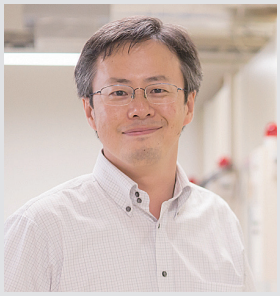
RESEARCH ACTIVITIES
Research Center of Integrative Molecular Systems

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

Biological Rhythm and Dynamics through Chemistry

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



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Professional Employment
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Awards
2016 The 13th (FY2016) JSPS PRIZE
2008 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
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2007 Young Scientist Prize, The Biophysical Society of Japan
2006 SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
2002 The Protein Society Annual Poster Board Award

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Keywords Biological Rhythm, Circadian Clock, Cyanobacteria

Living organisms on Earth evolved over time to adapt to daily environmental alterations, and eventually acquired endogenous time-measuring (biological clock) systems. Various daily activities that we perform subconsciously are controlled by the biological clock systems sharing three characteristics. First, the autonomic rhythm repeats with an approximately 24-hour (circadian) cycle (self-sustainment). Second, the period is unaffected by temperature (temperature compensation). Third, the phase of the clock is synchronized with that of the outer world in response to external stimuli (synchronization). We seek to explain these three characteristics, and consider the biological clock system of cyanobacteria to be an ideal experimental model.

The major reason that cyanobacteria are considered to be the ideal experimental model is that the core oscillator that possesses the three characteristics of the clock can be easily reconstructed within a test tube. When mixing the three clock proteins KaiA, KaiB, and KaiC with ATP, the structure and enzyme activity of KaiC change rhythmically during a circadian cycle. Taking advantage of this test tube experiment, we used an approach combining biology, chemistry, and physics to elucidate the means by which the clock system extends from the cellular to atomic levels.

Among the three Kai proteins, KaiC is the core protein of the oscillator. In the presence of KaiA and KaiB, KaiC revelas the rhythm of autophosphorylation and dephosphorylation; however, the cycle of this rhythm depends on the ATPase activity of KaiC independent of KaiA or KaiB. For example, when the ATPase activity of KaiC doubles as a result of amino acid mutations, the frequencies of both the *in vitro* oscillator and the intracellular rhythm also double (the cycle period is reduced to half). This mysterious characteristic is called a transmural hierarchy, in which the cycle (frequency) and even the temperature compensation both *in vitro* and *in vivo* are greatly affected (controlled) by the function and structure of KaiC.

How are the circadian activities and temperature compensation features encoded in KaiC and then decoded from it to propagate rhythms at the cellular level? We are committed to better understanding biological clocks and other dynamic systems through the chemistry of circadian ***rhythm***, ***structure***, and evolutionary ***diversity***.

Selected Publications

- D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
- A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
- A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* **8**, 8803 (2018).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. 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, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

1. *Structure*: Reasons for Seeking Structure and Dynamics of Circadian Clock Components in Cyanobacteria[1–3)]

A great deal of effort has been devoted to characterizing structural changes in the clock proteins along the circadian reaction coordinate.[1)] However, little is known about the mechanism driving the circadian cycle, even for the simple cyanobacterial protein KaiC that has ATPase and dual phosphorylation sites in its N-terminal C1 and C-terminal C2 domains, respectively. Nearly all KaiC structures reported to date share a nearly identical structure, and they do not appear to be suggestive enough to explain the determinants of circadian period length and its temperature compensation. We are studying the structural and dynamical origins in KaiC using high-resolution x-ray crystallography[2)] and quasielastic neutron scattering,[3)] respectively.

2. *Rhythm*: Cross-Scale Analysis of Cyanobacterial Circadian Clock System[3–5)]

KaiC ATPase is of particular interest here, as it finely correlates to the frequencies of *in vivo* as well as *in vitro* oscillations and also it is temperature compensated. This unique property has inspired us to develop an ATPase-based screening for KaiC clock mutants[4)] giving short, long, and/or temperature-dependent periods. A developed HPLC system with a 4-channel temperature controller has reduced approximately 80% of time costs for the overall screening process (Figure 1). Using the developed device, we are screening a number of temperature-dependent mutants of KaiC.[3)]

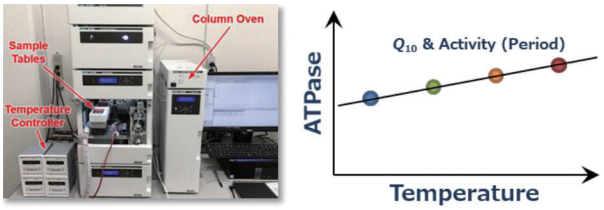


Figure 1. Development of a quick ATPase assay system.

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

3. beyond Evolutionary *Diversity*[6)]

In the presence of KaiA and KaiB, the ATPase activity of KaiC oscillates on a 24-hour cycle. KaiC is not capable of maintaining a stable rhythm on its own, but its activity was observed to fluctuate with reduced amplitude over time (Figure 2A). We have identified a signal component that is similar to damped oscillation, and propose that it encodes the specific frequency, equivalent to a 24-hour cycle.[1)]

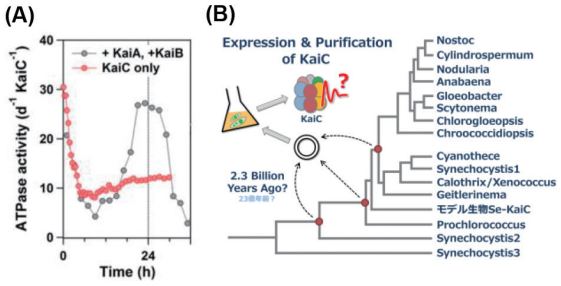


Figure 2. Damped oscillation of KaiC ATPase activity (**A**) and evolutionary diversity of cyanobacteria (**B**).

The habitats of cyanobacteria are diverse, so the space of their sequence is immense.[6)] Furthermore, some KaiA and KaiB genes are missing in several strains of cyanobacteria. This is understandable to some extent if KaiC possesses the specific frequency. Given our current understanding of this phenomenon, *what specific frequencies are possessed by KaiC homologues in other species and ancestral cyanobacteria?* (Figure 2B) If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

4. Bio-SAXS Activity in IMS[7)]

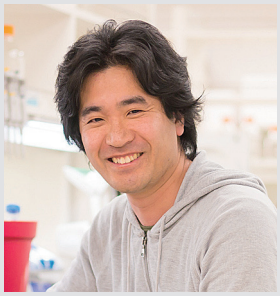
We have supported SAXS users so that they can complete experiments smoothly and publish their results.[7)]

References

1)S. Akiyama, *Circadian Rhythms in Bacteria and Microbiomes*, 138–145 (2021).
2) Y. Furuike, A. Mukaiyama, D. Ouyang, K. Ito-Miwa, D. Simon, E. Yamashita, T. Kondo and S. Akiyama, *bioRxiv* doi: 10.1101/2021.08.30.457330 (2021).
3) Y. Furuike, D. Ouyang, T. Tominaga, T. Matsuo, A. Mukaiyama, Y. Kawakita, S. Fujiwara and S. Akiyama, *bioRxiv* doi: 10.1101/2021.08.20.457041 (2021).
4) D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
5) K. Ito-Miwa, Y. Furuike, S. Akiyama and T. Kondo, *Proc. Natl. Acad. Sci. U. S. A.* **117**, 20926–20931 (2020). doi: org/10.1073/pnas.2005496117
6) A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
7) M. Okumura, S. Kanemura, M. Matsusaki, Y. H. Lee, S. Akiyama and K. Inaba, *Structure* **29**, 1–14 (2021).

Protein Design Using Computational and Experimental Approaches

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



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2013 Young Scientist Award, The 51st Annual Meeting of the Biophysical Society of Japan
2018 Morino Foundation for Molecular Science

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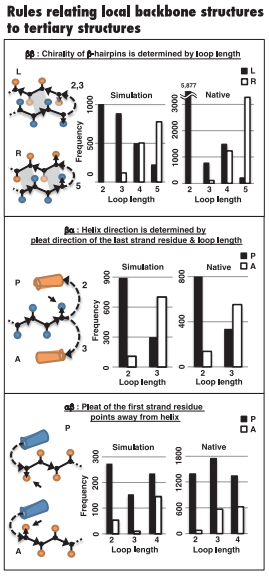
Keywords Protein Design for Structure and Function, Protein Folding, Structural Biology

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 new proteins. 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. Robust Folding of a De Novo Designed Ideal Protein Even with Most of the Core Mutated to Valine

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

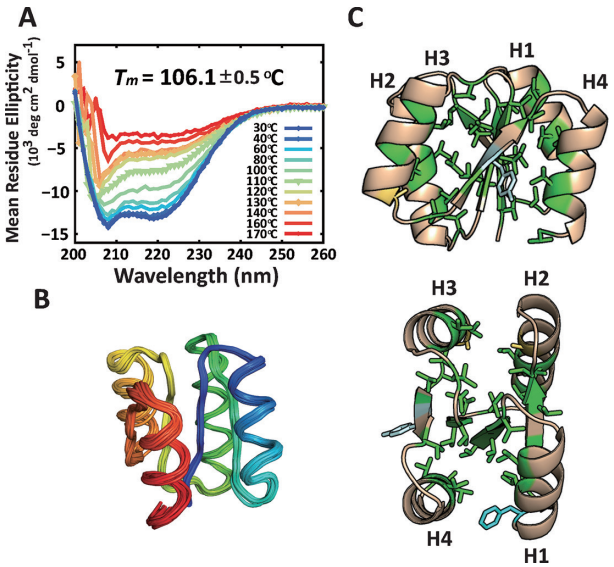


Figure 1. Experimental characterization of the designed protein with most of the core mutated to Val. (A) The far-UV CD spectra at various temperatures. (B) NMR structure. (C) Hydrophobic core side chains are shown in stick. Residues colored in green are valine.

2. Role of Backbone Strain in De Novo Design of Complex α/β Protein Structures

We have elucidated principles for designing ideal proteins with completely consistent local and non-local interactions which have enabled the design of a wide range of new αβ-proteins with four or fewer β-strands. The principles relate local backbone structures to supersecondary-structure packing arrangements of α-helices and β-strands. Here, we test the generality of the principles by employing them to design larger proteins with five- and six- stranded β-sheets flanked by α-helices. The designs are monomeric in solution with high thermal stability, and the nuclear magnetic resonance (NMR) structure of one was close to the design model, but for two others the order of strands in the β-sheet was swapped. Investigation into the origins of this strand swapping suggests that the global structures of the design models are more strained than the NMR structures. We incorporated explicit consideration of global backbone strain into our design methodology, and succeeded in designing proteins with the original unswapped strand arrangements. These results illustrate the value of experimental structure determination in guiding improvement of de novo design, and the importance of consistency between local, supersecondary, and global tertiary interactions in determining protein topology. The augmented set of principles should inform the design of larger functional proteins.

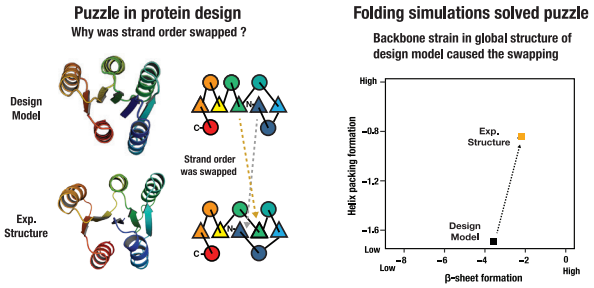


Figure 2. (left) The strand order swapping in de novo design of larger αβ-proteins has been a long-standing problem for the research team. (right) Backbone ensembles generated from folding simulations identified that backbone strain caused the strand swapping.

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1) R. Koga*, M. Yamamoto, T. Kosugi, N. Kobayashi, T. Sugiki, T. Fujiwara and N. Koga*, *Proc. Natl. Acad. Sci. U. S. A.* **117**, 31149–31156 (2020).

2) N. Koga*, R. Koga, G. Liu, J. Castellanos, G. T. Montelione and D. Baker*, *Nat. Commun.* **12**, 3921 (12 pages) (2021).

Awards

KOSUGI, Takahiro; The Young Scientist Excellence Award of Protein Science Society of Japan (PSSJ) (2021).
MITSUMOTO, Masaya; The Poster Excellence Award of the 1st Molecular Engine Workshop (2021).
MITSUMOTO, Masaya; The Poster Award of Protein Science Society of Japan (PSSJ) (2021).
KAIDA, Shingo; The Poster Award of Protein Science Society of Japan (PSSJ) (2021).

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

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Keywords Ultrafast Spectroscopy, Nonlinear Spectroscopy, Chemical Reaction Dynamics

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study the chemical reaction dynamics of the condensed-phase molecules. In particular, we focus on exploiting unique methodologies based on sub-10-fs pulses (*e.g.*, time-domain impulsive vibrational spectroscopy and multidimensional spectroscopy) and tracking molecular dynamics from electronic and structural viewpoints throughout the chemical reaction with exquisite temporal resolution. We also develop a novel methodology and light source to probe ultrafast dynamics of single molecules in the condensed phase at room temperature, with the aim to understand chemical reaction dynamics at the single-molecule level. Our particular interest rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our advanced spectroscopic approaches, we aim to establish a new avenue for the study of chemical reaction dynamics.

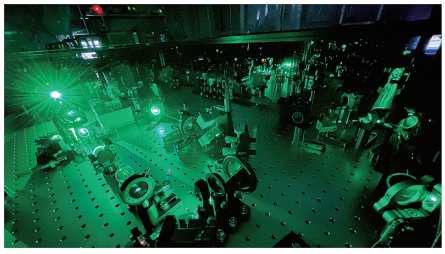

Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- H. Kuramochi and T. Tahara, "Tracking Ultrafast Structural Dynamics by Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, "Tracking Photoinduced Au–Au Bond Formation through Transient Terahertz Vibrations Observed by Femtosecond Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **141**, 19296–19303 (2019).
- H. Kuramochi, S. Takeuchi, H. Kamikubo, M. Kataoka and T. Tahara, "Fifth-Order Time-Domain Raman Spectroscopy of Photoactive Yellow Protein for Visualizing Vibrational Coupling in Its Excited State," *Sci. Adv.* **5**, eaau4490 (2019).
- H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photoreception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* **9**, 660–666 (2017).
- T. Fujisawa, H. Kuramochi, H. Hosoi, S. Takeuchi and T. Tahara, "Role of Coherent Low-Frequency Motion in Excited-State Proton Transfer of Green Fluorescent Protein Studied by Time-Resolved Impulsive Stimulated Raman Spectroscopy," *J. Am. Chem. Soc.* **138**, 3942–3945 (2016).
- H. Kuramochi, S. Takeuchi and T. Tahara, "Femtosecond Time-Resolved Impulsive Stimulated Raman Spectroscopy Using Sub-7-fs Pulses: Apparatus and Applications," *Rev. Sci. Instrum.* **87**, 043107 (2016).

1. Tracking Ultrafast Dynamics with Time-Domain Raman Spectroscopy

In traditional Raman spectroscopy, narrow-band light is irradiated on a sample, and its inelastic scattering, *i.e.*, Raman scattering, is detected. The energy difference between the Raman scattering and the incident light corresponds to the vibrational energy of the molecule, providing the Raman spectrum that contains rich information about the molecular-level properties of the materials. On the other hand, by using ultrashort optical pulses, it is possible to induce Raman-active coherent nuclear motion of the molecule and to observe the molecular vibration in real time. This time-domain Raman measurement can be combined with femtosecond photo-excitation triggering chemical changes, which enables tracking ultrafast structural dynamics in a form of "time-resolved" time-domain Raman spectroscopy, also known as time-resolved impulsive stimulated Raman spectroscopy (Figure 2). Through our extensive efforts, time-resolved impulsive stimulated Raman spectroscopy now realizes high sensitivity and a wide detection frequency window from THz to 3000 cm^{-1}, and has seen success in unveiling the molecular mechanisms underlying the efficient functions of complex molecular systems. We recently overviewed its application to the study on femtosecond structural dynamics of complex molecular systems such as photoresponsive proteins and molecular assemblies,[1] and reported another application to the ultrafast structural dynamics of a fluorescent protein.[2] In the latter, we studied excited-state proton transfer (ESPT) dynamics of LSSmOrange, which has been extensively used for multi-color bioimaging owing to its large Stokes shift. The chromophore of LSSm Orange takes a neutral form in the ground state, but the bright orange fluorescence is emitted from the anionic form that is generated through ESPT upon photoexcitation. This ESPT has been known to proceed in a biphasic manner, but its origin has been unknown. We investigated the chromophore structural dynamics during ESPT and unveiled that the chromophore exists in both *trans* and *cis* forms in the ground state, and they are simultaneously photoexcited and undergo ESPT in parallel with significantly different time scales.

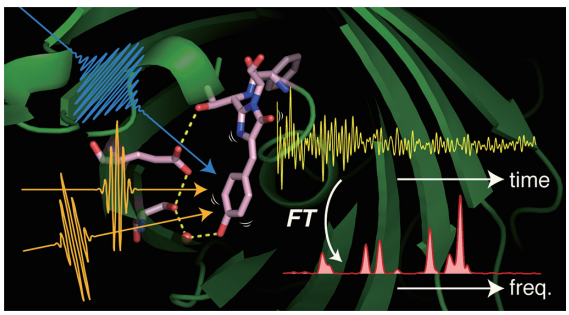

Figure 2. Schematic illustration of time-resolved time-domain Raman spectroscopy. Reprinted with permission from ref. 1. Copyright 2021 American Chemical Society.

2. Generation of Sub-10-fs Pulses with Ultrabroadband Spectral Coverage

Electronic/vibrational coherence has been used as a probe to gain detailed insights into the chemical reaction dynamics. Moreover, it has recently attracted tremendous interest as a control knob for directing and thus enhancing chemical reactions in the desired way. Observing and manipulating such coherences of the condensed phase polyatomic molecules inevitably require extremely short pulses with broad spectral coverage to monitor relevant electronic transitions thoroughly. Nevertheless, generating such ultrashort pulses has been primarily limited in the visible spectral region from the viewpoint of spectroscopic applications, where long-term high stability is required. We developed light sources to generate highly stable sub-10-fs pulses in a broad spectral coverage from UV to NIR. The light source is based on a Yb:KGW regenerative amplifier. Through various nonlinear optical processes such as optical parametric amplification, self-phase modulation, and subsequent sum-frequency mixing, we generate pulses tunable from 300–1400 nm with bandwidths that support the pulse duration well below 10 fs at Fourier transform limit, as shown in Figure 3. We compensate group delay dispersion of these pulses by a combination of chirped mirrors and a pulse shaper, and the intensity profiles of the compressed pulses retrieved from Frequency-Resolved Optical Gating (FROG) measurement show that the compressed pulses have a pulse duration as short as 4.5 fs. Applications of these pulses to ultrafast spectroscopy of functional molecules are now in progress.

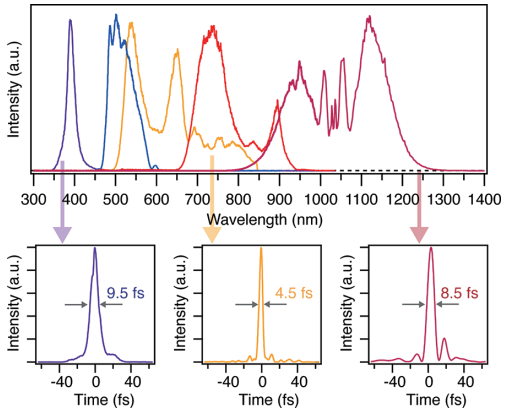

Figure 3. (Top) Typical spectra of the broadband pulses that support Fourier transform limit pulse duration of <10 fs. (Bottom) Intensity profiles of the compressed pulses retrieved from the FROG data.

References

1) H. Kuramochi and T. Tahara, *J. Am. Chem. Soc.* **143**, 9699–9717 (2021).
2) P. Kumar, E. Fron, H. Hosoi, H. Kuramochi, S. Takeuchi, H. Mizuno and T. Tahara, *J. Phys. Chem. Lett.* **12**, 7466–7473 (2021).

Awards

KURAMOCHI, Hikaru; The 13th Inoue Science Research Award (2021).
KURAMOCHI, Hikaru; The 13th Young Scientist Awards of the Japan Society for Molecular Science (2020).

Open up Future Electronics by Organic Molecules

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Keywords Organic Mott Insulator, Field Effect Transistors, Organic Spintronics

Organic molecules are attracting recent attention as new ingredients of electronic circuits. Our group focuses on the development of organic electronics in the next era by providing new mechanism and concepts of the device operation and fabrication. For example, an electronic phase transition is utilized for the ON/OFF switching of our field-effect-transistor (FET). This special FET is called an organic Mott-FET, where the conduction electrons in the organic semiconductor are solidified at the OFF state because of Coulomb repulsion among carriers. In the operation, these solidified electrons can be melted by applying a gate voltage, and show an insulator-to-metal transition so-called Mott-transition to be switched to the ON state. Because of this phase transition, a large electric response of the device can be achieved, resulting in the highest device mobility ever observed for organic FETs. In addition to this high performance, the Mott-FET is interesting in terms of superconductivity. Because the Mott-transition sometimes accompanies superconducting phase in between metal and insulator, modulation of gate electric field at low temperature may induce superconductivity. In fact, we have achieved first example of field-induced superconductivity in an organic FET. By combining a strain effect that can tune the bandwidth, this type of electric-field-induced superconducting transition can be utilized for mapping the phase diagram around the Mott-insulator as shown in Figure 1.

Another approach to the future electronics is the development of spintronic devices based on chirality of organic material. We aim to implement chirality-induced spin selectivity (CISS) effect into molecular devices that can generate spin-polarized current. This type of device is expected to realize spintronics devices without magnet or topological insulator.

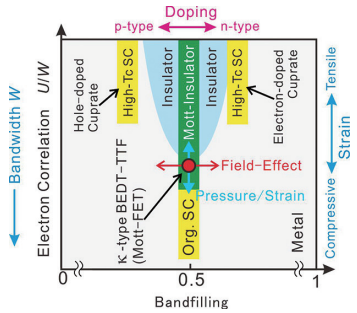

Figure 1. Phase diagram surrounding a Mott-insulator. SC denotes superconductor, while *U* and *W* are on-site Coulomb repulsion and bandwidth, respectively.

Selected Publications

- H. M. Yamamoto, "Phase-Transition Transistor Based on Organic Mott Insulators," *Bull. Chem. Soc. Jpn*. **94**, 2505–2539 (2021).
- Y. Kawasugi, K. Seki, S. Tajima, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Two-Dimensional Ground-State Mapping of a Mott-Hubbard System in a Flexible Field-Effect Device," *Sci. Adv.* **5**, eaav7282 (9 pages) (2019).
- M. Suda, Y. Thathong, V. Promarak, H. Kojima, M. Nakamura, T. Shiraogawa, M. Ehara and H. M. Yamamoto, "Light-Driven Molecular Switch for Reconfigurable Spin Filters," *Nat. Commun.* **10**, 2455 (7 pages) (2019).
- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).

1. Current-Induced Spin-Polarization in a Chiral Crystal $CrNb_3S_6$[1,2)]

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

We detected CISS-based spin transport phenomena in a monoaxial chiral dichalcogenide $CrNb_3S_6$. This material has chiral structure and metallic conduction, so that we could perform CISS experiments with metallic conduction regime. Spin polarization was detected in this chiral bulk crystal under a charge current flowing along the principal *c* axis at room temperature without magnetic field. The detection was made by an inverse spin Hall signal which is induced on the tungsten electrode that absorbs polarized spin from the chiral crystal. An inverse response was also observed when applying the charge current into the tungsten electrode, which implied an inverse CISS effect. The signal sign reversed in the device with the opposite chirality, which is consistent with the symmetry required for CISS effect. Furthermore, the spin signals were found over micrometer length scale in a nonlocal configuration. Such a robust generation and protection of the spin-polarized state can be discussed based on a one-dimensional model with an antisymmetric spin–orbit coupling.

In addition to the above experiments, we also detected bulk magnetization generated by applying electric current to the crystal using SQUID magnetometer (Figure 2). When the current amplitude was swept from negative to positive, the current-induced magnetization changed linearly. Directly detecting such magnetization by magnetometry enables one to estimate the number of spin-polarized electrons. Using this number, we evaluated the spin polarization rate within the framework of Boltzmann's equation and found that spin polarization generated by CISS effect was enhanced by 10^5 times inside this material. It seemed that effective magnetic field generated by CISS could reach 10^3 T at high current density, which again confirmed the robustness of CISS effect. We also observed that the current-induced magnetization increased in the vicinity of the phase boundary between paramagnetic and forced ferromagnetic phases, which could be attributed to the spin fluctuation associated with the phase transition. (SQUID = superconducting quantum interference device)

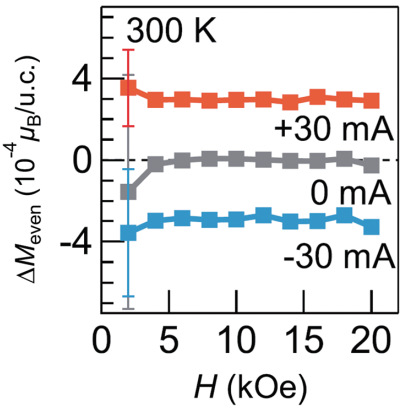

Figure 2. Detection of spin polarization in a chiral metal $CrNb_3S_6$. By applying electrical current, electron spins are polarized along the current direction by CISS effect. The amplitude of the magnetization is irrelevant to the applied magnetic field, which strongly supports the current-induced nature of this magnetization.

2. Spin Current Generation in a Chiral Organic Superconductor

Although centrosymmetric *s*- and *d*-wave superconductors are in a spin singlet state, a superconductor with broken mirror symmetry is expected to show spin triplet state, according to a theory developed by Edelstien.[3)] This means spin polarization can be generated by applying supercurrent in a chiral superconductor, whose magnetization direction depending on the lattice symmetry has been recently calculated by group theory.[4)] We have tested this idea by employing κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ (hereafter, κ-NCS) which is an organic superconductor with chiral and polar crystal lattice. The space group of this crystal is $P2_1$, and its handedness is defined by the relative arrangement between the anionic $Cu(NCS)_2$ and cationic BEDT-TTF. This handedness can be experimentally determined by X-ray diffraction or circular dichroism. After confirming pure enantiomeric lattice system, a thin crystal of κ-NCS has been laminated onto a resin substrate with pre-patterned gold and nickel electrodes. At temperature lower than superconducting *T*c, an electrical current was applied to induce spin magnetization. The spin polarization accumulated at the interface between κ-NCS and the magnetic electrode was detected as a voltage that is dependent on the magnetic field. By measuring the angle dependency of this magneto-voltaic signal, the direction of accumulated spin could be determined. The spin polarization direction was dependent on the specific location inside the crystal, and its arrangement was consistent with a magnetic quadrupole structure which has been hypothesized in a chiral molecule with CISS effect.
[BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]

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