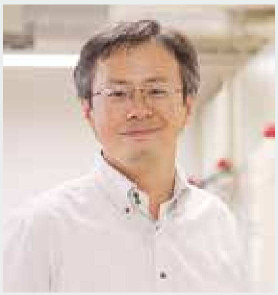
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

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

The Origin of 24 Hour Period in Cyanobacterial Clock System

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



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

Education

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

Professional Employment

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

Awards

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

Member

Assistant Professor
MUKAIYAMA, Atsushi
FURUIKE, Yoshihiko

Post-Doctoral Fellow
ABE, Jun
HIYAMA, Takuya

Visiting Scientist
GOUILLART, Louis*
YEW, Han Choi*
HUR, Anaa*

Technical Fellow
FUNAKI, Yukino
SHINTANI, Atsuko

Secretary
SUZUKI, Hiroko

Keywords Biological Clocks, Clock Proteins, Slow Dynamics

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

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

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

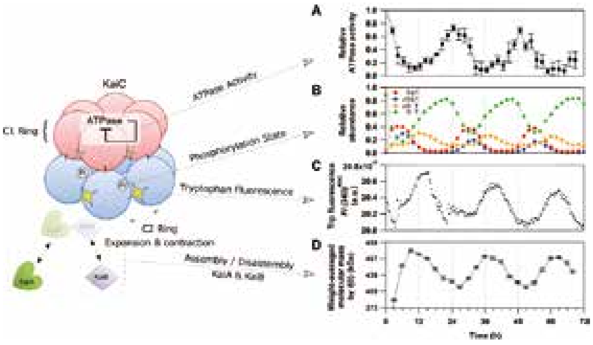


Figure 1. Circadian dynamics of cyanobacterial clock protein KaiC. The C1 and C2 domains in each protomer of KaiC are drawn as red and blue spheres, respectively. Expansion and contraction motions of the C2 ring (B, C) in solution serves as a timing cue for assembly/disassembly of KaiA and KaiB (D),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

Selected Publications

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

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

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.

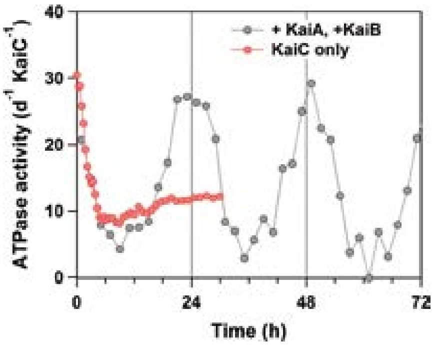


Figure 2. Time-course of KaiC ATPase activity.

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.

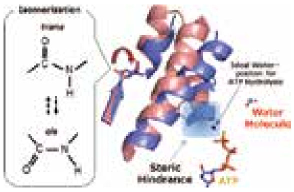


Figure 3. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

The 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[2)]

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

We have supported SAXS users so that they can complete experiments smoothly and publish their results.[3,4)]

4. Other Activities[3,5,6)]

We have conducted joint research projects in collaboration with other universities and research facilities.[3,5,6)]

References

1) 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).
2) Y. Furuike *et al.*, submitted.
3) Y. Furukawa, I. Anzai, S. Akiyama, M. Imai, F. J. C. Cruz, T. Saio, K. Nagasawa, T. Nomura and K. Ishimori, *J. Biol. Chem.* **291**, 4144–4155 (2016).
4) E. Nango, S. Akiyama, S. Maki-Yonekura, Y. Ashikawa, Y. Kusakabe, E. Krayukhina, T. Maruno, S. Uchiyama, N. Nuemket, K. Yonekura, M. Shimizu, N. Atsumi, N. Yasui, T, Hikima, M. Yamamoto, Y, Kobayash and A. Yamashita, *Sci. Rep.* **6**, 25745 (2016).
5) Y. Furukawa, Y. Suzuki, M. Fukuoka, K. Nagasawa, K. Nakagome, H. Shimizu, A. Mukaiyama and S. Akiyama, *Sci. Rep.* **6**, 20576 (2016).
6) I. Anzai, K. Toichi, E. Tokuda, A. Mukaiyama, S. Akiyama and Y. Furukawa, *Front. Mol. Biosci.* **3**, 40 (2016).

---

* IMS International Internship Program

Protein Design Using Computational and Experimental Approaches

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

KOGA, Nobuyasu
Associate Professor
[nkoga@ims.ac.jp]

Education

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

Professional Employment

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

Awards

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

Member

Assistant Professor
  KOSUGI, Takahiro
Research Fellow
  KOGA, Rie
  KONDO, Minako
  MORIWAKI, Yoshitaka
Graduate Student
  SAKUMA, Kouya
  NAKAMURA, Kengo
  YAMAMOTO, Mami
Secretary
  SUZUKI, Hiroko

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

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

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

Selected Publications

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

1. Principles for Designing Ideal Protein Structures

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

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

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

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

References

1) S. J. Fleishman, S. D. Khare, N. Koga and D. Baker*, *Protein Sci.* **20**, 753–757 (2011).
2) H. Kenzaki, N. Koga, N. Hori, R. Kanada, W. Li, K. Okazaki, X.-Q. Yao and S. Takada*, *J. Chem. Theory Comput.* **7**, 1979–1989 (2011).
3) N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, *Nature* **491**, 222–227 (2012).
4) J. Fang, A. Mehlich, N. Koga, J. Huang, R. Koga, M. Rief, J. Kast, D. Baker and H. Li*, *Nat. Commun.* **4**:2974 (2013).
5) Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).

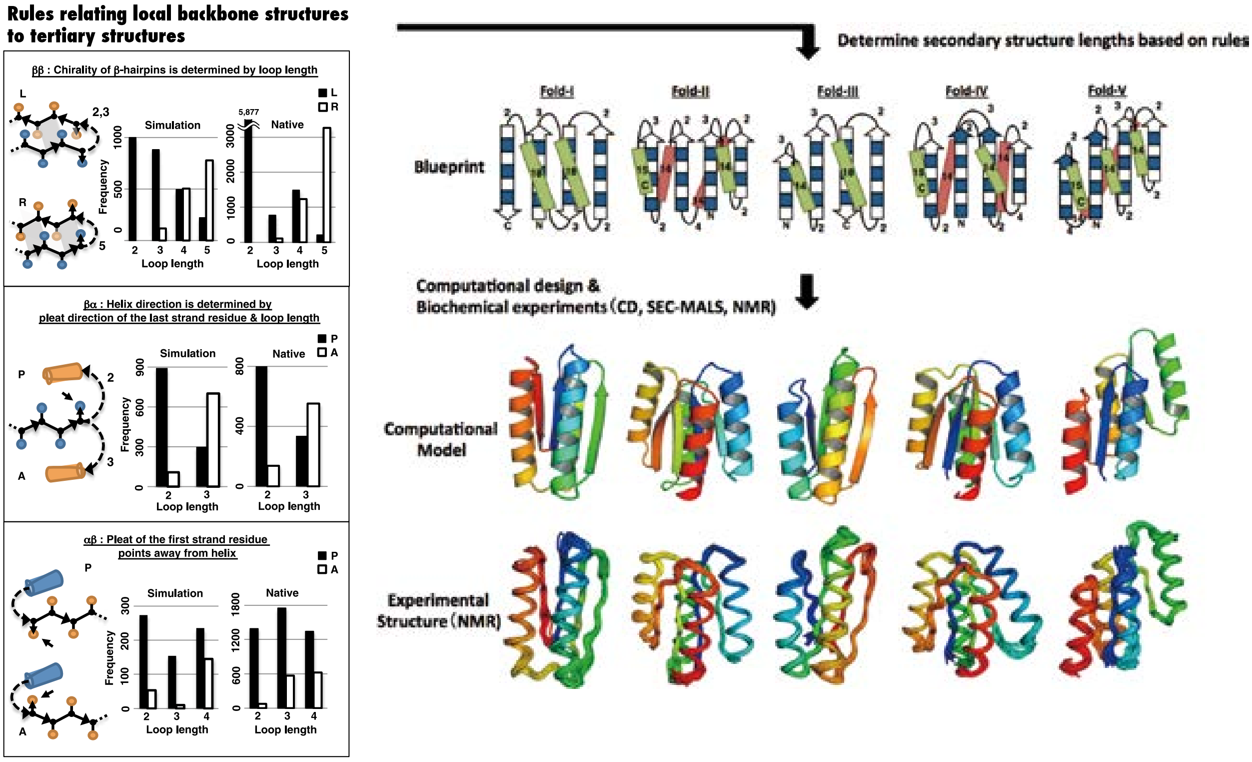


Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Visualization of Quantum Dynamical Nature Utilized Quantum Measurements

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

SHIKANO, Yutaka
Research Associate Professor
[yshikano@ims.ac.jp]

Education

2007	B.S. Tokyo Institute of Technology
2009	M.S. Tokyo Institute of Technology
2011	Ph.D. Tokyo Institute of Technology

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
2014	Visiting Associate Professor, Tokyo Institute of Technology

Awards

2013	FQXi Essay Contest Fourth Prize
2014	2013 Quantum Information Processing Top Reviewers
2014	Research Award, Research Foundation for Opto-Science and Technology
2015	Outstanding Referee of Physica A
2015	Outstanding Referee of Physics Letters A

Member
Research Fellow
  GOTO, Shin-itiro
Visiting Scientist
  ARNAULT, Pablo[*]
  ZHANG, Yu-Xiang[†]
  TUKIAINEN, Mikko[‡]
  AGRAWAL, Sristy[§]
Technical Fellow
  KAMO, Kyoko
  KATO, Mayuko
Secretary
  KONDO, Naoko
  SUZUKI, Sayuri

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.

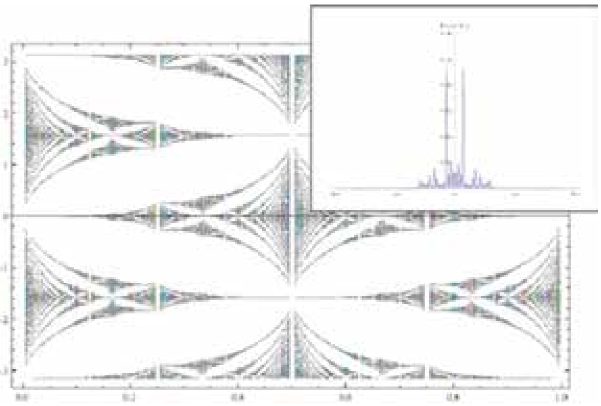


Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called 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* **82**, 031122 (7 pages) (2010).
- A. Noguchi, Y. Shikano, K. Toyoda and S. Urabe, "Aharonov-Bohm Effect in the Tunnelling of a Quantum Rotor in a 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. Generation Mechanism and Detection of Coherent Phonon in Bulk Solid[1,2]

Coherent optical phonons in bulk solid system play a crucial role in understanding and designing light-matter interactions and can be detected by the transient-reflectivity measurement. In this paper, we demonstrate spectrally resolved detection of coherent optical phonons in diamond from ultrashort infrared pump–probe measurements using optical bandpass filters. We show that this enhances the sensitivity approximately 35 times in measuring the coherent oscillations in the transient reflectivity compared with the commonly used spectrally integrated measurement. To explain this observation, we discuss its mechanism.

We also investigated the coherent phonon generation mechanism by irradiation of an ultrashort pulse with a simple two-level model. Our derived formulation shows that both impulsive stimulated Raman scattering (ISRS) and impulsive absorption (IA) simultaneously occur, and phonon wave packets are generated in the electronic ground and excited states by ISRS and IA, respectively. We identify the dominant process from the amplitude of the phonon oscillation. For short pulse widths, ISRS is very small and becomes larger as the pulse width increases. We also show that the initial phase is dependent on the pulse width and the detuning.

2. Exciton–Polariton Condensates in High Density Regime[3]

In a standard semiconductor laser, electrons and holes recombine via stimulated emission to emit coherent light, in a process that is far from thermal equilibrium. Exciton–polariton condensates—sharing the same basic device structure as a semiconductor laser, consisting of quantum wells coupled to a microcavity—have been investigated primarily at densities far below the Mott density for signatures of Bose-Einstein condensation. At high densities approaching the Mott density, exciton–polariton condensates are generally thought to revert to a standard semiconductor laser, with the loss of strong coupling. Here, we report the observation of a photoluminescence sideband at high densities that cannot be accounted for by conventional semiconductor lasing. This also differs from an upper-polariton peak by the observation of the excitation power dependence in the peak-energy separation. Our interpretation as a persistent coherent electron–hole–photon coupling captures several features of this sideband whereas many remain elusive. Understanding the observation will lead to a development in non-equilibrium many-body physics.

3. Operational Derivation of Physical Laws[4,5]

The resolution of the Maxwell's demon paradox linked thermodynamics with information theory through information erasure principle. By considering a demon endowed with a Turing-machine consisting of a memory tape and a processor, we attempt to explore the link towards the foundations of statistical mechanics and to derive results therein in an "operational" manner. Here, we present a derivation of the Boltzmann distribution in equilibrium as an example, without hypothesizing the principle of maximum entropy. Further, since the model can be applied to non-equilibrium processes, in principle, we demonstrate the dissipation–fluctuation relation to show the possibility in this direction.

4. Laser Cooling Mechanism of Optomechanics[6]

In the optomechanical cooling of a dispersively coupled oscillator, it is only possible to reach the oscillator ground state in the resolved sideband regime, where the cavity-mode line width is smaller than the resonant frequency of the mechanical oscillator being cooled. In this paper, we show that the dispersively coupled system can be cooled to the ground state in the unresolved sideband regime using an ancillary oscillator, which is coupled to the same optical mode via dissipative interaction. The ancillary oscillator has a resonant frequency close to that of the target oscillator; thus, the ancillary oscillator is also in the unresolved sideband regime. We require only a single blue-detuned laser mode to drive the cavity.

References

1) K. G. Nakamura, Y. Shikano and Y. Kayanuma, *Phys. Rev. B* **92**, 144304 (7 pages) (2015).
2) K. G. Nakamura, K. Ohya, H. Takahashi, T. Tsuruta, H. Sasaki, S. Uozumi, K. Norimatsu, M. Kitajima, Y. Shikano and Y. Kayanuma, *Phys. Rev. B* **94**, 024303 (7 pages) (2016).
3) T. Horikiri, M. Yamaguchi, K. Kamide, Y. Matsuo, T. Byrnes, N. Ishida, A. Löffler, S. Höfling, Y. Shikano, T. Ogawa, A. Forchel and Y. Yamamoto, *Sci. Rep.* **6**, 25655 (11 pages) (2016).
4) A. Hosoya, K. Maruyama and Y. Shikano, *Sci. Rep.* **5**, 17011 (9 pages) (2015).
5) Y. Shikano, in *It From Bit or Bit From It?* The Frontiers Collection, Springer; Switzerland, Chapter 10, pp. 113–118 (2015).
6) Y.-X. Zhang, S. Wu, Z.-B. Chen and Y. Shikano, *Phys. Rev. A* **94**, 023823 (11 pages) (2016).

---

* JSPS Summer Program from University Pierre et Marie Curie (UPMC) -Paris 6, France

† IMS International Internship Program from University of Science and Technology of China, China

‡ from University of Turku, Finland

§ from Indian Institute of Science Education and Research, Kolkata, India

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

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

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

Education

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

Professional Employment

2010	Postdoctoral Fellow, Tokyo Institute of Technology
2011	Assistant Professor, Kanagawa University
2012	JST-PRESTO Researcher (Additional post)
2013	Research Associate Professor, Institute for Molecular Science

Awards

2010	ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011	Tejima Doctoral Dissertation Award, Tokyo Institute of Technology

Member

Graduate Student
WATANABE, Akihiro*

Technical Fellow
IMAI, Yumiko
KUBOTA, Akiko

Secretary
KAWAI, Shigeko

Keywords Solid State Ionics, Oxyhydride, Battery

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

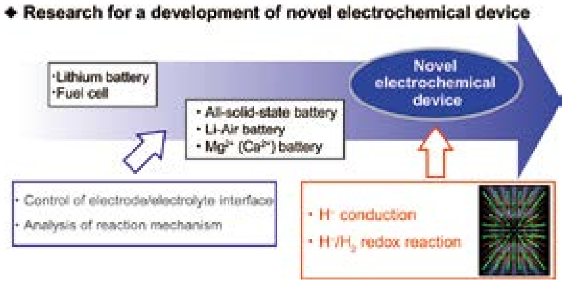


Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

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, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- G. Kobayashi, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).

1. Synthesis of H⁻ Conductive Oxyhydrides[1–4)]

Ionic charge carriers include a variety of species, such as Li^+, H^+, Ag^+, Cu^+, F^-, and O^{2-}, and their conductors have found applications in energy devices such as fuel cells and batteries. The conduction of hydride ions, H^-, is also attractive. These are similar in size to oxide and fluoride ions and show strong reducing properties with a standard redox potential of H^-/H_2 (–2.3 V) which is close to that of Mg/Mg^{2+} (–2.4 V). Hydride ion conductors may therefore be applied in energy storage/conversion devices with high energy densities. Here, we prepared a series of K_2NiF_4-type oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$, which are equipped with anion sublattices that exhibit flexibility in the storage of H^-, O^{2-}, and vacancies. An all-solid-state $Ti/La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}/TiH_2$ cell showed a redox reaction with hydrogen storage/desorption on the electrodes. The present success in the construction of an all-solid-state electrochemical cell exhibiting H^- diffusion confirms not only the capability of the oxyhydride to act as an H^- solid electrolyte but also the possibility of developing electrochemical solid devices based on H^- conduction.

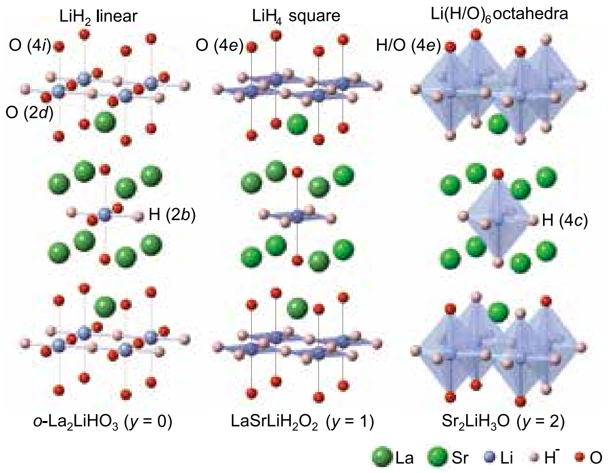


Figure 2. Crystal structures of $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0$, 1, 2). Lanthanum (and strontium) ions occupy the *A* sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the *B* site that are octahedrally coordinated 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[5)]

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

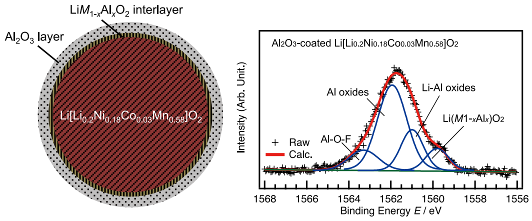


Figure 3. Schematic illustration and Al 1*s* HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

References

1) G. Kobayashi*, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno*, *Science* **351**, 1314–1317 (2016).

2) A. Watanabe, G. Kobayashi*, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry*, accepted.

3) G. Kobayashi*, A. Watanabe, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, under revision.

4) A. Watanabe, M. Yonemura, Y. Imai, K. Suzuki, M. Hirayama, R. Kanno and G. Kobayashi*, under revision.

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

---

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

Open up Future Electronics by Organic Molecules

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems

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

Education

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

Professional Employment

1998	Research Associate, Gakushuin University
1999	Special Postdoctral Fellow, RIKEN
2000	Research Scientist, RIKEN
2007	Senior Research Scientist, RIKEN
2012	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2012	Visiting Professor, Tokyo Institue of Technology
2015	Visiting Professor, Tohoku University

Awards

2009	RSC Publishing CrystEngComm Prize
2009	Young Scientist Awards, Japan Society for Molecular Science

Member
Assistant Professor
SUDA, Masayuki
IMS Research Assistant Professor
KAWAGUCHI, Genta
Technical Associate
URUICHI, Mikio
Graduate Student
YANG, Fan*
CHOOPPAWA, Tianchai
Secretary
KAWAI, Shigeko

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.

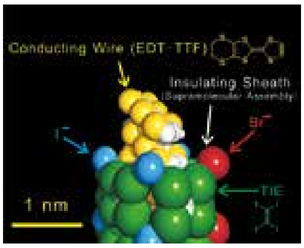


Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- Y. Kawasugi, K. Seki, Y. Edagawa, Y. Sato, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, “Electron–Hole Doping Asymmetry of Fermi Surface Reconstructed in a Simple Mott Insulator,” *Nat. Commun.* **7**, 12356 (8 pages) (2016).
- 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).

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 of this device 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.

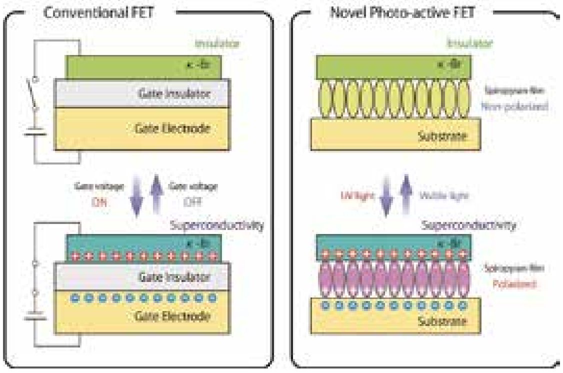


Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).

Award

SUDA, Masayuki; The 10th PCCP Prize (2016).

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)

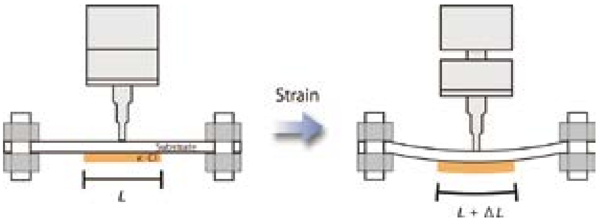


Figure 3. Side-view schematic for flexible organic Mott-FET device.

References

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

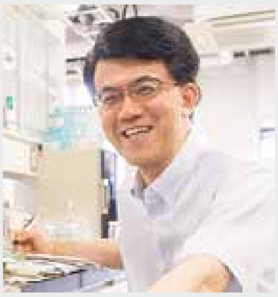
2) M. Suda, Y. Kawasugi, T. Minari, K. Tsukagoshi, R. Kato and H. M. Yamamoto, *Adv. Mater.* **26**, 3490–3495 (2014).

---

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

Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



SUZUKI, Toshiyasu
Associate Professor
[toshy@ims.ac.jp]

Education

1985 B.S. Nagoya University
1992 Ph.D. University of California, Santa Barbara

Professional Employment

1992 Assistant Professor, Institute for Molecular Science
1998 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
SAKAMOTO, Youichi
Post-Doctoral Fellow
KURODA, Yasuhiro
Secretary
WATANABE, Yoko

Keywords Organic Synthesis, Graphene Molecule, Organic Semiconductor

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

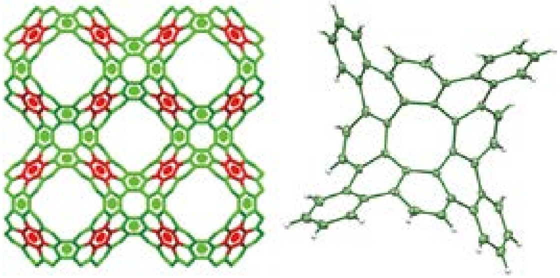


Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

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

1. Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops[1)]

Three *N*-substituted tetracyclo(2,7-carbazole)s have been synthesized to investigate the inner regions of nanohoops. One compound has a 5,5-dimethylnonane bridge between two neighboring *anti* carbazoles, which can be used as covalently bonded "methane probes." These probes near the ring center are strongly shielded by local ring currents and exhibited a singlet at $\delta = -2.70$ ppm in ^{1}H NMR. To visualize local and macrocyclic ring currents separately, we drew NICS (nucleus-independent chemical shift) contour maps of tetracyclo(9-methyl-2,7-carbazole) and [*n*]cycloparaphenylenes (CPPs). Local ring currents make the interior diatropic, and paratropic regions exist only outside the ring. Macrocyclic ring currents in [5] to [7]CPPs generate deshielding cones, which are typical of antiaromatic [4*n*]annulenes.

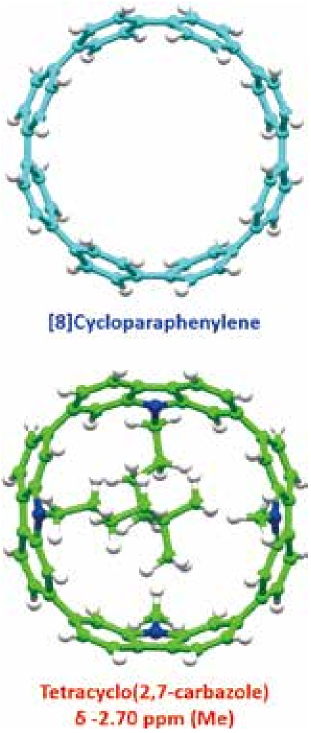


Figure 2. Optimized geometries of nanohoops by DFT calculations at the B3LYP/6-31G(d) level.

2. Ligand-Controlled Synthesis of [3]- and [4]Cyclo-9,9-dimethyl-2,7-fluorenes through Triangle- and Square-Shaped Platinum Intermediates[2)]

The syntheses of [3]- and [4]cyclo-9,9-dimethyl-2,7-fluorenes ([3] and [4]CFRs), cyclic trimer, and tetramers of 9,9-dimethyl-2,7-fluorene (FR), respectively, were achieved by the platinum-mediated assembly of FR units and subsequent reductive elimination of platinum. A triangle-shaped tris-platinum complex and a square-shaped tetra-platinum complex were obtained by changing the platinum ligand. The structure of the triangle complex was unambiguously determined by X-ray crystallographic analysis. Reductive elimination of each complex gave [3] and [4]CFRs. Two rotamers of [3]CFR were sufficiently stable at room temperature and were separated by chromatography. The physical properties of the CFRs were also investigated theoretically and experimentally.

References

1) Y. Kuroda, Y. Sakamoto, T. Suzuki, E. Kayahara and S. Yamago, *J. Org. Chem.* **81**, 3356–3363 (2016).
2) E. Kayahara, R. Qu, M. Kojima, T. Iwamoto, T. Suzuki and S. Yamago, *Chem. –Eur. J.* **21**, 18939–18943 (2015).

Three-Dimensional π-Electron Molecules

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems

HIGASHIBAYASHI, Shuhei
Assistant Professor

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

1. Butterfly- and Bowl-Shaped Molecules

We succeeded to create new butterfly-shaped$^{1)}$ (Figure 1) and bowl-shaped$^{2)}$ (Figure 2) π-conjugated molecules with embedded hydrazine structure. The butterfly-shaped molecules were synthesized by dimerization of heterocycles (dimethylacridine, phenothiazine, acridone). The bowl-shaped molecule with bicarbazole structure was synthesized by desulfurizatiion of butterfly-shaped biphenothiazine. The bowl-shaped molecule was found to undergo reversible two-electron oxidation, in which the shape of molecule was transformed between bowl and planar geometries (Figure 2).

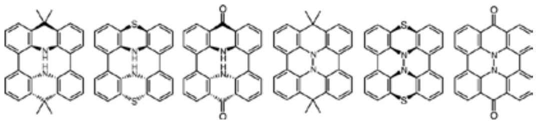


Figure 1. Butterfly- and bowl-shaped molecules.

Figure 2. Butterfly- and bowl-shaped molecules.

References

1) K. Yamamoto and S. Higashibayashi, *Chem. –Eur. J.* **22**, 663–671 (2016).
2) S. Higashibayashi, P. Pandit, R. Haruki, S. Adachi and R. Kumai, *Angew. Chem., Int. Ed.* **55**, 10830–10834 (2016).

Coordination Behavior of Heteroarenes to Palladium Centers

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems

YAMAMOTO, Koji
Assistant Professor

The coordination behavior of heteroarenes to palladium centers has attracted much attention since their coordination has been involved in Pd-catalyzed functionalization reactions of heteroarenes. However, heteroarene–palladium complexes have rarely been isolated, due to the labile nature of heteroarene–Pd complexes. In this project, synthesis and structural characterization of heteroarene–Pd complexes have been studied.$^{1,2)}$

1. σ-π Continuum in Indole–Pd^{II} Complexes

It has been proven that there is a σ-π continuum in heteroarene–metal complexes through isolation and systematic structural analysis of σ- and π-modes in indole–Pd^{II} complexes, while σ-mode has been assumed as the dominant mode for heteroarene–Pd interaction. The insight into the heteroarene–Pd interaction will provide a structural aspect on the key catalytic intermediates of palladium-catalyzed heteroarene transformations. Further study to verify the reactivity of σ-, σ/π-intermediate-, and π-complexes of indole is now underway.

Figure 1. σ-π Continuum in indole–Pd complexes.

References

1) K. Yamamoto, S. Kimura and T. Murahashi, *Angew. Chem., Int. Ed.* **55**, 5322–5326 (2016).
2) K. Yamamoto, Y. Ishikawa, S. Kimura and T. Murahashi, *C. R. Chim.* **18**, 785–789 (2015).