Synthesis of BEDT-BDTBS and Crystal Structures of Its Conducting Cation Radical Salts

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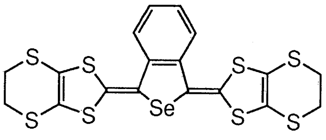
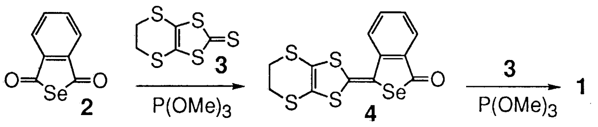
1,3-Bis(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3-dihydrobenzo[c]selenophene (BEDT-BDTBS) has been synthesized by a convenient method and the electric properties and X-ray crystal structures of its single-crystalline cation radical salts have been clarified.

Extension of donor π-systems is very important molecular design strategy not only to stabilize the dicationic state of the donor molecules by decreasing the Coulombic repulsive energy[1] but also to create high T_c organic superconductors by increasing the thickness of the effective conducting layer for the carrier distribution.[2] We have succeeded very recently in the synthesis of several heteroquinonoid-extended donors and have proved that the TCNQ complexes of some of these donors exhibit fairly high conductivities even when measured on compressed pellets.[3] However, the crystal structures of the conducting CT complexes of these donors have not been determined so far. The crystal growth and the intermolecular bonding interactions in the single-crystalline complexes will be much enhanced by the introduction of ladder-like array of sulfur atoms and/or selenium atom(s) with diffused *p*-orbitals.[4] Moreover, the electrochemical crystal growth of cation radical salts might take place more easily by the condensation of a benzene ring on the central heterocyclic ring which may reduce the solubility of the corresponding cation radical salts. To this end, we have now synthesized a new fused donor, BEDT-BDTBS, **1** and have clarified the electric properties and X-ray crystal structures of its single-crystalline cation radical salts, which are reported herein.

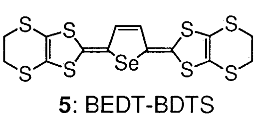


1: BEDT-BDTBS

The new donor, BEDT-BDTBS, **1** has been synthesized in a fairly good overall yield of 42% by a convenient, short-step method according to the routes depicted in Scheme 1.[5] The cyclic voltammogram of BEDT-BDTBS exhibited two pairs of reversible redox waves and the E_1^{ox} and E_2^{ox} values (+0.47 and +0.68 V *vs*. SCE in PhCN at 25 °C) are higher by 0.17 and 0.23 V respectively, than the corresponding oxidation potentials of non-fused donor, BEDT-BDTS, **5**.[3d] BEDT-BDTBS formed a 2:3 charge-transfer (CT) complex with TCNQ. Although the complex is stoichiometrically rich in the acceptor component, the complex exhibits room temperature conductivity of 4.9 Scm^{-1} on a compressed pellet and a very broad intra-stack CT absorption band[6] at 2800 cm^{-1} in the solid state electronic spectrum, characteristic of a segregated stacked structure in a mixed valene state (Table 1). We have succeeded in obtaining single-crystalline cation radical salts of BEDT-BDTBS, **1** with ClO_4, BF_4, ReO_4, and PF_6 by conventional electrochemical oxidation in chlorobenzene containing 10% volume of ethanol in the presence of the corresponding tetra-*n*-butylammonium salts under the constant current of 1 μA. Of these, the BF_4 and PF_6 salts exhibited fairly high conductivities as shown in Table 1. The PF_6 salt exhibited a semiconducting temperature dependence, but with a relatively small activation energy of E_a=0.066 eV in the range of room temperature to 80 K.



Scheme 1.



5: BEDT-BDTS

Table 1. Conductivities[a] and physical properties of TCNQ complex and single-crystalline radical cation salts of **1**

Anion	D : A	Form	σ_{RT} /Scm^{-1}	ν_{CT} /cm^{-1}	E_a /eV
TCNQ	2 : 3	Powder	4.9	2800	----[b]
BF_4	2 : 3	Prism	1.0	2800	----[c]
ClO_4	2 : 3	Prism	1.9×10^{-4}	> 4000	----[c]
ReO_4	2 : 3	Prism	3.2×10^{-2}	> 4000	----[c]
PF_6	----	Needle	2.8	3000	0.066

[a] The room temperature conductivities were measured by four-probe method. [b] To be measured. [c] The exact value was not obtained.

X ray crystal structural analysis of the ClO_4, BF_4, and ReO_4 salts, which are iso-morphous with each other, has been performed.[7] BEDT-BDTBS molecules, in the ClO_4 salt for an example, stack along the *c*-axis and the unit cell contains two pairs of a dimer in the donor column as seen in Figure 1.

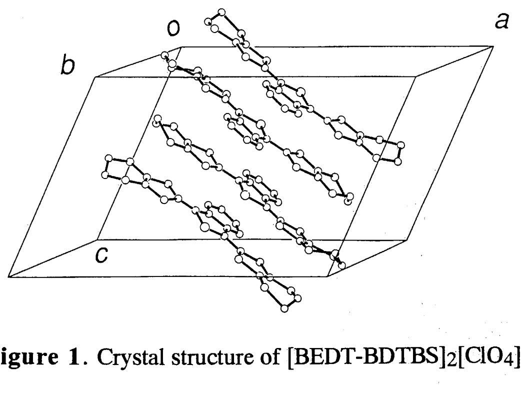


Figure 1. Crystal structure of $[BEDT\text{-}BDTBS]_2[ClO_4]_3$.

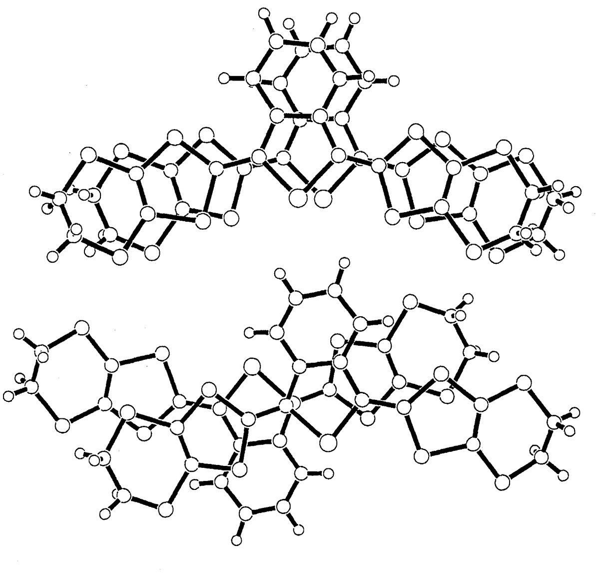


Figure 2. Overlapping mode of donor molecules in [BEDT-BDTBS]$_2$[ClO$_4$]$_3$, top: intra-dimer overlap, bottom: inter-dimer overlap.

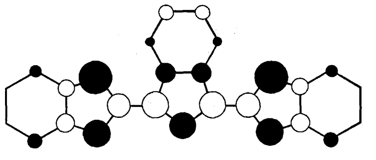


Figure 3. π-HOMO coefficients of BEDT-BDTBS, **1**.

The overlapping mode of the intra-dimer overlap (Figure 2, top) is of so-called ring-over-bond type, directing the central selenium atom to the same side of the molecule. In considering the π-HOMO coefficients of the donor molecule obtained from MNDO-PM3 calculation (Figure 3), it is revealed that a strong intermolecular HOMO-HOMO bonding interaction is achieved in the intra-dimer overlap. On the other hand, the inter-dimer overlapping mode (Figure 2, bottom) is a little complicated, and then, the intermolecular HOMO-HOMO bonding interaction in the inter-dimer overlapp appears to be weaker than that of the intra-dimer overlap. Indeed the inter-dimer overlap integral (c2) is about one tenth of the intra-dimer overlap integral (c1) in the ClO$_4$ salt (Figure 4). However, in the BF$_4$ salt exhibiting the 10^4 times higher conductivity than that of the ClO$_4$ salt, the overlap integral ratio of c1 (9.63×10^{-3}) to c2 (10.35×10^{-3}) is almost 1:1. From this evidence it is suggested that the packing mode providing a uniform stack or with fairly identical overlap integrals between c1 and c2 is important to induce a high conductivity. In the ClO$_4$ salt, the overlap integrals of the transverse directions (b, p1, and p2) are less than 1/20 of the intra-dimer overlap (c1). The donor molecules are separated from each other by the anion molecules in the transverse directions. A band structure and a semimetallic Fermi-surface of the BF$_4$ salt with one-dimensional nature were calculated by a tight-binding model based on an Extended Hückel molecular orbital. Investigation on the salts with octahedral anions is in progress.

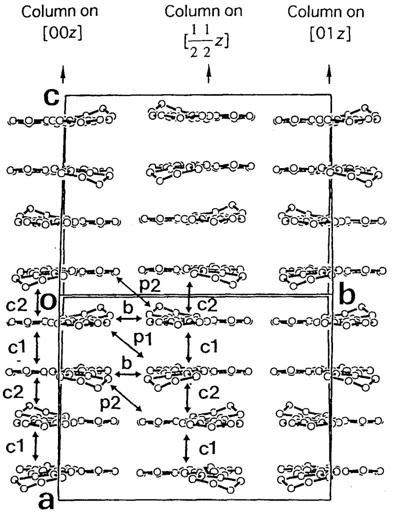


Figure 4. Molecular arrangement of donor units in [BEDT-BDTBS]$_2$[ClO$_4$]$_3$, viewed along the donor long axis. The overlap integrals, c1, c2, b, p1, and p2 are 10.74, 1.17, 0.39, 0.15, and -0.19×10^{-3}, respectively.

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References and Notes

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4 J. K. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. -H. Whangbo, "Organic Superconductors (Including Fullerenes)", Englewood Cliffs, NJ (1992).

5 Selected physical data of **1**: dark red needles, mp 281— 282 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$-CS$_2$) δ 3.37 (8H, mc, SCH$_2$CH$_2$S), 7.27 (2H, dd, *J*=6.0 and 3.2 Hz, H-5,6 of the benzoselenoquinoid, BSQ, ring), 7.39 (2H, dd, *J*=6.0 and 3.2 Hz, H-4,7 of the BSQ ring); ^{13}C NMR (CDCl$_3$-CS$_2$, 150 MHz) δ 29.7 and 29.9 (SCH$_2$CH$_2$S), 112.2 and 113.7 (C-4,5 of the dithiol ring), 116.9 (C-1,3 of the BSQ ring), 117.3 (C-2 of the dithiol ring), 124.2 (C-4,7 of the BSQ ring), 125.8 (C-5,6 of the BSQ ring), 138.3 (C-3a,7a of the BSQ ring); UV-VIS (THF) λ_{max}/nm (log ε) 507sh (3.80), 447 (4.53), 422sh (4.51), 396sh (4.22), 368 (4.15), 341sh (3.91).

6 J. B. Torrance, B. A. Scott, and F. B. Kaufman, *Solid State Commun.*, **17**, 1369 (1975).

7 The ClO$_4$, BF$_4$, and ReO$_4$ salts belong to a monoclinic system, space group of C2/c and Z=8 with cell dimensions: [BEDT-BDTBS]$_2$[ClO$_4$]$_3$ a=21.626(1), b=18.674(3), c=14.563(2) Å, β=116.949(7)°, V=5242(1) Å^3 (R=0.075 and R$_W$=0.066 for observed 1627 reflections with $I>4\sigma(I)$); [BEDT-BDTBS]$_2$[BF$_4$]$_3$ a=21.544(6), b=18.436(6), c=14.591(3) Å, β=116.97(2)°, V=5164(2) Å^3 (R=0.081 and R$_W$=0.070 for observed 823 reflections with $I>3\sigma(I)$, Reflection/Parameter Ratio= 2.54); [BEDT-BDTBS]$_2$[ReO$_4$]$_3$ a=21.98(2), b=19.24(1), c=14.425(7) Å, β=117.61(7)°, V=5405(6) Å^3.