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Magnetoresistance Effects Evidencing the π–d Interaction in Metallic Organic Conductors, (EDT-DSDTFVO)$_2$•MX$_4$ (M = Fe, Ga; X = Cl, Br)

Hideki Fujiwara,[*,†,§] Toshiki Hayashi,[†] Toyonari Sugimoto,[*,†,§] Hiroyuki Nakazumi,[‡] Satoru Noguchi,[||,§] Lin Li,[⊥] Keiichi Yokogawa,[⊥] Syuma Yasuzuka,[⊥] Keizo Murata,[*,⊥] and Takehiko Mori[*,#]

Department of Chemistry, Osaka Prefecture University, Osaka 599-8570, Japan, CREST, Japan Science and Technology Agency, Saitama 332-0012, Japan, Department of Applied Chemistry, Osaka Prefecture University, Osaka 599-8531, Japan, Department of Physics and Electronics, Osaka Prefecture University, Osaka 599-8531, Japan, Department of Molecular Materials Science, Osaka City University, Osaka 558-8585, Japan, and Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan

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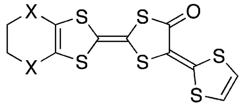
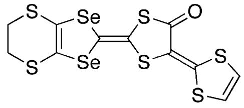
The 2:1 salts of a new donor molecule, EDT-DSDTFVO with MX$_4^-$ (M = Fe, Ga; X = Cl, Br) ions, were prepared. The crystal structures of the donor molecules had a β-type packing motif. All the salts essentially exhibited metallic behaviors despite the small upturns in the resistances below 30–70 K. A large negative magnetoresistance (MR) effect [–14.7% ($\rho_\perp$) at 4.0 K and 5 T] was observed in the FeCl$_4^-$ salt, while a positive MR effect [+4.0% ($\rho_\perp$) at 4.0 K and 5 T] was observed in the GaCl$_4^-$ salt, suggesting that there is a π–d interaction in the FeCl$_4^-$ salt. The pressure application suppressed the resistivity upturns, increased the negative MR effect (–17.7% at 9.5 kbar) in the FeCl$_4^-$ salt, and decreased the positive MR effect (+3.3% at 15 kbar) in the GaCl$_4^-$ salt.

Recent advances in organic molecular conductors have directed current interest toward developing unprecedented ferromagnetic molecular semiconductors and metals with a significant interaction between the conducting π electrons and localized π, d, or f spins.[1] Very recently, we prepared a 2:1 salt of a new donor molecule, ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolemethide (EDT-TTFVO, **1**) with a magnetic FeBr$_4^-$ ion, which displayed a ferromagnetic ordering of the Fe(III) d spins at ca. 1 K where its electrical conductivity was semiconducting.[2] Subsequently, in a 2:1 salt of the ethylenedioxy derivative of **1** (EDO-TTFVO, **2**) with a magnetic FeCl$_4^-$ ion, a metallic conducting behavior was maintained down to 0.3 K. Unfortunately, the Fe(III) d spins were antiferromagnetically ordered at ca. 3 K.[3] Accordingly, a selenium derivative of **1**, EDT-DSDTFVO (**3**), may have both a semiconducting or metallic conductivity and a ferromagnetic ordering at a temperature as high as possible because the introduction of the selenium atoms enhances the transverse intermolecular interaction, which stabilizes the metallic state at low temperatures. Herein, we report the metallic behaviors down to 4.2 K in the 2:1 salts of **3** with MX$_4^-$ (M = Fe, Ga; X = Cl, Br) ions, **3**$_2$•MX$_4$, and the distinctive difference of the magnetoresistance effects between **3**$_2$•FeX$_4$ and **3**$_2$•GaX$_4$, which provides evidence for significant π−d interactions in the FeX$_4^-$ salts.



1: X = S; EDT-TTFVO
2: X = O; EDO-TTFVO



3: EDT-DSDTFVO

Donor molecule **3**[4] was synthesized from 4,5-ethylenedithio-4′-5′-bis(cyanoethylthio)diselenadithiafulvalene with a method similar to that used to synthesize **1**.[5] The redox potentials of **3** measured in benzonitrile at 25 °C are +0.73

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* To whom correspondence should be addressed. E-mail: hfuji@c.s.osakafu-u.ac.jp (H.F.); toyonari@c.s.osakafu-u.ac.jp (T.S.); muratak@sci.osaka-cu.ac.jp (K.M.); takehiko@o.cc.titech.ac.jp (T.M.).

[†] Department of Chemistry, Osaka Prefecture University.

[§] CREST, Japan Science and Technology Agency.

[‡] Department of Applied Chemistry, Osaka Prefecture University.

[||] Department of Physics and Electronics, Osaka Prefecture University.

[⊥] Department of Molecular Materials Science, Osaka City University.

[#] Department of Organic and Polymeric Materials, Tokyo Institute of Technology.

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(4) Red powder. mp: 200−201 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.96 (d, J = 6.6 Hz, 1H), 6.85 (d, J = 6.6 Hz, 1H), 3.32 (s 4H). Anal. Calcd for C$_{11}$H$_6$OS$_6$Se$_2$: C, 26.19; H, 1.20. Found: C, 26.07; H, 1.37.

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10.1021/ic060034t CCC: $33.50

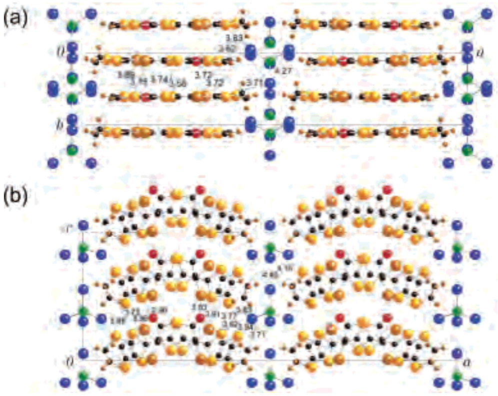

Figure 1. Crystal structure of $\mathbf{3}_2$•$FeBr_4$. The projections are down the (a) *ab* and (b) *ac* planes.

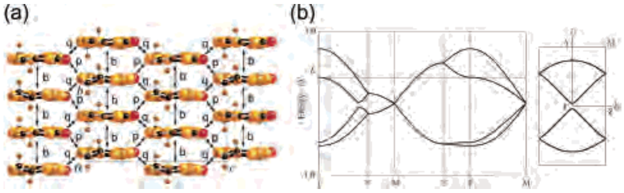

Figure 2. (a) β-type donor array in the *bc* plane and overlap integrals between the donor molecules in $\mathbf{3}_2$•$FeBr_4$ ($b = -28.1 \times 10^{-3}$, $p = 4.37 \times 10^{-3}$, and $q = 5.51 \times 10^{-3}$) and (b) the band dispersion and Fermi surface.

and +0.97 V vs Ag/AgCl, which are slightly higher than those of **1** under the same conditions (+0.66 and +0.92 V vs Ag/AgCl), suggesting that **3** possesses a slightly lower donating ability than **1**. A solution of **3** and 10 equiv of Et_4N•MX_4 (M = Fe, Ga; X = Cl, Br) in ethanol−chlorobenzene (1:9, v/v) was electrochemically oxidized with a constant current of 0.1 μA at 35 °C. Brown or black platelike crystals were grown on the anode after one week. Electron probe microanalysis indicated that each crystal had a 2:1 composition of **3** and MX_4^- ions. The crystal structure of $\mathbf{3}_2$•$FeBr_4$ was successfully solved.[6,7] Because the crystal lattice parameters are nearly identical to those of the $FeBr_4^-$ salt, a similar crystal structure should be applicable to the other MX_4^- salts despite their insufficient X-ray structure analyses. The crystal involved only one crystallographically independent donor molecule with an almost planar molecular structure. As can be seen from the projection down the *ab* plane (Figure 1a), the donor molecules are uniformly stacked with an equal interplanar distance of 3.57 Å and several S•••S(Se) contacts along the *b* axis. Furthermore, these stacking columns are aligned along the *c* axis, and the donor layer has a β-like packing motif (see Figures 1b and 2a). There are also several close contacts between the S and Se atoms of the donor molecules in neighboring columns, suggesting a strong intercolumnar interaction. On the other hand, the $FeBr_4^-$ ions intervene between the donor layers and are aligned in a uniform manner along the *b* axis but are arranged in a zigzag manner along the *c* axis. The Br•••Br distances between neighboring $FeBr_4^-$ ions are 4.16 and 4.27 Å (Figures 1a and b), which are much longer than the van der Waals contact distance (3.90 Å). In contrast, the $FeBr_4^-$ ions are in close contact with neighboring donor molecules as can be seen from the short Br•••S distances (3.62−3.83 Å), suggesting a strong π−d interaction between the donor molecules and the $FeBr_4^-$ ions.

The band calculation of $\mathbf{3}_2$•$FeBr_4$ was performed by a tight-binding method based on the extended Hückel approximation. As shown in Figure 2a, there are three different overlap integrals ($b = -28.1 \times 10^{-3}$, $p = 4.37 \times 10^{-3}$, and $q = 5.51 \times 10^{-3}$). The overlap integral along the stacking direction (*b*) is five to six times larger than those along the side-by-side directions (*p* and *q*), suggesting a quasi-one-dimensional electronic structure. On the basis of these overlap integrals, the band dispersion and Fermi surface were calculated as shown in Figure 2b. The band dispersion has a quarter-filled nature because of the 2:1 composition of **3** and $FeBr_4^-$ and the uniform stacking structure of **3**. The calculated Fermi surface has a two-dimensionality, but opens along the k_c direction, in a manner similar to the Fermi surface of $\mathbf{1}_2$•$FeBr_4$. Furthermore, the Fermi surface of $\mathbf{3}_2$•$FeBr_4$ is folded in half along the k_c (side-by-side) direction because the period of the crystal lattice along the side-by-side direction doubles (6.67 Å in $\mathbf{1}_2$•$FeBr_4$ and 13.28 Å in $\mathbf{3}_2$•$FeBr_4$), which probably results in the weakening of the low-dimensionality of the electronic structure and stabilizes the metallic state down to a lower temperature.

The in-plane and out-of-plane electrical resistivities ($\rho_{||}$ and $\rho_{\perp}$) of the platelike crystals were measured using a four-probe method down to 4.2 K. The $\rho_{||}$'s at room temperature ($\rho_{||rt}$'s) are small, 0.02−0.1 Ω cm, but the $\rho_{\perp}$'s at room temperature are larger, ca. 10^3 times. As shown in Figure 3a, the metallic conducting behaviors in $\rho_{||}$ are maintained until 30−70 K, but very small upturns occur below these temperatures. However, the increase is very small, and the values at 4.2 K are similar to $\rho_{||rt}$. Furthermore, because the estimated energy gaps below the temperature of the upturns are extremely small (1−3 meV), these salts are essentially metallic down to 4.2 K. Similar $\rho_{\perp}$−T behaviors are also observed. As shown in Figure 3, an applied pressure of ca. 7 kbar nearly suppresses these upturns of ρ.

The paramagnetic susceptibilities (χ_p) of polycrystalline samples of the $FeCl_4^-$ and $FeBr_4^-$ salts were measured at 0.1 T in the temperature range of 1.9−300 K. The temperature dependences of χ_p obey the Curie−Weiss law with a Curie constant (C) of 4.52 emu K mol^{-1} and a Weiss temperature (θ) of −0.3 K above 1.9 K for the $FeCl_4^-$ salt and with $C = 4.61$ emu K mol^{-1} and $\theta = -9.7$ K above 8 K for the $FeBr_4^-$ salt, indicating that the interactions between the Fe(III) ($S = 5/2$) d spins are very weak and fairly strong antiferromagnetic ones, respectively. As shown in Figure 1, the neighboring $FeBr_4^-$ ions have relatively long Br•••Br contacts to mediate the strong antiferromagnetic interaction

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(6) Crystal data for $\mathbf{3}_2$•$FeBr_4$: $C_{22}H_{12}O_2S_{12}Se_4FeBr_4$, $M = 1384.45$, orthorhombic, $a = 38.858(7)$ Å, $b = 7.144(1)$ Å, $c = 13.278(3)$ Å, $V = 3686.0(12)$ Å^3, $T = 100$ K, space group $Cmc2_1$, $Z = 4$, μ(Mo Kα) = 94.02 cm^{-1}. There were 24 144 reflections measured ($R_{int} = 0.078$), of which 4279 were used in all the SHELX-97 calculations. The final R and R_w were 0.066 and 0.157, respectively, based on all reflections. Because the donor molecule has an orientational disorder in the identical position, as if two donor molecules overlap in a head-to-tail manner and share terminal sulfur and carbon atoms on both sides with a occupancy ratio of ca. 0.727(2):0.273(2), only one orientation with a higher occupancy was drawn in the figures for clarity.

(7) The crystal plane corresponds to the conduction *bc* plane where the direction perpendicular to the crystal plane is the *a* axis.

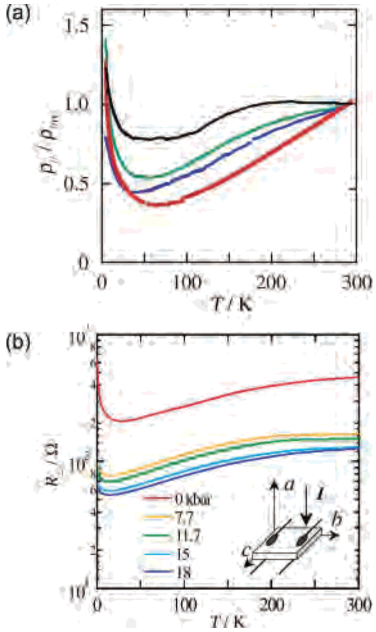

Figure 3. (a) Temperature dependence of $\rho_{\|}/\rho_{\|\mathrm{rt}}$ between 4.2 and 293 K for $GaCl_4^-$ (blue), $FeCl_4^-$ (black), $GaBr_4^-$ (green), and $FeBr_4^-$ salts (red). (b) Temperature dependence of the out-of-plane resistivities ($R_\perp$) under the indicated applied pressures for the $GaCl_4^-$ salt.

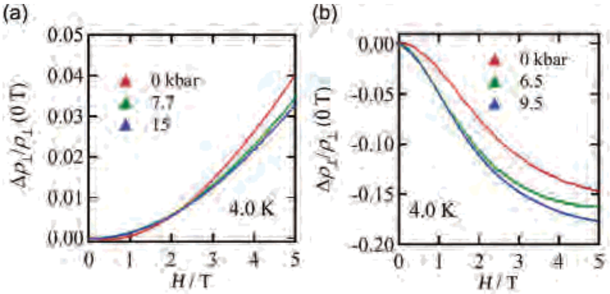

Figure 4. Magnetic field (H) dependence of the MR ratios [$\Delta\rho_\perp/\rho_\perp(0\ \mathrm{T})$] at 4.0 K under applied pressures in the H range up to 5 T for the (a) $GaCl_4^-$ and (b) $FeCl_4^-$ salts.

with $\theta = -9.7$ K. Accordingly, it is likely that the conducting π electrons on the donor columns mediate the strong interaction between the d spins through the π−d interaction. However, antiferromagnetic ordering of the Fe(III) d spins could not be recognized down to 1.9 K.

The magnetoresistance (MR) effects of $\mathbf{3}_2\cdot MX_4$ were investigated. An external magnetic field (H) was applied parallel to the *bc* conducting plane,[7] and the out-of-plane resistivities ($\rho_\perp$'s) were measured up to 5 T. The MR ratio is defined as $\Delta\rho_\perp/\rho_\perp(0\ \mathrm{T}) = [\rho_\perp(\mathrm{H\ T}) - \rho_\perp(0\ \mathrm{T})]/\rho_\perp(0\ \mathrm{T})$, where $\rho_\perp(\mathrm{H\ T})$ and $\rho_\perp(0\ \mathrm{T})$ are the resistivities at $H = \mathrm{H}$ and 0 T, respectively. Figure 4 shows the H dependence of $\Delta\rho_\perp/\rho_\perp(0\ \mathrm{T})$ at 4.0 K for the $GaCl_4^-$ and $FeCl_4^-$ salts. The $GaCl_4^-$ salt exhibits a positive MR effect, which is typical of normal nonmagnetic metals (+4.0% at 5 T). On the other hand, a negative MR effect where ρ decreases as H increases is observed in the magnetic $FeCl_4^-$ salt (−14.7% at 5 T). The latter value, especially, is unexpectedly large and is comparable to −13% at 1.5 K and 5 T in a semiconducting (4,5-dibromo-4′,5′-ethylenedithiotetrathiafulvalene)$_2\cdot$$FeBr_4$,[8] although the present $FeCl_4^-$ salt maintains an extremely high conductivity even at 4.0 K. The appearance of this negative MR effect in the $FeCl_4^-$ salt originates from a suppressed spin scattering resulting from a spin alignment with the applied field. This difference of the MR effects between the nonmagnetic $GaCl_4^-$ and magnetic $FeCl_4^-$ salts provides direct evidence that a π−d interaction exists in the $FeCl_4^-$ salt. Furthermore, an applied pressure enhances the negative MR effect [−16.3 (6.5 kbar) and −17.7% (9.5 kbar) at 5 T], which is in sharp contrast to the observations of the $GaCl_4^-$ salt [+3.5 (7.7 kbar) and +3.3% (15 kbar) at 5 T], as shown in Figure 4. These observations suggest that the π−d interaction is strengthened under applied pressures. The MR effects between the $FeBr_4^-$ and $GaBr_4^-$ salts were compared. Both salts show positive MR effects. However, the MR ratio for the $FeBr_4^-$ salt decreases by about 8% compared to that of the $GaBr_4^-$ salt [$\rho_\|$; +12.0% for the $GaBr_4^-$ salt and +4.1% for the $FeBr_4^-$ salt at 5 T and 1.3 K], which is probably caused by the superimposition of the negative MR component with the large positive component.

The magnitudes of the d−d (J_{dd}) and π−d ($J_{\pi\mathrm{d}}$) interactions were estimated using MO calculations.[9] The calculated J_{dd} is 0.43 K, which is smaller than that of $\mathbf{1}_2\cdot FeBr_4$ (0.78 K),[10] and is comparable to that of κ-(BETS)$_2\cdot$$FeBr_4$ [BETS = bis(ethylenedithio)tetraselenafulvalene] (0.36 K).[9] Furthermore, $J_{\pi\mathrm{d}}$ is 7.58 K, which is nearly identical to that of κ-(BETS)$_2\cdot$$FeBr_4$ (7.93 K). Because of the weak d−d interaction of this salt, detecting magnetic ordering will be difficult in the measurement temperature range, down to 1.9 K. However, the relatively large π−d interaction of this system allows the difference of the magnetoresistance effects between $\mathbf{3}_2\cdot FeX_4$ and $\mathbf{3}_2\cdot GaX_4$ to be realized.

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Supporting Information Available: An X-ray crystallographic file for $\mathbf{3}_2\cdot FeBr_4$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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