

Metal–Insulator Transition of Alloyed Radical Cation Salts, $(\text{Me}_x\text{EDO-TTF})_2\text{PF}_6$

Tsuyoshi Murata^{1,2,3}, Xiangfeng Shao², Hideki Yamochi², Gunzi Saito⁴, Mikio Uruichi⁵, Kyuya Yakushi⁵, and Koichiro Tanaka³

¹*Department of Chemistry, Graduate School of Science, Osaka University, Japan.*

²*Research Center for Low Temperature and Materials Sciences, Kyoto University, Japan.*

³*Institute for Integrated Cell-Material Sciences, Kyoto University, Japan.*

⁴*Research Institute, Meijo University, Japan.*

⁵*Institute for Molecular Science, Japan.*

Email: tmurata@chem.sci.osaka-u.ac.jp

Our recent research on ethylenedioxy-TTF (EDO-TTF) and its derivatives has demonstrated radical cation salts showing peculiar phase transitions. $(\text{EDO-TTF})_2\text{PF}_6$ salt shows a metal–insulator (M-I) phase transition right below room temperature ($T_{\text{MI}} = 279$ K) originating from the multi-instability (Peierls, charge-order, anion-order) [1]. This salt exhibits an ultra-fast and highly efficient photo-induced phase transition with strong electron-lattice interaction [2]. Methyl substituted EDO-TTF (MeEDO-TTF) affords a radical cation salt with PF_6^- showing a semiconductor–semiconductor first-order phase transition right above room temperature ($T_c = 303$ K) accompanying changes in charge-separation and molecular orientation [3]. Despite the differences in molecular shapes and features of radical cation salts, EDO-TTF and MeEDO-TTF afforded alloyed salts, $(\text{Me}_x\text{EDO-TTF})_2\text{PF}_6$.

Alloys were prepared by the electrocrystallization of the mixture of EDO-TTF and MeEDO-TTF in the presence of $(\text{Bu}_4\text{N})\text{PF}_6$ in EtOH. The x values of EDO-TTF rich alloys ($0 < x < 0.5$) nearly accorded with the donor mixing ratio in starting solution. At 300 K, the crystal structures of the alloys were isostructural to that of $(\text{EDO-TTF})_2\text{PF}_6$, the electronic structure of which shows a quasi-one dimensional nature (Fig. 1). Alloys in $0 < x < 0.1$ exhibited M–I transition, and the T_{MI} became lower with increasing x values ($T_{\text{MI}} = \sim 185$ K for $x = 0.1$).

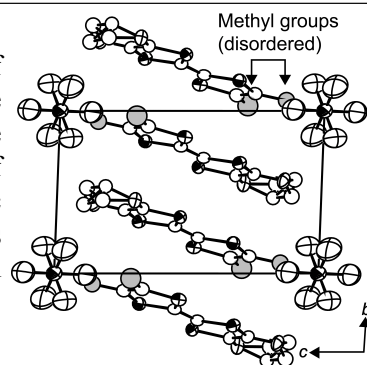
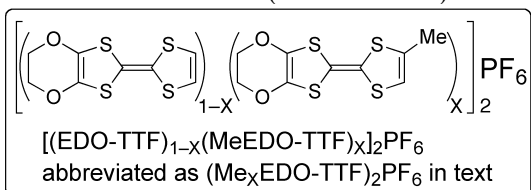


Fig. 1. Crystal structure of $(\text{Me}_x\text{EDO-TTF})_2\text{PF}_6$ ($x = 0.5$) at 300K.

[1] A. Ota *et al.*, *J. Mater. Chem.* 12 (2002) 2600.

[2] M. Collet *et al.*, *Science* 307 (2005) 86.

[3] X.-F. Shao *et al.*, *Chem. Mater.* 20 (2008) 7551.