PREPARATION, STRUCTURE, AND PROPERTIES OF 1,3-BIS (1,4-DITHIAFULVEN-6-YL)AZULENES[†]

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Abstract – Novel bis(1,3-dithiole) donors containing an azulene spacer unit have been prepared from 1,3-diformylazulene using a Wittig–Horner reaction. The cyclic voltammetry revealed that they are stronger electron donors than tetrathiafulvalene and show amphoteric characters. The structural features of a benzo-fused derivative were investigated by an X-Ray analysis. The spectroelectro-chemical studies on the methylthio derivative revealed that the cation radical and dication state show the longest absorption maxima at 612 and 721 nm, respectively.

Recently, electron donors composed of 1,3-dithiol-2-ylidene units and π-conjugated systems have attracted much attention due to their highly electron-donating abilities as well as decreased on-site Coulombic repulsion.[1] Their properties including those of charge-transfer complexes or cation radical salts can be varied by changing the π-conjugated systems. On the other hand, it is known that azulene and its derivatives are electron-rich non-benzenoid aromatic compounds and afford the corresponding cation radicals upon oxidation at relatively low potentials.[2] Therefore, the azulene nucleus is an attractive building block for new electron donors. Tetrathiafulvalene (TTF) derivatives (**1**)[3] and (**2**)[4] containing an azulene unit were reported previously. For the compound (**1**) the fused azulene ring was expected to act as a source of occilating dipole in the Little's superconduction theory. In the latter molecule the azulene unit was introduced as a ferromagnetic coupling unit. We have now designed the title bis(1,3-dithiole) donors (**3**) containing an azulene spacer unit for the following reasons. (*i*) Since the 1- and 3-positions of azulene have large atomic orbital coefficients in the HOMO, introduction of electron-donating 1,4-dithiafulvenyl groups into these positions would raise the HOMO energy level. Therefore, strong electron-donating abilities are expected for **3**. (*ii*) The cation radical (**3**·+) and dication (**3**²⁺) may be stabilized by an aromatic tropylium ring formed by oxidation. (*iii*) The extended π-conjugation and dipole moment of the azulene ring are


[†] Dedicated to Prof. Shô Itô on the occasion of his 77th birthday.

expected to enhance intermolecular interactions in the solid state. (*iv*) Since the dication species (3^{2+}) can be regarded as a pentamethinecyanine dye combined with a tropylium ring, their electronic spectra are of particular interest. In this report we describe the preparation, X-Ray analysis, and properties of the donors (**3**).

1

2

3

$3^{\bullet+}: * = \bullet$
$3^{2+}: * = +$
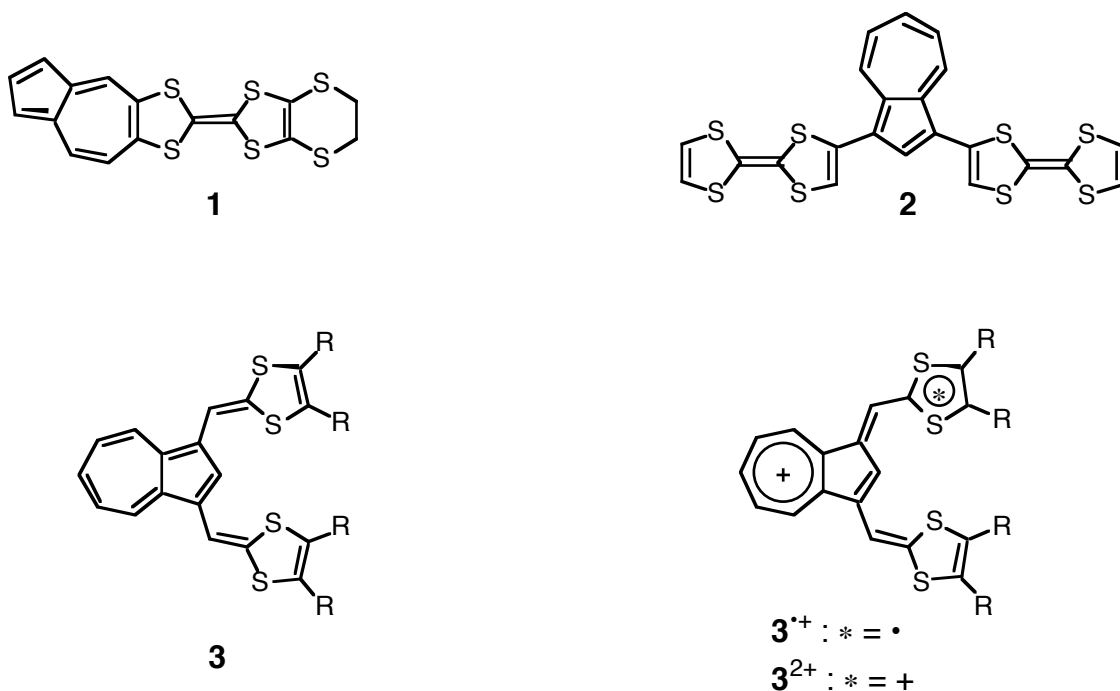
RESULTS AND DISCUSSION

Preparation. The new donors (**3a–d**) were prepared by a Wittig–Horner reaction of the corresponding carbanions derived from phosphonate esters (**5a–d**)[5] with 1,3-diformylazulene (**4**)[6] in 20–85% yields (Scheme 1). Although the reaction of **5a** with **4** using *n*-butyllithium as a base resulted in the formation of complex products mixture, the parent donor (**3a**) could be obtained using potassium *tert*-butoxide. All the spectral data and elemental analyses supported the structures of the new compounds.

a: R = H
b: R = SMe
c: R, R = SCH$_2$CH$_2$S
d: R, R = (CH=CH)$_2$
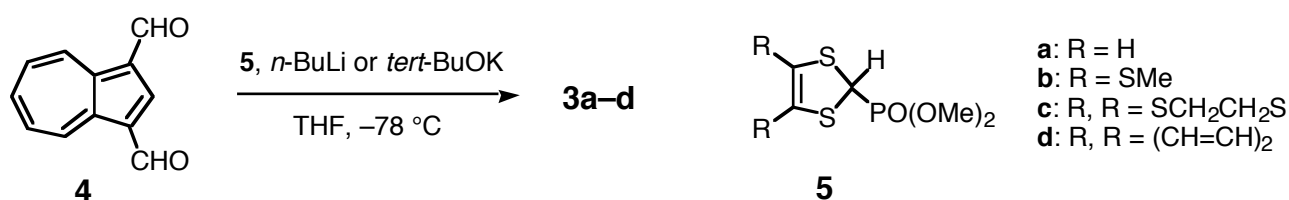
Scheme 1

Molecular orbital calculations. Prior to discuss the properties of the donors (**3**), we performed the MNDO-PM3 calculations[7] on the parent molecule (**3a**) in order to obtain information about the geometry as

completely planar conformation. The HOMO energy (–7.37 eV) of **3a** is much higher than that of TTF (–7.99 eV). Thus the donors (**3**) are expected to be stronger electron donors than TTF. The atomic orbital coefficients in the HOMO are distributed over the whole molecule, indicating a highly delocalized system involving a significant interaction between the azulene unit and the 1,4-dithiafulvenyl groups. On the other hand, **3a** has a lower LUMO (–1.55 eV) and hence a smaller HOMO–LUMO gap (5.82 eV) than those of azulene (–1.19 and 6.80 eV, respectively). These results indicate that the donors display an amphoteric electrochemical behavior and show longer absorption than that of azulene.

X-Ray analysis. In order to investigate the molecular and crystal structures of **3**, an X-Ray structural analysis of the benzo-fused derivative (**3d**) was carried out. The single crystal was obtained by recrystallization from toluene/ethanol. Although the PM3 calculations predicted the planar structure, the molecule takes a nonplanar conformation as shown in Figure 1. Namely, while one of the 1,4-dithiafulvenyl groups and the azulene moiety are in almost coplanar plane [torsion angle for C(2)–C(1)–C(11)–C(12): 4.1(9)°], the other one twists around the C(3)–C(19) bond [torsion angle for C(2)–C(3)–C(19)–C(20): 20.8(8)°]. Such a deformation of the molecule in the crystal can be accounted for by the
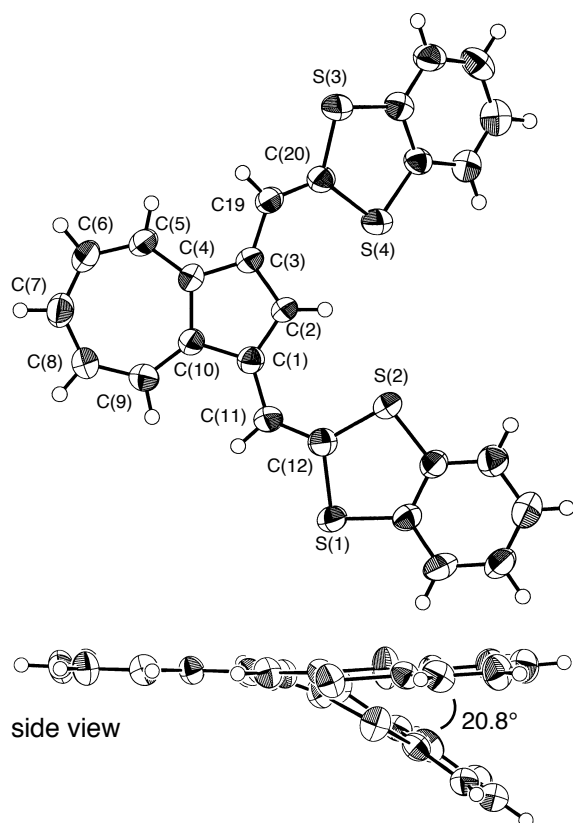

Figure 1. Molecular structure of **3d**. Selected bond lenghts (Å): C(1)–C(2) 1.400(7); C(1)–C(10) 1.438(6); C(2)–C(3) 1.407(6); C(3)–C(4) 1.417(6); C(4)–C(5) 1.382(6); C(4)–C(10) 1.487(7); C(5)–C(6) 1.369(7); C(6)–C(7) 1.387(8); C(7)–C(8) 1.357(8); C(8)–C(9) 1.398(7); C(9)–C(10) 1.376(7).
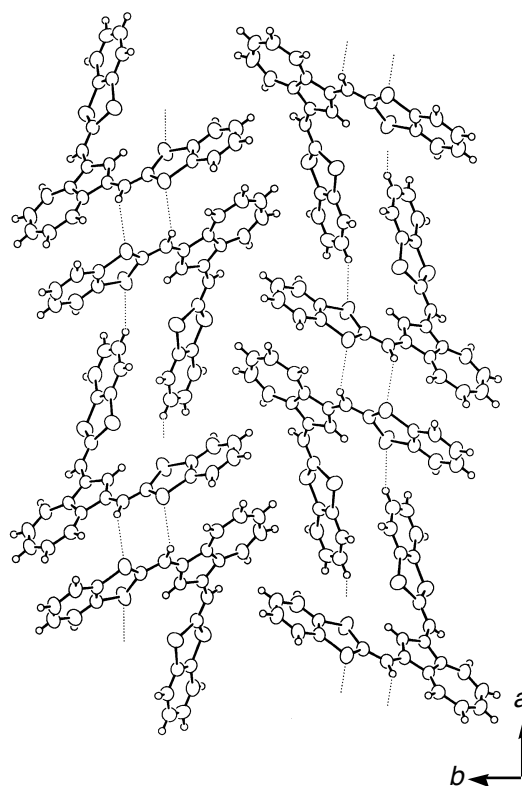

Figure 2. Crystal structure of **3d** viewed along the *c* axis. Dotted lines indicate short S⋯H contacts (< 3.0 Å).

crystal packing forces which make the molecule nonplanar to achieve the most effective molecular packing. The C(3)–C(19) bond [1.461(7) Å] is longer than the C(1)–C(11) bond [1.431(7) Å], and the C(19)–C(20) bond [1.346(7) Å] is shorter than the C(11)–C(12) bond [1.357(6) Å]. This fact suggests that the π-conjugation between the azulene moiety and the dithiafulvenyl group substituted on C(3) is diminished in the crystal due to the twisted conformation. On the other hand, the C(1)–C(10), C(4)–C(5), C(6)–C(7), and C(8)–C(9) bonds are slightly lengthened compared with the C(3)–C(4), C(9)–C(10), C(7)–C(8), and C(5)–C(6) bonds, respectively, suggesting that some bond alternations occur in the azulene ring. Figure 2 shows the crystal structure. The molecules are uniformly stacked along the c axis but the overlapping of the molecules is not so good. Although there are no intermolecular S···S interactions in the crystal, short intermolecular S···H contacts,[8] which are shorter than the sum of van der Waals radii (3.0 Å), are found.

Properties. The donors are air-stable deeply-colored crystals. The color of **3** in dichloromethane is greenish yellow. They show the longest absorption maxima at 733–762 nm, which are fairly longer than that of azulene. This reflects their smaller HOMO–LUMO gaps suggested by the MO calculations.

The electrochemical properties of the donors were investigated by cyclic voltammetry. The cyclic voltammogram of **3d** as a typical example is shown in Figure 3, and the redox potentials are summarized in Table 1 along with those for TTF and azulene measured under the same conditions. All the donors (**3**) show three pairs of one-electron oxidation waves, and the third ones corresponding to the formation of trication radicals (**3**$^{3+\bullet}$) are irreversible processes. The first oxidation potentials of **3** are lower than that of TTF, indicating that they are stronger donors than TTF as predicted by the PM3 calculations. The differences between the first and second oxidation potentials are slightly smaller than that of TTF, suggesting the reduced on-site Coulombic repulsion in the dication states. Alkylthio groups slightly lower the third oxidation potentials. In addition to the oxidation waves, they show an irreversible reduction peak at *ca*. –1.4 V. Despite the presence of the electron-donating dithiafulvenyl groups, the reduction potentials are considerably higher than that of azulene (–1.70 V), probably due to the expansion of π-conjugation. This amphoteric character of **3** is well consistent with the absorption data supporting the small HOMO–LUMO separation.
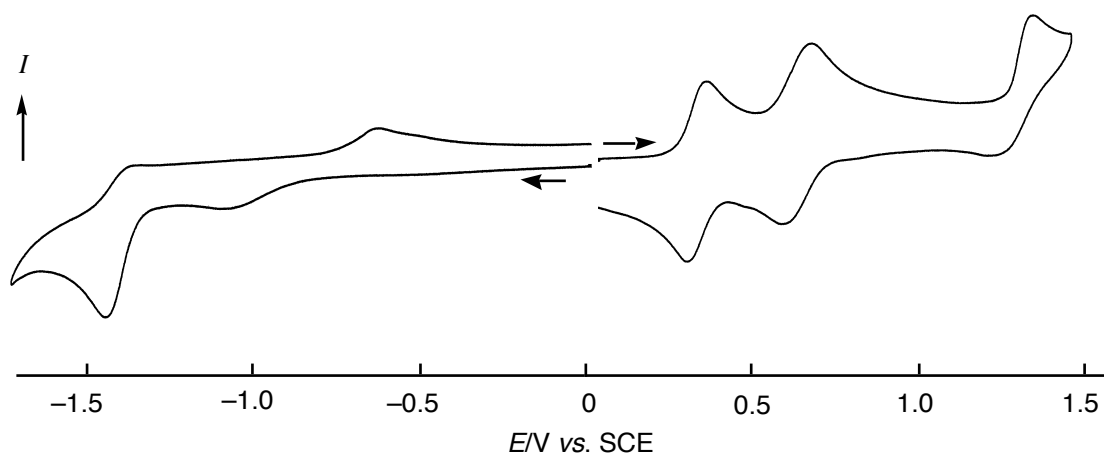

Figure 3. Cyclic voltammogram of **3d** in 0.1 M Bu$_4$NClO$_4$ /benzonitrile,

Table 1. Redox potentials of **3**[a]

Compound	E^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}	$E_2^{ox} - E_1^{ox}$
3a	-1.49^b	+0.21	+0.49	$+1.23^b$	0.28
3b	-1.42^b	+0.32	+0.58	$+1.07^b$	0.26
3c	-1.43^b	+0.29	+0.55	$+1.11^b$	0.26
3d	-1.46^b	+0.32	+0.62	$+1.32^b$	0.30
TTF	–	+0.38	+0.78	–	0.40
azulene	-1.70^b	$+0.98^b$	–	–	–

[a] Bu_4NClO_4 (0.1 M) in PhCN, Pt electrode, scan rate 100 mV s^{-1}, E/V *vs.* saturated calomel electrode (SCE). [b] Irreversible wave, peak potentials.

Next, we studied the spectroelectrochemistry of **3b** using a thin-layer working electrode in order to obtain the electronic spectra of the oxidized states. Upon oxidation at +0.50 V, where **3b** is oxidized to the cation radical (**3b**$^{•+}$), the color of the solution changed from yellow to dark blue and new absorptions at 612, 548, and 510 nm increased with isosbestic points at 365 and 493 nm as shown in Figure 4 (a). On the other hand, when the applied potential was further raised to +0.80 V, the spectrum of the cation radical disappeared and broad peaks at 721, 545, and 410 nm due to the dication (**3b**$^{2+}$) appeared [Figure 4 (b)]. The color turned to reddish purple. In this case, the spectral change is accompanied by isosbestic points at 380, 442, and 682 nm. The observation of the isosbestic points in both cases indicates that the redox
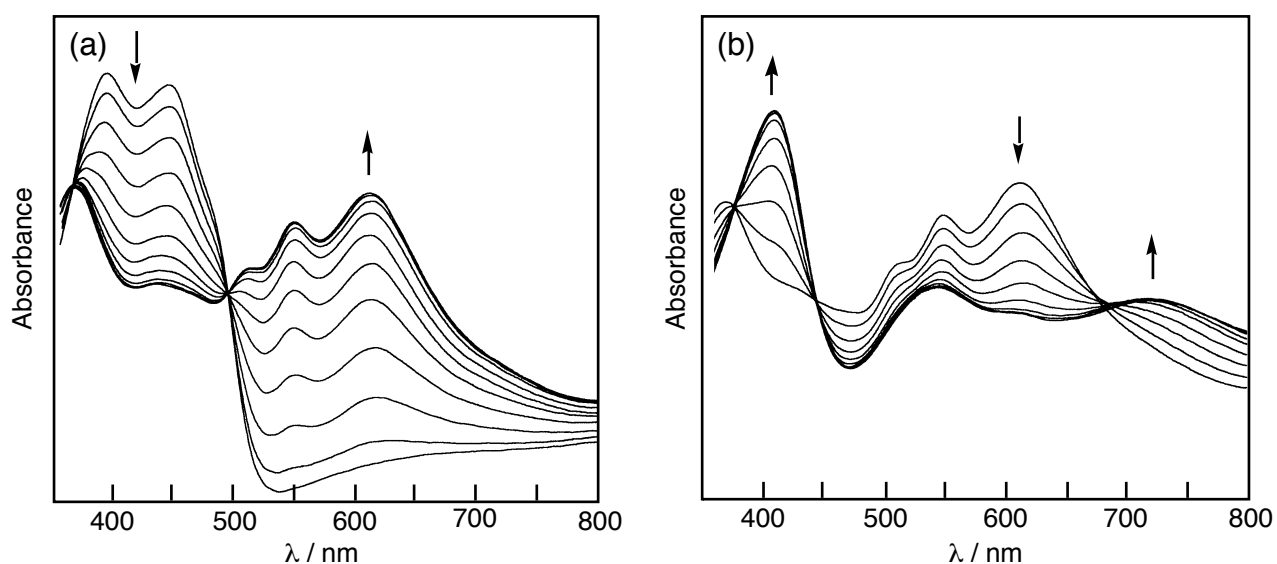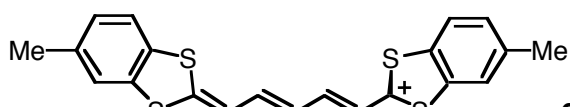

Figure 4. UV-VIS spectral changes during oxidation of (a) **3b** to **3b**$^{•+}$ at +0.5 V, (b) **3b**$^{•+}$ to **3b**$^{2+}$ at +0.8 V (in 0.1 M Bu_4NBF_4/PhCN with a thin-layer electrode at 3 min intervals).

processes take place cleanly. The spectrum of the neutral state could be restored upon reduction at –0.8 V. Therefore, **3** seem interesting as an electrochromic dye. The longest absorption maximum of **3b**$^{2+}$ (721 nm) is shorter than that of a previously reported pentamethinecyanine dye (**6**, 758 nm),[9] suggesting that the introduction of the electron-deficient tropylium ring into the cyanine system makes the absorption blue-shifted.

The donors (**3a**) and (**3d**) afforded tetracyanoquinodimethane (TCNQ) complexes whose electrical conductivities as a compressed pellet are 2.7×10^{-3} and 5.0×10^{-3} S cm^{-1}, respectively. The preparation of cation radical salts by electrochemical oxidation is now in progress.

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 JEOL JNM-LA400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer in DMSO-d$_6$. MS spectra (EI, 70 eV) were measured on a Shimadzu GCMS-QP1000EX spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 140 apparatus.

1,3-Bis(dithiafulven-6-yl)azulene (3a). To a solution of phosphonate ester (**5a**)[5a] (532 mg, 2.5 mmol) and 1,3-diformylazulene (**4**)[6] (180 mg, 1.0 mmol) in THF (15 mL) was added a solution of potassium *tert*-butoxide (418 mg, 3.7 mmol) in THF (5 mL) over a period of 5 min at –78 ℃ under nitrogen. The mixture was stirred for 4 h at –78 ℃ and allowed to warm to rt. The solution was poured into water (100 mL), and the precipitate was collected by filtration and washed with water followed by ethanol to give the title compound (**3a**) (66 mg, 20%) as deep brown prisms (from toluene). mp 228–229 ℃; IR (KBr) 1556, 1431, 1396, 823, 800, 729 cm^{-1}; ^{1}H-NMR δ 6.75 (2H, d, J = 6.6 Hz, dithiole-H), 6.81 (2H, d, J = 6.6 Hz, dithiole-H), 6.93 (2H, br t, J = 9.8 Hz, Az-5,7-H), 7.32 (2H, s, =CH–), 7.49 (1H, br t, J = 9.8 Hz, Az-6-H), 8.12 (1H, s, Az-2-H), 8.32 (2H, br d, J = 9.8 Hz, Az-4,8-H); ^{13}C-NMR δ 105.0, 118.2, 119.0, 122.5, 126.2, 127.7, 133.0, 134.1, 134.9, 140.4; UV (CH$_2$Cl$_2$) λ$_{max}$ (log ε) 230 (4.31), 270 (4.33), 317 (4.56), 382 (4.42), 439 (4.35), 762 (2.65) nm; MS m/z (rel. intensity) 356 (M$^+$, 100%). Anal. Calcd for C$_{18}$H$_{12}$S$_4$: C, 60.64; H, 3.39. Found: C, 60.37; H, 3.26.

1,3-Bis(2,3-bismethylthiodithiafulven-6-yl)azulene (3b). A solution of *n*-butyllithium in hexane (1.54 M, 0.9 mL, 1.43 mmol) was added to a solution of phosphonate ester (**5b**)[5b] (405 mg, 1.3 mmol) in THF (12 mL) at –78 ℃ under argon. After stirring for 10 min, **4** (110 mg, 0.60 mmol) was added to the solution. The mixture was stirred for 50 min at –78 ℃ and allowed to warm to rt. Water was added to the solution, and the product was extracted with dichloromethane. The extract was washed with water, dried over Na$_2$SO$_4$, and concentrated. The residue was separated by column chromatography (alumina / toluene) to give **3b** (274 mg, 85%) as deep brown prisms (from ethyl acetate). mp 92–94 ℃; IR (KBr) 2914, 1560, 1496, 1427, 1392, 1215, 968, 899, 731 cm^{-1}; ^{1}H-NMR δ 2.49 (12H, s, SCH$_3$), 7.09 (2H, br t, J = 9.8 Hz, Az-7,5-H), 7.38 (2H, s, =CH–), 7.62 (1H, br t, J = 9.8 Hz, Az-6-H), 8.01 (1H, s, Az-2-H), 8.41 (2H, br d, J = 9.8 Hz, Az-4,8-H); ^{13}C-NMR δ 18.2, 18.3, 108.2, 122.9, 123.5, 125.3,

(4.37), 443 (4.38), 745 (2.38) nm; MS m/z (rel. intensity) 540 (M$^+$, 100%). Anal. Calcd for $C_{22}H_{20}S_8$: C, 48.85; H, 3.73. Found: C, 49.08; H, 3.69.

The other compounds (**3c,d**) were synthesized by using the similar method. In these cases, the crude products were precipitated by addition of water and ethanol to the reaction mixture and collected by filtration. The data are as follows.

3c: 42%, deep brown needles (from toluene). mp 261–262 °C; IR (KBr) 1554, 1520, 1390, 1286, 1221, 733 cm^{-1}; ^{1}H-NMR δ 3.44 (8H, s, SCH$_2$CH$_2$S), 7.09 (2H, br t, J = 9.8 Hz, Az-5,7-H), 7.40 (2H, s, =CH–), 7.62 (1H, br t J = 9.8 Hz, Az-6-H), 7.84 (1H, s, Az-2-H), 8.41 (2H, br d, J = 9.8 Hz, Az-4,8-H); UV (CH$_2$Cl$_2$) λ$_{max}$ (log ε) 231 (4.56), 270 (4.42), 315 (4.65), 372 (4.49), 425 (4.39), 735 (2.67) nm; MS m/z (rel. intensity) 536 (M$^+$, 13%). Anal. Calcd for $C_{22}H_{16}S_8$: C, 49.22; H, 3.00. Found: C, 49.22; H, 3.13.

3d: 63%, deep brown needles (from toluene). mp 256 °C (decomp); IR (KBr) 1550, 1446, 1433, 1394, 733 cm^{-1}; ^{1}H-NMR δ 7.08 (2H, br t, J = 9.8 Hz, Az-5,7-H), 7.21–7.26 (4H, m, benzo-H), 7.42 (2H, s, =CH–), 7.49–7.55 (2H, m, benzo-H), 7.58–7.65 (3H, m, Az-6-H and benzo-H), 8.30 (1H, s, Az-2-H), 8.46 (2H, br d, J = 9.8 Hz, Az-4,8-H); ^{13}C-NMR δ 107.6, 121.5, 122.4, 123.4, 125.5, 125.9, 126.4, 128.2, 129.1, 134.6, 135.0, 135.2, 135.4, 140.5; UV (CH$_2$Cl$_2$) λ$_{max}$ (log ε) 204 (4.48), 231 (4.55), 271 (4.41), 315 (4.64), 373 (4.48), 426 (4.38), 733 (2.63) nm; MS m/z (rel. intensity) 456 (M$^+$, 100%), 316 (20), 271 (12), 228 (17). Anal. Calcd for $C_{26}H_{16}S_4$: C, 68.39; H, 3.53. Found: C, 68.67; H, 3.66.

TCNQ complex of 3a. A solution of the donor (**3a**) (10 mg, 0.028 mmol) in dichloromethane (20 mL) was added to a solution of TCNQ (6 mg, 0.029 mmol) in dichloromethane (10 mL) at rt. The resulting precipitate was collected by filtration and washed with a small amount of dichloromethane to give the complex (10 mg, 71%) as a black solid. mp > 300 °C; IR (KBr) 2195 (CN), 1560, 1506, 1496, 1473, 1342, 1309, 1274, 1234 cm^{-1}. Anal. Calcd for (**3a**)$_3$(TCNQ)$_4$·0.5CH$_2$Cl$_2$, $C_{102}H_{52}N_{16}S_{12}$ ·0.5CH$_2$Cl$_2$: C, 63.82; H, 2.77; N, 11.62. Found: C, 63.69; H, 2.81; N, 11.76.

TCNQ complex of 3d. This was prepared by the similar procedure. **3d** (20 mg, 0.044 mmol) and TCNQ (9 mg, 0.044 mmol) afforded the complex (17 mg, 89%) as a deep brown solid. mp > 300 °C; IR (KBr) 2197 (CN), 1560, 1493, 1315, 1228, 1117 cm^{-1}. Anal. Calcd for (**3d**)(TCNQ)$_2$, $C_{50}H_{24}N_8S_4$: C, 69.43; H, 2.80; N, 12.95. Found: C, 69.28; H, 3.08; N, 12.45.

Electrochemical and spectroelectrochemical 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 perchlorate (0.1 M) as supporting electrolyte in benzonitrile.

Spectroelectrochemical measurements were performed in a one-component cell containing a solution of **3b** (*ca.* 1 mM) and tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte in benzonitrile. A thin layer working electrode was constructed from glass and indium tin oxide (ITO) glass held together with a PTFE spacer. Pt wire and SCE were used as counter and reference electrodes, respectively.

X-Ray structural analysis of 3d. A brown needle-like single crystal having approximate dimensions of $0.50 \times 0.10 \times 0.10$ mm was prepared by recrystallization from toluene/ethanol. The data collections were performed on an Enraf-Nonius CAD4 diffractometer (40 kV, 26 mA) with graphite-monochromated Cu-Kα radiation ($\lambda = 1.54178$ Å) using ω–2θ scan technique. A total of 2338 reflections were measured up to $2\theta = 148.66°$ at room temperature. Crystal data are as follows: *MF* $C_{26}H_{16}S_4$, *MW* = 456.65, orthorhombic, space group Fdd2, $a = 32.39(1)$, $b = 44.374(7)$, $c = 5.9834(7)$ Å, $V = 8334(2)$ Å^3, $Z = 16$, $D_{calcd} = 1.456$ g cm^{-3}. The structure was solved by the direct method using the SHELXS-86 program.[10] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares method using the SHELXL-93 program.[11] Hydrogen atoms were included at calculated positions but not refined. The final R_1 and wR_2 are 0.0405 and 0.0935 for 1727 reflections with $I > 2\sigma(I)$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.206 and -0.385 e Å^{-3}, respectively.

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