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.

Exploitations of Novel Spectroscopic Methods for Material and Surface Science

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Division of Electronic Structure

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Professional Employment

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Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism

For the developments of novel functional materials, it is quite important to exploit new characterization methods based on advanced technology simultaneously. 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 synchrotron radiation and lasers.

The first topic is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism photoelectron emission microscopy, 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 a ultrahigh vacuum superconducting magnet and a liq. He cryostat. The XMCD apparatus is widely open for public usage and many researchers even from abroad visit every year. We are currently interested in metal phthalocyanine monolayers on nonmagnetic and ferromagnetic surfaces, whose electronic and magnetic properties are tunable by changing the central metal atom and/or modifying the ligand. Our recent achievement concerning vanadyl phthalocyanine will be presented in the next page.

The second topic is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (XPS) for polymer electrolyte fuel cells (PEFC) under working conditions. We have successfully installed ambient pressure (up to 3000 Pa) hard x-ray photoelectron spectrometer (Figure 1). We have designed in situ fuel cells under working conditions and have successfully recorded Pt 3d XPS (Figure 1) of Pt/C and PtCo/C cathode catalysts in PEFC.

Furthermore, we have just started the third topic of the picosecond time resolved x-ray absorption fine structure (XAFS) spectroscopy. The installation of a picosecond laser system was completed and the performance test using a short-lived photoexcited metal complex was successful.

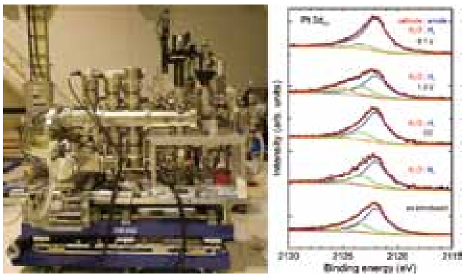

Figure 1. Ambient pressure hard x-ray photoelectron spectrometer (left) and typical Pt3d spectra from the Pt/C cathode catalyst in PEFC (right).

Selected Publications

- M. Dabrowski, T. R. F. Peixoto, M. Pazgan, A. Winkelmann, T. Nakagawa, Y. Takagi, T. Yokoyama, U. Bauer, F. Yildiz, F. Bisio, M. Przybylski and J. Kirschner, *Phys. Rev. Lett.* **113**, 067203 (2014).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **110**, 075901 (2013).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- X.-D. Ma, D. I. Bazhanov, O. Fruchart, F. Yildiz, T. Yokoyama, M. Przybylski, V. S. Stepanyuk, W. Hergert and J. Kirschner, *Phys. Rev. Lett.* **102**, 205503 (2009).
- T. Nakagawa, I. Yamamoto, Y. Takagi, K. Watanabe, Y. Matsumoto and T. Yokoyama, *Phys. Rev. B* **79**, 172404 (2009).
- T. Nakagawa and T. Yokoyama, *Phys. Rev. Lett.* **96**, 237402 (2006).

1. Structural and Magnetic Properties of Submonolayer Vanadyl Phthalocyanine[1,2]

Controlling a wide range of functionalities of metal complexes on substrate surfaces for the applications such as molecular spintronics, molecular devices, and molecular catalysis is of special importance. Metal phthalocyanine (MPc) is one of the most promising materials. Although extensive studies on late 3d transition metal Pc monolayers on metal surfaces have been reported, much less investigations have been conducted on early 3d transition metal Pcs. We have studied structural and magnetic properties of vanadyl phthalocyanine VOPc on Si(111) and Ag(111) single crystal surfaces and also ferromagnetic ultrathin Fe, Co and Ni films grown epitaxially on Cu(001), by means of soft x-ray absorption spectroscopy and x-ray magnetic circular dichroism using our synchrotron radiation facility UVSOR-III and other surface scientific methods.

Figures 2(a) and 2(b) show the N and O K-edge x-ray absorption spectra of 10 monolayer (ML) VOPc on Si(111), 0.6 ML VOPc on Si(111) and 1 ML VOPc on Ag(111). From these spectra, it is concluded that the adsorbed submonolayer VOPc is lying flat on both the surfaces and that on Si(111) the VOPc molecule adsorbs with the oxygen downward configuration due to the formation of the Si–O–V bond, while on Ag(111) the oxygen-up configuration is preferred because of a stronger interaction between Ag and the Pc π/π* orbitals. This is the first experimental proof for the oxygen-down configuration of MOPc on semiconductor surfaces, consistent with the theoretical prediction on the VOPc/GaAs system.

Figure 3 shows the V and Fe L-edge XMCD spectra of monolayer VOPc on 3 ML Fe films grown epitaxially on Cu(001). The Fe film exhibits perpendicular magnetic easy axis. The V L_{III}-edge signals are found to be reversed compared to the Fe ones; namely the V magnetic moment is antiparallel to the magnetic field. This indicates that the magnetic interaction between VOPc and Fe is antiferromagnetic even under ±5 T. The V L-edge spectra of VOPc on the Co film (not shown) reveal that the interaction between VOPc and Co is again antiferromagnetic, though the coupling seems to be considerably weaker. On the contrary, VOPc on the Ni films exhibits inherent paramagnetism without noticeable magnetic interaction between VOPc and Ni. This is consistent with a previous theoretical study that concluded much longer spacing between MPc and Ni than Fe and Co. The present observation of antiferromagnetic coupling between MPc and the ferromagnetic films is quite rare and VOPc should be a possible candidate for molecular magnetic devices to preserve or enhance the ferromagnetism of the substrate metals. Since VOPc itself seems to show the perpendicular easy axis with respect to the molecular plane, this molecule could be also suitable for perpendicular magnetic anisotropy.

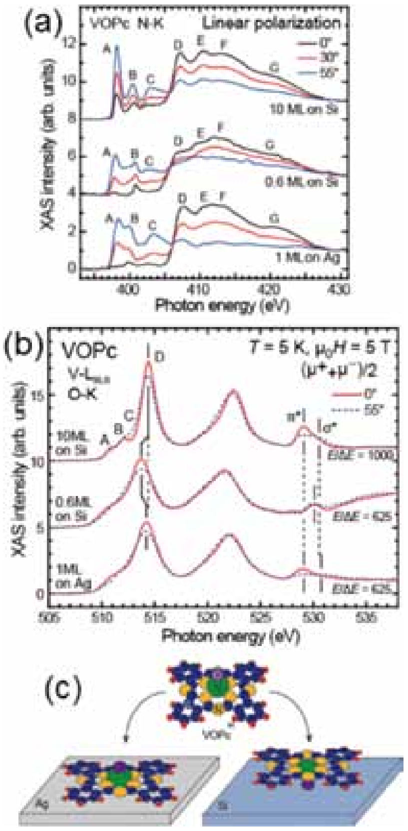

Figure 2. (a,b) N K-edge (a) and V L- and O K-edge x-ray absorption spectra of multilayer VOPc on Si(111), 0.6 ML VOPc on Si(111) and 1 ML VOPc on Ag(111). (c) Schematic structural views of adsorbed VOPc on Ag(111) and Si(111) surfaces.

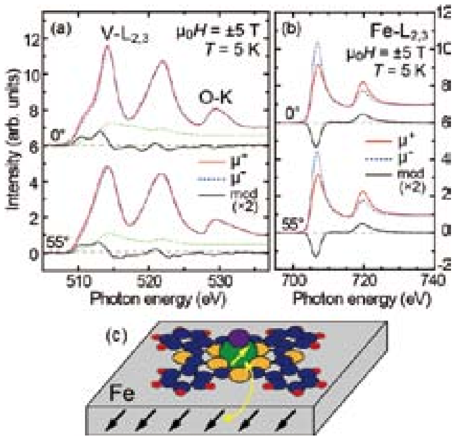

Figure 3. (a,b) V and Fe L-edge x-ray magnetic circular dichroism spectra of monolayer VOPc on 3 ML Fe films grown on Cu(001) recorded at $T = 5$ K and $H = \pm 5$ T. (c) Schematic views of antiferromagnetic interaction between VOPc and the Fe film.

References

1) K. Eguchi, Y. Takagi, T. Nakagawa and T. Yokoyama, *J. Phys. Chem. C* **117**, 22843–22851 (2013).

2) K. Eguchi, Y. Takagi, T. Nakagawa and T. Yokoyama, *J. Phys. Chem. C* **118**, 17633–17637 (2014).

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.

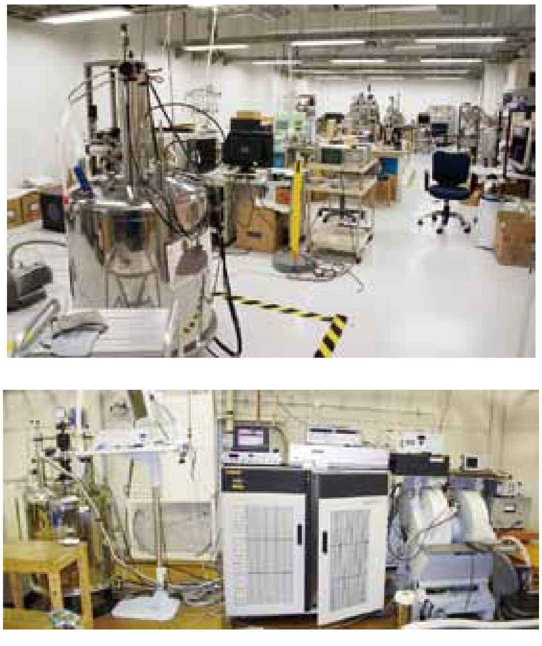

Figure 1. Solid state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- T. Terauchi, S. Sumi, Y. Kobayashi, T. Nakamura, K. Furukawa and Y. Misaki, "Stable Metallic State of $(TTPCOO)_2NH_4$ with Mobile Dopant," *Chem. Commun.* **50**, 7111–7113 (2014).
- S. Jin, K. Furukawa, M. Addicoat, L. Chen, S. Takahashi, S. Irle, T. Nakamura and D. Jiang, "Large Pore Donor–Acceptor Covalent Organic Frameworks," *Chem. Sci.* **4**, 4505–4511 (2013).

1. Magnetic Resonance Investigation of Self-Doped Type TTFCOO and TTPCOO Family Salts

^{1}H-NMR and High-Field ESR measurements were carried out for self-doped type organic conductors, ammonium tetrathiapentalene carboxylate $(TTPCOO)_2[(NH_4^{+1})_{1-x}(NH_3^0)_x]$ (hereafter we abbreviated as $TTPCOONH_4$ system), which are developed by NIMS group. While the pristine TTPCOOH molecules are closed-shell, self-doped type carrier is generated by substitution of the end group of (NH_3^0) with (NH_4^{+1}), which is regarded as a charge-reservoir. The π-extended system, TTPCOO, possessed a uni-axial g-tensor, indicating 2D isotropic structure such as herring-bone-like donor arrangements. NMR-relaxation rate shows the Korringa relation temperature dependence, and the ESR linewidth follows Elliot mechanism. These facts are apparent evidences of stable metallic state.

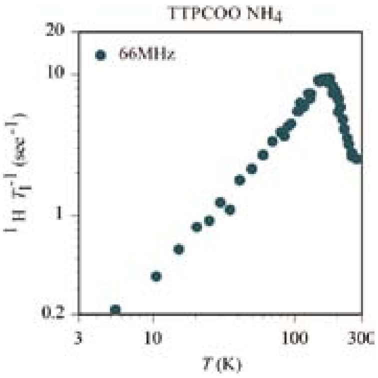

Figure 2. Temperature dependence of the ^{1}H-NMR spin–lattice relaxation rate T_1^{-1} for TTPCOO system. T-linear Korringa-like behavior down to 5 K indicates a stable metallic state.

Figure 2 shows the temperature dependence of the spin–lattice relaxation rate of $TTPCOONH_4$ system. A pronounced peak behavior observed at around 160K shows frequency dependence and is apparently originated from the proton motion. Since the relaxation of molecular motion is rapidly suppressed as lowering temperature, the nuclear spin relaxation at low temperatures (*i.e.* below 100 K) is mainly caused by the electron spins. In the low-temperature region, the ^{1}H NMR spin–lattice relaxation rate, T_1^{-1}, of $TTPCOONH_4$ system shows T-linear Korringa-like behavior down to 5 K. This observation clarifies that this system is metallic. It is contrast to the 1D spin diffusive relaxation behavior ($\sim T^{0.5}$) observed in a semiconductor $(TTFCOO)_2[(NH_4^{+1})_{1-x}(NH_3^0)_x]$. The continuous T-linear behavior of T_1^{-1} down to 5 K also shows that there is no low-dimensional instability and antiferromagnetic (SDW) transitions at low temperatures. No obvious line shift and line broadening with temperature also supports this scenario. These facts indicate that substitution of mainframe from TTF to π extended TTP is essential key to realize a stable metallic state by means of reduction of electron correlation (Coulomb repulsion) and dispersion force.

2. Time-Resolved ESR Spectroscopy Investigation of Photoconduction Mechanism in Covalent Organic Framework (COF) Materials

Covalent organic framework (COF) materials are porus crystalline materials. They attracted much attention because of their functionalities. Recently, a variety of COF materials based on the Donor–Acceptor (D–A) system have been developed. Jiang and coworkers synthesized a variety of D–A type COFs such as NDI-ZnPc, PyDI-ZnPC and ZnPc-NDI-HHTP. While molecules are connected by tight covalent bonds within the two-dimensional layers, the molecules stack to form one-dimensional columns perpendicular to the planes. They show pronounced photo-conducting behavior. The possible photo-conduction origin is the electron transfer between donor and acceptor. However, the detail mechanism is an open question. We performed time-resolved photo-excited ESR spectroscopy for a series of D–A type COF materials to investigate the photo-conduction mechanism. After photo-excitation to D–A type COFs, an ESR signal originated from the charge-separated state was observed, which could not be observed in isolated molecules. As for ZnPc-NDI-COF, we can observe the charge-separated ESR signal even at R.T., indicating long lifetime of the photo-excited carriers. Actually, the lifetime of the photo-excited charge-separated states in ZnPc-NDI-COF are estimated as 865 μs at 80 K and 1.8 μs at 280K.

References

1) K. Furukawa, T. Nakamura, Y. Kobayashi and T. Ogura, *J. Phys. Soc. Jpn.* **79**, 053701 (4 pages) (2010).

2) S. Jin, X. Ding, X. Feng, M. Supur, K. Furukawa, S. Takahashi, M. Addicoat, M. E. El-Khouly, T. Nakamura, S. Irle, S. Fukuzumi, A. Nagai and D. Jiang, *Angew. Chem., Int. Ed.* **52**, 2017–2021 (2013).

Organic Solar Cells

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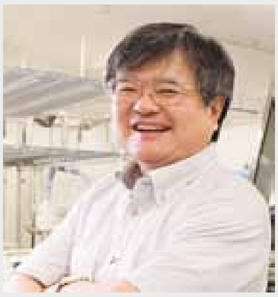

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Keywords Organic Semiconductors, Organic Solar Cells, Doping

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.

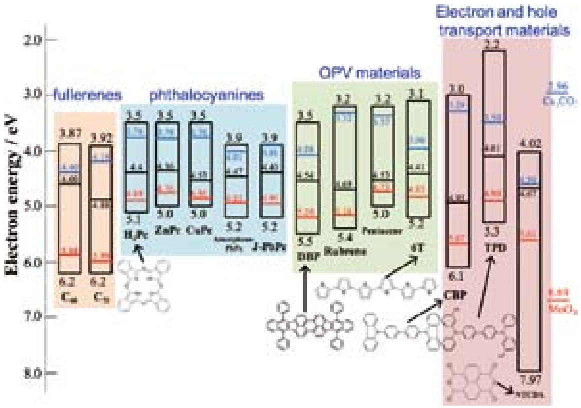

Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100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

Selected Publications

- 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).
- M. Kubo, K. Iketaki, T. Kaji and M. Hiramoto, "Conduction Type Control of Fullerene Films from *n*- to *p*-Type by Molybdenum Oxide Doping," *Appl. Phys. Lett.* **98**, 023302 (3 pages) (2011).
- M. Hiramoto, H. Fujiwara and M. Yokoyama, "Three-Layered Organic Solar Cell with a Photoactive Interlayer of Codeposited Pigments," *Appl. Phys. Lett.* **58**, 1062–1064 (1991).

1. Ionization Sensitization of Doping in Co-Deposited Organic Semiconductor Films

We have developed the *pn*-control technique by impurity doping for co-deposited films[1] such as C_{60}:H_2Pc (fullerene: metal-free phthalocyanine) since a key element for exciton dissociation in organic solar cells is having a co-deposited films. During the course of these studies, we made accurate estimates of the carrier concentrations generated by impurity doping by means of Kelvin band-mapping,[2] from which we found evidence of higher doping efficiencies for co-deposited films compared to those for the respective single films.

Figure 3 shows the dependence of the doping efficiency on the doping concentration for C_{60}:H_2Pc and their component films. The doping efficiency is defined by the ratio of the carrier concentration created to the molecular concentration of Cs_2CO_3. The doping efficiencies of single films of C_{60} and H_2Pc are around 10%. In contrast, those of the co-deposited films of C_{60}:H_2Pc are around 50%. Thus, we conclude that the doping efficiency was significantly enhanced in the co-deposited films.

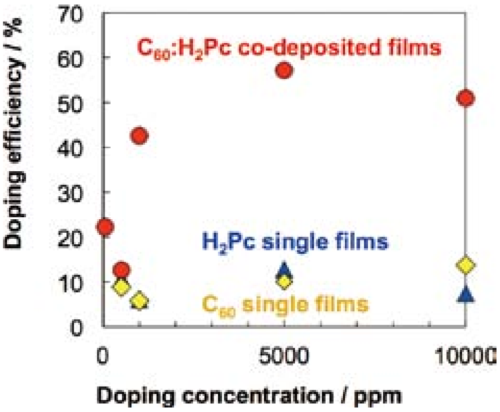

Figure 2. Dependence of doping efficiency on Cs_2CO_3 doping concentration for C_{60}:H_2Pc co-deposited films and their component films.

By making contact with C_{60}, since the electron transfer from the conduction band of H_2Pc to that of C_{60} (Figure 4(a), blue arrow) occurs accompanied with energetic relaxation (0.7 eV), the electron concentration in H_2Pc decreases. Due to the shift in equilibrium, the electrons liberated from the donor levels accelerate, *i.e.*, the ionization rate (doping efficiency) for donors increases only in the H_2Pc region. Figure 4(b) shows the cross sectional energy structures of charge separating H_2Pc/C_{60} superlattice after contact. In this model, the H_2Pc regions act as electron supplying layers to the C_{60} regions. The C_{60} regions act as electron transporting highways. Based on this model, we expected that the total ionization rate in H_2Pc:C_{60} co-deposited films would increase further by increasing the H_2Pc ratio and obtained the ionization rate of 97% at a H_2Pc:C_{60} ratio of 99:1.

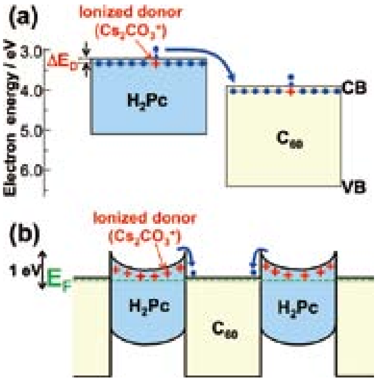

Figure 3. (a) Energy diagrams of Cs_2CO_3-doped H_2Pc and C_{60} single films before contact. CB, VB, and ΔE_D denote the conduction band, the valence band, and the activation energy of the donors, respectively. (b) Cross sectional energy structure of a Cs_2CO_3-doped H_2Pc/C_{60} superlattice model after contact.

2. Mapping of Band-Bending for Organic *pn*-Homojunctions

A precise band-mapping for organic *pn*-homojunctions, which have various balance of doping concentration between *p*- and *n*-type layers, was performed by measuring the film thickness dependence of the work function from both sides of the *pn*-homojunction interface using a Kelvin probe. Band-bending including the simultaneous development of depletion layer in underlying *n*-type layer induced by the deposition of *p*-type layer, and vice versa, should be taken into account for the precise fitting based on the Poisson equation. Validity of the conventional theory of space charge layer suggests that the dopants are spatially fixed even in the organic semiconductor films. The present result allows the precise design of the built-in potential in the organic solar cells.

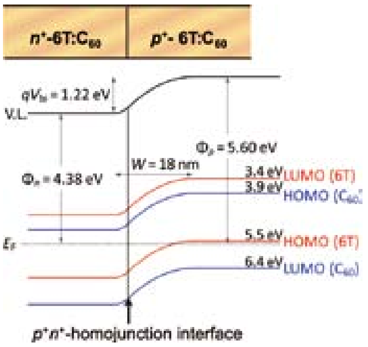

Figure 4. Energy band diagram of the p^+n^+-homojunction. VL, E_F, VB, and CB denote the vacuum level, Fermi level, the valence band and the conduction band, respectively.

References

1) M. Kubo, T. Kaji and M. Hiramoto, *Appl. Phys. Lett.* **103**, 263303 (2013).

2) Y. Shinmura, N. Ishiyama, T. Kaji and M. Hiramoto, *Appl. Phys. Express* **7**, 071601 (2014).

Two-Dimensional Polymers and Covalent Organic Frameworks

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Professional Employment

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Awards

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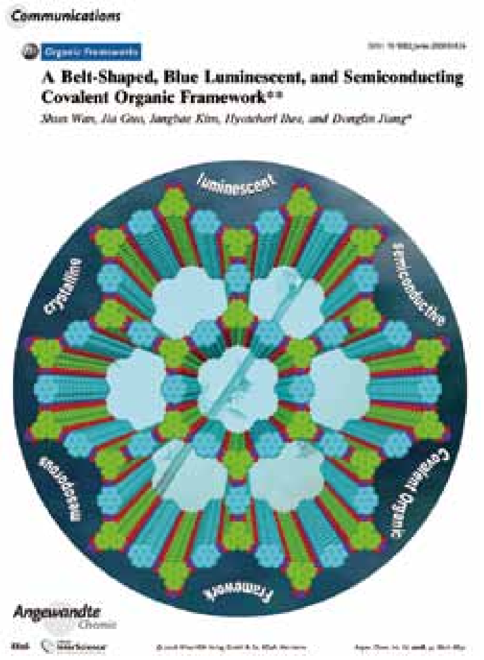
Keywords Two-Dimensional Covalent Polymer, Porous Organic Polymers

Two-dimensional (2D) polymers and their layered frameworks (covalent organic frameworks: COFs) are a class of crystalline porous materials that allow an atomically precise integration of organic components into a 2D or 3D periodicity. The COF materials are different from conventional polymers and typical porous meta-organic framework in the aspects structure, synthesis, and functions and have emerged as a new platform for designing advanced materials, including gas adsorption, catalysts, semicoductors, light-emitters, and active materials for batteries and polymer solar cells. We have pioneered the field of COFs by exploring molecular topologies, building blocks, linkages, and functions and applications.



Communications

A Belt-Shaped, Blue Luminescent, and Semiconducting Covalent Organic Framework**

Figure 1. The first semiconducting 2D COF.

Selected Publications

- X. Feng, X. Ding and D. Jiang*, "Covalent Organic Frameworks," *Chem. Soc. Rev.* **41**, 6010–6022 (2012).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Belt-Shaped, Blue Luminescent and Semiconducting Covalent Organic Framework," *Angew. Chem., Int. Ed.* **47**, 8826–8830 (2008) (VIP).
- S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang*, "A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes with Eclipsed 2D Polypyrene Sheets for Photocurrent Generation," *Angew. Chem., Int. Ed.* **48**, 5439–5442 (2009).
- J. Guo, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, S. Seki, S. Irle, M. Hiramoto, J. Gao and D. Jiang*, "Conjugated Organic Framework with Three-Dimensionally Ordered Stable Polymer with Delocalized π Clouds," *Nat. Commun.* **4**: 2736 doi: 10.1038/ncomms3736 (2013).

1. Azine-Linked 2D Polymers and COFs

To discover new covalent bonds for the construction of crystalline and permanent porous organic frameworks remains challenging in the field of reticular chemistry. Successful attempts to achieve COFs have been limited to few covalent bonds, including boronate, boroxine, borosilicate, imine, triazine, hydrazone, and squaraine linkages. Among them, only few examples of COFs have been reported to show enough high thermal and chemical stabilities, which however, are crucial for applications. In this context, to explore a robust linkage for the synthesis of COFs that meet the requirement in crystallinity, porosity, and stability is of critical importance for the further advancement of the field from the viewpoints of both basic research and technological application.

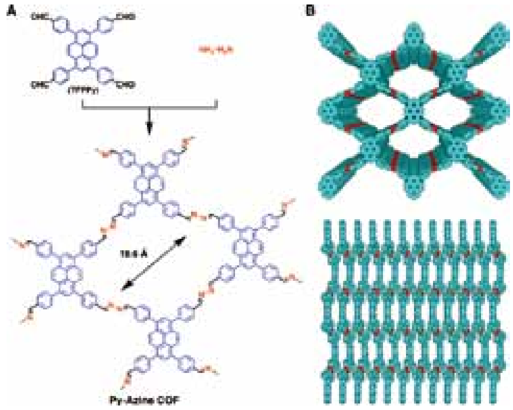


Figure 2. (A) Schematic representation of the Synthesis of the azine-linked COF (Py-Azine COF). (B) Top and side views of the AA stacking structure of the Py-Azine COF (sky blue: tetraphenylpyrene unit, red: nitrogen, H atoms are omitted).

Herein, we report the development of a new covalent bond based on the azine linkage for the synthesis of COFs that exhibit high crystallinity, high porosity, and robust chemical stability (Figure 2, Py-Azine COF). Condensation of hydrazine with 1,3,6,8-tetrakis(4-formylphenyl)pyrene under solvothermal conditions affords highly crystalline two-dimensional covalent organic frameworks. The pyrene units occupy the vertices and the diazabutadiene (–C=N–N=C–) linkers locate the edges of rohmbic-shaped polygon sheets, which further stack in an AA-stacking mode to afford periodically ordered pyrene columns and one-dimensional microporous channels. The azine-linked frameworks feature permanent porosity with high surface area and exhibit outstanding chemical stability. By virtue of the pyrene columnar ordering, the azine-linked frameworks are highly luminescence, whereas the azine units serve as open docking sites for hydrogen-bonding interactions. These synergestic functions of the vertices and edges units endow the azine-linked pyrene frameworks with extremely high sensitivity and selectivity in chemosensing, for example, the selective detection of 2,4,6-trinitrophenol explosive. We anticipate that the extension of the present azine-linked strategy would not only increase the structural diversity but also expand the scope of functions based on this highly stable class of covalent organic frameworks.

2. Pore Surface Engineering for Constructing Donor–Acceptor COFs

Two strategies have been established for the synthesis of donor–acceptor COFs. By using electron donor and acceptor as monomers, we have developed a covalent methodology for the synthesis of donor–acceptor COFs, whereas the skeletons are built from alternately linked donor and acceptor π-arrays and leave open channels unused. As an alternative way, we and other groups have explored a supramolecular approach by spatially confining electron acceptors within the open channels of electron-donating frameworks. Clearly, the former approach requires a planar conformation of the monomer units and is not applicable to the zero-dimensional molecules, such as buckyballs, a class of widely utilized electron acceptors. The second approach based on physical filling can load buckyballs; however, it encounters a problem on the fullerene elution from the channels.

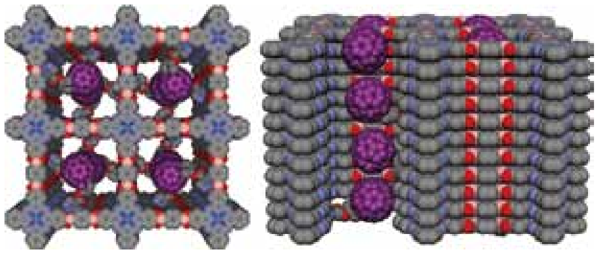


Figure 3. Surface engineering of pore walls for covalent linking of fullerenes to constitute donor–acceptor systems.

In this work, we developed a method for converting the open lattice of COFs into photoelectric structures in which electron-accepting buckyballs were spatially confined within the nanochannels via covalent anchoring on the channel walls (Figure 3). The donor–acceptor heterojunctions trigger photo-induced electron transfer and allow charge separation with radical species delocalized in the π-arrays, whereas the charge separation efficiency was dependent on the buckyball content. This new donor–acceptor strategy explores both skeletons and pores of COFs for charge separation and photoenergy conversions.

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Solid State NMR for Molecular Science

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Education

1994 B.S. Himeji Institute of Technology
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Keywords Solid State NMR, Biomolecules, Developments

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

We have been working on the methodology and hardware developments of solid state NMR and their applications such as structural biology and material science. We study for characterization of biomolecules such as peripheral membrane proteins and organic molecules such as natural products and synthetic polymers. Characterizations of several molecular materials in addition to biomolecules are under investigations with several corroborators using solid state NMR.

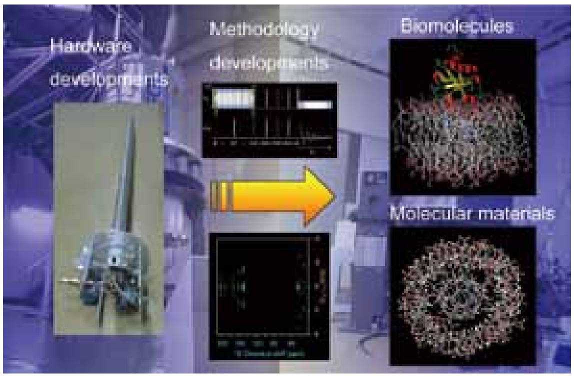

Figure 1. Outline of our studies.

Selected Publications

- J. Hu, R. Fu, K. Nishimura, L. Zhang, H. X. Zhou, D. D. Busath, V. Vijayvergiya and T. A. Cross, "Histidines, Heart of the Hydrogen Ion Channel from Influenza A Virus: Toward an Understanding of Conductance and Proton Selectivity," *Proc. Natl. Acad. Sci. U .S.A.* **103**, 6865–6870 (2006).
- K. Nishimura and A. Naito, "Remarkable Reduction of RF Power by ATANSEMA and DATANSEMA Separated Local Field in Solid-State NMR Spectroscopy," *Chem. Phys. Lett.* **419**, 120–124 (2006).
- 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).

1. Molecular Proximity Revealed by Solid State NMR

Molecular proximity is one of the important information to characterize structure and functions of various molecules. However, the isotope enrichments of those samples are difficult or limited. Thus, low sensitivity natural abundant isotopes must be observed. Furthermore, so far many of developed solid state NMR techniques have been designed for the study of isotope enriched sample. Thus methodology developments and analysis optimized for natural abundant samples are quite important.

We have been exploring to reveal molecular proximity of biomolecules and synthetic polymers without isotope enrichment based on different approaches.

^{1}H detection is one of the possibilities in order to overcome sensitivity issue for the observation of natural abundant samples. However, solid organic samples possess ^{1}H homonuclear dipolar coupling which results in significant broadening of spectra. Thus unlike solution NMR, it has been difficult to observe ^{1}H high resolution spectra for organic solids. However, high speed MAS technique has made a remarkable progress in the past decade. It enables to observe high resolution ^{1}H spectra only by using MAS and gives reliable isotropic chemical shifts.

We have attempted to reveal molecular proximity by observing high resolution ^{1}H spectra using ultra high speed MAS under ultra high field. With collaborators, we have successfully revealed molecular packing in silk fibroin based on accurately determined ^{1}H position in model peptide which obtained from the analysis of cross peak growing for ^{1}H-homonculear double quantum-single quantum correlation spectra[1,2] at various mixing time.

As an alternative approach, so far CRAMPS technique which utilize multiple pulse (MP) ^{1}H homonuclear dipolar decoupling under magic angle spinning has been used to observed high resolution ^{1}H spectra under magic angle spinning. In this technique, averaging cycle of ^{1}H homonuclear dipolar interaction based on MP must be short enough compare to the MAS rotation period in order to avoid interference between spin and sample rotations. Thus high power RF field is required for ^{1}H to satisfy above requirements. Furthermore, MP also scales down isotropic chemical shifts of ^{1}H simultaneously. Thus careful calibrations of experimental parameters are essential in order to observe correct isotropic chemical shifts. Using CRAMPS approach for ^{1}H dimension, it is possible to obtain high resolution ^{1}H-^{13}C heteronuclear correlation spectra under moderate speed MAS.

We are currently investigating intermolecular proximity of cage molecules with collaborator. By using ^{1}H-^{13}C heteronuclear correlation experiments under high field, it enables to detect intermolecular ^{1}H-^{13}C heteronuclear correlation based on heteronuclear dipolar couplings. Compared to ^{1}H-intermolecular correlation approach mentioned above, detectable distance range are limited and sensitivity is lower, however ^{13}C detection enables well resolved sharp signals.

2. Proton Localization in ZnO Nanorods Revealed by In-Situ ^{1}H-Magic Angle Spinning Solid State NMR Spectroscopy[3]

ZnO nanorods can be grown using aqueous solution. Unique shape of ZnO nanorods are studied for various applications such as biosensors, piezoelectric generators, dye-sensitized solar cells. Aqueous-grown ZnO nanorods might contain various kinds of impurities from source materials. Considering aqueous-growth of ZnO nanorods, we pay attention on incorpolated hydrogen atoms, which can act as shallow donors.

In this study, local environments of protons incorporated in aqueous grown ZnO nanorods at different temperatures and approaches were studied prepared by collaborator by in-situ ^{1}H-magic angle spinning solid state NMR spectroscopy. We found out that the amount of protons incorporated in ZnO nanorods were increased toward increase of temperature of hydrothermal synthesis. However those for annealed samples at 500 °C after thermal synthesis release protons toward increase of temperature of hydrothermal synthesis. Furthermore, protons incorporated in ZnO nanorods prepared by either hydrothermal synthesis using autoclave or microwave irradiations exhibited different proton concentrations and adsorptive activities. Those results indicate that adsorptive activity of protons incorporated in ZnO nanorods may vary depending on the preparation procedures.

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3) K. Ogata, S. Sasa, M. Inoue, M. Yano and K. Nishimura, to be submitted.

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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. Synthesis, Structure and Physical Properties of *N*-Boc-Pyrrole Derivatives for Organic Semiconductors

Planar π-conjugated molecules have been attracted much attention from the viewpoints of development of organic semiconductor devices.[1] To improve their low solubility, we synthesized several *N*-*tert*-butoxycarbonyl (Boc)-2,5- diarylpyrrole derivatives as precursors of organic semiconductors for the fabrication of solution-processed field-effect transistors. These compounds have nonplanar structures due to a steric hindrance between Boc group and aryl ones. Elimination of Boc group from the soluble precursors by annealing quantitatively afforded insoluble *N*-H-2,5-diarylpyrroles with planar structures. We investigated their spectral and electrochemical changes toward a film fabrication technology.

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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 (**MOSET**) and their integrated circuits.

1. Systematic Chemical Modulation of Molecular Wires

We have already elucidated the details of steady-state long-distance molecular conduction through a series of molecular wires **1**. As a next step, we have planed to develop the design principle for precise and wide-range control of electron-transport characteristics of single molecular wires. For this purpose, we have modulated the electronic structure of the wires **1** by systematic chemical modifications. Figure 1 shows the typical examples. The measurement of single molecular conductance of these wires is still in progress.

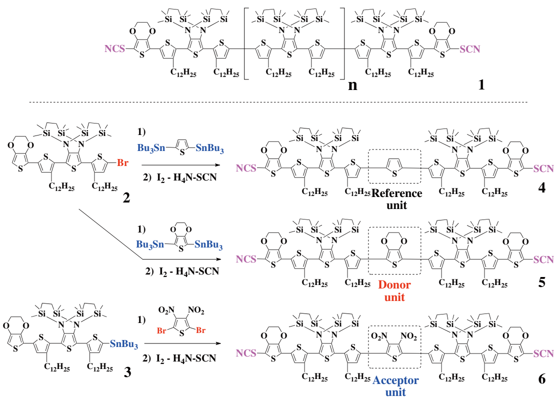

Figure 1. Synthetic scheme for molecular wires with modified electronic structure.

Visiting Professors

Visiting Professor

TAKENOBU, Taishi *(from Waseda University)*

Electronic Phase Control of Molecular Materials by Electric Double Layer Transistors

Charge carrier control is one of the key issues in the development of solid state physics and novel functional devices. Most famous device is field-effect transistor, in which material conductivity is controlled by accumulated charges at semiconductor/insulator interface. Beyond the simple enhancement of conductivity, high charge carrier accumulation can realize various phenomena, such as phase transition, magnetic ordering, and superconductivity. Electric double layers, formed at solid/electrolyte interfaces, induce extremely large electric fields, huge specific capacitance and high density charge accumulation, and, as the results, this method opens new route for novel functionalities. Because molecular materials have large variety of electronic and magnetic properties, we are investigating the physical properties of ionic liquid/molecular materials interfaces and are developing the method to combine single crystals of molecular solid with electric double layer transistors to discover novel phase transitions and functional devices.

Visiting Associate Professor

NAKANISHI, Takashi *(from National Institute for Materials Science)*

Self-Assembly Controlled Soft Materials of Multifunctional Spin-Active Molecules

Because of optoelectronic properties and single magnet molecule behavior, phthalocyaninato rare-earth metal double-decker complexes have received much attention. These complexes are expected to have application in spintronics as well as in electrochromic and optoelectronic devices. In our work we apply the concept of soft materialization to the double-decker phthalocyanines to achieve control over self-assembly and phase transition of the material. Our aim is to obtain solvent-free soft materials, including room temperature liquids and liquid crystals, with tunable intermolecular interactions and magnetic, electrochromic, and photoconductive properties. One kind of double-decker phthalocyanine is chosen as a “functional, spin-active unit” and multiple branched long-alkyl chains are attached as substituents. The synthesis, spectroscopy and electrochemistry, ESR analyses of these materials as well as their thermotropic behavior are deeply evaluated and further analysis such as electrochromic and photoconductive properties are currently under way.

Visiting Associate Professor

NEGISHI, Yuichi *(from Tokyo University of Science)*

Creation of Functionalized Metal Nanoclusters and Highly Active Photocatalytic Materials Using Thiolate-Protected Magic Gold Clusters

Advances in developments in nanotechnology have encouraged the creation of highly functionalized nanomaterials. Because of their nanoscale size (< 2 nm), thiolate-protected gold clusters ($Au_n(SR)_m$) exhibit size-specific physical and chemical properties not observed in bulk metals. Therefore, they have attracted attention as functional units or building blocks in nanotechnology. The highly stable, magic $Au_n(SR)_m$ clusters possess great potential as new nanomaterials. We are studying the following subjects related to magic $Au_n(SR)_m$ clusters: (1) establishing methods to enhance their functionality, (2) developing high-resolution separation methods and (3) utilizing the clusters as active sites in photocatalytic materials. Through these studies, we aim to create highly functional metal nanoclusters and apply them as highly active photocatalytic materials.