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 of Reactions, Functions, and Thermodynamic Properties in Biomolecular and Liquid Systems

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Keywords Complicated Dynamics, Reactions, Functions

Nonlinear intermolecular interactions cause complicated motions in condensed phases, *e.g.* liquids and biological systems. These motions are spatially and temporally heterogeneous and produce both static and dynamic properties of the systems. The spatiotemporal 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 spatiotemporal heterogeneous dynamics is essential to the elucidation of the structure, reactions, functions, and thermodynamic properties of the condensed phase systems.

We have investigated inter- and intra-molecular dynamics of water by using third-order nonlinear spectroscopy which can provide the detailed dynamics that are not available from conventional spectroscopy. We have revealed the molecular mechanism of ultrafast energy relaxation, which is one of dynamical features of water, *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 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 revealed the molecular origin of anomalous temperature dependence of isobaric specific heat of water by examining the spatiotemporal fluctuations in terms of specific heat.

We examine heterogeneous conformational dynamics in proteins by exploiting the ideas used in multi-dimensional spectroscopy and glassy dynamics. Currently, we investigate how enzymatic reactions proceed at a molecular level under complicated environmental fluctuations. In addition, we elucidate the emergence of functions, *e.g.* the circadian rhythm in Kai system, as a result of dynamics over a wide range of spatiotemporal scales.

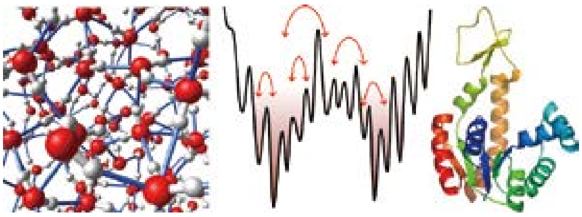

Figure 1. Schematic figure of rugged energy landscape (center) in supercooled water (left) and adenylate kinase (right).

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. Phys. Chem. B* **119**, 11068–11078 (2015).
- 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).
- J. Ono, S. Takada and S. Saito, *J. Chem. Phys. (Special Topic on Multidimensional Spectroscopy)* **142**, 212404 (13 pages) (2015).

1. Crucial Role of Low-Populated Conformations Facilitating Enzymatic Reactions: Example in Catalysis in Pin1 *cis-trans* Isomerase[1)]

Protein flexibility is essential for enzymes to function, yet the mechanism of catalysis has been highly controversial. Here we elucidate how protein and ligand conformational changes occur along the reaction by examining the *cis-trans* isomerization reaction catalyzed by Pin1 as an example. While free energy profiles can explain the catalytic effect, we show that the enzymatic reaction proceeds through specific conformations, which hereafter we call excited conformational state formed in the reactant. The transition trajectories therefore do not overcome the barrier in a simple stochastic manner. Furthermore, since the excited conformational state is formed by specific hydrogen bonds, the reaction occurs via bond-alternations and the excess energy is efficiently dissipated. As a result, the reaction path is direction-dependent and possesses directionality, *i.e.* different paths are used depending on the reactant character. We expect that the excited conformational states and specific bond switching mechanisms are embedded in broader enzymes.

2. A Reaction Model of Circadian Rhythm in Kai Proteins by Considering Elementary Reactions and Conformational Changes[2)]

Circadian clocks are biological timing system used in various organisms to anticipate daily changes in environment and to adjust their biological activity to the changes. Cyanobacteria are known as the simplest organisms showing a circadian rhythm, where the core oscillator is composed of only three proteins, KaiA, KaiB, and KaiC. KaiC consisting of two domains plays a central role in the circadian rhythm of Kai system, and has autokinase and autophosphatase activities. A periodic phosphorylation and dephosphorylation occur at Ser431 and Thr43 in KaiC. This periodic oscillation is generated with the help of KaiA and KaiB: KaiA promotes the phosphorylation, on the other hand KaiB inhibits KaiA to act on KaiC. Several important elementary processes have recently been unveiled, for example, the phosphorylation and dephosphorylation reactions and conformational changes that might switch between phosphorylation and dephosphorylation phases. It is, however, an open question to integrate these detailed experimental results and explain how the circadian phosphorylation occurs. In almost all previous mathematical models, only the phosphorylation/dephosphorylation reactions have been focused for the circadian rhythm of Kai system. In the present study, we propose a mathematical reaction model of the circadian rhythm in the Kai system based on conformational changes in KaiB and KaiC as well as elementary processes, such as ATP hydrolysis, ADP/ATP exchange, and phosphorylation/dephosphorylation reactions. As a result, an allosteric effect in the domains in KaiC is also considered in the current model. We find that the optimized parameters determined to reproduce the experimental data of the periodic phosphorylation can quantitatively reproduce not only the data of phosphorylation used in the optimization, but also various experimental data not used in the optimization, such as ATPase activity even when KaiA and/or KaiB are absent. In addition, the current model can successfully reproduce the synchronization of oscillation caused by environmental changes. The present study demonstrates that the circadian rhythm is regulated by conformational changes as well as elementary reactions.

3. Crucial Role of Fragmented and Isolated Defects in Persistent Relaxation of Deeply Supercooled Water[3)]

Water is the most common and the most intensively studied liquid in nature. Characteristic properties of water have been well elucidated for temperature above ~200 K. And yet a mystery still remains about the deeply supercooled region: Why and how can water stay in the liquid state even at very low temperature? Experiments show that amorphous ice when heated from very low temperature. undergoes a transition to a highly viscous liquid at 136 K and then crystallizes to ice at 150 K. This water glass transition temperature, T_G = 136 K, almost half of the ice melting temperature T_M, is much lower than what is expected from the general $T_G/T_M \approx 2/3$ rule of glass formers. The present study, performing extensive trajectory calculations, attempts to clarify what molecular mechanisms could be involved in promoting molecular motions in deeply supercooled water. We find that the structural and dynamical instabilities hidden behind the so-called “no man’s land” the experimentally inaccessible region for liquid water between 235 K and 150 K, strongly influence the properties of deeply supercooled water, through the fragmentation and the consequent isolation of high density (HD) clusters. The fragmentation that starts below 220 K, makes each larger HD cluster scattered into smaller clusters. When the fragmentation is completed at ~190 K, each scattered HD cluster contains only one or two defects. These isolated defects are hardly annihilated in the well-formed hydrogen bond network of low density (LD) molecules. We find that specific 3-coordinated defects play a crucial role to induce slow but persistent structural relaxations and thus lower the T_G of water. These defects are exactly the same ones essential in melting ice. The fragmentation of LD clusters in HD network takes place at the temperature of density maximum. The fragmentation scheme provides a unified picture on water properties in a wide temperature range.

References

1) T. Mori and S. Saito, to be submitted.
2) S. Koda and S. Saito, to be submitted.
3) S. Saito, B. Bagchi and I. Ohmine, submitted.

Theory for Optical Response in Nanostructures and Application to Unified Photonic and Electronic Devices

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Keywords Optical Response, Light-Matter Interaction, Nanodevices

Optical response of materials is undoubtedly essential for understanding their physicochemical properties. In conventional theoretical approaches to optical response of materials, two conditions are usually assumed:
(i) A scale of wavelength of an incident light is much longer than material size, *i.e.*, dipole approximation. Thus, a target material is well approximated by a point dipole and the dipole feels a spatially uniform electromagnetic field.
(ii) Electric polarization in a material induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an "optical near-filed." 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* 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. Electron dynamics in nanostructures interacting with an electromagnetic field is described by the time-dependent Kohn-Sham equation, whereas electromagnetic field dynamics is represented by the microscopic Maxwell's equations. The nonuniform LM interaction is considered 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 highly suitable for massively parallelized computations. Very recently, we newly developed a computational program called SALMON (Scalable Ab-initio Light-Matter simulator for Optics and Nanoscience) including all the functions of the GCEED. By using the SALMON, we are currently computationally designing unified photonic and electronic nanodevices.

We also performed computational design of heterogeneous catalysts to develop efficient and commercially appealing ones, thus reducing the use of expensive rare catalytic metals. The simulations were carried out by using the first-principles, *i.e.*, Car-Parrinello, molecular dynamics simulations.

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).
- K. Nobusada and T. Iwasa, "Oligomeric Gold Clusters with Vertex-Sharing Bi- and Triicosahedral Structures," *J. Phys. Chem. C* **111**, 14279–14282 (2007).
- M. Noda, K. Ishimura, K. Nobusada, K. Yabana and T. Boku, "Massively-Parallel Electron Dynamics Calculations in Real-Time and Real-Space: Toward Applications to Nanostructures of More than Ten-Nanometers in Size," *J. Comput. Phys.* **265**, 145–155 (2014).
- M. Noda, M. Yamaguchi and K. Nobusada, "Second Harmonic Excitation of Acetylene by the Optical Near Field Generated in a Porous Material," *J. Phys. Chem. C* **121**, 11687–11692 (2017).

1. Second Harmonic Excitation of Acetylene by the Optical Near Field Generated in a Porous Material[1)]

We perform first-principles calculations of the photoexcitation dynamics of an acetylene molecule in a metal organic framework, IRMOF-10. Resonant laser excitation of the IRMOF-10 generates an optical near field (ONF) around the two benzene rings that comprise the main framework of the IRMOF-10. Interestingly, along with the ONF of frequency ω, which synchronizes with the resonant frequency of the IRMOF-10, a second harmonic (= 2ω) component of the ONF is generated. The second harmonic component effectively excites the acetylene molecule at a frequency of 2ω, although the incident laser field is in tune with ω. It is noteworthy that the second harmonic excitation is caused by spatial nonuniformity of the ONF interaction. It is completely different from the conventional two-photon excitation and is much more efficient than the two-photon excitation by several orders of magnitude.

2. Development of Theoretical Approach for Describing Electronic Properties of Hetero-Interface Systems under Applied Bias Voltage[2)]

We have developed a theoretical approach for describing the electronic properties of hetero-interface systems under an applied electrode bias. The finite-temperature density functional theory is employed for controlling the chemical potential in their interfacial region, and thereby the electronic charge of the system is obtained. The electric field generated by the electronic charging is described as a sawtooth-like electrostatic potential. Because of the continuum approximation of dielectrics sandwiched between electrodes, we treat dielectrics with thicknesses in a wide range from a few nanometers to more than several meters. Furthermore, the approach is implemented in our original computational program called GCEED. Thus, the approach is capable of comprehensively revealing electronic structure changes in hetero-interface systems with an applied bias. We calculate the electronic structure of a SiO_2-graphene-boron nitride (BN) system in which an electrode bias is applied between the graphene layer and an electrode attached on the SiO_2 film. The electronic energy barrier between graphene and BN is varied with an applied bias, and the energy variation depends on the thickness of the BN film. This is because the density of states of graphene is so low that the graphene layer cannot fully screen the electric field generated by the electrodes. We have demonstrated that the electronic properties of hetero-interface systems are well controlled by the combination of the electronic charging and the generated electric field.

3. An Atomic-Level Insight into the Basic Mechanism Responsible for the Enhancement of the Catalytic Oxidation of Carbon Monoxide on a Cu/CeO_2 Surface[3)]

The reaction mechanisms of CO molecules interacting with a Cu/CeO_2 surface and related morphological modifications occurring upon removal of O atoms to generate CO_2 are investigated by first-principles dynamical simulations complemented by a free-energy sampling technique. We show that the reactivity of oxygen atoms located in the first layer in the vicinity of the Cu site is remarkably high because of a reduction of the O coordination number. Moreover, we evidence that the doped Cu atoms are responsible for an enhancement of the exposure of other surrounding O atoms, even below the first surface layer, which can then easily react with CO and are gradually removed from the system in the oxidation process. The underlying mechanism responsible for such a high catalytic reactivity of the Cu/CeO_2 surface toward CO oxidation is rationalized in terms of the characteristics of the doped Cu. In fact, this copper site is responsible for providing an increasing number of O atoms participating in the catalysis by exposing subsequently all O atoms in the vicinity which are likely to react with an approaching CO. This peculiarity of the Cu atoms extends to O atoms which initially can be deeply buried up to the fourth layer underneath the surface.

4. Large Hyperpolarizabilities of the Second Harmonic Generation Induced by Nonuniform Optical Near Fields[4)]

We studied the optical selection rules and hyperpolarizabilities of a second harmonic generation (SHG) induced by a nonuniform optical near field (ONF) on the basis of first-principles calculations. The excitations of the symmetric and asymmetric molecules para-dinitrobenzene (pDNB) and para-nitroaniline (pNA), respectively, were investigated according to the time-dependent density functional theory. By calculating the ONF excitation dynamics of symmetric pDNB, we demonstrated that the ONF causes the SHG even in symmetric materials because of nonuniformity of the field in space. To quantitatively evaluate the intensity of the SHG induced by the ONF, we estimated the first hyperpolarizability, $\beta(2\omega)$, of asymmetric pNA for both of the usual far-field light and ONF excitations. Our results showed that $\beta(2\omega)$ for the ONF excitation is 1–2 orders of magnitude larger than that for the far-field excitation when the distance between the source of the ONF and pNA is around 10 Å.

References

1) M. Noda, M. Yamaguchi and K. Nobusada, *J. Phys. Chem. C* **121**, 11687–11692 (2017).

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

3) K. Koizumi, K. Nobusada and M. Boero, *Phys. Chem. Chem. Phys.* **19**, 3498–3505 (2017).

4) M. Yamaguchi and K. Nobusada, *J. Phys. Chem. C* **120**, 23748–23755 (2016).

Award

NOBUSADA, Katsuyuki; Award for excellence in research projects using the HPCI System (2017).

Advanced Electronic Structure Theory in Quantum Chemistry

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Awards

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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.

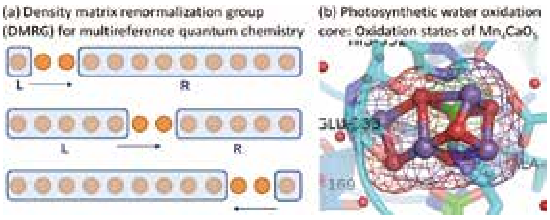

Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

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. Direct Observation of the Ultrafast Evolution of Open-Shell Biradical in Photochromic Radical Dimer[1)]

Delocalized biradicals have been extensively studied because of fundamental interests to singlet biradicals and several potential applications such as to two-photon absorption materials. However, many of the biradical studies only focus on the static properties of the rigid molecular structures. It is expected that the biradical properties of the delocalized biradicals are sensitive to the subtle changes of the molecular structures and their local environments. Therefore, the studies of the dynamic properties of the system will give further insight into stable radical chemistry. In this study, we directly probe the ultrafast dynamics of the delocalized biradical of a photochromic radical dimer, pentaarylbiimidazole (PABI), by time-resolved visible and infrared spectroscopies and quantum chemical calculations with the extended multistate complete active space second-order perturbation theory (XMS-CASPT2). While the photogenerated transient species was considered to be a single species of the biradical, the present ultrafast spectroscopic study revealed the existence of two transient isomers differing in the contributions of biradical character. The origin of the two metastable isomers is most probably due to the substantial van der Waals interaction between the phenyl rings substituted at the imidazole rings. Unraveling the temporal evolution of the biradical contribution will stimulate to explore novel delocalized biradicals and to develop biradical-based photofunctional materials utilizing the dynamic properties (**Figure 2**).

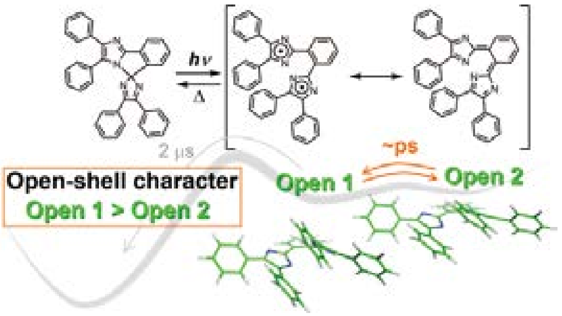

Figure 2. Quantum chemical calculations with XMS-CASPT2 method were performed on PABI in order to illuminate molecular- and electronic-level details of its photochromic ring opening and closing reaction.

2. Projector Augmented Wave Method Incorporated into Gauss-Type Atomic Orbital Based Density Functional Theory[2)]

The Projector Augmented Wave (PAW) method developed by Blöchl is well recognized as an efficient, accurate pseudopotential approach in solid-state density functional theory (DFT) calculations with the plane-wave basis. Here we present an approach to incorporate the PAW method into the Gauss-type function (GTF) based DFT implementation, which is widely used for molecular quantum chemistry calculations. The nodal and high-exponent GTF components of valence molecular orbitals (MOs) are removed or pseudized by the ultrasoft PAW treatment, while there is elaborate transparency to construct an accurate and well-controlled pseudopotential from all-electron atomic description and to reconstruct an all-electron form of valence MOs from the pseudo MOs. The smoothness of the pseudo MOs should benefit the efficiency of GTF-based DFT calculations in terms of elimination of high-exponent primitive GTFs and reduction of grid points in the numerical quadrature. The processes of the PAW method are divided into basis-independent and -dependent parts. The former is carried out using the previously developed PAW libraries libpaw and atompaw. The present scheme is implemented by incorporating libpaw into the conventional GTF-based DFT solver. The details of the formulations and implementations of GTF-related PAW procedures are presented. The test calculations are shown for illustrating the performance. With the near-complete GTF basis at the cc-pVQZ level, the total energies obtained using our PAW method with suited frozen core treatments converge to those with the conventional all-electron GTF-based method with a rather small absolute error (**Figure 3**).

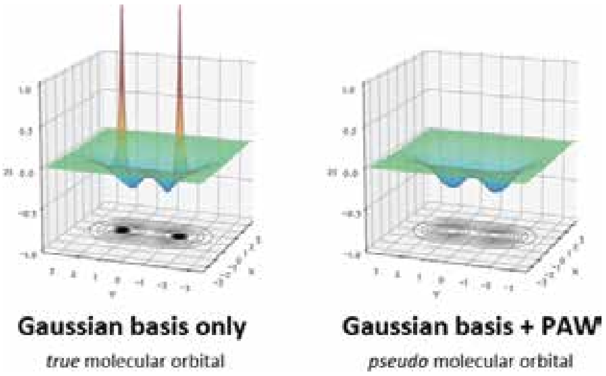

Figure 3. Plots of exact and pseudo molecular orbitals determined for the F_2 molecule with Gauss-type atomic basis functions without and with the PAW pseudopotential treatment.

References

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2) X.-G. Xiong and T. Yanai, *J. Chem. Theory Comput.* **13**, 3236–3249 (2017).

Award

YANAI, Takeshi; The 2017 Pople Medal of Asia-Pacific Conference of Theoretical and Computational Chemistry.

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Awards

2015	10th Condensed-Matter Science Prize, Japan
2016	10th Young Scientist Award of the Physical Society of Japan
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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.

Selected Publications

- A. Ishizaki and Y. Tanimura, "Quantum Dynamics of System Strongly Coupled to Low-Temperature Colored Noise Bath: Reduced Hierarchy Equations Approach," *J. Phys. Soc. Jpn.* **74**, 3131–3134 (2005).
- A. Ishizaki and G. R. Fleming, "Unified Treatment of Quantum Coherent and Incoherent Hopping Dynamics in Electronic Energy Transfer: Reduced Hierarchy Equation Approach," *J. Chem. Phys.* **130**, 234111 (10 pages) (2009).
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- A. Ishizaki and G. R. Fleming, "Quantum Coherence in Photosynthetic Light Harvesting," *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes, G. R. Fleming, L. X. Chen, A. Aspuru-Guzik, A. Buchleitner, D. D. F. Coker, G. S. Engel, R. van Grondelle, A. Ishizaki, D. M. Jonas, J. S. Lundeen, J. K. McCusker, S. Mukamel, J. P. Ogilvie, A. Olaya-Castro, M. A. Ratner, F. C. Spano, K. B. Whaley and X. Y. Zhu, "Using Coherence to Enhance Function in Chemical and Biophysical Systems," *Nature* **543**, 647–656 (2017).

1. Using Coherence to Enhance Function in Chemical and Biophysical Systems

Coherence phenomena arise from interference, or the addition, of wave-like amplitudes with fixed phase differences. Although coherence has been shown to yield transformative ways for improving function, advances have been confined to pristine matter and coherence was considered fragile. However, recent evidence of coherence in chemical and biological systems suggests that the phenomena are robust and can survive in the face of disorder and noise. We surveyed the state of recent discoveries, present viewpoints that suggest that coherence can be used in complex chemical systems, and discuss the role of coherence as a design element in realizing function.1)

2. Modeling of High Frequency Vibrational Motion in Quantum Dynamics of Singlet Fission Process

Singlet fission is a spin-allowed energy conversion process whereby a singlet excitation splits into two spin-correlated triplet excitations residing on adjacent molecules and has a potential to dramatically increase the efficiency of organic photovoltaics. Recent time-resolved nonlinear spectra of pentacene derivatives have shown the importance of high frequency vibrational modes in efficient fission. In this work, we explored impacts of vibration-induced fluctuations on fission dynamics through quantum dynamics calculations with parameters from fitting measured linear and nonlinear spectra. We demonstrated that fission dynamics strongly depends on the frequency of the intramolecular vibrational mode. Furthermore, we examined the effect of two vibrational modes on fission dynamics. Inclusion of a second vibrational mode creates an additional fission channel even when its Huang-Rhys factor is relatively small. Addition of more vibrational modes may not enhance fission *per se*, but can dramatically affect the interplay between fission dynamics and the dominant vibrational mode.2)

3. Spin Hall Effect without Space Inversion Symmetry

A master equation approach based on an optimized polaron tranThe spin Hall effect (SHE), first proposed almost half a century ago, has been investigated and observed in a large variety of systems including electrons in semiconductors such as GaAs and In GaAs, photons passing through an interface with a refractive index gradient, and atomic Bose-Einstein condensates subject to synthetic gauge fields. In all of these studies, the SHE arises from the spin–orbit interaction which requires space inversion symmetry (SIS) breaking. In this work, we showed that the SHE can appear in a totally different but equally broad class of many-body systems with SIS. In particular, we demonstrated that the SHE can emerge from the dipole–dipole interaction (DDI), which preserves SIS. The DDI-based SHE is expected to occur in, for example, heteronuclear molecules, strongly magnetic atoms, Rydberg excitations, electron gases, etc. The SHE arising from the DDI offers a complementary tool to generate spin currents, which constitutes an essential ingredient in spintronics.3)

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Awards

ISHIZAKI, Akihito; 18th Sir Martin Wood Prize (2016).
ISHIZAKI, Akihito; Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize (2017).

Theoretical Study on Photochemistry and Catalysis

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Education

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

Awards

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2009	QSCP Prize CMOA

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- IMS Fellow
  - YANG, Tao
- JSPS Invited Fellow
  - ZHAO, Xiang
- Post-Doctoral Fellow
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  - SADHUKHAN, Tumpa
- Visiting Scientist
  - JUNKAEW, Anchalee
  - NAMUANGRUK, Supawadee
  - CHIRAWAT, Chitpakdee
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  - SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

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

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

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

(2) Heterogeneous catalysis

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

(3) Photophysical chemistry

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

(4) Theoretical spectroscopy

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

Selected Publications

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

1. Structure and Reactivity of Nanolcluster Catalysts

In the supported nanocluster (NC) catalysts, the structure and electronic state of NC are relevant for the catalytic activity. We have investigated these factors together with bond activation of Cu-M binary NCs using DFT calculations.1) We adopted the computational model of $Cu_{38-n}M_n$ (M = Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au; n = 1, 2, and 6). In the most stable structure of $Cu_{37}M_1$ (M = Ru, Ph, Os, Ir, Group 7 and 8), the M atom takes the core position, while in $Cu_{37}M_1$ (M = Pd, Ag, Pt, Au, Group 9 and 10), it takes the shell (center or corner) position. The segregation energy defined by energy difference between the most stable $Cu_{37}M_1$ (core) and the next stable structure $Cu_{37}M_1$ (shell), was found to be proportional to d orbital population, suggesting that the M atom with unoccupied d orbitals tends to take the core position. Due to the alloy effects, the adsorption energy and bond activation to CO and NO are enhanced in binary NCs, for example, on $Cu_{32}Ru_6$ NC.

We also studied the single atom catalyst, $M_1/\gamma\text{-}Al_2O_3$ (M = Pd, Fe, Co, Ni) for the low-temperature CO oxidation and found that the +II oxidation state of the M atom is crucial for its catalytic activity. We have theoretically proposed that $Ni_1/\gamma\text{-}Al_2O_3$ is an alternative efficient catalyst that has low energy barriers.2)

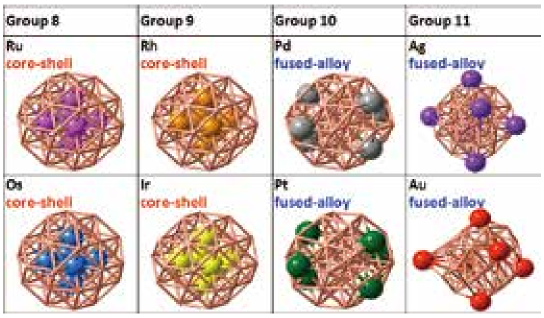

Figure 1. Stable structures of CuM (M = Ru, Rh, Pd, Ag, Os, Ir, Pt) NC.

2. Electronic Resonance States

For investigating the electronic resonance states, we have developed the complex absorbing potential (CAP)/SAC-CI method with new potential. We have systematically applied the method to the series of molecules; *i.e.* double-bond and hetero-aromatic compounds, DNA/RNA bases and their derivatives, and cyano-containing molecules.3) These successful applications showed that the CAP/SAC-CI method is a robust protocol for predicting the π* resonances of the molecules and clusters.

We also have developed another robust approach for locating the resonance states in the framework of extrapolation method; that is, analytic continuation of the coupling constant (ACCC) approach with some new stabilization potentials.4) The results for the model potential and some small molecules showed that ACCC SAC-CI is also a reliable approach for locating the electronic resonance states.

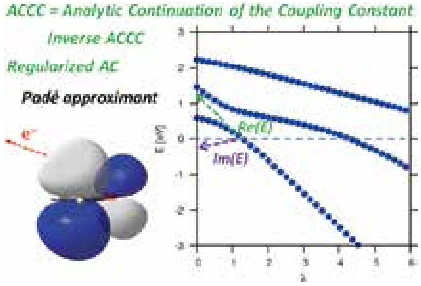

Figure 2. Analytic continuation of the coupling constant (ACCC) SAC-CI method for electronic resonance states.

3. Chemical Reaction under Extreme High Pressure

We have developed the theory for investigating the effects of high pressure on chemical reaction, XP-PCM (Polarizable Continuum Model for eXtreme Pressure). The pressure effects have been studied in the solid state physics, but, not so well in molecular systems. So far, there are accumulated experimental data of the pressure effects for molecular systems. We applied our method to the excited states of furan in condensed phase and found that level crossing and significant changes in valence-Rydberg mixing occur under the high pressure. In this work, we have investigated the pressure effects on chemical reaction, more specifically, Diels-Alder cycloaddition of cyclopentadiene and C_{60}.5) It was shown that the energy barrier drastically reduces and the reaction becomes even barrier-less under extreme high pressure.

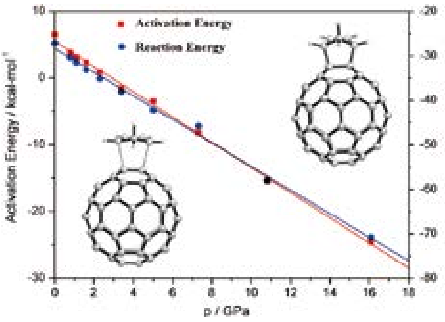

Figure 3. Extreme pressure effects on chemical reaction: Diels-Alder cycloaddition of cyclopentadiene and C_{60}.

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3) M. Ehara, Y. Kanazawa and T. Sommerfeld, *Chem. Phys.* **482**, 169–177 (2017).
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5) T. Yang, R. Fukuda, R. Cammi and M. Ehara, *J. Phys. Chem. A* **121**, 4363–4371 (2017).

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* IMS International Internship Program

Development of New Molecular Dynamics Algorithms for Biomolecular Systems

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Keywords Molecular Dynamics Simulation, Protein, Amyloid

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

We are also interested in amyloid fibrils, which are insoluble aggregates of misfolded fibrous proteins and associated with more than 20 human neurodegenerative diseases (Figure 2). For example, Alzheimer's disease is related to amyloid-β (Aβ) peptides. To overcome these diseases, it is essential to understand amyloid genesis and disruption. We perform such MD simulations of amyloid fibrils.

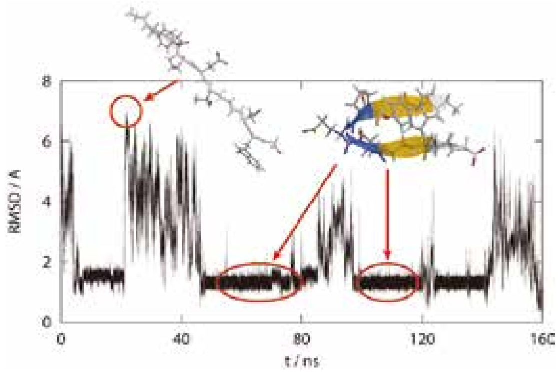

Figure 1. Time series of protein folding simulation.

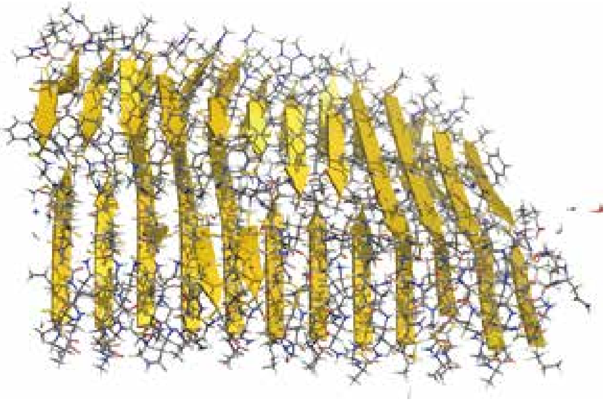

Figure 2. Snapshot of amyloid fibril.

Selected Publications

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

1. Molecular Dynamics Simulations Predict Only One End of Aβ Amyloid Fibril Has Open Conformations

To understand the amyloid extension mechanism, we must understand the amyloid fibril structure and fluctuation at the fibril end, which has not been revealed to date. We revealed these features by all-atom MD simulations of Aβ42 and Aβ40 fibrils in explicit water.[1)] The structure and fluctuation were observed to differ between the two ends, as shown in Figure 3. At the even end, the Aβ peptide always took a closed form wherein β1 and β2 were closely spaced. The Aβ peptide fluctuated more at the odd end and took an open form wherein the two β-sheets were well separated. The differences were attributed to the stronger β-sheet formation by the β1 exposed at the even end than the β2 exposed at the odd end. Along with the small fluctuations at the even end, these results explain why the fibril extends from one end only, as observed in experiments. Our MD results agree well with recent observations by high-speed atomic force microscopy.

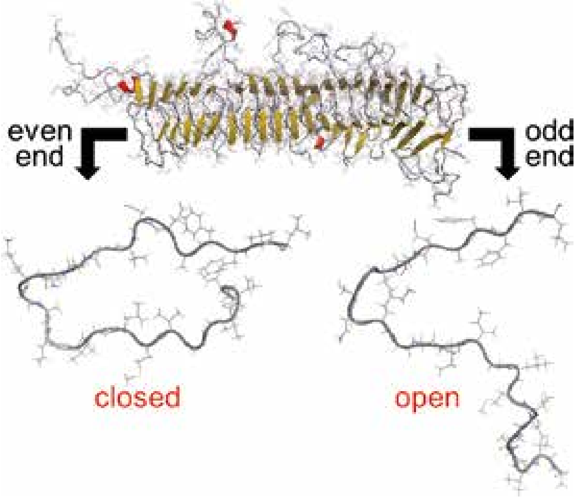

Figure 3. Typical conformation of an Aβ42 amyloid fibril and side views of the Aβ42 monomer at the even and odd ends.

2. Rapid QM/MM Approach for Biomolecular Systems under Periodic Boundary Conditions

A quantum mechanical/molecular mechanical (QM/MM) approach based on the density-functional tight-binding (DFTB) theory is a useful tool for analyzing chemical reaction systems in detail. In this study, an efficient QM/MM method was developed by the combination of the DFTB/MM and particle mesh Ewald (PME) methods.[2)] Because the Fock matrix, which is required in the DFTB calculation, is analytically obtained by the PME method, the Coulomb energy is accurately and rapidly computed. For assessing the performance of this method, DFTB/MM calculations and molecular dynamics simulation are conducted for a system consisting of two amyloid-β(1-16) peptides and a zinc ion in explicit water under periodic boundary conditions, as shown in Figure 4. As compared with that of the conventional Ewald summation method, the computational cost of the Coulomb energy by utilizing the present approach is drastically reduced.

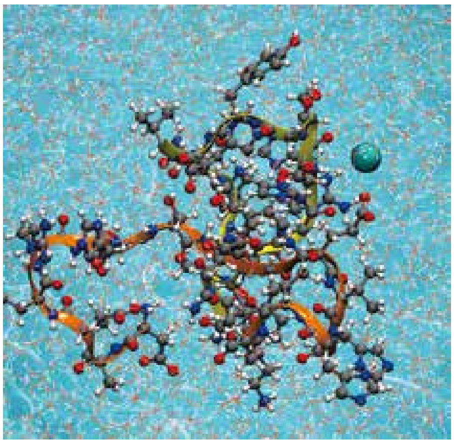

Figure 4. Test system consists of two amyloid-β(1-16) peptides, zinc ion, and water molecules.

3. Molecular Dynamics Simulation for Structural Basis of TRPA1 Inhibition by HC-030031

Pain is a harmful sensation that arises from noxious stimuli. Transient receptor potential ankyrin 1 (TRPA1) is one target for studying pain mechanisms. TRPA1 is activated by various stimuli such as noxious cold, pungent natural products and environmental irritants. Since TRPA1 is an attractive target for pain therapy, a few TRPA1 antagonists have been developed and some function as analgesic agents. Prof. Tominaga and his coworkers in National Institute for Physiological Sciences revealed that the TRPA1 antagonist HC-030031 (HC) failed to inhibit frog TRPA1 (fTRPA1) and zebrafish TRPA1 activity, but did inhibit human TRPA1 (hTRPA1). We collaborated with them and performed MD simulations of HC and hTRPA1 and found that HC stably binds to N855 in hTRPA1.[3)] These findings provide novel insights into the structure-function relationship of TRPA1 and could lead to the development of more effective analgesics targeted to TRPA1.

References

1) H. Okumura and S. G. Itoh, *Sci. Rep.* **6**, 38422 (9 pages) (2016).
2) H. Nishizawa and H. Okumura, *J. Comput. Chem.* **37**, 2701–2711 (2016).
3) R. Gupta, S. Saito, Y. Mori, S. G. Itoh, H. Okumura and M. Tominaga, *Sci. Rep.* **6**, 37460 (14 pages) (2016).

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Theoretical Studies on Molecular Aggregates

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Keywords Exciton, Energy and Charge Transfer, Organic Semiconductors

Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates exhibit characteristic optical and electronic properties that are not observed in isolated molecules. For example, their photophysical processes include electronic energy transfer and charge separations, which are desirable for low-cost electronic devices.

We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, energy conversions, and structure-property relationship.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave function can be delocalized by electronic couplings due to molecular interactions; it is modulated by molecular vibrations. It is thus essential to consider electronic couplings and electron–phonon couplings on the same footing. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. An electronic structure of an aggregate is described as tight-binding Hamiltonian with electronic couplings obtained from the fragment molecular orbital method. The energy or charge dynamics is described by quantum dynamics methods with incorporating finite-temperature effects and electron–phonon couplings. The combine computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

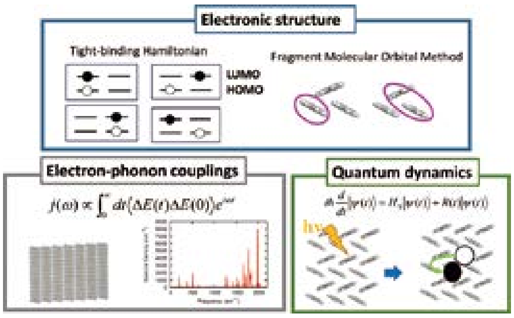

Figure 1. A combine approach to quantum dynamics in molecular aggregates.

We currently investigate electronic structures and exciton dynamics in organic optoelectronic materials, such as an organic/organic interface. We also develop an ab initio theory suitable to treat electronically excited states of large systems with reasonable accuracy, on the basis of a fragment-based approach and a many-body perturbation theory.

Selected Publications

- T. Fujita, J. C. Brookes, S. K. Saikin and A. Aspuru-Guzik, "Memory-Assisted Exciton Diffusion in the Chlorosome Light-Harvesting Antenna of Green Sulfur Bacteria," *J. Phys. Chem. Lett.* **3**, 2357–2361 (2012).
- T. Fujita, J. Huh, S. K. Saikin, J. C. Brookes and A. Aspuru-Guzik, "Theoretical Characterization of Excitation Energy Transfer in Chlorosome Light-Harvesting Antennae from Green Sulfur Bacteria," *Photosynth. Res.* **120**, 273–289 (2014).

1. Development of the Fragment Molecular Orbital Method for Calculating Non-Local Excitations in Large Molecular Systems[1)]

Predicting electronically excited states of large molecular systems is still a challenging issue in quantum chemistry. In this study, we develop an excited-state theory suitable to treat large systems based on the fragment molecular orbital (FMO) method and the configuration interaction single theory with localized molecular orbitals. Although the FMO method have been well established for calculating local excited states, it is not straightforward to compute non-local excited states. We thus develop the theory which can compute non-local excitation of large molecular systems.

The method is based on the configuration interaction single (CIS) theory and was designed to reproduce low-energy excited states for a whole system with small dimensions. In order to describe non-local excited-states for the whole system, configuration state functions (CSFs) were constructed from localized MOs and the CIS amplitudes of intrafragment excitation via ground-state FMO and MLFMO-CIS calculations. The excited states of the whole system were written as the superposition of fragment CSFs for local excitations and interfragment charge transfer (CT) excitations. Exploiting fragment CSFs allows for efficient truncation of the dimension of the excited-state Hamiltonian. The excited-state Hamiltonian represented with fragment CSFs are calculated, and the resulting generalized eigenvalue problem is solved to determine the excited states of the whole system. The one-electron part of the excited-state Hamiltonian was treated by the FMO-linear combination of molecular orbital method, while the two-electron parts were efficiently treated within the two-body expansion of the FMO.

The theory was implemented based on the ABINIT-MP program package. The accuracy and efficiency of the present theory were tested for illustrative examples of molecular dimer and clusters. For example, the excitation energies of the face-to-face benzene dimer as a function of intermolecular distance is shown in Figure 2. FMO-CIS can reproduce the results of conventional CIS with quantitative accuracy for relatively large intermolecular distance of $R > 4$ Å. The mean absolute error relative to the conventional CIS is 26 meV at $R = 4$ Å. Regarding that the equilibrium distance of the face-to-face benzene dimer is $R = 3.8$ Å, the present theory can work with reasonable accuracy for practical applications. Similar benchmark calculations for π-stacked systems and realistic molecular crystals have confirmed that the absolute errors of 50 meV are achievable for molecular assemblies in their equilibrium geometries.

The present theory can compute a large number of excited states in large molecular systems; in addition, it allows for the systematic derivation of a model exciton Hamiltonian. These feature are useful for studying excited-state dynamics in condensed molecular systems based on the ab initio electronic structure theory.

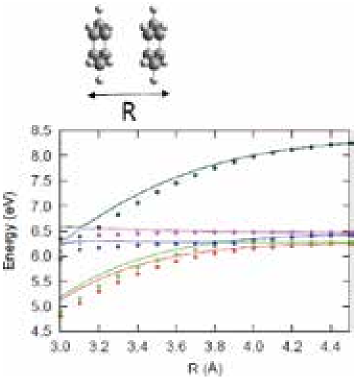

Figure 2. Excitation energies as a function of intermolecular distances from the conventional CIS (solid line) and the FMO-CIS (filled circles). The results shows energies of first six excited states.

2. Interfacial Charge Transfer States in the Pentacene/C_{60} Interface

The electronic structures at organic–organic interfaces comprising electron–donor and electron–accepter materials are of great importance in the performance of various electronic devices. In organic photovoltaic (OPV) devices, interfacial charge-transfer states play critical roles in both charge separation and charge recombination processes. Despite their critical importance, it is difficult to experimentally investigate the interfacial CT states.

In this study, we consider an organic/organic interface that in composed of pentacene molecules as electron donor and C_{60} molecules as electron acceptor. To characterize CT state manifold, we apply the FMO-based excited state theory to the pentacene/C_{60} interface containing about 50 molecules. The structure was extracted from a bilayer interface modeled by a molecular dynamics simulation. The calculated energy (1.1 eV) of the lowest CT state is in reasonable agreement with the experimental reported value. We have analyzed CT states in terms of electron–hole (e–h) separation and delocalization of electron or hole wave function. We have found that in the energy region lower than pentacene absorption, CT states are localized with their small e–h separations, while CT states are delocalized with larger e–h separation in higher-energy region. In addition, the mixing among the interfacial CT states and pentacene excited states enhance the delocalization of electron wavefunction over the pentacene and C_{60} molecules.

References

1) T. Fujita and Y. Mochizuki, submitted.
2) T. Fujita , Md. K. Alam and T. Hoshi, in preparation.

Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

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Keywords Theoretical Biophysics, Molecular Motors, Molecular Simulations

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

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

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

Selected Publications

- K. Okazaki, T. Sato and M. Takano, "Temperature-Enhanced Association of Proteins due to Electrostatic Interaction :A Coarse-Grained Simulation of Actin–Myosin Binding," *J. Am. Chem. Soc.* **134**, 8918–8925 (2012).
- K. Okazaki and G. Hummer, "Phosphate Release Coupled to Rotary Motion of F_1-ATPase," *Proc. Natl. Acad. Sci. U.S.A.* **110**, 16468–16473 (2013).
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- M. Sugawa, K. Okazaki, M. Kobayashi, T. Matsui, G. Hummer, T. Masaike and T. Nishizaka, "F_1-ATPase Conformational Cycle from Simultaneous Single-Molecule FRET and Rotation Measurements," *Proc. Natl. Acad. Sci. U.S.A.* **113**, E2916–E2924 (2016).

1. Mechanochemical Coupling Mechanism of F_1-ATPase

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

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

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

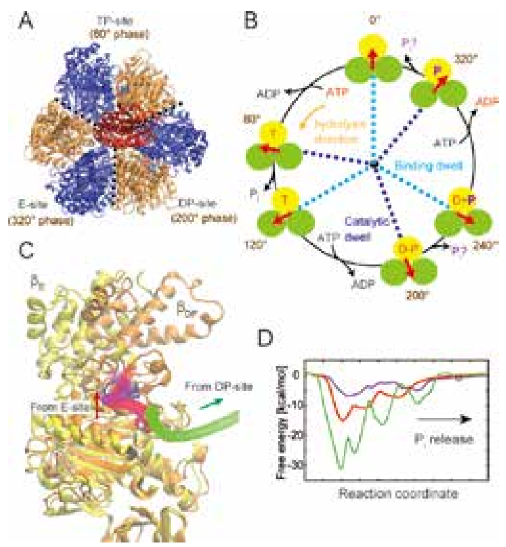

Figure 1. Mechanochemical coupling scheme and P_i release in F_1-ATPase.

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

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

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

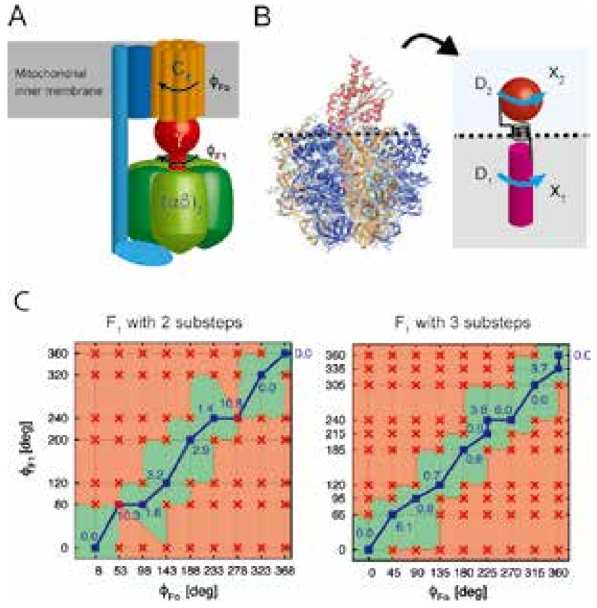

Figure 2. Viscoelastic model of F_oF_1-ATP synthase.

References

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

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

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

Theory and Computation of Reactions and Properties in Solutions and Liquids

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

ISHIDA, Tateki
Assistant Professor

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

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

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

2. Investigations of Ionic Liquids(1–2) with Molecular Dynamics Simulation

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

References

1) T. Ishida and H. Shirota, *J. Phys. Chem. B* **117**, 1136–1150 (2013).
2) S. Kakinuma, T. Ishida and H. Shirota, *J. Phys. Chem. B* **121**, 250–264 (2017).

Visiting Professors

Visiting Professor
SHIGETA, Yasuteru *(from University of Tsukuba)*

Theoretical Analyses on Functions of Biomolecules

Several biological functions, such as molecular recognition, enzyme catalysis, signal transduction, allosteric regulation, and protein folding, are strongly related to conformational transitions of biomolecules. In order to understand these biologically relevant phenomena, we have developed new algorithms for conformational search, a fragment molecular orbital method, first-principles molecular dynamics simulations and applied them to protein folding problems, energy transfer in proteins, and enzymatic reaction analyses. In particular, we have investigated conformational changes of a GDP binding form of FtsZ from Staphylococcus aureus, which are related to shrink of Z-ring during a cell fission processes by using a newly developed conformational search method. We also suggest a few amino acid residues that are important for recognition of GDP and thus the conformational changes.

Visiting Associate Professor
NAGATA, Yuki *(from Max Planck Institute for Polymer Research)*

Combined Simulation and Experiment Reveals Physics of Ice Interface

Our group aims at obtaining molecular level understanding of the structure and dynamics of aqueous liquid interfaces, with particular emphasis on water, thought ‘theoretical sum-frequency generation (SFG) spectroscopy.’ The main highlight in our group in 2016 and 2017 is the SFG probe of the ice interface. We worked on the water conformation near the ice nucleation protein, where we found that the hydrophobic and hydrophilic patterns would be crucial for ice nucleation (*Sci. Adv.* 2016). Further focus has been made on the anomaly of the ice surface melting, where we found the presence of the excess hydrogen bond at the top most ice layer at 200 K, through the formation of non-hexagonal ice (*PRL* 2017). The details of the peak assignment of the SFG spectra were also made (*JPCL* 2017). In addition, we have contributed to several review papers for vibrational spectroscopy of water (*Chem. Rev.* 2016), modeling of interface (*JPCB* 2016) and TMAO molecule (*PCCP* 2017). Through this, it was also very fruitful to start a new collaboration, in particular, with Prof. Wataru Mizukami (Kyusyu Univ.) who used to be a graduate student in IMS.

Visiting Associate Professor
KATO, Tsuyoshi *(from The University of Tokyo)*

Development of Effective Potential Theory for Quantal Dynamics

I am studying in the area of quantal molecular dynamics focusing on the developments of new methods to calculate the electronic and nuclear dynamics in molecules. I am constructing a time-dependent effective potential theory that could be used to calculate the exact time-dependent wave function of a many-electron system. During the development of the effective potential theory, I found a solution algorithm for the time-independent/dependent inverse Kohn-Sham problem in terms of the effective potential calculated for an exact time-dependent/stationary wave function. Given the exact time-dependent wave function describing quantal many-particle dynamics, my final goal is to establish a method to derive an exact effective single- and two-particle potentials out of the many-particle wave function in order to deepen the understanding of quantal dynamics in atoms and molecules.

RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction of atoms and molecules with optical fields with its possible applications to active control of atomic and molecular functionality and reactivity. We also develop novel light sources to promote those studies. The UVSOR Synchrotron Facility, closely collaborates with the Department.

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

Exploring Quantum-Classical Boundary

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

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

Awards
1998 Award by Research Foundation for Opto-Science and Technology
2007 JSPS Prize
2007 Japan Academy Medal
2009 Fellow of the American Physical Society
2012 Humboldt Research Award

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TAKEDA, Shuntaro*
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TANAKA, Akira
Post-Doctoral Fellow
ZHANG, Yichi
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Visiting Scientist
TIRUMALASETTY PANDURANGA, Mahesh†
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YAMAGAMI, Yukiko

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, as depicted schematically in Figure 1, and a bulk solid, envisaging the quantum-classical boundary connected smoothly.

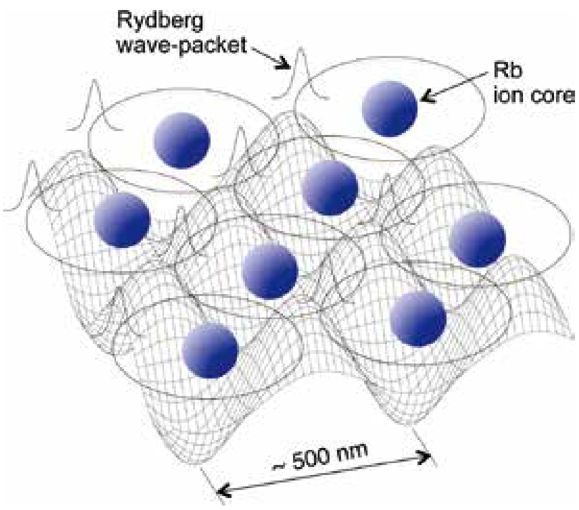

Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.2)

Selected Publications

- H. Katsuki *et al.*, "Visualizing Picometric Quantum Ripples of Ultrafast Wave-Packet Interference," *Science* **311**, 1589–1592 (2006).
- H. Katsuki *et al.*, "Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales," *Phys. Rev. Lett.* **102**, 103602 (2009).
- K. Hosaka *et al.*, "Ultrafast Fourier Transform with a Femtosecond-Laser-Driven Molecule," *Phys. Rev. Lett.* **104**, 180501 (2010).
- H. Goto *et al.*, "Strong-Laser-Induced Quantum Interference," *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, "All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth," *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, "Direct Observation of Ultrafast Many-Body Electron Dynamics in a Strongly-Correlated Ultracold Rydberg Gas," *Nat. Commun.* **7**, 13449 (2016).

1. Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas³⁾

Many-body correlations govern a variety of important quantum phenomena such as the emergence of superconductivity and magnetism. Understanding quantum many-body systems is thus one of the central goals of modern sciences. Here we demonstrate an experimental approach towards this goal by utilizing an ultracold Rydberg gas generated with a broadband picosecond laser pulse, as schematically depicted in Figure 2. We follow the ultrafast evolution of its electronic coherence by time-domain Ramsey interferometry with attosecond precision. The observed electronic coherence shows an ultrafast oscillation with a period of 1 femtosecond, whose phase shift on the attosecond timescale is consistent with many-body correlations among Rydberg atoms beyond mean-field approximations. This coherent and ultrafast many-body dynamics is actively controlled by tuning the orbital size and population of the Rydberg state, as well as the mean atomic distance. Our approach will offer a versatile platform to observe and manipulate non-equilibrium dynamics of quantum many-body systems on the ultrafast timescale.

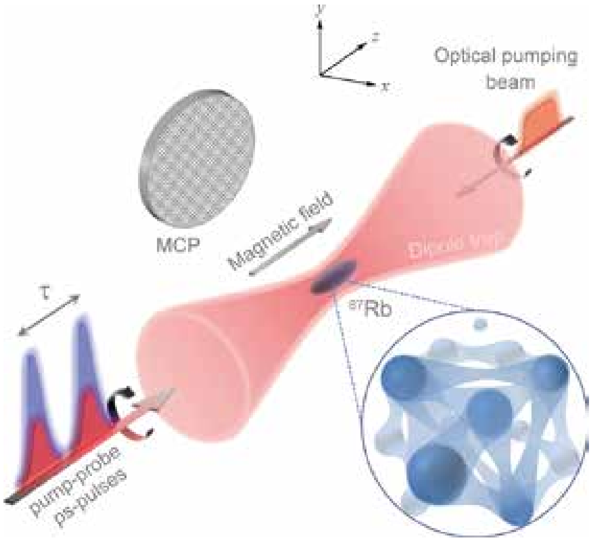

Figure 2. Schematic diagram of the experimental setup for the observation of ultrafast many-body electron dynamics in a strongly correlated ultracold Rydberg gas.³⁾

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1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
3) N. Takei *et al.*, *Nat. Commun.* **7**, 13449 (2016).

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† IMS International Internship Program

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

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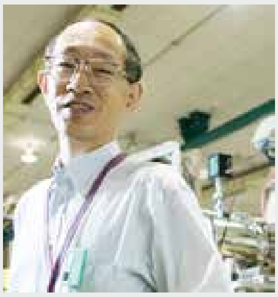
Division of Photo-Molecular Science III



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Education

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1981	Ph.D. The University of Tokyo

Professional Employment

1981	JSPS Postdoctoral Fellow
1982	Research Associate, The University of Tokyo
1988	Lecturer, The University of Tokyo
1989	Associate Professor, Kyoto University
1993	Professor, Institute for Molecular Science
1993	Professor, The Graduate University for Advanced Studies
1996	Visiting Professor, McMaster University, Canada
2008	Visiting Professor, Université P&M Curie - Paris VI, France
2011	Visiting Professor, Université Paris-Sud - Paris XI, France
2013	Visiting Professor, Freie Universität Berlin, Germany

Award

2015	The 68th Chemical Society of Japan (CSJ) Award

Member
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YAMANE, Hiroyuki
Post-Dctoral Fellow
YUZAWA, Hayato
Visiting Scientist
JU, Huanxin
CARLIER, Andy*
BOUVIER, Mathilde*
Secretary
INAGAKI, Itsuko
SUGIYAMA, Kayoko

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

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

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

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

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

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

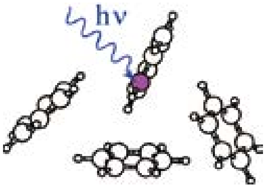

Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

Selected Publications

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

1. Liquid–Liquid Interfaces in Aqueous TEA Solution by Spatially-Resolved XAS

Aqueous triethylamine (TEA) solution shows a lower critical solution temperature (LCST) behavior,[1] in which two liquids are mixed at the lower temperature and are separated into two phases with the increase of temperature. This phase transition is contrary to normal and the mechanism of LCST has not yet been fully understood. We have observed local structures of liquid–liquid interfaces between TEA and water phases by spatially-resolved XAS with the resolution of 140 nm using a scanning transmission X-ray microscope (STXM) on UVSOR BL4U.[2] The liquid–liquid interfaces between TEA and water phases are formed from aqueous TEA solutions with the molar fraction of 0.4 at the temperature of 29.9 °C above LCST.

Figure 2(a) shows O K-edge XAS of water at different positions of the liquid–liquid interfaces. The inset shows the soft X-ray transmission image at 530 eV, in which the central part is a water phase and is surrounded by a TEA phase. We have estimated molar concentrations of water and TEA at different positions from the edge jumps of XAS in the O and C K-edges, respectively. It was confirmed that the mixing ratio of TEA and water determined in both the water and TEA phases are consistent with the phase diagram of TEA-water mixtures.[1]

Figure 2(b) shows the energy shift of the pre-edge peak (535 eV) in the O K-edge XAS at different positions. It is already known that the pre-edge peak is shifted to the lower photon energy when the hydrogen bond (HB) between water molecules is elongated/weakened. From the water to the TEA phase, the pre-edge peak is shifted to the lower energy. Because the amount of water is decreased with the direction of the TEA phase, the hydrophobic interaction of the ethyl group in TEA is dominant and the HB interaction of water molecules is decreased. Water and TEA molecules are coexisted in the TEA phase because the HB network of water is broken. The liquid–liquid interface between the water and TEA phases is formed with the balance of the hydrophobic interaction of TEA and the HB interaction of water molecules.

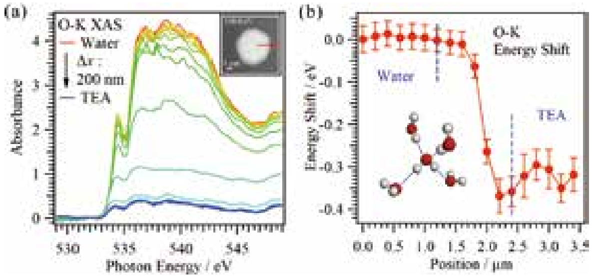

Figure 2. (a) O K-edge XAS of liquid–liquid interfaces at different positions. The inset shows soft X-ray transmission image at 530 eV. (b) Energy shift of the pre-edge peak as a function of position.

2. Delocalization of Charge-Transfer-Induced Valence Levels in Two-Dimensional Metal- Molecule Networks

Because of the large electron affinity, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) is well known as a strong electron accepter, and has been applied for the *p*-type doping of organic semiconductors and for the work-function control of metal electrodes. It is understood that the cyano group in the F_4TCNQ molecule plays a crucial role in the charge-transfer (CT) interaction. At the F_4TCNQ/Au(111) interface, in particular, the F_4TCNQ molecule forms a two-dimensional network via the cyano group with the segregated Au atom from the underlying Au(111) surface. In the present work, in order to investigate the electronic structure of the Au-F_4TCNQ network, we have studied the electronic structure of the F_4TCNQ/Au(111) interface by means of angle-resolved photoemission spectroscopy (ARPES) using synchrotron radiation at BL6U of the UVSOR Synchrotron.

From the low-energy electron diffraction (LEED), shown in Figure 3, it was found that the F_4TCNQ molecule on Au(111) forms a commensurate (5,2)(1,3) structure. Furthermore, the LEED image of F_4TCNQ/Au(111) does not show the 22×√3 herringbone pattern of Au(111) just around the (0,0) spot. This indicates the possibility of the Au-atom segregation from the Au(111) surface, which can introduce the formation of the Au-F_4TCNQ network.

Figure 3 shows the photoemission-angle (θ) dependence of ARPES for the clean Au(111) surface and the F_4TCNQ monolayer on Au(111) at 20 K using $h\nu = 45$ eV. Upon the deposition of F_4TCNQ, the Shockley-type surface state of Au(111) (labeled S) is almost quenched due to the presence of the strong chemical interaction, and the CT-induced electronic states are appeared at around 0.5 eV (labeled CT_1) and 1.5 eV (labeled CT_2) below the Fermi level. The CT_1 peak, which can be ascribed to LUMO (lowest-unoccupied molecular orbital) accepting a CT electron, shows a dispersive behavior with θ. The width of the dispersion of CT_1 is about 250 meV, and can be ascribed to the adatom-mediated intermolecular interaction in the Au-F_4TCNQ network, which was not observable at the physisorbed TCNQ/Au(111) interface.

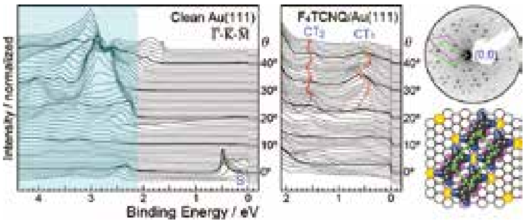

Figure 3. Photoemission-angle dependence of ARPES for the clean Au(111) and the F_4TCNQ monolayer on Au(111) at 20 K, measured at $h\nu = 45$ eV. The LEED image and the 2D ordering structure of the F_4TCNQ monolayer on Au(111) are shown in the right side.

References

1) F. Kohler and O. K. Rice, *J. Chem. Phys.* **26**, 1614 (1957).
2) T. Ohigashi *et al.*, *AIP Conf. Proc.* **1741**, 050002 (2016).

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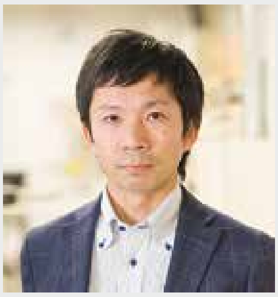
* IMS International Internship Program

Electronic Property of Functional Organic Materials

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



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Education

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2003	Postdoctoral Fellow, Wuerzburg University
2004	Assistant Professor, Chiba University
2007	Associate Professor, Chiba University
2009	Visiting Associate Professor, Institute for Molecular Science
2013	Adjunct Lecturer, The Open University of Japan
2013	Visiting Associate Professor, Soochow University
2014	Professor, Institute for Molecular Science
	Professor, The Graduate University for Advanced Studies
	Visiting Professor, Chiba University

Member

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IMS Fellow
MEISSNER, Matthias

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SUN, Zhengyi
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YAMAGUCHI, Takuma

Secretary
MASUDA, Michiko

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 even for solid phases due to weak 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 photoelectron-emission 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, very small gap-state DOS, weak band dispersion and dynamic electronic polarization. To elucidate what really impacts on the electronic states of 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). Seeing a modification of electron wave function upon weak electronic coupling as well as strong electron–phonon coupling is central issue on our agenda.

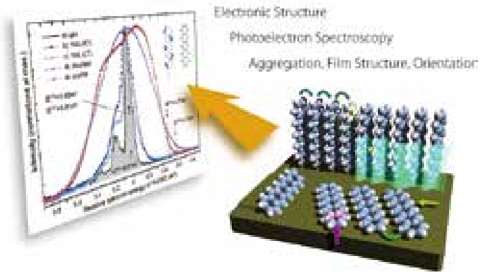

Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

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1. Hole–Phonon Coupling Effect on the Band Dispersion of Organic Molecular Semiconductors[1)]

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

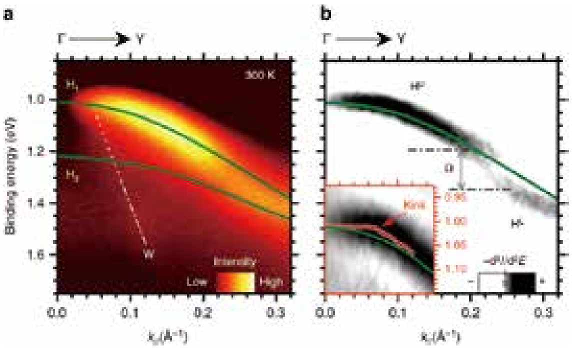

Figure 2. Renormalization of the energy-band dispersion of HOMO band of rubrene single crystal at 300 K. a) The photoelectron-emission intensity map by ARUPS. Binding energy vs. $k_{//}$ along the ΓY direction of the single crystal. Theoretical HOMO band dispersions are plotted as continuous green lines. The secondary-electron emission feature of W is overlapping (dashed line). b) Second derivative of ARUPS intensity map as obtained from data in a). The splitting of the HOMO band in two subband H^U and H^L is evidenced as separated by gap Ω. Inset: Magnification of second derivative map close to Γ point. Experimental H peak positions are also indicated by red circles and compared with theoretical band dispersion (continuous green line) to highlight the kink-like distortion.

2. Metal-Organic Interface Functionalization via Acceptor End Groups[2)]

The presence of functional groups in π-conjugated molecules not only determines the specific electronic and geometrical properties of the molecule, but also impacts the molecule–substrate and the molecule–molecule interactions. We reported a comprehensive study of the complex interface between perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) and the (111) surfaces of the three coinage metals. The specific structural, electronic, and chemical properties of the interface rendered by the different substrate reactivities are monitored with low-energy electron diffraction (LEED), x-ray standing waves (XSW), and ultraviolet and x-ray photelectron spectroscopy (UPS and XPS). In particular, the balance between molecule–substrate and molecule–molecule interactions is considered when interpreting the core-level spectra of the different interfaces. By presenting additional adsorption distances of the unsubstituted perylene, we show that the molecular functionalization via end groups with acceptor character facilitates the charge transfer from the substrate but it is not directly responsible for the associated short adsorption distances, demonstrating that this frequently assumed correlation is not necessarily correct.

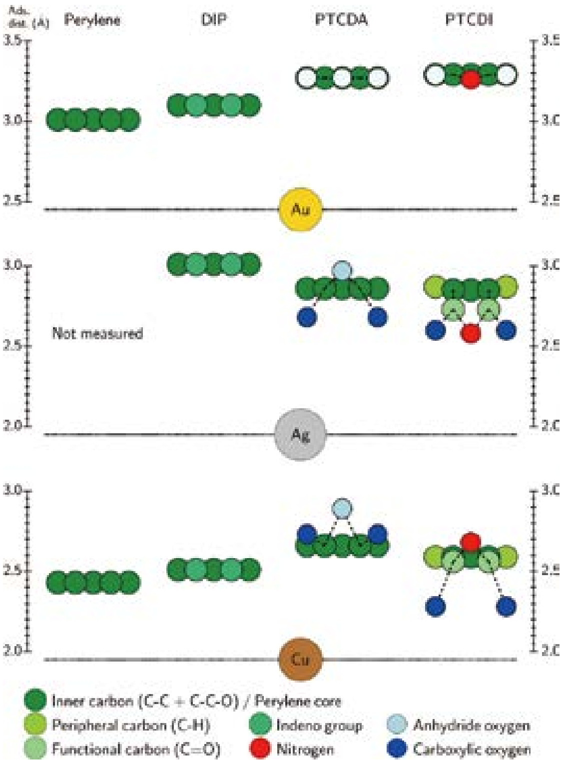

Figure 3. Adsorption distances extracted from XSW measurements for different perylene derivatives. Together with the data for perylene, DIP and PTCDA on Au(111), Ag(111) and on Cu(111). The adsorption distances on Au(111) have been corrected taking into account the surface reconstruction.

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Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Beam Physics, Astrobiology

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

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

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1. Light Source Technology Developments Based on Laser and Synchrotron

We have developed novel light source technologies using UVSOR-III electron storage ring and a dedicated experimental station BL1U which was constructed under the support of Quantum Beam Technology Program of JST/MEXT, for developing novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beam-line. The generation of coherent synchrotron radiation based on our original method was successfully demonstrated in collaboration with Lille Univ. and Nagoya Univ. Its application is under preparation, in collaborating with Osaka Univ. Optical vortex beam from undulators are intensively investigated in collaboration with Hiroshima Univ., Nagoya Univ., AIST and so on.

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 developed a unique method to produce ultra-short gamma-ray pulses in pico- and femtosecond range for the first time and demonstrated its potential as a powerful tool for material sciences by a photon-induced positron annihilation lifetime spectroscopy experiment, in collaboration with AIST. We have started developing an imaging technology for isotopes based on nuclear fluorescence resonance in collaboration with Kyoto Univ., AIST and JAEA. We have started reconstructing the resonator free electron laser on UVSOR-III, which will be used to produce intense gamma-rays through intra-cavity inverse Compton scattering.

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

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

We proposed several upgrade plans and have carried out all of them successfully. We designed a special electron beam optics intended to higher brightness. We designed necessary accelerator components, remodeled the machine and commissioned. We have designed six undulators and have successfully installed and commissioned all of them. 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 in the world.

We continue the efforts to improve the machine performance by introducing new technologies such as pulsed sextupole injection scheme. We are planning to replace some of the undulators to fit the changes of the users' requirements. Also, we are designing new accelerators for future project of the facility, such as linear accelerator based free electron laser or diffraction limited storage ring light source.

We are collaborating with Nagoya University Synchrotron Radiation Research Center (NUSR) for the accelerator developments at Aichi-SR. Accelerator magnets based on permanent magnets are being developed. Various high brightness electron sources are being developed and tested. New beam diagnostic technologies toward beam stabilization are being tested. Several PhD students from the University are involved. We are also collaborating with Accelerator Research Laboratory at KEK for the compact Energy Recovery Linac (cERL) project.

Figure 3. Optical Cavity for Resonator Free Electron Laser is under reconstruction at UVSOR-III.

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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.

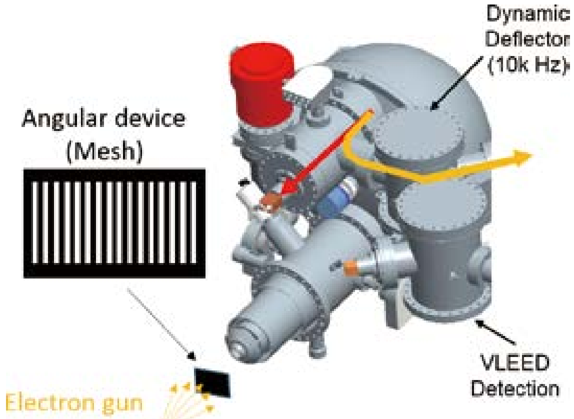

Figure 1. Schematic view of current spun-resolved ARPES system. Red and yellow arrows indicate the electron trajectory of conventional ARPES and spin-resolved ARPES, respectively.

Selected Publications

- K. Tanaka, T. Yoshida, A. Fujimori, D. H. Lu, Z.-X. Shen, X.-J. Zhou, H. Eisaki, Z. Hussain, S. Uchida, Y. Aiura, K. Ono, T. Sugaya, T. Mizuno and I. Terasaki, "Effects of Next-Nearest-Neighbor Hopping *t'* on the Electronic Structure of Cuprates," *Phys. Rev. B* **70**, 092503 (4 pages) (2004).
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- 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).
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1. Development of New Spin-Resolved ARPES

Spintronics is a rapidly emerging field of science and technology that will most likely have a significant impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin- and angle-resolved photoemission spectroscopy (spin-resolved ARPES) is one of the most powerful experimental techniques to investigate the magnetic properties of such materials, where one can know the "complete" information; energy, momentum, and spin, on electronic states of materials. Recent development of high energy- and angle-resolution photoelectron analyzer as well as the contemporary light sources such as third generation synchrotron radiation make it possible for the photoemission spectroscopy to investigate not only precise band structures but many body interactions of electrons in solids. However, appending the spin resolution is quite difficult because of an extremely low efficiency (10^{-4}) of Mott-type spin detections, and has not been established. Recently, very-low-energy-electron-diffraction (VLEED-type) spin detector with 100 times higher efficiency than that of conventional Mott-type one has been developed and spin-resolved ARPES has been started to be realized. So far, all the spin-resolved ARPES system in the world is using the single-channel detector and efficiency is still a problem. UVSOR Facility in Institute for Molecular Science equipped two public undulator-beamlines for ARPES, one was BL5U in the photon energy $h\nu$ region of 20–200 eV and the other BL7U of $h\nu$ = 6–40eV. Since the monochromator of BL5U was an old-style spherical grating type SGMTRAIN constructed in 1990s and the throughput intensity and energy resolution were poor, the whole beamline has been replaced to state-of-the-art monochromator and end station. The new beamline has been opened to users as high resolution and high flux ARPES beamline from FY2016. The newly developed electron lens system successfully achieved ~100 times better momentum resolution perpendicular to slit direction compared to the conventional ARPES. As a new function for this beamline, we have started high-efficient spin-resolved ARPES project with multi-channel detection as shown in Figure 1 (we call "image-spin" detection). Currently we successfully introduce electrons to the VLEED target position with maintaining the angle information emitted from the sample (Figure 2). If this new image-spin ARPES is realized, efficiency will be better than 100 times and the momentum resolution will be 10 times better than the current spin-resolved ARPES system in the world, which can be a breakthrough in this field.

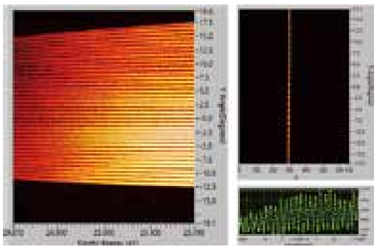

Figure 2. Detector images obtained by the electron trajectory with conventional ARPES (left) and spin-resolved ARPES (right).

2. Triple-Layer Splitting in Slightly-Overdoped $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ Observed by ARPES

It has been known that one of the most efficient ways to increase the critical temperature (T_c) of high-T_c cuprate superconductors (HTSCs) is to increase the number of neighboring CuO_2 planes (n). T_c generally increases from single-layer (n = 1), double-layer (n = 2), to tri-layer (n = 3) and then decreases for $n \geq 4$. Although several mechanisms have been proposed to explain the n dependence of T_c, it is still not clear because of the lack of detailed knowledge about the electronic structure of the multi-layer ($n \geq 3$) cuprates. We performed detailed low-photon-energy dependent ARPES study of slightly-overdoped tri-layer $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223, T_c = 110 K) in the superconducting states at UVSOR BL7U, and successfully observed the third band dispersion originated from the band splitting caused by hybridization between the CuO_2 planes. This is the first observation of three bands in Bi2223.[1,2] Surprisingly, each band shows different superconducting gaps as shown in Figure 3. We are performing temperature dependent study of those gaps to clarify which superconducting gap governs the T_c of this system.

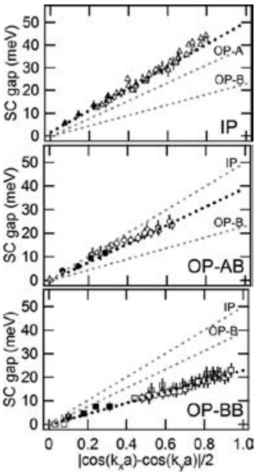

Figure 3. Superconducting gap of each band along the Fermi surface against d-wave form. The dashed lines are guides to the eye indicating the expected momentum dependence of a simple d-wave form.

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2) S. Ideta, K. Takashima, M. Hashimoto, T. Yoshida, A. Fujimori, H. Anzai, T. Fujita, Y. Nakashima, A. Ino, M. Arita, H. Namatame, M. Taniguchi, K. Ono, M. Kubota, D. H. Lu, Z.-X. Shen, K. M. Kojima and S. Uchida, *Phys. Rev. Lett.* **104**, 227001 (2010).

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

Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

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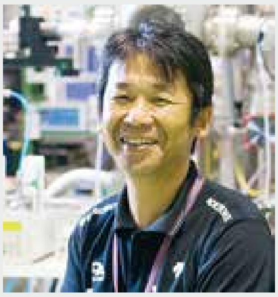

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Keywords Soft X-Ray Spectroscopy, Inner-Shell Excitation, Photodissociation Dynamics

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.

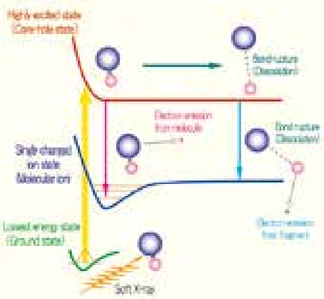

Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

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- H. Iwayama, T. Kaneyasu, Y. Hikosaka and E. Shigemasa, “Stability and Dissociation Dynamics of N_2^{++} Ions Following Core Ionization Studied by an Auger-Electron–Photoion Coincidence Method,” *J. Chem. Phys.* **145**, 034305 (8 pages) (2016).

1. Anisotropic Angular Distributions of CF_3^+ Fragment Ions Following Ultrafast Dissociation of CF_4

Following inner-shell excitation, the relaxation pathway of a molecular system involves complex fragmentation patterns, depending on the nature of the core-excited state (bound or dissociative), and/or of the final states reached after the whole relaxation process. In particular, elongation and breaking of chemical bonds can occur in many molecular systems during the lifetime of the excited state: In this case, the dissociation is defined as ultrafast, since typical lifetimes of core-excited states in molecules containing light atoms are of the order of few femtoseconds (see e.g. ref. 1)). Molecular fragmentation can also occur in a final state reached after resonant Auger decay, if such final state is unstable. In this case, the time scale for the breaking of the chemical bond is much longer. In this work, we performed resonant Auger-electron–ion coincidence measurements, which allowed us to enlighten the angular distributions of the fragments.

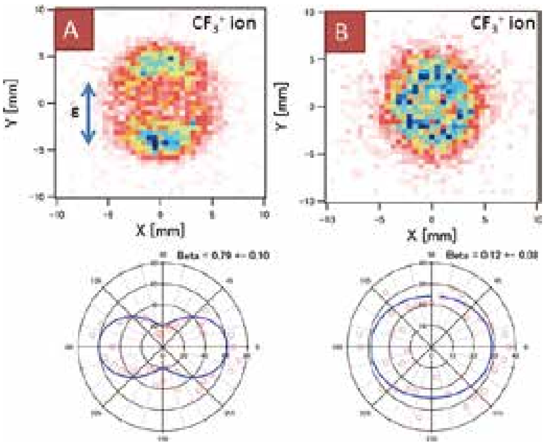

Figure 2. Angular distributions of CF_3^+ fragment ions taken in coincidence with resonant Auger electrons emitted after C 1s → LUMO excitation: (A) the lowest binding energy peak related to the ultrafast dissociation and (B) the second lowest peak corresponding to $3t_2^{-1}$ final states. The lower figures represent the results of the fitting procedures.

Figure 2 shows Angular distributions of CF_3^+ fragment ions taken in coincidence with resonant Auger electrons emitted after C 1s → LUMO excitation. The coincidence resonant Auger spectrum exhibits two broad peaks. The lower binding energy peak corresponds to the resonant Auger decay of the CF_3* fragment originated from ultrafast dissociation, while the higher is related to the molecular CF_4^+ final states ($3t_2^{-1}$).[2)] The angular distributions of CF_3^+ ions in panels (A) and (B) of Figure 2 have been taken in coincidence with the former and the latter peaks, respectively. The electric vector ε is vertical in both cases. It can immediately be seen that in the case of ultrafast fragmentation (A) the angular distribution of the CF_3^+ ions is quite asymmetric and peaked along the ε vector, while in the case of (B) the angular distribution is much more isotropic. These observations strongly suggest that the time scales of the two dissociation channels are different: For the ultrafast dissociation, the molecule has no time to rotate and the fragments are emitted according to the maintained orientation of the core-excited species, while for the dissociation after the resonant Auger decay, the molecule still keeps some memory of the excitation process before reassuming random orientation.

2. Limitations in Photoionization of Helium atoms by Extreme Ultraviolet Vortex

A circularly polarized extreme ultraviolet vortex (XUV) beam can be produced by a helical undulator. The XUV vortex beam carries not only spin angular momentum but also orbital angular momentum (OAM) with a helical wavefront. It is known that the nth harmonic off-axis radiation from a helical undulator carries OAM of $(n-1)\hbar$ per photon. According to recent theoretical works, it is predicted that a violation of the so-called electric dipole selection rules can be observed as a result of the transference of the OAM to the system. In order to investigate vortex-matter interactions in the short wavelength region experimentally, photoionization of helium atoms by the circularly polarized XUV vortex beam has been studied.

Figure 3 shows the angular distributions of photoelectrons measured for (A) the first, (B) second, and third harmonics, which correspond to plane-wave photons ($l = 0$), and the XUV vortices ($l = 1$ and $l = 2$), respectively. As seen in Figure 3, the angular distributions of photoelectrons are well reproduced by the dipole components alone, in contrast to the theoretical predictions. It is found that non-dipole transitions by vortex are hardly observable in conventional gas phase experiments.

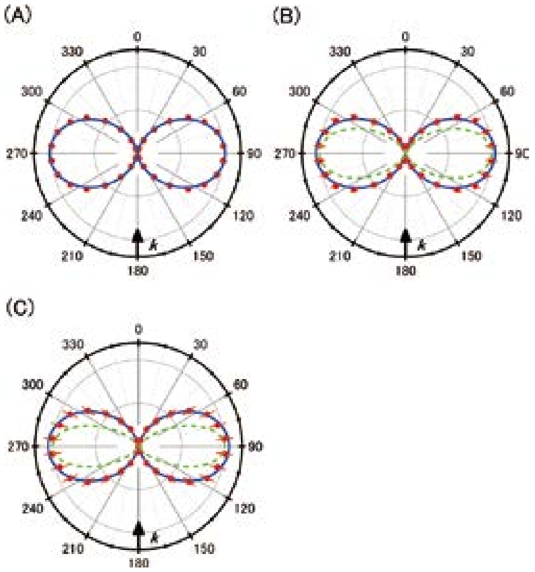

Figure 3. Angular distributions of 1s photoelectrons from helium atoms measured for (A) the first, (B) second, and (C) third harmonics from a helical undulator.

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

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

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

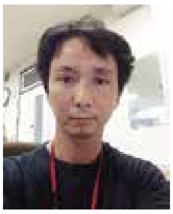
In the DSSCs, counter electrodes consist of Pt. The Pt electrode has some disadvantages such as cost and stability. Electrodes made of carbonaceous materials are candidates of substitutes for the Pt electrodes. To produce the carbon electrodes, we utilize the Langmuir-Blodgett (LB) technique. We have fabricated the LB films using fullerenes and their amphiphilic derivatives. We succeeded in producing homogeneous films on ITO glass substrates. The produced LB film electrodes were diagnosed by electrochemical methods. We found that the LB film electrodes exhibit the ionic charge- selective electron transfer (ICSET). The emergence of ICSET gives clue to utilize reactant selectivity of electrodes for suppressing side reactions which do not contribute to the efficiency of the cell.

2. Combined Study of Photoelectron Spectroscopy and Thermodynamic Measurements of ILs and Their Mixtures

We have started a research subject to apply the combined study of spectroscopic and thermodynamic measurements to the ILs. This combined study will allow us to understand the extraordinary characteristics of the ILs and their mixtures.

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

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research



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Assistant Professor

Computed tomography (CT) is a powerful technique for X-ray microscopy to observe 3-dimensional internal structure of a sample without any destructive process. Additionally, by scanning the energy of X-rays, reconstructed image of CT can contain quantitative photoabsorption data to realize 3-dimensional spectroscopy. We have been developing CT for a scanning transmission X-ray microscopy (STXM) in UVSOR by designing a sample rotation cell and adjusting parameters of the optical system.[1)]

We tried 3-dimensional structural analysis of an isolated cell nucleus of HeLaS_3 cell. The cell nucleus was fixed by glutaraldehyde and critical point drying to maintain its morphology. 50 STXM images of the nucleus on a tungsten needle were acquired with rotating the sample 3.6° each. In data acquisition, the X-ray energy of 280 eV, below C K-edge, was used for high transmission. The dwell time was 2 ms per a point and it took ~3 hours for measurement in total. A reconstructed cross sectional image and a 3-dimensional projection image are shown in Figure 1, where a voxel size is 80×80×80 nm^3. Network of actin filaments and nucleolus, round objects with high density, observed.

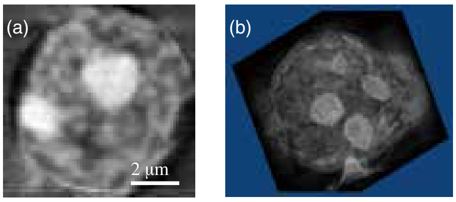

Figure 1. (a) Reconstructed cross sectional image and (b) 3-dimensional projection image of a cell nucleus.

Reference

1) T. Ohigashi *et al.*, *J. Phys.: Conf. Ser.*, in press.

Visiting Professors

Visiting Professor

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

Electronic Structure of Organic Molecules/Metal Interface

Fundamental questions about the adsorption of organic molecules on metal have gained importance also in applied research because the electronic structure at the interface between organic semiconductors and electrode metals (organic/metal interface) has a direct effect on the electric properties of various organic semiconductor devices. We have investigated how the electronic structure at the organic/metal interface is formed upon the adsorption of organic molecules by monitoring the modification of metal surface state (SS) induced by the adsorption of organic molecules using angle-resolved photoemission spectroscopy. Recently, we have focused on the interface between a well-ordered *n*-alkane monolayer and an Au(111) as an example of physisorption of organic molecule. We observed the shrinkage of quasi-free electron-like Fermi surface and enhancement of Rashba splitting of the SS upon the adsorption of the molecules. This substantial change in the metal SS directly shows that there is a certain amount of orbital interaction even in this ideal physisorption system. We have just started to investigate the other molecular systems.

Visiting Associate Professor

HIRAHARA, Toru *(from Tokyo Institute of Technology)*

Spin-Split States at the Surface/Interface of Nonmagnetic Ultrathin Films/Topological Materials

Recently there has been growing interest in utilizing the spin degree of freedom in electronic devices, the so-called *spintronics*. The conventional way is to use magnetic materials and manipulate the spin using a magnetic field. However, it is sometimes troublesome to apply a magnetic field to nano-scale materials and it is much easier to control the spin properties of materials using an electric field. By making use of the Rashba effect in which electrons become spin polarized in k-space due to spin–orbit coupling effects at the surface, such manipulation of electron spin with an electric field becomes possible, *i.e.*, a spin field effect transistor can be realized in such materials. We are developing a high-resolution spin- and angle- resolved photoemission spectroscopy measurement system equipped with *in situ* surface sample preparation facilities at BL-5U and characterize the novel spin property at the Rashba-split surface/interface states of nonmagnetic ultrathin films. We will also try to grow thin films of novel topological materials such as Dirac/Weyl/line-nodal semimetals. Furthermore, we will try to study the interplay between magnetism and the Rashba effect.

Visiting Associate Professor

KISHIMOTO, Tetsuo *(from University of Electro-Communications)*

Development towards Continuous Production of Bose-Einstein Condensates

Our goal is to realize continuous production of Bose-Einstein Condensates (BEC) based on all-optical techniques. By using sympathetic cooling techniques, this can further extend the possibility of realizing CW BECs for many other different atomic species or even molecules that are not eligible for direct evaporative cooling. So far we have explored the possibility of using the narrow $5S_{1/2}$–$6P_{3/2}$ cooling transition, however continuous loading of atoms into an optical dipole trap with this transition has not been successful so far. We have tuned this dipole trap to a special wavelength but the hyperfine states in the excited state experiences some vector light-shift, which may be the cause of insufficient cooling during the continuous loading. To avoid such vector shifts, currently we are moving toward the next approach of using a so called gray-molasses (GM) cooling with the $5S_{1/2}$–$6P_{1/2}$ transition. There has been no report of GM-cooling so far using such transitions with different principle quantum numbers.

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.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

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

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

Member
Assistant Professor
TAKAGI, Yasumasa
UEMURA, Yohei
Post-Doctoral Fellow
NAKAMURA, Takahiro
YU, Liwei
KOIDE, Akihiro
CHAVEANGHONG, Suwilai
Secretary
AOKI, Junko

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

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

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

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. In 2014, we successfully exploited near ambient pressure (up to ~5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8, and in 2017 eventually we have succeeded in real ambient pressure (100,000 Pa) HAXPES measurements. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated non-crystalline element by using the energy-resolved x-ray fluorescence detection technique. Fast time resolved XAFS measurement is difficult since the repetition frequencies of probe SR and pumping lasers are usually far different, requiring pulse picking of the SR probe and resultantly time resolved detection of only energy-integrated x-ray fluorescence. To detect energy- resolved x-ray fluorescence, a picosecond laser with high repetition rate (up to 1 MHz) was installed in Photon Factory Advanced Ring with single bunch operation (794 kHz). This allows us to investigate XAFS of low concentration elements using a slow but energy-resolved x-ray fluorescence detector.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Takagi *et al.*, *Appl. Phys. Lett.* **105**, 131602 (2014).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Wakisaka *et al.*, *Phys. Rev. B* **92**, 184408 (2015).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).

1. X-Ray Photoelectron Spectroscopy under Real Ambient Pressure Conditions[1)]

We have successfully developed a real ambient pressure (10^5 Pa) hard X-ray photoelectron spectroscopic system equipped with a differential pumping system at beamline BL36XU of SPring-8 for the first time in the world. Photoelectron spectra from gold single crystal were recorded using excitation light of 8 keV focused to 20×20 μm^2 and adopting an aperture diameter of 30 μm at the entrance of the electron lens (see Figures. 1(a)–(c)) and a working distance of 60 μm (see Figure 1(d)). The Au 4f and 3d$_{5/2}$ spectra were successfully measured by increasing the ambient pressure from 1 Pa to atmospheric pressure as shown in Figure 2 and demonstrated that the instrument is capable of measuring the photoelectron spectrum under atmospheric pressure.

The kit shown in Figure 1 allows us to keep the high vacuum pressure in the electron energy analyzer and the ambient pressure at the sample surface. Figure 2 clearly exemplifies successful observation of the photoelectron spectra at 10^5 Pa. The present system is widely applicable to various kinds of investigations as fuel cells under real working conditions, solid/liquid/gas interfaces, ambient pressure chemical reactions *etc*.

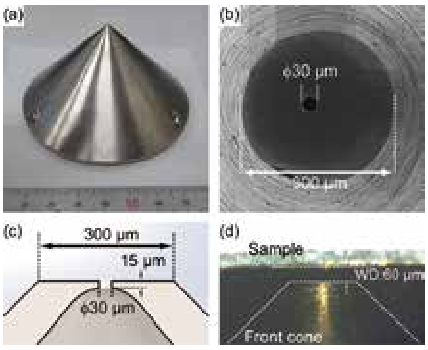

Figure 1. (a) Front cone of the electron energy analyzer. (b) Scanning electron microscope image of the aperture shaped at the top of the front cone. (c) Schematic diagram of the cross section of the aperture. (d) CCD microscopic image of the sample and the front cone at a WD of 60 μm.

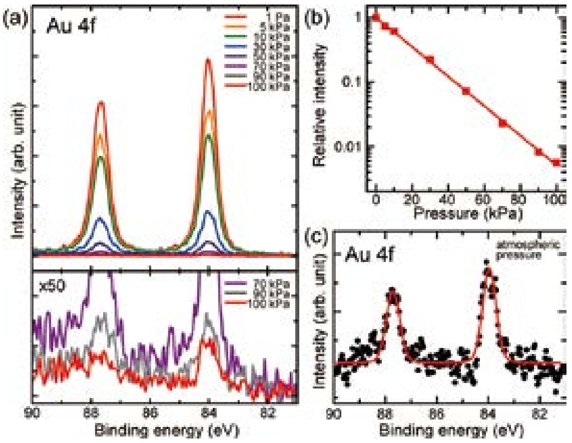

Figure 2. (a) Au 4f spectra recorded using 7.94 keV X-rays at pressures of 1 to 10^5 Pa. (b) Relative intensity of Au 4f$_{7/2}$ as a function of pressure. (c) Background subtracted Au 4f recorded at 10^5 Pa.

2. Capturing Local Structure Modulations of Photoexcited $BiVO_4$ by Ultrafast Transient XAFS[2)]

$BiVO_4$ is a promising material for fabricating practically useful photocatalysts and photoelectrodes, exhibiting a band-gap of ~2.5 eV and having the potential to excite electrons from the valence band to the conduction band and to form valence band holes by absorbing visible sunlight. In this work, ultrafast excitation of photocatalytically active $BiVO_4$ was characterized by femto- and picosecond transient X-ray absorption fine structure (XAFS) spectroscopy.

Figure 3 shows the transient Bi L$_3$-edge XAFS and their time dependence. An initial photoexcited state changed to a metastable state (<<500 fs) accompanied by a structural change with a time constant of ~14 ps. The structural change might stabilize holes on oxygen atoms since the interaction between Bi and O increases. A proposed diagram of the photoexcitation process of $BiVO_4$ is shown in Figure 4.

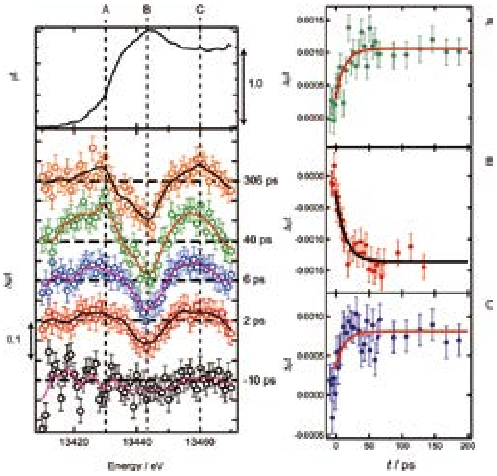

Figure 3. (Left) Bi L$_3$-edge XAFS spectra of the ground state (top) and the difference spectra of the excited states after the given delay times. (Right) Changes in X-ray absorption intensities at points A, B, and C.

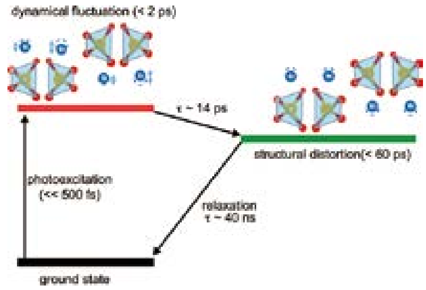

Figure 4. A proposed diagram of the photoexcitation process of $BiVO_4$.

References

1) Y. Takagi, T. Nakamura, L. Yu, S. Chaveanghong, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama, *Appl. Phys. Express* **10**, 076603 (2017).

2) Y. Uemura, D. Kido, A. Koide, Y. Wakisaka, Y. Niwa, S. Nozawa, K. Ichiyanagi, R. Fukaya, S. Adachi, T. Katayama, T. Togashi, S. Owada, M. Yabashi, K. Hatada, A. Iwase, A. Kudo, S. Takakusagi, T. Yokoyama and K. Asakura, *Chem. Commun.* **53**, 7314–7317 (2017).

Magnetic Resonance Studies for Functional Molecular-Based Solids

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Education

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1995	D.S. Kyoto University

Professional Employment

1992	Assistant Professor, Gakushuin University
1998	Associate Professor, Institute for Molecular Science
2003	Associate Professor, The Graduate University for Advanced Studies

Award

2017	The 22nd Outstanding Paper Award of the Physical Society of Japan

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IMS Research Assistant Professor
ASADA, Mizue
Secretary
YAMASAKI, Yumi

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. Nakamura, K. Furukawa, T. Terauchi and Y. Kobayashi, “Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate,” *Phys. Status Solidi RRL* **9**, 480–484 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, “Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex,” *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Magnetic Investigation of Iodine-Doped COF (Covalent-Organic-Framework)

COF materials are pours crystalline materials, which attract much attention because of their functionalities. We investigated the photoconduction mechanism by time-resolved ESR.[1)] Recently a two-dimensional (2D) crystalline covalent organic framework (sp^2c-COF) that is fully π-conjugated and constructed from all sp^2-carbons by C=C condensation reactions of tetrakis(4-formylphenyl)pyrene and 1,4-phenylenediacetonitrile.[2)] The sp^2c-COF can be chemically oxidized with iodine, and the generated radical spins are on the pyrene skeletons. To investigate the electronic states down to low-temperatures, we performed ESR and SQUID measurements for the 2D sp^2c-COF. An ESR signal appeared at $g = 2.003$, just after iodine doping. The ESR linewidth and g-values were almost constant regardless of the doping level. The ESR linewidth of 1.3 Gauss is narrow. The significant increase of ESR intensity indicates that high concentration spin injection realized. The χ_{spin} determined by ESR and SQUID measurements indicates the existing spin freedom down to the low temperature. Curious low-temperature behavior of spin system is also discussed.

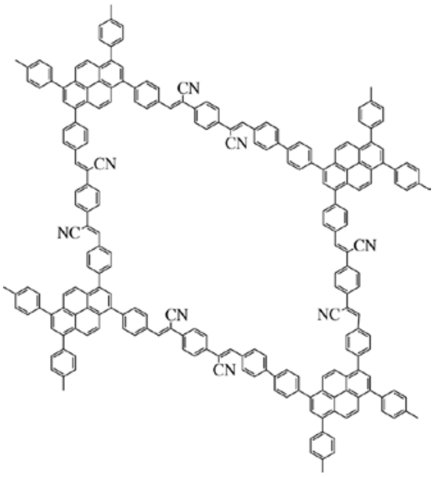


Figure 2. Molecular structure of sp^2c-COF.

2. Low-Temperature Electronic Phases in One-Dimensional Organic Conductors (TMT*C*F)$_2$*X*

One-dimensional conductors based on (TMTCF)$_2X$ (C = S, Se) are some of the most extensively studied materials among organic conductors. They possess various ground states including the spin-singlet (SS), commensurate antiferromagnetic state (C-AF), incommensurate spin density wave (IC-SDW) and superconductivity (SC), with applied pressures or counter anions, X. Moreover, findings of charge-ordering (CO) and related phenomena in (TMTTF)$_2X$ have attracted significant recent attention.

(TMTTF)$_2MF_6$ shows successive phase transitions as the temperature decreases. In paramagnetic region, these salts undergo a charge-ordering phase transitions. With synchrotron x-ray diffraction, we directly observed a slight structural difference owing to the effect of charge-order transition between two TMTTF molecules in a dimer for (TMTTF)$_2$PF$_6$.[3)] The charge distribution is estimated as 0.20e, which is close to that observed in NMR.

(TMTTF)$_2$Br undergoes antiferromagnetic transition at 16 K (T_N). But it is located on the proximity between C-AF and IC-SDW phase in the generalized phase diagram. To understand the electronic states on the boundary region between the commensurate antiferromagnetic phase and the incommensurate spin-density-wave (IC-SDW) phase in the generalized phase diagram for 1D organic conductors, we performed antiferromagnetic resonance (AFMR) and nuclear magnetic resonance (NMR) measurements for (TMTTF)$_2$Br. The angular dependence of the AFMR fields at 1.5 K is different from that at 4.8 K, and the temperature dependence of the two AFMR modes is enhanced below 5 K. Furthermore, ^{2}D-NMR measurements were performed to investigate charge distribution by quadrupole splitting at low temperatures. We found that the ^{2}D-NMR spectrum changes at ~4 K in the antiferromagnetic phase. Successive phase transition and a possible magnetic structure are discussed.

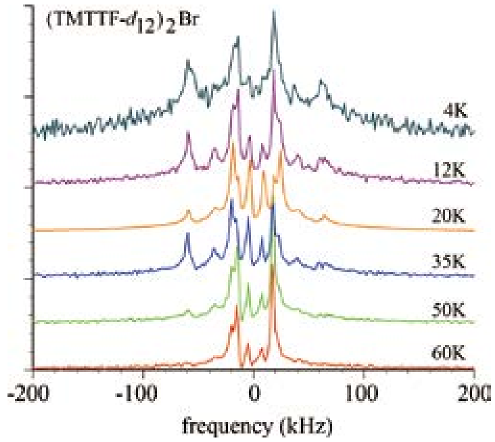


Figure 3. Temperature dependence of the ^{2}D-NMR spectra for deuterated (TMTTF)$_2$Br. Each spectrum is composed of several doublets because of quadrupole splitting.

References

1) S. Jin, M. Supur, M. Addicoat, K. Furukawa, L. Chen, T. Nakamura, S. Fukuzumi, S. Irle and D. Jiang, *J. Am. Chem. Soc.* **137**, 7817–7827(2015), and references therein.

2) T. E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen and D. Jiang, *Science* **357**, 673–676 (2017).

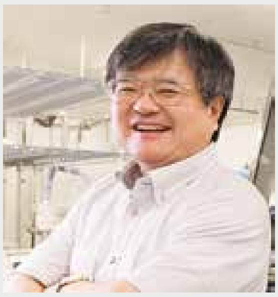
3) S. Kitou, T. Fujii, T. Kawamoto, N. Katayama, S. Maki, E. Nishibori, K. Sugimoto, M. Takata, T. Nakamura and H. Sawa, *Phys. Rev. Lett.* **119**, 065701 (2017).

Award

NAKAMURA, Toshikazu; The 22nd Outstanding Paper Award of the Physical Society of Japan (2017).

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions



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Education

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

Professional Employment

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

Awards

2017	11th JSAP Fellow Awards
2006	Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
2006	Research and Education Award, Osaka University
2004	Editor Award, Japanese Journal of Applied Physics

Member

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IZAWA, Seiichiro

Post-Doctoral Fellow
NAKAO, Satoru

Research Fellow
KIKUCHI, Mitsuru

Visiting Scientist
RAI, Nitish*

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SHINTAKU, Naoto

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SUGIHARA, Hidemi

Keywords Organic Semiconductors, Organic Solar Cells, ppm-Doping

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, *etc*. We have been focused on the 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.

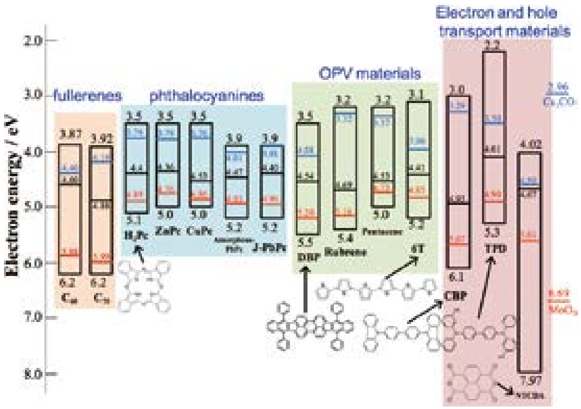

Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100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

Selected Publications

- C. Ohashi, S. Izawa, Y. Shinmura, M. Kikuchi, S. Watase, M. Izaki, H. Naito and M. Hiramoto, “Hall Effect in Bulk-Doped Organic Single Crystal,” *Adv. Mater.* **29**, 1605619 (6 pages) (2017).
- C. Ohashi, Y. Shinmura, M. Kubo and M. Hiramoto, “ppm-Doping Effects in the Simplest n^+p-Homojunction Organic Photovoltaic Cells,” *Org. Electron.* **27**, 151–154 (2015).
- M. Hiramoto, M. Kubo, Y. Shinmura, N. Ishiyama, T. Kaji, K. Sakai, T. Ohno, M. Izaki and M. Hiramoto, “Bandgap Science for Organic Solar Cells,” *Electronics* **3**, 351–380 (2014).

1. Hall Effect in Doped Organic Single Crystals

Control of *p*-type and *n*-type that holes and electrons are responsible for electric conduction, respectively, by the addition of a trace amount of impurity (doping) is the central technology in 20 century's inorganic single crystal electronics as represented by the silicon chips, the solar cells, and the light emitting diodes. The number of carriers created by doping and their moving speed (mobility) can be freely evaluated by Hall effect measurement using a magnetic field. However, in the field of organic electronics emerging in 21 century, no one has attempted not only to dope impurities into the organic single crystal itself but also the Hall effect measurement.

We combined the rubrene organic single crystal growth technique with the our original ultra-slow deposition technique of one billionth of a nanometer (10^{-9} nm) per second, which includes a rotating shutter having aperture, and have succeeded in producing the 1 ppm doped organic single crystal and in detecting the Hall effect signal for the first time (Figures 2 and 3). As an acceptor dopant, iron chloride (Fe_2Cl_6) was used.

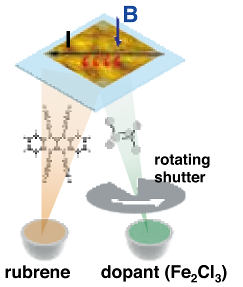

Figure 2. Ultra-slow co-deposition technique to produce the doped rubrene single crystal. Magnetic field (B) and excitation current (I) for Hall effect measurements are also shown.

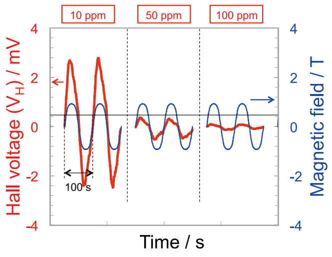

Figure 3. Hall voltage signals (red) observed under the application of AC magnetic field (blue) for the 50-, 100-, 500-, and 1000-ppm doped devices.

Hall voltage (V_H) signals were detected when applying a magnetic field to the $FeCl_3$-bulk-doped homoepitaxial layer (Figure 3). V_H showed a systematic decrease for the 50-, 100-, 500-, and 1000-ppm doped devices, respectively. This is due to the increase in the hole concentration (N) (Figure 4(a), red).

Two unique observations were observed for the doped single crystals.

(i) High ionization rate of dopant molecules: The doping efficiencies of a single crystal and amorphous films of rubrene were compared. The rubrene single crystal reached a maximum value of 24% at 100 ppm (Figure 4(b), red), which was significantly larger than the value of 1.2% for the amorphous film that formed from vacuum deposition (Figure 4(b), blue). We presume that the ionization rate was dominated by the density of hole traps.

(ii) Scattering effects from lattice disturbances: The Hall mobility (μ_H) decreased above 10 ppm (Figure 4(c)). We think that this could be attributed to hole scattering by doping-induced lattice disturbances, such as lattice distortion from the substitution of rubrene molecules with ionized and neutral dopant molecules, and the formation of various types of defects, such as dopants that were inserted at interstitial positons, the formation of doping-induced vacancies, *etc*.

The present results have the meaning of dawn of organic single crystal electronics similar to the silicon single crystal electronics. In future, organic single crystal devices such as high performance organic single crystal solar cells would be developed.

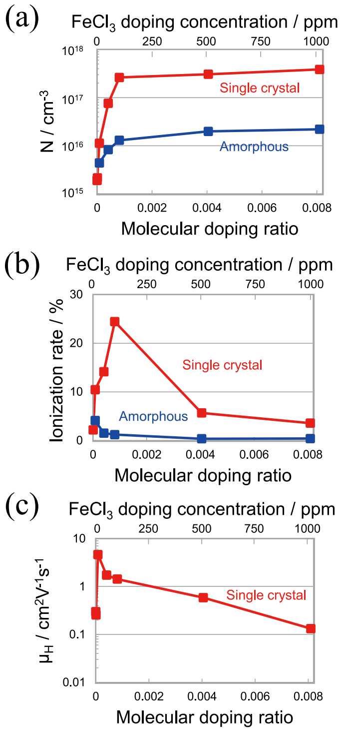

Figure 4. Dependences of (a) the hole concentration per unit volume (N), (b) the ionization rate, and (c) the Hall mobility (μ_H) on the molecular doping ratio (MR) and the $FeCl_3$ doping concentration by volume for doped single crystal (red curves). For comparison, the results for N and the ionization rate for vacuum deposited amorphous films are also shown (blue curves).

Award

HIRAMOTO, Masahiro; 11th JSAP Fellow Awards (2017).

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* IMS International Internship Program

Solid-State NMR for Molecular Science

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Education
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Professional Employment
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2001 Assistant Professor, Yokohama National University
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Associate Professor, The Graduate University for Advanced Studies

Award
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Member
Secretary
YAMAZAKI, Yumi

Keywords Solid State NMR, Biomolecules, Developments

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

We have been working on methodology and hardware developments of solid-state NMR and their applications for structural biology and material science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterizations of those molecules based on solid-state NMR are under investigations through collaborations with several research groups.

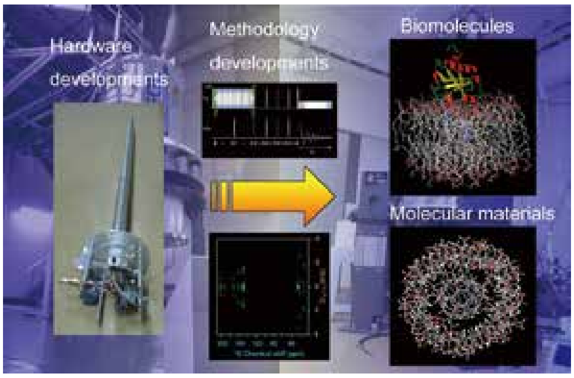

Figure 1. Outline of our studies.

Selected Publications

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

1. Characterization of Supramolecular Structure Based on Solid-State NMR[1)]

We have been collaborated with Prof. Eiji Yashima group in Nagoya university during a couple of years for the characterization of supramolecules developed in their research group. They have successfully reported that syndiotactic poly methyl methacrylate (st-PMMA) can hold into a preferred handed-helical conformation with an inner cavity in toluene in the presence of an optically active alcohol or amine accompanied by gelation. They have been explored to develop a strategy to encapsulate a helical peptide attached to C_{60} into the helical cavity of st-PMMA.

In this study, we have attempted to reveal the formation of inclusion complex composed of those molecules using solid-state NMR. Based on ^{13}C cross polarization magic angle spinning (CPMAS) and two-dimensional (2D) ^{1}H-^{13}C heteronuclear correlation (HETCOR) spectra at short contact time (CT) for st-PMMA, peptide-C_{60} and their complex, ^{1}H and ^{13}C signals were successfully assigned. Then 2D ^{1}H-^{13}C HETCOR spectra were acquired with various appropriate long CTs to obtain long distance correlations. With use of Lee-Goldburg (LG) ^{1}H homonuclear dipolar decoupled CPMAS at CT of 2.0 ms, ^{1}H-^{13}C correlations up to 4 Å apart may be detected.

Inter- and intra-molecular correlation peaks were observed in 2D ^{1}H-^{13}C HETCOR spectrum for peptide-C_{60} at CT of 2.0 ms between ^{1}H signals of peptide moieties and ^{13}C signals of C_{60}-moieties, suggesting random orientation of peptide-C_{60} in sample as shown in Figure 2(b). In contrast, apparent intermolecular correlation peaks between ^{1}H signals of methylene and methoxy groups of st-PMMA and ^{13}C signals of the C_{60} moieties were successfully observed in 2D ^{1}H-^{13}C HETCOR spectrum for complex at same CT as shown in Figure 2(c). On the other hand, the methylene and the methoxy groups in helical st-PMMA locate inside of helical cavity, in contrast to the methyl group locating out side of helical cavity of st-PMMA. Those experimental evidences are consistent when peptide-C_{60} is encapsulated into helical cavity of st-PMMA. Therefore, based on those analyses, formation of inclusion complex composed of those molecules was clearly proved.

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

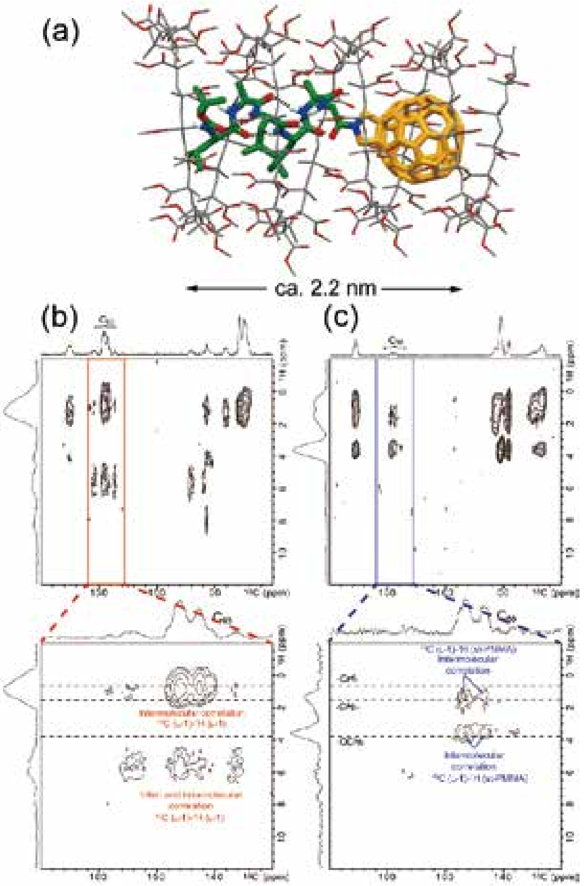

Figure 2. (a) Energy minimized supramolecular structure of st-PMMA/peptide-C_{60} inclusion complex. 2D solid-state NMR spectra of ^{1}H-^{13}C-heteronuclear correlation with LG-CPMAS at CT of 2.0 ms for (b) peptide-C_{60} and (c) complex, respectively.

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

Amyloid β (Aβ) peptides exhibit random structures in solution, however after incubation, those conform insoluble amyloid fibrils, which are found in senile plaque as hallmark of Alzheimer's disease. Although, their structures have been characterized precisely, molecular mechanism of formation of the amyloid fibrils in human brain has not been clarified. Accumulated evidences strongly suggest that an initial stage of aggregation may be promoted on surface of neuronal membrane, and ganglioside GM1 specifically interacting with Aβ may play important roles for the binding of Aβ to the surface of neuronal membrane. We have successfully determined oligomeric structure of Aβ(1-40) bound to the lipid bilayers consisting of neutral lipid of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) using solid-state NMR as reported in last year.[2)]

In current study, to clarify the contribution of GM1 in fibrillation process, we have been attempted to characterize oligomeric structure of Aβ(1-40) bound to lipid bilayers consisting of GM1 and DMPC. Sample preparation procedures were optimized to enhance spectral sensitivity and ^{13}C homo- and ^{13}C-^{15}N hetero-nuclear correlation spectra were acquired for sequential signal assignments. Currently, data is under investigation.

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2) M. Yagi-Utsumi, K. Kato and K. Nishimura, *PLoS One* **11**, 0146405 (10 pages) (2016).

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

Safety Office

TOMURA, Masaaki
Assistant Professor

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

1. A Novel Synthesis of Halogenated Oxa[9]helicenes and Dibromo Spiro-Lactone Derivative[1)]

A new class of halogenated oxa[9]helicene derivatives along with dibromo spiro-lactone were synthesized in excellent yields, and the compounds were successfully characterized by ^{1}H and ^{13}C NMR, high resolution mass spectroscopy and X-ray crystallographic analysis.

2. X-Ray Crystallographic Analyses of Heterocyclic and Organometallic Compounds[2,3)]

The X-ray crystallographic analyses of two heterocyclic and organometallic compounds have revealed their interesting structural natures and unique molecular aggregations.

References

1) M. Shahabuddin, M. Salim, M. Tomura, T. Kimura and M. Karikomi, *Tetrahedron Lett.* **57**, 5902–5906 (2016).
2) M. Tomura, *IUCrData* **2**, x171023 (2017).
3) M. Tomura, *IUCrData* **2**, x171059 (2017).

Multifunction Integrated Macromolecules for Molecular-Scale Electronics

Safety Office

TANAKA, Shoji
Assistant Professor

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

1. Development of Rigid-Rod Linkers for Mono-Molecular Integration of Quantum-Effect Device Modules

We have established the synthetic methods for typical **SET** modules based on building blocks (**1**). In this study, we developed rigid-rod linkers (**2-9**) for precise alignment of the device modules in single molecular skeleton. Figure 1 illustrates our synthetic strategy.

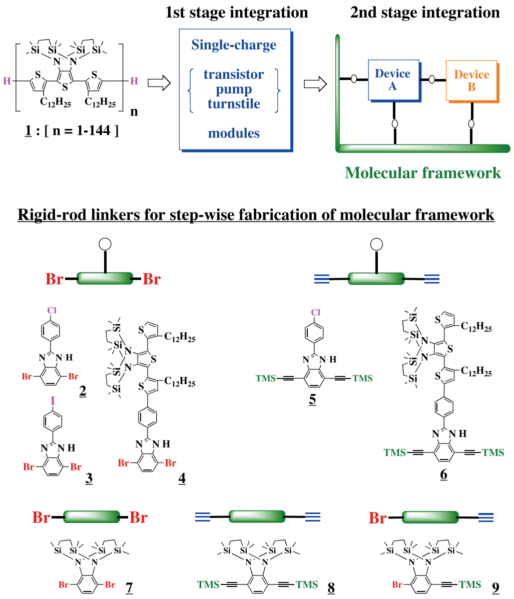

Figure 1. Synthetic strategy for precise integration of device modules.

Visiting Professors

Visiting Professor

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

Giant Seebeck Effect in Pure π-Conjugated Molecular Solids

The Seebeck effect is a well-known phenomenon where a voltage appears in a material with temperature gradient. The origin of the Seebeck effect has been generally explained by the transport coefficients of charge carriers under electric field and temperature gradient using the linear response theory where the interaction between carrier and phonon is included only as a rare event called 'scattering.' Recently, our group found that irregularly large Seebeck coefficients appear in pure π-conjugated molecular solids at a near room temperature range, of which magnitude is a hundred times larger than the prediction by the conventional theory. A strong charge-vibration coupling in molecular solids is considered to be a driving force of this phenomenon and both experimental and theoretical studies are under progress. Such a large Seebeck coefficient is also interesting from an application point of view because it possibly produces revolutionary simple thermoelectric generators being free from the series connection of hundreds of p- and n-type blocks.

Visiting Professor

TAJIMA, Naoya *(from Toho University)*

Quantum Transport Phenomena in Molecular Massless Dirac Fermion Systems

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

Visiting Associate Professor

YOSHIKAWA, Hirofumi *(from Kwansei Gakuin University)*

Development of Rechargeable Batteries Using Coordination Compounds as Cathode Materials

Recently, much attention has been focused on development of high-performance rechargeable batteries due to the global energy and environmental problems. Our research interest is to find novel cathode materials toward the next-generation rechargeable battery with a high capacity, a stable cycle performance, a rapid charging, and so on. We have examined battery performances of various organic and inorganic materials, which could take the place of the present general cathode materials, $LiCoO_2$ and $LiFePO_4$. Among various materials, porous redox-active coordination compounds are promising since they have an ionic conductive space and a robust structure. To realize a high capacity, a good cycle performance, and a rapid charging, we develop porous polyoxometalates and metal organic frameworks, and examine their battery performances. We also try to prepare their nanoparticles to increase electrochemical performances. Finally, we reveal these electrochemical reaction mechanism by using operando XAFS, XRD, solid-state NMR *etc.* and the obtained information is utilized to investigate new materials with high battery performances.

RESEARCH ACTIVITIES

Life and Coordination-Complex Molecular Science

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

Bioinorganic Chemistry of Metalloproteins Responsible for the Homeostasis Control

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

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

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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 focused on the elucidation of the structure and function relationships of metalloproteins responsible for the regulation of biological homeostasis.

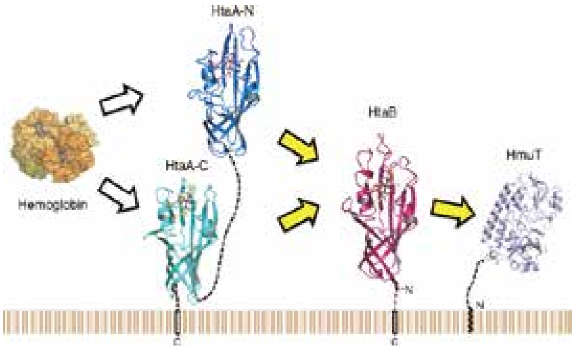

Figure 1. The protein machinery for heme uptake and transport in *Corynebacterium glutamicum*.

Selected Publications

- N. Muraki, C. Kitatsuji, M. Ogura, T. Uchida, K. Ishimori and S. Aono, "Structural Characterization of Heme Environmental Mutants of CgHmuT that Shuttles Heme Molecules to Heme Transporters," *Int. J. Mol. Sci.* **17**, 829 (2016).
- N. Muraki and S. Aono, "Structural Basis for Heme Recognition by HmuT Responsible for Heme Transport to the Heme Transporter in *Corynebacterium glutamicum*," *Chem. Lett.* **45**, 24–26 (2015).
- C. Kitatsuji, M. Ogura, T. Uchida, K. Ishimori and S. Aono, "Molecular Mechanism for Heme-Mediated Inhibition of 5-Aminolevulinic Acid Synthase 1," *Bull. Chem. Soc. Jpn.* **87**, 997–1004 (2014).
- Y. Okamoto, H. Sawai, M. Ogura, T. Uchida, K. Ishimori, T. Hayashi and S. Aono, "Heme-Binding Properties of HupD Functioning as a Substrate-Binding Protein in a Heme-Uptake ABC-Transporter System in *Listeria monocytogenes*," *Bull. Chem. Soc. Jpn.* **87**, 1140–1146 (2014).
- 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).

1. Structure and Function of Heme Uptake Machinery in *Corynebacterium glutamicum*

Most commensal or pathogenic bacteria have heme acquisition systems for utilizing host heme as an iron source. The heme acquisition systems consist of cell surface localized heme binding proteins and heme transport proteins. In several Gram-positive bacteria such as *Staphylococcus aureus* and *Bacillus anthracis*, the iron regulated surface determinant (Isd) proteins capture and transfer heme to ABC transporter-type heme transport proteins. Though a similar ABC-type heme transporter consisting of HmuT, HmuU, and HmuV proteins is used by *Corynebacteria glutamicum* and *Corynebacterium diphtheriae*, they adopt different heme binding proteins, HtaA and HtaB, instead of Isd proteins (Figure 1). The ABC-type heme transporter system is widely used for heme acquisition, which consists of an ATP-binding protein, heme permease, and heme-binding protein (substrate-binding protein).

In this work, we have studied the structural and functional relationships of heme-binding and heme-trnasport proteins, HtaA, HtaB and HmuT in *Corynebacterium glutamicum*. Where HtaA and HtaB act as heme-binding and heme-transport proteins in the heme acquisition system of HtaAB-HmuTUV for *Corynebacterium glutamicum*, HmuT is a substrate (heme) binding protein for the ABC-type heme transporter HmuUV. Our working hypothesis is that heme captured in HtaA is transferred into cytoplasm by the ABC-type HmuUV heme transporter, but the detailed molecular mechanisms of heme transport in these systems remain to be elucidated. In this work, the molecular mechanisms of heme acquisition in *Corynebacterium glutamicum* have been elucidated based on the structural analyses of HtaA, HtaB, and HmuT.

Sequence analysis identified a conserved region (CR) of approximately 150 amino acids that is duplicated in HtaA and present in a single copy in HtaB. HtaA consists of two homologous CRs in the N- and C-terminal regions. We have determined the crystal structures of the N-terminal and C-terminal CRs of HtaA (HtaA-N and HtaA-C, respectively) at the resolution of 2.0 and 1.3 Å, respectively. The crystal structure of HtaB has also been determined at the resolution of 1.7 Å. HtaA-N consists of 11 β strands and two short α helices and accommodates one heme molecules with Tyr58 located in the first α helix as an heme axial ligand. Tyr58 forms a hydrogen bond with His111 (Figure 2A). A heme propionate forms hydrogen bonds with Ser54 and Tyr201. Heme is accommodated in an open pocket formed by hydrophobic amino acid residues including Phe55, Val63, Ile118, Leu119, Phe146, Phe197, and Phe200. Phe200 forms π-π stacking with heme and heme propionate forms a hydrogen bond with Ser54. These residues including the axial ligand and residues involved in the hydrogen bonding interactions are responsible for heme recognition by HtaA-N, which are conserved among HtaA-C and HtaB, as shown in Figure 2.

We have also determined the crystal structure of HmuT at the resolution of 1.4 Å. HmuT consists of structurally similar two domains located in the N-terminal and C-terminal regions connected a long α helix. A single heme molecule is bound in the cleft between these domains. Heme iron is ligated by His141 and Tyr240, and Tyr240 forms a hydrogen bond with Arg242. There is no amino acid residue interacting heme except for His141 and Tyr240 indicating that heme is recognized by the axial ligation in HmuT. Intriguingly, HmuT binds a heme with two different orientations. As the protoheme bound to HmuT has an asymmetric structure, there are two possible orientations of heme when it is accommodated in the heme-binding site of HmuT.

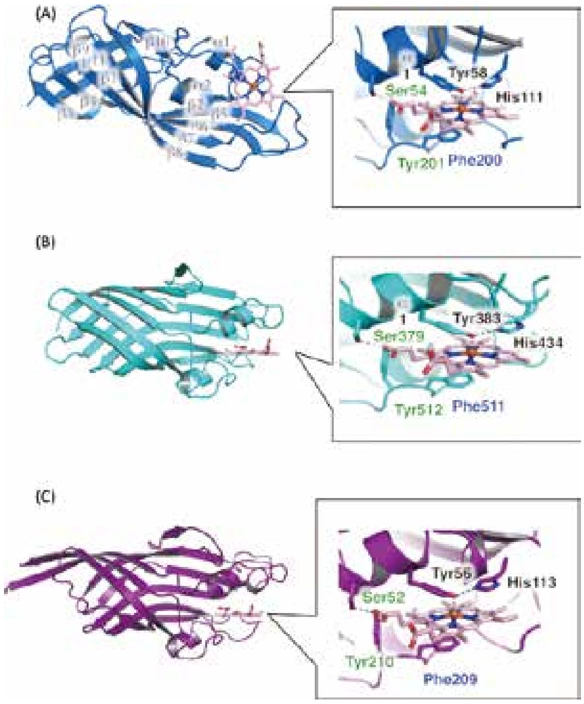

Figure 2. The crystal structures of (A) CgHtaA-N, (B) CgHtaA-C, and (C) CgHtaB with the close-up view of their heme binding sites.

2. A Novel Photosensor Protein CarH Using Vitamin B12 as a Photosensing Unit

We have studied the structure and function relationships of a novel photosensor protein CarH from *Thermus thermophilus* (*Tt*-CarH). In dark, adenosylcobalamin-bound CarH forms tetramer, which has a DNA binding ability. We have determined crystal structures of a C-terminal domain of *Tt*-CarH and full-length *Tt*-CarH at 2.5 Å and 3.0 Å resolution, respectively. *Tt*-CarH consists of an N-terminal DNA-binding domain and a C-terminal sensor domain. Adenosylcobalamin is bound in a cavity of the sensor domain with base-off form, where cobalt is coordinated by 5’-deoxyadenosine and His177 as axial ligands. The crystal structures suggest that interaction between adeonsyl group and surrounding amino acid residues plays a crucial role in photosensing by CarH.

* IMS International Internship Program

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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

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Education

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1991	Ph.D. The University of Tokyo

Professional Employment

1991	Assistant Professor, The University of Tokyo
1997	Lecturer, The University of Tokyo
2000	Professor, Nagoya City University
2008	Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience 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
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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.

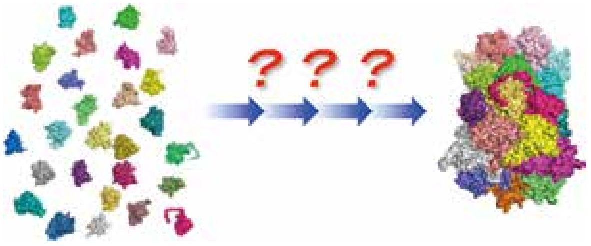

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- M. Yagi-Utsumi, T. Yamaguchi, Y. Uekusa and K. Kato, “NMR Characterization of the Conformations, Dynamics, and Interactions of Glycosphingolipids,” in *NMR in Glycoscience and Glycotechnology*, K. Kato and T. Peters, Eds., RSC Publishing; Cambridge, pp. 161–178 (2017).
- Y. Yamaguchi, H. Yagi and K. Kato, “Stable Isotope Labeling of Glycoproteins for NMR Study,” in *NMR in Glycoscience and Glycotechnology*, K. Kato and T. Peters, Eds., RSC Publishing; Cambridge, pp. 194–207 (2017).
- M. Yagi-Utsumi, T. Yamaguchi, R. Kitahara and K. Kato, “NMR Explorations of Biomolecular Systems with Rapid Conformational Exchanges,” in *Molecular Science of Fluctuations Toward Biological Functions*, M. Terazima, M. Kataoka, R. Ueoka and Y.Okamoto, Eds., Springer; Japan, pp. 87–103 (2016).
- M. Yagi-Utsumi and K. Kato, “Structural and Dynamic Views of GM1 Ganglioside,” *Glycoconjugate J.* **32**, 105–112 (2015).
- T. Satoh, T. Yamaguchi and K. Kato, “Emerging Structural Insights into Glycoprotein Quality Control Coupled with *N*-Glycan Processing in the Endoplasmic Reticulum,” *Molecules* **20**, 2475–2491 (2015).

1. Design and Creation of Neo-Glycomolecules Baced on Knowledge of Conformational Dynamics of Oligosaccharides

Exploration of the conformational spaces of flexible oligosaccharides is essential to gain deeper insights into their functional mechanisms. We characterized dynamic conformation of a high-mannose-type dodecasaccharide with a terminal glucose residue, a critical determinant recognized by molecular chaperones.[1] The dodecasaccharide was prepared by our developed chemoenzymatic technique, which uses ^{13}C labelling and lanthanide tagging to detect conformation-dependent paramagnetic effects by NMR spectroscopy. The NMR-validated molecular dynamics simulation visualized the dynamic conformational ensemble of the dodecasaccharide, thereby delineating the spatial distribution as well as the glycosidic linkage conformation of the terminal glucose determinant. Moreover, comparison of our results with previously reported crystallographic data indicates that the chaperone binding to its target oligosaccharides involves an induced-fit mechanism (Figure 2). Furthermore, our crystallographic data of glucosidase II revealed how the catalytic subunit recruits the regulatory subunit for cooperative recognition of the glucosylated high-mannose-type oligosaccharide, thereby providing structural basis of glycoprotein quality control in the endoplasmic reticulum.[2]

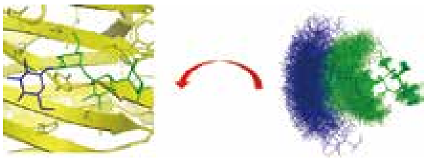

Figure 2. Comparison of our NMR-validated simulation results (right) with the previously reported crystallographic data (left) indicate that the chaperone binding to its target oligosaccharides involves an induced-fit mechanism.

We also attempted to design and develop *cyborg* supramolecular systems having unique molecular recognition properties. We successfully created a self-assembled, Lewis X-expressing glycocluster by hybridizing a spherical metal–organic complex with a synthetic oligosaccharide derivative.[3] The self-assembled glycoclusters exhibited homophilic hyper-assembly in aqueous solution in a Ca^{2+}-dependent manner through specific carbohydrate–carbohydrate interactions, offering a unique structural scaffold for functional biomimetic systems (Figure 3).

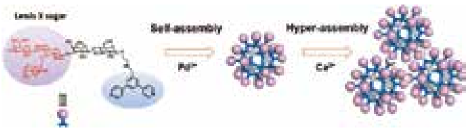

Figure 3. Ca^{2+}-dependent hyper-assembly of self-assembled glycoclusters mediated by specific carbohydrate–carbohydrate interactions.

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

Here we summarize our recent findings obtained by employing integrative biochemical and biophysical approaches for structural characterization of various biomolecular systems that involve proteins, including NMR spectroscopy, X-ray crystallography, solution scattering, and mass spectrometry (MS).

We determined a crystal structure of the human proteasome assembling chaperone PAC4 and characterized the interaction with its binding partner PAC3.[4] Furthermore, we applied native MS and small-angle neutron scattering data to structural characterization of the circadian clock protein complex.[5] Moreover, we successfully addressed the functional roles of the enzymes related to dystroglycanopathy, which is a major class of congenital muscular dystrophy caused by a deficiency of functional glycans on α-dystroglycan (αDG) with laminin-binding activity. By employing nanoLC-MS/MS analytical workflow in conjunction with a panel of mutated cells deficient in one of these enzymes, we revealed additional modifications on phosphorylated *O*-glycans of αDG, suggesting functional interplay among these enzymes through their interactions.[6]

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2) T. Satoh, T. Toshimori, M. Noda, S. Uchiyama and K. Kato, *Protein Sci.* **25**, 2095–2101 (2016).

3) G. Yan, T. Yamaguchi, T. Suzuki, S. Yanaka, S. Sato, M. Fujita and K. Kato, *Chem. –Asian J.* **12**, 968–972 (2017).

4) E. Kurimoto, T. Satoh, Y. Ito, E. Ishihara, K. Okamoto, M. Yagi-Utsumi, K. Tanaka and K. Kato, *Protein Sci.* **26**, 1080–1085 (2017).

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Awards

YOGO, Rina; The Best Poster Award, OIIB retreat (2016).

YUNOKI, Yasuhiro; The Young Scientist Award, The 4th Joint Nagoya Meeting: Future perspectives on structural/functional analyses and molecular design of biomolecules (2016).

YOGO, Rina; Poster Award, The 81st Annual Meeting of Chubu Branch, the Japanese Biochemical Society (2017).

YUNOKI, Yasuhiro; Poster Award, The 81st Annual Meeting of Chubu Branch, the Japanese Biochemical Society (2017).

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Operation and Design Principles of Biological Molecular Machines

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Professional Employment
2000 Research Associate, Japan Science and Technology Cooperation
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2005 Specially-Appointed Assistant Professor, Osaka University
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2013 Associate Professor, The University of Tokyo
2014 Professor, Institute for Molecular Science
Professor, Okazaki Institute for Integrative Bioscience
Professor, The Graduate University for Advanced Studies

Award
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Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

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

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

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

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

Selected Publications

- H. Isojima, R. Iino, Y. Niitani, H. Noji and M. Tomishige, “Direct Observation of Intermediate States during the Stepping Motion of Kinesin-1,” *Nat. Chem. Biol.* **12**, 290–297 (2016).
- A. Nakamura, T. Tasaki, D. Ishiwata, M. Yamamoto, Y. Okuni, A. Visootsat, M. Maximilien, H. Noji, T. Uchiyama, M. Samejima, K. Igarashi and R. Iino, “Direct Imaging of Binding, Dissociation, and Processive Movement of *Trichoderma reesei* Cel6A and Its Domains on Crystalline Cellulose,” *J. Biol. Chem.* **291**, 22404–22413 (2016).
- H. Ueno, Y. Minagawa, M. Hara, S. Rahman, I. Yamato, E. Muneyuki, H. Noji, T. Murata and R. Iino, “Torque Generation of *Enterococcus hirae* V-ATPase,” *J. Biol. Chem.* **289**, 31212–31223 (2014).
- 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).
- 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. One Nanometer Steps and Rate-Limiting Step of *Serratia marcescens* Chitinase A Resolved by Gold Nanoprobe[1)]

Serratia marcescens chitinase A (*Sm*ChiA) is a monomeric linear molecular motor moving on and hydrolyzing crystalline chitin processively. We have directly resolved steps and pauses in the motion of *Sm*ChiA with high-resolution single-molecule imaging analysis with gold nanoparticle. By using total internal reflection dark-field microscopy and 40-nm gold nanoparticle as a low-load probe, movement of *Sm*ChiA was observed at 1,000–2,000 frames/s with 0.3 nm localization precision (Figure 2). The step sizes were 1.1 nm and –1.2 nm for forward and backward steps (Figure 3), respectively, consistent with the length of the product, chitobiose (~1 nm). The ratio of forward to backward steps was 5.5, corresponding to the energy difference of 1.7 k_BT. Frequent backward steps and low energy difference indicate that *Sm*ChiA operates as the Brownian ratchet. Furthermore, detailed analysis of the distribution of pause duration revealed that the rate-limiting step of chemo-mechanical coupling of *Sm*ChiA is the decrystallization of single polymer chain from the crystalline chitin, not bond cleavage and product release. These results give us important insights to engineer non-natural chitinases which show better performances than the natural ones.

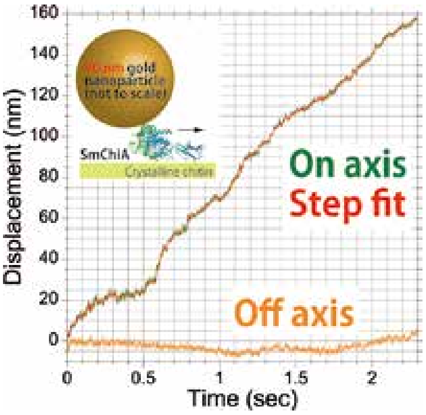

Figure 2. Example of stepping movement of *Sm*ChiA.

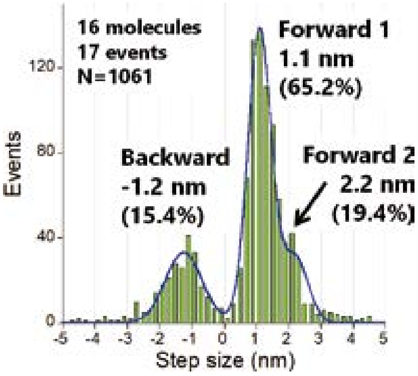

Figure 3. Distribution of step size of *Sm*ChiA.

2. Chemo-Mechanical Coupling Scheme of Rotary Molecular Motor *Enterococcus hirae* V_1-ATPase[2)]

A rotary molecular motor V-ATPase (Figure 4, left) is an ion pump driven by ATP hydrolysis. To understand the chemo-mechanical energy conversion mechanism, we conducted single-molecule analysis of V_1 moiety of *Enterococcus hirae* V-ATPase (Figure 4, right). We found that 120° steps (3 pausing positions per turn) reflecting the coordinations among three catalytic sites of V_1 were further divided into 40° and 80° substeps. At low ATP concentration ([ATP]), pause duration before 40° substep was dependent on [ATP], indicating that ATP binding triggers 40° substeps. On the other hand, at high [ATP], two time constants (both ~1 ms) independent on [ATP] were obtained. When slowly hydrolyzing ATPγS was used as a substrate, the pause before 40° step became longer (140 ms), indicating that cleavage of phosphate bond of ATP occurs during this pause. Time constant (2.5 ms) of pause duration before 80° step was also [ATP] independent. In the presence of ATPγS and high concentration of ADP, 80° backward steps were frequently observed, indicating that ADP binding triggers 80° forward step. From these results and rotation behavior of an arginine finger mutant, we proposed a model of chemo-mechanical coupling scheme of V_1 (Figure 5).

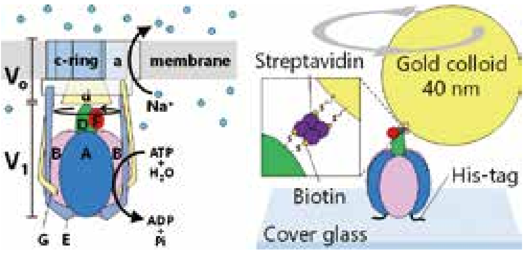

Figure 4. V-ATPase (left) and single-molecule rotation assay of V_1 (right).

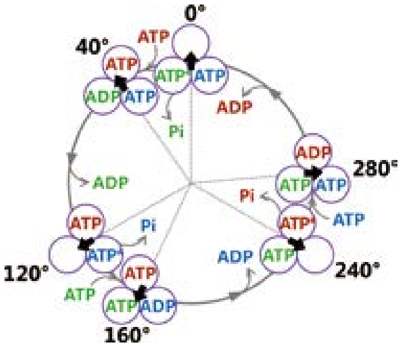

Figure 5. Chemo-mechanical coupling scheme of V_1.

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1) A. Nakamura and R. Iino, in preparation.
2) T. Iida, Y. Minagawa, H. Ueno, F. Kawai, T. Murata and R. Iino, in preparation.

A Supramolecular Chemical Approach to the Construction of Artificial Cells

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Professional Employment

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Keywords Artificial Cell, Origin of Life, Vesicle

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

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

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

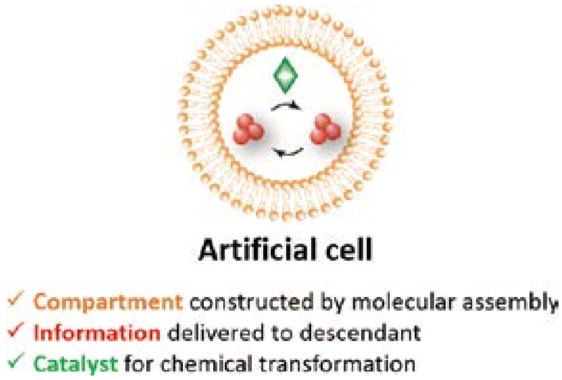

Figure 1. Artificial cell model. The replicating systems of the compartment and the information materials are combined. The reactions in the two replicating systems are accelerated by appropriate catalysts.

Selected Publications

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

1. An Artificial Cell Containing a Catalyst-Producing System

A cell is a self-organized system that can maintain its state via metabolism. Our previously developed artificial cellular system is robust, but it can self-reproduce only a specific state in the any environments.[1–3]

Here, our goal was to create a new artificial cellular system in which the GV self-organizes its composition spontaneously according to its environment. For a GV to self-reproduce (grow and divide spontaneously) and self-maintain, it is necessary to combine the metabolism and the compartment.[4] By introducing a cross-catalysis system (Figure 2), we constructed an artificial cell in which catalysts are produced. After addition of a membrane precursor aldehyde, the production of the catalyst and the membrane molecule was confirmed by nuclear magnetic resonance (NMR) and microscopic observation. In this system, the GV was reproduced by the catalyst, which catalyzed the production of the GV membrane lipid molecule. The GV membrane provides the field where the catalyst is synthesized.

In addition, by changing the composition of the vesicular membrane, the production of the catalyst and that of the membrane molecule fluctuated due to the components interacting each other; in effect, the artificial cell incorporated a negative feedback loop.

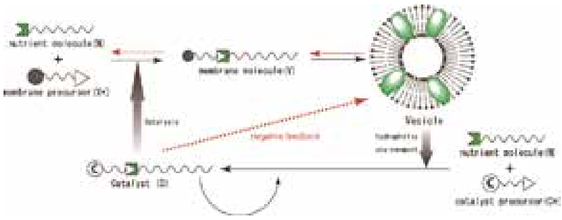

Figure 2. Scheme of our new artificial cellular system. The membrane molecules of the GV was synthesized by the catalyst produced in the GV.

We are also studying the oscillation in generation of membrane molecule and catalyst occurred by depletion of nutrient molecules.

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

Research on transforming oil droplets into vesicles by use of chemical reactions and self-assembly processes is expected to facilitate our understanding of the origin and definition of life from a chemistry perspective.

The mixing of an aqueous solution of an aldehyde containing an imidazole hydrochloride group with octylaniline led to the spontaneous formation of autocatalytic oil droplets[5] (Figure 3). An aldehyde-bearing quaternary ammonium salt that does not react well with octylaniline was added to this autocatalytic droplet system. As a result, the catalytic molecules that formed within the oil droplets promoted the condensation reaction between the octylaniline and the non-catalytic aldehyde, which ultimately led to the synthesis of vesicular membrane molecules with imine functionality within the molecular aggregates; thus self-reproducible oil droplets were successfully transformed into vesicles upon the addition of the membrane precursor.

In this way, we created a protocell model that can construct boundaries by using this new process that relies on the formation of robust vesicles through the use of an existing autocatalytic, self-reproducing oil drop system as a scaffold.

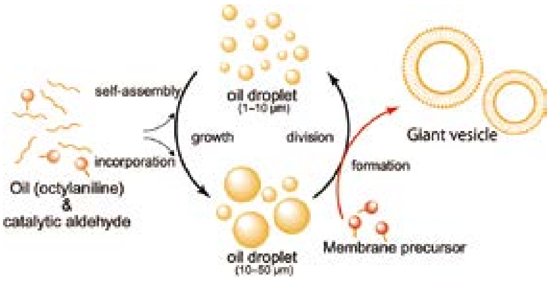

Figure 3. Scheme of the self-reproducing oil droplet (oil-in-water emulsion) and vesicular transformation system.

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

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1) K. Kurihara, M. Tamura, K-I. Shohda, T. Toyota, K. Suzuki and T. Sugawara, *Nat. Chem.* **3**, 775–781 (2011).
2) K. Kurihara, Y. Okura, M. Matsuo, T. Toyota, K. Suzuki and T. Sugawara, *Nat. Commun.* **6**, 8352 (2015).
3) L. Sheng and K. Kurihara, *Chem. Lett.* **45**, 598–600 (2016).
4) L. Sheng and K. Kurihara, *Chem. Commun.* **52**, 7786–7789 (2016).
5) Y. Natsume, H. Wen, T. Zhu, K. Itoh, L. Sheng and K. Kurihara, *J. Vis. Exp.* **119**, e55282 (2017).

Investigation of Molecular Mechanisms of Channels, Transporters and Receptors

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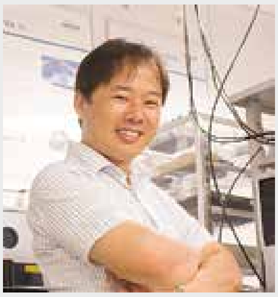

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Education

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2004	Ph.D. Kyoto University

Professional Employment

2003	JSPS Research Fellow
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2011	JST-PRESTO Researcher (concurrent post) (–2015)

Awards

2012	Morino Foundation for Molecular Science
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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.

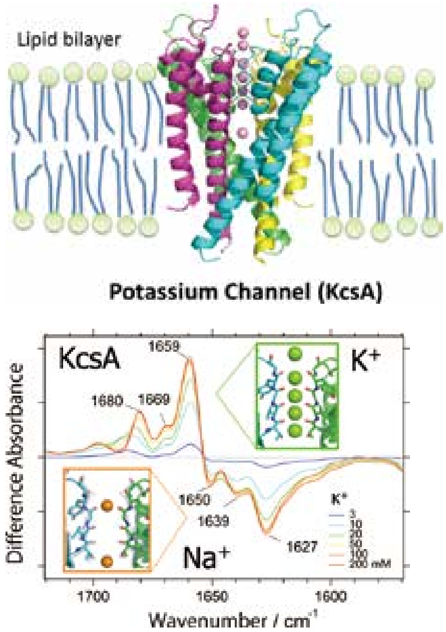

Figure 1. (top) X-ray crystal structure of a potassium ion channel, KcsA. (bottom) The ion-exchange induced difference infrared spectra of KcsA with different potassium ion concentration. The amide I bands are mainly originated from the carbonyl groups of the selectivity filter of KcsA.

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. Nucleotide Base Specificity of P2X Receptors[1]

P2X receptors are cation channels activated by adenosine-5'-triphosphate (ATP), which is a well-known biomolecule utilized for various biological activities. The ATP-gated cation channels sense extracellular ATP concentration and function for muscle contraction, taste signal transduction, nociception and so on. Three monomers form a trimeric structure and three nucleotide binding sites exist in the interfaces between two nearby monomers (Figure 2a).

X-ray crystal structure of P2X associated with cytidine-5'-triphosphate (CTP) was resolved (Figure 2a; the right bottom) and its functionality and nucleotide base specificity was examined by applying electrophysiological and spectroscopic measurements.

As shown in Figure 2b, ATP was tightly bound to WT and most of the bound ATP retained after 15–30 min wash. T189S, which loses a methyl group in the side chain, exhibited similar affinity for ATP, while T189V, which loses a hydroxyl group in the side chain, exhibited very low affinity for ATP. Therefore, the hydroxyl group in the side chain of T189 is very important for the ATP binding to P2X, which is consistent with the X-ray crystal structure (Figure 2a; the right top) showing that the hydroxyl group is located in hydrogen-bonding distance from the adenine ring of ATP. On the other hand, WT exhibited relatively higher affinity for CTP than T189S and T189V mutants, while both mutants exhibited similar affinity for CTP. Therefore, the hydroxyl group of T189 is not so important for the CTP binding to P2X, which is also supported by the X-ray crystal structure (Figure 2a; the right bottom).

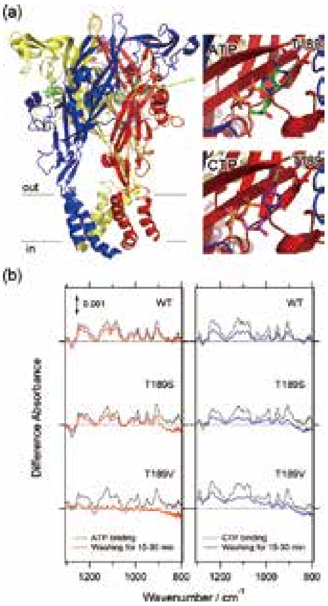

Figure 2. (a) X-ray crystal structure of P2X with ATP or CTP molecules. A nucleotide binding site is expanded in the right panel. The dotted lines indicate that the atoms of Thr189 and the nucleotides exist in hydrogen-bonding distance. (b) Ligand-binding-induced difference IR spectra of P2X measured for WT, T189S and T189V mutants with ATP or CTP.

2. UV-Sensing Protein in the Brain of a Marine Zooplankton[2]

Most of animals show some circadian (daily) behaviors. On the earth, two large-scale daily movements of biomass are known. One is human commuting and the other is daily vertical migration of zooplanktons. Zooplanktons move downward in water during daytime and upward at night, in order to avoid predators and UV damage from sunlight. Thus, it is important to understand how zooplankton species sense ambient UV signals.

Larva of the marine ragworm (*Platynereis dumerilii*) has been studied as a zooplankton model, and the larvae possess photoreceptor cells in the brain to control circadian swimming behavior. The brain photoreceptor cells express an opsin (named as c-opsin) that is closely related to visual pigments in our eyes. We expected that *Platynereis* c-opsin is involved in UV detection, and assessed spectral and biochemical properties of the opsin.

We purified the c-opsin protein that was expressed in mammalian cultured cells. The purified opsin showed an absorption maximum at 383-nm in the UV region (Figure 3a). Also, *Xenopus* oocytes expressing the opsin showed electrophysiological responses upon UV irradiation (Figure 3b). These results clearly indicate that the c-opsin is a UV-sensitive pigment. Mutagenesis analyses identified that a single amino acid residue is responsible for UV sensing. Thus, the single residue is essential for the opsin to achieve the ability to receive UV signals. Taken together, the c-opsin would enable the brain of *Platynereis* to sense ambient UV signals.

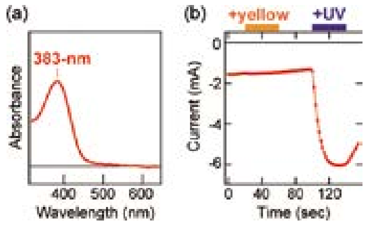

Figure 3. UV sensing ability of *Platynereis* c-opsin.
(a) Absorption spectrum of purified *Platynereis* c-opsin. (b) Photoresponses of a *Xenopus* oocyte expressing *Platynereis* c-opsin with a potassium channel GIRK1/GIRK2.

References

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2) H. Tsukamoto, I.-S. Chen, Y. Kubo and Y. Furutani, *J. Biol. Chem.* **292**, 12971–12980 (2017).

Award

FURUTANI, Yuji; The 3rd Biophysics and Physicobiology Editors' Choice Award (2016).

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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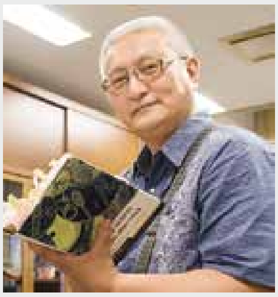
Division of Complex Catalysis



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

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

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  - HAMASAKA, Go
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  - PAN, Shiguang
- Post-Doctoral Fellow
  - NAGAOSA, Makoto
  - ROY, David
  - HIRATA, Shuichi
  - PUTRA, Anggi Eka
  - YAN, Shuo
  - KIM, Kiseong
- Graduate Student
  - ICHII, Shun
  - SHEN, Guanshuo
  - NIIMI, Ryoko
  - KAISER, Reinhard*
- Technical Fellow
  - TORII, Kaoru
  - TAZAWA, Aya
  - TSUCHIMOTO, Tatsushi
- Secretary
  - SASAKI, Tokiyo
  - HAZAMA, Kozue
  - TANIWAKE, Mayuko

Keywords Transition Metal Catalysis, Green Chemistry, Organic Synthesis

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

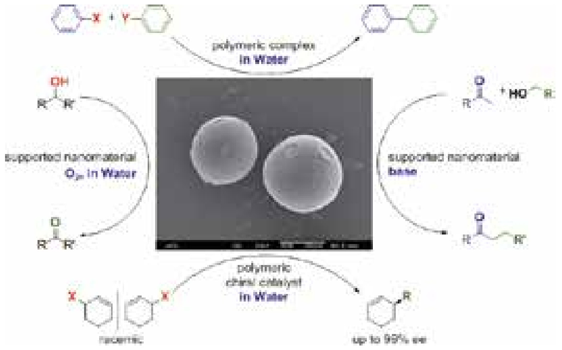

Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

Selected Publications

- 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).
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1. The Development of a Vesicular Self-Assembled Amphiphilic Platinum NCN-Pincer Complex and Its Catalytic Application to Hydrosilylation of Alkenes in Water[1)]

An amphiphilic platinum NCN-pincer complex bearing hydrophilic tri(ethylene glycol) and hydrophobic dodecyl chains was designed and synthesized for use as a new aqua-catalytic system. The complex self-assembled in aqueous medium to form bilayer vesicles that catalyzed the hydrosilylation of alkenes by dimethyl(phenyl)silane in water to give the hydrosilylated products in good yields. In contrast, the complex in its amorphous form did not promote the reaction efficiently, and thus, the formation of a vesicular structure was essential to promote the reaction.

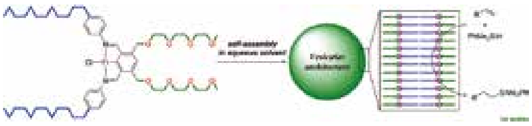

Figure 2. Hydrosilylation of styrene with dimethyl(phenyl)silane in water in the presence of a self-assembled vesicular amphiphilic platinum NCN-pincer complex.

2. Detailed Structural Analysis of a Self-Assembled Vesicular Amphiphilic NCN-Pincer Palladium Complex by Using Wide-Angle X-Ray Scattering and Molecular Dynamics Calculations[2)]

Wide-angle X-ray scattering experiments and all-atomistic molecular dynamics calculations were performed to elucidate the detailed structure of bilayer vesicles constructed by self-assembly of an amphiphilic palladium NCN-pincer complex. We found an excellent agreement between the experimental and calculated X-ray spectra and between the membrane thickness determined from a TEM image and that calculated from an electron-density profile, indicating that the calculated structure was highly reliable. The analysis of the simulated bilayer structure showed that the bilayer membrane could act as a nanoreactor. The self-assembled vesicles were shown to be catalytically active in a Miyaura–Michael reaction in water.

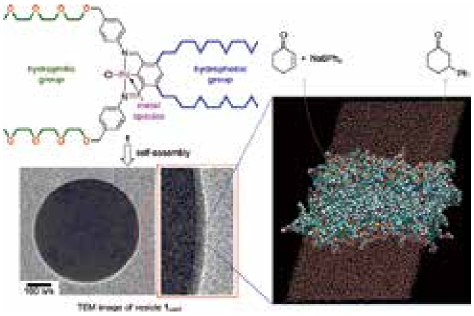

Figure 3. A self-assembled vesicular palladium NCN-pincer complex.

3. Palladium-Catalyzed Asymmetric Suzuki–Miyaura Cross Coupling with Homochiral Phosphine Ligands Having Tetrahydro-1*H*-imidazo[1,5-*a*]indole Backbone[3)]

Amphiphilic polystyrene-poly(ethylene glycol) resin-supported chiral imidazoindole phosphines (PS-PEG-L*) bearing PPh_2, P(*t*-Bu)$_2$, and P(*c*-Hex)$_2$ groups were designed and prepared with a view toward using them in aqueous heterogeneous asymmetric Suzuki–Miyaura biaryl coupling. The asymmetric coupling of 2-substituted 1-iodonaphthalenes and 2-substituted naphthalen-1-ylboronic acid took place in water under heterogeneous conditions in the presence of 10 mol% palladium of PS-PEG-L*-Pd complexes to give up to 94% ee of (*S*)-2,2'-disubstituted 1,1'-binaphthyls.

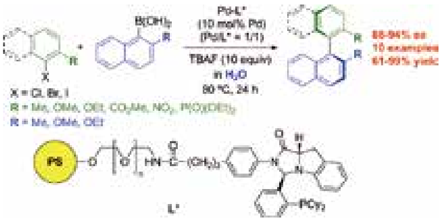

Figure 4. Palladium-catalyzed asymmetric biaryl coupling in water with a PS-PEG resin-supported imidazoindolephosphine.

4. Huisgen Cycloaddition with Acetylene Gas by Using an Amphiphilic Self-Assembled Polymeric Copper Catalyst[4)]

A copper-mediated Huisgen cycloaddition of flammable acetylene gas and a variety of organic azides proceeded smoothly by using our amphiphilic self-assembled polymeric copper catalyst MPPI-Cu to give the corresponding triazoles in high yield. MPPI-Cu was readily reused without loss of catalytic activity.

Figure 5. Huisgen cycloaddition of azides and acetylene in the presence of self-assembled polymeric copper catalyst.

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* carrying out graduate research on Cooperative Education Program of IMS with Charles University in Prague

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Keywords Organic Synthesis, Molecular Catalyst, Non-Covalent Interaction

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

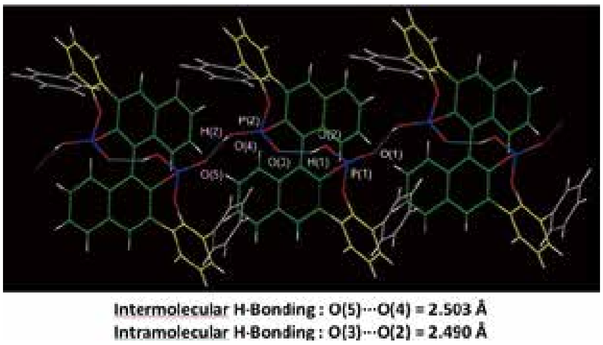

Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

Selected Publications

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

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

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

2. Design of Chiral Brønsted Acid Catalyst

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

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

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

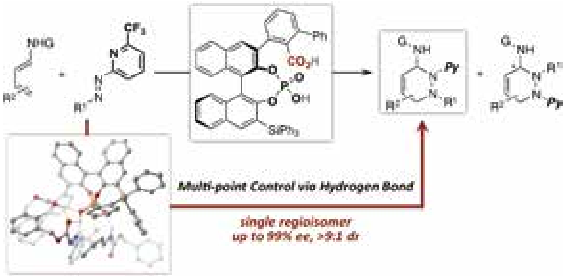

Figure 2. Chiral carboxylic acid–phosphoric acid-catalyzed azo-hetero-Diels–Alder reaction.

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

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

We found that pentafluoroiodebenzene was able to catalyze the allylation reaction of isoquinolines, quinolones, and pyridines with allylsilatrane, crotylsilatrane, and prenyl silatrane to give the corresponding product in good yield.[8)]

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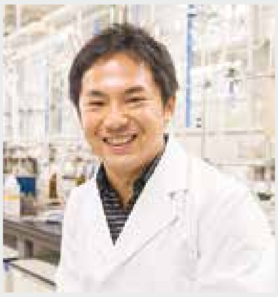
8) N. Momiyama *et al.*, under revision for resubmission.

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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Professional Employment

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2017	The 13th (FY 2016) JSPS Prize

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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.

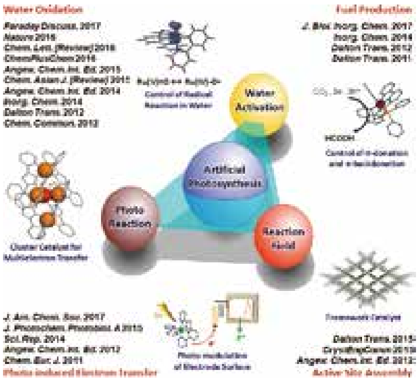

Figure 1. An overview of our work.

Selected Publications

- M. Yoshida, M. Kondo, M. Okamura, M. Kanaike, S. Haesuwannakij, H. Sakurai and S. Masaoka, "Fe, Ru, and Os Complexes with the Same Molecular Framework: Comparison of Structures, Properties and Catalytic Activities," *Faraday Discuss.* **198**, 181–196 (2017).
- V. K. K. Praneeth, M. Kondo, P.-M. Woi, M. Okamura and S. Masaoka, "Electrocatalytic Water Oxidation by a Tetranuclear Copper Complex," *ChemPlusChem* **81**, 1123–1128 (2016).
- M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S. Hayami, V. K. K. Praneeth, M. Yoshida, K. Yoneda, S. Kawata and S. Masaoka, "A Pentanuclear Iron Catalyst Designed for Water Oxidation," *Nature* **530**, 465–468 (2016).
- M. Yoshida, M. Kondo, S. Torii, K. Sakai and S. Masaoka, "Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant -SO_3^- Groups," *Angew. Chem., Int. Ed.* **54**, 7981–7984 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Fe, Ru, and Os Complexes with the Same Molecular Framework: Comparison of Structures, Properties and Catalytic Activities$^{1)}$

Water oxidation ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is a key reaction in energy conversion in natural and artificial photosynthesis. The development of artificial water oxidation catalysts (WOCs) has attracted growing interest in recent years due to the urgent need to solve the world's energy problems. Metal complexes containing group 8 metal centres (Fe, Ru, or Os) and water coordination sites can be regarded as the most attractive candidates for molecular WOCs, because such metal-aqua species can generate high-valent metal-oxo species, which are the key intermediates triggering the formation of the O–O bond, via stepwise electron removal involving concomitant proton loss.

In this study, we present the syntheses, crystal structures, spectroscopic and electrochemical properties, and water oxidation activities of a series of Fe(II), Ru(II), and Os(II) complexes bearing a pentadentate ligand and a monodentate ligand. The nature of the metal ions are extracted and discussed by comparing the difference of the structure, properties and reactivities among a series of group 8 metal complexes with the same molecular framework. The results will provide new insight into the design and development of group 8 metal-based molecular catalysts for water oxidation.

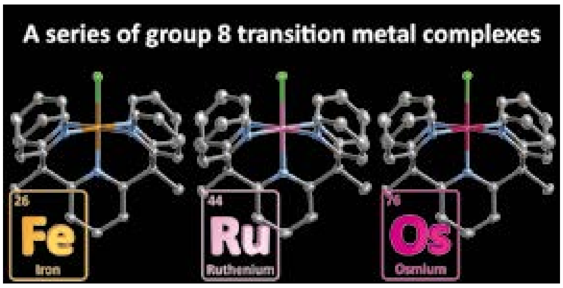

Figure 2. Crystal structures of the Fe, Ru, and Os Complexes.

2. Electrocatalytic Water Oxidation by a Tetranuclear Copper Complex$^{2)}$

Cu-based WOCs have attracted much interest among researchers due to the low cost and biological relevance of Cu.$^{3)}$ One of the most attractive targets in this field of research can be considered to be discrete multinuclear Cu complexes due to their homogeneity and multinuclearity. However, there are only a few reports on water oxidation catalysis by discrete multinuclear Cu complexes.

In this study, a novel tetranuclear copper-based water oxidation catalyst was designed and synthesized by using a new multinucleating ligand containing two proton dissociation sites, 1,3-bis(6-hydroxy-2-pyridyl)-1*H*-pyrazole. The copper complex showed electrocatalytic activity for water oxidation reactions under aqueous basic conditions (pH 12.5) with an overpotential of approximately 500 mV. UV/Vis absorption and energy-dispersive X-ray (EDX) spectroscopic techniques coupled with electrochemical analyses of the catalyst system strongly suggest that the tetranuclear copper complex works as a homogeneous system under the conditions used. The results demonstrate the utility of a discrete tetranuclear copper complex in water oxidation reactions.

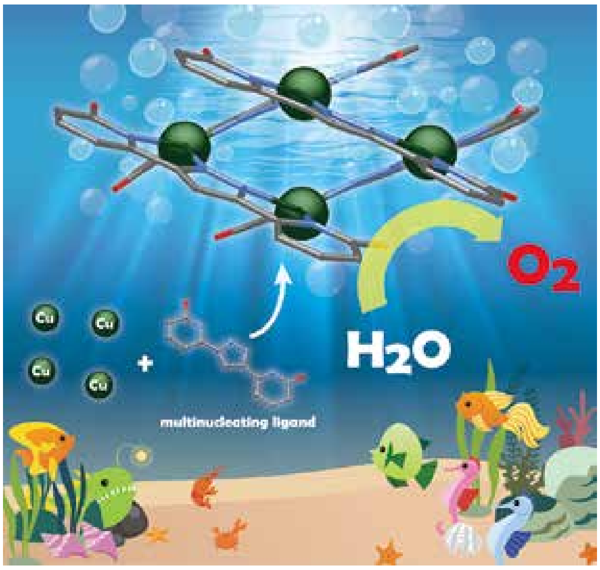

Figure 3. Water oxidation by the tetranuclear copper complex.

References

1) M. Yoshida, M. Kondo, M. Okamura, M. Kanaike, S. Haesuwannakij, H. Sakurai and S. Masaoka, *Faraday Discuss.* **198**, 181–196 (2017).

2) V. K. K. Praneeth, M. Kondo, P.-M. Woi, M. Okamura and S. Masaoka, *ChemPlusChem* **81**, 1123–1128 (2016).

3) M. Kondo and S. Masaoka, *Chem. Lett. [Highlight Review]* **45**, 1220–1231 (2016).

Awards

MASAOKA, Shigeyuki; The 13th (FY 2016) JSPS Prize (2017).
KONDO, Mio; Morita Science Research Award (2017).
CHINAPANG, Pondchanok; Excellent Poster Award, International Conference on Artificial Photosynthesis (2017).
IZU, Hitoshi; Excellent Poster Award, International Conference on Artificial Photosynthesis (2017).
ENOMOTO, Takafumi; Poster Award, 6th CSJ Chemistry Festa (2016).
OKAMURA, Masaya; KONDO, Mio; MASAOKA, Shigeyuki; Special Prize of the Nature Industry Award (2016).
ENOMOTO, Takafumi; Poster Prize, the 66th JSCC Symposium (2016).
ENOMOTO, Takafumi; Dalton Transactions Award (2016).

Control of Electron Transfer for Efficient Oxygenation Reactions

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Assistant Professor

Electron transfer is the most fundamental reaction to govern chemical reactions. To find an effective way to control electron transfer, electronic structures of key active species were investigated in detail with various techniques including absorption, ^{1}H and ^{2}H NMR, EPR, IR resonance Raman spectroscopy and magnetic susceptibility measurements. Correlations between electronic structures and electron transfer ability are the main focus.

1. Design and Synthesis of Photoactive Salen-Type Ligands

Salen-type ligands are well known as the most versatile framework for catalysts, because of the simple structure that is suitable for large-scale preparations and chemical modifications. The present study investigated a new method to incorporate excellent photochemical properties without sacrificing structural advantages of salen-type ligands.

The key concept is tautomerization of a salicylidene ring of a salen-type ligand, which converts a phenolate structure to a quinoidal structure. The resulting quinoidal salen-type ligand is expected to show better photochemical properties, because quinones having a quinoidal structure are excellent photocatalysts.

To compare photochemical properties of salen-type ligands in a quantitative manner, fluorescence properties of salen-type ligands with redox-inactive zinc(II) ion were investigated. One of the achievements is a finding that the steric bulk of a substituent on salicylidene rings in addition to the molecular space around the diamine moiety plays a critical role for high fluorescence emission efficiency. Another point is an electron-donating or electron-withdrawing substituent on salicylidene rings, which systematically alters an absorption/fluorescence wavelength.

Visiting Professors

Visiting Professor

OGOSHI, Sensuke *(from Osaka University)*

Transformation of Tetrafluoroethylene via Oxycupration

Organofluorine compounds have attracted much attention, mostly on account of their applications in a variety of research areas, including pharmaceutical, agrochemical, and materials science, and consequently substantial efforts have been devoted to the development of novel strategies for the construction of fluorinated organic compounds. Among these, fluoroalkyl ethers such as Ar–OCF_2CF_2–Ar' (Ar/Ar' = aryl) have garnered special attention, as they represent key structures in insecticides and lubricants. In addition, this structural motif is fascinating with respect to perfluoroalkoxylation of aromatic compounds. Most of practical approaches to the construction of Ar–OCF_2CF_2–Ar' moieties have to use the fluorinated starting materials that have very high greenhouse gas effect. Under these circumstances, we have to develop new reactions to allow us to produce those chemicals without using such starting materials. We have been focusing on the synthesis of a variety of fluorinated compounds by using tetrafluoroethylene (TFE) of which greenhouse gas effect is almost zero. So far, we have reported the transformation of TFE by Palladium catalyzed coupling reaction with aryl metals (Zn, B, Si) to give α,β,β-trifluorostyrene and nickel-catalyzed co-trimerization with ethylene and aldehyde. Although the introduction of both oxygen and carbon into TFE is the one of the most difficult reactions, the oxycupration of TFE allows us to the construction of Ar–OCF_2CF_2–Ar' moieties.

Visiting Associate Professor

SHOJI, Osami *(from Nagoya University)*

Gaseous Alkane and Benzene Hydroxylation Catalyzed by Cytochrome P450BM3 with the Assistance of Decoy Molecules

Cytochrome P450BM3 (P450BM3) is one of the most promising P450s for construction of biocatalysts because of its high monooxygenase activity. Because the substrate binding is crucial for the generation of active species of P450BM3 (Compound I), substrates whose structures are largely different from that of its native substrates (long-alkyl-chain fatty acids) cannot be hydroxylated by P450BM3. However, we found that P450BM3 starts to catalyze hydroxylation of nonnative substrates in the presence of perfluorinated carboxylic acids (PFCs) as inert dummy substrates (decoy molecules). Recently, we have succeeded in developing the next generation of decoy molecules by modifying the carboxylate of PFCs with amino acids and succeeded in enhancing the catalytic activity for gaseous alkanes. Furthermore, we have succeeded in crystallizing the *N*-perfluorononanoyl-*L*-tryptophan (PFC9-*L*-Trp)-bound form of P450BM3. The crystal structure analysis of PFC9-*L*-Trp-bound form of P450BM3 showed that the terminal of alkyl chain does not reach to the active site owing to the multiple hydrogen bonding interactions between the carboxyl and carbonyl groups of PFC9-*L*-Trp and amino acids located at the entrance of P450BM3. More recently, we have demonstrated that various carboxylic acids modified with amino acids (*N*-acyl amino acids) as well as amino acid dimers having a completely different structure from fatty acids can serve as decoy molecules. Benzene was more efficiently hydroxylated in the presence of these decoy molecules. Furthermore, we have succeeded in controlling the enantioselectivity of benzylic hydroxylation using these decoy molecules.

Visiting Associate Professor

TOSHA, Takehiko *(from RIKEN SPring-8 Center)*

Elucidation of Mechanism for Effective Chemical Reactions by Supracomplex Formation

Nitric Oxide (NO) plays diverse and significant roles in biological processes such as signal transduction, vasodilation and memory consolidation, despite its high cytotoxicity, raising the essential question of how biological systems control the action of NO to minimize its cytotoxic effect in cells. To answer this, we focus on microbial denitrification in which cytotoxic NO is produced as an intermediate product. However, denitrifying bacteria can grow without any damage from NO, suggesting that there is a system for effective NO elimination. As a possible system, we found from X-ray crystallography, mutagenesis and molecular dynamics simulation that NO-generating nitrite reductase (NiR) forms a complex with NO-decomposing nitric oxide reductase (NOR) to suppress the diffusion of NO. To further elucidate how the proteins involved in denitrification effectively catalyze the consecutive chemical reactions, we explore the possibility of their supracomplex formation using cryo-electron microscopic technique.

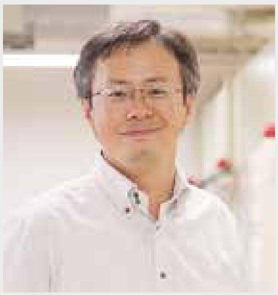
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

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

The Origin of 24 Hour Period in Cyanobacterial Clock System

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



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Education

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Professional Employment

2001	JSPS Research Fellow
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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

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

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Keywords Circadian Clock, Clock Proteins, Cyanobacteria

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

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

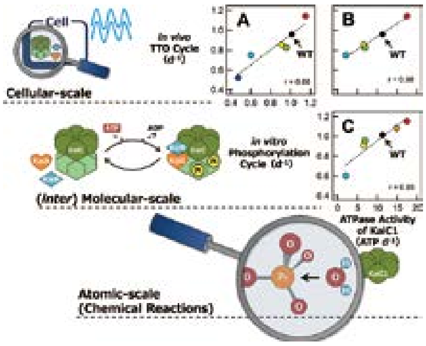

Figure 1. *Trans*-hierarchic nature of the circadian clock system in cyanobacteria. Cross-correlational plots (A–C) among frequency of *in vivo* transcription and translation oscillation (TTO) cycle, frequency of *in vitro* phosphorylation cycle, and ATPase activity of KaiC for cyanobacteria carrying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

Selected Publications

- Y. Furuike, J. Abe, A. Mukaiyama and S. Akiyama, *Biophys. Physicobiol.* **13**, 235–241 (2016).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, *Cell. Mol. Life Sci.* **69**, 2147–2160 (2012).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

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

In accordance with diurnal changes in the environment resulting from the Earth's daily rotation around its axis, many organisms regulate their biological activities to ensure optimal fitness and efficiency. The biological clock refers to the mechanism whereby organisms adjust the timing of their biological activities. The period of this clock is set to approximately 24 h. A wide range of studies have investigated the biological clock in organisms ranging from bacteria to mammals. Consequently, the relationship between the biological clock and multiple diseases has been clarified. However, it remains unclear how circadian rhythms are implemented.

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

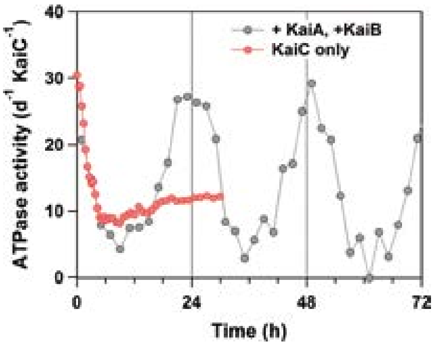

Figure 2. Time-course of KaiC ATPase activity.

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

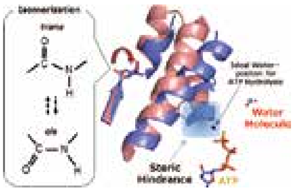

Figure 3. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

The fact that a water molecule, ATP, the polypeptide chain, and other universal biological components are involved in this regulation suggests that humans and other complex organisms may also share a similar molecular machinery.

2. Instrumentation for Studying Biological Clock Systems[2)]

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

3. Bio-SAXS Activity in IMS[3–5)]

We have supported SAXS users so that they can complete experiments smoothly and publish their results.[3–5)]

4. Other Activities

We have conducted joint research projects in collaboration with other universities and research facilities.

References

1) J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
2) Y. Furuike, J. Abe, A. Mukaiyama and S. Akiyama, *Biophys. Physicobiol.* **13**, 235–241 (2016).
3) S. Kanemura, M. Okumura, K. Yutani, T. Ramming, T. Hikima, C. Appenzeller-Herzog, S. Akiyama and K. Inaba K, *J. Biol. Chem.* **291**, 23952–23964 (2016).
4) I. Anzai, E. Tokuda, A. Mukaiyama, S. Akiyama, F. Endo, K. Yamanaka, H. Misawa and Y. Furukawa, *Protein Sci.* **26**, 484–496 (2017).
5) N. Nuemket, N. Yasui, Y. Kusakabe, Y. Nomura, N. Atsumi, S. Akiyama, E. Nango, Y. Kato, M. K. Kaneko, J. Takagi, M. Hosotani and A. Yamashita, *Nat. Commun.* **8**, 15530 (2017).

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* IMS International Internship Program

Protein Design Using Computational and Experimental Approaches

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Professional Employment

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2007	JSPS Postdoctoral Fellow for Research Abroad
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2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
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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

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

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

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

Selected Publications

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

1. Principles for Designing Ideal Protein Structures

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

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

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

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

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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.

4) Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).

5) Y.-R. Lin, N. Koga, S. M. Vorobiev and D. Baker*, *Protein Sci.* **26**, 2187–2194 (2017).

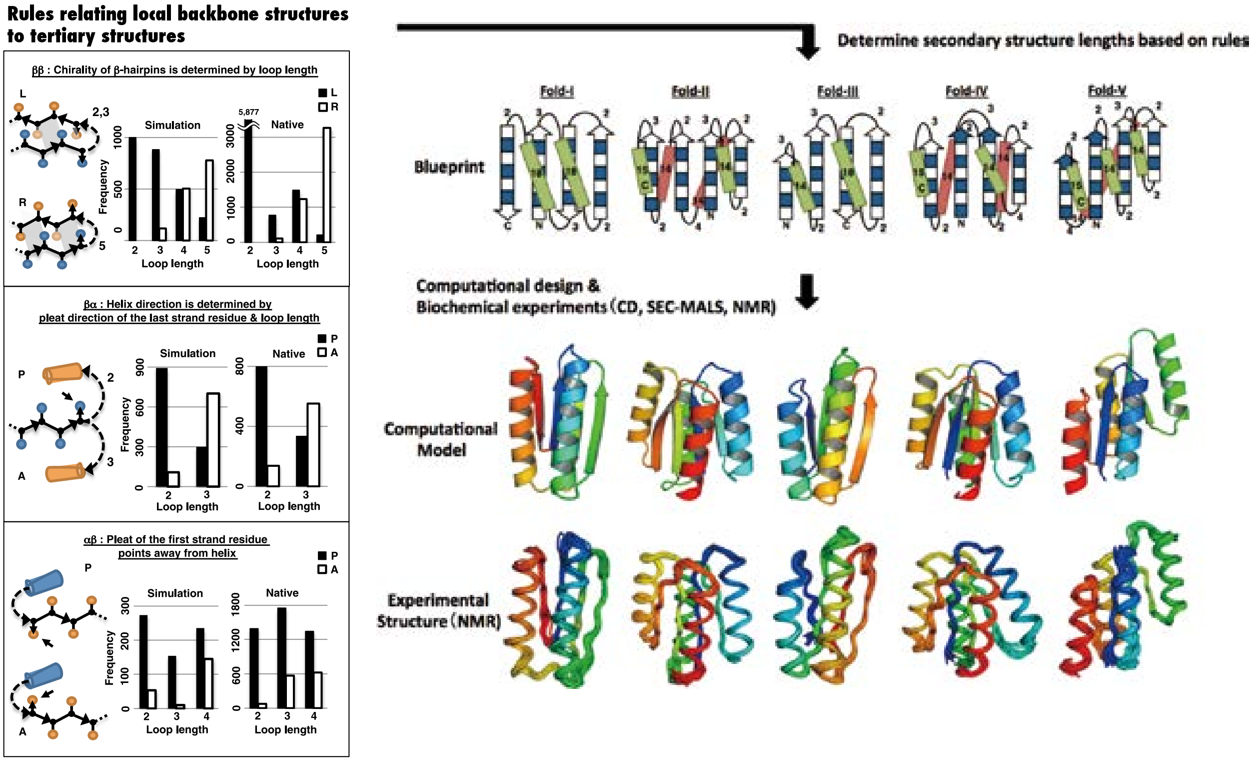

Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Visualization of Quantum Dynamical Nature Utilized Quantum Measurements

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2007	B.S. Tokyo Institute of Technology
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Professional Employment

2009	JSPS Research Fellow, Tokyo Institute of Technology
2011	JSPS Postdoctoral Fellow, Tokyo Institute of Technology
2011	Visiting Assistant Professor, Chapman University
2012	Research Associate Professor, Institute for Molecular Science
2014	Visiting Associate Professor, Tokyo Institute of Technology
2017	Project Associate Professor, The University of Tokyo

Awards

2013	FQXi Essay Contest Fourth Prize
2014	2013 Quantum Information Processing Top Reviewers
2014	Research Award, Research Foundation for Opto-Science and Technology
2015	Outstanding Referee of Physica A
2015	Outstanding Referee of Physics Letters A
2017	Reviewer Rewards for International Journal of Modern Physics B

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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.

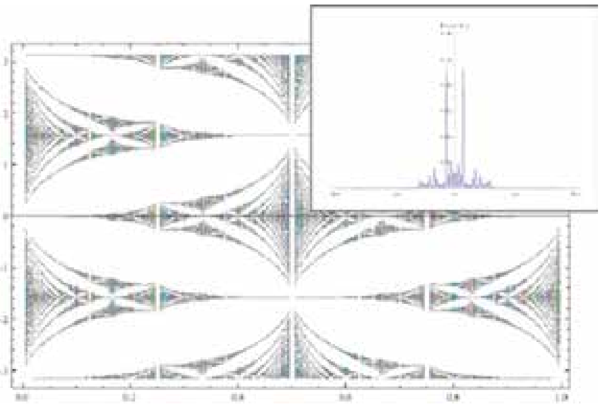

Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called 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* **82**, 031122 (7 pages) (2010).
- A. Noguchi, Y. Shikano, K. Toyoda and S. Urabe, "Aharonov-Bohm Effect in the Tunnelling of a Quantum Rotor in a 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. Exciton–Polariton Condensates in High Density Regime[1,2]

Exciton–polaritons are a coherent electron–hole–photon (e–h–p) system where condensation has been observed in semiconductor microcavities. In contrast to equilibrium Bose-Einstein condensation (BEC) for long lifetime systems, polariton condensates have a dynamical nonequilibrium feature owing to the similar physical structure that they have semiconductor lasers. One of the distinguishing features of a condensate to a laser is the presence of strong coupling between the matter and photon fields. Irrespective of its equilibrium or nonequilibrium nature, exciton–polariton have been observed to maintain strong coupling. We show that by investigating high density regime of exciton–polariton condensates, the negative branch directly observed in photoluminescence. This is evidence that the present e–h–p system is still in the strong coupling regime, contrary to past results where the system reduced to standard lasing at high density.

2. Large-Amplitude Quasi Phase Squeezed State[3]

Phase-squeezed light can enhance the precision of optical phase estimation. The larger the photon numbers are and the stronger the squeezing is, the better the precision will be. We propose an experimental scheme for generating phase-squeezed light pulses with large coherent amplitudes. In our scheme, one arm of a single-photon Mach-Zehnder interferometer interacts with coherent light via a non-linear optical Kerr medium to generate a coherent superposition state. Post-selecting the single photon by properly tuning a variable beam splitter in the interferometer yields a phase-squeezed output.

3. Visualization of Quantum States[4,5]

Since entanglement is not an observable *per se*, measuring its value in practice is a difficult task. Here we propose a protocol for quantifying a particular entanglement measure, namely concurrence, of an arbitrary two-qubit pure state via a single fixed measurement set-up by exploiting so-called weak measurements and the associated weak values together with the properties of the Laguerre-Gaussian modes. The virtue of our technique is that it is generally applicable for all two-qubit systems and does not involve simultaneous copies of the entangled state. We also propose an explicit optical implementation of the protocol.

4. Contact Geometry Description of Thermodynamics[6]

Contact geometry has been applied to various mathematical sciences, and it has been proposed that a contact manifold and a strictly convex function induce a dually flat space that is used in information geometry. Here, such a dually flat space is related to a Legendre submanifold in a contact manifold. In this paper contact geometric descriptions of vector fields on dually flat spaces are proposed on the basis of the theory of contact Hamiltonian vector fields. Based on these descriptions, two ways of lifting vector fields on Legendre submanifolds to contact manifolds are given. For some classes of these lifted vector fields, invariant measures in contact manifolds and stability analysis around Legendre submanifolds are explicitly given. Throughout this paper, Legendre duality is explicitly stated. In addition, to show how to apply these general methodologies to applied mathematical disciplines, electric circuit models and some examples taken from nonequilibrium statistical mechanics are analyzed.

5. Quantum Dynamical Simulation in Solid System[7]

One-dimensional discrete-time quantum walks (DTQWs) can simulate various quantum and classical dynamics and have already been implemented in several physical systems. This implementation needs a well-controlled quantum dynamical system, which is the same requirement for implementing quantum information processing tasks. Here, we consider how to realize DTQWs by Dirac particles toward a solid-state implementation of DTQWs.

References

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2) T. Horikiri, T. Byrnes, K. Kusudo, N. Ishida, Y. Matsuo, Y. Shikano, A. Löffler, S. Höfling, A. Forchel and Y. Yamamoto, *Phys. Rev. B* **95**, 245122 (5 pages) (2017).
3) F. Matsuoka, A. Tomita and Y. Shikano, *Quant. Stud.: Math. Found.* **4**, 159–169 (2017).
4) M. Tukiainen, H. Kobayashi and Y. Shikano, *Phys. Rev. A* **95**, 052301 (6 pages) (2017).
5) Y. Shikano, *AIP Conf. Proc.* **1871**, 020001 (7 pages) (2017).
6) S. Goto, *J. Math. Phys.* **57**, 102702 (41 pages) (2016).
7) Y. Shikano, *Interdiscip. Inform. Sci.* **23**, 33–37 (2017).

Award

SHIKANO, Yutaka; Reviewer Rewards for International Journal of Modern Physics B (2017).

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

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Keywords Solid State Ionics, Oxyhydride, Battery

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

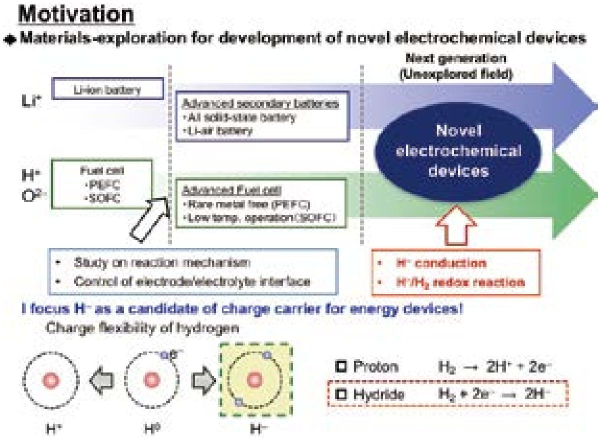

Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

Selected Publications

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

1. Synthesis of H⁻ Conductive Oxyhydrides[1–4]

Ionic charge carriers include a variety of species, such as Li^+, H^+, Ag^+, Cu^+, F^-, and O^{2-}, and their conductors have found applications in energy devices such as fuel cells and batteries. The conduction of hydride ions, H^-, is also attractive. These are similar in size to oxide and fluoride ions and show strong reducing properties with a standard redox potential of H^-/H_2 (–2.3 V) which is close to that of Mg/Mg^{2+} (–2.4 V). Hydride ion conductors may therefore be applied in energy storage/conversion devices with high energy densities. Here, we prepared a series of K_2NiF_4-type oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$, which are equipped with anion sublattices that exhibit flexibility in the storage of H^-, O^{2-}, and vacancies. An all-solid-state $Ti/La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}/TiH_2$ cell showed a redox reaction with hydrogen storage/desorption on the electrodes. The present success in the construction of an all-solid-state electrochemical cell exhibiting H^- diffusion confirms not only the capability of the oxyhydride to act as an H^- solid electrolyte but also the possibility of developing electrochemical solid devices based on H^- conduction.

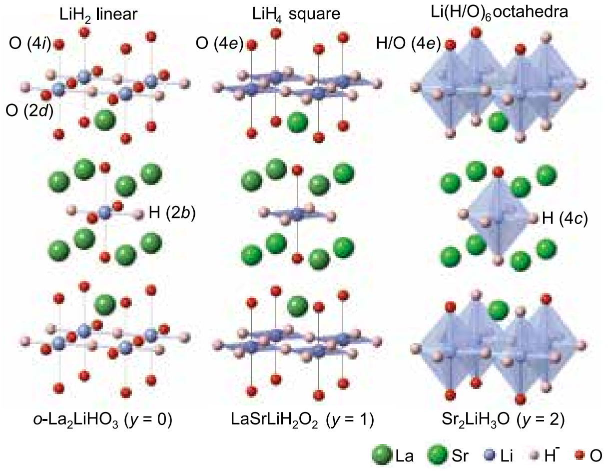

Figure 2. Crystal structures of $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0$, 1, 2). Lanthanum (and strontium) ions occupy the A sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the B site that are octahedrally coordinated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

2. High-Performance of Li-Rich Layered Cathode Materials through Combination of A_2O_3-Based Surface Modification and Stepwise Pre-Cycling[4]

Controlling the cathode/electrolyte interface by modifying the surface of the cathode material with metal oxides or phosphate is being explored as a possible strategy for improving the electrochemical performance of such materials. In this study, we synthesized Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ and investigated the crystal structure, the chemical bonding state from bulk to surface, and the influence of the surface modification on the electrochemical performance by X-ray diffraction, hard X-ray photoelectron spectroscopy (HAXPES), and galvanostatic charge/discharge reaction. It revealed that the surface-modification layer was composed of Li-Al oxides and Al oxides and that a $LiM_{1-x}Al_xO_2$ (M = transition metals) interlayer was formed between the modification layer and the $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particles (Figure 3). The cycling performance of the Li-rich layered oxide was enhanced by the surface modification with Al_2O_3. A discharge capacity of more than 310 mA h^{-1} and excellent cycling stability at 50 °C were achieved by the combination of the gradual Li-insetion/de-insertion process (stepwise precycling treatment) and the surface-modification.

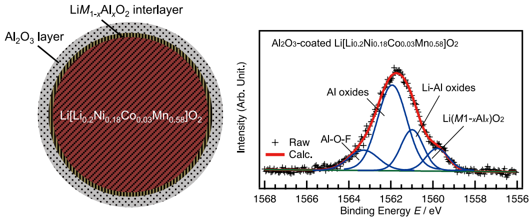

Figure 3. Schematic illustration and Al 1*s* HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

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3) G. Kobayashi, A. Watanabe, M. Yonemura, A. Kubota and R. Kanno, under revision.

4) A. Watanabe, M. Yonemura, Y. Imai, K. Suzuki, M. Hirayama, R. Kanno and G. Kobayashi, under revision.

5) G. Kobayashi*, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).

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* IMS International Internship Program

Open up Future Electronics by Organic Molecules

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2000	Research Scientist, RIKEN
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Awards

2009	RSC Publishing CrystEngComm Prize
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Keywords Molecular Conductors, Organic Superconducting Transistors, Supramolecular Nanowires

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

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

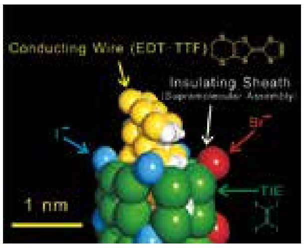

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

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

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

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

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

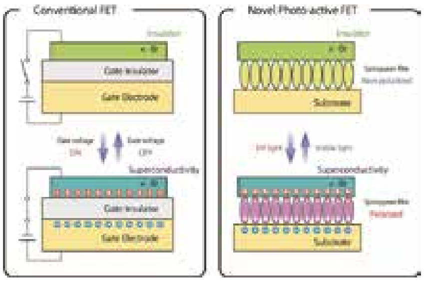

Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).
This figure shows p-type doping by molecular dipole-moment.

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

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

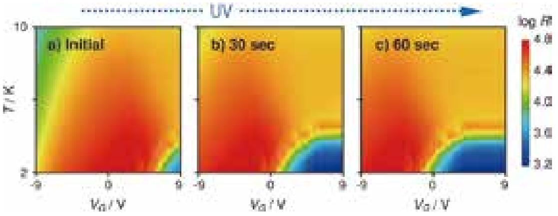

Figure 3. Emergence of n-type superconductivity by UV-irradiation. At the initial state (a), the device shows a normal ambipolar transistor behavior. After the UV-irradiation, superconducting region (blue) appears from electron-doped side (panels b and c).

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

Awards

SUDA, Masayuki; Young Scientist Awards, Japan Society for Molecular Science (2016).
SUDA, Masayuki; Ishida Prize, Nagoya University (2016).
SUDA, Masayuki; CSJ Award for Young Chemists, Chemical Society of Japan (2017).
SUDA, Masayuki; The 6th Young Scientist Award of National Institutes of Natural Sciences (2017).
SUDA, Masayuki; Morino Foundation for Molecular Science, Morino Foundation (2017).

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* IMS International Internship Program

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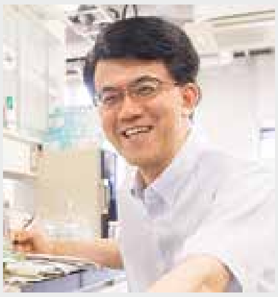
Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



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Keywords Organic Synthesis, Organic Semiconductor, Graphene Molecule

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

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

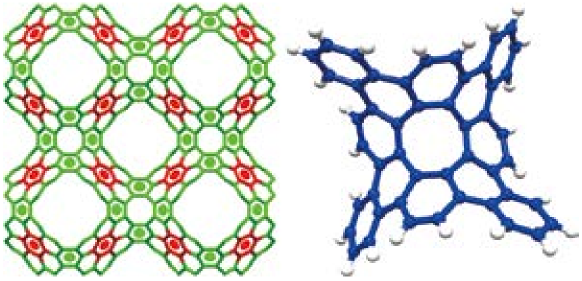


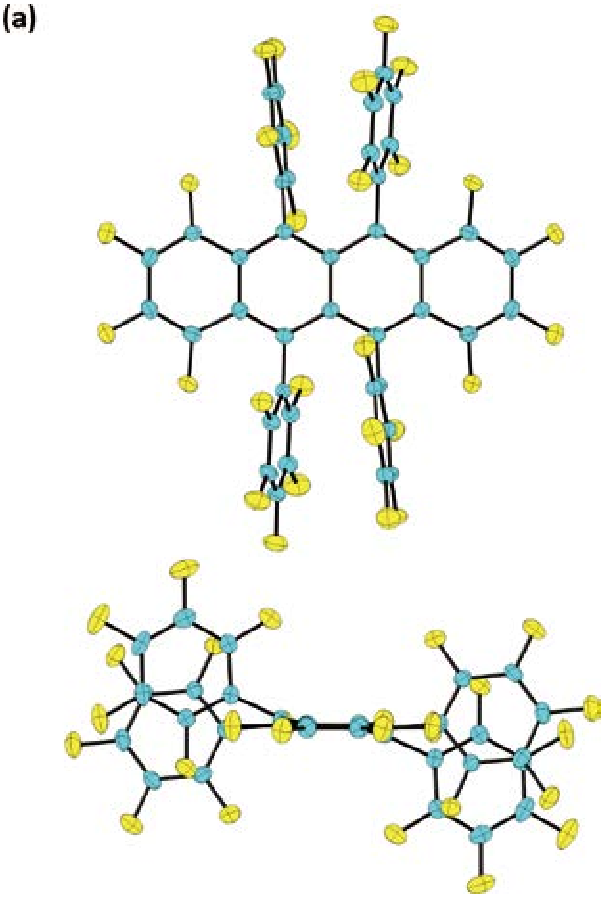
Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- 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).
- Y. Kuroda, Y. Sakamoto, T. Suzuki, E. Kayahara and S. Yamago, "Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops," *J. Org. Chem.* **81**, 3356–3363 (2016).

1. Perfluorinated and Half-Fluorinated Rubrenes: Synthesis and Crystal Packing Arrangements[1)]

Perfluororubrene (PF-RUB) has been synthesized by cycloaddition of perfluorinated 1,3-diphenylisobenzofuran and 1,4-diphenyl-2,3-didehydronaphthalene followed by reductive deoxygenation. This method was easily applied for the synthesis of half-fluorinated rubrene (F_{14}-RUB). The electrochemical measurements and DFT calculations indicate that perfluorination strongly lowers the HOMO and LUMO energies. Recrystallization and sublimation of PF-RUB gave two different crystals with planar and twisted conformations, respectively. In both cases, perfluorination leads to the formation of short C–F and F–F contacts and completely disrupts face-to-face π interactions. Single crystals of F_{14}-RUB were grown by sublimation, and twisted molecules display the two-dimensional π-stacking with a face-to-face distance of 3.54 Å.



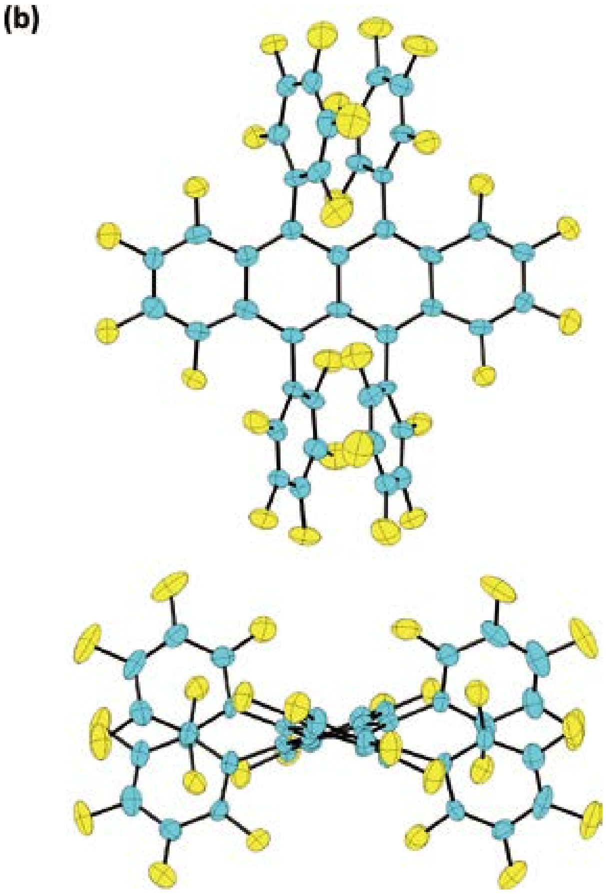


Figure 2. Planar (a) and twisted (b) conformations of perfluororubrene in two different crystal structures.

Reference

1) Y. Sakamoto and T. Suzuki, *J. Org. Chem.* **82**, 8111–8116 (2017).

RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

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

Development of Advanced Nano-Optical Imaging and Application to Nanomaterials

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Keywords Nano Optics, Plasmons, Chirality

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

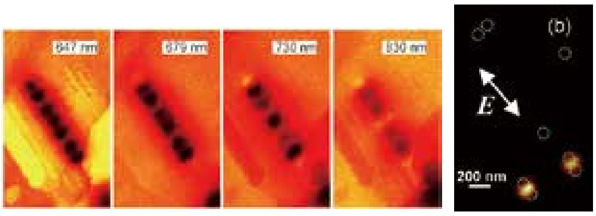

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right)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

Selected Publications

- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).
- H. Okamoto and K. Imura, "Near-Field Optical Imaging of Enhanced Electric Fields and Plasmon Waves in Metal Nanostructures," *Prog. Surf. Sci.* **84**, 199–229 (2009).

1. Circular Dichroism Microscopy Free from Commingling Linear Dichroism via Discretely Modulated Circular Polarization[1)]

Circular dichroism (CD) is a representative method to detect chirality in materials spectroscopically. Microscopy based on CD signals provides unique and powerful technique for the studies of nanomaterials with chiro-optical and magneto-optical functions, biomolecular systems, *etc*. One of difficulty in CD microscopy is commingling of linear birefringence (LB) and linear dichroism (LD) signals, that arise from optical anisotropy of the samples. Because LB and LD signal levels are in general much larger than that of CD, slight imperfections of optical components and nonlinearity (in particular from polarization modulation devices) cause commingling LB and LD signals to CD.

In this work, we developed a far-field CD imaging microscope with a device to suppress the commingling of LB and LD signals. CD signals are, in principle, free from the commingling influence of LD and LB if the sample is illuminated with pure circularly polarized light, with no linear polarization contribution. Based on this idea, we here propose a novel circular polarization modulation method to suppress the contribution of linear polarization, which enables high-sensitivity CD detection (10^{-4} level in optical density unit or mdeg level in ellipticity) for microscopic imaging at a nearly diffraction limited spatial resolution (sub-μm level). The highly sensitive, diffraction-limited local CD detection will make direct analyses of chiral structures and spatial mappings of optical activity feasible for μm- to sub-μm-sized materials and may yield a number of applications as a unique optical imaging method.

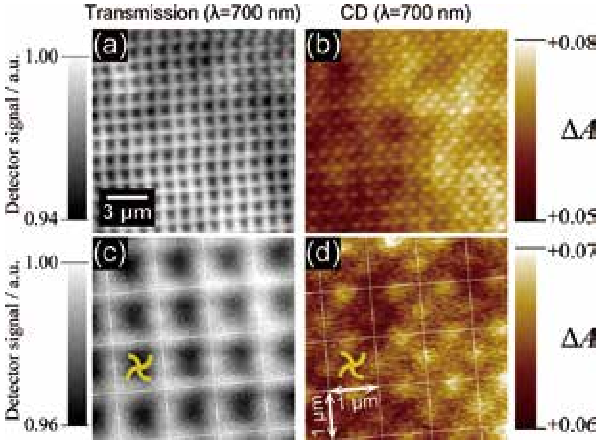

Figure 2. Transmission (a, c) and CD (b, d) images of the two-dimensional array of chiral (swirl-shaped) gold nanostructures. The wavelength of observation both for the transmission and CD images was 700 nm.[1)]

2. Near-Field Nonlinear CD Imaging of Single Gold Nanostructures[2)]

We demonstrated near-field nonlinear circular dichroism (CD) imaging of single rectangular (achiral) gold nanostructures using a two-photon excitation method. The gold rectangles were illuminated by pulses of circularly polarized light (CPL) to generate two-photon excitation images of the longitudinal plasmon modes. The observed images consisted of oval-shaped spatial features (corresponding to the antinodes of the plasmon modes) tilted from the long axis of the rectangles. The tilting direction depended on the handedness (left or right) of the CPL used for illumination, which led to the observation of a strong local dissymmetry of the two-photon excitation signals. The tilts of the oval features were not observed under linearly polarized pulse illumination with any polarization direction. The nonlinear CD images constructed from the differential two-photon excitation probability for left- and right-CPL pulses exhibited spatial features that were reasonably explained by the multipolar characters of the excited plasmon modes.

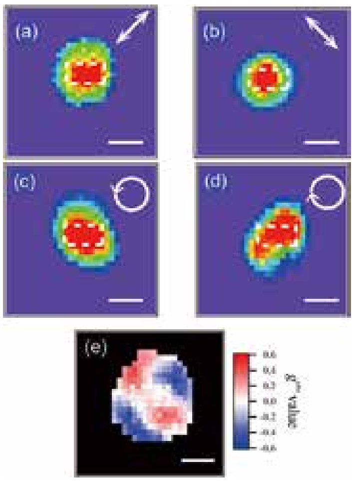

Figure 3. (a–d) Near-field two-photon excitation images of the rectangle at the excitation wavelength of 830 nm. Incident pulses are (a) linearly polarized, rotated by 45° from the long axis, (b) linearly polarized, rotated by −45° from the long axis, (c) left-circularly polarized, and (d) right-circularly polarized. (e) Near-field two-photon CD image evaluated from (c) and (d). The CD signals (g^{obs}) were not evaluated for the black areas outside the rectangular nanostructures because of low TPI-PL intensity. The dotted lines represent the approximate shape of the rectangle. Scale bars: 100 nm.[2)]

References

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2) Y. Nishiyama and H. Okamoto, *J. Phys. Chem. C* **120**, 28157–28162 (2016).

Awards

HASHIYADA, Shun; The Best Poster Presentation Award, NFO-14 (2016).
HASHIYADA, Shun; OSJ-OSA Joint Symposia Student Award (2016).

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Micro Solid-State Photonics

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Professional Employment

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1989	Research Associate, Fukui University
1993	Visiting Researcher, Stanford University (–1994)
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Awards

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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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Post-Doctoral Fellow
- SATO, Yoichi
- ZHENG, Lihe
- YAHIA, Vincent
- LIM, Hwanhong

Research Fellow
- KAUSAS, Arvydas
- KAWASAKI, Taisuke

Visiting Scientist
- LAFITTE-HOUSSAT, Eloïse*

Secretary
- ONO, Yoko
- INAGAKI, Yayoi

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

"*Micro Solid-State Photonics*," based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science. The engineered materials of micro and/or microchip solid-state, ceramic and single-crystal, lasers can provide excellent spatial mode quality and narrow linewidths with enough power. High-brightness nature of these lasers has allowed efficient wavelength extension by nonlinear frequency conversion, UV to THz wave generation. Moreover, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. The future may herald new photonics.

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

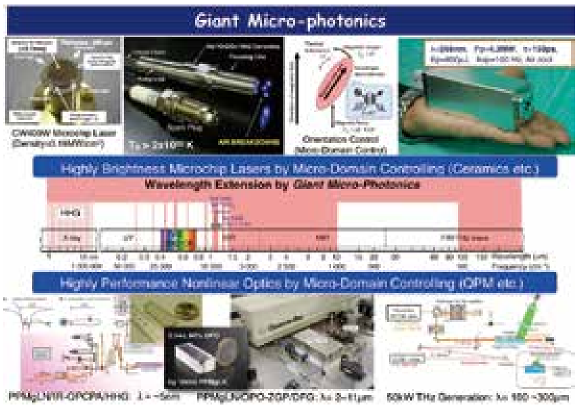

Figure 1. Giant micro-photonics.

Selected Publications

- H. Sakai, H. Kan and T. Taira, ">1 MW Peak Power Single-Mode High-Brightness Passively Q-Switched Nd^{3+}:YAG Microchip Laser," *Opt. Express* **16**, 19891–19899 (2008).
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1. >MW Peak Power at 266 nm, Low Jitter kHz Repetition Rate from Intense Pumped Microlaser

Intense pulse pumped microlaser is proposed for high peak power and low timing jitter at high repetition rate. It is based on Intense and Fast Pulse Pump (IFPP) technique, in which fast pulse pumps up the upper-level population and then dumps it rapidly by Q-switching. That could come close to complete pumping efficiency to reduce thermal problems and contribute to suppress the timing jitter of passively Q-switched laser. In this work, linearly polarized 1064 nm beam from [100]-cut YAG/Nd^{3+}:YAG and [110]-cut Cr^{4+}:YAG passively Q-switched microlaser is directly guided into nonlinear crystals to obtain 532 nm and 266 nm output. By implementing IFPP concept, over 1 MW peak power, 215 ps pulse duration, 1 kHz pulses at 266 nm with reduced standard deviation timing jitter of 37 ns were obtained.

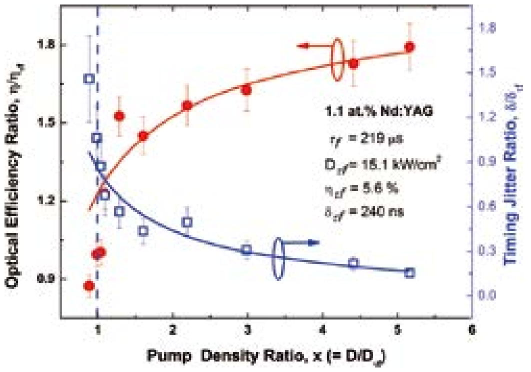

Figure 2. Optical efficiency ratio $\eta/\eta_{\tau f}$ and timing jitter ratio $\delta/\delta_{\tau f}$ as a function of pump power density ratio $D/D_{\tau f}$ at 1 kHz.

2. Sub-Nanosecond Laser Induced Air-Breakdown with Giant-Pulse Duration Tuned Nd:YAG Ceramic Micro-Laser by Cavity-Length Control

Laser induced breakdown (LIB) in air has been explained by different ways along pulse duration τ. Cascade ionization (CI) is considered as the mechanism for long pulse durations of over 1 ns. On the other hand, laser filamentation is alternative mechanism for fs pulses. However, for intermediate ps pulse, the mechanism is unclear due to a lack of knowledge about air-breakdown in sub-ns region and a contribution of multi-photon ionization. In addition, the knowledge about pulse duration dependence of breakdown energy in gas is practically useful for laser ignition. We first demonstrated a continuously giant-pulse duration tunable (0.5–9 ns) laser based on a short monolithic Nd:YAG/Cr:YAG ceramic by cavity-length control. LIB in laboratory air was investigated as a function of τ in sub-ns region using the developed laser. Air-breakdown threshold intensity I_{th} was measured using three different focusing conditions (Figure 3). We confirmed that (1) the measured I_{th} was almost constant at the longer τ than τ_{CI} named as limit-pulse-duration of CI, (2) I_{th} had ~τ^{-2} scaling for $\tau < \tau_{\mathrm{CI}}$, (3) the increase of I_{th} is not connected to a specific intensity level, and (4) τ_{CI} was not constant and depended on focusing conditions.

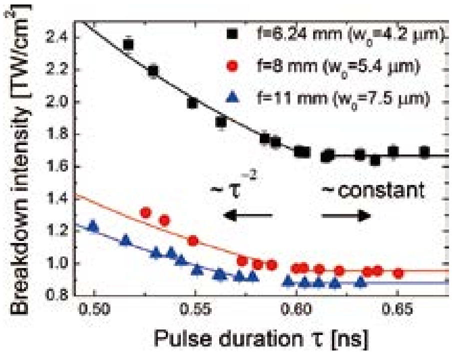

Figure 3. Measured breakdown threshold intensities as a function of pulse duration in laboratory air for three focusing conditions.

3. Damage Threshold Evaluation by Bulk-Shaped Nonlinear and Laser Materials

Laser-induced damage threshold (LIDT) of various optical materials, such as crystal quartz, YAG, and glass at sub-nanosecond pulse duration are evaluated. Bulk-shaped materials are used in the LIDT evaluation as shown in Figure 4, which can eliminate surface effects, such as adhesive dirt and polishing quality.

Evaluation were demonstrated using a laser source with 0.7-ns pulse-duration of 1.064 μm wavelength. LIDT of crystal quartz for piezoelectric and optical purpose were measured around 700 GW/cm^2 and 900 GW/cm^2, respectively. Also, LIDT of Nd:YAG and borosilicate glass were measured around 400 GW/cm^2 and 610 GW/cm^2, respectively.

Although conventional plate-shape measurement should be affected by its plate-surface condition, measurement using the bulk-shaped material can evaluate pure material characteristics.

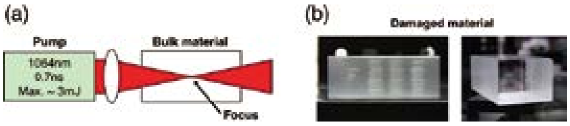

Figure 4. Laser-induced damage threshold evaluation using bulk-shaped material. (a) Set up of evaluation, (b) Example of damaged material.

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Ultrafast Laser Science

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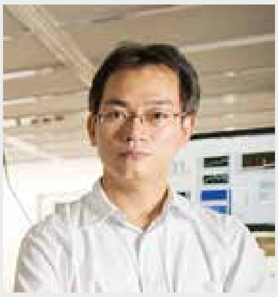

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Keywords Ultrafast Science, Laser Physics, Nonlinear Optics

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

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

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

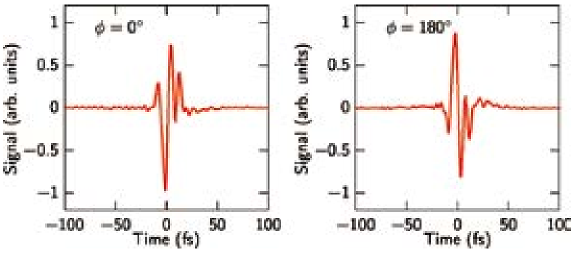

Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

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.

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

Selected Publications

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

1. Self-Referenced Waveform Measurement of Ultrashort Pulses

As is written in the previous page, it is still very difficult to directly sample an optical field transient on a time scale below the oscillation period. It has been naturally believed that the field oscillation can be detected only by using a reference pulse that has a shorter duration than the period of the oscillation.

In 2013, we proposed a new scheme of waveform characterization, frequency-resolved optical gating capable of carrier-envelope phase determination (FROG-CEP),[1)] which is based on a combination of frequency-resolved optical gating (FROG) with a carrier-envelope phase (CEP) sensitive time-domain nonlinear interferometer. The intensity and relative spectral phase of the target pulse are obtained from the FROG measurement, and the CEP is obtained from the nonlinear interferometer. Combining these data sets, we are able to retrieve a complete waveform of the target pulse. In this method, it is possible to measure a waveform with a reference pulse that has a longer duration than the period of the target pulse. The fact suggests that self-referenced waveform characterization is possible by using FROG-CEP.

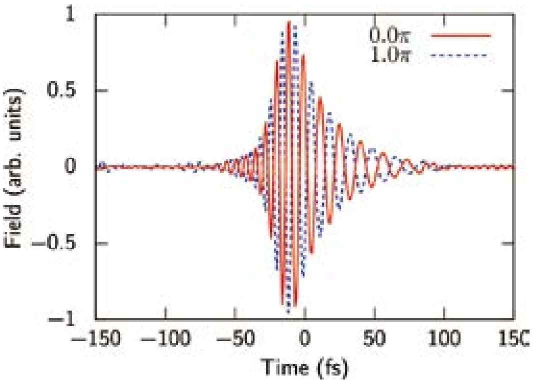

Figure 2. Retrieved electric-field in time domain. The solid line is the electric-field reconstructed with the method described in the text. The dotted line is the electric field where the CEP of the pulse is experimentally changed by π.

Here, we show the experimental demonstration of self-referenced FROG-CEP for few-cycle MIR pulses.[2)] We simultaneously measured a trace of second harmonic generation FROG (SHG-FROG) and interferogram between second harmonic (SH) and self-diffraction (SD) signals. The intensity and relative spectral phase of the target pulse are obtained from SHG-FROG, and the CEP is obtained from the interferogram. The retrieved waveform is shown in Figure 1.

2. Direct Amplification of 2 μm Femtosecond Pulses in a Tm:ZBLAN Fiber

Ultrafast lasers working in the 2 μm region have been attracting a lot of attention owing to a number of possible applications in various scientific and industrial fields. Thulium (Tm)-doped fiber lasers are one of the most promising candidates to generate ultrashort pulses in this wavelength region because of their broad emission spectra. Here we report the development of a fiber amplifier.

To develop high power, femtosecond light sources at the 2 μm region, the most straightforward method is the chirped-pulse amplification (CPA) technique. Another approach to build an ultrafast fiber laser amplifier is to make use of the nonlinearity within the fiber to broaden the spectrum rather than suppressing the nonlinearity. This approach was successful especially for developing ultrafast ytterbium-doped fiber laser amplifiers. However, the situation is quite different for Tm-doped fiber lasers because the fibers have anomalous dispersion around 2 μm region and thus the nonlinearity during amplification leads to wave breaking, which is usually considered detrimental.

We demonstrate direct generation of sub-50 fs pulses from a Tm-based fiber amplifier by utilizing nonlinearities within the amplifier fiber itself. Pulses with a duration of 48 fs are obtained at an average power of 2.5 W. The core-pumping scheme helped to obtain broad spectra extending into relatively short wavelength region around 1.7 μm. The setup uses no stretcher or compressor, resulting in an extremely simple system.[3)]

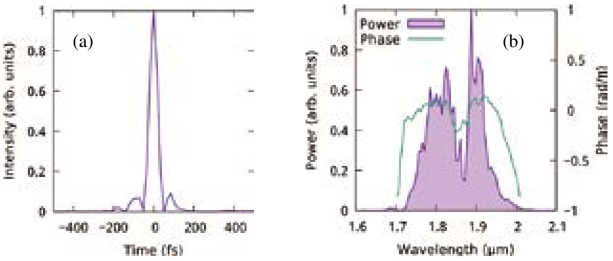

Figure 3. (a) Pulse shape retrieved from the FROG measurement. (b) Spectral intensity (blue solid curve) and phase (green dashed curve) profiles retrieved from the FROG measurement.

Figure 3 summarizes the results of FROG measurements of the amplified pulse. The pulse shape retrieved from the FROG measurement is shown in Figure 3(a). The duration of the pulse is as short as 48 fs, which is only 7% above the transform limit duration of 45 fs. The spectral intensity and phase profiles retrieved from the same FROG trace are shown in Figure 3(b). It can be seen that the phase is more or less flat for the main parts of the spectrum, whereas distorted in the region where the spectral intensity is relatively low.

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