J. Org. Chem. **1997,** *62,* 5567−5574

Syntheses, Unique Strained Molecular Structures, and Unusual Transannular Electronic Interactions of a Series of Crisscross-Overlapped Tetrathiafulvalenophanes[†]

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Received December 3, 1996[⊗]

A series of novel tetrathiafulvalenophanes has been synthesized, in which two tetrathiafulvalenes (TTF) are linked in a crisscross-overlapped arrangement by four alkylenedithio bridges. Their molecular structures were elucidated by X-ray crystal analyses, being characterized by the bent TTF skeletons as well as the unique stacking mode. The degree of the bend largely depends on both the length and conformational rigidity of the alkylenedithio chains. The short and rigid chains induce severe bending, which brings about a hypsochromical effect in the electronic absorption spectra. On the other hand, the long and flexible chains reduce the strain and make an inside cavity large enough to include a guest molecule. In addition, the less strained compounds can effect an intramolecular transannular Coulombic interaction between their two TTF units in solution, as demonstrated by multistage redox waves in the cyclic voltammograms. All the radical cation salts formed from these tetrathiafulvalenophanes have conductivities of the same order of $10^{-6}-10^{-7}$ S cm^{-1}, which are apparently independent of the donor and the counterion species.

Introduction

An area of TTF chemistry which in recent years has gained in importance is concerned with the development of dimeric TTFs.[1] This is based on the idea that a through-bond or through-space intramolecular interaction between the two TTF units might provide an opportunity to control the stoichiometry, band filling, and molecular assembly in desired conducting complexes.[2] Of a number of such compounds ever designed, tetrathiafulvalenophanes (TTF phanes), in which the two TTF units are stacked by two or more spacer bridges, are of particular interest, because they have unique nonplanar, double-layered structures, which might form molecular complexes different in crystal structure and solid properties from the usual ones based on the ordinary planar TTF donors. Until quite recently, however, only few examples of TTF phanes were known.[3] Recently we reported double-bridged TTF phanes **1**−**4**[4] and quadruple-bridged one **5**,[5] of which the former gave highly conductive molecular complexes. Such compounds are very useful in understanding the stacking interactions of conducting TTF complexes. There are a variety of modes for the stack of TTF. The crystal structures of highly conducting molecular complexes of TTF and related compounds generally comprise segregated stacks of the π-systems with a face-to-face arrangement along the stacks.[6] On the other hand, those of κ-type of recent superconductors are characterized by close packing of paired TTF units. More recently, an unusual crisscross-overlapped arrangement of TTFs was also found in the crystal structures of semiconducting salts, $(TTF)_3W_6O_{19}$ and $(TTF)_3Mo_6O_{19}$.[7] This unique stacking mode has stimulated our great interests in studying the unexplored chemistry of crisscross-overlapped TTF phanes. In this paper we wish to describe the synthesis, molecular structures, and properties of novel TTF phanes **6**.[8,9]

Results and Discussion

Synthesis. The general methodology of our synthesis of **6** is based on the stepwise construction of the two TTF units, which was achieved by double coupling reaction of the 1,3-dithiol-2-one intermediates mediated by triethyl phosphite. The key precursors for the construction of the first TTF unit, 4,5-bis[(ω-chloroalkyl)thio]-1,3-dithiol-2-ones (**9**), were synthesized by treatments of bis

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[†] Dedicated to Professor Soichi Misumi on the occasion of his 70th birthday.

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

(1) For a recent comprehensive review on dimeric TTFs, see: Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater.* **1996**, *8*, 203.

(2) Kaplan, M. L.; Haddon, R. C.; Wudl, F. *J. Chem. Soc., Chem. Commun.* **1977**, 388. Bechgaard, K.; Lerstrup, K.; Jørgensen, M.; Johannsen, I.; Christensen, J.; Larsen, J. *Mol. Cryst. Liq. Cryst.* **1990**, *181*, 161. Izuoka, A.; Kumai, R.; Tachikawa, T.; Sugawara, T. *Ibid.* **1992**, *218*, 213.

(3) Ippen, J.; Tao-pen, C.; Starker, B.; Schweitzer, D.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 67. Bertho-Thoraval, F.; Robert, A.; Souizi, A.; Boubekeur, K.; Batail, P. *J. Chem. Soc., Chem. Commun.* **1991**, 843; Adam, M.; Enkelmann, V.; Räder, H.-J.; Röhrich, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 309.

(4) Takimiya, K.; Aso, Y.; Ogura, F.; Otsubo, T. *Chem. Lett.* **1995**, 735.

(5) Matsuo, K.; Takimiya, K.; Aso, Y.; Ogura, F.; Otsubo, T. *Chem. Lett.* **1995**, 523.

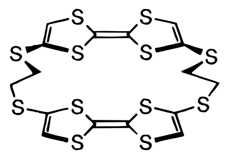
(6) Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*; Academic: San Diego 1987. Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors*; Prentice-Hall: New Jersey, 1992.

(7) Triki, S.; Ouahab, L.; Halet, J.-F.; Pe-a, O.; Padiou, J.; Grandjean, D.; Garrigou-Lagrange, C.; Delhaes, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1217.

(8) A preliminary communication has been published: Takimiya, K.; Shibata, Y.; Imamura, K.; Kashihara, A.; Aso, Y.; Otsubo, T.; Ogura, F. *Tetrahedron Lett.* **1995**, *36*, 5045.

(9) Sugawara and coworkers reported an independent synthesis of **6a** and **6b**: Tanabe, J.; Kudo, T.; Okamoto, M.; Kawada, Y.; Ono, G.; Izuoka, A.; Sugawara, T. *Chem. Lett.* **1995**, 579. Tanabe, J.; Ono, G.; Izuoka, A.; Sugawara, T.; Kudo, T.; Saito, T.; Okamoto, M.; Kawada, Y. *Mol. Cryst. Liq. Cryst.*, in press. They also reported preliminary X-ray crystal analyses of **6a** and **6b**: Tanabe, J.; Ono, G.; Izuoka, A.; Sugawara, T.; Kudo, T.; Saito, T.; Kawada, Y. *Abstracts of papers*; 1995 Symposium on Molecular Structure, Sendai; the Chemical Society of Japan: Tokyo, Japan, 1995; Abstract 3P092.

S0022-3263(96)02239-6 CCC: $14.00



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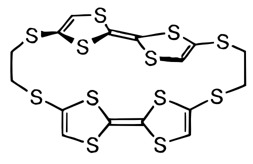

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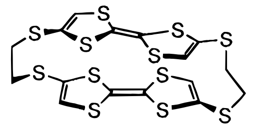

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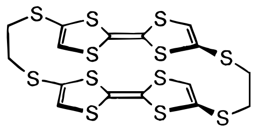

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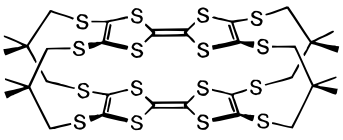

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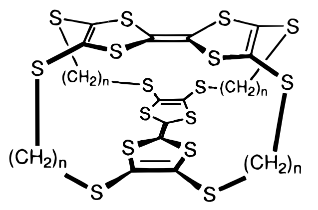
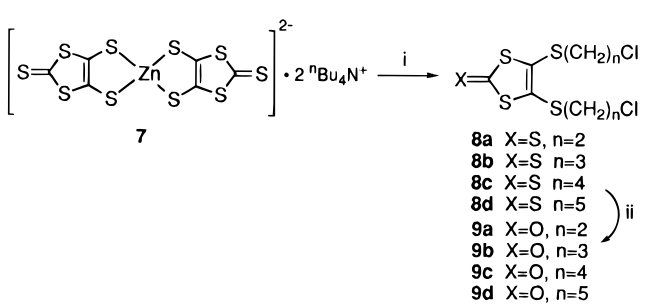


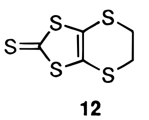
6a n=2
6b n=3
6c n=4
6d n=5

Scheme 1[a]



[a] Reagents and conditions: (i) $Br(CH_2)_nCl$, acetone, reflux; (ii) $Hg(OAc)_2$, $CHCl_3$–AcOH, rt.

(tetrabutylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate **7**[10] with the corresponding bromochloroalkanes, followed by oxidations of the resulting 1,3-dithiole-2-thiones **8** with mercury acetate according to Scheme 1. The preparation of 4,5-bis[(2-chloroethyl)thio]-1,3-dithiole-2-thione (**8a**), however, required a modification, because the reaction of **7** and 1-bromo-2-chloroethane produced 4,5-(ethylenedithio)-1,3-dithiole-2-thione **12** as a main product rather than the desired **8a**.



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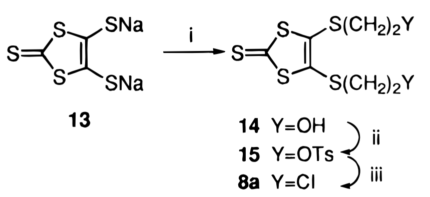
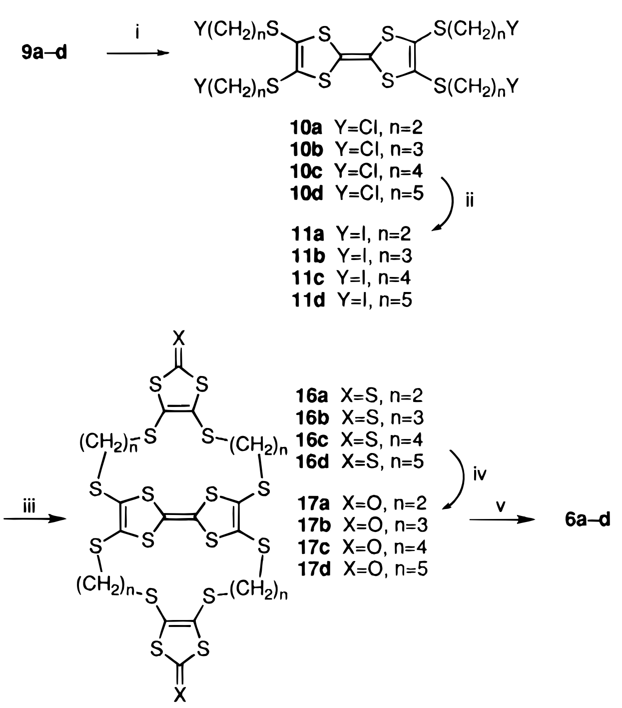
Scheme 2[a]



[a] Reagents and conditions: (i) $Cl(CH_2)_2OH$, EtOH, rt; (ii) TsCl, pyridine, rt; (iii) NaCl, DMF, 80 °C.

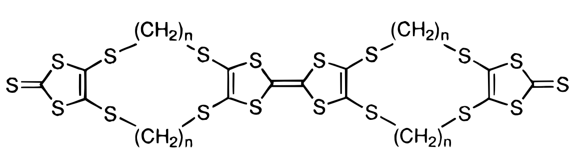
Scheme 3[a]



[a] Reagents and conditions: (i) $P(OEt)_3$, benzene, reflux; (ii) NaI, acetone–dioxane, reflux; (iii) zincate **7**, THF, reflux; (iv) $Hg(OAc)_2$, $CHCl_3$–AcOH, rt; (v) $P(OEt)_3$, toluene, reflux.

Alternatively, the diol **14** was prepared by the reaction of sodium 1,3-dithiole-2-thione-4,5-dithiolate **13** and 2-chloroethanol according to the reported procedure,[11] and easily converted via the tosylate **15** into **8a** (Scheme 2).

Self-coupling of **9** with triethyl phosphite gave tetrakis[(ω-chloroalkyl)thio]TTFs **10** in high yields, which, after halogen exchange with sodium iodide, were reacted with the zincate **7** to afford the bicyclic TTF compounds **16**, as shown in Scheme 3. In the last coupling reaction, it is possible to form another structural isomer **18**, which may lead to a parallel-overlapped TTF phane. However, the detectable product was only a single isomer, whose structure was confirmed on the basis of an X-ray crystal analysis of **16b** to be the precursor of the crisscross-overlapped TTF phane. As shown in Figure 1, the molecular geometry of **16b** clearly demonstrates that the



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(10) Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulphur* **1979**, *7*, 49.

(11) Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1639. Hansen, T. K.; Jørgensen, T.; Jensen, F.; Thygesen, P. H.; Christiansen, K.; Hursthouse, M. B.; Harman, M. E.; Malik, M. A.; Girmay, B.; Underhill, A. E.; Begtrup, M.; Kilburn, J. D.; Belmore, K.; Roepstorff, P.; Becher, J. *J. Org. Chem.* **1993**, *58*, 1359.

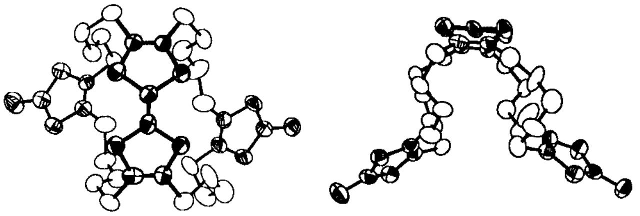


Figure 1. ORTEP drawings of **16b**: a top view (left) and a side view (right).

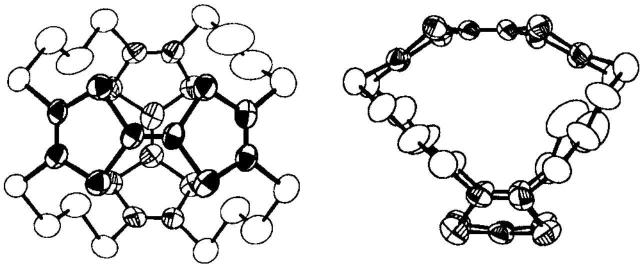


Figure 2. ORTEP drawings of **6a**: a top view (left) and a side view (right).

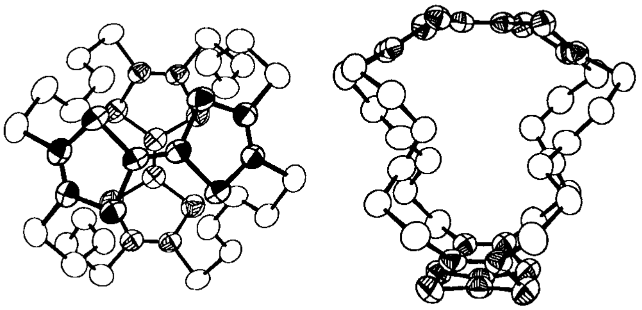


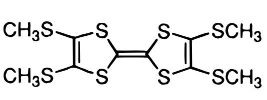
Figure 3. ORTEP drawings of **6c**: a top view (left) and a side view (right).

Figure 4. ORTEP drawings of **6d**: a top view (left) and a side view (right).

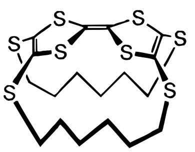
two dithiole rings are linked in the lateral direction of the central TTF moiety. In addition, both rings lie in the same space with respect to the TTF plane in such a way as to be easy to approach. This suggests that the intramolecular coupling forming the second TTF moiety may occur readily. Actually the intramolecular coupling reactions of the two 1,3-dithiole moieties, after the conversion to the diketones **17** with mercury acetate, proceeded smoothly to give the desired crisscross-overlapped TTF phanes **6** in good yields.

Molecular Structures. The unique molecular structures of the three TTF phanes **6a**, **6c**, and **6d** were elucidated by X-ray crystal analyses and depicted in Figures 2, 3, and 4, respectively.[9] The TTF rings are bent into a boat shape in varying degree and overlapped with each other in a crisscross-overlap arrangement. As expected, **6a** with the shortest ethylenedithio bridges has the most bent TTF structure, in which the dihedral angles defined by the central tetrathiaethylene part and the outer one range from 27 to 45°. As a result, the two TTF units are largely separated from each other far beyond van der Waals contact. In the case of **6c**, the butylenedithio bridges are expected to be long enough to be able to reduce the strain of the TTF moieties. However, the molecular structure of **6c** demonstrates that the dihedral angles are still large with 24−40°. There is a considerable conformational restriction in the butylene groups: nearly all methylenes are forced to take torsional gauche conformations to make the bridges rigid and stretched, so that they stand perpendicular to the TTF moieties against reduction of the strain. On the other hand, the molecular structure of **6d** with pentylenedithio bridges is fairly freed from such strain: all the bridged methylenes take anti conformations and the dihedral angles are only 6−17°. In addition, **6d** has an appropriate cavity whose size is large enough to include a chloroform molecule derived from solvent, as seen in Figure 4. In contrast, the inside cavities of **6a** and **6c** are too small to include such a guest species. Interestingly, a crystal of **6c** incorporates carbon disulfides in the lattice outside the molecules.

Spectroscopic Properties. It is well known that the electronic spectra of cyclophane compounds generally show marked bathochromic and hyperchromic shifts due to transannular electronic interactions between the two stacked π-electron chromophores.[12] The majority of the essence of the interactions is of exciton type rather than of charge-transfer type, so that the extent of such shifts largely depends on the overlapping orientation as well as on the transannular distance of the chromophores.[13] This means that crisscross-overlapped cyclophanes do not show so large a spectral change as parallel-overlapped ones, as previously observed for biphenylophanes.[14] Concordant with this, the electronic spectra of the present crisscross-overlapped TTF phanes demonstrate no shifts or rather hypsochromic shifts, as shown in Figure 5. Thus these spectra are roughly classified into the following two types: the electronic spectra of **6b** and **6d** have a remarkable resemblance to that of tetrakis(methylthio)-tetrathiafulvalene (TMT-TTF) as the normal reference, with an absorption edge reaching up to 500 nm. On the other hand, those of **6a** and **6c** are characterized by appearance of two definite peaks at around 260 and 330 nm with lack of the longest absorption. The latter change is speculated to be connected with the molecular structures characteristic of the bent TTF moieties described above. This speculation was supported by the fact that the electronic spectra of **6a** and **6c** are similar to that of **19**, which can be regarded as an appropriate model of a



TMT-TTF



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(12) Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes*; Academic Press, New York, 1983; Vols. I and II.

(13) Ferguson, J. *Chem. Rev.* **1986**, *86*, 958.

(14) Tani, K.; Seo, H.; Maeda, M.; Imagawa, K.; Nishiwaki, N.; Ariga, M.; Tohda, Y.; Higuchi, H.; Kuma, H. *Tetrahedron Lett.* **1995**, *36*, 1883.

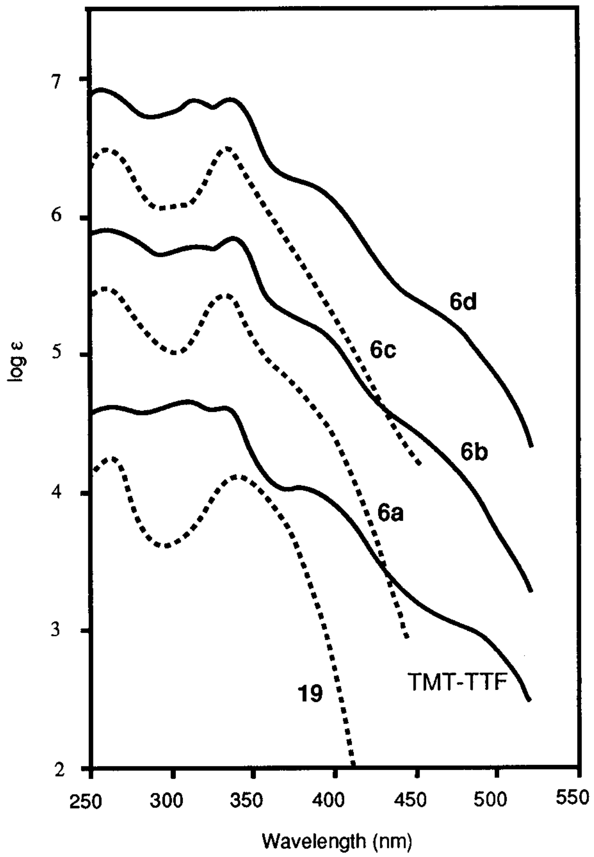

Figure 5. Electronic spectra of **6**, **19**, and TMT-TTF in THF. The spectra are displaced upward successively by 0.5 log ε unit from the bottom spectrum.

Table 1. Chemical Shifts of Central Fulvalenic Carbons of 6a–d and Related Compounds

compound	δ (ppm)	compound	δ (ppm)
6a	122.9	**6b**	112.9
6c	120.5	**6d**	112.5
19	129.1	TMT-TTF	111.0

bent TTF compound.[15] However, this discussion is based on the assumption that **6a** and **6c** adopt the same strained molecular structures in the solid and in solution. In addition, it may leave a question that **6b** with the shorter bridges has rather less strain than the higher homolog **6c**. A detailed examination of molecular structures suggests that **6b** has less conformational restriction in the bridged methylenes and, as a whole, a more flexible structure than **6c**.

A definitive evidence of the bent TTFs in solution was obtained in ^{13}C NMR measurements. Müllen et al. previously pointed out that the bending of the TTF moiety causes a noticeable downfield shift for the resonance of the central fulvalenic carbons.[16] Table 1 summarizes the chemical shifts of the fulvalenic carbons of the present TTF phanes together with two reference compounds, TMT-TTF and **19**. Evidently those of **6b** and **6d** are almost the same as that of TMT-TTF, supporting free-strain for these TTF phanes. On the other hand, those of **6a** and **6c** show significant downfield shifts as seen for **19**, indicating considerable bending of the TTF moieties.

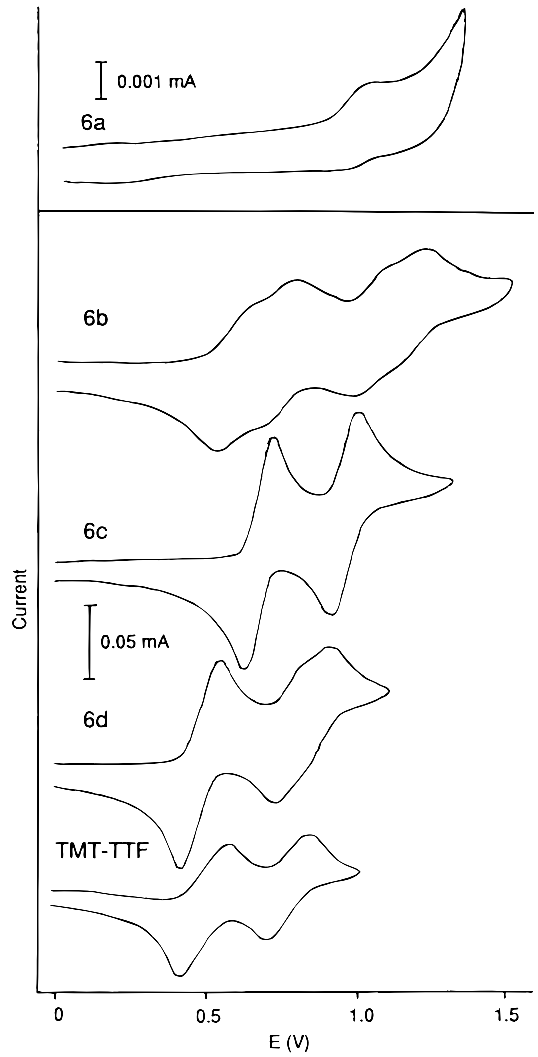

Figure 6. Cyclic voltammograms of **6** and TMT-TTF (1.0 × 10^{-3} mol dm^{-3} except for **6a**: 6.5 × 10^{-4} mol dm^{-3}) in benzonitrile containing 0.1 mol dm^{-3} ^{n}Bu$_4$NClO$_4$ as supporting electrolyte, Ag/AgCl reference electrode, 1 mm ∅ × 30 mm Pt-wire working electrode, scan rate 100 mV s^{-1}.

Table 2. Half-Wave Oxidation Potentials[a] (V) of 6, 19, and TMT-TTF

compound	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_{1/2}(4)$
6a	0.94[b]			
6b	0.57(1e)	0.70(1e)	0.98(1e)	1.11(1e)
6c	0.60(2e)		0.89 (2e)	
6d	0.46(2e)		0.74(1e)	0.85(1e)
19	1.01[b]			
TMT-TTF	0.49(1e)		0.71(1e)	

[a] Cyclic voltammetry was carried out at a scan rate of 100 mV s^{-1} with Pt working and counter electrodes and an Ag/AgCl reference electrode in 10^{-3} mol dm^{-3} benzonitrile solution containing 10^{-1} mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. [b] Irreversible anodic peak.

As is distinct from the above electronic spectroscopy, cyclic voltammetry provided important information on the transannular electronic interaction of the crisscross-overlapped TTF phanes **6**. Figure 6 demonstrates their voltammograms and Table 2 summarizes the half-wave oxidation potentials. The most strained molecule **6a** shows only one irreversible oxidation wave at an extraordinarily high potential (+0.94 V). Thus **6a** can no longer

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(15) Compound **19** was prepared by the intramolecular coupling reaction of the corresponding macrocyclic bis(1,3-dithiol-2-one), 2,9,11,13,15,22,24,26-octathiatricyclo[21.3.0.0^{10,14}]hexacosa-1(23),10(14)-diene-12,25-dione, mediated by triethyl phosphite.

(16) Röhrich, J.; Wolf, P.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1377.

behave as a good electron donor. This is due to the severe bending of the TTF moieties, because **19** also has a high oxidation potential (+1.01 V). On the other hand, the cyclic voltammogram of **6b** has four reversible redox waves, which each corresponds to a one-electron process. The splitting of the first and second waves as well as the third and fourth ones clearly supports that the two TTF moieties strongly interact with each other. The first half-wave oxidation potential (+0.57 V) is slightly higher than that of TMT-TTF (+0.49 V), but the second one (+0.70 V) is markedly higher. This indicates that the splitting is ascribed to intramolecular Coulombic repulsion of the resulting dicationic TTF species. Similar Coulombic repulsion is also responsible for the splitting and high potentials of the third (+0.98 V) and fourth (+1.11 V) oxidations as compared with the second one of TMT-TTF (0.71V). In contrast, **6c** shows only two reversible redox waves (+0.60 V and +0.89 V), which each corresponds to a two-electron process. Both the first and second half-wave oxidation potentials are somewhat higher than the respective ones of TMT-TTF, suggesting the bent structure of the TTF moieties. The equivalent redox behavior of the two TTF moieties indicates that there exists no Coulombic interaction between two TTF moieties of **6c**. These results are consistent with the above consideration of the molecular structure of **6c** based on the UV and ^{13}C-NMR spectra and X-ray analysis. Rather unusual phenomena were found for the redox process of **6d**: the first redox process occurs with a two-electron process, but the half-wave oxidation potential (+0.46 V) is a little lower than that (+0.49 V) of TMT-TTF. Such a low potential shift has been found for *peri*-naphthalene-inserted dimeric TTF by Iyoda et al.,[17] who suggest an attractive interaction of the two TTF moieties. Probably the monocationic species of the flexible compound **6d** can take a favorable conformation for transannular charge delocalization. On the other hand, the second oxidation process splits into two waves with high potentials (+0.74 V and +0.85 V), also demonstrating the emergence of Coulombic repulsion in the higher oxidation state. These voltammetric results suggest that **6b** and **6d** with less strained and interactive TTF units might be good electron donors for conducting molecular complexes.

Molecular Complexes. Formation of molecular complexes of **6** was examined by galvanostatic electrochemical crystallization in the presence of tetrabutylammonium perchlorate, hexafluorophosphate, or bromide. Although **6a** afforded no crystalline complexes as expected from the cyclic voltammetry, the others formed crystalline radical cation salts. As summarized in Table 3, the conductivities of all the salts are of the order of 10^{-6}–10^{-7} Scm^{-1}, independent of the donor and the counter ion species. The same low conductivities of the salts of **6b** and **6d** as those of **6c** fell short of our expectations. The crystal structure of the **6d**·Br complex explains a reason for its low conductivity. The TTF phane **6d** still maintains the inclusion ability even in the radical cation state, including an ethanol used as a co-solvent inside the cavity (Figure 7). Therefore, the TTF unit of **6d** can interact intermolecularly with the TTFs of the neighboring molecules but not intramolecularly with the other TTF of the same molecule. In addition, Figure 7 exhibits another interesting inclusion feature that the counter bromide is located at the entrance of the cavity. This suggests that more sophisticated crisscross-overlapped TTF phanes might be designed as novel host donor molecules which include the counter acceptor or anion inside the molecules.

Table 3. Radical Cation Salts of 6b−d

radical salt	appearance	D:A[a]	conductivity[b] (S cm^{-1})
6b·ClO_4	dark wine-red crystals	1:1	5.4×10^{-7}
6c·ClO_4	deep green crystals	1:1	6.2×10^{-7}
6d·ClO_4	deep green powder	1:2	7.3×10^{-7}
6b·PF_6	dark wine-red crystals	3:2	1.1×10^{-6}
6c·PF_6	black powder	1:1	1.3×10^{-6}
6d·PF_6	black needles	2:3	3.1×10^{-7}
6d·Br	black plates	1:1[c]	1.4×10^{-6} [d]

[a] Determined on the basis of elemental analyses. [b] Measured on a compressed pellet with a two-probe technique. [c] Determined by an X-ray analysis, which indicated inclusion of an additional ethanol. [d] Measured on a single crystal with a two-probe technique.

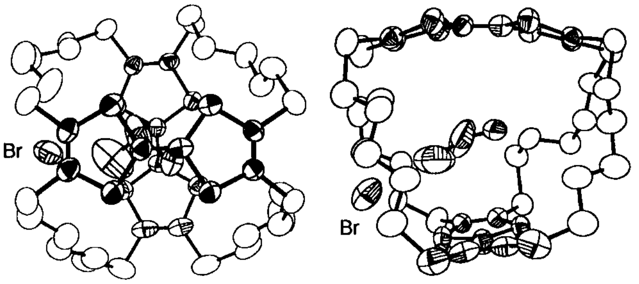

Figure 7. ORTEP drawings of **6d**·Br: a top view (left) and a side view (right).

Conclusion

A series of novel tetrathiafulvalenophanes, in which two tetrathiafulvalenes (TTF) are linked in a crisscross-overlapped arrangement by four alkylenedithio bridges, has been synthesized and elucidated by X-ray crystal analyses. Their unique molecular structures are characterized by the bent TTF skeletons and the inside cavity. The rigid compounds **6a** and **6c** have the severely bent TTFs with high oxidation potentials. On the other hand, the flexible ones **6b** and **6d** undergo transannular Coulombic interactions between the two TTF units in solution, but have the large cavities in the solid state, which include a guest molecule. These structural features are disadvantageous to the formation of conductive radical cationic salts of the crisscross-overlapped TTF phanes.

Experimental Section

General. Melting points are uncorrected. Nuclear magnetic resonance spectra were obtained in the indicated deuteriated solvents with Bruker AMX-400wb or JEOL Lambda 400 spectrometers operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C with TMS as the internal reference; chemical shifts (δ) are reported in parts per million. Mass spectral data were obtained on Shimadzu QP-2000 or Hitachi M-80B spectrometers using an electron impact ionization procedure. Infrared (IR) and UV-vis spectra were obtained on a Shimadzu FTIR-8100A spectrophotometer and on a Shimadzu UV-3100 spectrophotometer, respectively. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator. Elemental analyses were performed by Mr. Hideaki Iwatani, Microanalytical Laboratory in Department of Applied Chemistry, Faculty of Engineering, Hiroshima University. All chemicals and solvents are of reagent grade. All reactions were carried out under a nitrogen atmosphere with dry solvents. Column chromatography was carried out with Daisogel IR-60 (63−210

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[17] Kux, U.; Iyoda, M. *Chem. Lett.* **1994**, 2327.

μm). Bis(tetrabutylammonium)bis(1,3-dithiole-2-thione-4,5-dithiolato)zincate **7**,[10] 4,5-bis[(2-hydroxyethyl)thio]-1,3-dithiole-2-thione (**14**), and 4,5-bis[[(2-(tosyloxy)ethyl]thio]-1,3-dithiole-2-thione (**15**)[11] were synthesized according to the literature procedures.

General Procedure for Reaction of 7 with 1-Bromo-ω-chloroalkanes. Synthesis of 4,5-Bis[(3-chloropropyl)thio])-1,3-dithiole-2-thione (8b). To a solution of the zincate **7** (3.77 g, 4.00 mmol) in acetone (40 mL) was added 1-bromo-3-chloropropane (1.6 mL, 16 mmol), and the mixture was stirred at room temperature for 2 days. Evaporation of the solvent gave a viscous oil, which was dissolved in CH$_2$Cl$_2$ (50 mL). The solution was successively washed with saturated aqueous NaHCO$_3$ solution (2 × 50 mL) and water (2 × 50 mL), dried over MgSO$_4$, and then concentrated. The crude product was purified by column chromatography on silica gel with 1:1 CHCl$_3$/hexane to give 2.27 g (97%) of **8b** as a yellow oil. ^{1}H NMR (CDCl$_3$) δ 2.12 (quintet, $J = 6.6$ Hz, 4H), 3.06 (t, $J = 6.6$ Hz, 4H), 3.69 (t, $J = 6.6$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 32.0, 33.8, 42.8, 136.3, 210.7; IR (neat) 1050 cm^{-1}; MS (DI) *m/z* 350 (M$^+$). Anal. Calcd for C$_9$H$_{12}$Cl$_2$S$_5$: C, 30.76; H, 3.44. Found: C, 30.51; H, 3.47.

4,5-Bis[(4-chlorobutyl)thio]-1,3-dithiole-2-thione (8c). Reaction of **7** (6.60 g, 7.00 mmol) with 1-bromo-4-chlorobutane (3.2 mL, 28 mmol) in acetone (70 mL) for 2 days gave 4.79 g (91%) of **8c** as a yellow oil. ^{1}H NMR (CDCl$_3$) δ 1.87 (quintet, $J = 6.4$ Hz, 4H), 2.12 (quintet, $J = 6.4$ Hz, 4H), 3.06 (t, $J = 6.4$ Hz, 4H), 3.69 (t, $J = 6.4$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 26.8, 31.0, 36.0, 44.2, 136.1, 210.7; IR (neat) 1065 cm^{-1}; MS (DI) *m/z* 378 (M$^+$). Anal. Calcd for C$_{11}$H$_{16}$Cl$_2$S$_5$: C, 34.82; H, 4.25. Found: C, 34.63; H, 4.25.

4,5-Bis[(5-chloropentyl)thio]-1,3-dithiole-2-thione (8d). Reaction of **7** (18.7 g, 20.2 mmol) with 1-bromo-5-chloropentane (10.7 mL, 81 mmol) in acetone (250 mL) for 2 days gave 15.7 g (96%) of **8d** as a yellow oil. ^{1}H NMR (CDCl$_3$) δ 1.60−1.80 (m, 12H), 2.97 (t, $J = 6.6$ Hz, 4H), 3.64 (t, $J = 6.6$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 25.7, 28.2, 31.9, 36.5, 44.7, 136.1, 210.8; IR (neat) 1064 cm^{-1}; MS (DI) *m/z* 406 (M$^+$). Anal. Calcd for C$_{13}$H$_{20}$Cl$_2$S$_5$: C, 38.31; H, 4.95. Found: C, 38.27; H, 4.84.

Preparation of 4,5-Bis[(2-chloroethyl)thio]-1,3-dithiole-2-thione (8a). A mixture of the tosylate **15**[11] (557 mg, 0.597 mmol) and NaCl (560 mg, 9.57 mmol) in DMF (20 mL) was stirred at 80 °C for 12 h. The mixture was poured into ice−water (100 mL), and the resulting solid was collected by filtration and extracted with CH$_2$Cl$_2$ (50 mL). The extract was washed with H$_2$O (2 × 30 mL), dried over MgSO$_4$, and then concentrated. Column chromatography on silica gel with CH$_2$Cl$_2$ followed by recrystallization from CHCl$_3$ gave 300 mg (97%) of **8a** as yellow needles. Mp 68.0−68.5 °C; ^{1}H NMR (CDCl$_3$) δ 3.23 (t, $J = 7.5$ Hz, 2H), 3.72 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 38.3, 42.2, 136.0, 209.8; IR (KBr) 1067 cm^{-1}; MS (DI) *m/z* 322 (M$^+$). Anal. Calcd for C$_7$H$_8$Cl$_2$S$_5$: C, 26.00; H, 2.49. Found: C, 26.09; H, 2.53.

General Procedure for Oxidation of 8. Synthesis of 4,5-Bis[(2-chloroethyl)thio]-1,3-dithiol-2-one (9a). A suspension of Hg(OAc)$_2$ (636 mg, 2.00 mmol) in AcOH (5 mL) was added to a solution of **8a** (300 mg, 0.93 mmol) in CHCl$_3$ (20 mL), and the mixture was stirred at room temperature for 2 h. The resulting insoluble material was filtered off through a Celite pad, and the filtrate was successively washed with H$_2$O (2 × 30 mL) and saturated aqueous NaHCO$_3$ solution (2 × 30 mL), dried over MgSO$_4$, and then concentrated. Chromatography on silica gel with CH$_2$Cl$_2$ gave 267 mg (94%) of **9a** as a pale yellow solid. An analytical pure sample was obtained by further purification with preparative GPC and then recrystallization from hexane as pale yellow prisms. Mp 47−48 °C; ^{1}H NMR (CDCl$_3$) δ 3.20 (t, $J = 7.8$ Hz, 2H), 3.71 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 38.2, 42.2, 127.3, 188.3; IR (KBr) 1669 cm^{-1}; MS (DI) *m/z* 306 (M$^+$). Anal. Calcd for C$_7$H$_8$Cl$_2$OS$_4$: C, 27.36; H, 2.62. Found: C, 27.50; H, 2.55.

4,5-Bis[(3-chloropropyl)thio]-1,3-dithiol-2-one (9b). Reaction of **8b** (8.24 g, 23.5 mmol) with Hg(OAc)$_2$ (17.9 g, 56.4 mmol) in chloroform (200 mL) and acetic acid (200 mL) for 1 h gave 7.45 g (95%) of **9b** as a pale yellow oil. ^{1}H NMR (CDCl$_3$) δ 2.10 (quintet, $J = 6.6$ Hz, 4H), 3.03 (t, $J = 6.6$ Hz, 4H), 3.68 (t, $J = 6.6$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 31.9, 33.6, 42.7, 127.3, 189.1; IR (neat) 1669 cm^{-1}; MS (DI) *m/z* 334 (M$^+$). Anal. Calcd for C$_9$H$_{12}$Cl$_2$OS$_4$: C, 32.23; H, 3.61. Found: C, 32.15; H, 3.61.

4,5-Bis[(4-chlorobutyl)thio]-1,3-dithiol-2-one (9c). Reaction of **8c** (4.48 g, 11.9 mmol) with Hg(OAc)$_2$ (9.10 g, 28.6 mmol) in chloroform (100 mL) and acetic acid (10 mL) for 2 h gave 3.00 g (70%) of **9c** as a yellow oil. ^{1}H NMR (CDCl$_3$) δ 1.81−1.85 (m, 4H), 1.91−1.95 (m, 4H), 2.89 (t, $J = 6.6$ Hz, 4H), 3.52 (t, $J = 6.6$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 26.8, 31.0, 35.8, 44.2, 127.2, 189.5; IR (neat) 1669 cm^{-1}; MS (DI) *m/z* 362 (M$^+$). Anal. Calcd for C$_{11}$H$_{16}$Cl$_2$OS$_4$: C, 36.36; H, 4.44. Found: C, 36.31; H, 4.48.

4,5-Bis[(5-chloropentyl)thio]-1,3-dithiol-2-one (9d). Reaction of **8d** (9.77 g, 24.0 mmol) with Hg(OAc)$_2$ (18.4 g, 57.0 mmol) in chloroform (200 mL) and acetic acid (10 mL) for 2 h gave 9.15 g (97%) of **9d** as a yellow oil. ^{1}H NMR (CDCl$_3$) δ 1.56−1.62 (m, 4H), 1.65−1.71 (m, 4H), 1.76−1.84 (m, 4H), 1.69 (quintet, $J = 7.1$ Hz, 4H), 1.80 (quintet, $J = 6.5$ Hz, 4H), 2.87 (t, $J = 7.1$ Hz, 4H), 3.54 (t, $J = 6.5$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 25.7, 28.8, 31.9, 36.3, 44.7, 127.1, 189.6; IR (neat) 1671 cm^{-1}; MS (DI) *m/z* 390 (M$^+$). Anal. Calcd for C$_{13}$H$_{20}$Cl$_2$OS$_4$: C, 39.89; H, 5.15. Found: C, 39.88; H, 4.91.

General Procedure for Self-Coupling of 9. Synthesis of 2,3,6,7-Tetrakis[(2-chloroethyl)thio]-1,4,5,8-tetrathiafulvalene (10a). Into a refluxing solution of **9a** (267 mg, 0.87 mmol) in benzene (20 mL) was added triethyl phosphite (1.0 mL, 5.8 mmol), and the mixture was further refluxed for 12 h. The solvent was evaporated, and the residue was adsorbed to a small amount of silica gel, which was then placed on the top of silica gel column and developed with CHCl$_3$ to give the crude product. Recrystallization from CHCl$_3$/MeOH provided 188 mg (74%) of **10a** as orange fine crystals. Mp 160−161 °C; ^{1}H NMR (CS$_2$/CDCl$_3$) δ 3.16 (t, $J = 7.8$ Hz, 4H), 3.69 (t, $J = 7.8$ Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 37.8, 42.4, 110.8, 128.0; MS (DI) *m/z* 582 (M$^+$). Anal. Calcd for C$_{14}$H$_{16}$Cl$_4$S$_8$: C, 28.86; H, 2.77. Found: C, 29.09: H, 2.71.

2,3,6,7-Tetrakis[(3-chloropropyl)thio]-1,4,5,8-tetrathiafulvalene (10b). Reaction of **9b** (6.40 g, 19.1 mmol) with triethyl phosphite (33 mL, 190 mmol) in benzene (20 mL) for 12 h gave, after recrystallization from acetone/EtOH, 4.78 g (78%) of **10b** as orange needles. Mp 63−64 °C; ^{1}H NMR (CDCl$_3$) δ 2.10 (quintet, $J = 6.6$ Hz, 8H), 2.96 (t, $J = 6.6$ Hz, 8H), 3.65 (t, $J = 6.6$ Hz, 8H); ^{13}C NMR (CDCl$_3$) δ 32.1, 33.2, 42.9, 110.5, 128.1; MS (DI) *m/z* 638 (M$^+$). Anal. Calcd for C$_{18}$H$_{24}$Cl$_4$S$_8$: C, 33.87; H, 3.79. Found: C, 33.78; H, 3.73.

2,3,6,7-Tetrakis[(4-chlorobutyl)thio]-1,4,5,8-tetrathiafulvalene (10c). Reaction of **9c** (3.00 g, 8.29 mmol) with triethyl phosphite (29 mL, 160 mmol) in benzene (20 mL) for 16 h gave, after recrystallization from acetone, 2.59 g (90%) of **10c** as orange needles. Mp 52.5−53.0 °C; ^{1}H NMR (CDCl$_3$) δ 1.80 (quintet, $J = 6.8$ Hz, 8H), 1.92 (quintet, $J = 6.8$ Hz, 8H), 2.86 (t, $J = 6.8$ Hz, 8H), 3.57 (t, $J = 6.8$ Hz, 8H); ^{13}C NMR (CDCl$_3$) δ 26.9, 31.1, 35.5, 44.3, 110.4, 127.7; MS (DI) *m/z* 694 (M$^+$). Anal. Calcd for C$_{22}$H$_{32}$Cl$_4$S$_8$: C, 38.03 H, 4.64. Found: C, 37.79; H, 4.65.

2,3,6,7-Tetrakis[(5-chloropentyl)thio]-1,4,5,8-tetrathiafulvalene (10d). Reaction of **9d** (8.72 g, 22.0 mmol) with triethyl phosphite (64 mL, 370 mmol) in benzene (50 mL) for 20 h gave, after recrystallization from acetone, 12.9 g (78%) of **10d** as orange needles. Mp 39−40 °C; ^{1}H NMR (CDCl$_3$) δ 1.51−1.76 (m, 8H), 1.67 (quintet, $J = 7.1$ Hz, 8H), 1.80 (quintet, $J = 6.6$ Hz, 8H), 2.83 (t, $J = 7.1$ Hz, 8H), 3.54 (t, $J = 6.6$ Hz, 8H); ^{13}C NMR (CDCl$_3$) δ 25.6, 28.9, 31.9, 35.8, 44.7, 110.1, 127.6; MS (DI) *m/z* 750 (M$^+$). Anal. Calcd for C$_{26}$H$_{40}$Cl$_4$S$_8$: C, 41.59; H, 5.37. Found: C, 41.53; H, 5.32.

General Procedure for Halogen Exchange of 10. Synthesis of 2,3,6,7-Tetrakis[(2-iodoethyl)thio]-1,4,5,8-tetrathiafulvalene (11a). A mixture of **10a** (176 mg, 0.30 mmol) and NaI (450 mg, 3.0 mmol) in acetone (30 mL) and dioxane (5 mL) was refluxed for 3 days. After the solvent was evaporated, the resulting solid was extracted with CS$_2$ (30 mL), and the extract was successively washed with H$_2$O (2 × 30 mL) and 10% aqueous NaHSO$_3$ solution (30 mL) and dried over MgSO$_4$. Chromatography on silica gel with 1:1 CH$_2$Cl$_2$/CS$_2$ gave an orange solid, which was further purified by GPC and then recrystallized from CHCl$_3$ to give 204 mg (72%) of **11a** as orange needles. Mp 179−180 °C dec; ^{1}H NMR (CDCl$_3$) δ 3.23−

3.30 (m, 8H), 3.31−3.38 (m, 8H). Anal. Calcd for $C_{14}H_{16}S_8I_4$: C, 17.73; H, 1.70. Found: C, 17.80; H, 1.69.

2,3,6,7-Tetrakis[(3-iodopropyl)thio]-1,4,5,8-tetrathiafulvalene (11b). Reaction of **10b** (4.02 g, 6.29 mmol) with NaI (37.8 g, 252 mmol) in acetone (230 mL) and dioxane (80 mL) for 1 day gave, after recrystallization from acetone, 4.80 g (76%) of **11b** as orange needles. Mp 74−75 °C; ^{1}H NMR ($CDCl_3$) δ 2.12 (quintet, J = 6.6 Hz, 8H), 2.95 (t, J = 6.6 Hz, 8H), 3.33 (t, J = 6.6 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 4.2, 32.8, 36.7, 110.7, 128.0. Anal. Calcd for $C_{18}H_{24}I_4S_8$: C, 21.52; H, 2.40. Found: C, 21.77; H, 2.40.

2,3,6,7-Tetrakis[(4-iodobutyl)thio]-1,4,5,8-tetrathiafulvalene (11c). Reaction of **10c** (2.78 g, 4.01 mmol) with NaI (12.0 g, 80.1 mmol) in acetone (150 mL) and dioxane (50 mL) for 1 day gave, after recrystallization from acetone, 3.44 g (81%) of **11c** as orange needles. Mp 79−80 °C; ^{1}H NMR ($CDCl_3$) δ 1.76 (quintet, J = 6.8 Hz, 8H), 1.96 (quintet, J = 6.8 Hz, 8H), 2.84 (t, J = 6.8 Hz, 8H), 3.20 (t, J = 6.8 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 5.8, 30.4, 31.9, 35.1, 110.6, 127.8. Anal. Calcd for $C_{22}H_{32}I_4S_8$: C, 24.91 H, 3.04. Found: C, 25.15; H, 3.04.

2,3,6,7-Tetrakis[(5-iodopentyl)thio]-1,4,5,8-tetrathiafulvalene (11d). Reaction of **10d** (10.0 g, 13.3 mmol) with NaI (24.0 g, 160 mmol) in acetone (200 mL) and dioxane (50 mL) for 1 day gave, after recrystallization from acetone, 12.2 g (82%) of **11d** as orange needles. Mp 57−58 °C; ^{1}H NMR ($CDCl_3$) δ 1.54 (quintet, J = 6.7 Hz, 8H), 1.67 (quintet, J = 6.7 Hz, 8H), 1.86 (quintet, J = 6.7 Hz, 8H), 2.83, (t, J = 6.7 Hz, 8H), 3.20 (t, J = 6.7 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 6.5, 28.7, 32.9, 35.9, 39.3, 110.3, 127.7. Anal. Calcd for $C_{26}H_{40}I_4S_8$: C, 27.97; H, 3.61. Found: C, 27.99; H, 3.61.

General Procedure for Coupling of 7 and 11. Synthesis of 2,7:3,6-Bis[2′-thioxo-1′,3′-dithiole-4′,5′-diylbis(ethylenedithio)]-1,4,5,8-tetrathiafulvalene (16a). Two THF solutions (50 mL each) of the zincate **7** (310 mg, 0.34 mmol) and of **11a** (320 mg, 0.34 mmol) were added simultaneously into refluxing THF (100 mL) over a period of 8 h, and the mixture was further refluxed for 2 days. Evaporation of the solvent gave a reddish black tar, which was washed with acetone (200 mL) to afford a yellow solid (130 mg) containing **16a**. Because of the poor solubility of **16a**, the crude solid was used for the conversion to **17a** without further purification. An analytical sample was obtained by silica gel column chromatography with 2:1 CH_2Cl_2/CS_2 and subsequent recrystallization from CS_2 as yellow needles. Mp 270 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 2.88 (ddd, J = 5.0, 9.7, 13.9 Hz, 4H), 3.14 (ddd, J = 6.1, 9.7, 11.6 Hz, 4H), 3.23 (ddd, J = 5.0, 9.6, 11.6 Hz, 4H), 3.42 (ddd, J = 6.1, 9.6, 13.9 Hz, 4H); IR (KBr) 1076 cm^{-1}. Anal. Calcd for $C_{20}H_{16}S_{18}$: C, 28.82; H, 1.93. Found: C, 28.52; H, 1.93.

2,7:3,6-Bis[2′-thioxo-1′,3′-dithiole-4′,5′-diylbis(propane-1,3-diyldithio)]-1,4,5,8-tetrathiafulvalene (16b). Reaction of the zincate **7** (1.55 g, 1.64 mmol) and **11b** (1.50 g, 1.49 mmol) in THF (750 mL) for 36 h gave 601 mg of crude **16b** as a yellow solid. Silica gel chromatography and recrystallization from CS_2/hexane afforded an analytical pure sample of **16b** as yellow plates. Mp 231−232 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 2.01 (quintet, J = 6.9 Hz, 8H), 3.02 (t, J = 6.9 Hz, 8H), 3.03 (t, J = 6.9 Hz, 8H); IR (KBr) 1062 cm^{-1}. Anal. Calcd for $C_{24}H_{24}S_{18}$: C, 32.40; H, 2.72. Found: C, 32.39; H, 2.66.

2,7:3,6-Bis[2′-thioxo-1′,3′-dithiole-4′,5′-diylbis(butane-1,4-diyldithio)]-1,4,5,8-tetrathiafulvalene (16c). Reaction of the zincate **7** (1.89 g, 2.00 mmol) and **11c** (1.06 g, 1.00 mmol) in THF (400 mL) for 12 h gave 412 mg of crude **16c** as an orange solid. Silica gel chromatography and recrystallization from CS_2/hexane afforded an analytical pure sample of **16c** as yellow plates. Mp 199 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 1.77−1.89 (m, 16H), 2.80 (t, J = 6.8 Hz, 8H), 2.92 (t, J = 6.8 Hz, 8H); IR (KBr) 1062 cm^{-1}. Anal. Calcd for $C_{28}H_{32}S_{18}$: C, 34.82; H, 4.25. Found: C, 34.63; H, 4.25.

2,7:3,6-Bis[2′-thioxo-1′,3′-dithiole-4′,5′-diylbis(pentane-1,5-diyldithio)]-1,4,5,8-tetrathiafulvalene (16d). Reaction of the zincate **7** (3.17 g, 3.36 mmol) and **11d** (2.50 g, 2.24 mmol) in THF (500 mL) for 36 h gave 706 mg of crude **16d** as a reddish black solid. Silica gel chromatography and recrystallization from $CHCl_3$/MeOH afforded an analytical pure sample of **16d** as orange needles. Mp 201 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 1.56−1.62 (m, 8H), 1.67−1.76 (m, 16H), 2.77 (t, J = 6.8 Hz, 8H), and 2.90 (t, J = 6.8 Hz, 8H); IR (KBr) 1065 cm^{-1}. Anal. Calcd for $C_{32}H_{40}S_{18}$: C, 38.37; H, 4.02. Found: C, 38.13; H, 4.04.

General Procedure for Oxidation of 16. Synthesis of Bis[2′-oxo-1′,3′-dithiole-4′,5′-diylbis(ethylenedithio)]-1,4,5,8-tetrathiafulvalene (17a). To a suspension of crude **16a** (130 mg) in $CHCl_3$ (20 mL) was added a solution of $Hg(OAc)_2$ (100 mg, 0.31 mmol) in AcOH (3 mL). The mixture was stirred at room temperature for 12 h and then concentrated to give a white solid. The solid was extracted with CS_2 (50 mL), and the extract was successively washed with H_2O (2 × 50 mL) and saturated aqueous $NaHCO_3$ solution (2 × 50 mL) and dried over $MgSO_4$. Column chromatography on silica gel eluted with 2:1 CH_2Cl_2/CS_2 gave a pale yellow solid, which was further purified by preparative GPC to give 50 mg (18% based on **11a**) of **17a** as a pale yellow powder. Mp 254 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 2.87 (ddd, J = 5.0, 9.7, 13.9 Hz, 4H), 3.11 (ddd, J = 6.1, 9.7, 11.6 Hz, 4H), 3.20 (ddd, J = 5.0, 9.6, 11.6 Hz, 4H), 3.44 (ddd, J = 6.1, 9.6, 13.9 Hz, 4H); IR (KBr) 1667 cm^{-1}; MS m/z 800 (M$^+$). Anal. Calcd for $C_{20}H_{16}O_2S_{16}$: C, 29.98; H, 2.01. Found: C, 29.76; H, 1.94.

2,7:3,6-Bis[2′-oxo-1′,3′-dithiole-4′,5′-diylbis(propane-1,3-diyldithio)]-1,4,5,8-tetrathiafulvalene (17b). Reaction of crude **16b** (601 mg) with $Hg(OAc)_2$ (431 mg, 1.35 mmol) in $CHCl_3$ (20 mL) and AcOH (3 mL) for 12 h gave, after recrystallization from CS_2/hexane, 360 mg (28% based on **11b**) of **17b** as yellow plates. Mp 234 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 1.96 (quintet, J = 6.9 Hz, 8H), 2.97 (t, J = 6.9 Hz, 8H), 2.98 (t, J = 6.9 Hz, 8H); ^{13}C NMR ($CS_2/CDCl_3$) δ 29.5, 34.7, 34.9, 118.7, 127.1, 127.4, 189.4; IR (KBr) 1669 cm^{-1}. Anal. Calcd for $C_{24}H_{24}O_2S_{16}$: C, 33.62; H, 2.82. Found: C, 33.58; H, 2.83.

2,7:3,6-Bis[2′-oxo-1′,3′-dithiole-4′,5′-diylbis(butane-1,4-diyldithio)]-1,4,5,8-tetrathiafulvalene (17c). Reaction of crude **16c** (412 mg) with $Hg(OAc)_2$ (277 mg, 0.87 mmol) in $CHCl_3$ (30 mL) and AcOH (5 mL) for 12 h gave, after recrystallization from CS_2/hexane, 128 mg (14% based on **11c**) of **17c** as yellow plates. Mp 207−208 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 1.77 (quintet, J = 7.0 Hz, 8H), 1.86 (quintet, J = 7.0 Hz, 8H), 2.84 (t, J = 7.0 Hz, 8H,), 2.90 (t, J = 7.0 Hz, 8H); ^{13}C NMR ($CS_2/CDCl_3$) δ 28.2, 29.1, 35.0, 36.5, 114.0, 126.9, 128.1, 189.4; IR (KBr) 1671 cm^{-1}. Anal. Calcd for $C_{28}H_{32}O_2S_{16}$: C, 36.81; H, 3.53. Found: C, 37.09; H, 3.53.

2,7:3,6-Bis[2′-oxo-1′,3′-dithiole-4′,5′-diylbis(pentane-1,5-diyldithio)]-1,4,5,8-tetrathiafulvalene (17d). Reaction of crude **16d** (706 mg) with $Hg(OAc)_2$ (450 mg, 2.37 mmol) in $CHCl_3$ (70 mL) and AcOH (14 mL) for 12 h gave, after recrystallization from $CHCl_3$/MeOH, 428 mg (13% based on **11d**) of **17d** as orange plates. Mp 130−131 °C; ^{1}H NMR ($CS_2/CDCl_3$) δ 1.57−1.63 (m, 8H), 1.67−1.73 (m, 16H), 2.81 (t, J = 6.8 Hz, 8H), 2.88 (t, J = 6.8 Hz, 8H); ^{13}C NMR ($CS_2/CDCl_3$) δ 27.1, 28.6, 29.5, 35.6, 36.5, 112.6, 126.8, 127.3, 189.8; IR (KBr) 1669 cm^{-1}. Anal. Calcd for $C_{32}H_{40}O_2S_{16}$: C, 39.64; H, 4.16. Found: C, 39.46; H, 4.15.

General Procedure for Intramolecular Coupling of 17. Synthesis of Ethylenedithio-Bridged Tetrathiafulvalenophane (6a). Triethyl phosphite (0.72 mL, 4.2 mmol) was slowly added to a refluxing solution of **17a** (168 mg, 0.21 mmol) in toluene (50 mL), and the mixture was refluxed for additional 37 h. Evaporation of the solvent provided an orange solid, which was purified with silica gel column chromatography using CS_2 as an eluent and then recrystallized from CS_2/hexane to give 123 mg (76%) of **6a** as yellow needles. Mp 290 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 2.75−2.85 (m, 8H), 3.08−3.17 (m, 8H); ^{13}C NMR ($CS_2/CDCl_3$) δ 53.5, 122.9, 130.0; MS (DI) m/z 768 (M$^+$); UV-vis (THF) λ (log ϵ) 258 (4.46), 333 (4.47) nm. Anal. Calcd for $C_{20}H_{16}S_{16}$: C, 31.22; H, 2.10. Found: C, 31.01; H, 2.05.

Propane-1,3-diyldithio-Bridged Tetrathiafulvalenophane (6b). Reaction of **17b** (228 mg, 0.26 mmol) with triethyl phosphite (13.3 mL, 76.1 mmol) in toluene (100 mL) for 24 h gave, after recrystallization from CS_2/hexane, 139 mg (65%) of **6b** as orange crystals. Mp 278 °C dec; ^{1}H NMR ($CS_2/CDCl_3$) δ 2.11−2.20 (m, 8H), 2.75−2.80 (m, 16H); ^{13}C NMR ($CS_2/CDCl_3$) δ 32.7, 34.2, 112.9, 125.0; MS (DI) m/z 824 (M$^+$);

UV-vis (THF) λ (log ϵ) 263 (4.41), 313 (4.28), 338 (4.35), 384 (sh, 3.71), 468 (sh, 2.73) nm. Anal. Calcd for $C_{24}H_{24}S_{16}$: C, 34.92; H, 2.93. Found: C, 34.88; H, 2.89.

Butane-1,4-diyldithio-Bridged Tetrathiafulvalenophane (6c). Reaction of **17c** (294 mg, 0.32 mmol) with triethyl phosphite (4.5 mL, 26 mmol) in toluene (40 mL) for 2 days gave, after recrystallization from CS_2/hexane, 235 mg (83%) of **6c** as pale yellow needles. Mp 295 °C dec; ^{1}H NMR (CS_2/$CDCl_3$) δ 1.31−1.37 (m, 8H), 1.62−1.66 (m, 8H), 2.43−2.51 (m, 8H) and 2.95−3.01 (m, 8H); ^{13}C NMR (CS_2/$CDCl_3$) δ 27.0, 35.0, 120.5, 128.3; MS (DI) *m/z* 880 (M^+); UV-vis (THF) λ (log ϵ) 261 (4.49), 304 (sh, 4.08), 336 (4.50) nm. Anal. Calcd for $C_{29}H_{32}S_{18}$ (**3c**·CS_2): C, 36.37; H, 3.37. Found: C, 36.43; H, 3.36.

Pentane-1,5-diyldithio-Bridged Tetrathiafulvalenophane (6d). Reaction of **17d** (131 mg, 0.14 mmol) with triethyl phosphite (1.9 mL, 11 mmol) in toluene (10 mL) for 2 h gave, after recrystallization from $CHCl_3$/MeOH, 77 mg (61%) of **6d** as orange needles. Mp 265 °C dec; ^{1}H NMR (CS_2/$CDCl_3$) δ 1.44−1.49 (m, 8H), 1.68−1.77 (m, 16H), 2.65 (ddd, $J = 13.8$, 10.1, 6.4 Hz, 8H), 2.89 (ddd, $J = 13.8$, 10.1, 5.0 Hz, 8H); ^{13}C NMR (CS_2/$CDCl_3$) δ 29.2, 30.7, 35.9, 112.5, 126.0; MS (DI) *m/z* 936 (M^+); UV-vis (THF) λ (log ϵ) 258 (4.42), 314 (4.33), 336 (4.43), 388 (sh, 3.69), 474 (sh, 2.69) nm. Anal. Calcd for $C_{33}H_{41}S_{16}Cl$ (**3d**·$CHCl_3$): C, 37.49; H, 3.91. Found: C, 37.36; H, 3.98.

X-ray Crystallographic Analyses. X-ray diffraction experiments were performed at room temperature on a Rigaku AFC6S diffractometer or a Rigaku RASA7R diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å). The intensity data were measured using $\omega-2\theta$ scan technique. The structures were solved by direct methods and refined by full-matrix least-squares techniques with anisotropic temperature factors for the non-hydrogen atoms. The author has deposited atomic coordinates 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.

Acknowledgment. This work was supported by Grants-in-Aid of Scientific Research (Nos. 05453058, 06243105, 06453074, and 08740498) from the Ministry of Education, Science, Sports, and Culture, Japan. The authors also thank The Nishida Research Fund for fundamental organic chemistry and The Yazaki Memorial Foundation for Science and Technology for financial support.

Supporting Information Available: Synthetic procedures for compound **19** and characterization (3 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.

JO962239X