Radical-Cation Salts Based on Brominated and Chlorinated Ethylenedioxytetrathiafulvalenes

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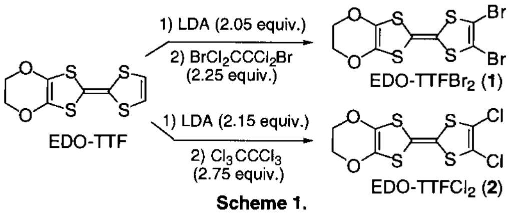
Radical-cation salts derived from 4,5-dibromo-4',5'-ethylenedioxy- and 4,5-dichloro-4',5'-ethylenedioxytetrathiafulvalenes (EDO-$TTFBr_2$ and EDO-$TTFCl_2$) showed metallic conductivities in spite of their electron-withdrawing substituents.

Highly polarizable electron donors have attracted current attention,[1] because weak interactions between polarizable substituents may lead to the formation of molecular networks with stacking columns in line with the crystal engineering,[2] and because intermolecular interactions between radical-cations in the complexes can be enhanced by electrostatic interaction to increase dimensionality of the molecular conductors.[3] Among them, the substitution of halogen atoms on the TTF framework has been extensively studied,[4,5] although the electronegativity of halogens, especially Cl and Br, decreases the donor properties, thus causing difficulty in forming molecular conductors. Recently, unsymmetrical TTF derivatives with iodine substituents have been reported to produce metallic radical-cation salts with unique three-dimensional structures.[6] We disclose here the synthesis of both brominated and chlorinated ethylenedioxytetrathiafulvalenes (**1** and **2**) and the electrical conductivities and crystal structures of radical-cation salts based on **1** and **2**.



Scheme 1.

The syntheses of **1** and **2** were carried out using the lithiation-halogenation procedure. Thus, the reaction of EDO-TTF[7] with LDA in THF at -78 °C for 40 min, followed by treatment with $BrCl_2CCCl_2Br$ at -78 °C to room temperature produced **1** in 74% yield.[8] Similarly, the treatment of EDO-TTF with LDA in THF at -78 °C for 40 min, followed by the reaction with hexachloroethane at -78 °C to room temperature produced **2** in 56% yield. The redox potentials of **1**, **2** and BEDT-TTF measured by cyclic voltammetry are shown in Table 1. Interestingly, the first oxidation potentials of **1** and **2** are only a little larger than that of BEDT-TTF.

Table 1. Redox potentials[a] of **1**, **2** and BEDT-TTF

Compound	$E^1_{1/2}$	$E^2_{1/2}$	ΔE ($E^2_{1/2}$ - $E^1_{1/2}$)
1	0.57	0.89	0.32
2	0.59	0.89	0.30
BEDT-TTF	0.52	0.83	0.31

[a] Conditions: n-Bu_4NClO_4, benzonitrile, room temperature, Pt working and counter electrodes. Potentials were measured against an Ag/Ag^+ electrode and converted to the value *vs* SCE (Fc/Fc^+ = 0.31 V).

Single crystals of the radical-cation salts based on **1** and **2** were prepared by the galvanostatic oxidation (ca. 1 μA) in 1,2-dichloroethane (DCE), 1,1,2-trichloroethane (TCE) or chlorobenzene (PhCl) containing the corresponding tetrabutylammonium salt. The structures of the radical-cation salts ($(\mathbf{1})_3{\cdot}I_3$, $(\mathbf{1})_3{\cdot}PF_6$, and $(\mathbf{2})_3{\cdot}PF_6$) were determined by X-ray analysis. The conducting behavior of the radical-cation salts derived from **1** and **2** is summarized in Table 2. Although **1** bears a marked structural resemblance to **2**, an appreciable difference was observed in the conducting behavior of their radical-cation salts. Thus, **1** formed the metallic I_3^- and AuI_2^- salts, whereas the I_3^- salt of **2** was a semiconductor. The 3:1 PF_6 salt of **1** was a semiconductor, but the 2:1 salt of **2** was metallic at room temperature with high conductivity. To our knowledge, no metallic radical-cation salt based on brominated and chlorinated TTF derivatives has been reported to date, whereas some metallic salts have been prepared from iodinated TTF derivatives. Thus, the metallic conducting behavior of $(\mathbf{1})_3{\cdot}I_3$, $(\mathbf{1})_2{\cdot}AuI_2$ and $(\mathbf{2})_2{\cdot}PF_6$ is the first example for the radical-cation salts derived from brominated and chlorinated TTF derivatives.

Table 2. Electrical conductivities of radical-cation salts

Donor	Anion	Solvent	D:A[a]	σ_{rt}/S cm^{-1} [b]
1	I_3^-	DCE[c]	3:1	9.9 (T_{MI} = 180 K)
1	PF_6^-	DCE	3:1	9.6 (E_a = 4.3 meV / 50 K) (E_a = 17.2 meV / 200 K)
1	AuI_2^-	TCE[d]	2:1[e]	22 (T_{MI} = 100 K)
2	I_3^-	PhCl	1:1	3.6×10^{-2}
2	PF_6^-	TCE	2:1	169 (T_{MI} = 262 K)

[a] Determined by X-ray analysis. [b] Room temperature conductivity measured on a single crystal by a four-probe technique. [c] 1,2-Dichloroethane. [d] 1,1,2-Trichloroethane. [e] Determined by elemental analysis.

The radical-cation salt $(\mathbf{1})_3{\cdot}I_3$ exhibits a metallic behavior down to 180 K and becomes semiconductive with a small activation energy of 0.01 eV below this temperature. The conducting behavior of $(\mathbf{2})_2{\cdot}PF_6$ is similar to that of $(\mathbf{1})_3{\cdot}I_3$ and its conductivity is more than one order of magnitude larger than that of the latter.

The crystal structures of $(\mathbf{1})_3{\cdot}I_3$ and $(\mathbf{2})_2{\cdot}PF_6$ determined by X-ray diffraction method are shown in Figures 1 and 2.[9] As shown in Figure 1, the radical-cation salt $(\mathbf{1})_3{\cdot}I_3$ possesses a segregated-stacking structure. The donor molecules are stacked in the *ac* plane in a head-to-tail mode, and the face-to-face distance between the donors is 3.56 Å. Interestingly, the iodine atoms are aligned along the *c* axis to form a chain structure with a distance of 3.38 Å. On the basis of the X-ray analysis, it is difficult to decide the structure of the iodide anion, *e.g.*, I_3^-, because of the large thermal atomic scattering factor of the iodine atoms. Therefore, the I_3^- structure of the iodide anion was determined by the elemental analysis and Raman spectra ($\nu_{I\text{-}I}$ = 105 cm^{-1} at 2–250 K) of the radical salt, which indicates no structural change at the temperatures measured. The central C-C distance (1.37 Å) of EDO-TTFBr$_2$ in (**1**)$_3$·I$_3$ shows a shorter distance than that (1.40 Å) of **1**·ClO$_4$[10], reflecting an expected smaller cationic charge in the donor molecule. The most remarkable feature of the crystal packing is the inter-column Br···O, Br···S and Br···I short contacts. As shown in Figure 1a, the Br···O and Br···S distances (3.34 and 3.65 Å, respectively) are 0.3-4% shorter than the sum of the van der Waals radii (Br···O: 3.35 and Br···S: 3.80 Å). In addition, the S···S contact (3.69 Å) along the *a* axis, which is shorter than the sum of the van der Waals radii (3.70 Å), forms a side-by-side overlap (*q* in Figure 1b). Interestingly, there is no intra-column short S···S distances less than the sum of van der Waals radii, while all intra-column Br···O and Br···S contacts (a, a', b and b' in Figure 1a) are longer than the sum of the van der Waals radii and are balanced by the S···S contacts in the donor column. The Br-I shortest distance (4.06 Å) is shorter than the sum of the van der Waals radii (4.10 Å), indicating a strong halogen-halogen interaction. Thus, each donor molecule is anchored by the iodide chain to form a metallic conducting path (*p* in Figure 1b).

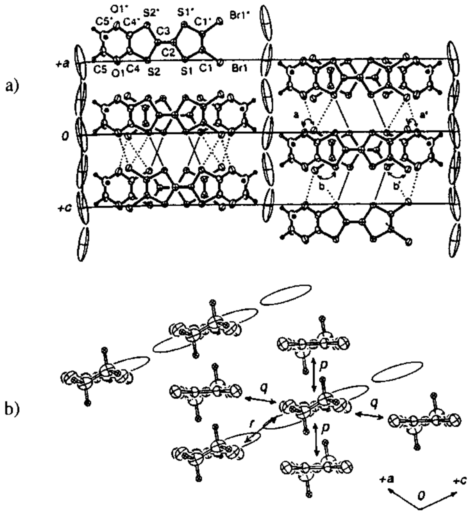


Figure 1. Crystal structure of $(1)_3 \cdot I_3$. a) Stacking along the *a* and *c* axis; the inter-column S•••S contact (3.69 Å) indicated by solid lines, the inter-column Br•••O and Br•••S distances by dotted lines [Br(1)•••O(1) = 3.34 and Br(1)•••S(2) = 3.65 Å), and the intra-column Br•••O and Br•••S distances by curved allows [a = 3.70, a' = 3.64, b = 3.96, and b' = 3.99 Å]. b) Stacking along the *b* axis; the solid arrows corresponding to overlap integrals (x 10^3) of the conduction orbitals (*p* = 22.8; *q* = -6.31; *r* = -3.82).

As shown in Figure 2, the donor molecule in (**2**)$_2$·PF$_6$ is stacked face-to-face with a head-to-tail mode along the *c* axis to form a segregated column. The intra-column S···S contacts [S(1)···S(4): 3.61 and S(2)···S(3): 3.64 Å] are 2% shorter than the sum of the van der Waals radii to form a metallic conducting path, where the two kinds of the face-to-face distances (3.47 and 3.48 Å) between the donors correspond to the overlap integrals *p1* and *p2* in Figure 2, respectively. Surprisingly, there is no inter-column S···S interaction, although the inter-column Cl···S contact (3.65 Å) is 3% shorter than the sum of the van der Waals radii (3.75Å). Thus, (**2**)$_2$·PF$_6$ possesses a typical one-dimensional donor layer structure, but the Cl···S short contact with two Cl···F interactions (3.47 and 3.70 Å), which are longer than the sum of the van der Waals radii (3.15 Å), may enhance the dimensionality.

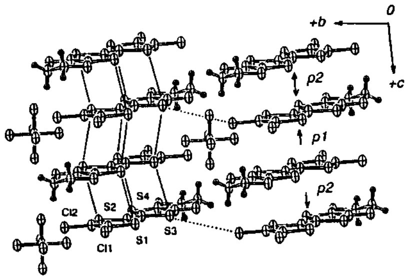


Figure 2. Crystal structure of $(2)_2 \cdot PF_6$; Stacking along the *c* axis; the intra-column short S•••S contacts [S(1)•••S(4) = 3.61, S(2)•••S(3) = 3.64 Å) by solid lines and the inter-column Cl•••S contact by dotted lines [Cl(2)•••S(3) = 3.42 Å). The solid arrows corresponding to overlap integrals (x 10^3) of the conduction orbitals (*p1* = 29.1; *p2* = 25.1).

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8 **1**: red needles, mp 167.5–168 °C; EI-MS *m/z* 422, 420, 418 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 4.267 (s, 4H); ^{13}C NMR (CDCl$_3$) δ 66.3, 101.6, 105.6, 110.2, 123.2. **2**, red needles, mp 175.5–176 °C (decomp.); EI-MS *m/z* 330 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 4.271 (s, 4H); ^{13}C NMR (CDCl$_3$) δ 66.3, 105.8, 106.8, 114.2, 123.2.

9 Crystal data. (**1**)$_3$·I$_3$: $C_8H_4O_2S_4Br_2I$, M = 547.07, monoclinic, space group $C_{2/c}$ (#15), a = 7.756(7) Å, b = 32.116(4) Å, c = 6.761(7) Å, β = 121.94(5)°, V = 1429(1) Å^3, T = 296 K, Z = 4, d_{calcd} = 2.542 g cm^{-3}, R = 0.045 and R_w = 0.056 for 1120 observed reflections out of 1652 unique reflections. (**2**)$_2$·PF$_6$: $C_8H_4O_2S_4Cl_2P_{0.50}F_3$, M = 403.75, triclinic, space group P-1 (#2), a = 9.29(2) Å, b = 11.68(2) Å, c = 6.948(4) Å, α = 90.8(2)°, β = 101.0(2)°, γ = 113.4(1)°, V = 675(2) Å^3, T = 296 K, Z = 2, d_{calcd} = 1.985 g cm^{-3}, R = 0.113 and R_w = 0.140 for 1820 observed reflections out of 3089 unique reflections.

10 E. Ogura, T. Takano, K. Hara, Y. Kuwatani, and M. Iyoda, unpublished results.