IV-C Development of Multi-Functional Molecular Systems

The molecules are usually assembled by weak intermolecular interactions and tend to retain their isolated electronic states even in the crystalline state. Consequently, the multi-functional systems can be constructed by assembling various molecules with different characters. Thus, the molecules are regarded as suitable building blocks for the bottom-up construction of the systems where various functions coexist.

Recently, “dual-action system” such as magnetic molecular conductors has attracted a considerable interest. We have discovered many molecular conducting systems exhibiting various dual-active electromagnetic properties such as the organic superconductor exhibiting a “superconductor → insulator transition” at low temperature (λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ ($0.35 < x < 0.5$) (1997)), the first antiferromagnetic organic superconductor exhibiting “antiferromagnetic superconductor → ferromagnetic metal transition” associated with meta-magnetic transition of magnetic anion layers around 1.6 T (κ-(BETS)$_2$FeBr$_4$ (1999–2002)), the first field-induced organic superconductor (λ-(BETS)$_2$FeCl$_4$ (2001)). The intriguing field-induced superconductivity was also observed in λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ and κ-(BETS)$_2$FeBr$_4$. Except these conductors, any hitherto-developed organic conductors scarcely show clear interplay between magnetic building blocks and conducting parts.

We have tried to prepare new TTF-type π donors with stable organic radical parts with the aim of developing new type of magnetic conductors. We are now trying to prepare new molecular conductors exhibiting spin-crossover behavior.

The large designability is another important feature of the molecular system. We have recently developed the single-component molecular metal based on the transition metal dithiolate complex with extended-TTF ligands. The fundamental idea of the molecular design of the single-component molecular metals is based on the development of multi-chalcogen π molecule with TTF-like skeleton and very small HOMO-LUMO gap. Recently the existence of the Fermi surface in the first single-component molecular metal, [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalene) was confirmed by the observation of de Haas-van Alphen oscillation at high magnetic field.

The host-guest molecular system is a good example showing the molecular assembly by weak interactions. By utilizing weak host-guest interaction of porous materials, we are now trying to obtain new functional molecular systems.

IV-C-1 Organic Metals and Superconductors Based on BETS (BETS = Bis(ethylenedithio) tetraselenafulvalene)

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

[*Chem. Rev.* **104**, 5265 (2004)]

Since the discovery of the first organic superconductors (TMTSF)$_2$X (TMTSF = tetramethyltetraselenafulvalene; X = PF$_6$, ClO$_4$, ...) about a quarter century ago, an extremely large progress has been achieved in the field of physics and chemistry of molecular conductors. When the metallic states of TMTSF conductors were found to be stable down to about 10 K, many chemists noticed the possibility of the existence of two-dimensional (2D) organic conductors with intermolecular 2D networks of peripheral chalcogen atoms of π molecules. In fact, by the observations of Shubnikov-de Haas (SdH) and de Haas-van Alphen (dHvA) oscillations in the subsequently developed BEDT-TTF (= bis(ethylenedithio)tetrathiafulvalene) superconductors with β- and κ-type molecular arrangements, the existence of ideally 2D organic π metal systems with stable metallic states was proved. However, in the midst of these rapid progress, an extraordinarily large impact was brought about by the discovery of high temperature cupper oxide superconductors. It became very serious for the chemists in this field to find new ways by making the best use of the merit of molecule-based systems. More than a decade ago, we started to try to prepare magnetic organic conductors based on BETS molecules and tetrahalide Fe^{3+} ions. Fortunately, the π-*d* interaction in BETS conductors was discovered to be fairly strong and we could obtain very unique magnetic organic superconductors. In this review, we have summarized our recent works on magnetic organic superconductors based on BETS and magnetic and non-magnetic anions MX$_4^-$ (M = Fe, Ga; X = Cl, Br). Many topics such as field-induced superconductivity of λ-(BETS)$_2$FeCl$_4$, λ-(BETS)$_2$FeBr$_x$Cl$_{4-x}$ and κ-(BETS)$_2$FeBr$_4$, superconductor-to-insulator transition of λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$, antiferromagnetic organic superconductors, κ-(BETS)$_2$FeX$_4$ and switching behavior of electrical properties of magnetic organic superconductors are described.

IV-C-2 Single-Component Molecular Metals with Extended-TTF Dithiolate Ligands

KOBAYASHI, Akiko[1]**; FUJIWARA, Emiko**[1]**; KOBAYASHI, Hayao**
([1]Univ. Tokyo)

[*Chem. Rev.* **104**, 5243 (2004)]

It has been believed for a long time that the formation of electronic bands and the generation of charge carriers by the intermolecular charge transfer between the molecules constituting the band (designated by A) and other chemical species (designated by B) are two essential requirements to design molecular metals. In some cases, both molecules A and B form conduction bands where the electron and the hole carriers are generated on both A and B molecules. This is the reason why the design of metals composed of single-component molecules is difficult. However, we have recently noticed the possibility of carrier generation even in the single-component molecular crystal and prepared the first example of the crystal of a neutral transition metal complex with extended-TTF ligands, [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate) exhibiting metallic behavior down to very low temperature. More recently, a direct experimental evidence for the Fermi surface in [Ni(tmdt)$_2$] was obtained by detecting the quantum oscillations in magnetization at very high magnetic field (or de Haas-van Alphen (dHvA) effect). Torque magnetometry measurements of single crystals of [Ni(tmdt)$_2$] using a sensitive microcantilever at low temperature revealed dHvA oscillatory signals for all directions of magnetic field, showing the presence of three-dimensional (3D) electron and hole Fermi surfaces. Thus the existence of single-component molecular metal has been definitely confirmed.

This review describes the frontier orbital engineering for the design of single-component molecular metal and present some examples of recently developed single-component molecular conductors with various extended-TTF ligands such as [Ni(dmdt)$_2$], [Au(tmdt)$_2$] exhibiting magnetic transition around 85 K without loss of its high conductivity and [Co(dt)$_2$] with unique dimeric conformation and high conductivity down to 0.6 K. Experimental evidences showing the validity of our idea on the molecular design of single-component molecular metals are also presented.

IV-C-3 Observation of Three-Dimensional Fermi Surfaces of Single-Component Molecular Metal, Ni(tmdt)$_2$

TANAKA, Hisashi[1]; TOKUMOTO, Madoka[1]; ISHIBASHI, Shouji[1]; GRAF, D.[2]; CHOI, E. S.[2]; BROOKS, J. S.[2]; YASUZUKA, Shyuma[3]; OKANO, Yoshinori; KOBAYASHI, Hayao; KOBAYASHI, Akiko[4]
([1]AIST; [2]Florida State Univ.; [3]Natl. Inst. Mater. Sci.; [4]Univ. Tokyo)

[*J. Am. Chem. Soc.* **126**, 10518 (2004)]

We have recently reported that the metal electrons can be spontaneously produced by self-assembling of the well-designed π complex molecules with TTF-like ligands and very small HOMO-LUMO gap. We have also reported that the first single-component molecular metal, [Ni(tmdt)$_2$] and analogous compounds show the very broad low-energy electronic excitation spectra in IR region, which undoubtedly shows the validity of our molecular design of the single-component molecular metals. However, considering that there has been no example of the molecular metal composed of single molecules before our discovery, unambiguous evidence will be desired to establish completely the existence of the metal electrons in the single-component molecular crystal. One of the most rigorous evidence may be the observation of de Haas-van Alphen oscillation. Since the crystals of [Ni(tmdt)$_2$] were very small, a new micro-cantilever technique of magnetization measurement was adopted using the hybrid magnet at the National High Magnetic Field Laboratory at Florida. The quantum oscillation observed for all the direction of the magnetic field suggested the existence of the three-dimensional Fermi surfaces.

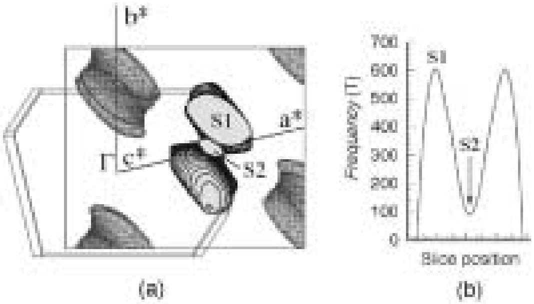


Figure 1. (a) Hole (black) and electron (gray) Fermi surfaces and the first Brillouin zone of [Ni(tmdt)$_2$]. The extremal hole orbits for the field applied parallel to *c** axis are also shown. (b) S1 and S2 are the corresponding extremal cross section sizes calculated by slicing Fermi surfaces.

IV-C-4 Syntheses, Structures and Physical Properties of New Nickel Bis(dithiolene) Complexes Containing TTF (Tetrathiafulvalene) Units

FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]; FUJIWARA, Hideki; KOBAYASHI, Hayao
([1]Univ. Tokyo)

[*Inorg. Chem.* **43**, 1122 (2004)]

To contribute to the development of single-component molecular metals, several nickel complexes with cyclohexeno-condensed or ethylenedioxy-substituted TTF (tetrathiafulvalene) dithiolate ligands, $(R_4N)_n$ [Ni(chdt)$_2$] [R = Me, n = 2: (**1**); R = ^{n}Bu, n = 1: (**2**); n = 0: (**3**)] and $(R_4N)_n$[Ni(eodt)$_2$] [R = Me, n = 2: (**4**); R = ^{n}Bu, n = 1: (**5**); n = 0: (**6**)], were prepared. X-Ray structures were determined on the monoanionic species (**2**) and (**5**). The tetra-*n*-butylammonium complexes of the monoanionic [Ni(chdt)$_2$] (**2**) with a 1:1 composition revealed that its magnetic susceptibility gave good agreement with the Bonner-Fisher model ($J/k_B = -28$ K), which was derived from the one-dimensional chains of anions with regular intervals. On the other hand, the magnetic susceptibility of tetra-*n*-butylammonium complexes of monoanionic [Ni(eodt)$_2$] (**5**) showed Curie-Weiss behavior ($C = 0.376$ K·emu·mol^{-1} and $\theta = -4.6$ K). Both of the monoanionic species (**2**) and (**5**) indicate that they belong to the $s = 1/2$ magnetic systems and have relatively large and anisotropic *g*-values, suggesting the contribution of the nickel 3*d* orbital. The electrical resistivity measurements were performed on the compressed pellets of the neutral species (**3**) and (**6**). The fairly large conductivities were obtained ($\sigma_{rt} = 1$–10 S·cm^{-1}). In addition, in spite of the compressed powder pellet sample, the neutral species (**6**) showed metallic behavior down to *ca.* 120 K and retained high conductivity even at 0.6 K [$\sigma(0.6\text{ K})/\sigma_{rt} \approx 1/30$], suggesting the crystal to be essentially metallic down to very low temperature. These electrical behavior and Pauli paramagnetism of (**6**) indicate the system to be a new single-component metal.

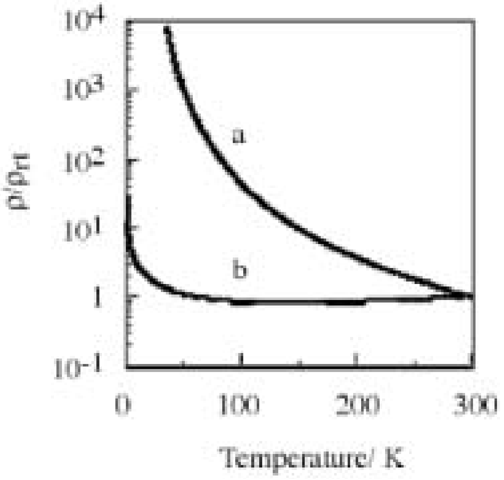


Figure 1. Temperature dependence of electrical resistivities of the neutral nickel complexes measured by use of the compressed pellets. (a)[Ni(chdt)$_2$] (**3**) and (b) [Ni(eodt)$_2$] (**6**).

IV-C-5 The Pressure Effect on the Antiferromagnetic and Superconducting Transitions of κ-(BETS)$_2$FeBr$_4$

OTSUKA, Takeo; CUI, HengBo; FUJIWARA, Hideki; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]**; KOBAYASHI, Akiko**[1]
([1]Univ. Tokyo)

[*J. Mater. Chem.* **14**, 1682 (2004)]

Among a wide variety of highly conducting molecular solids, a special group of conducting salts, so-called π–*d* system has attracted much concern in recent years, where π–*d* system is a class of complexes comprising π conducting electrons and localized magnetic moments of transition metal ions together in a crystal. The main interests in these systems are concentrated on the possible multi-functional properties originating from the interplay between localized magnetic moments and π metal electrons because the development of the multi-functional molecular conductors is considered to be an important step for realising molecular devices. However, up to now only a very limited number of systems are known to exhibit physical properties clearly reflecting π–*d* coupling. The first antiferromagnetic organic superconductor, κ-(BETS)$_2$FeBr$_4$ shows a unique successive phase transition from paramagnetic metal to antiferromagnetic metal to antiferromagnetic superconductor with lowering temperature. In order to examine the pressure effect on the antiferromagnetic and superconducting transition (T_N, T_c), the resistivity was measured up to 6 k bar along two directions. One direction is perpendicular to the conduction plane (*I*//*b* axis), and another is parallel to the conduction plane (*I*//*a*). These resistivities along the *a* and *b* axes gave almost the same temperature dependencies though the anisotropy of the resistivity is fairly large ($\rho_{//b}/\rho_{//a} \approx 200$ at room temperature). The pressure dependencies of T_N and T_c were obtained from the anomalies in the temperature dependencies of the resistivities. The value of T_c decreased with pressure and became less than 0.5 K around 4 kbar. While, T_N was enhanced at high pressure. The high-pressure resistivity measurements under magnetic field showed the critical magnetic field of metamagnetic transition increased gradually with pressure.

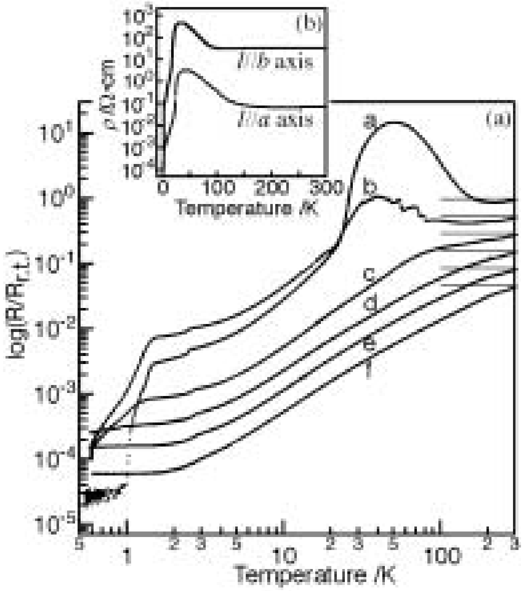


Figure 1. Temperature dependence of the resistivity of κ-(BETS)$_2$FeBr$_4$ at high pressure (< 5 kbar): a, 1 bar(ambient); b, 2 kbar; c, 3 kbar; d, 3.5 kbar; e, 4 kbar; f, 5 kbar. (b) The temperature dependencies of the resistivities of κ-(BETS)$_2$ FeBr$_4$ for *I*//*a* and *I*//*b* at ambient pressure.

IV-C-6 Crystal Structure of [(C$_2$H$_5$)$_2$(CH$_3$)$_2$N][Pd(dmit)$_2$]$_2$ at High Pressure

OKANO, Yoshinori; ADACHI, Takafumi[1]**;NARYMBETOV, Bakhyt**[2]**; KOBAYASHI, Hayao; ZHOU, Biau**[3]**; KOBAYASHI, Akiko**[3]
([1]SPring8, JASRI; [2]Uzbek Acad. Sci.; [3]Univ. Tokyo)

[*Chem. Lett.* 938 (2004)]

We have recently reported the crystal structure of high-pressure molecular superconductor, [(C$_2$H$_5$)$_2$ (CH$_3$)$_2$N][Pd(dmit)$_2$]$_2$ based on the high-pressure X-ray data obtained more than several years ago. The crystal of [(C$_2$H$_5$)$_2$(CH$_3$)$_2$N][Pd(dmit)$_2$]$_2$ belongs to the triclinic system. Since the (C$_2$H$_5$)$_2$(CH$_3$)$_2$N$^+$ cation is on the inversion center, the cation is disordered with taking two possible positions randomly at ambient pressure. The Pd(dmit)$_2$ molecules are stacked face-to-face to form dimeric columns along the *a* direction. Despite of the high room-temperature conductivity, the crystal becomes semiconducting at low temperature. But as mentioned above, the system shows a superconducting transition at high pressure at 2–7 kbar. However, in contrast to most of the molecular superconductors with stable metallic states above the critical pressures where the superconducting phases are suppressed, the insulating state appears above 7 kbar. The high-pressure X-ray experiments were made by using a specially designed diamond anvil cell. The crystals with typical dimensions of about 0.3 × 0.2 × 0.04 mm^3 were used.

The X-ray diffraction spots were detected by X-ray imaging plate system equipped with a rotating anode X-ray generator (MoKα). The crystal structure determination at 10 kbar was made using the 815 reflections ($I > 3\sigma(I)$). The correction for X-ray absorption by diamond anvil was not made. Due to the limited number of the observed reflections and the relatively large number of crystallographically independent atoms (41 non-hydrogen atoms of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$), the anisotropic temperature factors were used only for two Pd atoms. The structure refinements gave the final *R*-value of 0.105. The band structure at high-pressure was calculated based on the high-pressure structure. The calculated orbital levels of HOMO and LUMO at ambient pressure were significantly smaller than those at 10 kbar, which is considered to be related to the increase of planarity of $Pd(dmit)_2$ molecule (or π conjugation of the molecule) at high pressure.

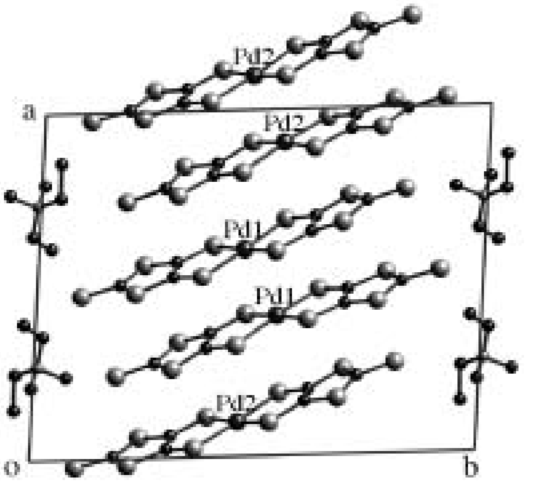


Figure 1. The crystal structure of $[(C_2H_5)_2(CH_3)_2N][Pd(dmit)_2]_2$ at 10 kbar.

IV-C-7 Synthesis, Structures and Physical Properties of a New Organic Conductor Containing a Stable PROXYL Radical

FUJIWARA, Hideki; LEE, Ha-Jin; CUI, HengBo; KOBAYASHI, Hayao; FUJIWARA, Emiko[1]; KOBAYASHI, Akiko[1]
([1]Univ. Tokyo)

[*Adv. Mater.* **16**, 1765 (2004)]

By the recent intensive studies on the molecule-based materials consisting of conducting organic layers and inorganic anion layers with localized magnetic moments, ferromagnetic metals, para- or antiferromagnetic superconductors and organic conductors exhibiting superconductor-to-insulator transition and field-induced superconductivity have been discovered. On the other hand, the development of organic ferromagnetic metals had been stimulated by the theoretical report that pointed out the possibility of the realization of ferromagnets employing the charge transfer complexes with stable organic radical substituents, and several research groups have investigated on the synthesis of donor or acceptor units bearing a stable radical part and reported cation radical salts based on such component molecules so far. However, it was quite difficult to obtain highly conducting cation radical salts because of so large steric hindrance of stable radical parts to construct the conduction pathway by stacking the conducting units such as the TTF (tetrathiafulvalene) skeleton. Recently, we have tried to overcome such problems by introducing π-extended donor skeletons which are regarded as being effective to establish sufficient intermolecular overlap integrals and π conduction bands which are indispensable for realizing the highly conducting complexes. We have discovered highly conducting cation radical salts by use of the bis-fused TTF skeleton called as TTP containing a PROXYL radical substituent and succeeded in the structure analysis of the AsF_6^- salt of cyclopenteno-fused TTP derivative carrying a stable PROXYL radical part having a 4:1 stoichiometry of D:A. Though the size of the crystal was very small (maximum dimension is about 0.15 mm) and the crystal quality was poor, we performed successfully a four-probe resistivity measurement. The crystal was semiconducting with the room temperature conductivity of about 1 S cm^{-1} and a small activation energy of 0.05 eV. The SQUID susceptibility measurements and ESR experiments suggested the coexistence of the localized PROXYL radical spins and π conduction electrons at high temperature ($T > 100$ K).

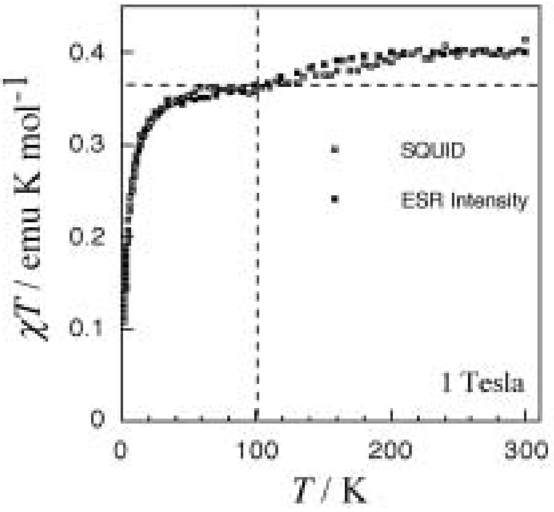


Figure 1. Temperature dependence of the χT values of $(TTP\text{-}PROXYL)_4AsF_6$ measured by SQUID (open square) and normalized ESR intensities.

IV-C-8 Anionic NaCl-Type Frameworks of $[Mn^{II}(HCOO)_3^-]$, Templated by Alkylammonium, Exhibit Weak Ferromagnetism

WANG, Zheming[1]; ZHANG, Bin[2];OTSUKA, Takeo; INOUE, Katsuya; KOBAYASHI, Hayao; KURMOO, Mohamedally[3]
([1]Peiking Univ; [2]Chinese Acad. Sci.; [3]Inst. Phys. Chim. Matériaux Strasbourg)

[*Dalton Trans.* 2209–2216 (2004)]

We present the synthesis, characterization by IR, TGA, single crystal X-ray structure and magnetic properties of a novel series of NaCl-type frameworks of [AmineH$^+$][Mn(HCOO)$_3$$^-$], templated by alkylammonium. The anionic NaCl-framework of [Mn (HCOO)$_3$$^-$] is counter-balanced by the alkylammonium cations located in the cavities of the framework to which they are hydrogen-bonded. The divalent manganese ions have octahedral geometry and are bridged by the formate in an *anti-anti* mode of coordination. All the compounds exhibit long-range antiferromagnetism below 9 K with a slight non-collinear arrangement of the moments. The canting, likely due to second-order spin-orbit coupling, is *via* a Dzyaloshinski-Moriya antisymmetric exchange mechanism. A spin-flop is observed in each case at fairly low fields. An orthorhombic to monoclinic transformation was observed for the protonated cyclotrimethyleneamine that is accompanied by localization of the cations into two positions below 240 K from the rapid dynamic flipping of the ring observed at room temperature.

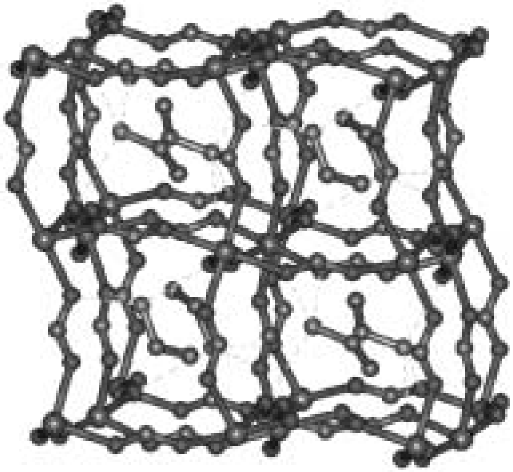


Figure 1. NaCl-type framework of [Mn^{II}(HCOO)$_3$$^-$] including annmonium cations ($CH_3CH_2NH_3^+$) in the cavity.

IV-C-9 Preparation and Properties of Novel Fe(III) Spin-Crossover Complexes with [Ni(dmit)$_2$] Anion

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

Spin-crossover phenomena are observed in transition metal complexes with d^4 to d^7 configuration under an appropriate octahedral ligand field. The spin conversion is induced by external perturbation such as temperature, pressure, light, and so on. Thus, the spin-crossover complexes are considered as a promising candidate for molecular switching materials. Recently, great attention has been attracted to development of novel multifunctional materials. We have explored possibility to control electrical conductivity by external perturbation. Since molecular-based conductors consist of relatively weak intermolecular interactions, bandwidth and bandfilling can be controlled by substitution with similar size and shape of constituents. The spin conversion between the low-spin and the high-spin states accompanies a remarkable structural change in coordination bond length. Therefore, electrical conductivity is expected to be controlled by embedding of the spin-crossover ion in molecular-based conductors. We have focused our attention upon the Fe(III) spin crossover complex, [Fe(qsal)$_2$]X, and the molecular-based conducting salt, M[Ni(dmit)$_2$] [qsalH = *N*-(8-quinolyl)-salicylaldimine, dmit = 4,5-dithiolato-1,3-dithiole-2-thione]. We have prepared and characterized novel Fe(III) spin crossover complexes with [Ni(dmit)$_2$] anion. The syntheses of [Fe(qsal)$_2$]$_2$[Ni(dmit)$_2$] and [Fe(qsal)$_2$][Ni(dmit)$_2$]·CH_3CN could be achieved by metathesis between [Fe(qsal)$_2$]Cl and $(Bu_4N)_2$[Ni(dmit)$_2$], and between [Fe(qsal)$_2$]Cl and (Bu_4N)[Ni(dmit)$_2$], respectively, in acetonitrile. The composition ratios of them were determined by microanalysis. Temperature dependence of $\chi_M T$ in [Fe(qsal)$_2$]$_2$[Ni(dmit)$_2$] revealed that a gradual spin transition from the low-spin to high-spin states occurred above 150 K. However, a complete spin conversion to the high-spin state could not be observed. On the other hand, temperature dependence of $\chi_M T$ in [Fe(qsal)$_2$][Ni(dmit)$_2$]·CH_3CN showed a wide hysteresis with about 35 K (Figure 1). These results suggested that there was no intermolecular interaction between [Fe(qsal)$_2$] ions in the 2:1 complex, whereas a strong cooperative interaction between them existed in the 1:1 complex. The crystal structure analyses were performed on a single crystal of both [Fe(qsal)$_2$]$_2$[Ni(dmit)$_2$] and [Fe(qsal)$_2$][Ni(dmit)$_2$]·CH_3CN. In [Fe(qsal)$_2$]$_2$[Ni (dmit)$_2$], crystallographical independent molecules were one [Fe(qsal)$_2$] ion and a half [Ni(dmit)$_2$] ion. No interaction was observed between neither [Fe(qsal)$_2$] nor [Ni(dmit)$_2$] ions. On the other hand, in [Fe(qsal)$_2$] [Ni(dmit)$_2$]·CH_3CN, two-dimensional network was formed by π-π interactions between the π-ligands in [Fe(qsal)$_2$] ion. These results were consistent to temperature dependence of magnetic behaviors. The LIESST (Light-induced excited spin state trapping) experiment and an attempt to obtain conducting complexes by electrocrystallization of [Fe(qsal)$_2$] [Ni(dmit)$_2$]·CH_3CN are now in progress.

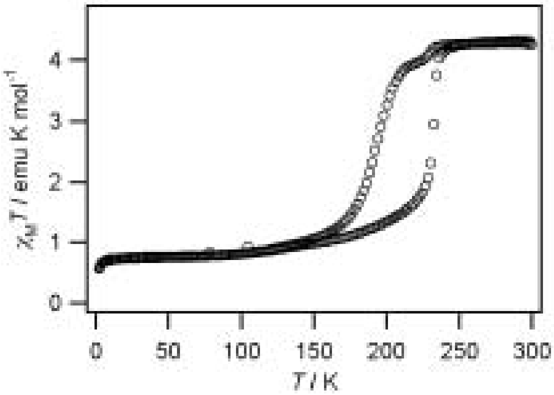


Figure 1. $\chi_M T$ *vs.* T plot of [Fe(qsal)$_2$][Ni(dmit)$_2$]·CH_3CN. Scan speed = 2 K min^{-1}, magnetic field = 5000 G.

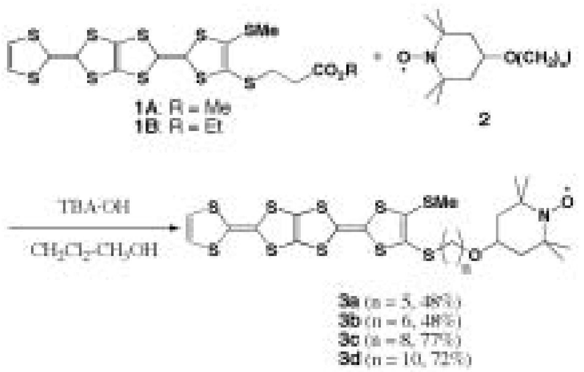
IV-C-10 Preparation and Characterization of Novel TTP Derivatives Connected with a Stable Organic Radical by a Long Covalent Bond Spacer

TAKAHASHI, Kazuyuki; CUI, HengBo;

FUJIWARA, Hideki[1]; KOBAYASHI, Hayao; FUJIWARA, Emiko[2]; KOBAYASHI, Akiko[2]
([1]Osaka Prefecture Univ.; [2]Univ. Tokyo)

Recently, great attention has been attracted to interplay between conducting electrons and localized spins to develop novel magneto-electronic materials. We have reported synthesis and properties of several π-donor molecules with stable organic radicals and their conducting complexes. However, since the radical part is usually bulky, we often encountered difficulties in the formation of the conduction path based on the overlap of π-donor parts. A moderate distance between the π-donor and organic radical parts is considered to decrease a hindrance to the formation of conduction path. Therefore, we have designed novel tetrathiapentalene (TTP) derivatives attached to a stable organic radical by a long covalent bond.

New TTP derivatives with stable TEMPO radicals (**3**) were synthesized by the reaction between S-protected TTPTM (**1**) and iodoalkyl-substitued TEMPO (**2**). These donors were isolated as a fine powder or film-like solid, and were unstable in air. Characterization of new donor molecules was carried out by MALDI-TOF mass spectroscopy, ESR spectra, and cyclic voltammetry. On the MALDI-TOF measurement, $[M+H]^+$ ions were observed in all new donors. ESR spectra showed triplet signals, indicating that there is a TEMPO radical in each molecule. Cyclic voltammogram of them revealed that the redox behavior of the donor part was independent of that of the TEMPO one. Preparation of the conducting complexes of these donors is now in progress.



Scheme 1. Synthesis of TTP donors with a stable TEMPO radical.

IV-C-11 Crystal Structures and Physical Properties of Novel Molecular Conductors Based on BETS and MX$_4^-$ (M = In, Tl; X = Cl, Br) Anions

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

So far we have reported many molecular conductors based on BETS and MX$_4^-$ (M = Fe, Ga; X = Cl, Br) anions with various structure types (α, θ, κ, λ, λ'). Among them, κ-(BETS)$_2$FeBr$_4$ and κ-(BETS)$_2$FeCl$_4$ are the first and second antiferromagnetic superconductors and λ-(BETS)$_2$FeCl$_4$ is the first organic conductor exhibiting a field-induced superconductivity. In λ-(BETS)$_2$FeCl$_4$, BETS molecules are stacked to form a tetradic column along the *a* axis. There exist many shortest distance between S(Se)···Cl and therefore the strong π-d interaction through Cl 3*p* orbitals is expected in λ-(BETS)$_2$FeCl$_4$. λ'-(BETS)$_2$GaBr$_4$ also has triclinic lattice and tetradic columns. But unlike superconducting λ-(BETS)$_2$GaCl$_4$, this salt seems to have a non-magnetic insulating ground state. Recently, we have found the salts with another modified λ-type structure, λ”-(BETS)$_2$TlBr$_4$. Similar to the λ-type structure, λ”-type has a triclinic unit cell. BETS molecules are staked to form 8-fold column, and tetrahedral TlBr$_4^-$ anions are arranged to take the orientation of “up–up–down–down” along the 8-fold BETS column. The crystal has a fairly high conductivity but slightly semiconducting. (BETS)$_3$InCl$_5$(PhCl)$_{0.5}$ has a unique three-dimensional donor arrangement, and retains its metallic state down to 120 K with high room-temperature conductivity (250 Scm^{-1}). Two-dimensional Fermi surface was obtained by tight-binding band calculation.

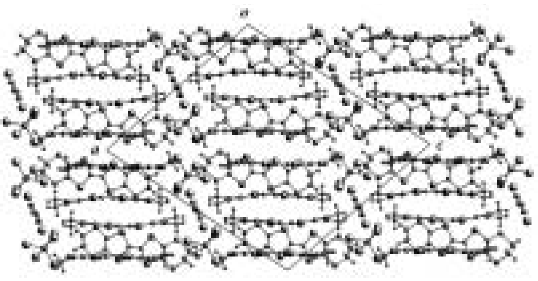


Figure 1. Crystal structure of (BETS)$_3$InCl$_5$(PhCl)$_{0.5}$.

IV-C-12 Structural and Physical Properties of Molecular Conductors Based on BEST and MX$_4^-$ (M = Fe, Ga, In; X = Cl, Br)

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

We have reported novel λ and κ-type salts based on BETS (bis(ethylenedithio)tetraselenafulvalene) and MX$_4^-$ (M = Fe; X = Cl, Br). These salts exhibit many unprecedented electro-magnetic properties originated from the interplay between π conduction electrons and localized 3*d* magnetic moments. Recently, we have prepared BEST (bis(ethylenediseleno)tetrathiafulvalene), and grew the crystals of molecular conductors using MX$_4^-$ (M = Fe, Ga, In; X = Cl, Br) anions. We obtained λ-BEST$_2$MCl$_4$ (M = Fe, Ga) and another triclinic modification, BEST$_2$MBr$_4$ (M = Fe, In). λ-BEST$_2$MCl$_4$ (M = Fe, Ga) is isostructural to λ-BEST$_2$ MCl$_4$ (M = Fe, Ga) but is semiconducting. In the crystal of BEST$_2$MBr$_4$ (M = Fe, In), BEST molecules form two kind of diadic columns along *b* axis. There exist many short S(Se)···Br contacts between BEST molecules and FeBr$_4^-$. Thus, it seems possible that intermolecular interaction through the intermolecular overlapping between π orbitals of BEST and d-like orbitals of the anion. The resistivity of $BEST_2FeBr_4$ takes minimum around 180 K (Fe salt).

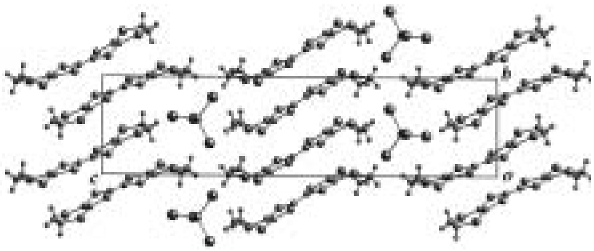


Figure 1. The crystal structure of $BEST_2FeBr_4$.

IV-C-13 Unsymmetrical Donors Fused with Pyridazine and Pyrazine Rings

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI, HengBo; KOBAYASHI, Hayao; FUJIWARA, Hideki[1]; FUJIWARA, Emiko[2]; KOBAYASHI, Akiko[2]
([1]Osaka Prefecture Univ.; [2]Univ. Tokyo)

We have reported the crystal structures and physical properties of a series of organic conductors consisting of Se-containing π donors, bis(ethylenedithio)tetraselenafulvalene (BETS) and metal tetrahalide monoanions such as κ -and λ-$(BETS)_2MX_4$ (M = Ga, Fe, In, Tl,…; X = Br, Cl). In order to enhance the interaction between donor and anion layers, we have synthesized unsymmetrical donors fused with a pyridazine ring and a pyrazine ring **2**–**4** and prepared several cation radical salts of **3** and PEDTTSeF (**2**) by electrochemical oxidation. The ReO_4^- salt of **3** has 1:1 donor-to-anion composition, which exhibited a semiconducting behavior (σ_{rt} = 0.45 S/cm, E_a = 0.094 eV). Whereas $(PEDTTSeF)_2FeX_4$ (X = Br, Cl) showed a metallic behavior down to 60 K (X = Cl) or 120 K (X = Br). The temperature dependence of magnetic susceptibility suggested very weak magnetic interactions between donors and anions.

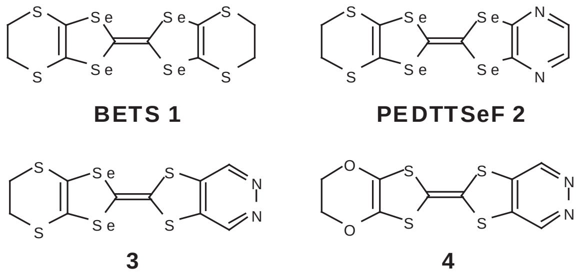
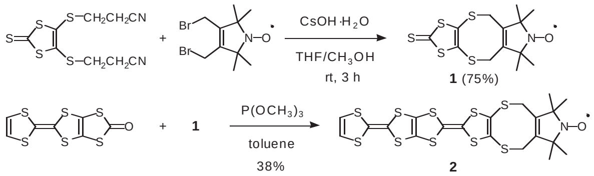


Figure 1. Molecular structures of organic donors.

IV-C-14 A Novel TTP Donor Containing a Stable Organic Radical

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI, HengBo; LEE, Ha-Jin; KOBAYASHI, Hayao; FUJIWARA, Hideki[1]; FUJIWARA, Emiko[2]; KOBAYASHI, Akiko[2]
([1]Osaka Prefecture Univ.; [2]Univ. Tokyo)

Development of magnetic conductors bearing both conductivity and magnetism has recently played a important role in the research of the multifunctionality of organic molecular materials. Recently, we have synthesized several organic donors containing a TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxyl) radical or a PROXYL (2,2,5,5-tetramethylpyrrolidin-1-yloxyl) radical. Among them, TTPPROXYL was found to produce interesting conductors exhibiting the coexistence of the conduction electrons and the localized spins. However, TTPPROXYL gives racemic compounds. So, a new TTP donor containing 2,2,5,5-tetramethyl-3-pyrrolin-1-yloxyl was synthesized as orange powder in 0.43% yield (14 steps from 2,2,6,6-tetramethyl-4-piperidinone). The preparation of cation radical salts by electrochemical oxidation is now in progress.

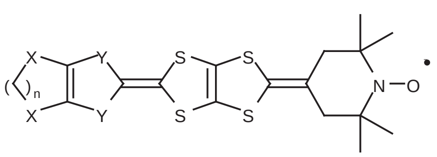


Scheme 1. Synthetic route of a new organic donor.

IV-C-15 Organic Conductors Containing a TEMPO Radical

OTSUBO, Saika; TAKAHASHI, Kazuyuki; CUI, HengBo; KOBAYASHI, Hayao; FUJIWARA, Hideki[1]; FUJIWARA, Emiko[2]; KOBAYASHI, Akiko[2]
([1]Osaka Prefecture Univ.; [2]Univ. Tokyo)

We have reported many intriguing electro-magnetic properties discovered in the magnetic organic superconductors based on Se-containing π donors BETS and magnetic transition metal anions FeX_4^- (X = Cl, Br). Besides BETS conductors, an attempt to obtain new type of magnetic organic conductors has been also performed by using donors containing a TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxyl) radical or NN (4,4,5,5-tetramethyl-2-imidazoline-1-oxyl-3-oxide). TEMPOET (**2**), which is constituted of ET part and TEMPO radical part, has been synthesized several years ago but no highly conducting salts has not been prepared yet. We have recently tried to prepare similar TEMPOET-type organic donors (**1**, **3**–**5**), which were synthesized by cross-coupling reaction and Horner-Wittig reaction (10–20% yield, 2 steps). Several cation radical salts with tetrahedral anions ($FeCl_4^-$, BF_4^-,…) were prepared by electrochemical oxidation. However, up to now, highly conducting salt could not be obtained.



1 (n = 1, X = Y = S)
2 (n = 1, X = Y = S) [**TEMPOET**]
3 (n = 3, X = Y = S)
4 (n = 2, X = S, Y = Se)
5 (n = 2, X = Se, Y = S)

Figure 1. Organic donors with TEMPO radical parts.