# **RESEARCH ACTIVITIES** Materials Molecular Science

Extensive development of new molecules, molecular systems and their higher-order assemblies is being conducted in the four divisions and in the research center for molecular scale nanoscience. Their electronic, optical and magnetic properties as well as reactivities and catalytic activities are being examined in an attempt to discover new phenomena and useful functions.

# Structures and Functions of Metal–Carbon Nano-Systems Produced from Metal-Acetylides

# Department of Materials Molecular Science Division of Electronic Structure



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Metal acetylides or metal ethynyl conpounds are made of the  $M^+-C^-$  ionic bonds. However, the ionic states of the acetylides are essentially metastable resulting in the segregation into metal-carbon or metal-organic polymer nanophases. Following to the invention of graphene-walled Mesoporous Carbon Nano Dendrides (MCND) by evaporating silver from dendroid silver acetylide crystals, we have invented copper nanowires and nanonets by removing the carbon, this time, and also 3D nanonets with copper skeletons with carbon mantles. These electron-conductive materials can be used for energy storage devices.

## 1. Invention of Electron-Conductive 3D Nanostructure Networks for Energy Storage Electrodes

As demonstrated by the invention of graphene-walled Mesoporous Carbon Nano-Dendrites (MCND), metal-acetylides are well suited for generating nanostructured conductive materials. In contrast to silver acetylide, copper acetylide or methylethynyl copper normally produces wire-type crystals. Copper methylacetylide (Cu-C=C-CH<sub>3</sub>) also produces wire type crystals bigger than those of copper acetylide as shown in the next section. These wire crystals form bundles of the wires and, owing to the catalytic activity of copper, all carbons are removed as volatile hydrocarbon gases leaving copper wires, or 3D copper nets (Figure 1-a). We also succeeded to generate Hollow Carbon Nets by removing copper and the methyl group from copper methylacetylene wire crystals. After the segregation reaction of the acetylide to copper nanoparticles, light hydrocarbon gases, and the carbon matrices with 3D connected net-type structures of 20~150 nm wires (Figure 1b), mild thermal activation and nitric acid treatment removes copper components from the hybrid materials leaving hollow carbon networks. This material allow to be heated at a high temperature producing conductive graphene and graphitic components around the wall region.

In the empty space of the carbon networks, one can fill tin nanoparticles or silicon submicron particles to make lithium ion batteries or other active metal particles for new batteries.



**Figure 1. a**: a SEM image of the 2D copper nanonets. **b**: Hollow Carbon Alveolus with graphitic walls. The body is a planer belt shape with many carbon balls connected each other.

# 2. Self-Assembly of Copper Methyl-Acetylide Nanowires

The methods for nanowire production by highly aniso-

tropic materials are usually based upon the binding with covalent bonds. The  $Cu_2C_2$  molecule is a new category of highly anisotropic crystal, which is based on ionic bonding with a highly anisotropic ligand of a  $C_2^{2-}$  unit. Crystal growth of metal atoms is expected to be isotropic and nanowire structures cannot be obtained by a normal method of crystal growth. Our strategy is that the insertion of an acetylenic functional group ( $C_2^{2-}$  unit) to metal element provides anisotropic properties. Metal acetylides can be a candidate compound to self-assemble into nanowire morphology.

The substituent effect was examined on nanowire generation of  $Cu_2C_2$ . We have succeeded in producing the copper methyl-acetylene ( $CuC_2CH_3$ ) nanowires by the simple selfassembly technique. The methyl substitution on an acetylene molecule, can also self-assemble into nanowire morphology through methyl-methyl hydrophobic intermolecular interaction in an aqueous solution. It may mean that an acetylenic or a methy-ethynyl functional group originally has anisotropic crystal growth properties.

It is very simple to produce  $CuC_2CH_3$  nanowires. The fabrication method for  $CuC_2CH_3$  nanowire involves bubbling methyl acetylene (propyne,  $HC_2CH_3$ ) gas into an ammonia solution of copper chloride (CuCl).<sup>1,2)</sup> Figure 2 shows a scanning electron microscopic (SEM) image of as-grown product of  $CuC_2CH_3$ . A mat with copper methyl acetylide nanowires was observed. It should be noticed that the amount of impure, amorphous product (not nanowire) for  $CuC_2CH_3$  is much smaller than that for  $Cu_2C_2$ . Not only purity of the  $CuC_2CH_3$  nanowire mats, but also the large surface area of them can link to the capability of good gas adsorbent, gas sensor, or gas storage materials. Indeed, we attempt to check the properties of this nano-material for hydrogen storage, catalysis and so on.



**Figure 2.** A SEM image of Cu−C≡C−CH<sub>3</sub> bundled nanowire crystals. Organometallic crystals are normally space-charged for SEM observation.

# 3. Weak Ferromagnetism in Chromium Acetylide Based Magnet

The interest in constructing a transition metal acetylide  $[M(C=C-R)_n]^{(m-n)+}$  based magnet has been stimulated, in part, by its superior optical properties that raise the possibility of using the materials in various magneto-optical devices.

Recently, we succeeded in constructing the first transition metal acetylide based magnet  $[CrCyclam(C=C-Ph)_2]$  [Ni (mdt)<sub>2</sub>](H<sub>2</sub>O). The crystal structure of the material is characterized by the centrosymmetric unit cell containing a pair of a

cation  $[CrCyclam(C=C-Ph)_2]^+$  (S = 3/2) and an anion [Ni  $(mdt)_2$ <sup>-</sup> (S = 1/2), and one water molecule. The cations and anions form one dimensional [3/2-1/2] ferrimagnetic chains. The inter-chain interaction between adjacent cations along the *a*-axis is mediated by the water molecules which are strongly bound to the cations by hydrogen bonds as shown in Figure 3b. Despite the centrosymmetry of the whole crystal, a water molecule can occupy only one of the two centrosymmetric sites, resulting in the local breakdown of the inversion symmetry between adjacent cations. The observed magnetic susceptibility is in good agreement with the theoretical value of the isolated [3/2-1/2] ferrimagnetic chains down to 3.8 K with the intra-chain interaction  $2J/k_{\rm B} = -5.7$  K. The weak interchain interaction through water molecules brings a magnetic phase transition at 3.7 K accompanied with a small spontaneous magnetization as shown in Figure 1d, indicating a weak-ferromagnetic ground state below the temperature. The remanent magnetization monotonically increases from 0.016 to 0.12  $\mu_B$  as the temperature decreases from 3.7 to 1.8 K, while coercive force approximately keeps a constant value of 0.8 mT in the temperature range of 2.9 < T < 3.7 K, followed by a rapid increase below 2.9 K, suggesting the existence of the second phase transition. The existence of the second phase transition is also evidenced by the AC susceptibility, but the detail of the transition remains unclear. The weak ferromagnetism is originated from the local symmetry breakdown that allows the Dzyaloshinsky-Moriya interaction between adjacent cations despite the centrosymmetry of the whole crystal.



**Figure 3.** a) The molecular structures. b) The inter-chain interaction path along the *a*-axis mediated by a water molecule. The red spheres indicate two crystallographically equivalent positions of the water molecule, and the dashed blue lines represent the hydrogen bonds between the oxygen atom of a water molecule and the hydrogen atom of cations. c) The temperature dependence of the  $\chi T$  value. The red solid line indicates the theoretical value calculated by the isolated [1/2–3/2] ferrimagnetic chain model with the intra-chain interaction 2*J*/k<sub>B</sub> = -5.7 K. d) The magnetization curves measured at 1.8, 3.3 and 4 K.

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# Characterization of Magnetic Ultrathin Films by Novel Spectroscopic Methods

# Department of Materials Molecular Science Division of Electronic Structure



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Novel properties of magnetic metal ultrathin films have been attractive both from fundamental interest and from technological requirements. We are interested in drastic modification of metal thin films by surface chemical treatment such as adsorption-induced spin transitions and morphological changes. The magnetic properties are characterized by means of several kinds of spectroscopic methods like MOKE (Magneto-Optical Kerr Effect) using lasers and XMCD (X-ray Magnetic Circular Dichroism) using UV-visible lasers and XMCD (Xray Magnetic Circular Dichroism) using synchrotron radiation soft X-rays.

Moreover, we have been exploiting new techniques based on UV photoemission magnetic circular dichroism (MCD) such as ultrafast time resolved UV MCD photoelectron emission microscopy (PEEM) for spatiotemporal magnetic imaging.

### 1. Observation of Two-Photon Photoemission Magnetic Circular Dichroism<sup>1)</sup>

In 2006, we discovered surprising enhancement of the UVvisible photoemission MCD from ultrathin Ni films on Cu (001) when the photon energy was tuned to the work function threshold.<sup>2)</sup> Based on this discovery, we succeeded in the first observation of UV MCD PEEM images of ultrathin magnetic films.<sup>3)</sup> This method allows us to perform in-laboratory MCD PEEM measurements instead of the usage of third-generation synchrotron radiation XMCD PEEM. Moreover, ultrafast UV MCD PEEM images were successfully obtained by using ultrashort pulsed lasers and a pump-and-probe technique.<sup>4)</sup>

Laser two-photon photoemission (2PPE) MCD should be also an attractive technique, because deeper valence bands can easily be detected without using vacuum UV light. In this work, we succeeded in the observation of significant enhancement in the 2PPE MCD near the work function threshold.

Figure 1(a) shows the MCD asymmetry of 12 monolayer (ML) Ni grown on Cu(001) as a function of excitation energy. An wavelength-tunable Ti:sapphire laser (80 MHz, 2.5 W, ~70

fs, 690–1050 nm) was employed in these measurements. The 4th-order harmonics for 1PPE (one-photon photoemission, hv = 5-6 eV) and the 2nd-order for 2PPE (hv = 2.5-3 eV). Noticeable enhancements of both the 1PPE and 2PPE MCD asymmetries are clearly observed in the vicinity of the work function threshold ( $\Phi = 5.15 \text{ eV}$ ). It is noted that the spectral features of the 1PPE and 2PPE MCD resemble each other and that the negative maximum (~7%) in the 2PPE MCD is strong enough to apply this phenomenon to MCD PEEM measurements.

Figure 1(b) depicts the laser incidence angle ( $\theta$ ) dependence of the 1PPE and 2PPE MCD asymmetries from the same sample. In the 1PPE, the function is rather constant, although the MCD asymmetry should basically be proportional to  $\cos\theta$  ( $\theta$  corresponds to the angle between the magnetization and the light propagation direction). The deviation from the  $\cos\theta$  function is ascribed to the presence of the reflected light. Actually, the dashed line in Figure 1(b), which shows the calculated result using dielectric constants, agrees well with the observation. On the contrary, huge further enhancement is observed in the 2PPE at the grazing laser incidence (~45°). The negative maximum reaches as much as ~28%. Since



**Figure 1.** (a) 1PPE and 2PPE MCD asymmetries as a function of excitation energy (*hv* and 2*hv* for 1PPE and 2*hv*, respectively). The sample is perpendicularly magnetized Ni(12ML)/Cu(001) at room temperature and the laser incidence angle was 0° (normal incidence). Noticeable enhancements near the work function threshold (5.15 eV) can be seen as negative maxima. (b) Incidence angle dependence of 1PPE and 2PPE MCD asymmetries. 2PPE MCD shows negative maxima at ~45° incidence. Dashed lines are the calculated results using a simple model.

PEEM experiments require grazing light incidence, the present finding is essentially important for the 2PPE MCD. The dashed line in Figure 1(b) again agrees fairly well with the observation. The calculation was done by assuming that only the first photon contributes to the MCD since the second photon excites the hot electron that is regarded as a free electron without spin-orbit coupling. Theoretical study is needed to understand the present observation in detail.

### 2. Structural and Magnetic Properties of Ultrathin Iron Nitride Eptaxial Films Grown on Cu(001)

Bulk iron nitrides exhibit various kinds of phases depending on the Fe/N stoichiometry, and many of the Fe-rich phases show ferromagnetism. It is interesting to investigate magnetic and structural properties of ultrathin iron nitride films. We have succeeded in the preparation of very flat ultrathin iron nitride films grown eptaxially on Cu(001) by the sequential process of depositing elemental Fe, subsequent N<sup>+</sup> bombardment, and annealing at ~670 K. Figures 2(a) and 2(b) show respectively the  $p4gm(2\times 2)$  LEED (low energy electron diffraction) pattern and the STM (scanning tunnel microscopy) of the 1 ML Fe<sub>2</sub>N film. The Fe/N stoichiometry of 2:1 was verified separately by the X-ray absorption spectra (XAS) intensity. A sharp LEED pattern in Figure 2(a) and a wide terrace observed in the STM image of Figure 2(b) confirm the extreme flatness of the film. The LEED I-V curves were measured and analyzed to determine quantitative surface structures. The surface structure obtained is shown in Figure 2(c). The surface Fe atoms are squeezed due to embedding of the N atoms, leading to the  $p4gm(2\times 2)$  reconstructed surface.

By conducting a similar preparation procedure, a 2 ML iron nitride epitaxial film was also obtained. Interestingly, the Fe/N stoichiometry is found to be 4:1 by XAS, and the tensor LEED analysis has elucidates that the topmost layer structure is nearly identical to that of 1 ML Fe<sub>2</sub>N, while the second layer contains only Fe, as seen in Figure 2(d). Such surface structures is found to mimic the bulk  $\gamma$ '-Fe<sub>4</sub>N structure, where Fe forms *fcc* lattice with the N atom located at the center of the



**Figure 2.** (a)  $p4gm(2\times2)$  LEED pattern, (b) STM images, and (c) surface structure of the 1 ML Fe<sub>2</sub>N film on Cu(001), and (d) that of the 2 ML Fe<sub>4</sub>N film on Cu(001). The surface structure was determined quantitatively by the tensor LEED analysis.

lattice. By neglecting the occurrence of the  $p4gm(2\times2)$  surface reconstruction, the 1 ML Fe<sub>2</sub>N/Cu(001) structure can be regarded as one  $\gamma$ '-Fe<sub>4</sub>N layer containing N, while the 2 ML Fe<sub>4</sub>N structure corresponds to the unit cell of  $\gamma$ '-Fe<sub>4</sub>N.

Magnetic properties were investigated by XMCD using the Beamline 4B of the UVSOR-II synchrotron radiation facility in IMS and our high-field & low-temperature XMCD apparatus recently developed.<sup>5)</sup> Figure 3(a) shows the angular dependent magnetization (M-H) curves of 1-4 ML iron nitride films on Cu(001). The *M*–*H* curves along the  $\theta = 0^{\circ}$  direction imply that the surface normal is a magnetically hard axis, while the grazing angle ( $\theta = 55^{\circ}$ ) data indicates an easy axis within the film plane. The total magnetic moments  $m = m_{spin} + m_{spin}$  $m_{\rm orb}$  and the direction dependent orbital magnetic moments  $m_{\rm orb}$  were obtained by the XMCD sum-rule analysis. The total magnetic moment m [Figure 3(a)] of 1 ML is rather small possibly due to the formation of strong chemical bonds between Fe and N. It increases with the thickness and seems to approach the bulk  $\gamma$ '-Fe<sub>4</sub>N value of 2.2  $\mu$ <sub>B</sub>. The orbital magnetic moment  $m_{\rm orb}$  [Figure 3(b)] is always larger in the in-plane (//) direction than in the perpendicular  $(\perp)$  direction. The difference between  $m_{\rm orb}^{\prime\prime}$  and  $m_{\rm orb}^{\perp}$  is ~0.06  $\mu_{\rm B}$ , which corresponds to the uniaxial magnetic anisotropy constant  $K_u$  of ~0.1 meV/atom. This implies semiquantitative agreement in the present macroscopic and microscopic observations. The large in-plane magnetic anisotropy of the present system is resulted from a large anisotropy in the spin-orbit interaction.



**Figure 3.** (a) Magnetization curves of 1–4 ML iron nitride films on Cu(001) at T = 5 K, recorded by the Fe L3-edge circularly polarized X-ray absorption intensity and (b) the angle dependent XMCD spectra of the same samples at T = 5 K and  $H = \pm 5$  T. The X-ray incident angles  $\theta = 0^{\circ}$  and 55° correspond respectively to normal and grazing magnetization measurements.

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# Advanced Design and In-Situ Time-Resolved Analysis of Catalyst Surfaces

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# 1. Advanced Design of Catalytically Active Structures at Surfaces

Although many useful chemicals have been produced by heterogeneous solid catalysts, the molecular-level design of heterogeneous catalyst surfaces has not been established yet. On heterogeneous catalyst surfaces with the limited accessibility of reactants, rate enhancement and new catalysis can often be obtained on novel unsaturated metal structures, which are hard to be isolated in homogeneous solutions. We have succeeded in preparing novel catalytically active structures on oxide surfaces for selective catalysis by attaching techniques of some organic acid-base catalysts or metal-complex catalysts.<sup>1–6)</sup>



Figure 1. The step-by-step preparation and photo-induced structural transformations of novel unsaturated Ru complexes on a SiO<sub>2</sub> surface for the selective photo-oxidation of cycloalkanes.<sup>1)</sup>

For examples, the photo-irradiation of a Ru complex supported on a SiO<sub>2</sub> surface was found to promote the selective formation of two different unsaturated Ru complexes under O<sub>2</sub> or N<sub>2</sub> atmosphere, one of whose structures with an appropriate Ru–H conformation efficiently catalyzed the selective photooxidation of cycloalkanes with O<sub>2</sub>. The active Ru complex immobilized at double sites on SiO<sub>2</sub> was prepared by the photo-induced selective elimination of a *p*-cymene ligand accompanied with dissociative coordination of a surface OH group to the unsaturated Ru center (Figure 1). The two supported Ru complexes were reversible for the structural transformation by photo-excitation with different wavelength and atmospheres.<sup>1)</sup>

### 2. Design of Molecular-Imprinted Metal-Complex Catalysts for Regio- and Shape-Selective Catalysis

Molecular imprinting of supported metal complex in which a specific ligand serves as a prescribed template is devoted to tailor-made design of catalyst architecture for selective integrated catalysis. A selective reaction cavity memorized the shape and coordination environment of a ligand, which is a template for molecular imprinting, can be selectively created right beside an unsaturated active metal atom on a support surface. We have designed and prepared a novel molecular-imprinted Ru-complex catalyst on a SiO<sub>2</sub> surface and succeeded in regulating the regio- and shapeselective epoxidation of limoene using O<sub>2</sub>.

A molecular-imprinted Ru-complex catalyst was prepared by following step-by-step procedures: (1) the attachment of a precursor Ru complex onto a SiO<sub>2</sub> surface, (2) the coordination of limonene-10-ol (template), which possesses a similar shape to an intermediate of terminal C=C bond epoxidation of limonene, (3) stacking of surface SiO2-matrix overlayers, and (4) the removal of the template ligand to create a shapeselective reaction space (cavity) on the active Ru site (Figure 2). The structures of the supported and molecular-imprinted catalysts were characterized by means of solid-state NMR, FT-IR, XRD, XRF, UV/Vis, BET, and XAFS. We found that the molecular-imprinted catalyst designed for the terminal C=C bond epoxidation of limonene exhibited fine shape selectivity discriminating a methyl group of alkene reactants and high regioselectivity for the epoxidation of the terminal C=C bond of limonene.



**Figure 2.** Design of a molecular-imprinted Ru-complex catalyst for the terminal C=C bond epoxidation of limonene.

We have also designed novel molecular-imprinted Ru catalysts for the asymmetric transfer hydrogenation of ketones. Molecular recognition sites spatially locating the imprinted matrix was designed at the molecularly imprinted catalyst surface for the first time.

### 3. In-Situ Time-Resolved XAFS and Raman Spectroscopy for Reaction Mechanism of Selective Alcohol Oxidation on Supported Vanadium Catalysts

Vanadium is one of the most active metals for oxidation catalysis and supported V catalysts on various oxide surfaces have been utilized for selective alcohol oxidation to aldehyde at low temperatures. Their catalytic activity and aldehyde selectivity highly depend on the structures of supported V species, however the catalytic reaction mechanism of selective alcohol oxidation has not been demonstrated yet. We have developed in-situ time-resolved energy-dispersive XAFS (DXAFS) and in-situ time-resolved Raman spectroscopy, which can monitor dynamic structural changes in active catalysts *under working conditions in real time*,<sup>7)</sup> and the structural kinetics and reaction mechanism of selective ethanol oxidation on V/SiO<sub>2</sub> and V/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were investigated.

Figure 3 shows a series of V K-edge DXAFS spectra recorded every 150 ms for the oxidation of ethanol on a V/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The analysis of DXANES spectra revealed rate constants and activation energies for the oxidation/reduction and symmetry changes of the active V catalyst. Ethanol smoothly reacted with V<sup>5+</sup> species, forming the stoichiometric amount of acetoaldehyde, and the V catalyst reduced with the rate constant of 0.19 s<sup>-1</sup>. The further adsorption of ethanol varied the symmetry of the supported V species with the rate constant of 0.12 s<sup>-1</sup>. When O<sub>2</sub> admitted to the reduced V catalyst, CO and CO<sub>2</sub> were obtained as major C products. The rate constants and activation energies for the V oxidation were estimated to be 1.59 s<sup>-1</sup> and 52 kJ mol<sup>-1</sup>, respectively. These results suggest

#### Awards

TADA, Mizuki; The 13<sup>th</sup> JSSRR Scientific Awards. TADA, Mizuki; The 1<sup>st</sup> Inoue Science Research Award. TADA, Mizuki; The 11<sup>th</sup> Morita Fellowship Award. that low acetoaldehyde selectivity on the V/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is caused by the oxidation process with O<sub>2</sub> on the reduced V species.

On the other hand, a SiO<sub>2</sub>-supported V catalyst exhibited high acetoaldehyde selectivity and there were no significant changes in in-situ V K-edge XAFS and Raman spectroscopy. On the SiO<sub>2</sub> surface, it is suggested that the bond breaking of a V–O–Si bond forms a V–O–Et species, which selectively converts to acetoaldehyde. The in-situ time-resolved DXAFS and Raman spectroscopy revealed the relationship between the structures of supported V species and their ethanol oxidation performances, the structural kinetics of the active V catalysts, and the reaction mechanism of the ethanol oxidation catalysis for the first time.



**Figure 3.** A series of V K-edge DXAFS spectra for the selective oxidation of ethanol on a  $V/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 553 K. DXAFS spectra were recorded every 150 ms and presented every 900 ms.

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# Optical Studies of Charge Ordering in Organic Conductors

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In organic conductors, kinetic energy is comparable with on-site and inter-site Coulomb energy. Due to this reason, many organic conductors are located in a boundary area between metallic and localized states, and thus various organic charge-transfer compounds show metal-insulator phase transition. Recently, charge-ordered (CO) state originated from Coulomb interaction is widely found in organic conductors, and the electronic phase diagrams of typical organic conductors are re-considered taking CO into account. The CO state attracts much attention, first because charge-mediated superconductivity is theoretically predicted in superconducting compounds neighbored on CO phase, second because some compounds in CO phase show ferroelectricity through the crystallization of conduction electrons, third because the narrow-band compounds have a poorly understood intermediate state between metallic and CO states. We have investigated the CO state and metallic state near CO employing infrared and Raman, and reflection spectroscopy.

# 1. Charge Order–Disorder Phase Transition in $\alpha$ '-(BEDT-TTF)\_2IBr\_2^1)

Among a variety of organic conductors, the  $\alpha$ -type BEDT-TTF salts shows rich properties such as charge order, superconductivity, zero-gap state, persistent photoconductivity, photoinduced phase transition, and non-linear optical response. Although  $\alpha$ '-(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> is not isostructural to  $\alpha$ -type BEDT-TTF salts, it has a herringbone molecular arrangement similar to  $\alpha$ -type BEDT-TTF salts. This compound shows an insulator-insulator phase transition differently from convensional metal-insulator transition. According to the x-ray diffraction study, no distinct structural change was reported at phase transition temperature. We elucidated the mechanism of this phase transition.

Kinetic energy arising from hopping process is directly correlated with bandwidth. To compare the bandwidth with other  $\alpha$ -type BEDT-TTF salts, the kinetic energy was esti-



**Figure 1.** Snapshot of order (top) and disorder (bottom) model. The blue circles denote holes (charge-rich sites). The dashed lines denote the inter-site Coulomb interaction. In ordered state, every charge-rich site is surrouded by two charge-rich sites (m = 2), whereas in disordered state various configurations (m = 0, ..., 6).are accessible as shown in the above figures.

mated from integration of optical conductivity in the farinfrared and infrared region. It was found that the kinetic energy of  $\alpha$ '-(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> is much smaller than other  $\alpha$ type BEDT-TTF) salts, and therefore the bandwidth is narrowest among the  $\alpha$ -type BEDT-TTF salts.

The investigation of infrared and Raman spectra of  $\alpha$ '-(BEDT-TTF)<sub>2</sub>IBr<sub>2</sub> with the aid of <sup>13</sup>C-substituted compound showed clear evidence that the low-temperature high-resistivity phase is a charge-ordered state. The horizontal stripe of charge order is most stable, but dislocation can be easily generated because a diagonal stripe is energetically very close to the horizontal stripe.

It was found from infrared and Raman spectra that the electrons are localized even in the high-temperature (HT) phase. In HT phase, however, inter-site hopping rate significantly increases, symmetry changes from P1 to P1, diagnostic vibronic mode which reflects order parameter vanishes, and the density of state near Fermi energy appears. All of these observations indicate that the HT phase is a dynamically disordered state. Therefore, this insulator-to-insulator transition is regarded as an order-disorder phase transition of localized charge. This localized electronic state in the whole temperature range is ascribed to the very narrow bandwidth.

Based on this picture, we proposed a simple electronic model using point charge approximation neglecting all transfer integrals. In this model, the energy states can be calculated from the electrostatic inter-site Coulomb energy (see Figure 2). Using this model, the energy states of charge-rich sites (holes) are calculated for ordered and disordered states. The estimation of the activation energies in low-temperature and high-temperature phase, resistivity jump can be qualitatively explained. The optical gap in low-temperature phase and the increase of optical weight in the gap region in high-temperature phase also is well explained by this model. The magnetic susceptibility is also consistent with this localized model.

Hydrostaic pressure suppresses the order-disorder transition temperature down to 100 K at 1.2 GPa, above which the phase transition changes the character such as a metal-insulator transition. The Raman spectrum was measured up to 2.3 GPa at various temperatures. The Raman spectrum also changes spectral features above 1.6 GPa. The author presents a pressure-temperature phase diagram using the spectral characteristic feature and electrical resistivity. The order-disorder transition extends up to 1.3 GP, above which metal-insulator transition appears. The insulating states above 1.3 GPa is a dimer-Mott state or density-wave state.

### 2. Direct Observation of Ferroelectric Domains Created by the Wigner Crystallisation of Electrons in an Organic Conductor<sup>2)</sup>

In an effort to materialize a novel class of ferroelectrics, the possibility of pure-electronic mechanisms of spontaneous polarization, draws recent attention.<sup>3)</sup> We have proposed in the previous study that an organic superconductor  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> could be a promising candidate of a compound corresponding to the above picture.<sup>4)</sup> In the present study, we examined to reveal the ferroelectric domains created in the organic complex by means of second-harmonic (SH) generation interferometry.

The ferroelectric transition in the compound is driven by Wigner crystallization of valence electrons. Since the charge ordering forms a pattern which is incompatible with the centric crystal symmetry underlying the valence charges. The domains created by such a transition that breaks centric symmetry, 180°



**Figure 2.** (a) Propagations of the excitation and SH light waves in the SH interferometry. (b) Transmission microscope image of a thin single crystal of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> used for the SH interference measurement. (c) and (d) show the SH contrast images measured from the rectangular region in (b) masured at above (140 K) and lower (50 K) temperature than the transition point (135 K), respectively.

polar domains, in which different domains have opposite polarizations, should be formed.

The SH intereferometry enables us to observe 180° polar domains that cannot be observed by a conventional microscope. Figure 1(a) illustrates the trajectory of the SH light waves in the interferometry. As shown in this sketch, the phase of SH wave generated from a domain is reversed from that of different domains of opposite polarization. On the SH beam generated by the specimen, harmonic beam produced by a single-domain nonlinear-optical crystal is overlaid as reference wave. The two beams interfere constructively or destructively depending on the phase difference, resulting in the SH contrast of domain structure.

Figure 1(b) shows the microscope image of the crystal used for the domain observations. Figures 1(c) and 1(d) show the SH images observed from the rectangular region in 1(b) at above (140 K) and lower (50 K) temperature than the transition point ( $T_{CO} = 135$  K), respectively. The SH image showed the drastic change from 1(c) to (d); the image was split into bright and dark regions representing the formation of polar domains.

The growth of macroscopic domains manifests that the polar state forms as a stable bulk phase in the complex, materializing the feasibility of the electronic mechanism of ferroelectric polarization. The visualization of domain structures is important as the first step for understanding the nature of the ferroelectric compounds. Furthermore, the ability of discerning different polarizations can be utilized as a means of non-destructive readout of information in memory applications of the compound.

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# Magnetic Resonance Studies for Molecular-Based Conductors

# Department of Materials Molecular Science Division of Electronic Properties



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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, highlycorrelated electron systems and functional materials. Competition between the electronic phases in molecular-based conductors has attracted much attention.<sup>1)</sup> 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.

# 1. <sup>13</sup>C NMR Study of the Chemical Pressure Effect in $(TMTTF)_2[(AsF_6)_x(SbF_6)_{1-x}] (x \sim 0.5)$

<sup>13</sup>C NMR measurements of  $(TMTTF)_2[(AsF_6)_x(SbF_6)_{1-x}]$ ( $x \sim 0.5$ ) alloy were performed in order to understand the chemical pressure effect and the electronic state at low temperatures. The charge-ordering transition temperature is the intermediate value between those of SbF\_6 and AsF\_6 salts. The broadening of NMR spectra and the weak temperature dependence of the spin-lattice relaxation rate at low temperatures indicate that this salt is situated in the vicinity of the phase boundary between the spin-Peierls and antiferromagnetic phases.

## 2. <sup>13</sup>C NMR Investigation of Low-Temperature States in One-Dimensional Organic Cation Radical Salt, (TMTTF)<sub>2</sub>SbF<sub>6</sub>, under High Pressures

<sup>13</sup>C nuclear magnetic resonance (NMR) measurements

under the application of hydrostatic pressure were carried out on the one-dimensional organic conductor,  $(TMTTF)_2SbF_6$ , to investigate the competed antiferromagnetic and spin-singlet ground states. The charge-ordering (CO) transition temperature,  $T_{CO}$ , (155 K at ambient pressure), decreased to 100 K under a pressure of 5 kbar, and was suppressed above 8 kbar. Under pressures between 5 kbar and 14 kbar, the low-pressure side antiferromagnetic state (AF-I) was suppressed. At the same time, a spin-gap phase was stabilized. Above 17 kbar, another antiferromagnetic phase appeared below approximately 15~20 K. A possible reentrant antiferromagnetic phase diagram is discussed from a microscopic point-of-view.



**Figure 1**. Temperature dependence of the <sup>13</sup>C NMR spectra of (TMTTF)<sub>2</sub>SbF<sub>6</sub> under a pressure of 25 kbar.

# 3. Anomalous Temperature Dependence of *g*-Tensor in Organic Conductor, $(TMTTF)_2X$ (X = Br, PF<sub>6</sub> and SbF<sub>6</sub>)

The magnetic properties of organic conductor  $(TMTTF)_2X$ (X = Br, PF<sub>6</sub> and SbF<sub>6</sub>), where TMTTF is tetramethyltetrathiafulvalene, were examined by electron spin resonance (ESR) spectroscopy, X-ray diffraction (XRD) of the single crystals, and quantum-chemical calculation of the g-tensor. In the case of salts with bulky counter anions such as the PF<sub>6</sub> and SbF<sub>6</sub>, an anomalous temperature dependence of the g-tensor was observed in the temperature range from 20 K to 296 K. This anomalous behavior of the g-tensor signifies the rotation of the principal axes as well as the shift of the principal values. The g-tensor of the Br salt is, however, temperature independent. No remarkable change in the intra-molecular structure as a function of temperature was observed for all salts. On the other hand, the distance between TMTTF and counter-anion molecules obviously decreases as the temperature decreases for the  $PF_6$  and the  $SbF_6$  salts, while thermal contraction is not remarkable for the Br salt. In order to clarify the origin of the anomalous behavior of the g-tensor, we investigated the possibility of deformation of the wave-function by the counteranion potentials using a quantum-chemical calculation for the actual crystal structures measured at low-temperatures. In this paper, we describe the first direct observation of the deformation of the frontier orbital by the counter anion potential for organic conductors. The intra-molecular spin-distribution as a function of temperature also is discussed from the microscopic point of view.

# 4. Spin-Dynamics in Vicinity of Phase Transition for Organic Conductor (TMTTF)<sub>2</sub>X

(TMTTF)<sub>2</sub>PF<sub>6</sub> shows unique electronic state with a charge ordering phase above the ground state. The spin dynamics in the vicinity of the spin-Peierls transition for the (TMTTF)<sub>2</sub>PF<sub>6</sub> were examined and compared with those for the typical spin-Peierls materials, MEM(TCNQ)<sub>2</sub>. The temperature dependence of the electron-spin relaxation rate,  $T_1^{-1}$  and  $T_2^{-1}$ , in the vicinity of the spin-Peierls transition was measured by pulsed-ESR spectroscopy. The FID signal was successfully detected and the relaxation rate for the condensed matter could be estimated. In the typical spin-Peierls system, MEM(TCNQ)<sub>2</sub>, decrease of the spin-lattice relaxation and increase of the spinspin relaxation were observed below the  $T_{sP}$ . On the other hand, an anomaly of the spin-spin relaxation rate was observed for the  $(TMTTF)_2PF_6$  below the  $T_{sP}$ , which suggests the reorientation of the charge. This behavior is not shown in typical spin-Peierls materials, and is peculiar to the spin dynamics of spin-Peierls materials with a charge ordering phase. This result is the first example of direct experimental estimation of the electron spin dynamics of the spin-Peierls transition.

# 5. ESR Investigation for Competed Electronic Phases in (TMTTF)<sub>2</sub>X

A Quasi-one-dimensional conductors based on TMTCF (C = S, Se) are some of the most extensively studied materials among organic conductors. They possess various ground states including the spin-Peierls (sP), antiferromagnetic state (AF), incommensurate spin density wave (IC-SDW) and superconductivity (SC), with applied pressures or counter anions, *X*. Findings of charge-ordering (CO) and related phenomena in  $(TMTTF)_2X$  have attracted significant recent attention. We have also investigated the completed ground states and CO phenomena observed in the intermediated temperature region from the viewpoint of magnetic resonance.

Based on recent systematic transport measurements for  $(TMTTF)_2X$  salts under ultra-high pressures, a possible modified generalized Pressure-Temperature phase diagram was proposed. However, this phase diagram is based on the preconceived idea that the spin-gap (spin-Peierls) phase, which is a quantum one-dimensional phase, is sandwiched between two antiferromagnetic phases. In a general sense, for conventional systems, antiferromagnetic phases are stabilized with finite inter-chain interactions with the application of pressure.

Therefore, in order to understand the whole phase diagram of the TMTCF-family salts, we prepared several TMTTF-family salts, such as  $(TMTTF)_2TaF_6$  and  $(TMTTF)_2I$ , and carried out ESR measurements. Both salts undergo antiferro-magnetic states, but the temperature dependences of the ESR properties are quite different. We discussed the competed electronic phases in  $(TMTTF)_2X$  from a view of microscopic.



**Figure 2.** Temperature dependence of the ESR parameters,  $\chi_{spin}$ ,  $\Delta H_{pp}$  and *g*-values, for (TMTTF)<sub>2</sub>TaF<sub>6</sub> and (TMTTF)<sub>2</sub>I.

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# **Topological Design of Sheet-Shaped Macromolecules and Organic Framewarks**

# Department of Materials Molecular Science Division of Molecular Functions



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Covalent organic frameworks (COFs) are porous and crystalline materials with pre-designable 2D and 3D polymer structures. Due to covalent linkage between components together with an elaborate control on structure parameters including porosity and composition, COFs are promising for the design of tailor-made porous materials for gas storages. Recently, co-condensation of triphenylene and pyrene monomers has been reported, to create a  $\pi$ -electronic COF that is semiconducting (TP-COF). The well-defined crystalline structure of COFs would have a high probability of forming conduction path that transports charge carriers across the framework. Inspired by this finding, we are interested in the synthesis of photofunctional COFs, especially photoconductive COF that requires photoinduced carrier generation and carrier transportation in the framework. Crystal engineering has demonstrated that high quality single crystals of certain  $\pi$ -conjugated arenes are photoconductive as the result of exciton migration over lattice followed by charge separation at molecule-electrode interface. To fulfill this prerequisite, we turned to the exploration of arene-based COF, which should retain crystal-latticelike highly ordered arene arrangement, can absorb photons of visible region, and is robust under irradiation. Herein, we report the first example of photoconductive COF, bearing eclipsed molecular order of arene building blocks in the framework (Figure 1, PPy-COF).

# 1. Toward Photoconductive Sheet-Shaped Macromolecules and COFs

We employed self-condensation of pyrene diboronic acid (Figure 1a, PDBA) for polymerization that would topologically integrate pyrene unit on edges and boronic ester ring at vertices (Figure 1), to assume uniform and single aromatic component of the framework. We found that under solvothermal condition it successfully leads to the desirable eclipsed alignment of 2D polypyrene sheets in the micrometer-scale cubes (Figure 1b). Such an ultimately superimposed stack together with uniform composition in sheet structure significantly facilitates exciton migration and carrier transportation. We highlight that PPy-COF harvests visible light and triggers photocurrent generation with a quick response to visible light irradiation, allows



**Figure 1.** Schematic representations of (a) the synthesis and (b) the framework of PPy-COF (Structure is based on quantum calculation and crystal lattice parameters; Red: B, White: O, Blue: Pyrene; H atoms are omitted for clarity).

repetitive switching of photocurrent without deterioration, and displays a large on-off ratio over  $8.0 \times 10^4$ .

FE SEM shows that PPy-COF adopts cubic shape, while no any other morphologies such as belt, fiber, sphere, or rod are present. Close checks at high magnification confirm that the cubes are in micrometer scale with similar dimension. HR TEM reveals the aligned 2D polymer sheets with face-to-face distance of about 3.4 Å, which is reasonable for  $\pi$ - $\pi$  stack. These observations indicate that self-condensation of PDBA leads to the formation of quite uniform cube-shaped COF with well-aligned polypyrene sheets.

To fully understand the structure of PPy-COF, we carried out PXRD analysis, quantum simulation and gas sorption experiments. PXRD measurement of PPy-COF displays a main peak at 4.6° due to 100 diffraction together with minor peaks at 9.3, 12.2 and 26.2° due to 200, 210, 001 diffractions, respectively. To elucidate the lattice packing, we first carried out quantum chemical calculation with Gaussian 03. Rev. C01 at PM3 level to optimize the geometry of pore unit structure and then performed molecular modeling and Pawley refinement by using Reflex, a software package for crystal structure determination from the PXRD pattern, implemented in Materials Studio modeling version 4.2. Simulation using P6/mmm space group with a = b = 22.16295 Å and c = 3.42066 Å results in a PXRD pattern that is in good agreement with the experimentally observed one. Therefore, the 2D polypyrene sheets stack along c axis in a perfectly eclipsed fashion, with all vertices and edges superimposed on those from neighbouring sheet, thus leaving aligned tubular channels with a pore diameter of 1.73 nm. Gas sorption measurement with N2 at 77 K displays typical type-I sorption profile, suggesting a microporous character. The BET surface area was evaluated to be 923 m<sup>2</sup>g<sup>-1</sup> and the pore width was 1.88 nm calculated by NLDFT method. These results indicate that PPy-COF is supermicroporous crystalline macromolecule with eclipsed alignment of polypyrene sheets.

Upon excitation at 414 nm, PPy-COF emits at 484 nm. In contrast, the simple solid of PDBA gives an emission at 421 nm. Therefore, the fluorescence of PPy-COF most likely originates from excimer, as a result of close packing of pyrene building blocks. Along this line, we further investigated the fluorescence anisotropy upon excitation with a polarized light. When a chromophore with a restricted Brownian motion is excited by a polarized light, it emits a polarized fluorescence. However, the fluorescence should be depolarized when the excitation energy migrates within the lifetime of the excited state. PDBA shows an anisotropy (p) value of 0.020. In contrast, PPy-COF under identical conditions exhibited a significantly depolarized fluorescence with an extremely low p value of 0.001. This value is much smaller than that of previously reported TP-COF (0.017). Unlike TP-COF that contains two alternatively linked components with difference in energy gaps, the exciton migration in the single component PPy-COF is facilitated, since it can flow "borderlessly" not only over the sheet plane but across the stacked layers as well.

The well-defined sheet structure together with superimposed layer alignment of PPy-COF would also benefit the flow of carriers. To verify this, we measured the electrical conductivity by using a two-probe method across a 10- $\mu$ mwidth Pt gap. PPy-COF displays an almost linear *I*–*V* profile in air at 25 °C, while the gap itself is silent, irrespective of voltage bias. In contrast, PDBA shows a low current under otherwise identical conditions. The electric current of PPy-COF can be on–off switched for many times. The relatively high electrical conductivity is clearly resulted from the highly aligned molecular order. Upon doping with iodine to induce hole generation, the electric current increased, suggesting that PPy-COF is a hole transporting material.

We investigated the photoconductivity of PPy-COF by casting a thin film of PPy-COF on Al electrode and vapor depositing 30-nm thick Au on the top of the film to fabricate sandwich-type electrodes. Indeed, on irradiation from Au side with visible light (> 400 nm) of a xenon lamp, PPy-COF is highly responsive and shows sharp rise in photocurrent generation to give a linear I-V profile. Moreover, the photocurrent can be repetitively switched for many times without deterioration at an on-off ratio over  $8.0 \times 10^4$ . Such a quick response together with a large on-off ratio is most likely related to the facilitated exciton migration and carrier transportation in PPy-COF. In sharp contrast, PDBA hardly shows response to light irradiation under otherwise identical conditions. On the other hand, TP-COF consisting of co-condensed triphenylene and pyrene network shows a low photocurrent with significantly decreased on-off ratio, which is only one-forth that of PPy-COF. Although 1,4-benzene diboronic acid forms a crystalline COF, which, however, eventually adopts staggered structure and hardly absorbs any photons in the visible region.

In summary, we demonstrate the first example of photoconductive COF, newly synthesized by self-condensation of pyrene diboronic acid under solvothermal condition. The ultimate alignment of 2D polypyrene sheets in perfectly eclipsed fashion leads to the formation of micrometer-scale cubes that favor exciton migration and carrier flow over the framework. PPy-COF harvests visible photons and triggers prominent photocurrent generation, displays quick response to light irradiation, and is capable of repetitive on–off photocurrent switching with large on–off ratio. These unique properties are unprecedented and thus constitute an important step to the utility of COFs in optoelectronics and photovoltaics.

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# Developments of New Techniques and Magnetically Aligned Lipid Bilayer System for Structural Biology Based on Solid State NMR Spectroscopy

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Solid state NMR is one of the useful tools to characterize dynamics and structures of molecules on amorphous condition without specific limitations. We are working on methodology developments of solid state NMR for structural biology and material science. Especially, we are focusing on elucidation of functions and dynamic structure of peripheral membrane protein bound to lipid bilayer surface based on solid state NMR. In the following, we show the newly developed solid state NMR techniques to enhance spectral sensitivity for aligned sample, and new lipid sample system enabling magnetically aligned planer lipid bilayers useful for structural characterization of peripheral membrane proteins. In addition, a study of molybdenum compounds was reported.

## 1. <sup>1</sup>H-<sup>13</sup>C Heteronuclear Polarization Transfer for Aligned Solid<sup>1)</sup>

Analysis of anisotropic interactions such as dipolar interaction and chemicals shift anisotropy in aligned sample give information of local molecular structure straightforwardly. Thus membrane proteins embedded in magnetically aligned lipid bilayer samples have been studied so far. In such experiment, heteronuclear polarization transfer from <sup>1</sup>H to rare nuclei such as <sup>13</sup>C and <sup>15</sup>N plays important role to enhance spectral sensitivities of rare nuclei. Recently, Jayanthi et al developed DAPT which is the INEPT type dipolar based heteronuclear polarization transfer technique to be used in aligned sample. However due to the lack of refocusing mechanism of <sup>1</sup>H carrier frequency offset in DAPT, performance of DAPT is quite poor.

In this study, we show improved version of DAPT, which is insensitive to <sup>1</sup>H carrier frequency offset. We refer developed technique to as refocused DAPT (REDAPT), which refocuses <sup>1</sup>H carrier frequency offset based on refocused multiple pulse technique which author developed. The performance of REDAPT was assessed using liquid crystalline molecule of 5CB as shown in Figure 1 (a). The practically obtained polarization transfer profile was shown in Figure 1 (b). Because of refocusing of <sup>1</sup>H carrier frequency offset in REDAPT, signal intensities were gradually decreased respect to the <sup>1</sup>H carrier frequency offset.



**Figure 1.** (a) REDAPT enhanced <sup>13</sup>C-NMR spectrum of 5CB liquid crystal at 20 °C. Plot of site 3 signals in 5CB obtained from REDAPT at mixing time of 264  $\mu$ s for various <sup>1</sup>H carrier frequency offsets.

### 2. A Bicelle Magnetically Aligned Planner Lipid Bilayers at Room Temperature for Structural Characterization of Membrane Bound Proteins by Solid State NMR<sup>2)</sup>

The properly hydrated mixture of saturated lipids possess-

ing short and long acyl-chains at proper composition forms planer lipid bilayer so called bicelle which can be magnetically aligned under static magnetic field at temperature from 30 to 40 °C. Bicelle is widely used in solid state NMR for structural characterization of membrane associated proteins. Triba *et al.*, proposed a bicelle prepared by mixture of saturated lipid 1,2dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and unsaturated lipid 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) for long acyl chain, and 1,2-dihexanoyl-snglycero-3-phosphocholine (DHPC) for short acyl chain lipid, respectively in order to achieve magnetic alignment at temperature lower than that of conventional bicelle. In the following we refer above bicelle to as POPC/DMPC/DHPC-bicelle.

In this study, we developed a new bicelle enabling better magnetic alignment at room temperature over POPC/DMPC/ DHPC-bicelle. Our developed bicelle consists of phosphatidylinositol 4, 5-bisphosphate (PIP<sub>2</sub>) in addition to above lipids at proper molar ratio. Orientational property of developed bicelle was compared to those for POPC/DMPC/DHPC-bicelle based on <sup>31</sup>P-NMR. As shown in Figure 2, (b) newly developed bicelle exhibited better magnetic alignment over (c) POPC/ DMPC/DHPC-bicelle. Furthermore, temperature range for magnetic alignment for developed bicelle was twice wider than that of POPC/DMPC/DHPC-bicelle. We have successfully developed new bicelle magnetically aligned at room temperature stably. New bicelle may be useful especially for structural characterization of membrane proteins which are sensitive to fluctuation depending on the sample temperature such as peripheral membrane proteins.

coupling and increase in equilibrium magnetization. Structural researches utilizing high-field NMR for quadrupolar nuclei such as <sup>95</sup>Mo have been recently reported. Studies of <sup>95</sup>Mo NMR can be classified by the oxidation number of molybdenum taking from Mo<sup>0</sup> to Mo<sup>VI</sup>. While solution <sup>95</sup>Mo NMR has accessed all species with the integer oxidation number, <sup>95</sup>Mo solid state NMR studies are limited to Mo<sup>0</sup>, Mo<sup>IV</sup> and Mo<sup>VI</sup>. Although the Mo<sup>V</sup> or Mo<sup>V,VI</sup> species frequently appear in polyoxomolybdates such as ε-Keggin anion and nanosized oxides with ring-, tube- and ball-structure, only several <sup>95</sup>Mo solution NMR spectra have been measured for Mo<sup>V</sup>. In this study, we investigated high-field solid-state <sup>95</sup>Mo NMR of Mo<sup>V,VI</sup> and Mo<sup>VI</sup> species in mixed valence polyoxomolybdates(V, VI).

Compounds used here are [Me<sub>3</sub>NH]<sub>6</sub>[H<sub>2</sub>Mo<sup>V</sup><sub>12</sub>O<sub>28</sub>(OH)<sub>12</sub>  $(Mo^{VI}O_3)_4]2H_2O$  (1) and  $[NMe_4]_2[NH_4]_8[(Mo^{VI}_6Mo^VO_{23})_2]$  $8H_2O$  (2) which have localized or delocalized d<sup>1</sup> electrons, respectively. As show in Figure 3, <sup>95</sup>Mo MAS NMR spectra were measured under moderate (9.4 T) and ultrahigh magnetic fields (21.8 T). By simulating the acquired NMR spectra and density functional theory (DFT) calculation for isolated anions, NMR parameters for each of molybdenum sites within the crystals were obtained. Despite different state of the d<sup>1</sup> electrons, a similar trend that exhibits large chemical shifts for Mo<sup>V</sup> in **1** and Mo<sup>V,VI</sup> in **2** was found. Highest-energy occupied molecular orbital(s) of the anions was mainly consisting of 4d atomic orbitals of Mo<sup>V</sup> or Mo<sup>V,VI</sup>. Then the large shift was ascribed to a paramagnetic deshielding term by magneticdipole allowed mixing of the occupied and virtual orbitals containing the 4d orbitals of these species.



**Figure 2.** (a) Schematic representation of bicelle. Dark and light gray colored areas indicate polar heads of short and long acyl chain lipids, respectively. (b) <sup>31</sup>P-NMR spectra of magnetically aligned POPC/ DMPC/ PIP<sub>2</sub>/DHPC-bicelle and (c) POPC/ DMPC/ PIP<sub>2</sub>/DHPC-bicelle at 16 °C, respectively.

# 3. <sup>95</sup>Mo NMR of Mixed Valence Polyoxomolybdates (V, VI)<sup>3)</sup>

Solid state NMR of half integer quadrupole nuclei benefits from recent development of high field magnets for highresolution NMR, because a higher field brings higher sensitivity and resolution by decrease in second-order quadrupole



**Figure 3.**  ${}^{95}$ Mo MAS NMR spectra of [NMe<sub>4</sub>]<sub>2</sub>[NH<sub>4</sub>]<sub>8</sub>[(Mo<sup>VI</sup><sub>6</sub>Mo<sup>V</sup> O<sub>23</sub>)<sub>2</sub>]8H<sub>2</sub>O under (i) 9.4 and (ii) 21.8 T. (a) and (b) show the observed and simulated spectra, respectively. (c–f) denote spectral components consisting of the spectrum (b).

- 1) To be submitted.
- 2) To be submitted.
- 3) To be submitted.

# **Organic Solar Cells**

Research Center for Molecular Scale Nanoscience Division of Molecular Nanoscience



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Organic solar cell is recognized as a future 3rd generation solar cell. Our group accomplished the world record conversion efficiency of 5.3% by ultra-high purification and nanostructure design.<sup>1,2)</sup> Moreover, a new organic solar cell having the sensitivity of near-infrared (NIR) region to 1050 nm like Si cell is successfully fabricated.

### 1. Efficient Organic *p-i-n* Solar Cells Having NIR Sensitivity by Using J-Aggregate of Pb Phthalocyanine

In 1991, we proposed *p-i-n* organic solar cells in which the *i*-interlayer is a codeposited film composed of *p*- and *n*-type organic semiconductors.<sup>3,4)</sup> *i*-interlayer acts as an efficient photocarrier generation layer.

Unfortunately, organic solar cells did not have sensitivity to near infrared (NIR) so far. Since there is a lot of NIR photon in the solar spectrum, they should be utilized in order to obtain photocurrent density reaching 30 mA/cm<sup>2</sup> like Si solar cells.

In order to solve this problem, we incorporated Pb phthalocyanine (PbPc) having shuttle-cock type molecular structure in *p-i-n* cell (Figure 1). *p*-type layer of ZnPc, codeposited *i*interlayer composed of  $C_{60}$  and PbPc, and *n*-type layer of  $C_{60}$ were successively deposited by vacuum evaporation on ITO glass substrate.

Figure 2(a) shows the spectral dependence external quantum efficiency (EQE) of short-circuit photocurrent. The present cell showed the NIR sensitivity to 1050 nm. Maximum EQE reached 43%, which is the largest value of NIR sensitivity



**Figure 1.** Structure of organic *p-i-n* cell incorporating PbPc:C<sub>60</sub> *i*-interlayer.

observed so far. Conversion efficiency by NIR light irradiation reached 2.3% (Figure 2(b)).

Codeposited *i*-interlayer was revealed to have nanostructure composed of 3 phases, *i.e.*, amorphous  $C_{60}$ , H-aggregate of PbPc, and J-aggregate of PbPc (Figure 3). This nanostructure has the efficient carrier generation ability due to 3-separated functions, *i.e.*, electron transport, hole transport, and photocarrier generation by NIR, respectively.



**Figure 2.** (a) Spectral dependence external quantum efficiency of short-circuit photocurrent. Absorption spectrum of PbPc: $C_{60}$  *i*-interlayer is also shown. Absorption peaks at 650 nm and 860 nm are attributed to H- and J-aggregates of PbPc. (b) Photourrent-voltage characteristic for *p*-*i*-*n* cell.



**Figure 3.** 3-function separated nanostructure consists of amorphous  $C_{60}$ , H-PbPc, and J-PbPc, which act as electron transport, hole transport, and photocarrier generation by NIR, respectively. Molecular stackings of H- and J-aggregates are also shown.

### 2. Hole-Transport Highway in Phthalocyanine:C<sub>60</sub> *i*-interlayer Showing Conversion Efficiency of 5.3%

Our group accomplished the world record conversion efficiency of 5.3% by *p-i-n* cell having *i*-interlayer composed of metal-free phthalocyanine (H<sub>2</sub>Pc) and seven-nine (7N, 99.99999%) purified C<sub>60</sub> (Figure 4).<sup>1,2)</sup> Utilization of entire visible light of solar spectrum without decreasing fill factor by incorporating 1  $\mu$ m-thick C<sub>60</sub>:H<sub>2</sub>Pc *i*-interlayer is essential to obtain large J<sub>sc</sub> value of 20 mAcm<sup>-2</sup> and efficiency of 5.3%.

Figure 5 shows the TEM image of 1  $\mu$ m-thick H<sub>2</sub>Pc:C<sub>60</sub> codeposited *i*-interlayer. H<sub>2</sub>Pc whisker structures having diameter of around 20 nm were clearly observed. Carrier is photogenerated at H<sub>2</sub>Pc whisker/C<sub>60</sub> interface and photogenerated holes are efficiently transported *via* this H<sub>2</sub>Pc whisker to electrode. This observation suggests that H<sub>2</sub>Pc hole-transport highway is formed in H<sub>2</sub>Pc:C<sub>60</sub> *i*-interlayer.

We also investigated the nanostructure of 1 µm-thick ZnPc:C<sub>60</sub> *i*-interlayer which showed essentially the same results to H<sub>2</sub>Pc:C<sub>60</sub> system. Figure 6 shows the schematic illustration of a ZnPc nanocrystal (a) and nanocrystals-connected nanostructure clarified by cross sectional SEM and XRD observations. (i) ZnPc nanocrystals having diameter of around 20 nm surrounded by amorphous C<sub>60</sub> (Figure 6(a)). (ii) ZnPc:C<sub>60</sub> thickness < 300 nm;  $\pi$ -stacking direction is parallel to the substrate electrode (Figure 6(a)(b)). (iii) 300 nm < ZnPc:  $C_{60}$  thickness < 1 µm;  $\pi$ -stacking direction is changed to be vertical to the electrodes (Figure 6(b)). Since photogenerated holes are transported via  $\pi$ -stacking, the present observation suggests the formation of hole-transport highway between two metal electrodes. Note that the H<sub>2</sub>Pc whisker structure in Figure 5 resembles to this hole-transport highway. Formation of such hole-transport highway is one of the reasons of 5.3% high efficiency of *p-i-n* cells.



**Figure 4.** (a) Photograph of 7N(99.99999%)- $C_{60}$  single crystals. (b) Current-voltage characteristics for *p-i-n* cell having 1 µm-thick H<sub>2</sub>Pc:  $C_{60}$  *i*-interlayer.



Figure 5. TEM image of 1 µm-thick H<sub>2</sub>Pc:C<sub>60</sub> codeposited *i*-interlayer.



**Figure 6.** (a) Schematic illustration of a ZnPc nanocrystal surrounded by  $C_{60}$ . (b) Schematic illustration of 1 µm-thick ZnPc: $C_{60}$  *i*-interlayer. Red arrows represent the direction of  $\pi$ -stacking, *i.e.*, hole transport direction. Hole-transport highway between electrodes is formed.

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# Development of Organic Semiconductors for Molecular Thin-Film Devices

# Research Center for Molecular Scale Nanoscience Division of Molecular Nanoscience



SUZUKI, Toshiyasu SAKAMOTO, Youichi WATANABE, Yoko Associate Professor Assistant Professor Secretary

Organic light-emitting diodes (OLEDs) and organic fieldeffect transistors (OFETs) based on  $\pi$ -conjugated oligomers have been extensively studied as molecular thin-film devices. Organic semiconductors with low injection barriers and high mobilities are required for highly efficient OLEDs and OFETs. Radical cations or anions of an organic semiconductor have to be generated easily at the interface with an electrode (or a dielectric), and holes or electrons must move fast in the semiconducting layer. Compared with organic p-type semiconductors, organic n-type semiconductors for practical use are few and rather difficult to develop. Recently, we found that perfluorinated aromatic compounds are efficient n-type semiconductors for OLEDs and OFETs.

### 1. High-Mobility Bottom-Contact Thin-Film Transistor Based on Anthracene Oligomer<sup>1)</sup>

The mobility in top- and bottom-contact thin-film transistors (TFTs) based on 2,2-bianthryl (**2A**) was improved. The mobility of the top-contact **2A**-TFT was improved from 0.25 to 1.0 cm<sup>2</sup>/Vs by octyltrichlorosilane (OTS) treatment of the SiO<sub>2</sub> gate-insulator surface. Large grains and clear step structures corresponding to the molecular length of **2A** were observed in the AFM image of a **2A** film deposited on the OTStreated SiO<sub>2</sub>. The bottom-contact **2A**-TFT with typical source– drain (S–D) electrodes of Cr/Au showed a non-linear rise in the output characteristics due to the large injection barrier between the work function of Au and the HOMO level of **2A**. The non-linear rise in the output characteristics was successfully improved by employing  $MoO_x$  as the carrier injection layer for the S–D electrodes. Consequently, the mobility of the bottom-contact **2A**-TFT with a  $MoO_x/Au$  electrode was improved to 1.0 cm2/Vs, which is comparable to that in the top-contact **2A**-TFT.



Figure 1. Structure of 2,2-bianthryl (2A).

# 2. Structure, Morphology, and Growth Dynamics of Perfluoropentacene Thin Films<sup>2)</sup>

We report high structural order in thin films of the organic semiconductor perfluoropentacene (PFP), which is a candidate material for n-type applications, deposited by vacuum sublimation on oxidized silicon wafers. Bragg reflections up to high order in both specular and grazing incidence geometries and a mosaicity of less than 0.01° demonstrate the well defined structure. The thin film entirely consists of crystallites with a structure close to the bulk phase without any contamination with a second phase. Real-time X-ray measurements show that PFP grows in a Stranski–Krastanov growth mode with the first monolayer wetting the substrate before 3d-growth sets in during growth of the second monolayer. Implications for its use are discussed.

### 3. Impact of Perfluorination on the Charge-Transport Parameters of Oligoacene Crystals<sup>3)</sup>

The charge-transport parameters of the perfluoropentacene and perfluorotetracene crystals are studied with a joint experimental and theoretical approach that combines gas-phase ultraviolet photoelectron spectroscopy and density functional theory. To gain a better understanding of the role of perfluorination, the results for perfluoropentacene and perfluorotetracene are compared to those for their parent oligoacenes, that is, pentacene and tetracene. Perfluorination is calculated to increase the ionization potentials and electron affinities by ~1 eV, which is expected to reduce significantly the injection barrier for electrons in organic electronics devices. Perfluorination also leads to significant changes in the crystalline packing, which greatly affects the electronic properties of the crystals and their charge-transport characteristics. The calculations predict large conduction and valence bandwidths and low hole and electron effective masses in the perfluoroacene crystals, with the largest mobilities expected along the  $\pi$ stacks. Perfluorination impacts as well both local and nonlocal vibrational couplings, whose strengths increase by a factor of about 2 with respect to the parent compounds.



Figure 2. Structures of perfluorotetracene and perfluoropentacene.

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# Building Photosynthesis by Artificial Molecules

# Research Center for Molecular Scale Nanoscience Division of Molecular Nanoscience



NAGATA, Toshi KON, Hiroki KAWAO, Masahiro MIURA, Takahiro TANEMURA, Hiroyo WANATABE, Yoko Associate Professor IMS Fellow IMS Fellow Graduate Student Technical Fellow Secretary

The purpose of this project is to build nanomolecular machinery for photosynthesis by use of artificial molecules. The world's most successful molecular machinery for photosynthesis is that of green plants—the two photosystems and related protein complexes. These are composed almost exclusively from organic molecules, plus a small amount of metal elements playing important roles. Inspired by these natural systems, we are trying to build up multimolecular systems that are capable of light-to-chemical energy conversion. At present, our interest is mainly focused on constructing necessary molecular parts.

### 1. Synthesis of A New, Ternary TEMPO-Porphyrin-Quinone Pool Molecule<sup>1)</sup>

Plant photosynthesis is one of the most important biological activities on this planet. It is of interest, both academic and industrial, to mimic this process by artificial chemical systems. To achieve this goal, it is useful for chemists to mimic individual processes of photosynthesis by use of artificial molecules. Although many aspects of natural photosynthesis have been modeled by use of artificial molecules, there are still many important features of photosynthesis that are yet unexplored by model chemists.

Among these disregarded features in photosynthesis, we have been focusing on the quinone pools. The quinone pools in biological systems consist of a collection of quinones embedded in special membranes, and they work as buffers between the redox enzymes embedded in the same membranes. Previously we reported our research on building a "singlemolecular" quinone pool by use of synthetic dendrimer molecules; in these molecules, the quinones were converted to quinols by irradiation in the presence of reducing agent (thiols).

Our "first-generation" quinone pool, however, lacked one important aspect. After giving an electron to the quinone, the oxidized porphyrin must receive an electron from the electron donor directly (Figure 1a). This is not always easy, because one-electron oxidation of a closed-shell molecule often requires high overpotential. To overcome this difficulty, it is desirable that the porphyrin has a neighboring catalytic site that oxidizes the substrate (electron donor) with low overpotential and supply electrons to the porphyrin (Figure 1b).



**Figure 1.** Pictorial representation of the quinone pools. P, Q, D, C denote pigment (porphyrin), quinone, electron donor, and catalytic site, respectively. The bold arrows indicate the flow of electrons. (a) A simple quinone-pool molecule, (b) a "ternary" quinone-pool molecule with a electrocatalytic site, (c) a schematic view of the oxidizing end of plant photosynthesis. OEC: oxygen evolving complex, PSII: photosystem II.

In this work, we present the first preparation of "ternary" quinone-pool molecules (Figure 2). As the electrocatalytic site, we featured TEMPO (2,2,6,6-tetramethylpiperidinyloxy free radical), which is known to catalyze oxidation of various organic substrates including alcohols, thiols, and alkenes. The choice of TEMPO was based on our previous finding that the TEMPO/porphyrin/quinone ternary system was effective for photochemical oxidation of alcohol.<sup>2)</sup>



Figure 2. The "ternary" quionone-pool molecule in this work.

### 2. Syntheses of the Terpyridine-Bipyridine Linked Binary Ligands, and Structural, Redox Properties of Their Cobalt Complexes<sup>3)</sup>

One of the necessary components for photosynthetic chemical conversion is the redox catalysts that generate useful chemicals from abundant source via electrochemical reactions. Transition metal complexes are especially important in this respect, because they are capable of facile single-electron transfer. Among the various transition metals, the 3d metals are particularly important because of their wide availability. However, the 3d metals are generally more substitution labile than the 4d and 5d congeners, so that a certain artifice is necessary in the ligand part to make useful complexes of 3d metals. It is noteworthy that many metalloenzymes use 3d metals in their active centers, where appropriate arrangement of donor atoms are provided by the amino acids embedded in the protein backbone.

We are currently studying "binary" ligands, in which the two different ligands are arranged closely so that the construction of mixed-ligand complexes are made easy and, at the same time, the connection is flexible enough for the complex to accommodate to the change of the chemical environments. We are particularly interested in cobalt complexes among the 3d metals, and previously we synthesized the terpyridinecatechol-Co(III) complexes and discussed their structural and redox properties. However, we would also like to work with Co(II) and Co(I) complexes, because Co(II) and Co(I) complexes exhibit various interesting chemistry, such as hydrogen production and formation of metal-carbon bonds, which should be useful in development of photosynthetic chemical conversion. On the other hand, the Co(II) and Co(I) complexes pose a greater synthetic challenge than the Co(III) complexes, because these ions are more labile towards ligands substitution than Co(III).

In this work, we report the syntheses of new terpyridinebased binary ligands, **1a-1d** and their Co(II) complexes, **2a-2d** and **2a'-2d'**. By using the bipyridine and terpyridine, the ligands act as the penta-dentate ligands and, one coordination site will be vacant. We found that the redox properties were greatly affected by ligand exchange at this "vacant" site, as well as by the length of the intervening methylene chains.



Figure 3. (a) The binary ligands 1a-d (n = 3-6). (b) The cobalt(II) complexes 2a-d (L = Cl, m = 1) and 2a'-d' (L = H<sub>2</sub>O, m = 2).



**Figure 4.** The ORTEP drawing of the complex cation of **2b**. [Reprinted with permission from ref. 3, Copyright (2009) American Chemical Society.]



Figure 5. The cyclic voltammograms of the cobalt complexes 2a-d and 2a'-d'. [Reprinted with permission from ref. 3, Copyright (2009) American Chemical Society.]

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# Chemistry of Bowl-Shaped Aromatic Compounds and Metal Nanocluster Catalysts

# Research Center for Molecular Scale Nanoscience Division of Molecular Nanoscience



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Associate Professor Assistant Professor **IMS Fellow** Post-Doctoral Fellow Post-Doctoral Fellow Visiting Scientist Graduate Student Graduate Student Graduate Student Graduate Student **Technical Fellow** Technical Fellow Secretary Secretary

Bowl-shaped  $\pi$ -conjugated compounds including partial structures of the fullerenes, which are called "buckybowls," are of importance not only as model compounds of fullerenes but also as their own chemical and physical properties. Heteroatom-containing buckybowls (heterobuckybowls) have also been expected to exhibit unique physical characters. For example, in solution they show the characteristic dynamic behavior such as bowl-to-bowl inversion. On the other hand, they sometimes favor stacking structure in a concave-convex fashion in the solid state, giving excellent electron conductivity. Furthermore, some buckybowls are conceivable to possess the bowl-chirality if the racemization process, as equal as bowl-tobowl inversion, is slow enough to be isolated. However, very few buckybowls/heterobuckybowls has been achieved for preparation mainly due to their strained structure, and no report on the preparation of chiralbowls has appeared. In the present project, we develop the rational route to the various kinds of buckybowls/heterobuckybowls with perfect chirality control using the organic synthesis approach.

We also investigate to develop novel catalytic properties of metal nanoclusters. We focus on the following projects: Preparation of size-selective gold nanoclusters supported by hydrophilic polymers and its application to aerobic oxidation catalysts: Synthetic application using metal nanocluster catalyst: Development of designer metal nanocluster catalyst using the highly- functionalized protective polymers: Catalytic activity of metal nanoclusters under the laser-irradiated conditions.

# 1. Preparation of $C_3$ Symmetric Homochiral *syn*-Trisnorbornabenzenes through Regio-Selective Cyclotrimerization of Enantiopure Iodonorbornenes<sup>1)</sup>

 $C_3$  symmetric homochiral (-)-*syn*-trisoxonorbornabenzene **1** possessing a rigid cup-shaped structure was synthesized through a novel regio-selective cyclotrimerization of enantiopure iodonorbornenes catalyzed by palladium nanoclusters. The yield of the cyclotrimerization was dependent on the stability of the palladium clusters, which was ascertained from the appearance and TEM images of the reaction mixtures. The efficient preparation of (-)-*syn*-**1** was established in short steps including the newly developed cyclotrimerization reaction.



The thus-prepared homochiral (-)-syn-1 can serve as a key intermediate for the synthesis of  $C_3$  symmetric homochiral cup-shaped molecules with a helical arrangement of substituents. Introduction of several types of substituents was well demonstrated through palladium-catalyzed coupling reactions with the corresponding phosphate and triflate of (-)-syn-1.



# 2. Effect of Electronic Structures of Au Clusters Stabilized by Poly (*N*-vinyl -2pyrrolidone) on Aerobic Oxidation Catalysis<sup>2)</sup>

Au clusters smaller than 1.5 nm and stabilized by poly (Nvinyl-2-pyrrolidone) (PVP) showed higher activity for aerobic oxidation of alcohol than those of larger size or stabilized by poly(allylamine) (PAA). X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy of adsorbed CO, and X-ray absorption near edge structure measurements revealed that the catalytically active Au clusters are negatively charged by electron donation from PVP, and the catalytic activity is enhanced with increasing electron density on the Au core. Based on similar observations of Au cluster anions in the gas phase, we propose that electron transfer from the anionic Au cores of Au:PVP into the LUMO ( $\pi^*$ ) of O<sub>2</sub> generates superoxo or peroxo-like species, which plays a key role in the oxidation of alcohol. On the basis of these results, a simple principle is presented for the synthesis of Au oxidation catalysts stabilized by organic molecules.



# 3. Aerobic Oxygenetion of Benzylic Ketones Promoted by Gold Nanocluster Catalyst<sup>3)</sup>

Au:PVP promoted the oxidation of benzylic ketones, including auto-oxidation-type bond cleavage reactions and  $\alpha$ -hydroxylation, under ambient conditions. The catalyst accelerates the formation of an  $\alpha$ -peroxide intermediate, from which bond cleavage spontaneously proceeds in aqueous solvent to give the auto-oxidation products. In contrast, the  $\alpha$ -hydroxylation product is obtained predominantly in DMSO solvent.



## 4. Intramolecular Addition of Toluene-Sulfonamide to Unactivated Alkenes Catalyzed by Gold Nanoclusters under Aerobic Conditions<sup>4)</sup>

Au:PVP catalyzed the intramolecular addition of tosyl amides to unactivated alkenes in EtOH under aerobic conditions.



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# Multifunction Integrated Macromolecules for Molecular-Scale Electronics

Research Center for Molecular Scale Nanoscience Division of Molecular Nanoscience



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Assistant Professor

We have been developing step-wise synthetic protocols for integrating molecule-based quantum device elements (quantum dots, wells, and tunnel junctions) within a single planar macromolecule. Our strategy is based on "modular architecture" using a library of versatile molecular building blocks. The flexible functionality of our building blocks is derived from the 3,4-diaminothiophene component, which can be easily modified to tune the structural and electronic properties of the main  $\pi$ -conjugated chain.

## 1. Step-Wise Synthesis of Molecular Wire Modules of Over 100 nm Lengths

We have finished the step-wise synthesis of precisely defined molecular wires of over 100 nm lengths (1-2). Now we have a series of wire modules of 1–166 nm lengths. These are not a final product, but a starting material for our next target system, that is, 2-dimension macromolecules of  $100 \times 100$  nm size. As a first step, we have synthesized multi-terminal modules (3-6), and set out to build up molecular ladder structures.





Figure 1. Structures of building blocks (1-6).

## 2. Isomeric Discriminating and Indiscriminating Assembly of Adsorbed Oligothiophenes on Ag(110)<sup>1)</sup>

Selective discriminating and indiscriminating assembly of isomeric oligothiophene derivatives is performed on a Ag(110) surface. The self-assembled structures are directly analyzed by using scanning tunneling microscopy. We demonstrate that the phase separation and phase mixing of s-*cis*- and s-*trans*-oligothiophenes can be controlled by "shape complementary intermolecular interactions" associated with the overall molecular shapes. The overall shapes of the s-*cis*- and s-*trans*-oligothiophenes are tuned by the length of alkyl side chains.

### 3. Electrical Resistance of Long Oligothiophene Molecules<sup>2)</sup>

The electrical resistance of single oligothiophene molecular wires with lengths ranging from 2.2 nm (5-mer) to 9 nm (23-mer) was measured by the break junction method. A linear relationship between the molecular length and resistance was found for molecules longer than 11 mer, whereas an exponential increase in the resistance was observed for molecules shorter than 11-mer. These results indicate that the carrier transport mechanism changes from tunneling to hopping at around 11–14-mer (5.6 nm).

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

# **Safety Office**



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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 ionradical 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 Linear Chain of Water Molecules Accommodated in a Macrocyclic Nanotube Channel<sup>1)</sup>

A macrocyclic tetramer of 2-phenyl-1,3,4-oxadiazole was synthesized, and its self-assembly was investigated. The macrocycle was stacked to form a one-dimensional (1D) columnar structure containing water molecules. The nanotube self-assembled into a bundle, which grew into a molecular wire. The association of the water molecules in the tubular cavity resulted in shielding of the 1D chain of water molecules by the nanotube; these macrocyclic nanotube channels are promising candidates for nanotechnological applications.



Figure 1. Bundle structure of the microcyclic nanotube.

### 2. Theoretical Study of Noncovalent Interactions Between Triple Bonds and Chlorine Atoms in Complexes of Acetylene and Some Chloromethanes<sup>2)</sup>

The intermolecular potential surfaces of the acetylene– chloromethane complexes containing C–Cl··· $\pi$  (triple bond) interaction were calculated by the HF and MP2 methods with cc-pVXZ (X = D, T, Q) basis sets. At the minimum, the intermolecular distances between the triple bond and chlorine atom range from 3.3 to 3.5 Å. The CCSD(T) method predicted that the binding energies of the acetylene complexes with CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> are –0.49, –0.77, –1.05 and –1.34 kcal/mol at the basis set limit, respectively.

# 3. Theoretical Study for a Complex of 1,2,5-Thiadiazole with Formic Acid<sup>3)</sup>

Ab initio and DFT calculations have been performed on a complex of 1,2,5-thiadiazole with formic acid. Fifteen local minima of the complex are found using the MP2/6-31G method. The three stable structures with the lowest total energies are examined at the HF, MP2 and B3LYP/6-311++G(2d,2p) levels. The first and second stable structures contain intermolecular O–H…N/C–H…O and S…O/O–H…N interactions, respectively. Their binding energies by MP2 corrected BSSE and ZPE are -7.0 and -7.2 kcal/mol, which indicate a great stabilization of the complex.

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# **Visiting Professors**



### Visiting Professor AWAGA, Kunio (from Nagoya University)

#### Research on Organic Radical Materials

Organic radicals are key materials in both solid-state and solution redox processes. Organic radical solids always exhibit semiconductive behavior, due to electrostatic repulsion between unpaired electrons and/or electron-lattice interactions. This strongly suggests a potential application of organic radicals to organic electronics. We are performing fundamental research on electrical and magnetic properties of

organic radical solids and application research on photo- and current-induced phenomena. We are also working on solid-state electrochemistry of insoluble self-assembled organic thin-films and transition metal complex clusters, targeting rechargeable batteries, functional electroches, and electrochromic devices.



### Visiting Professor NAKAZAWA, Yasuhiro (from Osaka University)

#### Construction of a Low-Temperature Calorimeter Equipped with a Dilution Refrigerator

Organic conductors, Organic magnets, and metal complexes are fascinating materials which give various interesting electronic phases at low temperatures. The electron-phonon interactions, electron correlations in low-dimensional lattices have been widely investigated in them. With a purpose of studying these subjects and finding novel electronic behaviors, we are developing a new thermal-relaxation

calorimeter for measuring heat capacity at extremely low-temperature region. The dilution refrigerator available under magnetic fields up to 16 T in the instrument center of IMS is utilized to get low-temperatures condition. The minimum temperature reached without sample cell was 21 mK and the cooling power at 100 mK was confirmed as 400  $\mu$ W. A chip-type resistance containing ruthenium-oxide thick film was calibrated against standard thermometer and it was mounted on the Ag-based calorimetry cell. The heat capacity of tiny single crystals with typical weight of 50–300  $\mu$ g can be measured with absolute precision in this temperature region. The microchip calorimetry devices obtained by the micro-fabrication technique will be installed in the dilution refrigerator in order to study  $\mu$ g class single crystal samples with high resolution.



### Visiting Professor SEKIYA, Hiroshi (from Kyushu University)

Spectroscopic Study on Intermolecular Interactions and Dynamics in Hydrogen-Bonded Clusters and Coordination and Solvation Structures of Transition Metal Ions

We investigate structures, intermolecular interactions, and multiple-proton/hydrogen transfer reactions in hydrogen-bonded clusters such as 7-azaindole(alcohol)<sub>n</sub>/(water)<sub>n</sub> (n = 1-3) in the gas phase to clarify multi-dimensional potentials and the tunneling effect by combining electronic and IR spectroscopy with

high-level quantum chemistry calculations. These studies provide specific features of multiple-proton/hydrogen transfer reactions that are different from single- and double-proton trasfer reactions. We also investigate the coordination and solvation structures of transition-metal ions.  $Ag^+(NH_3)_n$  and  $Ni^+(NH_3)_n$  are studied by infrared spectroscopy and quantum chemical calculations.  $Ag^+$  and  $Ni^+$  adopt tetrahedral and square-planar coordination, respectively. The results demonstrate a close relationship between the d-electron configurations of the metals and the geometric structures of the solvated complexes.