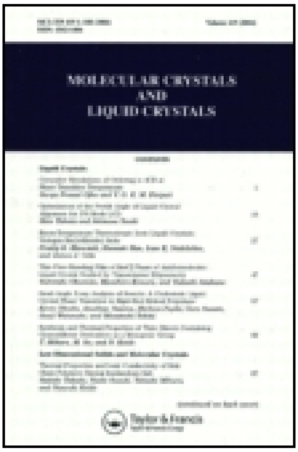

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Molecular Design and Development of Single-component Molecular Metals with Extended TTF Ligands

Akiko Kobayashi [a] , Wakako Suzuki [a] , Emiko Fujiwara [a] , Takeo Otsuka [a] , Hisashi Tanaka [b] , Yoshinori Okano [b] & Hayao Kobayashi [b]

[a] Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

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Molecular Design and Development of Single-component Molecular Metals with Extended TTF Ligands

AKIKO KOBAYASHI[a]*, WAKAKO SUZUKI[a],
EMIKO FUJIWARA[a], TAKEO OTSUKA[a], HISASHI TANAKA[b],
YOSHINORI OKANO[b] and HAYAO KOBAYASHI[b]

[a]*Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan and*
[b]*Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*

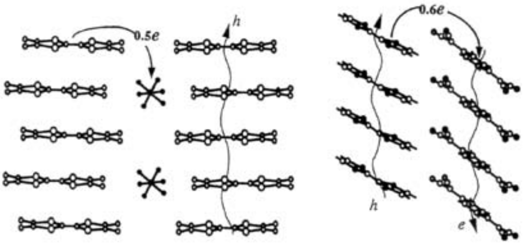
The novel neutral nickel complex with the extended TTF dithiolato ligand, trimethylenedithiotetrathiafulvalenedithiolate[$\mathrm{tmdt_2}^-=(\mathrm{S_6C_9H_6})_2{}^-$], have been synthesized. The single crystal of [Ni(tmdt)$_2$] was metallic down to 0.6 K. The crystal structure and electronic band structure calculation showed [Ni(tmdt)$_2$] is the first single-component molecular metal with three-dimensional Fermi surfaces. Metallic behavior was also found in the crystal of an analogous molecule, [Ni(dmdt)$_2$][$\mathrm{dmdt_2}^-$=dimethyltetrathiafulvalenedithiolate]. Similar highly conducting systems, [Au(dmdt)$_2$] and the molecular conductor with localized S=1/2 spins, [Cu(dmdt)$_2$] were also prepared.

Keywords: extended TTF ligand; single-component molecular metal; three-dimensional molecular metal

INTRODUCTION

The discovery of the first organic superconductor, (TMTSF)$_2$ PF$_6$ (TMTSF=tetramethyltetraselenafulvalene) in 1980 has opened the new era of organic conductors[1]. Its crystal structure gave a great hint to establish the molecular design to develop the organic conductor without one-dimensional metal instability. Since 1980, an extremely large number of molecular conductors have been developed, which have contributed to change the old image on molecular crystals, that is, the molecular crystal is nothing but an insulator.

The design of molecular metal composed of single component molecules was a very difficult problem in the field of molecular conductors. In contrast to the typical inorganic metals such as sodium and copper composed of single elements, all the molecular metals ever developed were consisted of more than two components. It has been long believed that the formation of electronic band structure and the charge transfer between the molecules (A) constructing the band and other chemical species (B) are two essential requirements to obtain metallic state. In some cases, both molecules A and B form conduction bands where the electron and hole carriers are generated by the charge transfer between A and B. This was the reason why more than two components were needed to construct molecular metals. For example, in $(TMTSF)_2PF_6$, TMTSF molecules form a conduction band and metal electrons are produced by electron transfer between TMTSF and PF_6 $[(TMTSF^{0.5+})_2(PF_6)^-]$(Figure 1). In the case of (TTF)(TCNQ)[2] with segregated columns of TTF and TCNQ, free carriers are generated in both columns by partial transfer between TTF and TCNQ ($TTF^{+0.6}TCNQ^{-0.6}$)(Figure 1).



$TMTSF_2PF_6$ (TTF)(TCNQ)

FIGURE 1 Formation of electronic bands and the generation of charge carriers due to a charge transfer in $(TMTSF)_2PF_6$ and (TTF)(TCNQ).

Even in the case of recently observed superconductivity obtained for C60 and aromatic hydrocarbons such as naphthalene, anthracene and tetracene in field effect transistor (FET) configulations, the injection of charges by the electric field is unavoidable[3]. The difficulty of the design of single-component molecular metal is naturally related to the fact that the molecule has usually even number of electrons and the highest occupied molecular orbital is doubly occupied.

There are trials to develop highly conducting systems by using stable organic radical molecules with singly occupied molecular orbitals. However, these molecules tend to produce narrow half-filled bands, where electrons will be localized by correlation even when the electronic band is formed. Thus, the spontaneous generation of free carriers in the molecular crystal composed of single-component molecules seemed almost impossible.

We have recently succeeded in preparing a single-component molecular metal with a stable metallic state down to very low temperatures using transition metal complex and obtained the guiding principle of molecular design of neutral metal composed of single-component molecule based on the metal complexes with extended-TTF dithiolato ligands:

In this report, we present the guiding principle of molecular design of a neutral metal composed of single-component molecule and the first single-component molecular metal $[Ni(tmdt)_2]$[4] and analogous compounds.

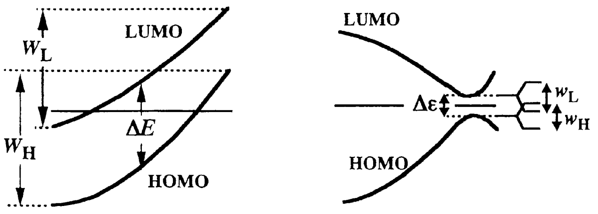
EXPERIMENT

All the synthetic procedures were carried out under a strictly inert atmosphere with the Schlenk technique. Synthesis of the ligand moieties with the cyanoethyl-protecting group was performed according to the reported method[5] and derived methods thereof. The diffraction experiment was made on a Rigaku MERCURY CCD system. Resistivities were measured using the four-probe method. The susceptibility measured with a SQUID magnetometer within the temperature range of 2-300 K.

RESULTS AND DISCUSSIONS

Design of a π Metal Band with Small HOMO-LUMO Gap

In the molecular crystal composed of single molecules the "partial charge transfer" must occur between the electronic band derived from HOMO and that from LUMO to generate the carriers. In order to realize such "charge transfer", the energy difference between HOMO and LUMO (ΔE) must be small compared with the band width ($\Delta E < (W_H + W_L)/2$, where W_H and W_L are widths of HOMO and LUMO bands, respectively) (Figure 2a). Since the band width of usual organic metal is a little less than 1 eV, the condition $\Delta E < (W_H + W_L)/2$ is assumed to be satisfied. Since the symmetry of HOMO is different from that of LUMO, the sign of intermolecular overlap intergal (S) (or transfer integral ($t = kS$; $k \sim 10$ eV)) of HOMO-HOMO interaction (S_{HH}) is apt to be different from that of LUMO-LUMO interaction (S_{LL}). This situation is serious especially in highly one-dimensional conductors. As illustrated in Figure 2b, HOMO and LUMO form "crossing bands", where HOMO-LUMO interaction destroys Fermi surfaces. One way to protect Fermi surface from HOMO-LUMO interaction (t_{HL}) is the enhancement of transverse interactions, which is almost the same condition required to stabilize the metallic state of molecular conductor against one-dimensional metal instability.



(a) (b)

FIGURE 2 Shematic drawing of band structure :(a) parallel band (b) crossing band.

If the energy gap ($\Delta\varepsilon$) produced by HOMO-LUMO interaction is less than the band width along the transverse direction (w_H, w_L) ($\Delta\varepsilon$☐ w_H, w_L), it is highly possible that the electrons and holes are generated and the system will become (semi-)metallic. Thus the enhancement of two-dimensional intermolecular interactions (that is, w_H and w_L) is essential. On the other hand, if we can realize the molecular arrangement where the sign of S_{HH} is same to that of S_{LL}, the system has "parallel bands". Then the Fermi surfaces are stable against HOMO-LUMO interaction (see Figure 2a).

Since HOMO of TTF-like p donor has the same sign on every sulfur (or selenium) atom (Figure 3), SHH has negative sign along the molecular stacking direction (that is, the direction of the largest interaction) in usual conducting system. But S_{LL} has a tendency to have opposite sign due to "intermolecular slipping configuration" frequently found in the crystals of molecular conductors where the neighbouring molecule is displaced along the long axis of the molecule. But if the adjacent molecule slips along the short axis of the molecule, S_{LL} becomes negative like as S_{HH}. Then the system has parallel bands and large Fermi surfaces derived from HOMO and LUMO bands.

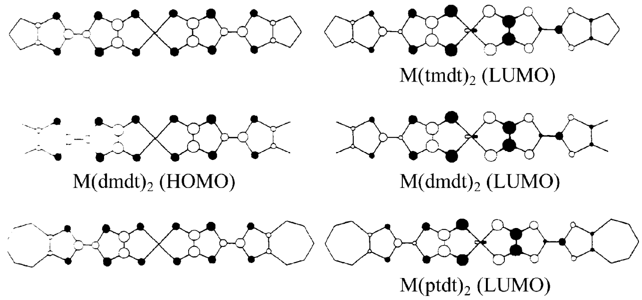


FIGURE 3 Schematic drawing of HOMO and LUMO of metal dithiolate complex.

Effective approach to design of molecules with small HOMO-LUMO gap is the utilization of transition metal complexes with extended π ligands having a TTF skeleton. If the interaction between the ligands and the central transition metal atom can be neglected, an energy level pair with a small energy separation (ΔE) would appear due to the weak interaction between the left and the right TTF-like ligands through the small π...π overlap of sulfur atoms ($S_{\pi\pi}$) separated by the central metal atom($\Delta E \approx 2kS_{\pi\pi}$). The resultant wave functions of these two states can be written as: $\phi_H=\phi_1+\phi_2$ and $\phi_L=\phi_1-\phi_2$ where ϕ_1 and ϕ_2 represent the left half and the right half of the ligand wave function. Ab initio MO calculations were recently performed on a [Ni(ptdt)$_2$] molecule, which show that the energy difference between HOMO and LUMO is very small. The comparison of the result of a simple extended Hükel tight-binding band calculation performed for a

[Ni(ptdt)$_2$] crystal with its electrical properties gives us a hint to establish the design of a metallic (or semi-metallic)crystal composed of single neutral molecules[6]. From the studies on this MO calculations and band structure calculations, the following guiding principles of molecular design of a "neutral metal" composed of a single component molecule was derived:

(1) The HOMO-LUMO energy gap of the constituent molecule must be small. The metal complex with extended-TTF ligands is a good candidate.

(2a) In systems with crossing bands, large HOMO-HOMO and LUMO-LUMO tansverse interactions are needed to produce semi-metallic Fermi surfaces. Molecules with a TTF-like skeleton have a great advantage in enhancing transverse intermolecular interactions.

(2b) Systems with parallel bands are desirable to obtain large metallic Fermi surfaces. That is, a suitable molecular arrangement must be realized, where the HOMO-HOMO overlap integral and the LUMO-LUMO integral have the same sign.

A Metallic Crystal Composed of a Single Component Molecule

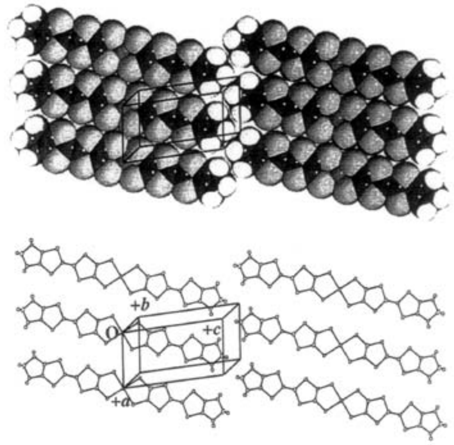
The single crystal of neutral [Ni(ptdt)$_2$], which has an extended TTF dithiolato ligands, is a narrow-gap semiconductor with a room temperature conductivity of 7 Scm^{-1} and has an unusual regular stacking structure[6]. The crystal structure determination revealed that [Ni(ptdt)$_2$] molecules are stacking one-dimensionally. This structual feature is very unusual considering that the neutral molecule usually has no attractive interaction with neibouring molecules except for the weak van der Waals interactions. Thus [Ni(ptdt)$_2$] seems to have a unique electronic structure which utilizes the close assembly of molecules. We calculated the ab initio molecular orbital calculations which shows that the HOMO and the LUMO are π-like molecular orbitals with b_{2g} and b_{1u} symmetries, respectively, with the HOMO-LUMO energy separation (ΔE) being very small. We perfomed tight-binding band calculation of [Ni(ptdt)$_2$] crystal based on HOMO and LUMO orbitals and obtained the guiding principle of molecular design of neutral metal composed of single component molecule mensioned in the previous section.

According to these guiding principle, we have prepared the first metallic crystal composed of single component molecules [Ni(tmdt)$_2$] (tmdt^{2-}=trimethylenetetrathiafulvalenedithiolate)[4,7].

The syntheses of tmdt ligand moiety with cyanoethylene group were performed according to the literature methods[5]. The oxidation of metal complexes was performed by electrochemical method and black plate crystals were obtained. The composition was determined by EPMA (electron probe microanalysis) and elemental analysis.

As shown in Figure 4, [Ni(tmdt)$_2$] molecules crystallize into very simple and compact structure with triclinic symmetry. Lattice constants are :a=6.376(3) Å, b=7.359(1), c=12.012(7), α=90.384(7)°, β=96.688(4), γ=103.587(4), triclinic $P\bar{1}$. The unit cell contains only one [Ni(tmdt)$_2$] molecule and half of the molecule is crystallographically independent. The molecule is ideally planar even at terminal trimethylene groups. It is very impressive that the neutral molecules form a closely packed structure. There are many short S...S contacts between the molecules neighboring in the ac plane and also along [111] direction. These structural features suggest that the system has three-dimensional intermolecular interactions.

The single-crystal resistivity measurement along the a axis was made down to 0.6 K using four-probe method. The room-temperature conductivity was 400 S cm^{-1} and the system retained metallic state down to 0.6 K (Figure 5). That is, neutral [Ni(tmdt)$_2$] crystal is the first single-component molecular metal. The resistivity measurement on a compacted powder sample also showed very high conductivity at room temperature (200 S cm^{-1}) and exhibited a metallic behavior down to 70 K. Below 70 K, the resistivity was slightly increased but the value at 4 K was less than the room-temperature value (Figure 5). These facts suggest the small anisotropy of the resistivity, which is consistent with three-dimensional nature of the system. The susceptibility was measured on polycrystalline samples by SQUID magnetometer down to 2K, which showed approximately temperature independent paramagnetic susceptibility consistent with Pauli paramagnetism of the system (Figure 5).



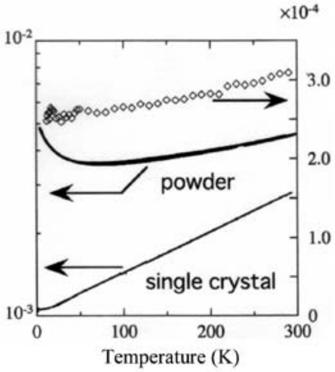
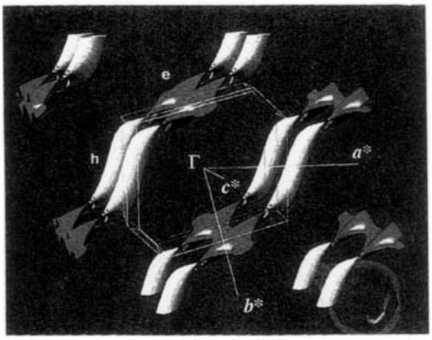


FIGURE 5 Resistivity and susceptibility measurements of Ni(tmdt)$_2$.

We performed tight-binding band calculation of [Ni(tmdt)$_2$] crystal. The intermolecular overlap integrals show that the system has a three-dimensional π band. As suggested previously, three-dimensional intermolecular interaction is considered to produce the sufficiently large Fermi surfaces even when HOMO and LUMO form the "crossing bands". Considering the difficulty in the precise estimation of ΔE, the band calculations were performed with varying ΔE, which revealed that the system has the three-dimensional Fermi surfaces for $\Delta E < 0.6$ eV. The calculated Fermi surface is shown in

Figure 6. The electron and hole Fermi surfaces are arranged alternately in the plane approximately parallel to the *a**-*b** and *c** axes.



Single-Component Magnetic Molecular Metals

The formation of a single component molecular metal opens the possibilities of developing various types of unprecedented functional molecular systems such as molecular superconductors, molecular ferromagnetic metals composed of single-component magnetic molecules, etc.

A novel type of "molecular metallic crystals" composed of [Ni(tmdt)$_2$] and an analogous molecule was discovered recently[7]. One of the next target of the single-component molecular metal is a development of single-component magnetic molecular metals.

We prepared single-component molecular conductors with magnetic ions (Cu^{2+}, Co^{2+}, ...) with TTF extended ligand such as tmdt and dmdt. Although good crystals have not been obtained yet, [Cu(dmdt)$_2$] has recently been shown to give a fairly high conducting crystal ($\sigma_{RT} \approx 4$ Scm^{-1}) with localized S=1/2 spins. A single crystal structure determination shows that the central Cu atom is coordinated by four sulfur atoms of two bidentate ligands with a distorted tetrahedral geometry. These dimeric ligand is almost perpendicular(80.3°) and dimeric ligand form such a closed-packed compact structure similar to κ-type ET or BETS superconductors[8]. Recently we have prepared [Au(dmdt)$_2$] , which is essentially metallic based on resistivity and magnetic susuceptibility measurements. [Au(tmdt)$_2$] is isomorphous to [Ni(tmdt)$_2$]. Experimental details will be shown in near future.

CONCLUSION

The guiding principle of molecular design of a neutral metal composed of single-component molecule was discussed and the first single component-molecular metal [Ni(tmdt)$_2$] was prepared according to this guiding principle. A single-component molecular metal will provide various possibilities for future studies on the development of new functional molecular systems.

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References

[1.] D. Jérome, M. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett.*, **L95**, 1416 (1980).
[2.] J. P. Ferraris, D. O. Cowan, V. Walatka Jr. and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
[3.] J.H. Schön, Ch. Kloc, B. Batlogg, *Nature*, **406**, 702 (2000).
[4.] H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki and A. Kobayashi, *Science*, **291**, 285 (2001).
[5.] L. Binet, J. M. Fabre, C. Montginoul, K. B. Simonsen and J. Becher, *J. Chem. Soc., Perkin Trans.* I, 783 (1996).
[6.] A. Kobayashi, M. Kumasaki, H. Torii, T. Tanaka,T. Adachi and B. Narymbetov, *J. Amer. Chem. Soc.*, **121**, 10763 (1999).
[7.] A. Kobayashi, H. Tanaka and H. Kobayashi, *J. Mater. Chem.*, **11**, 2078 (2001).
[8.] H. Kobayashi, K. Kawano, T. Naito and A. Kobayashi, *J. Mater. Chem.*, **5**, 1681 (1995).