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Communication

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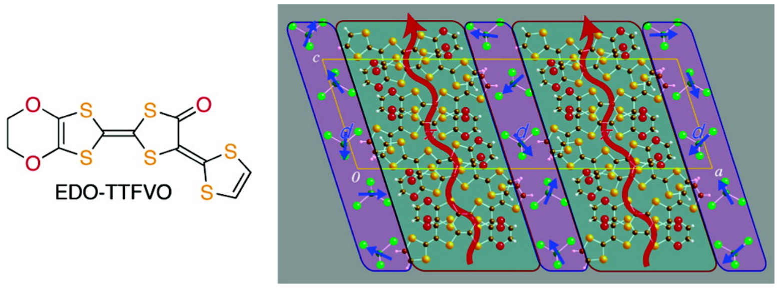

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COMMUNICATIONS

Stable Metallic Behavior and Antiferromagnetic Ordering of Fe(III) *d* Spins in (EDO-TTFVO)$_2$·FeCl$_4$

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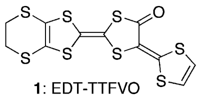
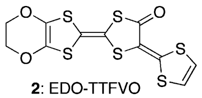
A number of conducting organic materials that incorporate localized spins have been prepared, and their conducting and magnetic properties have been investigated to understand the interaction between conducting π electrons and localized spins.[1] Several salts based on tetrathiafulvalene (TTF)-type donor molecules with magnetic anions showed interesting phenomena in which metallic and/or superconductivities and a magnetic ordered state coexist in the identical system and interact with each other, like a ferromagnetic metal of (ET)$_3$·[MnCr(C$_2$O$_4$)$_3$][2] and antiferromagnetic superconductors of κ-(BETS)$_2$·FeX$_4$ (X = Cl, Br),[3] where ET = bis(ethylenedithio)TTF and BETS = bis(ethylenedithio)tetraselenafulvalene. Especially in κ-(BETS)$_2$·FeBr$_4$, metamagnetism of the magnetic anion layer enabled a switching of the conductivity through the $\pi-d$ interaction and was realized a field-induced superconductivity around 12.5 T. To develop new types of magnetic molecular conductors, we focused on donor molecules with bent molecular structures and recently discovered a ferromagnetic ordering of Fe(III) *d* spins of the FeBr$_4^-$ ions at 1 K in the 2:1 FeBr$_4^-$ salt of EDT-TTFVO (ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolemethide, **1**).[4] However, this salt exhibited a metal-to-semiconductor transition around 170 K. To suppress such a transition, we noticed the introduction of an ethylenedioxy group because of its strong tendency to form stable metallic states as often observed in bis(ethylenedioxy)TTF (BO) salts. Here we report the crystal structure and physical properties of the 2:1 FeCl$_4^-$ salt of a new donor molecule, EDO-TTFVO (**2**) and clear the coexistence of stable metallic behavior down to 0.3 K and antiferromagnetic ordering of the Fe(III) *d* spins at 3 K.



1: EDT-TTFVO



2: EDO-TTFVO

The new donor molecule **2**[5] was synthesized according to the method similar to the synthesis of **1**.[6] Electrochemical oxidation of **2** was performed in chlorobenzene/ethanol (9:1, v/v) at 25 °C in the presence of Et$_4$N·FeCl$_4$ under a constant current of 0.1 μA, and after 1 week was obtained a black needlelike crystal of **2**$_2$·FeCl$_4$. The crystal structure analysis of this salt was performed.[7] There are two crystallographically independent donor molecules (**A** and **B**), and they are located on the mirror plane parallel to the molecular planes, indicating complete planarity of their molecular structures. As shown in Figure 1b, the donor molecules form **A**−**B**−**A**−**B**-type side-by-side arrays along the *c*-axis with several short S···S(O) contacts, suggesting a strong intermolecular interaction along the *c*-axis. In the *bc*-layer, the donor molecules construct two identical diagonal stackings like **A**−**A′**−**B**−**B′** along [0 2 1] and [0 2 −1] directions. This donor array resembles a β''-type packing motif. There is a relatively short hydrogen bond (CH···O, 2.87 Å) between the ethylenedioxy groups along the p1 direction, which might determine this characteristic packing motif as often observed in the BO salts. The FeCl$_4^-$ ions form a two-dimensional rectangular arrangement in the *bc*-plane with a short Cl···Cl contact (3.48 Å) along the *b*-axis. In addition, there is a short Cl···S contact (3.60 Å) between the 1,3-dithiole ring of the donor molecule and the FeCl$_4^-$ ion, suggesting a possibility of a strong $\pi-d$ interaction by virtue of the characteristic bent molecular structure of **2**.

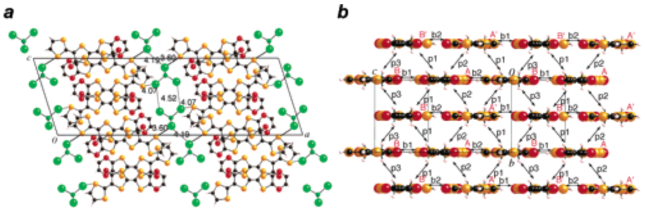


Figure 1. (a) Crystal structure of **2**$_2$·FeCl$_4$ projected down to the *ac*-plane. (b) Donor array in the *bc*-conduction plane and overlap integrals between the neighboring donor molecules in **2**$_2$·FeCl$_4$: b1 = 7.0 × 10^{-3}, b2 = 10.4 × 10^{-3}, p1 = 10.9 × 10^{-3}, p2 = −4.3 × 10^{-3}, and p3 = −3.5 × 10^{-3}.

The band calculation was performed by a tight-binding method based on an extended Hückel approximation (Figures 1b and 2a). There are two different overlaps (b1, 7.0 × 10^{-3}; and b2, 10.4 × 10^{-3}) along the side-by-side direction. The overlap integrals along the diagonal stacking are also relatively large, p1 (**A**−**B**), 10.9 × 10^{-3}; p2 (**A**−**A′**), −4.3 × 10^{-3}; and p3 (**B**−**B′**), −3.5 × 10^{-3}, and have almost the same order of amplitudes as b1 and b2, suggesting a two-dimensional interaction in the conduction *bc*-plane. As a result, the calculated Fermi surface has a two-dimensionality and closes along the Y−M line but opens along the Z−M line, giving rise to one closed ellipse around Z-point and two opened Fermi surfaces along the M−Y−M line (Figure 2a).

Electrical resistivity (ρ) of the single crystal was measured down to 0.3 K. The electrical conductivities measured along the conduction plane and perpendicular to the conduction plane are 8.4 and 0.02 S cm^{-1} at room temperature, respectively, and stable metallic behaviors were kept down to 0.3 K for both of the measurements, as shown in Figure 2b. Since all of the salts obtained so far by our donor molecules showed semiconducting behavior or metal-to-semiconductor transitions at relatively high temperature regions

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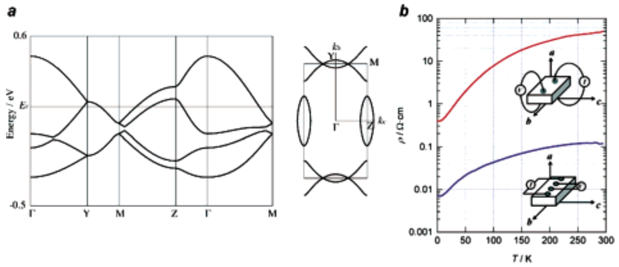

Figure 2. (a) Band dispersion and Fermi surface. (b) Temperature dependence of electrical resistivities down to 0.3 K measured along the conduction plane (blue) and perpendicular to the conduction plane (red).

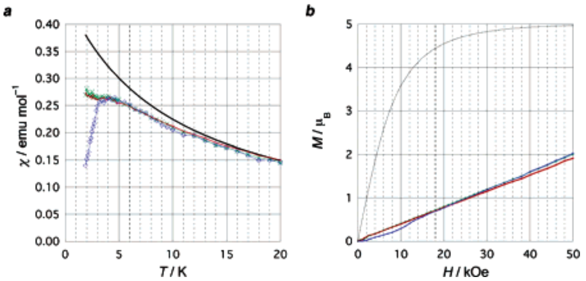

Figure 3. (a) Temperature dependence of χ in the temperature range of 1.9−20 K at 1 kOe and a Curie−Weiss fitting curve with $C = 4.45$ emu K mol^{-1} and $\theta = -9.8$ K (blue: $H \parallel a$; red: $H \parallel b$; green: $H \parallel c$). (b) H dependence of M in the H range of 0−50 kOe at 1.9 K and a Brillouin function with $g = 2.0$, $S = 5/2$, and $T = 1.9$ K (black).

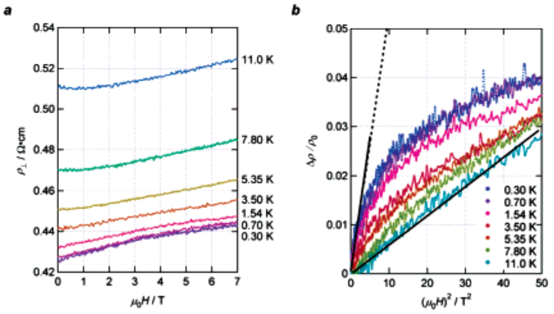

Figure 4. (a) Magnetic field (H) dependence of magnetoresistances up to 7 T at different temperatures of 0.30, 0.70, 1.54, 3.50, 5.35, 7.80, and 11.0 K. H and current (I) were applied perpendicular to the crystal plane (|| a-axis). (b) Magnetoresistance data in the form of H^2 plots.

above 100 K, this salt became the first stable metal down to 0.3 K. This stabilization of metallic state is considered to originate from the achievement of two-dimensional Fermi surfaces by the introduction of an ethylenedioxy group.

Magnetic susceptibilities (χ) were measured on several pieces of the single crystals that are aligned to the same orientation using a SQUID magnetometer. The measurements were performed by applying a magnetic field ($H = 1$ kOe) along the three crystallographic axes of the single crystal (a, b, and c-axes). The temperature dependence of χ above 15 K can be well fitted with the Curie−Weiss law with a Curie constant (C) of 4.45 emu K mol^{-1} and a Weiss temperature ($\theta = -9.8$ K), suggesting that a relatively strong antiferromagnetic interaction occurs preferentially between the d spins of the $FeCl_4^-$ ions. As shown in Figure 3, a sudden decrease of χ was observed below ca. 3 K only when H was applied along the a-axis. This indicates an antiferromagnetic ordering at $T_N \approx 3$ K with an easy-spin axis parallel to the a-axis. The magnetization (M) curve of $\mathbf{2}_2$•$FeCl_4$ measured at 1.9 K showed a spin−flop around 12 kOe when H was applied along the a-axis and a very slow increase of M compared to that of the Brillouin function with $g = 2.0$, $S = 5/2$, $T = 1.9$ K. Since the metallic state is still kept even when the antiferromagnetic ordering occurs, this salt can be listed as a new antiferromagnetic molecular metal at ambient pressure.

Figure 4a shows a series of the magnetoresistances (MR) up to 7 T from 0.30 to 11.0 K. H was applied along the a-axis, and the interplane resistivities, $\rho_\perp$ (current, $I \perp$ plane), were measured at different temperatures between 0.30 and 11.0 K. At 11.0 K, the MR increased quadratically with increasing H, which is simply explained in terms of the orbital effect by Lorentz force. With decreasing temperature, the magnetic field dependence of MR gradually changed from concave to convex curves near T_N, as seen in Figure 4a. In Figure 4b, a dramatic downward deviation from H^2 dependence was evident below T_N in high fields. It is expected that the alignment of d spins of the $FeCl_4^-$ ions is enhanced with increasing magnetic field and that the $\pi-d$ interaction becomes important below T_N. As a result, we consider that the strong downward deviation from H^2 is attributable to the suppression of the spin-scattering effect by d spins of the $FeCl_4^-$ ions with an application of H. Therefore, the observation of the deviation below T_N suggests the presence of the $\pi-d$ interaction in this system.

Molecular orbital calculation affords much larger $d-d$ interaction of this salt, $J_{dd} = 1.17$ K compared to $J_{dd} = 0.04$ K for κ-(BETS)$_2$•$FeCl_4$.[8] The calculated $\pi-d$ interaction, $J_{\pi d} = 2.91$ K, is also comparable to $J_{\pi d} = 3.12$ K for κ-(BETS)$_2$•$FeCl_4$. In the comparison with the κ-(BETS)$_2$•$FeCl_4$ salt ($T_N = 0.45$ K),[3a] the present $FeCl_4^-$ salt has characteristics of a higher T_N ($\approx$3.0 K) and an anomaly of magnetoresistances evidencing the stronger magnetic interactions.

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Supporting Information Available: An X-ray crystallographic file for the crystal of $\mathbf{2}_2$•$FeCl_4$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Compound **2**: a red powder; mp 224−225 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.95 (s, 1H), 4.28 (s, 4H). Anal. Calcd for $C_{11}H_6O_3S_6$: C, 34.90; H, 1.60. Found: C, 34.43; H, 1.85; MS (EI) *m/z* 378 (M^+).

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(7) Crystal Data for $\mathbf{2}_2$•$FeCl_4$: $C_{11}H_6Cl_2Fe_{0.5}O_3S_6$, $M = 477.36$, monoclinic, $a = 40.7(1)$, $b = 6.92(2)$, $c = 13.13(4)$ Å, $\beta = 107.96(4)°$, $V = 3518(17)$ Å^3, $T = 293$ K, space group $C2/m$, $Z = 8$, μ(Mo Kα) = 14.83 cm^{-1}, 41 590 reflections measured ($R_{int} = 0.064$), 5289 unique, of which 2522 were used in all calculations [$F^2 > 2.00\sigma(F^2)$]. The final R and Rw were 0.059 and 0.070, respectively.

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