HETEROCYCLES, Vol. 54, No. 2, pp. 833-848, Receivrd, 19th June, 2000

SYNTHESES, STRUCTURE AND CONDUCTING PROPERTIES OF HALOGENATED ETHYLENEDIOXYTETRATHIAFULVALENES[1]

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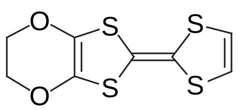
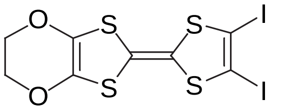
Abstract- 4,5-Diiodo-, 4,5-dibromo-, and 4,5-dichloro-4',5'-ethylenedioxytetrathiafulvalenes (EDO-TTFI_2, EDO-TTFBr_2, and EDO-TTFCl_2) were synthesized in moderate to good yields by the two routes. The first route contains the reaction of EDO-TTF with LDA, followed by quenching with halogenated reagents, and the second route consists of the $P(OR)_3$-mediated cross-coupling of 4,5-dihalogenated 1,3-dithiole-2-ones with 4,5-ethylenedioxy-1,3-dithiole-2-thione. The structures of EDO-TTFI_2 and EDO-TTFCl_2 were determined by X-Ray analysis. The radical-cation salts derived from EDO-TTFI_2, EDO-TTFBr_2, and EDO-TTFCl_2 show high conductivities, although these compounds contain electron-withdrawing halogens as the substituent.

INTRODUCTION

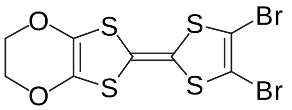
Highly polarizable electron donors have attracted current attention,[2] because weak interactions between polarizable substituents may lead to the formation of molecular networks with stacking columns in line with the crystal engineering,[3] and because intermolecular interactions between radical-cations in the complexes can be enhanced by electrostatic interaction to increase dimensionality of the molecular conductors.[4,5] Among them, the substitution of halogen atoms on the TTF framework has been extensively studied,[6,7] although the electronegativity of halogens decreases the donor properties, thus causing difficulty in forming molecular conductors. Previously, we reported the synthesis and unique conductivities of CT-complexes and radical salts of halogenated ethylenedithiotetrathiafulvalenes (EDT-TTFX_2's) and disclosed an interesting behavior of halogen-substituents in the crystals.[8] Our continuing interests in the weak interaction between halogens and chalcogens in crystals prompted us to investigate the halogenated derivatives of EDO-TTF (**1**). We report here the synthesis of EDO-TTFI$_2$ (**2**), EDO-TTFBr$_2$ (**3**), and EDO-TTFCl$_2$ (**4**) and the properties of their CT-complexes and radical salts, together with the X-Ray structures of **2**-**4** and their radical-cation salts.[1]



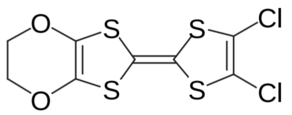
EDO-TTF **1**



EDO-TTFI$_2$ **2**



EDO-TTFBr$_2$ **3**

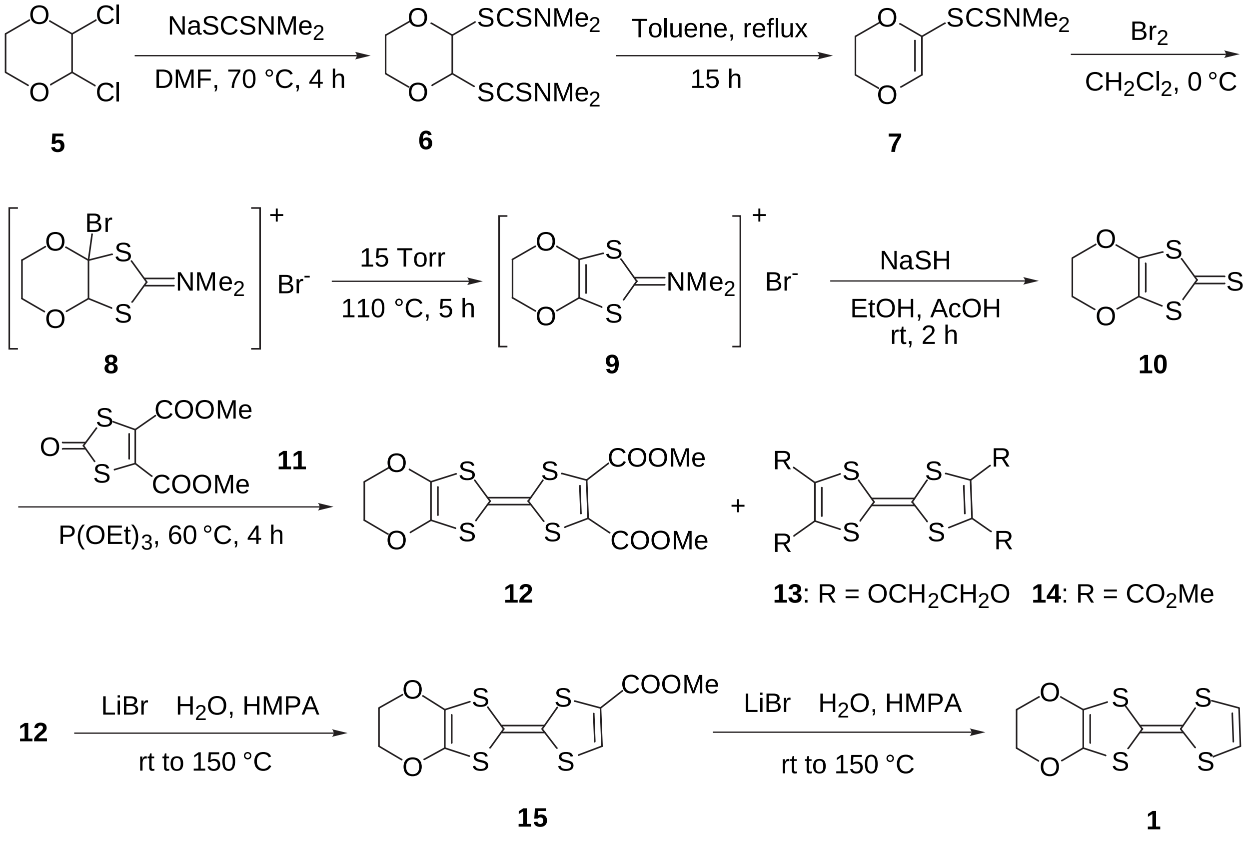


EDO-TTFCl$_2$ **4**

RESULTS AND DISCUSSION

Synthesis of Ethylenedioxytetrathiafulvalene (1).

EDO-TTF (**1**) was first synthesized in 1990,[9] but the total yield of **1** appeared not to be high enough to produce a gram-scale of **1**.[9,10] Therefore, we first improved the synthetic procedure of **1** (Scheme 1). The reaction of 1,2-dichlorodioxane (**5**) with sodium dimethyldithiocarbamate in DMF at 70 ℃ for 4 h afforded the bis(dithiocarbamate) (**6**) in 74% yield.[10,11a] Treatment of **6** in refluxing toluene for 15 h formed **7** in 95% yield. A similar reaction of **6** in DMSO yielded a mixture of products containing **7**. Bromination of **7** in CH_2Cl_2 at 0 ℃ produced the bromide (**8**) in quantitative yield, and dehydrobromination of **8** under

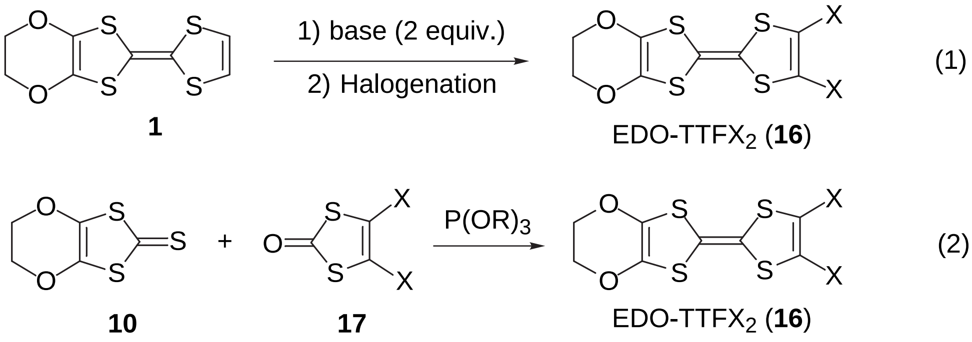


Scheme 1

reduced pressure at 110 °C afforded **9** in almost quantitative yield.[10, 11b] The reaction of **9** with sodium hydrogensulfide in ethanol-acetic acid at room temperature formed the thione (**10**) in 73% yield.[11b,12] The cross-coupling reaction of **10** with **11** in $P(OEt)_3$ at 60 °C for 4 h produced the diester (**12**) in 77% yield, together with small amounts of **13** and **14**.[9b,13] The decarboxylation of **12** with lithium bromide monohydrate in HMPA at room temperature to 150 °C afforded EDO-TTF (**1**) in 70% yield, together with the monoester (**15**) (20%). The monoester (**15**) can be converted into **1** in 50% yield under the similar decarbonylation conditions. Thus, **1** can be synthesized in 40% overall yield starting from **5**.

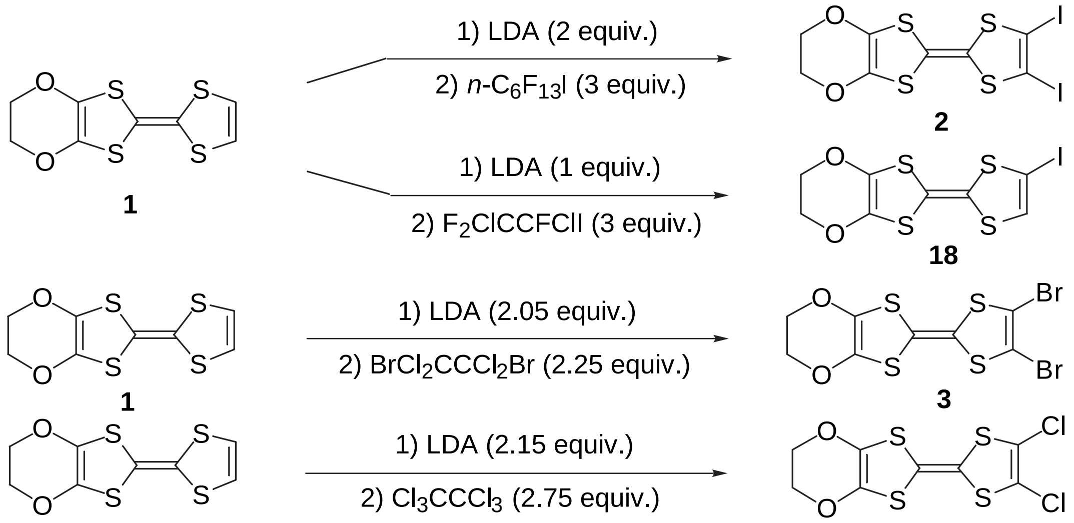
Synthesis of Halogenated Ethylenedioxytetrathiafulvalenes (2-4).

Halogenated tetrathiafulvalene and its derivatives have attracted considerable attention in recent years,[6,7] because of the unique crystal structures and electric conductivities of their CT-complexes and radical salts,[14] and because of the synthetic utilities as a building block for extended TTF systems.[15] The syntheses of **2, 3**, and **4** were attempted using the two synthetic routes shown in Scheme 2. The first route is based on the lithiation-halogenation sequence (eq. 1). Since TTF monoanions can be easily prepared from TTF and its derivatives with butyllithium or LDA and can be transformed into halogenated derivatives by treatment with alkyl halides or tosyl halides,[6,7] **1** can be converted into the corresponding anion which is halogenated to produce EDO-$TTFX_2$ (**16**). The second route is a cross-coupling reaction of the thione (**10**) with dihalogenated 1,3-dithiole-2-one (**17**) using trialkyl phosphite (eq. 2). The combination of **10** with electron-donating group and **17** with electron-withdrawing group may be necessary to produce the cross-coupling product **16** in good yield.



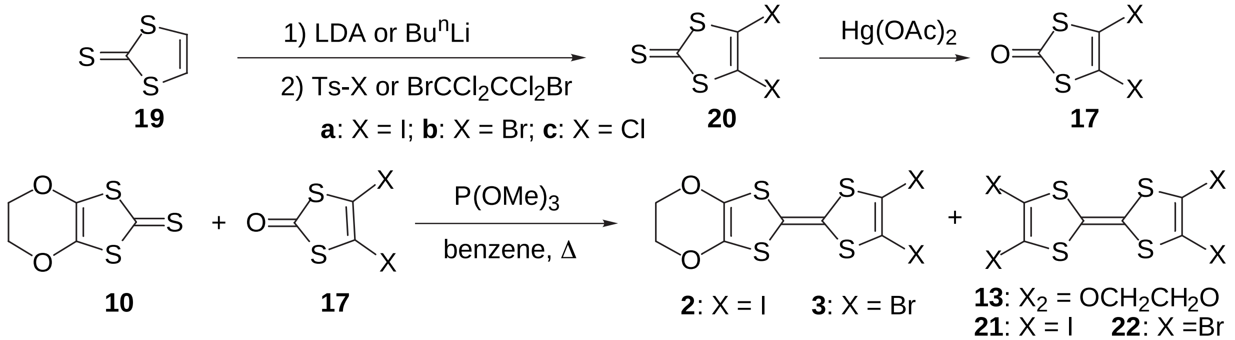
Scheme 2

At first, we investigated the route 1 (eq. 1). Although the reaction of EDT-TTF with 2 equiv. of LDA produces the vinylthio-thiolate anion *via* the cleavage of the ethylenedithio ring,[16] EDO-TTF (**1**) is fairly stable to a strong base like 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 (**18**) (Scheme 3).[17] In a similar manner, EDO-TTFI (**18**) was prepared selectively by the successive treatment of **1** with LDA (1 equiv.) in THF at -78 °C and $F_2ClCCFClI$ (3 equiv.) at the same temperature. In the case of the bromide (**3**), the reaction of **1** with LDA (2.15 equiv.) in THF at -78 °C for 40 min, followed by treatment with $BrCl_2CCCl_2Br$ (2.25 equiv.) at -78 °C to room temperature produced **3** in 74% yield. Similarly, treatment of **1** with LDA (2.05 equiv.) in THF at -78 °C for 40 min, followed by the reaction with hexachloroethane (2. 75 equiv.) at -78 °C to room temperature produced **4** in 56% yield. The dibromide (**3**) and the dichloride (**4**) were isolated by column chromatography on silica gel, followed by gell permeation chromatography (GPC) separation. Interestingly, no monobromide and monochloride were isolated in these reactions.



Scheme 3

Second, we attempted the route 2 (eq. 2). Recently, the synthesis of 4,5-diiodo-1,3-dithiole-2-one (**17a**) starting from **19** was reported.[7b] For the cross-coupling reaction of **10** with **17a**, $P(OMe)_3$ was found to be more effective than $P(OEt)_3$. Thus, the reaction of **10** and **17a** with $P(OMe)_3$ in refluxing benzene afforded **2** in 59% yield, together with **21** (29%) (Scheme 4). 4,5-Dibromo-1,3-dithiole-2-one (**17b**) was prepared from **19**. The reaction of **19** with Bu^nLi (1.01 equiv.) in THF at -78 ℃ for 1 h, followed by treatment with 1,2-dibromotetrachloroethane (2.19 equiv.) formed **20b** in 32% yield. Treatment of **20b** with $Hg(OAc)_2$ in CH_2Cl_2-acetic acid at room temperature led to **17b** in 95% yield. In a similr manner to the synthesis of the diiodide (**2**), the reaction of **10** and **17b** with $P(OMe)_3$ in refluxing benzene afforded **3** in 59% yield, together with bisethylenedioxytetrathiafulvalene (**13**) (4%) and **22** (15%). In the case of **17c**, however, the reaction of **19** with LDA or Bu^nLi in THF at -78 ℃, followed by treatment with *p*-toluenesufonyl chloride or hexachloroethane formed **20c** in low yield. Therefore, we could not attempt the reaction of **10** with **17c**. Although the lithiation-halogenation procedure is superior method for the synthesis of **2**-**4**, the cross-coupling method shown in Scheme 4 serves sometimes alternatively and can also produce a gram-scale of **2** and **3** without experimental difficulties.



Scheme 4

Structures and Properties of Halogenated Ethylenedioxytetrathiafulvalenes (2-4).

The oxidation potentials of TTF, EDO-TTF (**1**), BEDT-TTF, EDT-TTFX_2 (**2-4**), and EDO-TTFI (**18**) measured by cyclic voltammetry are shown in Table 1. Although all halogenated EDO-TTFs (**2-4**) show lower donor ability as compared to TTF and EDO-TTF (**1**), the oxidation potentials of **2-4** are comparable to those of BEDT-TTF which is a well-known donor for superconducting radical salts. The oxidation potentials of EDO-TTFI (**18**) also indicates good donor properties of this compound.

Table 1. Redox potentials of **1-4**, **18**, TTF and BEDT-TTF.[a]

Compound	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
TTF	0.36	0.73	0.37
EDO-TTF (**1**)	0.39	0.76	0.37
BEDT-TTF	0.52	0.83	0.31
EDO-TTFI2 (**2**)	0.51	0.84	0.33
EDO-TTFI (**18**)	0.45	0.80	0.35
EDO-TTFBr2 (**3**)	0.57	0.89	0.32
EDO-TTFCl2 (**4**)	0.59	0.89	0.30

[a] Conditions: $Bu^n{}_4NClO_4$, benzonitrile, room temperature, Pt working and counter electrodes. Potentials were measured against a Ag/Ag^+ electrode and converted to the value *vs* SCE ($Fc/Fc^+ = 0.46$ V).

Since **2** shows similar donor properties to BEDT-TTF (Table 1), the molecular structure and packing diagram of **2** have been determined by X-Ray analysis. The molecular and crystal structures of **2** are shown in Figure 1. The crystal lattice includes two crystallographically independent molecules which form pairs in the crystal (Figure 1c). The crystal of BEDT-TTF is composed of pairs of molecules,[18] whereas the crystal of BEDO-TTF (**13**) consists of sheets of molecules.[10] Therefore, the crystal structure of **2** is rather similar to that of BEDT-TTF instead of BEDO-TTF.

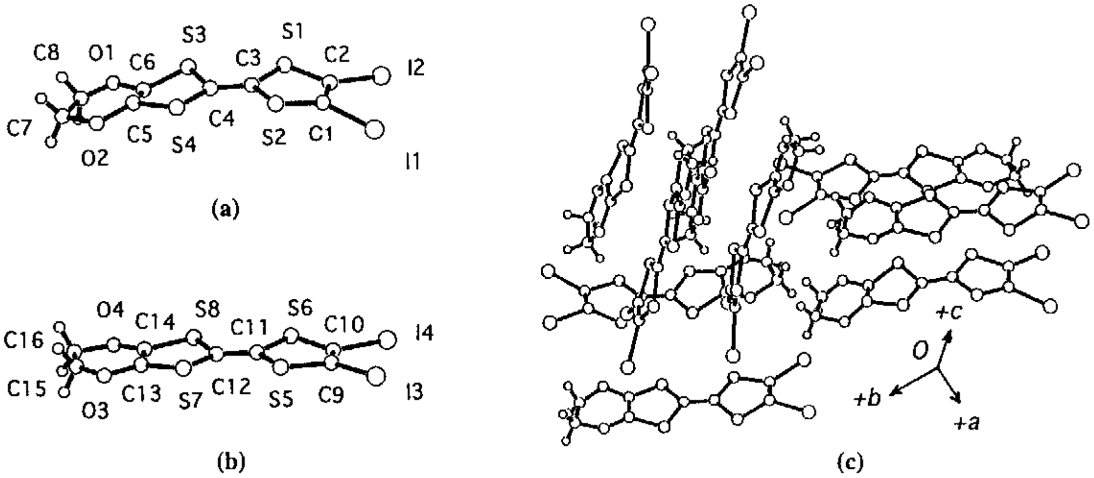


Figure 1. Crystal structure of **2**. (a) Side view of the non-planar form. (b) Side view of the planar form. (c) The head-to-head dimeric structure. [I(1)-C(1) 2.06(2), I(2)-C(2) 2.10(2), I(3)-C(9) 2.07(2), I(4)-C(10) 2.08(2), C(3)-C(4) 1.37(1), C(9)-C(10) 1.31(2), S(5)-C(9) 1.78(2), S(5)-C(11) 1.74(2), C(11)-C(12) 1.36(1), S(7)-C(12) 1.70(2), S(7)-C(13) 1.75(2), C(13)-C(14) 1.31(2), O(3)-C(13) 1.40(2), O(3)-C(15) 1.46(2) Å].

As shown in Figures 1a and 1b, one of the EDO-TTFI$_2$ molecules has a nonplanar structure, the other bearing an almost planar TTF core. Although **2** has a polar TTF framework due to iodine substituents, the dimeric structure proved to be a head-to-head manner instead of a normal head-to-tail structure (Figure 1c).[6d] It is worth noting that two short I•••O distances [I(1)-O(2) 3.37(1) and I(2)-O(1) 3.44(1)] between the iodine and oxygen on **2** was observed along the *c* axis. These I•••O distances are 3-5% shorter than the sum of the van der Waals radii (3.55 Å). The intermolecular I•••O interaction in **2** may cause one of the EDO-TTFI$_2$ molecules to force a nonplanar structure in the crystal. In contrast to **2**, the crystal structure of **4** consists of sheets of molecules (Figure 2c). The molecular structure of **4** is similar to those of other halogenated TTFs. The TTF core and two chlorine atoms in **4** show the high coplanarity, the maximum atomic deviation for the least-square plane being 0.0855 Å (Figure 2b). There is only one intermolecular short contact, and the S(3)•••Cl(1) distance (3.513(4) Å) is less than the sum of the van der Waals radii (3.65 Å).

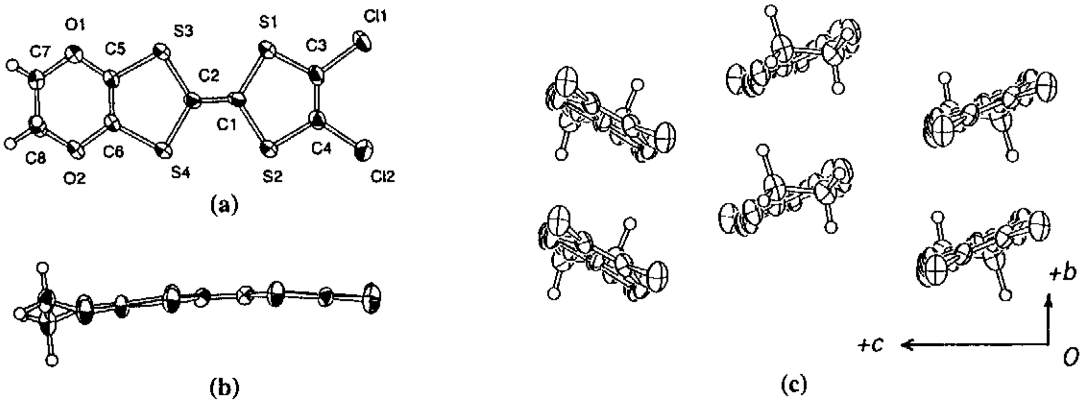


Figure 2. Crystal structure of **4**. (a) Top view. (b) Side view. (c) Packing diagram along the *a* axis. [Cl(1)-C(3) 1.750(9), Cl(2)-C(4) 1.688(10), S(1)-C(1) 1.753(9), S(1)-C(3) 1.73(1), S(3)-C(2) 1.748(9), S(3)-C(5) 1.755(4), O(1)-C(5) 1.35(1), C(1)-C(2) 1.29(1), C(3)-C(4) 1.29(1), C(5)-C(6) 1.31(1) Å].

Electric Conductivities of CT-complexes and Radical Cation Salts Derived from 2-4.

The new donors (**2-4** and **18**) formed single crystals of radical-cation salts with the anions and tetracyanoquinodimethane (TCNQ) examined except for **2**•TCNQ (Table 2). Preparation of TCNQ complexes with **2** and **18** was carried out by mixing a solution of **2** or **18** in CHCl$_3$ with a solution of TCNQ in MeCN. The radical-cation salts of **2-4** with I_3^-, $I_2\bullet(I^-)_2$, ClO_4^-, PF_6^-, $AuBr_2^-$,AuI_2^-, and Br^- were prepared by the galvanostatic oxidation (*ca.* 1 μA) in chlorobenzene (PhCl), 1,2-dichloroethane (DCE), 1,1,2-trichloroethane (TCE), THF, or CH$_2$Cl$_2$ 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 **18** with TCNQ is a semi-conductor. The radical-cation salts of **2** with ClO_4^-, PF_6^- and AuI_2^- exhibited high room-temperature conductivities; however, the radical-cation salts with I^- and Br^- showed conductivities as semi-conductors. It is known that the substitution of iodine on the TTF core causes sometimes different conducting behavior of the radical-cation salts as compared to the effect of bromine and chlorine, whereas chlorine exhibits a similar effect to bromine.[6d,14a]

Thus, the structures and conductivities of the radical-cation salts derived from **2** are somewhat different from those derived from **3**. In addition, an appreciable difference was observed in the conducting behavior of the radical-cation salts based on **3** and **4**. The donor (**3**) formed the metallic I_3^- and AuI_2^- salts, whereas the I_3^- salt of **4** was a semiconductor. The 3:1 PF_6 salt of **3** was a semiconductor, but the 2:1 salt of **4** 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. Therefore, the metallic conducting behavior of $(\mathbf{3})_3{\bullet}I_3$, $(\mathbf{3})_2{\bullet}AuI_2$ and $(\mathbf{4})_2{\bullet}PF_6$ is the first example for the radical-cation salts derived from brominated and chlorinated TTF derivatives.

Table 2. Electrical conductivities of radical-cation salts derived from **2-4** and **18**.

Donor	Acceptor	Solvent	D:A	σ_{rt}/S cm^{-1} [a]
2	TCNQ	$CHCl_3$, MeCN	1:1[b]	152
2	$I_2(I)_2$ [c]	PhCl	2:1[d]	1.8×10^{-3}
2	ClO_4	PhCl	2:1[d]	68 (T_{MI} = 50 K)
2	PF_6	TCE	3:1[b]	200 (E_a = 60 meV / 100 K) (E_a = 172 meV / 273 K)
2	AuI_2	DCE	2:1[d]	7.2 (T_{MI} = 40 K)
2	Br	CH_2Cl_2	2:1[d]	6.3×10^{-2}
18	TCNQ	$CHCl_3$, MeCN	2:1[d]	4.3×10^{-2}
3	I_3	DCE	3:1[d]	9.9 (T_{MI} = 180 K)
3	PF_6	DCE	3:1[d]	9.6 (E_a = 4.3 meV / 50 K) (E_a = 17.2 meV / 200 K)
3	AuI_2	TCE	2:1[b]	22 (T_{MI} = 100 K)
4	I_3	PhCl	1:1[d]	3.6×10^{-2}
4	PF_6	TCE	2:1[d]	169 (T_{MI} = 262 K)

[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 $Bu^n{}_4NI_3$. [d] Determined by X-Ray analysis.

The crystal structure of the unusual radical-cation salt $(\mathbf{2})_2{\bullet}I_2(I^-)_2$ in Table 2 was determined by X-Ray analysis (Figure 3). The crystal packing of $(\mathbf{2})_2{\bullet}(I_2)(I^-)_2$ 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}.

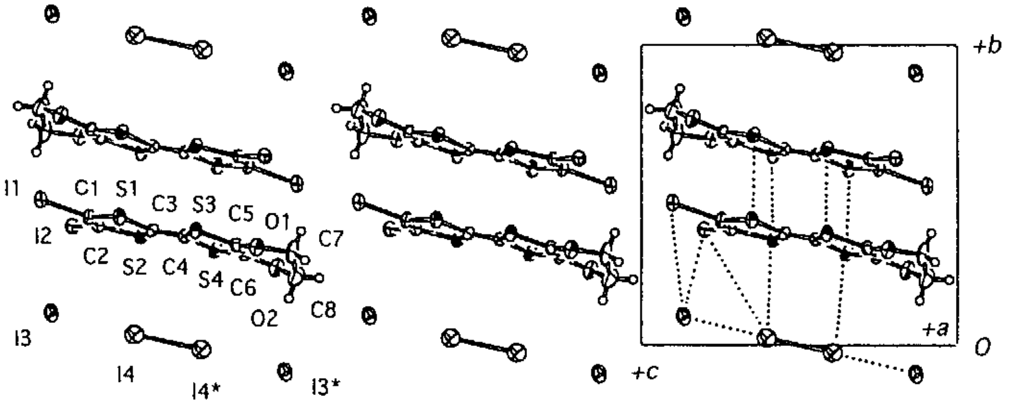
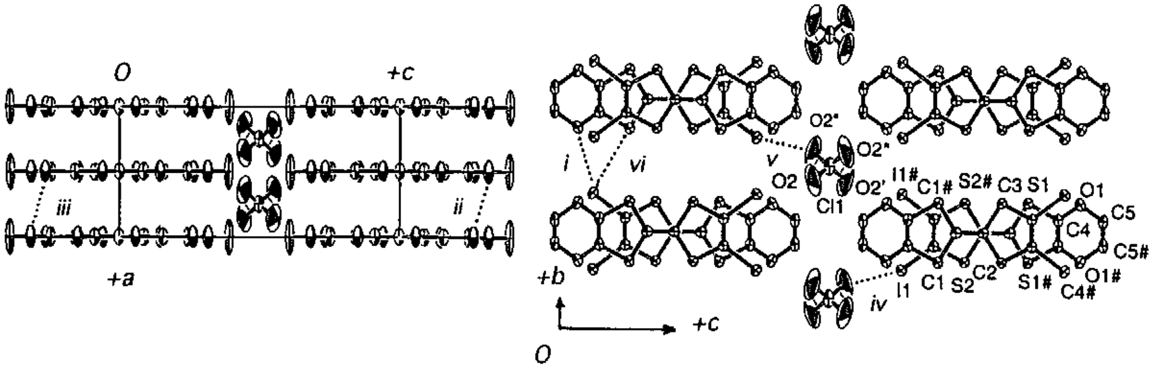


Figure 3. Packing diagram of $(\mathbf{2})_2\bullet I_2(I^-)_2$ along the *a* axis. Dotted lines show short contacts less than the sum of van der Waals radii. [I(1)-C(1) 2.107(7), S(1)-C(1) 1.751(8), S(1)-C(3) 1.732(8), S(3)-C(4) 1.722(7), S(3)-C(5) 1.735(8), O(1)-C(5) 1.354(9), C(1)-C(2) 1.32(1), C(3)-C(4) 1.390(10), C(5)-C(6) 1.35(1), 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(3)•••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 4. The EDO-TTFI$_2$ molecule locates on a crystallographic C_{2v} symmetry with two-fold axis passing through the C(2)-C(3) bond and the midpoint of the C(1)-C(1#), C(4)-C(4#), and C(5)-C(5#) bonds. The 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 (*i*-*v*) between the iodine and oxygen on the donor (I(1)-O(1) 3.375(1) Å) and between the donor's iodine and acceptor's oxygen (I(1)-O(2) 3.11 Å). These I•••O distances are 5-12% shorter than the sum of the van der Waals radii (3.55 Å), and the strong intermolecular I•••O interaction along the *a*, *b*, and *c* axes enhances the dimensionality. Surprisingly, there is no intra- and inter-column short S•••S distance less than the sum of van der Waals radii (3.70 Å), in spite of the intra-column I•••S interaction (I(1)•••S(1): *vi* 3.713(1) Å).

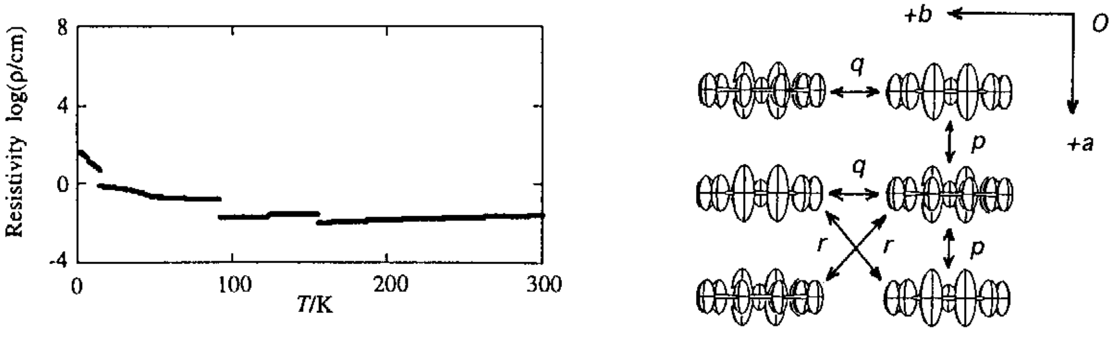


(a)

(b)

Figure 4. Packing diagram of $(\mathbf{2})_2\bullet ClO_4$. (a) Along the *b* axis. (b) Along the *a* axis. Dotted lines show short contacts less than the sum of van der Waals radii. [I(1)-C(1) 2.067(4), C(1)-S(2) 1.738(4), S(2)-C(2) 1.733(4), C(2)-C(3) 1.367(9), C(3)-S(1) 1.738(4), S(1)-C(4) 1.751(5), C(4)-O(1) 1.361(6), O(1)-C(5) 1.433(7), I(1)•••O(1): *i* 3.375(1), I(1)•••O(1): *ii* 3.689(7), I(1)•••O(1): *iii* 3.690(7), I(1)•••O(2): *iv* 3.110(7), I(1)•••O(2): *v* 3.111(7), I(1)•••S(1): *vi* 3.713(1) Å].

As shown in Figure 5a, (**2**)$_2$•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 (**2**)$_2$•ClO$_4$ may be due to its structurally enhanced dimensionality based on the I•••O interaction, although the crystal structure exhibits a typical one-dimentional stacking. The overlap integrals (p, q, and r) calculated show a good agreement with the one-dimentional conductivity (Figure 5b). As mentioned above, there is no intra- and inter-column short S•••S contact, while the intra- and inter-column I•••O and I•••S contacts are strong and less than the sum of van der Waals radii. Thus, each donor molecule is anchored by I•••O and I•••S contacts to form a metallic conducting path (p in Figure 5b).

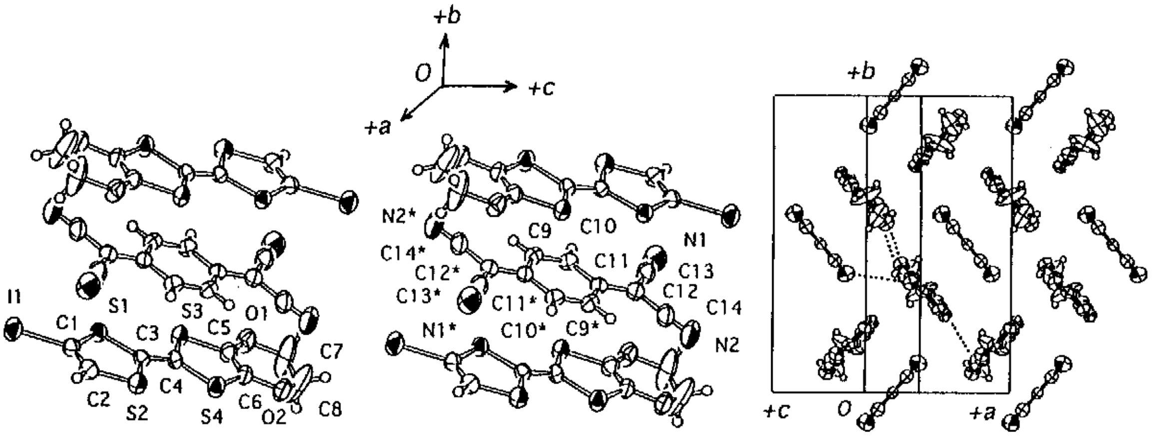


(a)

(b)

Figure 5. (a) Temperature dependence of the resistivity for (**2**)$_2$•ClO$_4$. (b) Packing diagram along the c axis. Overlap integrals (x 10^{-3}) of the conduction orbitals in (**2**)$_2$•ClO$_4$ are: p = 20.6; q = 6.22; r = 1.38.

The crystal structure of the CT-complex (**18**)$_2$•TCNQ shows an interesting stacking. As shown in Figure 6a, the donor (**18**) and acceptor (TCNQ) form a 2:1 mixed-stacked unit (DAD). The donor molecules in one unit are placed in staggered positions at the side edges of the adjacent DAD units (Figure 6b). Although



(a)

(b)

Figure 6. Crystal structure of (**18**)$_2$•TCNQ. (a) The 2:1 mixed-stacked structure. (b) Packing diagram. Dotted lines show short contacts less than the sum of van der Waals radii. [S(1)-C(1) 1.750(4), S(2)-C(2) 1.736(4), S(2)-C(3) 1.754(4), S(3)-C(4) 1.756(4), S(3)-C(5) 1.752(4), O(1)-C(5) 1.365(4), N(1)-C(13) 1.145(5), N(2)-C(14) 1.130(5), C(9)-C(10) 1.339(5), C(10)-C(11) 1.439(5), C(11)-C(12) 1.371(5), I(1)•••N(2) 3.068(4), S(1)•••S(2) 3.434(2), S(1)•••S(3) 3.618, S(3)•••S(3) 3.634(2) Å].

there is no short distance in the DAD unit less than the sum of van der Waals radii, the inter-column I•••N and S•••S interaction is fairly large. Thus, the I(1)•••N(2) distance (3.09 Å) is 15% shorter than the sum of van der Waals radii (3.65 Å), and the S(1)•••S(2), S(1)•••S(3), S(3)•••S(3) distances (3.43-3.63 Å) are 2-7% shorter than the sum of van der Waals radii. In the DAD unit, the degree of the charge transfer in TCNQ part was estimated to be 0.22,[19] reflecting the C≡N bond length (1.145 and 1.130 Å) in $(\mathbf{18})_2$•TCNQ [the C≡N bond length in TCNQ is 1.14 Å,[20]]. It is worth noting that $(\mathbf{18})_2$•TCNQ shows conductivity (4.3 x 10^{-3} S cm^{-1}) at room temperature. Since the CT-complex has a mixed stacked structure with a staggered packing, the room temperature conductivity of $(\mathbf{18})_2$•TCNQ is unusually high.

Our results reported here disclose that halogenated EDO-TTF derivatives may produce a new type of synthetic metals using the X•••S, X•••O, and X•••X interactions in the crystals. We believe that the radical-cation salts derived from **2-4** and **18** will develop a new aspect in the chemistry of molecular conductors using a new concept based on the crystal engineering.

EXPERIMENTAL

General Procedure. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-LA-500 and JEOL JNM-LA-400 instruments. Spectra are reported (in δ) referenced to Me_4Si. Unless otherwise indicated, $CDCl_3$ was used as solvent. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, and coupling constant (Hz). MS spectra were determined on a JEOL JMS-AX 500 instrument. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. Melting points were determined on a Yanaco Micro melting point apparatus MP-500D and are uncorrected. Elemental analyses were performed in the microanalysis laboratory of Tokyo Metropolitan University. Column chromatography was carried out with use of EM Reagents silica gel 60, 70-230 mesh ASTM, Daiso silica gel 1001W, or neutral alumina activity II-III, 70-230 mesh ASTM. Gel permeation liquid chromatography (GPC) was performed on AL LC-08 and LC-918 liquid chromatography instruments with JAIGEL-1H column (20 mm x 600 mm x 2) and chloroform as eluent. All solvents were dried by conventional procedures. 1,3-Dithiole-2-thione (**19**),[13] 4,5-diiodo-1,3-dithiole-2-thione (**20a**),[7b] and 4,5-diiodo-1,3-dithiole-2-one (**17a**)[7b] were prepared according to the published procedures.

2,3-Dichloro-1,4-dioxane (5).

To 1, 4-dioxane (88.1 g: 84.6 mL, 1.0 mol) was added dropwise SO_2Cl_2 (269.9 g: 161.6 mL, 2.0 mol) at 0 ℃ during 1 h, and then the mixture was stirred at 60 ℃ for 18 h. The mixture was cooled to rt, and gaseous nitrogen was bubbled through the mixture for 1 h. The product was purified by distillation under reduced pressure to afford **5** (114.5 g, 72 %) as a colorless liquid (bp 82-83 ℃ / 18 torr). ^{1}H-NMR (400 MHz) δ 5.88 (s, 2H), 4.20-4.22 (m, 2H), 3.57-3.60 (m, 2H).

2,3-Bis(dimethyldithiocarbamyl)-1,4-dioxane (6).

A solution of **5** (38.27 g, 0.244 mol) and sodium dimethyldithiocarbamate (91.56 g, 0.569 mol) in DMF (500 mL) was heated 60 ℃ for 3 h. The reaction mixture was cooled to rt and was diluted with water (500 mL). The colorless precipitates were filtered and washed with water. The solid was dissolved in $CHCl_3$. The solution was washed with brine, dried over $MgSO_4$, and evaporated to dryness. The solid product was purified by recrystallization from CH_2Cl_2-diisopropyl ether (1:1) to afford **6** (56.83 g, 71 %) as colorless crystals, mp 168.5-169.5 ℃ (CH_2Cl_2-diisopropyl ether) (lit.,[9a] 165-166 ℃); ^{1}H-NMR (400 MHz) δ 6.56 (s, 2H), 4.23 (d, 2H, J=8.5Hz), 3.78 (d, 2H, J=8.5Hz), 3.56 (s, 6H), 3.43 (s, 6H); ^{13}C-NMR (100 MHz) δ 193.2, 89.7, 62.2, 45.4, 41.8; MS (EI) *m/z* 327 (M^+).

2-Dimethyldithiocarbamyl-1,4-diox-2-ene (7).

A solution of 2,3-bis(dimethyldithiocarbamyl)-1,4-dioxane (**6**) (9.02 g, 27.6 mmol) in toluene (200 mL) was heated under reflux for 15 h. The reaction mixture was cooled to room temperature and evaporated *in vacuo*. The residue was purified by recrystallization from CH_2Cl_2-diisopropyl ether (1:1) to afford **7** (5.41 g, 95 %) as colorless crystals, mp 169-169.5 ℃ (CH_2Cl_2-diisopropyl ether) (lit.,[9a] 171 ℃); ^{1}H-NMR (400 MHz) δ 6.47 (s, 1H), 4.28-4.30 (m, 2H), 4.19-4.21 (m, 2H), 3.53 (s, 3H), 3.39 (s, 3H) ; ^{13}C-NMR (100 MHz) δ 195.1, 137.4, 128.0, 64.8, 64.2, 45.5, 41.7.

Bromination of 7.

To a cooled solution of **7** (10.5 g, 53.2 mmol) in CH_2Cl_2 (100 mL) was added dropwise a solution of Br_2 (2.8 mL, 54.3 mmol) in CH_2Cl_2 (8 mL) at 0 ℃ and the mixture was stirred for 1 h. The orange precipitates were filtered and washed with CH_2Cl_2 to afford the bromide (**8**) (19.7 g, 98%) which was used for further transformation. **8**: colorless crystals, mp 104-106 ℃ (CH_2Cl_2) (lit.,[9a] 105 ℃); ^{1}H-NMR (DMSO-d_6, 400 MHz) δ 4.52 (s, 1H), 4.14-4.27 (m, 4H), 3.61 (s, 3H), 3.56 (s, 3H); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ 183.9, 97.7, 96.9, 65.5, 60.7, 46.9, 46.9.

4,5-Ethylenedioxy-2-dimethylamino-1,3-dithiolium bromide (9).

The iminium salt **8** (18.1 g, 49.5 mmol) was placed in a 100-mL flask and heated 110 ℃ for 5 h under reduced pressure (15 Torr) to afford **9** (14.0 g, 99 %) as pale brown microcrystals, mp 171.5-172 ℃. UV (CH_2Cl_2) λ_{max} 270, 360 nm[9a]; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ 4.53 (s, 4H), 3.47 (s, 6H); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ 174.2, 128.0, 64.5, 46.1.

4,5-Ethylenedioxy-1,3-dithiole-2-thione (10).

To a solution of **9** (4.98 g, 17.5mmol) in EtOH (130 mL) and AcOH (130 mL) was added portionwise powdery NaSH (8.55 g, 153 mmol) with stirring. The reaction mixture was stirred at rt for 2 h and diluted with a mixture of CH_2Cl_2 (300 mL) and water (300 mL). The organic layer was separated and washed with brine and saturated $NaHCO_3$ solution successively. After dried $MgSO_4$, the organic solution was concentrated *in vacuo* and the residue was purified by chromatography on silica gel using CH_2Cl_2-hexane (1:1) as eluent. The eluent was concentrated to dryness and the residual solid was recrystallized from CH_2Cl_2 / hexane (1:1) to afford **10** (2.46 g, 73%) as yellow crystals, mp 144-144.5 ℃; ^{1}H-NMR (400 MHz) δ 4.38 (s, 4H); ^{13}C-NMR (100 MHz) δ 174.2, 128.0, 67.5, 66.5; MS *m/z* 192(M^+), 164, 128, 76; IR (KBr) 1597 (C=C), 1171 (C=S) cm^{-1}; HRMS calcd for $C_5H_4O_2S_3$ 191.9374, found 191.9359.

4,5-Ethylenedioxy-4',5'-bis(methoxycarbonyl)tetrathiafulvalene (12).
A mixture of the thione (**10**) (300 mg, 1.56 mmol) and **11** (535 mg, 2.29 mmol) was heated in triethyl phosphite (10 mL) at 60 ℃ under nitrogen for 4 h. After the reaction mixture was cooled to rt, triethyl phosphite was removed under reduced pressure to give a black residue which was separated by column chromatography on silica gel using CH_2Cl_2 / hexane (1:1) as eluent to afford **12** (304 mg, 70%), together with small anounts of bis(ethylenedioxy)tetrathiafulvalene (**13**) and tetrakis(methoxycarbonyl)-tetrathiafulvalene (**14**). **12**: purple crystals, mp 125.5-126 ℃ (CH_2Cl_2-hexane) (lit.,[9b] 122-123 ℃); ^{1}H-NMR (400 MHz) δ 4.27 (s, 4H), 3.84 (s, 6H); ^{13}C-NMR (100 MHz) δ 159.4, 131.8, 123.1, 108.7, 104.8, 66.1, 52.9; MS *m/z* 378 (M^+), 350, 320, 264, 216.

4,5-Ethylenedioxytetrathiafulvalene (1).
A mixture of **12** (2.19 g, 5.8 mmol) and LiBr•H_2O (6.11 g, 58.3 mmol) in HMPA (176 mL) was evacuated, and gaseous nitrogen was filled. The mixture was gradually heated from rt to 150 ℃ in a period of 1.5 h with stirring and stirred for 15 min at 150 ℃. The reaction mixture was cooled to rt and water was added. The mixture was extracted with CS_2. The organic layer was washed with brine and dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue was chromatographed on silica gel with CS_2 as eluent to afford **1** (1.06 g, 70%), together with the monoester (**15**) (371 mg, 20%). **1**: red needles, mp 92.0-92.5 ℃ ($CHCl_3$-hexane) (lit.,[9a] 92 ℃); ^{1}H-NMR (400 MHz) δ 6.33 (s, 2H), 4.26 (s, 4H); ^{13}C-NMR(100 MHz) δ 123.0, 118.8, 115.7, 98.4, 66.0; MS *m/z* 262 (M^+), 234, 178, 146, 102; HRMS calcd for $C_8H_6O_2S_4$ 261.9251, found 261.9243. **15**: red microcrystals, mp 166.5-167.0 ℃ (CH_2Cl_2-hexane); ^{1}H-NMR (400 MHz) δ 7.26 (s, 1H), 4.27 (s, 4H), 3.80 (s, 3H); MS *m/z* 320 (M^+), 292, 246, 204; HRMS calcd for $C_{10}H_8O_4S_4$ 319.9306, found 319.9287. The monoester (**15**) was converted into **1** (50%) under the similar conditions described above.

4,5-Diiodo-4',5'-ethylenedioxytetrathiafulvalene (2) by Iodination of 1.
To a solution of **1** (199 mg, 0.759 mmol) in THF (5 mL) was added LDA, which was prepared from Pr^i_2NH (372 mg, 3.69 mmol) and Bu^nLi (1.0 mL, 1.6 mmol, 1.6 M in hexane) in THF (2 mL), at -78 ℃ during 7 min under argon. The color of solution was changed to intensely orange. After being stirred at -78 ℃ for 50 min, perfluorohexyl iodide (1.24 g, 2.77 mmol) in THF (3 mL) was added at -78 ℃ during 7 min. The resulting red solution was stirred for 1 h at -78 ℃ and then was allowed to warm to rt. Saturated aq NH_4Cl was added and the mixture was extracted with CS_2. The organic layer was washed with brine and dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue was chromatographed on silica gel with CS_2 as eluent and was further purified by GPC to afford **2** (215 mg, 55%). **2**: red needles, mp 150 ℃ (decomp) (CH_2Cl_2-hexane); ^{1}H-NMR (400 MHz) δ 4.26 (s, 4H); ^{13}C-NMR (125 MHz) δ 123.1, 117.8, 103.4, 77.2, 66.1; MS *m/z* 514 (M^+), 388, 260; HRMS calcd for $C_8H_4O_2I_2S_4$ 513.7182, found 513.7166.

4,5-Ethylenedioxy-4'-iodotetrathiafulvalene (18) by Iodination of 1.
In a similar manner for the preparation of **2**, **1** (82 mg, 0.313 mmol) in THF (10 mL) was treated with LDA from Pr^i_2NH (56 mg, 0.555 mmol) and Bu^nLi (0.35 mL, 0.37 mmol, 1.06 M in hexane) in THF (2

mL) at -78 °C under argon. After being stirred at -78 °C for 50 min, $F_2ClCCFClI$ (253 mg, 0.94 mmol) in THF (3 mL) was added and the reaction mixture was stirred for 1 h at -78 °C and then was allowed to warm to rt. After aqueous work-up, **18** (100 mg, 82%) was isolated by column chromatography on silica gel with CS_2 as eluent, followed by GPC separation. **18**: orange needles, mp 78-79 °C (decomp) (CH_2Cl_2-hexane); ^{1}H-NMR (400 MHz) δ 6.43 (s, 1H), 4.34 (s, 4H); ^{13}C-NMR (125 MHz) δ 124.0, 123.2, 123.1, 116.8, 100.6, 66.2, 63.7; MS *m/z* 388 (M^+), 360; HRMS calcd for $C_8H_5O_2IS_4$ 387.8217, found 387.8223.

4,5-Dibromo-4',5'-ethylenedioxytetrathiafulvalene (3) by Bromination of 1.

In a similar manner for the preparation of **2**, **1** (300 mg, 1.14 mmol) in THF (5 mL) was treated with LDA from Pr^i_2NH (350 mg, 3.47 mmol) and Bu^nLi (1.5 mL, 2.45 mmol, 1.6 M in hexane) in THF (3 mL) at -78 °C under argon. After stirred at -78 °C for 40 min, $BrCl_2CCCl_2Br$ (830 mg, 2.55 mmol) in THF (3 mL) was added. After stirring at -78 °C to rt and then work-up, **3** (354 mg, 74%) was isolated by column chromatography on silica gel with CS_2 as eluent, followed by GPC separation. **3**: red needles, mp 169-170 °C (CH_2Cl_2-hexane); ^{1}H-NMR (500 MHz) δ 4.27 (s, 4H); ^{13}C-NMR (125 MHz) δ 123.2, 110.2, 105.6, 101.6, 66.3; MS *m/z* 424, 422, 420 (M^+), 368, 303, 260; HRMS calcd for $C_8H_4O_2{}^{79}Br{}^{81}BrS_4$ 421.7420, found 421.7403.

4,5-Dichloro-4',5'-ethylenedioxytetrathiafulvalene (4) by Chlorination of 1.

In a similar manner for the preparation of **2**, **1** (201 mg, 0.77 mmol) in THF (5 mL) was treated with LDA [Pr^i_2NH (350 mg, 3.47 mmol), Bu^nLi (1.5 mL, 2.45 mmol, 1.6 M in hexane), and THF (3 mL)]. After being stirred for 1 h at -78 °C, Cl_3CCCl_3 (498 mg, 2.10 mmol) in THF (3 mL) was added. After stirring for 1.7 h at -78 °C and then rt, **4** (142 mg, 56%) was isolated by column chromatography on silica gel with CS_2 as eluent, followed by GPC separation. **4**: red needles, mp 177.5-178 °C (CH_2Cl_2-hexane); ^{1}H-NMR (500 MHz) δ 4.27 (s, 4H); ^{13}C NMR (125 MHz) δ 123.2, 114.2, 106.8, 105.8, 66.3; MS *m/z* 334, 332, 330 (M^+), 214; HRMS calcd for $C_8H_4O_2{}^{35}Cl_2S_4$ 329.8471, found 329.8456.

4,5-Dibromo-1,3-dithiole-2-thione (20b).

To a solution of **19** (674 mg, 5.02 mmol) in THF (40 mL) was added Bu^nLi (3.3 mL, 5.05 mmol, 1.53 M in hexane) at -78 °C under argon. The mixture was stirred for 1 h at -78 °C. To the mixture was added $BrCl_2CCCl_2Br$ (3.75 g, 10.99 mmol) in THF (20 mL) at -78 °C and the resulting mixture was stirred for 3 h at -78 °C, allowed to warm to rt, and stirred at rt overnight. After aqueous work-up, the product was separated by column chromatography on silica gel using CS_2-hexane (1:1) as eluent to afford **20b** (462 mg, 32%). **20b**: yellow needles, mp 100.3-100.8 °C (CH_2Cl_2-hexane); ^{13}C-NMR (125 MHz) δ 208.7, 107.2; MS *m/z* 294, 292, 290 (M^+); IR (KBr) 1505 cm^{-1}; HRMS calcd for $C_3{}^{81}Br_2S_3$ 293.7488, found 293.7494.

4,5-Dibromo-1,3-dithiole-2-one (17b).

To a solution of **20b** (1.40 g, 4.78 mmol) in a mixture of $CHCl_3$ (100 mL) and acetic acid (100 mL) was added mercury(II) acetate (4.65 g, 14.6 mmol) under nitrogen. The reaction mixture was stirred for 2 h at rt. The resultant white precipitates were filtered off and washed with $CHCl_3$. The filtrate was washed with brine several times and then with sat. aq. $NaHCO_3$ solution to remove acetic acid. The organic layer was dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was passed through a short colum of silica gel with CH_2Cl_2 as eluent to afford **17b** (1.26 g, 95%). **17b**: colorless needles, mp 67.0-67.5 ℃ (CH_2Cl_2-hexane); ^{13}C-NMR (125 MHz) δ 188.5, 100.5; MS *m/z* 278, 276, 274 (M^+); IR (KBr) 1665 cm^{-1}; HRMS calcd for $C_3{}^{81}Br_2OS_2$ 277.2243, found 277.2216.

4,5-Diiodo-4',5'-ethylenedioxytetrathiafulvalene (2) by Cross-coupling.

A mixture of the thione (**10**) (199 mg, 1.03 mmol), the diiodide (**17a**) (374 mg, 1.01 mmol), and $P(OCH_3)_3$ (5 mL) was heated in refluxing benzene (10 mL) for 4 h. After the reaction mixture was cooled to rt, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel using CS_2-hexane (1:1) as eluent to afford EDO-TTFI$_2$ **2** (304 mg, 59%), together with tetraiodotetrathiafulvalene (TTFI$_4$) (104 mg, 29%).

4,5-Dibromo-4',5'-ethylenedioxytetrathiafulvalene (3) by Cross-coupling.

In a similar manner for the reaction of **10** with **17a**, the reaction of **10** (182 mg, 0.95 mmol) with **17b** (250 mg, 0.91 mmol) formed EDO-TTFBr$_2$ **3** (228 mg, 59%), together with TTFBr$_4$ (74 mg, 15%) and BEDO-TTF (13 mg, 4%).

X-Ray Structural Determination of 2 (Figure 1).

Crystals of **2** suitable for X-Ray structure analysis were obtained by slow recrystallization of **2** from (hexane-CH_2Cl_2), $C_8H_4O_2I_2S_4$, red needle of crystal size 0.12 x 0.14 x 0.30 mm; intensity data were collected using a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71069); crystal system orthorhombic, space group $Pna2_1$(No. 33); cell parameters: a = 14.561(1), b = 15.324(1), c = 12.046(2); V = 2687.8(4) Å^3; Z = 8; D_{calcd} = 2.541 g cm^{-3}; no. of reflections measured with $I > 3.00\sigma(I)$ 2001; R = 0.045, R_w = 0.044. Structural parameters of non-hydrogen atoms were refined anisotropically according to the full-matrix least-squares technique.

X-Ray Structural Determination of 4 (Figure 2).

Crystals of **4** were obtained by slow recrystallization of **4** from (hexane-CH_2Cl_2), $C_8H_4O_2Cl_2S_4$, red needle of crystal size 0.60 x 0.18 x 0.06 mm; intensity data were collected under the similar conditions described for **2**; crystal system monoclinic, space group $C_{2/c}$ (No. 15); cell parameters: a = 26.22(3), b = 4.01(9), c = 22.62(3); β = 107.8(1)°; V = 2261(49) Å^3; Z = 8; D_{calcd} = 1.946 g cm^{-3}; no. of reflections measured with $I > 3.00\sigma(I)$ 1551; R = 0.068, R_w = 0.051. Structural parameters of non-hydrogen atoms were refined anisotropically according to the full-matrix least-squares technique.

X-Ray Structural Determination of $(2)_2 \cdot I_2(I^-)_2$ (Figure 3).

Crystals of $(\mathbf{2})_2 \cdot I_2(I^-)_2$ were obtained by the galvanostatic oxidation (*ca.* 1 µA) of **2** with $Bu^n{}_4NI_3$ in chlorobenzene, $C_8H_4O_2I_4S_4$, black prism of crystal size 0.12 x 0.08 x 0.20 mm; intensity data were collected under the similar conditions described for **2**; crystal system monoclinic, space group $P2_1/a$ (No.

14); cell parameters: a = 11.196(2), b = 11.835(3), c = 13.392(2); β = 110.00(1)°; V = 1667.5(6) Å^3; Z = 4; D_{calcd} = 3.059 g cm^{-3}; no. of reflections measured with $I > 3.00\sigma(I)$ 2579; R = 0.033, R_w = 0.031.

X-Ray Structural Determination of $(2)_2$•ClO_4 (Figure 4).

Crystals of (**2**)$_2$•ClO_4 were obtained by the galvanostatic oxidation (*ca.* 1 μA) of **2** with $Bu^n{}_4NClO_4$ in chlorobenzene, $C_{16}H_8O_8ClI_4S_8$, black needle of crystal size 0.40 x 0.08 x 0.08 mm; intensity data were collected under the similar conditions described for **2**; crystal system orthorhombic, space group *Cmma* (No. 67); cell parameters: a = 7.14(1), b = 13.178(1), c = 15.628(2); V = 1469(2) Å3; Z = 2; D_{calcd} = 2.548 g cm^{-3}; no. of reflections measured with $I > 3.00\sigma(I)$ 2343; R = 0.037, R_w = 0.054. Structural parameters of non-hydrogen atoms were refined anisotropically according to the full-matrix least-squares technique.

X-Ray Structural Determination of 18•TCNQ (Figure 6).

Crystals of **18**•TCNQ were obtained by mixing a solution of **18** in $CHCl_3$ with a solution of TCNQ in MeCN, $C_{14}H_6N_2O_2IS_4$, black prism of crystal size 0.30 x 0.25 x 0.32 mm; intensity data were collected under the similar conditions described for **2**; crystal system monoclinic, space group $P2_1/a$ (No. 14); cell parameters: a = 8.176(3), b = 16.247(2), c = 12.967(2); β = 103.25(1)°; V = 1676.5(6) Å^3; Z = 4; D_{calcd} = 1.939 g cm^{-3}; no. of reflections measured with $I > 3.00\sigma(I)$ 2938; R = 0.030, R_w = 0.029. Structural parameters of non-hydrogen atoms were refined anisotropically and some hydrogen atoms were refined isotropically according to the full-matrix least-squares technique.

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