RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

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

Theoretical Studies on Heterogeneous Condensed Phase Dynamics

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Keywords Spatiotemporal Heterogeneous Dynamics, Liquids, Proteins

Nonlinear intermolecular interactions cause complicated motions in condensed phases, *e.g.* liquids and biological systems. These motions are spatially and temporally heterogeneous with a wide range of time and spatial scales and yield both static and dynamic properties of the systems. 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 dynamic heterogeneity. Our systematic analysis for various systems shows that the lifetime of dynamic heterogeneity is intimately related to configurational entropy and thus the temperature dependence of lifetime of dynamic heterogeneity is more sensitive to the fragility than that of α-relaxation time determined by one-time correlation function. In addition to the analysis of dynamic heterogeneity with multi-time correlation function, we have examined the molecular origin of anomalous temperature dependence of isobaric specific heat of water. The time scale involved in isothermal specific heat has been analyzed by analyzing complex specific heat. We examined the emergence of correlated motion in terms of the wavenumber (k) dependent complex specific heat and the shell-wise energy fluctuation.

We currently investigate how chemical reactions proceed in biological systems, *e.g.* clock protein KaiC, under complex fluctuations. We also examine the large conformational transitions and the time-dependent couplings between conformational dynamics in proteins by using the idea of multi-dimensional spectroscopy.

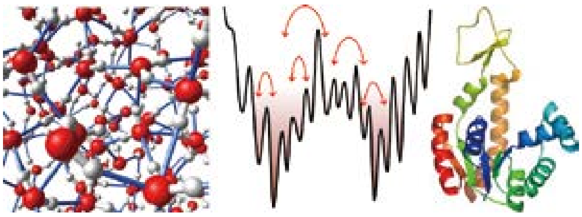

Figure 1. Schematic figure of rugged energy landscape (center) in supercooled water (left) and a biomolecule (right).

Selected Publications

- T. Yagasaki and S. Saito, *Acc. Chem. Res.* **42**, 1250–1258 (2009), *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013). S. Imoto, S. Xantheas and S. Saito, *J. Chem. Phys.* **139**, 044503 (7 pages) (2013).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, I. Ohmine and B. Bagchi, *J. Chem. Phys.* **138**, 094503 (7 pages) (2013).

1. Dynamic Heterogeneity in the Folding/Unfolding Transitions of FiP35[1)]

Molecular dynamics simulations have become an important tool in studying protein dynamics over the last few decades. Atomistic simulations on the order of micro- to milliseconds are becoming feasible and are used to study the state-of-the-art experiments in atomistic detail. Yet, analyzing the high-dimensional-long-temporal trajectory data is still a challenging task and sometimes leads to contradictory results depending on the analyses. To reveal the dynamic aspect of the trajectory, here we propose a simple approach which uses a time correlation function matrix and apply to the folding/unfolding trajectory of FiP35 WW domain [Shaw *et al.*, *Science* **330**, 341 (2010)]. The approach successfully characterizes the slowest mode corresponding to the folding/unfolding transitions and determines the free energy barrier indicating that FiP35 is not an incipient downhill folder. The transition dynamics analysis further reveals that the folding/unfolding transition is highly heterogeneous, *e.g.*, the transition path time varies by ~100 fold. We identify two misfolded states and show that the dynamic heterogeneity in the folding/unfolding transitions originates from the trajectory being trapped in the misfolded and half-folded intermediate states rather than the diffusion driven by a thermal noise. The current results help reconcile the conflicting interpretations of the folding mechanism and highlight the complexity in the folding dynamics. This further motivates the need to understand the transition dynamics beyond a simple free energy picture using simulations and single-molecule experiments.

2. Couplings between Hierarchical Conformational Dynamics from Multi-Time Correlation Functions and Two-Dimensional Lifetime Spectra: Application to Adenylate Kinase[2)]

An analytical method based on a three-time correlation function and the corresponding two-dimensional (2D) lifetime spectrum is developed to elucidate the time-dependent couplings between the multi-timescale conformational dynamics in heterogeneous systems such as proteins. In analogy with 2D NMR, IR, electronic, and fluorescence spectroscopies, the waiting-time dependence of the off-diagonal peaks in the 2D lifetime spectra can provide a quantitative description of the dynamical correlations between the conformational motions with different lifetimes. The present method is applied to intrinsic conformational changes of substrate-free adenylate kinase (AKE) using long-time coarse-grained molecular dynamics simulations. It is found that the hierarchical conformational dynamics arise from the intra-domain structural transitions among conformational sub-states of AKE by analyzing the one-time correlation functions and one-dimensional lifetime spectra for the donor–acceptor distances corresponding to single-molecule Förster resonance energy transfer experiments with the use of the principal component analysis. In addition, the complicated waiting-time dependence of the off-diagonal peaks in the 2D lifetime spectra for the donor–acceptor distances is attributed to the fact that the time evolution of the couplings between the conformational dynamics depends upon both the spatial and temporal characters of the system. The present method is expected to shed light on the biological relationship among the structure, dynamics, and function.

3. Ultrafast Dynamics of Liquid Water: Energy Relaxation and Transfer Processes of the OH Stretch and the HOH Bend[3)]

The vibrational energy relaxation and transfer processes of the OH stretching and the HOH bending vibrations in liquid water are investigated via the theoretical calculation of the pump–probe spectra obtained from non-equilibrium molecular dynamics simulations with the TTM3-F interaction potential. The excitation of the OH stretch induces an instantaneous response of the high frequency librational motions in the 600–1000 cm^{-1} range. In addition, the excess energy of the OH stretch of a water molecule quickly transfers to the OH stretches of molecules in its first hydration shell with a time constant of ~50 fs, followed by relaxation to the HOH bends of the surrounding molecules with a time constant of 230 fs. The excitation of the HOH bend also results in the ultrafast excitation of the high frequency librational motions. The energy of the excited HOH bend of a water molecule decays, with a time constant of 200 fs, mainly to the relaxation of the HOH bends of its surrounding molecules. The energies of the HOH bends were found to transfer quickly to the intermolecular motions via the coupling with the high frequency librational motions. The excess energy of the OH stretch or the HOH bend relaxes to the high frequency intermolecular librational motions and eventually to the hot ground state with a time scale of ~1 ps via the coupling with the librational and translational motions. The energy relaxation and transfer processes were found to depend on the local hydrogen bonding network; the relaxations of the excess energy of the OH stretch and the HOH bend of four- and five-coordinated molecules are faster than those of a three-coordinated molecule due to the delocalization of the vibrational motions of the former (four- and five-coordinated molecules) compared to those of the later (three-coordinated molecules). The present results highlight the importance of the high frequency intermolecular librational modes in facilitating the ultrafast energy relaxation process in liquid water via their strong nonlinear couplings with the intramolecular OH stretching and HOH bending vibrations.

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1) T. Mori and S. Saito, *J. Chem. Phys.* **142**, 135101 (7 pages) (2015).
2) J. Ono, S. Takada and S. Saito, *J. Chem. Phys., Special Topic: Multidimensional Spectroscopy* **142**, 212404 (13 pages) (2015).
3) S. Imoto, S. S. Xantheas and S. Saito, *J. Phys. Chem. B* **119**, 11068–11078 (2015).

Theory for Optical Response in Nanostructures and its Application to Functional Nanodevices

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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) Wavelength of incident light is considered to be much longer than molecular size, *i.e.*, dipole approximation. Thus, a target molecule is well approximated by a point dipole and the dipole feels a uniform electromagnetic field.
(ii) Electric polarization in a molecule induced by incident-light excitation inevitably generates a new electromagnetic field, referred to as an "optical near-filed." 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 very suitable for massively parallelized computations.

Very recently, we also started the theoretical studies of computational design of catalytic metal clusters supported on bulk surfaces. The simulations were carried out by using the first-principles molecular dynamics (MD) approach, *i.e.*, Car-Parrinello MD 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).
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- K. Nobusada and T. Iwasa, "Oligomeric Gold Clusters with Vertex-Sharing Bi- and Triicosahedral Structures," *J. Phys. Chem. C* **111**, 14279–14282 (2007).
- M. Noda, K. Ishimura, K. Nobusada, K. Yabana and T. Boku, "Massively-Parallel Electron Dynamics Calculations in Real-Time and Real-Space: Toward Applications to Nanostructures of More than Ten-Nanometers in Size," *J. Comput. Phys.* **265**, 145–155 (2014).

1. Two-Photon Absorption Induced by Electric Field Gradient of Optical Near-Field and its Application to Photolithography[1)]

An electric field gradient is an inherent property of the optical near-field (ONF). In this study, we have verified that the electric field gradient of the ONF intrinsically leads to two-photon absorption, demonstrating the optical response of a closely-placed dielectric nanoparticle and quantum dot system. The theoretical calculations were carried out by using a density matrix formalism and a classical Lorentz model. The electric field gradient of the ONF was found to cause two-photon absorption by an unusual mechanism. Furthermore, the absorption exhibits a non-monotonic dependence on the spatial arrangement of the nanosystem, completely different from that of conventional two-photon absorption induced by an intense electric field. The present two-photon absorption process was illustrated in a previous experimental observation, by reinterpreting the results of ONF photolithography. The present idea of the two-photon absorption due to the electric field gradient is not limited to the model system considered here. The idea provides a basis for fundamental optical responses in nanostructures and paves the way for the ONF excitation dynamics that are completely different from those of conventional optical response processes.

2. Reaction Pathway and Free Energy Landscape of Catalytic Oxidation of Carbon Monoxide Operated by a Novel Supported Gold–Copper Alloy Cluster[2)]

An insight into the catalytic activities of pure gold (Au_8) and gold-alloy ($CuAu_7$) clusters supported on either MgO(100) or graphene has been undertaken in the search for an efficient, yet commercially appealing production of Au-based nanocatalysts. The present set of first-principles dynamical simulations shows that the gold and gold-copper alloy clusters destabilize to various extents on MgO but preserve their structures on the graphene support at room temperature. Consequently, the Cu atom remains embedded inside the Au cluster on MgO, whereas it can be easily exposed on the cluster surface on the graphene substrate. This feature appears to be a general key issue to trigger the catalytic reaction and discloses new perspectives for a rational synthesis of supported Au-based catalysts relying on the intrinsic chemical character of Cu which possesses a stronger affinity to oxygen than Au. Indeed, the Cu atom acts as an active site for the approach of O_2 and keeps the molecule bound to the cluster. We clarified that the catalytic oxidation of CO occurs on the graphene-supported $CuAu_7$ in a highly selective Langmuir-Hinshelwood type reaction, addressing the long-standing controversy about the actual reaction mechanism for this type of catalysis. Our findings contribute to the development of efficient and commercially appealing supported alloy clusters driven by a proper choice of dopants and supports, thus reducing the use of expensive gold.

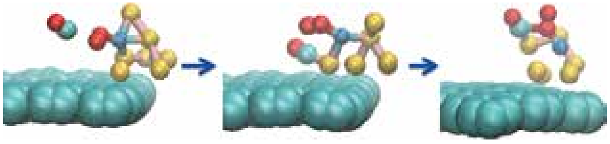

Figure 1. A first step of the Langmuir-Hinshelwood type reaction on $CuAu_7$ supported by graphene, obtained via Blue-Moon ensemble simulations. CO approaches the gold surface and reacts with O_2 anchored on the Cu active site, forming an intermediate for the subsequent CO_2 desorption.

3. Control of Optical Response of a Supported Cluster on Different Dielectric Substrates[3)]

We developed a theoretical approach for photo-induced electron dynamics at an interface, approximating a substrate as a dielectric continuum. Because electron dynamics is treated in real-time and real-space, the approach is applicable to various optical processes. We calculated optical absorption of Ag_n (n = 2, 54) supported on a dielectric substrate with a Drude-type dielectric function. Changes in ω_p and γ of the substrate differently altered the spectral peak position and intensity. By analyzing the time-dependent induced dipole and spatial configuration of induced electron density, we clarified the mechanism underlying spectral changes, relating to experimental results obtained in many research areas. Shifts in spectral peaks of Ag_2 were mainly determined by the strength of attractive and repulsive interactions with the substrate, and decreases in peak intensity were due to energy dissipation into the substrate. These peak shifts and intensity changes are related to the real and imaginary parts of $\varepsilon{-}1/\varepsilon{+}1$, respectively. We extended the approach to a nanostructure, Ag_{54}, and found another mechanism for changes in intensity, which is related to the real part of $\varepsilon{-}1/\varepsilon{+}1$. The spectral peak for Ag_{54} increases through interactions with the Ag substrate because of collective oscillations of electrons. The present method and the resulting insights contribute to a basic understanding of optical processes at an interface and to the development of optical devices that can be controlled by electronic properties of a substrate.

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3) K. Iida, M. Noda and K. Nobusada, *J. Chem. Phys.* **142**, 214702 (2015).

Advanced Electronic Structure Theory in Quantum Chemistry

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Keywords Electronic Structure Theory, Quantum Chemistry, Computational Chemistry

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

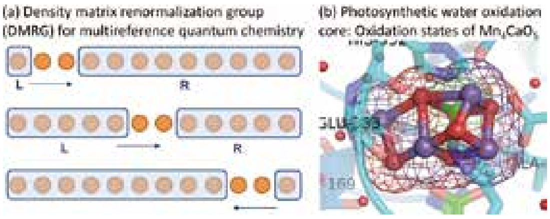

Figure 1. (a) Algorithm of density matrix renormalization group (DMRG) and (b) Its application to manganese cluster.

Selected Publications

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

1. Fully Internally Contracted Multireference Configuration Interaction Theory Using Density Matrix Renormalization Group

We present an extended implementation of the multireference configuration interaction (MRCI) method combined with the quantum-chemical density matrix renormalization group (DMRG). In the previous study, we introduced the combined theory, referred to as DMRG-MRCI, as a method to calculate high-level dynamic electron correlation on top of the DMRG wavefunction that accounts for active-space (or strong) correlation using a large number of active orbitals. The previous implementation achieved the MRCI calculations with the active space (24*e*,24*o*), which are deemed the record largest, whereas the inherent $O(N^9)$ complexity of computation was found a hindrance to use further large active space. In this study, an extended optimization of the tensor contractions is developed by explicitly incorporating the rank reduction of the decomposed form of the cumulant-approximated tensors into the factorization. It reduces the computational scaling (to $O(N^8)$) as well as the cache-miss penalty. The new DMRG-MRCI implementation is applied to the determination of the stability of the iron(IV)-oxo porphyrin relative to the iron(V) electronic isomer (electromer) using the active space (29*e*,29*o*) (including four second d-shell orbitals of iron) with triple-*z*-quality atomic orbital basis sets. The DMRG-MRCI model is shown to favor the triradicaloid iron(IV)-oxo state as the lowest-energy state and characterize the iron(V) electromer as thermally inaccessible, supporting the earlier experimental and density functional studies. This conflicts with the previous MR calculations using the restricted active space second-order perturbation theory with the similar-size active space (29*e*,28*o*) reported by Pierloot *et al*. [M. Radon, E. Broclawik, and K. Pierloot, *J. Chem. Theory Comput.* **7**, 898 (2011)], showing that the hypothetical iron(V) state indicated by recent laser flash photolysis (LFP) studies is likely thermally accessible because of its underestimated relative energy.

2. Scalar Relativistic Calculations of Hyperfine Coupling Constants Using *Ab Initio* DMRG[5)]

We have developed a new computational scheme for high-accuracy prediction of the isotropic hyperfine coupling constant (HFCC) of heavy molecules accounting for the high-level electron correlation effects as well as the scalar-relativistic effects. For electron correlation, we employed the *ab initio* DMRG method in conjunction with a complete active space model. The orbital-optimization procedure was employed to obtain the optimized orbitals required for accurately determining the isotropic HFCC. For the scalar-relativistic effects, we initially derived and implemented the Douglas-Kroll-Hess hyperfine coupling operators up to the third order by using the direct transformation scheme. A set of *4d* transition metal radicals consisting of Ag atom, PdH, and RhH_2 were chosen as test cases. Good agreement between the isotropic HFCC values obtained from DMRG/DKH3 and experiment was archived.

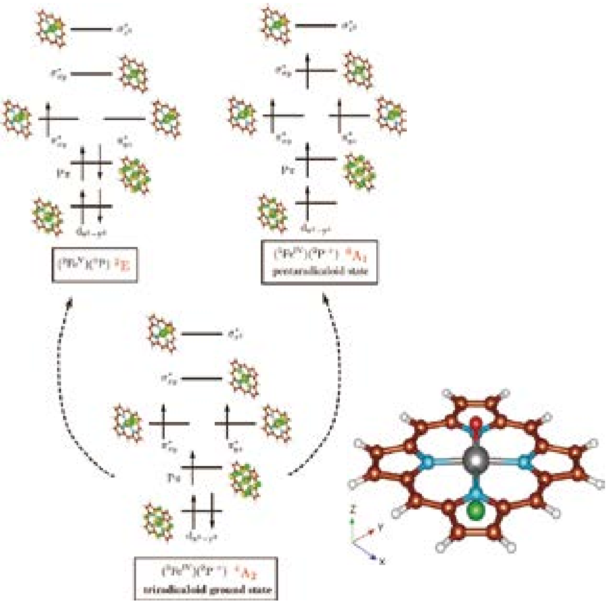

Figure 2. Electronic isomers of FeO(P)Cl molecule and their electronic configurations $^4A_2$ is a formal ground state; however, recent LFP analysis suggests the presence of the stable $^6A_1$ state.

References

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Award

KURASHIGE, Yuki; The Chemical Society of Japan Award for Young Chemists 2014.

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 heterojunction of Ag nanocluster supported by alumina surface in terms of H_2 activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

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

(4) Theoretical spectroscopy

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

Selected Publications

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

1. Complex Absorbing Potential (CAP) for Resonance States

Complex absorbing potentials (CAP) have been successfully applied in many contexts from nuclear physics, over vibrational predissociation and reactive scattering phenomena, to electronically metastable states. In the electronic structure, CAPs are used to characterize resonances, such as temporary anions and dianions, core ionized states (Auger decay), and molecules subjected to field ionization.

We have introduced new CAP forms and systematically examined their performances,$^{1)}$ for example, in double-bond and heteroaromatic molecules (Figure 1). The advantage of new CAPs is that they warp perfectly around the molecular systems with side chain or any monomer of a cluster.

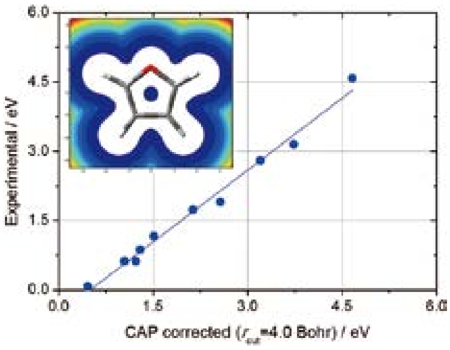

Figure 1. Correlation between calculated resonance energy and observed energy. A smooth Voronoi potential (example shown in the inset of the figure) was developed.

2. Modeling Molecular Systems at Extreme Pressure in Various Electronic States

Novel molecular photochemistry can be developed by combining high pressure and laser irradiation. For studying such high-pressure effects (order of GPa) on the confined electronic ground and excited states, we extend the PCM (polarizable continuum model) SAC (symmetry-adapted cluster) and SAC-CI (SAC-configuration interaction) methods to the PCM-XP (extreme pressure) framework.

The PCM-XP SAC/SAC-CI method was applied to furan (C_4H_4O) in cyclohexane at high pressure (1–60 GPa).$^{2)}$ The excitation energies of furan in cyclohexane show blue shift with increasing pressure, yet the extents of the blue shift significantly depend on the character of the excitations (Figure 2). The energy ordering of the lowest Rydberg and valence states alters under high-pressure. The pressure effects on the electronic structure are two-fold: A confinement of the molecular orbital and a significant change in valence-Rydberg mixing along the pressure.

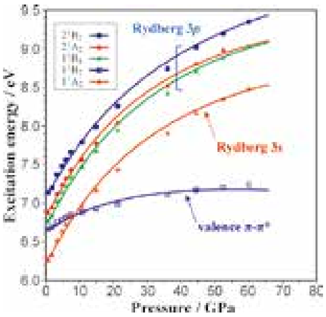

Figure 2. Variation of the excitation energies for furan calculated by the PCM-XP SAC-CI.

3. Bond Activation on Bimetallic Alloy Nanoclusters

Gold-Palladium (Au/Pd) bimetallic nanocluster (NC) catalysts have been extensively investigated because of their wide varieties of catalytic activity for various substrates. Recently, we have developed new catalysts for C–Cl bond activation under mild condition using Au/Pd NP supported on poly-*N*-vinylpyrrolidone (PVP); the Ullmann coupling of aryl chloride (ArCl).$^{3)}$

We have investigated the C–Cl bond activation on Au/Pd NC for the oxidative addition of ArCl, which is a key step of this homocoupling reaction (Figure 3).$^{4)}$ Some stable cage structures and spin states of Au/Pd NCs were found by using genetic algorithm (GA) and DFT calculations. Several low-lying oxidative addition pathways were obtained and some of them are thermally accessible via spin crossing and internal conversion.

The present computational protocol using GA combined with the DFT calculations is useful for investigating the structures and reactivity of the bimetallic NCs.

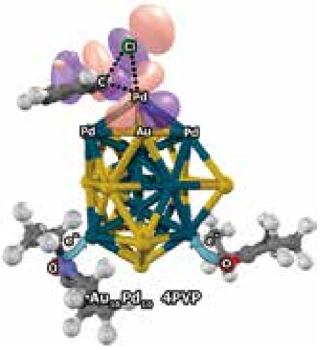

Figure 3. C–Cl bond activation on bimetallic Au/Pd nanocluster coordinated by PVP (polyvinylpyrolidon).

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2) R. Fukuda, M. Ehara and R. Cammi, *J. Chem. Theory Comput.* **11**, 2063–2076 (2014).
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* IMS International Internship Program

Development of New Molecular Dynamics Algorithms for Biomolecular Systems

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

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Education

1998 B.S. Keio University
2002 Ph.D. Keio University

Professional Employment

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

Award

2014 Academic Award of the Molecular Simulation Society of Japan

Member

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IMS Research Assistant Professor
MORI, Yoshiharu
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NISHIZAWA, Hiroaki
Graduate Student
NISHIKAWA, Naohiro*
Secretary
KAWAGUCHI, Ritsuko

Keywords Molecular Dynamics Simulation, Protein, Amyloid

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

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

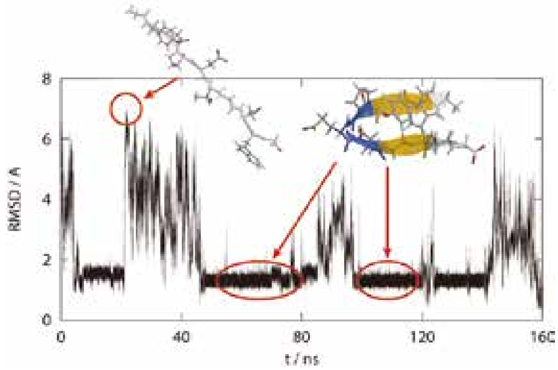

Figure 1. Time series of protein folding simulation.

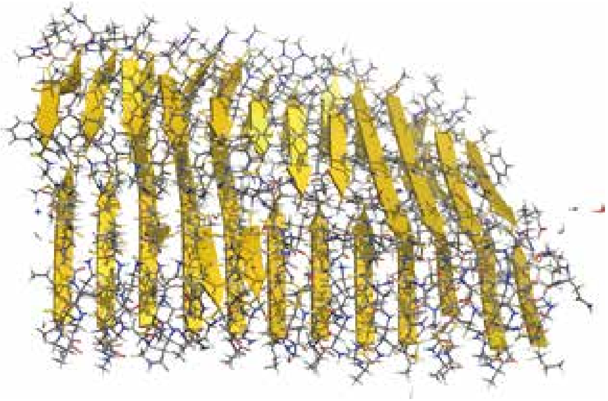

Figure 2. Snapshot of amyloid fibril.

Selected Publications

- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- S. G. Itoh and H. Okumura, "Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method," *J. Chem. Theory Comput.* **9**, 570–581 (2013).
- Y. Mori and H. Okumura, "Pressure-Induced Helical Structure of a Peptide Studied by Simulated Tempering Molecular Dynamics Simulations," *J. Phys. Chem. Lett.* **4**, 2079–2083 (2013).
- H. Okumura, "Temperature and Pressure Denaturation of Chignolin: Folding and Unfolding Simulation by Multibaric-Multithermal Molecular Dynamics Method," *Proteins* **80**, 2397–2416 (2012).

1. Dimerization Process of Amyloid-β(29-42) by the Hamiltonian Replica-Permutation Molecular Dynamics Simulations

In order to investigate the dimerization process and conformations of amyloid-β peptides, we applied the Hamiltonian replica-permutation method, which is a better alternative to the Hamiltonian replica-exchange method, to two amyloid-β(29-42) molecules in explicit water solvent.1) At the first step of the dimerization process, two amyloid-β(29-42) molecules came close to each other and had intermolecular sidechain contacts. When two molecules had the intermolecular sidechain contacts, the amyloid-β(29-42) tended to have intramolecular secondary structures, especially β-hairpin structures as in Figure 3. The two molecules had intermolecular β-bridge structures by coming much closer at the second step of the dimerization process. Formation of these intermolecular β-bridge structures were induced by the β-hairpin structures. The intermolecular β-sheet structures elongated at the final step. Structures of the amyloid-β(29-42) in the monomer and dimer states are also shown with the free-energy landscapes, which were obtained by performing efficient sampling in the conformational space in our simulations.

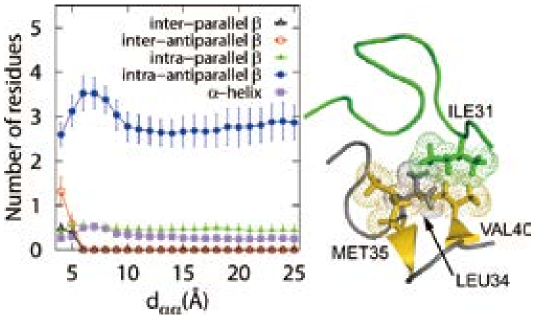

Figure 3. Ensemble-averages of the numbers of residues that have secondary structures at the corresponding intermolecular distance $d_{\alpha\alpha}$ (left) and a snapshot of a representative conformation at $d_{\alpha\alpha}$ = 8 Å (right).

2. Molecular Dynamics of the Structural Changes of Helical Peptides Induced by Pressure

An AK16 peptide and a C-peptide analog are experimentally known to form more helical structures under high pressure conditions than those at atmospheric pressure, even though most proteins usually unfold at high pressure as in Figure 4. To understand the pressure-induced structural changes of the two peptides, molecular dynamics simulations with the simulated tempering method for the isobaric-isothermal ensemble were performed in a wide pressure range from 0.1 MPa to 1.4 GPa.2) We found that the fraction of the folded state decreases once and then increases with increasing pressure for both peptides. The partial molar volume change of both peptides from the folded state to the unfolded state increases monotonically from a negative value to a positive value as pressure increases. By calculating the radius of gyration and interatomic distances of the AK16 peptide and the C-peptide analog, we found that these peptides are compressed under high-pressure conditions, which causes the folded state to be more stable at high pressure. Furthermore, we found that the salt bridge of the C-peptide analog is broken under high pressure.

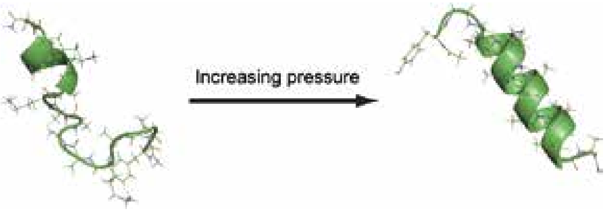

Figure 4. Coil structure of an AK16 peptide (left) and the helically folded structure of this peptide (right).

3. Comparison of Replica-Permutation Molecular Dynamics Simulations with and without Detailed Balance Condition

In the replica-permutation method (RPM), temperatures are not only exchanged between two replicas but also permutated among more than two replicas using the Suwa–Todo algorithm, which minimizes the rejection ratio in Monte Carlo trials. We verify the sampling efficiency of RPM that adopts Suwa–Todo algorithms with and without a detailed balance condition (DBC).3) To compare these techniques, molecular dynamics simulations of RPM with and without the DBC and the replica-exchange method (REM) were carried out for a chignolin molecule in explicit water. Although no difference in the numbers of folding and unfolding events was observed, the numbers of tunneling events of the two RPM simulations were larger than that of REM. This indicates that the minimization of the rejection ratio by the Suwa–Todo algorithm in RPM realizes efficient sampling. Furthermore, the sampling efficiency was slightly higher in the RPM without the DBC than in that with the DBC. The reason for this difference is also discussed.

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3) H. Nishizawa and H. Okumura, *J. Phys. Soc. Jpn.* **85**, 074801 (6 pages) (2015).

Award

OKUMURA, Hisashi; Academic Award of the Molecular Simulation Society of Japan (2014).

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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 focus on the projects both on ultrafast photoinduced electron energy transfer in the excited state in solution and on ionic liquids (ILs). The project on photoinduced electron energy transfer processes in the excited state in solution is aimed at the development of a theoretical method to investigate electron energy transfer including solvent motion and dynamics. On the other hand, ILs' projects are focused on the study of dynamical properties on ionic liquids using molecular dynamics simulation technique.

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

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

2. Investigations of Dynamical Properties on Ionic Liquids[1–2)]

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

References

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

Visiting Professors

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

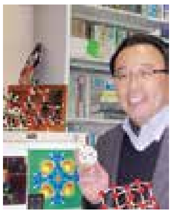
New Frontier of Hybrid Stochastic and Deterministic Electronic Structure Approaches

The vast majority of ab initio electronic structure methods are on the basis of deterministic disciplines, in which a compactification of an N-factorial CI expansion is of main interest. Nevertheless, the way to calculate strongly correlated systems with quasi-degeneracy and general excited states accurately still remains open. These objectives are of significant importance for entangled electronic states involving photoinduced phenomena in biochemistry and energy conversion processes in chemistry. We have recently developed the model space quantum Monte Carlo (MSQMC) method crossing the effective Hamiltonian formalism and full configuration interaction (FCI) QMC [*ST*, *J. Chem. Phys.* **138**, 164126 (2013)]. The method sidesteps the negative sign problem in QMC arising from quasi-degeneracy transcending the storage limitation for CI vectors. Promising results are obtained for the FCI potential energy curves of various excited states. We further extend MSQMC to energy independent partitioning (EIP) that enable us to obtain all of the FCI solutions in the model space simultaneously.

Visiting Professor
TAKADA, Shoji *(from Kyoto University)*

Computational Studies of Biomolecular Systems

I am studying in the area of computational molecular biophysics, primarily focusing on protein structure and dynamics. Even though thousands of X-ray crystal structures may provide impression that biomolecules are rigid material, in reality they are nano-scale molecules that work under thermal noise and, as such, they are dynamic. Given many crystal structures as snapshots, my ultimate goal is to understand dynamical functions of these molecules via computational analysis. Specifically, using coarse-grained molecular modeling approach, we study interplay between conformational dynamics and protein function, for adenylate kinase as a model protein. Adenylate kinase exerts large-amplitude motion that couples with binding to substrates, ATP and AMP. After binding and structural change, it catalyzes chemical reaction to obtain 2ADP, which is then released coupling with conformational dynamics. Modeling the entire process of this enzyme can be an ideal computational model for complete cycles of molecular machines.



Visiting Associate Professor
SUGIMOTO, Manabu *(from Kumamoto University)*

Computational Molecular Science for Chemical Design and Engineering

The quantum chemical method is a powerful and insightful tool for analyzing and predicting molecular structures and chemical phenomena. Our group is interested in applying electronic-structure methods for investigating molecular functions that are of practical importance. Our on-going research is twofold: One is direct application of the quantum methods. For example, we have recently carried out the calculations to characterize electronic excitations in supramolecular systems, and developed a computational scheme to study elastic deformation of a molecule by external force. We are also studying materials related to energy conversion such as hydrogen-production catalysts and those in photovoltaics. Another research is for development of chemoinformatics through which one would be able to learn, understand, investigate, predict, and design molecules and their chemistries. We are developing a computer system on the basis of our original electronic-structure database and new search engines. Our contribution is intended to enrich usefulness and uniqueness of Computational Molecular Science.

RESEARCH ACTIVITIES

RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction 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

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Division of Photo-Molecular Science I

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Education
1983 B.S. The University of Tokyo
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Professional Employment
1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
1993 Associate Professor, The University of Tokyo
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

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Assistant Professor
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NISHIYAMA, Yoshio
Post-Doctoral Fellow
KOWAKA, Yasuyuki
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HASHIYADA, Shun
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ISHIKAWA, Akiko
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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 molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies, and so forth.

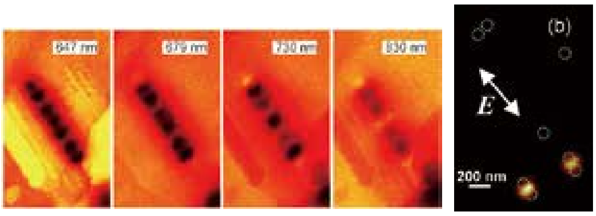

Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right)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

Selected Publications

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

1. Local Optical Activity in Achiral Two-Dimensional Gold Nanostructures[1,2]

Since the discovery of molecular chirality, the geometrical chirality of a material, which means that the material has a non-superposable mirror image, has been considered the prerequisite for exhibiting optical activity of the structural origin. Circular dichroism (CD, defined as the differential absorption of left and right circularly polarized light) is a representative measurement method of optical activity. We recently developed a scanning near-field CD microscope, which is capable of optical imaging with CD of a specimen as the signal with a spatial resolution beyond the diffraction limit of light, and applied the method to local optical activity measurements of plasmonic chiral nanostructures. In the present study, we report an experimental demonstration of nanoscale local CD activities for highly symmetric achiral (non-chiral) rectangular gold nanostructures.[1] Macroscopic CD spectral measurements of the nanostructure sample did not show any CD activity over the entire range of measured wavelengths, as expected from the achiral shape of the rectangle. In contrast, we found both locally positive and negative CD signals in a single rectangular nanostructure, whose spatial distribution was symmetric about the center of the rectangle, with strong CD signals at the corners (Figure 2(b)). The strong local CD signals in achiral material were also found in crescent (C-shaped) gold nanostructures.[2] These results demonstrate that the established selection rule of optical activity is not valid for local microscopic measurements, and suggest that strongly chiral optical fields are generated in the vicinities of plasmonic materials even if the materials are achiral.

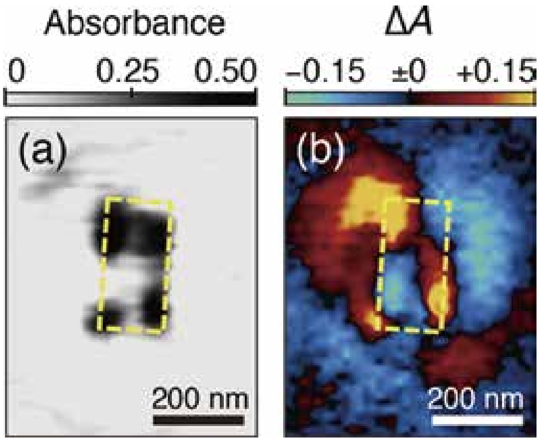

Figure 2. Near-field optical images (at 633 nm) of a rectangular gold nanostructure fabricated on a glass substrate via electron beam lithography and lift-off method.[1] (a) Transmission image. (b) CD image. Dashed yellow lines represent approximate shape of the nanostructure.

2. Plasmon Dephasing in Single Gold Nanorods Observed by Ultrafast Near-Field Optical Imaging[3]

We applied time-resolved near-field optical microscopic measurements with ultrashort light pulses of ~16 fs duration to observe plasmon dephasing processes in single gold nanorods. The correlation width of the time-resolved signal obtained at each position on the nanorod was broadened compared with the auto-correlation width of the pulse, because the plasmon dephasing was convolved on the system response function given by the pulse auto-correlation function. The correlation width maps of the rods (Figure 3) showed spatially oscillating patterns that look similar to the plasmon mode structures observed in the static near-field optical images (as typified with Figure 1). The spatial variation of the correlation widths was explained as arising from the position dependent contribution of the resonant plasmon excitation in the time-resolved signals relative to that of the non-resonant excitation. The dephasing times of the resonant plasmon modes were constant regardless of the excitation position, which is understood to be a consequence of the spatial coherence of the plasmon mode across the rod.

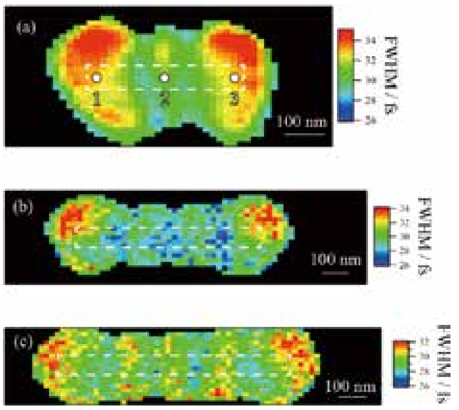

Figure 3. Correlation width maps obtained for time-resolved signals of gold nanorods with different dimensions.[3] Dashed white lines represent approximate shapes of the nanorods. The black parts outside of the nanorods are the areas where the correlation widths were not evaluated because of low signal intensities.

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3) Y. Nishiyama, K. Imaeda, K. Imura and H. Okamoto, *J. Phys. Chem. C* **119**, 16215–16222 (2015).

Award

HASHIYADA, Shun; Chemical Society of Japan Student Presentation Award 2015.

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Exploring Quantum-Classical Boundary

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Education
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Professional Employment
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2003 Professor, Institute for Molecular Science
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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
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2007 JSPS Prize
2007 Japan Academy Medal
2009 Fellow of the American Physical Society
2012 Humboldt Research Award

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TAKEDA, Shuntaro
Post-Doctoral Fellow
GOTO(SHIKANO), Haruka
Visiting Scientist
NGUYEN, Quynh*
RASTI, Soroush*
Graduate Student
MIZOGUCHI, Michiteru
KONDO, Norihisa†
Secretary
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.

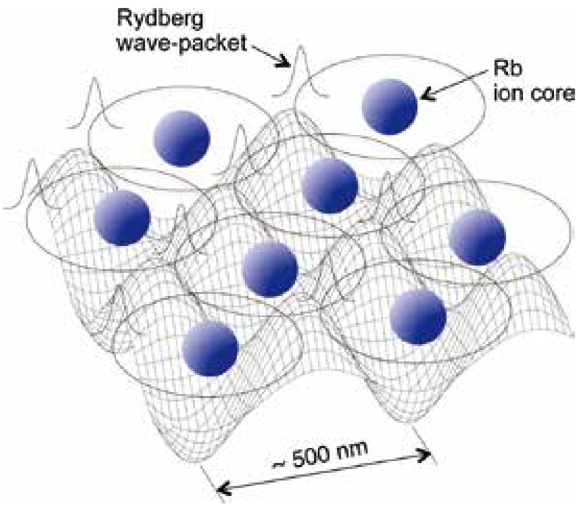

Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.2)

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).
- H. Katsuki *et al.*, “Real-Time Observation of Phase-Controlled Molecular Wave-Packet Interference,” *Phys. Rev. Lett.* **96**, 093002 (2006).

1. Manipulation and Visualization of Two-Dimensional Phase Distribution of Vibrational Wave Functions in Solid Parahydrogen Crystal[3]

Solid parahydrogen, which is known to have an exceptionally long vibrational coherence lifetime as a molecular solid, offers an ideal testbed to perform coherent control experiments in the condensed phase. Here we demonstrate the spatial manipulation and visualization of the relative phase of vibrational wave functions in solid parahydrogen. Spatial distribution of vibrational excitation is generated by femtosecond impulsive Raman excitation. It is shown that the imprinted initial phase can be manipulated by wave-front modulation of the excitation laser pulses with a spatial light modulator. An interferometric measurement is used to convert the spatial phase distribution of the vibrational wave functions to the amplitude distribution. We have confirmed that the spatial profile of the scattered anti-Stokes pulse reveals the spatial phase distribution of the wave functions. The read-and-write scheme demonstrated in this experiment is applicable to a broad range of Raman memory systems accessible by Λ-type transitions.

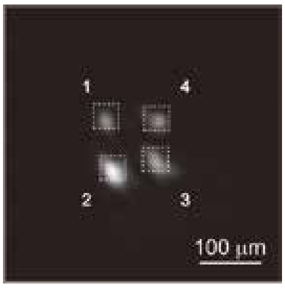

Figure 2. (a) O K-edge XAS of liquid water at different positions of liquid layerImage of the anti-Stokes pulse retrieved by irradiating a probe pulse into the p-H_2 crystal in which the 2×2 spatial distribution of the wave function is prepared by the impulsive Raman excitation (IRE).

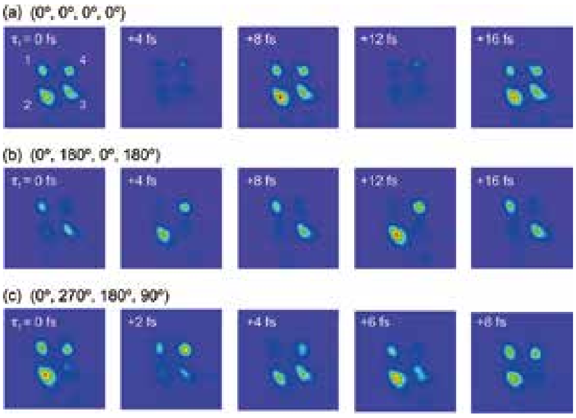

Figure 3. False color plots of the temporal evolution of the CCD images of the anti-Stokes pulse as the function of the delay τ_f between two IREs. The origin of τ_f ($\tau_f = 0$) is arbitrary and is set to 0 for the leftmost panel in each row (a), (b), or (c). The signal is retrieved by the irradiation of a probe pulse at its delay τ_{probe} ~ 250 ps. The delay τ_f is scanned around 25 ps. The first IRE encodes different relative phases among regions 1–4 shown in Figure 2. Note that the time step for (c) is half of the other two cases.

References

1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
3) H. Katsuki *et al.*, *Phys. Rev. B* **92**, 094511 (2015).

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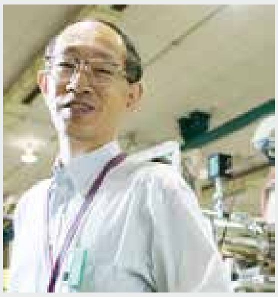
* IMS International Internship Program

† carrying out graduate research on Cooperative Education Program of IMS with Tokyo Institute of Technology

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

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



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

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

Soft X-rays with photon energies of 100–700 eV excite 1s inner-shell (K-shell) electrons of chemically important light elements such as C, N, and O to unoccupied states of molecules. The 1s electron is localized and bound by an atom in the system but is slightly affected by surrounding atoms and chemical bonds. Therefore, we can select a 1s electron in each atom in molecules by choosing different X-ray energies, and know each atomic component in the unoccupied state in the system. The excited electron in the unoccupied state is also affected by chemical environments. The intermolecular interaction effect is often less than 0.1 eV; therefore, a highly resolved soft X-ray spectrometer is necessary.

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

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

Highly brilliant soft X-rays for the chemical state analysis are available as synchrotron radiation from in-vacuum undulator-type insertion devices even on low-energy electron storage rings; *e.g.* 0.75 GeV UVSOR in IMS. In addition to experimental and instrumental developments at UVSOR-III BL3U, BL4U and BL6U, we are developing an original *ab initio* quantum chemical program package GSCF, which is optimized to calculation of molecular inner-shell processes.

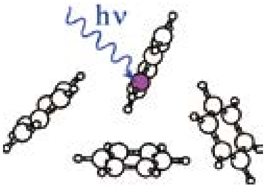

Figure 1. The C 1s excitation energy in interacting benzene molecules is dependent and selective on chemically different atomic sites.

Selected Publications

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

1. Optimization of Thin Liquid Layer Samples for Soft X-Ray Absorption Spectroscopy in Transmission Mode

In order to measure soft X-ray absorption spectroscopy (XAS) of liquid samples in transmission mode, it is necessary to optimize thickness of thin liquid layers and reduce non-uniformity of sample thickness in the X-ray absorbed/transmitted region. Recently, we have developed a liquid flow cell, in which the thin liquid layer is sandwiched between two Si_3N_4 or SiC membranes with Teflon spacers and is pressed by O-rings outside the membranes.[1] Although the liquid layer is easily assembled by our method, the thickness of liquid layer is not uniform at different positions due to the large window size (2 × 2 mm^2). To find the region of the uniform sample thickness in the X-ray absorbed/transmitted region of 200 μm × 200 μm (determined by our using orifice), we have developed a chamber-type XAS measurement system that is able to scan the sample position, and investigated the influence of the spectral shapes caused by the non-uniform thickness in the O K-edge XAS of liquid water at different sample positions.

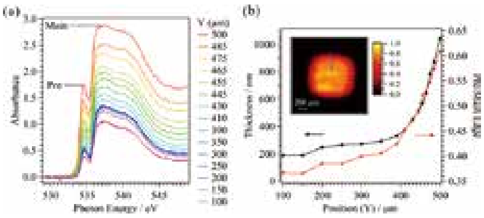

Figure 2. (a) O K-edge XAS of liquid water at different sample positions. The pre-edge at 535 eV and the main-edge at 538 eV are shown in the spectra. (b) Thickness of liquid water and Pre/Main ratio of XAS spectra as a function of sample positions. Inset shows the 2D images of the soft X-ray transmission at 550 eV, where the sample positions are scanned as indicated. The size of the present soft X-ray beam is 200 μm × 200 μm.

Figure 2(a) shows O K-edge XAS spectra of water at different positions of the liquid layer. The liquid thickness at different positions was estimated from the edge-jump of the XAS spectrum. It is also important to determine the intensity ratio of pre-edge at 535 eV to main-edge at 538 eV for the evaluation of the XAS spectra. Figure 2(b) shows the Pre/Main ratio and thickness at different sample positions. The thickness is constant when the sample position is within 300 μm from the center, and is increased when the position exceeds 300 μm. The Pre/Main ratio is nearly constant between 0.36 and 0.40 when the sample thickness is constant, but the Pre/Main ratio is increased at the larger and non-uniform thickness region. This behavior in the Pre/Main ratio is in agreement with the simulated behavior by using the absorbance of water for the non-uniform sample thickness.

2. Lateral Intermolecular Interaction in Two-Dimensional Superstructure of Organic Monolayers

The intermolecular interaction is a key issue in molecular electronic properties. In the present work, in order to examine the lateral intermolecular interaction in flat-lying molecular layers, we investigated the electronic structure of hexa-*peri*-hexabenzocoronene (HBC) monolayers on Au(111), which forms various superstructures, *e.g.*, (5×5)R0°, (3√3×3√3)R30°, and their mixture, depending on the preparation condition.

Figure 3 shows the low-energy electron diffraction (LEED) image, the surface Brillouin zone (SBZ), and the energy-vs.-momentum $E(\boldsymbol{k})$ map of the R0 and R30 phases of the HBC monolayer on Au(111) at 15 K, obtained by angle-resolved photoemission spectroscopy (ARPES). In the R0 phase, the highest occupied molecular orbital (HOMO, H_0) disperses in a narrow width by 20 meV only along the $\boldsymbol{k}_{\Gamma K}$ direction, and the HOMO-1 (H_1) disperses by 25 meV only along the $\boldsymbol{k}_{\Gamma M}$ direction. The opposite trend is observed in the R30 phase; that is, the HOMO disperses by 20 meV along the $\boldsymbol{k}_{\Gamma M}$ direction, and the HOMO-1 disperses by 25 meV along the $\boldsymbol{k}_{\Gamma K}$ direction. The observed dispersion and its $\boldsymbol{k}$ periodicity is dependent not on the substrate SBZ but on the molecular SBZ; therefore, the observed lateral band dispersion rationally arises from a long-range (direct or indirect) intermolecular π–π interaction.

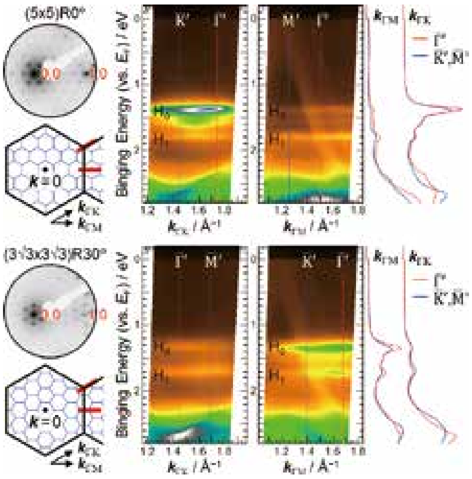

Figure 3. LEED, SBZ [black hexagon for Au(111) and blue hexagon for HBC], wherein the red line indicates the scanned region in ARPES, and the $E(\boldsymbol{k})$ map of HBC/Au(111) of the R0 and R30 phases at 15 K.

Reference

1) M. Nagasaka *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **177**, 130–134 (2010).

Award

YAMANE, Hiroyuki; The 2014 Young Scientist Award of the Japan Society for Molecular Science.

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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.

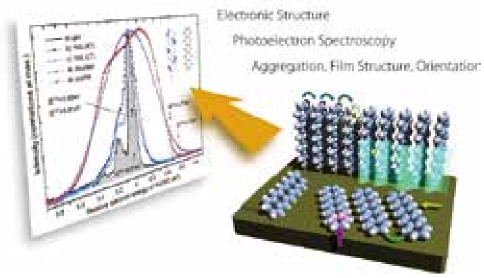

Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- F. Bussolotti, S. Kera, K. Kudo, A. Kahn and N. Ueno, "Gap States in Pentacene Thin Film Induced by Inert Gas Exposure," *Phys. Rev. Lett.* **110**, 267602 (5 pages) (2013).
- S. Duhm, Q. Xin, S. Hosoumi, H. Fukagawa, K. Sato, N. Ueno and S. Kera, "Charge Reorganization Energy and Small Polaron Binding Energy of Rubrene Thin Films by Ultraviolet Photoelectron Spectroscopy," *Adv. Mater.* **24**, 901–905 (2012).
- S. Kera, H. Yamane and N. Ueno, "First Principles Measurements of Charge Mobility in Organic Semiconductors: Valence Hole-Vibration Coupling in Organic Ultrathin Films," *Prog. Surf. Sci.* **84**, 135–154 (2009).

1. Charge Reorganization Energy and Small Polaron Energy of Molecular Films[1)]

Understanding of electron–phonon coupling as well as intermolecular interaction is required to discuss the mobility of charge carrier in functional molecular solids. We summarized recent progress in direct measurements of valence hole-vibration coupling in ultrathin films of organic semiconductors by using ultraviolet photoelectron spectroscopy (UPS). The experimental study of hole-vibration coupling of the highest occupied molecular orbital (HOMO) state in ordered monolayer film by UPS is essential to comprehend hole-hopping transport and small-polaron related transport in organic semiconductors. Only careful measurements can attain the high-resolution spectra and provide key parameters in hole-transport dynamics, namely the charge reorganization energy and small polaron binding energy. Analyses methods of the UPS-HOMO fine feature and resulting charge reorganization energy and small polaron binding energy are described for pentacene and perfluoropentacene films. Difference between thin-film and gas-phase results is discussed by using newly measured high-quality gas-phase spectra of pentacene. Methodology for achieving high-resolution UPS measurements for molecular films is also described.

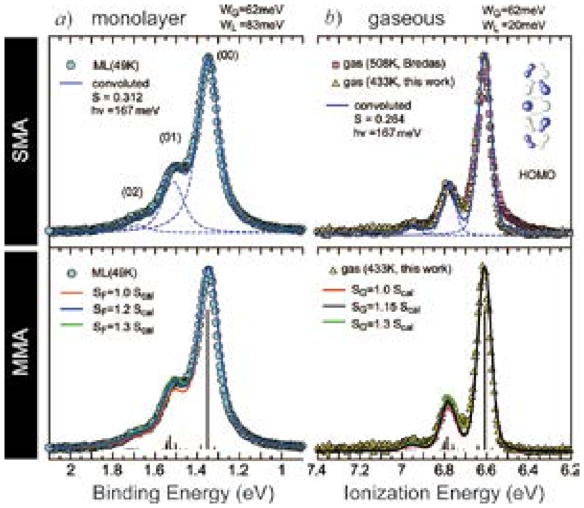

Figure 2. Comparison of HOMO band of pentacene between angle-integrated UPS for the monolayer (*a*, left panels) and gas-phase UPS (*b*, right panels). Convoluted curves by the single mode (SMA) and multimode (MMA) analyses of vibration coupling are also shown.

2. Impact of Molecular Orbital Distribution on Photoelectron Intensity[2)]

Ultraviolet photoelectron spectroscopy (UPS) is well established technique for studying the electronic structure of surfaces and interfaces. In the detail, however, the origins of the UPS spectral features are not clearly understood even for so-called van-der Waals molecular crystals formed by weak intermolecular interaction. For molecular monolayer films prepared on a metal substrate, the spectrum is complicated much more due to orbital hybridization and charge transfer, which lead to interface states and/or broadening of spectral features. In principle, photoelectrons can give us all of important information on electronic properties in the molecular systems, when we measure precisely the molecular sample prepared very carefully.

The recent development in the theoretical evaluation of photoelectron intensity from π-electronic states delocalized over a molecule is discussed. By comparing the experimental photoelectron angular distribution (PAD) from the organic molecular assemblies with computed PAD we show that the use of the initial-state orbitals by density functional theory and the final continuum states by multiple-scattering theory (MSMO) is suited for simulations of angle-resolved UPS (ARUPS) and PAD. We demonstrate that the ARPES and PAD simulations are useful to characterize the top five π-electronic states for picene ($C_{22}H_{14}$) film.

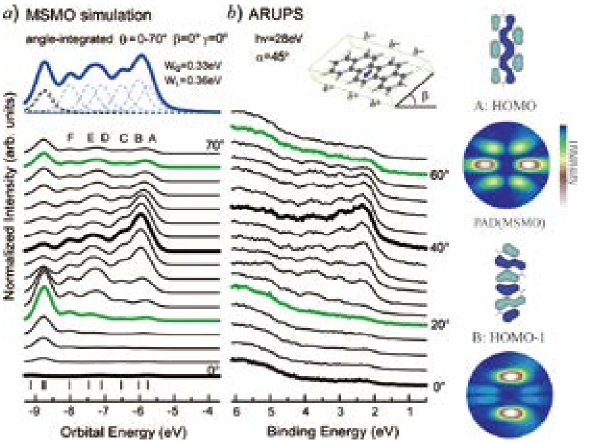

Figure 3. (a) Simulated ARUPS by MSMO calculation for an isolated picene molecule. b) Observed take-off angle θ dependence of ARUPS of picene film (10 nm) on graphite. The molecules are assumed to be lying-flat in the film. Each spectrum is produced by convoluting Voigt function for all states. Calculated PADs of top two MO states by MSMO are shown (right).

References

1) S. Kera and N. Ueno, *J. Electron Specrosc. Relat. Phenom.* **204**, 2–11 (2015).

2) Y. Liu, D. Ikeda, S. Nagamatsu, T. Nishi, N. Ueno and S. Kera, *J. Electron Specrosc. Relat. Phenom.* **195**, 287–292 (2014).

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Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Synchrotron Radiation, Free Electron Laser

UVSOR is a synchrotron light source to provide low energy synchrotron light ranging from terahertz wave to soft X-rays. Although it was constructed about 30 years ago, its performance is still in the world top level. This is the result of the continuous effort on improving the machine. Our research group 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 synchrotron radiation with various characteristics such as free electron laser, coherent synchrotron radiation and laser Compton gamma-rays. We are also investigating future light sources for the facility, such as a diffraction limited light source or a linac-based free electron laser source.

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

Selected Publications

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

1. Light Source Technology Developments Based on Laser and Synchrotron

We have developed novel light source technologies using UVSOR-III electron storage ring and external laser sources. Under the support of Quantum Beam Technology Program of JST/MEXT, a new experimental station dedicated for the source development studies were constructed. We modified a part of the accelerator to produce a space for new undulator system and dedicated beam-lines. The generation of coherent synchrotron radiation based on our original method was successfully demonstrated at the new site, in collaboration with Lille Univ. and Nagoya Univ. For the applications using coherent synchrotron radiation, the construction of the beam-line is in progress. Some basic researches on the optical vortex beam from helical undulators are in progress in collaboration with Hiroshima Univ. and KEK.

Laser Compton scattering is a method to produce mono-chromatic 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 succeeded in producing intense gamma-ray beam by using a fiber laser. 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

The UVSOR facility has been operational as a national synchrotron light source for lower energy photons from the terahertz wave to the soft X-rays. The machine was born as a low energy second generation light source and now it is 30 years old. We have proposed several upgrades and most of them have been carried out successfully. We designed a special electron beam optics intended to higher brightness. We designed accelerator components necessary for the new optics and have successfully remodeled and commissioned the machine with the new optics. 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 using new technologies such as pulsed sextupole injection scheme. 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. As a technology development towards the new facility, a superconducting RF electron gun has been developed in collaboration with KEK, which would produce high brightness electron beam with high repetition rate.

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

Award

ITO, Kenya; 2015 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.

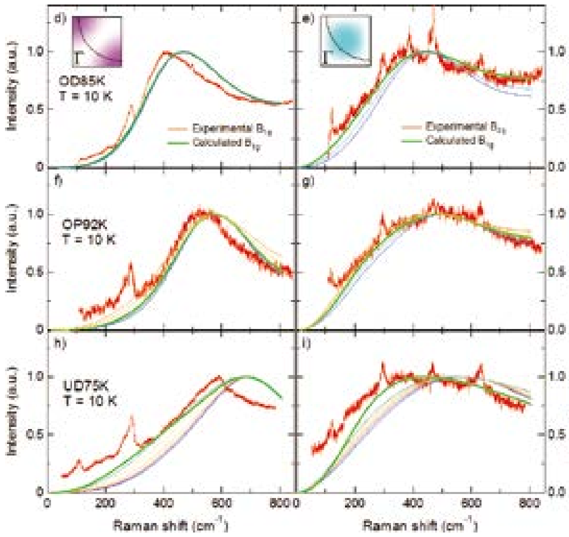

Figure 1. Calculation results of Bi2212 for B_{1g} and B_{2g} ERS spectra using ARPES spectra together with experimental ones.

Selected Publications

- K. Tanaka, T. Yoshida, A. Fujimori, D. H. Lu, Z.-X. Shen, X.-J. Zhou, H. Eisaki, Z. Hussain, S. Uchida, Y. Aiura, K. Ono, T. Sugaya, T. Mizuno and I. Terasaki, "Effects of Next-Nearest-Neighbor Hopping *t'* on the Electronic Structure of Cuprates," *Phys. Rev. B* **70**, 092503 (4 pages) (2004).
- K. Tanaka, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Distinct Fermi-Momentum-Dependent Energy Gaps in Deeply Underdoped Bi2212," *Science* **314**, 1910–1913 (2006).
- W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Abrupt Onset of a Second Energy Gap at the Superconducting Transition of Underdoped Bi2212," *Nature* **450**, 81–84 (2007).
- E. Uykur, K. Tanaka, T. Masui, S. Miyasaka and S. Tajima, "Coexistence of the Pseudogap and the Superconducting Gap Revealed by the *c*-Axis Optical Study of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$," *J. Phys. Soc. Jpn.* **82**, 033701 (4 pages) (2013).

1. Quantitative Comparison between ARPES and ERS on High-T_c Cuprate Superconductor

Both of ARPES and electronic Raman scattering (ERS) revealed two energy scales for the gap in different momentum spaces in the cuprates. However, the interpretations were different and the gap values were also different in two experiments. In order to clarify the origin of these discrepancies, we have directly compared experimental ARPES and ERS by using new calculation method of ERS through the Kubo formula.

It is well known that ARPES intensity is a function of matrix element, Fermi Dirac function and a spectral function $A(k,\omega)$. On the other hand, the electronic Raman response in the superconducting state can be described by Green's functions using the Kubo susceptibility. Since the imaginary part of Green's function is the spectral function, the electronic Raman responses can be calculated from ARPES spectra.

In this study, we have prepared $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) samples with three doping levels, namely, underdoped (UD75K: T_c = 75 K), optimally doped (OP92K: T_c = 92 K), and overdoped (OD85K: T_c = 85 K) samples and performed ARPES and ERS measurements on the same sample to directly compare the results. From ARPES spectra, we obtained $A(k,\omega)$ and calculated ERS spectra and compared to the experimental ERS spectra.

Figure 1 shows the calculated ERS spectra with different intensity distribution of $A(k,\omega)$ along the Fermi surface. Compared to the conventional ERS spectral calculation based on kinetic theory, our new calculation results reproduced spectral features much better (not shown). Especially B_{2g} spectra, which are sensitive to the nodal region in the momentum space, were well reproduced. Doping dependence of the best fitted intensity distribution of $A(k,\omega)$ shows that the spectral function confined in the nodal region distributes to the antinodal region as the doping level increases.

The peak energies of the calculated Raman spectra were plotted in Figure 2 together with the experimental Raman, ARPES and STM data. From B_{1g} spectra, which are sensitive to the antinodal region in the momentum space, we found that the ARPES antinodal gap is always larger than the experimental B_{1g} peak energy. Since the difference increases with underdoping, this difference is possibly caused by the pseudogap. In Figure 2, we also plotted the pseudogap energy determined by ARPES Bi2212 data taken at 100 K. The pseudogap increases rapidly with underdoping and it seems that the superconducting gap in ARPES is enhanced by underlying-high-energy-pseudogap.

The present results give us the following important messages. First, Raman and ARPES can be understood with the same gap profile. Namely, the nodal slope of gap profiles is doping independent, as reported by ARPES. The apparent doping dependence of the B_{2g} peak energy is caused by the change of spectral weight of $A(k,\omega)$ along the Fermi surface. Second, the antinodal gap of ARPES is a superconducting gap that is strongly affected by the pseudogap, whereas the Raman B_{1g} gap is moderately affected. This probe-dependent effect of the pseudogap is the main source for the difference between the Raman B_{1g} gap and the ARPES aninodal gap energies. Third, while the spectral weight of $A(k,\omega)$ is confined into the nodal region in the underdoped sample, the antinodal region gains spectral weight with doping and contributes to superconductivity. Although this is similar to the "Fermi arc" picture reported before, the Fermi surface area contributing to superconductivity in our results is larger than the Fermi arc area estimated from the normal state. All these findings reflect the unusual electronic states where superconductivity and pseudogap coexist even at the lowest temperature.

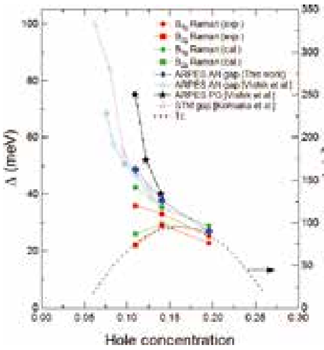

Figure 2. Doping dependence of the peak energies in Bi2212 obtained from ERS calculations in comparison to the experimental data from Raman, ARPES and STM measurements.

2. Development of New Spin-Resolved ARPES

UVSOR Facility in Institute for Molecular Science equips two public undulator-beamlines for ARPES: BL5U in the photon energy *h*ν region of 20–200 eV and BL7U of *h*ν = 6–40 eV. Since the monochromator of BL5U is an old-style spherical grating type SGM-TRAIN constructed in 1990s and the throughput intensity and energy resolution are poor, the beamline was planned to be replaced to state-of-the-art monochromator and end station with spin-resolved ARPES. The newly developed electron lens system successfully achieved ~100 times better momentum resolution perpendicular to slit direction compared to the conventional ARPES. The beamline will be open to users from FY2016.

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Electronic Structure and Decay Dynamics Following Core Hole Creation in Molecules

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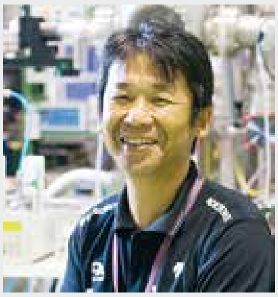
Division of Advanced Photochemistry



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

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

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

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

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

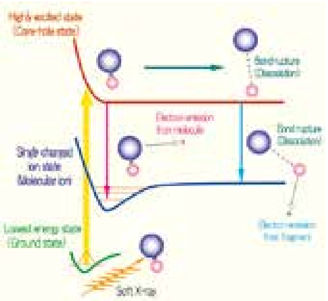

Figure 1. Schematic representation of the potential energy curves associated with the inner-shell excitation and subsequent de-excitation processes.

Selected Publications

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- M. N. Piancastelli, R. Guillemin, M. Simon, H. Iwayama and E. Shigemasa, "Ultrafast Dynamics in C 1s Core-Excited CF_4 Revealed by Two-Dimensional Resonant Auger Spectroscopy," *J. Chem. Phys.* **138**, 234305 (5 pages) (2013).

1. Ultrafast Dissociation of Inner-Shell Excited CF_4 Molecules Studied by an Auger-Electron–Ion Coincidence Method

Recently, we found a signature of ultrafast dissociation following C 1s → $\sigma^*(t_2)$ core excitation in CF_4 by using two dimensional electron spectroscopy.[1)] We observed Auger electrons from both CF_3^* fragment and CF_4^* parent molecule. This means that the Auger decay and dissociation processes take place on the same time scale and significantly compete with each other. In the current study, we have investigated anisotropic angular distributions of ejected CF_3^+ ions by using an Auger-electron–ion coincidence method. Since the CF bond involved in the C 1s → $\sigma^*(t_2)$ core excitation is immediately broken due to the ultrafast dissociation, anisotropic angular distributions of ejected the CF_3^+ ions are expected.

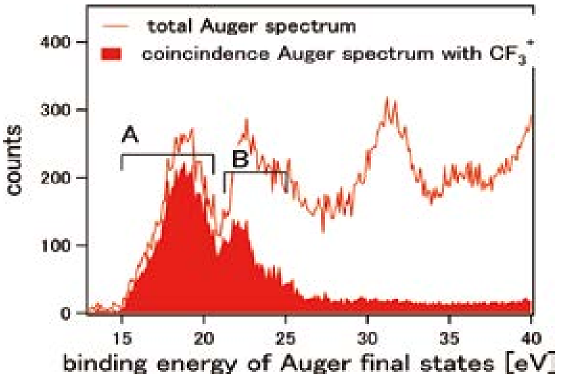

Figure 2. Non-coincident and coincident Auger electron spectra with CF_3^+ ions.

The Auger-electron–ion coincidence measurements were carried out on the undulator beamline BL6U at UVSOR. The radiation from an undulator was monochromatized by a variable included angle varied line-spacing plane grating monochromator. The electrons ejected at 54.7° with respect to the electric vector of the incident radiation were analyzed in energy by a double toroidal analyzer (DTA), while ions were extracted from the interaction region into a momentum spectrometer by a pulsed electric field according to the electron detection. Arrival position on the detector and time-of-flights of ions were recorded for every event. The pass energy of the DTA was set to 200 eV for observing the Auger electrons. The energy resolution was about 1.9 eV.

Figure 2 shows non-coincident and coincidence Auger spectra with CF_3^+ ions. It is seen that the CF_3^+ ions are coincident with electrons at the binding energy of 15 ~ 25 eV, where two peaks A and B are detected. For higher binding energies, we observed smaller fragment ions such as CF_2^+, CF^+ and C^+ (not shown here). From the previous work,[1)] the peaks A and B are attributable to the Auger electrons from the CF_3^* fragment and CF_4^* parent molecules, respectively.

Figures 3(a) and 3(b) show ion images of CF_3^+ fragments, which were taken in coincident with electrons at the peaks A and B, respectively. The angular distribution of CF_3^+ ions is considerably anisotropic in Figure 3(a), while almost isotropic angular distributions are seen in Figure 3(b). Two island-like structures along the polarization vector are clearly observed in Figure 3(a). This means that the core-excited CF_4 molecules lead to immediate CF bond breaking, which is the direct evidence of the ultrafast dissociation for the peak A. The detailed data analyses are now in progress.

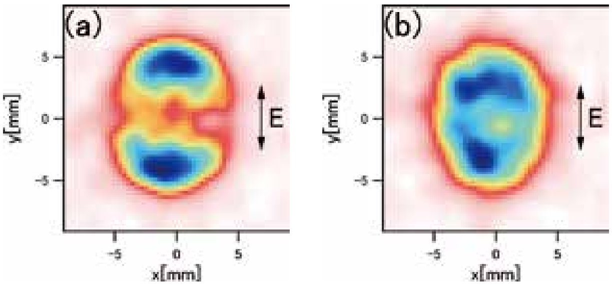

Figure 3. Ion images of CF_3^+ ions taken in coincident with Auger electrons at (a) peak A and (b) peak B.

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

The n_{th} harmonic radiation from a helical undulator carries orbital angular momentum (OAM) of $(n-1)\hbar$ per photon.[2,3)] This accelerator-based method efficiently generates the OAM photon beam in a wide wavelength range. As a first step of the application study of the OAM photon beam, we have investigated the interaction of the OAM photon and gas-phase atoms in which violation of the dipole selection rules is predicted.[4)]

The experiments were performed at the undulator beamline BL1U during the machine study operations. We observed the angular distributions of the He 1s photoelectrons by using an imaging spectrometer. The downstream part of the tandem APPLE-II undulators was used with horizontal and circular polarization modes. The OAM photon beams were obtained as the 2nd and 3rd harmonic radiation in the circular polarization mode.

Concerning the horizontal polarization and the fundamental radiation with circular polarization, the photoelectron angular distributions measured are fairly in agreement with those calculated by assuming the normal dipole transition. This confirms the validity of the analyzing procedure in the present study. The analysis of the photoionization by the OAM photon is in progress. Although preliminary result indicates the slight deviation from the dipole selection rule in the OAM photoionization, it is required to perform more precise measurements for unveiling the influence of the OAM photon.

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Micro Solid-State Photonics

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Awards

2004	Persons of Scientific and Technological Research Merits, Commendation by Minister of Education, Culture, Sports, Science and Technology, Japan
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2012	SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
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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-photonics," are promising. Moreover, the new generation of micro and/or microchip lasers by using orientation-controlled advanced ceramics can provide extreme high performances in photonics.

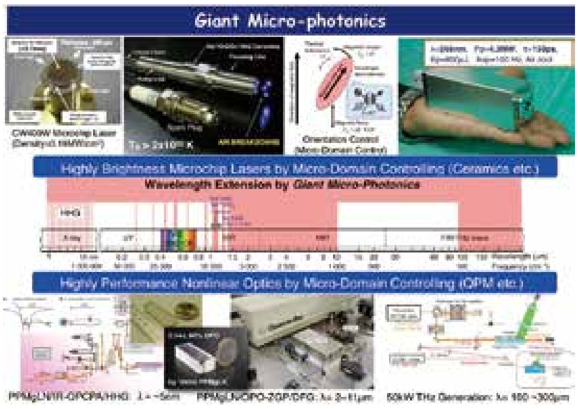

Figure 1. Giant micro-photonics.

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- H. Ishizuki and T. Taira, "Half-Joule Output Optical-Parametric Oscillation by Using 10-mm-Thick Periodically Poled Mg-Doped Congruent $LiNbO_3$," *Opt. Express*, **20**, 20002–20010 (2012).
- R. Bhandari, N. Tsuji, T. Suzuki, M. Nishifuji and T. Taira, "Efficient Second to Ninth Harmonic Generation Using Megawatt Peak Power Microchip Laser," *Opt. Express* **21**, 28849–28855 (2013).

1. Anisotropic Yb:FAP Laser Ceramics by Micro-Domain Control

Highly transparent Yb:FAP fluorapatite (FAP) ceramics were realized by use of slip casting under rotational magnetic field of 1.4 T from a electromagnet, even though the main crystal axis become a hard magnetization axis. This means that the enhancement of magnetic anisotropy by rare-earth doping is also effective for the orientation control even under the rotating magnetic field. X-ray and optical evaluations clearly gives the first evidence that our Yb:FAP ceramics have a laser-grade quality in the world. We confirmed the laser-grade quality of Yb:FAP ceramics by inserting into a lasing cavity with Nd:YVO_4 as a gain medium: It did not interrupt laser oscillation.

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.

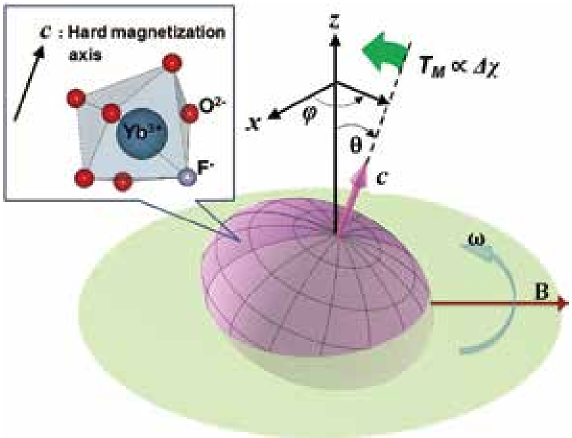

Figure 2. Schematic diagram for the spheroidal of magnetic energy of the processed particle under the rotating magnetic field. This particle is made of FAP doped with Yb^{3+}, of which main crystal axis is hard magnetization axis.

2. Compact Megawatt Peak Power 266 nm Laser at 1 kHz

Compact and stable megawatt peak power 266 nm laser at 1 kHz from sub-nanosecond passively Q-switched laser was demonstrated. In order to optimize thermal management and obtain stable UV laser operation at high repetition rate 1 kHz, we put forward to increase pump efficiency by employing higher pump power laser diode while maintaining the low depolarization ratio by fixing specific angle between <110>-cut Cr:YAG and <100>-cut composite YAG/Nd:YAG crystal. Megawatt peak power UV laser (266 nm) at 1 kHz is important for developing Time-of-Flight Mass Spectrometer with the technology of Single Photon Ionization (SPI).

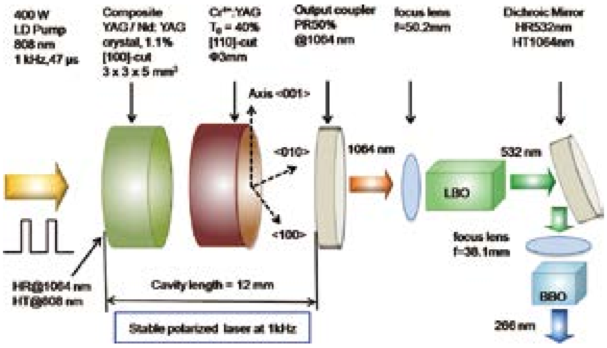

Figure 3. Schematic diagram of 266 nm laser at 1 kHz.

3. Optical Parametric Mid-Infrared Generation Pumped by Sub-Nanosecond Microchip Laser

Single-pass Mid-infrared optical-parametric generation (OPG) pumped by microchip laser with sub-nanosecond duration was demonstrated. Effective single-pass OPG with 1 mJ output energy using conventional PPMgLN could be realized. Broadband single-pass OPG could be also realized using chirped PPMgLN.

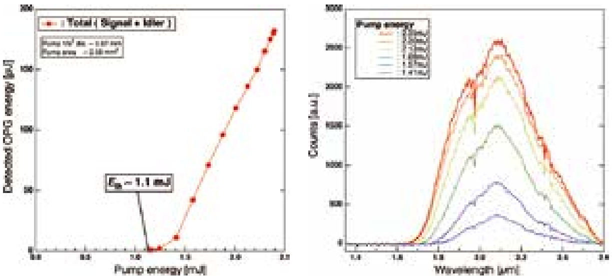

Figure 4. (a) OPG output on input pump energy, (b) OPG spectrum on various pumping energy, using a chirped PPMgLN.

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Ultrafast Laser Science

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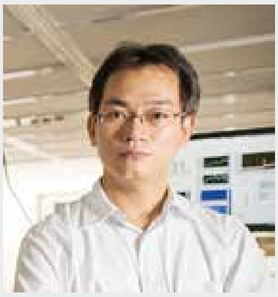

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Awards

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2015	Laser Research Development Award, the Laser Society of Japan

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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.

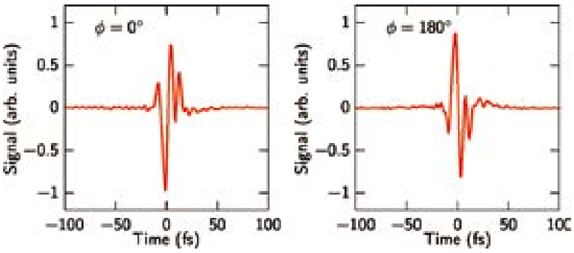

Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

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

Other than FROG-CEP, ultrabroadband mid-infrared continuum generation through filamentation 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).
- H. Shirai, C. Duchesne, Y. Furutani and T. Fuji, "Attenuated Total Reflectance Spectroscopy with Chirped-Pulse Upconversion," *Opt. Express* **22**, 29611–29616 (2014).
- 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).

1. Attenuated Total Reflectance Spectroscopy with Chirped-Pulse Upconversion1,2)

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) is a powerful tool to study liquid or solid samples in various scientific and industrial fields. However, the time resolution of the Fourier-transform infrared spectroscopy (FTIR) with the rapid scan mode is limited by the speed of the FTIR device which needs time (at least several milliseconds) for scanning the delay of the interferometer.

Chirped-pulse upconversion1) is a noteworthy method to improve the time resolution of IR spectroscopy. In this method, an infrared beam is upconverted into a visible beam and the spectrum is measured with a high performance visible dispersive spectrometer. Here, we report attenuated total reflectance (ATR) spectroscopy connected with chirped-pulse upconversion. Single-shot IR absorption spectrum measurement of liquids from 200 to 5500 cm^{-1} has been realized.2)

We performed a proof-of-principle experiment by continuously recording IR spectra while exchanging the liquid on the ATR prism from water to aceton and vice versa. The rapid solution exchanging system is a useful tool to study some biological samples at advanced time-resolved ATR-FTIR spectroscopy. It is possible to monitor the IR spectrum in realtime with initiating some chemical reactions by exchanging the solutions on the ATR crystal by using two pneumatic drive pump systems, which are generally used in a stopped flow system.

We show the absorption change at 1230 and 3400 cm^{-1} in the time domain in Figure 2. At 169 and 422 ms only water and aceton, respectively, should be on the ATR prism. 182 ms is the timing at which the exchange occurs. It is clear that the exchange is finished within 10 ms.

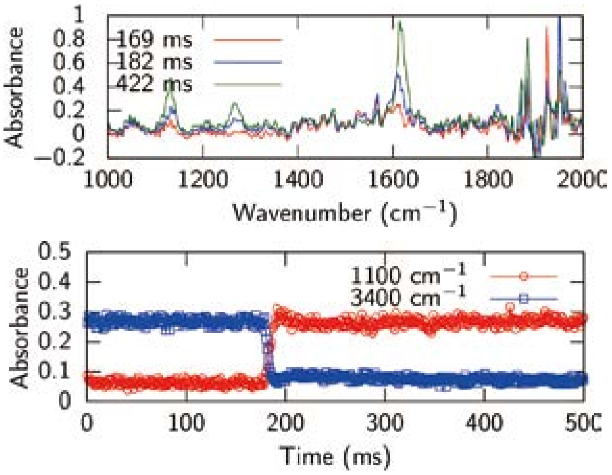

Figure 2. Measured dynamics of exchange of liquids with the rapid solution-exchange ATR-CPU system. Upper figure: Absorption spectra at each timing. Lower figure: Absorption change at each frequency.

2. Controlling the Carrier-Envelope Phase of Single-Cycle Mid-Infrared Pulses with Two-Color Filamentation5)

The rapid development of ultrafast laser technology in the last decade has made it possible to study dynamics of electrons in atoms and molecules on attosecond time scale. One of the most famous schemes of attosecond time-resolved spectroscopy is based on attosecond streaking, which is direct waveform measurement of few-cycle electric field using attosecond pulses. In this method, both an extreme ultraviolet attosecond pulse and the target pulse are focused into a noble gas, and measurement of the kinetic energy of the photoelectrons produced by the extreme ultraviolet pulse reflects the vector potential induced by the target field.

In 2013, Fuji *et al.* has developed a new waveform measurement scheme, frequency-resolved optical gating capable of carrier-envelope phase determination (FROG-CEP).3,4) The concept is based on a combination of frequency-resolved optical gating (FROG) and electro-optic sampling (EOS), which enables us to determine not only the intensity and (relative) phase profile but also carrier-envelope phase (CEP) at the same time. There are a lot of advantages of the new scheme, such as all-optical method, variety of nonlinear interactions, and possibility of single-shot measurement.

We applied the method for investigation of the phase of the single-cycle pulses generated through multi-color laser filamentation.5–7) We have experimentally found that the CEP variation depends on the frequency of the generated pulses. The phase of high frequency components of the generated pulses continuously and linearly changes with the relative phase between the two-color input pulses, on the other hand, the phase of the low frequency components takes only two discrete values. We have numerically simulated the CEP variation based on the two different models, four-wave mixing and photocurrent. Eventually, both the models are consistent with the experimental results.8)

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2) H. Shirai, C. Duchesne, Y. Furutani and T. Fuji, *Opt. Express* **22**, 29611–29616 (2014).
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7) T. Fuji, Y. Nomura and H. Shirai, *IEEE J. Quantum Electron.* **21**, 8700612 (2015).
8) Y. Nomura, Y.-T. Wang, A. Yabushita, C.-W. Luo and T. Fuji, *Opt. Lett.* **40**, 423–426 (2015).

Award

FUJI, Takao; NOMURA, Yutaka; SHIRAI, Hideto; Laser Research Development Award, the Laser Society of Japan (2015).

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* IMS International Internship Program

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

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

KATAYANAGI, Hideki
Assistant Professor

We have studied the mechanisms and kinetics of dissociative photoionization of fullerenes by means of the velocity map imaging spectroscopy. We now intend to apply the above gas phase spectroscopy to functional materials such as carbon nanotubes (CNTs). Additionally we apply the CNT and fullerene derivatives to a catalytic counter electrode (CE) in dye-sensitized solar cells (DSSCs).

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

We have obtained 2D velocity images of the fragments from C_{60}[1] and C_{70} with improved resolution. The 2D velocity images of fragments were found to be convolutions of isotropic center-of-mass velocity acquired by the C_2 emission and anisotropic velocity of C_{60} in the parent molecular beam.

2. Gas Phase Spectroscopy of CNTs

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

3. Development of the Counter Electrodes Using CNTs and Fullerene Derivatives and Evaluation of Their Feasibility for DSSCs

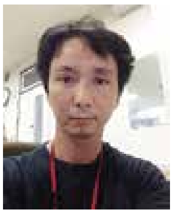
To improve efficiency, lifetime and cost of the DSSC, materials to make the CE need to be reconsidered. We prepared the CEs using commercial CNT aqueous dispersions and succeeded in fabricating DSSC cells which showed reasonable efficiency. We have started to make CEs using sulfonated fullerenes. We produced Langmuir-Blodgett (LB) films of the sulfonated fullerenes on glass substrates. We will evaluate the feasibility of the LB films for the DSSCs.

Reference

1) H. Katayanagi and K. Mitsuke, *Bull. Chem. Soc. Jpn.* **88**, 857–861 (2015).

Soft X-Ray Spectro-Microscopy for *In-Situ* Chemical Imaging

UVSOR Facility
Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji
Assistant Professor

A scanning X-ray transmission microscopy (STXM) is a powerful tool[1] for *in-situ* chemical imaging. In the present work, we have developed a humidity control sample cell for the chemical and morphological analysis of a fuel cell under the working condition, such as high temperature and high humidity. The sample cell is consisted of two silicon nitride windows with 100 nm thickness and a chamber. A small sensor (SHT7x, Sensirion AG) is placed near the sample in the chamber to monitor the humidity and the temperature. The chamber is equipped with three gas ports and the humidity of the sample can be controlled by flowing dry or humid helium gas in the sample cell.

With changing the humidity inside the sample cell from 8 to 83% at room temperature, a thin section (thickness of 100 nm) of the fuel cell has been observed. The optical density images of a porous polymer electrode of the fuel cell are shown in Figure 1. These images were acquired by using the photon energy at 285.5 eV and the dwell time per a pixel was 10 ms. In a high humidity condition, the area of the polymers (shown as white color) increases and the voids (shown in dark color) decreases. This result implies that the porous polymers are swelled by absorbing the water vapor.

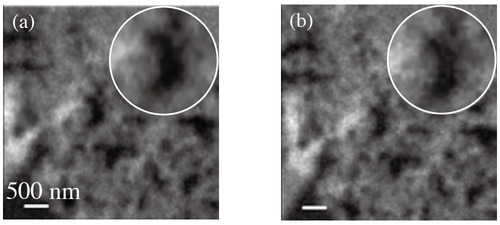


Figure 1. OD images of the electrode at the humidity of (a) 8% and (b) 83%. Inset images are blowup of the same area.

Reference

1) T. Ohigashi, H. Arai, T. Araki, N. Kondo, E. Shigemasa, A. Ito, N. Kosugi and M. Katoh, *J. Phys.: Conf. Ser.* **463**, 012006 (2013).

Visiting Professors

Visiting Professor

IMURA, Kohei *(from Waseda University)*

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

Near-field optical microcopy overcomes the diffraction limit of light and achieves a nanometer spatial resolution. We have developed various near-field spectroscopic methods such as transmission, non-linear excitation, ultrafast time-resolved imaging, and utilized them to study optical properties of nanomaterials. We have been extending these studies into two directions: (1) development of advanced super-resolution microscopy based on various microscopes, and (2) spatio-temporal control of elementary excitations and photochemical reactions using nanomaterials. We have developed near-field reflection microscope and cathodoluminescence electron microscope. The microscopy enables to visualize spatial distribution of eigen modes excited in nanomaterials on transparent and non-transparent substrate with a wide spectral range. Recently, we found that optical field distribution excited in the nanomaterials varies with amplitudes and phases of ultrashort pulses illuminated. This indicates that coherent control of elementary excitations and photochemical reactions are feasible in space and time resolved manner. We are currently exploring novel photochemical reaction schemes assisted with designed optical fields.

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. In last 15 years I have developed STM 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 2015, we glow two-dimensional molecular networks on an atomically-flat noble metal substrate. The surface structures are directly observed by STM. Subsequently, a magnetic metal is deposited on the network, then we can glow new two-dimensional magnetic nano-dot arrays. We study electronic and magnetic structures of the magnetic array by means of STM spectroscopy and the photoemission spectroscopy. All experiments are performed in ultra-high vacuum. We try to control electronic/quantum spin structures of magnetic arrays by using two-dimensional molecular networks.

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 plan to develop a high-resolution spin- and angle- resolved photoemission spectroscopy measurement system equipped with in situ sample preparation facilities at BL-5U and characterize the novel spin property at the Rashba-split surface/interface states of nonmagnetic ultrathin films.

RESEARCH ACTIVITIES

Materials Molecular Science

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

Exploitations of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

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Education

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1985	M.S. The University of Tokyo
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Professional Employment

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

Member

- Assistant Professor
  - TAKAGI, Yasumasa
  - UEMURA, Yohei
- Post-Doctoral Fellow
  - WANG, Heng
  - NAKAMURA, Takahiro
- Visiting Scientist
  - WAKISAKA, Yuki
  - CHAVEANGHONG, Suwilai*
- Technical Fellow
  - UOZUMI, Madoka
- Secretary
  - FUKUTOMI, Yukiyo
  - NAKANE, Kaori
  - AOKI, Junko

Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism

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 photoelectron emission microscopy, which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed in situ x-ray magnetic circular dichroism (XMCD) system using a ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD apparatus is extensively open for public usage and many domestic and foreign researchers visit every year. We are currently interested in transition-metal phthalocyanine monolayers on nonmagnetic and ferromagnetic surfaces, whose electronic and magnetic properties are tunable by changing the central metal atom and/or modifying the ligand. Our recent achievement will be presented in the next page.

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 spectroscopy is believed to be done under ultrahigh vacuum, recent material science requires in situ 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 element by using the *energy-resolved* x-ray fluorescence detection technique. Fast time resolved XAFS measurements are, however, usually difficult since the frequencies between normal SR (probe) and pumping lasers are far different, requiring pulse picking of the SR probe and resultantly time resolved detection of *energy-integrated* x-ray fluorescence. To solve this problem, a picosecond laser with high repetition rate (up to 1 MHz) was installed in Photon Factory Advanced Ring with single bunch operation (794 kHz). This allows us to investigate XAFS of low concentration elements using a slow but energy-resolved x-ray fluorescence detector.

Selected Publications

- K. Eguchi, T. Nakagawa, Y. Takagi and T. Yokoyama, *J. Phys. Chem. C* **119**, 9805 (2015).
- K. Eguchi, Y. Takagi, T. Nakagawa and T. Yokoyama, *J. Phys. Chem. C* **118**, 17633 (2014).
- Y. Takagi, H. Wang, Y. Uemura, E. Ikenaga, O. Sekizawa, T. Uruga, H. Ohashi, Y. Senba, H. Yumoto, H Yamazaki, S. Goto, M. Tada, Y. Iwasawa and T. Yokoyama, *Appl. Phys. Lett.* **105**, 131602 (2014).
- M. Dabrowski, T. R. F. Peixoto, M. Pazgan, A. Winkelmann, T. Nakagawa, Y. Takagi, T. Yokoyama, U. Bauer, F. Yildiz, F. Bisio, M. Przybylski and J. Kirschner, *Phys. Rev. Lett.* **113**, 067203 (2014).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- T. Nakagawa and T. Yokoyama, *Phys. Rev. Lett.* **96**, 237402 (2006).

1. Synthesis and Structural/Magnetic Properties of Vanadium Phthalocyanine[1)]

Controlling a wide range of functionalities of metal complexes on substrate surfaces for the applications such as molecular spintronics, molecular devices, and molecular catalysis is of special importance. Metal phthalocyanine (MPc) is one of the most promising materials. Although most 3d transition metal Pcs have been synthesized, ScPc or VPc has never been obtained because of high air sensitivity during the chemical synthesis. In this work, we have successfully prepared VPc monolayer and multilayer on Ag(111) in a ultrahigh vacuum (UHV) deposition technique. Moreover, we investigated structural and magnetic properties of monolayer and multilayer VPc using XAFS and XMCD.

VPc was synthesized by depositing H_2Pc and subsequent V metal on a clean and ordered Ag(111) surface. Monolayer VPc did not require any annealing process to complete the reaction $V + H_2Pc \rightarrow VPc + H_2$, while multilayer VPc needed annealing at 450 K. The identification of VPc was carried out by in-laboratory N1s XPS. The N1s XPS of H_2Pc shows two peaks assigned to iminic (–N=) and pyrrolic (–NH–) nitrogen, while that of metal Pc exhibits a single peak. The present observation of a single N1s peak clearly elucidate the successful synthesis of monolayer and multilayer VPc. From the V2p XPS, V is found to be divalent, as expected, although some amount of charge transfer from the substrate Ag(111) was observed in monolayer.

Linear polarization dependence of the N K-edge XAFS of VPc on Ag(111) has revealed flat-lying orientation of monolayer VPc and rather random orientation of multilayer. The V L-edge XAFS and XMCD have indicated complicated electronic structure of VPc due to strong configuration interaction between ${}^2E_g\ (3d_{xy})^2(3d\pi)^1$ and other configurations as $(3d_{xy})^2(3d_{z^2})^1$, similarly to other transition metal Pcs. The V L-edge XMCD spectra shown in Figure 1 suggest the doublet state in monolayer on Ag(111) and embedded in H_2Pc multilayer, while multilayer exhibits antiferromagnetism due to intermolecular exchange interaction.

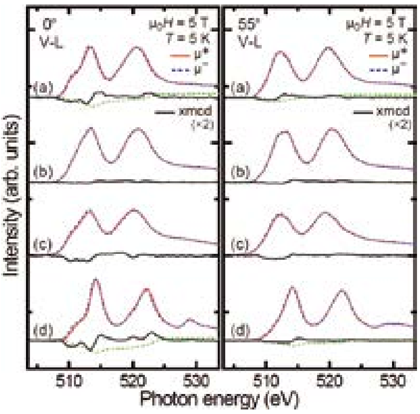

Figure 1. V L-edge XMCD of VPc on Ag(111) at incident x-ray angles of 0° (normal incidence, left panel) and 55° (grazing incidence, right panel): (a) monolayer embedded in multilayer H_2Pc, (b) multilayer, (c) monolayer and (d) VOPc monolayer as a reference.

2. Anomalous Structural Behavior in Metamagnetic Transition in FeRh Films

The FeRh intermetallic compound with ordered CsCl structure is known to exhibit an interesting metamagnetic transition from antiferromagnetic (AFM) to ferromagnetic (FM) phase with the temperature rise (T_C ~ 385 K), which would be applicable to thermally assisted recording/memory media. In this work, FeRh thin films have been investigated via temperature dependent XAFS spectroscopy in order to gain correlations between the magnetization and the local electronic and geometric structures.

According to the Fe and Rh K-edge XAFS, strong hybridization was found to exist between Fe and Rh. This Fe–Rh hybridization was revealed to decrease during the phase transition from the systematic change observed in the Fe K-edge XAFS. On the other hand, only the Debye-Waller factor of the Fe–Fe pair in the AFM phase was found to be considerably enhanced when compared with that in the FM phase, which was ascribed to local structural fluctuation inherent in the AFM phase itself. This anomalous feature is interpreted in consistent with the recent theoretical study proposing the local fluctuations of spin and structure by considering the different features of the exchange interactions in Fe–Rh and Fe–Fe. Therefore, we consider that the local Fe–Fe distance and the spin fluctuations play an important role for driving the metamagnetic transition, whereas the Fe–Rh hybridization is important for determining the static stability of each magnetic phase.

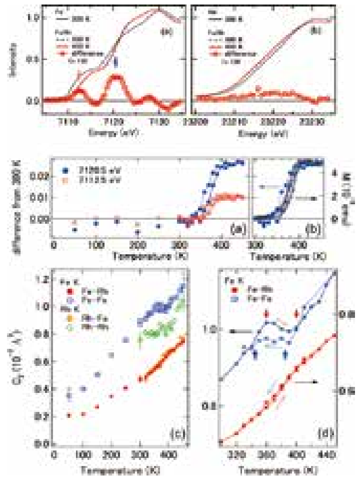

Figure 2. (a) Fe K-edge XAFS intensity at 7120.5 (blue) and 7112.5 (red) eV. (b) SQUID magnetization (black) compared to XAFS (7120.5 eV, blue). A slight T_C difference between SQUID and XAFS implies a difference in the phase transition nature between macroscopic and microscopic origins. (c,d) Debye-Waller factors for the atom pairs of the first nearest neighbor Fe–Rh and the second nearest neighbor Fe–Fe and Rh–Rh. Only the Fe–Fe pair exhibits an interesting anomaly.

Reference

1) K. Eguchi, T. Nakagawa, Y. Takagi and T. Yokoyama, *J. Phys. Chem. C* **119**, 9805 (2015).

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* IMS International Internship Program

Magnetic Resonance Studies for Functional Molecular-Based Solids

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1995	D.S. Kyoto University

Professional Employment

1992	Assistant Professor, Gakushuin University
1998	Associate Professor, Institute for Molecular Science
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ABE, Hitomi
YAMASAKI, Yumi

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

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

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

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

Selected Publications

- P. Pandit, K. Yamamoto, T. Nakamura, K. Nishimura, Y. Kurashige, T. Yanai, G. Nakamura, S. Masaoka, K. Furukawa, Y. Yakiyama, M. Kawanoe and S. Higashibayashi, “Acid/Base-Regulated Reversible Electron Transfer Disproportionation of N-N Linked Bicarbazole and Biacridine Derivatives,” *Chem. Sci.* **6**, 4160–4173 (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. Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate

We performed magnetic resonance investigation, including solid-state broad line NMR and high-field ESR measurements, of the π-extended self-doped organic conductor $(TTPCOO)_2[(NH_4^{+1})_{1-x}(NH_3^0)_x]$, and compared the results with those of first-generation $(TTFCOO)[(NH_4^{+1})_{1-x}(NH_3^0)_x]$. The observed principal values of the ESR g-tensor indicate that both salts have electron spins on TTF and TTP cation radical mainframe parts. In $(TTFCOO)[(NH_4^{+1})_{1-x}(NH_3^0)_x]$, the TTF forms a 1D uniform stacking structure, and the system is a narrow-gap semiconductor. The electron spin demonstrates 1D spin-diffusive behavior, which may be why this system is a semiconductor. On the other hand, in the π-extended system, TTPCOO, the uniaxial anisotropy of the g-tensor indicates a 2D isotropic structure such as a herring-bone-like or parallel cross like donor arrangement. The π-extended system should reduce the electronic correlation that stabilizes the metallic state. As a result, NMR-relaxation demonstrates the Korringa-like temperature dependence, and the ESR linewidth follows the Elliot mechanism. These facts are apparent evidence of a stable metallic state (itinerant electron spins are present). We demonstrate that advanced magnetic resonance measurements can effectively clarify the intrinsic characteristics and functionality of novel materials. Moreover, this one-pot process for synthesizing organic (semi-) conductors enables large-scale high-volume synthesis in a short time. Our next goal is to realize a one-pot functional organic system such as superconducting, ferromagnetic, or ferroelectric materials.

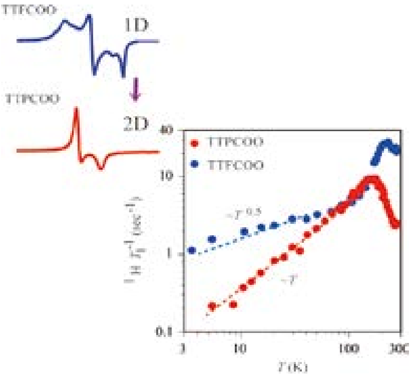

Figure 2. Metallic state in one-pot organic conductor, an ammonium tetrathiapentalene carboxylate based system is found. High-field ESR spectra showed a 2D isotropic structure such as a herring-bone-like donor arrangement. This is unlike the 1D ammonium tetrathiafulvalene carboxylate system. NMR-relaxation and the ESR linewidth provide strong evidence of a stable metallic state in the ammonium tetrathiapentalene carboxylate system.

2. Charge Ordering in Oxo-Bridged Dinuclear Ruthenium Mixed-Valence Complex by Magnetic Resonance Investigation

Solid-state broad line ^{1}H-NMR was carried out for an oxo-bridged dinuclear ruthenium mixed-valence complex. A pronounced peak in the ^{1}H-NMR T_1^{-1} was observed around 33 K. The frequency independence of the peak temperature of T_1^{-1} indicates that this anomaly is not a crossover phenomenon but a phase transition. This 33 K anomaly is a transition from an averaged-valence state to a trapped-valence state in $[RuORu]^{5+}$; that is, the averaged-valence $Ru^{3.5+}ORu^{3.5+}$ spontaneously breaks symmetry into $Ru^{3+}ORu^{4+}$ below 33 K. In other word, the electronic charge freedom is cooperatively frozen at 33 K. The observed abrupt decrease in T2 also indicates internal charge separation ($Ru^{3+}ORu^{4+}$). Because the 33 K anomaly is cooperative phenomena, the Ru^{3+} and Ru^{4+} charge configuration must be regularly arranged by necessity in the phase transition. Considering the crystal structure symmetry, one possible schematic charge configuration within the ac-plane is shown in Figure 3. Of course, this is mere speculation, and detailed structural measurements at a synchrotron radiation facility are required. Note also that the ruthenium-equivalent sites are connected by an inversion center in the $[RuORu]^{5+}$ complex, so the charge order state should be antiferroelectric. For applicable use, ferroelectric and/or multiferroic materials are desired. The development of dinuclear complexes with lower symmetry and stronger inter-molecular interactions is a good next step, and further investigations are already underway. However, we emphasize on the basis of this investigation that mixed-valence metal complexes are excellent candidates for electronic device materials.

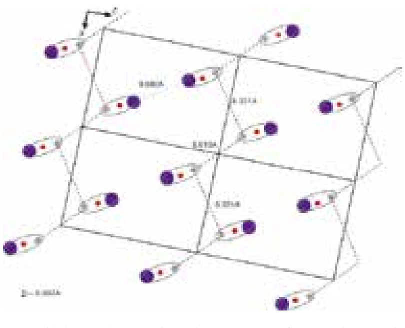

Figure 3. Possible schematic charge configuration within the ac-plane below 33 K.

References

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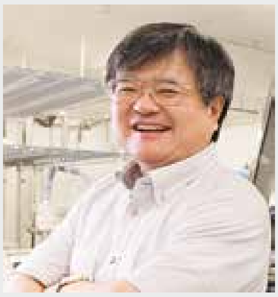
2) T. Nakamura, M. Yoshida, M. Kondo and S. Masaoka, submitted.

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions



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Education

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

Professional Employment

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

Awards

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

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NAKAO, Satoru

Research Fellow
SHINMURA, Yusuke
KUBO, Masayuki
KIKUCHI, Mitsuru
KATAYAMA, Mikimasa
HIROTA, Masaki

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OHASHI, Chika
SHINTAKU, Naoto

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SUGIHARA, Hidemi
KOBAYASHI, Megumi

Keywords Organic Semiconductors, Organic Solar Cells, Doping

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

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

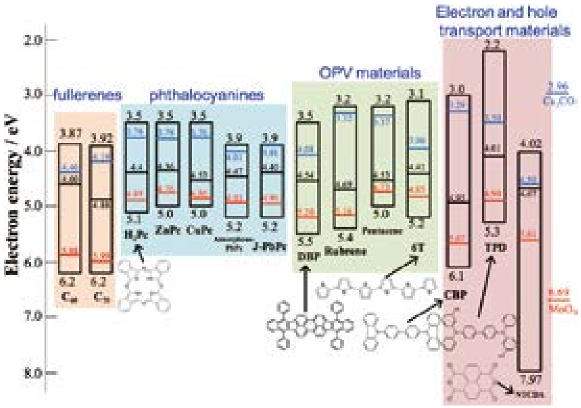

Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100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

Selected Publications

- M. Hiramoto, M. Kubo, Y. Shinmura, N. Ishiyama, T. Kaji, K. Sakai, T. Ohno, M. Izaki and M. Hiramoto, “Bandgap Science for Organic Solar Cells,” *Electronics* **3**, 351–380 (2014).
- M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, “Conduction Type Control of Fullerene Films from *n*- to *p*-Type by Molybdenum Oxide Doping,” *Appl. Phys. Lett.* **98**, 023302 (3 pages) (2011).
- M. Hiramoto, H. Fujiwara and M. Yokoyama, “Three-Layered Organic Solar Cell with a Photoactive Interlayer of Codeposited Pigments,” *Appl. Phys. Lett.* **58**, 1062–1064 (1991).

1. Effects of ppm-Level Doping in Organic Photovoltaic Cells Based on Minority Carrier Diffusion

The doping of organic semiconductors has mainly been in the concentration range of the order of a few %. We believe that a doping technique for very low concentrations of the order of parts per million should be developed. In this study, we clarified the effects of doping at the ppm-level.

Organic photovoltaic cells with *pn*-homojunctions in C_{60}:H_2Pc co-deposited films were fabricated. The donor (Cs_2CO_3) doping concentration in the *n*-layer was kept constant at 50 ppm. On the other hand, the acceptor (F_4-TCNQ) doping concentration in the *p*-layer was varied, *i.e.*, 0, 1, 3, 10, and 100 ppm. Figures 2 and 3 show the current-voltage characteristics and the energy band diagrams for the *pn*-homojunction cells.

(i) 0–1 ppm region

The fill factor (FF) increases from 0.37 (black solid curve) to 0.47 (blue solid curve) together with an increase of the forward dark current (black and blue broken curves)(Figure 2), *i.e.*, a decrease of the cell resistance (R_S) from 15.0 to 9.6 Ωcm^2. Acceptor doping inevitably introduces majority (hole) and minority carriers (electron) (Figures 3(a)). The increase in the majority carrier concentration causes R_S to decrease and FF to increase. Thus, the doping effect of extremely low concentrations of the order of 1 ppm was confirmed.

(ii) 1–10 ppm region

The short-circuit photocurrent (J_{SC}) increases (Figure 2, blue orange red solid curves). One can see that a *pn*-homojunction is formed and the built-in field (V_{bi}) increases from a small value at 1 ppm to a much larger value at 10 ppm (Figures 3(a) and 3(b)). One of the reasons for the increase in J_{SC} is the increase in carrier generation efficiency in a *pn*-homojunction with a depletion layer (red shaded regions). Moreover, the depth of the photocurrent generation region (σ) (blue shaded region) is clearly larger than the width of the depletion layer (W_{dep}) (red shaded region)(Figure 3(b)). Photocurrent generation in the region where there is no electric field (green double-headed arrow) occurs by the diffusion of minority carriers (electrons).

(iii) 10– 100 ppm region

J_{SC} decreased (Figure 2, red and green solid curves) due to narrower depletion layer and narrower diffusion length of minority carrier by impurity scattering (Figure 3(c)).

We believe that doping at the ppm-level offers a general method for optimizing the design of organic photovoltaic cells and other organic electronic devices.

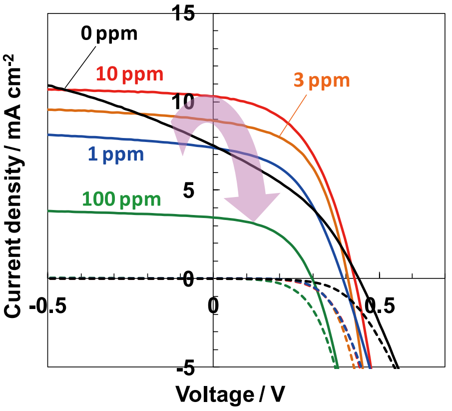

Figure 2. Current-voltage characteristics for the *pn*-homojunction cells. The doping concentrations of the *p*-layer are 0 (black), 1 (blue), 3 (orange), 10 (red), and 100 ppm (green).

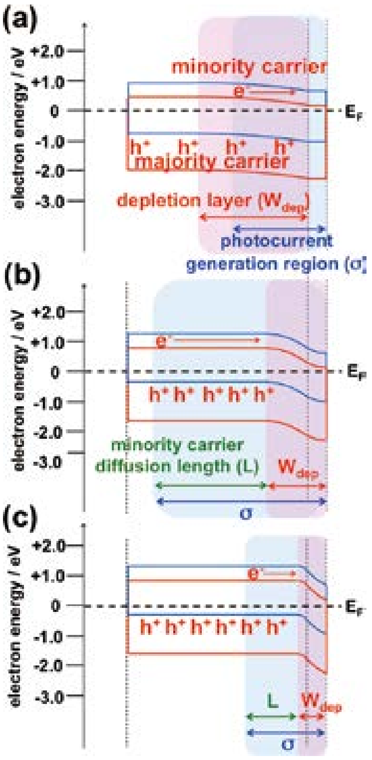

Figure 3. Energy structures of cells with doping concentrations of 1 (a), 10 (b), and 100 ppm (c).

Two-Dimensional Covalent Polymers and Organic Frameworks

Department of Materials Molecular Science
Division of Molecular Functions

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Associate Professor
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Education

1989	B.S. Zhejiang University
1992	M.S. Zhejiang University
1998	Ph.D. The University of Tokyo

Professional Employment

1997	JSPS Research Fellow
1998	JSPS Postdoctoral Fellow
1998	Assistant Professor, The University of Tokyo
2000	Group Leader, JST ERATO Aida Nanospace Project
2005	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2006	The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Japan
2006	Wiley Award, The Society of Polymer Science, Japan

Member

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JSPS Post-Doctoral Fellow
GU, Cheng
DALAPATI, Sasanka

Visiting Scientist
WEI, Hao

Graduate Student
XU, Hong
HUANG, Ning
WU, Yang
GAO, Jia
JIN, Enquan
TAO, Shanshan
WANG, Ping
XU, Qing

Secretary
SUZUKI, Sayuri

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

Covalent organic frameworks (COFs) are a class of porous polymers that enable the atomically precise incorporation of organic units into periodic structures, creating highly ordered π-columnar arrays and one-dimensional open channels. One significant structural feature is that they can be predesigned at both primary and high-order structure levels. COFs have emerged as a platform for materials design and functional explorations and exhibit great potential for applications in gas storage, manufacture of semiconductive and photoconductive devices, energy conversion and storage, and heterogeneous catalysis. The key to the design of COFs is their topology diagram, which defines the polygon size and shape and determines the crystal lattice. Hexagonal and tetragonal topologies have been exploited for the design of COFs with discrete pores and ordered skeletons. The introduction of new topologies is highly desired to broaden the structural diversity and application of COF materials.

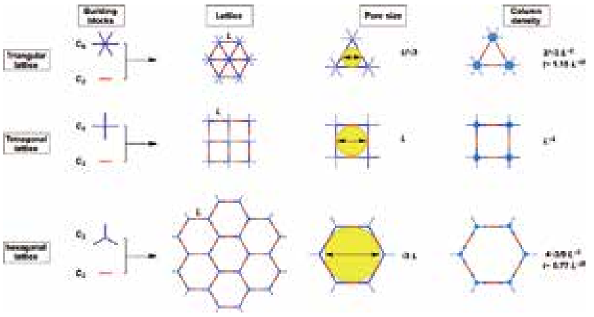

Figure 1. Comparison of topological diagrams for the synthesis of 2D COFs. The different diagrams required different building blocks and result in different lattices, π-densities, and pore sizes. The trigonal topology leads to the highest π-density and smallest pore size among the topologies thus far developed.

Selected Publications

- X. Feng, X. Ding and D. Jiang*, "Covalent Organic Frameworks," *Chem. Soc. Rev.* **41**, 6010–6022 (2012).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Belt-Shaped, Blue Luminescent and Semiconducting Covalent Organic Framework," *Angew. Chem., Int. Ed.* **47**, 8826–8830 (2008) (VIP).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes with Eclipsed 2D Polypyrene Sheets for Photocurrent Generation," *Angew. Chem., Int. Ed.* **48**, 5439–5442 (2009).
- X. Ding, J. Guo, X. Feng, Y. Honsho, J. Guo, S. Seki, P. Maitarad, A. Saeki, S. Nagase and D. Jiang, "Synthesis of Metallophthalocyanine Covalent Organic Frameworks That Exhibit High Carrier Mobility and Photoconductivity," *Angew. Chem., Int. Ed.* **50**, 1289–1293 (2011).
- X. Feng, L. Chen, Y. Honsho, O. Saengsawang, L. Liu, L. Wang, A. Saeki, S. Irle, S. Seki, Y. Dong and D. Jiang*, "An Ambipolar Covalent Organic Framework with Self-Sorted and Periodic Electron Donor-Acceptor Ordering," *Adv. Mater.* **24**, 3026–3031 (2012).
- J. Guo, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang*, "Conjugated Organic Framework with Three-Dimensionally Ordered Stable Polymer with Delocalized π Clouds," *Nat. Commun.* **4**: 2736 doi: 10.1038/ncomms3736 (2013).

1. Design of COFs with Trigonal Topology

In this study, we developed a strategy for the rational design and synthesis of a new class of COFs based on the triangular topology (Figure 1). The triangular topology consists of C_6-geometric vertices, which is the highest symmetry of a benzene system and has a potential to efficiently exploit space for titling organic units into a crystal lattice. With this geometry, a triangular COF would feature the smallest pore size and most dense π-columns among all of the COF materials. However, the triangular topology has not been reported for the practical synthesis of COFs. We demonstrate the synthesis of two triangular COFs (defined as HPB-COF and HBC-COF) by using two different C_6-symmetric vertices—one is hexaphenylbenzene (HPB), which is a typical propeller-shaped π-unit, and the other is hexabenzocoronene (HBC), which is a large graphitic π-unit—for Schiff-base polymerization with C_2-symmetric benzene linkers. These triangular COFs form supermicropores with pore sizes of as low as 12 Å, which is among the lowest reported for COFs, whereas the density of π-columns can reach 0.25 nm^{-2}, which exceeds those of the COFs and supramolecular π-arrays reported to date. These crystalline COFs exhibit excellent thermal and solvent stabilities. We demonstrate that the triangular COFs enable both intra- and inter-layer π-cloud delocalization and exhibit a prominent photoconductivity, with carrier mobilities as high as 0.7 cm^2 V^{-1} s^{-1}, which is among the highest reported for COFs and polygraphitic ensembles. These results suggest that the triangular topology is useful for designing COFs with unique structures to be used in a wide variety of applications, such as gas storage, catalysis, and the manufacture of sensing and semiconducting devices.

2. Light-Harvesting Porous π-Network Films: Cascade Exciton-Pumping Engines with Manipulated Speed and Efficiency

Light-harvesting antennae are the machinery for exciton pumping in natural photosynthesis, whereas cascade energy transfer through chlorophyll is key to long-distance, efficient energy transduction. Numerous artificial antennae have been developed. However, they are limited in their cascade energy-transfer abilities because of a lack of control over complex chromophore aggregation processes, which has impeded their advancement.

Here we report a viable approach for addressing this issue by using a light-harvesting porous polymer film in which a three-dimensional π-network serves as the antenna and micropores segregate multiple dyes to prevent aggregation. The porous organic polymer (POP) films are synthesized with a controlled thickness via the previously reported electrochemical method and emit bright blue luminescence. The three-dimensional π-network drastically enhances the interface of energy transfer to relay and acceptor dyes, whereas the nanopores within the film permit segregated molecular docking of multiple laser dyes with desired properties and in specific proportions. Mechanistic studies reveal that the light-harvesting films allow the integration of a cascade energy-transfer engine that functions in a vectorial and highly efficient manner and enables total control over the speed and efficiency of the energy transfer through tuning of the distribution and types of dye introduced. This film system allows for accurate and versatile luminescence engineering in producing thirty different luminescence hues, including blue, green, red and white (Figure 2). By virtue of the antenna effect, the films exhibit considerably amplified luminescence and gain exceptional quantum efficiencies. We envisage that replacement of the dyes with redox-active components may lead to application of the present technology for highly efficient photosynthesis and photoenergy conversion.

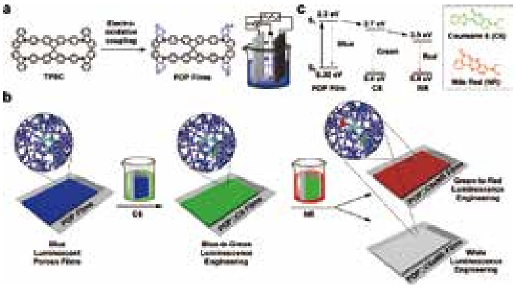

Figure 2. **a**, Schematic representation of the synthesis of POP films by the electro-oxidative coupling reaction. Inset: cell setup for electro-oxidative coupling for the preparation of POP thin films on ITO working electrode. **b**, Graphical protocol for the preparation of exciton-pumping films by dipping the films into the corresponding laser dye solutions of coumarin 6 and Nile red followed by rinsing. Inset: Enlarged circles show porous structures of the frameworks (blue: POP framework; sky blue: highlight of one TSPC unit; green: coumarin 6; red: nile red). **c**, Diagram of cascade energy transfer from the POP film to coumarin 6 and to Nile red. Inset: Chemical structures of coumarin 6 and Nile red.

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7) H. Xu and D. Jiang*, *Nat. Chem.* **6**, 564–566 (2014).
8) C. Gu, N. Huang, J. Gao, F. Xu, Y. Xu and D. Jiang*, *Angew. Chem., Int. Ed.* **53**, 4850–4844 (2014).
9) X. Chen, N. Huang, J. Gao, H. Xu, F. Xu and D. Jiang*, *Chem. Commun.* **50**, 6161–6163 (2014).
10) S. Jin, T. Sakurai, T. Kowalczyk, S. Dalapati, F. Xu, H. Wei, X. Chen, J. Gao, S. Seki, S. Irle and D. Jiang*, *Chem. –Eur. J.* **20**, 14608–14612 (2014) (Back Cover).

Award

GU, Cheng; MOF2014 Kobe Best Poster Award.

Solid-State NMR for Molecular Science

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Division of Molecular Functions

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Education
1994 B.S. Himeji Institute of Technology (University of Hyogo)
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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

Award
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Member
IMS Research Assistant Professor
OKUSHITA, Keiko
Secretary
YAMAZAKI, Yumi

Keywords Solid State NMR, Biomolecules, Developments

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

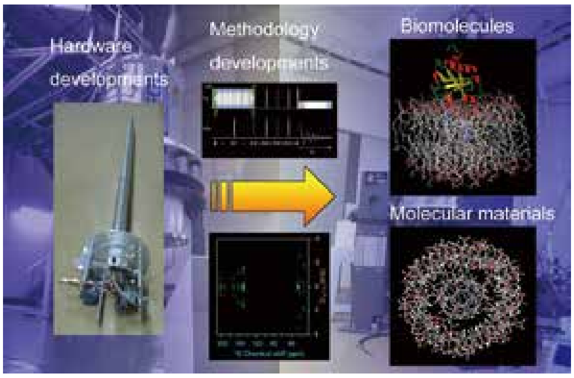

Figure 1. Outline of our studies.

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).
- K. Nishimura and A. Naito, "Remarkable Reduction of RF Power by ATANSEMA and DATANSEMA Separated Local Field in Solid-State NMR Spectroscopy," *Chem. Phys. Lett.* **419**, 120–124 (2006).
- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, "^{2}H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^{1}H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β-Sheet Structures by High Resolution ^{1}H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).

1. Characterization of Organic Materials Based on Solid-State NMR through Observation of Natural Abundant Isotopes

There are so many organic materials which are insoluble to organic solvents. Solid-state NMR is one of the powerful tools to characterize such molecules. For small organic molecules and polymers consisting of repeated local structures, ^{1}H and ^{13}C solid-state NMR spectra through observation of natural abundant isotopes retain reasonable spectral sensitivities. Thus various types of 2D ^{1}H-^{13}C hetero-nuclear correlation experiments can be performed. By combining with spectral-editing techniques, signal assignments for ^{1}H and ^{13}C nuclei may be achieved. In the following, we show some collaboration works for characterization of organic materials achieved by those techniques.

Dr. Higashibayashi and co-works in IMS discovered a new phenomenon in which N-N linked bicarbazole and tetramethylbiacridine derivatives undergo electron transfer disproportionation by acid stimuli. In order to elucidate molecular structure of N-N linked bicarbazole molecules at neutral condition in solid state, signal assignments of ^{1}H and ^{13}C nuclei for the molecule were successfully carried out based on the two types of 2D ^{1}H-^{13}C hetero-nuclear correlation experiments together with several spectral-editing techniques. The aromatic back born carbons exhibited two sets of signals that suggest either mixture of two different conformations or asymmetric local conformations respect to the symmetric axis of the molecule. Finally, the closed state of the molecules in solid state was successfully proved through the signal assignments.[1)]

Dr. Ito and co-workers successfully developed formal aryne/carbon monoxide copolymerization using [2.2.1.] oxabicyclic alkenes as aryne equivalents. For insoluble fractions in individual reaction step was evaluated by observing ^{13}C solid-state NMR spectra. All of ^{13}C signals were successfully assigned based on the several spectral editing techniques in solid-state NMR at individual reaction steps.[2)]

We are also collaborating with several other research groups for characterization of natural products and synthetic polymers and *etc.*, based on solid state NMR. Currently, new types of correlation experiments for such organic molecules without isotope enrichments are also under investigated.

2. Intermolecular Packing in *B. mori* Silk Fibroin Revealed by Solid-State NMR[3)]

We have been collaborated with Prof. Asakura's group during couple of years for characterization of silk model peptides using solid-state NMR. The group has been suggested that crystalline *Bombyx mori* silk in silk II form (the silk after spinning) is intrinsically heterogeneous anti-parallel β-sheets.

In this study, full assignments of high resolution ^{1}H solid state NMR spectra for model peptide (Alanine-Glycine)15 peptide was successfully obtained using ultra high speed magic angle spinning (MAS) probe under ultra high field 920 MHz spectrometer in IMS. Distinct heterogeneity was observed for both ^{1}H and ^{13}C spectra for the AG(15) peptide. A new model containing two different packing arrangement of anti-parallel β-sheets was proposed based on obtained results. Through the energetically minimized structure using CASTEP, chemical shifts for ^{1}H, ^{13}C and ^{15}N nuclei were calculated. The obtained new model structure was supported by both calculated and experimentally observed chemical shifts for those nuclei in addition to the ^{1}H-^{1}H proximities obtained through the analyses of 2D ^{1}H-double quantum MAS experiments. Thus intermolecular packing of *B. mori* silk fibroin has been solved in this study.

3. Selective Observation of ^{2}H Quadrupole Interaction by Two Dimensional Solid-State NMR in Paramagnetic Compounds[4)]

A simple 2D solid-state NMR correlation experiments exhibiting ^{2}H quadrupolar interaction in indirect dimension for paramagnetic compounds was developed. The method is based on a quadupole-echo sequence inserted with π pulses where the pulse spaces are incremented an asymmetric fashion with use of strong rf field pulses. Quadrupolar interaction can be analyzed by projected quadrupole spectrum in the indirect dimension of 2D spectrum obtained by this technique through the simulation of the quadrupole-echo sequence without considering the effect of the paramagnetic shift.

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2) S. Ito, W. Wang, K. Nishimura and S. Nozaki, *Macromolecules* **48**, 1959–1962 (2015).

3) T. Asakura, T. Ohata, S. Kametani, K. Okushita, K. Yazawa, Y. Nishiyama, K. Nishimura, A. Aoki, F. Suzuki, H. Kaji, A. Ulrich and M. Williamson, *Macromolecules* **48**, 28–36 (2015).

4) T. Iijima, T. Shimizu and K. Nishimura, *J. Magn. Reson.* **251**, 57–64 (2015).

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. (Dibenzoylmethanato)boron Difluoride Derivatives Containing Triphenylamine Moieties: A New Type of Electron-Donor/π-Acceptor System for Dye-Sensitized Solar Cells[1)]

(Dibenzoylmethanato)boron difluoride derivatives containing triphenylamine moieties were synthesized as a new type of electron-donor/π-acceptor system. These new compounds exhibited long-wavelength absorptions in the UV/Vis spectra, and reversible oxidation and reduction waves in cyclic voltammetry experiments. Their amphoteric redox properties are based on their resonance hybrid forms, in which a positive charge is delocalized on the triphenylamine moieties and a negative charge is localized on the boron atoms. Molecular orbital (MO) calculations indicate that their HOMO and LUMO energies vary with the number of phenylene rings connected to the difluoroboron-chelating ring. Dye-sensitized solar cells fabricated by using these compounds as dye sensitizers exhibited solar-to-electric power conversion efficiencies of 2.7–4.4%.

Reference

1) Y. Mizuno, Y. Yisilamu, T. Yamaguchi, M. Tomura, T. Funaki, H. Sugihara and K. Ono, *Chem. –Eur. J.* **20**, 13286–13295 (2014).

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. Molecular Design for Boosting Conductivity of Deca-Nanometer Scale Molecular Wires

We have already established the synthetic process for "single-nanometer scale" multi-terminal device systems. The next target is to fabricate the "deca-nanometer scale" systems. In this case, one of the fundamental issues is the insufficient conductivity of neutral (undoped) deca-nanometer molecular wires, and so we have been developing the various types of building block for boosting conductivity of long molecular wires by introducing redox-active cites into the conjugated main chain. Figure 1 shows the examples (**1-5**).

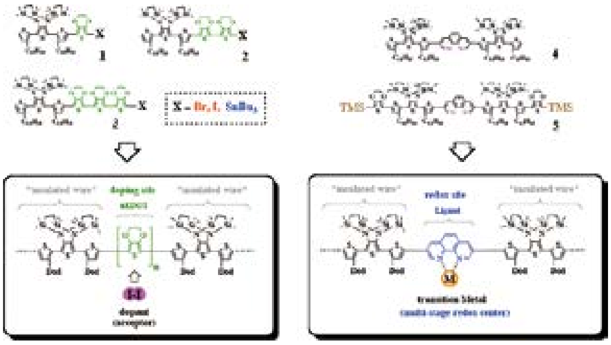

Figure 1. Building blocks for boosting conductivity of long molecular wires.

Visiting Professors

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

Electronic Phase Control of Molecular Materials by Electric Double Layer Transistors

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

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

Development of Multi-Functional Organic Liquids: Color & Spin toward Printable Memory Media

Because of optoelectronic properties and spin-active behavior, phthalocyaninato rare-earth metal double-decker complexes have received much attention. These complexes are expected to have application in spintronics as well as in electrochromic display and optoelectronic devices. In our work we apply the concept of “alkyl-π engineering” using flexible branched alkyl chains to the double-decker phthalocyanines to achieve control over self-assembly and of the material. Our aim is to obtain solvent-free soft materials, including room temperature liquids, with tunable intermolecular interactions and spin as well as electrochromic properties. A multi-functional, *i.e.*, electrochemically and organic radical (spin) active-switchable, electrochromic, as well as non-Newtonian type, room temperature solvent-free liquid of double-decker phthalocyanine has been successfully developed. The finding would be applicable to develop paintable spin & electrochromic switching memory devices.

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

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

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

RESEARCH ACTIVITIES

Life and Coordination-Complex Molecular Science

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

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
YOSHIOKA, Shiro
IMS Research Assistant Professor
MURAKI, Norifumi
Visiting Scientist
RILHAC, Vincent*
Secretary
NAKANE, Kaori

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.

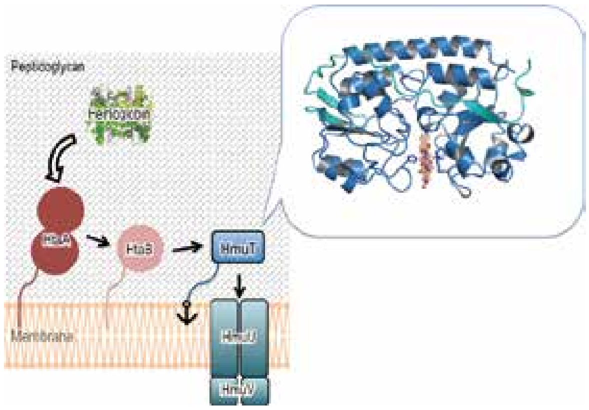

Figure 1. Schematic view of heme uptake system in *Corynebacterium glutamicum* and the crystal structure of HmuT that transports heme to the heme transporter HmuUV.

Selected Publications

- C. Kitatsuji, M. Ogura, T. Uchida, K. Ishimori and S. Aono, "Molecular Mechanism for Heme-Mediated Inhibition of 5-Aminolevulinic Acid Synthase 1," *Bull. Chem. Soc. Jpn.* **87**, 997–1004 (2014).
- Y. Okamoto, H. Sawai, M. Ogura, T. Uchida, K. Ishimori, T. Hayashi and S. Aono, "Heme-Binding Properties of HupD Functioning as a Substrate-Binding Protein in a Heme-Uptake ABC-Transporter System in *Listeria monocytogenes*," *Bull. Chem. Soc. Jpn.* **87**, 1140–1146 (2014).
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1. Structure and Function of CgHmuT that is a Heme Binding Protein for the ABC-Type Heme Transporter CgHmuUV

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 HmuT from *Corynebacterium glutamicum* (CgHmuT) by X-ray crystallography to elucidate the molecular mechanism of heme transport by CgHmuT.

The structure of CgHmuT was determined at a resolution of 1.42 Å. CgHmuT showed a basket handle shape, where a long α helix is connected the N- and C-terminal domains (Figure 1). There was a cleft between the N- and C-terminal domains, in which one heme molecule was accommodated with His141 and Tyr240 as axial ligands that were located at the loop regions in the N- and C-terminal domains, respectively. Intriguingly, it was shown that heme was accommodated in the heme-binding site of CgHmuT with two different orientations. As protoheme bound to CgHmuT has an asymmetric structure, there are two possible orientations of heme when it is accommodated in the heme-binding site of CgHmuT. When a single orientation of heme was assumed in the model refinement, the residual electron densities were observed in the F_O-F_C map. On the other hand, good fitting of the model into the electron densities was obtained without any residual electron densities when 1:1 mixture of two orientations of heme was assumed, indicating the existence of the two different orientation of heme in CgHmuT.

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 senor unit for light sensing. We are now working on CarH from *Thermus thermophilus* to elucidate the molecular mechanisms of photosensing and signal transduction of CarH.

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* IMS International Internship Program

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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Keywords Biomolecule, Dynamical Ordering, NMR

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

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

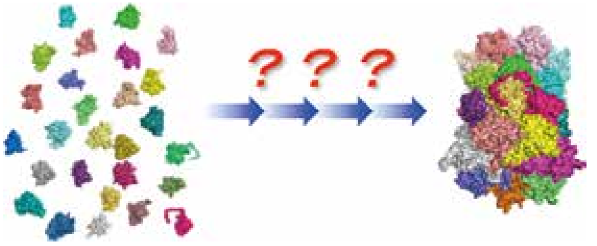

Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- M. Yagi-Utsumi 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).
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- Y. Kamiya, T. Satoh and K. Kato, “Molecular and Structural Basis for *N*-Glycan-Dependent Determination of Glycoprotein Fates in Cells,” *Biochim. Biophys. Acta, Gen. Subj.* **1820**, 1327–1337 (2012).

1. Exploration of Conformational Spaces of Flexible Oligosaccharides

Conformational dynamics are essential properties of biomacromolecules that are involved in molecular recognition events in living systems. The motional freedom of three-dimensional structures can endow them with adaptability to various interaction partners, occasionally in promiscuous fashions. We employed stable isotope- and lanthanide-assisted NMR approaches in conjunction with replica-exchange molecular dynamics (REMD) simulations to obtain atomic descriptions of the conformational dynamics of high-mannose-type oligosaccharides, which harbor intracellular glycoprotein-fate determinants in their triantennary structures.1) The experimentally validated REMD simulation provided quantitative views of the dynamic conformational ensembles of the complicated, branched oligosaccharides, and indicated significant expansion of the conformational space upon removal of a terminal mannose residue during the functional glycan-processing pathway (Figure 2).

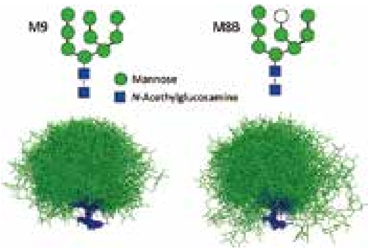

Figure 2. Superimpositions of 240 conformers derived from NMR-validated replica exchange MD simulations of the high-mannose-type M9 (left) and M8B (right) oligosaccharides.

2. Structural Characterization of Biomolecular Interactions Involved in Protein Fate Determination

Using NMR spectroscopy and X-ray crystallography, we characterized structures and interactions of multidomain proteins involved in fate determination of other proteins in living systems. In the endoplasmic reticulum, folding of newly synthetized proteins is facilitated through interaction with various proteins including molecular chaperones. We determined three-dimensional structures of the putative substrate-binding domains of UDP-glucose:glycoprotein glucosyltransferase (UGGT), a folding sensor enzyme, and protein disulfide isomerase (PDI), a folding catalyst, underscoring the importance of conformational changes in substrate recognition.2,3)

Many of proteins in cells are destroyed primarily by ubiquitin-/proteasome-mediated protein degradation system. We applied a paramagnetic NMR technique to determine the mode of substrate recognition by the Josephin domain of ataxin-3, which has an endo-type deubiquitinase activity.4) Moreover, our NMR study revealed that Ump1, a proteasome assembly chaperone, is an intrinsically unstructured protein and largely devoid of secondary structural elements.5)

Our NMR data also contributed to providing structural bases of interactions of amyloidogenic proteins with self-assembled spherical complex displaying a gangliosidic glycan cluster (collaboration with Dr. Sota Sato, Tohoku University and Dr. Makoto Fujita, the University of Tokyo) and with SorLA, a neuronal sorting receptor considered to be a major risk factor for Alzheimer's disease (in collaboration with Dr. Junichi Takagi, Osaka University).6,7)

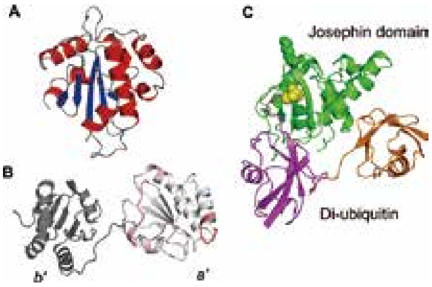

Figure 3. 3D Structures of (A) the Trx3 domain of UGGT, (B) PDI *b*'-*a*' domains, and (C) the Josephin domain of ataxin-3 complexed with di-ubiquitin.

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Awards

TONG, Zhu; Young Presentation Award, The 87th Annual Meeting of the Japanese Biochemical Society (2014).
YAGI-UTSUMI, Maho; Poster Presentation Award, The 3rd International Symposium of "Dynamical ordering of biomolecular systems for creation of integrated functions" (2015).
SIKDAR, Arunima; Poster Presentation Award, The Winter School of Sokendai/ Asian CORE Program (2015).

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Operation and Design Principles of Biological Molecular Machines

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Keywords Single-Molecule Biophysics, Molecular Machines, Molecular Motors

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

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

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

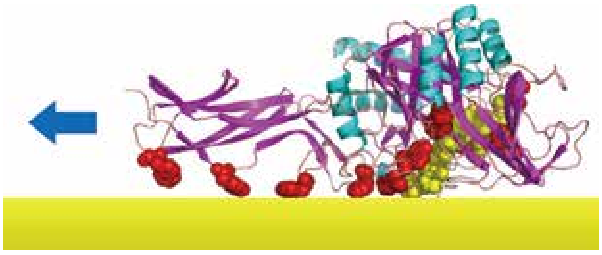

Figure 1. A linear molecular motor chitinase. Chitinase moves on the substrate crystalline chitin unidirectionally and processively, driven by the energy of hydrolysis of the chain end of the chitin.

Selected Publications

- R. Iino, 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_I," *J. Biol. Chem.* **289**, 14056–14065 (2014).
- R. Iino and H. Noji, "Intersubunit Coordination and Cooperativity in Ring-Shaped NTPases," *Curr. Opin. Struct. Biol.* **23**, 229–234 (2013).
- 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).
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- 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. Key Chemical Factors of Arginine Finger Catalysis of F_1-ATPase Clarified by an Unnatural Amino Acid Mutation[1)]

A catalytically important arginine, called Arg finger, is employed in many enzymes to regulate their functions through enzymatic hydrolysis of nucleotide triphosphates. F_1-ATPase, a rotary molecular motor, possesses Arg fingers which catalyze hydrolysis of adenosine triphosphate (ATP) for efficient chemo-mechanical energy conversion. In this study, we examined the Arg finger catalysis by single-molecule measurements for a mutant of F_1-ATPase in which the Arg finger is substituted with an unnatural amino acid of a lysine analogue, 2,7-diaminoheptanoic acid (Lyk). The use of Lyk, of which the side chain is elongated by one CH_2 unit so that its chain length to the terminal nitrogen of amine is set to be equal to that of arginine, allowed us to resolve key chemical factors in the Arg finger catalysis, *i.e.*, chain length matching and chemical properties of the terminal groups. Rate measurements by single-molecule observations showed that the chain length matching of the side-chain length is not a sole requirement for the Arg finger to catalyze the ATP hydrolysis reaction step, indicating the crucial importance of chemical properties of the terminal guanidinium group in the Arg finger catalysis. On the other hand, the Lyk mutation prevented severe formation of an ADP inhibited state observed for a lysine mutant and even improved the avoidance of inhibition compared with the wild-type F_1-ATPase. The present study demonstrated that incorporation of unnatural amino acids can widely extend with its high "chemical" resolution biochemical approaches for elucidation of the molecular mechanism of protein functions and furnishing novel characteristics.

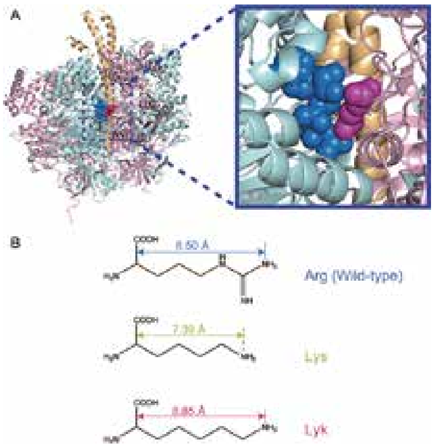

Figure 2. (A) Crystal structure of mitochondrial F_1–ATPase viewed from the side, β_{DP}/α_{DP} catalytic interface. The α, β, and γ subunits are shown in pearl pink, pearl blue, and pearl yellow, respectively. The "arginine finger" in the α subunit is shown by pink space-filling model. AMP-PNP bound to the catalytic site are shown by blue space-filling model. (B) Chemical structures and side-chain length of arginine (Arg, top), lysine (Lys, middle), and 2,7-diaminoheptanoic acid (Lyk, bottom).

2. High-Speed Angle-Resolved Imaging of Single Gold Nanorod with Microsecond Temporal Resolution and One-Degree Angle Precision[2)]

We developed two types of high-speed angle-resolved imaging methods for single gold nanorods (SAuNRs) using objective-type vertical illumination dark-field microscopy and a high-speed CMOS camera to achieve microsecond temporal and one-degree angle resolution. These methods are based on: (i) an intensity analysis of focused images of SAuNR split into two orthogonally polarized components and (ii) the analysis of defocused SAuNR images. We determined the angle precision (statistical error) and accuracy (systematic error) of the resultant SAuNR (80 nm × 40 nm) images projected onto a substrate surface (azimuthal angle) in both methods. Although both methods showed a similar precision of ~1° for the azimuthal angle at a 10 μs temporal resolution, the defocused image analysis showed a superior angle accuracy of ~5°. In addition, the polar angle was also determined from the defocused SAuNR images with a precision of ~1°, by fitting with simulated images. By taking advantage of the defocused image method's full revolution measurement range in the azimuthal angle, the rotation of the rotary molecular motor, F_1-ATPase, was measured with 3.3 μs time resolution. The time constants of the pauses waiting for the elementary steps of the ATP hydrolysis reaction and the torque generated in the mechanical steps have been successfully estimated. The high-speed angle-resolved SAuNR imaging methods will be applicable to the monitoring of the fast conformational changes of many biological molecular machines.

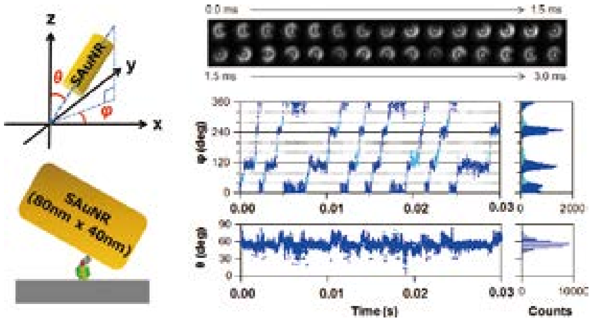

Figure 3. (Left) Schematic image of experimental system of rotation assay of F_1-ATPase using single gold nanorod (SAuNR) as a probe. (Right) Example of rotation of F_1-ATPase probed at 3.3 μs time resolution.

References

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2) S. Enoki, R. Iino, Y. Niitani, Y. Minagawa, M. Tomishige and H. Noji, *Anal. Chem.* **87**, 2079–2086 (2015).

Supramolecular Chemical Approach to Construction of Artificial Cell

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Keywords Artificial Cell, Origin of Life, Vesicle

Exploring the boundary between a living and non-living matter is one of the most challenging problems for contemporary scientists. In order to understand a cell, which is a minimum unit of life, synthesis of an artificial cell from supramolecular chemical approach is a plausible strategy, because simple molecular assemblies evolved to a simple cell on prebiotic earth. As shown in Figure 1, the key elements of a cell are compartment, information and catalyst, *i.e.* metabolism. We have tackled the construction of a chemical artificial cell endowed with these three elements.

In our laboratory, we aim to construct the two artificial cells using giant vesicles (GV) as compartment. One is an artificial cell which can proliferate from generation to generation. This work is a collaboration with Sugawara group (Kanagawa Univ.). The other research is an artificial cell incorporating catalyst producing system. The GV system can generate catalyst and membrane molecule by transforming each precursors, which makes it possible for GVs to proliferate with producing catalyst.

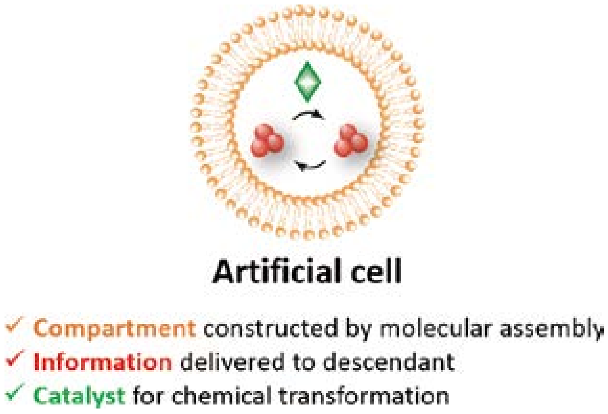

Figure 1. Artificial cell model
The replicating systems of compartment and the replicating system of information materials are combined. The reactions in the two replicating systems are accelerated by each proper catalysts.

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).
- T. Sugawara, K. Kurihara and K. Suzuki, “Constructive Approach towards Protocells,” in *Engineering of chemical complexity*, world scientific lecture notes in complex systems, World Scientific Pub. Co. Inc., pp. 359–374 (2013).

1. An Artificial Cell with a Primitive Cell Cycle

One of the approaches for exploring the origin of life or elucidating of the functions of life is construction of an artificial cell from supramolecular chemical approach.[1,2] In collaboration with Sugawara's group, artificial cells which have three basic elements of a cell; information (DNA), compartment (giant vesicle (GV): A supramolecular assembly of amphiphiles) and metabolism (synthetic catalyst) have been constructed.[3] The artificial cellular system consisted of amplification of DNA by polymerase chain reaction and self-reproduction of GV by addition of membrane lipid precursor. Although this GV proliferated with distribution of internal amplified DNA, it ceased at the 2nd generation because of depletion of internal information substances.

Now, we construct a recursive vesicular artificial cell system with proliferation cycles, collaborating with Sugawara group. By using the vesicular transport system,[4] the 2nd generation of GVs which have no PCR reagents after self-reproduction was replenished by fusing with the conveyer GVs encapsulating the PCR reagents (Figure 2). The replenished GV can amplify the internal DNA and yield 3rd generation of the GV after addition of membrane lipid precursor. The GV system with replenishing system was constructed.[5] This system would lead to an evolvable artificial cellular system.

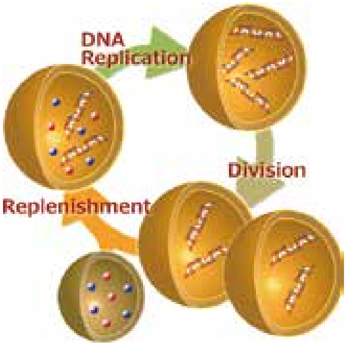

Figure 2. An artificial cell system with premitive cell cycle. After growth and division of GV, the substance-depleted GV was replenished by the vesicular fusion.

2. An Artificial Cell Containing a Catalyst-Producing System

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

Here, we aim to realize a new artificial cellular system in which the GV self-organize its own composition spontaneously according to the environment. In order for GV to self-reproduce and self-maintain, it is necessary to combine metabolism and compartment. By introducing the cross-catalysis system (Figure 3), we construct an artificial cell in which catalysts are produced. After addition of membrane precursor aldehyde, the production of catalyst and membrane molecule was confirmed by NMR, microscopy observation. In this system, the GV was reproduced by the catalyst which catalyze the production of the GV membrane lipid molecule. The GV membrane provides the field where the catalyst is synthesized.

In addition, by changing the composition of the vesicular membrane, the production of catalyst and membrane molecule was oscillated by interacting each other. This means that the artificial cell incorporating the negative feedback is realized.

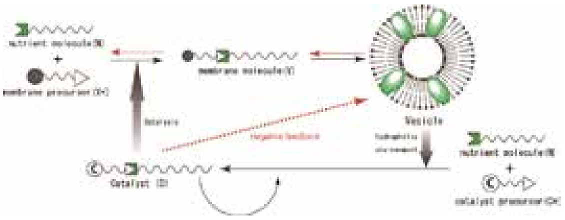

Figure 3. Scheme of new artificial cellular system. The membrane molecules of the GV was synthesized by the catalyst produced in the GV.

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

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Investigation of Molecular Mechanisms of Channels, Transporters and Receptors

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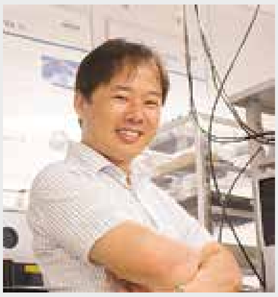

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Education
1999 B.S. Kyoto University
2004 Ph.D. Kyoto University

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

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

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Keywords Infrared Spectroscopy, Membrane Protein, Ion Channel

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

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

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

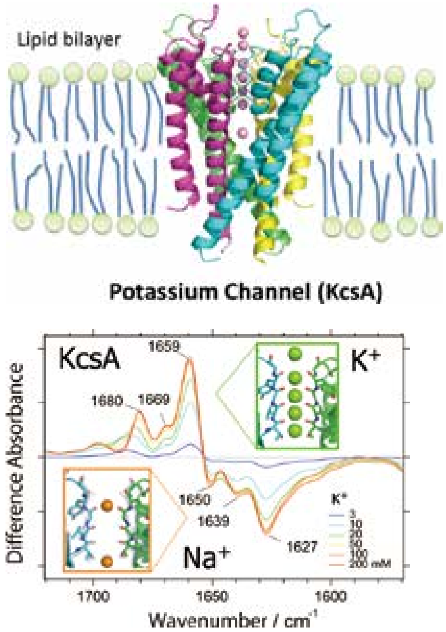

Figure 1. (top) X-ray crystal structure of a potassium ion channel, KcsA. (bottom) The ion-exchange induced difference infrared spectra of KcsA with different potassium ion concentration. The amide I bands are mainly originated from the carbonyl groups of the selectivity filter of KcsA.

Selected Publications

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

1. Light-Induced Structural Changes of Chimeras of Channelrhodopsin-1 and -2 from *Chlamydomonas reinhardtii*[1)]

Optogenetics is a powerful technique for manipulating specific neural activities by light stimulation, which has been rapidly growing up since discovery of light-gated cation channel, channelrhodopsin. There are two kinds of channelrhodopsin called channelrhodopsin-1 and -2 (ChR1 and ChR2) which are expressed in the eyespot of *Chlamydomonas reinhardtii*. Among them, ChR2 and its derivatives have been extensively utilized in optogenetics application. Alteration of channelrhodopsins to achieve a favorable electrophysiological response could be rationally applied when the molecular mechanisms of channelrhodopsin are understood well.

The basic architecture of channelrhodopsin is similar to other microbial rhodopsins which are composed of seven transmembrane helices with an all-*trans* retinal as the chromophore. Photoisomerization of the retinal chromophore upon light absorption causes conformational changes of the protein that result in opening of the channel gate and the influx of cations. The time course of the photocurrent upon continuous illumination of ChR2 shows a peak-and-plateau, while that of ChR1 shows a rectangular shape. The suppression just after the transient maximum photocurrent seen in ChR2 is denoted the “desensitization.”

In 2009, several types of ChR1/ChR2 chimeras were characterized using electrophysiological techniques. One of these chimeras consists of the first five transmembrane helices (TM1 to TM5) from ChR1 and the last two transmembrane helices (TM6 and TM7) from ChR2. This chimera is referred to as $\mathrm{ChR}_{5/2}$. Another chimera consists of TM1 and TM2 from ChR1 and TM3 to TM7 from ChR2. This chimera is referred to as $\mathrm{ChR}_{2/5}$ (for details, see Figure 2). These ChR1/ChR2 chimeras show larger photocurrents than the wild types, and their desensitization is significantly reduced upon continuous illumination. However, the molecular mechanism of suppression of desensitization has remained unknown.

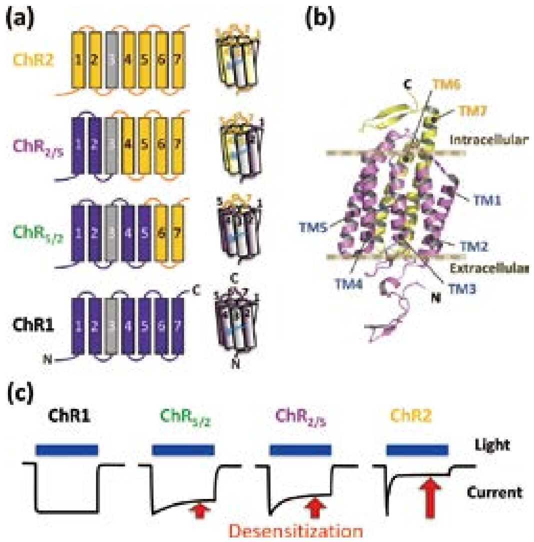

Figure 2. (a) Schematic representation of the chimeric channel rhodopsins. (b) The X-ray crystal structure of a chimeric channelrhodopsin called C1C2, which is nearly identical to $\mathrm{ChR}_{5/2}$. (c) The photocurrent profiles of ChR1, ChR2and the chimeras. This figure is adapted from ref. 1.

Fourier-transform infrared (FTIR) spectroscopy has revealed the molecular mechanisms underlying the photo-induced structural dynamics of various microbial rhodopsins, such as bacteriorhodopsin and halorhodopsin.[2)] We applied light-induced difference FTIR spectroscopy on ChR1/ChR2 chimeras and ChR2 with an aim to reveal the molecular basis underlying the differences in electrophysiological properties between them.

As a consequence, we found that ChR1/ChR2 chimeras exhibited structural changes distinct from those in ChR2 upon continuous illumination. In particular, the protonation state of a glutamate residue, Glu129, (Glu90 in ChR2 numbering) in the ChR chimeras is not changed as dramatically as seen in ChR2 as a negative band at 1718 cm^{-1} (Figure 3). Moreover, using mutants stabilizing particular photointermediates as well as time-resolved measurements, we identified some differences between the major photointermediates of ChR2 and ChR1/ChR2 chimeras. We couldn’t see any substantial change in the protonation state of Glu129 in $\mathrm{ChR}_{5/2}$ during the photocycle. Taken together, our data indicate that the gating and desensitizing processes in ChR1/ChR2 chimeras are different from those in ChR2 and that these differences should be considered in the rational design of new optogenetic tools based on channelrhodopsins.

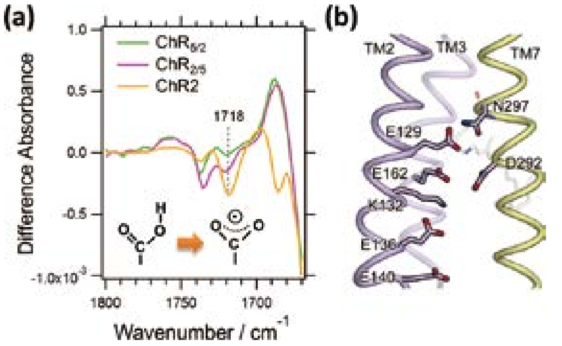

Figure 3. (a) Light-induced difference spectra in the C=O stretching region of carboxylic acid side chains. (c) The X-ray crystal structure of C1C2 shown along TM2 and TM7 helices. This figure is adapted from ref. 1.

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2) Y. Furutani*, K. Fujiwara, T. Kimura, T. Kikukawa, M. Demura and H. Kandori, *J. Phys. Chem. Lett.* **3**, 2964–2969 (2012).

(*; corresponding authors)

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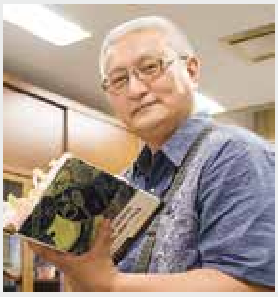
* IMS International Internship Program

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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



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Education
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2014 Distinguished Professor, Three George University
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2011 Deputy Research Project Leader, JST CREST (–2016)

Awards
1991 Eisai Award, Synthetic Organic Chemistry
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ICHII, Shun

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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.

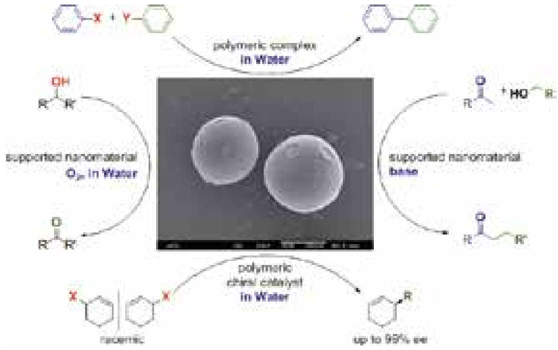

Figure 1. Typical Examples of Heterogeneous Aquacatalyses using Amphiphilic Polymer-Supported Metal Complexes and Metal Nanoparticles.

Selected Publications

- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Amphiphilic Self-Assembled Polymeric Copper Catalyst to Parts per Million Levels: Click Chemistry," *J. Am. Chem. Soc.* **134**, 9285–9290 (2012).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels," *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, "Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex," *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, "Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Pallasium Catalyst Supported on Amphiphilic Resin," *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, "A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water," *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, "Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane," *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. Enantioposition-Selective Copper-Catalyzed Azide–Alkyne Cycloaddition for Construction of Chiral Biaryl Derivatives[1,2]

A highly enantioposition-selective copper-catalyzed azide–alkyne cycloaddition (CuAAC) of dialkynes bearing prochiral biaryls has been developed for the construction of 1,2,3-triazoles bearing axially chiral biaryl groups in up to 76% yield and up to 99% ee.

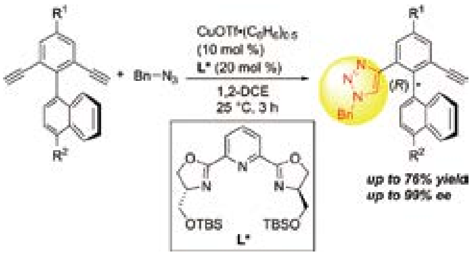

Figure 2. Enatioposition-selective copper-catalyzed azide–alkyne cycloaddition.

2. Continuous-Flow Oxidation of Alcohols and Hydrogenation of Olefines and Nitrobenzenes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Polymer[3,4]

We have developed a continuous-flow reaction system containing amphiphilic polymer-dispersion of platinum nanoparticles (ARP-Pt) packed in a catalyst cartridge to catalyze the aerobic oxidation of alcohols and the hydrogenation of olefins and nitrobenzenes. In the flow system using O_2, various alcohols were fully oxidized within 73 seconds (100–120 °C, 40–70 bar of the system pressure, 5 vol% of O_2) in water to give the corresponding carbonyl products in up to 99% yield. Olefins and nitrobenzenes underwent hydrogenation with the same flow system under H_2 (25 °C, 5–15 bar of the system pressure, 5 vol% of H_2) within 31 seconds to afford the corresponding hydrogenated products in up to 99% yield.

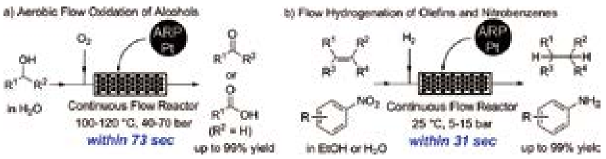

Figure 3. Continuous-flow oxidation of alcohols and hydrogenation of olefins and nitorobenzenes.

3. Palladium NNC-Pincer Complex: An Efficient Catalyst for Allylic Arylation at Perts Per Billion Levels[5]

Allylic arylation of allylic acetates by sodium tetraarylborates in the presence of ppb to ppm (molar) loadings of a palladium NNC-pincer complex catalyst in methanol at 50 °C gave the corresponding arylated products in excellent yields. Total turnover numbers of up to 500,000,000 and turnover frequencies of up to 11,250,000 h^{-1} were achieved.

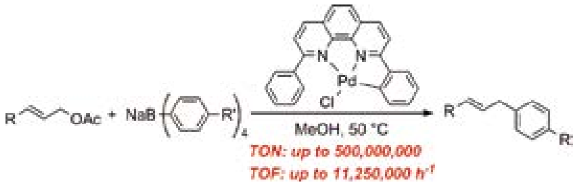

Figure 4. Allylic arylation of allylic acetates with sodium tetraarylborates in the presence of a palladium NNC-pincer complex.

4. Development of an Aquacatalytic System Based on the Formation of Vesicles of an Amphiphilic Palladium NNC-Pincer Complex[6]

Two amphiphilic palladium NNC-pincer complexes bearing hydrophilic tri(ethylene glycol) chains and hydrophobic dodecyl chains were designed and prepared for the development of a new aquacatalytic system. In water, these amphiphilic complexes self-assembled to form vesicles, the structures which were established by means of a range of physical techniques. When the catalytic activities of the vesicles were investigated in the arylation of terminal alkynes in water, they were found to catalyze the reaction of aryl iodides with terminal alkynes to give good yields of the corresponding internal alkynes. The formation of a vesicular structure was shown to be essential for efficient promotion of this reaction in water.

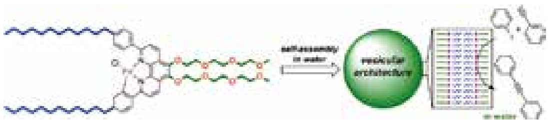

Figure 5. Cu-free Sonogashira reaction in water in the presence of a self-assembled vesicular amphiphilic palladium NNC-pincer complex.

References

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2) T. Osako and Y. Uozumi, *Synlett* **26**, 1475–1479 (2015).
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4) T. Osako, K. Torii, A. Tazawa and Y. Uozumi, *RSC Adv.* **5**, 45760–45766 (2015).
5) G. Hamasaka, F. Sakurai and Y. Uozumi, *Chem. Commun.* **51**, 3886–3888 (2015).
6) F. Sakurai, G. Hamasaka and Y. Uozumi, *Dalton Trans.* **44**, 7828–7834 (2015).

Award

OSAKO, Takao; The 4th NINS Prize for Young Scientists (2015).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Education

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Professional Employment

2005	Postdoctoral Fellow, Harvard University
2006	Assistant Professor, Tohoku University
2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2003	The Elizabeth R. Norton Prize for Excellence in Research in Chemistry, University of Chicago
2004	Abbott Laboratories Graduate Fellowship
2005	Damon Runyon Cancer Research Foundation Post Doctoral Research Fellowship
2008	Thieme Chemistry Journals Award
2014	The 17th Morita Science Research Award Central Glass Co., Ltd. Award in Organic Chemistry, Japan

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Keywords Organic Synthesis, Molecular Catalyst, Non-Covalent Interaction

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

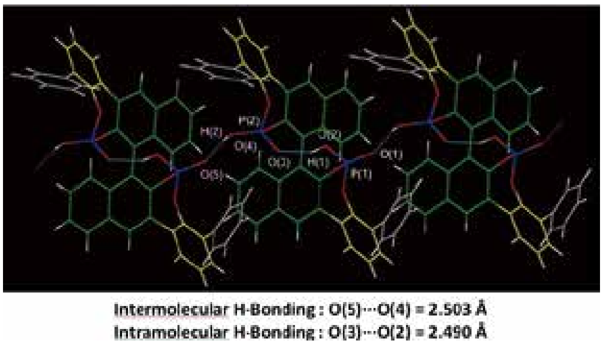

Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

Selected Publications

- T. P. Yoon and E. N. Jacobsen, *Science* **299**, 1691–1693 (2003).
- N. Momiyama and H. Yamamoto, "Brønsted Acid Catalysis of Achiral Enamine for Regio- and Enantioselective Nitroso Aldol Synthesis," *J. Am. Chem. Soc.* **127**, 1080–1081 (2005).
- N. Momiyama, H. Tabuse and M. Terada, "Chiral Phosphoric Acid-Governed Anti-Diastereoselective and Enantioselective Hetero-Diels–Alder Reaction of Glyoxylate," *J. Am. Chem. Soc.* **131**, 12882–12883 (2009).
- N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, "Design of Chiral Bis-Phosphoric Acid Catalyst Derived from (*R*)-3,3'-Di(2-hydroxy-3-arylphenyl)binaphthol: Catalytic Enantioselective Diels–Alder Reaction of α,β-Unsaturated Aldehydes with Amidodienes," *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).

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

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

2. Design of Chiral Brønsted Acid Catalyst

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

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

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.5,6) 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.7) 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.8)

3. Halogen Bond Donor Catalyzed Allylation Reaction of Isoquinoline with Allylsilatrane

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

We found that pentafluoroiodebenzene was able to catalyze the allylation reaction of isoquinoline with allylsilatrane to give the corresponding product in good yield.9)

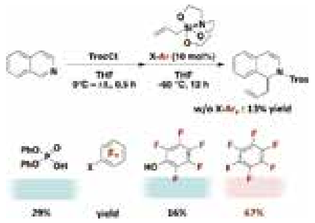

Figure 2. Halogen bond donor catalyzed allylation reaction. Comparison with Brønsted acid/hydrogen bond donor catalyst.

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3) N. Momiyama, H. Okamoto, M. Shimizu and M. Terada, *Chirality* **27**, 464–475 (2015). (Invited)
4) N. Momiyama, H. Okamoto, J. Kikuchi, T. Korenaga and M. Terada, under revision.
5) N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
6) N. Momiyama, K. Funayama, H. Noda, M. Yamanaka, N. Akasaka, S. Ishida, T. Iwamoto and M. Terada, under revision.
7) N. Momiyama, T. Narumi and M. Terada, *Chem. Commun.* **51**, 16976–16979 (2015).
8) N. Momiyama *et al.*, Manuscript in preparation.
9) N. Momiyama *et al.*, Manuscript in preparation.

Awards

MOMIYAMA, Norie; The 17th Morita Science Research Award (2014).
MOMIYAMA, Norie; Central Glass Co., Ltd. Award in Organic Chemistry, Japan (2014).

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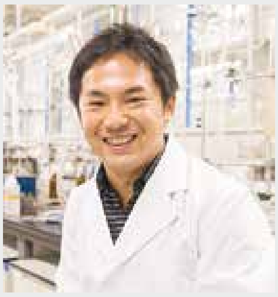
* carrying out graduate research on Cooperative Education Program of IMS with Tohoku University

Development of Functional Metal Complexes for Artificial Photosynthesis

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



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IZU, Hitoshi
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TANIWAKE, Mayuko
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Keywords Metal Complex, Water Oxidation, Artificial Photosynthesis

Artificial photosynthesis is a solar energy conversion technology that mimics natural photosynthesis, and considered to be one of the next big breakthroughs in energy. Our group studies the development of functional metal complexes toward the realization of artificial photosynthesis. Specific areas of research include (i) synthesis of ruthenium-based molecular catalysts for water oxidation and carbon dioxide reduction, (ii) creation of cluster catalysts for multi-electron transfer reactions, (iii) mechanistic investigation into water oxidation catalyzed by metal complexes, (iv) application of proton-coupled electron transfer toward multi-electron transfer reactions, (v) electrochemical evaluation of the activity of molecular catalysts for water oxidation and carbon dioxide reduction, (vi) electrochemical measurement of metal complexes in homogeneous solutions under photoirradiation, and (vii) development of reaction fields via self-assembly of molecular catalysts.

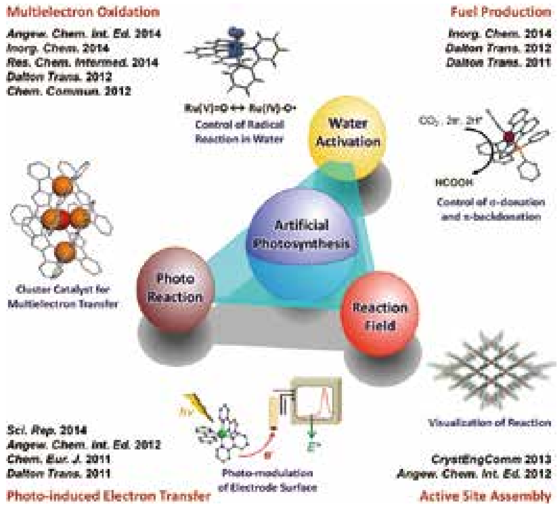


Figure 1. An overview of our work.

Selected Publications

- M. Yoshida, M. Kondo, S. Torii, K. Sakai and S. Masaoka, "Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant -SO_3^- Groups," *Angew. Chem., Int. Ed.* **54**, 7981–7984 (2015).
- M. Okamura and S. Masaoka, "Design of Mononuclear Ruthenium Catalysts for Low-Overpotential Water Oxidation," *Chem. –Asian J. [Focus Review]* **10**, 306–315 (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).
- G. Nakamura, M. Okamura, M. Yoshida, T. Suzuki, H. D. Takagi, M. Kondo and S. Masaoka, "Electrochemical Behavior of Phosphine-Substituted Ruthenium(II) Polypyridine Complexes with a Single Labile Ligand," *Inorg. Chem.* **53**, 7214–7226 (2014).
- A. Fukatsu, M. Kondo, M. Okamura, M. Yoshida and S. Masaoka, "Electrochemical Response of Metal Complexes in Homogeneous Solution under Photoirradiation," *Sci. Rep.* **4**, 5327 (2014).
- T. Itoh, M. Kondo, M. Kanaike and S. Masaoka, "Arene-Perfluoroarene Interactions for Crystal Engineering of Metal Complexes: Controlled Self-Assembly of Paddle-Wheel Dimers," *CrystEngComm* **15**, 6122–6126 (2013).

1. Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant -SO_3^- Groups1)

Rational molecular design of catalytic systems capable of smooth O–O bond formation is critical to the development of efficient catalysts for water oxidation. In this work, we developed a new ruthenium complex which bears pendant SO_3^- groups in the secondary coordination sphere: [Ru(terpy)(bpyms)(OH_2)] (terpy = 2,2':6',2''-terpyridine, bpyms = 2,2'-bipyridine-5,5'-bis(methanesulfonate)). Water oxidation driven by a Ce^{4+} oxidant is distinctly accelerated upon introduction of the pendant SO_3^- groups in comparisons to the parent catalyst, $[Ru(terpy)(bpy)(OH_2)]^{2+}$ (bpy = 2,2'-bipyridine). Spectroscopic, electrochemical, and crystallographic investigations concluded that the pendant SO_3^- groups promote the formation of an O–O bond via the secondary coordination sphere on the catalyst, whereas the influence of the pendant SO_3^- groups on the electronic structure of the $[Ru(terpy)(bpy)(OH_2)]^{2+}$ core is negligible. The results of this work indicate that modification of the secondary coordination sphere is a valuable strategy for the design of water oxidation catalysts.

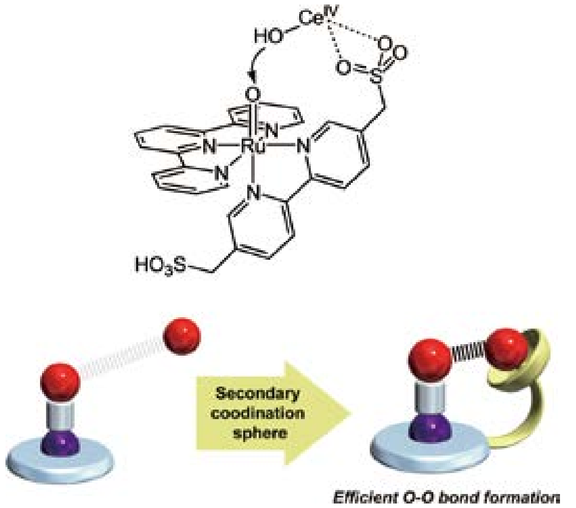


Figure 2. Schematic illustration of efficient O–O bond formation through modification of the secondary coordination sphere.

2. Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex2)

Mixed-valence (MV) complexes are excellent model systems for the investigation of electron-transfer phenomena in biophysical processes such as photosynthesis and in artificial electronic devices based on conjugated materials. Given that the electronic properties of MV states could be strictly controlled by the oxidation state of the dinuclear core, systematic investigations on the several oxidation states of dinuclear metal complexes are an interesting and important research topic. In this work, a series of $[\{(terpy)(bpy)Ru\}(\mu\text{-}O)\{Ru(bpy)(terpy)\}]^{n+}$ (**[RuORu]**$^{n+}$, terpy = 2,2';6',2''-terpyridine, bpy = 2,2'-bipyridine) was systematically synthesized and characterized in three distinct redox states (n = 3, 4, and 5 for $Ru^{II,III}_2$, $Ru^{III,III}_2$, and $Ru^{III,IV}_2$, respectively). The crystal structures of **[RuORu]**$^{n+}$ (n = 3, 4, 5) in all three redox states were successfully determined. X-ray crystallography showed that the Ru–O distances and the Ru–O–Ru angles are mainly regulated by the oxidation states of the ruthenium centers. X-ray crystallography and ESR spectra clearly revealed the detailed electronic structures of two mixed-valence complexes, $\mathbf{[Ru^{III}ORu^{IV}]^{5+}}$ and $\mathbf{[Ru^{II}ORu^{III}]^{3+}}$, in which each unpaired electron is completely delocalized across the oxo-bridged dinuclear core. These findings allow us to understand the systematic changes in structure and electronic state that accompany the changes in the redox state.

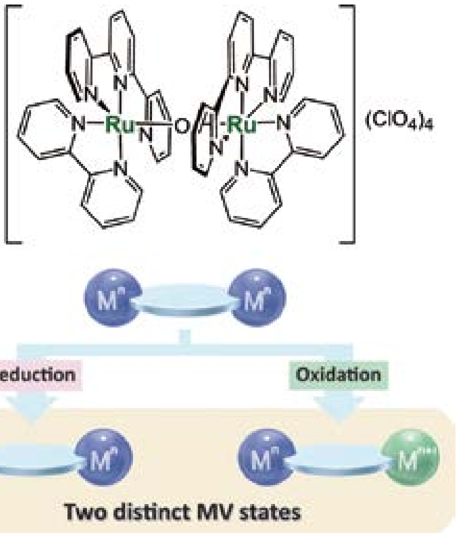


Figure 3. Two distinct MV states derived from a homovalent dimer.

References

1) 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).

2) 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).

Awards

FUKATSU, Arisa; Excellent Poster Award, International Conference on Artificial Photosynthesis (2014).
IZU, Hitoshi; Excellent Poster Award, The 4th CSJ Chemistry Festa (2014).
ITOH, Takahiro; CrystEngComm Poster Prize (2014).
ITOH, Takahiro; Poster Award, The 64th Conference of Japan Society of Coordination Chemistry (2014).

Control of Electron Transfer for Efficient Oxygenation Reactions

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

KURAHASHI, Takuya
Assistant Professor

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, ^{1}H and ^{2}H NMR, EPR, IR resonance Raman spectroscopy and magnetic susceptibility measurement. Correlations between electronic structures and electron transfer ability are investigated in detail.

1. Dioxygen Activation via Two-Electron Transfer from Hydroxide to Dioxygen Mediated By a Manganese(III) Complex

Although atmospheric dioxygen is regarded as the most ideal oxidant, O_2 activation for use in oxygenation reactions intrinsically requires a costly sacrificial reductant. This study investigated the use of inexpensive aqueous alkaline solution for O_2 activation. This study has clarified that a manganese(III) salen complex mediates O_2 activation in the presence of OH^- from 2 M KOH aqueous solution (Figure 1). Mechanistic investigation have shown that the reaction of Mn^{III}(salen)(Cl) with OH^- generates a transient species with strong reducing ability, which effects the reduction of O_2 by means of a manganese(II) intermediate.

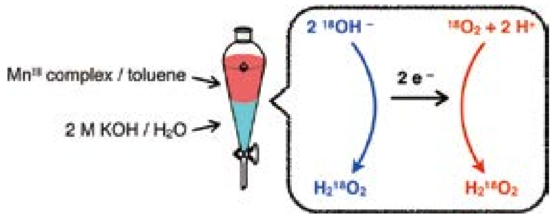


Figure 1. Isotope experiments to verify two-electron transfer from OH^- to O_2.

Visiting Professors

Visiting Professor

KATO, Masako *(from Hokkaido University)*

Construction of Photofunctional Metal Complexes and the Elucidation of Their Properties

In our research group, we focus on the creation of photofunctional metal complexes.

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

Visiting Professor

YORIMITSU, Hideki *(from Kyoto University)*

Synthesis of π-Conjugated Molecules by Means of Organometallics

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

Visiting Associate Professor

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

Development of an Auto-Sampling System Designed for Titration-SAXS Measurements

Various protein molecules concert with each other to express various biological functions. Because these multicomponent biological molecules weakly interact with each other, they can undergo regulatory dissociation and association upon inducing biological stimuli. In order to understand biological systems, we must, at first, aim to identify every possible unstable complex involved in the given multicomponent system, and then quantitatively analyze the interactions of these complex molecules. However, because of the complexity, it is generally difficult to apply conventional analytical methods to analyze such multi-component equilibrium systems. We have realized a new analytical method that would enable us to perform structure and interaction analyses on multi-component equilibrium systems. This was achieved by developing an auto-sampling system equipped with micro-fluidics technology. Applying this newly designed equipment to SAXS measurements, we can automatically collect numerous scattering profiles while altering the molar ratios of each component involved in the multi-component equilibrium; thus, enabling us to determine the system's free energy landscape of the multi-component equilibrium.

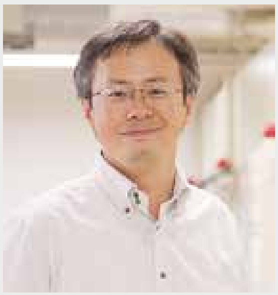
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

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

The Origin of 24 Hour Period in Cyanobacterial Clock System

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



AKIYAMA, Shuji
Professor
[akiyamas@ims.ac.jp]

Education

1997	B.E. Kyoto University
1999	M.E. Kyoto University
2002	Ph.D. Kyoto University

Professional Employment

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

Awards

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

Member

Assistant Professor
- MUKAIYAMA, Atsushi
- FURUIKE, Yoshihiko

Post-Doctoral Fellow
- ABE, Jun
- HIYAMA, Takuya

Visiting Scientist
- GOUILLART, Louis*

Technical Fellow
- FUNAKI, Yukino
- SHINTANI, Atsuko

Secretary
- SUZUKI, Hiroko

Keywords Biological Clocks, Clock Proteins, Slow Dynamics

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

KaiC, a core protein of the circadian clock in cyanobacteria, undergoes rhythmic structural changes over approximately 24 h in the presence of KaiA and KaiB (Kai oscillator). This slow dynamics spanning a wide range of both temporal and spatial scales is not well understood, and is central to a fundamental question: What determines the temperature-compensated 24 h period? The Kai oscillator reconstitutable *in vitro* is advantageous for studying its dynamic structure through a complementary usage of both X-ray crystallography and solution scattering, its transient response by using physicochemical techniques, and its molecular motion through a collaborative work with computational groups (Figure 1).

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

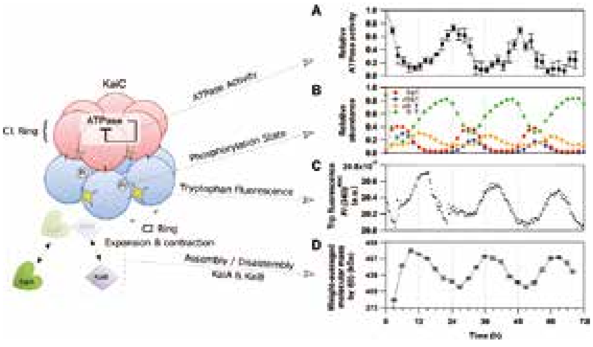


Figure 1. Circadian dynamics of cyanobacterial clock protein KaiC. The C1 and C2 domains in each protomer of KaiC are drawn as red and blue spheres, respectively. Expansion and contraction motions of the C2 ring (B, C) in solution serves as a timing cue for assembly/disassembly of KaiA and KaiB (D), and is interlocked with its C1 ATPase 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 System[1,2)]

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.

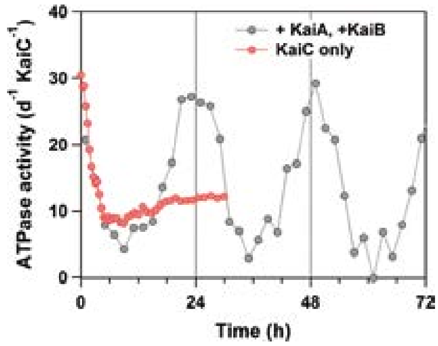


Figure 2. Time-course of KaiC ATPase activity.

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.

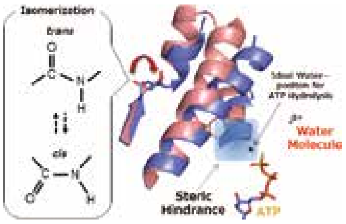


Figure 3. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

The circadian clock's period is independent of ambient temperature, a phenomenon known as temperature compensation. One KaiC molecule is composed of six identical subunits, each containing duplicated domains with a series of ATPase motifs. The asymmetric atomic-scale regulation by the aforementioned mechanism suggests a feedback mechanism that maintains the ATPase activity at a constant low level. Our results indicate that the circadian period is implemented as the time constant of the feedback mechanism mediated in this protein structure.

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

2. Instrumentation for Studying Biological Clock Systems[3)]

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,[3)] HPLC,[2)] 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[1,4)]

We are supporting motivated SAXS users so that they can complete experiments smoothly and publish their results.

References

1) A. Mukaiyama, M. Osako, T. Hikima, T. Kondo and S. Akiyama, *Biophysics* **11**, 79–84 (2015).
2) J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
3) Y. Furuike *et al.*, to be submitted.
4) R. Kojima, M. Okumura, S. Masui, S. Kanemura, M. Inoue, M. Saiki, H. Yamaguchi, T. Hikima T, M. Suzuki, S. Akiyama and K. Inaba, *Structure* **22**, 431–443 (2014).

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* IMS International Internship Program

Protein Design Using Computational and Experimental Approaches

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

KOGA, Nobuyasu
Associate Professor
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Education

2001	B.S. Kobe University
2006	Ph.D. Kobe University

Professional Employment

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

Awards

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

Member

Assistant Professor
KOSUGI, Takahiro

Research Fellow
KOGA, Rie

Graduate Student
SAKUMA, Kouya

Secretary
SUZUKI, Hiroko

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

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

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

Selected Publications

- N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, "Principles for Designing Ideal Protein Structures," *Nature* **491**, 222–227 (2012).
- J. Fang, A. Mehlich, N. Koga, J. Huang, R. Koga, M. Rief, J. Kast, D. Baker and H. Li, "Forced Protein Unfolding Leads to Highly Elastic and Tough Protein Hydrogels," *Nat. Commun.* **4**:2974 (2013).

1. Principles for Designing Ideal Protein Structures

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

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

References

1) S. J. Fleishman, S. D. Khare, N. Koga and D. Baker*, *Protein Sci.* **20**, 753–757 (2011).
2) H. Kenzaki, N. Koga, N. Hori, R. Kanada, W. Li, K. Okazaki, X.-Q. Yao and S. Takada*, *J. Chem. Theory Comput.* **7**, 1979–1989 (2011).
3) N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, *Nature* **491**, 222–227 (2012).
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).

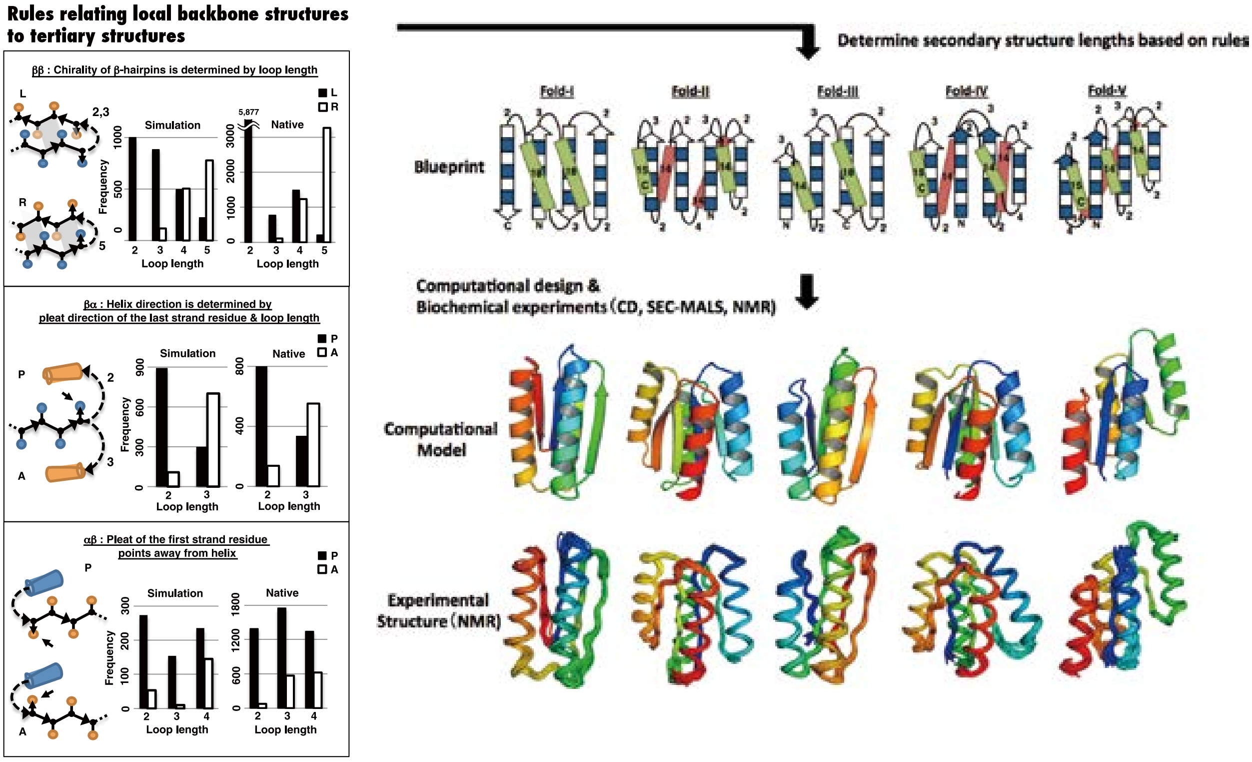

Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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

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Education

2008	D.Sc. Kyoto University

Professional Employment

2006	JPSP Research Fellow, Kyoto University
2008	JPSP Postdoctoral Fellow for Research Abroad, University of California, Berkeley
2010	Postdoctoral Fellow, Lawrence Berkeley National Laboratory
2012	Research Associate Professor, Institute for Molecular Science
2013	Fellow 2012–2013, Wissenschaftskolleg zu Berlin

Member
Post-Doctoral Fellow
FUJIHASHI, Yuta
Secretary
YAMADA, Mariko

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

Photosynthesis provides the energy source for essentially all living things on Earth, and its functionality has been one of the most fascinating mysteries of life. Photosynthetic conversion of the energy of sunlight into its chemical form suitable for cellular processes involves a variety of physicochemical mechanisms. The conversion starts with the absorption of a photon of sunlight by one of the light-harvesting pigments, followed by transfer of electronic excitation energy to the reaction center, where charge separation is initiated. At low light intensities, surprisingly, the quantum efficiency of the transfer is near unity. A longstanding question in photosynthesis has been the following: How does light harvesting deliver such high efficiency in the presence of disordered and fluctuating dissipative environments? Why does not energy get lost? At high light intensities, on the other hand, the reaction center is protected by regulation mechanisms that lead to quenching of excess excitation energy in light harvesting proteins. The precise mechanisms of these initial steps of photosynthesis are not yet fully elucidated from the standpoint of molecular science. Particularly, recent observations of long-lived beating phenomena in two-dimensional electronic spectra of photosynthetic pigment-protein complexes stimulated a huge burst of activity in an interdisciplinary community of molecular science and quantum physics.1)

Selected Publications

- A. Ishizaki and Y. Tanimura, “Quantum Dynamics of System Strongly Coupled to Low-Temperature Colored Noise Bath: Reduced Hierarchy Equations Approach,” *J. Phys. Soc. Jpn.* **74**, 3131–3134 (2005).
- A. Ishizaki and G. R. Fleming, “Unified Treatment of Quantum Coherent and Incoherent Hopping Dynamics in Electronic Energy Transfer: Reduced Hierarchy Equation Approach,” *J. Chem. Phys.* **130**, 234111 (10 pages) (2009).
- A. Ishizaki and G. R. Fleming, “Theoretical Examination of Quantum Coherence in a Photosynthetic System at Physiological Temperature,” *Proc. Natl. Acad. Sci. U.S.A.* **106**, 17255–17260 (2009).
- G. S. Schlau-Cohen, A. Ishizaki, T. R. Calhoun, N. S. Ginsberg, M. Ballottari, R. Bassi and G. R. Fleming, “Elucidation of the Timescales and Origins of Quantum Electronic Coherence in LHCII,” *Nat. Chem.* **4**, 389–395 (2012).
- A. Ishizaki, T. R. Calhoun, G. S. Schlau-Cohen and G. R. Fleming, “Quantum Coherence and Its Interplay with Protein Environments in Photosynthetic Energy Transfer,” *Phys. Chem. Chem. Phys.* **12**, 7319 (2010). [Invited perspective article]
- A. Ishizaki and G. R. Fleming, “Quantum Coherence in Photosynthetic Light Harvesting,” *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]

1. Impact of Environmentally Induced Fluctuations on Quantum Mechanically Mixed Electronic and Vibrational Pigment States in Photosynthetic Energy/Charge Transfer and 2D Electronic Spectra

Recently, nuclear vibrational contribution signatures in two-dimensional (2D) electronic spectroscopy have attracted considerable interest, in particular as regards interpretation of the oscillatory transients observed in light-harvesting complexes. These transients have dephasing times that persist for much longer than theoretically predicted electronic coherence lifetime. As a plausible explanation for this long-lived spectral beating in 2D electronic spectra, quantum-mechanically mixed electronic and vibrational states (vibronic excitons) were proposed by Christensson *et al.* [*J. Phys. Chem. B* **116**, 7449 (2012)] and have since been explored. In this work, we address a dimer that produces little beating of electronic origin in the absence of vibronic contributions, and examine the impact of protein-induced fluctuations upon electronic-vibrational quantum mixtures by calculating the electronic energy transfer dynamics and 2D electronic spectra in a numerically accurate manner. It was found that, at cryogenic temperatures, the electronic-vibrational quantum mixtures are rather robust, even under the influence of the fluctuations and despite the small Huang-Rhys factors of the Franck-Condon active vibrational modes. This results in long-lasting beating behavior of vibrational origin in the 2D electronic spectra. At physiological temperatures, however, the fluctuations eradicate the mixing, and hence, the beating in the 2D spectra disappears. Further, it was demonstrated that such 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 2D electronic spectra, contrary to speculations in recent publications.[1,2)]

The most significant aspect of this work is, of course, clarification of the confusion concerning the long-lived quantum beats observed in 2D electronic spectra of photosynthetic light harvesting systems. However, I would like to emphasize another significance of the work from the viewpoint of fundamental physics. In general, energy eigenstates due to quantum mixing among multiple states are obtained via mathematical diagonalization of Hamiltonians of interest. It should be noted that these are usually independent of any environmental factors such as temperatures and fluctuations, even though one considers quantum systems in condensed phases. Thus, once quantum delocalizatios are introduced "mathematically" (*i.e.* invariable coefficients in a linear combination), they are never destroyed by the environmental factors. However, the reality is not the case.[2)] In order to capture subtle robustness and fragility of quantum mixing under the influence of the fluctuations, we employed the beating amplitudes of the ground state bleaching pathways in 2D nonrephasing spectra "as a measure of the degrees of the quantum mixture between electronic and vibrational pigment states." This successfully visualizes the degrees of the quantum mixture between electronic and vibrational pigment states under the influence of protein-induced fluctuations at different temperatures.

2. Influence of Weak Vibrational-Electronic Couplings on 2D Electronic Spectra and Inter-Site Coherence in Weakly Coupled Photosynthetic Complexes

Coherence oscillations measured in two-dimensional (2D) electronic spectra of pigment-protein complexes may have electronic, vibrational, or mixed-character vibronic origins, which depend on the degree of electronic-vibrational mixing. Oscillations from intra-pigment vibrations can obscure the inter-site coherence lifetime, of interest in elucidating the mechanisms of energy transfer in photosynthetic light-harvesting. Huang-Rhys factors (S) for low-frequency vibrations in Chlorophyll and Bacteriochlorophyll are quite small ($S \leq 0.05$), so it is often assumed that these vibrations influence neither 2D spectra nor inter-site coherence dynamics. In this work, we explore the influence of S within this range on the oscillatory signatures in simulated 2D spectra of a pigment heterodimer. To visualize the inter-site coherence dynamics underlying the 2D spectra, we introduce a formalism which we call the "site-probe response." By comparing the calculated 2D spectra with the site-probe response, we show that an on-resonance vibration with Huang-Rhys factor as small as $S = 0.005$ and the most strongly coupled off-resonance vibrations ($S = 0.05$) give rise to long-lived, purely vibrational coherences at 77 K. We moreover calculate the correlation between optical pump interactions and subsequent entanglement between sites, as measured by the concurrence. Long-lived inter-site coherence and site entanglement increase with S at 77 K, and this dependence all but vanishes at physiological temperature, as environmentally-induced fluctuations destroy the vibronic mixing.[4,5)]

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Visualization of Quantum Dynamical Nature Utilized Quantum Measurements

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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.

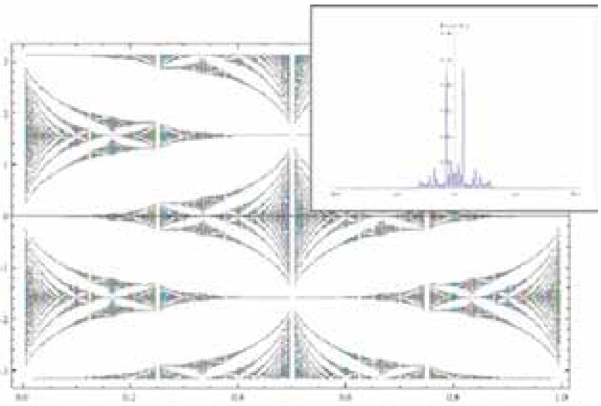

Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called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

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- Y. Shikano and A. Hosoya, "Weak Values with Decoherence," *J. Phys. A* **43**, 025304 (15 pages) (2010).
- Y. Shikano and H. Katsura, "Localization and Fractality in Inhomogeneous Quantum Walks with Self-Duality," *Phys. Rev. E* **83**, 031122 (7 pages) (2010).
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- H. Kobayashi, K. Nonaka and Y. Shikano, "Stereographical Visualization of a Polarization State Using Weak Measurements with an Optical-Vortex Beam," *Phys. Rev. A* **89**, 053816 (5 pages) (2014).

1. Quantum Measurement with Higher-Order Gaussian Modes[1)]

Through the von Neumann interaction followed by post-selection, we can extract not only the eigenvalue of an observable of the measured system but also the weak value. In this post-selected von Neumann measurement, the initial pointer state of the measuring device is assumed to be a fundamental Gaussian wave function. By considering the optical implementation of the post-selected von Neumann measurement, higher-order Gaussian modes can be used. In this paper, we consider the Hermite–Gaussian (HG) and Laguerre–Gaussian (LG) modes as pointer states and calculate the average shift of the pointer states of the post-selected von Neumann measurement by assuming the system observable A with $A^2 = I$ and $A^2 = A$ for an arbitrary interaction strength, where I represents the identity operator. Our results show that the HG and LG pointer states for a given coupling direction have advantages and disadvantages over the fundamental Gaussian mode in improving the signal-to-noise ratio (SNR). We expect that our general treatment of the weak values will be helpful for understanding the connection between weak- and strong-measurement regimes and may be used to propose new experimental setups with higher-order Gaussian beams to investigate further the applications of weak measurement in optical systems such as the optical vortex.

2. Quantum Measurement with Squeezing Technique[2)]

We investigate, within the weak measurement theory, the advantages of non-classical pointer states over semi-classical ones for coherent, squeezed vacuum, and Schroedinger cat states. These states are utilized as pointer state for the system operator A with property $A^2 = I$, where I represents the identity operator. We calculate the ratio between the signal-to-noise ratio (SNR) of non-post-selected and post-selected weak measurements. The latter is used to find the quantum Fisher information for the above pointer states. The average shifts for those pointer states with arbitrary interaction strength are investigated in detail. One key result is that we find the post-selected weak measurement scheme for non-classical pointer states to be superior to semi-classical ones. This can improve the precision of measurement process.

3. Single-Photon Nonlinearity Amplification by Post-Selection[3)]

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

4. Discrete-Time Quantum Walk as Quantum Dynamical Simulator[4,5)]

Discrete-time quantum walks can be regarded as quantum dynamical simulators since they can simulate spatially discretized Schroedinger, massive Dirac, and Klein-Gordon equations. Here, two different types of Fibonacci discrete-time quantum walks are studied analytically. The first is the Fibonacci coin sequence with a generalized Hadamard coin and demonstrates six-step periodic dynamics. The other model is assumed to have three- or six-step periodic dynamics with the Fibonacci sequence. We analytically show that these models have ballistic transportation properties and continuous limits identical to those of the massless Dirac equation with coin basis change.

5. NMR Sensitivity Improvement by Composite Pulse[6)]

ConCatenated Composite Pulses (CCCPs) are derived from various composite pulses widely employed in NMR and have been developed as high-precision unitary operations in Quantum Information Processing (QIP). CCCPs are robust against two systematic errors, pulse-length and off-resonance errors, in NMR simultaneously. We show experiments that demonstrate CCCPs are powerful and versatile tools not only in QIP but also in NMR measurements.

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

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Keywords Solid State Ionics, Oxyhydride, Battery

Chemical energy conversion/storage using electrochemical devices such as fuel cells and batteries will become increasingly important for future sustainable societies. 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.

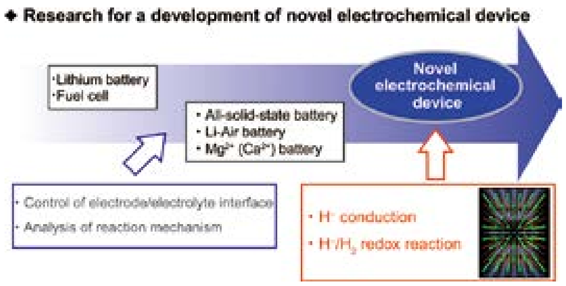

Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

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- G. Kobayashi, S.-I. Nishimura, M.-S. Park, R. Kanno, M. Yashima, T. Ida and A. Yamada, "Isolation of Solid Solution Phases in Size-Controlled Li_xFePO_4 at Room Temperature," *Adv. Funct. Mater.* **19**, 395–403 (2009).
- G. Kobayashi, A. Yamada, S.-I. Nishimura, R. Kanno, Y. Kobayashi, S. Seki, Y. Ohno and H. Miyashiro, *J. Power Sources* **189**, 397–401 (2009).
- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, I. Tanaka and R. Kanno, under revision (2015).
- G. Kobayashi, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).

1. Synthesis of H⁻ Conductive Oxyhydrides[1)]

Indeed, H^- conduction is particularly attractive for electrochemical devices such as fuel cells and batteries, because H^- has an ionic radius suitable for fast ion conduction and a strong reducing ability. The standard redox potential of H^-/H_2 (–2.3 V) is comparable with that of Mg/Mg^{2+} (–2.4 V); thus, effective utilization of the H^- conduction phenomenon and the H^-/H_2 redox reaction may be promising for application in new energy storage/conversion devices with high energy densities.

Here, we succeeded in the synthesis of a novel oxyhydride ($La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$) with a wide composition range and provide the first conclusive evidence of a pure H^- conduction phenomenon in oxide-based materials (Figure 2). Furthermore, the capability of this oxyhydride as a solid electrolyte was confirmed by discharging reaction of the all-solid-state H^- cell. H^- conductors are the new frontier materials in the research field of solid-state ionics and electrochemistry. We anticipate that our results provide a completely novel approach for the effective use of hydrogen in a range of devices.

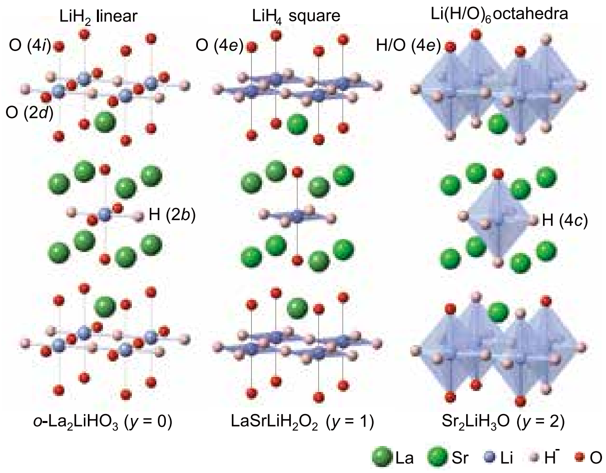

Figure 2. Crystal structures of $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0$, 1, 2). Lanthanum (and strontium) ions occupy the *A* sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the *B* site that are octahedrally coordinated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

2. High-Performance of Li-Rich Layered Cathode Materials through Combination of A₂O₃-Based Surface Modification and Stepwise Pre-Cycling[2)]

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

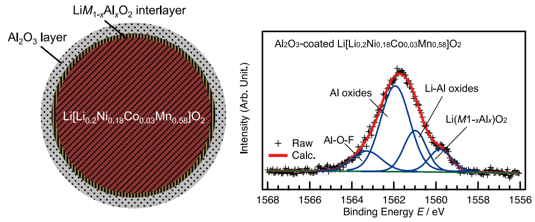

Figure 3. Schematic illustration and Al 1*s* HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

References

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

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Open up Future Electronics by Organic Molecules

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

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

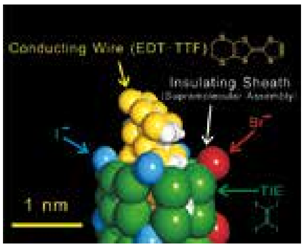

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- 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).
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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 SiO$_2$/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 SrTiO$_3$ is used as a back-gate substrate because of its larger thermal expansion coefficient (*ca.* 10 ppm/K) than Si. An aluminum oxide layer was grown by atomic layer deposition technique to form a gate dielectric on the substrate to form a FET device structure. 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 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.

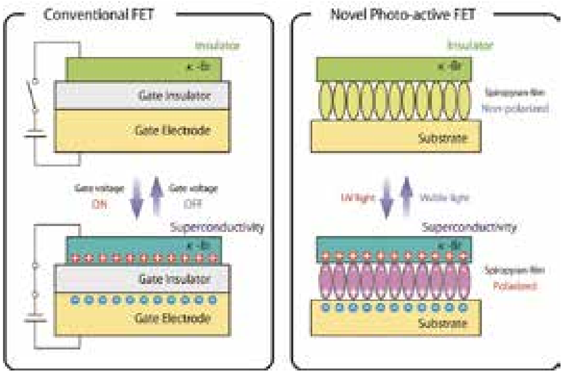

Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).

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 cm^2/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 cm^2/Vs. This high response of the device can be attributed to an increase of superconducting fraction at application of gate voltage. In order to examine the above hypothesis, we have applied a magnetic field up to 7 T. Indeed, the field-effect has been considerably suppressed because the superconducting phases are destroyed by the magnetic field. This electric-field-induced superconductivity seems to originate from a decrease of Coulomb repulsion among carriers by electrostatic doping effect.

(BEDT-TTF = bis(ethyelenedithio)tetrathiafulvalene)

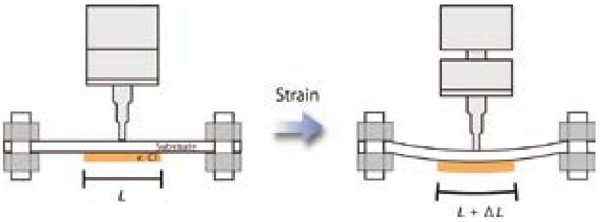

Figure 3. Side-view schematic for flexible organic Mott-FET device.

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2003 JSPS Fellow for Research Abroad, Massachusetts Institute of Technology
2005 JST-PRESTO Researcher
2007 Associate Professor, Osaka University
2010 JST-PRESTO Researcher
2012 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2015 Professor, Tokyo Institute of Technology

Awards
2007 The Chemical Society of Japan (CSJ) Award for Young Chemists
2007 The Japan Society of Coordination Chemistry (JSCC) Award for Young Chemists
2008 The Young Scientists' Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, and Technology, Japan
2010 Dalton Lectureship Award, Royal Society of Chemistry

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ISHIKAWA, Yuki
MASAI, Kohei
TERAMOTO, Masahiro
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Keywords Coordination Chemistry, Organometallic Chemistry, Mechanism of Catalysis

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

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

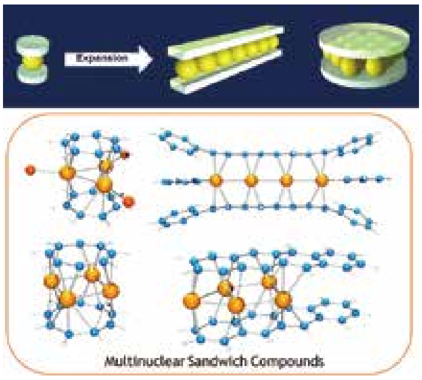

Figure 1. The concept of dimensionally extended sandwich structures and some examples of the multinuclear sandwich complexes.

Selected Publications

- T. Murahashi, T. Uemura and H. Kurosawa, "Perylene Tetrapalladium Sandwich Complexes," *J. Am. Chem. Soc.* **125**, 8436–8437 (2003).
- T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki and H. Kurosawa "Discrete Sandwich Compounds of Monolayer Palladium Sheets," *Science* **313**, 1104–1107 (2006).
- T. Murahashi, R. Inoue, K. Usui and S. Ogoshi, "Square Tetrapalladium Sheet Sandwich Complexes: Cyclononatetraenyl as a Versatile Face-Capping Ligand," *J. Am. Chem. Soc.* **131**, 9888–9889 (2009).
- T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi and H. Kurosawa, "Redox-Induced Reversible Metal Assembly through Translocation and Reversible Ligand Coupling in Tetranuclear Metal Sandwich Frameworks," *Nat. Chem.* **4**, 52–58 (2012).

1. Chemistry of Multinuclear Sandwich Complexes

Synthesis and Structural Elucidation of the Carotene Metal Chain Sandwich Complexes: $[\mathrm{Pd}_{10}(\beta\text{-carotene})_2][\mathrm{B(Ar^F)_4}]_2$ 1)

Carotenoids are naturally abundant pigments containing extended π-conjugated C=C double bond arrays. While the fascinating physical and chemical properties of carotenoids have been explored, their metal binding ability has been undeveloped. We found the remarkable multinuclear metal binding ability of β-carotene, through synthesis and characterization of bis-(β-carotene) decanuclear metal chain complexes.

It has been proven that bis-β-carotene π-framework can accommodate ten-Pd-atoms-array through remarkable multidentate bridging π-coordination. The decanuclear palladium complex $[\mathrm{Pd}_{10}(\mu_{10}\text{-}\beta\text{-carotene})_2][\mathrm{B(Ar^F)_4}]_2$ (**1**, $\mathrm{B(Ar^F)_4} = \mathrm{B(3,5\text{-}(CF_3)_2C_6H_3)_4}$) was synthesized by the redox-condensation reaction of $[\mathrm{Pd_2(CH_3CN)_6}][\mathrm{BF_4}]_2$ and excess $\mathrm{Pd_2(dba)_3 \cdot C_6H_6}$ in the presence of β-carotene at 60 °C (Figure 2). The molecular structures of the two isomers **1-meso** and **1-rac** were determined by X-ray crystallographic analysis (Figure 2). The decanuclear complexes **1-meso** and **1-rac** are the soluble and isolable organometallic clusters having a long metal chain.

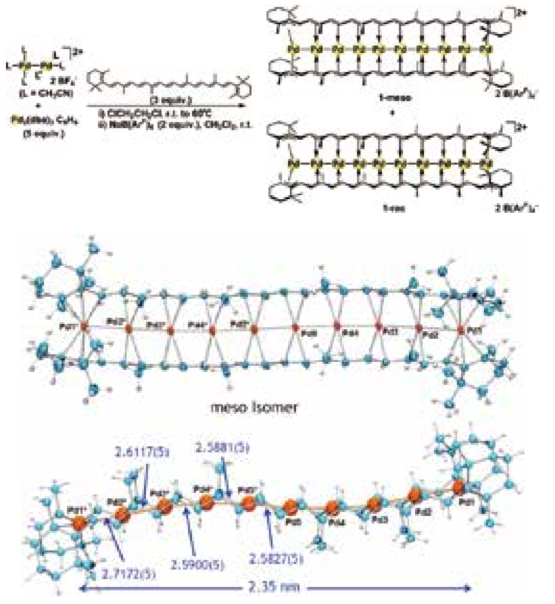

Figure 2. Synthesis of bis-carotene Pd_{10} chain complexes, and X-ray structure of the meso-isomer.

The metallo-carotene framework showed interesting multinuclear metalation-demetalation reactivity, allowing us to construct heterobimetallic decanuclear chain. The metal-deficient sandwich complex, $[\mathrm{Pd}_5(\beta\text{-carotene})_2][\mathrm{B(Ar^F)_4}]_2$ (**2-meso**) or $[\mathrm{Pd}_7(\beta\text{-carotene})_2][\mathrm{B(Ar^F)_4}]_2$ (**3-meso**), was obtained as a single product by demetalation from **1-meso** with CO in certain reaction conditions. Then metal-refilling with Pt^0 afforded the bimetallic $\mathrm{Pd_5Pt_3}$ chain complex $[\mathrm{Pd_5Pt_3}(\beta\text{-carotene})_2][\mathrm{B(Ar^F)_4}]_2$ (**4-meso**). Subsequent metalation of **4-meso** with Pd^0 gave decanuclear bimetallic chain complex $[\mathrm{Pd_5Pt_3Pd_2}(\beta\text{-carotene})_2][\mathrm{B(Ar^F)_4}]_2$ (**5-meso**) having alternative metal arrangement (Figure 3).

This work showed that natural extended π-conjugated unsaturated hydrocarbons can be utilized as the multi-dentate π-scaffolds for the construction of giant metal clusters.

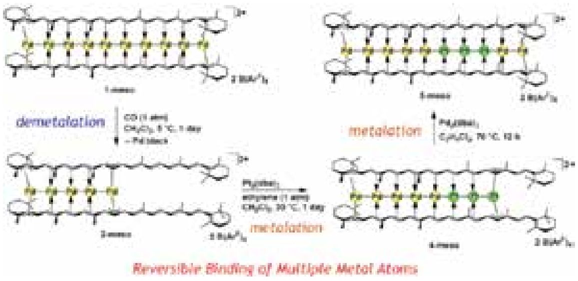

Figure 3. Demetalation-metalation sequence of metallo-carotene framework.

2. Reaction Mechanism of Highly Reactive Metal Complexes

Modulation of Cluster Binding Sites by the Backside-Ligand Effect2)

One of our main interests is in the elucidation of the reaction patterns and mechanisms of highly reactive transition metal complexes in relevance to catalysis. We developed a method to modulate the trinuclear cluster binding site by the backside-ligand effect. We found that the backside cyclooctatetraene (COT) ligand of the Pd_3 clusters significantly enhances the benzene binding ability at the Pd_3 cluster site, leading to the first μ_3-benzene-Pd_3 clusters which are stable in solution (Figure 4). Theoretical analysis supported the electronic stabilization effect of the backside COT ligand. The naphthalene binding by Pd_4 clusters was also attained by using a Pd_4 sheet bearing the backside COT ligand. These new aspects might represent a promising backside-ligand-modulation strategy to control the reactivity of metal clusters.

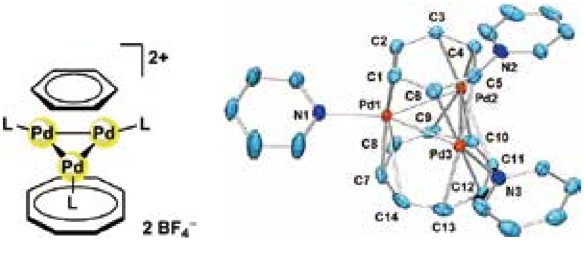

Figure 4. The first solution-stable μ_3-benzene Pd_3 cluster and its X-ray structure.

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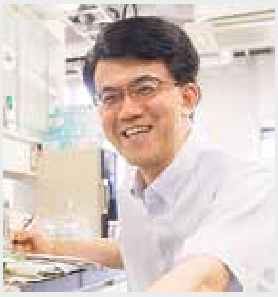
1) S. Horiuchi, Y. Tachibana, M. Yamashita, K. Yamamoto, K. Masai, K. Takase, T. Matsutani, S. Kawamata, Y. Kurashige, T. Yanai and T. Murahashi, *Nat. Commun.* **6**, 6742 (2015).
2) Y. Ishikawa, S. Kimura, K. Takase, K. Yamamoto, Y. Kurashige, T. Yanai and T. Murahashi, *Angew. Chem., Int. Ed.* **54**, 2482–2486 (2015).

Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



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Education

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1992 Ph.D. University of California, Santa Barbara

Professional Employment

1992 Assistant Professor, Institute for Molecular Science
1998 Associate Professor, Institute for Molecular Science
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WATANABE, Yoko

Keywords Organic Synthesis, Graphene Molecule, Organic Semiconductor

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

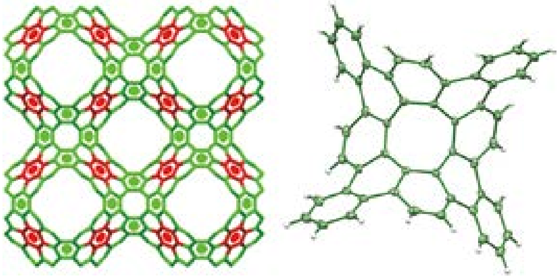

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato and S. Tokito, "Perfluoropentacene: High-Performance p-n Junctions and Complementary Circuits with Pentacene," *J. Am. Chem. Soc.* **126**, 8138–8140 (2004).
- T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki and S. Yamago, "Selective and Random Syntheses of [*n*]Cycloparaphenylenes (*n* = 8–13) and Size Dependence of their Electronic Properties," *J. Am. Chem. Soc.* **133**, 8354–8361 (2011).
- Y. Sakamoto and T. Suzuki, "Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene," *J. Am. Chem. Soc.* **135**, 14074–14077 (2013).

1. Interface Dipole and Growth Mode of Partially and Fully Fluorinated Rubrene on Au(111) and Ag(111)[1]

Thin films of fully and partially fluorinated rubrene deposited on Au(111) and Ag(111) were investigated using ultraviolet and X-ray photoelectron spectroscopy. We demonstrate that fluorination of the molecules is an efficient way for tuning the metal–organic interface dipole and the hole injection barrier. Moreover, the results indicate that the pronounced electrostatic dipole moment of partially fluorinated rubrene (F14-RUB) has a strong impact on the growth mode of these molecules. Most notably, we infer that the first layer of F14-RUB on Au(111) and Ag(111) is formed by molecules with alternating orientation of their dipole moments whereas the second layer shows a nearly uniform orientation.

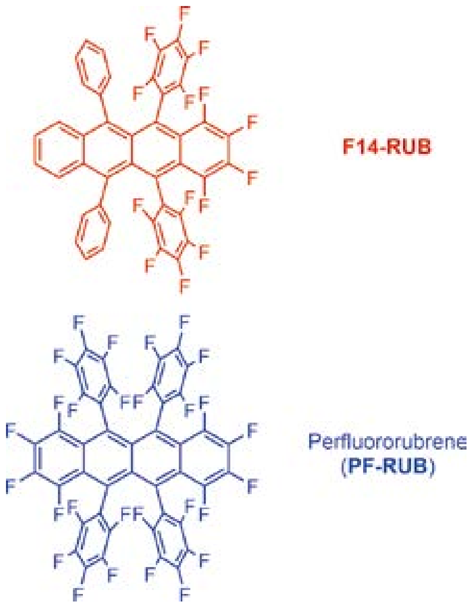

Figure 2. Chemical structures of partially and fully fluorinated rubrene.

2. Tetracyclo(2,7-carbazole)s: Aromaticity in Cycloparaphenylenes

The aromaticity of fullerenes and carbon nanotubes (CNTs) is the key to understand their thermal stability. The total of aromatic (diamagnetic) and antiaromatic (paramagnetic) ring currents can be estimated by the NMR magnetic shielding. In the case of C_{60}, some endohedral derivatives containing atoms (He and Xe) or small molecules (H_2 and H_2O) have been prepared, and their NMR spectra were obtained in solution. For example, the ^1H NMR spectrum of $H_2@C_{60}$ showed a singlet at –1.44 ppm, which was shifted by –5.98 ppm compared to free hydrogen in the same solvent. [*n*]Cycloparaphenylenes (CPPs) are the shortest models for armchair (*n*,*n*) CNTs. The NMR shielding at the ring center would be a good indicator to see the aromaticity of CPPs. Unlike fullerenes, it is difficult to keep atoms or small molecules within CPP rings. Therefore, it is necessary to design a CPP derivative with covalently bonded groups near the ring center. For this purpose, we have synthesized three *N*-substituted tetracyclo(2,7-carbazole)s, which are the derivatives of [8]CPP. Carbazole compounds are also interesting as p-type semiconductors and thermally activated delayed fluorescent materials.

Reference

1) F. Anger, H. Glowatzki, A. Franco-Cañellas, C. Bürker, A. Gerlach, R. Scholz, Y. Sakamoto, T. Suzuki, N. Koch and F. Schreiber, *J. Phys. Chem. C* **119**, 6769–6776 (2015).

Three-Dimensional π-Electron Molecules

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems

HIGASHIBAYASHI, Shuhei
Assistant Professor

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

Member
Post-Doctoral Fellow
PANDIT, Palash
YAMAMOTO, Koji

1. Acid/Base-Responsive Helicenes

We discovered a new phenomenon that N–N linked helical bicarbazole (BC) and tetramethylbiacridine (TBA) derivatives undergo reversible electron transfer disproportionation by acid/base stimuli with contrast photophysical and magnetic properties.[1] The reaction goes through an acid-triggered homolytic N–N bond cleavage reaction of BC or TBA.

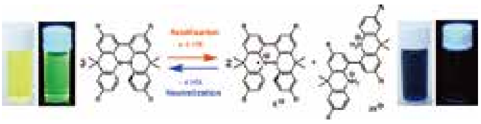

Figure 1. Acid/base-regulated electron transfer disproportionation.

2. Thermal Dynamics of Buckybowls

Buckybowls, bowl-shaped aromatic compounds, have a unique thermal dynamic behavior, *i.e.* bowl inversion. Thermal dynamics of a buckybowl dimer, bisumanenyl, was studied and elucidated by combination of NMR experiment and DFT calculation.[2]

References

1) P. Pandit, K. Yamamoto, T. Nakamura, K. Nishimura, Y. Kurashige, T. Yanai, G. Nakamura, S. Masaoka, K. Furukawa, Y. Yakiyama, M. Kawano and S. Higashibayashi, *Chem. Sci.* **6**, 4160–4173 (2015).
2) B. B. Shrestha, S. Karanjit, S. Higashibayashi, T. Amaya, T. Hirao and H. Sakurai, *Asian J. Org. Chem.* **4**, 62–68 (2015).