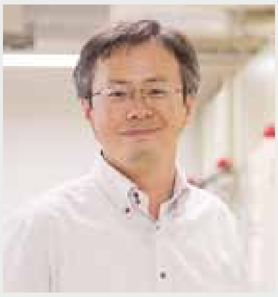
RESEARCH ACTIVITIES

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.

Molecular Origin of 24 Hour Period in Cyanobacterial Protein Clock

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



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Education

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

Professional Employment

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

Awards

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

Member
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Post-Doctoral Fellow
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Keywords Biological Clocks, Clock Proteins, Slow Dynamics

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

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

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

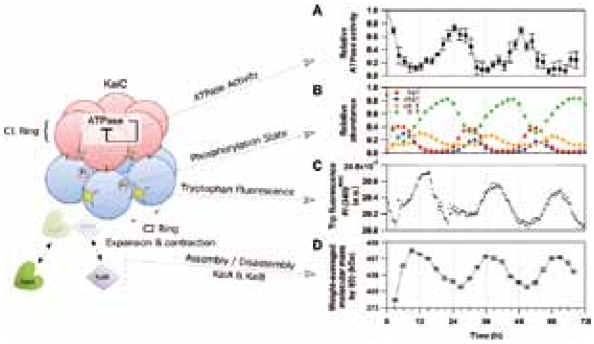

Figure 1. Circadian dynamics of cyanobacterial clock protein KaiC. The C1 and C2 domains in each protomer of KaiC are drawn as red and blue spheres, respectively. Expansion and contraction motions of the C2 ring (B, C) in solution serves as a timing cue for assembly/disassembly of KaiA and KaiB (D),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

Selected Publications

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

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* IMS International Internship Program

1. Tracking the Ticking of Cyanobacterial Clock Protein KaiC in Solution[3]

The ATPase activity of KaiC alone is strongly correlated with the oscillatory period of the Kai oscillator. This correlation suggests that the ATPase activity of KaiC is one of the period-determining factors of the Kai oscillator. Therefore, the determination of the structural change of KaiC interlocked with the ATPase activity is of great of importance.

To track the dynamic transition of KaiC, we recorded the time evolution of intrinsic tryptophan (Trp) fluorescence from KaiC contained in the Kai oscillator. KaiC is a dumbbell-shaped molecule composed of tandemly duplicated N-terminal (C1) and C-terminal (C2) domains. Six protomers are assembled into a hexamer to attain a double-doughnut shape. Two tryptophan (Trp) residues located in the protomer–protomer interface of the C2 domain can serve as a sensitive probe to monitor the potential structural transition of the C2 ring. The intensity of the Trp fluorescence from KaiC revealed a rhythmic fluctuation with the period of approximately 24 h (Figure 1, panel C). This is the first experimental evidence that demonstrated a dynamic structural transition of the C2 ring of KaiC in solution.

Concomitantly with the Trp-fluorescence dynamics, KaiC underwent a periodic change in its phosphorylation state (Figure 1, panel B). KaiC has the two phosphorylation sites, *i.e.*, Ser431 and Thr432, in the C2 domain, and both residues are phosphorylated and then dephosphorylated in a programmed sequence during the phosphorylation cycle as follows: KaiCS/pT → KaiCpS/pT → KaiCpS/T → KaiCS/T (where 'S' represents Ser431, 'pS' represents phosphorylated Ser431, 'T' represents Thr432, and 'pT' represents phosphorylated Thr432). Interestingly, the Trp fluorescence was maximized at the timing when the KaiCpS/T state was populated (Figure 1, panels B and C). The result suggests the Trp fluorescence is an excellent measure of the phosphor-coupled transition of the C2 ring in KaiC.

2. Visualization of Dynamic Structural Changes of KaiC Using Small-Angle X-Ray Solution Scattering Technique[1–3]

To visualize the C2-ring dynamics confirmed by tracking Trp fluorescence, we measured the small-angle x-ray scattering (SAXS) from KaiC in solution. To obtain the SAXS data of biological samples in solution, one must first record the scattering intensity of the sample and then that of the matching buffer in the separate experiment, and finally find the difference between two intensities. The cuvette used for conventional SAXS experiments has only a single observation chamber in order to ensure the qualitative subtraction of the scattering contributed by the solvent molecules. On the other hand, the use of the single-chamber cuvette makes both the experiment and analysis time-consuming.

To record the SAXS pattern of KaiC both efficiently and qualitatively, we designed and constructed an eight-chamber cuvette (octuplet cuvette), each chamber of which was fabricated so uniformly to ensure the inter-chamber subtraction. The developed cuvette enabled us to acquire SAXS dataset of KaiC roughly 10 times faster without any significant degradation of data quality.

On the basis of the obtained SAXS data, we built low-resolution models of the KaiC hexamer. The overall shape is almost unchanged in the transition from KaiCS/pT to KaiCpS/pT, whereas the radius of the C2 ring is dramatically enlarged in the subsequent transition from KaiCpS/pT to KaiCpS/T. The expanded C2 ring is partly contracted in the transition from KaiCpS/T to KaiCS/T, and is further contracted in the subsequent transition from KaiCS/T to KaiCS/pT. The present model suggests that KaiC ticks through expanding and contracting motions of the C2 ring.

The dynamic motion of the C2 ring uncovered throughout our study is chronobiologically meaningful, we believe, in terms of the elucidation of the key conformational change tightly coupled to the period-determining ATPase of KaiC. Our group is trying to improve spatio-temporal resolution of the experiments so as to draw a more dynamic and detailed picture of KaiC ATPase.

3. Instrumentation for the Molecular Origin of 24 Hour Period in Cyanobacterial Circadian Clock

How can biological-clock systems be so slow and stable? It is important to revisit the biological and structural backgrounds for the slowness and specificity both experimentally and theoretically. For this purpose, much effort has been focused on designing dedicated instrumentations for the molecular origin of the circadian period. We have made considerable improvements of instrument stability, signal-to-noise ratio, time resolution, temperature control, automated high-throughput measurements each for fluorescence tracking system,[1] auto-sampling device (unpublished work), HPLC (unpublished work), FTIR (unpublished work) and so on. Using the developed device, we recently succeeded in site-specific monitoring of conformational change of KaiC in solution, and also in identifying a core process of generating circadian periodicity in cyanobacterial circadian clock.[4]

4. Bio-SAXS Activity in IMS

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

References

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2) A. Mukaiyama, T. Kondo and S. Akiyama, *SPring-8 Research Frontiers 2011* 47–48 (2012).
3) S. Akiyama and T. Hikima, *J. Appl. Crystallogr.* **44**, 1294–1296 (2011).
4) A. Mukaiyama and S. Akiyama, Submitted.
5) R. Kojima, M. Okumura, S. Masui, S. Kanemura, M. Inoue, M. Saiki, H. Yamaguchi, T. Hikima T, M. Suzuki, S. Akiyama and K. Inaba, *Structure* **22**, 431–443 (2014).

Award

ABE, Jun; Best Presentation Award at Biophysical Society-Chubu-Annual Meeting (2014).

Protein Design Using Computational and Experimental Approaches

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Education

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

Professional Employment

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

Awards

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

Member
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SUZUKI, Hiroko

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

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

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

Selected Publications

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

1. Principles for Designing Ideal Protein Structures

Understanding the principles for protein folding is complicated by energetically unfavorable non-ideal features—for example kinked α-helices, bulged β-strands, strained loops and buried polar groups—that arise in proteins from evolutionary selection for biological function or from neutral drift. Here, we uncovered the principles for protein folding by designing "ideal" protein structures, which are stabilized by completely consistent local and non-local interactions. We discovered a set of rules relating local backbone structures (secondary structure patterns) to tertiary motifs (Figure 1 left), which were identified using a combination of folding simulations and analyses of naturally occurring proteins. Building backbone structures according to the rules (Figure 1 top right) and placing side chains stabilizing the backbone structures, we can readily design the proteins that have funnel-shaped folding energy landscapes leading into the target folded state. Using this approach, we designed sequences predicted to fold into ideal protein structures consisting of α-helices, β-strands and minimal loops, using the Rosetta program. Designs for five different topologies were found to be monomeric and very stable and to adopt structures in solution nearly identical to the computational models (Figure 1 bottom right). These results suggest that the tertiary folded structures are determined by the local backbone structures rather than the details of amino acid sequences.

References

1) S. J. Fleishman, S. D. Khare, N. Koga and D. Baker, *Protein Sci.* **20**, 753–757 (2011).
2) N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, *Nature* **491**, 222–227 (2012).
3) J. Fang, A. Mehlich, N. Koga, J. Huang, R. Koga, M. Rief, J. Kast, D. Baker and H. Li, *Nat. Commun.* **4**:2974 (2013).

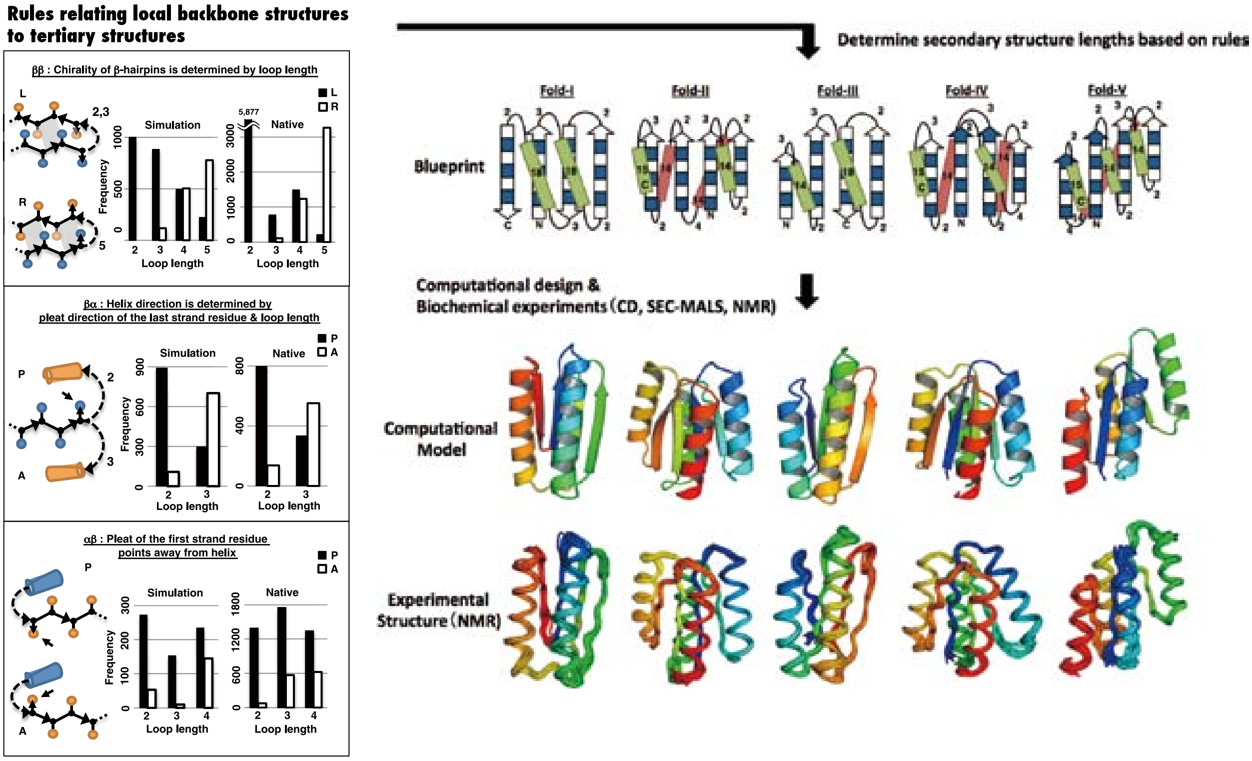

Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Awards

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

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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2010 Postdoctoral Fellow, Lawrence Berkeley National Laboratory
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FUJIHASHI, Yuta
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YAMADA, Mariko

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

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

Selected Publications

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

1. Impacts of Protein-Induced Fluctuations upon Quantum Mechanically Mixed Electronic and Vibrational States in Photosynthetic Energy Transfer and 2D Electronic Spectra

Initially, 2D electronic spectroscopic experiments were conducted for the Fenna-Mathews-Olson (FMO) complexes isolated from green sulfur bacteria at a cryogenic temperature, 77 K and revealed the presence of quantum beats lasting for 660 fs. [Engel, *et al. Nature* **446**, 782–786 (2007).] However, it is generally thought that the coherence at physiological temperatures is fragile compared to that at cryogenic temperatures because amplitudes of environmental fluctuations increase with increasing temperature. To clarify this issue, a theoretical examination on lifetimes of electronic coherence in the FMO complex. Consequently, it was predicted that electronic coherence in the FMO complex might persist for 700 fs and 300 fs at 77 K and 300 K, respectively.[2)] These theoretical predictions were consistent with the initial experimental observation at a cryogenic temperature and newer experimental results at physiological temperatures of the FMO complex. However, Panitchayangkoon *et al.* [*Proc. Natl. Acad. Sci. U.S.A.* **107**, 12766–12770 (2009).] showed that quantum beats in the FMO complex persist for at least 1.5 ps at a cryogenic temperature, while the theoretical model did not produce electronic coherence with lifetime of 1.5 ps. Hence, signatures of nuclear vibrational contributions in 2D spectroscopy have attracted great interest of late, in particular to interpret the oscillatory transients observed for light-harvesting complexes that persist much longer than predicted electronic dephasing times. Several independent publications have alluded to nuclear vibrational effects as an explanation for the long-lived beatings.

In photosynthetic pigment-protein complexes, the Huang-Rhys factors of chlorophyll/bacteriochlorophyll molecules are generally thought small, suggesting that the photophysics therein is primarily electronic in nature, rather than vibrational. Indeed, the recent 2D electronic experiments on BChl molecules in solution did not find significant vibrational coherences. Concerning this point, Christensson *et al.* [*J. Phys. Chem. B* **116**, 7449–7454 (2012).] proposed that resonance between electronic and Franck-Condon active vibrational states serves to create vibronic excitons, *i.e.* quantum mechanically mixed electronic and vibrational states. Such states have vibrational characters and have enhanced transition dipole moments owing to intensity borrowing from the strong electronic transitions. Along this line it was discussed that coherent excitation of the vibronic excitons produces oscillations in 2D signal that exhibit picosecond dephasing time. Tiwari, Peters, and Jonas pointed out that the excitonically mixed electronic and vibrational states lead to an enhancement of the excitation of vibrational coherences in the electronic ground state as well. [*Proc. Natl. Aca. Sci. U.S.A.* **110**, 1203–1208 (2013).] It was also argued that this effect could explain the long-lived oscillations in the FMO complex.

The quantum mechanically mixed electronic and vibrational states or the vibronic excitons are plausible as an explanation for long-lived spectral beatings in 2D electronic spectra. However, a question naturally arises concerning the interplay between the vibronic resonance and fluctuations in electronic energies induced by the environmental dynamics. In general, energy eigenstates due to quantum mixing of the electronic and vibrational excitations are obtained via diagonalization of the Hamiltonian comprising the Franck-Condon transition energies and electronic interactions. It should be noticed that these are independent of any information on the environment such as temperature, reorganization energy, and fluctuations. Concerning this point, Ishizaki and Fleming[3)] characterized the impact of the surrounding environments upon the quantum delocalization with the use of the concurrence. They visually demonstrated that smaller electronic coupling, larger reorganization energy, and higher temperature cause the dynamic localization, even in the case that two electronic states resonate in a coupled homo-dimer. Recently, Ishizaki[4)] explored the influence of timescales of the environment-induced fluctuations upon the quantum mixing between electron donor and acceptor molecules in photo-induced electron transfer reaction. It was demonstrated that fast fluctuation and correspondingly fast solvation destroys the quantum mixing between the donor and acceptor in the vicinity of the crossing point of the diabatic free energy surfaces, leading to a diabatic reaction, whereas slow fluctuation sustains the quantum mixing and prompts the electron transfer reaction in an adiabatic fashion. Therefore, it is natural to raise a question of whether dynamic interaction with the electronic and vibrational states and the environment will change the nature of the quantum mechanically mixed electronic and vibrational states.

The main purpose of this project is to explore impacts of environment-induced fluctuations upon the quantum mechanically mixed electronic and vibrational states through calculations of electronic energy transfer dynamics and 2D electronic spectra. Further, we investigated to what extent vibrational modes play a role in electronic energy transfer dynamics under the influence of the environment-induced fluctuations. We found that the quantum mechanically mixed electronic and vibrational states does not paly an important role in photosynthetic energy transfer dynamics contrary to the prediction by the community although they induced longer-lived quantum beats in 2D electronic spectra of photosynthetic light harvesting pigment-protein complexes.

References

1) A. Ishizaki and G. R. Fleming, *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012).
2) A. Ishizaki and G. R. Fleming, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 17255–17260 (2009).
3) A. Ishizaki and G. R. Fleming, *New J. Phys.* **12**, 055004 (13 pages) (2010).
4) A. Ishizaki, *Chem. Lett.* **42**, 1406–1408 (2013).

Ultimate Quantum Measurements for Quantum Dynamics

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Professional Employment

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

Awards

2013	FQXi Essay Contest Fourth Prize
2014	Research Award, Research Foundation for Opto-Science and Technology

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Keywords Quantum Measurement, Photophysics

Due to great development on experimental technologies, it is possible to capture quantum dynamics in some physical and chemical systems. On the other hand, all experiments are in principle open and dissipative systems. Up to now, the well explained experiments are approximated to the equilibrium situation. However, by recent technological development, some experiments reach to a transition from equilibrium to non-equilibrium situations. While there are the well-known tools on the non-equilibrium situations; the linear response theory and the Keldysh Green function method, this analysis cannot basically catch dynamical situations. Our goal is to construct the time-resolved theoretical models included the non-equilibrium situations. However, the quantum measurement theory is needed on measuring quantum dynamics, especially considering the measurement back action. Our current activities are to resolve how sensitive (quantum) measurement can we carry out in principle, to build up some toy models on quantum dynamic and to explain unique quantum-mechanical phenomena using precise quantum-state engineering technology.

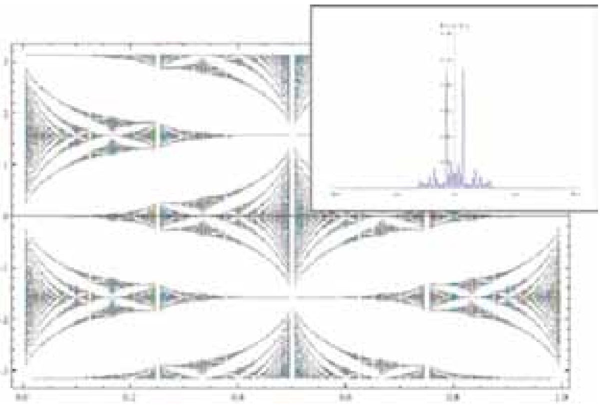

Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called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

Selected Publications

- Y. Shikano and A. Hosoya, "Weak Values with Decoherence," *J. Phys. A* **43**, 025304 (15 pages) (2010).
- Y. Shikano and H. Katsura, "Localization and Fractality in Inhomogeneous Quantum Walks with Self-Duality," *Phys. Rev. E* **83**, 031122 (7 pages) (2010).
- A. Noguchi, Y. Shikano, K. Toyoda and S. Urabe, "Aharonov-Bohm Effect with Quantum Tunneling in Linear Paul Trap," *Nat. Commun.* **5**, 3868 (6 pages) (2014).
- H. Kobayashi, K. Nonaka and Y. Shikano, "Stereographical Visualization of a Polarization State Using Weak Measurements with an Optical-Vortex Beam," *Phys. Rev. A* **89**, 053816 (5 pages) (2014).

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

We propose a stereographical-visualization scheme for a polarization state by two-dimensional imaging of a weak value with a single setup. The key idea is to employ Laguerre Gaussian modes or an optical vortex beam for a probe state in weak measurement. Our scheme has the advantage that we can extract information on the polarization state from the single image in which the zero-intensity point of the optical vortex beam corresponds to a stereographic projection point of the Poincaré sphere. We experimentally perform single-setup weak measurement to validate the stereographical relationship between the polarization state on the Poincaré sphere and the location of the zero-intensity point.

2. Quantum Measurement Sensitivity without Squeezing Technique[2)]

The weak measurement was proposed in the context of the time-symmetric quantum measurement without collapsing the quantum state. The weak value as the measurement outcome of the weak measurement can exceed the eigenvalue. By this fact, the signal can be amplified. This is called the weak-value amplification. To study the invisible region under the standard technique, there are several studies on the weak-value amplification. Here, the following question arises. How can the signal maximize? To solve this problem, the probe wave function should be changed from the Gaussian distribution, which is originally used. We show the probe wave function to maximize the shift while this mode is not the propagation mode in light.

3. Discrete Time Quantum Walk as Quantum Dynamical Simulator[3)]

Constructing a discrete model like a cellular automaton is a powerful method for understanding various dynamical systems. However, the relationship between the discrete model and its continuous analogue is, in general, nontrivial. As a quantum mechanical cellular automaton, a discrete-time quantum walk is defined to include various quantum dynamical behavior. Here we generalize a discrete-time quantum walk on a line into the feed-forward quantum coin model, which depends on the coin state of the previous step. We show that our proposed model has an anomalous slow diffusion characterized by the porous-medium equation, while the conventional discrete-time quantum walk model shows ballistic transport.

4. Aharonov-Bohm Effect with Quantum Tunneling[4)]

A quantum tunneling is also one of the unique quantum mechanical phenomena. However, nobody has yet measured a tunneling particle. There are still many quantum mysteries. While we have known that a tunneling particle can be coupled to an electromagnetic field, we have not yet demonstrated a coupling between a tunneling particle and a vector potential of the electromagnetic field. This effect is called the Aharonov-Bohm effect.

Our experimental setup done in Urabe group, Osaka University uses an ion trap system. The ion trap system is one of the great candidates to implement a quantum computer and a quantum simulation. Especially, a linear Paul trap, which is also used in our experiment, has the high scalability under the one-dimensional quantum system due to the great development of quantum information technology. While the two-dimensional structure of ions is very difficult to be cooled down in the linear Paul trap, we found that we can manipulate the almost ground state of the ion rotational motion by the laser cooling technique. This is a new quantum technology to implement a two-dimensional quantum simulation and a quantum computation used in a liner Paul trap. Then, we realized the almost ground state of rotational mode of three calcium ions arranged to a triangular structure. The distance between two ions is 6.8 micro meter. This ground state has the two structures, upward and downward triangles. This can be taken as the quantum rotor, which is often used in molecular science such as a diatomic molecule, with a quantum tunneling region. We confirmed that this transition is led by quantum tunneling even in the large tunneling region. Since we cannot distinguish clockwise and anticlockwise transitions, this system can be taken as the double-slit experiment. Changing the strength of the magnetic field, we showed that the transition probability was oscillated. This oscillation can be predicted by Aharonov-Bohm effect.

References

1) H. Kobayashi, K. Nonaka and Y. Shikano, *Phys. Rev. A* **89**, 053816 (5 pages) (2014).
2) Y. Shikano, "On Signal Amplification from Weak-Value Amplification," in *Kinki University Series on Quantum Computing Volume 9* "Physics, Mathematics, and All that Quantum Jazz," S. Tanaka, M. Bando and U. Gungordu, Eds., World Scientific; Singapore, pp. 91–100 (2014).
3) Y. Shikano, T. Wada and J. Horikawa, *Sci. Rep.* **4**, 4427 (7 pages) (2014).
4) A. Noguchi, Y. Shikano, K. Toyoda and S. Urabe, *Nat. Commun.* **5**, 3868 (6 pages) (2014).

Awards

SHIKANO, Yutaka; FQXi (Foundational Questions Institute) Essay Contest "It from Bit or Bit from It" Fourth Prize. (2013)
SHIKANO, Yutaka; 2013 Quantum Information Processing Top Reviewers.
SHIKANO, Yutaka; Research Foundation for Opto-Science and Technology Research Award (2014).

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† IMS International Internship Program from Institute for Theoretical Physics, Chinese Academy of China, China

‡ JSPS Summer Internship Program from University Pierre and Marie CURIE, France

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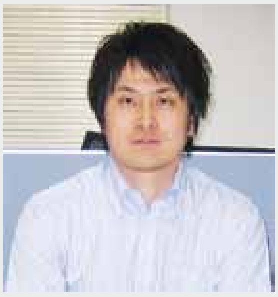
Study of Ion Conductive Materials for Novel Energy Storage/Conversion Devices

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



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Keywords Solid State Ionics, Oxyhydride, Battery, Energy Storage/Conversion

Recently, the demands for advanced electrochemical devices providing high energy density have been growing because of the expansion in application and a need for diversification of energy sources. In order to achieve the requirement, it will be essential not only to improve the existing devices such as lithium secondary batteries and fuel cells, but also to develop a novel energy storage/conversion system (Figure 1). In other words, a development of a novel electrochemical device possessing excellent battery performances that would be required in future is not an extension of the research on the existing devices. On the basis of these backgrounds, we are tackling two research topics; (i) improvement of battery performance with controlling the interface between electrode and electrolyte in lithium secondary batteries (ii) the exploration of novel ion conductive phenomena in solid.

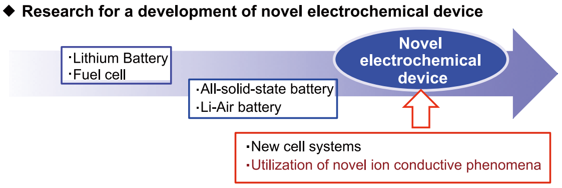

Figure 1. The concept of our research toward the realization of new electrochemical device.

(i) Control of the Cathode/Electrolyte-Interface in Lithium Batteries for Enhancement of the Performance

A surface modification of the cathode materials for lithium batteries with other metal oxides or phosphate is suggested as an effective method to inhibit the capacity degradation for lithium batteries. The main role of the surface modification layer has been considered the protection of a surface crystallinity of cathode materials from side reactions with electrolyte, but it has not been fully understood. To clarify the role of a surface modification, we examine the crystal structure of the modified cathode material, the chemical bonding state of coating layer and deterioration behavior of the cathode material using *ex situ* X-ray diffraction, transmission electron microscope and Hard X-ray photoelectron spectroscopy.

(ii) Synthesis and Property of Hydride Conductive Oxyhydride

We focus on hydride ions (H^-) as a new mobile ion. Hydride ion conductors are the new frontier materials in the research field of solid-state ionics and electrochemistry. Indeed, hydride ion conduction is particularly attractive for electrochemical devices such as fuel cells and batteries, because hydride ions have suitable ionic radii as mobile ions and strong reducing properties. The ionic radii of hydride ions are similar to oxide and fluoride ions, which may provide high ionic conduction in the crystal lattice. The standard potential for H^-/H_2 at about –2.3 V is comparable to the value of –2.4 V for Mg/Mg^{2+}; therefore, energy storage/conversion devices effectively utilizing a H^- conduction phenomenon and the redox reaction of H^-/H_2 are expected to show high energy density. However, the ionic conducting characteristics of hydride H^- ions are not established yet and the interplay between elementary H^- mobility, lattice structure, functional properties and materials synthesis are mostly lacking. Although a possibility of H^- conduction was indicated in several materials, the conclusive evidence for pure hydride ion conduction has not been provided yet, due to difficulties in identifying hydride ions. Recently, our group reported for the first time pure H^- conductivity in new oxyhydrides. We try to synthesis new H^- conductive materials on the basis of our previous works.

Open up Future Electronics by Organic Molecules

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Keywords Molecular Conductors, Organic Superconducting Transistors, Supramolecular Nanowires

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

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

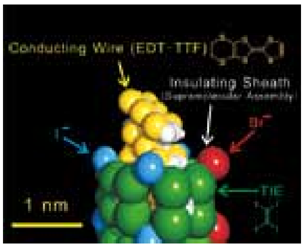

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- H. M. Yamamoto, M. Nakano, M. Suda, Y. Iwasa, M. Kawasaki and R. Kato, "A Strained Organic Field-Effect Transistor with a Gate-Tunable Superconducting Channel," *Nat. Commun.* **4**, 2379 (7 pages) (2013).
- H. M. Yamamoto, "Sheathed Nanowires Aligned by Crystallographic Periodicity: A Possibility of Cross-Bar Wiring in Three-Dimensional Space," *CrystEngComm* **16**, 2857–2868 (2014).
- Y. Kawasugi, H. M. Yamamoto, N. Tajima, T. Fukunaga, K. Tsukagoshi and R. Kato, "Field-Induced Carrier Delocalization in the Strain-Induced Mott Insulating State of an Organic Superconductor," *Phys. Rev. Lett.* **103**, 116801 (4 pages) (2009).
- H. M. Yamamoto, Y. Kosaka, R. Maeda, J. Yamaura, A. Nakao, T. Nakamura and R. Kato, "Supramolecular Insulating Networks Sheathing Conducting Nanowires Based on Organic Radical Cations," *ACS Nano* **2**, 143–155 (2008).

1. Field-Induced Superconductivity in an Organic Mott-FET[1)]

κ-(BEDT-TTF)Cu[N(CN)$_2$]Br (κ-Br) is an organic Mott-insulator at room-temperature, but turns into metallic and superconducting states at low temperature. In our previous works, a tensile strain from FET substrate altered its ground state into a Mott-insulating state, when its thin (100–300 nm) crystal was laminated on top of SiO$_2$/Si^{++} substrate and cooled down to low temperature. In those experiments the electronic state at low temperature became completely insulating because of the tensile strain that originates in mismatching of thermal expansion coefficients between κ-Br (30 ppm/K) and Si substrate (2 ppm/K). However, one can anticipate from the *T–P* (temperature *vs.* pressure) phase diagram that mixed electronic state between superconducting and Mott-insulating states can be realized when the tensile strain is much weaker. To achieve such a mixed state (or, percolate-superconducting state) in the device, where phase-separation occurs between superconducting and Mott-insulating states, we have chosen Nb-doped SrTiO$_3$ as a back-gate substrate because of its larger thermal expansion coefficient (*ca.* 10 ppm/K) than Si. An aluminum oxide layer was grown by atomic layer deposition technique to form a gate dielectric on the substrate. After lamination of κ-Br on the substrate, the Mott-FET device which showed a weakly insulating behavior at low temperature was fabricated (Figure 2).

Upon application of a positive gate voltage, the resistivity goes down and weakly metallic behavior is observed at $V_G > 2$ V. By further increasing the gate voltage up to 8 V, the device shows a sudden drop of resistivity around 5 K, which can be attributed to superconductivity. Taking into account of bistable IV characteristics observed in the low resistance region, the above transition can be understood as a percolation transition of superconducting islands that is induced by the electrostatic doping of electrons. The transition temperature increases as the gate voltage rises and saturates around $V_G = 11$ V. This result is the first example of field-induced superconductivity in organic materials, and can be utilized for uncovering a phase diagram of organic Mott system in the simultaneous control of band filling and band width.

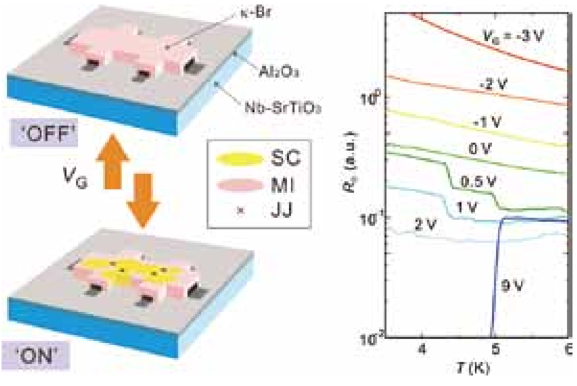

Figure 2. Device schematic (left) and temperature dependency of resistance at various gate voltages (right).

2. Strain-Tunable Organic FET with Strongly Correlated Electron Systems[2)]

Organic materials are soft and can be stretched even at low temperature. Our organic Mott-FETs are also soft enough to be compressed or expanded with a plastic substrate and show a band-width-controlled Mott/superconducting transitions. This kind of lattice modulation has been demonstrated in our recent experiments by mechanically pushing a poly-ethylene naphthalate (PEN) substrate covered with gold gate electrode and parylene-C dielectric from the back side (Figure 2). The organic Mott-insulator κ-(BEDT-TTF)Cu[N(CN)$_2$]Cl (κ-Cl) laminated on top of the substrate exhibited superconductor-to-insulator transition by bending the substrate where the surface has an effect of tensile strain in a longitudinal direction. The strain necessary for this transition is only 0.3% while the resistance change reached ten orders of magnitude, which demonstrates high sensitivity of the Mott-insulator. The phase diagram obtained by simultaneous scans of strain and temperature well reproduces that of hydrostatic pressure. This means that one-dimensional tensile strain corresponds to an effective negative pressure in κ-Cl system.

Then, a field-effect was examined by applying a gate electric field. The transfer characteristics at higher tensile strain showed only moderate device mobility of around 5 cm^2/Vs. When the system was forced to stay in a mixed phase state, where superconducting and Mott-insulating phases coexist, however, the electric-field-effect maximized to show device mobility up to 5900 cm^2/Vs. This high response of the device can be attributed to an increase of superconducting fraction at application of gate voltage. In order to examine the above hypothesis, we have applied a magnetic field up to 7 T. Indeed, the field-effect has been considerably suppressed because the superconducting phases are destroyed by the magnetic field. This electric-field-induced superconductivity seems to originate from a decrease of Coulomb repulsion among carriers by electrostatic doping effect.

(BEDT-TTF = bis(ethyelenedithio)tetrathiafulvalene)

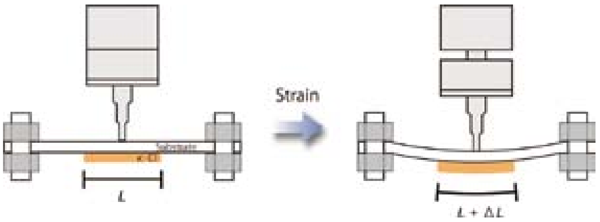

Figure 3. Side-view schematic for flexible organic Mott-FET device.

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2) M. Suda, Y. Kawasugi, T. Minari, K. Tsukagoshi, R. Kato and H. M. Yamamoto, *Adv. Mater.* **26**, 3490–3495 (2014).

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Synthetic Inorganic and Organometallic Chemistry of Transition Metals

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Keywords Coordination Chemistry, Organometallic Chemistry, Mechanism of Catalysis

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

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

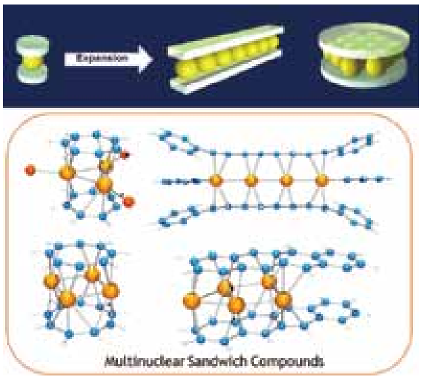

Figure 1. The concept of dimensionally extended sandwich structures and some examples of the multinuclear sandwich complexes.

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- T. Murahashi, T. Uemura and H. Kurosawa, "Perylene Tetrapalladium Sandwich Complexes," *J. Am. Chem. Soc.* **125**, 8436–8437 (2003).
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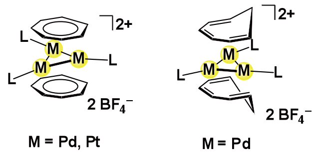
- T. Murahashi, R. Inoue, K. Usui and S. Ogoshi, "Square Tetrapalladium Sheet Sandwich Complexes: Cyclononatetraenyl as a Versatile Face-Capping Ligand," *J. Am. Chem. Soc.* **131**, 9888–9889 (2009).
- T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi and H. Kurosawa, "Redox-Induced Reversible Metal Assembly through Translocation and Reversible Ligand Coupling in Tetranuclear Metal Sandwich Frameworks," *Nat. Chem.* **4**, 52–58 (2012).

1. Chemistry of Multinuclear Sandwich Complexes

Synthesis and Structural Elucidation of Bis-Cyclooctatetraene Trimetal Sandwich Complexes

Our group has made research efforts to establish the generality of the metal sheet sandwich compounds. We have shown that several unsaturated hydrocarbon ligands such as [2.2]paracyclophane, cycloheptatriene, cycloheptatrienyl, and some polycyclic arenes behave as the excellent binders for triangular trimetal sheets.[2–6] Particularly, it has been shown that seven-membered unsaturated hydrocarbons, *i.e.*, tropylium and cycloheptatriene, serve as an excellent facial μ_3-binder for the triangular M_3L_3 core (M = Pd, Pt) (Scheme 1). However, it has not been verified whether larger π-conjugated carbocycles are able to form a simple triangular trimetal sandwich complex.



Scheme 1. The tropylium- and cycloheptatriene sandwich complexes.

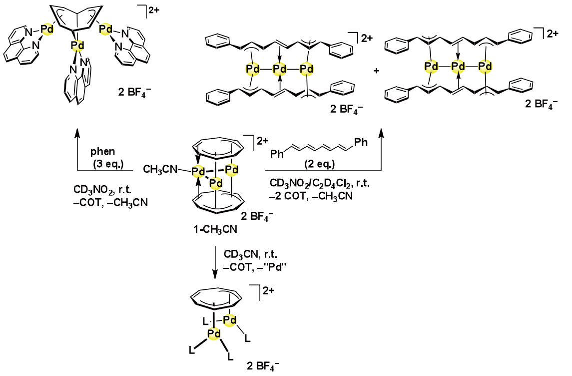
1,3,5,7-Cyclooctatetraene (COT) is a potentially useful eight-membered carbocyclic ligand for metal sheet sandwich complexes, in view of its greater number of C=C bonds and a flexible electron-donating/back-donating nature. A recent finding by Grubbs *et al.* represents the versatility of the COT ligand, *i.e.*, a homoleptic trimetal tris-COT complex, $Fe_3(\mu\text{-}COT)_3$, was isolated through a catalytic method.[7] Here, we successfully synthesized the first discrete bis-COT trimetal sandwich complexes.[8]

The bis-cyclooctatetraene Pd_3 sandwich complex $[Pd_3(\mu_3\text{-}C_8H_8)_2L][BF_4]_2$ (**1-CH₃CN**) was obtained by the reaction of $[Pd_2(CH_3CN)_6][BF_4]_2$ and $Pd_2(dba)_3$ in the presence of cyclooctatetraene (COT), followed by treatment with CH_3CN (eq. 1). Recrystallization in an aerobic condition gave a single crystal of **1-H₂O**. The structure of **1-H₂O** was determined by X-ray diffraction analysis. The cyclooctatetraene ligands coordinate to an isosceles Pd_3 triangle (Pd1–Pd2 = 2.7321(8) Å; Pd2–Pd3 = 2.7359(8) Å; Pd1···Pd3 = 3.0604(8) Å) through a $\mu_3\text{-}\eta^3\text{:}\eta^2\text{:}\eta^3$ mode. The sandwich structure seems to be related with that of a diphenyloctatetraene Pd_3 chain sandwich complex $[Pd_3\{Ph(CH{=}CH)_4Ph\}_2]^{2+}$ which exhibits the same $\mu_3\text{-}\eta^3\text{:}\eta^2\text{:}\eta^3$ coordination mode.[9]

A deep purple PPh_3 complex $[Pd_3(\mu_3\text{-}COT)_2(PPh_3)][BF_4]_2$ (**1-PPh₃**) or a PCy_3 complex $[Pd_3(\mu_3\text{-}COT)_2(PCy_3)][BF_4]_2$ (**1-PCy₃**) was obtained by treatment of **1-CH₃CN** with PPh_3 or PCy_3 (1 equiv.). In solution, **1-CH₃CN** and **1-PPh₃** showed a sharp singlet NMR signal for C_8H_8 protons or carbons at 25 °C. Lowering the temperature down to –90 °C of the related compound resulted in significant broadening of the resonance for the C_8H_8 protons, suggesting the dynamic fluxional rotation of the cyclooctatetraene ligands on the Pd_3 core.

(1)

The reactivity of **1-CH₃CN** with several coordinating substrates were investigated, and the results were summarized in Scheme 2, showing the substitutionally labile nature of the μ_3-COT ligands in the bis-COT Pd_3 sandwich complex.



Scheme 2. Facile dissociation of the COT ligand in $[Pd_3(\mu_3\text{-}C_8H_8)_2(CH_3CN)][BF_4]_2$ (**1-CH₃CN**).

2. Reaction Mechanism of Highly Reactive Metal Complexes

One of our main interests is in the elucidation of the reaction patterns and mechanisms of highly reactive transition metal complexes in relevance to catalysis. Synthetic and structural chemistry of the arenes and hetero-arenes transition metal complexes are now ongoing in our laboratory, and several new aspects have been gained recently.[10,11]

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8) T. Murahashi, S. Kimura, K. Takase, T. Uemura, S. Ogoshi and K. Yamamoto, *Chem. Commun.* **50**, 820–822 (2014).
9) T. Murahashi *et al.*, *J. Am. Chem. Soc.* **124**, 14288–14289 (2002).
10) T. Murahashi *et al.*, *J. Am. Chem. Soc.* **133**, 14908–14911 (2011).
11) T. Murahashi *et al.*, *Chem. Commun.* **49**, 4310–4312 (2013).

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* IMS International Internship Program

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

Development of Curved Graphene Molecules as Organic Semiconductors

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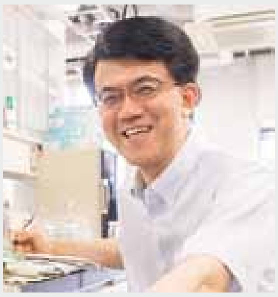

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Keywords Organic Synthesis, Graphene Molecule, Organic Semiconductor

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

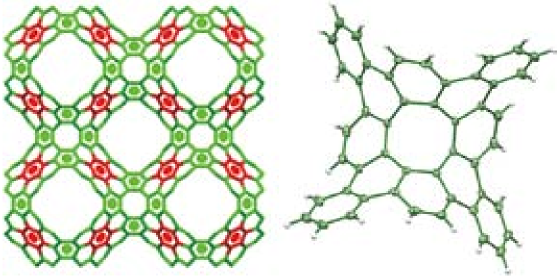

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

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

1. Tetrabenzo[8]circulene: Aromatic Saddles from Negatively Curved Graphene[1)]

An aromatic saddle was designed from the hypothetical three-dimensional graphene with the negative Gaussian curvature (Schwarzite P192). Two aromatic saddles, tetrabenzo[8]circulene (**TB8C**) and its octamethyl derivative **OM-TB8C**, were synthesized by the Scholl reaction of cyclic octaphenylene precursors. The structure of **TB8C** greatly deviates from planarity, and the deep saddle shape was confirmed by single-crystal X-ray crystallography. There are two conformers with the S_4 symmetry, which are twisted compared to the DFT structure (D_{2d}). The theoretical studies propose that the interconversion of **TB8C** via the planar transition state (125 kcal mol^{-1}) is not possible. However, the pseudorotation leads to a low-energy tub-to-tub inversion via the nonplanar transition state (7.3 kcal mol^{-1}). The ground state structure of **TB8C** in solution is quite different from the X-ray structure because of the crystal-packing force and low-energy pseudorotation. **OM-TB8C** is a good electron donor and works as the p-type semiconductor.

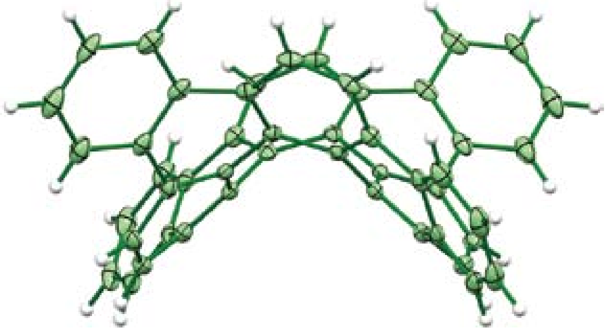

Figure 2. Single-crystal X-ray structure of **TB8C** from the side. The thermal ellipsoids are shown at 50% probability.

2. Synthesis and Physical Properties of a Ball-Like Three-Dimensional π-Conjugated Molecule[2)]

Curved π-conjugated molecules with closed and three-dimensional (3D) structures, such as fullerenes and carbon nanotubes, have been the subject of intensive research due to their potential applications in molecular electronics. However, basic molecular skeletons of 3D molecules are limited because of the lack of a rational and selective synthetic method by organic synthesis. We report the synthesis of a 3D π-conjugated molecule based on the platinum-mediated assembly of four molecules of a stannylated trisubstituted benzene derivative forming a hexanuclear platinum complex with an octahedral shape, from which reductive elimination of platinum gave the target molecule. As many supramolecular transition metal-ligand complexes with 3D cages and polyhedral structures have been synthesized by self-assembly of ligands and metals, the current assembly/reductive elimination strategy could provide a variety of new 3D π-conjugated molecules with different structures and topologies, which are challenging to obtain using conventional synthetic methods.

3. Synthesis, Characterization, and Properties of [4]Cyclo-2,7-pyrenylene: Effects of Cyclic Structure on the Electronic Properties of Pyrene Oligomers[3)]

A cyclic tetramer of pyrene, [4]cyclo-2,7-pyrenylene ([4]CPY), was synthesized from pyrene in six steps and 18% overall yield by the platinum-mediated assembly of pyrene units and subsequent reductive elimination of platinum. The structures of the two key intermediates were unambiguously determined by X-ray crystallographic analysis. DFT calculations showed that the topology of the frontier orbitals in [4]CPY was essentially the same as those in [8]cycloparaphenylene ([8]CPP), and that all the pyrene units were fully conjugated. The electrochemical analyses proved the electronic properties of [4]CPY to be similar to those of [8]CPP. The results are in sharp contrast to those obtained for the corresponding linear oligomers of pyrene in which each pyrene unit was electronically isolated. The results clearly show a novel effect of the cyclic structure on cyclic π-conjugated molecules.

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Chemistry of Buckybowls and Metal Nanocluster Catalysts

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2004	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
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Keywords Organic Synthesis, Buckybowl, Cluster Catalyst

Bowl-shaped π-conjugated compounds including partial structures of the fullerenes, which are called “buckybowls,” are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-to-bowl inversion, is slow enough to be isolated. Very few buckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiral bowls has appeared. In this project, we develop the rational route to the various buckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly-functionalized protective polymers.

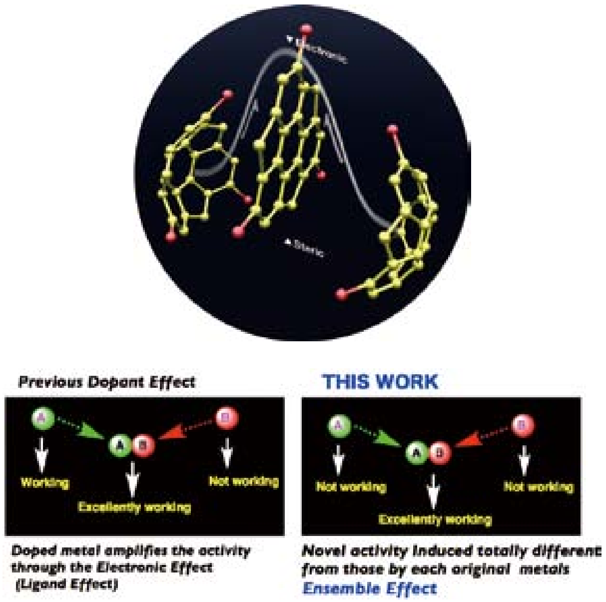

Figure 1. Dynamic behavior (bowl-inversion) of buckybowls and the concept of the bimetallic metal nanoclusters catalysts.

Selected Publications

- S. Higashibayashi and H. Sakurai, *J. Am. Chem. Soc.* **130**, 8592–8593 (2008).
- Q.-T. Tan, S. Higashibayashi, S. Karanjit and H. Sakurai, *Nat. Commun.* **3**:891 doi: 10.1038/ncomms1896 (2012).
- R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.* **134**, 20250–20253 (2012).
- S. Higashibayashi, S. Onogi, H. K. Srivastava, G. N. Sastry, Y.-T. Wu and H. Sakurai, *Angew. Chem., Int. Ed.* **52**, 7314–7316 (2013).

1. Correlation between Bowl-Inversion Energy and Bowl Depth in Substituted Sumanenes

The correlation between the bowl-inversion energy and the bowl depth for sumanenes monosubstituted with an iodo, formyl, or nitro group was investigated experimentally and by theoretical calculations. The bowl-inversion energies of the substituted sumanenes were determined experimentally by two-dimensional NMR exchange spectroscopy measurements. Various density functional theory methods were examined for the calculation of the structure and the bowl-inversion energy of sumanene, and it was found that PBE0, ωB97XD, and M06-2X gave better fits of the experimental value than did B3LYP. The experimental value was well reproduced at these levels of theory. The bowl structures and bowl-inversion energies of monosubstituted sumanenes were therefore calculated at the ωB97XD/6-311+G(d,p) level of theory. In both the experiments and the calculations, the correlation followed the equation $\Delta E = a\cos^4\theta$, where a is a coefficient, ΔE is the bowl-inversion energy, and $\cos\theta$ is the normalized bowl depth, indicating that the bowl inversion follows a double-well potential energy diagram.

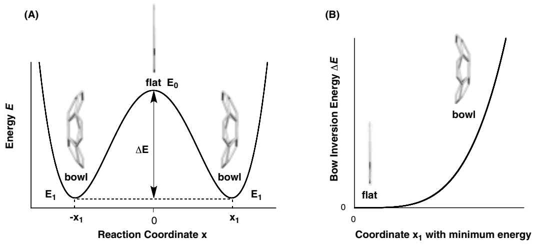

Figure 2. (A) Double-well potential of bowl-inversion and (B) correlation between bowl-inversion and bowl depth.

2. Columnar/Herringbone Dual Crystal Packing of Pyrenylsumanene and its Photophysical Properties

A single crystal of pyrenylsumanene was found to exhibit both columnar and herringbone crystal packing. The sumanene moieties form unidirectional columnar structures based on π-π stacking while the pyrene moieties generate herringbone structures due to CH–π interactions. The absorption and emission maxima of pyrenylsumanene were both red-shifted relative to those of sumanene and pyrene, owing to the extension of π-conjugation. Monomer emission with high quantum yield (0.82) was observed for pyrenylsumanene in solution, while excimer-type red-shifted emission was evident in the crystalline phase.

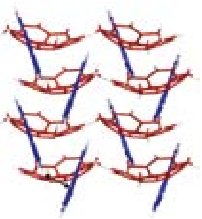

Figure 3. Side view of columns with a herringbone packing of the pyrene moiety due to CH–π interactions.

3. Bimetallic Gold/Palladium Alloy Nanoclusters: An Effective Catalyst for Ullmann Coupling of Chloropyridines under Ambient Conditions

An efficient method for the Ullmann coupling of chloropyridines catalyzed by poly(*N*-vinylpyrrolidone) (PVP)-stabilized bimetallic Au/Pd alloy nanoclusters (NCs) under ambient conditions is demonstrated. The reaction does not occur with either gold or palladium single-metal clusters alone, nor with a physical mixture of the two metals. The experimental results indicate that the inclusion of Au as a nearest heteroatom is crucial to initiate the coupling and its composition up to 50% is essential to accelerate the reaction. Unlikely to the conventional transition metal catalysis, 2-chloropyridine was found to be highly reactive as compare to 2-bromopyridine. From the UV-vis and ICP-AES, significant amount of leached Pd(II) was observed in the coupling with 2-bromopyrdine as compared with 2-chloropyridine, indicating the leaching process might be a crucial factor to diminish the reactivity of the coupling.

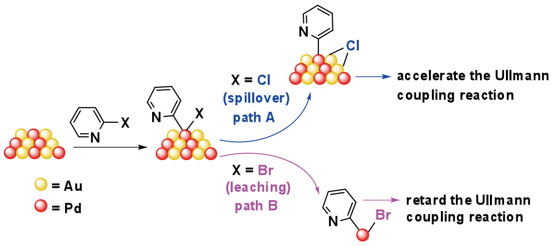

Figure 4. Mechanistic illustration of the activity of Au/Pd clusters in the Ullmann coupling with 2-chloro- or 2-bromo-pyridine. Path A represents the activation and path B represents the deactivation process.

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Awards

SAKURAI, Hidehiro; Distinguished Award on IUPAC Novel Materials and their Synthesis (2013).
SAKURAI, Hidehiro; The Chemical Society of Japan (CSJ) Award for Creative Work (2014).
HAESUWANNAKIJ, Setsiri; CSJ Student Presentation Award 2013 (2014).