Crystal Structure and Electrical Conducting Properties of [BEDT-BDTBT]$_3$[ReO$_4$]$_2$, an Organic Conductor Based on a Novel Benzo[c]thiophene-Extended Donor

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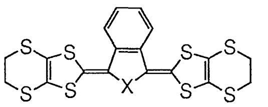
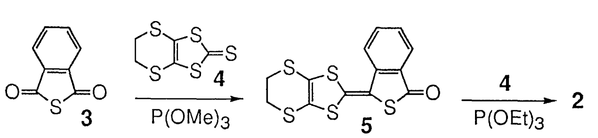
Conducting behavior and X-ray crystal structure of ReO$_4$ salt of a new benzo[c]thiophene-extended donor have been investigated, revealing that the packing mode as well as the donor to anion ratio varies distinctly by changing the central hetero atom.

In recent years, many kinds of conjugation-extended donors have been synthesized.[1] The organic conductors based on these extended donors are expected to show a high conductivity due to the small Coulombic repulsive energy and show a high superconducting transition temperature (Tc) due to the large effective volume of carrier delocalization.[2] We have proved for the first time that incorporation of sulfur atom(s) in the π-extending bridge stabilizes significantly cation radicals of the donors[1b,c] and have synthesized thieno- and selenienoquinonoid-extended donors affording metallic or highly conducting TCNQ complexes.[3] However, studies on the X-ray crystal structure analysis of the extended-donor based conducting complexes not involving a TTF skeleton are very rare,[4] although these materials are capable of generating conceptionally novel physical properties which have not been observed in the traditional TTF derivatives. Actually [BEDT-BDTBS]$_2$[X]$_3$ salts (X=ClO$_4$, BF$_4$, ReO$_4$) reported previously by us possess abnormally high formal charge of +3/2 per the donor molecule, nevertheless their conductivities are not so low.[4c] In order to obtain further information on this series of compounds, we have now synthesized new donor BEDT-BDTBT (**2**) and clarified that the crystal structure and the charge transfer extent of its ReO$_4$ salt are remarkably different from those of [BEDT-BDTBS]$_2$[ReO$_4$]$_3$,[4c] despite replacing only one central selenium atom by a sulfur atom in the donor.



1: X=Se: BEDT-BDTBS
2: X=S: BEDT-BDTBT



Scheme 1.

The synthetic route to the new donor BEDT-BDTBT (**2**) is outlined in Scheme 1.[5] The mono-capped **5** was synthesized in 80% yield by refluxing a toluene solution of thioanhydride **3**, thione **4**, and P(OMe)$_3$. The bis-capped **2** was synthesized in 49% yield by heating the reaction mixture at 120 °C without solvent. The first and second half-wave oxidation potentials of BEDT-BDTBT (E_1^{ox} = +0.43, E_2^{ox} = +0.65 V *vs* SCE) are much the same as those of BEDT-BDTBS (E_1^{ox} = +0.47, E_2^{ox} = +0.68 V *vs* SCE)[4c] in PhCN at 25 °C. BEDT-BDTBT (**2**) gave a 2:3 TCNQ complex exhibiting a room temperature conductivity (σ_{rt}) of 6.7 Scm^{-1} measured on a compressed pellet. Black needle-like single crystals of ReO$_4$ salt were harvested by the galvanostatic electrolysis (0.5 μA) of BEDT-BDTBT in chlorobenzene at 20 °C in the presence of Bu$_4$NReO$_4$. This salt showed σ_{rt} = 0.10 Scm^{-1}, semiconductive temperature dependence with Ea = 0.165 eV down to 180 K and was suitable for X-ray structure analysis.[6] As shown in Figure 1, the unit cell contains two donor layers stacking along the (a+c) axis.

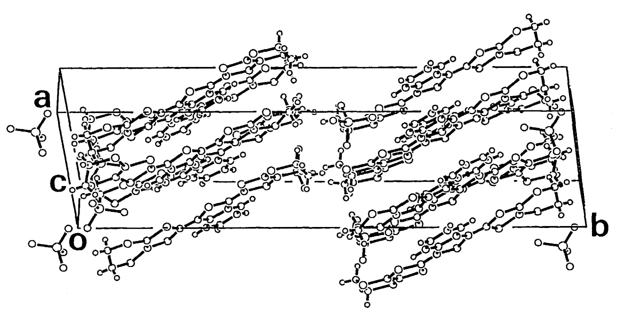


Figure 1. Crystal structure of [BEDT-BDTBT]$_3$[ReO$_4$]$_2$.

Each donor layer contains three crystallographically independent donor molecules A, B, and C in a unit cell and separated by intervening two ReO$_4$ layers. The molecules A, B, and C possess much the same bond lengths and bond angles and are almost planar while the ethylene carbons deviate from the optimal plane. The unit cell contains six donors and four anions demonstrating that the exact donor to anion ratio is [BEDT-BDTBT]$_3$[ReO$_4$]$_2$ and the formal charge on the BEDT-BDTBT molecule is +2/3. It is surprising that the value is distinctly different from the formal charge of +3/2 on the donor molecule of [BEDT-BDTBS]$_2$[ReO$_4$]$_3$.[4c] All the donors are stacking in face-to-face manner and directing the central sulfur atom to the same side within the layer (Figures 1 and 2) which is favorable for bringing about the intermolecular side-by-side S---S contacts. The C-S bond is shorter than the C-Se bond. Thus the BEDT-BDTBT is bent more than the BEDT-BDTBS, allowing the protruding benzene ring to meet the dent of the neighboring molecule in the side-by-side direction. In consequence, the anion can not get into the space along the donor short (a–c) axis, whereas four anions in the unit cell exist along the donor short axis of [BEDT-BDTBS]$_2$[ReO$_4$]$_3$. Thus the most interesting aspect of this comparison is that the central hetero atom governs roughly the donor packing motif, especially the donor to anion ratio of the cation radical salt, although the stoichiometry appears to be widely changeable due to the small Coulombic repulsion. There is no centrosymmetry between the trimers giving the stacking mode of A-B-C-A-B-C type repetition.

The interplanar distances between adjacent stacking molecules

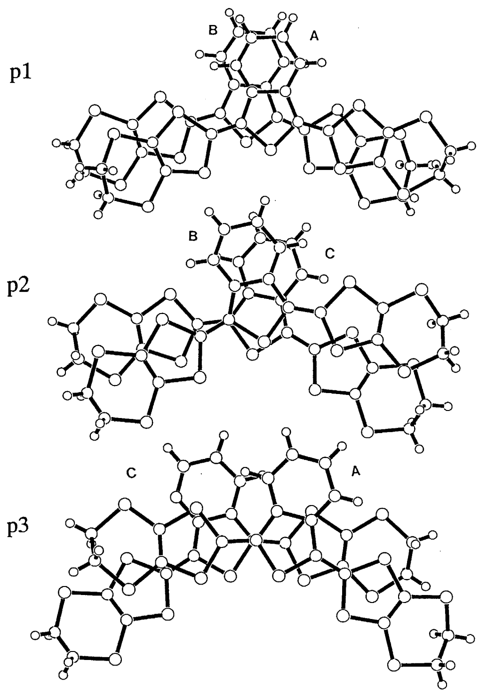


Figure 2. Overlapping modes of the donor molecules in [BEDT-BDTBT]$_3$[ReO$_4$]$_2$.

are 3.53 Å (A — B, p1 in Figure 3), 3.66 Å (B — C, p2), and 3.62 Å (C — A, p3). The overlap mode between the donors A and B is so-called ring-over-bond type with the slip distance along the donor long axis being about 1.12 Å. The donor B and C overlap mainly at the central part in a ring-over-ring type and in a crisscross type at the dithiol part. There are four short S---S contacts less than the sum of van der Waals radii (3.7 Å) and many S---S distances around 3.7 — 3.9 Å in the stack. The bonding interaction between C and A in the stack, namely the inter-trimer overlap, is relatively small since the slip distance along the donor long axis reaches to 2.0 Å, so that the central part of the donors can not overlap with each other, although several S---S distances around 3.7 — 3.9 Å exist in the stack.

The calculated intermolecular overlap integrals are listed in Table 1. The large intra-trimer overlap integrals (p1 and p2) are reasonable on considering the large π-HOMO coefficients (about 0.24) and the favorable short S---S contacts of the central sulfur atoms. The inter-trimer overlap integral, p3 is not very small as compared with the value of p1 and p2 indicating that the trimerization is weak in this salt. There are seven S---S contacts shorter than the sum of van der Waals radii in the side-by-side directions between the outer and dithiol sulfur atoms, nevertheless the overlap integrals along the transverse directions are about 1/10 of the values along the stack. This may be due to the smaller π-HOMO coefficients (about 0.057 — 0.024) on these sulfur atoms than the central one. Thus the band structure of this salt is almost one-dimensional along the stacking a+c axis. According to the stoichiometry, the energy band of this salt is 2/3 filled, then the Fermi level comes between the second and third bands owing to the trimerization.

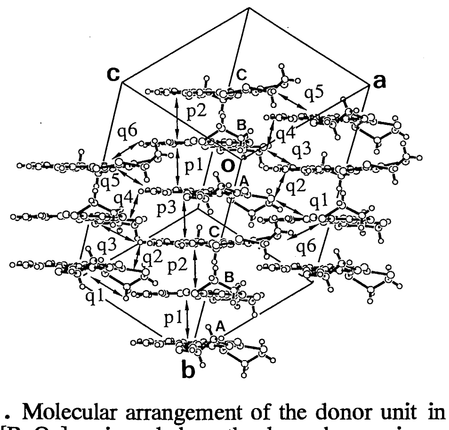


Figure 3. Molecular arrangement of the donor unit in [BEDT-BDTBT]$_3$[ReO$_4$]$_2$, viewed along the donor long axis.

Table 1. Intermolecular overlap integrals[a] ($S \times 10^3$) obtained from extended Hückel π-AO coefficients

Stacking direction	Side by side direction	
A—B: p1 = −14.0	q1 = 0.55	q4 = 0.46
B—C: p2 = −8.26	q2 = −0.48	q5 = −1.09
A—C: p3 = −5.89	q3 = −0.31	q6 = 0.21

[a] The overlap modes p1—p3 and q1—q6 are indicated in Figure 3.

References and Notes

1 For example: a) K. Takahashi, T. Nihira, K. Takase, and K. Shibata, *Tetrahedron Lett.*, **30**, 2091 (1989); b) K. Takahashi and T. Nihira, *Tetrahedron Lett.*, **30**, 5903 (1989); c) Y. Yamashita, Y. Kobayashi, and T. Miyashi, *Angew. Chem., Int. Ed. Engl.*, **28**, 1052 (1989); d) A. J. Moore and M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 157; e) Y. Misaki, N. Higuchi, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, and S. Tanaka, *Angew. Chem., Int. Ed. Engl.*, **34**, 1222 (1995) and references cited therein.

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5 Selected physical data of BEDT-BDTBT, **2**: orange fine needles, mp 288 — 290 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$-CS$_2$) δ 3.37 (8H, s, SCH$_2$CH$_2$S), 7.30 (2H, dd, J = 5.9 and 3.1 Hz, H-5,6 of the benzothienoquinoid, BTQ, ring), 7.43 (2H, dd, J = 5.9 and 3.1 Hz, H-4,7 of the BTQ ring); ^{13}C NMR (CDCl$_3$-CS$_2$, 150 MHz) δ 29.7 and 29.9 (SCH$_2$CH$_2$S), 112.7 and 113.1 (C-4,5 of the dithiol ring), 113.9 (C-1,3 of the BTQ ring), 119.0 (C-2 of the dithiol ring), 123.5 (C-4,7 of the BTQ ring), 126.0 (C-5,6 of the BTQ ring), 136.7 (C-3a,7a of the BTQ ring); UV-VIS (THF) λ_{max}/nm (log ε) 446 (4.45), 366 (4.12).

6 [BEDT-BDTBT]$_3$[ReO$_4$]$_2$ belongs to a triclinic system, space group of $P\bar{1}$ and Z = 2 with cell dimensions: a = 10.657(6), b = 34.590(8), c = 10.169(9) Å, α = 89.75(6)°, β = 113.46(4)°, γ = 96.69(4)°, V = 3412(4) Å^3 (R = 0.051 and R$_W$ = 0.061 for observed 5772 reflections with $I > 4.00\sigma(I)$).