



RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

The objective of the Department is understanding and prediction of static and dynamic properties, reactions, and functions in condensed phase including nanomaterials and biomolecular systems by developing novel theories and computational methods based on quantum mechanics, statistical mechanics, and solid state physics. The Department collaborates with Research Center for Computational Science on researches.

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

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



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Education

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Professional Employment

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2005 Professor, Institute for Molecular Science
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Keywords Reactions, Functions, Fluctuations

Many-body molecular systems, such as liquids and biomolecular systems, take disordered conformations, and show heterogeneous dynamics, due to complicated molecular interactions. Furthermore, various reactions and biological functions occur in these kinds of systems. Therefore, understanding of the complicated structures and dynamics is essential for the elucidation of the reactions and functions in the systems.

Multidimensional nonlinear spectroscopy can provide detailed information on dynamics that can not be obtained from conventional IR or Raman spectroscopy. We have developed computational methods of multidimensional nonlinear spectroscopy. As a result, we have revealed the molecular origin of the ultrafast energy relaxations and heterogeneous fluctuations in water based on theoretical two-dimensional (2D) IR spectra.

We have also explored the spatiotemporal heterogeneous dynamics in supercooled liquids referred to as the dynamic heterogeneity. Especially, we have examined the lifetime of dynamic heterogeneity by using the three-time correlation function of density fluctuation, and elucidated the relationship between the lifetime and fragility.

In addition, we have been examining the molecular origin of anomalous properties of water. By performing extensive molecular dynamics simulations, we find that structural and dynamical instabilities of water are hidden in the experimentally inaccessible region between 235 K and 150 K. We also

find a crucial role of specific three-coordinated defects in the structural relaxation and glass transition temperature. Now, we investigate how slow but persistent structural relaxations proceed at a very low temperatures to understand the freezing of motions toward the glass transition.

The heterogeneous conformational fluctuations/dynamics are also found in biomolecular systems. It is considered that such conformational dynamics are essential for biological functions. We examine the molecular mechanisms of biological functions, i.e., the efficient excitation energy transfer in photosynthetic proteins and the robust circadian rhythm in clock protein KaiC. In addition, we investigate dynamic effects of enzymatic reactions, and explore conformational change dynamics of proteins at the molecular level by using stochastic theory.

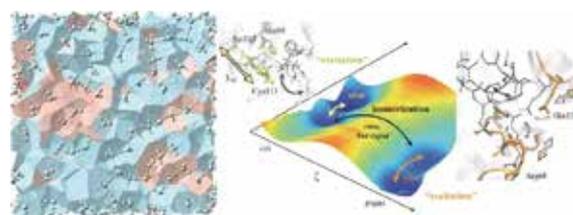


Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

Selected Publications

- T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013).
- T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019). (Perspective)
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018).
- J. Ono, S. Takada and S. Saito, *J. Chem. Phys. (Special Topic on Multidimensional Spectroscopy)* **142**, 212404 (13 pages) (2015).
- T. Mori and S. Saito, *J. Phys. Chem. Lett.* **10**, 474–480 (2019).

1. Thermodynamic Picture of Vitrification of Water through Complex Specific Heat and Entropy: A Journey through ‘No Man’s Land’¹⁾

We investigate thermodynamic properties of supercooled water across the “no man’s land” onto the formation of amorphous ice. The calculations are aided by very long computer simulations, often more than 50 μs long, with the TIP4P/2005 model potential. Density fluctuations that arise from the proximity to a putative liquid-liquid (LL) transition at 228 K, cast a long shadow on the properties of water, both above and below the LL transition. We carry out the calculations of the quantum mechanical static and frequency-dependent specific heats by combining seminal studies of Lebowitz, Percus, and Verlet and Grest and Nagel with the harmonic approximation for the density of states. The obtained values are in quantitative agreement with all available experimental and numerical results of specific heats for both supercooled water and ice. We calculate the entropy at all the state points by integrating the specific heat. We find that the quantum corrected-contributions of intermolecular vibrational entropy dominate the excess entropy of amorphous phases over the crystal over a wide range of temperatures. Interestingly, the vibrational entropy lowers the Kauzmann temperature, T_K , to 130 K, just below the experimental glass-to-liquid water transition temperature, T_g , of 136 K and the calculated T_g of 135 K in our previous study. A straightforward extrapolation of high temperature entropy from 250 K to below however would give a much higher value of $T_K \sim 190$ K.

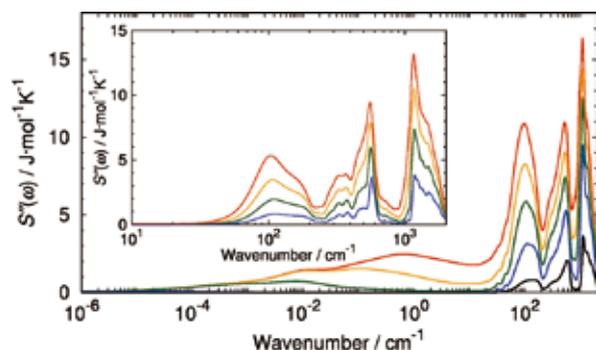


Figure 2. Imaginary part of complex entropy of (liquid, supercooled, and amorphous) water at 300 (red), 250 (orange), 220 (green), 180 (blue), and 100 (black) K. The inset shows those at 250 (red), 200 (orange), 150 (green), and 100 (blue) K of ice Ih.

2. Theory of Coherent Two-Dimensional Vibrational Spectroscopy²⁾

Two-dimensional (2D) vibrational spectroscopy has emerged as one of the most important experimental techniques useful to study the molecular structure and dynamics in con-

densed phases. Theory and computation have also played essential and integral roles in its development through the nonlinear optical response theory and computational methods such as molecular dynamics (MD) simulations and electronic structure calculations. In this article, we present the fundamental theory of coherent 2D vibrational spectroscopy and describe computational approaches to simulate the 2D vibrational spectra. The classical approximation to the quantum mechanical nonlinear response function is invoked from the outset. It is shown that the third-order response function can be evaluated in that classical limit by using equilibrium or non-equilibrium MD simulation trajectories. Another simulation method is based on the assumptions that the molecular vibrations can still be described quantum mechanically and that the relevant molecular response functions are evaluated by the numerical integration of the Schrödinger equation. A few application examples are presented to help the researchers in this and related areas to understand the fundamental principles and to use these methods for their studies with 2D vibrational spectroscopic techniques. In summary, this exposition provides an overview of current theoretical efforts to understand the 2D vibrational spectra and an outlook for future developments.

3. Site-Dependent Fluctuations Optimize Electronic Energy Transfer in the Fenna-Matthews-Olson Protein³⁾

Light absorbed by light-harvesting antennae is transferred to the reaction center (RC). The excitation energy transfer (EET) to the RC is known to proceed with nearly perfect quantum yield. However, understanding of EET is still limited at molecular level. Here, we examine the dynamics in the Fenna–Matthews–Olson (FMO) protein by developing an efficient molecular dynamics simulation that can properly describe the electronic properties of the bacteriochlorophylls. We find that the FMO protein consists of sites with heterogeneous fluctuations extending from fast to slow modulation. We also find that efficient EETs are facilitated by site-dependent fluctuations that enhance the resonance condition between neighboring sites with large site-energy differences and circumvent exciton trapping on the pathway to the RC. Knowledge of site-dependent fluctuations is an important component of understanding optimization of EET in photosynthetic systems.

References

- 1) S. Saito and B. Bagchi, *J. Chem. Phys.* **150**, 054502 (14 pages) (2019). (Featured Article)
- 2) T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019). (Perspective)
- 3) S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B*, in press.

Theoretical Studies on Novel Physical Properties Arising from Many-Body Interaction

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Education

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Professional Employment

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Awards

2008 L'Oréal-UNESCO Japan National Fellowships for Women in Science
2011 Best Poster Award in ISSS-6 Internal Symposium on Surface Science
2017 Young Scientist Award of the Physical Society of Japan
2019 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
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Keywords

Quantum Many-Body Interaction, Density Functional Theory, Quantum Field Theory

Quantum many-body interaction is a source of novel physical properties in the condensed matters. In our group, we develop theoretical methods by combining quantum field theory and density functional theory, and carry out collaborative research with experimental groups. As specific targets, we focus on magnetism in nanostructure and energy dissipation.

For magnetism in nanostructure, we are interested in the Kondo effect and spin-orbit interaction. The Kondo effect arises from the interaction between the localized spin and conduction electrons, which forms a characteristic many-body state so called the Kondo singlet state. The spin-orbit interaction originating from relativistic effect constrains the direction of magnetic moment to specific direction. We investigate the possibility of novel physical phenomena induced by these interactions in the nanostructure and molecules on surfaces.

For energy dissipation, we focus on the effect of electron-phonon interaction. The electron-phonon interaction is one of the most fundamental interactions in the condensed matter

physics, and the quantitative evaluation in realistic materials is highly demanding. We adopt the ab-initio calculation to analyze the signal of electron-phonon coupling in surface spectroscopy and thermal properties in various kind of solids.

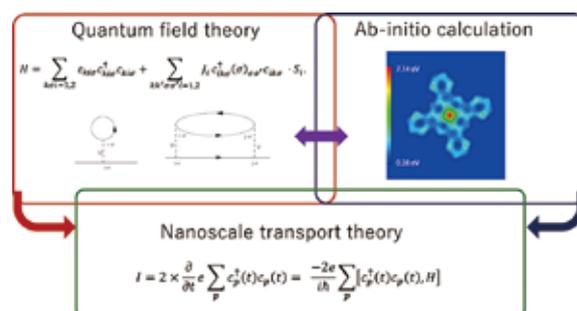


Figure 1. Schematic image of the theoretical method developed in our group.

Selected Publications

- E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi and M. Kawai, "Symmetry-Driven Novel Kondo Effect in a Molecule," *Phys. Rev. Lett.* **109**, 086602 (2012).
- E. Minamitani, R. Arafune, N. Tsukahara, Y. Ohda, S. Watanabe, M. Kawai, H. Ueba and N. Takagi, "Surface Phonon Excitation on Clean Metal Surfaces in Scanning Tunneling Microscopy," *Phys. Rev. B* **93**, 085411 (2016).
- E. Minamitani, N. Takagi and S. Watanabe, "Model Hamiltonian Approach to the Magnetic Anisotropy of Iron Phthalocyanine at

Solid Surfaces," *Phys. Rev. B* **94**, 205402 (2016).

- R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai and N. Takagi, "Single-Molecule Quantum Dot as a Kondo Simulator," *Nat. Commun.* **8**, 16012 (2017).
- E. Minamitani, R. Arafune, T. Frederiksen, T. Suzuki, S. M. F. Shahed, T. Kobayashi, N. Endo, H. Fukidome, S. Watanabe and T. Komeda, "Atomic-Scale Characterization of the Interfacial Phonon in Graphene/SiC," *Phys. Rev. B* **96**, 155431 (2017).

1. Simulating Lattice Thermal Conductivity in Semiconducting Materials Using High-Dimensional Neural Network Potential

Heat generation in semiconducting materials has become a critical problem in modern nanoscale electronics. To design semiconductor materials with better thermal manageability, efficient methods for theoretical simulation of the thermal conductivity are required.

The main carrier of heat in semiconductors is the phonon, which is a quantum of lattice vibration. Current methods of simulating lattice thermal conductivity require accurate prediction of the interatomic force in the solid. Density functional theory (DFT) calculation is one of the most well-established techniques for accurate force prediction, including the effect of changes in the electronic state with atomic displacement. However, the high computational cost limits the application of DFT calculation in thermal conductivity simulations.

We focus on the application of machine learning techniques for thermal conductivity simulations.¹⁾ Among various machine learning techniques, we chose the high-dimensional neural network potential (HDNNP) developed by Behler *et al.*^{2,3)} HDNNP can describe the relation between the total energy of a system and its atomic arrangement. The force acting on atoms can also be described by the HDNNP as shown in several previous studies, however, the accuracy of the prediction is limited. We showed that much higher accuracy can be obtained by training HDNNP parameters with a focus on force fitting. We chose crystalline Si and GaN as representative semiconducting materials with one and two atom types, respectively.

Figure 2 shows the compare the forces in the Si and GaN systems predicted by DFT and HDNNP. The root mean square error (RMSE) between force prediction from HDNNP and DFT calculation results was 25.5 meV/Å for Si and 37.8 meV/Å for GaN.

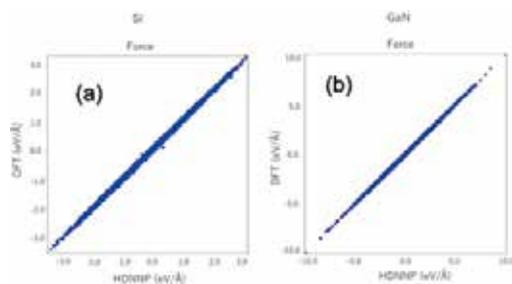


Figure 2. Comparison of interatomic forces in (a) Si and (b) GaN bulk crystals obtained by HDNNP and DFT calculations.

The phonon dispersion curves obtained using HDNNP agree well with the DFT calculation results and previous reports for both Si and GaN,^{4,5)} as shown in Figure 3. Then, we simulated the lattice thermal conductivity based on ALD

by combining HDNNP and phonopy package.⁶⁾ Figure 4 shows a comparison of the temperature dependence of the thermal conductivity obtained from the force predictions of HDNNP and VASP calculations. The deviation from the DFT calculation results is within 1% at 200 to 500 K for Si and within 5.4% from 200 to 1000 K for GaN.

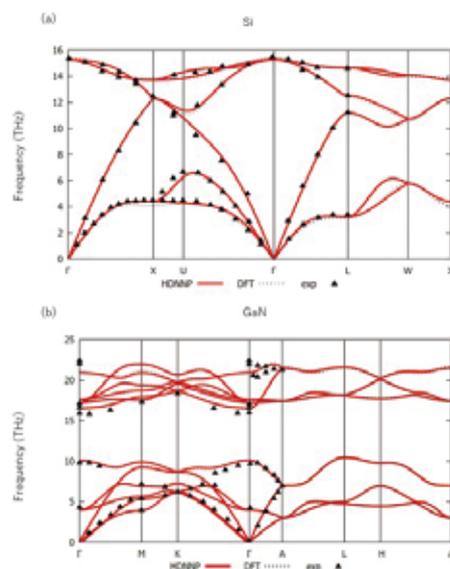


Figure 3. Comparison of phonon dispersions in (a) Si and (b) GaN obtained by HDNNP and DFT calculations. The experimental data for comparison were obtained from Ref. 4 for Si and Ref. 5 for GaN.

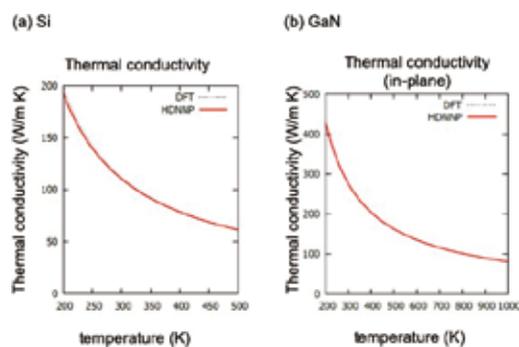


Figure 4. Comparison of thermal conductivities in (a) Si, (b) along the in-plane (100) direction in GaN obtained by HDNNP and DFT calculations.

References

- 1) E. Minamitani, M. Ogura and S. Watanabe, *Appl. Phys. Express*, in press.
- 2) J. Behler and M. Parrinello, *Phys. Rev. Lett.* **98**, 146401 (2007).
- 3) J. Behler, *Angew. Chem., Int. Ed.* **56**, 12828 (2017).
- 4) A. Ward and D. A. Broido, *Phys. Rev. B* **81**, 085205 (2010).
- 5) T. Ruf *et al.*, *Phys. Rev. Lett.* **86**, 906 (2001).
- 6) A. Togo, L. Chaput and I. Tanaka, *Phys. Rev. B* **91**, 094306 (2015).

Award

MINAMITANI, Emi; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize (2019).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Awards

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Keywords

Quantum Dissipative Systems in Complex Molecular Systems, Quantum Optics, Light-Matter Interaction

Quantum dynamic phenomena are ubiquitous in molecular processes, and yet remain a challenge for experimental and theoretical investigations. On the experimental side, it has become possible to explore molecules on a time scale down to a few femtoseconds. This progress in ultrafast spectroscopy has opened up real-time observation of dynamic processes in complex chemical and biological systems and has provided a strong impetus to theoretical studies of condensed phase quantum dynamics.

Essentially, any quantum systems can never be regarded as “isolated systems.” Quantum systems are always in contact with “the outside world,” and hence their quantum natures are sometimes sustained and sometimes destroyed. In condensed phase molecular systems, especially, quantum systems are affected by the huge amount of dynamic degrees of freedom such as solvent molecules, amino acid residues in proteins, and so forth. Balance between robustness and fragility of the quantum natures may dramatically alter behaviors of chemical dynamics and spectroscopic signals. Therefore, theoretical

tools to adequately describe (1) dynamical behaviors of quantum systems affected by the huge amount of dynamic degrees of freedom and (2) the interaction with radiation fields should be developed.

For this purpose, our research group has been tackling the following subjects:

- (1) Developments of condensed phase quantum dynamic theories
- (2) Quantum theories to describe dynamical and transport processes in materials and biological systems
- (3) Theoretical investigations on measurement and control with the use of atomic-molecular-optical (AMO) physics approaches.

In recent years, specifically, special attention is devoted to the subject (3). We have been examining whether ideas and concepts in the field of quantum science and technology would provide novel control knobs that supplement classical parameters in conventional spectroscopic tools such as frequencies and time delays.

Selected Publications

- A. Ishizaki, T. R. Calhoun, G. S. Schlau-Cohen and G. R. Fleming, “Quantum Coherence and Its Interplay with Protein Environments in Photosynthetic Energy Transfer,” *Phys. Chem. Chem. Phys.* **12**, 7319 (2010). [Invited perspective article]
- A. Ishizaki and G. R. Fleming, “Quantum Coherence in Photosynthetic Light Harvesting,” *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes *et al.*, “Using Coherence to Enhance Function in Chemical and Biophysical Systems,” *Nature* **543**, 647–656 (2017).
- T. P. Nguyen and A. Ishizaki, “Control of Excitation Energy

Transfer in Condensed Phase Molecular Systems by Floquet Engineering,” *J. Phys. Chem. Lett.* **9**, 1243 (2018).

- Y. Fujihashi, M. Higashi and A. Ishizaki, “Intramolecular Vibrations Complement the Robustness of Primary Charge Separation in a Dimer Model of the Photosystem II Reaction Center,” *J. Phys. Chem. Lett.* **9**, 4921 (2018).
- A. Kato and A. Ishizaki, “Non-Markovian Quantum-Classical Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases,” *Phys. Rev. Lett.* **121**, 647 (2018).

1. Quantum Dynamics Investigation on Chiral-Induced Spin Selectivity in Helical Molecules

Charge transfer processes in DNA have attracted considerable attention over several decades in relation with its possible role to the long-range oxidative damage of DNA. In recent years, however, a new dimension has been brought to this research field. Naaman and coworkers revealed that electrons transmitted through a double-stranded DNA molecule exhibited a preferred spin polarization at room temperature [*Science* **331**, 894 (2011)]. Similar effects were found in various chiral molecules. This effect is currently referred to as chirality induced spin selectivity. Such organic helical molecules are non-magnetic; nevertheless, they can serve as highly efficient spin filters. In this regard, chiral molecules are expected to open a new avenue in molecular spintronics.

In this work, we developed a theoretical framework to investigate quantum dynamics of spinful electrons in a helical molecule under the influence of both the spin-orbit interaction and the surrounding environment. In the literature, the Landauer theory has offered a way to calculate spin-dependent charge current under the assumption that electrons propagated freely across a conductor. Therefore, we focused on the quantum master equation approach. Furthermore, the geometric phase associated with the spin-orbit interaction has been analyzed, and it has been revealed that impacts of the phase upon the spin dynamics depends on individual paths.¹⁾

2. Generation of Pseudo-Sunlight via Quantum Entangled Photon Pairs and the Interaction with Molecular Systems

Light incident upon molecules trigger fundamental processes in diverse systems present in nature. However, under natural conditions such as sunlight illumination, it is impossible to assign known times for photon arrival owing to continuous pumping, and therefore, the photo-induced processes cannot be easily investigated. In time-resolved optical spectroscopy, in contrast, investigations on the processes can be conducted by synchronizing the initial excitations in the entire ensemble with pulsed laser and thereby amplifying the microscopic dynamics in a constructively interferential fashion. Hence, whether dynamics initiated by sunlight irradiation might be different from those detected with laser spectroscopy is still being debated.

In this work, we addressed quantum entangled photon pairs generated with the parametric down-conversion (PDC) in birefringent crystals. The photon number statistics obeys the geometric distribution rather than the Poisson distribution, and therefore, the entangled photons are expected to reproduce characteristics of the sunlight photons. Furthermore, it becomes possible to investigate photo-induced dynamical processes with quantitative underpinnings, because expressions of quantum states of the pseudo-sunlight photons can be theoretically obtained. We showed that the average photon number of the sunlight in a specific frequency spectrum, e.g., the visible light, can be reconstructed by adjusting the PDC crystal length and pump frequency, and thereby molecular dynamics induced by

the pseudo-sunlight can be investigated. The entanglement time, which is the hallmark of quantum entangled photons, can serve as a control knob to resolve the photon arrival times under the pseudo-sunlight irradiation, enabling investigations on real-time dynamics triggered by the pseudo-sunlight photons.²⁾

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

Manipulation of quantum systems is the basis for many promising quantum technologies. However, how quantum mechanical principles can be used to manipulate the dynamics of quantum dissipative systems remains unanswered because of strong decoherence effects arising from interaction with the surrounding environment. In this work, we demonstrate that electron transfer dynamics in molecular loop structures can be manipulated with the use of Floquet engineering by applying a laser field. Despite strong dephasing, the system's dynamics spontaneously breaks the chiral symmetry of the loop in a controllable fashion, followed by the generation of a robust steady-state electronic current without an external voltage. An exponential scaling law that relates the magnitude of the current to the system-environment coupling strength is revealed numerically. The breaking of chiral symmetry and the consequent controllable unidirectional flow of electrons could be employed to construct functional molecular electronic circuits.³⁾

4. Precise Determination of Excitation Energies in Condensed-Phase Molecular Systems Based on Exciton-Polariton Measurements

The precise determination of the excitation energies in condensed-phase molecular systems is important for understanding system-environment interactions as well as for the prerequisite input data of theoretical models used to study the dynamics of the system. The excitation energies are usually determined by fitting of the measured optical spectra that contain broad and unresolved peaks as a result of the thermally random dynamics of the environment. Herein, we propose a method for precise energy determination by strongly coupling the molecular system to an optical cavity and measuring the energy of the resulting polariton. The effect of thermal fluctuations induced by the environment on the polariton is also investigated, from which a power scaling law relating the polariton's linewidth to the number of molecules is obtained. The power exponent gives important information about the environmental dynamics.⁴⁾

References

- 1) A. Kato, T. Ikeda and A. Ishizaki, in preparation.
- 2) Y. Fujihashi, R. Shimizu and A. Ishizaki, submitted.
- 3) T. P. Nguyen and A. Ishizaki, *Phys. Rev. B* **99**, 064301 (2019).
- 4) T. P. Nguyen and A. Ishizaki, *Phys. Rev. Research* **1**, 033019 (2019).

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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Education

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Professional Employment

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

Awards

2009 APATCC Pople Medal
2009 QSCP Prize CMOA

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ZHAO, Pei
VIGNESH, K. R.
Visiting Scientist
ZHAO, Xiang
PRIYAKUMAR, Deva U
BOBUATONG, Karan
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SHIRAOGAWA, Takafumi
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KAWAGUCHI, Ritsuko
SUGIMOTO, Yukari

Keywords

Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

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

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

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

(2) Heterogeneous catalysis

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

Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

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

(4) Theoretical spectroscopy

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

Selected Publications

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

1. Theoretical Study on the Optical Properties of Multichromophoric Systems Based on an Exciton Approach: Modification Guidelines¹⁾

A degree of freedom of supramolecular and polymer design has been enhanced by recent advances in experimental techniques, where the design guidelines are demanded for developing optical materials. We propose post-modification strategy of emission and circularly polarized luminescence (CPL) of multichromophoric systems based on excitonic analysis. The strong decomposed CPL components originate from the interactions of exciton electric transition dipole moments between the chromophore and its adjacent monomers. The Frenkel-exciton decomposition analysis (FEDA) provides new possibilities for utilizing the potentials of multichromophoric systems.

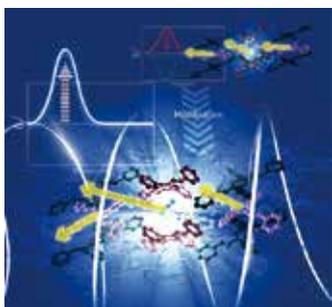


Figure 1. Post-modification strategy of emission and CPL of multichromophoric systems based on excitonic analysis.

2. Preferential Photoreaction in a Porous Crystal, Metal-Macrocyclic Framework: Pd^{II}-Mediated Olefin Migration over [2+2] Cycloaddition²⁾

A nano-sized confined space with well-defined functional surfaces has great potential to control the efficiency and selectivity of catalytic reactions. In this work, we report that a 1,6-diene, which normally forms an intramolecular [2+2] cycloadduct under photo-irradiation, preferentially undergoes a photo-induced olefin migration in a porous crystal, metal-macrocyclic framework (MMF), and alternatively [2+2] cycloaddition is completely inhibited in the confined space. A plausible reaction mechanism for olefin migration triggered by the photo-induced dissociation of the Pd–Cl bond is suggested based on UV-vis diffuse reflectance spectroscopy, single-crystal XRD, and MS-CASPT2 calculation. The substrate scope of the photo-induced olefin migration in MMF is also demonstrated.

3. Theoretical Insight into Configurational Selectivity of Functionalized Single-Walled Carbon Nanotubes Based on Clar Sextet Theory³⁾

Based on Clar's theory of the aromatic sextet, finite length

models of single-walled carbon nanotubes (SWNTs) have been utilized to study the configurational selectivity of modified SWNTs via covalent functionalization with organic substitutions by density functional theory calculations. After considering near-armchair, near-zigzag, and zigzag SWNTs with distinct chiralities, it is found that the parameter R of semiconducting SWNTs plays a significant role in determining stability difference of functionalized SWNTs, *i.e.*, SWNTs with $R = 2$ exhibit better configurational selectivity than those with $R = 1$ when binding the same substituent to the sidewall of SWNTs.

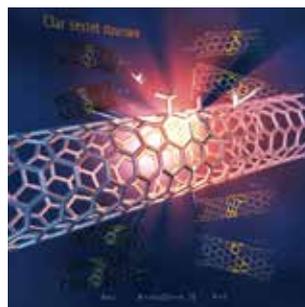


Figure 2. The configurational selectivity of modified SWNTs via covalent functionalization with organic substitutions to control the quantum dots.

4. Origin of Nb₂O₅ Lewis Acid Catalysis for Activation of Carboxylic Acids in the Presence of a Hard Base⁴⁾

The Nb₂O₅ surface catalyzes the amidation of carboxylic acids with amines via Nb⁵⁺ Lewis acid activation of the C=O group. In this work, DFT calculations were applied to theoretically investigate the C=O bond activation of a model carboxylic acid (acetic acid) on θ -Al₂O₃(110), anatase TiO₂(101), and T-Nb₂O₅(100) surfaces. The position of the mean DOS of the d -conduction band of the active metal site relative to the Fermi energy level correlates well with the efficiency in the C=O bond activation and, consequently, the catalytic activity for amidation. Unlike a classical understanding of strong acid sites of metal oxide surfaces, interaction of a carbonyl HOMO with a metal unoccupied d -orbital, covalent-like interaction between a carbonyl group and metal adsorption site, is relevant to the present system.

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Award

SHIRAOGAWA, Takafumi; Best Poster Award, The 22nd Annual Meeting of Japan Society of Theoretical Chemistry.

Development of New Simulation Algorithms and its Application to Protein Aggregates

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Keywords Molecular Dynamics Simulation, Protein, Amyloid

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

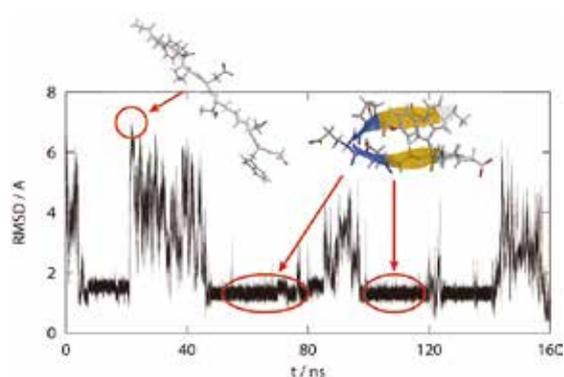


Figure 1. Time series of protein folding simulation.

We are also interested in protein aggregates such as spherical substances called oligomers and acicular substances called amyloid fibrils (Figure 2). These protein aggregates cause more than 30 kinds of diseases. For example, Alzheimer's disease is thought to be caused by aggregated amyloid- β ($A\beta$) peptides. To overcome these diseases, it is essential to understand the aggregate genesis and disruption of $A\beta$ peptides. We perform such MD simulations of oligomers and amyloid fibrils.

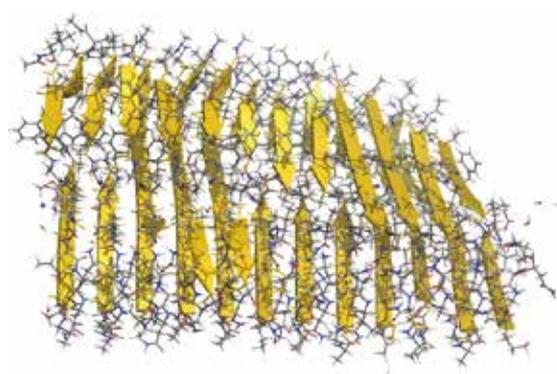


Figure 2. Snapshot of an $A\beta$ amyloid fibril.

Selected Publications

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- H. Okumura and S. G. Itoh, "Structural and Fluctuational Difference between Two Ends of $A\beta$ Amyloid Fibril: MD Simulation Predicts Only One End Has Open Conformations," *Sci. Rep.* **6**, 38422 (9 pages) (2016).
- 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).
- S. G. Itoh and H. Okumura, "Oligomer Formation of Amyloid- β (29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation," *J. Phys. Chem. B* **120**, 6555–6561 (2016).

1. Effects of a Hydrophilic/Hydrophobic Interface on Amyloid- β Peptides Studied by Molecular Dynamics Simulations and NMR Experiments

Oligomer formation of A β peptides is accelerated at a hydrophilic/hydrophobic interface. However, details of the acceleration mechanism have not been elucidated. To understand the effects of the interface on oligomerization at the atomic level, we performed all-atom MD simulations for an A β 40 monomer in the presence and absence of the hydrophilic/hydrophobic interface.¹⁾ Nuclear magnetic resonance experiments of A β 40 peptides with ganglioside micelles were also carried out in collaboration with Prof. Koichi Kato. We found that the A β peptides tend to gather at the hydrophilic/hydrophobic interface. That is, the local concentration of A β at the interface is higher than that in bulk water solution. In addition, β -hairpin structures are formed more at the interface than in the bulk water solution. In the β -hairpin structure, as shown in Figure 3, a part of the A β peptide extends straight and forms intramolecular hydrogen bonds. Therefore, another A β peptide that comes close to this peptide is easy to make intermolecular hydrogen bonds and tends to aggregate. In this way, we clarified that the reason for accelerating the aggregation of the A β peptides on the cell membrane surface is that not only the A β peptide tends to have high concentration on the cell membrane surface but also it takes a structure that tends to bind to each other. This discovery enables us to elucidate the mechanism by which the A β peptide aggregates on the membrane surface of nerve cells.

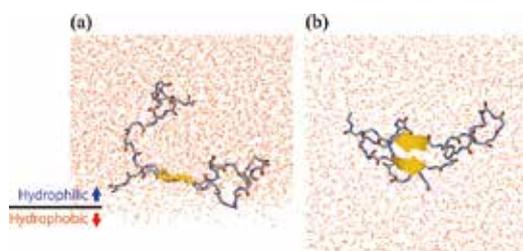


Figure 3. (a) An A β peptide that forms a β -hairpin structure at the hydrophilic/hydrophobic interface. (b) View from the bottom of panel (a).

2. Conformational Properties of an Artificial GM1 Glycan Cluster

Recent studies showed that monosialotetrahexosyl-ganglioside (GM1) clusters induce the pathological aggregation of A β peptide responsible for the onset and development of Alzheimer's disease. We first performed all-atom MD simulations to characterize the conformational properties of the artificial GM1 glycan cluster. We found that more than 65% of GM1 glycans are clustered by interchain hydrogen bonds, interchain hydrogen bonds are mainly formed between Neu5Ac and Gal', and pentamers were most frequently observed in the

metal-ligand complex. Our findings provide the physico-chemical properties of the artificial GM1 glycan cluster under the thermal fluctuations for understanding its protein recognition.

3. Conformational Change of Amyloid- β 40 in Association with Binding to GM1-Glycan Cluster

Interaction between A β peptide and GM1-glycan cluster is important for the earliest stage of the toxic aggregation on GM1 cluster. We then performed all-atom MD simulations of A β 40 on the artificial GM1-glycan cluster.³⁾ The GM1-glycan cluster facilitates the characterization of interactions between A β 40 and multiple GM1-glycans. We succeeded in observing the binding of A β 40 to the GM1-glycan cluster in all of our MD simulations. Our results indicate the importance of HHQ (13-15) segment of A β 40 for the GM1-glycan cluster recognition. The recognition mechanism of HHQ (13-15) segment is mainly explained by non-specific stacking interactions between side-chains of histidine and rings of sugar residues, in which the HHQ regime forms coil and bend structures. Moreover, we found that A β 40 exhibits helix structures at C-terminal side on the GM1-glycan cluster as in Figure 4. The helix formation is the initial stage of the pathological aggregation at ceramide moieties of GM1 cluster. The binding of Lys28 to Neu triggers the helix formation at C-terminus side because the formation of a salt bridge between Lys28 and Neu leads to change of intrachain interactions of A β 40. Our findings suggest that the pathological helix formation of A β 40 is initiated at GM1-glycan moieties rather than lipid ceramide moieties.

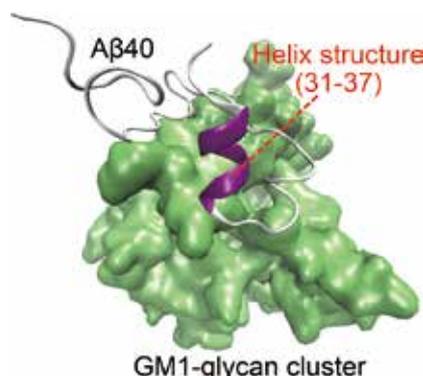


Figure 4. A typical snapshot of A β 40 with a helix structure formed in residues 31–37. Green colored molecule is the GM1-glycan cluster.

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Theoretical Studies on Molecular Aggregates

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Keywords Exciton, Energy and Charge Transfer, Organic Semiconductors

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

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

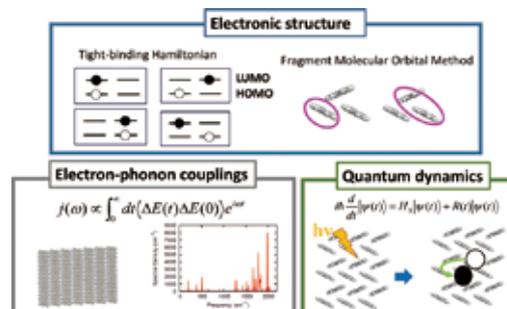


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

is used for simulating energy or charge dynamics by a quantum dynamics method, which incorporates finite-temperature effects and electron-vibration interactions. The combine computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

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

Selected Publications

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- T. Fujita and Y. Mochizuki, "Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems," *J. Phys. Chem. A* **122**, 3886–3898 (2018).

1. Development of Large-Scale GW Method for Applications to Organic Optoelectronic Materials¹⁾

Organic electronics based on π -conjugated molecules or polymers have attracted considerable attention due to their attractive features. Predicting the charged-transport levels or optical excitations is essential for understanding the electronic processes governing the device operation and for rationally designing novel materials. The successful theoretical descriptions of charged and neutral excited states require an accurate quantum mechanical method: In addition, the effects of polarizable environment must be appropriately taken into account. For example, an electron addition or removal of a molecule induces the polarization of the surrounding molecules, which results in the reduction of HOMO–LUMO gap. The polarization induced by the neutral excitation (creation of electron–hole pair) increases with increasing the electron–hole separation, leading to the relative stabilization of the charge-separated states. Note that such the environmental polarization is state-specific and cannot be treated by a standard electrostatic embedding scheme.

Here, we present a method that can treat both the electron correlation and the state-specific polarization, on the basis of the fragment molecular orbital and GW methods. The GW is a many-body Green's function theory and can offer an accurate and practical scheme to calculate a quasiparticle energy corresponding to an ionization potential or an electron affinity. Electronically excited states can be also computed in combination with Bethe-Salpeter equation method. In this study, we develop the large-scale GW method based on the FMO method. The implementation is based on the fragmentation approximation of the polarization function and the combined GW and Coulomb-hole plus screened exchange approximations for self-energies. As well as the ground-state polarization treated in the FMO method, the FMO-GW method can describe the state-specific polarization effect.

The fragment-based GW was demonstrated in application to the charge-transfer states formed across the pentacene (PEN)/C₆₀ bilayer heterojunction. The local interface structure approximately contains 2,000 atoms, with external molecules in the total bilayer heterojunction structure being treated by external point charges. The CT excitation energies were estimated from the quasiparticle energies and electron–hole screened Coulomb interactions and are in reasonable agree-

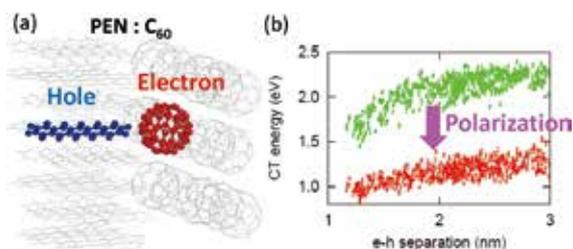


Figure 2. (a) The atomic structure of pentacene/C₆₀ local interface. (b) The CT excitation energy with respect to electron–hole separation.

ment with experimental estimates from the external quantum efficiency measurements. We highlight the impact of the induced polarization effects on the electron–hole energetics.

2. Polarization Energy of Pentacene Clusters²⁾

We investigate the electronic states of PEN clusters. The electronic states of PEN have been studied by calculations for an isolated molecule or molecular crystals. Although an isolated PEN molecule and PEN crystals have been well studied, the evolution of electronic states from the gas to the solid phase still remains unclear. In this study, we employ PEN clusters, (PEN)_N ($N = 3, 14, 33$), as model systems and consider the effects of molecular packing and intermolecular interactions on the electronic states. Figure 3(b) show the HOMO–LUMO gap and S₁ excitation energy of a PEN molecule in the central region in the cluster structures. The HOMO–LUMO gap and S₁ excitation energy of an isolated PEN molecule are 4.83 and 2.08 eV, respectively, at the GW@B3LYP/6-31G* level. The HOMO–LUMO gap decreases with increasing the cluster size. For the intramolecular excited states, the reduction of the HOMO–LUMO gap is compensated by the weakening of the electron–hole attraction, leaving the excitation energy unchanged.

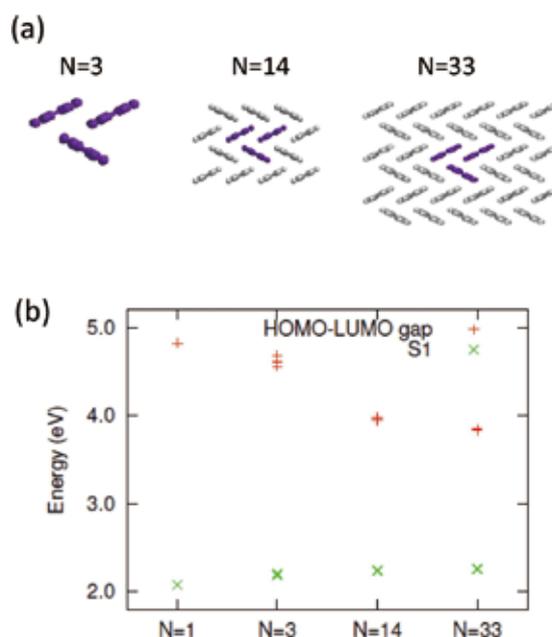


Figure 3. (a) The structures of PEN clusters. (b) The HOMO–LUMO gap and S₁ excitation energy of a pentacene molecule in the central regions in cluster structures.

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Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

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

Functional dynamics of biomolecular machines involve wide spectrum of intricate motions and reactions. In order to understand such dynamics, we need a multiscale approach to cover full range of these motions and reactions. Conventional atomistic molecular dynamics (MD) simulations alone cannot cover millisecond-long (or even longer) functional dynamics, especially for a large system like typical biomolecular machines. Thus, we use techniques like importance sampling, coarse-graining, and statistical/kinetic modeling to tackle this problem.

We have been working on biomolecular motors such as ATP synthase and chitinase. ATP synthase is a rotary motor that produces most of ATP required in the cell. It is composed of two rotary motors: F_0 and F_1 . F_0 motor is embedded in the membrane driven by proton gradient, while F_1 motor is driven

by ATP hydrolysis reaction. We studied how rotation of F_1 is caused by elementary steps such as product release from the catalytic site. Chitinase is a new type of molecular motor that uses hydrolysis energy of single chitin chain, a polysaccharide from exoskeleton of crab *etc.*, for its unidirectional motion. The sliding motion of chitin chain into the catalytic site of chitinase was studied by atomistic simulations. We also developed a novel framework to estimate free energy profiles and diffusion coefficient from single-molecule trajectories.

Transporters are membrane proteins that transport their substrates across the membrane. We have studied Na^+/H^+ antiporter that exchanges sodium ions and protons inside and outside the cell. The ion-transport cycle was simulated in atomic detail with the transition path sampling technique. The simulations predicted the mutation that can speed up the ion transport, which was confirmed by experiments. Another membrane-associated protein, F-BAR protein Pacsin1 that remodels the membrane, is our interest too. The curvature induction and sensing of Pacsin1 on the membrane was studied by multiscale MD simulations using both all-atom and coarse-grained models.

Selected Publications

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- K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, "Mechanism of the Electroneutral Sodium/Proton Antiporter PaNhaP from Transition-Path Shooting," *Nat. Commun.* **10**, 1742 (2019).

1. Mechanism of Unidirectional Motions of Chitinase

Processive cellulase and chitinase recently have been cast new light as a different type of biomolecular motors that use hydrolysis energy of polysaccharides for their unidirectional movements. With the high-precision single-molecule experiments, it was shown that chitinase SmChiA showed fast unidirectional movement of $\sim 50 \text{ nm s}^{-1}$ with 1-nm forward and backward steps.¹⁾ The rate constants of the hydrolysis reaction and decrystallization of single chitin chain were also clarified. The sliding motion of chitin chain into the catalytic site of chitinase was simulated by atomistic simulations. These results suggested that chitinase works by the burnt-bridge Brownian ratchet mechanism. We have been developing a novel framework to estimate its diffusion model from the single-molecule trajectories behind this mechanism too.

2. Mechanism of Na^+/H^+ Antiporter and Engineering of a Faster Transporter

Na^+/H^+ antiporters control pH and Na^+ concentration in the cell by exchanging sodium ions and protons across lipid membranes. They belong to the cation/proton antiporter (CPA) superfamily, and prevail in all domains of life. The archaeal Na^+/H^+ antiporters PaNhaP from *Pyrococcus abyssi* and MjNhaP1 from *Methanocaldococcus jannaschii* as well as human NHE1, which is linked to a wide spectrum of diseases from heart failure to autism and has no structure solved yet, are electroneutral antiporters of the CPA1 family, exchanging one proton against one sodium ion. As a model system in mechanistic studies of electroneutral Na^+/H^+ exchange, we studied the transport mechanism of PaNhaP.²⁾

Na^+/H^+ antiporters use the gradient of either sodium ion or proton to drive the uphill transport of the other ion (Figure 1A). The conformational transition of the transporter makes the ion-binding site accessible from either side of the membrane in the alternating manner. For PaNhaP, the inward-open conformation was obtained by X-ray crystallography, while the outward-open conformation is not known experimentally. We modelled the outward-open conformation by MDFF flexible fitting to the low-resolution outward-open structure of the homologous MjNhaP1 from cryo-EM, followed by the long equilibrium MD simulations. It was shown that the transporter domain moves $\sim 3.5 \text{ \AA}$ in the direction normal to the membrane to take the outward-open state (Figure 1B).

The inward-open and outward-open conformations described above only provides the end points of the ion-transport. The transition dynamics between the two states is central to the transport mechanism, revealing at once rate-limiting steps, substrate pathways, and the opening and closing of the gate preventing ion leakage. However, with ion exchange occurring on a timescale of seconds at ambient conditions, regular MD simulations are far too slow to resolve transitions. Instead, we can resort to importance sampling of

transition dynamics. To sample unbiased transition paths between the inward- and outward-open states, we used techniques from the transition path sampling.

In analysis of the transition paths, we found hydrophobic gates above and below the ion-binding site, which open and close in response to the domain motions (Figure 1C). From the reaction coordinate analysis, it was shown that open-close motion of the outside gate (Ile163-Tyr255) is a rate-limiting step of the alternating-access conformational change. Based on this result, we weakened the outside gate by mutating the residues to both alanine. It was expected that this mutation lowers the barrier and makes the ion transport faster. It was confirmed by experiments that the ion-transport speed of the mutant is indeed twice faster than the wild-type transporter.

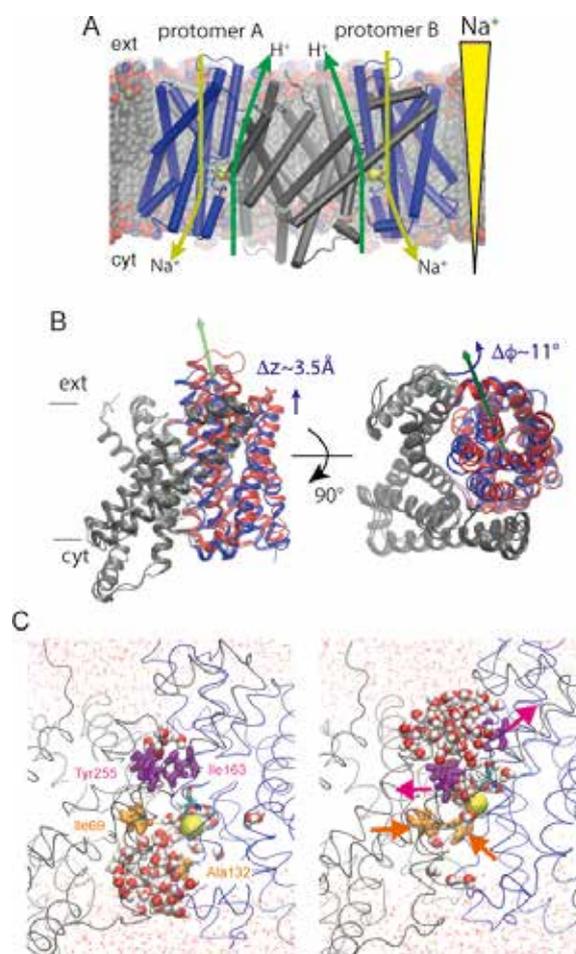


Figure 1. (A) PaNhaP dimer structure. (B) Comparison of the transporter domain between the inward-open (blue) and outward-open (red) states. (C) The outside (purple) and inside (orange) gates found in the transition paths.

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Theoretical Study of Heterostructures under Light and Voltage Bias

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Heterostructures consisting of different materials have various optical and electronic properties depending on their constituents and the interfacial region. We have studied the heterostructures under light and/or voltage bias using our developed first-principles computational program named SALMON.¹⁾

1. Photoexcited Electron Transfer in Silver/TiO₂ Heterostructure²⁾

The photoexcitation of heterostructures consisting of metallic nanoclusters and a semiconductor causes electron and resonance energy transfers and is extensively investigated to develop photocatalysis and optical devices. Using SALMON, we have studied photoexcited electron dynamics in a silver nanocluster/TiO₂ heterostructure. Excited electrons are directly transferred from the silver nanocluster to the TiO₂ layer without passing

through the silver conduction band because of photoinduced electrostatic interactions at the silver/TiO₂ interface.

2. Optical Near-Field Excitation of Silicon Semiconductor³⁾

We have clarified that direct interband transitions between different wavenumbers can occur in an indirect band gap semiconductor of silicon by an optical near field (ONF). The energy of the absorption edge can be reduced by the ONF excitation. Furthermore, a large number of transitions are induced by the ONF excitation of the realistic silicon system with a complex band structure more than that of a simplified model system.

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Theory and Computation of Reactions and Properties in Solutions and Liquids

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We are interested in the projects on ionic liquids (ILs). ILs' projects are focused on the unique dissolution process of cellulose polysaccharides, and the investigation of static and dynamical properties on ionic liquids including temperature effects.

1. Investigations of Dissolution and Decomposition Mechanisms of a Cellulose Fiber in Ionic Liquids¹⁾ with Molecular Dynamics Simulation

We studied dissolution and decomposition mechanisms of cellulose (I_β) polymers in ILs. In order to investigate motion of cellulose fibers and intermolecular interactions between cellulose molecules and cationic and anionic species in ILs, we carried out molecular dynamics simulation. We employed the 1-ethyl-3-methylimidazolium acetate IL solvent for target system. It was found out that the intermolecular interaction energy between cellulose polymers in the IL are reduced,

comparing with that in water. Also, it is shown that decomposition and solvation mechanisms of cellulose polymers can be interpreted not only by considering hydrogen bond strength between cellulose chains in the IL, but also by tracking both the intra- and inter-molecular (cellulose) hydrogen bond breaking processes in the IL.

2. Researches on Static and Dynamical Properties of Ionic Liquids: Molecular Origin of Low-k Peak of ILs and Dynamical Heterogeneity

We have investigated the molecular level origin of low-k peak (< 0.5 Å⁻¹) in the structure factor in ILs. In particular, we found out that the structure factor of heterocyclic ring parts in cations largely contribute to low-k peak in ILs. Also, we are going to carry out the study of dynamical properties of ILs, dynamical heterogeneity in ILs at room temperature with molecular dynamics simulation procedure.

Reference

- 1) T. Ishida, to be submitted to *J. Phys. Chem. B*, in preparation.

Visiting Professors



Visiting Professor
NAKANO, Masayoshi (*from Osaka University*)

Theoretical Study on Photofunctionalities of Open-Shell Molecular Systems

Through close collaboration between theoretical and experimental research groups, we have clarified a new structure-property correlation between diradical character and singlet–triplet energy gap for indenoindenodibenzothiophene diradicals: Inclusion of thiophenes within a quinoidal polycyclic hydrocarbon imparts appreciable diradical character yet retains the large singlet–triplet energy gap, a phenomenon that has no precedent in the literature. Theoretical investigation has revealed that the low aromatic character of thiophene and its electron-rich nature are the key properties leading to these unique findings. This new structure–property relationship is not only extremely important in the field of diradical chemistry and organic electronics, but also provides new insights into the versatility of π -electron chemical bonding. We have also developed a computational method for analyzing the singlet fission dynamics for molecular aggregates beyond dimer models. Using this method, we have clarified unique size and architecture dependences of SF dynamics, which will be useful for constructing novel design guidelines for highly-efficient SF materials.



Visiting Professor
NAKAYAMA, Akira (*from The University of Tokyo*)

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

A detailed understanding of the interface between liquid and metal-oxide is fundamental due to its relevance to the broad range of physicochemical phenomena and technological applications. To provide microscopic insight into the structures and dynamics at the liquid/metal-oxide interface, we perform the first-principles molecular dynamics simulations and unveil the intricate molecular process occurring at the interface. In this year, we have focused on the catalytic reactions at the water/CeO₂ and methanol/CeO₂ interfaces and investigated the role of acid-base and redox sites over CeO₂. In particular, we have worked on the following topics: (1) Substrate-specific adsorption of 2-cyanopyridine and hydration reaction over CeO₂. (2) The reaction mechanism for the direct synthesis of dimethyl carbonate from methanol and CO₂ over CeO₂ and ZrO₂. (3) Enhanced sampling employing the temperature-accelerated sliced sampling scheme for constructing multi-dimensional free energy landscape.



Visiting Associate Professor
KIM, Kang (*from Osaka University*)

Theoretical and Computational Research for Complex Fluids and Soft Matters

We are working on theoretical and simulation approaches to reveal various dynamical processes in complex fluids and soft matters. Recent topics in my research are related to slow dynamics in supercooled water. In particular, we have developed the cage jump model for the dynamics of supercooled water. The caged and jumping states of a water molecule are introduced with respect to the hydrogen-bond rearrangement process and describe the motion in supercooled states. It is then demonstrated from the molecular dynamics simulation that the characteristic length and time scales of cage jump motions provide a good description of the self-diffusion constant. Furthermore, using molecular dynamics simulations we have assessed the violations of the Stokes–Einstein and Stokes–Einstein–Debye relationships in supercooled water by the identification of timescales that appropriately characterize transport coefficients, such as translational diffusion constant, rotational relaxation time, and shear viscosity.





RESEARCH ACTIVITIES

Photo-Molecular Science

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

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

Exploring Quantum-Classical Boundary

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



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2009 Visiting Professor, The University of Tokyo (–2011)
2012 Visiting Professor, University of Heidelberg
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2007 Japan Academy Medal
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2012 Humboldt Research Award
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Keywords

Quantum-Classical Boundary, Quantum Technology, Attosecond Coherent Control

It is observed in a double-slit experiment by Tonomura and coworkers that single electrons recorded as dots on a detector screen build up to show an interference pattern, which is delocalized over the screen.¹⁾ This observation indicates that a delocalized wave function of an isolated electron interacts with the screen, which is composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as “collapse” in quantum theory, is often accepted as a discontinuous change, but a basic question arises: When and how the delocalized wave function becomes localized? Our objective is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this objective 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 array of ultracold rubidium (Rb) Rydberg atoms in an optical

lattice, as depicted schematically in Figure 1, envisaging the quantum-classical boundary connected smoothly.

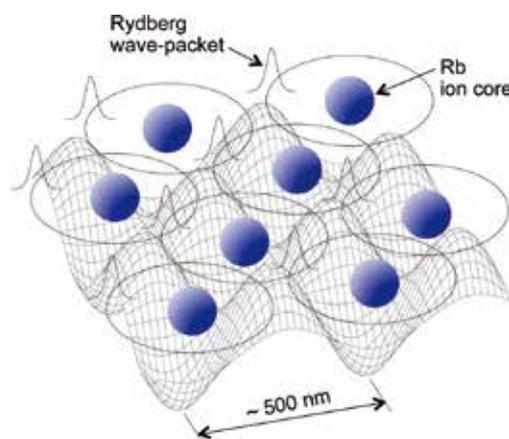


Figure 1. Schematic of the many-body system of ultracold Rydberg atoms.²⁾

Selected Publications

- H. Katsuki *et al.*, “Visualizing Picometric Quantum Ripples of Ultrafast Wave-Packet Interference,” *Science* **311**, 1589–1592 (2006).
- H. Katsuki *et al.*, “Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales,” *Phys. Rev. Lett.* **102**, 103602 (2009).
- K. Hosaka *et al.*, “Ultrafast Fourier Transform with a Femtosecond-Laser-Driven Molecule,” *Phys. Rev. Lett.* **104**, 180501 (2010).
- H. Goto *et al.*, “Strong-Laser-Induced Quantum Interference,” *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, “All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth,” *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, “Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas,” *Nat. Commun.* **7**, 13449 (2016).
- C. Liu *et al.*, “Attosecond Control of Restoration of Electronic Structure Symmetry,” *Phys. Rev. Lett.* **121**, 173201 (2018).

1. Development of an “Ultrafast Quantum Simulator” by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales^{3–5)}

Quantum many-body problems are at the heart of a variety of physical functionalities including superconductivity and magnetism in solid materials. It is extremely hard, however, to solve such quantum many-body problems. In solving the Hubbard model with 1000 particles, for example, the diagonalization would take 10 to the power of 573 years even with the world’s fastest supercomputers. In this project, we develop a novel quantum simulator that can simulate quantum many-body dynamics for more than 1000 particles within one nanosecond, combining our two unique experimental resources: “coherent control with attosecond precision”⁶⁾ and “a strongly-correlated ultracold Rydberg gas.”⁷⁾

We have completed a standard hardware of this ultrafast quantum simulator composed of an array of ultracold Rb atoms trapped in an optical lattice and excited to Rydberg levels with a coherent picosecond laser pulse, as schematically illustrated in Figure 2.^{3,4)} The broad bandwidth of the ps laser pulse has allowed us to excite the atoms in the neighboring lattice sites to Rydberg levels simultaneously for the first time. We expect that the overlap between their Rydberg orbitals could give rise to an exotic metal-like phase, where the electron could delocalize over the lattice.

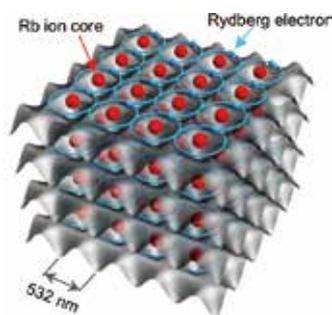


Figure 2. Schematic of the hardware of the ultrafast quantum simulator.^{3,4)}

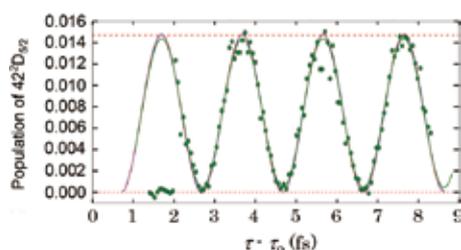


Figure 3. Time domain Ramsey interferometry of ultracold ⁸⁷Rb atoms with attosecond precision to be used as a readout interface of the ultrafast quantum simulator. Population of the 42²D_{5/2} Rydberg state is plotted as a function of the delay τ between two laser pulses, where $\tau_0 \sim 50$ ps. Adopted from Ref. 5).

We have also completed a readout interface of our ultrafast quantum simulator, which is the time domain Ramsey interferometry of ultracold Rydberg atoms with attosecond precision, whose contrast is almost 100% as shown in Figure 3.⁵⁾ The phase and visibility of this Ramsey interferogram are highly sensitive to the nature and strength of many-body interactions among the Rydberg atoms.

2. Application of an “Ultrafast Quantum Simulator” to Quantum Computing³⁾

We are developing a cold-atom based quantum annealer with the hardware of the ultrafast quantum simulator.⁸⁾ The cold-atom annealer has advantages against the one with the superconducting qubits. Those advantages include scalability and efficiency. All to all connections among physical bits necessary for quantum annealing could also be easier with cold atoms than superconducting qubits.

So far we have developed arbitrary two dimensional optical trap arrays for cold atoms, which are necessary for quantum annealing,⁸⁾ in tight collaborations with Hamamatsu Photonics K. K.³⁾ Their examples are shown in Figure 4, where we used a convex lens for clear visualization of the trap arrays. We have recently replaced this convex lens by an objective lens to realize the world’s smallest arbitrary trap array with its nearest neighbor distance now only 1.06 micron, which used to be typically ~ 4 micron in previous works.⁹⁾

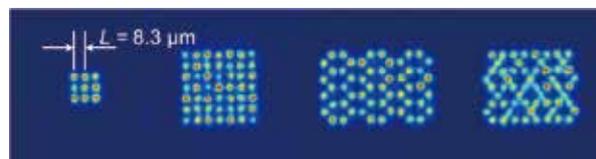


Figure 4. Examples of arbitrary optical trap arrays generated with a low NA convex lens ($L = 8.3 \mu\text{m}$; wavelength = 633 nm; NA = 0.0446), corresponding to $L = 640$ nm with NA = 0.75 at the wavelength 820 nm.³⁾

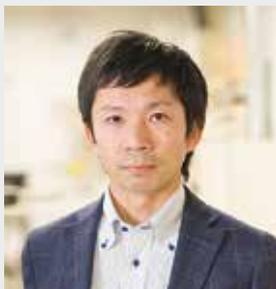
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- 2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
- 3) Patent Publication: US 2018/0292786 A1; JAPAN 2018-180179, “Quantum simulator and quantum simulation method,” H. Sakai (Hamamatsu Photonics K.K.), K. Ohmori (IMS) *et al.*, Oct. 11, 2018 (US); Nov. 15, 2018 (JAPAN).
- 4) White Paper 2018 on Manufacturing Industries published by Ministry of Economy Trade and Industry, JAPAN.
- 5) C. Liu *et al.*, *Phys. Rev. Lett.* **121**, 173201 (2018).
- 6) H. Katsuki *et al.*, *Acc. Chem. Res.* **51**, 1174–1184 (2018).
- 7) N. Takei *et al.*, *Nat. Commun.* **7**, 13449 (2016).
- 8) A. W. Glaetzle *et al.*, *Nat. Commun.* **8**, 15813 (2017).
- 9) D. Barredo *et al.*, *Science* **354**, 1021 (2016).

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Electronic Property of Functional Organic Materials

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Keywords

Photoelectron Spectroscopy, Molecular Assemble, Electronic State

Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However, the mechanisms and the origin of various device characteristics are still under debate. Scientific discussions were sometimes challenging because of long-standing beliefs that the electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to the weak van der Waals interaction. To reveal characteristics of FOM, it is key to precisely investigate the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the weak electronic interaction appears as small intensity modulations of fine features in photoelectron spectra, depending on the adsorption and aggregation conditions on the surface. Thanks to recent instrumentation improvements, we can assess hidden fine features in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small densities of gap states, weak band dispersion, and dynamic electronic polarization. To elucidate what really impacts the electronic states of the FOM in their assembly as well as at the interface upon weak interaction, an evaluation of the wave-function spread of the electronic states

would be very important because the interface states are described as a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Observing modifications of electron wave functions upon weak electronic coupling as well as strong electron–phonon coupling is a central issue on our agenda.

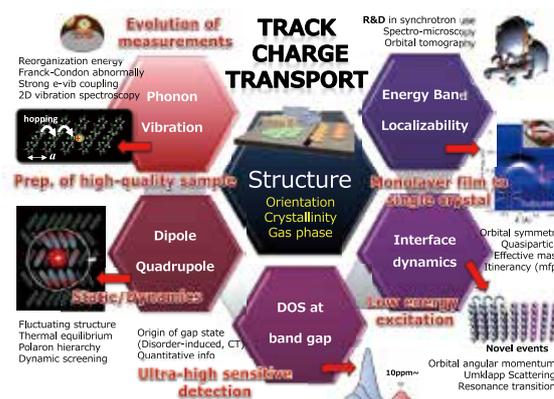


Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

Selected Publications

- S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, *J. Phys. D: Appl.*

Phys. **50**, 423002 (45 pages) (2017). [review]

- S. Kera and N. Ueno, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. Widely Dispersed Intermolecular Valence Bands of Epitaxially Grown Perfluoropentacene on Pentacene Single Crystals¹⁾

Strong intermolecular electronic coupling and well-ordered molecular arrangements enable efficient charge transport in semiconducting π -conjugated molecular solids. Molecular heteroepitaxy to form crystallized donor–acceptor molecular interfaces potentially leads to a novel strategy for creating efficient organic optoelectronic devices. In the present study, the crystallographic and electronic structures of a heteroepitaxial molecular interface, perfluoropentacene (PFP, $C_{22}F_{14}$) grown on pentacene single crystals (Pn-SCs, $C_{22}H_{14}$), were determined by means of grazing-incidence X-ray diffraction (GIXD) and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), respectively. GIXD revealed that PFP uniquely aligned its primary axis along the $[1\bar{1}0]$ axis of crystalline pentacene to form well crystallized overlayers. Valence band dispersion (at least 0.49 eV wide) was successfully resolved by ARUPS. This indicated a small hole effective mass and a significant transfer integral between the frontier molecular orbitals of the nearest-neighbor PFP molecules, ensuring the presumable occurrence of efficient band-like transport in the epitaxial PFP crystallites.

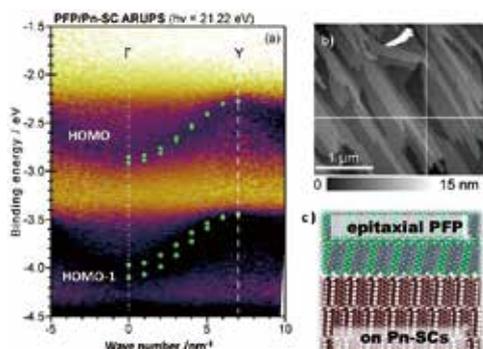


Figure 2. (a) ARUPS intensity map of the 4nm thick PFP overlayer on Pn-SC sample taken in the Γ – Y directions plotted on the E – K_{\parallel} plane. The theoretical band structures predicted by Yoshida *et al.* [*Phys. Rev. B* **92**, 075145 (2015)] are plotted as circles. (b) AFM image of a PFP (5nm)/Pn-SC substrate. The figure is after ref 1) with permission.

2. Molecular Parameters Responsible for Thermally Activated Transport in Doped Organic Semiconductors²⁾

Doped organic semiconductors typically exhibit a thermal activation of their electrical conductivity, whose physical origin is still under scientific debate. We disclose relationships between molecular parameters and the thermal activation energy (E_A) of the conductivity, revealing that charge transport is controlled by the properties of host–dopant integer charge transfer complexes (ICTCs) in efficiently doped organic

semiconductors. At low doping concentrations, charge transport is limited by the Coulomb binding energy of ICTCs, which can be minimized by systematic modification of the charge distribution on the individual ions. The investigation of a wide variety of material systems reveals that static energetic disorder induced by ICTC dipole moments sets a general lower limit for E_A at large doping concentrations. The impact of disorder can be reduced by adjusting the ICTC density and the intramolecular relaxation energy of host ions, allowing an increase of conductivity by many orders of magnitude. The observed correlation between E_A and the density of ICTCs indicates that the minimum achievable E_A is generally limited by the electrostatic disorder of ICTCs, which can be reduced by using large molecules or ICTCs with small dipole moments.

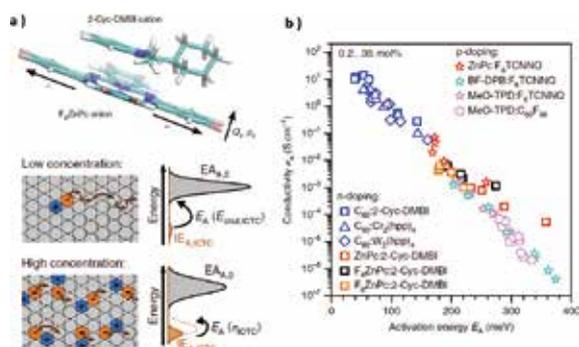


Figure 3. a) Simplified sketch of charge transport in different concentration regimes. At low doping concentrations, electron transport requires a dissociation of ICTCs into separated charges, resulting in an increase of E_A . At large doping concentrations and small distances between ICTCs, transport can be described ideally by electron transport between different ICTC configurations whose local energies change continuously and where multi-electron hops may also play a role. b) The change of conductivity with concentration goes along with a change of E_A . Starting from low doping concentrations, all material combinations investigated show a decrease of E_A with increasing doping concentration, explaining the increase of conductivity. The figure is after ref 2).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Introduction of novel momentum microscope launched at BL6U is started.

References

- 1) Y. Nakayama, R. Tsuruta, N. Moriya, M. Hikasa, M. Meissner, T. Yamaguchi, Y. Mizuno, T. Suzuki, T. Koganezawa, T. Hosokai, T. Ueba and S. Kera, *J. Phys. Chem. Lett.* **10**, 1312–1318 (2019). [Selected for Journal Cover]
- 2) M. Schwarze, C. Gaul, R. Schol, F. Bussolotti, A. Hofacker, K. S. Schellhammer, B. Nell, B. D. Naab, Z. Bao, D. Spoltore, K. Vandewal, J. Widmer, S. Kera, N. Ueno, F. Ortmann and K. Leo, *Nat. Mater.* **18**, 242–248 (2019).

Light Source Developments by Using Relativistic Electron Beams

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Keywords Accelerator, Beam Physics, Astrobiology

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



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

Selected Publications

- S. Bielawski, C. Evain, T. Hara, M. Hosaka, M. Katoh, S. Kimura, A. Mochihashi, M. Shimada, C. Szwaj, T. Takahashi and Y. Takashima, “Tunable Narrowband Terahertz Emission from Mastered Laser–Electron 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).
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- Y. Taira, T. Hayakawa and M. Katoh, “Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light,” *Sci. Rep.* **7**, 5018 (2017).
- S. Matsuba, K. Kawase, A. Miyamoto, S. Sasaki, M. Fujimoto, T. Konomi, N. Yamamoto, M. Hosaka and M. Katoh, “Generation of Vector Beam with Tandem Helical Undulators,” *Appl. Phys. Lett.* **113**, 021106 (2018).

1. Light Source Technology Developments Based on Laser and Synchrotron

We have been developing light source technologies at the UVSOR-III electron storage ring using a dedicated experimental station BL1U, which was constructed under the support of Quantum Beam Technology Program of JST/MEXT aiming to develop novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beam-line. In these years, we are focusing on generation of structured light, such as vortex beams and vector beams from undulators, in collaboration with Hiroshima Univ. and Nagoya Univ. We have already succeeded in producing such novel photon beams and are exploring their applications in collaboration with Saga Light Source and Toyama Univ.

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

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

We have carried out several upgrade plans successfully



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

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

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

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

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



Figure 3. Optical Cavity for Resonator Free Electron Laser.

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

Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

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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.

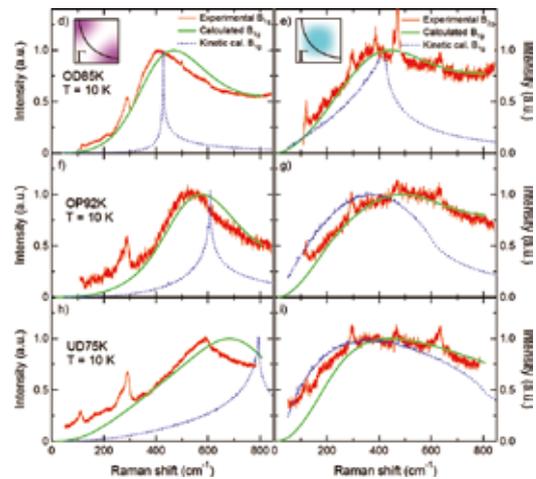


Figure 1. Comparison between experimental ERS spectra (red), calculated ERS spectra from ARPES (green), and kinetic theory (blue) for different carrier concentration of Bi2212 and different momentum space.

Selected Publications

- 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).
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- K. Tanaka, N. Hieu, G. Vincini, T. Masui, S. Miyasaka, S. Tajima and T. Sasagawa, "Quantitative Comparison between Electronic Raman Scattering and Angle-Resolved Photoemission Spectra in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ Superconductors: Doping Dependence of Nodal and Antinodal Superconducting Gaps," *J. Phys. Soc. Jpn.* **88**, 044710 (2019).

1. Quantitative Comparison between ARPES and ERS on High- T_c Cuprate Superconductor¹⁾

Both of ARPES and electronic Raman scattering (ERS) are powerful techniques which can obtain momentum-selected electronic structure. In the study of high- T_c cuprates superconductors, both techniques revealed two energy scales for the gap in different momentum spaces. 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 spectrum is a function of matrix element, Fermi Dirac function and a spectral function $A(k,\omega)$. On the other hand, ERS spectrum has been understood by simple model (so-called kinetic theory) for long time, where delta-function density of states along the Fermi surface is assumed. Therefore, quantitative analysis and discussion of ERS spectrum have been difficult. Using the Kubo formula, we noticed that the ERS spectrum can be written by square of the imaginary part of Green's function. This means that ERS spectrum can be calculated by ARPES spectrum, since the imaginary part of Green's function corresponds to the spectral function $A(k,\omega)$ in ARPES.

In this study, we have 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. For the samples, we prepared $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) with three doping levels, namely, underdoped (UD75K: $T_c = 75$ K), nearly optimally doped (OP92K: $T_c = 92$ K), and overdoped (OD85K: $T_c = 85$ K) samples.

Figure 1 shows the calculated ERS spectra. Here, it should be noted that the intensity distribution of $A(k,\omega)$ along the Fermi surface is an unknown parameter and we only showed the best fitted result. Compared to the conventional ERS spectral calculation based on kinetic theory (blue), our new calculation results (green) reproduced spectral features much better. Especially B_{2g} spectra, which is sensitive to the nodal region in the momentum space, were well reproduced. Doping dependence of the 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 (not shown).

The peak energies of the calculated ERS spectra were plotted in Figure 2 together with the experimental Raman, ARPES and STM data. From B_{1g} spectra, which is 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 spectrum can be well reproduced by

ARPES spectrum, and 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 antinodal 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 is larger than that estimated from the normal state ARPES as a Fermi arc. All these findings reflect the unusual electronic states where superconductivity and coexist even at the lowest temperature.

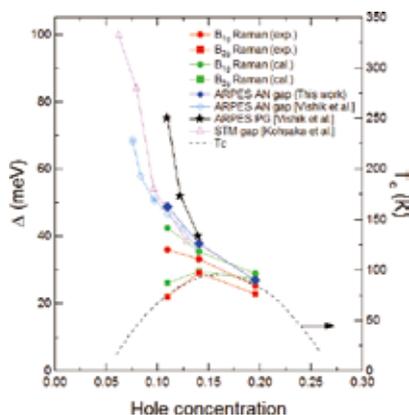


Figure 2. Doping dependence of the peak energies in Bi2212 obtained from ERS calculations in comparison to the experimental data from Raman, ARPES and STM measurements.

2. Development of Low Temperature 6-Axis Manipulator for High-Resolution ARPES

To perform high energy resolution ARPES measurements, the temperature of samples is important. We developed low temperature 6-axis manipulator by ourselves and achieved 4.5 K with tilting angle $-15 \sim 55$ deg. and azimuth angle ± 120 deg. This is one of the lowest temperature 6-axis manipulators in the synchrotron radiation facilities in the world.



Reference

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

Resonant Photoemission: Selective Access to Surface Atomic and Molecular Orbitals

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research



MATSUI, Fumihiko
Senior Researcher

The electronic properties and chemical reactivities of materials are closely related to the behavior of valence electrons near the Fermi level. Momentum-resolved valence-band photoelectron spectroscopy is a powerful technique to characterize such electrons. Furthermore, by tuning the excitation energy to the core-level absorption edge, valence electron can be resonantly selected and analyzed. In order to establish the reliability of this method, comprehensive measurement and understanding of the photoelectron emission process are important.¹⁾ BL6U at UVSOR is a beamline dedicated to valence band dispersion mapping with a practical photon energy range of 40 to 600 eV. Wide-acceptance-angle acquisition system enables measurement of full set of valence band dispersion data over several Brillouin zones.²⁾

1. Graphite Valence Band Dispersion in Resonance Auger Electron Spectra

Figure 1 shows a comparison of the angular distribution of graphite valence band between below and above the C 1s absorption threshold. The intensity of the π band with parabolic dispersion is enhanced at the π^* resonance due to “participant Auger electron process.” Until now, there was a common understanding that the angular distribution of Auger electron

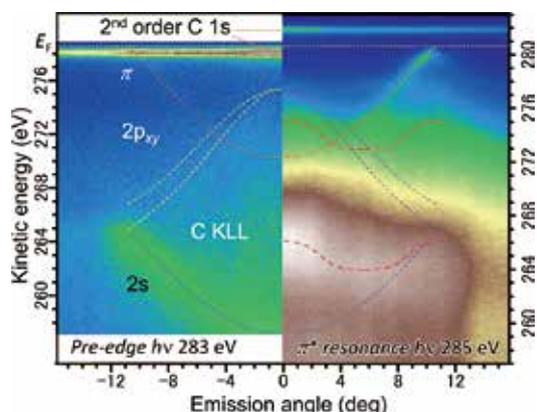


Figure 1. Angle-resolved photoelectron spectra below (left) and above (right) the C K edge threshold. Red dashed lines in the right panel are the newly found participant Auger electron dispersion features.

intensity is due to diffraction, not band dispersion. Here, we found that the resonant Auger electrons *do* carry band dispersion information. The red dashed curves show that momentum is conserved by the electrons involved in the “spectator Auger electron process.”

These experiments can only be performed on soft x-ray beamlines with low carbon contamination. In cooperation with the UVSOR technical team, we removed carbon from the beamline optics by O₂ photochemical etching and successfully experimented with this resonant photoelectron spectroscopy. The spectator Auger process at the C absorption edge was actively explored in the past to try to break specific chemical bonds by selecting antibonding orbitals as the transition destination of 1s electrons. The present success of resonance Auger electron experiments at the C K absorption edge is the basis for expanding the range of application to molecular adsorption systems.^{3,4)}

2. Momentum Microscope

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

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Local Structural Analyses of Liquids by Soft X-Ray Absorption Spectroscopy

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



NAGASAKA, Masanari
Assistant Professor

Soft X-ray absorption spectroscopy (XAS) is an element specific method to reveal local structures of liquids with the K-edges of C, N, and O. We have developed a liquid flow cell for XAS of liquids in transmission mode, where liquid thickness is controllable from 20 to 2000 nm.¹⁾ Local structures of several liquid samples have been investigated from the precise energy shift analyses of XAS peaks with the help of inner-shell calculations.^{2,3)}

1. Microheterogeneity in Aqueous Acetonitrile Solution

In microheterogeneity (MH), two liquids are mixed in macroscopic scale but are inhomogeneous in microscopic scale. We have investigated one of the simplest MH systems, aqueous acetonitrile solution, by using XAS. Molecular interactions of acetonitrile were measured in C and N K-edges, and

those of solvent water were separately observed in O K-edge. The energy shifts of the C≡N π^* peaks in C K-edge XAS show three concentration regions and especially a phase transition-like behavior. By comparing the energy shifts of XAS peaks with the inner-shell calculations, we have revealed that the MH state emerges when small acetonitrile clusters are formed by surrounding water with dipole interactions. By increasing the molar fraction of water, the MH state is diminished when the small acetonitrile clusters are taken into hydrogen bond network of water.

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Award

NAGASAKA, Masanari; The 8th Young Scientist Award of National Institutes of Natural Sciences.

Spectro-Microscopic Analysis of Lithium in an Electrode of a Lithium-Ion Battery

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji
Assistant Professor

Nowadays, lithium is an important element especially used for a secondary battery. To analyze chemical state and distribution of lithium in the battery, a scanning transmission X-ray microscope (STXM) will be a promising tool but an absorption edge in low energy, 55 eV, makes it difficult. Then, main issues are contamination of spectra by a lot of higher harmonic

lights from a monochromator and extremely short focal length of an optical element, a Fresnel zone plate (FZP). Recently, we overcame these issues by designing a new FZP and succeeded to have an access to Li K-edge by STXM at BL4U. Parameters of the new FZP are as follows; diameter of 240 μm , outermost zone width of 60 nm, gold pattern of 100 nm thick on a silicon substrate of 200 nm thick. The new FZP works as not only a focusing device of the X-rays but also as a filter for higher harmonics above 100 eV by Si L-edge (99 eV) absorption. From evaluation of the new FZP, intensities of the

higher harmonics light from 2nd to 5th orders for Li K-edge range are suppressed less than 1% of the 1st order light. Then, spatial resolution is below 85 nm at 90 eV.

An ultra-thin section of an electrode of a lithium-ion battery was measured around Li K-edge. The X-ray absorption spectra of LiCO_3 were obtained.

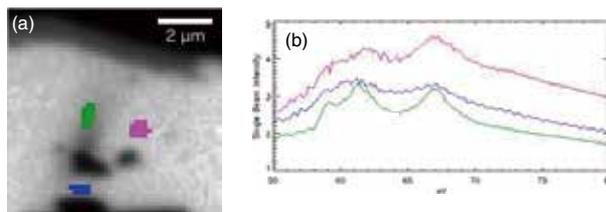


Figure 1. (a) Optical density image of an electrode of a lithium ion battery and (b) X-ray absorption spectra.

Reference

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Soft X-Ray Absorption Spectroscopy for Soft Matter

UVSOR Synchrotron Facility
Division of Advanced Photochemistry



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Assistant Professor

Recently we started to study soft matter with soft x-ray, whose energy region covers K-edge energies of light elements such as carbon, nitrogen and oxygen. Local chemical environments of liquid sample in a liquid cell¹⁾ was investigated by x-ray absorption spectroscopy (XAS).

1. Soft X-Ray Absorption Spectroscopy for Liquid-Crystal Materials

The liquid-crystal material is one of the most important soft matter. In addition to gas, liquid and solid phases, liquid-crystal materials have liquid-crystal phase between solid and liquid phases. In the case of nematic liquid-crystal phase, the rod-shaped organic molecules have no position order, but they

self-align to have long-range directional order with their long axes roughly parallel. To investigate a change of local chemical environments caused by a phase transition, we measured XAS spectra of liquid-crystal materials at carbon and nitrogen K edge in solid, liquid-crystal and liquid phases.

In XAS spectra at carbon and nitrogen K edges, we find several peaks which are corresponding to core excitations such as $1s\text{-to-}\pi^*$ core excitations. We assigned these peaks to each core excitations with the help of a quantum chemical program, StoBe. The peak intensities and structures of XAFS spectra are slightly different for each phase of sample. We obtained results suggesting that $\pi\text{-}\pi$ interactions of two molecules become weak after a phase transition from solid to liquid-crystal phases.

Reference

- 1) M. Nagasaka, H. Yuzawa and N. Kosugi, *J. Spectrosc. Relat. Phenom.* **200**, 293 (2015).

Visiting Professors



Visiting Professor
FUKUI, Ken-ichi (*from Osaka University*)

Ionic Liquid/Organic Semiconductor Interfaces for Efficient Carrier Transport

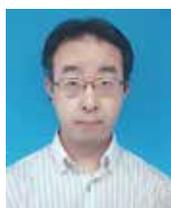
Local analyses of electrolyte/organic semiconductor electrode interfaces at controlled electrode potentials are of fundamental importance to understanding the origin and properties of the electric double layer (EDL) at the interfaces, which is necessary for their application to EDL-organic field effect transistors (OFETs). Ionic liquids (ILs) gated EDL-OFETs can be operated with ultralow voltage (~ 0.1 V), however, ILs sometimes cause operational instability due to their unusual interface structuring. By using an IL (EMIM-FSA) and rubrene crystal, IL-derived bias stress was observed, which increased operational voltage of the EDL-OFET by 33% in 2 h. Electrochemical FM-AFM and molecular dynamics (MD) simulation revealed that the formation of structured IL layer on the surface of hole-injected rubrene; anions in the IL monolayer probably trapped hole carriers by orienting their polar parts. Application of higher magnitude of OFF-state gate voltage reset the IL-derived bias stress immediately by separating the anion-hole pairs, but the same shift occurred in the same time scale by the local structural change of the interface.



Visiting Associate Professor
KANEYASU, Tatsuo (*from SAGA Light Source*)

Generation and Application of Structured Light in Synchrotron Light Sources

Novel undulators in synchrotron light sources can provide energy-tunable structured light at short wavelengths. We have been investigating the generation and application of structured light, such as vortex beams and vector beams, in the extreme ultraviolet (XUV) wavelength region in the UVSOR synchrotron facility. In exploring new applications of the structured light, a fundamental understanding of the light-matter interaction is crucial. We have investigated the characteristics of the structured light by using interference measurements and have applied it to the photoionization and photoexcitation study of rare-gas atoms. In addition, we started to study the potential of undulator radiation as longitudinally coherent wave packets suitable for the coherent control at short wavelengths. We are currently performing the coherent control experiments in photoexcitation of atoms using the undulator radiation in the XUV to soft x-ray range.



Visiting Associate Professor
KATSUKI, Hiroyuki (*from Nara Institute of Science and Technology*)

Coherent Control in Condensed Systems

Coherent control is a technique to manipulate quantum states of a target system utilizing the interference of wavefunctions. My research is focused on the coherent control in organic crystals and in strongly coupled systems. In the first case, we have recently demonstrated the control of multiple THz intramolecular oscillatory modes in a rubrene crystal. We are planning to apply this technique for the electronic excited states in which the electron-phonon interaction plays a key role in various physical properties such as carrier transportation and photoemission. In the second case, a typical example of the strong coupled system is a cavity exciton-polariton system, which is a mixture of cavity photons and atomic/molecular excitons. Cavity exciton-polaritons have gathered much attention due to its spontaneous formation of quantum coherence in the lowest energy ($k = 0$) state and succeeding coherent emission called polariton lasing, when the excitation fluence is above the threshold. We are now trying to artificially regulate the polariton flow towards the $k = 0$ state utilizing the stimulated scattering process.





RESEARCH ACTIVITIES

Materials Molecular Science

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

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science Division of Electronic Structure



YOKOYAMA, Toshihiko
Professor
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Education

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

Professional Employment

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

Member

Assistant Professor
KOITAYA, Takanori
YAMAMOTO, Kohei
Post-Doctoral Fellow
NAKAMURA, Takahiro
YU, Liwei
CHAVEANGHONG, Suwilai
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Graduate Student
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Secretary
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SHIBATA, Yuka
ISHIKAWA, Azusa

Keywords

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

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

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

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer

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

The third subject is the pico- and femtosecond pump-and-probe time resolved measurements using x-ray. Time-resolved x-ray absorption fine structure spectroscopy of photocatalysts WO_3 and BiVO_4 was performed and we have investigated those local geometric and electronic structures. Time-resolved measurement can be also applied to investigate the dynamics of magnetic materials with XMCD and other magneto-optical effects. We captured XMCD spectra of the photoinduced transient state. The real space image of magnetic domains can be retrieved from the diffraction patterns. We succeeded in capturing diffraction from magnetic domains and now considering the possibility of its application for time- and space-resolved imaging.

Within two years, two assistant professors Drs. Takagi and Uemura moved out and new assistant professors Drs. Koitaya and Yamamoto have joined our group. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation and lasers.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Uemura *et al.*, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).

1. Operando Observation of Sulfur Species Poisoning PEFC Studied by Near Ambient Pressure HAXPES¹⁾

PEFC is currently one of the most promising electrochemical energy conversion and storage technology. To achieve more highly efficient PEFC with longer life time, a continuous supply of more powerful materials and a further detailed understanding of the electrochemical properties of PEFC are essentially important. We have been investigating the degradation and poisoning mechanisms of PEFC using near ambient pressure *operando* HAXPES of PEFC under working conditions. We will here emphasize that the electric potentials of all chemical species in PEFC can be determined by HAXPES measurements and allow us to distinguish the location of the specimen; whether the S-containing species in PEFC is adsorbed on the electrode or solved in the electrolyte *etc.* In this work, we performed S 1s HAXPES measurements to observe sulfur species poisoning the PEFC cathode and anode electrodes, C-supported Pt nanoparticles in PEFC. Without artificial introduction of S-containing species, we observed several S species other than sulfonic acid group of Nafion: Anionic atomic S species adsorbed on the Pt nanoparticles, SO_3^{2-} in the electrolyte, and S in the C support. As a voltage applied between the cathode and anode increases, the adsorbed S species on the Pt nanoparticles at the cathode electrode are gradually diminished and completely disappear at ≥ 0.8 V due to oxidation reactions from adsorbed S to SO_3^{2-} and possibly SO_4^{2-} , but is reproduced with a decrease in the voltage. With oxygen introduction to the cathode electrode, no sulfur species except sulfonic acid group of Nafion were detected even at the lowest voltage. Schematic electric potential diagrams of the cathode, electrolyte and anode are depicted. Upon the voltage change, the electric double layer varies on the cathode, while it is kept constant (~ 1.0 V) on the anode. It is emphasized that the electric potentials of the chemical species observed by HAXPES can distinguish the location of the specimen; the SO_3^{2-} species is found not to be adsorbed on the electrode but to be solved in the electrolyte.

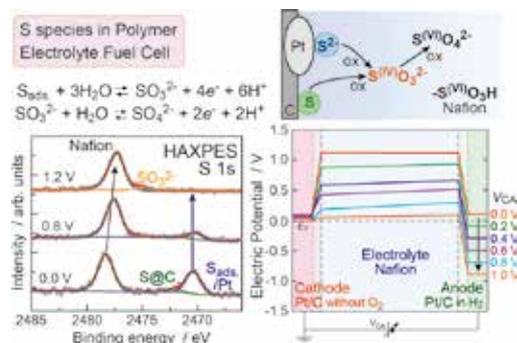


Figure 1. Various sulfur species observed in working PEFC that poison the electrode Pt nanoparticles. It is most important to note that HAXPES can determine the electric potentials of the electrolyte as well as the electrodes that are impossible fundamentally by any conventional electric method as probe contact *etc.*

2. Operando Observation of Methane Oxidative Coupling on Pd(110) by Soft X-Ray Ambient Pressure XPS

Chemical transformation of methane to valuable chemicals is an attracting but challenging research topic. Activation of inert methane molecules on metal or metal-oxide surfaces is an important process for catalytic conversion. In order to reveal reaction mechanisms of weakly adsorbed methane, spectroscopic measurements under ambient pressure condition are indispensable because of a small reactive sticking probability of methane. In this study, the oxidative coupling of methane to ethane on Pd(110) was investigated by ambient pressure soft x-ray photoelectron spectroscopy (XPS) and quadrupole mass spectroscopy (QMS). Figure 2(a) shows the QMS signal of produced ethane and the sample temperature as a function of elapsed time. The sample was exposed to 2.0 mbar O_2 and 5.7 mbar CH_4 throughout the entire experiment. The sample was first heated to 615 K (I). At this point, the reactivity of the sample was low, and the amount of produced ethane is negligible. The reactivity was significantly enhanced by temporary heating to 780 K. The produced ethane was clearly detected by QMS after cooling to 615 K (II). Figure 2(b) shows Pd 3d AP-XPS spectra at 615 K measured before and after heating the sample to 780 K. Observed three peaks were attributed to Pd oxide (PdO), oxygen-adsorbed Pd ($\text{O}_{\text{ad}}\text{-Pd}$), and metallic Pd (Pd). The relative intensity of the $\text{O}_{\text{ad}}\text{-Pd}$ and Pd peaks was increased after heating to 780 K, indicating partial reduction of the PdO thin film formed on Pd(110). These results show that the reactivity of Pd(110) significantly depends on the oxidation state of the surface; partially reduced PdO-Pd(110) is active for the methane oxidative coupling reaction.

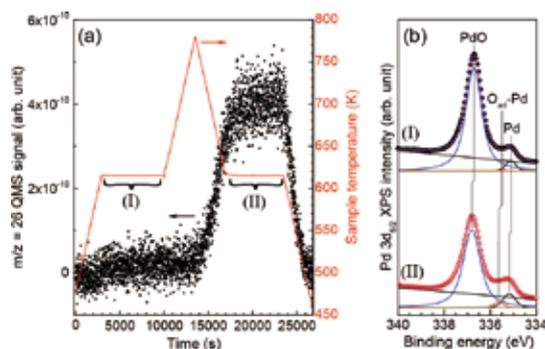


Figure 2. (a) The QMS signal of produced ethane ($m/z = 26$) and the sample temperature as a function of elapsed time. The Pd(110) sample was heated and cooled in the presence of 2.0 mbar O_2 and 5.7 mbar CH_4 gas mixture. AP-XPS measurements were performed at 615 K (I) and (II). (b) Pd 3d_{5/2} AP-XPS spectra ($h\nu = 1100$ eV) measured (I) before and (II) after heating the sample to 780 K. The sample temperature was kept at 615 K during the AP-XPS measurements.

Reference

- 1) L. Yu *et al.*, *J. Phys. Chem. C* **123**, 603–611 (2019).

* IMS International Internship Program

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Unique Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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Division of Electronic Structure



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Education

2007 B.S. Kyoto University
2011 Ph.D. The University of Tokyo

Professional Employment

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

Awards

2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
2014 39th Vacuum Science Paper Award
2018 PCCP Prize 2018
2018 CSJ Presentation Award 2018
2018 Encouragement Award, The Spectroscopic Society of Japan
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Secretary
YOKOTA, Mitsuyo

Keywords Water Molecule, Molecular Spectroscopy, Surface Science

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning probe microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used recently developed heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\text{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the hetero-

dine detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected $\text{Im}\chi^{(2)}$ SFG has a great advantage for direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

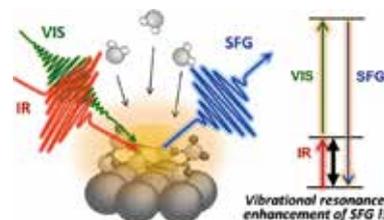


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, “Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film,” *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji *et al.*, “Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice,” *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- K. Shirai *et al.*, “Water-Assisted Hole Trapping at Highly Curved Surface of Nano-TiO₂ Photocatalyst,” *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- N. Aiga *et al.*, “Origins of Emergent High- T_c Ferroelectric Ordering in Heteroepitaxial Ice Film: Sum-Frequency Generation Spectroscopy of H₂O and D₂O Ice Films on Pt(111),” *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
- T. Sugimoto *et al.*, “Topologically Disordered Mesophase at Topmost Surface of Crystalline Ice Between 120 and 200 K,” *Phys. Rev. B* **99**, 121402(R) (2019).

1. Isotope Effects on Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Proton in Ice¹⁾

In the hydrogen-bond network of crystalline water ice, orientation of water molecules, *i.e.* configuration of protons, is strongly correlated and highly frustrated under the Pauling's ice rules. Materials with these constraints have a potential to exhibit dramatic and unusual responses to external stimuli. In fact, we have recently demonstrated that inversion-symmetry breaking at a heterointerface in isotope diluted HDO crystalline-ice film grown on Pt(111) induces high- T_c ferroelectric proton ordering.²⁾ However, the molecular-level origin of the emergent high- T_c ferroelectric ordering has been unclear.

We have tackled this problem to elucidate fundamental physics behind the heterointerface-induced ferroelectric proton ordering in the crystalline-ice film. Because an isotope shift in the critical temperature of ferro-to-paraelectric transition gives essential information about the mechanism of emergent ferroelectric ordering, we have conducted temperature programmed sum-frequency generation (SFG) spectroscopy of H₂O and D₂O ice films on Pt(111). Then, we found that the ferroelectric proton orderings in these films are extremely thermally robust: $T_c = 164$ K (H₂O) and 168 K (D₂O); these are more than twice as large as that of ferroelectric bulk ice XI ($T_c \sim 72$ K for H₂O, $T_c \sim 76$ K for D₂O). The observed small isotope shift in T_c of the ferroelectric ice films is beyond the conventional belief: High- T_c hydrogen-bonded ferroelectrics typically have large isotope shifts in T_c . This result indicates that not only nuclear quantum effects in the hydrogen-bond network of ice film but also the inter-adsorbate and adsorbate-substrate interactions at the ice/Pt interface are responsible for the thermal stability of ferroelectric ordering and its small isotope effect.

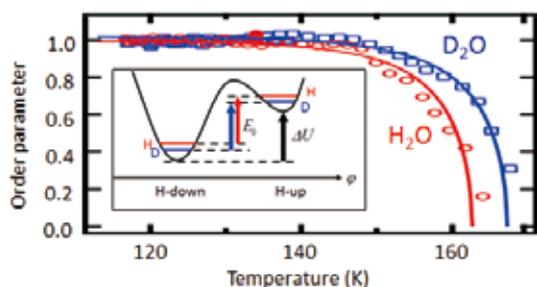


Figure 2. Temperature dependence of the ferroelectric order parameter of crystalline H₂O (red) and D₂O (blue) grown on Pt(111).

2. Unveiling Topologically Disordered Hydrogen-Bond Network at Surface Layer of Hexagonal Crystalline Ice^{3,4)}

The surface of crystalline water ice (hexagonal ice Ih) ubiquitous in nature plays a crucial role in a variety of phenomena in physics, chemistry, biology, geology, atmospheric and astronomical sciences. In 1859, Faraday first proposed that a layer of liquid water (quasi liquid) is present on the surface of crystalline ice below the bulk freezing temperature

of 273 K. Ever since, the nature of ice surface and the onset temperature of surface premelting have been intensely explored. Nowadays it is generally believed that the onset temperature of surface disordering of ice Ih is 200 K and the surface structure of ice Ih is perfectly ordered below this temperature. However, we have demonstrated for the first time that surface disordering of ice emerges at 120 K that is much lower than the traditionally believed premelting temperature of 200 K.

By combining surface-specific SFG spectroscopy and the state-of-the-art molecular dynamics simulations, we found that the topmost surface layer of ice Ih(0001) undergoes a cascade of structural transitions from solid to quasi-liquid phase via a liquid-crystal-like mesophase with a topologically disordered hydrogen-bond network between 120 and 200 K; this is in stark contrast to the traditional concept of premelting of ice surface as well as bulk melting of ice where a single first-order phase transition takes place from solid to liquid state at the melting temperature. Our result sheds new light on the effects of undercoordinated water molecules at the surface on melting behavior of ice and thus advances physics of two-dimensional surface phase transition of molecular crystal.

In addition, our finding casts profound impacts on many disciplines. Since the lower limit of temperature of the earth's atmosphere is ~ 120 K, the surface of crystalline ice Ih on earth is unlikely to be the perfectly ordered solid. The existence of glassy mesophase in the temperature range 120–200 K makes the structural and electronic features of ice surface in nature more inhomogeneous than they have ever been expected. The molecular-level structure and dynamics of ice surface clarified in the present study provide a new basis for elucidating the key properties of ice surface that are of great interest in a variety of heterogeneous processes in nature such as cloud seeding and electrification in atmosphere, catalytic destruction of Earth's ozone layer, and even molecular evolution in interstellar space.

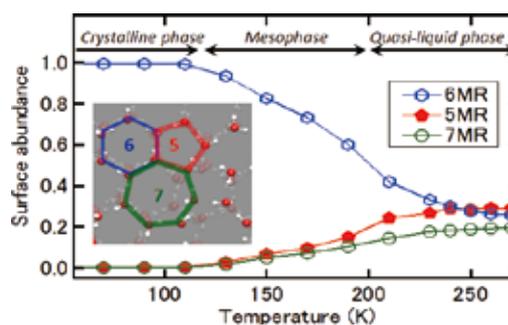


Figure 3. Temperature dependence of relative abundance of 5-, 6- and 7-membered rings at the topmost surface layer of hexagonal crystalline ice-Ih(0001).

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Magnetic Resonance Studies for Functional Molecular-Based Solids

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

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

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

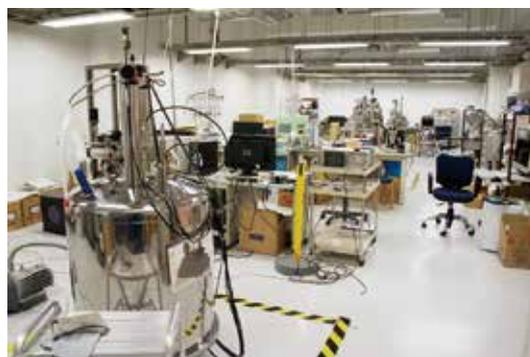


Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

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

Solid-state broad line $^1\text{H-NMR}$ (nuclear magnetic resonance) and ESR (electron spin resonance) were performed for an oxo-bridged dinuclear ruthenium $[\text{RuORu}]^{5+}$ ($\text{Ru}^{3.5+}\text{ORu}^{3.5+}$) mixed-valence complex. The $^1\text{H-NMR}$ spin-lattice relaxation rate T_1^{-1} was significantly enhanced, to below 100 K with a peak at approximately 33 K. The T_1^{-1} peak temperature was frequency-independent, indicating that this anomaly is a possible phase transition. Below approximately 40 K, an abrupt decrease of $^1\text{H-NMR}$ spin-spin relaxation time T_2 provides evidence of the appearance of inequivalent ^1H -sites (sudden decrease in symmetry). ESR spectra suddenly disappeared above 35 K. The electronic properties and possible charge ordering ($\text{Ru}^{3+}\text{ORu}^{4+}$) states in this mixed-valence compound are discussed from a microscopic point of view.

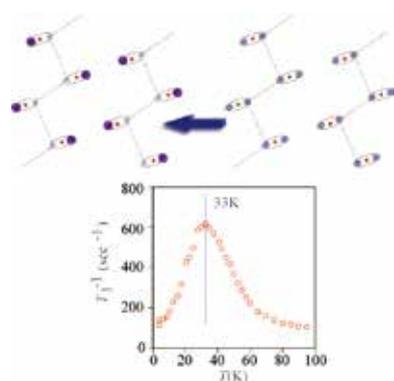


Figure 2. Temperature dependence of the $^1\text{H-NMR}$ spin-lattice relaxation rate T_1^{-1} of the $[\text{RuORu}]^{5+}$ complex. A schematic diagram of the ac -plane: The inter-molecular Ru–Ru interactions between each dinucleus are described here. Possible schematic charge configuration within the ac -plane below 33 K. Color code: Ru^{3+} , dark blue; Ru^{4+} , gray; $\text{Ru}^{3.5+}$, blue; O, red.

2. Effect of Cu Intercalation and Pressure on Excitonic Interaction in $1T\text{-TiSe}_2$

$1T\text{-TiSe}_2$ has a semimetallic band structure at room temperature and undergoes phase transition to a triple- q charge density wave (CDW) state with a commensurate superlattice structure ($2a \times 2a \times 2c$) below $T_c \approx 200$ K at ambient pressure. This phase transition is caused by cooperative phenomena involving electron–phonon and electron–hole (excitonic) interactions, and cannot be described by a standard CDW framework. By Cu intercalation or the application of pressure, this phase transition temperature is suppressed and superconductivity (SC) appears. However, it is not clear what kinds of order parameters are affected by these two procedures. We investigated the crystal structure of Cu_xTiSe_2 and pressurized $1T\text{-TiSe}_2$ around the SC state by synchrotron x-ray diffraction on single crystals. In the high-temperature phase, the variation of structural parameters for the Cu intercalation and application of pressure are considerably different. The relationship between the critical points of the CDW phase transition and

the SC dome are also different. The excitonic interaction appears to play an important role in the P – T phase diagram of $1T\text{-TiSe}_2$, but not in the x – T phase diagram.

3. Honeycomb Lattice Type CDW Formed by Cooperative Interaction in Cu Intercalated $1T\text{-TiSe}_2$

$1T\text{-TiSe}_2$ has attracted attention as an excitonic insulator. However, since the phase transition accompanying superlattice peaks has the q -vector connecting the Fermi surfaces of the three-dimensional shape of hole- and electron-pockets, it also suggests the CDW state due to the electron–phonon interaction. In order to understand the electronic state at the low-temperature, the control of chemical potential was attempted by electronic doping by Cu^+ intercalation. It has been found that phase transition occurs as a cooperative phenomenon between the honeycomb lattice type CDW corresponding to the nesting vector and the ordered state of the Cu^+ ions between TiSe_2 layers at a specific doping amount. The behavior of Cu^+ ions in highly doped regions suggests the two-dimensional liquid–solid state transition from the temperature dependence of the x-ray diffuse scattering.

4. Synthesis of a Protected Ribonucleoside Phosphoramidite-Linked Spin Label via an Alkynyl Chain at the 5' Position of Uridin

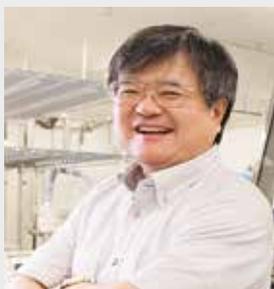
New spin-labeled nucleosides and an efficient synthetic route for the modified uridine amidite were developed. The spin-labeled part was the 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) group, and TEMPO was linked via an alkynyl chain at the 5' position of uridine. Three typical protecting groups, such as the *t*-butyldimethylsilyl (TBDMS) group at 2', the dimethoxytrityl (DMTr) group at 5', and the phosphoramidite group at 3', were introduced to induce an automated nucleic acid synthesizer. The TEMPO group at the 5' position in the uridine structure affected the introduction of the bulky protecting groups, such as the DMTr group at the 5' position and the TBDMS group at the 2' position. The EPR data revealed the presence of a nitroso radical in the structure of synthetic nucleoside compounds; however, RNA synthesized by an automated synthesis using TEMPO linked uridine phosphoramidite building block which was protected by TBDMS at 3' and DMTr at 5' was EPR silent.

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Organic Solar Cells

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Keywords Organic Semiconductors, Organic Solar Cells, ppm-Doping

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

So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching 10^{-9} nm s⁻¹ (Figure 1), in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of

open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.

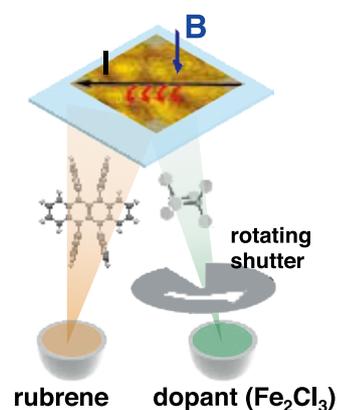


Figure 1. Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

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1. Lateral Multilayered Junction for Organic Solar Cells¹⁾

Bulkheterojunctions (blended junctions) are indispensable for organic solar cells. However, the fabrication of electron and hole transport routes in blended junction remains quite challenging. We proposed a novel concept of the structure of organic solar cell, namely, a lateral alternating multilayered junction (Figure 2). An essential point is that the photo-generated holes and electrons are laterally transported and extracted to the respective electrodes.

Minimum units of proposed junction are hole highway and electron highway. At first, we demonstrated that lateral extraction of photogenerated holes and electrons of the order of 1 mm in the hole and electron highways using ultra-high mobility organic films. Observed macroscopic value of milli-meter order is surprising long compared to the conventional value below 1 μm . Next, we demonstrated the successful operation of organic solar cell having a lateral alternating multilayered junction by combining the hole highway and electron highway. A total of 93% of the photogenerated electrons and holes are laterally collected over a surprising long distance (0.14 mm). The exciton-collection efficiency reaches 75% in a lateral alternating multilayered junction with a layer thickness of 10 nm. Therefore, the lateral junction is proved to have an ability to collect both excitons and carriers almost completely.

A lateral alternating multilayered junction can be regarded to be an alternative blended junction for organic solar cells. Advantage of a lateral cell is its unlimited thickness in the vertical direction. Therefore, tandem solar cells that can utilize the full solar spectrum can be freely designed. The present new concept paves the way to exceed the conversion efficiency of organic solar cells above 20%.

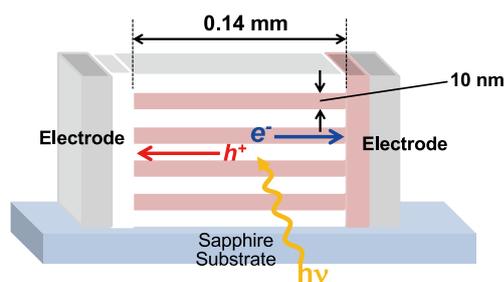


Figure 2. Lateral alternating multilayered junction. Present junction has layer thickness of 10 nm and lateral distance of 0.14 mm, *i.e.*, aspect ratio reaches 1.4×10^4 .

2. Organic *pn*-Homojunction Solar Cell²⁾

Formation of *pn*-homojunction in a single semiconductor material through doping is key for photocurrent generation in inorganic solar cells. In contrast, a donor/acceptor heterojunction is generally utilized in organic solar cells to split coulombically bound exciton forming in organic semiconductors. We reported an organic *pn*-homojunction solar cell showing high internal quantum efficiency of about 30%. *pn*-homojunction was created by co-deposition of *p* or *n* type dopants and an organic semiconductor. An increase of the photocurrent density by more than 8 times, from the undoped device to *pn*-homojunction device with 5% doping, was observed. The increase of photocurrent due to charge separation assisted by the built-in potential near the *pn*-homojunction interface that was controlled by doping concentration (Figure 3). The result demonstrated that the *pn*-homojunction interface in a single organic semiconductor layer formed by doping can achieve efficient charge separation and provide a suitable alternative to the donor/acceptor interface that has been considered necessary for photoconversion in organic solar cells.

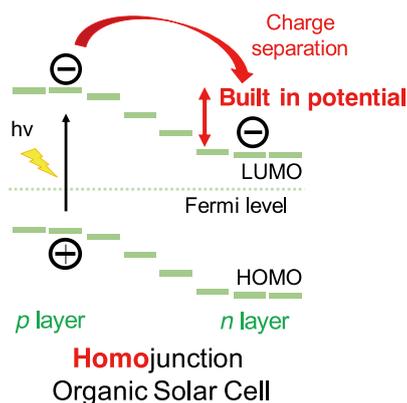


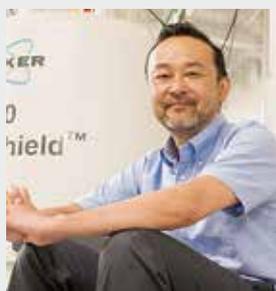
Figure 3. Schematic diagram of the working mechanism of organic *pn*-homojunction solar cells.

References

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Solid-State NMR for Molecular Science

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Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to 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 application to structural biology and materials science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

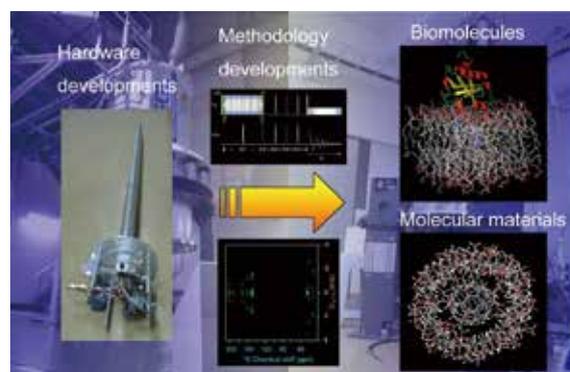


Figure 1. Outline of our studies.

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- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C- δ 1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
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1. Characterization of Fluorinated Synthetic Polymer Based on Solid-State NMR¹⁾

We have collaborated with a research group of Prof. Hiroki Fukumoto in Ibaraki university for the characterizations of fluorinated polymers newly designed in his group. Molecular design of polyaromatic hydrocarbons with fluorine unit is one of the central themes in investigation of functionalized organic materials such as *n*-type organic semiconductors and polymers for electronic devices. They have successfully developed new schemes of synthesis and copolymerization of fluorinated phenanthrene derivatives with hydroxyl groups based on the Mallory reaction using commercially available octafluorocyclopentene (OFCP). Since final polymers are insoluble in any organic solvents, we have utilized solid state NMR to characterize a polymerization state of this compound.

¹⁹F possesses as large a gyromagnetic ratio as ¹H. Therefore, ¹⁹F-X hetero-, and ¹⁹F homonuclear dipolar couplings are as large as those for ¹H. In order to observe ¹³C spectra in the presence of ¹⁹F, it is essential to decouple ¹⁹F during ¹³C detection, which requires a ¹H-¹⁹F-¹³C triple resonance probe. Since a ¹⁹F resonance frequency is very close to that for ¹H, it is usually difficult to isolate ¹H and ¹⁹F channels well. Therefore, although a ¹H-¹⁹F-X triple resonance probe is commercially available, it is commonly significantly expensive and their performances are limited. In addition, we do not possess such a probe. In order to overcome those problems, we have used high-speed magic angle spinning (MAS) techniques to attenuate ¹⁹F homonuclear- and ¹⁹F-¹³C heteronuclear dipolar couplings as much as possible.

¹³C observed solid-state NMR measurements for all the raw materials and polymers were carried out at spinning speed of 20 kHz using a ¹H-¹³C-¹⁵N triple resonance probe with an outer diameter of 2.5 mm at the ¹H-¹³C double resonance mode. ¹³C solid-state NMR spectra for the raw materials exhibited quite sharp signals, suggesting homogeneous local structures. In contrast, those for polymers showed broad signals, suggesting inhomogeneous local structures. Unfortunately, 2D correlation experiments were unable to be performed due to low sensitivity to the polymers. Only ¹³C signals for the carbons directly attached to fluorine disappeared due to the strong ¹³C-¹⁹F heteronuclear dipolar couplings. However, most of the observed ¹³C signals were successfully assigned based on a variety of 1D NMR spectra in combination of spectral editing techniques. Based on those analyses, the polymerization state of fluorinated phenanthrene derivatives was successfully characterized.

In addition, we have been working on collaboration work with two other research groups for the characterization of newly designed materials based on solid-state NMR.

2. Development of Solid-State NMR Probe

We have built a variety of solid-state NMR probes such as static and MAS probes for 400 MHz NMR, and a variable temperature MAS probe for 920 MHz ultra-high field NMR so far. Most of these probe buildings were achieved through major modifications of commercial probes. Since last year, we have been working on building an original solid-state NMR

probe which is fully compatible with commercial instruments currently used. Probe developments enable us to reduce costs for acquiring probes and open up possibilities to design new experiments which are tightly related to specifically designed hardware. Currently, we are building a solid-state ¹H-X double resonance MAS probe. It will be extended to triple resonance probes for ¹H-¹³C-¹⁵N. In the near future, we would like to incorporate special functions into our original probes.

3. Structural Characterization of Amyloid β Protein Oligomer Promoted on Lipid Bilayers Using Solid-State NMR

Amyloid β (A β) protein is disordered in solutions under diluted conditions, however it conforms insoluble amyloid fibrils, which are found in senile plaque as a hallmark of Alzheimer's disease. Although molecular structures of amyloid fibrils have been determined, its molecular process for fibrillation in vivo has not been clarified yet. However, accumulated evidences suggest that the fibrillation process may be promoted on neuronal cell membrane. Especially, it has been reported that A β specifically interacts with ganglioside GM1 which is one of the key lipids in lipid raft. Therefore, GM1 embedded into lipid bilayers composed of neutral lipid DMPC may be regarded as the most simplified model neuronal cell membrane. In order to clarify the role of GM1 in the fibrillation process, first, we have successfully determined the oligomeric structure of A β (1-40) induced on DMPC bilayers based on solid-state NMR.²⁾

In the current study, to clarify the contribution of GM1 in the fibrillation process, we have attempted to characterize the oligomeric structure of A β (1-40) bound to lipid bilayers consisting of GM1 and DMPC. In order to achieve reliable signal assignments, we have re-examined ¹³C-¹⁵N heteronuclear solid-state NMR correlation experiments because of low sensitivities for previously obtained spectra. Then the signal assignments have been completed together with 2D ¹³C homonuclear correlation data. Analysis of the secondary structure of A β based on the chemical shifts of assigned signals revealed that a disordered N-terminus was followed by two β -sheet structures from the middle region to the C-terminus. Comparison of secondary structures of A β in the absence and presence of GM1 in lipid bilayers suggests that the β -sheet structure in the middle region may be promoted through the interaction with GM1. In order to clarify intermolecular packing, ¹³C space through homonuclear correlation experiments were carried out at various mixing times for the sample with spin labeled A β at the C-terminus. The correlation spectra for spin labeled sample, Ser²⁶ signal clearly disappeared, suggesting the close location of Ser²⁶ residue and C-terminal spin center. Based on the obtained data, a molecular packing model is currently under construction.

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

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Education

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2010 D.S. Tokyo Institute of Technology

Professional Employment

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2011 Assistant Professor, Kanagawa University
2012 JST-PRESTO Researcher (Additional post)
2013 Research Associate Professor, Institute for Molecular Science
2018 Associate Professor, Institute for Molecular Science
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Awards

2010 ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011 Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018 The 39th Honda Memorial Young Researcher Award, The Honda Memorial Foundation
2018 The 7th Ishida Award, Nagoya University
2019 Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan

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Keywords Solid State Ionics, H⁻ Conductor, Battery

Chemical energy conversion/storage using electrochemical devices such as fuel cells and batteries will become increasingly important for future sustainable societies. As ion transport in solids is key for determining the performance of these devices, an improved understanding of the characteristics of existing electrode and electrolyte materials is required. For example, crystal structure, thermal stability, and reaction mechanisms are important to enhancing battery performance. Furthermore, the development of novel ion conduction phenomena through the synthesis of a new class of substances will be expected to lead to the creation of novel battery systems. In this context, I have concentrated my research efforts into two main areas: (i) Studies into the reaction mechanisms of cathodic materials for lithium secondary batteries; and (ii) The synthesis of new materials exhibiting hydride ion (H⁻) conductivity and the development of a novel battery system utilizing both the H⁻ conduction phenomenon and the H⁻/H₂ redox reaction.

Selected Publications

- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- G. Kobayashi, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**(2), 88–92 (2017).
- Y. Iwasaki, N. Matsui, K. Suzuki, Y. Hinuma, M. Yonemura, G. Kobayashi, M. Hirayama, I. Tanaka and R. Kanno, *J. Mater. Chem. A* **6**, 23457–23463 (2018).
- F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi, *Inorg. Chem.* **58**, 4431–4436 (2019).
- N. Matsui, G. Kobayashi, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).

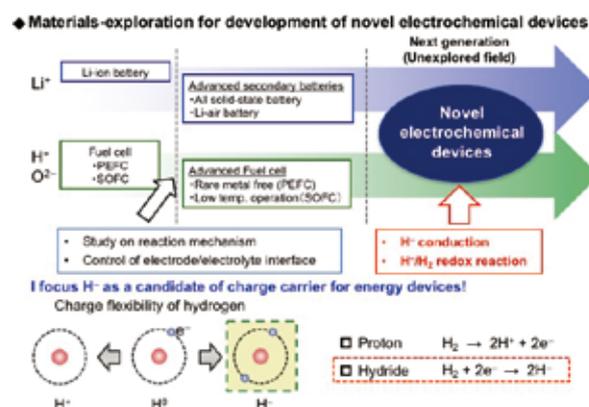


Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

1. Study on H⁻ Conductive Oxyhydrides¹⁻⁴⁾

Ionic charge carriers include a variety of species, such as Li⁺, H⁺, Ag⁺, Cu⁺, F⁻, and O²⁻, and their conductors have found applications in energy devices such as fuel cells and batteries. The conduction of hydride ions, H⁻, is also attractive. These are similar in size to oxide and fluoride ions and show strong reducing properties with a standard redox potential of H⁻/H₂ (-2.3 V) which is close to that of Mg/Mg²⁺ (-2.4 V). Hydride ion conductors may therefore be applied in energy storage/conversion devices with high energy densities. Here, we prepared a series of K₂NiF₄-type oxyhydrides, La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}, which are equipped with anion sublattices that exhibit flexibility in the storage of H⁻, O²⁻, and vacancies (Figure 2). An all-solid-state Ti/La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}/TiH₂ cell showed a redox reaction with hydrogen storage/desorption on the electrodes. The present success in the construction of an all-solid-state electrochemical cell exhibiting H⁻ diffusion confirms not only the capability of the oxyhydride to act as an H⁻ solid electrolyte but also the possibility of developing electrochemical solid devices based on H⁻ conduction.

More recently, we synthesized Ba₂SchO₃, a novel H⁻ conductive Sc-oxyhydride with the K₂NiF₄-type structure and confirmed its unique site selectivity for H⁻. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba₂SchO₃ selectively occupied the rock salt layer, in contrast to those of the observed isostructural Li-based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). This result indicated that anion arrangements in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H⁻ conducting materials.

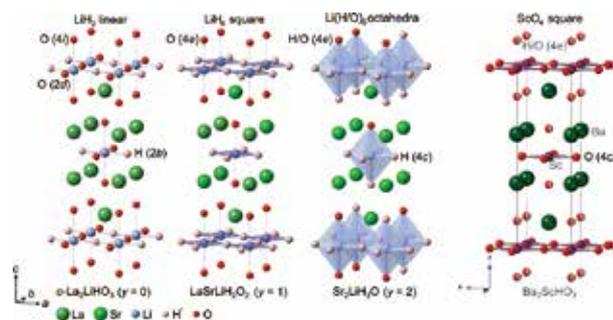


Figure 2. Crystal structures of H⁻ conductive oxyhydrides La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} ($x = 0, y = 0, 1, 2$) and Ba₂SchO₃.

2. High-Performance of Li-Rich Layered Cathode Materials through Al₂O₃-Surface Modification⁵⁾

Awards

KOBAYASHI, Genki; Tagawa Solid State Chemistry Awards (2019).

KOBAYASHI, Genki; 7th Ishida Award (2018).

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 Al₂O₃-coated Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ 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_xO₂ ($M =$ transition metals) interlayer was formed between the modification layer and the Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ particles (Figure 3). The cycling performance of the Li-rich layered oxide was enhanced by the surface modification with Al₂O₃. 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.

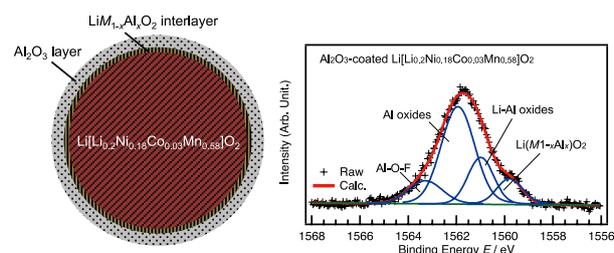


Figure 3. Schematic illustration and Al 1s HAXPES spectra of the 2 wt% Al₂O₃-coated Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ particle.

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- 2) N. Matsui, G. Kobayashi*, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- 3) A. Watanabe, G. Kobayashi*, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**, 88–92 (2017).
- 4) G. Kobayashi*, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno*, *Science* **351**, 1314–1317 (2016).
- 5) G. Kobayashi*, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).

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Visiting Professors



Visiting Professor

KISHINE, Jun-ichiro (*from The Open University of Japan*)

Theoretical Studies on Chiral Material Science

The concept of chirality is ubiquitous in natural sciences. However, until only recently, research fields on chirality had been fragmented into separated branches of physics, chemistry and biology. Even inside physics, a term “chiral” has been used in different meanings in condensed matter and high-energy physics. One of the most important mission of our project, on which the present workshop is based, is to integrate the scattered concepts of chirality and make a roadmap toward an attempt at synthesis of chiral material sciences. Let us remind the Laurence Barron’s definition of the true chirality, *i.e.*, true chirality is shown by systems existing in two distinct enantiomeric states that are interconverted by space inversion, but not by time reversal combined with any proper spatial rotation. The space inversion is a matter of geometrical symmetry, while time reversal is a matter of dynamical motion. This unambiguous definition clearly indicates that the concept of chirality ties geometry and dynamics. Conversion of geometry into dynamics naturally leads to material functionalities. The main purpose of this research project is to integrate these concepts in a unified manner.



Visiting Associate Professor

FURUKAWA, Ko (*from Niigata University*)

Electron Spin Dynamics of the Functional Materials

To develop the high-efficiency molecule-based device, it’s vital to clarify the mechanism of the functional molecules/materials. We investigate the mechanism of the solid-state functional materials in terms of the advanced electron spin resonance (ESR) spectroscopy such as high-field/high-frequency ESR, pulsed-ESR, time-resolved ESR, and so on. In recently, my main targets are the photo-induced conductivity/magnetic materials composed of a donor–acceptor (D–A) dyad. The charge-separated (CS) state induced by the electron transfer from the donor to the acceptor after the photolysis plays an important role of the functional efficiency of the photo-induced conductivity/magnetic properties. We investigated the CS state in the D–A dyad in terms of the spin dynamics by using the time-resolved ESR spectroscopy.



Visiting Associate Professor

OSHIMA, Yugo (*from RIKEN*)

Electron Spin Resonance Studies of a Bilayer-Type Molecular Ferromagnet (Et-4BrT)[Ni(dmit)₂]₂

Recently, several novel bilayer-type molecular magnets X[Ni(dmit)₂]₂, where dmit is 1,3-dithiol-2-thiole-4,5-dithiolate and X is a monovalent cation, have been developed by Kusamoto Group and Yamamoto Group in IMS. By taking the advantages of molecular design and the degree of freedom of the molecular arrangements, these novel molecular magnets take a bilayer structure, and the intralayer exchange interactions can be controlled by just substituting the asymmetric cation X. (Et-4BrT)[Ni(dmit)₂]₂ is one of these novel bilayer molecular magnets, which becomes a ferromagnet below 1 K. However, the magnetic moment only shows the half of the full saturation, and the mechanism of the ferromagnetism in this system is still under debate. In collaboration with Kusamoto Group and Yamamoto Group, we have studied the microscopic magnetic properties of (Et-4BrT)[Ni(dmit)₂]₂ by means of ESR spectroscopy. We have found that the ESR origin is only from one of the two layers and the other layer remains non-magnetic up to 24 T.



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

Bioinorganic Chemistry of Metalloproteins Responsible for Signal Sensing

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Keywords Bioinorganic Chemistry, Metalloproteins, Sensor Protein

Gas molecules such as O₂, NO, CO and ethylene are present in the environment and are endogenously (enzymatically) produced to act as signaling molecules in biological systems. Sensing these gas molecules is the first step in their acting as signalling molecules. Sensor proteins are usually required. Input signals generated by gas sensing have to transduce to output signals that regulate biological functions. This is achieved by biological signal-transduction systems. Recognition of the cognate gas molecules is a general mechanism of functional regulation for gas-sensor proteins. This induces conformational changes in proteins that controls their activities for following signal transductions. Interaction between gas molecules and sensor proteins is essential for recognition of gas molecules. Metal-containing prosthetic groups are widely used. In my research group, our research focuses on heme-based gas-sensor proteins and the signalling systems working with them.

The prosthetic group heme acts as the active center of hemeproteins that show a variety of functions, including O₂ or NO storage/transport, electron transfer, redox catalysis of various substrate, and dehydration of aldoxime. In the present

context, it acts as the active site for sensing of diatomic gas molecules such as NO, O₂, and CO. These gas molecules are able to bind to heme iron as an axial ligand, which is a reason why heme can be adapted as the active center for sensing gas molecules. Heme-based gas-sensor proteins constitute a major group in the gas-sensor proteins. Binding of a cognate gas molecule to heme is the initial step for gas sensing, which is followed by the signalling processes. The binding affinities of gas molecules, that measures of the sensitivities of the sensor proteins, can be controlled by heme environmental structures. Differences in the heme coordination structure of the axial ligand(s) and/or of interaction(s) between the heme-bound gas molecule and surrounding amino acid residue(s) in a heme pocket play important roles. They not only regulate the binding affinities of gas molecules but also discriminate one cognate effector gas molecule from others, allowing the sensor to respond with the proper signal transductions. We have been elucidating the relationships of structures and functions of heme-based sensor proteins by crystallographic, biochemical, biophysical, and molecular biological studies.

Selected Publications

- A. Pavlou, H. Yoshimura, S. Aono and E. Pinakoulaki, "Protein Dynamics of the Sensor Protein HemAT as Probed by Time-Resolved Step-Scan FTIR Spectroscopy," *Biophys. J.* **114**, 584–591 (2018).
- A. Pavlou, A. Loullis, H. Yoshimura, S. Aono and E. Pinakoulaki, "Probing the Role of the Heme Distal and Proximal Environment in Ligand Dynamics in the Signal Transducer Protein HemAT by Time-Resolved Step-Scan FTIR and Resonance Raman Spectroscopy," *Biochemistry* **56**, 5309–5317 (2017).
- N. Muraki, C. Kitatsuji, M. Ogura, T. Uchida, K. Ishimori and S. Aono, "Structural Characterization of Heme Environmental Mutants of CgHmuT that Shuttles Heme Molecules to Heme Transporters," *Int. J. Mol. Sci.* **17**, 829 (2016).
- N. Muraki and S. Aono, "Structural Basis for Heme Recognition by HmuT Responsible for Heme Transport to the Heme Transporter in *Corynebacterium glutamicum*," *Chem. Lett.* **45**, 24–26 (2015).
- C. Kitatsuji, M. Ogura, T. Uchida, K. Ishimori and S. Aono, "Molecular Mechanism for Heme-Mediated Inhibition of 5-Aminolevulinic Acid Synthase 1," *Bull. Chem. Soc. Jpn.* **87**, 997–1004 (2014).
- Y. Okamoto, H. Sawai, M. Ogura, T. Uchida, K. Ishimori, T. Hayashi and S. Aono, "Heme-Binding Properties of HupD Functioning as a Substrate-Binding Protein in a Heme-Uptake ABC-Transporter System in *Listeria monocytogenes*," *Bull. Chem. Soc. Jpn.* **87**, 1140–1146 (2014).

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

Hydrogenases are metalloenzymes that catalyze the oxidation of H_2 into electrons and protons and the reduction of protons into H_2 reversibly, which are expected as biocatalysts for fuel cells and H_2 production for clean and sustainable energy. Based on the differences of metal content and the structure of the active site, they are classified into three groups: FeFe-, NiFe-, and Fe-hydrogenases containing a dinuclear Fe unit linked to a [4Fe-4S] cluster, a hetero dinuclear Ni-Fe cluster, and a mononuclear Fe center, respectively. In addition to the enzymatic function of hydrogenases, some hydrogenase that is classified as a regulatory hydrogenase (RH) acts as a molecular hydrogen sensor.

RH consists of two subunits, a large subunit containing the Ni-Fe dinuclear complex and a small subunit containing iron-sulfur clusters. Though the Ni-Fe dinuclear complex in the large subunit is assumed to be the active site for H_2 sensing by RH, the molecular mechanisms of biosynthesis and maturation of the Ni-Fe dinuclear complex are not clear yet.

CO and CN^- ligands are coordinated to the Fe in the Ni-Fe dinuclear complex in RH. These CO and CN^- are biosynthesized and assembled into the metal clusters, for which several accessory and chaperone proteins are required. It is reported recently that HypX protein is responsible for CO biosynthesis for the maturation of Ni-Fe hydrogenases including RH, but the detailed molecular mechanism of CO biosynthesis by HypX is not elucidated. We are now elucidating the structural and functional relationships of the accessory protein HypX responsible for the construction of the Fe(CO) unit in the Ni-Fe dinuclear complex in RH. We have obtained single crystals of HypX and determined the crystal structure.

HypX consists of the N-terminal (residues 1-270) and the C-terminal (residues 289-542) domains with the C-terminal tail (residues 543-562) as shown in Figure 1. The N- and C-terminal domains are linked by a loop (residues 271-288). The N-terminal domain is composed of two subdomains, subdomains A (residues 1-151) and B (residues 182-270), which are linked by a long loop (residues 152-181). The subdomain A consists of six β -strands and five α -helices. It

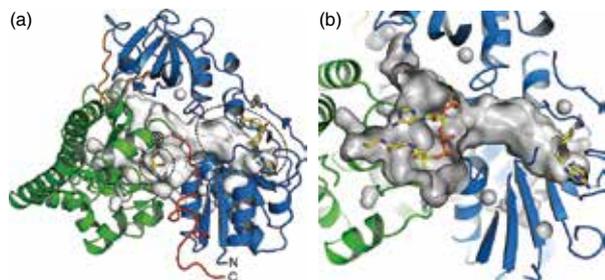


Figure 1. (a) Overall structure of HypX, in which the N-terminal domain (blue) and the C-terminal domain (green) are linked by a loop (orange). The cavity is shown in gray. (b) A sectional view of the cavity. CoA and THF are shown in the stick model.

forms a Rossmann-fold with a mixed parallel β -sheet, which is constructed by six β -strands that is sandwiched by two sets of two α -helices. The subdomain B has a barrel-helix framework as an oligonucleotide/oligosaccharide-binding (OB) fold consisting of six β -strands and one α -helix, in which six β -strands form an open barrel-like structure.

A continuous cavity connecting the N- and C-terminal domains is present in the interior of HypX. Coenzyme A (CoA) is bound in the C-terminal region of the cavity with a “folded conformation” in which adenine and pantetheine groups are stacked in parallel. The HypX-THF complex has been obtained by soaking HypX crystals with THF. THF is bound at the N-terminal region inside the cavity.

The crystallographic analyses reveal that HypX consists of the N- and C-terminal domains that are structurally homologous to the hydrolase domain of N^{10} -formyl-tetrahydrofolate (N^{10} -formyl-THF) dehydrogenase (FDH) and enoyl-CoA hydratase/isomerase (ECH/ECH), respectively. The comparison of amino acid sequences and crystal structures between HypX and FDH reveals that His and Asp among the catalytic triad are conserved at the corresponding positions (His74 and Asp109 in HypX). Though Ser among the catalytic triad is not conserved in HypX, Asp80 forms a hydrogen bond with τN of His74, which fixes the orientation of His74 as does Ser106 in FDH. Asp80 not only sustain a functional role for the fixation of the orientation of His74 but may enhance the catalytic activity of Asp109 through the hydrogen bonding network among His74, Asp80, and Asp109. Thus, HypX adopts a slightly modified catalytic triad for formyl-group transfer reaction. While 4-phosphopantetheine in ACP accepts formyl group from N^{10} -formyl-THF in the case of FDH, CoA will do so for HypX because it has the phosphopantetheine moiety identical to ACP.

While CoA adopts the folded conformation in HypX, an “extended conformation” of CoA, in which the ADP and pantetheine moieties are extended in a linear fashion, is observed in some CoA-dependent enzymes. We examined whether the extended conformation of CoA was also available in HypX and found that CoA is able to adopt the extended conformation in the A392F-I419F variant. Ala392 and Ile419 are located near the pantetheine moiety of the folded form of CoA, whose positions correspond to “a neck of a bottle” accommodating the pantetheine moiety of CoA in the folded form. Replacing Ala392 and Ile419 with Phe will narrow “the neck of a bottle,” which will destabilize the folded conformation of CoA by a steric hindrance to make the extended conformation of CoA more favorable because the residues 392 and 419 are no longer interacting with the pantetheine moiety of CoA in the extended conformation. In fact, we have found that CoA in the A392F-I419F variant adopts the extended conformation. Taken together, we propose the following reaction scheme of CO biosynthesis by HypX. HypX will catalyze two consecutive reactions, the formyl-group transfer from N^{10} -formyl-THF to CoA and decarbonylation of formyl-CoA, in the N- and C-terminal domains, respectively, to produce CO.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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Professor, The Graduate University for Advanced Studies
2006 Visiting Professor, Ochanomizu University
2013 Project Leader, JSPS Grant in Aid for Scientific Research on Innovative Areas “Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions”
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Awards

2000 The Pharmaceutical Society of Japan Award for Young Scientists
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Keywords Biomolecule Organization, NMR

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

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

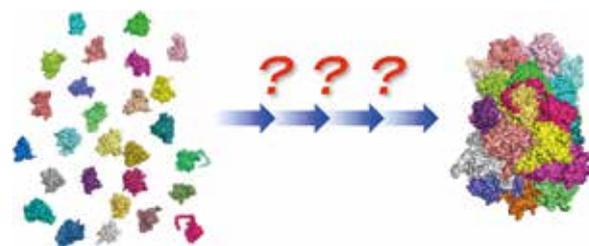


Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

dynamic structures and interactions of biomolecules at atomic level, in conjunction with the methodologies of molecular and cellular biology along with synthetic and computational technique.

Selected Publications

- S. Yanaka, R. Yogo, R. Inoue, M. Sugiyama, S. G. Itoh, H. Okumura, Y. Miyanoiri, H. Yagi, T. Satoh, T. Yamaguchi and K. Kato, “Dynamic Views of the Fc Region of Immunoglobulin G Provided by Experimental and Computational Observations,” *Antibodies* **8**, 39 (2019).
- T. Sekiguchi, T. Satoh, E. Kurimoto, C. Song, T. Kozai, H. Watanabe, K. Ishii, H. Yagi, S. Yanaka, S. Uchiyama, T. Uchihashi, K. Murata and K. Kato, “Mutational and Combinatorial Control of Self-Assembling and Disassembling of Human Proteasome α Subunits,” *Int. J. Mol. Sci.* **20**, 2308 (2019).
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- H. Yagi, S. Yanaka and K. Kato, “Structure and Dynamics of Immunoglobulin G Glycoproteins,” in *Glycobiophysics*, Y. Yamaguchi and K. Kato, Eds., Springer Nature; Singapore, pp. 219–235 (2018).
- T. Satoh and K. Kato, “Structural Aspects of ER Glycoprotein Quality-Control System Mediated by Glucose Tagging,” in *Glycobiophysics*, Y. Yamaguchi and K. Kato, Eds., Springer Nature; Singapore, pp. 149–169 (2018).

1. Exploration of Protein Assembly Dynamics

We characterized a variety of protein assembly systems using an integrative biophysical approach to provide deeper insights into the biomolecular organization. One of the most striking examples of sophisticated protein assembly is the formation of the proteasome, which is a huge enzyme complex harboring four layers of heteroheptameric rings (*i.e.*, two α and two β rings). We focused on the mechanisms underlying the formation of the α ring that comprises seven different but homologous α subunits. They are correctly assembled via transient interactions with assembly chaperones. We comprehensively characterized the assembly states of the α subunits of the human proteasome, thereby controlled their assembly and disassembly using mutational and combinatorial techniques.¹⁾ In addition, we provided a molecular and structural basis for the mechanism of α subunit assembly mediated by the chaperone complex as a molecular matchmaker²⁾ (Figure 2).

Our approach has been applied to other protein assembly systems.³⁾ We successfully characterized the interaction between cyanobacterial clock proteins through the combined use of NMR spectroscopy and native mass spectrometry.⁴⁾ Furthermore, we are addressing the molecular mechanisms underlying the environment-dependent self-assembly of proteins into filamentous structures, as exemplified by amyloid formation in microgravity and tardigrade protein assembly occurring during desiccation.

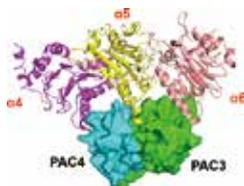


Figure 2. Three-dimensional model of the complex comprising the PAC3/PAC4 heterodimeric chaperon and proteasome subunits $\alpha 4$, $\alpha 5$, and $\alpha 6$.

2. Characterization of Structural Dynamics and Interactions of Immunoglobulin G Glycoproteins

Immunoglobulin G (IgG) molecules play pivotal roles in the immune system as multifunctional glycoproteins, coupling between antigen recognition and effector functions. The Fab region of each IgG binds to its specific antigen, whereas the Fc region interacts with the effector proteins typified by Fc γ receptors (Fc γ Rs), depending on Fc glycosylation, particularly fucosylation. To date, crystallographic studies have been performed to

elucidate the molecular mechanisms underlying IgG functions, primarily using isolated Fab and Fc fragments. We aimed to provide dynamic views of IgG-Fc by performing molecular dynamics (MD) simulations, which were experimentally validated using X-ray scattering and NMR spectroscopy. The results indicated that the dynamic conformational ensembles of Fc encompass most of the previously reported crystal structures in the free and Fc γ R-bound forms, although the major Fc conformers in solution significantly deviated from the crystal structures⁵⁾ (Figure 3). Furthermore, we found that glycans restrict the motional freedom of Fc and provide quaternary-structure plasticity via multiple intramolecular interaction networks. Particularly, the fucosylation of Fc glycans restricts the conformational freedom the proximal amino acid residue of functional importance, thereby preventing its interaction with Fc γ R11a, an Fc γ R isoform that mediates antibody-dependent cellular cytotoxicity. Moreover, based on integrated biophysical experiments, we demonstrated that the Fab portion of IgG is directly involved in its interaction with Fc γ R11a in addition to the canonical Fc-mediated interaction.⁶⁾ Our findings could inspire novel therapeutic antibody engineering targeting the previously unidentified receptor-interaction sites in IgG-Fab.

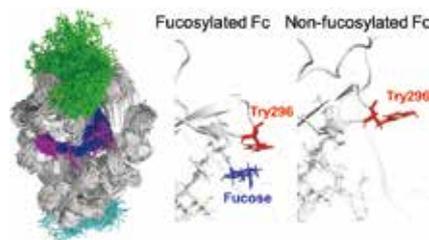


Figure 3. Dynamic views of the Fc region of IgG obtained by experimental and computational observations. This depiction shows the conformational ensemble of IgG-Fc derived from MD simulation (left) and the typical conformational snapshots of the functionally important tyrosine residue (Tyr296) derived from the major conformational states of the fucosylated (middle) and nonfucosylated (right) forms of Fc.

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Awards

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HONDA, Rena; Tokai Branch Chief Award, The Chemical Society of Japan (2019).

SAITO, Taiki; Young Scientist Award, The 6th Joint Nagoya Meeting: Future perspectives on structural/functional analyses and molecular design of biomolecules (2019).

KOFUJI, Kana; The Best Presentation Award, The Tokai Branch Meeting of the Pharmaceutical Society of Japan (2018).

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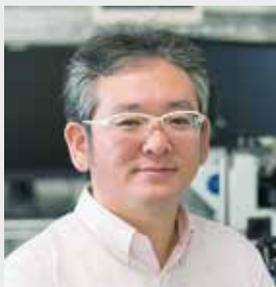
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Operation and Design Principles of Biological Molecular Machines

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Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

Activity of life is supported by various molecular machines made of proteins. Protein molecular machines are tiny, but show very high performance, and are superior to man-made machines in many aspects. One of the representatives of protein molecular machines is linear and rotary molecular motors (Figure 1). Molecular motors generate mechanical forces and torques that drive their unidirectional motions from the energy of chemical reaction or the electrochemical potential across the cell membrane.

We unveil operation principles of molecular motors with advanced single-molecule functional analysis and X-ray crystallographic structural analysis. With the help of computer science and robotic automation, we also engineer non-natural molecular motors to understand their design principles.

Selected Publications

- J. Ando, A. Nakamura, A. Visootsat, M. Yamamoto, C. Song, K. Murata and R. Iino, "Single-Nanoparticle Tracking with Angstrom Localization Precision and Microsecond Time Resolution," *Biophys. J.* **115**, 2413–2427 (2018).
- A. Nakamura, K. Okazaki, T. Furuta, M. Sakurai and R. Iino, "Processive Chitinase is Brownian Monorail Operated by Fast Catalysis after Peeling Rail from Crystalline Chitin," *Nat. Commun.* **9**, 3814 (2018).
- A. Nakamura, T. Tasaki, Y. Okuni, C. Song, K. Murata, T. Kozai, M. Hara, H. Sugimoto, K. Suzuki, T. Watanabe, T. Uchihashi, H. Noji and R. Iino, "Rate Constants, Processivity, and Productive Binding Ratio of Chitinase A Revealed by Single-Molecule Analysis," *Phys. Chem. Chem. Phys.* **20**, 3010–3018 (2018).
- F. Kawai, A. Nakamura, A. Visootsat and R. Iino, "Plasmid-Based One-Pot Saturation Mutagenesis and Robot-Based Automated Screening for Protein Engineering," *ACS Omega* **3**, 7715–7726 (2018).
- T. Uchihashi, Y. H. Watanabe, Y. Nakazaki, Y. Yamasaki, T. Watanabe, T. Maruno, S. Uchiyama, S. Song, K. Murata, R. Iino and T. Ando, "Dynamic Structural States of ClpB Involved in Its Disaggregation Function," *Nat. Commun.* **9**, 2147 (2018).
- H. Isojima, R. Iino, Y. Niitani, H. Noji and M. Tomishige, "Direct Observation of Intermediate States during the Stepping Motion of Kinesin-1," *Nat. Chem. Biol.* **12**, 290–297 (2016).
- A. Nakamura, T. Tasaki, D. Ishiwata, M. Yamamoto, Y. Okuni, A. Visootsat, M. Maximilien, H. Noji, T. Uchiyama, M. Samejima, K. Igarashi and R. Iino, "Direct Imaging of Binding, Dissociation, and Processive Movement of *Trichoderma reesei* Cel6A and Its Domains on Crystalline Cellulose," *J. Biol. Chem.* **291**, 22404–22413 (2016).



Figure 1. Protein molecular machines. (Left) A linear molecular motor chitinase A. (Center and Right) Rotary molecular motors F₁-ATPase and V₁-ATPase, respectively.

1. Rotational Substeps and Chemo-Mechanical Coupling Scheme of *Enterococcus hirae* V₁-ATPase¹

V₁-ATPase (V₁), the catalytic domain of an ion pump V-ATPase, is a rotary molecular motor and converts chemical energy of ATP hydrolysis into mechanical rotation. To understand chemo-mechanical coupling mechanism of *Enterococcus hirae* V₁ (EhV₁), we directly observed rotation of newly-constructed EhV₁ with gold nanoparticle probe. We found that 120° steps per ATP hydrolysis were divided into 40° and 80° substeps. In the main-pause before 40° substep, time constant was inversely proportional to ATP concentration ([ATP]) at low [ATP], indicating that ATP binds during the main-pause with rate constant of $1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. At high [ATP], [ATP]-independent two time constants (0.5, 0.7 ms) were obtained. One of two time constants was prolonged (143 ms) in rotation driven by slowly-hydrolyzable ATPγS, indicating that ATP cleavage occurs during the main-pause. In another subpause before 80° substep, [ATP]-independent time constant (2.5 ms) was obtained. Furthermore, in ATP-driven rotation of an arginine-finger mutant in the presence of ADP, -80° and -40° backward steps were observed. Time constants of the pauses before -80° backward and +40° recovery steps were inversely proportional to [ADP] and [ATP], respectively, indicating that these steps are triggered by ADP and ATP bindings. Assuming that backward steps are reverse reactions, we concluded that 40° and 80° substeps are triggered by ATP binding and ADP release, respectively. The remaining time constant in the main-pause was considered to be phosphate release. Combined with previous structural information, we propose a chemo-mechanical coupling scheme of EhV₁ including substeps, largely different from those of F₁-ATPases (Figure 2).

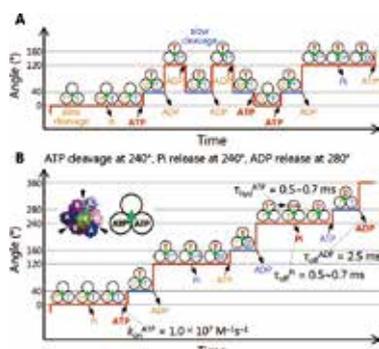


Figure 2. A model of chemo-mechanical coupling of EhV₁ including substeps and backward steps.

2. Multi-Color High-Speed Tracking of Single Biomolecules with Silver, Gold, Silver-Gold Alloy Nanoparticles²

Gold nanoparticles have been used as an imaging probe to track motions of single biomolecules. Since they show high scattering signals, single-particle tracking has been performed

with microsecond time resolution and nanometer localization precision. To investigate behaviors of various kinds of biomolecules simultaneously, increase of the color palette is necessary. Here we developed a multi-color, high-speed single-particle tracking system by using silver, gold, and silver-gold alloy nanoparticles. Peak wavelengths of plasmon resonance for silver and gold nanoparticles are around 400 nm and 530 nm, respectively, and those for silver-gold alloy nanoparticles can be modulated between 400 nm and 530 nm depending on their composition ratio. We constructed multi-color total internal reflection dark-field microscopy with multiple lasers at 404 nm for silver, 473 nm for silver-gold alloy, and 561 nm for gold nanoparticles. By using a spectrophotometer in the imaging optics, scattering images at each wavelength were projected onto the different portion of a two-dimensional detector (Figure 3 and 4). High contrast images of 30 nm silver, 30 nm silver-gold alloy, and 40 nm gold nanoparticles were simultaneously obtained at 404, 473, and 561 nm channels, respectively. With this system, diffusional motions of phospholipids in supported lipid membrane and stepping motions of kinesins along microtubules were observed with 2 nm localization precision and 100 μs time resolution. Furthermore, introduction of 649 nm laser enabled detection of plasmon coupling and transient dimer formation of two nanoparticles. Our method will pave the way to investigate operation mechanisms of complex biomolecular systems and multi-subunit biomolecular motors and machines.

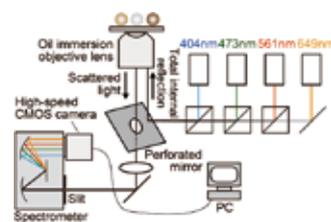


Figure 3. Spectrometer-based multi-color dark-field imaging system.

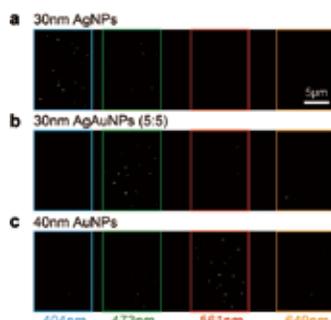


Figure 4. Spectrometer-based dark-field imaging of AgNPs, AgAuNPs (5:5), and AuNPs.

References

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A Supramolecular Chemical Approach to the Construction of Artificial Cells

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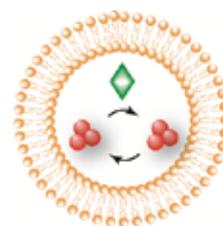
Keywords Artificial Cell, Origin of Life, Vesicle

The cell is the smallest unit of life, and the first simple cells evolved from simple molecular assemblies on prebiotic earth. To understand this transition from non-living to living structures, we use a supramolecular chemical approach. As shown in Figure 1, the key elements of a cell are a compartment, information, and a catalyst (*i.e.*, metabolism). We have attempted to construct a chemically based artificial cell endowed with these three elements.

In our laboratory, we constructed two types of artificial cells by using giant vesicles (GVs) as the compartment. The first, developed in collaboration with the Sugawara group (Kanagawa Univ.), is an artificial cell that can proliferate from generation to generation. We have improved this model by constructing a recursive vesicular artificial cell system with proliferation cycles. After self-reproduction, these second-generation GV's contain no PCR reagents by consuming and therefore cannot reproduce for a second time. However, the reagents can be replenished by using the vesicular transport system and changing the pH of the dispersion, resulting in the fusion of the GV's with conveyor GV's bearing the PCR reagents. After the PCR reagents are replenished, the GV can self-reproduce again. This system could lead to an evolvable artificial cellular system. The second type of artificial cell contains a catalyst-producing system. The GV system can

generate catalysts and membrane molecules by transforming their respective precursors. The catalysts that are produced facilitate the proliferation of the GV's.

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



Artificial cell

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

Figure 1. Artificial cell model. Materials containing heritable information are enclosed within a compartment. The reactions in the two replicating systems (compartment and information) are accelerated by appropriate catalysts. The reactions in the two replicating systems are accelerated by appropriate catalysts.

Selected Publications

- Y. Natsume, E. Noguchi and K. Kurihara, "Spontaneous Localization of Particles in Giant Vesicles Owing to Depletion Force," *J. Phys. Soc. Jpn.* **88**, 033001 (2019).
- M. Matsuo, Y. Kan, K. Kurihara, T. Jimbo, M. Imai, T. Toyota, Y.

Hirata, K. Suzuki and T. Sugawara, "DNA Length-Dependent Division of a Giant Vesicle-Based Model Protocell," *Sci. Rep.* **9**, 6916 (2019).

1. Spontaneous Formation of Liquid–Liquid Phase-Separated Droplets with Amino Acid Polymerization

In the prebiotic era, cooperative interaction between self-producing molecular aggregates and peptide polymers led to the emergence of primitive cells. Although the advanced membrane provides a field for catalytic reaction, it remains a mystery how cooperation between polymers and molecular aggregates occurred even in membraneless organisms like coacervate droplets. Therefore, we attempted to construct a liquid–liquid phase-separated droplet that self-reproduces by constructing a reaction system in which a peptide is produced by spontaneous polymerization of an amino acid derivative in water.

We synthesized an amino acid derivative (monomer) with two cysteine reactive sites at the N-terminus and a thioester at the C-terminus that spontaneously polymerizes in water to form a peptide. In order to prevent undesirable oxidation, a monomer precursor was obtained by crosslinking monomers with disulfide. After the addition of a reducing agent (dithiothreitol, DTT) to the monomer precursor solution, we observed the formation of droplets. We then added more precursor and DTT and examined the changes in particle size. The mean particle size increased and decreased rapidly immediately after the addition, confirming the self-reproducibility of the formed droplets. When the precursor and DTT were continuously added every 20 hours, the particle size of the droplets fluctuated recursively, indicating autocatalytic self-reproduction of the formed liquid–liquid phase-separated droplets. This autocatalytic droplet formation in this system is considered to be due to a physical mechanism: When a molecular assembly is created as the dehydration condensation proceeds and it forms a hydrophobic field, the assembly functions as a site for promoting dehydration condensation, thereby allowing the autocatalytic dehydration condensation to proceed.

The behavior of the interface formed by this chemical reaction replicates the autocatalytic self-reproduction that might have occurred in droplets formed by liquid–liquid phase separation on the primitive, prebiotic earth. In the future, we aim to construct the Droplet World Hypothesis by inducing the emergence of the primordial cell membrane via an internal chemical reaction or by functionally expressing biologically active molecular species, such as ribozymes, inside the droplet.

2. Self-Reproduction Model Using Particle-Localized Vesicles

Biopolymers inside cells change their structures around themselves, thereby increasing the free movement area. This entropic action is called the excluded volume effect. We prepared phospholipid vesicles containing densely packed colloidal particles as a model to show the excluded volume effect. When polystyrene beads of two different sizes were confined in the GV, a novel phenomenon was observed: Smaller beads were localized in the vicinity of the vesicle membrane. To explain this phenomenon theoretically, we assumed that an equilibrium osmotic pressure was realized between an outer phase containing a relatively large number of small particles and a separate inner phase.¹⁾ We constructed a second model based on the depletion effect.²⁾

Considering the relation between vesicular membrane area and the volume fraction of the particles, we hypothesize that increased membrane area would cause the vesicle to become unstable, and that stability could be restored by division into two spherical vesicles. We confirmed this by showing that when a fatty acid similar to a vesicular membrane molecule is added to particle-containing vesicles, the vesicles divide easily and frequently. To further assess this self-reproducing vesicle model, we are constructing a system can track morphological changes and analyze microscopy images.

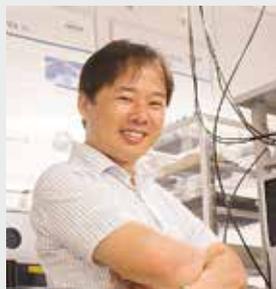
The purpose of this vesicular system is to achieve cellular behavior such as internal structure or membrane deformation without sophisticated biomaterials. Because this vesicular system is simple, it is possible to extract and analyze the contribution of the crowding effect to cell deformation. For this reason, applying data to simulation and modeling will be relatively easy in this system compared with other systems. Because this model excludes biopolymers with specific properties, the biopolymers' unique functions do not appear. Therefore, this vesicular system is expected to act as a primitive cell in which simple molecules interact loosely to express their function.

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Investigation of Molecular Mechanisms of Channels, Transporters and Receptors

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

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

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

Selected Publications

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

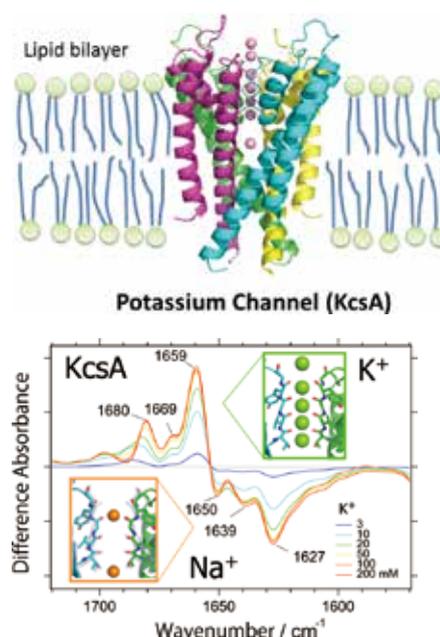


Figure 1. (top) X-ray crystal structure of a potassium ion channel, KcsA. (bottom) The ion-exchange induced difference infrared spectra of KcsA with different potassium ion concentration. The amide I bands are mainly originated from the carbonyl groups of the selectivity filter of KcsA.

1. Ion-Protein Interactions of MgtE Magnesium Channel with Magnesium or Calcium Ions and Its Implication for the Ion Selectivity¹⁾

Magnesium ion (Mg^{2+}) is vital for living systems and utilized for various biological processes. Calcium ion (Ca^{2+}) is also important as a second messenger inside the cell. Thus, the selective permeation of Mg^{2+} is not only prerequisite for homeostasis of internal Mg^{2+} concentration and also for avoiding unintended induction of calcium signaling.

MgtE is an ion channel highly selective to Mg^{2+} . The crystal structure of MgtE showed a dimeric structure with transmembrane domain and two cytosolic domains [N- and cystathionine- β -synthase (CBS) domains]. The transmembrane domains constitute a pore with a central cavity which is important for the ion selectivity to Mg^{2+} . In addition, the crystal structure of the transmembrane region with higher resolution revealed that a Mg^{2+} ion exists with hydrated water molecules in the cavity.

To elucidate the molecular mechanisms of the ion selectivity for Mg^{2+} of MgtE in more detail, we applied ion-exchange induced difference FTIR spectroscopy with an aid of computational methods. By changing electrolyte solution containing Mg^{2+} with that of Ca^{2+} , we obtained an infrared difference spectrum of MgtE which contains molecular information of the ion-protein interactions with Mg^{2+} or Ca^{2+} . Comparing the difference spectra of several site-directed mutant proteins of MgtE, we assigned antisymmetric and symmetric COO^- vibrations of Asp432 which was found to be crucial for the ion selectivity of MgtE.

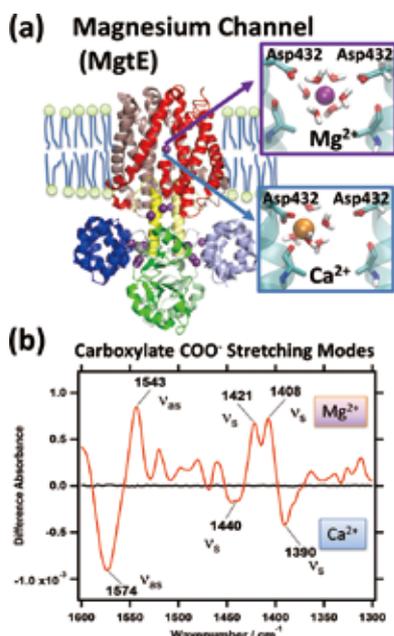


Figure 2. (a) The X-ray crystal structure of MgtE and snap shots of molecular dynamics simulation with Mg^{2+} or Ca^{2+} ion. (b) The ion-exchange induced difference infrared spectrum of MgtE in the carboxylate COO^- stretching region.

Moreover, from systematic measurements with the different ion concentrations, we estimated the dissociation constant relating to the central cavity and found that the value is much lower for Mg^{2+} (~ 0.3 mM) compared to that for Ca^{2+} (~ 80 mM). The difference of affinity is well consistent with the high selectivity for Mg^{2+} of MgtE elucidated by electrophysiological and biological methods. Difference in frequency of COO^- stretching vibrations of Asp432 in the central cavity suggests that ion-protein interactions with Mg^{2+} and Ca^{2+} are different from each other. To get more information about energetics of the ion-protein interactions and dynamics, we applied molecular dynamics simulation and normal mode analysis with quantum chemical calculation on MgtE with hydrated Mg^{2+} or Ca^{2+} in the cavity. We found that Mg^{2+} is more stable with hydrated configuration at the center between two Asp432 residues, but Ca^{2+} is easily captured by either of the residues and forms the direct interaction. In this way, our experimental and computational approach provided new insights for the ion selectivity of MgtE.

2. Detection of Ligand- or Light- Induced Structural Changes in G Protein-Coupled Receptors Using ATR-FTIR Spectroscopy

My group has developed attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy to trace and reveal structural features of membrane proteins involved in various important biological functions. Based on IR spectral changes, we have reported how functional properties of ion channels (an ATP-sensitive P2X receptor and a potassium channel TWIK1) are regulated. In order to extend the applicability of ATR-FTIR spectroscopy to other important membrane proteins, we tried to measure IR spectral changes of G protein-coupled receptors (GPCRs) upon agonist-binding or light-absorption since GPCRs are involved in many important cellular processes such as neuro- transmission, hormone perception, vision and olfaction.

Besides ligand-binding GPCR, we also tried to measure IR spectral changes of light-sensitive GPCR opsin. We previously reported that an opsin in the brain of a zooplankton is activated by UV light and inactivated by visible light. Through the ATR-FTIR techniques, IR spectral changes of the opsin upon activation and inactivation were successfully detected. Time-resolved IR measurements of the opsin as well as ligand-binding GPCR would reveal how signal reception (UV light absorption for the opsin and ligand-binding for GPCRs) evokes conformational changes in the GPCRs toward activated states.

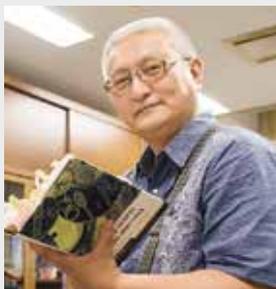
Reference

- 1) T. Kimura, V. A. Lorenz-Fonfria, S. Douki, H. Motoki, R. Ishitani, O. Nureki, M. Higashi and Y. Furutani, *J. Phys. Chem. B* **122**, 9681–9696 (2018).

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Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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2014 Distinguished Professor, Three George University
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2008 Research Project Leader, NEDO Project (–2012)
2011 Deputy Research Project Leader, JST CREST (–2016)
2014 Research Project Leader, JST ACCEL Project (–2019)

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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 transformations. In particular, we have recently been developing the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels. Thus, for example, a variety of palladium catalysts were designed and prepared promoting carbon–carbon bond forming reactions at ppm-ppb loading levels (Figure 1).

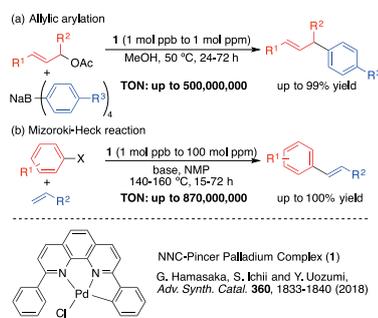


Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Complex.

Selected Publications

- R. David and Y. Uozumi, “Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at ppm-ppb Molecular Catalyst Loadings (review),” *Adv. Synth. Catal.* **360**, 602–625 (2018).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, “Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin,” *ACS Catal.* **7**, 7371–7377 (2017).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, “Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels,” *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
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- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, “Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane,” *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. Self-Assembled Polymeric Pyridine Copper Catalysts for the Huisgen Cycloaddition with Alkynes and Acetylene Gas: Application in Synthesis of Tazobactam¹⁾

Novel convoluted polymeric pyridine copper(I) catalysts PVPy-Cu were developed for Huisgen cyclization of organic azides with alkynes and acetylene gas. They were readily prepared by our molecular convolution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and poly(4-vinylpyridine) (PVPy) in the presence of sodium ascorbate with/without various sodium salts in water. Their structural investigation was conducted with XANES and EXAFS as well as DFT calculation. The Huisgen cycloaddition of a variety of alkynes and acetylene gas was carried out with 100 to 800 mol ppm Cu of PVPy-Cu in water whose turnover numbers reached up to 10,000. This catalytic system was applied to synthesis of tazobactam, an inhibitor of bacterial β -lactamases.

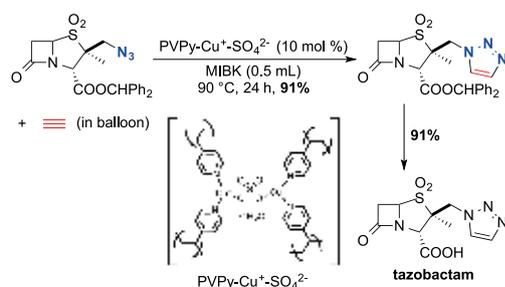


Figure 2. Synthesis of Tazobactam through the Huisgen Cyclization with Acetylene Gas Using a Polymeric Cu Catalyst.

2. Iterative Preparation of Platinum Nanoparticles in an Amphiphilic Polymer Matrix: Regulation of Catalytic Activity in Hydrogenation^{2,3)}

We have demonstrated that iteration of the seeded preparation of platinum nanoparticles dispersed in an amphiphilic polystyrene–poly(ethylene glycol) resin (ARP–Pt) regulates the activity of the catalyst in the hydrogenation of aromatic compounds in water and is accompanied by a slight modifi-

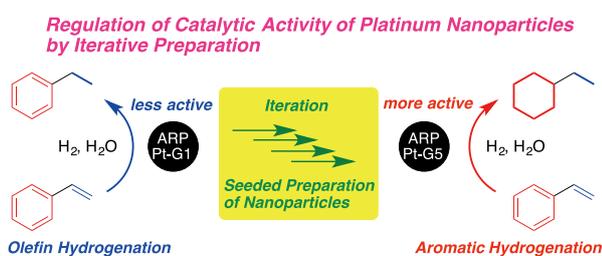


Figure 3. Regulated Hydrogenation with Iteratively Generated Polymeric nanoPt Catalysts.

cation of its structural properties. Platinum nanoparticles dispersed in the amphiphilic polymer prepared through four iterations (ARP–Pt G5) showed a much higher catalytic activity than that of the initial ARP–Pt (G1) in the hydrogenation of aromatic compounds in water. These results suggest that iteration of the seeded preparation of nanoparticles can be an effective method for the precise regulation of the catalytic activity and the structural properties of the resulting catalyst.

3. Solvent-Free A³ and KA² Coupling Reactions with Mol ppm Level Loadings of a Polymer-Supported Copper(II)-Bipyridine Complex for Green Synthesis of Propargylamines⁴⁾

A copper(II)–bipyridine complex immobilized on amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin (PS–PEG–BPy–CuBr₂) has been developed. The immobilized copper(II)–bipyridine complex at a mol ppm level of loading efficiently catalyzed the three-component coupling of aldehydes or ketones, amines, and alkynes (A³ or KA² coupling) under solvent-free conditions to give the corresponding propargylamines in good-to-excellent yields. Moreover, a ten-gram-scale green syntheses of propargylamines proceeded with excellent atom economy (*E* factor ≥ 0.38) through a solvent-free A³ coupling using 5 mol ppm of PS–PEG–BPy–CuBr₂. The total turnover number and turnover frequency of the catalyst reached as high as 178 800 and 7450 h⁻¹, respectively.



Figure 4. Preparation of Propargylamines by A³ Coupling Reaction with ppm Loading Level of a Polymeric Cu(II) Catalyst.

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- 4) S. Yan, S. Pan, T. Osako and Y. Uozumi, *ACS Sus. Chem. Eng.* **7**, 9097 (2019).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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Awards

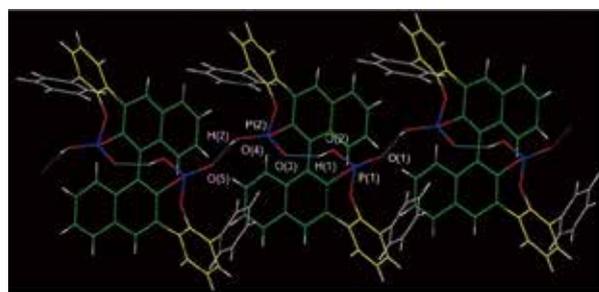
2003 The Elizabeth R. Norton Prize for Excellence in Research in Chemistry, University of Chicago
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The field of molecular catalysis has been an attractive area of research to realize efficient and new transformations in the synthesis of functional molecules. The design of ligands and chiral molecular catalysts has been recognized as one of the most valuable strategies; therefore, a great deal of effort has been dedicated to the developments. In general, “metal” has been frequently used as the activation center, and conformationally rigid, and C_2 - or pseudo C_2 symmetry has been preferably components for the catalyst design. To develop new type of molecular catalysis, we have focused on the use of hydrogen and halogen atom as activation unit, and have utilized conformationally flexible components in the molecular design of catalyst, which had not received much attention until recently. We hope that our approach will open the new frontier in chiral organic molecules from chiral molecular chemistry to chiral molecular science.



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

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

Selected Publications

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

1. Brønsted Acid Catalyzed Asymmetric Rearrangement: Asymmetric Synthesis of Linear Homoallylic Amines

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 homoallylic amines, we discovered chirality transferred formal 1,3-rearrangement of ene-aldimines in the presence of Brønsted acid, and developed it as synthetic method for variety of enantioenriched linear homoallylic amines.¹⁾ Furthermore, we studied details of reaction mechanism and succeeded catalytic asymmetric version of this rearrangement.²⁾ To the best our knowledge, our discovery is the first example of asymmetric formal [1,3]-rearrangement and the new entry of the synthetic methodology for the linear enantioenriched homoallylic amines.

2. Design of Chiral Brønsted Acid Catalyst

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

Perfluorinated aryls have emerged as an exquisite class of motifs in the design of molecular catalysts, and their electronic and steric alterations lead to notable changes in the chemical yields and the stereoselectivities. However, unfortunately, the distinctive potential of perfluorinated aryls has not been fully exploited as design tools in the development of chiral Brønsted acid catalysts. We developed the perfluoroaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deliver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino-ene reaction using aldehydes and FmocNH₂.³⁾

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

molecular design of a chiral Brønsted acid with two different acidic sites, chiral carboxylic acid-cyclic mono-phosphoric acid, was identified as a new and effective concept in asymmetric hetero-Diels-Alder reaction of 2-azopyridinoester with amidodienes.⁷⁾

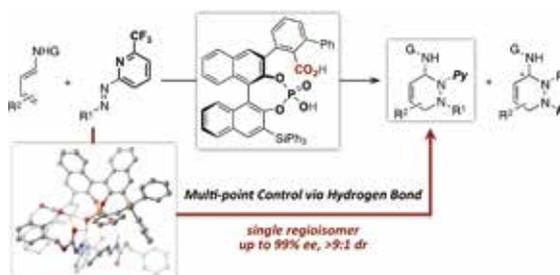


Figure 2. Chiral carboxylic acid-phosphoric acid-catalyzed azo-hetero-Diels-Alder reaction.

3. Design of Catalysis with Halogen Bond for Carbon-Carbon Bond Forming Reactions

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 LBs. 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 catalysis with halogen bond for carbon-carbon bond forming reactions.

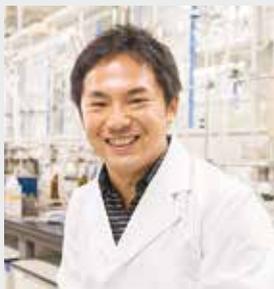
We found that perfluorinated iodoaryls are able to catalyze the Mukaiyama-type Mannich reaction and allylation reaction.⁸⁾

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- 4) N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
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- 8) N. Momiyama *et al.*, Six manuscripts in preparation.

Development of Functional Metal Complexes for Artificial Photosynthesis

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Metal Complex, Multi-Electron Transfer Reactions, Artificial Photosynthesis

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



Figure 1. An overview of our work.

Selected Publications

- V. K. K. Praneeth, M. Kondo, M. Okamura, T. Akai, H. Izu and S. Masaoka, "Pentamuclear Iron Catalysts for Water Oxidation: Substituents Provide Two Routes to Control Onset Potentials," *Chem. Sci.* **10**, 4628–4639 (2019).
- S. K. Lee, M. Kondo, M. Okamura, T. Enomoto, G. Nakamura and S. Masaoka, "Function-Integrated Ru Catalyst for Photochemical CO₂ Reduction," *J. Am. Chem. Soc.* **140**, 16899–16903 (2018).
- P. Chinapang, M. Okamura, T. Itoh, M. Kondo and S. Masaoka, "Development of a Framework Catalyst for Photocatalytic Hydrogen Evolution," *Chem. Commun.* **54**, 1174–1177 (2018).
- M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S.

- Hayami, V. K. K. Praneeth, M. Yoshida, K. Yoneda, S. Kawata and S. Masaoka, "A Pentamuclear Iron Catalyst Designed for Water Oxidation," *Nature* **530**, 465–468 (2016).
- M. Yoshida, M. Kondo, S. Torii, K. Sakai and S. Masaoka, "Oxygen Evolution Catalysed by a Mononuclear Ruthenium Complex bearing Pendant -SO₃⁻ Groups," *Angew. Chem., Int. Ed.* **54**, 7981–7984 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Development of Function-Integrated Ru Catalyst for Photochemical CO₂ Reduction¹⁾

The efficient conversion of solar energy into storable chemical fuels or useful chemicals is one of the major challenges in the 21st century. Particularly, visible-light driven photocatalytic reduction of CO₂ has attracted considerable attention because this technology can produce fuels and chemicals and counteract CO₂ emissions. The reaction is typically achieved by a system using a combination of two distinct functional units: A visible-light absorbing chromophore (photosensitizer, PS) and a catalyst (Cat). These systems require photoinduced electron transfer (ET) from the PS to the Cat to drive the reaction, and catalysis is largely affected by the efficiency of the ET process. Accordingly, optimization of the ET process with convergent modification of PS and Cat units is indispensable for efficient catalytic reactions.

A function-integrated catalyst, which can act as both PS and Cat, is a valuable alternative for photocatalytic CO₂ reduction. In this type of system, light absorption and subsequent CO₂ reduction proceed within one molecular unit. Thus, a reaction without an ET event between PS and Cat units can be achieved. However, the development of function-integrated catalysts that have (i) strong absorption in the visible-light region, (ii) high reaction rate, and (iii) high stability is still challenging.

In this study, we report efficient, visible-light-driven CO₂ reduction catalyzed by a function-integrated photocatalyst. The key to our success is the use of a phosphine-substituted Ru(II) polypyridyl complex, *trans*(*P,MeCN*)-[Ru^{II}(tpy)(pqn)(MeCN)]²⁺ (**RuP**, tpy = 2,2':6',2''-terpyridine; pqn = 8-(diphenylphosphanyl)quinoline, Figure 2). **RuP** exhibits an intense band at 475 nm due to MLCT transitions. Additionally, **RuP** catalyzes electrochemical CO₂ reduction at one of the lowest overpotentials among homogeneous catalysts. These two characteristics of **RuP** enabled the development of a function-integrated system with a catalytic performance superior to that of best-in-class counterparts.

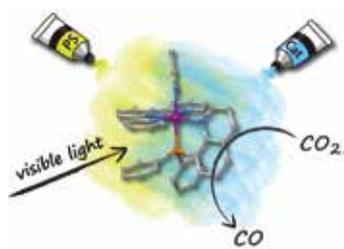


Figure 2. Function-integrated catalyst for visible-light driven CO₂ reduction.

Awards

MASAOKA, Shigeyuki; The 25th Gold Medal Prize (2019).

IZU, Hitoshi; Elsevier Best Poster Prize, 15th International Symposium on Applied Bioinorganic Chemistry (2019).

ENOMOTO, Takafumi; The School of Physical Sciences Dean's Award, SOKENDAI (2018).

LEE, Sze Koon; SOKENDAI Award (2018).

CHINAPONG, Pondchanok; The School of Physical Sciences Dean's Award, SOKENDAI (2018)

2. Water Oxidation Reaction Catalyzed by Pentanuclear Iron Complexes²⁾

Water oxidation ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) is considered the main bottleneck in the production of chemical fuels from sunlight and/or electricity. Recently, we demonstrated that a pentanuclear iron complex $[\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}(\mu_3\text{-O})(\text{bpp})_6]^{3+}$, $[\text{Fe}_5\text{-H}]^{3+}$ (Hbpp = bis(pyridyl)pyrazole), can serve as a highly active catalyst for electrocatalytic water oxidation. The reaction rate and durability of $[\text{Fe}_5\text{-H}]^{3+}$ are the highest among iron-based water oxidation catalysts reported thus far. However, a relatively large onset potential is required for the catalysis. Therefore, the development of a novel strategy for designing catalysts that can drive the reaction at low onset potentials is essential.

Here, we report two approaches for decreasing the onset potential of pentanuclear iron water oxidation systems. Two approaches involving the installation of substituents onto the Hbpp ligand have been demonstrated. Two kinds of ligands, one with electron-donating and the other with electron-withdrawing groups at the 4-position of the Hbpp have been employed, and the new pentanuclear complexes were constructed utilizing these ligands. The newly synthesized complexes catalyzed the oxidation of water with high Faradaic efficiencies, and the onset potentials of these complexes were lower than that of the parent complex. Mechanistic insights revealed that there are two methods for decreasing onset potentials: Control of the redox potentials of the pentanuclear complex and control of the reaction mechanism (Figure 3).

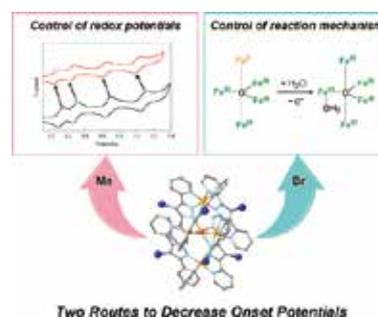


Figure 3. Two routes to control onset potentials of water oxidation in pentanuclear iron complexes.

References

- 1) S. K. Lee, M. Kondo, M. Okamura, T. Enomoto, G. Nakamura and S. Masaoka, *J. Am. Chem. Soc.* **140**, 16899–16903 (2018).
- 2) V. K. K. Praneeth, M. Kondo, M. Okamura, T. Akai, H. Izu and S. Masaoka, *Chem. Sci.* **10**, 4628–4639 (2019).

Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

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Keywords

Radical, Open-Shell Electronic States, Photonic-Electronic-Magnetic Properties

The molecules with open-shell electronic states can exhibit unique properties, which are difficult to achieve for conventional closed-shell molecules. Our group develops new open-shell organic molecules (= radicals) and metal complexes to create novel photonic-electronic-magnetic functions.

While conventional closed-shell luminescent molecules have been extensively studied as promising components for organic light-emitting devices, the luminescent properties of radicals have been much less studied because of its rarity and low chemical (photo-)stability. We have developed a novel luminescent organic radical PyBTM, which is highly stable at ambient condition and in the photoexcited state. We have also discovered that (i) PyBTM-doped molecular crystals exhibit photoluminescence with a room-temperature emission quantum yield of 89%, which is exceptionally high in radicals, and (ii) the doped crystals show drastic changes in the emission spectra by applying a magnetic field. This is the first observation of the magnetoluminescence in organic radicals. Our studies provide novel and unique insights in molecular photonics, electronics, and spintronics, and also contribute to

developing applied science for light-emitting devices.

Our group focuses on frustrated spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states can afford unusual electronic states attributed to the frustrated spins, providing exotic electrical and magnetic properties.

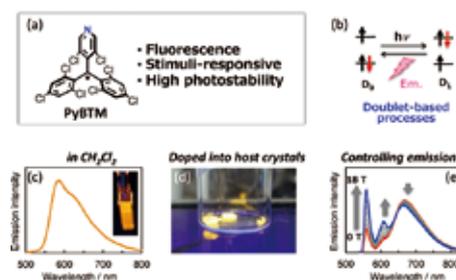


Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2 . (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

Selected Publications

- S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, "Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment," *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* **54**, 3731–3734 (2015).
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1. NIR Emission and Acid-Induced Intramolecular Electron Transfer Derived from a SOMO–HOMO Converted Non-Aufbau Electronic Structure

Some organic radicals violate the Aufbau principle and possess peculiar electronic structures in which the energy level of the SOMO (Singly Occupied Molecular Orbital) is formally lower than that of the highest occupied molecular orbital (HOMO). Radicals with such SOMO–HOMO converted electronic structures are attracting growing interest as promising candidates for unique stimulus-controlled molecular functions, which cannot be achieved using conventional radicals or closed-shell molecules. We prepared a novel organic radical with a SOMO–HOMO converted electronic structure, TPA-R*, a novel electron donor–acceptor hybrid of triphenylamine (an electron donor) and a stable polychlorinated diphenyl(4-pyridyl)methyl radical (an electron acceptor).¹⁾ TPA-R* exhibited fluorescence in the near-infrared region ($\lambda_{\text{max}} = 910 \text{ nm}$) in cyclohexane from a polar intramolecular charge-transfer excited state. Cyclic voltammetry, absorption spectroscopy, and DFT calculation revealed the inversion of the SOMO and HOMO levels in the electronic structure of TPA-R*. Addition of trifluoromethanesulfonic acid to TPA-R* caused a two-step change. Protonation initially occurred on the diphenylpyridyl-methyl radical moiety to form TPA-[RH]^{•+}. Further addition of the acid caused unprecedented intramolecular electron transfer from the triphenylamine moiety to the protonated radical moiety, generating [TPA]^{•+}-RH. TPA-[RH]^{•+} and [TPA]^{•+}-RH could be switched by changing the acidity of the solution. These results constitute the first example of the multistep switching behavior stimulated by a single external stimulus in the SOMO–HOMO converted non-Aufbau electronic structure and demonstrate its great potential for realizing unique molecular photonic and electronic functions.

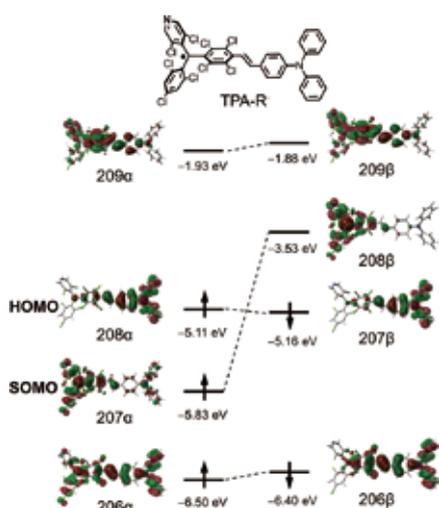


Figure 2. MO diagram of TPA-R* calculated using DFT (uB3LYP/6-31G*).

2. 1D Cu^{II}–Radical Heterospin System: Temperature-Dependent Jahn–Teller Distortion Correlated to π -Conjugation and Magnetic Properties

Jahn–Teller (JT) and pseudo-JT distortions modulate coordination geometry around the metal ion to decrease the energy of an electronic system, thereby affecting the physical properties of materials. Controlling the JT distortion is one promising approach to develop tunable physical properties or to reveal structure–property relationships. We prepared a new class of 1D chain complexes $[\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$ (hfac = hexafluoroacetylacetonato; bisPyTM²⁾ = bis(3,5-dichloro-4-pyridyl)(2,4,6-trichlorophenyl)methyl radical).³⁾ In the crystal, bisPyTM bridges two Cu^{II} ions via the nitrogen atoms to form a 1D –Cu^{II}(hfac)₂–bisPyTM– type zigzag chain structure (Figure 3). Importantly, the coordination geometry around the Cu^{II} atom continuously changes with temperature, where the JT axis rotates from the Cu–N1 bond direction at 298 K to the Cu–O1 bond direction at 93 K. This structural change induces changes in the mode of π -conjugation in the hfac moieties. Magnetic investigations revealed ferromagnetic (FM) interaction between spins on bisPyTM and Cu^{II}. The FM interaction was enhanced below 90 K due to the reorientation of the spin orbital ($d_{x^2-y^2}$ orbital) accompanied by the rotation of the JT axis on the Cu^{II} atom. The reorientation of the spin orbitals was supported by ESR spectroscopy and DFT calculation. Namely, the JT distortion, degree of freedom of π -conjugation, and magnetic properties in $[\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$ were coupled, resulting in unique temperature-dependent properties. The present study expands the scope of JT-active magnetic molecular compounds displaying controllable properties.

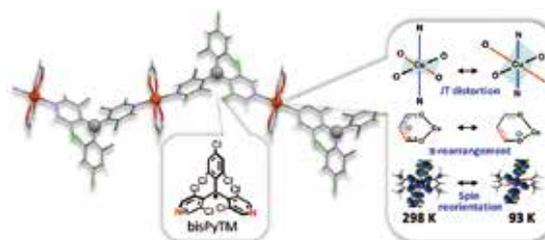


Figure 3. 1D chain structure of $[\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$. CF_3 groups in the hfac ligands are omitted for clarity.

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

Control of Electron Transfer for Efficient Oxygenation Reactions

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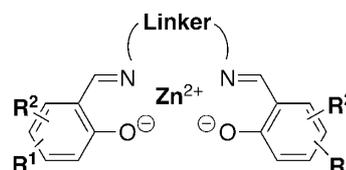
KURAHASHI, Takuya
Assistant Professor

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

1. Development of Photoactive Schiff Base Ligands for Photocatalytic Reactions

A Schiff base ligand such as salen, which is prepared from salicylaldehydes and amines, could be easily obtained in a

large scale and is also suitable for a wide variety of chemical modifications. This structural feature makes a Schiff base complex one of the most versatile framework for catalysts and materials. Some of Schiff base ligands shows relatively strong fluorescence, which has been used for sensory applications. But the photophysical properties of Schiff base ligands have not been fully exploited, and the mechanistic aspects of strong or weak fluorescence remains unknown. The present study explored a higher fluorescence quantum yield and longer emission wavelength by systematically changing the structure of salen-type Schiff base ligands with zinc ion shown in Figure 1.



$\text{R}^1, \text{R}^2 = \text{MeO-}, \text{Me-}, t\text{-Bu-}, \text{Ph-}, \text{Cl-}, \text{MeCO-}, \text{NO}_2\text{-}$

Figure 1. Schiff base complexes for fluorescence studies.

Visiting Professors



Visiting Professor
SAKURAI, Hidehiro (from *Osaka University*)

Nanoscience Based on the Synthetic Organic Chemistry

Bowl-shaped π -conjugated compounds including partial structures of the fullerenes or the cap structure of carbon nanotubes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties due to their unique structure. We have developed the rational routes to the various buckybowls, including sumanene, a C_{3v} -symmetric pristine buckybowl framework, and also investigate their chemical and physical properties. We also investigate to develop novel catalytic properties of metal nanoclusters protected by organic polymers and/or molecules. We focus on the following projects: Preparation of size-selective gold and gold-based alloy nanoclusters supported by hydrophilic polymers and its catalytic activity; Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers.



Visiting Professor
UCHIHASHI, Takayuki (from *Nagoya University*)

High-Speed AFM Reveals Accelerated Binding of Agitoxin-2 to K⁺ Channel by Induced-Fit

Agitoxin-2 (AgTx2) from scorpion venom is a potent blocker of Shaker-related K⁺ channels. Docking model of them has been elucidated; however, whether binding dynamics is described by a two-state (AgTx2-bound and AgTx2-unbound) model or more complicated mechanism such as induced-fit or conformational selection is still unclear. Here, we observed the binding dynamics of AgTx2 to the Shaker-mimicking KcsA channel using high-speed atomic force microscopy. We imaged repeated binding and dissociation of AgTx2 to the channel, and found that the affinity of the channel for AgTx2 increases during persistent binding of AgTx2 and decreases during persistent dissociation. We propose a four-state model including high- and low-affinity states of the channel with relevant rate constants. Induced-fit pathway is dominant that accelerates binding event 400 times. This is the first analytical imaging of scorpion toxin binding in real time, which is applicable to various biological dynamics including channel-ligands, DNA-modifier proteins, and antigen-antibody complexes.



Visiting Associate Professor
YAMADA, Teppei (from *Kyushu University*)

Thermocell and Ionic Motion in Soft Molecular Space

Recently we focus on the ionic motion in chiral nanospace. A porous metal–organic framework, Labtb, was synthesized with an enantioselective method. After the collaborative work with Prof. Okamoto and Dr. Narushima in IMS, high enantiomer-excess of Labtb in particle-level was visualized by circular dichroism imaging (*Chem. –Eur. J.* **10**, 6698–6702 (2019)). The obtained enantiomeric Labtb is highly stable from heat, chemicals and has 1D pore of ca. 13 Å in diameter, and we are searching the wide application of it.

I also intend to control the behavior of redox species by temperature response for constructing next-generation thermocell. Host–guest chemistry, (*Bull. Chem. Soc. Jpn.* **92**, 1142–1147 (2019); *Polymer J.* **50**, 761–769 (2019); *Chem. Sci.* **10**, 773–780 (2019)) and the chemistry of polythiolate (*ChemSusChem* **12**, 4014–4020 (2019)) were applied and high Seebeck coefficient was observed.

RESEARCH ACTIVITIES





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.

Biological Rhythm and Dynamics through Chemistry

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



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The Young Scientists' Prize
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2006 SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
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Keywords Biological Rhythm, Circadian Clock, Cyanobacteria

Living organisms on Earth evolved over time to adapt to daily environmental alterations, and eventually acquired endogenous time-measuring (biological clock) systems. Various daily activities that we perform subconsciously are controlled by the biological clock systems sharing three characteristics. First, the autonomic rhythm repeats with an approximately 24-hour (circadian) cycle (self-sustainment). Second, the period is unaffected by temperature (temperature compensation). Third, the phase of the clock is synchronized with that of the outer world in response to external stimuli (synchronization). We seek to explain these three characteristics, and consider the biological clock system of cyanobacteria to be an ideal experimental model.

The major reason that cyanobacteria are considered to be the ideal experimental model is that the core oscillator that possesses the three characteristics of the clock can be easily reconstructed within a test tube. When mixing the three clock proteins KaiA, KaiB, and KaiC with ATP, the structure and enzyme activity of KaiC change rhythmically during a circadian cycle. Taking advantage of this test tube experiment, we used an approach combining biology, chemistry, and physics

to elucidate the means by which the clock system extends from the cellular to atomic levels.

Among the three Kai proteins, KaiC is the core protein of the oscillator. In the presence of KaiA and KaiB, KaiC reveals the rhythm of autophosphorylation and dephosphorylation; however, the cycle of this rhythm depends on the ATPase activity of KaiC independent of KaiA or KaiB. For example, when the ATPase activity of KaiC doubles as a result of amino acid mutations, the frequencies of both the *in vitro* oscillator and the intracellular rhythm also double (the cycle period is reduced to half). This mysterious characteristic is called a transmurial hierarchy, in which the cycle (frequency) and even the temperature compensation both *in vitro* and *in vivo* are greatly affected (controlled) by the function and structure of KaiC.

How are the circadian activities and temperature compensation features encoded in KaiC and then decoded from it to propagate rhythms at the cellular level? We are committed to better understanding biological clocks and other dynamic systems through the chemistry of circadian **rhythm, structure**, and evolutionary **diversity**.

Selected Publications

- D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
- A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
- A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* **8**, 8803 (2018).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

1. Structure: Atomic-Scale Origins of Clock Slowness in Cyanobacterial Circadian Clock System¹⁾

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

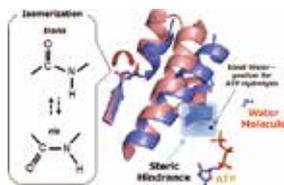


Figure 1. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

2. Rhythm: Transmural Hierarchy in Cyanobacterial Circadian Clock System^{2,3)}

KaiC ATPase is of particular interest here, as it finely correlates to the frequencies of *in vivo* as well as *in vitro* oscillations. This unique property has inspired us to develop an ATPase-based screening for KaiC clock mutants giving short, long, and/or temperature-dependent periods.²⁾ A developed HPLC system with a 4-channel temperature controller has reduced approximately 80% of time costs for the overall screening process (Figure 2).

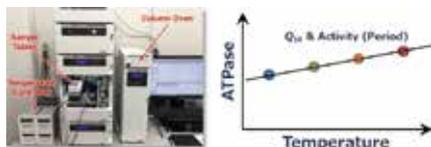


Figure 2. Development of a quick ATPase assay system.

How is the intra-molecular slowness encoded in KaiC (Figure 1) transmitted to the inter-molecular interactions with other Kai proteins? To address this question, a tryptophan residue was introduced in the N-terminal ring of KaiC as the fluorescent probe for KaiBC complex formation.³⁾ Our kinetic data indicated that KaiB exclusively selects the post-ATP-hydrolysis state of KaiC to form the KaiBC complex. This process follows a mechanism called conformational selection (CS), in which proteins (KaiC) first undergoes a structural change to form a specific intermediate. Ligands (KaiB) are

then recognized specifically through the intermediate state to form a tight ligand-protein complex. The CS mechanism is elegantly designed in KaiC so that the slow intra-molecular ATPase reaction in KaiC can be the rate-limiting step of the overall KaiBC complex formation.

3. beyond Evolutionary Diversity^{1,4)}

In the presence of KaiA and KaiB, the ATPase activity of KaiC oscillates on a 24-hour cycle. KaiC is not capable of maintaining a stable rhythm on its own, but its activity was observed to fluctuate with reduced amplitude over time (Figure 3A). We have identified a signal component that is similar to damped oscillation, and propose that it encodes the specific frequency, equivalent to a 24-hour cycle.¹⁾

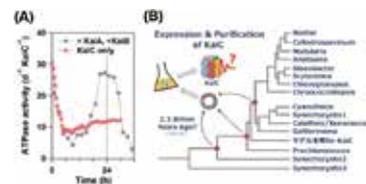


Figure 3. Damped oscillation of KaiC ATPase activity (A) and evolutionary diversity of cyanobacteria (B).

As this proposal is further discussed and verified, development of new studies is expected. Some KaiA and KaiB genes are missing in several strains of cyanobacteria. This is understandable to some extent if KaiC possesses the specific frequency. Given our current understanding of this phenomenon, *what specific frequencies are possessed by KaiCs and their homologues in other species and ancestral cyanobacteria?* (Figure 3B) The habitats of cyanobacteria are diverse, so the space of their sequence is immense.⁴⁾ If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

4. Bio-SAXS Activity in IMS^{5,6)}

We have supported SAXS users so that they can complete experiments smoothly and publish their results.^{5,6)}

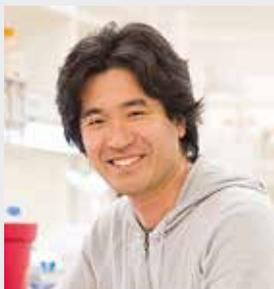
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- 5) M. Okumura, K. Noi, S. Kanemura, M. Kinoshita, T. Saio, Y. Inoue, T. Hikima, S. Akiyama, Y. Ogura and K. Inaba, *Nat. Chem. Biol.* **15**, 499–509 (2019).
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Protein Design Using Computational and Experimental Approaches

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2007 JSPS Postdoctoral Fellow for Research Abroad
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Keywords Structural Biology, Protein Folding, Protein Design for Structure and Function

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

Protein design holds promise for applications ranging from catalysis to therapeutics. There has been considerable recent progress in computationally designing proteins with

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

Selected Publications

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

1. Principles for Designing Ideal Protein Structures

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

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

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

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

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- 4) Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).
- 5) Y.-R. Lin, N. Koga, S. M. Vorobiev and D. Baker*, *Protein Sci.* **26**, 2187–2194 (2017).
- 6) S. Basak, R. P. Nobrega, D. Tavella, L. M. Deveau, N. Koga, R. Tatsumi-Koga, D. Baker, F. Massi* and C. R. Matthews*, *Proc. Natl. Acad. Sci. U. S. A.* **116**, 6806–6811 (2019).

Rules relating local backbone structures to tertiary structures

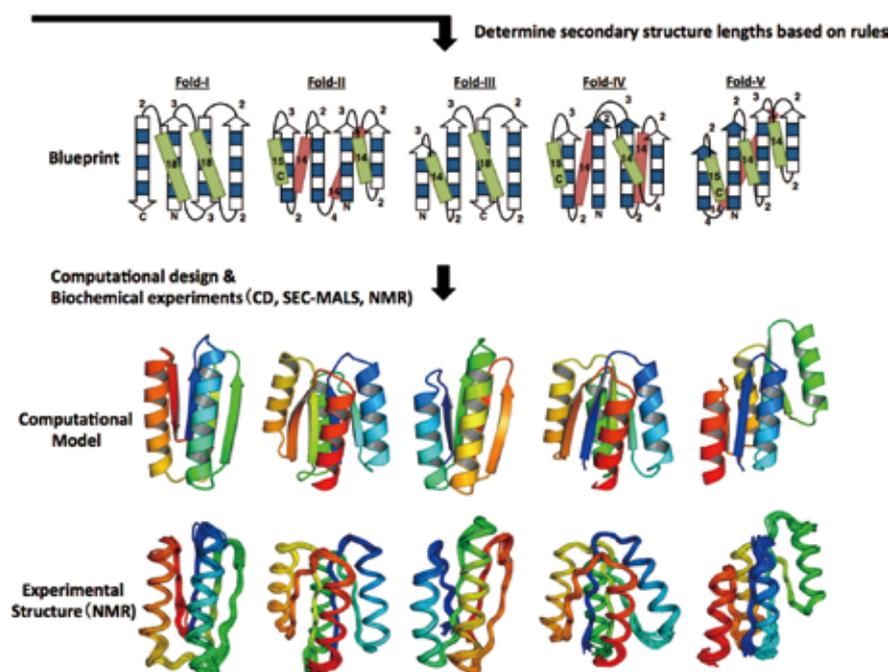
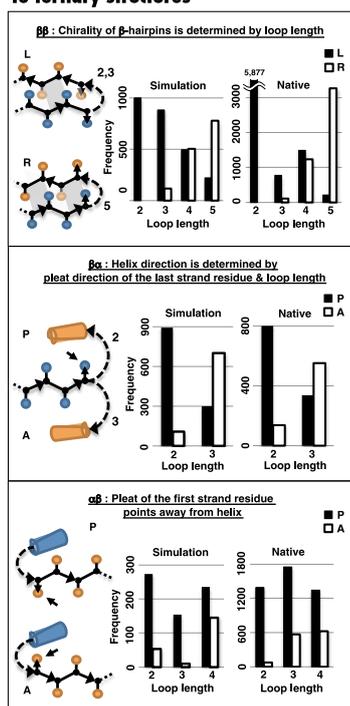


Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Open up Future Electronics by Organic Molecules

Research Center of Integrative Molecular Systems Division of Functional Molecular Systems



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Keywords Organic Mott Insulator, Field Effect Transistors, Organic Spintronics

Organic molecules are attracting recent attention as new ingredients of electronic circuits. Our group focuses on the 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. In the operation, 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 electric response of the device can be achieved, resulting in the highest device mobility ever observed for organic FETs. In addition to this high performance, the Mott-FET is interesting in terms of superconductivity. Because the Mott-transition sometimes accompanies superconducting phase in between metal and insulator, modulation of gate electric field at low temperature may induce superconductivity. In fact, we have achieved first example of field-induced superconductivity in an organic FET. By combining a strain effect that can tune the bandwidth, this type of electric-field-induced superconducting transition can

be utilized for mapping the phase diagram around the Mott-insulator as shown in Figure 1.

Another approach to the future electronics is the development of spintronic devices based on chirality of organic material. We aim to implement chirality-induced spin selectivity (CISS) effect into molecular devices that can generate spin-polarized current. This type of device is expected to realize spintronics devices without magnet or topological insulator.

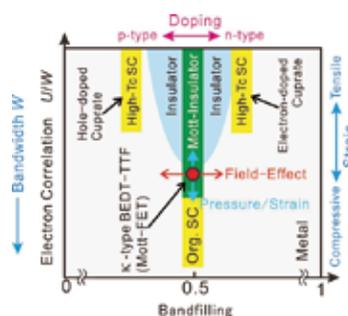


Figure 1. Phase diagram surrounding a Mott-insulator. SC denotes superconductor, while U and W are on-site Coulomb repulsion and bandwidth, respectively.

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- H. M. Yamamoto, M. Suda and Y. Kawasugi, "Organic Phase-Transition Transistor with Strongly Correlated Electrons," *Jpn. J. Appl. Phys.* **57**, 03EA02 (7 pages) (2018).
- Y. Kawasugi, K. Seki, Y. Edagawa, Y. Sato, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Electron-Hole Doping Asymmetry of Fermi Surface Reconstructed in a Simple Mott Insulator," *Nat. Commun.* **7**, 12356 (8 pages) (2016).
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- 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).

1. Light-Driven Spin Switching Device Using an Artificial Molecular Motor¹⁾

Artificial molecular switches and machines that enable the directional movements of molecular components by external stimuli have undergone rapid advances over the past several decades. Particularly, overcrowded alkene-based artificial molecular motors are highly attractive from the viewpoint of chirality switching during rotational steps. However, the integration of these molecular switches into solid-state devices is still challenging. In this study, solid-state spin-filtering devices that can switch the spin polarization direction by light irradiation or thermal treatment have been examined. We measured magnetoresistance of a device, in which M-cis form (Figure 2) of the motor is sandwiched by two electrodes as tunnelling layer, before and after photo irradiation. The magnetoresistance showed switching of spin polarization from up-spin selective to down-spin selective by the irradiation of light. This result indicates that the M to P chirality conversion by light is switching the spin of electrons that tunnel through the motor molecule because of CISS effect. We also confirmed that spin direction switching is possible in the next step, too, where heat treatment inverts the molecular chirality from P to M. During this study we found that the flexibility at the molecular scale is essential for the electrodes in solid-state devices using molecular machines. The same device operation was also confirmed by conductive AFM (atomic force microscope) measurement with magnetized tip. We also evaluated the strength of spin-orbit interaction by quantum chemical calculation, and found that state transitions between σ and π electron states are good to enhance the interaction. This result demonstrates a possibility of novel spintronics based on solid-state functionalities emerging from nano-sized motions of molecular switches.

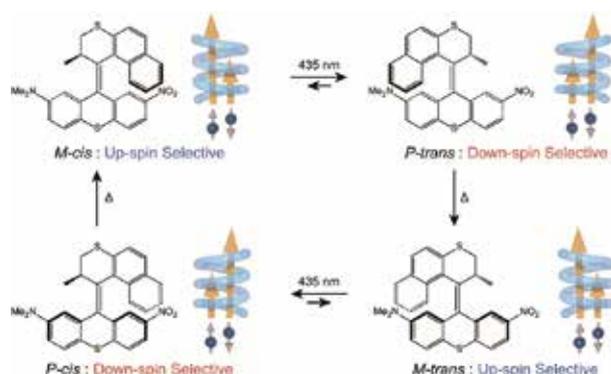


Figure 2. Spin selectivity switching by light irradiation and heat. The molecular motor has four steps for the 360 degree rotation, during which the four times chirality switching and associated spin switching occurs.

Award

YAMAMOTO, Hiroshi; The CSJ Award for Creative Work (2019).

2. Ambipolar Superconductivity in Organic Field-Effect Devices^{2,3)}

Because Mott-FET shows ambipolar operation, field-induced superconductivity in both p-type and n-type regimes is expected. This idea coincides with the fact that both hole-doped and electron-doped cuprates show superconductivity in the vicinity of Mott-insulator. We performed both FET and EDLT (electric double-layer transistor) measurement with organic Mott-insulator at low temperature. In the EDLT experiment, a flexible substrate was employed to tune not only the gate voltage but also the strain. With such a device, we could perform the scanning of bandwidth and bandfilling simultaneously. The phase diagram thus obtained at 5.5 K is shown in Figure 3.²⁾ This is the first experimental example of a phase diagram in which ambipolar superconductivity and strain-induced superconductivity are continuously surrounding the Mott-insulator. From theoretical insights, a p/n asymmetry evident in this diagram seems to originate in the band structure calculated without correlation. A similar ambipolar switching of superconductivity was also observed in Mott-FET with κ -(BEDT-TTF)₂Cu(NCS)₂.³⁾

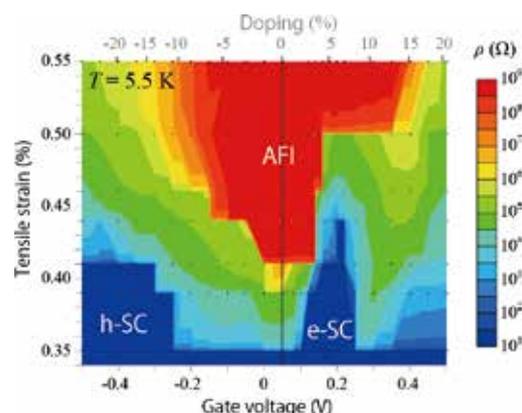


Figure 3. Emergence of both p-type (h-SC) and n-type (e-SC) superconductivity by gate voltage at various tensile strain. The strain is controlling electron correlation U/W while gate voltage controls bandfilling (see also Figure 1). AFI denotes antiferromagnetic insulator, meaning a Mott-insulating phase.

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Development of Graphene Molecules as Organic Semiconductors

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Keywords Organic Synthesis, Organic Semiconductor, Graphene Molecule

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

Perfluorination is a simple method to prepare an n-type semiconductor with the same molecular symmetry. It is impor-

tant to understand the impact of perfluorination on the solid-state structures and charge transport properties. We are currently working on the synthesis of new perfluorinated aromatic compounds.

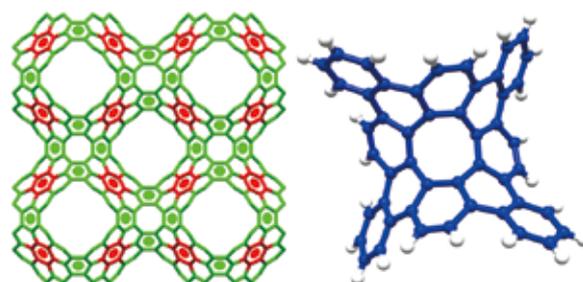


Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

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- Y. Sakamoto and T. Suzuki, "Perfluorinated and Half-Fluorinated Rubrenes: Synthesis and Crystal Packing Arrangement," *J. Org. Chem.* **82**, 8111–8116 (2017).

1. Brønsted Acid-Initiated Formal [1,3]-Rearrangement Dictated by β -Substituted Ene-Aldimines¹⁾

The rearrangement of ene-aldehydes is a useful reaction for affording homoallylic amines. Despite their utilities in synthetic chemistry, the rearrangement for accessing homoallylic amines substituted at the 2-position remains elusive. In this study, the Brønsted acid-initiated formal [1,3]-rearrangement of ene-aldehydes was developed to synthesize 2,4,4-substituted homoallylic amines that were otherwise inaccessible previously. Our study reveals an intermolecular pathway in which the rearrangement proceeds via a protonation-mediated 2-azaallenium cation.

2. Widely Dispersed Intermolecular Valence Bands of Epitaxially Grown Perfluoropentacene on Pentacene Single Crystals²⁾

Strong intermolecular electronic coupling and well-ordered molecular arrangements enable efficient transport of both charge carriers and excitons in semiconducting π -conjugated

molecular solids. Thus, molecular heteroepitaxy to form crystallized donor–acceptor molecular interfaces potentially leads to a novel strategy for creating efficient organic optoelectronic devices via the concomitance of these two requirements. In the present study, the crystallographic and electronic structures of a heteroepitaxial molecular interface, perfluoropentacene (PFP, C₂₂F₁₄) grown on pentacene single crystals (Pn-SCs, C₂₂H₁₄), were determined by means of grazing-incidence X-ray diffraction (GIXD) and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), respectively. GIXD revealed that PFP uniquely aligned its primary axis along the [1 $\bar{1}$ 0] axis of crystalline pentacene to form well-crystallized overlayers. Valence band dispersion (at least 0.49 eV wide) was successfully resolved by ARUPS. This indicated a significant transfer integral between the frontier molecular orbitals of the nearest-neighbor PFP molecules.

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RESEARCH ACTIVITIES





RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

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

Nano-Optical Imaging and Application to Nanomaterials

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Keywords Nano Optics, Plasmons, Chirality

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

ceeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials are also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

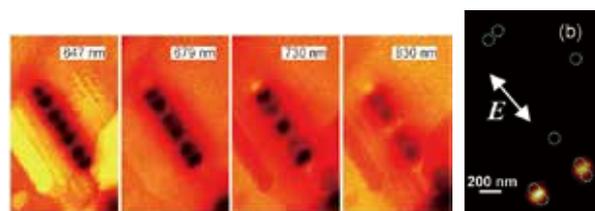


Figure 1. (Left four panels) Near-field transmission images of gold nanorod ($20 \text{ nm}^D \times 510 \text{ nm}^L$). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spherical 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).
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1. Active Control of Chiral Optical Near-Fields on a Single Metal Nanorod¹⁾

Chiral optical fields (typified by circularly polarized light) localized on the nanoscale enhance the chiral light–matter interaction, which may provide novel potential applications. This property enables the development of an ultrasensitive method for characterization of chiral molecules and nanoscale magnetic control realized by an all-optical method to interconnect spintronic nano-optical devices. A local chiral light source with switchable handedness or controllable chirality is indispensable for building such applications for practical use. In the current major method used for local chiral light generation, the handedness of the light is controlled by the handedness of the nanomaterial, which is not convenient when we need to change the handedness of the light. We experimentally achieve here generation and active control of a highly chiral local optical field by using a combination of an achiral gold nanorod and achiral linearly polarized optical field. By tilting the azimuth angle for the incident linear polarization relative to the axis of the nanorod, either left- or right-handed circularly polarized local optical fields can be generated. Our work may give us a chance to pioneer analytical applications of chiral optical fields and novel spintronic nano-optical devices.

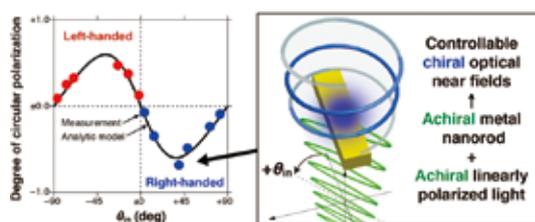


Figure 2. Right: Scheme of optical arrangement. A gold nanorod is illuminated by linearly polarized light with the E-field direction rotated for θ_m from the rod axis. Left: Experimentally obtained degree of circular polarization near the rod vs. polarization angle θ_m .¹⁾

2. Circularly Polarized Photoluminescence from Achiral Dye Molecules Induced by Plasmonic Two-Dimensional Chiral Nanostructures²⁾

Strong dissymmetry between left- and right-handed circularly polarized photoluminescence (PL) enhancement induced by 2-dimensional chiral gold nanostructures was found, which can be utilized to provide a circularly polarized luminescence source. Lightning-bolt-like (composed of two displaced rectangles) chiral plasmonic gold nanostructures were fabricated on a glass substrate and were adopted as materials to induce dissymmetry in PL enhancement. We employed achiral IR125 dye as an achiral molecular PL emitter with luminescence that was enhanced by near-field interaction between the chiral plasmon and the molecule. PL decay measurements confirmed that the PL enhancement arose from the plasmonic effect. Large PL enhancement dissymmetry factors $g \sim 0.14$ were obtained in the wavelength region near 800 nm. The dissymmetry of PL enhancement showed maximum amplitudes at

800–850 nm, which approximately correspond to the wavelength providing maximal extinction dissymmetry (~ 800 nm) of the lightning-bolt-like structure, and is resonant with a chiral multipolar plasmon mode. The dissymmetry was relatively small at the wavelength resonant with a dipolar plasmon mode.

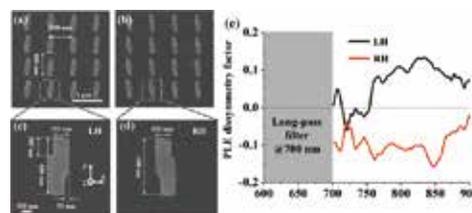


Figure 3. (a–d) Electron micrographs of chiral gold nanostructures. (e) Photoluminescence enhancement (PLE) dissymmetry spectra for luminescence from IR125 dye combined with left-handed (black) and right-handed (red) gold nanostructures.²⁾

3. Visualization of Enantiomeric Excess of Chiral Metal-Organic Framework Microparticles by Circular Dichroism Imaging³⁾

Circular dichroism (CD) microscopic images of microcrystalline particles of a microporous, robust, and chiral metal–organic framework (MOF) were observed to estimate enantiomer excess (ee) of the synthesized particles. La(btbt) (btbt = 1,3,5-tris(4-carboxylatephenyl)benzene), a thermally and chemically robust MOF, was employed in this study because it shows a chiral space group. Although La(btbt) has been obtained as a racemic conglomerate, enantioselective synthesis of La(btbt) was achieved via a chiral precursor complex consisting of lanthanum and homochiral phenylalanine. Methyl orange (MO) was introduced into the micropores of chiral La(btbt), which showed a strong induced CD signal for the absorption band of MO chromophores. High ee of the synthesized chiral La(btbt) was revealed by microscopic CD observation at the single particle-level. This result provides a facile way to obtain a robust MOF that has chiral nanospace, and demonstrates the potential utility of CD microscopy to define handedness of many microcrystalline particles at the same time.

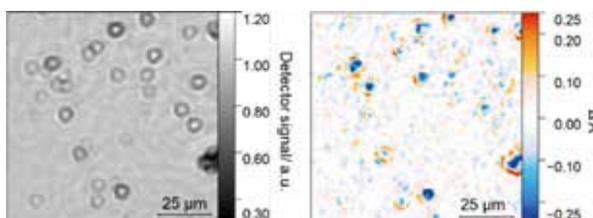


Figure 4. Transmission (left) and CD (right) microscopic images of $\text{MO}_{0.35}@\text{L-La}(\text{btbt})$.³⁾ Most of the particles showed the same CD signals.

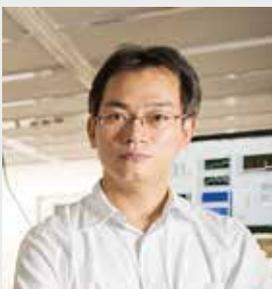
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Keywords Ultrafast Science, Laser Physics, Nonlinear Optics

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

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

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

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

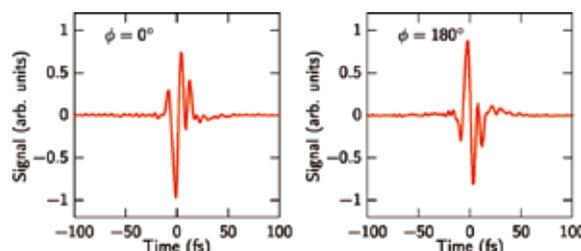


Figure 1. Infrared light waveforms measured with FROG-CEP. The phase difference between the two infrared pulses was clearly measured.

communication speed becomes 3 orders of magnitude faster. We believe that our method, FROG-CEP, becomes very important to realize such communication technology.

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

Selected Publications

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1. Development of Intense Femtosecond Lasers at $2\ \mu\text{m}$ ¹⁾

Intense ultrashort infrared pulse lasers are highly attractive in many research fields. Powerful femtosecond pulses in the vicinity of $2\ \mu\text{m}$ are desired for coherent mid-infrared or terahertz pulse generation, high harmonic generation in the water window soft x-ray region, and atmospheric sensing. In order to obtain intense femtosecond pulses around the $2\ \mu\text{m}$ wavelength region, one of the most widely used schemes is optical parametric amplification (OPA) with well-established ultrafast pump lasers such as Ti:sapphire or Yb lasers. However, OPA in general has a complicated design due to the requirement of the precise synchronization between the pump and seed pulses. This fact attracts a lot of attention to the development of solid-state lasers which directly generate high energy ultrashort pulses around $2\ \mu\text{m}$.

In this work we present a new table-top Tm:YAP laser system based on a diode-pumped ring cavity regenerative amplifier. The system generates 360 fs pulses at $2\ \mu\text{m}$ with the peak power of 2 GW after the compression.

The schematic of the system is shown in Figure 2. The seed source of the laser system is a Tm:ZBLAN fiber oscillator,²⁾ which generates $2\ \mu\text{m}$ pulses with the pulse energy of 4 nJ. The pulses are sent to a grating stretcher and then to a ZBLAN fiber pre-amplifier pumped by a laser diode at $794\ \text{nm}$.³⁾

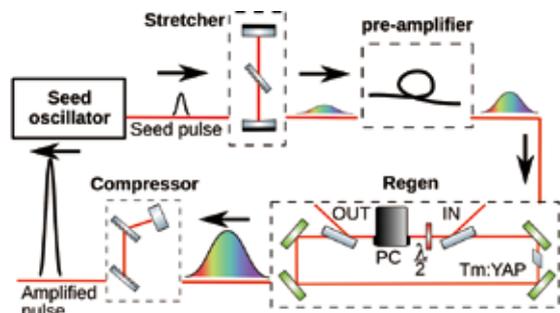


Figure 2. Schematic of the system. PC: Pockels cells.

The amplified seed pulses ($\sim 100\ \text{nJ}$) are picked with 1 kHz rate by a Pockel cell and are sent to a regenerative amplifier based on a Brewster-cut, 4% doped, 12 mm long Tm:YAP crystal which is pumped by another $794\ \text{nm}$ laser diode. The output power of the regenerative amplifier is 1.4 W with the absorbed pump power is 23.5 W at 45 round trips. The output pulse is compressed using a pair of gratings. The energy of the compressed pulse is 0.924 mJ.

The compressed pulse was characterized using a home-built SHG-FROG system. The temporal and spectral profile of the pulse obtained by the system are shown in Figure 3. The pulse duration is 360 fs.

The compressed pulses exhibit good beam profile and can be directly used to generate white light in bulk materials. Using only $15\ \mu\text{J}$ of the amplified pulse, we have generated

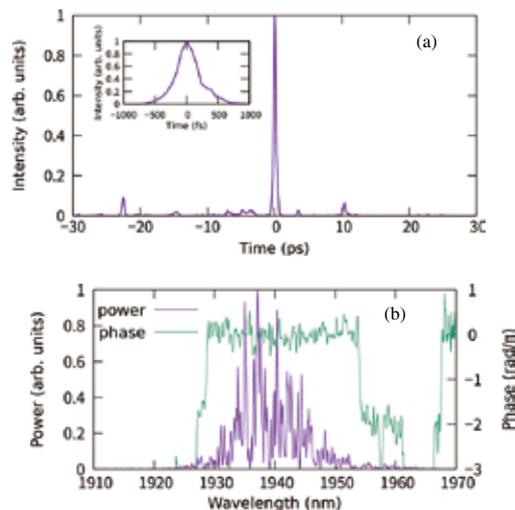


Figure 3. (a) Temporal profile of the pulse from the amplifier. Inset: Zoomed view of the main pulse peak. (b) Power spectrum and spectral phase of the pulse.

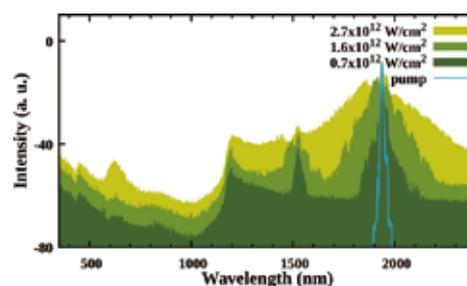


Figure 4. Variation of the generated white light with the changes of the pump intensity.

white light in a 3 mm YAG crystal. The white light spectra are shown in Figure 4.

Such properties combined with the good power scalability over a wide range of available pumping energies makes this scheme a viable candidate for direct application for mid-infrared OPA. In particular, the system exhibits a flexible electronic control on the obtainable output energy through changes in round trips, pumping energy, and repetition rate. The feature makes it a good candidate for many applications such as spectroscopy which would require a tight control over the light source. The proposed ring regenerative amplifier provides a versatile and simple infrared source that can be used in many of the current applications, in a compact table-top design.

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





RESEARCH ACTIVITIES

Division of Advanced Molecular Science

In this division, scientists of the first water are invited as “distinguished professors,” and the environment, in which they can devote themselves to their own research, is provided. The research in this division should be the last word in the field of molecular science.

Self-Assembling Molecular Systems Based on Coordination Chemistry

Division of Advanced Molecular Science



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Education

1980 B.S. Chiba University
1982 M.S. Chiba University
1987 Ph.D. Tokyo Institute of Technology

Professional Employment

1982 Researcher, Sagami Chemical Research Center
1988 Assistant Professor, Chiba University
1994 Associate Professor, Chiba University
1997 Associate Professor, Institute for Molecular Science
1999 Professor, Nagoya University
2002 Professor, The University of Tokyo
2018 Distinguished Professor, Institute for Molecular Science

Awards

1994 Progress Award in Synthetic Organic Chemistry, Japan
2000 Division Award of Chemical Society of Japan (Organic Chemistry)
2001 Tokyo Techno Forum 21 Gold Medal
2001 Japan IBM Award
2003 Nagoya Silver Medal
2004 Izatt-Christensen Award
2006 G. W. Wheland Award (Chicago University Lectureship Award)
2010 The Reona Esaki Award
2010 The JSCC Award
2011 3M Lectureship Award (University of British Columbia)
2012 Thomson Reuters Research Front Award 2012
2013 The Chemical Society of Japan (CSJ) Award
2013 Arthur C. Cope Scholar Award (ACS National Award)
2013 Merck-Karl Pfister Visiting Professorship (MIT Lectureship Award)
2014 ISNSCE 2014 Nanoprize
2014 Medal with Purple Ribbon
2014 Fred Basolo Medal (Northwestern University)
2018 Wolf Prize in Chemistry
2019 The Imperial Prize and the Japan Academy Prize

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Keywords Self-Assembly, Nano-Space, Coordination Chemistry

We are exploring new molecular materials with various three-dimensional architectures, utilizing the coordination chemistry. Especially, we are interested in materials, which possess inner space, because the inner space imparts new properties and functions to the materials. For example, we have developed a material called “crystalline sponge (CS),” which can accommodate many kinds of small molecules (Figure 1). Since the crystalline sponge can align the accommodated small molecules neatly in its inner space, we can carry out the structural elucidation of the accommodated molecules by the X-ray crystallography. This new structural elucidation technique is designated as “CS method,” and attracting broad interests, because this method enables the X-ray analysis without the crystallization of target molecules.

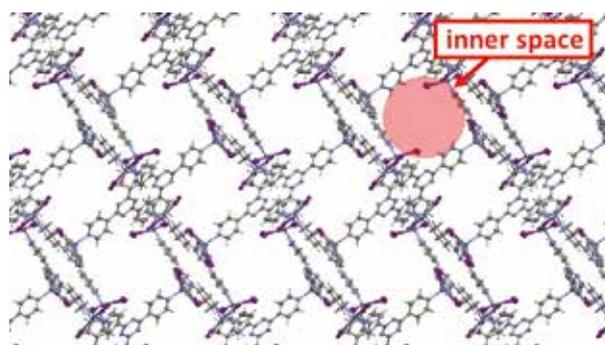


Figure 1. Network structure of the CS. There is inner space, into which various kinds of molecules could be introduced.

Selected Publications

- Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, “X-Ray Analysis on the Nanogram to Microgram Scale Using Porous Complexes,” *Nature* **495**, 461–466 (2013).
- D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, “Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components,” *Nature* **540**, 563–566 (2016).

1. Structural Elucidation of a Novel Natural Product, Tenebrathin, by the CS Method¹⁾

The natural product chemistry is one of the best fields, in which the CS method could be efficiently utilized. One of the goals of the natural product chemistry is an identification of new compounds with novel structures from nature. However, structures of natural products are, in many cases, very complex and hard to solve. But, if we use the CS method, we can easily and quickly observe the 3D-structure of target compounds. Thus, the CS method has a great potential to accelerate the study in the field of natural product chemistry.

To search for novel natural products, we investigated into metabolite of bacterium *Streptoalloteichus tenebrarius* NBRC 16177, and found a new compound, which we designated as tenebrathin (**1**). Firstly, the structure of **1** was investigated by the NMR (Nuclear Magnetic Resonance) analysis, and a partial structure of **1** could be solved. However, we could not know its complete structure. Actually, even though NMR is really strong approach to solve the structures of small molecules, NMR analysis is not a universal method. Sometimes, we encounter compounds, whose structures could not be solved by the NMR analysis. Moreover, the NMR analysis normally could not determine an absolute configuration. Thus, we subjected **1** to the CS method. As a result, the structure and the absolute configuration of **1** was clearly solved (Figure 2). These results have been obtained through a collaborative research with Prof. Ikuro Abe (the University of Tokyo, Japan).

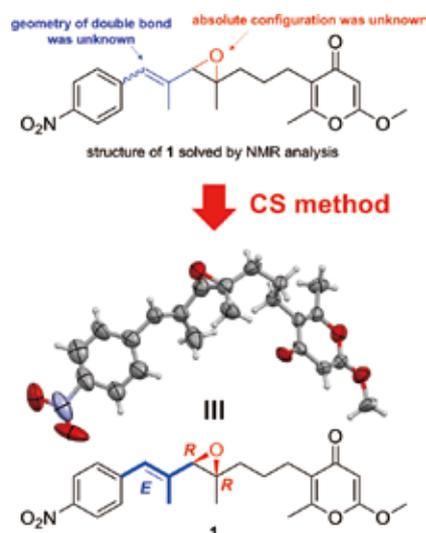


Figure 2. The chemical structure of **1**, and a crystal structure of **1**, which was observed by the CS method.

Award

FUJITA, Makoto; The Imperial Prize and the Japan Academy Prize (2019).

2. Structural Elucidation of a Biosynthetic Intermediate of Diosgenin²⁾

Diosgenin is a spiroketal steroidal natural product and one of the important compounds for the world steroid hormone industry, because diosgenin can be used as precursor of drugs. However, the biosynthetic pathway of diosgenin was unknown, and almost all diosgenin used in the industry are extracted from plant.

If we can solve the biosynthetic route of diosgenin, we would be able to pave the way for developing fermentative production process, which does not require the plant body to obtain diosgenin. Therefore, we tried to solve the biosynthetic pathway of diosgenin.

As a result, we identified enzymes responsible for the biosynthesis of diosgenin. At the same time, we also obtained compound **2**, a biosynthetic intermediate of diosgenin. However, only 1.5 mg of **2** could be obtained, and it was hard to determine its chemical structure only by the NMR and MS analysis. Therefore, we apply the CS method, and successfully elucidated the structure of **2** (Figure 3). These results have been obtained through a collaborative research with Prof. Jing-Ke Weng (Massachusetts Institute of Technology, USA).

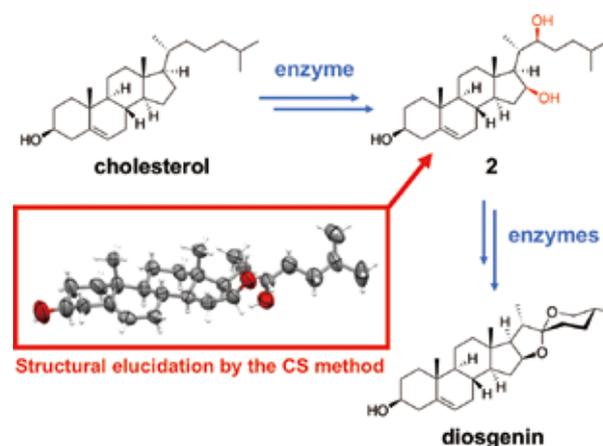


Figure 3. The biosynthetic pathway of diosgenin, and a crystal structure of **2**, which was observed by the CS method.

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RESEARCH ACTIVITIES





RESEARCH ACTIVITIES

Division of Research Innovation and Collaboration

As the open innovation hub managed by IMS and companies, we conduct the research projects in collaboration with Academia, Industry and Government.

Micro Solid-State Photonics

Division of Research Innovation and Collaboration



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Education

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

Professional Employment

1985 Researcher, Mitsubishi Electric Corp.
1989 Research Associate, Fukui University
1993 Visiting Researcher, Stanford University (–1994)
1998 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2018 Group Director, RIKEN SPring-8 Center
2019 Project Professor, Institute for Molecular Science

Awards

2004 Persons of Scientific and Technological Research Merits, Commendation by Minister of Education, Culture, Sports, Science and Technology, Japan
2010 OSA Fellow Award, The Optical Society (OSA)
2012 SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
2014 IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)
2018 IAPLE (The International Academy of Photonics and Laser Engineering) Fellow
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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: The world first laser ignited car, highly efficiency broad frequency conversions from the wavelength of 118nm VUV until 300–500 μ m THz waves, and so on. In addition, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. Lately, we propose a new architecture to realize a monolithic multi-disk laser by the surface activated bonding (SAB). This multiple thin-disk or chip gain medium for distributed face cooling (DFC) structure can manage the high-power and high-field laser with high-gain compact system. Besides, QPM-structured crystal quartz constructed by multiple plate stacking could be promising as a high-power and reliable VUV frequency conversion devices. These downsized and



Figure 1. TILA consortium toward “Laser Science and Innovation” by micro solid-state photonics.

modularized **tiny integrated lasers** (TILA) promise the extremely high-brightness lasers to open up the new science, such as laser driven electron accelerator toward table-top XFEL, and innovation by the compact power laser (Figure 1).

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1. High Peak Power Nd:YAG/Cr:YAG Ceramic Microchip Laser with Unstable Resonator¹⁾

A doughnut mode microchip laser was demonstrated by introducing a monolithic ceramic Nd:YAG/Cr⁴⁺:YAG chip in an unstable resonator to deliver laser pulses with an energy of 13.2 mJ and a pulse width of 476 ps, corresponding to a record peak power of 27.7 MW. The laser beam quality was characterized by $M^2 \sim 6$ at 10 Hz repetition rate. No significant degradation or change of beam pattern, pulse width, and M^2 was confirmed during energy scaling in the case of the unstable cavity, promising for further brightness improving. In comparison with a stable cavity, pulse broadening and M^2 increase was observed up to ~ 1.2 ns and ~ 10 , respectively, during energy scaling up to 18 mJ due to the beam pattern degradation.

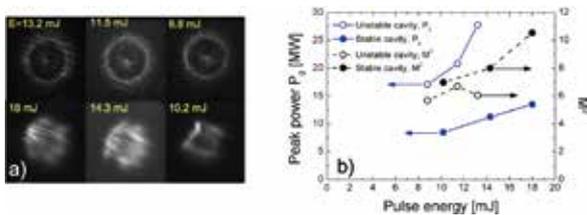


Figure 2. (a) Measured beam patterns and (b) peak power and M^2 at different pulse energies for unstable and stable cavity.

2. High-Brightness 100 Hz 190 mJ Micro-MOPA with the Gain Aperture^{2,3)}

High-brightness 100Hz repetition rate compact MOPA system has been developed. A microchip laser was used as an oscillator whose pulse shape and energy were improved through a Gain Aperture device (GA): After GA, energy was increased

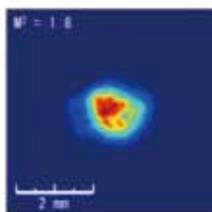


Figure 3. Beam profile under 190 mJ and 100 Hz operation.

from 2.8 mJ to 6.4 mJ, while beam quality factor was reduced from 3.2 to 1.2. The beam was then amplified through double-pass compact high-power amplifier. The strong intrinsic thermal lens of the amplifier has been efficiently compensated

Award

TAIRA, Takunori; Fellow, The Laser Society of Japan (2019).

by inserting a set of convex-concave lenses between first and second-pass, designed after ABCD matrix calculations. Without compensation, operation was limited to 10 Hz with output beam brightness reaching 18 PW/sr/cm², whereas compensation system allowed operation to 100 Hz with a brightness of 11 PW/sr/cm².

3. Spectral Phase Control of Interfering Chirped Pulses for High-Energy Narrowband Terahertz Generation⁴⁾

We show that high-order spectral phase fundamentally limits the efficiency of narrowband difference-frequency generation using chirped-pulse beating and resolve this limitation by introducing a novel technique based on tuning the relative spectral phase of the pulses. For optical terahertz generation, we demonstrate a 13-fold enhancement in conversion efficiency for 1%-bandwidth, 0.361 THz pulses, yielding a record energy of 0.6 mJ and exceeding previous optically-generated energies by over an order of magnitude. Our results prove the feasibility of millijoule-scale applications like terahertz-based electron accelerators and light sources and solve the long-standing problem of temporal irregularities in the pulse trains generated by interfering chirped pulses.

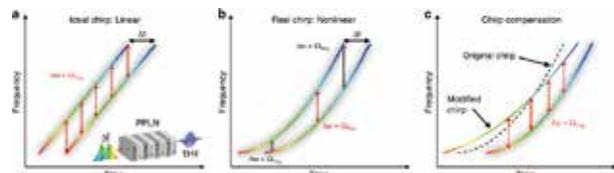


Figure 4. Chirp-and-delay concept. (a) Two broadband but linearly chirped and delayed pulses provide narrow spectral features with constant instantaneous difference frequency. (b) Due to higher order dispersion difference frequency varies along the pulse and limits the range where the provided difference frequency fulfils the phase matching condition in the PPLN. (c) Slightly tilting one of the pulses in time-frequency space regularizes difference frequency and thereby maximizes THz generation.

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