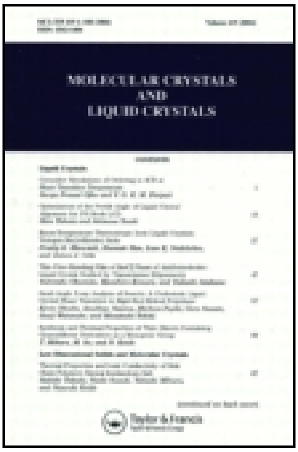

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Two-Dimensional Metallic ClO 4 Salt of a Novel Dihydrothiophene-Extended Donar, BO-HBDTT, with Relatively Narrow Band Width

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Two-Dimensional Metallic ClO_4 Salt of a Novel Dihydrothiophene-Extended Donar, BO-HBDTT, with Relatively Narrow Band Width

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A new dihydrothiophene-extended BEDO-TTF (BO) type donor, BO-HBDTT, was synthesized by a convenient method and gave metallic ClO_4, BF_4, and PF_6 salts. Of these the ClO_4 salt with β'' type donor arrangement showed two-dimensional metallic behavior and relatively narrow band width.

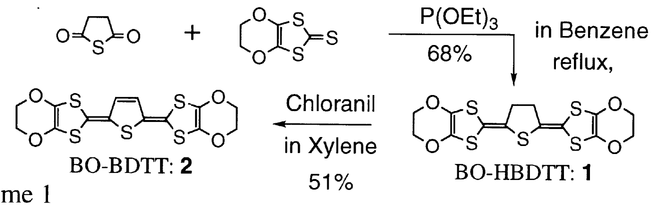
Keywords Dihydrothiophene-extended BO; ClO_4 salt; 2D metal; β'' type

INTRODUCTION

It has been known that BEDO-TTF produces a variety of metallic complexes with inorganic and organic counter components due to its strong aggregation property to form a layered structure connected by intrastack C–H---O and side-by-side heteroatom contacts.[1] For this reason, many of BEDO-TTF complexes have wide band width and their metallic states are stable down to below 20 K. Thus high T_C superconductors based on BEDO-TTF appear to be difficult to prepare according to the BCS theory.[2] To decrease band width and to make the metallic state more unstable, we have now designed and synthesized a new extended donor, BO-HBDTT, **1**, as well as BO-BDTT, **2** and clarified the crystal and electronic structures of the ClO_4 salt of **1**.

RESULTS AND DISCUSSION

The donors **1** and **2** were synthesized by the route shown in Scheme 1.[3]



Scheme 1

The E_1^{ox} and E_2^{ox} values of **1** (+0.53 and +0.75 V *vs* SCE) are higher than those of BEDO-TTF (+0.42 and +0.74 V *vs* SCE) in PhCN at 25 °C. Although the preparation of radical cation salts of **2** (E_1^{ox} =+0.19 V, E_2^{ox}=+0.37 V, *vs* SCE in PhCN) failed because of its instability, single-crystalline salts of **1** were grown by the conventional electrochemical oxidation in chlorobenzene.

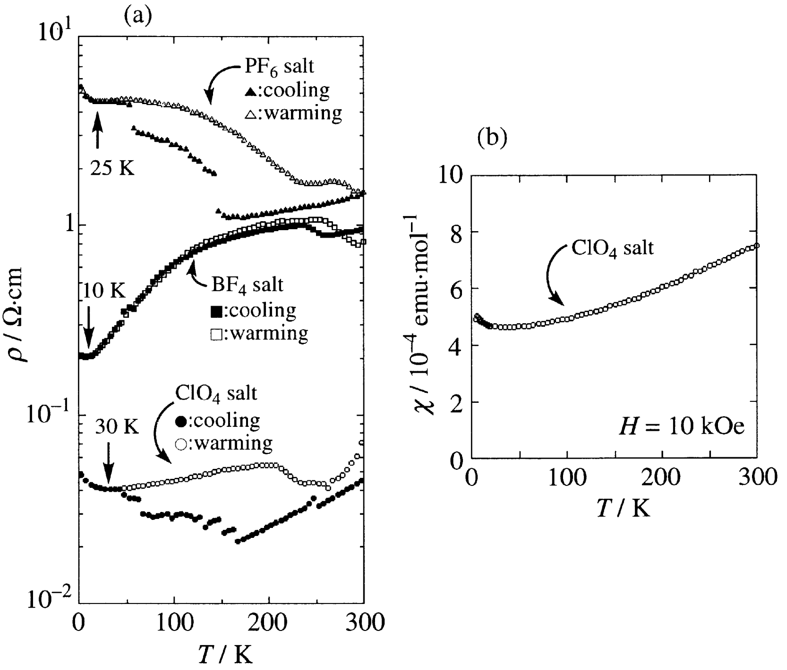


FIGURE 1. Temperature dependence of (a) the resistivities of $[\text{BO-HBDTT}]_5[ClO_4]_2[PhCl]_2$, $[\text{BO-HBDTT}]_2[BF_4][PhCl]$, and $[\text{BO-HBDTT}]_5[PF_6]_2[PhCl]_2$ and (b) the magnetic susceptibility of $[\text{BO-HBDTT}]_5[ClO_4]_2[PhCl]_2$.

$[BO\text{-}HBDTT]_5[ClO_4]_2[PhCl]_2$, $[BO\text{-}HBDTT]_2[BF_4][PhCl]$, and $[BO\text{-}HBDTT]_5[PF_6]_2[PhCl]_2$, showing room temperature conductivities of 22, 1.1, and 0.68 S cm^{-1}, are metallic from room temperature down to 30, 10, and 25 K, respectively (FIGURE 1 (a)). The temperature dependence of the magnetic susceptibility of the ClO_4 salt is almost invariable from room temperature down to 5 K (FIGURE 1 (b)), which is regarded as Pauli paramagnetism. Thus, at least the ClO_4 salt is metallic down to 5 K.

X-Ray crystal structure analysis of the ClO_4 salt[4] was performed, while the structure analyses of the BF_4 and PF_6 salts were unable. Due to the poor quality of the crystals despite of our many efforts and the spontaneous loss of the PhCl during the X-ray data collection, the conventional R factor of the structural analysis is 0.300 at present. The choice of the space group is unambiguous, since the refinements assuming the other symmetries have not afforded the adequate molecular shape or produced the same structure to that described below in the unit cell of lower symmetry. The donor molecules in the ClO_4 salt stack uniformly along the a-axis directing the central sulfur atom to the same side with the interplanar distance of 3.51(10) Å[5] (FIGURE 2). The overlap mode is so-called ring-over-atom type with the slip distance of 2.12(8) Å along the donor short axis.

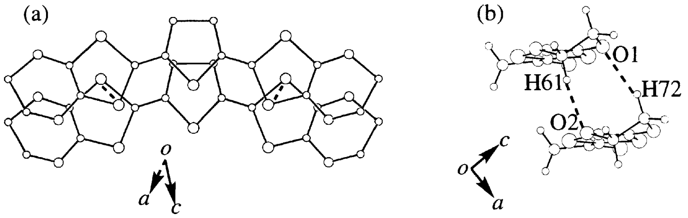


FIGURE 2 Intrastack intermolecular contacts in $[BO\text{-}HBDTT]_5[ClO_4]_2 [PhCl]_2$: (a) overlapping mode of donor molecule viewed along the a–c axis; (b) intrastack intermolecular hydrogen bond viewed along the donor long axis (b-axis).

There are two intrastack intermolecular short S---S contacts (3.68(9) Å) responsible for the 1,3-dithiole sulfur atoms.[6] More interestingly, there exist two short intrastack C–H---O contacts in both sides of the donor molecule participated with the four ethylenedioxy oxygen atoms and terminal ethylene protons of the neighboring donor molecules (O2–H61= O3–H131 = 2.72(9) Å, O1–H72 = O4–H142 = 2.74(8) Å). The C–H---

O angles (152—142°) are very close to the typical ones (152.7°). These intrastack C–H---O contacts appear to play an important role in determing the molecular packing motif, especially to bring about the uniform stack, since uniformly stacked donor arrangements are very rare in the salts based on 5-membered heterocycle-extended BEDT-TTF type donors.[7]

The donor molecules are coplanarly linked side-by-side (along the *a*+*c* axis) by the two short S---S contacts (3.46(3) Å) and two O---S contacts (3.33(4) Å) near to the van der Waals distance (3.32 Å), directing the central sulfur atom to the same side, but no slipping along the donor long axis was observed. Moreover, there exist two effective S---S interstack orbital overlaps along the oblique direction resulting relatively large overlap integral q (TABLE 1), although the S---S atomic distance (3.80(10) Å) is not so short.[8] Thus rigid and tight two-dimensional layered intermolecular networks are constructed along the *ac*-plane (FIGURE 3).

TABLE 1 Intermolecular overlap integrals[a] ($S \times 10^3$) of $[BO\text{-}HBDTT]_5[ClO_4]_2[PhCl]_2$ and $[BEDO\text{-}TTF]_{2.4}[I_3]$

Interaction	$[BO\text{-}HBDTT]_5[ClO_4]_2[PhCl]_2$	$[BEDO\text{-}TTF]_{2.4}[I_3]$
s (intrastack)	3.7	5.5
q (oblique)	–7.9	–13.0
p (transverse)	6.8	15.2

[a] The overlap modes s, q, and p are indicated in Figure 3. The overlap integrals for both salts were calculated using the same parameter.

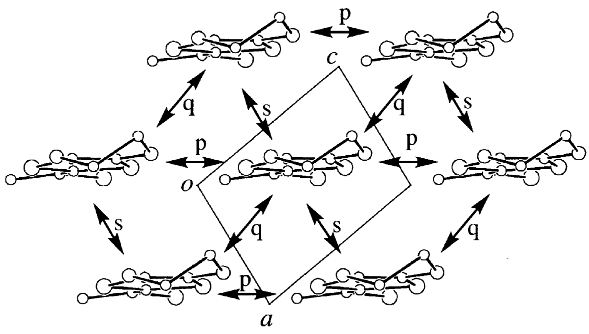


FIGURE 3 Molecular arrangement of donor molecules in $[BO\text{-}HBDTT]_5[ClO_4]_2[PhCl]_2$ viewed along the donor long axis (*b*-axis).

This donor packing mode is similar to that of $[\text{BEDO-TTF}]_{2.4}I_3$ salt[1] (β'' type)[9]. In comparison of the calculated intermolecular overlap integrals of our ClO_4 salt with those of the BEDO-TTF salt (TABLE 1), the intrastack interaction (s) is almost comparable with each other, but the values of the oblique (q) and transverse (p) interactions of our ClO_4 salt are about 2/5—3/5 of those of the I_3 salt. In consequence, the 2D character appears to be relatively enhanced in our ClO_4 salt ($p/s = 1.8$, $q/s = 2.1$) compared with the I_3 salt ($p/s = 2.76$, $q/s = 2.36$).

The 4/5 filled metallic band structure and calculated Fermi surface with 2D nature of the ClO_4 salt are depicted in FIGURE 4. The Fermi surface is composed of an ellipse centered around the X point.

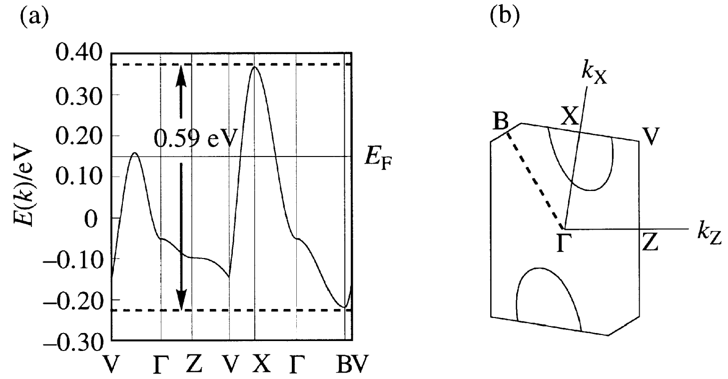


FIGURE 4 (a) Band structure and (b) Fermi surface of $[\text{BO-HBDTT}]_5[ClO_4]_2[PhCl]_2$.

Since the overlap along the *a* axis is smaller than those of the *c* and *a*+*c* axes, the ellipse is elongated along the k_X axis. This is a new 2D metal based on conjugation-extended type donors not incorporating the TTF skeleton.[10] As we expected first, the band width of our ClO_4 salt (0.59 eV) is about half of $[\text{BEDO-TTF}]_{2.4}I_3$ (1.13 eV). Thus, BO-HBDTT based salts with narrow band width and 2D character are of current interest in its possibilities for creation of high T_C organic superconductors.

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[3] Selected physical data of BO-HBDTT, **1:** yellow plates, mp 206—208 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.25 (8H, s, OCH_2CH_2O), 2.58 (4H, s, dihydrothienylene ring protons); ^{13}C NMR (150 MHz, $CDCl_3$) δ 34.50, 66.17, 107.40, 122.20, 122.50; UV-VIS (THF) λ_{max}/nm (log ε) 410 (2.76), 331 (sh, 4.22), 316 (4.28). BO-BDTT, **2**: Reddish brown powder, mp > 300 °C; ^{1}H NMR (200 MHz, $CDCl_3$-CS_2) δ 4.28 (8H, s, OCH_2CH_2O), 6.30 (2H, s, thienylene ring protons); UV-VIS (THF) λ_{max}/nm (log ε) 581 (sh, 3.31), 501 (3.39).

[4] Crystal data for $[BO\text{-}HBDTT]_5[ClO_4]_2[PhCl]_2$: $(C_{14}H_{12}O_4S_5)(ClO_4)_{0.4}(C_6H_5Cl)_{0.4}$: FW=489.38 monoclinic space group $P2_1/m$, a = 4.1(1), b = 41.91(10), c = 5.45(9) Å, β = 99(1)°, V = 913(31) Å^3 and Z = 2, (R = 0.300 and R_W = 0.337 for observed 1332 reflections with $I > 2.00\sigma(I)$). The stoichiometry was determined by the elemental analysis: Anal Found: C, 40.169; H, 2.842; S, 33.04%. Calcd for $C_{82}H_{70}O_{28}S_{25}Cl_4$: C, 40.251; H, 2.883; S, 32.76%. $[BO\text{-}HBDTT]_2[BF_4][PhCl]$: Anal Found: C, 40.603; H, 2.977; S, 31.70%. Calcd for $C_{34}H_{29}O_8S_{10}BF_4Cl$: C, 40.493; H, 2.898; S, 31.80%. $[BO\text{-}HBDTT]_5[PF_6]_2[PhCl]_2$: Anal Found: C, 39.037; H, 2.820; S, 31.64%. Calcd for $C_{82}H_{70}O_{20}S_{25}P_2F_{12}Cl_2$: C, 38.807; H, 2.780; S, 31.59%.

[5] Hereafter, estimated standard deviations in the least significant figure are given in parentheses.

[6] There are considerably large π-HOMO coefficients on all the S atoms of **1**. All the S and O atoms have the same phase reversing in the phase of the remaining all carbon atoms.

[7] K. Takahashi, T. Ise, T. Mori, H. Mori, and S. Tanaka, *Chem. Lett.*, **1996**, 1001; T. Ise, T. Mori, and K. Takahashi, *Chem. Lett.*, **1997**, 1013; K. Takahashi, T. Ise, T. Mori, H. Mori, and S. Tanaka, *Chem. Lett.*, **1998**, 1147.

[8] The magnitude of overlap integrals depends on the angle between the molecular plane and the intermolecular vector, not always proportional to the S---S distance: see the literature listed as reference [9].

[9] T. Mori, *Bull. Chem. Soc. Jpn.*, **71**, 2509 (1998).

[10] $[BO\text{-}HBDTT]_2[BF_4][PhCl]$ and $[BO\text{-}HBDTT]_5[PF_6]_2[PhCl]_2$ resemble $[BO\text{-}HBDTT]_5[ClO_4]_2[PhCl]_2$ in conducting and band