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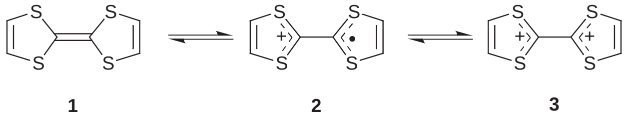
The synthesis, redox properties and X-ray crystal structures of two new tetrathiafulvalene-thiophene donors

Peter J. Skabara,[*a]† **Klaus Müllen,**[a] **Martin R. Bryce,**[b] **Judith A. K. Howard**[b] **and Andrei S. Batsanov**[b]

[a] *Max-Planck Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany*
[b] *Department of Chemistry, University of Durham, Durham, UK DH1 3LE*

The functionalisation of tetrathiafulvalene with thiophene units is reported *via* the synthesis of two multiredox compounds **4** and **5**. The two molecules represent a fused structure (**4**) and a TTF-thiophene system directly linked by a single bond (**5**); both compounds are endowed with 'free' 2,5-positions within the thiophene ring, making them accessible to polymerisation reactions. The solution electrochemistry of **4** and **5** reveals the redox properties of the two components: a three-stage oxidation process is seen in each case. Charge-transfer complexes have been prepared, using TCNQ or $TCNQF_4$ as the electron acceptor, with conductivities in the range of 10^{-4} to 0.22 S cm^{-1}. Compounds **4** and **5** have been studied by X-ray crystallography; the former exhibits *kappa*-packing whilst the latter shows a high degree of conjugation between the two donor moieties.

The outstanding redox properties of the π-electron donor tetrathiafulvalene (TTF) **1**, and its derivatives, are well documented; many charge-transfer salts incorporating TTF units exhibit metallic conductivity and even superconductivity.[1] TTF itself undergoes oxidation to the radical cation **2** and dication **3** *via* two reversible single-electron processes ($E^{1/2} = +0.34$ and $+0.71$ V *vs.* Ag/AgCl in acetonitrile, respectively). Generally, the oxidation of TTF compounds can be achieved by one of the following methods: (i) complexation with suitable electron acceptors (*e.g.* tetracyano-*p*-quinodimethane, TCNQ); (ii) *via* electrochemical techniques; (iii) by exposing the material to iodine vapour—a practice more commonly employed in the development of TTF-containing Langmuir–Blodgett (LB) films. The principal interest in TTF compounds focuses on the electronic behaviour of the corresponding stable radical intermediates which, as open-shell species, are directly associated with potential magnetic and conducting properties.

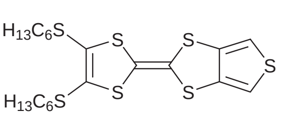


Scheme 1

Since the discovery of tetrathiafulvalene,[2] a multitude of TTF derivatives have been reported in the literature. This fact can be attributed to the meritorious donor ability and exceptional synthetic versatility of the molecule and its related 1,3-dithiole half-unit.[3] Among the TTF family of compounds are numerous examples of highly ordered solid state structures, whose self-assembly is usually promoted by intermolecular non-bonding chalcogen–chalcogen interactions providing a closely knit network of molecules with reduced intermolecular distances and electronic band-type superstructures. If the material comprises radical charged species, either as components in charge-transfer (CT) complexes or radical ion salts, then the formation of partially filled HOMO bands can lead to high levels of conductivity.

In recent years, several groups have prepared TTF systems covalently linked to other redox-active molecules. The purpose of these efforts has been manifold: improving donor ability by lowering oxidation potentials, integrating potential highly magnetic components, and producing materials capable of intramolecular charge-transfer have all been realised. Examples of such TTF systems incorporate other electron donors (*e.g.* ferrocene,[4] pyrrole,[5] selenophene,[6] thiophene[7] and phthalocyanines)[8] and electron acceptors (*e.g.* C_{60}).[9] The inclusion of TTF into redox-active polymeric materials is also a fascinating prospect. To this end, several attempts have been made at polymerising TTF-thiophene monomers, with only few reported to be successful.[7d,e]

In a previous communication, we have described the synthesis and electrochemistry of a novel fused TTF-thiophene donor **4**.[10] In this paper, we present this work and the X-ray crystal structure of **4** in detail, together with the synthesis, redox properties and X-ray structure of a new donor system, 4-(3-thienyl)tetrathiafulvalene **5**. Both compounds **4** and **5** are precursors to potentially fascinating polymer materials, however, herein we concentrate mainly on the π-electron donor ability of the two species.



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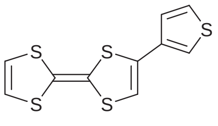

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Results and Discussion

Synthesis of TTF-thiophene donors

The preparation of **4** (Scheme 2) was achieved using an alternative route for the synthesis of the trithiocarbonate species **9**.[11] Conversion of diol **6**[12] to the dibromide **7** proceeded in 70% yield. Formation of the cyclic thioether **8**[13] (78%), followed by dehydrogenation with DDQ gave the thiophene derivative **9** (96%), which was finally oxidised to compound **10**[11] by treatment with mercuric acetate in 98% yield. The cross-coupling of half-units **10** and **13** in the presence of triethyl phosphite gave **4** in 20–30% yield, together with significant amounts of self-coupled products. (Ketone **13**, containing hexylthio side chains for improved solubility, was obtained using known synthetic methodology, *via* compounds **11** and **12**.)[14]

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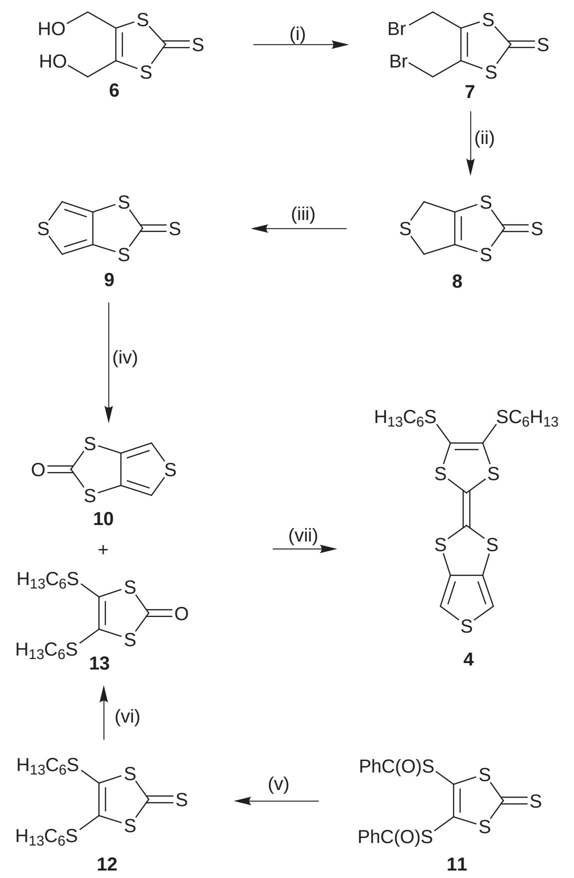
*E-mail: P.J.Skabara@shu.ac.uk
†Current address: Division of Chemistry, Sheffield Hallam University, Sheffield, UK S1 1WB

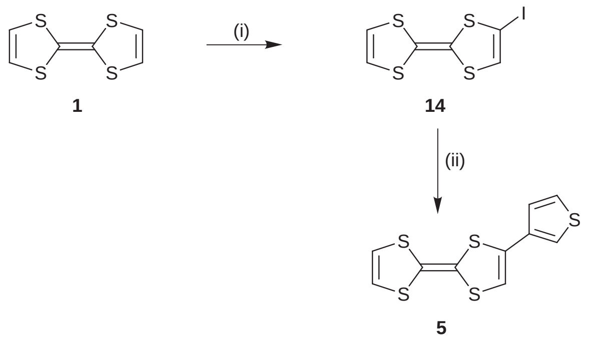


Scheme 2 *Reagents and conditions:* (i) CBr_4, PPh_3, dichloromethane; (ii) $Na_2S{\cdot}9H_2O$, ethanol–water; (iii) DDQ, toluene, reflux, 1.5 h; (iv) $Hg(OAc)_2$, acetic acid–chloroform; (v) NaOEt, EtOH, −10 °C, then $C_6H_{13}Br$; (vi) $Hg(OAc)_2$, acetic acid–chloroform; (vii) $P(OEt)_3$, 90 °C, 6 h

Compound **5** was prepared using standard Suzuki coupling methods (Scheme 3). 4-Iodotetrathiafulvalene[15] **14** was reacted in the presence of $Pd(PPh_3)_4$ with thiophene-3-boronic acid, using $Ba(OH)_2$ as base and a 1:1 mixture of monoglyme and water as the solvent. The reaction, which was allowed to stir at 80 °C in the dark and under nitrogen for several hours, afforded the product **5** in 31% yield.

Solution electrochemistry

The cyclic voltammetric data for compounds **4** and **5** are collated in Table 1, together with data for TTF **1**, for comparison. With both TTF-thiophene donors, two fully reversible single-electron waves are observed, corresponding to $E_1^{1/2}$ and $E_2^{1/2}$. These values (which are attributed to the behaviour of the TTF moiety in each donor species) are slightly raised compared to those of TTF, indicating an electron withdrawing effect of the pendant thiophene units. The oxidation potential of **4** may also be raised slightly by the presence of the alkylthio substituents.[16] Unsurprisingly, the $E_{1/2}$ values for compound **5** are almost identical to those of 4-(2-thienyl)tetrathiafulvalene ($E^{1/2} = +0.41$ and +0.80 V).[7b] Further substitution of TTF by thienyl groups has a detrimental effect on the donor ability of the TTF unit: positive shifts of 170 mV ($E_1^{1/2}$) and 130 mV ($E_2^{1/2}$) have been reported between the higher substituted analogues 4,5-bis(2-thienyl)tetrathiafulvalene and 4,4′,5,5′-tetrakis(2-thienyl)tetrathiafulvalene.[7c]



Scheme 3 *Reagents and conditions:* (i) Lithium diisopropylamide, THF, −78 °C, then $C_6F_{13}I$; (ii) $Pd(PPh_3)_4$, $Ba(OH)_2$, $CH_3OCH_2CH_2OCH_3$–H_2O (1:1), thiophene-3-boronic acid, 80 °C, 24 h

Table 1 Cyclic voltammetric data for TTF **1** and compounds **4** and **5**

compound	$E_1^{1/2}$/V	$E_2^{1/2}$/V	$E_3^{1/2}$/V
TTF **1**[a]	+0.23	+0.62	—
TTF **1**[b]	+0.34	+0.71	—
4[a]	+0.46	+0.83	+2.18
5[b]	+0.42	+0.79	+2.34[c]

Data were obtained in dichloromethane[a] or acetonitrile[b] *vs.* Ag/AgCl, 20 °C (except **4**, −30 °C), under argon, 0.1 M $TBAPF_6$ supporting electrolyte, 0.01 M substrate, 100 mV s^{-1} scan rate with *iR* compensation. All waves represent a reversible single-electron process, except [c]which is irreversible.

A third single-electron oxidation process is also observed for each of the donors **4** and **5** and is assigned to the thiophene component (the peak oxidation potential for unsubstituted thiophene is 2.06 V).[17] Whereas this oxidation wave is reversible for compound **4**, the same is found to be irreversible for 3-thienylTTF **5**.

Our failure to produce polymeric materials from either **4** or **5** under electrochemical conditions is mirrored by a number of groups who have tried to form polythiophenes bearing the TTF moiety. There are several possible reasons for this: (i) anodic polymerisation of thiophene involves the coupling of thiophene cation radicals.[18] It has been hypothesised that TTF may act as a radical scavenger towards the thiophene unit,[7e] thereby stabilising the thiophene radical cation and inhibiting the polymerisation sequence. In this instance, the charged species is allowed to diffuse away from the electrode surface to form soluble oligomers in solution. A similar behaviour in stabilisation is believed to predominate for (alkylthio)thiophenes: attempts at electropolymerising 3-(methylthio)-, 3-(ethylthio)- and 3,4-bis(ethylthio)-thiophenes have either failed,[19] or resulted in the formation of soluble oligomers,[20] due to the electron donating (and thus stabilising) effects of the β(β′) alkylthio side chains. (ii) The oxidation potentials of the thiophene units in compounds **4** and **5** are higher than that of thiophene; this is most probably due to the coulombic repulsion of the tricationic species generated in each case. In deference to polymerisation, these unusual triply charged molecules may be sufficiently unstable to react with either the solvent or the anion in solution to form by-products. This phenomenon has been observed previously in derivatised thiophene monomers with high oxidation potentials.[21] Further evidence to support this theory can be seen in the cyclic voltammogram of **4**,[10] which reveals an additional unexpected solitary cathodic peak at +1.46 V, suggesting some decomposition of the starting material. (iii) Of the two types of TTF-thiophene systems known to polymerise under electrochemical conditions,[7d,e] both polymerisations have been performed using nitrobenzene as the solvent; when other solvents were employed, no polymeric materials were obtained. The strategy behind this choice of solvent utilises the acceptor ability of nitrobenzene itself. It is believed that TTF forms a charge-transfer complex with the individual solvent molecules, thus decreasing the radical scavenging ability of the TTF moiety and allowing the thiophene unit to undergo polymerisation.[7e]

Table 2 Room temperature conductivity values and nitrile stretching frequencies of CT complexes of **1**, **4** and **5**

donor	acceptor	ratio	σ^a/S cm^{-1}	ν(CN)/cm^{-1}
TTF **1**	TCNQ	1 : 1	0.13	2202
4	TCNQ	1 : 1	3.0×10^{-4}	2206
4	TCNQF$_4$	1 : 1	6.7×10^{-3}	2191
5	TCNQ	1 : 1	0.22	2188

[a] Conductivity measurements were carried out using two-probe apparatus on compressed pellets.[23] The values given above represent the averages of five measurements of each CT complex.

However, on using these solvent conditions with monomers **4** and **5**, a dark precipitate formed at the anode in each experiment, indicating the formation of charge-transfer matter instead of polymerisation taking place.

Charge-transfer complexes

An alternative method for the polymerisation of thiophene derivatives involves the addition of a strong acceptor. This has been demonstrated by Wudl *et al.*,[22] who prepared poly(isothianaphthene) *via* the oxidation of isothianaphthene by TCNQ. When compound **4** was treated with TCNQ and TCNQF$_4$, the precipitate which formed in each case was found to be a CT complex (MALDI-TOF mass spectroscopy indicated the presence of monomer units, rather than oligomeric or polymeric species). A CT salt was also isolated when 4-(3-thienyl)TTF **5** was reacted with TCNQ. The conductivity values of the complexes (all of which are of 1 : 1 stoichiometry as judged by CHN analysis), were measured using two-probe apparatus[23] and the results are collated in Table 2 (TTF–TCNQ was also measured and used as a standard for our equipment). Complex **5**–TCNQ gave a conductivity slightly higher than that of TTF–TCNQ, whilst the complexes of donor **4** gave conductivity values several orders of magnitude lower, in the semiconductor range. The CN stretching frequencies of the above complexes are also given in Table 2. The CN peak for TTF–TCNQ (2202 cm^{-1}) is shifted with respect to that of neutral TCNQ (2222 cm^{-1}), and this is due to the influence of the delocalised radical anion in the former.[24] The shift in CN frequencies of the complexes of **4** and **5** are commensurate with those of reduced TCNQ and TCNQF$_4$ moieties (2226 cm^{-1} for neutral TCNQF$_4$), providing further evidence of charge-transfer material.

X-Ray crystallography

Molecule **4** (Fig. 1) has a non-crystallographic mirror symmetry. Its TTF-thiophene moiety adopts a boat conformation, folding along the S(2)···S(3) and S(4)···S(5) vectors by 10.8 and 16.3°, respectively. Both hexyl chains adopt almost ideal all-*trans* conformations. Molecules related *via* an inversion centre form rather loose dimers, overlapping with their parallel fused-ring systems (interplanar separation of 3.75 Å). The dimers are arranged into a *kappa*-type layer (Fig. 2), wherein each molecule participates in two S···S contacts closer than twice the van der Waals radius of sulfur (1.81 Å),[25] S(2)···S(5′) (and its equivalent) of 3.56 Å. Other S···S contacts are in the range of 3.70–3.85 Å. The layers are effectively separated from each other by hexyl chains, stretched in general normally to TTF-thiophene systems.

In molecule **5** (Fig. 3) the TTF moiety is folded by 10.5° along the S(1)···S(2) vector. The planar thiophene ring is nearly coplanar with the S(1)C(2)C(3)S(2) moiety. The C(2)—C(13) bond distance of 1.457(8) Å is typical for 'conjugated' single C(sp^2)—C(sp^2) bonds (mean 1.455 Å)[26] and much shorter than non-conjugated ones (1.478 Å)[26] indicating a considerable interaction between the π-electron systems of the thiophene and the TTF. The thiophene ring is disordered over

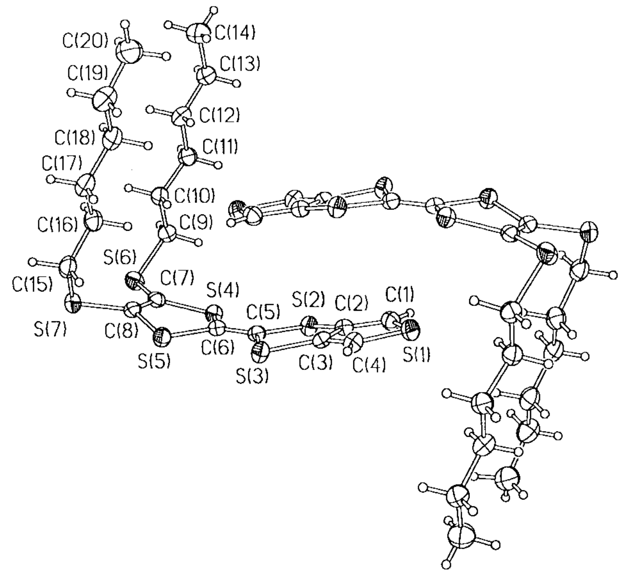


Fig. 1 Molecule **4**, showing 50% probability elipsoids and its inversion equivalent

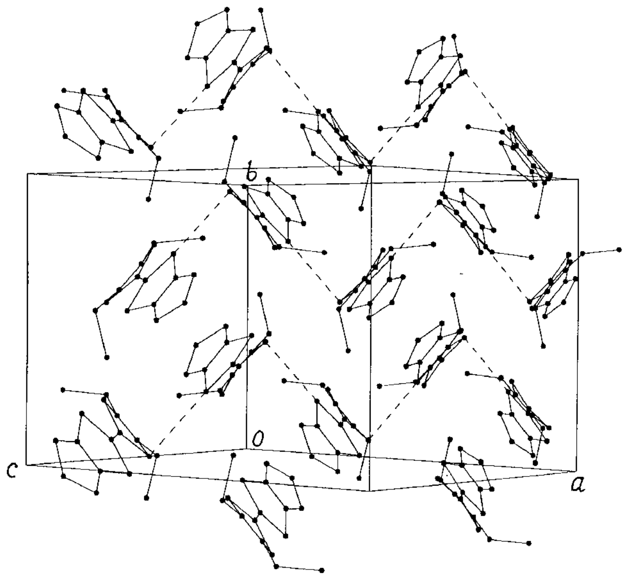


Fig. 2 *Kappa*-packing of **4** (hexyl groups omitted); projection on the (1 0 1) plane, showing S···S contacts <3.6 Å

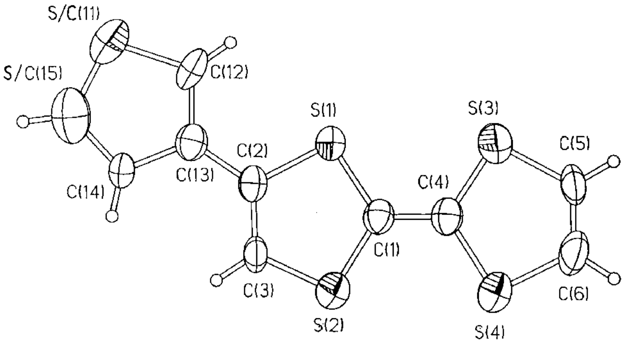


Fig. 3 Molecular structure of **5**, showing 50% probability elipsoids. The S/C(11) was refined as 85% sulfur and 15% carbon, S/C(15) *vice versa*

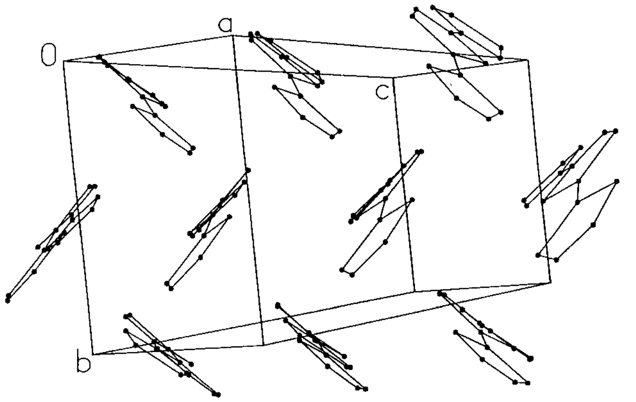


Fig. 4 Crystal packing diagram of **5**

two orientations, differing by the 180° rotation around the C(2)—C(13) bond, thus the observed bond distances in that ring are not meaningful. The crystal packing of **5** (Fig. 4) shows a perpendicular motif without short intermolecular contacts. All S···S contacts are ⩾3.8 Å, except one (3.51 Å) between S(4) and its inversion equivalent atom.

Conclusions

The synthesis of two new tetrathiafulvalene-thiophene systems **4** and **5** has been described. Under oxidative conditions, the propensity to form non-coupling charged intermediates, rather than oligomeric or polymeric species, is supported by the fact that compounds **4** and **5** form stable CT materials on reaction with TCNQ and TCNQF$_4$. The X-ray crystal structures of **4** and **5**, however, offer some interesting features: compound **4** crystallises with a high degree of order between the molecules, procured by an extensive network of close S···S intermolecular contacts, whilst compound **5** exhibits a high degree of π-delocalisation between the two donor units. Either of these characteristics could be beneficial to the corresponding polymer systems by: (i) increasing the dimensionality of the polymer material *via* the interaction of chalcogens between the chains, and (ii) integrating the TTF moiety into the electronic behaviour of the polythiophene backbone, on the basis of a highly conjugated TTF-thiophene link. In view of these results, our current efforts involve the synthesis of 2,5-dihalothiophene analogues of **4** and **5** as a means of functionalisation for chemical polymerisation.

Experimental

X-Ray crystallography

Table 3 Crystal data and experimental details

compound	**4**	**5**
formula	$C_{20}H_{28}S_7$	$C_{10}H_6S_5$
M	492.84	286.45
symmetry	monoclinic	monoclinic
T/K	150	293
λ/Å	1.54184	0.71073
a/Å	17.113(2)	5.886(1)
b/Å	12.259(2)	8.617(1)
c/Å	12.338(2)	23.146(2)
β (°)	110.42(1)	93.06(1)
U/Å^3	2425.8(7)	1172.3(3)
space group	$P2_1/c$	$P2_1/c$
Z	4	4
μ/cm^{-1}	60.4	9.5
D_c/g cm^{-3}	1.35	1.62
crystal size/mm	0.22 × 0.35 × 0.35	0.03 × 0.30 × 0.50
$2\theta_{max}$(°)	150	50.6
data total	4957	4766
data unique	4150	1880
data observed, $I > 2\sigma(I)$	3478	1387
R_{int} before/after abs. corr.	0.066, 0.047	0.077, 0.048
absorption correction	analytical[a]	integration[b]
transmission min, max	0.16, 0.40	0.68, 0.97
no. of refined variables	356	137
$wR(F^2)$, all data	0.147	0.214
$R(F)$, obs. data	0.039	0.061
$\Delta\rho_{max,min}$/e Å^{-3}	0.36, −0.32	0.46, −0.41

[a]TEXSAN software (ref. 28). [b]SHELXTL software (ref. 27).

The single-crystal X-ray diffraction experiment for **4** was carried out on a Rikagu AFC6S 4-circle diffractometer ($2\theta/\omega$ scan mode), using graphite monochromated Cu-Kα radiation and an Oxford Cryosystems open-flow N$_2$ cryostat. For **5**, the experiment was performed on a Siemens SMART 3-circle diffractometer with a CCD area detector, using graphite monochromated Mo-Kα radiation. A hemisphere of the reciprocal space was scanned by ω in frames of 0.3°. Both structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[27] All non-H atoms were refined with anisotropic displacement parameters. In **5** the thiophene ring is disordered over two orientations in which the sulfur atom occupies the positions 11 and 15, with the occupancies of 85(1) and 15(1)%, respectively. Other possible models of disorder, such as the partial presence of the α-thiophene substituent (*i.e.* sulfur in the positions 12 or 14) and the rotation of the whole molecule by 180° around the axis through S(1) and the midpoint of the S(2)—C(3) bond (the thiophene and dithiole rings overlapping), did not produce a consistent refinement. The disordered S and C atoms in overlapping positions were refined as a single atom. All H atoms were refined in isotropic approximation (**4**) or were treated as 'riding' (**5**). Crystal data and experimental details are listed in Table 3; atomic coordinates and thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC); see Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/103. Selected bond lengths are given in Table 4.

General

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 instrument. Infrared spectra

Table 4 Selected bond distances in Å in **4** and **5**

Compound **4**			
S(1)–C(1)	1.714(3)	S(1)–C(4)	1.719(3)
S(2)–C(2)	1.752(3)	S(2)–C(5)	1.762(3)
S(3)–C(3)	1.760(3)	S(3)–C(5)	1.767(3)
S(4)–C(6)	1.759(3)	S(4)–C(7)	1.769(3)
S(5)–C(8)	1.761(3)	S(5)–C(6)	1.761(3)
S(6)–C(7)	1.744(3)	S(6)–C(9)	1.814(3)
S(7)–C(8)	1.751(3)	S(7)–C(15)	1.817(4)
C(1)–C(2)	1.357(3)	C(2)–C(3)	1.425(4)
C(3)–C(4)	1.352(4)	C(5)–C(6)	1.331(4)
C(7)–C(8)	1.346(4)		
Compound **5**			
S(1)–C(1)	1.764(6)	S(1)–C(2)	1.768(5)
S(2)–C(3)	1.707(5)	S(2)–C(1)	1.740(6)
S(3)–C(5)	1.730(6)	S(3)–C(4)	1.755(6)
S(4)–C(6)	1.722(7)	S(4)–C(4)	1.744(6)
S/C(11)–C/S(15)	1.651(7)	S/C(11)–C(12)	1.706(5)
C/S(15)–C(14)	1.453(8)	C(1)–C(4)	1.363(8)
C(2)–C(3)	1.414(8)	C(2)–C(13)	1.457(8)
C(5)–C(6)	1.348(9)	C(12)–C(13)	1.459(8)
C(13)–C(14)	1.480(7)		

were recorded on a Nicolet FTIR spectrometer and mass spectra were determined with a Fison Instruments Trio 2000 or a Zab2-SE-FPD (VG Instruments). Elemental analyses were performed on a Carlo-Erba Strumentazione instrument. Cyclic voltammetry was performed using a BAS CV50W voltammetric analyser, using freshly distilled dichloromethane or acetonitrile as the solvent, with *iR* compensation. The syntheses of compounds **8**[13] and **9**[11] were achieved using alternative methods to those reported previously.

4,5-Bis(bromomethyl)-1,3-dithiole-2-thione 7

To a suspension of **6**[12] (2.00 g, 10.31 mmol) in dry dichloromethane (300 ml), under nitrogen, was added carbon tetrabromide (6.85 g, 20.63 mmol). Whilst stirring, a solution of triphenylphosphine (5.40 g, 20.61 mmol) in dry dichloromethane (100 ml) was added over 45 min. Evaporation of the solvent gave an oily brown residue, which was chromatographed using silica gel and dichloromethane–hexane (1 : 2 v/v) as the eluent. The product was recrystallised from dichloromethane–hexane to give a bright yellow solid (2.31 g, 70% yield); mp 124–126 °C (Found: C, 18.9; H, 1.3%; $C_5H_4Br_2S_3$ requires C, 18.8; H, 1.3%); *m/z* (FD) 320 (M^+); δ_H ($CDCl_3$) 4.33 (s); δ_C ($CDCl_3$) 208.4, 139.7 and 20.6; ν_{max} (KBr)/cm^{-1} 3023.3, 2960.5, 1198.5, 1058.2, 594.3 and 514.4.

4,6-Dihydrothieno[3,4-*d*]-1,3-dithiole-2-thione 8

A solution of **7** (2.00 g, 6.25 mmol) in THF–ethanol (250 ml, 4 : 1 v/v) and a solution of sodium sulfide nonahydrate (1.50 g, 6.25 mmol) in water–ethanol (250 ml, 4 : :1 v/v), were added simultaneously, over 45 min, to ethanol (200 ml) with vigorous stirring. Evaporation of the solvent afforded a yellow solid residue, which was leached with dichloromethane (3 × 150 ml). The resulting solution was washed with water, separated, dried ($MgSO_4$) and evaporated to leave a yellow solid. Recrystallisation from hexane–dichloromethane gave a yellow crystalline solid (0.94 g, 78% yield); mp 131–133 °C (Found: C, 31.5; H, 2.1%. $C_5H_4S_4$ requires C, 31.2; H, 2.1%); *m/z* (EI) 192 (M^+); δ_H ($CDCl_3$) 4.03 (s); δ_C ($CDCl_3$) 217.4, 138.6 and 35.1; ν_{max} (KBr)/cm^{-1} 2919.0, 2839.5, 1638.6, 1080.4, 1041.4 and 507.3.

Thieno[3,4-*d*]-1,3-dithiole-2-thione 9

To a solution of **8** (1.00 g, 5.21 mmol), under nitrogen in dry toluene (150 ml), was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.30 g, 5.73 mmol); the mixture was allowed to reflux for 1.5 h. After evaporation of the solvent, the product was extracted with dichloromethane (3 × 150 ml). The solution was washed with water (5 × 200ml), separated, dried ($MgSO_4$), and the residue chromatographed using silica gel and ethyl acetate–light petroleum (1 : 3 v/v) as the eluting solvent. Recrystallisation from ethyl acetate–light petroleum afforded the product as an orange solid (0.95 g, 96% yield); mp 139–141 °C (lit.,[29] 142 °C).

2-[4,5-Bis(hexylthio)-1,3-dithiol-2-ylidene]thieno[3,4-*d*]-1,3-dithiole 4

Compounds **10**[11] (0.75 g, 4.32 mmol) and **13** (2.25 g, 6.43 mmol) were added to neat freshly distilled triethyl phosphite (10 ml); the mixture was heated to 90 °C and left to stir at this temperature for 6 h. After cooling, the solution was chromatographed (silica gel), using hexane as the eluting solvent to remove triethyl phosphite, followed by dichloromethane–hexane (1 : 3 v/v) to isolate the product. Recrystallisation from dichloromethane–acetonitrile afforded bright yellow needles (0.53 g, 25% yield); mp 73–74 °C (Found C, 48.4; H, 5.7%; $C_{20}H_{28}S_7$ requires C, 48.7; H, 5.7%); *m/z* (FD) 492 (M^+); δ_H ($CDCl_3$) 6.88 (2H, s), 2.83 (4H, t, *J* 7.2 Hz), 1.65 (4H, m), 1.32 (12H, m) and 0.90 (6H, t, *J* 6.4 Hz); δ_C ($CDCl_3$) 136.0, 127.5, 113.8, 112.1, 112.0, 36.3, 31.3, 29.7, 28.2, 22.5 and 14.0; ν_{max} (KBr)/cm^{-1} 3087.8, 2948.3, 2922.7, 2853.6, 1459.5 and 768.8.

4-(3-Thienyl)tetrathiafulvalene 5

To a stirred solution of thiophene-3-boronic acid (0.22 g, 1.72 mmol) in dimethoxyethane–water (100 ml, 1 : 1 v/v), was added 4-iodotetrathiafulvalene[15a] **14** (0.63 g, 1.91 mmol). After the addition of barium hydroxide (0.5 g, 2.91 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.05 g, 0.04 mmol), the reaction was stirred at 80 °C in the dark, under nitrogen, for 24 h. Dichloromethane (200 ml) was added and the resulting mixture was washed with water. The organic layer was separated, dried ($MgSO_4$) and evaporated. The residue was chromatographed (silica gel), using dichloromethane–hexane (1 : 3 v/v) as the eluent to afford the product. Recrystallisation from dichloromethane–hexane gave orange crystals (0.15 g, 31% yield); mp 95–97 °C; *m/z* (EI) 286 (M^+); HRMS found 285.9076, $C_{10}H_6S_5$ requires 285.9073; δ_H ($CDCl_3$) 7.34 (1H, dd), 7.20 (2H, m), 6.43 (1H, s) and 6.34 (2H, s); δ_C ($CDCl_3$) 133.8, 131.1, 127.0, 125.6, 122.6, 119.4 and 113.6; ν_{max} (KBr)/cm^{-1} 3070.0, 2924.6, 2856.9, 1458.5, 870.8, 748.7 and 643.2.

General method for the preparation of CT complexes

To a solution of the donor (1 equiv.) in refluxing dichloromethane (for compound **4**), or acetonitrile (for compound **5**), was added a hot solution of TCNQ or $TCNQF_4$ (1 equiv.) in the same solvent. The mixture was heated gently at reflux for 10 min before allowing to cool. After several hours the charge-transfer material was collected by filtration.

Complex 4–TCNQ. Analysis found: C, 54.9; H, 4.7; N, 7.7%; $C_{32}H_{32}N_4S_7$ (a 1 : 1 complex) requires C, 55.1; H, 4.6; N, 8.0%; ν_{max} (KBr)/cm^{-1} 2921.6, 2852.2, 2206.2, 1508.1, 1469.5, 1423.2, 1313.3, 1186.0 and 767.5.

Complex 4–$TCNQF_4$. Analysis found: C, 49.9; H, 3.7; N, 7.5%; $C_{32}H_{28}F_4N_4S_7$ (a 1 : 1 complex) requires C, 50.0; H, 3.7; N, 7.3%; ν_{max} (KBr)/cm^{-1} 2926.7, 2856.8, 2191.1, 1630.4, 1386.4, 1313.6, 776.9 and 484.5.

Complex 5–TCNQ. Analysis found: C, 53.3; H, 2.0; N, 11.1%; $C_{22}H_{10}N_4S_5$ (a 1 : 1 complex) requires C, 53.9; H, 2.1; N, 11.4%; ν_{max} (KBr)/cm^{-1} 3062.4, 2925.9, 2187.9, 1642.1, 1314.8, 1122.5, 1084.1, 687.2 and 431.9.

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Note added in proof: After submission of this manuscript, the electropolymerisation of TTF-functionalised bithiophene derivatives was reported: L. Huchet, S. Akoudad and J. Roncali, *Adv. Mater.*, 1998, **10**, 541.

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