IV-E Development of Multi-Functional Molecular Systems

Since the molecules tend to retain their independence even in the solid state, the molecular systems can be considered to be suitable systems to construct multi-functional systems by assembling various molecular building blocks with different characters. We are trying to develop various new functional molecular materials such as single-component molecular conductors, photo-controllable magnetic conductors and dielectrically active porous molecular systems.

Recently, "dual-action organic conductors" such as magnetic molecular conductors have attracted a considerable interest. We have discovered unprecedented conductors exhibiting "superconductor → insulator transition," (λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$, BETS = bis(ethylendithio)tetraselenafulvalene) and the antiferromagnetic organic superconductors (κ-$(BETS)_2FeX_4$ X = Br, Cl) and the field-induced organic superconductor (λ-$(BETS)_2FeCl_4$, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$, κ-$(BETS)_2FeBr_4$). However, except these systems, there have been only a few systems showing clear synergetic actions between conduction and magnetic parts. Very recently, we have discovered "constant resistivity state (CRS)" below T_c in the system exhibiting superconductor → insulator transition at zero magnetic field (λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$, $x \approx 0.35$).

We have recently obtained a new κ-type BETS conductor with weakly ferromagnetic (canted antiferromagnetic) metal state and new molecular conductors exhibiting spin-crossover transition coupled with resistivity hysteresis and LIESST (Light-Induced Excited Spin State Trapping).

By utilizing weak host-guest interaction and polarizability of guest molecules, we have recently obtained new porous molecular systems with high-temperature polarizable and low-temperature unpolarizable states.

Besides these systems, we have recently developed the single-component molecular metals based on the transition metal with extended-TTF ligands. $Au(tmdt)_2$, which is isostructural to the first single-component molecular metal $Ni(tmdt)_2$ is the first molecular conductor where π conduction electron and antiferromagnetic order coexist above 100 K.

IV-E-1 Dielectric Properties of Porous Molecular Crystals Containing Polar Molecules

CUI, HengBo; TAKAHASHI, Kazuyuki; OKANO, Yoshinori; KOBAYASHI, Hayao; WANG, Zheming[1]; KOBAYASHI, Akiko[2]
([1]Peiking Univ.; [2]Univ. Tokyo)

[*Angew. Chem., Int. Ed.* **117**, 6666–6670 (2005)]

Recently molecular materials with porous coordination frameworks have aroused a considerable interest because of their various attractive properties arising from the synergy of the host lattice and guest molecules such as guest-switched spin crossover transition, gas sorption, molecular storage, and magnetic solvent sensor. However, to our knowledge, the reports on the dielectric properties of porous molecular materials seem to be very rare, though ferroelectric properties of molecular materials have recently attracted an increasing interest. We have recently obtained molecular systems exhibiting unprecedented dielectric properties by combining a porous ferrimagnetic molecular crystal, $[Mn(HCOO)_2]$ and polar guest molecules, H_2O and CH_3OH. $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ showed characteristic temperature-dependent dielectric constant for *E*//*a*, *b* but featureless behavior for *E*//*c*. It is very interesting that molecules confined in the narrow one-dimensional channel show a fairly sharp "transition-*like* behavior" because in general the system with strong one-dimensional nature hardly exhibits the phase transition.

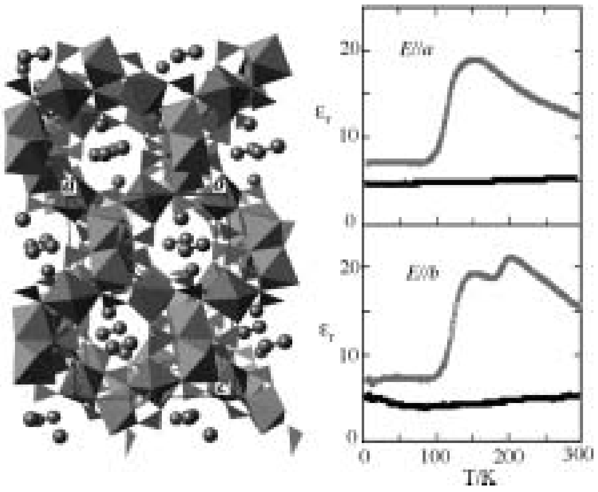

Figure 1. Crystal structure and dielectric constants of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$. The spheres in the channel are C and O atoms of the guest molecules. The black lines are the dielectric constants of the crystal without guest molecules.

IV-E-2 Giant Dielectric Constants of Porous Molecular Crystal with Guest Water Cluster

CUI, HengBo; LONG, La-Sheng; TAKAHASHI, Kazuyuki; OKANO, Yoshinori; KOBAYASHI, Hayao; KOBAYASHI, J. Akiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

Except for the ferroelectric (or anti-ferroelectric) materials, the heavy metal compounds such as $PbCl_2$ (ε_r = 33.5 (20 °C)), PbO (ε_r = 25.9 (20 °C)), and TlBr (ε_r = 30.3 (25 °C)) are known to be typical materials with large dielectric constants. It will be desirable to find a way to develop such highly polarizable materials without pernicious heavy metal atoms, especially molecular materials with dielectric properties switchable between high and low dielectric states. Since most molecules have no positional freedom in the crystalline state, the dielectric constants of molecular crystals are usually very small and almost temperature independent. On the other hand, there exist polar molecules with fairly large polarizabilities in the liquid state. Needless to say, the water is the exceptional system with very large dielectric constant, which becomes as high as 100 just above the freezing point (supercooled state). This value is about 40 times lager than that of benzene. We have examined the dielectric properties of water cluster formed in the channel of porous molecular crystal, $Cu_3La_2(NH(CH_2COO)_2)_6$ and found the extremely large enhancement of the dielectric constants around room temperature. To our surprise, the dielectric constant seems to exceed 200 at high temperature.

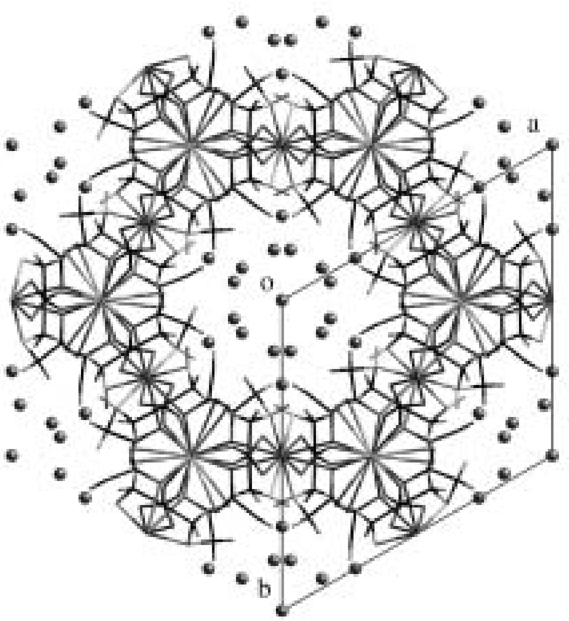

Figure 1. Crystal structure of $Cu_3La_2(NH(CH_2COO)_2)_6$ viewed along the *c* axis of the hexagonal porous crystal. The spheres in the channel are O atoms of water molecules forming one-dimensional water cluster.

IV-E-3 Synthesis and Characterization of a Porous Magnetic Diamond Framework Compound, $Co_3(HCOO)_6$, and Its N_2 Sorption Characteristic

WANG, Zheming[1]; ZHANG, Bin[2]; KURMOO, Mohamedally[3]; GREEN, Mark, A.[4]; OTSUKA, Takeo; KOBAYASHI, Hayao
([1]Peiking Univ.; [2]IC, CAS; [3]Univ. Louis Pasteur; [4]Royal Inst.)

[*Inorg. Chem.* **44**, 1230–1237 (2005)]

$[Co_3(HCOO)_6](CH_3OH)(H_2O)$, the iso-structural analogue of the porous magnet of coordination framework $[Mn_3(HCOO)_6](CH_3OH)(H_2O)$, was prepared by slow diffusion technique and characterized by X-ray and neutron diffraction methods, IR, TGA-DSC and BET and its magnetic properties measured. It crystallizes in the monoclinic system, space group $P2_1/c$, $a = 11.247(2)$, $b = 9.812(2)$, $c = 18.103(3)$ Å, $\beta = 127.245(3)°$, $V = 1590.3(5)$ Å^3, $Z = 4$, $R_1 = 0.0356$ (determined from single crystal data at 87 K) and it possesses a unit cell volume that is 10% smaller than $[Mn_3(HCOO)_6](CH_3OH)(H_2O)$ due to the smaller radius of Co^{2+} ion. The cell parameters, obtained from neutron powder data at 2 K, are $a = 11.309(2)$, $b = 9.869(1)$, $c = 18.201(3)$ Å, $\beta = 127.244(8)°$, $V = 1617.3(5)$ Å^3. The pore volume also reduces from 33% to 29% by replacing Mn by Co. The material exhibits an interesting diamond framework based on Co-centered $CoCo_4$ tetrahedral nodes, in which all metal ions have octahedral coordination geometry and all HCOO groups link the metal ions in *syn-syn*/*anti* modes. It displays high thermal stability up to 270 °C. The compound easily loses the guest molecules without loss of crystallinity and it partly re-absorbs water from the atmosphere. Significant N_2 sorption was observed for the desolvated framework suggesting the material possesses permanent porosity. The magnetic properties show a tendency to a 3D long-range magnetic ordering, probably antiferromagnetic with a spin canting arrangement below 2 K.

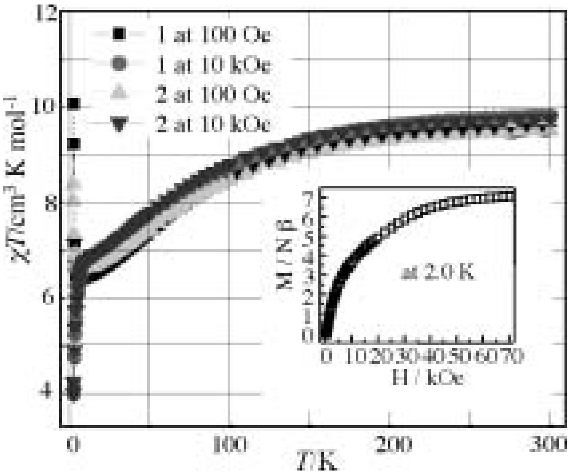

Figure 1. The temperature dependence of the magnetic susceptibility of **1** ($[Co_3(HCOO)_6](CH_3OH)(H_2O)$) and desolvated form **2** ($[Co_3(HCOO)_6]$) in applied field of 100 Oe and 10 kOe. Inset is the isothermal field dependent magnetization at 2.0 K for **1**. Magnetization at 70 kOe is 7.10 Nβ.

IV-E-4 Superconductivity and Voltex Phases in the Two-Dimensional Organic Conductor λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x = 0.45$)

UJI, Shinya[1]; TERASHIMA, Taichi[1]; YASUZUKA, Shuma[1]; TOKUMOTO, Madoka[2]; TANAKA, Hisashi[2]; KOBAYASHI, Akiko[3]; KOBAYASHI, Hayao
([1]Natl. Inst. Mater. Sci.; [2]AIST; [3]Univ. Tokyo)

[*Phys. Rev. B* **71**, 104525 (7 pages) (2005)]

Resistance measurements have been performed in two-dimensional organic conductor λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x = 0.45$) to investigate the superconducting properties. In magnetic field parallel to the layers, the superconducting (S) phase is stabilized in a wide magnetic field range, which is qualitatively understood by Jaccarino-Peter compensation mechanism. Depending on the internal field produced by the Fe 3d moments, three vortex phases in the S phase appear with increasing field. The superconducting transitions show characteristic field dependence, which is correlated to the voltex phases. In field perpendicular to the layers, the S phase appear only near the antiferromagnetic phase. The results for $x = 0.45$ are also compared with those for the isostructural nonmagnetic salt $x = 0$.

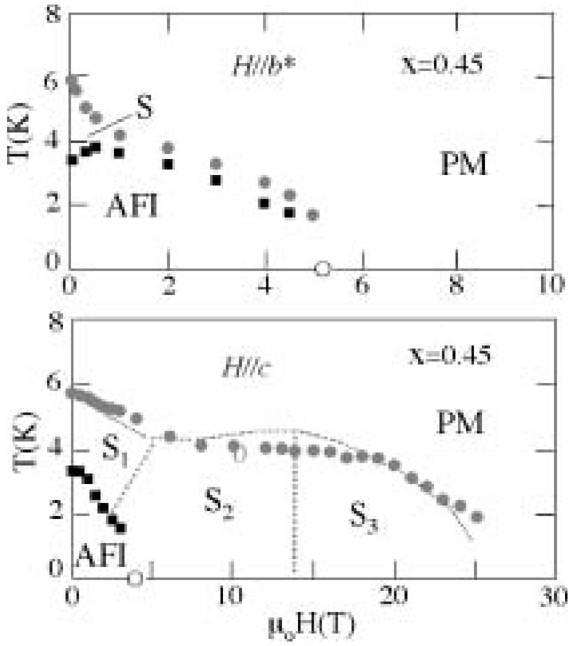

Figure 1. *T-H* phase diagram of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x = 0.45$) for *H*//*b** and *H*//*c*.

IV-E-5 Constant Resistivity State in the Field-Induced Organic Superconductor, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$

CUI, HengBo; TAKAHASHI, Kazuyuki; KOBAYASHI, Hayao; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

In 2001, Uji *et al.* have discovered the field-induced superconductivity (FISC) in two-demensional organic conductor, λ-$(BETS)_2FeCl_4$ with π-d coupled antiferromagnetic insulationg ground state below 8.5 K. Balicas *et al.* have found the FISC to be most stabilized around 33 T. Similar FISC states were also observed in a series of mixed-anion systems, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$. We have also reported the unprecedented resistivity switching between insulating, superconducting and metallic states in λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.4$). We have recently reexamined the resistivity of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.4$) up to 15 T at the temperature range down to 1 K. The crystal with $x = 0.37$ exhibited a superconducting transition at 4.6 K and superconductor-insulator transition around 2.3 K at zero magnetic field. But the superconducting state was changed to "the temperature- and field-independent resistivity state" with increasing magnetic field applied parallel to *ac* conduction plane. This constant resistivity state (CRS) was also observed in the crystals with $x \approx 0.39$, 0.37 (other crystal) and 0.30. But three crystals with *x*-value higher than 0.43 did not show CRS. The ratio of the resistivity of CRS (ρ_c) and the resistivity just above the superconducting transition (ρ_m), that is, ρ_m/ρ_c is linearly dependent on *x*. To our knowledge, λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x \approx 0.35$) is the first superconductor showing CRS.

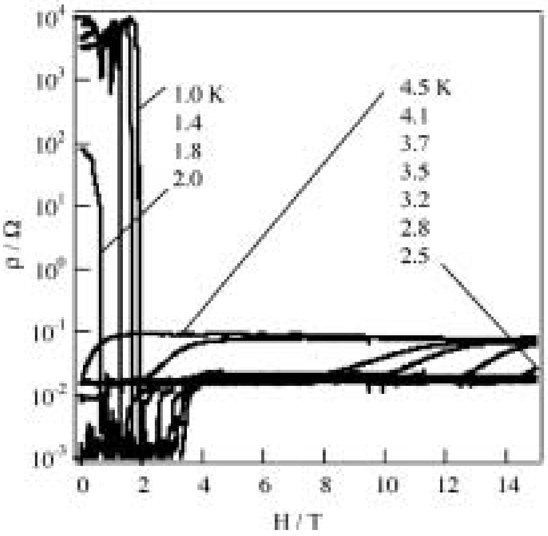

Figure 1. Low-temperature resistivity behavior of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x = 0.37$) under the magnetic field applied parallel to the *ac* conduction plane.

IV-E-6 (Tetrathiafulvalene)$[Fe^{III}(C_2O_4)Cl_2]$: An Organic-Inorganic Hybrid Exhibiting Canted Antiferromagnetism

ZHANG, Bin[1]; WANG, Zheming[2]; FUJIWARA, Hideki; KOBAYASHI, Hayao; KURMOO, Mohamedally[3]; INOUE, Katsuya[4]; MORI, Takehiko[5]; GAO, Song[2]; ZHANG, Yan[2]; ZHU, Daoben[1]
([1]IC CAS; [2]Peking Univ.; [3]Univ. Louis Pasteur; [4]Hiroshima Univ.; [5]TIT)

[*Adv. Mater.* **17**, 1988–1991 (2005)]

Over the past twenty years, the field of molecular materials has been decorated with a wide range of interesting compounds, based either on purely organic or inorganic molecules and organic-inorganic hybrids, exhibiting diverse electrical, magnetic and optical properties. While several electrical and magnetic ground states have been established and very well documented in the literature, the possibility of introducing novel properties with organic-inorganic hybrids remains a big challenge to date. The key feature of these hybrids is the interaction through space or through weak supramolecular contacts. While this can be quite strong between nearest neighbours having strong π-π overlap, especially those containing chalcogenides, the interactions between π-d are usually quite weak. To enhance the d-d super-exchange within the inorganic moiety, the use of 2D-polymeric anions containing oxalato bridges has been very successful to produce magnetic systems. On the other hand, it appears that chalogen-halogen contacts may be a good source for the π-d coupling in compounds containing isolated MX_4 anions. The present work is an attempt to mixed oxalate and halogen at the metal site of the anions to introduce d-d superexchange and π-d interaction in charge-transfer complex. Recently, two coordination compounds with $C_2O_4^{2-}$ and Cl^- have been reported and show ferromagnetic transition at 40 K and 70 K. We, therefore, present the first example of a TTF complex from a novel polymeric one-dimensional counter anion of iron that contains terminal chlorine and oxalate bridges. A new molecular-hybrid (TTF)[$Fe^{III}(C_2O_4)Cl_2$] displaying canted antiferromagnetism has been prepared and characterized. It is the first salt of TTF or its derivatives to contain a one-dimensional magnetic coordination polymer as anion. Due to π-d interaction, through short S···Cl, S···O contacts, a 3D-Néel state is stabilized at a rather high temperature of 20 K. It is a semiconductor with band gap of 1 eV.

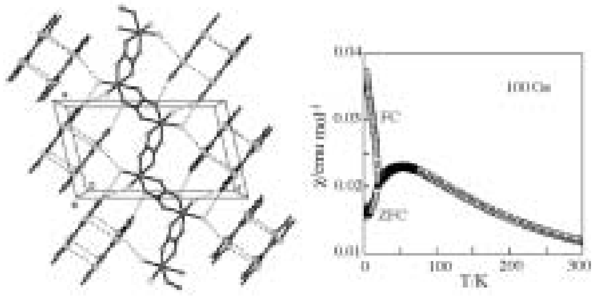

Figure 1. Crystal structure and zero-field cooling (ZFC) and field cooling (FC) M/H versus temperature curves of [TTF][Fe (C_2O_4)Cl_2].

IV-E-7 Development of Single-Component Molecular Metals

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([1]Univ. Tokyo)

[*J. Mater. Chem.* **15**, 3449–3451 (2005)]

Our recent studies on single-component molecular metals was introduced. The realization of molecular metal based on single-component molecules had been one of the long-standing challenges in the chemistry of molecular conductors since the discovery of semiconducting properties of molecular crystals around 1950. In contrast to typical inorganic metals composed of single elements, such as Na and Au, all of the molecular metals developed until 2000 are composed of more than two chemical species. However, we have proved that the metal electrons can be generated automatically by the self-assembling of the same kind of molecules. The novel nickel complex with the extended-TTF dithiolate ligand [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate) is the first three-dimensional single-component molecular metal with metallic state down to 0.6 K. The isostructural molecular conductor [Au(tmdt)$_2$] exhibited an antiferromagnetic transition around 110 K without loss of its high conductivity, which is extraordinarily high compared with the magnetic transition temperatures of the other molecular conductors ever developed. A brief description was also presented on "single-component alloy system" [Ni_xAu_{1-x}(tmdt)$_2$].

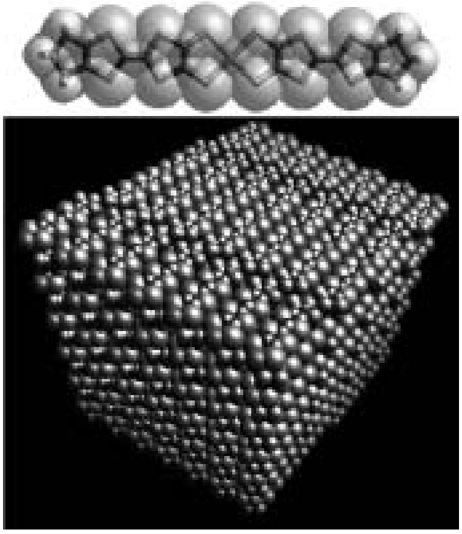


Figure 1. The molecular packing in single-component molecular metal [Au(tmdt)$_2$] which is the first molecular system exhibiting the coexistence of π conduction electrons and magnetic order above 100 K.

IV-E-8 Crystal Structures and Physical Properties of Single-Component Molecular Conductors Consisting of Nickel and Gold Complexes with Bis(trifluoromethyl)-tetrathiafulvalenedithiolate Ligands

SASA, Masaaki[1]; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]; ISHIBASHI, Shoji[2]; TERAKURA, Kiyoyuki[4]; OKANO, Yoshinori; FUJIWARA, Hideki; KOBAYASHI, Hayao
([1]Univ Tokyo; [2]AIST; [3]Hokkaiudo Univ.)

[*J. Mater. Chem.* **15**, 155–163 (2005)]

The neutral nickel and gold complexes with bis(trifluoromethyl)tetrathiafulvalenedithiolate ligands, [M(hfdt)$_2$] (M = Ni, Au) were prepared in order to examine the possibility of the development of single-component molecular conductors soluble to organic solvents. However, in contrast to the previous report, the crystals did not show any solubility to usual organic solvents. On the other hand, the crystal structure analysis showed unique two-dimensional layered structures, despite that the single-component molecular conductors usually tend to take compact three-dimensional molecular arrangement. Each layer is separated by the terminal CF_3 groups to form the "CF_3 bi-layer structure." The shortest intermolecular F···F distance (3.018 Å for [Ni(hfdt)$_2$] and 2.862 Å for [Au(hfdt)$_2$]) is significantly longer than the van der Waals F···F distance (2.70 Å) and the distribution of the frontier electrons is almost zero around the CF_3 bi-layer region. This is due to the strong F···F segregation effect, which will provide a useful way to control the molecular aggregation in the single-component molecular conductors. The extended-Hückel tight-binding band structure calculations and the *ab-initio* local density approximation (LDA) band structure calculations were made for [Ni(hfdt)$_2$], which can explain the semiconducting and non-magnetic properties of the system. The extended-Hückel tight-binding band structure calculations were also made for [Au(hfdt)$_2$]. The calculated band structure is consistent with weakly semiconducting and almost non-magnetic properties of [Au(hfdt)$_2$].

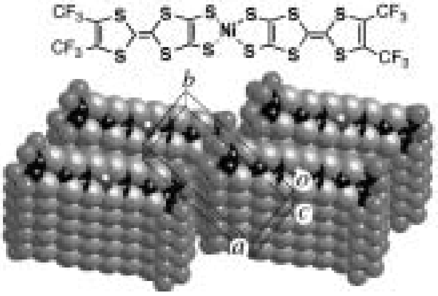


Figure 1. The molecular packing of [Ni(hfdt)$_2$].

IV-E-9 *Ab Initio* Electronic Structure Calculation of Single-Component Molecular Conductor Au(tmdt)$_2$ (Tmdt = Trimethylene-tetrathiafulvalenedithiolate)

ISHIBASHI, Shoji[1]; TANAKA, Hisashi[1]; TOKUMOTO, Madoka[1]; KOBAYASHI, Akiko[2]; KOBAYASHI, Hayao; TERAKURA, Kiyoyuki[3]
([1]AIST.; [2]Univ. Tokyo; [3]Hokkaido Univ.)

[*J. Phys. Soc. Jpn.* **74**, 843–846 (2005)]

We have investigated the electronic structure of Au(tmdt)$_2$ (tmdt = trimethylenetetrathiafulvalenedithiolate), which is a single-component conductor showing a magnetic phase transition around 100 K, by *ab initio* plane-wave pseudopotential calculations. A single band crosses the Fermi level. This band and the next band below are a result of the strongly hybridization between the two neighbouring molecular levels near the Fermi level (SOMO and HOMO-1) and the system is more properly described as quater-filled rather than half-filled in the strong correlation regime. The Fermi surface has corrugated-sheet-like parts nearly parallel to each other. Interband generalized susceptibility suggests the presence of a nesting vector $a^*/2$. Spin-polarized calculation on the doubled unit cell along the *a* axis results in an antiferromagnetic order. The nesting is not perfect and Fermi-surface pockets remain in the magnetic phase. The implications of the present calculations with regard to experimental results are discussed.

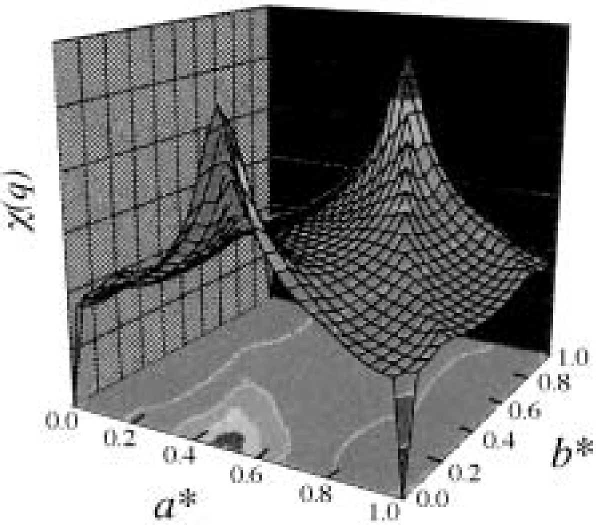


Figure 1. The interband generalized susceptibility of [Au(tmdt)$_2$].

IV-E-10 The Light-Induced Excited Spin State Trapping Effect on Ni(dmit)$_2$ Salt with an Fe(III) Spin-Crossover Cation: [Fe(qsal)$_2$][Ni(dmit)$_2$]·2CH$_3$CN

TAKAHASHI, Kazuyuki; CUI, HengBo; KOBAYASHI, Hayao; EINAGA, Yasuaki[1]; SATO, Osamu[2]
([1]Keio Univ.; [2]Kyushu Univ.)

[*Chem. Lett.* **34**, 1240–1241 (2005)]

Recently spin-crossover (SC) complexes have aroused a considerable attention in molecular materials scientists. Since the spin conversion between the low-spin (LS) and high-spin (HS) states can be induced by external perturbations such as temperature, pressure, and light, the introduction of the SC component is expected to give a switching ability to a molecular solid. The number of the reports of the LIESST effect on Fe(III) complexes is very rare. Therefore, realization of the LIESST in an Fe(III) SC component may be the first step to develop various photo-switchable molecular materials. We have focused our attention on the Fe(III) spin crossover complex, [Fe(qsal)$_2$][Ni(dmit)$_2$]·2CH$_3$CN [qsalH = *N*-(8-quinolyl)-salicylaldimine, dmit = 4,5-dithiolato-1,3-dithiole-2-thione]. Temperature dependence of $\chi_M T$ in [Fe(qsal)$_2$][Ni(dmit)$_2$]·2CH$_3$CN showed a cooperative spin transition (Figure 1a). On illumination with a diode laser (830 nm) at 5 K (Figure 1b), the magnetization of the complex gradually increased, indicating that the light-induced metastable HS state could be trapped. On heating after saturation of magnetization with light illumination, the relaxation from the metastable HS to the ground LS states was observed at around 40 K (T_{LIESST} = 46 K). The magnetization curve of the annealing sample followed that before illumination. This indicates that the change by light is completely reversible. Furthermore, the decease in magnetization by illuminating the metastble HS state with a diode laser (980 nm) suggests that the magnetism of the 1:1 complex can be controlled by light irradiation.

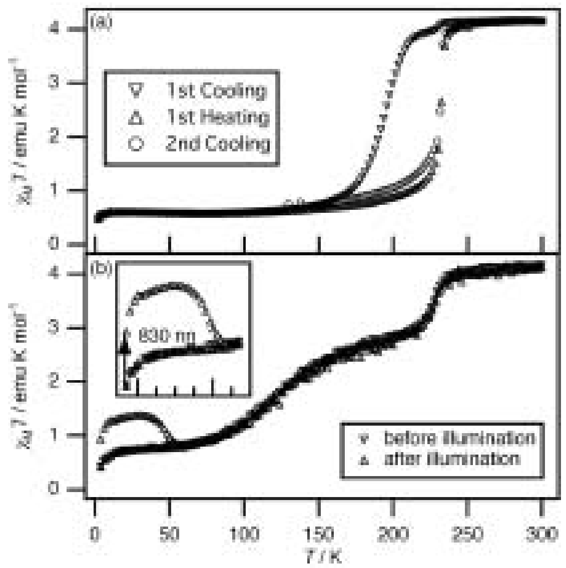


Figure 1. $\chi_M T$ *vs.* T plot of $[Fe(qsal)_2][Ni(dmit)_2]\cdot 2CH_3CN$: (a) Bulk sample, (b) the LIESST experiment of ground sample with an adhesive tape by using a diode laser (830 nm).

IV-E-11 Synergic Behavior between Spin and Conducting Property in $Ni(dmit)_2$ Salt with Fe(III) Spin-Crossover Cation

TAKAHASHI, Kazuyuki; CUI, HengBo; OKANO, Yoshinori; KOBAYASHI, Hayao; EINAGA, Yasuaki[1]; SATO, Osamu[2]
([1]Keio Univ.; [2]Kyushu Univ.)

Recently considerable interest has been attracted to the development of novel molecular-based conducting materials exhibiting the synergy between conductivity and magnetism. We have attempted to explore the possibility of “dynamic” and “reversible” control of electrical conducting state by external stimuli. It is well known that the conducting properties of molecular conductors are changed greatly by the small modification of their crystal structures. Since the spin transition between the low-spin (LS) and the high-spin (HS) states accompanies a remarkable structural change in coordination bond length and geometry, the electrical conductivity of conducting spin-crossover (SC) complex can be expected to be “dynamically” and “reversibly” controlled by a structural change involving the spin conversion. The conducting complex was prepared by electrocrystallization of $[Fe(qsal)_2][Ni(dmit)_2]\cdot 2CH_3CN$ in acetonitrile. The crystal structure analyses revealed that the ratio of $Fe(qsal)_2$ and $Ni(dmit)_2$ proved to be 1 to 3. $Ni(dmit)_2$ anions formed one-dimensional columns along the *b* axis and were arranged in a herringbone manner along the side-by-side direction. Temperature dependence of magnetic moment and electrical resistivity of the 1:3 complex were shown in Figure 1. As a result of the cooling and heating processes, the magnetic behavior showed a narrow hysteresis loop with width of 8 K between 90 and 120 K. The change in $\chi_M T$ value, which was larger than that estimated for the antiferromagnetic coupling of spins of $Ni(dmit)_2$, seemed to derive from the spin transition. The crystal showed a semiconducting behavior (σ_{RT} = 0.1 S cm^{-1}; E_a = 0.2 eV). Interestingly, a hysteresis loop of resistivity was observed in the temperature range of 90–120 K, which corresponds to the temperature range of the hysteresis of magnetic behavior. The relatively low resistivity in heating process is consistent with the compact molecular packing usually observed in the LS state. To our knowledge, this is the first observation of the resistivity anormaly coupled with spin transition.

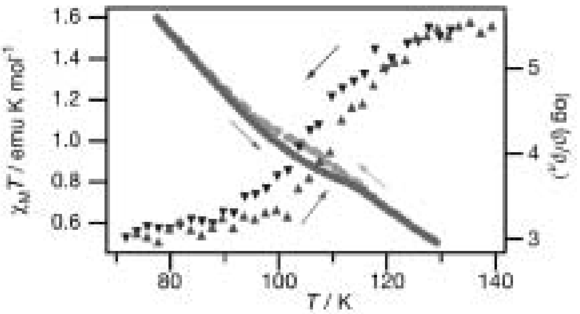


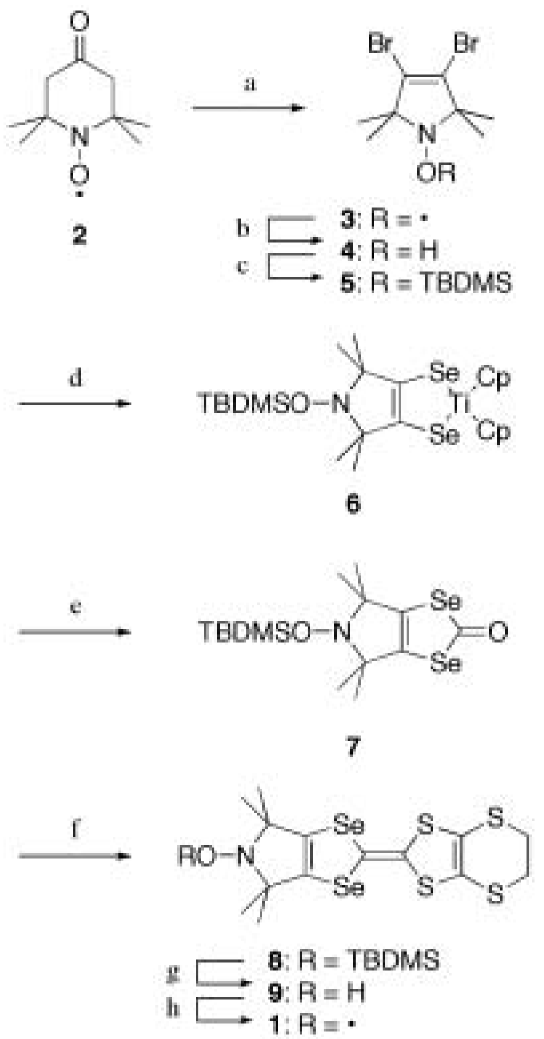
Figure 1. $\chi_M T$ *vs.* T plot (triangle, scale: left) and $\log(\rho/\rho_{rt})$ *vs.* T plot (circle, scale: right) of the 1:3 complex at the temperature range between 70 and 140 K.

IV-E-12 Synthesis and Molecular Structure of a Novel PROXYL-Fused π-Electron Donor, PROXYL-ET-STF

TAKAHASHI, Kazuyuki; KOBAYASHI, Hayao

The development of novel magneto-electronic properties based on the interplay between conducting electrons and localized spins has aroused a great attention in molecular materials. To realize the coupling between conducting π-electrons and the spins on the stable organic radical in purely organic systems is one of the targets in this field. Despite several reports of syntheses and physical properties of π-electron donor or acceptor molecules with stable organic radicals and their conducting complexes, the number of metallic complexes based on these donors is rare. Probably since the organic stable radicals are usually bulky, it is difficult to construct the conduction path based on the overlap of π-donor parts. In order to decrease a hindrance to the formation of conduction path, we have designed and synthesized PROXYL-fused π-electron donor, PROXYL-ET-STF.

Synthesis of PROXYL-ET-STF is summarized in Scheme 1. The donor was isolated as fine needles and stable in air. X-ray structural analysis was performed on a single crystal of the neutral donor molecule. The molecular structure of PROXYL-ET-STF was a little bent, but the radical part was almost parallel to the 1,3-diselenol ring. Donor molecules were stacked in a head-to-tail manner to form one-dimensional columns. These observations suggest that PROXYL-ET-STF is a promising donor to afford conducting complexes with a stable organic radical. Physicochemical properties and preparation of the conducting complexes of this donor are now in progress.



Scheme 1. Synthesis of PROXYL-ET.
(a) NaOBr; (b) Diphenylhydrazine; (c) TBDMSOTf; (d) t-BuLi, Se, Cp_2TiCl_2, THF; (e) triphosgene, THF; (f) 4,5-ethylenedithio-1,3-dithol-2-thione, $P(OMe)_3$, toluene; (g) TBAoF, THF; (h) Ag_2O, THF.