Charge Disproportionation in Semiconducting \(\theta\)-Type Salts of BTM-TTP and BSM-TTP

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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 \(\beta\)-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\(_6\), \(\beta\)- and \(\theta\)-types. The \(\beta\)-salt shows metallic behavior down to 5 K. In contrast, the \(\theta\)-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 \(\theta\)-salt suggests the weak localization of charge \([1b]\). In this study, we looked closely into the origin of semiconducting behavior of \(\theta\)-(BTM-TTP)\(_2\)SbF\(_6\).

According to the normal mode analysis based on B3LYP method, C=C stretching modes of neutral BTM-TTP and (BTM-TTP)\(_2\)ReO\(_4\) were assigned. Fig. 1 shows Raman spectra of \(\theta\)-(BTM-TTP)\(_2\)SbF\(_6\). The broad line width at 300 K suggests an inhomogeneous charge distribution. On lowering temperature, \(\nu_6^P\) band gradually sharpened with a blue shift. At the same time, \(\nu_6^R\), \(\nu_8^P\), and \(\nu_8^R\) bands developed from the spectral tail. Therefore, the origin of semiconducting nature is concluded as a charge disproportionation. Isostructural \(\theta\)-(BSM-TTP)\(_2\)PF\(_6\) will also be reported in this conference.

Fig. 1 Raman spectra of \(\theta\)-(BTM-TTP)\(_2\)SbF\(_6\) excited by a 568 nm laser. \(\nu_j^P\) and \(\nu_j^R\) denote the \(\nu_j\) mode at the charge-poor and rich sites, respectively.