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 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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Education

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Professional Employment

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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 2014, we successfully exploited near ambient pressure (up to ~5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8, and in 2017 eventually we have succeeded in real ambient pressure (100,000 Pa) HAXPES measurements. 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. Fast time resolved XAFS measurement is difficult since the repetition frequencies of probe SR and pumping lasers are usually far different, requiring pulse picking of the SR probe and resultantly time resolved detection of only energy-integrated x-ray fluorescence. To detect energy- resolved x-ray fluorescence, a picosecond laser with high repetition rate (up to 1 MHz) was installed in Photon Factory Advanced Ring with single bunch operation (794 kHz). This allows us to investigate XAFS of low concentration elements using a slow but energy-resolved x-ray fluorescence detector.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Takagi *et al.*, *Appl. Phys. Lett.* **105**, 131602 (2014).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Wakisaka *et al.*, *Phys. Rev. B* **92**, 184408 (2015).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).

1. X-Ray Photoelectron Spectroscopy under Real Ambient Pressure Conditions[1)]

We have successfully developed a real ambient pressure (10^5 Pa) hard X-ray photoelectron spectroscopic system equipped with a differential pumping system at beamline BL36XU of SPring-8 for the first time in the world. Photoelectron spectra from gold single crystal were recorded using excitation light of 8 keV focused to 20×20 μm^2 and adopting an aperture diameter of 30 μm at the entrance of the electron lens (see Figures. 1(a)–(c)) and a working distance of 60 μm (see Figure 1(d)). The Au 4f and $3d_{5/2}$ spectra were successfully measured by increasing the ambient pressure from 1 Pa to atmospheric pressure as shown in Figure 2 and demonstrated that the instrument is capable of measuring the photoelectron spectrum under atmospheric pressure.

The kit shown in Figure 1 allows us to keep the high vacuum pressure in the electron energy analyzer and the ambient pressure at the sample surface. Figure 2 clearly exemplifies successful observation of the photoelectron spectra at 10^5 Pa. The present system is widely applicable to various kinds of investigations as fuel cells under real working conditions, solid/liquid/gas interfaces, ambient pressure chemical reactions *etc*.

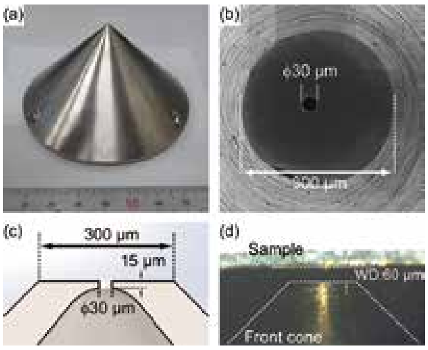

Figure 1. (a) Front cone of the electron energy analyzer. (b) Scanning electron microscope image of the aperture shaped at the top of the front cone. (c) Schematic diagram of the cross section of the aperture. (d) CCD microscopic image of the sample and the front cone at a WD of 60 μm.

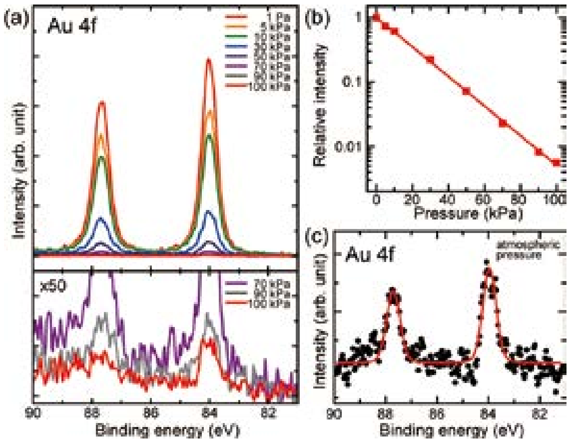

Figure 2. (a) Au 4f spectra recorded using 7.94 keV X-rays at pressures of 1 to 10^5 Pa. (b) Relative intensity of Au $4f_{7/2}$ as a function of pressure. (c) Background subtracted Au 4f recorded at 10^5 Pa.

2. Capturing Local Structure Modulations of Photoexcited $BiVO_4$ by Ultrafast Transient XAFS[2)]

$BiVO_4$ is a promising material for fabricating practically useful photocatalysts and photoelectrodes, exhibiting a bandgap of ~2.5 eV and having the potential to excite electrons from the valence band to the conduction band and to form valence band holes by absorbing visible sunlight. In this work, ultrafast excitation of photocatalytically active $BiVO_4$ was characterized by femto- and picosecond transient X-ray absorption fine structure (XAFS) spectroscopy.

Figure 3 shows the transient Bi L_3-edge XAFS and their time dependence. An initial photoexcited state changed to a metastable state (<<500 fs) accompanied by a structural change with a time constant of ~14 ps. The structural change might stabilize holes on oxygen atoms since the interaction between Bi and O increases. A proposed diagram of the photoexcitation process of $BiVO_4$ is shown in Figure 4.

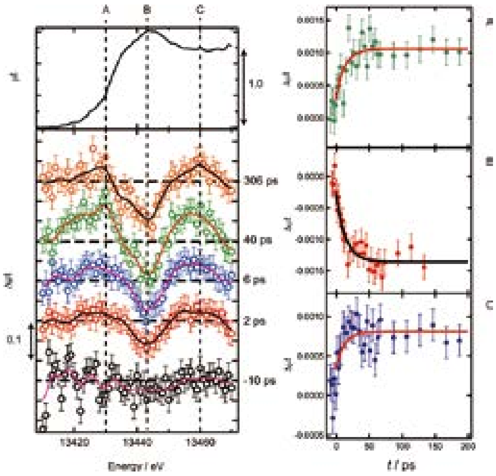

Figure 3. (Left) Bi L_3-edge XAFS spectra of the ground state (top) and the difference spectra of the excited states after the given delay times. (Right) Changes in X-ray absorption intensities at points A, B, and C.

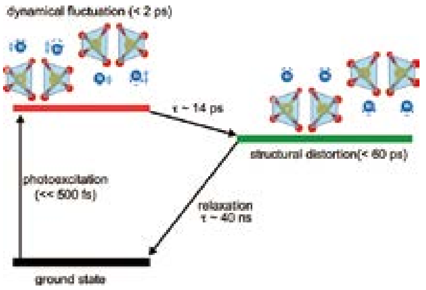

Figure 4. A proposed diagram of the photoexcitation process of $BiVO_4$.

References

1) Y. Takagi, T. Nakamura, L. Yu, S. Chaveanghong, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama, *Appl. Phys. Express* **10**, 076603 (2017).

2) Y. Uemura, D. Kido, A. Koide, Y. Wakisaka, Y. Niwa, S. Nozawa, K. Ichiyanagi, R. Fukaya, S. Adachi, T. Katayama, T. Togashi, S. Owada, M. Yabashi, K. Hatada, A. Iwase, A. Kudo, S. Takakusagi, T. Yokoyama and K. Asakura, *Chem. Commun.* **53**, 7314–7317 (2017).

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.

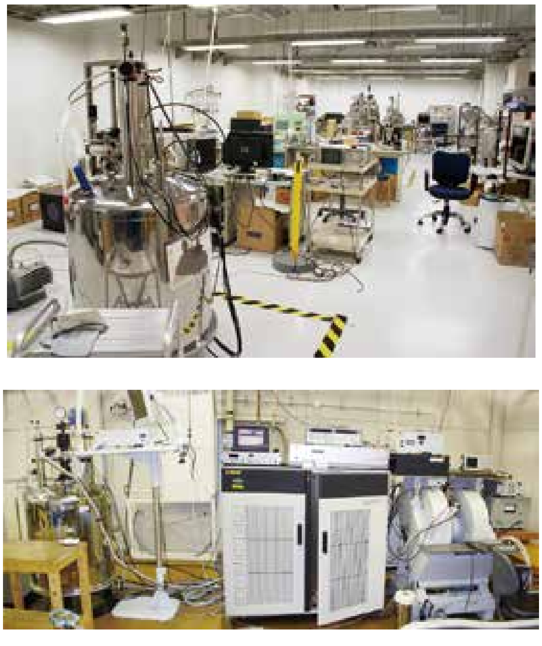


Figure 1. Solid-state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- T. Nakamura, K. Furukawa, T. Terauchi and Y. Kobayashi, "Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate," *Phys. Status Solidi RRL* **9**, 480–484 (2015).
- M. Yoshida, M. Kondo, T. Nakamura, K. Sakai and S. Masaoka, "Three Distinct Redox States of an Oxo-Bridged Dinuclear Ruthenium Complex," *Angew. Chem., Int. Ed.* **53**, 11519–11523 (2014).

1. Magnetic Investigation of Iodine-Doped COF (Covalent-Organic-Framework)

COF materials are pours crystalline materials, which attract much attention because of their functionalities. We investigated the photoconduction mechanism by time-resolved ESR.1) Recently a two-dimensional (2D) crystalline covalent organic framework (sp^{2}c-COF) that is fully π-conjugated and constructed from all sp^2-carbons by C=C condensation reactions of tetrakis(4-formylphenyl)pyrene and 1,4-phenylenediacetonitrile.2) The sp^{2}c-COF can be chemically oxidized with iodine, and the generated radical spins are on the pyrene skeletons. To investigate the electronic states down to low-temperatures, we performed ESR and SQUID measurements for the 2D sp^{2}c-COF. An ESR signal appeared at $g = 2.003$, just after iodine doping. The ESR linewidth and g-values were almost constant regardless of the doping level. The ESR linewidth of 1.3 Gauss is narrow. The significant increase of ESR intensity indicates that high concentration spin injection realized. The χ_{spin} determined by ESR and SQUID measurements indicates the existing spin freedom down to the low temperature. Curious low-temperature behavior of spin system is also discussed.

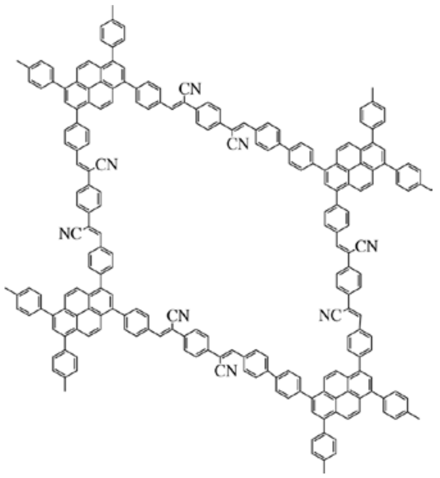


Figure 2. Molecular structure of sp^{2}c-COF.

2. Low-Temperature Electronic Phases in One-Dimensional Organic Conductors (TMT*C*F)$_2$*X*

One-dimensional conductors based on (TMTCF)$_2X$ (C = S, Se) are some of the most extensively studied materials among organic conductors. They possess various ground states including the spin-singlet (SS), commensurate antiferromagnetic state (C-AF), incommensurate spin density wave (IC-SDW) and superconductivity (SC), with applied pressures or counter anions, X. Moreover, findings of charge-ordering (CO) and related phenomena in (TMTTF)$_2X$ have attracted significant recent attention.

(TMTTF)$_2MF_6$ shows successive phase transitions as the temperature decreases. In paramagnetic region, these salts undergo a charge-ordering phase transitions. With synchrotron x-ray diffraction, we directly observed a slight structural difference owing to the effect of charge-order transition between two TMTTF molecules in a dimer for (TMTTF)$_2$PF$_6$.3) The charge distribution is estimated as 0.20e, which is close to that observed in NMR.

(TMTTF)$_2$Br undergoes antiferromagnetic transition at 16 K (T_{N}). But it is located on the proximity between C-AF and IC-SDW phase in the generalized phase diagram. To understand the electronic states on the boundary region between the commensurate antiferromagnetic phase and the incommensurate spin-density-wave (IC-SDW) phase in the generalized phase diagram for 1D organic conductors, we performed antiferromagnetic resonance (AFMR) and nuclear magnetic resonance (NMR) measurements for (TMTTF)$_2$Br. The angular dependence of the AFMR fields at 1.5 K is different from that at 4.8 K, and the temperature dependence of the two AFMR modes is enhanced below 5 K. Furthermore, ^{2}D-NMR measurements were performed to investigate charge distribution by quadrupole splitting at low temperatures. We found that the ^{2}D-NMR spectrum changes at ~4 K in the antiferromagnetic phase. Successive phase transition and a possible magnetic structure are discussed.

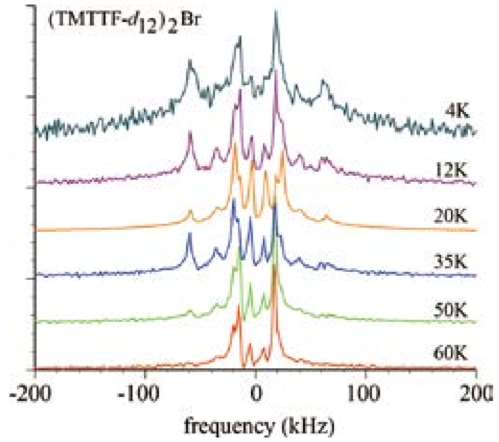


Figure 3. Temperature dependence of the ^{2}D-NMR spectra for deuterated (TMTTF)$_2$Br. Each spectrum is composed of several doublets because of quadrupole splitting.

References

1) S. Jin, M. Supur, M. Addicoat, K. Furukawa, L. Chen, T. Nakamura, S. Fukuzumi, S. Irle and D. Jiang, *J. Am. Chem. Soc.* **137**, 7817–7827(2015), and references therein.

2) 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).

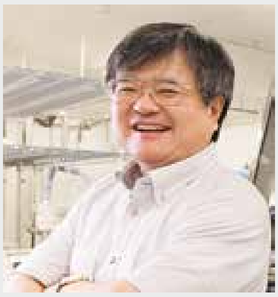
3) S. Kitou, T. Fujii, T. Kawamoto, N. Katayama, S. Maki, E. Nishibori, K. Sugimoto, M. Takata, T. Nakamura and H. Sawa, *Phys. Rev. Lett.* **119**, 065701 (2017).

Award

NAKAMURA, Toshikazu; The 22nd Outstanding Paper Award of the Physical Society of Japan (2017).

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions



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Education

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Professional Employment

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Awards

2017	11th JSAP Fellow Awards
2006	Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
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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 establishment of "bandgap science for organic solar cells." We believe that the following features are indispensable. (a) Organic semiconductors purified to sub-ppm level, at least seven nines (7N; 0.1 ppm), should be used. (b) A ppm-level doping technique should be developed. (c) Every individual organic semiconductor should be capable of displaying both *n*- and *p*-type characteristics by impurity doping alone, *i.e.*, complete *pn*-control should be developed. (d) Unintentional and uncontrollable doping by oxygen and water from air should be completely eliminated. (e) The doping technique should be applicable not only to single organic semiconductor films, but also to codeposited films consisting of two kinds of organic semiconductors since a key element for exciton dissociation in organic solar cells is having a co-deposited films.

Recently, we have showed that in principle, almost all single organic semiconductors can be controlled to both *n*-type and *p*-type by doping alone, similar to the case of inorganic semiconductors (Figure 1). This can be regarded as a foundation for the construction of high efficient organic solar cells.

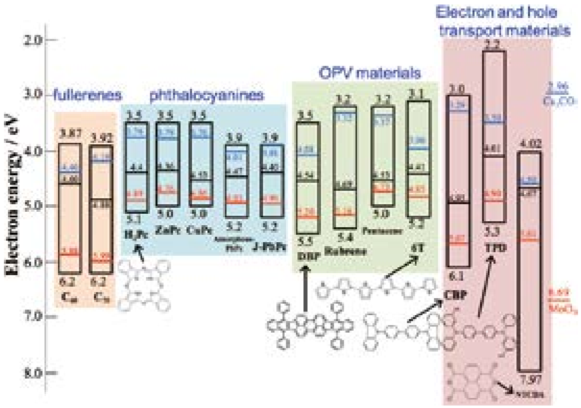

Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100 nm) are also shown.

Selected Publications

- 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).
- C. Ohashi, Y. Shinmura, M. Kubo and M. Hiramoto, "ppm-Doping Effects in the Simplest n^+p-Homojunction Organic Photovoltaic Cells," *Org. Electron.* **27**, 151–154 (2015).
- M. Hiramoto, M. Kubo, Y. Shinmura, N. Ishiyama, T. Kaji, K. Sakai, T. Ohno, M. Izaki and M. Hiramoto, "Bandgap Science for Organic Solar Cells," *Electronics* **3**, 351–380 (2014).

1. Hall Effect in Doped Organic Single Crystals

Control of *p*-type and *n*-type that holes and electrons are responsible for electric conduction, respectively, by the addition of a trace amount of impurity (doping) is the central technology in 20 century's inorganic single crystal electronics as represented by the silicon chips, the solar cells, and the light emitting diodes. The number of carriers created by doping and their moving speed (mobility) can be freely evaluated by Hall effect measurement using a magnetic field. However, in the field of organic electronics emerging in 21 century, no one has attempted not only to dope impurities into the organic single crystal itself but also the Hall effect measurement.

We combined the rubrene organic single crystal growth technique with the our original ultra-slow deposition technique of one billionth of a nanometer (10^{-9} nm) per second, which includes a rotating shutter having aperture, and have succeeded in producing the 1 ppm doped organic single crystal and in detecting the Hall effect signal for the first time (Figures 2 and 3). As an acceptor dopant, iron chloride (Fe_2Cl_6) was used.

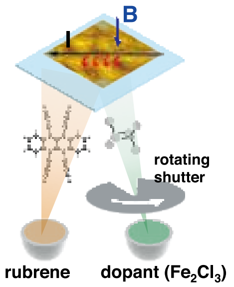

Figure 2. Ultra-slow co-deposition technique to produce the doped rubrene single crystal. Magnetic field (B) and excitation current (I) for Hall effect measurements are also shown.

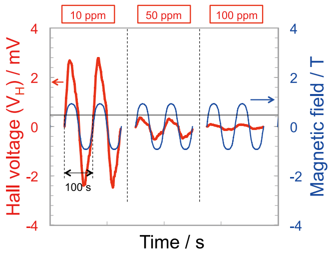

Figure 3. Hall voltage signals (red) observed under the application of AC magnetic field (blue) for the 50-, 100-, 500-, and 1000-ppm doped devices.

Hall voltage (V_H) signals were detected when applying a magnetic field to the $FeCl_3$-bulk-doped homoepitaxial layer (Figure 3). V_H showed a systematic decrease for the 50-, 100-, 500-, and 1000-ppm doped devices, respectively. This is due to the increase in the hole concentration (N) (Figure 4(a), red).

Two unique observations were observed for the doped single crystals.

(i) High ionization rate of dopant molecules: The doping efficiencies of a single crystal and amorphous films of rubrene were compared. The rubrene single crystal reached a maximum value of 24% at 100 ppm (Figure 4(b), red), which was significantly larger than the value of 1.2% for the amorphous film that formed from vacuum deposition (Figure 4(b), blue). We presume that the ionization rate was dominated by the density of hole traps.

(ii) Scattering effects from lattice disturbances: The Hall mobility (μ_H) decreased above 10 ppm (Figure 4(c)). We think that this could be attributed to hole scattering by doping-induced lattice disturbances, such as lattice distortion from the substitution of rubrene molecules with ionized and neutral dopant molecules, and the formation of various types of defects, such as dopants that were inserted at interstitial positons, the formation of doping-induced vacancies, *etc*.

The present results have the meaning of dawn of organic single crystal electronics similar to the silicon single crystal electronics. In future, organic single crystal devices such as high performance organic single crystal solar cells would be developed.

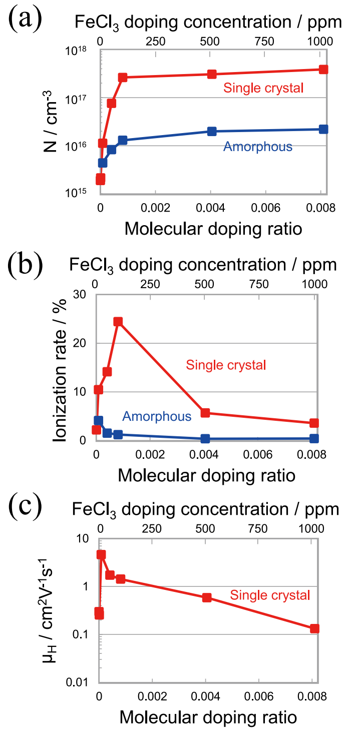

Figure 4. Dependences of (a) the hole concentration per unit volume (N), (b) the ionization rate, and (c) the Hall mobility (μ_H) on the molecular doping ratio (MR) and the $FeCl_3$ doping concentration by volume for doped single crystal (red curves). For comparison, the results for N and the ionization rate for vacuum deposited amorphous films are also shown (blue curves).

Award

HIRAMOTO, Masahiro; 11th JSAP Fellow Awards (2017).

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* IMS International Internship Program

Solid-State NMR for Molecular Science

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Education

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Professional Employment

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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.

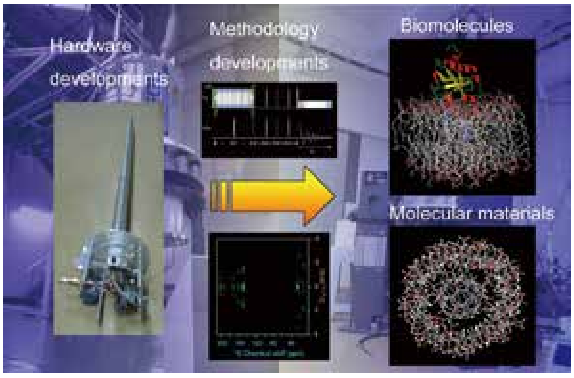

Figure 1. Outline of our studies.

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-δ1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, "^{2}H 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 ^{1}H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β-Sheet Structures by High Resolution ^{1}H 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-δ1 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. Characterization of Supramolecular Structure Based on Solid-State NMR[1)]

We have been collaborated with Prof. Eiji Yashima group in Nagoya university during a couple of years for the characterization of supramolecules developed in their research group. They have successfully reported that syndiotactic poly methyl methacrylate (st-PMMA) can hold into a preferred handed-helical conformation with an inner cavity in toluene in the presence of an optically active alcohol or amine accompanied by gelation. They have been explored to develop a strategy to encapsulate a helical peptide attached to C_{60} into the helical cavity of st-PMMA.

In this study, we have attempted to reveal the formation of inclusion complex composed of those molecules using solid-state NMR. Based on ^{13}C cross polarization magic angle spinning (CPMAS) and two-dimensional (2D) ^{1}H-^{13}C heteronuclear correlation (HETCOR) spectra at short contact time (CT) for st-PMMA, peptide-C_{60} and their complex, ^{1}H and ^{13}C signals were successfully assigned. Then 2D ^{1}H-^{13}C HETCOR spectra were acquired with various appropriate long CTs to obtain long distance correlations. With use of Lee-Goldburg (LG) ^{1}H homonuclear dipolar decoupled CPMAS at CT of 2.0 ms, ^{1}H-^{13}C correlations up to 4 Å apart may be detected.

Inter- and intra-molecular correlation peaks were observed in 2D ^{1}H-^{13}C HETCOR spectrum for peptide-C_{60} at CT of 2.0 ms between ^{1}H signals of peptide moieties and ^{13}C signals of C_{60}-moieties, suggesting random orientation of peptide-C_{60} in sample as shown in Figure 2(b). In contrast, apparent intermolecular correlation peaks between ^{1}H signals of methylene and methoxy groups of st-PMMA and ^{13}C signals of the C_{60} moieties were successfully observed in 2D ^{1}H-^{13}C HETCOR spectrum for complex at same CT as shown in Figure 2(c). On the other hand, the methylene and the methoxy groups in helical st-PMMA locate inside of helical cavity, in contrast to the methyl group locating out side of helical cavity of st-PMMA. Those experimental evidences are consistent when peptide-C_{60} is encapsulated into helical cavity of st-PMMA. Therefore, based on those analyses, formation of inclusion complex composed of those molecules was clearly proved.

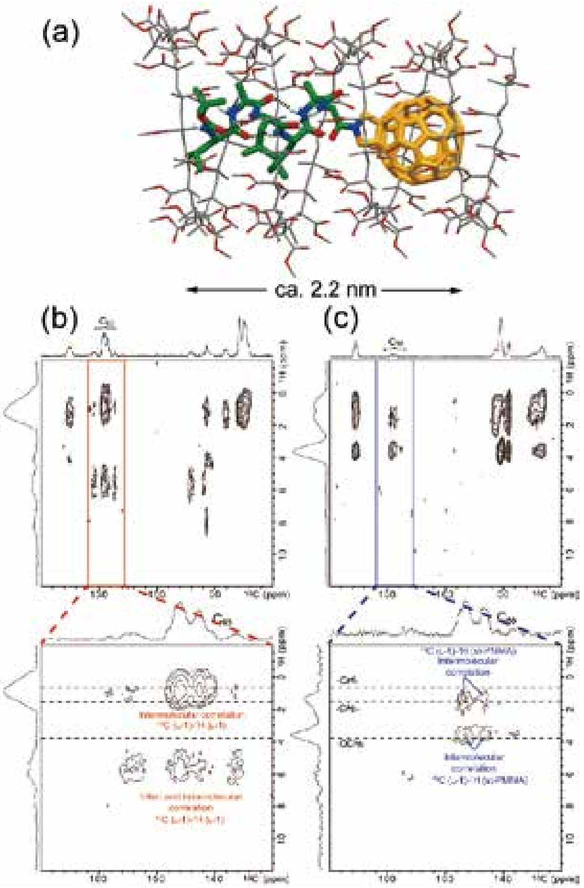

Figure 2. (a) Energy minimized supramolecular structure of st-PMMA/peptide-C_{60} inclusion complex. 2D solid-state NMR spectra of ^{1}H-^{13}C-heteronuclear correlation with LG-CPMAS at CT of 2.0 ms for (b) peptide-C_{60} and (c) complex, respectively.

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

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

Amyloid β (Aβ) 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 Aβ may play important roles for the binding of Aβ to the surface of neuronal membrane. We have successfully determined oligomeric structure of Aβ(1-40) bound to the lipid bilayers consisting of neutral lipid of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) using solid-state NMR as reported in last year.[2)]

In current study, to clarify the contribution of GM1 in fibrillation process, we have been attempted to characterize oligomeric structure of Aβ(1-40) bound to lipid bilayers consisting of GM1 and DMPC. Sample preparation procedures were optimized to enhance spectral sensitivity and ^{13}C homo- and ^{13}C-^{15}N hetero-nuclear correlation spectra were acquired for sequential signal assignments. Currently, data is under investigation.

References

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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. A Novel Synthesis of Halogenated Oxa[9]helicenes and Dibromo Spiro-Lactone Derivative[1)]

A new class of halogenated oxa[9]helicene derivatives along with dibromo spiro-lactone were synthesized in excellent yields, and the compounds were successfully characterized by ^{1}H and ^{13}C NMR, high resolution mass spectroscopy and X-ray crystallographic analysis.

2. X-Ray Crystallographic Analyses of Heterocyclic and Organometallic Compounds[2,3)]

The X-ray crystallographic analyses of two heterocyclic and organometallic compounds have revealed their interesting structural natures and unique molecular aggregations.

References

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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. Development of Rigid-Rod Linkers for Mono-Molecular Integration of Quantum-Effect Device Modules

We have established the synthetic methods for typical **SET** modules based on building blocks (**1**). In this study, we developed rigid-rod linkers (**2-9**) for precise alignment of the device modules in single molecular skeleton. Figure 1 illustrates our synthetic strategy.

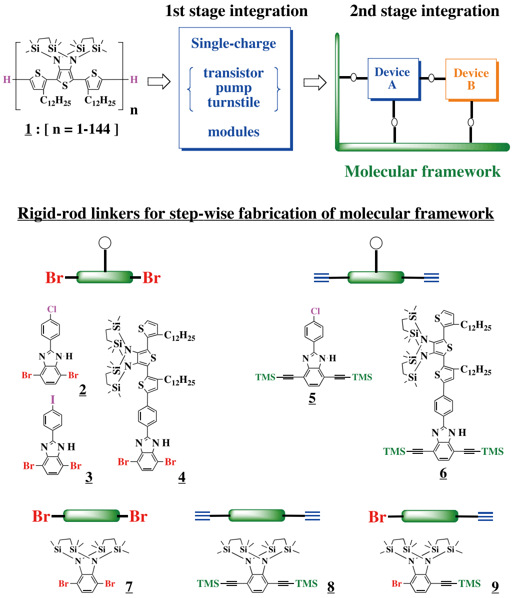

Figure 1. Synthetic strategy for precise integration of device modules.

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 well-known phenomenon where a voltage appears in a material with temperature gradient. The origin of the Seebeck effect has been generally explained by the transport coefficients of charge carriers under electric field and temperature gradient using the linear response theory where the interaction between carrier and phonon is included only as a rare event called ‘scattering.’ Recently, our group found that irregularly large Seebeck coefficients appear in pure π-conjugated molecular solids at a near room temperature range, of which magnitude is a hundred times larger than the prediction by the conventional theory. A strong charge-vibration coupling in molecular solids is considered to be a driving force of this phenomenon and both experimental and theoretical studies are under progress. Such a large Seebeck coefficient 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 found two dimensional massless Dirac fermion systems in an organic conductor α-(BEDT-TTF)$_2$I$_3$ under pressure. In contrast to graphene, this is the first bulk (multilayered) massless Dirac fermion system. Moreover, this massless Dirac fermion phase is close to the charge ordered insulating phase on the pressure–temperature phase diagram. Thus, this system provides the 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.

Visiting Associate Professor
YOSHIKAWA, Hirofumi *(from Kwansei Gakuin University)*

Development of Rechargeable Batteries Using Coordination Compounds as Cathode Materials

Recently, much attention has been focused on development of high-performance rechargeable batteries due to the global energy and environmental problems. Our research interest is to find novel cathode materials toward the next-generation rechargeable battery with a high capacity, a stable cycle performance, a rapid charging, and so on. We have examined battery performances of various organic and inorganic materials, which could take the place of the present general cathode materials, $LiCoO_2$ and $LiFePO_4$. Among various materials, porous redox-active coordination compounds are promising since they have an ionic conductive space and a robust structure. To realize a high capacity, a good cycle performance, and a rapid charging, we develop porous polyoxometalates and metal organic frameworks, and examine their battery performances. We also try to prepare their nanoparticles to increase electrochemical performances. Finally, we reveal these electrochemical reaction mechanism by using operando XAFS, XRD, solid-state NMR *etc.* and the obtained information is utilized to investigate new materials with high battery performances.