Thiophene-Functionalized TTF π-Electron Donors as Potential Precursors to Conducting Polymers and Organic Metals: Synthesis, Properties, Structure, and Electropolymerization Studies

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The synthesis and physical properties of a series of novel thiophene-substituted TTF electron donors (**6a**−**d**) are described. The cyclic voltammograms of **6a-d** exhibited two reversible one-electron redox waves, characteristic of TTF derivatives. Electropolymerization studies on compound **6a** in nitrobenzene indicate that no polymer formed on the working electrode, but a blue-colored intermediate was observed diffusing away from the electrode. In addition, the single-crystal X-ray structure of compound **6d** indicates that the central five-membered C_3S_2 rings are buckled and the ethylenedithiolo fragment adopts a twisted chair conformation. The pendant thiophene moieties are highly flexible, and short intermolecular interactions of 3.49 Å (S···S) and 3.45 Å (S···C) exist in the unit cell, resulting in the formation of a chain structure along the *c*-axis.

Introduction

Conducting polymers are emerging as a family of materials with considerable technological importance, with the potential applications for these compounds spanning the complete spectrum of materials science from lightweight batteries and electrochromic displays to artificial muscles and nerves and controlled-release medicine delivery systems.[1]

One particular class of conducting polymers, the polythiophenes (PTs), has attracted considerable attention because of the high electrical conductivities reported for the doped state in these materials,[2] resulting from the highly conjugated, structurally regular nature of the polymer backbone. The ability of PTs to form conducting composite materials with other polymers and the almost infinite possibilities of altering the physical properties of the polymer framework by chemical functionalization of the thiophene monomer are other attractive reasons for studying these compounds.[3]

Although modifcation of the physical properties of PT at the molecular level by grafting of specfic chemical funtionalities onto the monomer has been actively pursued, retaining the original properties of the polymer while embracing the intrinsic properties of the attached functionality during polymerization can prove problematic for a variety of reasons, including steric effects and reduced reactivity of the thiophene monomer after substitution.[3]

Despite these problems, some attention has focused on incorporating functionalities with specific properties, particularly redox active centers such as ferrocene,[4] bipyridyl,[5] and benzoquinone[6] into PTs. While the high oxidation potential of unsubstituted thiophene (+2.06 V[7]) would perhaps be expected to lead to electrolysis of the attached redox centers, under the strongly oxidizing conditions required to generate the PTs, the electrochemical behavior characteristic of these groups is generally still observed in the prepared polymer films.

The possibility of incorporating another extensively studied redox active molecule tetrathiafulvalene (TTF), into PTs, has also become an interesting proposition, because of the possibility of enhanced electrical conductivities in the resultant polymer.

Since the first preparation of TTF in 1970,[8] this π-electron donor and related analogues have assumed a central role in the development of organic metals and superconductors,[9] and more recently as building blocks in the new field of supramolecular chemistry.[10] The creation of 2- and 3-dimensional sheet and lattice structures in salts containing this donor and its analogues, through enhanced intermolecular S--S contacts, has resulted in metallic and even superconducting behavior at low temperatures.[11]

The concept of combining the ordered, large molecular weight polymers based on thiophene with the high conductivities observed in doped TTFs into a single framework is therefore an attractive goal from the viewpoint of preparing conducting, yet mechanically processable, polymeric systems.

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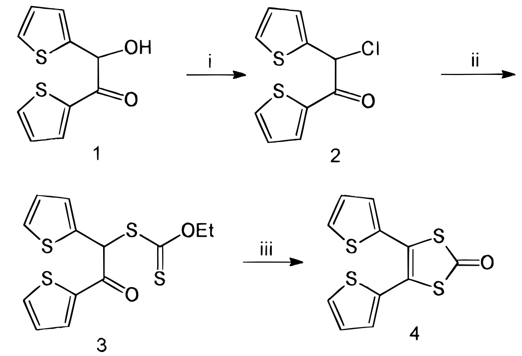
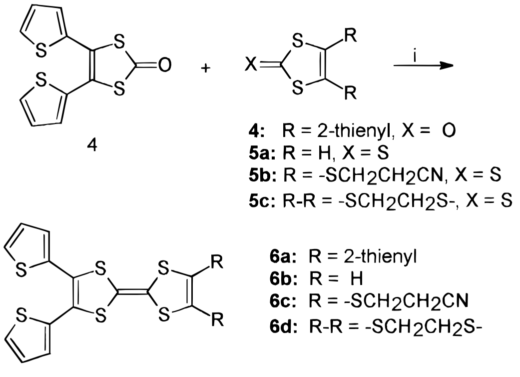
Scheme 1[a]



[a] (i) PPh$_3$, CH$_2$Cl$_2$/CCl$_4$ (1:2), rt, 24 h; (ii) KSC(S)OEt, Me$_2$CO, rt, 15 min; (iii) HBr/AcOH, rt, 1 h.

Scheme 2[a]



[a] (i) P(OEt)$_3$, 120 °C, 3−6 h.

The first report of a thiophene unit linked to TTF was by Bryce and co-workers,[12] but only one of the derivatives, in which the thiophene monomer was linked to the redox center *via* an ester group, appeared to form a polymer in solution. In 1993, Thobie-Gautier *et al.*[13] described the synthesis and electropolymerization studies on a 3-substituted thiophene linked to a TTF unit by a linear oxadecyl spacer.

In the present work, we report the synthesis and physical properties of a series of thiophene-functionalized TTF derivatives, in which the thiophene moieties are substituted in the 2-position and are linked directly to the TTF core. It is envisaged that because of the structure of these new derivatives they may serve as precursors to soluble, conducting polymeric systems and organic metals with novel electrical properties.

Results and Discussion

The key intermediate in the synthesis of the thiophene-substituted TTF derivatives was 4,5-bis(2-thienyl)-1,3-dithiol-2-one (**4**) and was prepared according to Scheme 1. Compounds **2** and **3** were somewhat unstable, and so were used in subsequent steps immediately without being characterized, while compound **4** was isolated as a yellow crystalline solid, in 30% overall yield. This compound was then allowed to react with a variety of bis-substituted 1,3-dithiole-2-thiones (**5a**−**c**) in triethyl phosphite to yield the corresponding TTF derivatives (**6a**−**d**), as in Scheme 2. Compounds **5a**,[14] **5b**,[15] and **5c**[16] were prepared according to literature methods. The derivatives **6a**−**d** were obtained as either red or orange crystalline solids (10−74% yield), after workup by flash column chromatography.

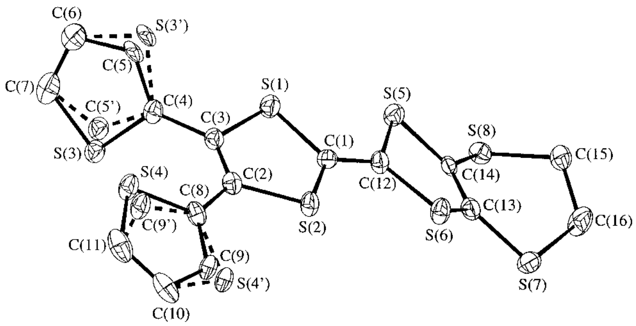


Figure 1. Molecular structure of BTEDT−TTF (**6d**) showing the crystallographic atom numbering scheme and also the two orientations for each of the disordered thiophene substituents (the atoms with major occupancies are indicated by solid lines and those with minor occupancies by dashed lines). Thermal ellipsoids are drawn at 50% probability level. The hydrogen atoms are omitted for clarity.

The single-crystal X-ray structure of one of the derivatives, compound **6a** has been published in a preliminary communication,[17] but in the present work single crystals of another derivative, 4,5-bis(2-thienyl)-4′,5′-bis(ethylenedithiolo)tetrathiafulvalene (**6d**), were grown by slow evaporation of a concentrated dichloromethane/methanol (1:1) mixture at room temperature. The structure was determined by X-ray diffraction methods (see the Experimental Section).

The structures of both compounds were determined in order to gain insight into how steric factors, as a result of thiophene substitution onto the TTF monomers, would affect their ability to form a closely interacting stack, and possibly lattice structures in the solid state through the presence of short intermolecular S--S contacts.

A general view of the molecular structure of **6d**, together with the crystallographic atom-numbering scheme, is shown in Figure 1, which also indicates both of the orientations of the two disordered thiophene substituents (see the Experimental Section). It is to be noted that orientational disorder in thiophene units is quite common and has been observed in many compounds, including **6a**. In the present compound, these two substituents were disordered between two orientations, one with 0.80:0.20 and the other with 0.72:0.28 occupancy ratios. Considering only the most densely populated conformer, one thiophene is nearly perpendicular to the S(1)S(2)C(2)C(3) plane, while the other lies nearly parallel to it, as shown by the dihedral angles C(2)−C(3)−C(4)−S(3) = −71.5(7) and C(3)−C(2)−C(8)−S(4) = −16.4(8)°. Similar arrangements were also observed in **6a**, where the corresponding dihedral angles are 93.5(3) and −18.0(4)°. In fact, the orientations of the thiophene substituents on TTF appear to be quite flexible in this type of species and are determined by the requirements of minimum interligand interactions and by packing requirements.

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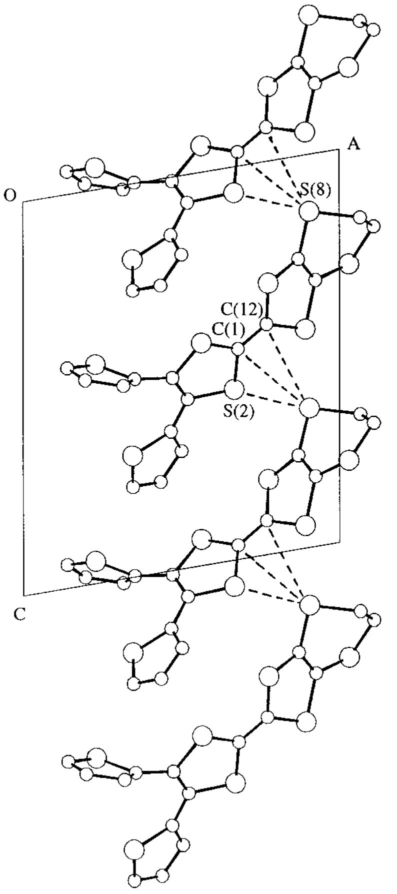

Figure 2. Intermolecular contacts between molecules in compound **6d** related by *c*-glide and forming a chain along *c*.

The S−C and C−C bond lengths and interbond angles in **6d** are as expected and comparable with the corresponding values in **6a**. The central C_2S_4 core of the TTF unit is planar within 0.024(6) Å, but each five-membered C_3S_2 ring is buckled, with fold angles of 13.5(3) and 26.7(3)° along the S(1)--S(2) and S(5)--S(6) axes, respectively. The larger buckling of the second ring may be attributed to the greater strain due to the six-membered ring involving the ethylenedithiolo moiety. The C−S−C angles at S(5) and S(6) are also somewhat narrower than the equivalent angles at S(1) and S(2) [93.0(2) and 92.9(2) *vs* 95.1(2) and 95.6(2)°]. Similarly, the angle at S(8) is also significantly narrower than that at S(7) [96.1(2) *vs* 103.8(2)°]. These differences in the chemically equivalent bond angles also seem to result from the above-mentioned strain. The six-membered ring adopts a twisted chair conformation, similar to that observed in the structure of the unsubstituted donor EDT−TTF, which was reported recently by Cassoux *et al.*[18] The corresponding fold angles in this molecule along the S(1)--S(2) and S(5)--S(6) axes were 12 and 17°, respectively. The structure of this molecule was characterized by a face-to-face, head-to-tail arrangement of the EDT−TTF molecules, forming (EDT−TTF)$_2$ dimers approximately orthogonal to each other. The shortest intermolecular S--S contact present between adjacent dimers was 3.64 Å.

The structure of **6d** revealed the presence of several short intermolecular contacts involving a pair of non-hydrogen atoms. The lengths of these contacts are 3.495(4) [S(8)--S(2) (at *x*, 0.5 − *y*, 0.5 + *z*)], 3.450(5) [S(8)---C(1) (at *x*, 0.5 − *y*, 0.5 + *z*)] and 3.558(7) Å [S(8)--C(12), (at *x*, 0.5 − *y*, 0.5 + *z*)], which suggests that the molecules in the unit cell of **6d** pack fairly closely and form a chain along the *c*-axis (see Figure 2). The shortest C···C and S···S intermolecular contacts in EDT−TTF were 3.45 and 3.57 Å, respectively.

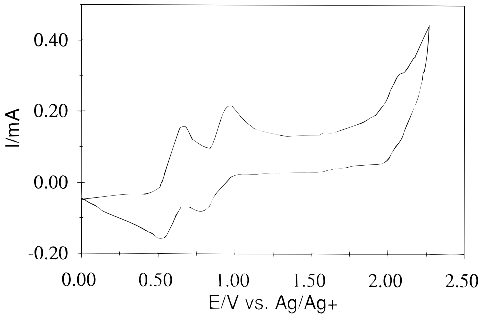

Figure 3. Cyclic voltammogram of BTBC−TTF (**6c**) in MeCN {$Bu_4N{\cdot}BF_4$ (0.1 mol dm^{-3}) under nitrogen at 20 °C *vs* Ag wire, Pt electrode, 100 mV s^{-1}}.

Table 1. Electrochemical Properties of the Thiophene-Substituted TTF Derivatives (6a−d)

compound[a]	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)
TTF	+0.23	+0.62
BEDT−TTF	+0.40	+0.63
6a	+0.48	+0.87
6b	+0.31	+0.74
6c	+0.30	+0.58
6d	+0.51	+0.88

[a] 0.02 mol dm^{-3} of substrate, Bu_4NPF_6 (0.1 mol dm^{-3}) in dry CH_2Cl_2 at 20 °C, *vs* Ag wire, Pt button electrode, 100 mVs $^{-1}$.

The solution electrochemistry of these new TTF derivatives was investigated using cyclic voltammetry in dichloromethane, at a platinum electrode (see Table 1). The cyclic voltammograms of all four compounds (**6a**−**d**) showed behavior typical of TTF derivatives,[19] in which two reversible, or quasi reversible, redox waves were present. These waves corresponded to the sequential oxidation of the TTF core to form the radical−cationic (TTF$^{\bullet+}$) and dicationic (TTF^{2+}) species, respectively. The $E_{1/2}$ values for the compounds **6a**, **6b**, and **6d** are, as expected, higher than for the parent TTF, this being reflected in the electron-withdawing nature of the attached thiophene moieties resulting in higher oxidation potentials. This data agrees well with previously published results[20] for the mono(2-thienyl)-substituted TTF ($E_{1/2}$ = +0.41 and +0.80 V; benzonitrile, 20 °C, Bu_4NClO_4 *vs* Ag/AgCl, Pt electrode), in which the quoted $E_{1/2}$ values were also higher than for TTF.

The influence of the electron-withdrawing thiophene groups can clearly be seen when comparing compounds **6a** and **6b**. The addition of two extra thiophene units to the former results in a shift in $E_{1/2}^1$ and $E_{1/2}^2$ of 170 and 130 mV, respectively.

The cyclic voltammogram of **6c**, however, exhibited unusually low $E_{1/2}^1$ and $E_{1/2}^2$ values. It is unclear at this stage as to why the presence of the (cyanoethyl)thio chains in this derivative reduces these values relative to **6b**, but this may be a function of the solvent. However, when the electrochemistry of this compound was studied

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in acetonitrile under the same conditions, the values obtained ($E_{1/2}{}^1 = +0.56$, $E_{1/2}{}^2 = +0.85$) were comparable to the values recently reported for a series of bis-substituted (cyanoethyl)thio TTF derivatives.[21] The low solubility of **6a**, **6b**, and **6d** in acetonitrile prevented detailed investigation of their solution electrochemistry in this solvent, but changes in the oxidation potentials of various TTF derivatives as a result of solvatochromic effects, have been reported previously.[19]

The oxidation of the thiophene moieties in the present derivatives occurs at slightly higher potentials than for unsubstituted thiophene. The voltammograms of monomers **6a**−**d** all exhibited a peak at potentials greater than +2.10 V,[22] corresponding to oxidation of these thiophene units. This slight increase in the oxidation potential may be related to the lower diffusion coefficients of the TTF−substituted thiophenes, as compared to thiophene.

Attempts were made to electropolymerize monomer **6a**, using potentiostatic, potentiodynamic (0 to +2.20 V), and galvanostatic techniques, but these were unsuccessful, and no polymer film was observed growing on the working electrode. However, a blue-colored intermediate was always seen to diffuse away from the electrode, which is reminiscent of the blue color of the radical cation of thiophene. Some deposition of material did occur on the electrode, but further voltammetric studies indicated that this was not of a polymeric nature.

It is apparent that if the polymer were to form, the delocalization of the charge, in all the monomers studied, would have involved the TTF moiety. However, as the monomers are already in the dicationic state prior to oxidation of the thiophene units, the delocalization of the charge would clearly involve an “quasi-aromatic TTF”. Electropolymerization would therefore disrupt the aromatic nature of the TTF core, which is energetically unfavorable, hence the difficulties experienced in trying to prepare a polymer.

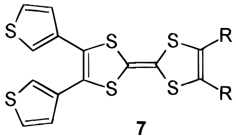
The potential that these derivatives may have as organic metals has also been investigated using both chemical and electrochemical techniques. Attempts have been made to grow single crystals of radical cation salts of compound **6a**, using standard electrocrystallization techniques[23] on platinum electrodes, over a range of current densities (1.25−7.0 μA cm^{-2}). Solutions of the donor (3 mM) and suitable cations, Bu_4NHSO_4 and Bu_4NI_3 (0.1 M), in dry, degassed nitrobenzene were added to standard 20 mL capacity H-cells, and a constant current was applied to the solution over a period of several weeks. If no crystal growth was observed on the anode, the current density was increased by *ca.* 0.5 μA cm^{-2} every couple of days. Unfortunately, even over the wide range of current densities used in the present experiments, it was not possible to prepare crystalline samples of either the HSO_4 or I_3 salts of **6a**. This may be a function of the solvent, or because the donor is unstable at high current densities over long periods of time, and these variables are being studied at the present time.

The possibility of chemically oxidizing **6a** using iodine and the acceptor molecule TCNQ (7,7,8,8,-tetracyano-*p*-quinodimethane) has also been investigated. The ability of TCNQ to form charge transfer complexes with organic donor molecules has been well documented,[24] as has the use of iodine as an oxidant in the preparation of conducting salts of the electron donor BEDT−TTF bis(ethylenedithiolo)tetrathiafulvalene.[25] Unfortunately, when **6a** dissolved in benzonitrile was exposed to iodine vapor and when solutions of **6a** and TCNQ dissolved in CH_2Cl_2 were mixed, there was no reaction and the unreacted donor was recovered. This apparent lack of reactivity with these two oxidants is probably reflected in the higher oxidation potential of **6a** compared to TTF and BEDT−TTF. It may be that the use of stronger oxidants will enable partially oxidized salts to be prepared.

Conclusions

A series of novel thiophene-functionalized TTF derivatives has been prepared and characterized. The electrochemical properties of these compounds have been studied using cyclic voltammetry, and attempts were made to electropolymerize derivative **6a**. The inability of monomer **6a** to undergo electropolymerization in nitrobenzene has dictated that other, more suitable target compounds are required in order to move the present work forward.

We are currently examining the behavior of similar derivatives possessing the general structure of compound **7**, in which the TTF unit is linked to the thiophene on the 3-position of the ring. This is in order to avoid the necessity of conjugation through the TTF core during electropolymerization of the monomer.



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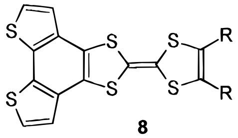

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Furthermore, we are also investigating the synthesis and electrochemical properties of derivatives of compound **8**, in which the 3-substituted thiophene units are fused together. The results of these studies will be published in due course.

Experimental Section

General Experimental. 2,2′-Theonin was purchased from Maybridge Chemicals, U.K., and used without futher purification. Triethyl phosphite was purchased from Aldrich and distilled under argon prior to use. All reactions utilizing triethyl phosphite were performed under a dry argon atmosphere. Compounds **5a**−**c** were prepared according to literature methods.[14−16] All ^{1}H- and ^{13}C-NMR data were recorded in $CDCl_3$ relative to TMS. Electrochemical studies were carried out using a three-electrode cell. The potential control was accomplished using a potentiostat (Hi-Tek Type DT2101) and waveform generator (Hi-Tek PPR1). The working electrode was a Pt disk (6 mm diameter), while a Pt flag served as a counter electrode. All potentials are quoted against Ag wire.

4,5-Bis(2-thienyl)-1,3-dithiol-2-one (4). 2,2′-Theonin (**1**) (5.43 g, 24.24 mmol) was dissolved in a mixture of CCl_4 (50 mL) and CH_2Cl_2 (25 mL); PPh_3 (12.7 g, 48.4 mmol) was added, and the mixture was stirred overnight at room temperature. The solution was then diluted with ether (100 mL) and filtered

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through a silica plug. The remaining solid residue was dissolved in CH_2Cl_2 (20 mL) and precipitated again by the addition of ether (100 mL) and petrol (50 mL). The solution was also passed through the silica pad, and after adsorption onto silica the combined filtrates were further purified by flash column chromatography [ether/petrol (30:70)]. After removal of the solvent, compound **2** (4.61 g) was obtained as a yellow oil and used immmediately in the next step. **2** (4.60 g) was dissolved in acetone (20 mL), and potassium *o*-ethyl xanthate (3.35 g, 20.9 mmol) was added. After the mixture was stirred at room temperature for 15 min, ether (150 mL) was added and the solution was filtered through a silica plug. The filtrate was adsorbed onto silica and was further purified by flash column chromatography [ether/petrol (30:70)]. Removal of the solvent yielded compound **3** (4.20 g) as a yellow oil. This oil (4.20 g) was dissolved in AcOH (10 mL), HBr (48% solution in AcOH, 20 mL) was added, and the mixture was stirred vigorously at room temperature for 1 h. CH_2Cl_2 (50 mL) and water (200 mL) were added, and the organic layer was separated. The aqueous layer was further extracted with CH_2Cl_2 (3 × 25 mL), and the combined extracts were washed with saturated $NaHCO_3$ (2 × 25 mL) and brine (2 × 20 mL) solutions. The solution was dried and adsorbed onto silica and the crude product purified by flash column chromatography (3% ether in petrol). Removal of the solvent *in vacuo*, followed by recrystallization of the residue from petrol/ether, yielded **4** as pale yellow needles (2.00 g, 30% yield): mp 93−95 °C; R_f (silica, 3% ether in petrol) = 0.27; FAB-MS *m/z* 282 (M^+); ^{1}H-NMR 7.37 (dd, 2H), 7.10 (dd, 2H), 7.02 (dd, 2H); ^{13}C-NMR 188.86, 131.77, 129.99, 128.61, 127.38, 122.88; IR (Nujol, cm^{-1}) 3099, 1650. Anal. Calcd $C_{11}H_6S_4O$: C, 46.78; H, 2.12. Found: C, 46.81; H, 2.17.

4,4′,5,5′-Tetrakis(2-thienyl)tetrathiafulvalene {TT-TTF} (6a). Compound **4** (0.37 g, 1.31 mmol) was dissolved in $P(OEt)_3$ (20 mL) and heated to 120 °C for 3 h. The dark orange solution was placed in a freezer overnight, and the red precipiate filtered off, washed with MeOH (50 mL), and air-dried. Recrystallisation of the red solid from CH_2Cl_2/ MeOH yielded **6a** as bright red needles (0.25g, 74%), mp 242−243 °C, *Rf* (silica, CH_2Cl_2) = 0.86; FAB-MS *m/z* 532 (M^+); ^{1}H-NMR 7.33 (dd, 4H), 7.10 (dd, 4H), 7.00 (dd, 4H); ^{13}C-NMR 129.32, 127.77, 127.10, 77.50, 76.99, 76.49. Anal. Calcd $C_{22}H_{12}S_8$: C, 49.60; H, 2.25; S, 48.14. Found: C, 49.47; H, 2.13; S, 47.88.

4,5-Bis(2-thienyl)tetrathiafulvalene {BT−TTF} (6b). Compounds **4** (0.24 g, 0.84 mmol) and **5a** (0.28 g, 2.1 mmol) were dissolved in $P(OEt)_3$ (10 mL) and heated to between 110 and 120 °C for 4 h. The solution was cooled and placed in a freezer for 4 h, and the orange precipitate obtained was filtered off, washed with MeOH, and air-dried. The solid was purified by repeated flash column chromatography (silica/CH_2Cl_2). The main fraction was treated with activated charcoal, and after filtration and removal of the solvent *in vacuo* the residue obtained was recrystallized from Me_2CO/2-propanol to yield **6b** as an orange waxy solid (0.15 g, 48%): mp 126−128 °C; R_f (silica, CH_2Cl_2) = 0.87; FAB-MS *m/z* 368 (M^+); ^{1}H-NMR: 7.32 (dd, 2H), 7.10 (dd, 2H), 7.00 (dd, 2H), 6.32 (s, 2H); ^{13}C-NMR 129.25, 127.69, 127.08, 119.07, 77.53, 77.02, 76.51. Anal. Calcd for $C_{14}H_8S_6$: C, 45.62; H, 2.19. Found: C, 45.75; H, 2.11.

4,5-Bis(2-thienyl)-4′,5′-bis[(2′-cyanoethyl)thio]tetrathiafulvalene {BTBC−TTF} (6c). Compounds **4** (0.4 g, 1.42 mmol) and **5b** (0.43 g, 1.41 mmol) were dissolved in $P(OEt)_3$ (20 mL) and heated to 120 °C for 3 h. The solution was placed in the freezer, and the red solid obtained was filtered off, washed with MeOH, and air-dried. The solid was purified by flash column chromatography (silica, CH_2Cl_2), and after filtering and evaporation of the desired fraction, **6c** was obtained as a red crystalline solid (0.11 g, 15%): mp 125−127 °C; R_f (silica, CH_2Cl_2) = 0.38; FAB-MS *m/z* 540 (M^+); ^{1}H-NMR 7.33 (dd, 2H), 7.10 (dd, 2H), 7.00 (dd, 2H), 3.10 (t, 4H), 2.80 (t, 4H); ^{13}C-NMR 129.49, 128.03, 127.21, 117.47, 77.97, 77.53, 77.02, 76.52, 31.33, 18.91. Anal. Calcd $C_{20}H_{16}S_8N_2$: C, 44.58; H, 2.62; N, 5.20. Found: C, 44.51; H, 2.44; N, 5.05.

4,5-Bis(2-thienyl)-4′,5′-bis(ethylenedithiolo)tetrathiafulvalene {BTEDT−TTF} (6d). Compounds **4** (0.25 g, 0.88 mmol) and **5c** (0.2 g, 0.89 mmol) were dissolved in $P(OEt)_3$ (10 mL) and heated to 110 °C for 6.5 h. The solution was cooled to room temperature and then placed in a freezer overnight. The orange precipitate obtained was filtered off, washed with MeOH, and air-dried. The solid was purified by flash column chromatography {silica, CH_2Cl_2/hexane (4:1)}, and recrystallization of the middle fraction from CH_2Cl_2/MeOH yielded **6c** as an orange crystalline solid (0.04 g, 10%): mp 153−155 °C; R_f (silica/CH_2Cl_2) = 0.87; EI-MS *m/z* 458 (M^+); ^{1}H-NMR 7.32 (m, 2H), 7.10 (m, 2H), 7.00 (m, 2H), 3.31 (s, 4H); ^{13}C-NMR 129.35, 127.84, 127.12, 77.52, 77.02, 76.51, 31.99, 30.23. Anal. Calcd for $C_{16}H_{10}S_8$: C, 41.89; H, 2.18. Found: C, 41.72; H, 2.02.

X-ray Crystallography. All measurements were made at 120 K using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator using Mo Kα radiation (λ = 0.710 69 Å) by following procedures described elsewhere.[26]

Crystal data: chemical formula $C_{16}H_{10}S_8$ (FW 458.72); monoclinic; space group $P2_1/c$; a = 11.408(2), b = 11.604(2), and c = 13.883(3) Å; β = 99.54(3)°; V = 1812.4(6) Å^3; Z = 4; D_c = 1.681 mg m^{-3}; μ(Mo Kα) = 0.981 mm^{-1}, $F(000)$ = 936.

The structure was solved by direct methods (SHELXS86),[27] and refined on F^2 by full-matrix least squares (SHELXL93)[28] using all unique data corrected for Lorentz and polarization factors. Absorption effects were ignored. Both the C_4H_3S rings were found to be disordered orientationally, each rotating by 180° about the $CC(C_3H_3S)$ axis. Best results were obtained by assigning 0.80/0.20 occupancies to the ring containing S(3) and 0.72/0.28 occupancies to the ring containing S(4). All non-hydrogen atoms were anisotropic, the displacement coefficients for a given pair of atoms being tied together. The S−C and C−C bonds involving the disordered atoms were constrained to remain 1.75(1) and 1.39(1) Å, respectively. The hydrogen atoms of the disordered C_4H_3S rings were ignored; those on C(15) and C(16) were included in calculated positions (riding model) with $U_{iso} = 1.2U_{eq}$ (parent). The weighting scheme used was $w = [\sigma^2(F_o^2) + (0.0382P)^2]^{-1}$ where $P = [\max(F_o^2) + 2(F_c^2)]/3$. Final R (on F) and R_w (on F^2) were 0.0725 and 0.0987, respectively, for all 2742 data and 0.0426 and 0.0839 for 1762 data with $I > 2\sigma(I)$. Sources of scattering factors were as previously described.[28] The diagram was drawn with SNOOPI.[29] The atomic coordinates, anisotropic displacement coefficients, hydrogen atom parameters, bond lengths and angles, and structure factor tables are available from the Cambridge Crystallographic Data Centre.[30]

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(29) Davies, K. SNOOPI Program for Crystal Drawing, University of Oxford, 1983.

(30) The author has deposited atomic coordinates for **6d** 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.