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Synthesis and Electronic Properties of Bilayer Type Molecular Conductors Based on Asymmetrical Donor Molecules

M. Uebe, H. Cui, R. Kato

Condensed Molecular Materials Laboratory RIKEN, 2-1 Hirosawa, Wakoshi, Saitama, 351-0198, Japan, email: masashi.uebe@riken.jp

Molecular conductors have been reported to realize various electronic properties different from those of inorganic materials based on molecular design. We synthesized asymmetrical donor molecules for searching unique crystal structures and electronic properties. For example, an asymmetrical donor molecule TMET-STF is a hybrid between HMTSF that prefers a one-dimensional column structure and BEDT-TTF that tends to take a two-dimensional molecular arrangement. In particular, the crystal of a BF₄ salt, (TMET-STF)_2BF₄, has two crystallographically independent cation radical layers, which is called bilayer structure. The band structure calculation indicates that the one conduction layer has a quasi-one-dimensional Fermi surface and the other layer a cylindrical two-dimensional Fermi surface. [1, 2] (TMET-STF)_2BF₄ is an ambient pressure superconductor at about 4.1 K. A small resistance anomaly around 100 K and a metal-insulator transition around 13 K were also observed and such complicated behavior is supposed due to the bilayer structure. In order to develop molecular conductors and new superconductors with bilayer structure induced by asymmetry of molecules, we have newly synthesized asymmetrical donor molecules, TMET-TTF, ETTM-STF, and TMET-TSF, and prepared their cation radical salts. X-ray structure analysis revealed that BF₄ and the ClO₄ salts have bilayer structure similar to that of (TMET-STF)_2BF₄ (Fig. 1). We will present crystal and electronic structures and physical properties of (TMET-TTF)_2X, (ETTM-STF)_2X, and (TMET-TSF)_2X (X = BF₄, ClO₄).

References