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Organic Metals Based on an Asymmetric π Donor PEDT-TSF, $(\text{PEDT-TSF})_2\text{FeX}_4$ (PEDT-TSF = Pyrazinoethylenedithiotetraselenafulvalene; X = Cl, Br)

Saika Otsubo, Kazuyuki Takahashi,* HengBo Cui, Yoshinori Okano, and Hayao Kobayashi
Institute for Molecular Science, and CREST, Japan Science and Technology Agency, Myodaiji, Okazaki 444-8585

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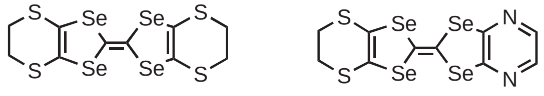
$(\text{PEDT-TSF})_2\text{FeCl}_4$ is the first κ-type organic metal based on an asymmetric π donor with a pyrazine ring, PEDT-TSF. $(\text{PEDT-TSF})_2\text{FeBr}_4$ has another type of metallic layers composed of unique tetradic PEDT-TSF columns, suggesting that PEDT-TSF is a suitable donor to afford metallic conductors. The extended Hückel tight-binding band examination showed a suitable choice of the atomic orbital parameters to be essential to obtain reasonable results.

Recently, synergetic action of metallic π electrons and localized magnetic moments of transition metal atoms incorporated in the organic conductors have attracted a considerable interest. However, only a few systems[1] have been known to exhibit significant π–d coupling except the systems such as λ-$(\text{BETS})_2\text{Fe}_x\text{Ga}_{1-x}\text{Cl}_4$ $(0 < x < 1)$ and κ-$(\text{BETS})_2\text{FeBr}_4$ (BETS = bis(ethylenedithio)tetraselenafulvalene) that show various unprecedented π–d coupled electromagnetic properties.[2,3] The intermolecular short contacts between sulphur or selenium atoms of the donors and halogen atoms of the anions are essential to realize strong π–d coupling. Such short contacts through halogen atoms are known as "halogen bonding."[4] Recently, construction of supramolecular structures in organic conductors by iodine bonding has been reported.[5] In order to search for the suitable donors to construct magnetic organic conductors, we have focused on a TTF-like asymmetric π donor with peripheral nitrogen atoms, PEDT-TSF, which is expected to be a potential "halogen-bonding acceptor." Several years ago, we have synthesized PEDT-TSF (Scheme 1) and obtained various metallic conductors of PEDT-TSF with linear (Au(CN)_2^- and AuBr_2^-), tetrahedral (BF_4^-, ClO_4^-, and ReO_4^-), and octahedral (PF_6^- and AsF_6^-) anions.[6] In this paper, we describe the structures and physical properties of PEDT-TSF conductors with typical tetrahalide anions such as FeCl_4^-, GaCl_4^-, and FeBr_4^-.



BETS PEDT-TSF

Scheme 1.

PEDT-TSF was prepared according to the previously reported procedure[6] and the crystals of FeCl_4^-, GaCl_4^-, and FeBr_4^- salts were prepared electrochemically. X-ray crystal structure analysis of FeCl_4^- salt revealed that the crystal is the first κ-type conductor of PEDT-TSF (Figure 1).[7] PEDT-TSF molecules are dimerized with head-to-head intermolecular overlapping to form κ-type donor layer having a head-to-tail dimer arrangement. There are many intermolecular Se (S)···Se (S) contacts shorter than the van der Waals distance (e.g., Se···Se: 3.579, 3.711, and 3.729 Å; Se···S: 3.391, 3.635, and 3.675 Å; S···S: 3.586 Å). Whereas the shortest Se···N distance of 3.517 Å is comparable to the corresponding van der Waals distance (3.50 Å). There is no short contact between chlorine atoms of FeCl_4^- anion and hetero atoms of PEDT-TSF, suggesting that the self-assembling nature of the donor molecule surpasses the halogen bonding. Similar strong self-assembling nature of PEDT-TSF has been also observed in $(\text{PEDT-TSF})_2\text{BF}_4$.[6]

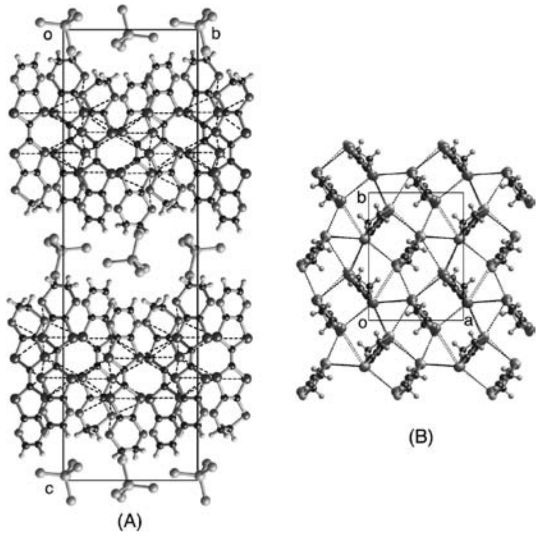


Figure 1. (A) Crystal structure of κ-$(\text{PEDT-TSF})_2\text{FeCl}_4$. The broken lines indicate short intermolecular contacts. (B) κ-Type molecular arrangement of PEDT-TSF.

The temperature dependence of the resistivity of κ-$(\text{PEDT-TSF})_2\text{FeCl}_4$ showed a metallic behavior down to about 60 K ($\sigma(\text{RT}) \approx 10\,\text{S cm}^{-1}$). Considering the insufficient quality of the crystals, the sluggish resistivity increase at low temperature ($\sigma(300\,\text{K})/\sigma(4\,\text{K}) \approx 3$) does not seem to be intrinsic nature of the crystal. The SQUID susceptibility measurements showed Curie paramagnetism of high-spin Fe^{3+} moments ($\theta = -0.08\,\text{K}$). This is consistent with no short contact between donor and anion, and between anions.

The GaCl_4^- salt was found to be isostructural to κ-$(\text{PEDT-TSF})_2\text{FeCl}_4$ salt.[8] The temperature dependence of the resistivity was metallic down to 20 K. As reported before,[6] in spite of a slight resistivity increase at low temperature, the crystal seems to be essentially metallic down to 4 K ($\sigma(300\,\text{K}) \approx 50\,\text{S cm}^{-1}$, $\sigma(\text{RT})/\sigma(4\,\text{K}) \approx 2$).

X-ray examination of $(\text{PEDT-TSF})_2\text{FeBr}_4$[9] showed that the crystal was not isotructural to κ-$(\text{PEDT-TSF})_2\text{MCl}_4$ (M = Fe and Ga) and also previously reported PEDT-TSF salts with tetrahedral anions.[6] The donors are stacked alternately in a head-to-tail manner with a large slip distance to form tetradic zig-zag columns (Figure 2). There are many intermolecular short

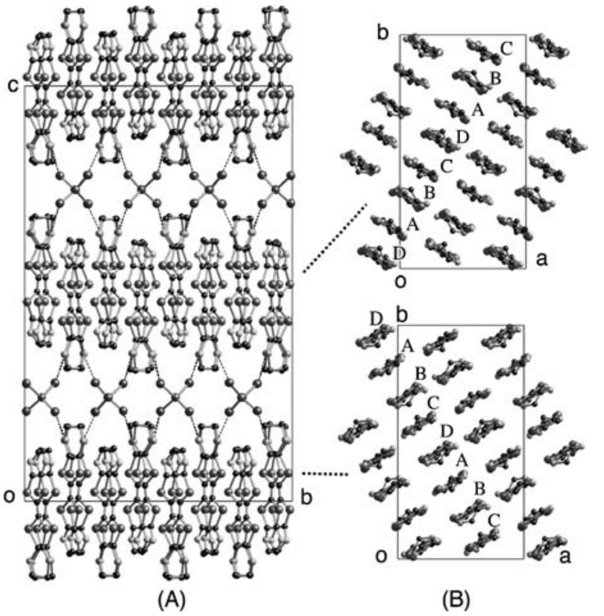


Figure 2. (A) Crystal structure of (PEDT-TSF)$_2$FeBr$_4$. The doted line is the eight S···Br contacts shorter than van der Waals distance (3.80 Å). (B) Molecular arrangements of the adjacent donor layers.

Se···Se, and Se···N contacts (e.g., Se···Se: 3.475, 3.496, and 3.507 Å; Se···N: 3.285, 3.314, and 3.338 Å). In addition, there are a number of short S···Br contacts (3.65–3.74 Å) between donor and anion layers, whose distances are quite close to those observed in κ-(BETS)$_2$FeBr$_4$. These short S···Br contacts suggest that the self-assembling ability of donors is comparable to halogen-bonding effect between Br and S atoms. The temperature dependence of the susceptibilities exhibited Curie–Weiss behavior ($\theta = -13.3$ K). However, no magnetic transition was observed down to 2 K. The crystal showed a weakly metallic behavior down to about 50 K ($\sigma(\mathrm{RT}) \approx 10\,\mathrm{S\,cm^{-1}}$).

The extended Hückel tight-binding band calculation has been useful to search and design organic metals and magnetic organic conductors. The atomic parameters usually used in the extended Hückel band calculation of organic conductors gave unsatisfactory results. Therefore, another type of molecular orbital (MO) calculations such as MOPAC (PM3, AM1), Gaussian (STO-3G, 3-21G) was performed. In order to reproduce essentially the same results by extended Hückel calculation, suitable choice of atomic parameters was important.[10] It was found that HOMO (the highest occupied molecular orbital) of PEDT-TSF has opposite signs on N and S (Se) atoms (Figure 3). It is well known that HOMO of π donor of TTF-family has the same sign on every heteroatom (S and Se), which is crucial to realize two-dimensional metallic band. In fact, the extended Hückel tight-binding band calculation of κ-(PEDT-TSF)$_2$FeCl$_4$ gave essentially two-dimensional but slightly open Fermi surfaces. The tight-binding band examination of (PEDT-TSF)$_2$FeBr$_4$ also suggested that the system is two-dimensional metal or extremely narrow gap semiconductor, which is consistent with the weakly metallic behavior of the system.

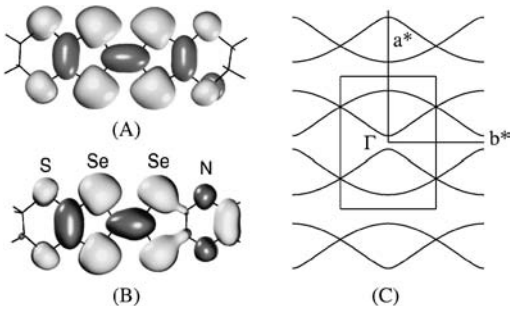


Figure 3. HOMOs of (A) BETS and (B) PEDT-TSF of κ-(PEDT-TSF)$_2$FeCl$_4$. The black and light gray parts of HOMO represent plus and minus regions of the wave functions, respectively. (C) Cross section of Fermi surfaces.

In summary, metallic properties of κ-(PEDT-TSF)$_2$MCl$_4$ (M = Fe and Ga) and (PEDT-TSF)$_2$FeBr$_4$ indicate that PEDT-TSF is a suitable donor to construct various types of organic metal layers. If we can select appropriate magnetic anions with halogen bonding especially containing bromine atoms, the construction of novel organic/inorganic composite magnetic conductors will be highly possible.

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7 The crystal data of κ-(PEDT-TSF)$_2$FeCl$_4$: orthorhombic, $P2_12_12_1$, $a = 8.125(4)$, $b = 11.058(5)$, $c = 37.57(2)$ Å, $V = 3386(2)$ Å^3, $Z = 4$, $R = 0.067$. No polymorphism was observed by the measurement of several crystals.

8 The crystal data of κ-(PEDT-TSF)$_2$GaCl$_4$: orthorhombic, $P2_12_12_1$, $a = 8.147(3)$, $b = 11.060(5)$, $c = 37.50(2)$ Å, $V = 3369(2)$ Å^3, $Z = 4$, $R = 0.061$.

9 The crystal data of (PEDT-TSF)$_2$FeBr$_4$: monoclinic, $C2/c$, $a = 13.990(9)$, $b = 25.41(5)$, $c = 38.77(2)$ Å, $\beta = 95.195(3)^\circ$, $V = 13727(14)$ Å^3, $Z = 8$, $R = 0.095$. No polymorphism was observed by the measurement of several crystals.

10 Among various sets of the previously reported AO parameters, the following parameters were adopted: IQ (eV) and $\zeta =$ -13.6, 1.3 (H, 1s); -21.4, 1.625 (C, 2s); -11.4, 1.625 (C, 2p); -26, 1.875 (N, 2s); -14.8, 1.65 (N, 2p); -20, 1.817 (S, 3s); -13.3, 1.817 (S, 3p); -20.5, 2.44 (Se, 4s); -14.4, 2.07 (Se, 4p).

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