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Conjugation-Extended Tetrathiafulvalene Analogues Involving a Central Aromatic 5-Membered Heterocyclic Linking Group

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Conjugation-extended tetrathiafulvalene analogues, 2,5-bis(1,4-dithiafulven-6-yl)thiophene (**2a**), 2,5-bis[2,3-bis(methoxycarbonyl)-1,4-dithiafulven-6-yl]thiophene, and 2,5-bis(1,4-dithiafulven-6-yl)furan, involving an aromatic heterocyclic linking group have been synthesized by the Wittig condensation reaction of 2,5-thiophene- and 2,5-furandicarbaldehydes with 1,3-dithiol-2-ylidenetributylphosphorane and its 4,5-bis(methoxycarbonyl) derivative. The electrochemical redox properties of these compounds in solution have been investigated by cyclic voltammetry in order to evaluate the effect of the linking group on the donating ability and the thermodynamic stability of the radical cations. Whereas the radical cations are not so stable, complexes of **2a** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and iodine were found to show relatively high conductivities ($((1.0—1.1)\times10^{-3}\ \mathrm{S\,cm^{-1}})$) on a compressed pellet at room temperature.

Conjugation-extended tetrathiafulvalene (TTF) analogues containing an extended π-framework between the 1,3-dithiole rings of TTF[1)] are expected as promising electron donors for organic metals, since the extended conjugation decreases the intramolecular Coulomb repulsive energy[2)] and hence increases the stability of the dication state of the corresponding donor, relative to that of TTF. Recently we have synthesized thienoquinonoid-extended TTF analogues **1** (R = Me and R–R = –(CH=CH)$_2$– (dibenzo derivative))[3,4)] which undergo two step one-electron oxidation reactions generating the very stable radical cation and the dication species and giving 7,7,8,8-tetracyanoquinodimethane (TCNQ) and iodine complexes with relatively high electroconductivities. However, the strategies to control the redox potentials of these heterocycle-extended donors have not been well-known so far. To this end, further investigation is needed in order to clarify the effect of the linking group on the electrochemical properties which closely correlate with the electroconductivities of their molecular complexes or radical salts.

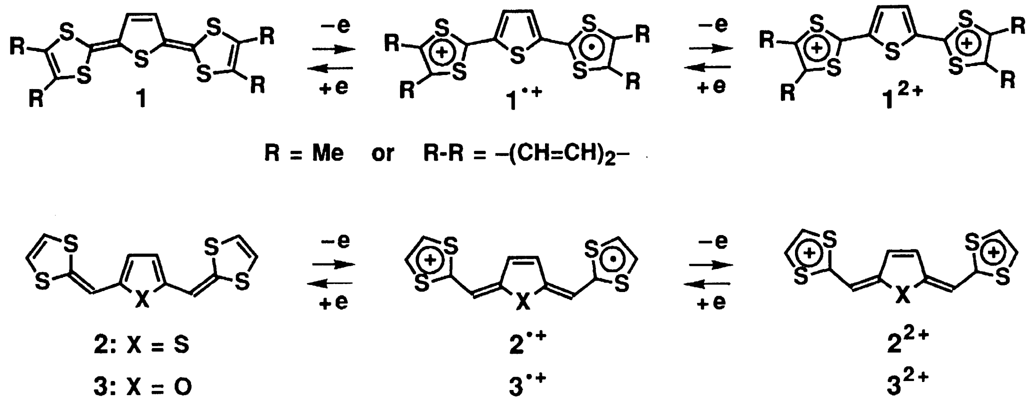
The thienoquinonoid linking group of **1** itself can achieve aromaticity at the oxidation stage of the system. On the other hand, the linking group of **2** and **3** involving a heteroaromatic thiophene or a furan ring at the neutral states should be destabilized by achieving a nonaromatic thienoquinonoid or furoquinonoid structure at the oxidation stage of the system as shown in Scheme 1. Therefore, the redox behavior of conjugation-extended tetrathiafulvene type compounds **2** and **3** appears to be very much helpful to evaluate the effect of the linking groups on stabilizing the radical cations or on determining oxidation potentials of the conjugation-extended TTF analogues.

Very recently, A. Gorgues et al.[5)] and M. P. Cava et al.,[6)] have independently reported the synthesis and redox properties of **2**, **3**, and pyrrole analogues. Herein we report our own results[7)] on the synthesis and solution redox behavior of extended-donors **2a,b** and **3**, together with the conductivities of the complexes of **2a** with several electron acceptors.

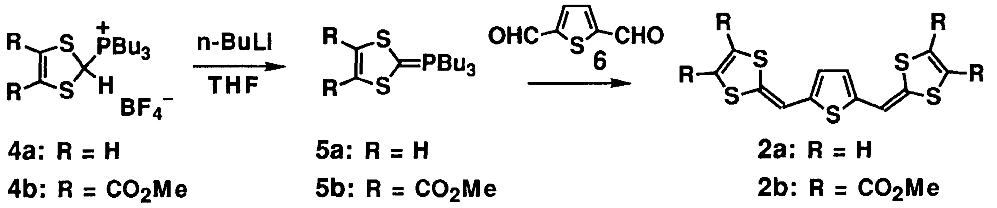
Results and Discussion

The donor **2a** was synthesized as shown in Scheme 2 by the Wittig condensation of 2,5-thiophenedicarbaldehyde (**6**) with tributyl-1,3-dithiol-2-ylidenephosphoranes (**5a**) obtained in situ by deprotonation of tributyl-1,3-dithiol-2-ylphosphonium salts (**4a**)[8)] with butyllithium in THF at −78 °C.[9)] By the Wittig reaction of **6** with 4,5-bis(methoxycarbonyl) derivative **5b**, generated in situ by treating **4b**[10)] with butyllithium, a 1 : 1 mixture of **2b** and mono-capped 5-[2,3-bis(methoxycarbonyl)-1,4-dithiafulven-6-yl]thiophene-2-carbaldehyde was formed even when 3 equiv of **5b** was used for the reaction. The mixture was allowed to react again with a further amount of **5b** to produce **2b** in satisfactory yield. Demethoxycarbonylation of **2b** with lithium bromide monohydrate in hexamethylphosphoric triamide (HMPA)[11)] was attempted, but **2a** was not obtained, presumably because **2b** is unstable under the reaction conditions (Scheme 2). The Wittig condensation of the phosphorane **5a** with 2,5-furandicarbaldehyde (**7**) proceeded smoothly at −78 °C in THF to give the furyl analogue **3** as pale yellow needles (Scheme 3). The present Wittig reaction using a butyllithium base in THF has proved to be very much effective especially for the preparation of **2a** and **3**, in contrast to the fact that M. P. Cava et al.[6)] obtained only undesired mono-capped monoaldehydes when a triethylamine base was used instead of butyllithium in the Wittig reaction and obtained the desired compounds **2a** and **3** in relatively lower yield by the Wittig-Horner type reaction.

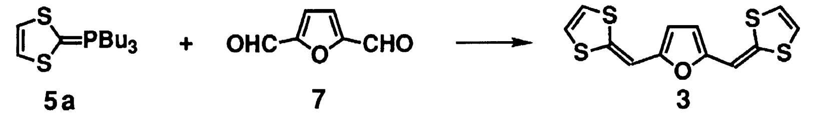
The electrochemical redox behavior of the donors **2a,b** and **3** has been studied by cyclic voltammetry, and the peak potentials (E_{pa}) and the half-wave oxidation potentials (E^{ox}) are summarized in Table 1. The donor **2a** displays only a one-step two-electron wave that was not resolved even if measurements was carried out at different sweep speeds. The oxidation of **2a**, however, can occur in two step one-electron processes at



Scheme 1.



Scheme 2.



Scheme 3.

Table 1. Electrochemical Data[a] (V vs. SCE) of **2a**, **2b**, **3**, and Reference Compounds **1** (R=Me) and TTF

Compound	$E_{\mathrm{pa}}1$	$E_{\mathrm{pa}}2$	ΔE_{pa}	E_1^{ox}	E_2^{ox}	Reversibility
2a	+0.43 (2e)		ca. 0	+0.40 (2e)		Pseudo-reversible
2b	+0.67	+0.78	0.11	+0.62	+0.74	Pseudo-reversible
3	+0.29	+0.36	0.07	+0.23[b]	+0.30[b]	Reversible
1 (R=Me)	+0.11	+0.37	0.26	+0.05	+0.32	Reversible
TTF	+0.38	+0.75	0.37	+0.32	+0.69	Reversible

a) Obtained by cyclic voltammetry: 1.0 mmol dm^{-3} in MeCN with 0.1 mol dm^{-3} Et_4NClO_4, scan rate: 50 mV s^{-1}, reference electrode: SCE. b) Divided from a reversible and nearly coalescent peak according to the Myers–Shain method.

two proximate potentials since two separate oxidation peaks (ΔE_{pa}=0.1 V) have been observed by thin layer cyclic voltammetry[5] and BAS CV-27 potentiostat.[6,12] The donor **2b** can be oxidized in two-step one-electron transfer reactions, but the difference between the first and second oxidation peak potentials is also very small (ΔE_{pa}=0.11 V). The donor **3** gives one nearly coalescent wave which can be divided into two one-electron steps according to the Myers–Shain method,[13] because the wave is clearly reversible and the first oxidation wave is observed as a small shoulder of the second oxidation wave. Consequently ΔE_{pa} value can be determined to be 0.07 V for **3**.[14]

Thus one of characteristics of the redox behavior for **2a**,**b**, and **3** is their smaller ΔE_{pa} value than that of the thienoquinonoid-extended donor **1** (R=Me).[3] This can be ascribable to the decreased intramolecular Coulomb repulsion in the dication state for the formers which involve two additional sp^2 carbon atoms in the linking bridge, and also to the formation of less stable radical cations and/or dications in **2a**,**b** and **3**, in which the conjugative interaction between the terminal 1,3-dithiole rings and the central heterocyclic ring is not significantly enhanced due to the relatively labile, namely not rigid conformations of **2a**,**b** and **3** as compared with that of **1**. The conformational change would be associated with the rotation of the 1,3-dithiole rings about the intercyclic single bonds. Indeed, the redox waves of furan analogue **3** are reversible, whereas those of **2a** and **2b** are quasi-reversible, in which the corresponding

Table 2. Room Temperature Conductivity Data for the Complexes of **2a** with Electron Acceptors

Acceptor	Stoichiometry[a)] Donor : Acceptor	Conductivity[b)] $\sigma_{\mathrm{r.t.}}$/S cm^{-1}	ΔE (D, A) V
DDQ	1 : 1	1.0×10^{-3}	−0.14
I_2	1 : 2	1.1×10^{-3}	—
TCNQ	2 : 3	1.1×10^{-5}	+0.16

a) Determined by the elemental analysis of the complexes. b) Two-probe compressed pellet measurement.

reduction segments are smaller than the oxidation ones of the cycles. From these facts it is suggested that $\mathbf{2a}^{2+}$ and $\mathbf{2b}^{2+}$ would be kinetically unstable in solution.[15)]

The first oxidation potentials ($E_1{}^{\mathrm{ox}}$) of **2a** and **3** are higher by about 0.18—0.35 V than that of **1** (R=Me),[3)] indicating that the electron donating ability is reduced in the more highly extended donors **2a** and **3** as compared with **1**. This phenomenon is contrary to the cases of the ethanediylidene-,[16)] *p*-benzoquinonoid-,[17,1c)] and 2,5-thienoquinonoid-[3,4)] extended TTF analogues whose donating abilities are higher than that of TTF. Whereas further detailed investigation based on the theoretical argument is needed before deducing definite conclusion, the higher oxidation potentials of **2a** and **3** might be attributed to the loss of the aromatic stabilization of the central linking heterocycles in the radical cations. The radical cation of **1** can acquire an extra stabilization energy by aromatization of the central bridging ring in the oxidation state. In accord with this explanation, the donor **3** involving a less aromatic furan ring exhibits a lower oxidation potential than **2a** involving a more aromatic thiophene ring. Thus the oxidation potentials of this kind of extended donors can be dictated by the aromatic stabilization or non-aromatic destabilization of the central bridging ring induced in the course of the oxidation reactions. In addition to this, another factor of stabilizing radical cations by the nitrogen atom is also significant in the case of the pyrrole derivatives.[6)]

The donor **2a** formed a violet-black complex with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in a stoichiometry of 1 : 1, exhibiting the room temperature electroconductivity of 1.0×10^{-3} S cm^{-1} as shown in Table 2. The electron accepting ability of DDQ seems to be too strong for **2a** to meet a partial change transfer (CT) condition, since the ΔE (D, A) value (−0.14 V) is out of the narrow range of $-0.02\ \mathrm{V}<\Delta E(\mathrm{D, A})<0.34\ \mathrm{V}$ which has been given as a guide line to achieve a partial CT condition.[18)] In particular, the complex showed no carbonyl band of DDQ in the IR spectrum and showed as intense absorption maximum being ascribable to the radical cation of **2a** at 686 nm in the electronic spectrum.[19)] Therefore, the complex is fully ionic, nonetheless showed a somewhat high conductivity in contrast to the complete charge transfer systems,[20,21)] such as TTF–TCNQF$_4$ and tetrathiatetracene (TTT)–TCNQF$_4$, which are invariably insulators. Apparently the conductivity of the iodine complex of **2a** is in the same order of magnitude with that of the DDQ complex of **2a**. The relatively high conductivity achieved in the DDQ and iodine complexes of **2a** would be perhaps associated with the reduced on-site Coulomb repulsive energy in the dication state of **2a**, which destabilizes the transition to a Mott-type insulator.[2a)]

The TCNQ complex of **2a** can be expected to be in a partial CT condition, since the ΔE (D, A) value of the complex falls within the narrow range.[18)] However, the room temperature conductivity of the TCNQ complex of **2a** measured on the compressed pellet is relatively low (Table 2), whereas the degree of CT (Z) determined by the ν_{CN} (2195 cm^{-1}) in the IR spectrum is 0.68. Taking the high conductivity of the TCNQ complex of **1** (R=Me: 1.3×10^{-2} S cm^{-1})[3)] into account, the low conductivity of the TCNQ complex of **2a** can be attributed to the non-planar and relatively labile conformation of the donor molecule **2a**, in which a close intermolecular face-to-face contact in the stacks would be difficult to attain. Indeed the intermolecular attractive forces appear to be relatively weak in the TCNQ complex of **2a** compared with that of the TCNQ complex of **1**, since the former complex tends to separate into two components on washing with polar solvents such as acetone and acetonitrile. In an acetonitrile solution of 5.7×10^{-5} mol dm^{-3} concentration, TCNQ complex of **2a** showed no absorption band ascribable to the complex.

In conclusion, the present study demonstrates the synthesis and electrochemical properties of conjugation-extended donors, **2a**, **2b**, and **3**. The higher oxidation potentials of **2a** and **3** as compared with that of **1** are attributed to the loss of the aromaticity of the central bridging ring in the course of the oxidation reactions. The difference between the first and second oxidation peak potentials (ΔE_{pa}=0.1—0.07 V) is significantly smaller than that of **1** (ΔE_{pa}=0.26 V). This can be ascribable not only to the decreased intramolecular Coulomb repulsion in the dication states, but also to the occurrence of the conformational changes during the redox process. Indeed the donor **2a** afforded charge transfer complexes with TCNQ and DDQ, and a radical cation salt with iodine, of which the DDQ and iodine complexes exhibited relatively high conductivities of (1.0—1.1)$\times10^{-3}$ S cm^{-1}.

Experimental

Melting points (uncorrected) were determined with a Yanagimoto MP-J3 melting point apparatus. The IR and electronic spectra (UV) were measured by using a Horiba FT-300 and a Hitachi U-3210 spectrophotometer, respectively; the NMR spectra were measured in $CDCl_3$ with a Varian XL-200 spectrometer using TMS as an internal standard. The assignments of all signals were made by employing a first-order analysis with the aid of a two-dimensional carbon-proton shift correlation technique. The mass spectra were taken on a JEOL-JMS-HX-110 mass spectrometer.

The cyclic voltammograms were taken on a Yanagimoto P-1100 polarographic analyzer.

Preparation of Tributyl-1,3-dithiol-2-ylphosphonium Tetrafluoroborate (4a).[8] To a solution of 1,3-dithiolium tetrafluoroborate (500 mg, 2.63 mmol) in dry acetonitrile (3.0 ml) was added dropwise tributylphosphine (0.69 ml, 559 mg, 2.76 mmol). The resulting yellow solution was stirred under nitrogen for 2 h at room temperature. Dry ether (70 ml) was added and the precipitated dithiolyl salt **4a** was collected by filtration and recrystallized from acetonitrile–ether to give a pure **4a** (890 mg, 86% yield): Colorless powder; mp 70—72 °C; IR (KBr) $\nu_{\max}$ 3080, 1456, 1295, 1130—1000, 940, 810, and 740 cm^{-1}. Found: C, 46.13; H, 7.98; S, 16.15%. Calcd for $C_{15}H_{30}S_2BF_4P$: C, 45.92; H, 7.71; S, 16.35%.

Preparation of 2,5-Bis(1,4-dithiafulven-6-yl)thiophene (2a). Butyllithium in hexane (1.83 ml, 3.0 mmol) was syringed into a stirred solution of the phosphonium salt **4a** (1.18 g, 3.0 mmol) in dry THF (60 ml) at −78 °C under argon atmosphere. An immediate color change of the solution occurred from pale yellow to yellow. After 1 h at −78 °C, a solution of thiophenedicarbaldehyde (**6**) (140 mg, 1.0 mmol) in dry THF (10 ml) was added dropwise into the reaction mixture. After stirring for 2 h at −78 °C, the mixture was allowed to warm to 0 °C over 3 h and then stirred for further 6 h at room temperature. The solvent was evaporated under reduced pressure, and the residue was treated with water and extracted with dichloromethane. The combined extracts were washed with brine and dried over Na_2SO_4. Solvent evaporation and chromatography of the residue on silica-gel column by eluting with a 4 : 1 mixture of hexane–ethyl acetate provided the crude product (222 mg, 71% yield) which was recrystallized from ethanol to give a pure **2a** (203 mg): Brownish red crystals; mp 147—149 °C (decomp); MS (DEI) *m*/*z* (rel intensity) 312 (M$^+$, 100); IR (KBr) $\nu_{\max}$ 3060, 1562, 1520, 1430, 1090, 1050, and 800 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ=6.36 (4H, s, H-4′,4″,5′,5″) 6.72 (2H, s, H-6′,6″), 6.80 (2H, s, H-3,4); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=106.7 (C-6′,6″), 118.1 (C-4′,4″,5′,5″), 123.7 (C-3,4), 133.6 (C-2′,2″), 139.3 (C-2, 5); UV-vis (CH_2Cl_2) $\lambda_{\max}$ ($\log\varepsilon$) 319 (3.94), 424 (4.44), 448 nm (4.45). Found: C, 46.07; H, 2.92; S, 51.10%. Calcd for $C_{12}H_8S_5$: C, 46.12; H, 2.58; S, 51.30%.

Preparation of 2,5-Bis[2,3-bis(methoxycarbonyl)-1,4-dithiafulven-6-yl]thiophene (2b). To a solution of **4b** (1.53 g, 3.0 mmol) in dry THF (40 ml) was added butyllithium in hexane (1.83 ml, 3.0 mmol) at −78 °C under argon atmosphere. After 1 h at −78 °C, a solution of **6** (140 mg, 1.0 mmol) in dry THF (1.0 ml) was added dropwise. The mixture was stirred for 2 h at −78 °C, then allowed to warm to 0 °C over 3 h, and finally to room temperature. After being stirred for 6 h at room temperature, the resulting mixture was worked up as usual and chromatographed on silica-gel column by eluting with dichloromethane to give a 1 : 1 mixture of **2b** and mono-capped 5-[2,3-bis(methoxycarbonyl)-1,4-dithiafulven-6-yl]thiophene-2-carbaldehyde (393.7 mg). The mixture was dissolved in dry THF (40 ml) and treated again with phosphorane **5b** (prepared in situ from **4b** (1.43 g, 2.8 mmol) and butyllithium in hexane (1.72 ml, 2.82 mmol)) in a similar procedure to that described above. The crude product obtained after the usual workup was chromatographed on silica-gel column by eluting with dichloromethane to give **2b** (400 mg, 73% yield) which was recrystallized from a 1 : 1 mixture of benzene–methanol to give a pure **2b**: Brownish red needles; mp 164—165 °C; MS (DEI) *m*/*z* (rel intensity) 544 (M$^+$, 100); IR (KBr) $\nu_{\max}$ 1760, 1726, 1715, 1580, 1427, 1280, and 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ=3.83 (12H, s, Me), 6.60 (2H, s, H-6′, 6″), 6.83 (2H, s, H-3,4); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=53.37 (Me), 53.45 (Me), 159.78 (C=O), 160.02 (C=O), 108.71 (C-6′, 6″), 125.23 (C-3,4), 130.07 (C-2,5), 131.77 (C-2′,2″), 139.02 (C-4′,4″,5′,5″); UV-vis (CH_2Cl_2) $\lambda_{\max}$ ($\log\varepsilon$) 310 (3.99), 414 (4.49), 432 nm (4.49). Found: C, 43.88; H, 3.22; S, 29.15%. Calcd for $C_{20}H_{16}O_8S_5$: C, 44.10; H, 2.96; S, 29.44%.

Preparation of 2,5-Bis(1,4-dithiafulven-6-yl)furan (3). In a similar procedure to that described above, the phosphonium salt **4a** (1.42 g, 3.63 mmol) was treated with butyllithium in hexane (2.28 ml, 3.63 mmol) and then with furandicarbaldehyde (150 mg, 1.21 mmol). The reaction mixture was allowed to warm to 0 °C over 4 h, and then to room temperature. After being stirred for 6 h at room temperature, the mixture was worked up as usual and the residue was chromatographed on silica-gel column by eluting with a 4 : 1 mixture of hexane–ethyl acetate to give crude **3** (241 mg, 67.2% yield). The pure **3** was isolated after recrystallization from ethanol: Yellow needles; mp 136—137 °C; MS (DEI) *m*/*z* (rel intensity) 296 (M$^+$, 100); IR (KBr) $\nu_{\max}$ 3064, 1572, 1522, 1489, 1230, 1174, 1041, 800, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ=6.19 (2H, s, H-3,4), 6.34 (4H, s, H-4′,4″,5′,5″), 6.44 (2H, s, H-6′,6″); ^{13}C NMR ($CDCl_3$, 50 MHz) δ=101.4 (C-3,4), 108.1 (C-6′,6″), 117.5 (C-4′,4″ or C-5′,5″), 118.6 (C-5′,5″ or C-4′,4″), 134.0 (C-2′, 2″), 150.5 (C-2,5); UV-vis (CH_2Cl_2) $\lambda_{\max}$ ($\log\varepsilon$) 318 (4.09), 367 (4.15), 412 (4.27), 436 nm (4.29). Found: C, 48.42; H, 2.72; S, 43.01%. Calcd for $C_{12}H_8OS_4$: C, 48.62; H, 2.72; S, 43.27%. HRMS: Calcd for $C_{12}H_8OS_4$: M, 295.9458. Found: *m*/*z* 295.9438.

Preparation of the Molecular Complexes of 2a with Acceptors. Two hot saturated solutions of equimolar amounts of **2a** and the acceptor in carbon disulfide or acetonitrile were mixed and concentrated. The precipitated complex was collected by filtration, washed with a little amount of benzene or acetonitrile, and dried in vacuo. Conductivities are listed in Table 2.

[**2a**][DDQ]: Black needles; UV-vis (MeCN) $\lambda_{\max}$ 261, 349, 424, 448, 686, and 1024 nm; IR (KBr) $\nu_{\max}$ 1500, 1460, 1410, 1382, 1300—1250, 1200, 1140, and 1070 cm^{-1}. Found: C, 44.11; H, 1.65; N, 4.93; S, 29.55%. Calcd for $C_{20}H_8O_2N_2S_2Cl_2$: C, 44.52; H, 1.49; N, 5.19; S, 29.72%.

[**2a**][I]$_{4.0}$: Dark violet needles, UV-vis (MeCN) $\lambda_{\max}$ 230, 293, 363, 566, 686, 810, and 1024 nm; IR (KBr) $\nu_{\max}$ 1480, 1442, 1300, 1230, 1190, 1120, and 1070 cm^{-1}. Found: C, 17.39; H, 1.08; S, 19.38; I, 61.47%. Calcd for $C_{12}H_8S_5I_4$: C, 17.57; H, 0.98; S, 19.55; I, 61.89%.

[**2a**]$_2$[TCNQ]$_3$: Black prisms; IR (KBr) $\nu_{\max}$ 2195, 1594, 1542, 1508, 1498, 1382, 1296, 1176, and 1128 cm^{-1}. Found: C, 57.98; H, 2.99; N, 13.30; S, 25.74%. Calcd for $C_{60}H_{28}S_{10}N_{12}$: C, 58.23; H, 2.80; N, 13.58; S, 25.91%.

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