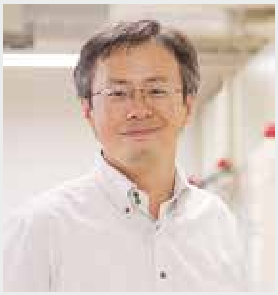
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

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

The Origin of 24 Hour Period in Cyanobacterial Clock System

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



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2003	RIKEN Special Postdoctoral Researcher
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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

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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.

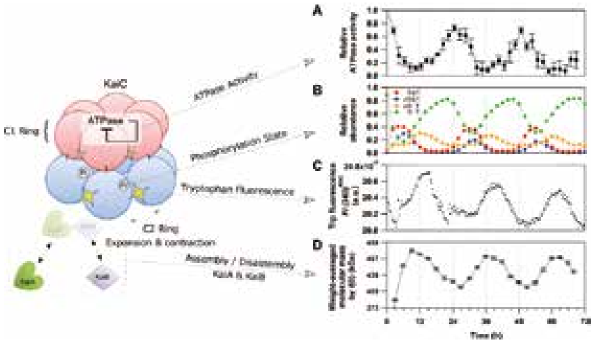

Figure 1. Circadian dynamics of cyanobacterial clock protein KaiC. The C1 and C2 domains in each protomer of KaiC are drawn as red and blue spheres, respectively. Expansion and contraction motions of the C2 ring (B, C) in solution serves as a timing cue for assembly/disassembly of KaiA and KaiB (D),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

Selected Publications

- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, *Cell. Mol. Life Sci.* **69**, 2147–2160 (2012).
- A. Mukaiyama, M. Osako, T. Hikima, T. Kondo and S. Akiyama, *Biophysics* **11**, 79–84 (2015).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).

1. Atomic-Scale Origins of 24 Hour Period in Cyanobacterial Clock System[1,2]

In accordance with diurnal changes in the environment resulting from the Earth's daily rotation around its axis, many organisms regulate their biological activities to ensure optimal fitness and efficiency. The biological clock refers to the mechanism whereby organisms adjust the timing of their biological activities. The period of this clock is set to approximately 24 h. A wide range of studies have investigated the biological clock in organisms ranging from bacteria to mammals. Consequently, the relationship between the biological clock and multiple diseases has been clarified. However, it remains unclear how circadian rhythms are implemented.

Our group have addressed this question using cyanobacteria. The cyanobacterial circadian clock can be reconstructed by mixing three clock proteins (KaiA, KaiB, and KaiC) and ATP. As shown in Figure 2, KaiC ATPase activity exhibits a robust circadian oscillation in the presence of KaiA and KaiB. Astonishingly, the temporal profile of KaiC ATPase activity exhibited an attenuating and oscillating component even in the absence of KaiA and KaiB. A detailed analysis revealed that this signal had a frequency of 0.91 d^{-1}, which approximately coincided with the 24 h period. KaiC is thus the source of a steady cycle that is in tune with the Earth's daily rotation.

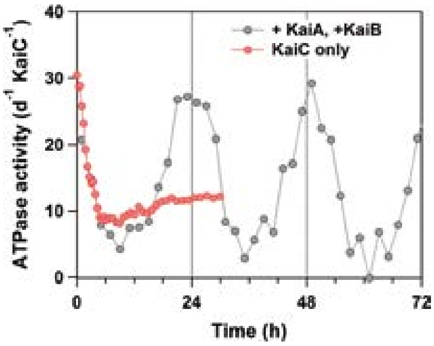

Figure 2. Time-course of KaiC ATPase activity.

To identify the structural origins, the N-terminal domain of KaiC was analyzed using high-resolution x-ray crystallography. The resultant atomic structures revealed the underlying cause of KaiC's slowness relative to other ATPases (Figure 3). A water molecule is prevented from attacking into the ideal position (a black dot in Figure 3) for the ATP hydrolysis by a steric hindrance near ATP phosphoryl groups. In addition, this hindrance is surely anchored to a spring-like structure derived from polypeptide isomerization. The ATP hydrolysis, which involves access of a water molecule to the bound ATP and reverse isomerization of the polypeptide, is expected to require a significantly larger amount of free energy than for typical ATP hydrolysis. Thus, the three-dimensional atomic structure discovered by us explains why the ATPase activity of KaiC is so much lower (by 100- to 1,000,000-fold) than that of typical ATPase molecules.

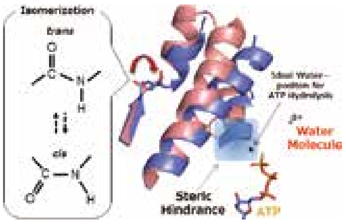

Figure 3. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

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

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

2. Instrumentation for Studying Biological Clock Systems[3]

We have improved stability over time, signal-to-noise ratio, time resolution, temperature control, automated high-throughput measurements each for fluorescence tracking system, auto-sampling device,[3] HPLC,[2] FTIR, and small-angle x-ray scattering (SAXS). The developed devices were utilized successfully in identifying a core process of generating circadian periodicity in cyanobacterial circadian clock.[1,2]

3. Bio-SAXS Activity in IMS[1,4]

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

References

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3) Y. Furuike *et al.*, to be submitted.
4) R. Kojima, M. Okumura, S. Masui, S. Kanemura, M. Inoue, M. Saiki, H. Yamaguchi, T. Hikima T, M. Suzuki, S. Akiyama and K. Inaba, *Structure* **22**, 431–443 (2014).

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* IMS International Internship Program

Protein Design Using Computational and Experimental Approaches

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Professional Employment

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2006	Postdoctoral Fellow, Kobe University
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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
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Awards

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

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Secretary
SUZUKI, Hiroko

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

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

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

Selected Publications

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

1. Principles for Designing Ideal Protein Structures

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

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

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

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

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3) N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, *Nature* **491**, 222–227 (2012).

4) J. Fang, A. Mehlich, N. Koga, J. Huang, R. Koga, M. Rief, J. Kast, D. Baker and H. Li*, *Nat. Commun.* **4**:2974 (2013).

5) Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).

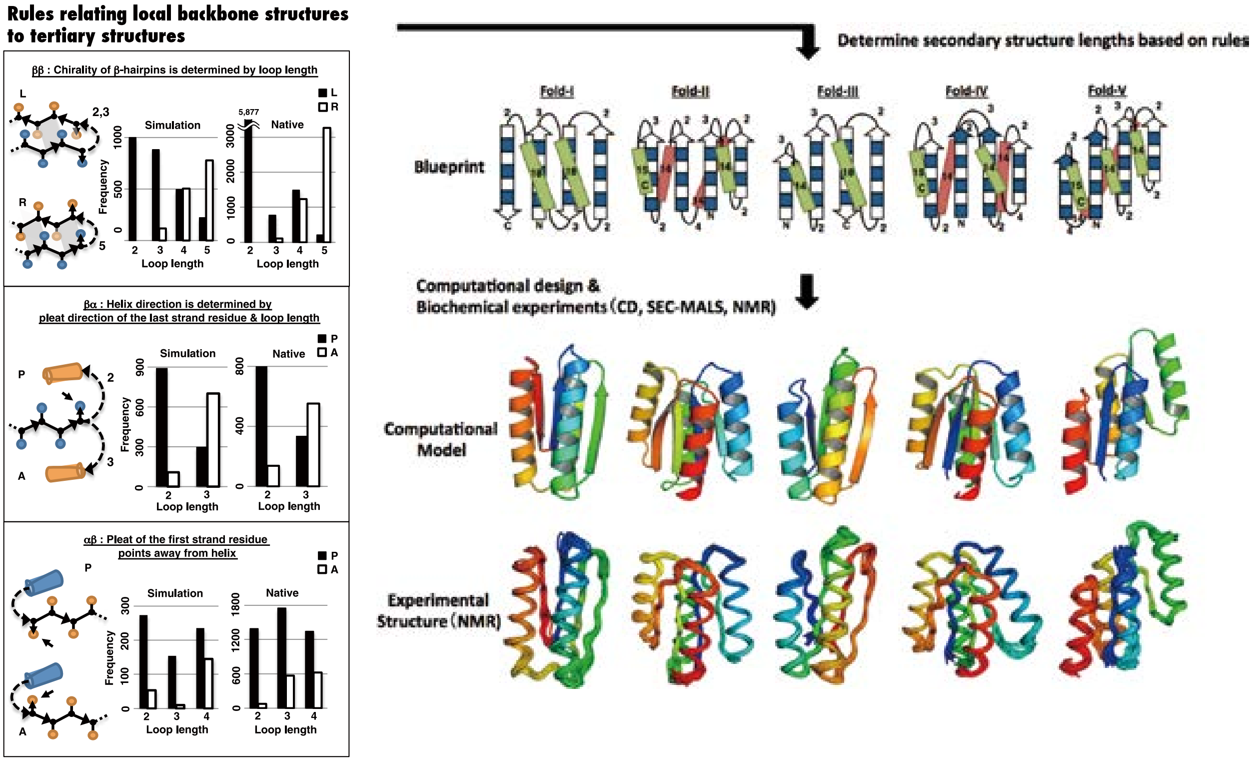

Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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

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

Selected Publications

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

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

Recently, nuclear vibrational contribution signatures in two-dimensional (2D) electronic spectroscopy have attracted considerable interest, in particular as regards interpretation of the oscillatory transients observed in light-harvesting complexes. These transients have dephasing times that persist for much longer than theoretically predicted electronic coherence lifetime. As a plausible explanation for this long-lived spectral beating in 2D electronic spectra, quantum-mechanically mixed electronic and vibrational states (vibronic excitons) were proposed by Christensson *et al.* [*J. Phys. Chem. B* **116**, 7449 (2012)] and have since been explored. In this work, we address a dimer that produces little beating of electronic origin in the absence of vibronic contributions, and examine the impact of protein-induced fluctuations upon electronic-vibrational quantum mixtures by calculating the electronic energy transfer dynamics and 2D electronic spectra in a numerically accurate manner. It was found that, at cryogenic temperatures, the electronic-vibrational quantum mixtures are rather robust, even under the influence of the fluctuations and despite the small Huang-Rhys factors of the Franck-Condon active vibrational modes. This results in long-lasting beating behavior of vibrational origin in the 2D electronic spectra. At physiological temperatures, however, the fluctuations eradicate the mixing, and hence, the beating in the 2D spectra disappears. Further, it was demonstrated that such electronic-vibrational quantum mixtures do not necessarily play a significant role in electronic energy transfer dynamics, despite contributing to the enhancement of long-lived quantum beating in 2D electronic spectra, contrary to speculations in recent publications.[1,2]

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

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

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

References

1) Y. Fujihashi, G. R. Fleming and A. Ishizaki, *J. Chem. Phys.* **142**, 212403 (2015).
2) A. Ishizaki and G. R. Fleming, *New J. Phys.* **12**, 055004 (13 pages) (2010).
3) Y. Fujihashi, G. R. Fleming and A. Ishizaki, *J. Chin. Chem. Soc.* (2015), in press. DOI: 10.1002/jccs.201500100.
4) D. M. Monahan, L. Whaley-Mayda, A. Ishizaki and G. R. Fleming, *J. Chem. Phys.* **143**, 065101 (2015).
5) D. M. Monahan, L. Whaley-Mayda, A. Ishizaki and G. R. Fleming, *Ultrafast Phenomena XIX (Springer Proceedings in Physics)* **162**, 553 (2015).

Visualization of Quantum Dynamical Nature Utilized Quantum Measurements

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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.

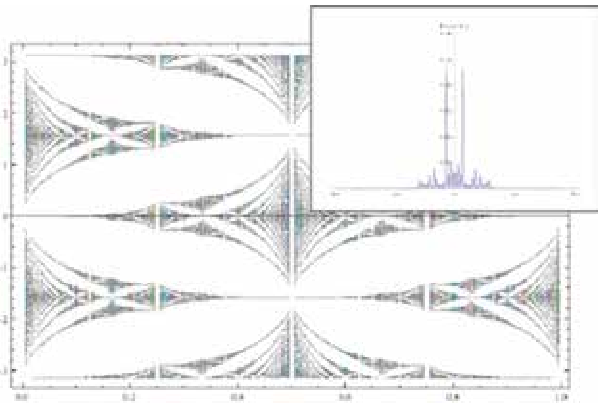

Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called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

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

2. Quantum Measurement with Squeezing Technique[2)]

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

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

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

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

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

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

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

References

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

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

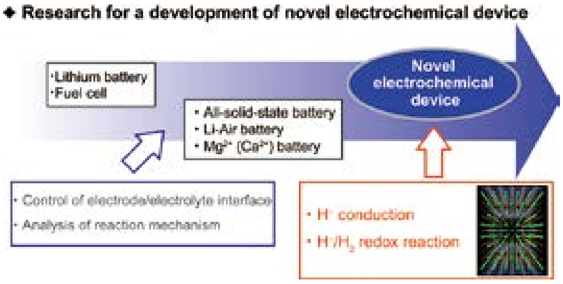

Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

Selected Publications

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

1. Synthesis of H^- Conductive Oxyhydrides$^{1)}$

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

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

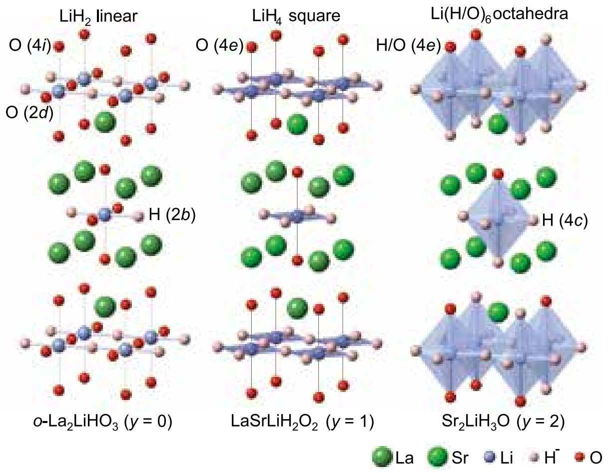

Figure 2. Crystal structures of $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0$, 1, 2). Lanthanum (and strontium) ions occupy the *A* sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the *B* site that are octahedrally coordinated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

2. High-Performance of Li-Rich Layered Cathode Materials through Combination of A_2O_3-Based Surface Modification and Stepwise Pre-Cycling$^{2)}$

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

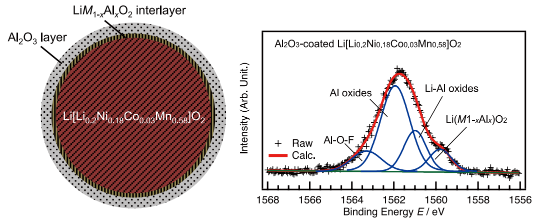

Figure 3. Schematic illustration and Al 1*s* HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

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1) G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, I. Tanaka and R. Kanno, under revision.

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

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Open up Future Electronics by Organic Molecules

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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.

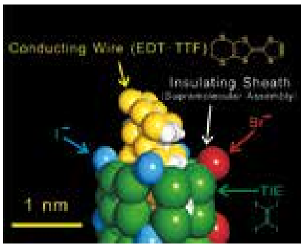

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).
- H. M. Yamamoto, M. Nakano, M. Suda, Y. Iwasa, M. Kawasaki and R. Kato, "A Strained Organic Field-Effect Transistor with a Gate-Tunable Superconducting Channel," *Nat. Commun.* **4**, 2379 (7 pages) (2013).
- H. M. Yamamoto, "Sheathed Nanowires Aligned by Crystallographic Periodicity: A Possibility of Cross-Bar Wiring in Three-Dimensional Space," *CrystEngComm* **16**, 2857–2868 (2014).
- 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).

1. Light-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 became completely insulating because of the tensile strain that originates in mismatching of thermal expansion coefficients between κ-Br (30 ppm/K) and Si substrate (2 ppm/K). However, one can anticipate from the *T–P* (temperature *vs.* pressure) phase diagram that mixed electronic state between superconducting and Mott-insulating states can be realized when the tensile strain is much weaker. To achieve such a mixed state (or, percolate-superconducting state), Nb-doped SrTiO$_3$ is used as a back-gate substrate because of its larger thermal expansion coefficient (*ca.* 10 ppm/K) than Si. An aluminum oxide layer was grown by atomic layer deposition technique to form a gate dielectric on the substrate to form a FET device structure. Moreover, we have covered this oxide layer with photochromic self-assembled monolayer (SAM-layer: Figure 2, right panel) in order to make it photo-active.

Upon irradiation of UV-light, the resistivity at 2 K goes down quickly and low-resistance state was observed after 180 sec. By performing resistance measurement with sweeping temperature, it turned out that Mott-insulating part of the device became superconducting by the above UV-light irradiation, which was confirmed by a sudden drop of resistivity around 7 K. This is because of the hole-doping at the FET interface that is induced by strong internal dipole moment of the SAM-layer. This mechanism was also confirmed by dual-gate action of this device, where gate-induced carriers worked cooperatively with the photo-induced carriers. This result is the first example of light-induced superconductivity in FET devices, and allows remote control of superconducting device without direct wiring.

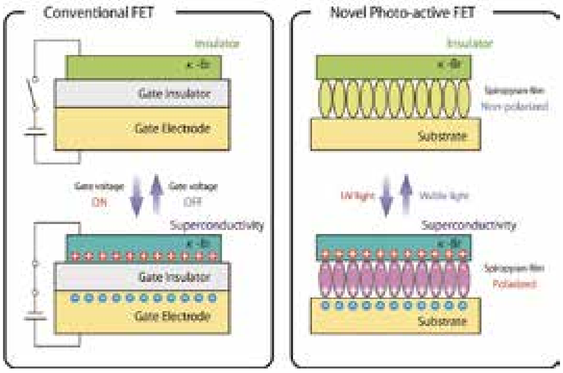

Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).

2. Strain-Tunable Organic FET with Strongly Correlated Electron 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 3). The organic Mott-insulator κ-(BEDT-TTF)Cu[N(CN)$_2$]Cl (κ-Cl) laminated on top of the substrate exhibited superconductor-to-insulator transition by bending the substrate where the surface has an effect of tensile strain in a longitudinal direction. The strain necessary for this transition at 5 K is only 0.3% while the resistance change reached ten orders of magnitude, which demonstrates high sensitivity of the Mott-insulator. The phase diagram obtained by simultaneous scans of strain and temperature well reproduces that of hydrostatic pressure. This means that one-dimensional tensile strain corresponds to an effective negative pressure in κ-Cl system.

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

(BEDT-TTF = bis(ethyelenedithio)tetrathiafulvalene)

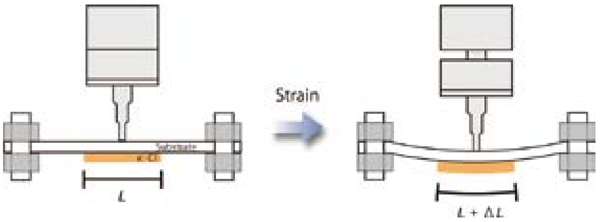

Figure 3. Side-view schematic for flexible organic Mott-FET device.

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1) M. Suda, R. Kato and H. M. Yamamoto, *Science* **347**, 743–746 (2015).

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 is sandwiched between two cyclic unsaturated hydrocarbons. Recently, our group discovered that multinuclear sandwich complexes exist as the stable and isolable molecules (Figure 1). These findings expand the structural concept of sandwich compounds from zero-dimension to one- and two dimensions, and provide a new opportunity to develop a novel class of organo-metal cluster compounds. Multinuclear sandwich complexes showed unique chemical properties stemming from their (π-conjugated unsaturated hydrocarbon)-(multinuclear metal) hybrid structures.

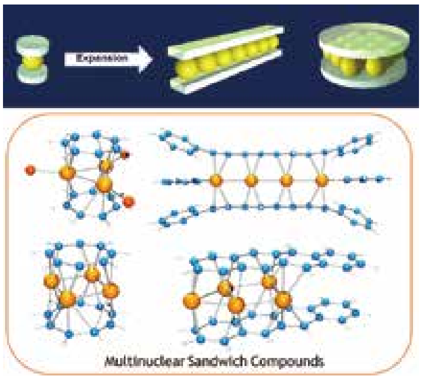

Figure 1. The concept of dimensionally extended sandwich structures and some examples of the multinuclear sandwich complexes.

Selected Publications

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

1. Chemistry of Multinuclear Sandwich Complexes

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

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

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

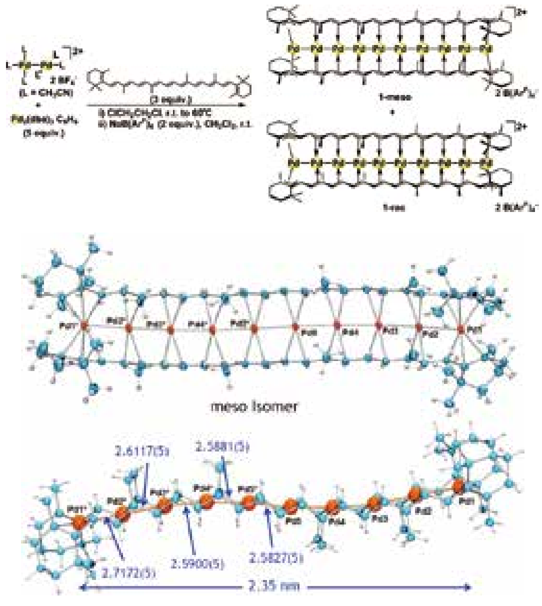

Figure 2. Synthesis of bis-carotene Pd_{10} chain complexes, and X-ray structure of the meso-isomer.

The metallo-carotene framework showed interesting multinuclear metalation-demetalation reactivity, allowing us to construct heterobimetallic decanuclear chain. The metal-deficient sandwich complex, $[Pd_5(\beta\text{-carotene})_2][B(Ar^F)_4]_2$ (**2-meso**) or $[Pd_7(\beta\text{-carotene})_2][B(Ar^F)_4]_2$ (**3-meso**), was obtained as a single product by demetalation from **1-meso** with CO in certain reaction conditions. Then metal-refilling with Pt^0 afforded the bimetallic Pd_5Pt_3 chain complex $[Pd_5Pt_3(\beta\text{-carotene})_2][B(Ar^F)_4]_2$ (**4-meso**). Subsequent metalation of **4-meso** with Pd^0 gave decanuclear bimetallic chain complex $[Pd_5Pt_3Pd_2(\beta\text{-carotene})_2][B(Ar^F)_4]_2$ (**5-meso**) having alternative metal arrangement (Figure 3).

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

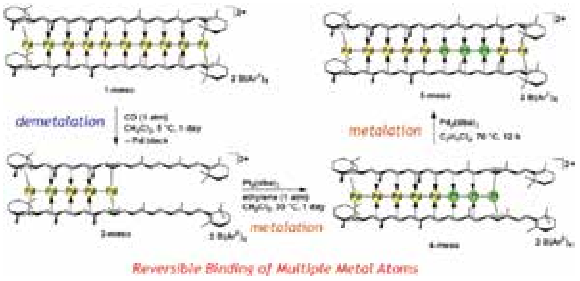

Figure 3. Demetalation-metalation sequence of metallo-carotene framework.

2. Reaction Mechanism of Highly Reactive Metal Complexes

Modulation of Cluster Binding Sites by the Backside-Ligand Effect[2)]

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

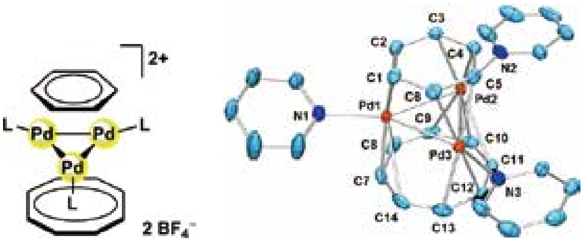

Figure 4. The first solution-stable μ_3-benzene Pd_3 cluster and its X-ray structure.

References

1) S. Horiuchi, Y. Tachibana, M. Yamashita, K. Yamamoto, K. Masai, K. Takase, T. Matsutani, S. Kawamata, Y. Kurashige, T. Yanai and T. Murahashi, *Nat. Commun.* **6**, 6742 (2015).

2) Y. Ishikawa, S. Kimura, K. Takase, K. Yamamoto, Y. Kurashige, T. Yanai and T. Murahashi, *Angew. Chem., Int. Ed.* **54**, 2482–2486 (2015).

Development of Curved Graphene Molecules as Organic Semiconductors

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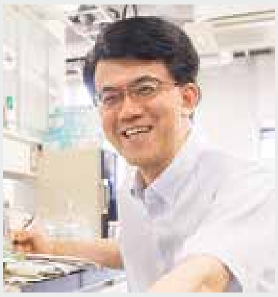

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Keywords Organic Synthesis, Graphene Molecule, Organic Semiconductor

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.

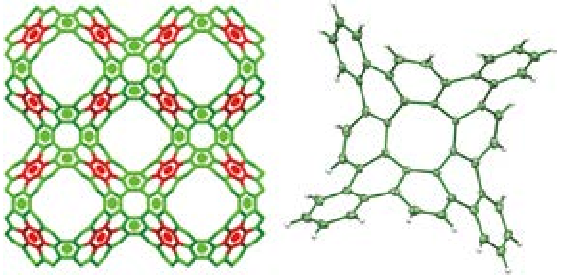

Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

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

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

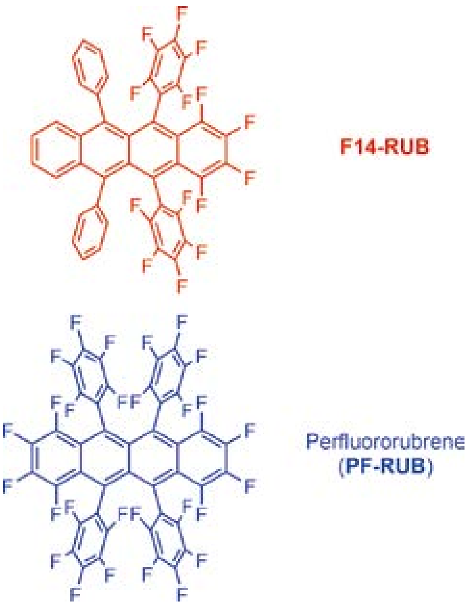

Figure 2. Chemical structures of partially and fully fluorinated rubrene.

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

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

Reference

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

Three-Dimensional π-Electron Molecules

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

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1. Acid/Base-Responsive Helicenes

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

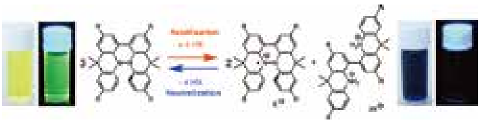

Figure 1. Acid/base-regulated electron transfer disproportionation.

2. Thermal Dynamics of Buckybowls

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

References

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