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

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Many molecular conductors have been reported because they can realize various electronic properties different from inorganic materials based on molecular design by using synthetic method. We synthesized new asymmetrical donor molecules for searching interesting crystal structures and electronic properties. For example, an asymmetrical donor molecule TMET-STF is a hybrid type molecule between HMTSF that is likely to take a one-dimensional column structure and BEDT-TTF that prefers a two-dimensional molecular arrangement (Fig. 1). The BF₄ salt of this molecule, (TMET-STF)₂BF₄, has two crystallographically independent cation radical layers, which is called bilayer structure. The band structure calculation indicates that each conducting layer has a quasi-one-dimensional Fermi surface and a cylindrical two-dimensional Fermi surface, respectively (Fig. 2) [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 are observed above the superconducting transition temperature, and this complicated behavior is induced by the bilayer structure (Fig. 3). Furthermore, the ClO₄ salt also has a bilayer structure like the BF₄ salt. On the other hand, the Au(CN)₂ salt has a one-dimensional column structure similar to HMTSF salts and the PF₆ salt has two-dimensional structure similar to (BEDT-TTF)₂PF₆. Depending on counter anions, cation radical salts of asymmetrical donor exhibit various crystal structures and show interesting



Fig. 2 The crystal structure and Fermi surface of (TMET-STF)₂BF_{4.}



Fig. 3 Temperature dependence of $(TMET-STF)_2BF_4$ at ambient pressure.

electronic states. This motivated us to develop molecular conductors and superconductors with the bilayer structure induced by the asymmetry of molecules. We synthesized a donor TMET-TTF where sulfur atoms substitute for selenium atoms within TMET-STF and prepared its cation radical salts (Fig. 1). In our previous synthetic work for asymmetrical donor molecules, including TMET-STF, we employed the conventional coupling reaction using trialkyl phosphate. In this coupling reaction, however, two symmetrical byproducts

are formed along with the asymmetrical donor molecule, and thus the yield of the target compound is low. In addition, when the selenocarbonyl group is used for the coupling reaction as starting material, it is necessary to use highly toxic hydrogen selenide. To synthesize efficiently only the aimed asymmetric donor TMET-TTF, we used the reaction developed by Yamada et al. which uses a dibutyltin complex and an ester compound of each donor unit in the presence of a Lewis acid catalyst such as Me₃Al. We then obtained cation radical salts with various counter anions using the electrochemical crystal growth method. X-ray crystal structure analysis revealed that the BF4 and ClO4 salts have a bilayer structure similar to (TMET-STF)₂BF₄ as shown in Fig. 4. (TMET-TTF)₂BF₄ has another type of crystal structure that is based on one-dimensional column formation. The PF₆ salt also has a one-dimensional column structure. At ambient pressure, the BF₄, ClO₄ and PF₆ salts of TMET-TTF are all semiconductors. Figure 5 shows temperature-dependent resistivity of the bilayer-type (TMET-TTF)₂BF₄ under pressure. The



Fig. 4 The crystal structures of (a) $(TMET-TTF)_2BF_4$ and (b) $(TMET-TTF)_2ClO_4$.



Fig.5 Temperature and pressure dependence of (TMET-TTF)₂BF₄.

resistivity decreased with the application of pressure. At 2.9 GPa, the system became metallic and kept the metal state down to ca. 100 K. Above 4.6 GPa, the system remained metallic down to the lowest temperature.

In future, we plan to synthesis new asymmetrical donor molecules containing selenium atoms in order to enhance intermolecular interactions and prepare cation radical salts with various counter anions.

References

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