TETRACYANOQUINODIMETHANES FUSED WITH 1,2,5-THIADIAZOLE AND PYRAZINE UNITS

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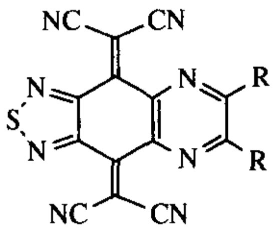
Abstract - 1,2,5-Thiadiazolopyrazino-TCNQs underwent reversible four-stage one-electron reduction and gave conductive CT complexes with some donors. The X-ray structural analysis of the unsubstituted derivative revealed that the coplanar "sheet"-like network was formed by interatomic contacts of S--N≡C and H--N≡C in crystal.

Electron acceptors fused with heterocycles are of interest because the metal-insulator transition can be suppressed by the interheteroatom interactions.[1] For example, the bis[1,2,5]thiadiazolo derivative (2) of tetracyanoquinodimethane (TCNQ) gave a charge-transfer (CT) complex with tetraselenatetracene which showed the metallic behavior down to 1.5 K.[2] The X-ray structural analysis of 2 revealed the existence of strong intermolecular interaction of S--N≡C,[3] which was also observed in anion-radical salts of 2.[4] Two-dimensional conductivity in $(n\text{-Bu})_3NMe^+$ $2^{-\bullet}$ salt is especially interesting because it showed the possibility of electron transfer along the direction of S--N≡C contacts. On the other hand, electron acceptors possessing large π-electron systems have been known to be favored in forming highly conducting organic solid because of the reduced intra- and intermolecular Coulombic repulsion in their anion radicals. If the negative charge on one molecule delocalizes to a neighboring molecule through the intermolecular interaction, there can be a new way to get planar and enlarged π-electron systems without extending the π-framework of a single molecule (Scheme 1). We report here the preparation and properties of 1,2,5-thiadiazolopyrazino-TCNQs, 1, the promising candidates for this purpose.



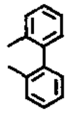
(1)

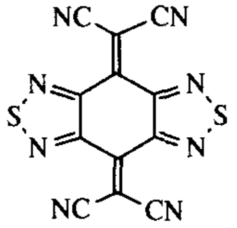
a: R=H

b: R=Me

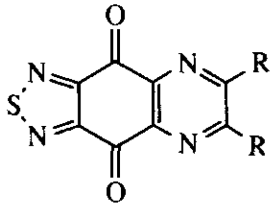
c: R=Ph

d: R,R=





(2)



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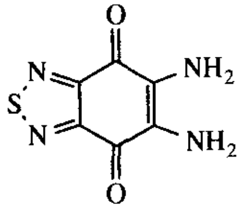
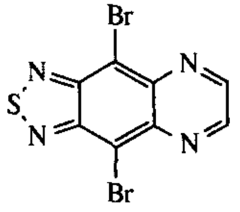
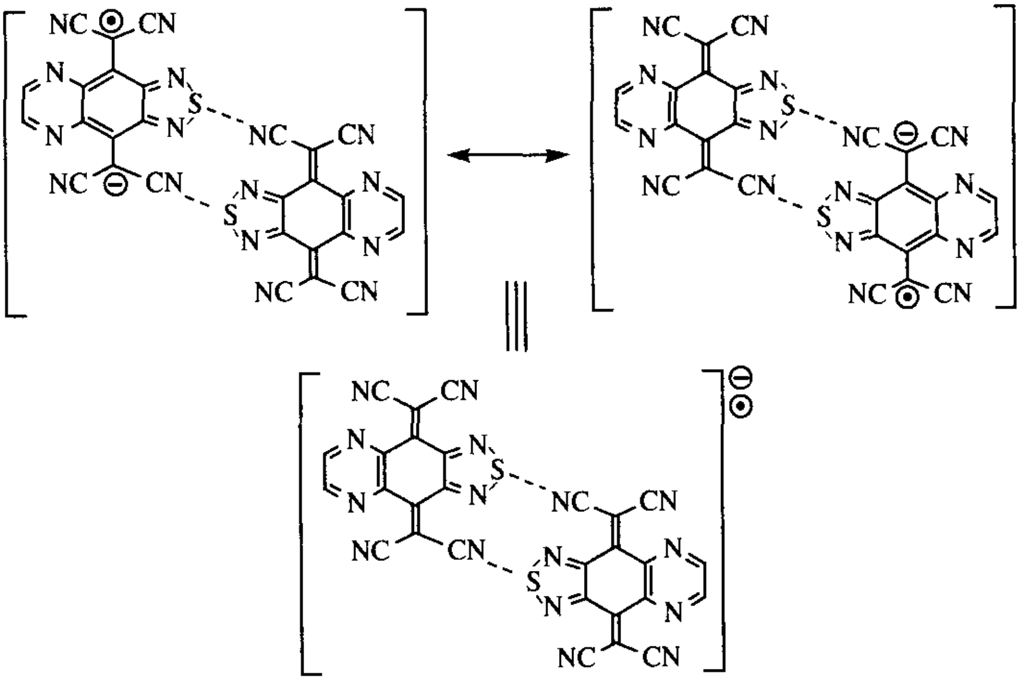


(4)



(5)

Scheme 1



enlarged π-electron system

RESULTS AND DISCUSSION

Preparation. Acceptors (**1a** - **1d**) were prepared by the condensation reactions of the corresponding quinones (**3a** - **3d**) with malononitrile in the presence of $TiCl_4$ and dry pyridine. Quinones (**3a** - **3d**) were obtained by the reactions of 5,6-diaminobenzo[*c*][1,2,5]thiadiazole (4)[5] with the corresponding 1,2-diketones, respectively. Because the preparation of **1a** was in low yield and unreproducible, another preparation was pursued by using 4,9-dibromo[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (**5**) as a precursor. However, **4** did not react with t-butylmalononitrile,[6] malononitrile anion in the presence of Pd(II) catalyst,[7] or tetracyanoethylene oxide.[8]

X-ray analysis. In order to investigate the molecular structure as well as the possible interheteroatom interactions, structural analysis of **1a** was carried out. It figured out a planar geometry for **1a** with the largest deviation of 0.13 Å from the molecular plane at N(5) (Figure 1). Molecular deformation into a butterfly shape was not observed. The twisting angles for dicyanomethylene groups are only 2.2° [C(4)=C(10)] and 2.7° [C(3)=C(9)], showing the negligible steric repulsion between the cyano groups and the lone pairs of pyrazine nitrogens.[9] The most striking feature in crystal is the formation of a nearly coplanar "sheet"-like arrangement of molecules (Figure 2) which resembles that in **5**. In the "sheet", molecule **A** was connected with molecule **B** to form a coplanar dyad by S(1)--N(6)≡C(12) (3.08 Å) contacts which are quite shorter than the sum of van der Waals radii (S--N, 3.35 Å).[10] Molecule **A** was further connected with molecule **C** by another kind of S(1)--N(5)≡C(11) (3.13 Å) contacts. There exist two kinds of H--N≡C contacts in the sheet, which may also contribute to the "sheet" formation by hydrogen bond type interaction. The "sheet" stacks to infinite layer. One-dimensional columnar stack of **1a** is formed along the b axis with the molecular overlaps shown in Figure 3. The observed dyad formation in **1a** suggests the possibility that the negative charge in **1a**$^{-\bullet}$ can delocalize over two molecules as depicted in Scheme 1.

Redox properties. Reduction potentials of **1a** - **1d** were measured by cyclic voltammetry and summarized in Table 1 together with those of 2 and TCNQ. Acceptors (**1a** - **1d**) underwent reversible four-stage one-electron reduction like 2. The lower E_1 values of **1a** - **1d** than that of TCNQ are due to a decrease in the contribution of quinoid structure by annelation of heterocycles. It is noteworthy that K_{sem} values are much smaller than that of TCNQ. Because the X-ray analysis showed the planar geometry for **1a**, the contraction of K_{sem} is due to the smaller Coulombic repulsion in their anion radicals.

Substitution at the pyrazine ring of **1a** little affected the redox properties. Reduction potentials of **1c** are quite similar to those of **1a**, indicating that bulky phenyl groups no longer affect the molecular geometry of **1a**. Elec-

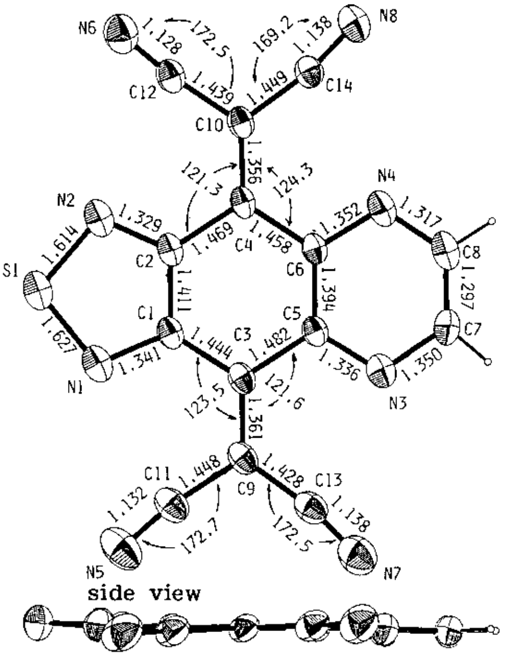


Figure 1. Thermal ellipsoid of **1a**, showing the bond distances and selected bond angles.

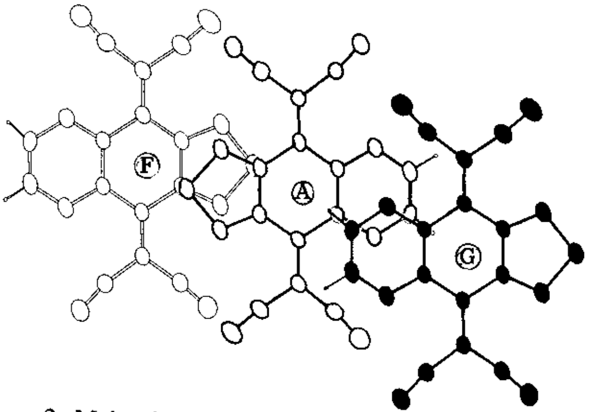


Figure 3. Molecular overlap in **1a**. The interplanar distances are 3.57 Å for molecule **A** and **F**, and 3.42 Å for **A** and **G**. Dihedral angle is 0.0° for two cases. Molecules A, F, and G are related by the following symmetry operations: **A** (x, y, z); **F** (-x, -y, -z); **G** (-x, 1-y -z).

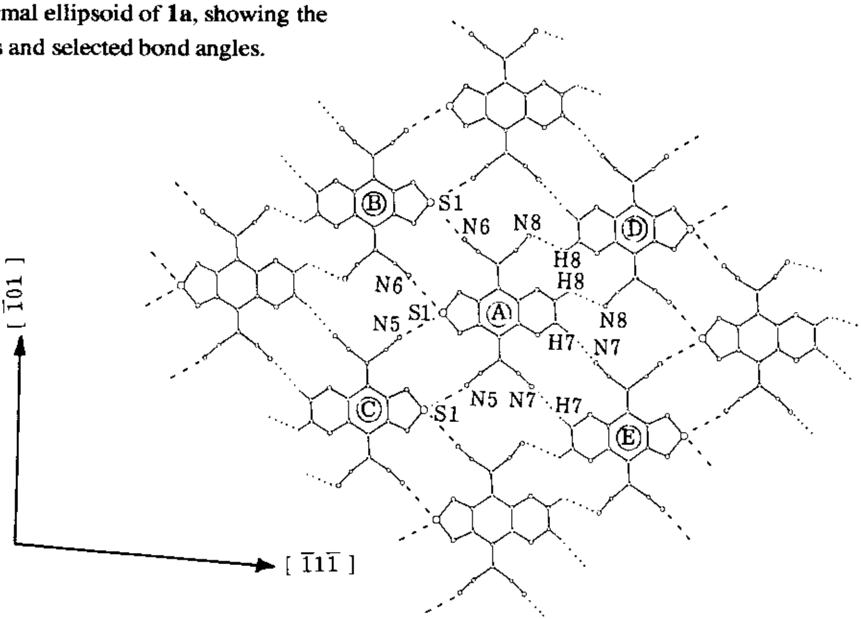


Figure 2. Nearly coplanar "sheet" network in **1a**. S(1) -- N(6)$\equiv$C(12) (3.08 Å) and S(1) -- N(5)$\equiv$C(11) (3.13 Å) contacts are shown by broken lines. Angles for S-N-C atomic array are 171.6° and 166.1°, respectively. N(8) -- H(8)-C(8) (2.54 Å) and N(7) -- H(7)-C(7) (2.64 Å) contacts are shown by dotted line. Angles for N-H-C atomic array are 127.5° and 172.0°, respectively. The deviations between neighboring molecular planes are 0.44 Å, 0.64 Å, 0.50 Å, and 0.29 Å for molecules **A** and **B**, **A** and **C**, **A** and **D**, and **A** and **E**, respectively. Molecules **A** - **E** are related by the following symmetry operations: **A** (x, y, z); **B** (-x, -y, 1-z); **C** (1-x, -y -z); **D** (-1-x, 1-y, -z); **E** (-x, 1-y, -1-z).

tron donating property of the methyl groups resulted in lowering of reduction potentials of **1b** compared with **1a**. This effect is more significant for E_3 and E_4 than for E_1 and E_2, indicating that E_3 and E_4 correspond to the reduction of 1,2,5-thiadiazolo[3,4-*g*]quinoxaline skeleton. In fact, E_1 of **5** (-1.17 V in MeCN) is close to E_3 of **1a**. On the other hand, annelation of phenanthrene moiety resulted in higher values for E_3 and E_4. The small difference between E_3 and E_4 indicates the delocalization of negative charge over 1,2,5-thiadiazolo[3,4-*i*]dibenzo[*a,c*]phenazine skeleton in the trianion radical of **1d**, which resulted in the facile reduction of $\mathbf{1d}^{3-\bullet}$ to $\mathbf{1d}^{4-}$.

CT complexes and anion radical salts. Acceptors **1a** and **1b** formed crystalline CT complexes with donors (Table 2) whereas **1c** did not. Because the redox properties of **1c** is similar to that of **1a**, no complexation of **1c** can be accounted for by the steric effects of bulky phenyl groups which prevent the effective face-to-face overlap of molecules in crystal. It is noteworthy that tetrathiatetracene (TTT) - **1a** (1:1) complex exhibits a good electrical conductivity. Although similar degree of charge transfer is indicated from the CN stretching frequencies for TTT - **1a** and TTT - **1b**, the conductivity of the latter is lower by 10^3 than that of the former. These results suggest that the interatomic contact of H--N≡C in **1a** is also important to form a favorable molecular arrangement for high conductivity. The good conductivity in bis(*N*-methylbenzothiazolinylidene) - **1b** is due to the 1:2 molar ratio of the complex resulting in the incomplete charge transfer from the donor to **1b**.

Formation of anion radical salts was examined for **1b** and **1c**. Reaction of **1b** with LiI in MeCN afforded a blue green anion radical [λ_{max}/nm (log ε), 663 (4.31), 598 (3.85), 362 (3.86), 316 (4.20)], which was isolated as a stable salt with 1:1 molar ratio. Although this salt is completely charge transferred, the electrical resistivity is quite lower (ρ, 1.9 x 10^2 Ωcm) than the usual simple salts ("Mott insulators")[11] such as $Li^+TCNQ^{-\bullet}$ (ρ, 2 x 10^5 Ωcm).[12] The observed good conductivity of $Li^+\mathbf{1b}^{-\bullet}$ indicates that the decreased Coulombic repulsion allows the easy disproportionation of $\mathbf{1b}^{-\bullet}$ to $\mathbf{1b}^0$ and $\mathbf{1b}^{2-}$. Other salts of $\mathbf{1b}^{-\bullet}$ and $\mathbf{1c}^{-\bullet}$ summarized in Table 3 were obtained by similar reduction of **1b** and **1c** with the corresponding iodides in MeCN. Anion radical of **1c** did not crystallize with Li^+, Na^+, or K^+ as a counter ion, which may be due to the dissimilarity of molecular sizes. Because of the incomplete charge transfer, the 2:3 salt of N-methyl-1,10-phenanthrolinium and $\mathbf{1c}^{-\bullet}$ exhibits a good electrical conductivity.

This work has revealed that 1,2,5-thiadiazolopyrazino-TCNQs gave stable anion radical salts and conductive complexes with some donors. Although the formation of enlarged π-electron system by interheteroatom interactions was not confirmed, the dyad formation of **1a** by S--N≡C contacts suggests the possibility of charge delocalization over two molecules in $\mathbf{1}^{-\bullet}$.

Table 1. Reduction potentials[a] and semiquinone formation constants[b] of **1a** - **1d**, **2**, and TCNQ

	E_1	E_2	$\log K_{sem}$	E_3	E_4
1a	-0.01	-0.46	7.76	-1.35	-1.75[c]
1b	-0.06 (+0.03)	-0.52 (-0.46)	7.93 (8.45)	-1.48 (-1.44)	-1.92[c] (-1.88[c])
1c	0.00 (+0.12)	-0.41 (-0.33)	7.07 (7.76)	-1.32 (-1.32)	-1.74[c] (-1.79[c])
1d	-[d] (+0.06)	-[d] (-0.41)	-[d] (8.10)	-[d] (-1.18)	-[d] (-1.59[c])
2	-0.02	-0.49	8.10	-1.21	-1.76
TCNQ	+0.18 (+0.28)	-0.36 (-0.29)	9.31 (9.83)	<-2.0 (<-2.0)	<-2.0 (<-2.0)

[a] E/V vs SCE, 0.1 mol dm^{-3} Et_4NClO_4, Pt wire, scan rate 100 mV s^{-1} in MeCN. E^{ox} of ferrocene is +0.38 V. Values in parentheses are those measured in DMF (E^{ox} of ferrocene is +0.44 V). [b] $K_{sem} = [A^{-\cdot}]^2/[A^0][A^{2-}]$. $\log K_{sem} = (E_1 - E_2) / 0.058$. [c] Quasi-reversible wave. Values were calculated as E_p + 0.03 V. [d] Values were not obtained because of its very low solubility.

Table 2. Molar ratios,[a] CN stretching frequencies, and electrical resistivities[b] of CT complexes

complex	D:A ratio	ν_{CN} / cm^{-1}	ρ_{RT} / Ωcm
tetrathiatetracene - **1a**	1:1	2187	30
tetrathiatetracene - **1b**	1:1	2188	1.1×10^4
tetrathiafulvalene - **1b**	1:1	2208	6.7×10^4
2,3,5,6-tetramethyl-*p*-phenylenediamine - **1b**	1:1	2198	4.7×10^4
bis(*N*-methylbenzothiazolinylidene) - **1b**	1:2	2167	64

[a] Determined on the basis on elemental analyses. [b] Measured on compaction pellets by a two-probe method at room temperature.

Table 3. Molar ratios,[a] CN stretching frequencies, and electrical resistivities[b] of anion radical salts

salt	molar ratio	ν_{CN} / cm^{-1}	ρ_{RT} / Ωcm
Li^+**1b**$^{-\cdot}$	1:1	2171	1.9×10^2
Et_4N^+(**1b**)$_2^{-\cdot}$	1:2	2172	1.3×10^3
Et_4N^+(**1c**)$_2^{-\cdot}$	1:2	2166	7.9×10^2
N-Methyl-1,10-phenanthrolinium **1b**$^{-\cdot}$	1:1	2165	7.8×10^4
(*N*-Methyl-1,10-phenanthrolinium)$_2$ (**1c**)$_3^{2-}$	2:3	2167	61

[a] Determined on the basis on elemental analyses. [b] Measured on compaction pellets by a two-probe method at room temperature.

EXPERIMENTAL SECTION

Preparation of [1,2,5]Thiadiazolo[3,4-*g*]quinoxaline-4,9-dione (3a). To a suspension of 5,6-diaminobenzo[*c*][1,2,5]thiadiazole-4,7-dione (**4**)[5] (3.00 g, 15.3 mmol) in 95% acetic acid (525 ml) was added 40% aqueous glyoxal (60 ml, 471 mmol), and the mixture was stirred for 3 h at room temperature. After 500 ml of water was added, grayish precipitates were filtrated, washed with water and MeOH. Purification by sublimation (300 °C, 10^{-2} Torr) gave **3a** (2.77 g, 83%) as greenish yellow crystals. mp > 400 °C; ir (KBr) 1708 cm^{-1}; ^1H nmr (200 MHz, DMSO-d_6) δ 9.18 (s); ms m/z 218 (M^+). Anal. Calcd for $C_8H_2N_4O_2S$: C, 44.04; H, 0.92; N, 25.68. Found: C, 44.25; H, 0.75; N, 25.80.

Preparation of 6,7-Dimethyl[1,2,5]thiadiazolo[3,4-*g*]quinoxaline-4,9-dione (3b). A suspension of diamine (**4**) (1.89 g, 9.63 mmol) and diacetyl (19.8 g, 230 mmol) in nitromethane (220 ml) was heated under reflux for 2 h. After evaporation of solvent, the crude product was chromatographed on Al_2O_3 (dichloromethane elution). Recrystallization from dichloromethane - EtOH afforded **3b** as orange crystals (1.40 g, 57%). mp 199 - 199.5 °C; ir (KBr) 1700 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 2.87 (s); ms m/z 246 (M^+). Anal. Calcd for $C_{10}H_6N_4O_2S$: C, 48.78; H, 2.46; N, 22.75; S, 13.02. Found: C, 48.33; H, 2.38; N, 22.43; S, 12.98.

Preparation of 6,7-Diphenyl[1,2,5]thiadiazolo[3,4-*g*]quinoxaline-4,9-dione (3c). A suspension of diamine (**4**) (119 mg, 0.608 mmol) and benzil (443 mg, 2.11 mmol) in acetic acid (30 ml) was heated for 21 h at 65 °C. After cooling, greenish precipitates were filtrated and washed with water and EtOH. Purification by sublimation (235 °C, 10^{-2} Torr) gave **3c** (169 mg, 75%) as yellow crystals. mp 331 - 333 °C; ir (KBr) 1708 cm^{-1}; ^1H nmr (200 MHz, DMSO-d_6) δ 7.43–7.51 (6H, m), 7.56-7.63 (4H, m); ms m/z 370 (M^+). Anal. Calcd for $C_{20}H_{10}N_4O_2S$: C, 64.86; H, 2.72; N, 15.13. Found: C, 64.63; H, 2.47; N, 15.20.

Preparation of [1,2,5]Thiadiazolo[3,4-*i*]dibenzo[*a*,*c*]phenazine-4,15-dione (3d). A suspension of diamine (**4**) (81.3 mg, 0.414 mmol) and phenanthrene-5,6-dione (208 mg, 1.00 mmol) in acetic acid (20 ml) was heated for 6.5 h at 70 °C. After cooling, yellow precipitates were filtrated and washed with EtOH. Purification by sublimation (350 °C, 10^{-2} Torr) gave **3d** (85.6 mg, 56%) as red crystals. mp 438 - 443 °C; ir (KBr) 1703 cm^{-1}; ^1H nmr (200 MHz, DMSO-d_6) δ 7.93–8.08 (4H, m), 8.96 (2H, d, J = 8.4 Hz), 9.31 (2H, dd, J = 7.6, 1.6 Hz); ms m/z 368 (M^+). Anal. Calcd for $C_{20}H_8N_4O_2S$: C, 65.21; H, 2.19; N, 15.21; S. 8.70. Found: C, 65.35; H, 2.12; N, 15.14; S, 8.50.

Preparation of 4*H*,9*H*-4,9-bis(dicyanomethylene)[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (1a). To a suspension of diketone **3a** (508 mg, 2.33 mmol) in dry dichloromethane (200 ml) were added dropwise $TiCl_4$ (17.3 g, 91.0 mmol) at room temperature and then a dry dichloromethane solution (60 ml) containing malononitrile (514 mg, 7.77 mmol) and dry pyridine (7.5 ml) at -50 °C over 1.5 h. After stirring for 60 h at -30 °C, 600 ml of cold ether was added at -50 °C to give green precipitates, which were quickly collected and washed with MeOH and water. The solid product was dissolved in dichloromethane (400 ml) and acetone (90 ml), and the solution was washed with dil. HCl and dried over Na_2SO_4. Evaporation of solvent and chromatographic separation on SiO_2 (dichloromethane - ether, 50 : 1) afforded **1a** (42.3 mg, 6%) as yellow crystals. mp 260 - 320 °C (decomp.); ir (KBr) 2213 cm^{-1}; ^1H nmr (200 MHz, DMSO-d_6) δ 10.00 (s); ms m/z 314 (M^+). Correct analytical values were obtained for the CT complex with tetrathiatetracene (*vide infra*).

Preparation of 4*H*,9*H*-4,9-bis(dicyanomethylene)-6,7-dimethyl[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (1b). To a suspension of diketone **3b** (856 mg, 3.47 mmol) in dry dichloromethane (300 ml) were added dropwise $TiCl_4$ (5.27 g, 27.8 mmol) at room temperature and then a dry dichloromethane solution (150 ml) containing malononitrile (851 mg, 12.9 mmol) and dry pyridine (17 ml) at -70 °C over 1.5 h. After stirring for 6 h at -30 °C and for 1 h at -10 °C, 3 mol dm^{-3} HCl (240 ml) was added. The mixture was extracted with dichloromethane, and the extract was washed with water and dried over Na_2SO_4. Evaporation of solvent and recrystallization from MeCN afforded **1b** (836 mg, 71%) as yellow fibers. mp 230 - 245 °C (decomp.); ir (KBr) 2216 cm^{-1}; ^1H nmr (60 MHz, $CDCl_3$) δ 2.83 (s); ms m/z 342 (M^+); uv (MeCN) λmax (log ε) 391 (4.56), 372 (4.51), 313 (4.51), 303 (4.29, sh), 236 nm (4.13). Anal. Calcd for $C_{16}H_6N_8S$: C, 56.14; H, 1.47; N, 32.73; S, 9.36. Found: C, 56.16; H, 1.56; N, 32.47; S, 9.06.

Preparation of 4*H*,9*H*-4,9-bis(dicyanomethylene)-6,7-diphenyl[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (1c). To a suspension of diketone **3c** (268 mg, 0.724 mmol) in dry dichloromethane (150 ml) were added dropwise $TiCl_4$ (3.45 g, 18.2 mmol) at room temperature and then a dry dichloromethane solution (100 ml) containing malononitrile (274 mg, 4.15 mmol) and dry pyridine (15 ml) at -50 °C over 1.5 h. After stirring for 6 h at -30 °C and for 2 h at -10 °C, 3 mol dm^{-3} HCl (300 ml) was added. The mixture was extracted with dichloromethane, and the extract was washed with water and dried over Na_2SO_4. Evaporation of solvent and the residue was washed with EtOH. Recrystallization from dichloromethane - n-hexane afforded **1c** (236 mg, 70%)

as red crystals. mp 326 - 328 °C (decomp.); ir (KBr) 2214 cm^{-1}; ^{1}H nmr (60 MHz, CDCl$_3$) δ 7.7 - 7.9 (4H, m), 7.2 - 7.5 (6H, m); ms m/z (relative intensity) 466 (M$^+$, 100), 440 (M$^+$ - CN, 24), 439 (26). Anal. Calcd for $C_{26}H_{10}N_8S$: C, 66.94; H, 2.16; N, 24.02; S, 6.87. Found: C, 66.92; H, 1.87; N, 23.74; S, 6.82.

Preparation of 4*H*,15*H*-4,15-bis(dicyanomethylene)[1,2,5]thiadiazolo[3,4-*i*]dibenzo[*a*,*c*]-phenazine (1d). To a suspension of diketone **3d** (83.6 mg, 0.227 mmol) in dry dichloromethane (30 ml) were added dropwise TiCl$_4$ (510 mg, 2.68 mmol) at room temperature and then a dry dichloromethane solution (20 ml) containing malononitrile (44.4 mg, 0.672 mmol) and dry pyridine (2 ml) at -70 °C over 15 min. After stirring for 4 h at -10 °C and for 2 h at room temperature, 3 mol dm^{-3} HCl (60 ml) was added and orange precipitates were filtrated and washed with MeOH. Recrystallization from dioxane gave **1d** as orange crystals (68.0 mg, 59%). mp 365 - 385 °C (decomp.); ir (KBr) 2213 cm^{-1}; ^{1}H nmr spectrum could not be measured because of its very low solubility; ms m/z (relative intensity) 464 (M$^+$, 95), 463 (M$^+$-1, 100) 438 (M$^+$ - CN, 27). Anal. Calcd for $C_{26}H_8N_8S \cdot 0.5C_4H_8O_2$: C, 66.14; H, 2.38; N, 22.04. Found: C, 66.05; H, 2.16; N, 21.79.

Preparation of 4,9-Dibromo[1,2,5]thiadiazolo[3,4-*g*]quinoxaline (5). To a solution of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole[13] (4.00 g, 10.4 mmol) in acetic acid (50 ml) was added portionwise Fe powder (7.02 g, 126 mmol) at 100 °C. After heating at 100 °C for 1.5 h, 10 ml of EtOH was added. The mixture was heated for another 1.5 h. After cooling, precipitates were filtrated and extracted with ethyl acetate for 11 h (soxhlet). Evaporation of solvent followed by recrystallization from EtOH gave 5,6-diamino-4,7-dibromobenzo[*c*][1,2,5]thiadiazole (6) (2.36 g, 70%) as pale yellow needles. mp 257 - 260 °C; ir (KBr) 3410, 3320, 1620, 1460 cm^{-1}; ^{1}H nmr (90 MHz, DMSO-d$_6$) δ 5.1 (br s), ms m/z (relative intensity) 326 (M$^+$, 10), 324 (M$^+$, 100), 322 (M$^+$, 12). Anal. Calcd for $C_6H_4N_4Br_2S$: C, 22.24; H, 1.24; N, 17.29; S, 9.90. Found: C, 22.29; H, 1.29; N, 17.07; S, 9.71.

A suspension of powdered diamine (6) (827 mg, 2.55 mmol) and 2,3-dihydroxy-1,4-dioxane (625 mg, 5.20 mmol) in acetic acid (170 ml) was stirred for 6.5 h at room temperature. After evaporation of solvent, 400 ml of water was added and the mixture was extracted with dichloromethane. The extract was washed with brine and dried over Na$_2$SO$_4$. Chromatographic separation on SiO$_2$ (dichloromethane elution) gave **5** (537 mg, 65%) as orange fibers. mp 170 - 210 °C (decomp.); ir (KBr) 1255, 970, 895 cm^{-1}; ^{1}H nmr (90 MHz, CDCl$_3$) δ 9.03 (s); ms m/z (relative intensity) 348 (M$^+$, 19), 346 (M$^+$, 100), 344 (M$^+$, 43). Anal. Calcd for $C_8H_2N_4Br_2S$: C, 27.77;

H, 0.58; N, 16.19. Found: C, 27.68; H, 1.24; N, 16.08.

Preparation of CT complexes. Tetrathiafulvalene - **1b** complex was obtained by the following direct method. To a hot dichloromethane solution (15 ml) of **1b** (83.0 mg, 0.242 mmol) was added a solution of tetrathiafulvalene (68.0 mg, 0.329 mmol) in dichloromethane (2 ml). The solution was cooled to room temperature, and separated brown solid (87.0 mg, 66%) was filtrated and dried *in vacuo*, mp 230-231 °C (decomp.). Anal. Calcd for $C_{22}H_{10}N_8S_5$: C, 48.34; H, 1.84; N, 20.50; S, 29.32. Found: C, 48.58; H, 1.65; N, 20.50; S. 29.62.

Other complexes were prepared by a direct method. CT complexes with TTT were obtained by using a soxhlet extractor because of the very low solubility of TTT in dichloromethane.

TTT - **1a** (1:1); black powder, mp > 360 °C. Anal. Calcd for $C_{32}H_{10}N_8S_5{\cdot}H_2O$: C, 56.13; H, 1.77; N, 16.36. Found: C, 56.14; H, 1.79; N, 16.29.

TTT - **1b** (1:1); dark green powder, mp > 400 °C. Anal. Calcd for $C_{34}H_{14}N_8S_5$: C, 58.77; H, 2.03; N, 16.13; S, 23.07. Found: C, 58.80; H, 1.81; N, 16.03; S, 22.87.

2,3,5,6-tetramethyl-*p*-phenylenediamine - **1b** (1:1); brown powder, mp 280-300 °C (decomp.). Anal. Calcd for $C_{26}H_{22}N_{10}S{\cdot}0.5H_2O$: C, 60.57; H, 4.50; N, 27.17; S, 6.22. Found: C, 60.35; H, 4.00; N, 27.06; S, 6.32.

Bis(*N*-methylbenzothiazolinylidene) - **1b** (1:2); grayish green powder, mp > 400 °C. Anal. Calcd for $C_{48}H_{26}N_{18}S_4{\cdot}H_2O$: C, 57.59; H, 2.82; N, 25.18; S, 12.81. Found: C, 57.28; H, 2.55; N, 25.42; S, 12.42.

Preparation of anion radical salts. Li^+**1b**$^{-\cdot}$ salt was obtained as follows. To a hot MeCN solution (50 ml) of **1b** (504 mg, 1.57 mmol) was added a solution of LiI (1.07 g, 8.03 mmol) in MeCN (20 ml). The solution was cooled to room temperature and separated violet precipitates (534 mg, 96%) was filtrated and dried *in vacuo*, mp > 400 °C. Anal. Calcd for $C_{16}H_6N_8SLi{\cdot}0.25H_2O$: C, 54.32; H, 1.85; N, 31.67. Found: C, 54.29; H, 1.84; N, 31.52.

Other salts were obtained by similar reactions with the corresponding iodides in MeCN.

Et_4N^+(**1b**)$_2^{-\cdot}$ (1:2); black-violet fibers, mp > 400 °C. Anal. Calcd for $C_{40}H_{32}N_{17}S_2$: C, 58.31; H, 4.04; N, 28.90. Found: C, 58.38; H, 3.92; N, 28.67.

N-Methyl-1,10-phenanthrolinium **1b**$^{-\cdot}$ (1:1); violet powder, mp > 400 °C. Anal. Calcd for $C_{29}H_{17}N_{10}S{\cdot}0.5H_2O$: C, 63.73; H, 3.32; N, 25.63; S, 5.87. Found: C, 63.91; H, 2.90; N, 25.53; S, 5.91.

$Et_4N^+(\mathbf{1c})_2^{-\bullet}$ (1:2); black needles, mp 237 - 238 °C (decomp.). Anal. Calcd for $C_{60}H_{40}N_{17}S_2{\bullet}0.5H_2O$: C, 67.21; H, 3.85; N, 22.21. Found: C, 67.46; H, 3.63; N, 21.99.

(*N*-Methyl-1,10-phenanthrolinium)$_2$ $(\mathbf{1b})_3^{2-}$ (2:3); black fibers, mp 258 - 259 °C (decomp.). Anal. Calcd for $C_{102}H_{52}N_{28}S_3$: C, 69.38; H, 2.97; N, 22.21; S, 5.45. Found: C, 69.61; H, 2.48; N, 22.12; S, 5.58.

X-ray structural analysis of 1a. A yellow plate-like crystal with a dimension of 0.2 x 0.35 x 0.18 mm was grown by a vapor-diffusion method from dichloromethane - n-hexane. A total of 4593 independent reflections within $2\theta = 64°$ was collected by using graphite monochromated MoKα radiation ($\lambda = 0.71049$ Å) on an AFC-5R automated four-circle diffractometer with a rotating anode (200 mA, 45 kV). Crystal data are as follows: MF $C_{14}H_2N_8S$, MW 314.29, triclinic, $P\bar{1}$, $a = 7.997(1)$, $b = 12.491(3)$, $c = 7.215(2)$ Å, $\alpha = 103.70(2)$, $\beta = 110.41(1)$, $\gamma = 87.98(2)°$, $V = 655.4(2)$ Å^3, $Z = 2$, and $Dc = 1.59$ g cm^{-3}. The structure was solved by the direct method using RANTAN81[14] program with some difficulty. By supposing the space group to be noncentrosymmetric $P1$, two molecules were appeared in the E-map which were related by a center of symmetry. After transformation of the space group to $P\bar{1}$, atomic parameters of non-hydrogen atoms were refined by the block-diagonal least-squares method. All the hydrogen atoms were picked up from the D-map and included in the refinement with isotropic temperature factors. No absorption correction was applied ($\mu = 2.472$ cm^{-1}). The final R value is 8.33% for 2573 reflections with $|Fo| > 3\sigma\ |Fo|$. The estimated standard deviations are 0.005 - 0.008 Å for bond distances and 0.2 - 0.6° for bond angles, respectively. All the calculations were carried out on an ACOS 2020 computer at Tohoku University by using applied library programs of UNICS III system.[15] Atomic parameters, thermal parameters, bond distances and angles, structure factors are deposited as supplementary material.

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