RESEARCH ACTIVITIES Theoretical and Computational Molecular Science

The goal of the Department is to predict and elucidate static and dynamic properties, reactions, and functions in condensed phase including biomolecular and heterogeneous catalytic 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



SAITO, Shinji Professor [shinji@ims.ac.jp]

Education

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

Professional Employment

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

Member

Assistant Professor MORI, Toshifumi KODA, Shin-ichi JSPS Post-Doctoral Fellow MATSUMURA, Yoshihiro

Post-Doctoral Fellow MAURYA, Manish Graduazte Student KALATHINGAL, Mahroof ZHU, Zhe Secretary

CHIBA, Fumika

Keywords

Reactions, Functions, Fluctuations

Many-body molecular systems, such as (supercooled) liquids and biomolecules, exhibit complex fluctuations. Furthermore, in these systems, various physical properties and biological functions are created and chemical reactions proceed under the fluctuations. We aim to elucidate the properties, functions, and reactions by investigating fluctuations and dynamics of the many-body molecular systems.

We investigate fluctuations and dynamics of liquids by developing computational methods for multi-dimensional nonlinear spectroscopy that can reveal detailed dynamical infomation not available from conventional linear spectroscopy. Consequently, we revealed the molecular origins of ultrafast energy relaxation and time evolution of inhomogeneous fluctuations in liquid water. In supercooled liquids, rare and non-uniform structural changes, called dynamic heterogeneity, are induced by fluctuations. We elucidated the relationship between the lifetime of the dynamic heterogeneity and the fragility using the three-time correlation function of density fluctuations.

We study the molecular origin of anomalous properties of liquid water. We revealed that the anomalies of liquid water are related to the structural and dynamical instabilities hidden in the experimentally inaccessible region and the physical reason of the low glass transition temperature of liquid water.

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), C. R. Baiz *et al.*, *Chem. Rev.* 120, 7152–7218 (2020).
- K. Kim and S. Saito, J. Chem. Phys. (Special Topic on Glass Transition) 138, 12A506 (12 pages) (2013).

We currently investigate how rare but persistent structural relaxation of liquid water proceeds towards the glass transition temperature.

Complex conformational fluctuations and changes can be observed in biomolecular systems. Such conformational dynamics are considered to be essential for biological functions. We examine the relationship between fluctuation and biomolecular function found in the robust circadian rhythm of the clock protein KaiC and the efficient excitation energy transfer in photosynthetic systems. We investigate dynamic effects of enzymatic reactions, and find the importance of prearranged states for the rare but persistent enzymatic reactions. Furthermore, we examine dynamic disorder in conformational changes of proteins at the molecular level.



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).

- S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* 149, 124504 (8 pages) (2018), S. Saito and B. Bagchi, *J. Chem. Phys.* 150, 054502 (14 pages) (2019).
- T. Mori and S. Saito, J. Phys. Chem. Lett. 10, 474-480 (2019).
- S. Saito, M. Higashi and G. R. Fleming, J. Phys. Chem. B 123, 9762–9772 (2019).

1. Dissecting the Dynamics during Enzyme Catalysis: A Case Study of Pin1 Peptidyl-Prolyl Isomerase¹⁾

Free energy surfaces have played a central role in studying protein conformational changes and enzymatic reactions over decades. Yet, free energy barriers and kinetics are highly dependent on the coordinates chosen to define the surface, and furthermore, the dynamics during the reactions are often overlooked. Our recent study on the Pin1-catalyzed isomerization reaction has indicated that the isomerization transition events remarkably deviate from the free energy path, highlighting the need to understand the reaction dynamics in more detail. To this end, here we investigate the reaction coordinates that describe the transition states of the free energy and transition pathways by minimizing the cross-entropy function. We show that the isomerization transition events can be expressed by the concerted changes in the improper torsion angle ζ and nearby backbone torsional angles of the ligand, whereas the transition state of the free energy surface involves changes in a broad range of coordinates including multiple protein-ligand interactions. The current result supports the previous finding that the isomerization transitions occur quickly from the conformational excited states, which is in sharp contrast to the slow and collective changes suggested from the free energy path. Our results further indicate that the coordinates derived from the transition trajectories are not sufficient for finding the transition states on the free energy surfaces due to the lack of information from conformational excited states.

2. An Alternative Interpretation of the Slow KaiB-KaiC Binding of the Cyanobacterial Clock Proteins²⁾

The biological clock of cyanobacteria is composed of three proteins, KaiA, KaiB, and KaiC. The KaiB–KaiC binding brings the slowness into the system, which is essential for the long period of the circadian rhythm. However, there is no consensus as to the origin of the slowness due to the prebinding conformational transition of either KaiB or KaiC. In this study, we propose a simple KaiB–KaiC binding scheme in a hexameric form with an attractive interaction between adjacent bound KaiB monomers, which is independent of KaiB's conformational change. We then show that the present scheme can explain several important experimental results on the binding, including that used as evidence for the slow conformational transition of KaiB. The present result thus indicates that the slowness arises from KaiC rather than KaiB.

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 the 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 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.

4. Molecular Mechanism of Acceleration and Retardation of Collective Orientation Relaxation of Water Molecules in Aqueous Solutions⁴⁾

The collective orientation relaxation (COR) of water molecules in aqueous solutions is faster or slower with the increase in concentration of the solutions than that in pure water; for example, acceleration (deceleration) of the COR is observed in a solution of sodium chloride (tetramethylammonium chloride) with increasing concentration. However, the molecular mechanism of the solution and concentration dependence of the relaxation time of the COR has not yet been clarified. We theoretically investigate the concentration dependence of the COR of water molecules in solutions of tetramethylammonium chloride (TMACl), guanidinium chloride (GdmCl), and sodium chloride (NaCl). Based on the Mori-Zwanzig equation, we identify two opposing factors that determine the COR of water molecules in any aqueous solution: The correlation of dipole moments and the single-molecule orientation relaxation. We reveal the molecular mechanism of the concentration dependence of the relaxation time of the COR in the TMACl, GdmCl, and NaCl solutions in terms of these two factors.

- 1) T. Mori and S. Saito, J. Chem. Theory Comput. 16, 3396–3407 (2020).
- 2) S.-i. Koda and S. Saito, Sci. Rep. 10, 10439 (7 pages) (2020).
- 3) S. Saito, M. Higashi and G. R. Fleming, J. Phys. Chem. B 123, 9762–9772 (2019).
- N. Moritsugu, T. Nara, S.-i. Koda, K. Tominaga and S. Saito, to be submitted.

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

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



Associate Professor

[eminamitani@ims.ac.jp]

Education

- 2005 B.S. Osaka University
- Ph.D. Osaka University 2010

Professional Employment

- 2010 Postdoctoral Fellow, Osaka University
- Special Postdoctral Researcher, RIKEN 2011
- Assistant Professor, The University of Tokyoy 2013
 - 2015 Lecturer, Cornell University
 - 2019
 - Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

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 The Young Scientists' Prize

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 electronphonon interaction. The electron-phonon interaction is one of the most fundamental interactions in the condensed matter

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).

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.

Member Assistant Professor

Secretary

SHITADE, Atsuo Research Fellow

HINODE, Kenji

AKABA, Atsuko

OKUGAWA, Shinichi



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

- 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).
- E. Minamitani, M. Ogura and S. Watanabe, "Simulating Lattice Thermal Conductivity in Semiconducting Materials Using High-Dimensional Neural Network Potential," Appl. Phys. Express 12, 095001 (2019).

1. Superconductivity in Chemically Doped 2D Materials

Layered materials have been investigated for a long time owing to their tunable features, which enable various applications. Amongst them, superconductivity has recently attracted considerable attention. Although several types of 2D superconductors have been experimentally and/or theoretically investigated, most of them are metallic/semimetallic materials, such as metal atomic layers on semiconductor surfaces, layered materials such as FeSe and NbSe₂, and electron-doped graphene. The other class of 2D superconductors is doped 2D semiconductors or insulators.

We focused on hexagonal boron nitride (h-BN) as a candidate for a 2D superconductor. Bulk h-BN has a wide bandgap of approximately 6 eV, and it exists in the monolayer form. Although the application of h-BN as an inert and atomically flat insulating layer to realize novel 2D-material-based electronics has been widely investigated, its possibility as a superconductor has been untapped until recently. In our previous study, we reported that a Li-intercalated h-BN bilayer became a phonon-induced superconductor with a $T_{\rm c}$ of up to 25 K, thereby indicating that both the phonon properties and electron-phonon coupling (EPC) in doped h-BN are appropriate for realizing superconductivity.1) However, the fabrication of a superconducting Li-intercalated h-BN bilayer is experimentally challenging, as the stacking order of the h-BN sheets must differ from that of the original bulk structure to attain a high T_c . To seek a promising candidate for an h-BN-based superconductor with a more experimentally feasible structure than the bilayer structure, we investigated the properties of doped monolayer h-BN by using ab-initio calculation of electron-phonon interaction.

Consequently, we reveal that Sr- and Ba-doped monolayer h-BN and Ca-doped monolayer h-BN with 3.5% tensile strain are energetically stable and become superconductors.²⁾ The estimated T_{cs} from McMillan–Allen–Dynes formula are approximately 5.83, 1.53, and 10.7 K, respectively. Interestingly, the T_{cs} for the Ca-, Sr-, and Ba doped graphene are lower than 0.5K.

To clarify the difference between h-BN and graphene, we analysed the electronic band structure depicted in Figure 2. The projection of the DOS from the adsorbate s-orbital onto the electronic-band structures indicated the presence of adsorbate bands that crossed the Fermi level in all systems. These bands correspond to the interlayer state reported in previous studies. In doped graphene systems, the interlayer state is crucial for determining T_c . However, the similarity in the interlayer state between doped graphene and h-BN indicates that the T_c in these systems is governed by other factors. Other than the interlayer states, several bands that originated from h-BN and graphene orbitals crossed the Fermi level.

These band structures around the Fermi level resulted in Fermi surfaces of different shapes and positions, as depicted in Figure 3. In both the h-BN and graphene cases, the Fermi surface around the K point originates from the interlayer state, and those around the Γ point correspond to the band from the h-BN or graphene states. The shape of the Fermi surfaces from the interlayer states resembled each another in both the doped h-BN and graphene cases, except for the size of the pocket.



Figure 2. Electronic band dispersions and DOS for doped h-BN and graphene.

However, the shapes of the inner Fermi surfaces around the Γ point between the doped h-BN and graphene cases differed significantly. In the doped h-BN case, the inner Fermi surface exhibited a snowflake-like shape, but it was hexagram-like in the doped graphene case. The projection of the k-resolved EPC (λ_k) shows that the electron–phonon interaction in the inner Fermi surface is crucial for determining T_c . Compared with doped graphene, the doped h-BNs exhibited greater λ_k in general in the Brillouin zone. The most prominent enhancement in λ_k was observed around the Γ point.



Figure 3. Fermi surfaces and k-resolved EPC projected on Fermi surface in doped h-BN and graphene.

The enhancement in λ_k around the Γ point in the Ca-doped h-BN is attributed to the spatial distribution of the wavefunction of the electronic states induced by the lower symmetry compared to the graphene case. These results indicate that instead of tuning the interlayer state, reducing the symmetry and introducing strong adsorbate–substrate interactions are alternative strategies to increase the T_c of doped 2D semiconductors/insulators.

Other Ongoing Projects:

- Geometric Spin–Orbit Coupling and Chirality-Induced Spin Selectivity

- Ab-Initio Calculation of Heat Generation in Semiconductors

- N. H. Shimada, E. Minamitani and S. Watanabe, *Appl. Phys. Express* 10, 9 (2017).
- N. H. Shimada, E. Minamitani and S. Watanabe, J. Phys.: Condens. Matter 32, 435002 (2020).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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



ISHIZAKI, Akihito Professor [ishizaki@ims.ac.jp]

Education

2008 D.S. Kyoto University

Professional Employment

- 2006 JPSP Research Fellow, Kyoto University
- 2008 JPSP Postdoctoral Fellow for Research Abroad, University of California, Berkeley
- 2010 Postdoctoral Fellow, Lawrence Berkeley National Laboratory 2012 Research Associate Professor, Institute for Molecular
- Science 2013 Fellow 2012–2013, Wissenschaftskolleg zu Berlin
- 2013 Pellow 2012–2013, Wissenschartskolleg zu Berlin 2016 Professor, Institute for Molecular Science
- Professor, The Graduate University for Advanced Studies Visiting professor, Nagoya University

Awards

- 2015 10th Condensed-Matter Science Prize, Japan
- 2016 10th Young Scientist Award of the Physical Society of Japan
- 2016 18th Sir Martin Wood Prize
- 2017 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
- 2020 JSPS Prize
- 2020 Japan Academy Medal

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

Selected Publications

- 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).
- A. Kato and A. Ishizaki, "Non-Markovian Quantum-Classical

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.

Member Assistant Professor

Secretary

NGUYEN, Thanh Phuc Post-Doctoral Fellow

FUJIHASHI, Yuta

AKABA, Atsuko

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.

Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases," *Phys. Rev. Lett.* **121**, 647 (2018).

- Y. Fujihashi, R. Shimizu and A. Ishizaki, "Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules," *Phys. Rev. Res.* **2**, 023256 (2020).
- A. Ishizaki, "Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy," J. Chem. Phys. 153, 051102 (2020). [Editor's Pick]

1. Precise Determination of Excitation Energies 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 proposed 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 was also investigated, from which a power scaling law relating the polariton's linewidth to the number of molecules was obtained.¹

2. Controlling the Nonadiabatic Electron Transfer Reaction Rate through Molecular Vibration Polaritons

Recent experiments showed that the chemical reaction rate is modified by strongly coupling a nuclear vibration mode to the single mode of an optical cavity. Herein we investigated how the rate of an electron-transfer reaction depends on the molecule-cavity coupling. We found two main factors that determine the modification of the reaction rate: The relative shifts of the energy levels induced by the coupling and the mixing of the ground and excited states of molecular vibration in the ground state of the hybrid molecule-plus-cavity system through which the Franck-Condon factor between the initial and final states of the transition is altered. The effect of the mixing of molecular vibrational states on the reaction rate is, however, suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton, and thus should be observed in a system containing a small number of molecules. In contrast, the effect of the relative shifts of the energy levels should be essentially independent of the number of molecules coupled to the cavity.³⁾

3. Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules

Light incident upon molecules triggers 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 due to continuous pumping, and therefore the photoinduced processes cannot be easily investigated. In this work, we demonstrated theoretically that the characteristics of sunlight photons, such as photon number statistics and spectral distribution, can be emulated through a quantum entangled photon pair generated with para-

Awards ISHIZAKI, Akihito; 16th JSPS Prize (2020). ISHIZAKI, Akihito; 16th Japan Academy Medal (2020). metric down-conversion (PDC). We showed that the average photon number of sunlight in a specific frequency spectrum, *e.g.*, the visible light, could be reconstructed by adjusting the PDC crystal length and pump frequency, and thereby the molecular dynamics induced by the pseudo-sunlight could 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, enabling investigations on real-time dynamics triggered by pseudo-sunlight photons.⁴⁾

4. Probing Excited-State Dynamics with Quantum Entangled Photons

Quantum light is a key resource for promoting quantum technology. One such class of technology aims to improve the precision of optical measurements using engineered quantum states of light. In this study, we investigate transmission measurement of frequency-entangled broadband photon pairs generated via parametric down-conversion with a monochromatic laser. It is observed that state-to-state dynamics in the system under study are temporally resolved by adjusting the path difference between the entangled twin beams when the entanglement time is sufficiently short. The non-classical photon correlation enables time-resolved spectroscopy with monochromatic pumping. It is further demonstrated that the signal corresponds to the spectral information along antidiagonal lines of, for example, two-dimensional Fouriertransformed photon echo spectra. This correspondence inspires us to anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.⁵⁾

5. Prerequisites for Relevant Spectral Density and Convergence of Reduced Density Matrices at Low Temperatures

Hierarchical equations of motion approach with the Drude– Lorentz spectral density has been widely employed in investigating quantum dissipative phenomena. However, it is often computationally costly for low-temperature systems because a number of Matsubara frequencies are involved. In this work, we examined a prerequisite required for spectral density, and demonstrated that relevant spectral density significantly reduced the number of Matsubara terms to obtain convergent results for low temperatures.²⁾

- 1) T. P. Nguyen and A. Ishizaki, Phys. Rev. Res. 1, 033019 (2019).
- 2) T. P. Nguyen, Q. T. Pham and A. Ishizaki, *Sci. Rep.* **10**, 7318 (2020).
- Y. Fujihashi, R. Shimizu and A. Ishizaki, *Phys. Rev. Res.* 2, 023256 (2020).
- 4) A. Ishizaki, J. Chem. Phys. 153, 051102 (2020). [Editor's Pick]
- 5) A. Ishizaki, J. Phys. Soc. Jpn. 89, 015001 (2020).

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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

1,	Education 1988 B.E. Kyoto University 1990 M.E. Kyoto University 1993 Ph.D. Kyoto University Professional Employment	VIGNESH, K. R. Visiting Scientist ZHAO, Xiang PRIYAKUMAR, Deva U BOBUATONG, Karan Graduate Student
	 1993 Postdoctral Fellow, Institute for Fundamental Chemistry 1994 JSPS Postdoctoral Fellow 1994 Visiting Researcher, Heidelberg University (-1995) 1995 Assistant Professor, Kyoto University 2002 Associate Professor, Kyoto University 	KANAZAWA, Yuki SHIRAOGAWA, Takafumi Secretary KAWAGUCHI, Ritsuko
EHARA, Masahiro Professor [ehara@ims.ac.jp]	 2002 Indecedent ryots chirotechy solutions 2008 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) 	SUGIMOTO, Yukari
	Awards 2009 APATCC Pople Medal 2009 QSCP Prize CMOA	

Keywords

Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

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

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

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states. (2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at heterojunction of Ag nanocluster supported by alumina surface in terms of 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

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).

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.

Member

Post-Doctoral Fellow

ZHAO, Pei

(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.

- 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 Design of Photofunctional Molecular Aggregates for Optical Properties: An Inverse Design Approach¹⁾

Properties of molecular aggregates are defined by their composition and structure. It is becoming possible to control these elements via advances in experimental techniques, and therefore the design guidelines are demanded for developing efficient optical materials. Here we propose a theoretical design approach for photofunctional molecular aggregates using an inverse design framework, the linear combination of atomic potentials (LCAP). The Frenkel exciton model coupled with the LCAP is introduced for designing systems with desired optical properties by gradient-guided optimization searches in terms of constituent molecules in chemical space of molecular aggregates. We have applied this approach to design one-dimensional molecular aggregates having locally maximized absorption and/or circular dichroism (CD) intensities as an example. By exploring a small fraction of the vast chemical space of 10²⁶ possible systems varying in composition and structure, we successfully obtained the optimal aggregates. The optimal structure-photofunction relationships were investigated from the designed systems. The present method is useful to design photofunctional molecular aggregates and accelerate optical material discoveries.



Figure 1. Schematic representation of the inverse design of photofunctional molecular aggregates with desired optical properties.

2. Importance of the Pd and Surrounding Site in Hydrosilylation of Internal Alkynes by Pd-Au Alloy Catalyst²⁾

Hydrosilylation is one of the key reactions in the formation of carbon–silicon bonds, where the addition of Si–H bonds occurs across the unsaturated bond in organic compounds. The Pd–Au alloy catalyst has been developed for the hydrosilylation of internal alkynes as well as α , β -unsaturated ketones under mild conditions. Herein, density functional theory calculations were utilized to study the mechanism of the hydrosilylation reaction of internal alkynes on the Pd–Au catalyst. The calculated energy profiles show that the reaction follows the Chalk–Harrod mechanism. The Pd site acts as the adsorption site and the reactive center as observed in experiments. The surrounding Pd–Au bridge and Au sites are also relevant for the bond activation and accepting the substrates or intermediates during the reaction, which is characteristic in the Pd–Au alloy catalysts and not available in the homogeneous catalyst. The present picture of the relevance of the Pd atomic site and its surrounding Pd–Au bridge or Au sites will be useful for developing the alloy catalysts for the related catalytic reactions.



Figure 2. Hydrosilylation on the Pd-Au Alloy Catalyst.

3. Theoretical Study on ³¹P NMR Chemical Shifts of P-Modified CHA Zeolites³⁾

The modification of zeolites with phosphorus is a widely adopted method to tune the acidity and consequently the catalytic properties in terms of activity, shape selectivity, and hydrothermal stability. The ³¹P MAS NMR spectra of phosphorus-modified chabazite (P-CHA) zeolites have been observed during the hydrothermal treatment to probe the structural changes of phosphorus species in zeolites. Theoretical calculations on the ³¹P and ²⁷Al NMR chemical shifts have been systematically performed to disclose the possible phosphorus species of intra- and extra-framework and the structural changes during the hydrothermal treatment. The present theoretical results provide useful information regarding the ³¹P NMR chemical shifts in P-CHA, which will significantly improve the ³¹P NMR assignments in future experiments.



Figure 3. ³¹P NMR chemical shifts of P-CHA zeolites.

References

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- P. Zhao, B. Boekfa, T. Nishitoba, N. Tsunoji, T. Sano, T. Yokoi, M. Ogura and M. Ehara, *Microporous Mesoporous Mater.* 294, 109908 (2020).

Award

SHIRAOGAWA, Takafumi; Poster Award, The 13th Annual Meeting of Japan Society for Molecular Science (2019).

Development of New Simulation Algorithms and its Application to Protein Aggregates

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



OKUMURA, Hisashi Associate Professor [hokumura@ims.ac.jp]

Education

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

Professional Employment

- 2002 Postdoctoral Fellow, The University of Tokyo
- 2002 Research Associate, Institute for Molecular Science
- 2004 Research Associate, The Graduate University for Advanced Studies
- 2006 Research Lecturer, Nagoya University
- 2008 Research Assistant, Rutgers University
- 2009 Assistant Research Professor, Rutgers University
- 2009 Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced
- Studies 2018 Associate Professor, Exploratory Research Center on Life
- and Living Systems (ExCELLS)
- Award
- 2014 Academic Award of the Molecular Simulation Society of Japan

Member Assistant Professor ITOH, Satoru G. Post-Doctoral Fellow TANIMOTO, Shoichi Graduate Student YAMAUCHI, Masataka MIYAZAWA, Kazuhisa FUKUHARA, Daiki Secretary KAWAGUCHI, Ritsuko

Keywords

Molecular Dynamics Simulation, Protein, Amyloid

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



Figure 1. Time series of protein folding simulation.

Selected Publications

- H. Okumura and S. G. Itoh, "Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations," J. Am. Chem. Soc. 136, 10549–10552 (2014).
- H. Okumura and S. G. Itoh, "Structural and Fluctuational Difference between Two Ends of Aβ Amyloid Fibril: MD Simulation Predicts Only One End Has Open Conformations," *Sci. Rep.* 6, 38422 (9 pages) (2016).

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 β) peptides. To overcome these diseases, it is essential to understand the aggregate genesis and disruption of A β peptides. We perform such MD simulations of oligomers and amyloid fibrils.



Figure 2. Snapshot of an Aβ amyloid fibril.

- 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 Amyloidβ(29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation," *J. Phys. Chem. B* 120, 6555–6561 (2016).

1. Molecular Dynamics Simulations of Amyloid-β(16-22) Peptide Aggregation at Air–Water Interfaces

The formation of A β oligomers is accelerated at hydrophilic-hydrophobic interfaces, such as the cell membrane surface and air-water interface. To understand the effects of the interface on oligomerization at the atomic level, we performed MD simulations of aggregation of A β (16–22) peptides at air-water interfaces.¹⁾ First, 100 randomly distributed A β (16–22) peptides (Figure 3(a)) moved to the interface (Figure 3(b)). The high concentration of peptides then accelerated their aggregation and formation of antiparallel β -sheets. Two layers of oligomers were observed near the interface. In the first layer from the interface, the oligomer with less β -bridges exposed the hydrophobic residues to the air. The second layer consisted of oligomers with more β -bridges that protruded into water. They are more soluble in water because the hydrophobic residues are covered by N- and C-terminal hydrophilic residues that are aligned well along the oligomer edge. These results indicate that amyloid protofibril formation mainly occurs in the second layer.



Figure 3. (a) Initial conformation of 100 A β (16–22) peptides (blue) and water molecules (red) with air–water interfaces. (b) Side view of the final conformation of A β (16–22) peptides. The water molecules are not shown here. The blue frames indicate the air–water interfaces.

2. Development of Replica Sub-Permutation Method for Efficient Molecular Dynamics Simulations

We proposed an improvement of the replica-exchange and replica-permutation methods, which we call the replica subpermutation method (RSPM).²⁾ Instead of considering all permutations, this method uses a new algorithm referred to as sub-permutation to perform parameter transition, as in Figure 4. The RSPM succeeds in reducing the number of combinations between replicas and parameters without the loss of sampling efficiency. For comparison, we applied the replica sub-permutation, replica-permutation, and replica-exchange methods to a β -hairpin mini protein, chignolin, in explicit water. We calculated the transition ratio and number of tunneling events in the parameter space, the number of foldingunfolding events, the autocorrelation function, and the autocorrelation time as measures of sampling efficiency. The results indicate that among the three methods, the proposed RSPM is the most efficient in both parameter and conformational spaces.



Figure 4. This image shows sub-permutation candidates for a fourreplica system. The replica sub-permutation method succeeds in improving sampling efficiency both in parameter and conformational spaces.

- H. Okumura and S. G. Itoh, J. Chem. Phys. 151, 095101 (12 pages) (2020).
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Theoretical Studies on Molecular Aggregates

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



FUJITA, Takatoshi Research Associate Professor [tfujita@ims.ac.jp]

Education

- 2006 B.H.D. Kobe University
- 2008 M.S. Kobe University
- 2011 Ph.D. Kobe University

Professional Employment

- 2010 JSPS Research Fellow (DC2)
- 2011 JSPS Postdoctoral Fellow (PD)
- 2012 Postdoctral Fellow, Harvard University
- 2015 Postdoctral Fellow, Kyoto University
- 2016 Research Associate Professor, Institute for Molecular Science

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, 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 are obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian

Selected Publications

• T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, "Coherent Dynamics of Mixed Frenkel and Charge Transfer Excitons in Dinaphtho[2,3-*b*:2'3'-*f*]thieno[3,2-*b*]-thiophene Thin Films: The Importance of Hole Delocalization," *J. Phys. Chem. Lett.* **7**, 1374–1380 (2016).



Member Secretary

CHIBA, Fumika

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 combined 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 manybody perturbation theory to predict electronic levels at higher accuracy.

 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 FMO-Based Exciton Model within GW/BSE¹⁾

Organic optoelectronic devices based on π -conjugated molecules or polymers have attracted considerable attention due to their attractive features. Predicting the electronically excited states is essential for understanding the optoelectronic processes governing the device operation and for rationally designing novel materials. However, accurate calculations of electronic states of organic materials which contain a lot of organic molecules or polymers are still challenging task. Successful theoretical descriptions require an accurate quantum mechanical method. In addition, the effects of polarizable environment must be appropriately taken into account.

In this study, we present the large-scale GW/Bethe-Salpeter equation (BSE) method that enables the computations of delocalized excited states in large molecular assemblies. The many-body Green's function method within the GW approximation can offer practical schemes to calculate electronic states within reasonable accuracy. However, the applications of GW and GW/BSE to large systems were difficult because of their considerable computational times. Here, we develop large-scale GW/BSE method for large systems based on the fragment molecular orbital methods. We have proposed the fragmentation approximations of total polarization functions and Δ COHSEX approximation that neglects the dynamical polarization of surrounding fragments. We have confirmed that the FMO-GW/BSE method enables accurate calculations of localized electronic states in large systems. Furthermore, the FMO-GW/BSE method was combined with the exciton model to calculate delocalized excited states in molecular aggregates. In the exciton model, the excited-state Hamiltonian for an entire system is calculated in the diabatic basis and then diagonalized to approximate the adiabatic excited states. The FMO-based exciton model utilizes the fragment configuration state functions (CSFs) for intrafragment excited states and for interfragment charge-transfer states, and the excited-state Hamiltonian at the GW/BSE level is calculated in the basis of fragment CSFs. We have shown that the results of unfragmented calculations can be reasonably reproduced; thus, the present FMO-GW/BSE method can offer efficient and practical schemes for investigating realistic molecular aggregates.

2. Revisiting the Electronic Structure of PEN/C₆₀ Bilayer Heterojunctions²⁾

Molecular orientations and interfacial morphologies have critical effects on the electronic states of donor/acceptor interfaces and thus on the performance of organic photovoltaic devices. Here, we investigate the charge-transfer (CT) states in pentacene(PEN)/C₆₀ interfaces as model systems and highlight the polarization and delocalization effects. The effects of polarization and delocalization on the interfacial CT states are schematically represented in Figure 2. In a gas phase (Figure 2 (a)), the energy of the CT state is given by the highestoccupied molecular orbital (HOMO) energy of a donor molecule, the lowest-unoccupied molecular orbital (LUMO) energy of an acceptor molecule, and the Coulomb interaction between the electron and the hole. The solid-state polarization effects reduce the energy gap between the donor HOMO and the acceptor LUMO (Figure 2 (b)) and weakens the e-h interaction. In a solid phase, the electron or hole wave function can be delocalized over multiple acceptor or donor molecules, and delocalized CT states can be formed (Figure 2 (c)). This charge delocalization can further shift the energy gap and



Figure 2. Schematics of solid-state effects on the interfacial charge-transfer states.

possibly weaken the e-h interaction.

In this study, we explore the energy levels and CT states at the organic donor/acceptor interfaces on the basis of the fragment-based GW/BSE approach. The face-on and edge-on orientations of pentacene/C₆₀ bilayer heterojunctions have employed as model systems. The FMO-GW/BSE calculations were performed for the local interface structures in the face-on and edge-on bilayer heterojunctions, which contain approximately 2,000 atoms. Calculated energy levels and CT state absorption spectra are in reasonable agreements with those obtained from experimental measurements. We found that the dependence of the energy levels on interfacial morphology is predominantly determined by the electrostatic contribution of polarization energy, while the effects of induction contribution in the edge-on interface are similar to those in the face-on. Moreover, the delocalized CT states contribute to the main absorption peak in the edge-on interface, while the face-on interface features relatively localized CT states in the main absorption peak. The impact of the interfacial morphologies on the polarization and charge delocalization effects is analyzed in detail.

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- 2) T. Fujita, Y. Noguchi and T. Hoshi, Materials 13, 2728 (2020).

Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

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



OKAZAKI, Kei-ichi Research Associate Professor [keokazaki@ims.ac.jp]

Education

- 2004 B.S. Kyoto University
- 2006 M.S. Kobe University
- 2009 Ph.D. Kobe University

Professional Employment

- 2007 JSPS Research Fellow (DC2), Kobe University
- 2009 JSPS Postdoctoral Fellow (PD), Waseda University
- 2010 Part-time Lecturer, Waseda University
- 2012 JSPS Postdoctoral Fellow for Research Abroad, National Institutes of Health, U.S.A.
- 2014 Postdoctoral Fellow, Max Planck Institute of Biophysics, Germany
- 2016 Research Associate Professor, Institute for Molecular Science

Award

2014 Early Career Award in Biophysics, Biophysical Society of Japan

Keywords

Theoretical Biophysics, Molecular Motors, Transporter

Functional dynamics plays an important role when biomolecular machines fulfill their functions. Motor proteins move on the rail or rotate relative to the stator unidirectionally by using chemical 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, coarsegraining, 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, 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 chemical-state-dependent free energy profile and diffusion coefficient from single-molecule trajectories.

Member

Secretary

Post-Doctoral Fellow

CHIBA, Fumika

MAHMOOD, Md Iqbal JAUNET-LAHARY, Titouan

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

- K. Okazaki and G. Hummer, "Phosphate Release Coupled to Rotary Motion of F₁-ATPase," *Proc. Natl. Acad. Sci. U.S.A.* 110, 16468–16473 (2013).
- K. Okazaki and G. Hummer, "Elasticity, Friction, and Pathway of γ-Subunit Rotation in F_oF₁-ATP Synthase," *Proc. Natl. Acad. Sci.* U.S.A. 112, 10720–10725 (2015).
- 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).

 M. I. Mahmood, H. Noguchi and K. Okazaki "Curvature Induction and Sensing of the F-BAR Protein Pacsin1 on Lipid Membranes via Molecular Dynamics Simulations," *Sci. Rep.* 9, 14557 (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. We used single-molecule trajectories to estimate an underlying diffusion model with chemical-state-dependent free energy profile.¹⁾ To consider nonequilibrium trajectories driven by the chemical energy consumed by biomolecular motors, we developed a novel framework based on a hidden Markov model, wherein switching among multiple energy profiles occurs reflecting the chemical state changes in motors. The chemical-state-dependent free energy profile underlying the burnt-bridge Brownian ratchet mechanism of processive chitinase was determined.¹⁾

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 ~3.5 Å 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 iontransport. The transition dynamics between the two states is central to the transport mechanism, revealing at once ratelimiting 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.

- K. Okazaki, A. Nakamura and R. Iino J. Phys. Chem. B 124, 6475– 6487 (2020).
- K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, *Nat. Commun.* 10, 1742 (2019).

Theory and Computation of Reactions and Properties in Solutions and Liquids

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

We are interested in the projects on

ionic liquids (ILs). ILs' projects are

focused on the unique dissolution pro-

cess of cellulose polysaccharides, and

the investigation of statical and dynami-

cal properties on ionic liquids includ-



ISHIDA, Tateki Assistant Professor

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, our results suggest that the

enhancement of the flexibility of rigid cellulose chains triggered by the breakage of intrachain H-bonds due to anions starts decomposition processes accompanied by dissolution processes due to the intercalation of cations, synergistically, and, then, both dissolution and decomposition processes are executed simultaneously.

2. Researches on Statical 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 Ang.⁻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, J. Phys. Chem. B 124, 3090-3102 (2020).

Visiting Professors



Visiting Professor MORI, Hirotoshi (from Chuo University)

Electronic Structure Informatics for Designing Functional Liquid Materials

Mixed liquids exhibit various chemical functions depending on their composition and mixing ratio. Contrary to its fundamental scientific importance, however, the chemistry of mixing is an area where molecular level knowledge is not still enough. With the backgrounds, we have been challenging the predictive chemistry of functional liquid materials by developing a novel *ab initio* molecular simulation

method with conventional computational cost (Effective fragment potential molecular dynamics; EFP-MD) and a data science approach. In fiscal 2020, we worked on the prediction of Henry's constant values related to the absorption of various industrial exhaust gases for non-aqueous mixed solutions (mixed ionic liquids, ionic liquids/organic solvent mixtures) which supports environmental chemical engineers shortly. We will proceed with our research aiming at the construction of statistical thermodynamic theory for real systems that predict mixed thermodynamics.



Visiting Professor YANASE, Youichi (from Kyoto University)

Theoretical Study of Exotic Quantum Phases

We are working on theoretical studies of exotic quantum phases such as unconventional superconductivity, parity-violating antiferromagnet, quantum liquid crystal, and topological state of matter. In particular, my recent interest focuses on quantum phases lacking global or local space inversion symmetry. For instance, we classified such quantum phases in terms of multipole moment with the use of group

theory, and explored emergent electromagnetic responses, such as magnetopiezoelectric effect and chiral photocurrent. Furthermore, a rigorous and gauge-invariant formulation of multipole moment was given by the thermodynamic definition, which is directly related to the magnetoelectric effect. Superconductivity induced by multipole fluctuations was clarified. To develop the functionality of superconductors, we showed a giant superconducting Edelstein effect in topological superconductors. By considering a light-matter interaction, we proposed laser-induced topological superconductivity in TMD.



Visiting Associate Professor HIGASHI, Masahiro (from Kyoto University)

Theoretical Study on the Excited-State Reactions in Condensed Phases

We are theoretically investigating chemical reactions and physical properties in condensed phases such as solutions and proteins. In particular, we are focusing on the excited-state reaction dynamics in condensed phases. Theoretical studies on the excited-state reaction dynamics of large systems is still one of most challenging tasks due to the high computational cost of electronic structure calculations for excited

states and adequate statistical samplings required for molecular dynamics simulations. To overcome this difficulty, we have been developing several efficient methods combining electronic structure calculations and molecular dynamics simulations. Recently, we analyzed the excitation energy transfer in a light-harvesting complex by using our developed methods. The calculated excitation energies of pigments and their fluctuations are in quantitative agreement with the experimental ones. It is found that the fluctuations of pigments are largely affected by the individual protein environments and that the efficient excitation energy transfer is achieved by the site-dependent fluctuations.

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 condensedphase 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



OHMORI, Kenji Professor [ohmori@ims.ac.jp]

Educa	Ition	IMS Research Assistant Professor
1987	B. E. The University of Tokyo	TOMITA Takafumi
1992	Ph.D. The University of Tokyo	Post Destaral Follow
Profes	ssional Employment	
1992	Research Associate, Tohoku University	BHARTI Vineet
2001	Associate Professor, Tohoku University	KUNIMI Masava
2003	Professor, Institute for Molecular Science	Craduata Student
	Professor, The Graduate University for Advanced Studies	Graduate Student
2004	Visiting Professor, Tohoku University (–2005)	
2007	Visiting Professor, Tokyo Institute of Technology (-2008)	
2009	Visiting Professor, The University of Tokyo (–2011)	Mahesh
2012	Visiting Professor, University of Heidelberg	
2014	Visiting Professor, University of Strasbourg (–2016)	Secretary
Award	ls	KAWAMOTO, Minako
1998	Award by Research Foundation for Opto-Science and	
	Technology	
2007	JSPS Prize	
2007	Japan Academy Medal	
2009	Fellow of the American Physical Society	
2012	Humboldt Research Award	
2017	Hiroshi Takuma Memorial Prize of Matsuo Foundation	

Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology of Japan

Keywords

Quantum-Classical Boundary, Quantum Simulation, Quantum Computing

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

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 Ultra-

array of ultracold rubidium (Rb) Rydberg atoms, as depicted schematically in Figure 1, envisaging the quantum-classical boundary connected smoothly.

Member Assistant Professor

> SUGAWA, Seij DE LÉSÉLEUC, Sylvain



Figure 1. Metal-like quantum gas. A schematic of the many-body system of ultracold Rydberg atoms, where electronic wave functions spatially overlap between neighboring atoms.^{2,7)}

fast 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).
- M. Mizoguchi et al., "Ultrafast Creation of Overlapping Rydberg Electrons in an Atomic BEC and Mott-Insulator Lattice," Phys. Rev. Lett. 124, 253201 (2020).

1. Development of an "Ultrafast Quantum Simulator" by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales^{3–9)}

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"⁸⁾ and "a strongly-correlated ultracold Rydberg gas."⁹⁾

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 (ps) laser pulse, as schematically illustrated in Figure $2.^{3,4,6,7)}$ 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. With this standard hardware, we have succeeded in creating an exotic electronic state with spatially overlapping wave-functions as shown schematically in Figure $2.^{7)}$ The degree of spatial overlap is actively tuned with ~50 nanometer precision. This exotic metal-like quantum gas under exquisite control opens up a completely new regime of many-body physics for simulating ultrafast many-body electron dynamics dominated by Coulomb interactions.⁷⁾



Figure 2. Schematic of the standard hardware of the ultrafast quantum simulator.^{3,4,7)}

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.



Figure 3. Time domain Ramsey interferometry of ultracold ⁸⁷Rb atoms with attosecond precision to be used as a readout interface of the ultrafast quantum simula-

tor. Population of the $42^2D_{5/2}$ 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).

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.¹⁰⁾ 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,¹⁰ in tight collaborations with Hamamatsu Photonics K. K.³) Their examples are shown in Figure 4, the world's smallest arbitrary trap arrays whose nearest neighbor distance is only ~1 micron, which used to be typically ~4 micron in previous works.¹¹

We have recently succeeded in loading a single atom into each trap of those arbitrary arrays, and reassembling those atoms with an optical tweezer. Accordingly we can prepare an array of atoms we desire, as exemplified in Figure 5.



Figure 4. Examples of the world's smallest arbitrary arrays of optical traps.³⁾

Before reassembly	After reassembly
9996	0000
0000	0000
@ @ @ @	0000

Figure 5. Assembly of an arbitrary array of single Rb atoms.

3. Engineering Quantum Wave-Packet Dispersion with a Strong Nonresonant Femtosecond Laser Pulse¹²⁾

A non-dispersing wave packet has been attracting much interest from various scientific and technological viewpoints. However, most quantum systems are accompanied by anharmonicity, so that retardation of quantum wave-packet dispersion is limited to very few examples only under specific conditions and targets. Here we demonstrate a conceptually new and universal method to retard or advance the dispersion of a quantum wave packet through "programmable time shift" induced by a strong non-resonant femtosecond laser pulse. A numerical simulation has verified that a train of such retardation pulses stops wave-packet dispersion.

Our ultrafast quantum simulator operates with atomic Rydberg levels,^{3–9)} whose level structure is anharmonic, so that its wave packet is dispersed and broadened quickly. The new control method for wave-packet dispersion developed here would serve as an enabling technology for our ultrafast quantum simulator to enhance its functionality for quantum simulation and computing.

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- 2) K. Ohmori, Found. Phys. 44, 813-818 (2014).
- US Patent (3rd Nov. 2020) "Quantum Simulator and Quantum Simulation Method," H. Sakai (Hamamatsu Photonics K.K.), K. Ohmori (IMS) *et al.*, and one more patent publication.
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- 5) C. Liu et al., Phys. Rev. Lett. 121, 173201 (2018).
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Electronic Property of Functional Organic Materials

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

KERA, SatoshiProfessorIkera@ims.ac.jp]	Education 1996 B.E. Chiba University 1998 M.E. Chiba University 2001 Ph.D. Chiba University Professional Employment 1998 1998 JSPS Research Fellow 2001 Research Associate, Chiba University 2003 Research Associate, Institute for Molecular Science 2003 Postdoctoral Fellow, Wuerzburg University 2004 Assistant Professor, Chiba University 2005 Associate Professor, Chiba University 2006 Visiting Associate Professor, Institute for Molecular Science 2013 Adjunct Lecturer, The Open University of Japan 2014 Professor, Institute for Molecular Science 2015 Visiting Associate Professor, Soochow University 2014 Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting Professor, Chiba University 2019 Visiting Professor, Kyoto University, Hiroshima University 2020 Visiting Professor, Tohoku University	Post-Doctoral Fellow YAMADA, Kazuto Visiting Scientist YANG, Jinpeng MADUWANTHA, Kaveendra Graduate Student NAKAMURA, Takuto [†] Secretary HAGIWARA, Hisayo
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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 have been redundant 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 essential to investigate precisely the electronic structure at various interfaces, including organicorganic and organic-inorganic (metal/semiconductor) contacts. Recently we realized that the weak electronic interaction manifests itself as small intensity modulations of fine structures 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, narrow band dispersion, and dynamic electronic polarization. To elucidate what really impacts on 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

Selected Publications

- Y. Nakayama, S. Kera and N. Ueno, J. Mater. Chem. C 8, 9090– 9132 (2020). [review]
- S. Kera, T. Hosokai and S. Duhm, J. Phys. Soc. Jpn. 87, 061008 (7 pages) (2018). [review]

electronic states is 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.

Member IMS Fellow

HASEGAWA, Yuri



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.

- 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. The Role of Initial and Final States in Molecular Spectroscopies: A Case Study of DBP^{1,2)}

Interpreting experimental spectra of organic semiconductor films is challenging, and understanding the relationship between experimental data obtained by different spectroscopic techniques, UPS, IPES, 2PPE and optical absorption requires a careful consideration of the initial and final states for each process. We present a coherent framework that is capable of treating on equal footing most spectroscopies. We develop a simple model for the expected energy level positions by the spectroscopies and relate them to the energies of molecular states. Molecular charging energies in photoionization processes, as well as adsorption energies and the screening of molecular charges due to environmental polarization, are taken into account as the main causes for shifts of the measured spectroscopic features. We explain the relationship between these quantities, as well as with the transport gap, the optical gap and the exciton binding energy.¹⁾

Our considerations serve as a model for weakly interacting systems where wave function hybridizations between adjacent molecules are negligible as demonstrated for DBP films on graphite.²)



Figure 2. a) Scheme of the typical spectroscopic processes in UPS, 2PPE, IPES, and optical absorption in relation to the initial and final states. b) Thickness dependences of XeI-UPS and IPES (LEIPS) of DBP films on graphite. The energy positions of bilayer (BL) are shifted from wetting layer (WL) of monolayer. The figure is after ref 1,2).

2. Impacts of Electrostatic Interactions on the Energy Levels of Organic Semiconductor Blends³⁾

Halogenation of conjugated molecules represents a powerful approach to tune the electronic structure of molecular thin films through inductive effects and long-range intermolecular electrostatic interactions. We provide a comprehensive experimental and theoretical analysis of the prototypical blend formed by pentacene (PEN) and perfluoropentacene (PFP) to relate structure with electronic properties. We find a mixed-stack structural motif in standing and lying orientations depending on the substrate nature. In the standing orientation, the ionization potential lies in between the values of the pure components, in line with the established picture of averaged molecular quadrupole moments. For the lying orientation, however, we experimentally observe an ionization potential lower than both pristine values, which seems at odds with this simple rationale. Electrostatic simulations based on the knowledge of the atomistic structure of the films capture the complex experimental scenario for both orientations. In particular, the ultralow ionization potential of films formed by lying molecules is identified as a signature of the monolayer structure, where quadrupolar interactions are responsible for a difference of ca. 0.4 eV in the highest occupied molecular orbital energy as compared to thicker films with the same molecular orientation.



Figure 3. (a) UPS of blends PEN/PFP films of lying orientation on graphite. The spectra of PEN and PFP monolayers are shown as reference. b) Calculated energy levels of PEN:PFP layers; black and green bars correspond to the IPs of PEN and PFP, respectively. The calculated intensity (bar height) depends on the depth z of the ionized layer from the surface in Figure 3c). The figure is after ref 3).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope is started at BL6U.⁴⁾

- T. Kirchhuebel, O. L. A. Monti, T. Munakata, S. Kera, R. Forker and T. Fritz., *Phys. Chem. Chem. Phys.* 21, 12730–12747 (2019).
- 2) T. Kirchhuebel, S. Kera et al., J. Phys. Chem. C 124, 19622–19638 (2020).
- 3) G. D'Avinol, S. Kera et al., Chem. Mater. 32, 1261-1271 (2020).
- 4) F. Matsui et al., Jpn. J. Appl. Phys. 59, 067001 (2020).

Light Source Developments by Using Relativistic Electron Beams

UVSOR Synchrotron Facility Division of Advanced Accelerator Research



KATOH, Masahiro Project Professor [mkatoh@ims.ac.jp]

Education

- 1982 B.S. Tohoku University
- 1997 Ph.D. Tohoku University

Professional Employment

- 1986 Reseach Associate, National Laboratory for High Energy Physics
- 2000 Associate Professor, Institute for Molecular Science2004 Professor, Institute for Molecular Science
- Professor, The Graduate University for Advanced Studies 2019 Professor, Hiroshima University
- Project Professor, Institute for Molecular Science

Member

Assistant Professor FUJIMOTO, Masaki

Post-Doctoral Fellow SALEHI, Elham

Graduate Student KIMURA, Shinnosuke* KOSUGI, Naoki* NAKAO, Kaito* HORI, Haruki*

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–Eelectron Beam Interaction," *Nat. Phys.* 4, 390–393 (2008).
- M. Shimada, M. Katoh, M. Adachi, T. Tanikawa, S. Kimura, M. Hosaka, N. Yamamoto, Y. Takashima and T. Takahashi, "Transverse-Longitudinal Coupling Effect in Laser Bunch Slicing," *Phys. Rev. Lett.* **103**, 144802 (2009).
- M. Katoh, M. Fujimoto, H. Kawaguchi, K. Tsuchiya, K. Ohmi, T. Kaneyasu, Y. Taira, M. Hosaka, A. Mochihashi and Y. Takashima, "Angular Momentum of Twisted Radiation from an Electron in Spiral Motion," *Phys. Rev. Lett.* 118, 094801 (2017).
- 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).
- Y. Hikosaka, T. Kaneyasu, M. Fujimoto, H. Iwayama and M. Katoh, "Coherent Control in the Extreme Ultraviolet and Attosecond Regime by Synchrotron Radiation," *Nat. Commun.* 10, 4988 (2019).
- T. Kaneyasu, Y. Hikosaka, M. Fujimoto, H. Iwayama and M. Katoh, "Controlling the Orbital Alignment in Atoms Using Cross-Circularly Polarized Extreme Ultraviolet Wave Packets," *Phys. Rev. Lett.* **123**, 233401 (2019).

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 develope 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 beamline consisting of mirrors and a monochromator whose arrangement can be flexibly changed according to the types of the experiments.

In these years, we are focusing on generation of spatially structured light, such as optical vortex beams and optical vector beams from undulators, in collaboration with Hiroshima Univ. and Nagoya Univ. We have succeeded in producing such novel photon beams and are exploring their applications. More recently, we have started exploring the possibility utilizing the temporal structure of undulator radiation, in collaboration with Saga Light Source and Toyama Univ. So far, we have been demonstrated the coherent controls of atoms by using radiation from two undulators arranged in tandem. It has been widely believed that such experiments were possible only with precisely controlled laser beam. Our results may open a new research field on the application of synchrotron radiation.

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. 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 Electron Synchrotrons

We carried out several upgrade plans on UVSOR electron synchrotron since 2000. We designed a special 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 commissioned them. Moreover, 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 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. For a long-term plan, we continue the design studies on the new low emittance optics of the present synchrotron and on new accelerator systems such as a linear accelerator based free electron laser or a diffraction limited storage ring light source.

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



Figure 3. UVSOR BL1U experimental station for source development studies.

Development and Utilization of Novel Quantum Beam Sources Using a High Energy Electron Beam

UVSOR Synchrotron Facility Division of Beam Physics and Diagnostics Research

TAIRA, Yoshitaka Associate Professor yostaira@ims.ac.jp]	 Education 2007 B.S. Nagoya University 2009 M.S. Nagoya University 2012 Ph.D. Nagoya University Professional Employment 2011 JSPS Research Fellow 2012 Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST) 2018 Senior Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST) 2020 Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies Awards 2010 Student Presentation Award, The 23rd Annual Meeting of the Japanese Society for Synchrotron Radiation Research 2010 Young Researcher Best Presentation Award, The 53rd Annual Meeting of the Japanese Society of Radiation Chemistry 2011 Nagoya University Outstanding Graduate Student Award 2012 Oral Presentation Award, The 9th Annual Meeting of Particle Accelerator Society of Japan 2012 Young Researcher Best Presentation Award, 12th International Symposium on Radiation Physics 2013 Young Researcher Best Presentation Award, Beam Physics Workshop 2015
Keywords F	ectron Beams, Synchrotron Radiation, Gamma-Rays

Our group develop new electromagnetic wave sources using a high energy electron beam. In the UVSOR-III electron storage ring at the Institute for Molecular Science, a 750-MeV electron beam can be generated. Electromagnetic waves in a wide frequency range from ultraviolet waves to gamma-rays are emitted by interacting the electron beam with magnetic fileds and lasers.

Laser Thomson (Compton) scattering is a method to generate a high energy gamma-ray by the interaction between a high energy electron and a laser. We have developed ultrashort pulsed gamma-rays with the pulse width of sub-ps to ps range by using 90-degree laser Thomson scattering (Figure 1). We applied this ultra-short pulsed gamma-rays to gamma induced positron annihilation lifetime spectroscopy (GiPALS).

- Selected Publications
 Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, "Generation of Energy-Tunable and Ultra-Short-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring," *Nucl. Instrum. Methods Phys. Res., Sect. A* 652, 696 (2011).
- Y. Taira, H. Toyokawa, R. Kuroda, N. Yamamoto, M. Adachi, S. Tanaka and M. Katoh, "Photon-Induced Positron Annihilation Lifetime Spectroscopy Using Ultrashort Laser-Compton-Scattered Gamma-Ray Pulses," *Rev. Sci. Instrum.* 84, 053305 (2013).

A positron is an excellent probe of lattice defects in solids and of free volumes in polymers at the sub-nm to nm scale. GiPALS enables defect analysis of a thick material in a few cm because positrons are generated throughout a bulk material via pair production. Our group is conducting research on improving the properties of the material by using GiPALS.

Member

Post-Doctoral Fellow

SALEHI, Elham



Figure 1. Schematic illustration of 90-degree laser Thomson scattering.

- Y. Taira, T. Hayakawa and M. Katoh, "Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light," *Sci. Rep.* **7**, 5018 (2017).
- Y. Taira and M. Katoh, "Gamma-Ray Vortices Emitted from Nonlinear Inverse Thomson Scattering of a Two-Wavelength Laser Beam," *Phys. Rev. A* **98**, 052130 (2018).
- Y. Taira and M. Katoh, "Generation of Optical Vortices by Nonlinear Inverse Thomson Scattering at Arbitrary Angle Interactions," *Astrophys. J.* 860, 45 (2018).

1. Gamma-Induced Positron Annihilation Lifetime Spectroscopy (GiPALS)

Positron lifetime spectrum is calculated by measuring the time difference between a reference signal and a detector output for the annihilation gamma-rays, which is emitted when a positron annihilates with an electron inside material. A reference signal is the output of a photodiode located near the injection position of a laser. A BaF₂ scintillator and a photo-multiplier tube is utilized to detect the annihilation gamma-rays. Two detectors are arranged at 180 degrees because two annihilation gamma-rays are generated at 180-degree direction. The annihilation gamma-rays are generated to whole solid angle. Therefore array detectors are effective to increase the count rate of the annihilation gamma-rays and to reduce the measurement time. We have developed the array detector using 10 detectors with a help of Equipment Development Center (Figure 2).



Figure 2. Positron lifetime measurement system using 10 detectors.

Users can currently utilize GiPALS at BL1U in UVSOR-III. A result of defect analysis for a GAGG scintillator was published in 2020.¹⁾

We plan to change the laser injection position to increase the ultra-short pulsed gamma-ray intensity in the next fiscal year. In the current laser injection position, the opposite side of the laser injection window is the vacuum duct. Thus, the laser hits the vacuum duct and generates gas. This gas induces the background gamma-rays, which is generated by the interaction with an electron beam. As a result, the laser cannot be tightly focused and therefore the intensity of the gamma-ray is weak. The laser can be focused down to few tens of micrometers at the new laser injection position. We estimate that the intensity of the gamma-rays will be increased more than 20 times.

On the other hand, we are planning to develop other measurement technique for the annihilation gamma-rays, such as a three-dimensional distribution imaging technique for defects, spin polarized positrons generated from circularly polarized gamma-rays, and age-momentum correlation (AMOC).

2. Short Wavelength Optical Vortices

An optical vortex is an electromagnetic wave with a

helical phase structure. When an optical vortex beam is viewed in a plane transverse to the direction of propagation, an annular intensity profile is observed due to the phase singularity at the center axis. An important consequence of the optical vortex is that it carries orbital angular momentum (OAM) due to the helical phase structure.

While fundamental and applied research on optical vortices using visible wavelength lasers is widely studied, much less has been done in ultraviolet, X-rays, and gamma-rays energy ranges. We have proposed for the first time a method to generate a gamma-ray vortex using nonlinear inverse Thomson scattering of a high energy electron and an intense circularly polarized laser.²⁾ In our method, the circularly polarized laser is important because the helical phase structure arises from the transverse helical motion of the electron inside the circularly polarized laser field. When peak power of a laser achieves terawatt class, high harmonic gamma-rays are generated. Only gamma-rays more than the first harmonic carry OAM. High harmonic gamma-rays show the annular intensity distribution due to this characteristic.

There are few facilities in the world, where can carry out the experiment for the nonlinear inverse Thomson scattering using an intense circularly polarized laser in terawatt class. We carried out the experiment at Kansai Photon Science Institute in Japan, where a 150 MeV microtron and a petawatt laser are available. Although we were not able to achieve the measurement of an annular intensity distribution of high harmonic gamma-rays, we plan to continue the experiment this year.

On the other hand, optical vortices in the ultraviolet wavelength range can be generated using a helical undulator. Similar with a nonlinear inverse Thomson scattering, an electron obeys a helical trajectory inside an undulator. Therefore, high harmonic radiation emitted from a helical undulator forms the helical phase structure.

Generation of an optical vortex from a helical undulator has been demonstrated at UVSOR-III. Recently, we newly revealed that undulator radiation with the phase structure can be generated from an elliptically polarized undulator. We derived the analytic expressions for the emitted electric fields were fully derived and the radiation's phase structure was found to change according to polarization. Average phase gradients of the undulator's radiation were measured using a double slit interferometer. The measured phase gradients of the first through third harmonics were compared with the calculated results. The results were submitted to the journal.

- K. Fujimori, M. Kitaura, Y. Taira, M. Fujimoto, H. Zen, S. Watanabe, K. Kamada, Y. Okano, M. Katoh, M. Hosaka, J. Yamazaki, T. Hirade, Y. Kobayashi and A. Ohnishi, *Appl. Phys. Express* 13, 085505 (4 pages) (2020).
- Y. Taira, T. Hayakawa and M. Katoh, *Sci. Rep.* 7, 5018 (9 pages) (2017).

Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

UVSOR Synchrotron Facility Division of Advanced Solid State Physics



TANAKA, Kiyohisa Associate Professor [k-tanaka@ims.ac.jp]

Education

- 2000 B.S. The University of Tokyo
- 2005 Ph.D. The University of Tokyo

Professional Employment

- 2005 Postdoctoral Fellow, Stanford University and Lawrence Berkeley National Laboratory
- 2008 Assistant Professor, Osaka University
- 2013 Associate Professor, Osaka University
- 2014 Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

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). ARPES is a powerful experimental technique, directly measuring the energy (E) and momentum (k) relation, namely the band structure of solids. In the last quarter of a century, the energy resolution and angular resolution of ARPES have improved almost three order of magnitude better, which makes us possible to address the fine structure of the electronic structure near the Fermi level: Superconducting gap, kink structure and so on. The main target materials of our group is high- $T_{\rm c}$ superconductors, such as cuprates and iron pnictides and use UVSOR-III as a strong light source.

Our group is also developing high-efficiency spin-resolved ARPES system. Spintronics is a rapidly emerging field of science and technology that will most likely have a significant

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).
- W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Abrupt Onset of a Second Energy Gap at the Superconducting Transition of Underdoped Bi2212," *Nature* 450, 81–84 (2007).
- K. Tanaka, N. Hieu, G. Vincini, T. Masui, S. Miyasaka, S. Tajima

impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spinresolved ARPES is one of the most powerful experimental techniques to investigate the magnetic properties of such materials.

Member Assistant Professor

IDETA, Shin-ichiro Graduate Student

HOSOYA Tomoki*

FURUTA Kanji*



and T. Sasagawa, "Quantitative Comparison between Electronic Raman Scattering and Angle-Resolved Photoemission Spectra in $Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconductors: Doping Dependence of Nodal and Antinodal Superconducting Gaps," *J. Phys. Soc. Jpn.* **88**, 044710 (2019).

 S. Ideta, N. Murai, M. Nakajima, R. Kajimto and K. Tanaka, "Experimental Investigation of the Suppressed Superconducting Gap and Double-Resonance Mode in Ba_{1-x}K_xFe₂As₂," *Phys. Rev. B* 100, 235135 (7 pages) (2019).

1. Quantitative Comparison between ARPES and ERS on Multilayer Cuprates Superconductor¹⁾

It has been well known that one of the most efficient ways to increase the critical temperature (T_c) of high- T_c cuprate superconductors (HTSCs) is to increase the number of neighboring CuO₂ planes (*n*). T_c of the optimally doped region $(T_{c:max})$ generally increases from single layer (*n* = 1), double layer (*n* = 2), to triple layer (*n* = 3) and then decreases for *n* > 4. In order to explain the *n* dependence of T_c , several mechanisms have been proposed. However, it has been unclear which parameter governs the *n* dependence of $T_{c:max}$ because of the lack of detailed knowledge about the electronic structure of the multilayer cuprates. In this study, we have performed angleresolved photoemission spectroscopy (ARPES) and electronic Raman scattering (ERS) to clarify the electronic structure of optimally doped triple-layer Bi₂Sr₂Ca₂Cu₃O_{10+δ} (Bi2223) which has the highest $T_{c:max}$ (~110 K) among Bi-based HTSCs.

Since the superconducting gap in the cuprates has a *d*-wave symmetry, we need *k*-selective experimental probes. Although ARPES and ERS are the most powerful *k*-selective probes, the gap sizes estimated from these two techniques are not always identical. To clarify the origin of the discrepancy, we have examined a direct comparison of ARPES and ERS through the Kubo formula analysis. In a previous study on the double layer Bi2212, we proved that this method is valid and advantageous.²⁾

In ERS study on optimally doped Bi2223, we found that B_{1g} spectra, which is sensitive to the antinodal region in the *k*-space, showed double peaks as shown in Figure 1a (blue curve). This is the first observation of multiple peaks in B_{1g} spectra in HTSCs. On the other hand, ARPES study on Bi2223 reveals two Fermi surfaces (FSs), which can be attributed the FS closer to the Γ point to that of the outer CuO₂ plane (OP) and the other to that of the inner CuO₂ plane (IP), assuming that the doping level is higher in the OP than in the IP. From those observations, we think that the double peak in ERS is originated from two different bands which form different FSs observed by ARPES.

To confirm our interpretation of the double peak, we calculated the Raman spectra from the ARPES, using the Kubo formula. For triple layer compounds, by separating the IP and OP bands of ARPES, we can calculate their separate contribution to the Raman spectra, and verify if the two B_{1g} Raman peaks truly originate from the two separate bands. The ARPES intensities for the IP and OP bands were separated by a Gaussian fit of the energy distribution curves using three Gaussian peaks, one for the IP and OP band each and one for the high energy incoherent intensity that originates from the strong correlations effects in the antinodal part of the *k*-space.

The calculated B_{1g} and B_{2g} Raman spectra for the optimally doped Bi2223 are compared with the experimental ones in Figure 1. One can find that the calculated spectra from the ARPES data successfully reproduce the experimental Raman spectra. The striking result is that, in the B_{1g} configuration, the IP and OP bands exhibit peaks at different energies that are close to the experimental B_{1g} peak energies. Here the OP peak position is slightly underestimated, which may be due to the fact that a small portion of the antinodal part of the momentum space is missing in our input ARRPES data. By summing the separate contribution of IP and OP, we obtain a thick orange line. A rather good correspondence of the calculated and experimental IP and OP peaks provides strong proof that the double B_{1g} Raman peak truly originates from the two separate bands of Bi2223 and, therefore, that it is a signature of the double superconducting gap of this material.

This results clarify systematic doping dependence of superconducting gaps of IP and OP in ERS, which reveals that the both the pair-breaking energy and the gap ratio are larger in triple layer cuprates than in single and double layer cuprates (not shown).



Figure 1. Comparison of the Raman spectra calculated from the ARPES (orange cruve) and the experimentally observed Raman spectra (blue curve) for B_{1g} (a) and B_{2g} (b) polarizations. The red and green curves are obtained from the ARPES data for the OP and IP, respectively. In the total curve IP+OP (thick orange), the contributions both from IP and OP are taken into account

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

We have developed low temperature 6-axis manipulator for high energy resolution ARPES measurements and achieved one of the lowest temperature 6-axis manipulators in



the synchrotron radiation facilities in the world. To achieve lower temperature, we have started computational thermal simulation.

Figure 2. Modeling and simulation of thermal analysis for 6-axis manipulator.

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Photoelectron Momentum Microscope at IMS

UVSOR Synchrotron Facility Division of Beam Physics and Diagnostics Research



MATSUI, Fumihiko Senior Researcher

The demand for photoelectron micro-spectroscopy and spectromicroscopy to characterize the electronic properties of microstructures is growing rapidly. Photoelectron spectroscopy resolved in three-dimensional momentum space with a microscopic field of view is realized by combining a so-called Momentum Microscope

(MM) with a soft X-ray synchrotron radiation source. We built a new MM station at BL6U,¹⁾ an undulator-based soft X-ray beamline. This station opens the door to direct observation of the Fermi surface of μ m-sized crystals, which was difficult with conventional ARPES-type hemispherical analyzers.

1. Momentum Microscope

As shown in Figure 1, the system consists of a photoemission electron microscope (PEEM) lens, a hemispherical deflection analyzer as an imaging-type energy filter, and a 2D detector with a CMOS camera. The details of the specification evaluation result are described elsewhere.¹⁾ In brief, the energy resolution of the analyzer was estimated to be 20 meV at pass energy of 20 eV. The spatial resolution in the microscopy mode was evaluated to be about 50 nm. The momentum resolution of 0.012 Å⁻¹ has been achieved. The position of sample stage facing to the analyzer is precisely controlled by a hexapod. Samples can be cooled down to 8 K and heated up to 400 K.

Since a high voltage is applied between the sample and the PEEM lens, it is essential that the sample be flat. We have developed a technique to cleanly cleave sub-mm-sized crystals in the ultra-high vacuum condition. Figure 2 shows a valence band measurement with a wide **k** acceptance of 6 Å⁻¹ in diameter.



Figure 1. Schematic drawing of the momentum microscope.¹⁾

2. Original Electron Analyzers

Furthermore, we are aiming at highly efficient and comprehensive measurement of spin distribution as the final goal. *Omnidirectional photoelectron acceptance lens* $(OPAL)^{2}$ together with *Projector for electron spectroscopy with collimator analyzer* (PESCATORA)³⁾ enables photoelectron holography measurement of the full hemisphere. Moreover, we invented *Right angle deflection imaging analyzer* (RADIAN)⁴⁾ for spin vector analysis with *k/r*-space resolution. We are expanding the MM system based on our original device developments.



Figure 2. (a) Photoelectron angular distribution and (b) band dispersion of the cleaved graphite crystal surface.



Figure 3. (a) Photograph of the omnidirectional photoelectron acceptance lens (OPAL). (b) 1-keV electron trajectory at the sample surface. (c) Performance of electrons emitted in full hemisphere.²⁾

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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



to reveal local structures of liquids with the K-edges of light elements (C, N, and O). We have investigated local structures of several liquids by using a liquid flow cell for XAS in transmission mode.¹⁾ In this year, we have developed two techniques for applying

Soft X-ray absorption spectroscopy

(XAS) is an element specific method

NAGASAKA, Masanari Assistant Professor

XAS to the low energy region below 200 eV including K-edges of Li and B and L-edges of Si, P, S, and Cl, as described below.

1. Development of Soft X-Ray Transmission Argon Gas Window

XAS in the low energy region is difficult since transmitted soft X-rays mostly consist of high order X-rays due to the low transmission of first order X-rays. We have proposed the soft X-ray transmission argon gas window that removes high order X-rays by the absorption of Ar L-edges (240 eV).²⁾

2. Development of Photoelectron Based Soft X-Ray Detector

We have developed a photoelectron based soft X-ray (PBSX) detector that removes high order X-rays.³⁾ In this detector, the Au 4f photoelectrons emitted by first order X-rays are separated from those by the high order X-rays using a difference in kinetic energy of photoelectrons.

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Award

NAGASAKA, Masanari; YUZAWA, Hayato; KOSUGI, Nobuhiro; Analytical Sciences Hot Article Award (2020).

Development of a Surface-Sensitive Detection Method for Scanning Transmission X-Ray Microscopy

UVSOR Synchrotron Facility Division of Beam Physics and Diagnostics Research



OHIGASHI, Takuji Assistant Professor

A scanning transmission X-ray microscope (STXM) obtains 2-dimensional X-ray absorption of a sample to obtain chemical status. Generally, the STXM gives us integrated (bulk) information of the sample along a path of the X-ray. Alternative approach of the STXM is to detect secondary electron from the sample by using a channeltron. The detection of the secondary

electron enables us to obtain information of near surface of the sample because of escape depth of the secondary electrons around a few nm. Additionally, this technique overcomes a main difficulty of the STXM by measuring a thick sample which cannot be penetrated by the X-rays.

A channeltron is used as a detector for the secondary electron and is placed upstream of the sample. This optical system can obtain an X-ray transmission image and a secondary electron image simultaneously. As a test sample, a thin section of blended polymer on a copper grid was measured. The energy of the X-ray was 400 eV and the dwell was 500 ms per pixel. In Figure 1(b), an empty space indicated by a dotted circle also shows higher signals of the secondary electron than those from the blended polymer. This problem is under discussion.



Figure 1. (a) An X-ray transmission image and (b) a secondary electron image of a thin section of blended polymer on a copper grid. Scale bars are $5 \mu m$.

Resonant Soft X-Ray Scattering Measurements for Liquid-Crystal Materials

UVSOR Synchrotron Facility Division of Advanced Photochemistry



IWAYAMA, Hiroshi Assistant Professor

We study soft matters such as liquid-crystal materials with soft x-ray, whose energy region covers K-edge energies of carbon, nitrogen and oxygen. Soft matters exhibit their intriguing properties due to mesoscopic physical structures by self-organizations. To understand properties of soft matters, we need to investigate their structure in the mesoscopic scale.

1. Development of Resonant Soft X-Ray Scattering Measurements

Resonant soft x-ray scattering measurements can probe mesoscopic structures and periodic spatial variations of the

orientation of molecules with both elemental and chemical environment sensitivity and have orders of magnitude scattering intensity enhancement over conventional small angle (non-resonant) x-ray scattering, which is sensitive only to the electron density modulations.

In this year, we developed an equipment for resonant soft x-ray scattering measurements. Since soft x-rays are strongly absorbed by air, all soft x-ray paths should be in high vacuum. In addition, a thickness of sample must be less than 1 micrometer to obtain transmitted scattered lights.

We were successful in developing the equipment and now confirmed vacuum test and sample holder test. Our equipment can probe structures in the range from 62 Å to 170 Å. A first sample will be liquid-crystal materials which show a twisted structure. The experiments will be performed at BL3U of UVSOR in September 2020.

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 ruburene 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 immediately reset the IL-derived bias stress 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 Professor SHIMADA, Kenya (from Hiroshima University)

High-Resolution Angle-Resolved Photoemission Study of Correlated Materials

In order to understand the physical properties of solids, we are studying the electronic structures by means of high-resolution angle-resolved photoemission spectroscopy (ARPES) using synchrotron radiation. We have also developed an ARPES system using an ultraviolet laser (hv = 6.36 eV) to pursuit ultimate spatial, energy, and angular resolutions (<10 μ m, <1meV, <0.05°). By combining synchrotron

radiation and laser ARPES measurements as well as extensive density functional theory (DFT) calculations, we could elucidate the termination dependent electronic structures of an antiferromagnetic topological insulator $MnBi_4Te_7$. The topological surface state is gapped for quintuple-layer (QL) termination but gapless for the septuple-layer (SL) termination. The spin texture is expected to be different for both terminations. While the DFT calculations reasonably reproduce the s-p electron bands, it is still challenging to predict magnetic 3d electronic bands. In the case of oxygen adsorbed Fe(100) surface states, we found significant deviations from the DFT results due to momentum- and orbital-dependent electron correlation effects.



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

Coherent Control in Condensed Systems

My research is focused on the ultrafast dynamics and coherent control in the condensed systems, especially in strongly coupled systems. We have recently demonstrated the ultrafast visible-pump THzprobe measurement of the carrier dynamics in a thin film of CH₃NH₃PbBr₃. As the pump photon energy changes around the bandgap, we can observe the drastic change of the THz transmission intensity. The

results are analyzed based on the efficiency of the Auger-like process which is only observable for free carriers, and it is shown that the thermal excitation of the excitons to generate free carriers in the conduction band is not efficient in this material.

We are interested in a vibrational strong-coupling system in which a mid infrared photon is mixed with molecular vibrational quanta and forms a polaritonic quasi-particle. This phenomenon accompanies the local deformation of the potential surface, which can modulate the wave packet motion on the potential. Our final goal is the control of the wave packet motion and the photochemical reaction based on the modulation of the potential surface.

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



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

Selected Publications

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- T. Yokoyama and K. Eguchi, Phys. Rev. Lett. 107, 065901 (2011).
- M. Dabrowski et al., Phys. Rev. Lett. 113, 067203 (2014).
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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 (10⁵ Pa) HAXPES measurements for the first time using Beamline 36XU of SPring-8. This work was supported by the NEDO Fuel Cell project.

Member Assistant Professor

The third subject is the pico- and femtosecond pump-andprobe 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 spaceresolved imaging.

Recently, new assistant professors Drs. Koitaya and Yamamoto joined our group. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation and lasers.

- Y. Takagi et al., Appl. Phys. Express 10, 076603 (2017).
- Y. Uemura et al., Chem. Commun. 53, 7314 (2017).
- Y. Takagi et al., Acc. Chem. Res. 51, 719 (2018).
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1. Quick *Operando* Ambient Pressure Hard X-Ray Photoelectron Spectroscopy for Reaction Kinetic Measurements of Polymer Electrolyte Fuel Cells¹⁾

Polymer electrolyte fuel cells (PEFCs) are 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. To study catalytic reaction mechanisms, it is generally quite important to investigate reaction kinetics with time-resolved experimental techniques.

In this work, we have designed and constructed a quick operando ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) measurement system for the investigations of reaction kinetics in electrochemical cells under working conditions. The HAXPES measurements can be performed at typical pressures of 1×10^4 Pa (maximum 1×10^5 Pa) with the typical time resolution of ~200 ms. To accumulate time-resolved spectra with sufficient signal-to-noise ratios, repeated cycles of the chemical reactions are conducted based on the repeated-cycle time-tagged method, requiring the identity of each event and the time trigger. As demonstrative experiments, we have successfully observed time-resolved operando Pt 3d_{5/2} and S 1s HAXPES from the Pt/C cathode catalyst of PEFCs. In the Pt $3d_{5/2}$ HAXPES, we have evaluated the reaction kinetics of the Pt oxidation/reduction processes at the cathode upon abrupt change of the cathodeanode bias voltage between 0.4 and 1.2 V. In the S 1s HAXPES for measurements of S species poisoning fuel cells, we have studied the contaminated anionic S adsorption and desorption kinetics on the Pt nanoparticles at the cathode. The results are comparatively discussed with previous findings.



Figure 1. (left) Schematic view of the quick *operando* HAXPES measurement system installed at hard x-ray undulator station BL36XU of SPring-8. (right) Examples of time dependence of the HAXPES results. The upper panel depicts the Pt oxidation process upon an abrupt step of the bias voltage. The lower panel gives the Pt-adsorbed S desorption process upon a similar bias voltage variation.

2. Photoinduced Anisotropic Distortion as the Electron Trapping Site of WO₃ Studied by Ultrafast W L₁-Edge X-Ray Absorption Spectroscopy with Full Potential Multiple Scattering Calculations²⁾

Understanding excited states of photocatalysts is significant to improve their activity for water splitting reaction. X-ray absorption fine structure (XAFS) spectroscopy using X-ray free electron lasers (XFEL) is a powerful method to address dynamic changes in electronic states and structures of photocatalysts in the excited state in ultrafast short time scales. The ultrafast atomic-scale local structural change in photoexcited WO₃ was observed by W L₁ edge XAFS spectroscopy using an XFEL. An anisotropic local distortion around the W atom could reproduce well the spectral features at a delay time of 100 ps after photoexcitation based on full potential multiple scattering calculations. The distortion involved the movement of W to shrink the shortest W-O bonds and elongate the longest one. The movement of the W atom could be explained by the filling of the d_{xy} and d_{zx} orbitals, which were originally located at the bottom of the conduction band with photoexcited electrons.



Figure 2. Schematic view of the ultrafast dynamics of WO_3 after ultraviolet laser excitation studied by the x-ray free electron laser.



Figure 3. Experimental and calculated time-dependent W L₁-edge XAFS spectra of WO₃. Significant more distortion of the local structure around W in the photoexcited state is elucidated.

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Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

Department of Materials Molecular Science Division of Electronic Structure

 SUGIMOTO, Toshiki Associate Professor SUGIMOTO, Toshiki Associate Professor SUGIMOTO, Toshiki Associate Professor SUGIMOTO, Toshiki Associate Professor Young Scientist Award, 33rd Annual Meeting of the SSSJ Young Scientist Award, 2018 Young Scientist Award 2018 Sub Presentation Award 2018 Sub Proceentation for Molecular Science Young Scientist Awards of the Japan Society for Molecular Science Young Scientist Award of the Physical Society of Japan

Keywords

Water Molecules, Nonlinear Optical Spectroscopy, Surface & Interface 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 hydrogenbond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning prove 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-

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- 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).
- T. Sugimoto et al., "Topologically Disordered Mesophase at Top-

dyne 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 Im $\chi^{(2)}$ SFG has a great advantage to 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.

Member Assistant Professor

SAKURAI, Atsunori



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

most Surface of Crystalline Ice Between 120 and 200 K," *Phys. Rev. B* **99**, 121402(R) (2019).

- F. Kato *et al.*, "Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice," *J. Phys. Chem. Lett.* 11, 2524–2529 (2020).
- T. Sugimoto *et al.*, "Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces," *Phys. Chem. Chem. Phys.* 29, 16435–17012 (2020).
1. Direct Evidence for Markedly Enhanced Surface Proton Activity of Crystalline Ice¹⁾

Hydrated protons on the ice surfaces critically influence physical and chemical properties of ices. They are generated solely by the thermal ionization of water molecules ($H_2O \Leftrightarrow$ $H^+ + OH^-$) in pure water molecular systems. Therefore, the proton activity inherent to water ice is determined by the amount and mobility of hydrated protons derived from the autoionization. Considerable discussions have been made, yet not been settled, on whether the activity of hydrated protons is substantially enhanced at the surface of water ice.

Very recently, we succeeded in directly and quantitatively demonstrating for the first time that the proton activity is significantly enhanced at the surfaces of low-temperature ice. On the basis of simultaneous experimental observation of the H/D isotopic exchange of water molecules at the surface and in the interior of double-layer crystalline-ice films composed of H₂O and D₂O (Figure 2), we reported three major discoveries of the unique enhancement of surface proton activity: (1) proton activity proved by the H/D exchange at the topmost surface is at least three orders of magnitude higher than in the interior even below 160 K; (2) the enhanced proton activity is dominated by autoionization process of water molecules rather than proton transfer process at ice surface; (3) as a consequence of surface promoted autoionization, the concentration of surface hydrated protons is more than six orders of magnitude higher than that in the bulk.

We also found that the cooperative structural fluctuations^{2–4)} allowed in the undercoordinated surface molecules but inhibited in the fully coordinated interior molecules facilitate the autoionization and dominate the proton activity at the ice surface. Because the lower limit of temperature of the earth's atmosphere is ~120 K around the mesopause, the surface of crystalline ice on earth is unlikely to be solidly ordered but would inevitably be highly fluctuated. In nature, such dynamic features facilitate the autoionization of water molecules and thus enhance the proton activity at the surface of crystalline ice.



Figure 2. Simultaneous observation of the H/D isotopic exchange of water molecules at the surface and in the interior of double-layer ice films composed of H_2O and D_2O .

2. Thickness Dependent Homogeneous Crystallization of Ultrathin Amorphous Ice⁵⁾

The crystallization mechanism and kinetics are fundamen-

Awards

tally important for thermal stability of amorphous materials. The crystallization of amorphous materials is generally triggered by spontaneous creation of crystalline nuclei. Two processes are distinguishable in terms of the place where crystallized nuclei are formed: *Heterogeneous nucleation* at the surface of material or the interface with the other material, and *homogeneous nucleation* in the bulk. In general, the surface and interface of amorphous thin films serve as nucleation sites. Therefore, it has been traditionally believed that crystallization of amorphous ice thin films also proceeds via the heterogeneous nucleation.

We have focused on the ultrathin films of amorphous ice grow on Pt(111) substrate and systematically investigated the crystallization process by varying the thickness of the films from a few nm to several tens of nm. Simultaneously monitoring the crystallization processes at the surface and in the interior of ice films, we found that the crystallization proceeds via homogeneous nucleation irrespective of the film thickness. This discovery overturned the conventional idea that the crystallization of amorphous ice thin films is initiated by heterogeneous nucleation. Furthermore, we found that the crystallization kinetics and temperature of amorphous ice thin films are highly modulated depending on the thickness of the film (Figure 3), although crystallization itself proceeds via the homogeneous nucleation mechanism. The structural analysis of hydrogen bonds based on vibrational spectroscopy revealed that the strength of hydrogen bonds in the thermodynamically most relaxed amorphous ice films (the state just before crystallization) changes significantly with the film thickness, which shows an evidence of a peculiar size effect.



Figure 3. Thickness dependence of the distribution of O–H···O hydrogen bond length (\bigcirc), crystallization rate (\triangle) and temperature (\diamondsuit) of the amorphous ice thin films on Pt(111).

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Organic Solar Cells

Department of Materials Molecular Science Division of Molecular Functions



HIRAMOTO, Masahiro Professor [hiramoto@ims.ac.jp]

Education

- 1984 B.E. Osaka University
 1986 Ph.D (Engineering) Osaka University
 Professional Employment
 1984 Technical Associate, Institute for Molecular Science
 1988 Research Associate, Osaka University
 1997 Associate Professor, Osaka University
 2008 Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
 Awards
 2017 Fellow Award of Japan Society of Applied Physics
 2006 Paper award, Molecular Electronics & Bioelectronics divis
- 2006 Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
- 2006 Research and Education Award, Osaka University
- 2004 Editor Award, Japanese Journal of Applied Physics

Keywords

Organic Semiconductors, ppm-Doping, Lateral Junction

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. Last year, we proposed a novel concept of the structure of organic solar cell, namely, a lateral multilayered junction (Figure 1). An essential point is that the photogenerated holes and electrons are laterally transported and extracted to the respective electrodes. We also investigated the reduction of open-circuit voltage loss in organic solar cells by using high-mobility organic semiconductors (Figure 2). On the other hand, we have been focused on the research on the ppmlevel doping effects in organic semiconductor films and organic single crystals for organic solar cells. 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, 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.

Member Assistant Professor

Secretary

IZAWA, Seiichiro Research Fellow

YABARA, Yusuke

PALASSERY ITHIKKAL, Jaseela

SUGIHARA, Hidemi

NAKAMURA, Yuka

Graduate Student

LEE, Jihyun



Figure 1. Lateral multilayered junction which can replace the blended junction.

Selected Publications

- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* **30**, 1801236 (15 pages) (2018). [Invited Progress Report]
- M. Kikuchi, M. Hirota, T. Kunawong, Y. Shinmura, M. Abe, Y.Sadamitsu, A. M. Moh, S. Izawa, M. Izaki, H. Naito and M.

Hiramoto, "Lateral Alternating Donor/Acceptor Multilayered Junction for Organic Solar Cells," *ACS Appl. Energy Mater.* **2**, 2087– 2093 (2019).

 S. Izawa, N. Shintaku, M. Kikuchi and M. Hiramoto, "Importance of Interfacial Crystallinity to Reduce Open-Circuit Voltage Loss in Organic Solar Cells," *Appl. Phys Lett.* 115, 153301 (2019).

1. Reduction of Open-Circuit Voltage Loss in Organic Solar Cells¹⁾

Reducing the energy loss in output voltage is critically important for further enhancing the efficiency of organic solar cells. In this work, we showed that the organic solar cells with high mobility and highly crystalline donor and acceptor materials can reduce an open-circuit voltage ($V_{\rm oc}$) loss.

Two-layer cells consisting of C8-BTBT and C_n-PTCDI (Figure 2(a)), which acts as the donor and acceptor were fabricated. V_{oc} increases in the order of C3 < C6 < C8 of C_n-PTCDI (Figure 2(a)) and reached to thermodynamic (Shockley–Queisser) limit (Figure 2(b), red dots). Simultaneously, electron mobility increases by the suppression of molecular vibration of π -stacking due to the increase of crystallinity by fastener effect by increasing the chain length (C3 < C6 < C8). V_{oc} increase can be reasonably explained by the suppression of non-radiative (vibrational) recombination from CT (charge transfer) exciton (D⁺/A⁻) to ground state (D/A) (Figure 2(c)).

By using the high mobility (band conductive) organic semiconductors, high efficient organic solar cells would be realized by reducing $V_{\rm oc}$ loss.



Figure 2. (a) J–V characteristics of C8-BTBT/ C_n -PTCDI cells. (b) $V_{\rm oc}$ vs. CT state energy. (c) Non-radiative recombination from CT state to ground state.

2. Ultra-Thick Blended Layer up to 10 μm in Organic Solar Cells²⁾

Blended layer thickness of organic solar cells made with small molecules has limitation up to the order of a few hundred nm which is still not enough to absorb whole solar light. In this work, we succeeded to operate the organic solar cells having 10- μ m-thick photoactive blended layer, consisting of zinc phthalocyanine (ZnPc), and fullerene (C₆₀).

A method of co-evaporant induced crystallization³⁾ was used for the deposition of $ZnPc:C_{60}$ codeposited films. Co-evaporant molecule (polydimethylsiloxane; PDMS) acts as a liquid in the vacuum, which induces the crystallization and phase separation of the codeposited film. The cross-sectional image of co-deposited films with a co-evaporant show the columnar structures of ZnPc and C₆₀ which offer the vertical transport routes for holes and electrons (Figure 3, inset).

With co-evaporant, short-circuit photocurrent (J_{sc}) and fill factor (FF) showed almost constant value up to the surprising blended layer thickness of 10 µm (Figure 3, blue diamonds). However, without co-evaporant, they steeply decreased within several hundred nm (Figure 3, green crosses). Photocurrent density of 20 mAcm⁻² and the conversion efficiency (PCE) of 4.3% were observed. Whole solar light absorption by ultrathick blended layer fabricated by co-evaporant will open the way to realize the high efficient small-molecular type organic solar cells.



Figure 3. Dependence of cell performance on blended layer thickness. Inset: Phase separated columnar structure made by co-evaporant induced crystallization.

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Solid-State NMR for Molecular Science

Department of Materials Molecular Science Division of Molecular Functions



NISHIMURA, Katsuyuki Associate Professor [nishimur@ims.ac.jp]

Education

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

Professional Employment

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

Award

2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

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, solidstate NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their 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.



Member Secretary

YOKOTA, Mitsuyo

Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1," *Biochim. Biophys. Acta, Biomembr.* 1788, 2575–2583 (2009).
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- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ¹H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β-Sheet Structures by High Resolution ¹H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* 48, 11199–

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- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* 1834, 1034–1043 (2013).
- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* 11, 0146405 (10 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* 56, 791–795 (2017).

1. Development of Solid-State NMR Probe

We have built a variety of solid-state NMR probes such as static and MAS ¹H-X double resonance probes for 400 MHz NMR, and a variable temperature ¹H-X double resonance MAS probe for 920 MHz ultra-high field NMR so far. Most of these probe buildings were achieved through major modifications of commercial probes. During the past few years, we have been working on building an original solid-state NMR probe which is fully compatible with commercial instruments currently used.

We have built original narrow bore solid-state NMR ¹H-X ("X" indicates variable resonant frequency) double resonance magic angle spinning (MAS) probe for 2.5 mm outer diameter (O.D.) sample tube used for 400 MHz (9.4 T) NMR spectrometer. The developed probe was built with originally designed parts except for spinning and spinning rate detection modules which were purchased from NMR company. The capacitive matching network design composed of commercially available non-magnetic variable capacitors was used. Balun type electric circuit was incorporated into ¹H channel, in which reduces to half the effective voltage of tuning capacitor and also minimize antenna effect of rf coil and rf inhomogeneity, especially at high field. Low frequency X channel was enabled to change largely its tunable frequency range to observe various nuclei by exchanging additional non-magnetic capacitors from bottom of the probe. The used network design may be compatible at higher fields by changing the parts related to resonant frequency.

Currently, the designs of individual parts are further updated and parts positions in the probe are further optimized to improve performance of the probe and access to the parts for the maintenance of the probe. ¹H-¹³C-¹⁵N triple resonance MAS probe was re-designed based on improved ¹H-X double resonance probe and is under building. We would like to replace two NMR modules purchased from NMR company to original ones. Therefore, we are currently attempting to design original spinning module for 4 mm sample tube in which a little bit easier than that for 2.5 mm sample tube. Probe developments enable to reduce cost for acquiring probes and open up possibilities to design new experiments which are tightly related to specifically designed hardware. In near future, we would like to incorporate special functions into our original probes.

2. 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 $A\beta$ 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 $A\beta$ (1-40) induced on DMPC bilayers based on solid-state NMR.¹ We have been collaborated with Prof. Kato group in IMS for those $A\beta$ studies.

In the current study, A β (1-40) oligomer induced on lipid bilayers consisting of GM1 and DMPC have been attempted to characterize using solid-state NMR. All of essential solid-state NMR experiments such as ¹³C-homonuclear- and, ¹³C-¹⁵N heteronuclear correlation experiments for signal assignments and dipolar coupling based ¹³C-homonuclear correlation experiments to obtain distance information were completed.

As reported in last report, analysis of secondary structure of $A\beta$ based on the chemical shifts of assigned signals revealed that disordered N-terminus followed by two β -sheet structures from middle region to C-terminus, in which differ from the one induced on DMPC bilayers.

During a year, the signal assignments were reconfirmed and dipolar coupling based ¹³C-homonuclear correlation experiments were performed for the sample of $[U^{-13}C, {}^{15}N] A\beta$ diluted with natural abundant A β at various mixing times to differentiate intra- and intermolecular correlations. Then intraand intermolecular distance information was extracted through the analyses of those NMR data. By considering the result of paramagnetic relaxation enhancements (PRE) experiments as reported last year, promising intermolecular packing model was successfully obtained from the NMR data.

Currently, precise molecular structure of $A\beta$ together with intermolecular packing configuration is under investigations based on NMR data with combination of computational science through collaboration with Prof. Okumura group in IMS.

3. Structural Characterizations of Molecular Materials Using Solid-State NMR

We have also been working on collaboration works with two other research groups, Prof. Yoshito Tobe in Osaka university and Prof. Nobuyuki Nishi in Aichi university of education for the characterizations of newly designed molecular materials based on solid-state NMR. Those projects are underway.

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

RESEARCH ACTIVITIES

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

Department of Materials Molecular Science Division of Molecular Functions



KOBAYASHI, Genki Associate Professor [gkobayashi@ims.ac.jp]

Education

- 2006 B.E. Kanazawa University
- 2008 M.E. Tokyo Institute of Technology
- 2010 D.S. Tokyo Institute of Technology

Professional Employment

- 2010 Postdoctoral Fellow, Tokyo Institute of Technology
- 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 Associate Professor, The Graduate University for Advanced Studies

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 Fundation
- 2018 The 7th Ishida Award, Nagoya University
- 2019 Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan
- 2019 Morino Foundation for Molecular Science

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

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.

battery system utilizing both the H^- conduction phenomenon and the $H^-\!/H_2$ redox reaction.

Member Assistant Professor

TAKEIRI, Fumitaka Graduate Student

NAWAZ, Haq

Technical Fellow

Secretary

IMAL Yumiko

SUZUKI, Ai

KUBOTA, Akiko

OKAMOTO, Kei

AYU. Nur Ika Puii*

UCHIMURA, Tasuku





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).
- H. Nawaz, F. Takeiri, A. Kuwabara and M. Yonemura and G. Kobayashi, *Chem. Commun.* 56, 10373–10376 (2020).

1. Study on H⁻ Conductive Oxyhydrides¹⁻⁵⁾

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. A hydride ion (H⁻,) is an attractive charge carrier because it exhibits promising features for fast ionic conduction; namely, monovalence, suitable ionic size similar to that of F⁻ and O²⁻, and high polarizability. Furthermore, its strong reducing properties with a standard redox potential of H^-/H_2 (-2.3 V) which is close to that of Mg/Mg²⁺ (-2.4 V) may be applied in energy storage/conversion devices with high energy densities. In 2016, we synthesized 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 upper) and demonstrated pure H⁻ conduction properties in the oxyhydrides. The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state $Ti/La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}/TiH_2$ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using Hconduction phenomena.



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 Ba₂MHO₃ (M = Sc, Y).

More recently, we synthesized novel H⁻ conductive oxyhydrides, Ba₂*M*HO₃ (M = Sc, Y), 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 Ba₂*M*HO₃ selectively occupied the rock-salt layer, in contrast to those of the observed isostructural Libased oxyhydrides that preferentially occupy the perovskite layer (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O led to the formation of the $[Ba_2H_2]$ layers. These results indicate that anion ordering in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H⁻ conducting materials.

2. High-Performance of Li-Rich Layered Cathode Materials through A₂O₃-Surface Modification⁶⁾

Controlling the cathode/electrolyte interface by surface modification of cathode materials with metal oxides or phosphate is being explored as a possible strategy for improving the electrochemical performance of such materials. We synthesized Al2O3-coated Li[Li0.2Ni0.18Co0.03Mn0.58]O2 and investiated 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 surfacemodification layer was composed of Li-Al oxides and Al oxides and that a $\text{Li}M_{1-x}\text{Al}_x\text{O}_2$ (M = transition metals) interlayer was formed between the modification layer and the Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]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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- H. Nawaz, G. Kobayashi* *et al.*, *Chem. Commun.* 56, 10373–10376 (2020).
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- 6) G. Kobayashi* et al., J. Power Sources 303, 250–256 (2016).

Award

KOBAYASHI, Genki; Morino Foundation for Molecular Science (2019).

* carrying out graduate research on Cooperative Education Program of IMS with High Energy Accelerator Research Organization

Clarification of the Energy Conversion Mechanism at the Surface and Interface by Scanning Probe Microscopy

Instrument Center



Surface and interface are the places for energy conversion processes in physics, chemistry, and biology. The detailed mechanism of such energy conversion processes is yet to be clarified. The reaction at the interface between the electrode and electrolyte of rechargeable batteries are a typical system of the energy conversion. At the interface in lithium ion battery, which

MINATO, Taketoshi Senior Researcher

is most widely used rechargeable battery,¹⁾ the energy transfer is proceeded by the insertion and extraction of the carrier ions at the interface during the charge and discharge reactions. Also, at the interface, the carrier ions, counter ions, solvents, additives, and crystal structures of the electrode surface forms characteristic structures that induce different properties from the material bulk. Traditionally, the reaction mechanism at the interface has been discussed based on electrochemical measurements. However, the nature of the interface is still unclear due to the difficulty of the analysis of the buried interface.



Figure 1. The scanning probe microscope system for the analysis of electrochemical reactions installed in the instrument center of Institute for Molecular Science.

Scanning probe microscopy (SPM) is an excellent technique to analyze the geometric, mechanical, electric, and electronic properties at the surfaces and interfaces. Thus, it has been employed for the analysis of the energy conversion processes. SPM can directly access to the buried interfaces such as the interface between electrode and electrolyte and has abilities to provide important information to clarify the reaction mechanism. In 2020, two specially designed SPMs have been launched at the instrument center of the Institution for Molecular Science. One is designed for the analysis of the geometric, mechanical, electric, and electronic properties at the surface and interface under photo excitation or magnetic field with high resolution. The another is solely designed for the analysis under electrochemical reactions (Figure 1). Using the two SPM systems, both the physical properties and the reaction mechanism of the energy conversion processes at the surface and interface could be clarified.



Figure 2. A Faraday current mapping on SiN/Pt obtained by scanning electrochemical microscopy in 5 mM hexamine RuCl₃ and 0.1 M KNO₃ aqueous solution. Cantilever: Pt; counter electrode: Pt, reference electrode: Ag, sample potential: -0.1 V (vs reference), image size: 25 μ m × 6 μ m.

In electrochemical devices, the local distribution of the reactions at the interface between the electrode and electrolyte strongly influences the device performances. The direct observation of the local distribution at the interface provides important information that aids the understanding of the reaction mechanism of the system. Using the SPM system with the specially designed cantilever having Pt tip, the local distribution of the electrochemical reactions was visualized. Figure 2 shows an example of the mapping of the electrochemical reaction on SiN/Pt in hexamine RuCl₃ electrolyte. The bright area shows the area with higher Faraday current than the dark area. The higher Faraday current is caused by the redox reactions of Ru ions in the electrolyte. From the simultaneous observation of the mechanical properties of the electrode surface using the SPM, the bright and dark areas are assigned to the regions of Pt and SiN, respectively. The results reveal the high reactivity of the Pt in the reaction. Employing this technique in the present and innovative battery systems,^{1–3)} the local distribution of the reactions in the batteries can be visualized. This will avail more vital information for the design of new energy devices.

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- H. Konishi, R. Takekawa, T. Minato, Z. Ogumi and T. Abe, *Chem. Phys. Lett.* **755**, 137785 (2020).

Visiting Professors



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

Theoretical Studies on Chiral Material Science

We focus on chirality-induced phenomena in solids. (1) Magnetic response of a highly nonlinear soliton lattice in a monoaxial chiral helimagnet: We presented a theory of nonlinear magnetic response of a chiral soliton lattice state in a monoaxial chiral helimagnet under an oscillating magnetic field. (2) Tensile deformations of the magnetic chiral soliton lattice probed by Lorentz transmission electron microscopy:

We considered the case of a chiral soliton lattice subjected to uniaxial elastic strain. We found that the strain induced anisotropies give rise to three distinct non-trivial spin textures, depending on the nature of the strain, and we show how these states may be identified by their signatures in Lorentz transmission electron microscopy (TEM). (3) Chirality-Induced Spin-Polarized State of a Chiral Crystal: Chirality-induced spin transport phenomena are investigated at room temperature without magnetic fields in a monoaxial chiral dichalcogenide $CrNb_3S_6$. We found that spin polarization occurs in these chiral bulk crystals under a charge current flowing along the principal *c* axis.



Visiting Associate Professor FURUKAWA, Ko (from Niigata University)

Advanced ESR Study of Molecule-Based 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 advanced electron spin resonance (ESR) spectroscopy such as high-field/high-frequency ESR, time-resolved ESR, pulsed-ESR and so on. Recently, our themes are following three (I) spin dynamics

study of molecule-based materials with the complex function combined to photoconductivity and photo-induced magnetic properties, (II) operand ESR study of the alternative catalyst for oxygen reduction reaction (ORR) in fuel cell, and (III) The ESR study aimed to investigate the paddy soil environments and to identify the rice cultivar from the trace metal in the rice bran.



Visiting Associate Professor OSHIMA, Yugo (from RIKEN)

Microscopic Studies of the Bilayer-Type Molecular Ferromagnet (Et-4BrT)[Ni(dmit)2]2 by ESR

Recently, a novel type of ferromagnet has been developed by Kusamoto Group and Yamamoto Group in IMS. The novel molecular ferromagnet $(Et-4BrT)[Ni(dmit)_2]_2$, where dmit is 1,3-dithiol-2-thiole-4,5-dithiolate and Et-4BrT is ethyl-4-bromothiazolium, takes a bilayer structure, and becomes ferromagnetic below 1 K. We are considering that this ferromagnet is the first realization of the Nagaoka-Penn ferromagnetism, where the ferromagnetism is achieved by the light hole-doping of the insulating Ni(dmit)_2

layer owing to the internal dipole moment of the monovalent cation Et-4BrT. In collaboration with Kusamoto Group and Yamamoto Group, we have investigated the microscopic electronic state of (Et-4BrT)[Ni(dmit)₂]₂ by high-frequency ESR. We have found that ESR lineshape largely changes below 30 K, which is probably due to the effect of doping from the cation site. We are now developing an ESR sample holder for field-effect transistors (FETs), so that we can control precisely the electrical doping of (Et-4BrT)[Ni(dmit)₂]₂ by means of FET structure, and investigate its change of magnetic properties by ESR spectroscopy.

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 Metal Homeostasis and Signal Sensing

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



AONO, Shigetoshi Professor [aono@ims.ac.jp]

Education

- 1982 B.S. Tokyo Institute of Technology 1987 Ph.D. Tokyo Institute of Technology
- Professional Employment
- 1988 Postdoctoral Fellow, Georgia University
- 1989 Assistant Professor, Tokyo Institute of Technology
- Associate Professor, Japan Advanced Institute of Science and Technology
- 2002 Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience (–2018) Professor, The Graduate University for Advanced Studies
- 2018 Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Keywords

Bioinorganic Chemistry, Metalloproteins, Sensor Protein

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

Selected Publications

- N. Muraki, C. Kitatsuji, Y. Okamoto, T. Uchida, K. Ishimori and S. Aono, "Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria," *Chem. Commun.* 55, 13864–13867 (2019).
- N. Muraki, K. Ishii, S. Uchiyama, S. G. Itoh, H. Okumura and S. Aono, "Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase," *Commun. Biol.* 2, 385 (12 pages) (2019).
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- A. Pavlou, A. Loullis, H. Yoshimura, S. Aono and E. Pinakoulaki,

function relationships of metalloproteins responsible for the regulation of biological homeostasis.

Member Assistant Professor

MURAKI, Norifumi IMS Research Assistant Professor

TAKEDA, Kouta

Post-Doctoral Fellow

NAM. Daveon

MURAKI, Megumi

NAKANE, Kaori

Technical Fellow

Secretary

I am also working on gas sensor proteins. 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 signaling 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 signaltransduction 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 transition metal-based gas-sensor proteins and the signaling systems working with them.

"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).

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

Regulatory hydrogenase (RH) that acts as a H_2 sensor 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 complexe in RH. These CO and CN^- are biosynthesized and assembled into the metal clusters, for which several accessory and chaperone proteins are required, as shown in Figure1. In 2019, we have determined the crystal structure of HypX, which catalyzes CO biosynthesis for the ligand of the Ni-Fe complex in RH, to find that HypX adopt coenyzme A (CoA) as a cofactor for CO biosynthesis using formyl-tetrahydrofolate as a substrate to form formyl-CoA, and that formyl-CoA is the reaction intermediate to form CO.



Figure 1. Reaction scheme of the biosynthesis and maturation of the Ni-Fe dinuclear complex for the active site in RH.

CO produced by HypX is used as a ligand of the iron in the NiFe(CN)₂(CO) center of NiFe hydrogenases. The Fe (CN)₂(CO) unit of the NiFe dinuclear center is assembled in the HypC/HypD complex as a scaffold. The binding site of the Fe(CN)₂(CO) unit is proposed to be located at the bottom of a tunnel ca. 20 Å deep inside from the protein surface in the HypC/HypD complex, to which Fe is initially bound and then CN⁻ and CO ligands bind to the Fe. If CO produced by HypX is diffused into solvent, it will be inefficient for the assembly of the Fe(CN)₂(CO) unit in the HypC/HypD. It may be a solution to utilize CO produced by HypX effectively is that HypX and HypC/HypD form a complex. The SEC analyses reveal the formation of HypC/HypD and HypC/HypD/HypX complexes as described below.

HypC (10.4 kDa in monomer) and HypD (45.0 kDa in monomer) are eluted from a Superdex75 column with an apparent mass of 21.6 kDa and 35.5 kDa, respectively, indicating that HypC and HypD exist as a homo-dimer and monomer in solution, respectively. The mixture of HypC and HypD is eluted with an apparent mass of 76.4 kDa. Though this result indicates the formation of the complex between HypC and HypD (probably (HypC)₂HypD complex), its quaternary structure is not clear at present. The mixture of HypC, HypD, and

HypX was eluted from a Superdex200 column with an apparent mass of 119.7 kDa, suggesting the formation of the 1:1:1 complex of HypC, HypD, and HypX. The structural characterization of this complex is now in progress.

2. Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria

Corynebacteria including *Corynebacterium diphtheriae* and *Corynebacterium glutamicum*, which are classified as a high GC content Gram-positive bacteria (Actinomycetes), adopt a different heme uptake machinery (Hta/Hmu system). It consists of the membrane-bound heme binding/transport proteins (HtaA and HtaB) and the ABC-type heme transporter system (HmuTUV). HtaA and HtaB consist of two and one CR (Conserved Region) domains, respectively, which are responsible for heme binding/transport. In this study, we have determined the crystal structures of HtaA and HtaB from *C. glutamicum* to understand the structural basis of the hemeuptake in Corynebacteria.

Though these interactions and the overall structure are conserved among HtaA and HtaB, the orientation of heme is different from one another. Good fitting of the model into the electron density of heme was obtained with the single orientation of heme for HtaA. On the other hand, assuming a 1:1 mixture of two orientations of heme was needed to obtain good fitting for the electron density of heme in HtaB. Thus, heme is accommodated with a mixture of two different orientations in HtaB unlike HtaA. The difference of the heme orientation suggests that heme transfer reaction between HtaA and HtaB proceeds through the HtaA/HtaB complex formation.

We also determined the crystal structure of the apo-form of H434A-HtaA at a resolution of 2.0 Å. Though the holoform of H434A-HtaA is a monomer, the apo-form of this variant was dimer. The N-terminal region (Ser364-Gly391) including the β 1 strand and the α 1 helix in each protomer are separated from the core region and each β 1 strand is swapped between two protomers to form a domain-swapped dimer (Figure 2).



Figure 2. The structure of the apo-form of H343A-HtaA. The chains A and B are shown in orange and light green, respectively. A dotted line in the chain B is a disordered region including the α 2 helix.

The structure of the domain-swapped dimer of apo-HtaA would be a model of a reaction intermediate for the heme transfer. In the domain-swapped dimer, the chain A would be a model of the holo-HtaA because it is superimposable to the structure of the holo-HtaA. The chain B in the domain-swapped dimer would be a model of the apo-HtaB in the holo-HtaA/ apo-HtaB complex.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

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



KATO, Koichi Professor [kkatonmr@ims.ac.jp] Director, ExCELLS

Education

- 1986 B.S. The University of Tokyo
- 1991 Ph.D. The University of Tokyo

Professional Employment

- 1991 Assistant Professor, The University of Tokyo
- 1997 Lecturer, The University of Tokyo
- 2000 Professor, Nagoya City University
- Professor, Institute for Molecular Science
 Professor, Okazaki Institute for Integrative Bioscience (-2018)
 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"
- 2018 Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Awards

- 2000 The Pharmaceutical Society of Japan Award for Young Scientists
- 2011 The Pharmaceutical Society of Japan Award for Divisional Scientific Promotions
- 2011 The 48th Baelz Prize

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 selforganized 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

Selected Publications

- S. Yanaka, R. Yogo and K. Kato, "Biophysical Characterization of Dynamic Structures of Immunoglobulin G," *Biophys. Rev.* 12, 637– 645 (2020).
- 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).
- K. Kato, H. Yagi and T. Yamaguchi, "NMR Characterization of the Dynamic Conformations of Oligosaccharides," in *Modern Magnetic Resonance*, 2nd Edition, G. A. Webb, Ed., Springer International Publishing, pp. 737–754 (2018).



Member Assistant Professor

> YAGI-UTSUMI, Maho YANAKA, Saeko

Post-Doctoral Fellow

Visiting Scientist

Graduate Student

SUZUKI, Tatsuya

GOH, Ean Wai*

WILASRI, Thunchanok*

HIRANYAKORN, Methanee

SEKIGUCHI, Taichiro

YUNOKI, Yasuhiro[†]

UMEZAWA, Fumiko[†]

YOGO, Rina[†]

SAITO, Taiki[†]

KOFUJI, Kana[†]

SASAKI, Yudai †

YAMADA, Rino[†]

ISONO, Yukiko

TANAKA, Kei

FUKUTOMI. Yukie

Technical Fellow

Secretary

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.

- T. Yamaguchi and K. Kato, "Molecular Dynamics of Gangliosides," in *Gangliosides*, S. Sonnino and A. Prinetti, Eds., Methods in Molecular Biology, Humana Press; New York, vol. 1804, pp. 411–417 (2018).
- K. Kato and T. Satoh, "Structural Insights on the Dynamics of Proteasome Formation," *Biophys. Rev.* 10, 597–604 (2018).
- K. Kato, S. Yanaka and H. Yagi, "Technical Basis for Nuclear Magnetic Resonance Approach for Glycoproteins," in *Experimental Approaches of NMR Spectroscopy*, The Nuclear Magnetic Resonance Society of Japan, Ed., Springer Nature; Singapore, pp. 415– 438 (2018).

1. Conformational Dynamics of Post-Translational Protein Modifiers

A majority of proteins encoded in genomes of limited size are post-translationally diversified by covalent modifications such as glycosylation and ubiquitination. The modifiers, *i.e.*, glycans and ubiquitin (Ub) chains, carry distinct biological information in forms of "glycocode" and "Ub code," respectively, which are read out by specific interacting proteins. Because these modifiers possess considerable degrees of motional freedom, we develop methodologies for characterizing their conformational dynamics in solution by NMR spectroscopy.

Our NMR analyses enabled the quantification of populations of individual conformers of Lys48-linked Ub chains, which serve as tags for proteasomal degradation. The data indicate that the most distal Ub unit in the Ub chains is the most apt to expose its interaction surface with the Ub-recognizing proteins. We also demonstrate that a mutational modification of the distal end of the Ub chain can remotely affect the solvent exposure of the interaction surfaces of the other Ub units, suggesting that Ub chains could be unique design frameworks for the creation of allosterically controllable multidomain proteins.¹⁾

We also developed an approach to improve the proteinbinding affinity of an oligosaccharide by remodeling its conformational space in the precomplexed state. In this approach, based on NMR-validated molecular dynamics simulations, we created an oligosaccharide analogue with an increased population of on-pathway metastable conformers that were originally very minor but exclusively accessible to the target protein without steric hindrance (Figure 2).²⁾



Figure 2. Remodeling of the oligosaccharide conformational space in the prebound state to improve lectin-binding affinity.

2. Integrative Biophysical Approaches to Exploring Protein Assembly Dynamics

The integrative biophysical approaches we have been

developing in collaboration with several research groups in ExCELLS and our external research network could be successfully applied to a variety of biomolecular assembling systems, yielding fruitful results in the past year, as summarized below (Figure 3).

We revealed that the two functionally unannotated archaeal proteins, PbaA and PF0014, are co-assembled into a unique ancient Greek tholos-like architecture, offering a novel framework for designing functional protein cages.³⁾ We successfully visualized the dynamic process by which the antibodies bound to antigens in membranes spontaneously assemble to form a hexameric ring structure, thereby recruiting complement component C1q on the membrane, which is the initial step of complement-mediated cell lysis.⁴⁾ Assembly of amyloid β (A β) under microgravity conditions were explored using the International Space Station, showing that the A β fibrillization process significantly slowed down in the microgravity environment, giving rise to distinct morphologies of A β .⁵⁾

Furthermore, we demonstrated that the cargo receptor complex responsible for the intracellular transportation of blood coagulation factors V and VIII recognizes 10-amino acid sequence built into these glycoproteins as a "passport" in the secretory pathway.⁶⁾ The secretion levels of recombinant glycoproteins were significantly increased simply by tagging it with the passport sequence. Our findings offer a potentially useful tool for improving the production yields of recombinant glycoproteins of biopharmaceutical interest.



Figure 3. Integrative biophysical approaches to exploring protein assembly dynamics. The simulated model structure of the PbaA/PF0014 complex superimposed onto the cryo-EM map (a), high-speed AFM image of IgG hexamers formed on membrane (b), distinct morphologies of A β fibrils formed under microgravity conditions (c).

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- 2) T. Suzuki et al. Biochemistry 59, 3180-3185 (2020).
- 3) M. Yagi-Utsumi et al. Sci. Rep. 10, 1540 (2020).
- 4) S. Yanaka et al. Int. J. Mol. Sci. 21, 147 (2020).
- 5) M. Yagi-Utsumi et al. NPJ Micorgravity 6, 17 (2020).
- 6) H. Yagi et al. Nat. Commun. 11, 1368 (2020).

Awards

SAITO, Taiki; Young Scientist Award, The Japanese Biochemical Society Chubu Branch (2019). UMEZAWA, Fumiko; Young Scientist Award, the 3rd Glycolleague (2019). YUNOKI, Yasuhiro; poster prize, the 26th Annual Meeting of the Japanese Society for Chronobiology (2019).

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

Operation and Design Principles of Biological Molecular Machines

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



IINO, Ryota Professor [iino@ims.ac.jp]

Education

- 1995 B.E. Kyoto University
- 1997 M.E. Kyoto University
- 2003 Ph.D. Nagoya University

Professional Employment

- 2000 Research Associate, Japan Science and Technology Cooperation
- 2002 Research Associate, Japan Science and Technology Agency
- 2005 Specially-Appointed Assistant Professor, Osaka University
- 2006 Assistant Professor, Osaka University
- 2011 Lecturer, The University of Tokyo
- 2013 Associate Professor, The University of Tokyo 2014 Professor, Institute for Molecular Science
 - 14 Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience (–2018) Professor, The Graduate University for Advanced Studies

Award

2012 Emerging Investigator. Lab on a Chip., The Royal Society of Chemistry, U.K.

Member Assistant Professor NAKAMURA, Akihiko ANDO, Jun OTOMO, Akihiro Post-Doctoral Fellow TAKEDA, Kimitoshi KIM. Ju-Youna Visiting Scientist NOJIMA, Tatsuya HONSA, Monique* YANG, Ling' Graduate Student VISOOTSAT, Akasit IIDA, Tatsuya Technical Fellow YAMAMOTO, Mayuko OKUNI, Yasuko KON, Yayoi Secretary NAKANE, Kaori

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. With the help of site-saturation mutagenesis and robot-based automation, we also engineer non-natural molecular motors to understand their design principles.



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

Selected Publications

- J. Ando, A. Nakamura, M. Yamamoto, C. Song, K. Murata and R. Iino, "Multicolor High-Speed Tracking of Single Biomolecules with Silver, Gold, Silver-Gold Alloy Nanoparticles," *ACS Photonics* 6, 2870–2883 (2019).
- T. Iida, Y. Minagawa, H. Ueno, F. Kawai, T. Murata and R. Iino, "Single-Molecule Analysis Reveals Rotational Substeps and Chemo-Mechanical Coupling Scheme of *Enterococcus hirae* V₁-ATPase," *J. Biol. Chem.* 294, 17017–17030 (2019).
- 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).
- 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).

1. Small Stepping Motion of Processive Dynein Revealed by Load-Free High-Speed Single-Particle Tracking¹⁾

Cytoplasmic dynein is a dimeric motor protein which processively moves along microtubule. Its motor domain (head) hydrolyzes ATP and induces conformational changes of linker, stalk, and microtubule binding domain (MTBD) to trigger stepping motion. Here we applied scattering imaging of gold nanoparticle (AuNP) to visualize load-free stepping motion of processive dynein (Figure 2). We observed artificially-dimerized chimeric dynein, which has the head, linker, and stalk from Dictyostelium discoideum cytoplasmic dynein and the MTBD from human axonemal dynein, whose structure has been well-studied by cryo-electron microscopy. One head of a dimer was labeled with 30 nm AuNP, and stepping motions were observed with 100 µs time resolution and sub-nanometer localization precision at physiologically-relevant 1 mM ATP. We found 8 nm forward and backward steps and 5 nm side steps, consistent with on- and off-axes pitches of binding cleft between $\alpha\beta$ -tubulin dimers on the microtubule. Probability of the forward step was 1.8 times higher than that of the backward step, and similar to those of the side steps. One-head bound states were not clearly observed, and the steps were limited by a single rate constant. Our results indicate dynein mainly moves with biased small stepping motion in which only backward steps are slightly suppressed.



Figure 2. (Top) Schematic of single-molecule imaging of dynein motion. (Middile) Typical trajectory of motion. (Bottom) Distribution of step size in on- and off-axis.

2. Single-Molecule Imaging Analysis Reveals the Mechanism of a High-Catalytic-Activity Mutant of Chitinase A from Serratia marcescens²⁾

Chitin degradation is important for biomass conversion and has potential applications for agriculture, biotechnology, and the pharmaceutical industry. Chitinase A from the Gramnegative bacterium Serratia marcescens (SmChiA, Figure 3) is a processive enzyme that hydrolyzes crystalline chitin as it moves linearly along the substrate surface. In a previous study, the catalytic activity of SmChiA against crystalline chitin was found to increase after the tryptophan substitution of two phenylalanine residues (F232W and F396W), located at the entrance and exit of the substrate binding cleft of the catalytic domain, respectively. However, the mechanism underlying this high catalytic activity remains elusive. In this study, single-molecule fluorescence imaging and high-speed atomic force microscopy were applied to understand the mechanism of this high-catalytic-activity mutant. A reaction scheme including processive catalysis was used to reproduce the properties of SmChiA WT and F232W/F396W, in which all of the kinetic parameters were experimentally determined. High activity of F232W/F396W mutant was caused by a high processivity and a low dissociation rate constant after productive binding. The turnover numbers for both WT and F232W/F396W, determined by the biochemical analysis, were well-replicated using the kinetic parameters obtained from single-molecule imaging analysis, indicating the validity of the reaction scheme. Furthermore, alignment of amino acid sequences of 258 SmChiA-like proteins revealed that tryptophan, not phenylalanine, is the predominant amino acid at the corresponding positions (Phe-232 and Phe-396 for SmChiA). Our study will be helpful for understanding the kinetic mechanisms and further improvement of crystalline chitin hydrolytic activity of SmChiA mutants.



Figure 3. (A) Structural model of *Sm*ChiA bound to crystalline chitin. (B and C) Side and bottom views of aromatic amino acid residues (cyan and pink) and bound chitin (yellow) in the catalytic cleft of *Sm*ChiA and OfChi-h.

References

J. Ando *et al.*, *Sci. Rep.* **10**, 1080 (2020).
 A, Visootsat *et al.*, *J. Biol. Chem.* **295**, 1915–1925 (2020).

Awards

NAKAMURA, Akihiko; Early Career Award in Biophysics, 2019 Annual Meeting of the Biophysical Society of Japan (2019). IIDA, Tatsuya; Student Presentation Award, 2019 Annual Meeting of the Biophysical Society of Japan (2019).

A Supramolecular Chemical Approach to the Construction of Artificial Cells

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



KURIHARA, Kensuke Research Associate Professor (–March, 2020) [kkurihara@ims.ac.jp]

Education

- 2005 B.S. The University of Tokyo
- 2010 Ph.D. The University of Tokyo

Professional Employment

- 2010 Technical Assistant, The University of Tokyo
- 2013 Postdoctoral Fellow, Research & Education Platform for
- Dynamics Living States, The University of Tokyo
- 2014 Research Associate Professor, Institute for Molecular Science Research Associate Professor, Okazaki Institute for
- Integrative Bioscience (OKAZAKI ORION Project) (-2018) 2018 Research Associate Professor, Exploratory Research Center
- on Life and Living Systems 2020 Project Researcher, Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

Award

2018 Kurita Outstanding Research Award

Keywords

Artificial Cell, Origin of Life, Droplet

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 secondgeneration GVs 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 GVs with conveyer GVs bearing the PCR reagents. After the PCR reagents are replenished, the GV can selfreproduce 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

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 et al., "Environment-Sensitive Intelligent Self-

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

Member

Secretary

Post-Doctoral Fellow

HIRATA, Yuiko

Visiting Scientist

MATSUO, Munevuki

FUKUTOMI, Yukiyo

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

Reproducing Artificial Cell with a Modification-Active Lipo-Deoxyribozyme," *Micromachines* **11**, 606 (2020). doi:10.3390/ mi11060606

1. Construction of a LLPS-Droplet Based Model Protocell

In the prebiotic era, cooperative interaction between selfproducing 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. Since a coacervate droplet as a model of early life was created by Oparin about 100 years ago, interesting primitive cell models using coacervate droplets have been created. However, construction of the self-reproduction of coacervate droplets and the spontaneous formation of peptides, which are the constituents of the coacervate droplets has not been realized in the same environment. In the present study, we designed and synthesized a molecule that has both a peptide and a droplet formation site to enable the formation of the coacervate droplets. We attempted to construct a liquidliquid 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. A detailed analysis of the particle size distribution measurements based on dynamic light scattering revealed that the growth of the droplets can be classified into two stages: The initial autocatalytic droplet formation and the fusion of the 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.

Furthermore, we conceived that this liquid-liquid phase separation droplet would be useful as a place to integrate biomolecules representing other origin-of-life hypotheses (e.g., RNA world, lipid world, etc.). Therefore, we attempted to investigate whether this droplet would incorporate those biomolecules. We added 20 mer RNA fragments, DNA fragments, and phospholipids to the droplets. By fluorescence microscopy observation and Raman microspectroscopy, it was found that the droplet was consisted of the hydrophobic center region and the hydrophilic peripheral region. The highly hydrophobic lipids were concentrated in the central region of the droplets and highly hydrophilic nucleic acids concentrated in the peripheral region. This hydrophilic and hydrophobic property was clear compared to the empty droplets. We suspect that the water contained in the hydrophilic region may have been replaced by nucleic acids.

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.

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

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

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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).

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).
- G. Hamasaka, T. Muto and Y. Uozumi, "Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an

Amphiphilic Palladium Pincer Complex," *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).

Member Visiting Professor

MASE, Toshiaki

- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, "Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Pallasium Catalyst Supported on Amphiphilic Resin," *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, "A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water," *Angew. Chem., Int. Ed.* 46, 704–706 (2007).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, "Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane," *J. Am. Chem. Soc.* 128, 15994–15995 (2006).

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Pd Comples.

(a) Allylic arylation

NaB

OAc

(b) Mizoroki-Heck reaction

-R3

1 (1 mol ppb to 1 mol ppm

MeOH. 50 °C. 24-72 h

TON: up to 500,000,000

1 (1 mol ppb to 100 mol ppm) base, NMP 140-160 °C, 15-72 h

TON: up to 870.000.000

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

NNC-Pincer Palladium Complex (1)

G. Hamasaka, S. Ichii and Y. Uozumi, Adv. Synth. Catal. 360, 1833-1840 (2018)

up to 99% vield

up to 100% vield

1. Arylation of Terminal Alkynes by Aryl lodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate¹⁾

Arylation of terminal alkynes (16 varieties) by aryl iodides (28 varieties) was achieved with a mol ppm loading level of palladium catalyst, where a variety of functional groups including heteroarenes were tolerated. Thus, the arylations were carried out in the presence of palladium acetate at ppm loadings and potassium carbonate in ethanol at 80 °C to give the corresponding internal alkynes in good to excellent yields. Synthesis of 2-phenyl-3-(phenylalkynyl)benzofuran was achieved by iterative use of the alkyne arylation under mol ppm catalytic conditions. Reaction-rate analysis, transmission electron microscopic (TEM) examination of the reaction mixture, and mercury-amalgamation test were performed to gain insight into the active species of the highly active ppm catalytic species. TEM examination of the reaction mixture revealed that palladium nanoparticles were generated in situ under the reaction conditions, and their cluster size was variable during the catalytic reaction. A variation in size of palladium particles suggested that the composition-decomposition process of Pd aggregates should take place in situ via monomeric palladium(0) species and/or fine palladium(0) clusters, which might be real catalytic species in this reaction.



Figure 2. Arylation of Terminal Alkynes with a mol ppm Loading Level of a Palladium Catalyst.

2. Second-Generation *meta*-Phenolsulfonic Acid–Formaldehyde Resin as a Catalyst for Continuous-Flow Esterification²⁾

A second-generation *m*-phenolsulfonic acid–formaldehyde resin (PAFR II) catalyst was prepared by condensation polymerization of sodium *m*-phenolsulfonate and paraformaldehyde in an aqueous H₂SO₄ solution. This reusable, robust acid resin catalyst was improved in both catalytic activity and stability, maintaining the characteristics of the previous generation catalyst (*p*-phenolsulfonic acid–formaldehyde resin). PAFR II was applied in the batchwise and continuous-flow direct esterification without water removal and provided higher product yields in continuous-flow esterification than any other commercial ion-exchanged acid catalyst tested.





3. The Hiyama Cross-Coupling Reaction at Parts Per Million Levels of Pd: In Situ Formation of Highly Active Spirosilicates in Glycol Solvents³⁾

A palladium NNC-pincer complex at a 5 molppm loading efficiently catalyzed the Hiyama coupling reaction of aryl bromides with aryl(trialkoxy)silanes in propylene glycol to give the corresponding biaryls in excellent yields. This method was applied to the syntheses of adapalene and a biaryl-type liquid-crystalline compound, as well as to the derivatization of dextromethorphan and norfloxacin. ESI-MS and NMR analyses of the reaction mixture suggested the formation of pentacoordinate spirosilicate intermediates in situ. Preliminary theoretical studies revealed that the glycol-derived silicate intermediates formed in situ are quite reactive silicon reagents in the transmetalation step.



Figure 4. Hiyama Cross-Coupling Catalyzed by ppm Palladium NNC-Pincer Complex in Glycol Solvents.

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- S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. –Asian J.* 14, 3850– 3854 (2019).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

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



MOMIYAMA, Norie Associate Professor [momiyama@ims.ac.jp]

Education

- 2000 B.S. Nagoya University
- 2005 Ph.D. The University of Chicago

Professional Employment

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

Awards

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

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- 2008 Thieme Chemistry Journals Award
- 2014 The 17th Morita Science Research Award Central Glass Co., Ltd. Award in Organic Chemistry, Japan

Member Assistant Professor OHTSUKA, Naoya Post-Doctoral Fellow FUJINAMI, Takeshi Graduate Student HORI, Tatsuaki OISHI, Shunya OTA, Hino KATO, Masayuki KOTANI, Shunsuke Secretary USHIDA, Hinano

Keywords

Synthetic Chemistry, Molecular Catalyst, Non-Covalent Interaction

The field of molecular catalysis has been an attractive area of research to realize efficient and new transformations in the synthesis of functional molecules. The design of ligands and chiral molecular catalysts has been recognized as one of the most valuable strategies; therefore, a great deal of effort has been dedicated to the developments. In general, "metal" has been frequently used as the activation center, and conformationally rigid catalyst framework 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 non-covalent interactions as organizing forces of catalyst framework 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.

Selected Publications

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

selective Diels–Alder Reaction of α , β -Unsaturated Aldehydes with Amidodienes," *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).

N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamanishi, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, "Molecular Design of a Chiral Brønsted Acid with Two Different Acidic Sites: Regio-, Diastereo-, and Enantioselective Hetero-Diels–Alder Reaction of Azopyridine-carboxylate with Amidodienes Catalyzed by Chiral Carboxylic Acid–Monophosphoric Acid," *J. Am. Chem. Soc.* 138, 11353–11359 (2016).





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

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 perfluoaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deriver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino–ene reaction using aldehydes and 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 azohetero-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 Mannich-type reaction and allylation reaction.⁸⁾

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- 6) N. Momiyama, T. Narumi and M. Terada, *Chem. Commun.* 51, 16976–16979 (2015).
- 7) 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, J. Am. Chem. Soc. 138, 11353–11359 (2016).
- 8) N. Momiyama *et al.*, Two manuscripts: Submitted; four manuscripts under preparation for submission.

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

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

	Education 2003 B.S. The University of Tokyo 2010 Ph.D. The University of Tokyo Professional Employment 2005 Sony Corporation 2010 Postdoctoral Fellow, RIKEN 2012 Project Assistant Professor, The University of Tokyo 2013 Assistant Professor, The University of Tokyo 2019 Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies	Graduate Student KIMURA, Shun* KATO, Soshi ISHIHARA, Mei FUJISAWA, Mayu Secretary MASUDA, Michiko
KUSAMOTO, Tetsuro Associate Professor [kusamoto@ims.ac.jp]	 2019 Research Encouragement Award, Japan Society of Coordination Chemistry 2010 Research Award, Graduate School of Science, the University of Tokyo 2008 BCSJ Award, The Chemical Society of Japan 	

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 openshell 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

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(2,4,6trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* 54, 3731–3734 (2015).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Luminescence, Sta-

developing applied science for light-emitting devices.

Our group focuses on strongly-interacted spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states enables unique molecular materials with exotic electrical and magnetic properties, such as superconductors, ferromagnets, and quantum spin liquids.

Member Assistant Professor

MATSUOKA, Ryota



Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH₂Cl₂. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

bility, and Proton Response of an Open-Shell (3,5-Dichloro-4pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical," *Angew. Chem., Int. Ed.* **53**, 11845–11848 (2014).

 T. Kusamoto, H. M. Yamamoto, N. Tajima, Y. Oshima, S. Yamashita and R. Kato, "Bilayer Mott System with Cation---Anion Supramolecular Interactions Based on Nickel Dithiolene Anion Radical: Coexistence of Ferro- and Antiferro-Magnetic Anion Layers and Large Negative Magnetoresistance," *Inorg. Chem.* 52, 4759–4761 (2013).

1. Construction of Supramolecular Two-Dimensional Network Mediated via Sulfur's σ-Holes in Conducting Molecular Crystals

Metal bis(dithiolato) complexes are attractive class of multi-functional molecular systems showing magnetic, conducting, and optical properties, such as superconductivity, ferromagnetism, quantum spin liquid, and NIR absorption. These properties depend highly on the arrangement of molecules in the solid state; therefore, controlling the arrangement (i.e., crystal structure) plays a crucial role for achieving novel or desired properties. We have focused on a σ -hole bond as an efficient noncovalent supramolecular interaction to control the arrangement of metal bis(dithiolato) complexes, with a goal of developing exotic magneto-conducting phenomena in molecular system. The σ -hole bond is observed between electrondeficient region on an atomic surface, so-called o-hole, and an electron-rich moiety in a molecule. Halogen and chalcogen atoms possess one and two σ -holes capable of forming supramolecular bonds with high directionality. We have developed novel conducting molecular solids based on platinum bis (dithiolato) complex anion radicals, (Et-4XT)₂[Pt(mnt)₂]₃ (X = Br, I; Et-4BrT = ethyl-4-bromothiazolium, Et-4IT = ethyl-4iodothiazolium, mnt = maleonitriledithiolato).^{1,2)} In their crystal structures, $X_{cation}{\cdots}N_{anion}$ and $S_{cation}{\cdots}N_{anion}$ $\sigma\text{-hole}$ bonds (i.e., halogen bond and chalcogen bond) were detected between the cation and the lone pairs of -CN moieties in the anion, forming a two-dimensional (2D) supramolecular network. The arrangement of the ions was similar in the two compounds (X = I and X = Br), while the orientation of the cations and the stacking manner of the anions along the direction perpendicular to the 2D supramolecular network were different (Figure 2). Such structural differences are attributed to the strength of the halogen bond, which is greater in iodine than in bromine, and resulted in distinct differences in their physical properties. For example, stronger trimerization of the anions in (Et-4IT)₂[Pt(mnt)₂]₃ enhanced antiferromagnetic interaction between the spins on the anions. These results suggest that sulfur-mediated chalcogen bonds can be robust enough to dominate the primary arrangement of



Figure 2. Chemical and crystal structures of (Et-4XT)₂[Pt(mnt)₂]₃ (X = Br, I).

molecules and the resulted physical properties, even in the presence of the other noncovalent intermolecular interactions or even upon the atomic replacements. Sulfur-based chalcogen bonds would be effective to realize desired structures and properties in molecular materials, while understanding the hierarchy of the noncovalent interactions operated in the crystal would be important for the precise crystal engineering.

2. Magnetoluminescence as Unique Photofunctions of Open-Shell Molecules

Controlling the spin state of open-shell molecules is a promising strategy for developing unique photochemical and photophysical properties, which are difficult to realize with conventional closed-shell molecules. We have shown that PyBTM doped into aH-PyBTM molecular crystals demonstrates new luminescent properties for organic radicals attributed to interplay between spin and luminescence.³⁾ Crystals containing 10 wt% PyBTM displayed PyBTM monomer- and PyBTM excimer-centered emissions and magnetic-field-sensitive luminescence, i.e., magnetoluminescence. We have revealed that changes in spin multiplicities of aggregated radicals contribute to the magnetic-field effect. To date, magnetoluminescence of stable radicals has been observed only in a few pure organic radicals. We are developing novel PyBTM-ligated metal complexes to expand the variety of materials showing magnetoluminescence behaviour, with a goal of realizing novel spin-sensitive photofunctions. We succeeded in observing excimer-like emission and magnetoluminescence behaviour in PyBTM-ligated zinc complexes doped into host crystals (Figure 3). Detailed investigations are in progress.



Figure 3. (left) Emission spectra of PyBTM-ligated zinc complex doped into host crystals at 4.2 K under magnetic fields. (right) Difference emission spectra (Δ intensity) under magnetic fields compared with the spectrum under 0 T.

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- C. Ohde, T. Kusamoto, K. Nakabayashi, S. Ohkoshi and H. Nishihara, *Cryst. Growth Des.* 17, 2203–2210 (2017).
- C. Ohde, T. Kusamoto and H. Nishihara, J. Magn. Magn. Mater. 497, 165986 (2020).
- 3) S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, Angew. Chem., Int. Ed. 57, 12711–12715 (2018).

Award

KUSAMOTO, Tetsuro; Research Encouragement Award, Japan Society of Coordination Chemistry (2019).

Design and Synthesis of Three-Dimensional Organic Structures

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



SEGAWA, Yasutomo Associate Professor [segawa@ims.ac.jp]

Education

- 2005 B.S. The University of Tokyo
- 2007 M.S. The University of Tokyo
- 2009 Ph.D. The University of Tokyo

Professional Employment

- 2009 Assistant Professor, Nagoya University
- 2013 Designated Associate Professor, Nagoya University
- 2013 Group Leader and Project Coordinator, JST ERATO Itami Molecular Nanocarbon Project (until 2020)
- 2020 Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Award

- 2013 RSC PCCP Prize
- 2014 Akasaki Award
- 2017 Chemical Society of Japan Award for Young Chemists2018 The Commendation for Science and Technology by the Minister
 - of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
- 2019 Nozoe Memorial Award for Young Organic Chemists

Keywords

π-Conjugated Molecules, Molecular Topology, 3D Network Polymer

Aromatic compounds are potentially useful as functional electronic materials. However, the controlled synthesis and assembly of three-dimensional complex molecules are still very difficult, especially for the crystal engineering of organic molecules. This group aims to create novel topological and reticular organic structures by using synthetic organic chemistry and geometric insights.

To achieve our purpose, this group will start electrondiffraction crystallography (MicroED) for the rapid structure determination of organic compounds. While X-ray crystallography is a general and reliable method for structure determination, it requires ~0.1 mm single crystals and making such crystal sometimes needs tremendous times and efforts. Since electron beam have much higher diffraction intensity than X-ray, structural analysis can be performed even with ultrasmall crystals (1 μ m or less). There are many fields such as covalent organic crystals with a three-dimensional structure

Selected Publications

- Y. Saito, K. Yamanoue, Y. Segawa and K. Itami, "Selective Transformation of Strychnine and 1,2-Disubstituted Benzenes by C–H Borylation," *Chem* **6**, 985–993 (2020).
- Y. Segawa, D. R. Levine and K. Itami, "Topologically Unique Molecular Nanocarbons," Acc. Chem. Res. 52, 2760–2767 (2019).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* 365, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* 356, 172–175 (2017).

and molecules with complex molecular topologies, where structural analysis has not been sufficiently developed.

Member Graduate Student

Secretary

WATANABE, Kosuke*

TANIWAKE, Mayuko



Figure 1. Design and synthesis of π -conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

- T. Yoshidomi, T. Fukushima, K. Itami and Y. Segawa, "Synthesis, Structure, and Electrochemical Property of a Bimetallic Bis-2-Pyridylidene Palladium Acetate Complex," *Chem. Lett.* 46, 587– 590 (2017).
- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* 48, 11963–11965 (2012).
- Y. Segawa, M. Yamashita and K. Nozaki, "Boryllithium: Isolation, Characterization, and Reactivity as a Boryl Anion," *Science* 314, 113–115 (2006).

1. Synthesis and Reactivity of Highly Strained Belt-Shaped Polycyclic Aromatic Hydrocarbons

We performed the synthesis of novel π -conjugated molecules with high strain energies and the investigation of its structural properties.^{2–4)}

The synthesis of cycloiptycene derivatives was achieved in each one step from (6,6)carbon nanobelt (Figure 2).³⁾ It was revealed that the carbon nanobelt was reacted as a diene in the Diels–Alder reaction with arynes and alkynes. Structures of all products were identified by X-ray crystallography to confirm that the Diels–Alder reactions took place at the six central benzene rings of the carbon nanobelt. DFT calculations indicated that the release of strain energy is the driving force to proceed the Diels–Alder reaction. By using this method, we have successfully synthesized cyclotetracosiptycene, the largest iptycene ever synthesized.



Figure 2. Diels–Alder reaction of (6,6)carbon nanobelt with alkynes and arynes for the formation of cycloiptycene derivatives.

The synthesis, structure, and properties of methylenebridged [6]cycloparaphenylene ([6]CPP), a nonalternant aromatic belt, were investigated (Figure 3).²⁾ This belt-shaped methylene-bridged [6]CPP, in which each phenylene unit is tethered to its neighbors by methylene bridges, was constructed through 6-fold intramolecular nickel-mediated arylaryl coupling of triflate-functionalized pillar[6]arene in 18% isolated yield. As compared to the analogous [6]CPP, the methylene bridges coplanarize neighboring paraphenylene units and enhance the degree of π -conjugation, which results in a significant decrease in energy gap. Moreover, the incorporation of small molecules in the defined pocket of methylenebridged [6]CPP makes it an attractive supramolecular architecture. Methylene-bridged [6]CPP is characterized by high internal strain energy reaching 110.2 kcal mol⁻¹, attributed to its restricted structure. This work not only exhibits an efficient



Figure 3. Synthesis of a nonalternant aromatic belt.

strategy to construct a new family of aromatic belt, but also showcases their properties, which combine the merits of CPPs and pillararenes.

2. Development of a Direct Octagon-Forming Annulation Reaction by Palladium Catalyst

The discoveries of new forms of carbon have always opened doors to new science and technology. In 1991, threedimensional (3D) periodic carbon crystals with negative Gaussian curvatures that consist of six- and eight-membered rings were proposed. To realize these 3D periodic carbon crystals, methods for creating polyaromatic structures embedding eight-membered rings must be developed. Here the two annulative coupling reactions that form an eight-membered ring through catalytic C-H functionalization are reported (Figure 4).1) Bay-chlorinated polyaromatics undergo either annulative dimerization or cross-coupling with biphenylene in the presence of a palladium catalyst to form various hitherto inaccessible polyaromatics embedding an eight-membered ring. The threefold annulative cross-coupling of 1,5,9-trichlorotriphenylene allowed construction of a highly curved nanocarbon. The present work not only demonstrates the potential of annulative coupling for constructing octagonal nanocarbons but also provides a conceptual pathway for the synthetic realization of 3D periodic carbon crystals.

Based on this result, our group has started the Joint Research Program in IMS with Murakami group. Our group will support the rapid structural determination of targeted π -conjugated molecules, their synthetic intermediates, as well as active species of transition metal catalysts.



Figure 4. Palladium-catalyzed octagon-forming annulation reaction.

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Visiting Professors



Visiting Professor FUKAZAWA, Aiko (from Kyoto University)

Renaissance of Nonbenzenoid π -Conjugated Systems toward Functional Materials

The work of our group has focused on exploring functional organic compounds with unusual with superb optical and/or electronic properties, based on the molecular designs of novel π -conjugated scaffolds as well as unusual functional groups. In particular, we have recently proposed a rational design of stable yet unusual π -conjugated systems based on the characteristics of nonbenzenoid hydrocarbons, *i.e.*, dehydro-

annulenes, non-alternant hydrocarbons, and fulvalenes, by the fusion of (hetero)arenes with small magnitude of aromaticity. In this year, we have succeeded in synthesizing several thiophene-fused antiaromatic π -systems, such as dithieno[*a*,*e*]pentalenes and their nitrogen-doped analogues. These thiophene-fused antiaromatics exhibit high thermal stability even without bearing bulky substituents while retaining pronounced antiaromatic character. These features give rise to characteristic long-wavelength absorption as well as aggregation behavior of these compounds.



Visiting Professor WATANABE, Rikiya (from RIKEN)

Single Molecule Physiology

Our study aims to understand cellular functions using a bottom-up approach from the single molecule level. To achieve this, we are attempting to elucidate the mechanism by which individual biomolecules or their networks function in a precise manner, by developing novel single-molecule techniques using multidisciplinary approaches, including biophysics, bioMEMS, and chemical biology. In addition, we are

developing a methodology to investigate correlations between genetic mutations, dysfunctions, and diseases with single molecule sensitivity, which would provide new insights for biological as well as pharmaceutical studies.



Visiting Associate Professor UEDA, Akira (from Kumamoto University)

Development of Purely Organic Molecular Materials with Unique Structural/Electronic Properties Design and synthesis of novel molecular materials have been a central issue for the development of molecular science. Our group has continuously focused on purely organic molecular materials with unique crystal/electronic structures and physical properties. Very recently, we have succeeded in the development of a novel neutral radical molecular conductor with a partially charge-transferred structure. Interestingly,

this material forms a two-dimensional conducting layer like BEDT-TTF salts, resulting in a much higher electrical conductivity than that of the conventional neutral radical conductors. These results suggest that this material is a possible candidate of a purely organic single-component molecular metal or superconductor. The magnetic properties and phase transition behavior of this material are of interest and thus will be investigated in the near future.

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

AKIYAMA, ShujiProfessor[akiyamas@ims.ac.jp]	Education 1997 B.E. Kyoto University 1999 M.E. Kyoto University 2002 Ph.D. Kyoto University Professional Employment 2001 JSPS Research Fellow 2002 JSPS Postdoctoral Fellow 2003 RIKEN Special Postdoctoral Researcher 2005 JST-PRESTO Researcher 2008 Junior Associate Professor, Nagoya University 2011 Associate Professor, Nagoya University 2012 Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Awards 2016 2018 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientist' Prize 2007 Young Scientist Prize, The Biophysical Society of Japan 2006 SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering 2002 The Protein Society Annual Poster Board Award	PURUIKE, Yoshihiko Post-Doctoral Fellow OUYANG, Dongyan Graduate Student SIMON, Damien Technical Fellow WASHIO, Midori TAKAYA, Mari SUGISAKA, Kanae WADA, Kotoe Secretary SUZUKI, Hiroko

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

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.

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

Member Assistant Professor

MUKAIYAMA, Atsushi

Among the three Kai proteins, KaiC is the core protein of the oscillator. In the presence of KaiA and KaiB, KaiC revelas 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 transmural 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*.

Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).

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- 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 System^{1,2)}

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 (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, requires a much larger amount of free energy than for typical ATP hydrolysis. The atomic structure explains why the ATPase activity of KaiC is so much lower (by 100- to 1,000,000-fold) than that of typical ATPases.²⁾



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^{3–5)}

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.³⁾ 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.⁴⁾ 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-liming step of the overall KaiBC complex formation.

We also collaborated with Drs. Ito-Miwa and Kondo (Nagoya University) to identify a series of KaiC mutations altering circadian periods dramatically, from 0.6 to 6.6 d.^{5})

3. beyond Evolutionary *Diversity*^{1,6)}

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**).

The habitats of cyanobacteria are diverse, so the space of their sequence is immense.⁶⁾ Furthermore, 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 KaiC homologues in other species and ancestral cyanobacteria?* (Figure 3B) If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

4. Bio-SAXS Activity in IMS⁷⁾

We have supported SAXS users so that they can complete experiments smoothly and publish their results.⁷⁾

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Protein Design Using Computational and Experimental Approaches

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

KOGA, Nobuyasu Associate Professo [nkoga@ims.ac.jp]	 Formation and the second state of the second state of	JSPS Post-Doctral Fellow KOBAYASHI, Naoya Post-Doctoral Fellow KOGA, Rie KONDO, Minako MINAMI, Shintaro Graduate Student SAKUMA, Kouya MITSUMOTO, Masaya YAMADA, Hiroko KAIDA, Shingo Secretary SUZUKI, Hiroko
Keywords	Protein Design for Structure and Function, Protein Folding, Structural Biology	,

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

Protein molecules spontaneously fold into unique threedimensional 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.

Member Assistant Professor

KOSUGI, Takahiro

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).
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- S. Basak, R. P. Nobrega, D. Tavella, L. M. Deveau, N. Koga, R. Koga, D. Baker, F. Massi and C. R. Matthews, "Networks of Electrostatic and Hydrophobic Interactions Modulate the Complex Folding Free Energy Surface of a Designed βα Protein," *Proc. Natl. Acad. Sci. U. S. A.* 116, 6806–6811 (2019).

1. Principles for Designing Ideal Protein Structures

We uncovered the principles for protein folding by designing "ideal" protein structures, which are stabilized 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), which were identified using a combination of folding simulations and analyses of naturally occurring proteins. Building backbone structures according to the rules, 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 have succeeded in designing ideal protein structures for five different topologies. These results suggest that the local backbone structures determine the tertiary folded structures rather than the details of amino acid sequences.





Figure 1. Rules relating local backbone structures to tertiary motifs.

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 demonstrated that the control is afforded by the resulting extended rule set by designing a series of proteins within the same fold but considerable variation in secondary structure length, loop geometry, β -strand registry, and overall shape. These extended design principles would provide the foundation for custom design of protein structures performing desired functions.

3. Robust Folding of De Novo Designed Ideal Protein Even with Most of the Core Filled with Valine

De novo designed ideal proteins, which are stabilized completely consistent local and non-local interactions, exhibit a remarkable property of extremely high thermal stability, compared with naturally occurring proteins. Whereas nonlocal interactions such as tight hydrophobic core packing have been traditionally considered to be crucial for protein folding and stability, the rules suggest the importance of local backbone structures in protein folding. We studied the robustness of folding of de novo designed proteins to the reduction of the hydrophobic core, by extensive mutation of large hydrophobic residues (Leu, Ile) to smaller ones (Val) for one of the designs. Surprisingly, even after 10-residue mutations from all of Leu and Ile to Val, a mutant with most of the core filled with Val was found to not be a molten globule and fold into the same backbone structure as the original design, with high stability. These results highlight the significance of local backbone structures for the folding ability and high thermal stability of designed proteins.



Figure 2. Experimental characterizations of the design with most of the core filled with Val.

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Elucidation of Function, Structure, and Dynamics of Condensed-Phase Molecular Systems by Advanced Ultrafast Laser Spectroscopy

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



KURAMOCHI, Hikaru Associate Professor [hkuramochi@ims.ac.jp]

Education

- 2007 B.S. Tokyo Institute of Technology
- 2013 Ph.D. Tokyo Institute of Technology
- Professional Employment
- 2013 Special Postdoctoral Researcher, RIKEN
- 2016 Research Scientist, RIKEN
- 2017 JST-PRESTO Researcher
- 2020 Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

- 2017 The 8th Research Incentive Award of RIKEN
- 2017 The Spectroscopical Society of Japan Award for Young Scientists
- 2019 RSC PCCP Prize
- 2020 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
- 2020 Morino Foundation for Molecular Science

Keywords

Ultrafast Spectroscopy, Chemical Reaction Dynamics, Ultrashort Pulse Generation and Control

Chemical reactions of polyatomic molecular systems proceed on complex potential energy surfaces (PESs) with a vast degree of freedom of nuclear coordinates. For understanding molecular mechanisms underlying the chemical reactions, it is essential to map out the PESs and visualize how the molecules migrate and change its structure thereon. To this end, it is necessary to track the change of the electronic/vibrational structure of the molecule from the reactant all the way down to the product, with temporal resolution as high as possible.

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study chemical reaction dynamics of the condensed-phase molecular systems. In particular, we exploit unique methodologies using sub-10-fs pulses (*e.g.*, ultrafast time-domain Raman spectroscopy and multidimensional electronic/vibrational spectroscopy), and track the molecular dynamics from the electronic and structural viewpoints, throughout the chemical reaction with an exquisite temporal resolution. Our particular interest

Selected Publications

- H. Kuramochi, S. Takeuchi and T. Tahara, "Femtosecond Time-Resolved Impulsive Stimulated Raman Spectroscopy Using Sub-7-fs Pulses: Apparatus and Applications," *Rev. Sci. Instrum.* 87, 043107 (2016).
- T. Fujisawa, H. Kuramochi, H. Hosoi, S. Takeuchi and T. Tahara, "Role of Coherent Low-Frequency Motion in Excited-State Proton Transfer of Green Fluorescent Protein Studied by Time-Resolved Impulsive Stimulated Raman Spectroscopy," *J. Am. Chem. Soc.* 138, 3942–3945 (2016).
- H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photo-

rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as photoreceptor proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our unique spectroscopic tools, we aim to establish a new avenue for the study of chemical reaction dynamics.

Member Secretary

ITO, Atsuko



Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

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- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, "Tracking Photoinduced Au–Au Bond Formation through Transient Terahertz Vibrations Observed by Femtosecond Time-Domain Raman Spectroscopy," J. Am. Chem. Soc. 141, 19296–19303 (2019).

1. Realtime Observation of the Structural Changes upon Photoinduced Tight Bond Formation

Realtime observation of chemical bond formation and subsequent nuclear rearrangements is one of the ultimate goals of chemical science. Nevertheless, such attempts have been long hampered by a technical difficulty to trigger bond formation at well-defined, desired timing. The dicyanoaurate complex trimer ([Au(CN)₂–]₃) is the best suitable system in order to achieve this aim because the tight covalent Au–Au bonds are formed upon photoexcitation. Despite the apparent simplicity of the system, however, recent time-resolved studies failed to construct a consistent picture of its structural dynamics.

We used femtosecond time-resolved impulsive stimulated Raman spectroscopy to track ultrafast structural dynamics of the [Au(CN)₂⁻] trimer upon the photoinduced Au–Au bond formation. This ultrafast "time-resolved time-domain" Raman technique allows us to monitor the change of the vibrational structure on the femtosecond timescale by inducing and observing coherent molecular vibrations at arbitrary timings with ultrashort pulses. The obtained femtosecond time-resolved Raman data reveal that the Au–Au stretching vibration at ~90 cm⁻¹ exhibits a gradual frequency upshift in a few picoseconds, demonstrating a continuous bent-to-linear structural change on the triplet-state potential energy surface upon the Au–Au bond formation. This comprehensive ultrafast spectroscopic study settles the controversy on this prototypical molecular assembly.¹



Figure 2. Schematic illustration of the structural changes in $[Au(CN)_2^-]_3$ upon photoinduced tight Au–Au bond formation.

2. Femtosecond Polarization Switching of the [CrCo] Dinuclear Complex Crystal

Polarization switching has been considered a promising key operating principle of next-generation sensors and memory devices. Ferroelectric compounds have been extensively studied as promising candidates because they exhibit polarization switching upon application of the external electric field or heating. However, the speed (and thus efficiency) of the polarization switching in these materials is often limited by the change in the molecular structure, which occurs on the picoseconds or longer time scale. Also, the polarization state of the ferroelectric compounds is, in many cases, dependent on their domain structure, making it difficult to realize large polarization at the macroscopic scale.

The crystal of the [CrCo] dinuclear complex has been shown to exhibit polarization switching upon the photoinduced phase transition.²⁾ Because the molecular orientation is well defined inside the crystal and the phase transition is accompanied by the charge transfer that does not require the change in the molecular structure, it has potential to realize the fast polarization switching at the macroscopic scale.

We studied photoinduced polarization switching dynamics in the crystal of the [CrCo] dinuclear complex by ultrafast pump–probe spectroscopy in the visible and mid-infrared regions. Our data clearly show that the photoinduced polarization switching is an ultrafast process with a time constant of 280 fs, demonstrating itself as the fastest polarization switching material realized using the metastable state. Moreover, the pump–probe data in the visible region reveal pronounced appearance of coherent nuclear wavepacket motion with a frequency as low as 22 cm⁻¹, which we attribute to a lattice vibrational mode. The pronounced non-Condon effect for its resonance Raman enhancement implies that this mode couples the relevant electronic states, thereby facilitating the ultrafast polarization switching.³



Figure 3. Schematic illustration of the change in the spin state associated with the phase transition. b) Time-resolved absorption spectra obtained after photoexcitation with the 9-fs pulse centered at 520 nm. c) Temporal profiles of the transient absorption signals.

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Awards

KURAMOCHI, Hikaru; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award (2020).

KURAMOCHI, Hikaru; Morino Foundation for Molecular Science (2020).

Open up Future Electronics by Organic Molecules

Research Center of Integrative Molecular Systems Division of Functional Molecular Systems



YAMAMOTO, Hiroshi Professor [yhiroshi@ims.ac.jp]

Education

- 1993 B.S. The University of Tokyo
- 1998 Ph.D. The University of Tokyo

Professional Employment

- 1998 Research Associate, Gakushuin University
- 1999 Special Postdoctral Fellow, RIKEN
- 2000 Research Scientist, RIKEN
- 2007 Senior Research Scientist, RIKEN
- 2012 Professor, Institute for Molecular Science
- Professor, The Graduate University for Advanced Studies Awards
- 2009 RSC Publishing CrystEngComm Prize
- 2009 Young Scientist Awards, Japan Society for Molecular Science
- 2010 RIKEN-ASI Award for the Young Scientist
- 2019 The CSJ Award for Creative Work
- 2020 NAGAI Foundation for Science & Technology Academic Award

Member Assistant Professor SUDA, Masavuki HIROBE, Daichi IMS Research Assistant Professor KAWAGUCHI, Genta Visiting Scientist SAENNAWA, Wiyada* PACHARIYANGKUN, Anna KUMSAMPAO Jakkapan Graduate Student MORISHIMA, Masaki AIZAWA, Hiroki NABEI, Yoji NAKAJIMA, Ryota Technical Fellow MURATA, Ryosuke Secretary SUZUKI, Ai

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 insulatorto-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

Selected Publications

- 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, S. Tajima, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Two-Dimensional Ground-State Mapping of a Mott-Hubbard System in a Flexible Field-Effect Device," *Sci. Adv.* 5, eaav7282 (9 pages) (2019).

be utilized for mapping the phase diagram around the Mottinsulator 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.

- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* 347, 743–746 (2015).
- H. M. Yamamoto, M. Nakano, M. Suda, Y. Iwasa, M. Kawasaki and R. Kato, "A Strained Organic Field-Effect Transistor with a Gate-Tunable Superconducting Channel," *Nat. Commun.* 4, 2379 (7 pages) (2013).

1. Current-Induced Spin-Polarization in a Chiral Crystal $CrNb_3S_6^{1,2)}$

CISS effect has remarkable ability which generates highly polarized spin current even with light element molecules. However, its extension to inorganic chiral materials has not been well investigated. Moreover, detection of CISS effect in metals that show ohmic response is quite interesting because one can discuss the CISS-based spin polarization in terms of band theory if metallic CISS effect in linear response regime is observed. So far, however, CISS experiments have been investigated only in tunnelling conduction regime.

We detected CISS-based spin transport phenomena in a monoaxial chiral dichalcogenide CrNb₃S₆. This material has chiral structure and metallic conduction, so that we could perform CISS experiments with metallic conduction regime. Spin polarization was detected in this chiral bulk crystal under a charge current flowing along the principal c axis at room temperature without magnetic field. The detection was made by an inverse spin Hall signal which is induced on the tungsten electrode that absorbs polarized spin from the chiral crystal (Figure 2). An inverse response was also observed when applying the charge current into the detection electrode, which implied an inverse CISS effect. The signal sign reversed in the device with the opposite chirality, which is consistent with the symmetry required for CISS effect. Furthermore, the spin signals were found over micrometer length scale in a nonlocal configuration. Such a robust generation and protection of the spin-polarized state can be discussed based on a one-dimensional model with spin-momentum locking.

In addition to the above experiments, we also detected bulk magnetization generated by applying electric current to the crystal. When the current amplitude was swept from



Figure 2. Detection of spin polarization in a chiral metal $CrNb_3S_6$. By applying electrical current (1), electron spins are polarized along the current direction by CISS effect. Then the spin current is diffused into W electrode (2) and generate a voltage by inverse spin Hall effect (3).

negative to positive, the current-induced magnetization changed linearly. Directly detecting such magnetization by magnetometry enables one to estimate the number of spin-polarized electrons. Using this number, we evaluated the spin polarization rate within the framework of Boltzmann's equation and found that spin polarization generated by CISS effect was enhanced by 10^5 times inside this material. It seemed that effective magnetic field generated by CISS could reach 10^3 T at high current density, which again confirmed the robustness of CISS effect. We also observed that the current-induced magnetization increased in the vicinity of the phase boundary between paramagnetic and forced ferromagnetic phases, which could be attributed to the spin fluctuation associated with the phase transition.

2. Anomalous Superconducting Phase in an Organic Field-Effect Device³⁾

We have achieved simultaneous control of bandwidth and bandfilling for organic Mott-insulators by using field effect device that can control the lattice strain to the organic crystal to observe the phase diagram for superconducting state. A new superconducting field-effect transistor (FET) in the vicinity of bandwidth-controlled Mott transition has been developed using molecular strongly correlated system κ-(BEDT-TTF)₂ Cu[N(CN)₂]Br laminated on CaF₂ substrate. This device exhibited significant cooling-rate dependence of resistance below about 80 K, associated with glass transition of terminal ethylene group of BEDT-TTF molecule, where more rapid cooling through glass transition temperature leads to the decrease in bandwidth. We demonstrated that the FET properties such as ON/OFF ratio and polarity can be changed by utilizing cooling rate. Therefore, this is another device that can control both bandwidth and bandfilling of an organic Mottinsulator simultaneously, to find phase diagram associated with superconducting and Mott-insulating phases. By analyzing the FET behaviors of the device at different cooling rates, an enhanced superconducting state at exactly half-filling was discovered.

[BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]

References

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- A. Inui, R. Aoki, Y. Nishiue, K. Shiota, Y. Kousaka, H. Shishido, D. Hirobe, M. Suda, J. Ohe, J. Kishine, H. M. Yamamoto and Y. Togawa, *Phys. Rev. Lett.* **124**, 166602 (2020).
- 3) G. Kawaguchi and H. M. Yamamoto, Crystals 9, 605 (2019).

Award

YAMAMOTO, Hiroshi; NAGAI Foundation for Science & Technology Academic Award (2020).
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

Center for Mesoscopic Sciences Division of Supersensitive Measurements



OKAMOTO, Hiromi Professor [aho@ims.ac.jp]

Education

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

Professional Employment

- 1985 Research Associate, Institute for Molecular Science
- 1990 Research Associate, The University of Tokyo
- 1993 Associate Professor, The University of Tokyo
- 2000 Professor, Institute for Molecular Science
- Professor, The Graduate University for Advanced Studies Award
- 2012 The Chemical Society of Japan (CSJ) Award for Creative Work
- 2020 The Commendation for Science and Technology by the MEXT Awards for Science and Technology Research Category

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 nearfield 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 Ramanscattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metalnanostructure 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-

Selected Publications

- H. Okamoto, "Local Optical Activity of Nano- to Microscale Materials and Plasmons," J. Mater. Chem. C 7, 14771–14787 (2019).
- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local

ceeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chirooptical 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.

Member Assistant Professor

> NARUSHIMA, Tetsuya YOSHIZAWA, Daichi

Project Assistant Professor (NINS)

YAMANISHI, Junsuke

ISHIKAWA, Akiko

NOMURA. Emiko

AHN, Hyo-Yong

Post-Doctoral Fellow

Visiting Scientist

Technical Fellow

Secretary

WU, Yi-Ju*



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

Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).

 H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," J. Phys. Chem. Lett. 4, 2230–2241 (2013).

1. Roles of Superchirality and Interference in Chiral Plasmonic Biodetection¹⁾

Chiral plasmonic nanostructures enable ≤pg detection and characterization of biomaterials. The sensing capabilities are associated with the chiral asymmetry of the near fields, which locally can be greater than equivalent circularly polarized light, a property referred to as superchirality. However, sensing abilities do not simply scale with the magnitude of superchirality. We show that chiral molecular sensing is correlated to the thickness of a nanostructure. This observation is reconciled with a previously unconsidered interference mechanism for the sensing phenomenon. It involves the "dissipation" of optical chirality into chiral material currents through the interference of fields generated by two spatially separated chiral modes. The presence of a chiral dielectric causes an asymmetric change in the phase difference, resulting in asymmetric changes to chiroptical properties. Thus, designing a chiral plasmonic sensor requires engineering a substrate that can sustain both superchiral fields and an interference effect.



Figure 2. Simulated CD spectra for gammadions of h = 5 nm, 30 nm, and 100 nm when light is incident upon their top (blue) and bottom (red) faces. Top three: Encapsulated by an achiral layer. Their mean is shown in black and is ~0 in all cases. Bottom three: Encapsulated by a chiral layer. The mean of the two incidences is shown in black.

2. Spectral Properties of Chiral Electromagnetic Near Fields Created by Chiral Plasmonic Nanostructures²⁾

The surface-enhanced chiral-optical spectroscopy is based on the interaction of chiral molecules with chiral electromagnetic near field localized on a chiral plasmonic nanostructure. It is of fundamental importance to reveal the spectral characteristics of chiral near fields for maximizing the chiral interaction. We investigated relations between near field and far field polarization characteristics of the chiral plasmonic nanostructures, using electromagnetic simulations. We found that spectral features of chiral near fields created by the nanostructures intercorrelate with those of far field optical rotation. This finding may provide us a method to characterize and design the chiral near field.



Figure 3. Simulated far-field circular dichroism η_{FF} (blue) and optical rotation θ_{FF} (red) spectra (top) and near-field circular dichroism η_{NF} spectrum (bottom) of a gold gammadion-shaped nanostructure (width 450 nm) by the finite-difference time-domain method.

3. Circularly Polarized Two-Photon-Induced Luminescence from Plasmonic Two-Dimensional Chiral Au Nanostructures³⁾

A chiral nanostructure, which exhibits optical activity, absorbs different amounts of left-handed circularly polarized (LCP) and right-handed circularly polarized (RCP) light. In this work, we report the observation of dissymmetry between twophoton-induced LCP and RCP photoluminescence from plasmonic two-dimensional (2D) chiral Au nanostructures. Under excitation by linearly polarized femtosecond pulses from a mode-locked Ti:sapphire laser with a low incident power of 3 mW, the 2D chiral plasmonic nanostructure yields circularly polarized two-photon-induced photoluminescence (TPIPL) due to resonance with a chiral multipolar plasmon mode of the nanostructure. The handedness of the circularly polarized TPIPL was dependent on the handedness of the chiral plasmonic nanostructure. The chiral nature of TPIPL may find potential applications in optical devices, sensing of chiral molecular environments in biological systems, and so forth.



Figure 4. (a,b) Left- and right-circularly polarized TPIPL spectra of the chiral nanostructures. Insets: SEM and TPIPL microscopic images of the left- (a) and right-handed (b) chiral gold nanostructures. (c) Dissymmetry factor (g) spectra of TPIPL for the chiral and achiral nanostructures. (d) CD spectra of the chiral nanostructures.

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- S. Hashiyada, K. Endo, T. Narushima, Y. Togawa and H. Okamoto, J. Phys.: Conf. Ser. 1220, 012050 (2019).
- 3) K. Q. Le and H. Okamoto, J. Phys.: Conf. Ser. 1220, 012004 (2019).

Award

OKAMOTO, Hiromi; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology Awards for Science and Technology Research Category (2020).

Center for Mesoscopic Sciences as an Interdepartmental Facility

OKAMOTO, Hiromi OHMORI, Kenji IINO, Ryota EHARA, Masahiro SUGIMOTO, Toshiki MINAMITANI, Emi NARUSHIMA, Tetsuya YOSHIZAWA, Daichi NOMURA, Yutaka OKANO, Yasuaki NOMURA, Emiko Director, Professor Professor Professor Associate Professor Associate Professor Assistant Professor Assistant Professor Assistant Professor Technical Associate Secretary

As the succeeding organization of former Laser Research Center for Molecular Science, Center for Mesoscopic Sciences continues development of new experimental apparatus and methods to open groundbreaking research fields in molecular science, in collaboration with other departments and facilities. Those new apparatus and methods will be served as key resources in advanced collaboration with the researchers from the community of molecular science. The targets cover:

- novel quantum-control schemes based on intense and ultrafast lasers
- novel optical imaging and nanometric microscopy and spectroscopy

- novel method of analysis for mesoscopic phenomena and so forth.

The Center also possesses several general-purpose instruments for laser-related measurements (commercial as well as in-house developed), and lends them to researchers in IMS who conduct laser-based studies, so as to support and contribute to their advanced researches.

RESEARCH ACTIVITIES Division of Advanced Molecular Science

The division consists of two sections. In the first one, 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 section should be the last word in the field of molecular science.

In the second section, we invite researchers in the universities performing unique researches in the field of molecular science as cross-appointment faculty members, and provide the research environment to enable research activity with advanced facilities in IMS.

Self-Assembling Molecular Systems Based on Coordination Chemistry

3M Lectureship Award (University of British Columbia)

Arthur C. Cope Scholar Award (ACS National Award) Merck-Karl Pfister Visiting Professorship (MIT Lectureship Award)

Thomson Reuters Research Front Award 2012 2013 The Chemical Society of Japan (CSJ) Award

Fred Basolo Medal (Northwestern University)

The Imperial Prize and the Japan Academy Prize

Division of Advanced Molecular Science

	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 to 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
	2019 Distinguished Professor, The University of Tokyo
	Awards
	1994 Progress Award in Synthetic Organic Chemistry, Japan
FUJITA, Makoto	2000 Division Award of Chemical Society of Japan (Organic Chemistry)
Distinguished Professor	2001 Tokyo Techno Forum 21 Gold Medal
	2001 Japan IBM Award
[mfujita@ims.ac.jp]	2003 Nagova Silver Medal
	2004 Izatt-Christensen Award
	2006 G W Wheland Award (Chicago University Lectureship
FUJITA, Makoto Distinguished Professor [mfujita@ims.ac.jp]	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)

Member

IMS Research Assistant Professor MITSUHASHI, Takaaki Post-Doctoral Fellow CHAN, Kwun Wa Graduate Student ALBERTSMA, Jelco* CHEN, Jiazhuo[†] KAGEYAMA, Ko[†] YOUNGCHEOL, Jung[†] YU, Zhengsu[†] WADA, Naoki† ZHOU, Boyu[†] Secretary MASUDA, Michiko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

Award)

2010 2010

2011 2012

2013

2013

2014 2014

2014

2018

2019 2020 The Reona Esaki Award

ISNSCE 2014 Nanoprize

Medal with Purple Ribbon

The 73rd Chunichi Cultural Award

Wolf Prize in Chemistry

The JSCC Award

We are designing new self-assembled molecular systems based on coordination chemistry, and apply the molecular system to various research fields. One of these examples is a molecular system called "crystalline sponge (CS)." The CS is a porous crystal, which can accommodate various kinds of small molecules, and align the accommodated molecules neatly in its inner space. Actually, we can observe the structure of the small molecules neatly aligned in the CS by the X-ray crystallography (Figure 1). Therefore, we can use the CS for the structure elucidation of the small molecules. This technique developed by us is called "CS method." The CS method has a potential to accelerate the various kinds of researches, in which the structure elucidation of novel compounds is required.



Figure 1. One example of the crystalline sponge method analysis result. Orange molecules are accommodated molecules, and green one is a framework of the crystalline sponge.

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. The CS Method Accelerates an Attempt to Create Artificial Natural Products

The natural products, compounds isolated from nature, exhibit great structural diversity and complexity. Such diversity and complexity of the natural products are generated by enzymatic reactions in organisms such as plants and bacteria. The enzymes can convert simple substrates into complex natural products. The natural products can be utilized for many kinds of purposes, such as medicines, industrial materials, and so on. Therefore, it can be said that the natural products are attractive resource for the exploration into useful compounds. However, recently, it becomes difficult to obtain new natural products with novel structures, because almost all types of natural products, which can be easily isolated, are considered to be already found through long history of natural product chemistry.

One way to solve this problem is a chemo-enzymatic approach. In this approach, we prepare unnatural synthetic substrates. Then, the substrates are converted into complex artificial molecules by enzymes, which is involved in the biosynthesis of natural products. In this way, we can expand the diversity of small molecules, using the biosynthetic mechanism of the natural products. One of the bottle-necks of this approach is the structural elucidation of the enzyme products, because the products often possess complex and unexpected structures. We consider that the CS method can solve this problem, since this method enables rapid structural elucidation of small molecules.

2. The CS Method Analysis of Artificial Indole-Containing Compound¹⁾



Figure 2. A) Reaction catalyzed by TleB in nature. B) Enzyme reaction to produce **1** and **6** from unnatural substrate **5**.

Award

FUJITA, Makoto; The 73rd Chunichi Cultural Award (2020).

We elucidated a structure of a compound 1 generated by reaction using a biosynthetic enzyme, TleB, which is involved in a biosynthesis of 2 (Figure 2). In nature, TleB accepts 3 as a substrate and produce 4 (Figure 2A). However, it was found that unnatural substrate 5 could also be accepted by TleB, and 1 and 6 were generated (Figure 2B). Even though the structure elucidation of 6 could be accomplished by the NMR, MS, and single-crystal X-ray diffraction study, that of 1 could not be determined by the conventional methods. Therefore, we subjected 1 to the CS method, and succeeded in the structure elucidation.

3. The CS Method Analysis of Artificial Natural Products Produced by Enzymatic Cyclization Reaction²⁾

One of the important reactions to form basic skeletons of the natural products is a cyclization reaction. When a chemically synthesized unnatural substrate **7** was converted by an enzymatic cyclization reaction, **8** was generated (Figure 3). **8** has a novel structure, but its structure could not be determined by the NMR analysis. Thus, the structure of **8** was revealed by the CS method.



Figure 3. Enzyme reaction to produce 8 from 7.

- I. Morita, T. Mori, T. Mitsuhashi, S. Hoshino, Y. Taniguchi, T. Kikuchi, K. Nagae, N. Nasu, M. Fujita, T. Ohwada and I. Abe, *Angew. Chem., Int. Ed.* 59, 3988–3993 (2020).
- 2) T. Mitsuhashi, L. Barra, Z. Powers, V. Kojasoy, A. Cheng, F. Yang, Y. Taniguchi, T. Kikuchi, M. Fujita, D. J. Tantillo, J. A. Porco and I. Abe, *Angew. Chem.*, *Int. Ed.* 59, in press (2020).

Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

Division of Advanced Molecular Science (Department of Materials Molecular Science, Electronic Structure)



KIMURA, Shin-ichi Professor (Cross Appointment) [kimura@ims.ac.jp]

Education

- 1988 B.S. Tohoku University
- 1990 M.S. Tohoku University
- 1991 Ph.D. Tohoku University

Professional Employment

- 1991 JSPS Postdoctoral Fellow, Tohoku University
- 1993 Research Associate, Kobe University
- 1993 Research Associate, Institute for Molecular Science
- 1998 Associate Professor, Kobe University
- 2002 Associate Professor, Institute for Molecular Science
- 2013 Professor, Osaka University
- 2020 Professor (Cross Appointment), Institute for Molecular Science

Awards

- 2001 Young Incentive Award, Japanese Society for Synchrotron Radiation Research
- 2008 The Commendation for Science and Technology by MEXT, Japan Science and Technology Prize (Research Field)
 2008 Morita Memorial Prize

Keywords

Condensed Matter, Biological Materials, Optical Property

Physical and chemical properties of solids, such as conductivity, magnetism, superconductivity and chemical reactions, and also life phenomena, such as redox and photosynthesis, originate from microscopic electronic and molecular vibrations and/or molecular movements based on quantum mechanics in materials and their interactions. To clarify the microscopic states provides us not only the knowledge of the origins of the physical properties and life phenomena but also the clarification of hidden functionalities. The information is useful for the creation of novel functional properties. To visualize the microscopic state, we also develop novel spectroscopic techniques using synchrotron radiation, high brilliant electron beams, and other so-called quantum beams. Recently, we have successfully developed a novel electron spectroscopy, namely resonant electron-energy-loss spectroscopy, as shown in Figure 1, to detect element-specific plasmons. Based on the obtained information of electronic structures, we are aiming to develop novel physical properties of new materials.

Selected Publications

- S. Kimura, T. Ito, M. Sakai, E. Nakamura, N. Kondo, K. Hayashi, T. Horigome, M. Hosaka, M. Katoh, T. Goto, T. Ejima and K. Soda, "SAMRAI: A Variably Polarized Angle-Resolved Photoemission Beamline in the VUV Region at UVSOR-II," *Rev. Sci. Instrum.* 81, 053104 (7 pages) (2010).
- S. Kimura, T. Iizuka, H. Miyazaki, A. Irizawa, Y. Muro and T. Takabatake, "Electronic-Structure-Driven Magnetic Ordering in a Kondo Semiconductor CeOs₂Al₁₀," *Phys. Rev. Lett.* **106**, 056404 (4 pages) (2011).



Member Secretary

ISHIKAWA, Azusa

Figure 1. Resonant electron-energy-loss spectroscopy (rEELS) apparatus developed by our group. The apparatus consists of a high-brilliant spin-polarized electron gun and a photoelectron spectrometer.

- S. Kimura and H. Okamura, "Infrared and Terahertz Spectroscopy of Strongly Correlated Electron Systems under Extreme Conditions," *J. Phys. Soc. Jpn.* **82**, 021004 (28 pages) (2013). [review]
- K. Hagiwara, Y. Ohtsubo, M. Matsunami, S. Ideta, K. Tanaka, H. Miyazaki, J. E. Rault, P. Le Fèvre, F. Bertran, A. Taleb-Ibrahimi, R. Yukawa, M. Kobayashi, K. Horiba, H. Kumigashira, K. Sumida, T. Okuda, F. Iga and S. Kimura, "Surface Kondo Effect and Non-Trivial Metallic State of the Kondo Insulator YbB₁₂," *Nat. Commun.* 7, 12690 (7 pages) (2016).

1. Non-Trivial Surface States of Samarium Hexaboride at the (111) Surface¹⁾

The peculiar metallic electronic states observed in the Kondo insulator, samarium hexaboride (SmB_6), has stimulated considerable attention among those studying non-trivial electronic phenomena. However, experimental studies of these states have led to controversial conclusions mainly to the difficulty and inhomogeneity of the SmB_6 crystal surface.

In this work, the detailed electronic structure of SmB_6 is revealed by angle-resolved photoelectron spectroscopy measurements of the three-fold (111) surface, where only two inequivalent time-reversal-invariant momenta (TRIM) exists. We observe the metallic two-dimensional state was dispersed across the bulk Kondo gap. Its helical in-plane spin polarization around the surface TRIM indicates that SmB_6 is topologically non-trivial, according to the topological classification theory for weakly correlated systems. Based on these results, we propose a simple picture of the controversial topological classification of SmB_6 .

We expect that this discovery could provide a new, fertile playground for the following researches about the concert effect between electron correlation and topology. It would also be applicable for future spintronic technologies.



Figure 2. (a) Crystal structure of SmB_6 . A shaded area is the (111) surface studied in the current work. (b) Surface electronic structure of SmB_6 obtained by angle-resolved photoelectron spectroscopy. Bright area represents the electrons with corresponding wavenumber (Fermi surface). A solid hexagon is the zone boundary determined from surface periodicity.

2. Relaxation Dynamics of [Re(CO)₂(bpy) {P(OEt)₃}₂](PF₆) in TEOA Solvent Measured by Time-Resolved Attenuated Total Reflection Terahertz Spectroscopy²)

To reveal highly efficient photocatalytic properties of an

artificial photosynthesis material $[Re(CO)_2(bpy){P(OEt)_3}_2]$ (PF₆), we have directly observed the photo-induced relaxation dynamics and reductive quenching process of the photoexcited state on a photosynthesis material in Triethanolamine (TEOA) solvent as an electron donor by time-resolved attenuated total reflection spectroscopy in the terahertz (THz) region. The spectrum of the complex in TEOA has an intermolecular vibrational mode between the complex and TEOA molecules, which reflects the precursor of the reductive quenching process. The intermolecular vibrational mode has three-step relaxation process in a picosecond timescale after photoexcitation, where firstly the triplet metal-to-ligand charge transfer excited state is vibrationally cooled down, secondly the distance between Re and TEOA is reduced by the rotation of TEOA molecules due to dipole-dipole interaction accelerated by heat transfer, and finally electrons transfer from TEOA to Re. These observations provide us the detailed information of the electron transfer process of photocatalytic properties of $[Re(CO)_2(bpy){P(OEt)_3}_2](PF_6)$ in TEOA solvent.



Figure 3. The schematic figures of the temporal evolution from I to III of the interaction between photocatalyst $[Re(CO)_2(bpy){P(OEt)_3}_2]^+$ as a photocatalyst and TEOA molecules as reductants.

- Y. Ohtsubo, Y. Yamashita, K. Hagiwara, S. Ideta, K. Tanaka, R. Yukawa, K. Horiba, H. Kumigashira, K. Miyamoto, T. Okuda, W. Hirano, F. Iga and S. Kimura, *Nat. Commun.* 10, 2298 (7 pages) (2019).
- 2) P. N. Nguyen, H. Watanabe, Y. Tamaki, O. Ishitani and S. Kimura, *Sci. Rep.* 9, 11772 (7 pages) (2019).

Innovative Catalysis Development Based on Radiant Right Spectroscopy

Division of Advanced Molecular Science (Department of Photo-Molecular Science, Photo-Molecular Science III)

Member Secretary HAGIWARA, Hisayo



Keywords

Organometallic Catalyst, Peptide-Based Material, X-Ray Spectroscopy

For future sustainable development, we promote research development of advanced catalysts based on element strategy criteria. Non-precious metal such as iron, nickel, cobalt, and cupper catalysts are investigated for synthetic transformation of various organic molecules related to pharmaceutical and photoelectronic materials. To elucidate the precise catalytic properties and mechanism, X-ray absorption spectroscopy (XAS) and various radiant right spectroscopies provided at UVSOR are used, where development of a solution-phase in situ XAS spectroscopic techniques and system will be intensively conducted for the study of homogeneous organometallic catalysts. Multidisciplinary research covered on DFT and XAS spectroscopy is also conducted to achieve an efficient structural determination technique being never accessible by the conventional XAS-based structural analysis. Using these cutting-edge spectroscopic technologies, we aim to promote innovative catalyst research which enable us highly efficient transformation of extremely unreactive organic molecules such as simple aromatic compounds, CO₂, and biomass into valuable functional materials.



Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

Selected Publications

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1. DFT-XAS-Based Mechanistic Investigation of Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate^{1,2)}

Pd-catalyzed oxidative coupling reaction of phthalate esters is a well-known industrial process for the production of biphenyl compounds which can be readily converted into biphenyl tetracarboxylic dianhydride (BPDA), being an important monomer of polyimides. Equation 1 shows a typical



procedure of the oxidative coupling, where dimethyl phthalate 3 readily couples in the presence of catalytic amounts of Pd(OAc)₂ 1a and Cu(OAc)₂ 2a to afford the corresponding biphenyls 4 and 5. Despite the widespread use of this process, the precise reaction mechanism had still remained unclear due to the severe reaction condition and the complex Pd/Cu heterobimetallic catalyst system including paramagnetic Cu(II) species, both which hamper the conventional analysis based on solution-phase NMR. To solve such problems in mechanistic study of homogeneous catalysis, we conducted to use XAS which enables element specific analysis to determine the oxidation state and the geometry of catalytic species.^{3,4)} Recently, we have succeeded to elucidate the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate as shown in Scheme 1. The oxidation states and the local coordination geometries of catalytic intermediates 1d, 1c, and 2a were determined under the stoichiometric conditions of each reaction path. DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of



Scheme 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAFS analysis.

these intermediates. This research is first to provide a clear answer to the long-term debate on the reaction mechanism in the last three decades and demonstrated that XAS is the powerful tool for the mechanistic study on homogeneous transition-metal-catalyzed reactions, being difficult by means of the conventional solution-phase NMR analysis.

2. XAFS-Based Structural Study on Flexible Organometallic Systems^{5–7)}

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal with sufficient size and quality for X-ray crystallography. We conducted DFT-XAS-based structural analysis of such flexible molecule. Recently, Prof. Uemura and Benjamin found a flexible MOF prepared from $[Zn_2(BDC)_2(DABCO)]_n$ and polystyrene which has a polymer-threaded multi-layered structure after removing the DABCO pillar ligand. The polymer-threaded extremely flexible molecular scaffolds showed no clear diffraction pattern except for a broad peak. To determine the molecular structure of this flexible MOF system, we carried out Zn K-edge and O K-edge XAS. A DFT-based simulation of both XAS spectra clearly demonstrated that $[Zn_2(BDC)_2]_n$ -monolayer was preserved well in the turbo-stratic phase without DABCO pillar.

Another successful application was achieved in the structure determination of rotaxane-linked iron porpyrin dimer in which two units of iron-porpyrin or phtalocyanine were interlocked through highly flexble quadruplet axials. Fe K-edge XAS-based structural analysis supproted with DFT-MD-based simulation succefully provides the precise local coordionation geometry of iron centers in highly flexible supramolecular system.

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Micro Solid-State Photonics

Division of Research Innovation and Collaboration



TAIRA. Takunori Project Professor [taira@ims.ac.jp]

Education

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

Professional Employment

- Researcher, Mitsubishi Electric Corp. 1985
- 1989 Research Associate, Fukui University
- Visiting Researcher, Stanford University (-1994) 1993 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
- 2019 LSJ (The Laser Society of Japan) Fellow

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 300-500µm 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 highpower and high-field laser with high-gain compact system. Besides, QPM-structured crystal quartz constructed by multiplate stacking could be promising as a high-power and reliable VUV frequency conversion devices. These downsized and

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Tiny Integrated Laser (TILA) Consortium TILA Disruptive Innovations can occur: Characteristics: limit the number of potential consum Consumption: take place in incon ient, centralized set ting: Ref. 'Seeing What's xt", C.M.Christ sen (2004) Modular interface Value network ownsize + a rial / Device New Mate Tiny Integ rated La R Power de Bandwidth ergy de nsity - Efficiency elength Reliability · Cost, e m quality

Member Program Manager SANO, Yuji

Visiting Professor

KAWASE, Kodo

Post-Doctoral Fellow

TAKEYA. Kei

SATO, Yoichi

ZHENG. Lihe*

YAHIA, Vincent

LIM. Hwanhong

KAUSAS, Arvvdas

MATSUDA, Miho

KOBAYASHI, Jun

INAGAKI, Yayoi

Research Fellow

Technical Fellow

ONO, Yoko

Secretary

ISHIZUKI, Hideki

Visiting Associate Professor

YOSHIDA, Mitsuhiro

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. Polarity Inversion of Crystal Quartz Using a Quasi-Phase Matching Stamp¹⁾

Stress-induced polarity inversion of crystal quartz using a quasi-phase matching (QPM) stamp is proposed for a QPM frequency conversion quartz device (Figure 2). Fabrication of QPM structure in x-cut quartz plate could be realized using the periodically patterned QPM stamp. Also, second-harmonic 532 nm generation with 16.8 kW peak intensity was demonstrated using a QPM quartz device with QPM period of 124 µm (3rd-order QPM) to confirm its polarity-inverted structure (Figure 3).



Figure 2. (a) Set up for the QPM stamp method, (b) Etched periodic pattern in *x*-cut plate.



Figure 3. (a) Set up for SHG experiment, (b) SHG characteristics using a QPM quartz.

2. High Peak-Power Near-MW Laser Pulses by Third Harmonic Generation at 355 nm in Ca₅(BO₃)₃F Nonlinear Single Crystals²⁾

In this work, the performance of $Ca_5(BO_3)_3F$ (CBF) single crystals (Figure 4) was investigated for the third harmonic generation at 355 nm. A high energy conversion efficiency of 16.9% at 355 nm was reached using a two-conversion-stage setup. First, using a high peak power, passively Q-switched Nd³⁺:YAG/Cr⁴⁺:YAG microlaser based gain aperture in micro-



Figure 4. Ca(BO₃)₃F crystal growth by TSSG method using 20 wt% LiF flux.



Figure 5. Experimental data on THG for uncoated CBF crystal and comparison with LBO crystal (anti-reflection coating) in terms of output UV energy (a) and of conversion efficiency (b).

MOPA, the second harmonic at 532 nm was achieved with lithium triborate (LBO) crystal, reaching 1.35 MW peak power. On a second step, laser pulses at 355 nm were generated using a 5 mm-long CBF crystal growth by TSSG method with energy, pulse duration and peak power of 479 μ J, 568 ps and 0.843 MW, respectively (Figure 5). These results are currently the highest reported for CBF material.

3. Remote Laser Analysis Technique in Harsh Environment^{3,4)}

In this study, a compact fiber-optic laser-induced breakdown spectroscopy (LIBS) system was developed using a microchip laser (MCL) with a monolithic Nd:YAG/Cr:YAG composite ceramic, for remote analysis of hazardous environments, such as nuclear reactor cores (Figure 6). Short duration laser pulses exhibiting a near-Gaussian beam profile were obtained. The output properties of the laser, such as pulse energy, repetition rate, temporal shape, and beam profile, were measured in view of their applicability to LIBS analysis and were found suitable for the purpose of this research (Figure 7). Spectra of zirconium metal were obtained, and signal intensity was further enhanced by applying multi-burst mode irradiation to the target. The results of this study reveal that the fiber-optic microchip-laser induced breakdown spectroscopy system is advantageous for efficient remote analysis of hazardous environments and is suitable for analyzing the inside of nuclear reactor cores.



Figure 6. Concept of remote laser analysis technique (LIBS) in harsh environment, such as nuclear reactor cores of Fukushima.



Figure 7. Instead of high power laser fiber delivering system, we have developed a fiber-optic microchip-laser induced breakdown spectros-copy system for efficient remote analysis of hazardous environments.

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