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# TRANSVERSE CONDUCTION AND METAL-INSULATOR TRANSITION IN β-(BEDT-TTF)$_2$PF$_6$

Hayao KOBAYASHI,* Takehiko MORI,† Reizo KATO,† Akiko KOBAYASHI,†
Yukiyoshi SASAKI,† Gunzi SAITO,†† and Hiroo INOKUCHI††
Department of Chemistry, Faculty of Science, Toho University,
Funabashi, Chiba 274
† Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Tokyo 113
†† Institute for Molecular Science, Okazaki 444

In the crystal of β-(BEDT-TTF)$_2$PF$_6$, BEDT-TTF (bis(ethylenedithiolo)-tetrathiafulvalene) molecules are arranged side-by-side. The anisotropy of the electrical resistivity shows that β-(BEDT-TTF)$_2$PF$_6$ is the first organic conductor where the conductivity is the largest along the direction parallel to the molecular plane. The metal-insulator transition is observed at 297 K. The thermoelectric power corresponds to that due to the hole conduction in highly correlated system.

Most of the organic molecular metals ever known can be regarded as one-dimensional (1-D) systems. The crystals contain segregated stacks of donor and/or acceptor molecules. Recently, we have reported a new-type 2-D organic metal, (BEDT-TTF)$_2$ClO$_4$(C$_2$H$_3$Cl$_3$)$_{0.5}$ which retain the metallic conductivity down to 1.4 K.[1,2] BEDT-TTF molecules do not stack face-to-face and the band structure is quite different from that of typical 1-D metals.[3]

In this paper, we report the crystal structure and metal-insulator transition of β-(BEDT-TTF)$_2$PF$_6$, whose conductivity is the largest in the direction parallel to the molecular plane.

Single crystals of β-(BEDT-TTF)$_2$PF$_6$ were obtained by the electrochemical oxidation.[4] The crystal data are: orthorhombic, space group, Pnna, $a = 14.960(4)$,

$b = 32.643(7)$, $c = 6.664(2)$ Å and $V = 3254.6$ Å$^3$. The crystal structure is shown in Fig. 1. The small intermolecular overlapping (Fig. 2) and no intermolecular short contact indicate a weak interaction along the a axis. On the other hand, each BEDT-TTF molecule has four intermolecular short S...S contacts along the c axis (Fig. 3). Similar molecular arrangement can be seen in (BEDT-TTF)$_2$ClO$_4$(C$_2$H$_3$Cl$_3$)$_{0.5}$[2] and α-(BEDT-TTF)$_2$PF$_6$.[4] This tendency for side-by-side arrangement of BEDT-TTF molecules indicates a significant transverse intermolecular interaction through sulfur atoms.

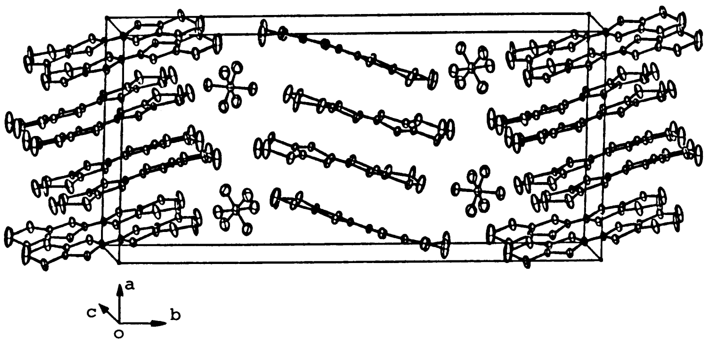

Fig. 1. Crystal structure of β-(BEDT-TTF)$_2$PF$_6$

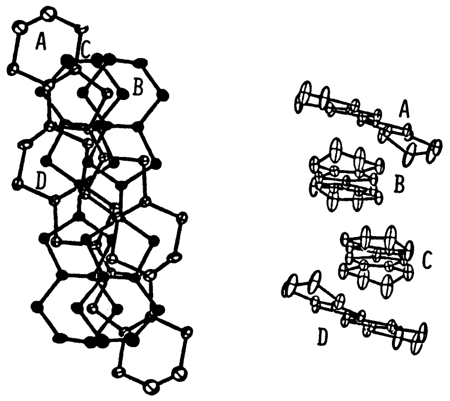

Fig. 2. Intermolecular overlapping. The molecules A, B, C and D form a repeating unit along the a axis.

The importance of the transverse interaction can be also seen from the anisotropy of the electrical resistivity. The resistivities were measured along the a, b and c axes ($\rho_a$, $\rho_b$ and $\rho_c$ (Fig. 4)) by the four probe method. As shown in Fig. 4, β-(BEDT-TTF)$_2$PF$_6$ is most conductive along the c axis and shows a sharp metal-insulator transition near 297 K ($=T_c$). The anisotropy of the resistivity increases rapidly around $T_c$. Above $T_c$, $\rho_c : \rho_a : \rho_b = 1 : 50 : 10^4$. This indicates that β-(BEDT-TTF)$_2$PF$_6$ is the first organic conductor whose transverse resistivity ($\rho_c$) is much lower than the parallel resistivity ($\rho_a$). The minimum value of $\rho_c$ is 0.1 - 0.05 Ωcm, which is somewhat larger than the room temperature resistivity of (BEDT-TTF)$_2$ClO$_4$(C$_2$H$_3$Cl$_3$)$_{0.5}$ (0.04 Ωcm)

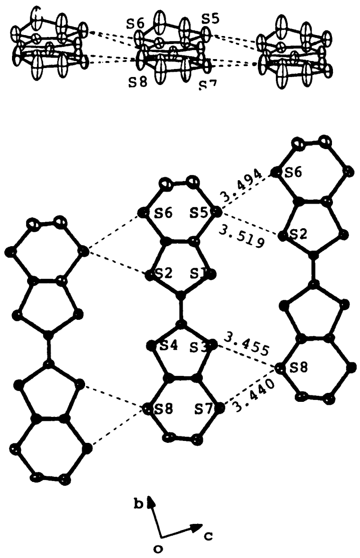

Fig. 3. Side-by-side arrangement of BEDT-TTF.

The activation energies of $\rho_a$, $\rho_b$ and $\rho_c$ ($T < T_c$) are 0.24, 0.20 and 0.23 eV, respectively.

In the organic molecular metals hitherto known, the 1-D metallic properties are originated mainly from the intermolecular pπ-pπ interaction along the stack. In other words, the pπ orbitals of the HOMO break the isolated state of the molecules. However, the crystal structure and the anisotropy of the electrical resistivity of β-(BEDT-TTF)$_2$PF$_6$ suggest that the organic compounds can be metallic in the absence of the column structure.

Since the organic metals whose band structures are not ideally one-dimensional ((TMTSF)$_2$X (X = ClO$_4$, PF$_6$, BF$_4$,...),[5] (TST)$_2$Cl[6]) always contain chalcogen atoms in the π-conjugated system, the chalcogen atoms are considered to be essential for the appearance of the two-dimensionality. Berlinsky et al.[7] showed that the HOMO of TTF is composed mainly of 3pπ and 3dπ orbitals of the sulfur atoms. The coefficients of 3pπ and 3dπ atomic orbitals are 0.424 and 0.225, respectively. Similar mixing of pπ and dπ orbitals can be expected in BEDT-TTF. Unlike α-(BEDT-TTF)$_2$PF$_6$ and (BEDT-TTF)$_2$ClO$_4$(C$_2$H$_3$Cl$_3$)$_{0.5}$, β-(BEDT-TTF)$_2$PF$_6$ has no short intermolecular S...S contact except for the contacts between the molecules approximately on the same plane (see Fig. 3). The shortest intermolecular S...S distance along the a axis is 3.73 Å, which is larger than the van der Waals distance of S...S (3.70 Å). The side-by-side arrangement is not suited for pπ-pπ interaction, but it is not so unfavorable for dπ-dπ interaction. Therefore, even if the intermolecular

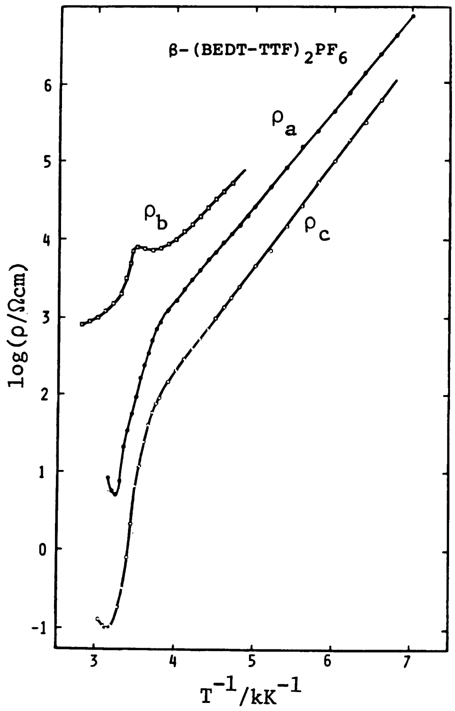

Fig. 4. Electrical resistivities of β-(BEDT-TTF)$_2$PF$_6$ along the a, b and c axes.

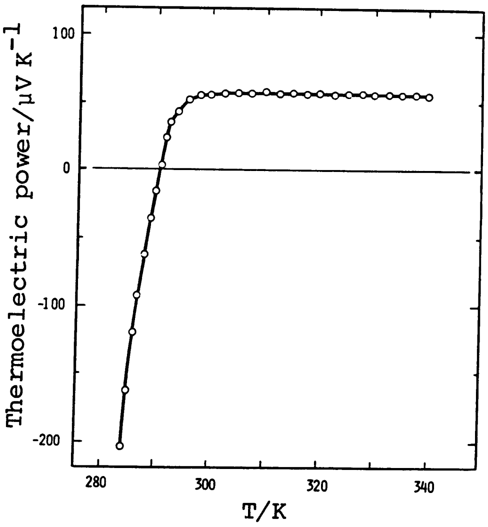

Fig. 5. Thermoelectric power of β-(BEDT-TTF)$_2$PF$_6$.

pπ-pπ interaction is small, the dπ-dπ interaction may be considerably large. Thus, it may be possible that the chalcogen atoms in the π-conjugated system can break the isolated state of the molecule to form a metallic band along the transverse direction.

The thermoelectric power (TEP) also shows the metal-insulator transition (Fig. 5). The temperature dependence of TEP is quite similar to that of highly conducting quarter-filled-band TCNQ salts such as quinolinium-$TCNQ_2$ and acridinium-$TCNQ_2$.8) In these TCNQ salts, TEP tends to saturate to a value of -60 μV/K at high temperature, which is considered to be an evidence for strong Coulomb correlation. In the case of the 1 : 2 complex, TEP is $-k/e \ln 2 (= -59.8\ \mu V/K)$. The TEP of β-$(BEDT\text{-}TTF)_2PF_6$ is 58 μV/K above $T_c$, which corresponds to that due to the hole conduction in the system with a strong onsite Coulomb repulsion. Strong Coulomb correlation or a narrow bandwidth is consistent with the relatively small conductivity in the metallic state.

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