

The Effect of a Methyl Group Incorporated in EDO-TTF

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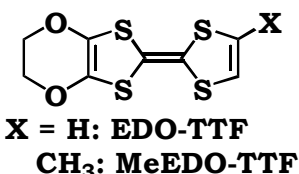
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Most of the radical cation salts of EDO-TTF contained the head-to-tail type columnar stacks or multimers of donor molecules. The former type of assembly provided quasi-one-dimensional (Q1D) electronic structures, and no EDO-TTF complexes showed metallic behavior at cryogenic temperature, while the multi-instability of the complexes is of interest [1]. Contrary, MeEDO-TTF afforded complexes with the donor layers consisting only of head-to-head type stacking [2]. In these cases, two-dimensional (2D) electronic structures were estimated from the crystal structures. Consistently, (MeEDO-TTF)₂X (X = BF₄, ClO₄) exhibited metallic behavior down to 10 K (the lowest temperature examined). Although the high-temperature phase was isostructural to these complexes, (MeDO-TTF)₂PF₆ showed no metallic behavior but a semiconductor-semiconductor transition at just above room temperature (303 K) [3]. Comparing the magnitudes of intermolecular interactions, it is concluded that these complexes are located near to the border between metal and semiconductor. The vibrational spectra detected the charge disproportionation more or less for all of them. Additionally, MeEDO-TTF also provided the complexes, the donor layers of which consisted solely with head-to-tail type donor stacking to show Q1D and localized electronic structures [4].

The methyl group incorporated in EDO-TTF brought about the ability to increase the dimensionality of the electronic structure of complexes to 2D one, while the magnitudes of intermolecular interactions were suppressed in these cases.



[1] H. Yamochi and G. Saito, in Multifunctional Conducting Molecular Materials, eds. G. Saito et al., RSC Publishing, Cambridge, UK. (2007), pp. 107-114.

[2] X.F. Shao *et al.*, J. Mater. Chem., 18 (2008) 2131.

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

[4] X.F. Shao *et al.*, Chem. Mater., 21 (2009) 1085.