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

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Abstract – In order to develop new redox systems which undergo reversible structural changes by electron transfer, bis(1,3-benzodithiolium)-type dications (52+) containing a biaryl unit have been synthesized by hydride abstraction of the corresponding bis(1,3-benzodithiol-2-yl)biaryls (8). Reduction of 52+ with zinc gave the corresponding intramolecular cyclization products (6), which reverted to 52+ 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 (12+/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 (32+/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 (52+/6) containing a biaryl unit as a new dynamic redox system (Scheme 2). It is known that bis(1,3-benzodithiolium)-type dications construct reversible redox couples with

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2,2'-bi-1,3-benzodithioles.\textsuperscript{4} Therefore, for this system it is expected that two-electron reduction of the dica
tions (5\textsuperscript{2+}, open forms) affords the corresponding cyclization products (6, closed forms) via a diradical
species (5\textsuperscript{2-}) and two-electron oxidation of the resulting 6 reproduces the starting dica
tions (5\textsuperscript{3+}) by ring-opening. In the course of the interconversion between the two forms, the dihedral angle of the
biaryl unit would change;\textsuperscript{2,3} the biaryl units should adopt twisted and coplanar conformations in the open
forms (5\textsuperscript{3+}) and closed forms (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
(5\textsuperscript{3+}) 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 (5\textsuperscript{3+}), are strong
chromophores.\textsuperscript{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 (1\textsuperscript{2+}/2
and 3\textsuperscript{2+}/4) possessing bulky redox-active units. This may be advantageous to further modification of the
present system.

![Scheme 1](image-url)
RESULTS AND DISCUSSION

The dication salts \((5^{2+})(\text{BF}_4^-)_2\) were prepared according to Scheme 3. Acid-catalyzed condensation\(^6\) of dialdehydes \((7)\)\(^7\)\(^8\) with 1,2-benzenedithiol in refluxing benzene gave the corresponding bis(1,3-benzodithioles) \((8)\) 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 \(\text{^{13}C}\)-NMR signal corresponding to the C-2 position of the 1,3-benzodithiolium ring in the downfield region (\(\delta = 188.2—189.9\)) supports the structures of the dications.

Redox properties of the dications were investigated by both chemical and electrochemical ways. When zinc power was added to a solution of dication salts \((5^{2+})(\text{BF}_4^-)_2\), 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 \(\text{^{13}C}\)-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.
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). 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 \(\varepsilon =\)
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 CH$_2$Cl$_2$.](image)

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 ($^1$H: 400 MHz; $^{13}$C: 100 MHz) or a JNM-LA300 ($^1$H: 300 MHz; $^{13}$C: 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-toluensulfonic 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 C₁₁₈H₆₈S₆: 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 C₁₁₈H₆₈S₆: 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 C₁₂₀H₁₈₁₄S₆: 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) $\lambda_{\text{max}}$ (log $\varepsilon$) 286 (4.00), 391 (4.51) nm; Anal. Calcd for C$_{22}$H$_{12}$S$_4$(BF$_4$)$_2$: C, 42.66; H, 2.36; N, 2.98. Found: C, 42.84; H, 2.29; N, 2.71.

The other dication salts (5b,c$^{2+}$(BF$_4$)$_2$) were synthesized by a similar method.

5b$^{2+}$(BF$_4$)$_2$: 91%; orange prisms; mp 235–238 °C (decomp.) (from MeCN/Et$_2$O); IR (KBr) 3099, 1479, 1371, 1346, 1105, 1084, 1036, 858, 762 cm$^{-1}$; $^1$H-NMR (300 MHz, CD$_3$CN) $\delta$ = 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); $^{13}$C-NMR (100 MHz, CD$_3$CN) $\delta$ = 127.08, 132.05, 132.13, 133.93, 141.95, 142.67, 144.58, 188.21; UV-Vis (MeCN) $\lambda_{\text{max}}$ (log $\varepsilon$) 253 (4.01), 295 (3.78), 348 (4.01), 433 (4.61) nm; Anal. Calcd for C$_{22}$H$_{12}$S$_4$(BF$_4$)$_2$: C, 41.14; H, 1.88. Found: C, 41.26; H, 1.91.

5c$^{2+}$(BF$_4$)$_2$: 76%; yellow prisms; mp 247–251 °C (decomp.) (from MeCN/Et$_2$O); IR (KBr) 3057, 1479, 1332, 1284, 1255, 1036, 760 cm$^{-1}$; $^1$H-NMR (100 MHz, CDCl$_3$) $\delta$ = 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); $^{13}$C-NMR (75 MHz, CD$_3$CN) $\delta$ = 126.82, 129.36, 131.67, 132.62, 133.86, 134.19, 137.75, 187.94, 148.76, 197.89; UV-Vis (MeCN) $\lambda_{\text{max}}$ (log $\varepsilon$) 251 (4.23), 284 (3.97), 376 (4.51) nm; Anal. Calcd for C$_{22}$H$_{10}$S$_4$(BF$_4$)$_2$: C, 49.55; H, 2.56. Found: C, 49.48; H, 2.57.

Reduction of dication salt (5a$^{2+}$(BF$_4$)$_2$) to closed form (6a): To a solution of 5a$^{2+}$(BF$_4$)$_2$ (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 CH$_2$Cl$_2$. 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$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 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); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ = 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$_4$: C, 56.37; H, 2.58. Found: C, 56.42; H, 2.54.

The other dication salts (5b,c$^{2+}$(BF$_4$)$_2$) 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$^{-1}$; $^1$H-NMR (300 MHz, CDCl$_3$) $\delta$ = 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); $^{13}$C-NMR (75 MHz, CDCl$_3$) $\delta$ = 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$_4$: 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; ¹H-NMR (300 MHz, CDCl₃) 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) ¹³C-NMR (100 MHz, CDCl₃) 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 C₂₆H₁₆S₄: C, 68.38; H, 3.53. Found: C, 68.32; H, 3.42.

Oxidation of closed form (6a) to open form (5a²⁺)(SbCl₆⁻)²⁻: To a solution of 6a (5 mg, 0.011 mmol) in dry CH₂Cl₂ (1 mL) was added tris(p-bромophenyl)aminium hexachloroantimonate (17 mg, 0.028 mmol) at rt. After stirring for 1h, the resulting precipitate was filtered off, washed with CH₂Cl₂ followed by Et₂O to give 5a²⁺(SbCl₆⁻)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; ¹H-NMR (400 MHz, CD₃CN) δ = 7.90–7.94 (4H, AA'BB', benzo-H), 8.16 (2H, d, J = 5.6 Hz, Th₄₄'-H), 8.30 (2H, d, J = 5.6 Hz, Th₅₅'-H), 8.41–8.45 (4H, AA'BB', benzo-H); Anal. Calcd for C₂₂H₁₂S₆(SbCl₆)₂•CH₂Cl₂: C, 22.59; H, 1.15. Found: C, 22.36; H, 1.15. The ¹H-NMR spectrum was almost the same as that of BF₄ salt.

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

**5b²⁺ (SbCl₆⁻)²⁻**: 99%; yellow solid; mp 180–182 °C (decomp.); IR (KBr) 3015, 1477, 1371, 1346, 1294, 1107, 1002, 860, 750 cm⁻¹; ¹H-NMR (300 MHz, CD₃CN) δ = 7.57 (2H, d, J = 5.0 Hz, Th₄₄'-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, Th₅₅'-H); Anal. Calcd for C₂₂H₁₂S₆(SbCl₆)₂•CH₂Cl₂: C, 22.59; H, 1.15. Found: C, 22.48; H, 1.22.

**5c²⁺ (SbCl₆⁻)²⁻**: 96%; yellow solid; mp 184–186 °C; IR (KBr) 3084, 1585, 1552, 1435, 1281, 1253, 1105, 999, 764, 756 cm⁻¹; ¹H-NMR (300 MHz, CD₃CN) 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 C₂₆H₁₆S₄(SbCl₆)₂•CH₂Cl₂: 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-Kα radiation (λ = 0.71070 Å) at 296 K. All the structures were solved by the direct method using the SHELXS-86 program. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares method on F2 using the SHELXL-93 program. 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 5a**2+ (BF4)2(MeCN)2: C22H12S6B2F8(CH3CN)2, M = 724.40, monoclinic, space group P2/n, a = 10.242(2), b = 7.4352(13), c = 20.264(4) Å, β = 101.238(4)°, V = 1513.6(5) Å³, Z = 2, Dc = 1.589 g cm⁻³, F(000) = 732, μ(Mo-Kα) = 5.24 cm⁻¹, crystal dimensions = 0.35 × 0.15 × 0.10 mm, 14703 reflections collected, 3417 independent (Rint = 0.0675), R1 = 0.0700 and wR2 = 0.1732 for 3134 data with I > 2σ(I). CCDC 616235.

**Crystal data for 5b**2+ (BF4)2: C22H12S6B2F8, M = 642.30, monoclinic, space group P21/c, a = 7.3216(5), b = 24.961(2), c = 14.8710(14) Å, β = 110.110(4)°, V = 2552.1(3) Å³, Z = 4, Dc = 1.672 g cm⁻³, F(000) = 1288, μ(Mo-Kα) = 6.08 cm⁻¹, crystal dimensions = 0.30 × 0.30 × 0.10 mm, 20457 reflections collected, 5804 independent (Rint = 0.0538), R1 = 0.0734 and wR2 = 0.1905 for 4846 data with I > 2σ(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) Å, β = 115.239(3)°, V = 1996.4(5) Å³, Z = 4, Dc = 1.559 g cm⁻³, F(000) = 960, μ(Mo-Kα) = 6.92 cm⁻¹, crystal dimensions = 0.35 × 0.30 × 0.25 mm, 8643 reflections collected, 2154 independent (Rint = 0.0389), R1 = 0.0328 and wR2 = 0.0855 for 2055 data with I > 2σ(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.
REFERENCES AND NOTES


6. J. Nakayama, K. Ueda, and M. Hoshino, Synthesis, 1977, 770. We used p-toluenesulfonic acid as an acid catalyst instead of HCl gas. When the experimental condition described in this literature was applied to the present synthesis, a complex mixture was formed.


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,b2+) 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,b2+) 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.
