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annual review

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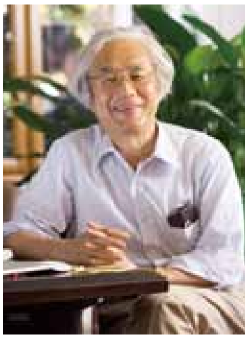


The Institute for Molecular Science (IMS) is one of the world's core research facilities for molecular science and is also a center for inter-university joint research in Japan. It sets an extremely wide range of research goals, from understanding the behavior of individual molecules to that of collective molecular processes on the scale of life forms and in space. Currently, the IMS is engaged in five (four plus one) areas of research: Theoretical and computational molecular science, Photo-molecular science, Materials molecular science, and Life and coordination-complex molecular science. A new research Center of Integrated 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. In addition to these research divisions, IMS has six Research facilities and centers; UVSOR Facility, Laser Research Center for Molecular Science, Instrument Center facilitated with various molecular detectors, for example, 920MHz and 800MHz NMR, and Equipment Development Center. IMS also operates the Research Center for Computational Science and Okazaki Institute for Integrative Bioscience (OIIB), jointly with National Institute for Physiological Sciences and National Institute for Basic Biology in the same campus.

This Annual Review 2014 is a summary of research activities during September 2013–August 2014. 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 five special programs in the institute basis; (i) a computational chemistry program of TCCI (Theoretical and Computational Chemistry Initiative) as a part of CMSI (Computational Materials Science Initiative) in HPCI (High Performance Computational Infrastructure), (ii) Nano science project, called Nanotechnology Platform from July 2012. (iii) Extreme photonics in collaboration with RIKEN, (iv) COE of molecular and materials simulations as a joint program of NINS, and (v) Photon Frontier Network Consortium for Photon Science and Technology in collaboration with Japan Atomic Energy Research Institute, Osaka University and Kyoto University. With two IMS own international programs for Asia, namely, EXODASS (EXchange prOgram for the Development of Asian Scientific Society) and Asian Core, IMS has invited active young scientists from various East Asian countries to carry out collaborative researches. EXODASS Program is the post-JENESYS starting from 2011, and aims to provide the opportunity of internship for young researchers (*e.g.*, master's and doctoral students and postdoctoral researchers) from Asian countries to stay in IMS laboratories related to the basic research for environmental and energy problems. Asian Core program also has now become IMS's own project, continuing to strengthen the tie among the four key institutes of Chemical Physics in Asia, namely, KAIST in Korea, IAMS in Taiwan, ICCAS in China and IMS in Japan.

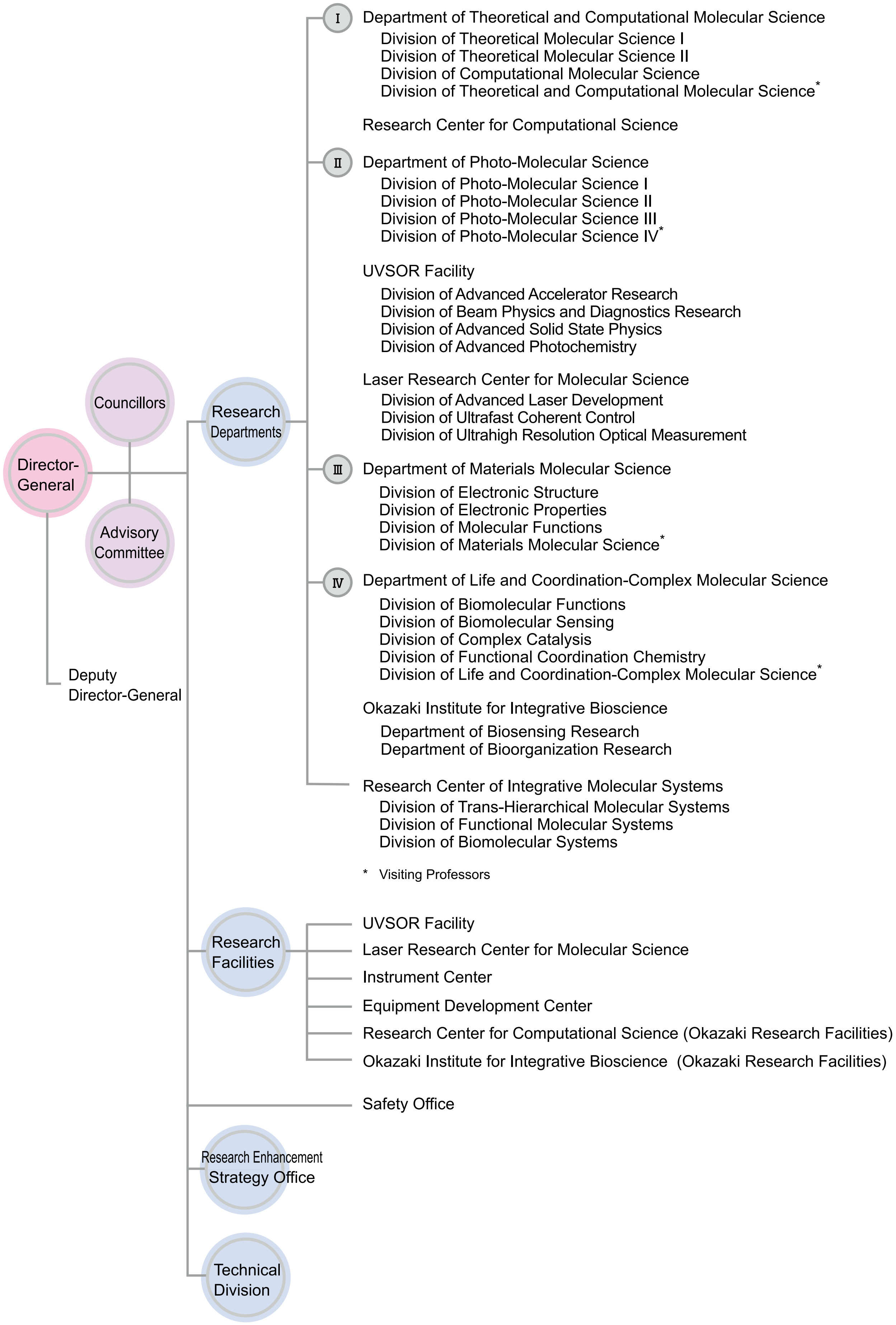
Many new faculty members have joined the IMS faculty in the period of September 2013–August 2014. Dr. Satoshi Kera from Chiba University, an expert of photoelectron spectroscopy and developing functional organic materials, has started his new position as a full professor of Photo-Molecular Science III section. Dr. Ryota Iino from the University of Tokyo, an expert on the single-molecule biophysics, especially, on molecular machines and molecular motors, is now a full professor of Okazaki Institute for Integrative Bioscience and also of Life and Coordination-Complex Molecular Science division. Three new associate professors have also joined our faculty in the same period; both Dr. Nobuyasu Koga from Washington University and Dr. Genki Kobayashi from Kanagawa University become members of Research Center of Integrative Molecular Systems, and Dr. Norie Momiyama from Tohoku University a member of Life and Coordination-Complex Molecular Science division. Professor Koga conducts the protein design by using computational and experimental approaches. Professor Kobayashi is developing effective synthesis methods of oxyhydrides, and to find a new functional materials providing hydride conductivity and novel electronic property. Professor Momiyama is exploring novel synthetic methods to develop highly functional chiral organic molecules.

IMS is continuing to employ a new scientific perspective with the newly founded CIMoS research center, mentioned above, and by trying to establish a new center ("precision multiscale measurement and analysis center") to develop the precision measurement and analysis methods to explore the spatiotemporal (time and spatial) development of multiscale molecular systems. We do expect your advice and support for creating this new era of molecular science.

September, 2014

OHMINE, Iwao
Director-General, Institute for Molecular Science

ORGANIZATION



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NAGASE, Shigeru	Senior Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University
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TANAKA, Koji	Professor, Institute for Integrated Cell-Material Sciences, Kyoto University
KUWAJIMA, Kunihiro	Adjunct Professor, The Center for the Promotion of Integrated Sciences, The Graduate University for Advanced Studies

ACTIVITIES IN EDUCATION AND COLLABORATION

Graduate Programs

IMS is one of the leading national research institutes for natural science. For graduate education, IMS has two departments of The Graduate University of Advanced Studies [SOKENDAI]: 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: Photochemistry and photophysics, Materials science, Coordination chemistry and catalysis, Biochemistry and biophysics, and Theoretical and computational molecular science.

In the 1st and 2nd years of the 5-year doctoral course, the programs emphasize the general science education in English and the laboratory rotation at three different research groups lasting about one month each. 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: (1) Basic Course (standard course), (2) The Advanced Research Course (studying abroad for 3 months), (3) Project Research Course (plan, develop, and execute large-scale research projects), (4) Development Research Course (internship at a company).

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 May, 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, and stay for 1–2 weeks to use various kinds of research equipments in our research facilities such as the UVSOR Facility 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 house.

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	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 researches and students from MOU partnership institutions

International Symposia

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

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 mechanics and statistical mechanics to predict and understand the structures, chemical reactions, and functions of molecules in gas and condensed phases including nano- and bio-systems.

Theoretical Studies on Heterogeneous Condensed Phase Dynamics

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Education

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

Professional Employment

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

Member
Assistant Professor
MORI, Toshifumi
IMS Fellow
ONO, Junichi
Secretary
KONDO, Naoko

Keywords Spatio-Temporal Heterogeneous Dynamics, Liquids, Proteins

Nonlinear intermolecular interactions cause complicated motions in condensed phases, *e.g.* liquids and biological systems. These motions are spatially and temporally heterogeneous with a wide range of time and spatial scales and yield both static and dynamic properties of the systems. In particular, heterogeneity plays important role in strongly-interacting systems, *e.g.* supercooled and ionic liquids, and biological systems. The spatio-temporal non-uniform motions known as dynamic heterogeneity are considered to be a clue to understand supercooled liquids and glass transition. Furthermore, heterogeneous reaction rates have been found in biological systems. Therefore, understanding of spatio-temporal heterogeneous dynamics is essential to the elucidation of the structure, thermodynamics, dynamics, and functions of the systems.

We have been investigating inter- and intra-molecular dynamics of water by third-order nonlinear spectroscopy which provide the detailed dynamics that are not available from conventional IR spectroscopy. We examined two-dimensional IR spectra and the energy relaxation and revealed the molecular mechanism of the ultrafast energy relaxation, which is one of dynamical features of water, *i.e.* the fast energy relaxation is caused by the nonlinear strong coupling between the libration motion and other intra- and inter-molecular vibrational motions.

We have also investigated the dynamics of supercooled liquids. We quantified the lifetime of dynamic heterogeneity by introducing the three-time correlation function of density fluctuation, which is sensitive to the time evolution of dynamic heterogeneity. Our systematic analysis for various systems shows that the lifetime of dynamic heterogeneity is intimately related to configurational entropy and thus the temperature dependence of lifetime of dynamic heterogeneity is more sensitive to the fragility than that of α-relaxation time determined by one-time correlation function. In addition to the analysis of dynamic heterogeneity with multi-time correlation function, we have examined the molecular origin of anomalous temperature dependence of isobaric specific heat of water. The time scale involved in isothermal specific heat has been analyzed by analyzing complex specific heat. We examined the emergence of correlated motion in terms of the wavenumber (k) dependent complex specific heat and the shell-wise energy fluctuation.

Currently, we are investigating how slow motions, which are involved in functions, are induced in biological molecules.

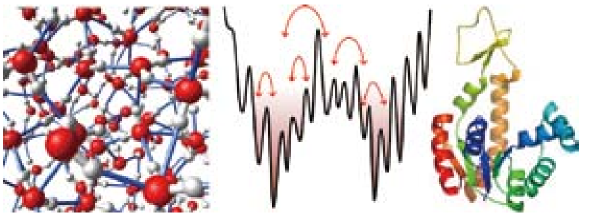

Figure 1. Schematic figure of rugged energy landscape (center) in supercooled water (left) and a biomolecule (right).

Selected Publications

- T. Yagasaki and S. Saito, *Acc. Chem. Res.* **42**, 1250–1258 (2009); *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013).
- S. Imoto, S. Xantheas and S. Saito, *J. Chem. Phys.* **139**, 044503 (7 pages) (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).

1. Anomalous Dynamics of Supercooled Water in "No Man's Land"

There exists no experimental study on dynamics of supercooled water between 155 K and 232 K, though several conjectures have been put forward. We carry out extensive molecular dynamics simulations from room temperatures down to as low as 130 K. Relaxation times are found to vary over twelve orders of magnitude in traversing this range, with occurrence of multiple anomalies. Structural, dynamical and thermodynamic properties all show a crossover, around 225 K, to a different, low density liquid state with different dynamical properties. On further cooling, this low density liquid again undergoes a dynamical transition around 197 K region where the density reaches its minimum, the dynamical heterogeneity starts to decrease after reaching maximum, and Stokes-Einstein relation, which is violated above 197 K, is recovered below 197 K. The temperature dependence of the relaxation times reveals three distinct branches, with discontinuities around 225 K and 197 K. From analysis of clusters of liquid-like and ice-like molecules, we attribute the latter anomalies to a pseudo-spinodal decomposition where the clusters of liquid-like molecules become fragmented (as if in a reverse percolation transition) and the small high density liquid droplets get surrounded by the dominant low density liquid. The third low temperature branch that appears below 197 K is studied here for the first time and is quite distinct from previous two branches. The relaxation time of this low temperature branch grows rapidly and the fitted relaxation time is projected to cross the 100 s mark around 135 K. We find that the number of defects in the liquid-like clusters serves as a good order parameter to describe this rapid growth. The approach to the amorphous ice is driven both by the rapid disappearance of the liquid-like droplets (below 180 K) and a simultaneous slow down of relaxation.

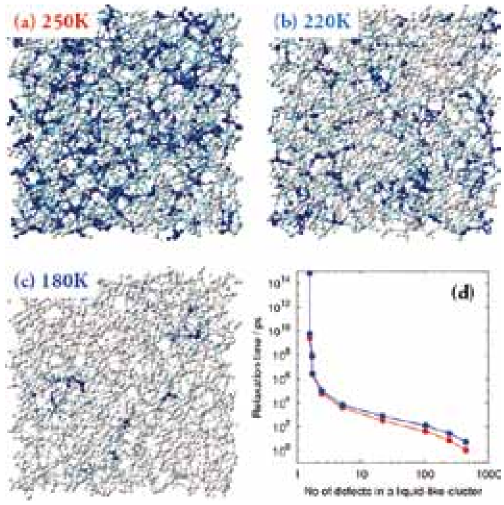

Figure 2. Snapshots of supercooled liquid water at (a) 250, (b) 220, and (c)180 K. (d) Relationship between the number of molecules in a liquid-like cluster and the relaxation times of translational (red curve) and rotational (blue curve) motions. A liquid-like cluster consists of HB defects and their first hydration molecules. Colored molecules in (a)–(c) are liquid-like clusters.

2. Theoretical Study on Excited States of Bacteriochlorophyll *a* in Solutions with Density Functional Assessment

We investigate the excited-state properties of bacteriochlorophyll *a* (BChl *a*) in triethylamine, 1-propanol, and methanol by using the quantum mechanical and molecular mechanical (QM/MM) reweighting free energy SCF method, which is an efficient geometry optimization method of a QM subsystem on a QM/MM free energy surface. We employ the time-dependent density functional theory for the excited-state electronic structure calculations with several density functionals. However, no prevalent functional can reproduce the experimental results, *i.e.* the absorption and reorganization energies of BChl *a* in solutions. We optimize the parameter μ in the range-separated hybrid functionals to reproduce the differences of the absorption energies in three solvents. The CAM-B3LYP functional with $\mu = 0.20$ can also reproduce the reorganization energies in triethylamine almost quantitatively. We examine the origin of the difference of the absorption energies in the three solutions. It is considered that the density functional with an adjusted parameter is essential to the understanding of the excited-state properties of BChl *a* in proteins and also the mechanism of the photosynthetic systems.

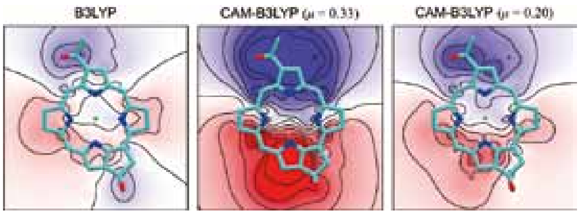

Figure 3. Functional dependence of the change in electrostatic potential of BChl *a* on the Q_y excitation in 1-propanol. The electrostatic potential distribution is calculated at the ground-state optimized geometry. Positive and negative values are shown by red and blue colors, respectively.

References

1) S. Saito, I. Ohmine and B. Bagchi, to be published.
2) M. Higashi, T. Kosugi, S. Hayashi and S. Saito, *J. Phys. Chem. B* (2014), in press.

Theory for Optical Near-Field Response and its Application to Functional Nanodevices

Department of Theoretical and Computational Molecular Science
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Education

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Professional Employment

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YAMADA, Mariko

Keywords Optical Near-Field, Light-Matter Interaction, Nanodevices

Optical response of molecules is undoubtedly essential for understanding their physicochemical properties. In conventional theoretical approaches to optical response of molecules, two conditions are usually assumed: (i) Wavelength of incident light is considered to be much longer than molecular size, *i.e.*, dipole approximation. Thus, a target molecule is well approximated by a point dipole and the dipole feels a uniform electromagnetic field. (ii) Electric polarization in a molecule induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an "optical near-filed," according to Maxwell's equations. However, such a self-consistent light-matter (LM) interaction between electron and electromagnetic field dynamics is ignored. Recent development of nanofabrication and nano-optical techniques requires a more general optical response theory fully taking account of *nonuniform and self-consistent* light-matter (LM) interactions.

We have developed a generalized theoretical description of full (nonuniform and self-consistent) LM interactions with the aim of understanding the optical near-field excitation dynamics in nanostructures of more than ten-nanometers in size. Electron dynamics in nanostructures interacting with an electromagnetic field is described by the time-dependent Kohn-Sham (TDKS) equation based on minimal coupling Hamiltonian with Coulomb gauge. On the other hand, electromagnetic field dynamics is represented by the microscopic Maxwell's equations. The nonuniform LM interaction is taken into account in the vector potential and the self-consistent LM interaction is described by solving the electron and electromagnetic field coupled equations self-consistently. The coupled equations are solved numerically by using our developed computational program (GCEED: *Grid-based Coupled Electron and Electromagnetic field Dynamics*). Our computational approach is based on a finite-difference method in real-time and real-space. Since the approach employs very simple algorithms, it is very suitable for massively parallelized computations. We have achieved the parallelized calculations with more than 660,000 cores in the K computer (Kobe RIKEN), which is one of the worldwide leading supercomputers.

Selected Publications

- K. Nobusada and K. Yabana, "Photoinduced Electric Currents in Ring-Shaped Molecules by Circularly Polarized Laser Pulses," *Phys. Rev. A* **75**, 032518 (7 pages) (2007).
- T. Iwasa and K. Nobusada, "Nonuniform Light-Matter Interaction Theory for Near-Field-Induced Electron Dynamics," *Phys. Rev. A* **80**, 043409 (11 pages) (2009).
- Y. Kubota and K. Nobusada, "Exciton–Polariton Transmission in Quantum Dot Waveguides and a New Transmission Path due to Thermal Relaxation," *J. Chem. Phys.* **134**, 044108 (8 pages) (2011).

1. Massively-Parallel Electron Dynamics Calculations in Real-Time and Real-Space: Toward Applications to Nanostructures of More Than Ten-Nanometers in Size[1)]

A highly efficient program of massively parallel calculations for electron dynamics has been developed in an effort to apply the method to optical response of nanostructures of more than ten-nanometers in size. The approach is based on time-dependent density functional theory calculations in real-time and real-space. The computational code is implemented by using simple algorithms with a finite-difference method in space derivative and Taylor expansion in time-propagation. Since the computational program is free from the algorithms of eigenvalue problems and fast-Fourier-transformation, which are usually implemented in conventional quantum chemistry or band structure calculations, it is highly suitable for massively parallel calculations. Benchmark calculations using the K computer at RIKEN demonstrate that the parallel efficiency of the program is very high on more than 60,000 CPU cores. The method is applied to optical response of arrays of C_{60} orderly nanostructures of more than 10 nm in size. The computed absorption spectrum is in good agreement with the experimental observation.

The present computation is one of the largest first-principles calculations of photoinduced electron dynamics in nanostructures. It is highly expected that nanostructures of up to ~50 nm in size with a quantum confinement effect are promising materials in developing next-generation quantum devices with valuable functions. The first-principles calculations of excitation dynamics in such huge nanostructures are really unprecedented in molecular and material science. The present computational approach paves a new way of theoretically designing these devices at a real nanoscale.

2. First-Principles Computational Visualization of Localized Surface Plasmon Resonance in Gold Nanoclusters[2)]

We have studied the cluster-size dependence of localized surface plasmon resonance (LSPR) for Au_n clusters of up to $n = 1414$ (3.9 nm in diameter) by performing first-principles photoinduced electron dynamics calculations. The maximum cluster size is unprecedentedly large in comparison with those addressed in previous, fully quantum mechanical, calculations of optical response in real cluster systems. The computations enable us to see that LSPR gradually grows and its peak position redshifts (blueshifts) with increasing (decreasing) cluster size. These computed results are in good agreement with experimental observations. The localized surface charge distributions are visualized in real space, vividly illustrating the conduction electrons oscillate in a collective manner. From the visualization, LSPR has proven to be discernible at $n \sim 146$, although the optical responses for $Au_n (n \leq 146)$ are still mostly in a quantum regime because a quantum confinement effect remains predominant. The charge oscillation occurs in two regions, the outermost surface region and the inner region. The surface charge responds in synchronization with the applied laser field, whereas the inner charge oscillates locally around each gold atom in a direction opposite to the surface charge distribution. This is clear evidence of a screening effect caused by the d-electrons. The present quantum mechanically accurate description of LSPR in gold nanoclusters provides valuable information when utilizing the properties of LSPR in developing plasmonic functional devices.

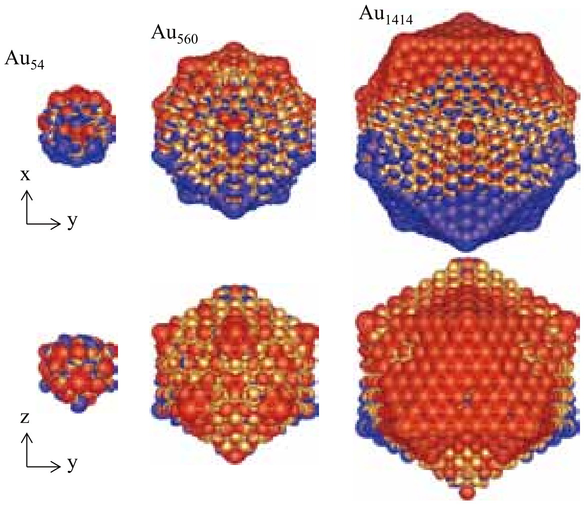

Figure 1. Photoinduced densities of LSPR for Au_n (n = 54, 560, and 1414).

3. Nonsuperatomic $[Au_{23}(SC_6H_{11})_{16}]^-$ Nanocluster Featuring Bipyramidal Au_{15} Kernel and Trimeric $Au_3(SR)_4$ Motif[3)]

We report the X-ray structure of a cyclohexanethiolate-capped $[Au_{23}(SR)_{16}]^-$ nanocluster (counterion: tetraoctylammonium, TOA^+). The structure comprises a cuboctahedron-based bipyramidal Au_{15} kernel, which is protected by two staple-like trimeric $Au_3(SR)_4$ motifs, two monomeric $Au(SR)_2$ and four plain bridging SR ligands. Electronic structure analysis reveals nonsuperatomic feature of $[Au_{23}(SR)_{16}]^-$ and confirms the Au_{15} kernel and surface motifs. The Au_{15} kernel and trimeric staple motif are unprecedented and offer new insight in understanding the structure evolution of gold nanoclusters.

References

1) M. Noda, K. Ishimura, K. Nobusada, K. Yabana and T. Boku, *J. Comput. Phys.* **265**, 145–155 (2014).
2) K. Iida, M. Noda, K. Ishimura and K. Nobusada, *J. Phys. Chem. A* **118**, 11317–11322 (2014).
3) A. Das, T. Li, K. Nobusada, C. Zeng, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.* **135**, 18264–18267 (2013).

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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Education

1997	B.S. The University of Tokyo
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

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

Member

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IMS Fellow
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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.

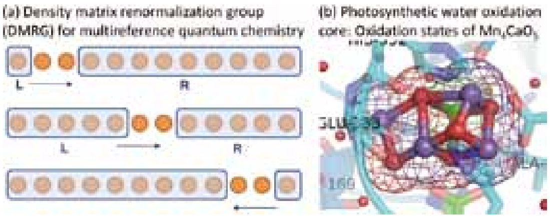

Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

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. Radical O–O Coupling Reaction in Diferrate-Mediated Water Oxidation Studied with Multireference Wave Function Theory[1)]

Recently, the water oxidation catalyzed by potassium ferrate K_2FeO_4 was investigated on the basis of experimental kinetic isotope effect analysis assisted by density functional calculations, revealing the intramolecular oxo-coupling mechanism within a di-iron(VI) intermediate, or diferrate [Sarma *et. al.*, *J. Am. Chem. Soc.* **134**, 15371 (2012)]. Here, we reported a detailed examination of this diferrate-mediated O–O bond formation using scalable multireference electronic structure theory. High-dimensional correlated many-electron wave functions beyond one-electron picture were computed with *ab initio* DMRG method along the O–O bond formation pathway. The necessity of using large active space arises from the description of complex electronic interactions and varying redox states both associated with two-center antiferromagnetic multivalent iron–oxo coupling. Dynamic correlation effects on top of the active space DMRG wave functions were additively accounted for by complete active space second-order perturbation (CASPT2) and multireference configuration interaction (MRCI) based methods, which were recently introduced by our group. These multireference methods were capable of handling the double shell effects in the extended active space treatment. The calculations with CAS(36e,32o), which is far over conventional limitation, provide a quantitatively reliable prediction of potential energy profiles and confirmed the viability of direct oxo coupling. (**Figure 2**).

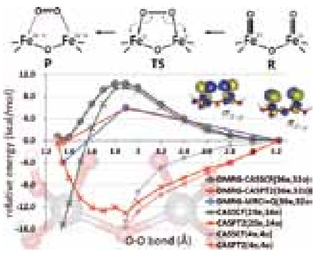

Figure 2. Diferrate-mediated O–O bond formation was studied using *ab initio* DMRG theory with large-size active space CAS(36e,32o) in conjunction with dynamic correlation correction.

2. Toward Reliable Prediction of Hyperfine Coupling Constants Using *Ab Initio* Density Matrix Renormalization Group Method[2)]

The DMRG method was used in conjunction with the CASCI and CASSCF methods to evaluate hyperfine coupling constants (HFCCs) for a series of diatomic $^2\Sigma$ radicals (BO, CO^+, CN, and AlO) and vinyl (C_2H_3) radical. The electron correlation effects on the computed HFCC values were systematically investigated using various levels of active space, which were increasingly extended from single valence space to large-size model space entailing double valence and at least single polarization shells. In addition, the core correlation was treated by including the core orbitals in active space. Reasonably accurate results were obtained by the DMRG-CASSCF method involving orbital optimization, while DMRG-CASCI calculations with Hartree-Fock orbitals provided poor agreement of the HFCCs with the experimental values. To achieve further insights into the accuracy of HFCC calculations, the orbital contributions to the total spin density were analyzed at a given nucleus, which is directly related to the FC term and is numerically sensitive to the level of correlation treatment and basis sets. This work serves as the first study on the performance of the *ab initio* DMRG method for HFCC prediction.

3. Flexible Nuclear Screening Approximation to the Two-Electron Spin–Orbit Coupling Based on *Ab Initio* Parameterization[3)]

The derivation, implementation, and validation of a new approximation to the two-electron spin–orbit coupling (SOC) terms was reported. The approximation, referred to as flexible nuclear screening spin–orbit (FNSSO), is based on the effective one-electron spin–orbit operator and accounts for two-electron SOC effects by screening nuclear charges. A highly flexible scheme for the nuclear screening is developed, mainly using parameterization based on *ab initio* atomic SOC calculations. Tabulated screening parameters are provided for contracted and primitive Gaussian-type basis functions of the ANO-RCC basis set for elements from H to Cm. A model to correct for the effect of spin–orbit splitting of transition metal *d* orbitals on their SOC matrix elements was introduced. The method is applied to a representative set of molecules, and compared to exact treatment and other approaches at the same level of relativistic theory. The calculated SOC matrix elements are in very good agreement with their "exact" values; deviation below 1% is observed on average.

References

1) Y. Kurashige, M. Saitow, J. Chalupský and T. Yanai, *Phys. Chem. Chem. Phys.* **16**, 11988–11999 (2014).
2) L. N. Tran, Y. Kurashige and T. Yanai, *J. Chem. Theory Comput.* **10**, 1953–1967 (2014).
3) J. Chalupský and T. Yanai, *J. Chem. Phys.* **139**, 204106 (14 pages) (2013).
4) F. Liu, Y. Kurashige, T. Yanai and K. Morokuma, *J. Chem. Theory Comput.* **9**, 4462–4469 (2013).
5) Y. Kurashige, *Mol. Phys.* **112**, 1485–1494 (2014).
6) S. Sharma, T. Yanai, G. H. Booth, C. J. Umrigar and G. K.-L. Chan, *J. Chem. Phys.* **140**, 104112 (8 pages) (2014).
7) T. V. Harris, Y. Kurashige, T. Yanai and K. Morokuma, *J. Chem. Phys.* **140**, 054303 (10 pages) (2014).

Awards

YANAI, Takeshi; Laureate, International Academy of Quantum Molecular Science 2013.
YANAI, Takeshi; Young Scientist Awards of the Japan Society for Molecular Science 2013.
KURASHIGE, Yuki; MORINO Foundation for Molecular Science 2014.

Theoretical Study on Photochemistry and Catalysis

Department of Theoretical and Computational Molecular Science
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Education

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

Professional Employment

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

Awards

2009	APATCC Pople Medal
2009	QSCP Prize CMOA

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    YANG, Tao
    DANG, Jing-Shuang
Visiting Scientist
    HANSEN, Jared A.
    IMPENG, Sarawoot*
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    SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photophysical Chemistry, 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 nanocluster catalysis

Metal nanoclusters supported by metal oxides or polymers achieves 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 hetero-junction of Ag nanocluster supported by alumina surface in terms of H_2 activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

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

(4) Theoretical spectroscopy

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

Selected Publications

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

1. Perturbative PCM SAC-CI Method

Ultraviolet-visible spectroscopies of molecules are commonly measured in solutions. Polar solvents are often used for solubility; solvent effects on the spectra are, therefore, considerable. Quantum chemical methods are useful for assigning and understanding the spectra and excited-state properties. For efficient calculations of the electronic excitations and absorption spectra of molecules in solutions, a perturbative approximation of the state specific polarizable continuum model (PCM) symmetry-adapted cluster configuration interaction (SAC-CI) method is proposed. This first-order PCM SAC-CI method considers the solvent effects on the energies of excited states up to the first-order with using the zeroth-order wavefunctions. This method can avoid the costly iterative procedure of the self-consistent reaction field (SCRF) calculations. The first-order PCM SAC-CI calculations well reproduce the results obtained by the iterative method for various types of excitations of molecules in polar and nonpolar solvents. The first-order contribution is significant for the excitation energies. The results obtained by the zeroth-order PCM SAC-CI, which considers the fixed ground-state reaction field for the excited-state calculations, are deviated from the results by the iterative method about 0.1 eV, and the zeroth-order PCM SAC-CI cannot predict even the direction of solvent shifts in *n*-hexane for many cases.

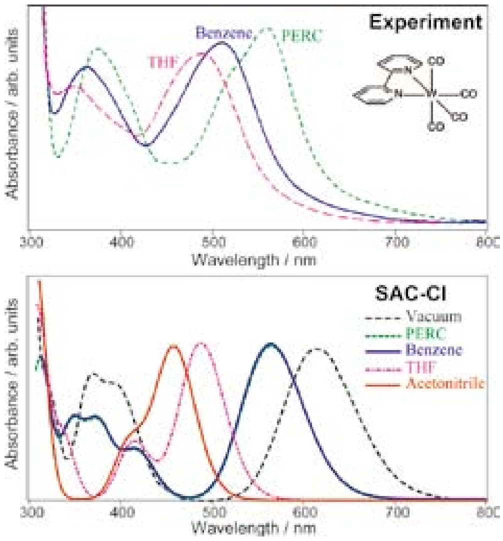

Figure 1. The observed and SAC-CI simulated absorption spectra of W(CO)$_4$(bpy).

The first-order PCM SAC-CI is applied to studying the solvatochromisms of (2,2'-bipyridine)tetracarbonyltungsten [W(CO)$_4$(bpy), bpy = 2,2'-bipyridine] and bis(pentacarbonyl tungsten)pyrazine [(OC)$_5$W(pyz)W(CO)$_5$, pyz = pyrazine]. The SAC-CI calculations reveal the detailed character of the excited states and the mechanisms of solvent shifts. The energies of metal to ligand charge transfer (MLCT) states are significantly sensitive to solvents. The first-order PCM SAC-CI well reproduces the observed absorption spectra of the tungsten carbonyl complexes in several solvents.

2. H_2 Activation on Ag/Al_2O_3 Dual Perimeter Sites

The catalytic activity of supported metal nanoparticles depends on the metal-support interaction and metal size. Supported silver nanoparticles have been the focus of research because of their characteristic catalytic activity. This work aims to theoretically elucidate the role of the interface perimeter site between the Ag cluster and alumina support for H_2 dissociation by applying the periodic density functional theory (DFT) calculations.

H_2 dissociation by Ag clusters supported on the θ-Al_2O_3 (110) surface has been investigated using DFT calculations. The crucial role of the dual perimeter site of Ag cluster and the surface oxygen (O) site of the alumina support is demonstrated with three theoretical models: anchored cluster, isolated cluster, and anchored cluster on hydroxylated alumina. The heterolytic cleavage of H_2 at the silver–alumina interface, yielding Ag–H$^{\delta-}$ and O–H$^{\delta+}$, is thermodynamically and kinetically preferred compared with H_2 cleavage at two Ag atomic sites on top of the Al_2O_3-supported Ag cluster and the homolytic cleavage of H_2 on the isolated Ag cluster. The hydroxylation at the O site of the alumina reduces the H_2 dissociation activity, which indicates that the interfacial bare O site is indispensible. It is concluded that the interfacial cooperative mechanism between the Ag cluster and Lewis acid-base pair site (bare Al–O site) is essentially relevant for the H_2 activation over Ag-loaded Al_2O_3 catalysts.

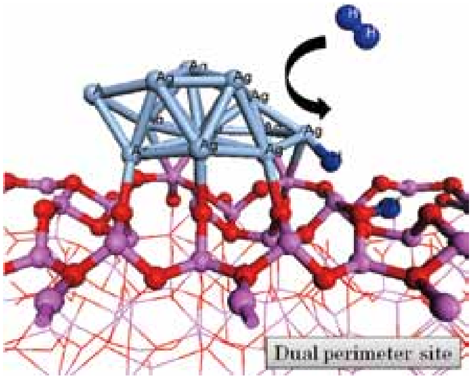

Figure 2. Ag$_{13}$ cluster on θ-Al_2O_3(110) surface. A model for investigating H_2 activation mechanisms with DFT calculations.

References

1) R. Fukuda, M. Ehara and R. Cammi, *J. Chem. Phys.* **140**, 064114 (15 pages) (2014).

2) P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, *J. Phys. Chem. C* **118**, 7996–8006 (2014).

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* IMS International Internship Program

Development of New Molecular Dynamics Algorithms for Biomolecular Systems

Department of Theoretical and Computational Molecular Science
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Education

1998	B.S. Keio University
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Professional Employment

2002	Postdoctoral Fellow, The University of Tokyo
2002	Research Associate, Institute for Molecular Science
2004	Research Associate, The Graduate University for Advanced Studies
2006	Research Lecturer, Nagoya University
2008	Research Assistant, Rutgers University
2009	Assistant Research Professor, Rutgers University
2009	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Member

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NISHIKAWA, Naohiro*
Secretary
KAWAGUCHI, Ritsuko

Keywords Molecular Dynamics Simulation, Protein, Amyloid

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

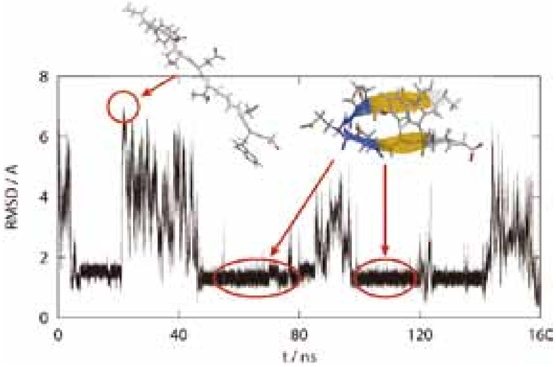


Figure 1. Time series of protein folding simulation.

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.

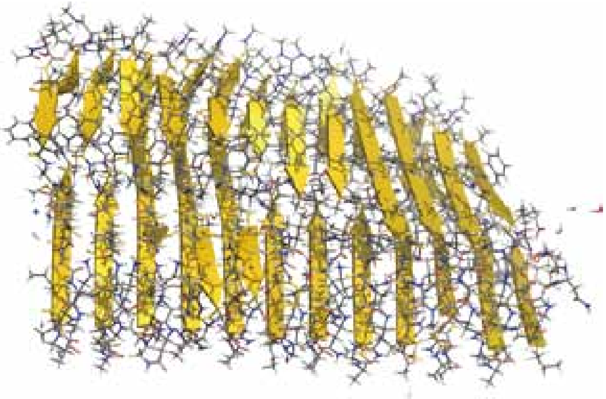


Figure 2. Snapshot of amyloid fibril.

Selected Publications

- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- S. G. Itoh and H. Okumura, "Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method," *J. Chem. Theory Comput.* **9**, 570–581 (2013).
- 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).
- H. Okumura, "Temperature and Pressure Denaturation of Chignolin: Folding and Unfolding Simulation by Multibaric-Multithermal Molecular Dynamics Method," *Proteins* **80**, 2397–2416 (2012).

1. Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations

There are some experimental reports that cavitation disrupts amyloid fibrils. However, it is still unknown how the cavitation or bubble in water disrupts the amyloid fibrils at atomic level. In order to answer this problem, we performed nonequilibrium molecular dynamics simulations of an Aβ fibril in explicit water.[1)] We used twelve Aβ(17–42) peptide molecules, 10169 water molecules, and twelve sodium ions as counter ions. The simulation was started from the experimentally-known amyloid oligomer structure in the amyloid fibril. To express supersonic wave, sinusoidal pressure was applied between –100 MPa and 300 MPa. Snapshots of this simulation are illustrated in Figure 3. When the pressure was decreased to a negative value of –100 MPa from a room pressure, a bubble formation was observed around the transmembrane region, in which all the amino acid residues were hydrophobic. Even after the bubble size increased, the secondary structures of the oligomer were maintained. When the pressure was increased to a positive value, the bubble shrank and collapsed, and the oligomer was disrupted. At this time, most water molecules attacked the hydrophilic residues in nontransmembrane region.

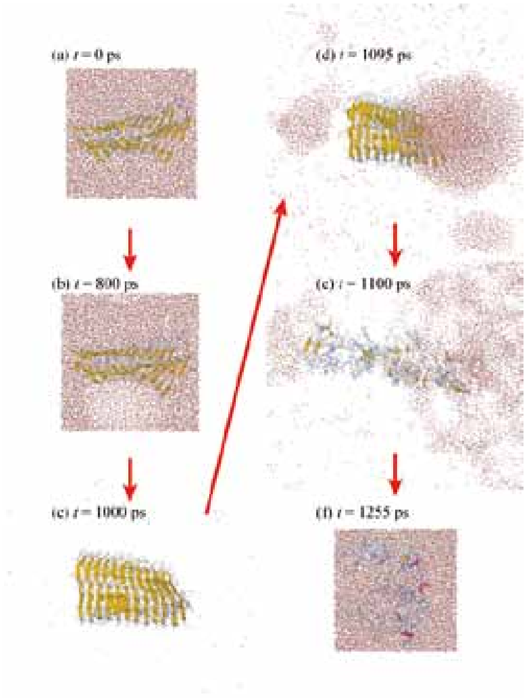


Figure 3. Snapshots of the non-equilibrium MD simulation of the amyloid-β fibril in explicit water.

2. Development of Hamiltonian Replica-Permutation Method

We propose the Hamiltonian replica-permutation method (RPM) (or multidimensional RPM) for molecular dynamics and Monte Carlo simulations, in which parameters in the Hamiltonian are permuted among more than two replicas with the Suwa-Todo algorithm.[2)] We apply the Coulomb RPM, which is one of realization of the Hamiltonian RPM, to an alanine dipeptide and to two amyloid-β(29–42) molecules. The Hamiltonian RPM realizes more efficient sampling than the Hamiltonian replica-exchange method. We illustrate the protein misfolding funnel of amyloid-β(29–42) and reveal its dimerization pathways.

3. Manifold Correction Method for the Nosé-Hoover and Nosé-Poincaré Molecular Dynamics Simulations

We introduce the manifold correction method to MD simulations with the Nosé-Hoover and Nosé-Poincaré thermostats.[3)] The manifold correction method was originally developed in astronomy, as an accurate numerical method for many body systems. Because the Nosé-Hoover thermostat is not a symplectic algorithm, the quantity which is conserved analytically is not conserved but increases in actual MD simulations. Using the manifold correction method, this quantity is completely conserved, and it makes the MD simulation stable. Because the conservation of this quantity is required in the proof that the Nosé-Hoover thermostat gives the canonical ensemble, the manifold correction method guarantees to provide the correct statistical ensemble. Although the time development of the Nosé-Poincaré thermostat is described as a symplectic algorithm, if the interatomic potential energy is truncated, the Nosé-Poincaré thermostat is no longer symplectic. In this case, the Hamiltonian increases, and temperature cannot be controlled. Applying the manifold correction method to the Nosé-Poincaré thermostat, the Hamiltonian becomes conserved and temperature can be appropriately controlled.

References

1) H. Okumura and S. G. Itoh, *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
2) S. G. Itoh and H. Okumura, *J. Comput. Chem.* **34**, 2493–2497 (2013).
3) H. Okumura, S. G. Itoh, A. M. Ito, H. Nakamura and T. Fukushima, *J. Phys. Soc. Jpn.* **83**, 024003 (5 pages) (2014).

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

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 currently focus on 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 describe electron energy transfer including solvent motion and dynamics. On the other hand, ILs' projects concentrate the study of dynamical properties on ionic liquids using molecular dynamics simulation technique.

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

We have developed a procedure for tracing the time-dependent evolution of the electronic structure of a solute molecule in solution, coupling an electronic structure theory with solvent motion. We have extended this method for investigating electron energy transfer processes in the excited state in solution. It is shown that the coupling between solvation dynamics 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 Dynamical Properties on Ionic Liquids$^{1–2)}$

We focus on, in particular, the dynamical properties on ionic liquids (ILs). With molecular dynamics simulation, it have been found out that ILs indicate unique collective dynamics. We have investigated interesting dynamical heterogeneity in ILs at room temperature. Also, we have studied spatial heterogeneity.

References

1) T. Ishida, "The Dynamical Properties on Ionic Liquids: Insights from Molecular Dynamics Study," in *Ionic Liquids—New Aspects for the Future*, J. Kadokawa, Ed., InTech; Rijeka, Croatia, pp. 3–29 (2013).

2) T. Ishida and H. Shirota, *J. Phys. Chem. B* **117**, 1136–1150 (2013).

Visiting Professors

Visiting Professor

TEN-NO, Seiichiro *(from Kobe University)*

New Frontier of Hybrid Stochastic and Deterministic Electronic Structure Approaches

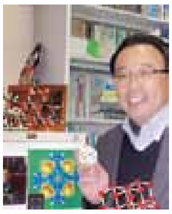
The vast majority of ab initio electronic structure methods are on the basis of deterministic disciplines, in which a compactification of an N-factorial CI expansion is of main interest. Nevertheless, the way to calculate strongly correlated systems with quasi-degeneracy and general excited states accurately still remains open. These objectives are of significant importance for entangled electronic states involving photoinduced phenomena in biochemistry and energy conversion processes in chemistry. We have recently developed the model space quantum Monte Carlo (MSQMC) method crossing the effective Hamiltonian formalism and full configuration interaction (FCI) QMC [*ST*, *J. Chem. Phys.* **138**, 164126 (2013)]. The method sidesteps the negative sign problem in QMC arising from quasi-degeneracy transcending the storage limitation for CI vectors. Promising results are obtained for the FCI potential energy curves of various excited states for C_2, N_2, and O_2 molecules [Y. Ohtsuka and *ST*, unpublished (2014)]. The method has been also applied to the oxygen evolving center of the photo system II for low-lying spin states.

Visiting Professor

TAKADA, Shoji *(from Kyoto University)*

Computational Studies of Biomolecular Systems

I am studying in the area of computational molecular biophysics, primarily focusing on protein structure and dynamics. Even though thousands of X-ray crystal structures may provide impression that biomolecules are rigid material, in reality they are nano-scale molecules that work under thermal noise and, as such, they are dynamic. Given many crystal structures as snapshots, my ultimate goal is to understand dynamical functions of these molecules via computational analysis. Specifically, my current research includes 1) protein folding and conformational dynamics, 2) biomolecular motors, and 3) gene dynamics, together with 4) methodology development used in these topics. Protein folding and conformational dynamics is a basis to understand all the protein functions. Many proteins undergo substantial conformational change upon binding to their partner molecules, which form a molecular switch. How these molecular switch is regulated is, in my view, one of the most fundamental problems in protein science.



Visiting Associate Professor

SUGIMOTO, Manabu *(from Kumamoto University)*

Computational Molecular Science for Chemical Design and Engineering

The quantum chemical method is a powerful and insightful tool for analyzing and predicting molecular structures and chemical phenomena. Our group is interested in applying electronic-structure methods for investigating molecular functions that are of practical importance. Our on-going research is twofold: One is direct application of the quantum methods. Recently we have been studying spectral properties of supramolecular metal-ion sensors in collaboration with experimentalists. We have been successful to reveal the electronic mechanism for metal-ion sensing. We are also studying photochemical water splitting by graphitic carbon nitride. Its chemical property is expected to provide rich information for designing artificial photosynthesis. Another research is for development of chemoinformatics through which one would be able to learn, understand, investigate, predict, and design molecules and their chemistries. We are developing a system on the basis of our original electronic-structure database and new search engines. Our contribution is intended to enrich usefulness and uniqueness of Computational Molecular Science.

RESEARCH ACTIVITIES

RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction between molecules and optical fields with its possible applications to active control of molecular functionality and reactivity. We also develop novel light sources to promote those studies. Two research facilities, the Laser Research Center for Molecular Science and the UVSOR, closely collaborate with the Department.

The core topics of the Department include ultrahigh-precision coherent control of gas- and condensed-phase 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.

Development of Advanced Near-Field Spectroscopy Imaging and Application to Nanomaterials

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

Award
2012 The Chemical Society of Japan (CSJ) Award for Creative Work

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Keywords Near-Field Optical Microscopy, Plasmons, Excited States of Nanomaterials

There is much demand for the studies of local optical properties of molecular assemblies and materials, to understand nanoscale physical and chemical phenomena and/or to construct nanoscale optoelectronic devices. Scanning near-field optical microscopy (SNOM) is an imaging method that enables spatial resolution beyond the diffraction limit of light. Combination of this technique with various advanced spectroscopic methods may provide direct probing methods for dynamics in nanomaterials and nanoscale functionalities. It may yield essential and basic knowledge to analyze origins of characteristic features of the nanomaterial systems. We have constructed apparatuses of near-field spectroscopy and microscopy for excited-state studies of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable near-field measurements of two-photon induced emission, femtosecond time-resolved signals, and circular dichroism, in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatiotemporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are given 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, and so forth.

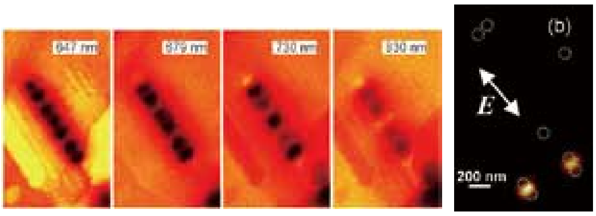

Figure 1. (Left four panels) Near-field transmission images of gold nanorod ($20\ \text{nm}^D \times 510\ \text{nm}^L$). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic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

Selected Publications

- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).
- H. Okamoto, "Nanooptical Studies on Physical and Chemical Characteristics of Noble Metal Nanostructures," *Bull. Chem. Soc. Jpn.* **86**, 397–413 (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. Plasmon-Mode Analysis of Gold Nanodisks[1)]

Spatial and spectral properties of plasmons in noble metal nanoparticles are strongly influenced by the geometry of the particles. We previously demonstrated that standing wave functions of plasmon modes of gold nanorods (1-dimensional system) could be visualized by near-field microscopy. In the present study we visualized plasmon-modes for gold nanodisks (2-dimensional system) fabricated by the electron-beam lithography lift-off method. Near-field transmission spectrum of a single nanodisk exhibited multiple plasmon resonances in the visible to near-infrared region. Near-field transmission images observed at these resonance wavelengths show wavy spatial features depending on the wavelength of observation, which are much more complicated than those of the 1-dimensional rods. Theoretical analysis is indispensable to clarify the origins of the spatial features of the modes. For this purpose, numerical simulations with a novel theoretical formalism based on spatial correlation between electromagnetic fundamental modes inside and outside of the disc were performed. Simulated images reproduced the observed spatial structures excited in the disc.

Compared with other electromagnetic simulation methods frequently used for the analysis of plasmons, such as finite-difference time-domain (FDTD) method, the present method is advantageous in its capability of mode-based analysis of the electromagnetic fields. Mode-analysis of the simulated images indicates that the spatial features observed in the transmission images originate mainly from a few fundamental modes of the disc. The relative phases of the collective oscillation of electrons in the lobes observed near-field images were also clarified by this analysis.

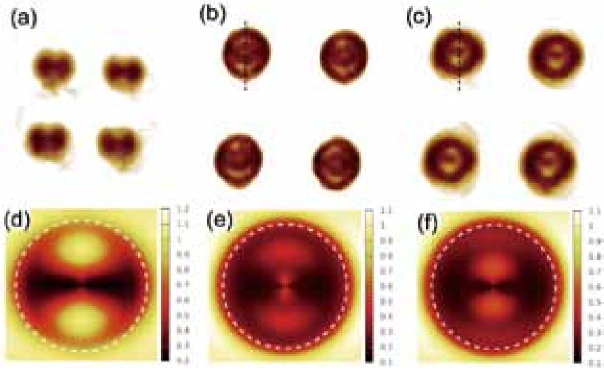

Figure 2. Observed (a–c) and simulated (d–f) near-field transmission images of gold nanodisks (thickness 35 nm).[1)] The diameters of the disks were 400 nm (a,d) and 800 nm (b,c,e,f). The wavelengths of observation and calculation were 780 nm (a,d), 710 nm (b), 790 nm (c), 705 nm (e), and 765 nm (f).

2. Strong Nanoscale Local Optical Activity in 2-D Chiral Metal Nanostructures

Nanostructures with chiral shapes show optical activity. Chiral metal nanostructures are expected to yield particularly strong optical activity arising from plasmon resonances. We recently developed a near-field circular dichroism (CD) imaging system with 100-nm-scale spatial resolution.

In the present work, we measured near-field CD images of S-shaped gold nanostructures and compared the results with the macroscopically obtained CD spectrum.[2)] Local CD signals of both handedness coexisted in the individual nanostructures, and the spatial distribution of the CD reflected the chiral symmetry of the nanostructure (Figure 3). When integrated over the entire nanostructure, the local CD signal was approximately 1% of the maximum of the local CD signal, which approximately coincided with the macroscopic CD signal. This indicates that there are possibly prominent nanoscale local CD signals even if only a tiny CD signal is observed macroscopically. We also studied developing optical activity with increasing chirality.[3)] We measured 2-D nanostructures composed of two symmetrically arranged C-shaped partial structures with various distances between them, which formed an “S” structure when the two partial structures were contacted. The chirality formed with the two partial structures caused an enhanced local optical activity when the partial structures were close enough to each other, even without a physical contact between them.

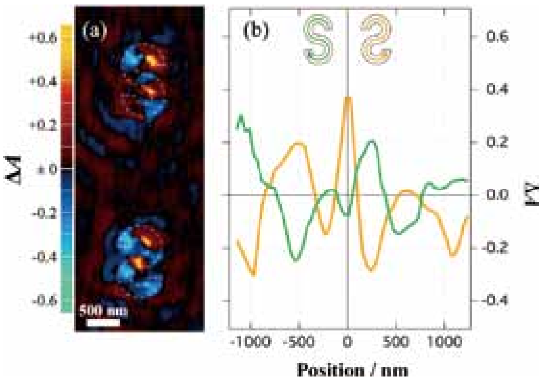

Figure 3. Near-field CD images of “S” shaped gold nanostructures (thickness 35 nm) observed at 785 nm (a) and the line profiles along the curves of the structures (b).[2)]

References

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2) T. Narushima and H. Okamoto, *J. Phys. Chem. C* **117**, 23964–23969 (2013).

3) T. Narushima, S. Hashiyada and H. Okamoto, *ACS Photonics* **1**, 732–738 (2014).

Awards

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NISHIYAMA, Yoshio; Best Presentation Award, The Spectroscopical Society of Japan (2014).

Design and Reconstruction of Molecular Quantum States of Motion

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Keywords Molecular Spectroscopy, Ultrafast Laser Science, Coherent Control

Molecules are vital existence. In a gas-phase ensemble at room temperature, they are, in an average, flying away by a few hundred meters, making turns almost reaching to 10^{11} times, and shaking themselves more than 10^{13} times within the duration of only one second. The ultimate goal this research group has been aiming to is to capture the lively figures of molecules moving in such a dynamic manner and to have a perfect command over the molecular motions. Here lasers with ultimate resolution in time and energy domains are employed complementally and cooperatively for this purpose.

When a gaseous molecular sample is irradiated by an intense nonresonant ultrashort laser pulse, the rotation of the molecules is coherently excited to create a rotational quantum wave packet (WP). We developed a method to explore the nonadiabatic excitation in a quantum-state resolved manner and applied it to diatomic and symmetric-top molecules. It has been shown that the state distribution is a useful experimental source for verifying the excitation process. When a pair of excitation pulses is implemented, partial control of rotational-state distribution has been achieved. In a favorable case, the double-pulse excitation has enabled us to reconstruct experimentally a rotational WP thus created. The sense of rotation can also be controlled, yielding to a rotational WP exhibiting angular-momentum orientation.

Nonadiabatic interaction with an intense ultrashort laser field can also coherently excite vibration of molecule. We have succeeded in creating and observing WPs pertinent to intermolecular vibrations of several molecular clusters in their vibronic ground states.

In the course of the control over molecular motion with high-resolution lasers, we constructed an optical parametric amplifier (OPA), to realize rapid adiabatic passage (RAP), which drives coherent population transfer from an initial quantum state to a target state with 100% efficiency. The laser system is consisted with BiBO crystals, which are seeded by a phase-modulated cw beam in the 1,040–1,070 nm region. Two-stage pre-amplification by Yb-doped fibers are implemented for stable injection to the OPA. The frequency chirp in the OPA pulse was actively controlled. Down/up chirps with up to 500 MHz shift were demonstrated. The output pulse energy was ~40 mJ, which is sufficient for two-photon RAP.

Selected Publications

- H. Hasegawa and Y. Ohshima, “Decoding the State Distribution in a Nonadiabatic Rotational Excitation by a Nonresonant Intense Laser Field,” *Phys. Rev. A* **74**, 061401 (4 pages) (R) (2006).
- H. Hasegawa and Y. Ohshima, “Quantum State Reconstruction of a Rotational Wave Packet Created by a Nonresonant Intense Femto-Second Laser Field,” *Phys. Rev. Lett.* **101**, 053002 (4 pages) (2008).
- K. Kitano, H. Hasegawa and Y. Ohshima, “Ultrafast Angular-Momentum Orientation by Linearly Polarized Laser Fields,” *Phys. Rev. Lett.* **103**, 223002 (4 pages) (2009).
- Y. Ohshima and H. Hasegawa, “Coherent Rotational Excitation by Intense Nonresonant Laser Fields,” *Int. Rev. Phys. Chem.* **29**, 619–663 (2010).
- S. Miyake and Y. Ohshima, “Injection-Seeded Optical Parametric Amplifier for Generating Chirped Nanosecond Pulses,” *Opt. Express* **21**, 5269–5274 (2013).

1. New Ion-Imaging Apparatus for Molecular Wave-Packet Dynamics Studies

To characterize the rotational wave-packet dynamics, ion imaging is one of the direct and powerful methods. In a conventional 2D ion imaging with a typical camera-based technique, only a 2D projection of the 3D particle distribution is observed. When the particle distribution is cylindrically symmetric, the original 3D distribution can be reconstructed from the 2D projection by utilizing a mathematical procedure (*e.g.*, inverse Abel transformation). However, we sometimes encounter non-Abel-invertable cases, such as unidirectional molecular rotation. Although 3D imaging techniques could be successfully applied for such a case, a 2D detector has many advantages over a 3D detector: Higher multi-hit capability, lower cost, and simpler setup.

In this study, we designed and built up a new 2D ion imaging apparatus. We installed a 2D imaging unit (MCP/screen/camera) and a repeller plate electrode in the middle of the flight tube of a typical imaging apparatus. A jet-cooled gaseous molecular sample was irradiated by the output of a Ti:Sapphire laser. The molecules were multiply ionized and then exploded within the laser duration (Coulomb explosion). The ion fragments were first accelerated perpendicularly to the laser propagation direction. At the time when the ions of interest arrived at the repeller, a fast high voltage pulse was applied to the repeller to push the ions perpendicularly to the imaging unit.

For dynamics studies, we carried out time-resolved pump–probe experiments on N_2 molecules by using circularly polarized light as a probe to explode molecules of all orientation angles. Pump pulse used was a linearly polarized light (800 nm, 120 fs, ~50 TW/cm^2), which induced rotational wave-packet dynamics. Figure 1 shows selected 2D polar plots for the Coulomb exploded fragment distribution of N^{3+}, recorded at various delay time between the linearly polarized pump and the circularly polarized probe pulses. This delay-dependent anisotropic distribution of the fragments directly correlates to the 2D slice of the molecular-axis probability distribution in the 3D laboratory frame, and the clear manifestation of spatio-temporal propagation of the rotational wave packet created by an impulsive strong laser field.

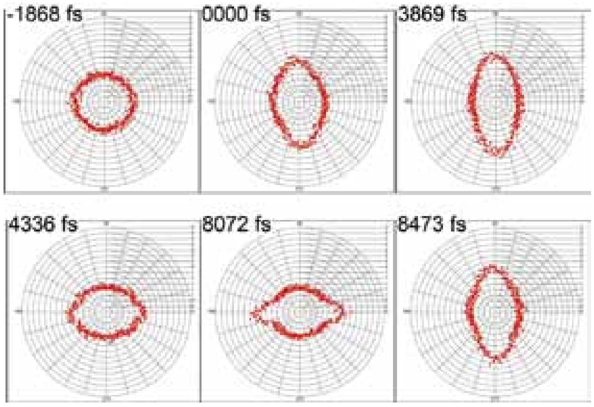

Figure 1. Delay-time dependent 2D distribution of Coulomb exploded N^{3+} fragments.

Owing to the multi-hit counting (*ca.* up to 150 events) for a single camera shot in the present imaging setup, we could record the snapshots with the time increment as small as 66.7 fs, within reasonable total data accusation time of 5 hours for 20 ps duration

2. Consideration of Coherent Population Transfer by Actively Phase-Controlled Nanosecond Laser Pulses

We have considered possible application of the newly developed ns OPA to advanced coherent population transfer and coherent control including chiral discrimination.

The constructed OPA is designed to produce the chirped signal and idler waves, of which energy difference is in the range of 0–400 cm^{-1}. Thus, by using the two beams as pump and Stokes pulses for stimulated Raman excitation, we will realize coherent population transfer in low-frequency Raman transitions. We numerically verified the robustness in the population transfer efficiency against the change of pulse intensity.

The amplification bandwidth of the constructed OPA is *ca.* 20 cm^{-1}. Multiple seeding beams can be amplified if their frequencies are covered in the OPA bandwidth, and multiple signal and idler waves with frequency chirp can be derived. This affords us to realize multiple chirped adiabatic Raman passage (CARP) within a single ns pulse operation. We numerically examined a ladder climbing coherent population transfer, $J = 0 \rightarrow 2 \rightarrow 4 \rightarrow 6 \rightarrow 8$, via CARP (Figure 2). As shown in the right panel, almost 90% of the initial population can be transferred to the final target state by setting the chirp rate and the seeding frequencies appropriately.

The seeding beam can be phase-modulated at up to 40 GHz. The relative optical phase between the carrier (ω_1) and the side band (ω_2) is precisely adjusted to that of the modulating microwave (MW) frequency (ω_3). Then, we can interfere constructively or destructively the stimulated Raman excitation pathway driven by ω_1 and ω_2 with the dipole transition pathway by ω_3. Among such quantum-control scenarios, the most interesting may be the realization of chiral discrimination. Here we numerically examined CARP excitation coupled with a resonant MW field and confirmed almost perfect enatio-selective population control.

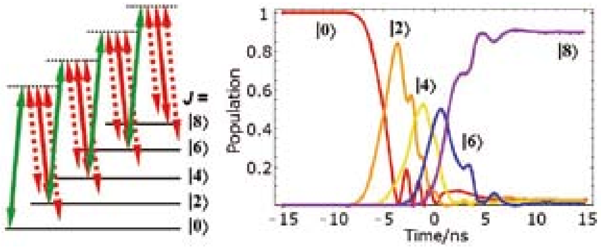

Figure 2. Rotational ladder climbing by multiple CARP process within a single-pulse OPA operation. (Light): Schematic energy levels and CARP transitions. (Right): Population change for five rotational levels involved.

Exploring Quantum-Classical Boundary

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Keywords Quantum-Classical Boundary, Coherent Control, Attosecond

It is observed in a double-slit experiment by Tonomura and coworkers that single electrons recorded as dots on a detector screen build up to show an interference pattern, which is delocalized over the screen.1) This observation indicates that a delocalized wave function of an isolated electron interacts with the screen, which is 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 and a bulk solid, envisaging the quantum-classical boundary connected smoothly.

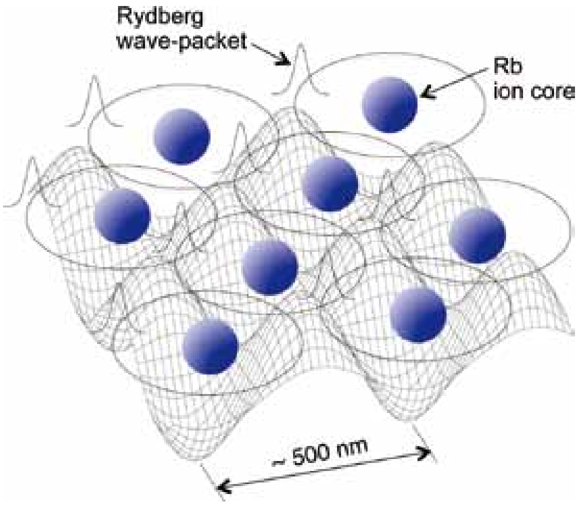

Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.2)

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. Hosak *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).

1. All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth[3)]

In a bulk solid, optical control of atomic motion provides a better understanding of its physical properties and functionalities. Such studies would benefit from active control and visualization of atomic motions in arbitrary directions, yet, so far, mostly only one-dimensional control has been shown. Here we demonstrate a novel method to optically control and visualize two-dimensional atomic motions in a bulk solid. We use a femtosecond laser pulse to coherently superpose two orthogonal atomic motions in crystalline bismuth. The relative amplitudes of those two motions are manipulated by modulating the intensity profile of the laser pulse, and these controlled motions are quantitatively visualized by density functional theory calculations. Our control-visualization scheme 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.

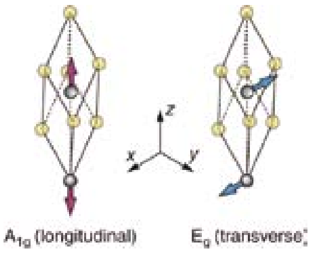

Figure 2. Crystal unit cell structure of Bi and the orientation of the A_{1g} (longitudinal) and E_g (transverse) phonon motions.

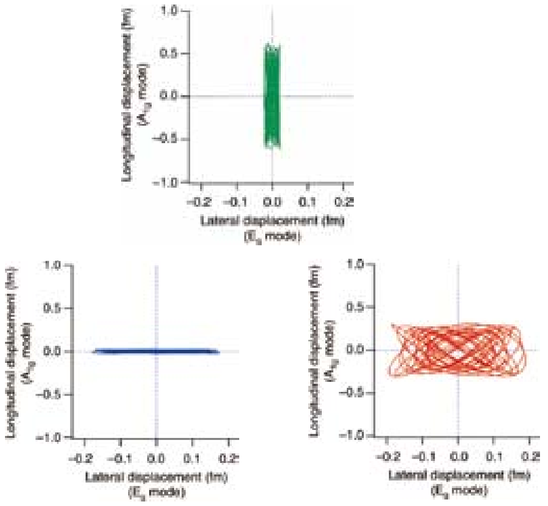

Figure 3. Traces of the atomic motions within a unit cell of Bi. Each trace represents the trajectory within the time window from 0.82 to 10.48 ps.

2. Ultrafast Coherent Control of an Ultracold Rydberg Gas[2)]

We employ an ensemble of ultracold Rb atoms as a model system to mimic a bulk solid. The model system offers longer coherence lifetime and more tunable parameters such as interatomic distance and interactions than a bulk solid. Since the interatomic distance is not shorter than submicrometers in this model system, longer than that of a bulk solid by more than three orders of magnitude, we generate Rydberg electronic wave-packets in those Rb atoms to induce interatomic interactions. Moreover these interactions can be actively tuned by changing the principal quantum numbers of Rydberg levels to be excited; the higher quantum numbers give larger diameters of Rydberg orbitals and hence stronger interactions. Briefly, a picosecond laser pulse produces Rydberg electronic wave-packets in laser-cooled Rb atoms. We measure the temporal evolution of those Rydberg wave-packets. We also measure the interferogram of two Rydberg wave-packets generated in each atom with a phased pair of picosecond laser pulses, whose delay is scanned in steps of attoseconds. Those temporal evolutions and interferograms of Rydberg wave-packets are measured as a function of the atom density, which can be converted to an atom–atom distance. We have observed that the interferogram is phase-shifted when we change the atom density. This observation suggests that the interatomic interactions have been induced by Rydberg wave-packets in Rb atoms. We plan to load these ultracold Rydberg atoms into an optical lattice to have better-defined interatomic configurations, as shown in Figure 1. Our ultrafast coherent control of an ultracold Rydberg gas could lead to the development of a novel simulator of quantum many-body dynamics.

3. Theoretical/Numerical Study on Strong-Laser-Induced Interference in the B State of I_2[4)]

In the B state of I_2, strong-laser-induced interference (SLI) was recently observed in the population of each vibrational eigenstate within a wave packet, which was initially prepared by a pump pulse and then strongly modulated by an intense femtosecond near-infrared (NIR) laser pulse. It was suggested that the interference as a function of the time delay occurs between the eigenstate reached by Rayleigh scattering and that by Raman scattering. To verify this mechanism and further discuss its characteristics, we theoretically/numerically study the SLI by adopting a two-electronic-state model of I_2. Numerical simulation reasonably reproduces the experimental signals and confirms the theoretical consequences, which include the π-phase shifts between Stokes and anti-Stokes transitions and (practically) no contribution from the energy shifts induced by the NIR pulse.

References

1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
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4) Y. Ohtsuki *et al.*, *Phys. Chem. Chem. Phys.* **16**, 5689 (2014).

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

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

Soft X-rays cannot pass through air or through liquid water due to photoabsorption processes of N_2, O_2, and H_2O molecules. Such strong interaction of soft X-rays can be used in highly sensitive chemical state analysis of thin samples by X-ray absorption spectroscopy (XAS).

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 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, and know each atomic component in the unoccupied state in the system. The excited electron in the unoccupied state is also affected by chemical environments. The intermolecular interaction effect is often less than 0.1 eV; therefore, a highly resolved soft X-ray spectrometer is necessary.

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 sample cells, detection systems, and spectro-microscopic techniques in X-ray absorption spectroscopy (XAS) for resonant excitation, and resonant and non-resonant 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 as synchrotron radiation from in-vacuum undulator-type insertion devices even on low-energy electron storage rings; *e.g.* 0.75 GeV UVSOR in IMS. In addition to 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.

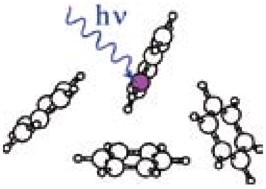

Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

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. *In Operando* Soft X-Ray Absorption Spectroscopy with Potential Modulation Applied to Electrochemical Reaction

In order to investigate local structures of electrolytes in electrochemical reactions under the same scan rate as a typical value 100 mV/s in cyclic voltammetry (CV), we have developed an *in operando* observation system for electrochemical reactions by soft X-ray absorption spectroscopy (XAS) with a potential modulation method. XAS spectra of electrolytes are measured by using a transmission-type liquid flow cell with built-in electrodes. The electrode potential is swept with a scan rate of 100 mV/s at a fixed photon energy, and soft X-ray absorption coefficients at different potentials are measured at the same time. By repeating the potential modulation at each fixed photon energy, it is possible to measure XAS of electrochemical reaction at the same scan rate as in CV. As shown in Figure 2, we have successfully measured the Fe 2p (L-edge) XAS spectra of aqueous iron sulfate solutions and the change in valence of Fe ions at different potentials in the Fe redox reaction.

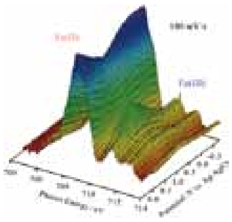

Figure 2. 3D plots of Fe 2p XAS spectra in the electrochemical reaction of aqueous iron sulfate solution under CV (100 mV/s scan).

2. *In Situ* Soft X-Ray Absorption Spectroscopy Applied to Hydration Reaction of Cyanopyrazine on Titanium Oxide Catalyst

In situ observation of liquid substrate conversion in solid–liquid heterogeneous catalytic reactions is difficult due to disturbance of the solvent and substrate itself. In this work, the hydration reaction of cyanopyrazine to produce pyrazinamide on TiO_2 catalyst ($PzCN + H_2O \rightarrow PzCONH_2$) has been successfully measured by the C K-edge and N K-edge XAS in transmission mode. Spectral change in both the C K-edge and N K-edge XAS, due to decreasing reactants PzCN and increasing products $PzCONH_2$, is clearly observed in spite of the coexistence of bulk liquid components PzCN, H_2O and solvent EtOH. The time dependence indicates that the hydration is the first order reaction. This result is also consistent with the linear relationship found in the Arrhenius plot, which is obtained from temperature dependent XAS measurements.

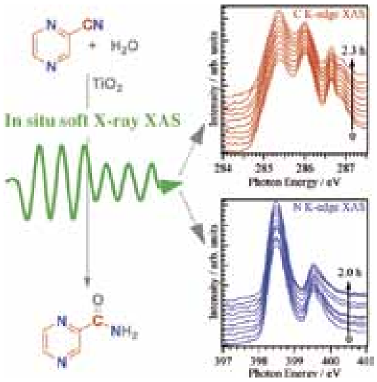

Figure 3. C K-edge (red) and N K-edge (blue) XAS spectra for the catalytic hydration reaction from cyanopyrazine to pyrazinamide.

3. Orbital-Specific Valence-Band Dispersion in α-Phase Crystalline Films of Cobalt Phthalocyanine

The valence band structure of α-crystalline cobalt phthalocyanine (CoPc) films grown on Au(111) is investigated by using angle-resolved photoemission spectroscopy (ARPES). The time-dependent photo-induced change in the ARPES peaks is noticed in shape and energy of the highest occupied molecular orbital (HOMO, C 2p) and HOMO-1 (Co 3d) of CoPc, and is misleading the interpretation of the electronic properties of CoPc films. By successfully avoiding such serious radiation damage, the clear valence-band dispersion has been first observed, showing that orbital-specific behaviors are attributable to the interplay of the intermolecular π–π and π–d interactions. The HOMO band dispersion by 0.1 eV gives the lower limit of the hole mobility for α-CoPc of 28.9 $cm^2 V^{-1} s^{-1}$ at 15 K. The non-dispersive character of the splitted HOMO-1 bands indicates that the localization of the spin state is a possible origin of the antiferromagnetism.

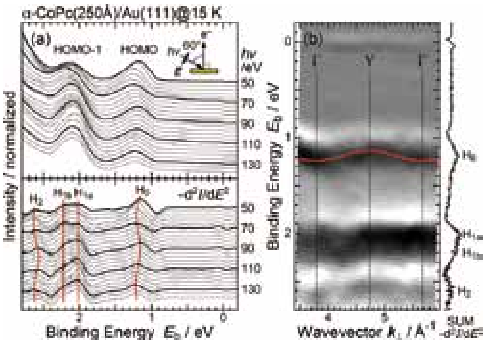

Figure 4. Intermolecular $E(\boldsymbol{k}_\perp)$ in the α-CoPc film on Au(111) at 15 K. (a) *h*ν-dependent normal-emission ARPES spectra. (b) $E(\boldsymbol{k}_\perp)$ map with the tight-binding fitting for the HOMO-band dispersion (red curve).

Awards

NAGASAKA, Masanari; The 2014 JSSRR Scientific Award (Japanese Society for Synchrotron Radiation Research).
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Electronic Property of Functional Organic Materials

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2009	Visiting Associate Professor, Institute for Molecular Science
2013	Adjunct Lecturer, The Open University of Japan
2013	Visiting Associate Professor, Soochow University
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Keywords Photoelectron Spectroscopy, Molecular Film, 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 its origin of various device characteristics are still under debate. Scientific mysteries would be raised because people have believed that electronic structure of FOM would be conserved as in an isolated molecule for solid phases due to van der Waals interaction. To reveal characteristics of FOM the key investigation would be on precise experiments on the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the impacts of weak interaction on the electronic structure would be appeared as small intensity modulation of photoemission fine features depending on adsorption and aggregation on the surface. By recent development in the instrumental we can assess hidden fine structures in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, weak band dispersion and dynamic electronic polarization. To elucidate what really happens for the FOM at the interface upon weak interaction, an evaluation on the wave-function spread of the electronic states would be very important because the interface states for the physisorbed systems are described to be a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization).

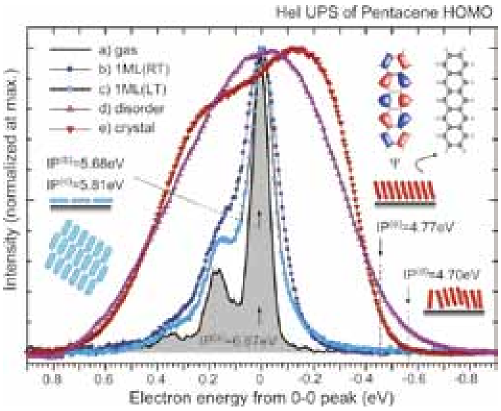

Figure 1. Wide variety in the feature of ultraviolet photoelectron spectra (UPS) for the HOMO band region taken for pentacene molecule in various aggregations (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- Q. Xin, S. Duhm, F. Bussolotti, K. Akaike, Y. Kubozono, H. Aoki, T. Kosugi, S. Kera and N. Ueno, "Accessing Surface Brillouin Zone and Band Structure of Picene Single Crystals," *Phys. Rev. Lett.* **108**, 226401 (5 pages) (2012).
- S. Duhm, Q. Xin, S. Hosoumi, H. Fukagawa, K. Sato, N. Ueno and S. Kera, "Charge Reorganization Energy and Small Polaron Binding Energy of Rubrene Thin Films by Ultraviolet Photoelectron Spectroscopy," *Adv. Mater.* **24**, 901–905 (2012).
- S. Kera, H. Yamane and N. Ueno, "First Principles Measurements of Charge Mobility in Organic Semiconductors: Valence Hole-Vibration Coupling in Organic Ultrathin Films," *Prog. Surf. Sci.* **84**, 135–154 (2009).

1. Impact of Intermolecular Interaction on the Reorganization Energy of Molecules[1)]

Organic semiconductors are molecular solids with specific charge transport properties due to weak intermolecular interaction. The transport properties of organic single crystals and organic thin films are far from being adequately understood. Important subjects still to be understood are related to molecular and lattice vibrations (phonons) and their coupling to a charge carrier. The electron–phonon interaction depends on the molecular structure and their packing motif and therefore it can impact both molecular site energies and transfer integrals. The overall strength of local electron–phonon coupling observed in highly-resolved UPS is given by the relaxation energy between neutral and ionized states, and the reorganization energy associated.

We investigated the impacts of perfluorination on the electronic structure of pentacene (PEN) monolayer on graphite and hole–vibration coupling, which is specified by the reorganization energy and the binding energy of molecular polaron. We demonstrate that electron-withdrawing property of F atom mediates increase in spatial spread of highest-occupied molecular orbital (HOMO), which contributes significantly to increase in the vibronic-satellite intensity, and then leads to significant increase in reorganization energy. This contribution is much larger than an opposite contribution by lowering of vibration energies by perfluorination of PEN.

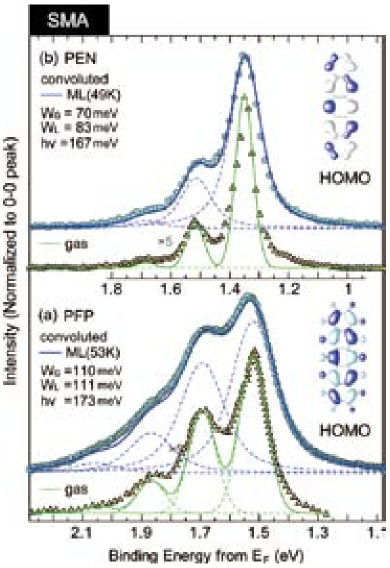

Figure 2. Comparison of HOMO band between gaseous HeI UPS (triangles) and angle-integrated UPS (circles) for the monolayer of perfluoropentacene (PFP) (a) and PEN (b), compared with convoluted curves by the single mode analysis of vibration coupling.

2. Mechanism of Energy-Level Alignment: Gap States Induced by Inert Gas Exposure[2)]

Energy level alignment (ELA) at organic-substrate and organic–organic interfaces is a crucial issue for any organic-based device, given that the interface electronic structure controls the charge injection process in the organic semiconductor. Despite considerable effort, however, there still remains a mystery why some organic semiconductors, such as PEN, always show p-type charge transport property while some others, such as C_{60}, show n-type property without heavy intentional doping, that is the transport property seems to be determined by molecule itself. Therefore, a consensus on ELA mechanism has yet to be reached.

We examined the energy distribution of density-of-gap state (DOGS) of the order of 10^{16} states $eV^{-1}cm^{-3}$, which is comparable to DOGS detected by electrical measurements, in an organic layer by means of ultralow background, high sensitivity UPS technique. We investigate PEN deposited on SiO_2/Si(100) and Au(111) substrates at 295 K. The impact of exposure to 1-atm of inert N_2 atmosphere on the PEN electronic properties is evaluated. Despite the absence of chemical interaction between N_2 and PEN molecules, the DOGS and ELA at the PEN/SiO_2 interface are strongly modified by the exposure to N_2 gas. This effect is ascribed to the structural disorder caused by N_2 molecules penetrating into the PEN film. A similar effect is observed upon exposure to Ar, while in case of O_2 exposure, the DOGS formation is accelerated, presumably because of the difference in the chemical properties of the gas molecules.

The present results demonstrate that structural disorder has a significant impact on the electronic properties and interfacial ELA. This is related to the nature of organic semiconductor crystals, which consists of low-symmetry molecules held together by weak intermolecular forces. The results also have great practical significance, as they show that organic layer processing in inert atmosphere does affect the electronic structure of the organic semiconductor, a point which had not been understood so far.

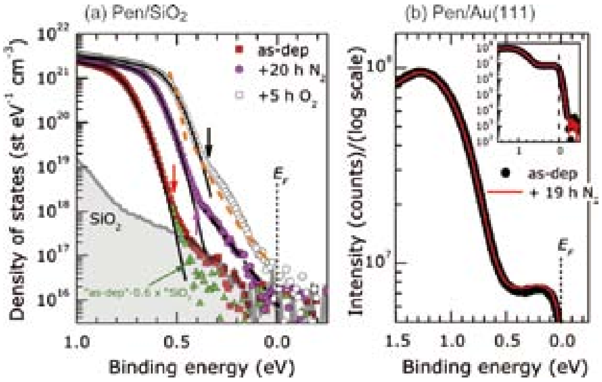

Figure 3. (a) DOS (log scale plot) of as-deposited, N_2-exposed, and O_2-exposed PEN film on SiO_2 by XeI-UPS. (b) XeI-UPS of as-deposited PEN film on Au(111) before and after N_2 exposure.

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2) F. Bussolotti, S. Kera, K. Kudo, A. Kahn and N. Ueno, *Phys. Rev. Lett.* **110**, 267602 (5 pages) (2013).

Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Synchrotron Radiation, Free Electron Laser

UVSOR is a synchrotron light source to provide 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 have 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 synchrotron radiation with various characteristics such as free electron laser, coherent synchrotron radiation and laser Compton gamma-rays. We are also investigating future light sources for the facility, such as a diffraction limited light source or a linac-based free electron laser source.

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

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- S. Bielawski, C. Evain, T. Hara, M. Hosaka, M. Katoh, S. Kimura, A. Mochihashi, M. Shimada, C. Szwaj, T. Takahashi and Y. Takashima, “Tunable Narrowband Terahertz Emission from Mastered Laser–Eelectron Beam Interaction,” *Nat. Phys.* **4**, 390–393 (2008).
- M. Shimada, M. Katoh, M. Adachi, T. Tanikawa, S. Kimura, M. Hosaka, N. Yamamoto, Y. Takashima and T. Takahashi, “Transverse-Longitudinal Coupling Effect in Laser Bunch Slicing,” *Phys. Rev. Lett.* **103**, 144802 (2009).
- T. Tanikawa, M. Adachi, H. Zen, M. Hosaka, N. Yamamoto, Y. Taira and M. Katoh, “Observation of Saturation Effect on Vacuum Ultraviolet Coherent Harmonic Generation at UVSOR-II,” *Appl. Phys. Express* **3**, 122702 (3 pages) (2010).
- Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, “Generation of Energy-Tunable and Ultrashort-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring,” *Nucl. Instrum. Methods Phys. Res., Sect. A* **652**, 696–700 (2011).
- I. Katayama, H. Shimosato, M. Bito, K. Furusawa, M. Adachi, M. Shimada, H. Zen, S. Kimura, N. Yamamoto, M. Hosaka, M. Katoh and M. Ashida, “Electric Field Detection of Coherent Synchrotron Radiation in a Storage Ring Generated Using Laser Bunch Slicing,” *Appl. Phys. Lett.* **100**, 111112 (2012).
- Y. Taira, H. Toyokawa, R. Kuroda, N. Yamamoto, M. Adachi, S. Tanaka and M. Katoh, “Photon-Induced Positron Annihilation Lifetime Spectroscopy Using Ultrashort Laser-Compton-Scattered Gamma-Ray Pulses,” *Rev. Sci. Instrum.* **84**, 053305 (2013).

1. Light Source Technology Developments Based on Laser and Synchrotron and Their Applications to Molecular Science

We have demonstrated that coherent synchrotron radiation of various properties could be generated in an electron storage ring by using an external laser source. This research was supported by the Quantum Beam Technology Program of JST/MEXT. Under this support, a new experimental station has been constructed. The generation of coherent synchrotron radiation at the new site was successfully demonstrated in collaboration with Lille Univ. and Nagoya Univ. Some basic researches on coherent synchrotron radiation have been conducted with an ultrafast terahertz detector in collaboration with Karlsruhe Institute of Technology, Lille Univ., Nagoya Univ. and Kyoto Univ. Applications using coherent synchrotron radiation are under preparation. Some basic researches on the optical vortex beam have been started in collaboration with Hiroshima Univ.

Figure 2. Twin Polarization-variable Undulators for Coherent Synchrotorn Radiation generation.

Laser Compton scattering is a method to produce monochromatic and energy-tunable gamma-ray pulses. Laser pulses are injected to the storage ring and are scattered by the relativistic electrons circulating in the ring. We have developed a method to produce ultra-short gamma-ray pulses and have demonstrated a photon-induced positron annihilation lifetime spectroscopy experiment, in collaboration with AIST. We have started constructing a system to produce intense gamma-rays by using an optical cavity, in collaboration with Kyoto Univ.

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

The UVSOR facility has been operational as a national synchrotron light source for lower energy photons from the terahertz wave to the soft X-rays. The machine was born as a low energy second generation light source and now it is 30 years old. However, the accelerators have been upgraded continuously. We have succeeded in introducing a specially designed electron beam optics intended to higher brightness. We have succeeded in commissioning six undulators. We have succeeded in introducing a novel operation mode called Top-up operation, in which the electron beam intensity is kept quasi-constant at a high beam current, 300 mA. As the result of all these efforts, now, the machine is the brightest synchrotron light sources among the low energy machines below 1 GeV.

We continue upgrading the machine, year by year. In 2014, one old undulator at BL5U was remodeled. Now it has become capable of producing any polarization, such as horizontal and vertical linear polarizations and left and right circular polarizations. The non-linear focusing forces produced by such undulators make significant effects on the beam injection and storage. We are developing correction scheme for these non-linear effects.

Figure 3. Remodeling of Variable Polarization Undulator at BL5U.

Award

INAGAKI, Toshiki; 2013 Annual Meeting Award of the Particle Accelerator Society of Japan.

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Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials 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.

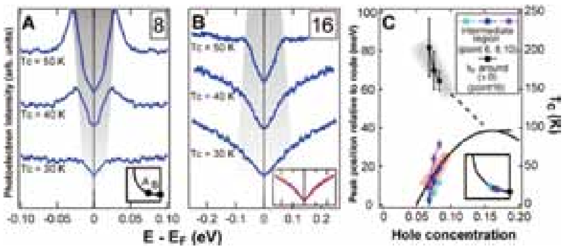

Figure 1. The symmetrized ARPES spectra of heavily underdoped Bi2212 at (A) the tip of the Fermi Arc region and (B) the antinodal region. Their corresponding locations on the Fermi surface are shown in the inset of (A).

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

1. ARPES Study on High-T_c Cuprate Superconductors

Two decades after the discovery of first high temperature superconductors, the microscopic mechanism of high-T_c superconductivity remains elusive. In conventional superconductors, it has been well established that electrons form so-called Cooper pairs to give rise to superconductivity. The pair binding manifests itself as an energy gap in many spectroscopic measurements. This energy gap, known as superconducting gap, appears at the superconducting transition temperature T_c where the resistance also vanishes. For high temperature superconductors, the story is more complicated. Over a wide region of compositions and temperatures, there exists an energy gap well above T_c. This energy gap is called "pseudogap," because there is no direct correlation to the superconducting transition. The origin of this pseudogap and its relation to the superconducting gap are believed to hold the key for understanding the mechanism of high-T_c superconductivity—one of the outstanding problems in condensed matter physics. In this regard, we performed ARPES measurements on the highly underdoped cuprate superconductor $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ (Bi2212) to clarify the doping dependence of the gap structure. Through a systematic study of heavily underdoped Bi2212 samples with T_c = 30, 40, and 50K, two distinct energy gaps along the Fermi surface were identified in different parts of the momentum space: A small gap along with a sharp coherence peak near the nodal region and a relatively large gap near the antinodal region. Remarkably, these two energy gaps exhibit opposite trends with doping as shown in Figure 1A and 1B. Panel A displays the data taken at the tip of the "Fermi-Arc"—the region along the Fermi surface where a coherence peak is observed, while panel B shows the data from the antinodal region. As indicated by the shaded area, the gap associated with the Fermi Arc region is reduced as the doping level and T_c decrease, while the gap in the antinodal region increases. The complete doping evolution of these two energy gaps is summarized in panel C. The doping dependence of the gap magnitude in the antinodal region (black circles and dashed line) is consistent with the well-studied pseudogap behavior. The unexpected doping evolution of the gap in the Fermi Arc region (colored symbols and solid line), on the other hand, is the new discovery of this work. Based on these observations, we proposes a picture of two energy gaps coexisting in different regions of the momentum space. The gap associated with the Fermi Arc region is most likely the superconducting gap as evidenced by the existence of a coherence peak in ARPES spectra and a positive correlation between the gap magnitude and T_c. The pseudogap in the antinodal region may, however, arise from another mechanism such as Umklapp scattering by the antiferromagnetic correlations or competing states, such as stripes, polaronic behavior, or a charge-density-wave. This two-gap scenario not only provides natural explanation of the new ARPES results, but also resolves the contradictory results on the superconducting gap deduced from different experimental techniques.

This two-gap scenario has two important implications that could be important for developing a microscopic theory of high-T_c superconductivity. First, the pseudogap near the antinodal region in these deeply underdoped samples is unlikely a precursor state of the superconducting state, as had been suggested previously. Instead, it is more likely a state that competes with the superconducting state. Second, these data suggest that the weakened superconductivity in the underdoped regime arises not only from the loss of phase coherence associated with the decrease in the superfluid density but also due to the weakening of the pairing amplitude. In this case, a mechanism for the superconducting gap reduction could be related to the shrinkage of the coherent Fermi surface with less doping, leading to a smaller phase space for pairing.

2. Development of New Spin-Resolved ARPES

UVSOR Facility in Institute for Molecular Science equips two public undulator-beamlines for ARPES, one is BL5U in the photon energy *hν* region of 20–200 eV and the other BL7U of *hν* = 6–40 eV. Since the monochromator of BL5U is an old-style spherical grating type SGMTRAIN constructed in 1990s and the throughput intensity and energy resolution are poor, the beamline was planned to be replaced to state-of-the-art monochromator and end station. Then we designed a new spin and angle-resolved photoemission spectroscopy instrument with variable photon energy and polarization. We employed a Monk-Gillieson-type variableline-spacing plane-grating monochromator covering the photon energy of 20–200 eV. The end station shown in Figure 2 will equip a VLEED spin detector for spin-resolved ARPES. The beamline is constructed in FY2013–FY2014 and will be opened to users from FY2015.

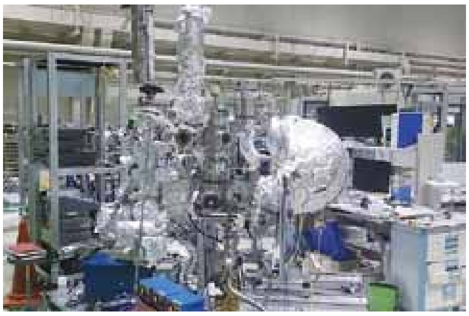

Figure 2. Picture of the new spin-resolved ARPES end station of BL5U, UVSOR-III.

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2) W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, *Nature* **450**, 81–84 (2007).

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Electronic Structure and Decay Dynamics in Following Core Hole Creation in Molecules

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Keywords Soft X-Ray Spectroscopy, Inner-Shell Excitation, Photodissociation Dynamics

The detailed comprehension of the electronic structure of molecules is an important step toward understanding the chemical and physical properties of matter, and also provides a link between atomic and solid-state physics. Information on photoexcitation, photoionization, and photodissociation processes derived from molecular spectroscopy is of fundamental importance, and also useful in various scientific disciplines, including astrophysics, planetary sciences, radiation chemistry, and biology.

Synchrotron radiation combined with a suitable monochromator is a powerful research tool for systematic investigations of outer- and inner-shell excitation and ionization processes in molecules, because the spectral range matches the binding energies of the valence and core electrons of the elements which form molecules of physical and chemical interest, namely low-Z molecules. In order to promote inner-shell electrons of low-Z molecules efficiently, it is indispensable to utilize monochromatized synchrotron radiation in the soft X-ray region.

Inner-shell excited states of low-Z molecules relax mainly through Auger decay, leading to the formation of highly excited singly or multiply charged molecular ions with outer-shell holes. These molecular ions are in general quite unstable, and immediately break apart into fragment ions and neutrals. The electronic relaxation and dissociation processes are coupled, and depend on the electronic and geometrical structure of the molecules.

The major aim for investigating molecular inner-shell excitation is to determine what happens to molecules following the excitation and ionization of an inner-shell electron by using various spectroscopic techniques to define the initial photoexcitation process itself, and to characterize and correlate the electrons, ions, neutrals, and metastables that are produced as a result.

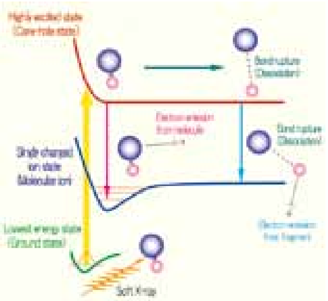

Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

Selected Publications

- E. Shigemasa and N. Kosugi, "Molecular Inner-Shell Spectroscopy. ARPIS Technique and its Applications," in *Advances in Chemical Physics*, Eds., S.A. Rice and A. Dinner, Wiley; New York, **Vol. 147**, p. 75–126 (2011).
- M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, "Ultrafast Dynamics in C 1s Core-Excited CF_4 Revealed by Two-Dimensional Resonant Auger Spectroscopy," *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).

1. Decay Processes Following Sulfur 2p Photoexcitation in OCS Studied by High-Resolution Two-Dimensional Electron Spectroscopy

In the current study, angle-resolved two dimensional (2D) electron spectroscopy,[1] where resonant Auger-electron spectra are recorded as a function of the photon energy, has been applied to the de-excitation processes in the S 2p excitation region of OCS, with previously unprecedented resolution.

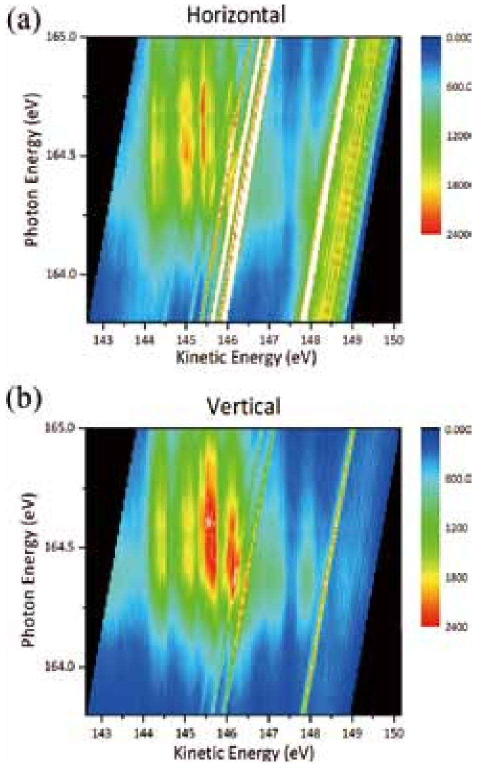

Figure 2. 2D maps of resonant Auger electron spectra after the S $2p_{3/2} \rightarrow \pi^*$ excitation of OCS, measured at horizontal (a) and vertical (b) directions relative to the electric vector of the incident radiation.

The 2D measurements were performed on the soft x-ray beam line BL6U at UVSOR. The undulator radiation was monochromatized by a variable included angle, varied line-spacing plane grating monochromator. For 2D electron spectroscopy, the monochromator bandwidth was set to ΔE_{Ph} ~20 meV at $h\nu = 165$ eV. The kinetic energy of the emitted electrons was measured by a hemispherical electron energy analyzer (MBS-A1) placed at a right angle with respect to the incident photon beam direction. The direction of the electric vector was set to be either parallel (horizontal) or perpendicular (vertical) to the axis of the electrostatic lens of the analyzer. The energy resolution of the analyzer was set to ΔE_k ~15 meV.

Figure 2 shows 2D maps of resonant Auger electron spectra following the S $2p_{3/2} \rightarrow \pi^*$ resonant excitation of OCS measured in the horizontal (a) and vertical (b) directions. The diagonal lines can be attributed to valence photoelectron lines, and clearly show vibrational side bands indicating that the net energy resolution is much better than 50 meV.

Clear island-like structures elongated in the vertical direction can be seen in both Figure 2(a) and Figure 2(b) in the kinetic energy region from 144 to 148 eV. In sharp contrast to the valence photoelectron lines, these structures do not show strong anisotropic angular distributions. To our knowledge, no detailed assignments have previously been given to them. In order to understand the origins of the structures, sophisticated theoretical calculations are highly desired.

2. Lifetime Broadening of Atomic Lines Produced upon Ultrafast Dissociation of HCl and HBr[2]

The excitation of a core electron to the lowest unoccupied antibonding orbital in a molecule reduces the molecular bond strength and in general populates a dissociative state. When the timescales of the nuclear motion and of the core–hole relaxation are similar, this leads to a peculiar situation which has been named ‘ultrafast dissociation.’ Here, the excited state starts to dissociate, and electronic decay can occur at any point during the dissociation, up to the point where dissociation can be considered as completed. The first evidence for such a process was reported in 1986 by Morin and Nenner.[3]

In the present study we revisit ultrafast dissociation following Cl $2p_{3/2}$ excitation in HCl and Br $3d_{5/2}$ excitation in HBr. The improved experimental resolution allows us to observe in detail the line-widths of both the atomic and molecular peaks. The atomic peaks are observed to be broader than the molecular vibrational peaks which are due to direct photoionization. We suggest that this broadening is due to the lifetime of the neutral, core-excited Cl* or Br* atomic fragment and can be retrieved from our experimental data.

The experiments were carried out at BL6U. The kinetic energies of electrons emitted perpendicular to the photon beam direction were measured by the MBS-A1. The energy resolution was set to ~12 meV or ~6 meV. The degree of linear polarization of the incident light was calibrated by measurements with rare gazes and found to amount to 90–100%. The direction of the electric vector was set to be either parallel or perpendicular to the axis of the electrostatic lens of the analyzer.

After careful analysis of the experimental data, the Lorentzian broadenings of the atomic peaks in HCl and HBr were found to be 96±5 meV and 91±5 meV, respectively. We suggest that these values correspond in good approximation to the lifetimes of the $2p_{3/2}$ hole in the Cl* atom and the $3d_{5/2}$ hole in the Br* atom.

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3) P. Morin and I. Nenner, *Phys. Rev. Lett.* **56**, 1913–1916 (1986).

Micro Solid-State Photonics

Laser Research Center for Molecular Science
Division of Advanced Laser Development

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

Education

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

Professional Employment

1985	Researcher, Mitsubishi Electric Corp.
1989	Research Associate, Fukui University
1993	Visiting Researcher, Stanford University (–1994)
1998	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

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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  SATO, Yoichi
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  KAUSAS, Arvydas
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Secretary
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  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.

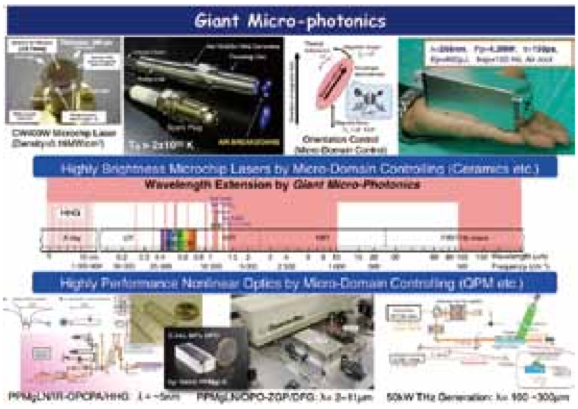

Figure 1. Giant micro-photonics.

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. Timing Jitter Control of a Passively Q-Switched Nd:YVO_4/Cr^{4+}:YAG Laser by the Use of a Coupled Cavity

Timing jitter was measured in Nd:YVO_4/Cr:YAG passively Q-switched laser. Primary results with coupled cavity as shown in Figure 2 showed reduction of timing jitter by one order of magnitude down to 450 ns (2σ value), 40 μJ pulse energy and 2.5 ns pulse duration.

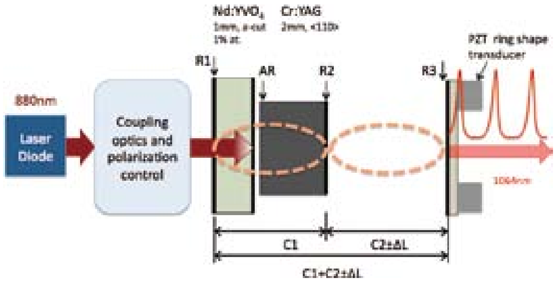

Figure 2. Schematic view of the Nd:YVO_4/Cr^{4+}:YAG passively Q-switched laser.

2. Highly Accurate Interferometric Evaluation of Thermal Expansion and *dn*/*dT* of Optical Materials

Thermo-mechanical and -optical properties of $Y_3Al_5O_{12}$ (YAG), YVO_4, and $GdVO_4$ were evaluated with high accuracy. Evaluation procedure that was established by authors enabled to suppress evaluation errors less than 2%, by means of the detection of temperature deviations in interferometric fringes on transmittance as shown in Figure 3.

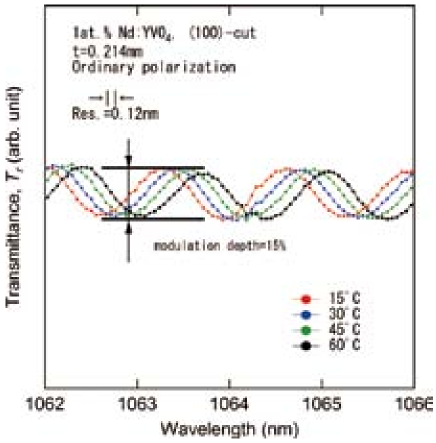

Figure 3. Temperature dependence of interferometric fringes in Nd:YVO_4.

Measured thermal expansion coefficient for YAG, [100]-YVO_4, [001]-YVO_4, [001]-$GdVO_4$, and [001]-$GdVO_4$ were 6.13, 1.76, 8.24, 1.19, and 7.26 × 10^{-6}/K at room temperature. Temperature coefficients of refractive index for YAG, YVO_4 in ordinary and extraordinary polarization, and $GdVO_4$ in ordinary and extraordinary polarization at room temperature for the wavelength of 1.06 μm were 12.1, 15.5, 8.41, 15.2, and 9.92 × 10^{-6}/K, respectively.

This work was ranked the fourth place in TOP-10 downloaded articles in June 2014 from OSA's Optical Materials Express.

3. Improvement of Laser-Beam Distortion in Large-Aperture PPMgLN Device by Using *X*-Axis Czochralski-Grown Crystal

Large-aperture periodically poled Mg-doped $LiNbO_3$ device using *X*-axis Czochralski-grown MgLN crystal was proposed to avoid a laser-beam distortion problem, as shown in Figure 4. Availability of periodic poling in 5-mm-thick MgLN and compatibility of wavelength-conversion characteristics in QPM-OPO were evaluated by comparing with conventional arrangement using *Z*-axis-grown crystal.

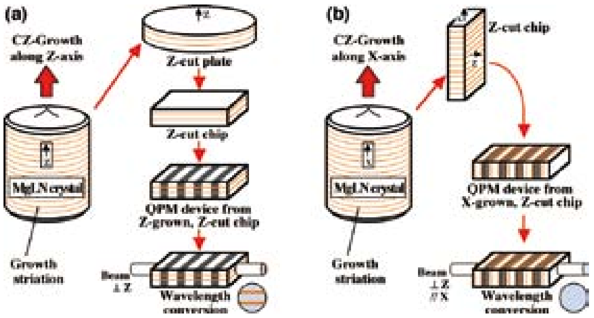

Figure 4. PPMgLN device fabricated from (a) *Z*-axis CZ-grown crystal, and (b) *X*-axis CZ-grown crystal.

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2) Y. Sato and T. Taira, *Opt. Mater. Express* **4**, 876–888 (2014).
3) H. Ishizuki and T. Taira, *Opt. Express* **22**, 19668 (2014).

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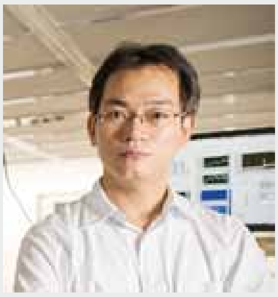
Ultrafast Laser Science

Laser Research Center for Molecular Science
Division of Advanced Laser Development



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Education

1994 B.S. University of Tsukuba
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Professional Employment

1999 Assistant Professor, The University of Tokyo
2002 JSPS Postdoctral Fellowship for Research Abroad, Vienna University of Technology (–2004)
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

1999 Encouragement Award, The Optical Society of Japan
2008 Kondo Award, Osaka University

Member

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NOMURA, Yutaka
IMS Fellow
SHIRAI, Hideto
Viiting Scientist
YEH, Tien-Tien*
DUCHESNE, Constance†
Secretary
KAWAI, Shigeko
MASUDA, Michiko

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 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 phase determination. Our method does not need attosecond pulses, even self-referencing is possible. The electric field oscillation 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.

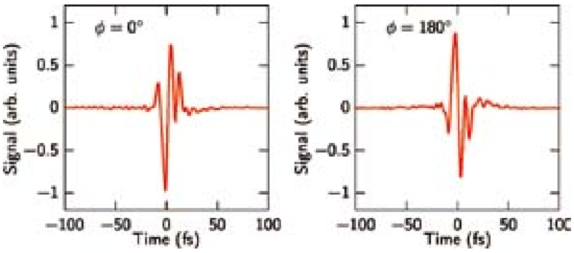

Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

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

Selected Publications

- Y. Nomura, H. Shirai, K. Ishii, N. Tsurumachi, A. A. Voronin, A. M. Zheltikov and T. Fuji, "Phase-Stable Sub-Cycle Mid-Infrared Conical Emission from Filamentation in Gases," *Opt. Express* **20**, 24741–24747 (2012).
- 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, Y. T. Wang, T. Kozai, H. Shirai, A. Yabushita, C. W. Luo, S. Nakanishi and T. Fuji, "Single-Shot Detection of Mid-Infrared Spectra by Chirped-Pulse Upconversion with Four-Wave Difference Frequency Generation in Gases," *Opt. Express* **21**, 18249–18254 (2013).
- T. Fuji, "Single-Shot Broadband Mid-Ir Spectra Measured in the Visible via Upconversion," *Laser Focus World* **49**, 9 (1 page) (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).

1. Frequency-Resolved Optical Gating Capable of Carrier-Envelope Phase Determination (FROG-CEP)[1,2]

Recent progress of the coherent light synthesis technology has brought the generation of single-cycle pulses within our reach. To exploit the full potential of such a single-cycle pulse in any applications, it is highly important to obtain the full information of its electric field.

There has been a method to measure the oscillation of light wave using attosecond (as = 10^{-18} s) pulses (attosecond streaking, [*Science* **305**, 1257]), however, a huge high vacuum system is necessary for the measurement since attosecond pulses, which are in XUV region, are absorbed in air.

Here, we propose a novel pulse characterization scheme, which enables us to determine not only the intensity and phase profiles of ultrashort pulses but also their absolute carrier-envelope phase values without using attosecond pulses. The method is based on a combination of frequency-resolved optical gating and electro-optic sampling.

We have demonstrated the method by characterizing phase-stable sub-single-cycle 7 fs infrared pulses generated through filamentation[3,4] by using a 30 fs reference pulse, which is much longer than the period of the carrier-wavelength of the characterized pulse. We have also demonstrated that the method has the capability of single-shot measurements. The self-referencing possibility of the method has been also discussed with numerical simulations. The results of our numerical simulations have clearly shown that it is possible to retrieve few-cycle 800 nm pulses with the absolute CEP information by self-referencing. It has turned out that approximately one octave spectrum and reasonable compression quality are necessary for the self-referencing, which is rather reasonable requirement for the waveform characterization of few-cycle pulses whose CEP becomes important. In principle, the concept has no limitation to characterize few-cycle pulses on measurable pulse duration or applicable wavelength regions thanks to the self-referencing possibility.

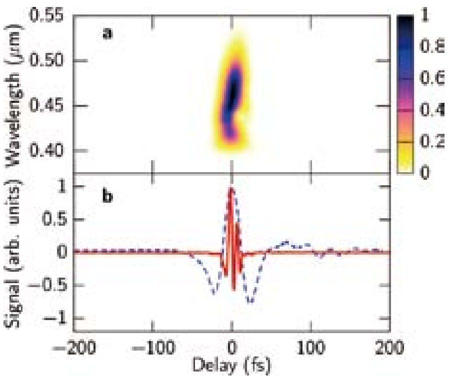

Figure 2. Experimental results of FROG-CEP. (a) The XFROG trace and (b) EOS signal measured in the experiment (blue dashed curve). The red solid curve shows the electric field reconstructed from the experimental data.

2. Sub-50-fs Pulse Generation from Thulium-Doped ZBLAN Fiber Laser Oscillator[5]

Passively mode-locked fiber lasers operating around 1 μm and 1.5 μm have been extensively studied over the past decades. In recent years, thulium-doped fiber lasers have attracted significant attention because they extend the operating wavelength toward 2 μm region, which will be useful for various fields such as medical applications, remote sensing, micromachining, high harmonic generation, and mid-infrared generation. In particular, broad emission spectra of thulium-doped fibers make them ideal candidates for ultrashort pulse sources in this wavelength region. However, it is not trivial to obtain ultrashort pulses from fiber lasers where the effect of the dispersion from long fibers is quite significant.

An interesting approach would be using fibers made of materials with less dispersion. Fluoride glass known as ZBLAN (ZrF_4–BaF_2-LaF_3-AlF_3-NaF) has high transmittance in the mid-infrared region. The property of low absorption suggests that it also has low dispersion in the mid-infrared region. However, the property has been overlooked and no previous work has utilized ZBLAN fibers for developing ultrafast laser oscillators.

In this work, we have developed a passively mode-locked laser oscillator based on thulium-doped ZBLAN fibers pumped by a cw Ti:sapphire laser. Output pulses with the average power of 13 mW are obtained at the repetition rate of 67.5 MHz with the pump power of 140 mW. Thanks to low dispersion of ZBLAN, the spectra of the output beam was as broad as 300 nm at 30 dB below the peak. The generated pulses was compressed down to 45 fs, which is the shortest pulses generated from laser oscillators operating around 2 μm wavelength region to the best of our knowledge.

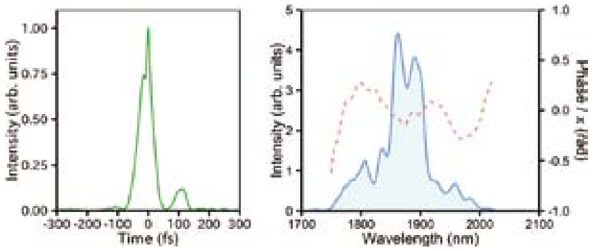

Figure 3. Measured pulse shape (Left). Measured spectral profile (Right, filled blue curve) and phase (Right, dashed red curve).

References

1) Y. Nomura, H. Shirai and T. Fuji, *Nat. Commun.* **4**, 2820 (2013).
2) H. Shirai, Y. Nomura and T. Fuji, *IEEE Photonics J*. **6**, 3300212 (2014).
3) Y. Nomura, H. Shirai, K. Ishii, N. Tsurumachi, A. A. Voronin, A. M. Zheltikov and T. Fuji, *Opt. Express* **20**, 24741–24747 (2012).
4) T. Fuji and Y. Nomura, *Appl. Sci.* **3**, 122–138 (2013).
5) Y. Nomura and T. Fuji, *Opt. Express* **22**, 12461–12466 (2014).

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* EXODASS Program

† IMS International Internship Program

Dissociative Photoionization Studies of Fullerenes and Carbon Nanotubes and Their Application to Dye-Sensitized Solar Cells

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

KATAYANAGI, Hideki
Assistant Professor

We have observed the dissociative photoionization of the fullerenes. We studied the mechanisms and kinetics of C_2 release reactions from the fullerenes on the basis of the yield curves and the scattering velocity distributions of the fragments. We now intend to apply the above gas phase spectroscopy to functional materials such as carbon nanotubes (CNTs). Additionally we utilize the CNT to a catalytic counter electrode in dye-sensitized solar cells (DSSCs). This research aims at understanding the electron transfer phenomena from CNTs both in gas phase and in condensed phase.

1. Mass Resolved Velocity Map Imaging of Doubly Charged Photofragments from C_{60} and C_{70}

We have obtained 2D velocity images of the fragments from C_{60} and C_{70}. The 2D velocity images of fragments were found to be convolutions of isotropic center-of-mass velocity acquired by the C_2 emission and anisotropic velocity of C_{60} in the parent molecular beam.

2. Gas Phase Spectroscopy of CNTs

We have started to build a vacuum apparatus for the gas phase spectroscopy of CNTs. With the apparatus we will first perform experiments using the fullerenes and then improve the apparatus to achieve experiments using CNTs.

3. Development and Evaluation of CNT Catalytic Counter Electrodes for DSSCs

To improve photovoltaic energy conversion efficiency of the DSSC, the rate of charge transfer reaction on the counter electrode is important. We prepared the counter electrodes using commercial CNT aqueous dispersions. We have started the impedance spectroscopy of the CNT electrodes in order to elucidate the effect of series resistance of the electrodes on the performance of DSSC.

In-situ Soft X-Ray Spectromicroscopic Study of Chemical and Biological Systems

UVSOR Facility
Division of Beam Physics and Diagnostics Research

OHIGASHI, Takuji
Assistant Professor

We have constructed a scanning transmission X-ray microscope (STXM) beamline in the soft X-ray region at BL4U in the UVSOR-III facility.$^{1,2)}$ One of the advantages of the STXM is a high tolerance for environments of samples. For example, vacuum is not required for samples and even the samples in water can be observed by using soft X-rays in the water window region (282 ~ 539 eV). This advantage enables the STXM to perform *in-situ* observation easily combined with a long working distance. Hence, we have been developing *in-situ* sample cells for the STXM measurement.

A schematic image of cross section of a liquid flow sample cell is shown in Figure 1. This sample cell uses two silicon nitride membranes of 100 nm thick as windows sealed by two O-rings. Liquid flows between a gap of the two membranes by using a tubing pump. Then, the gap width (*i.e.* thickness of the liquid) can be tuned by the pressure of helium gas in a main STXM chamber. As a test measurement, by changing the liquid from pure water to ethanol simply, their absorption spectra around oxygen 1s were measured (Figure 2). Recently, a window membrane with gold electrodes pettern was developed and *in-situ* measurement of electro-chemistry was performed.

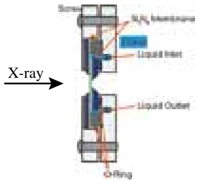

Figure 1. A liquid flow cell in section.

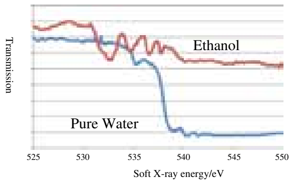

Figure 2. Transmission spectra of pure water and ethanol.

References

1) T. Ohigashi, H. Arai, T. Araki, N. Kondo, E. Shigemasa, A. Ito, N. Kosugi and M. Katoh, *J. Phys.: Conf. Ser.* **463**, 012006 (2013).
2) T. Ohigashi, H. Arai, N. Kondo, M. Sakai, K. Hayashi, E. Shigemasa, A. P. Hitchcock, N. Kosugi and M. Katoh, *UVSOR Activity Report* **40**, 43 (2013).

Visiting Professors

Visiting Professor

NODA, Susumu *(from Kyoto University)*

Strong Coupling of Single Atoms to Photonic Crystal Cavity Field

We have investigated photonic crystal structures which enable modification of propagation properties of an electromagnetic field and also tight confinement of the field to a tiny resonator. Accordingly the field strength inside the resonator is much enhanced and therefore the field can be strongly coupled to a quantum emitter such as a quantum dot even at a single photon level. Such a nanostructure device would be suitable for applications in optical communication and future quantum information processing in terms of its scalability. We have studied the strong coupling of the cavity field with a quantum dot and also the Purcell effect. Recently we have been interested in adopting a single cold atom as a quantum emitter, which shows much longer coherence time and therefore would be desirable for future application. Cold atoms are first loaded into a magneto-optical trap and then one of them is captured in tightly-focused optical tweezers. A movable lens-positioner can translate the position of the focal point, thereby transferring the trapped atom to the vicinity of the photonic crystal cavity. With this technique, the strong coupling of the single atom with the cavity field will be studied.

Visiting Professor

ITO, Atsushi *(from Tokai University)*

X-Ray Spectromicroscopy of Biomedical Specimens

Soft X-ray microscopy has a great advantage over other microscopies in the mapping of light elements or molecules containing such elements at high resolution. The mapping is realized with soft X-ray scanning microscope (STXM) using an unique imaging method X-ray spectromicroscopy which utilizes distinctive spectral features of elements and molecules, that is, absorption edges and XANES profiles observed in the vicinity of the absorption edge. To apply to biomedical specimens, XANES profiles have been surveyed for a variety of biomolecules such as DNA, proteins (histone and albumin), sulfur-containing amino acids, calcium-containing biomolecules and iron-containing proteins at the C-K, N-K, O-K, S-L, Ca-L and Fe-L absorption edges in the soft X-ray region. One of the most interesting and useful results obtained in this survey is that DNA and histone, a nuclear protein, exhibited significantly different spectra at the N-K edge, suggesting the possibility to image DNA and proteins in cellular nuclei separately. We are now interested in the time dependence of distribution pattern of DNA and proteins in nuclei that undergo apoptosis.

Visiting Associate Professor

HATSUI, Takaki *(from RIKEN SPring-8 Center)*

Atomistic Dynamics in Metal-Semiconductor-Oxide (MOS) Transistor

This year, we have investigated on the static behavior of MOS transistors. MOS transistors are widely used in semiconductor industry. One of the bottlenecks in achieving the lower power consumption is random telegraph noise. In order to avoid the malfunctioning arising from the noise, the supply voltages should be higher than the optimal condition, resulting higher power consumption. The noise behavior in this study was investigated by manufacturing a transistor-element group of a fully-depleted silicon-on-insulator (FD-SOI) MOS transistors at a technology node equivalent to 350 nm node. The FD-SOI CMOS transistors haves a substrate terminal where we can externally control the vertical field in MOS channel. The low frequency drain-source noise around 100 Hz was measured at different substrate voltages. For a transistor ($L = 0.4$ μm/$W = 1.0$ μm) with high RTS noise was selected. At the substrate voltage of 0 V, the transistor shows prominent RTS noise; current shows two distinct levels with a difference of 1×10^{-8} A. At lower substrate voltage of –5 V, the RTS noise completely disappeared. Traditionally, this phenomenon was explained in terms of a defect in channel and channel depth within a classical band theory. In this study, this phenomenon was interpreted within an atomistic model based on quantum mechanics.

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 fuel cells, solar cells and field effect transistors are investigated in this department.

Exploitations of Novel Spectroscopic Methods for Material and Surface Science

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Division of Electronic Structure

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Education

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1990	Ph.D. The University of Tokyo

Professional Employment

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

Member
Assistant Professor
  TAKAGI, Yasumasa
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Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism

For the developments of novel functional materials, it is quite important to exploit new characterization methods based on advanced technology simultaneously. 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 synchrotron radiation and lasers.

The first topic is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism photoelectron emission microscopy, 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 a ultrahigh vacuum superconducting magnet and a liq. He cryostat. The XMCD apparatus is widely open for public usage and many researchers even from abroad visit every year. We are currently interested in metal phthalocyanine monolayers on nonmagnetic and ferromagnetic surfaces, whose electronic and magnetic properties are tunable by changing the central metal atom and/or modifying the ligand. Our recent achievement concerning vanadyl phthalocyanine will be presented in the next page.

The second topic is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (XPS) for polymer electrolyte fuel cells (PEFC) under working conditions. We have successfully installed ambient pressure (up to 3000 Pa) hard x-ray photoelectron spectrometer (Figure 1). We have designed in situ fuel cells under working conditions and have successfully recorded Pt 3d XPS (Figure 1) of Pt/C and PtCo/C cathode catalysts in PEFC.

Furthermore, we have just started the third topic of the picosecond time resolved x-ray absorption fine structure (XAFS) spectroscopy. The installation of a picosecond laser system was completed and the performance test using a short-lived photoexcited metal complex was successful.

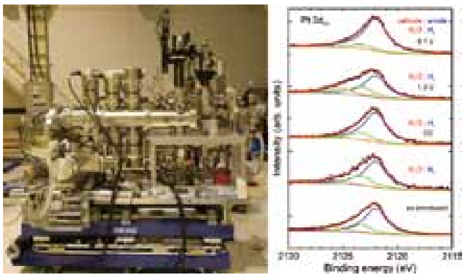

Figure 1. Ambient pressure hard x-ray photoelectron spectrometer (left) and typical Pt3d spectra from the Pt/C cathode catalyst in PEFC (right).

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- M. Dabrowski, T. R. F. Peixoto, M. Pazgan, A. Winkelmann, T. Nakagawa, Y. Takagi, T. Yokoyama, U. Bauer, F. Yildiz, F. Bisio, M. Przybylski and J. Kirschner, *Phys. Rev. Lett.* **113**, 067203 (2014).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- X.-D. Ma, D. I. Bazhanov, O. Fruchart, F. Yildiz, T. Yokoyama, M. Przybylski, V. S. Stepanyuk, W. Hergert and J. Kirschner, *Phys. Rev. Lett.* **102**, 205503 (2009).
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1. Structural and Magnetic Properties of Submonolayer Vanadyl Phthalocyanine[1,2]

Controlling a wide range of functionalities of metal complexes on substrate surfaces for the applications such as molecular spintronics, molecular devices, and molecular catalysis is of special importance. Metal phthalocyanine (MPc) is one of the most promising materials. Although extensive studies on late 3d transition metal Pc monolayers on metal surfaces have been reported, much less investigations have been conducted on early 3d transition metal Pcs. We have studied structural and magnetic properties of vanadyl phthalocyanine VOPc on Si(111) and Ag(111) single crystal surfaces and also ferromagnetic ultrathin Fe, Co and Ni films grown epitaxially on Cu(001), by means of soft x-ray absorption spectroscopy and x-ray magnetic circular dichroism using our synchrotron radiation facility UVSOR-III and other surface scientific methods.

Figures 2(a) and 2(b) show the N and O K-edge x-ray absorption spectra of 10 monolayer (ML) VOPc on Si(111), 0.6 ML VOPc on Si(111) and 1 ML VOPc on Ag(111). From these spectra, it is concluded that the adsorbed submonolayer VOPc is lying flat on both the surfaces and that on Si(111) the VOPc molecule adsorbs with the oxygen downward configuration due to the formation of the Si–O–V bond, while on Ag(111) the oxygen-up configuration is preferred because of a stronger interaction between Ag and the Pc π/π* orbitals. This is the first experimental proof for the oxygen-down configuration of MOPc on semiconductor surfaces, consistent with the theoretical prediction on the VOPc/GaAs system.

Figure 3 shows the V and Fe L-edge XMCD spectra of monolayer VOPc on 3 ML Fe films grown epitaxially on Cu(001). The Fe film exhibits perpendicular magnetic easy axis. The V L_{III}-edge signals are found to be reversed compared to the Fe ones; namely the V magnetic moment is antiparallel to the magnetic field. This indicates that the magnetic interaction between VOPc and Fe is antiferromagnetic even under ±5 T. The V L-edge spectra of VOPc on the Co film (not shown) reveal that the interaction between VOPc and Co is again antiferromagnetic, though the coupling seems to be considerably weaker. On the contrary, VOPc on the Ni films exhibits inherent paramagnetism without noticeable magnetic interaction between VOPc and Ni. This is consistent with a previous theoretical study that concluded much longer spacing between MPc and Ni than Fe and Co. The present observation of antiferromagnetic coupling between MPc and the ferromagnetic films is quite rare and VOPc should be a possible candidate for molecular magnetic devices to preserve or enhance the ferromagnetism of the substrate metals. Since VOPc itself seems to show the perpendicular easy axis with respect to the molecular plane, this molecule could be also suitable for perpendicular magnetic anisotropy.

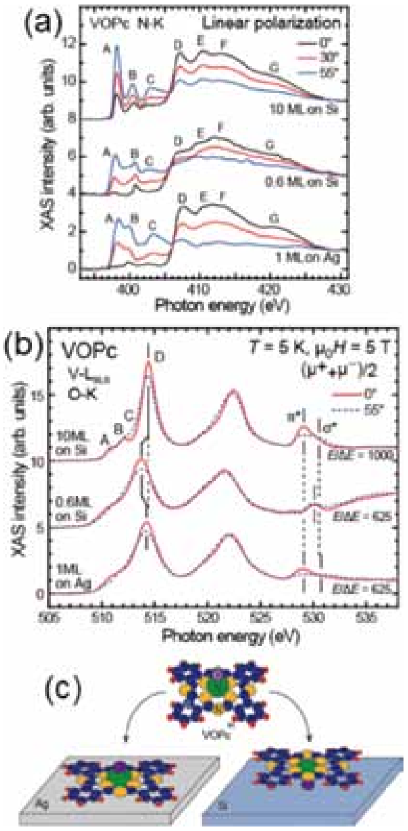

Figure 2. (a,b) N K-edge (a) and V L- and O K-edge x-ray absorption spectra of multilayer VOPc on Si(111), 0.6 ML VOPc on Si(111) and 1 ML VOPc on Ag(111). (c) Schematic structural views of adsorbed VOPc on Ag(111) and Si(111) surfaces.

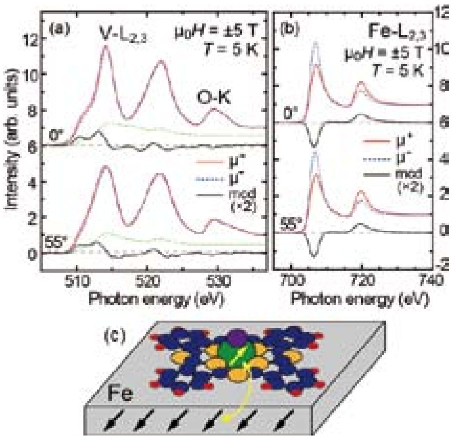

Figure 3. (a,b) V and Fe L-edge x-ray magnetic circular dichroism spectra of monolayer VOPc on 3 ML Fe films grown on Cu(001) recorded at T = 5 K and H = ±5 T. (c) Schematic views of antiferromagnetic interaction between VOPc and the Fe film.

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2) K. Eguchi, Y. Takagi, T. Nakagawa and T. Yokoyama, *J. Phys. Chem. C* **118**, 17633–17637 (2014).

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.

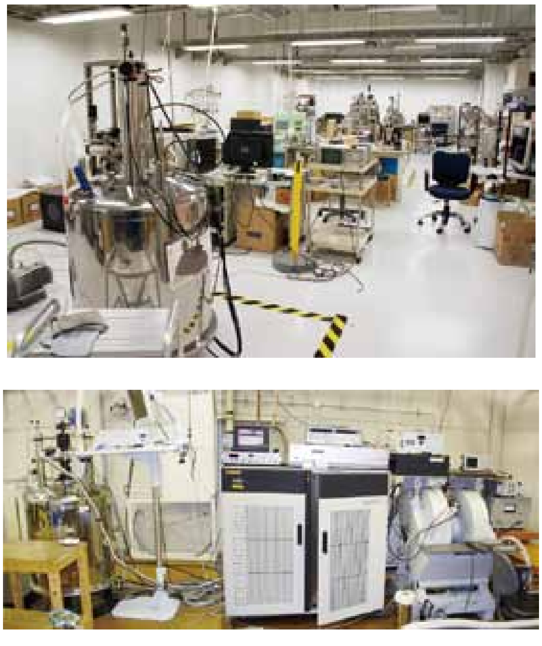

Figure 1. Solid state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- T. Terauchi, S. Sumi, Y. Kobayashi, T. Nakamura, K. Furukawa and Y. Misaki, "Stable Metallic State of $(TTPCOO)_2NH_4$ with Mobile Dopant," *Chem. Commun.* **50**, 7111–7113 (2014).
- S. Jin, K. Furukawa, M. Addicoat, L. Chen, S. Takahashi, S. Irle, T. Nakamura and D. Jiang, "Large Pore Donor–Acceptor Covalent Organic Frameworks," *Chem. Sci.* **4**, 4505–4511 (2013).

1. Magnetic Resonance Investigation of Self-Doped Type TTFCOO and TTPCOO Family Salts

^{1}H-NMR and High-Field ESR measurements were carried out for self-doped type organic conductors, ammonium tetrathiapentalene carboxylate $(TTPCOO)_2[(NH_4^{+1})_{1-x}(NH_3^0)_x]$ (hereafter we abbreviated as $TTPCOONH_4$ system), which are developed by NIMS group. While the pristine TTPCOOH molecules are closed-shell, self-doped type carrier is generated by substitution of the end group of (NH_3^0) with (NH_4^{+1}), which is regarded as a charge-reservoir. The π-extended system, TTPCOO, possessed a uni-axial g-tensor, indicating 2D isotropic structure such as herring-bone-like donor arrangements. NMR-relaxation rate shows the Korringa relation temperature dependence, and the ESR linewidth follows Elliot mechanism. These facts are apparent evidences of stable metallic state.

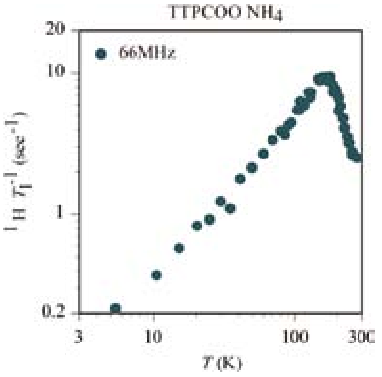

Figure 2. Temperature dependence of the ^{1}H-NMR spin–lattice relaxation rate T_1^{-1} for TTPCOO system. T-linear Korringa-like behavior down to 5 K indicates a stable metallic state.

Figure 2 shows the temperature dependence of the spin–lattice relaxation rate of $TTPCOONH_4$ system. A pronounced peak behavior observed at around 160K shows frequency dependence and is apparently originated from the proton motion. Since the relaxation of molecular motion is rapidly suppressed as lowering temperature, the nuclear spin relaxation at low temperatures (*i.e.* below 100 K) is mainly caused by the electron spins. In the low-temperature region, the ^{1}H NMR spin–lattice relaxation rate, T_1^{-1}, of $TTPCOONH_4$ system shows T-linear Korringa-like behavior down to 5 K. This observation clarifies that this system is metallic. It is contrast to the 1D spin diffusive relaxation behavior ($\sim T^{0.5}$) observed in a semiconductor $(TTFCOO)_2[(NH_4^{+1})_{1-x}(NH_3^0)_x]$. The continuous T-linear behavior of T_1^{-1} down to 5 K also shows that there is no low-dimensional instability and antiferromagnetic (SDW) transitions at low temperatures. No obvious line shift and line broadening with temperature also supports this scenario. These facts indicate that substitution of mainframe from TTF to π extended TTP is essential key to realize a stable metallic state by means of reduction of electron correlation (Coulomb repulsion) and dispersion force.

2. Time-Resolved ESR Spectroscopy Investigation of Photoconduction Mechanism in Covalent Organic Framework (COF) Materials

Covalent organic framework (COF) materials are porus crystalline materials. They attracted much attention because of their functionalities. Recently, a variety of COF materials based on the Donor–Acceptor (D–A) system have been developed. Jiang and coworkers synthesized a variety of D–A type COFs such as NDI-ZnPc, PyDI-ZnPC and ZnPc-NDI-HHTP. While molecules are connected by tight covalent bonds within the two-dimensional layers, the molecules stack to form one-dimensional columns perpendicular to the planes. They show pronounced photo-conducting behavior. The possible photoconduction origin is the electron transfer between donor and acceptor. However, the detail mechanism is an open question. We performed time-resolved photo-excited ESR spectroscopy for a series of D–A type COF materials to investigate the photo-conduction mechanism. After photo-excitation to D–A type COFs, an ESR signal originated from the charge-separated state was observed, which could not be observed in isolated molecules. As for ZnPc-NDI-COF, we can observe the charge-separated ESR signal even at R.T., indicating long lifetime of the photo-excited carriers. Actually, the lifetime of the photo-excited charge-separated states in ZnPc-NDI-COF are estimated as 865 μs at 80 K and 1.8 μs at 280K.

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Organic Solar Cells

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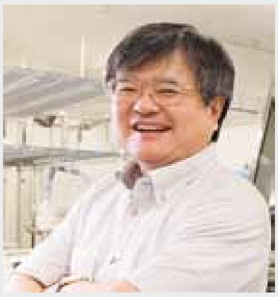

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Keywords Organic Semiconductors, Organic Solar Cells, Doping

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 establishment of “bandgap science for organic solar cells.” We believe that the following features are indispensable. (a) Organic semiconductors purified to sub-ppm level, at least seven nines (7N; 0.1 ppm), should be used. (b) A ppm-level doping technique should be developed. (c) Every individual organic semiconductor should be capable of displaying both *n*- and *p*-type characteristics by impurity doping alone, *i.e.*, complete *pn*-control should be developed. (d) Unintentional and uncontrollable doping by oxygen and water from air should be completely eliminated. (e) The doping technique should be applicable not only to single organic semiconductor films, but also to codeposited films consisting of two kinds of organic semiconductors since a key element for exciton dissociation in organic solar cells is having a co-deposited films.

Recently, we have showed that in principle, almost all single organic semiconductors can be controlled to both *n*-type and *p*-type by doping alone, similar to the case of inorganic semiconductors (Figure 1). This can be regarded as a foundation for the construction of high efficient organic solar cells.

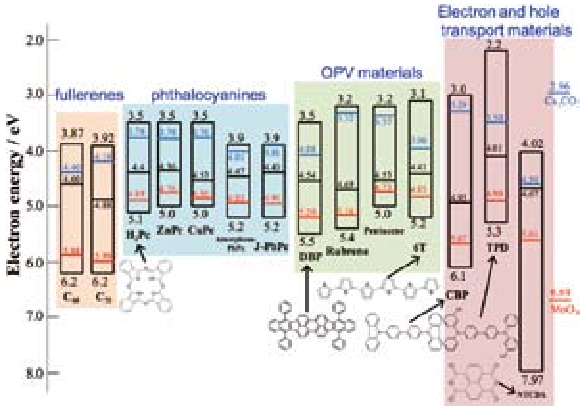

Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100 nm) are also shown.

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- M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, “Conduction Type Control of Fullerene Films from *n*- to *p*-Type by Molybdenum Oxide Doping,” *Appl. Phys. Lett.* **98**, 023302 (3 pages) (2011).
- M. Hiramoto, H. Fujiwara and M. Yokoyama, “Three-Layered Organic Solar Cell with a Photoactive Interlayer of Codeposited Pigments,” *Appl. Phys. Lett.* **58**, 1062–1064 (1991).

1. Ionization Sensitization of Doping in Co-Deposited Organic Semiconductor Films

We have developed the *pn*-control technique by impurity doping for co-deposited films[1] such as C_{60}:H_2Pc (fullerene: metal-free phthalocyanine) since a key element for exciton dissociation in organic solar cells is having a co-deposited films. During the course of these studies, we made accurate estimates of the carrier concentrations generated by impurity doping by means of Kelvin band-mapping,[2] from which we found evidence of higher doping efficiencies for co-deposited films compared to those for the respective single films.

Figure 3 shows the dependence of the doping efficiency on the doping concentration for C_{60}:H_2Pc and their component films. The doping efficiency is defined by the ratio of the carrier concentration created to the molecular concentration of Cs_2CO_3. The doping efficiencies of single films of C_{60} and H_2Pc are around 10%. In contrast, those of the co-deposited films of C_{60}:H_2Pc are around 50%. Thus, we conclude that the doping efficiency was significantly enhanced in the co-deposited films.

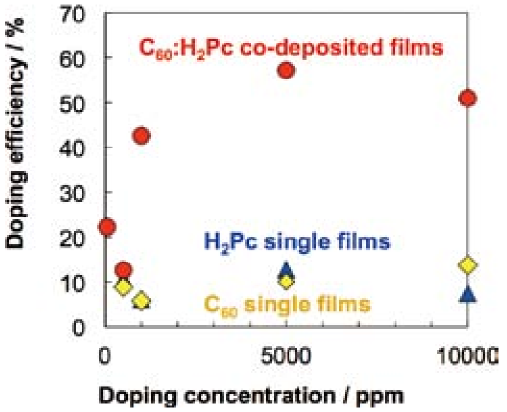

Figure 2. Dependence of doping efficiency on Cs_2CO_3 doping concentration for C_{60}:H_2Pc co-deposited films and their component films.

By making contact with C_{60}, since the electron transfer from the conduction band of H_2Pc to that of C_{60} (Figure 4(a), blue arrow) occurs accompanied with energetic relaxation (0.7 eV), the electron concentration in H_2Pc decreases. Due to the shift in equilibrium, the electrons liberated from the donor levels accelerate, *i.e.*, the ionization rate (doping efficiency) for donors increases only in the H_2Pc region. Figure 4(b) shows the cross sectional energy structures of charge separating H_2Pc/C_{60} superlattice after contact. In this model, the H_2Pc regions act as electron supplying layers to the C_{60} regions. The C_{60} regions act as electron transporting highways. Based on this model, we expected that the total ionization rate in H_2Pc:C_{60} co-deposited films would increase further by increasing the H_2Pc ratio and obtained the ionization rate of 97% at a H_2Pc:C_{60} ratio of 99:1.

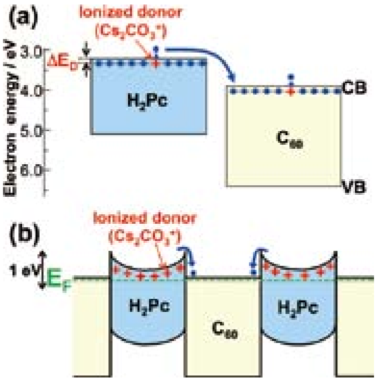

Figure 3. (a) Energy diagrams of Cs_2CO_3-doped H_2Pc and C_{60} single films before contact. CB, VB, and ΔE_D denote the conduction band, the valence band, and the activation energy of the donors, respectively. (b) Cross sectional energy structure of a Cs_2CO_3-doped H_2Pc/C_{60} superlattice model after contact.

2. Mapping of Band-Bending for Organic *pn*-Homojunctions

A precise band-mapping for organic *pn*-homojunctions, which have various balance of doping concentration between *p*- and *n*-type layers, was performed by measuring the film thickness dependence of the work function from both sides of the *pn*-homojunction interface using a Kelvin probe. Band-bending including the simultaneous development of depletion layer in underlying *n*-type layer induced by the deposition of *p*-type layer, and vice versa, should be taken into account for the precise fitting based on the Poisson equation. Validity of the conventional theory of space charge layer suggests that the dopants are spatially fixed even in the organic semiconductor films. The present result allows the precise design of the built-in potential in the organic solar cells.

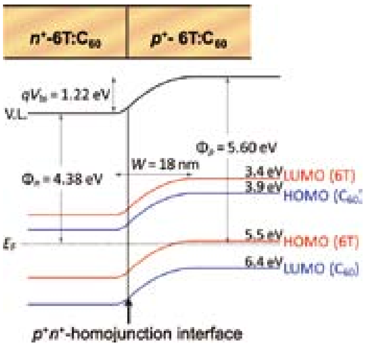

Figure 4. Energy band diagram of the p^+n^+-homojunction. VL, E_F, VB, and CB denote the vacuum level, Fermi level, the valence band and the conduction band, respectively.

References

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2) Y. Shinmura, N. Ishiyama, T. Kaji and M. Hiramoto, *Appl. Phys. Express* **7**, 071601 (2014).

Two-Dimensional Polymers and Covalent Organic Frameworks

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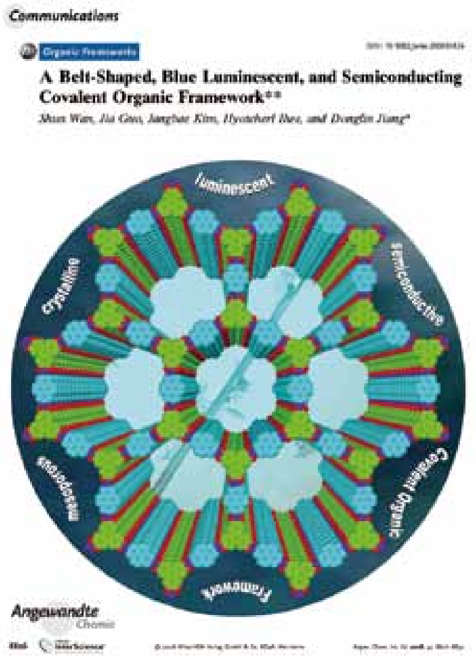
Keywords Two-Dimensional Covalent Polymer, Porous Organic Polymers

Two-dimensional (2D) polymers and their layered frameworks (covalent organic frameworks: COFs) are a class of crystalline porous materials that allow an atomically precise integration of organic components into a 2D or 3D periodicity. The COF materials are different from conventional polymers and typical porous meta-organic framework in the aspects structure, synthesis, and functions and have emerged as a new platform for designing advanced materials, including gas adsorption, catalysts, semicoductors, light-emitters, and active materials for batteries and polymer solar cells. We have pioneered the field of COFs by exploring molecular topologies, building blocks, linkages, and functions and applications.



Communications

A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework**

Figure 1. The first semiconducting 2D COF.

Selected Publications

- X. Feng, X. Ding and D. Jiang*, "Covalent Organic Frameworks," *Chem. Soc. Rev.* **41**, 6010–6022 (2012).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Belt-Shaped, Blue Luminescent and Semiconducting Covalent Organic Framework," *Angew. Chem., Int. Ed.* **47**, 8826–8830 (2008) (VIP).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes with Eclipsed 2D Polypyrene Sheets for Photocurrent Generation," *Angew. Chem., Int. Ed.* **48**, 5439–5442 (2009).
- J. Guo, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang*, "Conjugated Organic Framework with Three-Dimensionally Ordered Stable Polymer with Delocalized π Clouds," *Nat. Commun.* **4**: 2736 doi: 10.1038/ncomms3736 (2013).

1. Azine-Linked 2D Polymers and COFs

To discover new covalent bonds for the construction of crystalline and permanent porous organic frameworks remains challenging in the field of reticular chemistry. Successful attempts to achieve COFs have been limited to few covalent bonds, including boronate, boroxine, borosilicate, imine, triazine, hydrazone, and squaraine linkages. Among them, only few examples of COFs have been reported to show enough high thermal and chemical stabilities, which however, are crucial for applications. In this context, to explore a robust linkage for the synthesis of COFs that meet the requirement in crystallinity, porosity, and stability is of critical importance for the further advancement of the field from the viewpoints of both basic research and technological application.

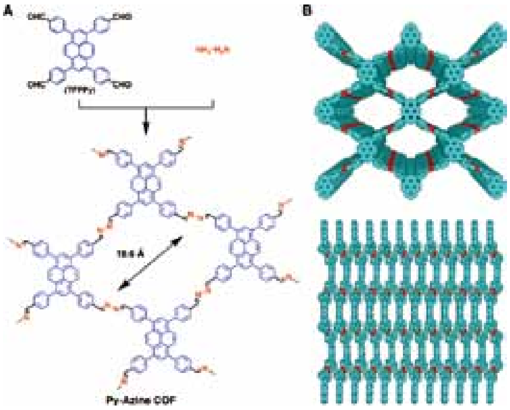


Figure 2. (A) Schematic representation of the Synthesis of the azine-linked COF (Py-Azine COF). (B) Top and side views of the AA stacking structure of the Py-Azine COF (sky blue: tetraphenylpyrene unit, red: nitrogen, H atoms are omitted).

Herein, we report the development of a new covalent bond based on the azine linkage for the synthesis of COFs that exhibit high crystallinity, high porosity, and robust chemical stability (Figure 2, Py-Azine COF). Condensation of hydrazine with 1,3,6,8-tetrakis(4-formylphenyl)pyrene under solvothermal conditions affords highly crystalline two-dimensional covalent organic frameworks. The pyrene units occupy the vertices and the diazabutadiene (–C=N–N=C–) linkers locate the edges of rohmbic-shaped polygon sheets, which further stack in an AA-stacking mode to afford periodically ordered pyrene columns and one-dimensional microporous channels. The azine-linked frameworks feature permanent porosity with high surface area and exhibit outstanding chemical stability. By virtue of the pyrene columnar ordering, the azine-linked frameworks are highly luminescence, whereas the azine units serve as open docking sites for hydrogen-bonding interactions. These synergestic functions of the vertices and edges units endow the azine-linked pyrene frameworks with extremely high sensitivity and selectivity in chemosensing, for example, the selective detection of 2,4,6-trinitrophenol explosive. We anticipate that the extension of the present azine-linked strategy would not only increase the structural diversity but also expand the scope of functions based on this highly stable class of covalent organic frameworks.

2. Pore Surface Engineering for Constructing Donor–Acceptor COFs

Two strategies have been established for the synthesis of donor–acceptor COFs. By using electron donor and acceptor as monomers, we have developed a covalent methodology for the synthesis of donor–acceptor COFs, whereas the skeletons are built from alternately linked donor and acceptor π-arrays and leave open channels unused. As an alternative way, we and other groups have explored a supramolecular approach by spatially confining electron acceptors within the open channels of electron-donating frameworks. Clearly, the former approach requires a planar conformation of the monomer units and is not applicable to the zero-dimensional molecules, such as buckyballs, a class of widely utilized electron acceptors. The second approach based on physical filling can load buckyballs; however, it encounters a problem on the fullerene elution from the channels.

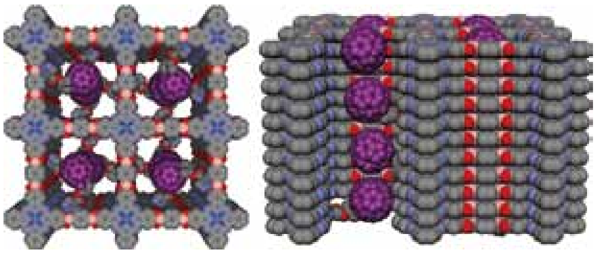


Figure 3. Surface engineering of pore walls for covalent linking of fullerenes to constitute donor–acceptor systems.

In this work, we developed a method for converting the open lattice of COFs into photoelectric structures in which electron-accepting buckyballs were spatially confined within the nanochannels via covalent anchoring on the channel walls (Figure 3). The donor–acceptor heterojunctions trigger photoinduced electron transfer and allow charge separation with radical species delocalized in the π-arrays, whereas the charge separation efficiency was dependent on the buckyball content. This new donor–acceptor strategy explores both skeletons and pores of COFs for charge separation and photoenergy conversions.

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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 molecules is the first step. There are varieties of important molecules which are insoluble to any solvent and functional at amorphous state. Solid state NMR enables to obtain variety of information for such molecules at atomic resolution without significant restrictions and damage of molecules. Thus solid state NMR is one of the essential tools for the characterization of those molecules.

We have been working on the methodology and hardware developments of solid state NMR and their applications such as structural biology and material science. We study for characterization of biomolecules such as peripheral membrane proteins and organic molecules such as natural products and synthetic polymers. Characterizations of several molecular materials in addition to biomolecules are under investigations with several corroborators using solid state NMR.

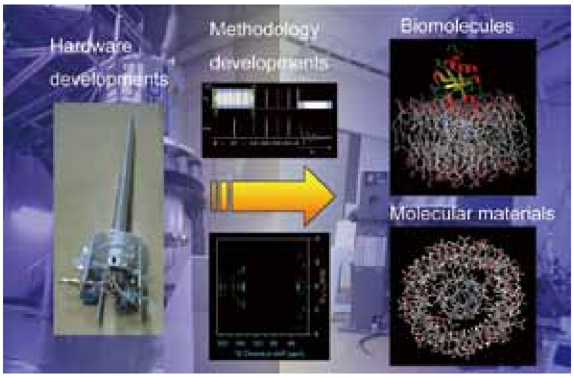

Figure 1. Outline of our studies.

Selected Publications

- J. Hu, R. Fu, K. Nishimura, L. Zhang, H. X. Zhou, D. D. Busath, V. Vijayvergiya and T. A. Cross, "Histidines, Heart of the Hydrogen Ion Channel from Influenza A Virus: Toward an Understanding of Conductance and Proton Selectivity," *Proc. Natl. Acad. Sci. U .S.A.* **103**, 6865–6870 (2006).
- K. Nishimura and A. Naito, "Remarkable Reduction of RF Power by ATANSEMA and DATANSEMA Separated Local Field in Solid-State NMR Spectroscopy," *Chem. Phys. Lett.* **419**, 120–124 (2006).
- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
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- 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).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).

1. Molecular Proximity Revealed by Solid State NMR

Molecular proximity is one of the important information to characterize structure and functions of various molecules. However, the isotope enrichments of those samples are difficult or limited. Thus, low sensitivity natural abundant isotopes must be observed. Furthermore, so far many of developed solid state NMR techniques have been designed for the study of isotope enriched sample. Thus methodology developments and analysis optimized for natural abundant samples are quite important.

We have been exploring to reveal molecular proximity of biomolecules and synthetic polymers without isotope enrichment based on different approaches.

^{1}H detection is one of the possibilities in order to overcome sensitivity issue for the observation of natural abundant samples. However, solid organic samples possess ^{1}H homonuclear dipolar coupling which results in significant broadening of spectra. Thus unlike solution NMR, it has been difficult to observe ^{1}H high resolution spectra for organic solids. However, high speed MAS technique has made a remarkable progress in the past decade. It enables to observe high resolution ^{1}H spectra only by using MAS and gives reliable isotropic chemical shifts.

We have attempted to reveal molecular proximity by observing high resolution ^{1}H spectra using ultra high speed MAS under ultra high field. With collaborators, we have successfully revealed molecular packing in silk fibroin based on accurately determined ^{1}H position in model peptide which obtained from the analysis of cross peak growing for ^{1}H-homonculear double quantum-single quantum correlation spectra[1,2] at various mixing time.

As an alternative approach, so far CRAMPS technique which utilize multiple pulse (MP) ^{1}H homonuclear dipolar decoupling under magic angle spinning has been used to observed high resolution ^{1}H spectra under magic angle spinning. In this technique, averaging cycle of ^{1}H homonuclear dipolar interaction based on MP must be short enough compare to the MAS rotation period in order to avoid interference between spin and sample rotations. Thus high power RF field is required for ^{1}H to satisfy above requirements. Furthermore, MP also scales down isotropic chemical shifts of ^{1}H simultaneously. Thus careful calibrations of experimental parameters are essential in order to observe correct isotropic chemical shifts. Using CRAMPS approach for ^{1}H dimension, it is possible to obtain high resolution ^{1}H-^{13}C heteronuclear correlation spectra under moderate speed MAS.

We are currently investigating intermolecular proximity of cage molecules with collaborator. By using ^{1}H-^{13}C heteronuclear correlation experiments under high field, it enables to detect intermolecular ^{1}H-^{13}C heteronuclear correlation based on heteronuclear dipolar couplings. Compared to ^{1}H-intermolecular correlation approach mentioned above, detectable distance range are limited and sensitivity is lower, however ^{13}C detection enables well resolved sharp signals.

2. Proton Localization in ZnO Nanorods Revealed by In-Situ ^{1}H-Magic Angle Spinning Solid State NMR Spectroscopy[3]

ZnO nanorods can be grown using aqueous solution. Unique shape of ZnO nanorods are studied for various applications such as biosensors, piezoelectric generators, dye-sensitized solar cells. Aqueous-grown ZnO nanorods might contain various kinds of impurities from source materials. Considering aqueous-growth of ZnO nanorods, we pay attention on incorpolated hydrogen atoms, which can act as shallow donors.

In this study, local environments of protons incorporated in aqueous grown ZnO nanorods at different temperatures and approaches were studied prepared by collaborator by in-situ ^{1}H-magic angle spinning solid state NMR spectroscopy. We found out that the amount of protons incorporated in ZnO nanorods were increased toward increase of temperature of hydrothermal synthesis. However those for annealed samples at 500 °C after thermal synthesis release protons toward increase of temperature of hydrothermal synthesis. Furthermore, protons incorporated in ZnO nanorods prepared by either hydrothermal synthesis using autoclave or microwave irradiations exhibited different proton concentrations and adsorptive activities. Those results indicate that adsorptive activity of protons incorporated in ZnO nanorods may vary depending on the preparation procedures.

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3) K. Ogata, S. Sasa, M. Inoue, M. Yano and K. Nishimura, to be submitted.

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

Safety Office

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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, Structure and Physical Properties of *N*-Boc-Pyrrole Derivatives for Organic Semiconductors

Planar π-conjugated molecules have been attracted much attention from the viewpoints of development of organic semiconductor devices.[1] To improve their low solubility, we synthesized several *N*-*tert*-butoxycarbonyl (Boc)-2,5- diarylpyrrole derivatives as precursors of organic semiconductors for the fabrication of solution-processed field-effect transistors. These compounds have nonplanar structures due to a steric hindrance between Boc group and aryl ones. Elimination of Boc group from the soluble precursors by annealing quantitatively afforded insoluble *N*-H-2,5-diarylpyrroles with planar structures. We investigated their spectral and electrochemical changes toward a film fabrication technology.

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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 (**MOSET**) and their integrated circuits.

1. Systematic Chemical Modulation of Molecular Wires

We have already elucidated the details of steady-state long-distance molecular conduction through a series of molecular wires **1**. As a next step, we have planed to develop the design principle for precise and wide-range control of electron-transport characteristics of single molecular wires. For this purpose, we have modulated the electronic structure of the wires **1** by systematic chemical modifications. Figure 1 shows the typical examples. The measurement of single molecular conductance of these wires is still in progress.

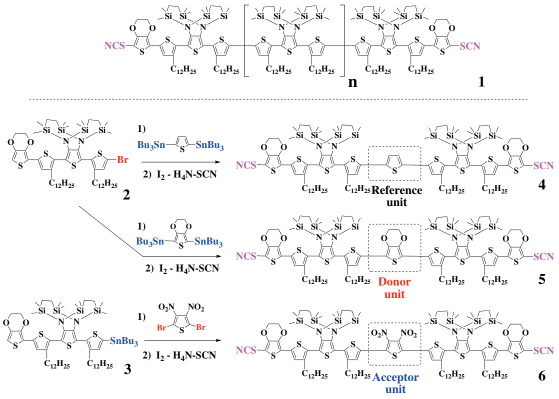

Figure 1. Synthetic scheme for molecular wires with modified electronic structure.

Visiting Professors

Visiting Professor
TAKENOBU, Taishi *(from Waseda University)*

Electronic Phase Control of Molecular Materials by Electric Double Layer Transistors

Charge carrier control is one of the key issues in the development of solid state physics and novel functional devices. Most famous device is field-effect transistor, in which material conductivity is controlled by accumulated charges at semiconductor/insulator interface. Beyond the simple enhancement of conductivity, high charge carrier accumulation can realize various phenomena, such as phase transition, magnetic ordering, and superconductivity. Electric double layers, formed at solid/electrolyte interfaces, induce extremely large electric fields, huge specific capacitance and high density charge accumulation, and, as the results, this method opens new route for novel functionalities. Because molecular materials have large variety of electronic and magnetic properties, we are investigating the physical properties of ionic liquid/molecular materials interfaces and are developing the method to combine single crystals of molecular solid with electric double layer transistors to discover novel phase transitions and functional devices.

Visiting Associate Professor
NAKANISHI, Takashi *(from National Institute for Materials Science)*

Self-Assembly Controlled Soft Materials of Multifunctional Spin-Active Molecules

Because of optoelectronic properties and single magnet molecule behavior, phthalocyaninato rare-earth metal double-decker complexes have received much attention. These complexes are expected to have application in spintronics as well as in electrochromic and optoelectronic devices. In our work we apply the concept of soft materialization to the double-decker phthalocyanines to achieve control over self-assembly and phase transition of the material. Our aim is to obtain solvent-free soft materials, including room temperature liquids and liquid crystals, with tunable intermolecular interactions and magnetic, electrochromic, and photoconductive properties. One kind of double-decker phthalocyanine is chosen as a “functional, spin-active unit” and multiple branched long-alkyl chains are attached as substituents. The synthesis, spectroscopy and electrochemistry, ESR analyses of these materials as well as their thermotropic behavior are deeply evaluated and further analysis such as electrochromic and photoconductive properties are currently under way.

Visiting Associate Professor
NEGISHI, Yuichi *(from Tokyo University of Science)*

Creation of Functionalized Metal Nanoclusters and Highly Active Photocatalytic Materials Using Thiolate-Protected Magic Gold Clusters

Advances in developments in nanotechnology have encouraged the creation of highly functionalized nanomaterials. Because of their nanoscale size (< 2 nm), thiolate-protected gold clusters ($\mathrm{Au}_n(\mathrm{SR})_m$) exhibit size-specific physical and chemical properties not observed in bulk metals. Therefore, they have attracted attention as functional units or building blocks in nanotechnology. The highly stable, magic $\mathrm{Au}_n(\mathrm{SR})_m$ clusters possess great potential as new nanomaterials. We are studying the following subjects related to magic $\mathrm{Au}_n(\mathrm{SR})_m$ clusters: (1) establishing methods to enhance their functionality, (2) developing high-resolution separation methods and (3) utilizing the clusters as active sites in photocatalytic materials. Through these studies, we aim to create highly functional metal nanoclusters and apply them as highly active photocatalytic materials.

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 division. During this year, associate professors Toshi Nagata, Hidehiro Sakurai (Research Center of Integrative Molecular Systems), Hiroshi Fujii (Okazaki Institute for Integrative Bioscience), who had joined this department under concurrent appointments, were promoted to move out from IMS. Dr. Norie Momiyama was recruited to be an associate professor of the Division of Complex Catalysis in June 2014. Dr. Ryota Iino was also recruited as a full professor of the Okazaki Institute for Integrative Bioscience in June, and simultaneously offered a concurrent appointment of this department.

Bioinorganic Chemistry of Metal-Containing Sensor Proteins

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

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Professional Employment
1988 Postdoctoral Fellow, Georgia University
1989 Assistant Professor, Tokyo Institute of Technology
1994 Associate Professor, Japan Advanced Institute of Science and Technology
2002 Professor, Institute for Molecular Science
Professor, Okazaki Institute for Integrative Bioscience
Professor, The Graduate University for Advanced Studies

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Keywords Bioinorganic Chemistry, Metalloproteins, Sensor Protein

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

Heme shows many biological functions. The most popular function is to be used as a prosthetic group in heme proteins. Heme proteins show a variety of functions including oxygen transport/storage, electron transfer, oxidase, peroxidase, oxygenase, catalase, and dehydratase. In addition to these functions, a new function of hemeprotein has been found recently, which is a sensor of diatomic gas molecules or redox change. In these heme-based sensor proteins, the heme acts as the active site for sensing the external signal such as gas molecules and redox change. Heme also shows a novel biological function as a signaling molecule for transcriptional and translational regulation. In these systems, heme-sensing proteins sense a heme molecule to regulate biological processes. We are now working on the heme-based gas sensor proteins, heme-dependent transcriptional regulation, and bacterial heme transport systems.

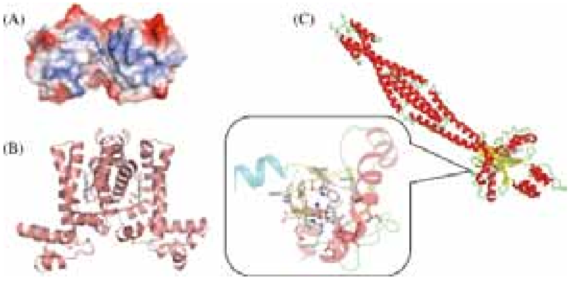

Figure 1. Structures of (A) the heme-transport protein HmuT, (B) the heme-sensing transcriptional regulator HrtR, and (C) the heme-based sensor protein Aer2.

Selected Publications

- S. Aono, "The Dos Family of Globin-Related Sensors Using PAS Domains to Accommodate Haem Acting as the Active Site for Sensing External Signals," *Adv. Microb. Physiol.* **63**, 273–327 (2013).
- H. Sawai, M. Yamanaka, H. Sugimoto, Y. Shiro and S. Aono, "Structural Basis for the Transcriptional Regulation of Heme Homeostasis in *Lactococcus lactis*," *J. Biol. Chem.* **287**, 30755–30768 (2012).
- H. Sawai, H. Sugimoto, Y. Shiro and S. Aono, "Structural Basis for Oxygen Sensing and Signal Transduction of the Heme-Based Sensor Protein Aer2 from *Pseudomonas aeruginosa*," *Chem. Commun.* **48**, 6523–6525 (2012).
- S. Aono, "Novel Bacterial Gas Sensor Proteins with Transition-Metal-Containing Prosthetic Groups as Active Sites," *Antioxid. Redox Signaling* **16**, 678–686 (2012).

1. Molecular Mechanism for Heme-Mediated Inhibition of 5-Aminolevulinic Acid Synthase 1$^{1)}$

Mammalian 5-aminolevulinic acid synthase 1 (ALAS1), an isozyme expressed in all cell types, catalyzes the first reaction in the heme biosynthetic pathway in mitochondria. Heme regulates ALAS1 function at multiple levels including the regulation of transcription, translation, mitochondrial import, protein degradation and enzyme activity to maintain intracellular heme concentrations at appropriate range. In this study, we elucidated the molecular mechanism of heme-mediated regulation of enzymatic activity for rat ALAS1. ALAS1 has three putative heme regulatory motifs (HRMs), two of which were found to be the ferric heme binding sites in ALAS1. Though the electronic absorption and resonance Raman spectroscopy have demonstrated that ^{110}Cys and ^{527}Cys are ferric heme binding sites in ALAS1, heme binding to ^{110}Cys and ^{527}Cys was not responsible for heme-mediated inhibition of ALAS1 activity. Rather, ALAS1 activity will be inhibited by heme binding with hydrophobic interactions to the succinyl-CoA binding pocket. The heme binding to the HRMs in ALAS1 was found not to be responsible for heme-mediated inhibition of ALAS1 activity. Though heme binding to ^{110}Cys and/or ^{527}Cys in the HRMs is not involved in the feedback regulation of ALAS1 activity, it would be responsible for the oxidative modification of ALAS1 that might regulate the heme-mediated proteolysis.

We also found that protoporphyrin IX (PpIX), a reaction intermediate of heme biogenesis, inhibited ALAS1 activity more efficiently compared with heme, indicating the presence of multiple pathways for the feedback regulation of ALAS1 activity. The intracellular accumulation of PpIX, which may be caused by unbalance between PpIX synthesis and iron chelation to PpIX to produce heme, causes severe damage to cells. Thus, it makes sense that PpIX functions as an effector of the feedback regulation of ALAS1 to shut down its activity to prevent from accumulation of PpIX under iron limitation.

2. Heme-Binding Properties of HupD Functioning as a Substrate-Binding Protein in a Heme-Uptake ABC-Transporter System in *Listeria monocytogenes*$^{2)}$

Iron is an essential element for all organisms, which is used as a component of iron-containing proteins such as hemoproteins and iron-sulfur proteins responsible for a variety of biological processes. Pathogenic bacteria need to thieve iron from host organisms for their growth. Since heme iron involved in hemoglobin is the most abundant iron source for pathogenic bacteria infected in vertebrate, these bacteria have evolved sophisticated acquisition systems of heme from their host organisms.

Recently, it is reported that a Gram-positive pathogen *L. monocytogenes* that cause listeriosis has three Fur-regulated heme-uptake systems: the *srtB* region coding sortase-anchored proteins and a putative ABC transporter, the *fhu* and *hup* operons coding putative ABC transporters for ferric hydroxamates and hemin respectively. An ABC-type transporter system HupDGC is the primary heme transporter system and is most crucial to virulence for *L. monocytogenes*. HupD, the substrate-binding protein in the HupDGC transporter, is reported to be specific for heme, but the detailed properties of HupD for heme-binding remains to be elucidated. In this work, heme-binding properties of HupD from *L. monocytogenes* were characterized by spectroscopic and mutagenesis studies.

Titration of apo-tHupD with hemin revealed that apo-HupD takes up 1 mol equivalent of heme to form a 1:1 complex, as shown in Figure 2. UV-vis absorption, EPR, and resonance Raman spectroscopy have revealed that HupD binds a heme with two histidine residues as the axial ligand. ^{105}His and ^{259}His are identified as the axial ligands by site-directed mutagenesis. HupD is the first example of the heme-binding protein having bis-histidine coordination environment among heme-binding proteins working in the bacterial heme acquisition systems. While mutation of ^{259}His to Ala resulted in a loss of heme-binding ability of HupD, the H105A variant of HupD retained heme-binding ability with lower heme-binding affinity compared with wild type. These results suggest that ^{259}His is an essential ligand for heme acquisition by HupD and that ^{105}His might be responsible for the regulation of heme-binding affinity of HupD during heme transport process.

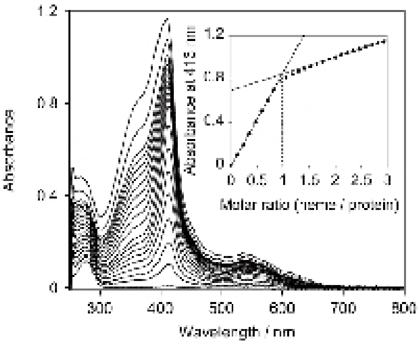

Figure 2. Spectral changes upon titration of apo-HupD with hemin. Inset: Titration curve of hemin binding to apo-HupD measured at 413 nm in 50 mM Tris-HCl (pH 7.4).

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Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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Education

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Professional Employment

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1997	Lecturer, The University of Tokyo
2000	Professor, Nagoya City University
2008	Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience 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"

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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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.

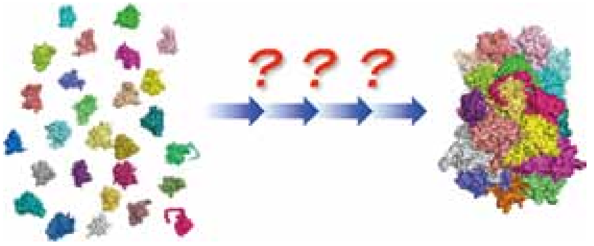

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- Y. Kamiya, T. Satoh and K. Kato, "Recent Advances in Glycoprotein Production for Structural Biology: Toward Tailored Design of Glycoforms," *Curr. Opin. Struct. Biol.* **26**, 44–53 (2014).
- Y. Zhang, T. Yamaguchi and K. Kato, "New NMR Tools for Characterizing the Dynamic Conformations and Interactions of Oligosaccharides," *Chem. Lett.* **42**, 1455–1462 (2013).
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- K. Kato and Y. Yamaguchi, "Glycoproteins and Antibodies: Solution NMR Studies," in *Encyclopedia of Magnetic Resonance*, John Wiley; Chichester, **vol.3**, pp. 1779–1790 (2012).
- O. Serve, Y. Kamiya and K. Kato, "Redox-Dependent Chaperoning, Following PDI Footsteps," *Proteomics Res. J.* **3**, 69–79 (2012).
- Y. Kamiya, M. Yagi-Utsumi, H. Yagi and K. Kato, "Structural and Molecular Basis of Carbohydrate–Protein Interaction Systems as Potential Therapeutic Targets," *Curr. Pharm. Des.* **17**, 1672–1684 (2011).

1. Dynamic Orchestration of Proteasomes

Recently accumulated evidence has demonstrated that the assembly of the eukaryotic 26S proteasome is not due to spontaneous self-organization but due to an ordered process assisted by several proteins called 'proteasome assembly chaperones' that transiently associate with the assembly intermediates at certain steps in the proteasome assembly pathway.

To provide structural basis for quaternary structure formation of the proteasome and its consequent activation, we conducted structural study by employing X-ray crystallography and NMR spectroscopy. By inspection of our structural data, a working model is proposed in which the proteasome assembly chaperones Pba3-Pba4 and Nas2 act as molecular matchmakers and offer checkpoints, respectively, during the proteasome formation (Figure 2).[1,2] The proteasome assembly chaperones can be potential therapeutic targets for drug discovery.[3]

We also performed conformational characterization of an intrinsically disordered protein in complex with an archaeal proteasome activator, PbaB, by NMR spectroscopy combined with small-angle neutron scattering using an inverse contrast matching method.[4]

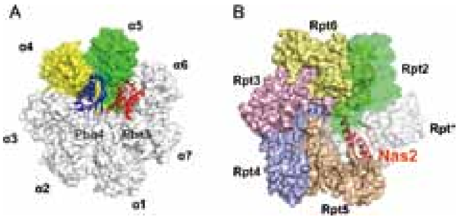

Figure 2. 3D models of (A) the proteasome α-ring complexed with the Pba3–Pba4 heterodimer and (B) the proteasome ATPase ring complexed with Nas2.

2. Functional Mechanisms of Glycans

The carbohydrate chains displayed on proteins play pivotal roles in a variety of molecular recognition events on cell surfaces as well as in intracellular environments. The intermolecular interaction systems involving the carbohydrate moieties could be potential therapeutic targets for various diseases.

In the early secretory pathway, *N*-glycans serve as tags recognized by cargo receptors having lectin activities. Our crystallographic data provide structural basis for disparate sugar-binding specificities in the homologous cargo receptors ERGIC-53 and VIP36, the former of which shows a broader specificity and lower binding affinity to the high-mannose-type oligosaccharides, irrespective of the presence or absence of the nonreducing terminal glucose residue at the D1 arm (Figure 3).[5]

Dystroglycanopathy is a major class of congenital muscular dystrophy that is caused by a deficiency of functional glycans on α-dystroglycan (α-DG) with laminin-binding activity. We demonstrated that a product of a recently identified causative gene for dystroglycanopathy, AGO61, is indispensable for the formation of laminin-binding glycans of α-DG. Furthermore, our results indicate that functional α-DG glycosylation was primed by AGO61-dependent GlcNAc modifications of specific threonine-linked mannosyl moieties of α-DG. These findings provide a key missing link for understanding how the physiologically critical glycan motif is displayed on α-DG and provides new insights on the pathological mechanisms of dystroglycanopathy.[6]

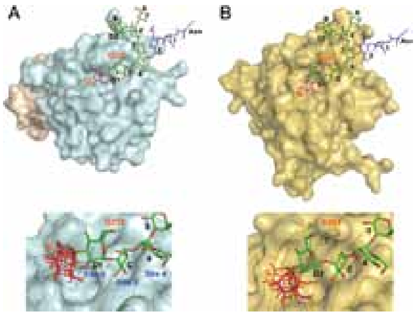

Figure 3. Structural models of the lectin domains of (A) ERGIC-53 and (B) VIP36 with monoglucosylated high-mannose-type oligosaccharides.

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Awards

YAMAGUCHI, Takumi; Presentation Award, The 7th Symposium on Biofunctional Chemistry (2013).
YAMAGUCHI, Takumi; The 3rd NINS Prize for Young Scientists (2014).

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Operation and Design Principles of Biological Molecular Machines

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Keywords Single-Molecule Biophysics, Molecular Machines, Molecular Motors

Activity of life is supported by various molecular machines made of proteins and nucleic acids. These biological molecular machines show high performance such as reaction specificity and energy conversion efficiency, and are superior to man-made machines in some aspects.

One of the representatives of the 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 potential energy.

We will unveil operation principles of biological molecular motors and machines with single-molecule techniques based on optical microscopy. We will also try to create new biological molecular motors and machines to understand their design principles. Our ultimate goal is controlling living organisms with created molecular machines.

Figure 1. A linear molecular motor chitinase. Chitinase moves on the substrate crystalline chitin unidirectionally and processively, driven by the energy of hydrolysis of the chain end of the chitin.

Selected Publications

- R. Iino and H. Noji, "Intersubunit Coordination and Cooperativity in Ring-Shaped NTPases," *Curr. Opin. Struct. Biol.* **23**, 229–234 (2013).
- R. Iino and H. Noji, "Operation Mechanism of F_oF_1-Adenosine Triphosphate Synthase Revealed by Its Structure and Dynamics," *IUBMB Life* **65**, 238–246 (2013).
- Y. Shibafuji, A. Nakamura, T. Uchihashi, N. Sugimoto, S. Fukuda, H. Watanabe, M. Samejima, T. Ando, H. Noji, A. Koivula, K. Igarashi and R. Iino, "Single-Molecule Imaging Analysis of Elementary Reaction Steps of *Trichoderma reesei* Cellobiohydrolase I (Cel7A) Hydrolyzing Crystalline Cellulose I_α and III_I," *J. Biol. Chem.* **289**, 14056–14065 (2014).
- Y. Minagawa, H. Ueno, M. Hara, Y. Ishizuka-Katsura, N. Ohsawa, T. Terada, M. Shirouzu, S. Yokoyama, I. Yamato, E. Muneyuki, H. Noji, T. Murata and R. Iino, "Basic Properties of Rotary Dynamics of the Molecular Motor *Enterococcus hirae* V_1-ATPase," *J. Biol. Chem.* **288**, 32700–32707 (2013).
- R. Watanabe, K. V. Tabata, R. Iino, H. Ueno, M. Iwamoto, S. Oiki and H. Noji, "Biased Brownian Stepping Rotation of F_oF_1-ATP Synthase Driven by Proton Motive Force," *Nat. Commun.* **4**, 1631 (2013).
- 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. Rotary Dynamics of *Enterococcus hirae* V$_1$-ATPase[1]

V-ATPases are rotary molecular motors that generally function as proton pumps. We characterized the rotary dynamics of the V$_1$ moiety of *Enterococcus hirae* V-ATPase (EhV$_1$, Figure 2A) using single-molecule analysis employing a load-free probe (Figure 2B). EhV$_1$ rotated in a counterclockwise direction, exhibiting two distinct rotational states, namely clear and unclear, suggesting unstable interactions between the rotor and stator. The clear state was analyzed in detail to obtain kinetic parameters. The rotation rates obeyed Michaelis-Menten kinetics with a maximal rotation rate (V_{max}) of 107 revolutions/s and a Michaelis constant (K_m) of 154 µM at 26 °C. At all ATP concentrations tested, EhV$_1$ showed only three pauses separated by 120°/turn, and no substeps were resolved, as was the case with *Thermus thermophilus* V$_1$-ATPase (TtV$_1$). At 10 µM ATP ($<<K_m$), the distribution of the durations of the ATP-waiting pause fit well with a single-exponential decay function. The second-order binding rate constant for ATP was 2.3×10^6 M^{-1} s^{-1}. At 40 mM ATP ($>>K_m$), the distribution of the durations of the catalytic pause was reproduced by a consecutive reaction with two time constants of 2.6 and 0.5 ms. These kinetic parameters were similar to those of TtV$_1$. Our results identified the common properties of rotary catalysis of V$_1$-ATPases that are distinct from those of F$_1$-ATPases and furthered our understanding of the general mechanisms of rotary molecular motors.

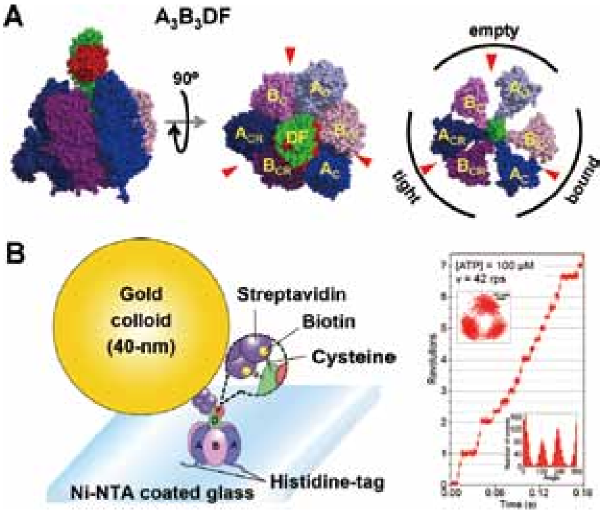

Figure 2. (A) Crystal structure of EhV$_1$. (B) Left, Schematics of the single-molecule rotation assay of EhV$_1$. Right, Example of the rotary motion.

2. Mechanism of Different Susceptibilities of Cellulose I$_\alpha$ and III$_I$ to Hydrolysis by a Linear Molecular Motor Cellulase[2]

A cellulase, *Trichoderma reesei* Cel7A (*Tr*Cel7A) is a linear molecular motor that directly hydrolyzes crystalline celluloses into water-soluble cellobioses. It has recently drawn attention as a tool that could be used to convert cellulosic materials into biofuel. However, detailed mechanisms of action, including elementary reaction steps such as binding, processive hydrolysis, and dissociation, have not been thoroughly explored because of the inherent challenges associated with monitoring reactions occurring at the solid/liquid interface. The crystalline cellulose I$_\alpha$ and III$_I$ were previously reported as substrates with different crystalline forms and different susceptibilities to hydrolysis by *Tr*Cel7A. We observed that different susceptibilities of cellulose I$_\alpha$ and III$_I$ are highly dependent on enzyme concentration, and at nanomolar enzyme concentration, *Tr*Cel7A shows similar rates of hydrolysis against cellulose I$_\alpha$ and III$_I$. Using single-molecule fluorescence microscopy and high-speed atomic force microscopy, we also determined kinetic constants of the elementary reaction steps for *Tr*Cel7A against cellulose I$_\alpha$ and III$_I$. These measurements were performed at picomolar enzyme concentration in which density of *Tr*Cel7A on crystalline cellulose was very low. Under this condition, *Tr*Cel7A displayed similar binding and dissociation rate constants for cellulose I$_\alpha$ and III$_I$ and similar fractions of productive binding on cellulose I$_\alpha$ and III$_I$. Furthermore, once productively bound, *Tr*Cel7A processively hydrolyzes and moves along cellulose I$_\alpha$ and III$_I$ with similar translational rates. With structural models of cellulose I$_\alpha$ and III$_I$, we proposed that different susceptibilities at high *Tr*Cel7A concentration arise from surface properties of substrate, including ratio of hydrophobic surface and number of available lanes (Figure 3).

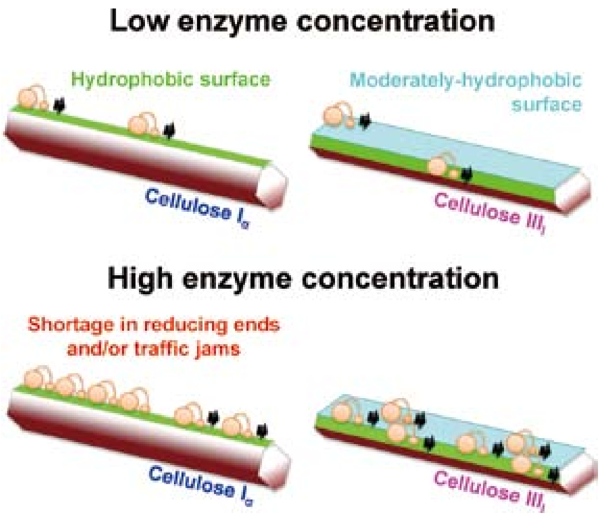

Figure 3. A model of different susceptibilities of cellulose I$_\alpha$ and III$_I$ to hydrolysis by *Tr*Cel7A.

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Structure-Function Relationship of Metalloenzymes

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Keywords Metalloenzyme, Reaction Intermediate, Reaction Mechanism

Metalloproteins are a class of biologically important macromolecules, which have various functions such as oxygen transport, electron transfer, oxidation, and oxygenation. These diverse functions of metalloproteins have been thought to depend on the ligands from amino acid, coordination structures, and protein structures in immediate vicinity of metal ions. In this project, we are studying the relationship between the electronic structures of the metal active sites and reactivity of metalloproteins.

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1. Oxygen-Atom Transfer from Iodosylarene Adducts of a Manganese(IV) Salen Complex: Effect of Arenes and Anions on I(III) of the Coordinated Iodosylarene[1)]

This paper reports preparation, characterization, and reactivity of iodosylarene adducts of a manganese-(IV) salen complex. In order to systematically investigate steric and electronic factors that control reactivity and selectivity, we prepared iodosylarene adducts from iodosylbenzene, iodosylmesitylene, 2,4,6-triethyliodosylbenzene, and pentafluoroiodosylbenzene. We also investigated the effect of anions on I(III) by using chloride, benzoate, and *p*-toluenesulfonate. Spectroscopic studies using ^{1}H NMR, electron paramagnetic resonance, infrared spectroscopy, and electrospray ionization mass spectrometry show that these iodosylarene adducts are manganese(IV) complexes bearing two iodosylarenes as external axial ligands. Reactions with thioanisole under the pseudo-first-order conditions show that the electron-withdrawing pentafluorophenyl group and the *p*-toluenesulfonate anion on I(III) significantly accelerate the oxygen-atom transfer. The high reactivity is correlated with a weakened I–OMn bond, as indicated by IR spectroscopy and mass spectrometry. Stoichiometric reactions with styrenes show that both enantioselectivity and diastereoselectivity are dependent on the arenes and anions on I(III) of the coordinate iodosylarenes. Notably, the pentafluorophenyl group and the *p*-toluenesulfonate anion suppress the *cis*-to-*trans* isomerization in the epoxidation of *cis*-β-methylstyrene. The present results show that iodosylarene adducts of manganese(IV) salen complexes are indeed active oxygen-atom-transfer reagents and that their reactivity and selectivity are regulated by steric and electronic properties of the arenes and anions on I(III) of the coordinated iodosylarenes.

2. Di-μ-oxo Dimetal Core of Mn^{IV} and Ti^{IV} as a Linker Between Two Chiral Salen Complexes Leading to the Stereoselective Formation of Different *M*- and *P*-Helical Structures[2)]

Because of restricted rotational freedom along the metal–metal axis, a di-μ-oxo dimetal core could be an excellent building block to create dinuclear compounds with well-defined stereochemistry, but their stereoselective synthesis remains a challenge. We herein report the formation of di-μ-oxo dimanganese(IV) complexes with tetradentate salen ligands bearing different degrees of steric bulk, in order to study stereochemical aspects of the dimerization reaction that potentially generates multiple stereoisomers. X-ray crystallography shows that the di-μ-oxo dimanganese(IV) complex with salen, where salen is (*R*,*R*)-*N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, adopts a unique structure in which two salen complexes are arranged in an *M*-helical fashion. According to the solution study using ^{1}H, ^{2}H NMR, and circular dichroism spectroscopies, the dimerization reaction is highly diastereoselective in the presence of the *tert*-butyl group at the 3/3' position as a determinant steric factor. In contrast, the di-μ-oxo dititanium(IV) complex with the same salen ligand was previously reported to afford an opposite *P*-helical dimer. The present DFT study clarifies that a less-covalent Ti–O bonding causes a distortion of the di-μ-oxo dititanium(IV) core structure, generating a completely different framework for interligand interaction. The present study provides a solid basis to understand the stereochemistry for the formation of the di-μ-oxo dimetal core.

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Supramolecular Chemical Approach to Construction of Artificial Cell

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Keywords Artificial Cell, Supramolecular Chemistry, Giant Vesicle

Exploring the boundary between a living and non-living matter is one of the most challenging problems for scientists. In order to understand a cell, which is a minimum unit of life, synthesis of an artificial cell from supramolecular chemical approach is a plausible strategy. By using a giant vesicle (GV), which is a supramolecular assembly of amphiphiles, as compartment, we constructed an artificial cellular system in which self-reproduction of GV and the amplification of internal DNA were combined. Such a constructive approach would be a powerful method of elucidating not only the boundary but also the origin of life.

In our laboratory, we aim to construct the following artificial cells: An artificial cell having a cycle of proliferation and an artificial cell which can be self-organized according to its environment.

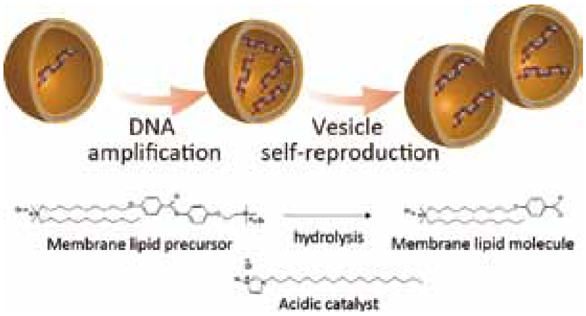

Figure 1. Proliferation of our artificial cellular system based on giant vesicle and structural formula of the molecules in the system.

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).
- T. Sugawara, K. Kurihara and K. Suzuki, “Constructive Approach towards Protocells,” in *Engineering of chemical complexity*, world scientific lecture notes in complex systems, World Scientific Pub. Co. Inc., pp. 359–374 (2013).
- K. Kurihara, K. Takakura, K. Suzuki, T. Toyota and T. Sugawara, “Cell-Sorting of Robust Self-Reproducing Giant Vesicles Tolerant to a Highly Ionic Medium,” *Soft Matter* **6**, 1888–1891 (2010).

1. An Artificial Cell Incorporating a Proliferation Cycle

One of the approaches for exploring the origin of life or elucidating of the functions of life is construction of an artificial cell from chemical approach.[1,2] We have constructed artificial cell which has three basic elements of a cell; information (DNA), compartment (giant vesicle: A supramolecular assembly of amphiphiles) and metabolism (synthetic catalyst).[3] The proliferation of the artificial cell was consisted of amplification of DNA and self-reproduction of GV. This vesicle is consisted of phospholipids, cationic synthesized molecules and cationic catalysts. Here, we added some phospholipids to the GVs for resistance of highly ionic medium and high temperature. First, we encapsulated template DNA and PCR reagents into the GVs and performed polymerase chain reaction to the GV dispersion and then the internal DNA was amplified. Second, we added a precursor of the GV membrane lipid molecule to the GV dispersion subjected to thermal cycles. After addition of the precursor, the GV proliferated accompanying with amplified DNA. From flow cytometric analysis, we found that the division of the GVs was accelerated by the amount of the amplified DNA in the GVs. We speculated that this complex formed by synthetic catalyst and the amplified DNA acted as an active scaffold of hydrolysis of membrane lipid precursor. This result means that information and compartment were combined.

However, this system ceased at the 2nd generation of GV because it does not have a cycle of growth and division. Now, we are constructing the recursive GV system with proliferation cycles, collaborating with Sugawara group (Kanagawa University). By using our vesicular transport system,[4] the 2nd generation of GVs which have no PCR reagents after self-reproduction was replenished by fusing with the conveyer GVs encapsulating the PCR reagents. The replenished GV can amplify the internal DNA and yield 3rd generation of the GV after addition of membrane lipid precursor. This system would lead to an evolvable artificial cellular system.

2. An Artificial Cell Incorporating a Cross-Catalysis System

A cell is a self-organized system which is able to maintain its state due to metabolism. The previous artificial cellular system have been so robust that it can self-reproduce only specific state in the any environments.

We aim to realize a new artificial cellular system in which the GV self-organize its own composition spontaneously according to the environment. In order for GV to self-reproduce and self-maintain, it is necessary to combine metabolism and compartment. We are constructing an artificial cell incorporating a cross-catalysis system. In this system, the GV was reproduced by the catalyst which catalyze the production of the GV membrane lipid molecule. The GV membrane provides the field where the catalyst is synthesized. In addition, by changing the packing parameter of the catalysts on the membrane, the GV collapse when the number of the catalyst increased substantially. This means that the artificial cell incorporating the negative feedback is realized.

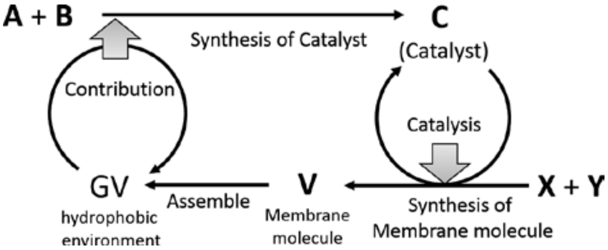

Figure 2. Scheme of new artificial cellular system. The membrane molecules of the GV was synthesized by the catalyst produced in the GV.

References

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2) T. Sugawara, K. Kurihara and K. Suzuki, "Constructive approach towards protocells," in *Engineering of chemical complexity*, world scientific lecture notes in complex systems, World Scientific Pub. Co. Inc., pp. 359–374 (2013).

3) K. Kurihara, M. Tamura, K-I. Shohda, T. Toyota, K. Suzuki and T. Sugawara, *Nat. Chem.* **3**, 775–781 (2011).

4) K. Suzuki, R. Aboshi, k. Kurihara and T. Sugawara, *Chem. Lett.* **41**, 789–791 (2012).

Investigation of Molecular Mechanisms of Channels, Transporters and Receptors

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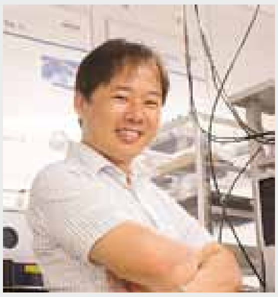

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Keywords Infrared Spectroscopy, Membrane Protein, Ion Channel

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.

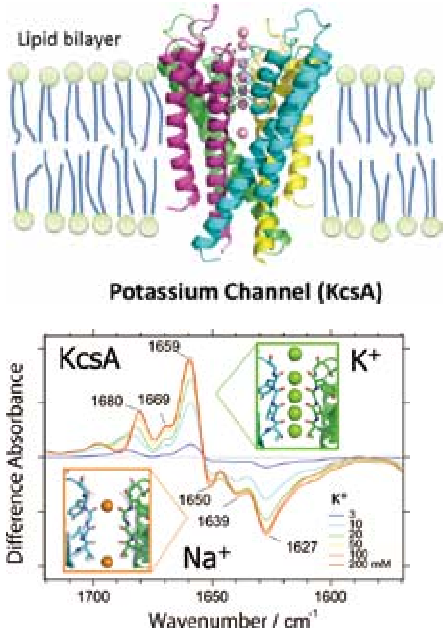

Figure 1. (top) X-ray crystal structure of a potassium ion channel, KcsA. (bottom) The ion-exchange induced difference infrared spectra of KcsA with different potassium ion concentration. The amide I bands are mainly originated from the carbonyl groups of the selectivity filter of KcsA.

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. Formation of Host–Guest Complexes on Gold Surface Investigated by Surface-Enhanced IR Absorption Spectroscopy1)

Surface-enhanced infrared absorption with attenuated total reflection (ATR-SEIRA) is a powerful tool for studying molecular systems at the monolayer level.

Ionophores capture guest ions selectively and carry them across interfaces efficiently. One of crown ethers, 18-crwon-6 (18C6) is one of well known ionophores for a potassium ion. Molecular mechanisms of the ion selectivity of 18C6 have been investigated by SEIRA spectroscopy as a cooperative research with Assoc. Prof. Inokuchi in Hiroshima University.

Thiol derivatives of 18C6 [2-(6-mercaptohexyloxy)methyl-18-crown-6 (18C6-C_1OC_6-SH) and 2-(mercaptomethyl)-18-crown-6 (18C6-C_1-SH)] were synthesized and chemisorbed on a gold surface (Figure 2). Aqueous solutions of MCl salts (M = alkali metals) were put on it to form M^+•18C6-C_1OC_6 and M^+•18C6-C_1 complexes. Infrared spectra of these complexes in the 2000–900 cm^{-1} region were obtained by SEIRA spectroscopy.

As a result, the SEIRA spectra of 18C6 with K^+ are very similar to those with Rb^+ and Cs^+, but largely different from those with Li^+ and Na^+. Moreover, it was demonstrated that the affinity for K^+ is higher than those for other alkali cations. Obtained results proved that SEIRA spectroscopy is a powerful method to examine the structure of host-guest complexes and the solvent effect on them in solutions.

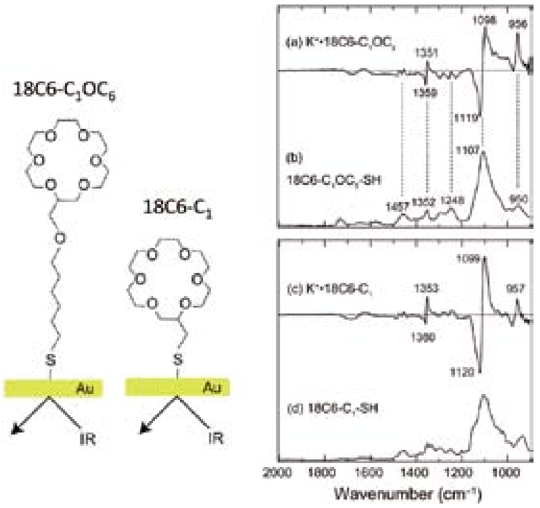

Figure 2. (left) Schematic figures of crown ethers immobilized on the gold surface through a S–Au bond. (right) SEIRA spectra of crown ethers 18C6-C1OC6 (a) and 18C6-C1 (c) recorded after addition of 0.1 M KCl solution. The absorption spectra of the crown ethers (b) and (d) were recorded by a conventional ATR-FTIR method. This figure is reproduced from ref. 1.

2. Deformation of β-Sheet Structures of the GroEL Apical Domain Induced at Sub-Micellar Detergent Condition2)

SEIRA spectroscopy is a useful tool to analyze protein structure as well. GroEL is a chaperonin which refolds denatured proteins with a cofactor GroES by utilizing hydrolysis energy of ATP. Dr. Jin Chen, who was an IMS research assistant professor in Prof. Kuwajima's Group in Okazaki Institute for Integrative Bioscience, studied the property of GroEL for formation of protein nanofibers at sub-micellar detergent condition. To understand the molecular mechanism of the fiber formation, SEIRA analysis on the GroEL apical domain was performed (Figure 3).

The data clearly showed SDS-dependent deformation of β-sheet structures in the GroEL apical domain, which would promote the formation of the nanofiber in the later stage.

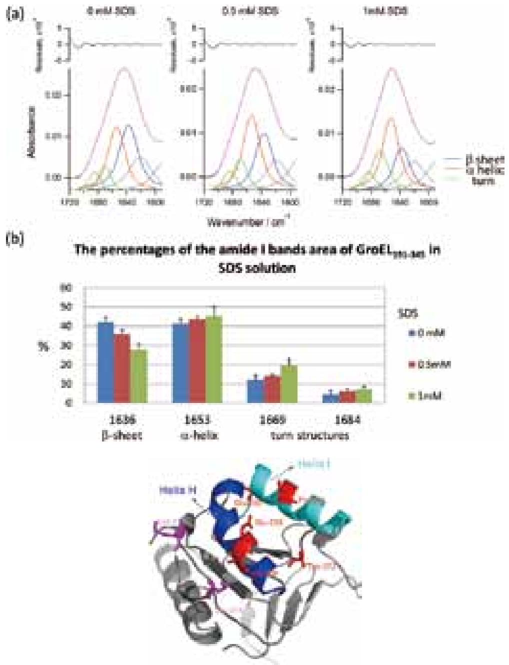

Figure 3. (a) The SEIRA spectra of GroEL apical domain recorded in SDS solution (0, 0.5, and 1 mM). The amide I bands are analyzed by band fitting method. (b) The effect of SDS on the secondary structures of GroEL apical domain. (c) The X-ray crystal structure of GroEL apical domain. This figure is adapted from ref. 2.

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2) J. Chen*, H. Yagi, Y. Furutani, T. Nakamura, A. Inaguma, H. Guo, Y. Kong and Y. Goto, *Sci. Rep.* **4**:5614 (2014).
(*; corresponding authors)

Awards

FURUTANI, Yuji; The 2013 Young Scientist Awards of the Japan Society for Molecular Science.
FURUTANI, Yuji; The 1st BIOPHYSICS Editors' Choice Award (2014).

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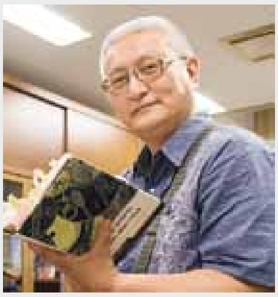
* IMS International Internship Program

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)

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, Prize for Science and Technology

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KOBAYASHI, Noboru
SAKURAI, Fumie
TSUJI, Hiroaki
YAN, Shuo
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TORII, Kaoru
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Secretary
SASAKI, Tokiyo
FUKUSHIMA, Tomoko

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.

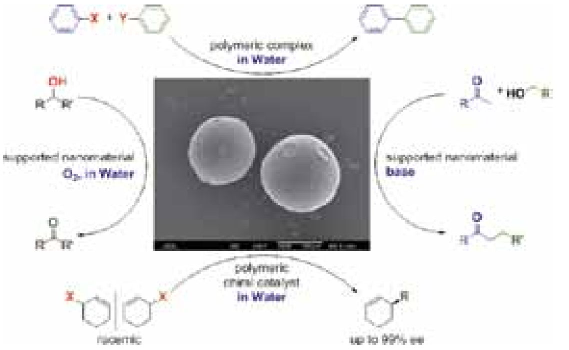

Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

Selected Publications

- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Amphiphilic Self-Assembled Polymeric Copper Catalyst to Parts per Million Levels: Click Chemistry," *J. Am. Chem. Soc.* **134**, 9285–9290 (2012).
- 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. A Palladium-Nanoparticles and Sillicon-Nanowire-Array Hybrid: A Platform for Catalytic Heterogeneous Reactions[1)]

We report the development of a silicon nanowire array-stabilized palladium nanoparticle catalyst, SiNA-Pd. Its use in the palladium-catalyzed Mizoroki-Heck reaction, the hydrogenation of an alkene, the hydrogenolysis of nitrobenzene, the hydrosilylation of an α,β-unsaturated aldehyde, and the C–H bond functionalization reactions of thiophenes and indoles achieved a quantitative production with high reusability. The catalytic activity reached several hundred-mol ppb of palladium, reaching a TON of 2,000,000.

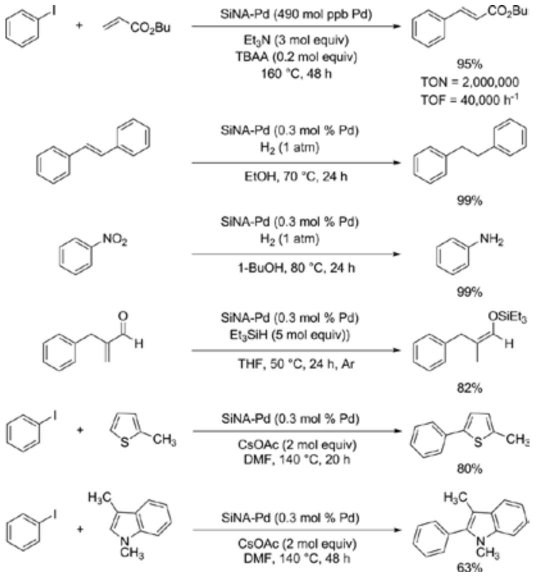

Figure 2. The Mizoroki-Heck reaction, the hydrogeneation of an alkene, the hydrogenolysis of nitrobenzene, the hydrosilation of an α,β-unsaturated aldehyde, and the C–H bond functionalization reactions of a thiophen and a indole catalyzed by SiNA-Pd.

2. Direct Dehydrative Esterification of Alcohols and Carboxylic Acids with a Macroporous Polymeric Acid Catalyst[2)]

A macroporous polymeric acid catalyst was prepared for the direct esterification of carboxylic acids and alcohols that proceeded at 50–80 °C without removal of water to give the corresponding esters with high yield. Flow esterification for the synthesis of biodiesel fuel was also achieved by using a column-packed macroporous acid catalyst under mild conditions without removal of water.

Figure 3. Direct dehydrative esterification of alchols and carboxylic acids with a macroporous polymeric acid catalyst.

3. Asymmetric Sonogashira Coupling with a Chiral Palladium Imidazoindole Phosphine Complex[3)]

The asymmetric Sonogashira coupling of 1-(2,6-dibromophenyl)naphthalene or 4,16-dibromo[2,2]paracyclophane with various terminal alkynes was carried out with a palladium complex of a homochiral imidazoindole phosphine, a derivative of a (3*R*,9a*S*)-2-aryl-[3-(2-dialkylphosphanyl)phenyl] tetrahydro-1*H*-imidazo[1,5*a*]indol-1-one, to give the corresponding axially chiral monoalkynylated biaryl products with up to 72% enantiomeric excess.

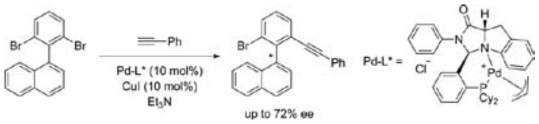

Figure 4. Asymmetric Sonogashira coupling with a chiral palladium imidazoindolephosphine complex.

References

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2) M. Minakawa, H. Baek, Y. M. A. Yamada, J. W. Han and Y. Uozumi, *Org. Lett.* **15**, 5798–5801 (2013).
3) H. Zhou and Y. Uozumi, *Synlett* **24**, 2550–2554 (2013).

Award

UOZUMI, Yasuhiro; The Commendation for Science and Technology by the Minister of MEXT, Prize for Science and Technology (2014).

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 Associate Professor, The Graduate University for Advanced Studies

Awards

2003	The Elizabeth R. Norton Prize for Excellence in Research in Chemistry, University of Chicago
2004	Abbott Laboratories Graduate Fellowship
2005	Damon Runyon Cancer Research Foundation Post Doctoral Research Fellowship
2008	Thieme Chemistry Journals Award

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Secretary
WATANABE, Yoko

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.

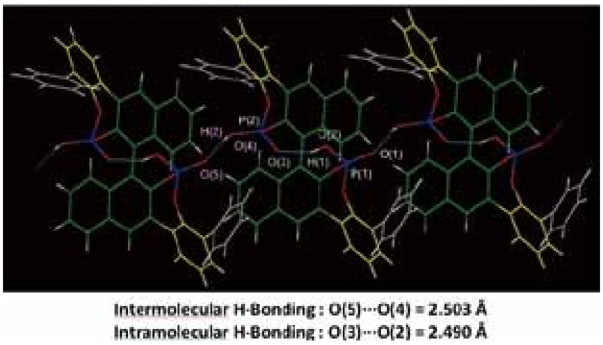


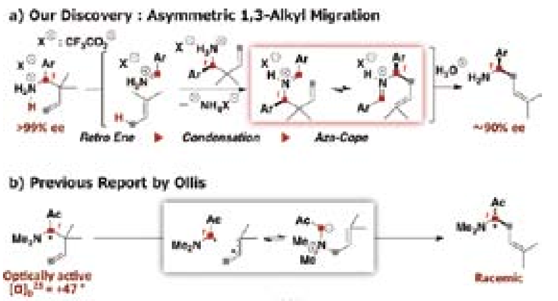
Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

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).

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.



JCS Perkin I 1980, 1458.

Figure 2. 1,3-Alkyl migration of 1-substituted-3-buten-1-amine. a) Our discovery, b) Previous report by Ollis *et al.*

2. Design of C_1 Symmetric Chiral Bis-Phosphoric Acid: Catalytic Enantioselective Diels–Alder Reaction of Acrolein with Amidodienes

We recently developed (*R*)-3,3'-di(2-hydroxy- 3-arylphenyl) binaphthol derived pseudo-C_2 symmetric chiral bis-phosphoric acid which efficiently catalyzed enantioselective Diels–Alder reaction of α,β-unsaturated aldehydes with amidodienes.3) Two cyclic phosphoric acid motifs introduced between the $C_{\mathrm{Naph}}(2)$ and $C_{\mathrm{Ar}}(2)$ positions and between the $C_{\mathrm{Naph}}(2')$ and $C_{\mathrm{Ar}}(2)$ positions represents a characteristic feature of our catalysts. On the basis of our early hypothesis and recent results, the intramolecular hydrogen bonding between two acidic moieties seems to be deeply related to control an atropisomeric behavior of catalyst structure; however, none of systematic study have been employed with respect to the importance of hydrogen bond in the molecular design of chiral catalysts.

We designed a new C_1 symmetric chiral bis-phosphoric acid that possesses an electron-withdrawing group at the $C_{\mathrm{Naph}}(3')$–$C_{\mathrm{Ar}}(3)$, $C_{\mathrm{Ar}}(5)$.4) We found that (i) the stereodynamic behavior of atropisomeric biaryls was controlled by the intervention of hydrogen bond, (ii) the requisite catalyst activity was served by the electronic effect at the $C_{\mathrm{Naph}}(3')$–$C_{\mathrm{Ar}}(3)$, and (iii) the precise distinction of asymmetric reaction space was realized by the different substitution at the $C_{\mathrm{Naph}}(3)$–$C_{\mathrm{Ar}}(3)$ and the $C_{\mathrm{Naph}}(3')$–$C_{\mathrm{Ar}}(3)$.

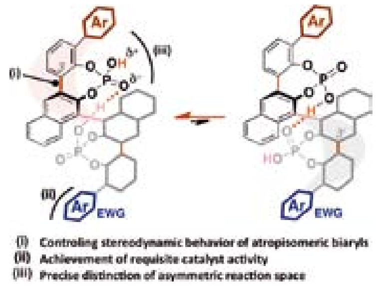


Figure 3. Molecular design of chiral C_1 symmetric bis-phosphoric acid.

3. Halogen Bond Donor Catalyzed Allylation Reaction of Isoquinoline 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 pentafluoroiodebenzene was able to catalyze the allylation reaction of isoquinoline with allylsilatrane to give the corresponding product in good yield.5)

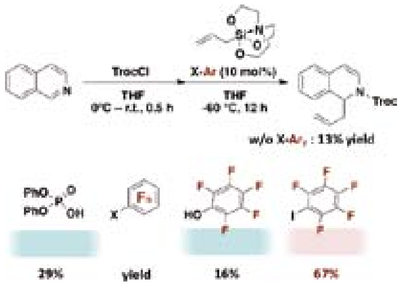


Figure 4. Halogen bond donor catalyzed allylation reaction. Comparison with Brønsted acid/hydrogen bond donor catalyst.

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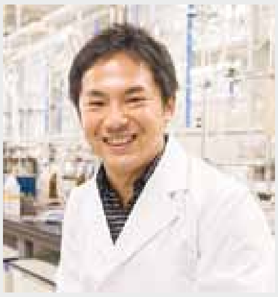
3) N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
4) N. Momiyama, K. Funayama, H. Noda, M. Yamanaka, N. Akasaka, S. Ishida, T. Iwamoto and M. Terada, Manuscript in preparation.
5) N. Momiyama, H. Nishimoto, Y. Kamata and M. Terada, Manuscript 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

2002	JSPS Research Fellow (DC2)
2004	Research Assistant (Postdoc), University of Liverpool
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

Member

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Post-Doctoral Fellow
- VIJAYENDRAN, Praneeth

Graduate Student
- NAKAMURA, Go
- OKAMURA, Masaya
- ITOH, Takahiro
- OKABE, Yuki
- CHINAPANG, Pondchanok
- LIU, Ke
- FUKATSU, Arisa
- FUKAHORI, Yukino
- IZU, Hitoshi
- ENOMOTO, Takafumi

Technical Fellow
- KUGA, Reiko
- KANAIKE, Mari
- SHIBATA, Akane

Secretary
- TANIWAKE, Mayuko

Keywords Metal Complex, Water Oxidation, 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 energy. Our group studies the development of functional metal complexes toward the realization of artificial photosynthesis. Specific areas of research include (i) synthesis of ruthenium-based molecular catalysts for water oxidation and carbon dioxide reduction, (ii) creation of cluster catalysts for multi-electron transfer reactions, (iii) mechanistic investigation into water oxidation catalyzed by metal complexes, (iv) application of proton-coupled electron transfer toward multi-electron transfer reactions, (v) electrochemical evaluation of the activity of molecular catalysts for water oxidation and carbon dioxide reduction, (vi) electrochemical measurement of metal complexes in homogeneous solutions under photoirradiation, and (vii) development of reaction fields via self-assembly of molecular catalysts.

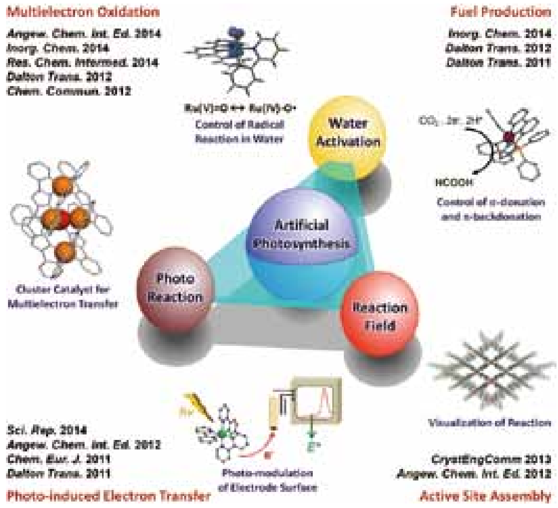

Figure 1. An overview of our work.

Selected Publications

- 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).
- G. Nakamura, M. Okamura, M. Yoshida, T. Suzuki, H. D. Takagi, M. Kondo and S. Masaoka, "Electrochemical Behavior of Phosphine-Substituted Ruthenium(II) Polypyridine Complexes with a Single Labile Ligand," *Inorg. Chem.* **53**, 7214–7226 (2014).
- A. Fukatsu, M. Kondo, M. Okamura, M. Yoshida and S. Masaoka, "Electrochemical Response of Metal Complexes in Homogeneous Solution under Photoirradiation," *Sci. Rep.* **4**, 5327 (2014).
- T. Itoh, M. Kondo, M. Kanaike and S. Masaoka, "Arene-Perfluoroarene Interactions for Crystal Engineering of Metal Complexes: Controlled Self-Assembly of Paddle-Wheel Dimers," *CrystEngComm* **15**, 6122–6126 (2013).
- M. Okamura, M. Yoshida, R. Kuga, K. Sakai, M. Kondo and S. Masaoka, "A Mononuclear Ruthenium Complex Showing Multiple Proton-Coupled Electron Transfer toward Multi-Electron Transfer Reactions," *Dalton Trans.* **41**, 13081–13089 (2012).
- A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka and K. Sakai, "Kinetics and DFT Studies on Water Oxidation by Ce^{4+} Catalyzed by $[Ru(terpy)(bpy)(OH_2)]^{2+}$," *Chem. Commun.* **48**, 239–241 (2012).

1. Electrochemical Response of Metal Complexes in Homogeneous Solution under Photoirradiation[1)]

Photoinduced electron transfer (PET) is a key process in reactions that convert light energy to electrical or chemical energy, both in natural and artificial systems. The efficiency of PET, which largely affects the performance of these systems, is correlated with the redox properties of the photoexcited molecule, which transfers electrons or holes during the PET reaction. Hence, determining the redox potentials of photoexcited molecules is of great significance not only for understanding the mechanisms of PET reactions but also for achieving highly efficient light-energy conversion systems. Electrochemical analysis under photoirradiation should enable the measurement of the redox potentials of excited species. However, reports of the direct electrochemical detection of photoexcited molecules have been limited to only a few examples in which specialized photoelectrochemical instrumentation was required. This limitation may be due to the difficulty to avoid the complication of voltammogram profiles that arises from the unintended side effects of photoirradiation, such as temperature increases and enhanced mass transfer. Thus, the redox potentials of excited states have more commonly been indirectly estimated using the 0-0 transition energy (E_{00}) or the quenching rate constant (k_q). Therefore, the establishment of a versatile methodology for electrochemical measurements under photoirradiation will provide new insights into PET phenomena.

To establish a simple method for directly determining the redox potentials of the photoexcited states of metal complexes, electrochemical measurements under several conditions were performed. The electrochemical response was largely influenced not only by the generation of photoexcited molecules but also by the convection induced by photoirradiation, even when the global temperature of the sample solution was unchanged. The suppression of these unfavourable electrochemical responses was successfully achieved by adopting well-established electrochemical techniques. Furthermore, as an initial demonstration, the photoexcited state of a Ru-based metal complex was directly detected, and its redox potential was determined using a thin layer electrochemical method.

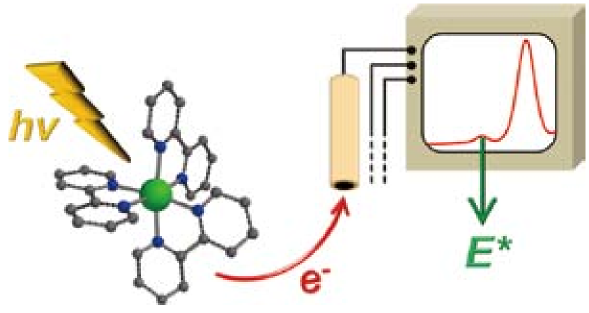

Figure 2. Schematic illustration of electrochemical measurement of a metal complex under photoirradiation.

2. Phosphine-Substituted Ruthenium(II) Polypyridine Complexes with a Single Labile Ligand[2)]

Ruthenium(II) polypyridine complexes with a single labile ligand have been widely studied as catalysts for many chemical reactions including water oxidation, CO_2 reduction, and photoinduced chemical conversions. One of the key strategies in developing ruthenium polypyridine catalysts with novel properties and reactivities is the introduction of phosphine ligands because their σ-donating and π-accepting abilities can influence electronic structures of the ruthenium center. However, few studies examining substitution of phosphine for pyridine moiety have been reported; there have been only a few works of diphosphine-coordinated ruthenium(II) polypyridine complexes, and no crystal structures have been reported. Thus, the investigation of phosphine-substituted ruthenium(II) polypyridine complexes with a single labile is important not only for the design and development of new catalysts but also for an understanding of their basic properties.

We report the synthesis, structural characterization, and electrochemical and spectroscopic properties of a series of ruthenium(II) polypyridine complexes containing 8-(diphenylphosphanyl)quinoline (Pqn), *trans*(P,MeCN)-[Ru(trpy)(Pqn)(MeCN)]$(PF_6)_2$ (*trans*-**PN**) and *cis*(P,MeCN)-[Ru(trpy)(Pqn)(MeCN)]$(PF_6)_2$ (*cis*-**PN**), or 1,2-bis(diphenylphosphanyl)benzene (dppbz), [Ru(trpy)(dppbz)(MeCN)]$(PF_6)_2$ (**PP**). Effects of the number and position of phosphine donors on the structures and electronic properties were investigated on the basis of comparisons with [Ru(trpy)(bpy)(MeCN)]$(PF_6)_2$ (**NN**). The electrochemical measurements of these complexes showed distinct behavior in their reduction reactions; reduction of *cis*-**PN** resulted in *cis–trans* isomerization to *trans*-**PN**, and that of **PP** proceeded via a two electron-transfer reaction. The mechanism of these electrochemical behaviors was explained in conjunction with the liberation of a monodentate labile ligand.

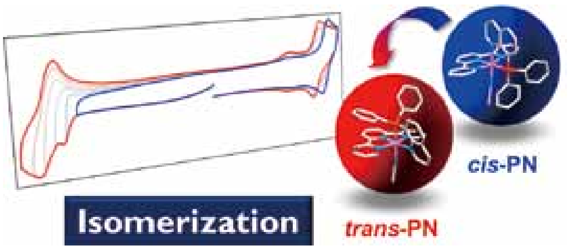

Figure 3. Cyclic voltammograms showing redox-induced *cis–trans* isomerization from *cis*-**PN** to *trans*-**PN**.

References

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2) G. Nakamura, M. Okamura, M. Yoshida, T. Suzuki, H. D. Takagi, M. Kondo and S. Masaoka, *Inorg. Chem.* **53**, 7214–7226 (2014).

Award

OKAMURA, Masaya; Student Lecture Award, The 63rd Conference of Japan Society of Coordination Chemistry (2013).

Visiting Professors

Visiting Professor

KATO, Masako *(from Hokkaido University)*

Construction of Photofunctional Metal Complexes and the Elucidation of Their Properties

In our research group, we focus on the creation of photofunctional metal complexes. **Fabrication of new multichromic materials:** Platinum(II) complexes exhibit characteristic luminescence by assembling. Taking advantage of the characteristic metallophilic interactions between Pt ions, our laboratory have developed new Pt(II) complexes with diimine or cyclometalating ligands exhibiting unique multichromic behaviors. **Fabrication of novel 3d-metal complexes with intense luminescence:** In order to effectively utilize elements, it is important that common metals should be used to fabricate materials with strong emissivity. We have developed various Cu(I) complexes exhibiting intense luminescence. **Fabrication of new photocatalysts based on redox-active organic ligands:** The strategy of our group to contribute to the energy issues is to construct novel photocatalytic systems using common metals instead of precious metals. By using a redox-active ligand, *o*-phenylenediamine, we found a simple metal-complex system for photochemical hydrogen evolution without extra photosensitizers.

Visiting Associate Professor

YORIMITSU, Hideki *(from Kyoto University)*

Synthesis of π-Conjugated Molecules by Means of Organometallics

Porphyrins are an important class of compounds that occur in nature, playing the vital roles in biologically important phenomena such as oxygen transport, oxygen storage, and photosynthesis. Additionally, they constitute useful functional molecules in the field of advanced organic material sciences including organic photovoltaics. These important functions largely rely on their highly conjugated, 18π electronic, aromatic core. Peripheral functionalizations of the core have hence been attracting considerable attentions since they effectively alter the electronic and steric natures of the parent porphyrins to create new π-rich molecules and properties. Along this line, we have been interested in the following topics. 1) Catalytic selective direct arylation of porphyrin periphery, 2) Oxidative fusions of *meso*-(diarylamino)porphyrins and the properties of nanoazagraphene products, 3) Generation and reactions of porphyrinyl Grignard reagents, 4) Synthesis and properties of porphyrin oligomers.

Visiting Associate Professor

KAMIKUKBO, Hironari *(from Nara Institute of Science and Technology)*

Excited-State Proton Transfer in Photoactive Yellow Protein

Green fluorescent protein (GFP) has been used as an effective tool in various biological fields. The large Stokes shift resulting from an excited-state proton transfer (ESPT) is the basis for the application of GFP. The chromophore of GFP is known to be involved in a hydrogen-bonding network. Previous X-ray crystallographic and FTIR studies suggest that a proton wire along the hydrogen-bonding network plays a role in the ESPT. In order to examine the relationship between the ESPT and hydrogen-bonding network within proteins, we prepared an artificial fluorescent protein using a light-sensor protein, photoactive yellow protein (PYP). Although PYP emits little fluorescence, we succeeded to reconstitute an artificial fluorescent PYP (PYP-coumarin) by substituting the pCA with its trans-lock analog 7-hydroxycoumarin. Spectroscopic studies with PYP-coumarin revealed that the chromophore takes an anionic form at neutral pH, but is protonated by lowering pH. Both the protonated and deprotonated forms of PYP-coumarin emit intense fluorescence, as compared with the native PYP. In addition, both the deprotonated and protonated forms show identical λ_{max} values in their fluorescence spectra, indicating that ESPT occurs in the artificial fluorescent protein.

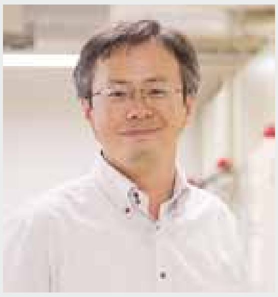
RESEARCH ACTIVITIES

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.

Molecular Origin of 24 Hour Period in Cyanobacterial Protein Clock

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



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Education

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

Professional Employment

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

Awards

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
2002	The Protein Society Annual Poster Board Award

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SUZUKI, Hiroko

Keywords Biological Clocks, Clock Proteins, Slow Dynamics

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 (Figure 1).

Our mission is to explore the frontier in molecular science of the cyanobacterial circadian clock from many perspectives. This Annual Report summarizes our recent activities.

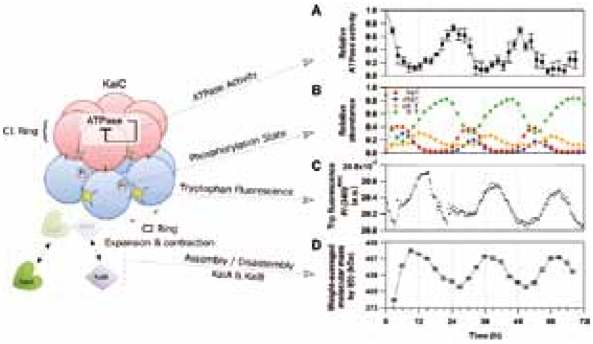

Figure 1. Circadian dynamics of cyanobacterial clock protein KaiC. The C1 and C2 domains in each protomer of KaiC are drawn as red and blue spheres, respectively. Expansion and contraction motions of the C2 ring (B, C) in solution serves as a timing cue for assembly/disassembly of KaiA and KaiB (D), and is interlocked with its C1 ATPase udder a control of negative-feedback regulation (A).

Selected Publications

- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).
- 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).

* IMS International Internship Program

1. Tracking the Ticking of Cyanobacterial Clock Protein KaiC in Solution[3)]

The ATPase activity of KaiC alone is strongly correlated with the oscillatory period of the Kai oscillator. This correlation suggests that the ATPase activity of KaiC is one of the period-determining factors of the Kai oscillator. Therefore, the determination of the structural change of KaiC interlocked with the ATPase activity is of great of importance.

To track the dynamic transition of KaiC, we recorded the time evolution of intrinsic tryptophan (Trp) fluorescence from KaiC contained in the Kai oscillator. KaiC is a dumbbell-shaped molecule composed of tandemly duplicated N-terminal (C1) and C-terminal (C2) domains. Six protomers are assembled into a hexamer to attain a double-doughnut shape. Two tryptophan (Trp) residues located in the protomer–protomer interface of the C2 domain can serve as a sensitive probe to monitor the potential structural transition of the C2 ring. The intensity of the Trp fluorescence from KaiC revealed a rhythmic fluctuation with the period of approximately 24 h (Figure 1, panel C). This is the first experimental evidence that demonstrated a dynamic structural transition of the C2 ring of KaiC in solution.

Concomitantly with the Trp-fluorescence dynamics, KaiC underwent a periodic change in its phosphorylation state (Figure 1, panel B). KaiC has the two phosphorylation sites, *i.e.*, Ser431 and Thr432, in the C2 domain, and both residues are phosphorylated and then dephosphorylated in a programmed sequence during the phosphorylation cycle as follows: KaiCS/pT → KaiCpS/pT → KaiCpS/T → KaiCS/T (where ‘S’ represents Ser431, ‘pS’ represents phosphorylated Ser431, ‘T’ represents Thr432, and ‘pT’ represents phosphorylated Thr432). Interestingly, the Trp fluorescence was maximized at the timing when the KaiCpS/T state was populated (Figure 1, panels B and C). The result suggests the Trp fluorescence is an excellent measure of the phosphor-coupled transition of the C2 ring in KaiC.

2. Visualization of Dynamic Structural Changes of KaiC Using Small-Angle X-Ray Solution Scattering Technique[1–3)]

To visualize the C2-ring dynamics confirmed by tracking Trp fluorescence, we measured the small-angle x-ray scattering (SAXS) from KaiC in solution. To obtain the SAXS data of biological samples in solution, one must first record the scattering intensity of the sample and then that of the matching buffer in the separate experiment, and finally find the difference between two intensities. The cuvette used for conventional SAXS experiments has only a single observation chamber in order to ensure the qualitative subtraction of the scattering contributed by the solvent molecules. On the other hand, the use of the single-chamber cuvette makes both the experiment and analysis time-consuming.

To record the SAXS pattern of KaiC both efficiently and qualitatively, we designed and constructed an eight-chamber cuvette (octuplet cuvette), each chamber of which was fabricated so uniformly to ensure the inter-chamber subtraction. The developed cuvette enabled us to acquire SAXS dataset of KaiC roughly 10 times faster without any significant degradation of data quality.

On the basis of the obtained SAXS data, we built low-resolution models of the KaiC hexamer. The overall shape is almost unchanged in the transition from KaiCS/pT to KaiCpS/pT, whereas the radius of the C2 ring is dramatically enlarged in the subsequent transition from KaiCpS/pT to KaiCpS/T. The expanded C2 ring is partly contracted in the transition from KaiCpS/T to KaiCS/T, and is further contracted in the subsequent transition from KaiCS/T to KaiCS/pT. The present model suggests that KaiC ticks through expanding and contracting motions of the C2 ring.

The dynamic motion of the C2 ring uncovered throughout our study is chronobiologically meaningful, we believe, in terms of the elucidation of the key conformational change tightly coupled to the period-determining ATPase of KaiC. Our group is trying to improve spatio-temporal resolution of the experiments so as to draw a more dynamic and detailed picture of KaiC ATPase.

3. Instrumentation for the Molecular Origin of 24 Hour Period in Cyanobacterial Circadian Clock

How can biological-clock systems be so slow and stable? It is important to revisit the biological and structural backgrounds for the slowness and specificity both experimentally and theoretically. For this purpose, much effort has been focused on designing dedicated instrumentations for the molecular origin of the circadian period. We have made considerable improvements of instrument stability, signal-to-noise ratio, time resolution, temperature control, automated high-throughput measurements each for fluorescence tracking system,[1)] auto-sampling device (unpublished work), HPLC (unpublished work), FTIR (unpublished work) and so on. Using the developed device, we recently succeeded in site-specific monitoring of conformational change of KaiC in solution, and also in identifying a core process of generating circadian periodicity in cyanobacterial circadian clock.[4)]

4. Bio-SAXS Activity in IMS

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

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2) A. Mukaiyama, T. Kondo and S. Akiyama, *SPring-8 Research Frontiers 2011* 47–48 (2012).
3) S. Akiyama and T. Hikima, *J. Appl. Crystallogr.* **44**, 1294–1296 (2011).
4) A. Mukaiyama and S. Akiyama, Submitted.
5) R. Kojima, M. Okumura, S. Masui, S. Kanemura, M. Inoue, M. Saiki, H. Yamaguchi, T. Hikima T, M. Suzuki, S. Akiyama and K. Inaba, *Structure* **22**, 431–443 (2014).

Award

ABE, Jun; Best Presentation Award at Biophysical Society-Chubu-Annual Meeting (2014).

Protein Design Using Computational and Experimental Approaches

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Education

2001	B.S. Kobe University
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Professional Employment

2003	JSPS Research Fellow
2006	Postdoctoral Fellow, Kobe University
2007	Postdoctoral Fellow, Kyoto Universtiy
2007	JSPS Postdoctoral Fellow for Research Abroad
2009	Postdoctoral Fellow, University of Washington
2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2014	JST-PRESTO Researcher (additional post) (–2017)

Awards

2013	Young Scientist Award, The 13th Annual Meeting of the Protein Science Society of Japan
2013	Young Scientist Award, The 51st Annual Meeting of the Biophysical Society of Japan

Member
Research Fellow
KOGA, Rie
Secretary
SUZUKI, Hiroko

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).
- J. Fang, A. Mehlich, N. Koga, J. Huang, R. Koga, M. Rief, J. Kast, D. Baker and H. Li, "Forced Protein Unfolding Leads to Highly Elastic and Tough Protein Hydrogels," *Nat. Commun.* **4**:2974 (2013).

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 tertiary folded structures are determined by the local backbone structures rather than the details of amino acid sequences.

References

1) S. J. Fleishman, S. D. Khare, N. Koga and D. Baker, *Protein Sci.* **20**, 753–757 (2011).
2) N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, *Nature* **491**, 222–227 (2012).
3) J. Fang, A. Mehlich, N. Koga, J. Huang, R. Koga, M. Rief, J. Kast, D. Baker and H. Li, *Nat. Commun.* **4**:2974 (2013).

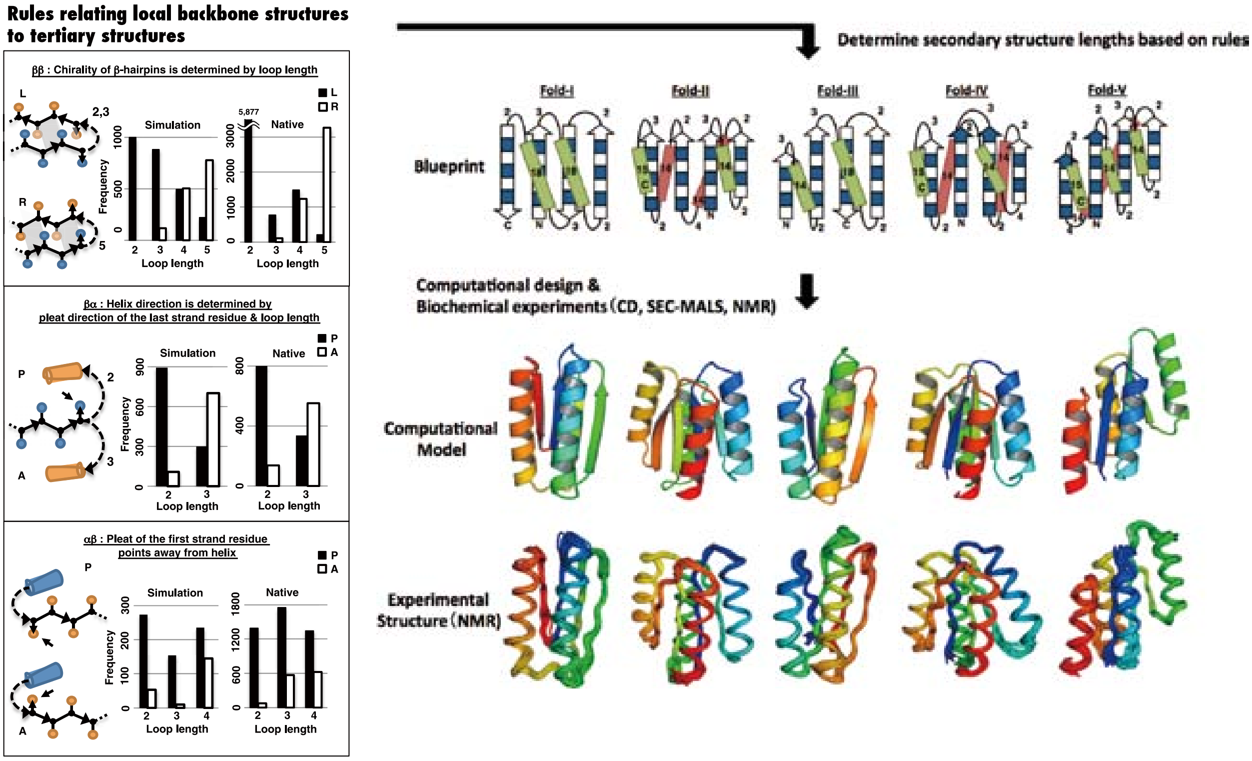

Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Awards

KOGA, Nobuyasu; Young Scientist Award, The 13th Annual Meeting of the Protein Science Society of Japan 2013.
KOGA, Nobuyasu; Young Scientist Award, The 51st Annual Meeting of the Biophysical Society of Japan 2013.

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Education

2008	D.Sc. Kyoto University

Professional Employment

2008	JPSP Postdoctoral Fellow for Research Abroad, University of California, Berkeley
2010	Postdoctoral Fellow, Lawrence Berkeley National Laboratory
2012	Research Associate Professor, Institute for Molecular Science

Member

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FUJIHASHI, Yuta

Secretary
YAMADA, Mariko

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

Photosynthesis provides the energy source for essentially all living things on Earth, and its functionality has been one of the most fascinating mysteries of life. 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.[1)]

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).
- A. Ishizaki and G. R. Fleming, "Theoretical Examination of Quantum Coherence in a Photosynthetic System at Physiological Temperature," *Proc. Natl. Acad. Sci. U.S.A.* **106**, 17255–17260 (2009).
- G. S. Schlau-Cohen, A. Ishizaki, T. R. Calhoun, N. S. Ginsberg, M. Ballottari, R. Bassi and G. R. Fleming, "Elucidation of the Timescales and Origins of Quantum Electronic Coherence in LHCII," *Nat. Chem.* **4**, 389–395 (2012).
- 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]

1. Impacts of Protein-Induced Fluctuations upon Quantum Mechanically Mixed Electronic and Vibrational States in Photosynthetic Energy Transfer and 2D Electronic Spectra

Initially, 2D electronic spectroscopic experiments were conducted for the Fenna-Mathews-Olson (FMO) complexes isolated from green sulfur bacteria at a cryogenic temperature, 77 K and revealed the presence of quantum beats lasting for 660 fs. [Engel, *et al. Nature* **446**, 782–786 (2007).] However, it is generally thought that the coherence at physiological temperatures is fragile compared to that at cryogenic temperatures because amplitudes of environmental fluctuations increase with increasing temperature. To clarify this issue, a theoretical examination on lifetimes of electronic coherence in the FMO complex. Consequently, it was predicted that electronic coherence in the FMO complex might persist for 700 fs and 300 fs at 77 K and 300 K, respectively.2) These theoretical predictions were consistent with the initial experimental observation at a cryogenic temperature and newer experimental results at physiological temperatures of the FMO complex. However, Panitchayangkoon *et al.* [*Proc. Natl. Acad. Sci. U.S.A.* **107**, 12766–12770 (2009).] showed that quantum beats in the FMO complex persist for at least 1.5 ps at a cryogenic temperature, while the theoretical model did not produce electronic coherence with lifetime of 1.5 ps. Hence, signatures of nuclear vibrational contributions in 2D spectroscopy have attracted great interest of late, in particular to interpret the oscillatory transients observed for light-harvesting complexes that persist much longer than predicted electronic dephasing times. Several independent publications have alluded to nuclear vibrational effects as an explanation for the long-lived beatings.

In photosynthetic pigment-protein complexes, the Huang-Rhys factors of chlorophyll/bacteriochlorophyll molecules are generally thought small, suggesting that the photophysics therein is primarily electronic in nature, rather than vibrational. Indeed, the recent 2D electronic experiments on BChl molecules in solution did not find significant vibrational coherences. Concerning this point, Christensson *et al.* [*J. Phys. Chem. B* **116**, 7449–7454 (2012).] proposed that resonance between electronic and Franck-Condon active vibrational states serves to create vibronic excitons, *i.e.* quantum mechanically mixed electronic and vibrational states. Such states have vibrational characters and have enhanced transition dipole moments owing to intensity borrowing from the strong electronic transitions. Along this line it was discussed that coherent excitation of the vibronic excitons produces oscillations in 2D signal that exhibit picosecond dephasing time. Tiwari, Peters, and Jonas pointed out that the excitonically mixed electronic and vibrational states lead to an enhancement of the excitation of vibrational coherences in the electronic ground state as well. [*Proc. Natl. Aca. Sci. U.S.A.* **110**, 1203–1208 (2013).] It was also argued that this effect could explain the long-lived oscillations in the FMO complex.

The quantum mechanically mixed electronic and vibrational states or the vibronic excitons are plausible as an explanation for long-lived spectral beatings in 2D electronic spectra. However, a question naturally arises concerning the interplay between the vibronic resonance and fluctuations in electronic energies induced by the environmental dynamics. In general, energy eigenstates due to quantum mixing of the electronic and vibrational excitations are obtained via diagonalization of the Hamiltonian comprising the Franck-Condon transition energies and electronic interactions. It should be noticed that these are independent of any information on the environment such as temperature, reorganization energy, and fluctuations. Concerning this point, Ishizaki and Fleming3) characterized the impact of the surrounding environments upon the quantum delocalization with the use of the concurrence. They visually demonstrated that smaller electronic coupling, larger reorganization energy, and higher temperature cause the dynamic localization, even in the case that two electronic states resonate in a coupled homo-dimer. Recently, Ishizaki4) explored the influence of timescales of the environment-induced fluctuations upon the quantum mixing between electron donor and acceptor molecules in photo-induced electron transfer reaction. It was demonstrated that fast fluctuation and correspondingly fast solvation destroys the quantum mixing between the donor and acceptor in the vicinity of the crossing point of the diabatic free energy surfaces, leading to a diabatic reaction, whereas slow fluctuation sustains the quantum mixing and prompts the electron transfer reaction in an adiabatic fashion. Therefore, it is natural to raise a question of whether dynamic interaction with the electronic and vibrational states and the environment will change the nature of the quantum mechanically mixed electronic and vibrational states.

The main purpose of this project is to explore impacts of environment-induced fluctuations upon the quantum mechanically mixed electronic and vibrational states through calculations of electronic energy transfer dynamics and 2D electronic spectra. Further, we investigated to what extent vibrational modes play a role in electronic energy transfer dynamics under the influence of the environment-induced fluctuations. We found that the quantum mechanically mixed electronic and vibrational states does not paly an important role in photosynthetic energy transfer dynamics contrary to the prediction by the community although they induced longer-lived quantum beats in 2D electronic spectra of photosynthetic light harvesting pigment-protein complexes.

References

1) A. Ishizaki and G. R. Fleming, *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012).
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3) A. Ishizaki and G. R. Fleming, *New J. Phys.* **12**, 055004 (13 pages) (2010).
4) A. Ishizaki, *Chem. Lett.* **42**, 1406–1408 (2013).

Ultimate Quantum Measurements for Quantum Dynamics

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2013	FQXi Essay Contest Fourth Prize
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- DI MOLFETTA, Giuseppe[‡]
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Keywords Quantum Measurement, Photophysics

Due to great development on experimental technologies, it is possible to capture quantum dynamics in some physical and chemical systems. On the other hand, all experiments are in principle open and dissipative systems. Up to now, the well explained experiments are approximated to the equilibrium situation. However, by recent technological development, some experiments reach to a transition from equilibrium to non-equilibrium situations. While there are the well-known tools on the non-equilibrium situations; the linear response theory and the Keldysh Green function method, this analysis cannot basically catch dynamical situations. Our goal is to construct the time-resolved theoretical models included the non-equilibrium situations. However, the quantum measurement theory is needed on measuring quantum dynamics, especially considering the measurement back action. Our current activities are to resolve how sensitive (quantum) measurement can we carry out in principle, to build up some toy models on quantum dynamic and to explain unique quantum-mechanical phenomena using precise quantum-state engineering technology.

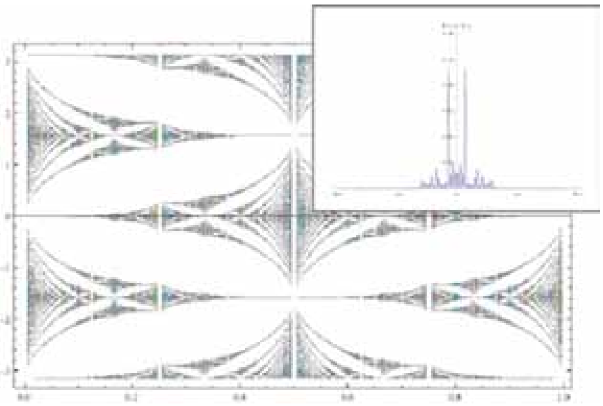

Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called Hofstadter's butterfly to show the multi-fractal structure.

Selected Publications

- Y. Shikano and A. Hosoya, "Weak Values with Decoherence," *J. Phys. A* **43**, 025304 (15 pages) (2010).
- Y. Shikano and H. Katsura, "Localization and Fractality in Inhomogeneous Quantum Walks with Self-Duality," *Phys. Rev. E* **83**, 031122 (7 pages) (2010).
- A. Noguchi, Y. Shikano, K. Toyoda and S. Urabe, "Aharonov-Bohm Effect with Quantum Tunneling in Linear Paul Trap," *Nat. Commun.* **5**, 3868 (6 pages) (2014).
- H. Kobayashi, K. Nonaka and Y. Shikano, "Stereographical Visualization of a Polarization State Using Weak Measurements with an Optical-Vortex Beam," *Phys. Rev. A* **89**, 053816 (5 pages) (2014).

1. Quantum Measurement with Higher Order Gaussian Modes¹⁾

We propose a stereographical-visualization scheme for a polarization state by two-dimensional imaging of a weak value with a single setup. The key idea is to employ Laguerre Gaussian modes or an optical vortex beam for a probe state in weak measurement. Our scheme has the advantage that we can extract information on the polarization state from the single image in which the zero-intensity point of the optical vortex beam corresponds to a stereographic projection point of the Poincaré sphere. We experimentally perform single-setup weak measurement to validate the stereographical relationship between the polarization state on the Poincaré sphere and the location of the zero-intensity point.

2. Quantum Measurement Sensitivity without Squeezing Technique²⁾

The weak measurement was proposed in the context of the time-symmetric quantum measurement without collapsing the quantum state. The weak value as the measurement outcome of the weak measurement can exceed the eigenvalue. By this fact, the signal can be amplified. This is called the weak-value amplification. To study the invisible region under the standard technique, there are several studies on the weak-value amplification. Here, the following question arises. How can the signal maximize? To solve this problem, the probe wave function should be changed from the Gaussian distribution, which is originally used. We show the probe wave function to maximize the shift while this mode is not the propagation mode in light.

3. Discrete Time Quantum Walk as Quantum Dynamical Simulator³⁾

Constructing a discrete model like a cellular automaton is a powerful method for understanding various dynamical systems. However, the relationship between the discrete model and its continuous analogue is, in general, nontrivial. As a quantum mechanical cellular automaton, a discrete-time quantum walk is defined to include various quantum dynamical behavior. Here we generalize a discrete-time quantum walk on a line into the feed-forward quantum coin model, which depends on the coin state of the previous step. We show that our proposed model has an anomalous slow diffusion characterized by the porous-medium equation, while the conventional discrete-time quantum walk model shows ballistic transport.

4. Aharonov-Bohm Effect with Quantum Tunneling⁴⁾

A quantum tunneling is also one of the unique quantum mechanical phenomena. However, nobody has yet measured a tunneling particle. There are still many quantum mysteries. While we have known that a tunneling particle can be coupled to an electromagnetic field, we have not yet demonstrated a coupling between a tunneling particle and a vector potential of the electromagnetic field. This effect is called the Aharonov-Bohm effect.

Our experimental setup done in Urabe group, Osaka University uses an ion trap system. The ion trap system is one of the great candidates to implement a quantum computer and a quantum simulation. Especially, a linear Paul trap, which is also used in our experiment, has the high scalability under the one-dimensional quantum system due to the great development of quantum information technology. While the two-dimensional structure of ions is very difficult to be cooled down in the linear Paul trap, we found that we can manipulate the almost ground state of the ion rotational motion by the laser cooling technique. This is a new quantum technology to implement a two-dimensional quantum simulation and a quantum computation used in a liner Paul trap. Then, we realized the almost ground state of rotational mode of three calcium ions arranged to a triangular structure. The distance between two ions is 6.8 micro meter. This ground state has the two structures, upward and downward triangles. This can be taken as the quantum rotor, which is often used in molecular science such as a diatomic molecule, with a quantum tunneling region. We confirmed that this transition is led by quantum tunneling even in the large tunneling region. Since we cannot distinguish clockwise and anticlockwise transitions, this system can be taken as the double-slit experiment. Changing the strength of the magnetic field, we showed that the transition probability was oscillated. This oscillation can be predicted by Aharonov-Bohm effect.

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4) A. Noguchi, Y. Shikano, K. Toyoda and S. Urabe, *Nat. Commun.* **5**, 3868 (6 pages) (2014).

Awards

SHIKANO, Yutaka; FQXi (Foundational Questions Institute) Essay Contest “It from Bit or Bit from It” Fourth Prize. (2013)
SHIKANO, Yutaka; 2013 Quantum Information Processing Top Reviewers.
SHIKANO, Yutaka; Research Foundation for Opto-Science and Technology Research Award (2014).

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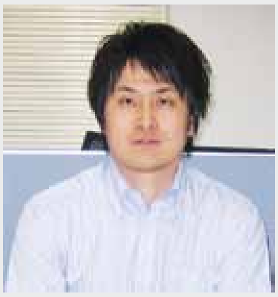
Study of Ion Conductive Materials for Novel Energy Storage/Conversion Devices

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



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Keywords Solid State Ionics, Oxyhydride, Battery, Energy Storage/Conversion

Recently, the demands for advanced electrochemical devices providing high energy density have been growing because of the expansion in application and a need for diversification of energy sources. In order to achieve the requirement, it will be essential not only to improve the existing devices such as lithium secondary batteries and fuel cells, but also to develop a novel energy storage/conversion system (Figure 1). In other words, a development of a novel electrochemical device possessing excellent battery performances that would be required in future is not an extension of the research on the existing devices. On the basis of these backgrounds, we are tackling two research topics; (i) improvement of battery performance with controlling the interface between electrode and electrolyte in lithium secondary batteries (ii) the exploration of novel ion conductive phenomena in solid.

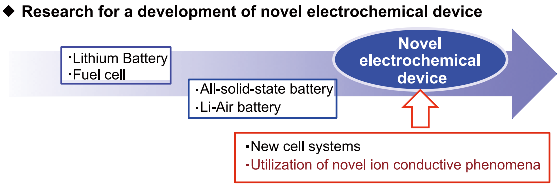

Figure 1. The concept of our research toward the realization of new electrochemical device.

(i) Control of the Cathode/Electrolyte-Interface in Lithium Batteries for Enhancement of the Performance

A surface modification of the cathode materials for lithium batteries with other metal oxides or phosphate is suggested as an effective method to inhibit the capacity degradation for lithium batteries. The main role of the surface modification layer has been considered the protection of a surface crystallinity of cathode materials from side reactions with electrolyte, but it has not been fully understood. To clarify the role of a surface modification, we examine the crystal structure of the modified cathode material, the chemical bonding state of coating layer and deterioration behavior of the cathode material using *ex situ* X-ray diffraction, transmission electron microscope and Hard X-ray photoelectron spectroscopy.

(ii) Synthesis and Property of Hydride Conductive Oxyhydride

We focus on hydride ions (H^-) as a new mobile ion. Hydride ion conductors are the new frontier materials in the research field of solid-state ionics and electrochemistry. Indeed, hydride ion conduction is particularly attractive for electrochemical devices such as fuel cells and batteries, because hydride ions have suitable ionic radii as mobile ions and strong reducing properties. The ionic radii of hydride ions are similar to oxide and fluoride ions, which may provide high ionic conduction in the crystal lattice. The standard potential for H^-/H_2 at about –2.3 V is comparable to the value of –2.4 V for Mg/Mg^{2+}; therefore, energy storage/conversion devices effectively utilizing a H^- conduction phenomenon and the redox reaction of H^-/H_2 are expected to show high energy density. However, the ionic conducting characteristics of hydride H^- ions are not established yet and the interplay between elementary H^- mobility, lattice structure, functional properties and materials synthesis are mostly lacking. Although a possibility of H^- conduction was indicated in several materials, the conclusive evidence for pure hydride ion conduction has not been provided yet, due to difficulties in identifying hydride ions. Recently, our group reported for the first time pure H^- conductivity in new oxyhydrides. We try to synthesis new H^- conductive materials on the basis of our previous works.

Open up Future Electronics by Organic Molecules

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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.

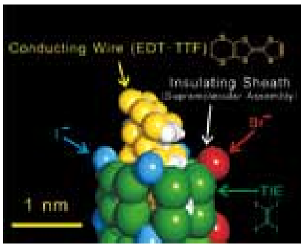

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- 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).
- Y. Kawasugi, H. M. Yamamoto, N. Tajima, T. Fukunaga, K. Tsukagoshi and R. Kato, "Field-Induced Carrier Delocalization in the Strain-Induced Mott Insulating State of an Organic Superconductor," *Phys. Rev. Lett.* **103**, 116801 (4 pages) (2009).
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1. Field-Induced Superconductivity in an Organic Mott-FET[1)]

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. In our previous works, a tensile strain from FET substrate altered its ground state into a Mott-insulating state, when its thin (100–300 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 tensile strain that originates in mismatching of thermal expansion coefficients between κ-Br (30 ppm/K) and Si substrate (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 can be realized when the tensile strain is much weaker. To achieve such a mixed state (or, percolate-superconducting state) in the device, where phase-separation occurs between superconducting and Mott-insulating states, we have chosen Nb-doped SrTiO$_3$ 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. After lamination of κ-Br on the substrate, the Mott-FET device which showed a weakly insulating behavior at low temperature was fabricated (Figure 2).

Upon application of a positive gate voltage, the resistivity goes down and weakly metallic behavior is observed at $V_G > 2$ V. By further increasing the gate voltage up to 8 V, the device shows a sudden drop of resistivity around 5 K, which can be attributed to superconductivity. Taking into account of bistable IV characteristics observed in the low resistance region, the above transition can be understood as a percolation transition of superconducting islands that is induced by the electrostatic doping of electrons. The transition temperature increases as the gate voltage rises and saturates around $V_G = 11$ V. This result is the first example of field-induced superconductivity in organic materials, and can be utilized for uncovering a phase diagram of organic Mott system in the simultaneous control of band filling and band width.

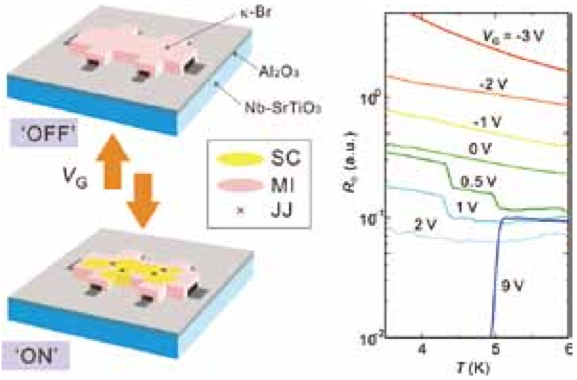

Figure 2. Device schematic (left) and temperature dependency of resistance at various gate voltages (right).

2. Strain-Tunable Organic FET with Strongly Correlated Electron Systems[2)]

Organic materials are soft and can be stretched even at low temperature. Our organic Mott-FETs are also soft enough to be compressed or expanded with a plastic substrate and show a band-width-controlled Mott/superconducting transitions. This kind of lattice modulation has been demonstrated in our recent experiments by mechanically pushing a poly-ethylene naphthalate (PEN) substrate covered with gold gate electrode and parylene-C dielectric from the back side (Figure 2). The organic Mott-insulator κ-(BEDT-TTF)Cu[N(CN)$_2$]Cl (κ-Cl) laminated on top of the substrate exhibited superconductor-to-insulator transition by bending the substrate where the surface has an effect of tensile strain in a longitudinal direction. The strain necessary for this transition is only 0.3% while the resistance change reached ten orders of magnitude, which demonstrates high sensitivity of the Mott-insulator. The phase diagram obtained by simultaneous scans of strain and temperature well reproduces that of hydrostatic pressure. This means that one-dimensional tensile strain corresponds to an effective negative pressure in κ-Cl system.

Then, a field-effect was examined by applying a gate electric field. The transfer characteristics at higher tensile strain showed only moderate device mobility of around 5 cm^2/Vs. When the system was forced to stay in a mixed phase state, where superconducting and Mott-insulating phases coexist, however, the electric-field-effect maximized to show device mobility up to 5900 cm^2/Vs. This high response of the device can be attributed to an increase of superconducting fraction at application of gate voltage. In order to examine the above hypothesis, we have applied a magnetic field up to 7 T. Indeed, the field-effect has been considerably suppressed because the superconducting phases are destroyed by the magnetic field. This electric-field-induced superconductivity seems to originate from a decrease of Coulomb repulsion among carriers by electrostatic doping effect.

(BEDT-TTF = bis(ethyeleneditihio)tetrathiafulvalene)

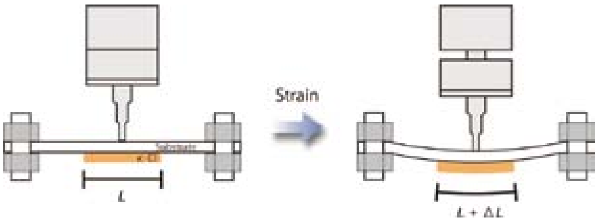

Figure 3. Side-view schematic for flexible organic Mott-FET device.

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2) M. Suda, Y. Kawasugi, T. Minari, K. Tsukagoshi, R. Kato and H. M. Yamamoto, *Adv. Mater.* **26**, 3490–3495 (2014).

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Synthetic Inorganic and Organometallic Chemistry of Transition Metals

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2007 The Japan Society of Coordination Chemistry (JSCC) Award for Young Chemists
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Keywords Coordination Chemistry, Organometallic Chemistry, Mechanism of Catalysis

Our research focuses mainly on two topics in inorganic and organometallic chemistry: i) Synthesis and structural elucidation of a new class of transition metal complexes; ii) elucidation of reaction patterns and mechanism of reactive transition metal complexes. Novel synthetic methods are developed to realize a new class of transition metal complexes. Some transition metal complexes are converted to more reactive forms, and their reaction mechanisms are elucidated. The research leads to development of fundamental concepts of transition metal chemistry.

The "sandwich" structure is one of the fundamental structural motifs for transition metal complexes. Most of sandwich complexes contain a mononuclear metal moiety between parallel cyclic unsaturated hydrocarbon ligands. On the other hand, it had been difficult to synthesize a stable sandwich complex in which a metal assembly are sandwiched between two cyclic unsaturated hydrocarbons. Recently, our group discovered that multinuclear sandwich complexes exist as the stable and isolable molecules (Figure 1). These findings expand the structural concept of sandwich compounds from zero-dimension to one- and two dimensions, and provide a new opportunity to develop a new class of organo-metal cluster compounds. Multinuclear sandwich complexes showed unique chemical properties stemming from their (π-conjugated unsaturated hydrocarbon)-(multinuclear metal) hybrid structures.

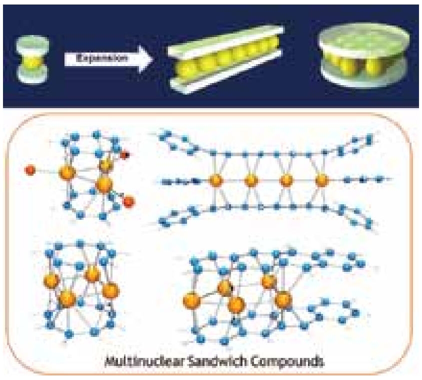

Figure 1. The concept of dimensionally extended sandwich structures and some examples of the multinuclear sandwich complexes.

Selected Publications

- T. Murahashi, T. Uemura and H. Kurosawa, "Perylene Tetrapalladium Sandwich Complexes," *J. Am. Chem. Soc.* **125**, 8436–8437 (2003).
- T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki and H. Kurosawa "Discrete Sandwich Compounds of Monolayer Palladium Sheets," *Science* **313**, 1104–1107 (2006).
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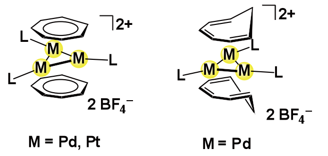
- T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi and H. Kurosawa, "Redox-Induced Reversible Metal Assembly through Translocation and Reversible Ligand Coupling in Tetranuclear Metal Sandwich Frameworks," *Nat. Chem.* **4**, 52–58 (2012).

1. Chemistry of Multinuclear Sandwich Complexes

Synthesis and Structural Elucidation of Bis-Cyclooctatetraene Trimetal Sandwich Complexes

Our group has made research efforts to establish the generality of the metal sheet sandwich compounds. We have shown that several unsaturated hydrocarbon ligands such as [2.2]paracyclophane, cycloheptatriene, cycloheptatrienyl, and some polycyclic arenes behave as the excellent binders for triangular trimetal sheets.[2–6] Particularly, it has been shown that seven-membered unsaturated hydrocarbons, *i.e.*, tropylium and cycloheptatriene, serve as an excellent facial μ_3-binder for the triangular M_3L_3 core (M = Pd, Pt) (Scheme 1). However, it has not been verified whether larger π-conjugated carbocycles are able to form a simple triangular trimetal sandwich complex.

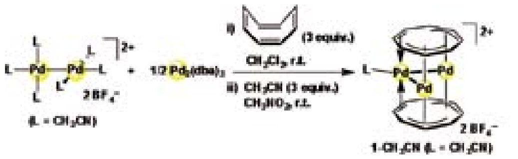


Scheme 1. The tropylium- and cycloheptatriene sandwich complexes.

1,3,5,7-Cyclooctatetraene (COT) is a potentially useful eight-membered carbocyclic ligand for metal sheet sandwich complexes, in view of its greater number of C=C bonds and a flexible electron-donating/back-donating nature. A recent finding by Grubbs *et al.* represents the versatility of the COT ligand, *i.e.*, a homoleptic trimetal tris-COT complex, $Fe_3(\mu\text{-}COT)_3$, was isolated through a catalytic method.[7] Here, we successfully synthesized the first discrete bis-COT trimetal sandwich complexes.[8]

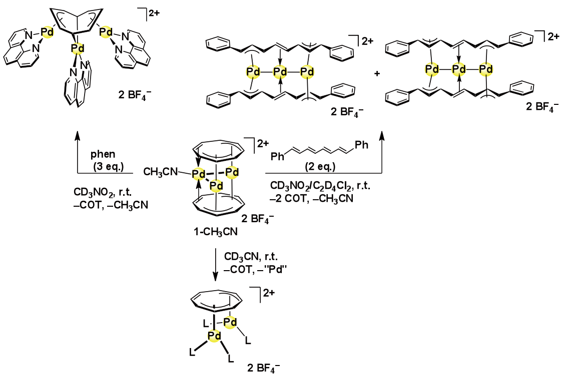
The bis-cyclooctatetraene Pd_3 sandwich complex $[Pd_3(\mu_3\text{-}C_8H_8)_2L][BF_4]_2$ (**1-CH₃CN**) was obtained by the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ and $Pd_2(dba)_3$ in the presence of cyclooctatetraene (COT), followed by treatment with CH_3CN (eq. 1). Recrystallization in an aerobic condition gave a single crystal of **1-H₂O**. The structure of **1-H₂O** was determined by X-ray diffraction analysis. The cyclooctatetraene ligands coordinate to an isosceles Pd_3 triangle (Pd1–Pd2 = 2.7321(8) Å; Pd2–Pd3 = 2.7359(8) Å; Pd1···Pd3 = 3.0604(8) Å) through a μ_3-η^3:η^2:η^3 mode. The sandwich structure seems to be related with that of a diphenyloctatetraene Pd_3 chain sandwich complex $[Pd_3\{Ph(CH{=}CH)_4Ph\}_2]^{2+}$ which exhibits the same μ_3-η^3:η^2:η^3 coordination mode.[9]

A deep purple PPh_3 complex $[Pd_3(\mu_3\text{-}COT)_2(PPh_3)][BF_4]_2$ (**1-PPh₃**) or a PCy_3 complex $[Pd_3(\mu_3\text{-}COT)_2(PCy_3)][BF_4]_2$ (**1-PCy₃**) was obtained by treatment of **1-CH₃CN** with PPh_3 or PCy_3 (1 equiv.). In solution, **1-CH₃CN** and **1-PPh₃** showed a sharp singlet NMR signal for C_8H_8 protons or carbons at 25 °C. Lowering the temperature down to –90 °C of the related compound resulted in significant broadening of the resonance for the C_8H_8 protons, suggesting the dynamic fluxional rotation of the cyclooctatetraene ligands on the Pd_3 core.



(1)

The reactivity of **1-CH₃CN** with several coordinating substrates were investigated, and the results were summarized in Scheme 2, showing the substitutionally labile nature of the μ_3-COT ligands in the bis-COT Pd_3 sandwich complex.



Scheme 2. Facile dissociation of the COT ligand in $[Pd_3(\mu_3\text{-}C_8H_8)_2(CH_3CN)][BF_4]_2$ (**1-CH₃CN**).

2. Reaction Mechanism of Highly Reactive Metal Complexes

One of our main interests is in the elucidation of the reaction patterns and mechanisms of highly reactive transition metal complexes in relevance to catalysis. Synthetic and structural chemistry of the arenes and hetero-arenes transition metal complexes are now ongoing in our laboratory, and several new aspects have been gained recently.[10,11]

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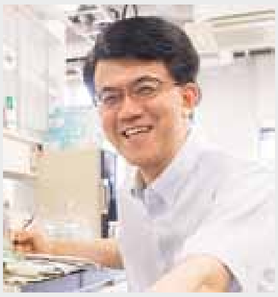
* IMS International Internship Program

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

Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



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1992 Ph.D. University of California, Santa Barbara

Professional Employment

1992 Assistant Professor, Institute for Molecular Science
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Keywords Organic Synthesis, Graphene Molecule, Organic Semiconductor

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. It is interesting to see how the curvature influences the structure and properties of the graphene molecule. We are currently working on the synthesis of aromatic saddles and belts.

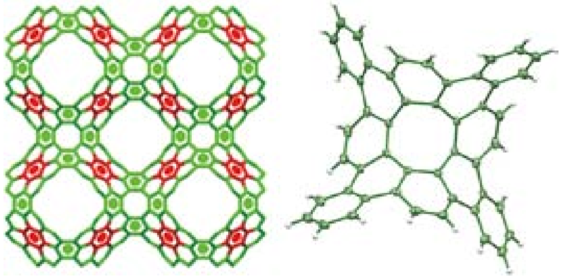

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato and S. Tokito, "Perfluoropentacene: High-Performance p-n Junctions and Complementary Circuits with Pentacene," *J. Am. Chem. Soc.* **126**, 8138–8140 (2004).
- 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).

1. Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene[1)]

An aromatic saddle was designed from the hypothetical three-dimensional graphene with the negative Gaussian curvature (Schwarzite P192). Two aromatic saddles, tetrabenzo[8]circulene (**TB8C**) and its octamethyl derivative **OM-TB8C**, were synthesized by the Scholl reaction of cyclic octaphenylene precursors. The structure of **TB8C** greatly deviates from planarity, and the deep saddle shape was confirmed by single-crystal X-ray crystallography. There are two conformers with the S_4 symmetry, which are twisted compared to the DFT structure (D_{2d}). The theoretical studies propose that the interconversion of **TB8C** via the planar transition state (125 kcal mol^{-1}) is not possible. However, the pseudorotation leads to a low-energy tub-to-tub inversion via the nonplanar transition state (7.3 kcal mol^{-1}). The ground state structure of **TB8C** in solution is quite different from the X-ray structure because of the crystal-packing force and low-energy pseudorotation. **OM-TB8C** is a good electron donor and works as the p-type semiconductor.

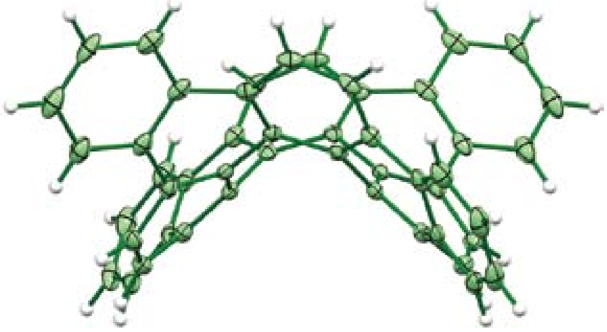

Figure 2. Single-crystal X-ray structure of **TB8C** from the side. The thermal ellipsoids are shown at 50% probability.

2. Synthesis and Physical Properties of a Ball-Like Three-Dimensional π-Conjugated Molecule[2)]

Curved π-conjugated molecules with closed and three-dimensional (3D) structures, such as fullerenes and carbon nanotubes, have been the subject of intensive research due to their potential applications in molecular electronics. However, basic molecular skeletons of 3D molecules are limited because of the lack of a rational and selective synthetic method by organic synthesis. We report the synthesis of a 3D π-conjugated molecule based on the platinum-mediated assembly of four molecules of a stannylated trisubstituted benzene derivative forming a hexanuclear platinum complex with an octahedral shape, from which reductive elimination of platinum gave the target molecule. As many supramolecular transition metal-ligand complexes with 3D cages and polyhedral structures have been synthesized by self-assembly of ligands and metals, the current assembly/reductive elimination strategy could provide a variety of new 3D π-conjugated molecules with different structures and topologies, which are challenging to obtain using conventional synthetic methods.

3. Synthesis, Characterization, and Properties of [4]Cyclo-2,7-pyrenylene: Effects of Cyclic Structure on the Electronic Properties of Pyrene Oligomers[3)]

A cyclic tetramer of pyrene, [4]cyclo-2,7-pyrenylene ([4]CPY), was synthesized from pyrene in six steps and 18% overall yield by the platinum-mediated assembly of pyrene units and subsequent reductive elimination of platinum. The structures of the two key intermediates were unambiguously determined by X-ray crystallographic analysis. DFT calculations showed that the topology of the frontier orbitals in [4]CPY was essentially the same as those in [8]cycloparaphenylene ([8]CPP), and that all the pyrene units were fully conjugated. The electrochemical analyses proved the electronic properties of [4]CPY to be similar to those of [8]CPP. The results are in sharp contrast to those obtained for the corresponding linear oligomers of pyrene in which each pyrene unit was electronically isolated. The results clearly show a novel effect of the cyclic structure on cyclic π-conjugated molecules.

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Chemistry of Buckybowls and Metal Nanocluster Catalysts

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2014	Professor, Osaka University

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2014	The Chemical Society of Japan (CSJ) Award for Creative Work

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- JSPS Post-Doctoral Fellow
  - DHITAL, Raghu Nath
- Post-Doctoral Fellow
  - PANDIT, Palash
  - MAITY, Prasenjit
  - YAMAMOTO, Kohji
- Visiting Scientist
  - THONGPAEN, Jompol
  - TUNGJITGUSONGUN, Vithawas
  - TRAN, Uyen Phuoc Nhat
  - LIU, Wenting
  - EVERLE, Fabian F.
  - MEKSERIWATTANA, Wid
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  - KAEWMATI, Patcharin
  - KARANJIT, Sangita
  - SHRESTHA, Binod Babu
  - NGAMSOMPRASERT, Niti
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  - OKABE, Yuki
- Secretary
  - SASAKI, Tokiyo
  - HAZAMA, Kozue

Keywords Organic Synthesis, Buckybowl, Cluster Catalyst

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. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. Very few buckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiral bowls has appeared. In this project, we develop the rational route to the various buckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers.

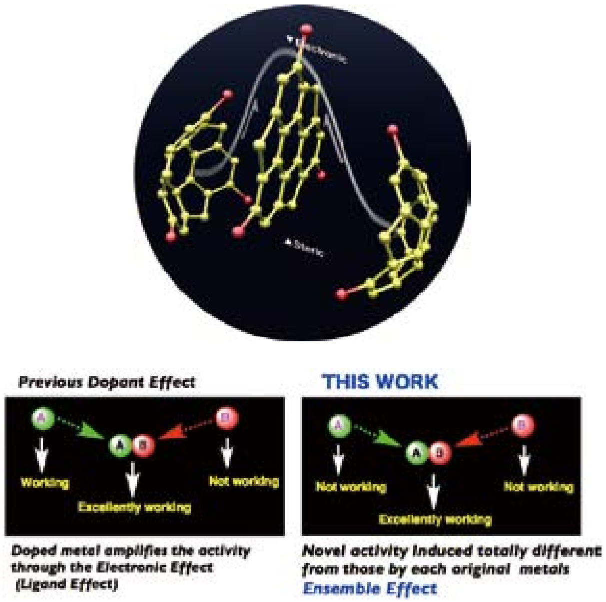

Figure 1. Dynamic behavior (bowl-inversion) of buckybowls and the concept of the bimetallic metal nanoclusters catalysts.

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- S. Higashibayashi and H. Sakurai, *J. Am. Chem. Soc.* **130**, 8592–8593 (2008).
- Q.-T. Tan, S. Higashibayashi, S. Karanjit and H. Sakurai, *Nat. Commun.* **3**:891 doi: 10.1038/ncomms1896 (2012).
- R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.* **134**, 20250–20253 (2012).
- S. Higashibayashi, S. Onogi, H. K. Srivastava, G. N. Sastry, Y.-T. Wu and H. Sakurai, *Angew. Chem., Int. Ed.* **52**, 7314–7316 (2013).

1. Correlation between Bowl-Inversion Energy and Bowl Depth in Substituted Sumanenes

The correlation between the bowl-inversion energy and the bowl depth for sumanenes monosubstituted with an iodo, formyl, or nitro group was investigated experimentally and by theoretical calculations. The bowl-inversion energies of the substituted sumanenes were determined experimentally by two-dimensional NMR exchange spectroscopy measurements. Various density functional theory methods were examined for the calculation of the structure and the bowl-inversion energy of sumanene, and it was found that PBE0, ωB97XD, and M06-2X gave better fits of the experimental value than did B3LYP. The experimental value was well reproduced at these levels of theory. The bowl structures and bowl-inversion energies of monosubstituted sumanenes were therefore calculated at the ωB97XD/6-311+G(d,p) level of theory. In both the experiments and the calculations, the correlation followed the equation $\Delta E = a\cos^4\theta$, where a is a coefficient, ΔE is the bowl-inversion energy, and $\cos\theta$ is the normalized bowl depth, indicating that the bowl inversion follows a double-well potential energy diagram.

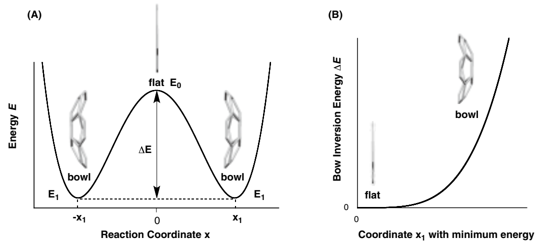

Figure 2. (A) Double-well potential of bowl-inversion and (B) correlation between bowl-inversion and bowl depth.

2. Columnar/Herringbone Dual Crystal Packing of Pyrenylsumanene and its Photophysical Properties

A single crystal of pyrenylsumanene was found to exhibit both columnar and herringbone crystal packing. The sumanene moieties form unidirectional columnar structures based on π-π stacking while the pyrene moieties generate herringbone structures due to CH–π interactions. The absorption and emission maxima of pyrenylsumanene were both red-shifted relative to those of sumanene and pyrene, owing to the extension of π-conjugation. Monomer emission with high quantum yield (0.82) was observed for pyrenylsumanene in solution, while excimer-type red-shifted emission was evident in the crystalline phase.

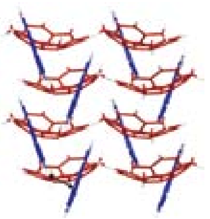

Figure 3. Side view of columns with a herringbone packing of the pyrene moiety due to CH–π interactions.

3. Bimetallic Gold/Palladium Alloy Nanoclusters: An Effective Catalyst for Ullmann Coupling of Chloropyridines under Ambient Conditions

An efficient method for the Ullmann coupling of chloropyridines catalyzed by poly(*N*-vinylpyrrolidone) (PVP)-stabilized bimetallic Au/Pd alloy nanoclusters (NCs) under ambient conditions is demonstrated. The reaction does not occur with either gold or palladium single-metal clusters alone, nor with a physical mixture of the two metals. The experimental results indicate that the inclusion of Au as a nearest heteroatom is crucial to initiate the coupling and its composition up to 50% is essential to accelerate the reaction. Unlikely to the conventional transition metal catalysis, 2-chloropyridine was found to be highly reactive as compare to 2-bromopyridine. From the UV-vis and ICP-AES, significant amount of leached Pd(II) was observed in the coupling with 2-bromopyrdine as compared with 2-chloropyridine, indicating the leaching process might be a crucial factor to diminish the reactivity of the coupling.

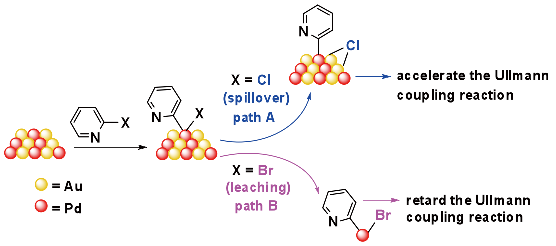

Figure 4. Mechanistic illustration of the activity of Au/Pd clusters in the Ullmann coupling with 2-chloro- or 2-bromo-pyridine. Path A represents the activation and path B represents the deactivation process.

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1) B. B. Shrestha, S. Karanjit, S. Higashibayashi and H. Sakurai, *Pure Appl. Chem.* **86**, 747–753 (2014).
2) B. B. Shrestha, S. Higashibayashi and H. Sakurai, *Beilstein J. Org. Chem.* **10**, 841–847 (2014).
3) R. N. Dhital, C. Kamonsatikul, E. Somsook and H. Sakurai, *Catal. Sci. Tech.* **3**, 3030–3035 (2013).

Awards

SAKURAI, Hidehiro; Distinguished Award on IUPAC Novel Materials and their Synthesis (2013).
SAKURAI, Hidehiro; The Chemical Society of Japan (CSJ) Award for Creative Work (2014).
HAESUWANNAKIJ, Setsiri; CSJ Student Presentation Award 2013 (2014).

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 (1978–2013).

UVSOR Facility

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IWAYAMA, Hiroshi	Assistant Professor
MATSUNAMI, Masaharu	Assistant Professor
OHIGASHI, Takuji	Assistant Professor
KONOMI, Taro	Assistant Professor
HORIGOME, Toshio	Technical Associate
HASUMOTO, Masami	Technical Associate
YAMAZAKI, Jun-ichiro	Technical Associate
HAYASHI, Kenji	Technical Associate
KONDO, Naonori	Technical Associate
SAKAI, Masahiro	Technical Associate
TESHIMA, Fumitsuna	Technical Associate
TOKUSHI, Tetsunari	Technical Fellow
INAGAKI, Yuichi	Technical Fellow
HAYASHI, Ken-ichi	Technical Fellow
MINAKUCHI, Aki	Technical Fellow
HAGIWARA, Hisayo	Secretary

Outline of UVSOR

Since the first light in 1983, UVSOR has been successfully operated as one of the major synchrotron light sources in Japan. After the major upgrade of the accelerators in 2003, UVSOR was renamed to UVSOR-II and became one of the world brightest low energy synchrotron light source. In 2012, it was upgraded again and has been renamed to UVSOR-III. The brightness of the electron beam was increased further. Totally, six undulators were installed. The storage ring is operated fully in the top-up mode, in which the electron beam intensity is kept constant.

The UVSOR accelerator complex consists of a 15 MeV injector linac, a 750 MeV booster synchrotron, and a 750 MeV 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 operation is also conducted about two weeks per year, which provides pulsed synchrotron radiation (SR) for time-resolved experiments.

Eight bending magnets and six undulators are available for providing SR. The bending magnet with its radius of 2.2 m provides SR with the critical energy of 425 eV. There are fifteen beam-lines operational. They can be classified into two categories. Eleven of them are the so-called “Open beamlines,” which are open to scientists of universities and research institutes belonging to the government, public organizations, private enterprises and those of foreign countries. The other three beam-lines are the so-called “In-house beamlines,” which are mainly used by the research groups within IMS. We have 1 soft X-rays (SX) station equipped with a double-crystal monochromator, 7 EUV and SX stations with a grazing incidence monochromator, 3 VUV stations with a normal incidence monochromator, 2 (far) infrared station equipped with FT interferometers and 1 beam-line for light source development without monochromator.

Figure 1. UVSOR electron storage ring and synchrotron radiation beam-lines.

Collaborations at UVSOR

Variety of investigations related to molecular/material science is carried out at UVSOR by IMS researchers. In addition, many researchers outside IMS visit UVSOR to conduct their own research works. The number of visiting researchers per year tops about 800, whose affiliations extend to 60 different institutes. International collaboration is also pursued actively and the number of visiting foreign researchers reaches over 80, across about 10 countries. UVSOR invites new/continuing proposals for research conducted at the open beamlines twice a year. The proposals from academic and public research organizations (charge-free) and from enterprises (charged) are acceptable. The fruits of the research activities using SR at UVSOR are published as a UVSOR ACTIVITY REPORT annually.

Recent Developments

In spring, 2013, we had two month shut-down for a reconstruction work at an undulator beam-line BL5U. The undulator at BL5U, which had been constructed about 20 years ago, was remodeled. Now it has become capable of producing any polarization, such as horizontal and vertical linear polarizations and left and right circular polarizations.

The endstation of BL5U has started to be renewed to perform higher energy resolution ARPES experiments. This endstation will have new capability to obtain spin- and spatial-dependence of the electronic structure of solids using new spin detector and micro-focused beam. This beam-line will be open for users from 2015.

Figure 2. Current situation of new ARPES beam-line BL5U.

Reserch Highlight

Solid-state functionalities of organic molecules are governed not only by individual molecular properties but also by their intermolecular interactions. This concerted interplay dominates a key process of the electric conduction in functional molecular systems. In this work, we have investigated the intermolecular energy-*vs*-momentum $E(\boldsymbol{k})$ relation, originating from the molecular stacking periodicity, of sub-100-meV scale in metal phthalocyanine (MPc) crystalline films. The small $E(\boldsymbol{k})$ relation of MPc with different terminal groups and central metals are sensitive and essential to characterize the intermolecular interaction in terms of the intermolecular distance, the molecular conformation, and the orbital symmetry.

Figure 3 shows the emission angle (θ) dependence of the angle-resolved photoemission (ARPES) spectra and its intensity map for the flat-lying monolayer and crystalline films of ZnPc on Au(111) at 15 K. For the monolayer, the dispersive and non-dispersive peaks appear around the binding energy (E_b) of 0 ~ 0.32 eV and 0.74 eV, respectively. The parabolic dispersion at E_b = 0 ~ 0.32 eV is derived from the Shockley State (SS) of the Au(111) surface, which is modified by the complex interplay of molecule–substrate interactions. The non-dispersive peak at E_b = 0.74 eV is derived from the highest occupied molecular orbital (HOMO) of C 2p (π) character in ZnPc. The observed HOMO-peak intensity shows a sharp θ dependence with the maximum at θ = 34°. This is due to the reflection of the spatial electron distribution of HOMO. For the ZnPc crystalline film, the SS band of Au(111) is suppressed and the HOMO peak is stabilized as E_b ~ 1.3 eV. Since the ZnPc molecule deposited on Au(111) shows the Stranski-Krastanov growth, the quite weak substrate signal of E_F appears and is utilized for the energy calibration for the precise $E(\boldsymbol{k})$ measurement. The θ dependence of the HOMO-peak intensity in the ZnPc crystalline film is almost the same as that in the ZnPc monolayer; that is, the molecular orientation indicates the layer-by-layer growth in the crystalline domain and induces orbital delocalization. Indeed, the HOMO peak of the ZnPc crystalline film shows a small dispersive behavior with θ. Such a dispersive behavior is not observed in the monolayer film and is related to the delocalized band formation.

In order to investigate the $\boldsymbol{k}$ component along the π-π stacking direction ($\boldsymbol{k}_\perp$), we measured the normal emission ARPES as a function of the photon energy ($h\nu$) for crystalline films of various MPc (H_2Pc, MnPc, CoPc, ZnPc, and F_{16}ZnPc) on Au(111) at 15 K. From this systematic experiment, we revealed quite small but different $E(\boldsymbol{k}_\perp)$ relations. The transfer integral ($t_\perp$) of the C 2p band is found to be dependent on the intermolecular distance ($a_\perp$) with the 75±5 meV/Å relation. Furthermore, we observed the different dispersion phase and periodicity, depending on the terminal group and central metal in MPc, which originate from the site-specific intermolecular interaction induced by substituents.1)

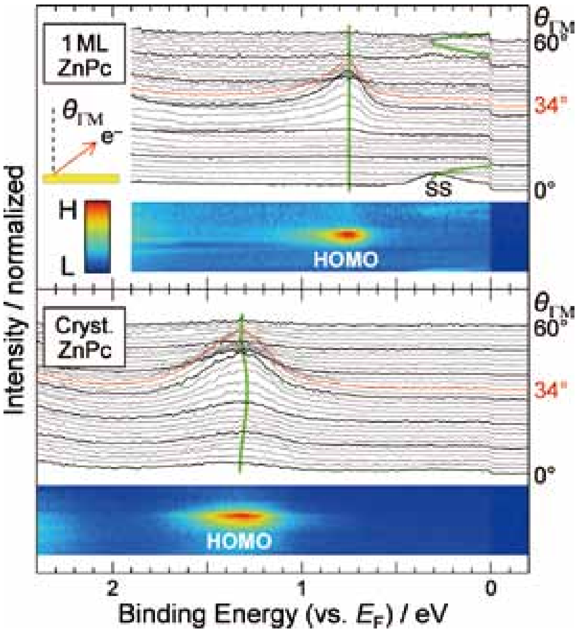

Figure 3. The θ dependence of the ARPES spectra ($h\nu$ = 45 eV) and its intensity map for the monolayer and crystalline films of ZnPc on Au(111) at 15 K.

Reference

1) H. Yamane and N. Kosugi, *Phys. Rev. Lett.* **111**, 086602 (2013).

Laser Research Center for Molecular Science

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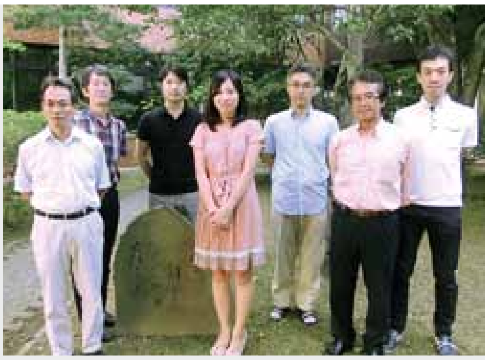
OHMORI, Kenji	Professor
OHSHIMA, Yasuhiro	Professor
TAIRA, Takunori	Associate Professor
FUJI, Takao	Associate Professor
ISHIZUKI, Hideki	Assistant Professor
NOMURA, Yutaka	Assistant Professor
OKANO, Yasuaki	Technical Associate
MASUDA, Michiko	Secretary
KAWAI, Shigeko	Secretary



The Center aims to develop new experimental apparatus and methods to open groundbreaking research fields in molecular science, in collaboration with the Department of Photo-Molecular Science. Those new apparatus and methods will be served as key resources in advanced collaborations with the researchers from the community of molecular science. The main targets are (1) advanced photon sources covering wide energy ranges from terahertz to soft X-day regions; (2) novel quantum-control schemes based on intense and ultrafast lasers; and (3) high-resolution optical imaging and nanometric microscopy. The center also serves as the core of the joint research project "Extreme Photonics" between IMS and RIKEN.

Two of full-time associate professors and their research groups belong to the Center. The groups promote research projects targeting mainly on developments of novel laser light sources for molecular science. The Center also possesses several general-purpose instruments for laser-related measurements, and lends them to researchers in IMS who conduct laser-based studies, so as to support and contribute to their advanced researches.

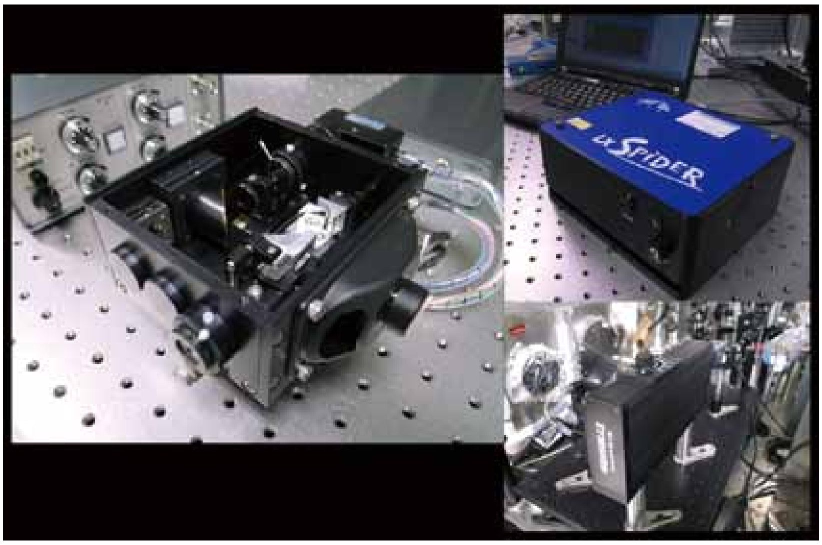


Figure 1. (left) A Fringe-Resolved Autocorrelation (FRAC) apparatus for sub-10 fs pulse characterization designed in the Center. (upper right) Spectral Phase Interferometry for Direct Electric-Field Reconstruction (SPIDER) and (lower right) Frequency-Resolved Optical Gating (FROG) apparatuses for general-purpose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

Instrument Center

OHSHIMA, Yasuhiro	Director
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OKANO, Yoshinori	Technical Associate
MIZUKAWA, Tetsunori	Technical Associate
MAKITA, Seiji	Technical Associate
NAKANO, Michiko	Technical Associate
UEDA, Tadashi	Technical Associate
OTA, Akiyo	Secretary
NAKAGAWA, Nobuyo	Secretary

Instrument Center was organized in April of 2007 by integrating the general-purpose 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 research by utilizing general-purpose instruments. The staffs of Instrument Center maintain the best condition 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 (JEOL JNM-ECA 920, JNM-ECA 600, and JNM-LA500, JNM-ECS400, and Bruker AVANCE800), matrix assisted laser desorption ionization (MALDI) mass spectrometer (Voyager DE-STR), powder X-ray diffractometer (Rigaku RINT-Ultima III), circular dichroism (CD) spectrometer (JASCO JW-720WI), differential scanning calorimeter (MicroCal VP-DSC), and isothermal titration calorimeter (MicroCal iTC200), scanning electron microscope (SEM; JEOL JEM-6700F(1), JED-2201F), focused ion beam (FIB) machine (JEOL JEM-9310FIB(P)), 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), superconducting quantum interference devices (SQUID; Quantum Design MPMS-7 and MPMS-XL7), powder X-ray diffractometer (MAC Science MXP3), 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 spectro-photometer (SPEX Fluorolog2), X-ray fluorescence spectrometer (JEOL JSX-3400RII), UV-VIS-NIR spectro-photometer (Hitachi U-3500), Raman microscope (Renishaw INVIA REFLEX532), excimer/dye laser system (Lambda Physics LPX105i/LPD3002), Nd^+: YAG-laser pumped OPO laser (Spectra Physics GCR-250/Lambda Physics Scanmate OPPO), excimer laser (Lambda Physics Complex 110F), and picosecond tunable laser system (Spectra Physics Tsunami/Quantronix Titan/Light Conversion TOPAS), SEM (Hitachi SU6600), electron spectrometers for chemical analysis (ESCA) (Omicron EA-125), high-resolution transmission electron microscope (TEM; JEOL JEM-3100FEF), and FTIR spectrometer (Bruker IFS 66v/S). In the fiscal year of 2013, Instrument Center accepted almost 140 applications from institutions outside IMS. Instrument Center also maintains helium liquefiers in the both campus and provides liquid helium to users. Liquid nitrogen is also provided as general coolants used in many laboratories in the Institute. The staffs of Instrument Center provide consultation for how to treat liquid helium, and provide various parts necessary for low-temperature experiments. Instrument Center supports also the Inter-University Network for Common Utilization of Research Equipments.

Figure 1. 600 MHz NMR spectrometer (JEOL JNM-ESA600).

Figure 2. Pulse ESR for Q-band (Bruker E680).

Figure 3. Raman microscope (Renishaw INVIA REFLEX532).

Equipment Development Center

YAMAMOTO, Hiroshi	Director
MIZUTANI, Nobuo	Technical Associate
AOYAMA, Masaki	Technical Associate
YANO, Takayuki	Technical Associate
KONDOU, Takuhiko	Technical Associate
YOSHIDA, Hisashi	Technical Associate
UTCHIYAMA, Kouichi	Technical Associate
TOYODA, Tomonori	Technical Associate
TAKADA, Noriko	Technical Associate
NAKANO, Michiko	Technical Associate
SUGITO,Shouji	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.

ARM-Microcontroller-Based Rotary Solenoid Driver

WA laser-shutter device, which can block a laser beam synchronizing with external control signals as trigger, is one of the basic elements in optical systems. In this work, we have developed a driver unit to control a shutter device, which consists of a bi-stable rotary-solenoid and a shutter plate, operated with TTL level trigger at a repetition rate up to 10 Hz (Figure 1).

Specifications of the driver are as follows: First, it detects the rising edge of the trigger, then, generates a Phase-A output to drive the rotary solenoid clockwise with a predetermined duration. Next, it detects the falling edge of the trigger, and generates a Phase-B output to drive the solenoid counter-clockwise with a predetermined duration. The tunable ranges of Phase-A and -B durations are from 1 ms to 99 ms with the step of 1 ms.

Conventionally, we used a combination of standard logic ICs for driving a circuit synchronized with a trigger. In this case, we adopted the module of LPC1114FBD48/302, the ARM microcontroller by NXP. We set one of the pins of ARM module as an input, and set interrupts on both edges of the trigger (rising and falling). ARM module identifies rising or falling edge in the interrupt handler, and outputs Phase A or Phase B. (Figure 2).

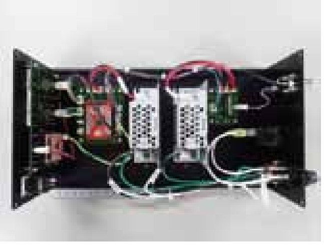


Figure 1. Photo of the rotary solenoid driver.

The duration of the each output is adjustable with a rotary encoder which is connected to the ARM module. Increasing or decreasing of the value is performed by detecting the rotation direction of the rotary encoder. The value is displayed on a LCD by another ARM module. We adopted I2C for communication between two ARM modules.

Figure 2. The input–output characteristics of the rotary solenoid driver.

Cathode Plug for Superconducting Electron Emitter

A new electron source is required for the development of next generation synchrotron radiation system. A cathode plug that will be used for photo-cathode with back-side irradiation has been fabricated (Figure 3). The plug is designed to be able to hold a photo-cathode substrate on the top, and can be fixed with screw on the cathode holder. The photo-cathode substrate, whose size is 5 × 5 × 0.5 mm^3, is requested to stay in the same plane with the plug's top-edge plane, and therefore cannot be fixed by using a holding plate mounting on it. At the same time, fixing of the substrate by side-holding makes it bending and inclining, which arises another undesirable problems. In order to address these issues, we have designed a new substrate-holding cathode plug with elastic parallel hinge structure. The tightness of the hinge was optimized to meet the best result of finite-element-method calculation by ANSYS program (Figure 4), so that accurate fixing of photo-cathode substrate has finally been achieved.

Figure 3. Cathode plug for electron emission.

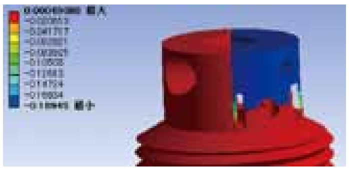


Figure 4. Analysis result for the elastic hinge calculated by ANSYS.

Research Center for Computational Science

SAITO, Shinji	Director, Professor
EHARA, Masahiro	Professor
OKUMURA, Hisashi	Associate Professor
OONO, Hitoshi	Assistant Professor
ISHIDA, Tateki	Assistant Professor
FUKUDA, Ryoichi	Assistant Professor
ITOH, G. Satoru	Assistant Professor
MIZUTANI, Fumiyasu	Technical Associate
NAITO, Shigeki	Technical Associate
SAWA, Masataka	Technical Associate
IWAHASHI, Kensuke	Technical Associate
MATSUO, Jun-ichi	Technical Associate
NAGAYA, Takakazu	Technical Associate
TOYA, Akiko	Secretary
ISHIHARA, Mayumi	Secretary

Research Center for Computational Science provides state-of-the-art computational resources to academic researchers in molecular science and related fields, *e.g.* quantum chemistry, molecular simulations, and solid state physics. The computer systems consist of Fujitsu PRIMERGY RX300, PRIME HPC FX10 and PRIMERGY CX250, SGI UV2000. 713 users in 185 project groups from a wide range of molecular science have used in 2013. Large scale calculations, for example the formation of fullerenes, conformation searches using non-Boltzmann ensemble methods, and nonlinear spectroscopy of liquids, have been performed with the systems. The Center also provides a number of application programs, for example Gaussian 09, GAMESS, Molpro, AMBER, and NAMD. The Center offers the Quantum Chemistry Literature Database, which has been developed by the Quantum Chemistry Database Group in collaboration with staff members of the Center. The latest release, QCLDB II Release 2013, contains 130,782 data of quantum chemical studies. Detailed information on the hardware and software is available on the web site (http://ccportal.ims.ac.jp/).

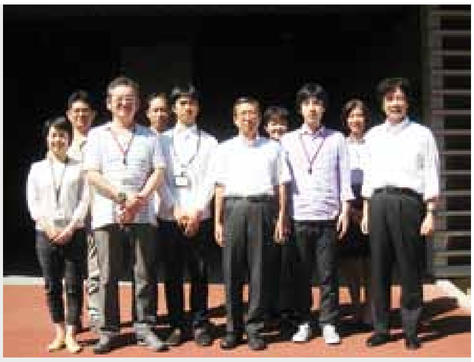
In addition to the provision of computational resources, the Center contributes to the so-called next-generation supercomputer project which is conducted by the government. In 2010, Computational Material Science Initiative (CMSI) was established, after the research field which consists of molecular science, solid state physics, and material science was selected as one of the research fields which scientific breakthroughs are expected by using the next-generation supercomputer. The Center contributes to CMSI by providing up to 20% of its computational resource.

Figure 1. Fujitsu PRIMERGY CX300.

Figure 2. SGI UV2000.

Okazaki Institute for Integrative Bioscience

AONO, Shigetoshi	Professor
KATO, Koichi	Professor
IINO, Ryota	Professor
FUJII, Hiroshi	Associate Professor
KURIHARA, Kensuke	Research Associate Professor
KURAHASHI, Takuya	Assistant Professor
YOSHIOKA, Shiro	Assistant Professor
YAMAGUCHI, Takumi	Assistant Professor
MURAKI, Norifumi	IMS Research Assistant Professor
YAGI-UTSUMI, Maho	OIIB Research Assistant Professor
TANIZAWA, Misako	Secretary
TANAKA, Kei	Secretary



The main purpose of Okazaki Institute for Integrative Bioscience (OIIB) is to conduct interdisciplinary, molecular research on various biological phenomena such as signal transduction, differentiation and environmental response. OIIB, founded in April 2000, introduces cutting edge methodology from the physical and chemical disciplines to foster new trends in bioscience research. OIIB is a center shared by and benefited from all three institutes in Okazaki, thus encouraging innovative researches adequately in advance of academic and social demands. OIIB has started the research programs, “Okazaki ORION Project” and “BioNEXT Program” from 2014. The research groups of three full professors and one associate professor who have the position in IMS join OIIB to be involved in these research projects. The research activities of these groups are as follows.

Aono group is studying the bioinorganic chemistry of metalloproteins that show a novel function. They elucidated the structure and function relationships of the heme-based sensor proteins in which a heme was the active site for sensing gas molecules such as CO and O_2. They are also studying the structure and function relationships of transcriptional regulators and metal transport proteins that are responsible for metal homeostasis in bacteria. Iino group is studying operation mechanism of molecular machines using single-molecule techniques based on optical microscopy. Especially they focus on new rotary and linear molecular motors. In this year, they directly visualized rotation of a rotary molecular motor *Enterococcus hirae* V1-ATPase, and determined kinetic parameters for all elementary reaction steps of a linear molecular motor *Trichoderma reesei* Cel7A. They also applied single-molecule techniques to a synthetic molecular rotor double-decker porphyrin, and directly visualized the rotary motion for the first time. Kato group is studying structure, dynamics, and interactions of biological macromolecules using nuclear magnetic resonance (NMR) spectroscopy, X-ray crystallography, and other biophysical methods. In particular, they conducted studies aimed at elucidating the dynamic structures of glycoconjugates and proteins for integrative understanding of the mechanisms underlying their biological functions. In this year, they successfully elucidated the working mechanisms of proteasome assembly chaperones, Nas2 and Pba3–Pba4, the carbohydrate recognition modes of the cargo receptor complex, ERGIC-53–MCFD2, and the functional role of a product of a recently identified causative gene for dystroglycanopathy, AGO61. Fujii group is studying molecular mechanisms of metalloenzymes, which are a class of biologically important macromolecules having various functions such as oxygen transport, electron transfer, oxygenation, and signal transduction, with synthetic model complexes for the active site of the metalloenzymes. In this year, they studied molecular mechanisms of metalloenzymes relating to monooxygenation reactions and denitification processes. Kurihara group is studying an artificial cell based on a giant vesicle constructed from organic chemical approach. Their goal is to realize an artificial cell in which elements such as information, container and metabolism interact each other. In this year, they studied cross-catalytic vesicular system: A vesicle is reproduced by the catalyst which was synthesized in the vesicle, *i.e.* interaction between container and metabolism.

Safety Office

UOZUMI, Yasuhiro	Director
TOMURA, Masaaki	Assistant Professor
TANAKA, Shoji	Assistant Professor
SUZUI, Mitsukazu	Technical Associate
NAGATA, Masaaki	Technical Associate
UEDA, Tadashi	Technical Associate
TAKAYAMA, Takashi	Technical Associate
SAKAI, Masahiro	Technical Associate
MAKITA, Seiji	Technical Associate
KONDO, Naonori	Technical Associate
ONITAKE, Naoko	Secretary
TSURUTA, Yumiko	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 comprised 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.

A management system for chemical substances (mainly for commercial chemicals) was launched in May 2014 and has been steered by the Office. This office acknowledged a task force chaired by Prof. Yamamoto, which has drawn the specifications of the system up.

SUPPORTING STAFF

Research Enhancement Strategy Office

KOSUGI, Nobuhiro	Head	SHIMODE, Ayako	Technical Fellow
AKIYAMA, Shuji	Vice-Head	MIZUNO, Hisayo	Secretary
HARADA, Miyuki	Technical Associate	NAKANE, Junko	Secretary
NAKAMURA, Rie	Technical Fellow	HAGIWARA, Hisayo	Secretary
TAUCHI, Kumi	Technical Fellow	NAGASONO, Hisayo	Secretary
KAMIYA, Miho	Technical Fellow	SUZUKI, Satomi	Secretary

Technical Division

SUZUI, Mitsukazu	Head
YAMANAKA, Takaya	Technical Associate
MINAMINO, Satoshi	Technical Associate
UCHIYAMA, Koichi	Technical Associate
MIZUNO, Hitoshi	Technical Fellow
SUGIYAMA, Kayoko	Secretary

Information Office

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

The Technical Division is an organization of the technical staff which supports research facilities of IMS. The technical staffs are assigned to support the research by using their professional skills of mechanical engineering, electrical engineering, instrumental analysis, optical technology, computer engineering, cryogenic technology, and the SOR technology, *etc*.

In addition, the Technical Division supports IMS facilities by managing Safety Office, Research groups, Public Affairs Office, Archives and Information Office.

The annual meeting for technical staff of research Institute and Universities was organized in 1975 and since then the meeting has been regularly held every year. We aim toward a higher technology and exchange discussion concerning the various technical problems related to our technology.

Special Research Projects

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

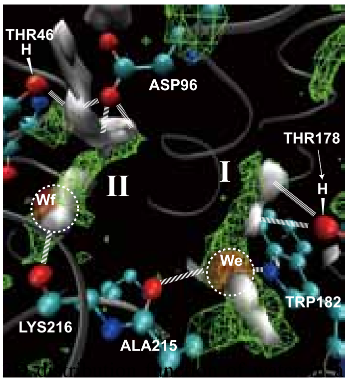
(a) The Ministry of Education, Culture, Sports, Science and Technology
HPCI Strategic Program "The Strategic Program for Innovation Research (SPIRE)"
Field 2 "New Materials and Energy Creation"
"Construction of Innovative High Performance Computing Infrastructure (HPCI)"
(b) Extreme Photonics
(c) MEXT Nanotechnology Platform Program
Platform of Molecule and Material Synthesis
(d) Inter-University Network for Efficient Utilization of Research Equipments
(e) Consortium for Photon Science and Technology (C-PhoST)

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

(a) The Ministry of Education, Culture, Sports, Science and Technology HPCI Strategic Program "The Strategic Program for Innovation Research (SPIRE)" Field 2 "New Materials and Energy Creation" "Construction of Innovative High Performance Computing Infrastructure (HPCI)"

HPCI strategy programs "SPIRE" aims to promote scientific research using "K-computer" at RIKEN Advanced Institute for Computational Science. In the strategic filed 2 of SPIRE, the Institute for Solid State Physics (ISSP) of the University of Tokyo, Institute for Molecular Science (IMS), and Institute for Material Research (IMR) of Tohoku University were selected as strategic organizations. The project started in September 2010 for "Computational Material Science: Turning the Headwaters of Basic Science into a Torrent of Innovations in Functional Materials and Energy Conversion" as a strategic target. To promote the activities of the strategic organizations, a new community "Computational Materials Science Initiative (CMSI)" consisting of research fields of condensed matter physics, molecular science and materials science was launched.

Theoretical and Computational Chemistry Initiative (TCCI) at IMS completed the activities of the 2013 fiscal year: (1) TCCI continued to contribute on making "Road-Map for Computational Science" to clarify the requests for post-K computers, such as computing speed, memory size, and other specifications, (2)TCCI organized the fourth TCCI workshop, the third symposium for communicating with experimental chemists, and the other one for industry–academic partnership, (3)TCCI also sponsored the seventeenth summer school of Molecular Simulations, two TCCI winter colleges (molecular simulations, and quantum chemistry), and one workshop for massively parallel programming, (4)Research Center for Computational Science (RCCS) continued to provide a part of its computing resources to the SPIRE project as one of the actvities of TCCI, and (5)TCCI and RCCS started to promote several software developed in "Next Generation Integrated Nanoscience Simulation Software Development" project, which had been completed by the end of FY 2011.



protein computed with the MC-MOZ method.

In the following years, TCCI is going to pursue the activities above and promote the research using K-computer and the computational molecular science field.

(b) Extreme Photonics

Institute for Molecular Science has a long-standing tradition of promoting spectroscopy and dynamics of molecules and molecular assemblies. Accordingly, photo-molecular science is one of the major disciplines in molecular science. This field is not confined in the traditional spectroscopy, but makes solid basis for other disciplines including nanoscience and bioscience, *etc*. Therefore, continuing developments in spectroscopy and microscopy are vital to enhance our abilities to elucidate more complex systems in time and spatial domains. In order to achieve full developments of photo-molecular science, we need to pursue three branches in developing: (1) new light source, (2) new spatio-temporally resolved spectroscopy, and (3) new methods to control atomic and molecular dynamics. Since 2005, we have started the program of "Extreme Photonics" in collaboration with the RIKEN institute. Currently 6 groups in IMS are involved in this program, and the specific research titles are as follows:

(1) Development of new light sources

TAIRA, Takunori	Micro Solid-State Photonics
FUJI, Takao	Coherent Synthesis of Femtosecond Pulses over the UV-IR Range
KATOH, Masahiro	Coherent Synchrotron Radiation

(2) Development of new spatio-temporally resolved spectroscopy

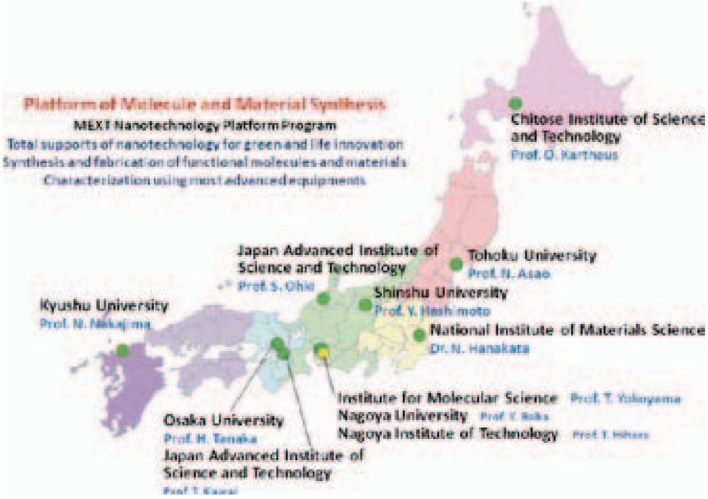
OKAMOTO, Hiromi	Development of Extreme Time-Resolved Near-Field Spectroscopy

(3) Development of new methods to control atomic and molecular dynamics

OHMORI, Kenji	Development of Attosecond Coherent Control and Its Applications
OHSHIMA, Yasuhiro	Quantum-State Manipulation of Molecular Motions by Intense Coherent Laser Pulses

(c) 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 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 amounted 123 (103 non-proprietary and 20 proprietary proposals, excluding applications from IMS) and the total number of days used for the supports is 2488 (2379 days for non-proprietary proposals and 109 days for proprietary ones).



List of Supports in IMS (FY2013)

Supporting Element		Responsible Persons		Charging Persons
Platform Management		T. Yokoyama, Y. Kaneko, M. Inoue		Y. Funaki, Y. Toyama, M. Yokota, K. Nakane
Organization Management in IMS		T. Yokoyama		
UVSOR Synchrotron Radiation	Scanning Transmission X-Ray Microscopy	M. Katoh	N. Kosugi	T. Ohigashi, Y. Inagaki
	X-Ray Magnetic Circular Dichroism		T. Yokoyama	Y. Takagi, M. Uozumi, Y. Uemura
	Microstructure Fabrication	M. Katoh	M. Suzui, M. Aoyama	N. Takada, T. Kondou
Electron Microscopy	300kV Transmission Electron Microscopy	Y. Ohshima		T. Ueda
	Field Emission Scanning Electron Microscopy			S. Nakao
	Focus Ion Beam Processing			
Molecular Properties	Electron Spectroscopy for Chemical Analysis	Y. Ohshima	N. Kosugi	M. Sakai
	Electron Spin Resonance		T. Nakamura	M. Fujiwara
	Superconducting Quantum Interference Device			
	Microscopic Raman Spectroscopy		H. Yamamoto	M. Uruichi
	Fourier Transform Far Infrared Spectroscopy			
High Field NMR	920 MHz NMR Solutions & Solids	Y. Ohshima	K. Kato, K. Nishimura	T. Yamaguchi M. Nakano
	800 MHz Solutions, Cryostat Probe		K. Kato	T. Yamaguchi
	600 MHz Solids		K. Nishimura	
Functional Molecular Synthesis and Molecular Device Fabrication	Organic Thin Film Solar Cells	T. Yokoyama	M. Hiramoto	T. Kaji
	Organic Field Effect Transistors		H. Yamamoto	M. Suda, M. Uruichi
	Molecular Catalysts		M. Tada	S. Muratsugu
	Functional Organic Synthesis		H. Sakurai	S. Higashibayashi
	Large Scale Quantum Mechanical Calculations		M. Ehara	R. Fukuda
	Magnetic Thin Films		T. Yokoyama	Y. Takagi, M. Uozumi, Y. Uemura

(d) Inter-University Network for Efficient Utilization of Research Equipments

It is highly important to improve the supporting environment for research and education in the field of science and engineering. Nowadays, advanced research instruments are indispensable for conducting research and education in high standard. To install such sophisticated instruments, significant amount of budgets is necessary. In 2007, for constructing a national-wide network to provide the easy access to high-level equipments to researchers and students in universities all over Japan, the 5 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. 73 national universities all over Japan have been participating to the network. They are grouped into 12 regions and in each region the regional committee discusses and determines the operation of regional network system 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 every public and private universities. Since 2010, the project name has been changed as "Inter-University Network for Efficient Utilization of Research Equipments," still keeping the original strategy and stable functioning. In June 2014, the number of user registrants amounts to more than 9000 in 147 universities/institutions covering more than 2300 laboratories in Japan. Usage of the network reaches to a few thousands per month since April 2010, and keeps growing in numbers.

(e) Consortium for Photon Science and Technology (C-PhoST)

In order to establish strong bases in the research and education in optical science, a new 10-year program “Photon Frontier Network” has been started in 2008 by the Ministry of Education, Culture, Sports, Science and Technology (MEXT). Consortium for Photon Science and Technology (C-PhoST) is the one of two research consortia of Photon Frontier Network. It is composed of 4 Core Organizations headed by Principal Investigators (written in parentheses): Osaka University (R. Kodama), JAEA (A. Sugiyama), Kyoto University (S. Noda) and Institute for Molecular Science (K. Ohmori). The major strength of this Consortium is the collaboration between the specialists in three fields: High power lasers, semiconductor lasers, and coherent control. Emphasis is placed in the education to foster young researchers capable of taking leaderships in scientific projects through participation to the forefront researches taking place at C-PhoST and also participation to international collaboration activities.

Okazaki Conference

The 73rd Okazaki Conference
Coherent and Incoherent Wave Packet Dynamics

(October 30–November 2, 2013)

Organizers: M. Shapiro (*Univ. British Columbia*), K. Ohmori (*IMS*), Y. Ohshima (*IMS*)

The topics discussed at the Coherent and Incoherent Wave Packet Dynamics colloquium are at a forefront of a number of rapidly expanding interdisciplinary areas of research, spanning atomic, molecular, and optical physics, condensed-matter physics, chemical physics, physical chemistry, quantum optics, and quantum information, with the number of groups interested in applying coherent control to such diverse areas of research increasing rapidly from year to year. Of particular interest will be the implementations of recent technological breakthroughs in molecular and laser science, which offer new ways of creating and manipulating molecular processes using quantum effects.

The main objectives of the workshop are: 1) To discuss strategies of making progress in subfields which have so far resisted the application of coherent control. 2) To advance innovative future technologies, and in particular the development of new optical tools to exercise control on the nanoscale. 3) To discuss ways of enhancing the interactions between theoreticians and experimentalists that are absolutely crucial for making progress in such an interdisciplinary field. 4) To lay the foundation for a strong and vibrant hub of activity in coherent control across the Pacific, which will facilitate the exchange of UBC and Japanese scientists and students and the organization of joint workshops and conferences. 5) To make the public more aware of the tremendous potentials of coherent control, and UBC's leadership in this field.

As for the public event, the participants enjoyed an excursion to Asuke village, which is a historical village that used to be a hub of salt trading along "Sanshu Highway" in Edo era. They also enjoyed Samurai performance played by a volunteer group in Okazaki. These events helped participants to develop their personal friendships.

Listed below is the list of invited speakers.

Prof. Ilya Averbukh (Weizmann Institute of Science)
Prof. Thomas Baumert (University of Kassel)
Prof. Jianshu Cao (Massachusetts Institute of Technology)
Prof. Akihito Ishizaki (Institute for Molecular Science)
Prof. Ronnie Kosloff (The Hebrew University of Jerusalem)
Prof. Roman Krems (The University of British Columbia)
Prof. Robert J. Levis (Temple University)
Prof. Valery Milner (The University of British Columbia)
Prof. Takamasa Momose (The University of British Columbia)
Prof. Kazutaka Nakamura (Tokyo Institute of Technology)
Prof. Ed Narevicius (Weizmann Institute of Science)
Prof. Keith Nelson (Massachusetts Institute of Technology)
Prof. Yasuhiro Ohshima (Institute for Molecular Science)
Prof. Hiromi Okamoto (Institute for Molecular Science)
Dr. Leonardo Pachon (University of Toronto)
Dr. Benjamin Sussman (National Research Council, Canada)
Prof. Matthias Weidemuller (University of Heidelberg)

The colloquium yielded a coherent control network across a variety of disciplines raging from atomic physics to biosciences. It has also laid the foundation for a strong and vibrant hub of activity in coherent control across the Pacific between UBC and Japanese scientists, and has made the public more aware of the tremendous potentials of coherent control and UBC's leadership in this field.

The invited speakers gave excellent lectures on the frontiers of a variety of disciplines ranging from AMO physics, nano-sciences, condensed matter physics, and biosciences from a viewpoint of quantum coherence. There was a good balance between experimentalists and theoreticians. Such arrangement of speakers activated interdisciplinary discussion among all the participants to discuss each subject for its new perspective and concept, and to further promote coherent control network across those various disciplines.

Examples of innovative approaches or creative ways of knowing that were developed or expanded through this Colloquium are as follows.

1) New schemes of optical control and observation of molecular rotation, strong-laser induced molecular dissociation and ionization, high bit-rate information processing with molecular vibration, formation of ultracold molecules, and ultracold molecular collisions.
2) Exploring many-body physics with ultracold Rydberg gases and ultracold molecules in an optical lattice.
3) Optical control of collective motion in condensed phases such as plasmon, coherent phonons, and photo-induced phase transitions in bulk solids and nano-materials.
4) Exploring the role of coherence in biological systems such as photosynthesis and circadian rhythm.

The colloquium generated a new research model in which coherent control, which has originally been developed for isolated small molecules, is now being applied to many-body systems ranging from strongly correlated ensembles of ultracold atoms and molecules to biological systems such as photosynthesis. Such active control offers a new possibility for better understanding of those complicated many-body phenomena than that obtained by passive observation.

The colloquium has demonstrated a possibility of new collaborations of two different disciplines such as ultracold physics and ultrafast coherent control, quantum optics and photosynthesis, and quantum information processing and molecular science. It has also promoted collaborations in each discipline among top researchers of Canada, USA, Europe, Israel, and Japan.

Although we initially planned to simulate the exchange of idea and concepts between participants belonging to different research fields, the varieties and diversities of the topics discussed in the colloquia were far more extended than we expected. Some representative examples, exhibiting the present state-of-the-art status of coherent control, includes: Creation of a uni-directionally rotating molecular ensemble with its internal energy reaching to hundred times of thermal ensembles, bimolecular reaction with finely tuned collisional energy ranging from a few tens of K to mK, and spatio-temporal tracking of excitation-energy transfer from a single ultracold Rydberg atom to surrounding ground-state atoms. Still, the discussions were not simply scattered into each specific problems, but always linked to a common concept, *i.e.*, coherent/incoherent nature of the systems under discussions. It was impressive to observe unexpectedly intensive exchange of thoughts between the researchers with different disciplines.

At the beginning, we had always to spend some times to clarify the difference in meaning of the same words or terms among the people with different research backgrounds, before we were able to find out the bottom line of the discussions we shared in the colloquia. After managing this little bit time-consuming process, it became possible to extract the similarity in the underlying physics and the uniqueness of each system, from apparently different two phenomena observed in separated fields, *e.g.*, energy transfer in ultracold atoms and bio-systems. It was also of much appreciation to find out plenty of possibilities of state-of-the-art new technology developed in some research field transferable to a far remote scientific area, for instance, ultrafast laser technology to be implemented in ultracold atomic physics and coherent control of molecular degrees of freedom into quantum information processing.

This article was reprinted from Wall Colloquia Abroad Report, Peter Wall Institute for Advanced Studies, The University of British Columbia.

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. Development of Polarized Quantum Beam Sources and their Applications to Molecular Science

KATOH, Masahiro *(IMS)*
KOBAYASHI, Kensei (*Yokohama Natl. Univ.*)
YAMAMOTO, Naoto (*Nagoya Univ.*)
AKITSU, Takashiro (*Tokyo Univ. Sci.*)
OHGAKI, Hideaki (*Kyoto Univ.*)
KURIKI, Masao (*Hiroshima Univ.*)
TOYOKAWA, Hiroyuki (*AIST*)
KIMURA, Shin-ichi *(Osaka Univ.)*

By using particle accelerator technologies, polarized quantum beams of various kinds can be produced, which can be powerful tools for molecular science. In this joint study program, we have been developing techniques to produce polarized quantum beams and exploring their applications. The major part of the researches has been carried out in the UVSOR facility.

We have succeeded in producing intense circular polarized UV and VUV radiation by using polarization-variable undulators and free electron lasers. We successfully demonstrated that they could be a powerful tool for the investigations on the photon induced chirality on the bio-molecules.[1,2] Towards higher intensity polarized photon beams, we developed a new undulator system called optical klystron and installed it in the ring (Figure 1). The ordinary undulator radiation is useful for experiments that requires wide tunability of the wavelength from UV to VUV but does not require very high intensity. Some experiments on the base metal complexes utilizing these polarized lights have started by the Tokyo Univ. Sci. team. We have successfully demonstrated the generation of coherent VUV radiation by using the undulator and an external laser, based on Coherent Harmonic Generation (CHG) technique. The CHG radiation is also polarization variable and has much higher peak intensity than the ordinary undulator radiation. A combined use of the CHG radiation and coherent terahertz radiation, which is generated simultaneously, is under preparation.

We successfully demonstrated the generation of polarized gamma-rays by using a technique called Laser Compton Scattering (LCS) in collaboration with AIST. Laser photons are injected to the electron beam and are scattered off, and they are converted to gamma-rays via inverse Compton scattering process. The polarity of the gamma-rays can be changed by changing that of the laser photons. We have successfully demonstrated that these gamma-ray photons can be used for the photon-induced positron annihilation lifetime spectroscopy.[3] The possible applications utilizing their polarization are being explored.

In Nagoya University, a polarized electron source has been developed based on an electron gun technology using the GaAs photocathode. The spin polarization higher than 90% has been demonstrated.[4] In collaboration with the Nagoya University team, we have been developing a spin polarized electron source at UVSOR. Some experiments on the chirality of the bio-molecules has been started. An inverse photoelectron spectroscopy system is being developed in collaboration with Osaka University team.

Based on the results on this joint study program, several research projects have started, based on other grants, such as Astrobiology program of CNSI, NINS, Grant-in-Aid for Scientific Research, and so on.

Figure 1. Twin Polarization-variable Undulator System at UVSOR-III.

References

1) J. Takahashi, H. Shinojima, M. Seyama, Y. Ueno, T. Kaneko, K. Kobayashi, H. Mita, M. Adachi, M. Hosaka and M. Katoh, *Int. J. Mol. Sci.* **10**, 3044–3064 (2009).
2) H. Nishino, M. Hosaka, M. Katoh and Y. Inoue, *Chemistry* **19**, 13929–13936 (2013).
3) Y. Taira, H. Toyokawa, R. Kuroda, N. Yamamoto, M. Adachi, S. Tanaka and M. Katoh, *Rev. Sci. Instrum.* **84**, 053305 (2013).
4) N. Yamamoto, X. G. Jin, A. Mano, T. Ujihara, Y. Takeda, S. Okumi, T. Nakanishi, T. Yasue, T. Koshikawa, T. Ohshima, T. Saka and H. Horinaka, *J. Phys.: Conf. Ser.* **298**, 012017 (2011).

B. Development of a Power Delivery IC for Wavelength Selective Organic Solar Cells

MIYAMOTO, Jun-ichi (*Chubu Univ.*)
HIRAMOTO, Masahiro (*IMS*)
KAJI, Toshihiko (*IMS*)
SATO, Motoyasu (*Chubu Univ.*)
ITOH, Hibiki (*Chubu Univ.*)
KATO, Akira (*Chubu Univ.*)

The present project aims at new solar cell system symbiotic with plants. The system uses mainly green-yellow wavelength region, unnecessary for the photosynthesis. One of the research elements is a development of a photocurrent extraction system with a small loss from circuit network connecting the vast number of cells. The system is realized by the Integrated Circuits, based on a new concept, named as a Power Delivery IC (PDIC).

The PDIC block diagram is shown in Figure 1. The voltage drop of the transfer-gate depends on the current flow. But it can be designed to be smaller by enlarging the transistor width. It means that the power of each solar cell can be taken out with little loss in comparison with a conventional one. The transfer-gate goes OFF, when the generated voltage of a cell drops below the reference voltage, preventing the power loss toward the non-active cell. The PDIC also notifies the locations of non-active cells outside, by outputting the memory data. Since the non-active cells are easily detected, they can be replaced in order to sustain whole system performance.

The PDIC was designed, and was fabricated with the 0.18μm CMOS process. The PDIC timing chart is shown in Figure 2, obtained by the actual chip evaluation. Note that the circuits consume the DC power only during the period of activating comparators (MONEN = high.). It is easy to make the PDIC power consumption negligibly small, since the climate changing speed is very slow as an order of second, or even millisecond.

Dye Sensitized Solar Cells (DSSC) are connected to the 4 stage PDIC for power generation system. Figure 3 depicts AC and DC characteristics of the output, PWSUM (power summation). It is shown that in case of 4 active cells, the PWSUM drivability increases and the power is accumulated by PDIC. Actually, because of the performance variation among cells, the total drivability did not exactly equal to 4 times of one cell active case.

The PDIC concept has been successfully verified by evaluating the actual chip. The device concept can be applied not only to DSSC, but also to organic solar cells. In other words, the PDIC, the combination IC of analog & digital circuits and power transistors, enables to accumulate low-density energy source, widely spread over in nature, effectively.

This work is supported by VLSI Design and Education Center, the University of Tokyo in collaboration with Synopsys, Inc., and Cadence Design Systems, Inc.

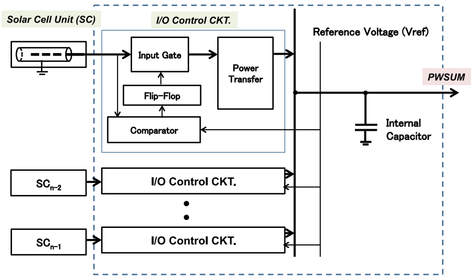


Figure 1. Block Diagram of PDIC. The interface with each Solar Cell is not a conventional blocking diode but a CMOS transfer-gate. The comparator detects whether a cell is active or not, by comparing the generated voltage by a Solar Cell with the reference voltage. The information is stored in the memory, which controls the gate of transfer-gates. The electric power obtained by each active cell is accumulated on the internal capacitor.

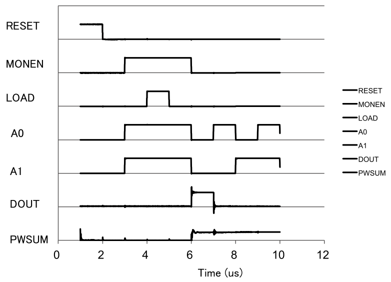


Figure 2. PDIC Timing Chart. At first, the RESET turns all the transfer-gates OFF. Then, the MONEN (Monitor Enable) makes comparator active, and the status of a Solar Cell is loaded in the memory at the LOAD timing. In the Figure, because only one cell is active, DOUT goes high only when the address of the SC, (A0, A1) equals to (0, 0). The accumulated power appears on the PWSUM (Power Summation).

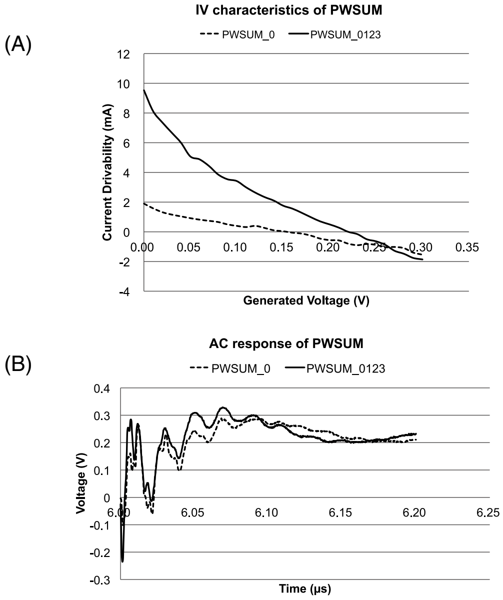


Figure 3. DC (a) and AC (b) Characteristics of PDIC connected to DSSC in both cases of 4 active cells (PWSUM_0123) and just one active cell (PWSUM_0). The PWSUM waveforms correspond to those in Figure 2 between 6 μs and 6.2 μs.

(2) Research Symposia

(From Oct. 2013 to Sep. 2014)

Dates	Theme	Chair
Oct. 3– 4, 2013	Photo-Controllable Electronic Phases in Molecular Conductors	**YAMAMOTO, Hiroshi**
Oct. 25–26, 2013	Future Materials Initiative from π-System Figuration with Multi-Discipline Integration	**ISOBE, Hiroyuki** **SAKURAI, Hidehiro**
Nov. 18–19, 2013	Developing New Ideas Based on the History of Rhodopsin Studies	**IMAMOTO, Yasushi** **FURUTANI, Yuji**
Nov. 25–27, 2013	IMS Asian International Symposium Korea-Japan Seminars on Biomolecular Sciences—Experiments and Simulations	**KATO, Koichi**
Dec. 18–19, 2013	Survey and Perspective of Material Science by Advanced ESR Studies	**OTA, Hitoshi** **NAKAMURA, Toshikazu**
Mar. 12–13, 2014	Structure and Function of Metal Clusters and Coordination Polymers	**NORO, Shin-ichiro** **MURAHASHI, Tetsuro**
Sep. 27, 2014	Molecular Science in the Cell Nucleus	**URISU, Tsuneo** **FURUTANI, Yuji** **SAITO, Shinji**
Jun. 15, 2014	Preparation Meeting for 54th Young Researchers Society for Molecular Science, 2014 Summer School	**FUKUDA, Masahiro** **FURUTANI, Yuji**
Jul. 21–23, 2014	12th ESR Summer School	**TANAKA, Ayaka** **NAKAMURA, Toshikazu**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2013–Mar. 2014		Apr. 2014–Sep. 2014		Total		
		Regular	NanoPlat	Regular	NanoPlat	Regular	NanoPlat	Sum
Special Projects		0		1		1		1
Research Symposia		6		1		7		7
Research Symposia for Young Researchers		0		2		2		2
Cooperative Research		32	24	30	32	62	56	118
Use of Facility	Instrument Center	17	43	14	54	31	97	128
	Equipment Development Center	4	4	3	9	7	13	20
Use of UVSOR Facility		70	30	67	22	137	52	189
Use of Facility Program of the Computer Center						185*		185*

* from April 2013 to March 2014

Collaboration Programs

(a) International 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
Okazaki Conference "Coherent and Incoherent Wave Packet Dynamics"	OHMORI, Kenji (IMS) OHSHIMA, Yasuhiro (IMS) SHAPIRO, Moshe (Univ. British Columbia, Canada)	2013.10.30–11.2	IMS
Workshop at German Science Days in Kyoto "Use of Accelerator-Based Photon Sources: Present State and Perspectives"	RÜHL, Eckart (Freie Univ. Berlin, Germany) KOSUGI, Nobuhiro (IMS)	2013.10.26	Kyoto University
ESR Workshop at Institute for Molecular Science —Toward International Cooperation—	NAKAMURA, Toshikazu (IMS)	2013.10.28–29	IMS
Joint IMS-KU (Kasetsart Univ. Thailand) Workshop "Joint IMS-KU Workshop on Molecular Sciences towards Green Sustainability"	HANNONGBUA, Supa (KU, Thailand) EHARA, Masahiro (IMS)	2014.1.5–1.6	Kasetsart University, Bangkok, Thailand
IMS Asian International Symposium "6th Japan-Korea Seminars on Biomolecular Science—Experiments and Simulations"	AONO, Shigetoshi (IMS) JEONG, Hawoong (KAIST, Korea) KATO, Koichi (IMS) KUWAJIMA, Kunihiro (SOKENDAI) LEE, Jooyoung (KIAS, Korea)	2013.11.25–11.27	IMS
SOKENDAI Asian Winter School "Innovations and Challenges in Molecular Science: From Basics to Cutting-Edge Researches"	MASAOKA, Shigeyuki (IMS) YANAI, Takeshi (IMS) SAKURAI, Hidehiro (IMS)	2013.12.10–12.13	IMS
EXODASS Mini Symposium	SAKURAI, Hidehiro (IMS)	2013.12.11	IMS
IMS Asian CORE (with ICCAS, KAIST, IAMS) "Asian CORE Winter School on Frontiers of Molecular, Photo- and Material Sciences"	UOZUMI, Yasuhiro (IMS) CHEN, Kuei-Hsien (IAMS) TAKAHASHI, Kaito (IAMS)	2014.2.24–2.26	Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan
Meeting with MOU Partner "CU (Chulalongkorn Univ., Thailand)-IMS Faculty Exchange Meeting"	SAKURAI, Hidehiro (IMS)	2014.2.25	IMS
Meeting with MOU Partner "NTU (Nanyang Technological Univ., Singapore)-IMS Faculty Exchange Meeting"	SAKURAI, Hidehiro (IMS)	2014.3.3	IMS

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

Category	Number of People	
	Overseas	Domestic
IMS International Internship Program (EXODASS program incl.)	33*	–
SOKENDAI Asian Winter School (2013.12.10–2013.12.13)	29	14

* from Sep. 2013 to Aug. 2014

(c) IMS International Collaboration

Category	Number of People
International Joint Research Programs	59
International Use of Facilities Programs	34

* from Sep. 2013 to Aug. 2014

(d) MOU Partnership Institutions

IMS has concluded academic exchange and agreements with overseas institutions.

The agreements encourage

- Exchange of researchers
- Internship of students
- Joint research symposia

Institution	Period	Accept	Send
The Korean Chemical Society, Physical Chemistry Division [Korea]	2010.11–2014.11	11	0
Institute of Atomic and Molecular Sciences (IAMS) [Taiwan]	2011. 2–2017. 2	0	18
Institute of Chemistry Chinese Academy of Science (ICCAS) [China]	2008. 9–2018. 9	1	0
Korea Advanced Institute of Science and Technology (KAIST) [Korea]	2012. 9–2016. 9	0	0
École Nationale Supérieure de Chimie de Paris (ENSCP) [France]	2009.10–2014.10 2014.10–2019.10	10	1
Indian Association for the Cultivation of Science (IACS) [India]	2013. 3–2017. 3	4	1
Freie Universität Berlin (FUB) [Germany]	2013. 6–2016. 6	7	1

* from Sep. 2013 to Aug. 2014

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

Institution	Period	Accept	Send
Chulalongkorn University, Faculty of Science [Thailand]	2010.4–2015.10	16	4
Kasetsart University, Faculty of Science [Thailand]	2011.3–2016.3	3	0
Mahidol University, Faculty of Science [Thailand]	2014.3–2019.3	3	1
Nanyang Technological University, College of Science [Singapore]	2014.3–2019.3	1	1
University of Malaya, Faculty of Science [Malaysia]	2014.3–2019.3	10	1

* from Sep. 2013 to Aug. 2014

AWARDS

UOZUMI, Yasuhiro Life and Coordination-Complex Molecular Science	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology (Research Category) “Development of Fine Organic Molecular Transformations with Water-Compatible Heterogeneous Catalysts”
YANAI, Takeshi Theoretical and Computational Molecular Science	The 2013 Young Scientist Awards of the Japan Society for Molecular Science “Development and Its Application of Multireference Electronic Structure Theory Based on Ab Initio Density Matrix Renormalization Group”
TAIRA, Takunori Laser Research Center for Molecular Science	IEEE Fellow “Contributions to the Field of Solid-State Lasers and Nonlinear Optics, in Particular Micro Solid-State Photonics”
FURUTANI, Yuji Life and Coordination-Complex Molecular Science	The 2013 Young Scientist Awards of the Japan Society for Molecular Science “Elucidation of Molecular Mechanisms of Membrane Proteins by Using Infrared Spectroscopy”
SAKURAI, Hidehiro Research Center of Integrative Molecular Systems	Chemical Society of Japan Award for Creative Work “Non-Planar π-Conjugated Compound “Buckybowl” Based on Synthetic Organic Chemistry”
SHIKANO, Yutaka Research Center of Integrative Molecular Systems	Resarch Award, Research Foundation for Opto-Science and Technology “Theoretical Study on Quantumness of Photon using Weak Measurement Theory”
KURASHIGE, Yuki Theoretical and Computational Molecular Science	Morino Foundation for Molecular Science (2014) “Development of Quantum-Chemical Density-Matrix Renormalization Group Theory and Applications to Metalloenzymes”
NAGASAKA, Masanari Photo-Molecular Science	Young Scientist Award of the Japanese Society for Synchrotron Radiation Research “Local Structural Analyses of Molecular Systems and Development of In-Situ Observation Methods by Soft X-Ray Spectroscopy”
KAJI, Toshihiko Materials Molecular Science	2013 M&BE Award for Young Researcher “Co-Evaporant Induced Crystalline Donor:Acceptor Blends in Organic Solar Cells”
YAMAGUCHI, Takumi Life and Coordination-Complex Molecular Science	Presentation Award, The 7th Symposium on Biofunctional Chemistry “Paramagnetic NMR Analyses of Conformational Dynamics of Oligosaccharides by Introducing of a Lanthanide-Probe” The 3rd NINS Prize for Young Scientists “Elucidation of Conformational Dynamics and Functional Mechanisms of Oligosaccharides by Nuclear Magnetic Resonance Spectroscopy”

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 2013–August 2014) are listed below.

(1) Attendance at an Okazaki Conference

Prof. Baumert, Thomas	Univ. Kassel	Germany	Oct. ’13–Nov. ’13
Prof. Sussman, Benjamin J.	Natl. Res. Council Canada	Canada	Oct. ’13–Nov. ’13
Prof. Avebukh, Ilya	Weizmann Inst. of Sci.	Israel	Oct. ’13–Nov. ’13
Prof. Cao, Janshu	Massachusetts Inst. of Tech.	U.S.A.	Oct. ’13–Nov. ’13
Prof. Kosloff, Ronnie	Hevrew Univ. of Jerusalem	Israel	Oct. ’13–Nov. ’13
Prof. Krems, Roman	Univ. of British Columbia	Canada	Oct. ’13–Nov. ’13
Prof. Levis, Rovert J.	Temple Univ.	U.S.A.	Oct. ’13–Nov. ’13
Dr. Milner, Valerie	Univ. of British Columbia	Canada	Oct. ’13–Nov. ’13
Prof. Momose, Takamasa	Univ. of British Columbia	Canada	Oct. ’13–Nov. ’13
Prof. Wridemuller, Matthias	Univ. of Heidelberg	Germany	Oct. ’13–Nov. ’13
Mr. Han, Alex	Univ. of British Columbia	Canada	Oct. ’13–Nov. ’13
Dr. Pachon, Leonardo	Univ. of Toronto	Canada	Oct. ’13–Nov. ’13
Prof. Narevicius, Edvardas	Weizmann Inst. of Sci.	Israel	Oct. ’13–Nov. ’13
Prof. Nelson, Keith	Massachusetts Inst. of Tech.	U.S.A.	Oct. ’13–Nov. ’13

(2) IMS Councillor

Prof. Fleming, Graham	Univ. of California, Berkeley	U.S.A.	Oct. ’13
Prof. WALES, David John	Univ. of Cambridge	U.K.	Nov. ’13 Mar. ’14–Apr. ’14
Prof. Hitchcock, Adam	McMaster Univ.	Canada	Jan. ’14–Feb. ’14
Prof. O'Halloran, Thomas	Northwestern Univ.	U.S.A.	Mar. ’14

(3) IMS Visiting Professor or Associate Professor from Abroad

Prof. Aziz, Emad	Freie Univ. Berlin	Germany	Jun. ’14–Dec. ’14

(4) JSPS Post-Doctoral or Ronpaku Fellow

Mr. Di Molfetta, Giuseppe	Univ. Pierre and Marie Curie	France	Jun. ’14–Aug. ’14
Dr. Hua, Duy Huu	Kansas State Univ.	U.S.A.	Aug. ’14

(5) IMS Visiting Scientist

Prof. Rueh, Eckart	Freie Univ. Berlin	Germany	Sep. ’13
Prof. Flesch, Roman	Freie Univ. Berlin	Germany	Sep. ’13
Dr. Kuechler, Sarah	Freie Univ. Berlin	Germany	Sep. ’13
Dr. Lin, Ming-Wei	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Sep. ’13
Dr. Hsu, Yao-Chen	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Sep. ’13
Dr. Shiu, Hung-Wei	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Sep. ’13
Dr. Lai, Yu-Ling	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Sep. ’13
Mr. Qin, Zhisheng	McMaster Univ.	Canada	Sep. ’13 Dec. ’13
Ms. Jia, Ti Tee	Univ. Malaya	Malaysia	Sep. ’13–Dec. ’13
Dr. Aruua, Ruben Dario	Univ. of Tasmania	Australia	Oct. ’13
Mr. Kim, Hyo Sung	POSTECH	Korea	Oct. ’13
Prof. MacLachan, Mark J.	Univ. of British Columbia	Canada	Oct. ’13
Prof. Stepien, Marcin Lukasz	Univ. of Wroslaw	Poland	Oct. ’13
Prof. Benerji, Natalie Renuka	Ecole Plytechnic Federal of Lausanne	Switzerland	Oct. ’13
Prof. Siegel, Jay S.	Tianjin Univ.	China	Oct. ’13
Prof. Kruger, Anke	Univ. Wurzburg	Germany	Oct. ’13
Prof. Wu, Jishan	Natl. Univ. of Singapore	Singapore	Oct. ’13
Mr. Son, Yeong Seop	POSTECH	Korea	Oct. ’13
Mr. Tungjitgusongun, Vithawas	Mahidol Univ.	Thailand	Oct. ’13–Dec. ’13
Ms. Tien, Yeh Tien	Natl. Chiao Tung Univ.	Taiwan	Oct. ’13–Dec. ’13
Mr. Impeng, Sarawoot	Kasesart Univ.	Thailand	Oct. ’13–Dec. ’13
Ms. Li, Binbin	Nanyang Technological Univ.	Singapore	Oct. ’13–Dec. ’13

LIST OF VISITING FOREIGN SCHOLARS

Prof. Dalagan, Juliet	Xavier Univ.-Ateneo de Cagayan	Philippines	Oct. ’13–Dec. ’13
Dr. Khongprcha, Pipat	Kasetsart Univ.	Thailand	Oct. ’13–Dec. ’13
Dr. Padungros, Panuwat	Chulalongkorn Univ.	Thailand	Oct. ’13–Dec. ’13
Mr. Wang, Yu-Fu	Tamkang Univ.	Taiwan	Oct. ’13–Mar. ’14
Mr. Jung, Sung Won	POSTECH	Korea	Oct. ’13–Mar. ’14
Ms. Chinapang, Pondchanok	Chulalongkorn Univ.	Thailand	Oct. ’13–Mar. ’14
Mr. Shin, Woojong	POSTECH	Korea	Nov. ’13
Mr. Wnag, Hsaui-Tsu	Natl. Tsinghua Univ.	Taiwan	Nov. ’13
Prof. Pong, Way-Faung	Tamkang Univ.	Taiwan	Nov. ’13
Prof. Chiou, Jan-Wern	Natl. Univ. of Kaohsing	Taiwan	Nov. ’13
Prof. Han, Sang Wook	POSTECH	Korea	Nov. ’13
Mr. Oon Han, Thomas Loke	Univ. of Western Australia	Australia	Nov. ’13–Dec. ’13
Ms. Wenting, Liu	Shanghai Univ.	China	Nov. ’13–Dec. ’13
Ms. Uyen, Tran Phuoc Nhat	Ho Chi Minh Univ. of Tech.	Vietnam	Nov. ’13–Dec. ’13
Dr. Srnec, Martin	Inst. of Organic Chemistry and Biochemistry AS CR	Czech	Dec. ’13
Dr. Rulisek, Lubomir	Inst. of Organic Chemistry and Biochemistry AS CR	Czech	Dec. ’13
Dr. Lin, Ming-Wei	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Dec. ’13
Dr. Shiu, Hung-Wei	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Dec. ’13
Ms. Lai, Yu-Ling	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Dec. ’13
Mr. Chang, Chiao-Kai	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Dec. ’13
Mr. Chiou, Guan-Chiun	Natl. Synchrotron Radiation Res. Cent.	Taiwan	Dec. ’13
Dr. Rosendahl, Scott	McMaster Univ.	Canada	Jan. ’14–Feb. ’14
Ms. Jo, Jihee	Chosun Univ.	Korea	Jan. ’14–Feb. ’14
Prof. Lim, Jong Kuk	Chosun Univ.	Korea	Jan. ’14–Feb. ’14
Mr. Eberle, Fabian	Freie Univ. Berlin	Germany	Jan. ’14–Mar. ’14
Mr. Hansen, Jared	Michigan State Univ.	U.S.A.	Jan. ’14–May. ’14
Mr. Zhu, Xiaohui	McMaster Univ.	Canada	Jan. ’14–May. ’14
Prof. Rachatasakorn, Pitoon	Chulalongkorn Univ.	Thailand	Feb. ’14
Prof. Parasuk, Vudhichai	Chulalongkorn Univ.	Thailand	Feb. ’14
Prof. Chavasiri, Warinthorn	Chulalongkorn Univ.	Thailand	Feb. ’14
Prof. Insin, Numpon	Chulalongkorn Univ.	Thailand	Feb. ’14
Prof. Srisa-Art, Monphichar	Chulalongkorn Univ.	Thailand	Feb. ’14
Prof. Wacharasindhu, Sumrit	Chulalongkorn Univ.	Thailand	Feb. ’14
Prof. Wanichwecharungrung, Supar	Chulalongkorn Univ.	Thailand	Feb. ’14
Prof. Wu, Shengjun	Nanjing Univ.	China	Feb. ’14
Mr. Knee, George C.	Univ. of Oxford	U.K.	Feb. ’14–Mar. ’14
Dr. Zhu, Xuanmin	Univ. of Sci. and Tech. of China	China	Feb. ’14–Mar. ’14
Mr. Zhang, Yu-xiang	Nanjin Univ.	China	Feb. ’14–Mar. ’14
Prof. Loh, Zhi Heng	Nanyang Technological Univ.	Singapore	Mar. ’14
Prof. Hiraoo, Hajime	Nanyang Technological Univ.	Singapore	Mar. ’14
Prof. Yeow, Edwin	Nanyang Technological Univ.	Singapore	Mar. ’14
Prof. Sum, Tze Chien	Nanyang Technological Univ.	Singapore	Mar. ’14
Prof. Tan, Howe-Siang	Nanyang Technological Univ.	Singapore	Mar. ’14
Mr. Pipart, Franck	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Mar. ’14–Aug. ’14
Mr. LECUYER, Thomas	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Mar. ’14–Aug. ’14
Ms. Duchesne, Constance	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Mar. ’14–Aug. ’14
Ms. Le Gulluche, Anne-Charlotte	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Mar. ’14–Aug. ’14
Ms. Wolanin, Julie	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Mar. ’14–Aug. ’14
Ms. Pamela, Jeppson	Western Michigan Univ.	U.S.A.	Apr. ’14
Prof. Paraan, Francis	Univ. of the Philippines Diliman	Philippines	May. ’14
Dr. Victoria, Maria	Philippine General Hospital	Philippines	May. ’14
Prof. Sommerfeld, Thomas	Southeastern Louisiana Univ.	U.S.A.	May. ’14
Ms. Islam, Zeba	Indian Inst. of Tech., Bombay	India	May. ’14–Jun. ’14
Mr. Jhunjhunwala, Tarun	Indian Inst. of Tech., Bombay	India	May. ’14–Jun. ’14
Mr. Zhang, Yu-Xiang	Xidian Univ.	China	May. ’14–Jul. ’14
Prof. Priyakumar, U. Deva	Int. Inst. of Information Tech., Hyderabad	India	May. ’14–Aug. ’14
Dr. Pan-In, Porntip	Chulalongkorn Univ.	Thailand	Jun. ’14
Dr. VEIS, Libor	J. Heyrovský Inst. of Physical Chemistry	Czech	Jun. ’14–Jul. ’14

Dr. Rosendahl, Scott	McMaster Univ.	Canada	Jun. ’14–Jul. ’14
Mr. Luo, Ben Bin-Bin	Univ. of Western Australia	Australia	Jun. ’14–Jul. ’14
Mr. Honter, Lauchran Thomas	Univ. of Western Australia	Australia	Jun. ’14–Jul. ’14
Ms. Noikham, Medena	Mahidol Univ.	Thailand	Jun. ’14–Aug. ’14
Mr. Mekseriwattana, Wid	Mahidol Univ.	Thailand	Jun. ’14–Aug. ’14
Mr. Peuvot, Kevin	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Jun. ’14–Aug. ’14
Mr. Zeng, Qingcong	The Univ. of Queensland	Australia	Jun. ’14–Sep. ’14
Mr. Shin, Woojong	POSTECH	Korea	Jul. ’14
Mr. Ryu, Sae Hee	POSTECH	Korea	Jul. ’14
Mr. Wang, HsiaoTsu	Natl. Tsinghua Univ.	Taiwan	Jul. ’14
Mr. Hsieh, ShangHsien	Tamkang Univ.	Taiwan	Jul. ’14
Dr. Marika, Savarese	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Jul. ’14
Mr. Kim, Jimin	POSTECH	Korea	Jul. ’14
Mr. Kim, Keun Su	POSTECH	Korea	Jul. ’14
Dr. Arrua, Dario	Univ. of Tasmania	Australia	Jul. ’14
Mr. Seo, Jungjin	Yonsei Univ.	Korea	Jul. ’14
Mr. Kim, Beom Seo	Yonsei Univ.	Korea	Jul. ’14
Mr. Kyung, Wonshik	Yonsei Univ.	Korea	Jul. ’14
Mr. Turek, Yusuf	Chinese Academy of Sci.	China	Jul. ’14–Sep. ’14
Prof. NASSIRI, Mohammadreza	Ferdowsi Univ. of Mashhad	Iran	Jul. ’14–Dec. ’14
Prof. Lim, Jong Kuk	Chosun Univ.	Korea	Aug. ’14
Prof. Park, Seung Ryong	Incheon Natl. Univ.	Korea	Aug. ’14
Mr. Cho, Soo Hyun	Yonsei Univ.	Korea	Aug. ’14
Mr. Kim, Bum Seo	Yonsei Univ.	Korea	Aug. ’14
Mr. Seo, Jungjin	Yonsei Univ.	Korea	Aug. ’14
Mr. Kwon, Junyoung	Yonsei Univ.	Korea	Aug. ’14
Ms. Chinapang, Pondchanok	Chulalongkorn Univ.	Thailand	Aug. ’14–Sep. ’14

(6) Visitor to IMS

Prof. Bisht, Prem B.	Indian Inst. of Tech. Madras	India	Oct. ’13
Prof. Bittl, Robert	Freie Univ. Berlin	Germany	Oct. ’13
Prof. Agapie, Theodor	California Inst. of Tech.	U.S.A.	Oct. ’13
Prof. Ahnm, Tae Kyu	Sungkyunkwan Univ.	Korea	Nov. ’13
Prof. Hiers, Jean Cyrille	Univ. of Burgundy	France	Nov. ’13
Dr. Kim, Jong Yun	Korea Inst. for Advanced Study	Korea	Nov. ’13
Mr. Sim, Jun	Soongsil Univ.	Korea	Nov. ’13
Dr. Kang, Ranhee	Seoul Natl. Univ.	Korea	Nov. ’13
Dr. Kim, Min-Kyu	Korea Inst. of Ocean Sci. and Tech.	Korea	Nov. ’13
Dr. Cheng, Qianyi	Korea Inst. for Advanced Study	Korea	Nov. ’13
Dr. Nam, Minkyung	Korea Inst. for Advanced Study	Korea	Nov. ’13
Dr. Heo, Seungryong	Korea Inst. for Advanced Study	Korea	Nov. ’13
Prof. Choi, Sun	Ewha Womans Univ.	Korea	Nov. ’13
Prof. Eom, Soo Hyun	Gwangju Inst. of Sci. and Tech.	Korea	Nov. ’13
Prof. Lee, Nam Ki	POSTECH	Korea	Nov. ’13
Prof. Yoon, Sug-il	Kangwon Natl. Univ.	Korea	Nov. ’13
Prof. Yu, Jaehoon	Seoul Natl. Univ.	Korea	Nov. ’13
Prof. Lee, Jinwoo	Kwangwoon Univ.	Korea	Nov. ’13
Prof. Cha, Sun-Shin	Korea Inst. of Ocean Sci. and Tech.	Korea	Nov. ’13
Prof. Rhee, Young Min	POSTECH	Korea	Nov. ’13
Prof. Shin, Seokmin	Seoul Natl. Univ.	Korea	Nov. ’13
Prof. Hyeon, Changbong	Korea Inst. for Advanced Study	Korea	Nov. ’13
Prof. Lee, Jooyoung	Korea Inst. for Advanced Study	Korea	Nov. ’13
Prof. Seok, Chaok	Seoul Natl. Univ.	Korea	Nov. ’13
Prof. Lee, Weontae	Yonsei Univ.	Korea	Nov. ’13
Prof. Lee, Julian	Soongsil Univ.	Korea	Nov. ’13
Dr. Manavalan, Balachandran	Korea Inst. for Advanced Study	Korea	Nov. ’13
Dr. Joung, Jong Young	Korea Inst. for Advanced Study	Korea	Nov. ’13
Dr. Joung, In Suk	Korea Inst. for Advanced Study	Korea	Nov. ’13

LIST OF VISITING FOREIGN SCHOLARS

Prof. Joo, Keehyoung	Korea Inst. for Advanced Study	Korea	Nov. ’13
Prof. Lindau, Evert Ingolf	Stanford Univ.	U.S.A.	Dec. ’13
Prof. Haacke, Stefan	Inst. of Physics and Chemistry of Mater. of Strasbourg	France	Dec. ’13
Prof. Avarvari, Narcis	CNRS, Univ. of Angers	France	Dec. ’13
Mr. Nguyen, Guong(Viet)	Hanoi Univ. of Sci. and Tech.	Vietnam	Dec. ’13
Ms. Fitriastuti, Dhina	Gadjah Mada Univ.	Indonesia	Dec. ’13
Mr. Ang, Chung Yen	Nayang Technological Univ.	Singapore	Dec. ’13
Ms. Sugiarta, Cynthia (komalasari)	Gadjah Mada Univ.	Indonesia	Dec. ’13
Ms. Songhao, Jittikarn	Chulalongkorn Univ.	Thailand	Dec. ’13
Mr. Sae-Lee, Tinnakorn	Chiang Mai Univ.	Thailand	Dec. ’13
Mr. Sukato, Rnagsarit	Chulalongkorn Univ.	Thailand	Dec. ’13
Ms. Boonsri, Manutchanok	Chulalongkorn Univ.	Thailand	Dec. ’13
Ms. Pothipor, Chamari	Chiang Mai Univ.	Thailand	Dec. ’13
Mr. Saputra, Andrian	Gadjah Mada Univ.	Indonesia	Dec. ’13
Mr. Kang, Yuetong	Tsinghua Univ.	China	Dec. ’13
Mr. Jusuf, Daniel (oktavianto)	Gadjah Mada Univ.	Indonesia	Dec. ’13
Mr. Song, Qiao	Tsinghua Univ.	China	Dec. ’13
Ms. Pasma, Satriani (Aga)	Natl. Univ. of Malaysia	Malaysia	Dec. ’13
Ms. Kerdpol, Khanittha	Chiang Mai Univ.	Thailand	Dec. ’13
Ms. Tan, Si Yu	Nanyang Technological Univ.	Singapore	Dec. ’13
Ms. Nguyen, (kim) Truc	Nanyang Technological Univ.	Singapore	Dec. ’13
Prof. EBESSEN, Thomas	Strasbourg Univ.	France	Jan. ’14
Prof. Beller, Matthias	Univ. of Rostoch	Germany	Jan. ’14
Prof. PETEK, Hrvoje	Univ. of Pittsburgh	U.S.A.	Feb. ’14
Prof. Bera, Jitendra K.	Indian Inst. of Tech. Kanpur	India	Feb. ’14
Dr. Kedem, Yaron	Nordic Inst. for Theoretical Physics	Sweden	Feb. ’14
Dr. Großmann, Frank	Dresden Univ. of Tech.	Germany	Mar. ’14
Prof. Promarak, Vinich	Suranaree Univ. of Tech.	Thailand	Apr. ’14
Prof. Jungsuttiwong, Siriporn	Ubon Ratchathani Univ.	Thailand	Apr. ’14
Dr. Namuangruk, Supawadee	Natl. NanoTech. Cent.	Thailand	Apr. ’14
Prof. Carlo, Adamo	Ecole Natl. Superieure de Chimie de Paris (Cheime Paris Tech)	France	Apr. ’14
Prof. Frenking, Gernot	Philipps-Univ. of Marburg	Germany	Apr. ’14
Dr. Choowongkomon, Kiattawee	Kasetsart Univ.	Thailand	Apr. ’14
Prof. Huang, Yen-Chieh	Natl. Tsinghua Univ.	Taiwan	Apr. ’14
Prof. Sorokina, Irina T.	Norwegian Univ. of Sci. and Tech.	Norway	Apr. ’14
Mr. Liu, Zuosheng	Univ. of Beijing	China	Apr. ’14
Prof. Zhang, Zhigang	Univ. of Beijing	China	Apr. ’14
Dr. Son, Seyeong	Chungbuk Natl. Univ.	Korea	Apr. ’14
Prof. Sorokin, Evgeni	Vienna Univ. of Tech.	Austria	Apr. ’14
Prof. Müller-Dethlefs, Klaus	Univ. of Manchester	U.K.	May ’14
Dr. GENES, Claudiu	Univ. of Innsbruck	Austria	May ’14
Prof. PUPILLO, Guido	Univ. of Strasbourg and CNRS	France	May ’14
Prof. G. Narahari, Sastry	Indian Inst. of Tech., CSIR	India	Jun. ’14
Prof. Li, Yongfang	Chinese Academy of Sci.	China	Jul. ’14
Dr. Ibrahim, Heide Nadda	Natl. Inst. of Scientific Res.	Canada	Jul. ’14
Mr. Thallmair, Sebastian	Ludwig-Maximilians-Univ. München	Germany	Jul. ’14

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

Theoretical and Computational Molecular Science

K. KIM, S. SAITO, K. MIYAZAKI, G. BIROLI and D. R. REICHMAN, "Dynamic Length Scales in Glass-Forming Liquids: An Inhomogeneous Molecular Dynamics Simulation Approach," *J. Phys. Chem. B* **117**, 13259–13267 (2013).

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R. JIN and K. NOBUSADA, "Doping and Alloying in Atomically Precise Gold Nanoparticles," *Nano Res.* **7**, 285–300 (2014).

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F. LIU, Y. KURASHIGE, T. YANAI and K. MOROKUMA, "Multireference *Ab Initio* Density Matrix Renormalization Group (DMRG)-CASSCF and -CASPT2 Study on the Photochromic Ring-Opening of Spiropyran," *J. Chem. Theory Comput.* **9**, 4462–4469 (2013).

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Y. KURASHIGE, "Multireference Electron Correlation Methods with Density Matrix Renormalisation Group Reference Functions," *Mol. Phys.* **112**, 1485–1494 (2014).

S. SHARMA, T. YANAI, G. H. BOOTH, C. J. UMRIGAR and G. K.-L. CHAN, "Spectroscopic Accuracy Directly from Quantum Chemistry: Application to Ground and Excited States of Beryllium Dimer," *J. Chem. Phys.* **140**, 104112 (8 pages) (2014).

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L. N. TRAN, Y. KURASHIGE and T. YANAI, "Toward Reliable Prediction of Hyperfine Coupling Constants Using *Ab Initio* Density Matrix Renormalization Group Method: Diatomic Radicals as Test Cases," *J. Chem. Theory Comput.* **10**, 1953–1967 (2014).

Y. KURASHIGE, M. SAITOW, J. CHALUPSKÝ and T. YANAI, "Radical O–O Coupling Reaction in Diferrate-Mediated Water Oxidation Studied with Multireference Wave Function Theory," *Phys. Chem. Chem. Phys.* **16**, 11988–11999 (2014).

M. EHARA, R. FUKUDA, C. ADAMO and I. CIOFINI, "Chemically Intuitive Indexes for Charge-Transfer Excitation Based on SAC-CI and TD-DFT Calculations," *J. Comput. Chem.* **34**, 2498–2501 (2013).

R. FUKUDA and M. EHARA, "Electronic Excited States and Electronic Spectra of Biphenyl: A Study Using Many-Body Wavefunction and Density Functional Theories," *Phys. Chem. Chem. Phys.* **15**, 17426–17434 (2013).

J. A. HANSEN, M. EHARA and P. PIECUCH, "Aerobic Oxidation of Methanol to Formic Acid on Au_8^-: Benchmark Analysis Based on Completely Renormalized Coupled-Cluster and Density Functional Theory Calculations," *J. Phys. Chem. A* **117**, 10416–10427 (2013).

Y. MORISAWA, M. YASUNAGA, R. FUKUDA, M. EHARA and Y. OZAKI, "Electronic Transitions in Liquid Amides Studied Using Attenuated Total Reflection Far-Ultraviolet Spectroscopy and Quantum Chemical Calculations," *J. Chem. Phys.* **139**, 154301 (9 pages) (2013).

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M. TASHIRO, M. EHARA, S. KUMA, Y. MIYAMOTO, N. SASAO, S. UETAKE and M. YOSHIMURA, "Iodine Molecule for Neutrino Mass Spectroscopy: Ab Initio Calculation of Spectral Rate," *Prog. Theor. Exp. Phys.* 013B02 (21 pages) (2014).

M. PROMKATKAEW, S. SURAMITR, T. KARPKIRD, S. WANICHWEACHARUNGRANG, M. EHARA and S. HANNONGBUA, "Photophysical Properties and Photochemistry of the Substituted Cinnamates and Cinnamic Acids for UVB Blocking Function: Effect of Hydroxy, Nitro, and Fluoro Substitutions at Ortho-, Meta- and Para-Position," *Photochem. Photobiol. Sci.* **13**, 583–594 (2014).

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S. IMPENG, P. KHONGPRACHA, C. WARAKULWIT, B. JANSANG, J. SIRIJARAENSRE, M. EHARA and J. LIMTRAKUL, "Direct Oxidation of Methane to Methanol on Fe-O Modified Graphene," *RSC Adv.* **4**, 12572–12578 (2014).

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).

L. HEDIN, M. TASHIRO, P. LINUSSON, J. H. D. ELAND, M. EHARA, K. UEDA, V. ZHAUNERCHYK, L. KARLSSON and R. FEIFEL, "Single Site Double Core Level Ionization of OCS," *Chem. Phys.* **439**, 111–116 (2014).

P. MAITARAD, S. NAMUANGRUK, D. ZHANG, L. SHI, H. LI, B. BOEKFA, L. HUANG and M. EHARA, "Metal-Porphyrin: A Potential Catalyst for N_2O Direct Decomposition by Theoretical Reaction Mechanism Investigation," *Environ. Sci. Technol.* **48**, 7101–7110 (2014).

H. TSUJI, H. A. FORGARTY, M. EHARA, R. FUKUDA, D. CASHER, K. TAMAO, H. NAKATSUJI and J. MICHL, "Electronic Transitions of Conformationally Controlled Tetrasilanes with Wide Range of SiSiSiSi Dihedral Angles," *Chem. –Eur. J.* **20**, 9431–9441 (2014).

H. KUNIYASU, A. SANAGAWA, T. NAKAJIMA, T. IWASAKI, N. KAMBE, K. BOBUATONG and M. EHARA, "Halogen Exchange by Reaction of $CpRu(PPh_3)_2Cl$ with MeC(O)X (X = Br, I) and Its Mechanistic Study," *J. Organomet. Chem.* **769**, 34–37 (2014).

H. OKUMURA and S. G. ITOH, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
H.-L. CHIANG, C.-J. CHEN, H. OKUMURA and C.-K. HU, "Transformation between α-Helix and β-Sheet Structures of One and Two Polyglutamine Peptides in Explicit Water Molecules by Replica-Exchange Molecular Dynamics Simulations," *J. Comput. Chem.* **35**, 1430–1437 (2014).
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S. G. ITOH and H. OKUMURA, "Hamiltonian Replica-Permutation Method and Its Applications to an Alanine Dipeptide and Amyloid-β(29-42) Peptides," *J. Comput. Chem.* **34**, 2493–2497 (2013).

I. TAKASHIMA, A. KANEGAE, M. SUGIMOTO and A. OJIDA, "Aza-Crown-Ether-Appended Xanthene: Selective Ratiometric Fluorescent Probe for Silver(I) Ion Based on Arene–Metal Ion Interaction," *Inorg. Chem.* **53**, 7080–7082 (2014).
I. TAKASHIMA, M. KINOSHITA, R. KAWAGOE, S. NAKAGAWA, M. SUGIMOTO, I. HAMACHI and A. OJIDA, "Design of Ratiometric Fluorescent Probes Based on Arene–Metal-Ion Interactions and Their Application to Cd^{II} and Hydrogen Sulfide Imaging in Living Cells," *Chem. –Eur. J.* **20**, 2184–2192(2014).

Photo-Molecular Science

T. NARUSHIMA and H. OKAMOTO, "Strong Nanoscale Optical Activity Localized in Two-Dimensional Chiral Metal Nanostructures," *J. Phys. Chem. C* **117**, 23964–23969 (2013).
K. IMURA, K. UENO, H. MISAWA, H. OKAMOTO, D. McARTHUR, B. HOURAHINE and F. PAPOFF, "Plasmon Modes in Single Gold Nanodiscs," *Opt. Express* **22**, 12189–12199 (2014).
T. NARUSHIMA, S. HASHIYADA and H. OKAMOTO, "Nanoscopic Study on Developing Optical Activity with Increasing Chirality for Two-Dimensional Metal Nanostructures," *ACS Photonics* **1**, 732–738 (2014).

M. HAYASHI and Y. OHSHIMA, "Sub-Doppler Electronic Spectra of the Benzene–$(H_2)_n$ Complexes," *J. Phys. Chem. A* **117**, 9819–9830 (2013).
M. KONDOH, Y. OHSHIMA and M. TSUBOUCHI, "Ion Effects on the Structure of Water Studied by Terahertz Time-Domain Spectroscopy," *Chem. Phys. Lett.* **591**, 317–322 (2014).
C. NIIDA, M. NAKAJIMA, Y. SUMIYOSHI, Y. OHSHIMA, H. KOHGUCHI and Y. ENDO, "FTMW Spectroscopy and Determination of the 3-Dimensional Potential Energy Surface for Ar–CS," *J. Chem. Phys.* **140**, 104310 (8 pages) (2014).

H. KATSUKI, J. C. DELAGNES, K. HOSAKA, K. ISHIOKA, H. CHIBA, E. S. ZIJLSTRA, M .E. GARCIA, H. TAKAHASHI, K. WATANABE, M. KITAJIMA, Y. MATSUMOTO, K .G. NAKAMURA and K. OHMORI, "All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth," *Nat. Commun.* **4**, 2801 (7 pages) (2013).
Y. OHTSUKI, H. GOTO, H. KATSUKI and K. OHMORI, "Theoretical/Numerical Study on Strong-Laser-Induced Interference in the B State of I_2," *Phys. Chem. Chem. Phys.* **16**, 5689–5697 (2014).
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T. OHIGASHI, H. ARAI, T. ARAKI, N. KONDO, E. SHIGEMASA, A. ITO, N. KOSUGI and M. KATOH, "Construction of the Scanning Transmission X-Ray Microscope Beamline at UVSOR," *J. Phys.: Conf. Ser.* **463**, 012006 (4 pages) (2013).
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H. KONDOH, Y. HIGASHI, M. YOSHIDA, Y. MONYA, R. TOYOSHIMA, K. MASE, K. AMEMIYA, F. TSUKIOKA, M. NAGASAKA, Y. IWASAWA, H. ORITA, K. MUKAI and J. YOSHINOBU, "Structure and Photo-Induced Charge Transfer of Pyridine Molecules Adsorbed on TiO_2(110): A NEXAFS and Core-Hole-Clock Study," *Electrochemistry* **82**, 341–345 (2014).

H. NISHINO, M. HOSAKA, M. KATOH and Y. INOUE, "Photoreaction of rac-Leucine in Ice by Circularly Polarized Synchrotron Radiation: Temperature-Induced Mechanism Swithing from Norrish Type II to Deamination," *Chem. –Eur. J.* **19**, 13929–13936 (2013).
E. ROUSSEL, C. EVAIN, M. LE PARQUIER, C. SZWAJ, S. BIELAWSKI, M. HOSAKA, N. YAMAMOTO, Y. TAKASHIMA, M. SHIMADA, M. ADACHI, H. ZEN, S. KIMURA and M. KATOH, "Transient Response of Relativistic Electron Bunches to Wave-Number Selected Perturbations near the Micro-Bunching Instability Threshold," *New J. Phys.* **16**, 063027 (11 pages) (2014).
E. ROUSSEL, C. EVAIN, C. SZWAJ, S. BIELAWSKI, J. RAASCH, P. THOMA, A. SCHEURING, M. HOFHERR, K. ILIN, S. WÜNSCH, M. SIEGEL, M. HOSAKA, N. YAMAMOTO Y. TAKASHIMA, H. ZEN, T. KONOMI, M. ADACHI, S. KIMURA and M. KATOH, "Microbunching Instability in Relativistic Electron Bunches: Direct Observations of the Microstructures Using Ultrafast YBCO Detectors," *Phys. Rev. Lett.* **113**, 094801 (5 pages) (2014).

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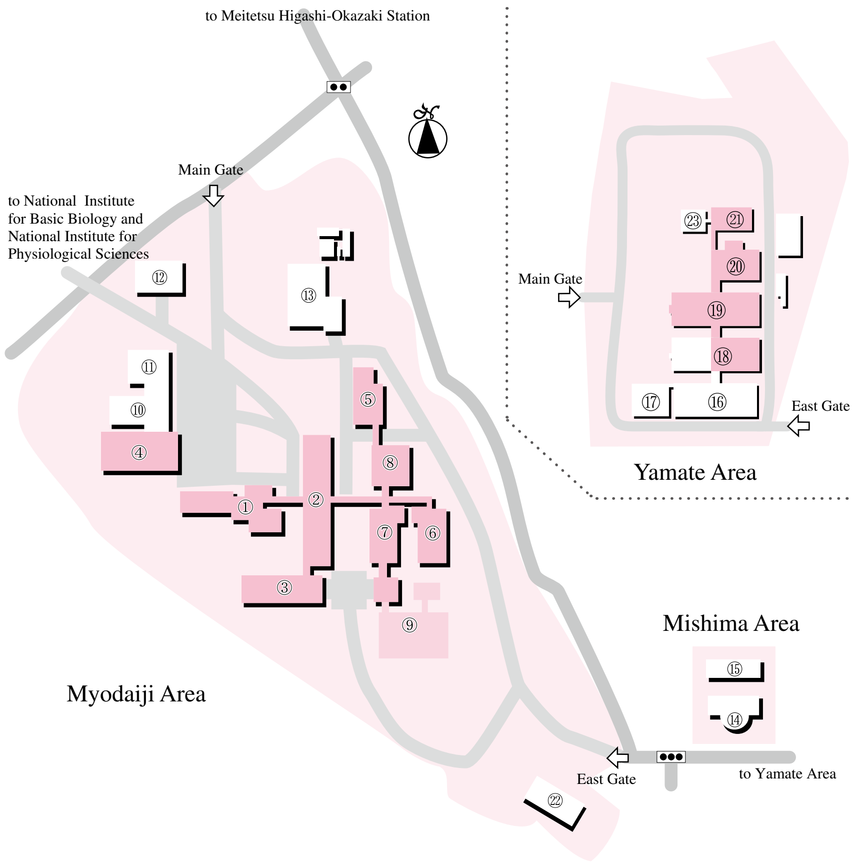

1. Research Office Building
2. Main Laboratory Building
3. South Laboratory Building
4. Research Center for Computational Science
5. Low-Temperature Facilities Building
6. Instrument Center
7. Laser Research Center for Molecular Science
8. Equipment Development Center
9. UVSOR Facility
10. Central Administration
11. Library
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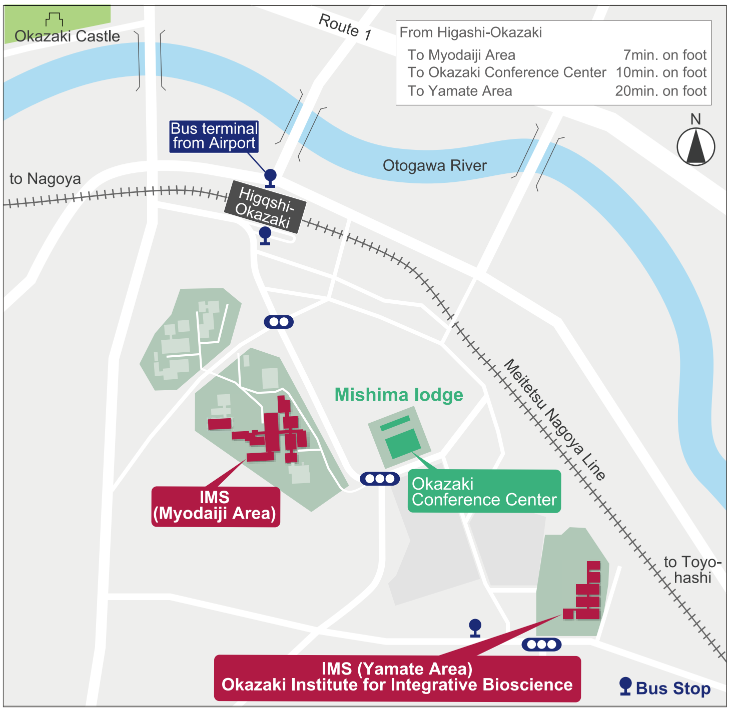

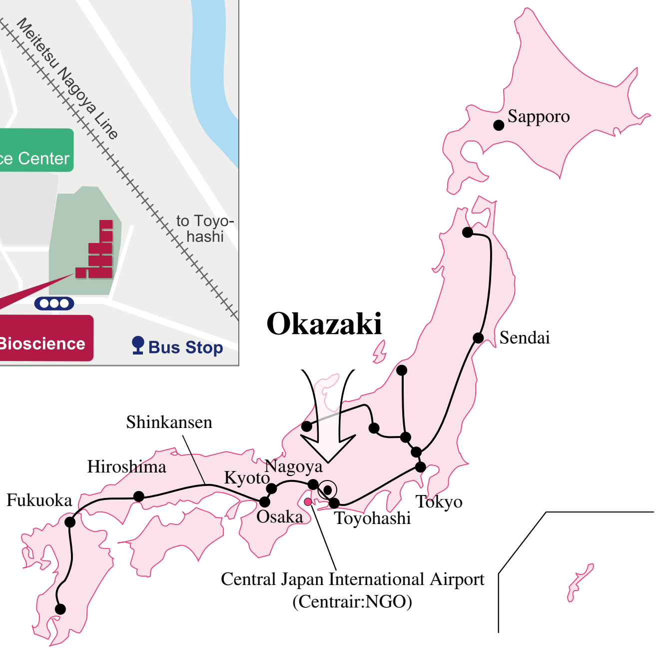

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