4,5-Diiodo-4',5'-ethylenedioxytetrathiafulvalene and Its Metallic Radical Salts

Yoshiyuki Kuwatani, Eiji Ogura, Hiroyuki Nishikawa, Isao Ikemoto, and Masahiko Iyoda*
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-03

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4,5-Diiodo-4',5'-ethylenedioxy-TTF (EDO-$TTFI_2$) was synthesized in moderate yield by the reaction of EDO-TTF with LDA, followed by quenching with $CF_3(CF_2)_5I$. Although EDO-TTF contains electron-withdrawing iodine as the substituent, this compound has a similar donor ability to BEDT-TTF. The radical-cation salt (EDO-$TTFI_2)_2$•ClO_4 shows a metallic conductivity down to 50 K, reflecting the strong I•••O interaction.

Halogenated tetrathiafulvalene and its derivatives have attracted considerable attention in recent years,[1] because of the unique crystal structures and electrical conductivities of their CT-complexes and radical-cation salts, and because of their synthetic utility as a building block for extended TTF systems.[2] Previously, we reported the synthesis and unique conductivities of CT-complexes and radical-cation salts of halogenated ethylenedithiotetrathia-fulvalenes (EDT-$TTFX_2$'s) and disclosed an interesting behavior of halogen-substituents in the crystals.[1f,1i] Our continuing interest in the weak interaction between halogens and calcogens in crystals prompted us to investigate the halogenated derivatives of ethylenedioxy-TTF (EDO-TTF **1**). We report here the synthesis of EDO-$TTFI_2$ **2** and EDO-TTFI **3** and the properties of the CT-complexes and radical-cation salts of **2**, together with the X-ray structures of **2** and its radical-cation salt.

Although the reaction of EDT-TTF with 2 equiv. of LDA produces the vinylthio-thiolate anion via the cleavage of the ethylenedithio ring,[3] EDO-TTF **1** is fairly stable to a strong base such as LDA at low temperature. Thus, the treatment of **1** with 2 equiv. of LDA in THF at -78 °C, followed by the reaction with 3 equiv. of $CF_3(CF_2)_5I$ at -78 - 0 °C produced EDO-$TTFI_2$ **2** in 55% yield, together with a small amount of monoiodide **3**.[4,5] In a similar manner, EDO-TTFI **3** was prepared selectively by the successive treatments of **1** with LDA (1 equiv.) in THF at -78 °C and $F_2ClCCFClI$ (3 equiv.) at the same temperature.[5]

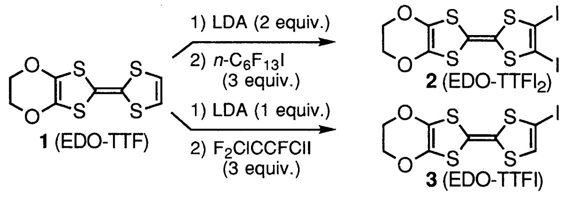

Table 1. Redox potentials[a] of TTF, BEDT-TTF, and **1-3**

Compound	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
TTF	0.36	0.73	0.37
BEDT-TTF	0.52	0.83	0.31
1	0.37	0.73	0.36
2	0.51	0.84	0.33
3	0.47	0.83	0.36

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

The oxidation potentials of TTF, BEDT-TTF, and **1-3** measured by cyclic voltammetry are shown in Table 1. Although **2** and **3** show lower donor ability as compared with TTF and EDO-TTF **1**, the oxidation potentials of **2** and **3** are comparable to those of BEDT-TTF which is a well-known donor for superconducting radical salts. Interestingly, the crystal structure of **2**[6] is rather similar to that of BEDT-TTF[7] instead of BEDO-TTF[8].

The new donors **2** and **3** formed single crystals of radical-cation salts with tetracyanoquinodimethane (TCNQ) and the anions examined (Table 2). Preparation of TCNQ complexes with **2** and **3** was carried out by mixing a solution of **2** or **3** in $CHCl_3$ with a solution of TCNQ in CH_3CN. The radical-cation salts of **2** with I_2•$(I^-)_2$, ClO_4^-, PF_6^-, $AuBr_2^-$, and Br^- were prepared by electrochemical oxidation in chlorobenzene, 1,1,2-trichloroethane (TCE), THF, or CH_2Cl_2 containing tetrabutylammonium salts of acceptor anions. As shown in Table 2, **2** produces a metallic complex with TCNQ (degree of CT based on IR spectrum: Z = 0.63), whereas the complex of **3** with TCNQ is a semi-conductor. In addition, the radical-cation salts of **2** with ClO_4^-, PF_6^- and $AuBr_2^-$ exhibited high room-temperature conductivities; however, the radical-cation salts with I^- and Br^- showed conductivities as semi-conductors.

Table 2. Electrical conductivities of radical-cation salts

Donor	Acceptor	Solvent	D:A	σ_{rt}/S cm^{-1} [a]
2	TCNQ	$CHCl_3,CH_3CN$	1:1[b]	152
2	$I_2\,(I)_2$ [c]	PhCl	2:1[d]	$1.8x10^{-3}$
2	ClO_4	PhCl	2:1[d]	68
2	PF_6	TCE[e]	3:1[b]	200
2	$AuBr_2$	THF	3:1[b]	24
2	Br	CH_2Cl_2	2:1[d]	$6.3x10^{-2}$
3	TCNQ	$CHCl_3,CH_3CN$	2:1[d]	$4.3x10^{-2}$

[a]Room-temperature conductivity measured by a four-probe technique. [b]Determined by elemental analysis. [c]Prepared by electrochemical oxidation of **2** in the presence of *n*-Bu_4NI_3. [d]Determined by X-ray analysis. [e]1,1,2-Trichloroethane.

The crystal structure of the unusual radical-cation salt $(\mathbf{2})_2$•$I_2(I^-)_2$ was determined by X-ray analysis (Figure 1).[9] The crystal packing of $(\mathbf{2})_2$•$(I_2)(I^-)_2$ shows that two donors and four iodines are stacked along the *b* axis to form a mixed-stacking structure. The central iodine molecule has a crystallographic S_2 symmetry, and the packing of the molecules in the crystal show that a pair of EDO-$TTFI_2$'s lies on a crystallographic center of inversion. The distance between the donor best plane and iodine atoms is ca. 3.40 Å, whereas the face-to-face distance between the two donors is ca. 3.51Å. There are many intermolecular contacts less than the sum of van der Waals radii. Thus, the I(1)•••I(3), I(2)•••I(3), S(1)•••S(4), S(2)•••S(3), and S(4)•••O(1) distances are 3.4024(8), 3.399(1), 3.4034(9), 3.514(3), 3.517(3), and 2.953(6) Å, respectively, which are much less than the I•••I, S•••S, S•••O van der Waals distances (I: 2.15 Å; S: 1.85 Å; O: 1.40 Å). Although iodide ions usually form a chain structure with an odd number of atoms such as I^-, I_3^-, I_5^-, etc., the I_4^{2-} chain consists of an iodine molecule (I_2) and two iodides (I^-). To our knowledge, this is the first report of the structure of I_4^{2-}. In accord with the mixed-stacking structure as a 1:1 radical-cation salt, the room temperature conductivity of $(\mathbf{2})_2\bullet(I_2)(I^-)_2$ is 1.8×10^{-3} S cm^{-1}.

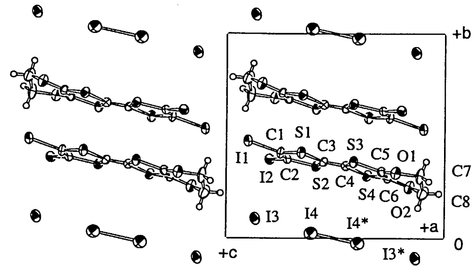

Figure 1. Crystal structure of $(\mathbf{2})_2\bullet(I_2)(I^-)_2$. [I(4)-I(4*) 2.808(1); I(1)•••I(3) 3.4025(8); I(2)•••I(3) 3.399(1); I(2)•••I(4) 3.977(1); I(3)•••I(4) 3.4034(9); I(4)•••S(3) 3.910(2); I(4*)•••S(4) 3,937(2); I(4)•••S(3) 3.981(2); I(4)•••S(2) 3,991(2); S(1)•••S(4) 3.514(3); S(2)•••S(3) 3.517(3); S(3)•••S(4) 3.613(3); S(4)•••O(1) 2.953(6) Å].

The crystal structure of $(\mathbf{2})_2\bullet ClO_4$ is shown in Figure 2.[10] Two crystallographically independent donor molecules are stacked along the *a* axis in a head-to-tail mode, and the face-to-face distance between the donors is 3.57 Å. The most remarkable feature of the crystal packing is the two types of short I•••O distances between the iodine and oxygen on the donor (3.33-3.51 Å) and between the donor's iodine and acceptor's oxygen (3.20-3.23 Å). These I•••O distances are 1-10% shorter than the sum of the van der Waals radii (3.55 Å), and the strong intermolecular I•••O interaction along *a*, *b*, and *c* axes enhances the dimensionality. Surprisingly, there is no intermolecular short S•••S distance less than the sum of van der Waals radii (3.70 Å).

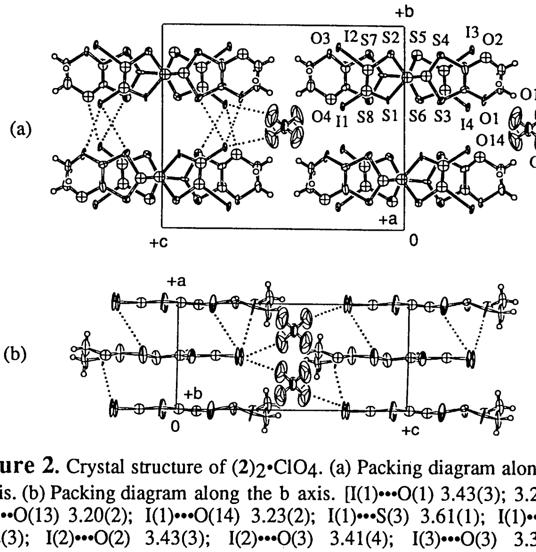

Figure 2. Crystal structure of $(\mathbf{2})_2\bullet ClO_4$. (a) Packing diagram along the a axis. (b) Packing diagram along the b axis. [I(1)•••O(1) 3.43(3); 3.20(2); I(1)•••O(13) 3.20(2); I(1)•••O(14) 3.23(2); I(1)•••S(3) 3.61(1); I(1)•••S(8) 3.92(3); I(2)•••O(2) 3.43(3); I(2)•••O(3) 3.41(4); I(3)•••O(3) 3.33(3); I(3)•••S(7) 3.83(2); I(4)•••O(1) 3.51(4); I(4)•••O(4) 3.32(3); I(1)•••O(11) 3.23(2); I(1)•••O(12) 3.22(2); I(4)•••S(3) 3.90(3); I(4)•••S(8) 3.20(2) Å].

As shown in Figure 3, $(\mathbf{2})_2\bullet ClO_4$ exhibits a metallic behavior down to 50 K and undergoes moderate metal-semiconductor transition below this temperature. A fairly low metal-insulator transition temperature of $(\mathbf{2})_2\bullet ClO_4$ may be due to its structurally enhanced dimensionality based on the I•••O interaction. Although radical-cation salts derived from diiodoethylenedithiodithiadiselenafulvalene have been recently reported to show a metallic conductivity,[11] we believe that the radical-cation salts derived from **2** disclose a new aspect in the chemistry of molecular conductors.

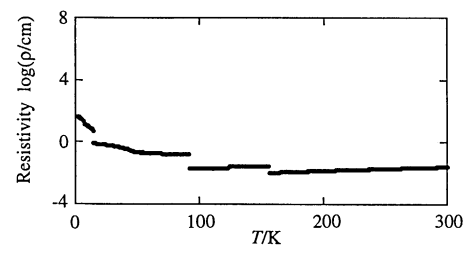

Figure 3. Temperature dependence of the resistivity for $(\mathbf{2})_2\bullet ClO_4$.

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References and Notes

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4 The synthesis of EDO-$TTFI_2$ **2** and EDO-TTFI **3** using the coupling of iodinated 1,3-dithiole-2-ones with 4,5-ethylenedioxy-1,3-dithiole-2-thione, see: T. Imakubo, H. Sawa, and R. Kato, *Synth. Metals*, in press.

5 **2**: red cryst., mp 150 °C (decomp.), MS (m/z) 514 (M^+); ^1H NMR (CD_2Cl_2-CS_2 1:1) δ 4.291 (s); ^{13}C NMR (CD_2Cl_2-CS_2 1:1) δ 66.05, 77.15, 103.39, 117.80, 123.07. **3**: orange cryst., mp 78.2-78.9 °C, MS (m/z) 388 (M^+); ^1H NMR ($CDCl_3$) δ 4.343 (s, 4H), 6.428 (s, 1H).

6 Crystal data for **2**: $C_8H_4O_2S_4I_2$, FW = 514.17, orthorhombic, space group $Pna2_1$ (#33); $a = 14.561(1)$ Å, $b = 15.324(1)$ Å, $c = 12.046(2)$ Å, $V = 2687.8(4)$ $Å^3$, $Z = 8$, $d_{calcd} = 2.541$ g cm^{-3}. The detailed structural analysis will be published in a full report.

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9 Crystal data for $\mathbf{2}\bullet I_2$: $C_8H_4O_2S_4I_4$, FW = 767.98, monoclinic, space group $P2_1/a$ (#14); $a = 11.196(2)$ Å, $b = 11.835(3)$ Å, $c = 13.392(2)$ Å, $\beta = 110.00(1)°$, $V = 1667.5(6)$ $Å^3$, $Z = 4$, $d_{calcd} = 3.059$ g cm^{-3}. The structure was solved by direct method using SIR92, full matrix least-squares refinement yielding the final R value of 0.033 ($R_W = 0.031$) for 2579 independent reflections [$2\theta \le 55.0°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC7R diffractometer using Mo-Kα radiation ($\lambda = 0.71069$ Å) and ω-2θ scan.

10 Crystal data for $(\mathbf{2})_2\bullet ClO_4$: $C_{16}H_8O_8S_8ClI_4$, FW = 767.98, triclinic, space group $P\bar{1}$ (#2); $a = 7.14(1)$ Å, $b = 13.178(1)$ Å, $c = 15.628(2)$ Å, $\alpha = 90.004(10)°$, $\beta = 89.97(4)°$, $\gamma = 89.98(4)°$, $V = 1469(2)$ $Å^3$, $Z = 2$, $d_{calcd} = 2.548$ g cm^{-3}. The structure was solved by direct method using SHELX86, full matrix least-squares refinement yielding the final R value of 0.034 ($R_W = 0.042$) for 2125 independent reflections [$2\theta \le 55.0°$, $I > 3.00\sigma(I)$] using Mo-Kα radiation and ω-2θ scan.

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