

## IV-E Control of Electronic States in Molecular Conductors with Chemical and Physical Methods

The electronic state of the molecular conductor is quite sensitive to molecular arrangement and orientation that are governed by the inter-molecular interaction. Design of the inter-molecular interaction is indispensable in the rational development of molecular conductors to still higher forms. An introduction of supramolecular chemistry is a possible solution to this problem. We have developed various molecular conductors containing supramolecular assemblies based on two types of supramolecular interactions, the iodine-based halogen bond and the tellurium-based secondary bond. It has been demonstrated that the supramolecular interaction has the ability to tune the molecular arrangement and orientation and thus provides a route for the formation of novel molecular materials.

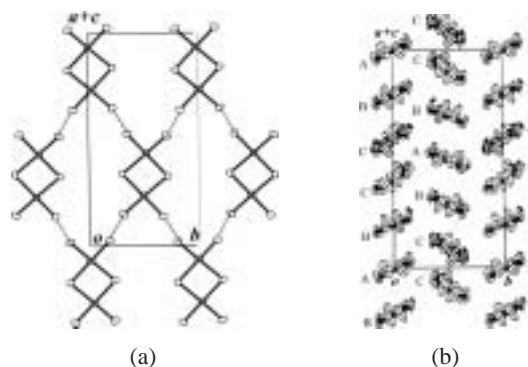
On the other hand, the electronic state of molecular conductors can be quite sensitive to the pressure (including chemical pressure) application. Recent development of the uniaxial stress and strain methods has enabled selective or anisotropic regulation of the inter-molecular interaction and has provided a powerful means to search for novel electronic states. We have examined the uniaxial strain effect and have found unusual electronic states in the organic narrow-gap semiconductor, the supramolecular conductor, and the two-dimensional strongly correlated system based on the metal dithiolene complex.

### IV-E-1 Structural and Physical Properties of New Conducting Cation Radical Salts with Te-Based Counter Anions, Tetraiodotellurate(II) and Hexaiodotellurate(II)

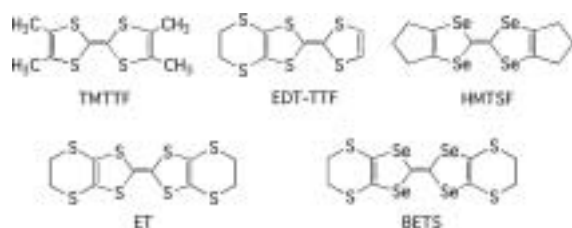
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We have prepared and characterized several cation radical salts of organic donors (TMTTF, EDT-TTF, ET, BETS and HMTSF; scheme) with two novel planar Te-based dianions,  $\text{TeI}_4^{2-}$  and  $\text{Te}_2\text{I}_6^{2-}$ .  $(\text{ET})_5\text{Te}_2\text{I}_6$  **1** and  $(\text{BETS})_5\text{Te}_2\text{I}_6$  **2** are isostructural. In these  $\text{Te}_2\text{I}_6^{2-}$  salts, intermolecular short I...I contacts form a supramolecular corrugated anion sheet (Figure 1a). Donor arrangement is similar to the  $\alpha$ -type (Figure 1b). With lowering temperature, the resistivity of **1** shows a gradual increase followed by a sharp upturn at 110 K. **2** is metallic down to 120 K and shows a gradual increase of the resistivity followed by a clear transition to an insulating state around 60 K. Crystal structure of  $(\text{ET})_4\text{TeI}_4$  **3** is based on the “herring bone” arrangement of ET molecules similar to the  $\alpha$ -type. **3** shows a semiconductive behavior around room temperature followed by a transition to an insulating state at 210 K.  $(\text{EDT-TTF})_4\text{TeI}_4$  **4**, a semiconductor, exhibits a unique two-dimensional arrangement of dimerized EDT-TTF molecules.



**Figure 1.** Crystal structure of **1**: a)  $\text{Te}_2\text{I}_6^{2-}$  anion network. b) end-on projection of ET molecules.



**Scheme 1.** Molecular structures of organic donors used in this work.