Institute for Molecular Science

annual review

2018

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Editorial Committee 2018

Institute for Molecular Science (IMS) is one of the world's core research facilities for molecular science and is also a center for inter-university joint research in Japan. It sets an extremely wide range of research goals, from understanding the behavior of individual molecules to that of collective molecular systems. These molecular systems have close relation to scientific understanding of biology, engineering and space sciences. Currently, IMS is engaged in six (four plus two) areas of research: Theoretical and computational molecular science, Photo-molecular science, Materials molecular science, and Life and coordination-complex molecular science. Research Center of Integrative Molecular Systems (CIMoS), the fifth research division of IMS, has started from April, 2013 to develop the highly functional molecular systems such as molecular rhythms, sensing and response, and even self-repair. Starting from April 2017, Center for Mesoscopic Sciences (CMS) is launched to develop innovative methodology of studying mesoscopic molecular systems, covering from theoretical methods to leading-edge measurement methods. In addition to these research divisions, IMS has three research facilities; UVSOR Synchrotron Facility, Instrument Center facilitated with various molecular detectors, and Equipment Development Center. IMS also operates the Research Center for Computational Science, jointly with National Institute for Physiological Sciences and National Institute for Basic Biology in the same campus. Okazaki Institute for Integrative Bioscience (OIIB) has accomplished its role to foster new trends in bioscience research since April 2000, and starting from April 2018, Exploratory Research Center on Life and Living Systems (ExCELLS) is launched directly under the National Institute of Natural Science.

Annual Review 2018 is a summary of research activities performed in IMS during September 2017–August 2018. The individual research groups at IMS are making steady progress in basic research on molecular structures, reactions and functions demonstrating "novel molecular capabilities," as reported in this Review. In addition to these individual activities, IMS conducts the six special programs in the institute basis: (i) Emerging innovation in computational science of energy from post-K computer; (ii) Nano science project, called Nanotechnology Platform from July 2012; (iii) MEXT Photon Frontier Network program for Photon Science and Technology in collaboration with Osaka University, Kansai Photon Science Institute, and Kyoto University (ended in March 2018); (iv) Inter-University Network for Common Utilization of Research Equipments cooperated with 72 Japanese National Universities; (v) Project on trans-hierarchical studies of materials and biological systems with molecular observations, as a joint program of NINS; (vi) IMS runs several international collaboration programs and also owns two internship programs for young scientists: Institute for Molecular Science International Internship Program (IMS-IIP) and IMS-IIP in Asia (IMS-IIPA). IMS-IIPA provides the opportunity of internship for young researchers (*e.g.*, master's and doctoral students, postdoctoral researchers and young faculty members of MOU partners) from Asian countries to stay in IMS laboratories related to the basic research.

Four new members have joined the IMS faculty in the period of September 2017–August 2018. Dr. Makoto Fujita of The University of Tokyo, an expert in self-assembling molecular systems based on coordination chemistry, has concurrently started his new position as a Distinguished Professor of IMS in Division of Advanced Molecular Science. Two new associate professors have also joined our faculty in the same period; both Dr. Genki Kobayashi, research associate professor of IMS and Dr. Toshiki Sugimoto from Kyoto University have become members of Department of Materials Molecular Science. Professor Kobayashi is developing effective material for hydride ion conductors for energy devices. Professor Sugimoto is exploring physicochemical properties and quantum dynamics of molecular aggregates at solid surfaces. Dr. Fumihiko Matsui from Nara Institute of Science and Technology has joined our UVSOR Synchrotron Facility as a Senior Researcher. Dr. Matsui studies both surface science and solid state physics with his expertise in developing novel microscope for x-ray and photoelectron spectroscopies, that are placed in synchrotron facilities. On the other hand, three faculty members, one senior professor and two young associate professors have left IMS. Professor Kosugi left for The Institute of Materials Structure Science (IMSS) of High Energy Accelerator Research Organization (KEK), and Professor Yanai left for Nagoya University. Much to our regret, Professor Nobusada passed away in January after some years of medical treatment. May his soul rest in peace. We deeply thank to these three professors for their important contributions to IMS and wish Professor Kosugi and Yanai success in their new environments. Many new young faculty members as assistant professors have joined IMS in this period. Also, Dr. Eiji Shigemasa, associate professor of IMS, became the manager of the technical division after the leave of Mr. Mitsukazu Suzui to the National Astronomical Observatory of Japan.

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

September, 2018

Maki Kawai

KAWAI, Maki
Director General, Institute for Molecular Science

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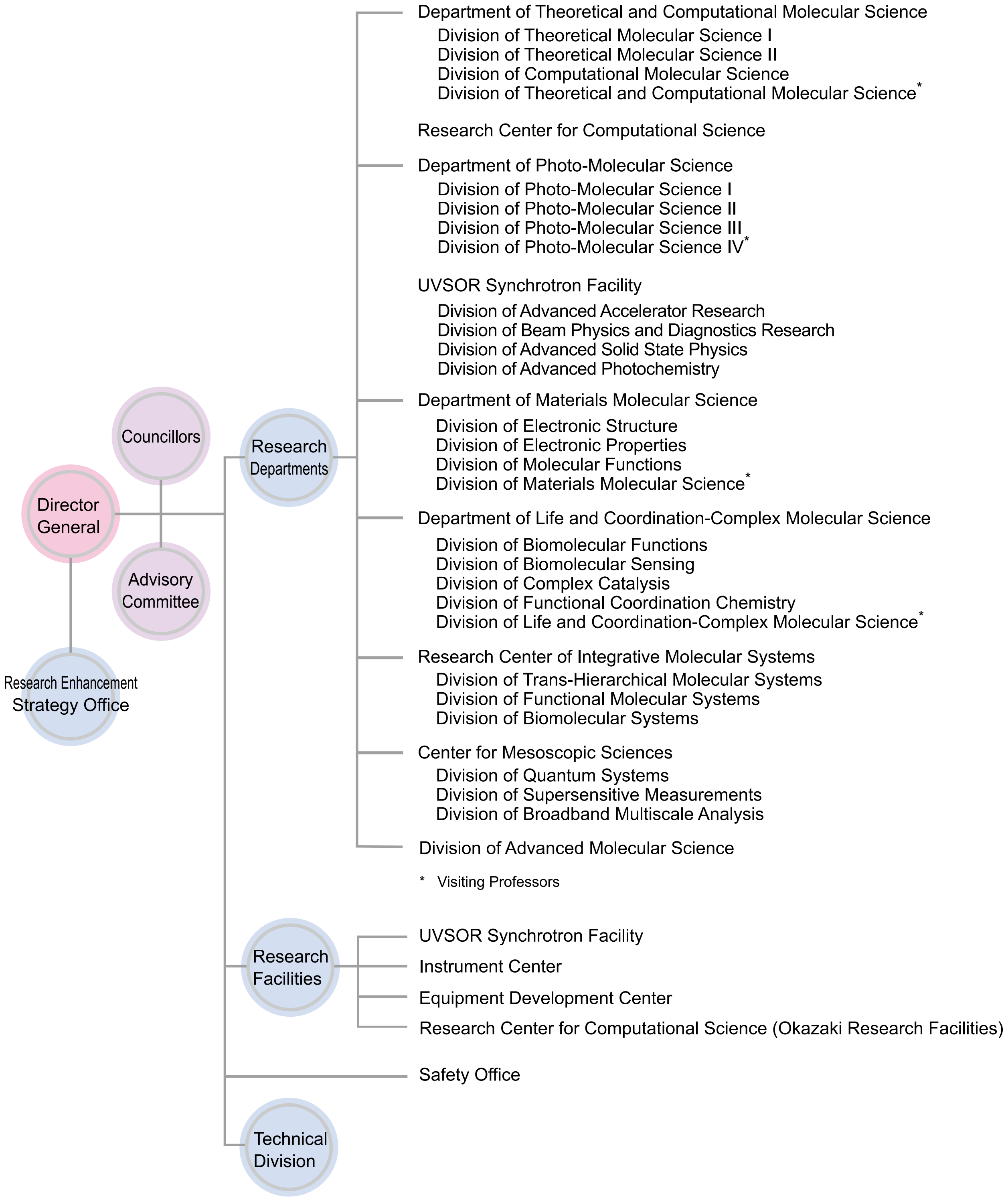
ORGANIZATION



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* Two of the councillors are selected among distinguished foreign scientists.

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YOKOYAMA, Toshihiko	Professor, Institute for Molecular Science

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NAGAKURA, Saburo	Professor Emeritus, The Graduate University for Advanced Studies and The University of Tokyo
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IWATA, Suehiro	Professor Emeritus, The Graduate University for Advanced Studies
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KITAGAWA, Teizo	Professor Emeritus, The Graduate University for Advanced Studies and The University of Hyogo
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NISHI, Nobuyuki	Professor Emeritus, The Graduate University for Advanced Studies
YAKUSHI, Kyuya	Professor Emeritus, The Graduate University for Advanced Studies
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NAGASE, Shigeru	FIFC Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University
HIRATA, Fumio	Fellow, Toyota Physical and Chemical Research Institute
TANAKA, Koji	Specially Appointed Professor, Institute for Integrated Cell-Material Sciences, Kyoto University
KUWAJIMA, Kunihiro	Professor Emeritus, The Graduate University for Advanced Studies and The University of Tokyo
OHMINE, Iwao	Professor Emeritus, The Graduate University for Advanced Studies

ACTIVITIES IN EDUCATION AND COLLABORATION

Graduate Programs

IMS is one of the leading national research institutes in natural science. For graduate education, IMS has two departments in Graduate School of Physical Sciences, SOKENDAI (The Graduate University for Advanced Studies): Department of Structural Molecular Science and Department of Functional Molecular Science. One year is divided into two terms, the first semester (April-to-September) and the second semester (October-to-March).

The graduate education at IMS focuses on the molecular sciences. Each graduate student can study molecular science under guidance of the IMS faculty members in the following areas: Photomolecular science, materials molecular science, biomolecular and coordination molecular science, and theoretical and computational molecular science.

In the 1st and 2nd years of the 5-year doctoral course, the programs emphasize the scientific education related to the expertises of IMS laboratories. By providing such opportunities, the program seeks to help students develop extensive knowledge on physical sciences and high degree of professional quality as well as to help them prepare for the education in their 3rd to 5th years of the 5-year doctoral course.

Young scientists and graduate students from abroad are also encouraged to visit IMS through several opportunities such as the IMS Open Campus and Lecture in June, Summer Training Program in August, and Asian Winter School in addition to IMS International Internship Program as shown below.

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

It is our goal to develop new theoretical and computational methods based on quantum and statistical mechanics to predict and understand structures, chemical reactions, and functions of molecules in condensed phases including nano- and biomolecular-systems.

Theoretical Studies of Reactions, Functions, and Fluctuations in Many-body Molecular Systems

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

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Education

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

Professional Employment

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

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KODA, Shin-ichi
Post-Doctoral Fellow
MATSUMURA, Yoshihiro
ANDO, Yoshimichi
Graduate Student
KALATHINGAL, Mahroof
MORITSUGU, Norifumi
Secretary
SUZUKI, Sayuri

Keywords Heterogeneous Dynamics, Reactions, Functions

In many-body molecular systems, such as liquids and biomolecular systems, nonlinear intermolecular interactions induce complicated motions. The motions are spatially and temporally heterogeneous, and yield static, dynamic, and thermodynamic properties of the systems. The spatiotemporal heterogeneous motions known as dynamic heterogeneity are found in supercooled liquids. In bio-molecular systems, which show slow conformational fluctuations, time-dependent reaction rates are often observed. Furthermore, biological functions are produced in complicated fluctuations with a wide range of timescales. Therefore, understanding of spatiotemporal heterogeneous dynamics is essential to the elucidation of the structure, reactions, functions, and fluctuations in these complicated systems.

We have investigated inter- and intra-molecular dynamics of water by using third-order nonlinear spectroscopy which can provide the detailed dynamics that are not available from conventional spectroscopy. We have revealed the molecular mechanism of ultrafast energy relaxation, which is one of dynamical features of water, is caused by the nonlinear strong coupling between the libration motion and other intra- and inter-molecular vibrational motions.

We have also investigated heterogeneous dynamic of supercooled liquids. In particular, we have quantified the lifetime of dynamic heterogeneity by introducing the three-time correlation function of density fluctuation. We have found that the temperature dependence of lifetime of dynamic heterogeneity obtained from the three-time correlation functions is very sensitive to the fragility, that is the three-time correlation function is sensitive to the configurational entropy.

We have also revealed the molecular origin of anomalous temperature dependence of isobaric specific heat of water by examining the so-called complex specific heat. Recently, we have investigated the structure and dynamics of deeply supercooled water. We have found the new dynamic transitions due to the instability of high- and low-density clusters in waters and also deciphered a crucial role of specific hydrogen-bond defects in persistent structural relaxations involved in low glass transition of water.

These days, we examine complicated conformational fluctuations of proteins by using the ideas of stochastic theory. We also investigate how chemical reactions and glass transitions proceed at the molecular level and how biological functions and thermal properties of liquids are generated under complicated fluctuations with a wide range of timescales.

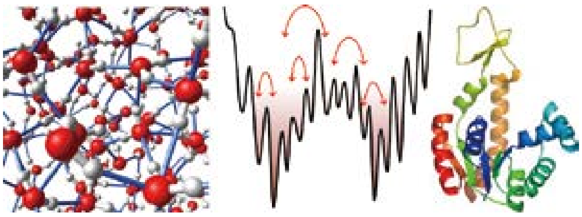

Figure 1. Schematic figure of rugged energy landscape (center) in supercooled water (left) and adenylate kinase (right).

Selected Publications

- T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, I. Ohmine and B. Bagchi, *J. Chem. Phys.* **138**, 094503 (7 pages) (2013), S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018).
- J. Ono, S. Takada and S. Saito, *J. Chem. Phys. (Special Topic on Multidimensional Spectroscopy)* **142**, 212404 (13 pages) (2015).

1. Conformational Excitation and Non-Equilibrium Transition Facilitate Enzymatic Reactions: Application to Pin1 Peptidyl-Prolyl Isomerase(1)

Conformational flexibility of proteins is essential for protein function and enzyme catalysis. Yet, how proteins' conformational rearrangements and dynamics contribute to the chemical step of enzyme catalysis has remained highly controversial over decades. In order to unravel protein's role in enzyme catalysis, it is necessary to understand the static and dynamic mechanisms of enzyme catalysis simultaneously. In this respect, here we study Pin1 peptidyl-prolyl isomerase, and reveal the structural and dynamic aspects of catalytic isomerization step in molecular detail. From the static and fully-equilibrium perspective, the hydrogen bond interactions within Pin1 as well as between Pin1 and ligand are found to rearrange along the minimum free energy path of isomerization. In sharp contrast, the transition dynamics reveal that isomerization transitions are very rapid; slow protein conformational rearrangements cannot simultaneously occur with the isomerization reaction, and the reaction instead proceeds in a non-equilibrium manner. We further reveal that distinctive protein conformational rearrangements and hydrogen bonds, necessary to stabilize the transition state, need to be prepared a priori, *i.e.* as a conformational excited state within the reactant equilibrium. The present results reveal that the catalytic isomerization reaction does not occur as a simple thermal activation from the equilibrium directly to the transition state, indicating the importance of protein conformational flexibility and the presence of favorable conformations for the isomerization reactions. The current findings add a novel perspective of the Pauling's view on the enzymatic reactions in which the reactions proceed thermally from reactants to stabilized transition state and products.

2. A Reaction Model of the Cyanobacterial Circadian Rhythm Considering the Interplay among Multiple Domain-Specific Conformational Changes of KaiC(2)

The clock proteins of cyanobacteria KaiABC constitute a biological clock with a temperature-compensated circadian period. KaiC forms a homo-hexamer with the two ring-shaped domains, C1 and C2, which allosterically communicate each other to generate the circadian rhythm. Experiments have found that several conformational changes of C1 and/or C2 are involved in the communication. However, detailed interplay among them remains elusive. We propose a mathematical model explicitly considering the interplay among the multiple domain specific conformational changes. In this model, the whole process, where the chemical reactions of ligands induce the (dis) assembly of KaiA and KaiB via the conformational changes, is represented only by the rate equations of them without any effective simplification. We show that the present model with automatically optimized rate or equilibrium constants can qualitatively reproduce various experimental data including temperature dependence of phosphorylation oscillation and ATPase activity. We also discuss a possible mechanism of the temperature compensation of period in association with the interplay among the domain-specific conformational changes, and find that some conformational changes induced by the slow and temperature-compensated ATP hydrolysis in C1 make the duration of phosphorylation temperature-compensated.

3. Theoretical Approach to Dynamical Disorder of Chemical Processes: Application to Bovine Pancreatic Trypsin Inhibitor Protein(3)

Chemical processes in many-body molecular systems proceed under thermal fluctuations over wide spatiotemporal scales. One example is the conformational dynamics of proteins, which is highly heterogeneous and closely related to their functions. Although the dynamical disorder model has been introduced to characterize and understand the process correlated with dynamical fluctuations, the molecular aspects are not well established. Recent achievements in single-molecule spectroscopy and ultralong-time molecular dynamics simulation enabled us to access rich time series data with the molecular details and encouraged us to explore the theoretical framework for the single molecule kinetics. In this study, we develop the analytical framework for the time series data based on the theory of stochastic process, to clarify the dynamical correlations of state transition processes. The framework is applied to the 1ms-length molecular dynamics simulation of the conformational dynamics of bovine pancreatic trypsin inhibitor protein in aqueous solutions. Conformational states can be detected as isomers of dihedral angles in the vicinity of a disulfide bond; experimentally three states are observed and several other transient states are also found in the simulations. The present method developed in this study can decipher that the transient states are dynamically coupled with the transitions between the three states, although complex behaviors are averaged out in experiments.

References

1) T. Mori and S. Saito, to be submitted.
2) S. Koda and S. Saito, to be submitted.
3) Y. Matsumura and S. Saito, to be submitted.

Advanced Electronic Structure Theory in Quantum Chemistry

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

YANAI, Takeshi
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(–March, 2018)
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Education
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2001 Ph.D. The University of Tokyo

Professional Employment
2001 Postdoctoral Fellow, The University of Tokyo
2002 Postdoctoral Fellow, Pacific Northwest National Laboratory
2002 Postdoctoral Fellow, Oak Ridge National Laboratory
2005 Postdoctoral Fellow, Cornell University
2007 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2018 Professor, Nagoya University

Awards
2008 Chemical Physics Letters Most Cited Paper 2003-2007 Award
2009 The Wiley-International Journal of Quantum Chemistry Young Investigator Award
2013 Laureate, International Academy of Quantum Molecular Science
2013 Japan Society of Molecular Science
2017 Pople Medal of Asia-Pacific Conference of Theoretical and Computational Chemistry

Member
IMS Research Assistant Professor
SAITOW, Masaaki
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Secretary
YAMADA, Mariko

Keywords Electronic Structure Theory, Quantum Chemistry, Computational Chemistry

Computational quantum chemistry, that is, practicing quantum chemical theory using computers, is now considered to be a powerful means to provide detailed analysis of chemical phenomena. The focus of our group is to develop methods and algorithms of molecular electronic structure calculations, which are capable of supplying electronic-level interpretation and reliable prediction of chemical characters, reactivity, energetics, and spectroscopic properties of molecular systems. Also, we are interested in applying the methods to challenging chemical systems. Recently, we have developed advanced multireference methods to describe highly-correlated many-electron wavefunction, which cannot be qualitatively accounted for with mean-field or one-electron theory (*e.g.*, density functional theory). The multireference wavefunction need be represented with a quantum superposition of multiple electron configurations; however, this gives rise to a high computational expense because the degree of the superposition is in general exponentially dependent on the system size. We approach the multireference problems using the density matrix renormalization group (DMRG), which is originally a method of condensed matter physics to solve strong correlation phenomena in physical models. We developed an efficient implementation for adapting DMRG to quantum chemical calculation, in which the DMRG is exploited to describe static correlation in combination with the complete active space (CAS) model. Our DMRG-based methods have shown to be capable of handling very large correlation space, which far exceeds the limitation of conventional methods. We have further introduced a scheme to additively account for dynamic correlation on top of active-space DMRG wavefunction. Using these methods, we carried out chemical applications to multireference electronic systems, ranging from organic material molecules, such as radicals of graphene nanoribbons, to transition metal complexes, such as tetranuclear manganese cluster.

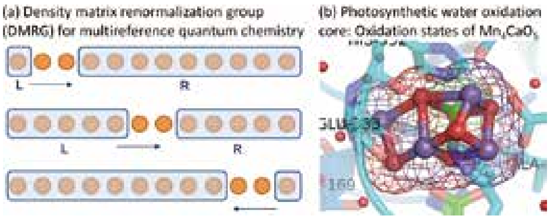


Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

Selected Publications

- Y. Kurashige and T. Yanai, “High-Performance *Ab Initio* Density Matrix Renormalization Group Method: Applicability to Large-Scale Multireference Problems for Metal Compounds,” *J. Chem. Phys.* **130**, 234114 (21 pages) (2009).
- W. Mizukami, Y. Kurashige and T. Yanai, “More π Electrons Make a Difference: Emergence of Many Radicals on Graphene Nanoribbons Studied by *Ab Initio* DMRG Theory,” *J. Chem. Theory Comput.* **9**, 401–407 (2013).
- Y. Kurashige, G. K-L. Chan and T. Yanai, “Entangled Quantum Electronic Wavefunctions of the Mn_4CaO_5 Cluster in Photosystem II,” *Nat. Chem.* **5**, 660–666 (2013).

1. Multistate Complete Active Space Second Order Perturbation Theory Based on Density Matrix Renormalization Group Reference States[1)]

We present the development of the multistate multireference second-order perturbation theory (CASPT2) with multi-root references, which are described using the density matrix renormalization group (DMRG) method to handle a large active space. The multistate first-order wave functions are expanded into the internally contracted (IC) basis of the single-state single-reference (SS-SR) scheme, which is shown to be the most feasible variant to use DMRG references. The feasibility of the SS-SR scheme comes from two factors: First, it formally does not require the fourth-order transition reduced density matrix (TRDM); and second, the computational complexity scales linearly with the number of the reference states. The extended multistate (XMS) treatment is further incorporated, giving suited treatment of the zeroth-order Hamiltonian despite the fact that the SS-SR based IC basis is not invariant with respect the XMS rotation. In addition, the state-specific fourth-order reduced density matrix (RDM) is eliminated in an approximate fashion using the cumulant reconstruction formula, as also done in the previous state-specific DMRG-cu(4)-CASPT2 approach. The resultant method, referred to as DMRG-cu(4)-XMS-CASPT2, uses the RDMs and TRDMs of up to third-order provided by the DMRG calculation (**Figure 2**). The multistate potential energy curves of the photoisomerization of diarylethene derivatives with CAS(26e,24o) are presented to illustrate the applicability of our theoretical approach (**Figure 3**).

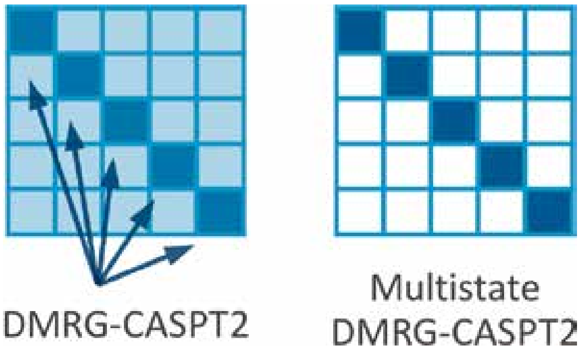
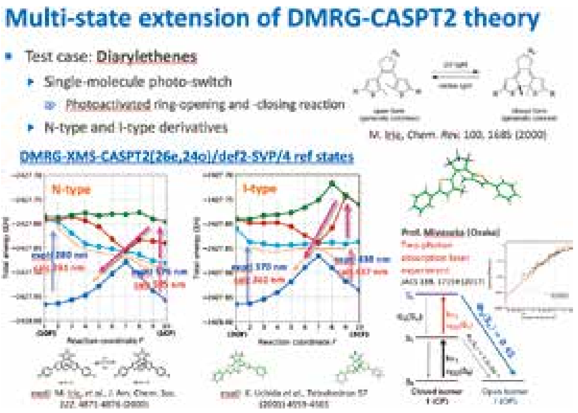


Figure 2. Development of multistate multireference perturbation theory with density matrix renormalization group references.


Multi-state extension of DMRG-CASPT2 theory

- Test case: Diarylethenes
  - Single-molecule photo-switch
    - Photoactivated ring-opening and -closing reaction
  - N-type and I-type derivatives

M. Irie, Chem. Rev. 100, 1685 (2000)

DMRG-XMS-CASPT2(26e,24o)/def2-SVP/4 ref states

Prof. Miyasaka (Osaka)

Figure 3. Application of DMRG-XMS-CASPT2 theory for studying potential energy curves of S_0–S_3 states of two types of diarylethene derivatives with use of large active space, CAS(26e,24o), considering four reference states.

2. Robust and Efficient Relativistic Complete Active Space Self-Consistent Field[2)]

We report a highly efficient algorithm using density fitting for the relativistic complete active space self-consistent field (CASSCF) method, which is as efficient as, but significantly more stable than, the algorithm previously reported. Our algorithm is based on the second-order orbital update scheme with an iterative augmented Hessian procedure, in which the density-fitted orbital Hessian is directly contracted to the trial vectors. Using this scheme, each microiteration is made less time consuming than one Dirac–Hartree–Fock iteration, while macroiteration converges quadratically. In addition, we show that the CASSCF calculations with the Dirac–Gaunt and Dirac–Breit interactions can be sped up by means of approximate orbital Hessians computed with the Dirac–Coulomb interaction. It is demonstrated that our algorithm can also be applied to systems under an external magnetic field, for which all of the molecular integrals are computed using gauge-including atomic orbitals.

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2) R. D. Reynolds, T. Yanai and T. Shiozaki, *J. Chem. Phys.* **149**, 014106 (2018).

Award

SAITOW, Masaaki; 2017 Molecular Physics Early Career Researcher Prize.

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Awards

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Keywords Quantum Dissipative Systems, Energy/Charge Transfer Dynamics, Photosynthetic Light Harvesting

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. Quantum dynamics of energy/charge transfer dynamics in condensed phase molecular systems such as protein environments are remarkable examples of such phenomena.

Photosynthetic conversion of the energy of sunlight into its chemical form suitable for cellular processes involves a variety of physicochemical mechanisms. The conversion starts with the absorption of a photon of sunlight by one of the light-harvesting pigments, followed by transfer of electronic excitation energy to the reaction center, where charge separation is initiated. At low light intensities, surprisingly, the quantum efficiency of the transfer is near unity. A longstanding question in photosynthesis has been the following: How does light harvesting deliver such high efficiency in the presence of disordered and fluctuating dissipative environments? Why does not energy get lost? At high light intensities, on the other hand, the reaction center is protected by regulation mechanisms that lead to quenching of excess excitation energy in light harvesting proteins. The precise mechanisms of these initial steps of photosynthesis are not yet fully elucidated from the standpoint of molecular science. Particularly, recent observations of long-lived beating phenomena in two-dimensional electronic spectra of photosynthetic pigment-protein complexes stimulated a huge burst of activity in an interdisciplinary community of molecular science and quantum physics.

Selected Publications

- A. Ishizaki and Y. Tanimura, "Quantum Dynamics of System Strongly Coupled to Low-Temperature Colored Noise Bath: Reduced Hierarchy Equations Approach," *J. Phys. Soc. Jpn.* **74**, 3131–3134 (2005).
- A. Ishizaki and G. R. Fleming, "Unified Treatment of Quantum Coherent and Incoherent Hopping Dynamics in Electronic Energy Transfer: Reduced Hierarchy Equation Approach," *J. Chem. Phys.* **130**, 234111 (10 pages) (2009).
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- A. Ishizaki, T. R. Calhoun, G. S. Schlau-Cohen and G. R. Fleming, "Quantum Coherence and Its Interplay with Protein Environments in Photosynthetic Energy Transfer," *Phys. Chem. Chem. Phys.* **12**, 7319 (2010). [Invited perspective article]
- 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).

1. Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering

Excitation energy transfer (EET) is one of the most important processes in both natural and artificial chemical systems including, for example, photosynthetic complexes and organic solar cells. The EET rate, however, is strongly suppressed when there is a large difference in the excitation energy between the donor and acceptor molecules. We have demonstrated both analytically and numerically that the EET rate can be greatly enhanced by periodically modulating the excitation energy difference. The enhancement of EET by using this Floquet engineering, in which the system's Hamiltonian is made periodically time-dependent, is found to be efficient even in the presence of strong fluctuations and dissipations induced by the coupling with a huge number of dynamic degrees of freedom in the surrounding molecular environments. The shift of the optimal driving frequency as moving from the homogeneous to the inhomogeneous broadening limits can be used to probe the nuclear motion dynamics of the environment.1)

2. Control of Quantum Dynamics of Electronic Excitation Transfer in Molecular Loop Structures: Spontaneous Breaking of Chiral Symmetry

Manipulation of quantum systems is the basis for many promising quantum technologies. How quantum mechanical principles can be used to manipulate dynamics of quantum dissipative systems is, however, still elusive because of strong decoherence effects arising from the interaction with the surrounding environment. We have demonstrated that electronic excitation transfer dynamics in molecular loop structures can be manipulated with the use of the Floquet engineering, in which the Franck-Condon transition frequency is temporally modulated in a periodic manner. Despite strong dephasing, the system's dynamics spontaneously breaks the chiral symmetry of the loop in a controllable fashion, followed by the generation of a steady-state current of electronic excitation. The breaking of chiral symmetry and the consequent controllable unidirectional flow of electronic excitations could be employed to construct functional molecular circuits for energy transport.2)

3. Non-Markovian Quantum-Classical Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases

In organic photovoltaic systems, a photogenerated molecular exciton in the donor domain dissociates into a hole and an electron at the donor–acceptor heterojunction, and subsequently separates into free charge carriers that can be extracted as photocurrents. The recombination of the once-separated electron and hole is a major loss mechanism in photovoltaic systems, which controls their performance. Hence, efficient photovoltaic systems need built-in ratchet mechanisms, namely, ultrafast charge separation and retarded charge recombination. In order to obtain insight into the internal working of the experimentally observed ultrafast long-range charge separation and protection against charge recombination, we theoretically investigate a potential ratchet mechanism arising from the combination of quantum delocalization and its destruction by performing numerically accurate quantum-dynamics calculations on a model system. We demonstrate that the non-Markovian effect originating from the slow polaron formation strongly suppresses the electron-transfer reaction back to the interfacial charge-transfer state stabilized at the donor–accepter interface and that it plays a critical role in maintaining the long-range electron–hole separation.3)

4. Intramolecular Vibrations Complement the Robustness of Primary Charge Separation in the Photosystem II Reaction Center

The energy conversion of oxygenic photosynthesis is triggered by primary charge separation in proteins at the photosystem II (PSII) reaction center (RC). Several time-resolved spectroscopic studies have reported that the primary charge separation in the PSII RC take place on subpicosecond time scale. However, it is one order of magnitude faster than the time constant of the charge separation starting from the special pair in the well-investigated purple bacterial RC, despite similarities in their arrangement of the pigments. As the coupling strengths between electron donors and acceptors are usually thought to be on the order of tens of wavenumbers, the precise mechanisms that enable subpicosecond charge separation in the PSII RC are to a large extent unknown.

To address the above question, we investigated the impacts of the protein environment and intramolecular vibrations on primary charge separation at the PSII RC. This was accomplished by combining the quantum dynamic theories of condensed phase electron transfer with quantum chemical calculations to evaluate the vibrational Huang-Rhys factors of chlorophyll and pheophytin molecules. We reported that individual vibrational modes play a minor role in promoting charge separation, contrary to the discussion in recent publications. Nevertheless, these small contributions accumulate to considerably influence the charge separation rate, resulting in subpicosecond charge separation almost independent of the driving force and temperature. We suggested that the intramolecular vibrations may complement the robustness of the charge separation in the PSII RC against the inherently large static disorder of the involved electronic energies.4)

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4) Y. Fujihashi, M. Higashi and A. Ishizaki, *J. Phys. Chem. Lett.* **9**, 4921–4929 (2018).

Theoretical Study on Photochemistry and Catalysis

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Awards

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Keywords Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

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

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

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

(2) Heterogeneous catalysis

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

(3) Photophysical chemistry

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

(4) Theoretical spectroscopy

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

Selected Publications

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

1. Frenkel-Exciton Decomposition Analysis of CD and CPL for Multichromophoric Systems1)

Recently, a method to calculate the absorption and circular dichroism (CD) spectra based on the exciton coupling has been developed. In this work, the method was utilized for the decomposition of the CD and circularly polarized luminescence (CPL) spectra of a multichromophoric system into chromophore contributions for recently developed through-space conjugated oligomers. The method which has been implemented using rotatory strength in the velocity form and therefore it is gauge-invariant, enables us to evaluate the contribution from each chromophoric unit and locally excited state to the CD and CPL spectra of the total system. The excitonic calculations suitably reproduced the full calculations of the system, as well as the experimental results. We demonstrated that the interactions between electric transition dipole moments of adjacent chromophoric units are crucial in the CD and CPL spectra of the multichromophoric systems, while the interactions between electric and magnetic transition dipole moments are not negligible.

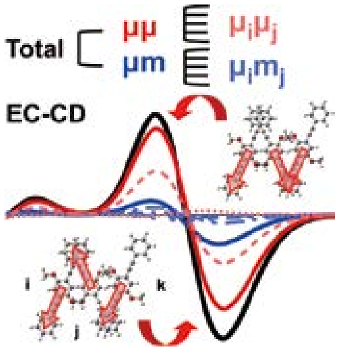

Figure 1. Frenkel-exciton decomposition analysis (FEDA) of CD spectra for through-space conjugated trimer.

2. Fluorescent Imaging Biological Probes of Nucleic Acids2)

Photophysical properties of exciton-controlled hybridization-sensitive fluorescent oligonucleotide (ECHO) probes which show strong emission in the near-infrared region via hybridization to the target DNA and/or RNA strand have been investigated using the SAC-CI and TD-DFT calculations. The monomer and dimer (H-aggregate) of fluorescent cyanine chromophores whose excitation is challenging for TD-DFT methods, have been examined. The present results support for the experimentally suggested mechanism of strong fluorescence and suppression of the probe. The SAC-CI method well reproduced the experimental transition energies, while the quantitative prediction by TD-DFT calculations was difficult for these chromophores. Stokes shifts of these chromophores were qualitatively reproduced by the theoretical calculations.

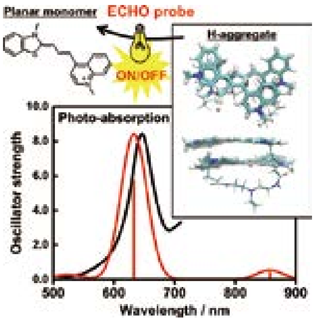

Figure 2. Photophysical properties of exciton-controlled hybridization-sensitive fluorescent oligonucleotide probe.

3. Nickel-Catalyzed Coupling Reaction of Alkyl Halides with Aryl Grignard Reagents in the Presence of 1,3-Butadiene: Mechanistic Studies of Four-Component Coupling and Competing Cross-Coupling Reactions3)

We investigated the mechanism, substituent effects, and origins of the selectivity of nickel-catalyzed four-component coupling reaction of alkyl fluorides, aryl Grignard reagents, and two molecules of 1,3-butadiene that affords a 1,6-octadiene carbon framework bearing alkyl and aryl groups at 3- and 8-positions, respectively, and the competing cross-coupling reaction. The C–C bond formation of alkyl fluorides with the γ-carbon of anionic nickel complexes leads to the four-component coupling product, whereas the cross-coupling product is yielded via nucleophilic attack of the Ni center toward alkyl fluorides. These steps are found to be the rate-determining and selectivity-determining steps of the whole catalytic cycle, in which the C–F bond of alkyl fluorides is activated by Mg cation rather than Li or Zn cation. ortho-Substituent(s) of aryl Grignard reagents suppressed the cross-coupling reaction leading to the selective formation of the four-component products. Such steric effects of the ortho-substituent(s) were clearly demonstrated by crystal structure characterizations of ate complexes and DFT calculations. The present mechanistic study offers new insight into anionic complexes, which are proposed as the key intermediates in catalytic transformations though detailed mechanisms are not established in many cases, and demonstrates their synthetic utility as promising intermediates for C–C bond forming reactions, providing useful information for developing efficient and straightforward multi-component reactions.

References

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2) T. Shiraogawa, G. Candel, R. Fukuda, I. Chiofini, C. Adamo, A. Okamoto and M. Ehara, *J. Comput. Chem.*, in press.

3) T. Iwasaki, A. Fukuoka, W. Yokoyama, X. Min, I. Hisaki, T. Yang, M. Ehara, H. Kuniyasu and N. Kambe, *Chem. Sci.* **9**, 2195–2211 (2018).

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Development of New Molecular Dynamics Algorithms for Biomolecular Systems

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2018 Associate Professor, Exploratory Research Center on Life and Living Systems

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Keywords Molecular Dynamics Simulation, Protein, Amyloid

Biomolecules such as proteins and peptides have complicated free-energy landscape with many local minima. The conventional canonical-ensemble molecular dynamics (MD) simulations tend to get trapped in a few of the local-minimum states. To overcome these difficulties, we have proposed new generalized-ensemble algorithms, such as 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 amyloid fibrils, which are insoluble aggregates of misfolded fibrous proteins and associated with more than 20 human neurodegenerative diseases (Figure 2). For example, Alzheimer's disease is related to amyloid-β (Aβ) peptides. To overcome these diseases, it is essential to understand amyloid genesis and disruption. We perform such MD simulations of amyloid fibrils.

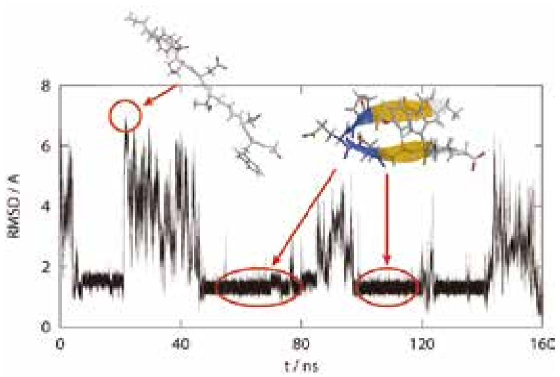

Figure 1. Time series of protein folding simulation.

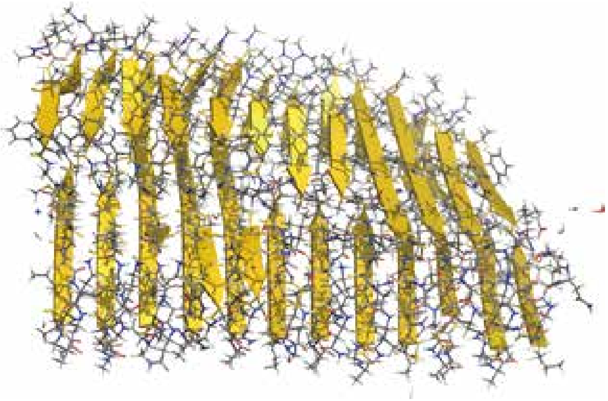

Figure 2. Snapshot of amyloid fibril.

Selected Publications

- Y. Mori and H. Okumura, "Pressure-Induced Helical Structure of a Peptide Studied by Simulated Tempering Molecular Dynamics Simulations," *J. Phys. Chem. Lett.* **4**, 2079–2083 (2013).
- S. G. Itoh and H. Okumura, "Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method," *J. Chem. Theory Comput.* **9**, 570–581 (2013).
- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- S. G. Itoh and H. Okumura, "Oligomer Formation of Amyloid-β(29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation," *J. Phys. Chem. B* **120**, 6555–6561 (2016).

1. Development of Isothermal-Isobaric Replica-Permutation Method and Its Application to Chignolin

We developed a two-dimensional replica-permutation molecular dynamics (MD) method in the isothermal-isobaric ensemble.[1)] The replica-permutation method is a better alternative to the replica-exchange method. It was originally developed in the canonical ensemble. This method employs the Suwa-Todo algorithm, instead of the Metropolis algorithm, to perform permutations of temperatures and pressures among more than two replicas so that the rejection ratio can be minimized. We showed that the isothermal-isobaric replica-permutation method performs better sampling efficiency than the isothermal-isobaric replica-exchange method. We applied this method to a β-hairpin mini protein, chignolin. In this simulation, we observed not only the folded state but also the misfolded state. We calculated the temperature and pressure dependence of the fractions of the folded, misfolded, and unfolded states. Differences in partial molar enthalpy, internal energy, entropy, partial molar volume, and heat capacity were also determined, and agreed well with experimental data. We observed a new phenomenon that misfolded chignolin becomes more stable under high-pressure conditions. We also revealed this mechanism of the stability as follows: TYR2 and TRP9 side chains cover the hydrogen bonds that form a β-hairpin structure as in Figure 3. The hydrogen bonds are protected from the water molecules that approach the protein as the pressure increases.

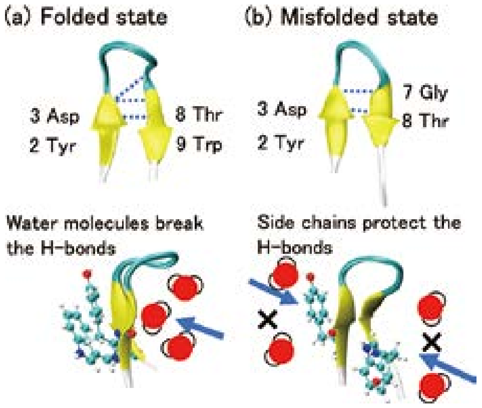

Figure 3. Schematic figure of the mechanism by which misfolded chignolin becomes stable under high-pressure conditions.

2. Classical Molecular Dynamics Simulation to Understand Role of a Zinc Ion for Aggregation of Amyloid-β Peptides

Metal ions such as those of copper and zinc are considered to accelerate initial formation of amyloid fibril of Aβ peptides. In this study, the role of a zinc ion for Aβ peptide aggregation was investigated by the classical MD simulations.[2)] The MD results indicated that the negatively-charged residues gained large stabilization in the existence of a zinc ion. On the other hand, histidine and tyrosine which were reported as making a bond with a metal ion were slightly stabled. Therefore, a zinc ion is thought of as combining with histidine or tyrosine after being attracted by negatively-charged residues, because these residues exist near negatively-charged residues. These results indicate that the metal-containing system needs to be treated by quantum-mechanical techniques.

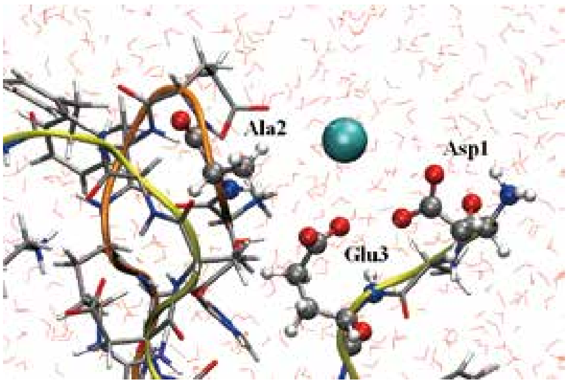

Figure 4. A snapshot around the zinc ion. Asp1 and Glu3 of one Aβ(1–16) peptide and Ala2 of the other Aβ(1–16) peptide exist near the zinc ion.

3. Antigen-Dependent Fluorescence Response of Anti-c-Myc Quenchbody Studied by Molecular Dynamics Simulations

We performed metadynamics MD simulations to reveal mechanism of antigen-dependent fluorescence response observed for site-specifically fluorescent-labeled single-chain antibody against c-Myc peptide antigen.[3)] We found that V_H and V_L bind with each other only when the antigen exists and that the fluorophore labeled at the N-terminus of V_H interacts with Trp103 most stably. These results support the mechanism proposed from previous experiments: In the absence of antigen, Trp residues are partially exposed at the interface of V_H and quench the fluorophore. In the presence of antigen, the Trp residues are buried in the interface between V_H and V_L, and the quenching is eliminated.

References

1) M. Yamauchi and H. Okumura, *J. Chem. Phys.* **147**, 184107 (15 pages) (2017).
2) H. Nishizawa and H. Okumura, *J. Comput. Chem. Jpn.* **17**, 76–79 (2018).
3) Y. Mori, H. Okumura, T. Watanabe and T. Hohsaka, *Chem. Phys. Lett.* **698**, 223–226 (2018).

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Theoretical Studies on Molecular Aggregates

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Keywords Exciton, Energy and Charge Transfer, Organic Semiconductors

Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates can exhibit remarkable optical and electronic properties that are not observed in isolated molecules. We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, and energy conversions, and structure-property relationship. Our research also include the developments of theoretical and computational methods.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave functions can be delocalized over many molecules by intermolecular electronic couplings. By contrast, the wave functions can be localized because of the static disorder and interactions with nuclear degree of freedom. Therefore, successful theoretical descriptions require the inclusions of electronic couplings, static disorder, and electron–phonon or electron–vibration interaction. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. Electronic states of an aggregate is obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian is used for simulating energy or charge dynamics by a quantum dynamics method, which incorporates finite-temperature effects and electron–vibration interactions. The combine computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

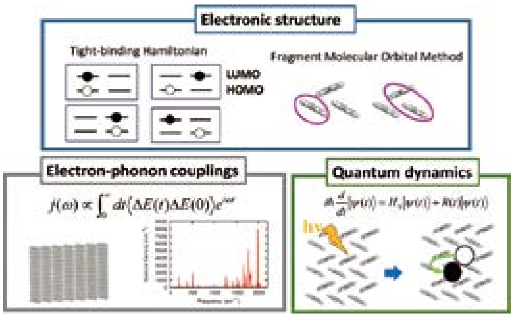

Figure 1. A combine approach to quantum dynamics in molecular aggregates.

We currently investigate electronic states and quantum dynamics at organic interfaces. We also develop the many-body perturbation theory to predict electronic levels at higher accuracy.

Selected Publications

- T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, "Coherent Dynamics of Mixed Frenkel and Charge Transfer Excitons in Dinaphtho[2,3-*b*:2'3'-*f*]thieno[3,2-*b*]-thiophene Thin Films: The Importance of Hole Delocalization," *J. Phys. Chem. Lett.* **7**, 1374–1380 (2016).
- T. Fujita and Y. Mochizuki, "Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems," *J. Phys. Chem. A* **122**, 3886–3898 (2018).

1. Interfacial Charge-Transfer States at Organic Bilayer Heterojunction$^{1)}$

The electronic structures at organic–organic interfaces comprising electron-donor and electron-accepter materials are of great importance in the performance of the organic solar cells. In particular, the interfacial charge-transfer (ICT) state—an electron-hole pair formed across the donor/acceptor interface—plays an essential role in charge photogeneration because it is an intermediate for both charge separation and charge recombination processes. Despite their critical importance, it is difficult to experimentally investigate the interfacial CT states.

Here, we performed ab initio excited-state calculations to investigate the ICT states formed at a pentacene/C_{60} bilayer heterojunction modeled by molecular dynamics simulations. The model bilayer heterojunction structures contain approximately 1.8×10^5 atoms, and their local interface regions containing 2,000 atoms were treated quantum mechanically, embedded in the electrostatic potentials from remaining parts. Therefore, the charge delocalization effect, structural disorder, and the resulting heterogeneous electrostatic and polarizable environments were taken into account in the excited-state calculations. The computed energies of the low-lying ICT states are in reasonable agreement with experimental estimates. By comparing the edge-on and face-on configurations of the pentacene/C_{60} interfaces, we highlight the influence of interfacial morphologies on the energetics and charge delocalization of ICT states. We found that, in the edge-on configuration, the pentacene absorption region is resonant with dense delocalized ICT states, resulting in the formation of hybridized states. The hybridization enhances the delocalization of ICT states, owing to their electron wave functions extending across the pentacene/C_{60} interface. In addition, the delocalized ICT state can be directly accessed by photoexcitation, borrowing absorption intensity from pentacene excited states. Such the optically-bright delocalized ICT states enable photoinduced long-range electron transfer through the extended electron wave functions, giving rise to rapid charge separations.

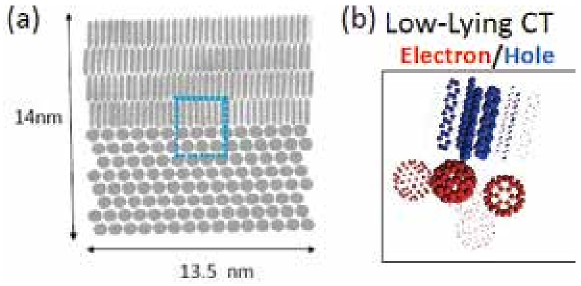

Figure 2. (a) The atomic structure of pentacene/C_{60} bilayer heterojunction. (b) Visualization of electron (red) and hole (blue) wave functions that constitute the low-lying CT state.

2. Development of Many-Body Green's Function Method for Large Molecular Systems$^{2)}$

The GW many-body Green's function approach has been established as an accurate and efficient method to predict the electronic levels. Within the GW method, the dielectric function is computed for screened Coulomb interaction, and the self-energy is approximated from the Green's function and the screened Coulomb potential. The GW method can be combined with the Bethe-Salpeter equation to obtain electronically excited states. The GW/BSE method have been applied to isolated molecules or periodic systems. However, they were not applied to interface systems because large and disordered system must be treated.

We develop the fragment-based GW method suitable to treat large molecular systems in heterogeneous polarizable environments, on the basis of the fragment molecular orbital (FMO) method. The Green's function of a total system is approximated from fragment Green's functions that are calculated by fragment molecular orbitals and is expanded up to two-body terms. The screened Coulomb potential is approximated from the sum of intrafragment density-response functions, with interfragment polarization terms being neglected. The approximations of the Green's function and screened Coulomb potential lead to the many-body expansion of the self-energy; this expansion is essentially equivalent to the many-body expansion of the Fock matrix in the FMO method. To deal with large molecular systems, the present implementation relies on the Coulomb hole plus screened exchange (COHSEX) approximation, which is the static limit of GW. The accuracy of the FMO-COHSEX method is demonstrated in comparison to conventional COHSEX results for organic molecular aggregates. We confirmed that the present fragmentation approach can provide resonantly accurate results, and the mean absolute errors of quasiparticle energies less than 0.1 eV have been achieved for valence orbitals. We also investigate the accuracy of the COHSEX approximation for describing the effects of molecular aggregation of electronic states, by comparing them to the GW method. Although the COHSEX fails to quantitatively determine quasiparticle energies, it was found to successfully describe the molecular aggregation effects on electronic states, such as induced polarization and dispersion effects. As an illustrative application of the present method, we consider the electronic states of the pentacene thin film. We discuss the impact of induced polarization effect in the heterogeneous environment, highlighting the gap renormalization and the polarization-induced localization. The application shows that our fragment-based GW method is useful to study electronic structures of molecular aggregates in complex environments.

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2) T. Fujita and Y. Noguchi, in preparation.

Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

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2011	Postdoctoral Fellow, National Institutes of Health, U.S.A.
2012	JSPS Postdoctoral Fellow for Research Abroad
2013	Postdoctoral Fellow, Max Planck Institute of Biophysics, Germany
2016	Research Associate Professor, Institute for Molecular Science

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Keywords Theoretical Biophysics, Molecular Motors, Molecular Simulations

Functional dynamics plays an important role when biomolecular machines fulfill their functions. For example, motor proteins walk on the rail or rotate relative to the stator by using ATP hydrolysis energy. Transporter proteins transport their substrates across the membrane by changing their conformation between inward-open and outward-open conformations. We aim to understand design principles of these precise, yet dynamic nano-machines developed by nature.

Functional dynamics of biomolecular machines involve wide spectrum of intricate motions and reactions. In order to understand such dynamics, we need a multiscale approach to cover full range of these motions and reactions. Conventional atomistic molecular dynamics simulations alone cannot cover millisecond-long (or even longer) functional dynamics, especially for a large system like typical biomolecular machines with more than hundreds of thousand atoms including water molecules. Thus, we use both atomistic and coarse-grained molecular simulations, as well as kinetic models based on statistical mechanics, to tackle this problem.

We have been working on ATP synthase that produces most of ATP required for living activities. The ATP synthase is composed of two rotary motors, F_o and F_1. The F_o motor is embedded in membrane and its rotation is driven by proton gradient. The F_1 motor is a catalytic part that produces ATP from ADP and P_i. However, the F_1 motor by itself (F_1-ATPase) rotates the central stalk, γ-subunit, in the opposite direction by hydrolyzing ATP. Thus, the two motors are driven by different energy sources and rotate in the opposite directions. In order to understand how ATP synthase works, we have to look into both individual motors and ATP synthase as a whole.

We are also working on other types of biomolecular machines like chitinase that shows a unidirectional motion by hydrolyzing chitin, Na^+/H^+ antiporter that exchanges sodium ions and protons inside and outside the cell. Methodological development and application of sampling rare events are our interests too.

Selected Publications

- K. Okazaki and G. Hummer, “Phosphate Release Coupled to Rotary Motion of F_1-ATPase,” *Proc. Natl. Acad. Sci. U.S.A.* **110**, 16468–16473 (2013).
- K. Okazaki and G. Hummer, “Elasticity, Friction, and Pathway of γ-Subunit Rotation in F_oF_1-ATP Synthase,” *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).
- M. Sugawa, K. Okazaki, M. Kobayashi, T. Matsui, G. Hummer, T. Masaike and T. Nishizaka, “F_1-ATPase Conformational Cycle from Simultaneous Single-Molecule FRET and Rotation Measurements,” *Proc. Natl. Acad. Sci. U.S.A.* **113**, E2916–E2924 (2016).
- H. Jung, K. Okazaki and G. Hummer, “Transition Path Sampling of Rare Events by Shooting from the Top,” *J. Chem. Phys.* **147**, 152716 (2017).
- 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). doi:10.1038/s41467-018-06362-3

1. Mechanochemical Coupling Mechanism of F_1-ATPase

Many single-molecule studies as well as crystallographic studies have clarified how the γ-subunit rotation is coupled to ATP hydrolysis reactions at three catalytic sites of F_1. As summarized in Figure 1B, main points are, 1) 120° step inferred from three-fold symmetry is further divided into 80° and 40° substeps, 2) the 80° substep is driven by ATP binding and ADP release, 3) the 40° substep is driven by P_i release and ATP hydrolysis reaction, 4) typical crystal structures correspond to catalytic dwell (before 40° substep). There are still some remaining questions, though. What is the timing of P_i release: Just after the hydrolysis reaction or after ADP release? What conformation does it take in ATP-binding dwell (before 80° substep)?

We resolved the timing of P_i release by using atomistic molecular dynamics simulations.$^{1)}$ The question is, essentially, from which catalytic site, DP-site or E-site, P_i is released. Since the P_i release takes ~millisecond, a biasing method called metadynamics was employed to facilitate the functional dynamics. Different pathways were observed depending on the site P_i was released. From the E-site it went through P-loop toward outside of the ring structure, while from the DP-site it went through switch II toward inside of the ring structure (Figure 1C). We estimated mean first-passage time from free energy profile (Figure 1D) and diffusion coefficient and concluded that P_i is release from the E-site. That is, P_i is released after ADP release, which is unique among other members of ATPases.

We also identified conformational state of the ATP-binding dwell by combining single-molecule FRET measurements and systematic structural analysis.$^{2)}$ We found that an ε-inhibited *E. Coli* structure that has half-closed β_{DP} and loose $\alpha\beta_E$ interface is consistent with the conformation taken in the ATP-binding dwell.

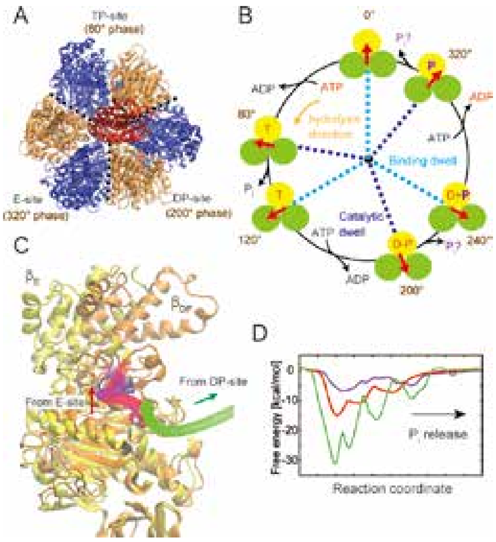

Figure 1. Mechanochemical coupling scheme and P_i release in F_1-ATPase.

2. Torsional Elasticity and Friction of Rotor in F_oF_1-ATP Synthase

It has been known that there is a symmetry mismatch between F_o c-ring and F_1 $\alpha_3\beta_3$ ring. The F_1 $\alpha_3\beta_3$ ring has (pseudo) three-fold symmetry, while the F_o c-ring in animal mitochondria has 8-fold symmetry. Thus, the common rotor, γ-subunit, has to rotate by 120° steps (or 80°+40° substeps) in F_1 part, while it has to rotate by 45° steps in F_o part. Therefore, it has to have torsional elasticity to solve the mismatch. In order to estimate torsional elasticity as well as viscosity of the γ-rotation, we built a simple viscoelastic model (Figure 2B) and fitted it against atomistic simulation trajectories in which external torque was applied on γ.$^{3)}$

The estimated torsional elasticity is consistent with values from single-molecule experiments. By using this elasticity, we identified pathways and associated free energies of the coupled F_oF_1 rotation (Figure 2C). It turned out that with the two-substep F_1 the pathway is blocked by high-energy states. To solve this situation, F_1 needs three substeps as was measured for human mitochondrial F_1 recently. From the estimated torsional friction, we predict that γ-rotation can rotate as fast as 1 MHz and this fast rotation can be observed with an attached bead as small as 20 nanometer diameter.

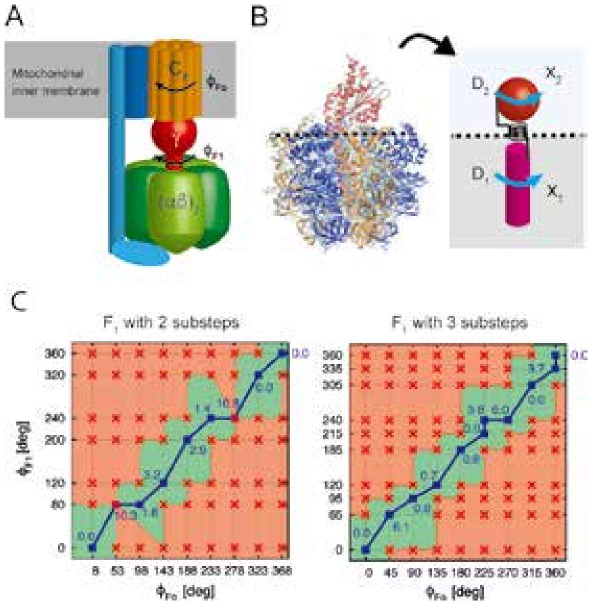

Figure 2. Viscoelastic model of F_oF_1-ATP synthase.

References

1) K. Okazaki and G. Hummer, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 16468–16473 (2013).

2) M. Sugawa, K. Okazaki, M. Kobayashi, T. Matsui, G. Hummer, T. Masaike and T. Nishizaka, *Proc. Natl. Acad. Sci. U.S.A.* **113**, E2916–E2924 (2016).

3) K. Okazaki and G. Hummer, *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).

Electronic Properties of Heterostructures Controlled by Applied Bias and Light

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

IIDA, Kenji
Assistant Professor

Heterostructures under applied bias and/or light irradiation have been extensively investigated in relation to the development of optical and electronic devices. To reveal their electronic functions, it is required to clarify the details of the electronic structure under applied bias and the photoinduced electronic interactions at the atomic scale.

1. Optical Response of Heterostructures

We have studied optical response of heterostructures using a first-principles computational program in which electron dynamics is directly calculated in real-time and real-space. This program can be applied to complex optical phenomena such as optical near-field excitation of nanostructures by carrying out massively parallel calculations. Using the program, we have shown that the photoexcitation of a MoS_2-graphene heterostructure induces the electron transfer from graphene to MoS_2. It is revealed that the photoexcitation causes the electron dynamics inherent in atomically-thin interfacial regions.1)

2. Electronic Structure Change by Applied Electrode Bias

We have been developing a theoretical approach for describing the electronic structure of heterostructures under applied bias.2) It has been shown that change in the electronic properties of heterostructures by an applied bias strongly depends on the atomic scale details of the interfacial region. We further extend the developed approach to address photoexcited systems under an applied bias.

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1) K. Iida, M. Noda and K. Nobusada, *J. Phys. Chem. C*, in press.
2) K. Iida, M. Noda and K. Nobusada, *J. Chem. Phys.* **146**, 084706 (10 pages) (2017).

Theory and Computation of Reactions and Properties in Solutions and Liquids

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

ISHIDA, Tateki
Assistant Professor

We are interested in the projects both on ultrafast photoinduced electron energy transfer in the excited state in solution and on ionic liquids (ILs). The project on photoinduced electron energy transfer processes in the excited state in solution is aimed at the development of a theoretical method to study electron energy transfer. Also, ILs' projects are focused on the investigation of dynamical properties on ionic liquids including temperature effects and the unique dissolution process of cellulose polysaccharides using molecular dynamics simulation technique.

1. The Theoretical Investigation of Photoinduced Electron Energy Transfer Processes in the Excited State in Solution1)

We have developed a procedure for investigating the time-dependent evolution of the electronic structure of a solute molecule in solution, coupling an electronic structure theory with solvent motion. It is shown that the coupling between solvation processes and a fast intramolecular electron energy transfer is likely to play an important role in the emergence of photoinduced unique functionalities in biochemical and metal complex systems.

2. Investigations of Ionic Liquids1–2) with Molecular Dynamics Simulation

We focus on the dynamical properties on ionic liquids (ILs). With molecular dynamics simulation procedure, it have been reported that ILs show unique collective dynamics. In addition, we have investigated interesting dynamical heterogeneity in ILs at room temperature. Also, we have studied the solvation mechanism of cellulose polymer in ILs.

References

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2) T. Ishida, in preparation.

Visiting Professors

Visiting Professor

NAKANO, Masayoshi *(from Osaka University)*

Theoretical Study on Photofunctionalities of Open-Shell Molecular Systems

Recently, the unique electronic structures and highly efficient functionalities in open-shell singlet molecules have attracted much attention both theoretically and experimentally. First, we have clarified the open-shell character dependences of the second hyperpolarizability γ for rectangular-shaped tetraradicaloid models, such as diradical dimers, using numerically exact solutions of the extended Hubbard model. The system shows two kinds of enhancements of the γ components, $\gamma_{\rm intra}$ and $\gamma_{\rm inter}$ (caused, respectively, by intra- and intermolecular diradical interactions): (i) a system with a large $y_{\rm intra}$ ($y_{\rm inter}$) (> ~0.4) exhibits the enhancement of a single component of γ, $\gamma_{\rm inter}$ ($\gamma_{\rm intra}$), at the intermediate $y_{\rm inter}$ ($y_{\rm intra}$) region (~0.3–0.4), and (ii) the system exhibits a further enhancement of both components of γ ($\gamma_{\rm intra}$ and $\gamma_{\rm inter}$) at the region where $y_{\rm intra} \sim y_{\rm inter}$ with small values (≤ ~0.3). The obtained relationships are verified by using ab initio quantum chemical calculations of the realistic tertraradical models of a 4,4'-bis(1,2,3,5-dithiazdiazolyl) (BDTDA) dimer and a disilene dimer. Second, we have investigated the y–γ correlation of a new class of open-shell NLO molecules, alkaline earth metal inverse sandwich complexes, and found that the y value can be controlled by the metal species (Ca, Mg) and ring ligands (cyclopentadienyl, cyclooctatetraene). A combination of higher period alkaline earth metal and larger organic antiaromatic ($4n\pi$) ring is found to enhance the γ due to the intermediate diradical character and large effective diradical distance.

Visiting Associate Professor

NAKAYAMA, Akira *(from Hokkaido University)*

First-Principles Simulations of the Molecular Process at the Interface of Liquid/Metal-Oxide

A detailed understanding of the interface between liquid and metal-oxide is fundamental due to its relevance to the broad range of physicochemical phenomena and technological applications. To provide insight into microscopic structures and dynamics at the interface, we perform the first-principles molecular dynamics simulations and unveil the intricate molecular process occurring at the liquid/metal-oxide interface. In this year, we have focused on the catalytic reactions at the water/CeO_2 and methanol/CeO_2 interfaces and investigated the role of acid-base and redox sites over CeO_2. In particular, we have worked on the following topics: (1) Structure and dynamical properties of water molecules at the water/CeO_2 interface. (2) Substrate-specific adsorption of 2-cyanopyridine and hydration reaction over CeO_2. (3) Formation of a strong base site by hybridization of 2-cyanopyridine and CeO_2. (4) The reaction mechanism for the direct synthesis of dimethyl carbonate from methanol and CO_2 over CeO_2.

Visiting Associate Professor

KIM, Kang *(from Osaka University)*

Theoretical and Computational Research for Complex Fluids and Soft Matters

We are working on theoretical and simulation approaches to reveal various dynamical processes in complex fluids and soft matters. Recent topics frequently occurred in my research are multiple time and length scales in disordered and glassy systems. In particular, we have revealed the spatio-temporal structures of dynamic heterogeneities using molecular dynamics simulations. It is demonstrated that those spatially heterogeneous dynamics are closely relevant with the anomalous rheological behaviors including the violation of Stokes-Einstein relation. Furthermore, we have developed a supercooled liquid model, for which we can systematically control the manner of structural relaxation widely ranging from silica-like to metallic-like glasses.

RESEARCH ACTIVITIES

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 collaborates with the Department.

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

Exploring Quantum-Classical Boundary

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Education

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Professional Employment

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2003	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2004	Visiting Professor, Tohoku University (–2005)
2007	Visiting Professor, Tokyo Institute of Technology (–2008)
2009	Visiting Professor, The University of Tokyo (–2011)
2012	Visiting Professor, 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
2009	Fellow of the American Physical Society
2012	Humboldt Research Award
2017	Hiroshi Takuma Memorial Prize of Matsuo Foundation
2018	Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology of Japan

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MENG, Zengming
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TIRUMALASETTY PANDURANGA, Mahesh*
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CHEW, Yee Lai
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KAWAMOTO, Minako

Keywords Quantum-Classical Boundary, Quantum Technology, Coherent Control

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 a bulk solid composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as “collapse” in quantum mechanics, is often accepted as a discontinuous event, but a basic question arises: When and how the delocalized wave function becomes localized? Our dream is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this dream 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 such as an ensemble of ultracold Rydberg atoms, as depicted schematically in Figure 1, and a bulk solid, envisaging the quantum-classical boundary connected smoothly.

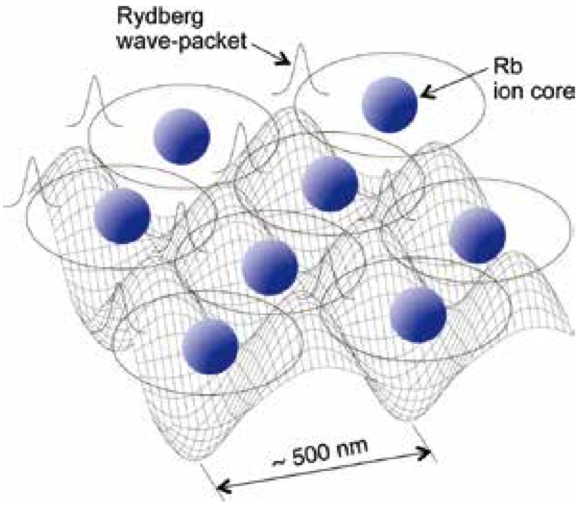

Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.[2)]

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,” *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, “All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth,” *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, “Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas,” *Nat. Commun.* **7**, 13449 (2016).

1. Ultrafast Coherent Control of Condensed Matter with Attosecond Precision[3)]

Coherent control is a technique to manipulate wave functions of matter with light. Coherent control of isolated atoms and molecules in the gas phase is well-understood and developed since the 1990s, whereas its application to condensed matter is more difficult because its coherence lifetime is shorter. We have recently applied this technique to condensed matter samples, one of which is solid *para*-hydrogen (p-H_2). Intramolecular vibrational excitation of solid p-H_2 gives an excited vibrational wave function called a "vibron," which is delocalized over many hydrogen molecules in a manner similar to a Frenkel exciton. It has a long coherence lifetime, so we have chosen solid p-H_2 as our first target in the condensed phase. We shine a time-delayed pair of femtosecond laser pulses on p-H_2 to generate vibrons. Their interference results in modulation of the amplitude of their superposition. Scanning the interpulse delay on the attosecond time scale gives a high interferometric contrast, which demonstrates the possibility of using solid p-H_2 as a carrier of information encoded in the vibrons.

In the second example, we have controlled the terahertz collective phonon motion, called a "coherent phonon," of a single crystal of bismuth. We employ an intensity-modulated laser pulse, whose temporal envelope is modulated with terahertz frequency by overlap of two positively chirped laser pulses with their adjustable time delay. This modulated laser pulse is shined on the bismuth crystal to excite its two orthogonal phonon modes. Their relative amplitudes are controlled by tuning the delay between the two chirped pulses on the attosecond time scale. Two-dimensional atomic motion in the crystal is thus controlled arbitrarily. The method is based on the simple, robust, and universal concept that in any physical system, two-dimensional particle motion is decomposed into two orthogonal one-dimensional motions, and thus, it is applicable to a variety of condensed matter systems.

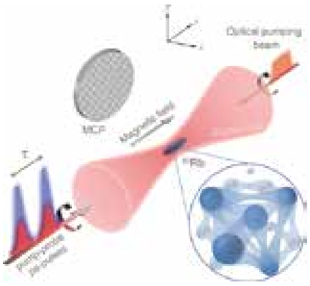

Figure 2. Schematic diagram of the experimental setup for the observation of ultrafast many-body electron dynamics in a strongly correlated ultracold Rydberg gas.[3)]

In the third example, the double-pulse interferometry used for solid p-H_2 has been applied to many-body electronic wave functions of an ensemble of ultracold rubidium Rydberg atoms, hereafter called a "strongly correlated ultracold Rydberg gas," as shown in Figure 2. This has allowed the observation and control of many-body electron dynamics of more than 40 Rydberg atoms interacting with each other. This new combination of ultrafast coherent control and ultracold atoms offers a versatile platform to precisely observe and manipulate nonequilibrium dynamics of quantum many-body systems on the ultrashort time scale.

2. Attosecond Control of Electronic Structure Symmetry Restoration[4)]

Laser pulses can break the electronic structure symmetry of atoms and molecules by preparing a superposition of states with different irreducible representations. Here, we discover the reverse process, symmetry restoration, by means of two circularly polarized laser pulses. The laser pulse for symmetry restoration is designed as copy of the pulse for symmetry breaking. Symmetry restoration is achieved if the time delay is chosen such that the superposed states have the same phases at the temporal center. This condition must be satisfied with precision of a few attoseconds. Numerical simulations are presented for the C_6H_6 molecule and ^{87}Rb atom as shown in Figure 3. The experimental feasibility of symmetry restoration is demonstrated by means of high-contrast time-dependent Ramsey interferometry of the ultracold ^{87}Rb atom.

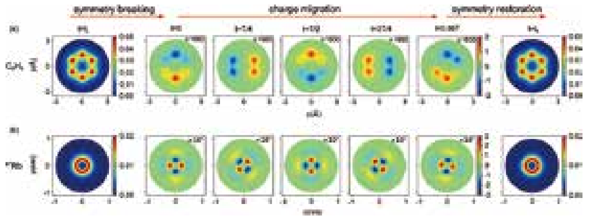

Figure 3. Numerical simulations of the evolutions of electronic densities upon laser-induced symmetry breaking, charge migration, and symmetry restoration in the (a) C_6H_6 molecule and (b) ^{87}Rb atom. The central panels show snapshots of the time-dependent parts of their electronic densities.[4)]

References

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3) H. Katsuki *et al.*, *Acc. Chem. Res.* **51**, 1174–1184 (2018).
4) C. Liu *et al.*, *Phys. Rev. Lett.* **121**, 173201 (2018).

Awards

OHMORI, Kenji; Hiroshi Takuma Memorial Prize of Matsuo Foundation (2017).
OHMORI, Kenji; Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology of Japan (2018).

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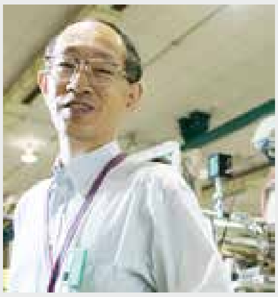
‡ carrying out graduate research on Cooperative Education Program of IMS with Nara Institute of Science and Technology

Local Chemical State Analysis Using Soft X-Rays: Experiment and Theory

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



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Education

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Professional Employment

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1982	Research Associate, The University of Tokyo
1988	Lecturer, The University of Tokyo
1989	Associate Professor, Kyoto University
1993	Professor, Institute for Molecular Science
1993	Professor, The Graduate University for Advanced Studies
2018	Director, Institute of Materials Structure Science, KEK
1996	Visiting Professor, McMaster University, Canada
2008	Visiting Professor, Université P&M Curie - Paris VI, France
2011	Visiting Professor, Université Paris-Sud - Paris XI, France
2013	Visiting Professor, Freie Universität Berlin, Germany

Award

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YUZAWA, Hayato

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VU, Anna A.*

Secretary
INAGAKI, Itsuko

Keywords X-Ray Spectroscopy, Local Chemical State Analysis, Quantum Chemistry

This research group has strong international network in the field of soft X-ray molecular sciences using world-leading advanced synchrotron radiation facilities for more than 20 years.

Soft X-rays cannot pass through air or bulk water due to photoabsorption of N_2, O_2, and H_2O molecules. Such strong photoabsorption can be used in highly sensitive chemical state analysis of thin or dilute samples, because soft X-rays with photon energies of 100–700 eV excite 1s inner-shell (K-shell) electrons of chemically important light elements such as C, N, and O selectively to unoccupied states of molecules. The 1s electron is localized and bound by an atom in the system but is slightly affected by surrounding atoms and chemical bonds. Therefore, we can select a 1s electron in each atom in molecules by choosing different X-ray energies with 10–100 meV accuracy, and know each atomic component and chemical environment in the unoccupied state.

In order to realize *in situ* and *in operando* chemical state analysis revealing local electronic structures and weak intermolecular interactions in molecular systems such as organic solids, liquids, aqueous solutions, and molecular clusters, we are developing and improving several kinds of thin sample cells, detection systems, and spectro-microscopic techniques in X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). We are also using resonant and non-resonant X-ray emission spectroscopy (XES) and angle-resolved photoelectron spectroscopy (ARPES).

Sample thickness should be optimized below 1 μm to get optimal absorbance in XAS. For inhomogeneous samples, the 10 nm-scale spatial resolution is necessary. It is also important to reduce the radiation damage of samples due to strong light-matter interaction in the soft X-ray region.

Highly brilliant soft X-rays for the chemical state analysis are available on our UVSOR-III Synchrotron in IMS. In addition to quite unique experimental and instrumental developments at UVSOR-III BL3U, BL4U and BL6U, we are developing an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

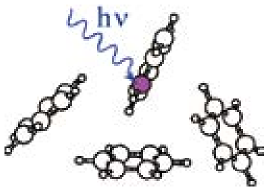

Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

Selected Publications

- M. Nagasaka, H. Yuzawa, T. Horigome, A. P. Hitchcock and N. Kosugi, "Electrochemical Reaction of Aqueous Iron Sulfate Solutions Studied by Fe L-Edge Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. C* **117**, 16343–16348 (2013).
- M. Nagasaka, K. Mochizuki, V. Leloup and N. Kosugi, "Local Structures of Methanol-Water Binary Solutions Studied by Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. B* **118**, 4388–4396 (2014).
- H. Yamane and N. Kosugi, "Substituent-Induced Intermolecular Interaction in Organic Crystals Revealed by Precise Band Dispersion Mesurements," *Phys. Rev. Lett.* **111**, 086602 (5 pages) (2013).

1. Temperature Dependent Structural Changes in Liquid Benzene

Benzene is the simplest aromatic molecule with a possibility of several kinds of intermolecular π–π interactions. Since ordered liquids are key structures to study chemical and biological phenomena in the liquid state, ordered structures of benzene confined in nanopores have been extensively studied, whereas those in the liquid state are still unknown. In this study, we address fundamental questions whether ordered structures of benzene are formed in the liquid state by using carbon K-edge X-ray absorption spectroscopy (XAS) as a sensitive local probe.

The experiments were performed at soft X-ray undulator beamline BL3U at UVSOR-III Synchrotron. Figure 2(a) shows C K-edge XAS of liquid benzene at different temperatures. The energy shifts of the solid at −193 °C1) and clusters2) from the gas peak are −55 meV and −70 meV, respectively. The energy shift of liquid benzene is between the gas and the solid at −193 °C. Figure 2(b) shows the energy shift of the π* peak of liquid benzene relative to benzene gas as a function of temperature. The π* peak of liquid benzene shows a lower energy shift with increasing temperature. Although the π* peak of liquid benzene should be approaching that of gaseous benzene with increasing temperature, the experimentally observed energy shift of the π* peak goes into the opposite direction.

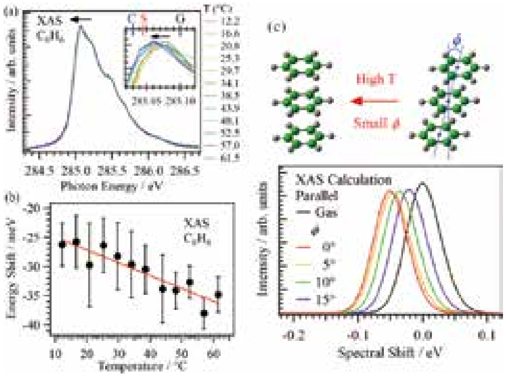

Figure 2. (a) C K-edge XAS of liquid benzene at different temperatures. (G), (S), and (C) are the peaks of gas, solid, and clusters, respectively. (b) Energy shifts of the π* peak as a function of temperature. (c) Calculated spectral shifts of parallel structures at the different angles ϕ, which become smaller at higher temperatures (*T*).

For understanding the characteristic temperature behavior of the π* peak shift in C K-edge XAS of liquid benzene, we have performed molecular dynamics simulation and inner-shell calculation based on quantum chemistry. In radial distribution functions of parallel structures in liquid benzene, the components of small intermolecular distance become abundant by increasing temperature. Figure 2(c) shows inner-shell spectra of benzene trimers at different angle ϕ in parallel structures. The π* peaks show lower energy shifts with decreasing the tilt angle ϕ of the parallel displaced structures. Since the angle ϕ in the parallel displaced structure becomes smaller by increasing temperature, these spectral shifts suggest that parallel displaced structures in liquid benzene are changed to sandwich (parallel non-displaced) structures for the higher temperature.

2. Microfluidics of Liquid Mixtures Observed by Spatially-Resolved XAS

Microfluidics is a technique for efficient chemical reactions, interfaces, and transport processes in the liquid phase.3) Although XAS is an element specific method to reveal structures of liquids by microfluidics, the application of XAS to microfluidics is difficult since soft X-rays cannot deeply penetrate a microfluidic cell. In this study, we have developed a microfluidic cell, where a T-shape microfluidic setup with the width and thickness of 50 μm is made of PDMS resin and is covered by a 100 nm thick Si_3N_4 membrane.

Figure 3(a) shows a soft X-ray fluorescence image of the T-shape microfluidic cell excited by soft X-rays at 550 eV. The spatial resolution of this image is 30 × 30 μm^2. The fluorescence shows high intensity at the water part and low intensity at the pyridine part. A laminar flow of pyridine and water is observed in the mixed part of the microfluidic cell. As shown in Figure 3(b), the π* peak of pyridine in N K-edge XAS shows a higher energy shift from the pyridine to water part across the mixed part due to the formation of hydrogen bond between pyridine and water.4) This energy shift indicates that the phase separation in the laminar flow is clearly observed by spatially resolved XAS. This spectroscopic technique will be applicable to only to liquid mixtures but also to chemical and biological reactions.

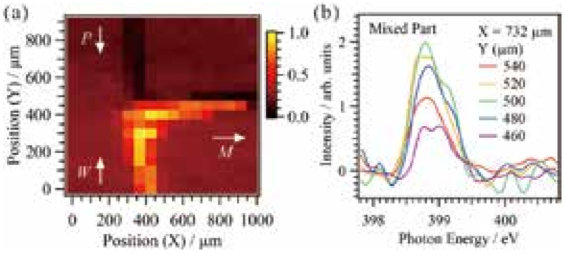

Figure 3. Soft X-ray fluorescence image of a T-shaped microfluidic cell excited by soft X-rays at 550 eV. Pyridine (*P*) and water (*W*) flow in the upper and lower sides, respectively, and the laminar flow is observed in the mixed part (*M*). (b) N K-edge XAS at different positions in the mixed part shown in (a). The horizontal position is fixed to *X* = 732 μm, and the vertical position is scanned.

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4) M. Nagasaka *et al.*, *Z. Phys. Chem.* **232**, 705 (2018).

Award

NAGASAKA, Masanari; Young Scientist Awards of the Japan Society for Molecular Science (2017).

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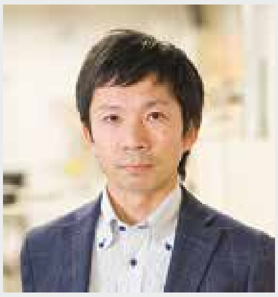
* IMS International Internship Program

Electronic Property of Functional Organic Materials

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



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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

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MASUDA, Michiko

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 were sometimes challenging 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 key to precisely investigate the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the weak electronic interaction appears as small intensity modulations of fine features 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, weak band dispersion, and dynamic electronic polarization. To elucidate what really impacts 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 would be 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.

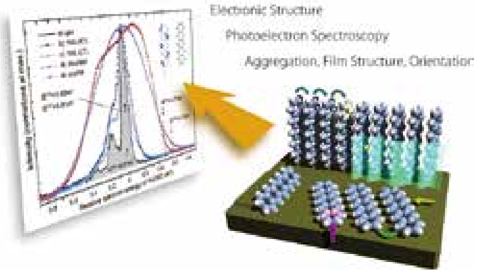

Figure 1. Scheme of a rich assortment of structures of functional molecular materials and spectral features of ultraviolet photoelectron spectroscopy (UPS) for the highest occupied molecular orbital (HOMO), measured for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- S. Kera, T. Hosokai and S. Duhm, "Characteristics of Organic–Metal Interaction: A Perspective from Bonding Distance to Orbital Delocalization," *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, "Origin and Role of Gap States in Organic Semiconductor: As the Nature of Organic Molecular Crystals," *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]
- S. Kera and N. Ueno, "Photoelectron Spectroscopy on the Charge Reorganization Energy and Small Polaron Binding Energy of Molecular Film," *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. Evolution of Intermolecular Energy Bands in Organic Thin Films[1)]

In organic semiconductors, the hole and electron transport occurs through the intermolecular overlaps of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), respectively. A measure of such intermolecular electronic coupling is the transfer integral (t), which can experimentally be observed as energy level splittings or the width of the respective energy bands. Quantum chemistry textbooks describe how an energy level splits into two levels in molecular dimers, into three levels in trimers and evolves into an energy band in infinite systems, a process that has never been observed for the LUMO or beyond dimers for the HOMO. In this work, our new technique, low-energy inverse photoelectron spectroscopy (LEIPS), was applied to observe the subtle change of the spectral line shape of a LUMO-derived feature while we used ultraviolet photoelectron spectroscopy (UPS) to investigate the occupied states. We show at first that tin-phthalocyanine molecules (SnPc) grow layer-by-layer in quasi one-dimensional stacks on graphite, and then discuss a characteristic and systematic broadening of the spectral line shapes of both HOMO and LUMO. The results are interpreted as energy-level splittings due to the intermolecular electronic couplings. On the basis of the Hückel approximation, we determined the transfer integrals for HOMO−1, HOMO, and LUMO to be ~15 meV, ~100 meV, and ~128 meV, respectively.

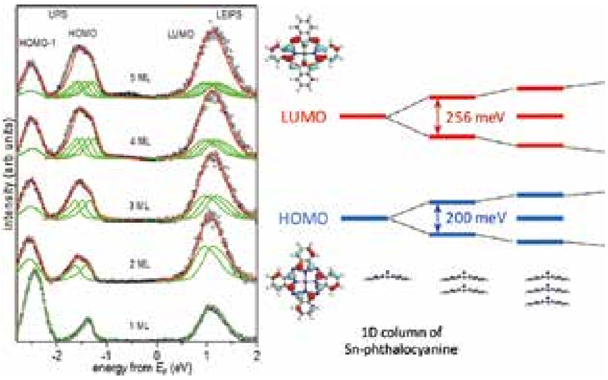

Figure 2. Left: Combined UPS and LEIPS spectra of SnPc films prepared on graphite (HOPG), with the thickness ranging between 1 and 5 monolayer (ML). The experimental data (open circles) are reproduced with the sum (red lines) of several spectral line shapes of the 1 ML peak (green lines) based on the energy levels calculated by Hückel model. Right: Energy splittings of HOMO and LUMO due to intermolecular orbital interaction. Corresponding orbital distributions are schematically shown together with quasi one-dimensional molecular stacking.

2. Efficient Organic Semiconductor Doping[2)]

Doping plays a crucial role in semiconductor physics, with n-doping being controlled by the ionization energy of the impurity relative to the conduction band edge. In organic semiconductors, efficient doping is dominated by various effects that are currently not well understood. Here, we simulate and experimentally measure, with direct and inverse photoemission spectroscopies, the density of states and the Fermi level position of the prototypical materials C_{60} and zinc phthalocyanine n-doped with highly efficient benzimidazoline radicals (2-Cyc-DMBI). We simulate the electronic states of nanoclusters with different molecules in the centre surrounded by up to 14 additional C_{60} molecules to describe the near-field dielectric screening of charge distributions, and evaluate various charging states of the molecules in the centre of the clusters and their charging energies (EA and IP), and thereby construct the DOS of the doped system. We study the role of doping-induced gap states, and, in particular, of the difference Δ_1 between the electron affinity of the undoped material and the ionization potential of its doped counterpart. We show that this parameter is critical for the generation of free carriers and influences the conductivity of the doped films. Efficient dopants should be optimized with regard to the molecular doping parameter Δ_1, which is crucial in organic semiconductors but does not exist in traditional inorganic semiconductors because of the strong screening of electrostatic effects in inorganic materials.

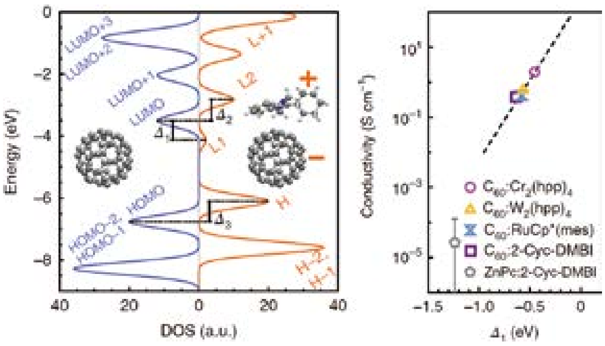

Figure 3. Left: DOS for neutral C_{60} (blue) and charged C_{60} next to a dopant (orange) in neat C_{60} bulk (14 molecules). Energy zero is aligned to vacuum and a Gaussian broadening of 0.2 eV is applied for illustration purposes. The introduction of dopants modifies the DOS of neat C_{60} considerably. While almost all levels of the anion shift upwards, the only one that shifts downwards is the occupied former LUMO of C_{60} (L1). Right: Conductivities in n-doped C_{60} at 2% concentration against Δ_1 for various molecular dopants. Tuning of Δ_1 may provide alternative strategies to optimize the electronic properties of organic semiconductors.

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2) C. Gaul, M. Schwarze, S. Schellhammer, F. Bussolotti, S. Kera, Z. Bao, G. Cuniberti, K. Leo and F. Ortmann, *Nat. Mater.* **17**, 439–444 (2018).

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* JSPS Summer Program

Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Beam Physics, Astrobiology

UVSOR is a synchrotron light source providing low energy synchrotron light ranging from terahertz wave to soft X-rays. Although it was constructed about 30 years ago, its performance is still in the world top level. This is the result of the continuous effort on improving the machine. Our research group has been developing accelerator technologies toward producing bright and stable synchrotron light, such as high brightness electron beam optics, novel insertion devices or state-of-the-art beam injection technique. We have been also developing novel light source technologies toward producing photons with novel properties, such as free electron laser, coherent synchrotron radiation, optical vortices and laser Compton gamma-rays. We are also investigating beam physics which would be the basis of the novel light source technologies. We are exploring a future plan for the facility.

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

Selected Publications

- S. Bielawski, C. Evain, T. Hara, M. Hosaka, M. Katoh, S. Kimura, A. Mochihashi, M. Shimada, C. Szwaj, T. Takahashi and Y. Takashima, "Tunable Narrowband Terahertz Emission from Mastered Laser–Eelectron Beam Interaction," *Nat. Phys.* **4**, 390–393 (2008).
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- 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).
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- S. Matsuba, K. Kawase, A. Miyamoto, S. Sasaki, M. Fujimoto, T. Konomi, N. Yamamoto, M. Hosaka and M. Katoh, "Generation of Vector Beam with Tandem Helical Undulators," *Appl. Phys. Lett.* **113**, 021106 (2018).

1. Light Source Technology Developments Based on Laser and Synchrotron

We have developed novel 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 for developing novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beam-line. In these years, we are focusing on generation of structured light, such as vortex beams and vector beams from undulators, in collaboration with Hiroshima Univ. and Nagoya Univ. We have succeeded in producing such novel photon beams from undulators for the first time. We are exploring their applications in collaboration with Saga Light Source and Toyama Univ.

We have been investigating laser Compton scattering at BL1U to produce monochromatic and energy-tunable gamma-rays. Now we are exploring their applications such as isotope imaging based on nuclear fluorescence resonance in collaboration with Kyoto Univ., AIST and QST, photon-induced positron annihilation lifetime spectroscopy in collaboration with Yamagata Univ. and AIST and an experimental verification on Delbruck scattering in collaboration with QST, AIST and Kyoto Univ. We have reconstructed the resonator free electron laser to produce more intense gamma-rays through intra-cavity inverse Compton scattering. Moreover, theoretically we have proven that vortex photons carrying orbital angular momentum can be produced by non-linear Compton scattering of circularly polarized photons. We are planning its experimental demonstration at BL1U in collaboration with AIST.

2. Accelerator Technology Developments for Synchrotron Light Source and Free Electron Laser

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

Currently, the storage ring is stably operated for many of the users, however, the requirements from the users for the stability is getting higher and higher. We are improving cooling water system and developing various feedback systems. As a near future upgrade plan, we are considering to replace some of the undulators to fit the changes of the users' requirements on the wavelength. As a long term plan, we have designed new accelerator systems such as a linear accelerator based free electron laser or diffraction limited storage ring light source. We are going to continue improving these plans.

We are collaborating with Nagoya University Synchrotron Radiation Research Center (NUSR) for the accelerator technology developments. Accelerator magnets based on permanent magnets are being developed, which would contribute to the power consumption saving in the future plan. Various high brightness electron sources are being developed and tested. New beam diagnostic technologies toward beam stabilization are being developed. Several PhD students from the University are involved in these studies.

We are also collaborating with Accelerator Research Laboratory at KEK for the compact Energy Recovery Linac (cERL) project, which is a novel electron accelerator toward a diffraction-limited synchrotron light source and a free electron laser.

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

Figure 3. Optical Cavity for Resonator Free Electron Laser.

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

Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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IKEMOTO, Masafumi†
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Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials has 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), a powerful tool in studying the electronic structure of complex materials, based on synchrotron radiation.

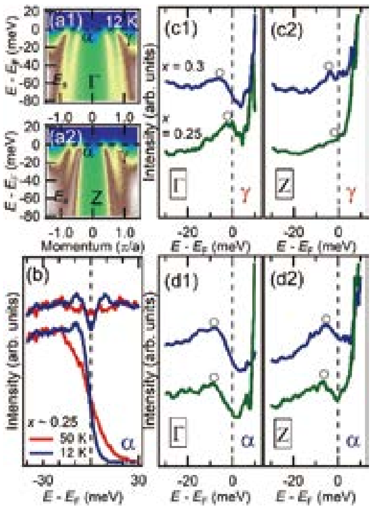

Figure 1. The superconducting (SC)-gap distribution on the hole FSs of K-Ba122 (x ~ 0.25). (a1)–(b2) The photoemission intensities taken along two momentum cuts near the BZ center with 21 and 32 eV photons. (b) Temperature dependence of ARPES spectra on K-Ba122 (x ~ 0.25) of k_F position at the Γ point. (c1), (c2) EDCs of the γ band at k_F position divided by Fermi-Dirac (FD) distribution function for K-Ba122 (x ~ 0.25, 0.3). (d1) and (d2) are the same as in panel (c1) and (c2) of the α band. The gray circles in (c1)–(d2) are guides to the eyes for the value of the superconducting gap.

Selected Publications

- K. Tanaka, T. Yoshida, A. Fujimori, D. H. Lu, Z.-X. Shen, X.-J. Zhou, H. Eisaki, Z. Hussain, S. Uchida, Y. Aiura, K. Ono, T. Sugaya, T. Mizuno and I. Terasaki, "Effects of Next-Nearest-Neighbor Hopping t' on the Electronic Structure of Cuprates," *Phys. Rev. B* **70**, 092503 (4 pages) (2004).
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- E. Uykur, K. Tanaka, T. Masui, S. Miyasaka and S. Tajima, "Coexistence of the Pseudogap and the Superconducting Gap Revealed by the c-Axis Optical Study of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$," *J. Phys. Soc. Jpn.* **82**, 033701 (4 pages) (2013).

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

1. Suppression of Superconducting Gap on $Ba_{1-x}K_xFe_2As_2$ Observed by Angle-Resolved Photoemission Spectroscopy

Iron-based superconductors have a complex phase diagram with the antiferromagnetic, structural, and superconducting (SC) transition phases as well as high-T_c cuprates superconductors.[1] Recently, nematicity, defined as broken rotational symmetry [a trigonal (C_4)-to-orthorhombic (C_2) structural transition], has shed light on the understanding of the mechanism on the iron-based superconductivity in the underdoped regime. In hole-doped $BaFe_2As_2$ (Ba122) system, thermal expansion, specific heat, and neutron diffraction measurements of $Ba_{1-x}Na_xFe_2As_2$ and $Ba_{1-x}K_xFe_2As_2$ (K- Ba122) at a certain hole concentration have revealed the magnetic order without C_4 symmetry breaking in the underdoped regime.[2] Besides, these materials show that the SC transition temperature (T_c) is suppressed between the SC phase and the C_4-magnetic phase by ~20–50%. Although these intriguing physical properties have been come into the open in the hole-doped Ba122 system universally, the microscopic mechanism of the C_4-magnetic phase and the T_c suppression has been unclear yet. In this study, we performed ARPES study on underdoped K-Ba122 (x ~ 0.25, T_c ~ 26 K) with the C_4-magnetic phase and T_c suppression, to elucidate the mechanism of superconductivity.

Figures 1(a1) and 1(a2) show the ARPES intensity plot as a function of energy and momentum taken at hν = 21 eV and 32 eV, corresponding to the Γ and Z points, respectively. We observe at least two hole bands for Γ using s polarization, indicating that the degenerated d_{yz}, d_{xz} bands and the d_{xy} band are observed at the Γ point. Hereafter, hole bands at the BZ center are designated as α, β, and γ for the inner, middle, and outer hole FSs, respectively.

In order to elucidate the character of the SC gap on the hole FSs, Figure 1(b) shows the temperature dependence of the near-E_F ARPES spectrum measured across T_c (~26 K) at Fermi momentum (k_F) for the α band. The EDC shows a SC peak in the SC state (12 K) while that disappears in the normal state (50 K). To eliminate the effect of the Fermi-Dirac (FD) distribution function, we have symmetrized the ARPES spectra measured above and below T_c as shown in Figure 1(b). On decreasing temperature, the spectral weight near E_F is transferred to high binding energy below T_c and the symmetrized EDC shows a peak at ~10 meV, suggesting the opening of a SC gap. FD-function-divided EDCs obtained from K-Ba122 (x = 0.25 and 0.3) at the k_F's of the α and γ bands are shown in Figures 1(c1)–2(d2) for comparison. While the SC peak (x = 0.3) is far from the E_F, indicating that the SC gap is observed on the α and γ FSs, we found that the SC peak of x ~ 0.25 moves towards E_F, which indicates the decrease or almost close of SC gaps for the γ band.

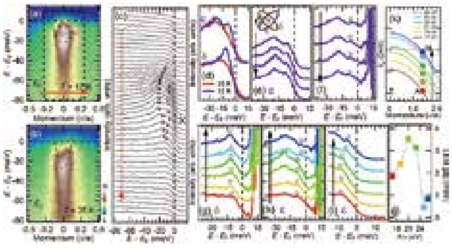

Figure 2. The SC-gap distribution on the electron FSs of K-Ba122 (x ~ 0.25). (a), (b) The photoemission intensities taken at the momentum cut at the BZ corner with 23 eV photons below and above T_c, respectively. (c) Raw spectra of the data in (a) enclosed by a dotted line. (d): Temperature dependence of ARPES spectra for ε and δ bands at k_F. (e), (f) Raw spectra at k_F and that divided by the Fermi-Dirac function on the ε band taken at 23 eV photons. (g), (h) k_z dependence of the spectra divided Fermi-Dirac function measured on the ε and δ electron bands. (i), (j) The expansion of the spectra on the ε FS in the vicinity of E_F and the leading-edge midpoint for each EDC of (i), respectively. Measured k_z's are taken at 17 eV–26 eV photons, corresponding to the k_z of the Γ-Z points shown in (k). The gray circles on the spectra are guides to the eyes for the peak position, reflecting SC gaps.

Figure 2 gives the detailed SC gap distribution of the electron bands designated as ε and δ for the inner and outer electron FSs, respectively. To precisely determine the SC gap size and its momentum dependence, we have performed an ARPES study at several k_F and k_z points of the ε and δ bands. For the k_z direction, while the SC gap for the δ band shows an isotropic gap [Figure 2(g)], the EDC peak position reflecting the SC gap for the ε band does not seem to be constant, namely, the peak position as shown by a gray circle decreases in going from the A to M points [Figure 2(i)]. This indicates that an anisotropic SC gap is exhibited along the k_z direction for the ε FS.

The present ARPES study indicates that the T_c suppression of K-Ba122 (x ~ 0.25) corresponds to the suppressed SC gap on the γ FS and the k_z dependent SC gap on the ε FS. According to the previous ARPES study, the SC gap size on hole FSs was almost identical in optimally doped K-Ba122, which was interpreted by the s^{++}-wave SC gap symmetry due to orbital fluctuations. Though SC gaps on the α and β FSs of K-Ba122 (x ~ 0.25) are identical, that on the γ FS seems not to be explained directly by the orbital fluctuation. The SC gap might be suppressed in the presence of the C_4-magnetic fluctuation, assuming that the presence of the C_4 symmetry of the electronic structure with disappearance of the orbital order. We also find that the ARPES intensity plots of K-Ba122 (x = 0.21, 0.3) at the BZ center show the band folding of the electron-like band, which is known to be observed below the SDW transition temperature in the underdoped regime, but disappears in x ~ 0.25 sample (not shown). Probably recently reported antiferroic electronic instability is suppressed around x ~ 0.25 because of the C_4-magnetic phase fluctuation. Thus, the experimental evidence indicates that the SC gap on the γ FS of K-Ba122 (x ~ 0.25) is strongly influenced by the C_4- magnetic phase.

2. Development of Micro-Focused Beam ARPES

A soft X-ray beamline BL5U has been open for users from 2016 and used as high energy resolution ARPES beamline. By introducing a final focusing mirror close to the sample position (~50 mm), the synchrotron light whose original size was 400 (H) × 120 (V) is successfully focused to 23 (H) × 40 (V) μm. ARPES study on small samples or inhomogeneous samples is now available.

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Comprehensive Photoelectron Diffraction and Spectroscopy for Surface Science

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

MATSUI, Fumihiko
Senior Researcher

Visualization of three-dimensional atomic arrangements of surfaces, interfaces, nanostructures, and molecular adsorbates is essential in materials science and engineering. This is accomplished by holographic reconstruction of element-specific photoelectron diffraction from the localized core level. Furthermore, the electronic properties and chemical reactivity of materials are closely related to the behavior of valence electrons near the Fermi level. Momentum-resolved valence-band (VB) photoelectron spectroscopy is a powerful technique to characterize such electrons. We have been working on the development of wide-acceptance-angle electron energy analyzers for photoelectron angular distribution measurement. In order to establish the reliability of these methods, comprehensive measurement and understanding of the photoelectron emission process are important.1)

1. Valence Band Atomic Orbital Analysis of Layered Compounds

BL6U at UVSOR is a beamline dedicated to VB dispersion mapping with a practical photon energy range of 45 to 600 eV. Wide-acceptance-angle acquisition system enables measurement of full set of VB dispersion data over several Brillouin zones.2) The cross sections of VB from $MoSe_2$ along the $\Gamma_{00\ 11}$M and $\Gamma_{00\ 12}$M directions are shown in Figure 1(a) and (b), respectively, together with the ab initio simulations. The interlayer interaction induces the splitting of the band degenerated at A point into two at Γ point. Band A, B, and C appeared intense at the $\Gamma_{00\ 11}$M plane, while their counterparts, Band A', B', and C' appeared intense at the $\Gamma_{00\ 12}$ M plane. We found that the two split bands appear alternatively in the Brillouin zones along the k_z direction. This 4π-periodic k_z oscillation was also observed for graphite3) and was explained by considering the photoelectron interference from atomic orbitals within the unit cell, *i.e.* photoelectron structure factor. We expanded this concept to the layered compound and investigated the bonding characters of these bands.

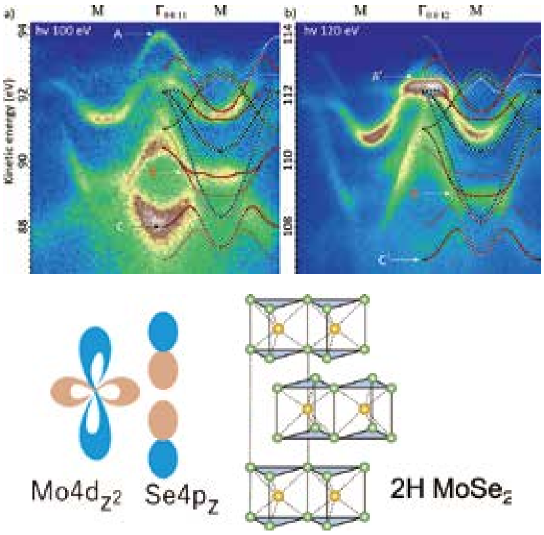

Figure 1. Cross section of $MoSe_2$ VB along the (a) $\Gamma_{00\ 11}$M and (b) $\Gamma_{00\ 12}$M directions together with ab initio simulation. Pairs of black and red dotted curves appear alternatively in the Brillouin zones along the k_z direction. Mo4d_{z^2} is the key-player orbital.

2. Momentum Microscope & PESCATORA

Conventionally, azimuthal and polar scans of sample orientation were required for the angle-resolved photoelectron spectroscopy and diffraction measurements. Aforementioned wide-acceptance-angle acquisition system combines a special mesh for gathering photoelectrons emitted into wide solid angle and a mechanical lens deflector for two-dimensional data acquisition. Alternatively, display-type analyzers enable the direct observation of wide-solid-angle photoelectron intensity distribution from a selected point without changing the angles of incident light or the sample orientation. By combining a photoelectron emission microscope column and two hemispherical deflection analyzers, *i.e. momentum microscope*, iso-energy photoelectron intensity k_x–k_y distribution can be obtained with high-momentum, energy, and spatial resolutions. My mission is to install state-of-the-art momentum microscope to UVSOR and establish a comprehensive photoemission experimental station.

Furthermore, we have recently invented a new type of display-type analyzer called **P**rojector for **ESCA to Re**al space **A**nalysis (PESCATORA) using an electrostatic lens making the trajectory of photoelectrons emitted within 1π steradian into parallel rays and a fine tube array plate as a collimator for energy and angular distribution analysis, realizing the detection of photoelectron diffraction with a high angle resolution.4)

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Photoelectron Spectroscopy of Ionic Liquids and Thin Films Made of Fullerenes and Their Application to Photoelectrochemistry

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

KATAYANAGI, Hideki
Assistant Professor

Electrodes made of fullerenes and their derivatives and electrolytes containing ionic liquids (ILs) are used in the photovoltaic devices such as dye-sensitized solar cells (DSSCs). Both electronic structures and mesoscopic mixing schemes of the materials are key issues which affect their efficiency and lifetime. These structures of materials can be investigated using a combined study of spectroscopic and thermodynamic measurements.

1. Fabrication of LB Film Electrodes of Sulfonated Fullerenes and Evaluation of Their Feasibility for the DSSCs

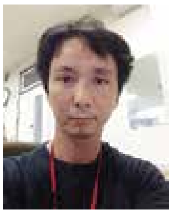
Carbon electrodes are candidates of substitutes for the Pt electrodes which are used in the most of present DSSC cells. To produce the carbon electrodes suitable for DSSC, we utilize the Langmuir-Blodgett (LB) technique and sulfonated fullerenes as building blocks. We first used stearic acid and oleic acid to find out suitable conditions for producing thin and homogeneous LB films. We then fabricated the LB monolayers and multilayers of fullerene/fatty acid mixtures and the sulfonated fullerenes. We found that even the LB monolayers of sulfonated fullerenes have electrochemical reactant selectivity. We are trying to produce homogeneous multilayer films and examine the suitability for DSSC.

2. Stimulation Induced Phase Transition of Crystals of Salicylideneaniline Derivatives

Some crystals have solid phase transition induced by small energy such as mechanical forces and light irradiation. We have measured the Raman spectra of the crystals of salicylideneaniline derivatives before and after the phase transition. The Raman spectra were found to change gradually during the period of the phase transition. We will analyze the change of the Raman spectra and elucidate mechanisms of the transition. Knowledge on the phase transition induced by the small energy in three-dimensional space gives us clue to understand a key to control self-organization in two-dimensional films.

Observation of 3-Dimensional Chemical Nano-Structures of a Cell Nucleus

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji
Assistant Professor

Computed tomography (CT) is a powerful technique to observe 3-dimensional (3D) structure of a sample without any destructive process. In regard to relationship between spatial resolution and transmittance, CT by using a scanning transmission soft X-ray microscope (STXM) is a suitable combination. Moreover, this combination also enables to perform 3D spectro-microscopy by changing energies of incoming X-rays.$^{1)}$

3D distributions of DNA and protein in an isolated cell nucleus of a HeLa S3 at stage 0 (*i.e.* normal cell) were observed. The cell nucleus was fixed by glutaraldehyde and critical point drying without any additional staining. Since X-ray absorption spectra of DNA and protein show remarkable difference in N K-edge, 50 images stacks around N K-edge were acquired with rotating the sample 3.6° each (180° in total). The 3D distributions of DNA and protein were reconstructed after fitting each reference X-ray absorption spectra to the energy stacks. A projection image of 3D distribution of DNA and cross sectional images of distributions of DNA and protein are shown in Figure 1.$^{2)}$ Several cell nucleoli with high density and framework-like structures are clearly observed in Figure 1(b).

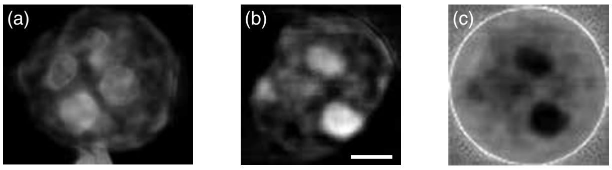


Figure 1. (a) A projection image of 3D distribution of DNA and cross sectional images of distributions of (b) DNA and (c) protein. Scale bar is 2 μm.

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Decay and Dissociation Dynamics of Core Excited Atoms, Molecules and Clusters

UVSOR Synchrotron Facility
Division of Advanced Photochemistry

IWAYAMA, Hiroshi
Assistant Professor

Core excited molecules are highly unstable and relaxes by Auger electron emission for light elements. The stability and dissociation dynamics of the Auger final states depend on their charge states and electronic states. We have investigated them by using an Auger-electron-photoion coincidence technique.

1. Intermolecular Coulombic Decay of Core Excited Nitrogen Molecular Clusters

Intermolecular Coulombic decay is an efficient electronic relaxation of excited molecules placed in a loosely bound chemical system (such as a hydrogen bounded or van-der-Waals-bounded cluster). This decay process ionize neighboring molecules to excited one and eject low-energy electrons, which play an important role in DNA damage induced ionizing radiation. Recently, it was proposed that emission site and energy of the electron released during this process can be controlled by coupling the ICD to a resonant core excitation.[1)]

We investigated ICD process of core excited nitrogen molecular clusters by using Auger-electron ion coincidence technique.[2)] Since ICD process lower the double ionization threshold, we measured binding energy of Auger states corresponding to double ionizations. Compared to isolated nitrogen molecules, we observed lowering of double ionization threshold for nitrogen molecular clusters.

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Award

IWAYAMA, Hiroshi; The 19th Young Scientist Awards of the Atomic Collision Society of Japan (2018).

Visiting Professors

Visiting Professor

KANAI, Kaname *(from Tokyo University of Science)*

Electronic Structure of Donor and Acceptor Interface in Organic Photovoltaics

It have been reported that microscopic structure at donor and acceptor (D/A) interface in organic photovoltaics has a key impact on the device performance. Especially, it has been believed that mixture inhomogeneity of donor and acceptor molecules at the interface significantly influences the efficiencies of free-charge generation and recombination. However, effects of the mixture inhomogeneity on the D/A interface remains elusive yet. Recently, we have been trying to figure out how the mixture inhomogeneity of donor and acceptor molecules affects the interface electronic structure at the D/A interface using photoemission spectroscopy (PES) at BL2B beamline of the UVSOR synchrotron facility. We found that the relatively strong intermolecular interaction between sexithiophenes (6T) and perfluorinated Cu-phthalocyanines (F_{16}CuPc) is key to have disordered molecular arrangements at the D/A interface by STM measurements. Now, we are trying to catch the subtle changes in the energy distribution of the molecular levels of 6T and F_{16}CuPc, respectively, in the mixed films using PES compared with isolated 6T and F_{16}CuPc's films.

Visiting Associate Professor

KANEYASU, Tatsuo *(from SAGA Light Source)*

Generation and Application of Vortex Beams from Synchrotron Light Source

A vortex light beam having a helical wavefront carries orbital angular momentum (OAM) as well as the spin angular momentum associated with its circular polarization. Recently, it was found that the harmonic radiation from a helical undulator carries an OAM. This novel feature of the undulator radiation will allow us to utilize vortex beam at short wavelengths, and may open up new applications in synchrotron radiation research. In exploring new applications of the vortex beams, a fundamental understanding of the role of the OAM in the light-matter interaction is crucial. We have investigated the characteristics of the vortex beam in the extreme ultraviolet (XUV) region and applied it to the photoionization study of rare-gas atoms. To explore the vortex-atom interaction which is hardly observable in the conventional gas-phase experiment, we are developing a new experimental setup based on the combined use of laser and synchrotron light sources. In addition we plan to study the XUV vector beam which has space-varying polarization, and its interaction with atoms.

RESEARCH ACTIVITIES

Materials Molecular Science

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

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

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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

Assistant Professor
TAKAGI, Yasumasa*
UEMURA, Yohei†
KOITAYA, Takanori

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NAKAMURA, Takahiro
YU, Liwei
KOIDE, Akihiro
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Secretary
AOKI, Junko

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

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

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD measurement system contains ultrahigh vacuum sample preparations chamber, with which one can clean substrates (substrate single crystals *etc*.), deposit materials (metallic and molecular magnets *etc*.) and characterize the samples using low energy electron diffraction, reflection high energy electron diffraction and Auger electron spectroscopy. The apparatus is extensively open for public usage and many domestic and foreign researchers visit us every year.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time using Beamline 36XU of SPring-8. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated non-crystalline element by using the energy-resolved x-ray fluorescence detection technique. We have investigated local geometric and electronic structures of the photoexcited states of photocatalysts as WO_3 and $BiVO_4$ which are known to be active for visible light. In WO_3, the photoexcited state around W is ascribed to the electron polaron like state since W is reduced from hexavalent to pentavalent and the local geometric structure around W is significantly distorted.

Within this one year, two assistant professors Drs. Takagi and Uemura moved out and a new assistant professor Dr. Koitaya has just joined our group and one position is now open. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation and lasers.

Selected Publications

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- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Uemura et al., Angew. Chem. Int. Ed. 55, 1364 (2015).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).

1. Local Thermal Expansions and Lattice Strains in Elinvar Alloy[1)]

It is well known that local structures in mixed crystals are often different from lattice structures that are expected crystallographically. Even when the crystal shows clear x-ray diffraction patterns, there should exist strains in the crystal that cannot be solved by the x-ray diffraction analysis. In this work, we have investigated local thermal expansions and lattice strains in the Elinvar alloy $\mathrm{Fe}_{49.66}\mathrm{Ni}_{42.38}\mathrm{Cr}_{5.49}\mathrm{Ti}_{2.47}$ (Ni Span C) and the stainless steel SUS304 $\mathrm{Fe}_{71.98}\mathrm{Ni}_{9.07}\mathrm{Cr}_{18.09}\mathrm{Mn}_{0.86}$ (AISI304) were investigated by the temperature-dependent Cr, Fe, and Ni *K*-edge EXAFS measurements, combined with the path-integral effective classical potential Monte Carlo (PIECP MC) theoretical simulations. From the EXAFS analysis of the Elinvar alloy, the local thermal expansion around Fe is found to be considerably smaller than the ones around Ni and Cr (see Figure 1). This observation can be understood simply because Fe in the Elinvar alloy exhibit an incomplete Invar-like effect. Moreover, in both the Elinvar and SUS304 alloys, the local thermal expansions and the lattice strains around Cr are found to be larger than those around Fe and Ni. From the PIECP MC simulations of both the alloys, the first-nearest neighbor Cr-Fe pair shows extraordinarily large thermal expansion, while the Cr-Cr pair exhibits quite small or even negative thermal expansion. These findings consequently indicate that the lattice strains in both the Elinvar and SUS304 alloys are concentrated predominantly on the Cr atoms. Although the role of Cr in stainless steel has been known to inhibit corrosion by the formation of surface chromium oxide, the present investigation may interestingly suggest that the Cr atoms in the bulk play a hidden new role of absorbing inevitable lattice strains in the alloys.

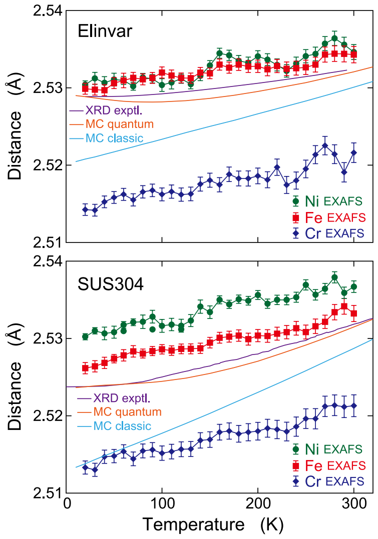

Figure 1. Temperature dependence of the interatomic distances in the Elinvar and SUS304 alloys. The Fe, Ni, and Cr *K*-edge EXAFS analysis are given, together with the results from the powder x-ray diffraction and the calculated results obtained by the present PIECP and the classical MC simulations.

2. Direct Electric Potential Measurements of Electrode Components in an Operating Fuel Cell by Ambient Pressure XPS[2)]

X-ray Photoelectron spectroscopy is usually utilized to investigate chemical states of the elements of interest in various materials. This technique also has the advantage of providing electric potentials of each component in functional materials without using probe electrodes. We performed operando hard X-ray photoelectron spectroscopy (HAXPES) measurements with an 8 keV excitation source to measure the shift in electron kinetic energies as a function of the voltages of all the components at the anode and cathode electrodes of a polymer electrolyte fuel cell (PEFC). At the cathode electrode, when we increase the voltage between the cathode and anode from 0.2 to 1.2 V, the O 1s and F 1s peaks shift to a lower binding energy and the magnitude of the energy shift is equal to the voltage. The Pt 3d and C 1s peaks do not shift with the voltage since platinum nanoparticles and carbon supports at the cathode electrode have ground contact. In contrast to the cathode electrode, the peak shifts of all the components at the anode electrode show the same amount of shift as the voltages. The results are summarized in Figure 2. It is clear that the change in the potential difference occurs only in an electrical double layer at the interface between the cathode electrode (Pt/C) and the electrolyte (Nafion and water), and that the anode electrode is in equilibrium as a pseudo-hydrogen electrode. It should be noted that the electric potential variation of the cathode electrode in a PEFC under a power generation condition was also directly detected by operando HAXPES, although the electric double layer is a well-established concept but is not easy to observe directly.

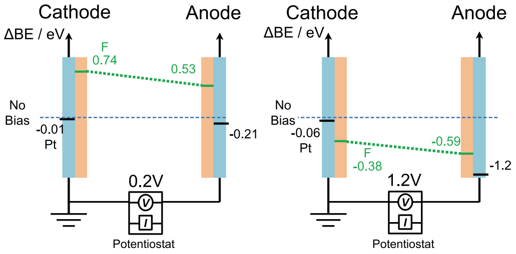

Figure 2. Electric potential diagram of each component in PEFC, where light blue bars correspond to cathode and anode electrodes of Pt (C shows the same potential) and orange to electrolyte Nafion (F and O). At the voltage of 1.2 V between the cathode and anode, a well-known two-step electric double layer is clearly observed (right panel). On the other hand, at 0.2 V, the electrolyte interestingly shows more positive potentials at both the cathode and anode electrodes (left panel).

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Unique Structures, Physicochemical Properties and Quantum Dynamics of Molecular Aggregates at Solid Surfaces

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2009 M.S. The University of Tokyo
2011 Ph.D. The University of Tokyo

Professional Employment
2011 JSPS Research Fellow (DC2)
2011 JSPS Postdoctoral Fellow (PD)
2012 Assistant Professor, Kyoto University
2016 PRESTO Researcher, Japan Science and Technology Agency
2018 Associate Professor, Institute for Molecular Science
2018 Associate Professor, The Graduate University for Advanced Studies

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
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Keywords Water Molecule, Molecular Spectroscopy, Surface Science

Materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. In the case of common water ice, protons in the hydrogen-bond network are strongly correlated and highly frustrated under the Bernal-Fowler-Pauling ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton system. It is, however, extremely difficult to directly access the local configuration of protons and their ordering dynamics through traditional experimental approaches. Moreover, the strongly correlated protons inevitably lose ergodicity at low temperature. These problems prevent us from fully understanding cooperative thermodynamic and electric responses of the many-body protons to external stimuli at the low temperature.

To open up a new route to unveil hidden exotic properties of many-body protons in ice, we have investigated a possibility of interface-induced ferroelectric proton ordering by focusing on heteroepitaxially grown crystalline-ice films on metal substrates as model systems. We have used recently developed phase-resolved sum-frequency generation (SFG) vibrational spectroscopy with heterodyne detection in an ultrahigh vacuum chamber. $\mathrm{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibits positive and negative sign for net-H-up orientation (protons pointing toward vacuum) and net-H-down orientation (toward substrate), respectively. Thus, heterodyne-detected SFG has a great advantage to directly observing local configuration of protons that cannot be investigated through other traditional experimental methods.

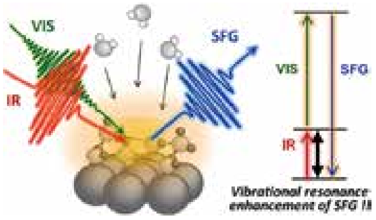

Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe and Y. Matsumoto, “Emergent High-T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film,” *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji, T. Sugimoto, T. Ishisyama, A. Morita, K. Watanabe and Y. Matsumoto, “Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice,” *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, “Origins of Emergent High-T_c Ferroelectric Ordering in Heteroepitaxial Ice Film: Sum-Frequency Generation Spectroscopy of H_2O and D_2O Ice Films on Pt(111),” *Phys. Rev. B* **97**, 075410 (21 pages) (2018).

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

1. Emergent High-T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Proton in Ice$^{1,2)}$

In the hydrogen-bond network of common water ice, protons are strongly correlated and highly frustrated under the ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton systems. Nevertheless, because of the difficulties in directly observing and quantitatively estimating the local configuration of protons and their ordering dynamics with traditional experimental techniques, little has been understood about thermodynamic properties of the protons especially at low temperature, where quantum effects are of potential importance on the emergence of the ordered state deeply hidden under the highly degenerated configurational disorder. Although materials containing strongly correlated and highly frustrated degree of freedom have a potential to exhibit dramatic and unusual response to external stimuli, it has widely been assumed nowadays that inversion-symmetry breaking at heterointerfaces such as crystalline ice films on solid surfaces has no ability to induce protonic ordering.

In contrast to the current belief, we have demonstrated emergent ferroelectric proton ordering in heteroepitaxial ice film on model platinum substrate.$^{1,2)}$ We found such an exotic proton ordering is thermodynamically stable and has an extremely high critical temperature of ~170 K (Figure 2). Anisotropic interaction and protolysis driven by electrostatistics at the interface is a key factor in stimulating exotic ferroelectric ordering of protons in the many-body correlated proton system. The concept of significant increase in T_c by heterointerface also suggests the ubiquity of ferroelectric ice in nature such as space and polar stratosphere.

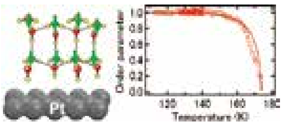

Figure 2. Schematic illustration of net-H-down ferroelectric ordering in ice film on Pt(111) and temperature dependence of the order parameter η normalized by the value at 120 K (red circle).

2. Unveiling Unique Hydrogen-Bond Structure of Ice Surface$^{3)}$

Water ice is one of the most abundant solid substances in nature and its surface plays crucial roles in a variety of processes in physics, chemistry and earth planetary science: Surface premelting for unusual slipperiness in skating and skiing, sublimation and condensation in the atmospheric air and planetary systems, charge generation and separation in thunder cloud, heterogeneous reactions in the Earth's ozone layer and interstellar space, *etc*. Because ice is hydrogen bonded aggregate of water molecules, its surface physicochemical properties are dominated not only by the lattice translational structure (position of oxygen atoms) but also by the sublattice structure (orientations of water molecules or configurations of hydrogen atoms) of ice surface.

A surface of solid is not confined to its topmost layer, but consists of transition layers extending to the bulk: Subsurface. As a result of abrupt truncation of materials, the lattice and electronic structures of surface generally differ from those of the bulk, which results in unique physicochemical properties and heterogeneous processes of solid surface. Thus, structural relaxation and reconstruction at solid surface have been intensively studied by low energy electron diffraction, ion and X-ray scattering, and transmission electron microscopy. Although these conventional analytical techniques have been successfully applied to strongly bonded materials: Metals and semiconductors, they cannot be well applied to fragile and insulating solid substances composed of soft molecular systems such as water ice.

To clarify subsurface structure of ice, we have conducted phase-resolved SFG spectroscopy of ice Ih(0001) and analysed the spectra by molecular dynamics simulations combined with ab initio quantum calculations.$^{4)}$ We found that observed bipolar band shape of the SFG spectra of isotope-diluted OH chromophores is a sensitive indicator of structural rumpling uniquely emerging at the subsurface of ice (Figure 3). In the outermost subsurface between the first (B1) and second (B2) bilayer, the hydrogen bond of O_{B1}–H···O_{B2} is weaker than that of O_{B1}···H–O_{B2}. This implies that subsurface O–O distance is laterally altered, depending on the direction of O–H bond along the surface normal: H-up or H-down, which is in stark contrast to bulk hydrogen bonds. This new finding uncovers how water molecules undercoordinated at the topmost surface influence on the subsurface structural rumpling associated with orientational frustration inherent in water ice. The structural rumpling would play key roles in a variety of anomalous physical and chemical properties of ice surface in nature.

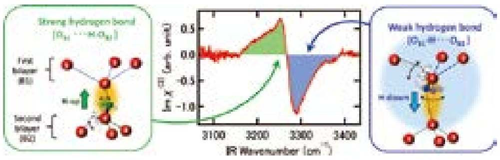

Figure 3. Schematic illustration of subsurface hydrogen-bond network between first and second bilayer of ice-Ih(0001) and the experimentally observed Im$\chi^{(2)}$ spectrum for the hydrogen-bonded OH-stretching band of isotope diluted ice Ih(0001).

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1) T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Nat. Phys.* **12**, 1063–1068 (2016).
2) N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
3) O. Yuji, T. Sugimoto, T. Ishisyama, A. Morita, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **96**, 115405 (14 pages) (2017).

Awards

SUGIMOTO, Toshiki; PCCP Prize 2018.
SUGIMOTO, Toshiki; CSJ Presentation Award 2018.
SUGIMOTO, Toshiki; Encouragement Award, The Spectroscopic Society of Japan (2018).
SUGIMOTO, Toshiki; Morino Foundation for Molecular Science (2018).

Magnetic Resonance Studies for Functional Molecular-Based Solids

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Keywords Organic Conductor, Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR)

Magnetic resonance measurements are advantageous for studying fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Developing an understanding of the electronic phases and functionality of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems and functional materials. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics, and to explore novel functionalities in the field of material science.

In this study, we performed broad-line NMR and ESR measurements on molecular-based conductors to understand electron spin dynamics and functionality in low-temperature electronic phases.

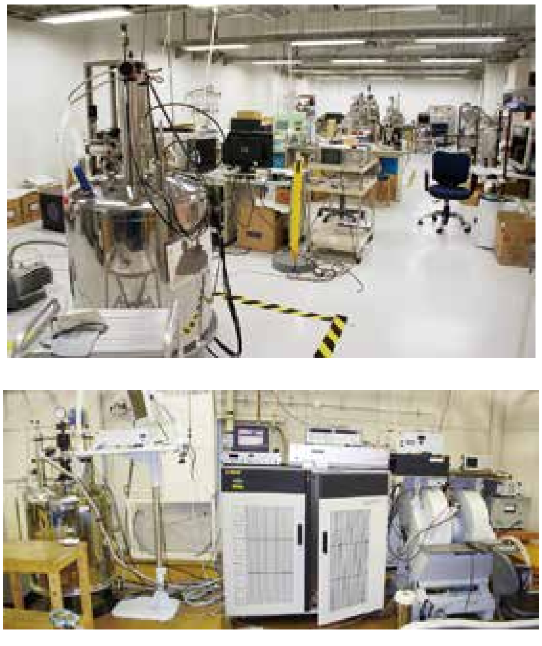

Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- S. Kitou, T. Fujii, T. Kawamoto, N. Katayama, S. Maki, E. Nishibori, K. Sugimoto, M. Takata, T. Nakamura and H. Sawa, *Phys. Rev. Lett.* **119**, 065701 (2017).
- T. E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen and D. Jiang, *Science* **357**, 673–676 (2017).

1. Magnetic Resonance Investigation for Possible Antiferromagnetic Sub-Phase in $(TMTTF)_2Br$

The ground state of $(TMTTF)_2X$ has been believed to be the C-AF(II) phase in the generalized phase diagram so far. Actually, the electronic state of $(TMTTF)_2Br$ at 4.2 K is clarified as a commensurate antiferromagnetic state with wave vector Q = (1/2, 1/4, 0), and the spin configuration is –up–0–down–0–. We performed AFMR and ^{2}D-NMR measurement to understand ground state of $(TMTTF)_2Br$. AFMR measurements shows the increase of the staggered magnetization of the sub-lattice below 4 K. As for ^{2}D-NMR, the nuclear quadrupole relaxation was dominant through electric field gradient. According to the ^{2}D-NMR spectra, the peak number decreases and broad back ground appear at 4 K, suggesting that charge (spin) configuration changes to inhomogeneous or incommensurate. Considering the AFMR and ^{2}D-NMR experimental results, the possible explanation of 4 K anomaly observed in $(TMTTF)_2Br$ is commensurate to incommensurate successive phase transition. Although the step-like 4 K anomaly observed in AFMR support a homogeneous phase transition, we cannot rule out the possibility of homogeneous effect such as discomesuration state at present. At least, we can say that a phase ϕ change anomaly of antiferromagnetic spin configuration occurs around 4 K. It is also very surprising and intriguing, the sub-magnetic phase detected in the present work appears at a temperature around $T_N/4$. Similarly $(TMTSF)_2X$ salts undergo sub-phases at $T_{SDW}/3$ in which the coexistence between CDW and SDW. Further investigation is ongoing, and supports from theoretical approaches for spin and charge distribution are awaited.

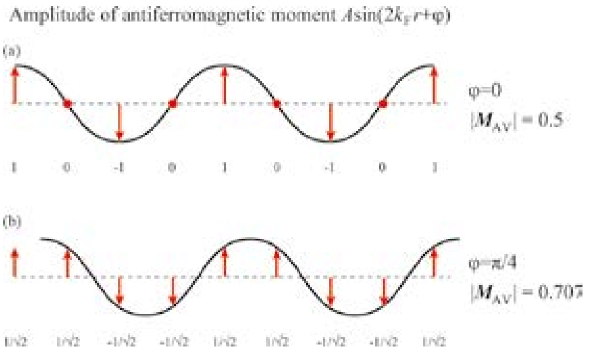

Figure 2. Schematic antiferromagnetic spin configuration for 1/4-filled 1D system along the 1D chain. (a) Spin configuration assuming the antiferromagnetic amplitude follows $A\sin(2k_F r+\phi)$ with $\phi = 0$. The magnetic structure of $(TMTTF)_2Br$ at 4.2 K is thought to have this configuration. (b) Spin configuration assuming $A\sin(2k_F r+\phi)$ with $\phi = \pi/4$.

2. Possibility of Dielectric Material: Nuclear Magnetic Resonance of Oxo-Bridged Dinuclear Ruthenium Mixed-Valence Complex

Since the discovery of mixed-valence compounds such as the Creutz-Taube type complex, the development of mixed-valence compounds and the spectroscopic study of the mixed-valence state have advanced significantly. Investigations into dinuclear and one-dimensional mixed-valence compounds such as those in the diethylbiferrocenium families and halogen-bridged platinum mixed-valence complexes have been particularly significant. The discovery of one-dimensional partial oxidation mixed valence platinum complexes has led to the development of organic conductor research. As for rare earth mixed valence compounds, the electronic properties of (resonance inner 4*f* orbitals) have been attracting much attention. These compounds gave us rich and interesting physical phenomena such as heavy fermion, Kondo-lattice, unconventional superconductivity and non-Fermi liquid. Their fundamental characteristics and electronic nature have been clarified through extensive study. On the other hand, along with the progress of recent research, it is also a fact that new and interesting unresolved problems exist as follows. Possible topological Kondo insulators in rare earth mixed valence compounds have been proposed and discussed. Extensive studies have been carried out for electronic phases in exotic systems such as manganite, magnetite, copper oxide, and so on.

However, recent developments of mixed valence phenomena mainly focus on intermetallic compounds and oxides. There are few studies on electronic states in metal complexes and molecular compounds. The recent progress in charge-ordering and multiferroic phenomena in the field of solid-state physics enhances the desire to redevelop interesting materials. Mixed-valence compounds offer interesting characteristics, such as multi-redox potential, spin-multiplet configurations, a variety of possible building blocks, and potential inter-molecular interactions. Moreover, from the viewpoint of material science, materials that can assume unique valence states and magnetic properties are strongly desired. There is growing momentum toward the research and development of mixed-valence compounds from an electronic functionality point of view. We are interested in systems with moderate valence fluctuations, because intermediate valence and spin states are advantageous for use in electromagnetic switching devices.

Recently, a series of oxo-bridged dinuclear ruthenium mixed-valence complex was systematically synthesized and characterized in three distinct redox states. We focus on the air-stable $[RuORu]^{5+}$ ($Ru^{3+}ORu^{4+}$) complex, and on a description of its electronic properties.

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2) T. Enomoto, M. Kondo, M. Asada, T. Nakamura and S. Masaoka, *J. Phys. Chem. C* **122**, 11282–11287 (2018).
3) T. Nakamura, T. Ikoma and K. Yamada, *Appl. Magn. Reson.* **49**, 755–756(2018).

Organic Solar Cells

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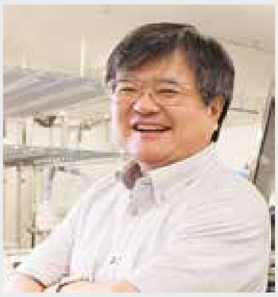

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Professional Employment

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

Awards

2017	11th JSAP Fellow Awards
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Keywords Organic Semiconductors, Organic Solar Cells, ppm-Doping

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. We have been focused on the research on the ppm-Level doping effects in organic semiconductor films and organic single crystals for organic solar cells. We believe that the following features are indispensable. (i) A ppm-doping strategy should be performed on sub-ppm purified organic semiconductors together with the total removal of oxygen from the air, which acts as an external dopant. (ii) Perfect *pn*-control, namely, any single or blended organic semiconductors should exhibit either *n* or *p*-type behavior only by impurity doping. (iii) To precisely clarify the nature of the doping effects, ppm doping in the bulk of organic semiconductor single crystals with few grain boundaries should be performed.

So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching 10^{-9} nm s^{-1} (Figure 1), in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.

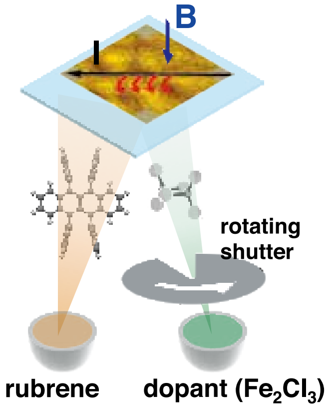

Figure 1. Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

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- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* 1801236 (15 pages) (2018). [Invited Progress Report]
- S. Izawa, N. Shintaku and M. Hiramoto, "Effect of Band Bending and Energy Level Alignment at the Donor/Acceptor Interface on Open-Circuit Voltage in Organic Solar Cells," *J. Phys. Chem. Lett.* **9**, 2914–2918 (2018).
- C. Ohashi, S. Izawa, Y. Shinmura, M. Kikuchi, S. Watase, M. Izaki, H. Naito and M. Hiramoto, "Hall Effect in Bulk-Doped Organic Single Crystal," *Adv. Mater.* **29**, 1605619 (6 pages) (2017).

1. Controlling Open-Circuit Voltage in Organic Solar Cells by Impurity Doping[1)]

Doping, addition of trace amount of *p*-type and *n*-type impurities, to form the *pn* junction is the central technology in inorganic solar cells. However, the doping effect on the energy-level alignment and the performance in organic solar cells (OSCs) are still unclear. Here, we report that the addition of *p*-type (MoO_3) and *n*-type (Cs_2CO_3) dopants into a donor layer in phthalocyanine/fullerene planar heterojunction OSCs controls the open-circuit voltage (V_{OC}). The V_{OC} decreased to 0.36 V when a *p*-type dopant was added to the donor layer, whereas it increased to 0.52 V with an *n*-type dopant. In contrast to the previous reports where *p*-type dopants were usually added to the donor layer, the *n*-type dopant was found to increase the V_{OC}. Energy-level mapping revealed that the origin of the V_{OC} change was the vacuum level shifts occurring near the donor/acceptor (D/A) interface because of the Fermi-level alignment (Figure 2). The results demonstrated that the V_{OC}s in OSCs are largely affected by the energy-level shift near the D/A interface that could be controlled by *p*-type and *n*-type doping.

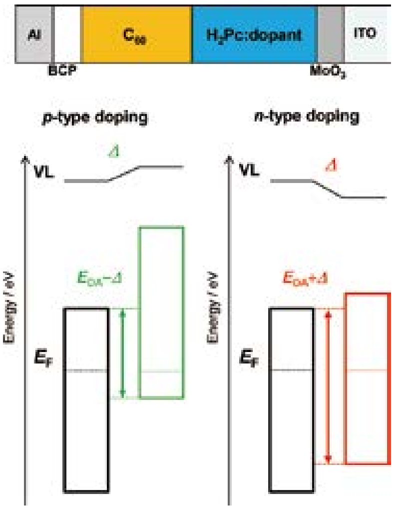

Figure 2. Schematic of the Fermi level alignment at the D/A interface when the phthalocyanine layer is doped with *p*-type and *n*-type dopants.

2. Effect of Trap-Assisted Recombination on Open-Circuit Voltage Loss in Phthalocyanine/Fullerene Solar Cells[2)]

Large energy losses in V_{OC} are still an issue for the photoconversion efficiency of OSCs. We clarify the relationship between charge recombination and V_{OC} loss for phthalocyanine/fullerene planar heterojunction OSCs. We quantify the V_{OC} loss relative to the charge-transfer state energy by the temperature dependence of V_{OC}. The charge recombination order obtained from impedance measurements indicates the presence of trap-assisted recombination (Figure 3). Our results suggest that the V_{OC} losses are caused by the broad distribution of the tail state near the D/A interface. Thus, reducing the number of trap states near the D/A interface could lead to an increase in V_{OC}.

The present results offer the method to increase the open-circuit voltage of organic solar cells.

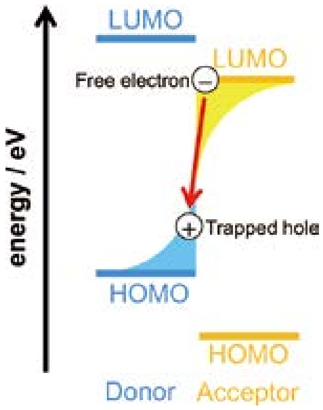

Figure 3. Schematics of the charge recombination process. Trapped holes recombining with free electrons.

References

1) N. Shintaku, M. Hiramoto and S. Izawa, *J. Phys. Chem. C* **122**, 5248–5253 (2018).
2) N. Shintaku, M. Hiramoto and S. Izawa, *Org. Electron.* **55**, 69–74 (2018).

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Solid-State NMR for Molecular Science

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Associate Professor, The Graduate University for Advanced Studies

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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 are varieties of important molecules, which are insoluble to any solvents and functional at amorphous state. Solid-state NMR enables to obtain variety of information at atomic resolution without damages of 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 applications for structural biology and material science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterizations of those molecules based on solid-state NMR are under investigations through collaborations with several research groups.

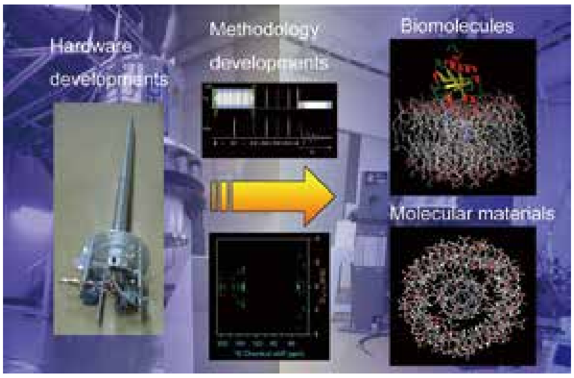

Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, "^{2}H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^{1}H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β-Sheet Structures by High Resolution ^{1}H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
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- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).

1. Extractions of Multiple Distance Information among Carbons Simultaneously from Uniformly ^{13}C Labeled Biomolecules Based on Solid-State NMR[1)]

There are number of organic materials, which are insoluble to any solvent. Solid-state NMR is one of the most powerful tools to provide molecular information for such samples at intact conditions. We have been carried out collaboration studies with many research groups for characterizations of those molecules. We have been collaborated with Prof. Tetsuro Asakura group in Tokyo university agriculture and technology during a couple of years for the characterizations of molecular structure and packing of silk fibroin using solid-state NMR and successfully reported several collaboration works at past.

In this study, applicability of a standard analysis approach developed for proton driven spin diffusion (PDSD) to dipolar assisted rotational resonance (DARR) experiment was verified to extract precise distance information simultaneously for uniformly ^{13}C labeled biomolecules. DARR spectra at several mixing times from 10 to 400 ms were acquired for [U-^{13}C] Ala tetra peptide microcrystal possessing antiparallel β-sheet structure whose atomic coordinates were determined from X-ray crystallography. Normalized cross peak intensities among coupled sites were plotted respect to the mixing times. Then the best fit curves were calculated based on two different approaches with and without considering experimentally obtained zero-quantum line shape function. The obtained distances were compared with the ones from X-ray crystallography. The obtained interatomic distances were well fit to the ones from X-ray crystallography in the range of 1.0–6.0 Å with the standard deviation of 0.244 Å, without considering the zero-quantum line-shape functions.

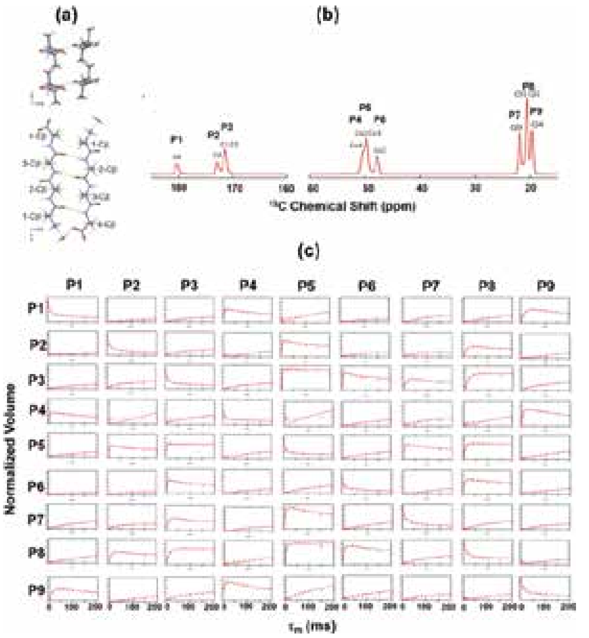

Figure 2. (a) X-ray crystallographic structure and (b) the ^{13}C CP/MAS spectrum of [U-^{13}C] AP-β-Ala$_4$. The bold numbers in (b) correspond to the numbers of the following matrix element numbers. (c) Build-up curves of AP-β-Ala$_4$ observed with DARR. The numbers shown for the peaks observed and labeled in (b).

Currently, we are also collaborating with several other research groups for characterizations of natural products, newly designed synthetic polymers, and new molecular materials, based on solid-state NMR.

2. Structural Characterization of Amyloid Peptide Oligomer Promoted on Lipid Bilayers Using Solid-State NMR

Amyloid β (Aβ) peptides exhibit random structures in solution, however after incubation, those conform insoluble amyloid fibrils, which are found in senile plaque as hallmark of Alzheimer's disease. Although, their structures have been characterized precisely, molecular mechanism of formation of the amyloid fibrils in human brain has not been clarified. Accumulated evidences strongly suggest that an initial stage of aggregation may be promoted on surface of neuronal membrane, and ganglioside GM1 specifically interacting with Aβ may play important roles for the binding of Aβ to the surface of neuronal membrane.

In current study, to clarify the contribution of GM1 in fibrillation process, we have been attempted to characterize oligomeric structure of Aβ(1-40) bound to lipid bilayers consisting of GM1 and DMPC. NMR measurements for sequential signal assignments have been completed. Currently, additional ^{13}C through space homonuclear correlation spectra are under measurements for the sample whose 4 types of amino-acid residues are selectively ^{13}C enriched to verify validity of signal assignments obtained from the analyses of various ^{13}C homonuclear and ^{13}C-^{15}N heteronuclear correlation spectra. In addition, correlation peaks among remote sites in ^{13}C through space homonuclear correlation spectra are under investigation to clarify intermolecular packing of Aβ (1-40).

Currently, we are also collaborating with other research groups for characterizations of amyloid fibrils using solid-state NMR.

Reference

1) A. Naito, K. Okushita, K. Nishimura, G. S. Boutis, A. Aoki and T. Asakura, *J. Phys. Chem. B* **122**, 2715–2724 (2018).

Study on Ion Conductive Materials for Novel Energy Storage/Conversion Devices

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2018	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

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2010	ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011	Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018	The 39th Honda Memorial Young Researcher Award, The Honda Memorial Fundation

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Keywords Solid State Ionics, Oxyhydride, Battery

Chemical energy conversion/storage using electrochemical devices such as fuel cells and batteries will become increasingly important for future sustainable societies. As ion transport in solids is key for determining the performance of these devices, an improved understanding of the characteristics of existing electrode and electrolyte materials is required. For example, crystal structure, thermal stability, and reaction mechanisms are important to enhancing battery performance. Furthermore, the development of novel ion conduction phenomena through the synthesis of a new class of substances will be expected to lead to the creation of novel battery systems. In this context, I have concentrated my research efforts into two main areas: (i) Studies into the reaction mechanisms of cathodic materials for lithium secondary batteries; and (ii) The synthesis of new materials exhibiting hydride ion (H^-) conductivity and the development of a novel battery system utilizing both the H^- conduction phenomenon and the H^-/H_2 redox reaction.

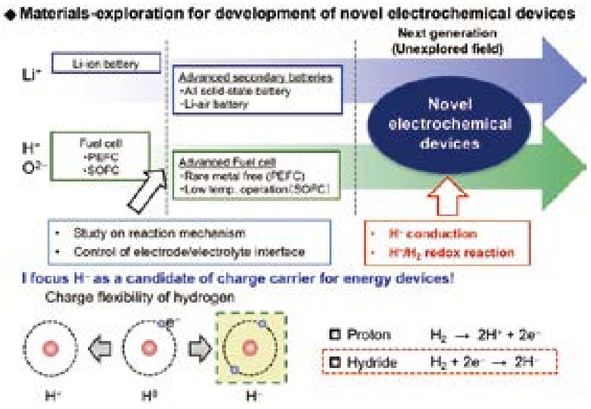

Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

Selected Publications

- G. Kobayashi, S.-I. Nishimura, M.-S. Park, R. Kanno, M. Yashima, T. Ida and A. Yamada, "Isolation of Solid Solution Phases in Size-Controlled Li_xFePO_4 at Room Temperature," *Adv. Funct. Mater.* **19**, 395–403 (2009).
- G. Kobayashi, A. Yamada, S.-I. Nishimura, R. Kanno, Y. Kobayashi, S. Seki, Y. Ohno and H. Miyashiro, *J. Power Sources* **189**, 397–401 (2009).
- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- G. Kobayashi, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).
- A. Watanabe, G. Kobayashi*, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85(2)**, 88–92 (2017).

1. Synthesis of H$^-$ Conductive Oxyhydrides[1–6]

Ionic charge carriers include a variety of species, such as Li$^+$, H$^+$, Ag$^+$, Cu$^+$, F$^-$, and O^{2-}, and their conductors have found applications in energy devices such as fuel cells and batteries. The conduction of hydride ions, H$^-$, is also attractive. These are similar in size to oxide and fluoride ions and show strong reducing properties with a standard redox potential of H$^-$/H$_2$ (–2.3 V) which is close to that of Mg/Mg^{2+} (–2.4 V). Hydride ion conductors may therefore be applied in energy storage/conversion devices with high energy densities. Here, we prepared a series of K$_2$NiF$_4$-type oxyhydrides, La$_{2-x-y}$Sr$_{x+y}$LiH$_{1-x+y}$O$_{3-y}$, which are equipped with anion sublattices that exhibit flexibility in the storage of H$^-$, O^{2-}, and vacancies. An all-solid-state Ti/La$_{2-x-y}$Sr$_{x+y}$LiH$_{1-x+y}$O$_{3-y}$/TiH$_2$ cell showed a redox reaction with hydrogen storage/desorption on the electrodes. The present success in the construction of an all-solid-state electrochemical cell exhibiting H$^-$ diffusion confirms not only the capability of the oxyhydride to act as an H$^-$ solid electrolyte but also the possibility of developing electrochemical solid devices based on H$^-$ conduction.

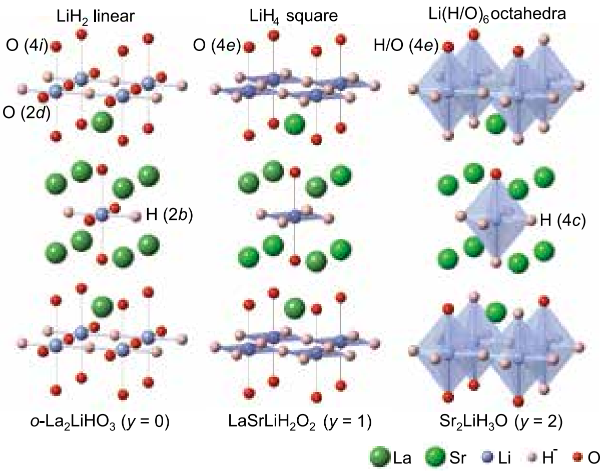

Figure 2. Crystal structures of H$^-$ conductive oxyhydrides La$_{2-x-y}$Sr$_{x+y}$LiH$_{1-x+y}$O$_{3-y}$ (x = 0, y = 0, 1, 2). Lanthanum (and strontium) ions occupy the *A* sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the *B* site that are octahedrally coordinated with anions. The coordination environment around lithium ions continuously changes with a change in the O/H$^-$ ratio. The four axial sites of the Li-anion octahedra (anion sites in Li-anion planes perpendicular *s*-axis) prefer to be occupied by H$^-$.

2. High-Performance of Li-Rich Layered Cathode Materials through Combination of A$_2$O$_3$-Based Surface Modification and Stepwise Pre-Cycling[7]

Controlling the cathode/electrolyte interface by modifying the surface of the cathode material with metal oxides or phosphate is being explored as a possible strategy for improving the electrochemical performance of such materials. In this study, we synthesized Al$_2$O$_3$-coated Li[Li$_{0.2}$Ni$_{0.18}$Co$_{0.03}$Mn$_{0.58}$]O$_2$ and investigated the crystal structure, the chemical bonding state from bulk to surface, and the influence of the surface modification on the electrochemical performance by X-ray diffraction, hard X-ray photoelectron spectroscopy (HAXPES), and galvanostatic charge/discharge reaction. It revealed that the surface-modification layer was composed of Li-Al oxides and Al oxides and that a LiM_{1-x}Al$_x$O$_2$ (M = transition metals) interlayer was formed between the modification layer and the Li[Li$_{0.2}$Ni$_{0.18}$Co$_{0.03}$Mn$_{0.58}$]O$_2$ particles (Figure 3). The cycling performance of the Li-rich layered oxide was enhanced by the surface modification with Al$_2$O$_3$. A discharge capacity of more than 310 mA h^{-1} and excellent cycling stability at 50 °C were achieved by the combination of the gradual Li-insetion/de-insertion process (stepwise precycling treatment) and the surface-modification.

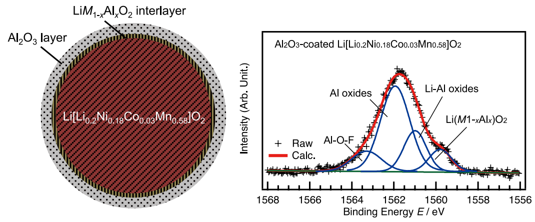

Figure 3. Schematic illustration and Al 1*s* HAXPES spectra of the 2 wt% Al$_2$O$_3$-coated Li[Li$_{0.2}$Ni$_{0.18}$Co$_{0.03}$Mn$_{0.58}$]O$_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

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2) G. Kobayashi*, A. Watanabe, N. I. P. Ayu, B. Miao, Y. Hinuma, Y. Noda, A. Kubota, F. Takeiri, M. Yonemura, N. Shibata, I. Tanaka and R. Kanno, under revision.

3) N. Matsui, G. Kobayashi*, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno*, *J. Am. Ceram. Soc.*, in press.

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Award

KOBAYASHI, Genki; The 39th Honda Memorial Young Researcher Award (2018).

Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

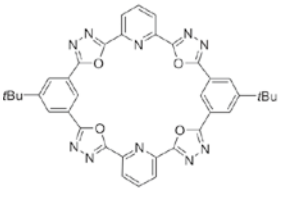
Safety Office

TOMURA, Masaaki
Assistant Professor

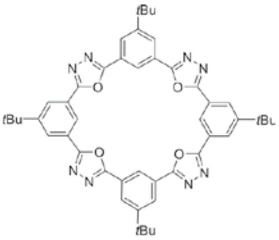
Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional organic materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form unique molecular assemblies. In this project, novel functional organic materials based on various heterocycles were synthesized and their physical and structural properties were investigated.

1. Synthesis and Crystal Structure of a Novel Macrocyclic Compound for a Supramolecular Nanotube[1)]

The novel macrocyclic compound (N-MC) was synthesized as a nitrogen analog of a macrocyclic compound (C-MC). The crystal structure of N-MC was investigated by an X-ray crystallographic analysis, and the crystal was characterized by a step-like columnar structure, which is different from the supramolecular nanotube structure of C-MC. The molecular framework and the number of *tert*-butyl groups affected the molecular arrangement in the crystal.



N-MC



C-MC

Reference

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Multifunction Integrated Macromolecules for Molecular-Scale Electronics

Safety Office

TANAKA, Shoji
Assistant Professor

Recently a single electron tunnel device (**SET**) has attracted much attention as an ultra-low-power device. In this project, to establish an innovative fabrication process for **SET** systems, we have been developing step-wise synthetic protocols for mono-molecular single-electron tunnel devices and their integrated circuits (**MOSET IC**).

1. Efficient Step-Wise Chain Extension of Rigid-Rod Linkers for Molecular Framework

We have developed an efficient synthetic route for step-wise chain extension of rigid-rod linkers (**1-4**). Figure 1 illustrates the synthetic scheme. In Sonogashira reactions, the removal of diacetylene by-product is frequently time consuming, but in our scheme, the separation is easy based on the difference in polarity of the silyl protecting groups.

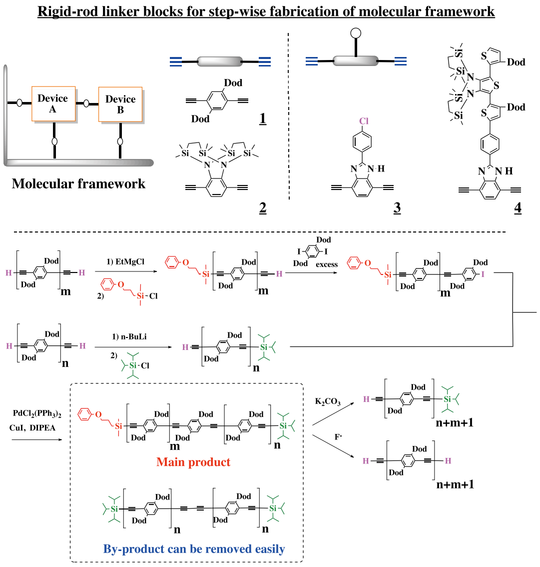

Figure 1. Representative synthetic scheme for step-wise chain extension of building blocks **1-4**.

Visiting Professors

Visiting Professor

NAKAMURA, Masakazu *(from Nara Institute of Science and Technology)*

Giant Seebeck Effect in Pure π-Conjugated Molecular Solids

The Seebeck effect is a phenomenon where a voltage appears in a material with temperature gradient. Its origin has been generally understood by the transport coefficients of charge carriers under electric field and temperature gradient where the charge–vibration interaction is included only as ‘scattering.’ We found that irregularly large Seebeck coefficients appear in thin films of pure π-conjugated molecules, of which magnitude is 100 times larger than the prediction by the conventional theory. A strong charge–vibration coupling is considered to be the driving force of the giant Seebeck effect (GSE). Recently, the GSE was first observed also in single crystals of π-conjugated molecules and was confirmed to vanish by increasing carrier concentration under light irradiation. Experimental and theoretical studies are under progress. The GSE is also interesting from an application point of view because it possibly produces revolutionary simple thermoelectric generators being free from the series connection of hundreds of p- and n-type blocks.

Visiting Professor

TAJIMA, Naoya *(from Toho University)*

Quantum Transport Phenomena in Molecular Massless Dirac Fermion Systems

We have discovered first bulk (multilayered) two-dimensional massless Dirac fermion systems in an organic conductor α-(BEDT-TTF)$_2$I$_3$ under pressure. This system shows next to the charge ordered insulating phase on the temperature–pressure phase diagram. Thus, this system provides a testing ground for the investigation of physical phenomena in strongly correlated Dirac particles. In this work, we develop the field effect transistor channeled by this system and then aim at the detection of (fractional) quantum Hall effect and new type of quantum pheneomena.

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, membrane-anchored proteins, biological-clock proteins, metalloproteins, glycoconjugates, and molecular chaperone. Coordination-complex divisions aim to develop molecular catalysts and functional metal complexes for transformation of organic molecules, water oxidation and reduction, and molecular materials such as molecular wires. Interdisciplinary alliances in this department aim to create new basic concepts for the molecular and energy conversion through the fundamental science conducted at each divisions.

Bioinorganic Chemistry of Metalloproteins Responsible for Signal Sensing

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

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Education

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

Professional Employment

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

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YOSHIOKA, Shiro
MURAKI, Norifumi
Secretary
NAKANE, Kaori

Keywords Bioinorganic Chemistry, Metalloproteins, Sensor Protein

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 signalling 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 heme-based gas-sensor proteins and the signalling systems working with them.

The prosthetic group heme acts as the active center of hemeproteins that show a variety of functions, including O_2 or NO storage/transport, electron transfer, redox catalysis of various substrate, and dehydration of aldoxime. In the present context, it acts as the active site for sensing of diatomic gas molecules such as NO, O_2, and CO. These gas molecules are able to bind to heme iron as an axial ligand, which is a reason why heme can be adapted as the active center for sensing gas molecules. Heme-based gas-sensor proteins constitute a major group in the gas-sensor proteins. Binding of a cognate gas molecule to heme is the initial step for gas sensing, which is followed by the signalling processes. The binding affinities of gas molecules, that measures of the sensitivities of the sensor proteins, can be controlled by heme environmental structures. Differences in the heme coordination structure of the axial ligand(s) and/or of interaction(s) between the heme-bound gas molecule and surrounding amino acid residue(s) in a heme pocket play important roles. They not only regulate the binding affinities of gas molecules but also discriminate one cognate effector gas molecule from others, allowing the sensor to respond with the proper signal transductions. We have been elucidating the relationships of structures and functions of heme-based sensor proteins by crystallographic, biochemical, biophysical, and molecular biological studies.

Selected Publications

- A. Pavlou, H. Yoshimura, S. Aono and E. Pinakoulaki, "Protein Dynamics of the Sensor Protein HemAT as Probed by Time-Resolved Step-Scan FTIR Spectroscopy," *Biophys. J.* **114**, 584–591 (2018).
- A. Pavlou, A. Loullis, H. Yoshimura, S. Aono and E. Pinakoulaki, "Probing the Role of the Heme Distal and Proximal Environment in Ligand Dynamics in the Signal Transducer Protein HemAT by Time-Resolved Step-Scan FTIR and Resonance Raman Spectroscopy," *Biochemistry* **56**, 5309–5317 (2017).
- N. Muraki, C. Kitatsuji, M. Ogura, T. Uchida, K. Ishimori and S. Aono, "Structural Characterization of Heme Environmental Mutants of CgHmuT that Shuttles Heme Molecules to Heme Transporters," *Int. J. Mol. Sci.* **17**, 829 (2016).
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- Y. Okamoto, H. Sawai, M. Ogura, T. Uchida, K. Ishimori, T. Hayashi and S. Aono, "Heme-Binding Properties of HupD Functioning as a Substrate-Binding Protein in a Heme-Uptake ABC-Transporter System in *Listeria monocytogenes*," *Bull. Chem. Soc. Jpn.* **87**, 1140–1146 (2014).

1. Protein Dynamics and Signal Transduction of Heme-Based Oxygen Sensor Protein HemAT-Bs

HemAT from *Bacillus subtilis* (HemAT-*Bs*) is a heme-based O_2 sensor protein responsible for aerotaxis (chemotaxis toward molecular oxygen) control in this bacterium. It consists of the N-terminal sensor domain in which heme acts as an oxygen sensing site and C-terminal signaling domain. The binding of O_2 to the heme induces a conformational change in the sensor domain of HemAT-*Bs*, triggering intramolecular signal transductions to result in the regulation of the chemotactic signaling in *B. subtilis*. An important issue to understand the signal transduction mechanism of HemAT-*Bs* is to reveal the pathway to transmit the conformational changes induced upon ligand binding/dissociation to/from the heme. In this study, we have elucidated conformational changes upon CO ligand dissociation from the heme for full-length wild-type HemAT, and the Y70F (B-helix), L92A (E-helix), T95A (E-helix), and Y133F (G-helix) HemAT mutants by time-resolved step-scan FTIR spectroscopy.

These mutations perturb hydrogen bonding and electrostatic interactions between the heme-bound ligand and the surrounding amino acid residues. While Tyr70 and Thr95 in the distal heme pocket form hydrogen bonds to the heme-bound O_2, a reversible hydrogen bond formation/cleavage takes place between Tyr133 and His123 upon ligand binding/dissociation to/from the heme in the proximal heme pocket. Rebinding of CO to the heme is biphasic in the sensor domain and full-length HemAT as well as in the mutants, with the exception of the Y133F mutant protein. The monophasic rebinding of CO in Y133F suggests that the ligand rebinding process is significantly affected in the absence of the hydrogen bond between Tyr133 and His123 residue in the proximal heme pocket.

Time-resolved step-scan FTIR studies reveal the spectral components to discrete substructures, which originate from a helical structure that is solvated (1638 cm^{-1}) and a native helix that is protected from solvation by interhelix tertiary interactions (1654 cm^{-1}). The full-length protein is characterized by an additional amide I absorbance at 1661 cm^{-1}, which is attributed to disordered structure suggesting that further protein conformational changes occur in the presence of the signaling domain in the full-length protein. The kinetics monitored within the amide I absorbance of the polypeptide backbone in the sensor domain exhibit two distinct relaxation phases (t_1 = 24 and t_2 = 694 μs), whereas that of the full-length protein exhibits monophasic behavior for all substructures in a time range of t = 1253–2090 μs. These observations can be instrumental in monitoring helix motion and the role of specific mutants in controlling the dynamics in the communication pathway from the sensor to the signaling domain. The kinetics observed for the amide I relaxation for the full-length protein indicate that the discrete substructures within full-length HemAT, unlike those of the sensor domain, relax independently.

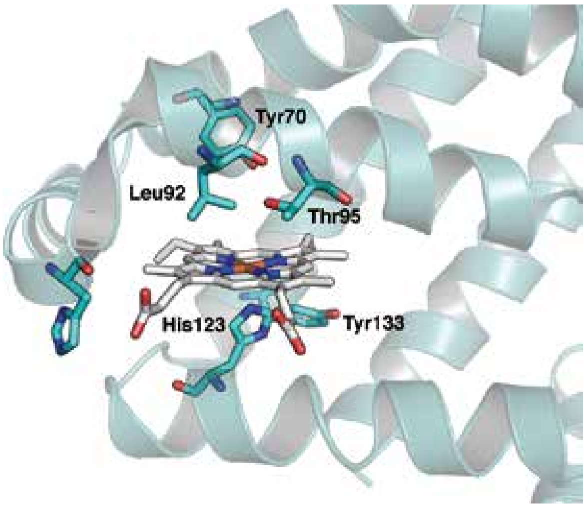

Figure 1. Heme environmental structure of HemAT-*Bs*.

2. Molecular Mechanisms for Biosynthesis and Maturation of Hydrogen Sensing Regulatory Hydrogenase

Regulatory hydrogenase (RH), HoxJ, and HoxA proteins consist a H_2-dependent regulatory system of gene expression for proteins involved in hydrogen metabolism, in which RH acts as a molecular hydrogen sensor. RH consists of two subunits, a large subunit containing the Ni-Fe dinuclear complex and a small subunit containing iron-sulfur clusters. Though the Ni-Fe dinuclear complex in the large subunit is assumed to be the active site for H_2 sensing by RH, the molecular mechanisms of biosynthesis maturation of the Ni-Fe dinuclear complex and RH protein remain elusive. Several accessory proteins are involved in the formation of the Ni-Fe complex and its insertion into the large subunit to mature RH. We are now elucidating the structural and functional relationships of the accessory protein HypX responsible for the construction of the Fe(CO) unit in the Ni-Fe dinulear complex in RH. We have obtained single crystals of HypX and the crystallographic analyses of HypX are now in progress.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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

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Education

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

Professional Employment

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

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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YANAKA, Saeko
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SUZUKI, Tatsuya
FUKUDA, Shingo
Visiting Scientist
JITYUTI, Benchawan
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HIRANYAKORN, Methanee
HONDA, Rena
SEKIGUCHI, Taichiro
YOGO, Rina*
YUNOKI, Yasuhiro*
SAITO, Taiki*
KOFUJI, Kana*
MATSUO, Muneyuki†
Technical Fellow
ISONO, Yukiko
OKADA, Tomo
OHNISHI, Kazue
Secretary
TANAKA, Kei

Keywords Biomolecule, Dynamical Ordering, NMR

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

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

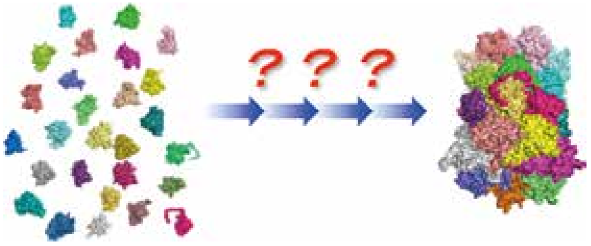

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- K. Kato, H. Yagi and T. Yamaguchi, “NMR Characterization of the Dynamic Conformations of Oligosaccharides,” in *Modern Magnetic Resonance, 2nd Edition*, G. A. Webb, Ed., Springer International Publishing, pp. 737–754 (2018).
- T. Yamaguchi and K. Kato, “Molecular Dynamics of Gangliosides,” in *Gangliosides*, S. Sonnino and A. Prinetti, Eds., Methods in Molecular Biology, Humana Press; New York, **vol. 1804**, pp. 411–417 (2018).
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- T. Ikeya, D. Ban, D. Lee, Y. Ito, K. Kato and C. Griesinger, “Solution NMR Views of Dynamical Ordering of Biomacromolecules,” *Biochim. Biophys. Acta, Gen. Subj.* **1862**, 287–306 (2018).

1. Characterization of Structural Dynamics and Interactions of Immunoglobulin G Glycoprotein

Immunoglobulin G (IgG) is a major serum glycoprotein that exerts antibody functions in the immune system, coupling antigen recognition in the Fab region with a variety of effector functions promoted in the Fc region. Therefore, detailed exploration of the structural dynamics and interactions of IgG is essential to gain deeper insights into their immune functions. We characterized the interaction of IgG-Fc with its cognate receptor (FcγR) using small-angle neutron scattering and molecular dynamics simulation.[1,2] The results revealed conformational deformation of Fc upon the interactions, underscoring the significance of existence of the *N*-glycans of these glycoproteins. In particular, our studies demonstrate that core fucosyaltion of the Fc *N*-glycans disrupts optimum intermolecular interactions mediated by the complex-type *N*-glycan at specific position of FcγRIIIa.[2,3]

We also characterized the antibody interactions using stable-isotope-assisted NMR spectroscopy. We established spectral assignments of FcγRIIIb and IgG-Fc.[4,5] Moreover, we successfully observed methyl-TROSY peaks originating from IgG with a molecular mass of 150 kDa, employing tailored deuteration.[6] On this technical basis, we conducted *in-serum* NMR observation detecting semi-specific antibody interactions in physiologically relevant heterogeneous environments.[4,6]

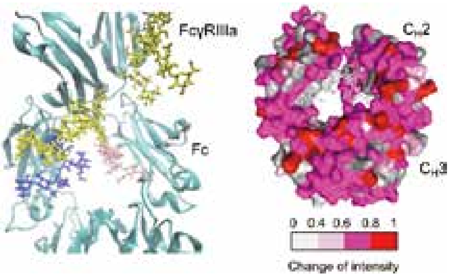

Figure 2. The dynamic view of IgG and its interactions.
Left figure: A snapshot from molecular dynamics simulation of Fc-FcγRIIIa complex. Right: Mapping of the interactions of IgG-Fc and serum components.

2. Dynamical Structures of Biomolecules toward Understanding the Mechanisms Underlying Their Functions

Our group employs multilateral biophysical and biochemical approaches for characterizing dynamical structures of various biomolecular systems that involve proteins, by integrating NMR spectroscopy, X-ray crystallography, high-speed atomic force microscopy, small-angle X-ray scattering, and cryo-electron microscopy. Our data demonstrated a two-step process for the disassembly mechanism of the eukaryotic proteasome, suggesting that scrap-and-build processes are involved in proteasome formation.[7] Based on structural information, we successfully endowed a functionally undefined archaeal protein with proteasome-activating activity by modifying its flexible C-terminal segment.[8] Furthermore, we revealed that an endoplasmic reticulum enzyme UGGT has a flexible modular structure in which the smaller catalytic domain is tethered to the larger folding-sensor region with variable spatial arrangements, offering structural insights into its working mechanism in the glycoprotein quality control system.[9] On the other hand, we created a series of synthetic neoglycolipids displaying functional glycotopes.[10] Surprisingly, the neoglycolipid micelles evoked selective apoptosis in undifferentiated neural stem cells. This serendipitous finding may offer a new strategy for controlling neural cell fates using artificial glycoclusters.

References

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Awards

YOGO, Rina; Poster Presentation Award, The 6th International Symposium on “Dynamical Ordering and Integrated Functions” (2018).

YAGI-UTSUMI, Maho; The Pharmaceutical Society of Japan Award for Young Scientists '18, The Pharmaceutical Society of Japan (2018).

SAITO, Taiki; Poster Presentation Award, ExCELLS Young Scientists Forum 2018 (2018).

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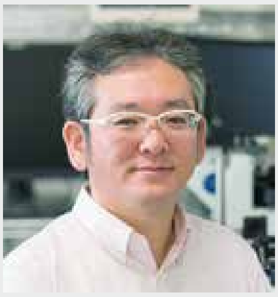
† carrying out graduate research on Cooperative Education Program of IMS with the University of Tokyo

Operation and Design Principles of Biological Molecular Machines

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



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Education

1995	B.E. Kyoto University
1997	M.E. Kyoto University
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Professional Employment

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

Award

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

Member
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Visiting Scientist
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BOORLA, Veda*
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VISOOTSAT, Akasit
IIDA, Tatsuya
Technical Fellow
YAMAMOTO, Mayuko
OKUNI, Yasuko
Secretary
NAKANE, Kaori

Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

Activity of life is supported by various molecular machines made of proteins. Protein molecular machines are tiny, but show very high performance, and are superior to man-made machines in many aspects.

One of the representatives of protein molecular machines is linear and rotary molecular motors (Figure 1). Molecular motors generate mechanical forces and torques that drive their unidirectional motions from the energy of chemical reaction or the electrochemical potential across the cell membrane.

We will unveil operation principles of molecular motors with advanced single-molecule functional analysis and structural analysis. With the help of computer science, we will also engineer new, non-natural molecular motors to understand their design principles. Our ultimate goal is controlling living organisms with created molecular machines.

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

Selected Publications

- A. Nakamura, T. Tasaki, Y. Okuni, C. Song, K. Murata, T. Kozai, M. Hara, H. Sugimoto, K. Suzuki, T. Watanabe, T. Uchihashi, H. Noji and R. Iino, “Rate Constants, Processivity, and Productive Binding Ratio of Chitinase A Revealed by Single-Molecule Analysis,” *Phys. Chem. Chem. Phys.* **20**, 3010–3018 (2018).
- F. Kawai, A. Nakamura, A. Visootsat and R. Iino, “Plasmid-Based One-Pot Saturation Mutagenesis and Robot-Based Automated Screening for Protein Engineering,”*ACS Omega* **3**, 7715–7726 (2018).
- T. Uchihashi, Y. H. Watanabe, Y. Nakazaki, Y. Yamasaki, T. Watanabe, T. Maruno, S. Uchiyama, S. Song, K. Murata, R. Iino and T. Ando, “Dynamic Structural States of ClpB Involved in Its Disaggregation Function,” *Nat. Commun.* **9**, 2147 (2018).
- H. Isojima, R. Iino, Y. Niitani, H. Noji and M. Tomishige, “Direct Observation of Intermediate States during the Stepping Motion of Kinesin-1,” *Nat. Chem. Biol.* **12**, 290–297 (2016).
- A. Nakamura, T. Tasaki, D. Ishiwata, M. Yamamoto, Y. Okuni, A. Visootsat, M. Maximilien, H. Noji, T. Uchiyama, M. Samejima, K. Igarashi and R. Iino, “Direct Imaging of Binding, Dissociation, and Processive Movement of *Trichoderma reesei* Cel6A and Its Domains on Crystalline Cellulose,” *J. Biol. Chem.* **291**, 22404–22413 (2016).
- H. Ueno, Y. Minagawa, M. Hara, S. Rahman, I. Yamato, E. Muneyuki, H. Noji, T. Murata and R. Iino, “Torque Generation of *Enterococcus hirae* V-ATPase,” *J. Biol. Chem.* **289**, 31212–31223 (2014).
- T. Uchihashi, R. Iino, T. Ando and H. Noji, “High-Speed Atomic Force Microscopy Reveals Rotary Catalysis of Rotorless F_1-ATPase,” *Science* **333**, 755–758 (2011).

1. Single-Nanoparticle Tracking with Angstrom Localization Precision and Microsecond Time Resolution[1]

Gold nanoparticle (AuNP) has been used as a probe of single-molecule imaging of molecular motors. We investigated lower limit of the localization precision in dark-field imaging of AuNP. We confirmed that the localization precision is inversely proportional to square root of photon number, and the lower limit is determined by detector saturation. To overcome the limit, we developed an axicon lens-based annular illumination total internal reflection dark-field microscopy, which illuminates AuNP with high laser intensity to obtain high signal intensity and observes AuNP with small image pixel size to avoid detector saturation. As results, with 40 nm AuNP, 1.3 Å and 5.4 Å localization precisions have been achieved at 1 ms and 33 μs time resolutions, respectively (Figure 2). We then observed transition pathways from bound to unbound states of the kinesin-1 head (Figure 3). During transitions, large leftward trails were not observed along the microtubule short axis indicating that the rear head passes the microtubule-bound leading head from the right, which results in unidirectional rotation of kinesin-1.

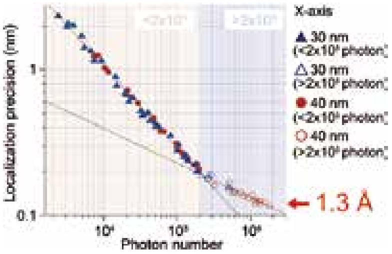

Figure 2. Photon number dependence of the localization precision for the 40 nm and 30 nm AuNPs.

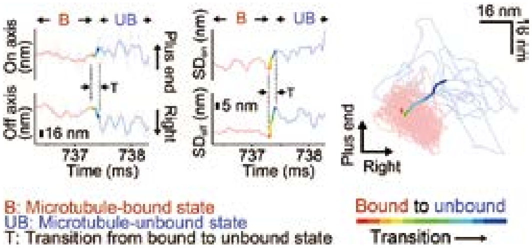

Figure 3. Transition from bound to unbound state of the kinesin-1 head labeled with 40 nm AuNP at 10 μs time resolution.

2. Processive Chitinase Is Brownian Monorail Operated by Fast Catalysis after Peeling Rail from Crystalline Chitin[2]

Processive chitinase is a linear molecular motor which moves on the surface of crystalline chitin driven by processive hydrolysis of single chitin chain (Figure 4). Here, we analysed the mechanism underlying unidirectional movement of *Serratia marcescens* chitinase A (*Sm*ChiA) using high-precision single-molecule imaging, X-ray crystallography, and all-atom molecular dynamics simulation. *Sm*ChiA showed fast unidirectional movement of ~50 nm s^{-1} with 1-nm forward and backward steps, consistent with the length of reaction product chitobiose. Analysis of the kinetic isotope effect revealed fast substrate-assisted catalysis with time constant of ~3 ms. Decrystallisation of the single chitin chain from crystal surface is the rate-limiting step of movement with time constant of ~17 ms, achieved by binding free energy at the product binding site of *Sm*ChiA (Figure 5). Our results demonstrate that *Sm*ChiA operates as a burnt-bridge Brownian ratchet wherein the Brownian motion along the single chitin chain is rectified forward by substrate-assisted catalysis.

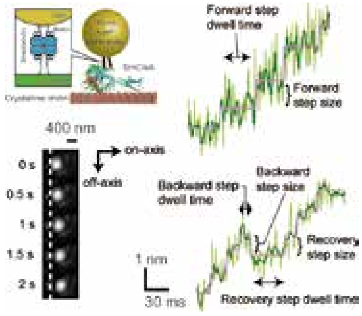

Figure 4. Examples of image and trajectory of *Sm*ChiA probed by 40 nm AuNP.

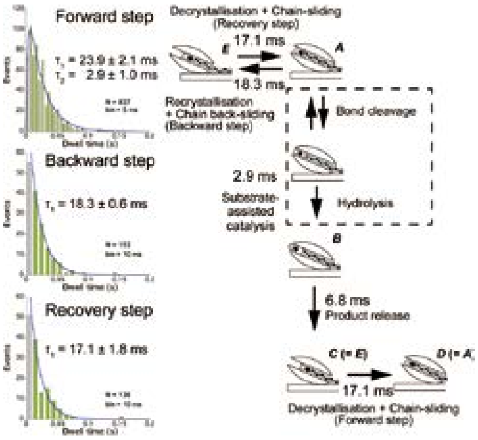

Figure 5. Distribution of dwell times and summary of time constants of elementally steps.

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Award

ANDO, Jun; Young Scientist Presentation Award of the Spectroscopical Society of Japan 2017 (2017).

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* IMS International Internship Program

A Supramolecular Chemical Approach to the Construction of Artificial Cells

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Professional Employment

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2013	Postdoctoral Fellow, Research & Education Platform for Dynamics Living States, The University of Tokyo
2014	Research Associate Professor, Institute for Molecular Science
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Member
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Keywords Artificial Cell, Origin of Life, Vesicle

Exploring the boundary between living and non-living matter is one of the most challenging problems for contemporary scientists. To understand the cell, which is considered the smallest unit of life, a plausible strategy is to synthesize an artificial cell by using a supramolecular chemical approach, because simple molecular assemblies at one time evolved to create the simple cell on prebiotic earth. As shown in Figure 1, the key elements of a cell are the compartment, information, and a catalyst (*i.e.*, metabolism). We have attempted to construct a chemically based artificial cell endowed with these three elements.

In our laboratory, we attempted to construct two artificial cells by using giant vesicles (GVs) as the compartment. One, developed in collaboration with the Sugawara group (Kanagawa Univ.), is an artificial cell that can proliferate from generation to generation. Now, we have constructed a recursive vesicular artificial cell system with proliferation cycles. By using the vesicular transport system, the second generation GVs, which contain no PCR reagents after self-reproduction, can be replenished by fusing them with conveyer GVs bearing the PCR reagents by changing the pH of the dispersion. After the PCR reagents are replenished, the GV can self-reproduce again. This system could lead to an evolvable artificial cellular system. The other artificial cell is an artificial cell that contains a catalyst-producing system. The GV system can generate catalysts and membrane molecules by transforming their respective precursors, thereby facilitating the proliferation of the GVs with the produced catalyst.

We are now tackling the creation of artificial cells that mimic cellular dynamics, such as cytoskeleton formation in the cell.

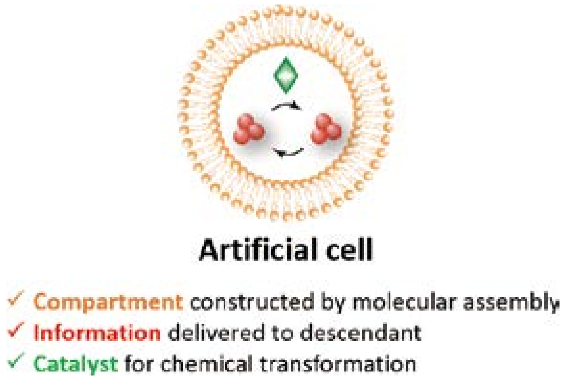

Figure 1. Artificial cell model. The replicating systems of the compartment and the information materials are combined. The reactions in the two replicating systems are accelerated by appropriate catalysts.

Selected Publications

- K. Kurihara, M. Tamura, K-I. Shohda, T. Toyota, K. Suzuki and T. Sugawara, "Self-Reproduction of Supramolecular Giant Vesicles Combined with the Amplification of Encapsulated DNA," *Nat. Chem.* **3**, 775–781 (2011).
- K. Kurihara, Y. Okura, M. Matsuo, T. Toyota, K. Suzuki and T. Sugawara, "A Recursive Vesicle-Based Model Protocell with a Primitive Cell Cycle," *Nat. Commun.* **6**, 8352 (2015).

1. An Artificial Cell Using a Self-Reproducing Oil Droplet as a Scaffold

A cell is a self-organized system that can maintain its state via metabolism. Our previously developed artificial cellular system is robust, but it can self-reproduce only a specific state in the any environments.[1–3] Research on transforming oil droplets into vesicles by use of chemical reactions and self-assembly processes is expected to facilitate our understanding of the origin and definition of life from a chemistry perspective.

The mixing of an aqueous solution of an aldehyde containing an imidazole hydrochloride group with octylaniline led to the spontaneous formation of autocatalytic oil droplets[5] (Figure 2). An aldehyde-bearing quaternary ammonium salt that does not react well with octylaniline was added to this autocatalytic droplet system. As a result, the catalytic molecules that formed within the oil droplets promoted the condensation reaction between the octylaniline and the non-catalytic aldehyde, which ultimately led to the synthesis of vesicular membrane molecules with imine functionality within the molecular aggregates; thus self-reproducible oil droplets were successfully transformed into vesicles upon the addition of the membrane precursor.

We will construct an oil droplet system that synthesizes peptides (simple proteins) and an oil droplet system that forms vesicles. The former is an oil droplet that incorporates amino acids and synthesizes peptides internally. In addition, peptide synthesis inside the vesicles is performed using a water-soluble condensing agent through our developed water-in-oil emulsion centrifugation method.[5]

2. Vesicular System Containing Peptide Synthesis

In the prebiological era, cooperative interaction of spontaneously polymerizing polymer and self-producing molecular aggregates led to the emergence of primitive cells. Although the membrane potentially provides a reactive field of catalytic reaction, it remains the mystery the cooperation between polymer and molecular aggregates occur without advanced catalyst.

Therefore, we designed and synthesized monomer precursors that spontaneously peptide-polymerized in a reductive water and generated molecular aggregates as the polymerization reaction proceeds. This monomer precursor has disulfide and thioester sites. In the first step of the reaction, the disulfide of the monomer precursor is reduced and a thiol-bearing monomer is produced. Next, benzylmercaptan, which generates the oil droplet, is eliminated by replacing the thiol of the monomer. Finally, the occurrence of S-N acyl transfer forms amide bonds (native chemical ligation).

From the reaction trace by NMR spectrum, the release of benzylmercaptan and subsequent formation of amide bond were detected. Furthermore, as turbidity increased with progress of reaction, the reaction solution formed cell-size oil droplets under microscope observation. These results mean that benzylmercaptan forms oil droplets without layer separation because the generated peptides stabilize the interface. In this system, since spontaneous polymerization of polymer and oil droplet generation are coupled, application of this system to artificial cells is expected.

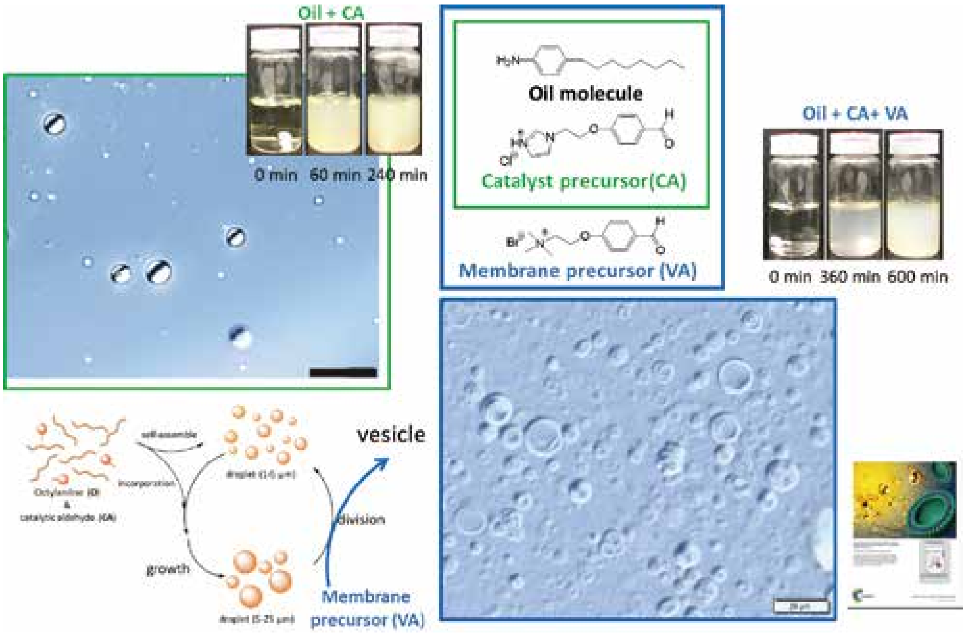

Figure 2. Scheme of the self-reproducing oil droplet (oil-in-water emulsion) and vesicular transformation system.

References

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2) K. Kurihara, Y. Okura, M. Matsuo, T. Toyota, K. Suzuki and T. Sugawara, *Nat. Commun.* **6**, 8352 (2015).

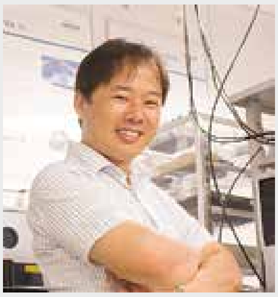
3) L. Sheng and K. Kurihara, *Chem. Lett.* **45**, 598–600 (2016).

4) L. Sheng and K. Kurihara, *Chem. Commun.* **52**, 7786–7789 (2016).

5) Y. Natsume, H. Wen, T. Zhu, K. Itoh, L. Sheng and K. Kurihara, *J. Vis. Exp.* **119**, e55282 (2017).

Investigation of Molecular Mechanisms of Channels, Transporters and Receptors

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



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2004 Ph.D. Kyoto University

Professional Employment
2003 JSPS Research Fellow
2004 JSPS Postdoctoral Fellow
2006 Assistant Professor, Nagoya Institute of Technology
2009 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2011 JST-PRESTO Researcher (concurrent post) (–2015)

Awards
2012 Morino Foundation for Molecular Science
2013 The 2013 Young Scientist Awards of the Japan Society for Molecular Science

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INABA, Kayo
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SHIMIZU, Atsuko

Keywords Infrared Spectroscopy, Membrane Protein, Ion Channel

Membrane proteins are important for homeostasis and signaling of living cells, which work as ion channel, ion pump, various types of chemical and biophysical sensors, and so on. These proteins are considered as one of important targets for biophysical studies. Our main goal is to clarify molecular mechanisms underlying functions of the channels, transporters and receptors mainly by using stimulus-induced difference infrared spectroscopy, which is sensitive to the structural and environmental changes of bio-molecules.

We applied attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy to extract ion-binding-induced signals of various kinds of membrane proteins. For example, KcsA is a potassium channel, which is highly selective for K^+ over Na^+, and the selectivity filter binds multiple dehydrated K^+ ions upon permeation. Shifts in the peak of the amide-I signals towards lower vibrational frequencies were observed as K^+ was replaced with Na^+ (Figure 1). These vibrational modes give us precise structural information of the selectivity filter. Moreover, by changing concentrations of K^+ in buffer solutions, we can estimate affinity of the selectivity filter for K^+ ions.

Recently, we have developed a rapid-buffer exchange apparatus for time-resolved ATR-FTIR spectroscopy, which can be utilized for studying dynamics of structural transition in membrane proteins.

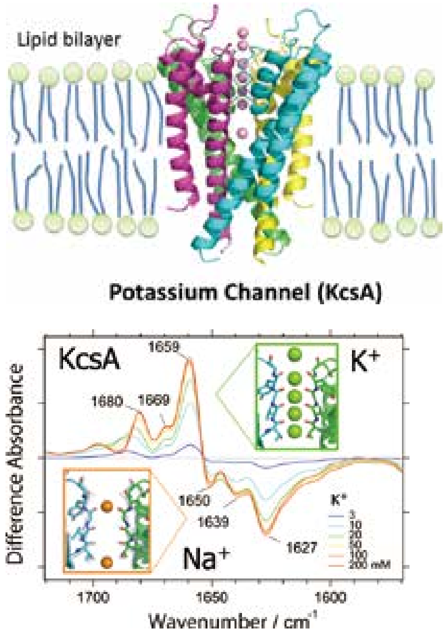

Figure 1. (top) X-ray crystal structure of a potassium ion channel, KcsA. (bottom) The ion-exchange induced difference infrared spectra of KcsA with different potassium ion concentration. The amide I bands are mainly originated from the carbonyl groups of the selectivity filter of KcsA.

Selected Publications

- Y. Furutani *et al.*, "ATR-FTIR Spectroscopy Revealed the Different Vibrational Modes of the Selectivity Filter Interacting with K^+ and Na^+ in the Open and Collapsed Conformations of the KcsA Potassium Channel," *J. Phys. Chem. Lett.* **3**, 3806–3810 (2012).
- Y. Furutani *et al.*, "Development of a Rapid Buffer-Exchange System for Time-Resolved ATR-FTIR Spectroscopy with the Step-Scan Mode," *Biophysics* **9**, 123–129 (2013).

1. Ion–Protein Interactions of TWIK1 Potassium Channel with Alkali Metal Cations and Its Implication for the Ion Selectivity[1)]

Potassium channels are selectively permeable to potassium ions (K^+) in cell membrane and function for shaping neuroral signals in nerve cells or maintaining ionic compositions in various cells. The ion selectivity of potassium channels for K^+ over Na^+ is extremely high (typically 1000:1 ratio). The molecular mechanism of the selectivity has been greatly understood by determination of three-dimensional structure of a bacterial potassium channel, KcsA, which stimulates further discussion on the potassium selectivity. As we have shown in previous studies, infrared spectroscopy can detect molecular vibrations and could be a key technique for studying ion–protein interactions in membrane proteins. Indeed, ion-exchange induced difference FTIR spectroscopy successfully discriminated structures of the selectivity filter of the KcsA channel interacting with each kind of alkali metal cations.[2)]

Two-pore domain potassium channel possesses two pore domains in a monomer unit and composes the ion selectivity filter by forming a dimer instead of a conventional tetramer. Among them, TWIK1 shows the peculiar ion selectivity in which sodium ions permeate under low potassium concentration or acidic pH in the extracellular side. The pseudo fourfold rotational symmetry along the pore axis may cause the low potassium selectivity. To understand the molecular mechanism underlying the low potassium selectivity of TWIK1, we applied ion-exchange induced difference FTIR spectroscopy on this protein. Then, we compared the difference spectra of a high potassium selective variant, T118I, and a L228F variant, which is altered on the filter but known to be unaffected to the ion selectivity, with those of the wild-type TWIK-1.

The ion-exchange induced difference spectra in the amide-I region of WT, T118I and L228F are basically similar to the previous spectrum obtained in KcsA. Especially, we found that the 1680-cm^{-1} band would be a general marker band for the selectivity filter interacting with potassium ions. Interestingly, the band at 1680 cm^{-1} shifts to ~1690 cm^{-1} upon replacing K^+ with Rb^+ or Cs^+ in the T118I and L228F variants, but not in WT. The titration experiments provided quantitative information about affinity of the channels with potassium ions and T118I exhibited the highest affinity. Thus, we conclude that the low potassium selectivity of TWIK-1 is well correlated with the structural dynamics of the filter region and its affinity to potassium ions.

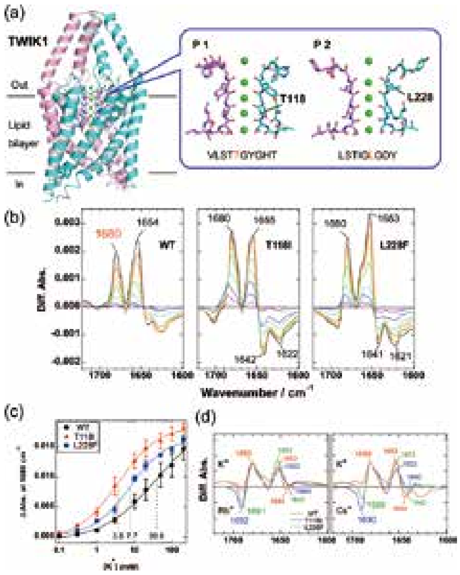

Figure 2. (a) The selectivity filter of TWIK1. (b) The difference IR spectra of WT, T118I and L228F mutants. (c) K^+-concentration dependence for the 1680-cm^{-1} band (d) The difference spectra upon replacement with Rb^+ or Cs^+.

2. PDMS-Based Microfluidic Device for Infrared Spectroscopy with an Electro-Chemical Reaction[3)]

Microfluidic technique is a promising method for characterizing chemical and biological reactions with low sample consumption. Polydimethylsiloxane (PDMS) is transparent under visible light and is a soft material, which widely used for making microfluidic devices feasible for various kinds of experimental techniques. A paper applying FTIR microspectroscopy with a PDMS microfluidic device was published as a collaborative work with Dr. M. Srisa-Art in Chulalongkorn University, Thailand. After that, Mr. A. Suea-Ngam stayed in our group as an IMS-IIPA internship student. He tried to fabricate a droplet-based microfluidics coupled with amperometric detection using chip-based carbon paste electrodes (CPEs) for FTIR spectro-electrochemistry. We succeeded to demonstrate infrared spectroscopy of electrochemical reactions of ferrocyanide ($[Fe(CN)_6]^{4-}$) in the microchannel.

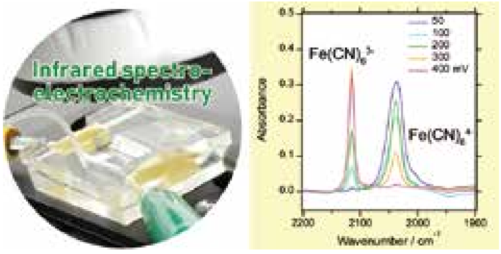

Figure 3. Infrared spectro-electrochemistry in PDMS device.

References

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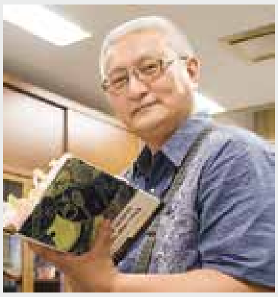
2) Y. Furutani, *Biophys. Rev.* **10**, 235–239 (2018).
3) A. Suea-Ngam, M. Srisa-Art and Y. Furutani, *Bull. Chem. Soc. Jpn.* **91**, 728–734 (2018).

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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



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

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

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

Member

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    - KOTORA, Martin
- Assistant Professor
    - OSAKO, Takao
    - HAMASAKA, Go
- Post-Doctoral Fellow
    - PAN, Shiguang
    - HIRATA, Shuichi
    - PUTRA, Anggi Eka
    - KIM, Kiseong
    - SUGIYAMA, Yuya
- Graduate Student
    - ICHII, Shun
    - SHEN, Guanshuo
    - NIIMI, Ryoko
    - TANI, Kazuki
- Technical Fellow
    - TORII, Kaoru
    - TAZAWA, Aya
- Secretary
    - SASAKI, Tokiyo
    - TANIWAKE, Mayuko

Keywords Transition Metal Catalysis, Green Chemistry, Organic Synthesis

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, *etc.*) organic transformation processes. In one active area of investigation, we are developing the heterogeneous aquacatalytic systems. Various types of catalytic organic molecular transformations, *e.g.* carbon–carbon bond forming cross-coupling, carbon–heteroatom bond forming reaction, aerobic alcohol oxidation, *etc.*, were achieved in water under heterogeneous conditions by using amphiphilic polymer-supported transition metal complexes and nanoparticles (**Figure 1**), where self-concentrating behavior of hydrophobic organic substrates inside the amphiphilic polymer matrix played a key role to realize high reaction performance in water.

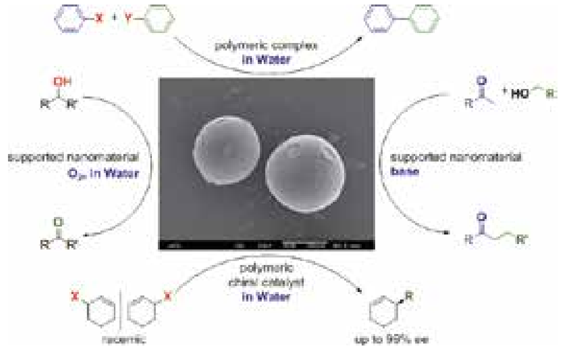

Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

Selected Publications

- 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).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, "Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane," *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin[1)]

A chemoselective continuous-flow hydrogenation of aldehydes catalyzed by a dispersion of platinum nanoparticles in an amphiphilic polymer (ARP-Pt) has been developed. Aromatic and aliphatic aldehydes bearing various reducible functional groups, such as keto, ester, or amide groups, readily underwent flow hydrogenation in aqueous solutions within 22 seconds in a continuous-flow system containing ARP-Pt to give the corresponding primary benzylic or aliphatic alcohols in up to 99% yield with excellent chemoselectivity. Moreover, the long-term continuous-flow hydrogenation of benzaldehyde for eight days was realized, and the total turnover number of the catalyst reached 997. The flow hydrogenation system provides an efficient and practical method for the chemoselective hydrogenation of aldehydes bearing reducible functional groups.

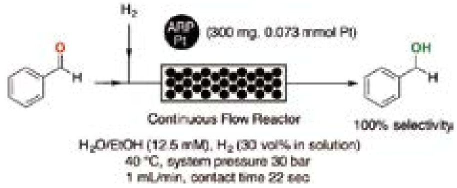

Figure 2. Aqueous continuous flow hydrogenation of benzaldehyde in water in the presence of amphiphilic resin-supported nano particles of platinum (ARP-Pt).

2. A Palladium NNC-Pincer Complex as an Extremely Efficient Catalyst Precursor for the Mizoroki–Heck Reaction[2,3)]

The Mizoroki–Heck reaction of aryl halides (iodides, bromides, or chlorides) with activated alkenes in the presence of a palladium NNC-pincer complex at ppb to ppm loadings gave the corresponding internal alkenes in excellent yields. The total turnover number and turnover frequency reached up to 8.70×10^8 and 1.21×10^7 h^{-1} (3.36×10^3 s^{-1}), respectively.

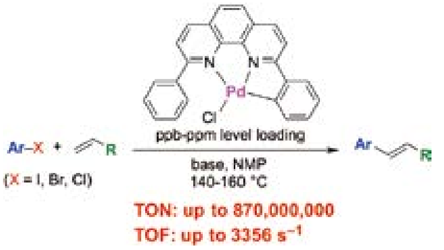

Figure 3. Heck reaction with a mol ppb loading level of an NNC-pincer palladium complex.

The catalyst was applied in a ten-gram-scale synthesis of the UV-B sunscreen agent octinoxate (2-ethylhexyl 4-methoxycinnamate). Reaction-rate analyses, transmission electron microscopic examination of the reaction mixture, and poisoning tests suggested that a monomeric palladium species is the catalytically active species in the catalytic cycle.

3. Aqueous Asymmetric 1,4-Addition of Arylboronic Acids to Enones Catalyzed by an Amphiphilic Resin-Supported Chiral Diene Rhodium Complex Under Batch and Continuous-Flow Conditions[4)]

A rhodium–chiral diene complex immobilized on amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin (PS–PEG–diene*–Rh) has been developed. The immobilized rhodium–chiral diene complex (PS–PEG–diene*–Rh) efficiently catalyzed the asymmetric 1,4-addition of various arylboronic acids to cyclic or linear enones in water under batch conditions to give the corresponding β-arylated carbonyl compounds in excellent yields and with excellent enantioselectivity. The catalyst was readily recovered by simple filtration and reused 10 times without loss of its catalytic activity and enantioselectivity. Moreover, a continuous-flow asymmetric 1,4-addition in a flow reactor containing PS–PEG–diene*–Rh proceeded efficiently at 50 °C with retention of high enantioselectivity. Long-term continuous-flow asymmetric 1,4-addition during 12 hours readily gave the desired product on a ten-gram scale with high enantioselectivity.

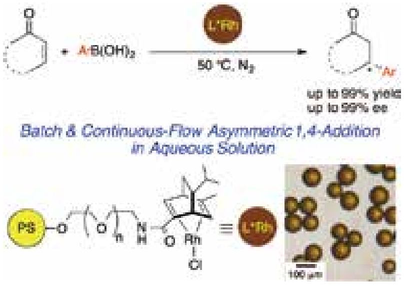

Figure 4. Asymmetric 1,4-addition of aryl boronic acids to enones in the presence of a PS–PEG resin-supported homochiral rhodium complex.

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3) G. Hamasaka, S. Ichii and Y. Uozumi, *Adv. Synth. Catal.* **360**, 1833–1840 (2018).
4) G. Shen, T. Osako, M. Nagaosa and Y. Uozumi, *J. Org. Chem.* **83**, 7380–7387 (2018).

Awards

OSAKO, Takao; Thieme Chemistry Journals Award 2018 (2018).
HAMASAKA, Go; Mitsubishi Gas Chemical Award in Synthetic Organic Chemistry, Japan (2018).
HAMASAKA, Go; The Chemical Society of Japan Lecture Award for Young Chemists (2018).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Division of Complex Catalysis

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

Professional Employment
2005 Postdoctoral Fellow, Harvard University
2006 Assistant Professor, Tohoku University
2014 Associate Professor, Institute for Molecular Science
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Awards
2003 The Elizabeth R. Norton Prize for Excellence in Research in Chemistry, University of Chicago
2004 Abbott Laboratories Graduate Fellowship
2005 Damon Runyon Cancer Research Foundation Post Doctoral Research Fellowship
2008 Thieme Chemistry Journals Award
2014 The 17th Morita Science Research Award
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Keywords Organic Synthesis, Molecular Catalyst, Non-Covalent Interaction

The field of molecular catalysis has been an attractive area of research to realize efficient and new transformations in the synthesis of functional molecules. The design of ligands and chiral molecular catalysts has been recognized as one of the most valuable strategies; therefore, a great deal of effort has been dedicated to the developments. In general, "metal" has been frequently used as the activation center, and conformationally rigid, and C_2- or pseudo C_2 symmetry has been preferably components for the catalyst design. To develop new type of molecular catalysis, we have focused on the use of hydrogen and halogen atom as activation unit, and have utilized conformationally flexible components in the molecular design of catalyst, which had not received much attention until recently. We hope that our approach will open the new frontier in chiral organic molecules from chiral molecular chemistry to chiral molecular science.

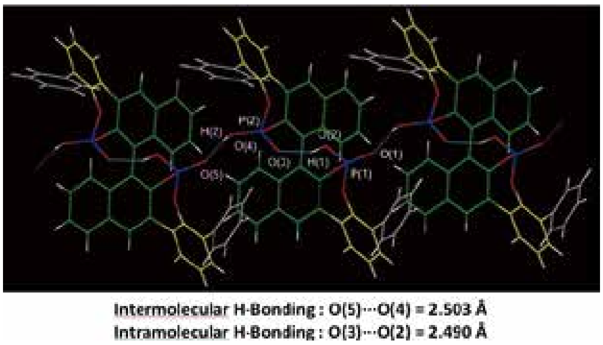

Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

Selected Publications

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

1. Brønsted Acid Catalyzed Asymmetric 1,3-Alkyl Migration of 1,2,2-Substituted Butenyl Amines: Asymmetric Synthesis of Linear Homoprenylamines

Allylation of imines with allylic metal reagents has been one of the most valuable tools to synthesize enantioenriched homoallylic amines. Due to the inherent nature of allylic metal reagent, however, regioselectivity has been a long-standing subject in this area. To develop the synthetic reaction for enantioenriched linear homoprenylic amines, we discovered chirality transferred 1,3-alkyl migration of 1,2,2-substituted butenyl amines in the presence of trifluoromethyl acetic acid, and developed it as synthetic method for variety of enantioenriched linear homoprenylic amines.1) In sharp contrast, Ollis *et al.* previously reported that chirality was significantly dropped in 1,3-alkyl migration of *N*,*N*-dimethyl-1-substituted-3-buten-1-amine.2) To the best our knowledge, our discovery is the first example of chirality transferred 1,3-alkyl migration and the new entry of the synthetic methodology for the linear enantioenriched homoallylic amines.

2. Design of Chiral Brønsted Acid Catalyst

Chiral Brønsted acid catalysis has been recognized as one of the useful tools in asymmetric synthesis. We have contributed to this area by focusing on the use of perfluoroaryls and C_1-symmetric design.

Perfluorinated aryls have emerged as an exquisite class of motifs in the design of molecular catalysts, and their electronic and steric alterations lead to notable changes in the chemical yields and the stereoselectivities. However, unfortunately, the distinctive potential of perfluorinated aryls has not been fully exploited as design tools in the development of chiral Brønsted acid catalysts. We developed the perfluoaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deriver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino–ene reaction using aldehydes and $\mathrm{FmocNH_2}$.3)

We have developed (*R*)-3,3’-di(2-hydroxy- 3-arylphenyl) binaphthol derived chiral bis-phosphoric acid which efficiently catalyzed enantioselective Diels–Alder reaction of acroleins with amidodienes.4,5) We demonstrated that two phosphoric acid groups with individually different acidities can play distinct roles in catalyst behavior through hydrogen bonding interactions. Hence, we were interested to explore whether a combination of *different acidic functional groups*, in particular an aryl phosphinic acid-phosphoric acid, would function as an efficient Brønsted acid catalyst. We developed a Brønsted acid with two different acidic sites, aryl phosphinic acid-phosphoric acid, and its catalytic performance was assessed in the hetero-Diels–Alder reaction of aldehyde hydrates with Danishefsky’s diene, achieving high reaction efficiency.6) Furthermore, molecular design of a chiral Brønsted acid with two different acidic sites, chiral carboxylic acid–cyclic mono-phosphoric acid, was identified as a new and effective concept in asymmetric hetero-Diels–Alder reaction of 2-azopyridinoester with amidodienes.7)

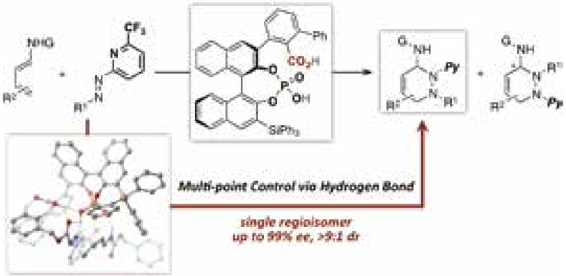

Figure 2. Chiral carboxylic acid–phosphoric acid-catalyzed azo-hetero-Diels–Alder reaction.

3. Halogen Bond Donor Catalyzed Reaction of *N*-Heteroaromatics with Allylsilatrane

Halogen bonds are attractive non-covalent interactions between terminal halogen atoms in compounds of the type R–X (X = Cl, Br, I) and Lewis bases LB. It has been known that strong halogen bonds are realized when “R” is highly electronegative substituents such as perfluorinated alkyl or aryl substituents. We recently developed synthetic methodology for perfluorinated aryl compounds, and applied it for the development of chiral Brønsted acid catalysts. On the basis of our achievements, we have examined it to develop halogen bond donor catalyzed allylation reaction.

We found that iodopentafluorobenzene was able to catalyze the reaction of isoquinolines, quinolines, and pyridines with allylsilatrane, crotylsilatrane, and prenyl silatrane to give the corresponding products in good yields.8)

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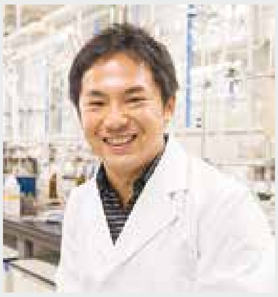
5) N. Momiyama, K. Funayama, H. Noda, M. Yamanaka, N. Akasaka, S. Ishida, T. Iwamoto and M. Terada, *ACS Catal.* **6**, 949–956 (2016).
6) N. Momiyama, T. Narumi and M. Terada, *Chem. Commun.* **51**, 16976–16979 (2015).
7) N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamanishi, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).
8) N. Momiyama *et al.*, Manuscript in preparation.

Development of Functional Metal Complexes for Artificial Photosynthesis

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



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Education

1999	B.S. Doshisha University
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Professional Employment

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2005	Research Associate, Kyushu University
2007	Assistant Professor, Kyushu University
2009	JST PRESTO Researcher
2011	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Award

2017	The 13th (FY 2016) JSPS Prize

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CHINAPANG, Pondchanok
Graduate Student
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IZU, Hitoshi
ENOMOTO, Takafumi
IWAMI, Hikaru
KACHI, Mami
TASAKI, Masahiro
AKAI, Takuya
FUJISAWA, Mayu
ISHIHARA, Mei
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MATSUDA, Miho
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TANIWAKE, Mayuko
NOGAWA, Kyoko

Keywords Metal Complex, Multi-Electron Transfer Reactions, Artificial Photosynthesis

Artificial photosynthesis is a solar energy conversion technology that mimics natural photosynthesis, and considered to be one of the next big breakthroughs in the research field. Our group studies the development of functional metal complexes toward the realization of artificial photosynthesis. Specific areas of research include (i) creation of cluster catalysts for multi-electron transfer reactions, (ii) frontier-orbital engineering of metal complexes for multi-electron transfer reactions, (iii) application of proton-coupled electron transfer toward multi-electron transfer reactions, (iv) electrochemical analysis of catalytic reactions, (v) development of novel photo-induced electron transfer systems, (vi) establishment of electrochemical method for the photoreactions of metal complexes in homogeneous solutions, and (vii) development of framework catalysts for small molecule conversion via the self-assembly of catalyst modules.

Figure 1. An overview of our work.

Selected Publications

- S. K. Lee, M. Kondo, G. Nakamura, M. Okamura and S. Masaoka, "Low-Overpotential CO_2 Reduction by Phosphine-Substituted Ru(II) Polypyridyl Complex," *Chem. Commun.* **54**, 6915–6918 (2018).
- T. Enomoto, M. Kondo, M. Asada, T. Nakamura and S. Masaoka, "Near-IR Light-Induced Electron Transfer via Dynamic Quenching," *J. Phys. Chem. C* **122**, 11282–11287 (2018).
- P. Chinapang, M. Okamura, T. Itoh, M. Kondo and S. Masaoka, "Development of a Framework Catalyst for Photocatalytic Hydrogen Evolution," *Chem. Commun.* **54**, 1174–1177 (2018).
- M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S. Hayami, V. K. K. Praneeth, M. Yoshida, K. Yoneda, S. Kawata and S. Masaoka, "A Pentanuclear Iron Catalyst Designed for Water Oxidation," *Nature* **530**, 465–468 (2016).
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- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Low-Overpotential CO_2 Reduction by Phosphine-Substituted Ru(II) Polypyridyl Complex[1)]

Catalytic CO_2 reduction into liquid fuels and commodity chemicals under benign condition has drawn tremendous attention, not only as a means to decrease the competition for limited fossil fuel reserves but also help to reduce the concentration of atmospheric CO_2. There are a continuously increasing number of molecular catalysts to convert CO_2 into fuels, such as HCOOH and deeply reduced products. In addition, the reduction of CO_2 to carbon monoxide (CO) is also favourable because a wide variety of fuels and commodity chemicals can be produced from CO via Fischer–Tropsch synthesis. Therefore, the development of a catalyst that can convert CO_2 to CO is an attractive research target.

In this study, we investigated electrochemical CO_2 reduction by a polypyridyl Ru complex with a mixed phosphine-pyridine and a labile ligands. Electrochemical measurements and controlled potential electrolysis revealed that the complex can promote electrocatalytic CO_2 reduction to produce CO at a lower overpotential than those of the relevant metal-complex-based catalysts. Mechanistic investigations using spectroscopic measurements clarified that the introduction of a phosphine donor at the *trans* position to the labile ligand is the key to reduce the overpotential for CO_2 reduction. In other words, a simple introduction of a phosphine moiety to the ligand largely affect the reactivity of the Ru centre, which collectively allow the complex to reduce CO_2 at a low overpotential. The results presented in this work provides a novel versatile strategy to reduce the overpotential of molecular catalysts for CO_2 reduction, which is possibly applicable to a wide variety of catalytic systems.

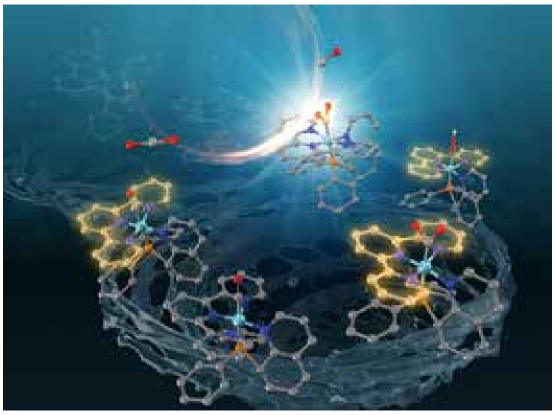

Figure 2. CO_2 reduction catalyzed by the ruthenium complex.

2. Development of a Framework Catalyst for Photocatalytic Hydrogen Evolution[2)]

The photocatalytic production of H_2 from water is a promising way to provide a sustainable and environmentally friendly chemical fuels. Thus far, considerable efforts have been devoted to the development of molecular-based homogeneous photocatalytic systems. However, homogeneous systems are considered unsuitable for future practical applications because of their moderate reusability and stability, for which heterogeneous photocatalytic systems are rather advantageous.

In this study, we propose an effective approach to construct a heterogeneous photocatalytic system based on the supramolecular assembly of molecular catalyst modules. In this system, a discrete catalyst module, which has a metal-complex-based catalytic centre (catalytic node) and intermolecular interaction sites (molecular connector), can be assembled into an ordered structure via non-covalent interactions to afford a heterogeneous framework catalyst. Therefore, our system provides two prominent features: (1) well-defined catalytic sites attributed to the molecular-based modules and (2) reusability and high durability based on the heterogeneous nature. The controlled self-assembly of a catalyst module composed of a Rh(II) paddle-wheel dimer bearing 1,8-naphthalimide-based moieties afforded a novel heterogeneous framework catalyst. The framework catalyst exhibited long-lived activity for photocatalytic hydrogen production from water and was easily reused without considerable loss of catalytic activity. The present work offer novel strategy constructing molecular-based heterogeneous catalytic systems for small molecular conversions.

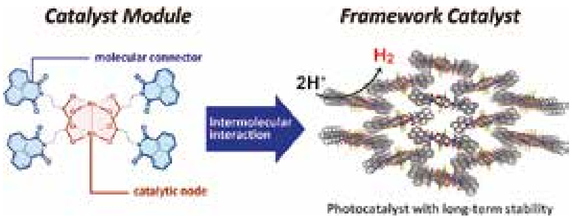

Figure 3. Construction of a framework catalyst via the self-assembly of catalyst modules.

References

1) S. K. Lee, M. Kondo, G. Nakamura, M. Okamura and S. Masaoka, *Chem. Commun.* **54**, 6915–6918 (2018).

2) P. Chinapang, M. Okamura, T. Itoh, M. Kondo and S. Masaoka, *Chem. Commun.* **54**, 1174–1177 (2018).

Awards

KONDO, Mio; Chemical Society of Japan Award for Young Women Chemists (2018).
KONDO, Mio; The 7th Young Scientists Award of National Institutes for Natural Sciences (2018).
CHINAPANG, Pondchanok; CSJ Student Presentation Award 2017, The 98th CSJ Annual Meeting (2018).
CHINAPANG, Pondchanok; Poster Prize, the 67th JSCC Symposium (2017).
LEE, Sze Koon; Chemistry Letters Young Award, The 4th Japan-Taiwan-Singapore-Hong Kong Quadrilateral Symposium on Coordination Chemistry (2017).
IZU, Hitoshi; Oral Award, Interdisciplinary Symposium for Up-and-Coming Material Scientists 2017 (ISUMS2017) (2017).
IZU, Hitoshi; Poster Award, The 50th symposium on Chemical and Biochemical Oxidation (2017).

Control of Electron Transfer for Efficient Oxygenation Reactions

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Division of Biomolecular Functions

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Assistant Professor

Electron transfer is the most fundamental reaction to govern chemical reactions. To find an effective way to control electron transfer, electronic structures of key active species were investigated in detail with various techniques including absorption, ^{1}H and ^{2}H NMR, EPR, IR resonance Raman spectroscopy and magnetic susceptibility measurements. Correlations between electronic structures and electron transfer ability are the main focus. The insight obtained from electronic structural studies is utilized to create a new catalyst, which is applied for the reactions of gaseous methane under photoirradiation.

1. Reactions of Gaseous Methane as a Substrate

One of the problems for the reactions of gaseous hydrocarbon substrates is low solubility in organic catalyst solution. To overcome this problem, a new reaction system using fine bubbles of methane gas is constructed. In this system, an organic catalyst solution is dispersed by fine bubbles in aqueous solution. Aqueous solution serves as a coolant and also plays a role in extracting methanol product from organic catalyst solution.

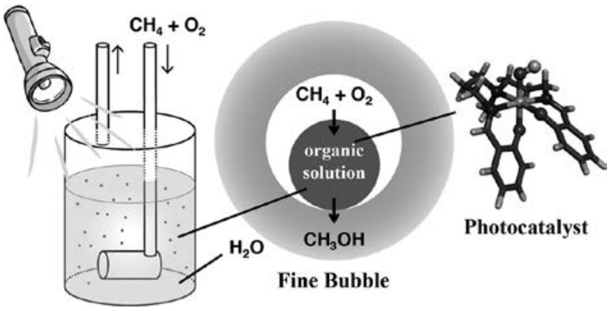


Figure 1. Photocatalytic Methane Oxygenation using Fine Bubbles under Biphasic Conditions.

Visiting Professors

Visiting Professor

SAKURAI, Hidehiro *(from Osaka University)*

Nanoscience Based on the Synthetic Organic Chemistry

Bowl-shaped π-conjugated compounds including partial structures of the fullerenes, which are called "buckybowls," are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. Very few buckybowls has been achieved for preparation mainly due to their strained structure. We develop the rational route to the various buckybowls and investigate their physical properties. We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold and gold-based alloy nanoclusters supported by hydrophilic polymers and its catalytic activity: Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers.

Visiting Professor

UCHIHASHI, Takayuki *(from Nagoya University)*

Dynamic Structural States of ClpB Involved in Its Disaggregation Function Revealed by High-Speed Atomic Force Microscopy

Protein disaggregation machines, ClpB in bacteria belonging to the AAA+ superfamily, refolds toxic protein aggregates into the native state in cooperation with the cognate Hsp70 partner. The ring-shaped hexamers of ClpB uses ATP to unfold and thread its protein substrate through the central pore. However, their function-related structural dynamics has remained elusive. We directly visualized the ClpB using high-speed atomic force microscopy (HS-AFM) to gain a mechanistic insight into its disaggregation function. The HS-AFM movies demonstrated massive conformational changes of the hexameric ring during the ATPase reaction, from a round ring to a spiral and even to a pair of twisted half-spirals. HS-AFM observations of Walker-motif mutants unveiled crucial roles of ATP binding and hydrolysis in the oligomer formation. Furthermore, repressed and hyperactive mutations resulted in significantly different oligomeric forms. These results lead to a comprehensive view for the ATP-driven oligomeric-state transitions that enable ClpB to disentangle protein aggregates.

Visiting Associate Professor

YAMADA, Teppei *(from Kyushu University)*

Ionic Motion in Soft Molecular Space

Dynamics of ionic species are affected by the surrounding intermolecular interaction, Madelung potential as well as the external electric field. We intended to control the intermolecular interaction of ions in the molecular scale by designing the molecular assembly. To date, the phase transition of the rotating mode of tetraethylammonium in plastic crystal phase was investigated (*J. Am. Chem. Soc.* 291–297 (2018); *Chem. Lett.* 497–499 (2018)). Ionic motion in the ionic crystal was also applied as an electrolyte of thermocell (*Chem. Lett.* 261–264 (2018)). Recently we focus on the ionic motion in chiral nanospace. A porous metal–organic framework, Labtb, was synthesized with an enantioselective method. After the collaborative work with Prof. Okamoto and Dr. Narushima in IMS, high enantiomer-excess of Labtb in particle-level was visualized by circular dichroism imaging (a paper to be submitted). The obtained enantiomeric Labtb is highly stable from heat, chemicals and has 1D pore of *ca.* 13 Å in diameter, and we are searching the wide application of it.

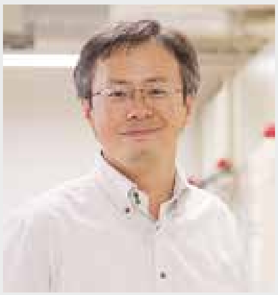
RESEARCH ACTIVITIES

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.

The Origin of 24 Hour Period in Cyanobacterial Clock System

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



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Education

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Professional Employment

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2003	RIKEN Special Postdoctoral Researcher
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2008	Junior Associate Professor, Nagoya University
2011	Associate Professor, Nagoya University
2012	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Awards

2016	The 13th (FY2016) JSPS PRIZE
2008	The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Japan
2007	Young Scientist Prize, The Biophysical Society of Japan
2006	SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
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Keywords Circadian Clock, Clock Proteins, Cyanobacteria

Circadian (approximately 24 h) clocks are endogenous time-keeping systems encapsulated in living cells, enabling organisms to adapt to daily fluctuation of exogenous environments on the Earth. These time-keeping systems, found ubiquitously from prokaryotes to eukaryotes, share the three characteristics. First, the circadian rhythmicity of the clocks persists even without any external cues (self-sustainability). Second, the period is little dependent on ambient temperature (temperature compensation). Third, the phase of the clock can be reset by external stimuli such as lightning, humidity, or temperature so as to be synchronized to the external phase (synchronization).

KaiC, a core protein of the circadian clock in cyanobacteria, undergoes rhythmic structural changes over approximately 24 h in the presence of KaiA and KaiB (Kai oscillator). This slow dynamics spanning a wide range of both temporal and spatial scales is not well understood, and is central to a fundamental question: What determines the temperature-compensated 24 h period? The Kai oscillator reconstitutable *in vitro* is advantageous for studying its dynamic structure through a complementary usage of both X-ray crystallography and solution scattering, its transient response by using physicochemical techniques, and its molecular motion through a collaborative work with computational groups (Abe *et al. Science* 2015). Our mission is to explore the frontier in molecular science of the circadian clock system from many perspectives.

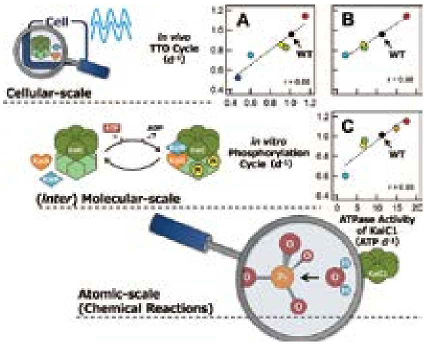

Figure 1. *Trans*-hierarchic nature of the circadian clock system in cyanobacteria. Cross-correlational plots (A–C) among frequency of *in vivo* transcription and translation oscillation (TTO) cycle, frequency of *in vitro* phosphorylation cycle, and ATPase activity of KaiC for cyanobacteria carrying period-modulating KaiC mutants (circles). Fine correlations in three panels indicate regulatory mechanisms of KaiC ATPase as the core basis for *trans*-hierarchic nature of cyanobacterial circadian clock system.

Selected Publications

- Y. Furuike, J. Abe, A. Mukaiyama and S. Akiyama, *Biophys. Physicobiol.* **13**, 235–241 (2016).
- 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, *Cell. Mol. Life Sci.* **69**, 2147–2160 (2012).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

1. Atomic-Scale Origins of 24 Hour Period in Cyanobacterial Clock System[1,2]

The cyanobacterial circadian clock can be reconstructed *in vitro* by mixing three clock proteins (KaiA, KaiB, and KaiC) and ATP. As shown in Figure 2, KaiC ATPase activity exhibits a robust circadian oscillation in the presence of KaiA and KaiB. Astonishingly, the temporal profile of KaiC ATPase activity exhibited an attenuating and oscillating component even in the absence of KaiA and KaiB. A detailed analysis revealed that this signal had a frequency of 0.91 d^{-1}, which approximately coincided with the 24 h period. KaiC is thus the source of a steady cycle that is in tune with the Earth's daily rotation.

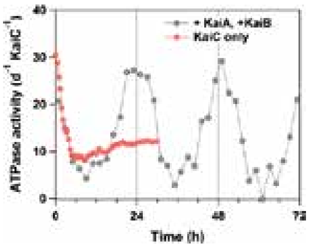

Figure 2. Time-course of KaiC ATPase activity.

To identify the structural origins of slowness encoded in KaiC (Figures 1B & 1C), its N-terminal ATPase domain was analyzed using high-resolution x-ray crystallography. A water molecule is prevented from attacking into the ideal position (a black dot in Figure 3) for the ATP hydrolysis by a steric hindrance near ATP phosphoryl groups. In addition, this hindrance is surely anchored to a spring-like structure derived from polypeptide isomerization. The ATP hydrolysis, which involves access of a water molecule to the bound ATP and reverse isomerization of the polypeptide, is expected to require a significantly larger amount of free energy than for typical ATP hydrolysis. The atomic structure discovered by us explains why the ATPase activity of KaiC is so much lower (by 100- to 1,000,000-fold) than that of typical ATPase molecules.

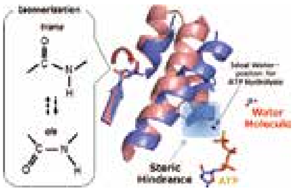

Figure 3. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

2. *Trans*-Hierarchic Nature of Cyanobacterial Circadian Clock System[3]

How is the intra-molecular slowness encoded in KaiC (Figures 2 and 3) transmitted to the inter-molecular interactions with other Kai proteins? Protein-ligand interactions are often discussed whether a structural change of the protein comes before or after the ligand binding (Figure 4). The conformational selection (CS) scheme predicts that the protein first undergoes a structural change to form a specific intermediate. The ligand is then recognized specifically through the intermediate state to form a tight ligand-protein complex. On the other hand, in the induced-fit (IF) scheme, the ligand and protein form an encountered complex without meaningful structural changes, and then both the ligand and protein undergo structural changes to form the tight protein-ligand complex. Under the ligand-saturating conditions, the rate of forming the protein-ligand complex differs between CS (k_f) and IF ($k_f + k_b$) schemes (Figure 4).

A tryptophan residue was introduced in the N-terminal ring of KaiC as the fluorescent probe for KaiBC complex formation.[3] Our detailed analysis of the kinetic data indicated that KaiB exclusively selects the post-ATP-hydrolysis state of KaiC to form the KaiBC complex. The CS mechanism is elegantly designed in KaiC so that the slow intra-molecular reaction (k_f: The slow rate of ATPase) in KaiC can be the rate-liming step of the overall KaiBC complex formation.

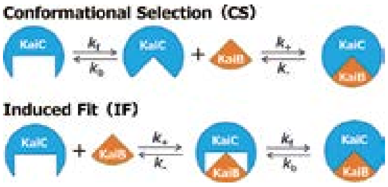

Figure 4. Conformational selection and induced-fit schemes.

3. Instrumentation for Studying Biological Clock Systems[4]

We have improved stability over time, signal-to-noise ratio, time resolution, temperature control, automated high-throughput measurements each for fluorescence tracking system,[3] auto-sampling device,[4] HPLC,[1] FTIR, and small-angle x-ray scattering (SAXS). The developed devices were utilized in identifying the core process of generating circadian periodicity in cyanobacterial circadian clock.[2,3]

4. Bio-SAXS Activity in IMS[5]

We have supported SAXS users so that they can complete experiments smoothly and publish their results.[5]

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1) S. Akiyama, A. Mukaiyama, J. Abe and Y. Furuike, *Biological Clocks: With Reference to Suprachiasmatic Nucleus*, 73–77 (2017).
2) 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).
3) A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* **8**, 8803 (2018).
4) Y. Furuike, J. Abe, A. Mukaiyama and S. Akiyama, *Biophys. Physicobiol.* **13**, 235–241 (2016).
5) Submitted.

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* IMS International Internship Program

Protein Design Using Computational and Experimental Approaches

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2014 JST-PRESTO Researcher (additional post) (–2017)
2018 Associate Professor, Exploratory Research Center on Life and Living Systems

Awards

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

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

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

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

Selected Publications

- N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, “Principles for Designing Ideal Protein Structures,” *Nature* **491**, 222–227 (2012).
- Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, “Control over Overall Shape and Size in De Novo Designed Proteins,” *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).

1. Principles for Designing Ideal Protein Structures

Understanding the principles for protein folding is complicated by energetically unfavorable non-ideal features—for example kinked α-helices, bulged β-strands, strained loops and buried polar groups—that arise in proteins from evolutionary selection for biological function or from neutral drift. Here, we uncovered the principles for protein folding by designing "ideal" protein structures, which are stabilized by completely consistent local and non-local interactions. We discovered a set of rules relating local backbone structures (secondary structure patterns) to tertiary motifs (Figure 1 left), which were identified using a combination of folding simulations and analyses of naturally occurring proteins. Building backbone structures according to the rules (Figure 1 top right) and placing side chains stabilizing the backbone structures, we can readily design the proteins that have funnel-shaped folding energy landscapes leading into the target folded state.

Using this approach, we designed sequences predicted to fold into ideal protein structures consisting of α-helices, β-strands and minimal loops, using the Rosetta program. Designs for five different topologies were found to be monomeric and very stable and to adopt structures in solution nearly identical to the computational models (Figure 1 bottom right). These results suggest that the local backbone structures determine the tertiary folded structures rather than the details of amino acid sequences.

2. Control over Overall Shape and Size in De Novo Designed Proteins

To achieve fine control over protein shape and size within a particular topology, we have extended the design rules by systematically analyzing the codependences between the lengths and packing geometry of successive secondary structure elements and the backbone torsion angles of the loop linking them. We demonstrate the control afforded by the resulting extended rule set by designing a series of protein with the same fold but considerable variation in secondary structure length, loop geometry, β-strand registry, and overall shape. Solution NMR structures of four designed proteins for two different folds show that protein shape and size can be precisely controlled within a given fold. These extended design principles provide the foundation for custom design of protein structures performing desired functions.

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4) J. Fang, A. Mehlich, N. Koga, J. Huang, R. Koga, M. Rief, J. Kast, D. Baker and H. Li*, *Nat. Commun.* **4**, 2974 (2013).
5) Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).
6) Y.-R. Lin, N. Koga, S. M. Vorobiev and D. Baker*, *Protein Sci.* **26**, 2187–2194 (2017).

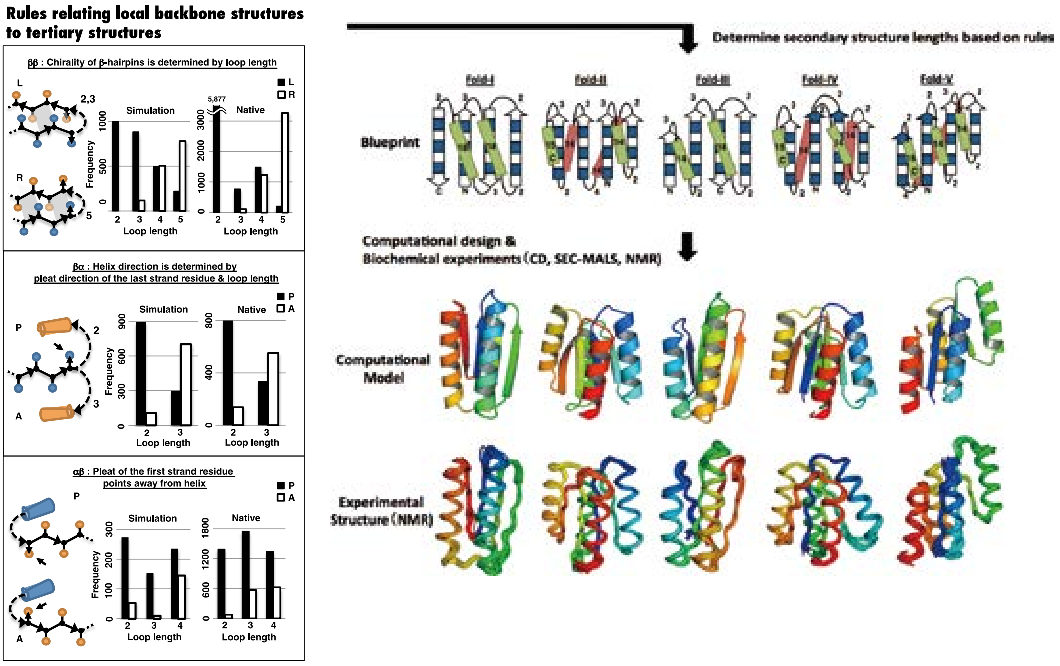

Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Award

KOGA, Nobuyasu; Morino Foundation for Molecular Science (2018).

Open up Future Electronics by Organic Molecules

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Education
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Awards
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Keywords Molecular Conductors, Organic Superconducting Transistors, Supramolecular Nanowires

Organic molecules are attracting recent attention as new ingredients of electronic circuits. Their functionalities have been developed considerably, but are still to be explored and advanced. Our group focuses on a development of organic electronics in the next era by providing new mechanism and concepts of the device operation and fabrication. For example, an electronic phase transition is utilized for the ON/OFF switching of our field-effect-transistor (FET). This special FET is called an organic Mott-FET, where the conduction electrons in the organic semiconductor are solidified at the OFF state because of Coulomb repulsion among carriers. However, these solidified electrons can be melted by applying a gate voltage, and show an insulator-to-metal transition so-called Mott-transition to be switched to the ON state. Because of this phase transition, a large response of the device can be achieved, resulting in the highest device mobility ever observed for organic FETs. At the same time, Mott-transition is known for its relevance to superconductivity. Not only in organic materials but also in inorganic materials such as cuprates, Mott-transition is frequently associated with superconducting phase at low temperature. Indeed, our organic FET shows an electric-field-induced superconducting transition at low temperature.

Another approach to the future electronics is a three-dimensional (3D) patterning of molecular devices using crystal engineering. Because each molecule can be designed to show different functionalities, it should be attractive to construct nano-structured devices by self-assembly. We are especially focusing on a development of supramolecular nanowires that allow 3D periodic wiring in nano-scale. By encapsulating a 1D array of conducting molecules in a channel formed inside 3D supramolecular network, it is possible to construct a sheathed nanowires aligned in a periodic order as shown in Figure 1.

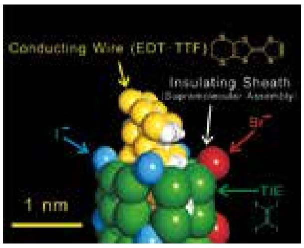

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- Y. Kawasugi, K. Seki, Y. Edagawa, Y. Sato, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Electron–Hole Doping Asymmetry of Fermi Surface Reconstructed in a Simple Mott Insulator," *Nat. Commun.* **7**, 12356 (8 pages) (2016).
- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).
- H. M. Yamamoto, M. Nakano, M. Suda, Y. Iwasa, M. Kawasaki and R. Kato, "A Strained Organic Field-Effect Transistor with a Gate-Tunable Superconducting Channel," *Nat. Commun.* **4**, 2379 (7 pages) (2013).
- H. M. Yamamoto, "Sheathed Nanowires Aligned by Crystallographic Periodicity: A Possibility of Cross-Bar Wiring in Three-Dimensional Space," *CrystEngComm* **16**, 2857–2868 (2014).

1. Light-Induced Superconductivity in an Organic Mott-FET[1,2)]

κ-(BEDT-TTF)Cu[N(CN)$_2$]Br (κ-Br) is an organic Mott-insulator at room-temperature, but turns into metallic and superconducting states at low temperature. (BEDT-TTF = bis(ethyelenedithio)tetrathiafulvalene) In our previous works, a tensile strain from FET substrate altered κ-Br's ground state into a Mott-insulating state, when its thin (*ca.* 100 nm) crystal was laminated on top of SiO$_2$/Si^{++} substrate and cooled down to low temperature. In those experiments the electronic state at low temperature became completely insulating because of the large tensile strain that originates in mismatching of thermal expansion coefficients between κ-Br (30 ppm/K) and Si (2 ppm/K). However, one can anticipate from the *T–P* (temperature *vs*. pressure) phase diagram that mixed electronic state between superconducting and Mott-insulating states will be realized when the tensile strain is much weaker. To achieve such a mixed state (or, percolate-superconducting state), Nb-doped SrTiO$_3$ is used as a back-gate substrate because of its larger thermal expansion coefficient (*ca.* 10 ppm/K) than Si. An aluminum oxide layer was grown by atomic layer deposition technique to form a gate dielectric on the substrate to form a FET device structure. With this type of FET substrate, we have achieved an electric-field-induced superconductivity in κ-Br.

Recently, we have inserted a photochromic self-assembled monolayer (SAM layer: Figure 2, right panel) into this device in order to make it photo-active. We have employed a photochromic molecule 'spiropyran' whose UV-converted isomer 'merocyanin' is known to exhibit zwitter-ionic structure. Because the photochromic molecules are aligned in the same direction in the SAM, a strong electric field can be generated by photo-irradiation, when the spiropyran is converted into the merocyanin form. Thus, excess carriers can be injected to the FET interface due to the strong dipole moment of merocyanin.

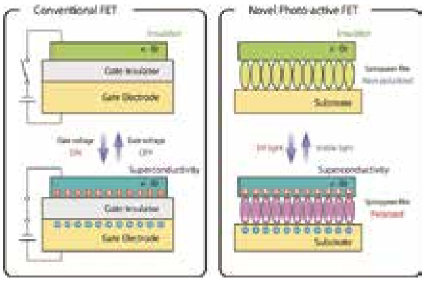

Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).
This figure shows p-type doping by molecular dipole-moment.

A κ-Br thin crystal is mounted on the SAM/Al$_2$O$_3$/Nb-SrTiO$_3$ substrate, and cooled down to low temperature. The resistance of the device showed weakly insulating temperature dependence, suggesting a percolate-superconducting state. Upon irradiation of UV-light, the resistivity at 5 K went down quickly and low-resistance state was observed after 180 sec. Temperature dependence of resistivity showed sudden drop around 7 K, confirming superconducting transition after the UV-light irradiation. Reverse photo-reaction by visible light led the phase transition back to the insulating state again. The switching of this device seems to originate from the light-induced formation of internal dipole moment in the SAM-layer, which resulted in a hole-doping at the FET interface. This speculation was confirmed by dual-gate experiment of this device, where gate-induced hole carriers worked cooperatively with the light-induced carriers. This result is the first example of light-induced superconductivity in FET devices, and allows remote control of superconducting device without direct wiring.

One can invert the direction of the molecule and its related electric field by designing a photochromic SAM molecule with different geometry. By such a strategy, we were able to achieve n-type light-induced superconductivity as shown in Figure 3. In this device, the threshold gate voltage for superconducting transition was shifted in the negative direction, as the UV irradiation proceeded. This implies that the light-induced carrier is an electron. These photo-active devices pave the way for new type of photo-electronics.

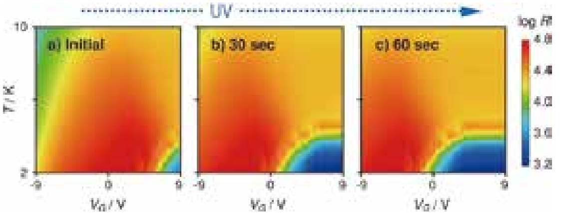

Figure 3. Emergence of n-type superconductivity by UV-irradiation. At the initial state (a), the device shows a normal ambipolar transistor behavior. After the UV-irradiation, superconducting region (blue) appears from electron-doped side (panels b and c).

References

1) M. Suda, R. Kato and H. M. Yamamoto, *Science* **347**, 743–746 (2015).
2) M. Suda, N. Takashina, S. Namuangruk, N. Kungwan, H. Sakurai and H. M. Yamamoto, *Adv. Mater.* **29**, 1606833 (2017).

Awards

SUDA, Masayuki; The 12th Condensed-Matter Science Prize (2017).
SUDA, Masayuki; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize (2018).

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* IMS International Internship Program

Development of Graphene Molecules as Organic Semiconductors

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Keywords Organic Synthesis, Organic Semiconductor, Graphene Molecule

Graphene and curved graphenes have been extensively investigated by both chemists and physicists because of their unique structures and properties. C_{60} fullerene is spherical and has the positive Gaussian curvature. Carbon nanotubes (CNTs) have the cylindrical structures with the zero Gaussian curvature. The introduction of curvatures to graphene changes the dimensionality and electronic properties. For example, graphene is a two-dimensional zero-gap semiconductor with the ambipolar character (both p- and n-types). C_{60} is a zero-dimensional n-type semiconductor, and CNTs are one-dimensional p-type semiconductors or metals. Three-dimensional graphenes with the negative Gaussian curvature were proposed as shown in Figure 1. It is interesting to see how the curvature influences the structure and properties of the graphene molecule.

Perfluorination is a simple method to prepare an n-type semiconductor with the same molecular symmetry. It is important to understand the impact of perfluorination on the solid-state structures and charge transport properties. We are currently working on the synthesis of new perfluorinated aromatic compounds.

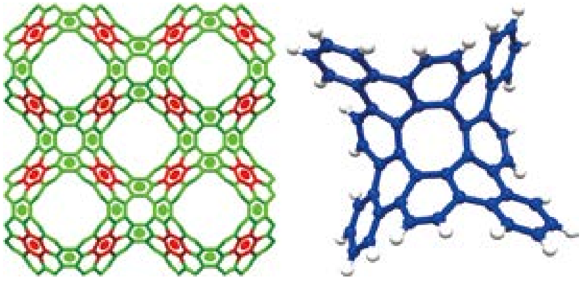

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki and S. Yamago, “Selective and Random Syntheses of [*n*]Cycloparaphenylenes (n = 8–13) and Size Dependence of their Electronic Properties,” *J. Am. Chem. Soc.* **133**, 8354–8361 (2011).
- Y. Sakamoto and T. Suzuki, “Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene,” *J. Am. Chem. Soc.* **135**, 14074–14077 (2013).
- Y. Kuroda, Y. Sakamoto, T. Suzuki, E. Kayahara and S. Yamago, “Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops,” *J. Org. Chem.* **81**, 3356–3363 (2016).
- Y. Sakamoto and T. Suzuki, “Perfluorinated and Half-Fluorinated Rubrenes: Synthesis and Crystal Packing Arrangement,” *J. Org. Chem.* **82**, 8111–8116 (2017).

1. Perfluorination of Rylene Compounds for Electronics and Optoelectronics

Perfluorination of aromatic compounds is a simple method of exchanging all hydrogen with fluorine, and it is possible to convert a p-type semiconductor to an n-type one.[1] Although the molecular weight greatly increases, the melting point, sublimation temperature, and stability do not change so much. Therefore, perfluorinated aromatic compounds can be handled under similar conditions. As seen in pentacene ($C_{22}H_{14}$) and perfluoropentacene ($C_{22}F_{14}$), the size and symmetry of the hydrogen molecule and the fluorine form are comparable. Because of this advantage, comparative study is easy and contributes to a deep understanding of molecular properties. In this research, we decided to fluorinate the rylene compound as a new target.

The rylene compound is an oligomer in which the 1,8 and 4,5 positions of naphthalene ($C_{10}H_8$) are connected.[2] Perylene (dimer, $C_{20}H_{12}$), terrylene (trimer, $C_{30}H_{16}$), and quarterrylene (tetramer, $C_{40}H_{20}$) have been known for a long time. Oligomers up to octamer have been reported as derivatives with solubilizing groups. Rylene compounds are interesting in the following three points. (1) High efficiency singlet fission (SF) can be expected. (2) Perylene derivatives such as diindenoperylene (DIP, $C_{32}H_{16}$) and dibenzotetraphenylperiflanthene (DBP, $C_{64}H_{36}$) have been frequently used for organic solar cells, and reports on organic thin films have increased. (3) Polyrylene corresponds to an armchair-type graphene nanoribbon (GNR) with the minimum width.

In collaboration with the Momiyama group, we synthesized some fluorinated naphthalene monomers and are working on perfluorinated perylene.

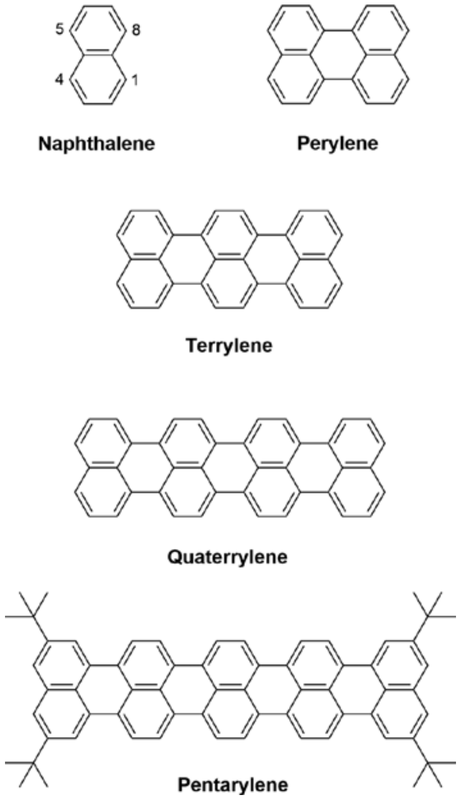

Figure 2. Chemical structures of naphthalene to pentarylene.

References

1) Y. Sakamoto and T. Suzuki, *J. Org. Chem.* **82**, 8111–8116 (2017).
2) J. T. Markiewicz and F. Wudl, *ACS Appl. Mater. Interfaces* **7**, 28063–28085 (2015).

RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

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

Nano-Optical Imaging and Application to Nanomaterials

Center for Mesoscopic Sciences
Division of Supersensitive Measurements

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Education
1983 B.S. The University of Tokyo
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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

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Keywords Nano Optics, Plasmons, Chirality

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

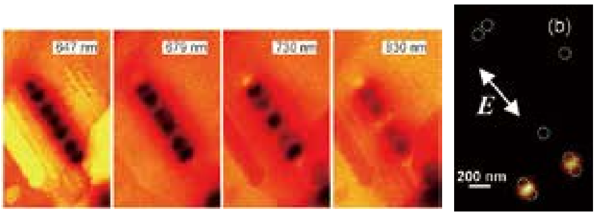

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right)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

Selected Publications

- H. Okamoto, 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).
- H. Okamoto and K. Imura, "Near-Field Optical Imaging of Enhanced Electric Fields and Plasmon Waves in Metal Nanostructures," *Prog. Surf. Sci.* **84**, 199–229 (2009).

1. Imaging Chirality of Optical Fields near Achiral Metal Nanostructures Excited with Linearly Polarized Light¹⁾

Chiral systems respond differently to left- and right-handed circularly polarized light macroscopically. As a consequence, only chiral materials show intrinsic macroscopic optical activity, and only chiral systems generate circularly polarized light from linearly polarized incident light. In the nanoscopic regime, in contrast to this general rule for macroscopic cases, it is theoretically expected that achiral (nonchiral) systems can locally generate circularly polarized fields. Here, we report experimental evidence for that situation in achiral systems consisting of gold nanostructures and linearly polarized incident light. The local circularly polarized fields were visualized by near-field polarimetry imaging. In this novel method, linearly polarized near-field radiation illuminates the sample, and the polarization state (ellipticity and rotational angle of polarization) of the far-field scattered light was measured at each position of excitation on the nanostructure, to construct the image. We found that highly circularly polarized fields were generated in the peripheries of the nanostructures, and the spatial features of the observed circularly polarized fields were qualitatively reproduced by a simple oscillating dipole model. The present results may provide a novel technique to produce controllable circularly polarized optical fields in nanospaces, the demonstration of which is now under way.

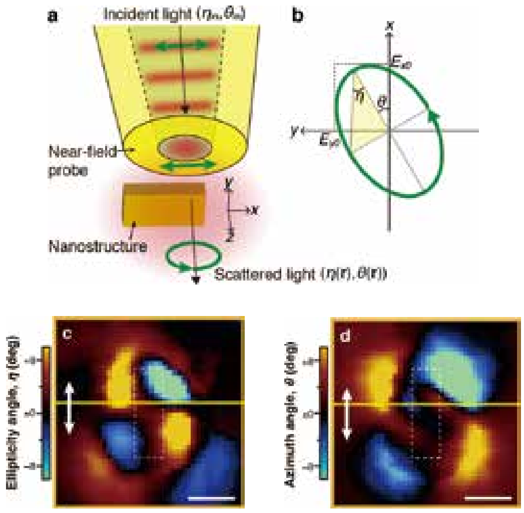

Figure 2. (a) Scheme of near-field polarimetry. (b) Definitions of ellipticity (η) and rotation (θ) angles. (c) Ellipticity and (d) optical rotation images (at 800 nm) of nano-rectangle. Scale bar: 100 nm.¹⁾

2. Nanoscale Chiral Surface Relief of Azo-Polymers Induced by Near-Field Optical Angular Momentum Light²⁾

An optical vortex with orbital angular momentum (OAM) can be used to induce micrometer-scale chiral structures in various materials. Such chiral structures enable the generation of a near-field OAM light on a sub-wavelength scale, thereby leading to nanoscale mass-transport. We found formation of a nanoscale chiral surface relief (diameter ~400 nm) in azo-polymers due to near-field OAM light based on this principle. We analyzed near-field intensity and polarization state distributions in the periphery of the chiral structures using the near-field polarimetry imaging.

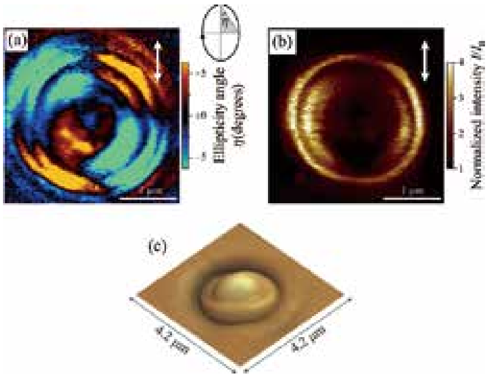

Figure 3. a) Near-field ellipticity, (b) near-field extinction, and (c) topographic images of left-handed spiral relief structure of azo-polymer fabricated with OAM light (532 nm).²⁾

3. Super-Resolution Optical Trapping: Theoretical Prediction of Nanoparticle Manipulation Using Nonlinear Optical Response³⁾

Optical manipulation of nanoparticles (NPs) with nanoscale precision is one of goals of nanomaterials science. A way to realize this is the usage of localized surface plasmon resonances. The electric fields near metallic structures are highly localized, which generate sufficient force to trap NPs, and the optical nonlinearity of NPs appears at the same time. In this study, we propose a scheme of spatially highly confined (beyond the diffraction limit) optical trap of the NP into a particular hotspot of the metallic nanostructure array. The scheme is based on the optical nonlinearity of NPs, and utilizes two kinds of structured light: Gaussian and Laguerre-Gaussian beams. The principle resembles that of stimulated emission depletion microscope, one of the major techniques of super-resolution microscope. The simulation results show the significant role of the optical nonlinearity in plasmon trappings. They are expected to open up new degrees of freedom to manipulate NPs.

References

1) S. Hashiyada, T. Narushima and H. Okamoto, *ACS Photonics* **5**, 1486–1492 (2018).
2) K. Masuda *et al.*, *Opt. Express* **26**, 22197–22207 (2018).
3) M. Hoshina, N. Yokoshi, H. Okamoto and H. Ishihara, *ACS Photonics* **5**, 318–323 (2018).

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* IMS International Internship Program (Graduate Student from National Chiao Tung University, Taiwan)

Micro Solid-State Photonics

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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

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)

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  ZHENG, Lihe
  YAHIA, Vincent
  LIM, Hwanhong
Research Fellow
  KAUSAS, Arvydas
  KAWASAKI, Taisuke
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Secretary
  ONO, Yoko
  INAGAKI, Yayoi

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

"*Micro Solid-State Photonics*," based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science. The engineered materials of micro and/or microchip solid-state, ceramic and single-crystal, 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, UV to THz wave generation. Moreover, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. The future may herald new photonics.

Giant pulse > 10 MW was obtained in 1064nm microchip lasers using micro-domain controlled materials. The world first laser ignited gasoline engine vehicle, giant-pulse UV (355 nm, 266 nm) and efficient VUV (118 nm) pulse generations have been successfully demonstrated. Also, few cycle mid-IR pulses for atto-second pulses are demonstrated by LA-PPMgLN. We have developed new theoretical models for the micro-domain control of anisotropic laser ceramics. These functional micro-domain based highly brightness/brightness-temperature compact lasers and nonlinear optics, so to speak "Giant Micro-photonics," are promising. Moreover, the new generation of micro and/or microchip lasers by using orientation-controlled advanced ceramics can provide extreme high performances in photonics.

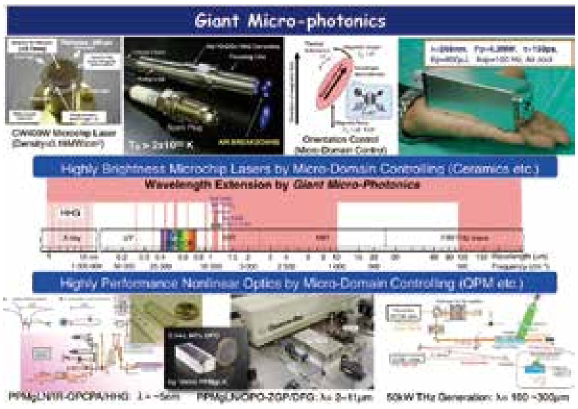


Figure 1. Giant micro-photonics.

Selected Publications

- H. Sakai, H. Kan and T. Taira, ">1 MW Peak Power Single-Mode High-Brightness Passively Q-Switched Nd^{3+}:YAG Microchip Laser," *Opt. Express* **16**, 19891–19899 (2008).
- M. Tsunekane, T. Inohara, A. Ando, N. Kido, K. Kanehara and T. Taira, "High Peak Power, Passively Q-Switched Microlaser for Ignition of Engines," *IEEE J. Quantum Electron.* **46**, 277–284 (2010).
- T. Taira, "Domain-Controlled Laser Ceramics toward Giant Micro-Photonics," *Opt. Mater. Express* **1**, 1040–1050 (2011).
- H. Ishizuki and T. Taira, "Half-Joule Output Optical-Parametric Oscillation by Using 10-mm-Thick Periodically Poled Mg-Doped Congruent $LiNbO_3$," *Opt. Express*, **20**, 20002–20010 (2012).
- R. Bhandari, N. Tsuji, T. Suzuki, M. Nishifuji and T. Taira, "Efficient Second to Ninth Harmonic Generation Using Megawatt Peak Power Microchip Laser," *Opt. Express* **21**, 28849–28855 (2013).

1. Thermal Reduction through Distributed Face Cooling (DFC) in a High Power Giant-Pulse Tiny Laser

Sapphire/Nd^{3+}:YAG based DFC chip was obtained with thermal reduction as compared with those from conventional Nd^{3+}:YAG chip. The CW diode laser pumped round-trip cavity loss was 0.51% from a 9-disk DFC chip, which was close to theoretically calculated total Fresnel reflection loss of 0.2% from 8 Sapphire/Nd^{3+}:YAG interfaces. The depolarization ratio from 8-disk DFC chip was 40 times lower than that from YAG/Nd^{3+}:YAG chip. The DFC chip underwent no crack at pump power of 86 W while Nd^{3+}:YAG single chip suffered crystal crack under pump power around 54 W, as shown in Figure 2.

Over megawatt peak power from DFC tiny integrated laser was demonstrated at 1 kHz with 3-pulse burst modes. It is concluded that DFC structure could relieve thermal effects as expected.

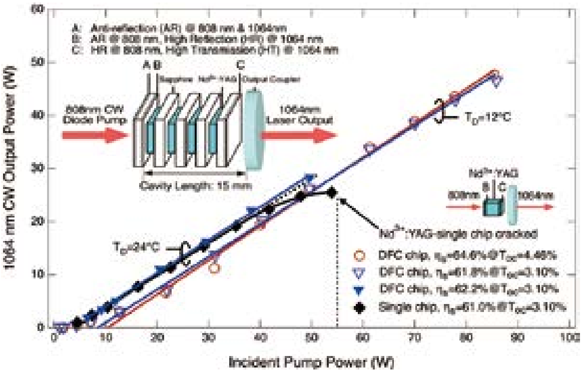


Figure 2. Output power from DFC chip under continuous wave laser pump. T_D is the temperature of diode laser.

2. Q-switching Laser Oscillation of Microdomain-Controlled Yb:FAP Laser Ceramics

The process control of microdomains with quantum mechanical calculations is expected to increase the optical power extracted per unit volume in gain media. Design of extensive variables allows us to evaluate the crystalline magnetic anisotropy in microdomains. Using this process control, we generate over 2 kW laser output from orientation-controlled microdomains made of Yb:Fluoroapatite (FAP).

In Figure 3, we compared the repetition rate and extraction energy density as the figure of merit for Giant-microphotonics, where our microdomain-controlled Yb:FAP laser ceramics showed excellent future possibility of power scaling.

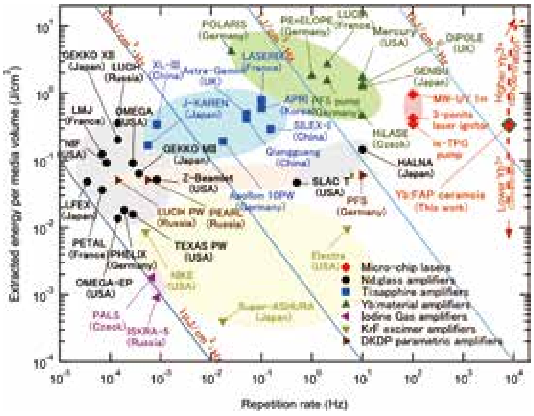


Figure 3. The figure of merit for Giant-microphotonics.

3. Crystal Quartz for High-Intensity, Sub-Nanosecond Wavelength Conversion

Crystal quartz for high-intensity wavelength conversion was evaluated. Pure durability of crystal quartz for sub-ns pulse region at 1.064 μm irradiation was measured as 602 GW/cm^2, which was 2-times higher than undope YAG crystal. QPM-structured quartz constructed by multi-plate stacking was evaluated by a sub-ns high-energy MCL-MOPA pumping. Maximum SH energy of 250 μJ could be obtained at E_p = 52 mJ with conversion efficiency of 0.48% as shown in Figure 4(a). Increasing characteristics of maximum E_{SH} on plate-stacking number N at E_p = 50~55 mJ is shown in Figure 4(b). Our experimental results well fitted the N^2-characteristics of the QPM characteristics.

As a result, availability of crystal quartz for high-intensity wavelength conversion could be demonstrated. QPM quartz is expected for both high-intensity operation and short-wavelength conversion.

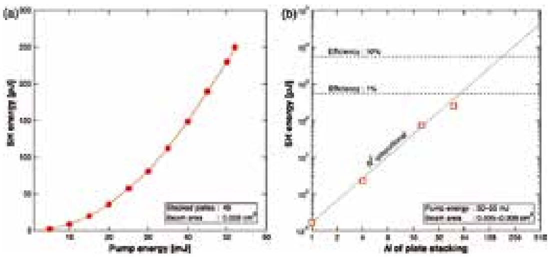


Figure 4. (a) SH energy on pump energy at N = 48, and (b) SH energy on stack number N.

References

1) L. H. Zheng, A. Kausas and T. Taira, *Opt. Mater. Express* **7**, 3214–3221 (2017).
2) Y. Sato, J. Akiyama and T. Taira, *Sci. Rep.* **7**, 10732 (2017).
3) H. Ishizuki, V. Yahia and T. Taira, *Opt. Mater. Express* **8**, 1259–1264 (2018).

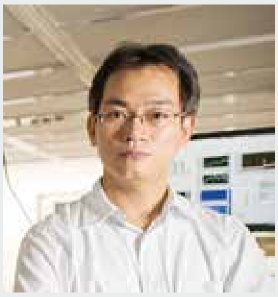
Award

TAIRA, Takunori; The Commendation for Lazer Advancement of Taizan Prize (2017).

* IMS International Internship Program

Ultrafast Laser Science

Center for Mesoscopic Sciences
Division of Broadband Multiscale Analysis



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Education

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2004 Guest Researcher, Max-Planck-Insitute of Quantum Optics
2006 Research Scientist, RIKEN
2008 Senior Scientist, RIKEN
2010 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards

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Keywords Ultrafast Science, Laser Physics, Nonlinear Optics

Light is very common in daily life, on the other hand, light has many interesting physical properties, for example, constancy of velocity, wave-particle duality, *etc*. The study of light itself is still important in modern physics.

Light is electro-magnetic field, same as radio wave, however, the measurement of the waveform of light is not easy task even in the 21st century. The difficulty comes from the extremely fast oscillation of the light wave. The oscillation frequency of light wave is the order of hundred terahertz (THz $= 10^{12}$ Hz), in other words, the oscillation period of light wave is the order of femtosecond (fs $= 10^{-15}$ s).

In 2013, we have developed a new method for the measurement of light wave. It is called FROG-CEP, frequency-resolved optical gating capable of carrier-envelope determination. Our method does not need attosecond pulses, even self-referencing is possible. The electric field oscillations of infrared light with the period of several femtoseconds were clearly measured with the method as is shown in Figure 1.

Currently, amplitude modulation and phase modulation are common encoding techniques in optical communication. If we can encode information in the shape of the light wave itself, the communication speed becomes 3 orders of magnitude faster. We believe that our method, FROG-CEP, becomes very important to realize such communication technology.

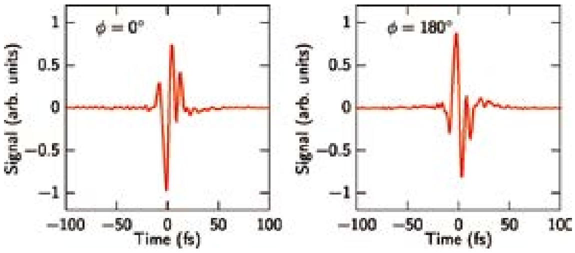

Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

Other than FROG-CEP, ultrabroadband mid-infrared continuum generation through filamentation, single-shot detection of ultrabroadband mid-infrared spectra, and development of 2 μm ultrafast lasers have been realized in our laboratory. We are developing such cutting edge technologies for ultrafast laser science.

Selected Publications

- T. Fuji and Y. Nomura, "Generation of Phase-Stable Sub-Cycle Mid-Infrared Pulses from Filamentation in Nitrogen," *Appl. Sci.* **3**, 122–138 (2013).
- Y. Nomura, H. Shirai and T. Fuji, "Frequency-Resolved Optical Gating Capable of Carrier-Envelope Phase Determination," *Nat. Commun.* **4**, 2820 (11 pages) (2013).
- Y. Nomura M. Nishio, S. Kawato and T. Fuji, "Development of Ultrafast Laser Oscillators Based on Thulium-Doped ZBLAN Fibers," *IEEE J. Sel. Top. Quantum Electron.* **21**, 0900107 (7 pages) (2015).
- T. Fuji, Y. Nomura and H. Shirai, "Generation and Characterization of Phase-Stable Sub-Single-Cycle Pulses at 3000 cm^{-1}," *IEEE J. Sel. Top. Quantum Electron.* **21**, 8700612 (12 pages) (2015).
- T. Fuji, H. Shirai and Y. Nomura, "Ultrabroadband Mid-Infrared Spectroscopy with Four-Wave Difference Frequency Generation," *J. Opt.* **17**, 094004 (9 pages) (2015).
- H. Shirai, Y. Nomura and T. Fuji, "Self-Referenced Measurement of Light Waves," *Laser Photonics Rev.* **11**, 1600244 (6 pages) (2017).

1. High Harmonic Generation in Solids Driven by Sub-Cycle Mid-Infrared Pulses from Two-Color Filamentation

High-harmonic generation (HHG) is one of the most important nonlinear processes for the generation of attosecond pulses. In the last few years, HHG in solid materials is attracting a lot of attention in the fields of ultrafast science and solid-state physics. Since the atomic density is much higher in solids than in gases, solid-state HHG would be much more efficient than the HHG in atomic gases. The solid-state HHG would be a key technology to realize a compact solid-state attosecond pulse generator or petahertz electronics.

Naturally, experimental study with well-characterized single-cycle or sub-cycle pulses is one of the most straightforward approaches to investigate highly nonlinear process. Here, we report the demonstration of the HHG in a Si membrane driven by carrier-envelope phase (CEP) controlled sub-cycle mid-infrared (MIR) pulses generated through two-color filamentation.

The light source was based on a Ti:Sapphire multipass amplifier system. The generation scheme of the sub-cycle MIR pulses is the same as that published before.[1,2] In brief, the fundamental (800 nm, ω_1) and second-harmonic (400 nm, ω_2) pulses were gently focused into nitrogen, in which the sub-cycle MIR pulse (ω_0) was generated by using four-wave mixing ($\omega_1 + \omega_1 - \omega_2 \rightarrow \omega_0$) through filamentation. As is the case with the difference frequency generation, the CEP of the MIR pulse is passively stabilized.

Figure 2(a) shows a typical power spectrum and (absolute) spectral phases of the MIR pulses obtained with FROG-CEP measurements.[3] The spectrum covers the entire MIR region, corresponding to more than three octaves, and the spectral phase has some nonlinear term; namely, the pulse is slightly chirped. The pulse duration of the MIR pulse is estimated as ~8.5 fs at FWHM, corresponding to 0.64 optical cycles at 4 μm center wavelength. The waveforms of MIR pulses for the phases of −0.10π and −0.77π at 4 μm are shown in Figure 2(b). We can control the CEP of the MIR pulse very precisely by tilting the delay plate on a kinematic mount with a piezo-electric inertia actuator.

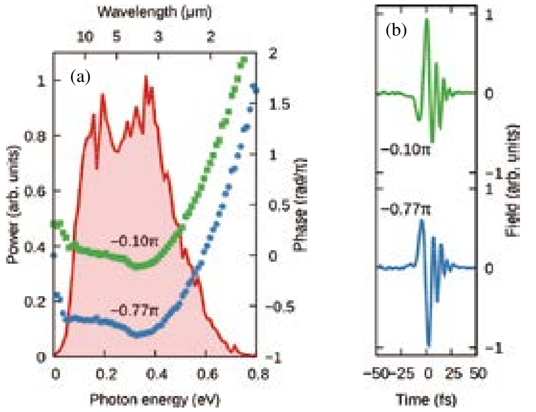

Figure 2. a) Power spectrum (shaded curve) and (absolute) spectral phases (closed circles and squares) of the MIR pulses obtained with the FROG-CEP technique. (b) Retrieved waveforms of the MIR pulses.

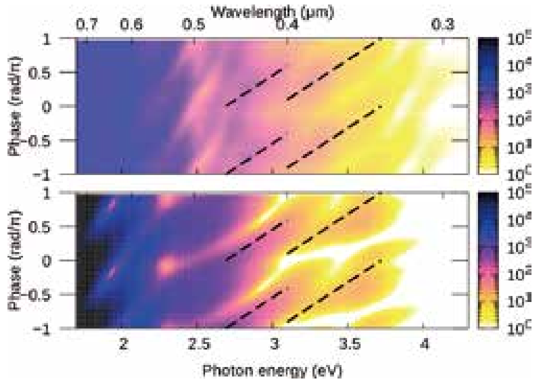

Figure 3. CEP dependence of the HH spectrum. (a) Experimental result. (b) Numerical simulation result obtained from optical Bloch equations.

Figure 3(a) shows the CEP dependence of the high-harmonic (HH) spectrum. We continuously recorded the HH spectra while scanning the CEP from −π to π. The HH spectra reach <300 nm, the ultraviolet region. The spectrum shifts to the higher photon energy region by increasing the CEP (indicated by dotted lines), and the same spectrum appears every π phase shift.

To investigate the complex structure and CEP dependence of the HH spectrum, we numerically simulated the CEP dependence of the HH spectrum based on the optical Bloch equations generalized to the case of a two-band semiconductor. In this numerical simulation, we used the waveform of the sub-cycle MIR pulse measured with FROG-CEP as a driving field.

Figure 3(b) shows the simulation result of the CEP dependence of the HH spectrum. As is the case with the experimental results in Figure 3(a), the spectral shape shifts to a higher photon energy region by increasing the CEP of the MIR pulse, and the same spectrum appears at every π phase shift. In addition, discontinuous change of the CEP dependence of the HH spectrum at around 3.1 eV, which corresponds to the direct band gap energy, is also reproduced [see dashed lines in Figures 3(a) and 3(b)]. We believe that the CEP dependence change is due to the increase in the imaginary part of the refractive index at around the direct band gap. In this simulation, the main features of the experimental result are qualitatively reproduced.

References

1) T. Fuji and Y. Nomura, *Appl. Sci.* **3**, 122 (2013).
2) T. Fuji, Y. Nomura and H. Shirai, *IEEE J. Sel. Top. Quantum Electron.* **21**, 8700612 (2015).
3) Y. Nomura, H. Shirai and T. Fuji, *Nat. Commun.* **4**, 2820 (2013).

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* IMS International Internship Program

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

RESEARCH ACTIVITIES

Division of Advanced Molecular Science

World-class researchers leading the frontiers of molecular science are invited as “distinguished professors.” The environment to devote themselves to research will be provided. We support top-level research in the field of molecular science.

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, Chiba University
1994	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

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)
2015	John Osborn Lecturer (Strasbourg University)
2016	Merit Award of The Naito Foundation
2018	Wolf Prize in Chemistry

Member
Secretary
WATANABE, Yoko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

Our laboratory is exploring the construction of new molecular materials through metal-directed self-assembly. By using coordination bonds with appropriate bond energy and well-defined geometries as the driving force of self-assembly, a variety of three-dimensional architectures have been constructed at will. Among these nanostructures, we are particularly interested in hollow frameworks with a large inner space, where new properties and functions are developed. Recent outstanding results include the self-assembly of gigantic $M_{30}L_{60}$ and $M_{48}L_{96}$ spherical complexes. We are also interested in reproducing solution reactions within the pore of self-assembled porous complexes. In due course, we have recently developed a new X-ray technique that does not require the crystallization of target compounds (crystalline sponge method). This innovative analysis method is attracting considerable interests of not only academia but also industries such as pharmaceutics and foods companies.

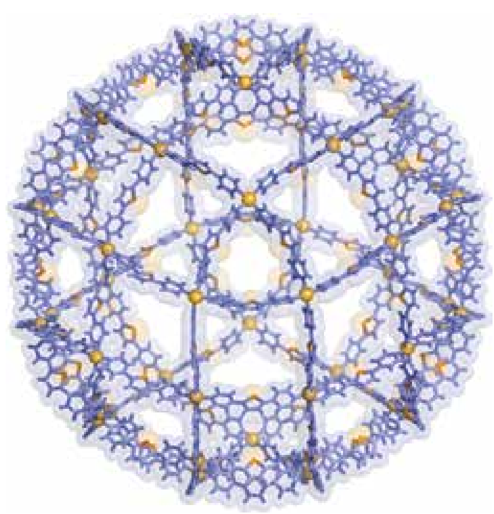

Figure 1. X-ray structure of $M_{48}L_{96}$ complex.

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, H. Yokoyama, N. Mizuno, T. Kumasaka and M. Fujita, "Self-Assembly of $M_{30}L_{60}$ Icocidodecahedron," *Chem* **1**, 91–101 (2016).
- D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, "Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components," *Nature* **540**, 563–566 (2016).

1. Self-Assembly of Molecular Polyhedra

Rational control of the self-assembly of large structures is one of the key challenges in chemistry, and is believed to become increasingly difficult and ultimately impossible as the number of components involved increases. We have achieved in the self-assembly of a series of large spherical structures which belong to Platonic or Archimedean polyhedra containing up to 30 palladium ions coordinated by up to 60 bent organic bidentate ligands by considering their geometries and topologies.[1,2] We have also found the functionality in the large inner spaces of these structures such as protein encapsulation,[3] size-regulated synthesis of nanoclusters and so on.

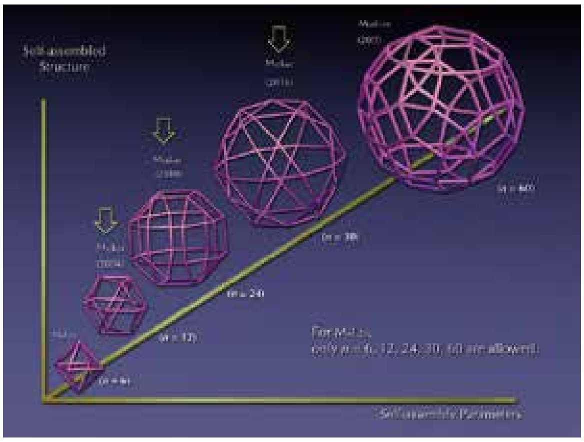

Figure 2. Series of large polyhedral structures.

Recently we serendipitously obtained the self-assembly of a spherical structure[4] that contains 30 palladium ions and 60 bent ligands, but belongs to a shape family that has not previously been observed experimentally (Figure 1). The new structure consists of a combination of 8 triangles and 24 squares, and has the symmetry of a tetravalent Goldberg polyhedron. Tetravalent Goldberg polyhedra have not previously been reported at the molecular level, although their topologies have been predicted using graph theory. We use graph theory to predict the self-assembly of even larger tetravalent Goldberg polyhedra, which should be more stable, enabling another member of this polyhedron family to be assembled from 144 components: 48 palladium ions and 96 bent ligands.

2. Crystalline Sponge Method

X-ray single crystal diffraction (SCD) analysis is one of the most effective methods for the structure determination and is the only one practical way to determine the absolute structure of molecules. However, it has the intrinsic limitation that the target molecules must be obtained as single crystals. We have reported a new protocol for SCD analysis that does not require the crystallization of samples.[5] In our method, tiny crystals of porous complexes are soaked in a solution of a target, where the complexes can absorb and orient the target molecules in the pores. The crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks. As the SCD analysis is carried out with only one tiny crystal, the required sample amount is of the nano-to-microgram order. This method can be applied to many varieties of molecules including oily materials which never crystallize in principle. With chiral guests, the space group of the crystal turned into chiral, enabling the determination of absolute configuration of the guests by anomalous scattering effect from the host heavy atoms (Zn and I).

This method has been applied to natural product chemistry, synthetic chemistry, and pharmaceutical research so far. For example, the absolute configurations of elatenyne, first isolated in 1986, was reliably determined by the crystalline sponge method after 30 years. It had not been unequivocally confirmed because of its almost achiral meso-formed core structure that results in nearly zero [α]D specific rotation. This faint chirality, defined only by the slight difference in the two alkyl side-chains, was precisely discriminated by crystalline sponge method. The total amount required for the experiments was only ~100 μg and the majority of this (95 μg) could be recovered after the experiments. Here, our group will widen and deepen this method more scientifically in close coordination with Nanotechnology Platform which started from 2018 at IMS.

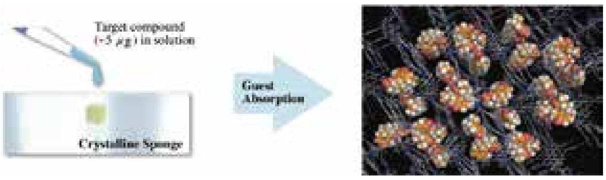

Figure 3. Schematic representation of crystalline sponge method.

References

1) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi and M. Fujita, *Science* **328**, 1144–1147 (2010).
2) D. Fujita, Y. Ueda, S. Sato, H. Yokoyama, N. Mizuno, T. Kumasaka and M. Fujita, *Chem* **1**, 91–101 (2016).
3) D. Fujita, K. Suzuki, S. Sato, M. Yagi-Utsumi, Y. Yamaguchi, N. Mizuno, T. Kumasaka, M. Takata, M. Noda, S. Uchiyama, K. Kato and M. Fujita, *Nat. Commun.* **3**, 1093 (2012).
4) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, *Nature* **540**, 563–566 (2016).
5) Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, *Nature* **495**, 461–466 (2013).

Award

FUJITA, Makoto; Wolf Prize in Chemistry (2018).

RESEARCH ACTIVITIES

RESEARCH FACILITIES

The Institute includes five research facilities. This section describes their latest equipment and activities. For further information please refer to previous IMS Annual Review issues (1978–2017).

UVSOR Synchrotron Facility

KERA, Satoshi	Director, Professor
KATOH, Masahiro	Professor
TANAKA, Kiyohisa	Associate Professor
MATSUI, Fumihiko	Senior Researcher
IWAYAMA, Hiroshi	Assistant Professor
OHIGASHI, Takuji	Assistant Professor
IDETA, Shin-ichiro	Assistant Professor
FUJIMOTO, Masaki	Assistant Professor
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YAMAZAKI, Jun-ichiro	Technical Associate
HAYASHI, Kenji	Technical Associate
KONDO, Naonori	Technical Associate
SAKAI, Masahiro	Technical Associate
TESHIMA, Fumitsuna	Technical Associate
YANO, Takayuki	Technical Associate
MAKITA,Seiji	Technical Associate
HORIGOME, Toshio	Specially Appointed Technical Associate
YUZAWA, Hayato	Specially Appointed Technical Associate
MINAKUCHI, Aki	Technical Fellow
HAGIWARA, Hisayo	Secretary
INAGAKI, Itsuko	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 approximately 50 meters in circumference, is regularly operated in the top-up mode, in which the electron beam current is kept constant, 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 storage ring is normally operated under multi-bunch mode with partial filling. The single bunch top-up operation for time-resolved measurements or low current measurements is also conducted for two weeks per year.

Figure 1. UVSOR-III electron storage ring, radiation shield wall, and beamlines/endstations.

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

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

Beamline	Monochromator / Spectrometer	Energy Range	Targets	Techniques
BL1U	Free electron laser	1.6 - 13.9 eV	Gas Liquid Solid	Irradiation
BL1B	Martin-Puplett FT-FIR	0.5 - 30 meV	Solid	Reflection Absorption
BL2A	Double crystal	585 eV - 4 keV	Solid	Reflection Absorption
BL2B	18-m spherical grating (Dragon)	23 - 205 eV	Solid	Photoemission
BL3U	Varied-line-spacing plane grating (Monk-Gillieson)	60 - 800 eV	Gas Liquid Solid	Absorption Photoemission Photon-emission
BL3B	2.5-m off-plane Eagle	1.7 - 31 eV	Solid	Reflection Absorption
BL4U	Varied-line-spacing plane grating (Monk-Gillieson)	130 - 700 eV	Gas Liquid Solid	Absorption (Microscopy)
BL4B	Varied-line-spacing plane grating (Monk-Gillieson)	25 eV - 1 keV	Gas Solid	Photoionization Photodissociation Photoemission
BL5U	Varied-line-spacing plane grating (Monk-Gillieson)	20 - 200 eV	Solid	Photoemission
BL5B	Plane grating	6 - 600 eV	Solid	Calibration Absorption
BL6U*	Variable-included-angle varied-line-spacing plane grating	40 - 800 eV	Gas Solid	Photoionization Photodissociation Photoemission
BL6B	Michelson FT-IR	4 meV - 2.5 eV	Solid	Reflection Absorption
BL7U	10-m normal incidence (modified Wadsworth)	6 - 40 eV	Solid	Photoemission
BL7B	3-m normal incidence	1.2 - 25 eV	Solid	Reflection Absorption

Yellow columns represent undulator beamlines.
* In-house beamline.

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). In total, fourteen beamlines are now operating and except for BL1U and BL6U they are so-called "public beamlines," which are open to scientists from universities, governmental research institutes, public and private enterprises, and also to overseas scientists. Other two beamlines 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. Since 2018, BL1U is partly opened for using as public beamline.

From the viewpoint of photon energies, we have 1 SX station equipped with a double-crystal monochromator, 7 SX stations with a grazing incidence monochromator, 3 VUV stations with a normal incidence monochromator, two IR/THz stations equipped with Fourier transform interferometers and 1 beamline for light source development without any monochromators.

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 number of visiting researchers per year tops > 1200, whose come from > 60 different institutes. International collaboration is also pursued actively, and the number of visiting foreign researchers reaches ~70 from 13 countries. 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

A soft X-ray beamline BL5U has been open for users since 2016 and used as high-energy resolution ARPES beamline. By introducing a final focusing mirror close to the sample position (~50 mm), the synchrotron light whose original size was 400 (H) × 120 (V) is successfully focused to 23 (H) × 40 (V) μm. ARPES study on small samples or inhomogeneous samples is now available.

Beamline BL4U has been open for users since 2013 and used as high-resolution X-ray transmission microscopy (STXM). The extension of the photon energy range is demanded to cover much broaden research field. Adopting Fresnel zone plate for low-energy range, we are approaching to get 50 eV which may cover Li K-edge. Although it is challenging how to optimize the optical parameters, BL4U will be an unique and attractive beamline for studying varisou novel materials including solid battery.

The UVSOR accelerators have been operated for more than 30 years. We have been upgrading and replacing the machine components, such as magnet power supplies or RF power amplifiers, to continue the stable operation. In these years, troubles occurred on some core components, such as the vacuum chambers and the magnets. We are carefully planning their replacements with short shutdown periods and under the limitation of the facility budget.

Reserch Highlights[1)]

Understanding the mechanism of charge transfer in functional molecular solids, the electronic structure measurement, especially of the energy-band dispersion, is requested for molecular materials. However the electronic structure measurement has not been well achieved due to experimental difficulties for the molecular solids. More importantly, the dynamic interaction between the traveling charges and the molecular vibrations is critical for the charge transport in organic semiconductors. However, a direct evidence of the expected impact of the charge–phonon coupling on the band dispersion of organic semiconductors is yet to be provided. We reported on the electronic properties of rubrene single crystal as investigated by angle resolved ultraviolet photoelectron spectroscopy using low-excitation photon energy. A gap opening and kink-like features in the rubrene electronic band dispersion are observed thanks to high-energy and momentum resolutions in BL7U. In particular, the latter results in a large enhancement of the hole effective mass, well above the limit of the theoretical estimations. The results are consistent with the expected modifications of the band structures in organic semiconductors as introduced by hole–phonon coupling effects and represent an important experimental step toward the understanding of the charge localization phenomena in organic materials.

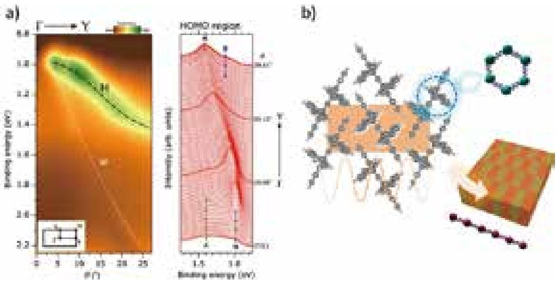

Figure 2. Renormalization of the energy-band dispersion of highest-occupied molecular orbital (HOMO) band of rubrene single crystal at 300 K by coupling collective phonons and intramolecular vibrations. a) Angle-resolved photoelectron spectra recorded along ΓY direction of the single crystal. The intensity map as a function of the emission angle θ is also shown (left). The HOMO (H) dispersion is indicated by dash dotted black curve as guides for the eye. The feature W due to secondary electron emission which reflects the density of states and band dispersion of unoccupied states is superimposed. b) Schematic of the molecular orientation in the crystalline a-b plane of rubrene single crystal. Images of collective phonon in the crystal and local intramolecular vibration are also shown.

Reference

1) F. Bussolotti *et al.*, *Nat. Commun.* **8**, 173–179 (2017).

Center for Mesoscopic Sciences

OKAMOTO, Hiromi	Director, Professor
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FUJI, Takao	Associate Professor
(the late) NOBUSADA, Katsuyuki	Associate Professor
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YOSHIZAWA, Daichi	Assistant Professor
ISHIZUKI, Hideki	Assistant Professor
NOMURA, Yutaka	Assistant Professor
SHIRAI, Hideto	IMS Research Assistant Professor
OKANO, Yasuaki	Technical Associate
MASUDA, Michiko	Secretary
NOMURA, Emiko	Secretary

As the succeeding organization of former Laser Research Center for Molecular Science, Center for Mesoscopic Sciences continues development of new experimental apparatus and methods to open groundbreaking research fields in molecular science, in collaboration with other departments and facilities. Those new apparatus and methods will be served as key resources in advanced collaboration with the researchers from the community of molecular science. The targets cover:

- advanced photon sources ranging from terahertz to soft X-ray regions
- novel quantum-control schemes based on intense and ultrafast lasers
- novel optical imaging and nanometric microscopy

and so forth.

The Center also possesses several general-purpose instruments for laser-related measurements (commercial as well as in-house developed), and lends them to researchers in IMS who conduct laser-based studies, so as to support and contribute to their advanced researches.

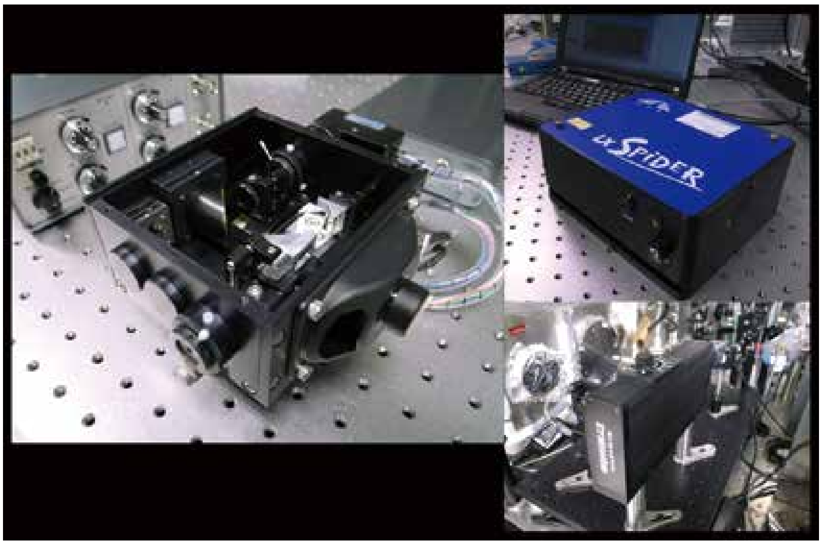

Figure 1. (left) A Fringe-Resolved Autocorrelation (FRAC) apparatus for sub-10 fs pulse characterization designed in the Center. (upper right) Spectral Phase Interferometry for Direct Electric-Field Reconstruction (SPIDER) and (lower right) Frequency-Resolved Optical Gating (FROG) apparatuses for general-purpose ultrashort pulse characterization.

Instrument Center

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UEDA, Tadashi	Technical Associate
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HIGASHI, Yosuke	Nano. Platform Manager
NODA, Ippei	Nano. Platform Coordinator
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NAGAO, Haruyo	Technical Fellow
IKI, Shinako	Technical Fellow
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SHIBATA, Yuka	Secretary
ITO, Sumie	Secretary

Instrument Center was organized in April of 2007 by integrating the general-purpose and state-of-the-art facilities of Research Center for Molecular Scale Nanoscience and Laser Research Center for Molecular Science. The mission of Instrument Center is to support the in-house and external researchers in the field of molecular science, who intend to conduct their researches by utilizing general-purpose and state-of-the-art instruments. The staffs of Instrument Center maintain the best conditions of the machines, and provide consultation for how to use them. The main instruments the Center now maintains in Yamate campus are: Nuclear magnetic resonance (NMR) spectrometers (JNM-ECA 600 for solutions, JNM-ECS400 for solutions and Bruker AVANCE800 Cryoprobe for solutions), matrix assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometer (microflex LRF, Bruker Daltonics), powder X-ray diffractometer (Rigaku RINT-Ultima III), circular dichroism (CD) spectrometer (JASCO JW-720WI), differential scanning calorimeter (MicroCal VP-DSC), isothermal titration calorimeter (MicroCal iTC200), solid-state calorimeter (Rigaku DSC8231/TG-DTA8122), scanning electron microscope (SEM; JEOL JEM-6700F), focused ion beam (FIB) processing machine (JEOL JEM-9310FIB), and elemental analyzer (J-Science Lab Micro Corder JM10). In the Myodaiji campus, the following instruments are installed: Electron spin resonance (ESR) spectrometers (Bruker E680, E500, EMX Plus), NMR spectrometer (Bruker AVANCE600 for solids), superconducting quantum interference devices (SQUID; Quantum Design MPMS-7 and MPMS-XL7), solution X-ray diffractometer (Rigaku NANO-Viewer), single-crystal X-ray diffractometers (Rigaku Mercury CCD-1, CCD-2, RAXIS IV, and 4176F07), thermal analysis instruments (TA TGA2950, DSC2920, and SDT2960), fluorescence spectrometer (SPEX Fluorolog2), X-ray fluorescence spectrometer (JEOL JSX-3400RII), UV-VIS-NIR spectrometer (Hitachi U-3500), Raman microscope (Renishaw INVIA REFLEX 532), nanosecond excimer/dye laser system (Lambda Physics LPX105i/LPD3002), Nd:YAG pumped OPO laser (Spectra Physics GCR-250/Lambda Physics Scanmate OPPO), fluorinated excimer laser (Lambda Physics Complex 110F), picosecond tunable laser system (Spectra Physics Tsunami/Quantronix Titan/Light Conversion TOPAS), low vacuum analytical SEM (Hitachi SU6600), electron spectrometers for chemical analysis (ESCA) (Omicron EA-125), angle resolved ultraviolet photoelectron spectroscopy (ARUPS) for functional band structures (VG-Scienta DA30), and FTIR spectrometer (Bruker IFS 66v/S). In the fiscal year of 2017, Instrument Center accepted 115 applications from outside and the total user time amounted 2,483 days for outside and 748 days for in-house with 34 equipments. Instrument Center also maintains helium liquefiers in the both campus and provides liquid helium to users (53,622 L/year). Liquid nitrogen is also provided as general coolants used in many laboratories in the Institute (41,042 L/year). The staffs of Instrument Center provide consultation for how to treat liquid helium, and provide various parts necessary for low-temperature experiments. Instrument Center organizes the Inter-University Network for Common Utilization of Research Equipments and the Molecule and Material Synthesis Platform in the Nanotechnology Platform Program supported by Ministry of Education, Culture, Sports, Science and Technology. These special programs are described in the other chapter of the booklet.

Equipment Development Center

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KONDOU, Takuhiko	Technical Associate
TOYODA, Tomonori	Technical Associate
TAKADA, Noriko	Technical Associate
NAKANO, Michiko	Technical Associate
KIMURA, Sachiyo	Technical Associate
KIKUCHI, Takuro	Specially Appointed Technical Associate
KIMURA, Kazunori	Specially Appointed Technical Associate
SAWADA, Toshihiro	Technical Fellow
YOSHIDA, Hisashi	Technical Fellow
URANO, Hiroko	Secretary

Researches and developments 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 two work sections, mechanics and electronics, are engaged in developing state-of-the-art experimental instruments in collaboration with scientists. We expanded our service to other universities and research institutes since 2005, to contribute to the molecular science community and to improve the technology level of the center staffs. A few selected examples of our recent developments are described below.

Development of a Special Shape Coil

We are developing a special shape electromagnetic coil that can generate rotating magnetic field inside a cavity. This rotating filed is important for aligning particles dispersed in a liquid. Since the shape and arrangement of coils affect the flow of magnetic flux with large complexity, it is not easy to estimate the direction and strength of magnetic flux generated by the coils. Therefore, computer-aided engineering is very important to help the designing. At the same time, we are fabricating the prototype model and evaluating the flow of magnetic flux by comparing the simulation and measurement result.

First, we have fabricated a winding machine to roll up wires in a customized way. Next, we have fabricated a simple shaped coil (wire diameter 0.6 mm, 725 turns), and measured generated magnetic flux density by a Gauss meter. As the result of comparison between the results of simulation and experiments, a good matching was confirmed. (Figure 1)

Now, we are not only optimizing the shape and material of the coil, but also developing a novel fabrication method for a special shaped coil.

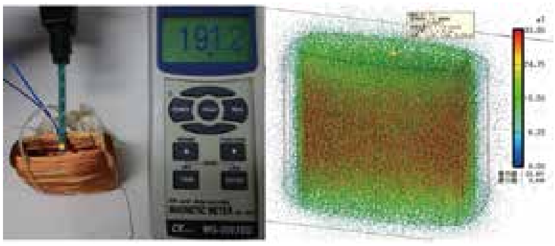

Figure 1. Measurement of magnetic flux density generated in a coil and result of CAE: 191.2 Gauss on experiment, 192 Gauss on CAE.

Signal Fan-Out Buffer and Distributor

When we distribute a signal from photo diode/MCP/Photo-Multiplier Tube (PMT) to an oscilloscope or a data acquisition system, we normally use BNC T type adapter and coaxial cable. However, such connections cause huge attenuation and/or degradation of the signal.

Our Signal Fan-out buffer and Distributor (SFD) can output copied input signal (up to ±5V, 20 MHz) to multiple channels (up to 8), and can prevent degradation of signal using driving circuit by THS3001ID (Texas Instruments). In addition, SFD indicates, by two-color LED, the polarity of input/output signals, as well as connection/ disconnection of cables using unique detection circuit by JFET operational amplifier ADA4610-2ARZ (Analog Devices). By the latter function, the users can grasp unexpected dropouts and disconnections of cables visually.

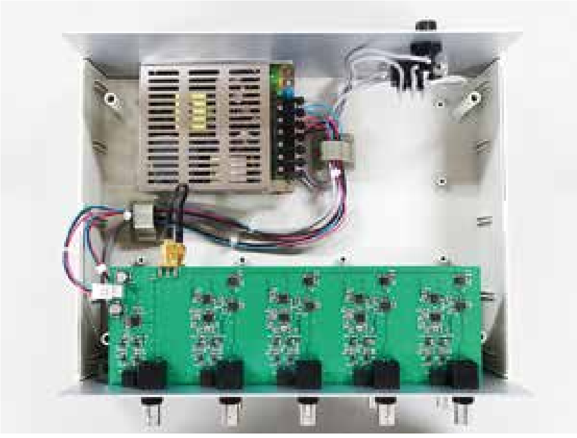

Figure 2. Inside view of Signal Fan-out Buffer and Distributor.

Research Center for Computational Science

SAITO, Shinji	Director, Professor
EHARA, Masahiro	Professor
OKUMURA, Hisashi	Associate Professor
OONO, Hitoshi	Assistant Professor
ISHIDA, Tateki	Assistant Professor
ITOH, Satoru G.	Assistant Professor
ITO, Soichi	Assistant Professor
UCHIYAMA, Ikuo	Assistant Professor
MIZUTANI, Fumiyasu	Technical Associate
IWAHASHI, Kensuke	Technical Associate
NAITO, Shigeki	Technical Associate
SAWA, Masataka	Technical Associate
MATSUO, Jun-ichi	Technical Associate
NAGAYA, Takakazu	Technical Associate
KAMIYA, Motoshi	Specially Appointed Technical Associate
TOYA, Akiko	Secretary
ISHIHARA, Mayumi	Secretary
KONDO, Naoko	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, and physiology. Our systems consist of NEC LX (406Rh-2, 110-Rh1, 108Th-4G; since Oct. 2017), Fujitsu PRIME HPC FX10, Fujitsu PRIMERGY (RX300 and CX2550; until Sep. 2017), and SGI UV2000 (until Sep. 2017). The NEC LX 406Rh-2 and 110-Rh1 combined system, named "Molecular Simulator," is ranked 93rd position in the TOP500 supercomputer list in June 2018. 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 a number of application programs to the users: Gaussian, GAMESS, Molpro, AMBER, Gromacs, and so on. The supercomputer systems had been used by 837 researchers from 224 groups in fiscal year 2017. Some of the computational resources are provided to the following projects: Post-K Supercomputer Priority Issues 5 and 7, Post-K Exploratory Challenge: Challenge of Basic Science—Exploring Extremes through Multi-Physics and Multi-Scale Simulations, Professional development Consortium for Computational Materials Scientists (PCoMS), and Elementary Strategy Initiative to Form a Core Research Center.

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. QCLDB had been developed by the Quantum Chemistry Database Group in collaboration with members of the center. 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, which are very important physical properties in vibrational spectrum analyses. 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/).

Figure 1. NEC LX.

Figure 2. Fujitsu PRIME HPC FX10.

Safety Office

UOZUMI, Yasuhiro	Director
TOMURA, Masaaki	Assistant Professor
TANAKA, Shoji	Assistant Professor
SHIGEMASA, Eiji	Technical Associate
UEDA, Tadashi	Technical Associate
TAKAYAMA, Takashi	Technical Associate
SAKAI, Masahiro	Technical Associate
MAKITA, Seiji	Technical Associate
KONDO, Naonori	Technical Associate
MIZUTANI, Nobuo	Technical Associate
TSURUTA, Yumiko	Secretary
KAMO, Kyoko	Secretary

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

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

Research Enhancement Strategy Office

OKAMOTO, Hiromi	Professor, Head
YAMAMOTO, Hiroshi	Professor (in charge of Foreign Affairs)
AKIYAMA, Shuji	Professor (in charge of Personnel Affairs)
IINO, Ryota	Professor (in charge of Public Affairs)
ISHIZAKI, Akihito	Professor (in charge of Facilities/Buildings and Foreign Affairs)
SHIGEMASA, Eiji	Technical Associate (in charge of General Affairs)
FUKUI, Yutaka	URA (Administrative Associate, Assistant to Head)

HARADA, Miyuki	URA (Technical Associate)
GOTO, Asako	URA (Administrative Associate)
NAGASONO, Hisayo	URA (Administrative Associate)
NAKAMURA, Rie	Technical Fellow
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HAGIWARA, Hisayo	Secretary
SUZUKI, Satomi	Secretary
SUGIYAMA, Kayoko	Secretary
OHHARA, Kyoko	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 Division

SHIGEMASA, Eiji	Head
UCHIYAMA, Koichi	Technical Associate

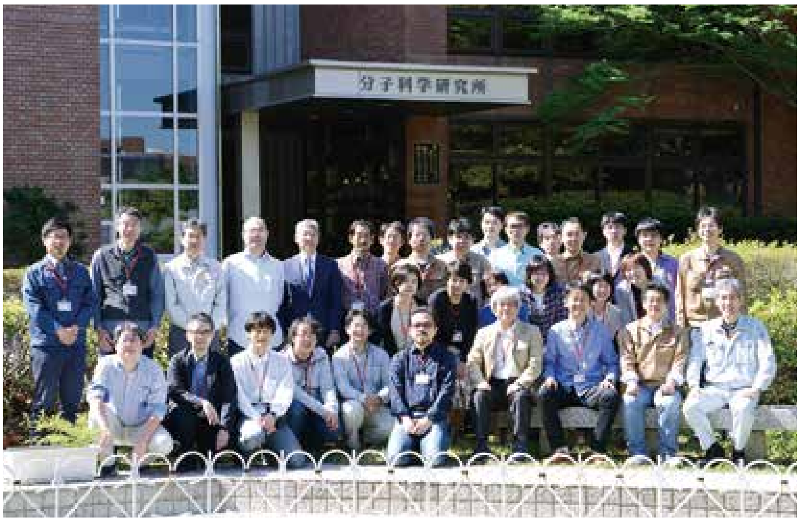
Information Office

OHHARA, Kyoko	Secretary
TSURUTA, Yumiko	Secretary
KAMO, Kyoko	Secretary

The Technical Division was established in 1975 as an organization of technical staffs who technically support in-house and outside scientists. Each technical staff with professional skills belongs to individual research facilities or centers such as the UVSOR Synchrotron Facility, the Research Center for Computational Science, the Instrument Center, the Equipment Development Center, or the Center for Mesoscopic Sciences.

In addition, several members belonging to the Technical Division 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 problems related to our technology and engineering. Our best endeavors have been, and will be made, to promote the advanced research of IMS.



Special Research Projects

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

(a) The Ministry of Education, Culture, Sports, Science and Technology (MEXT)
Flagship Project, Priority Research Issue
"Development of New Fundamental Technologies for High-Efficiency Energy Creation, Conversion/Storage, and Use"
(b) MEXT Nanotechnology Platform Program
Platform of Molecule and Material Synthesis
(c) Inter-University Network for Efficient Utilization of Research Equipments

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

(a) The Ministry of Education, Culture, Sports, Science and Technology (MEXT) Flagship Project, Priority Research Issue, "Development of New Fundamental Technologies for High-Efficiency Energy Creation, Conversion/Storage, and Use"

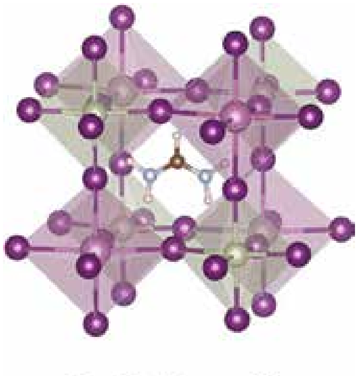
A new supercomputer, the so-called post-K computer, is being developed by RIKEN as the successor to the K computer and is expected to help to solve various social and scientific problems. Nine priority research issues have been defined by the government, and at the same time, software development is also in progress. IMS leads one of the priority research issues, "Development of New Fundamental Technologies for High-Efficiency Energy Creation, Conversion/Storage, and Use" in collaboration with Kobe University, RIKEN, the University of Tokyo, the National Institute for Materials Science (NIMS), Nagoya University, Okayama University, Hokkaido University, and Waseda University, incorporating 47 institutions including 17 companies.

We propose to perform state-of-the-art calculations to unravel the following issues. Branch A: Production and storage of alternative energy sources using solar cells and artificial photosynthesis; Branch B: Conversion and storage of energies produced in fuel cells and rechargeable batteries; Branch C: Separation, recovery, and storage of methane and CO_2 and effective use of energies and resources produced by catalytic reactions. We will also collaborate with experimentalists in academia and researchers in industries to establish new energy technologies which are highly efficient, inexpensive, environmentally clean, and sustainable.

Because of the limitation of current computer performance, conventional computational research has typically focused on isolated and/or subtotal systems to obtain partial information about the mechanism of the total system. The highly integrated computer resources of the post-K computer will be powerful enough to make such research obsolete; Post-K will open frontiers to establish a new academic standard in computational chemistry and physics, and will facilitate understanding of complex phenomena in real materials and heterogeneous systems.

The midterm evaluation on the project was performed by MEXT in the financial year of 2017. In response to the comments of the evaluation committee, we have introduced a working group to confirm the current status of materials informatics to explore possible application to the subjects in the projects.

"The first collaborative symposium for experimental and industrial researchers" was held focusing on the theme of "Light Energy Conversion" in Kobe on December 11. Four researchers outside the project gave invited lectures and had a panel discussion. The fourth annual symposium of the project was also held in Kobe on December 12. During these symposia, a total 71 participants joined the discussions. Furthermore, the research and development plan for the priority research issue "Development of New Fundamental Technologies for High-Efficiency Energy Creation, Conversion/Storage, and Use" was refined and submitted to MEXT. We plan to maintain similar activities for the duration of the Flagship project.

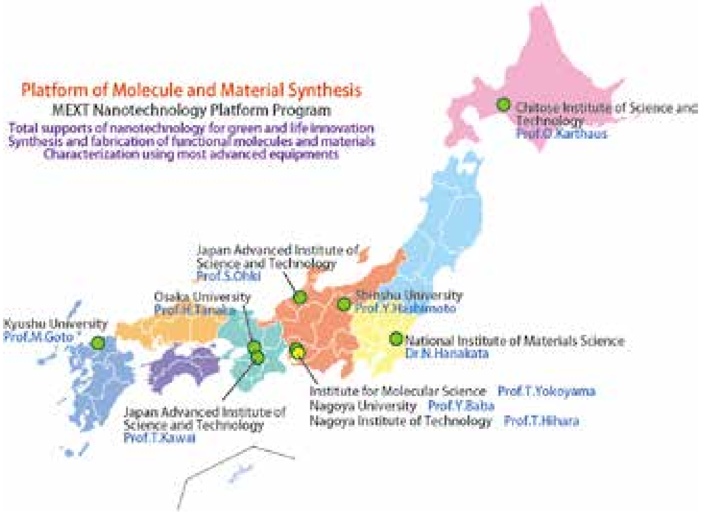


Double Perovskite

New material candidates were found in this project for "non-toxic perovskite solar cells" by searching based on highly efficient material screening using the K computer. Novel 51 low-toxic halide perovskites were discovered, most of which were newly proposed in this study. *J. Phys. Chem. Lett.* **8**, 4826–48319 (2017)

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

Since July 2012, Nanotechnology Platform Program supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT) has been conducted in order to promote public usage of various nanotechnology facilities. This program will continue until March 2022 and consists of three platforms of nanostructure analysis, nanoprocessing, and molecule and material synthesis, together with the management center of the platforms. Each platform constitutes of about ten organizations all over Japan. IMS conducts a representative core organization of the Molecule and Material Synthesis Platform. All the organizations in this platform are shown in Figure. In this platform, to promote green and life innovation researches using nanotechnology related techniques not only for universities and government institutes but also for private companies, we will open various kinds of our facilities with total supports including molecular synthesis, materials fabrications, characterization, data analysis and scientific discussion. We will encourage applications not only to each element, but to combined usage of several supporting elements for biotechnology and green chemistry. In IMS, the number of accepted proposals in FY2017 amounted 201 (170 non-proprietary and 31 proprietary proposals, excluding in-house applications from IMS) and the total number of days used for the supports is 3362 (3175 days for non-proprietary proposals and 187 days for proprietary ones).



List of Supports in IMS (FY2018)

Supporting Element		Responsible Persons	Charging Persons
Platform Management		T. Yokoyama	M. Ohara, Y. Toyama, Y. Shibata
Organization Management in IMS			Y. Hyodo, Y. Funaki, M. Yokota
UVSOR Synchrotron Radiation	X-Ray Magnetic Circular Dichroism	T. Yokoyama	T. Koitaya
Microstructure Fabrication	Maskless Lithography with Step Gauge	H. Yamamoto	E. Shigemasa, M. Aoyama, N. Takada, T. Kondou
	3D Optical Surface Profiler		
Equipment Development	Machine Shop		E. Shigemasa, M. Aoyama, T. Kondou, T. Toyota
Electron Microscopy	Field Emission Scanning Electron Microscopy	T. Yokoyama	Y. Matsuo
	Low vacuum Analytical Scanning Electron Microscopy		Y. Matsuo, M. Sakai
	Focus Ion Beam Processing		Y. Matsuo
X-rays	Single Crystal X-Ray Diffractometer		M. Fujiwara
	Low Temperature Single Crystal X-Ray Diffractometer for Microcrystals		Y. Okano
	Powder X-Ray Diffractometer		M. Fujiwara
	X-Ray Fluorescence Analysis		T. Ueda
	Small Angle X-Ray Scattering for Solutions	S. Akiyama	A. Mukaiyama

Electron Spectroscopy	Electron Spectroscopy for Chemical Analysis	T. Yokoyama	M. Sakai, Y. Inagaki
	Angle Resolved Ultraviolet Photoelectron Spectroscopy for Functional Band Structures	S. Kera, K. Tanaka	S. Ideta
Electron Spin Resonance	Pulsed High Field ESR	T. Yokoyama, T. Nakamura	M. Asada, S. Iki, M. Fujiwara
	X-Band CW ESR	T. Yokoyama	S. Iki, M. Fujiwara
	X, Q-Band CW ESR		
SQUID	Superconducting Quantum Interference Device		S. Iki, M. Fujiwara
Thermal Analysis	Differential Scanning Calorimeter (Solutions)		T. Mizukawa, H. Nagao
	Isothermal Titration Calorimeter (Solutions)		
	Calorimeter for solids		M. Fujiwara
Mass Spectrometer	Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer		T. Mizukawa, K. Fujikawa
Spectroscopy	Microscopic Raman Spectroscopy		M. Uruichi
	Fourier Transform Far Infrared Spectroscopy		
	Fluorescence Spectroscopy		T. Ueda
	Ultraviolet & Visible Absorption Spectroscopy		
	Circular Dichroism		T. Mizukawa, K. Fujikawa
Lasers	Picosecond Laser		T. Ueda
High Field NMR	800 MHz Solutions, Cryostat Probe	K. Kato	M. Yagi, S. Yanaka, Y. Isono
	600 MHz Solids	K. Nishimura	
	600 MHz Solutions	T. Yokoyama	T. Mizukawa, H. Nagao
Functional Molecular Synthesis and Molecular Device Fabrication	Organic Thin Film Solar Cells	M. Hiramoto	
	Organic Field Effect Transistors	H. Yamamoto	M. Suda
	Functional Organic Synthesis	N. Momiyama	A. Izumiseki, N. Ohtsuka
	Large Scale Quantum Mechanical Calculations	M. Ehara	S. Ito
	Magnetic Thin Films	T. Yokoyama	T. Koitaya
	Metal Complexes	S. Masaoka	M. Kondo
	Inorganic Materials	G. Kobayashi	
	Biomolecule System	S. Akiyama	A. Mukaiyama, Y. Furuike

(c) 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. They are grouped into 12 local regions and in each region the regional committee discusses and determines the operation of regional network systems with the hub university chairing. There is no barrier for every user to access to any universities beyond his/her regional group. From 2009, the registered equipments are open to the researchers and students of all the public (prefectural *etc.*) and private universities. Since 2010, the project has been renamed “Inter-University Network for Common Utilization of Research Equipments” still keeping the original strategy and stable functioning. In this year, we have launched a new reservation and charging system that is more user-friendly, convenient and safe for a long period. The number of registered users amounts to 10,000 in 325 universities/institutions/companies covering over 3,000 laboratories in Japan (August, 2018). Usage of the network reaches almost 11,000 times per month and keeps growing in numbers. Moreover, we have actively provide various opportunities where technical staffs and users can improve their technical skills and frankly communicate with each other.

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. Molecular Simulation on Structural Change of Tritium-Substituted Polymeric Materials by Decay from Tritium to Helium-3

FUJIWARA, Susumu (*Kyoto Inst. Tech.*)
MIZUGUCHI, Tomoko (*Kyoto Inst. Tech.*)
SAKAI, Wataru (*Kyoto Inst. Tech.*)
NAKAMURA, Hiroaki (*NIFS*)
HATANO, Yuji (*Univ. Toyama*)
SAITO, Seiki (*National Inst. Tech., Kushiro College*)
SAIKI, Toshiharu (*Keio Univ.*)
OTSUKA, Takao (*RIKEN*)
KENMOTSU, Takahiro (*Doshisha Univ.*)
SAITO, Shinji (*IMS*)

Tritium is radioactive hydrogen and is generated not only in nature but also by human activity. Since the range of beta rays emitted from tritium is short, external exposure is not problematic and protection against internal exposure is important. Particularly, damage of macromolecules such as polymeric materials and DNA caused both by beta rays and by the event where substituted tritium decays to helium-3 is regarded as problems. However, the molecular mechanism of the damage of macromolecules is still an unsolved problem. Effects of radiation on macromolecules are classified into three categories: (1) direct action, (2) indirect action, and (3) decay effect. Although there have been numerous experimental and computer simulation studies on the damage of macromolecules through direct and indirect action, any studies have not been conducted on the damage of macromolecules through decay effect because of the difficulties in extracting the decay effect only.

In this project, we aim to predict the structural change of tritium-substituted macromolecules such as polymeric materials and DNA by a beta decay to helium-3 using molecular dynamics simulations.

Three meetings were held at IMS room 302. Not only the core members (the applicants of this project) but also other related collaborators attended these meetings. The first two meetings were held to discuss course of action for this project on May 24 and October 6, 2017. The third meeting was held to discuss the progress and a future plan of this project on February 22–23, 2018.

(2) Research Symposia

(From Oct. 2017 to Sep. 2018)

Dates	Theme	Chair
Nov. 4, 2017	Cutting-Edge Researches in Coordination Chemistry and Photochemistry	**MASAOKA, Shigeyuki**
Nov. 16–18, 2017	New Developments of Quantum Beams for Materials and Life Sciences	**KATOH, Masahiro**
Jan. 26–27, 2018	Molecular Science of Batteries: Frontier of Interplay between Theory and Experiment	**YAMASHITA, Koichi** **EHARA, Masahiro**
Mar. 4– 5, 2018	Stimuli and Responses—What Will Coordination Compounds Mediate?	**TSUGE, Kiyoshi** **MASAOKA, Shigeyuki**
May 29–30, 2018	Emergence of Novel Chemistry Created by Merging Chemistry and Information Science	**ADSCHIRI, Tadafumi** **YAMAMOTO, Hiroshi**
Jun. 1– 2, 2018	Symposium on Materials Science for Building New Elemental Strategies	**KOBAYASHI, Genki**
Jun. 10, 2018	Interplay between Light and Nanomaterials: For the Future of Molecular Science	**SAITO, Shinji**

Jun. 29–30, 2018	Recent Advances in Quantum State Control Using Organic Devices	**KAGAWA, Fumitaka** **YAMAMOTO, Hiroshi**
Jul. 8–11, 2018	Fronteir Bioorganization Forum 2018	**KATO, Koichi**
Jun. 10, 2018	Meeting for Lectures at 58th Summer School on Molecular Science for Young Scientists	**KATO, Fumiaki** **FURUTANI, Yuji**
Aug. 31–Sep. 2, 2018	Synthetic, Biological, and Hybrid Molecular Engines	**KINBARA, Kazushi** **IINO, Ryota**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2017–Mar. 2018		Apr. 2018–Sep. 2018		Total		
		Regular	NanoPlat	Regular	NanoPlat	Regular	NanoPlat	Sum
Special Projects		1		2		3		3
Research Symposia		4		5		9		9
Research Symposia for Young Researchers		0		1		1		1
Cooperative Research		38	33	22	31	60	64	124
Use of Facility	Instrument Center		74		77	0	151	151
	Equipment Development Center	1	4	1	5	2	9	11
Use of UVSOR Facility		84	23	98	1	182	24	206
Use of Facility Program of the Computer Center						224*		224*

* from April 2017 to March 2018

Collaboration Programs

(a) International and Inter-Institutional Collaboration Symposia

Several international symposia and workshops in molecular science are held in IMS and in Japan. Some workshops are organized with our MOU partners for international collaboration in the MOU partner's country as well as in Japan:

Program	Coordinator	Date	Place
Japan-China Joint Interdisciplinary Symposium on Coordination-Based Hybrid Materials	IMAOKA, Takane (Tokyo Tech) MASAOKA, Shigeyuki (IMS)	2017.6.24	IMS
NANOTEC-IMS Joint Symposium	YAMAMOTO, Hiroshi (IMS) CHINSIRIKUL, Wannee (NANOTEC)	2017.10.30	NANOTEC, Thailand
Cutting-Edge Researches in Coordination Chemistry and Photochemistry	MASAOKA, Shigeyuki (IMS)	2017.11.4	IMS
SOKENDAI Asian Winter School "Challenges for New Frontiers in Molecular Science: From Basics to Advanced Researches"	KOGA, Nobuyasu (IMS) NISHIMURA, Katsuyuki (IMS)	2017.12.15	IMS
IMS Asian International Symposium 10th Korea-Japan Seminar on Biomolecular Science "Frontier Bioorganization Forum 2018"	KATO, Koichi (ExCELLS, IMS) AONO, Shigetoshi (ExCELLS, IMS) NISHIDA, Motohiro (ExCELLS, NIPS) AOKI, Kazuhiro (ExCELLS, NIBB) YAGI-UTSUMI, Maho (ExCELLS, IMS) JOO, Taiha (POSTECH) KAWAI, Maki (IMS) RYU, Sunmin (POSTECH) KIM, Tae Kyu (PNU) KERA, Satoshi (IMS) SAITO, Shinji (IMS)	2018.7.8–7.10	IMS
1st IMS-SKKU-UJN Symposium on Structure and Dynamics of Small and Large Molecules	KANG, Baotao (UJN) LEE, Jing Yong (SKKU) SAITO, Shinji (IMS)	2018.8.15–8.17	University of Jinan, China
The 79th Okazaki Conference "Synthetic, Biological, and Hybrid Molecular Engines"	KINBARA, Kazushi (Tokyo Tech) IINO, Ryota (IMS)	2018.8.31–9.2	IMS

(b) IMS International Internship Programs and SOKENDAI International Lecture & Training Courses

Category	Number of People	
	Overseas	Domestic
IMS International Internship Program (IMS-IIP)	24*	–
SOKENDAI Asian Winter School (2017.12.15)	7†	1

* from Sep. 2017 to Aug. 2018, † include the IMS-IIP students

(c) IMS International Collaboration

Category	Number of People
International Joint Research Programs	71
International Use of Facilities Programs	48

from Sep. 2017 to Aug. 2018

(d) MOU Partnership Institutions

IMS has concluded academic exchange and 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]	2014.11–2018.11	0	0
Institute of Atomic and Molecular Sciences (IAMS) [Taiwan]	2017. 2–2020. 2	5	3
Institute of Chemistry, Chinese Academy of Science (ICCAS) [China]	2013. 9–2018. 9	0	0
Korea Advanced Institute of Science and Technology (KAIST) [Korea]	2016. 9–2020. 9	0	0
École Nationale Supérieure de Chimie de Paris (ENSCP) [France]	2014.10–2019.10	6	1
Helmholtz Zentrum Berlin (HZB) [Germany] Freie Universität Berlin (FUB) [Germany]	2016. 6–2019. 6	13	1
Indian Institute of Science Education and Research Kolkata (IISER Kolkata) [India]	2015.10–2019.10	5	0
Indian Institute of Science (IISc) [India]	2015.10–2019.10	1	0
National Nanotechnology Center, National Science and Technology Development Agency (NANOTEC/NSTDA) [Thailand]	2017.10–2022.10	2	6
Sungkyunkwan University (SKKU) [Korea]	2018. 4–2022. 3	1	0
University of Oulu [Finland]	2018. 5–2021. 5	8	2

from Sep. 2017 to Aug. 2018

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

Institution	Period	Accept	Send
Chulalongkorn University, Faculty of Science [Thailand]	2010. 4–2020. 3	4	9
Kasetsart University, Faculty of Science [Thailand]	2011. 3–2021. 4	3	0
Mahidol University, Faculty of Science [Thailand]	2014. 3–2019. 3	0	0
Nanyang Technological University, College of Science [Singapore]	2014. 3–2019. 3	0	0
University of Malaya, Faculty of Science [Malaysia]	2014. 3–2019. 3	2	0

from Sep. 2017 to Aug. 2018

Director General Maki Kawai Received Medal with Purple Ribbon Honor in Autumn 2017

It is our great pleasure to report here that our Director General Maki Kawai was awarded Medal with Purple Ribbon Honor in autumn 2017. This medal is one of the prizes given by the Emperor to those who outstandingly contributed to the academic, artistic, technological, or sports achievements.

She graduated from the Department of Chemistry, Faculty of Science at the University of Tokyo in 1975 and received a PhD degree (Rigaku Hakushi) in 1980. She became chief scientist, director of Surface Chemistry Laboratory in Riken (Shunin Kenkyu-in) in 1991, professor at the University of Tokyo in 2004, executive director of Riken (Riji) in 2010, and eventually came to IMS as director general in 2016.

She has extensively been investigating surface physical chemistry such as catalytic reactions on solid surfaces, thin film growth of functional metal oxides, thermophysics and dynamics of surface adsorbed molecules, surface single molecule spectroscopy, single molecule reaction control, and so forth. She has provided numerous pioneering academic achievements that are now well known fundamental concepts in surface chemistry and physics.

During her stay at Riken and the University of Tokyo, she established a new scientific field of “nanomolecular science” on atomically well-defined solid surfaces. She exploited vibrational action spectroscopy and reaction control methodology of single molecules; using scanning tunnel microscopy (STM), chemical reactions of single molecules were successfully realized by exciting the adsorbed molecules electronically and/or vibrationally, and furthermore as vibrational spectroscopy of single molecules, action spectroscopy was developed by monitoring the probabilities of chemical reactions as a function of the kinetic energy of incident electrons. These methodologies are now well known techniques throughout the world for the dynamical analysis of adsorbed molecules on solid surfaces.

In the next stage, she has devoted her efforts to lower energy and more highly resolved spectroscopy of single molecules. She succeeded in the observation of electron spin resonant excitations of paramagnetic single molecules adsorbed on surfaces. This achievement is highly praised as a construction of a new scientific field of surface single molecular magnetism. In her sequential studies, she found a switching of magnetic anisotropy in Fe phthalocyanine molecules and discovered a peculiar Kondo effect in which orbital magnetic moments participate as well as spin magnetic moments. Especially, the latter finding gave a great influence to the field of solid state physics. We will here deeply respect her strong belief and consequent achievements to pursue lower energy and higher resolution in single molecular spectroscopy for the investigations of different scientific fields of chemical reactions and solid state physics using a unique method of scanning tunnel microscopy.

So far she has been awarded for many times, especially CSJ (Chemical Society of Japan) Award 2008, IUPAC 2015 Distinguished Women in Chemistry or Chemical Engineering, Gerhard Ertl Lecture Award 2015, AVS (American Vacuum Society) Medard W Welch Award 2016, 5th Diels-Planck-Lecture Award *etc*. In the meanwhile, she worked as a representative researcher in Grant-in-Aid for Scientific Research on Priority Areas of “Surface Chemistry of Condensed Molecules” and “Electron Transport through a Molecule at Metal Electrode” and in JST Presto of “Structures and Control of Interfaces.” In these projects, she also promoted trainings of young scientists with an excellent leadership. She has also devoted her efforts to tremendous number of government committee members as Intellectual Property Strategy Headquarters Experts Committee (Cabinet Office, 2003–2007), Sciences Council Committee (Ministry of Education, Culture, Sports, Science and Technology, 2004–2005), Education Rebuilding Council (Cabinet Office, 2013–) *etc*. to give important scientific and technological suggestions. Especially, in Intellectual Property Strategy Headquarters Experts Committee during the period of Prime Minister Koizumi Junichiro, she claimed importance of scientific and technological innovations leading to the present strategies in Japanese scientific and technological policies. In Education Rebuilding Council, she contributed significantly to the summaries of proposals concerning many kinds of contemporary issues as children bullying in compulsory educational schools, reforms in bridging between high schools and universities etc. Moreover, she worked quite actively also in foreign countries as Chair of Surface Science Division in International Union for Vacuum Science, Technique and Applications (IUVSTA), a committee member of European Research Council (for evaluation of large scale budgets), an evaluation committee member of Fritz-Haber-Institut in Max-Planck-Gesellschaft. Although Japanese researchers seldom work as members in these western committees, she has made valuable contributions to the developments of these international scientific communities and to important international presence of Japan as well.

Director General Maki Kawai has been engaged in deepening of scientific principles based on physical chemistry and exploiting analytical methodology, has led nanomolecular science all over the world, has devoted efforts to training young scientists, international relationship in research environments, and enrichment and development of education. She is definitely a rare researcher who can play an important role in scientific governmental administration, overlooking Japanese scientific communities from an international view point. She was awarded Medal with Purple Ribbon Honor in autumn 2017 for these reasons.

We will be courteously pleased with her present decoration and will expect her excellent perspective decisions in the administration of Institute for Molecular Science as well as further development of IMS. Congratulations.

AWARDS

2018 Wolf Prize in Chemistry
“Pioneering Reticular Chemistry via Metal-Organic Frameworks and Covalent Organic Framework”

The 2018 Wolf Prize in Chemistry has been awarded to Professor Makoto Fujita for his research on metal-guided synthesis and “for conceiving metal-directed assembly principles leading to large highly porous complexes.”

Professor Fujita introduced the concept of “metal-guided synthesis” or “metal-directed self-assembly” for creating large, stable cyclic and three-dimensional molecular structures. The 3D structures form a regular “cage” that can be used as “containers” for other molecules. One revolutionary application of these structures is to capture other molecules within those spaces allowing the use of standard X-ray crystallography to determine structures without the need to obtain a crystallized sample. This method, also known as the “crystalline sponge method,” should make a paradigm shift in a wide variety of scientific fields.

OHMORI, Kenji Photo-Molecular Science	Hiroshi Takuma Memorial Prize of Matsuo Foundation “Development of Coherent Control with Attosecond Precision and Its Applications” The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology Prizes for Science and Technology Research Category “Development of Coherent Control with Attosecond Precision and Its Applications”
NOBUSADA, Katsuyuki Theoretical and Computational Molecular Science	The HPCI Research Project Award for Excellent Achievement “Computational Design of Functional Fields with Novel Optical Properties Induced by Near-Field Light Excitation”
SUGIMOTO, Toshiki Materials Molecular Science	Morino Foundation for Molecular Science 2018 “Emergent Properties and Dynamics of Molecular Aggregates Induced by Inversion-Symmetry Breaking at Solid Surfaces”
KOBAYASHI, Genki Materials Molecular Science	The 39th Honda Memorial Young Researcher Award “Study on Ion Conductive Materials for Next-Generation Energy Devices”
KOGA, Nobuyasu Research Center of Integrative Molecular Systems	Morino Foundation for Molecular Science 2018 “Studies on Design Principle for Ideal Protein Structures”
TAIRA, Takunori Center for Mesoscopic Sciences	The Commendation for Lazer Advancement of Taizan Prize “Pioneer Work in Downsizing of Solid-State Lasers and Nonlinear Optics”
NAGASAKA, Masanari Photo-Molecular Science	The 10th Young Scientist Awards of the Japan Society for Molecular Science “Operando Observation of Liquid and Liquid–Liquid Interface by Soft X-Ray Absorption Spectroscopy”
IWAYAMA, Hiroshi UVSOR Synchrotron Facility	The 19th Young Scientist Awards of the Atomic Collision Society of Japan “Interaction and Relaxation Process of Rare Gas Clusters Irradiated by Intense EUV-FEL Pulses”
YAGI-UTSUMI, Maho Life and Coordination-Complex Molecular Science	The Pharmaceutical Society of Japan Award for Young Scientists '18 “NMR Characterization of Conformational Dynamics and Molecular Assemblies of Proteins”
ANDO, Jun Life and Coordination-Complex Molecular Science	Young Scientist Presentation Award of the Spectroscopical Society of Japan 2017 “Alkyne-Tag SERS Screening for Identifying Small-Molecule-Binding Sites in Proteins”

OSAKO, Takao Life and Coordination-Complex Molecular Science	Thieme Chemistry Journals Award 2018
HAMASAKA, Go Life and Coordination-Complex Molecular Science	Mitsubishi Gas Chemical Award in Synthetic Organic Chemistry, Japan “Development of Highly Efficient Aquacatalytic Systems Based on Immobilization of Amphiphilic Transition Metal Complexes onto Solid Supports” The Chemical Society of Japan Lecture Award for Young Chemists “Development of New Reaction Systems Driven by Assembly of Molecular Transition Metal Catalysts”
KONDO, Mio Life and Coordination-Complex Molecular Science	The Chemical Society of Japan Award for Outstanding Young Women Chemists “Development of Function-Integrated Metal Complex Catalysts for Small Molecule Conversion” The 7th Young Scientist Award of National Institutes of Natural Sciences “Development of Function-Integrated Metal Complex Catalysts for Production of Chemical Fuels”
SUDA, Masayuki Research Center of Integrative Molecular Systems	The 12th Condensed-Matter Science Prize “Phase Control between Mott Insulators and Superconductors Utilizing Photoisomerization Reactions” The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists’ Prize “Development of Novel Molecular Devices Based on a New Photo-Control Method for Interface Dipoles”

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 (September 2017–August 2018) are listed below.

(1) Attendance at an Okazaki Conference

Prof. Bryant, Zev	Stanford Univ.	U.S.A.	Aug. ’18
Prof. Ces, Oscar	Imperial College London	U.K.	Aug. ’18
Prof. Choi, Jong Hyun	Purdue Univ.	U.S.A.	Aug. ’18
Dr. Yifei, Zhang	Columbia Univ.	U.S.A.	Aug. ’18
Prof. Huc, Ivan	Ludwig-Maximilians-Univ.	Germany	Aug. ’18
Dr. Gennerich, Arne	Albert Einstein College of Medicine	U.S.A.	Aug. ’18
Prof. Rapenne, Gwénaël	Univ. Paul Sabatier	France	Aug. ’18
Prof. Huang, Possu	Stanford Univ.	U.S.A.	Aug. ’18

(2) IMS Councillor

Prof. Petek, Hrvoje	Univ. of Pittsburgh	U.S.A.	Dec. ’17 Apr. ’18
Prof. Umbach, Eberhard	Univ. of Würzburg	Germany	Mar. ’18

(3) IMS Visiting Scientist

Dr. Lai, Yu Ling	NSRRC	Taiwan	Sep. ’17 Dec. ’17 Aug. ’18
Dr. Shiu, Hung Wei	NSRRC	Taiwan	Sep. ’17 Dec. ’17 Aug. ’18
Dr. Yu, Li Chung	NSRRC	Taiwan	Sep. ’17 Dec. ’17 Aug. ’18
Prof. Hu, Chin-Kun	Acad. Sinica	Taiwan	Sep. ’17
Prof. Ruehl, Eckart	Free Univ. of Berlin	Germany	Sep. ’17 Mar. ’18
Mr. Yamamoto, Kenji	Free Univ. of Berlin	Germany	Sep. ’17 Mar. ’18
Dr. Flesch, Roman	Free Univ. of Berlin	Germany	Sep. ’17 Mar. ’18
Dr. Klossek, Andre	Free Univ. of Berlin	Germany	Sep. ’17 Mar. ’18
Dr. Rancan, Fiorenza	Free Univ. of Berlin	Germany	Sep. ’17 Mar. ’18
Mr. T. P., Mahesh	Indian Inst. of Sci. Education and Res., Kolkata	India	Sep. ’17–Oct. ’17 Dec. ’17–Mar. ’18 Jun. ’18–Sep. ’18
Prof. Hirata, So	Univ. of Illinois	U.S.A.	Sep. ’17–Oct. ’17 Nov. ’17–Dec. ’17
Dr. Salehi, Elham	Inst. for Res. in Fundamental Sci.	Iran	Sep. ’17–Nov. ’17
Ms. Teanwarawat, Jitpinan	Kasetsart Univ.	Thailand	Sep. ’17–Jan. ’18
Mr. Kammarabut, Jirayu	Chulalongkorn Univ.	Thailand	Sep. ’17–Jan. ’18
Mr. Paisuwan, Waroton	Chulalongkorn Univ.	Thailand	Sep. ’17–Feb. ’18
Mr. Zhao, Pei	Xi’an Jiaotong Univ.	China	Sep. ’17–Mar. ’18
Mr. Marguet, Bastien	Ecole Normale Superieure Paris-Saclay	France	Sep. ’17–Aug. ’18
Dr. Dubinskiy, Mark	U.S. Army Laboratory	U.S.A.	Oct. ’17
Prof. Mackenzie, Jacob	Univ. of Southampton	U.K.	Oct. ’17
Dr. Stenhouse, Henry	Univ. of Southampton	U.K.	Oct. ’17
Dr. Cante, Silvia	Univ. of Southampton	U.K.	Oct. ’17
Dr. Cini, Luigi	Univ. of Southampton	U.K.	Oct. ’17
Dr. Ertel, Klaus	Central Laser Facility, STFC	U.K.	Oct. ’17
Dr. Peterson, Alan	Spectra-Physics Lasers	U.S.A.	Oct. ’17
Dr. Kafka, Jim	Spectra-Physics Lasers	U.S.A.	Oct. ’17

Dr. Qui, Gang	CRYSLASER INC.	China	Oct. ’17
Dr. Wang, Fang	CRYSLASER INC.	China	Oct. ’17
Prof. Kubecek, Vaclav	Czech Technical Univ.	Czech	Oct. ’17
Dr. Cech, Miroslav	Czech Technical Univ.	Czech	Oct. ’17
Dr. Jelinkova, Helena	Czech Technical Univ.	Czech	Oct. ’17
Dr. Jelinek, Michal	Czech Technical Univ.	Czech	Oct. ’17
Dr. Frank, Milan	Czech Technical Univ.	Czech	Oct. ’17
Dr. Thomas Metzger	TRUMPF	Germany	Oct. ’17
Prof. Huttula, Marko	Univ. of Oulu	Finland	Oct. ’17 Feb. ’18
Mr. Immonen, Esa-Ville	Univ. of Oulu	Finland	Oct. ’17
Mr. Zwick, Christian	Univ. of Jena	Germany	Oct. ’17–Nov. ’17
Dr. Boekfa, Bundet	Kasetsart Univ.	Thailand	Oct. ’17–Dec. ’17
Mr. Nirun, Ruankaew	Kasetsart Univ.	Thailand	Oct. ’17–Jan. ’18
Dr. Zheng, Hong	Xi’an Jiaotong Univ.	China	Oct. ’17–Mar. ’18
Ms. Subramaniam, Jeevithra	Univ. of Malaya	Malaysia	Oct. ’17–Jun. ’18
Prof. Bagchi, Biman	Indian Inst. of Sci. Bangalore	India	Nov. ’17
Prof. List, Benjamin	Max-Planck-Inst. für Kohlenforschung	Germany	Nov. ’17
Mr. Wen, Chenhaoping	Fudan Univ.	China	Nov. ’17–Dec. ’17
Mr. Yu, Tianlun	Fudan Univ.	China	Nov. ’17–Dec. ’17
Mr. Lou, Xia	Fudan Univ.	China	Nov. ’17–Dec. ’17
Dr. Fang, Yifei	Fudan Univ.	China	Nov. ’17–Dec. ’17
Prof. Yang, Jinpen	Yangzhou Univ.	China	Nov. ’17–Jan. ’18
Ms. Makmuang, Sureerat	Chulalongkorn Univ.	Thailand	Nov. ’17–Apr. ’18
Ms. Vu, Anna	Free Univ. of Berlin	Germany	Nov. ’17–Sep. ’18
Dr. Unruangsri, Junjuda	Chulalongkorn Univ.	Thailand	Dec. ’17–Jan. ’18
Prof. Chiu, Chaowen	Tamkang Univ.	Taiwan	Jan. ’18–Feb. ’18
Dr. Dong, Chung Li	Acad. Sinica	Taiwan	Jan. ’18–Feb. ’18
Dr. Shirolkar, Mandar	Natl. Univ. of Kaohsiung	Taiwan	Jan. ’18–Feb. ’18
Mr. Huang, Yucheng	Tamkang Univ.	Taiwan	Jan. ’18–Feb. ’18
Prof. Zhao, Xiang	Xi’an Jiaotong Univ.	China	Jan. ’18–Feb. ’18 Aug. ’18
Dr. Teh, Swe Jyan	Univ. of Malaya	Malaysia	Jan. ’18–Mar. ’18
Ms. Jityuti, Benchawan	Srinakharinwirot Univ.	Thailand	Jan. ’18–Sep. ’18
Mr. Corral, Pablo	Paul Scherrer Inst.	Switzerland	Feb. ’18
Mr. Kong, Xiangrui	Univ. of Gothenburg	Sweden	Feb. ’18
Prof. Prisle, Nonne	Univ. of Oulu	Finland	Feb. ’18
Mr. Michailoudi, Georgia	Univ. of Oulu	Finland	Feb. ’18
Dr. Lin, Jack	Univ. of Oulu	Finland	Feb. ’18
Mr. Chattrairat, Kunanon	King Mongkut’s Inst. of Tech. Ladkrabang	Thailand	Feb. ’18–Mar. ’18
Mr. Hagenlocher, Jan	Eberhard Karls Univ. Tubingen	Germany	Feb. ’18–Mar. ’18
Mr. Berkemeyer, Janis	Free Univ. of Berlin	Germany	Mar. ’18
Dr. Arrua, Dario	Univ. of South Australia	Australia	Mar. ’18
Dr. Khodabandeh, Aminreza	Univ. of South Australia	Australia	Mar. ’18
Prof. Brown, Leonid	Univ. of Guelph	Canada	Mar. ’18
Mr. Vignon, Paul	Ecole Natl. Supérieure de Chimie de Paris (Cheime Paris Tech)	France	Apr. ’18
Mr. Perrot, Armand	Ecole Natl. Supérieure de Chimie de Paris (Cheime Paris Tech)	France	Apr. ’18
Ms. Daugas, Louise	Ecole Natl. Supérieure de Chimie de Paris (Cheime Paris Tech)	France	Apr. ’18
Mr. Toniolo, Paul	Ecole Natl. Supérieure de Chimie de Paris (Cheime Paris Tech)	France	Apr. ’18
Mr. De Montgolfier, Jean-Vincent	Ecole Natl. Supérieure de Chimie de Paris (Cheime Paris Tech)	France	Apr. ’18
Mr. Cassouret, Florent	Ecole Natl. Supérieure de Chimie de Paris (Cheime Paris Tech)	France	Apr. ’18
Prof. Kadodwala, Malcolm	Univ. of Glasgow	U.K.	Apr. ’18
Dr. Supawadee, Namuangruk	Natl. Nanotechnology Cent.	Thailand	Apr. ’18–May ’18
Ms. P.I., Jaseela	Affiliated to Calicut Univ.	India	Apr. ’18–May ’18
Dr. Anchalee, Junkaew	Natl. Nanotechnology Cent.	Thailand	Apr. ’18–Jun. ’18
Mr. Nam, Yeonsig	Sungkyunkwan Univ.	Korea	Apr. ’18–Jul. ’18
Dr. Amsalem, Patrick	Humboldt Univ. zu Berlin	Germany	May ’18–Jun. ’18
Dr. Park, Soohyung	Humboldt Univ. zu Berlin	Germany	May ’18–Jun. ’18
Dr. Schultz, Thorsten	Humboldt Univ. zu Berlin	Germany	May ’18–Jun. ’18

Mr. Mandal, Niladri Shekhar	Indian Inst. of Sci. Education and Res., Kolkata	India	May ’18–Jul. ’18
Mr. Das, Soumik	Indian Inst. of Sci. Education and Res., Kolkata	India	May ’18–Aug. ’18
Dr. Morimoto, Takahiro	Univ. of California, Berkeley	U.S.A.	Jun. ’18
Dr. Ismail, Mostafa	Univ. of Oulu	Finland	Jun. ’18
Dr. Patanen, Minna	Univ. of Oulu	Finland	Jun. ’18
Mr. Jung, Woobeen	Seoul Natl. Univ.	Korea	Jun. ’18–Jul. ’18
Mr. Kim, Younsik	Seoul Natl. Univ.	Korea	Jun. ’18–Jul. ’18
Dr. Kanaev, Andrei	LSPM-CNRS	France	Jun. ’18–Jul. ’18
Dr. Feldbach, Eduard	Univ. of Tartu	Estonia	Jun. ’18–Jul. ’18
Prof. Museur, Luc	Univ. Paris 13	France	Jun. ’18–Jul. ’18
Mr. Chiu, Ding-Shiang	Natl. Chiao Tung Univ.	Taiwan	Jun. ’18–Aug. ’18
Mr. Sheersh, Boorla Veda	Indian Inst. of Tech. Kharagpur	India	Jun. ’18–Aug. ’18
Mr. Schaal, Maximilian	Univ. of Jena	Germany	Jun. ’18–Sep. ’18
Mr. Metzger, Christian	Univ. of Würzburg	Germany	Jun. ’18–Sep. ’18
Ms. Wiyada, Saennawa	Suranaree Univ. of Tech.	Thailand	Jun. ’18–Apr. ’19
Prof. Ju, Huanxin	Univ. of Sci. and Tech. of China	China	Jul. ’18
Mr. Ma,Jun	Univ. of Sci. and Tech. of China	China	Jul. ’18
Prof. Chen, Shuangming	Univ. of Sci. and Tech. of China	China	Jul. ’18
Prof. Long, Ran	Univ. of Sci. and Tech. of China	China	Jul. ’18
Prof. Chiu, Chao Wen	Natl. Univ. of Kaohsiung	Taiwan	Jul. ’18
Dr. Hwang, Ing-Shouh	Acad. Sinica	Taiwan	Jul. ’18
Dr. Chuang, Cheng-Hao	Acad. Sinica	Taiwan	Jul. ’18
Dr. Hsu, Wei-Hao	Acad. Sinica	Taiwan	Jul. ’18
Dr. R. S., Swathi	Indian Inst. of Sci. Education and Res.	India	Jul. ’18
Mr. Cho, Soohyun	Yonsei Univ.	Korea	Jul. ’18
Prof. Abedin, Kazi	Sultan Qaboos Univ.	Oman	Jul. ’18–Sep. ’18
Dr. Ceolin, Denis	Synchrotron SOLEIL	France	Aug. ’18
Mr. Klaiphet, Kanchanasuda	Suranaree Univ. of Tech.	Thailand	Aug. ’18
Ms. Saisopa, Thanit	Suranaree Univ. of Tech.	Thailand	Aug. ’18

(4) Visitor to IMS

Prof. Françoise Remacle	Univ. of Liege	Belgium	Sep. ’17
Mr. Furfari, Domenico	Airbus Operations GmbH	Germany	Sep. ’17
Prof. Byer, Robert L.	Stanford Univ.	U.S.A.	Sep. ’17
Prof. Dekorsy, Thomas	German Aerospace Cent.	Germany	Sep. ’17
Mr. Trbola, Johannes	Dausinger + Giesen GmbH	Germany	Sep. ’17
Prof. Ho, Wilson	Univ. of California	U.S.A.	Oct. ’17
Prof. Patnaik, Archita	IIT Madras	India	Nov. ’17
Prof. Heberle, Joachim	Free Univ. of Berlin	Germany	Jan. ’18
Prof. Nam, Ki Tae	Seoul Natl. Univ.	Korea	Mar. ’18
Dr. Lee, Hye-Eun	Seoul Natl. Univ.	Korea	Mar. ’18
Mr. Ahn, Hyo-Yong	Seoul Natl. Univ.	Korea	Mar. ’18
Prof. Hagan, David	Univ. of Central Florida	U.S.A.	Aug. ’18

Theoretical and Computational Molecular Science

P. PONGPRAYOON and T. MORI, "Critical Role of Dimer Formation in Monosaccharide Binding to Human Serum Albumin," *Phys. Chem. Chem. Phys.* **20**, 3249–3257 (2018).
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J. WEN, T. UTO, J. CHALUPSKÝ, D. L. CASHER, G. RAABE, J. FLEISCHHAUER, T. YANAI, H. TSUJI, K. KOMATSU and J. MICHL, "Magnetic Circular Dichroism of an Unaromatic Planar [8]Annulene," *J. Phys. Org. Chem.* **31(8)**, e3854 (16 pages) (2018). DOI: 10.1002/poc.3854
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N. T. PHUC and A. ISHIZAKI, "Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering," *J. Phys. Chem. Lett.* **9**, 1243–1248 (2018).

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R. ZHAO, K. YUAN, S. ZHAO, X. ZHAO and M. EHARA, "Quantum Chemical Insight into La_2C_{96}: Metal Carbide Fullerene La_2C_2@C_{94} versus Dimetallofullerene La_2@C_{96}," *Inorg. Chem.* **56**, 11883–11890 (2017).
K. TAKAGI, K. ITO, Y. YAMADA, T. NAKASHIMA, R. FUKUDA, M. EHARA and H. MASU, "Synthesis and Optical Properties of Excited-State Intramolecular Proton Transfer Active π-Conjugated Benzimidazole Compounds: Influence of Structural Rigidification by Ring Fusion," *J. Org. Chem.* **82**, 12173–12180 (2017).
T. IWASAKI, A. FUKUOKA, W. YOKOYAMA, X. MIN, I. HISAKI, T. YANG, M. EHARA, H. KUNIYASU and N. KAMBE, "Nickel-Catalyzed Coupling Reaction of Alkyl Halides with Aryl Grignard Reagents in the Presence of 1,3-Butadiene: Mechanistic Studies of Four-Component Coupling and Competing Cross-Coupling Reactions," *Chem. Sci.* **9**, 2195–2211 (2018).
T. SHIRAOGAWA, M. EHARA, S. JURINOVICH, L. CUPELLINI and B. MENNUCCI, "Frenkel-Exciton Decomposition Analysis of Circular Dichroism and Circularly Polarized Luminescence for Multichromophoric Systems," *J. Comput. Chem.* **39**, 931–935 (2018).
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A. JUNKAEW, S. NAMUANGRUK, P. MAITARAD and M. EHARA, "Silicon-Coordinated Nitrogen-Doped Graphene as a Promising Metal-Free Catalyst for N_2O Reduction by CO: A Theoretical Study," *RSC Adv.* **8**, 22322–22330 (2018).
T. IWASAKI, X. MIN, A. FUKUOKA, L. ZHU, R. QIU, T. YANG, M. EHARA, A. SUDALAI and N. KAMBE, "Ni-Catalyzed Dimerization and Hydroperfluoroarylation of 1,3-Dienes," *J. Org. Chem.* **83**, 9267–9277 (2018).
R. FUKUDA, S. SAKAI, N. TAKAGI, M. MATSUI, M. EHARA, S. SAKAKI, S. HOSOKAWA and T. TANAKA, "Mechanisms of NO–CO Reaction over Highly Dispersed Cuprous Oxide on γ-Alumina Catalyst Using Metal-Support Interfacial Site in the Presence of Oxygen: Similarity to and Difference from Biological Systems," *Catal. Sci. Technol.* **8**, 3833–3845 (2018).

Y. MORI, H. OKUMURA T. WATANABE and T. HOHSAKA, "Antigen-Dependent Fluorescence Response of Anti-c-Myc Quenchbody Studied by Molecular Dynamics Simulations," *Chem. Phys. Lett.* **698**, 223–226 (2018).
H. NISHIZAWA and H. OKUMURA, "Classical Molecular Dynamics Simulation to Understand Role of a Zinc Ion for Aggregation of Amyloid-β Peptides," *J. Comput. Chem., Jpn.* **17**, 76–79 (2018).

M. YAMAUCHI and H. OKUMURA, “Development of Isothermal-Isobaric Replica-Permutation Method for Molecular Dynamics and Monte Carlo Simulations and Its Application to Reveal Temperature and Pressure Dependence of Folded, Misfolded, and Unfolded States of Chignolin,” *J. Chem. Phys.* **147**, 184107 (15 pages) (2017).

T. FUJITA and Y. MOCHIZUKI, “Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems,” *J. Phys. Chem. A* **122**, 3886–3898 (2018).

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T. YATSUI, H. SAITO, K. NISHIOKA, B. LEUSCHEL, O. SOPPERA and K. NOBUSADA, “Effects of a Power and Photon Energy of Incident Light on Near-Field Etching Properties,” *Appl. Phys. A: Mater. Sci. Process.* **123**, 751 (6 pages) (2017).

T. YATSUI, M. YAMAGUCHI and K. NOBUSADA, “Nano-Scale Chemical Reactions Based on Non-Uniform Optical Near-Fields and Their Applications,” *Prog. Quantum Electron.* **55**, 166–194 (2017).

T. YATSUI, H. SAITO and K. NOBUSADA, “Angstrom-Scale Flatness Using Selective Nano-Scale Etching,” *Beilstein J. Nanotechnol.* **8**, 2181–2185 (2017).

K. KOIZUMI, M. HATAKEYAMA, M. BOERO, K. NOBUSADA, H. HORI, T. MISONOU and S. NAKAMURA, “How Seaweeds Release the Excess Energy from Sunlight to Surrounding Sea Water,” *Phys. Chem. Chem. Phys.* **19**, 15745–15753 (2017).

H. MATSUI, S. ITO and M. NAKANO, “Open-Shell Character Dependences of Second Hyperpolarizability in Two-Dimensional Tetraradicaloids,” *J. Phys. Chem. A* **122**, 3680–3687 (2018).

S. TAKAMUKU and M. NAKANO, “Diradical Character and Second Hyperpolarizability of Alkali Earth Metal Inverse Sandwich Complexes Involving Cyclopentadienyl and Cyclooctatetraene Ligands,” *Eur. J. Inorg. Chem.* **2018**, 2894–2899 (2018).

S. MUHAMMAD, M. NAKANO, A. AL-SEHEMI, A. CHAUDHARY, A. IRFAN, T. TONAMI, R. KISHI, Y. KITAGAWA and S. ITO, “Exploring the Novel Donor-Nanotube Archetype as Efficient Third-Order Nonlinear Optical Material: Asymmetric Open-Shell Carbon Nanotubes,” *Nanoscale* **10**, 16345–16944 (2018).

T. NAGAMI, J. FUJIYOSHI, T. TONAMI, K. WATANABE, K. OKADA, R. KISHI, M. NAKANO, B. CHAMPAGNE and V. LIÉGEOIS, “Evaluation of Aromaticity for Open-Shell Singlet Dicyclopenta-Fused Acenes and Polyacenes Based on Magnetically Induced Current,” *Chem. –Eur. J.* **24**, 13457–13466 (2018).

Photo-Molecular Science

M. NAGASAKA, H. YUZAWA and N. KOSUGI, “Intermolecular Interactions of Pyridine in Liquid Phase and Aqueous Solution Studied by Soft X-Ray Absorption Spectroscopy,” *Z. Phys. Chem.* **232**, 705–722 (2018).

M. NAGASAKA, H. YUZAWA, T. HORIGOME and N. KOSUGI, “Reliable Absorbance Measurement of Liquid Samples in Soft X-Ray Absorption Spectroscopy in Transmission Mode,” *J. Electron Spectrosc. Relat. Phenom.* **224**, 93–99 (2018).

M. NAGASAKA, H. YUZAWA and N. KOSUGI, “Interaction between Water and Alkali Metal Ions and Its Temperature Dependence Revealed by Oxygen K-Edge X-Ray Absorption Spectroscopy,” *J. Phys. Chem. B* **121**, 10957–10964 (2017).

H. YAMANE, A. CARLIER and N. KOSUGI, “Orbital-Specific Electronic Interaction in Crystalline Films of Iron Phthalocyanine Grown on Au(111) Probed by Angle-Resolved Photoemission Spectroscopy,” *Mater. Chem. Front.* **3**, 609–614 (2018).

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M.-H. LI, H.-H. YEH, Y.-H. CHIANG, U-S. JENG, C.-J. SU, H.-W. SHIU, Y.-J. HSU, N. KOSUGI, T. OHIGASHI, Y.-A. CHEN, P.-S. SHEN, P. CHEN and T.-F. GUO, “Highly Efficient 2D/3D Hybrid Perovskite Solar Cells via Low-Pressure Vapor-Assisted Solution Process,” *Adv. Mater.* **30**, 1801401 (13 pages) (2018).

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T. GEJO, M. OURA, T. TOKUSHIMA, Y. HORIKAWA, H. ARAI, S. SHIN, V. KIMBERG and N. KOSUGI, “Resonant Inelastic X-Ray Scattering and Photoemission Measurement of O_2: Direct Evidence for Dependence of Rydberg-Valence Mixing on Vibrational States in O 1s-Rydberg States,” *J. Chem. Phys.* **147**, 044310 (7 pages) (2017).

C. YOU, F. XIA, Y. ZHAO, Y. ZHANG, Y. SHENG, Y. WU, X.-C. HANG, F. CHEN, H. MA, K. SHEN, Z. SUN, T. UEBA, S. KERA, C. ZHANG, H. ZHANG, Z.-K. CHEN and W. HUANG, “Probing Triplet Excited States and Managing Blue Light Emission of Neutral Tetradentate Platinum (II) Complexes,” *J. Phys. Chem. Lett.* **9**, 2285–2292 (2018).

Y. KASHIMOTO, K. YONEZAWA, M. MEISSNER, M. GRUENEWALD, T. UEBA, S. KERA, R. FORKER, T. FRITZ and H. YOSHIDA, “The Evolution of Intermolecular Energy Bands of Occupied and Unoccupied Molecular States in Organic Thin Films,” *J. Phys. Chem. C* **122**, 12090–12097 (2018).

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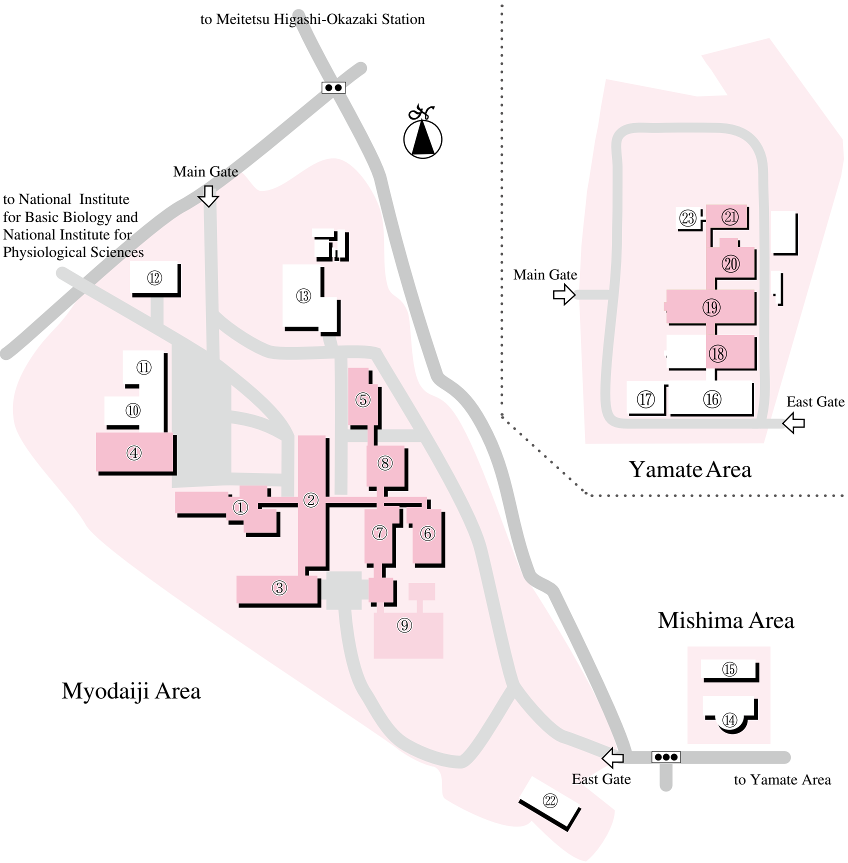
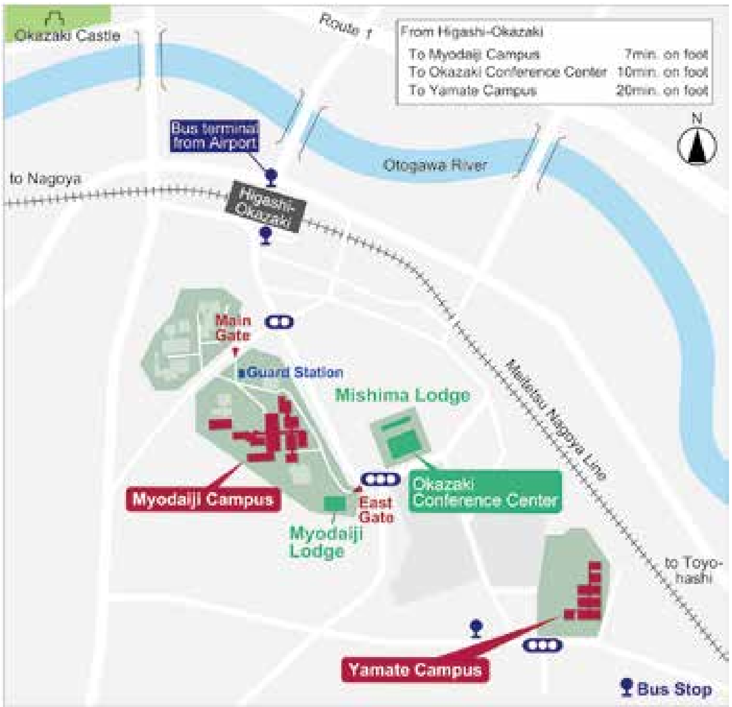
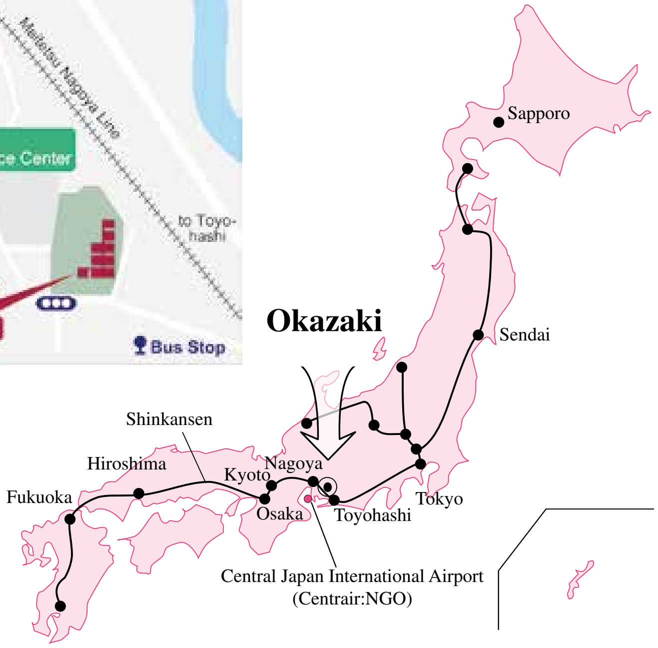
MAPS



1. Research Office Building
2. Main Laboratory Building
3. South Laboratory Building
4. Research Center for Computational Science
5. Low-Temperature Facilities Building
6. Instrument Center
7. Laser Facility Bldg.
8. Equipment Development Center
9. UVSOR Synchrotron Facility
10. Central Administration
11. Library
12. Faculty Club
13. Power Station
14. Okazaki Conference Center
15. Mishima Lodge
16. Yamate Bldg. 1A
17. Yamate Bldg. 1B
18. Yamate Bldg. 2
19. Yamate Bldg. 3
20. Yamate Bldg. 4
21. Yamate Bldg. 5
22. Myodaiji Lodge
23. NIBB Center of Interuniversity Bio-Backup Project





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