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New Tetrathiafulvalene Donors with Extended Peripheral Substituents by Addition of Heterocycles: Synthesis, Properties, and Molecular Structures

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Syntheses of the bis(heterocycle)-fused bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) derivatives **7** and **8**, the heterocycle-fused BEDT-TTF, methylenedithio(ethylenedithio)tetrathiafulvalene (MET), and ethylenedithiotetrathiafulvalene derivatives **9**−**11**, and the 1,3-dioxolane derivative of MET **12a** and its analogues **12b**−**d** are described. The heterocycle-fused ketones **17** and **19** with cis ring fusions could be prepared by the BF_3-promoted reaction of tin dithiolate **13** with dihaloheterocycles **15** and **16** in good yields, respectively, and served as key intermediates for the $(RO)_3P$- and/or Me_3Al-promoted coupling syntheses of these new tetrathiafulvalene donors **7**−**12**. Further, the electrochemical properties of new donors **8**−**12** by the use of cyclic voltammetry and the molecular structures of **9a**, **10a**, **11**, and **12a** by X-ray crystallographic analyses are also reported.

Introduction

Ever since the discovery of the first metallic charge-transfer complex composed of TTF (tetrathiafulvalene, **1**, Figure 1) and TCNQ (tetracyanoquinodimethane),[1] modifications of the TTF skeleton have received considerable attention from synthetic chemists in exploration of new molecular-based organic metals.[2] Among those modifications known to date, the heterocycle-fused TTF donors, such as BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene, **2**], MET [methylenedithio(ethylenedithio)-tetrathiafulvalene, **3**], EDT-TTF (ethylenedithiotetrathiafulvalene, **4**), and MDT-TTF (methylenedithiotetrathiafulvalene, **5**), are very attractive π-electron donors because most of them have produced organic superconductors.[3] In particular, BEDT-TTF (**2**) has yielded the largest number of superconducting salts, and it is now well-known that the additional sulfur atoms accompanied by fusion of a 1,4-dithiane ring onto both sides of the prototype TTF molecule play an important part in the formation of two-dimensional conducting S···S networks in the BEDT-TTF-based superconductors.[4] Therefore, one synthetic method for the construction of new TTF donors leading to conducting salts with enhanced dimensionality of conduction might be the addition of another heterocycle onto the existing one or both outer rings in the known heterocycle-fused TTF derivatives, and to this end, the bis(dioxane)-fused BEDT-TTF derivative [BDDT-TTF (**6**)] has been already synthesized.[5] Further appearance of such a π-electron donor bearing extended sub-

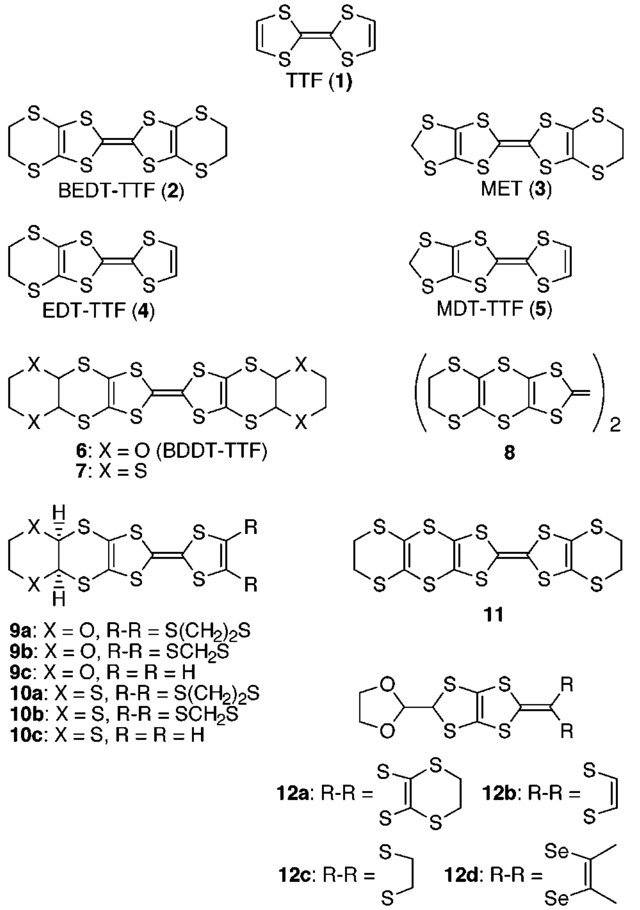

Figure 1.

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stituents by the σ-bond framework on the periphery of the TTF core would be of interest in preparation of new molecular-based conductors.[6]

Meanwhile, we have found that the combination of organotin dichalcogenolates with Me_3Al as a Lewis acid is versatile for the formation of the internal carbon−carbon double bonds of unsymmetrical TTF derivatives, DSDTF (diselenadithiafulvalene) derivatives, and TTF-fused donors.[7] Our next search for the synthetic possibilities presented by the combination of dichalcogenostannanes and a Lewis acid involved the use of the BF_3-promoted reaction of organotin dithiolates with 1,2-dihaloheterocycles in order to develop a synthetic route to new TTF donors with extended periphery by addition of several heterocycles.[8] We now describe a detailed study of the syntheses of new bis(heterocycle)-fused BEDT-TTF derivatives **7** and **8** and the heterocycle-fused BEDT-TTF, MET, and EDT-TTF derivatives **9**−**11**, as well as the electrochemical characterization of **8**−**11** and X-ray crystallographic analyses of **9a**, **10a**, and **11**. Further, in the course of this work, we found that the synthesis of the 1,3-dioxolane derivative of MET **12a** and its analogues **12b**−**d** can be accomplished via the Me_3Al-mediated rearrangement.[9] We also present the synthesis and electrochemical properties of these new donors together with an X-ray structural analysis of **12a**.

Results and Discussion

Preparation of Precursors for Two Coupling Syntheses. Synthetic routes to our final products in this study are based on two coupling reactions, viz., the $(RO)_3P$-promoted coupling reaction between 1,3-dithiole-2-chalcogenones (eq 1, Scheme 1) and the Me_3Al-promoted coupling reaction[7] between organotin dithiolates and esters (eq 2). As shown in Scheme 2, preparation of the chalcogenones and the tin-masked dithiolates as reactants used for these coupling reactions was effected via the BF_3-promoted reactions of tin dithiolates **13** and **14** with dihalides **15** and **16** as key steps. Tin dithiolate **13** was accessible by our reported procedure,[7c] and **14** could be obtained by treatment of $(Bu_4N)_2[Zn(dmit)_2]$ (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) with Cl_2SnBu_2 in THF at room temperature (92% yield). These tin dithiolates **13** and **14** reacted smoothly with commercially available *trans*-2,3-dichloro-1,4-dioxane (**15**) in the presence of $BF_3 \cdot OEt_2$ to give ketone **17** and thione **18** as single stereoisomers in 91% and 63% yields, respectively. An X-ray crystallographic analysis of **17** confirmed the cis stereochemistry for two methine protons (Figure 2). Also, the methine protons of **18** are presumably in the cis position, since reaction of **18** with $Hg(OAc)_2$ in THF−AcOH resulted in the production of the ketone **17** (81% yield). The exclusively cis stereoselectivity in these reactions appears to be due

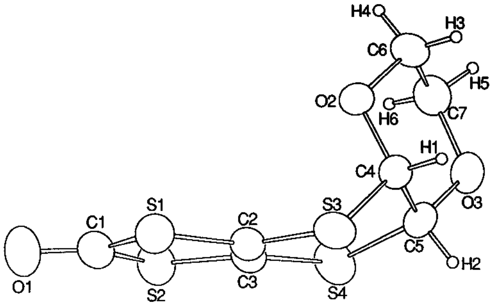
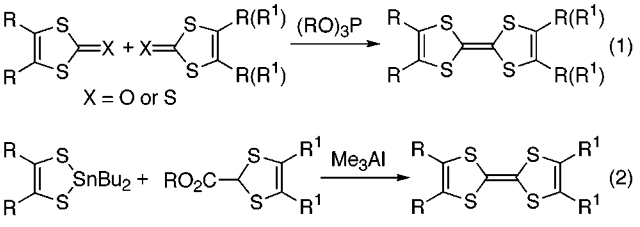
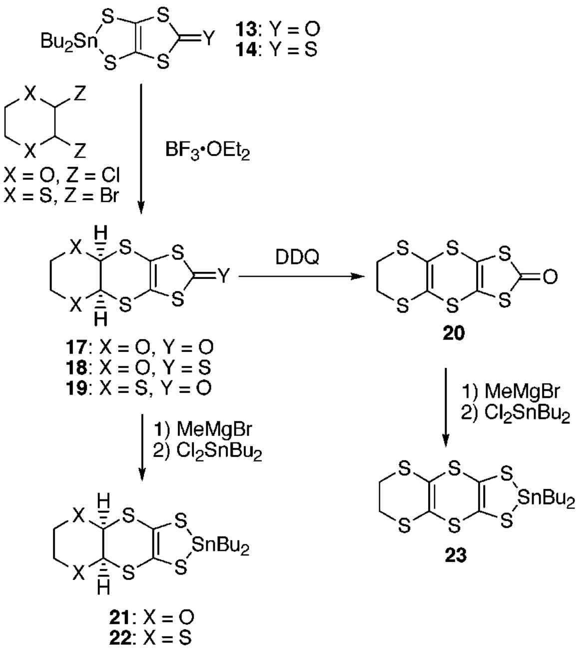


Figure 2. Molecular structure of **17**.

Scheme 1



Scheme 2



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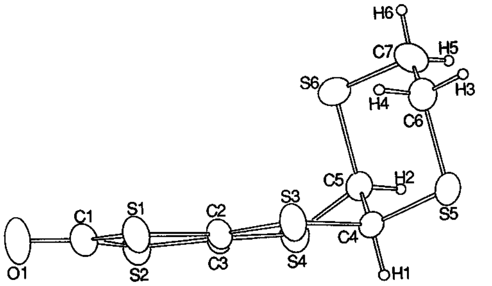
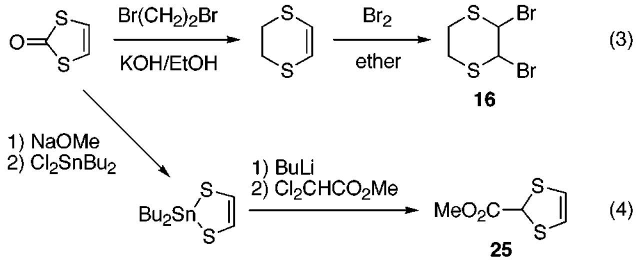


Figure 3. Molecular structure of **19**.

Scheme 3



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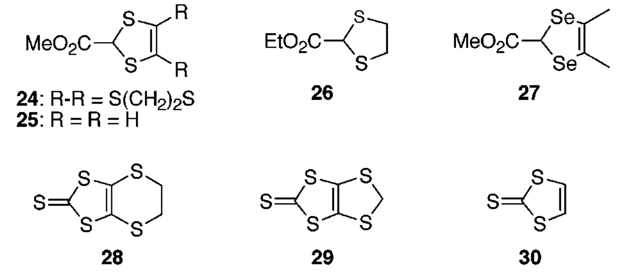
to the participation of an S_N1-like mechanism, since the formation of trans isomers requires the substitution reaction via a strictly S_N2 process in the use of *trans*-dichlorodioxane.[5b] It is thus noteworthy that an alternative synthetic route to the known dioxane-fused ketone **17** and thione **18** was accomplished via the BF_3-promoted reaction.[5] In addition, bromination of 5,6-dihydro-1,4-dithiin[10] derived from 1,3-dithiol-2-one gave the unstable dibromide **16** (eq 3, Scheme 3), which subsequently reacted with tin dithiolate **13** with the aid of $BF_3{\cdot}OEt_2$ to produce the dithiane-fused ketone **19** as a single stereoisomer in 68% yield. An X-ray crystallographic study of **19** revealed that the dithiane ring was condensed by cis fusion (Figure 3), in analogy to the dioxane ring of **17**. Oxidation of the carbon−carbon single bond between two *S*,*S*-acetals of **19** was achieved by treatment with DDQ in boiling toluene for 2 days, furnishing the dihydrodithiin-fused ketone **20** in 60% yield. However, introduction of the carbon−carbon double bond between two *S*,*O*-acetals of **17** was unsuccessful under similar conditions. Grignard reaction of the resulting ketones **17**, **19**, and **20** followed by trapping with Cl_2SnBu_2 gave the tin-masked dithiolates **21**−**23** as precursors for the Me_3Al-promoted coupling synthesis, which were used for the next reaction without purification through silica gel chromatography. As described in the earlier report,[7e] esters **24** and **27** (Figure 4) used for the Me_3Al-promoted coupling reaction could be prepared via a tin/lithium transmetalation reaction. A sequence of analogous reactions afforded ester **25** in 38% yield (eq 4, Scheme 3). Finally, the readily prepared and/or commercially available thiones **28**−**30** were used for the $(RO)_3P$-promoted coupling reaction.

Synthesis of the Dioxane-Fused BEDT-TTF, MET, and EDT-TTF Derivatives. Although we first attempted the synthesis of the dioxane-fused BEDT-TTF derivative **9a** by the Me_3Al-promoted coupling reaction of tin dithiolate **21** with ester **24**, the desired product **9a** could not be obtained, as mentioned later. So, the $(RO)_3P$-promoted coupling reaction of ketone **17** with thiones **28**−**30** was examined to synthesize the dioxane-fused BEDT-TTF, MET, and EDT-TTF derivatives **9a**−**c**. The results are summarized in Table 1. Cross-coupling reaction between **17** and 2 equiv of **28** using $(EtO)_3P$ as a trialkyl phosphite reagent gave the desired product **9a** in 22% yield (entry 1). The cis configuration for the 1,4-dioxane ring of **9a** was confirmed by an X-ray crystallography (vide infra). The same product was obtained in relatively higher yield when the cross-coupling reaction was carried out by the use of $(MeO)_3P$ in place of $(EtO)_3P$ (entry 2). Similarly, the $(MeO)_3P$-promoted coupling reaction with **29** produced **9b** in 17% yield (entry 3). However, **9c** was not obtained by use of the same molar excess of $(MeO)_3P$ as employed for the synthesis of **9a** and **9b** (entry 4). Thus, we used a large excess of $(MeO)_3P$ to obtain **9c** (entry 5).



24: R-R = S(CH2)2S
25: R = R = H
26
27
28
29
30

Figure 4.

Oxidation potentials by cyclic voltammograms (CVs) of the dioxane-fused donors **9a**−**c** are summarized in Table 2. The CVs of **9a** and **9c** showed two pairs of reversible redox waves, whereas that of **9b** consisted of one pair of reversible redox waves and one irreversible oxidation wave. For comparison with BEDT-TTF (**2**) and BDDT-TTF (**6**),[11] the oxidation potentials for these compounds were measured under identical conditions. The E_1 value of the dioxane-fused BEDT-TTF derivative **9a** is higher by 0.04 V than that of **2**, indicating that the appended dioxane ring causes a decrease of the electron-donating ability, whereas this value is equal to that of **6**. While roughly the same ΔE ($E_2 - E_1$) values are observed between **9a** and **6**, the ΔE ($E_2 - E_1$) value of **9a** is slightly larger than that of **2**, implying a slight increase in the on-site Coulombic repulsion involved in the formation of a dicationic species. The E_1 value of the MET derivative **9b** is comparable to that of **9a**, and the EDT-TTF derivative **9c** shows a lower E_1 value than those of **9a** and **9b**.

A single crystal of the BEDT-TTF derivative **9a** suitable for an X-ray crystallographic study was obtained by recrystallization from carbon disulfide. As shown in Figure 5, **9a** has a nonplanar structure, in which the dioxane ring is forced to incline toward the outer ethylene group linking two S atoms. Evidently, the whole molecular structure of **9a** is bulkier than that of BEDT-TTF (**2**), but the dioxane ring added to the BEDT-TTF skeleton results in no significant deformation of the molecular structure of BEDT-TTF itself.[12]

Synthesis of the Bis(dithiane)-Fused BEDT-TTF Derivative. Synthesis of the bis(dithiane)-fused BEDT-

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[10] For an alternative synthesis of this compound, see: Kato, R.; Kobayashi, H.; Kobayashi, A. *Synth. Metals* **1991**, *41−43*, 2093−2096.

[11] Preparation of this compound by the coupling reaction between **17** and **18** was carried out according to ref 5a.

[12] For the molecular structure of BEDT-TTF, see: Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 301−302.

Table 1. Cross-Coupling Reaction of Ketone 17 with Thiones 28−30

entry	thione (equiv)	$(RO)_3P$ (equiv)	solvent	temp[a] (°C)	reaction time (h)	product	yield (%)[b]
1	**28** (2)	$(EtO)_3P$ (23)	benzene	100	4	**9a**	22
2	**28** (2)	$(MeO)_3P$ (23)	benzene	100	3	**9a**	35
3	**29** (2)	$(MeO)_3P$ (23)	benzene	100	3	**9b**	17
4	**30** (2)	$(MeO)_3P$ (23)	benzene	100	3	**9c**	*c*
5	**30** (2)	$(MeO)_3P$ (85)	benzene	100	3	**9c**	13

[a] Oil bath temperature. [b] After column chromatography on silica gel followed by recrystallization. [c] There was no detectable amount of **9c**.

Table 2. Oxidation Potentials[a] of 9a−c, 2, and 6

compd	E_1	E_2	ΔE ($E_2 - E_1$)
9a	0.67	0.92	0.25
9b	0.67	0.87[b]	0.20
9c	0.59	0.86	0.27
BEDT-TTF (**2**)	0.63	0.86	0.23
BDDT-TTF (**6**)	0.67	0.93	0.26

[a] In $PhCN{:}CS_2 = 1{:}1$. [b] Irreversible wave.

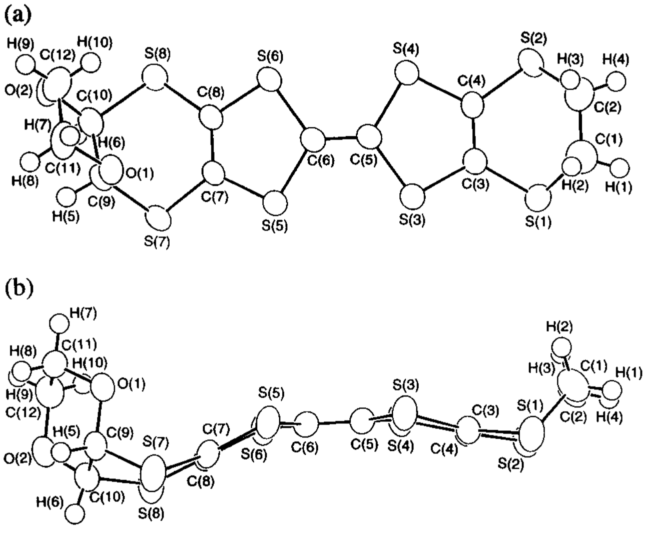

Figure 5. Molecular structure of **9a**: (a) top view, (b) side view.

TTF derivative **7** was carried out by the self-coupling reaction of ketone **19** in neat $(EtO)_3P$ at 120 °C, and the desired product was obtained in 9% yield along with small amounts of the recovered ketone **19**. In the synthesis of BDDT-TTF (**6**) by phosphite-coupling reaction between **17** and **18**, it has been reported that the formation of two diastereomers of **6** can be confirmed by a ^1H NMR spectrum study.[5] On the other hand, the assignment for the two diastereomers of **7** could not be clearly made on the basis of ^1H NMR analysis due to their insolubility in appropriate solvents (e.g., $CDCl_3$, THF-d_8, and $CDCl_3{-}CS_2$) for the analysis; however, it is presumed that the two diastereomers were formed in the course of the self-coupling reaction, since the difference in conformational energy between two diastereomers of **7**, similarly to those of **6**, does not seem to be large enough to enable the exclusive formation of one diastereomer.[6] The insolubility of **7** in most organic solvents also did not allow us to obtain its satisfactory CV data.

Synthesis of the Dithiane-Fused BEDT-TTF, MET, and EDT-TTF Derivatives. Our first synthesis of the dithiane-fused BEDT-TTF derivative **10a** and the EDT-TTF derivative **10c** employed the Me_3Al-promoted reaction of tin dithiolate **22** with esters **24** and **25**. In each case the yield of the desired product was 11%. Thus, we examined cross-coupling reaction of ketone **19** with thiones **28** and **30** to improve the yields of **10a** and **10c**. In addition, a similar reaction using ketone **19** and thione **29** was attempted to obtain the dithiane-fused MET derivative **10b**. The results are summarized in Table 3. For the synthesis of **10a**, the yields were dependent on the molar equivalent of thione **28**, on the phosphite reagent (trimethyl or triethyl phosphite), and on the reaction temperature (entries 1−4). Cross-coupling reaction using 2 equiv of thione **28** and $(EtO)_3P$ as a phosphite reagent with a temperature of 100 °C gave the highest yield (entry 4). Similarly, the use of 2 equiv of thione **29** in place of 1 equiv of **29** could enhance the yield of **10b** (entries 5 and 6). However, in contrast to the cross-coupling synthesis of **10a**, the yields of **10c** from cross-coupling reactions were lower than that obtained from the Me_3Al-promoted reaction, even though $(EtO)_3P$ in place of $(MeO)_3P$ was used (entries 7 and 8).

The CVs of the BEDT-TTF derivative **10a** and the EDT-TTF derivative **10c** showed two pairs of reversible redox waves and one pair of quasi-reversible redox waves: the first two oxidation waves could be defined while the latter was not well-defined, and the CV of the MET derivative **10b** exhibited two pairs of reversible redox waves and one poorly defined oxidation wave. Table 4 summarizes the oxidation potentials of **10a**−**c** together with that of the dioxane-fused BEDT-TTF derivative **9a** measured under the same conditions. The E_1 value of **10a** is lower by 0.04 V than that of **9a**, suggesting that electron-donating ability is enhanced by the replacement of the dioxane ring with the dithiane

Table 3. Cross-Coupling Reaction of Ketone 19 with Thiones 28−30

entry	thione (equiv)	$(RO)_3P$	solvent	temp[a] (°C)	reaction time (h)	product	yield (%)[b]
1	**28** (1)	$(MeO)_3P$	benzene	100	3	**10a**	9
2	**28** (2)	$(MeO)_3P$	benzene	100	3	**10a**	32
3	**28** (2)	$(MeO)_3P$	toluene	130	3	**10a**	21
4	**28** (2)	$(EtO)_3P$	benzene	100	3	**10a**	50
5	**29** (1)	$(EtO)_3P$	benzene	100	3	**10b**	17
6	**29** (2)	$(EtO)_3P$	benzene	100	3	**10b**	26
7	**30** (2)	$(MeO)_3P$	benzene	100	3	**10c**	trace
8	**30** (2)	$(EtO)_3P$	benzene	100	3	**10c**	3

[a] Oil bath temperature. [b] After column chromatography on silica gel followed by recrystallization.

Table 4. Oxidation Potentials[a] of 10a−c and 9a

compd	E_1	E_2	ΔE ($E_2 - E_1$)
10a	0.61	0.91[b]	0.30
10b	0.60	0.92[b]	0.32
10c	0.52	0.85[b]	0.33
9a	0.65	0.94	0.29

[a] In PhCN. [b] One other poorly defined peak exists at a more anodic potential.

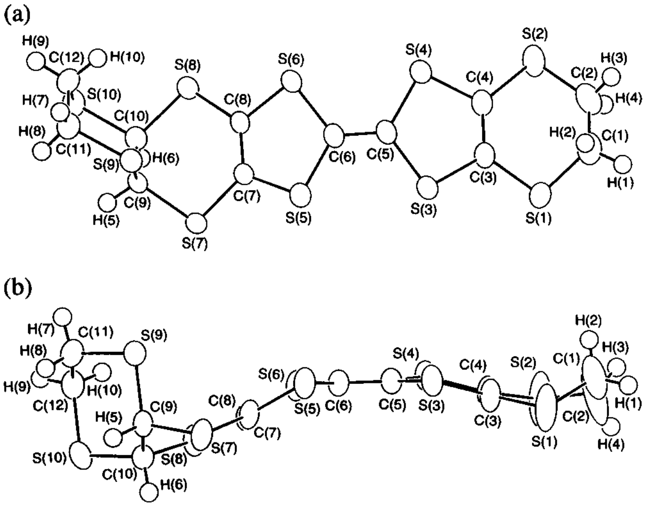

Figure 6. Molecular structure of **10a**: (a) top view, (b) side view.

ring, and the ΔE ($E_2 - E_1$) value of **10a** is comparable to that of **9a**. There is no remarkable difference between the E_1 values of **10a** and **10b** and the E_1 value of **10c** is lower than those of **10a** and **10b**.

A single crystal of the dithiane-fused BEDT-TTF derivative **10a** was obtained by recrystallization from carbon disulfide, and its molecular structure was determined by X-ray crystallography (Figure 6). The molecular structure of **10a** resembles that of its dioxane analogue **9a** (see Figure 5), though the crystallographic data of **10a** differs from those of **9a**.

Synthesis of the Bis(dihydrodithiin)- and Dihydrodithiin-Fused BEDT-TTF Derivatives. The self-coupling reaction using $(EtO)_3P$ was explored with the objective of converting ketone **20** into the bis(dihydrodithiin)-fused BEDT-TTF derivative **8**. The coupling reaction of **20** in neat $(EtO)_3P$ at 120 °C gave **8** in 56% yield. For the synthesis of the dihydrodithiin-fused BEDT-TTF derivative **11**, we employed the Me_3Al-promoted coupling reaction. Reaction of the tin-masked dithiolate **23** with ester **24** in the presence of Me_3Al produced **11** in 37% yield. Because of this moderate yield, no attempt was made to examine the phoshite-coupling synthesis of **11**.

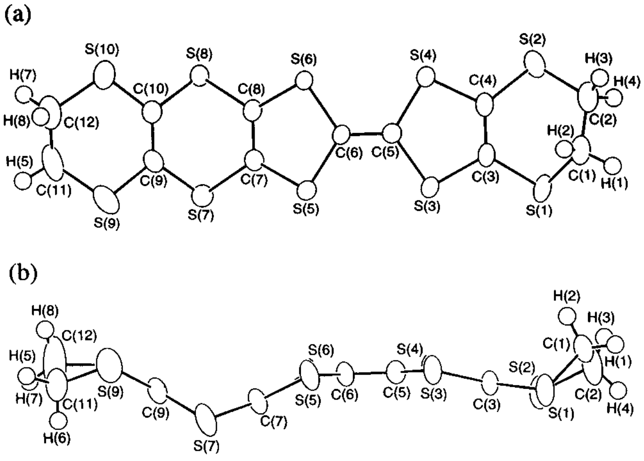

Figure 7. Molecular structure of **11**: (a) top view, (b) side view.

Table 5. Synthesis of 12a−d via Me3Al-Mediated Reaction of Tin Thiolate 21 with Esters 24−27

entry	ester	reaction temp	reaction time	product	yield (%)[a]
1	**24**	−78 °C → rt[b]	4 days	**12a**	3[c]
2	**24**	−78 °C → rt	overnight	**12a**	14[c]
3	**24**	−78 °C → rt	2 days	**12a**	16[c]
4	**25**	−78 °C → rt	2 days	**12b**	14[d]
5	**26**	−78 °C → rt	2 days	**12c**	14[c]
6	**27**	−78 °C → rt	2 days	**12d**	27[c]

[a] Overall yield from ketone **17**. [b] Room temperature. [c] After column chromatography on silica gel followed by recrystallization. [d] After column chromatography on silica gel.

The oxidation potentials of **8** and **11** were measured by cyclic voltammetry under the same conditions as used for the measurement of the dithiane-fused BEDT-TTF **10a** [**8**, $E_1 = +0.68$ V, $E_2 = +0.94$ V; **11**, $E_1 = +0.67$ V, $E_2 = +0.95$ V, $E_3 = +1.52$ V (vs SCE)]. In the CV of **8**, one other poorly defined peak existed at a more anodic potential. The electron-donating abilities of **8** and **11** estimated by their E_1 values are almost equal, whereas the E_1 value of **11** is higher by 0.06 V than that of its dithiane analogue **10a** (+0.61 V), indicating that introduction of the C═C bond between two *S*,*S*-acetals decreases the donating ability. On the other hand, when comparing the ΔE ($E_2 - E_1$) values of **11** (0.28 V) and **10a** (0.30 V), the presence of the additional C═C bond proves to induce a slight reduction in the on-site Coulombic repulsion.

An X-ray crystallographic study of a single crystal of **11** obtained by recrystallization from carbon disulfide revealed that the crystal was solvated with the composition $(\mathbf{11})_2CS_2$. The molecular structure of **11** in this crystal exhibits a nonplanar conformation, in which the molecule is bent around each individual intramolecular S···S axis existing in the five heterocycles and contains four tetrathioethylene medium planes (Figure 7).

Synthesis of the Dioxolane Derivative of MET and Its Analogues. As already mentioned, though an attempt to synthesize the dioxane-fused donor **9a** by the Me_3Al-promoted reaction of tin dithiolate **21** with ester **24** was unsuccessful, this reaction resulted in the production of a new MET derivative with a 1,3-dioxolane ring **12a** on the basis of the Me_3Al-mediated rearrangement of the existing two *S*,*O*-acetals in the two fused six-membered heterocycles to the five-membered cyclic *O*,*O*- and *S*,*S*-acetals. It was noted that, for synthesis of **12a**, the addition order of Me_3Al, tin dithiolate **21**, and ester **24** affected the yield of the product. Initially, to a CH_2Cl_2 solution of **21** was added at −78 °C a hexane solution of Me_3Al, and then a CH_2Cl_2 solution of ester **24** was added (entry 1 in Table 5). Under these operating conditions, clean reaction did not take place, and the yield of **12a** was only 3%. An alternative addition order, (i) ester **24**, (ii) Me_3Al, and then (iii) tin dithiolate **21**, led to an increase in the yield of **12a** (entry 2). However, the length of the reaction time had only a negligible influence on the yield of **12a** (entry 3). By the procedure used to obtain entry 3, reaction of **21** with ester **25** gave the

Table 6. Oxidation Potentials[a] of 12a−d

compd	E_1	E_2	E_3	ΔE ($E_2 - E_1$)
12a	0.57	0.84	1.58	0.27
12b	0.53	0.92		0.39
12c	0.62	1.02		0.40
12d	0.53	0.83	1.58	0.30

[a] In PhCN.

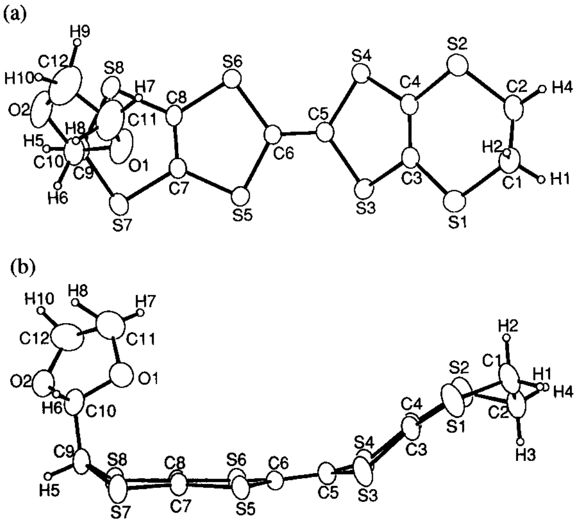

Figure 8. Molecular structure of **12a**: (a) top view, (b) side view.

dioxolane derivative of MDT-TTF **12b** (entry 4), and reaction with ester **26** furnished the derivative of MDHT [methylenedithio(dihydro)tetrathiafulvalene][7d] **12c** (entry 5). In addition, the derivative of DSDTF **12d** could be obtained by reaction with ester **27** in 27% overall yield from ketone **17**.

The CVs data for the dioxolane derivatives **12a**−**d** are summarized in Table 6. The CV of **12b** consisted of two pairs of reversible redox waves, whereas those of **12a** and **12d** showed three pairs of reversible redox waves though the π-electron system of **12a**, or **12d** is the same as that of **12b**. The CV of the derivative of MDHT **12c** exhibited two pairs of reversible redox waves, and the E_1 value of **12c** is higher by 0.09 V than that of **12b**. The E_1 values of **12b** (0.53 V in PhCN and 0.54 V in CH_3CN) are higher than those of MDT-TTF (**5**, 0.47 V in PhCN and 0.49 V in CH_3CN) measured under identical conditions, suggesting that the electron-donating ability is decreased by the existence of a 1,3-dioxane ring.

The molecular structure of **12a** was confirmed by an X-ray crystallographic analysis of its single crystal obtained by recrystallization from carbon disulfide (Figure 8). The dioxolane ring is attached perpendicularly to the MET molecule via a single bond, and the MET framework itself is curved toward the dioxolane ring. Accordingly, the dioxolane ring appended to the MET molecule makes it bulkier than most donors so far prepared.

Conclusion

The BF_3-promoted reaction of tin-masked dithiolates with dihaloheterocycles followed by $(RO)_3P$- or Me_3Al-promoted coupling reaction provides a new TTF family containing a bis-fused heterocycle or a biheterocycle on either or both sides of the TTF core. Although the molecular structures of several compounds belonging to this TTF family are nonplanar and bulky, we have already found that the dioxane-fused BEDT-TTF derivative **9a** produces the metallic radical-cation salts[13] and also that the dioxolane derivative of MET **12a** forms a metallic charge-transfer complex with TCNQ.[9] Therefore, our ongoing work is aimed at further development of organic metals derived from bulky TTF donors, described herein, and clarification of the steric effects of the bulky substituents on the formation of conducting salts.

Experimental Section

General Methods. Melting points were measured in open capillaries and are uncorrected. ^1H NMR spectra and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. ^1H NMR chemical shifts are expressed in parts per million (δ) relative to $CHCl_3$ (δ 7.24) as an internal reference. For ^{13}C NMR chemical shifts, the reference was the center peak of chloroform-*d* (δ 77.0).

The cyclic voltammetric measurement was carried out at room temperature under nitrogen in $PhCN/CS_2$ (v/v = 1/1), PhCN, or CH_3CN containing Bu_4NClO_4 (0.1 M) as a supporting electrolyte at 50 mV s^{-1} by use of platinum working and counter electrodes, and a SCE (saturated calomel electrode) as the reference electrode.

The data of X-ray structures were collected on an Enraf-Nonius CAD-4 (for **17**, **19**, **10a**, and **12a**) and a Mac Science MXC18 [for **9a** and $(\mathbf{11})_2CS_2$] diffractometers equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using the $\omega - 2\theta$ scan technique. All calculations were performed using the Molen structure determination system (for **17**, **19**, **10a**, and **12a**) and CRYSTAN (MacScience) [for **9a** and $(\mathbf{11})_2CS_2$].

Air- and/or moisture-sensitive reactions were carried out in a dry reaction vessel.

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under an argon atmosphere unless otherwise noted. All other solvents were dried by appropriate procedures and stored over molecular sieves. Boron trifluoride diethyl etherate was distilled and stored prior to use. MeMgBr/THF, NaOMe/MeOH, ^nBuLi/hexane, Me_3Al/hexane, $(Bu_4N)_2[Zn(dmit)_2]$, 2,3-dichrolo-1,4-dioxane (**15**), ethyl 1,3-dithiolan-2-carboxylate (**26**), 4,5-ethylenedithio-1,3-dithiole-2-thione (**28**), and 1,3-dithiole-2-thione (**30**) were purchased and used without further titration or purification. 1,3-Dithiol-2-one could be obtained by reaction of **30** with $Hg(OAc)_2$ in THF−AcOH[7e] in 78% yield. 4,5-Methylenedithio-1,3-dithiole-2-thione (**29**), though commercially available, could be prepared by reaction of $(Bu_4N)_2[Zn(dmit)_2]$ with 6 equiv of dibromomethane in refluxing THF under nitrogen for 1.5 h in 90% yield after column chromatography on silica gel followed by recrystallization from hexane−$CHCl_3$.

2,2-Dibutyl-2-stanna-1,3-dithiolo[4,5-*d*]-1,3-dithiole-2-thione (14). To a solution of $(Bu_4N)_2[Zn(dmit)_2]$ (2.83 g, 3.00 mmol) in THF (15 mL) was added a solution of Cl_2SnBu_2 (1.83 g, 6.02 mmol) in THF (6 mL) at room temperature under nitrogen. After stirring for 1 h at that temperature, water was added, and the aqueous layer was extracted with several portions of $CHCl_3$. The extracts were combined, dried over $MgSO_4$, concentrated under reduced pressure, and purified by column chromatography on silica gel using CH_2Cl_2 as an eluent to give 2.38 g (5.54 mmol) of **14** (92% yield): orange powder; mp 157 °C dec from CH_2Cl_2−hexane; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 6 H), 1.38 (sixtet, J = 7.3 Hz, 4 H), 1.63−1.88 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 24.8, 26.7, 27.7, 128.5, 211.5.

4,5-(1,4-Dioxanediyl-2,3-dithio)-1,3-dithiol-2-one (17) from Tin Thiolate 13. To a solution of tin dithiolate **13** (3.96 g, 9.58 mmol) in $CHCl_3$ (50 mL) was added 1.1 mL (10 mmol)

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[13] Yamada, J.; Tanaka, S.; Anzai, H.; Sato, T.; Nishikawa, H.; Ikemoto, I.; Kikuchi, K. *J. Mater. Chem.* **1997**, *7*, 1311−1312.

of 2,3-dichloro-1,4-dioxane (**15**) at room temperature under nitrogen, and then 2.5 mL (20 mmol) of $BF_3{\cdot}OEt_2$ was added. After the reaction mixture was stirred at room temperature for 3 h, aqueous $NaHCO_3$ was added, and the resulting suspension was filtered through Celite. 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. Column chromatography of the residue on silica gel by using hexane−CH_2Cl_2 as an eluent gave 2.31 g (8.67 mmol) of **17** (91% yield): pale orange plate; mp 144 °C from EtOH; ^1H NMR ($CDCl_3$) δ 3.73 (m, 2 H), 4.06 (m, 2 H), 5.48 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 63.4, 78.9, 115.1, 189.4; MS, *m/z* (% relative intensity) 268 ($M^+ + 2$, 7), 266 (M^+, 36), 86 (100); HRMS (EI) calcd for $C_7H_6O_3S_4$ 265.9200, measured 265.9198. Anal. Calcd for $C_7H_6O_3S_4$: C, 31.56; H, 2.27. Found: C, 31.80; H, 2.31

4,5-(1,4-Dioxanediyl-2,3-dithio)-1,3-dithiole-2-thione (18). To a solution of tin dithiolate **14** (2.15 g, 5.01 mmol) in $CHCl_3$ (50 mL) was added 0.54 mL (5.0 mmol) of 2,3-dichloro-1,4-dioxane (**15**) at room temperature under nitrogen, and then 1.23 mL (10 mmol) of $BF_3{\cdot}OEt_2$ was added. After stirring at room temperature overnight, the same workup and purification as described above furnished 891 mg (3.15 mmol) of **18** (63% yield): reddish-brown needles; mp 180 °C dec from EtOH; ^1H NMR ($CDCl_3$) δ 3.74 (m, 2 H), 4.06 (m, 2 H), 5.50 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 63.5, 78.2, 124.7, 209.6; MS, *m/z* (% relative intensity) 284 ($M^+ + 2$, 8), 282 (M^+, 37), 86 (100); HRMS (EI) calcd for $C_7H_6O_2S_5$ 281.8971, measured 281.8970. Anal. Calcd for $C_7H_6O_2S_5$: C, 29.76; H, 2.14. Found: C, 29.71; H, 2.42.

4,5-(1,4-Dioxanediyl-2,3-dithio)-1,3-dithiol-2-one (17) from Thione 18. To a solution of thione **18** (518 mg, 1.83 mmol) in THF (distilled from CaH_2, 50 mL) was added a solution of $Hg(OAc)_2$ (0.93 g, 2.93 mmol) in acetic acid (29 mL) in one portion at room temperature. After stirring was continued vigorously for 1 h, the same workup as described previously[7e] was carried out. Column chromatography of the crude product on silica gel by using hexane−CH_2Cl_2 as an eluent gave 396 mg (1.49 mmol) of **17** (81% yield).

5,6-Dihydro-1,4-dithiin. To a mixture of 1,3-dithiol-2-one (3.40 g, 28.7 mmol) and potassium hydroxide (14.5 g, 258 mmol) in EtOH (287 mL) under nitrogen was added 19.8 mL (230 mmol) of 1,2-dibromoethane. After the reaction mixture was heated under reflux for 1 h, 5% HCl solution and water were sequentially added, and the resulting mixture was filtered through Celite. The aqueous layer was extracted with several portions of CH_2Cl_2, and the extracts were combined, dried over $MgSO_4$, and concentrated. Column chromatography of the residue on silica gel by using pentane and pentane−CH_2Cl_2 as eluents afforded 2.84 g (24.0 mmol) of a light yellow oil (84% yield), the ^1H and ^{13}C NMR spectra of which were identical with those of the authentic samples prepared according to the literature method:[11] ^1H NMR ($CDCl_3$) δ 3.18 (s, 4 H), 6.07 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.3, 114.3.

2,3-Dibromo-1,4-dithiane (16). To a solution of 5,6-dihydro-1,4-dithiin (1.09 g, 9.22 mmol) in ether (distilled form P_2O_5, 33 mL) at −78 °C was added dropwise 0.47 mL (9.12 mmol) of bromine via a syringe. After the reaction mixture was allowed to warm to 0 °C, the resulting precipitate was filtered off and washed with hexane to give 1.99 g (7.16 mmol) of **16** as a pale brown powder, which was immediately used for the next reaction due to its lability: ^1H NMR ($CDCl_3$) δ 2.74 (m, 2 H), 3.42 (m, 2 H), 5.52 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 25.1, 53.5.

4,5-(1,4-Dithianediyl-2,3-dithio)-1,3-dithiol-2-one (19). To a solution of tin dithiolate **13** (2.02 g, 4.89 mmol) and the crude **16** (1.33 g, 4.78 mmol) in $CHCl_3$ (49 mL) was added 1.25 mL (9.86 mmol) of $BF_3{\cdot}OEt_2$ at room temperature under nitrogen. After the reaction mixture was stirred at room temperature for 2 h, the same workup and purification procedures as used for the preparation of **17** from **13** furnished 989 mg (3.31 mmol) of **19** (68% yield): pale yellow needles; mp 167 °C from EtOH; ^1H NMR ($CDCl_3$) δ 2.98 (m, 2 H), 3.15 (m, 2 H), 4.89 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.3, 45.6, 110.3, 188.5; MS, *m/z* (% relative intensity) 300 ($M^+ + 2$, 8), 298 (M^+, 29), 118 (100); HRMS (EI) calcd for $C_7H_6OS_6$ 297.8743, measured 297.8747. Anal. Calcd for $C_7H_6OS_6$: C, 28.16; H, 2.03. Found: C, 28.20; H, 2.17.

4,5-(5,6-Dihydro-1,4-dithiindiyl-2,3-dithio)-1,3-dithiol-2-one (20). A mixture of **19** (500 mg, 1.68 mmol) and DDQ (574 mg, 2.53 mmol) in toluene (16 mL) was refluxed for 2 days, and the resulting suspension was filtered through a Celite pad, the Celite being then washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel using hexane−CH_2Cl_2 as an eluent to give 300 mg (1.01 mmol) of **20** (60% yield) and 168 mg (0.56 mmol) of the recovered **19**, which could be recycled: pale yellow powder; mp 163 °C dec from EtOH−CH_2Cl_2; ^1H NMR ($CDCl_3$) δ 3.27 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 30.7, 120.2, 122.2, 191.0; MS, *m/z* (% relative intensity) 298 ($M^+ + 2$, 33), 296 (M^+, 100), 268 (53), 116 (36), 88 (93); HRMS (EI) calcd for $C_7H_4OS_6$ 295.8586, measured 295.8602. Anal. Calcd for $C_7H_4OS_6$: C, 28.35; H, 1.36. Found: C, 28.45; H, 1.60

Conversion of Ketones (17, 19, and 20) into Tin Dithiolates (21−23) via Grignard Reaction. These compounds were prepared by the procedure described in the earlier report[7e] unless otherwise noted.

4,5-(1,4-Dioxanediyl-2,3-dithio)-2,2-dibutyl-2-stanna-1,3-dithiole (21): yellow powder; mp 109−110 °C; ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3 H), 0.91 (t, J = 7.3 Hz, 3 H), 1.34 (m, 4 H), 1.49−1.87 (m, 8 H), 3.64 (m, 2 H), 4.07 (m, 2 H), 5.28 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 21.8, 23.1, 26.6, 26.7, 27.5, 28.1, 63.2, 79.5, 116.7.

4,5-(1,4-Dithianediyl-2,3-dithio)-2,2-dibutyl-2-stanna-1,3-dithiole (22). The reaction of ketone **19** with MeMgBr in THF was carried out for 4 h: pale brown powder; mp 104−105 °C; ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 6 H), 1.35 (sixtet, J = 7.3 Hz, 4 H), 1.56−1.88 (br, 8 H), 2.88 (m, 2 H), 3.12 (m, 2 H), 4.70 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.3, 23.0, 26.6, 26.7, 27.7, 28.0, 28.1, 46.8, 112.2.

4,5-(5,6-Dihydro-1,4-dithiindiyl-2,3-dithio)-2,2-dibutyl-2-stanna-1,3-dithiole (23): brown powder; mp 76 °C; ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 6 H), 1.34 (sixtet, J = 7.3 Hz, 4 H), 1.58−1.85 (m, 8 H), 3.20 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.6, 23.7, 26.7, 27.7, 30.6, 120.4, 126.4.

2,2-Dibutyl-2-stanna-1,3-dithiole. In a 200-mL flask with a septum inlet was placed 1.18 g (10 mmol) of 1,3-dithiol-2-one, and this flask was cooled in a water bath. After a methanol solution of NaOMe (1M × 20 mL, 20 mmol) was added to that flask via a syringe under nitrogen, the reaction mixture was stirred for 10 min and then cooled to − 78 °C. To the cooled mixture was added dropwise for 1 h a solution of 3.03 g (10 mmol) of Cl_2SnBu_2 in THF (100 mL), and the reaction mixture was allowed to warm to 0 °C. Water was added, the mixture was extracted with several portions of CH_2Cl_2, and the extracts were combined. The combined extracts were dried over $MgSO_4$, concentrated in vacuo, and purified by column chromatography on silica gel using hexane−CH_2Cl_2 as an eluent to afford 1.94 g (6.0 mmol) of a pale yellow oil (60% yield): ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 6 H), 1.35 (sixtet, J = 7.3 Hz, 4 H), 1.30−1.80 (m, 8 H), 6.44 (s, 2 H, $J_{H,Sn}$ = 63.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.6, 22.2, 26.6, 27.9, 120.0.

Methyl 1,3-Dithiole-2-carboxylate (25). To a solution of 725 mg (2.24 mmol) of 2,2-dibutyl-2-stanna-1,3-dithiole in THF (23 mL) at −78 °C under nitrogen was added dropwise for 10 min a hexane solution of ^nBuLi (1.64 M × 2.8 mL, 4.59 mmol). After stirring was continued for 20 min at that temperature, a solution of commercially available methyl dichloroacetate (0.24 mL, 2.32 mmol) in THF (12 mL) was added dropwise for 30 min, and the reaction mixture was allowed to warm to 0 °C. Saturated aqueous NH_4Cl solution was added, the mixture was extracted with several portions of CH_2Cl_2, and the extracts were combined. The combined extracts were dried over $MgSO_4$, concentrated under reduced pressure, and purified by column chromatograghy on silica gel using hexane and hexane−CH_2Cl_2 as eluents to give 137 mg (0.84 mmol) of **25** (38% yield): pale orange oil; ^1H NMR ($CDCl_3$) δ 3.75 (s, 3 H), 5.31 (s, 1 H), 5.98 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 51.8, 53.4, 116.2, 169.2; MS, *m*/*z* (% relative intensity) 164 ($M^+ + 2$, 3), 162 (M^+, 31), 103 (100).

General Procedure for Cross Coupling Reaction of Ketone 17 and Thiones 28−30. Entry 2 in Table 1 is representative. In a 100-mL flask under nitrogen were placed ketone **17** (533 mg, 2.0 mmol), thione **28** (898 mg, 4.0 mmol), benzene (33 mL), and trimethyl phosphite (5.4 mL, 46 mmol). The mixture was heated over an oil bath at 100 °C and kept at that temperature for 3 h with stirring. After cooling to room temperature, water was added and the mixture was extracted with several portions of carbon disulfide. The extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by silica gel column chromatography using CS_2 and $CS_2-CH_2Cl_2$ as eluents, followed by recrystallization from CS_2−EtOH, furnished 312 mg (0.70 mmol) of **9a** (35% yield).

(1,4-Dioxanediyl-2,3-dithio)ethylenedithiotetrathiafulvalene (DOET, 9a): orange plate; mp 179 °C dec from CS_2; ^{1}H NMR ($CDCl_3-CS_2$) δ 3.24 (m, 2 H), 3.31 (m, 2 H), 3.68 (m, 2 H), 4.04 (m, 2 H), 5.40 (s, 2 H); MS, *m*/*z* (% relative intensity) 444 ($M^+ + 2$, 3), 442 (M^+, 8), 356 (11), 86 (100), 76 (90); HRMS (EI) calcd for $C_{12}H_{10}O_2S_8$ 441.8447, measured 441.8469. Anal. Calcd for $C_{12}H_{10}O_2S_8$: C, 32.55; H, 2.28. Found: C, 32.84; H, 2.40.

(1,4-Dioxanediyl-2,3-dithio)methylenedithiotetrathiafulvalene (DOMT, 9b). This compound was purified by silica gel column chromatography using hexane−CH_2Cl_2 as an eluent, followed by recrystallization from CS_2−EtOH; dark red powder: mp 173 °C dec from $CHCl_3$−EtOH; ^{1}H NMR ($CDCl_3-CS_2$) δ 3.69 (m, 2 H), 4.04 (m, 2 H), 4.82 (d, J = 9.8 Hz, 1 H), 5.04 (d, J = 9.8 Hz, 1 H), 5.41 (s, 2 H); MS, *m*/*z* (% relative intensity) 428 (M^+, 1), 342 (2), 236 (24), 86 (100), 58 (82); HRMS (EI) calcd for $C_{11}H_8O_2S_8$ 427.8290, measured 427.8297. Anal. Calcd for $C_{11}H_8O_2S_8$: C, 30.81; H, 1.88. Found: C, 30.59; H, 2.03.

(1,4-Dioxanediyl-2,3-dithio)tetrathiafulvalene (DOT, 9c): greenish-yellow powder; mp 154 °C dec from CS_2−EtOH; ^{1}H NMR ($CDCl_3$) δ 3.69 (m, 2 H), 4.06 (m, 2 H), 5.41 (s, 2 H), 6.31 (s, 2 H); MS, *m*/*z* (% relative intensity) 354 ($M^+ + 2$, 22), 352 (M^+, 74), 266 (83), 86 (100); HRMS (EI) calcd for $C_{10}H_8O_2S_6$ 351.8849, measured 351.8847.

Bis(1,4-dithianediyl-2,3-dithio)tetrathiafulvalene (BDTET, 7). In a 30-mL flask under nitrogen were placed ketone **19** (203 mg, 0.68 mmol) and triethyl phosphite (6.8 mL). After the mixture was heated at 120 °C for 1.5 h with stirring, the suspension was cooled to 0 °C and diluted with hexane. The resulting precipitate was filtered off, washed with hexane, and purified by column chromatography on silica gel using CS_2 as an eluent, followed by recrystallization from CS_2−EtOH, to gave 15 mg (0.03 mmol) of **7** (9% yield): pale red powder; mp 222 °C dec from CS_2−EtOH; MS, *m*/*z* (% relative intensity) 566 ($M^+ + 2$, 10), 564 (M^+, 18), 118 (62), 76 (100); HRMS (EI) calcd for $C_{14}H_{12}S_{12}$ 563.7588, measured 563.7587. Anal. Calcd for $C_{14}H_{12}S_{12}$: C, 29.76; H, 2.14. Found: C, 29.64; H, 2.19.

(1,4-Dithianediyl-2,3-dithio)ethylenedithiotetrathiafulvalene (DTET, 10a) via Me_3Al-Promoted Reaction. To a solution of the crude tin dithiolate **22** (2.0 mmol based on **19**) in CH_2Cl_2 (20 mL) was added a hexane solution of Me_3Al (1.08 M × 3.7 mL, 4.0 mmol) at −78 °C under nitrogen. After stirring at that temperature for 1.5 h, the reaction mixture was brought up to room temperature, and then a solution of ester **24** (485 mg, 1.9 mmol) in CH_2Cl_2 (10 mL) was added. The reaction mixture was stirred overnight before being quenched with saturated aqueous $NaHCO_3$. The resulting mixture was filtered through Celite, 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 hexane and CS_2 as eluents, followed by recrystallization from CS_2, giving 104 mg (0.22 mmol) of **10a** (11% yield): reddish-orange plate; mp 202 °C dec from CS_2; ^{1}H NMR ($CDCl_3-CS_2$) δ 2.94 (m, 2 H), 3.12 (m, 2 H), 3.27 (m, 4 H), 4.79 (s, 2 H); MS, *m*/*z* (% relative intensity) 474 (0.6, M^+), 356 (3), 118 (100), 76 (100); HRMS (EI) calcd for $C_{12}H_{10}S_{10}$ 473.7990, measured 473.7974. Anal. Calcd for $C_{12}H_{10}S_{10}$: C, 30.35; H, 2.12. Found: C, 30.46; H, 2.14.

(1,4-Dithianediyl-2,3-dithio)tetrathiafulvalene (DTT, 10c) via Me_3Al-Promoted Reaction. This compound was synthesized from the crude tin dithiolate **22** (1.25 mmol based on **19**) and ester **25** (1.99 mmol) in the presence of Me_3Al (2.48 mmol) by the same procedure as described above, except that the mixture of **22** and Me_3Al was stirred at −78 °C for 1 h prior to the addition of ester **25** at room temperature: orange powder; mp 189 °C dec from CS_2−EtOH; ^{1}H NMR ($CDCl_3-CS_2$) δ 2.94 (m, 2 H), 3.13 (m, 2 H), 4.79 (s, 2 H), 6.30 (s, 2 H); MS, *m*/*z* (% relative intensity) 386 (17, $M^+ + 2$), 384 (47, M^+), 266 (100), 118 (80), 76 (40); HRMS (EI) calcd for $C_{10}H_8S_8$ 383.8392, measured 383.8392.

General Procedure for Cross Coupling Reaction of Ketone 19 and Thiones 28−30. Entry 4 in Table 3 is representative. In a 50-mL flask under nitrogen were placed ketone **19** (149 mg, 0.50 mmol), thione **28** (224 mg, 1.0 mmol), benzene (8.3 mL), and triethyl phosphite (2.3 mL, 13 mmol). The mixture was heated over an oil bath at 100 °C and kept at that temperature for 3 h with stirring. After the resulting suspension was cooled to 0 °C and diluted with hexane, the precipitate was filtered off and washed with hexane. Purification by silica gel column chromatography using CS_2 as an eluent, followed by recrystallization from CS_2, gave 121 mg (0.25 mmol) of **10a** (50% yield).

(1,4-Dithianediyl-2,3-dithio)methylenedithiotetrathiafulvalene (DTMT, 10b): brownish-yellow powder; mp 193 °C dec from CS_2; ^{1}H NMR ($CDCl_3-CS_2$) δ 2.94 (m, 2 H), 3.13 (m, 2 H), 4.80 (s, 2 H), 4.86 (d, J = 9.8 Hz, 1 H), 5.01 (d, J = 9.8 Hz, 1 H); MS, *m*/*z* (% relative intensity) 460 (0.5, M^+), 342 (0.8), 236 (25), 118 (100), 90 (78). Anal. Calcd for $C_{11}H_8S_{10}$: C, 28.67; H, 1.75. Found: C, 28.43; H, 1.70.

Bis(5,6-dihydro-1,4-dithiindiyl-2,3-dithio)tetrathiafulvalene (BDHDI-TTF, 8). This compound was synthesized from ketone **20** by the procedure used for the preparation of **7**, except that the mixture of **20** and triethyl phosphite was heated for 2 h: yellow powder; mp 264 °C dec from CS_2−EtOH; ^{1}H NMR ($CDCl_3-CS_2$) δ 3.23 (s, 8 H); MS, *m*/*z* (% relative intensity) 562 (3, $M^+ + 2$), 560 (5, M^+), 384 (33), 356 (20), 88 (39), 76 (100); HRMS (EI) calcd for $C_{14}H_8S_{12}$ 559.7275, measured 559.7273. Anal. Calcd for $C_{14}H_8S_{12}$: C, 29.97; H, 1.44. Found: C, 30.31; H, 1.55.

(5,6-Dihydro-1,4-dithiindiyl-2,3-dithio)ethylenedithiotetrathiafulvalene (DHDIET, 11). To a solution of the crude tin dithiolate **23** (0.71 mmol based on **20**) in CH_2Cl_2 (10 mL) was successively added a hexane solution of Me_3Al (1.07 M × 1.3 mL, 1.39 mmol) and a CH_2Cl_2 (10 mL) solution of ester **24** (177 mg, 0.70 mmol) at −78 °C under nitrogen. After the reaction mixture was allowed to warm to room temperature and stirred overnight, the same workup and purification as described in preparation of **10a** via Me_3Al-promoted reaction, followed by recrystallization from CS_2-hexane, furnished 125 mg (0.26 mmol) of **11** (37% yield): orange needles; mp 231 °C dec for $(\mathbf{11})_2CS_2$ from CS_2; ^{1}H NMR ($CDCl_3-CS_2$) δ 3.23 (s, 4 H), 3.28 (s, 4 H); MS, *m*/*z* (% relative intensity) 474 (29, $M^+ + 2$), 472 (54, M^+), 384 (100), 356 (77), 88 (89), 76 (75); HRMS (EI) calcd for $C_{12}H_8S_{10}$ 471.7833, measured 471.7817. Anal. Calcd for $(\mathbf{11})_2CS_2$ ($C_{25}H_{16}S_{22}$): C, 29.38; H, 1.58. Found: C, 29.49; H, 1.54.

A Typical Procedure for Synthesis of the Dioxolane Derivatives. Synthesis of **12a** (entry 3 in Table 6) is representative. To a solution of ester **24** (0.80 mmol) in CH_2Cl_2 was added a hexane solution of Me_3Al (1.02 M × 1.6 mL, 1.63 mmol) at −78 °C under nitrogen, and then a CH_2Cl_2 (8.0 mL) solution of the crude tin dithiolate **21** (377 mg, 0.80 mmol based on **17**) was added. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 2 days. The usual workup and purification by silica gel column chromatography using hexane and hexane−$CHCl_3$ as eluents, followed by recrystallization from $CHCl_3$−EtOH, afforded 58 mg (0.13 mmol) of **12a** (16% yield from ketone **17**).

[(1,3-Dioxolan-2-yl)methylidynedithio]ethylenedithiotetrathiafulvalene (DO-MET, 12a): orange needles; mp 178 °C dec from CS_2; ^{1}H NMR ($CDCl_3$) δ 3.27 (m, 4 H), 4.00 (m, 4 H), 5.05 (d, $J = 5.6$ Hz, 1 H), 5.20 (d, $J = 5.6$ Hz, 1 H); MS, *m/z* (% relative intensity) 444 (13, $M^+ + 2$), 442 (37, M^+), 380 (24), 307 (59), 73 (100); HRMS (EI) calcd for $C_{12}H_{10}O_2S_8$ 441.8447, measured 441.8467. Anal. Calcd for $C_{12}H_{10}O_2S_8$: C, 32.55; H, 2.28. Found: C, 32.57; H, 2.45.

[(1,3-Dioxolan-2-yl)methylidynedithio]tetrathiafulvalene (DO-MDT, 12b): brownish-yellow needles; mp 113−114 °C from CS_2−EtOH; ^1H NMR ($CDCl_3$) δ 4.00 (m, 4 H), 5.05 (d, $J = 5.4$ Hz, 1 H), 5.21 (d, $J = 5.4$ Hz, 1 H), 6.31 (s, 2 H); MS, *m/z* (% relative intensity) 354 (26, $M^+ + 2$), 352 (100, M^+), 279 (54), 146 (24), 73 (48); HRMS (EI) calcd for $C_{10}H_8O_2S_6$ 351.8849, measured 351.8848. Anal. Calcd for $C_{10}H_8O_2S_6$: C, 34.06; H, 2.29. Found: C, 34.04; H, 2.40.

[(1,3-Dioxolan-2-yl)methylidynedithio]dihydrotetrathiafulvalene (DO-MDHT, 12c): light brown plate; mp 137 °C dec from $CHCl_3$−EtOH; ^1H NMR ($CDCl_3$) δ 3.44 (m, 4 H), 3.98 (m, 4 H), 5.02 (d, $J = 5.9$ Hz, 1 H), 5.20 (d, $J = 5.9$ Hz, 1 H); MS, *m/z* (% relative intensity) 356 (20, $M^+ + 2$), 354 (71, M^+), 281 (68), 148 (28), 73 (100); HRMS (EI) calcd for $C_{10}H_{10}O_2S_6$ 353.9005, measured 353.8987. Anal. Calcd for $C_{10}H_{10}O_2S_6$: C, 33.87; H, 2.84. Found: C, 33.93; H, 2.86.

Dimethyl[(1,3-Dioxolan-2-yl)methylidynedithio]diselenadithiafulvalene (DMDO−STF, 12d): dark red powder; mp 198 °C dec from $CHCl_3$−EtOH; ^1H NMR ($CDCl_3$) δ 1.98 (s, 6 H), 3.99 (m, 4 H), 5.02 (d, $J = 5.6$ Hz, 1 H), 5.20 (d, $J = 5.6$ Hz, 1 H); MS, *m/z* (% relative intensity) 476 (100, $M^+ + 2$), 474 (77, M^+), 403 (44), 401 (40), 270 (19), 268 (18), 73 (77); HRMS (EI) calcd for $C_{12}H_{12}O_2S_6{}^{80}Se_2$ 475.8051, measured 475.8052. Anal. Calcd for $C_{12}H_{12}O_2S_4Se_2$: C, 30.38; H, 2.55. Found: C, 30.28; H, 2.57.

Crystal data for 17:[14] $C_7H_6O_3S_4$, $M = 266.38$, monoclinic, space group $P2_1$, $a = 9.182(1)$ Å, $b = 5.461(2)$ Å, $c = 9.920(1)$ Å, $\beta = 91.19(1)°$, $V = 497.3(2)$ Å^3, $Z = 2$, $D_c = 1.779$ g cm^{-3}, $\mu = 8.9$ cm^{-1}, $F(000) = 272$. The $\omega{-}2\theta$ scan technique was used to a maximum 2θ of 70°. Cell constants were determined from 25 carefully centered reflections in the range 26.5° < 2θ < 35.6°. The structure was solved by the Patterson method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.021$, $R_w = 0.029$ for 1926 observed [$I \geq 3\sigma(I)$] reflections from 2368 unique data.

Crystal data for 19:[14] $C_7H_6OS_6$, $M = 298.51$, monoclinic, space group $P2_1/c$, $a = 5.171(2)$ Å, $b = 11.269(3)$ Å, $c = 18.897(1)$ Å, $\beta = 90.10(2)°$, $V = 1101.2(6)$ Å^3, $Z = 4$, $D_c = 1.800$ g cm^{-3}, $\mu = 11.6$ cm^{-1}, $F(000) = 608$. The $\omega{-}2\theta$ scan technique was used to a maximum 2θ of 70°. Cell constants were determined from 25 carefully centered reflections in the range 24.2° < 2θ < 42.3°. The structure was solved by the Patterson method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.038$, $R_w = 0.042$ for 1824 observed [$I \geq 3\sigma(I)$] reflections from 4841 unique data.

Crystal data for 9a:[14] $C_{12}H_{10}O_2S_8$, $M = 442.72$, monoclinic, space group $P2_1/n$, $a = 12.005(3)$ Å, $b = 21.532(2)$ Å, $c = 6.571(2)$ Å, $\beta = 96.93(3)°$, $V = 1686.1(9)$ Å^3, $Z = 4$, $D_c = 1.741$ g cm^{-3}, $\mu = 26.85$ cm^{-1}, $F(000) = 272$. The $\omega{-}2\theta$ scan technique was used to a maximum 2θ of 55°. Cell constants were determined from 25 carefully centered reflections in the range 25° < 2θ < 30°. The structure was solved by a direct method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.043$, $R_w = 0.049$ for 2852 observed [$I \geq 2\sigma(I)$] reflections from 3604 independent reflections.

Crystal data for 10a:[14] $C_{12}H_{10}S_{10}$, $M = 474.85$, triclinic, space group Po(1,¯), $a = 8.788(1)$ Å, $b = 9.998(2)$ Å, $c = 11.126(2)$ Å, $\alpha = 80.09(1)°$, $\beta = 68.01(1)°$, $\gamma = 82.17(1)°$, $V = 890.0(3)$ Å^3, $Z = 2$, $D_c = 1.772$ g cm^{-3}, $\mu = 11.82$ cm^{-1}, $F(000) = 484$. The $\omega{-}2\theta$ scan technique was used to a maximum 2θ of 80°. Cell constants were determined from 25 carefully centered reflections in the range 35.9° < 2θ < 39.6°. The structure was solved by a direct method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.052$, $R_w = 0.047$ for 5307 observed [$I \geq 3\sigma(I)$] reflections from 8935 unique data.

Crystal data for $(11)_2CS_2$:[14] $C_{25}H_{16}S_{22}$, $M = 1021.84$, monoclinic, space group $p2_{1/n}$, $a = 12.330(7)$ Å, $b = 24.22(1)$ Å, $c = 6.553(4)$ Å, $\beta = 98.01\ (5)°$, $V = 1938.3(2)$ Å^3, $Z = 4$, $D_c = 1.617$ g cm^{-3}, $\mu = 10.85$ cm^{-1}, $F(000) = 518$. The $\omega{-}2\theta$ scan technique was used to a maximum 2θ of 60°. Cell constants were determined from 38 carefully centered reflections in the range 20° < 2θ < 30°. The structure was solved by a direct method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.068$, $R_w = 0.084$ for 3318 observed [$I \geq 3\sigma(I)$] reflections from 3745 unique data.

Crystal Data for 12a:[14] $C_{12}H_{10}O_2S_8$, $M = 442.72$, monoclinic, space group $P2_1/n$, $a = 6.322(1)$ Å, $b = 25.093(2)$ Å, $c = 10.637(1)$ Å, $\beta = 93.62(1)°$, $V = 1684.1(3)$ Å^3, $Z = 4$, $D_c = 1.746$ g cm^{-3}, $\mu = 10.2$ cm^{-1}, $F(000) = 904$. The $\omega{-}2\theta$ scan technique was used to a maximum 2θ of 80°. Cell constants were determined from 25 carefully centered reflections in the range 26.5° < 2θ < 35.6°. The structure was solved by the Patterson method and refined by full-matrix least-squares analysis (anisotropic for non-hydrogen atoms) to $R = 0.045$, $R_w = 0.051$ for 6244 observed [$I \geq 1.5\sigma(I)$] reflections from 10416 unique data.

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Supporting Information Available: ^1H NMR spectra of 2,2-dibutyl-2-stanna-1,3-dithiole and compounds **9c**, **10c**, **14**, **16**, **21**, **22**, **23**, and **25** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.