



RESEARCH ACTIVITIES

Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three Divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells and field effect transistors are investigated in this department.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science Division of Electronic Structure



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1994 Lecturer, The University of Tokyo
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2002 Professor, Institute for Molecular Science
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Keywords

X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard X-Ray Photoelectron Spectroscopy

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD measurement system contains ultrahigh vacuum sample preparations chamber, with which one can clean substrates (substrate single crystals *etc.*), deposit materials (metallic and molecular magnets *etc.*) and characterize the samples using low energy electron diffraction, reflection high energy electron diffraction and Auger electron spectroscopy. The apparatus is extensively open for public usage and many domestic and foreign researchers visit us every year.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer

electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time using Beamline 36XU of SPring-8. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated non-crystalline element by using the energy-resolved x-ray fluorescence detection technique. We have investigated local geometric and electronic structures of the photoexcited states of photocatalysts as WO_3 and BiVO_4 which are known to be active for visible light. In WO_3 , the photoexcited state around W is ascribed to the electron polaron like state since W is reduced from hexavalent to pentavalent and the local geometric structure around W is significantly distorted.

Within this one year, two assistant professors Drs. Takagi and Uemura moved out and a new assistant professor Dr. Koitaya has just joined our group and one position is now open. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation and lasers.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Uemura *et al.*, *Angew. Chem. Int. Ed.* **55**, 1364 (2015).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).

1. Local Thermal Expansions and Lattice Strains in Elinvar Alloy¹⁾

It is well known that local structures in mixed crystals are often different from lattice structures that are expected crystallographically. Even when the crystal shows clear x-ray diffraction patterns, there should exist strains in the crystal that cannot be solved by the x-ray diffraction analysis. In this work, we have investigated local thermal expansions and lattice strains in the Elinvar alloy $\text{Fe}_{49.66}\text{Ni}_{42.38}\text{Cr}_{5.49}\text{Ti}_{2.47}$ (Ni Span C) and the stainless steel SUS304 $\text{Fe}_{71.98}\text{Ni}_{9.07}\text{Cr}_{18.09}\text{Mn}_{0.86}$ (AISI304) were investigated by the temperature-dependent Cr, Fe, and Ni *K*-edge EXAFS measurements, combined with the path-integral effective classical potential Monte Carlo (PIECP MC) theoretical simulations. From the EXAFS analysis of the Elinvar alloy, the local thermal expansion around Fe is found to be considerably smaller than the ones around Ni and Cr (see Figure 1). This observation can be understood simply because Fe in the Elinvar alloy exhibit an incomplete Invar-like effect. Moreover, in both the Elinvar and SUS304 alloys, the local thermal expansions and the lattice strains around Cr are found to be larger than those around Fe and Ni. From the PIECP MC simulations of both the alloys, the first-nearest neighbor Cr-Fe pair shows extraordinarily large thermal expansion, while the Cr-Cr pair exhibits quite small or even negative thermal expansion. These findings consequently indicate that the lattice strains in both the Elinvar and SUS304 alloys are concentrated predominantly on the Cr atoms. Although the role of Cr in stainless steel has been known to inhibit corrosion by the formation of surface chromium oxide, the present investigation may interestingly suggest that the Cr atoms in the bulk play a hidden new role of absorbing inevitable lattice strains in the alloys.

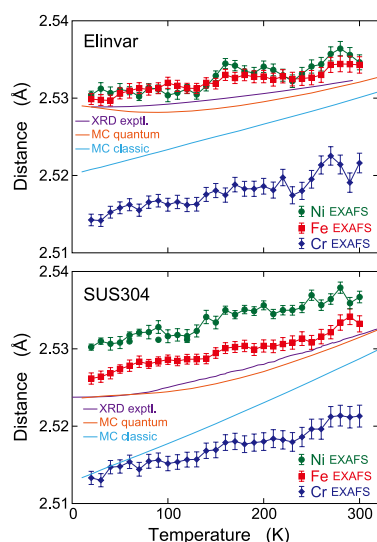


Figure 1. Temperature dependence of the interatomic distances in the Elinvar and SUS304 alloys. The Fe, Ni, and Cr *K*-edge EXAFS analysis are given, together with the results from the powder x-ray diffraction and the calculated results obtained by the present PIECP and the classical MC simulations.

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2. Direct Electric Potential Measurements of Electrode Components in an Operating Fuel Cell by Ambient Pressure XPS²⁾

X-ray Photoelectron spectroscopy is usually utilized to investigate chemical states of the elements of interest in various materials. This technique also has the advantage of providing electric potentials of each component in functional materials without using probe electrodes. We performed operando hard X-ray photoelectron spectroscopy (HAXPES) measurements with an 8 keV excitation source to measure the shift in electron kinetic energies as a function of the voltages of all the components at the anode and cathode electrodes of a polymer electrolyte fuel cell (PEFC). At the cathode electrode, when we increase the voltage between the cathode and anode from 0.2 to 1.2 V, the O 1s and F 1s peaks shift to a lower binding energy and the magnitude of the energy shift is equal to the voltage. The Pt 3d and C 1s peaks do not shift with the voltage since platinum nanoparticles and carbon supports at the cathode electrode have ground contact. In contrast to the cathode electrode, the peak shifts of all the components at the anode electrode show the same amount of shift as the voltages. The results are summarized in Figure 2. It is clear that the change in the potential difference occurs only in an electrical double layer at the interface between the cathode electrode (Pt/C) and the electrolyte (Nafion and water), and that the anode electrode is in equilibrium as a pseudo-hydrogen electrode. It should be noted that the electric potential variation of the cathode electrode in a PEFC under a power generation condition was also directly detected by operando HAXPES, although the electric double layer is a well-established concept but is not easy to observe directly.

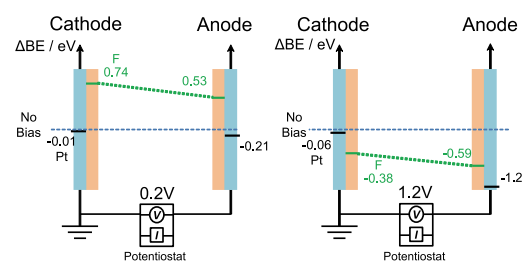


Figure 2. Electric potential diagram of each component in PEFC, where light blue bars correspond to cathode and anode electrodes of Pt (C shows the same potential) and orange to electrolyte Nafion (F and O). At the voltage of 1.2 V between the cathode and anode, a well-known two-step electric double layer is clearly observed (right panel). On the other hand, at 0.2 V, the electrolyte interestingly shows more positive potentials at both the cathode and anode electrodes (left panel).

References

- 1) T. Yokoyama, A. Koide and Y. Uemura, *Phys. Rev. Mater.* **2**, 023601 (2018).
- 2) L. Yu, Y. Takagi, T. Nakamura, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa, G. Samjeské and T. Yokoyama, *Phys. Chem. Chem. Phys.* **19**, 30798 (2017).

Unique Structures, Physicochemical Properties and Quantum Dynamics of Molecular Aggregates at Solid Surfaces

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Awards

2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
2014 39th Vacuum Science Paper Award
2018 PCCP Prize 2018
2018 CSJ Presentation Award 2018
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Keywords

Water Molecule, Molecular Spectroscopy, Surface Science

Materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. In the case of common water ice, protons in the hydrogen-bond network are strongly correlated and highly frustrated under the Bernal-Fowler-Pauling ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton system. It is, however, extremely difficult to directly access the local configuration of protons and their ordering dynamics through traditional experimental approaches. Moreover, the strongly correlated protons inevitably lose ergodicity at low temperature. These problems prevent us from fully understanding cooperative thermodynamic and electric responses of the many-body protons to external stimuli at the low temperature.

To open up a new route to unveil hidden exotic properties of many-body protons in ice, we have investigated a possibility of interface-induced ferroelectric proton ordering by focusing on heteroepitaxially grown crystalline-ice films on metal substrates as model systems. We have used recently

developed phase-resolved sum-frequency generation (SFG) vibrational spectroscopy with heterodyne detection in an ultrahigh vacuum chamber. $\text{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibits positive and negative sign for net-H-up orientation (protons pointing toward vacuum) and net-H-down orientation (toward substrate), respectively. Thus, heterodyne-detected SFG has a great advantage to directly observing local configuration of protons that cannot be investigated through other traditional experimental methods.

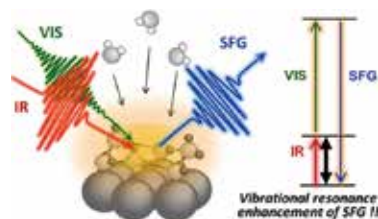


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe and Y. Matsumoto, "Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film," *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji, T. Sugimoto, T. Ishiyama, A. Morita, K. Watanabe and Y. Matsumoto, "Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice," *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, "Origins of Emergent High- T_c Ferroelectric Ordering in Heteroepitaxial Ice Film: Sum-Frequency Generation Spectroscopy of H_2O and D_2O Ice Films on Pt(111)," *Phys. Rev. B* **97**, 075410 (21 pages) (2018).

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1. Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Proton in Ice^{1,2)}

In the hydrogen-bond network of common water ice, protons are strongly correlated and highly frustrated under the ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton systems. Nevertheless, because of the difficulties in directly observing and quantitatively estimating the local configuration of protons and their ordering dynamics with traditional experimental techniques, little has been understood about thermodynamic properties of the protons especially at low temperature, where quantum effects are of potential importance on the emergence of the ordered state deeply hidden under the highly degenerated configurational disorder. Although materials containing strongly correlated and highly frustrated degree of freedom have a potential to exhibit dramatic and unusual response to external stimuli, it has widely been assumed nowadays that inversion-symmetry breaking at heterointerfaces such as crystalline ice films on solid surfaces has no ability to induce protonic ordering.

In contrast to the current belief, we have demonstrated emergent ferroelectric proton ordering in heteroepitaxial ice film on model platinum substrate.^{1,2)} We found such an exotic proton ordering is thermodynamically stable and has an extremely high critical temperature of ~ 170 K (Figure 2). Anisotropic interaction and protolysis driven by electrostatics at the interface is a key factor in stimulating exotic ferroelectric ordering of protons in the many-body correlated proton system. The concept of significant increase in T_c by heterointerface also suggests the ubiquity of ferroelectric ice in nature such as space and polar stratosphere.

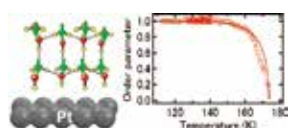


Figure 2. Schematic illustration of net-H-down ferroelectric ordering in ice film on Pt(111) and temperature dependence of the order parameter η normalized by the value at 120 K (red circle).

2. Unveiling Unique Hydrogen-Bond Structure of Ice Surface³⁾

Water ice is one of the most abundant solid substances in nature and its surface plays crucial roles in a variety of processes in physics, chemistry and earth planetary science: Surface premelting for unusual slipperiness in skating and skiing, sublimation and condensation in the atmospheric air and planetary systems, charge generation and separation in thunder cloud, heterogeneous reactions in the Earth's ozone layer and interstellar space, *etc.* Because ice is hydrogen bonded aggregate of water molecules, its surface physico-

chemical properties are dominated not only by the lattice translational structure (position of oxygen atoms) but also by the sublattice structure (orientations of water molecules or configurations of hydrogen atoms) of ice surface.

A surface of solid is not confined to its topmost layer, but consists of transition layers extending to the bulk: Subsurface. As a result of abrupt truncation of materials, the lattice and electronic structures of surface generally differ from those of the bulk, which results in unique physicochemical properties and heterogeneous processes of solid surface. Thus, structural relaxation and reconstruction at solid surface have been intensively studied by low energy electron diffraction, ion and X-ray scattering, and transmission electron microscopy. Although these conventional analytical techniques have been successfully applied to strongly bonded materials: Metals and semiconductors, they cannot be well applied to fragile and insulating solid substances composed of soft molecular systems such as water ice.

To clarify subsurface structure of ice, we have conducted phase-resolved SFG spectroscopy of ice Ih(0001) and analysed the spectra by molecular dynamics simulations combined with *ab initio* quantum calculations.⁴⁾ We found that observed bipolar band shape of the SFG spectra of isotope-diluted OH chromophores is a sensitive indicator of structural rumpling uniquely emerging at the subsurface of ice (Figure 3). In the outermost subsurface between the first (B1) and second (B2) bilayer, the hydrogen bond of $O_{B1}-H\cdots O_{B2}$ is weaker than that of $O_{B1}\cdots H-O_{B2}$. This implies that subsurface O-O distance is laterally altered, depending on the direction of O-H bond along the surface normal: H-up or H-down, which is in stark contrast to bulk hydrogen bonds. This new finding uncovers how water molecules undercoordinated at the topmost surface influence on the subsurface structural rumpling associated with orientational frustration inherent in water ice. The structural rumpling would play key roles in a variety of anomalous physical and chemical properties of ice surface in nature.

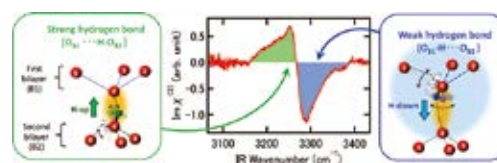


Figure 3. Schematic illustration of subsurface hydrogen-bond network between first and second bilayer of ice-Ih(0001) and the experimentally observed $\text{Im}\chi^{(2)}$ spectrum for the hydrogen-bonded OH-stretching band of isotope diluted ice Ih(0001).

References

- 1) T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Nat. Phys.* **12**, 1063–1068 (2016).
- 2) N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
- 3) O. Yuji, T. Sugimoto, T. Ishiyama, A. Morita, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **96**, 115405 (14 pages) (2017).

Awards

SUGIMOTO, Toshiki; PCCP Prize 2018.

SUGIMOTO, Toshiki; CSJ Presentation Award 2018.

SUGIMOTO, Toshiki; Encouragement Award, The Spectroscopic Society of Japan (2018).

SUGIMOTO, Toshiki; Morino Foundation for Molecular Science (2018).

Magnetic Resonance Studies for Functional Molecular-Based Solids

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Keywords

Organic Conductor, Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR)

Magnetic resonance measurements are advantageous for studying fundamental electronic properties and for understanding the detailed electronic structures of molecular based compounds. Developing an understanding of the electronic phases and functionality of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems and functional materials. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics, and to explore novel functionalities in the field of material science.

In this study, we performed broad-line NMR and ESR measurements on molecular-based conductors to understand electron spin dynamics and functionality in low-temperature electronic phases.

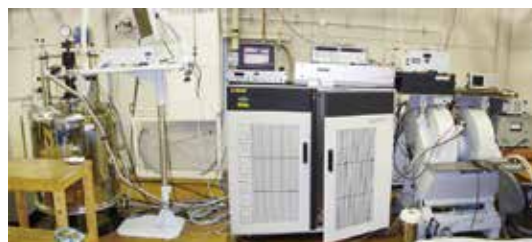
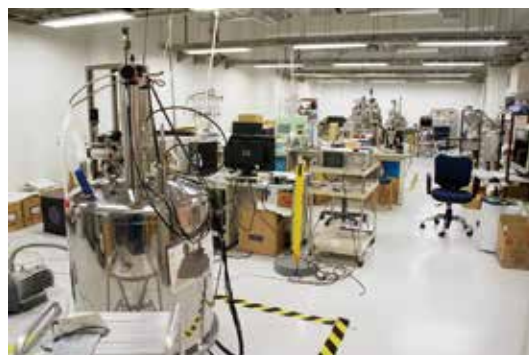


Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- S. Kitou, T. Fujii, T. Kawamoto, N. Katayama, S. Maki, E. Nishibori, K. Sugimoto, M. Takata, T. Nakamura and H. Sawa, *Phys. Rev. Lett.* **119**, 065701 (2017).
- T. E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen and D. Jiang, *Science* **357**, 673–676 (2017).

1. Magnetic Resonance Investigation for Possible Antiferromagnetic Sub-Phase in (TMTTF)₂Br

The ground state of (TMTTF)₂X has been believed to be the C-AF(II) phase in the generalized phase diagram so far. Actually, the electronic state of (TMTTF)₂Br at 4.2 K is clarified as a commensurate antiferromagnetic state with wave vector $Q = (1/2, 1/4, 0)$, and the spin configuration is –up–down–0–. We performed AFMR and ²D-NMR measurement to understand ground state of (TMTTF)₂Br. AFMR measurements shows the increase of the staggered magnetization of the sub-lattice below 4 K. As for ²D-NMR, the nuclear quadrupole relaxation was dominant through electric field gradient. According to the ²D-NMR spectra, the peak number decreases and broad background appear at 4 K, suggesting that charge (spin) configuration changes to inhomogeneous or incommensurate. Considering the AFMR and ²D-NMR experimental results, the possible explanation of 4 K anomaly observed in (TMTTF)₂Br is commensurate to incommensurate successive phase transition. Although the step-like 4 K anomaly observed in AFMR support a homogeneous phase transition, we cannot rule out the possibility of homogeneous effect such as discommensuration state at present. At least, we can say that a phase ϕ change anomaly of antiferromagnetic spin configuration occurs around 4 K. It is also very surprising and intriguing, the sub-magnetic phase detected in the present work appears at a temperature around $T_N/4$. Similarly (TMTSF)₂X salts undergo sub-phases at $T_{SDW}/3$ in which the coexistence between CDW and SDW. Further investigation is ongoing, and supports from theoretical approaches for spin and charge distribution are awaited.

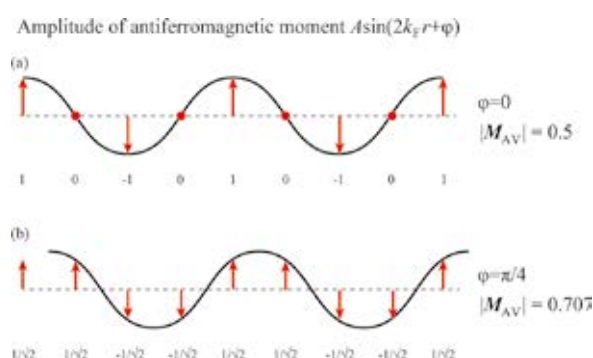


Figure 2. Schematic antiferromagnetic spin configuration for 1/4-filled 1D system along the 1D chain. (a) Spin configuration assuming the antiferromagnetic amplitude follows $A \sin(2k_F r + \phi)$ with $\phi = 0$. The magnetic structure of (TMTTF)₂Br at 4.2 K is thought to have this configuration. (b) Spin configuration assuming $A \sin(2k_F r + \phi)$ with $\phi = \pi/4$.

2. Possibility of Dielectric Material: Nuclear Magnetic Resonance of Oxo-Bridged Dinuclear Ruthenium Mixed-Valence Complex

Since the discovery of mixed-valence compounds such as

the Creutz-Taube type complex, the development of mixed-valence compounds and the spectroscopic study of the mixed-valence state have advanced significantly. Investigations into dinuclear and one-dimensional mixed-valence compounds such as those in the diethylbiferrocenium families and halogen-bridged platinum mixed-valence complexes have been particularly significant. The discovery of one-dimensional partial oxidation mixed valence platinum complexes has led to the development of organic conductor research. As for rare earth mixed valence compounds, the electronic properties of (resonance inner 4f orbitals) have been attracting much attention. These compounds gave us rich and interesting physical phenomena such as heavy fermion, Kondo-lattice, unconventional superconductivity and non-Fermi liquid. Their fundamental characteristics and electronic nature have been clarified through extensive study. On the other hand, along with the progress of recent research, it is also a fact that new and interesting unresolved problems exist as follows. Possible topological Kondo insulators in rare earth mixed valence compounds have been proposed and discussed. Extensive studies have been carried out for electronic phases in exotic systems such as manganite, magnetite, copper oxide, and so on.

However, recent developments of mixed valence phenomena mainly focus on intermetallic compounds and oxides. There are few studies on electronic states in metal complexes and molecular compounds. The recent progress in charge-ordering and multiferroic phenomena in the field of solid-state physics enhances the desire to redevelop interesting materials. Mixed-valence compounds offer interesting characteristics, such as multi-redox potential, spin-multiplet configurations, a variety of possible building blocks, and potential inter-molecular interactions. Moreover, from the viewpoint of material science, materials that can assume unique valence states and magnetic properties are strongly desired. There is growing momentum toward the research and development of mixed-valence compounds from an electronic functionality point of view. We are interested in systems with moderate valence fluctuations, because intermediate valence and spin states are advantageous for use in electromagnetic switching devices.

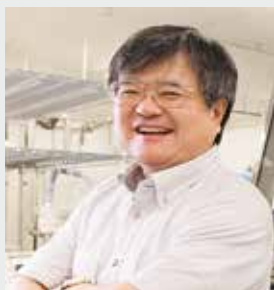
Recently, a series of oxo-bridged dinuclear ruthenium mixed-valence complex was systematically synthesized and characterized in three distinct redox states. We focus on the air-stable $[\text{RuORu}]^{5+}$ ($\text{Ru}^{3+}\text{ORu}^{4+}$) complex, and on a description of its electronic properties.

References

- 1) M. Asada and T. Nakamura, *Phys. Rev. B* **96**, 125120 (6pages) (2017).
- 2) T. Enomoto, M. Kondo, M. Asada, T. Nakamura and S. Masaoka, *J. Phys. Chem. C* **122**, 11282–11287 (2018).
- 3) T. Nakamura, T. Ikoma and K. Yamada, *Appl. Magn. Reson.* **49**, 755–756(2018).

Organic Solar Cells

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Education

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Professional Employment

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Awards

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2006 Research and Education Award, Osaka University
2004 Editor Award, Japanese Journal of Applied Physics

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Keywords Organic Semiconductors, Organic Solar Cells, ppm-Doping

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. We have been focused on the research on the ppm-Level doping effects in organic semiconductor films and organic single crystals for organic solar cells. We believe that the following features are indispensable. (i) A ppm-doping strategy should be performed on sub-ppm purified organic semiconductors together with the total removal of oxygen from the air, which acts as an external dopant. (ii) Perfect *pn*-control, namely, any single or blended organic semiconductors should exhibit either *n* or *p*-type behavior only by impurity doping. (iii) To precisely clarify the nature of the doping effects, ppm doping in the bulk of organic semiconductor single crystals with few grain boundaries should be performed.

So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching 10^{-9} nm s⁻¹ (Figure 1), in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of

open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.

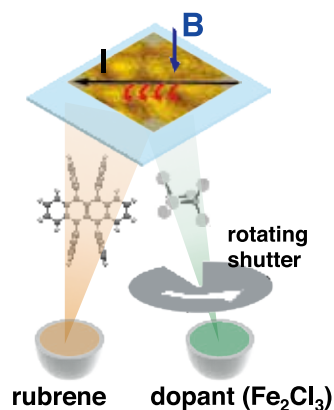


Figure 1. Ultra-slow co-deposition technique to produce the doped rubrene single crystal for Hall effect measurements.

Selected Publications

- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* 1801236 (15 pages) (2018). [Invited Progress Report]
- S. Izawa, N. Shintaku and M. Hiramoto, "Effect of Band Bending and Energy Level Alignment at the Donor/Acceptor Interface on Open-Circuit Voltage in Organic Solar Cells," *J. Phys. Chem. Lett.* **9**, 2914–2918 (2018).
- C. Ohashi, S. Izawa, Y. Shinmura, M. Kikuchi, S. Watase, M. Izaki, H. Naito and M. Hiramoto, "Hall Effect in Bulk-Doped Organic Single Crystal," *Adv. Mater.* **29**, 1605619 (6 pages) (2017).

1. Controlling Open-Circuit Voltage in Organic Solar Cells by Impurity Doping¹⁾

Doping, addition of trace amount of *p*-type and *n*-type impurities, to form the *pn* junction is the central technology in inorganic solar cells. However, the doping effect on the energy-level alignment and the performance in organic solar cells (OSCs) are still unclear. Here, we report that the addition of *p*-type (MoO_3) and *n*-type (Cs_2CO_3) dopants into a donor layer in phthalocyanine/fullerene planar heterojunction OSCs controls the open-circuit voltage (V_{OC}). The V_{OC} decreased to 0.36 V when a *p*-type dopant was added to the donor layer, whereas it increased to 0.52 V with an *n*-type dopant. In contrast to the previous reports where *p*-type dopants were usually added to the donor layer, the *n*-type dopant was found to increase the V_{OC} . Energy-level mapping revealed that the origin of the V_{OC} change was the vacuum level shifts occurring near the donor/acceptor (D/A) interface because of the Fermi-level alignment (Figure 2). The results demonstrated that the V_{OC} s in OSCs are largely affected by the energy-level shift near the D/A interface that could be controlled by *p*-type and *n*-type doping.

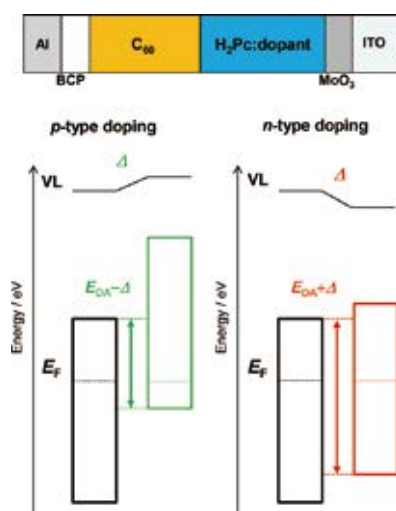


Figure 2. Schematic of the Fermi level alignment at the D/A interface when the phthalocyanine layer is doped with *p*-type and *n*-type dopants.

2. Effect of Trap-Assisted Recombination on Open-Circuit Voltage Loss in Phthalocyanine/Fullerene Solar Cells²⁾

Large energy losses in V_{OC} are still an issue for the photo-conversion efficiency of OSCs. We clarify the relationship between charge recombination and V_{OC} loss for phthalocyanine/fullerene planar heterojunction OSCs. We quantify the V_{OC} loss relative to the charge-transfer state energy by the temperature dependence of V_{OC} . The charge recombination order obtained from impedance measurements indicates the presence of trap-assisted recombination (Figure 3). Our results suggest that the V_{OC} losses are caused by the broad distribution of the tail state near the D/A interface. Thus, reducing the number of trap states near the D/A interface could lead to an increase in V_{OC} .

The present results offer the method to increase the open-circuit voltage of organic solar cells.

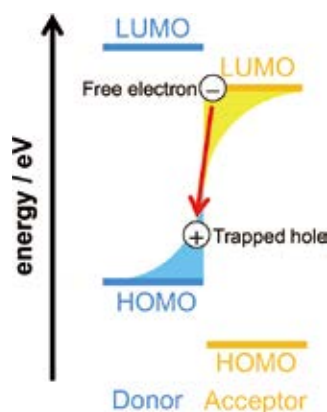


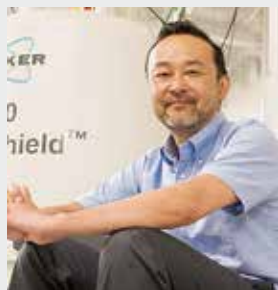
Figure 3. Schematics of the charge recombination process. Trapped holes recombining with free electrons.

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- 2) N. Shintaku, M. Hiramoto and S. Izawa, *Org. Electron.* **55**, 69–74 (2018).

Solid-State NMR for Molecular Science

Department of Materials Molecular Science Division of Molecular Functions



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Education

1994 B.S. Himeji Institute of Technology (University of Hyogo)
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Professional Employment

1999 Postdoctoral Fellow, National High Magnetic Field Laboratory, Florida State University
2001 Assistant Professor, Yokohama National University
2006 Associate Professor, Institute for Molecular Science
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2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

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Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There are varieties of important molecules, which are insoluble to any solvents and functional at amorphous state. Solid-state NMR enables to obtain variety of information at atomic resolution without damages of molecules and significant restrictions. Thus solid-state NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their applications for structural biology and material science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterizations of those molecules based on solid-state NMR are under investigations through collaborations with several research groups.

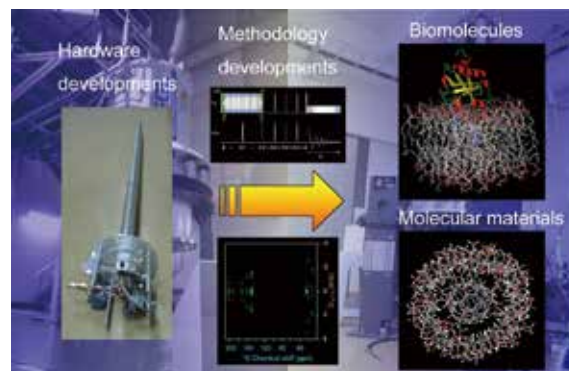


Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C- δ 1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, " ^2H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^1H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β -Sheet Structures by High Resolution ^1H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C- δ 1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).

1. Extractions of Multiple Distance Information among Carbons Simultaneously from Uniformly ^{13}C Labeled Biomolecules Based on Solid-State NMR¹⁾

There are number of organic materials, which are insoluble to any solvent. Solid-state NMR is one of the most powerful tools to provide molecular information for such samples at intact conditions. We have been carried out collaboration studies with many research groups for characterizations of those molecules. We have been collaborated with Prof. Tetsuro Asakura group in Tokyo university agriculture and technology during a couple of years for the characterizations of molecular structure and packing of silk fibroin using solid-state NMR and successfully reported several collaboration works at past.

In this study, applicability of a standard analysis approach developed for proton driven spin diffusion (PDS) to dipolar assisted rotational resonance (DARR) experiment was verified to extract precise distance information simultaneously for uniformly ^{13}C labeled biomolecules. DARR spectra at several mixing times from 10 to 400 ms were acquired for $[\text{U-}^{13}\text{C}]$ Ala tetra peptide microcrystal possessing antiparallel β -sheet structure whose atomic coordinates were determined from X-ray crystallography. Normalized cross peak intensities

among coupled sites were plotted respect to the mixing times. Then the best fit curves were calculated based on two different approaches with and without considering experimentally obtained zero-quantum line shape function. The obtained distances were compared with the ones from X-ray crystallography. The obtained interatomic distances were well fit to the ones from X-ray crystallography in the range of 1.0–6.0 Å with the standard deviation of 0.244 Å, without considering the zero-quantum line-shape functions.

Currently, we are also collaborating with several other research groups for characterizations of natural products, newly designed synthetic polymers, and new molecular materials, based on solid-state NMR.

2. Structural Characterization of Amyloid Peptide Oligomer Promoted on Lipid Bilayers Using Solid-State NMR

Amyloid β ($\text{A}\beta$) peptides exhibit random structures in solution, however after incubation, those conform insoluble amyloid fibrils, which are found in senile plaque as hallmark of Alzheimer's disease. Although, their structures have been characterized precisely, molecular mechanism of formation of the amyloid fibrils in human brain has not been clarified. Accumulated evidences strongly suggest that an initial stage of aggregation may be promoted on surface of neuronal membrane, and ganglioside GM1 specifically interacting with $\text{A}\beta$ may play important roles for the binding of $\text{A}\beta$ to the surface of neuronal membrane.

In current study, to clarify the contribution of GM1 in fibrillation process, we have been attempted to characterize oligomeric structure of $\text{A}\beta(1-40)$ bound to lipid bilayers consisting of GM1 and DMPC. NMR measurements for sequential signal assignments have been completed. Currently, additional ^{13}C through space homonuclear correlation spectra are under measurements for the sample whose 4 types of amino-acid residues are selectively ^{13}C enriched to verify validity of signal assignments obtained from the analyses of various ^{13}C homonuclear and ^{13}C - ^{15}N heteronuclear correlation spectra. In addition, correlation peaks among remote sites in ^{13}C through space homonuclear correlation spectra are under investigation to clarify intermolecular packing of $\text{A}\beta(1-40)$.

Currently, we are also collaborating with other research groups for characterizations of amyloid fibrils using solid-state NMR.

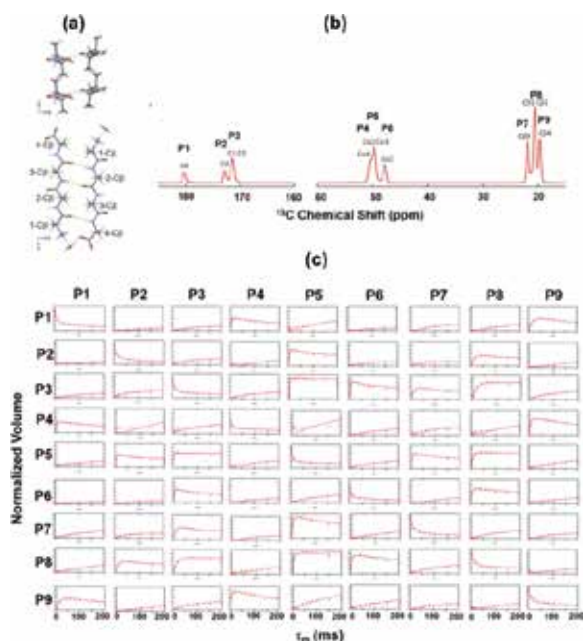


Figure 2. (a) X-ray crystallographic structure and (b) the ^{13}C CP/MAS spectrum of $[\text{U-}^{13}\text{C}]$ AP- β -Ala₄. The bold numbers in (b) correspond to the numbers of the following matrix element numbers. (c) Build-up curves of AP- β -Ala₄ observed with DARR. The numbers shown for the peaks observed and labeled in (b).

Reference

- 1) A. Naito, K. Okushita, K. Nishimura, G. S. Boutis, A. Aoki and T. Asakura, *J. Phys. Chem. B* **122**, 2715–2724 (2018).

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

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Education

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

Professional Employment

2010 Postdoctoral Fellow, Tokyo Institute of Technology
2011 Assistant Professor, Kanagawa University
2012 JST-PRESTO Researcher (Additional post)
2013 Research Associate Professor, Institute for Molecular Science
2018 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards

2010 ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011 Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018 The 39th Honda Memorial Young Researcher Award, The Honda Memorial Foundation

Member

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IMAI, Yumiko
KUBOTA, Akiko
NISHIKAWA, Masako
Secretary
SUZUKI, Ai

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.

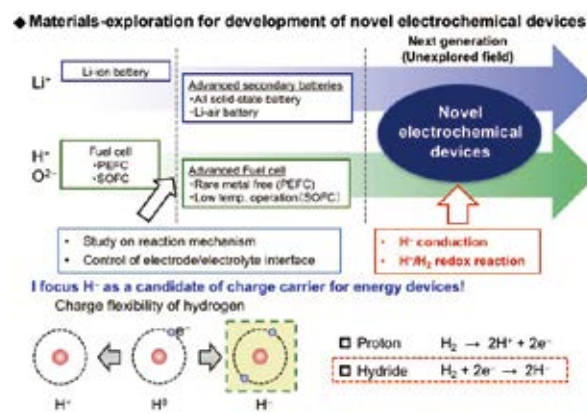


Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

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_3FePO_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).
- A. Watanabe, G. Kobayashi*, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**(2), 88–92 (2017).

1. Synthesis of H⁻ Conductive Oxyhydrides¹⁻⁶⁾

Ionic charge carriers include a variety of species, such as Li⁺, H⁺, Ag⁺, Cu⁺, F⁻, and O²⁻, 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⁻/H₂ (−2.3 V) which is close to that of Mg/Mg²⁺ (−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 K₂NiF₄-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⁻, O²⁻, and vacancies. An all-solid-state Ti/La_{2-*x-y*}Sr_{*x+y*}LiH_{1-*x+y*}O_{3-*y*}/TiH₂ 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.

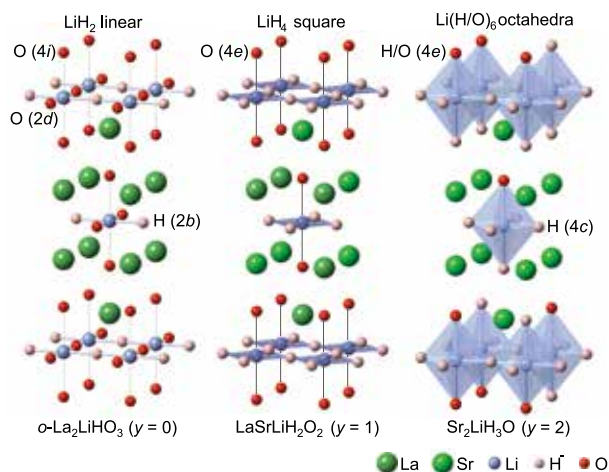


Figure 2. Crystal structures of H⁻ conductive oxyhydrides La_{2-*x-y*}Sr_{*x+y*}LiH_{1-*x+y*}O_{3-*y*} (*x* = 0, *y* = 0, 1, 2). Lanthanum (and strontium) ions occupy the A sites of the layered perovskite-type structure (A₂BX₄) that are 12-fold coordinated with anions. Lithium occupies the B site that 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 Al₂O₃-Based Surface Modification and Stepwise Pre-Cycling⁷⁾

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 Al₂O₃-coated Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ 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_{*x*}O₂ (*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}]O₂ particles (Figure 3). The cycling performance of the Li-rich layered oxide was enhanced by the surface modification with Al₂O₃. 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.

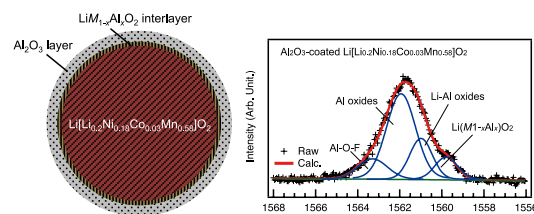


Figure 3. Schematic illustration and Al 1s HAXPES spectra of the 2 wt% Al₂O₃-coated Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O₂ particle. The observed data, the calculated results, and the background are shown as black crosses and red, blue, and green lines, respectively.

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- 1) F. Takeiri, A. Watanabe, H. Nawaz, N. I. P. Ayu, M. Yonemura, T. Ogawa, A. Kuwabara, R. Kanno and G. Kobayashi*, under revision.
- 2) G. Kobayashi*, A. Watanabe, N. I. P. Ayu, B. Miao, Y. Hinuma, Y. Noda, A. Kubota, F. Takeiri, M. Yonemura, N. Shibata, I. Tanaka and R. Kanno, under revision.
- 3) N. Matsui, G. Kobayashi*, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno*, *J. Am. Ceram. Soc.*, in press.
- 4) Y. Iwasaki, N. Matsui, K. Suzuki, Y. Hinuma, M. Yonemura, G. Kobayashi, M. Hirayama, I. Tanaka and R. Kanno*, *J. Mater. Chem. A*, in press.
- 5) A. Watanabe, G. Kobayashi*, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85**, 88–92 (2017).
- 6) 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).
- 7) 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).

Award

KOBAYASHI, Genki; The 39th Honda Memorial Young Researcher Award (2018).

Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

Safety Office



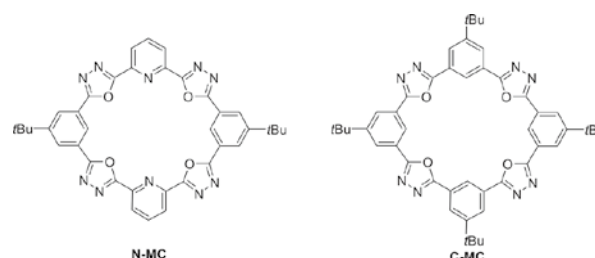
TOMURA, Masaaki
Assistant Professor

Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional organic materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form unique molecular assemblies. In this project, novel functional organic materials based on various heterocycles were synthesized and their physical and structural properties were investigated.

1. Synthesis and Crystal Structure of a Novel Macrocyclic Compound for a Supramolecular Nanotube¹⁾

The novel macrocyclic compound (N-MC) was synthesized as a nitrogen analog of a macrocyclic compound (C-MC).

The crystal structure of N-MC was investigated by an X-ray crystallographic analysis, and the crystal was characterized by a step-like columnar structure, which is different from the supramolecular nanotube structure of C-MC. The molecular framework and the number of *tert*-butyl groups affected the molecular arrangement in the crystal.



Reference

- 1) K. Ono, S. Karasuda and M. Tomura, *Heterocycles* **94**, 2209–2214 (2017).

Multifunction Integrated Macromolecules for Molecular-Scale Electronics

Safety Office



TANAKA, Shoji
Assistant Professor

Recently a single electron tunnel device (SET) has attracted much attention as an ultra-low-power device. In this project, to establish an innovative fabrication process for SET systems, we have been developing step-wise synthetic protocols for mono-molecular single-electron tunnel devices and their integrated circuits (MOSET IC).

1. Efficient Step-Wise Chain Extension of Rigid-Rod Linkers for Molecular Framework

We have developed an efficient synthetic route for step-wise chain extension of rigid-rod linkers (1-4). Figure 1 illustrates the synthetic scheme. In Sonogashira reactions, the removal of diacetylene by-product is frequently time consuming, but in our scheme, the separation is easy based on the difference in polarity of the silyl protecting groups.

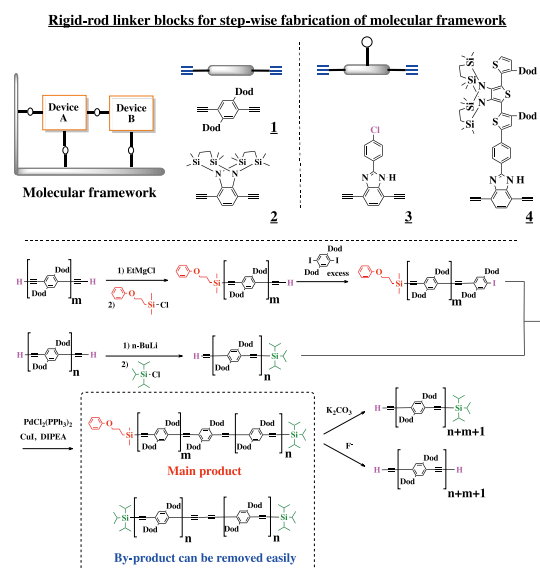


Figure 1. Representative synthetic scheme for step-wise chain extension of building blocks 1-4.

Visiting Professors



Visiting Professor

NAKAMURA, Masakazu (*from Nara Institute of Science and Technology*)

Giant Seebeck Effect in Pure π -Conjugated Molecular Solids

The Seebeck effect is a phenomenon where a voltage appears in a material with temperature gradient. Its origin has been generally understood by the transport coefficients of charge carriers under electric field and temperature gradient where the charge–vibration interaction is included only as ‘scattering.’ We found that irregularly large Seebeck coefficients appear in thin films of pure π -conjugated molecules, of which magnitude is 100 times larger than the prediction by the conventional theory. A strong charge–vibration coupling is considered to be the driving force of the giant Seebeck effect (GSE). Recently, the GSE was first observed also in single crystals of π -conjugated molecules and was confirmed to vanish by increasing carrier concentration under light irradiation. Experimental and theoretical studies are under progress. The GSE is also interesting from an application point of view because it possibly produces revolutionary simple thermoelectric generators being free from the series connection of hundreds of p- and n-type blocks.



Visiting Professor

TAJIMA, Naoya (*from Toho University*)

Quantum Transport Phenomena in Molecular Massless Dirac Fermion Systems

We have discovered first bulk (multilayered) two-dimensional massless Dirac fermion systems in an organic conductor α -(BEDT-TTF)₂I₃ under pressure. This system shows next to the charge ordered insulating phase on the temperature–pressure phase diagram. Thus, this system provides a testing ground for the investigation of physical phenomena in strongly correlated Dirac particles. In this work, we develop the field effect transistor channeled by this system and then aim at the detection of (fractional) quantum Hall effect and new type of quantum phenomena.