Crystal Structures and Conducting Properties of PF_6 and AsF_6 Salts of a Novel Benzo[c]furan-Extended Donor: The Role of Inter-Column Interactions

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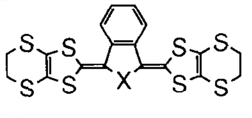
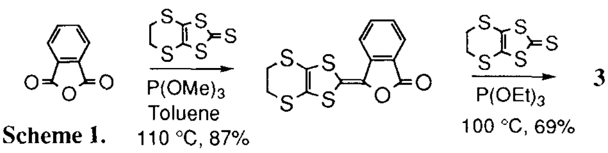
The PF_6 and AsF_6 salts of a new benzo[c]furan-extended donor have been prepared. It has been clarified that the inter-column interactions connecting the tetrameric donor columns play an important role in the conduction of these salts.

Although a large number of TTF based organic conductors have been investigated so far,[1] studies on conducting complexes based on extended-donors with a high electrical conductivity are not many[2] and detailed information on this regard is limited.[3] In such a situation, we have recently synthesized fused heterocycle-extended donors, BEDT-BDTBS (**1**)[4] and BEDT-BDTBT (**2**)[5] as well as their cation radical salts, and have demonstrated that the donor to anion ratio varies remarkably from 2:3 to 3:2 by replacing only one hetero atom of the central ring of the donors from Se to S atom. In order to know further insights into the correlation between the donor structure and solid state properties of the conducting radical cation salts, we have now synthesized an oxygen analogue, BEDT-BDTBF (**3**) and its PF_6 and AsF_6 salts, and clarified their unusual crystal structures having one-dimensional band structure brought about by a unique inter-column interaction.



1 (X=Se): BEDT-BDTBS
2 (X=S): BEDT-BDTBT
3 (X=O): BEDT-BDTBF

The new donor BEDT-BDTBF (**3**)[6] has been synthesized as shown in Scheme 1, starting from phthalic anhydride and 4,5-ethylenedithio-1,3-dithiole-2-thione.



Scheme 1.

The oxidation of **3** occurred in reversible two-step one-electron process in cyclic voltammetry, exhibiting the half-wave oxidation potentials of E_1^{ox} = +0.37 and E_2^{ox} = +0.53 V *vs.* SCE in PhCN at 25 °C. The E_1^{ox} value is lower by 0.1 V than that of **2**[5] and is much the same as that of TTF. Actually **3** formed a 1:1 TCNQ complex showing a room temperature conductivity of 4.8 Scm^{-1} on a compressed sample.

Single-crystalline PF_6 and AsF_6 salts of **3** were grown by the conventional electrochemical oxidation (0.1 μA) in chlorobenzene with 10% of EtOH at 20 °C. Both of the salts showed semiconducting temperature dependence with E_a = 0.191 (PF_6 salt) and 0.190 eV (AsF_6 salt) in the temperature range from room temperature to 160 K. However, the PF_6 salt exhibited a fairly high room temperature conductivity of 7.3 Scm^{-1} which is 26 times higher than that of the AsF_6 salt (σ_{rt} = 0.28 Scm^{-1}).

From X-ray crystal structure analysis,[7] it has been revealed that the PF_6 and AsF_6 salts are iso-morphous with each other and have very unusual crystal structures. The unit cell contains eight donors and four anions, giving a donor to anion ratio of 2:1, from which the formal charge on BEDT-BDTBF is determined to be +0.5. The eight donors form a pair of tetramers. The tetramer is constructed with crystallographycally independent four donor molecules A, B, C, and D with much the same bond lengths (Figure 1). Therefore, there is no charge separation among these donors.

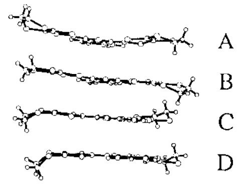


Figure 1. Stacking structure of the donors A, B, C, and D.

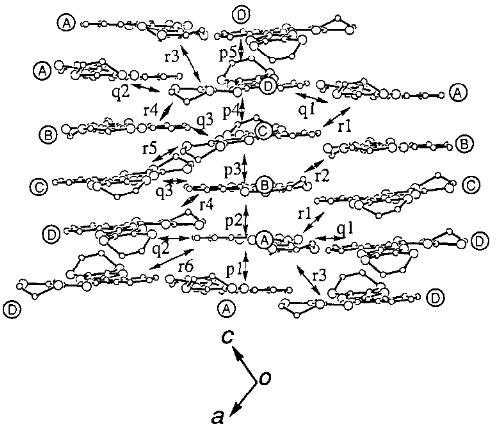


Figure 2. Donor arrangement in $[BEDT\text{-}BDTBF]_2[PF_6]$.

There is a center of symmetry between the tetramers. Thus, the donors stack in a ABCDDCBA manner along the *–a+c* axis (Figure 2) with the interplanar distances of 3.38—3.65 Å. The PF_6 or AsF_6 anions are located in the space between the conducting a-c plane. As shown in Figure 3, the overlapping modes between A and B, and C and D are quite favorable for giving a high intermolecular HOMO-HOMO bonding interaction because they are so called ring-over-bond types directing the central oxygen atom to the same side and all the S and O atoms have the same phase reversing in the phase of the remaining all carbon atoms of **3**, similar to the HOMO of BEDT-TTF. In

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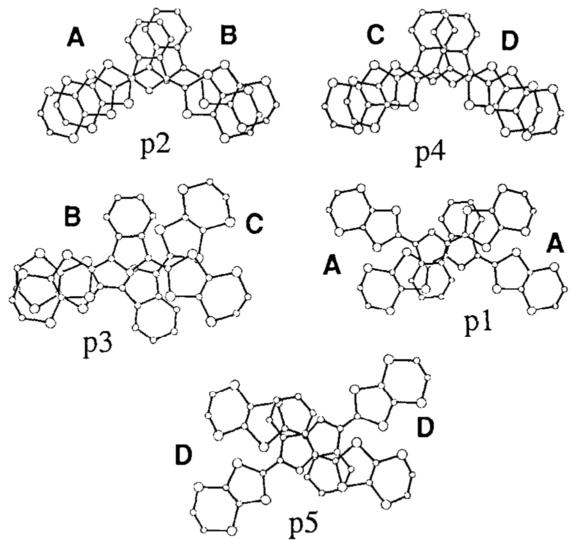

Figure 3. Overlapping modes of BEDT-BDTBF in [BEDT-BDTBF]$_2$[PF$_6$] and [BEDT-BDTBF]$_2$[AsF$_6$].

Table 1. Intermolecular overlap integrals[a] ($S \times 10^3$) of [BEDT-BDTBF]$_2$[PF$_6$] and [BEDT-BDTBF]$_2$[AsF$_6$]

Intra-column			Inter-column		
Anion:	PF$_6$	AsF$_6$	Anion:	PF$_6$	AsF$_6$
(Intra-tetramer)			q1 =	−0.7	−0.2
p2 =	−7.0	−6.7	q2 =	−0.3	−0.3
p3 =	−5.3	−5.6	q3 =	0.2	0.1
p4 =	−8.0	−7.7	r1 =	0.5	0.0
			r2 =	1.6	0.3
(Inter-tetramer)			r3 =	1.3	0.2
			r4 =	0.4	0.0
p1 =	−0.3	1.2	r5 =	−0.3	0.1
p5 =	−0.4	0.0	r6 =	−0.2	−0.8

[a] The overlap modes p1—p5, q1—q3, and r1—r6 are indicated in Figure 2.

consequence, the calculated overlap integrals p2 and p4 are significantly large in the PF$_6$ and AsF$_6$ salts as shown in Table 1. The overlapping modes between B and C, A and A, and D and D are much more complicated. However, as compared with the values of p2 and p4, there is no significant difference in the value of p3, although B and C overlap only at ethylendithio-1,3-dithiole rings. In contrast, the overlap integrals p1 (A–A) and p5 (D–D), overlapping only at the central part of the donor molecules, are less than 1/10th of p3. This is reasonable because the ethylendithio-1,3-dithiole rings have large π-HOMO coefficients and the 2pπ orbital of the central O atom is smaller than the 3pπ orbitals of the S atoms. The inter-tetramer overlap integrals p1 and p5 are very small as compared with intra-tetramer ones, in consequence, the tetramerization is fairly strong in these two salts.

Quite interestingly, there exist two fairly large inter-column overlap integrals r2 and r3 along the *a*- and *c*-axis, respectively, in the PF$_6$ salt as shown in Table 1 and Figure 2. Of these, the r3 appears to play an important role in the conduction, because the interactions (r3) combine all the tetramers belonging to the all neighboring columns along the *c*-axis.[8] The interactions (r2) are not important for the conduction, since r2 combines only one side of the neighboring column, resulting in a dimerization of the columns. Hence, the band structure of [BEDT-BDTBF]$_2$[PF$_6$] is one-dimensional along the *c*-axis, although the donor stacks along the −*a*+*c* axis. On the other hand, the r3 as well as r2 are very small in the AsF$_6$ salt as shown in Table 1. Thus the high and low conductivities of PF$_6$ and AsF$_6$ salts, respectively, can be mainly ascribed to the difference in the overlap integral of r3. The lattice constants along the *b*- and *a*- axes of the AsF$_6$ salt are larger than those of the PF$_6$ salt. Therefore the large AsF$_6$ anion increases the unit cell volume, and then the key inter-column overlap integral r3 is significantly decreased probably by the slipping of the donor molecules along the *a*- or *b*-axis in the AsF$_6$ salt. In consequence, the salts with smaller tetrahedral anions, if we can grow them, are expected to show metallic properties. We have no data to answer the question why these two salts show almost identical activation energies. This may be attributed to the difference in the mobility of holes in a logical sense.

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6 Selected physical data of BEDT-BDTBF, **3**: orange needles, mp 249 °C (decomp); ^{1}H NMR (600 MHz, CDCl$_3$-CS$_2$) δ 3.35 (8H, s, SCH$_2$CH$_2$S), 7.33 (2H, mc, H-5,6 of the benzofuroquinoid, BFQ, ring), 7.43 (2H, mc, H-4,7 of the BFQ ring); ^{13}C NMR (CDCl$_3$-CS$_2$, 150 MHz) δ 29.75 and 29.81 (SCH$_2$CH$_2$S), 101.6 (C-1,3 of the BFQ ring), 111.2 and 113.1 (C-4,5 of the dithiole ring), 121.2 (C-4,7 of the BFQ ring), 127.4 (C-5,6 of the BFQ ring), 130.8 (C-3a,7a of the BFQ ring), 139.1 (C-2 of the dithiole ring); UV-VIS (THF) λ_{max}/nm (log ε) 469 (4.58), 441 (4.46), 362 (4.24).

7 Crystal data for [BEDT-BDTBF]$_2$[PF$_6$]: triclinic space group $P\bar{1}$, a = 17.456(5), b = 18.586(6), c = 16.788(4) Å, α = 100.39(2)°, β = 116.46(2)°, γ = 64.86(2)°, V = 4414(4) Å^3 and Z = 2, (R = 0.064 and R_W = 0.068 for observed 9702 reflections with $I > 5.00\sigma(I)$); for [BEDT-BDTBF]$_2$[AsF$_6$]: triclinic space group $P\bar{1}$, a = 17.658(4), b = 18.691(3), c = 16.684(4) Å, α = 100.02(2)°, β = 116.77(2)°, γ = 64.98(1)°, V = 4454(1) Å^3 and Z = 2, (R = 0.070 and R_W = 0.064 for observed 9332 reflections with $I > 2.50\sigma(I)$)

8 The overlap integral r3 is induced by up and down type overlaps at the ethylenedithio groups of the donors A and D belonging to the neighboring colunms.