# Room temperature structural transition in the (MeEDO-TTF)$_2$PF$_6$ salt

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A material which exhibits the reversible interconversion between two stable states induced by the external stimuli can be applied as switching system. The switching phenomena were observed in the organic cation radical salts; for example, (EDO-TTF)$_2$PF$_6$ shows the peculiar thermally- and photo-induced phase transition.[1] The molecular flexibility and small π-electron system of EDO-TTF play an important role for this peculiarity.
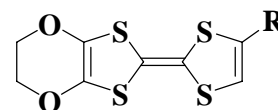
R= H: EDO-TTF
Me: MeEDO-TTF

To further explore variety of switching systems in the conducting charge-transfer complexes, a minor chemical modification of EDO-TTF was carried out. Here, we report the MeEDO-TTF cation radical salts with PF$_6$ anion, which showed polymorphism and one of the modifications exhibited a first-order phase transition associated with the structural modulation at around room temperature.

Electrocrystallization of MeEDO-TTF with PF$_6$ anion under the different conditions afforded three kinds of cation radical salts having the same composition of donor : anion = 2 : 1; black powder (**1**),[2] green plate (**2**), and black plate (**3**). For **1** and **2**, the single crystals were not obtained yet, and hence the conductivities were measured on the compressed pellets.

Despite the same compositions and similar optical absorption spectra at room temperature, these three modifications exhibited different transport properties. **1** was a semiconductor with good conductivity at room temperature (σ_{rt} = 3 S cm^{-1}). **2** showed weak metallic behavior down to around 150 K with σ_{rt} = 30 S cm^{-1}. **3** showed a semiconductor-semiconductor first-order phase transition at 302 – 304 K associated with the jump of the magnetic susceptibility χ and resistivity ρ (Fig. 1). The existence of the bistable state, therefore, shows the potential to be used for the molecular switching system.

In the high-conducting phase (H phase), **3** showed very similar crystal structure to that of the stable metal of (MeEDO-TTF)$_2$BF$_4$.[3] Two donor molecules were crystallographically unique and located on the mirror plane except for the terminal ethylene groups. Needless to say, all of the donor molecules were parallel to each other. The anion showed isotropic rotational disorder with the central phosphorous atom located on the mirror plane. In the low-conducting phase (L phase), on the other
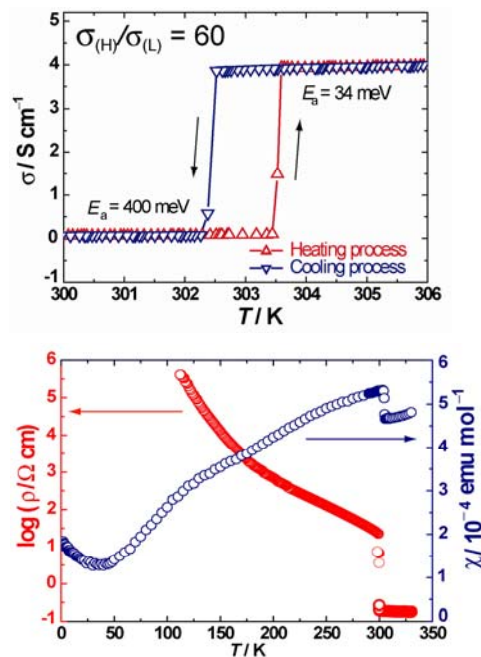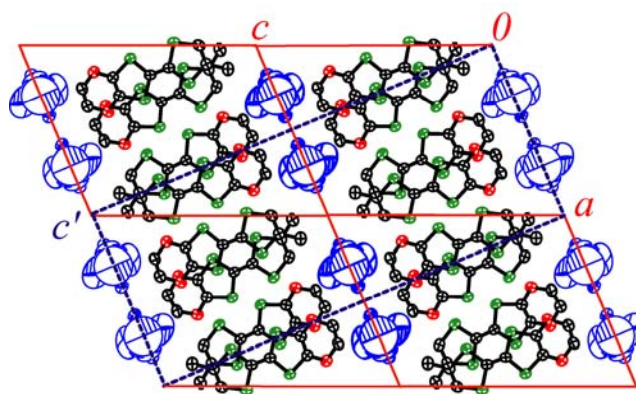
Fig. 1. Hysteresis loop of σ (top panel) and the temperature dependence of χ and ρ in the whole temperature region of **3** (bottom panel).

hand, **3** crystallized in orthorhombic system with the asymmetric unit containing one donor and half of anion. The donor molecule was approximately planar, and the anion showed a uniaxial rotational disorder. Unlike the *H* phase, the side-by-side two neighboring donor molecules were twisted with an angle of 6º in the *L* phase. To find the structural relationship between the *H* and *L* phases, the unit cells at 302 K were compared in Fig. 2. Based on the structure of the *H* phase, the unit cell of the *L* phase was doubled along the $2c + a$ direction. Although the magnitudes of the intermolecular overlap integrals were small ($< 10^{-2}$), the calculated band structures for both of the *H* and *L* phases provided two-dimensional Fermi surfaces. The existences of the Fermi surfaces are inconsistent with the transport properties for both of the phases.

In the *L* phase, only one donor molecule is crystallographically unique, therefore, the charge ordering state is not expected. Also, the two-dimensional

Fig. **2**. The structural relationship between the *H* and *L* phases of **3** at 302 K. The red solid and blue dashed lines indicate the unit cells of the *H* and *L* phases projected on the *ac*-plane, respectively. Although this figure depicts the molecular packing of the *H* phase, the illustration for the *L* phase is almost identical to this one, except the magnitude of the thermal ellipsoids of fluorine atoms.
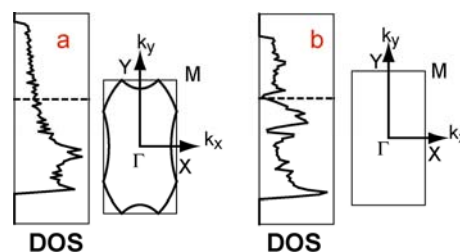
Fig. **3**. Calculated density of states (DOS) and Fermi surfaces for the low-conducting phase of **3**. Based on the crystal structure (a) observed at 290 K, and (b) assumed by atomic displacement of 0.1 Å along the *a*-axis.

feature of the Fermi surface excludes the Peierls instability. To understand the semiconducting nature, the effects of the small molecular motion on the electronic structures were examined. Since the intermolecular overlap integrals were moderately small in this salt, the band structures were sensitive to the small structural modulations. For example, in the *L* phase, when the positions of donor molecules at $x \approx 0.0$ and 0.5 were shifted +0.1 and −0.1 Å along the *a*-axis, respectively, the gap was formed at the Fermi level (see Fig. 3). By applying the similar assumption, a gap was also opened at the Fermi level for the *H* phase. Thus, the molecular motions have significant effects to the electronic structures in both phases of this salt. When the crystal consists of the domains in which the small displacements of the donor molecules from the averaged positions take place, the semiconducting states are available.

In conclusion, cation radical salts $(MeEDO-TTF)_2PF_6$ showed polymorphism, among which the black plates (**3**) exhibited a first-order phase transition at around room temperature. The difference and relationship of crystal structures between the high- and low-conducting phases were examined. To understand the transport properties at both above and below the transition temperature, the existence of the local molecular displacements was proposed, in the light of the estimated sensitivity of the band structures to the molecular motions.

1. (a) A. Ota *et al., J. Mater. Chem.*, 2002, **12**, 2600-2602; (b) M. Chollet *et al., Science*, 2005, **307**, 86-89.

2. X. F. Shao *et al.,* Molecular Structure Meeting at Shizuoka, Japan, 20-23th, Sept, 2006, 2D05.

3. X. F. Shao *et al.,* Spring Meeting of Chemical Society of Japan at Osaka, 25-28th, March, 2007, 2G3-02.