

**SYNTHESIS AND PROPERTIES OF NOVEL
BIS(1,3-BENZODITHOLIUM)-TYPE DICATIONS CONTAINING A
BIARYL UNIT: NEW REDOX SYSTEMS UNDERGOING REVERSIBLE
STRUCTURAL CHANGES BY ELECTRON TRANSFER**

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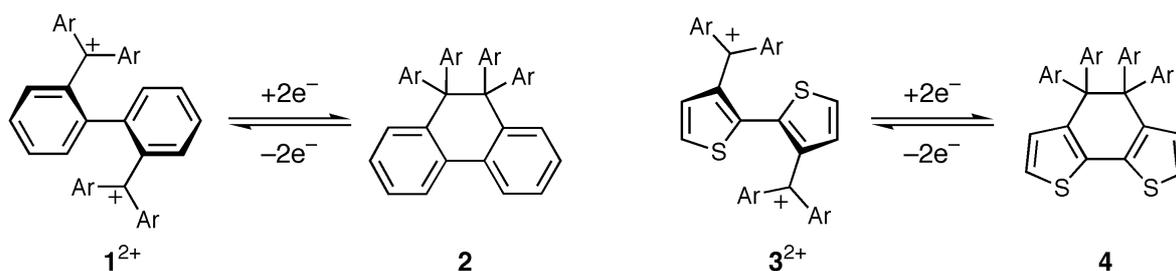
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Abstract – In order to develop new redox systems which undergo reversible structural changes by electron transfer, bis(1,3-benzoditholium)-type dications (**5**²⁺) containing a biaryl unit have been synthesized by hydride abstraction of the corresponding bis(1,3-benzodithiol-2-yl)biaryls (**8**). Reduction of **5**²⁺ with zinc gave the corresponding intramolecular cyclization products (**6**), which reverted to **5**²⁺ by oxidation. Cyclic voltammetry also showed the efficient interconversion between both states. X-Ray analyses revealed that the twist angle of the biaryl unit decreases largely by reductive intramolecular cyclization.

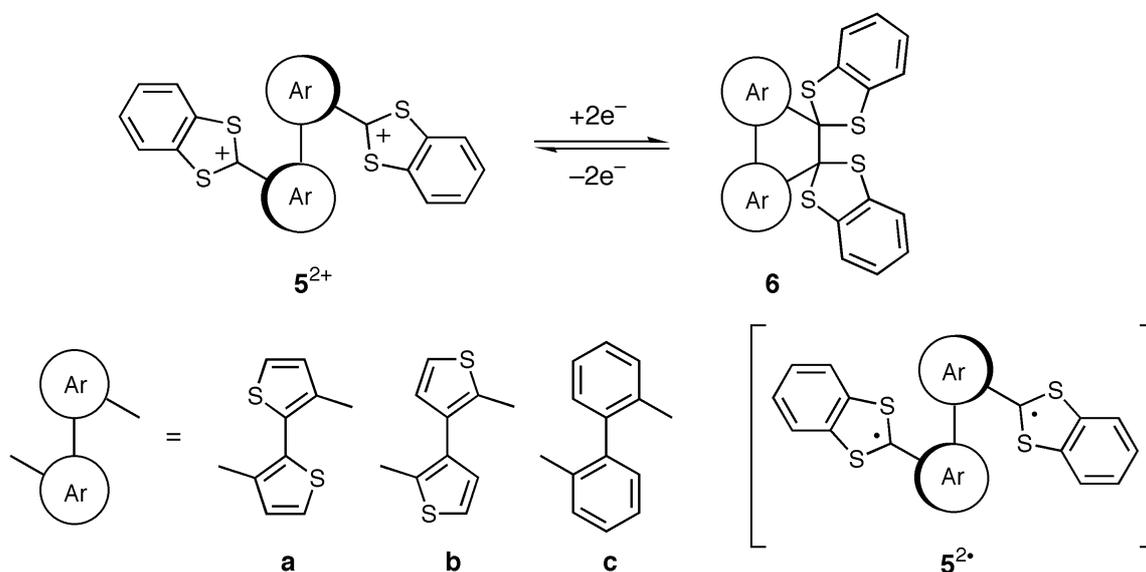
INTRODUCTION

Organic redox systems undergoing reversible structural changes upon electron transfer are called ‘dynamic redox systems’ and have attracted much attention for applications, such as molecular switches.¹ Recently, Suzuki *et al.* have studied extensively on various types of redox systems represented by common structures (**1**²⁺/**2**) and shown that they are useful to construct novel redox responsive systems which show distinct structural and spectral changes by an electrochemical stimulus (Scheme 1).² In these systems, the structural changes are based on the redox-induced intramolecular cyclization and ring-opening reactions. On the other hand, Nishida and co-workers reported redox responsive oligothiophenes containing a closely related redox couple (**3**²⁺/**4**), in which the twist angle of the central bithienyl unit can be controlled by electron transfer.³ We have now designed a redox couple (**5**²⁺/**6**) containing a biaryl unit as a new dynamic redox system (Scheme 2). It is known that bis(1,3-benzoditholium)-type dications construct reversible redox couples with

2,2'-bi-1,3-benzodithioles.⁴ Therefore, for this system it is expected that two-electron reduction of the dication ($\mathbf{5}^{2+}$, open forms) affords the corresponding cyclization products ($\mathbf{6}$, closed forms) *via* a diradical species ($\mathbf{5}^{2\cdot}$) and two-electron oxidation of the resulting $\mathbf{6}$ reproduces the starting dication ($\mathbf{5}^{2+}$) by ring-opening. In the course of the interconversion between the two forms, the dihedral angle of the biaryl unit would change;^{2,3} the biaryl units should adopt twisted and coplanar conformations in the open forms ($\mathbf{5}^{2+}$) and closed forms ($\mathbf{6}$), respectively. The present redox system has the following features based on the 1,3-benzodithiole ring systems introduced as a redox-active unit. (i) The dication states ($\mathbf{5}^{2+}$) should be stabilized by the formation of the aromatic 1,3-benzodithiolium rings. (ii) 2-Aryl-1,3-benzodithiolium units, which are incorporated in the open forms ($\mathbf{5}^{2+}$), are strong chromophores.⁵ Thus, distinct color changes are expected during the interconversion. (iii) The molecules of the both forms are structurally simple compared to the previously reported systems ($\mathbf{1}^{2+}/\mathbf{2}$ and $\mathbf{3}^{2+}/\mathbf{4}$) possessing bulky redox-active units. This may be advantageous to further modification of the present system.



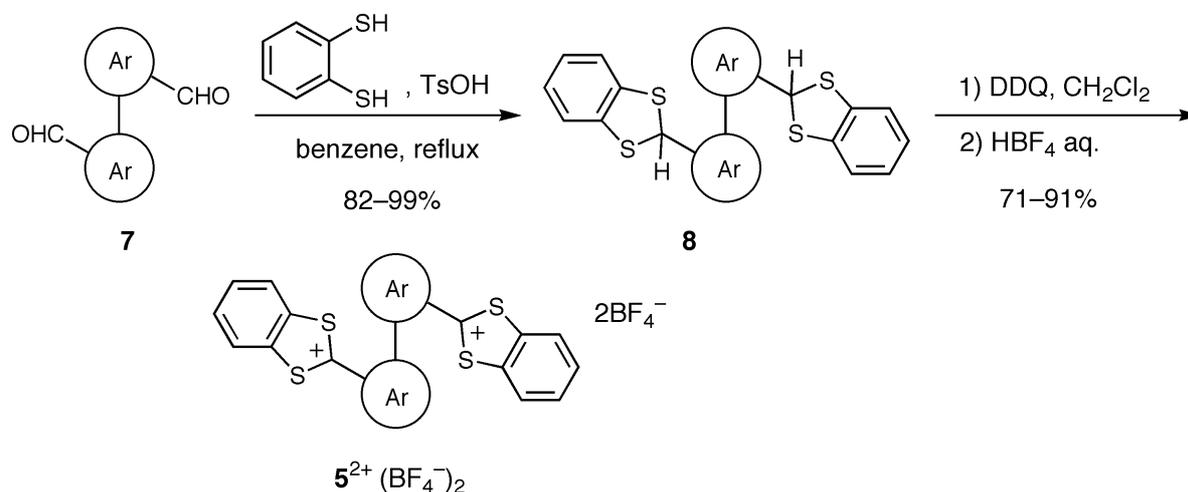
Scheme 1



Scheme 2

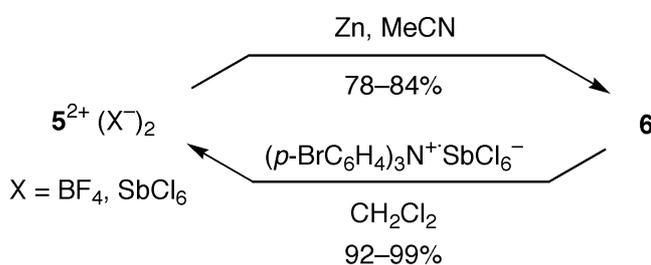
RESULTS AND DISCUSSION

The dication salts (5^{2+})(BF_4^-)₂ were prepared according to Scheme 3. Acid-catalyzed condensation⁶ of dialdehydes (**7**)^{7,8} with 1,2-benzenedithiol in refluxing benzene gave the corresponding bis(1,3-benzodithiole)s (**8**) in 82–99% yields. Hydride abstraction of **8** with DDQ followed by exchange of the counterions by addition of tetrafluoroboric acid gave the dications (5^{2+}) as air-stable BF_4^- salts in 71–91% yields. When trityl tetrafluoroborate was used as a hydride abstraction reagent, a mixture of mono- and dications was formed. The observation of a ¹³C-NMR signal corresponding to the C-2 position of the 1,3-benzodithiolium ring in the downfield region ($\delta = 188.2\text{--}189.9$) supports the structures of the dications.



Scheme 3

Redox properties of the dications were investigated by both chemical and electrochemical ways. When zinc powder was added to a solution of dication salts (5^{2+})(BF_4^-)₂, the color of the solution immediately disappeared and the closed forms (**6**) were obtained in 78–84% yields. The structures of **6** were determined based on the spectroscopic data, especially the ¹³C-NMR signal at *ca.* 80 ppm corresponding to the quaternary sp^3 carbon atoms of the 1,3-benzodithiole rings.⁹ Chemical oxidation of the closed forms (**6**) with two equiv. of tris(*p*-bromophenyl)aminium hexachloroantimonate in dichloromethane reproduced the corresponding dications (5^{2+}) as SbCl_6^- salts in good yields (92–99%). These results show that the interconversion between the open and closed forms occurs efficiently.



Scheme 4

The electrochemical properties were examined by cyclic voltammetry (CV). The cyclic voltammograms of the dication salt (**5c**²⁺) and neutral compound (**6c**) in benzonitrile are shown in Figure 1 as typical examples. In the CV of **5c**²⁺, it is irreversibly reduced at E_{pc} of +0.28 V to give a new compound which shows an anodic peak at E_{pa} of +1.30V [Figure 2 (a)], which is in complete agreement with the oxidation peak potential of **6c** [Figure 2 (b)]. Therefore, this new anodic peak observed in the CV of **5c**²⁺ can be assigned to the oxidation of the electrochemically generated closed form (**6c**). In the case of the CV of **6c**, a cathodic peak of the open form (**5c**²⁺) was observed after the oxidation of **6c**. The cyclic voltammograms were almost unchanged during the repetition of scans, suggesting the high chemical reversibility of the interconversion. The bithienyl derivatives (**5a,b**²⁺) showed the similar electrochemical behavior (E_{pc}/V : **5a**²⁺, +0.14; **5b**²⁺, +0.16, E_{pa}/V : **6a**, +1.29; **6b**, +1.33).¹⁰ While the E_{pa} values are close to each other, the E_{pc} values of the bithienyl derivatives (**5a,b**²⁺) are lower than that of **5c**²⁺, suggesting that the dication states (**5a,b**²⁺) are stabilized by electron-donating thienyl groups. The large separation of reduction and oxidation peaks is typical for redox systems which undergo C–C bond formation and cleavage upon electron transfer and indicates a high electrochemical bistability of the present redox systems **5**²⁺/**6**.¹⁻³

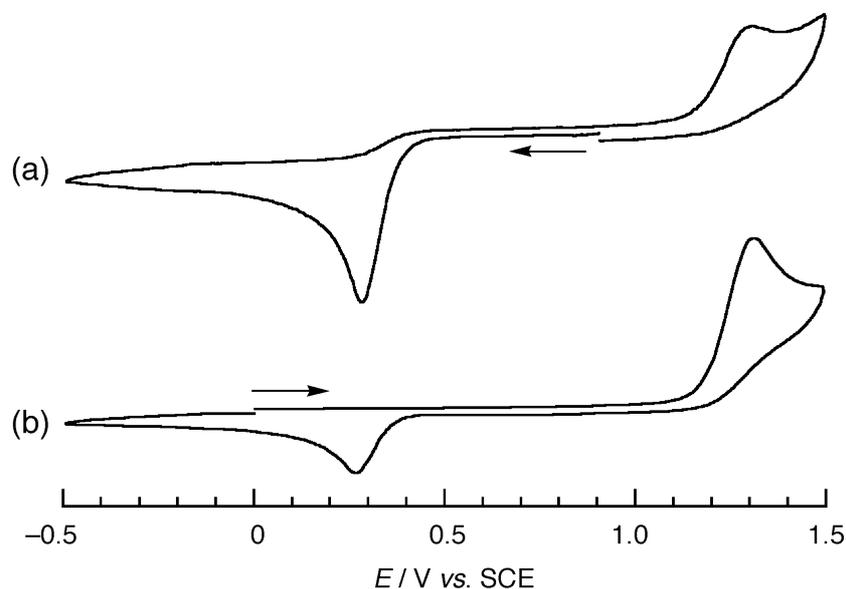


Figure 1. Cyclic voltammograms of (a) **5c**²⁺ and (b) **6c** in benzonitrile.

In order to investigate the molecular geometries of the open and closed forms, X-Ray analyses were carried out on the dication salts (**5a,b**²⁺) and the neutral compound (**6a**). The ORTEP drawings are shown in Figure 2. The molecules of **5a**²⁺ and **5b**²⁺ have C_2 and approximate C_2 symmetries, respectively and are twisted around the central C–C bond to avoid steric and electrostatic repulsions between the two 1,3-benzodithiolium rings [Figure 2 (a), (b)]. The dihedral angle (94.8°) formed by the

two thiophene rings of **5b**²⁺ is much larger than that for **5a**²⁺ (61.0°).¹¹ The 2-thienyl-1,3-benzodithiolium moieties are slightly twisted (dihedral angle: **5a**²⁺, 23.9°; **5b**²⁺, 12.4 and 16.3°). The better coplanarity of these moieties in **5b**²⁺ would lead to a higher degree of conjugation interactions between the 2-thienyl and 1,3-benzodithiolium rings. In contrast to the dication states, the dihedral angle (8.3°) of the bithienyl unit in the molecule of the neutral state (**6a**) decreases largely by ring closure as shown in Figure 2 (c). The central six-membered ring adopts a half-chair conformation. The bond length of the newly formed C–C bond is 1.583(3) Å. Although X-Ray analyses for the other closed forms were not carried out at present, the molecular structures of **6b,c** are considered to be similar to that of **6a** owing to their restricted conformational freedom.

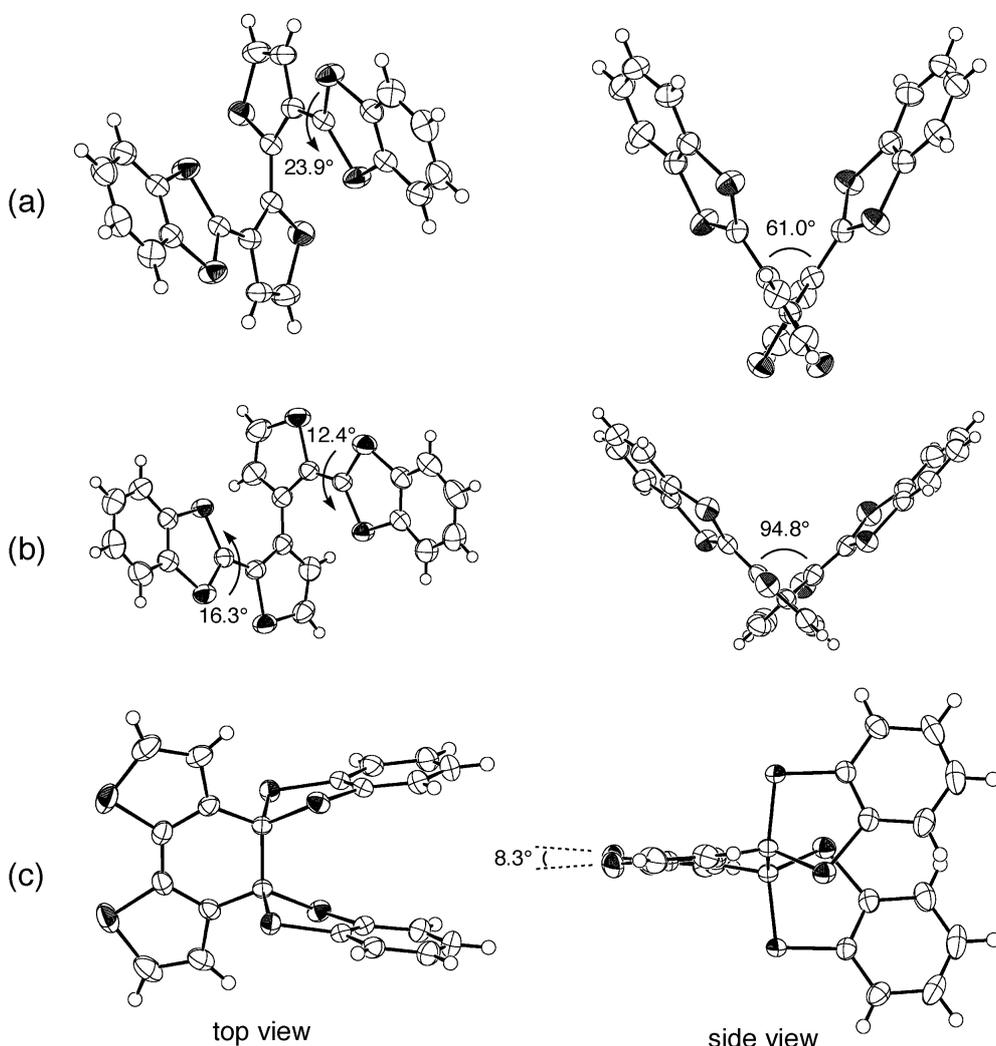


Figure 2. ORTEP drawings of (a) **5a**²⁺, (b) **5b**²⁺, and (c) **6a**. Counterions and solvent molecules are omitted. Values shown in the top views of the dications indicate the dihedral angles between the thiophene and 1,3-benzodithiolium rings.

UV-Vis spectra of the open and closed forms (**5b**²⁺, **6b**) in MeCN are shown in Figure 3. The dications (**5**²⁺) show yellow to orange color in the solution. The absorption maxima of **5a–c**²⁺ are 391 (log ϵ =

4.51), 433 (4.61), and 376 (4.51) nm, respectively. The longer wavelength for **5b**²⁺ is probably due to the higher coplanarity of the 2-(2-thienyl)-1,3-benzodithiolium moieties as mentioned above. On the other hand, the closed forms (**6**) did not show absorption in visible region. These distinct color changes indicate that the present redox couples are interesting as an electrochromic system.

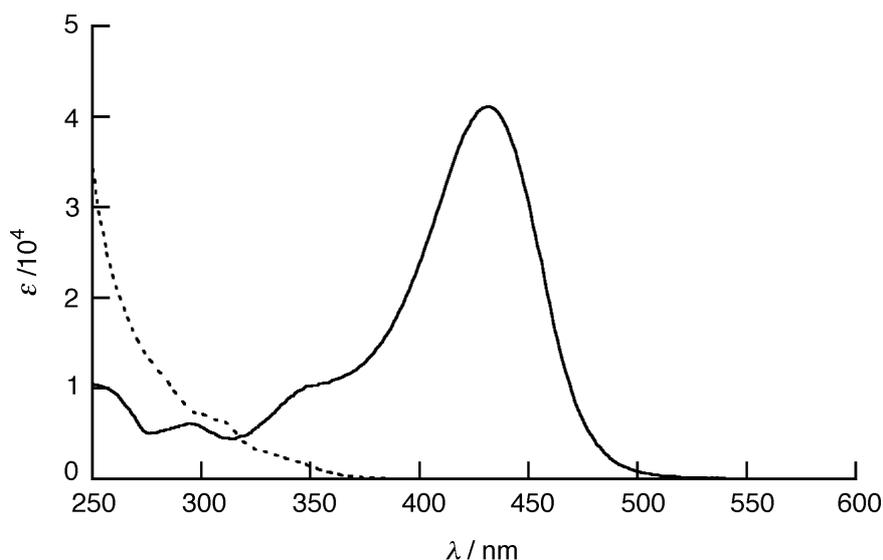


Figure 3. UV-Vis spectra of **5b**²⁺ (solid line) in MeCN and **6b** (broken line) in CH₂Cl₂.

In conclusion, we have succeeded in construction of the new redox couples (**5**²⁺/**6**) showing the distinct structural and spectral changes upon electron transfer. Introduction of appropriate functional groups, such as a molecular recognition site, to the present redox system would afford other interesting systems showing additional functions based on the structural change. Investigations along this line are now in progress and will be reported elsewhere.

EXPERIMENTAL

General. Melting points were measured on a Yanagimoto hot stage melting point apparatus and are uncorrected. IR and UV-VIS spectra were recorded on a JEOL Diamond-20 and a Shimadzu UV-260 spectrophotometers, respectively. NMR spectra were recorded with a JEOL JNM-LA400 (¹H: 400 MHz; ¹³C: 100 MHz) or a JNM-LA300 (¹H: 300 MHz; ¹³C: 75 MHz) spectrometer. MS and HRMS spectra were measured on a Shimadzu GCMS-QP1000EX and a JEOL JMS-777V spectrometer, respectively. Elemental analyses were performed on a Perkin-Elmer Model 240 or a Yanaco MT-6 apparatus.

Compound (8a): A solution of dialdehyde (**7a**) (200 mg, 0.90 mmol), *p*-toluenesulfonic acid monohydrate (17 mg, 0.09 mmol), and 1,2-benzenedithiol (282 mg, 1.98 mmol) in benzene (20 mL) was heated under reflux for 5 h. To the solution was added sat. NaHCO₃ aq (15 mL) and the mixture was extracted with CH₂Cl₂. The extract was dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on alumina (toluene/hexane, 1:1) to give **8a** (416 mg, 98%) as colorless prisms: mp 186–187 °C (from toluene/hexane); IR (KBr) 3105, 3055, 2922, 1442, 1244, 1230, 1115, 837, 742 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃), δ = 6.00 (2H, s, S-CH-S), 7.04–7.09 (4H, AA'BB', benzo-H), 7.19–7.23 (4H, AA'BB', benzo-H), 7.35 (4H, s, Th-H); ¹³C-NMR (100 MHz, CDCl₃) δ = 49.19, 122.11, 125.86, 127.19, 127.48, 128.02, 137.32, 141.49; MS *m/z* (rel. intensity, %) 470 (M⁺, 11), 329 (100), 296 (92), 190 (29), 153 (20), 77 (14); Anal. Calcd for C₂₂H₁₄S₆: C, 56.13; H, 3.00. Found: C, 55.88; H, 2.94.

The other compounds (**8b,c**) were synthesized by a similar method.

8b: 99%; colorless prisms; mp 242–243 °C (from toluene/hexane); IR (KBr) 3091, 2918, 1564, 1442, 1433, 1346, 1257, 1119, 858, 796, 737 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ = 6.24 (2H, d, *J* = 0.6 Hz, S-CH-S), 6.88 (2H, d, *J* = 5.1 Hz, Th-4,4'-H), 7.04–7.10 (4H, AA'BB', benzo-H), 7.18–7.23 (4H, AA'BB', benzo-H), 7.28 (2H, dd, *J* = 5.1, 0.6 Hz, Th-5,5'-H); ¹³C-NMR (75 MHz, CDCl₃) δ = 50.51, 122.16, 125.45, 126.08, 128.48, 132.95, 136.95, 141.62; MS *m/z* (rel. intensity, %) 470 (M⁺, 1.6), 329 (100), 296 (40), 190 (19), 153 (17); HRMS–EI Calcd for C₂₂H₁₄S₆: *m/z* 469.9420; Found: 469.9418 (dev. –0.3 ppm).

8c: 82%; colorless prisms; mp 205–206 °C (from toluene/hexane); IR (KBr) 3055, 2949, 1564, 1473, 1446, 1429, 1253, 1122, 760, 746 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ = 5.90 (2H, s, S-CH-S), 7.00–7.06 (4H, m, benzo-H), 7.13–7.21 (6H, m, benzo-H and biphenyl-H), 7.33–7.43 (4H, m, biphenyl-H), 8.04–8.07 (2H, m, biphenyl-H); ¹³C-NMR (100 MHz, CDCl₃) δ = 52.88, 121.90, 121.99, 125.74, 125.75, 128.00, 128.42, 128.97, 129.76, 137.31, 137.35, 137.68, 138.58; MS *m/z* (rel. intensity, %) 458 (M⁺, 2), 317 (100), 284 (24), 165 (80); Anal. Calcd for C₂₆H₁₈S₄: C, 68.08; H, 3.96. Found: C, 68.15; H, 4.17.

Dication salt (5a²⁺)(BF₄⁻)₂: To a solution of **8a** (50 mg, 0.11 mmol) in dry CH₂Cl₂ (5 mL) was added DDQ (96 mg, 0.42 mmol) at rt. After stirring for 30 min, 42% fluoroboric acid (3 mL) was added to the solution, and the mixture was further stirred for 30 min. The resulting precipitate was collected by filtration, washed with CH₂Cl₂, and purified by reprecipitation from MeCN/diethyl ether to give **5a²⁺(BF₄⁻)₂** (48 mg, 71%) as orange prisms: mp 243–244 °C (from MeCN/Et₂O); IR (KBr) 3111, 1522, 1402, 1377, 1273, 1084, 1036, 850, 756 cm⁻¹; ¹H-NMR (300 MHz, CD₃CN) δ = 7.88–7.95 (4H, AA'BB', benzo-H), 8.16 (2H, d, *J* = 5.5 Hz, Th-4,4'-H), 8.30 (2H, d, *J* = 5.5 Hz, Th-5,5'-H), 8.40–8.46 (4H, AA'BB', benzo-H); ¹³C-NMR (100 MHz, CD₃CN) δ = 127.30, 131.00, 132.15, 133.16, 136.55, 138.84,

142.79, 189.91; UV-Vis (MeCN) λ_{\max} (log ϵ) 286 (4.00), 391 (4.51) nm; Anal. Calcd for $C_{22}H_{12}S_6(BF_4)_2 \cdot (CH_3CN)_{1.5}$: C, 42.66; H, 2.36; N, 2.98. Found: C, 42.84; H, 2.29; N, 2.71.

The other dication salts (**5b,c²⁺**)(BF₄⁻)₂ were synthesized by a similar method.

5b²⁺ (BF₄⁻)₂: 91%; orange prisms; mp 235–238 °C (decomp.) (from MeCN/Et₂O); IR (KBr) 3099, 1479, 1371, 1346, 1105, 1084, 1036, 858, 762 cm⁻¹; ¹H-NMR (300 MHz, CD₃CN) δ = 7.54 (2H, d, J = 5.0 Hz, Th-4,4'-H), 7.84–7.87 (4H, AA'BB', benzo-H), 8.33–8.36 (4H, AA'BB', benzo-H), 8.63 (2H, d, J = 5.0 Hz, Th-5,5'-H); ¹³C-NMR (100 MHz, CD₃CN) δ = 127.08, 132.05, 132.13, 133.93, 141.95, 142.67, 144.58, 188.21; UV-Vis (MeCN) λ_{\max} (log ϵ) 253 (4.01), 295 (3.78), 348 (4.01), 433 (4.61) nm; Anal. Calcd for $C_{22}H_{12}S_6(BF_4)_2$: C, 41.14; H, 1.88. Found: C, 41.26; H, 1.91.

5c²⁺ (BF₄⁻)₂: 76%; yellow prisms; mp 247–251 °C (decomp.) (from MeCN/Et₂O); IR (KBr) 3057, 2911, 1587, 1552, 1435, 1284, 1255, 1036, 760 cm⁻¹; ¹H-NMR (300 MHz, CD₃CN) δ = 7.79–7.82 (2H, m, biphenyl-H), 7.92–8.08 (8H, m, benzo-H and biphenyl-H), 8.31–8.33 (2H, m, biphenyl-H), 8.43–8.49 (4H, AA'BB', benzo-H); ¹³C-NMR (75 MHz, CD₃CN) δ = 126.82, 129.36, 131.67, 132.62, 133.86, 134.19, 137.75, 187.94, 148.76, 197.89; UV-Vis (MeCN) λ_{\max} (log ϵ) 251 (4.23), 284 (3.97), 376 (4.51) nm; Anal. Calcd for $C_{26}H_{16}S_4(BF_4)_2$: C, 49.55; H, 2.56. Found: C, 49.48; H, 2.57.

Reduction of dication salt (5a²⁺**)(BF₄⁻)₂ to closed form (**6a**):** To a solution of **5a²⁺** (BF₄⁻)₂ (25 mg, 0.089 mmol) in dry MeCN (2 mL) was added zinc powder (100 mg) at rt. After stirring for 1 h, the precipitate was filtered off and washed with CH₂Cl₂. The filtrate and washings were combined and concentrated. The residue was purified by column chromatography on alumina (toluene/hexane, 1:1) to give **6a** (14 mg, 78%) as colorless prisms: mp 203–204 °C (from toluene/hexane); IR (KBr) 3107, 3055, 1563, 1444, 1431, 1122, 1109, 837, 735, 710, 679 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ = 7.00 (8H, s, benzo-H), 7.20 (2H, d, J = 5.1 Hz, Th-4, 4'-H), 7.43 (2H, d, J = 5.1 Hz, Th-5, 5'-H); ¹³C-NMR (100 MHz, CDCl₃) δ = 80.14, 121.09, 123.72, 125.24, 128.55, 130.25, 137.85, 137.96; MS m/z (rel. intensity, %) 468 (M⁺, 30), 328 (100), 296 (41), 234 (12); Anal. Calcd for $C_{22}H_{12}S_6$: C, 56.37; H, 2.58. Found: C, 56.42; H, 2.54.

The other dication salts (**5b,c²⁺**)(BF₄⁻)₂ were reduced by a similar method.

6b: 84%; colorless prisms; mp 213–216 °C (decomp.) (from toluene/hexane); IR (KBr) 3099, 3060, 1566, 1446, 1431, 1122, 852, 739, 715 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ = 6.96–7.03 (8H, m, benzo-H), 7.21 (2H, d, J = 5.1 Hz, Th-4,4'-H), 7.39 (2H, d, J = 5.1 Hz, Th-5,5'-H); ¹³C-NMR (75 MHz, CDCl₃) δ = 80.47, 120.99, 124.46, 125.36, 128.19, 129.02, 132.40, 140.62; MS m/z (rel. intensity, %) 468 (M⁺, 32), 328 (100), 296 (53); HRMS–FAB Calcd for $C_{22}H_{12}S_6$: m/z 467.9263; Found: 467.9265 (dev. +0.4 ppm).

6c: 78%; colorless prisms; mp 254–255 °C (from toluene/hexane); IR (KBr) 3054, 1446, 1429, 1122, 746 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ = 6.86–6.89 (2H, m, biphenyl-H), 6.94–7.06 (4H, m, benzo-H), 7.18–7.21 (2H, m, biphenyl-H), 7.38–7.50 (4H, m, benzo-H), 7.82 (2H, dd, J = 8.4, 1.5 Hz, biphenyl-H), 8.19 (2H, dd, J = 8.4, 1.5 Hz, biphenyl-H) $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 82.18, 121.19, 121.44, 124.92, 125.29, 125.48, 129.07, 129.25, 129.55, 131.86, 137.33, 137.64, 137.68 MS m/z (rel. intensity, %) 456 (M^+ , 19), 316 (100), 284 (31); Anal. Calcd for $\text{C}_{26}\text{H}_{16}\text{S}_4$: C, 68.38; H, 3.53. Found: C, 68.32; H, 3.42.

Oxidation of closed form (6a) to open form (5a^{2+})(SbCl_6^-)₂: To a solution of **6a** (5 mg, 0.011 mmol) in dry CH_2Cl_2 (1 mL) was added tris(*p*-bromophenyl)aminium hexachloroantimonate (17 mg, 0.028 mmol) at rt. After stirring for 1h, the resulting precipitate was filtered off, washed with CH_2Cl_2 followed by Et_2O to give 5a^{2+} (SbCl_6^-)₂ (11 mg, 92%) as yellow solid: mp 182–184 °C (decomp.); IR (KBr) 3111, 1520, 1491, 1396, 1279, 1265, 1105, 1005, 852, 775, 760 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CD_3CN) δ = 7.90–7.94 (4H, AA'BB', benzo-H), 8.16 (2H, d, J = 5.6 Hz, Th-4,4'-H), 8.30 (2H, d, J = 5.6 Hz, Th-5,5'-H), 8.41–8.45 (4H, AA'BB', benzo-H); Anal. Calcd for $\text{C}_{22}\text{H}_{12}\text{S}_6(\text{SbCl}_6)_2 \cdot \text{CH}_2\text{Cl}_2$: C, 22.59; H, 1.15. Found: C, 22.36; H, 1.15. The $^1\text{H-NMR}$ spectrum was almost the same as that of BF_4 salt.

The other compounds (**6b,c**) were oxidized by a similar method.

5b²⁺ (SbCl_6^-)₂: 99%; yellow solid; mp 180–182 °C (decomp.); IR (KBr) 3015, 1477, 1371, 1346, 1294, 1107, 1002, 860, 750 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CD_3CN) δ = 7.57 (2H, d, J = 5.0 Hz, Th-4,4'-H), 7.87–7.90 (4H, AA'BB', benzo-H), 8.34–8.38 (4H, AA'BB', benzo-H), 8.65 (2H, d, J = 5.0 Hz, Th-5,5'-H); Anal. Calcd for $\text{C}_{22}\text{H}_{12}\text{S}_6(\text{SbCl}_6)_2 \cdot \text{CH}_2\text{Cl}_2$: C, 22.59; H, 1.15. Found: C, 22.48; H, 1.22.

5c²⁺ (SbCl_6^-)₂: 96%; yellow solid; mp 184–186 °C; IR (KBr) 3084, 1585, 1552, 1435, 1281, 1253, 1105, 999, 764, 756 cm^{-1} ; $^1\text{H-NMR}$ (300 MHz, CD_3CN) δ = 7.80–7.83 (2H, m, biphenyl-H), 7.92–8.08 (8H, m, benzo-H and biphenyl-H), 8.30–8.32 (2H, m, biphenyl-H), 8.43–8.48 (4H, m, benzo-H); Anal. Calcd for $\text{C}_{26}\text{H}_{16}\text{S}_4(\text{SbCl}_6)_2 \cdot \text{CH}_2\text{Cl}_2$: C, 26.79; H, 1.50. Found: C, 26.44; H, 1.50.

Electrochemical measurements. Cyclic voltammetry was performed in a three-compartment cell with a Pt disc working electrode, Pt wire counter electrode, and saturated calomel reference electrode (SCE). 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. All solutions were purged with nitrogen and retained under the inert atmosphere during the experiment. The

half wave potential of the ferrocene/ferrocenium couple was observed at +0.56 V under the same conditions.

X-Ray structural analyses. Reflection data were collected on a Rigaku Mercury CCD area detector using Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$) at 296 K. All the structures were solved by the direct method using the SHELXS-86 program.¹² The non-hydrogen atoms were refined anisotropically by full-matrix least-squares method on F_2 using the SHELXL-93 program.¹³ Hydrogen atoms were included at calculated positions but not refined. All the structures have been deposited as CIF files at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Crystal data for 5a²⁺ (BF₄⁻)₂(MeCN)₂: C₂₂H₁₂S₆B₂F₈·(CH₃CN)₂, $M = 724.40$, monoclinic, space group $P2_1/n$, $a = 10.242(2)$, $b = 7.4352(13)$, $c = 20.264(4) \text{ \AA}$, $\beta = 101.238(4)^\circ$, $V = 1513.6(5) \text{ \AA}^3$, $Z = 2$, $D_c = 1.589 \text{ g cm}^{-3}$, $F(000) = 732$, $\mu(\text{Mo-K}\alpha) = 5.24 \text{ cm}^{-1}$, crystal dimensions = $0.35 \times 0.15 \times 0.10 \text{ mm}$, 14703 reflections collected, 3417 independent ($R_{\text{int}} = 0.0675$), $R_1 = 0.0700$ and $wR_2 = 0.1732$ for 3134 data with $I > 2\sigma(I)$. CCDC 616235.

Crystal data for 5b²⁺ (BF₄⁻)₂: C₂₂H₁₂S₆B₂F₈, $M = 642.30$, monoclinic, space group $P2_1/c$, $a = 7.3216(5)$, $b = 24.961(2)$, $c = 14.8710(14) \text{ \AA}$, $\beta = 110.110(4)^\circ$, $V = 2552.1(3) \text{ \AA}^3$, $Z = 4$, $D_c = 1.672 \text{ g cm}^{-3}$, $F(000) = 1288$, $\mu(\text{Mo-K}\alpha) = 6.08 \text{ cm}^{-1}$, crystal dimensions = $0.30 \times 0.30 \times 0.10 \text{ mm}$, 20457 reflections collected, 5804 independent ($R_{\text{int}} = 0.0538$), $R_1 = 0.0734$ and $wR_2 = 0.1905$ for 4846 data with $I > 2\sigma(I)$. CCDC 616236.

Crystal data for 6a: C₂₂H₁₂S₆, $M = 468.68$, monoclinic, space group $C2/c$, $a = 16.819(3)$, $b = 11.822(2)$, $c = 11.100(2) \text{ \AA}$, $\beta = 115.239(3)^\circ$, $V = 1996.4(5) \text{ \AA}^3$, $Z = 4$, $D_c = 1.559 \text{ g cm}^{-3}$, $F(000) = 960$, $\mu(\text{Mo-K}\alpha) = 6.92 \text{ cm}^{-1}$, crystal dimensions = $0.35 \times 0.30 \times 0.25 \text{ mm}$, 8643 reflections collected, 2154 independent ($R_{\text{int}} = 0.0389$), $R_1 = 0.0328$ and $wR_2 = 0.0855$ for 2055 data with $I > 2\sigma(I)$. CCDC 616237.

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DEDICATION

It is our pleasure to dedicate this paper to Professor Satoshi Omura on the occasion of his 70th birthday.

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9. The ¹³C-NMR spectrum of the biphenyl derivative (**6c**) shows six kinds of aromatic carbon signals of the spiro-1,3-benzodithiole moiety, suggesting that the inversion of the central six-membered ring is sufficiently slow under the measurement time scale.
10. Second irreversible reduction peaks were observed for the bithienyl derivatives (**5a,b**²⁺) at -0.20 and -0.18 (weak) V, respectively. When the potential sweep was reversed after the second reduction peak, any other oxidation peaks additional to the oxidation of **6** were observed in reverse scan. Reasonable assignment of these second reduction process is unclear at present.
11. Differences in the molecular structures of the dications (**5a,b**²⁺) revealed by the X-Ray analyses may be caused by various effects such as conjugation interactions between the heteroaromatic rings, intramolecular steric interactions, crystal packing effects, and the influence of the counterions.
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