PREPARATION, PROPERTIES, AND OXIDATION OF NOVEL BIS(1,3-DITHIOLE) COMPOUNDS CONTAINING A DI(2-THIENYL)METHANE UNIT†

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Abstract – *Novel bis(1,3-dithiole) compounds* (**5**) and (**6**) containing a di(2-thienyl)methane unit have been prepared by either a Wittig or a Wittig–Horner reaction. These compounds showed irreversible cyclic voltammetric behavior. Oxidation products of **5** and **6** were strongly dependent on the substituents (R_1) on the C6-carbon atoms of the 1,4-dithiafulvenyl groups. In the case of R_1 = H (**5**), intermolecular coupling giving a redox-active oligomer selectively occurred. On the other hand, when R_1 was methyl, **6** underwent deprotonation by oxidation to give the corresponding stable dithienylmethyl cations showing intense absorptions in the near-infrared region (> 900 nm in MeCN).

On the development of organic conducting charge-transfer complexes or ion radical salts, the high stability of the charged states of their components is one of the most important requirements.[1] From this point of view, electron-donors or acceptors in which electron transfer is accompanied by chemical reactions have been considered quite useless. However, if the reaction processes and the resulting products can be identified properly, these compounds seem useful to explore the novel type of chemical reactions induced by electron transfer. Moreover, it is expected that the reaction can be applied to the preparation of novel compounds. In this connection, we reported that extended bis(1,3-dithiole) donors (**1**), which show irreversible oxidation waves in the cyclic voltammograms, underwent deprotonation from the dication states

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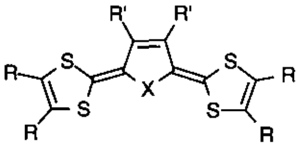
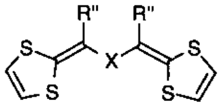
†Dedicated to Prof. Shigeru Oae on the occasion of his 77th birthday.

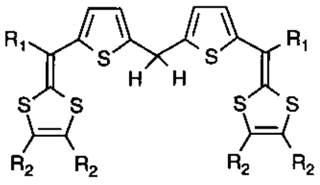
by oxidation to give novel interesting deeply-colored cations (**2**).[2] Molecules (**3**) containing a methylene group adjacent to electron-donating moieties such as a 1,3-dithiole unit seem to undergo a similar reaction to give the corresponding methyl cations (**4**). In order to prove the generality of this type of reaction and to apply it to the preparation of novel cations, we have now designed bis(1,3-dithiole) compounds (**5**) and (**6**) containing a dithienylmethane unit. These systems are considered as vinylogues of **3** extended by two thiophene units. The resulting cations (**7**) and (**8**) are expected to be stabilized by electron-donating groups and to show interesting properties owing to their extended π-conjugation caused by the insertion of the thiophene units. We report here the preparation, redox properties, and oxidation of **5** and **6**.[3]



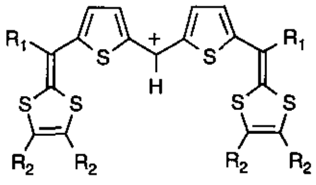
1 X = CH_2 **2** X = CH^+



3 X = CH_2 **4** X = CH^+



5 R_1 = H **6** R_1 = Me

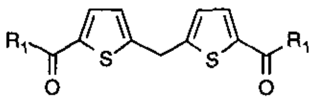


7 R_1 = H **8** R_1 = Me

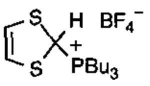
R_2, R_2
a H
b SMe
c SCH_2CH_2S
d benzo

RESULTS AND DISCUSSION

Preparation and Redox Properties. The new 1,3-dithiole compounds (**5**) and (**6**) were prepared by either a Witttig reaction of phosphonium salt (**11**)[4] (for **5a**) or a Wittig-Horner reaction of phosphonate esters (**12a–d**)[5] with aldehyde (**9**)[6] or ketone (**10**)[6] in 47–94% yields. For comparison, dimethyl derivatives (**13**) and (**14**) were synthesized by the similar method from the corresponding carbonyl compounds[6] in 65 and 69% yields, respectively.



9 R_1 = H **10** R_1 = Me



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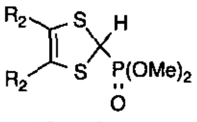
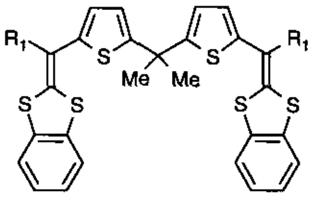


12a–d



13 R_1 = H **14** R_1 = Me

The X-ray molecular structure of the ethylenedithio derivative (**6c**) is shown in Figure 1. The two thiophene rings are orthogonal, while the thienyldithiafulvenyl subunits are nearly planar with the largest deviations of 0.39 and 0.63 Å from the mean planes. The interatomic distances (3.01 and 3.02 Å) between the sulfur atoms of the thiophene and the dithiole are shorter than the sum of the van der Waals radii (3.70 Å), indicating that there exist attractive interactions between them.[7]

In order to investigate the electrochemical behavior of the compounds (**5**) and (**6**), cyclic voltammetry experiments were carried out. The typical examples of the cyclic voltammograms (CVs) of **5d** and **6d** are shown in Figure 2 along with the corresponding dimethyl derivatives (**13**) and (**14**), and the redox potentials are summarized in Table 1. Both CVs of **5** and **6** showed irreversible oxidation waves at E_{pa}. In the reverse scan new reduction waves due to the oxidation products caused by subsequent chemical reactions were observed at lower potentials of E_{pc}(new). However, the shapes of the CVs were strongly dependent upon the substituents R_1 on the C6-carbons of the dithiafulvenyl groups. In the case of $R_1 = H$, both **5** and **13** exhibit almost the same cyclic voltammetric behavior. Thus, the methyl groups on the central carbon atom do not affect the subsequent reaction. This result indicates that **5** do not undergo deprotonation by oxidation, but another reaction takes place. The details will be discussed later in this paper. On the other hand, **14** showed a reversible redox wave in the potential range of –0.5 to 1.10 V. Thus, it can be concluded that the new reduction peaks [E_{pc}(new)] observed in the CV of **6** correspond to the reduction of the cations (**8**) which arose from deprotonation subsequent to electrochemical oxidation of **5**.

Isolation and Characterization of Cations. Oxidation of **6a–d** with one equivalent of nitrosyl tetrafluoroborate ($NOBF_4$) in dichloromethane at room temperature gave the corresponding cation salts (**8a–d**)·BF_4 in 32–48% yields. Although only ^1H nmr spectrum of **8b**·BF_4 was obtained because of the low solubilities of the other cations, the structure of **8b** is supported by the presence of the signals assignable to the methine proton at δ 7.50 (1H, s) and the thienyl protons at δ 6.91 (2H, d, J = 4.9 Hz) and 7.27 (2H, d, J = 4.9 Hz). Attempted preparation of the cation salts (**7a–d**)·BF_4 by oxidation of **5a–d** gave only a small amount of unidentified products. The cations (**8a–d**) were also obtained by hydride abstraction of **6a–d** with an equimolecular amount of trityl tetrafluoroborate in dichloromethane in 50–87% yields. The successful preparation of **7b**·BF_4 was achieved by using this method in 88% yield. The cations are fairly stable in both solid and solution states, and the ^1H nmr spectrum of **8b**·BF_4 in CD_3CN did not change after storage at room temperature under air for several months.

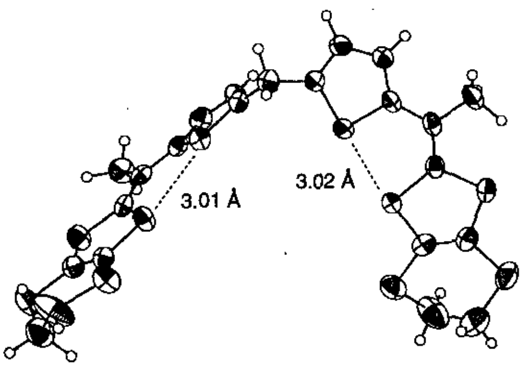


Figure 1. X-ray molecular structure of **6c**.

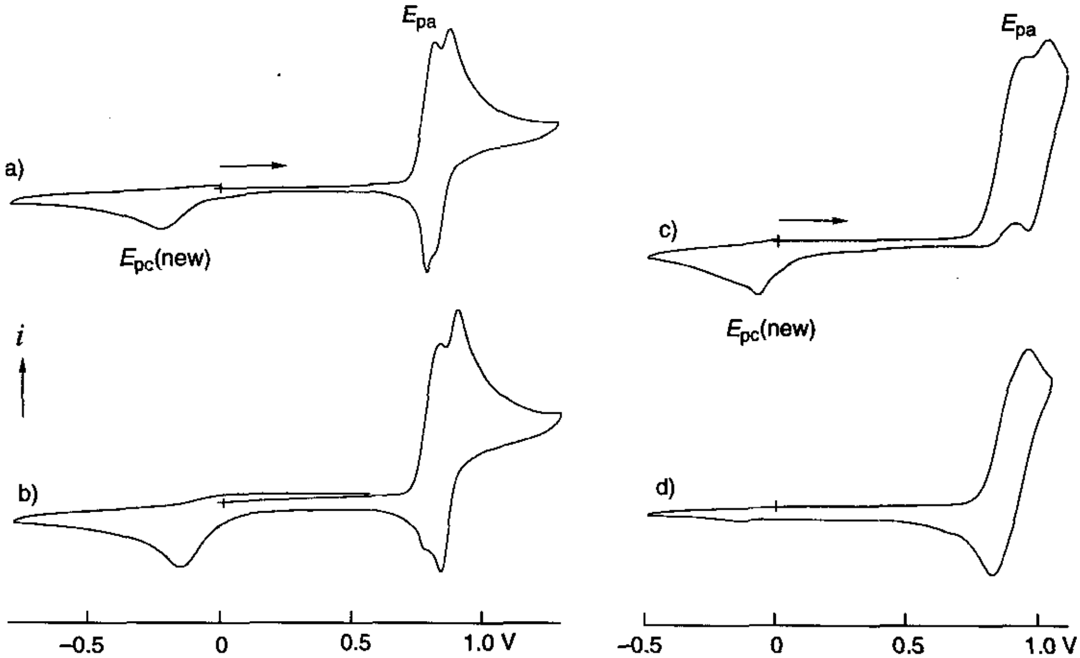


Figure 2. Cyclic voltammograms of a) **5d**, b) **13**, c) **6d**, and d) **14**. Bu_4NBF_4 (0.1 M) in benzonitrile, Pt electrode, scan rate 100 mV s^{-1}, *E*/V *vs.* saturated calomel electrode (SCE).

Table 1. Redox potentials of the compounds (**5**) and (**6**).[a]

Compound	E_{pa}	E_{pc}(new)	Compound	E_{pa}	E_{pc}(new)
5a	0.69	–0.10	**6a**	0.82	–0.13
5b	0.72	–0.30	**6b**	0.82	–0.04
5c	0.72	–0.30	**6c**	0.82	–0.05
5d	0.83	–0.23	**6d**	0.93	–0.08

[a] Measured in benzonitrile.

The CVs of the cations (**8a–c**) in benzonitrile showed both oxidation and reduction waves, although the CV of **8d** could not be obtained due to its low solubility. The reduction potentials are in complete agreement with E_{pc}(new) for **6a–c**. The three-stage one-electron oxidation waves corresponding to the formation of the dication radical, trication, and tetracation radical were observed for **8b** at 0.91, 1.15, and 1.39 V, respectively (Figure 3).

In order to investigate the structure of the cations, an X-ray structural analysis was carried out on **7b**·BF_4. The single crystal was obtained by recrystallization from acetonitrile. There exist two crystallographically independent molecules (molecule I and molecule II) in the crystal. The molecular structure of molecule II with bond lengths is shown in Figure 4. Although there are differences in the conformations of the methylthio groups, the geometries of the π-skeleton of the molecules I and II are similar to each other. The molecules have an approximate C_2 symmetry. The thienyldithiafulvene moieties are almost planar. The two thiophene rings form dihedral angles of 9.7° (molecule I) and 18.0° (molecule II). The decrease in bond alternations is found in the carbon-framework of the molecule. Namely, while the C23–C24, C25–C26, C27–C28, C33–C34, C35–C36, and C37–C38 bonds are lengthened, the C24–C25, C26–C27, C34–C35, and C36–C37 ones are shortened compared with the corresponding bond lengths of **6c**. Furthermore, the average bond length of C28–S12, C28–S13, C38–S17, and C38–S18 bonds (1.73 Å) is slightly shorter than that of **6c** (1.76 Å). These observations indicate the polymethine cyanine like structure of the cation.[8] The molecules I and II form a dimer in the crystal as shown in Figure 5. Each dimer is connected by the counteranion BF_4^- with short F···H contacts (< 2.67 Å) to form a ladder-like network.

The cations (**7b**) and (**8a–d**) show intense absorptions in the near-infrared region (*ca.* 900–980 nm in acetonitrile) due to their polymethine cyanine type structure.[9] The spectrum of **8b** in acetonitrile is shown in Figure 6 (solid line), and the longest absorption maxima are summarized in Table 2. These values are considerably longer than that of some di(2-thienyl)methyl cation derivatives[8,10] and 1,3-dithiolium dyes[11] owing to the expansion of π-conjugation. The alkylthio groups on the 1,3-dithiole rings make the absorptions much red-shifted. The absorption maxima observed in solution are over the absorption region for the Ga–As laser diode (780–840 nm). However, the absorptions are blue-shifted in thin films, and **8b** showed the maximum at 824 nm as a thin film (Figure 6, broken line). This finding indicates that they are interesting as near-infrared absorbing dyes. Recently much attention has been focused on the near-infrared absorbing dyes for optical memory media.[12]

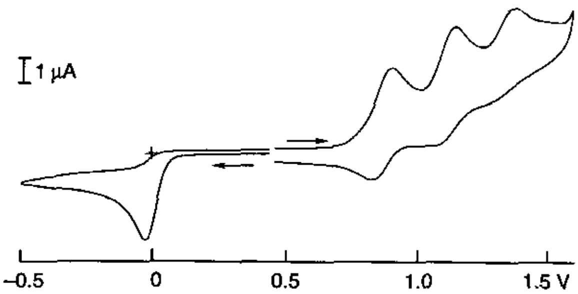


Figure 3. Cyclic voltammogram of **8b**·BF_4. Bu_4NBF_4 (0.1 M) in PhCN, Pt electrode, scan rate100 mV s^{-1}, *E*/V *vs*. SCE.

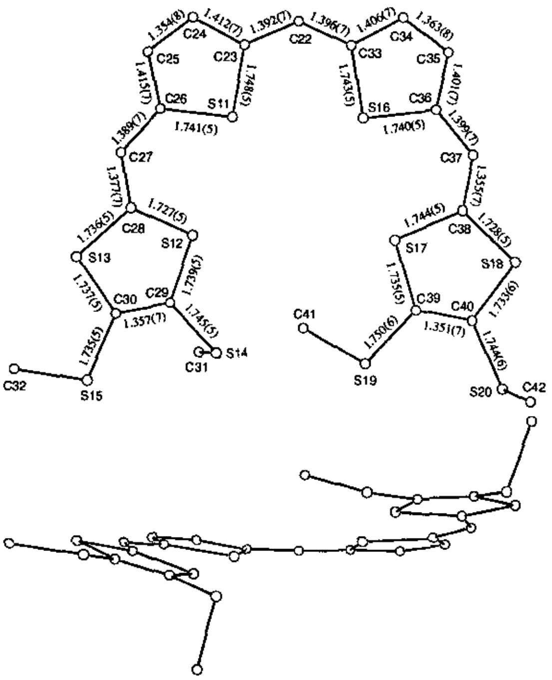


Figure 4. Two views of **7b** (Molecule II) . Hydrogen atoms are omitted.

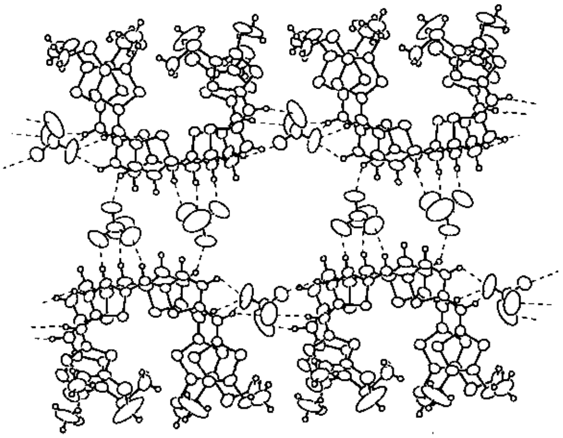


Figure 5. Crystal structure of **7b**·BF_4. Broken lines indicate short F···H contacts (< 2.67 Å).

Table 2. Longest absorption maxima of the cations in acetonitrile.

Cation	λ_{max} / nm (log ε)
7b	938 (4.76)
8a	921 (4.85)
8b	950 (4.69)
8c	976 (4.38)
8d	906 (4.56)

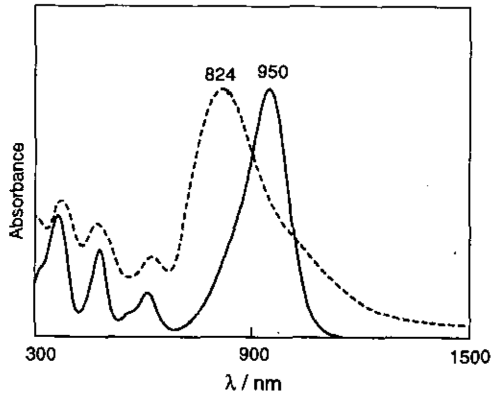
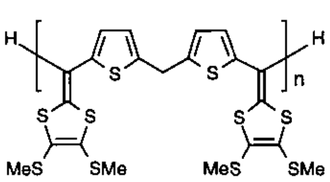


Figure 6. Absorption spectra of **8b**·BF_4 in acetonitrile (—) and as a thin film (---).

Formation of Redox-Active Oligomers. As described above, the cyclic voltammetric experiments suggested that the compounds (**5**) do not undergo deprotonation by oxidation. Because it is known that 1,4-dithiafulvene derivatives possessing an eliminable hydrogen atom on the C6-carbon undergo oxidative dimerization at the 6-position to give 1,2-bis(1,3-dithiol-2-ylidene)ethane derivatives,[13] the compounds (**5**) seem to undergo intermolecular coupling by oxidation. When **5b** was oxidized with tris(4-bromophenyl)aminium hexachloroantimonate, a sparingly soluble black solid was obtained as an oxidized form. Treatment of the product with hydrazine hydrate gave a neutral product as a brown solid. The gel-permeation chromatography analysis of the product showed a weight-average molecular weight of 6177 (polystylene standard) with a polydispersity of 1.5. These data indicate that the product is an oligomer (**15**) composed of about ten monomer units. The new reduction peaks $[E(\text{new})_{\text{pc}}]$ observed in the CVs of **5** can be attributed to the reduction of an intermediate (**16**). This interpretation is supported by the fact that 1,3-benzodithiolium cation[14] is reduced at a peak potential of –0.24 V *vs.* SCE in benzonitrile.

The absorption maximum (372 nm) of **15** in dichloromethane is red-shifted by only 8 nm compared with that of the monomer (**5b**). A similar relationship was observed between the absorption wavelengths of a closely related compound (**17**) (λ_{max} 352 nm) and its dimer (**18**) (λ_{max} 362 nm).[13e] The oligomer showed only one redox wave in the CV, and the oxidation peak potential (0.69 V) is slightly lower than that of the monomer (**5b**) ($E_{\text{pa}} = 0.72$ V). These spectral and electrochemical properties indicate that the degree of intramolecular interaction between the monomer units is small probably due to steric interactions. Since the oligomer (**15**) can be regarded as an assembly of the extended TTF (**18**), it seems interesting as a novel redox active oligomer presented by a general structure, –D–σ–D–σ–D–σ–, in which electronically isolated donor units are connected by σ-linkage.[15]



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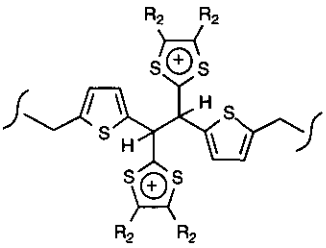

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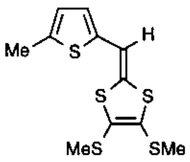

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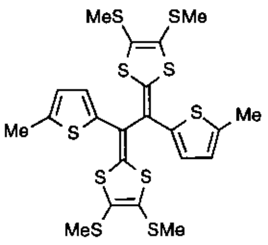

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EXPERIMENTAL

General. Melting points were measured on a Yanaco MP-500D melting point apparatus and are uncorrected. Ir and uv spectra were recorded on a Perkin-Elmer FTIR 1600 and a Shimadzu UV-3101PC spectrophotometer, respectively. Unless otherwise stated, ^{1}H (400 MHz) and ^{13}C (100 MHz) nmr spectra were measured on a JEOL JNM-GX400 spectrometer. 270 MHz ^{1}H nmr spectra were measured on a JEOL JNM-EX270 spectrometer. EI (70 eV) and FAB (Xe, 7kV) mass spectra were measured on a Shimadzu GCMS-QP1000EX and a Shimadzu Kratos CONCEPT 1S spectrometer, respectively. Elemental analyses were performed on a Yanaco MT-3 CHN CORDER. Gpc analysis were performed by using a Shimadzu LC-9A liquid chromatograph with a Tosoh TSK–GEL G3000HHR column (7.8 nm × 30 cm) and tetrahydrofuran as a solvent. Cyclic voltammetry experiments were performed in a three-compartment cell with a Pt disc working electrode, Pt wire counter electrode, and saturated calomel reference electrode. Measurements were made with a Toho Technical Research Polarization Unit PS-07 potentiostat / galvanostat with a scan rate of 100 mV s^{-1}. The cell contained a solution of a substrate (*ca.* 1 mM) and tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte in benzonitrile or dichloromethane. All solutions were purged with argon and retained under the inert atmosphere during the experiment.

Bis[5-(1,4-dithiafulven-6-yl)-2-thienyl]methane (5a). Aq. NaOH (10%, 5 ml, 15 mmol) was added to a solution of the aldehyde (**9**)[6] (300 mg, 1.27 mmol) and the phosphonium salt (**11**)[4] (1.05 g, 2.68 mmol) in dichloromethane (5 ml), and the mixture was vigorously stirred for 10 min at room temperature. The resulting solid was washed with water, followed by ethanol to give the compound (**5a**) (486 mg, 94%) as colorless needles (from $ClCH_2CH_2Cl$). mp 190–191 °C (decomp.); ir (KBr) 3056, 1567, 1303, 1046, 821, 801, 650, 502 cm^{-1}; ^{1}H nmr ($CDCl_3$) δ 4.31 (2H, s, CH_2), 6.32 (2H, d, J = 6.7 Hz, dithiole-H), 6.34 (2H, d, J = 6.7 Hz, dithiole-H), 6.67 (2H, s, =CH), 6.70 (2H, d, J = 3.7 Hz, Th-H), 6.80 (2H, d, J = 3.7 Hz, Th-H); ^{13}C nmr ($CDCl_3$) δ 30.80, 106.68, 117.89, 122.81, 125.69, 134.06, 140.25, 140.90; uv (CH_2Cl_2) λ_{max} (log ε) 246 (3.99), 362 (4.42), 375 (4.40, sh) nm; ms *m/z* (rel. intensity) 408 (M$^+$, 100), 306 (60), 153 (49), 95 (21), 69 (30). Anal. Calcd for $C_{17}H_{12}S_6$: C, 49.97; H, 2.96. Found: C, 49.87; H, 3.05.

5b: A solution of BuLi in hexane (1.63 M, 0.91 ml, 1.48 mmol) was added to a solution of phosphonate ester (**12b**)[5] (510 mg, 1.68 mmol) in THF (10 ml) at –78 °C under argon. After stirring for 10 min, the aldehyde (**9**) (160 mg, 0.68 mmol) was added to the solution. The mixture was stirred for 30 min at

–78 °C and allowed to warm to room temperature. To the solution was added water (30 ml), and the product was extracted with dichloromethane. The extract was washed with water, dried over Na_2SO_4, and concentrated. The residue was separated by column chromatography (alumina / toluene) to give the compound (**5b**) (299 mg, 75%) as yellow needles (from acetone). mp 82–83 °C; ir (KBr) 2914, 1570, 1498, 1426, 1298, 800, 504 cm^{-1}; ^1H nmr ($CDCl_3$) δ 4.43 (6H, s, SMe), 4.40 (6H, s, SMe), 4.30 (2H, s, CH_2), 6.59 (2H, s, =CH), 6.69 (2H, d, J = 3.5 Hz, Th-H), 6.80 (2H, d, J = 3.5 Hz, Th-H); ^{13}C nmr ($CDCl_3$) δ 18.85, 19.00, 30.75, 108.44, 123.68, 124.86, 125.71, 127.65, 129.54, 139.34, 141.63; uv (CH_2Cl_2) λ_{max} (log ε) 256 (4.04), 364 (4.28) nm; ms *m/z* (rel. intensity) 592 (M^+, 100), 153 (52), 91 (74). Anal. Calcd for $C_{21}H_{20}S_{10}$: C, 42.54; H, 3.40. Found: C, 42.56; H, 3.43.

The other compounds (**5c,d**), (**6a–d**), (**13**), and (**14**) were synthesized from the corresponding carbonyl compounds[6] by using the similar method (Wittig–Horner reaction). In the cases of the compounds (**5c,d**) and (**6c,d**), the products were isolated directly by addition of water and ethanol to the reaction mixture without extraction. The data are as follows.

5c: 92%; yellow needles (from $ClCH_2CH_2Cl$). mp 207–209 °C (decomp.); ir (KBr) 1561, 1518, 1284, 820, 796, 509 cm^{-1}; ^1H nmr ($CDCl_3$) δ 3.32 (8H, s, SCH_2CH_2S), 4.29 (2H, s, CH_2), 6.63 (2H, s, =CH), 6.69 (2H, d, J = 3.7 Hz, Th-H), 6.80 (2H, d, J = 3.7 Hz, Th-H); uv (CH_2Cl_2) λ_{max} (log ε) 257 (4.06), 371 (4.26), 396 (4.08, sh) nm; ms (FAB) *m/z* 588 (M^+). Anal. Calcd for $C_{21}H_{16}S_{10}$: C, 42.83; H, 2.74. Found: C, 42.60; H, 2.83.

5d: 71%; colorless plates (from toluene). mp 226–228 °C (decomp.); ir (KBr) 3051, 1577, 1557, 1448, 1432, 1124, 826, 743 cm^{-1}; ^1H nmr ($CDCl_3$) δ 4.34 (2H, s, CH_2), 6.68 (2H, s, =CH), 6.78 (2H, d, J = 3.7 Hz, Th-H), 6.84 (2H, d, J = 3.7 Hz, Th-H), 7.11–7.13 (4H, m, benzo-H), 7.22–7.24 (4H, m, benzo-H); uv (CH_2Cl_2) λ_{max} (log ε) 247 (4.20), 354 (4.44), 369 (4.39, sh) nm; ms *m/z* (rel. intensity) 508(M^+, 100), 356 (42), 261 (27), 209 (22), 203 (30), 190 (24), 178 (32), 153 (38) 108 (24). Anal. Calcd for $C_{25}H_{16}S_6$: C, 59.02; H, 3.17. Found: C, 59.21; H, 3.36.

6a: 47%; colorless needles (from acetone). mp 74–75 °C; ir (KBr) 3059, 1556, 1519, 1420, 1236, 986, 803, 786, 643, 594 cm^{-1}; ^1H nmr ($CDCl_3$) δ 2.14 (6H, s, Me), 4.29 (2H, s, CH_2), 6.35 (2H, d, J = 6.7 Hz, dithiole-H), 6.37 (2H, d, J = 6.7 Hz, dithiole-H), 6.82 (2H, d, J = 3.7 Hz, Th-H), 6.85 (2H, d, J = 3.7 Hz, Th-H); ^{13}C nmr ($CDCl_3$) δ 23.77, 30.63, 112.78, 117.79, 118.76, 122.70, 125.50, 130.80, 140.33, 143.58; uv (CH_2Cl_2) λ_{max} (log ε) 247 (4.17), 359 (4.50), 367 (4.44, sh) nm; ms *m/z* (rel. intensity) 436(M^+, 100), 334 (33), 225 (13), 167 (13), 103 (10). Anal. Calcd for $C_{19}H_{16}S_6$: C, 52.26;

H, 3.69. Found: C, 52.29; H, 3.78.

6b: 70%; yellow needles (from $CHCl_3$–EtOH). mp 90–91 °C; ir (KBr) 2915, 1553, 1499, 1424, 969, 897, 792, 786 cm^{-1}; ^1H nmr ($CDCl_3$) δ 2.11 (6H, s, Me), 2.42 (6H, s, SMe), 2.45 (6H, s, SMe), 4.29 (2H, s, CH_2), 6.82 (4H, s, Th-H); ^{13}C nmr ($CDCl_3$) δ 18.86, 18.93, 22.51, 30.55, 114.60, 123.43, 125.48, 126.03, 126.42, 126.82, 140.90, 142.68; uv (CH_2Cl_2) λ_{max} (log ε) 256 (4.05), 360 (4.22) nm; ms *m/z* (rel. intensity) 620 (M^+, 100), 558 (13), 470 (16), 320 (14), 249 (18), 167 (36), 135 (26), 91 (66). Anal. Calcd for $C_{23}H_{24}S_{10}$: C, 44.48; H, 3.90. Found: C, 44.50; H, 3.88.

6c: 93%; yellow prisms (from $CHCl_3$–hexane). mp 167–168 °C; ir (KBr) 1557, 1527, 1516, 1409, 1286, 801, 791 cm^{-1}; ^1H nmr ($CDCl_3$) δ 2.13 (6H, s, Me), 3.31 (8H, s, SCH_2CH_2S), 4.28 (2H, s, CH_2), 6.81 (4H, s, Th-H); uv (CH_2Cl_2) λ_{max} (log ε) 257 (4.06), 367 (4.18) nm; ms (FAB) *m/z* 616 (M^+). Anal. Calcd for $C_{23}H_{20}S_{10}$: C, 44.77; H, 3.27. Found: C, 44.57; H, 3.38.

6d: 86%; colorless needles (from $CHCl_3$–hexane). mp 159–160 °C; ir (KBr) 3057, 2908, 1571, 1547, 1448, 784, 735 cm^{-1}; ^1H nmr ($CDCl_3$) δ 2.21 (6H, s, Me), 4.32 (2H, s, CH_2), 6.85 (2H, d, *J* = 3.7 Hz, Th-H), 6.94 (2H, d, *J* = 3.7 Hz, Th-H), 7.08–7.11 (4H, m, benzo-H), 7.23–7.27 (4H, m, benzo-H); uv (CH_2Cl_2) λ_{max} (log ε) 246 (4.04), 352 (4.14), 364 (4.09) nm; ms *m/z* (rel. intensity) 536 (M^+, 100), 153 (63), 69 (42). Anal. Calcd for $C_{27}H_{20}S_6$: C, 60.41; H, 3.76. Found: C, 60.25; H, 3.84.

2,2-Bis[5-(1,4-beznodithiafulven-6-yl)-2-thienyl]propane (13). 65%; pale yellow solid. mp 130–138 °C; ir (KBr) 2966, 1573, 1552, 1447, 1432, 801, 741 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.88 (6H, s, Me), 6.66 (2H, s, =CH), 6.75 (2H, d, *J* = 3.7 Hz, Th-H), 6.81 (2H, d, *J* = 3.7 Hz, Th-H), 7.08–7.13 (4H, m, benzo-H), 7.20–7.23 (2H, m, benzo-H), 7.25–7.29 (2H, m, benzo-H); ms *m/z* (rel. intensity) 536 (M^+, 14), 521 (100). Anal. Calcd for $C_{27}H_{20}S_6$: 535.98894. Found: *m/z* 535.99069.

2,2-Bis[5-(6-methyl-1,4-benzodithiafulven-6-yl)-2-thienyl]propane (14). 69%, pale yellow needles (from acetone). mp 115 – 120 °C; ir (KBr) 2967, 1571, 1547, 1449, 1434, 1123, 792, 739 cm^{-1}; ^1H nmr (400 MHz, $CDCl_3$) δ 1.88 (6H, s, Me), 2.21 (6H, s, =CMe), 6.83 (2H, d, *J* = 3.7 Hz, Th-H), 6.93 (2H, d, *J* = 3.7 Hz, Th-H), 7.08–7.12 (4H, m, benzo-H), 7.22–7.27 (4H, m, benzo-H); ms *m/z* (rel. intensity) 564 (M^+, 49), 549 (100), 302 (25), 275 (37), 153 (47). Anal. Calcd for $C_{29}H_{24}S_6$: C, 61.65; H, 4.28. Found: C, 61.47; H, 4.27.

Isolation of cation salt 8a·BF$_4$ (General procedure). Method A: Argon was bubbled into a stirred solution of the compound (**6a**) (100 mg, 0.23 mmol) in dichloromethane (10 ml). To this solution was added $NOBF_4$ (28 mg, 0.24 mmol) in acetonitrile (1 ml) at room temperature. After addition, argon bubbling was continued for 10 min. The mixture was stirred for further 20 min, and the resulting solid was collected by filtration and washed with dichloromethane to give the cation salt (**8a**)·**BF_4** (50 mg, 42%). **Method B**: Trityl tetrafluoroborate (80 mg, 0.24 mmol) was added to a solution of **6a** (100 mg, 0.23 mmol) in dichloromethane (5 ml) at room temperature under argon. The mixture was stirred for 1 h, and the resulting solid was collected by filtration and washed with dichloromethane to give the cation salt (**8a**)·**BF_4** (104 mg, 87%): black solid (from AcOH). mp *ca.* 250 °C (decomp.); ir (KBr) 1557, 1348, 1193, 1151, 1086, 1053, 986, 742 cm^{-1}; uv (MeCN) λ_{max} (log ε) 324 (4.21), 362 (4.18), 458 (4.70), 547 (3.85), 590 (3.86), 921 (4.85) nm. Anal. Calcd for $C_{19}H_{15}BF_4S_6$: C, 43.68; H, 2.89. Found: C, 43.06; H, 2.93.

The other cation salts were prepared by the similar method. The data are as follows.

8b·BF_4: Method A: 32%; Method B: 83%; black solid (from AcOH). mp 177–179 °C (decomp); ir (KBr) 1555, 1353, 1149, 1088, 1052, 986, 736 cm^{-1}; ^1H nmr (CD_3CN) δ 2.11 (6H, s, Me), 2.53 (12H, br s, SMe), 6.91 (2H, d, *J* = 4.9 Hz, Th-H), 7.27 (2H, d, *J* = 4.9 Hz, Th-H), 7.50 (1H, s, CH); uv (MeCN) λ_{max} (log ε) 254 (4.25), 367 (4.38), 484 (4.24), 617 (3.95), 950 (4.69) nm. Anal. Calcd for $C_{23}H_{23}BF_4S_{10}$: C, 39.08; H, 3.28. Found: C, 38.80; H, 3.33.

8c·BF_4: Method A: 38%; Method B: 50%; black solid (from AcOH). mp > 300 °C; ir (KBr) 1557, 1451, 1424, 1344, 1194, 1152, 1091, 1052, 985, 737 cm^{-1}; uv (MeCN) λ_{max} (log ε) 377 (4.16), 501 (4.00), 645 (3.86), 976 (4.38) nm. Anal. Calcd for $C_{23}H_{19}BF_4S_{10}$: C, 39.31; H, 2.72. Found: C, 38.39; H, 2.74.

8d·BF_4: Method A: 48%; Method B: 64%; black fine needles. mp 281–283 °C (decomp.); ir (KBr) 1557, 1364, 1197, 1155, 1094, 1057, 986, 738 cm^{-1}; uv (MeCN) λ_{max} (log ε) 352 (4.37), 463 (4.26), 583 (3.78), 906 (4.56) nm. Anal. Calcd for $C_{27}H_{19}BF_4S_6$: C, 52.09; H, 3.08. Found: C, 51.80; H, 3.27.

7b·BF_4: Trityl tetrafluoroborate (56 mg, 0.17 mmol) was added to a solution of **5b** (100 mg, 0.17 mmol) in dichloromethane (2 ml) at room temperature under argon. The mixture was stirred for 1 h, and the resulting solid was collected by filtration and washed with a small amount of dichloromethane to give the cation salt (**7b**)·**BF_4** (101 mg, 88%) as a dark green solid (from AcOH). mp 228 – 236 °C (decomp.); ir (KBr) 1518, 1459, 1386, 1293, 1171, 1139, 1064, 711 cm^{-1}; uv (MeCN) λ_{max} (log ε) 369 (4.49), 480 (4.40), 604 (4.02), 938 (4.76) nm. Anal. Calcd for $C_{21}H_{19}BF_4S_{10}$: C, 37.16; H, 2.82. Found: C, 36.76; H, 2.84.

Oxidative oligomerization of 5b. Tris(4-bromophenyl)aminium hexachloroantimonate (140 mg, 0.17 mmol) was added to a solution of **5b** (100 mg, 0.17 mmol) in dichloromethane (10 ml) at room temperature. The mixture was stirred for 2 h, and the resulting solid was collected by filtration and washed with dichloromethane to give a dark blue solid (94 mg). To a suspension of this solid (59 mg) in dichloromethane was added hydrazine hydrate (0.05 ml, 1 mmol), and the mixture was stirred for 5 min. An insoluble solid was removed by filtration, and the filtrate was washed with water, dried over Na_2SO_4, and concentrated *in vacuo* to give the oligomer (**18**) (10 mg, 10%) as a brown solid; uv (CH_2Cl_2) λ_{max} 372 nm. Gpc analysis indicated weight- and number-average molecular weights of 6177 and 4241 (polystylene standard), respectively.

X-ray structural analyses. All of the data collections were performed on an Enraf-Nonius CAD4 diffractometer (40 kV, 30 mA) with graphite-monochromated Cu-Kα radiation (λ = 1.541 Å) using ω–2θ scan technique.

6c: A pale yellow prism-like single crystal with a dimension of 0.30 × 0.30 × 0.10 mm was prepared by recrystallization from 1,2-dichloroethane. A total of 5395 reflections was collected up to 2θ = 140°. Crystal data are as follows: $C_{23}H_{20}S_{10}$, M = 617.09, monoclinic, space group, $P2_1/a$, a = 10.551(2), b = 24.797(3), c = 9.907(2) Å, β = 94.30(1)°, V = 2584.8(8) Å^3, Z = 4, D_{calcd} = 1.59 g cm^{-3}. The structure was solved by the direct method using the SHELX86 program and refined by the block-diagonal least squares analysis based on F values using the UNICS III program package. The positions of all hydrogen atoms were calculated using the HYCO80 program. All the non-hydrogen atoms were refined with anisotropic temperature factors. At the final stage, all hydrogen atoms were included in the refinement with isotropic factors. The final R value was 7.28% for 3944 reflections with $|F_o| > 3\sigma|F_o|$. The largest electron density in the D-map after the final refinement was 0.80 e/Å^3. These calculations were carried out in the Computer Center of Institute for Molecular Science.

7b·BF$_4$: A black prism-like single crystal with a dimension of 0.50 × 0.25 × 0.10 mm was obtained by slow recrystallization from acetonitrile. A total of 12055 reflections was collected up to 2θ= 148.6°. Crystal data are as follows: $C_{21}H_{19}S_{10}BF_4$, M = 678.78, triclinic, space group $P\bar{1}$, a = 14.7572(6), b = 14.9204(8), c = 15.4377(6) Å, α = 96.523(4), β = 110.719(3), γ = 111.367(4)°, V = 2843.7(3) Å^3, Z = 4, D_{calcd} = 1.59 g cm^{-3}. The structure was solved by the direct methods using the SHELXS86 program and expanded by Fourier techniques using the DIRDIF92 program. The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were included at calculated positions but not refined. The final R value was 5.30% for 7973 reflections with $I > 3\sigma(I)$. The largest electron density in the D-map after the final refinement was 0.64 e/Å^3. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

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