Design, Preparation, and Characterization of Novel ET Salts with Supramolecular Assembly. Sheet, Chain, and Pore Structures Based on Difluorotetraiodobenzene

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To control the donor/anion ratio of an ET (= bis(ethylenedithio)tetrathiafulvalene) salt, an anionic supramolecular assembly was designed. The supramolecular assembly based on 1,4-difluoro-2,3,5,6-tetraiodobenzene (DFTIB) and the bromide anion thus afforded an ET salt with desired 3:1 donor/anion ratio, while it also gave three other salts with unexpected structures. These salts showed semiconductive behaviors in the resistivity.

The control ability of the supramolecular assembly over crystal structure is attracting wide current interest as a tool for crystal engineering.[1] We have been trying to utilize this character of the supramolecular assembly for the development of new molecular conductors with the aid of iodine-containing neutral molecules,[2–4] because the physical properties of molecular conductors are strongly dependent on their crystal structures.[5] To design the crystal structure and the donor/anion ratio, we have recently noticed that the unit area of the anion layer is important. Since the supramolecular assemblies often form rigid two-dimensional (2D) anion layer, the unit area of the layer can be defined much clearer than discrete anion systems. For instance, *p*-bis(iodoethynyl)benzene (*p*BIB) and Cl^- form supramolecular assembly whose unit area contains one negative charge within 90 Å^2.[3] Since one ET molecule is known to occupy 25–30 Å^2 in the conduction layer,[6] the ET molecules are obliged to form the unusual 3:1 organic metal $(ET)_3Cl(pBIB)$ and possess the averaged charge of +1/3. Notably, the number of the +1/3-charged system is still limited despite of the interests in their physical properties with uncommon band filling, especially in comparison with the well-known +1/2-charged systems.

According to this condition for the +1/3-charged system (the 2D anion layer with ~90 Å^2/unit/e$^-$), we can design another anionic supramolecular structure for the preparation of 3:1 salts. Provided that the tetraiodobenzene forms rectangular lattice as shown in Figure 1, the unit cell with one negative charge should have an area of about 88 Å^2. This value is comparable to that of the *p*BIB system. Therefore, this anionic layer is expected to provide a new 3:1 ET salt, hopefully with metallic conduction associated with another donor arrangement. This letter describes expected and unexpected results of our crystal design.

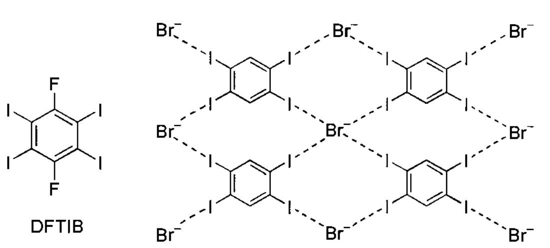

Figure 1. Molecular formula for DFTIB (left) and expected 2D supramolecular sheet formed by bromide anions and tetraiodobenzene (right). The size of the rectangular unit in the right figure is expected to be *ca.* 8 Å in height and *ca.* 11 Å in width, resulting the area of 88 Å^2.

In practice, we used 1,4-difluoro-2,3,5,6-tetraiodobenzene (DFTIB) rather than the simple tetraiodobenzene because of the requirement for electron-deficiency of the iodine atoms (tetraiodobenzene did not afford good crystals). The galvanostatic oxidation of a chlorobenzene solution dissolving ET, DFTIB, and tetraphenylphosphonium bromide afforded four salts $(ET)_3Br(DFTIB)$, $(ET)_2Br_2(DFTIB)$, $(ET)_2Br_2(DFTIB)_3(CB)_x$ (CB = chlorobenzene), and $(ET)_3Br_2(DFTIB)$. X-ray diffraction measurements revealed crystal structures of the former three and lattice constants for the last one.[7] The chemical formula for the last one was determined by the EPMA measurement.

The electric resistivities of the four salts were measured by the standard four-probe method. All of them exhibit semiconductive temperature dependence. The r. t. resistivities are ca. 3×10^0, 1×10^2, 1×10^0, and 3×10^2 Ω cm for $(ET)_3Br(DFTIB)$, $(ET)_2Br_2(DFTIB)$, $(ET)_2Br_2(DFTIB)_3(CB)_x$, and $(ET)_3Br_2(DFTIB)$, respectively. The activation energies are 0.11, 0.17, 0.07, and 0.12 eV, respectively. As for $(ET)_3Br(DFTIB)$, two resistivity anomalies were observed at 200 and 240 K.

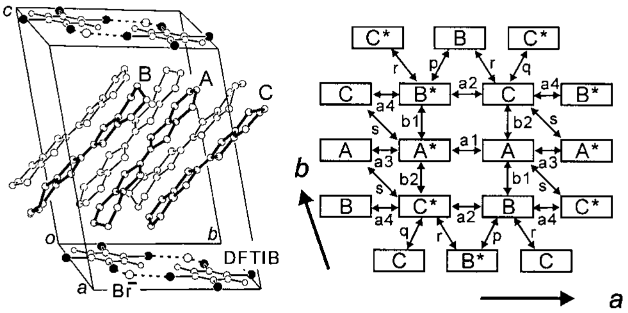

Figure 2. Crystal structure of $(ET)_3Br(DFTIB)$ along with the schematic donor arrangement viewed along the long axes of the donor molecules. The overlap integrals (*S*) are as follows (Overlaps smaller than 1×10^{-3} are omitted for clarity): $S(\mathbf{a1}) = -3.07$, $S(\mathbf{a2}) = -2.47$, $S(\mathbf{a3}) = -2.59$, $S(\mathbf{a4}) = -1.41$, $S(\mathbf{b1}) = -7.84$, $S(\mathbf{b2}) = -6.38$, $S(\mathbf{p}) = 3.36$, $S(\mathbf{q}) = 1.73$, $S(\mathbf{r}) = -8.23$, $S(\mathbf{s}) = 1.11 \times 10^{-3}$. Hydrogen atoms in the left figure are omitted for clarity.

The crystal structure of $(ET)_3Br(DFTIB)$ is shown in Figure 2, in which the expected rectangular lattice of DFTIB and Br^- is formed. The rectangle exhibits the height of 8.0 Å and the width of 10.9 Å. According to our designing principle, resulting anion area of 87 Å^2 corresponds to three ET molecules (29 Å^2 for each). In fact, the donor/anion ratio of this salt is 3:1. This fact justifies our designing strategy.

From crystallographic point of view, the unit cell of $(ET)_3Br(DFTIB)$ contains six ET molecules and two bromide anions. The distances between Br^- and the iodine atoms (3.25–3.33 Å) are quite shorter than the corresponding van der Waals contacts (3.80 Å). These strong and directional interactions are indicated as dotted lines in Figure 2. As for the donor molecules, three (A, B, and C) molecules are crystallographically independent. The longitudinal axes of B and C are almost parallel to one another while that of A is twisted against those of B and C by ca. 30º. This structure is similar to so called δ-type,[8] although the repeating unit is composed of three donors in this case.

To investigate the electronic nature of this salt, the tight-binding band calculation based on extended Hückel MO was carried out.[9] In the calculation, the HOMO levels for the donor molecules are assumed to be equal as a first approximation, although the calculated donors' charges based on their bond lengths[10] indicate slight charge separation (ca. +0.5 for A and ca. +0.3 for B and C). The overlap integrals between HOMOs are shown in Figure 2. The conducting layer parallel to the ***ab*** plane is composed of two donor-chains (···B*A*C*··· and ···CAB···) interrelated by the inversion symmetry. The inter-chain interactions are relatively weak and thus the conduction band is dispersive in the ***b****** direction, forming quasi-1D Fermi surfaces as shown in Figure 3. Although this result indicates metallic character, the salt exhibited semiconductive temperature dependence in its resistivity as mentioned above. The origin of this semiconducting character is an open question and will be discussed elsewhere.

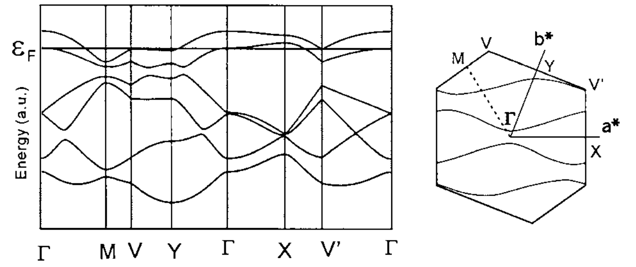

Figure 3. Band structure of $(ET)_3Br(DFTIB)$.

Anyway, we have successfully proved that the donor/anion ratio can be controlled by fabricating the supramolecular assembly. Our designing principle, however, is based on the layered structure. If this limitation is removed, other donor/anion ratio would be possible. Indeed, the DFTIB molecule coupled with the Br^- anion also gave unexpected supramolecular and crystal structures. In $(ET)_2Br_2(DFTIB)$, DFTIB and Br^- form 1D chain structure as illustrated in Figure 4. The period of the two-fold ET stack is equal to the 1D chain period, affording the donor/anion ratio of 1:1.

In another 1:1 salt $(ET)_2Br_2(DFTIB)_3(CB)_x$, the Br^- and DFTIB construct very unique supramolecular structure which contains 1D rectangular pores with the size of ca. 3 × 6 Å^2 as shown in Figure 5. These pores accommodate the solvent molecules (chlorobenzene), some atoms of which are observed as residual electron peaks. The accurate structure of the solvent, however, could not be fixed due to the heavy disorder. To maintain this unique supramolecular structure, interactions other than the anion···iodine interaction are employed: the iodine atoms of DFTIB are coordinated by the fluorine atoms and the π-electrons of the benzene rings as well as the bromide anions. These interesting interactions would enrich the possibility of the future crystal design, although predicting such motifs remains difficult so far.

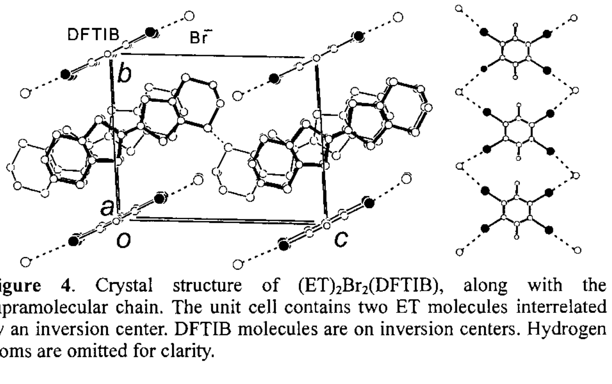

Figure 4. Crystal structure of $(ET)_2Br_2(DFTIB)$, along with the supramolecular chain. The unit cell contains two ET molecules interrelated by an inversion center. DFTIB molecules are on inversion centers. Hydrogen atoms are omitted for clarity.

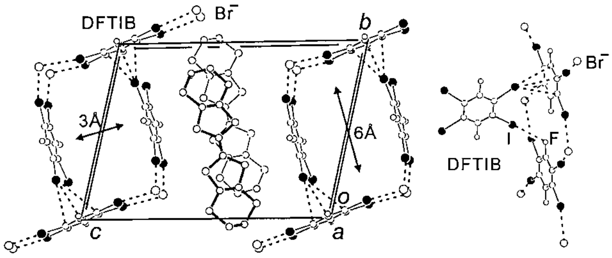

Figure 5. Crystal structure of $(ET)_2Br_2(DFTIB)_3(CB)_x$, along with the enlargement of the I···π and I···F interactions. The donor molecules form 1D conduction column.

In conclusion, we have proposed the designing principle of supramolecular assembly in the ET salts with layered structures in order to obtain an expected donor/anion ratio. The select molecule, DFTIB, provided the expected 3:1 salt and additional three other salts, two of which were revealed to have unexpected non-layered structures.

References and Notes

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6 Some of the calculated anion areas per ET molecule are as follows: 24.8 Å^2 for α-$(ET)_2I_3$, 27.7 Å^2 for β-$(ET)_2I_3$, and 27.7 Å^2 for κ-$(ET)_2Cu(NCS)_2$.

7 Crystal data for $(ET)_3Br(DFTIB)^-$: $C_{36}H_{24}F_2BrI_4S_{24}$, FW = 1851.54, triclinic, $P\bar{1}$, 1), a = 13.428, b = 13.546, c = 17.487 Å, α = 99.73, β = 105.87, γ = 107.46º, V = 2807.2 Å^3, Z = 2, D_{calc} = 2.190 g cm^{-3}, R = 0.087 for unique 10530 reflections. Crystal data for $(ET)_2Br_2(DFTIB)$: $C_{13}H_8FBrI_2S_8$, FW = 773.40, triclinic, $P\bar{1}$, a = 7.884, b = 11.069, c = 12.999 Å, α = 84.34, β = 84.80, γ = 71.46º, V = 1068.2 Å^3, Z = 2, D_{calc} = 2.404 g cm^{-3}, R = 0.070 for unique 3919 reflections. Crystal data for $(ET)_2Br_2(DFTIB)_3(CB)_x$: $C_{19}H_{12}F_3BrI_6S_8$, FW = 1851.54, triclinic, $P\bar{1}$, a = 7.840, b = 13.276, c = 17.967 Å, α = 99.99, β = 102.21, γ = 98.86º, V = 1764.36 Å^3, Z = 2, D_{calc} = 2.626 g cm^{-3}, R = 0.083 for unique 7682 reflections. Crystal data for $(ET)_3Br_2(DFTIB)$: monoclinic, a = 14.145, b = 24.717, c = 21.409 Å, β = 90.381º, V = 7484.9 Å^3.

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