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.
Metal acetylides or metal ethynyl compounds are made of the $M^+\text{–C}^- \text{ionic bonds. However, the ionic states of the acetylides are essentially metastable resulting in the segregation into metal-carbon or metal-organic polymer nanophases. This segregation still maintains $M^+\text{–C}^- \text{ionic bonds around the interfaces of the metal wire, particles, and dendritic sponges exhibiting various functions depending on the metal species.}$

1. **Increased Electric Conductance through Physisorbed Oxygen on Copper Nanocables Sheathed in Carbon**

Solid gas sensors, which are operated at high temperature, are normally based on chemisorption for modification of the electronic band conduction. Sensing of $O_2$ has been widely investigated. Recent advances in nanotechnology allow $O_2$ sensors, such as carbon nanotubes, to work at lower temperatures. We found that copper nanocables sheathed in carbon can detect physisorbed $O_2$ at room temperature by just measuring electric resistance. We have recently reported a low-cost, simple, and large-scale production method of nanowires involving the self-assembly of copper acetylide ($Cu_2C_2$) molecules in an aqueous solution. The conductance of a pressed tablet of nanocables fabricated by annealing $Cu_2C_2$ nanowires varies reversibly with adsorption and desorption of $O_2$ at room temperature.

$Cu_2C_2$ nanocables consist of metallic $Cu$ nanowires sheathed in amorhous carbon layers. It is very simple to produce a sensor using $Cu_2C_2$ nanocables. Current-voltage ($I$-$V$) measurement of the $Cu_2C_2$ nanocables was carried out under $O_2$-$N_2$ gas mixtures with a total pressure of 1 atm. The $Cu_2C_2$ nanocables exhibited an ohmic, proportional $I$-$V$ character. The constant voltage used for the measurement was typically 1 V. Figure 1 shows the transient conductivity on the $Cu_2C_2$ nanocables obtained by alternately exposing the nanocables to pure $O_2$ (1 atm) and pure $N_2$ (1 atm) gas. The conductance more than doubled during the 10-min $O_2$ exposures, and recovered reversibly during the subsequent $N_2$ exposures. It must be noted that the reversible fluctuations in conductance were observed at room temperature. The presence of the charged species changes the semiconductor’s Fermi level and the conduction of carriers. However, reversible absorption and desorption cycles at room temperature are generally believed to involve physisorption of molecules. Physisorption of $O_2$, which is not accompanied by charge transfer, is extremely unlikely to modify the electronic band structure for sensing by conductance.

![Figure 1. a: Reversible changes in $Cu_2C_2$ nanocable conductivity. The resistance of the $Cu_2C_2$ nanocables decreased under $O_2$. b: TEM image of a $Cu_2C_2$ nanocable.](image)

2. **Template-Free Fabrication of One-Dimensional Ag Nanoparticle Arrays**

Development of a new facile preparation method of onedimensional (1D) metal nanoparticle (NP) arrays is significant for both application and fundamental studies. We demonstrate a new facile and mass productive fabrication method for diameter-controlled 1D NP arrays via decomposition of silver phenylacetylide [Ag-C=C-C-Ph] nanowires. The ligand dissocia-
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3. Dendric Nano-Sponge of Silver Acetylide (Ag₂C₂) and Its Conversion to Silver Dendric-Skeletons Sheathed in Carbon Mantle

In contrast to the wire-type nano-structure formation of copper acetylide, silver acetylide (Ag₂C₂) produces nanosponge composed of dendric nano-rods with diameters of 20–30 nm under a certain synthetic condition as seen in Figure 3. Annealing at a temperature lower than 85 °C exhibits the segregation into inner silver and outer carbon with maintaining the dendric shape. This heating procedure in vacuum sometimes causes explosive reaction when the temperature of the powder increases this upper limit. Nitric acid treatment removes metallic silver but remains carbon and a small amount of silver strongly bound to carbon. EDS and TGA spectra of this sample revealed the presence of the remaining metallic silver. BET area (number of molecules adsorbed x area per an N₂ molecule) is estimated to be 157 m²/g from the BET adsorption isotherm equation for the acid treated sample. Although the characterization of the residual silver remains, we expect high catalytic activities of the silver on the carbon sponge with mesopore structures.

4. Hollow Graphitic Nano-Polyhedrons Produced from Silver Acetylide (Ag₂C₂)

A thoughtful graduate student can sometimes have a chance to change a bad accident to a very lucky discovery of a new material. The student performed the explosive reaction in a glass tube situated in a vacuum and collected the carbon product left inside the tube. Silver was evaporated and coated a mirror film inside the inner surface of the glass tube. Then he observed the TEM images of the carbon products. What he saw is the carbon onion type graphitic nano-structures with large empty holes, as shown in Figure 4. Strangely or reasonably, most of graphite layers are straight with bent corners with angles 90° ~ 120°. The SEM image in Figure 4-d shows the polyhedron balls of 20–100 nm. The presence of many defects (holes and layer mismatchings) in the graphitic shells suggests the potentials for gas storage.

Figure 4. a: TEM image of Hollow Graphitic Polyhedrons. The part in the black frame is expanded in b. c: Another expanded TEM image exhibiting imperfect graphitic shells. d: SEM image of the samples.

Award
NISHIJO, Junichi; Excellent Presentation Award, 87th Spring Meeting of Chemical Society of Japan.
Characterization of Magnetic Ultrathin Films by Novel Spectroscopic Methods

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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 synchrotron radiation. Moreover, we are exploiting a new technique of ultraviolet (UV) magnetic circular dichroism (MCD) photoelectron emission microscopy (PEEM) in order to perform spatiotemporal magnetic imaging.

1. Enhanced Photoemission Magnetic Circular Dichroism Using Free Electron Laser at UVSOR-II

In 2006, we discovered surprising enhancement of the visible/ultraviolet photoemission MCD when the photon energy was tuned to the work function threshold. In the previous experiments, we employed Cs-coated films in order to reduce and control the work function of the magnetic thin film samples. It is essentially important to verify the enhancement of the photoemission MCD of the pure metal thin films without Cs deposition for the exclusion of some possible Cs-induced changes of the electronic structure. In this work, we have measured a magnetization curve of clean Ni films on Cu(001) by using a free electron laser (FEL) at UVSOR-II that is tunable and extremely intense.

Figure 1(a) shows the magnetization curve of 8 monolayer (ML) Ni on Cu(001) obtained by the total photoemission MCD measurement in the applied external magnetic field using the FEL, whose photon energy was tuned around the work function of Ni. The MCD asymmetry, defined as \( \frac{I_{\text{left}} - I_{\text{right}}}{I_{\text{left}} + I_{\text{right}}} \) where \( I_{\text{left}} \) and \( I_{\text{right}} \) are the photoemission intensities using left- and right-circularly polarized lights, respectively, is found to be ±5%. The value is around two orders of magnitude more intense than the conventional MOKE measurement, as in our previous observations. Moreover, we have measured a photoemission MCD magnetization curve of Gd-coated Ni on Cu(001) by using a HeCd laser. The work function is again close to the photon energy. The result is shown in Figure 1(b). A similar enhancement of the photoemission MCD was observed.

We have consequently confirmed that the enhancement of photoemission MCD around the work function threshold is a universal behavior, applicable to photoelectron emission microscopy. This work was carried out in collaboration with the UVSOR machine group of Prof. M. Kato and Dr. M. Hosaka (present affiliation: Nagoya University).


The enhancement of the photoemission magnetic circular dichroism in the UV region paves a new way to develop UV MCD PEEM for the investigation of nanostructured magnetism. At present, MCD PEEM is performed as XMCD PEEM using third-generation synchrotron radiation X-ray sources. UV MCD PEEM allows us to do in-laboratory experiments when tunable deep UV lasers are available. Moreover, when ultrashort pulsed lasers are employed, pump-and-probe UV MCD PEEM measurements provide us a time resolving
power of ~100 fs rather easily, which is two to three orders of magnitude faster than the present standard experiments using the third-generation synchrotron radiation sources. In the present experiment, we have constructed an UV laser PEEM apparatus and have successfully observed the first UV MCD PEEM images of the ultrathin film.2)

Figure 2 (left) is our UV MCD PEEM apparatus. In this experiment, as we had no deep UV lasers available, the Ni films was coated with Cs to match the work function to the photon energies of the employed UV lasers. A right panel of Figure 2 shows the magnetic image of the Cs-coated 12 ML Ni film on Cu(001) using a Ti:sapphire laser (second harmonics 400 nm). The image was given by the subtraction between the two images obtained by using the left- and right-circularly polarized lights. Beautiful magnetic domains can be seen; the light and dark areas are ascribed to the downward and upward magnetizations, respectively. This is the first observation of the UV MCD PEEM of the ultrathin film; although the UV MLD PEEM images (MLD: Magnetic Linear Dichroism) have been already reported, the results was given for a thick Fe film of 100 nm, and the contrast is only 0.19%.4)

We have succeeded in the observation of two-photon MCD PEEM of the same sample using a Ti:sapphire fundamental light (800 nm). Preliminary pump-and-probe data were also obtained with the time resolution of ~100 fs, which show the magnetization recovery with the time evolution. The experiments are in progress in collaboration with Prof. Y. Matsumoto (present affiliation: Kyoto University) and Dr. K. Watanabe.

Figure 2. (left) Photo of our UV MCD PEEM apparatus (Elmitec, PEEMSpector) and (right) UV MCD PEEM image of Cs-coated 12 ML Ni on Cu(001), taken using the second-order harmonics of a Ti:sapphire laser (400 nm). In inset, the magnetization curve of a similar film is also shown.

3. Magnetism of Self-Assembled Co Nanorods Grown on Cu(110)-(2x3)N

Magnetic properties of low dimensional magnets has recently attracted much interest due to their importance for further dense magnetic recording media. From the view point of fundamental physics, these materials are interesting for their magnetic anisotropy, Curie/blocking temperature. In this work, we have investigated structural and magnetic properties of self-assembled Co nanorods3) with ~1 nm thick grown on Cu(110)-(2x3)N. This work was performed in collaboration with Prof. F. M. Leibsle (University of Missouri, Kansas, U. S.

References

Awards
1. Extremely High Stability of Glutathione-Protected Au$_{25}$ Clusters against Core Etching$^{1)}$

It is well known that so-called magic-numbered clusters can be preferentially populated by dissociative excitation of larger precursors, because the energy required for removal of a single atom from a magic-numbered cluster is higher than from a neighbor. Thus, if the Au atoms can be removed sequentially from preformed thiolated-protected gold (Au:SR) clusters, one can anticipate a population growth of certain stable Au$_n$:SR clusters. Chemical etching by free thiols is one feasible method for core size reduction of the Au:SR clusters. The etching rate of Au$_n$:SR clusters must be determined as a function of core size, in order to provide a synthesis for well-defined Au$_n$:SR$_m$ clusters in large quantity, as well as to provide information regarding the stability of Au$_n$:SR$_m$. In the present paper, we studied etching reactions of Au$_n$:SR$_m$ clusters with $(n,m) = (10,10), (15,13), (18,14), (22,16), (25,18), (29,20), (33,22), (39,24)$ by free glutathione (GSH). It was found that Au$_{25}$:SG clusters show higher stability against etching than the others and as a result two different reaction modes are operative depending on the core size. The Au$_n$:SG$_m$ (n < 25) clusters are completely oxidized to Au(1):SG complexes while Au$_n$:SG$_m$ (n ≥ 25) clusters are etched into Au$_{25}$:SG by free GSH molecules. On the basis of this observation, a model is proposed to explain our recent finding that Au$_{25}$:SG$_{15}$ clusters are selectively formed during the reaction of triphenylphosphine-stabilized Au$_{11}$ clusters and an excess amount of GSH.

2. Formation of Alkanethiolate-Protected Gold Clusters with Unprecedented Core Sizes in the Thiolation of Polymer-Stabilized Gold Clusters$^{2)}$

We have investigated magic-number sequences of octadecanethiolate-protected gold (Au:SC$_{18}$) clusters obtained by thiolation of gold clusters stabilized by poly(N-vinyl-2-pyrrolidone) (PVP). The Au:SC$_{18}$ clusters were prepared by the reaction of C$_{18}$SH and PVP-stabilized Au clusters. Four samples were fractionated by recycling size exclusion chromatography (SEC) of the as-prepared Au:SC$_{18}$ clusters, and their core sizes were determined to be 8, 11, 21, 26 kDa by using laser desorption ionization mass spectrometry. Unexpectedly, the sequence of these core sizes is different from that (8, 14, 22, and 29 kDa) obtained by conventional reduction of Au(I)–SC$_{18}$ polymers, which is governed by kinetic factors. The present finding shows that the Au:SR (R = organic group) clusters with a high tolerance to thiol etching can be systematically synthesized by first populating precursory Au clusters in a PVP matrix with subsequent thiolation of the preformed Au clusters. Optical spectroscopy shows that the electronic structure changes drastically with a core size in the size range between ca. 40 and ca. 140 atoms.

3. Thiolate-Induced Structural Reconstruction of Gold Clusters Probed by $^{197}$Au M"ossbauer Spectroscopy$^{3)}$

Several research groups have recently synthesized Au:SR clusters with well-defined chemical compositions, such as Au$_{25}$(SR)$_{18}$, Au$_{38}$(SR)$_{24}$, and Au$_{55}$(SR)$_{32}$, using size-separation techniques in combination with mass spectrometry. Nevertheless, geometric structures of Au:SR have not been determined experimentally mainly due to the unavailability of single crystals of these compounds. The lack of structural information for small Au:SR clusters hinders a full understanding of the origin of their stability and novel properties (e.g. photoluminescence, magnetism, and optical activity).

In the present study, we investigated the structures of a series of glutathionate-protected gold clusters, Au$_n$:SG$_m$ with $n = 10–45$, using $^{197}$Au M"ossbauer spectroscopy, which allows us to probe the local environment of the Au sites via isomer shift (IS) and quadrupole splitting (QS). The spectral analysis, with the help of recent theoretical results on methanethiolated gold clusters, revealed that Au–SG oligomeric rings are preferentially formed around the Au core. Specifically, a core-in-
cage structural motif theoretically predicted for \([\text{Au}_{25}(\text{SCH}_2)_{18}]^{2+}\) explains the Mössbauer spectra of \([\text{Au}_{25}(\text{SG})_{18}]^{2+}\) fairly well and thereby explains the high stability against the core etching reaction. The positive IS and QS values for the Au cores of \([\text{Au}_{4}(\text{SG})_{n}]^{2+}\) suggest a nontrivial effect of thiolate ligation on the electronic structure of the underlying gold clusters.

4. Synthesis of Biicosahedral Gold Clusters, \([\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_6\text{H}_{2n+1})_5\text{Cl}_2]^{2+} (n = 2–18)\)\(^4\)

Metal clusters have been gaining growing interest as elementary units of functional materials and building blocks of optoelectronic devices because of the novelty and controllability of their properties. Probably the most interesting aspect of “cluster-assembled materials” is that new collective properties can be imparted by controlling the distance between and arrangement of individual clusters. It is not trivial, however, to achieve this goal, since the interaction between clusters has to be enhanced without causing them to coalesce. One approach that has the potential to achieve such contradictory requirements is to use “magic clusters” as building units, since the interaction between these clusters is suppressed due to their inherent stability arising from their closed electronic and geometrical structures.

This paper reports the first chemical synthesis of \([\text{Au}_{25}]\) cluster compounds in which two icosahedral \([\text{Au}_{13}]\) units are directly connected by sharing a single vertex atom. The chemical reaction between \([\text{Au}_{14}(\text{PPh}_3)_8\text{Cl}_2]^{2+}\) and \(n\)-alkanethiol \(\text{C}_n\text{H}_{2n+1}\text{SH} (n = 2, 8, 10, 12, 14, 16, 18)\) serendipitously yielded stable \([\text{Au}_{25}]\) cluster compounds with the formula, \([\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_6\text{H}_{2n+1})_5\text{Cl}_2]^{2+}\). Single-crystal X-ray structural analysis of \([\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_6\text{H}_5\text{Cl}_2(\text{SbF}_6))_2\) revealed that the \([\text{Au}_{25}]\) core is constructed by bridging two icosahedral \([\text{Au}_{13}]\) clusters with thiolates sharing a vertex atom (Figure 1). Optical absorption spectroscopy showed that coupling between the \([\text{Au}_{13}]\) building blocks gives rise to new electronic levels in addition to those of the \([\text{Au}_{13}]\) constituents.

Figure 1. ORTEP drawing of the molecular structure of \([\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_6\text{H}_5\text{Cl}_2]^{2+}\). Thermal ellipsoids are drawn at the 50% probability level.

5. Effect of Ag-Doping on the Catalytic Activity of Polymer-Stabilized Au Clusters in Aerobic Oxidation of Alcohol\(^5\)

We have recently showed that Au clusters (\(\phi = 1.3\pm0.3\) nm) stabilized by a representative hydrophilic polymer, poly(N-vinyl-2-pyrrolidone) [PVP; \(\text{C}_8\text{H}_{12}\text{ON}]\), work as catalysts for various types of aerobic oxidation in water under mild conditions.\(^6\) The \([\text{Au}:\text{PVP}]\) clusters not only work as practical catalysts for aerobic oxidations, but also provide an ideal opportunity to address fundamental questions regarding the reaction mechanism. Most importantly, a wet chemical approach has enabled us to prepare monodisperse \([\text{Au}:\text{PVP}]\) clusters in the core-size range of 1.3–10 nm and to study the size dependent catalytic activity. The catalytic activity per unit cluster surface was found to increase with decreasing size, which is associated with non-metallic electronic structures. With the knowledge about size effect in hand, we have launched a further investigation into the nature of the active site of the small \([\text{Au}:\text{PVP}]\) by tuning the charge state of \([\text{Au}\] via impurity doping.

A set of nearly monodisperse Au–Ag alloy clusters (size range 1.6 to 2.2 nm) with various Ag content (5–30%) was prepared by the co-reduction method in the presence of PVP. The catalytic activities of the Au–Ag:PVP clusters were investigated for aerobic oxidation of \(p\)-hydroxybenzyl alcohol as a model reaction to understand the effect of Ag on the catalytic activity of Au clusters. It was found that the rate constants per unit surface area for Au–Ag:PVP clusters with small Ag content (< 10%) were larger than those of non-metallic \([\text{Au}:\text{PVP}]\) clusters of comparable size. The enhancement of the catalytic activity by Ag doping is discussed in light of the electronic structure of the Au–Ag cores probed by X-ray photoelectron spectroscopy. The present results indicate that the partial anionic character of the Au core is important for the aerobic oxidation reactions of \([\text{Au}:\text{PVP}]\) clusters.

References

Awards
NEGISHI, Yuichi; PCCP Award.
TSUKUDA, Tatsuya; GOLD 2006 Best Presentation Award.
In many organic charge-transfer salts, the electronic state of charge carriers is located at the boundary between localized and delocalized states. Recently the charge ordering (CO) originated from the localization of the charge carriers is widely found in organic conductors, and the electronic phase diagrams of typical organic conductors are re-considered taking CO into account. We are interested in the CO state, first because a CO phase is neighbored on a superconducting phase, wherein a new type of pairing mechanism for superconductivity is theoretically predicted, second because some compounds in a CO phase shows ferroelectricity, the origin of which is attributable to the electronic displacement, third because the narrow-band compounds have an inhomogeneous intermediate state between metallic and CO states. We employ infrared and Raman spectroscopy to study the CO state, since the infrared and Raman spectra change dramatically at the CO phase-transition temperature.

1. Two-Phase Coexistence in the Monovalent–Divalent Phase Transition of Dineopentylbiferrocene-Fluorotetracyanoquinodimethane, ((npBifc)\textsuperscript{n+}(F\textsubscript{1}TCNQ)\textsubscript{3}n–), \textsuperscript{1)}

Dineopentylbiferrocene-fluorotetracyanoquinodimethane, ((npBifc)\textsuperscript{n+}(F\textsubscript{1}TCNQ)\textsubscript{3}n–), undergoes a monovalent \((n = 1)\)– to-divalent \((n = 2)\) phase transition. The phase-transition behavior was studied using the magnetization, \(\chi T\), which showed a continuous increase in the temperature interval of \(-60\) K from 160 to 100 K. Mochida et al. suggested the coexistence of LT and HT phases to explain the continuous transformation. If a domain structure causes the continuous phase transformation, the domain size seems to be microscopic like spin-crossover compounds and relaxor ferroelectrics. Contrary to this expectation, we found macroscopic domains in the temperature interval of gradual phase transformation. In this temperature interval, we found that the Bragg peaks split into two groups which correspond to the monovalent and divalent phases.

![Figure 1. Position dependence of the Raman spectrum at 120 K. The Raman band at 1447 cm\(^{-1}\) appears in a monovalent \((n = 1)\) state, whereas the 1432 cm\(^{-1}\) band appears in a divalent \((n = 2)\) state. We have measured 11 points with the laser spot of 2 \(\mu\)m diameter. In the region A, only the 1432 cm\(^{-1}\) band is observed, whereas in other region C, 1447 cm\(^{-1}\) band is observed. At the boundary B, both are observed.](image-url)
Below 100 K, the Bragg peaks of monovalent phase are completely replaced by the Bragg peaks of divalent phase. In addition, we found a strong position dependence of the Raman spectrum (See Figure 1). Both experiments show that the macroscopic domains of monovalent and divalent phases coexist in the transition temperature region. This finding is unique, because two macroscopic domains stably exist in a wide temperature interval near the gradual phase transformation. We consider that the large volume contraction (ΔV/V ~ 0.03) at ~130 K is related to the stableness of the macroscopic coexistent domains. We examined a simple Landau-Ginzburg model including volumetric strain. According to this model, a stable coexistent state is obtained near the transition temperature region, and the coexistent temperature range increases as the elastic compliance and/or the volumetric strain is large. However, this model is very preliminary, and more realistic theory is necessary to fully understand the stable coexistent state.

2. Infrared and Raman Study of the Charge-Ordered State in the Vicinity of the Superconducting State in a Organic Conductor β-(meso-DMBEDT-TTF)2PF6

The competition between charge ordering and superconductivity has been attracting attention, because in systems in which such competition occurs, charge fluctuation possibly contributes to the superconductivity pairing mechanism. Such competition can be depicted in an electronic phase diagram. From this viewpoint, the insulating charge-ordered (CO) phase in the vicinity of the superconducting phase has been studied in both organic and inorganic compounds.

β-(meso-DMBEDT-TTF)2PF6 is possibly the typical compound, in which CO is competing with SC to be a ground state. We present spectroscopic evidence for the charge ordering in β-(meso-DMBEDT-TTF)2PF6 below ~70 K. The infrared and Raman spectra abruptly changed at ~70 K, and the amplitude of charge order was estimated to be 0.5 from the splitting of the infrared-active C=C stretching mode. The coexistence of the high-temperature and low-temperature signals was observed in a narrow temperature range (~4 K) at the phase transition temperature. The pressure and temperature phase diagram was obtained in the vicinity of the superconducting phase. The checkerboard-type charge-order (CCO) phase is not adjacent to the superconducting phase, but the short-range ordered charge-ordering (SRO) phase is next to the superconducting (SC) phase. The coexistent region significantly expands under the hydrostatic pressure. In the coexistent region, the crystal is inhomogeneous not only in macroscopic scale but also in mesoscopic scale.

3. Charge Ordered State and Frustration of the Site-Charges in (ET)3Te2I6 and (BETS)2Te2I6

The θ-type ET salt is most extensively studied for the charge-ordering (CO) phase transition. As the crystal lattice is uniform with herringbone structure, several electronic configurations are frustrating above the phase transition. The low-temperature horizontal CO is stabilized by the structural transformation, that is, electron-lattice interaction as well as Coulomb interaction takes part in the phase transition. To examine the role of Coulomb interaction, we have studied (ET)3Te2I6 and (BETS)2Te2I6 [ET = bis(ethylenedithio) tetra-thiafulvalene and BETS = bis(ethylenedithio) tetrathiafulvalene], whose organic layer takes the non-uniform lattice with a herringbone structure. We have studied x-ray structural analysis, temperature dependence of vibrational spectra and temperature dependence of electrical resistivity under the uni-axial strain for (ET)3Te2I6 and (BETS)2Te2I6. In the low-temperature insulating phase for each salt, a charge sensitive mode, ν2, exhibits a peak splitting, and a vibronic ν3 mode shows the factor group splitting. This observation confirms the charge ordered state. The distribution of the site charges is determined from the factor group analysis of the vibronic ν3 mode, and the site charge takes an inner distribution. This result is in agreement with that suggested from the x-ray crystal structure analysis of the ET-salt. In the high temperature conducting phase, the vibronic ν3 mode is smeared out whereas the frequencies of the two charge sensitive modes are almost unchanged in the whole temperature range. We have proposed the model that the highly conducting state is ascribed to the frustration between the inner distribution in the insulating state and the other charge distribution, which contributes to reducing the inter-site Coulomb interaction along the stacking and diagonal directions, respectively. Our conjecture is supported from the temperature dependence of the electrical resistivity under the uni-axial strain.

References
RESEARCH ACTIVITIES

Electrical Properties of Single-Component Molecular Crystals

Since the discovery of the first single-component molecular metal, \([\text{Ni}(\text{tmdt})_2]\) (tmdt = trimethyleneetrahydrofulvalenedithiolate), many analogous systems consisting of the transition metal complex molecules with similar extended-TTF type ligands were developed. However, the single-component molecular superconductor has not been developed yet. We have tried to prepare and characterize new analogous systems. The trial to examine the condition to metallize the insulating crystal of planar \(\pi\) donor molecule was made by using diamond anvil high-pressure cell.

1. Resistance Measurements of Microcrystals of Single-Component Molecular Metals Using Finely Patterned Interdigitated Electrodes

One of the largest problems in the studies on single-component molecular metals is the difficulties in the growth of sufficiently large single crystals. Therefore almost all the resistivity measurements ever made were performed on compacted crystalline powder pellets, which prevent to see the intrinsic resistivity behavior of the system. Recently, we have made the two-probe resistivity measurements on the as-grown polycrystalline samples of \([\text{Au}(\text{tmdt})_2]\) (tmdt = trimethyleneetrahydrofulvalenedithiolate) using finely patterned interdigitated electrodes and confirmed the system to be antiferromagnetic molecular metal with unprecedentedly high magnetic transition temperature \((T_N = 110 \text{ K})\). We used the commercially available gold or platinum electrodes with gap between interdigitated electrodes was 5 \(\mu\)m and the width of electrodes was 10 \(\mu\)m. The microcrystals were grown on the interdigitated electrodes electrochemically from the acetonitrile solution containing \((\text{Me}_4\text{N})[\text{Au}(\text{tmdt})_2]\) and \((n-\text{Bu}_4\text{N})\text{PF}_6\). The resistivity measurements showed metallic behavior down to 3 K where the resistance ratio \(\rho(3 \text{ K})/\rho(300 \text{ K})\) was 0.4. Despite of large decrease in the susceptibility at \(T_N\) suggesting the disappearance of a considerably large part of the Fermi surface, the resistivity showed no distinct anomaly around 110 K. This work was made under the collaboration with Dr. Hishashi Tanaka (AIST), Prof. Madoka Tokumoto (National Defense Academy) and Prof. Akiko Kobayashi (Nihon University).

2. Structures and Physical Properties of Highly Conducting Single-Component Molecular Conductors Substituted with Selenium Atoms, \([\text{M}(\text{tmstfdt})_2]\) (M = Ni and Au, tmstfdt = trimethylenediselenadi-thiafulvalenedithiolate)

With the aim of obtaining the single-component molecular metals with larger intermolecular interactions, that is, stronger
metallic properties, we have tried to prepare \([M(mstfdt)\_2] (M = Ni, Au)\) with Se-containing extended-TTF ligands, mstfdt. Microcrystals of \([M(mstfdt)\_2]\) were grown by electrochemical oxidation of \((Me\_4N)\_n[M(mstfdt)\_2] (n = 1 (Au), 2 (Ni))\) in the presence of tetra-n-butylammonium perchlorate in THF or acetonitrile. The crystal structures of \([M(mstfdt)\_2]\) were determined by synchrotron radiation X-ray powder diffraction experiments. The crystals \([Ni(mstfdt)\_2]\) and \([Au(mstfdt)\_2]\) are isostructural to each other and have very simple triclinic unit cells with only one molecule on the lattice point. Although resistivity measurements were made on compressed polycrystalline pellet samples, the room temperature resistivities were very high \((\rho(RT) = 10^{-2} \, \Omega \, cm (Ni), 10^{-1} (Au))\). Furthermore, \([Ni(mstfdt)\_2]\) showed metallic behavior down to about 50 K and kept high conductivities even at 4.2 K \((\rho(RT) = \rho(4 K))\). That is, \([Ni(mstfdt)\_2]\) is a new Se-containing single-component molecular metal. On the other hand, the resistivity of \([Au(mstfdt)\_2]\) increased slowly with lowering temperature. Magnetic measurements indicated Pauli paramagnetic behavior for \([Ni(mstfdt)\_2]\) and antiferromagnetic transition below 10 K for \([Au(mstfdt)\_2]\). This work were made under the collaboration with Dr. Emiko Fujiwara (the University of Tokyo) and Akiko Kobayashi (the University of Tokyo and Nihon University).

3. Possibility of Metallization of \(\pi\) Molecular Crystal at High Pressure

It may be said that the science on the molecular conductors was started by the pioneer works by Eley, Varanyan, Akamatu and Inokuchi around the middle of 20 century, who examined the conducting properties of the crystals of neutral \(\pi\) molecules such as phthalocyanine and condensed aromatic hydrocarbons. Since then an extremely large progress has been achieved in the field of molecular conductors. The first one-dimensional organic metal, \((TTF)(TCNQ)\) and the first organic superconductor, \((TMTSF)\_2PF\_6\) were reported in 1973 and 1980, respectively and through the examination of these systems and analogous molecular conductors, the requirements for the design of molecular metals became clear. That is, (1) the formation of conduction band by suitable molecular arrangement and (2) the carrier generation by charge transfer (CT) between the molecules forming conduction band and other chemical species were found to be two essential requirements. Due to the large success in the development of “CT-type molecular metals and superconductors,” almost all the chemists seemed to believe until recently that the crystal consisting of single kind of molecule could not be highly conducting at least at ambient pressure. However we have succeeded to develop the first single-component molecular metal in 2001 by designing the transition metal complex molecule with extremely small HOMO-LUMO gap and fairly large intermolecular interactions. It may be imagined that more straightforward way to metallize the single-component molecular crystal will be to apply extremely high pressure.

We have recently examined the possibility of metallization of the crystal of \(\pi\) donor molecule tetramethyltetradurophthalene (TMTTeN) up to 30 GPa by performing high-pressure four-probe resistivity measurements using diamond anvil cell (DAC). The crystal of TMTTeN has monoclinic lattice with space group \(P2\_1/c\) and the lattice constants of \(a = 10.130 \, \text{Å}, b = 6.069, c = 13.549, \beta = 110.572^\circ, V = 779.8 \, \text{Å}^3, Z = 2\). The room-temperature resistivity \((\rho(RT))\) decreased smoothly with increasing pressure at \(P < 10 \, \text{GPa}\), almost constant at \(11 < P < 16 \, \text{GPa}\) and decreased again at \(17 < P < 25 \, \text{GPa}\). \(\rho(RT)\) became as small as \(1.4 \times 10^{-3} \, \Omega \, cm\) at 30 GPa. To our best knowledge, all the hitherto reported molecular conductors with \(\rho(RT)\) smaller than \(10^{-2} \, \Omega \, cm\) are metallic at around room temperature. However, TMTTeN was not metallic at least around room temperature. These results seem to support our conjecture that it is very difficult to metallize the crystal without destroying the molecular structure.

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Magnetic Resonance Studies for Molecular-Based Conductors

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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 of these materials enables us to perform systematic investigations of low-dimensional, highly-correlated electron systems. Competition between the electronic phases in molecular-based conductors has attracted much attention. The investigations of such electronic phases by means of magnetic resonance measurements are important to understanding unsolved fundamental problems in the field of solid state physics.

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

1. Redistribution of Charge in the Proximity of the Spin-Peierls Transition: $^{13}$C NMR Investigation of (TMTTF)$_2$PF$_6$

Organic conductors, (TMTTF)$_2$X, have been extensively studied and are well-known quasi-one-dimensional conductors possessing various ground states, for example, spin-Peierls, antiferromagnetic, and superconductivity states realized by the application of pressure or variation of the counter-anion, $X$. However, recent progress in the investigation of charge-ordering (CO) phenomena has cast doubts on the validity of the simple Mott-Hubbard insulator model. TMTTF-based salts show a resistivity minimum at $T_\rho$ in the paramagnetic phase because of 1D electronic Umklapp processes. Below $T_\rho$, they are well described with a localized picture. At low-temperatures, most of them undergo charge-ordering transitions in the intermediate paramagnetic states between $T_\rho$ and the phase-transition temperature toward the ground state.

In our previous report, the charge configuration patterns of the charge-ordering phases in the intermediate paramagnetic states, such as $\cdot-O-O-O-O-o-(2k_F)$ and $\cdot-O-o-O-O-o-(4k_F)$ along the stacking axes, were determined for several TMTTF salts by ESR linewidth anisotropy analysis. We also clarified that the long-range Coulomb interaction along the stacking axis plays an essential role stabilizing the charge-ordering phases in the intermediate paramagnetic states. However, the driving force and charge configuration of the ground state have not yet been clarified.

For example, the ground states of (TMTTF)$_2$SbF$_6$ (antiferromagnet) and (TMTTF)$_2$AsF$_6$ (spin-Peierls) are different from each other, although they possess the same charge configuration pattern in the intermediate paramagnetic phase. Moreover, the coexistence of two orders was established along with the existence of a tetracritical point in the temperature/pressure phase diagram. Hence, it is also an open question whether charge separation in the spin-Peierls phase of (TMTTF)$_2$MF$_6$ is likely or unlikely.

In this study, we performed pulsed $^{13}$C NMR measurements on (TMTTF)$_2$PF$_6$ to determine its low-temperature electric states. (TMTTF)$_2$PF$_6$ shows a charge-ordering phase in the intermediate paramagnetic state below 65 K, and undergoes the spin-Peierls phase-transition at around 18 K. These Figure 1. Temperature dependence of $^{13}$C NMR spectra of (TMTTF)$_2$PF$_6$. Measurements were performed at the so-called magic-angle configuration. The inset shows two inequivalent inner (solid large circles) and outer (small circles) $^{13}$C sites in the zigzag TMTTF chains.
two successive phase-transition temperatures are the closest to each other among the family of TMTTF salts at ambient pressure. We present the electronic properties of this compound from a microscopic point of view.

2. Possible One-Dimensional Helical Conductor: Hexa-Peri-Hexabenzocoronene Nanotube

The discovery of electrically conductive carbon nanotube materials has expanded interest in exploring novel materials for functional electronic devices. Recently, new nanotubular objects have been developed by Aida and co-workers using novel hexa-peri-hexabenzocoronene (HBC) amphiphiles bearing hydrophilic oxyalkylene chains and lipophilic dodecyl chains. The amphiphilic HBC molecules have two lipophilic alkyl chains on one side, and two hydrophilic chains on the opposite side. Self-assembled graphitic nanotubes were obtained by cooling a hot tetrahydrofuran solution of the HBC derivative to room temperature. The HBC molecules stack to form well-defined nanotubes with a helical array of a large number of π-stacked HBC units. In ordinary carbon nanotubes, the conjugated two-dimensional π-molecular wave functions are spread on the surfaces of the nanotubes. However, in the case of the HBC nanotubes, the π-conjugated columns stack in the direction of the one-dimensional chain. The HBC nanotubes possess a uniform diameter of 20 nm with a wall thickness of 3 nm. Since the HBC molecules have a closed-shell, the resistivity of the pristine HBC nanotube is very high (~MΩcm). By chemical oxidation using iodine, however, the HBC nanotubes show high electrical conductivity.

There have been remarkable recent developments in structural measurement techniques such as scanning electron microscopy (SEM) and X-ray crystallography. However, the HBC nanotubes are not crystalline and the iodine-doped phases are not stable in a vacuum: when placed in a vacuum, the iodine-doped HBC nanotubes return to reversibly to the form of pristine HBC nanotubes. Hence, it is difficult to use such structural measurement techniques for the iodine-doped HBC nanotubes. Magnetic resonances measurements, on the other hand, are non-contact, low-energy spectroscopy techniques that are powerful even for non-crystalline materials. Moreover, with magnetic resonance investigations we can obtain not only static information but also dynamic details. In order to understand the origin and dynamics of charged carriers, in the present study, ESR and 1H NMR measurements were carried out on the iodine-doped HBC nanotubes.

3. Anomalous Temperature Dependence of g-Tensor in Organic Conductor, (TMTTF)₂X (X = Br, PF₆ and SbF₆)

The band-structures of organic conductors are deduced from frontier orbitals (for example, the highest occupied molecular orbital from a donor molecule) estimated by molecular orbital calculations applying the tight-binding approximation. The Fermi surfaces thus calculated are consistent with those estimated from quantum vibration and/or angular dependence magneto-resistance experiments. Most of the physical phenomena associated with organic conductors can be explained within a framework where the frontier orbital is treated as one rigid atomic orbital in an alkaline metal. It is commonly believed that the counter anions themselves do not affect the electronic properties of organic conductors.

An anomalous behavior of the g-tensor — a shift in principal value and rotation of the principal axes— was observed in (TMTTF)₂X salts with decreasing temperature. This behavior cannot be explained by a precursor effect (short-range magnetic fluctuation) just above the magnetic long-range order nor by molecular arrangement change.

In this study, we examined the magnetic properties for (TMTTF)₂X (X = Br, PF₆ and SbF₆) with ESR spectroscopy, X-ray diffraction, and quantum-chemical calculation of the g-tensor. We attempted to explain the anomalous behavior of the g-tensor using a scenario where the symmetry of the frontier orbital is deformed by the external counter-anion potential. The intra-molecular spin-distribution as a function of temperature is discussed from the microscopic point of view.

References
Macromolecular and Supramolecular Approaches to Spin-Functional Soft Materials

The first-row transition metal ions of $d^4$–$d^7$ electronic configuration are of interest, due to their possibility for the coexistence of two spin states, i.e. low-spin and high-spin states. Under certain conditions, the two spin states are known to switch in response to external perturbations caused by changes in temperature and pressure or photoexcitation. This phenomenon, referred to as spin transition or spin crossover, leads to changes in the magnetic and optical properties of the materials and has great potential for memory, display, and sensor applications. Solid or crystalline inorganic materials have been studied most extensively so far as potential spin-crossover materials, and some show reversible spin transition in a narrow temperature range. On the other hand, recent attention has been focused on soft materials with spin-crossover properties, as these materials can be processed easily by casting and tuned by molecular design. However, because of a larger freedom of molecular ordering, one may anticipate a possible loss of long-range cooperativity among the spin-transition sites, with the result of non-abrupt spin crossover, as often observed in solution.

Recently, we have designed a series of dendritic triazole derivatives, which serve as bidentate ligands that covalently bridge the iron(II) centers to form rigid coordination polymers, whose spin-transition properties are controlled by the dimensions of the dendritic ligand.1,2 Herein, we review our recent work on macromolecular and supramolecular approaches to the synthesis of newly designed spin-functional soft materials, with a focus on the possibility for the control of spin state and spin–spin interaction.

1. Synthesis and Functions of Multi Metallosalen Wheels

Salen units, due to their high binding affinity for various metal ions, are useful building blocks for the construction of functional materials such as spin-crossover crystalline solids, components of molecular magnet, and catalysts for organic transformation and polymerization.

By appending dendritic metallosalen complexes with different generation numbers to di-, tri-, and hexakis-substituted benzene cores, a series of multi metallosalen wheels having different geometry and numbers of salen units on the exterior surface were synthesized (Figure 1) and unambiguously characterized by NMR and MALDI-TOF MS measurements. These molecular wheels are unique in that their metal sites are located on the identical single layer of the dendritic framework and thus allows for a clear correlation between function and structure. Studies on spin and catalytic functionalities are in progress.

Figure 1. Schematic Representation of Multi Salen Wheels bearing 24 Metal Ions On the Exterior Surface.
2. Synthesis and Functions of TEG-Tethered Iron–Triazolate One Dimensional Chain

A series of newly designed Fe(II)-triazolate coordination polymers with TEG-tethered dendritic wedges \( (G^n_{\text{trz}})\text{Fe} \) (Figure 2; \( n = \text{number of the generation of benzyl ether dendritic wedge; } \text{m} = \text{number of TEG chains} \) ) were synthesized and their spin-crossover properties were investigated both in solution and solid.

![Figure 2. Schematic Representation of TEG-tethered Dendritic Iron–Triazolate Polymers.](image)

TEG-tethered dendritic triazoles \( (G^n_{\text{trz}}) \) with different numbers of TEG chains on the exterior surface were synthesized by convergent method and unambiguously characterized by NMR, MALDI-TOF-MS, IR measurements. Polymerization of \( G^n_{\text{trz}} \) with \( \text{Fe}(\text{MeSO}_3)_2 \) in MeOH at room temperature afford a series of coordination polymers \( (G^n_{\text{trz}})\text{Fe} \) with iron–triazolate backbone encapsulated in TEG-tethered dendritic wedges. These dendritic polymers are highly soluble in THF, MeOH, EtOH, \( \alpha \)-propanol to give a stable solution over a long period. Since the ‘naked’ iron–triazolate polymer is not soluble, TEG-tethered dendritic wedges not only enhanced solubility but also prevented the polynuclear chain from decomposition in solution.

A MeOH solution of \( (G^2_{\text{trz}})\text{Fe} \) at room temperature was colored violet, characteristic of low-spin state, and discolored upon heating at 30 °C, whilst after cooling at 20 °C, the solution turned to violet again. This thermally induced coloration-discoloration process is reversible without any deterioration for many times. The above color change suggests that thermal spin crossover takes place even in MeOH. In fact, temperature variable electronic absorption spectroscopy display a heating profile with a decrease at 450-nm absorption band, originated from \( d-d \) absorption band of the low-spin state, together with the appearance of a new peak centered at 750 nm, characteristics of the high-spin state. The spin transition temperature was thus estimated to be 25 °C. This is also the case for \( G^0_{\text{trz}}\text{Fe} \) with one TEG chain on the dendritic surface, to show a spin transition temperature at 25 °C. On the other hand, \( G^3_{\text{trz}}\text{Fe} \) with three TEG chains on the surface of the dendritic wedges although displayed a reversible spin crossover in MeOH but with a much low transition temperature at 6 °C.

\( (G^1_{\text{trz}})\text{Fe} \) and \( (G^2_{\text{trz}})\text{Fe} \) bearing large dendritic wedges were highly soluble in MeOH but displayed a colorless solution at room temperature, indicating a high-spin state of the focal metal chain. Upon cooling at 0 °C, the solution turned to violet, as a result of spin transition to low-spin state. The spin transition temperature in MeOH were estimated to be 8 and 5 °C, respectively. Therefore, when the size of dendritic wedge becomes large, the temperature for spin transition in MeOH decreased. In sharp contrast to the case of \( G^0_{\text{trz}}\text{Fe} \), solid samples of \( (G^1_{\text{trz}})\text{Fe} \) and \( (G^2_{\text{trz}})\text{Fe} \) retain high spin state even upon cooling at −78 °C. All these observations indicate that the TEG-tethered dendritic wedges play an important role in spin transition of the focal iron-triazolate chain.

XRD measurements of \( (G^0_{\text{trz}})\text{Fe}, (G^1_{\text{trz}})\text{Fe}, \) and \( (G^2_{\text{trz}})\text{Fe} \) exhibit that these dendrimers form hexagonal columnar structures. TEG-tethered dendritic wedges in the solution likely adopt stretched conformation, therefore, the decrease of spin transition temperature in solution is predominately affected by the size of the dendritic wedges. A large dendritic wedge causes steric hindrance between the neighboring metal sites and thus decreases the polymerization degree of the focal iron-triazolate chain. As a result, the spin transition temperature decreased. On the other hand, in solid state, the TEG chains become shrink to give a global conformation. Such a conformational change result in further increment of the steric hindrance between the two neighboring dendritic wedges, and eventually the focal iron-triazolate chain becomes distort, especially in the case of high-generation \( (G^1_{\text{trz}})\text{Fe} \) and \( (G^2_{\text{trz}})\text{Fe} \). Therefore, the TEG-tethered dendritic wedges not only greatly improved the solubility of rigid coordination polymer chain, but much importantly through conformational change enables magneto-optical switching of the focal iron-triazolate chain.

References

Award
Jiang, Donglin; SPSJ Wiley Award 2006.
We are currently developing a novel solid state NMR technique to be used for material science and structural biology. Currently, we focus to develop a methodology to characterize membrane bound proteins such as peripheral membrane proteins under fully hydrated sample condition, to reveal their native structures and dynamics. Solid state NMR is one of the useful tools to characterize dynamics of such insoluble proteins. For this reason, we have developed a new technique to observe motionally averaged weak heteronuclear dipolar coupling.

1. A Novel Technique to Examine Local Dynamics of Biomolecules by Means of Magnified, Motionally Averaged, Weak Heteronuclear Dipolar Couplings by Solid State NMR Spectroscopy

Fully hydrated membrane proteins in lipid bilayers undergo lateral diffusion and are known to exhibit significant dynamics. When the motions are that the tensor interaction has effective axial symmetry, all the motional information can be referred to this axis and is expressed in terms of a single order parameter. In order to characterize local mobility of such biomolecules, we have explored to determine their segmental order parameters by observing motionally averaged, weak heteronuclear dipolar interaction, under magic angle spinning (MAS). For this purpose, we have developed a new separated local field technique, scalar coupling refocused effectively magnified dipolar field-chemical shift (SCREM-DIPSHIFT) correlation spectroscopy, to determine motionally averaged, weak heteronuclear dipolar coupling, under MAS. A pulse sequence is shown in Figure 1(a). This method greatly magnifies the detection sensitivity for heteronuclear dipolar couplings 4 times over the conventional ones, by only recoupling of heteronuclear dipolar interaction based on interference between sign changes of average Hamiltonian of heteronuclear dipolar interaction under $^1$H homonuclear dipolar decoupling.

For Figure 1, (a) Pulse sequence of INEPT-SCREM-DIPSHIFT under MAS. BLEW12+/– is multiple-pulse to generate the same form of average Hamiltonian for heteronuclear dipolar interaction with opposite signs with suppression of $^1$H homonuclear dipolar decoupling. The thin- and thick- blacked bars indicate $\pi/2$ and $\pi$ pulses, respectively. $\tau_r$ is rotor period and ‘$m$’ and ‘$n$’ are integer. (b) Molecular structure of POPC. (C) $^{13}$C-NMR slice spectra acquired with sequence (a) without (upper column.) and maximally reduced signal (lower column) due to magnified $^1$H-$^{13}$C dipolar coupling for POPC in MLVs. Experimentally determined dynamic order parameters were indicated inside of bottom spectrum.
and spatial modulation by MAS. Furthermore, the one also refocuses scalar coupling evolution during dipolar evolution time. One can therefore determine extremely averaged, weak dipolar coupling with lower limit of a hundred Hz for $^{1}H-^{13}C$ spin pair, which corresponds to dynamic order parameter of 0.0043 with single rotor cycle at spinning speed less than 3 kHz. Total experimental time can also be appreciably reduced, as compared with acquiring full 2D-NMR spectra. Furthermore, by extending dipolar evolution time of multiple of unit cycle, lower detection limit can be extended as much as possible depending on effective $T_{2}$ under $^{1}H$ homonuclear dipolar decoupling multiple-pulse sequence of observed nuclei.

To prove efficacy and usefulness of this technique, we characterized lipids in fully hydrated multi-lamella vesicles (MLVs), 1-palmitoyl-2-oleyl-sn-glycero-3-phosphocholine (POPC). The time evolution of the recouped, motionally averaged, weak $^{1}H-^{13}C$ heteronuclear dipolar interactions was monitored by reduced high resolution NMR signal of natural abundant $^{13}C$ nuclei, prepared by either $^{1}H$ coherence transfer based on through-bond $J$-coupling mediated rotor synchronized INEPT or single pulse excitation of $^{13}C$ polarization. Dipolar couplings in each residue were determined by fitting the curves of reduced signals for $^{1}H-^{13}C$ 2-spin, $^{1}H-^{13}C$ 3-spin system $^{1}H-^{13}C-^{13}C$ 4-spin system for CH and CH$_{2}$ and CH$_{3}$, respectively. The segmental order parameters were shown in Figure 1 (c) with slice $^{13}C$ NMR spectra without and with maximally reduced signals. The obtained segmental order parameters for POPC in MLVs were slightly smaller, but similar as reported for saturated lipids. Further developments to characterize the local structures are in progress.

2. A Study of Local Mobility for Phospholipase C $\delta 1$-Pleckstlin Homology Domain Bound to Fully Hydrated Multi-Lamella Vesicles by Solid State NMR$^{2}$

A peripheral membrane protein, phospholipase C (PLC)-$\delta 1$, is one of membrane proteins related to signal transduction by conducting hydrolytic cleavage of phosphatidylinositol-4,5-bisphosphate (PIP$_{2}$) on the surface of membrane bilayers and is known as one of essential proteins for mammals. Pleckstlin homology (PH) domain of PLC-$\delta 1$ has been recognized as PIP$_{2}$ binding domain. In current study, characterization of local mobility of PLC-$\delta 1$ PH domain bound to fully hydrated MLVs was explored. $[3-^{13}C]$Ala-labeled PLC-$\delta 1$ PH domain was expressed as GST fusion protein in E Coli in $[3-^{13}C]$Ala contained in M9 culture and purified by affinity chromatography. The purified one was attached to the surface of MLVs prepared from POPC and PIP$_{2}$ with molar ratio 20:1. The molar ratio of protein to lipids was prepared to 1:20. PLC-$\delta 1$ PH domain bound to MLVs were precipitated by ultracentrifuge of 6 hours at 541000 xg at 4 °C. They were packed into sample tube as same way as mentioned above. Solid state NMR experiments were carried out under the same condition mentioned above. The magnified recoupling effects of motionally averaged weak $^{1}H-^{13}C$ heteronuclear dipolar interactions were monitored as signal reduction of high resolution $^{13}C$ spectra of isotope enriched methyl carbon of Ala residues in PLC-$\delta 1$ PH domain by SCREM-DIPSHIFT. Individual dipolar couplings were determined by fitting curves of the reduced signals for $^{1}H_{3}-^{13}C$ 4-spin system with rotation effect around the C$_{3}$ rotation axis. Dynamic order parameters (0 < DOP < 1.0), were determined by the normalizing motionally averaged heteronuclear dipolar couplings with the one in rigid limit. Figure 2 (a) shows high resolution solid state NMR spectra with reduced signals due to recoupled heteronuclear dipolar couplings of methyl region. Dynamic order parameters for all Ala residues in PLC-$\delta 1$ PH domain were determined similarly. Figure 2 (b) illustrates preliminary result of a pictorial representation of local mobility of PLC-$\delta 1$ PH domain bound to fully hydrated POPC/PIP$_{2}$-MLVs, based on experimentally determined dynamic order parameters. The information of local mobility of PLC-$\delta 1$ PH domain may give the understanding of a detailed mechanism as to a relationship between structure and function of PH domain, which is bound to PIP$_{2}$. To the best of our knowledge, this is first example of successfully characterized local mobility for peripheral membrane protein bound to fully hydrated lipid bilayers by solid state NMR.

Figure 2. Pictorial representation of local mobility of PLC-$\delta 1$ PH domain bound to fully hydrated POPC/PIP$_{2}$ lipid bilayers surface of MLVs based on the experimentally determined order parameters (red colored) of Ala residues in PLC-$\delta 1$ PH domain. Light blue spheres indicate the location of Ala residues in PLC-$\delta 1$ PH domain. A model structure has been generated from the combination of X-ray derived structure bound to Inositol-1,4,5-triphosphate in the crystal and POPC lipid bilayers calculated from MD simulation.

References
2) N. Uekama, M. Okada, H. Yagisawa, S. Tuzi and K. Nishimura, to be submitted.
RESEARCH ACTIVITIES

Construction and Nano-scale Measurements of Molecular Nanostructures for Molecular Electronics

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Molecular electronics is a relatively new and fascinating area of research. However, as most single organic molecules are not conductive in a classical sense, long-range electronic transport through single molecules is unlikely to be useful for practical electronic circuits. Our group is interested in composites of conductive nano-materials with functional organic molecules as attractive bases for molecular electronics. Structures such as carbon nanotubes and metal nanoparticles incorporating functional organic molecules have been shown to be possible candidates. We have prepared two dimensional, one dimensional Au nano-particle assemblies using organic molecules, and carbon nanotube/organic molecule composites. Their electric properties were studied using nanogap electrodes and PCI-AFM.

The subjects of our group can be classified into three categories: (1) Preparation and self organization of functional organic molecules, metal nano-particles, and carbon nanotubes, (2) development of new scanning microscopic methods, and (3) development of new lithographic technique utilizing self assembling of molecules. By the combination of these three theme we are aiming to realize molecular scale electronics.

1. Metal-Semiconductor Transition Induced Visible Fluorescence in Single Walled Carbon-Nanotube/Noble Metal Nanoparticle Composites¹)

We show that single walled carbon nanotube (SWNT) bundles emit visible fluorescence in the presence of noble metal nanoparticles and nanorods in the solid state. Conductivity measurements with metallic nanotubes, isolated from pristine SWNTs show that they become semiconducting in the presence of the metal nanoparticles. Nanoparticle binding increases the defects in the nanotube structures which is evident in the Raman spectra. The metal–semiconductor transition removes the non-radiative decay channels of the excited states enabling visible fluorescence. Nanotube structures are imaged using this emission with resolution below the classical limits.

2. A New Utilization of Organic Molecules for Nanofabrication Using the Molecular Ruler Method²)

Oligothiophenes and porphyrin oligomers were exploited as new molecules for the “molecular ruler” (MR) method in the form of simple molecular monolayers. When handled in air, oligothiophenes yielded extremely homogeneous nanogaps about 30 nm wide, while handling under N₂ produced nanoscale gaps of around 10 nm between parent and daughter structures. The difference between these two results indicated that it was possible to control the width of this gap by varying the extent of oxidation of the oligothiophenes. Porphyrin oligomers also yielded nanogaps about 10 nm wide. Therefore, these two types of molecules are promising candidates for use in MR methods.

3. Scanning Tunneling Microscopy Investigation of Vanadyl and Cobalt(II) Octaethylporphyrin Self-Assembled Monolayer Arrays on Graphite³)

Two-dimensional crystals of [2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine] vanadium(IV) oxide and cobalt(II) (VOOEP and CoOEP, respectively) at the interface of 1-tetradecene and highly oriented pyretic graphite (HOPG) were studied by scanning tunneling microscopy (STM). The lattice parameters were determined for VOOEP (a = 1.6±0.1 nm, b = 1.46±0.05 nm, Γ = 61±3°) and CoOEP (a = 1.48±0.08 nm, b = 1.42±0.07 nm, Γ = 62.0±4°). The lattice parameters were calibrated using the HOPG lattice as a reference. The center metal dependence observed by high-resolution STM analysis of octaethylporphyrin and the differences between VOOEP and CoOEP are proved.
4. Different I-V Characteristic of Single Electron Tunneling Induced by Using Double-Barrier Tunneling Junctions with Differing Symmetric Structures

I-V characteristics of single electron tunneling from a symmetric and an asymmetric double-barrier tunneling junction (DBTJ) were examined. A single Au nanoparticle was trapped in nanogap whose size was precisely controlled using a combination of electron beam lithography and molecular rulertchnique. Though the symmetric junction showed a monotonic rise with a bias beyond the Coulomb gap voltage, the asymmetric junction showed Coulomb staircases. The capacitance of the junction estimated from the fitting curves using the Coulomb conventional theory was consistent with the capacitance calculated from the observed structure. The authors quantitatively found the correlation between the electrical and structural properties of DBTJ.

5. Halide Anion Mediated Dimer Formation of a meso-Unsubstituted N-Confused Porphyrin

The new N-confused porphyrin (NCP) derivatives, meso-unsubstituted b-alkyl, 3-oxo-N-confused porphyrin (3-oxo-NCP) and related macrocycles, were synthesized from appropriate pyrrolic precursors via a [3+1] type condensation reaction. 3-Oxo-NCP forms a self-assembled dimer in dichloromethane solution that is stabilized by complementary hydrogen bonding interactions arising from the peripheral amide-like moieties. The protonated form of 3-oxo-NCP was observed to bind halide anions (F-, Cl-) through the outer NH and the inner pyrrolic NH groups, affording a dimer in dichloromethane solution. The structure of the chloride-bridged dimer in the solid state was determined by X-ray diffraction analysis.


Electrodes with a gap size of 15 ~ 80 nm could be bridged by porphyrin molecular wires with 50 ~ 300 nm length. The porphyrin units could be coordinated with Au nano-particles having pyridinyl moiety. The device with both the porphyrin and Au nano-particles showed photo-response characteristics while those without the Au nano-particles showed no response.

7. Synthesis of Dendron Protected Porphyrin Wires and Preparation of a One-Dimensional Assembly of Gold Nanoparticles Chemically Linked to the π-Conjugated

A one-dimensional assembly of gold nanoparticles chemically bonded to π-conjugated porphyrin polymers was prepared on a chemically modified glass surface and on an undoped naturally oxidized silicon surface by the following methods: π-conjugated porphyrin polymers were prepared by oxidative coupling of 5,15-diethynyl-10,20-bis-(4-dendron)phenyl porphyrin, and its homologues (larger than 40-mer) were collected by analytical gel permeation chromatography. The porphyrin polymers were deposited using the Langmuir-Blodgett method on substrate surfaces, which were then soaked in a solution of gold nanoparticles (2.7±0.8 nm protected with r-dodecanethiol and 4-pyrindineethanethiol). The topographical images of the surface observed by tapping mode atomic force microscopy showed that the polymers could be dispersed on both substrates, with a height of 2.8±0.5 nm on the modified glass and 3.1±0.5 nm on silicon. The height clearly increased after soaking in the gold nanoparticle solution, to 5.3±0.5 nm on glass and 5.4±0.7 nm on silicon. The differences in height corresponded to the diameter of the gold nanoparticles bonded to the porphyrin polymers. The distance between gold nanoparticles observed in scanning electron microscopic images was ca. 5 nm, indicating that they were bonded at every four or five porphyrin units.

References

Awards
MIYAKE, Yusuke; Outstanding Research Award, AsiaNano 2006.
MIYAKE, Yusuke; Best Poster Award, International Scanning Probe Microscopy Conference 2007.

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RESEARCH ACTIVITIES

Development of Organic Semiconductors for Molecular Thin-Film Devices

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WATANABE, Yoko  Secretary

Organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) based on π-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. Perfluoropentacene and Perfluorotetracene: Syntheses, Crystal Structures, and FET Characteristics

We have synthesized perfluoropentacene and perfluorotetracene as potential n-type semiconductors for organic field-effect transistors (OFETs). Perfluoropentacene and perfluorotetracene are dark blue and reddish-orange crystalline solids, respectively. The HOMO-LUMO gaps of perfluorinated acenes are smaller than those of the corresponding acenes. The reduction potential of perfluoropentacene is almost the same as that of C₆₀, which is known as an excellent n-type semiconductor for FETs. Perfluoropentacene and perfluorotetracene are planar molecules that adopt herringbone structures with the angles of 91.2° and 91.1°, respectively. The short C–C contacts less than the sum of van der Waals radii were observed for both perfluorinated acenes. The interplanar distances are shorter than the layer separation of graphite, which may lead to high electron mobility along the stacking directions.

We report the synthesis and characterization of perfluorinated tetracene; a material with potential applications in organic electronics. The electrochemical behavior of the compound is analyzed by differential pulse voltammetry, and compared with that of tetracene. The structure of perfluorotetracene is planar as observed for pentacene. We also report a comparative Raman spectroscopic study of tetracene and perfluorotetracene in relation to their π-conjugational properties. Density functional theory calculations have been also performed, at the B3LYP/6-31G** level, to assess information regarding the topologies and energies of the frontier molecular orbitals around the gap, and about the vibrational normal modes associated with the Raman features selectively enhanced by the π-conjugation.

3. Optical Properties of Pentacene and Perfluoropentacene Thin Films

The optical properties of pentacene (PEN) and perfluoropentacene (PFP) thin films on various SiO₂ substrates were studied using variable angle spectroscopic ellipsometry. Structural characterization was performed using X-ray reflectivity and atomic force microscopy. A uniaxial model with the optic axis normal to the sample surface was used to analyze the ellipsometry data. Strong anisotropy was observed and enabled the direction of the transition dipole of the absorption bands to be determined. Furthermore, comparison of the optical constants of PEN and PFP thin films with the absorption spectra of the monomers in solution shows significant changes due to the crystalline environment. Relative to the monomer spectrum the HOMO-LUMO transition observed in PEN (PFP) thin film is reduced by 210 meV (280 meV). Surprisingly, a second absorption band in the PFP thin film shows a slight blueshift (40 meV) compared to the spectrum of the monomer with its transition dipole perpendicular to that of the first absorption band.

4. The Effect of Fluorination on Pentacene/Gold Interface Energetics and Charge Reorganization Energy

The energy level alignment at interfaces between conjugated organic semiconductors and metals is recognized as a key factor determining the performance of organic-based (opto-) electronic devices. Experimentally, the hole injection barriers (HIBs) at organic/metal interfaces can be directly determined by ultraviolet photoelectron spectroscopy (UPS). In addition, angle-resolved UPS (AR-UPS) allows to assess important aspects of surface molecular orientation. In the present work, we used this method to investigate interfaces between two prototypical organic semiconductors pentacene (PEN) and perfluoropentacene (PFP) and Au. PEN can successfully be used as active material in organic field-effect transistors (OFETs) with high hole mobility of up to 5.5 cm²/Vs. The fabrication of integrated circuits requires also high electron mobility OFETs, which turns out to be difficult to achieve with pentacene, with reported electron mobilities up to 0.04 cm²/Vs. One approach to improve n-type performance of OFETs was to use perfluoropentacene, resulting in high electron mobilities of more than 0.2 cm²/Vs. Commonly, Au is used as source and drain contact metal in OFETs. Therefore, the interface energetics between organic semiconductors and Au are of interest, since charges have to be transported across these interfaces and minimized contact resistance is sought for. PEN and PFP monolayers on Au(111) exhibited very similar HIBs (0.60 eV vs. 0.65 eV), despite the significantly higher IE of the perfluorinated PEN analog. φ of Au(111) decreased upon PEN adsorption by 0.95 eV, while the decrease was only 0.5 eV for PFP. In the simple model of the “push-back” effect of surface metal electrons due to adsorption of molecules, our findings imply a larger bonding distance of PFP on Au compared to PEN. For PFP, four different layers away from Au were identified by significantly different HOMO binding energies, spreading by 0.8 eV. This spread was only 0.4 eV for PEN, and two layers could be resolved. PEN and PFP monolayers on Au(111) exhibited large charge reorganization energies, pointing towards strong charge localization at the interface.

References
Building Photosynthesis by Artificial Molecules

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. An Approach towards Artificial Quinone Pools by Use of Photo- and Redox-Active Dendritic Molecules

Mimicking individual processes of photosynthesis by use of artificial molecules is an interesting approach for chemists to build up new systems for light-to-chemical energy conversion. In this respect, particular success has been, and is being, achieved by studies on photoinduced electron transfer, models of antenna systems and oxygen evolving complexes. However, many other features of photosynthesis are still unexplored by model chemists. The quinone pool is one of such disregarded features.

We built a “single-molecular” quinone pool by use of synthetic molecules (Figure 1). The molecules are based on dendrimers with well-defined size and shape. A porphyrin (photoactive group) is attached at the center, and multiple quinones are attached at internal positions of the dendrimer.

When these molecules were irradiated with visible light (λ > 500 nm) in the presence of 4-tert-butylthiophenol, the quinones were gradually converted to the corresponding quinols. Figure 2 shows the time-dependent change of $^1$H NMR under these conditions. This reaction is triggered by photoexcitation of the porphyrin. A particularly interesting observation in Figure 2 is that the quinones of all layers in G3Q$_{14}$P were converted to quinols at similar apparent rates. We attribute this apparent layer independence of the conversion rate to the photoinduced exchange of quinone/quinol.
2. Rigid Tricarboxylate Ligands Derived from Triarylmesitylenes and Their Metal Complexes

Carboxylate ligands are widely found in active sites of metalloenzymes. From the synthetic point of view, however, there is one long-standing problem about metal-carboxylate clusters; carboxylate ligands can exist in various coordination modes (monodentate, $\eta^1$-bridging, $\eta^2$-bridging with syn/anti variations, etc.), hence it is very difficult to predict what structure(s) will result under particular reaction conditions. Even preformed clusters can easily rearrange to give products with very different structures.

To overcome these general difficulties in metal carboxylate chemistry, we developed a new tricarboxylate ligand 1, which is designed suitably to bind to a particular trinuclear $M_3(\mu_3-O)$ core (Figure 3). The ligand 1 is a derivative of syn-2,4,6-tris(2'-X-aryl)-1,3,5-trimethylbenzene (triarylmesitylene), in which the three side chains (X) of the aryl groups are fixed in the same side of the central mesitylene ring because of the restricted rotation of the aryl-mesityl bonds. In addition, the carboxylate groups at the end of the side chains are located in suitable positions to bind to a $M_3(\mu_3-O)$ core.

We successfully prepared the triiron complex $[\text{Fe}_3(\mu_3-O)(\text{1})_2(\text{H}_2\text{O})_3]\text{FeCl}_4$ and characterized by X-ray crystallography (Figure 4). Interestingly, the similar compound lacking the 1,3,5-methyl groups did not give the similar complex. Such difference was rationalized by the molecular dynamic (MD) simulations (Figure 5). This ligand will serve as useful building blocks for constructing difficult metal clusters as observed in the photosynthetic oxygen-evolving center.

3. Reconstitution of the Water-Oxidizing Complex in Photosystem II Using Synthetic Mn Complexes: Production of Hydrogen Peroxide

Oxygen evolution is one of the most important, and most enigmatic, processes in plant photosynthesis. The function is performed at the oxygen-evolving complex (OEC), which contains, among others, four manganese ions as essential cofactors. The OEC resides at the oxidizing terminal of Photosystem II (PS2). Since the PS2 is a very efficient biomolecular device for photoinduced charge separation, replacing the OEC with other metal complexes is an interesting approach for developing new functions of photoinduced chemical conversion.

We attempted the reconstitution of the OEC with several dinuclear complexes of Mn(II) and Mn(IV). The reconstituted PS2 samples with these compounds regained the electron-transfer capability, but the oxygen evolution capability was less efficient. More interestingly, it was shown that hydrogen peroxide was produced by these reconstituted PS2 samples. This is the first example of reconstituted PS2 samples that exhibit non-natural photochemical functions.

Figure 5. The MD trajectory of 1 (left) and that lacking the 1,3,5-methyl groups (right).

References


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Chemistry of Bowl-Shaped Aromatic Compounds and Metal Nanocluster Catalysts

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Bowl-shaped π-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-to-bowl 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 chiralbuckybowls 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. Synthesis of an Enantiopure syn-Benzocyclotrimer through Regio-Selective Cyclotrimerization of Halonorbornenes under Palladium Nanocluster Conditions

An enantiopure syn-benzocyclotrimer (1) was selectively synthesized from an enantiopure halonorbornene (2) through regio-selective cyclotrimerization catalyzed by palladium nanoclusters. The yield of 1 was dependent on the stability of the palladium clusters, which was ascertained from the appearance and TEM images of the reaction mixtures. The thus-prepared enantiopure benzocyclotrimer will serve as a key intermediate for the synthesis of $C_{3v}$ symmetric chiral buckybowls.

Table 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>BuNX</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield of 1 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BuNBr 100 mol %</td>
<td>Na$_2$CO$_3$ 250 mol %</td>
<td>DMSO</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>BuNOAc 100 mol %</td>
<td>Na$_2$CO$_3$ 1000 mol %</td>
<td>1,4-dioxane</td>
<td>34%</td>
</tr>
<tr>
<td>3</td>
<td>BuNOAc 300 mol %</td>
<td>Na$_2$CO$_3$ 1000 mol %</td>
<td>1,4-dioxane</td>
<td>42%</td>
</tr>
<tr>
<td>4</td>
<td>BuNOAc 500 mol %</td>
<td>Na$_2$CO$_3$ 1000 mol %</td>
<td>1,4-dioxane</td>
<td>47%</td>
</tr>
<tr>
<td>5</td>
<td>BuNOAc 1000 mol %</td>
<td>Na$_2$CO$_3$ 1000 mol %</td>
<td>1,4-dioxane</td>
<td>53%</td>
</tr>
</tbody>
</table>

Figure 1.
Photographs and typical TEM images of the reaction mixtures under the conditions listed in entries 1, 2, 4, and 5 in Table 1 are shown in Figure 1. Judging from the appearance of the reaction mixtures, the Pd nanoclusters were well dispersed in the order of (B) < (C) < (D) which was consistent with the amount of Bu$_2$NOAc. The amount of precipitation of Pd black was observed in the opposite order, (B) > (C) > (D). The TEM images supported these observations. In Table 1, we show the result using the conditions which are considered typical reaction conditions for generation of Pd nanoclusters (Entry 1: Figure 1A). Indeed, the appearance of (A) was similar to that of (D), indicating the formation of nanoclusters. However, a considerable degree of aggregation of clusters was observed in the TEM images as well as in those of (B). Although both clusters in (C) and (D) were well dispersed judging from the TEM images, the concentration of clusters was much higher in (D), consistent with their appearance. These observations strongly suggest that the generation of Pd nanoclusters in appropriate conditions might be very important and that an excess amount of Bu$_2$NOAc could realize well-dispersed nanoclusters.

2. Synthetic Application of PVP-Stabilized Au Nanocluster Catalyst to Aerobic Oxidation of Alcohols in Aqueous Solution under Ambient Conditions

Gold nanoclusters (φ = 1.3 nm) stabilized by poly(N-vinyl-2-pyrrolidone) (Au:PVP) were found to show a high catalytic activity toward the aerobic oxidation of alcohols. Various kinds of primary and secondary alcohols were converted to the corresponding carboxylic acids and ketones, respectively, in basic aqueous media at 300–360 K under air.

3. Lewis Acid Character of Zero-Valent Gold Nanoclusters under Aerobic Conditions: Intramolecular Hydroalkoxylation of Alkenes

Gold nanoclusters stabilized by poly(N-vinyl-2-pyrrolidone) (Au:PVP NCs, φ = 1.3 nm) behave as Lewis acid catalyst in aqueous media under aerobic conditions, to promote the intramolecular hydroalkoxylation of unactivated alkenes. Molecular oxygen generates a reaction center having the Lewis acidic character on the surface of Au NCs in which constituent gold atoms are formally in zero-valence state.

Table 2. The role of molecular oxygen in the cyclization of 1a.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>conditions</th>
<th>yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au:PVP(1:3)</td>
<td>under air</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>Au:PVP(1:3)</td>
<td>under degassed conditions</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Au:PVP(9:5)</td>
<td>under air</td>
<td>0</td>
</tr>
</tbody>
</table>

A possible mechanism is shown in Scheme 1. The reaction is initiated by formation of key intermediate A, which possesses an electron-deficient site generated by adsorption of O$_2$ onto the surface of the Au NCs. A acts as a Lewis acid, activating both the alkoxide and alkene by adsorption onto the surface (B), and giving C by the insertion of an alkene into the O–Au bond. From C, neither β-elimination, O$_2$ insertion, nor protonation proceeds; only homolytic dissociation takes place, generating the radical intermediate D, which afforded 2 via hydrogen abstraction from DMF accompanied by the regeneration of free Au NCs. Judging from the decrease in the reaction rate in DMF-d$_7$, all the steps between A and D may be in equilibrium.

References

Awards
KAMIYA, Ikuyo; Best Poster Presentation Award, The 3rd Organic Chemistry Young Researchers’ Workshop, Nagoya University.
HIGASHIBAYASHI, Shuhei; Best Presentation Award, The 87th Spring Meeting, Chemical Society of Japan.
HIGASHIBAYASHI, Shuhei; Best Poster Presentation Award, Symposium on Molecular Chirality 2007.
HIGASHIBAYASHI, Shuhei; Best Poster Presentation Award, The 17th International Symposium on Olefin Metathesis.
Our research seeks the underlying molecular basis for the function of biological macromolecules. In particular, we are interested in the function of molecular machines that work in the cellular processes involving protein folding, transport and degradation, and of glycoproteins playing important roles in the humoral and cellular immune systems. By use of ultra-high field NMR spectroscopy, we aim to elucidate the three-dimensional structure, dynamics, and interactions of proteins and glycoconjugates at the atomic level. Here we report stable-isotope-assisted NMR studies of IgG-Fc glycoprotein, NEDD8 and protein disulfide isomerase.

1. Structural Comparison of Fucosylated and Nonfucosylated Fc Fragments of Human Immunoglobulin G1

Removal of the fucose residue from the oligosaccharides attached to Asn297 of human immunoglobulin G1 (IgG1) results in a significant enhancement of antibody-dependent cellular cytotoxicity (ADCC) via improved IgG1-binding to Fcγ receptor IIIa (FcγRIIIa). To provide a structural insight into the mechanisms of affinity enhancement, we determined the crystal structure of non-fucosylated Fc fragment and compared it with that of fucosylated Fc. The overall conformations of the fucosylated and non-fucosylated Fc fragments were similar except for hydration mode around Tyr296. Stable-isotope-assisted NMR analyses confirmed the similarity of the overall structures between fucosylated and non-fucosylated Fc fragments in solution. These data suggest that the glycoform-dependent ADCC enhancement is attributed to a subtle conformational alteration in a limited region of IgG1-Fc. Furthermore, the electron density maps revealed that the traces between Asp280 and Asn297 of our fucosylated and non-fucosylated Fc crystals were both different from those in previously reported isomorphous Fc crystals.
2. Direct Interactions between NEDD8 and Ubiquitin E2 Conjugating Enzymes Upregulate Cullin-Based E3 Ligase Activity

Although cullin-1 neddylation is crucial for the activation of SCF ubiquitin E3 ligases, the underlying mechanisms for NEDD8-mediated activation of SCF remain unclear. We demonstrated by NMR and mutational studies that NEDD8 binds the ubiquitin E2 (UBC4), but not NEDD8 E2 (UBC12). Our data imply that NEDD8 forms an active platform on the SCF complex for selective recruitment of ubiquitin-charged E2s in collaboration with RBX1, and thereby upregulates the E3 activity.

Figure 2. Identification of the binding sites on NEDD8 and UBC4.
(a,b) Mapping of the perturbed residues of NEDD8 (a) and UBC4 (b) upon binding to each other. Residues are highlighted in red on the crystal structures of NEDD8 and UBC4. Red gradient indicates the strength of the perturbation. Blue, residues involved in the interaction with the RING-finger domain in the crystal structure of c-Cbl (PDB 1FBV); gray, prolines; yellow, catalytic cysteine (C85).

3. NMR Assignments of the b’ and a’ Domains of Thermophilic Fungal Protein Disulfide Isomerase

Protein disulfide isomerase (PDI) is a folding assistant in the endoplasmic reticulum that catalyzes the formation, breakage and rearrangement of disulfide bonds of its substrate proteins. PDI comprises four structural domains, a, b, b’, a’ plus C-terminal extension. To gain insight into the functions of PDI, we initiated NMR structure determinations of the b’ and a’ domains of thermophilic fungal PDI expressed in E. coli. Backbone NH signals of these domains were completely assigned except for His367 in the a’ domain. In total, 87% (b’ domain) and 86% (a’ domain) of the observable proton signals were assigned. The secondary chemical shifts indicate that both domains assume thioredoxin folds.

Figure 3. 1H-15N HSQC spectra of 1 mM uniformly 13C/15N-labeled b’ domain (a) and a’ domain (b) of thermophilic fungal PDI in the presence of 10 mM [2H10]dithiothreitol. Backbone amide cross peaks are indicated with assignments. The residue numbering of intact PDI was applied for each domain.

References

Awards
UTSUMI, Maho; Physical Pharma Forum 2007 (The Pharmaceutical Society of Japan, Division of Physical Sciences) Award of Superior Excellence.
UTSUMI, Maho; 71st The Japanese Biochemical Society, Chubu Branch, Award for Young Scientists.

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya City University
Development of Multifunction Integrated Macromolecules for Molecular-Scale Electronics

Research Center for Molecular Scale Nanoscience
Division of Molecular Nanoscience

TANAKA, Shoji
Assistant Professor

The concept of molecular-scale electronics is now realized for individual components such as wire, diode, switch, and memory cell, but the fabrication of complete molecular-scale circuits remains challenging because of the difficulty of connecting molecular modules to one another. Monomolecular Integration technology, which integrates the wiring, transistors, and the required passive elements on a single macromolecule, has been proposed as a promising solution to this problem. In this project we have been developing the architecture of this novel class of macromolecules and the protocols for their purposive organization on metal or semiconductor substrate surfaces.

1. Multipurpose Building Blocks for over 10 nm Long π-Conjugated System

“Stepwise synthesis” is the most flexible tool to construct tailor-made π-conjugated macromolecules with well-defined functions for nanoscience and technology, however, the stepwise fabrication of over 10 nm long molecular skeleton is still a great challenge. As a solution to this problem, we have developed a series of versatile building blocks (1-2) as shown in Figure 1, which are active for typical Pd or Ni-catalyzed Ar–Ar coupling reactions. It is facile to access to a wide variety of 1–75 nm long π-conjugated macromolecules from the combination of these blocks and 1–10 nm long molecular modules so far reported (3–9). The synthetic examples are presented in Figure 2.

![Molecular structures of building blocks (1-9).](image)

**Figure 1.** Molecular structures of building blocks (1-9).

![Synthetic examples of precisely-defined α-oligothiophene derivatives.](image)

**Figure 2.** Synthetic examples of precisely-defined α-oligothiophene derivatives.
Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species, and extended π-conjugation decreases Coulombic repulsion. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form novel molecular assemblies. In this project, new electron acceptors, donors, and donor-acceptor compounds based on heterocycles such as 1,2,5-thiadiazole and 1,3-dithiole were synthesized and their physical properties, including those of the charge-transfer complexes or ion-radical salts, were investigated. Unique crystal structures were constructed by using weak intermolecular interactions such as hydrogen bonding or heteroatom contacts.

1. Synthesis and Electroluminescence Properties of fac-Tris(2-phenylpyridine)-iridium Derivatives Containing Hole-Accepting Moieties

For effective organic electroluminescent (EL) devices, we synthesized fac-tris(2-phenylpyridine)iridium [Ir(ppy)3] derivatives containing hole-trapping moieties, such as diphenylamine, carbazole, and phenoxazine. Their photoluminescent maxima were observed around the maximum of Ir(ppy)3. These values were slightly shifted depending on the hole-trapping moieties. EL devices using an Ir complex with diphenylamine exhibited high EL performance because 1,1-bis[4-(di-p-tolylamino)phenyl]cyclohexane was employed as a hole-transporting layer. The maximum external quantum efficiency was recorded as 12.2%, which is comparable to that observed in a device using Ir(ppy)3.

2. Synthesis and Photoluminescence Properties of BF2 Complexes with 1,3-Diketone Ligands

BF2 complexes with 1,3-diketone ligands were synthesized, and their optical and electrochemical properties were studied. The colors of the complexes varied depending on the structures of the 1,3-diketone ligands. The absorption and emission maxima of the complexes with 1,3-diaryl-1,3-diketone ligands were considerably red shifted as compared to those of the complexes with 1-aryl-3-trifluoromethyl-1,3-diketone ligands, suggesting an extended p-conjugation of the 1,3-diaryl-1,3-diketone moieties. The molar absorption coefficients and quantum yields of the complexes with 1,3-diaryl-1,3-diketone ligands were larger than those of the complexes with 1-aryl-3-trifluoromethyl-1,3-diketone ligands. Cyclic voltammetry measurements revealed that the reduction potentials of the BF2 complexes were higher than those of the free ligands. These complexes exhibited various emission colors in the solid states due to the intermolecular interactions.

References
Visiting Professors

Visiting Professor
BABA, Yoshinobu (from Nagoya University)

Biomolecular Imaging by Quantum Dot
We developed new materials, which are synthesized by conjugation of quantum dots (QD) and biomolecules, including DNA, enzyme, and lectin. The QD-biomolecule conjugated materials are applied to single molecule imaging of real-time interaction between DNA and enzyme, real-time imaging of single DNA molecule trafficking into a single cell, and differentiation of a single cancer cell by selective labeling of QD-lectin conjugate and imaging. These techniques are extremely useful to understand the mechanism of an enzymatic reaction at the single molecule level, to enhance the gene transfection efficiency in the gene therapy, and to develop novel technology for cancer diagnosis in the very early stage of cancer.

Visiting Associate Professor
HIGUCHI, Masayoshi (from National Institute for Materials Science)

Creation of Novel Organic-Metallic Hybrid Polymers and their Electrochromic Functions
Organic-metallic hybrid polymers are expected to have unique electrochemical, photochemical, magnetic, or catalytic properties based on strong interaction between organic modules and metal ions. Novel hybrid polymers are formed by complexation of iron(II) acetate with bis(terpyridyl)benzenes as an organic module. The polymers have specific colors based on the metal-to-ligand charge transfer and the color disappears by electrochemical oxidation of the polymer. The electrochromic properties are caused by electrochemical redox of metal ions in the polymers. Interestingly, a single film of the hybrid polymer including both iron(II) and cobalt(II) ions shows multi-color electrochromic change: red, blue, and colorless at 0, 0.6, and 1.0 V vs. Ag/Ag⁺, respectively. The hybrid polymers with excellent electrochromic functions will be applied to “electronic papers,” one of next generation displays.

Visiting Associate Professor
MAEDA, Hiromitsu (from Ritsumeikan University)

Pyrrole-Based Molecular Assemblies and Supramolecular Structures
Acyclic π-conjugated oligopyrrole derivatives, though less extensively studied so far, often potentially have even more advantages as anion receptors and metal coordination ligands than cyclic ones. This is due to the formation of versatile complexes and supramolecular assemblies, although they require conformation changes by guest binding. Of the linear oligopyrroles, oligomeric derivatives of dipyrrins bridged by π-conjugated spacers behave as building subunits and form coordination oligomers and discrete coordination nanorings. On the other hand, pyrrole oligomers with hydrogen bonding accepting site(s) have yielded unique morphologies as supramolecular assemblies and micro- and nanometer-scale structures by means of hydrogen bonding interactions. Furthermore, a new class of acyclic anion receptors, namely BF₂ complexes of dipyrrolyldiketones, have been shown to interact with anions by means of both pyrrole NH and bridging CH interactions. Ring inversion of pyrrole rings have been found to be essential to capture anions using these binding sites. Aryl-substitution of the receptors as π-extended derivatives has enabled the formation of assemblies such as supramolecular organogels that can be controlled by the addition of anions.