



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

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 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, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD apparatus is extensively open for public usage and many domestic and foreign researchers visit every year. We are currently interested in transition-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 will be presented in the next page.

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

polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopy is believed to be done under ultrahigh vacuum, recent material science requires in situ measurements under working conditions. We have installed nearly ambient pressure (up to 5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8. We have successfully investigated Pt 3d HAXPES of Pt/C, PtCo/C and PtNi/C cathode catalysts in PEFC under working conditions to reveal degradation mechanism of PEFC. 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 element by using the *energy-resolved* x-ray fluorescence detection technique. Fast time resolved XAFS measurements are, however, usually difficult since the frequencies between normal SR (probe) and pumping lasers are far different, requiring pulse picking of the SR probe and resultantly time resolved detection of *energy-integrated* x-ray fluorescence. To solve this problem, 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

- K. Eguchi, T. Nakagawa, Y. Takagi and T. Yokoyama, *J. Phys. Chem. C* **119**, 9805 (2015).
- K. Eguchi, Y. Takagi, T. Nakagawa and T. Yokoyama, *J. Phys. Chem. C* **118**, 17633 (2014).
- Y. Takagi, H. Wang, Y. Uemura, E. Ikenaga, O. Sekizawa, T. Uruga, H. Ohashi, Y. Senba, H. Yumoto, H. Yamazaki, S. Goto, M. Tada, Y. Iwasawa and T. Yokoyama, *Appl. Phys. Lett.* **105**, 131602 (2014).
- 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).
- T. Nakagawa and T. Yokoyama, *Phys. Rev. Lett.* **96**, 237402 (2006).

1. Synthesis and Structural/Magnetic Properties of Vanadium Phthalocyanine¹⁾

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 most 3d transition metal Pcs have been synthesized, ScPc or VPc has never been obtained because of high air sensitivity during the chemical synthesis. In this work, we have successfully prepared VPc monolayer and multilayer on Ag(111) in a ultrahigh vacuum (UHV) deposition technique. Moreover, we investigated structural and magnetic properties of monolayer and multilayer VPc using XAFS and XMCD.

VPc was synthesized by depositing H₂Pc and subsequent V metal on a clean and ordered Ag(111) surface. Monolayer VPc did not require any annealing process to complete the reaction $V + H_2Pc \rightarrow VPc + H_2$, while multilayer VPc needed annealing at 450 K. The identification of VPc was carried out by in-laboratory N1s XPS. The N1s XPS of H₂Pc shows two peaks assigned to iminic (–N=) and pyrrolic (–NH–) nitrogen, while that of metal Pc exhibits a single peak. The present observation of a single N1s peak clearly elucidate the successful synthesis of monolayer and multilayer VPc. From the V2p XPS, V is found to be divalent, as expected, although some amount of charge transfer from the substrate Ag(111) was observed in monolayer.

Linear polarization dependence of the N K-edge XAFS of VPc on Ag(111) has revealed flat-lying orientation of monolayer VPc and rather random orientation of multilayer. The V L-edge XAFS and XMCD have indicated complicated electronic structure of VPc due to strong configuration interaction between 2E_g ($3d_{xy})^2(3d\pi)^1$ and other configurations as $(3d_{xy})^2(3d_z)^1$, similarly to other transition metal Pcs. The V L-edge XMCD spectra shown in Figure 1 suggest the doublet state in monolayer on Ag(111) and embedded in H₂Pc multilayer, while multilayer exhibits antiferromagnetism due to intermolecular exchange interaction.

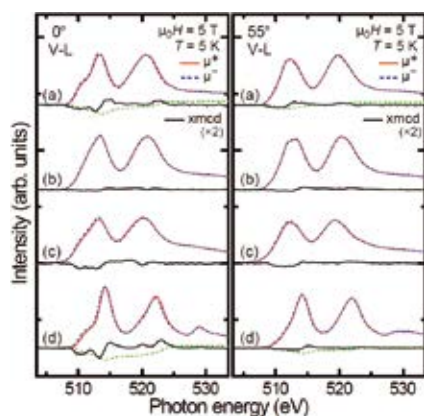


Figure 1. V L-edge XMCD of VPc on Ag(111) at incident x-ray angles of 0° (normal incidence, left panel) and 55° (grazing incidence, right panel): (a) monolayer embedded in multilayer H₂Pc, (b) multilayer, (c) monolayer and (d) VOPc monolayer as a reference.

2. Anomalous Structural Behavior in Metamagnetic Transition in FeRh Films

The FeRh intermetallic compound with ordered CsCl structure is known to exhibit an interesting metamagnetic transition from antiferromagnetic (AFM) to ferromagnetic (FM) phase with the temperature rise ($T_C \sim 385$ K), which would be applicable to thermally assisted recording/memory media. In this work, FeRh thin films have been investigated via temperature dependent XAFS spectroscopy in order to gain correlations between the magnetization and the local electronic and geometric structures.

According to the Fe and Rh K-edge XAFS, strong hybridization was found to exist between Fe and Rh. This Fe–Rh hybridization was revealed to decrease during the phase transition from the systematic change observed in the Fe K-edge XAFS. On the other hand, only the Debye-Waller factor of the Fe–Fe pair in the AFM phase was found to be considerably enhanced when compared with that in the FM phase, which was ascribed to local structural fluctuation inherent in the AFM phase itself. This anomalous feature is interpreted in consistent with the recent theoretical study proposing the local fluctuations of spin and structure by considering the different features of the exchange interactions in Fe–Rh and Fe–Fe. Therefore, we consider that the local Fe–Fe distance and the spin fluctuations play an important role for driving the metamagnetic transition, whereas the Fe–Rh hybridization is important for determining the static stability of each magnetic phase.

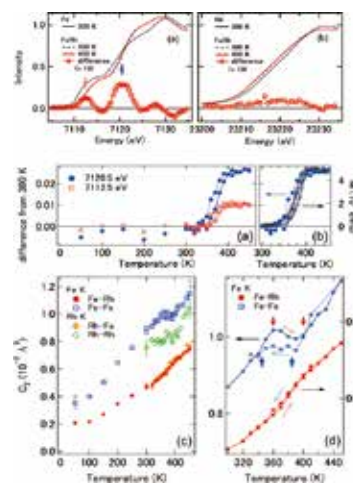


Figure 2. (a) Fe K-edge XAFS intensity at 7120.5 (blue) and 7112.5 (red) eV. (b) SQUID magnetization (black) compared to XAFS (7120.5 eV, blue). A slight T_C difference between SQUID and XAFS implies a difference in the phase transition nature between macroscopic and microscopic origins. (c,d) Debye-Waller factors for the atom pairs of the first nearest neighbor Fe–Rh and the second nearest neighbor Fe–Fe and Rh–Rh. Only the Fe–Fe pair exhibits an interesting anomaly.

Reference

- 1) K. Eguchi, T. Nakagawa, Y. Takagi and T. Yokoyama, *J. Phys. Chem. C* **119**, 9805 (2015).

Magnetic Resonance Studies for Functional Molecular-Based Solids

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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.

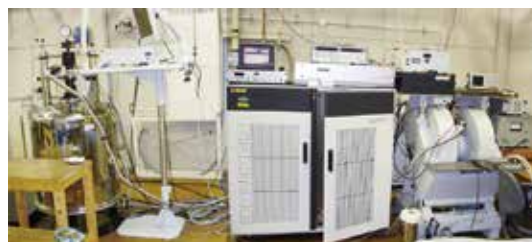
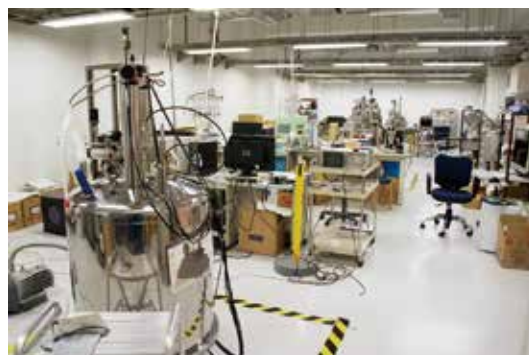


Figure 1. Solid state broad-line NMR system (above). Multi-frequency pulsed ESR system (below).

Selected Publications

- P. Pandit, K. Yamamoto, T. Nakamura, K. Nishimura, Y. Kurashige, T. Yanai, G. Nakamura, S. Masaoka, K. Furukawa, Y. Yakiyama, M. Kawano and S. Higashibayashi, "Acid/Base-Regulated Reversible Electron Transfer Disproportionation of N-N Linked Bicarbazole and Biacridine Derivatives," *Chem. Sci.* **6**, 4160–4173 (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. Microscopic Evidence of a Metallic State in the One-Pot Organic Conductor, Ammonium Tetrathiapentalene Carboxylate

We performed magnetic resonance investigation, including solid-state broad line NMR and high-field ESR measurements, of the π -extended self-doped organic conductor (TTPCOO)₂[(NH₄⁺)_{1-x}(NH₃⁰)_x], and compared the results with those of first-generation (TTFCOO)[(NH₄⁺)_{1-x}(NH₃⁰)_x]. The observed principal values of the ESR g -tensor indicate that both salts have electron spins on TTF and TTP cation radical mainframe parts. In (TTFCOO)[(NH₄⁺)_{1-x}(NH₃⁰)_x], the TTF forms a 1D uniform stacking structure, and the system is a narrow-gap semiconductor. The electron spin demonstrates 1D spin-diffusive behavior, which may be why this system is a semiconductor. On the other hand, in the π -extended system, TTPCOO, the uniaxial anisotropy of the g -tensor indicates a 2D isotropic structure such as a herring-bone-like or parallel cross like donor arrangement. The π -extended system should reduce the electronic correlation that stabilizes the metallic state. As a result, NMR-relaxation demonstrates the Korringa-like temperature dependence, and the ESR linewidth follows the Elliot mechanism. These facts are apparent evidence of a stable metallic state (itinerant electron spins are present). We demonstrate that advanced magnetic resonance measurements can effectively clarify the intrinsic characteristics and functionality of novel materials. Moreover, this one-pot process for synthesizing organic (semi-)conductors enables large-scale high-volume synthesis in a short time. Our next goal is to realize a one-pot functional organic system such as superconducting, ferromagnetic, or ferroelectric materials.

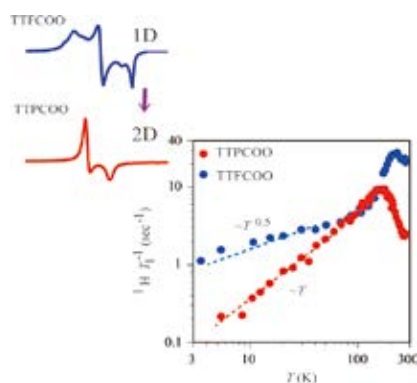


Figure 2. Metallic state in one-pot organic conductor, an ammonium tetrathiapentalene carboxylate based system is found. High-field ESR spectra showed a 2D isotropic structure such as a herring-bone-like donor arrangement. This is unlike the 1D ammonium tetrathiapentalene carboxylate system. NMR-relaxation and the ESR linewidth provide strong evidence of a stable metallic state in the ammonium tetrathiapentalene carboxylate system.

2. Charge Ordering in Oxo-Bridged Dinuclear Ruthenium Mixed-Valence Complex by Magnetic Resonance Investigation

Solid-state broad line ¹H-NMR was carried out for an oxo-bridged dinuclear ruthenium mixed-valence complex. A pronounced peak in the ¹H-NMR T_1^{-1} was observed around 33 K. The frequency independence of the peak temperature of T_1^{-1} indicates that this anomaly is not a crossover phenomenon but a phase transition. This 33 K anomaly is a transition from an averaged-valence state to a trapped-valence state in [RuORu]⁵⁺; that is, the averaged-valence Ru^{3.5+}ORu^{3.5+} spontaneously breaks symmetry into Ru³⁺ORu⁴⁺ below 33 K. In other words, the electronic charge freedom is cooperatively frozen at 33 K. The observed abrupt decrease in T₂ also indicates internal charge separation (Ru³⁺ORu⁴⁺). Because the 33 K anomaly is cooperative phenomena, the Ru³⁺ and Ru⁴⁺ charge configuration must be regularly arranged by necessity in the phase transition. Considering the crystal structure symmetry, one possible schematic charge configuration within the ac -plane is shown in Figure 3. Of course, this is mere speculation, and detailed structural measurements at a synchrotron radiation facility are required. Note also that the ruthenium-equivalent sites are connected by an inversion center in the [RuORu]⁵⁺ complex, so the charge order state should be antiferroelectric. For applicable use, ferroelectric and/or multiferroic materials are desired. The development of dinuclear complexes with lower symmetry and stronger inter-molecular interactions is a good next step, and further investigations are already underway. However, we emphasize on the basis of this investigation that mixed-valence metal complexes are excellent candidates for electronic device materials.

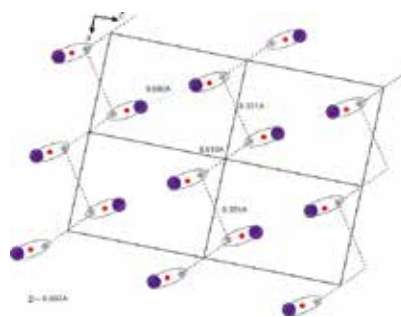
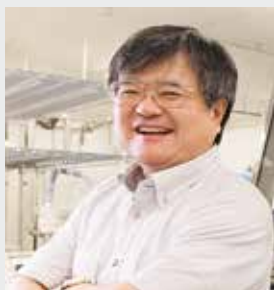


Figure 3. Possible schematic charge configuration within the ac -plane below 33 K.

References

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- 2) T. Nakamura, M. Yoshida, M. Kondo and S. Masaoka, submitted.

Organic Solar Cells

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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.

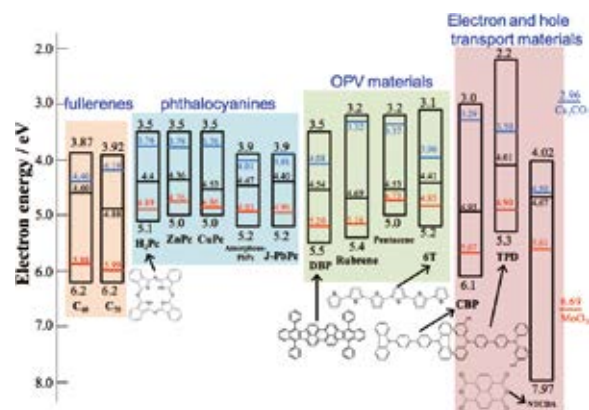


Figure 1. Energy diagrams of various organic semiconductor films. The black, red, and blue lines show the energetic position of E_F for non-doped, acceptor dopant (MoO_3)-doped, and donor dopant (Cs_2CO_3)-doped films. The doping concentration is 3,000 ppm. E_F values for MoO_3 and Cs_2CO_3 films (100 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. Effects of ppm-Level Doping in Organic Photovoltaic Cells Based on Minority Carrier Diffusion

The doping of organic semiconductors has mainly been in the concentration range of the order of a few %. We believe that a doping technique for very low concentrations of the order of parts per million should be developed. In this study, we clarified the effects of doping at the ppm-level.

Organic photovoltaic cells with *pn*-homojunctions in C₆₀:H₂Pc co-deposited films were fabricated. The donor (CS₂CO₃) doping concentration in the *n*-layer was kept constant at 50 ppm. On the other hand, the acceptor (F₄-TCNQ) doping concentration in the *p*-layer was varied, *i.e.*, 0, 1, 3, 10, and 100 ppm. Figures 2 and 3 show the current-voltage characteristics and the energy band diagrams for the *pn*-homojunction cells.

(i) 0–1 ppm region

The fill factor (FF) increases from 0.37 (black solid curve) to 0.47 (blue solid curve) together with an increase of the forward dark current (black and blue broken curves) (Figure 2), *i.e.*, a decrease of the cell resistance (R_S) from 15.0 to 9.6 Ωcm^2 . Acceptor doping inevitably introduces majority (hole) and minority carriers (electron) (Figures 3(a)). The increase in the majority carrier concentration causes R_S to decrease and FF to increase. Thus, the doping effect of extremely low concentrations of the order of 1 ppm was confirmed.

(ii) 1–10 ppm region

The short-circuit photocurrent (J_{SC}) increases (Figure 2, blue orange red solid curves). One can see that a *pn*-homojunction is formed and the built-in field (V_{bi}) increases from a small value at 1 ppm to a much larger value at 10 ppm (Figures 3(a) and 3(b)). One of the reasons for the increase in J_{SC} is the increase in carrier generation efficiency in a *pn*-homojunction with a depletion layer (red shaded regions). Moreover, the depth of the photocurrent generation region (σ) (blue shaded region) is clearly larger than the width of the depletion layer (W_{dep}) (red shaded region) (Figure 3(b)). Photocurrent generation in the region where there is no electric field (green double-headed arrow) occurs by the diffusion of minority carriers (electrons).

(iii) 10–100 ppm region

J_{SC} decreased (Figure 2, red and green solid curves) due to narrower depletion layer and narrower diffusion length of minority carrier by impurity scattering (Figure 3(c)).

We believe that doping at the ppm-level offers a general method for optimizing the design of organic photovoltaic cells and other organic electronic devices.

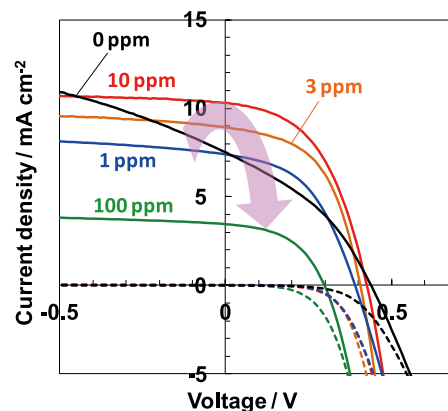


Figure 2. Current-voltage characteristics for the *pn*-homojunction cells. The doping concentrations of the *p*-layer are 0 (black), 1 (blue), 3 (orange), 10 (red), and 100 ppm (green).

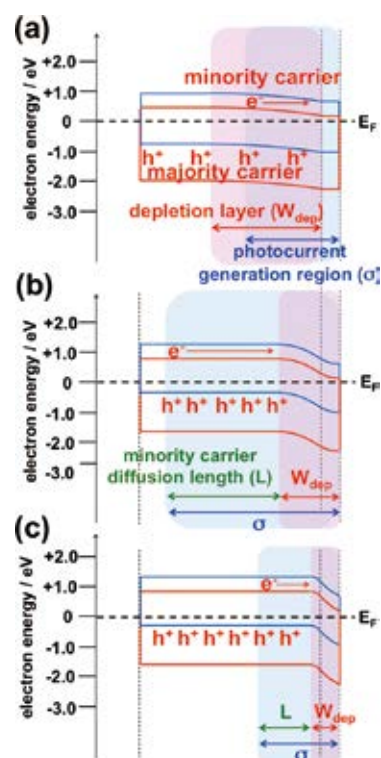


Figure 3. Energy structures of cells with doping concentrations of 1 (a), 10 (b), and 100 ppm (c).

Two-Dimensional Covalent Polymers and Organic Frameworks

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Keywords

Two-Dimensional Covalent Polymer, Covalent Organic Frameworks, Porous Organic Polymers

Covalent organic frameworks (COFs) are a class of porous polymers that enable the atomically precise incorporation of organic units into periodic structures, creating highly ordered π -columnar arrays and one-dimensional open channels. One significant structural feature is that they can be pre-designed at both primary and high-order structure levels. COFs have emerged as a platform for materials design and functional explorations and exhibit great potential for applications in gas storage, manufacture of semiconductive and photoconductive devices, energy conversion and storage, and heterogeneous catalysis. The key to the design of COFs is their topology diagram, which defines the polygon size and shape and determines the crystal lattice. Hexagonal and tetragonal topologies have been exploited for the design of COFs with discrete pores and ordered skeletons. The introduction of new topologies is highly desired to broaden the structural diversity and application of COF materials.

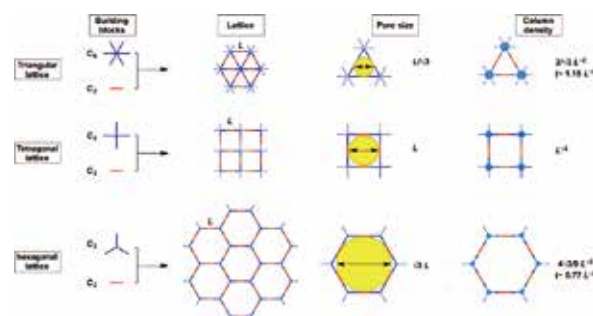


Figure 1. Comparison of topological diagrams for the synthesis of 2D COFs. The different diagrams required different building blocks and result in different lattices, π -densities, and pore sizes. The trigonal topology leads to the highest π -density and smallest pore size among the topologies thus far developed.

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).
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- X. Ding, J. Guo, X. Feng, Y. Honsho, J. Guo, S. Seki, P. Maitarad, A. Saeki, S. Nagase and D. Jiang, "Synthesis of Metallophthalocyanine Covalent Organic Frameworks That Exhibit High Carrier Mobility and Photoconductivity," *Angew. Chem., Int. Ed.* **50**, 1289–1293 (2011).
- X. Feng, L. Chen, Y. Honsho, O. Saengsawang, L. Liu, L. Wang, A. Saeki, S. Irle, S. Seki, Y. Dong and D. Jiang*, "An Ambipolar Covalent Organic Framework with Self-Sorted and Periodic Electron Donor-Acceptor Ordering," *Adv. Mater.* **24**, 3026–3031 (2012).
- 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. Design of COFs with Trigonal Topology

In this study, we developed a strategy for the rational design and synthesis of a new class of COFs based on the triangular topology (Figure 1). The triangular topology consists of C_6 -geometric vertices, which is the highest symmetry of a benzene system and has a potential to efficiently exploit space for tiling organic units into a crystal lattice. With this geometry, a triangular COF would feature the smallest pore size and most dense π -columns among all of the COF materials. However, the triangular topology has not been reported for the practical synthesis of COFs. We demonstrate the synthesis of two triangular COFs (defined as HPB-COF and HBC-COF) by using two different C_6 -symmetric vertices—one is hexaphenylbenzene (HPB), which is a typical propeller-shaped π -unit, and the other is hexabenzocoronene (HBC), which is a large graphitic π -unit—for Schiff-base polymerization with C_2 -symmetric benzene linkers. These triangular COFs form supermicropores with pore sizes of as low as 12 Å, which is among the lowest reported for COFs, whereas the density of π -columns can reach 0.25 nm⁻², which exceeds those of the COFs and supramolecular π -arrays reported to date. These crystalline COFs exhibit excellent thermal and solvent stabilities. We demonstrate that the triangular COFs enable both intra- and inter-layer π -cloud delocalization and exhibit a prominent photoconductivity, with carrier mobilities as high as 0.7 cm² V⁻¹ s⁻¹, which is among the highest reported for COFs and polygraphitic ensembles. These results suggest that the triangular topology is useful for designing COFs with unique structures to be used in a wide variety of applications, such as gas storage, catalysis, and the manufacture of sensing and semiconducting devices.

2. Light-Harvesting Porous π -Network Films: Cascade Exciton-Pumping Engines with Manipulated Speed and Efficiency

Light-harvesting antennae are the machinery for exciton pumping in natural photosynthesis, whereas cascade energy transfer through chlorophyll is key to long-distance, efficient energy transduction. Numerous artificial antennae have been developed. However, they are limited in their cascade energy-transfer abilities because of a lack of control over complex chromophore aggregation processes, which has impeded their advancement.

Here we report a viable approach for addressing this issue by using a light-harvesting porous polymer film in which a three-dimensional π -network serves as the antenna and micropores segregate multiple dyes to prevent aggregation. The porous organic polymer (POP) films are synthesized with a controlled thickness via the previously reported electrochemical method and emit bright blue luminescence. The three-dimensional π -network drastically enhances the interface of energy transfer to relay and acceptor dyes, whereas the nanopores within the film permit segregated molecular docking of multiple laser dyes with desired properties and in specific proportions.

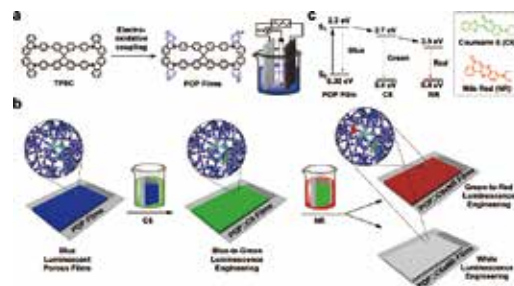


Figure 2. **a**, Schematic representation of the synthesis of POP films by the electro-oxidative coupling reaction. Inset: cell setup for electro-oxidative coupling for the preparation of POP thin films on ITO working electrode. **b**, Graphical protocol for the preparation of exciton-pumping films by dipping the films into the corresponding laser dye solutions of coumarin 6 and Nile red followed by rinsing. Inset: Enlarged circles show porous structures of the frameworks (blue: POP framework; sky blue: highlight of one TSPC unit; green: coumarin 6; red: Nile red). **c**, Diagram of cascade energy transfer from the POP film to coumarin 6 and to Nile red. Inset: Chemical structures of coumarin 6 and Nile red.

Mechanistic studies reveal that the light-harvesting films allow the integration of a cascade energy-transfer engine that functions in a vectorial and highly efficient manner and enables total control over the speed and efficiency of the energy transfer through tuning of the distribution and types of dye introduced. This film system allows for accurate and versatile luminescence engineering in producing thirty different luminescence hues, including blue, green, red and white (Figure 2). By virtue of the antenna effect, the films exhibit considerably amplified luminescence and gain exceptional quantum efficiencies. We envisage that replacement of the dyes with redox-active components may lead to application of the present technology for highly efficient photosynthesis and photoenergy conversion.

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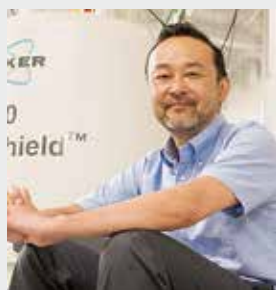
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Award

GU, Cheng; MOF2014 Kobe Best Poster Award.

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)
- 1999 Ph.D. Himeji Institute of Technology (University of Hyogo)

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
- Associate Professor, The Graduate University for Advanced Studies

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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 characterization 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 corroborations with several research groups.

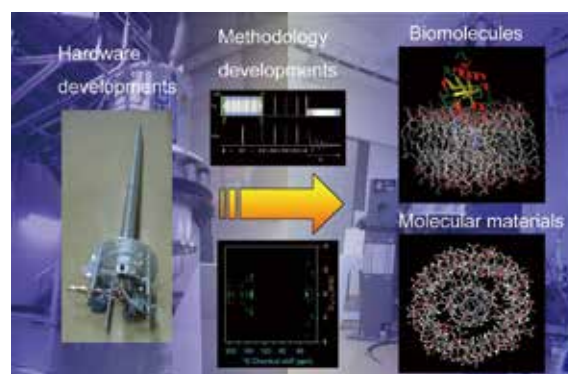


Figure 1. Outline of our studies.

Selected Publications

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1. Characterization of Organic Materials Based on Solid-State NMR through Observation of Natural Abundant Isotopes

There are so many organic materials which are insoluble to organic solvents. Solid-state NMR is one of the powerful tools to characterize such molecules. For small organic molecules and polymers consisting of repeated local structures, ^1H and ^{13}C solid-state NMR spectra through observation of natural abundant isotopes retain reasonable spectral sensitivities. Thus various types of 2D ^1H - ^{13}C hetero-nuclear correlation experiments can be performed. By combining with spectral-editing techniques, signal assignments for ^1H and ^{13}C nuclei may be achieved. In the following, we show some collaboration works for characterization of organic materials achieved by those techniques.

Dr. Higashibayashi and co-workers in IMS discovered a new phenomenon in which N-N linked bicarbazole and tetramethylbiacridine derivatives undergo electron transfer disproportionation by acid stimuli. In order to elucidate molecular structure of N-N linked bicarbazole molecules at neutral condition in solid state, signal assignments of ^1H and ^{13}C nuclei for the molecule were successfully carried out based on the two types of 2D ^1H - ^{13}C hetero-nuclear correlation experiments together with several spectral-editing techniques. The aromatic back born carbons exhibited two sets of signals that suggest either mixture of two different conformations or asymmetric local conformations respect to the symmetric axis of the molecule. Finally, the closed state of the molecules in solid state was successfully proved through the signal assignments.¹⁾

Dr. Ito and co-workers successfully developed formal aryne/carbon monoxide copolymerization using [2.2.1.] oxabicyclic alkenes as aryne equivalents. For insoluble fractions in individual reaction step was evaluated by observing ^{13}C solid-state NMR spectra. All of ^{13}C signals were successfully assigned based on the several spectral editing techniques in solid-state NMR at individual reaction steps.²⁾

We are also collaborating with several other research groups for characterization of natural products and synthetic polymers and *etc.*, based on solid state NMR. Currently, new types of correlation experiments for such organic molecules without isotope enrichments are also under investigated.

2. Intermolecular Packing in *B. mori* Silk Fibroin Revealed by Solid-State NMR³⁾

We have been collaborated with Prof. Asakura's group during couple of years for characterization of silk model

peptides using solid-state NMR. The group has been suggested that crystalline *Bombyx mori* silk in silk II form (the silk after spinning) is intrinsically heterogeneous anti-parallel β -sheets.

In this study, full assignments of high resolution ^1H solid state NMR spectra for model peptide (Alanine-Glycine)₁₅ peptide was successfully obtained using ultra high speed magic angle spinning (MAS) probe under ultra high field 920 MHz spectrometer in IMS. Distinct heterogeneity was observed for both ^1H and ^{13}C spectra for the AG(15) peptide. A new model containing two different packing arrangement of anti-parallel β -sheets was proposed based on obtained results. Through the energetically minimized structure using CASTEP, chemical shifts for ^1H , ^{13}C and ^{15}N nuclei were calculated. The obtained new model structure was supported by both calculated and experimentally observed chemical shifts for those nuclei in addition to the ^1H - ^1H proximities obtained through the analyses of 2D ^1H -double quantum MAS experiments. Thus intermolecular packing of *B. mori* silk fibroin has been solved in this study.

3. Selective Observation of ^2H Quadrupole Interaction by Two Dimensional Solid-State NMR in Paramagnetic Compounds⁴⁾

A simple 2D solid-state NMR correlation experiments exhibiting ^2H quadrupolar interaction in indirect dimension for paramagnetic compounds was developed. The method is based on a quadrupole-echo sequence inserted with π pulses where the pulse spaces are incremented an asymmetric fashion with use of strong rf field pulses. Quadrupolar interaction can be analyzed by projected quadrupole spectrum in the indirect dimension of 2D spectrum obtained by this technique through the simulation of the quadrupole-echo sequence without considering the effect of the paramagnetic shift.

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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. (Dibenzoylmethanato)boron Difluoride Derivatives Containing Triphenylamine Moieties: A New Type of Electron-Donor/ π -Acceptor System for Dye-Sensitized Solar Cells¹⁾

(Dibenzoylmethanato)boron difluoride derivatives containing triphenylamine moieties were synthesized as a new type of electron-donor/ π -acceptor system. These new compounds exhibited long-wavelength absorptions in the UV/Vis spectra, and reversible oxidation and reduction waves in cyclic voltammetry experiments. Their amphoteric redox properties are based on their resonance hybrid forms, in which a positive charge is delocalized on the triphenylamine moieties and a negative charge is localized on the boron atoms. Molecular orbital (MO) calculations indicate that their HOMO and LUMO energies vary with the number of phenylene rings connected to the difluoroboron-chelating ring. Dye-sensitized solar cells fabricated by using these compounds as dye sensitizers exhibited solar-to-electric power conversion efficiencies of 2.7–4.4%.

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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. Molecular Design for Boosting Conductivity of Deca-Nanometer Scale Molecular Wires

We have already established the synthetic process for “single-nanometer scale” multi-terminal device systems. The next target is to fabricate the “deca-nanometer scale” systems. In this case, one of the fundamental issues is the insufficient

conductivity of neutral (undoped) deca-nanometer molecular wires, and so we have been developing the various types of building block for boosting conductivity of long molecular wires by introducing redox-active sites into the conjugated main chain. Figure 1 shows the examples (1-5).

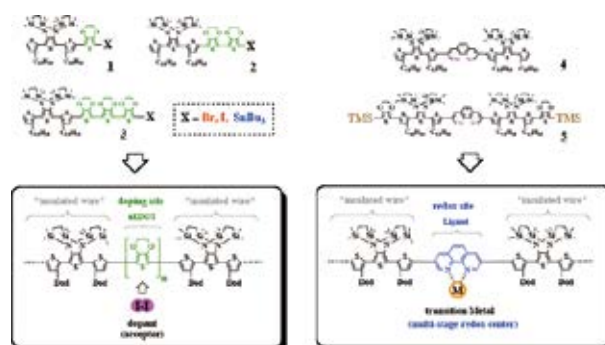


Figure 1. Building blocks for boosting conductivity of long molecular wires.

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*)

Development of Multi-Functional Organic Liquids: Color & Spin toward Printable Memory Media

Because of optoelectronic properties and spin-active 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 display and optoelectronic devices. In our work we apply the concept of “alkyl- π engineering” using flexible branched alkyl chains to the double-decker phthalocyanines to achieve control over self-assembly and of the material. Our aim is to obtain solvent-free soft materials, including room temperature liquids, with tunable intermolecular interactions and spin as well as electrochromic properties. A multi-functional, *i.e.*, electrochemically and organic radical (spin) active-switchable, electrochromic, as well as non-Newtonian type, room temperature solvent-free liquid of double-decker phthalocyanine has been successfully developed. The finding would be applicable to develop paintable spin & electrochromic switching memory devices.



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 ($\text{Au}_n(\text{SR})_m$) 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 $\text{Au}_n(\text{SR})_m$ clusters possess great potential as new nanomaterials. We are studying the following subjects related to magic $\text{Au}_n(\text{SR})_m$ 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.

RESEARCH ACTIVITIES

