Syntheses, Structure and Properties of Vinylogous EDO-TTFs

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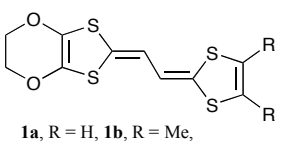
BEDO-TTF provides many two-dimensional metallic cation radical salts with various size and shape of counter components, because of their self-assembling ability [1]. To obtain a variety of physical properties, the self-assembling ability would be suppressed by chemical modification. EDO-TTF which have suppressed this ability, affords the cation radical salts with many types of packing motifs. Among them, $(EDO\text{-}TTF)_2PF_6$ salt shows a metal-insulator (MI) transition and an ultra-fast photo-induced phase transition (PIPT) at around room temperature [2]. To explore the materials with various electronic structures, we synthesized vinylogous EDO-TTFs **1b-d** by the phosphite-mediated cross-coupling reactions and **1a** could be obtained by demethoxycarbonylation of **1d** (Fig. 1). Although the TCNQ complexes of **1b** and **1c** show low electrical conductivity due to DDAA-type alternate stacking, the cation radical salt $(\mathbf{1b})_2PF_6$ shows metallic behavior down to T_{MI} = 185 K (Fig. 2). Donor packing motif of the PF_6 salt is resemble in that of $(EDO\text{-}TTF)_2PF_6$ (Fig. 3). Low temperature structure analyses revealed that the phase transition of the PF_6 salt is originated from the charge disproportionation.



1a, R = H, **1b**, R = Me,
1c, R = SMe, **1d**, R = CO_2Me

Fig. 1. Vinylogous EDO-TTFs.

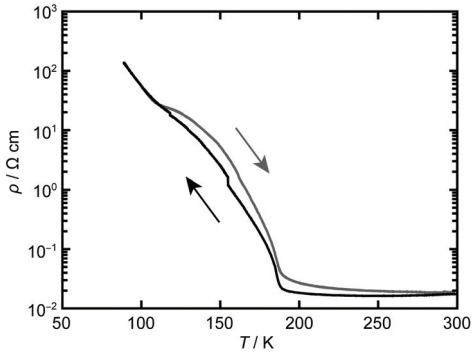


Fig. 2. Temperature dependence of the resistivity of $(\mathbf{1b})_2PF_6$.

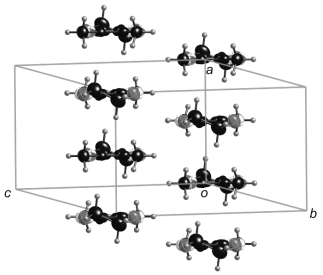


Fig. 3. Donor sheet structure of $(\mathbf{1b})_2PF_6$.

[1] S. Horiuchi *et al.*, J. Am. Chem. Soc. **118** (1996) 8604.
[2] M. Chollet *et al.*, Science **307** (2005) 86.