1770 *Chem. Mater.* **2001,** *13,* 1770−1777

Tetrathiafulvalene Derivatives Linking a Dichalcogenolane Ring through the σ-Bond: New Donor Components for Organic Metals

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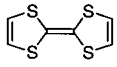
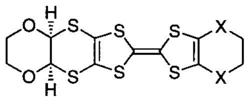
Received October 23, 2000. Revised Manuscript Received February 27, 2001

A synthetic study of the dioxolane derivatives of methylenedithio(ethylenedithio)-tetrathiafulvalene (MET), bis(methylenedithio)tetrathiafulvalene (MT), and methylenedithiotetrathiafulvalene, their dithiolane analogues, and the oxathiolane derivative of MET has been undertaken to explore new organic metals. A practically useful preparation of the biheterocycle-fused 1,3-dithiol-2-ones as building blocks for these dichalcogenolane-linked tetrathiafulvalene (TTF) donors has been realized via the newly developed BF_3-promoted reactions. The effect of the additional linked dichalcogenolane ring on the electron-donating ability is investigated by cyclic voltammetry. An X-ray crystallographic analysis of the oxathiolane-linked MET reveals that its molecular structure is isostructural with that of its dithiolane analogue but not bulkier than that of its dioxolane analogue. Several of the present TTF donors have produced metallic charge-transfer materials, two of which are characterized by X-ray crystallography. In the crystal structure of the 7,7,8,8-tetracyanoquinodimethane complex of the dioxolane-linked MT that exhibits metallic-like behavior around room temperature, the donor molecules are stacked head-to-tail to form the dimers, which are connected by C−H···O hydrogen bonds. On the other hand, in the metallic AsF_6 salt of the dioxolane-linked MET stable down to 2.0 K, the donor molecules are stacked head-to-head to form two-dimensional sheets despite the dioxolane ring being perpendicularly attached to the MET molecule.

Introduction


TTF (**1**)



DOET (**2**: X = S)
DOES (**3**: X = Se)

Tetrathiafulvalene (TTF, **1**) derivatives serve as important π-electron donors for the development of molecular-based organic metals and superconductors,[1,2] and a variety of studies on modification of the TTF skeleton have been made.[3] One major trend in these studies has focused on the construction of TTF-type donors with extended π-conjugation, whereas our own interest in this field has involved the use of TTF derivatives with the periphery extended by the σ-bond framework containing heteroatoms as donor components to develop new organic metals.[4] Our early work revealed that DOET (**2**)[5] and DOES (**3**), in each of which a cis-fused heterobicyclic system is condensed on one

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(1) See recent conference proceedings: (a) Proceedings of ICSM '96, Snowbird, *Synth. Met.* **1997**, *84−86*. (b) Proceedings of ICSM '98, Montpellier, *Synth. Met.* **1999**, *101−103*.

(2) For organic superconductors, see: (a) Ishiguro, T.; Yamaji, K.; Saito, G. *Organic Superconductors*, 2nd ed.; Fulde, P., Ed.; Springer Ser. Solid-State Sci.; Springer: Berlin, 1998; Vol. 88. (b) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes) Synthesis, Structure, Properties and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992.

(3) For recent reviews, see: (a) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11−23. (b) Becher, J.; Lau, J.; Mørk, P. In *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley−VCH: Weinheim, 1998; pp 198−233. (c) Papavassiliou, G. C.; Terzis, A.; Delhaes, P. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; J. Wiley & Sons: Chichester, 1997; Vol. 1, pp 151−227. (d) Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater.* **1996**, *8*, 203-211. (e) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1996**, *18*, 1−294. (f) Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481−1496.

(4) (a) Yamada, J.; Nishikawa, H.; Kikuchi, K. *J. Mater. Chem.* **1999**, *9*, 617−628. (b) Yamada, J. In *Recent Research Developments in Organic Chemistry*; Pandalai, S. G., Ed.; Transworld Research Network: Trivandrum, 1998; Vol. 2, pp 525−545. (c) Yamada, J.; Tanaka, S.; Segawa, J.; Hamasaki, M.; Hagiya, K.; Anzai, H.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *J. Org. Chem.* **1998**, *63*, 3952−3960.

(5) Abbreviations for the TTF derivatives used herein: DOET, (1,4-dioxanediyl-2,3-dithio)ethylenedithiotetrathiafulvalene; DOES, (1,4-dioxanediyl-2,3-dithio)ethylenediselenotetrathiafulvalene; DO-MET, (1,3-dioxolan-2-yl)methylenedithio(ethylenedithio)tetrathiafulvalene; MET, methylenedithio(ethylenedithio)tetrathiafulvalene; DO-MMT, (1,3-dioxolan-2-yl)methylenedithio(methylenedithio)tetrathiafulvalene; DO-MDT, (1,3-dioxolan-2-yl)methylenedithiotetrathiafulvalene; DT-MET, (1,3-dithiolan-2-yl)methylenedithio(ethylenedithio)tetrathiafulvalene; DT-MMT, (1,3-dithiolan-2-yl)methylenedithio(methylenedithio)tetrathiafulvalene; DT-MDT, (1,3-dithiolan-2-yl)methylenedithiotetrathiafulvalene; OT-MET, (1,3-oxathiolan-2-yl)methylenedithio(ethylenedithio)tetrathiafulvalene; BEDT-TTF, bis(ethylenedithio)tetrathiafulvalene.

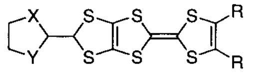
10.1021/cm000842x CCC: $20.00

Table 1. Preparation of Ketones 9b,c[a]

entry	substrate	reagent (equiv)	solvent	BF_3·OEt_2 (equiv)	reaction time (d)	product (yield, %)
1	**8**	1,2-ethanedithiol (1.2)	$CHCl_3$	10	2	**9b** (95)
2	**8**	2-mercatpoethanol (1.2)	$CHCl_3$	10	2	**9c** (10)
3	**8**	1,2-ethanedithiol (1.2)	$CHCl_3$	2	5	**9b** (82)
4	**8**	2-mercaptoethanol (1.2)	$CHCl_3$	2	5	—[b]
5	**9a**	2-mercaptoethanol (1.2)	$CHCl_3$	10	2	**9c** (33)
6	**9a**	2-mercaptoethanol (1.2)	CH_2Cl_2	10	2	**9c** (40)

[a] All reactions were carried out at 25−30 °C. [b] No detectable amount of **9c**.

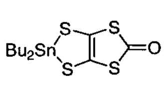
side of the TTF core, produce metallic cation-radical salts, including β-$(DOET)_2BF_4$ and β-$(DOES)_2(AuI_2)_{0.75}$.[6,7] In the course of investigation of these bulky TTF donors, we also found a metallic 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex of DO-MET (**4a**), though this donor seems to be much bulkier than DOET and DOES because the dioxolane ring is perpendicularly attached to the MET molecule.[8] This result prompted us to pursue further a search for new organic metals derived from the dioxolane-linked TTF derivatives and related compounds because such a search would result in a further extension of the molecular design for donor components, providing new organic metals as well as donor packing modes conducive to metallic electronic structures. Following our initial communication,[9] we now describe the detailed synthesis and electrochemical properties of a series of novel TTF donors with an appended dichalcogenolane ring: DO-MET (**4a**), DO-MMT (**4b**), DO-MDT (**4c**), DT-MET (**5a**), DT-MMT (**5b**), DT-MDT (**5c**), and OT-MET (**6**), including the molecular structure of OT-MET (**6**). We also report the electrical conducting behavior of their charge-transfer (CT) materials and the crystal structures of (DO-MMT)(TCNQ) and $(DO\text{-}MET)_2AsF_6$.



4a (DO-MET): X = Y = O, R-R = $S(CH_2)_2S$
4b (DO-MMT): X = Y = O, R-R = SCH_2S
4c (DO-MDT): X = Y = O, R = R = H
4d: X = Y = O, R = R = CO_2Me
5a (DT-MET): X = Y = S, R-R = $S(CH_2)_2S$
5b (DT-MMT): X = Y = S, R-R = SCH_2S
5c (DT-MDT): X = Y = S, R = R = H
5d: X = Y = S, R = R = CO_2Me
6 (OT-MET): X = O, Y = S, R-R = $S(CH_2)_2S$

Results and Discussion

Synthesis. Our strategy for synthesizing the present TTF donor system was based on the $(MeO)_3P$-mediated cross-coupling reaction, and to this end, a synthetic method for the preparation of new ketones **9a**−**c** utilized for this reaction was developed. Treatment of the dioxane-fused ketone **8**, which was available by reaction of tin dithiolate **7** with *trans*-2,3-dichloro-1,4-dioxane in the presence of 2 equiv of BF_3·OEt_2 for 3 h,[4c,8] with an excess of BF_3·OEt_2 (10 equiv) in $CHCl_3$ at room temperature for 1 day, induced isomerization of the bis-fused six-membered heterocycle to the five-membered biheterocycle, affording the dioxolane-attached ketone **9a** in 80% yield together with a trace amount of **8**.[10] The ratio of **9a**:**8** determined by ^1H NMR was 46:1. The pure ketone **9a** could be obtained by recrystallization from $CHCl_3$−EtOH. Similarly, the use of 10 equiv of BF_3·OEt_2 in the reaction of **7** with *trans*-2,3-dichloro-1,4-dioxane under the same conditions as those used for the isomerization of **8** furnished an 8:1 mixture of **9a** and **8** in 89% yield.



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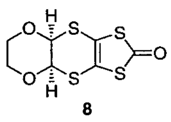

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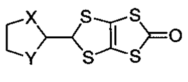
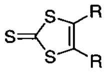


9a: X = Y = O
9b: X = Y = S
9c: X = O, Y = S



10a: R-R = $S(CH_2)_2S$
10b: R-R = SCH_2S
10c: R = R = CO_2Me

We next examined the reaction of **8** with 1,2-ethanedithiol and 2-mercaptoethanol in the presence of BF_3·OEt_2 to prepare the dithiolane- and oxathiolane-attached ketones **9b**,**c** because we anticipated that the BF_3-promoted isomerization of **8** to **9a** followed by the dithio- and oxathio-acetalization of **9a** with the aid of BF_3·OEt_2 could progress. The results are summarized in Table 1. As expected, **8** reacted with 1,2-ethanedithiol in the presence of 10 equiv of BF_3·OEt_2 to give **9b** in 95% yield (entry 1). In contrast, reaction with 2-mercaptoethanol under the same conditions afforded **9c** in only 10% yield, and a mixture of **9a** and **8** (4.4:1) was isolated in 18% yield (entry 2). In addition, even by the use of only 2 equiv of BF_3·OEt_2 in the reaction of **8** with 1,2-ethanedithiol for a prolonged reaction time, **9b** was obtained in 82% yield along with a 13% recovery of **8** (entry 3), but reaction of **8** with 2-mercaptoethanol under the same conditions could not give **9c** (80% recovery of **8**, entry 4). In entries 3 and 4, the isomerization of **8** most probably did not take place because **9a** was not detected. Accordingly, it is unlikely that the conversion of **8** into **9b** necessarily proceeds via **9a**.[11]

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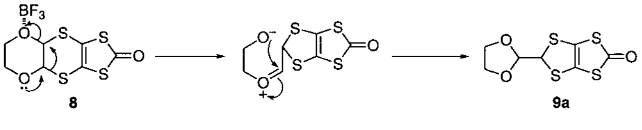
[6] (a) Nishikawa, H.; Ishikawa, H.; Sato, T.; Kodama, T.; Ikemoto, I.; Kikuchi, K.; Tanaka, S.; Anzai, H.; Yamada, J. *J. Mater. Chem.* **1998**, *8*, 1321−1322. (b) Yamada, J.; Tanaka, S.; Anzai, H.; Sato, T.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *J. Mater. Chem.* **1997**, *7*, 1311−1312.

[7] The other metallic DOET salts have been reported, see: Kotov, A. I.; Buravov, L. I.; Konovalikhin, S. V.; Dyachenko, O. A.; Yagubskii, E. B.; Malfant, I.; Courcet, T.; Cassoux, P.; Akimoto, J.; Honda, K.; Mizuno, M. *Synth. Met.* **1999**, *102*, 1630−1631.

[8] Yamada, J.; Hamasaki, M.; Jinih, O.; Tanaka, S.; Hagiya, K.; Anzai, H. *Tetrahedron Lett.* **1997**, *38*, 3439−3442.

[9] For a preliminary communication and conference proceedings, see: (a) Yamada, J.; Oka, R.; Anzai, H.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *Tetrahedron Lett.* **1998**, *39*, 7709−7712. (b) Yamada, J.; Oka, R.; Anzai, H.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *Synth. Met.* **1999**, *102*, 1701−1702.

[10] A postulated mechanism for the isomerization of **8** to **9a** is shown below.



On the other hand, it is possible that **9c** is formed via **9a** and the oxathioacetalization of **9a** is fairly slow. On the basis of this working hypothesis, our attempt to improve the yield of **9c** was successful with the use of **9a** instead of **8** under the same conditions as shown in entry 2 (16% recovery of **9a**, entry 5). Furthermore, varying the reaction solvent from $CHCl_3$ to CH_2Cl_2 resulted in enhanced yield of up to 40% (10% recovery of **9a**, entry 6).[12]

Synthesis of DO-MET (**4a**), DO-MMT (**4b**), **4d**, DT-MET (**5a**), DT-MMT (**5b**), **5d**, and OT-MET (**6**) was attained by cross-coupling of the resulting ketones **9a-c** with 2 equiv of thiones **10a**−**c** using $(MeO)_3P$ as a phosphite reagent in toluene at 110 °C for 2 h in the following yields: DO-MET (**4a**), 80%; DO-MMT (**4b**), 58%; **4d**, 96%; DT-MET (**5a**), 94%; DT-MMT (**5b**), 66%; **5d**, 72%; OT-MET (**6**), 83%. It is noted that, in the $(MeO)_3P$-mediated reaction of **9b** with **10a**, the use of benzene in place of toluene as a solvent gave BEDT-TTF as a self-coupling product in 92% yield along with the recovered **9b** (80%) and caused essentially no yield of DT-MET (**5a**). Demethoxycarbonylation of **4d** and **5d** was performed by heating with $LiBr{\cdot}H_2O$ (10 equiv) in HMPA at 90 °C for 1 h and then at 130 °C for 1 h, furnishing DO-MDT (**4c**) and DT-MDT (**5c**) in 52% and 63% yields, respectively.

Electrochemical Properties. We have already reported the redox behavior of DO-MET (**4a**) and DO-MDT (**4c**).[4c,8] For comparison with these donors, the redox behavior of DO-MMT (**4b**), DT-MET (**5a**), DT-MMT (**5b**), DT-MDT (**5c**), and OT-MET (**6**) was investigated by cyclic voltammetry under the same conditions. Three pairs of reversible redox waves were observed for DT-MET (**5a**), DT-MMT (**5b**), DT-MDT (**5c**), and OT-MET (**6**), whereas DO-MMT (**4b**) showed three reversible oxidation waves and another irreversible one, whose peak current appeared at the most anodic potential and was smaller than those of the other three oxidation waves. The three reversible oxidation waves of these compounds probably arise from two redox-active 1,3-dithiole rings of the TTF core and the dichalcogenolane-attached 1,3-dithiolane ring fusing onto the TTF molecule.[13] The reason for the appearance of the fourth small oxidation wave (corresponding to E_4) in DO-MMT (**4b**) has not yet been fully elucidated. The oxidation potentials of a series of the dichalcogenolane-linked TTF donors are summarized in Table 2. In three dithiolane-linked TTF donors, the same E_1 value is observed between DT-MET (**5a**) and DT-MMT (**5b**), and DT-MDT (**5c**) showed the lowest E_1 value, presumably because of the absence of the outer alkylenedithio group acting as an electron-withdrawing group. Although a similar tendency can be found in the dioxane- and dithiane-fused TTF donor systems,[4c] this is not the case for the dioxolane-linked TTF donor system. That is, the E_1 value of DO-MMT (**4b**) is lower than that of DO-MET (**4a**) and comparable to that of DO-MDT (**4c**). The E_1, E_2, and E_3 values of OT-MET (**6**), a hybrid of DO-MET (**4a**) and DT-MET (**5a**), are very similar to those of DT-MET (**5a**) rather than to those of DO-MET (**4a**).

Table 2. Oxidation Potentials of the Dichalcogenolane-Linked TTF Donors[a]

compound	E_1	E_2	E_3	E_4	E ($E_2 - E_1$)
DO-MET (**4a**)[b]	0.57	0.84	1.58		0.27
DO-MMT (**4b**)	0.53	0.76	1.38	1.56[c]	0.23
DO-MDT (**4c**)[b]	0.53	0.92			0.39
DT-MET (**5a**)	0.55	0.83	1.63		0.28
DT-MMT (**5b**)	0.55	0.77	1.57		0.22
DT-MDT (**5c**)	0.48	0.80	1.67		0.32
OT-MET (**6**)	0.55	0.83	1.64		0.28

[a] V vs saturated calomel electrode (SCE); 0.1 M $n\text{-}Bu_4NClO_4$ in PhCN; Pt electrode; at room temperature; under nitrogen; scan rate 50 mV s^{-1}. [b] Cited from refs 4c and 8. [c] Irreversible wave.

Molecular Structure of OT-MET (6). An X-ray diffraction analysis of the neutral OT-MET (**6**) was undertaken for comparison with the molecular structures of DO-MET (**4a**)[4c,8] and DT-MET (**5a**).[9] The OT-MET (**6**) molecule crystallized as a 1:1 racemic mixture in the monoclinic space group $P2_1/a$ and is isostructural with the DT-MET (**5a**) molecule (Figure 1). Hence, similarly to the molecular structure of DT-MET (**5a**), the whole molecular structure of OT-MET (**6**) is less bulky than that of DO-MET (**4a**).

Preparation and Electrical Conducting Behavior of the CT Materials. As communicated by us earlier,[8] DO-MET (**4a**) and DO-MDT (**4c**) reacted with TCNQ at room temperature in 1,1,2-trichloroethane (TCE) and CH_3CN, respectively, to give CT complexes. Similarly, TCNQ complexes of DO-MMT (**4b**) and DT-MMT (**5b**) were obtained at room temperature in TCE. Although DT-MET (**5a**), DT-MDT (**5c**), and OT-MET (**6**) form no crystalline CT complex with TCNQ under similar reaction conditions, heating at 80 °C in TCE enabled us to obtain small amounts of their TCNQ complexes. On the other hand, CT complexes of the present dichalcogenolane-linked TTF donors with a stronger acceptor, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$), were all obtainable at room temperature in TCE or CH_3CN. Preparation of the cation-radical salts with various counteranions was examined by the controlled-current electrocrystallization method[14] in TCE, 5% EtOH-TCE, or PhCl.

Table 3 summarizes the electrical conducting behavior of the thus-obtained CT materials. From the DO-MET (**4a**) donor, in addition to its metallic TCNQ complex,[15]

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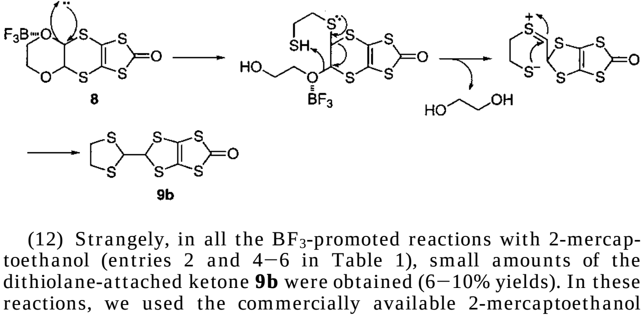
(11) As an alternative speculation for the formation of **9b**, we assume that this reaction proceeds via the cleavage of the *O,S*-acetal of **8** by nucleophilic attack of the sulfur atom of 1,2-ethanedithiol, as shown below.



(12) Strangely, in all the BF_3-promoted reactions with 2-mercaptoethanol (entries 2 and 4−6 in Table 1), small amounts of the dithiolane-attached ketone **9b** were obtained (6−10% yields). In these reactions, we used the commercially available 2-mercaptoethanol containing no 1,2-ethanedithiol, so that the reason for the production of **9b** is, at present, far from clear.

(13) The latter 1,3-dithiolane ring is not always redox-active because the cyclic voltammogram for DO-MDT (**4c**) consists of two pairs of reversible redox waves; see Table 2.

(14) (a) Nishikawa, H.; Sato, T.; Kodama, T.; Ikemoto, I.; Kikuchi, K.; Anzai, H.; Yamada, J. *J. Mater. Chem.* **1999**, *9*, 693−696. (b) Anzai, H.; Delrieu, J. M.; Takasaki, S.; Nakatsuji, S.; Yamada, J. *J. Cryst. Growth* **1995**, *154*, 145−150.

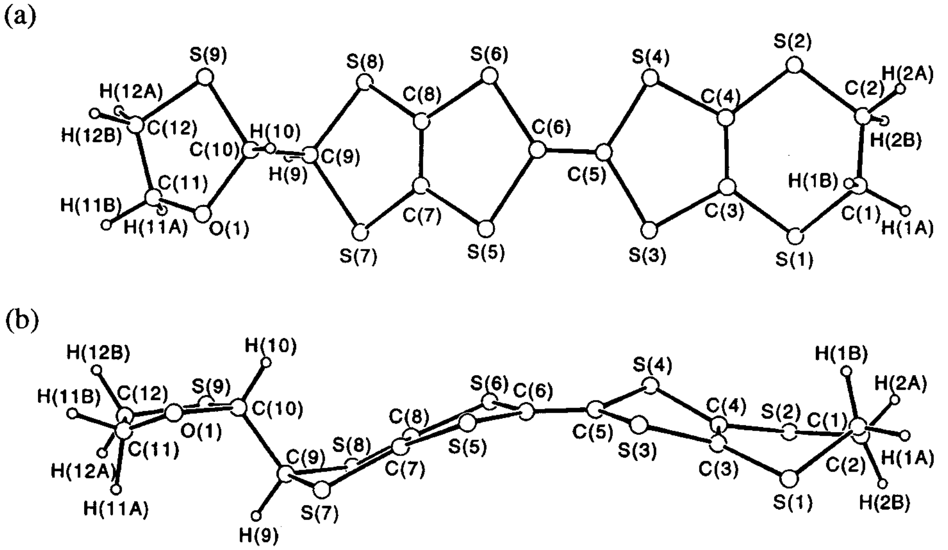


Figure 1. Top (a) and side (b) views of the molecular structure of OT-MET (**6**).

the metallic BF_4 and AsF_6 salts were obtained, and they retained the metallic state essentially down to 2.6 and 2.0 K, respectively, as shown in Figure 2.[16] Suitable single crystals of the TCNQ complex with DO-MMT (**4b**) for four-probe conductivity and thermoelectric power measurements were prepared by recrystallization from TCE with slow concentration. The resistivity of this complex exhibited metallic-like temperature dependence around room temperature and then a resistive minimum near 280 K (Figure 3a), which is almost coincident with the zero-crossing temperature of the thermoelectric power (Figure 3b). The thermoelectric power measurement suggested that the main charge carrier is a hole in the temperature range within the metallic-like region but changes to an electron near 280 K. In contrast to the metallic-like TCNQ complex, the $TCNQF_4$ complex with DO-MMT (**4b**) showed a low room-temperature conductivity. So it seems likely that the donor and $TCNQF_4$ molecules in this complex form alternating mixed stacks due to a complete charge transfer on each donor molecule induced by the strong electron-accepting ability of $TCNQF_4$; the same can be said for the $TCNQF_4$ complex with DO-MET (**4a**). Although single crystals of the DO-MMT (**4b**) salts with the used anions were not obtained by electrocrystallization in TCE, a compressed pellet of the AuI_2 salt exhibited weak metallic behavior down to near 240 K. The dithiolane-linked MET, DT-MET (**5a**), produced the metallic AuI_2, BF_4, PF_6, and AsF_6 salts with metal-to-insulator transitions, which is in contrast to the report that the parent MET donor yields the semiconducting ClO_4, PF_6, and ReO_4 salts.[17] However, unfortunately, we were unable to obtain crystals of these metallic salts with suitable quality for X-ray diffraction analyses, even by varying the solvent used for electrocrystallization from TCE to 5% EtOH-TCE or PhCl. In addition, the racemic OT-MET (**6**) donor gave a metallic BF_4 salt down to near 100 K despite the fact that the measurement was taken on a compressed pellet. Unlike DO-MET (**4a**), DO-MMT (**4b**), DT-MET (**5a**), and OT-MET (**6**) donors that provided the metallic CT materials, the DO-MDT (**4c**), DT-MMT (**5b**), and DT-MDT (**5c**) donors failed to yield any metallic CT materials with the organic and inorganic acceptors we so far examined.

Crystal Structures. From among single crystals of the CT complexes and salts listed in Table 3, the crystal structures of the (DO-MMT)(TCNQ) complex and the $(DO\text{-}MET)_2AsF_6$ salt were determined by X-ray diffraction analyses.

The crystal structure of (DO-MMT)(TCNQ) is depicted in Figure 4. In this complex, the DO-MMT molecules are stacked head-to-tail along the [101] direction to form β-type two-dimensional (2D) sheets, where intermolecular C−H···O hydrogen bonds exist within a pair of donor molecules (Figure 4a) and there are some large intermolecular overlaps, calculated on the basis of the extended Hückel method, between stacks as well as within a stack (Figure 4b). The formation of hydrogen-bonded dimers is understood by considering that the DO-MMT molecule has the relatively acidic methylene group activated by two sulfur atoms. When the overlap integrals of the donor molecules in this complex are compared with those in (BEDT-TTF)(TCNQ), which exhibits electron conduction in the metallic state,[18] three

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(15) Our attempt to obtain appropriate single crystals of this complex for conductivity measurement and X-ray diffraction study by recrystallization from TCE with slow cooling or slow concentration, by the diffusion method in TCE, or by using THF instead of TCE as the solvent used for recrystallization was unsuccessful.

(16) On the resistive behavior of the DO-MET (**4a**) salt with the PF_6^- anion, the sample dependence was observed. We carried out conductivity measurements on four different crystals of this salt. The resistivity of the first crystal specimen decreased in a weak metallic fashion upon cooling from room temperature to near 100 K, after which the resistivity showed a change to semiconductive behavior with some jumps. On the other hand, the other three crystal specimens exhibited semiconducting behavior with very small thermal activation energies [$E_a = 5-8$ meV (>200 K)] upon cooling from room temperature. These observations may be attributed to differences in crystal defects. However, because of the flaky shape of the crystals, further investigation such as X-ray diffraction analysis and conductive anisotropy measurements could not be carried out. In Table 3, the conducting data of one crystal specimen chosen from among three very small gap semiconductors are given as the conductive properties of this salt. The description concerning the conductive behavior of this salt, which is added to ref 8 as a note, is made on the first crystal specimen.

(17) Beno, M. A.; Geiser, U.; Kini, A. M.; Wang, H. H.; Carlson, K. D.; Miller, M. M.; Allen, T. J.; Schlueter, J. A.; Proksch, R. B.; Williams, J. M. *Synth. Met.* **1988**, *27*, A209−A217.

(18) Mori, T.; Inokuchi, H. *Solid State Commun.* **1986**, *59*, 355−359.

Table 3. Conducting Behavior of the CT Materials Based on the Dichalcogenolane-Linked TTF Donors

donor	acceptor	D:A[a]	solvent	σ_{rt}/S cm$^{-1\ b}$
DO-MET(**4a**)	TCNQ	1:1	TCE[c]	12^{d} (metallic)[e]
	$TCNQF_4$	1:1	TCE	$7.1 \times 10^{-4\ d}$ ($E_a = 380$ meV)
	I_3	1:1	TCE	$1.9 \times 10^{-1\ d}$ ($E_a = 170$ meV)
	AuI_2	1:1	TCE	$5.0 \times 10^{-2\ f}$ ($E_a = 77$ meV)
	BF_4	5:2	TCE	22^{f} (metallic ≥ 2.6 K)
	ClO_4	—[g]	TCE	20^{f} ($E_a = 16$ meV)
	PF_6	5:2	5% EtOH-TCE	7.3^{f} ($E_a = 6$ meV)
	AsF_6	2:1[h]	PhCl	9.4^{f} (metallic ≥ 2.0 K)
DO-MMT(**4b**)	TCNQ	1:1	TCE	63^{f} (metallic-like ≈ rt[i])
	$TCNQF_4$	1:1	TCE	$8.7 \times 10^{-5\ d}$ ($E_a = 260$ meV)
	I_3	2:1	TCE	6.7^{d} ($E_a = 23$ meV)
	AuI_2	3:1	TCE	11^{d} (metallic ≥ 240 K)
	BF_4	3:1	TCE	$5.2 \times 10^{-1\ d}$ ($E_a = 31$ meV)
	ClO_4	2:1	TCE	$1.3 \times 10^{-1\ d}$ ($E_a = 33$ meV)
	PF_6	5:2	TCE	$2.4 \times 10^{-2\ d}$ ($E_a = 76$ meV)
	AsF_6	3:1	TCE	$5.2 \times 10^{-2\ d}$ ($E_a = 48$ meV)
DO-MDT(**4c**)	TCNQ	5:4	CH_3CN	9.1^{d} ($E_a = 60$ meV)[j]
	$TCNQF_4$	1:1	CH_3CN	$<10^{-6\ d}$
	I_3	1:1	PhCl	$1.8 \times 10^{-6\ d}$
	AuI_2	2:1	PhCl	$6.3 \times 10^{-1\ f}$ ($E_a = 130$ meV)
	BF_4	1:1	PhCl	$2.2 \times 10^{-4\ f}$ ($E_a = 380$ meV)
	ClO_4	—[g]	PhCl	$<10^{-6\ f}$
	PF_6	5:2	PhCl	$3.8 \times 10^{-2\ d}$ ($E_a = 280$ meV)
	AsF_6	2:1	PhCl	$2.2 \times 10^{-2\ d}$ ($E_a = 260$ meV)
DT-MET(**5a**)	TCNQ	—[k]	TCE	$<10^{-7\ f}$
	$TCNQF_4$	1:1	TCE	$4.0 \times 10^{-6\ d}$
	I_3	3:1	TCE	$3.2 \times 10^{-1\ d}$ ($E_a = 15$ meV)
	AuI_2	5:3	TCE	13^{f} (metallic ≥ 35 K)
	BF_4	2:1	TCE	7.0^{f} (metallic ≥ 110 K)
	ClO_4	—[g]	TCE	$9.5 \times 10^{-2\ d}$ ($E_a = 58$ meV)
	PF_6	3:2	TCE	1.5^{f} (metallic ≥ 55 K)
	AsF_6	3:1	TCE	19^{f} (metallic ≥ 60 K)
DT-MMT(**5b**)	TCNQ	1:1	TCE	$1.1 \times 10^{-2\ d}$ ($E_a = 200$ meV)
	$TCNQF_4$	1:1	TCE	$<10^{-6\ d}$
	I_3	1:1	TCE	$2.1 \times 10^{-2\ d}$ ($E_a = 200$ meV)
	AuI_2	3:1	TCE	$1.4 \times 10^{-1\ f}$ ($E_a = 87$ meV)
	BF_4	3:1	TCE	$2.9 \times 10^{-3\ d}$ ($E_a = 230$ meV)
	ClO_4	—[g]	TCE	$2.1 \times 10^{-2\ f}$ ($E_a = 140$ meV)
	PF_6	3:1	TCE	$2.5 \times 10^{-3\ f}$ ($E_a = 150$ meV)
	AsF_6	3:1	TCE	$4.0 \times 10^{-3\ f}$ ($E_a = 170$ meV)
DT-MDT(**5c**)	TCNQ	—[k]	TCE	$<10^{-7\ f}$
	$TCNQF_4$	1:1	TCE	$<10^{-6\ d}$
	I_3	2:1	TCE	$3.6 \times 10^{-2\ d}$ ($E_a = 110$ meV)
	AuI_2	3:2	TCE	$3.8 \times 10^{-2\ d}$ ($E_a = 130$ meV)
	BF_4	1:1	TCE	$<10^{-7\ f}$
	ClO_4	—[g]	TCE	$6.0 \times 10^{-6\ f}$
	PF_6	1:1	TCE	$< 10^{-6\ f}$
OT-MET(**6**)	TCNQ	—[k]	TCE	$1.2 \times 10^{-1\ f}$ ($E_a = 50$ meV)
	$TCNQF_4$	1:1	TCE	$1.0 \times 10^{-3\ d}$ ($E = 280$ meV)
	I_3	2:1	TCE	8.2^{d} ($E = 8$ meV)
	AuI_2	1:1	TCE	3.1^{d} ($E_a = 25$ meV)
	BF_4	2:1	TCE	7.5^{d}(metallic ≥ 100 K)
	ClO_4	—[g]	TCE	1.6^{d} ($E_a = 37$ meV)
	PF_6	5:2	TCE	$1.8 \times 10^{-1\ d}$ ($E_a = 32$ meV)
	AsF_6	—[k]	TCE	$9.1 \times 10^{-2\ f}$ ($E_a = 66$ meV)

[a] Determined by elemental analysis unless otherwise noted. [b] Room-temperature conductivity measured by a four-probe technique. [c] 1,1,2-Trichloroethane. [d] Measured on a compressed pellet. [e] See ref 8. [f] Measured on a single crystal. [g] Not determined because this salt may explode during analysis. [h] Determined by X-ray diffraction analysis. [i] Room temperature. [j] Cited from ref 8. [k] Not determined due to insufficient amount of sample for elemental analysis.

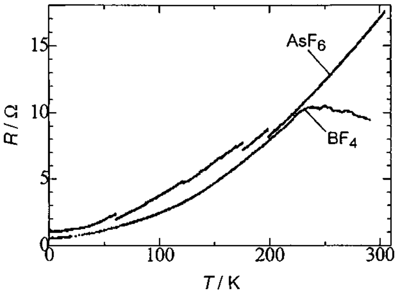

Figure 2. Temperature dependence of resistance for the metallic DO-MET (**4a**) salts.

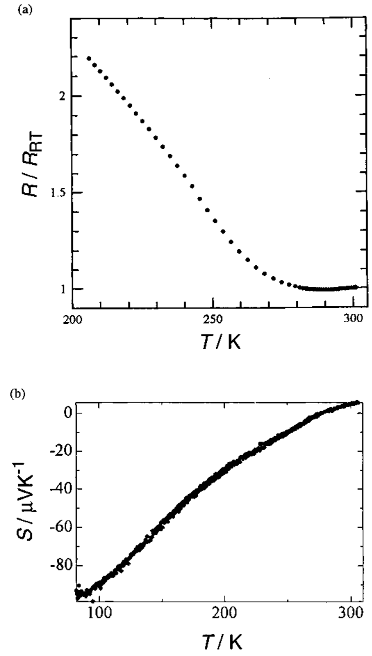

Figure 3. Temperature dependence of relative resistance (a) and thermoelectric power (b) for the TCNQ complex with DO-MMT (**4b**).

larger values (the c, p2, and q1 directions shown in Figure 4b) are estimated, which suggests a 2D conducting sheet with tight donor packing responsible for the above-mentioned hole conduction in the metallic-like state. On the other hand, TCNQ molecules form one-dimensional stacks along the *c* axis with some dimerization (Figure 4a), which appears to bring about the transition to the semiconductive state below near 280 K.

The crystal structure of $(DO\text{-}MET)_2AsF_6$ is shown in Figure 5. In this salt, the DO-MET molecules are stacked head-to-head with a constant interplanar spacing of 3.70 Å along the *a* axis and also to a considerable extent mutually shifted so as to avoid the steric hindrance of the dioxolane ring (Figure 5a). Nevertheless, the intermolecular overlap integral within a stack (the a direction shown in Figure 5b) is appreciable, though smaller than those between stacks (the p1, p2, q1, and q2 directions shown in Figure 5b), thereby leading to the 2D electronic structure responsible for the metallic behavior down to low temperatures. According to the X-ray analysis, the occupation probability of the AsF_6^- anion is nearly 0.5 and the fluorine atoms could not be found down to at least 120 K so that the anions probably rotate freely above 120 K.

Conclusion

As one thrust of our approach to the development of new organic metals, we focused our attention, herein, on the extension of TTF donors by linking a dichalcogenolane ring through the σ-bond. This thrust would be anomalous from the viewpoint of the conventional molecular design for π-electron donors leading to organic metals. However, in fact, several of the present TTF donors produced the metallic CT materials, some of which maintained the metallic state down to low temperatures. We also demonstrated the possibility that,

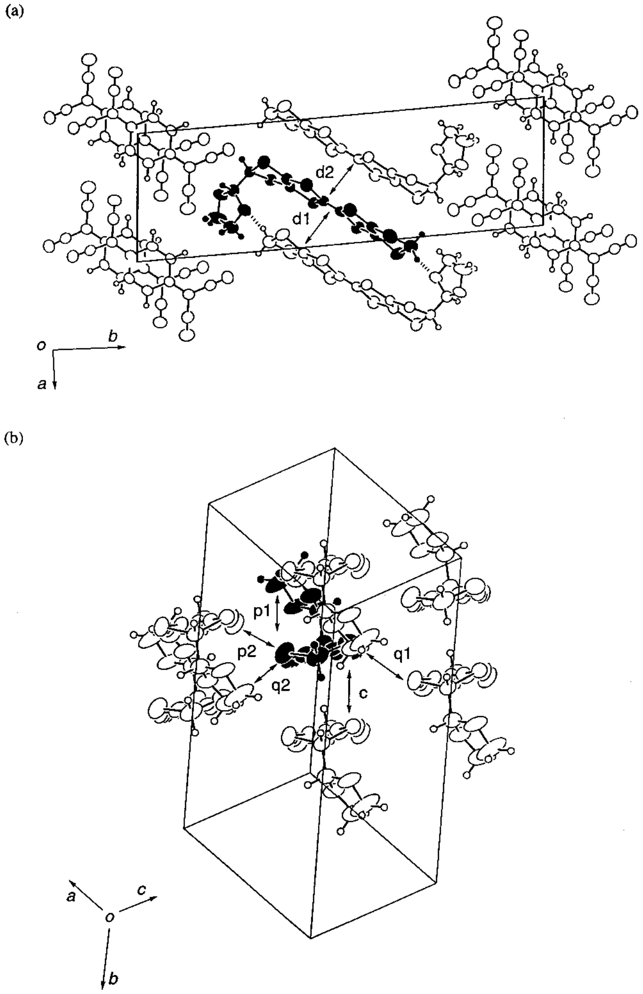

Figure 4. Crystal structure of (DO-MMT)(TCNQ). (a) Intermolecular hydrogen bonds [3.251(6) Å] are indicated by dotted lines. Intermolecular face-to-face distances of the DO-MMT column are 3.67 (d1) and 3.65 (d2) Å and those of the TCNQ column are 3.34 and 3.26 Å. (b) Within the donor molecular layer, intermolecular overlap integrals ($\times 10^{-3}$) c, p1, p2, q1, and q2 are 10.4, 20.3, 12.6, 20.4, and −1.95, respectively.

even if a sterically bulky appendage such as the dioxolane ring in axial-like position, which could hinder the face-to-face interaction, exists on the donor molecule, donor packing with 2D character is realized by an unexpected mode. Another possibility is that the hydrogen-bonded interaction arising from the linked oxygen-containing heterocycle plays an active role in controlling the crystal structures. Further pursuit of these possibilities is the subject of continued interest in our laboratories, which is anticipated to lead to the development of molecular-based organic metals with more exciting donor packing motifs and solid-state properties.

Experimental Section

General and Material. All reactions were carried out in a dry reaction vessel under nitrogen. Melting points were determined in open capillaries and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded at 400 and 100 MHz, respectively, and their chemical shifts are expressed in parts per million (δ) relative to $CHCl_3$ (δ 7.24) for ^{1}H NMR and the center peak of $CDCl_3$ (δ 77.0) for ^{13}C NMR. Cyclic voltammetry measurements were carried out under the same conditions as described in the earlier report.[4c] Electrical conductivity was measured by the four-probe technique using gold wire contacted to the surface of a compressed pellet or a single crystal with gold, silver, or carbon paste. Thermoelectric power measurement and calculation of the overlap integrals were performed according to the corresponding methods described in our earlier report.[14a] All solvents were reagent grade and distilled prior to use, except CS_2 that was used as received. Boron trifluoride diethyl etherate was fractionally distilled and stored before use. Compound **10b** was prepared by our reported method.[4c] Trimethyl phosphite was distilled from sodium and stored before use. TCNQ was purified by recrystallization from CH_3CN, whereas $TCNQF_4$ was used as received. Tetra-*n*-butylammonium tetrafluoroborate, perchlorate, and hexafluorophosphate were used as received, whereas tetra-*n*-butylammonium triiodide, diiodoaurate, and hexafluoroarsenate were prepared by the standard procedures.

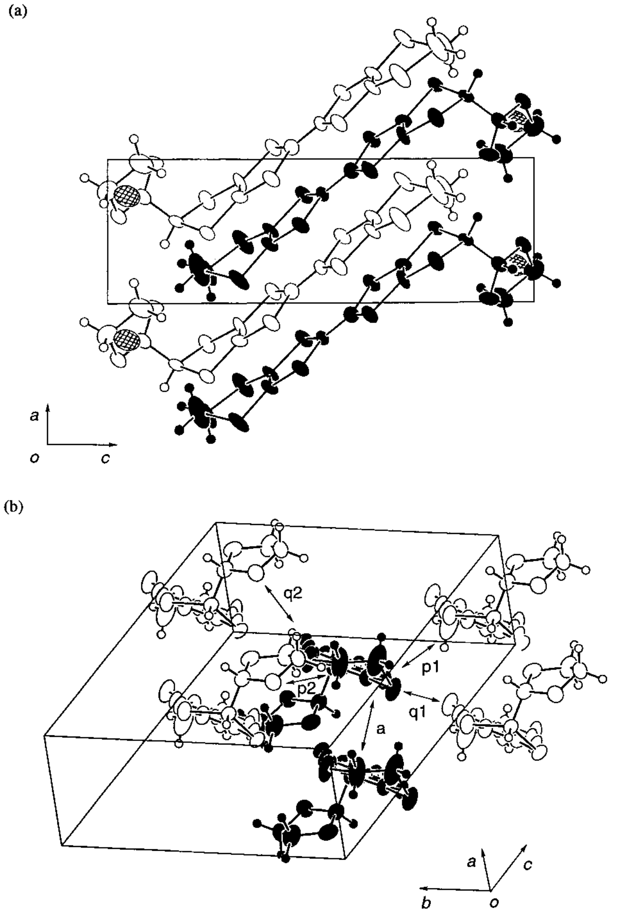

Figure 5. Crystal structure of $(DO\text{-}MET)_2AsF_6$. (a) The front molecules shown by darkly shaded circles stack head-to-head with a constant interplanar spacing of 3.70 Å. The As atoms are indicated by reticulated circles. (b) Intermolecular overlap integrals ($\times 10^{-3}$) a, p1, p2, q1, and q2 are 3.27, 14.2, 9.34, −13.3, and 12.2, respectively.

4,5-[(1,3-Dioxolan-2-yl)methylenedithio]-1,3-dithiol-2-one (9a). To a solution of the dioxane-fused ketone **8** (533 mg, 2.0 mmol) in $CHCl_3$ (20 mL) was added 2.5 mL (20 mmol) of $BF_3{\cdot}OEt_2$ at room temperature. After the reaction mixture was stirred for 1 day, aqueous $NaHCO_3$ was added, and the resulting suspension was filtered through a Celite pad, the Celite then being washed with $CHCl_3$. The aqueous layer was extracted with several portions of $CHCl_3$, and the extracts were combined, dried over $MgSO_4$, and then concentrated under reduced pressure. The residue was chromatographed on silica gel using CH_2Cl_2 as an eluent to give 424 mg (1.6 mmol) of a 46:1 mixture of **9a** and **8** (80% yield). Purification of **9a** was carried out by recrystallization from $CHCl_3$−EtOH: pale brown powder; mp 70 °C dec; ^{1}H NMR ($CDCl_3$) δ 3.93−4.09 (m, 4 H), 4.98 (d, $J = 5.4$ Hz, 1 H), 5.14 (d, $J = 5.4$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 57.7, 66.2, 104.0, 111.6, 192.7; MS (EI), *m*/*z* (% relative intensity) 268 ($M^+ + 2$, 7), 266 (M^+, 32), 73 (100); HRMS (EI) calcd for $C_7H_6O_3S_4$ (M^+) 265.9200, measured 265.9207. Anal. Calcd for $C_7H_6O_3S_4$: C, 31.56; H, 2.27. Found: C, 31.32; H, 2.19.

4,5-[(1,3-Dithiolan-2-yl)methylenedithio]-1,3-dithiol-2-one (9b). Entry 1 in Table 1 is representative. To a solution of **8** (533 mg, 2.0 mmol) in $CHCl_3$ (20 mL) was added 0.20 mL (2.4 mmol) of 1,2-ethanedithiol at room temperature, and then 2.5 mL (20 mmol) of $BF_3{\cdot}OEt_2$ was added. After the solution was stirred continuously for 2 days, the same workup and purification as described above, except for using *n*-hexane−CH_2Cl_2 as an eluent for silica gel column chromatography, gave 577 mg (1.9 mmol) of **9b** (95% yield): pale yellow powder; mp 140 °C from CH_2Cl_2−EtOH; ^1H NMR ($CDCl_3$) δ 3.18−3.28 (m, 4 H), 4.77 (d, $J = 9.8$ Hz, 1 H), 4.84 (d, $J = 9.8$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.4, 60.2, 64.2, 110.4, 192.6; MS (EI), *m*/*z* (% relative intensity) 300 ($M^+ + 2$, 7), 298 (M^+, 26), 105 (100); HRMS (EI) calcd for $C_7H_6OS_6$ (M^+) 297.8743, measured 297.8743. Anal. Calcd for $C_7H_6OS_6$: C, 28.16; H, 2.03. Found: C, 27.80; H, 2.00.

4,5-[(1,3-Oxathiolan-2-yl)methylenedithio]-1,3-dithiol-2-one (9c). Entry 6 in Table 1 is representative. To a solution of the dioxolane-added ketone **9a** (266 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) were successively added 0.08 mL (1.2 mmol) of 2-mercaptoethanol and 1.3 mL (10 mmol) of $BF_3{\cdot}OEt_2$ at room temperature. After the solution was stirred for 2 days, the same workup and purification as described above, except for using CS_2−CH_2Cl_2 as an eluent for silica gel column chromatography, gave 113 mg (0.40 mmol) of **9c** (40% yield): grayish-brown powder; mp 114 °C dec from CH_2Cl_2−EtOH; ^1H NMR ($CDCl_3$) δ 2.99−3.08 (m, 2 H), 4.02−4.08 (m, 1 H), 4.21−4.26 (m, 1 H), 5.01 (d, $J = 7.8$ Hz, 1 H), 5.40 (d, $J = 7.8$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.0, 60.5, 72.5, 88.8, 110.8, 111.6, 192.5; MS (EI), *m*/*z* (% relative intensity) 284 ($M^+ + 2$, 9), 282 (M^+, 34), 89 (100); HRMS (EI) calcd for $C_7H_6O_2S_5$ (M^+) 281.8971, measured 281.8992. Anal. Calcd for $C_7H_6O_2S_5$: C, 29.76; H, 2.14. Found: C, 29.82; H, 2.17.

(1,3-Dioxolan-2-yl)methylenedithio(ethylenedithio)-tetrathiafulvalene (DO-MET, 4a). In a 50-mL flask were placed 266 mg (1.0 mmol) of ketone **9a**, 449 mg (2.0 mmol) of thione **10a**, 10 mL of toluene, and 10 mL of $(MeO)_3P$. After the mixture was heated over an oil bath at 110 °C and kept at that temperature for 2 h with stirring, water was added and the aqueous layer was extracted with several portions of CS_2. The combined extracts were dried over $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography on silica gel using CS_2 and CS_2−CH_2Cl_2 as eluents to give 356 mg (0.80 mmol) of **4a** (80% yield), whose ^1H NMR spectrum was identical to that of the authentic sample reported in ref 4c.

(1,3-Dioxolan-2-yl)methylenedithio(methylenedithio)-tetrathiafulvalene (DO-MMT, 4b). This compound was synthesized from **9a** and **10b** according to the procedure described above: reddish-orange needles; mp 170 °C dec from CS_2; ^1H NMR ($CDCl_3$−CS_2) δ 3.94−4.05 (m, 4 H), 4.88 (d, $J = 9.8$ Hz, 1 H), 4.99 (d, $J = 9.8$ Hz, 1 H), 5.07 (d, $J = 5.4$ Hz, 1 H), 5.19 (d, $J = 5.4$ Hz, 1 H); MS (EI), *m*/*z* (% relative intensity) 430 ($M^+ + 2$, 37), 428 (M^+, 100), 355 (25), 73 (60); HRMS (EI) calcd for $C_{11}H_8O_2S_8$ (M^+) 427.8290, measured 427.8309. Anal. Calcd for $C_{11}H_8O_2S_8$: C, 30.82; H, 1.88. Found: C, 30.57; H, 1.90.

[(1,3-Dioxolan-2-yl)methylenedithio]bis(methoxy-carbonyl)tetrathiafulvalene (4d). After a mixture of ketone **9a** (133 mg, 0.50 mmol) and thione **10c** (250 mg, 1.0 mmol) in $(MeO)_3P$ (5 mL)/toluene (5 mL) was heated at 110 °C for 2 h, the reaction mixture was concentrated under reduced pressure and chromatographed on silica gel using CS_2−CH_2Cl_2 and CH_2Cl_2 as eluents to give 227 mg (0.48 mmol) of **4d** (96% yield): dark-brown needles; mp 120 °C from CS_2; ^1H NMR ($CDCl_3$) δ 3.82 (s, 6 H), 3.93−4.07 (m, 4 H), 5.07 (d, $J = 5.4$ Hz, 1 H), 5.20 (d, $J = 5.4$ Hz); MS (EI), *m*/*z* (% relative intensity) 470 ($M^+ + 2$, 28), 468 (M^+, 93), 395 (34), 262 (23), 73 (100); HRMS (EI) calcd for $C_{14}H_{12}O_6S_6$ (M^+) 467.8958, measured 467.8944. Anal. Calcd for $C_{14}H_{12}O_6S_6$: C, 35.88; H, 2.58. Found: C, 35.72; H, 2.45.

(1,3-Dithiolan-2-yl)methylenedithio(ethylenedithio)-tetrathiafulvalene (DT-MET, 5a). After a mixture of ketone **9b** (149 mg, 0.50 mmol) and thione **10a** (224 mg, 1.0 mmol) in $(MeO)_3P$ (5 mL)/toluene (5 mL) was heated at 110 °C for 2 h, the reaction mixture was cooled to 0 °C and diluted with *n*-hexane. The resulting precipitate was filtered off, washed with *n*-hexane, and chromatographed on silica gel using CS_2 as an eluent to give 223 mg (0.47 mmol) of **5a** (94% yield): orange plate; mp 168 °C dec from CS_2; ^1H NMR ($CDCl_3$−CS_2) δ 3.15−3.34 (m, 8 H), 4.85 (d, $J = 9.8$ Hz, 1 H), 4.88 (d, $J = 9.8$ Hz, 1 H); MS (EI), *m*/*z* (% relative intensity) 476 ($M^+ + 2$, 11), 474 (M^+, 22), 369 (20), 105 (40), 76 (100); HRMS (EI) calcd for $C_{12}H_{10}S_{10}$ (M^+) 473.7990, measured 473.8007. Anal. Calcd for $C_{12}H_{10}S_{10}$: C, 30.35; H, 2.12. Found: C, 30.16; H, 2.16.

(1,3-Dithiolan-2-yl)methylenedithio(methylenedithio)-tetrathiafulvalene (DT-MMT, 5b). This compound was synthesized from **9b** and **10b** according to the procedure described above, except for using CS_2 and CS_2−CH_2Cl_2 as eluents for silica gel column chromatography: brownish-orange powder; mp 175 °C dec from CS_2; ^1H NMR ($CDCl_3$−CS_2) δ 3.16−3.26 (m, 4 H), 4.84 (d, $J = 9.8$ Hz, 1 H), 4.87 (d, $J = 9.8$ Hz, 1 H), 4.88 (d, $J = 9.8$ Hz, 1 H), 5.01 (d, $J = 9.8$ Hz, 1 H); MS (EI), *m*/*z* (% relative intensity) 462 ($M^+ + 2$, 2.5), 460 (M^+, 5.5), 355 (6.8), 105 (39), 76 (100); HRMS (EI) calcd for $C_{11}H_8S_{10}$ (M^+) 459.7833, measured 459.7821. Anal. Calcd for $C_{11}H_8S_{10}$: C, 28.67; H, 1.75. Found: C, 28.74; H, 1.66.

[(1,3-Dithiolan-2-yl)methylidynedithio]bis(methoxy-carbonyl)tetrathiafulvalene (5d). This compound was prepared from **9b** and **10c** by the procedure used for the synthesis of **5b**: blackish-brown needles; mp 173 °C from CS_2; ^1H NMR ($CDCl_3$−CS_2) δ 3.15−3.26 (m, 4 H), 3.83 (s, 6 H), 4.85 (d, $J = 9.8$ Hz, 1 H), 4.90 (d, $J = 9.8$ Hz, 1 H); MS (EI), *m*/*z* (% relative intensity) 502 ($M^+ + 2$, 22), 500 (M^+, 59), 395 (100), 262 (32), 105 (19); HRMS (EI) calcd for $C_{14}H_{12}O_4S_8$ (M^+) 499.8501, measured 499.8503. Anal. Calcd for $C_{14}H_{12}O_4S_8$: C, 33.57; H, 2.42. Found: C, 33.35; H, 2.28.

(1,3-Oxathiolan-2-yl)methylidynedithio(ethylenedithio)-tetrathiafulvalene (OT-MET, 6). This compound was synthesized from **9c** and **10a** according to the procedure used for the synthesis of **4a**: orange plate; mp 153−155 °C dec from CS_2; ^1H NMR ($CDCl_3$−CS_2) δ 2.98−3.03 (m, 2 H), 3.21−3.34 (m, 4 H), 4.02−4.08 (m, 1H), 4.18−4.23 (m, 1 H), 5.07 (d, $J = 8.8$ Hz, 1 H), 5.48 (d, $J = 8.8$ Hz, 1 H); MS (EI), *m*/*z* (% relative intensity) 460 ($M^+ + 2$, 45), 458 (M^+, 100), 369 (22), 89 (56); HRMS (EI) calcd for $C_{12}H_{10}OS_9$ (M^+) 457.8218, measured 457.8246. Anal. Calcd for $C_{12}H_{10}OS_9$: C, 31.41; H, 2.20. Found: C, 31.16; H, 2.11.

General Procedure for Demethoxycarbonylation. A typical procedure is described for the synthesis of DO-MDT (**4c**). In a 30-mL flask were placed 217 mg (0.46 mmol) of **4d** and 4.6 mL of HMPA, and stirring in vacuo was continued for 1 h to remove volatile amines dissolved in HMPA. After 482 mg (4.6 mmol) of $LiBr{\cdot}H_2O$ was added to that flask, the mixture was heated over an oil bath at 90 °C for 1 h and then at 130 °C for 1 h. The reaction mixture was cooled to room temperature and purified by column chromatography on silica gel using CS_2−CH_2Cl_2 as an eluent, giving 84 mg (0.24 mmol) of **4c** (52% yield), whose ^1H NMR spectrum was identical to that of the authentic sample reported in ref 4c.

(1,3-Dithiolan-2-yl)methylenedithiotetrathiafulvalene (DT-MDT, 5c). Pale orange needles; mp 158−160 °C dec from $CHCl_3$-EtOH; ^1H NMR ($CDCl_3$−CS_2) δ 3.15−3.25 (m, 4 H), 4.87 (dd, $J = 10.3$, 10.3 Hz, 2 H), 6.32 (s, 2 H); MS (EI), *m*/*z* (% relative intensity) 386 ($M^+ + 2$, 40), 384 (M^+, 100), 279 (33), 105 (5); HRMS (EI) calcd for $C_{10}H_8S_8$ (M^+) 383.8392, measured 383.8393. Anal. Calcd for $C_{10}H_8S_8$: C, 31.22; H, 2.10. Found: C, 31.13; H, 2.02.

General Procedure for Preparation of TCNQ and $TCNQF_4$ Complexes. All reactions were carried out on a 0.1- or 0.05-mmol scale. After 1 equiv of TCNQ or $TCNQF_4$ was added to a solution of the donor dissolved in a minimum amount of TCE or CH_3CN, the mixture was stirred at room temperature overnight and concentrated under reduced pressure. When no crystalline CT complex was obtained by this procedure (in the cases of the reaction of **5a**, **5c**, or **6** with

Table 4. Selected Crystallographic Data for 6, (4b)(TCNQ), and (4a)$_2$AsF$_6$

	6	(**4b**)(TCNQ)	(**4a**)$_2$AsF$_6$
formula	$C_{12}H_{10}OS_9$	$C_{23}H_{12}N_4O_2S_8$	$C_{24}H_{20}O_4S_{16}AsF_6$
formula wt	458.75	632.85	1074.50
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$
crystal color	orange	black	black
crystal size (mm)	0.4 × 0.3 × 0.05	0.6 × 0.5 × 0.1	0.3 × 0.25 × 0.01
a (Å)	18.59(1)	8.0813(4)	5.086(2)
b (Å)	9.663(3)	24.418(3)	11.500(3)
c (Å)	10.159(3)	6.707(2)	15.080(5)
α (deg)		90.35(2)	99.01(2)
β (deg)	104.79(4)	105.77(1)	90.16(3)
γ (deg)		95.495(8)	91.09(2)
V (Å^3)	1765(1)	1267.2(4)	871.0(5)
temp (K)	295	295	298
Z	4	2	1
D_c (g cm^{-3})	1.73	1.66	2.05
μ (mm^{-1})	1.13	0.737	1.02
no. of reflections	5712	7971	5791
no. of unique data points	5693	7392	4113
obsd data	1427 [$I > 3\sigma(I)$]	3449 [$I > 3\sigma(I)$]	1962 [$I > 3\sigma(I)$]
R, R_w	0.104, 0.130	0.049, 0.042	0.074, 0.085
GOF	2.85	2.68	2.56

TCNQ), the same amount of the solvent as that used for the reaction was again added and then the mixture was heated at 80 °C for an appropriate time (2 h for the reaction of **5a** or **5c** with TCNQ; 4 h for the reaction of **6** with TCNQ) and concentrated in vacuo. The residue was recrystallized from the solvent used for the reaction with slow cooling or slow concentration, except the TCNQF$_4$ complexes of **5a** and **5c**, which were washed well with CS$_2$ due to their insufficient solubilities in hot TCE.

General Procedure for Electrocrystallization. According to the controlled-current electrocrystallization technique,[14] the cation-radical salt was prepared from the corresponding donor (0.08 mmol) and tetra-*n*-butylammonium salt (0.32 mmol) in the organic solvent (16 mL) at 20 °C under nitrogen for 35 days. In all cases, the current was controlled through a personal computer.

X-ray Structure Determination. The data of X-ray structures were collected on an Enraf-Nonius CAD-4 [for **6** and (**4b**)(TCNQ)] and a MacScience MXC18 four-circle [for (**4a**)$_2$AsF$_6$] diffractometers equipped with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation using the $\omega-\theta$ scan technique to a maximun 2θ of 60° at room temperature (295 or 298 K). The data of (**4a**)$_2$AsF$_6$ were corrected using empirical (ψ scans) absorption corrections. All structures were solved by the direct method. The structures of **6** and (**4b**)(TCNQ) were refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms). The structure of (**4a**)$_2$AsF$_6$ was refined by full-matrix least-squares analysis (anisotropic for C, O, S, and As atoms and isotropic for H atoms), and the refinement was carried out by fixing the occupancy of As atom to 0.5 from the population analysis of the As atom (the converged value being 0.56). The fluorine atoms could not be found because there was no peak around the As atom in the difference Fourier map after the refinement. No diffuse line and no satellite peak were observed from room temperature to at least 120 K. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation [for **6** and (**4b**)(TCNQ)] and the CRYSTAN program [MacScience, for (**4a**)$_2$AsF$_6$]. Crystallographic data are summarized in Table 4.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (10640565) from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: Figures for the temperature dependence of resistance of the metallic **4b**-, **5a**-, and **6**-based salts and combustion analytical data for the CT materials listed in Table 3 (PDF). Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **6**, (**4b**) (TCNQ), and (**4a**)$_2$AsF$_6$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM000842X