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Novel Bis-Fused π-Electron Donors for Organic Metals: 2-(1,3-Dithiol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene

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Bis-fused π-electron donors composed of tetrathiafulvalene (TTF) and 2-(thiopyran-4-ylidene)-1,3-dithiole (TPDT), 2-(1,3-dithiol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (**1a**, TPDT-TTP), and its derivatives (**1b**−**d**, **2a**−**d**) have been synthesized as donor components for organic conductors. An X-ray structure analysis of bis(methylthio)-**1** (**1c**) revealed that the TPDT-TTP skeleton is almost planar except for the outer 1,3-dithiole ring, and that the crystal has a two-dimensional "θ-type" arrangement of molecules. The cyclic voltammograms of TPDT-TTPs exhibit four pairs of single-electron redox waves. The first oxidation potential (E_1) of **1a** (+0.37 V vs SCE, in PhCN) is comparable to that of TTF (+0.35 V) and is higher by 0.1 V than that of TPDT (+0.27 V). The observed substituent effect on E_1 values suggests that the first one-electron oxidation mainly occurs in the 2-(thiopyran-4-ylidene)-1,3-dithiole (TPDT) moiety. On the other hand, on-site coulombic repulsion estimated from the $E_2 - E_1$ value is lower than in TTF and TPDT. MNDO MO calculations reveal that all the sulfur atoms in the 1,3-dithiole rings have the same phase in the HOMO, a condition necessary for realization of effective transverse intermolecular interaction. The present donors have produced many charge-transfer complexes and cation radical salts showing relatively high conductivity ($\sigma_{rt} = 10^{-1}$−10^{1} S cm^{-1}), several of which display metallic temperature dependence.

Introduction

Recently, compounds that act as π-electron donors have received considerable attention in the context of the preparation of organic conductors.[1,2] In particular, the modification of tetrathiafulvalene (TTF) has been popular because TTF and its derivatives have been structural components of many organic superconductors.[3] In general, the modification of TTF has served one of two purposes. The first is to increase the dimensionality of conducting salts, which has usually been achieved by introduction of alkylchalcogeno substituents onto the TTF skeleton[4] and/or the exchange of the sulfur atoms of TTF with the larger chalcogenides such as selenium or tellurium.[5] The second goal has been to decrease on-site coulombic repulsion in the dication state, which is realized by the insertion of a π-electron spacer unit between two 1,3-dithiole rings of TTF,[2d,6] or by linkage of two or three TTF units.[2e,7] The first condition is essential in order to suppress the metal to insulator transition at low temperature characteristic of the usual one-dimensional metals.[8] In fact, all of the TTF donors that have afforded ambient superconductors so far have satisfied this requirement. But the design and preparation of donor molecules that satisfy both of the principles mentioned above are now of particular interest in the search for new organic metals that are stable at low temperature. Bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (BDT-TTP),[9] is one of the most promising donors. We have recently synthesized many BDT-TTP derivatives,[10] several of which have produced metallic cation radical salts stable to low temperatures (≤4.2 K).[10,11] In this context, bis-fused 1,3-dithiole donors having different skeletons from TTF are also attractive targets. 2-(Thiopyran-4-ylidene)-1,3-dithiole (TPDT),[12]

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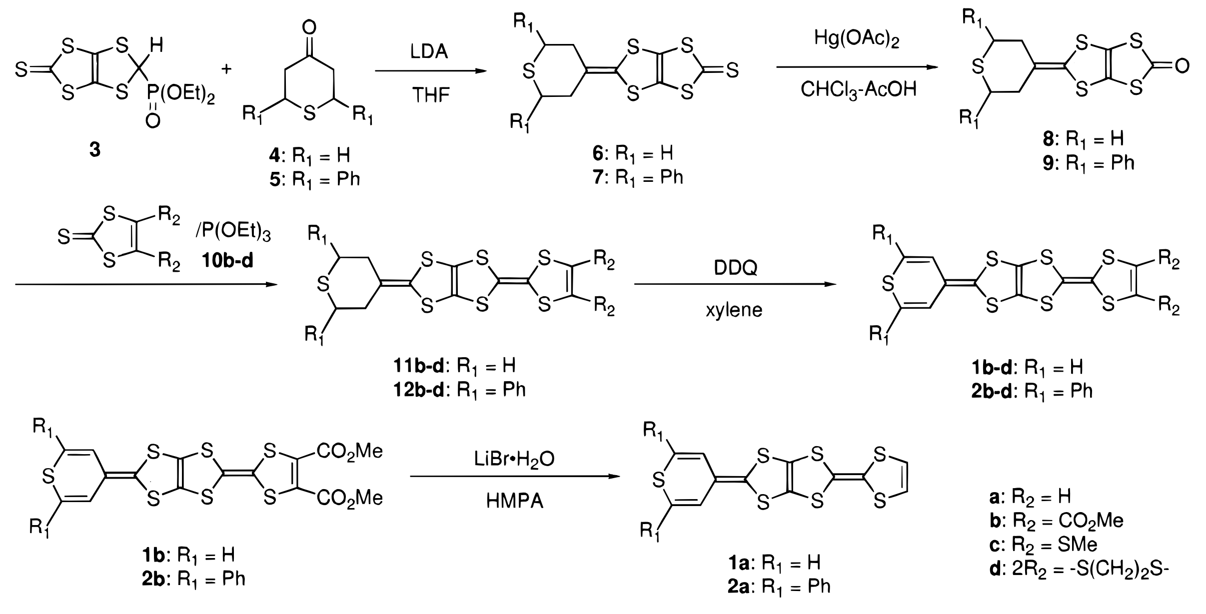
Scheme 1

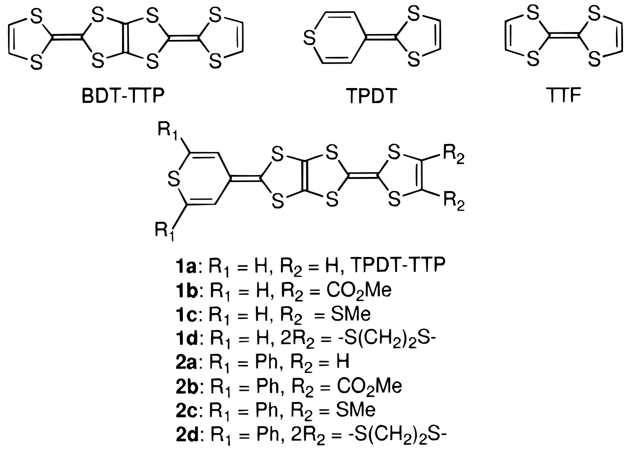


which possesses an unsymmetrical π-framework, is an interesting donor because unsymmetrical donors are available for the stabilization of metallic states at low temperatures. In fact several unsymmetrical derivatives of TTF, tetraselena- and diselenadithia-fulvalene have produced superconducting cation radical salts.[13] In this article, we report the synthesis, structure, and electrochemical properties of various derivatives of 2-(1,3-dithiol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (TPDT-TTP, **1a**)[14] which is a bis-fused donor composed of TTF and TPDT. Furthermore, the conducting properties of their charge-transfer (CT) complexes and cation radical salts are described.

Results and Discussion

Synthesis. The syntheses of TPDT-TTPs were achieved as shown in Scheme 1. Treatment of a phosphorus reagent for a Wittig−Horner reaction (**3**)[4e] with an equimolar amount of LDA in the presence of tetrahydrothiopyran-4-one (**4**) or 2,6-diphenyltetrahydrothiopyran-4-one (**5**) in THF at −78 °C gave 1,3-dithiole-2-thione **6** or **7** in 67 and 85% yield, respectively. The reaction of **6, 7** with an excess of mercury(II) acetate in chloroform−acetic acid (1:1, v/v) at room temperature afforded the corresponding 1,3-dithiol-2-ones (**8**, **9**) in the respective yields of 92 and 90%. When the ketones **8**, **9** were cross-coupled with various 1,3-dithiole-2-thiones (**10b**-**d**) in neat triethyl phosphite at 80 °C, the corresponding tetrahydro derivatives of **1** (**11b**-**d**) and **2** (**12b**-**d**) were obtained in 40−73% yields. Dehydrogenation of **11** and **12** was carried out by treatment with an excess of DDQ in refluxing xylene to give the target donors (**1b-d** and **2b-d**) in 59−98% yields. In the synthesis of TPDT derivatives, the dehydrogenation was carried out by using *p*-chloranil in refluxing benzene or toluene.[12] Sandman et al. had reported that the yield of bis(methoxycarbonyl)-TPDT considerably decreased (84 → 10%) when DDQ was used as a dehydrogenation reagent.[12c] However, it was quantitatively obtained by DDQ dehydrogenation in our case. The differing result of Sandman et al. and ourselves is probably due to several differences in experimental conditions such as reaction temperature, concentration of substrates, reaction time, etc. The

Chart 1



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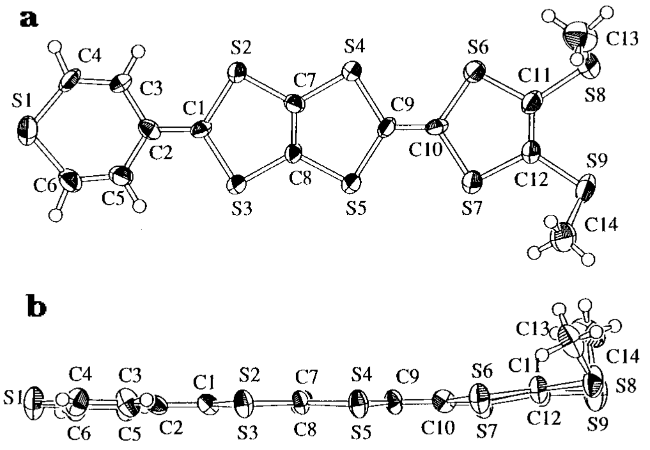

Figure 1. Molecular structure of **1c** with atomic numbering scheme (a) and the side view (b); selected bond lengths (Å): S(1)–C(4), 1.72(2); S(1)–C(6), 1.74(2); S(2)–C(1), 1.77(2); S(2)–C(7), 1.75(2); S(3)–C(1), 1.76(2); S(3)–C(8), 1.73(2); S(4)–C(7), 1.75(2); S(4)–C(9), 1.77(2); S(5)–C(8), 1.75(1); S(5)–C(9), 1.76(2); S(6)–C(10), 1.77(2); S(6)–C(11), 1.75(1); S(7)–C(10), 1.76(2); S(7)–C(12), 1.75(2); S(8)–C(11), 1.77(2); S(8)–C(13), 1.76(2); S(9)–C(12), 1.75(1); S(9)–C(14), 1.74(3); C(1)–C(2), 1.36(2); C(2)–C(3), 1.46(2); C(2)–C(5), 1.43(2); C(3)–C(4), 1.33(2); C(5)–C(6), 1.33(2); C(7)–C(8), 1.33(2); C(9)–C(10), 1.33(2); C(11)–C(12), 1.33(2).

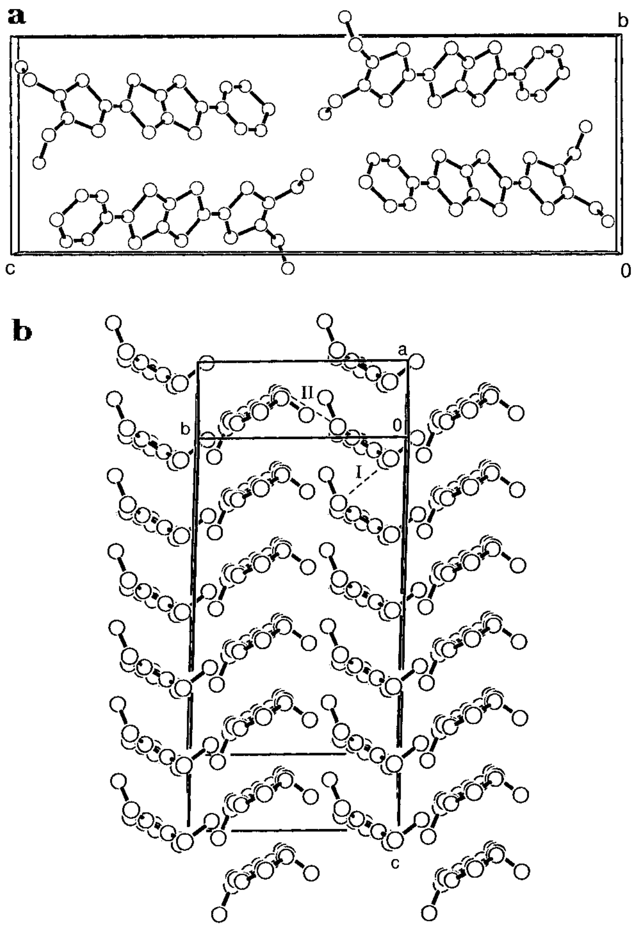

Figure 2. Crystal structure of **1c**: (a) viewed along *a*-axis; (b) viewed along the molecular long axis, showing intermolecular S–S contacts (≤3.70 Å) with dotted lines; S(5)–S(6), 3.68(2) Å for I, S(2)–S(3), 3.63(2) Å for II.

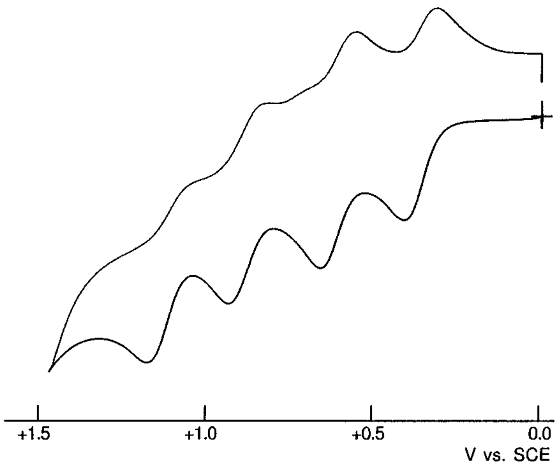

Figure 3. Cyclic voltammogram of **2d** in benzonitrile at 25 °C.

unsubstituted derivatives **1a** and **2a** were obtained in 45 and 62% yields, respectively, by the demethoxycarbonylation of **1b** and **2b** with an excess (10 mol equiv) of LiBr·H_2O in HMPA at 90 °C and then at 130 °C. All of the donors are stable solids and considerably less soluble in organic solvents than the corresponding TTF and TPDT derivatives.

Molecular and Crystal Structures of 1c. From among the newly prepared donors, single crystals of **1c** were obtained by recrystallization from CS_2–benzonitrile, and its molecular and crystal structures were determined in an X-ray structure analysis.[21] The molecular structure is shown in Figure 1. The TPDT-TTP skeleton is almost planar except for the outer 1,3-dithiole ring, which is slightly tilted with a dihedral angle of 9.5°. The methylthio groups are bent upward from the molecular plane. In the crystal **1c**, molecules are stacked in a head-to-head manner, while they are arranged in a head-to-tail manner along the transverse direction (Figure 2a). The present arrangement of molecules is similar to the donor array in θ-(BEDT-TTF)$_2$I$_3$ which is a 2D metal showing superconductivity at 3.6 K (Figure 2b).[15] The interplanar distance of the stack is 3.48 Å. There are S–S contacts less than the sum of the van der Waals radii (3.70 Å) in both the intra- and the interstack; S(5)–S(6), 3.68(2) Å for the intrastack, S(2)–S(3), 3.63(2) Å for the interstack. This result indicates that **1c** is expected to produce two-dimensional metals if it has the same arrangement in the molecular complexes.[16]

Electrochemical Properties. The electrochemical properties of TPDT-TTP derivatives were investigated by cyclic voltammetry. Figure 3 shows the cyclic voltammogram of **2d** in benzonitrile. All the donors show four pairs of redox waves, all of which correspond to single-electron transfers, given that the peak current of each step is almost the same, and that there are four redox-active units (three 1,3-dithiole rings and one thiopyrane one). The redox potentials are summarized in Table 1 together with those of the related compounds measured under identical conditions. The first oxidation potential (E_1) of **1a** (+0.37 V vs SCE) is lower by 0.07 V than that

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[15] Kobayashi, H.; Kato, R.; Kobayashi, A.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1986**, 833.

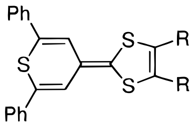
[16] Though the array of donors in neutral state has not been well correlated with that in a partially oxidized state, two-dimensional array of neutral molecules has been expected to be available for construction of two-dimensional conductors. For examples; (a) Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 301. (b) Martin, J. D.; Canadell, E.; Becker, J. Y.; Bernstein, J. *Chem. Mater.* **1993**, *5*, 1199. (c) Batsanov, A. S.; Bryce, M. R.; Cooke, G.; Heaton, J. N.; Howard, J. A. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1701. (d) Bryce, M. R.; Cooke, G.; Dhindsa, A. S.; Ando, D. J.; Hursthouse, M. B. *Tetrahedron Lett.* **1992**, *33*, 1783.

Table 1. Redox Potentials of 1, 2, and Their Related Compounds in PhCN (V vs SCE, 25 °C)

compound	E_1	E_2	E_3	E_4[a]	$E_2 - E_1$
1a	+0.37	+0.60	+0.94	+1.11	0.23
1c	+0.38	+0.63	+0.93	+1.10	0.25
2a	+0.35	+0.58	+0.89	+1.15	0.23
2b	+0.38	+0.64	+1.07	+1.30	0.26
2c	+0.36	+0.61	+0.89	+1.12	0.25
2d	+0.36	+0.61	+0.88	+1.18	0.25
BDT-TTP	+0.44	+0.62	+1.05 [a]	+1.13	0.18
TTF	+0.35	+0.77			0.42
TPDT	+0.28	+0.69			0.41
13a	+0.27	+0.63			0.36
13b	+0.50	+0.80			0.30
13c	+0.34	+0.63			0.29

[a] Irreversible step. Anodic peak potentials.

Chart 2



13a: R = H
13b: R = CO_2Me
13c: R = SMe

of BDT-TTP. The increase in donating ability is expected to be perturbed by almost half, as in the case of TTF and TPDT, because the number of redox-active sites (1,3-dithiole rings) of BDT-TTP is twice those of TTF. However, the difference in the E_1 values of **1a** and BDT-TTP is identical to that between TTF and TPDT. Such a significant perturbation to the donating ability of the bis-fused donor system indicates that the positive charge of $(\text{TPDT-TTP})^{\bullet+}$ lies on the TPDT moiety, not on the TTF. The E_1 value of diphenyl substituted TPDT-TTP (**2a**) is slightly lower by 0.02 V than that of **1a**, suggesting an enhancement of the donating ability by substitution of weak electron-donating phenyl groups. In contrast, E_1 values of **1a** and **2a** are comparable to that of TTF (+0.35 V), and are higher by ca. 0.1 V than those of TPDT (+0.28 V) and diphenyl-TPDT (**13a**, +0.27 V). Such a decrease of donating ability upon fusion of two donors is also observed in other bis-fused donors such as BDT-TTP and DTEDT (2-(1,3-dithiol-2-ylidene)-5-(2-ethanediylidene-1,3-dithiole)-1,3,4,6-tetrathiapentalene).[17] Compounds **2** exhibit very weak substituent effects on E_1 values. For example, **2b** which has strongly electron-withdrawing methoxycarbonyl groups, has an E_1 value higher by only 0.03 V than the unsubstituted derivative **2a**, while the corresponding TPDT **13b** has a higher E_1 value, by 0.3 V, than **13a**. Thus, the donating ability of **2b** is slightly weaker than that of TTF and is superior to that of BEDT-TTF ($E_1 = +0.51$ V). The results described in this section suggest that the positive charge of $(\text{TPDT-TTP})^{\bullet+}$ exists primarily on the more donating TPDT part, and that the weaker donating TTF moiety plays the role of a sulfur-based substituent. This is consistent with the E_1 value of **2a** being identical with that of **13c**. The same situation exists with DTEDT.[17b] On the other hand, the ΔE (= $E_2 - E_1$) value of **1a** (0.23 V) and **2a** (0.23 V) is smaller by ca. 0.13−0.19 V than those of TTF (0.42 V),TPDT (0.41 V) and **13a** (0.36 V). This result strongly suggests that the on-site coulombic repulsion in the dication of TPDT-TTP decreases relative to that in TTF and TPDT by delocalization of the two positive charges over the entire molecule.

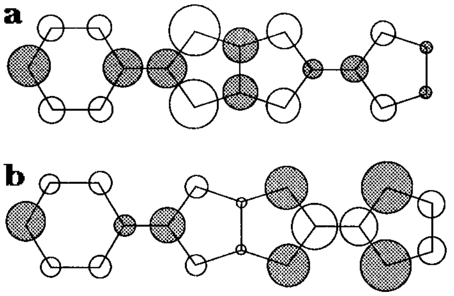


Figure 4. Atomic coefficients of TPDT-TTP in the HOMO (a) and in the HOMO-1 (b). The radii of the circles are approximately proportional to the LCAO coefficients.

Molecular Orbital Calculation. Molecular orbital calculations on TPDT-TTP were carried out by the semiempirical MNDO method using the Gaussian 90 program.[18] The geometry was fully optimized assuming that the symmetry was C_{2v}. Figure 4 shows the HOMO and the 2nd HOMO (HOMO-1) of TPDT-TTP. Thus, the HOMO of TPDT-TTP is composed of those of TTF[19] and TPDT which interact in-phase with each other. In contrast, HOMO-1 is constructed from an out-of-phase interaction between the HOMOs of each TTF and TPDT unit. In the HOMO of TPDT-TTP, all sulfur atoms in the 1,3-dithiole rings have the same phase. Thus, effective transverse intermolecular interaction is expected in its cation radical salts, which is an indispensable requirement for realization of two-dimensional electronic structures.

Preparation and Properties of Charge-Transfer Complexes and Cation Radical Salts. Most TPDT-TTP donors reacted with tetracyano-*p*-quinodimethane (TCNQ) and tetra-*n*-butylammonium triiodide to give the corresponding TCNQ complexes and I_3 salts. The other cation radical salts were prepared by an electrochemical oxidation of the donor at a constant current in the presence of the corresponding tetra-*n*-butylammonium salt as electrolyte. The electrical conductivity of the charge-transfer salts obtained was measured using the four-probe technique with gold paste contacts. The results are summarized in Table 2. The parent TPDT-TTP (**1a**) gave a highly conducting TCNQ complex and an I_3 salt, whose conductivities on compressed pellets were high values of 37 and 6.0 S cm^{-1} at room temperature, respectively. Unfortunately both salts showed semiconductive temperature dependence of conductivity, however, their activation energies (E_a) were very small (ca. 0.02 eV), suggesting that their single crystals are expected to exhibit metallic conductive behavior. Compressed pellets of TCNQ and the I_3 salt of **1c** were poorly conductive semiconductors compared to those of **1a**. In contrast, cation radical salts of **1c** with octahedral anions (PF_6, AsF_6, and SbF_6) showed high conductivities (σ_{rt} = 10^1 S cm^{-1}). They exhibited metallic temperature dependence near room temperature, and a metal to semiconductor transition was observed at 150−250 K (Figure

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Table 2. Electrical Properties of TCNQ Complexes and Cation Radical Salts of 1 and 2

donor	acceptor	D:A[a]	ν_{CN}[b]	σ_{rt}, S cm^{-1} [c]	E_a, eV
1a	TCNQ	1:1	2196	37	0.019
	I_3	2:1		6.0	0.021
1c	TCNQ	1:1	2195	1.8	0.009−0.032
	ClO_4	5:3		1.0×10^{-1} [d]	0.090
	BF_4	5:4		1.5[d]	0.067
	ReO_4	3:2		1.3×10^{-2}	0.14
	PF_6	5:3		53[d]	$T_{MI} = 170$ K
	AsF_6	5:3		12[d]	$T_{MI} = 150$ K
	SbF_6	2:1		16	$T_{MI} = 250$ K
	I_3	3:2		4.0×10^{-1}	0.064
1d	TCNQ	1:1	2196	13	$T_{MI} = 230$ K
	ClO_4	*e*		2.8×10^{-1} [d]	0.11
	BF_4	*e*		20[d]	0.026
	PF_6	*e*		6.4×10^{-2} [d]	0.15
	AsF_6	*e*		2.8×10^{-2} [d]	0.15
	I_3	4:1		3.2	$T_{MI} = 230$ K
2a	TCNQ	4:3	2195	2.6×10^{-1}	0.036
	I_3	3:2		4.9×10^{-1}	0.034
2b	TCNQ	7:4	2183	1.2×10^{-1}	0.062
	I_3	5:3		3.7×10^{-1}	0.056
2c	TCNQ	4:3	2197	1.1	0.039
	I_3	5:4		2.2×10^{-1}	0.063
2d	I_3	4:3		1.2×10^{-1}	0.079

[a] Determined based on elemental analyses. [b] From IR spectra. [c] Measured on a compressed pellet using the four-probe technique. [d] Measured on a single crystal. [e] Not determined because adequate quantity of samples for elemental analyses could not be obtained.

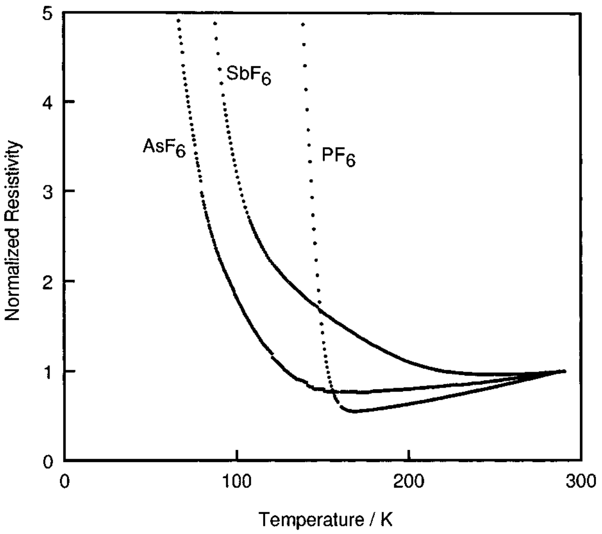

Figure 5. Conducting behavior of metallic cation radical salts of **1c**.

5). The metal to semiconductor transition temperature (T_{MI} = 250 K) of the SbF_6 salt was higher than those of the others due to the conductivity measurement being taken on a compressed pellet. We believe that its T_{MI} becomes lower in a single crystal. On the other hand, the TCNQ complex and I_3 salt of **1d** on compressed pellets also displayed metallic conductivity down to ca. 230 K, while most of the salts with tetrahedral and octahedral anions showed low conductivities of 10^{-1}-10^{-2} S cm^{-1} in single crystals. Diphenyl-substituted derivatives **2** afforded poorly conducting TCNQ complexes and I_3 salts ($\sigma_{rt} = 10^{-1}-10^{1}$ S cm^{-1} on compressed pellets) compared to the corresponding **1**, all of which were semiconductors with E_a values of 0.034−0.079 eV. It is noteworthy that **2b** gave a relatively high conducting TCNQ complex and I_3 salt ($\sigma_{rt} = 10^{-1}$ S cm^{-1}) in spite of the presence of strongly electron-withdrawing methoxycarbonyl groups.

Conclusion

In summary, we have synthesized many derivatives of bis-fused π-electron donors containing the TPDT moiety. X-ray structure analysis of **1c** reveals that the crystal has a two-dimensional θ-type arrangement of molecules. The CV data of TPDT-TTPs indicate that the positive charge in $(TPDT\text{-}TTP)^{\bullet+}$ mainly lies on the TPDT moiety. Several derivatives of TPDT-TTP afford metallic cation radical salts. This is the first example of metallic salts in which the donors possess the TPDT moiety. The results described here indicate that fusion of two donor units is a viable strategy for the formation of metallic molecular complexes.

Experimental Section

General. THF was freshly distilled under argon over sodium and benzophenone prior to use. Triethyl phosphite was distilled under argon by fractional distillation. Mixed xylene was dried and distilled under argon over CaH_2.

4,5-(Tetrahydrothiopyran-4-ylidenemethylenedithio)-1,3-dithiole-2-thione (6). To a solution of 4,5-(diethoxyphosphinylmethylenedithio)-1,3-dithiole-2-thione (**3**) (1.34 g, 3.88 mmol) and tetrahydrothiopyran-4-one (**4**) (498 mg, 4.29 mmol) in 140 mL of dry THF was added dropwise 0.5 M LDA (7.80 mL, 3.90 mmol) for 20 min at −78 °C under argon. The resultant precipitate was filtered off and washed with water and then with MeOH and dried *in vacuo*. The THF filtrate was directly column chromatographed on silica gel with dichloromethane as the eluent and evaporated. The residue was column chromatographed again on silica gel with CS_2 as the eluent. Compound **6** (809 mg, 2.62 mmol) was totally obtained as yellow microcrystals in 67% yield: mp 215 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1594, 1490 (C=C), 1419, 1251, 1177, 1070 (C=S); ^{1}H-NMR (CS_2−$CDCl_3$, 90 MHz) δ 2.76−2.38 (m, 8H); MS *m/z* 308 (M^+). Anal. Calcd for $C_9H_8S_6$: C, 35.04; H, 2.61; S, 62.35. Found: C, 34.92; H, 2.44; S, 62.50.

4,5-[(2,6-Diphenyltetrahydrothiopyran-4-ylidene)methylenedithio]-1,3-dithiole-2-thione (7). Compound **7** was obtained in 85% by the similar method as mentioned above from **3** and 2,6-diphenyltetrahydrothiopyran-4-one (**5**): orange microcrystals; mp 237−238 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1600, 1513, 1490 (C=C), 1196, 1067 (C=S); ^{1}H-NMR (CS_2−acetone-d_6, 90 MHz) δ 7.4−7.1 (m, 10H), 4.1−3.9 (m, 2H), 2.9−2.4 (m, 4H); MS *m/z* 460 (M^+). HRMS *m/z* Calcd for $C_{21}H_{16}S_6$: 459.9576. Found: 459.9551.

4,5-(Tetrahydrothiopyran-4-ylidenemethylenedithio)-1,3-dithiol-2-one (8). To a solution of **6** (600 mg, 1.94 mmol) in a mixture of chloroform (45 mL) and acetic acid (45 mL) was added mercury(II) acetate (1.55 g, 4.86 mmol) under argon, and the reaction mixture was stirred at room temperature for 2 h. The resultant white precipitate was filtered off and washed with CS_2. The filtrate was washed five times with water to remove acetic acid. The organic layer was dried over Na_2SO_4 and evaporated. After chromatographic separation on silica gel with CS_2, **8** (521 mg, 1.78 mmol) was obtained as greenish white microcrystals in 92% yield: mp 177 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1676 (C=O), 1590 (C=C), 1425, 1276; ^{1}H-NMR (CS_2−C_6D_6, 90M Hz) δ 2.6−2.1 (m, 8H); MS *m/z* 292 (M^+). Anal. Calcd for $C_9H_8OS_5$: C, 36.96; H, 2.76; S, 54.81. Found: C, 36.72; H, 2.65; S, 54.98.

4,5-[(2,6-Diphenyltetrahydrothiopyran-4-ylidene)methylenedithio]-1,3-dithiol-2-one (9). Compound **9** was obtained in 90% by the similar method as mentioned above from **7**: greenish white microcrystals; mp 179 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1683 (C=O), 1596, 1493 (C=C), 1450, 1253; ^{1}H-NMR (CS_2−C_6D_6, 90 MHz) δ 7.4−7.1 (m, 10H), 4.1−3.7 (m, 2H), 2.9−2.3 (m, 4H); MS *m/z* 444 (M^+). HRMS *m/z* Calcd for $C_{21}H_{16}OS_5$: 443.9804. Found: 443.9674. Anal. Calcd for $C_{21}H_{16}OS_5$: C, 56.72; H, 3.63; S, 36.05. Found: C, 56.53; H, 3.47; S, 35.81.

2-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-5-(tetrahydrothiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (11b). Compound **8** (140 mg, 0.480 mmol) and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**10b**) (252 mg, 1.01 mmol) was heated in triethyl phosphite (12 mL) at 80 °C under argon for 2 h. After the reaction mixture was cooled to room temperature, the resultant brown precipitate was filtered off, washed with *n*-hexane, and then dried *in vacuo*. Further purification could not be carried out because of its extremely low solubility for the common solvents. Compound **11b** (174 mg, 0.352 mmol) was obtained as dark brown powder in 73% yield: mp 225 °C dec; IR (KBr) ν (cm^{-1}) 1751, 1736 (C=O), 1585 (C=C), 1439, 1269 (C-O); HRMS *m/z* Calcd for $C_{16}H_{14}O_4S_7$: 493.8936. Found: 493.8949.

The other derivatives of **11** and **12** were obtained by the similar procedure mentioned above.

2-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-5-(tetrahydrothiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (11c). Obtained in 44% from **8** and **10c** after column chromatography on silica gel with CS_2: reddish orange microcrystals; mp 183 °C dec (recrystallized from chlorobenzene); IR (KBr) ν (cm^{-1}) 1607, 1497 (C=C), 1421, 1318, 1272; ^{1}H-NMR ($CS_2-C_6D_6$, 90 MHz) δ 2.6−2.1 (m, 8H), 2.17 (s, 6H); MS *m/z* 470 (M$^+$). Anal. Calcd for $C_{14}H_{14}S_9$: C, 35.71; H, 3.00; S, 61.29. Found: C, 35.50; H, 2.75; S, 61.27.

2-(4,5-Ethylenedithio-1,3-dithiol-2-ylidene)-5-(tetrahydrothiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (11d). Obtained in 51% from **8** and **10d** after washing thoroughly with CS_2 in order to eliminate bis(ethylenedithio)tetrathiafulvalene as the homo-coupling product of **10d**: reddish brown microcrystals; mp 204 °C dec (recrystallized from *o*-dichlorobenzene); IR (KBr) ν (cm^{-1}) 1598, 1551 (C=C), 1411, 1334, 1274; HRMS *m/z* Calcd for $C_{14}H_{12}S_9$: 467.8425. Found: 467.8460; Anal. Calcd for $C_{14}H_{12}S_9$: C, 35.86; H, 2.58. Found: C, 35.75; H, 2.69.

2-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-5-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (12b). Obtained in 70% from **9** and **10b** after column chromatography on silica gel with CS_2-CH_2Cl_2 (v/v =1:1) as the eluent; dark brown powder; mp 202−203 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1733 (C=O), 1580, 1493 (C=C), 1432, 1257 (C−O); ^{1}H-NMR (CS_2−acetone-d_6, 270 MHz) δ 7.3−7.1 (m, 10H), 4.00−3.92 (m, 2H), 3.76 (s, 6H), 2.77−2.51 (m, 4H); MS *m/z* 646 (M$^+$). Anal. Calcd for $C_{28}H_{22}O_4S_7$: C, 51.98; H, 3.43; S, 34.69. Found: C, 51.81; H, 3.39; S, 34.87.

2-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-5-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (12c). Obtained in 40% from **9** and **10c** after column chromatography on silica gel with CS_2 as the eluent; orange microcrystals; mp 200 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1596, 1492 (C=C), 1451, 1422, 1271; ^{1}H-NMR (CS_2−acetone-d_6, 90 MHz) δ 7.4−7.1 (m, 10H), 4.08−3.84 (m, 2H), 2.74−2.48 (m, 4H), 2.40 (s, 6H); MS *m/z* 622 (M$^+$). Anal. Calcd for $C_{26}H_{22}S_9$: C, 50.12; H, 3.56; S, 46.32. Found: C, 49.83; H, 3.71; S, 46.16.

2-(4,5-Ethylenedithio-1,3-dithiol-2-ylidene)-5-(2,6-diphenyltetrahydrothiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (12d). Obtained in 54% from **9** and **10d** after column chromatography on silica gel with CS_2 as the eluent: light pink microcrystals; mp 225 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1598, 1492 (C=C), 1451, 1409, 1285; ^{1}H-NMR (CS_2−acetone-d_6, 270 MHz) δ 7.3−7.1 (m, 10H), 4.0−3.9 (m, 2H), 3.30 (s, 4H), 2.80−2.48 (m, 4H); MS *m/z* 620 (M$^+$). Anal. Calcd for $C_{26}H_{20}S_9$: C, 50.29; H, 3.25; S, 46.47. Found: C, 50.03; H, 3.02; S, 46.60.

2-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (1b). A solution of DDQ (153 mg, 0.676 mmol) in mixed xylene (30 mL) was added dropwise for 20 min to a solution of **11b** (120 mg, 0.243 mmol) in mixed xylene (80 mL) at reflux under argon. After additional 10 min, the hot reaction mixture was filtered and the filtrate was ice-cooled. The resultant precipitate was filtered off and washed with acetonitrile and *n*-hexane and dried *in vacuo*. Compound **1b** (99.1 mg, 0.202 mmol) was obtained as brown solid in 83% yield. The analytically pure sample was obtained after recrystallization from chlorobenzene: mp 217-218 °C dec; IR (KBr) ν (cm^{-1}) 1746, 1721 (C=O), 1574 (C=C), 1434, 1250 (C−O); HRMS *m/z* Calcd for $C_{16}H_{10}O_4S_7$: 489.8623. Found: 489.8608; Anal Calcd for $C_{16}H_{10}O_4S_7$: C, 39.16; H, 2.05. Found: C, 39.43; H, 2.14.

The other derivatives of **1** and **2** were obtained by the similar procedure mentioned above.

2-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (1c). Obtained in 79% from **11c** after column chromatography on silica gel with CS_2 as the eluent; orange platelike crystal: mp 183−184 °C dec (recrystallized from 1,2-dichloroethane); IR (KBr) ν (cm^{-1}) 1514, 1502 (C=C), 1421, 1295; UV ($CHCl_3$) λ (nm) (log ϵ) 401 (4.06), 368 (4.34), 343 (4.38), 323 (4.36), 266 (4.15); ^{1}H-NMR (CS_2−acetone-d_6, 90M Hz) δ 6.12 (d, J = 5.4 Hz, 4H), 2.40 (s, 6H); MS *m/z* 466 (M$^+$). Anal. Calcd for $C_{14}H_{10}S_9$: C, 36.02; H, 2.16; S, 61.81. Found: C, 35.75; H, 2.14; S, 61.84.

2-(4,5-Ethylenedithio-1,3-dithiol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (1d). Obtained in 59% from **11d** after column chromatography with hot CS_2 as the eluent: yellowish brown microcrystals; mp 198 °C dec (recrystallized twice from chlorobenzene); IR (KBr) ν (cm^{-1}) 1618, 1501 (C=C), 1415, 1292; ^{1}H-NMR ($CS_2-C_6D_6$, 270 MHz) δ 5.87 (d, J = 5.4 Hz, 4H), 2.92 (s, 4H); MS *m/z* 464 (M$^+$). Anal. Calcd for $C_{14}H_8S_9$: C, 36.18; H, 1.73. Found: C, 36.46; H, 1.87.

2-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-5-(2,6-diphenylthiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (2b). Obtained in 88% from **12b** after column chromatography on silica gel with $CS_2-CH_2Cl_2$ (v/v = 1:1) as the eluent: brown microcrystals; mp 181−182 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1720 (C=O), 1577, 1486 (C=C), 1431, 1239 (C−O); UV ($CHCl_3$) λ (nm) (log ϵ) 427 (4.35), 347 (4.19), 262 (4.47), 250 (4.48); ^{1}H-NMR ($CS_2-C_6D_6$, 90 MHz) δ 7.5−7.3 (m, 10H), 6.29 (s, 2H), 3.59 (s, 6H); MS *m/z* 642 (M$^+$). Anal. Calcd for $C_{28}H_{18}O_4S_7$: C, 52.31; H, 2.82; S, 34.91. Found: C, 52.26; H, 2.72; S, 34.88.

2-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-5-(2,6-diphenylthiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (2c). Obtained in 98% from **12c** after column chromatography on silica gel with CS_2 as the eluent: red microcrystals; mp 161 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1593, 1484 (C=C), 1443, 1303, 1233; UV ($CHCl_3$) λ (nm) (log ϵ) 428 (4.37), 354 (4.27), 253 (4.51); ^{1}H-NMR ($CS_2-C_6D_6$, 90 MHz) δ 7.5−7.3 (m, 10H), 6.26 (s, 2H), 2.21 (s, 6H). Anal. Calcd for $C_{26}H_{18}S_9$: C, 50.45; H, 2.93; S, 46.62. Found: C, 50.05; H, 2.85; S, 46.66.

2-(4,5-Ethylenedithio-1,3-dithiol-2-ylidene)-5-(2,6-diphenylthiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (2d). Obtained in 64% from **12d** after column chromatography on silica gel with CS_2 as the eluent: reddish brown platelike crystals; mp 191−192 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1594, 1484 (C=C), 1443, 1287, 1234; UV ($CHCl_3$) λ (nm) (log ϵ) 430 (4.36), 356 (4.28) 340 (4.26), 250 (4.52); ^{1}H-NMR (CS_2−acetone-d_6, 90 MHz) δ 7.6−7.2 (m, 10H), 6.30 (s, 2H), 3.34 (s, 4H); MS *m/z* 616 (M$^+$). Anal. Calcd for $C_{26}H_{16}S_9$: C, 50.62; H, 2.61; S, 46.77. Found: C, 50.50; H, 2.60; S, 46.72.

2-(1,3-Dithiol-2-ylidene)-5-(thiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (1a). A mixture of **1b** (95.6 mg, 0.195 mmol) and LiBr·H_2O (204 mg, 1.95 mmol) in HMPA (30 mL) was vacuumed for 1 h to eliminate the trace of amines of the solvent. The mixture was stirred at 90 °C for 1 h and then at 130°C for 1 h under bubbling argon gas. The reaction mixture was cooled to room temperature and extracted for three times with benzene. The organic layer was washed three times with distilled water and dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. The residue was column chromatographed on silica gel with CS_2 as the eluent and recrystallized from chlorobenzene to afford **1a** (32.5 mg, 0.087 mmol) as orange microcrystals in 45% yield: mp 200−201 °C dec; IR (KBr) ν (cm^{-1}) 1541, 1497 (C=C), 1296, 1205; UV ($CHCl_3$) λ (nm) (log ϵ) 402 (4.04), 377 (4.30), 328 (4.37), 275 (4.08); ^{1}H-NMR ($CS_2-C_6D_6$, 90 MHz) δ 6.75 (s, 2H), 5.86 (d, J = 5.4 Hz, 4H); MS *m/z* 374 (M$^+$). HRMS *m/z* Calcd for $C_{12}H_6S_7$:

373.8514. Found: 373.8539. Anal Calcd for $C_{12}H_6S_7$: C, 38.48; H, 1.61. Found: C, 38.75; H, 1.49.

2-(1,3-Dithiol-2-ylidene)-5-(2,6-diphenylthiopyran-4-ylidene)-1,3,4,6-tetrathiapentalene (2a). Compound **2a** was obtained in 62% by the similar method as mentioned above from **2b** after column chromatography on silica gel with CS_2 as the eluent: reddish brown microcrystals; mp 169 °C dec (recrystallized from CS_2−EtOH); IR (KBr) ν (cm^{-1}) 1596, 1507, 1485 (C═C), 1443, 1297, 1253; UV ($CHCl_3$) λ (nm) (log ϵ) 430 (4.33), 350 (4.20), 252 (4.44); ^{1}H-NMR (CS_2−acetone-d_6, 90 MHz) δ 7.6−7.2 (m, 10H), 6.49 (s, 2H), 6.31 (s, 2H); MS m/z 526 (M^+). Anal. Calcd for $C_{24}H_{14}S_7$: C, 54.72; H, 2.68; S, 42.60. Found: C, 54.98; H, 2.96; S, 42.68.

General Procedure for Preparation of TCNQ Complexes and I_3 Salts. Hot solutions of donor molecule and TCNQ or tetra-*n*-butylammonium triiodide in chlorobenzene or 1,1,2-trichloroethane were mixed, and the resultant precipitate was collected by filtration. TCNQ complex was washed with CS_2 and CH_3CN and dried in vacuo. I_3^- salt was washed with CS_2 and MeOH and dried *in vacuo*. The ratio of donor and TCNQ or I_3^- was determined by elemental analysis.

General Procedure for Preparation of Cation Radical Salts. Cation radical salts of **1c** and **1d** were prepared by electrochemical oxidation in chlorobenzene−ethanol (17:1, v/v) at a constant current of 0.1−0.5 μA in the presence of the corresponding tetra-*n*-butylammonium salts at 20 °C for **1c** and 50 °C for **1d** for 1−3 weeks. The crystals obtained were washed with EtOH and were air-dried at room temperature. The ratio of donor and anion was determined by elemental analysis.

X-ray Diffractional Analysis of 1c. Crystal data: $C_{14}H_{10}S_9$, $M = 466.77$, monoclinic, space group $P2_1/c$, $a = 5.21(8)$ Å, $b = 11.11(6)$, $c = 30.82(6)$ Å, $\beta = 92.0(6)°$, $V = 1784(28)$ Å^3, $Z = 4$, $D_c = 1.737$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu = 11.10$ cm^{-1}, $F(000) = 952.00$. A dark red plate crystal of dimensions 0.94 × 0.16 × 0.03 mm crystallized from CS_2−benzonitrile was used for X-ray measurement at 293 K on a Rigaku AFC7R diffractometer equipped with graphite monochromated MoKα radiation and a 12 kW rotating anode generator. Cell constants were determined from 25 carefully centered reflections in the range $20.33 < 2\theta < 26.96°$. Intensity data were collected to a maximum 2θ value of 60.8° by the $\omega-2\theta$ scan technique. The total number of independent reflections measured was 5546, of which 1413 were considered to be observed [$I > 3.00\sigma(I)$]. The structure was solved by direct methods (SHELXS86).[20,21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The structure was refined by full-matrix least squares to $R = 0.068$, $Rw = 0.074$.

Electrochemical Measurement. The cyclic voltammetry system used in this experiment was composed of a Yanaco polarographic analyzer Model P-1100, a Graphtec X-Y recorder Model WX-1200. The measurement was performed in benzonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate as a supporting electrolyte by use of platinum working and counter electrodes, and a Yanaco saturated calomel electrode (SCE) Model MR-P2A as reference electrode (scan rate: 50 mV/s).

Electrical Conductivity Measurement. Electrical conductivity with four-probe technique was measured on using Huso Electro Chemical System HESS 994 Multi-channel four-terminal conductometer. Electrical contacts were achieved with a gold paste.

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(20) Sheldrick, G. M. *Crystallographic Computing 3*; Oxford University Press: New York, 1985; p 175.

(21) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.