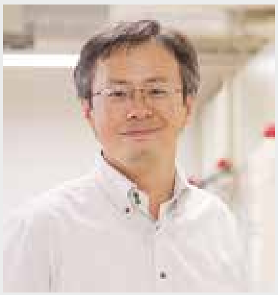
RESEARCH ACTIVITIES

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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Professional Employment
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2008 Junior Associate Professor, Nagoya University
2011 Associate Professor, Nagoya University
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Awards
2016 The 13th (FY2016) JSPS PRIZE
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 Circadian Clock, Clock Proteins, Cyanobacteria

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 (Abe *et al. Science* 2015). Our mission is to explore the frontier in molecular science of the circadian clock system from many perspectives.

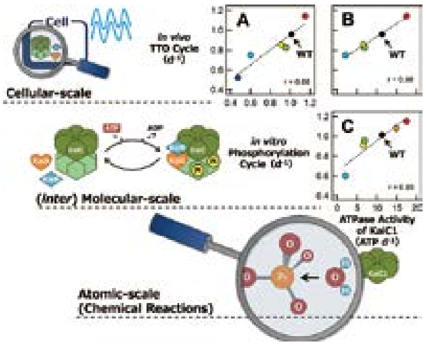

Figure 1. *Trans*-hierarchic nature of the circadian clock system in cyanobacteria. Cross-correlational plots (A–C) among frequency of *in vivo* transcription and translation oscillation (TTO) cycle, frequency of *in vitro* phosphorylation cycle, and ATPase activity of KaiC for cyanobacteria carrying period-modulating KaiC mutants (circles). Fine correlations in three panels indicate regulatory mechanisms of KaiC ATPase as the core basis for *trans*-hierarchic nature of cyanobacterial circadian clock system.

Selected Publications

- Y. Furuike, J. Abe, A. Mukaiyama and S. Akiyama, *Biophys. Physicobiol.* **13**, 235–241 (2016).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, *Cell. Mol. Life Sci.* **69**, 2147–2160 (2012).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

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.

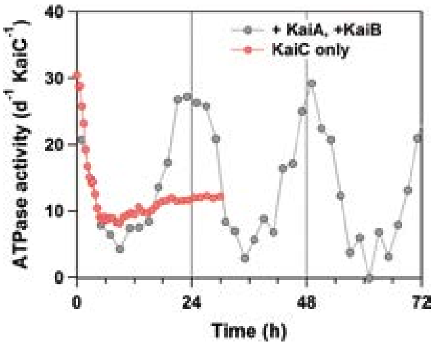

Figure 2. Time-course of KaiC ATPase activity.

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.

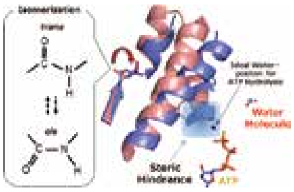

Figure 3. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

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[3–5)]

We have supported SAXS users so that they can complete experiments smoothly and publish their results.[3–5)]

4. Other Activities

We have conducted joint research projects in collaboration with other universities and research facilities.

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, J. Abe, A. Mukaiyama and S. Akiyama, *Biophys. Physicobiol.* **13**, 235–241 (2016).

3) S. Kanemura, M. Okumura, K. Yutani, T. Ramming, T. Hikima, C. Appenzeller-Herzog, S. Akiyama and K. Inaba K, *J. Biol. Chem.* **291**, 23952–23964 (2016).

4) I. Anzai, E. Tokuda, A. Mukaiyama, S. Akiyama, F. Endo, K. Yamanaka, H. Misawa and Y. Furukawa, *Protein Sci.* **26**, 484–496 (2017).

5) N. Nuemket, N. Yasui, Y. Kusakabe, Y. Nomura, N. Atsumi, S. Akiyama, E. Nango, Y. Kato, M. K. Kaneko, J. Takagi, M. Hosotani and A. Yamashita, *Nat. Commun.* **8**, 15530 (2017).

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* IMS International Internship Program

Protein Design Using Computational and Experimental Approaches

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2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
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Keywords Structural Biology, Protein Folding, Protein Design for Structure and Function

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

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

Selected Publications

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

1. Principles for Designing Ideal Protein Structures

Understanding the principles for protein folding is complicated by energetically unfavorable non-ideal features—for example kinked α-helices, bulged β-strands, strained loops and buried polar groups—that arise in proteins from evolutionary selection for biological function or from neutral drift. Here, we uncovered the principles for protein folding by designing "ideal" protein structures, which are stabilized by completely consistent local and non-local interactions. We discovered a set of rules relating local backbone structures (secondary structure patterns) to tertiary motifs (Figure 1 left), which were identified using a combination of folding simulations and analyses of naturally occurring proteins. Building backbone structures according to the rules (Figure 1 top right) and placing side chains stabilizing the backbone structures, we can readily design the proteins 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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2) N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, *Nature* **491**, 222–227 (2012).

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

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

5) Y.-R. Lin, N. Koga, S. M. Vorobiev and D. Baker*, *Protein Sci.* **26**, 2187–2194 (2017).

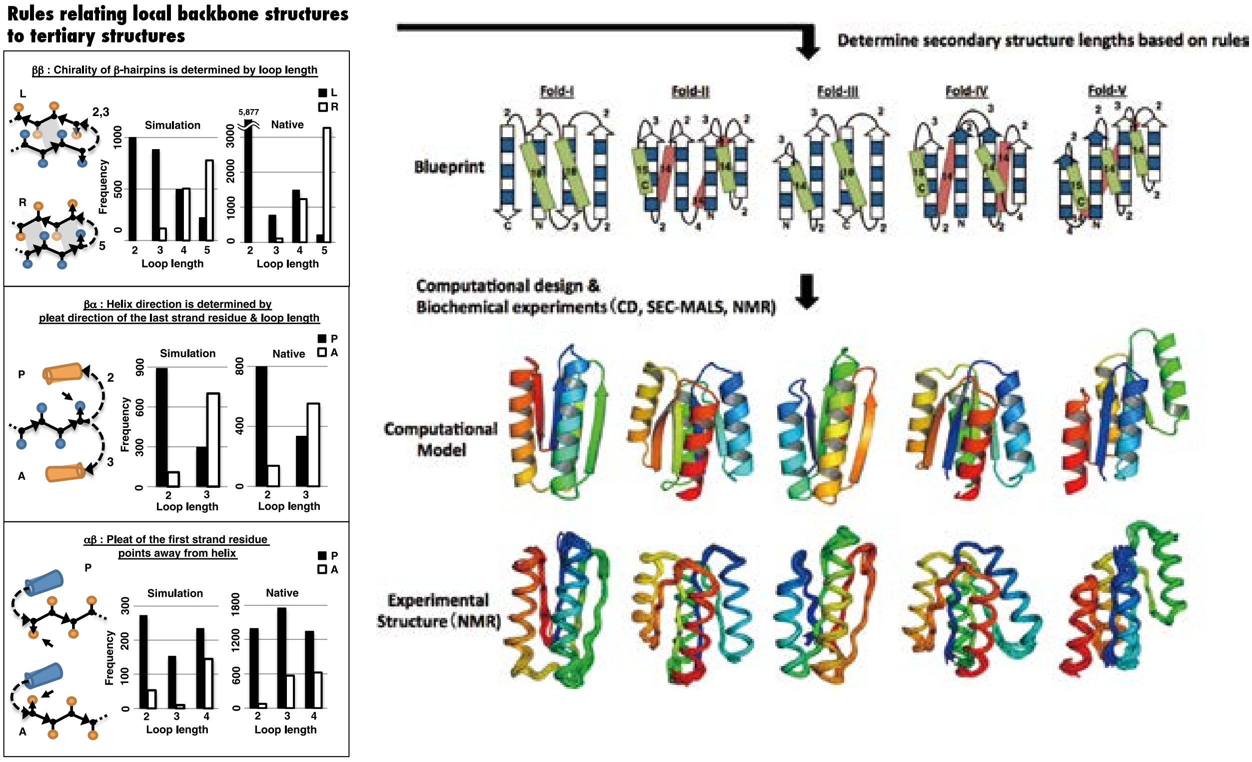

Figure 1. Left: Rules relating local backbone structures to tertiary motifs. Right: De novo designed protein structures.

Visualization of Quantum Dynamical Nature Utilized Quantum Measurements

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2012 Research Associate Professor, Institute for Molecular Science
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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
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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.

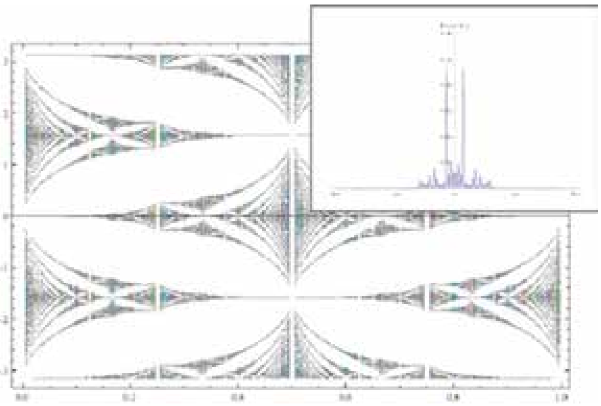

Figure 1. Example of the complex but regular phenomena from the simple law; the discrete-time quantum walk, which is a mathematical toy model to be defined as a quantum-mechanical analogue of the random walk. The probability distribution is depicted in the left top panel. This main distribution is called 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* **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. Exciton–Polariton Condensates in High Density Regime[1,2]

Exciton–polaritons are a coherent electron–hole–photon (e–h–p) system where condensation has been observed in semiconductor microcavities. In contrast to equilibrium Bose-Einstein condensation (BEC) for long lifetime systems, polariton condensates have a dynamical nonequilibrium feature owing to the similar physical structure that they have semiconductor lasers. One of the distinguishing features of a condensate to a laser is the presence of strong coupling between the matter and photon fields. Irrespective of its equilibrium or nonequilibrium nature, exciton–polariton have been observed to maintain strong coupling. We show that by investigating high density regime of exciton–polariton condensates, the negative branch directly observed in photoluminescence. This is evidence that the present e–h–p system is still in the strong coupling regime, contrary to past results where the system reduced to standard lasing at high density.

2. Large-Amplitude Quasi Phase Squeezed State[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 will be. 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 non-linear 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.

3. Visualization of Quantum States[4,5]

Since entanglement is not an observable *per se*, measuring its value in practice is a difficult task. Here we propose a protocol for quantifying a particular entanglement measure, namely concurrence, of an arbitrary two-qubit pure state via a single fixed measurement set-up by exploiting so-called weak measurements and the associated weak values together with the properties of the Laguerre-Gaussian modes. The virtue of our technique is that it is generally applicable for all two-qubit systems and does not involve simultaneous copies of the entangled state. We also propose an explicit optical implementation of the protocol.

4. Contact Geometry Description of Thermodynamics[6]

Contact geometry has been applied to various mathematical sciences, and it has been proposed that a contact manifold and a strictly convex function induce a dually flat space that is used in information geometry. Here, such a dually flat space is related to a Legendre submanifold in a contact manifold. In this paper contact geometric descriptions of vector fields on dually flat spaces are proposed on the basis of the theory of contact Hamiltonian vector fields. Based on these descriptions, two ways of lifting vector fields on Legendre submanifolds to contact manifolds are given. For some classes of these lifted vector fields, invariant measures in contact manifolds and stability analysis around Legendre submanifolds are explicitly given. Throughout this paper, Legendre duality is explicitly stated. In addition, to show how to apply these general methodologies to applied mathematical disciplines, electric circuit models and some examples taken from nonequilibrium statistical mechanics are analyzed.

5. Quantum Dynamical Simulation in Solid System[7]

One-dimensional discrete-time quantum walks (DTQWs) can simulate various quantum and classical dynamics and have already been implemented in several physical systems. This implementation needs a well-controlled quantum dynamical system, which is the same requirement for implementing quantum information processing tasks. Here, we consider how to realize DTQWs by Dirac particles toward a solid-state implementation of DTQWs.

References

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2) T. Horikiri, T. Byrnes, K. Kusudo, N. Ishida, Y. Matsuo, Y. Shikano, A. Löffler, S. Höfling, A. Forchel and Y. Yamamoto, *Phys. Rev. B* **95**, 245122 (5 pages) (2017).
3) F. Matsuoka, A. Tomita and Y. Shikano, *Quant. Stud.: Math. Found.* **4**, 159–169 (2017).
4) M. Tukiainen, H. Kobayashi and Y. Shikano, *Phys. Rev. A* **95**, 052301 (6 pages) (2017).
5) Y. Shikano, *AIP Conf. Proc.* **1871**, 020001 (7 pages) (2017).
6) S. Goto, *J. Math. Phys.* **57**, 102702 (41 pages) (2016).
7) Y. Shikano, *Interdiscip. Inform. Sci.* **23**, 33–37 (2017).

Award

SHIKANO, Yutaka; Reviewer Rewards for International Journal of Modern Physics B (2017).

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

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2011	Tejima Doctoral Dissertation Award, Tokyo Institute of Technology

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NISHIKAWA, Masako

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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. As ion transport in solids is key for determining the performance of these devices, an improved understanding of the characteristics of existing electrode and electrolyte materials is required. For example, crystal structure, thermal stability, and reaction mechanisms are important to enhancing battery performance. Furthermore, the development of novel ion conduction phenomena through the synthesis of a new class of substances will be expected to lead to the creation of novel battery systems. In this context, I have concentrated my research efforts into two main areas: (i) Studies into the reaction mechanisms of cathodic materials for lithium secondary batteries; and (ii) The synthesis of new materials exhibiting hydride ion (H^-) conductivity and the development of a novel battery system utilizing both the H^- conduction phenomenon and the H^-/H_2 redox reaction.

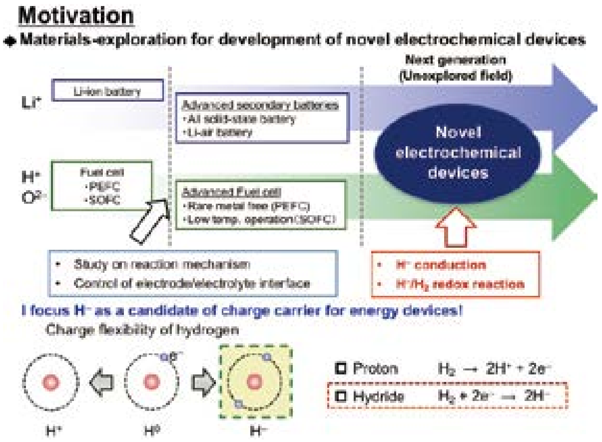

Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

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.

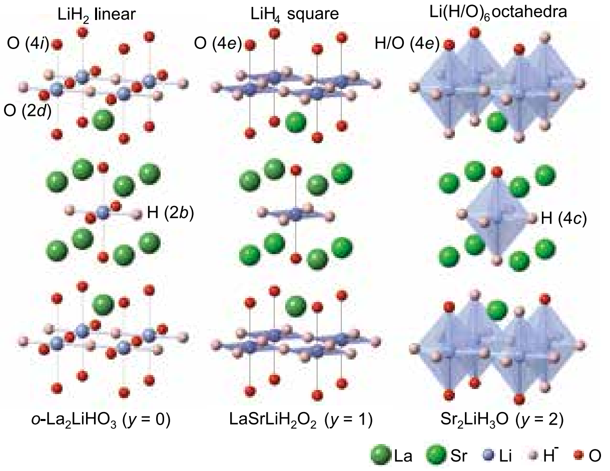

Figure 2. Crystal structures of $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0$, 1, 2). Lanthanum (and strontium) ions occupy the A sites of the layered perovskite-type structure (A_2BX_4) that are 12-fold coordinated with anions. Lithium occupies the B site that are octahedrally coordinated 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[4]

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.

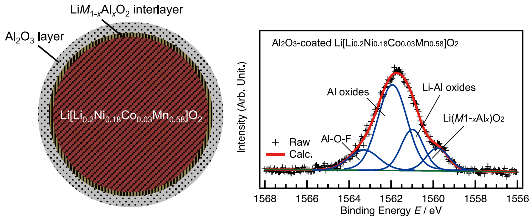

Figure 3. Schematic illustration and Al 1s HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

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3) G. Kobayashi, A. Watanabe, M. Yonemura, A. Kubota 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).

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* IMS International Internship Program

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.

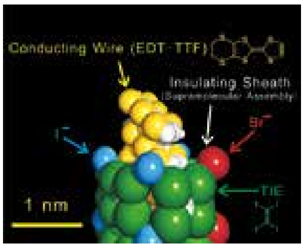

Figure 1. Crystal structure of supramolecular nanowire.

Selected Publications

- 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[1,2]

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. (BEDT-TTF = bis(ethyelenedithio)tetrathiafulvalene) In our previous works, a tensile strain from FET substrate altered κ-Br's ground state into a Mott-insulating state, when its thin (*ca.* 100 nm) crystal was laminated on top of SiO$_2$/Si^{++} substrate and cooled down to low temperature. In those experiments the electronic state at low temperature became completely insulating because of the large tensile strain that originates in mismatching of thermal expansion coefficients between κ-Br (30 ppm/K) and Si (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 will 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. With this type of FET substrate, we have achieved an electric-field-induced superconductivity in κ-Br.

Recently, we have inserted a photochromic self-assembled monolayer (SAM layer: Figure 2, right panel) into this device in order to make it photo-active. We have employed a photochromic molecule 'spiropyran' whose UV-converted isomer 'merocyanin' is known to exhibit zwitter-ionic structure. Because the photochromic molecules are aligned in the same direction in the SAM, a strong electric field can be generated by photo-irradiation, when the spiropyran is converted into the merocyanin form. Thus, excess carriers can be injected to the FET interface due to the strong dipole moment of merocyanin.

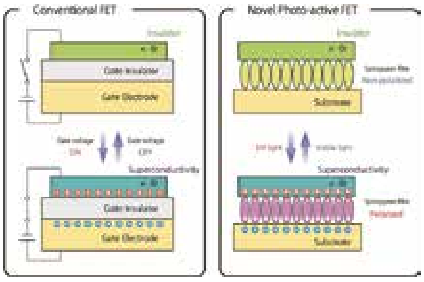

Figure 2. Device schematic for conventional superconducting FET (left) and our photo-active FET (right).
This figure shows p-type doping by molecular dipole-moment.

A κ-Br thin crystal is mounted on the SAM/Al$_2$O$_3$/Nb-SrTiO$_3$ substrate, and cooled down to low temperature. The resistance of the device showed weakly insulating temperature dependence, suggesting a percolate-superconducting state. Upon irradiation of UV-light, the resistivity at 5 K went down quickly and low-resistance state was observed after 180 sec. Temperature dependence of resistivity showed sudden drop around 7 K, confirming superconducting transition after the UV-light irradiation. Reverse photo-reaction by visible light led the phase transition back to the insulating state again. The switching of this device seems to originate from the light-induced formation of internal dipole moment in the SAM-layer, which resulted in a hole-doping at the FET interface. This speculation was confirmed by dual-gate experiment of this device, where gate-induced hole carriers worked cooperatively with the light-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.

One can invert the direction of the molecule and its related electric field by designing a photochromic SAM molecule with different geometry. By such a strategy, we were able to achieve n-type light-induced superconductivity as shown in Figure 3. In this device, the threshold gate voltage for superconducting transition was shifted in the negative direction, as the UV irradiation proceeded. This implies that the light-induced carrier is an electron. These photo-active devices pave the way for new type of photo-electronics.

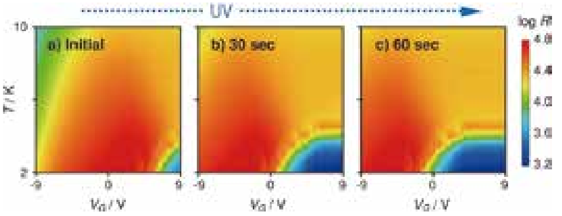

Figure 3. Emergence of n-type superconductivity by UV-irradiation. At the initial state (a), the device shows a normal ambipolar transistor behavior. After the UV-irradiation, superconducting region (blue) appears from electron-doped side (panels b and c).

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1) M. Suda, R. Kato and H. M. Yamamoto, *Science* **347**, 743–746 (2015).
2) M. Suda, N. Takashina, S. Namuangruk, N. Kungwan, H. Sakurai and H. M. Yamamoto, *Adv. Mater.* **29**, 1606833 (2017).

Awards

SUDA, Masayuki; Young Scientist Awards, Japan Society for Molecular Science (2016).
SUDA, Masayuki; Ishida Prize, Nagoya University (2016).
SUDA, Masayuki; CSJ Award for Young Chemists, Chemical Society of Japan (2017).
SUDA, Masayuki; The 6th Young Scientist Award of National Institutes of Natural Sciences (2017).
SUDA, Masayuki; Morino Foundation for Molecular Science, Morino Foundation (2017).

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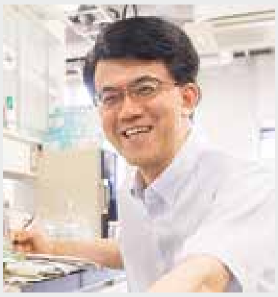
* IMS International Internship Program
† carrying out graduate research on Cooperative Education Program of IMS with Tokyo Institute of Technology

Development of Curved Graphene Molecules as Organic Semiconductors

Research Center of Integrative Molecular Systems
Division of Functional Molecular Systems



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Keywords Organic Synthesis, Organic Semiconductor, Graphene Molecule

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

Perfluorination is a simple method to prepare an n-type semiconductor with the same molecular symmetry. It is important to understand the impact of perfluorination on the solid-state structures and charge transport properties. We are currently working on the synthesis of new perfluorinated aromatic compounds.

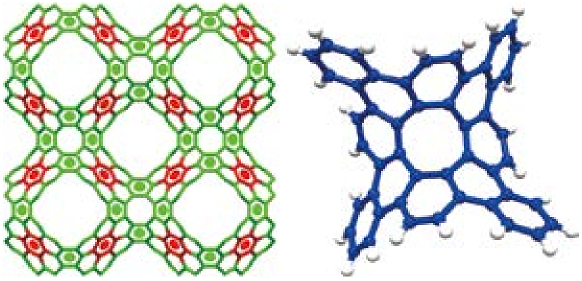


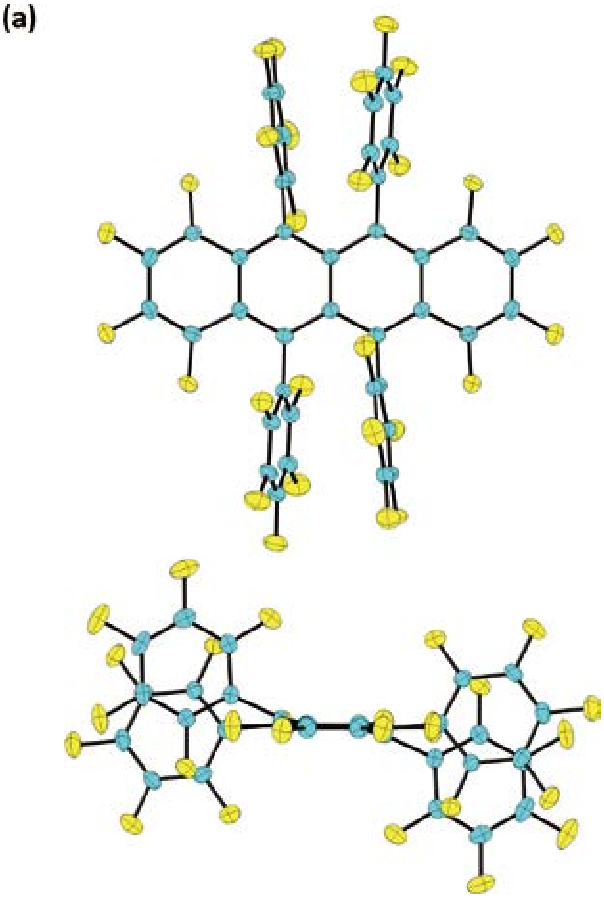
Figure 1. Schwarzite P192 (left) as a hypothetical 3D graphene with the negative Gaussian curvature. Tetrabenzo[8]circulene (right) as a repeating molecular unit for Schwarzite P192.

Selected Publications

- 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).
- Y. Kuroda, Y. Sakamoto, T. Suzuki, E. Kayahara and S. Yamago, "Tetracyclo(2,7-carbazole)s: Diatropicity and Paratropicity of Inner Regions of Nanohoops," *J. Org. Chem.* **81**, 3356–3363 (2016).

1. Perfluorinated and Half-Fluorinated Rubrenes: Synthesis and Crystal Packing Arrangements[1)]

Perfluororubrene (PF-RUB) has been synthesized by cycloaddition of perfluorinated 1,3-diphenylisobenzofuran and 1,4-diphenyl-2,3-didehydronaphthalene followed by reductive deoxygenation. This method was easily applied for the synthesis of half-fluorinated rubrene (F_{14}-RUB). The electrochemical measurements and DFT calculations indicate that perfluorination strongly lowers the HOMO and LUMO energies. Recrystallization and sublimation of PF-RUB gave two different crystals with planar and twisted conformations, respectively. In both cases, perfluorination leads to the formation of short C–F and F–F contacts and completely disrupts face-to-face π interactions. Single crystals of F_{14}-RUB were grown by sublimation, and twisted molecules display the two-dimensional π-stacking with a face-to-face distance of 3.54 Å.



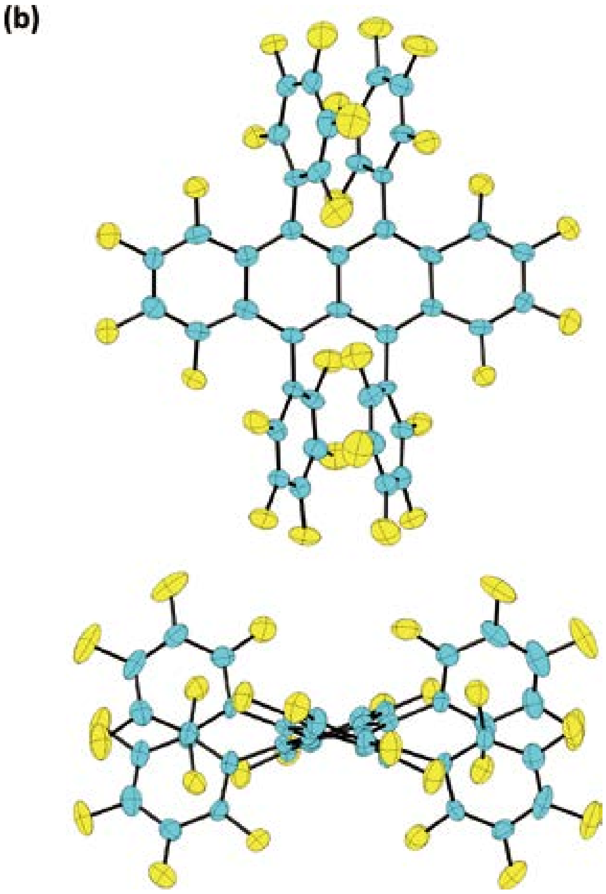


Figure 2. Planar (a) and twisted (b) conformations of perfluororubrene in two different crystal structures.

Reference

1) Y. Sakamoto and T. Suzuki, *J. Org. Chem.* **82**, 8111–8116 (2017).