Crystal Structures and Electrical Properties of 1:1 and 4:1 PF_6 Salts of BO–HBDTT with an α'-Type Donor Arrangement

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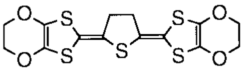
Crystal structures and electronic properties of [BO–HBDTT][PF_6] and [BO–HBDTT]$_4$[PF_6] have been clarified. The donor packing patterns in these salts can be basically classified into α'-type, in which the donor stacks in the twisted overlap mode regarding the 1,3-dithiole rings. Intrastack intermolecular C–H···O contacts play an important role in the metallic nature of [BO–HBDTT]$_4$[PF_6].

Quite recently, we have unexpectedly found that 2,5-bis(4,5-ethylenedioxy-1,3-dithiol-2-ylidene)-2,3,4,5-tetrahydrothiophene (BO–HBDTT), a new conjugation elongated BEDO–TTF type donor yielded a two-dimensional metallic salt, [BO–HBDTT]$_5$[ClO_4]$_2$[PhCl]$_2$ showing metallic behavior down to 30 K.[1] From this fact it is suggested that BO–HBDTT could be a promising donor for organic conductors. Then, the preparation of other cation radical salts based on BO–HBDTT is of considerable interest. Herein we report crystal and electronic structures of two kinds of PF_6 salts of BO–HBDTT, which have an α'-type donor arrangement. One of them showed a metallic nature.



BO–HBDTT

Brown plate-like single crystals of [BO–HBDTT][PF_6] and black needle-like single crystals of [BO–HBDTT]$_4$[PF_6] were harvested by the galvanostatic electrolysis of BO–HBDTT in chlorobenzene and in THF, respectively, at 20 °C in the presence of Bu_4NPF_6. [BO–HBDTT][PF_6] showed σ_{rt} = 0.18 S cm^{-1}, semiconducting temperature dependence with E_a = 0.069 eV down to 210 K. On the other hand, [BO–HBDTT]$_4$[PF_6] showed a fairly high conductivity, σ_{rt} = 16 S cm^{-1}, and is metallic down to 200 K (Figure 1).

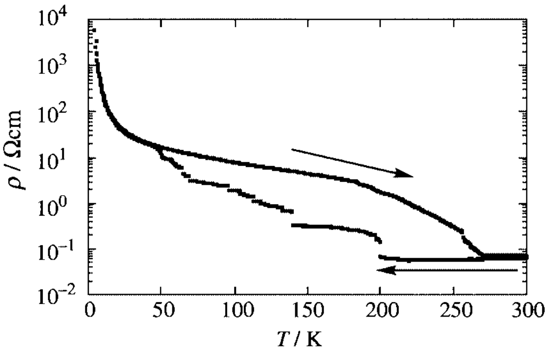


Figure 1. Temperature dependence of the resistivity of [BO–HBDTT]$_4$[PF_6].

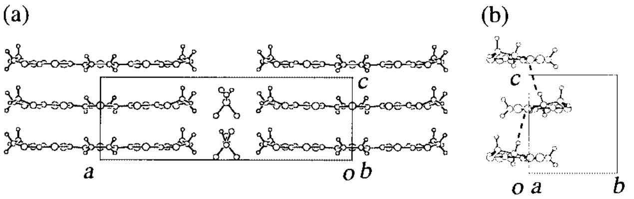


Figure 2. Crystal structure of [BO–HBDTT]$_4$[PF_6]: (a) viewed along the b-axis; (b) intrastack intermolecular hydrogen bond viewed along the a-axis. The unit cell contains 0.5 anions.

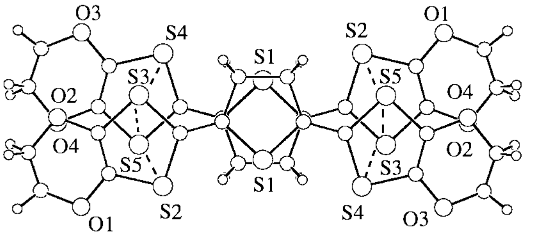


Figure 3. Stacking mode of donor molecules in [BO–HBDTT][PF_6] and [BO–HBDTT]$_4$[PF_6] viewed along the c-axis. Dotted lines indicate chalcogen atom contacts.

From X-ray crystal analysis, it was revealed that both salts belong to the same space group and have the same donor arrangement.[2] The donor molecules stack uniformly along the c-axis (Figure 2a) directing the central sulfur atom to the opposite side without slipping (Figure 3). The interplanar distance is 3.53 Å. This overlap mode is quite favorable to avoiding the steric repulsion of the central ethylene moiety. Interestingly, there exist short intrastack C–H···O contacts in both sides of the donor molecule participated with the ethylenedioxy oxygen atoms and the terminal ethylene protons of the neighboring donor molecules (O2–H12 = O4–H6 = 2.52 Å for the 1:1 salt and 2.96 Å for the 4:1 salt) (Figure 2b). There are also short interstack C–H···O contacts along the oblique directions (O1–H9 = O3–H3 = 2.66 Å for the 1:1 salt and 2.71 Å for the 4:1 salt) (Figure 4). The intrastack C–H···O contacts appear to play an important role to bring about the uniform stack, since uniformly stacked donor arrangement is very rare in the salts based on 5-membered heterocycle-extended BEDT–TTF type donors.[3] Thus incorporation of ethylenedioxy moieties in conjugation elongated donor molecules is a very usefull molecular design strategy to make metallic organic conductors with uniform segregated columns.[4]

The overlap mode of the 1,3-dithiole rings in Figure 3 closely resembles the twisted overlap mode in δ- and α'-phase BEDT–TTF salts.[5] The twisted overlap mode has never been observed in BEDO–TTF family. It has been known that many

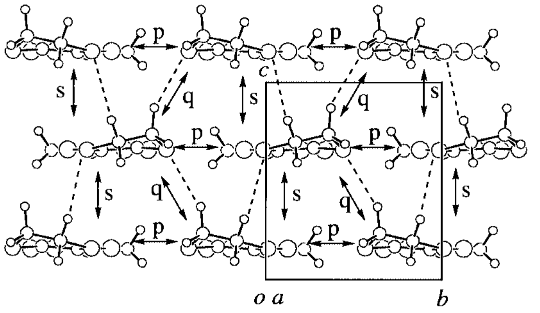


Figure 4. Molecular arrangement of donor molecules in [BO–HBDTT][PF_6] and [BO–HBDTT]$_4$[PF_6] viewed along the donor long axis (*a*-axis). Dotted lines indicate intermolecular C–H···O contacts.

Table 1. Calculated intermolecular overlap integrals[a] (S × 10^3) of [BO–HBDTT][PF_6] and [BO–HBDTT]$_4$[PF_6]

Interaction type	1 : 1	4 : 1
s (stacking direction)	–10.41	–10.26
p (side-by-side direction)	2.96	2.93
q (oblique direction)	–2.56	–2.32

[a] The overlap modes s, p, and q are indicated in Figure 4.

of organic conductors with such a twisted overlap mode are insulating or exhibit fairly high metal-insulator transition temperatures.[5] Therefore, twisted overlap mode and metallic nature of the present 4:1 PF_6 salt down to 200 K are very unusual and novel from the view point of genealogy of BEDO–TTF- or BEDT–TTF-based organic conductors.

Although intrastack intermolecular S···S distances (3.83–3.87 Å) (Figure 3) are not so short, the calculated intrastack overlap integral, s (Table 1) is fairly large.[6] The donor packing pattern of the 1:1 and 4:1 PF_6 salts is shown in Figure 4. The donor molecules are coplanarly linked side-by-side (along the *b* axis) by the two short S···S contacts (3.49 Åfor the 1:1 salt and 3.50 Å for the 4:1 salt) and two O···S contacts (3.37 Åfor the 1:1 salt and 3.30 Å for the 4:1 salt) near to the van der Waals distance (3.32 Å), directing the central sulfur atom to the same side (Figure 4). In spite of the short S···S contacts, the calculated overlap integral in side-by-side direction, p (Table 1) is not so large.[6] In the oblique directions along the *b–c* and *b+c* axes, donors are arranged directing the central sulfur atom to the opposite side (Figure 4). Along the oblique directions (q), effective intermolecular S···S overlaps are possible since the 1,3-dithiole rings of the donor in each adjacent column are coming close. In consequence, the magnitude of the calculated overlap integral, q is as large as that of p (Table 1).

Thus, the layered intermolecular π-electron overlapping networks are constructed along the *bc*-plane. The intrastack overlap integral, s is about three times larger than those of inter-column overlap integrals, p and q (Table 1). Therefore, the PF_6 salts have quasi-one-dimensional character along the stacking direction.

Interestingly, the donor packing pattern of the PF_6 salts (Figure 4) is similar to those of α'-type [BEDT–TTF]$_2$[X] salts: X=$AuBr_2$, $Au(CN)_2$, or $Ag(CN)_2$,[7,8] while the PF_6 salts are composed of the extended BEDO–TTF type of donor. The α'-type of donor arrangement has never been found so far in the BEDO–TTF salts. It should be noted that the α'-type BEDT–TTF salts have strongly dimerized structures and are one-dimensional along the side-by-side direction showing insulating nature.[5] In contrast, the present PF_6 salts are one-dimensional along the stacking direction having a uniform stacking structure and the 4:1 PF_6 salt has a metallic nature. Thus, the 4:1 PF_6 salt is the first example of α'-type salt with a metallic nature and belongs to the BEDO–TTF family.

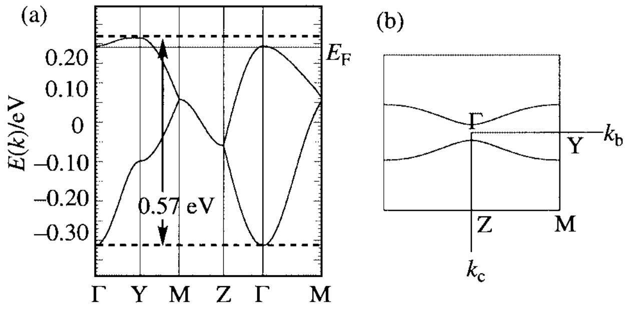


Figure 5. (a) Band structure and (b) Fermi surface of [BO–HBDTT]$_4$[PF_6], calculated by the tight binding approximation method.

Metallic band structures were calculated by the tight binding approximation method for the 1:1 and 4:1 PF_6 (Figure 5a) salts. The calculated bandwidth of both of the PF_6 salts is 0.57 eV. Both salts have quasi-one-dimensional Fermi surfaces open out into the k_b direction (Figure 5b). The semiconducting character of the 1:1 PF_6 salt appears to be commonly reasonable since it is a perfect electron transfer system.

References and Notes

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2 Crystal data for [BO–HBDTT][PF_6]: fw = 549.54 orthorhombic space group $Pmc2_1$, a = 21.250(4), b = 6.271(2), c = 7.068(4) Å, V = 944.2(5) Å^3 and Z = 2, (R = 0.114 and R_w = 0.140 for observed 756 reflections with $I > 3.00\sigma(I)$). [BO–HBDTT][PF_6]$_{0.25}$: fw = 440.82 orthorhombic, space group $Pmc2_1$, a = 21.188(4), b = 6.2844(2), c = 7.075(4) Å, V = 942.1(3) Å^3 and Z = 2, (R = 0.065 and R_w = 0.080 for observed 850 reflections with $I > 3.00\sigma(I)$). The 4:1 donor to anion ratio is also confirmed by elemental analysis.
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