JOURNAL OF
Materials
CHEMISTRY
Feature Article

Molecular design and development of single-component molecular metals

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Received 23rd March 2001, Accepted 1st May 2001
First published as an Advance Article on the web 4th June 2001

This article discusses the requirements for designing single component molecular metals, derived from the results of crystal structure analyses, electrical resistivity measurements and extended Hückel tight-binding band calculations, performed on molecular conductors composed of single-component molecules of [Ni(ptdt)$_2$] (ptdt = propylenedithiotetrathiafulvalenedithiolate) with extended TTF-ligands. The design of π molecules with a small HOMO–LUMO gap and a TTF-like skeleton is a key step to developing single-component molecular metals. A new approach is proposed to reduce HOMO–LUMO gaps. The preparation and characterization of a single-component three-dimensional molecular metal based on an analogous neutral transition metal complex molecule, [Ni(tmdt)$_2$] (tmdt = trimethylenetetrathiafulvalenedithiolate) are reported. The details of the procedures for its synthesis are presented. Black crystals of this compound were obtained by the electrochemical method. In the crystal, which has a triclinic unit cell containing only one molecule, the planar [Ni(tmdt)$_2$] molecules are closely packed to form the lattice plane (02$\bar{1}$). There are intermolecular short S⋯S contacts which indicate that the system is a three-dimensional conductor. The resistivity measurements show that the system is metallic down to 0.6 K. The extended Hückel tight-binding band calculation gave three-dimensional semi-metallic Fermi surfaces. A metallic crystal was also prepared with an analogous molecule [Ni(dmdt)$_2$] (dmdt = dimethyltetrathiafulvalenedithiolate). The formation of a single component molecular metal opens the possibilities of developing various types of unprecedented functional molecular systems such as single component molecular superconductors, ferromagnetic metals composed of single component magnetic molecules, molecular metals (or superconductors) soluble in organic solvent, *etc.*

Introduction

The first clear evidence for the existence of degenerated metal electrons in molecular crystals was obtained in 1973 through the observation of Peierls instability or giant Kohn anomaly by X-ray and neutron diffuse scattering experiments on a partially oxidized platinum complex, $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$.[1] The characteristic one-dimensional metal properties of $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ and analogous platinum complexes observed around 1970,[2,3] and further observed in an organic metal (TTF)(TCNQ) and its analogs,[4] attracted a large interest from physicists and chemists, opening a new era of low-dimensional molecular metals. In 1980, the first organic superconductor Bechgaard salt was discovered.[5] From then on, extensive efforts have been devoted to develop new types of molecular metals and superconductors. Nowadays, a number of organic superconductors, including the first molecular superconductors based on transition metal complexes, (TTF)[Ni(dmit)$_2$]$_2$ have been reported.[6] Furthermore, new types of organic superconductors such as organic superconductors with paramagnetic anions,[7] antiferromagnetic organic superconductors[8,9] and even molecular conductors exhibiting unprecedented superconductor-to-insulator transitions[10] and field-induced superconducting transitions[11] have been recently discovered.

Thus, the field of molecular conductors has expanded tremendously in the last three decades. However, in the field of metallization of molecular crystals, a difficult problem remains unsolved. It has been believed for a long time that the formation of electronic bands and the generation of charge carriers due to a charge transfer between 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 by the charge transfer between A and B. This is the reason why the design of metals composed of single-component molecules is difficult. For example, in the first organic superconductor (TMTSF)$_2$PF$_6$, TMTSF (tetramethyltetraselenafulvalene) molecules form a conduction band and metal electrons are produced by electron transfer between TMTSF and PF$_6$ [$(TMTSF^{+0.5})_2(PF_6)^-$]. In the case of (TTF)(TCNQ) with segregated columns of TTF and TCNQ, free carriers are generated in both columns by partial charge transfer between TTF and TCNQ ($TTF^{+0.6}TCNQ^{-0.6}$). Needless to say, similar carrier generation processes are also required in conducting organic polymers (*e.g.* chemical doping of polyacetylene[12]). Even in the case of recently observed superconductivity obtained for C_{60} and aromatic hydrocarbons such as naphthalene, anthracene and tetracene in field effect transistor (FET) configurations,[13] the injection of charges by the electric field is unavoidable. The difficulty in designing a single-component molecular metal is naturally related to the fact that molecules usually have an even number of electrons and that 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.[14] 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

DOI: 10.1039/b102865k

spontaneous generation of free carriers in the molecular crystal composed of single-component molecules seemed almost impossible.[15]

However, 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 molecules with extended-TTF ligands.[16] Another approach using gold dithiolene complexes has been also reported.[17,18]

Few remarks on the general concept in the design of a π metal band

In this paper, the design of π molecular metals is discussed based on the simple extended Hückel tight-binding band picture. Here, a π molecular metal stands for the metal composed of molecules with the frontier orbitals [the highest occupied molecular orbital (HOMO) and/or the lowest unoccupied molecular orbital (LUMO)] with a "π character". When the crystal structure of the first organic superconductor $(TMTSF)_2PF_6$ with a two-dimensional Se···Se network was reported,[19] it gave us a clue as to how to design molecular metals with two-dimensional π metal bands, despite the fairly strong one-dimensional character suggested from the extended Hückel tight-binding band calculation.[20] Another conductor which gave us an important hint was a platinum dithiolate complex, $(H_3O)_xLi_yPt(mnt)_2{\cdot}zH_2O$ exhibiting a metal–insulator (MI) transition around 220 K [mnt = 1,2-dicyano-1,2-ethylenedithiolate (maleonitriledithiolate)] (Fig. 1).[21] In spite of the apparent similarity of the chemical formula with the partially oxidized one-dimensional platinum complexes, the crystal structure of this $Pt(mnt)_2$ conductor showed that the frontier orbital responsible for the formation of the conduction band in this complex is not the $5d_{z^2}$ orbital of the central platinum atom but the π orbitals (including the dπ orbital of the Pt atom) delocalized over the dithiolene ligands.[21,22] In other words, the character of the frontier orbital is drastically changed by using dithiolate ligands. Consequently, this platinum dithiolate complex can be regarded as a π metal system where intermolecular S···S contacts play an essential role to form a conduction band similar to the case of organic conductors based on TTF-like π donor molecules. Through these studies, the organic conductors and the conductors based on metal dithiolate complexes were unified into the same group of π molecular conductors composed of "multi-sulfur (or selenium) π molecules" where common concepts of molecular design can be applied.

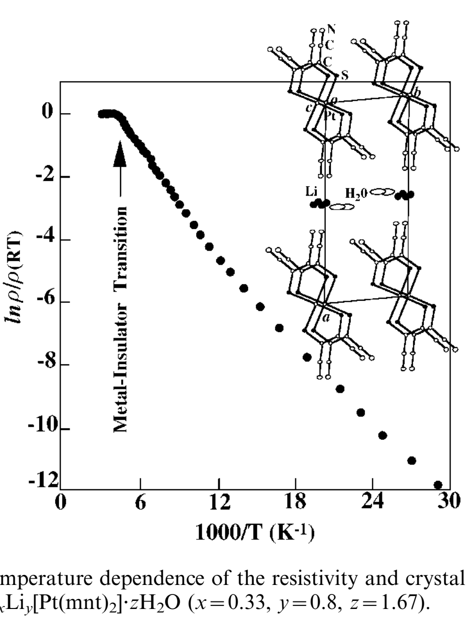


Fig. 1 Temperature dependence of the resistivity and crystal structure of $(H_3O)_xLi_y[Pt(mnt)_2]{\cdot}zH_2O$ ($x = 0.33$, $y = 0.8$, $z = 1.67$).

As mentioned above, the "partial charge transfer" must occur between the electronic band derived from HOMO and that from LUMO to generate the carriers in the molecular crystal composed of single molecules. In order to realize such a "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 the widths of the HOMO and the LUMO bands, respectively) (Fig. 2a). Since the band width for an ordinary organic metal is slightly less than 1 eV, ΔE must be less than 1 eV. In the following discussion, we assume that the condition $\Delta E < (W_H + W_L)/2$ is satisfied. Since the symmetry of HOMO is different from that of LUMO, the sign of the intermolecular overlap integral (S) (or the transfer integral ($t = kS$; $k \approx -10$ eV)) of HOMO–HOMO interaction (S_{HH}) is likely to be different from that of LUMO–LUMO interaction (S_{LL}). This situation is serious especially in highly one-dimensional conductors. As illustrated in Fig. 2b, HOMO and LUMO form "crossing bands", where HOMO–LUMO interaction destroys (t_{HL}) Fermi surfaces.[23] One way to protect the Fermi surface from HOMO–LUMO interaction is the enhancement of transverse interactions, which is almost the same condition required to stabilize the metallic state of a molecular conductor against one-dimensional metal instability. If the energy gap ($\Delta\varepsilon$) produced by HOMO–LUMO interaction is less than the band width in 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 becomes (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 a molecular arrangement where S_{HH} and S_{LL} have the same sign, the system has "parallel bands". Then the Fermi surfaces are stable for the HOMO–LUMO interaction (see Fig. 2a). Since HOMO of a TTF-like π donor has the same sign on every sulfur (or selenium) atom (Fig. 3a), S_{HH} has a negative sign along the molecular stacking direction (that is, the direction of the largest interaction) in an ordinary conducting system. However, S_{LL} tends to have an opposite sign due to "intermolecular slipping configuration" frequently found in crystals of molecular conductors where the neighboring molecule is displaced along the long axis of the molecule (an example will be presented later in the band structure of the $[Ni(ptdt)_2]$ system). Nevertheless, if the adjacent molecule slips along the short axis of the molecule, S_{LL} becomes negative in the same way as S_{HH}. Then, the system has parallel bands and large Fermi surfaces derived from HOMO and LUMO bands. To our knowledge, there are only a small number of molecular conductors with parallel bands. One example which we found more than 15 years ago is $(DBTTF)[Ni(dmit)_2]$ (DBTTF = dibenzotetrathiafulvalene) with segregated columns of DBTTF and $Ni(dmit)_2$, as found in (TTF)(TCNQ).[24,25] In order to avoid confusion, note that the "parallel band" of $(DBTTF)[Ni(dmit)_2]$, which means that the sign of the HOMO–HOMO interaction along the DBTTF column is the same as that of the LUMO–LUMO interaction along the $Ni(dmit)_2$ column, is different from the "parallel band" discussed in this paper where HOMO and LUMO of single-component molecules form "parallel bands".

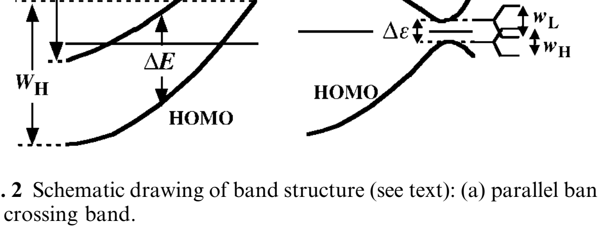


Fig. 2 Schematic drawing of band structure (see text): (a) parallel band (b) crossing band.

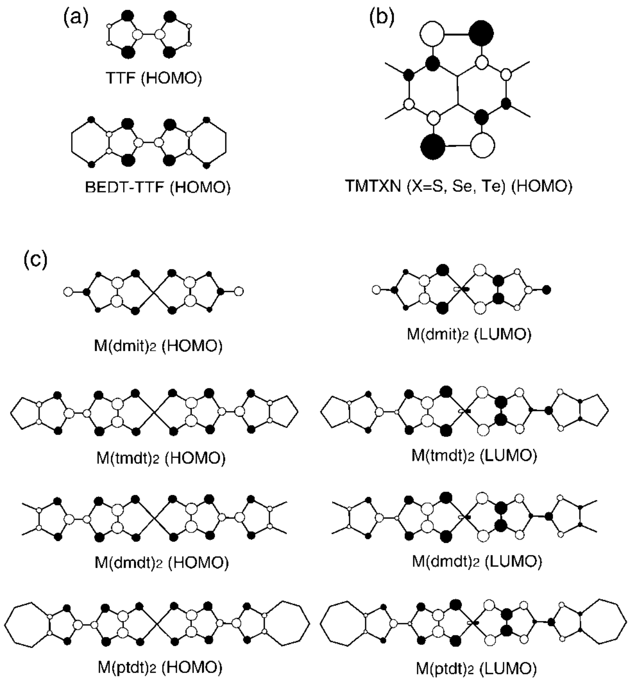


Fig. 3 (a) Schematic drawing of (a) HOMO of TTF-like π donor molecule (b) HOMO of TMTXN (X = S, Se, Te) molecule (*e.g.*, TMTSeN = tetramethyltetraselenonaphthalene) and (c) HOMO and LUMO of metal dithiolate complex.

Considering that the symmetry of HOMO of Ni(dmit)$_2$ is the same as that of a TTF-donor (see Figs 3a and c), however, it can be easily imagined that the intermolecular overlapping mode of Ni(dmit)$_2$ along the column satisfies the condition to form a "parallel band".

As mentioned later, we have recently examined the crystal structure and the electrical properties of a neutral nickel complex with an extended TTF-ligand (ptdt, propylenedithiotetrathiafulvalenedithiolate), Ni(ptdt)$_2$, in order to examine the requirements for designing single-component molecular metals.[26] From these studies, the following requirements for the development of single component molecular metals were suggested: (1) a small HOMO–LUMO energy gap (2a) large transverse interactions, which will permit the formation of (semi-)metallic Fermi surfaces even in systems with crossing bands. (2b) molecular arrangement into parallel bands.

Design of molecules with a small HOMO–LUMO gap

(1) Multi-chalcogen π molecule with eclipsed dimer structure

Among the above-mentioned requirements, requirement (1) seems to be the most difficult to satisfy. Tanaka *et al.* have prepared a molecule composed of aromatic heterocycles and a novel non-classical thiophene with pyrazine–dihydropyrazine whose lowest-energy absorption edge was observed at about 2100 nm, indicating a small HOMO–LUMO gap ($\approx$0.6 eV).[27] It can be easily imagined that the HOMO–LUMO gap will decrease with extending conjugated π systems. Fused porphyrin prepared by Osuka *et al.* is another example of a molecule with small electronic excitation energies.[28] The absorption maximum of fused triporphyrin was observed at about 1250 nm (1.0 eV) and the absorption shows a strong red shift with increasing numbers of fused porphyrins. However, it seems almost impossible for these molecules to satisfy requirement (2a) (or (2b)). On the other hand, requirement (2a), which is essential to produce Fermi surfaces even in a system with crossing bands, can be considered to be the same requirement as for designing two-dimensional metals, which was intensively studied in the 1980s through systematic crystal and electronic structure examinations performed on various molecular conductors based on multi-sulfur (or selenium) π molecules.[22,24] In other words, the constituent molecule must be a multi-sulfur (or a chalcogen) π molecule with a TTF-like skeleton. As mentioned before, HOMO of TTF-like donors have the same sign on every chalcogen atom (see Fig. 3a), which means that the intermolecular interaction through chalcogen···chalcogen contacts can additively contribute to enhance intermolecular interactions. Thus, the close intermolecular transverse contacts present in these systems mean that large transverse intermolecular interactions have been realized. This is not always true in other organic conductors composed of different multi-sulfur π donor molecules. For example, in the case of the well-known π donors TTN (or TSN) (tetrathionaphthacene, which is frequently abbreviated as TTN or TSN), TSeN and TTeN with peripheral chalcogen atoms, HOMO has a node on the chalcogen–chalcogen bond, which tends to cancel transverse HOMO–HOMO interactions through chalcogen atoms (Fig. 3b).[29] These facts show the advantage of TTF-donors in the design of two-dimensional molecular metals.

In the course of systematic studies on molecular conductors based on multisulfur π molecules, we have examined crystal structures of several M(dmit)$_2$ (M = Ni, Pd, Pt) conductors of $[R^+][M(dmit)_2]_2$ (R^+ = ammonium cation; M = Ni, Pd, Pt, ...). Compared to Ni(dmit)$_2$, Pd(dmit)$_2$ and Pt(dmit)$_2$ molecules have a strong tendency to form dimeric stacks.[22,30,31] Consequently, in contrast to Ni(dmit)$_2$ conductors where LUMO is mainly responsible for the formation of the conduction band, the conduction bands of Pd(dmit)$_2$ conductors are formed from HOMOs. As illustrated in Fig. 4, the energy level of the antibonding combination of two HOMOs (ϕ_{H-}) is higher than the energy level of the bonding combination of two LUMOs (ϕ_{L+}) due to the strong intradimer HOMO–HOMO and LUMO–LUMO interactions. Consequently, ϕ_{H+} forms a three-quarter filled band in the crystal of the $[R^+][Pd(dmit)_2]_2$ conductor. This means that ΔE for Pd(dmit)$_2$ is less than the intradimer interactions ($t_{HH}+t_{LL}$), which suggests that the energy level of ϕ_{L+} (E_{L+}) can be made comparable to that of ϕ_{H-} (E_{H-}) by controlling the intradimer interactions. It should be noted that the ideally eclipsed overlapping of Pd(dmit)$_2$ is important, where the intradimer HOMO–LUMO interaction (t_{HL}) is zero due to the symmetry (approximately D_{2h}). In other configurations, it will be difficult to obtain almost degenerated ϕ_{H+} and ϕ_{L-} owing to t_{HL}.

Considering the "HOMO–LUMO inversion" of Pd(dmit)$_2$, there is a possibility of designing π molecules with almost degenerated HOMO (ϕ_{H+}) and LUMO (ϕ_{L-}) by constructing eclipsed dimer molecules. Thus, if "Pd(dmit)$_2$ (or Pd(dddt)$_2$ (dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate))-like dimer molecule" having a cyclophane structure could be

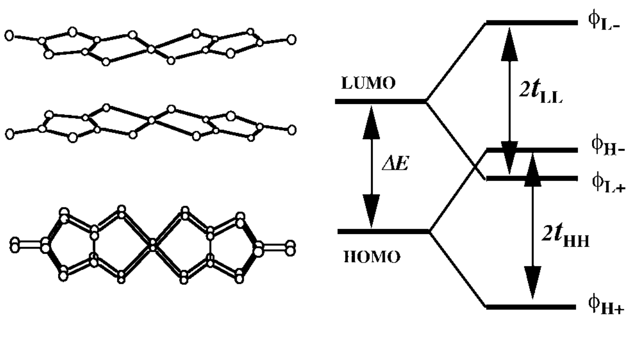


Fig. 4 Structure of the [Pd(dmit)$_2$] dimer and its energy level scheme. HOMO and LUMO of [Pd(dmit)$_2$] are split into two levels by the strong intradimer HOMO–HOMO and LUMO–LUMO interactions to form four electronic levels (see text).

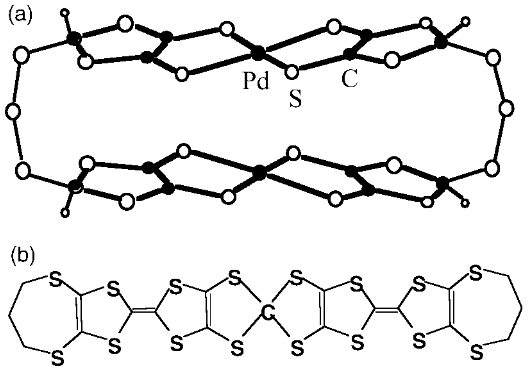


Fig. 5 Model of (a) hypothetical cyclophane-type Pd–dithiolate complex molecule and (b) hypothetical molecule "C(ptdt)$_2$".

prepared, it might be a candidate representing a molecule with a small HOMO–LUMO gap (Fig. 5a). If we can design cyclophane-type TTF-like π organic donors with a small HOMO–LUMO gap and a large intradimer interaction, a similar situation would be obtained.[32]

(2) Metal dithiolate complex with extended TTF-ligands

Another approach to design π molecules with a small HOMO–LUMO gap is the utilization of transition metal complexes with extended π ligands having a TTF skeleton (see Fig. 6).[33–36] 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. Unlike ϕ_H, ϕ_L can be mixed with the dπ orbital of the central metal atom. Therefore, the energy level of ϕ_L will change.

In order to obtain a more precise picture of the symmetries and the energy levels of HOMO and LUMO of metal complexes with TTF-like ligands, *ab initio* MO calculations were recently performed on a [Ni(ptdt)$_2$] molecule.[26] Since the details of the calculations have been already reported, only the results necessary for the present discussion are briefly presented. The calculation of the singlet ground state of [Ni(ptdt)$_2$] based on the optimized molecular structure, which has a good planarity and has approximately a D_{2h} symmetry except for the propylenedithio group, showed the symmetries of b_{2g} for HOMO and b_{1u} for LUMO, which are similar to those of the dmit metal complexes. The schematic drawings of HOMO and LUMO orbitals are shown in Fig. 3c, whose respective symmetries are consistent with the above discussion. It is noteworthy that HOMO (and LUMO) of every dithiolene complex in Fig. 3c have the same symmetry. Comparison of the results of calculations performed on the lowest triplet state and the singlet state suggests that the energy difference between HOMO and LUMO is very small.

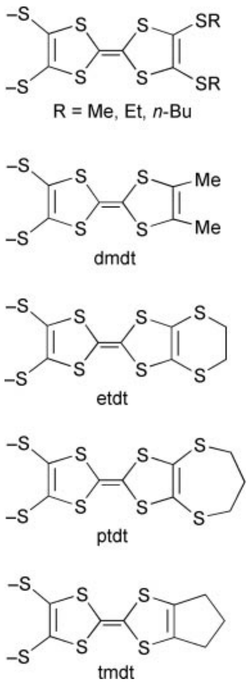


Fig. 6 Selected extended π ligands having a TTF skeleton.

These results are prompting us to "design" a different type of π molecule where two TTF-like molecules are weakly bonded through one atom. Let us consider a hypothetical molecule where the Ni atom of Ni(ptdt)$_2$ is replaced by a C atom (see Fig. 5b). At first, a similar discussion seems possible. However, there is a crucial difference between these two molecules concerning the role of the central atom. In Ni(ptdt)$_2$, the oxidation state of the central Ni metal atom can be considered to be +2 (Ni^{2+}). This means that each TTF ligand π orbital (the lowest vacant orbital) will accept one electron from the Ni^{2+} atom and the resultant ϕ_H state obtained by the bonding combination of ϕ_1 and ϕ_2 is doubly occupied. However, the $\phi_L(=\phi_1-\phi_2)$ state is vacant. Thus, the energy separation between HOMO (ϕ_H) and LUMO (ϕ_L) can be small. However, in the case of "C(ptdt)$_2$", such a "π electron transfer" from the central C atom cannot be expected. Therefore, both ϕ_H and ϕ_L are doubly occupied (or completely vacant). Consequently, the small HOMO–LUMO separation cannot be expected.

Molecular design of a metallic crystal composed of a single component molecule

In this section, a possible way to realize a neutral metallic compound composed of a single component molecule will be discussed based on the band structure and the electrical properties of [Ni(ptdt)$_2$].[26]

Band structure calculation

The crystal of neutral [Ni(ptdt)$_2$] molecules is a narrow-gap semiconductor with a room temperature conductivity of 7 S cm^{-1} (Fig. 7),[26] which is much higher than the conductivities of the crystal of neutral [Ni(dmit)$_2$] ($\sigma_{RT} = 3.5 \times 10^{-3}$ S cm^{-1})[37] and other usual neutral molecular crystals. The electrical resistivity shows a monotonous increase down to 60 K with a very small activation energy (≈0.03 eV). The crystal structure of neutral [Ni(ptdt)$_2$] indicates that the

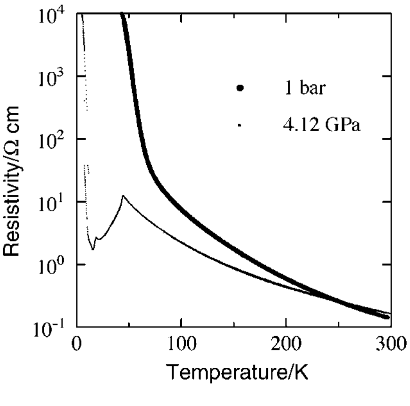


Fig. 7 Resistivities of [Ni(ptdt)$_2$] at ambient pressure and at 4.12 GPa.[25]

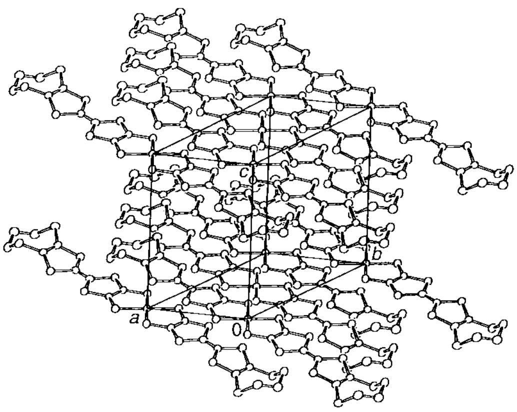


Fig. 8 Crystal structure of [Ni(ptdt)$_2$] at 90 K. The Ni(ptdt)$_2$ molecules regularly stack along the [100] direction.

intermolecular overlap is larger than in the (Me$_4$N)[Ni(ptdt)$_2$] complex (Fig. 8).[35] This structural feature is very unusual, considering that the neutral molecule usually has no attractive interactions between the neighboring molecules except for weak van der Waals interactions. Thus the [Ni(ptdt)$_2$] crystal seems to have a unique electronic structure which realizes the close assembly of the molecules.

The comparison of the result of a simple extended Hückel 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. The intra-stack overlap integrals along the [100] direction are 14.5×10^{-3} for the LUMO–LUMO overlap integral and -12.4×10^{-3} for the HOMO–HOMO overlap integral. While the overlap integral along the transverse direction is about 1/14 of that along the "chain direction" for LUMO–LUMO and 1/6 for HOMO–HOMO. Therefore, the electronic band structure of [Ni(ptdt)$_2$] is essentially one-dimensional. Since the sign of the HOMO–HOMO integral along [100] is different from that of the LUMO–LUMO integral, the system has crossing bands (see the energy dispersion curves presented in Fig. 9). Needless to say, the Fermi surfaces of a purely one-dimensional conductor with crossing bands will be destroyed by the HOMO–LUMO interaction even if it is very small. Although the calculated HOMO–LUMO overlap integral was very small (2.6×10^{-4}), the band structure of [Ni(ptdt)$_2$] calculated for $\Delta E < 0.5$ eV indicates extremely small electron and hole pockets (Fig. 9).[26] This implies that even a small HOMO–LUMO interaction can cause the Fermi surfaces to vanish in the case of a "crossing band system" with a strong one-dimensionality. Therefore, the enhancement of two-dimensionality is considered to be essential to obtain significant Fermi surfaces. Considering the difficulties in accurately evaluating weak intermolecular interactions, the conducting behavior of the [Ni(ptdt)$_2$] crystal can be qualitatively explained by the simple tight-binding band calculation, despite the fact that the system is not a semi-metal but a narrow-gap semiconductor. It is possible to imagine that the semiconducting state of this system with a fairly high conductivity and a very small activation energy can be easily changed into a metallic state by applying pressure. However, the electronic structure of [Ni(ptdt)$_2$] is different from that of ordinary molecular conductors where only HOMO (or LUMO) is responsible for the formation of the conduction bands. In fact, a [Ni(ptdt)$_2$] crystal retains the essential semiconducting properties up to 7 GPa.[26]

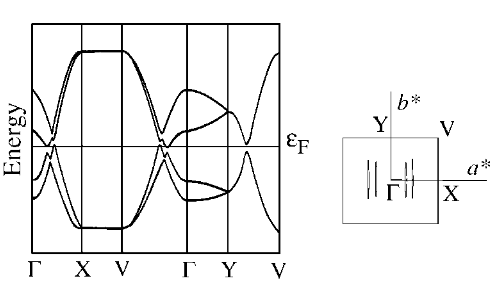


Fig. 9 Band energies and Fermi surfaces of [Ni(ptdt)$_2$] calculated by assuming ΔE (HOMO–LUMO gap) = 0.1 eV.

On the basis of these band structure examinations, 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. As mentioned before, the metal complex with extended-TTF ligands is a good candidate.

(2a) In systems with crossing bands, large HOMO–HOMO and LUMO–LUMO transverse 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) Alternatively, systems with parallel bands are desirable (especially in a system with a strong one-dimensionality) 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. As mentioned before, Fermi surfaces of a system with parallel bands are stable with respect to HOMO–LUMO interactions. Unlike the sign of the intermolecular overlap integral of HOMO–HOMO of TTF-like molecules, that of LUMO–LUMO depends on the overlapping mode. The sign of the overlap integral of LUMO–LUMO must be minus to realize a parallel band. For example, if the molecules adopt an overlapping mode where the neighboring molecule is displaced along the short axes of the molecule, parallel bands will be generated.

Development of a molecular metal composed of a single component molecule

Recently, we have prepared a Ni complex with extended-TTF ligands, tmdt (trimethylenetetrathiafulvalenedithiolate) and dmdt (dimethyltetrathiafulvalenedithiolate). Considering that the amplitudes of HOMO and LUMO of [Ni(ptdt)$_2$] are small for the sulfur atoms of the terminal trimethylenedithio group (see Fig. 3c), the sulfur atoms in the terminal rings are not important in the construction of the metal band. Therefore, we selected a more planar and shorter extended-TTF ligand with a trimethylene group (or a dimethyl group) instead of thioalkyl groups in order to increase molecular interactions. The crystal and the band structure analyses and the resistivity measurements of the crystal of [Ni(tmdt)$_2$] revealed that we had obtained the first three-dimensional metal composed of single-component planar molecules.

Crystal structure

Neutral [Ni(tmdt)$_2$] molecules crystallize into a very simple triclinic structure (Fig. 10a).[16] The unit cell contains only one molecule. The central Ni atoms are on the lattice points and half of the molecule is crystallographically independent. The molecule is ideally planar even in the terminal trimethylene group, and the planar molecules are closely packed in the crystal plane (02$\bar{1}$)(Fig. 10e). The average Ni–S is 2.177(7) Å and the S–Ni–S angle is 92.29(4)° at 123 K. The C=C bond length in the tetrathiafulvalene group is 1.362(5) Å. A comparison of the average C=C bond lengths in [Ni(tmdt)$_2$] and [Ni(ptdt)$_2$] is shown in Table 1. [Ni(tmdt)$_2$] molecules have S···S transverse short contacts (3.350(2)–3.675(2) Å) along the [100] direction, which is shown in Fig. 10b. There are two types of overlap modes, and in both cases almost half of the molecules are overlapped (Fig. 10c). The average interplanar

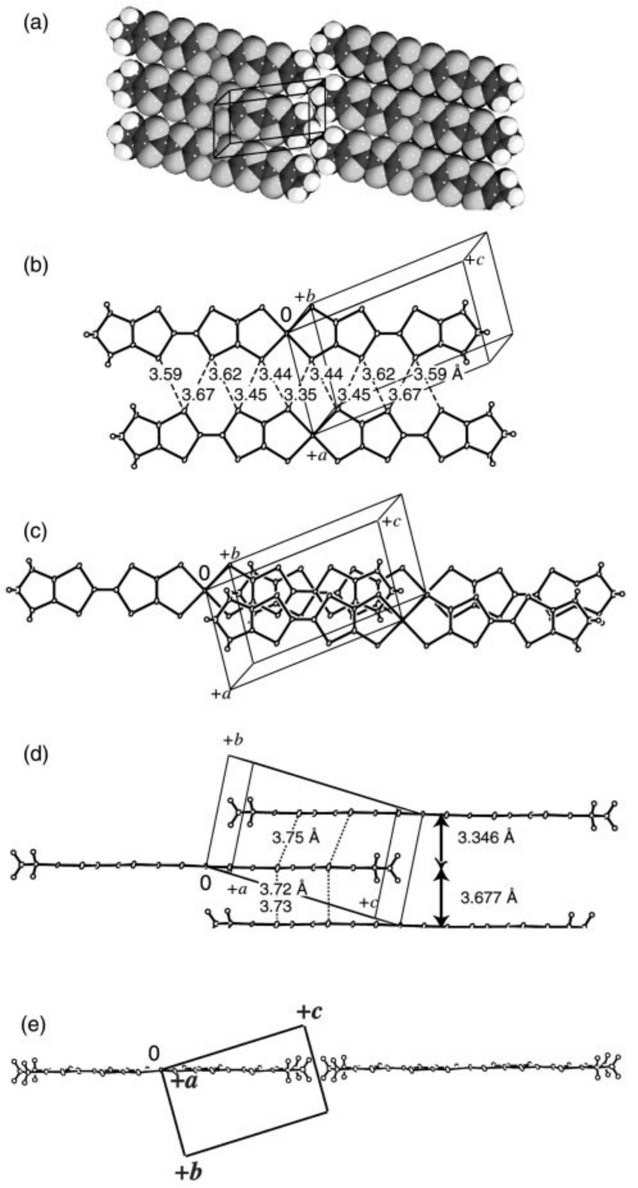
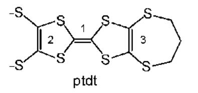
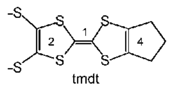


Fig. 10 (a) Crystal structure and molecular packing of [Ni(tmdt)$_2$]. (b) Crystal structure viewed along the perpendicular axis of the molecular plane and intermolecular short contacts along the *a* axis. (c) Overlap modes of [Ni(tmdt)$_2$]. (d) Side view of the molecular stacking and interplanar distances with S···S short contacts. (e) Side view of the molecules closely packed in the crystal plane (02$\bar{1}$).

distance between the molecules on (0,0,0) and (1,1,1) is 3.346 Å, and between molecules on (0,0,0) and (1,0,1) is 3.677 Å, which are shown in Fig. 10d. These structural features suggest that the system has three-dimensional intermolecular interactions.

Table 1 The comparison of the bond length of Ni–S and the average C=C bond lengths in neutral [Ni(ptdt)$_2$] and [Ni(tmdt)$_2$] 1, 2, 3 and 4 indicate C=C bond lengths (Å) in neutral [Ni(ptdt)$_2$] and [Ni(tmdt)$_2$]





	1	2	3	4	Ni–S
[Ni(ptdt)$_2$](296 K)	1.380(7)	1.384(8)	1.384(8)	—	2.183(1)
[Ni(ptdt)$_2$](90 K)	1.373(10)	1.36(1)	1.348(10)	—	2.186(1)
[Ni(tmdt)$_2$](123 K)	1.362(5)	1.352(6)	—	1.333(6)	2.177(1)

Electrical conductivity and magnetic susceptibility of [Ni(tmdt)$_2$] and an analogous system

The single crystal conductivity measurements of [Ni(tmdt)$_2$] were made nearly along the *a* axis down to 0.6 K using the four-probe method. The room temperature conductivity was 400 S cm^{-1}, which is almost one order of magnitude greater than those of typical BEDT-TTF organic superconductors (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene). The metallic behavior was observed down to 0.6 K (Fig. 11).[16] A compacted powder sample also gave high conductivity [σ(RT) = 200 S cm^{-1}] and exhibited metallic behavior down to 70 K, suggesting that a small anisotropy of the resistivity exists, which is consistent with the three-dimensional intermolecular short contacts.

Molecular crystals composed of single component molecules have been so far considered to be typical molecular crystals whose electrical properties are insulating. However, owing to their crystal structure and their resistivity, [Ni(tmdt)$_2$] crystals have removed the boundary between molecular crystals and metallic crystals.

The susceptibility measured on a polycrystalline sample with a SQUID magnetometer within the temperature range of 2–300 K exhibited a weakly temperature-dependent paramagnetic susceptibility (2.6–3.1 × 10^{-4} emu mol^{-1}), which is consistent with the metallic nature of the system (Fig. 11). The diamagnetic component of the magnetic susceptibility was estimated to be −4.6 × 10^{-4} emu mol^{-1} by using the diamagnetic susceptibility of [Ni(tmdt)$_2$] derived from the magnetic susceptibility of (Me$_4$N)$_2$[Ni(tmdt)$_2$].

Metallic behavior was also found in the crystal of an analogous molecule, [Ni(dmdt)$_2$]. The room-temperature conductivity measured on the sample of compressed pellet was 3–4 × 10^2 S cm^{-1} and retained metallic behavior down to 230 K. Below this temperature the resistivity gradually increased but was still highly conductive even at 4 K (Fig. 12). The magnetic susceptibility was measured on a polycrystalline sample from room temperature to 2 K. The magnetic properties are quite similar to [Ni(tmdt)$_2$]. The magnetic susceptibility was 2.9 × 10^{-4} emu mol^{-1} at room temperature and gradually decreased with lowering temperature (Fig. 12). Therefore, the crystal of [Ni(dmdt)$_2$] is the second single component molecular metal at liquid helium temperature.

Band structure calculation

As shown in Fig. 3c, HOMO and LUMO of [Ni(tmdt)$_2$] are similar to those of [Ni(ptdt)$_2$]. The intermolecular overlap integrals were given in Table 2. The anisotropy of the

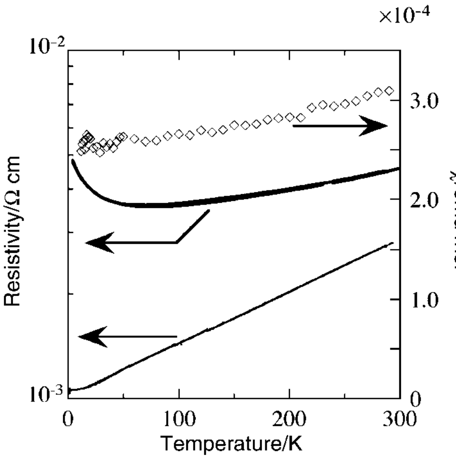


Fig. 11 Temperature dependence of the resistivities of single crystal (approximately along the *a* axis) (·) and compacted pellet (●) and magnetic susceptibility χ (◇) of [Ni(tmdt)$_2$] crystals.

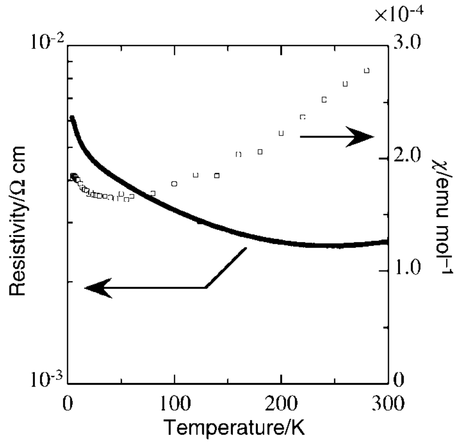
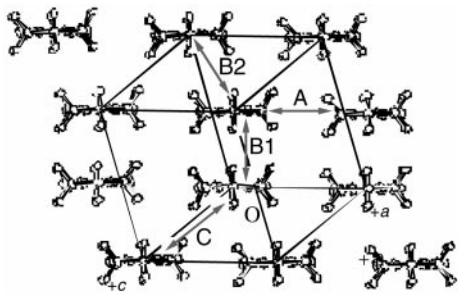


Fig. 12 Temperature dependence of the resistivities of compacted pellet (●) and magnetic susceptibility χ (□) of [Ni(dmdt)$_2$] crystals.

intermolecular interactions is quite different from that of [Ni(ptdt)$_2$]. The interstack overlap integrals along the [111] direction are 6.5×10^{-3} for LUMO–LUMO and -7.5×10^{-3} for the HOMO–HOMO overlap integrals and those along the [101] direction are 2.3×10^{-3} for the LUMO–LUMO and -3.4×10^{-3} for the HOMO–HOMO overlap integrals, respectively. There are large overlap integrals along the [001] direction for the LUMO–LUMO 4.4×10^{-3} and for the HOMO–HOMO -5.1×10^{-3}. These results show that the system has three-dimensional π bands. According to the previous discussion, three-dimensional system having large "transverse intermolecular interactions" in two directions is considered to be able to have fairly large Fermi surfaces even when the HOMO and LUMO form "crossing bands." Extended Hückel MO calculations estimated ΔE to be 0.10 eV, which is approximately the same as for [Ni(ptdt)$_2$] (0.12 eV). Furthermore, this is consistent with the result of *ab initio* calculation which suggested a small ΔE. Since the precise estimation of the value of ΔE is difficult, the band calculations were performed with varying ΔE. The system has semi-metallic Fermi surfaces for $\Delta E < 0.6$ eV. The calculated Fermi surfaces for $\Delta E = 0.1$ eV are shown in Fig. 13. Upper and lower bands are mixed around the Fermi energy (ε_F) and form electron and hole Fermi surfaces. The density of state of [Ni(tmdt)$_2$] is calculated for $\Delta E = 0.1$ eV (Fig. 14). The band width was estimated to be 0.75 eV. The cross section of the Fermi surfaces at (ξa^*, ηb^*, $0.3c^*$) and the band energy dispersion curves are given in Fig. 15 to show the crossing band character of the electronic structure.

Table 2 Overlap integrals of HOMO and LUMO ($\times 10^{-3}$) of [Ni(tmdt)$_2$] at 123 K



	A	B1	B2	C
HOMO–HOMO	3.3	6.5	2.3	4.4
LUMO–LUMO	3.6	−7.5	−3.4	−5.1
HOMO–LUMO	0.0	−7.1	−2.8	−4.8

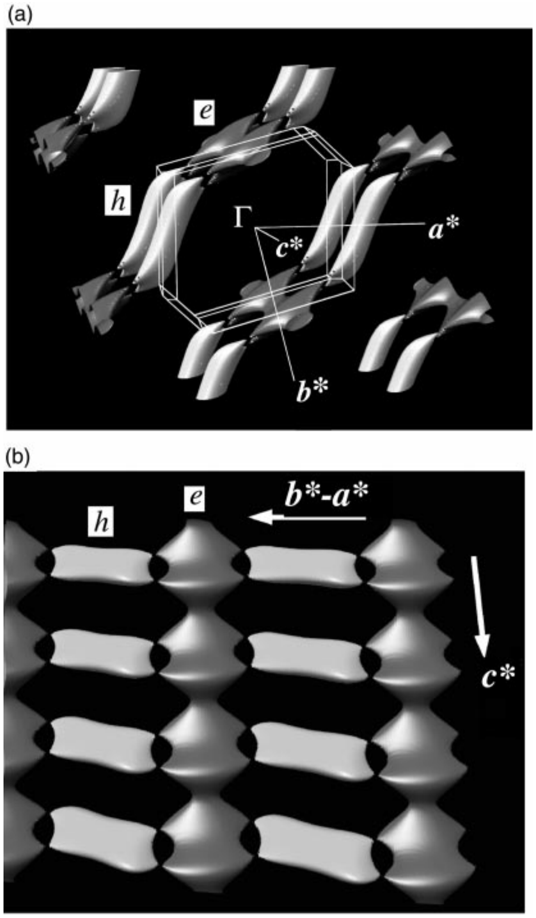


Fig. 13 Calculated electron (*e*) and hole (*h*) Fermi surfaces. The overlap integrals are given in Table 2 and ΔE is assumed to be 0.1 eV.

Possible functions of single component molecular metals

Since a novel type of "molecular metallic crystal" composed of [Ni(tmdt)$_2$] and an analogous molecule was discovered recently, it may be worthwhile to consider new possibilities for the development of new functional molecules provided by this discovery. (1) Although superconductivity was not discovered in the crystal of [Ni(tmdt)$_2$] down to 0.6 K, possibilities are large in the development of single-component molecular superconductors. As mentioned above, the Fermi surfaces of the [Ni(tmdt)$_2$] crystal are strongly diminished by the crossing band properties of the electronic structure. If we can design a single-component molecular metal with a large Fermi surface (or a large state density at Fermi energy $D(\varepsilon_F)$) by controlling the sign and the magnitude of intermolecular HOMO–HOMO, LUMO–LUMO and HOMO–LUMO interactions, it may be possible to prepare a single-component molecular superconductor. (2) Similar to metal elements such as Na and Cu, [Ni(tmdt)$_2$] molecules self-assemble to form

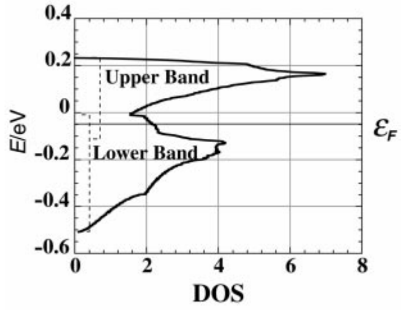


Fig. 14 Density of states of [Ni(tmdt)$_2$] calculated assuming a ΔE of 0.1 eV.

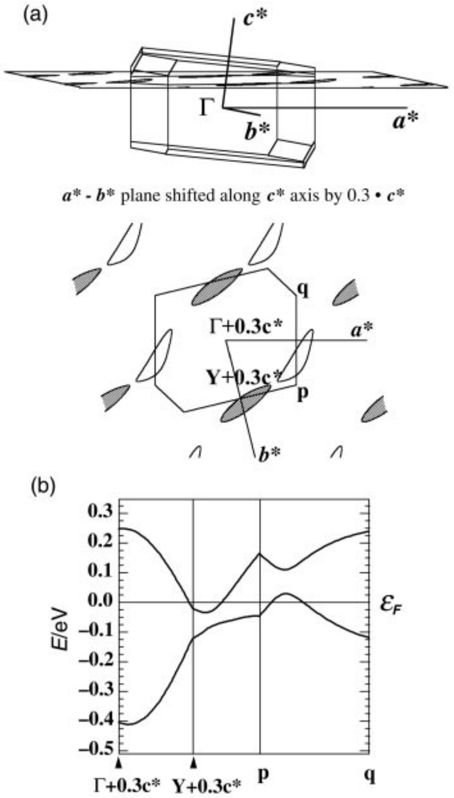


Fig. 15 Cross section of Fermi surfaces at (ξa^*, ηb^*, $0.3c^*$) and the corresponding band energy.

metallic crystals. However, needless to say, there are many differences between an atom and a molecule. Designability is one of the most advantageous nature of the molecule. Although a non-magnetic element such as Na and Cu cannot be changed into a magnetic element such as Fe and Co, [Ni(tmdt)$_2$] can be converted into a magnetic molecule by replacing the central Ni^{2+} atom with magnetic atoms such as Cu^{2+} and Co^{2+} (Fig. 16a). It is well known that the Curie temperature (T_c) for ferromagnetic crystals composed of single organic molecules such as *p*-nitrophenyl nitronyl nitroxide† is very low,[38] but the transition temperature of a molecular ferromagnet is expected to be much higher if the intermolecular magnetic interaction is mediated by conduction electrons. Therefore, magnetic molecular conductors with high T_c will be expected when using magnetic analogs of [Ni(tmdt)$_2$]. Although good crystals have not been obtained yet, [Cu(dmdt)$_2$] has recently been shown to give a fairly high conducting crystal with localized $S=\frac{1}{2}$ spins.[39] (3) New functional systems related to the solubility of the molecule might be also derived. As reported, we have prepared [Ni(ptdt)$_2$] with a propylenedithio group in order to improve the solubility of the molecule and succeeded in obtaining fairly good crystals.[26] It is expected that the solubility will be enhanced by using long alkyl-chain substituents (Fig 16b). It might be possible that a metallic (or highly conducting) crystal soluble in organic solvent can be obtained. Considering the high conductivities of the compacted powder pellets of [Ni(tmdt)$_2$] and [Ni(dmdt)$_2$], soluble metals would provide the possibility of a new method of electrical wiring. Soluble magnetic metals (or conductors) would be another possibility. If the size of dithiolene ligands can be reduced, it should be possible to design conducting liquid crystals. (4) Besides designability, the anisotropy of the molecule should provide another function. If we can manipulate [Ni(tmdt)$_2$] molecules to arrange one-dimensionally in a face-to-face manner, the array of molecules would generate a metallic state because HOMO and LUMO form parallel bands (see Fig. 16c). The band width can be controlled by slipping the molecule along the molecular short axis. On the other hand if we can arrange the molecules in such manner that the left-side of one molecule overlaps the right-side of the adjacent molecule, this array would become semiconducting because HOMO and LUMO form a crossing band. Thus, various electronic properties can be realized owing to the anisotropy of the molecule.

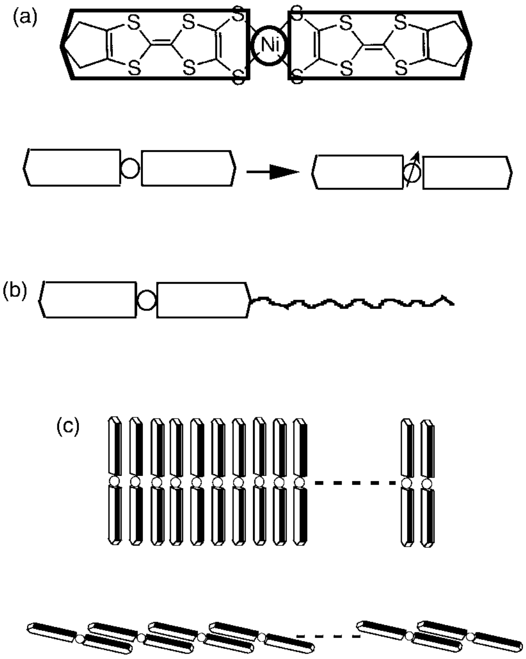


Fig. 16 Illustration of possible functions for metal dithiolate complexes with extended-TTF ligands. (a) Design of magnetic molecules by incorporation of a magnetic moment from which a magnetic single component molecular metal might be produced. (b) Design of a molecule from which a molecular conductor soluble in organic solvent might be developed. (c) Molecular arrangement producing a metallic band (top) and semiconducting band (bottom).

Experimental

Synthesis

All of the synthetic procedures (Scheme 1) 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[40] and derived methods thereof. The synthetic procedures of [Ni(dmdt)$_2$] and [Ni(tmdt)$_2$] are described in the following paragraphs, and other metal complexes (Pd, Cu, Co) were also obtained by almost similar methods.

(1) 2,3-Bis(2-cyanoethylsulfanyl)-6,7-dimethyltetrathiafulvalene: dmdt(C$_2$H$_4$CN)$_2$ 3a

Triethylamine (10 ml) was added to an acetonitrile solution (200 ml) of 4,5-dimethyl-1,3-dithiolium hexafluorophosphate **1a** (1.80 g, 6.5 mmol) and triphenyl[4,5-bis(2′-cyanoethylsulfanyl)-1,3-dithiol-2-yl]phosphonium tetrafluoroborate **2** (4.05 g, 6.5 mmol). The yellow mixture gradually turned into an orange solution. After stirring the solution for 1 hour, the solvent was removed by evaporation. Purification by silica-gel-column chromatography (CH$_2$Cl$_2$) gave 2.30 g of yellow needle crystals **3a** (88% yield).

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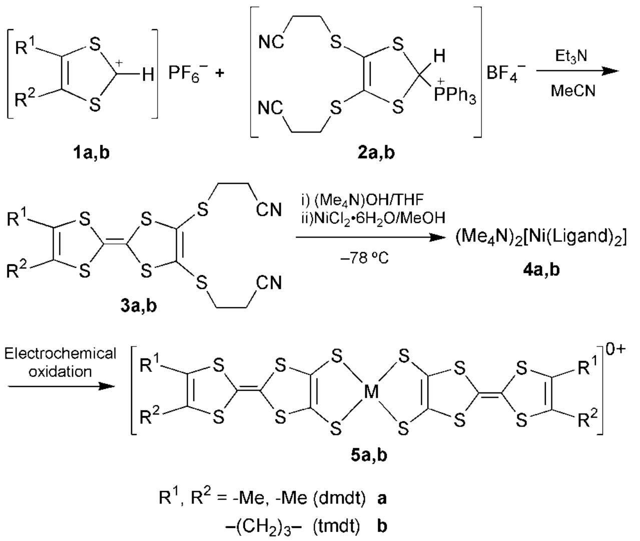
†The IUPAC name for *p*-nitrophenyl nitronyl nitroxide is 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazol-3-ium-1-oxyl.



Scheme 1

(2) $(Me_4N)_2[Ni(dmdt)_2]$ 4a

The coordination of ligands to metals was performed at low temperature. The dmdt ligand **3a** (200 mg, 0.50 mmol) was dissolved in THF (7 ml) at −78 °C and a methanol solution of 25% $(Me_4N)OH$ (1.1 ml, 3.0 mmol) was added to the solution. The mixture was warmed to room temperature gradually, and the orange solution turned to a vivid pink suspension. After cooling down to −78 °C again, $NiCl_2{\cdot}6H_2O$ (59.4 mg, 0.25 mmol) dissolved in methanol solution (5 ml) was added to the reddish suspension. After the suspension was stirred overnight and slowly warmed up to room temperature, the corresponding metal complex **4a** (180 mg, 94% yield) could be obtained by filtration.

(3) Neutral $[Ni(dmdt)_2]$ 5a

Black plate crystals of neutral $[Ni(dmdt)_2]$ were obtained electrochemically from an acetonitrile solution containing $(Me_4N)_2[Ni(dmdt)_2]$ in H-shape glass cells with Pt electrodes, by applying a 0.2 μA current for 14 days. The crystals obtained were insoluble in conventional organic solvents and stable in air. The composition was determined by electron probe X-ray microanalysis and elemental analysis.

Results of an elemental analysis: found% (calcd.%) C, 29.76 (29.67); H, 1.92 (1.87); N, 0.00 (0.00); S, 59.19 (59.40). The calcd.% is calculated as neutral $[Ni(dmdt)_2]$, $C_{16}H_{12}NiS_{12}$.

(4) 2,3-Bis(2-cyanoethylsulfanyl)-6,7-trimethylenetetrathiafulvalene: $tmdt(C_2H_4CN)_2$ 3b

Triethylamine (6.5 ml) was added to an acetonitrile solution (120 ml) of 4,5-trimethylene-1,3-dithiolium hexafluorophosphate **1b** (1.16 g, 4.0 mmol) and triphenyl[4,5-bis(2′-cyanoethylsulfanyl)-1,3-dithiol-2-yl]phosphonium tetrafluoroborate **2** (2.51 g, 4.0 mmol). The yellow mixture gradually turned into an orange solution. After stirring the solution for 1 hour, the solvent was removed by evaporation. The purification by silica-gel-column chromatography (CH_2Cl_2) gave 1.25 g of yellow needle crystals **3b** (75% yield).

(5) $(Me_4N)_2[Ni(tmdt)_2]$ 4b

The coordination of ligands to metals was performed at low temperature. The tmdt ligand **3b** (200 mg, 0.48 mmol) was dissolved in THF (7 ml) at −78 °C and a methanol solution of 25% $(Me_4N)OH$ (1.0 ml, 2.7 mmol) was added to the solution. The mixture was warmed to room temperature gradually, and the orange solution turned into a reddish suspension. After cooling down to −78 °C again, $NiCl_2{\cdot}6H_2O$ (57.0 mg, 0.24 mmol) dissolved in methanol solution (3 ml) was added to the reddish suspension. After the suspension was stirred overnight and slowly warmed up to room temperature, the corresponding metal complex **4b** (180 mg, 91% yield) could be obtained by filtration.

(6) Neutral $[Ni(tmdt)_2]$ 5b

Black plate crystals of neutral $[Ni(tmdt)_2]$ were obtained electrochemically from an acetonitrile solution containing $(Me_4N)_2[Ni(tmdt)_2]$ in H-shaped glass cells with Pt electrodes by applying 0.2 μA current for 20 days. The crystals obtained were insoluble in conventional organic solvents and stable in air. The composition was determined by electron probe X-ray microanalysis and elemental analysis. The results of an elemental analysis: found% (calcd.%) C, 32.33 (32.18); H, 1.83 (1.80); N, 0.00 (0.00); S, 57.02 (57.28). The calcd. % is calculated as neutral $[Ni(tmdt)_2]$, $C_{18}H_{12}NiS_{12}$.

Cyclic voltammetry

Cyclic voltammetry (CV) of $tmdt(C_2H_4CN)_2$, $dmdt(C_2H_4CN)_2$, $(Me_4N)_2[Ni(tmdt)_2]$ and $(Me_4N)_2[Ni(dmdt)_2]$ was carried out in acetonitrile using $(Bu_4N)ClO_4$ as supporting electrolytes at 100 mV s^{-1} over the potential range −1.8–2.0 V. The working and counter electrode were platinum and the reference electrode was Ag/Ag$^+$. These results are listed in Table 3. The CV data of these compounds indicate that the peaks at −0.80 V of $(Me_4N)_2[Ni(tmdt)_2]$ and −0.79 V of $(Me_4N)_2[Ni(dmdt)_2]$ appears to correspond to the process $Ni(tmdt)_2^{2-}{\rightarrow}Ni(tmdt)_2^{-}$ and $Ni(dmdt)_2^{2-}{\rightarrow}Ni(dmdt)_2^{-}$, and the peaks at −0.46 V and −0.48 V seem to correspond to the processes of $Ni(tmdt)_2^{-}{\rightarrow}Ni(tmdt)_2^{0}$ and $Ni(dmdt)_2^{-}{\rightarrow}Ni(dmdt)_2^{0}$. E_1 peaks of both $(Me_4N)_2[Ni(tmdt)_2]$ and $(Me_4N)_2[Ni(dmdt)_2]$ are irreversible.

Crystal structure determination of neutral $[Ni(tmdt)_2]$[26]

Crystal structure determination was performed using a black crystal with a size of 0.1 × 0.05 × 0.03 mm^3. As the size of the crystal was very small, a diffraction experiment was made on a Rigaku MERCURY CCD system at 123 K to collect a sufficient number of reflections. The lattice constants are: $a = 6.376(3)$, $b = 7.359(1)$, $c = 12.012(7)$ Å, $\alpha = 90.384(7)$, $\beta = 96.688(4)$, $\gamma = 103.587(4)°$, $V = 543.7(4)$ Å^3 with space group $P\bar{1}$, $Z = 1$. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R-value based on observed 9576 reflections was 0.098 and based on the selected 5905 reflections [$I > 2.0(I)$] was 0.069.

Conclusion

We presented the basic idea on the design of a single component molecular metal. The crucial step is the development

Table 3 Cyclic voltammetry of ligands and Ni complexes (V *vs.* Ag/Ag$^+$) 0.1 M (n-$Bu_4N)ClO_4$/MeCN WE;Pt, CE;Pt, RE;Ag/Ag$^+$0.1 M (n-$Bu_4N)ClO_4$/MeCN

	E_2/V	E_1/V	E_2-E_1/V
$dmdt(C_2H_4CN)_2$	+0.47	+0.16	0.31
$tmdt(C_2H_4CN)_2$	+0.46	+0.16	0.30
$ptdt(C_2H_4CN)_2$	+0.55	+0.29	0.26

	E_1/V^a	E_2/V	E_3/V	E_2-E_3/V
$(Me_4N)_2[Ni(dmdt)_2]$	+0.40	−0.48	−0.79	0.31
$(Me_4N)_2[Ni(tmdt)_2]$	+0.55	−0.46	−0.80	0.34
$(Me_4N)_2[Ni(ptdt)_2]$	+1.05	−0.30	−0.60	0.30

^{a}Irreversible

of a molecule with a small HOMO–LUMO gap and a TTF-skeleton. Needless to say, in the π conjugated system, the HOMO–LUMO gap can be reduced by extending the π systems. However, we propose a new idea to reduce the HOMO–LUMO gap, which will be useful in future studies on the development of new functional molecular systems because the properties of the molecular system are mainly governed by the nature of frontier orbitals. We reported the synthesis, the structure analysis and the physical properties of the first single-component three-dimensional molecular metal [Ni(tmdt)$_2$] with a stable metallic state down to very low temperatures. An analogous single-component molecular crystal [Ni(dmdt)$_2$] is also metallic down to low temperatures. The discovery of a single-component molecular metal will provide various possibilities for future studies on the development of new functional molecular systems.

Acknowledgements

The authors thank Mr Y. Okano for the band structure calculations on [Ni(tmdt)$_2$]. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References

1 R. Comes, M. Lambert, H. Launois and H. R. Zeller, *Phys. Rev.*, 1973, **B8**, 571; B. Renker, l. Pintchovius, W. Glaser, H. Rietschel, R. Comes, L. Liebert and W. Drexel, *Phys. Rev. Lett.*, 1974, **32**, 836; H. J. Deiseroth and H. Shultz, *Phys. Rev. Lett.*, 1974, **33**, 963.

2 K. Krogmann and H. D. Hausen, *Z. Anorg. Allg. Chem.*, 1968, **358**, 67; K. Krogmann, *Angew. Chem., Int. Ed.*, 1969, **8**, 35.

3 P. S. Gomm and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, 1972, 334; T. W. Thomas, M. M. Labes, M. M. Gomm and A. E. Underhill, *J. Chem. Soc., Chem. Commun.*, 1972, 322.

4 J. P. Ferraris, D. O. Cowan, V. Walatka Jr. and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948; "*Chemistry and Physics of One-dimensional Metals*" ed. by H. J. Keller, NATO ASI, **Series B, Volume 25**, 1977.

5 D. Jérome, M. Mazaud, M. Ribault and K. Bechgaard, *J. Phys. Lett.*, 1980, **41**, L95.

6 L. Brossard, M. Ribault, L. Valade and P. Cassoux, *Physica B & C (Amsterdam)*, 1986, **143**, 378; P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.

7 A. W. Graham, M. Kurmoo and P. Day, *J. Chem. Soc., Chem Commun.*, 1995, 2061; M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hurtsthouse, J. M. Caufield, J. Singleton, L. Ducasse and P. Guionneau, *J. Am. Chem. Soc.*, 1995, **117**, 12209.

8 E. Ojima, H. Fujiwara, K. Kato, H. Kobayashi, H. Tanaka, A. Kobayashi, M. Tokumoto and P. Cassoux, *J. Am. Chem. Soc.*, 1999, **121**, 5581; H. Fujiwara, E. Ojima, Y. Nakazawa, B. Zh. Narymbetov, K. Kato, H. Kobayashi, A. Kobayashi, M. Tokumoto and P. Cassoux, *J. Am. Chem. Soc.*, 2001, **123**, 306.

9 T. Otsuka, A. Kobayashi, Y. Miyamoto, J. Kiuchi, N. Wada, E. Ojima, H. Fujiwara and H. Kobayashi, *Chem. Lett.*, 2000, 732.

10 H. Kobayashi, A. Sato, E. Arai, H. Akutsu, A. Kobayashi and P. Cassoux, *J. Am. Chem. Soc.*, 1997, **119**, 12392.

11 S. Uji, H. Shinagawa, T. Terashima, C. Terakura, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka and H. Kobayashi, *Nature*, 2001, 908.

12 T. Ito, H. Shirakawa and S. Ikeda, *J. Polym. Sci., Polym. Chem., Ed.*, 1974, **12**, 11; H. Shirakawa, E. J. Louis, A. G. MacDiamid, C. K. Chiang and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, 578.

13 J. H. Schön, Ch. Kloc and B. Batlogg, *Nature*, 2000, **406**, 702; J. H. Schön, Ch. Kloc and B. Batlogg, 2000, **408**, 549.

14 For example: T. M. Barclay, A. W. Codes, R. H. de Laat, J. D. Goddard, R. C. Haddon, D. Y. Jeter, R. C. Mawhinney, R. T. Oakley, T. T. M. Palstra, G. W. Patenaude, R. W. Reed and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1997, **119**, 2633.

15 P. Cassoux, *Science*, 2001, **291**, 263.

16 H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki and A. Kobayashi, *Science*, 2001, **291**, 285.

17 N. C. Schiødt, T. Bjørnholm, K. Bechgaard, J. J. Neumeier, C. Allgeier, C. S. Jacobsen and N. Thorup, *Phys. Rev. B*, 1996, **53**, 1773.

18 D. Belo, H. Alves, E. B. Lopes, M. T. Duarte, V. Gama, R. T. Henriques, M. Almeida, A. Pérez-Benítez, C. Rovira and J. Veciana, *Chem. Eur. J.*, 2001, **7**, 511.

19 N. Thorup, G. Rindorf, H. Soling and K. Bechgaard, *Acta. Cryst. B*, 1981, **37**, 1236.

20 T. Mori, A. Kobayashi, Y. Sasaki and H. Kobayashi, *Chem. Lett.*, 1982, 1923.

21 A. E. Underhill and M. M. Ahmad, *J. Chem. Soc., Chem. Commun.*, 1982, 390; A. Kobayashi, T. Mori, Y. Sasaki, H. Kobayashi, M. M. Ahmad and A. E. Underhill, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3262.

22 A. Kobayashi and H. Kobayashi, Chapter 5 in *Handbook of Organic Conductive Molecules and Polymers*, **Vol. 1**, ed., H. S. Nalwa, John Wiley & Sons, Chichester, New York, 1997.

23 The band energy ε(k) can be obtained from the simple equation, $(\varepsilon_H(k)-\varepsilon(k))(\varepsilon_L(k)-\varepsilon(k))-t_{HL}{}^2=0$. That is, $\varepsilon_\pm(k)=[(\varepsilon_H(k)+\varepsilon_L(k))\pm\{(\varepsilon_H(k)-\varepsilon_L(k))^2+4t_{HL}{}^2\}^{1/2}]/2$, where $\varepsilon_H(k)$ and $\varepsilon_L(k)$ are the band energies of the system without HOMO–LUMO interaction and $\varepsilon_\pm$ are those of upper and lower bands (see Fig. 2). If $\varepsilon_H(k_o)=\varepsilon_L(k_o)$ (that is, the two bands cross with each other at $k=k_o$), $\varepsilon_\pm(k_o)=\varepsilon_H(k_o)\pm|t_{HL}|$. Thus, the upper and lower bands are separated by the energy gap of $2|t_{HL}|$, which means the disappearance of the Fermi surfaces. Contrary to this, the Fermi surfaces of the parallel bands are stable against the HOMO–LUMO interaction.

24 A. Kobayashi, H. Kim, Y. Sasaki, R. Kato and H. Kobayashi, *Solid State Commun.*, 1987, **62**, 57.

25 R. Kato, H. Kobayashi, A. Kobayashi and Y. Sasaki, *Chem. Lett.*, 1985, 131.

26 A. Kobayashi, H. Tanaka, M. Kumasaki, H. Torii, B. Narymbetov and T. Adachi, *J. Am. Chem. Soc.*, 1999, **121**, 10763.

27 S. Tanaka and Y. Yamashita, *Synth. Met.*, 1997, **84**, 229; S. Tanaka, private communications.

28 A. Tsuda, H. Furuta and A. Osuka, *Angew. Chem., Int. Ed.*, 2000, **39**, 2549.

29 E. Arai, H. Fujiwara, H. Kobayashi, A. Kobayashi, K. Takimiya, T. Otsubo and F. Ogura, *Inorg. Chem.*, 1998, **37**, 2850; E. Ojima *et al.*, to be submitted.

30 A. Kobayashi, A. Miyamoto, H. Kobayashi, A. Clark and A. E. Underhill, *Chem. Lett.*, 1991, 2163; A. Kobayashi, A. Miyamoto, H. Kobayashi, A. Clark and A. E. Underhill, *J. Mater. Chem.*, 1991, **1**, 827; H. Kobayashi, K. Bunn, T. Naito, R. Kato and A. Kobayashi, *Chem. Lett.*, 1992, 1909.

31 A. Kobayashi, A. Sato, T. Naito and H. Kobayashi, *Mol. Cryst. Liq. Cryst.*, 1996, **284**, 85.

32 The studies on cyclophane donor–acceptor systems by Staab *et al.* showed that if the cyclophane "links" were short enough to constrain orientations they tended to induce the non-planarity in the π-electron systems, whereas longer chains which did not produce this non-planarity failed to achieve the same structural constraints [R. Reimann and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, 1978, **17,** 374; H. A. Staab, G. H. Knaus, H.-E. Henke and C. Krieger, *Chem. Ber.*, 1983, **116**, 2785]. These facts seem to suggest the difficulty of the design of the molecular metals based on the cyclophane-type multi-sulfur molecules. On the other hand, the heavily bent structure of [Pd(dmit)$_2$] molecules in the conducting crystals seems to show that the molecular deformation is not always disadvantageous to construct the conduction bands [A. Kobayashi, H. Kim, Y. Sasaki, K.Murata, R. Kato and H. Kobayashi, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 361]. Furthermore, considering the phenomena of the self-assembly of molecules, the strict constraint of the dimerized molecules by short chains seems not to be an inevitable condition. We have recently examined the molecular structure of a novel trisulfide double-bridged TTF dimer with a cyclophane-type structure [H. Fujiwara, E. Arai and H. Kobayashi, *J. Mater. Chem.*, 1998, **8**, 829]. The TTF dimer takes a loosely overlapping conformation in the neutral state but the dimer molecule takes a more rigid conformation in the cation state, which is of course related to the stabilization of the electronic energy by the extraction of an electron from the molecular orbital derived from the anti-bonding conbination of HOMOs of TTF molecules. Probably the eclipsed conformation will be realized automatically if the crystal composed of TTF-dimers is stabilized by the metal band formation.

33 N. L. Narvor, N. Robertson, T. Weyland, J. D. Killburn, A. E. Underhill, M. Webster, N. Svenstrup and J. Becker, *J. Chem.*

Soc., Chem. Commun., 1996, 1363; N. L. Narvor, N. Robertson, E. Wallace, J. D. Killburn, A. E. Underhill, P. N. Bartlett and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1996, 823.

34 M. Nakano, A. Kuroda, T. Maikawa and G. Matsubayashi, *Mol. Cryst. Liq. Cryst.*, 1996, **284**, 301.

35 M. Kumasaki, H. Tanaka and A. Kobayashi, *J. Mater. Chem.*, 1998, **8**, 301; A. Kobayashi, M. Kumasaki and H. Tanaka, *Synth. Met.*, 1999, **102**, 1768.

36 K. Ueda, M. Goto, M. Iwamatsu, T. Sugimoto, S. Endo, N. Toyota, K. Yamamoto and H. Fujita, *J. Mater. Chem.*, 1998, **8**, 2195; Y. Misaki, Y. Tani, M. Taniguchi, T. Maitani, K. Tanaka and K. Bechgaard, *Mol. Cryst. Liq. Cryst.*, 2000, **343**, 59.

37 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.

38 M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, *Chem. Phys. Lett.*, 1991, **186**, 401.

39 H. Tanaka, H. Kobayashi, W. Suzuki and A. Kobayashi, to be submitted.

40 L. Binet, J. M. Fabre, C. Montginoul, K. B. Simonsen and J. Becher, *J. Chem. Soc., Perkin Trans. 1*, 1996, 783.