



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 Heterogeneous Dynamics and Protein Functions

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Spatiotemporal Heterogeneous Dynamics, Functions, Liquids

Nonlinear intermolecular interactions cause complicated motions in condensed phases, *e.g.* liquids and biological systems. These motions are spatially and temporally heterogeneous with a wide range of time and spatial scales and yield both static and dynamic properties of the systems. 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, thermodynamics, dynamics, and functions 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 IR spectroscopy. We have examined the detailed fluctuations in water by calculating two-dimensional IR spectra of water. 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 dy-

namic 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 complex specific heat.

We currently investigate how chemical reactions proceed in biological systems, *e.g.* clock protein KaiC, under complex conformational fluctuations. We also examine heterogeneous conformational dynamics of proteins by exploiting the ideas of multi-dimensional spectroscopy and glassy dynamics.

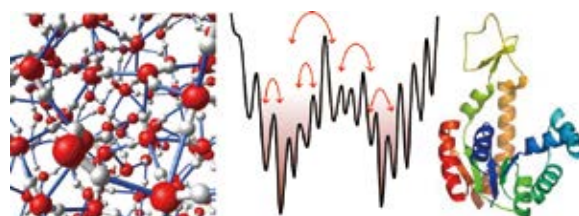


Figure 1. Schematic figure of rugged energy landscape (center) in supercooled water (left) and adenylate kinase (right).

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. Quantitative Evaluation of Site Energies and Their Pigment Fluctuations in the Fenna-Matthews-Olson Complex with an Efficient Method for Generating Potential Energy Surfaces¹⁾

We develop an efficient method to generate an accurate semi-global potential energy surface of a molecule in condensed phases with low computational cost. We apply the method to the analysis of the site energies and their fluctuations of bacteriochlorophyll (BChl) a pigments in the Fenna-Matthews-Olson (FMO) complex using the density functional properly describing the ground and excited states of BChl a in solution in our previous work (*J. Phys. Chem. B* **118**, 10906–10918 (2014)). The errors of the potential energies calculated from the present and QM/MM methods are small: ~1 kcal/mol for both the ground and excited states. The calculated site energies are in good agreement with the experimentally fitted results. The calculated spectral density also agrees with the experimentally available data. The spectral densities of BChl 2 and BChl 5 are much larger than those of the other five sites. The present method is expected to reveal the efficient excitation energy transfer in light-harvesting antennas.

2. Molecular Mechanism behind the Fast Folding/Unfolding Transitions of Villin Headpiece Subdomain: Hierarchy and Heterogeneity²⁾

Proteins involve motions over a wide range of spatial and temporal scales. While the large conformational changes such as folding and functioning are slow and appear to occur in a highly cooperative manner, how the hierarchical dynamics over different timescales play a role during these slow transitions has been of great interest over the decades. Here we study the folding mechanism of the villin headpiece subdomain (HP35) to understand the molecular mechanism behind this prototypical fast-folding protein. The ~400 μ s molecular dynamics (MD) trajectories obtained by Piana *et al.* [Piana, S. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **109**, 17845 (2012)] are analyzed in detail. By extracting the slowest mode from the trajectories, which is responsible for the folding/unfolding transitions, and by analyzing the transition events along this mode, we find that the transitions occur in a heterogeneous manner. Detailed analysis of the individual transition events shows that the folding/unfolding transitions occur via two qualitatively different pathways, *i.e.* the unfolding triggered from the C-terminal (α_3 helix) and from the N-terminal (α_1 – α_2 loop). Non-native contacts are also found to contribute in slowing down the transitions. The folding of HP35 thus proceeds in a segmental manner rather than cooperatively at the sub-microsecond timescale. The Lys \rightarrow Nle mutation is found to speed up the transitions by rigidifying the α_3 helix, *i.e.* suppressing one transition pathway. The analysis of the microsecond dynamics in the single-molecule Förster resonance energy transfer efficiency trajectories, which are calcu-

lated from the MD data, reveals that the folding/unfolding transitions in the NleNle mutant can be fitted with a two-state model, whereas those in WT appear to be more complex and involves multiple timescales. This may be due to the similarity in the timescale of the transition events and overall folding/unfolding transitions in WT. The present study demonstrates that a protein as small as HP35 already involves heterogeneous characters during folding/unfolding transitions when the hierarchical dynamics at molecular level is considered, thus heterogeneity can be a general characteristic in protein folding.

3. Multiple Transitions of Water on Its Path to Low Density Amorphous Ice³⁾

Amorphous ice is ubiquitous in the Universe, being a major constituent of meteorites and asteroids. It is mechanically stable at very low temperatures and is different from its crystalline counterpart, ice Ih. However, the mechanism of its formation from low temperature water is still not understood. The amorphous ice, when heated from below, undergoes a glass transition to a highly viscous liquid at 136 K, then crystallizes at 150 K, while liquid water when supercooled below its freezing temperature itself freezes at 227 K. Our difficulty to understand the formation of amorphous ice stems from the inaccessibility of liquid water to experiments between 227 K and 150 K, a temperature range well-known as “no man’s land.” We study the entire process of vitrification of water by extensive molecular dynamics simulations. We find that vitrification of water occurs in three distinct stages, accompanied by two sharp changes in fragility. A large scale density fluctuation between the high density liquid (HDL) and the low density liquid (LDL) that appears near 220 K, profoundly influences the entire transformation process. It undergoes a further dynamical transition at ~195 K where we find the dynamical heterogeneity to decrease sharply, and rather suddenly. This transition occurs by a fragmentation of macroscopic HDL, leading to the formation of a state where small, non-spherical, fast relaxing, high density droplets containing 3- and 5-coordinated defects exist in the slow low density network of 4-coordinated water molecules. The fragmentation scenario explains well the observed density minimum of water at 190 K. We also find that particular 3-coordinated defects with two HB acceptors and one HB donor are involved in structural changes in water. It is found, furthermore, that the presence of LDL predominantly formed by 4-coordinated molecules leads to a significant decrease of the glass transition temperature of water.

References

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- 3) S. Saito, B. Bagchi and I. Ohmine, to be submitted.

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

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Keywords

Optical Near-Field, Light-Matter Interaction, Nanodevices

Optical response of molecules is undoubtedly essential for understanding their physicochemical properties. In conventional theoretical approaches to optical response of molecules, two conditions are usually assumed:

- (i) A scale of wavelength of incident light is considered to be much longer than molecular size, *i.e.*, dipole approximation. Thus, a target molecule is well approximated by a point dipole and the dipole feels a spatially uniform electromagnetic field.
- (ii) Electric polarization in a molecule induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an “optical near-field.” 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 of more than ten-nanometers in size. Electron dynamics in nanostructures interacting with an electromagnetic field is described by the time-dependent

Kohn-Sham (TDKS) equation, whereas electromagnetic field dynamics is represented by the microscopic Maxwell’s equations. The nonuniform LM interaction is taken into account in the vector potential and the self-consistent LM interaction is described by solving the electron and electromagnetic field coupled equations self-consistently. The coupled equations are solved numerically by using our developed computational program (GCEED: *Grid-based Coupled Electron and Electromagnetic field Dynamics*). Our computational approach is based on a finite-difference method in real-time and real-space. Since the approach employs very simple algorithms, it is highly suitable for massively parallelized computations. By using GCEED, we are currently computationally designing unified photonic and electronic nanodevices.

We also launched a new project of 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. The theoretical approach allows us to treat dynamical chemical reaction processes taking account of the effects of temperature and nonequilibrium interactions between clusters and supports.

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 Tricosahedral 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. Yamaguchi and K. Nobusada, “Indirect Interband Transition Induced by Optical Near Fields with Large Wave Numbers,” *Phys. Rev. B* **93**, 195111 (2016).

1. Indirect Interband Transition Induced by Optical Near Fields with Large Wave Numbers¹⁾

Optical near fields (ONFs) have Fourier components with large wave numbers that are two or three orders of magnitude larger than those of far-field propagating light owing to their nonuniformity in space. By utilizing these large wave numbers, the ONF is expected to induce an indirect interband transition between Bloch states having different wave numbers and directly generate an electron–hole pair without electron–phonon coupling. We perform time-dependent dynamics calculations of a one-dimensional periodic potential with an indirect band-gap structure and demonstrate that the ONF definitely induces an indirect interband transition. Instead of using the general Bloch boundary condition, which is usually imposed in conventional band structure calculations, we adopt an alternative boundary condition, the Born–von Karman boundary condition, to appropriately treat indirect interband transitions. The calculated absorption spectra for the far-field and ONF excitations show different absorption edges and spectral patterns. We argue that this difference can be experimentally measured as evidence of the effects of the large wave numbers of the ONF.

2. Reducing the Cost and Preserving the Reactivity in Noble-Metal-Based Catalysts: Oxidation of CO by Pt and Al–Pt Alloy Clusters Supported on Graphene²⁾

The oxidation mechanisms of CO to CO₂ on graphene-supported Pt and Pt–Al alloy clusters are elucidated by reactive dynamical simulations. The general mechanism evidenced is a Langmuir–Hinshelwood (LH) pathway in which O₂ is adsorbed on the cluster prior to the CO oxidation. The adsorbed O₂ dissociates into two atomic oxygen atoms thus promoting the CO oxidation. Auxiliary simulations on alloy clusters in which other metals (Al, Co, Cr, Cu, Fe, Ni) replace a Pt atom have pointed to the aluminum doped cluster as a special case. In the nanoalloy, the reaction mechanism for CO oxidation is still a LH pathway with an activation barrier sufficiently low to be overcome at room temperature, thus preserving the catalyst efficiency. This provides a generalizable strategy for the design of efficient, yet sustainable, Pt-based catalysts at reduced cost.

3. Interface Electronic Properties Between a Gold Core and Thiolate Ligands: Effects on an Optical Absorption Spectrum in Au₁₃₃(SPh-*t*Bu)₅₂³⁾

We analyze the electronic structures and optical absorption spectrum of Au₁₃₃(SPh-*t*Bu)₅₂, particularly in terms of

interface electronic properties between the Au core and the thiolate ligands. Computations are performed by using the time-dependent density functional theory approach in real-time and real-space that has recently been developed by our group. Local density of states analysis reveals a relationship between an icosahedral Au core and a thiolate-protected Au cluster; Au atoms associated with the edge or surface sites of the icosahedral core anchor the ligands to the core, whereas Au atoms associated with the apex sites bridge two thiolates forming –S–Au–S– bonds. We compare the optical absorption spectrum of Au₁₃₃(SPh-*t*Bu)₅₂ with that of an icosahedral Au₁₄₆ bare cluster to clarify effects of the ligands on the optical absorption. The absorption intensity for Au₁₃₃(SPh-*t*Bu)₅₂ is obviously higher than that for the bare cluster. The significant increase in the optical absorption of Au₁₃₃(SPh-*t*Bu)₅₂ is attributed to mutual enhancement of electric polarizations induced both in the Au core and in the thiolate ligands. The effect of the enhancement is computationally visualized by analyzing the electric fields generated in the Au core and the thiolate ligands.

4. Nonlinear Optical Response Induced by a Second-Harmonic Electric-Field Component Concomitant with Optical Near-Field Excitation⁴⁾

Electron dynamics excited by an optical near field (ONF) in a two-dimensional quantum dot model was investigated by solving a time-dependent Schrödinger equation. It was found that the ONF excitation of the electron caused two characteristic phenomena: A two-photon absorption and an induction of a magnetic dipole moment with a strong third-harmonic component. By analyzing the interaction dynamics of the ONF and the electron, we explained that the physical mechanism underlying these phenomena was the second-harmonic electric-field component concomitant with the near-field excitation originating from the nonuniformity of the ONF. Despite a *y*-polarized ONF source, the second-harmonic component of an *x*-polarized electric field was inherently generated. The effect of the second-harmonic electric-field component is not due to usual second-order nonlinear response but appears only when we explicitly consider the electron dynamics interacting with the ONF beyond the conventional optical response assuming the dipole approximation.

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- 2) K. Koizumi, K. Nobusada and M. Boero, *Chem. –Eur. J.* **22**, 5181 (2016).
- 3) K. Iida, M. Noda and K. Nobusada, *J. Phys. Chem. C* **120**, 2753 (2016).
- 4) M. Yamaguchi and K. Nobusada, *Phys. Rev. A* **92**, 043809 (2015).

Advanced Electronic Structure Theory in Quantum Chemistry

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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 calcula-

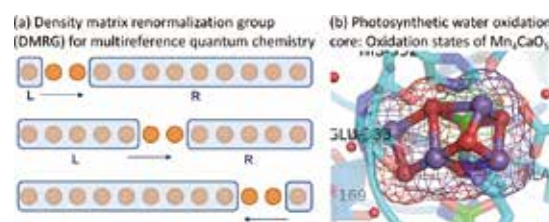


Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

tion, 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.

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 Nano-

ribbons 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. Computational Evidence of Inversion of 1L_a and 1L_b -Derived Excited States in Naphthalene Excimer Formation from Highly-Correlated *ab initio* Multireference Theory²⁾

The naphthalene molecule has two important lowest-lying singlet excited states, denoted 1L_a and 1L_b . Association of the excited and ground state monomers yields a metastable excited dimer (*excimer*), which emits characteristic fluorescence. Here, we report a first computational result based on *ab initio* theory to corroborate that the naphthalene excimer fluorescence is 1L_a parentage, resulting from inversion of 1L_a and 1L_b -derived dimer states. This inversion was hypothesized by earlier experimental studies; however, it has not been confirmed rigorously. In this study, the advanced multireference (MR) theory based on density matrix renormalization group (DMRG) theory using unprecedented large-size active space for describing significant electron correlation effects is used to provide accurate potential energy curves (PECs) of the excited states. The results evidenced the inversion of the PECs and accurately predicted transition energies for excimer fluorescence and monomer absorption. Traditional MR calculations with smaller active spaces and single-reference theory calculations exhibit serious inconsistencies with experimental observations.

The excimer formation is driven by the strong 1L_a 's attractive intermolecular interaction arising from a mixing of excitation resonance (ER) and charge resonance (CR) configurations. At large distance $r(R-R) = 5.2$ Å, $^1L_a^-$ and $^1L_b^-$ states are both characterized by near 100% ER. In $^1L_a^-$, the CR character rises up to 40% for the excimer formation, while it remains negligible in $^1L_b^-$. This near CR-free character in $^1L_b^-$ is an interesting finding; the previous semi-empirical approaches were unable to unveil it. Since the transition dipole moment of the monomer 1L_b is much smaller than that of 1L_a , the attractive interaction in $^1L_b^-$ driven by ER alone should be far weaker than that in $^1L_a^-$. In the presence of the transition dipole–transition dipole interaction, the attractive interaction in $^1L_a^-$ is further pronounced by the growth of its CR character, as modeled by the semi-empirical approach. These imbalanced intermolecular interactions underlie the mechanism of the inversion of the two excitation levels.

2. Theoretical Investigation into Pentanuclear Iron Catalyst Designed for Water Oxidation³⁾

Quantum chemistry calculations were performed on the pentanuclear iron complex and its reaction intermediates using density functional theory (DFT). The catalyst based on the complex was recently developed by Masaoka group; it was

Naphthalene excimer: DMRG-CASPT2 study

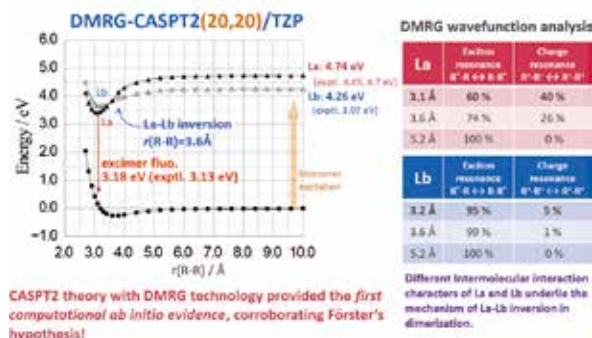


Figure 2. The potential energies of naphthalene dimer of ground, 1L_a and 1L_b excited states as a function of intermolecular distance. DMRG wavefunction analysis showing the weights of exciton and charge resonance characters of the DMRG-CASSCF wavefunction.

revealed that it here has a remarkable ability to catalyze water oxidation with significant efficiency and robustness. We first examined the viability of water attack reaction. Potential energy surface scan calculations were carried out to derive a reaction pathway of the insertion of a single water to the cluster. Our computational model showed that the coordination of water to activation iron site occurs with activation barrier of 14 kcal/mol. Next, we assume that the reaction proceeds to the coordination of another water and sequential or simultaneous deprotonation, affording cofacial Fe=O radical units. It was found that these top and bottom iron sites play a role as oxidants that withdraw two electrons from water-coordinated activation iron sites during deprotonation; so, intramolecular electron rearrangement takes place between central sites and up-down sites, and they assist generation of reactive high-valence iron-oxo species. Importantly, the number of electrons are conserved in the step. This system was found a mixed valence system involving three kinds of valence, Fe^{II} , Fe^{III} , and Fe^{IV} , simultaneously. Such remarkable redox flexibility is perhaps responsible for high efficiency of catalytic core. In addition, our computational investigation indicated that the O–O bond formation proceeds from the mixed-valence $Fe^{II}_2Fe^{III}(Fe^{IV}=O)_2$ intermediate with a reaction barrier of less than 10 kcal mol⁻¹.

References

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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]
- Y. Fujihashi, G. R. Fleming and A. Ishizaki, "Impact of Environmentally Induced Fluctuations on Quantum Mechanically Mixed Electronic and Vibrational Pigment States in Photosynthetic Energy Transfer and 2D Electronic Spectra," *J. Chem. Phys.* **142**, 212403 (12 pages) (2015).

1. Influences of Quantum Mechanically Mixed Electronic and Vibrational Pigment States in 2D Electronic Spectra of Photosynthetic Systems: Strong Electronic Coupling Cases

In 2D electronic spectroscopy studies, long-lived quantum beats have recently been observed in photosynthetic systems, and several theoretical studies have suggested that the beats are produced by quantum mechanically mixed electronic and vibrational states. Concerning the electronic-vibrational quantum mixtures, the impact of protein-induced fluctuations was examined by calculating the 2D electronic spectra of a weakly coupled dimer with the Franck-Condon active vibrational modes in the resonant condition [Fujihashi *et al.*, *J. Chem. Phys.* **142**, 212403 (2015)]. This analysis demonstrated that quantum mixtures of the vibronic resonance are rather robust under the influence of the fluctuations at cryogenic temperatures, whereas the mixtures are eradicated by the fluctuations at physiological temperatures. However, this conclusion cannot be generalized because the magnitude of the coupling inducing the quantum mixtures is proportional to the inter-pigment electronic coupling. In this study, we explore the impact of the fluctuations on electronic-vibrational quantum mixtures in a strongly coupled dimer with an off-resonant vibrational mode. Toward this end, we calculate energy transfer dynamics and 2D electronic spectra of a model dimer that corresponds to the most strongly coupled bacteriochlorophyll molecules in the Fenna-Matthews-Olson complex in a numerically accurate manner. The quantum mixtures are found to be robust under the exposure of protein-induced fluctuations at cryogenic temperatures, irrespective of the resonance. At 300 K, however, the quantum mixing is disturbed more strongly by the fluctuations, and therefore, the beats in the 2D spectra become obscure even in a strongly coupled dimer with a resonant vibrational mode. Further, the overall behaviors of the energy transfer dynamics are demonstrated to be dominated by the environment and coupling between the 0–0 vibronic transitions as long as the Huang-Rhys factor of the vibrational mode is small. The electronic-vibrational quantum mixtures do not necessarily play a significant role in electronic energy transfer dynamics despite contributing to the enhancement of long-lived quantum beating in the 2D spectra.¹⁾

2. Fluctuations in Electronic Energy Affecting Singlet Fission Dynamics and Mixing with Charge Transfer State: Quantum Dynamics Study

Singlet fission is a spin-allowed process by which a singlet excited state is converted to two triplet states. To understand

mechanisms of the ultrafast fission via a charge transfer (CT) state, one has investigated the dynamics through quantum-dynamical calculations with the uncorrelated fluctuation model; however, the electronic states are expected to experience the same fluctuations induced by the surrounding molecules because the electronic structure of the triplet pair state is similar to that of the singlet state except for the spin configuration. Therefore, the fluctuations in the electronic energies could be correlated, and the 1D reaction coordinate model may adequately describe the fission dynamics. In this work we develop a model for describing the fission dynamics to explain the experimentally observed behaviors. We also explore impacts of fluctuations in the energy of the CT state on the fission dynamics and the mixing with the CT state. The overall behavior of the dynamics is insensitive to values of the reorganization energy associated with the transition from the singlet state to the CT state, although the coherent oscillation is affected by the fluctuations. This result indicates that the mixing with the CT state is rather robust under the fluctuations in the energy of the CT state as well as the high-lying CT state.²⁾

3. A Variational Master Equation Approach to Quantum Dynamics with Off-Diagonal Coupling in a Sub-Ohmic Environment

A master equation approach based on an optimized polaron transformation is adopted for dynamics simulation with simultaneous diagonal and off-diagonal spin–boson coupling. Two types of bath spectral density functions are considered, the Ohmic and the sub-Ohmic. The off-diagonal coupling leads asymptotically to a thermal equilibrium with a nonzero population difference $P_z(t \rightarrow \infty) \neq 0$, which implies localization of the system, and it also plays a role in restraining coherent dynamics for the sub-Ohmic case. Since the new method can extend to the stronger coupling regime, we can investigate the coherent–incoherent transition in the sub-Ohmic environment. Relevant phase diagrams are obtained for different temperatures. It is found that the sub-Ohmic environment allows coherent dynamics at a higher temperature than the Ohmic environment.³⁾

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- 3) K.-W. Sun, Y. Fujihashi, A. Ishizaki and Y. Zhao, *J. Chem. Phys.* **144**, 204106 (8 pages) (2016).

Awards

ISHIZAKI, Akihito; 10th Condensed-Matter Science Prize, Japan (2015).

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Theoretical Study on Photochemistry and Catalysis

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Keywords

Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

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

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

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

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at hetero-junction of Ag nanocluster supported by alumina surface in terms of H₂ activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy

Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

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

(4) Theoretical spectroscopy

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

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, “SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution,” *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, “Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser,” *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, “CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions,” *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, “Cooperative H₂ Activation at Ag Cluster/θ-Al₂O₃ Dual Perimeter Sites: A DFT Study,” *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Low-Lying Resonances of Standard and Rare DNA and RNA Bases

The character and efficiency of electron transfer or electron injection in DNA and RNA play a crucial role in various biological processes. This process is relevant to the more general question of charge transfer in DNA, and much experimental and theoretical effort has been devoted to the study of electron attachment to the vacant π^* molecular orbitals (MOs) of DNA bases. In low-energy (< 3 eV) electron-induced processes, so-called transient or temporary negative ions, also referred to as resonance states, are early key intermediates in the damage of DNA strands.

We have investigated low-lying π^* resonance states of DNA and RNA bases by the recently developed projected complex absorbing potential (CAP)/SAC-CI method using a smooth Voronoi potential as CAP.¹⁾ In addition to these standard bases, three modified forms of cytosine, which serve as epigenetic or biomarkers, were investigated. A strong correlation between the computed positions and the observed ETS values is demonstrated, clearly suggesting that the present computational protocol should be useful for predicting the π^* resonances of DNA and RNA bases (Figure 1).

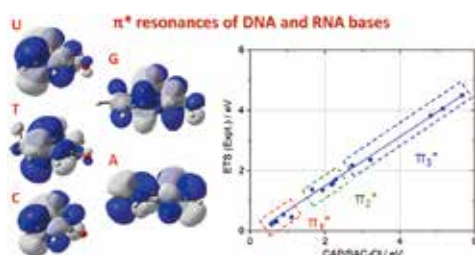


Figure 1. Correlation between calculated resonance energy and observed energy.

2. Donor- π -Acceptor Organic Dyes for a Dye-Sensitized Solar Cell

The electronic structure and photophysical properties of five coumarin-based donor- π -acceptor (D- π -A)-type organic dyes for a dye-sensitized solar cell (DSSC) have been investigated using the TDDFT and SAC-CI methods.²⁾ Theoretical calculations including the solvent effect in state-specific and linear-response scheme reproduced the experimental UV/Vis absorption spectra of these dyes satisfactorily. The π -spacers, thiophene and thiophene-phenylene mixed units, affect the planarity of the molecular structures which is relevant to the photophysical properties and charge polarization. Energy levels of the frontier orbitals and charge separation were analyzed and the thiophene linker was found to be effective for the electron injection in DSSC. The adsorption of these dyes on the TiO₂ anatase (101) surface and the electron injection mechanism were also investigated using a dye-(TiO₂)₃₈ cluster model employing PBE and TD-CAM-B3LYP calculations, respectively. The possible direct electron injection

mechanism was suggested in the present coumarin-based D- π -A dyes in a dye-TiO₂ interacting system.

3. Bond Activation on Bimetallic Alloy Nanoclusters

Bimetallic nanoparticles (NP) have been shown to exhibit certain advantages over pure NPs in catalysis due to synergistic effect. It is common to disperse NPs in polymer matrix such as polyvinylpyrrolidone (PVP) to prevent flocculation, which imparts considerable electronic effects on the NPs.

In this work, interactions between aqueous solutions of N-ethylpyrrolidone (EP, system chosen to model the monomeric form of PVP) and Au/Pd bimetallic NPs, which are relevant in catalysis,³⁾ have been investigated using molecular dynamics simulations and density functional theory (DFT) method.⁴⁾ The interactions of NP with the environment were studied at various concentrations of aqueous solutions of EP to examine the strength of NP-EP and NP-water interactions. Free energy calculations show that the EP adsorption on NP is preferred over the adsorption of water (Figure 2). Extensive analysis of the interactions of the NPs with various concentrations of aqueous EP suggests existence of isolated water molecules that may take part in reactions. Adsorption of unexpectedly large numbers of EP molecules was found to be possible leading to accumulation of the electron density on the Au/Pd NPs, which have previously been shown to enhance the catalytic activity of NPs.

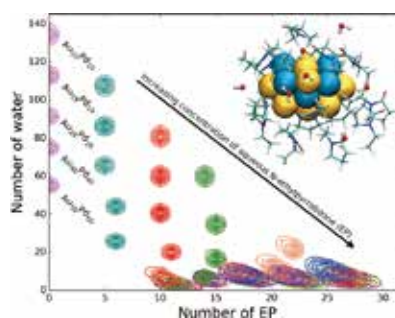


Figure 2. Number of EP and water molecules adsorbed on Au/Pd NC depending on the concentration of EP.

References

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- 3) R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.* **134**, 20250–20253 (2012).
- 4) A. Gupta, B. Boekfa, H. Sakurai, M. Ehara and U. Deva Priyakumar, *J. Phys. Chem. C* **120**, 17454–17464 (2016).

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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.

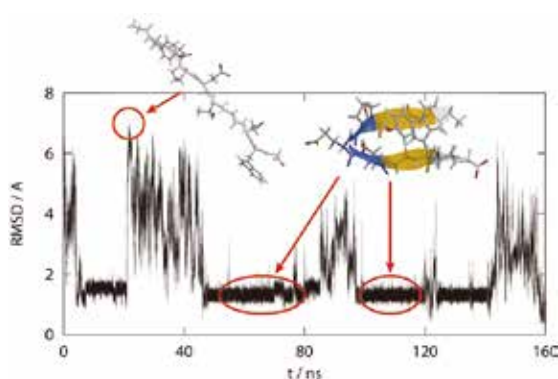


Figure 1. Time series of protein folding simulation.

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

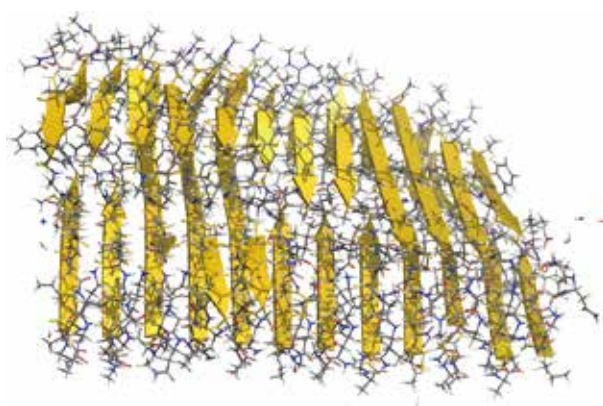


Figure 2. Snapshot of amyloid fibril.

Selected Publications

- 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. Oligomer Formation of Amyloid- β (29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation

Oligomers of amyloid- β peptides ($A\beta$) are formed during the early stage of the amyloidogenesis process and exhibit neurotoxicity. The oligomer formation process of $A\beta$ and even that of $A\beta$ fragments are still poorly understood, though understanding of these processes is essential for remedying Alzheimer's disease. In order to better understand the oligomerization process of the C-terminal $A\beta$ fragment $A\beta$ (29-42) at the atomic level, we performed the Hamiltonian replica-permutation molecular dynamics simulation with $A\beta$ (29-42) molecules using the explicit water solvent model.¹⁾ We observed that oligomers increased in size through the sequential addition of monomers to the oligomer, rather than through the assembly of small oligomers. Moreover, solvent effects played an important role in this oligomerization process.

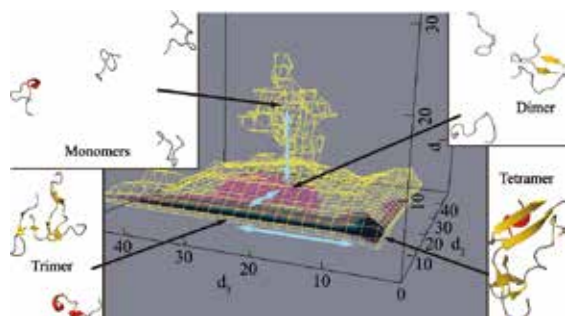


Figure 3. Free-energy surface and typical conformations of four $A\beta$ (29-42) molecules.

2. Simulated Tempering Based on Global Balance or Detailed Balance Conditions: Suwa-Todo, Heat Bath, and Metropolis Algorithms

Simulated tempering (ST) is a useful method to enhance sampling of molecular simulations. When ST is used, the Metropolis algorithm, which satisfies the detailed balance condition, is usually applied to calculate the transition probability. Recently, an alternative method that satisfies the global balance condition instead of the detailed balance condition has been proposed by Suwa and Todo. In this study, ST method with the Suwa-Todo algorithm is proposed.²⁾ Molecular dynamics simulations with ST are performed with three algorithms (the Metropolis, heat bath, and Suwa-Todo algorithms) to calculate the transition probability. Among the three algorithms, the Suwa-Todo algorithm yields the highest acceptance ratio and the shortest autocorrelation time. These suggest

that sampling by a ST simulation with the Suwa-Todo algorithm is most efficient. In addition, because the acceptance ratio of the Suwa-Todo algorithm is higher than that of the Metropolis algorithm, the number of temperature states can be reduced by 25% for the Suwa-Todo algorithm when compared with the Metropolis algorithm.

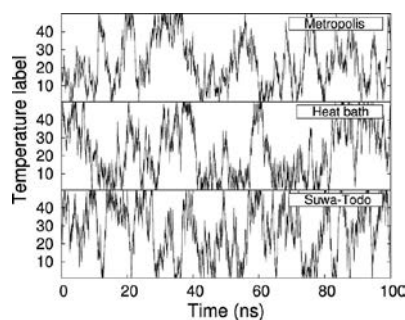


Figure 4. Time series of the temperature label in the simulations with the Metropolis, heat bath, and Suwa-Todo algorithms

3. Conformation Study of ϵ -Cyclodextrin: Replica-Exchange Molecular Dynamics Simulations

There is growing interest in large-ring cyclodextrins (LR-CDs) which are known to be good host molecules for larger ligands. The isolation of a defined size LR-CD is an essential prerequisite for studying their structural properties. Unfortunately the purification procedure of these substances turned out to be very laborious. Finally the problem could be circumvented by a theoretical consideration: The replica exchange molecular dynamics (REMD) simulation offers an ideal approach for studying the conformational change of ϵ -cyclodextrin (CD10), a smaller representative of LR-CDs. Three carbohydrate force fields and three solvent models were tested.³⁾ The conformational behavior of CD10 was analyzed in terms of the flip (turn) of the glucose subunits within the macrocyclic ring. In addition a ranking of conformations with various numbers of turns was performed. Our findings might be also helpful in the temperature controlled synthesis of LR-CDs as well as other experimental conditions, in particular for the host-guest reaction.

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- 1) S. G. Itoh and H. Okumura, *J. Phys. Chem. B* **120**, 6555–6561 (2016).
- 2) Y. Mori and H. Okumura, *J. Comput. Chem.* **36**, 2344–2349 (2015).
- 3) W. Khuntawee, T. Rungrotmongkol, P. Wolschann, P. Pongsawasdi, N. Kungwan, H. Okumura and S. Hannongbua, *Carbohydr. Polym.* **141**, 99–105 (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 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

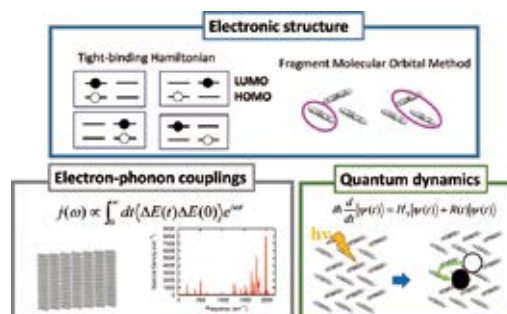


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

incorporating finite-temperature effects and electron-phonon couplings. The combine computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in molecular aggregates.

We currently investigate exciton dynamics in organic semiconductors, and structure-property relationships in ion-based π -conjugated molecular systems. We also study statistical-mechanics theories for predicting supramolecular structures in solution, and a many-body approach for excited-state calculations.

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. Coherent Dynamics of Mixed Frenkel and Charge-Transfer Excitons¹⁾

There has been a growing interest in electronic properties in organic semiconductors due to their broad applications for electronic devices. Optical properties of organic molecular aggregates have been traditionally explained in terms of Frenkel exciton model, which describes an electronic excited state as a bound electron–hole pair. In recent years, great attention has been focused on charge-transfer excitons—a state where electron and hole can be located in separate regions. The CT excitons play essential roles in singlet fission and charge separations at donor/acceptor interfaces.

In this study, we focus on a p-type organic semiconductor, dinaphtho[2,3-b:2'3'-f]thieno[3,2-b]-thiophene (DNTT). A time-resolved spectroscopy study suggests that mixed Frenkel and CT excitons are formed in DNTT thin films after the optical excitation. Although the degree of CT characters in excited states has been discussed, its role in excitation dynamics has remained unclear. We investigate optical properties and exciton dynamics in the DNTT. The excited states of DNTT aggregates are described by tight-binding Hamiltonian combined with electronic couplings. Exciton dynamics coupled to molecular vibrations is modeled by a stochastic Schrödinger equation with spectral densities derived from molecular dynamics simulations and excited-state calculations.

The calculated absorption spectrum is in qualitative agreement with the experimental one. Our theory predicts that the low-energy Frenkel exciton band consists of 8 to 47% of CT character. The obtained excitonic Hamiltonian was used to simulate real-time quantum dynamics with incorporating exciton–phonon interactions in atomistic details. We observe the mixing of CT excitons with Frenkel state in 50 fs after the excitation. Accordingly, an electron–hole separation increases and shows an oscillation pattern as a result of delocalization of electron and hole and electron–hole Coulomb interactions.

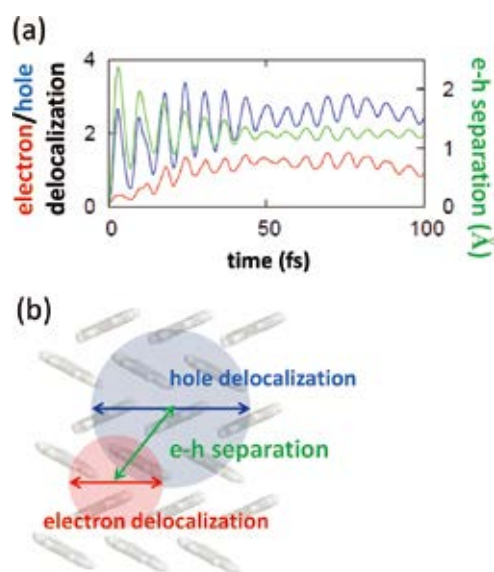


Figure 2. Ultrafast dynamics of mixed Frenkel-CT excitons in DNTT. (a) Electron and hole delocalization lengths, and electron–hole separations. (b) A schematic picture.

2. Polymorphism and Optoelectronic Properties of Anion-Responsible Molecules

π -conjugated molecules, especially aromatic hydrocarbons, show characteristic electronic and optical properties. The planar geometries are useful for constructions of stacking assemblies. Maeda and co-workers have proposed ion-based π -conjugated systems based on dipyrrolyldiketone difluoroboron (BF_2) complexes. Mixed with anion and cationic π -conjugated molecules, they form ion-based molecular assemblies.

Here, we consider the dipyrrolyldiketone BF_2 . This molecule shows the polymorphism of solid-state assemblies with different stacking modes. They have distinct optical and charge transport properties, which depend on their molecular stacking and interactions. In this study, we calculate charge mobility based on fragment molecular orbital calculations for transfer integrals and Marcus theory for charge transfer. Charge mobility is obtained from diffusion constants by Master equation with the hopping rates. Calculated hole mobility correlates well with time-resolved microwave conductivity measurements, suggesting that hole transport is responsible for the photoconductivity.

3. Solution Theories for Nano-Sized Hydrophobic Molecules

Solvation free energy (SFE) is most important thermodynamics quantities in solution chemistry. Molecular dynamics simulations combined with thermodynamic integration or free energy perturbation can offer exact computations of SFEs within statistical error and force fields employed. However, it requires large computational time especially for nano-sized molecular systems. Accurate and efficient estimations of SFEs is still challenging.

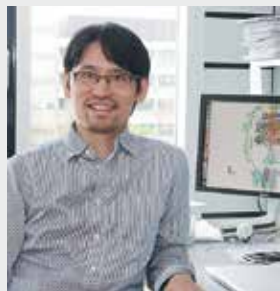
Here, we investigate the accuracy of approximate solution theories for calculating hydration free energies (HFEs) of nano-sized hydrophobic molecules. Energy representation and three-dimensional reference interaction site model (3D-RISM) with different closures were compared with molecular dynamics simulations with the Bennett acceptance ratio. The HFEs from approximate theories are in reasonable agreement for relatively small hydrophobic solutes. However, they show considerable errors in HFEs of large hydrophobic solutes and predict artificial solute-size dependence of the HFEs. A recently-proposed empirical correction based on a partial molar volume (PMV) of a solute significantly improves the 3D-RISM results in such a way that they become qualitatively agreement with the BAR. The success of the PMV correction is discussed in terms of asymptotic behaviors of HFEs in a limit of large solute size.

Reference

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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_0 and F_1 . The F_0 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).
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- K. Okazaki and G. Hummer, "Elasticity, Friction, and Pathway of γ -Subunit Rotation in F_0F_1 -ATP Synthase," *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).
- M. Sugawa, K. Okazaki, M. Kobayashi, T. Matsui, G. Hummer, T. Masaïke 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 F₁-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 F₁. 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 released 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.

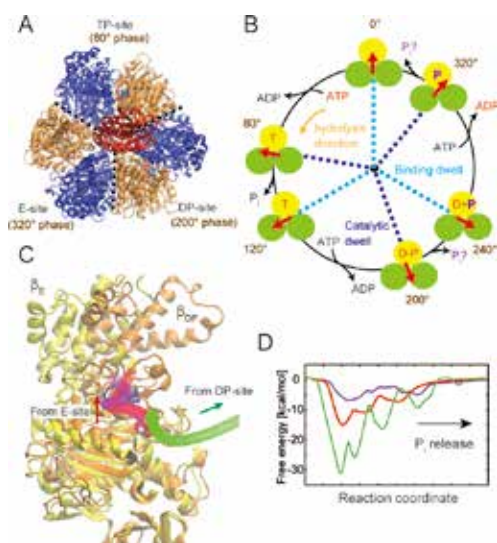


Figure 1. Mechanochemical coupling scheme and P_i release in F₁-ATPase.

2. Torsional Elasticity and Friction of Rotor in F₀F₁-ATP Synthase

It has been known that there is a symmetry mismatch between F₀ c-ring and F₁ $\alpha_3\beta_3$ ring. The F₁ $\alpha_3\beta_3$ ring has (pseudo) three-fold symmetry, while the F₀ 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 F₁ part, while it has to rotate by 45° steps in F₀ 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 F₀F₁ rotation (Figure 2C). It turned out that with the two-substep F₁ the pathway is blocked by high-energy states. To solve this situation, F₁ needs three substeps as was measured for human mitochondrial F₁ recently. From the estimated torsional friction, we predict that γ -rotation can be as fast as 1 MHz and this fast rotation can be observed with an attached bead as small as 20 nanometer diameter.

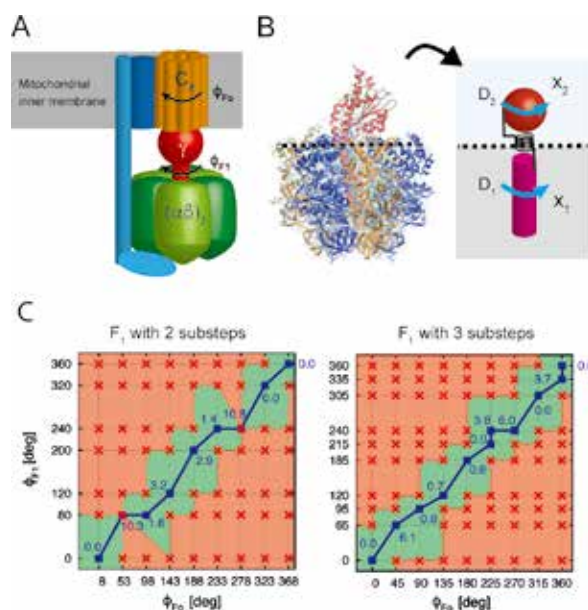


Figure 2. Viscoelastic model of F₀F₁-ATP synthase.

References

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- 2) M. Sugawa, K. Okazaki, M. Kobayashi, T. Matsui, G. Hummer, T. Masaïke 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 and the unique dissolution process of cellulose polysaccharides using molecular dynamics simulation technique.

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

We have developed a procedure for 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.

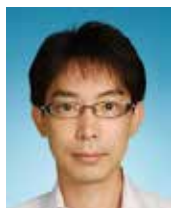
2. Investigations of Ionic Liquids¹⁻²⁾ with Molecular Dynamics Simulation

We focus on the dynamical properties on ionic liquids (ILs). With molecular dynamics simulation procedure, it has 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, *AIP Conference Proceedings for 8th International Conference of Computational Methods in Sciences and Engineering (ICCMSE) 2010, AIP Conf. Proc.* **1642**, pp. 518–521 (2015).
- 2) T. Ishida and H. Shirota, *J. Phys. Chem. B* **117**, 1136–1150 (2013).

Visiting Professors



Visiting Professor

SHIGETA, Yasuteru (*from University of Tsukuba*)

Computational Analyses on Biological Functions at the Atomic Scale

Life is a system that converts a variety of energy (mechanical, electrostatic, thermal, chemical, information, and so forth) into each other to maintain itself. For the understanding and controlling phenomena in the life, elucidation of the relationship between the three-dimensional conformational changes and biological functions of proteins at the atomic scale has become one of the most important issues. However, these conformational changes are induced as slow dynamics upon collective motions, including biologically relevant large-amplitude fluctuations of proteins. Our group develops an efficient conformational search method using molecular dynamics simulations and investigates dynamics of proteins that drive specific biological functions on the basis of quantum mechanical and statistical physics-based methods.



Visiting Associate Professor

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

Combined Simulation and Experiment Reveals Physics of Aqueous Interface

Our group aims at obtaining molecular-level understanding of the structure and dynamics of aqueous liquid interfaces, with particular emphasis on water. To this end, by using molecular dynamics (MD) simulations, we have made a direct connection to experiments using 'theoretical sum-frequency generation (SFG) spectroscopy'—both in aiding the interpretation of experimental results, as well as designing novel experiments and experimental schemes. We have interrogated the molecular conformation of water at the water-air and water-lipid interface as well as the effects of surface-active molecules on the conformation of the interfacial water molecules. One research highlights that the water's O–H group near zwitterionic lipids orients *up* toward lipid uniformly, although zwitterionic lipids can be, in principle, electronegative/positive. Having established an excellent agreement between SFG simulation and experiment, we also predicted the molecular mechanism of water evaporation from MD simulation. It turned out that the evaporation is not stochastic process, but has certain pathway for transferring the momentum of water.



Visiting Associate Professor

KATO, Tsuyoshi (*from The University of Tokyo*)

Development of Quantal Dynamical Theory and Its Application to Molecular Dynamics

I am studying in the area of quantal molecular dynamics mainly focusing on the developments of new methods to calculate the electronic and nuclear dynamics in molecules interacting with strong laser field. Currently, 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 Kohn-Sham problem, and presently I am analyzing the relations among some exact wave function theories and density functional theory. 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. Consequently, we are able to use the notions, that are deduced from the analysis of the properties of the exact effective potentials, within the quantum optimal control theory as well as to analyze the chemical reactions.





RESEARCH ACTIVITIES

Photo-Molecular Science

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

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

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

Department of Photo-Molecular Science Division of Photo-Molecular Science I



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Education

1983 B.S. The University of Tokyo
1991 Ph.D. The University of Tokyo

Professional Employment

1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
1993 Associate Professor, The University of Tokyo
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Award

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

Member

Assistant Professor
NARUSHIMA, Tetsuya
IMS Research Assistant Professor
NISHIYAMA, Yoshio*
Visiting Scientist;
JSPS Invited Fellow
JACK, Calum†
Post-Doctoral Fellow
LE, Quang Khai
Graduate Student
HASHIYADA, Shun
Technical Fellow
ISHIKAWA, Akiko
Secretary
NOMURA, Emiko

Keywords

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

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

lar 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, and so forth.

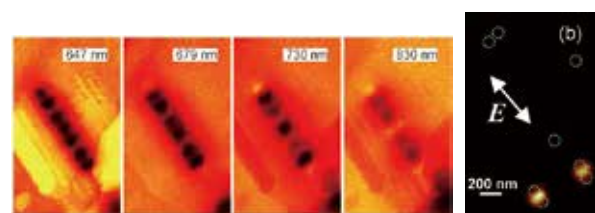


Figure 1. (Left four panels) Near-field transmission images of gold nanorod ($20 \text{ nm}^D \times 510 \text{ nm}^L$). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates 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. Observation of Plasmon Wave Packet Motions via Femtosecond Time-Resolved Near-Field Imaging Techniques^{1,2)}

The generation and dynamics of plasmon wave packets in single gold nanorods were observed at a spatiotemporal scale of 100 nm and 10 fs via time-resolved near-field optical microscopy. Because an ultrashort pulse has a broad spectral width, one can excite more than two resonant modes of materials if their frequency range is covered with the pulse spectrum. In this study, dynamics after excitation of single plasmon mode (for a relatively low aspect ratio rod) and that after multi-mode excitation (for a relatively high aspect ratio rod) were compared.

When a single plasmon mode was excited, time-resolved signals showed single-exponential decay profiles reflecting the dephasing of the mode, and time-resolved near-field image feature was essentially independent of time. In contrast, if two plasmon modes of a nanorod were excited coherently with an ultrashort near-field pulse, a decay and revival feature of the time-resolved signal was obtained, which reflected the reciprocating motion of the wave packet. The time-resolved near-field images were also indicative of the wave packet motion. At some period of time after the excitation, the spatial features of the two modes appeared alternately (Figure 2(a)), showing motion of plasmonic wave crests along the rod. The wave packet propagation was clearly demonstrated from this observation with the aid of a simulation model (Figure 2(b,c)). The present experimental scheme opens the door to coherent control of plasmon-induced optical fields in a nanometer spatial scale and femtosecond temporal scale.

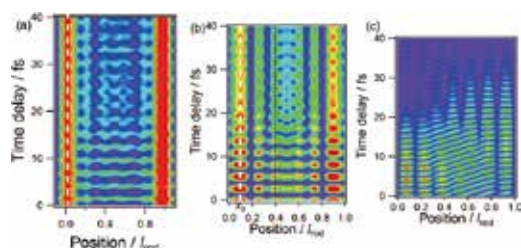


Figure 2. (a) Time variation (ordinate) of line profiles of transient near-field images of a gold nanorod along the rod axis (abscissa). At ~ 20 fs, two different features of plasmon modes appear alternately with a period of ~ 3 fs. (b) Model simulation of a position-time profile of excitation probability that corresponds to the near-field observation in panel (a), which qualitatively reproduced the characteristic feature observed at ~ 20 fs. (c) Simulated time evolution of the plasmon wave packet after local excitation with a single ultrashort pulse at a position x_0 in panel (b). Propagation of the wave packet from left to right (0–15 fs), reflection at the right end, and back propagation to left (20–40 fs) are observed.²⁾

Awards

HASHIYADA, Shun; Excellent poster award 2015, Japan Society for Molecular Science.

NISHIYAMA, Yoshio; The OMC outstanding award, Optical Manipulation Conference 2016.

2. Optical Activity Governed by Local Chiral Structures in Two-Dimensional Curved Metallic Nanostructures³⁾

Chiral nanostructures show macroscopic optical activity. Local optical activity and its handedness are not uniform in the nanostructure, and are spatially distributed depending on the shape of the nanostructure. In this study we fabricated curved chain nanostructures made of gold by connecting two or more arc structures in a two-dimensional plane. Spatial features of local optical activity in the chain structures were evaluated with near-field circular dichroism (CD) imaging. The electromagnetic simulation predicted that local optical activity appears at inflection points where arc structures are connected, and the handedness of the local optical activity was dependent on the handedness of the local chirality at the inflection point. In the near-field CD images of fabricated chain nanostructures, the local optical activity was found to be determined by the handedness of the inflection point, for the fabricated chain structures having two or more inflection points, consistent with the simulation. The local optical activity was thus governed primarily by the local chirality of the inflection points for the gold chain structures.

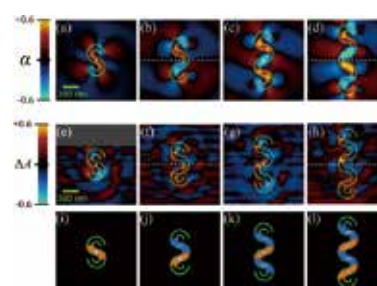


Figure 3. (a–d) Spatial distribution of theoretically calculated electric field intensity difference (α) for curved chain structures. (e–h) Spatial distribution of local CD signal (ΔA) observed with a near-field CD microscope for chain structures. (i–l) Schematic representations of the measured CD signal distribution in panels (e–h). The wavelength of observation was 785 nm for both the calculation and the imaging experiment. The inflection points gave local CD signals whose signs were determined by the handednesses (chirality) of the local structures, except for the minimal chain (“S” structure).³⁾

References

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- 2) Y. Nishiyama, K. Imura and H. Okamoto, *Nano Lett.* **15**, 7657–7665 (2015).
- 3) T. Narushima, S. Hashiyada and H. Okamoto, *Chirality* **28**, 540–544 (2016).

* Present Address: Kanazawa University

† Graduate Student from University of Glasgow

Exploring Quantum-Classical Boundary

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



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Education

1987 B. E. The University of Tokyo
1992 Ph.D. The University of Tokyo

Professional Employment

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

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

Member

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SOMMER, Christian
TAKEDA, Shuntaro
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TANAKA, Akira
Post-Doctoral Fellow
GOTO(SHIKANO), Haruka
Visiting Scientist
SOUQUET BASIÈGE, Hubert*
TIRUMALASETTY PANDURANGA, Mahesh*
Graduate Student
MIZOGUCHI, Michiteru
RASTI, Soroush
KONDO, Norihisa†
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INAGAKI, Itsuko
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 and a bulk solid, envisaging the quantum-classical boundary connected smoothly.

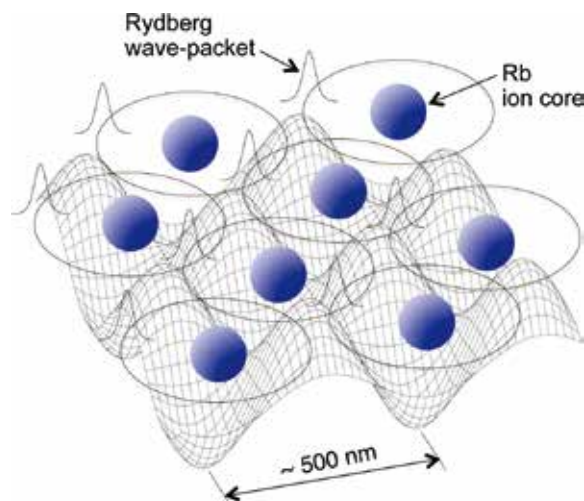


Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.²⁾

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,” *arXiv:1504.03635* (2015).

1. Time Domain Ramsey Interferometry with Interacting Rydberg Atoms³⁾

We theoretically investigate the dynamics of a gas of strongly interacting Rydberg atoms subject to a time domain Ramsey interferometry protocol. The many-body dynamics is governed by an Ising-type Hamiltonian with long range interactions of tunable strength. We analyze and model the contrast degradation and phase accumulation of the Ramsey signal and

identify scaling laws for varying interrogation times, ensemble densities and ensemble dimensionalities.

References

- 1) K. Tonomura *et al.*, *Am. J. Phys.* **57**, 117 (1989).
- 2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
- 3) C. Sommer *et al.*, *arXiv:1604.02314* (2016).

Awards

TAKEDA, Shuntaro; Young Scientist Award of the Physical Society of Japan (2016).

TAKEDA, Shuntaro; Inoue Research Award for Young Scientists (2016).

* IMS International Internship Program

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

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



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Education

1976 B.S. Kyoto University
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

Awards

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

Member

Assistant Professor
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YAMANE, Hiroyuki
JSPS Post-Dctoral Fellow
YUZAWA, Hayato

Secretary

NAKANE, Junko
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 N₂, O₂, and H₂O 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 photo-

electron 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.

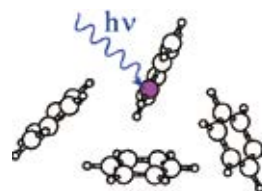


Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

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 Measurements," *Phys. Rev. Lett.* **111**, 086602 (5 pages) (2013).

1. Local Structures of Liquid Benzene Studied by C K-Edge Soft X-Ray Absorption Spectroscopy at Different Temperatures

Recently, we reported C K-edge X-ray absorption spectroscopy (XAS) of benzene in gas, cluster and solid phases.^{1,2)} Although solid benzene mainly shows T-shaped structures, liquid benzene shows both T-shaped and parallel structures. In this work, we have measured C K-edge XAS of liquid benzene at different temperatures by using a transmission-type liquid flow cell,³⁾ and studied the temperature effect of the molecular interaction.

Figure 2(a) shows C K-edge XAS of liquid benzene at different temperatures. The C 1s $\rightarrow \pi^*$ peak shows adiabatic (0, 0) transition and vibrational fine structures at the higher photon energy. Figure 2(b) shows the energy shifts of (0, 0) transition peaks of liquid benzene from gas as a function of temperature. The π^* peak shows a shift to the lower photon energy by increasing the temperature. The energy shift of liquid benzene relative to the gas phase is 29.4 meV at 25.3 °C. This shift is smaller than in solid benzene and clusters, which is 55 meV²⁾ and 70 meV,¹⁾ respectively.

The lower energy shift of the π^* peak is caused by induced polarization with surrounding molecules. Because the molecular distance in solid phase is smaller than that in liquid phase, the π^* peak in solid phase shows lower photon energy shifts than that in liquid phase. We have performed molecular dynamics simulations of liquid benzene at different temperatures. The molecular distance in the T-shaped structure shows longer distances at higher temperatures. On the other hand, we found that the molecules in the parallel structure are getting close to each other by increasing the temperature. The lower energy shifts of the π^* peak at higher temperatures would be derived from this parallel structure. In the near future, we will discuss the molecular interaction in liquid benzene by correlating C K-edge XAS results with infrared spectroscopy and molecular dynamics simulations.

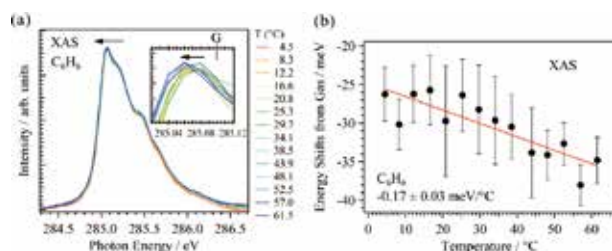


Figure 2. (a) C K-edge XAS of liquid benzene at different temperatures. The inset shows the maximum of the C 1s $\rightarrow \pi^*$ transition in greater detail. (b) Energy shifts of C 1s $\rightarrow \pi^*$ (0, 0) transition peak of liquid benzene relative to gaseous benzene as a function of temperature.

2. Site-Specific Organic/Metal Interaction Revealed from Shockley-Type Interface State

The Shockley state is a well-known surface state associated with the breakdown of the bulk-crystal periodicity at the surface, and can be observed by using angle-resolved photoemission spectroscopy (ARPES). In the present work, we have applied the Shockley-state measurement to the well-ordered monolayer of Co phthalocyanine (CoPc) on Au(111), in order to study the site-specific organic/metal interfacial interaction quantitatively.

The Shockley state of CoPc/Au(111) is compared with that of H₂Pc/Au(111) and that of the clean Au(111) at 23 K in Figure 3. The observed Shockley state of both CoPc/Au(111) and H₂Pc/Au(111), labeled S', shows the energy shift of about 120 meV towards the Fermi level (E_F) from that of the clean Au(111) surface. The observed upshift of the Shockley state upon adsorption originates from the exchange interaction of surface electron systems by CoPc. Furthermore, one more dispersive band just below E_F is observed for CoPc/Au(111), labeled X, which is not observable for H₂Pc/Au(111).

We found from the temperature dependence of ARPES for CoPc/Au(111) that peaks S' and X can be ascribed to the Shockley state modified by the site-specific interfacial interaction at the Pc-ligand site and the central-metal Co site in the molecule, respectively. Using the relation of $E_a = 0.106 \Delta E_{SS}$, where E_a and ΔE_{SS} are the adsorption energy and the shift in the Shockley state, respectively,⁴⁾ we determined the site-specific interfacial bonding strength in CoPc/Au(111) at 23 K as $E_a = 13.0 \text{ meV}/\text{\AA}^2$ at the Pc-ligand site and $E_a = 45.9 \text{ meV}/\text{\AA}^2$ at the central-metal Co site.

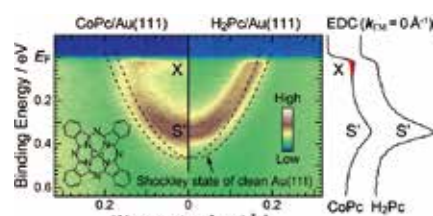


Figure 3. The E - k map around the Shockley state for CoPc/Au(111) and H₂Pc/Au(111) at 23 K, together with the best-fit curve of the Shockley state for the clean Au(111) at 23 K (black dashed curve).

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Awards

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Electronic Property of Functional Organic Materials

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Keywords

Photoelectron Spectroscopy, Molecular Film, Electronic State

Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However the mechanisms and its origin of various device characteristics are still under debate. Scientific mysteries would be raised because people have believed that electronic structure of FOM would be conserved as in an isolated molecule for solid phases due to van der Waals interaction. To reveal characteristics of FOM the key investigation would be on precise experiments on the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the impacts of weak interaction on the electronic structure would be appeared as small intensity modulation of 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 happens for the FOM at the interface upon weak interaction, an evaluation on the wave-function

spread of the electronic states would be very important because the interface states for the physisorbed systems are described to be a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Seeing a modification of electron wave function upon weak electronic coupling as well as strong electron–phonon coupling is central issue on our agenda.

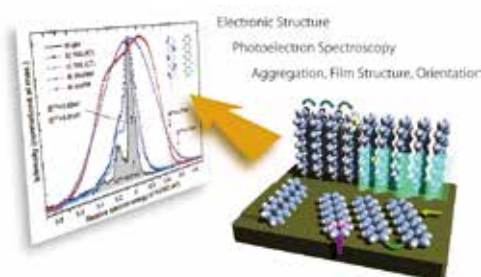


Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

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- S. Kera, H. Yamane and N. Ueno, “First Principles Measurements of Charge Mobility in Organic Semiconductors: Valence Hole-Vibration Coupling in Organic Ultrathin Films,” *Prog. Surf. Sci.* **84**, 135–154 (2009).

1. Charge Transfer States Appear in the π -Conjugated Pure Hydrocarbon Molecule on Cu(111)¹⁾

Understanding the metal and adsorbed molecule interaction is required to discuss the mechanism of charge transfer in functional molecular solids. We report on the results of experimental and theoretical studies on the electronic structure of gas-phase diindenoperylene (DIP) and DIP-monolayer (ML) on Cu(111). Vapor-phase ultraviolet photoelectron spectroscopy (UPS) was realized for 11.3 mg of DIP, giving reference orbital energies of isolated DIP, and UPS and inverse photoemission spectroscopy of DIP-ML/graphite were performed to obtain DIP-ML electronic states at a weak interfacial interaction. Furthermore, first-principles calculation clearly demonstrates the interfacial rearrangement. These results provide evidence that the rearrangement of orbital energies, which is realized in HOMO–LUMO and HOMO–HOMO-1 gaps, brings partially occupied LUMO through the surface-induced aromatic stabilization (SIAS) of DIP, a pure hydrocarbon molecule, on Cu(111) surface. It has been considered in SIAS, that a site-specific interaction between the heteroatoms in adsorbate molecules and the substrate plays a key role, while the present results demonstrated that the heteroatoms are not necessarily required for the formation of the charge transfer states through SIAS. In passing, it was reported that no charge transfer states are formed at the interface of perylene on Ag(111) and Cu(111), suggesting that the perylene core alone does not play a role in the CT state formation. We therefore conclude that a combination of a specific chemical structure and functional groups leading to the flexibility of the molecular skeleton is a key requirement of SIAS on metal substrates, even if the functional groups do not involve heteroatoms such as indeno-groups in DIP.

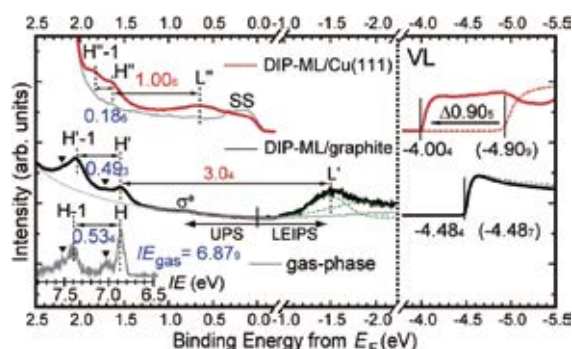


Figure 2. Comparison of He I UPS of DIP-ML on Cu(111) (red), Xe I UPS and LEIPS of DIP-ML on graphite (black), and gas-phase UPS (gray). The right panel shows vacuum levels before (dashed curves) and after (solid curves) DIP deposition. Spectra of clean surfaces of Cu(111) and graphite are also shown (pale gray). SS indicates the surface states of clean Cu(111). The gas-phase spectrum is shown in ionization energy for comparison with DIP MLs. Vibration satellites in the gas phase and DIP-ML-graphite spectra are indicated by

inverted triangles. Weak features marked by σ^* in UPSs of DIP-ML-graphite and the graphite substrate are the conduction band features of graphite.

2. Mechanism for Doping Induced p Type C₆₀ Using Thermally Evaporated Molybdenum Trioxide (MoO₃) as a Dopant²⁾

Thermally evaporated molybdenum trioxide (MoO₃) doped C₆₀ films, which could change n type features of pristine C₆₀ to form a p type mixed C₆₀ layer, are investigated by x-ray and ultraviolet photoelectron spectroscopy. It is found that C₆₀ HOMO progressively shifts closer to the Fermi level after increased MoO₃ doping concentration, and final onset of C₆₀ HOMO is pinned at binding energy of 0.20 eV, indicating the formation of p type C₆₀ films. It is proposed that in charge transfer induced p type C₆₀ formation, due to large electron affinity of MoO₃ (6.37 eV), electrons from HOMO of C₆₀ could easily transfer to MoO₃ to form cations and therefore increase hole concentration, which could gradually push C₆₀ HOMO to the Fermi level and finally form p type C₆₀ films. Moreover, clear different types of C₆₀ species have been confirmed from UPS spectra in highly doped films.

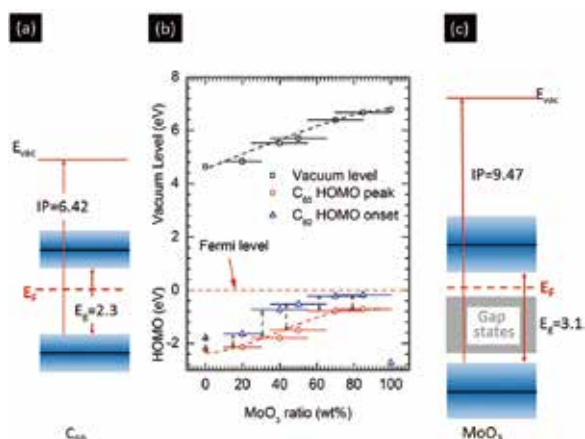


Figure 3. Evolution of energy level of MoO₃-doped C₆₀ film with MoO₃ ratios. (a) and (c) Energy level diagram for pristine C₆₀ and MoO₃ films respectively; (b) summarized HOMO peak of C₆₀, HOMO onset of C₆₀ and vacuum level as a function of different MoO₃ doping ratios are shown according to the Fermi level position.

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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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- E. Roussel, C. Evain, C. Szwaj, S. Bielawski, J. Raasch, P. Thoma, A. Scheuring, M. Hofherr, K. Ilin, S. Wunsch, M. Siegel, M. Hosaka, N. Yamamoto, Y. Takashima, H. Zen, T. Konomi, M. Adachi, S. Kimura and M. Katoh, "Microbunching Instability in Relativistic Electron Bunches: Direct Observations of the Microstructures Using Ultrafast YBCO Detectors," *Phys. Rev. Lett.* **113**, 094801 (2014).

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 electron sources are being developed and tested. New beam diagnostic technologies 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.

Award

YAMAGUCHI, Kenta; 2016 Annual Meeting Award of the Particle Accelerator Society of Japan.

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Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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Keywords

Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials has attracted more attentions in the last few decades because of their unusual and fascinating properties such as high- T_c superconductivity, giant magnetoresistance, heavy fermion and so on. Those unique properties can offer a route toward the next-generation devices. We investigate the mechanism of the physical properties as well as the electronic structure of those materials by using angle-resolved photoemission spectroscopy (ARPES), a powerful tool in studying the electronic structure of complex materials, based on synchrotron radiation.

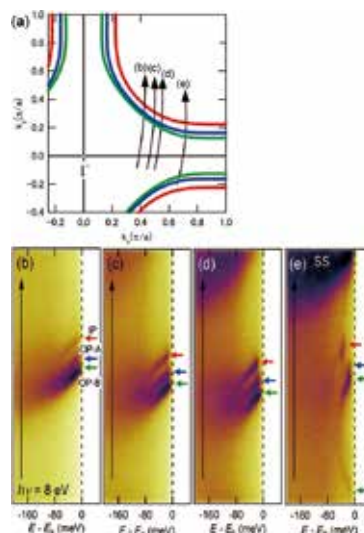


Figure 1. ARPES intensity plot of slightly-overdoped Bi2223 taken with $h\nu = 8$ eV along FS.

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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1. Triple-Layer Splitting in Slightly-Overdoped $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ 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 $n \geq 4$. Several mechanisms have been proposed to explain the n dependence of T_c . According to the tunneling mechanism of Cooper pairs between the CuO_2 planes, $T_{c,\text{max}}$ should increase with increasing n . However if one takes into account the charge imbalance between the planes and the existence of competing order, $T_{c,\text{max}}$ takes a maximum at $n = 3$ in agreement with experiment. Meanwhile, T_c shows tendency to increase with next-nearest-neighbor Cu–Cu hopping parameter t , which increases with the number of CuO_2 planes. Also, T_c increases with decreasing degree of out-of-plane disorder. So far, which governs the n dependence of $T_{c,\text{max}}$ has been unclear because of the lack of detailed knowledge about the electronic structure of the multi-layer cuprates.

In the case of Bi-based HTSCs, the optimum T_c ($T_{c,\text{max}}$) increases from the single-layer $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ (Bi2201, $T_{c,\text{max}} = 35$ K), the double-layer $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212, $T_{c,\text{max}} = 95$ K) to the tri-layer $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (Bi2223, $T_{c,\text{max}} = 110$ K). Angle-resolved photoemission spectroscopy (ARPES) studies of double-layer Bi2212 and four-layer $\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_8\text{F}_2$ (F0234) have revealed the splitting of band dispersions and Fermi surfaces (FSs). In Bi2212, hybridization between the two CuO_2 planes causes splitting into the bonding and anti-bonding bands. The ARPES study on F0234 has indicated two energy bands due to the different hole concentrations of the outer CuO_2 planes and the inner CuO_2 planes, and correspondingly two FS sheets have been observed. In the previous ARPES results on the tri-layer Bi2223 have revealed only two FSs originated different hole concentrations of inner (IP) and outer (OP) CuO_2 planes and band splitting has not been observed. In the present study, we performed detailed low-photon-energy dependent ARPES study of slightly-overdoped Bi2223 in the superconducting states ($T = 12$ K) at UVSOR BL7U, and successfully observed the third band dispersion originated by the band splitting.

In Figures. 1(b)–(e), we plot ARPES intensity taken with $h\nu = 8$ eV along FS, where the momentum positions in the k -space are shown in Figure 1(a). Three different band dispersions have been clearly observed as indicated by three arrows. By comparing the band positions in the momentum space to previous report, we have found that the band located in the center indicated by blue arrow is the newly observed band. Here, it should be noted that the intensity of each band strongly depended on the energy of incident photons and this results could not be obtained if the synchrotron light source was not used where the photon energy of the measurements is tunable.

In Figure 2, the symmetrized ARPES intensity against the

Fermi level around $k_x \sim 0.54$ (\AA^{-1}) is plotted. It clearly shows that three bands have different superconducting gaps.

The present results give us the following important messages. First, there is strong interaction between CuO_2 planes in Bi2223. Since this interaction has not been observed in four-layer F0234, it can be a critical factor to achieve the highest T_c . Second, it is not obvious why three bands show different superconducting gap size. To clarify the relationship between the interaction between CuO_2 planes and high- T_c superconductivity, it is necessary to perform temperature dependent measurements along the FS to define the Fermi arc region which should strongly contribute to the superconductivity.

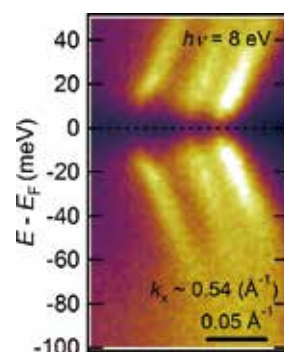


Figure 2. The symmetrized ARPES intensity against the Fermi level around $k_x \sim 0.54$ (\AA^{-1}).

2. Development of New Spin-Resolved ARPES

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 $h\nu = 6$ –40 eV. 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 from FY2016. The newly developed electron lens system successfully achieved ~ 100 times better momentum resolution perpendicular to slit direction compared to the conventional ARPES. Together with the image-spin detection, which is under development, one should be able to obtain spin information of materials with much higher efficiency than the conventional spin-resolved ARPES.

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Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

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Keywords

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

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

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

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

The electronic relaxation and dissociation processes are coupled, and depend on the electronic and geometrical structure of the molecules.

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

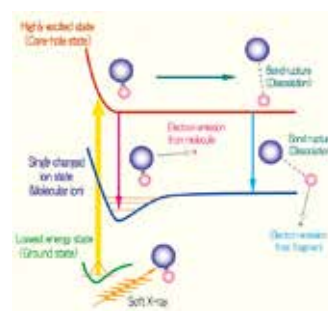


Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

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- H. Iwayama, T. Kaneyasu, Y. Hikosaka and E. Shigemasa, "Stability and Dissociation Dynamics of N_2^{2+} Ions Following Core Ionization Studied by an Auger-Electron-Photoion Coincidence Method," *J. Chem. Phys.* **145**, 034305 (8 pages) (2016).

1. Site-Specific Production of H_3^+ Ions Following Core Ionization of CH_3Cl

Trihydrogen cation H_3^+ is one of the most interesting molecules in diverse fields from chemistry to astronomy because it is the simplest triatomic molecule and plays an important role in the interstellar. While the H_3^+ ions can be mainly generated from the proton transfer reactant ($\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$), it was shown that unimolecular reactions of soft x-ray irradiated CH_3X molecules ($\text{X} = \text{Cl}, \text{OH}, \text{CN}, \text{etc.}$) also have a contribution of H_3^+ formation in the interstellar.¹⁾

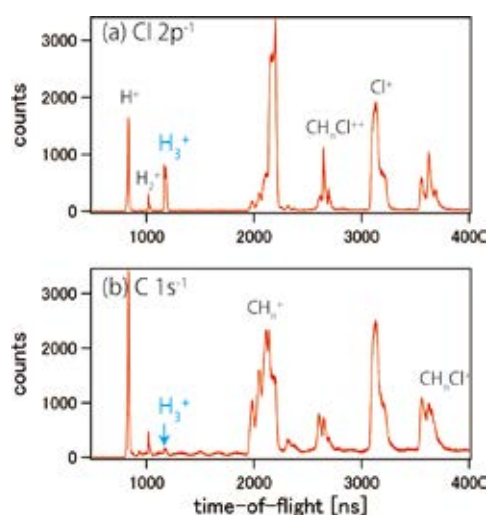


Figure 2. Time-of-flight spectra of ions taken in coincidence with (a) Cl 2p and (b) C 1s photoelectrons.

In this work, we investigate the H_3^+ production mechanism of soft x-ray irradiated CH_3Cl molecules with using an Auger-electron-ion coincidence technique, which allows us to correlate Auger final dicationic states with product ions. From coincidence Auger spectra, we reveal dicationic states which form the H_3^+ ions.

Figure 2 shows total ion TOF spectra following the Cl 2p and C 1s photoionization. Main fragment ions are H_n^+ ($n = 1, 2, 3$), CH_n^+ ($n = 0-3$), Cl^+ and CH_nCl^+ ($n = 0, 1, 2$). CH_3Cl^+ ions were not observed since the parent molecules following the Auger decay are doubly charged. Doubly charged ions such as Cl^{2+} and $\text{CH}_n\text{Cl}^{2+}$ ($n = 0-3$) were also observed. The most remarkable difference in fragmentation between the Cl 2p and C 1s photoionization is the relative abundance of H_3^+ ions. The relative intensity of H_3^+ ions for the Cl 2p photoionization is ten times larger than that for the C 1s photoionization. In order to correlate the production of H_n^+ ($n = 1, 2, 3$) ions with the Auger final states, we have measured the coincidence Auger spectra. It is clearly seen that the formation of the H_3^+ ions is related to only the lowest band around the binding energy of 32 eV for both the Cl 2p and C 1s photoionization. In order to understand the mechanism of such a site-specific production of the H_3^+ ions, theoretical calculations for the Auger final states of the CH_3Cl molecule are highly desired.

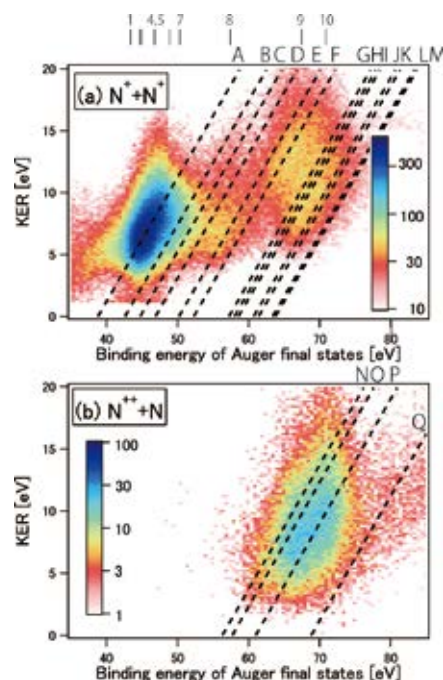


Figure 3. Two-dimensional Auger-electron-photoion coincidence maps for (a) $\text{N}_2^{2+} \rightarrow \text{N}^+ + \text{N}^+$ and (b) $\text{N}^{2+} + \text{N}$ dissociation pathways.

2. Photoionization of Helium Atoms by Higher Harmonic Radiation from a Helical Undulator

A core shell electron in a molecule can be promoted to unoccupied orbitals when a photon energy is tuned to resonances. For light elements ($Z < 26$), the Auger decay is the dominant process after the core excitation, and various ionic states are formed through the Auger electron emissions. The stability and dissociation dynamics of the Auger final states depend on their charge states and electronic states, which can be investigated by using an Auger-electron-photoion coincidence technique. In this work, we investigate the stability and dissociation dynamics of core excited N_2 molecules.²⁾

Two-dimensional Auger-electron-photoion coincidence maps are shown in Figure 3. The maps reveal diagonal structures, indicating correlations between Auger-electron binding energies and ion KERs. These correlations come from the fact that the KER is equal to the difference between the binding energy of the Auger final state and the dissociation limit energy. The dissociation limit energy corresponds to the binding energy at the dissociation asymptote, and depends on the electronic states of atomic fragments in addition to charge states. From the correlations in Figure 3, we have derived the dissociation limits of dissociative Auger final states. It is also found that the $X\ ^1\Sigma_g^+$, $A\ ^1\Pi_u$, and $c\ ^3\Sigma_u^+$ states are associated with the formation of metastable dicationic states.

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Micro Solid-State Photonics

Laser Research Center for Molecular Science Division of Advanced Laser Development



TAIRA, Takunori
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Education

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

Professional Employment

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

Awards

2004 Persons of Scientific and Technological Research Merits, Commendation by Minister of Education, Culture, Sports, Science and Technology, Japan
2010 OSA Fellow Award, The Optical Society (OSA)
2012 SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
2014 IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)

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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-

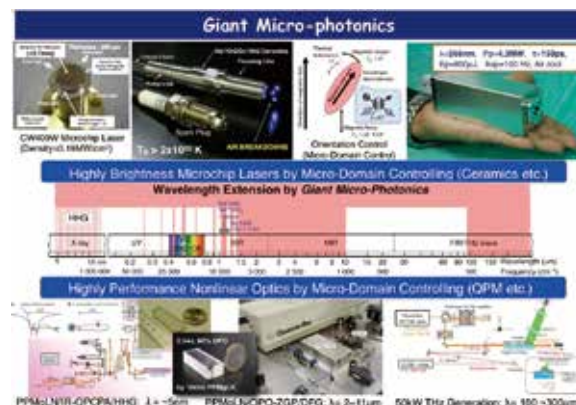


Figure 1. Giant micro-photonics.

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.

Selected Publications

- H. Sakai, H. Kan and T. Taira, “>1 MW Peak Power Single-Mode High-Brightness Passively Q-Switched Nd³⁺:YAG Microchip Laser,” *Opt. Express* **16**, 19891–19899 (2008).
- M. Tsunekane, T. Inohara, A. Ando, N. Kido, K. Kanehara and T. Taira, “High Peak Power, Passively Q-Switched Microlaser for Ignition of Engines,” *IEEE J. Quantum Electron.* **46**, 277–284 (2010).
- T. Taira, “Domain-Controlled Laser Ceramics toward Giant Micro-Photonics,” *Opt. Mater. Express* **1**, 1040–1050 (2011).
- H. Ishizuki and T. Taira, “Half-Joule Output Optical-Parametric Oscillation by Using 10-mm-Thick Periodically Poled Mg-Doped Congruent LiNbO₃,” *Opt. Express*, **20**, 20002–20010 (2012).
- R. Bhandari, N. Tsuji, T. Suzuki, M. Nishifuji and T. Taira, “Efficient Second to Ninth Harmonic Generation Using Megawatt Peak Power Microchip Laser,” *Opt. Express* **21**, 28849–28855 (2013).

1. Giant-Pulse Nd:YVO₄ Microchip Laser with MW-Level Peak Power by Emission Cross-Sectional Control

Giant-pulse generation laser realized by the emission cross-section control of a gain medium in a passively Q-switched Nd:YVO₄ microchip laser with a Cr⁴⁺:YAG saturable absorber. Up to 1.17 MW peak power and 1.03 mJ pulse energy were obtained with a 100 Hz repetition rate. By combining the Nd:YVO₄ crystal with a Sapphire plate, lower temperature difference between a pump region in the gain crystal and a crystal holder was obtained which helped to keep the cavity in stability zone at elevated temperatures and allowed the achievement of the high peak power for this laser system.

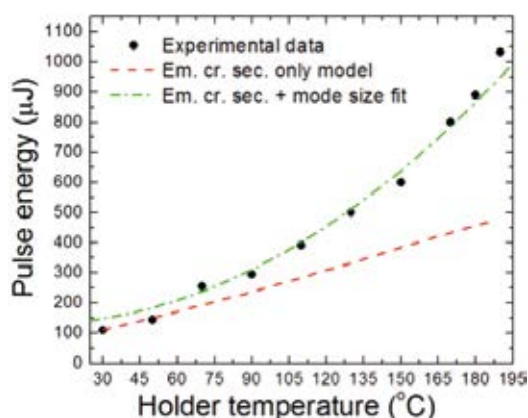


Figure 2. Experimental results of giant-pulse Sapphire/Nd:YVO₄ micro-laser.

2. Optical Gain in the Anisotropic Yb:FAP Laser Ceramics

Currently well-aligned anisotropic laser ceramics can be produced by only the orientation control by slip-casting under the magnetic field, therefore our methods should be the solution for appreciating advantages of anisotropic laser gain media and ceramic gain media, simultaneously. We fabricated Yb:FAP fluorapatite (FAP) ceramics by means of 1.4-T rotational magnetic field. If it can perform the optical amplification, it can be the best candidate of the gain medium for lasers with the extreme high brightness.

The experimental setup is shown in Figure 3. Uncoated *c*-cut Yb:FAP ceramic sample with the thickness of 0.6 mm was positioned with Brewster angle to the optical path. The fluorescence from the sample was detected by the spectrometer through the pump-cut filter (both of setup-a and -b) and the mirror-2 (only setup-b). As a result, fluorescence from anisotropic Yb:FAP laser ceramics was amplified to 2.8 times by constructing an optical resonator.

This amplification indicates that the laser-diode pumping formed the optical gain comparable to the optical loss in Yb:FAP ceramics. We are now expecting we can realize laser oscillation by use of the optical gain in Yb:FAP ceramics.

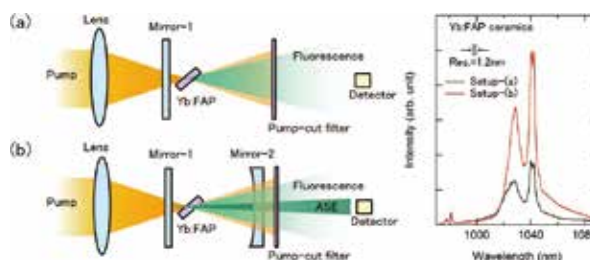


Figure 3. Experimental setup for the detection of fluorescence from Yb:FAP ceramics and their signals. (a) Without output coupler. (b) With output coupler.

3. Periodic Laminar Structured Quartz for Quasi-Phase Matched Wavelength Conversion

Crystal quartz, used in the first second harmonic generation (SHG) by Franken *et al.* in 1961, is one of major non-linear material. Although its excellent optical properties, such as short absorption edge and high laser-damage threshold, its small birefringence has limited practical applications by conventional birefringent phase matching scheme.

Recent progress of laser-system development enabled to use intense short pulses with narrow spectra between ps and sub-ps pulse region, and periodic laminar structure (PLS) quartz pumped by the intense laser have become practical choice for next-generation wavelength-conversion device.

Figure 4(a) shows improvement of SHG-green output energy by PLS quartz. Resulting SHG by 48-plates stacking was increased 500 times higher than single-plate, non-phase matched SHG. Figure 4(b) shows SHG output on input pump energy of 48-plates PLS quartz. Maximum output energy of 8 μJ with 0.54 ns pulse duration could be obtained. Wavelength conversions such as third and forth harmonic generation by PLS quartz pumped by intense MCL can be also expected.

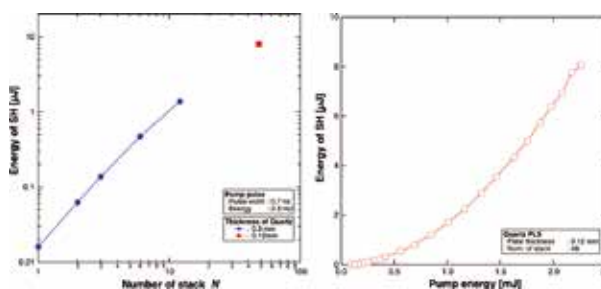


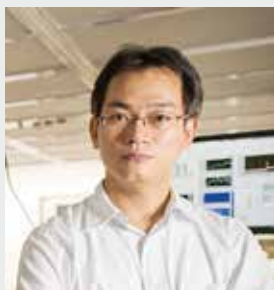
Figure 4. (a) Improvement of SHG output by PLS, (b) SHG output on input pump energy at 48-plates PLS.

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- 3) H. Ishizuki and T. Taira, *The 63rd JSAP Spring meeting 2016*, 21a-S611-4 (Mar. 19–22, 2016).

Ultrafast Laser Science

Laser Research Center for Molecular Science Division of Advanced Laser Development



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2002 JSPS Postdoctoral Fellowship for Research Abroad, Vienna University of Technology (–2004)
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2006 Research Scientist, RIKEN
2008 Senior Scientist, RIKEN
2010 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards

1999 Encouragement Award, The Optical Society of Japan
2008 Kondo Award, Osaka University
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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 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 oscillation of infrared light with the period of several femtoseconds were clearly measured with the method as is shown in Figure 1.

Currently, amplitude modulation and phase modulation are common encoding techniques in optical communication. If we can encode information in the shape of the light wave itself,

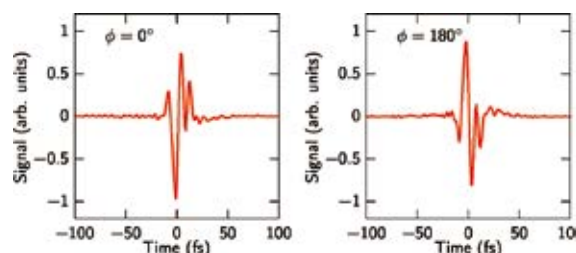


Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

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 and single-shot detection of ultrabroadband mid-infrared spectra has 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).
- Y. Nomura, Y.-T. Wang, A. Yabushita, C.-W. Luo and T. Fuji, "Controlling the Carrier-Envelope Phase of Single-Cycle Mid-Infrared Pulses with Two-Color Filamentation," *Opt. Lett.* **40**, 423–426 (2015).
- T. Fuji, Y. Nomura and H. Shirai, "Generation and Characterization of Phase-Stable Sub-Single-Cycle Pulses at 3000 cm^{-1} ," *IEEE J. Sel. Top. Quantum Electron.* **21**, 8700612 (12 pages) (2015).
- T. Fuji, H. Shirai and Y. Nomura, "Ultrabroadband Mid-Infrared Spectroscopy with Four-Wave Difference Frequency Generation," *J. Opt.* **17**, 094004 (9 pages) (2015).

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 or solid-state lasers are one of the most promising candidates to generate ultrashort pulses in this wavelength region because of their broad emission spectra. We have developed an oscillator based on a Tm-doped ZBLAN ($\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$) fiber which delivers 41 fs pulses at 2 μm .^{1,2} Here we report the development of the amplifier for the oscillator output.

1. Chirped-Pulse Amplifier Based on Thulium-Doped ZBLAN Fibers

ZBLAN ($\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$) is fluoride glass known for high transmittance in the mid-infrared region. This suggests the ZBLAN glass has low material dispersion, which fact would be suitable for ultrafast amplifier system.

Here we demonstrate a chirped-pulse amplifier (CPA) system based on ZBLAN fibers. The experimental setup consists of an oscillator, a stretcher, an amplifier, and a compressor. The pulses from the oscillator are stretched with a normal-dispersion ZBLAN fiber with the core diameter of 5 μm (group velocity dispersion $\sim +30\text{ fs}^2/\text{mm}$). After propagating through the 15-m-long ZBLAN fiber, the pulses are stretched to $\sim 25\text{ ps}$ with $\sim 50\%$ transmission efficiency. After all the optics, the average power of the stretched pulses is 12 mW.

The stretched pulses are sent into the core of a 3.8-m-long, Tm-doped, large-mode-area double-clad ZBLAN fiber. The core of the fiber has a diameter of 32 μm and NA of 0.08, whereas the first clad has a diameter of 200 μm and NA of 0.5. The concentration of Tm ion in the core is 2 mol%.

The fiber is pumped in the counter-propagating direction, *i.e.*, from the side of the non-doped fiber, with a laser diode (LD) operating around 793 nm. When the output power of the LD is increased to 20 W, the maximum output power of 4.5 W is obtained. The slope efficiency is $\sim 29\%$ if we assume the pump coupling efficiency to be 90%.

Figure 1(a) shows the spectrum of the amplifier output, extending over more than 100 nm. This value is much less compared to the oscillator spectral width of 350 nm, which could be explained by gain narrowing effect and strong absorption of Tm ion in the short wavelength region.

The amplified pulses are compressed with a compressor comprised of a pair of transmission grating with grooves of 560 mm^{-1} . The average power after the compressor is 2.5 W. The compressed pulses are characterized with a home-built frequency-resolved optical gating (FROG) device designed for pulses around 2 μm region. A typical FROG trace and the pulse retrieved from it are shown in Figure 1(b) and (c). From this result, the duration of the compressed pulse is determined as 150 fs.

2. Ring Cavity Diode-Pumped Tm:YAP Regenerative Amplifier

To obtain higher pulse energy, we have developed an amplifier based on a solid-state laser, namely, diode pumped Tm:YAP regenerative amplifier.

The CPA system consists of a Tm:ZBLAN fiber oscillator, grating stretcher, ring-cavity regenerative amplifier and grating compressor. The Regenerative amplifier is based on Brewster-cut 4% doped 12 mm long 6.5 $^\circ\text{C}$ water cooled Tm:YAP crystal end-pumped by 794 nm InGaAs diodes, being reimaged into 400 μm spot on the crystal. The CPA system is seeded by 90 fs 52 MHz 4 nJ Tm:ZBLAN fiber oscillator. The seed pulses are sent to the Martinez type stretcher based on a 550 gr/mm transmissive grating and concave mirror with the group delay dispersion of 16 ps^2 , which is necessary to avoid damage and non-linear effects while operating at high energies. The regenerative amplifier generates $>0.9\text{ mJ}$ pulses at 1 kHz repetition rate, or, by decreasing repetition rate to 250 Hz, it is possible to extract up to 2.0 mJ pulses.

Even though the cavity is nitrogen purged (to 9% residual humidity level), the high water vapor absorption leads to generation of strongly modulated spectrum. Measured spectrum supports 0.46 ps duration, but recompression with 560 gr/mm gratings Treacy compressor results in autocorrelation of 1 ps spike with strong 10^8 ps long pedestal, which can be cleaned out by stronger dehumidifying.

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- 1) Y. Nomura and T. Fuji, *Opt. Express* **22**, 12461–12466 (2014).
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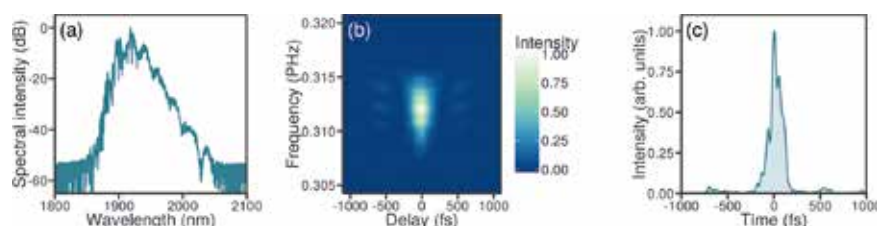


Figure 2. Output after amplification. (a) An output spectrum after the amplifier. (b) A FROG trace measured after compression. (c) The pulse shape retrieved from the FROG trace shown in (b).

Award

NOMURA, Yutaka; The 5th Young Scientist Award of National Institutes of Natural Sciences (2016).

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

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



KATAYANAGI, Hideki
Assistant Professor

Electrodes made of fullerenes and their derivatives and electrolytes containing ionic liquids (ILs) are used in the photovoltaic devices such as dye-sensitized solar cells (DSSCs) 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 fullerenes and carbon nanotubes are

candidates of substitutes for the Pt electrodes. To produce the carbon electrodes, we utilize the Langmuir-Blodgett (LB) technique which has low burden on the environment. Additionally, the LB technique has ability to make ordered structure. 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 are now trying to apply photoelectron spectroscopy to understand the electronic structures of the films which is essential to the efficiency of photovoltaic devices.

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

We have just 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.

3-Dimensional Spectro-Microscopy

UVSOR Facility
Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji
Assistant Professor

Scanning transmission X-ray microscopy (STXM) can realize nano-scale 2-dimensional (2D) chemical state analysis without any destructive process, in combination of soft X-ray absorption spectroscopy with nano-focused X-ray beams obtained by using a Fresnel zone plate (FZP). This STXM technique can be extended to nano-scale 3D analysis based on a computed tomography (CT) method; however, the short working distance (typically, less than 0.5 mm) problem inherent in the FZP applied to the soft X-ray region has to be solved.

We designed a special compact sample cell for CT by using a two-phase stepping motor (shown in Figure 1(a)). As a feasibility test of this method, polystyrene spheres of diameter of 5 μm were used as a standard sample, though 5 μm is a little thicker than the focal depth of the present nano-focused beam. STXM images were successfully obtained with rotating the sample by 3.6° each, and 50 STXM images were acquired in total, where the photon energy was 280 eV and the dwell time

was 3 ms per a pixel. A reconstructed 3-dimensional volume image was obtained as shown in Figure 2. We will plan to apply this technique to μm -scale samples with heterogeneous chemical components.

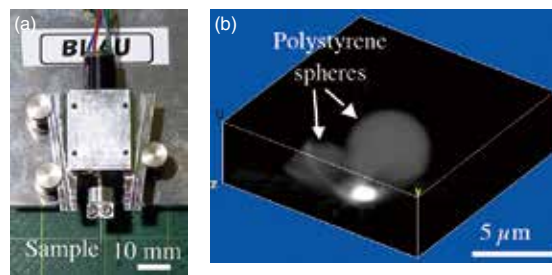


Figure 1. (a) A sample cell for computed tomography and (b) 3-dimensional volume image of polystyrene spheres.

Reference

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Visiting Professors



Visiting Professor
IMURA, Kohei (*from Waseda University*)

Development of Advanced Super-Resolution Microscopy and Their Application to Nanomaterials

Elementary excitations in nanomaterials generate amplified optical fields in the vicinity of the materials. Near-field interactions of molecules with the localized fields provide new frameworks in optical excitations. In order to utilize the novel optical excitation schemes for various applications, understanding of the near-field light-matter interaction is crucial. Near-field optical microscopy, which achieves a super-resolution, is promising for this purpose. Spectroscopic methods in the near-field optical microscope, however, have not been well developed. We have been extending the near-field optical microscope to linear- and non-linear spectroscopic imaging methods. Recently, we have developed reflection and ultrafast near-field imaging methods, and applied them to study optical properties of nanomaterials. We found that giant nonlinearity is effectively induced at the localized fields in the nanomaterials. We are currently extending these studies to controlling linear and non-linear optical properties of nanomaterials in space and time resolved manner. The study will open the door to coherent control of elementary excitations and photochemical reactions.



Visiting Associate Professor
YAMADA, Toyo Kazu (*from Chiba University*)

Dimensional Dependence of Organic Molecular Electronic States

Scanning tunneling microscopy (STM) has been used to visualize material topology with an atomic scale. For 2000–2016, I have developed spin-polarized STM setups to visualize not only atomic structures of materials but also electronic, spin, and quantum structures combined with spectroscopy techniques. 1-nm-size nano-materials, such as nano-magnets, single atoms, single molecules, and graphene nano-ribbons have been studied for realizing new nano-electronic devices with low cost, low power consumption, and high performance. In 2016, we have developed a new low-temperature STM setup and now try to fabricate two-dimensional molecular networks on an atomically-flat noble metal substrate. Subsequently, a magnetic metal will be deposited on the network, and try to make a new two-dimensional magnetic nano-dot array.



Visiting Associate Professor
HIRAHARA, Toru (*from Tokyo Institute of Technology*)

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

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.



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. Currently we are exploring different laser cooling transitions in the fine structure of the 6P levels in 87-Rubidium atoms to obtain higher phase space density. As a separate project from this, we have also started to seek for a new method to manipulate quantum gas with high spatial resolution, using special wavelengths. With these special wavelengths, AC Stark effect from the irradiated laser light will be cancelled out on one of the hyperfine ground sublevels of the atoms, while there will be AC Stark effects on all the other sublevels. So far we are searching for such special wavelengths by spectroscopic measurements, using thermal vapor gas of rubidium.





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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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 a 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 near-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. We have installed nearly ambient pressure (up to ~5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8. We have successfully investigated Pt 3d HAXPES of Pt/C, PtCo/C and PtNi/C cathode catalysts in PEFC under working conditions to reveal degradation mechanism of PEFC. 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.

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- 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. Uemura *et al.*, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
- Y. Wakisaka *et al.*, *Phys. Rev. B* **92**, 184408 (2015).
- K. Eguchi *et al.*, *J. Phys. Chem. C* **119**, 9805 (2015).

1. Ultrafast Structure Determination of Photocarrier in WO₃ Photocatalyst¹⁾

The utilization of solar energies is one of the most fascinating and important research subjects to achieve a future society less dependent on fossil fuels. Many photocatalysts have extensively been developed over last several decades in order to produce hydrogen from water without the generation of harmful pollutants. Recently, tungsten trioxide WO₃ has received much attention since its band gap is 2.6–2.8 eV, implying that it functions as an active photocatalyst under visible light irradiation. In the present work, we have investigated femto- and picosecond structure transformation of photoexcited WO₃ by pump-and-probe time-resolved x-ray absorption fine structure (XAFS) spectroscopy using x-ray free electron laser SACLA in Harima and synchrotron radiation PF-AR (single bunch operation) in Tsukuba.

Figure 1 shows the W L_{III}-edge x-ray absorption near edge structure (XANES) of photoexcited WO₃ recorded in SACLA and the time evolution at x-ray energy point C in Figure 1 is depicted in Figure 2. The shift of the edge energy to a lower x-ray energy side is clearly observed, accompanied by the reduction of the white-line intensity. This implies that the W

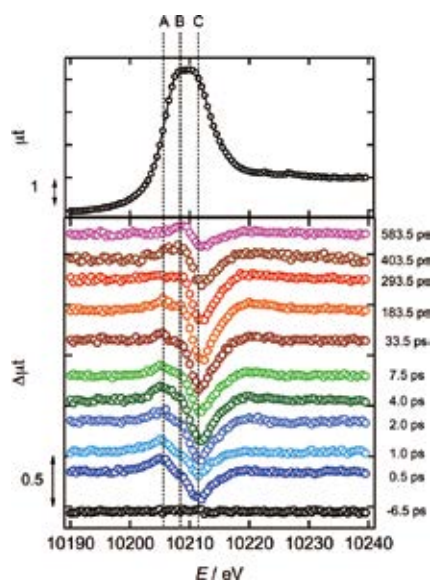


Figure 1. W L_{III}-edge XAFS of the ground state WO₃ and the time evolution of the spectral difference after the photoexcitation (400 nm, 0.070 fs) recorded in SACLA. The time resolving power is ~0.7 ps.

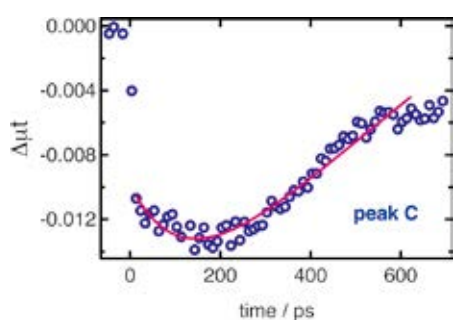


Figure 2. Time evolution of the difference spectra at energy point C in Figure 1.

ions are reduced from hexavalent to pentavalent. From Figure 2 and other results of W L_{III}-edge extended x-ray absorption fine structure (EXAFS) and W L_I-edge XANES, we can deduce the photoexcitation process as

- 1) fast formation of the photocarrier (<0.7 ps)
- 2) local structural distortion of WO₆ octahedra (140 ps)
- 3) decay of the photoexcited state (1800 ps).

The local structure distortion of the photocarrier in WO₃ is exemplified, suggesting the usefulness of the time resolved XAFS experiments.

2. Local Thermal Properties of Functional Materials as Magnetic Alloys^{2–4)} and Gold Nanoclusters Studied by Temperature Dependent EXAFS⁵⁾

We have extensively been studying local thermal properties such as local thermal expansion and local vibrational amplitude between atom pairs by means of the temperature dependent EXAFS technique, together with the computational simulations based on the path-integral effective classical potential theory. In the FeNi invar alloy²⁾ that shows almost no thermal expansion up to 400 K, we concluded that the absence of thermal expansion at very low temperature originates from the vibrational quantum effect, and found the different local thermal expansion between Fe and Ni, which cannot be detected with the x-ray diffraction. In the martensitic MnNi alloy,³⁾ Mn exhibits large thermal expansion along the tetragonal *a* axis due to the anti-Invar effect and negligibly small thermal expansion along the *c* axis due to the cooperative Invar effect. In metamagnetic FeRh intermetallic compound,⁴⁾ only the Debye-Waller factor of the Fe–Fe pair in the antiferromagnetic phase was found to be enhanced significantly, indicating that the local spin and Fe–Fe distance fluctuations play an important role in driving the metamagnetic transition. In thiolated gold nanoclusters,⁵⁾ we elucidated the hierarchy in the bond stiffness in Au₂₅(SC₂H₄Ph)₁₈, Au₃₈(SC₂H₄Ph)₂₄ and Au₁₄₄(SC₂H₄Ph)₆₀. Longer and more flexible Au–Au bonds locate at the icosahedral-based gold surface, while shorter stiffer Au–Au bonds are distributed along the radial direction and form a cyclic structural backbone of the rigid Au–SR oligomers.

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- 4) Y. Wakisaka, Y. Uemura, T. Yokoyama, H. Asakura, H. Morimoto, M. Tabuchi, D. Ohshima, T. Kato and S. Iwata, *Phys. Rev. B* **92**, 184408 (2015).
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Magnetic Resonance Studies for Functional Molecular-Based Solids

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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.

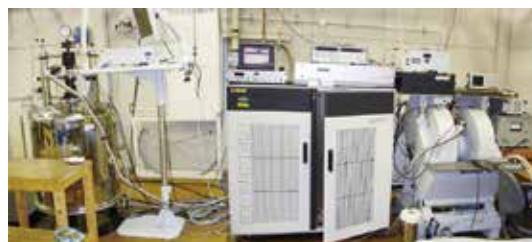
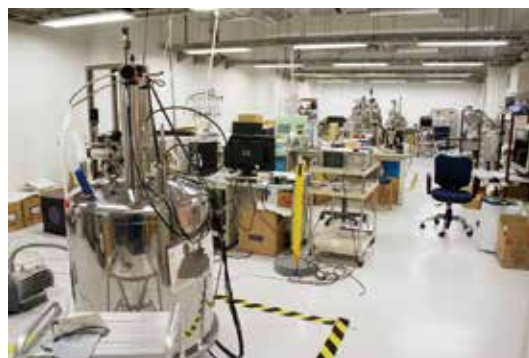


Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

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- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, “Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex,” *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Curious Electronic Phases and ESR Behaviors in One-Dimensional Organic Conductors (TMTCF)₂X

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)₂Br 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. Previously, we examined the magnetic structure of the antiferromagnetic state of (TMTTF)₂Br by ¹H-NMR spectroscopy at 4.2 K. We clarified that the wave-number of the antiferromagnetic state is commensurate $Q = (1/2, 1/4, 0)$ with amplitude $0.14\mu_B/\text{molecule}$ at 4.2 K.¹⁾ The commensurate antiferromagnetic state of (TMTTF)₂Br was also confirmed by ¹³C-NMR measurements. Recently anomalous ¹³C-NMR spectra change was observed in (TMTTF)₂Br below 4.2 K.²⁾ This observation suggests possible successive phase transition around 4.2 K. Hence we also investigated antiferromagnetic resonance (AFMR) of a single crystal of (TMTTF)₂Br. The X-band ESR experiments were carried out using Bruker Elexsys 500 with Oxford Cryostat E910. The temperature range was between 1.5 K and 10 K. Figure 2 shows the angular dependence of the antiferromagnetic resonance (AFMR) modes (normal mode and spin-flop mode) at 4.8 K and 1.5 K. The AFMR modes seem to enhance at 1.5 K, indicating development of the magnetic moment of the AF sub-lattices even at low-temperatures ($T \ll T_N/2$). Temperature dependence of the two AFMR modes also shows anomalous increase below 5 K. According to the detailed analysis of the AFMR experiment results, the shift of the AFMR field suggests change of the magnetization of the AF sub-lattice (namely, the amplitude of the AF).³⁾ Possible sub-phases in the antiferromagnetic state are discussed.

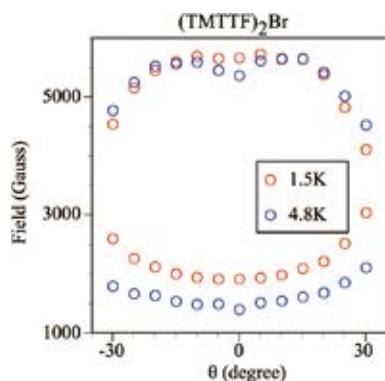


Figure 2. Angular dependence of the anti-ferromagnetic resonance in (TMTTF)₂Br (easy-intermediate plane: 9.5 GHz).

2. Effect of Spin–Orbit Interaction and Topological Gap for ESR Spectra in Low-Dimensional Organic Conductors

Recently theoretical investigation by Oshikawa proposed that strong spin–orbit interaction causes additional ESR satellite signal and g -shift in 1D metallic system.⁴⁾ So, we reexamined detailed X-band ESR spectra (satellite, line-shape, line-width) for low-dimensional metallic systems. Firstly, we focused on a 1D organic conductor (TMTSF)₂ClO₄, which shows stable metallic state down to 1 K. Since the TMTSF molecule contains heavy selenium elements, there are considerable spin–orbit interactions. When we apply the static magnetic field along 1D conducting direction ($H_0//a$), a tiny satellite peak was appeared below 12 K. In the case of $H_0//c^*$, we cannot observe any satellite peak. We also performed 2D metallic system, BEDT-TTF salts. A series of BEDT-TTF salts with low-symmetry shows anomalous g -shift at low-temperatures. We discuss relationship between the tiny band gap and anomalous ESR behavior observed in low-dimensional metallic systems.

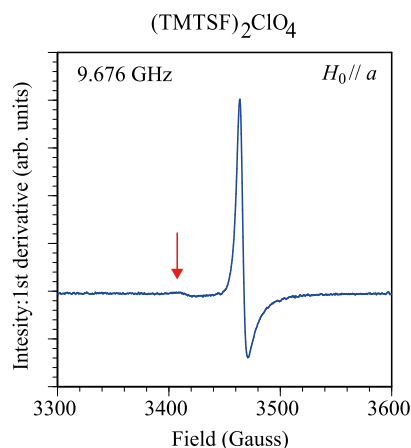


Figure 3. ESR spectra of (TMTSF)₂ClO₄ at 8 K with the static magnetic field along 1D conducting direction ($H_0//a$). A tiny satellite peak was appeared below 12 K.

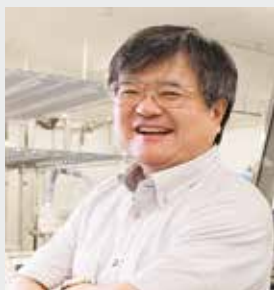
These works were supported by a Grant-in-Aid for Scientific Research B (No. 20340095) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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- 4) M. Oshikawa, *54th SEST (Japan ESR society) annual meeting* SB-05 (2015.11).

Organic Solar Cells

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Keywords

Organic Semiconductors, Organic Solar Cells, ppm-Doping

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

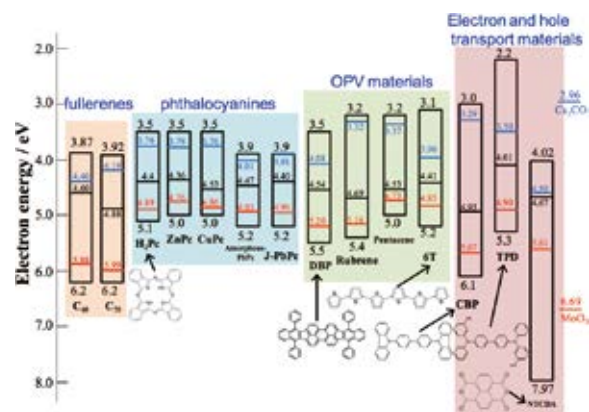


Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100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

Selected Publications

- C. Ohashi, 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).
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Organic Solar Cells,” *Electronics* **3**, 351–380 (2014).

- M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, “Conduction Type Control of Fullerene Films from *n*- to *p*-Type by Molybdenum Oxide Doping,” *Appl. Phys. Lett.* **98**, 023302 (3 pages) (2011).

1. Effects of Doping at the ppm Level in Simple n^+p -Homojunction Organic Photovoltaic Cells

We believe that a doping technique for very low concentrations of the order of parts per million should be developed. In this study, we adopted the simplest n^+p -homojunction cell that has a one-sided abrupt junction (Figure 2). The acceptor (FeCl_3) doping concentration in the p -layer was varied from the extremely low concentration of 1 ppm up to 1,000 ppm.

Figure 3(a) shows the dependences of short-circuit photocurrent (J_{sc}) and the fill factor (FF) on doping concentration. The doping effect of extremely low concentrations of the order of 1 ppm was confirmed. The doping effects can be divided into three regions. From 0 to 10 ppm, both FF and J_{sc} increase rapidly. From 10 to 100 ppm, J_{sc} still increases while FF maintains a constant value. From 100 to 1,000 ppm, both J_{sc} and FF decrease.

Figure 3(b) shows the dependences of the fill factor (FF) and the cell resistance (R_s) on doping concentration from 0 to 100 ppm. Clearly, R_s decreases and FF increases from 0 to 10 ppm. Once acceptor doping is performed, holes and electrons inevitably act as majority and minority carriers, respectively. Thus, we conclude that the increase in FF at 10 ppm doping is due to the appearance of majority carriers in the p -layer.

Figure 3(c) shows the dependences of J_{sc} and the built-in potential (V_{bi}) on doping concentration from 0 to 1,000 ppm. Clearly, there is a close relationship between J_{sc} and V_{bi} . In particular, there are simultaneous increases in J_{sc} and V_{bi} at the relatively low doping concentrations of 10 and 100 ppm. Based on these considerations, we conclude that the increase in J_{sc} is due to the increase in V_{bi} , that is, the formation of an n^+p -homojunction.

The decreases in FF and J_{sc} from 100 to 1,000 ppm doping (Figure 3(a)) are caused by the decrease in mobility of the majority carriers as a result of the disturbance of hopping transport by dopant molecules and by the decrease in the width of depletion layer, respectively.

The most important technical significance of the doping is the intentional design of built-in potentials in the cells. We believe that a new design concept that includes the doping technology needs to be developed in order to realize a high-performance cell.

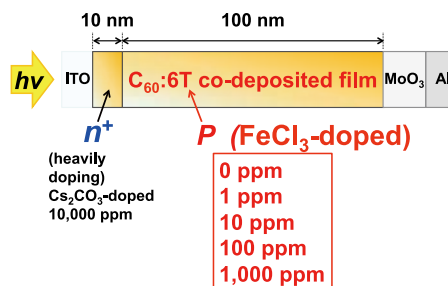


Figure 2. Structure of n^+p -homojunction cell with a one-sided abrupt junction.

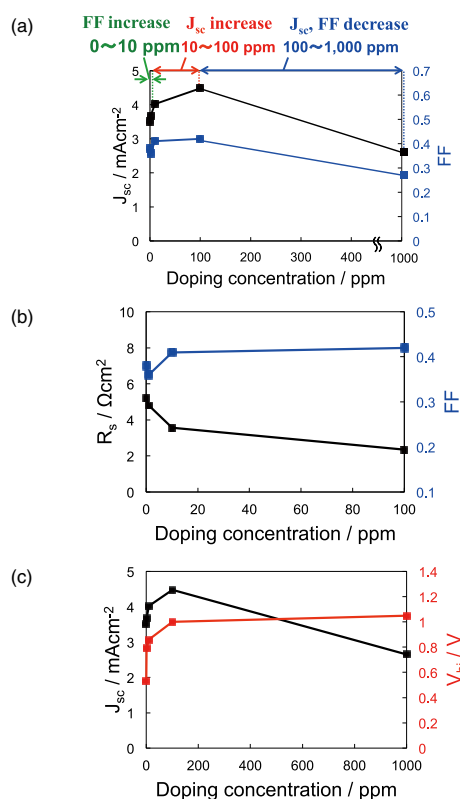


Figure 3. (a) Dependences of short-circuit photocurrent (J_{sc}) and the fill factor (FF) on doping concentration. (b) Dependences of FF and the cell resistance (R_s) on doping concentration. (c) Dependences of J_{sc} and the built-in potential (V_{bi}) on doping concentration.

Two-Dimensional Polymers and Covalent Organic Frameworks

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Keywords

Two-Dimensional Covalent Polymer, Covalent Organic Frameworks, Porous Organic Polymers

Two-dimensional (2D) polymers and their layered frameworks (covalent organic frameworks: COFs) are a class of crystalline porous materials that enable precise integration of organic components into periodicities. Different from conventional polymers and typical porous zeolite materials in the aspects structure, synthesis, and functions, COF materials have emerged as a new platform for designing advanced multiple functional materials, including gas adsorption, catalysts, semiconductors, light-emitters, and active materials for batteries and solar cells. We have pioneered the field of COFs by exploring molecular design principle, synthetic reactions, functions and applications.

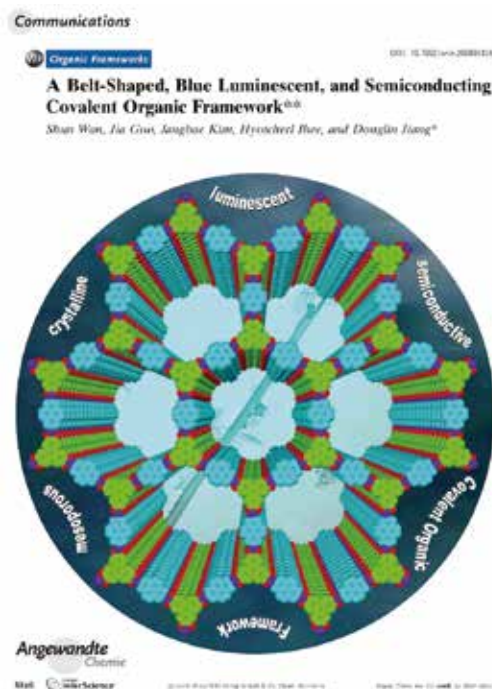


Figure 1. The first semiconducting 2D COF.

Selected Publications

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- J. Guo, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ilhee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang*, "Conjugated Organic Framework with Three-Dimensionally Ordered Stable Polymer with Delocalized π Clouds," *Nat. Commun.* **4**: 2736 doi: 10.1038/ncomms3736 (2013).

1. Radical Covalent Organic Frameworks for Capacitive Energy Storage

Organic radicals have received considerable attentions because their unpaired electrons endow the materials with unusual electronic, magnetic, optical, and redox properties. In this study, we developed a facile and general strategy that converts a conventional COF to an outstanding redox-active platform for energy storage *via* post-synthetic channel-wall functionalization with organic radicals. With this achievement, we show a new platform based on radical COFs for energy storage. We demonstrated this strategy using a conventional imine-linked NiP-COF (Figure 2) as a scaffold with nickel porphyrin at the vertices and TEMPO radicals on the walls.

The radical frameworks with open-accessible polyradicals immobilized on the pore walls undergo rapid and reversible redox reactions, leading to capacitive energy storage with high

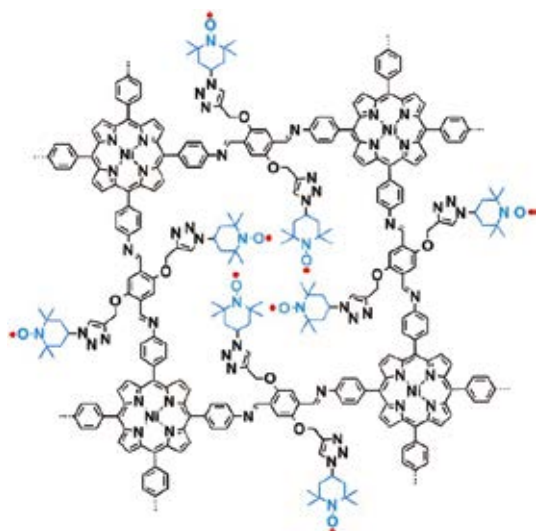


Figure 2. A NiP-COF with TEMPO radicals immobilized on the walls.

capacitance, high-rate kinetics, and robust cycle stability. The results suggest that channel-wall functional engineering with redox-active species will be a facile and versatile strategy to explore COFs for energy storage. Our results reveal the enormous potential of COFs as an appealing platform for construction of electrode materials for energy storage. We anticipate that the present post-synthetic channel-wall engineering strategy will be critical to exploring COF materials for high-performance energy storage and power supply.

2. A Photoresponsive Smart Covalent Organic Framework

Materials with structures that are transformable in response to external stimuli, such as light, heat and pressure, are attracting increasing attention because of their broad applications in various fields. In particular, when the structural transformations are accompanied by changes in physiochemical properties, these materials are considered “smart” and “dynamic” and can function as stimuli-responsive materials.

Two-dimensional covalent organic polymers (2D COPs) and their layered covalent organic frameworks (COFs) are a class of crystalline porous polymers that allow atomically precise integration of organic units into periodic columnar π -arrays and ordered one-dimensional (1D) open channels. The integration of stimuli-responsive π -units into COFs is likely to yield structurally-dynamic frameworks in which the structure can be transformed upon external stimulation. However, a “smart” COF is unprecedented and the possibility of structural transformation is to be exemplified.

The anthracene units stacked in the π -columns of Ph-An-COF are responsive to irradiation, which induces interlayer $[4\pi + 4\pi]$ cycloaddition reactions, causes conformational

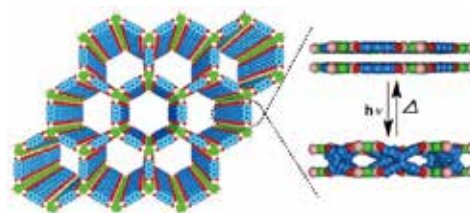


Figure 3. Anthracene-based photoresponsive COF.

changes of the π -columns, and triggers a structural transformation of the layers. These photoinduced hierarchical transformations are reversible by virtue of the thermally allowed reversibility of the cycloaddition reaction. Notably, the structural transformations are accompanied by profound changes in properties and functions, including gas adsorption, π -electronic adsorption and luminescence. Our results demonstrate the first example of photoresponsive structurally-dynamic COFs and suggest that COFs could be designed as “smart” materials whose gas-adsorption, molecular storage, sensing, and semiconducting properties are controllable by external stimuli.

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Solid-State NMR for Molecular Science

Department of Materials Molecular Science Division of Molecular Functions



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Education

- 1994 B.S. Himeji Institute of Technology (University of Hyogo)
- 1999 Ph.D. Himeji Institute of Technology (University of Hyogo)

Professional Employment

- 1999 Postdoctoral Fellow, National High Magnetic Field Laboratory, Florida State University
- 2001 Assistant Professor, Yokohama National University
- 2006 Associate Professor, Institute for Molecular Science
- Associate Professor, The Graduate University for Advanced Studies

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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 characterization 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.

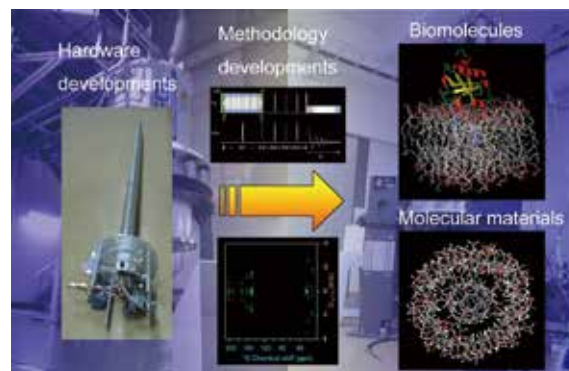


Figure 1. Outline of our studies.

Selected Publications

- J. Hu, R. Fu, K. Nishimura, L. Zhang, H. X. Zhou, D. D. Busath, V. Vijayvergiya and T. A. Cross, "Histidines, Heart of the Hydrogen Ion Channel from Influenza A Virus: Toward an Understanding of Conductance and Proton Selectivity," *Proc. Natl. Acad. Sci. U.S.A.* **103**, 6865–6870 (2006).
- 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- δ 1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, " ^2H 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 ^1H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β -Sheet Structures by High Resolution ^1H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C- δ 1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- 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).

1. Membrane Induced Dichotomous Conformation of Amyloid β (1-40) Bound to Lipid Bilayers¹⁾

Various neurodegenerative disorders are ascribed to pathogenic molecular processes involving conformational transitions of amyloidogenic proteins into toxic aggregates characterized by their β -structure. Accumulating evidence indicate that neural cell membranes provide platforms for such conformational transitions of pathogenic proteins. Amyloid β (A β) is a major player in the onset and developments of Alzheimer's disease. Prof. K. Kato group in IMS has successfully determined monomeric structure of A β (1-40) bound to glycolipid GM1 embedded in micelles using solution NMR. However the membrane bound A β are not accessible with solution NMR techniques, because of its slow molecular tumbling. So we collaborate with Prof. K. Kato group to characterize A β oligomers induced on the surface of lipid bilayers composed of neutral lipids prior to formation of amyloid fibril using solid-state NMR.

Fully hydrated uniformly ^{13}C -, and ^{15}N isotope enriched A β (1-40) bound to DMPC vesicles were lyophilized immediately after preparation of sample in order to capture oligomeric state of A β and used for solid-state NMR measurements. Sequential signal assignments were carried out using solid-state NMR techniques of ^{13}C homonuclear scholar coupling based homonuclear correlation experiment of *constant time uniform cross peak COSY* (CT-UCCOSY) under magic angle spinning (MAS), in conjunction with ^{13}C observed *double cross polarization* (DCP) based NCO and NCA heteronuclear correlation experiments. All of observed signals were successfully assigned to C-terminal segment of A β (1-40) from Val₂₄ to Val₃₉. Through the inspection of conformational dependent isotropic chemical shifts using TALOS-N, the conformation of C-terminal segment of A β (1-40) was identified to as β -structure. In order to clarify intermolecular packing of the C-terminal segment of A β (1-40), dipolar coupling based

through-space homonuclear correlation experiments of *dipolar assisted rotational resonance* (DARR) were carried out with various mixing times up to 400 ms to obtain correlation among carbons up to 6 Å apart. The DARR spectra exhibited correlation peaks among carbons in same and adjacent residues. Therefore, intermolecular arrangement of the C-terminal segments of A β (1-40) was identified to as parallel β -sheet structure. The obtained structure of A β (1-40) bound to DMPC bilayers differs from any of reported ones such as monomer on lipids and fibrils conformed in the absence and the presence of lipids. The oligomeric structure of A β on DMPC bilayers suggests structural transition of A β from α to β is occurred at oligomeric state on lipid bilayers.

2. Characterizations of Organic and Inorganic Materials Based on Solid-State NMR through Observations of Natural Abundant Isotopes^{2,3)}

There are a number of organic materials, which are insoluble to any solvents. Solid-state NMR is one of the most powerful tools to provide molecular information for such samples at intact conditions. Especially, for small organic molecules and polymers consisting of repeated local structures, ^1H and ^{13}C solid-state NMR spectra through the observations of those natural abundant isotopes retain reasonable spectral sensitivities. Combination of ultra high-field and ultra high-speed MAS also enables high-resolution spectra for ^1H as demonstrated in the past collaboration works.

We have been collaborated with several research groups to characterize molecular structures of various types of materials using solid-state NMR. During a year, our group contributed to provide molecular information of several molecular materials such as newly designed synthetic polymers²⁾ for collaboration with Prof. Jiang group in JAIST and also inorganic materials³⁾ for collaboration with Prof. Iijima group in Yamagata Univ.

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

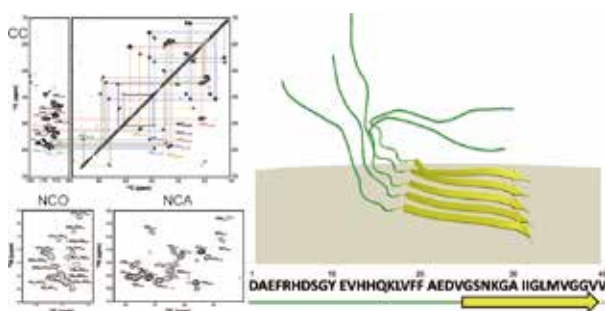


Figure 2. ^{13}C -homonuclear and ^{13}C - ^{15}N heteronuclear correlation spectra of [U- ^{13}C , ^{15}N] A β (1-40) bound to DMPC lipid bilayers acquired by solid-state NMR (right side). The proposed topology model of A β (1-40) bound to DMPC lipid bilayers (left side).

References

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- 2) N. Huang, L. Zhai, D. E. Couprie, M. A. Addicoat, K. Okushita, K. Nishimura, T. Heine and D. Jiang, *Nat. Commun.* **7**, 12325 (12 pages) (2016).
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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. X-Ray Crystallographic Analyses of Heterocyclic and Aromatic Compounds

The X-ray crystallographic analyses of five heterocyclic

and aromatic compounds have revealed their interesting structural natures and unique molecular aggregations. A large number of short intermolecular S...S and S...N contacts are observed in the crystal structures of [1,3]dithiolo[4,5-*c*][1,2,5]thiadiazole-5-thione, 2-thioxo-[1,3]dithiolo[4,5-*b*]pyrazine-5,6-dicarbonitrile and dimethyl 2-([1,3]dithiolo[4,5-*c*][1,2,5]thiadiazol-5-ylidene)-1,3-dithiole-4,5-dicarboxylate. In the bis(tetra-*n*-butylammonium) bis(5,6-dicyanopyrazine-2,3-dithiolato- κ^2S,S')nickel(II) complex, the centrosymmetric dianion is planar, with an r.m.s. deviation of 0.031(1) Å. We have also found a novel hydrate isomer of cyananilic acid, dihydrate derivative. The cyananilate dianion molecule is planar with an r.m.s. deviation of 0.011(2) Å and is located on an inversion center. The cyananilate molecules are linked via the oxonium ions with intermolecular O-H...O and O-H...N interactions.

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. Synthesis of 10 nm-Long Molecular Linkers for Supramolecular Architecture

We have already established the synthetic process for a series of “single-nanometer scale” devices. In the current study, we have synthesized long molecular linkers for supramolecular approaches, which are one of the key parts for the integration of nanosize devices to “deca~hecto-nanometer scale” electronic circuits. Figure 1 shows the examples.

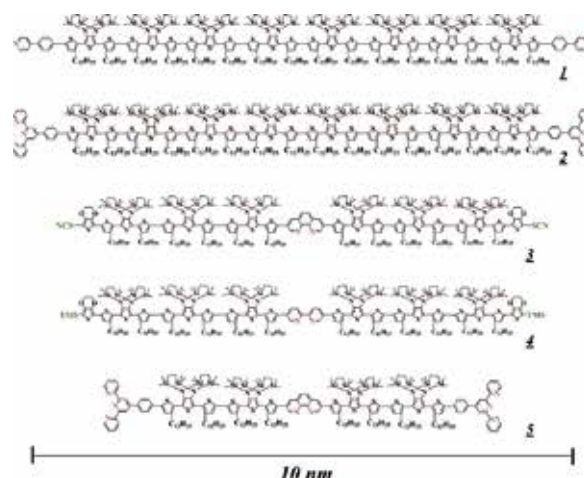


Figure 1. Examples of long molecular linkers with coordination sites.

Visiting Professors



Visiting Professor

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

Giant Seebeck Effect in Pure Fullerene Thin Films

The small thermal conductivity of molecular solids is beneficial for their thermoelectric applications. If Seebeck coefficients were sufficiently large to compensate for the relatively small electrical conductivity, these materials would be promising candidates for thermoelectric devices. In this work, the thermoelectric properties of C_{60} were studied by in situ measurements under ultrahigh vacuum after the deposition of a pure C_{60} thin film. An exceptionally large Seebeck coefficient of more than 150 mV/K was observed as a steady-state thermoelectromotive force. Even considering several extreme but realistic conditions, conventional semi-classical thermoelectric theories cannot explain this giant Seebeck effect.



Visiting Associate Professor

YOSHIKAWA, Hirofumi (*from Kwansei Gakuin University*)

Development of High Performance Rechargeable Batteries Using Various Molecular Materials

Recently, much attention has been focused on development of high-performance rechargeable batteries due to the global energy and environmental crises. Our research interest is to find novel cathode materials toward the next-generation rechargeable battery. In order to realize a high capacity, a stable cycle performance, a rapid charging, and so on, we examine battery performances of various materials such as organic and inorganic compounds, nanomaterials *etc.*, which can take the place of the present general cathode materials, transition metal oxides. We also try to nano-hybridize these materials with nano-carbons such as single-walled carbon nanotubes, graphenes, and mesoporous carbons, to increase electrochemical performances by utilizing electrical double layer capacitance of nanocarbons. Finally, we reveal these electrochemical reaction mechanism by using operando XAFS, XRD, solid-state NMR *etc.* and it is utilized to investigate new materials with high battery performances.



Visiting Associate Professor

TAJIMA, Naoya (*from Toho University*)

Quantum Transport Phenomena in Molecular Massless Dirac Fermion Systems

Two dimensional (2D) massless Dirac fermion systems was realized in an organic conductor α -(BEDT-TTF) $_2$ I $_3$ under pressure. This material with layered structure and tilted Dirac cones belongs to a broad category of 2D massless Dirac fermion systems. Moreover, the interaction between Dirac particles are strong. Thus, this system provides us with a testing ground for the quantum transport of multilayered massless Dirac fermion systems. In this work, we develop the field effect transistor channeled by this system and then aim at the detection of (fractional) quantum Hall effect.





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

Professional Employment

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

Member

Assistant Professor
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DESFRAŃÇOIS, Claire*
Secretary
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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.

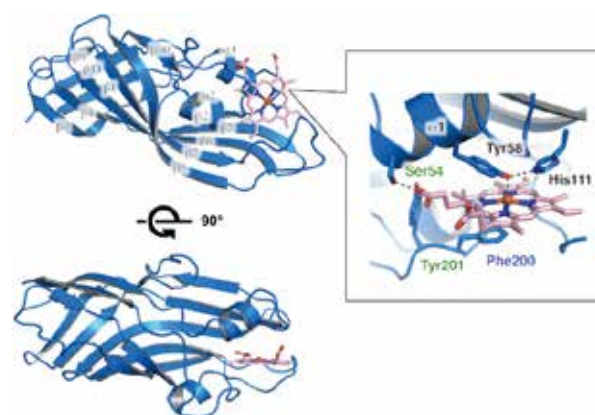


Figure 1. The crystal structure of CgHtaA-N and the close-up view of heme binding site in CgHtaA-N.

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-Amino-levulinic 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*

As iron is an essential trace element for most of organisms, they develop sophisticated iron acquisition systems. Pathogenic bacteria can use heme as an iron source partly because heme is the most abundant iron species in their host. However, there is little free heme molecule as most of heme molecules are tightly bound to hemoproteins as a prosthetic group. Therefore, some heme acquisition system is required to use heme in hemoproteins as an iron source.

In Gram-negative bacteria, hemophores that are secreted to the extracellular medium acquire heme from hemoproteins and transport it to a specific outer membrane receptor. The outer membrane receptor transports heme across the outer membrane to the periplasmic space, where a periplasmic heme-binding protein binds heme to transport it to an ABC-type heme transporter. On the other hand, in Gram-positive bacteria, heme uptake occurs by direct interaction between hemoproteins or heme and the membrane anchored proteins responsible for heme binding and transport. In a Gram-positive bacterium *Corynebacterium glutamicum*, heme is captured by the membrane anchored heme binding proteins, HtaA and HtaB proteins, and then heme is transferred to HmuT, which is a heme-binding protein for the ABC-type heme transporter HmuUV. Heme is transported into cytoplasm by this ABC transporter. While this heme uptake process is proposed based on the genetic and microbiological studies, the molecular mechanisms of heme uptake/transport are not obvious mainly due to a lack of structural information of these proteins. We have characterized HtaA, HtaB, and HmuT from *Corynebacterium glutamicum* (CgHmuT) by X-ray crystallography to elucidate the molecular mechanism of heme transport and uptake.

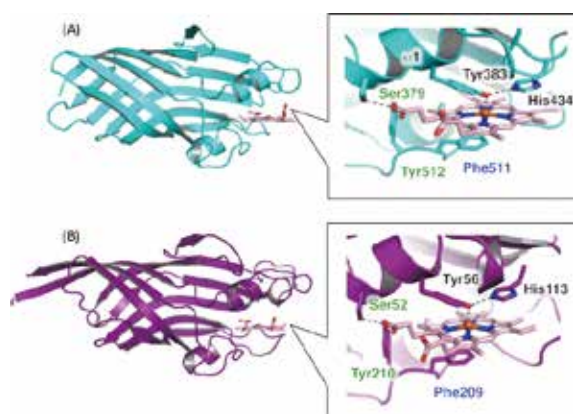


Figure 2. The crystal structures of (A) CgHtaA-C and (B) CgHtaB with the close-up view of their heme binding sites.

HtaA consists of two homologous domains, HtaA-N and HtaA-C. We have determined the structure of CgHtaA-N at a

resolution of 2.0 Å (Figure 1). HtaA-N consists of 11 β -strands and 2 short α -helices and binds a heme molecule with Tyr58 as an axial ligand in a hydrophobic pocket. Tyr58 forms a hydrogen bond with His111, which may regulate the heme binding affinity of HtaA-N. Phe200 forms π - π stacking with heme and heme propionate forms a hydrogen bond with Ser54.

The crystal structures of CgHtaA-C and CgHtaB have also been determined as shown in Figure 2. The whole structures of CgHtaA-N, CgHtaA-C, and CgHtaB are superimposable and the heme environmental structures are highly conserved among them including the axial ligand, hydrogen bonding interaction between Tyr and His, and heme propionate and Ser, and π - π stacking of heme and Phe.

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

Vitamin B12 is well known as a cofactor for the B12-dependent enzymes that catalyze carbon skeleton rearrangement or elimination reactions, where Co-C bond hemolysis takes place to form the radical species as the reaction intermediate. Recently, a novel biological function of vitamin B12 has been reported: A photosensor protein CarH utilizes adenosylcobalamin (vitamin B12) as its sensor unit for light sensing. We have determined the crystal structure of CarH from *Thermus thermophilus* to elucidate the molecular mechanisms of photosensing and signal transduction of CarH (Figure 3). CarH forms homo-tetramer and each subunit binds an adenosylcobalamin (AdoCbl). The protomer of CarH consists of the

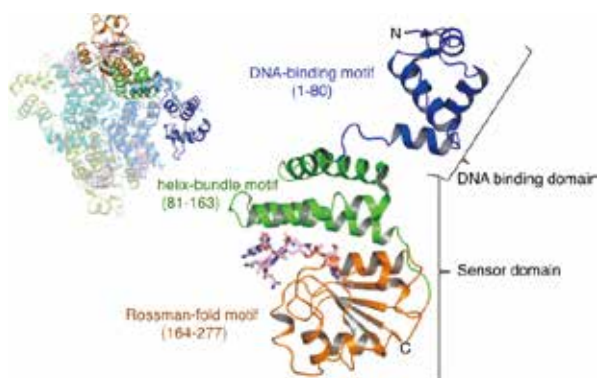


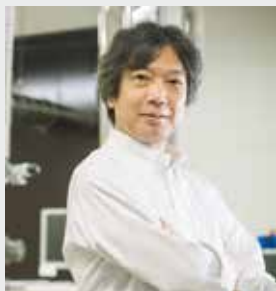
Figure 3. The crystal structures of AdoCbl-bound CarH.

DNA-binding and sensor domains as shown in Figure 3. The sensor domain consists of the helix-bundle motif and Rossmann-fold motif, between of which AdoCbl is accommodated.

AdoCbl-bound CarH is photosensitive and dissociation of tetramer to monomer takes place upon photo irradiation. The adenosyl group is dissociated from Co ion upon photosensing, which is a trigger of the change of CarH quaternary structure.

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
2011 The 48th Baelz Prize

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Secretary
TANAKA, Kei

Keywords Biomolecule, Dynamical Ordering, NMR

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

Toward an integrative understanding of the principles behind the biomolecular ordering processes, we conduct multidisciplinary approaches based on detailed analyses of



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

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.

Selected Publications

- 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).
- Y. Zhang, T. Yamaguchi, M. Yagi-Utsumi, Y. Kamiya, Y. Sakae, Y. Okamoto and K. Kato, "Conformational Dynamics of Oligosaccharides Characterized by Paramagnetism-Assisted NMR Spectroscopy in Conjunction with Molecular Dynamics Simulation," in *Advances in Experimental Medicine and Biology*, Springer; Switzerland, **842**, pp. 217–230 (2015).
- T. Yamaguchi and K. Kato, "Paramagnetism-Assisted Nuclear Magnetic Resonance Analysis of Dynamic Conformations and Interactions of Oligosaccharides," in *Glycoscience: Biology and Medicine*, Springer; Japan, **1**, pp. 137–145 (2014).

1. Characterization of Dynamic Process of Protein Assembly and Disassembly

In our group, various physicochemical and biochemical approaches are integrated to characterize assembly and disassembly of proteins exemplified by formation of proteasomes and cargo receptor complexes. The core part of the eukaryotic proteasome contains heteroheptameric rings compose of α 1-7 subunits. Among these homologous subunits, α 7 is spontaneously assembled into a homotetrasecamer having a double ring structure as shown by our crystallographic analysis. Intriguingly, our native mass spectrometric (MS) data indicate that this double ring is disrupted upon addition of α 6, suggesting that proteasome formation involves the disassembly of non-native oligomers, which are assembly intermediates.¹⁾ Furthermore, we characterized the pH-dependent coiled-coil interactions of yeast putative cargo receptors (Emp46p and Emp47p), identifying the key residue that controls this interaction.²⁾ These results contribute toward understanding the molecular mechanisms underlying the dynamic cargo receptor assembly in the yeast secretory pathway. Our findings will provide a framework for designing molecular assembly and disassembly systems mediated by intermolecular interactions.

2. Structural Basis of Drug-Induced Conformational Change of HIV-1 Reverse Transcriptase

Human immunodeficiency virus type 1 reverse transcriptase (HIV-1 RT) is an important target for antiviral therapy against acquired immunodeficiency syndrome. Using NMR and native MS methods, we characterized the interactions between the heterodimeric HIV-1 RT enzyme and non-nucleoside reverse transcriptase inhibitors with different inhibitory activities.^{3,4)} We also applied a paramagnetism-assisted NMR technique for detecting the inhibitor-induced conformational change of HIV-1 RT, offering a strategy to identify allosteric inhibitors.⁵⁾ Our approaches thus provide useful tools in protein-based drug screening in developing anti-HIV drugs.

3. Interactions of Amyloidogenic Proteins with Membranes and Molecular Chaperones

Lipid membranes provide active platform for dynamic interactions of a variety of biomolecules on cell surfaces. Our

solid-state NMR data of amyloid β (A β) employing 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) vesicle as model membrane have elucidated the membrane-induced dichotomous conformation of A β , in which the disordered N-terminal segment is followed by the stable C-terminal β strand, providing an insight into the molecular processes of the conformational transition of A β coupled with its assembly into parallel β structures (Figure 2).⁶⁾

It has been proposed that molecular chaperones actively contribute to the suppression of toxic aggregate formation of various neurodegenerative disordered proteins. We identified a *chaperone-philic* binding motif of α -synuclein on the basis of NMR data and determined the crystal structure of its complex with the substrate-binding domains of protein disulfide isomerase (PDI) (Figure 2).⁷⁾ Our findings provided a structural basis for the mechanism underlying the redox-dependent substrate binding of PDI.

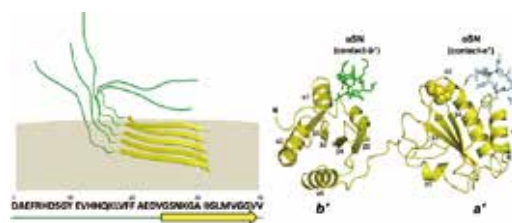


Figure 2. Structural model of A β (1–40) bound to DMPC bilayers characterized by solid-state NMR analyses (left). Crystal structure of the oxidized PDI b'–a' domains complexed with the α SN peptide (right).

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Awards

YOGO, Rina; Best Presentation Award, The Tokai Branch Meeting of the Pharmaceutical Society of Japan (2015).

TONG, Zhu; Poster Presentation Award, The 4th International Symposium of “Dynamical ordering of biomolecular systems for creation of integrated functions” (2015).

TONG, Zhu; Young Scientist Award, The 12th Forum of the Glycoscience base for Chubu (2015).

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Operation and Design Principles of Biological Molecular Machines

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Keywords

Molecular Machines, Protein Engineering, Single-Molecule Analysis

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

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

We will unveil operation principles of molecular motors with single-molecule functional analysis and advanced structural analysis. With the help of computer science, we will also engineer new, non-natural molecular machines 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

- S. Enoki, R. Iino, Y. Niitani, Y. Minagawa, M. Tomishige and H. Noji, "High-Speed Angle-Resolved Imaging of Single Gold Nanorod with Microsecond Temporal Resolution and One-Degree Angle Precision," *Anal. Chem.* **87**, 2079–2086 (2015).
- A. Yukawa, R. Iino, R. Watanabe, S. Hayashi and H. Noji, "Key Chemical Factors of Arginine Finger Catalysis of F_1 -ATPase Clarified by an Unnatural Amino Acid Mutation," *Biochemistry* **54**, 472–480 (2015).
- R. Iino, H. Ueno, Y. Minagawa, K. Suzuki and T. Murata, "Rotational Mechanism of *Enterococcus hirae* V_1 -ATPase by Crystal-Structure and Single-Molecule Analyses," *Curr. Opin. Struct. Biol.* **31**, 49–56 (2015).
- 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_β ," *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. Direct Observation of Intermediate States during the Stepping Motion of Kinesin-1¹⁾

The dimeric motor protein kinesin-1 walks along microtubules by alternately hydrolyzing ATP and moving two motor domains ('heads'). Nanometer-precision single-molecule studies demonstrated that kinesin takes regular 8-nm steps upon hydrolysis of each ATP; however, the intermediate states between steps have not been directly visualized. Here, we employed high-temporal resolution dark-field microscopy to directly visualize the binding and unbinding of kinesin heads to or from microtubules during processive movement (Figure 2). Our observations revealed that upon unbinding from microtubules, the labeled heads were displaced rightward and underwent tethered diffusive movement. Structural and kinetic analyses of wild-type and mutant kinesins with altered neck linker lengths provided evidence that rebinding of the unbound head to the rear-binding site is prohibited by a tension increase in the neck linker and that ATP hydrolysis by the leading head is suppressed when both heads are bound to the microtubule, thereby explaining how the two heads coordinate to move in a hand-over-hand manner.

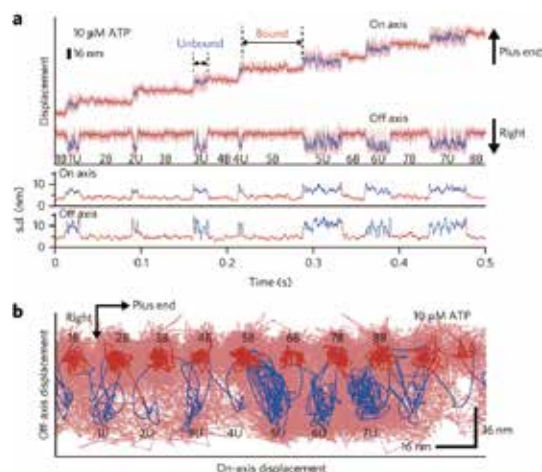


Figure 2. (a) Typical trace for the centroid position of the gold probe attached to a kinesin head (light red lines), toward the microtubule long axis (on axis) and perpendicular to the microtubule axis (off axis). Red and blue lines depict the median-filtered traces (window size of 51 frames) for the bound and unbound states, respectively. Lower panel shows the s.d. of on- and off-axis positions for each time frame t (calculated as $[t-20, t+20]$). (b) Two-dimensional plot of the gold probe shown in a. Numbers denote the temporal order of the bound (B) and unbound (U) states.

2. Direct Imaging of Binding, Dissociation, and Processive Movement of *Trichoderma reesei* Cel6A and Its Domains on Crystalline Cellulose²⁾

Trichoderma reesei Cel6A (TrCel6A) is a cellobiohydrolase

that hydrolyzes crystalline cellulose into cellobiose. Here, we observed the binding, dissociation, and movement of single-molecule intact TrCel6A on a crystalline cellulose, in addition to isolated catalytic domain (CD), cellulose-binding module and linker (CBM-Linker), and CBM (Figure 3). The CBM-Linker had a binding rate constant almost half that of intact TrCel6A, whereas those of the CD and CBM were only one-tenth of intact TrCel6A. These results indicate that the linker region largely contributes to initial binding on crystalline cellulose. After binding, all samples showed slow and fast dissociations, likely caused by the two different bound states due to the heterogeneity of cellulose surface. The CBM showed much higher (12-times) specificity to the high-affinity site than to the low-affinity site, whereas the CD did not, suggesting that the CBM leads the CD to the hydrophobic surface of crystalline cellulose. The intact molecules showed slow, processive movements (8.8 ± 5.5 nm/s) in addition to fast diffusional movements (30–40 nm/s), whereas the CBM-Linker, the CD, and a full-length but catalytically inactive mutant showed only fast diffusional movements. These results suggest that in addition to direct binding, surface diffusion also contributes to the searching of the hydrolysable point of the cellulose chains. The duration time constant for the processive movement was 7.7 s. Our results reveal the role of each domain in the elementary steps of the reaction cycle and provide the first direct evidence of the processive movement of TrCel6A on crystalline cellulose.

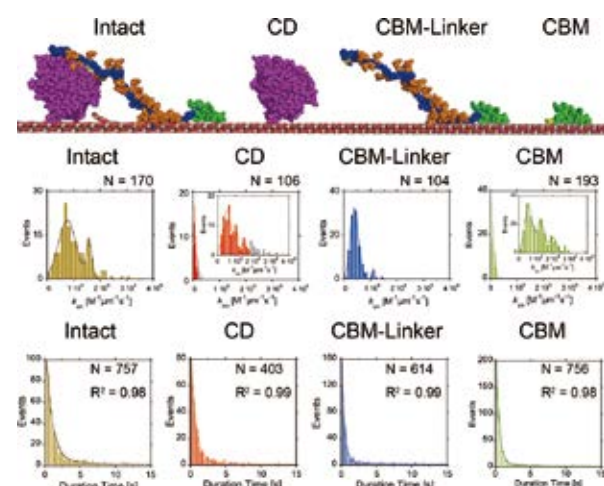


Figure 3. (Top) Domain structures of Intact, CD, CBM-Linker, and CBM of TrCel6A. (Middle) Distributions of the binding rate constant. (Bottom) Distributions of the duration time on cellulose.

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A Supramolecular Chemical Approach to the Construction of Artificial Cells

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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 GV, which contain no PCR reagents after self-reproduction, can be replenished by fusing them with conveyer GV 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.



- ✓ **Compartment** constructed by molecular assembly
- ✓ **Information** delivered to descendant
- ✓ **Catalyst** for chemical transformation

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

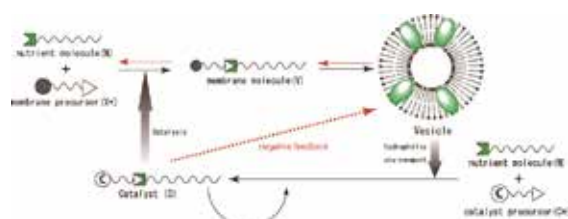


Figure 2. Scheme of our new artificial cellular system. The membrane molecules of the GV was synthesized by the catalyst produced in the GV.

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 droplets⁵⁾ (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.

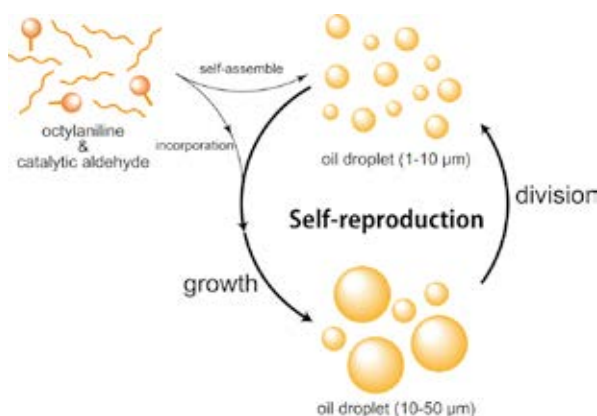


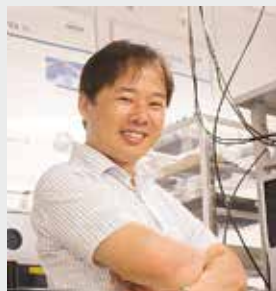
Figure 3. Scheme of the self-reproducing oil droplet (oil-in-water emulsion) system.

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- 3) K. Takakura, T. Yamamoto, K. Kurihara, T. Toyota, K. Ohnuma and T. Sugawara, *Chem. Commun.* **50**, 2190–2192 (2014).
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Investigation of Molecular Mechanisms of Channels, Transporters and Receptors

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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.

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).

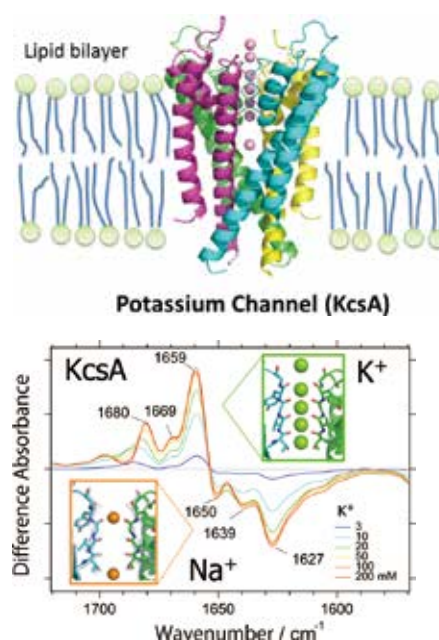


Figure 1. (top) X-ray crystal structure of a potassium ion channel, KcsA. (bottom) The ion-exchange induced difference infrared spectra of KcsA with different potassium ion concentration. The amide I bands are mainly originated from the carbonyl groups of the selectivity filter of KcsA.

1. Molecular Characteristics of a Mammalian Photoreceptive Protein, Melanopsin for Non-Visual Function¹

Animals use external light signals not only for vision but also for “non-visual” functions such as regulation of biological clock. In particular, mammals including human receive ambient light through retina, leading to photoentrainment of the circadian clock and pupil responses. It had been thought that visual cells (rods and cones) are only photoreceptor cells in mammalian retina, but recent studies have shown that small population of retinal ganglion cells are also photoreceptive and play important roles in the non-visual photoreception. Since the intrinsically photoreceptive retinal ganglion cells (ipRGCs) show extremely low photosensitivity (less than 1/10,000-fold sensitivity of visual cells), mammals can detect condition of ambient light in a wide dynamic range by using ipRGCs as well as visual cells. Thus, lowering the photosensitivity of ipRGCs is important for non-visual photoreception in mammals.

ipRGCs express a photoreceptive protein melanopsin. Like visual pigments in rods and cones, melanopsin is a member of the opsin family, and it consists of a protein moiety with seven transmembrane α -helices and the chromophore retinal. Interestingly, the amino acid sequence of melanopsin is more similar to that of invertebrate visual pigment rather than to that of vertebrate visual pigment (Figure 2a). In this context, we speculated that mammalian melanopsins possess

some molecular characteristics contributing to the low photosensitivity of ipRGCs. We thus compared biochemical, spectroscopic and electrophysiological properties of mouse and human melanopsins with those of closely related invertebrate melanopsin and visual pigment.

We expressed mouse and human melanopsin in mammalian cultured cells, and purified them through immuno-affinity chromatography. The purified proteins were kept at 37 °C in the dark, and subsequent spectral changes were recorded. During the incubation, the mammalian melanopsins showed time-dependent loss of absorbance at ~470-nm, indicating that they spontaneously hydrolyze the Schiff base linkage with the retinal (Figure 2, b and c). In contrast, such a hydrolysis was not observed in invertebrate melanopsin and visual pigment, both of which are closely related to mammalian melanopsins (Figure 2, d and e). Interestingly, human melanopsin showed the hydrolysis much faster (~10-fold) than mouse one whereas their sequences are very similar (~80% identity). Electrophysiological analyses using *Xenopus* oocytes expressing human or mouse melanopsin confirmed that the faster retinal release in human melanopsin occurs in cells, too.

These results indicate that mammalian melanopsins can lose their photoreceptive ability by spontaneous hydrolysis and release of the retinal chromophore. This characteristic would have an effect to lower photosensitivity of melanopsin-expressing cells (Figure 3). Our findings suggest that molecular

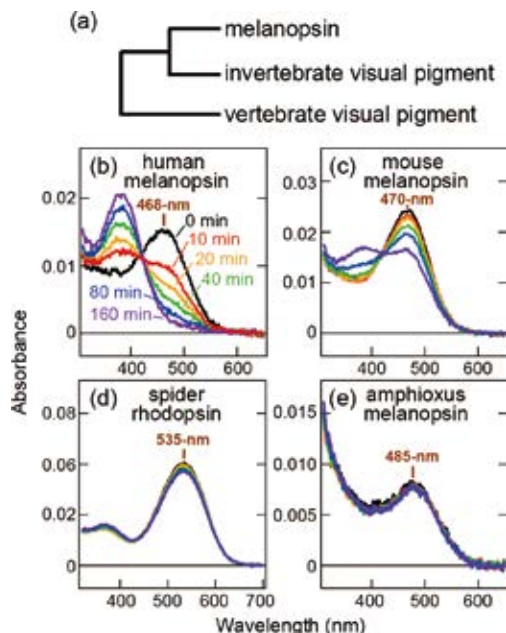


Figure 2. (a) Schematic representation of phylogenetic relationship of melanopsin, invertebrate visual pigment and vertebrate visual pigment. (b)–(e) Absorption spectra showing time-dependent loss of absorbance in the visible region for human melanopsin (b), mouse melanopsin (c), jumping spider rhodopsin, an invertebrate visual pigment (d), and an invertebrate amphioxus melanopsin (e). Panels (b)–(e) are adopted from ref. 1.

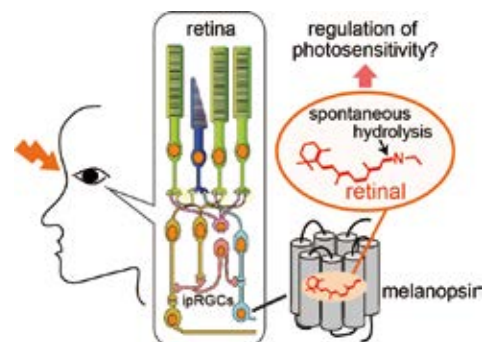


Figure 3. Our model illustrating how molecular characteristics of melanopsin contributes to non-visual photoreception in mammals. The spontaneous hydrolysis would play an important role in lowering photosensitivity of the cells.

characteristics of mammalian melanopsin are tuned for their non-visual photoreception. In addition, the further destabilized retinal attachment in human melanopsin would result in further lowered photosensitivity of human ipRGCs. This “enhanced” characteristic of human melanopsin might reflect adaptation to bright environment humans live.

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- 1) H. Tsukamoto*, Y. Kubo, D. L. Farrens, M. Koyanagi, A. Terakita and Y. Furutani, *J. Biol. Chem.* **290**, 27176–27187 (2015).

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Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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Professor, The Graduate University for Advanced Studies
2007 Research team leader, RIKEN
2014 Distinguished Professor, Three George University
2003 Research Project Leader, JST CREST Project (–2008)
2008 Research Project Leader, NEDO Project (–2012)
2011 Deputy Research Project Leader, JST CREST (–2016)
2014 Research Project Leader, JST ACCEL Project (–2019)

Awards

1991 Eisai Award, Synthetic Organic Chemistry
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2007 MEXT Ministerial Award for Green Sustainable Chemistry
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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.

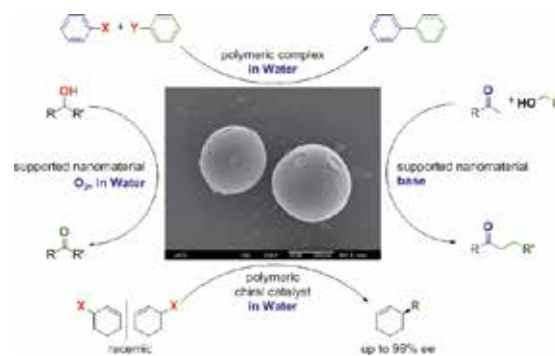


Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

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

1. A Vesicular Self-Assembled Amphiphilic Palladium NNC-Pincer Complex-Catalyzed Allylic Arylation of Allyl Acetates with Sodium Tetraarylborates in Water¹⁾

The allylic arylation of various allyl acetates with sodium tetraarylborates proceeded in water in the presence of a vesicular self-assembled amphiphilic palladium NNC-pincer complex to give the corresponding arylated products in high yield, whereas the same complex as an amorphous powder did not promote the reaction efficiently. The formation of a vesicular structure was therefore shown to be essential for efficient promotion of the reaction.

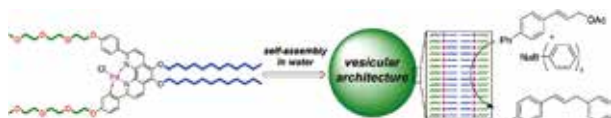


Figure 2. Allylic arylation reaction in water in the presence of a self-assembled vesicular amphiphilic palladium NNC-pincer complex.

2. Organoborane-Catalyzed Hydrogenation of Unactivated Aldehydes with a Hantzsch Ester as a Synthetic NAD(P)H Analogue²⁾

We have developed a method for the hydrogenation of unactivated aldehydes, using a Hantzsch ester as a NAD(P)H analogue in the presence of an electron-deficient triarylborane as a Lewis acid catalyst. Thus, tris[3,5-bis(trifluoromethyl)phenyl]borane efficiently catalyzes the hydrogenation of aliphatic aldehydes with a Hantzsch ester in 1,4-dioxane at 100 °C to give the corresponding aliphatic primary alcohols in up to 97% yield. Aromatic aldehydes also undergo the hydrogenation, even at 25 °C, to furnish the corresponding aromatic primary alcohols in up to 100% yield.

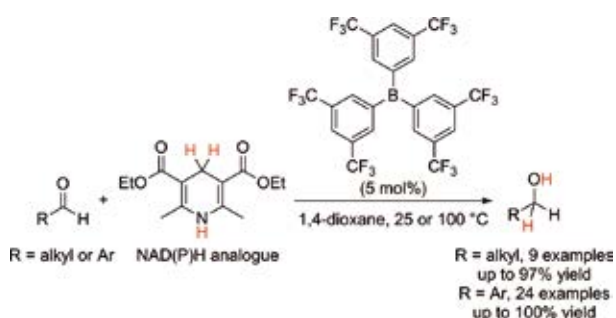


Figure 3. Organoborane-catalyzed hydrogenation of aldehydes with a Hantzsch ester.

3. Recyclable Polystyrene-Supported Copper Catalysts for the Aerobic Oxidative Homocoupling of Terminal Alkynes³⁾

Polystyrene-supported copper(II) *N,N,N',N'*-tetraethyldi-

ethylenetriamine [Cu(II)–TEDETA] complexes were prepared by immobilization of TEDETA onto crosslinked polystyrene resin, followed by complexation with copper salts. The polystyrene-immobilized CuSO₄–TEDETA complex efficiently catalyzed the oxidative homocoupling of terminal alkynes under air to give the corresponding 1,3-diynes in up to 99% yield. The catalyst was easily recovered by simple filtration and reused eight times without significant loss of catalytic activity.

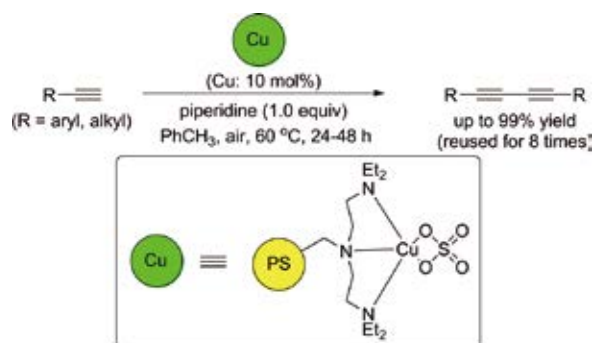


Figure 4. Homocoupling of terminal alkynes in the presence of a polystyrene-supported copper catalyst.

4. Instantaneous Click Chemistry by a Copper-Containing Polymeric-Membrane-Installed Microflow Catalytic Reactor⁴⁾

Instantaneous Huisgen cycloaddition has been achieved by developing a novel catalytic dinuclear-copper-complex-containing polymeric-membrane-installed microflow device. The microflow device instantaneously promotes the click reaction with a variety of alkynes and organic azides to afford the corresponding triazoles in quantitative yield.

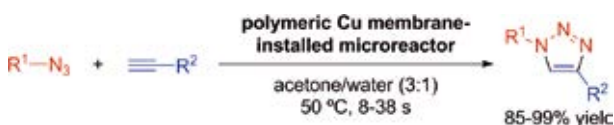


Figure 5. Homocoupling of terminal alkynes in the presence of a polystyrene-supported copper catalyst.

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Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Awards

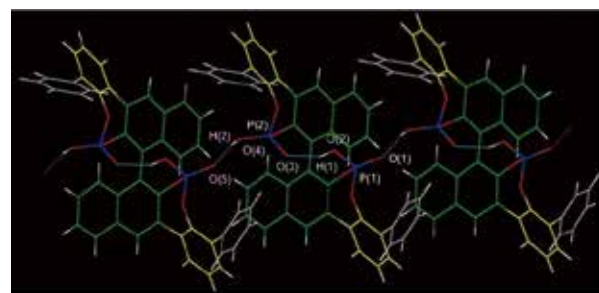
2003 The Elizabeth R. Norton Prize for Excellence in Research in Chemistry, University of Chicago
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Keywords Organic Synthesis, Molecular Catalyst, Non-Covalent Interaction

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.



Intermolecular H-Bonding: O(5)⋯O(4) = 2.503 Å
Intramolecular H-Bonding: O(3)⋯O(2) = 2.490 Å

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 Enantio-

selective 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 Azopyridine-carboxylate with Amidodienes Catalyzed by Chiral Carboxylic Acid–Monophosphoric Acid,” *J. Am. Chem. Soc.*, in press (2016). DOI: 10.1021/jacs.6b07150

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 of 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 perfluoroaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deliver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino-ene reaction using aldehydes and FmocNH_2 .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⁾

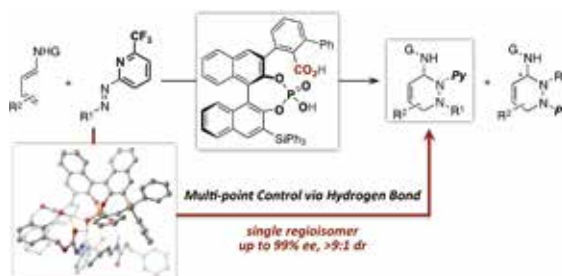


Figure 2. Chiral carboxylic acid-phosphoric acid-catalyzed azo-hetero-Diels-Alder reaction.

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 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) 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.

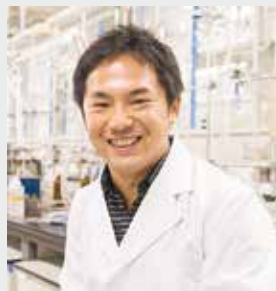
We found that pentafluoroiodobenzene was able to catalyze the allylation reaction of isoquinolines, quinolones, and pyridines with allylsilatrane to give the corresponding product in good yield.⁸⁾

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- 8) N. Momiyama *et al.*, Manuscript in preparation.

Development of Functional Metal Complexes for Artificial Photosynthesis

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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.

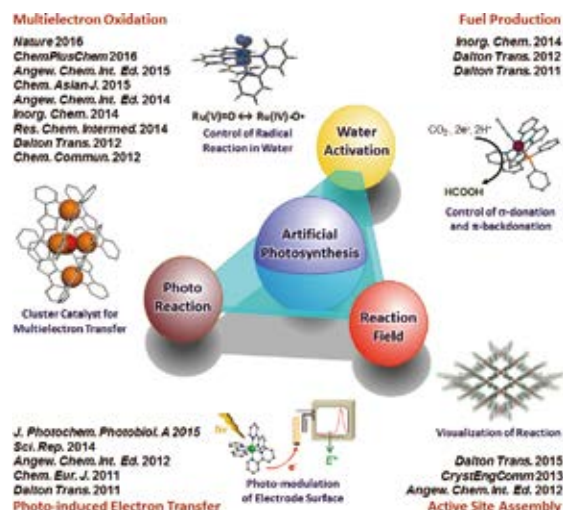


Figure 1. An overview of our work.

Selected Publications

- M. 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).
- T. Itoh, M. Kondo, H. Sakamoto, K. Wakabayashi, M. Kanaïke, K. Itami and S. Masaoka, "Porous Frameworks Constructed by Non-Covalent Linking of Substitution-Inert Metal Complexes," *Dalton Trans.* **44**, 15334–15342 (2015).
- A. Fukatsu, M. Kondo, Y. Okabe and S. Masaoka, "Electrochemical Analysis of Iron-Porphyrin-Catalyzed CO_2 Reduction under Photoirradiation," *J. Photochem. Photobiol. A* **313**, 143–148 (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. A Pentanuclear Iron Catalyst Designed for Water Oxidation¹⁾

Water oxidation ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) is considered the main bottleneck in the production of chemical fuels from sunlight and/or electricity. In nature, the oxidation of water is efficiently catalysed by the oxygen-evolving complex (OEC) in photosystem II (PSII). Because extraction of the OEC is extremely difficult, various synthetic molecular catalysts have been investigated over the last decades. However, the development of efficient, robust and abundant metal-based molecular catalysts remains a challenge. In this work, we show a water oxidation reaction catalysed by a pentanuclear iron complex. Electrochemical analysis revealed that the pentairon complex exhibits rich redox flexibility with six different oxidation states between Fe^{II}_5 and Fe^{III}_5 , in which the Fe^{III}_5 state is the active species for oxidising water. A computational investigation indicated that the O–O bond formation proceeds from the mixed-valence $\text{Fe}^{\text{II}}_2\text{Fe}^{\text{III}}(\text{Fe}^{\text{IV}}=\text{O})_2$ intermediate with a reaction barrier of less than 10 kcal mol^{-1} . The turnover frequency of the water oxidation catalyst was determined to be $1,900 \text{ s}^{-1}$, which is considerably greater than that of the OEC ($100\text{--}400 \text{ s}^{-1}$). Our findings indicate that efficient water oxidation catalysts can be created based on multinuclear iron complexes with redox flexibility and adjacent water-activation sites.

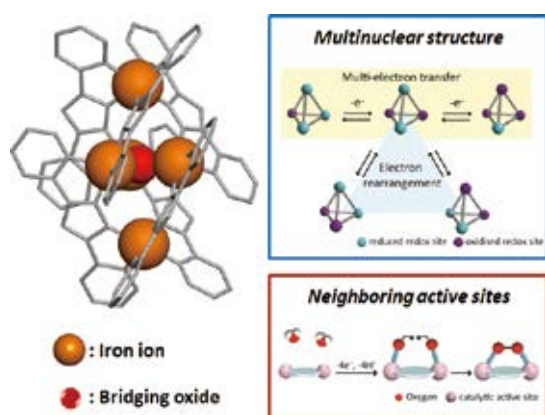


Figure 2. Structure (a) and characteristics (b) of the Fe_5 catalyst.

2. Electrochemical Analysis of Iron-Porphyrin-Catalyzed CO_2 Reduction under Photoirradiation²⁾

To understand the mechanisms of solar-to-fuel conversion

reactions, electrochemical responses of catalysts should be investigated under photoirradiation because the electrochemical process proceeds subsequent to the photochemical process. However, in general, the electrochemical and photochemical properties of molecular catalysts are separately evaluated using different experimental setups. In this study, the photochemical reaction of a metal-complex-based catalyst was analyzed by electrochemical measurements. A well-known catalyst for the CO_2 reduction reaction, *meso*-tetraphenylporphyrin iron(III) chloride ($\text{Fe}(\text{tpp})\text{Cl}$), was selected as the target analyte. Although the analysis of the electrochemical response of $\text{Fe}(\text{tpp})\text{Cl}$ under photoirradiation with conventional cyclic voltammetry (CV) was not allowed, the adaptation of thin layer cyclic voltammetry (TLCV) enabled us to detect the photochemical reaction of $\text{Fe}(\text{tpp})\text{Cl}$. The influence of photoirradiation on the electrochemical property of $\text{Fe}(\text{tpp})\text{Cl}$ was investigated both under Ar and CO_2 atmospheres. Although the thin layer cyclic voltammograms of $\text{Fe}(\text{tpp})\text{Cl}$ upon photoirradiation under an Ar atmosphere were almost the same as those measured in the dark, the measurements under a CO_2 atmosphere clearly indicated the change of the electrochemical response upon photoirradiation. The detailed analysis of this phenomenon revealed that the photoinduced decarbonylation reaction regenerates the original $[\text{Fe}^{\text{II}}(\text{tpp})]$ complex under photoirradiation.

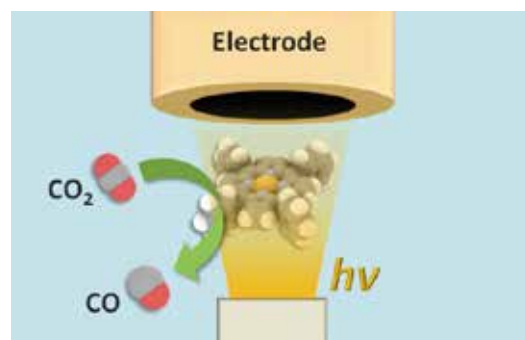


Figure 3. Electrochemical CO_2 reduction under photoirradiation.

References

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- 2) A. Fukatsu, M. Kondo, Y. Okabe and S. Masaoka, *J. Photochem. Photobiol. A* **313**, 143–148 (2015).

Awards

ENOMOTO, Takafumi; Outstanding Student Prize, Tokai Branch of the Chemical Society of Japan (2016).

LEE, Sze Koon; Poster Award, The Winter School of Asian-Core Program (2016).

ENOMOTO, Takafumi; Poster Award, The 27th Symposium on Photochemistry and Photophysics of Coordination Compounds (2016).

FUKATSU, Arisa; IZU, Hitoshi; ENOMOTO, Takafumi; Presentation Award, SOKENDAI Physical Science Student Seminar (2016).

ENOMOTO, Takafumi; Adobe Award (the excellence award), SOKENDAI Physical Science Student Seminar (2016).

Control of Electron Transfer for Efficient Oxygenation Reactions

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Electron transfer is the most fundamental reaction to govern chemical reactions. To find an effective way to control electron transfer, transient active species were prepared at low temperature under inert atmosphere. Electronic structures of these active species were investigated with various techniques including absorption, ^1H and ^2H NMR, EPR, IR resonance Raman spectroscopy and magnetic susceptibility measurement. Correlations between electronic structures and electron transfer ability are investigated in detail.

1. Reductive Manganese Species Related to Dioxygen Activation

The previous study has shown that a manganese(III) salen

complex mediates O_2 activation in the presence of OH^- from 2 M KOH aqueous solution.¹⁾ This study investigated an active species that is responsible for dioxygen activation in this reaction. Then, the reaction of a manganese(III) salen complex with Bu_4NOH was carefully carried out at low temperature (-80°C). It was found that a new species with characteristic visible absorptions is generated. Cyclic voltammetry shows that the Mn(III)/Mn(IV) redox of the new species appears at $-0.31\text{ V vs Fc/Fc}^+$, which is drastically lower than that of the starting manganese(III) complex by 1.13 V. According to the ^1H and ^2H NMR spectra, the new species is assigned as a six-coordinate anionic $[\text{Mn}^{\text{III}}(\text{salen})(\text{OH})_2]^-$ complex. Magnetic susceptibility measurements show the spin state is changed from $S = 2$ for the starting complex to $S = 1$ for the new species.

Reference

1) T. Kurahashi, *Inorg. Chem.* **54**, 8356–8366 (2015).

Visiting Professors



Visiting Professor
OGOSHI, Sensuke (*from Osaka University*)

Transformation of Unsaturated Carbonyl Compounds via Nickelacycles

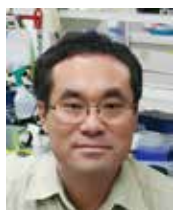
Chemists no longer doubt the importance of a methodology that could activate and utilize aldehydes in organic syntheses since many products prepared from them support our daily life. Tremendous effort has been devoted to the development of these methods using main-group elements and transition metals. Thus, many organic chemists have used an activator–(aldehyde oxygen) interaction, namely, η^1 coordination, whereby a Lewis or Brønsted acid activates an aldehyde. In the field of coordination chemistry, η^2 coordination of aldehydes to transition metals by coordination of a carbon–oxygen double bond has been well-studied; this activation mode, however, is rarely found in transition-metal catalysis. In view of the distinctive reactivity of an η^2 -aldehyde complex, unprecedented reactions via this intermediate are a distinct possibility. We have been focusing on the formation of an η^2 -aldehyde complex and its application to catalytic reactions. The key to success is efficient formation of oxa-nickelacycles generated by oxidative cyclization with carbon–carbon unsaturated bond. These nickelacycle allow us to develop new transformation of unsaturated carbonyl compounds.



Visiting Associate Professor
SHOJI, Osami (*from Nagoya University*)

Development of Novel Biocatalysts Based on Substrate Misrecognition of Enzymes

Gaseous alkanes such as methane and ethane are important fuels and potential chemical feedstock, but the selective hydroxylation of gaseous alkanes is a long-standing challenge and a current topic of interest considering increasing industrial and economic requirements. Although cytochrome P450s (P450s) are capable of breaking strong C–H bonds of hydrocarbons, the substrate specificity of cytochrome P450s makes them unsuitable for the hydroxylation of gaseous small alkanes, because P450s, especially those isolated from bacteria, recognize their specific substrates by intermolecular interactions to ensure their specificity and efficiency. We focused on the substrate misrecognition of P450s induced by inert dummy substrates (decoy molecules) that have a structural similarity to their natural substrates. We have demonstrated that even wild-type P450BM3 can catalyze the hydroxylation of gaseous alkanes such as ethane and propane by the addition perfluorinated carboxylic acids as decoy molecules. We believe that the catalytic turnover rate and coupling efficiency for hydroxylation of non-native substrates would be further improved by optimizing the structure of decoy molecules based on the crystal structure of P450BM3 with 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 question, we focus on microbial denitrification, a form of anaerobic respiration, in which nitrate is reduced to dinitrogen through nitrite, NO and nitrous oxide. In denitrification, cytotoxic NO is produced as an intermediate product, but denitrifying bacteria can grow without any damage from NO, suggesting that there is a system for effective NO elimination. As a possible system, we recently found that NO-generating nitrite reductase (NiR) forms a complex with NO-decomposing nitric oxide reductase (NOR) to suppress the diffusion of NO. On the basis of this result, we further analyze the structure and function of the NOR:NiR complex by X-ray crystallography, mutagenesis, and time-resolved spectroscopic methods.





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

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Professor, The Graduate University for Advanced Studies

Awards

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2007 Young Scientist Prize, The Biophysical Society of Japan
2006 SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
2002 The Protein Society Annual Poster Board Award

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Keywords Biological Clocks, Clock Proteins, Slow Dynamics

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

KaiC, a core protein of the circadian clock in cyanobacteria, undergoes rhythmic structural changes over approximately 24 h in the presence of KaiA and KaiB (Kai oscillator). This slow dynamics spanning a wide range of both temporal and spatial scales is not well understood, and is central to a fundamental question: What determines the temperature-compensated 24 h period? The Kai oscillator reconstitutable *in vitro* is advantageous for studying its dynamic structure through a complementary usage of both X-ray crystallography and solution scattering, its transient response by using physico-chemical techniques, and its molecular motion through a

collaborative work with computational groups (Figure 1).

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

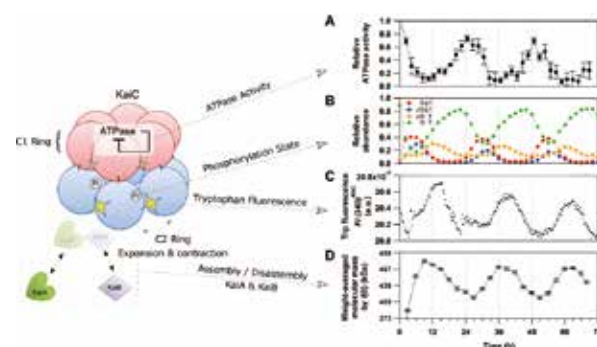


Figure 1. Circadian dynamics of cyanobacterial clock protein KaiC. The C1 and C2 domains in each protomer of KaiC are drawn as red and blue spheres, respectively. Expansion and contraction motions of the C2 ring (B, C) in solution serves as a timing cue for assembly/disassembly of KaiA and KaiB (D),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

Selected Publications

- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, *Cell. Mol. Life Sci.* **69**, 2147–2160 (2012).
- A. Mukaiyama, M. Osako, T. Hikima, T. Kondo and S. Akiyama, *Biophysics* **11**, 79–84 (2015).
- 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).

1. Atomic-Scale Origins of 24 Hour Period in Cyanobacterial Clock System¹⁾

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.

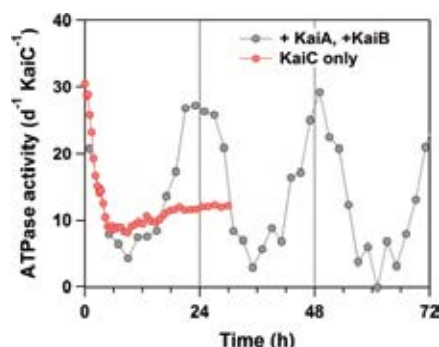


Figure 2. Time-course of KaiC ATPase activity.

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.

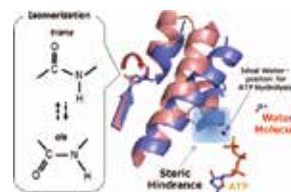


Figure 3. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

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 Systems²⁾

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^{3,4)}

We have supported SAXS users so that they can complete experiments smoothly and publish their results.^{3,4)}

4. Other Activities^{3,5,6)}

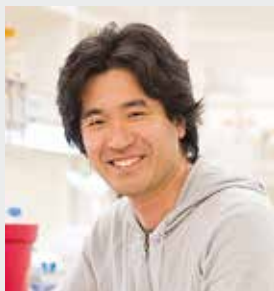
We have conducted joint research projects in collaboration with other universities and research facilities.^{3,5,6)}

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Protein Design Using Computational and Experimental Approaches

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Education

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

Awards

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

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

1. Principles for Designing Ideal Protein Structures

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

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

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

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

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

Rules relating local backbone structures to tertiary structures

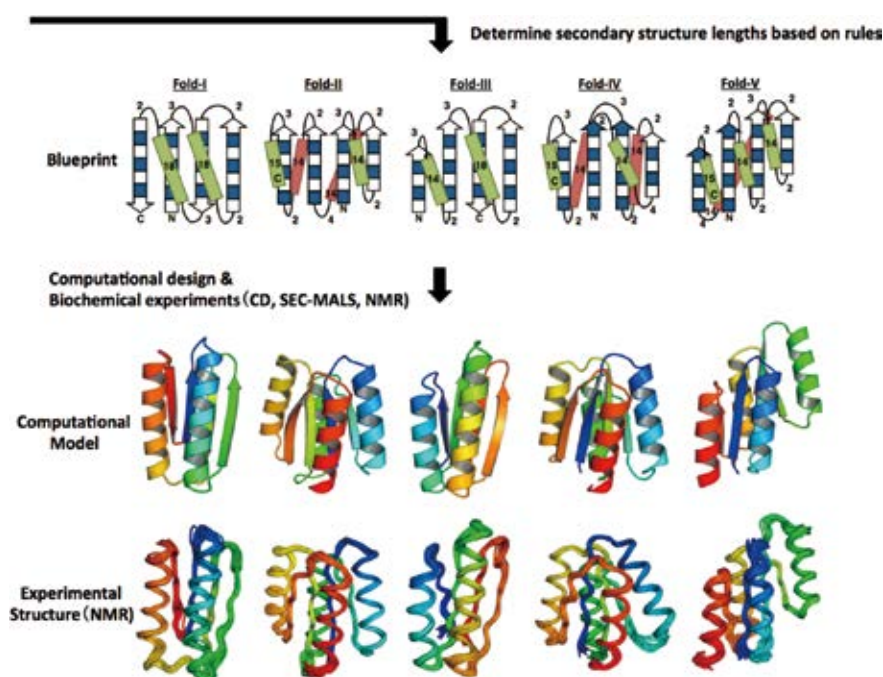
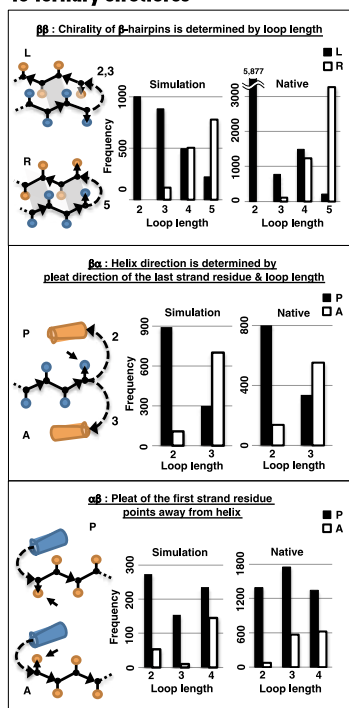


Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Visualization of Quantum Dynamical Nature Utilized Quantum Measurements

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Education

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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
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Awards

2013 FQXi Essay Contest Fourth Prize
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2015 Outstanding Referee of Physics Letters A

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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.

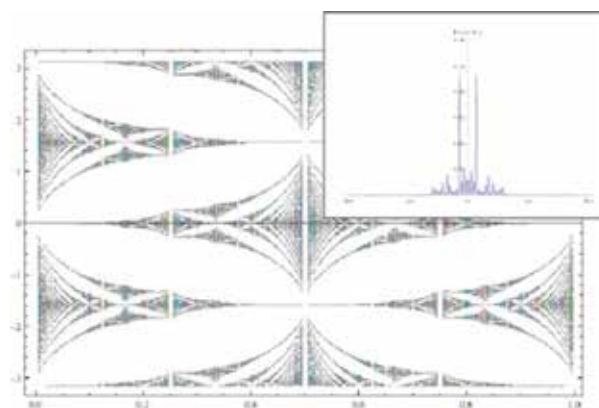


Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called 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. Generation Mechanism and Detection of Coherent Phonon in Bulk Solid^{1,2)}

Coherent optical phonons in bulk solid system play a crucial role in understanding and designing light-matter interactions and can be detected by the transient-reflectivity measurement. In this paper, we demonstrate spectrally resolved detection of coherent optical phonons in diamond from ultra-short infrared pump-probe measurements using optical band-pass filters. We show that this enhances the sensitivity approximately 35 times in measuring the coherent oscillations in the transient reflectivity compared with the commonly used spectrally integrated measurement. To explain this observation, we discuss its mechanism.

We also investigated the coherent phonon generation mechanism by irradiation of an ultrashort pulse with a simple two-level model. Our derived formulation shows that both impulsive stimulated Raman scattering (ISRS) and impulsive absorption (IA) simultaneously occur, and phonon wave packets are generated in the electronic ground and excited states by ISRS and IA, respectively. We identify the dominant process from the amplitude of the phonon oscillation. For short pulse widths, ISRS is very small and becomes larger as the pulse width increases. We also show that the initial phase is dependent on the pulse width and the detuning.

2. Exciton-Polariton Condensates in High Density Regime³⁾

In a standard semiconductor laser, electrons and holes recombine via stimulated emission to emit coherent light, in a process that is far from thermal equilibrium. Exciton-polariton condensates—sharing the same basic device structure as a semiconductor laser, consisting of quantum wells coupled to a microcavity—have been investigated primarily at densities far below the Mott density for signatures of Bose-Einstein condensation. At high densities approaching the Mott density, exciton-polariton condensates are generally thought to revert to a standard semiconductor laser, with the loss of strong coupling. Here, we report the observation of a photoluminescence sideband at high densities that cannot be accounted for by conventional semiconductor lasing. This also differs from an upper-polariton peak by the observation of the excitation power dependence in the peak-energy separation. Our interpretation as a persistent coherent electron-hole-photon coupling captures several features of this sideband whereas many remain elusive. Understanding the observation will lead to a development in non-equilibrium many-body physics.

3. Operational Derivation of Physical Laws^{4,5)}

The resolution of the Maxwell's demon paradox linked thermodynamics with information theory through information erasure principle. By considering a demon endowed with a Turing-machine consisting of a memory tape and a processor, we attempt to explore the link towards the foundations of statistical mechanics and to derive results therein in an "operational" manner. Here, we present a derivation of the Boltzmann distribution in equilibrium as an example, without hypothesizing the principle of maximum entropy. Further, since the model can be applied to non-equilibrium processes, in principle, we demonstrate the dissipation-fluctuation relation to show the possibility in this direction.

4. Laser Cooling Mechanism of Optomechanics⁶⁾

In the optomechanical cooling of a dispersively coupled oscillator, it is only possible to reach the oscillator ground state in the resolved sideband regime, where the cavity-mode line width is smaller than the resonant frequency of the mechanical oscillator being cooled. In this paper, we show that the dispersively coupled system can be cooled to the ground state in the unresolved sideband regime using an ancillary oscillator, which is coupled to the same optical mode via dissipative interaction. The ancillary oscillator has a resonant frequency close to that of the target oscillator; thus, the ancillary oscillator is also in the unresolved sideband regime. We require only a single blue-detuned laser mode to drive the cavity.

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- 6) Y.-X. Zhang, S. Wu, Z.-B. Chen and Y. Shikano, *Phys. Rev. A* **94**, 023823 (11 pages) (2016).

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

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2010 D.S. Tokyo Institute of Technology

Professional Employment

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2011 Assistant Professor, Kanagawa University
2012 JST-PRESTO Researcher (Additional post)
2013 Research Associate Professor, Institute for Molecular Science

Awards

2010 ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011 Tejima Doctoral Dissertation Award, Tokyo Institute of Technology

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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. Ion conductive materials are used as electrodes or solid electrolytes, and are key for determining the performance of these devices. Therefore, much better understanding characteristics of existing electrodes/electrolytes materials such as crystal structure, thermal stability and their reaction mechanism is important for achieving enhancement of battery performances. On the other hand, finding novel ion conduction phenomena through synthesis of a new class of substances leads to a creation of new battery systems. Our group focuses mainly on two research topics; (i) Control of an electrode/electrolyte interface in lithium secondary batteries for enhancement of battery performance (ii) Synthesis of new materials possessing a hydride ion (H^-) conductivity and development of a novel battery system utilizing the H^- conduction phenomenon and H^-/H_2 redox reaction.

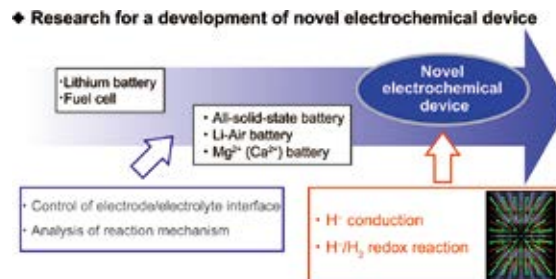


Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

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_3FePO_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 Oxyhydrides¹⁻⁴⁾

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, $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$, which are equipped with anion sublattices that exhibit flexibility in the storage of H^- , O^{2-} , and vacancies. An all-solid-state $\text{Ti}/\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}/\text{TiH}_2$ 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.

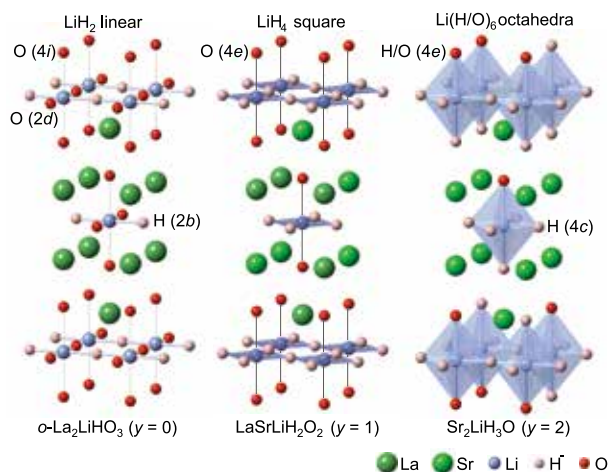


Figure 2. Crystal structures of $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$ ($x = 0, y = 0, 1, 2$). Lanthanum (and strontium) ions occupy the A sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the B site that are 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 Al_2O_3 -Based Surface Modification and Stepwise Pre-Cycling⁵⁾

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 $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ 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 $\text{LiM}_{1-x}\text{Al}_x\text{O}_2$ (M = transition metals) interlayer was formed between the modification layer and the $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ 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-inset/de-insertion process (stepwise precycling treatment) and the surface-modification.

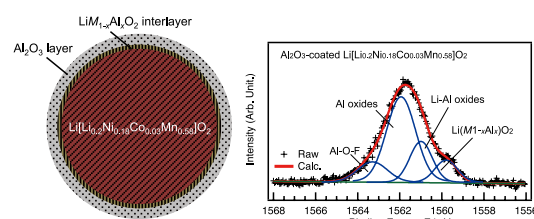


Figure 3. Schematic illustration and Al 1s HAXPES spectra of the 2 wt% Al_2O_3 -coated $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Co}_{0.03}\text{Mn}_{0.58}]\text{O}_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

References

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Open up Future Electronics by Organic Molecules

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Keywords

Molecular Conductors, Organic Superconducting Transistors, Supramolecular Nanowires

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

low temperature.

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

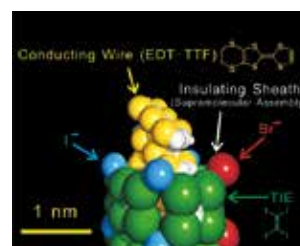


Figure 1. Crystal structure of supramolecular nanowire.

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- Y. Kawasaki, 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-FET¹⁾

κ -(BEDT-TTF)Cu[N(CN)₂]Br (κ -Br) is an organic Mott-insulator at room-temperature, but turns into metallic and superconducting states at low temperature. In our previous works, a tensile strain from FET substrate altered its ground state into a Mott-insulating state, when its thin (100–300 nm) crystal was laminated on top of SiO₂/Si⁺⁺ substrate and cooled down to low temperature. In those experiments the electronic state became completely insulating because of the tensile strain that originates in mismatching of thermal expansion coefficients between κ -Br (30 ppm/K) and Si substrate (2 ppm/K). However, one can anticipate from the T - P (temperature vs. pressure) phase diagram that mixed electronic state between superconducting and Mott-insulating states can be realized when the tensile strain is much weaker. To achieve such a mixed state (or, percolate-superconducting state), Nb-doped SrTiO₃ 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. Moreover, we have covered this oxide layer with photochromic self-assembled monolayer (SAM-layer: Figure 2, right panel) in order to make it photo-active.

Upon irradiation of UV-light, the resistivity of this device at 2 K goes down quickly and low-resistance state was observed after 180 sec. By performing resistance measurement with sweeping temperature, it turned out that Mott-insulating part of the device became superconducting by the above UV-light irradiation, which was confirmed by a sudden drop of resistivity around 7 K. This is because of the hole-doping at the FET interface that is induced by strong internal dipole moment of the SAM-layer. This mechanism was also confirmed by dual-gate action of this device, where gate-induced carriers worked cooperatively with the photo-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.

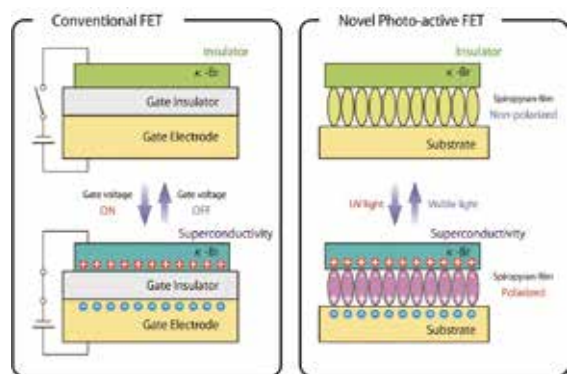


Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).

Award

SUDA, Masayuki; The 10th PCCP Prize (2016).

2. Strain-Tunable Organic FET with Strongly Correlated Electron Systems²⁾

Organic materials are soft and can be stretched even at low temperature. Our organic Mott-FETs are also soft enough to be compressed or expanded with a plastic substrate and show a band-width-controlled Mott/superconducting transitions. This kind of lattice modulation has been demonstrated in our recent experiments by mechanically pushing a poly-ethylene naphthalate (PEN) substrate covered with gold gate electrode and parylene-C dielectric from the back side (Figure 3). The organic Mott-insulator κ -(BEDT-TTF)Cu[N(CN)₂]Cl (κ -Cl) laminated on top of the substrate exhibited superconductor-to-insulator transition by bending the substrate where the surface has an effect of tensile strain in a longitudinal direction. The strain necessary for this transition at 5 K is only 0.3% while the resistance change reached ten orders of magnitude, which demonstrates high sensitivity of the Mott-insulator. The phase diagram obtained by simultaneous scans of strain and temperature well reproduces that of hydrostatic pressure. This means that one-dimensional tensile strain corresponds to an effective negative pressure in κ -Cl system.

Then, a field-effect was examined by applying a gate electric field. The transfer characteristics at higher tensile strain showed only moderate device mobility of around 5 cm²/Vs. When the system was forced to stay in a mixed phase state, where superconducting and Mott-insulating phases coexist, the electric-field-effect maximized to show device mobility up to 5900 cm²/Vs. This high response of the device can be attributed to an increase of superconducting fraction at application of gate voltage. In order to examine the above hypothesis, we have applied a magnetic field up to 7 T. Indeed, the field-effect has been considerably suppressed because the superconducting phases are destroyed by the magnetic field. This electric-field-induced superconductivity seems to originate from a decrease of Coulomb repulsion among carriers by electrostatic doping effect.

(BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene)

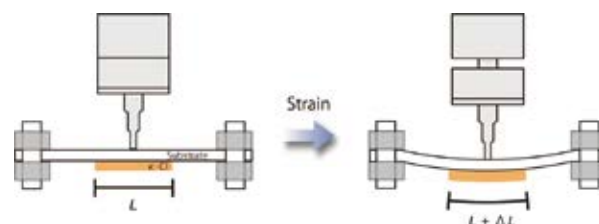


Figure 3. Side-view schematic for flexible organic Mott-FET device.

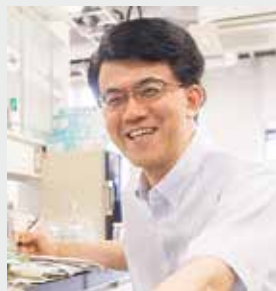
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Development of Curved Graphene Molecules as Organic Semiconductors

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Keywords Organic Synthesis, Graphene Molecule, Organic Semiconductor

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

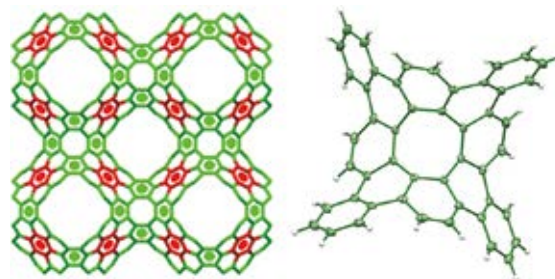


Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato and S. Tokito, "Perfluoropentacene: High-Performance p-n Junctions and Complementary Circuits with Pentacene," *J. Am. Chem. Soc.* **126**, 8138–8140 (2004).
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- Y. Sakamoto and T. Suzuki, "Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene," *J. Am. Chem. Soc.* **135**, 14074–14077 (2013).

1. Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops¹⁾

Three *N*-substituted tetracyclo(2,7-carbazole)s have been synthesized to investigate the inner regions of nanohoops. One compound has a 5,5-dimethylnonane bridge between two neighboring *anti* carbazoles, which can be used as covalently bonded “methane probes.” These probes near the ring center are strongly shielded by local ring currents and exhibited a singlet at $\delta = -2.70$ ppm in ^1H NMR. To visualize local and macrocyclic ring currents separately, we drew NICS (nucleus-independent chemical shift) contour maps of tetracyclo(9-methyl-2,7-carbazole) and [*n*]cycloparaphenylenes (CPPs). Local ring currents make the interior diatropic, and paratropic regions exist only outside the ring. Macrocyclic ring currents in [5] to [7]CPPs generate deshielding cones, which are typical of antiaromatic [*4n*]annulenes.

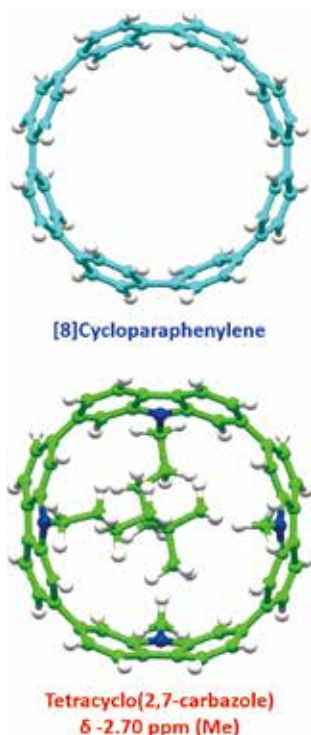


Figure 2. Optimized geometries of nanohoops by DFT calculations at the B3LYP/6-31G(d) level.

2. Ligand-Controlled Synthesis of [3]- and [4]Cyclo-9,9-dimethyl-2,7-fluorenes through Triangle- and Square-Shaped Platinum Intermediates²⁾

The syntheses of [3]- and [4]cyclo-9,9-dimethyl-2,7-fluorenes ([3] and [4]CFRs), cyclic trimer, and tetramers of 9,9-dimethyl-2,7-fluorene (FR), respectively, were achieved by the platinum-mediated assembly of FR units and subsequent reductive elimination of platinum. A triangle-shaped tris-platinum complex and a square-shaped tetra-platinum complex were obtained by changing the platinum ligand. The structure of the triangle complex was unambiguously determined by X-ray crystallographic analysis. Reductive elimination of each complex gave [3] and [4]CFRs. Two rotamers of [3]CFR were sufficiently stable at room temperature and were separated by chromatography. The physical properties of the CFRs were also investigated theoretically and experimentally.

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Three-Dimensional π -Electron Molecules

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Organic molecules possessing three-dimensional (3D) curved π -conjugated structures are attractive research targets in organic synthesis, physical organic chemistry, and organic material science. My research interest is the creation of new 3D π -conjugated organic molecules, the elucidation of properties, and the application in material science.

1. Butterfly- and Bowl-Shaped Molecules

We succeeded to create new butterfly-shaped¹⁾ (Figure 1) and bowl-shaped²⁾ (Figure 2) π -conjugated molecules with embedded hydrazine structure. The butterfly-shaped molecules were synthesized by dimerization of heterocycles (dimethyl-acridine, phenothiazine, acridone). The bowl-shaped molecule with bicarbazole structure was synthesized by desulfurization of butterfly-shaped biphenothiazine. The bowl-shaped molecule was found to undergo reversible two-electron oxidation,

in which the shape of molecule was transformed between bowl and planar geometries (Figure 2).

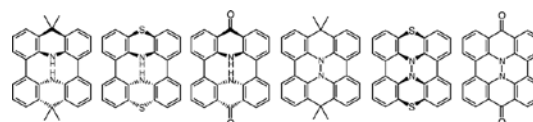


Figure 1. Butterfly- and bowl-shaped molecules.

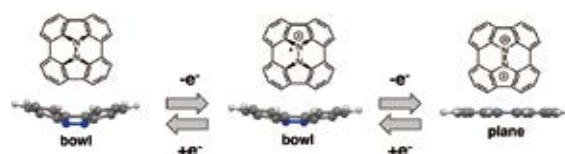


Figure 2. Butterfly- and bowl-shaped molecules.

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Coordination Behavior of Heteroarenes to Palladium Centers

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The coordination behavior of heteroarenes to palladium centers has attracted much attention since their coordination has been involved in Pd-catalyzed functionalization reactions of heteroarenes. However, heteroarene–palladium complexes have rarely been isolated, due to the labile nature of heteroarene–Pd complexes. In this project, synthesis and structural characterization of heteroarene–Pd complexes have been studied.^{1,2)}

arene–Pd interaction will provide a structural aspect on the key catalytic intermediates of palladium-catalyzed heteroarene transformations. Further study to verify the reactivity of σ -, σ/π -intermediate-, and π -complexes of indole is now underway.

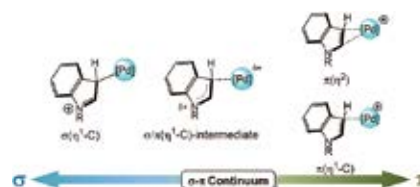


Figure 1. σ - π Continuum in indole–Pd complexes.

1. σ - π Continuum in Indole–Pd^{II} Complexes

It has been proven that there is a σ - π continuum in heteroarene–metal complexes through isolation and systematic structural analysis of σ - and π -modes in indole–Pd^{II} complexes, while σ -mode has been assumed as the dominant mode for heteroarene–Pd interaction. The insight into the hetero-

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