Charge Disproportionation in Semiconducting θ-Type Salts of BTM-TTP and BSM-TTP

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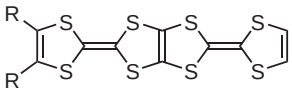

BDT-TTP: R = H
BTM-TTP: R = SCH_3
BSM-TTP: R = $SeCH_3$

Most radical cation salts of BDT-TTP exhibit metallic behavior down to cryogenic temperature because of the self-assembling nature which strongly prefers a uniform β-type arrangement. However, even introduction of a relatively small-sized substituent into BDT-TTP molecule brings about a major change in the strong preference. For example, methylthio groups are added to give BTM-TTP [1a], and the electrocrystallization of which affords two kinds of 2:1 salts with SbF_6, β- and θ-types. The β-salt shows metallic behavior down to 5 K. In contrast, the θ-salt is semiconducting, but the electrical property should be interpreted with caution. The structural analysis reveals that only one BTM-TTP molecule is crystallographically unique, and the closed Fermi surface is calculated, which is quite characteristic of two-dimensional metal. The magnetic susceptibility of θ-salt suggests the weak localization of charge [1b]. In this study, we looked closely into the origin of semiconducting behavior of θ-$(BTM\text{-}TTP)_2SbF_6$.

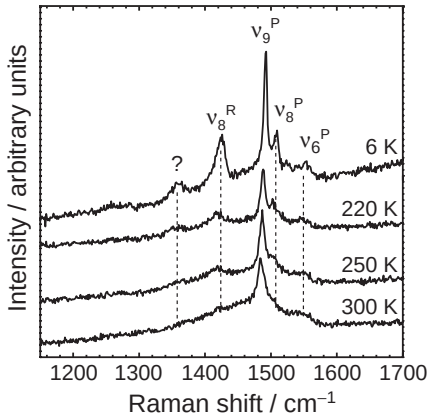

Fig. 1 Raman spectra of θ-$(BTM\text{-}TTP)_2SbF_6$ excited by a 568 nm laser. ν_j^P and ν_j^R denote the ν_j mode at the charge-poor and rich sites, respectively.

According to the normal mode analysis based on B3LYP method, C=C stretching modes of neutral BTM-TTP and $(BTM\text{-}TTP)ReO_4$ were assigned. Fig. 1 shows Raman spectra of θ-$(BTM\text{-}TTP)_2SbF_6$. The broad line width at 300 K suggests an inhomogeneous charge distribution. On lowering temperature, ν_9^P band gradually sharpened with a blue shift. At the same time, ν_8^R, ν_8^P, and ν_6^P bands developed from the spectral tail. Therefore, the origin of semiconducting nature is concluded as a charge disproportionation. Isostructural θ-$(BSM\text{-}TTP)_2PF_6$ will also be reported in this conference.

[1] a) Y. Misaki *et al*., Chem. Lett. 22 (1993) 729; b) M. Noda *et al*., Chem. Lett. 37 (2008) 396.