JOURNAL OF
Materials
CHEMISTRY
Communication

A novel metal–insulator phase transition observed in $(EDO\text{-}TTF)_2PF_6$†

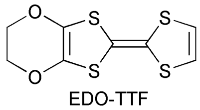
Akira Ota,* Hideki Yamochi* and Gunzi Saito*

Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, 606-8502, Japan. E-mail: yamochi@kuchem.kyoto-u.ac.jp; Fax: +81 75 753 4000; Tel: +81 75 753 4036

Received 1st July 2002, Accepted 17th July 2002
First published as an Advance Article on the web 2nd August 2002

$(EDO\text{-}TTF)_2PF_6$ shows a novel metal–insulator phase transition, which complies with the cooperative features of the Peierls transition, charge ordering, and anion ordering.

In organic conductors, the following kinds of metal–insulator (MI) transitions are known.[1] The *Peierls* transition and *anion ordering* (AO) are associated with significant lattice modulations.[1a–e] In both cases, the conducting molecules translate to form a frozen lattice distortion, while the transition to the *spin density wave*,[1a,b] charge localization (*Mott transition*),[1c] and *charge ordering* (CO) states[1f–h] are known to extinguish the Fermi surface without prominent structural changes except for a special case (*vide infra*). Additionally, *Anderson localization*, in which the carriers are localized due to the local potential of the defects and/or localized impurities, is reported to result in an insulating state without the deformation of the conducting path.[1c,i] In this communication, a new type of MI transition observed in the complexes of ethylenedioxytetrathiafulvalene (EDO-TTF) is reported. The mechanism by which the transition occurs is interpreted to be a combination of the Peierls, CO, and AO transitions.



EDO-TTF

The electrocrystallization of EDO-TTF[2] in the presence of $(tetrabutylammonium)PF_6$ in ethanol afforded black elongated plates with a typical size of 0.1 × 0.5 × 1.0 mm^3. The composition was determined by crystal structure analysis to be $(EDO\text{-}TTF)_2PF_6$. By using conventional four- and two-probe methods for the room temperature (RT) and low temperature (LT) phases, respectively, the temperature dependence of the electrical resistivity was measured. As shown in Fig. 1, a metallic behavior was observed down to *ca.* 280 K, and then the resistivity jumped, clearly showing the occurrence of an MI transition. Below this MI transition temperature (T_{MI}), the resistivity showed a semiconducting temperature dependence with an activation energy of 0.52 eV.‡

The temperature dependence of the static magnetic susceptibility (χ) showed hysteresis at around T_{MI} (Fig. 2), indicating that the MI transition is a first-order one. The magnitude of χ (= 2.5×10^{-4} emu (mol of complex)$^{-1}$) of the RT phase is reasonable for the Pauli paramagnetism of an organic metal based on a TTF derivative. The annihilation of χ below T_{MI} is understood to be due to the nesting of the Fermi surface with the MI transition as described below.

In the RT phase, EDO-TTF molecules, in which the π-system showed an almost planar shape and the terminal ethylene group exhibited disorder due to flipping, formed a structurally two-dimensional conducting layer parallel to the *ab*-plane.§ Consistent with the metallic behavior around RT, the tight binding approximated band calculation based on the crystal structure of the donor layer resulted in the quasi

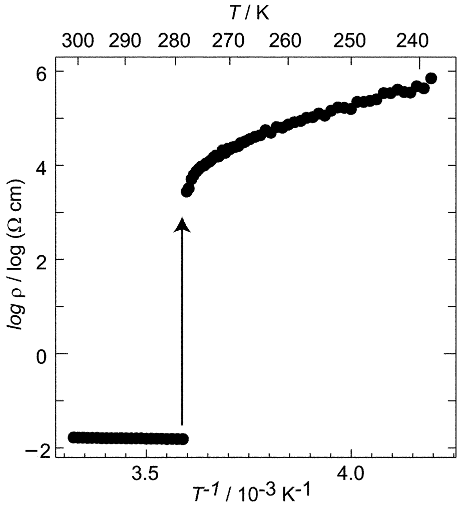


Fig. 1 Temperature dependence of resistivity (ρ) of $(EDO\text{-}TTF)_2PF_6$. The conductivities at 300 and 260 K are 6.0 × 10 S cm^{-1} and 1.4×10^{-5} S cm^{-1}, respectively.

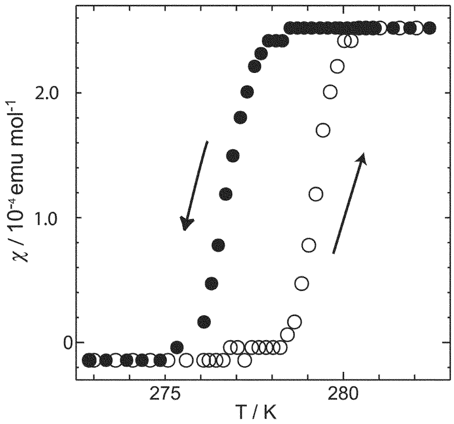


Fig. 2 Temperature dependence of the static magnetic susceptibility (χ) of $(EDO\text{-}TTF)_2PF_6$. Closed and open circles correspond to the data on cooling and heating, respectively.

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†Electronic supplementary information (ESI) is available: Raman spectra data for $(EDO\text{-}TTF)_2X$ (X = PF_6 and AsF_6) and comparison of the RT and LT phases for X = PF_6. See http://www.rsc.org/suppdata/jm/b2/b206293c/

DOI: 10.1039/b206293c

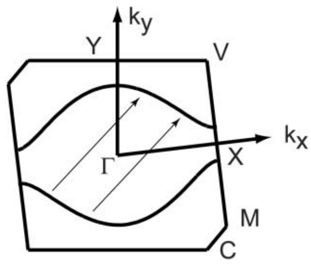

Fig. 3 The calculated Fermi surface based on the RT crystal structure of (EDO-TTF)$_2$PF$_6$. Thin arrows indicate the estimated nesting vector of (a^*+b^*)/2.

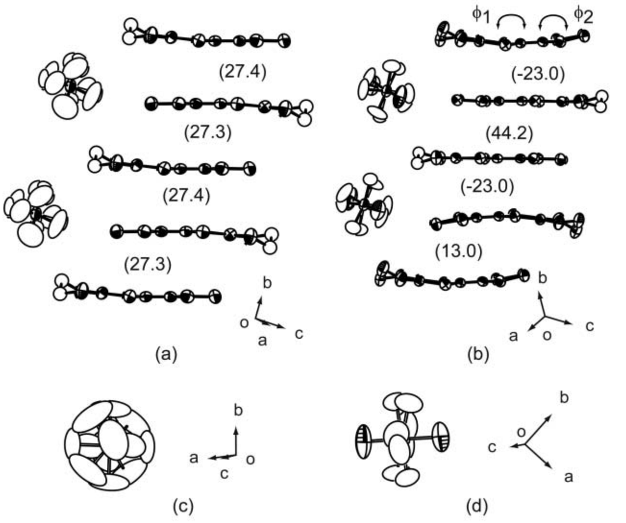

Fig. 4 The side views of a donor column and PF$_6$ anions (a) above and (b) below the MI transition temperature (RT and 260 K), respectively. Hydrogen atoms are omitted for simplicity. The numbers in parentheses indicate the overlap integrals in 10^{-3} units. At RT the dihedral angles are ϕ_1, ϕ_2 = 6.0°, 0.3°, while at 260 K they are 11.1°, 7.9° for the bent and 0.8°, 2.1° for the planar molecule, respectively (ϕ_1 and ϕ_2 represent the dihedral angles between the central C$_2$S$_4$ and terminal C$_2$O$_2$S$_2$ and C$_2$S$_2$ parts, respectively). (c) and (d) depict the anion projected onto the *ab*-plane at RT and 260 K, respectively. The vertical direction corresponds to the donor stacking axis in each of these. For (a)–(d), the atoms, for which site occupancy factors are equal to and less than unity, are depicted by shaded and open ellipsoids, respectively.

one-dimensional (1D) Fermi surface with considerable warping, which is susceptible to the nesting vector of (a^* + b^*)/2 (Fig. 3).[3] The cavity formed by the head-to-tail stacking of the donor molecules accommodated the counter anion (Fig. 4a). The PF$_6$ anions were located at the center of inversion and showed almost isotropic rotational disorder. Even by assuming two orientations of the anion to express the rotational disorder, the equivalent temperature factor (U_{eq}) of each fluorine atom was rather large.

The most striking feature of the LT phase, the deformation of half of the donor molecules was observed, could be the origin of the destructive behavior at around T_{MI}.‡ One of the crystallographically independent EDO-TTF molecules deformed into the bent shape of the π-moiety, which resembled that in the neutral crystals. At the central part of the π-moiety, the dihedral angles between the planar parts changed by more than 5°, while another EDO-TTF molecule showed a more flattened π-system than that observed in the RT phase, as shown in Fig. 4b. The donor column consisted of tetramers of BFFB, where B and F denote the bent and flat molecules, respectively.

In the LT phase, the unit cell is doubled along the diagonal direction between the *a*- and *b*-axes compared with those at RT, which corresponds to the nesting of the Fermi surface. Contrary to the almost uniform stack above T_{MI}, the intermolecular overlap integrals below T_{MI} show significant alternation with the formation of the tetramers (Fig. 4b). These features indicate that the MI transition includes the *Peierls* character in which electron–phonon coupling takes an important role.

From the comparison of the bond length[4] and the peak shifts of the Raman spectra,†¶ it is shown that the B molecules are almost neutral, and the F molecules have a charge close to +1 in the LT phase, indicating the CO nature of this MI transition. For example, the central carbon–carbon double bonds of EDO-TTF showed a bond length of 1.318(6) Å , 1.365(5) Å, 1.346(5) Å, 1.381(5) Å in the neutral donor, in the RT phase, B and F molecules in the LT phase, respectively. The pattern of the CO is a rare [0, +1, +1, 0] type,[1f–h] corresponding to the [B, F, F, B] tetramer. The quarter filled 1D electronic systems are expected to result in the CO pattern of the [0, +1, 0, +1] type, which is mainly concerned with the nearest-neighbor coulombic (electron–electron) interactions. It is plausible that the instantaneous coupling between the lattice modulation and the electron–electron correlation *i.e.* the coupling of the Peierls and CO character leads to the peculiar CO pattern in this system. To our knowledge, an MI transition associated with the distinct deformation of the conducting component molecules similar to our case has only been reported for κ-(BEDT-TTF)$_4$PtCl$_6$(Benzonitrile) (in which BEDT-TTF represents bis(ethylenedithio)-TTF).[5] In this case, however, the MI transition is associated only with CO but not with the *Peierls* and AO features.

As for the disorder of the PF$_6$ anion, the mode is modified by the MI transition. The isotropic rotation in the RT phase is restricted to a uni-axial rotation (Fig. 4c, and d). In the LT phase, the positions of a couple of the fluorine atoms, which are located to give a F–P–F bond angle of 178.5(2)°, are expressed by only one site for each. Also, the decrease in the temperature factors is distinct. In the LT phase, the averaged U_{eq}'s for the fluorine atoms are reduced to *ca.* 60% of that of the RT phase even only 20 K below T_{MI}, while the other atoms, except the disordered ethylene carbon atoms, showed a reduction of the U_{eq}'s of *ca.* 10%. Associated with the modulation of the disorder, the structural environment is changed at T_{MI}. In the LT phase, the anion is no longer located at a special position and forms a new periodicity corresponding to the nesting vector of the Fermi surface. The phosphorus atoms are arranged uniformly along the donor stacking axis at a distance of 7.343(0.6) Å at RT, while they show periodic alternation with distances of 6.962(2) Å and 7.873(2) Å at 260 K, which corresponds to the tetrameric alternation of the donor molecules. Although the rotation of the anion is not completely frozen in the LT phase of this salt, the reduction of the disorder with a fixed molecular axis of the anion and the formation of the new lattice periodicity are accounted for by AO.[1a,b] In our case, the new periodicity corresponds to the nesting of the Fermi surface as in the case of (tetramethyl-tetraselenafulvalene)$_2$ReO$_4$, and contributes to the MI transition.

Summarizing the analysis of the MI transition observed here, the mechanism complies with the simultaneous cooperation of the *Peierls*, CO and AO features, in which molecular deformation is associated with changes in the crystal and electronic structures. In other words, the transition involves concurrent couplings of the electron–phonon, electron–electron interactions, and the molecular degree of freedom. Recently, we observed the same type of MI transition in the isostructural complex, (EDO-TTF)$_2$AsF$_6$ at a lower temperature (*ca.* 268 K).¶‖ The occurrence of the same type of transition in another salt indicates the necessity of concurrent coupled mechanisms in this transition. The flexibility of the molecules in functional materials will lead to the exotic physical properties and functions suggested by this novel MI transition.

Acknowledgements

The authors acknowledge Professor M. Iyoda, Tokyo Metropolitan University, for his kind suggestions about the synthetic method of EDO-TTF. The authors thank Dr O. Drozdova, IMS, for her kind offer of the optical data of (EDO-TTF)$_2$AsF$_6$ prior to its publication. Also, this work is supported by a Grant-in-Aids from the Ministry of Education, Science, Sports, and Culture, Japan (COE Research on Elements Science, No. 12CE2005) and a Grant-in-Aid for JSPS fellows.

Notes and references

‡The single crystals were extremely brittle during the phase transition. To prevent the samples from cracking, the conductivity measurements on the LT phase were carried out by the two-probe method using an annealed gold wire of 10 μm diameter with a very slow cooling rate (1–2 K h^{-1}). For the X-ray data collection of the LT phase, the crystal was cooled at a slow rate of −6 K h^{-1} prior to the measurements being taken.

§*Crystal structure analysis*: an imaging plate type diffractometer (MacScience DIP-2020K) was used for the data collection of (EDO-TTF)$_2$PF$_6$ (C$_{16}$H$_{12}$S$_8$O$_4$PF$_6$) at RT and at 260 K with Mo-Kα radiation (λ = 0.71073 Å): black rods (0.35 × 0.2 × 0.15 mm^3) at RT, triclinic, $P\bar{1}$, a = 7.197(0.9) Å, b = 7.343(0.6) Å, c = 11.948(1) Å, α = 93.454(7)°, β = 75.158(6)°, γ = 97.405(7)°, V = 605.0(1) Å^3, Z = 1, d_{calcd} = 1.838 g cm^{-3}. A total of 2281 reflections were collected ($2\theta_{\max} \leqslant 52°$), 2218 independent, 1986 observed ($I_o \geqslant 2\sigma(I_o)$), structure solution by direct methods (CrystanGM 6.2), refinement against F^2 with all observed reflections (SHELXL97) (187 parameters). The positions of the H atoms were calculated and considered isotropically according to a riding model. $R1$ = 0.0564. At 260 K, triclinic, $P\bar{1}$, black rods, a = 9.822(1) Å, b = 11.000(2) Å, c = 11.487(2) Å, α = 101.865(8)°, β = 99.128(8)°, γ = 90.445(8)°, V = 1198.1(3) Å^3, Z = 2, d_{calcd} = 1.838 g cm^{-3}. A total of 4169 reflections were collected ($2\theta_{\max} \leqslant 52°$), 3950 independent, 3283 observed ($I_o \geqslant 2\sigma(I_o)$), structure solution by direct methods (CrystanGM 6.2), refinement against F^2 with all observed reflections (SHELXL97) (352 parameters). The positions of the H atoms were calculated and considered isotropically according to a riding model. $R1$ = 0.0415. CCDC reference numbers 157198 (RT) and 157199 (260 K). See http://www.rsc.org/suppdata/jm/b2/b206293c/ for crystallographic files in CIF or other electronic format.

¶The exact charge distribution in our tetramer is estimated as +0.1, +0.9, +0.9, +0.1 from the preliminary results of the Raman spectra: O. Drozdova, K. Yakushi, A. Ota, H. Yamochi, G. Saito, to be published.

||*Crystal data for (EDO-TTF)$_2$AsF$_6$ at RT*: triclinic, $P\bar{1}$, black rods, a = 7.224(2), b = 7.354(1), c = 12.093(2) Å, α = 93.35(1)°, β = 74.822(9)°, γ = 97.08(1)°, V = 615.1(2) Å^3, Z = 1. At 230 K: triclinic, $P\bar{1}$, a = 9.771(8), b = 10.990(9), c = 11.341(8) Å, α = 101.78(4)°, β = 100.06(4)°, γ = 89.89(5)°, V = 1173(2) Å^3, Z = 2. The details will be published in elsewhere.

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