# 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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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

#### 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.

to elucidate the means by which the clock system extends from the cellular to atomic levels.

Member Assistant Professor

MUKAIYAMA, Atsushi

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*.

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*: Atomic-Scale Origins of Clock Slowness in Cyanobacterial Circadian Clock System<sup>1,2)</sup>

To identify the structural origins of slowness encoded in KaiC, its N-terminal ATPase domain was analyzed using high-resolution x-ray crystallography.<sup>1)</sup> Water molecules are prevented from attacking into the ideal position (Figure 1) 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, requires a much larger amount of free energy than for typical ATP hydrolysis. The atomic structure explains why the ATPase activity of KaiC is so much lower (by 100- to 1,000,000-fold) than that of typical ATPases.<sup>2)</sup>



Figure 1. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

### 2. *Rhythm*: Transmural Hierarchy in Cyanobacterial Circadian Clock System<sup>3–5)</sup>

KaiC ATPase is of particular interest here, as it finely correlates to the frequencies of *in vivo* as well as *in vitro* oscillations. This unique property has inspired us to develop an ATPase-based screening for KaiC clock mutants giving short, long, and/or temperature-dependent periods.<sup>3)</sup> A developed HPLC system with a 4-channel temperature controller has reduced approximately 80% of time costs for the overall screening process (Figure 2).



Figure 2. Development of a quick ATPase assay system.

How is the intra-molecular slowness encoded in KaiC (Figure 1) transmitted to the inter-molecular interactions with other Kai proteins? To address this question, a tryptophan residue was introduced in the N-terminal ring of KaiC as the fluorescent probe for KaiBC complex formation.<sup>4)</sup> Our kinetic data indicated that KaiB exclusively selects the post-ATP-hydrolysis state of KaiC to form the KaiBC complex. This process follows a mechanism called conformational selection (CS), in which proteins (KaiC) first undergoes a structural change to form a specific intermediate. Ligands (KaiB) are then recognized specifically through the intermediate state to form a tight ligand-protein complex. The CS mechanism is

elegantly designed in KaiC so that the slow intra-molecular ATPase reaction in KaiC can be the rate-liming step of the overall KaiBC complex formation.

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  $6.6 \text{ d.}^{5}$ )

### 3. beyond Evolutionary *Diversity*<sup>1,6)</sup>

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 3A). 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.<sup>1)</sup>



**Figure 3.** 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.<sup>6)</sup> 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 3B) If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

### 4. Bio-SAXS Activity in IMS<sup>7)</sup>

We have supported SAXS users so that they can complete experiments smoothly and publish their results.<sup>7)</sup>

#### References

- 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).
- S. Akiyama, Circadian Rhythms in Bacteria and Microbiomes, in press (2020).
- 3) D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* 20, 2789–2800 (2019).
- A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* 8, 8803 (2018).
- 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) I. Anzai, E. Tokuda, S. Handa, H. Misawa, S. Akiyama and Y. Furukawa, *Free Radical Biol. Med.* 147, 187–199 (2020).

# **Protein Design Using Computational and Experimental Approaches**

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

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Keywords	Protein Design for Structure and Function, Protein Folding, Structural Biolog	1

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

Protein molecules spontaneously fold into unique threedimensional 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.

Member Assistant Professor

KOSUGI, Takahiro

#### 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).
- P. Nordenfelt, T. Moore, S. Mehta, J. Kalappurakkal, V. S. Swaminathan, N. Koga, T. Lambert, D. Baker, J. Waters, R. Oldenbourg, T. Tani, S. Mayor, C. M. Waterman and T. Springer,

"Direction of Actin Flow Dictates Integrin LFA-1 Orientation during Leukocyte Migration," Nat. Commun. 8, 2047 (2017).

- · Y. Lin, N. Koga, S. M. Vorobiev and D. Baker, "Cyclic Oligomer Design with De Novo αβ-Proteins," Protein Sci. 26, 2187-2194 (2017)
- S. Basak, R. P. Nobrega, D. Tavella, L. M. Deveau, N. Koga, R. Koga, D. Baker, F. Massi and C. R. Matthews, "Networks of Electrostatic and Hydrophobic Interactions Modulate the Complex Folding Free Energy Surface of a Designed Ba Protein," Proc. Natl. Acad. Sci. U. S. A. 116, 6806-6811 (2019).

# 1. Principles for Designing Ideal Protein Structures

We uncovered the principles for protein folding by designing "ideal" protein structures, which are stabilized 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), which were identified using a combination of folding simulations and analyses of naturally occurring proteins. Building backbone structures according to the rules, and placing side chains stabilizing the backbone structures, we can readily design the proteins which have funnel-shaped folding energy landscapes leading into the target folded state. Using this approach, we have succeeded in designing ideal protein structures for five different topologies. These results suggest that the local backbone structures determine the tertiary folded structures rather than the details of amino acid sequences.





Figure 1. Rules relating local backbone structures to tertiary motifs.

## 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 demonstrated that the control is afforded by the resulting extended rule set by designing a series of proteins within the same fold but considerable variation in secondary structure length, loop geometry,  $\beta$ -strand registry, and overall shape. These extended design principles would provide the foundation for custom design of protein structures performing desired functions.

### 3. Robust Folding of De Novo Designed Ideal Protein Even with Most of the Core Filled with 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 nonlocal 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 2. Experimental characterizations of the design with most of the core filled with Val.

#### References

- 1) R. Koga\* and N. Koga\*, *Biophys. Physicobiol.* 16, 304–309 (2019).
- 2) 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).

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

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



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#### Education

- 2007 B.S. Tokyo Institute of Technology
- 2013 Ph.D. Tokyo Institute of Technology
- Professional Employment
- 2013 Special Postdoctoral Researcher, RIKEN
- 2016 Research Scientist, RIKEN
- 2017 JST-PRESTO Researcher
- 2020 Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

- 2017 The 8<sup>th</sup> Research Incentive Award of RIKEN
- 2017 The Spectroscopical Society of Japan Award for Young Scientists
- 2019 RSC PCCP Prize
- 2020 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
- 2020 Morino Foundation for Molecular Science

#### Keywords

Ultrafast Spectroscopy, Chemical Reaction Dynamics, Ultrashort Pulse Generation and Control

Chemical reactions of polyatomic molecular systems proceed on complex potential energy surfaces (PESs) with a vast degree of freedom of nuclear coordinates. For understanding molecular mechanisms underlying the chemical reactions, it is essential to map out the PESs and visualize how the molecules migrate and change its structure thereon. To this end, it is necessary to track the change of the electronic/vibrational structure of the molecule from the reactant all the way down to the product, with temporal resolution as high as possible.

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study chemical reaction dynamics of the condensed-phase molecular systems. In particular, we exploit unique methodologies using sub-10-fs pulses (*e.g.*, ultrafast time-domain Raman spectroscopy and multidimensional electronic/vibrational spectroscopy), and track the molecular dynamics from the electronic and structural viewpoints, throughout the chemical reaction with an exquisite temporal resolution. Our particular interest

#### Selected Publications

- 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).
- 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, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photo-

rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as photoreceptor proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our unique spectroscopic tools, we aim to establish a new avenue for the study of chemical reaction dynamics.

Member Secretary

ITO, Atsuko



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

reception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* 9, 660–666 (2017).

- 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, 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).

### 1. Realtime Observation of the Structural Changes upon Photoinduced Tight Bond Formation

Realtime observation of chemical bond formation and subsequent nuclear rearrangements is one of the ultimate goals of chemical science. Nevertheless, such attempts have been long hampered by a technical difficulty to trigger bond formation at well-defined, desired timing. The dicyanoaurate complex trimer ( $[Au(CN)_2^-]_3$ ) is the best suitable system in order to achieve this aim because the tight covalent Au–Au bonds are formed upon photoexcitation. Despite the apparent simplicity of the system, however, recent time-resolved studies failed to construct a consistent picture of its structural dynamics.

We used femtosecond time-resolved impulsive stimulated Raman spectroscopy to track ultrafast structural dynamics of the [Au(CN)<sub>2</sub><sup>-</sup>] trimer upon the photoinduced Au–Au bond formation. This ultrafast "time-resolved time-domain" Raman technique allows us to monitor the change of the vibrational structure on the femtosecond timescale by inducing and observing coherent molecular vibrations at arbitrary timings with ultrashort pulses. The obtained femtosecond time-resolved Raman data reveal that the Au–Au stretching vibration at ~90 cm<sup>-1</sup> exhibits a gradual frequency upshift in a few picoseconds, demonstrating a continuous bent-to-linear structural change on the triplet-state potential energy surface upon the Au–Au bond formation. This comprehensive ultrafast spectroscopic study settles the controversy on this prototypical molecular assembly.<sup>1</sup>



**Figure 2.** Schematic illustration of the structural changes in  $[Au(CN)_2^-]_3$  upon photoinduced tight Au–Au bond formation.

## 2. Femtosecond Polarization Switching of the [CrCo] Dinuclear Complex Crystal

Polarization switching has been considered a promising key operating principle of next-generation sensors and memory devices. Ferroelectric compounds have been extensively studied as promising candidates because they exhibit polarization switching upon application of the external electric field or heating. However, the speed (and thus efficiency) of the polarization switching in these materials is often limited by the change in the molecular structure, which occurs on the picoseconds or longer time scale. Also, the polarization state of the ferroelectric compounds is, in many cases, dependent on their domain structure, making it difficult to realize large polarization at the macroscopic scale.

The crystal of the [CrCo] dinuclear complex has been shown to exhibit polarization switching upon the photoinduced phase transition.<sup>2)</sup> Because the molecular orientation is well defined inside the crystal and the phase transition is accompanied by the charge transfer that does not require the change in the molecular structure, it has potential to realize the fast polarization switching at the macroscopic scale.

We studied photoinduced polarization switching dynamics in the crystal of the [CrCo] dinuclear complex by ultrafast pump–probe spectroscopy in the visible and mid-infrared regions. Our data clearly show that the photoinduced polarization switching is an ultrafast process with a time constant of 280 fs, demonstrating itself as the fastest polarization switching material realized using the metastable state. Moreover, the pump–probe data in the visible region reveal pronounced appearance of coherent nuclear wavepacket motion with a frequency as low as 22 cm<sup>-1</sup>, which we attribute to a lattice vibrational mode. The pronounced non-Condon effect for its resonance Raman enhancement implies that this mode couples the relevant electronic states, thereby facilitating the ultrafast polarization switching.<sup>3)</sup>



**Figure 3.** Schematic illustration of the change in the spin state associated with the phase transition. b) Time-resolved absorption spectra obtained after photoexcitation with the 9-fs pulse centered at 520 nm. c) Temporal profiles of the transient absorption signals.

#### References

- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, J. Am. Chem. Soc. 141, 19296–19303 (2019).
- 2) S. Kanegawa, Y. Shiota, S. Kang, K. Takahashi, H. Okajima, A. Sakamoto, T. Iwata, H. Kandori, K. Yoshizawa and O. Sato, *J. Am. Chem. Soc.* **138**, 14170–14173 (2016).
- 3) H. Kuramochi, G. Aoyama, H. Okajima, A. Sakamoto, S. Kanegawa, O. Sato, S. Takeuchi and T. Tahara, *Angew. Chem., Int. Ed.* 59, 15865–15869 (2020).

#### Awards

KURAMOCHI, Hikaru; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award (2020).

KURAMOCHI, Hikaru; Morino Foundation for Molecular Science (2020).

# Open up Future Electronics by Organic Molecules

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#### 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 Awards
- 2009 RSC Publishing CrystEngComm Prize
- 2009 Young Scientist Awards, Japan Society for Molecular Science
- 2010 RIKEN-ASI Award for the Young Scientist
- 2019 The CSJ Award for Creative Work
- 2020 NAGAI Foundation for Science & Technology Academic Award

Member Assistant Professor SUDA, Masavuki HIROBE, Daichi IMS Research Assistant Professor KAWAGUCHI, Genta Visiting Scientist SAENNAWA, Wiyada\* PACHARIYANGKUN, Anna KUMSAMPAO Jakkapan Graduate Student MORISHIMA, Masaki AIZAWA, Hiroki NABEI, Yoji NAKAJIMA, Ryota Technical Fellow MURATA, Ryosuke Secretary SUZUKI Ai

#### 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 insulatorto-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

#### Selected Publications

- H. M. Yamamoto, M. Suda and Y. Kawasugi, "Organic Phase-Transition Transistor with Strongly Correlated Electrons," *Jpn. J. Appl. Phys.* **57**, 03EA02 (7 pages) (2018).
- 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).

be utilized for mapping the phase diagram around the Mottinsulator 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.

- 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).

# 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<sub>3</sub>S<sub>6</sub>. 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 (Figure 2). An inverse response was also observed when applying the charge current into the detection 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 spin-momentum locking.

In addition to the above experiments, we also detected bulk magnetization generated by applying electric current to the crystal. When the current amplitude was swept from



**Figure 2.** Detection of spin polarization in a chiral metal  $CrNb_3S_6$ . By applying electrical current (1), electron spins are polarized along the current direction by CISS effect. Then the spin current is diffused into W electrode (2) and generate a voltage by inverse spin Hall effect (3).

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.

# 2. Anomalous Superconducting Phase in an Organic Field-Effect Device<sup>3)</sup>

We have achieved simultaneous control of bandwidth and bandfilling for organic Mott-insulators by using field effect device that can control the lattice strain to the organic crystal to observe the phase diagram for superconducting state. A new superconducting field-effect transistor (FET) in the vicinity of bandwidth-controlled Mott transition has been developed using molecular strongly correlated system κ-(BEDT-TTF)<sub>2</sub> Cu[N(CN)<sub>2</sub>]Br laminated on CaF<sub>2</sub> substrate. This device exhibited significant cooling-rate dependence of resistance below about 80 K, associated with glass transition of terminal ethylene group of BEDT-TTF molecule, where more rapid cooling through glass transition temperature leads to the decrease in bandwidth. We demonstrated that the FET properties such as ON/OFF ratio and polarity can be changed by utilizing cooling rate. Therefore, this is another device that can control both bandwidth and bandfilling of an organic Mottinsulator simultaneously, to find phase diagram associated with superconducting and Mott-insulating phases. By analyzing the FET behaviors of the device at different cooling rates, an enhanced superconducting state at exactly half-filling was discovered.

[BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]

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#### Award

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