BENZIDINE TYPE ELECTRON DONORS FUSED WITH 1,2,5-CHALCOGENADIAZOLE UNITS[1]

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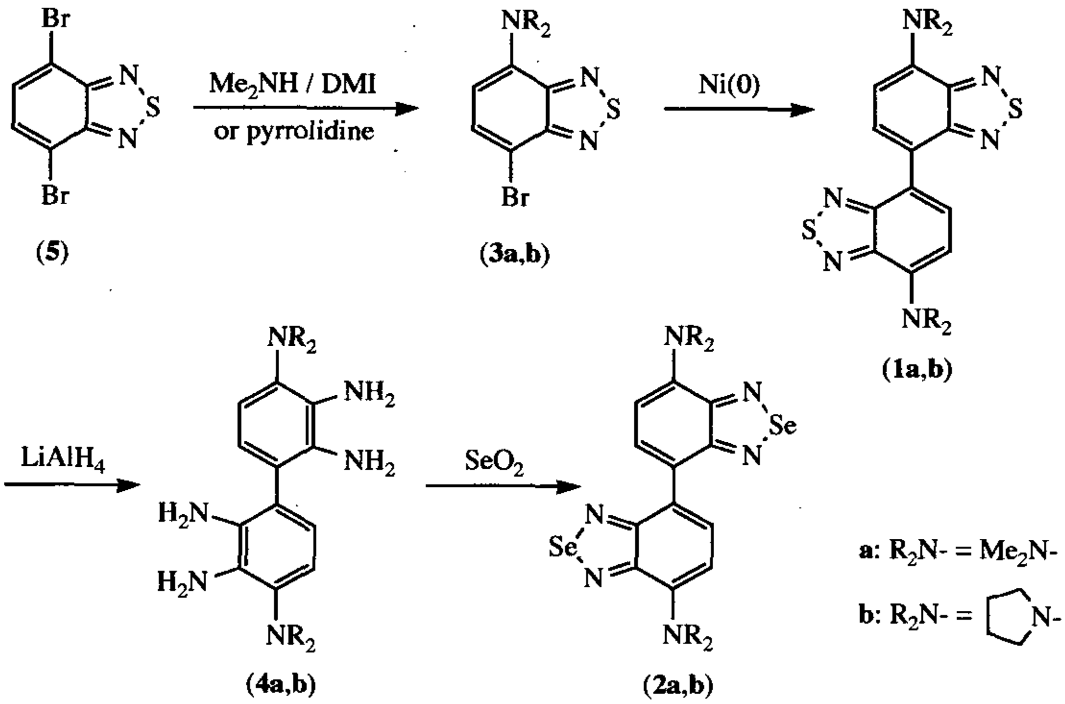
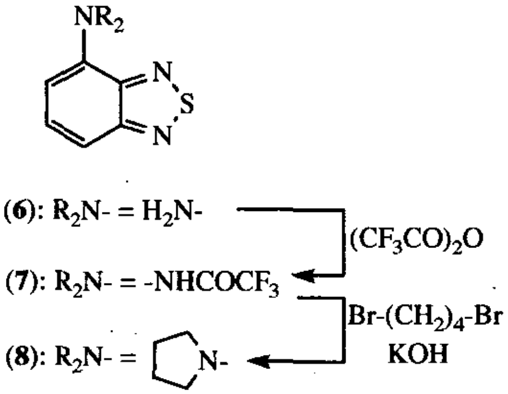
Abstract-The title electron donors (**1** and **2**) were prepared from 4-bromo-7-dialkylaminobenzo[*c*][1,2,5]thiadiazole (**3**). They are electrochemically amphoteric, and the absorption maxima in the 500-550 nm region were assigned to the intramolecular charge-transfer (CT) bands. The X-ray analyses of **1b** and **1b**$^{+\bullet}$$PF_6^-$ revealed that the twisted geometry of **1b** became planar upon one-electron oxidation, and a coplanar "ribbon"-like network was formed by S•••N interactions in the crystal of **1b**$^{+\bullet}$$PF_6^-$.

Aromatic amines have been known as strong electron donors,[2,3] and *p*-phenylenediamines and benzidines are the representative examples of the Wurster-type redox systems.[4] Recently considerable attention has been focused on organic redox systems due to their intriguing behaviors such as electrical conduction and ferromagnetism in the solid. Because these properties are largely affected by the molecular arrangement in crystal, prediction and regulation of crystal structures are the central problems to be explored in detail. The "engineering" of molecular arrangements is also of significant importance in other areas such as solid-state reactions, and weakly attractive intermolecular interactions can be used for the crystal engineering.[5] In this connection, the electrostatic interaction between heterocycles may be a useful tool for this purpose, which is suggested by various types of molecular networks formed by the chalcogen - nitrogen contacts in the crystal of 1,2,5-chalcogenadiazole derivatives.[6] We report here the preparation and properties of benzidine derivatives fused with chalcogenadiazole units, which were designed in anticipation of the interheteroatom interactions affecting their crystal structures.

Scheme I



Scheme II



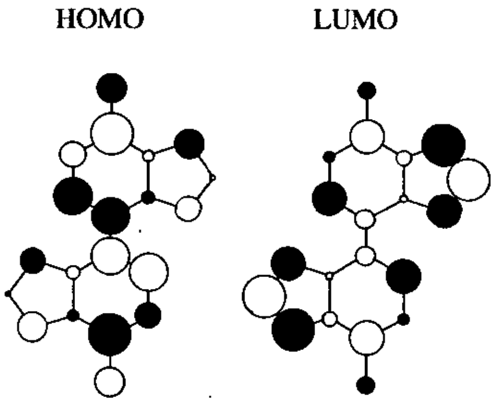


Figure1. HOMO and LUMO of **1** ($R_2N- = H_2N-$) obtained by the simple HMO method. The areas of the circles are proportional to the squares of the LCAO coefficients.

RESULTS AND DISCUSSION

Preparation. Reactions of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**5**)[7] with dimethylamine in 1,3-dimethyl-2-imidazolidinone (DMI) and with neat pyrrolidine afforded 7-dialkylamino derivatives (**3a**) and (**3b**), respectively (Scheme I). They were subjected to the reductive coupling by using a Ni(0) catalyst[8] to give benzidine derivatives fused with 1,2,5-thiadiazole units (**1a,b**). Reductions of **1a** and **1b** with $LiAlH_4$ afforded air sensitive hexamines (**4a,b**), and subsequent reactions with SeO_2 gave **2a** and **2b** fused with 1,2,5-selenadiazole rings. 4-(1-Pyrrolidinyl)benzo[*c*][1,2,5]thiadiazole (**8**) was prepared from 4-aminobenzo[*c*][1,2,5]thiadiazole (**6**)[9] (Scheme II) in order to compare the spectral properties with those of **1b** possessing the same chromophore.

Redox properties and electronic spectra. As shown in Table 1, the first oxidation potentials (E_1^{ox}) of **1** and **2** are the nearly same as that of *N,N,N',N'*-tetramethylbenzidine (TMB), and the cation radical of **1b** was successfully isolated as PF_6^- and I_3^- salts by electrochemical oxidation in THF. The lower oxidation potentials of **1b** and **2b** than **1a** and **2a** are due to the stronger electron donating property of the pyrrolidinyl group than the dimethylamino group.[10] It is noteworthy that the difference (ΔE_{ox}) between E_1^{ox} and E_2^{ox} is much smaller in **1** or **2** than in TMB, showing that $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ can be oxidized more easily to the dications than $TMB^{+\bullet}$. Because $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ are expected to possess planar geometries (*vide infra*), smaller ΔE_{ox} values indicate the reduced Coulombic repulsion by the annelation of heterocyclic π-systems, and the effect is larger in **2** containing Se with larger polarizability than S. On the other hand, **1** and **2** underwent reversible one-electron reduction, exhibiting their amphoteric character. Their stronger electron affinities than TMB may arise from the annelation of electron-withdrawing heterocycles, and comparisons of ΔE_{sum} values indicate that the selenadiazole derivatives (**2**) possess higher amphotericity than the thiadiazole derivatives (**1**). This finding is in accord with the fact that unsubstituted benzo[*c*][1,2,5]selenadiazole has a smaller ΔE_{sum} value than benzo[*c*][1,2,5]thiadiazole.[11]

In the electronic spectra of **1** and **2**, broad absorption maxima appeared in the 500-550 nm region and absorption coefficients were not affected by concentration. These absorptions were assigned to the intramolecular CT bands from the benzidine skeleton to the electron-withdrawing heterocycles by considering the orbital coefficient distribution in HOMO and LUMO (Figure 1). The similar absorption in the visible region was observed in the spectrum of **8** although its absorption maximum (460 nm in CH_2Cl_2) is shifted hypsochromically by 60 nm compared with **1b** possessing the same chromophore. This shift implies the presence of π-conjugation between two chromophores through the C4-C4' bond in **1b**, so that the perpendicularly twisted structure seems inappropriate for **1b**.

Table 1. Redox potentials[a] and absorption maxima of benzidine type donors, **1a**, **1b**, **2a**, **2b**, and TMB

	E_1^{ox}	E_2^{ox}	ΔE_{ox}^{b}	E_1^{red}	ΔE_{sum}^{c}	λ_{max}^{d}
1a	+0.56[e] (+0.59)	- (+0.75[f])	- (0.16)	-1.50	2.06	488
1b	+0.43 (+0.48)	+0.52 (+0.71)	0.09 (0.23)	-1.60	2.03	520
2a	+0.45[e] (ca.+0.50[g])	- (+0.63[f])	- (ca. 0.13)	-1.40	1.85	504
2b	+0.34[e] (+0.34)	- (+0.51[f])	- (0.17)	-1.49	1.83	552
TMB	+0.49 (+0.49)	+0.64 (+0.76[f])	0.15 (0.27)	<-2.0	< 2.49	-

[a] E / V vs SCE, 0.1 mol dm^{-3} Et_4NClO_4 in DMF, Pt wire, scan rate 100 mV s^{-1}. E^{ox} of ferrocene is +0.45 V. Values in parentheses are those measured in CH_2Cl_2 (0.1 mol dm^{-3} $n$$Bu_4NClO_4$, E^{ox} of ferrocene is +0.52 V). [b] $\Delta E_{ox} = E_2^{ox} - E_1^{ox}$. [c] $\Delta E_{sum} = E_1^{ox} - E_1^{red}$. [d] Intramolecular CT bands in CH_2Cl_2, values in nm. [e] One-wave two-electron processes. [f] Irreversible waves. Values were calculated as E_p - 0.03 V. [g] The exact value could not be obtained because of the small separation of E_1^{ox} and E_2^{ox}.

X-ray structural analyses. The X-ray analysis of **1b** revealed that the two molecular halves are related by a crystallographic 2-fold axis, and the molecule possesses a twisted geometry around the central C4-C4' bond (Figure 2). Although the van der Waals (vdW) contacts[12] between the orthohydrogens (H6 and H6') and nitrogen atoms (N2' and N2) of heterocycles may result in a twisted structure, the twisting angle is 43.4°, which is much smaller than those in 8,8'-biquinolyl (83.2°)[14] and 2,2'-dimethylbenzidine (86°)[5] and rather close to those in 3,3'-dimethylbenzidine (41°)[15] and 3,3'-dichlorobenzidine (21°)[16] having no substituent at the ortho-positions. Furthermore, the bond distance of C4-C4' is 1.478(12) Å, corresponding to 20% of double bond character.[17] These structural features indicate the π-conjugation between two molecular halves in **1b**, which is in accord with the conclusion obtained by comparisons of electronic spectra. On the other hand, molecules are packed in crystal without remarkable intermolecular interactions, and no interheteroatom contact of S•••N was observed in neutral **1b**. Although the molecular halves are arranged in a face-to-face manner as shown in Figure 3, the π-orbital overlap causing the HOMO-LUMO or NHOMO-LUMO interaction seems less important because the interplaner distance (3.72 Å) and N(3)•••C(3) contacts (3.70 Å) are much longer than the sum of vdW radii of N•••C (3.25 Å).[13]

The geometry of **1b** was drastically changed upon one-electron oxidation. Thus, two crystallographically independent molecules of **1b**$^{+\bullet}$ exhibit planar structures in the **1b**$^{+\bullet}PF_6^-$ crystal, and the twisting around the central bond is negligible (4.6° and 3.6° for molecule-**A** and -**B**, respectively). The enhanced double bond character in the central bond in **1b**$^{+\bullet}$ is expected by the MO consideration and may result in the geometrical change although this idea could not be supported by comparisons of the bond distances [1.47(4) Å and 1.49(4) Å in molecule-**A** and -**B**, respectively] in **1b**$^{+\bullet}$ with that in **1b** because of the large observational errors. On the other hand, intramolecular contacts between orthohydrogens[18] and heterocyclic nitrogens get closer due to the planar geometry in **1b**$^{+\bullet}$. Their N•••H distances and C-H•••N angles are 1.9-2.1 Å and 127-134°, respectively, suggesting the C-H•••N hydrogen bonding[19] through these contacts. Both molecule-**A** and -**B** are connected by S•••N contacts along the c axis, resulting in the formation of infinite "ribbon"-like networks on the ac plane (Figure 4). Although the S•••N distances (3.33-3.39 Å) are the nearly same as the sum of vdW radii (3.35 Å),[12] the coplanar arrangement of molecules is indicative of the attractive interaction through these contacts. The "ribbon" network of molecule-**A** and that of molecule-**B** are stacked alternately along the b axis (Figure 5) affording two different types of molecular overlapping. One is a favorable overlap for the interaction of SOMOs of **1b**$^{+\bullet}$ (Figure 4) with the short interplanar distance (3.21 Å) and causes the "dyad" formation in the crystal. The other is observed between the "dyads" (Figure 6), and the π-orbitals are scarcely overlapped with the longer interplanar distance (3.44 Å). The low conductivity of this salt (σ_{powder}, 9.1 x 10^{-6} S cm^{-1}) can be accounted for by the "dyad" formation in the crystal. By changing the counter ion from PF_6^- to I_3^- the conductivity was raised by a factor of five (σ_{powder}, 4.5 x 10^{-5} S cm^{-1}), suggesting the improved π-orbital overlapping in **1b**$^{+\bullet}I_3^-$ salt.

In summary, multistage redox systems with electrical amphotericity were constructed by the annelation of electron withdrawing heterocycles to the benzidine skeleton. Their planar cation radicals less suffer the Coulombic repulsion due to the enlarged π-electron system, and the infinite network in crystal was formed by the attractive interaction between heterocycles.

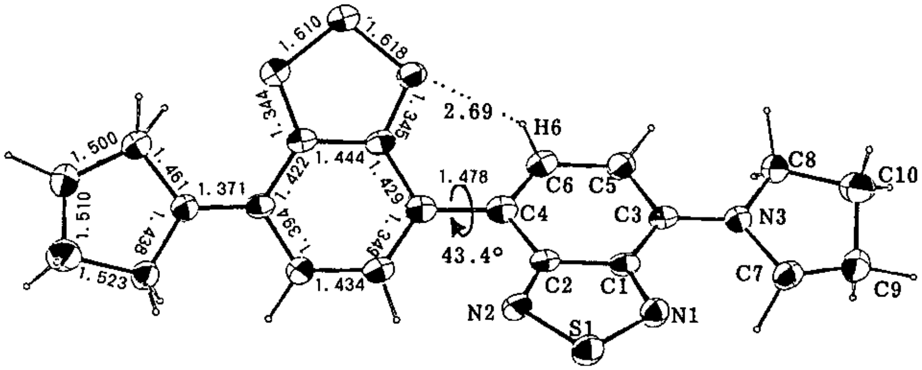


Figure 2. Thermal ellipsoids of **1b** viewed perpendicular to the least-square plane of the molecular half. In the molecular half, the benzothiadiazole unit and N3, C8, and C10 atoms lie on a coplane with the largest deviation of 0.07 Å at C10. Deviations of C7 and C9 from this plane are 0.3 Å and 0.7 Å, respectively.

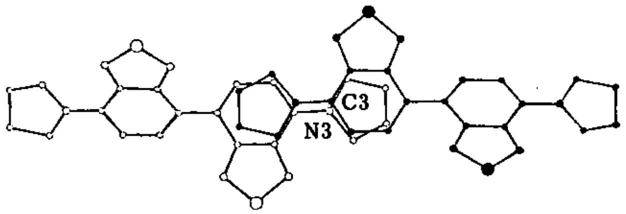


Figure 3. Molecular overlapping pattern in **1b**. Interatomic distance of N(3)•••C(3) is 3.70Å.

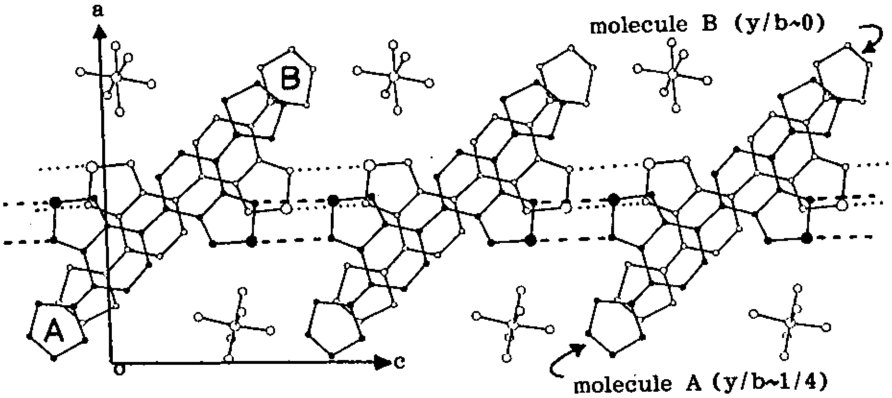


Figure 4. Coplanar "ribbon"-like networks in $\mathbf{1b}^{+\bullet}\mathrm{PF}_6^-$ by S•••N contacts (3.33 and 3.39 Å in molecule-**A**; 3.34 and 3.35 Å in molecule-**B**). Molecule **A** and **B** form a dyad by face-to-face overlapping.

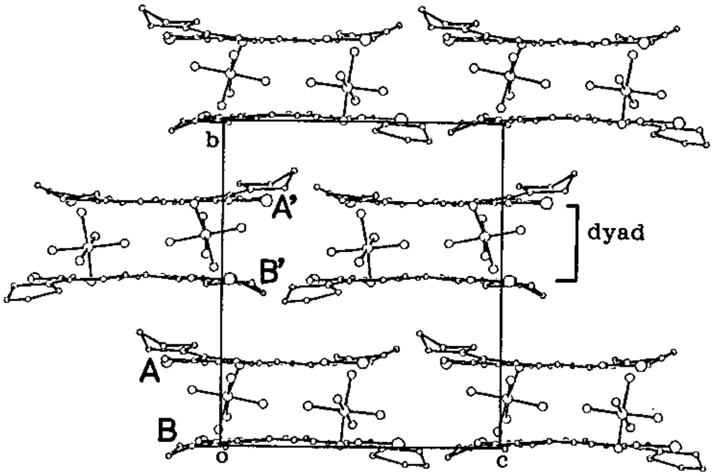


Figure 5. Crystal structure of $\mathbf{1b}^{+\bullet}\mathrm{PF}_6^-$ viewed along the a axis. S•••N contacts were not shown for clarity.

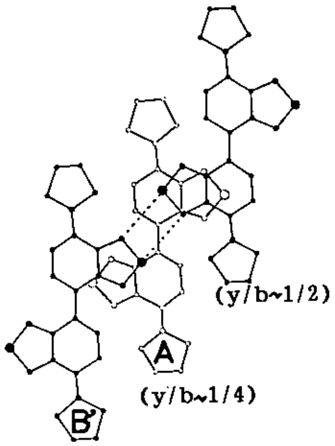


Figure 6. Molecular overlapping pattern between dyads in $\mathbf{1b}^{+\bullet}\mathrm{PF}_6^-$.

EXPERIMENTAL SECTION

Preparation of 4-Bromo-7-dimethylaminobenzo[c][1,2,5]thiadiazole (3a). To a solution of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**5**)[7] (720 mg, 2.4 mmol) in 30 ml of 1,3-dimethyl-2-imidazolidinone (DMI) was introduced dry gaseous dimethylamine for 4 h at 180 °C. After cooling, the mixture was poured into water and extracted with CCl_4. The extract was washed with water and brine, and then dried over Na_2SO_4. Evaporation of solvent followed by chromatographic separation on SiO_2 (CH_2Cl_2 / *n*-hexane, 1:1) afforded **3a** (510 mg) as orange needles in 81% yield. mp 91-93 °C; ir (KBr) 2900, 2800, 1578, 1540, 1492 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 1H), 6.20 (d, J = 8.1 Hz, 1H), 3.11 (s, 6H); ms m/z 257 (M^+). Anal. Calcd for $C_8H_8N_3BrS$: C, 37.22; H, 3.12; N, 16.28. Found: C, 37.11; H, 3.10; N, 16.19.

Preparation of 4,4'-Bis(7-dimethylaminobenzo[c][1,2,5]thiadiazolyl) (1a). Under a nitrogen atmosphere, a solution of **3a** (470 mg, 1.8 mmol) in 3 ml of dry THF was added to a THF solution (3 ml) of Ni(0)[8] prepared by the reduction of $(Ph_3P)_2NiBr_2$ (440 mg, 0.6 mmol) with Zn powder (190 mg, 2.9 mmol) and Et_4NI (470 mg, 1.8 mmol). The whole mixture was heated at 50 °C for 24 h. After evaporation of the solvent, the residue was extracted with benzene (soxhlet). The reddish extract was chromatographed on Al_2O_3 (CH_2Cl_2 / *n*-hexane, 1:1), and recrystallization from benzene gave 300 mg of **1a** as red plates in 92% yield. mp 225-226 °C; ir (KBr) 2860, 1550, 1494, 1355, 805 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 8.04 (d, J = 9.0 Hz, 2H), 6.71 (d, J = 9.0 Hz, 2H), 3.28 (s, 12H); uv (CH_2Cl_2) λmax (log ε) 266 (4.64), 310 (4.30, sh), 488 nm (4.14); ms m/z (relative intensity) 356 (M^+, 30), 357 (M^++1, 100), 358 (M^++2, 18). Anal. Calcd for $C_{16}H_{16}N_6S_2$: C, 53.91; H, 4.52; N, 23.58. Found: C, 54.06; H, 4.77; N, 23.28.

Preparation of 4,4'-Bis(dimethylamino)-2,2',3,3'-tetraaminobiphenyl (4a). To a suspension of **1a** (240 mg, 0.65 mmol) in 50 ml of dry ether was added $LiAlH_4$ (260 mg, 6.5 mmol) by small portions under nitrogen, and the mixture was stirred for 24 h at room temperature. Excess $LiAlH_4$ was quenched by adding water-saturated ether, and the mixture was poured into water. The ethereal extract was dried over Na_2SO_4, and evaporation of solvent afforded the crude hexamine (**4a**) (210 mg, 89%) as a pale orange solid, which was purified by sublimation to give air sensitive colorless rods. mp 57-58 °C; ir (KBr) 3400, 3300, 2930, 2820, 2780, 1485 cm^{-1}; ^1H nmr (90 MHz, $CDCl_3$) δ 6.67 (s, 4H), 3.60 (br s, 8H), 2.68 (s, 12H); ms m/z 300 (M^+). Anal. Calcd for $C_{16}H_{24}N_6$: C, 63.97; H, 8.05; N, 27.98. Found: C, 65.20; H, 8.42; N, 24.65 (Correct analytical values could not be obtained because of its lability).

Preparation of 4,4'-Bis(7-dimethylaminobenzo[c][1,2,5]selenadiazolyl) (2a). Because of the lability of **4a**, higher yield of **2a** was achieved when **4a** was used without isolation and purification. Thus, to the ethereal extract obtained by the reaction of **1a** (220 mg, 0.62 mmol) with $LiAlH_4$ (240 mg, 6.3 mmol) was added an aqueous solution (5 ml) of SeO_2 (300 mg, 2.7 mmol), and the mixture was stirred vigorously for 23 h at room temperature. Most of ether was evaporated, and the mixture was extracted with CH_2Cl_2. Chromatographic separation on Al_2O_3 (CH_2Cl_2) followed by recrystallization from $CHCl_3$/EtOH (5:1) afforded 142 mg of **2a** as red plates in 51% yield over two steps. mp 217-220 °C (decomp.); ir (KBr) 2940, 2830, 2790, 1536, 1480, 1360, 1056 cm^{-1}; ^{1}H nmr (90 MHz, $CDCl_3$) δ 7.75 (d, J = 7.7 Hz, 2H), 6.59 (d, J = 7.7 Hz, 2H), 3.23 (s, 12H); uv (CH_2Cl_2) λmax (log ε) 270 (4.37), 326 (4.31), 332 (4.32), 338 (4.32), 504 nm (3.91); ms m/z 450 (M^+). Anal. Calcd for $C_{16}H_{16}N_6Se_2{\bullet}0.5H_2O$: C, 42.15; H, 3.56; N, 18.32. Found: C, 41.84; H, 3.73; N, 18.30.

Preparation of 4-Bromo-7-(1-pyrrolidinyl)benzo[c][1,2,5]thiadiazole (3b). A solution of **5** (4.59 g, 15.3 mmol) in 10 ml of pyrrolidine was heated under reflux for 8 h under nitrogen. After cooling, reddish needles of **3b** (4.10 g, 86%) was filtrated, washed with EtOH, and dried *in vacuo*. mp 109-111 °C; ir (KBr) 2950, 2850, 1495 cm^{-1}; ^{1}H nmr (90 MHz, $CDCl_3$) δ 7.55 (d, J = 9.0 Hz, 1H), 6.10 (d, J = 9.0 Hz, 1H), 3.80 (m, 4H), 2.05 (m, 4H); ms m/z (relative intensity) 284 (M^++1, 81), 283 (M^+, 43), 282 (M^+-1, 100). Anal. Calcd for $C_{10}H_{10}N_3BrS$: C, 42.27; H, 3.55; N, 14.79. Found: C, 42.67; H, 3.46; N, 14.48.

Preparation of 4,4'-Bis(7-(1-pyrrolidinyl)benzo[c][1,2,5]thiadiazole) (1b). Similarly to the case of **1a**, **3b** (4.10 g, 14.4 mmol) was reacted with Ni(0) in THF for 42 h at 50 °C. Evaporation of solvent afforded a black solid which was extracted with benzene (soxhlet). The extract was concentrated to dryness and the residue was suspended in 120 ml of hot EtOH. Filtration of the insoluble purple powder gave 2.30 g of **1b** in 78% yield. mp 236-238 °C; ir (KBr) 2950, 2840, 1550 cm^{-1}; ^{1}H nmr (90 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 2H), 6.46 (d, J = 8.1 Hz, 2H), 3.93 (m, 8H), 2.12 (m, 8H); uv (CH_2Cl_2) λmax (log ε) 274 (4.55), 316 (4.21, sh), 520 nm (4.08); ms m/z 408 (M^+). Anal. Calcd for $C_{20}H_{20}N_6S_2{\bullet}0.5H_2O$: C, 57.53; H, 5.07; N, 20.13. Found: C, 57.26; H, 4.78; N, 19.94.

Preparation of 4,4'-Bis(1-pyrrolidinyl)-2,2',3,3'-tetraaminobiphenyl (4b). To a suspension of **1b** (160 mg, 0.39 mmol) in 50 ml of dry ether was added $LiAlH_4$ (100 mg, 2.5 mmol) by small portions under nitrogen, and the mixture was stirred for 72 h at room temperature. Excess $LiAlH_4$ was quenched with water, and the mixture was extracted with ether. Evaporation of solvent afforded 128 mg of crude hexamine (**4b**) as pale orange crystals in 93% yield, which was purified by sublimation (170 °C, 10^{-2} Torr) to give colorless plates. mp 209-211

°C; ir (KBr) 3400, 3320, 2950, 2800, 1480 cm^{-1}; ^{1}H nmr (90 MHz, $CDCl_3$) δ 6.67 (s, 4H), 3.53 (br s, 8H), 3.08 (m, 8H), 1.95 (m, 8H); ms m/z 352 (M^+). Anal. Calcd for $C_{20}H_{28}N_6$: C, 68.94; H, 6.94; N, 24.12. Found: C, 68.47; H, 7.93; N, 23.80 (Correct analytical values could not be obtained because of its lability).

Preparation of 4,4'-Bis(7-(1-pyrrolidinyl)benzo[c][1,2,5]selenadiazolyl) (2b). To a solution of crude hexamine **4b** (50 mg, 0.14 mmol) in CH_2Cl_2 (20 ml) was added powdered SeO_2 (78 mg, 0.70 mmol), and the mixture was stirred for 30 min at room temperature. Dark violet filtrate was collected by suction. The insoluble material was thoroughly washed with water and EtOH, and the residue was extracted with CH_2Cl_2 (soxhlet). The extract and the violet filtrate were combined and chromatographed on Al_2O_3 (CH_2Cl_2) giving violet powder of **2b** (56 mg) in 79% yield. mp 300-305 °C (decomp.); ir (KBr) 2960, 2860, 1540 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$) δ 7.76 (d, J = 7.6 Hz, 2H), 6.30 (br d, 2H), 3.86 (m, 8H), 2.07 (m, 8H); uv (CH_2Cl_2) λmax (log ε) 298 (4.51), 324 (4.36), 552 nm (4.01); ms m/z 502 (M^+). Anal. Calcd for $C_{20}H_{20}N_6Se_2 \cdot 0.5H_2O$: C, 46.98; H, 4.14; N, 16.44. Found: C, 47.23; H, 4.13; N, 16.20.

Preparation of 4-(Trifluoroacetylamino)benzo[c][1,2,5]thiadiazole (7). To a solution of 4-aminobenzo[*c*][1,2,5]thiadiazole (**6**)[9] (2.01 g, 13.3 mmol) in 20 ml of CCl_4 was added $(CF_3CO)_2O$ (8.92 g, 42.4 mmol), and the mixture was heated under reflux for 1 h. After evaporation of solvent, recrystallization of the residue from petroleum ether afforded 2.55 g of faintly orange plates of **7** in 78% yield. mp 85-88 °C; ir (KBr) 3380, 1725, 1619, 1563, 1190-1144 cm^{-1}; ^{1}H nmr (90 MHz, $CDCl_3$) δ 9.13 (br s, 1H), 8.47 (d, J = 6.3 Hz, 1H), 7.55-7.95 (m, 2H); ms m/z 247 (M^+). Anal. Calcd for $C_8H_4N_3OF_3S$: C, 38.87; H, 1.63; N, 17.00; S, 12.97. Found: C, 39.12; H, 1.36; N, 16.93; S, 13.01.

Preparation of 4-(1-Pyrrolidinyl)benzo[c][1,2,5]thiadiazole (8). To a solution of **7** (2.06 g, 8.35 mmol) and 1,4-dibromobutane (7.23 g, 33.5 mmol) in dry acetone (40 ml) was added portionwise 3.1 g (54 mmol) of crashed KOH at 100 °C. After heating under reflux for 7 h, the mixture was concentrated to dryness. The residue was suspended in water and extracted with CH_2Cl_2. Chromatographic separation on Al_2O_3 (CH_2Cl_2) afforded bright orange crystals of **8** (1.28 g) in 75% yield. mp 84-85 °C; ir (KBr) 2950, 2820, 1520, 732 cm^{-1}; ^{1}H nmr (200 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.5, 7.5 Hz, 1H), 7.20 (d, J = 8.5 Hz, 1H), 6.23 (d, J = 7.5 Hz, 1H), 3.03 (m, 4H), 2.06 (m, 4H); uv (CH_2Cl_2) λmax (log ε) 266 (4.47), 304 (3.60), 316 (3.56), 460 nm (3.70); ms m/z (relative intensity) 205 (M^+, 100), 204 (M^+-1, 14). Anal. Calcd for $C_{10}H_{11}N_3S$: C, 58.51; H, 5.40; N, 20.47. Found: C, 58.60; H, 5.49; N, 20.35.

Preparation of cation radical salts of 1b. A solution of **1b** (20 mg, 0.05 mmol) in 3 ml of THF containing 0.1 mol dm^{-3} nBu$_4$NPF$_6$ or nBu$_4$NI$_3$ was electrolyzed by applying constant current of 10 μA for 3 d. Cation radical salts of **1b**$^{+\bullet}$PF$_6^-$ and **1b**$^{+\bullet}$I$_3^-$ were obtained as black thin plates or black rods, respectively.

1b$^{+\bullet}$PF$_6^-$: mp 149-153 °C; ir (KBr) 1560, 1190, 830 cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_6F_6PS_2$: C, 43.40; H, 3.64; N, 15.18. Found: C, 43.55; H, 4.01; N, 14.83.

1b$^{+\bullet}$I$_3^-$: mp 150-160 °C; ir (KBr) 1555, 1190 cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_6I_3S_2$: C,30.44; H, 2.55; N, 10.65. Found: C, 30.79; H, 2.79; N, 10.46.

X-ray structural analysis of 1b. A dark red plate-like crystal with a dimension of 0.3 x 0.3 x 0.08 mm was obtained by recrystallization from chlorobenzene/CH$_3$CN, and used for the data collection on an AFC-5R automated four-circle diffractometer with a rotating anode (200 mA, 45 kV) at 13 °C. A total of 2157 independent reflections within $2\theta = 55°$ was collected by using graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71049$ Å) with a scan speed of 4° min^{-1} and the ω - 2θ scan mode of $(1.2 + 0.3 \tan\theta)°$. Crystal data are as follows: orthorhombic, Pbcn (No. 60), a = 13.205(2), b = 7.783(1), c = 18.167(2) Å, V = 1867.1(5) Å^3, Z = 4, D_{calcd} = 1.453 g cm^{-3}. The structure was solved by the direct method by using RANTAN81 program with some modification. Atomic parameters of non-hydrogen atoms were refined by the block-diagonal least-squares method with anisotropic temperature factors. Most of hydrogen atoms were picked up from the D-map, and the positions of H5 and H92 were calculated geometrically. They were included in the refinement at the final stage with isotropic temperature factors. The final R value is 7.93% for 946 reflections with $|Fo| > 3\sigma|Fo|$ (No. of parameters, 168). The largest electron density in the D-map after the final refinement is 0.41 e/Å^3. No absorption correction was applied ($\mu = 2.916$ cm^{-1}). All the calculations were carried out on an ACOS 2020 computer at Tohoku University by using applied library programs of UNICS III system. The estimated standard deviations are 0.007 - 0.015 Å for bond distances and 0.3 - 0.8° for bond angles, respectively, within the non-hydrogen atoms.

X-ray structural analysis of 1b$^{+\bullet}$PF$_6^-$. A black thin plate-like crystal with a dimension of 0.35 x 0.20 x 0.05 mm was obtained by an electrochemical oxidation of **1b** in THF, and used for the data collection. A total of 4219 reflections within $2\theta = 50°$ was collected on an AFC-5 four-circle diffractometer (25 mA, 50 kV) by using graphite monochromated MoK$_\alpha$ radiation with the ω - 2θ scan mode of 3° min^{-1} and scan width of $(1.25 + 0.5 \tan\theta)°$. Intensities of the higher angle reflections ($35° < 2\theta < 50°$) were very weak probably because of the small size and low quality of the crystal. Several larger crystals were proved to be twinned. Another data set was collected on an AFC-5R diffractometer (MoK$_\alpha$, 200 mA, 45 kV) on the same specimen, which was also used for the structure solution. However, the former data set gave a more satisfactory result in the refinement than the latter. Crystal data are as follows: monoclinic, $P2_1$ (No. 4), a = 14.125(3), b = 13.355(3), c = 11.656(2) Å, β = 91.69(1)°, V = 2197.9(8) $Å^3$, Z = 4, D_{calcd} = 1.658 g cm^{-3}. The structure was solved by the direct method and successive R factor method with some difficulty. There are two crystallographically independent molecules in the crystal whose molecular planes are parallel to the ac plane, and coplanar two-dimensional "sheets" are formed at y/b = 0, 1/4, 1/2, and 3/4. Because these molecules cannot be related by a mirror symmetry or an inversion center, the space group is $P2_1$ but not $P2_1/m$ with higher symmetry. The atomic parameters were refined by using block-diagonal least-squares method with anisotropic temperature factors for S and P, and isotropic ones for C, N, and F. Hydrogen atoms were not included in the refinement because of a small number of reflections available for the refinement. Higher angle reflections ($40° < 2\theta < 50°$) were omitted because of their very weak intensities and large observational errors. The final R value is 12.69% for 1580 non-zero reflections within 2θ = 40° (No. of parameters, 312). The largest residual electron density is 0.81 e/$Å^3$. No absorption correction was applied (μ = 3.728 cm^{-1}). Comparisons of the bond distances and angles of **1b**$^{+\bullet}$ with those of neutral **1b** make no sense because of their large estimated standard deviations (0.03 - 0.08 Å for distances and 1 - 4° for angles, respectively).

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