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Exceptional electron donating ability of an extended tetrathiafulvalene derivative

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Abstract—We report the synthesis, crystal structures and redox chemistry of two new TTF derivatives bearing fused triaryl units. Both compounds show significant planarisation within conjugated regions, assisted by close intramolecular S···O contacts. The extended-TTF analogue displays multi-redox activity and can be oxidised sequentially to the tetracation species.

The π-electron donor tetrathiafulvalene (TTF) and its derivatives have been studied extensively for their use in a variety of applications such as organic metals and superconductors,[1] Langmuir–Blodgett films,[2] molecular sensors,[3] non-linear optics,[4] field effect transistors[5] and photovoltaics.[4] In many cases, the bulk electronic properties of TTF derivatives stem from their potential to self-assemble into well-defined structures featuring close intermolecular contacts. Such interactions are particularly beneficial where charge transport is of concern. From this viewpoint, derivatisation of the TTF framework affords the possibility of integrating additional valuable features into the molecule, namely: (i) enhanced redox behaviour, (ii) stronger and more widespread intermolecular interactions and (iii) control of the shape of the molecule itself. In recent work,[6] we have shown that 1-3-dithiole-2-thione species, appended with fused 2,5-diphenylthiophene and 2,5-diphenylfuran derivatives, are efficient electron donors capable of undergoing two reversible oxidation processes to afford the corresponding radical cation and dication species. *ortho*-substitution of the phenyl rings with methoxy groups induces planarisation of the triaryl units through intramolecular S···O interactions and this situation is responsible for enhanced stabilisation of the products of oxidation. In this paper, we present the first soluble TTF derivatives bearing fused 4,6-bis(2,4-dimethoxyphenyl)thieno[3,4-*d*][1,3]dithiole and 4,6-bis(2,4-dimethoxyphenyl)furano[3,4-*d*][1,3]dithiole moieties and discuss the novel geometrical and electrochemical features that are attributed to the incorporation of these triaryl units.

Due to the insolubility of symmetrical TTF derivatives derived from compounds such as **1**,[6] we attempted to synthesise the unsymmetrical derivatives **4** and **10**, bearing ethylenedithiodithiole units. Compound **4** was prepared according to Scheme 1. Thus, **1** was stirred at 80 °C with oxone **2**[7] in the presence of trimethyl phosphite to afford the cross-coupled product **3** in 26% yield. The cyanoethylene protecting groups of **3** were removed by CsOH in THF and the resulting dithiolate intermediate was reacted immediately with 1,2-dibromoethane to give the product in 57% yield. The reason for proceeding in two steps from the oxone **2**, rather than using the ethylenedithio analogue, resides in the easy separation of **3** and tetracyanoethylsulfanyl-TTF.

Scheme 2 depicts the route towards the π-extended TTF analogue **10**. Methylation of compounds **5** and **1** was achieved using methyl triflate, to give the dithiolium salts **6a**,**b** in 73% and 81% yield, respectively. Compounds **7a**,**b** were isolated from the reactions of **6a**,**b** with sodium borohydride (79% and 88% yields). Treatment of **7a**,**b** with triflic acid gave salts **8a**,**b** in 67% and 74% yield, but these materials proved to be unstable and slowly decomposed upon isolation. The phosphonium

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Keywords: Tetrathiafulvalene; Synthesis; X-ray crystallography; Electrochemistry.

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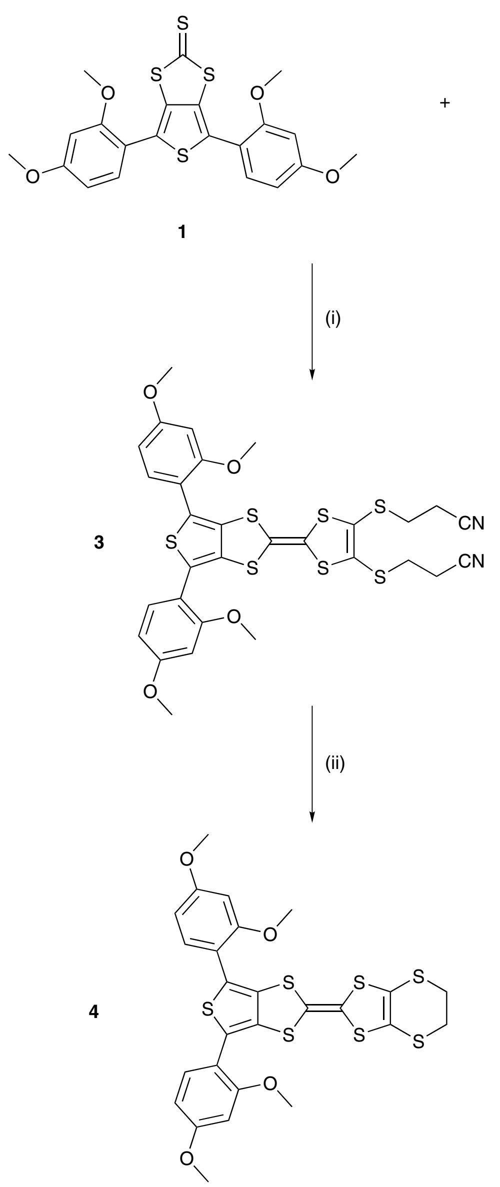


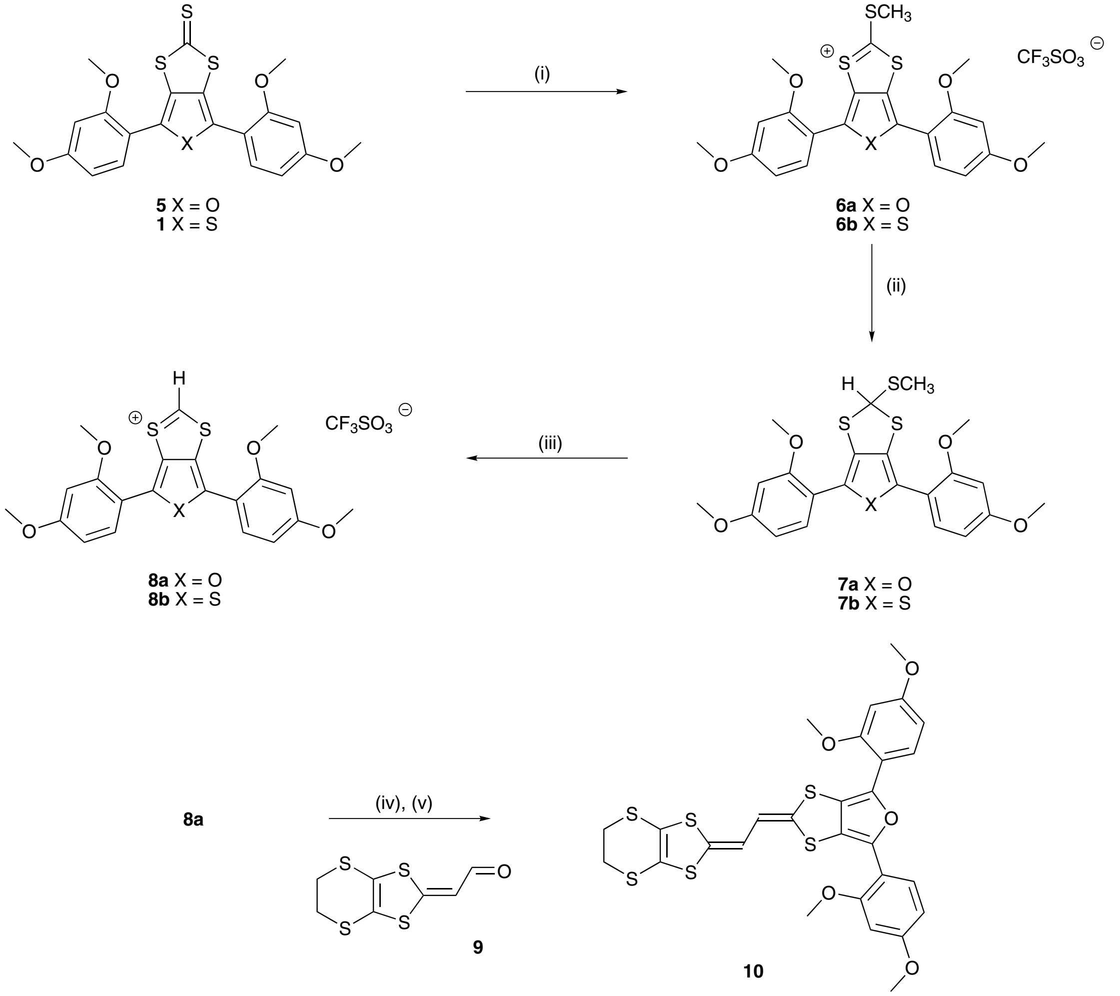
Scheme 1. Reagents and conditions: (i) P(OMe)$_3$, toluene, 80 °C, 12 h; (ii) THF, CsOH, then 1,2-dibromoethane.

salt of **8a** was prepared by reaction of the latter with triphenyl phosphine in THF. After treatment in situ with *n*-BuLi at −78 °C, compound **9**[8] was added to give the product **10** in 71% yield.[9] Unfortunately, we were not able to repeat this procedure for salt **8b** to give the thiophene analogue of **10**.

Recrystallisation of compounds **4** (CHCl$_3$–EtOH 10/2 v/v) and **10** (toluene) gave single crystals suitable for X-ray crystallographic analysis. Compound **4**[10] displays two intramolecular short S···O contacts[11] (Fig.1(a)), the first involving one *o*-methoxy group and the adjacent dithiole ring (2.948(7) Å) and the other between the second *o*-methoxy substituent and the sulfur of the thiophene ring (2.626(7) Å). The latter interaction is associated with a reasonable degree of planarity between the corresponding benzene ring and the thiophene unit; the torsion angle between these two cyclic units is 11.8°. The second benzene ring is twisted significantly away from the plane of the thiophene unit, with a torsion angle of 44.4°. Compound **4** forms dimers in the solid state through intermolecular S···S contacts (3.296(8) Å) between the S(5) atoms of the ethylenedithio fragment. There are no further significant intermolecular short contacts. Compound **10**[12] crystallises as a 1:1 toluene solvate and shows a high degree of planarity (Fig.1(b)). Two S···O interactions (2.777(3) and 2.754(2) Å) are observed exclusively between the *o*-methoxy substituents and the corresponding sulfurs of the adjacent dithiole ring. Hydrogen bonding is also observed between the marked hydrogens of the two benzene rings (Fig.1(b)) and the oxygen atom of the furan unit (2.313(3) and 2.309(2) Å). This arrangement of short contacts is also evident in the oxone analogue of compound **5**[6] and is thought to be responsible for the high degree of planarity within the triaryl fragment, which comprises the two benzene rings and the thienofurano unit. The torsion angle between benzene A and the furan is 0.03°, whilst that between ring B and the furan heterocycle is 4.2°. There are no close intermolecular interactions in the crystal structure of compound **10**, apart from weak H-bonds involving aliphatic C–H groups.

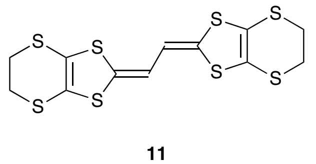
The redox properties of compounds **4** and **10** have been studied by cyclic voltammetry.[13] Compound **4** undergoes two reversible oxidation processes at +0.56 and +0.97 V, respectively. A third irreversible peak is also observed at +1.47 V. Compound **1** also undergoes two reversible oxidation processes at +0.86 and +1.16 V. From these values it can be concluded that the first oxidation of **4** is attributed to the TTF unit of the molecule, whilst the second oxidation originates from the triaryl component. The third redox process is also assumed to arise from the triaryl fragment and its irreversible nature is probably due to the high potential at which this oxidation takes place.

The cyclic voltammogram of compound **10** is depicted in Figure 2. In contrast to the electrochemical behaviour of **4**, the extended TTF analogue is oxidised to the tetracation through four sequential, reversible oxidation processes ($E_1^{1/2} = +0.35\,\mathrm{V}$, $E_2^{1/2} = +0.76\,\mathrm{V}$, $E_3^{1/2} = +1.09\,\mathrm{V}$ and $E_4^{1/2} = +1.25\,\mathrm{V}$). The first two oxidation processes are assigned to the extended TTF unit. Comparing the electrochemistries of compounds **4** and **10**, the key role of the additional vinylene spacer group between the two dithiole rings is to minimise couloumbic repulsion within the dication of the TTF species. In comparison with the values reported for the symmetrical bis(ethylenedithio) analogue **11** ($E_1^{1/2} = +0.48$ and $E_2^{1/2} = +0.71$ vs Ag/AgCl in dichloromethane),[14] $E_1^{1/2}$ for **10** is 130 mV lower, whilst $E_2^{1/2}$ is higher by 50 mV. E_1 for compound **10** is therefore assigned to the triaryl fused dithiole, leaving the 4,5-ethylenedithio1,3-dithiole ring as the site for E_2. The difference between the first two redox processes for each compound ($E_2 - E_1$) is 0.23 V for **11** and 0.41 V for **10**. This discrepancy is due to the unsymmetrical nature of compound **10** and the stronger electron donating effect of the triaryl moiety, compared to the relatively unchanged donor ability of the 4,5-ethylenedithio1,3-dithiole unit. It is surprising to see



Scheme 2. Reagents and conditions: (i) $CF_3SO_3CH_3$, CH_2Cl_2; (ii) $NaBH_4$, CH_3CN/IPA; (iii) CF_3SO_3H, CH_2Cl_2; (iv) PPh_3, THF, rt; (v) *n*-BuLi, −78 °C, then **9**.

that molecule **10** undergoes two further reversible oxidation processes, despite the inevitability of strong coulombic repulsion within the triaryl unit. The extended TTF **12** with two dithiafulvenyl arms is also known to lead to a tetracation state, but with an irreversible fourth oxidation step.[15] Compared to compound **1**, $E_3^{1/2}$ and $E_4^{1/2}$ for **10** are 230 and 90 mV higher than the corresponding redox processes and are slightly inferior to those observed for **12** ($E_3^{1/2} = 1.15$ V and $E_4^{1/2} = 1.40$ V). Undoubtedly, this increase in redox potentials is due to coulombic factors, but the overall reversibility of the oxidation processes, together with the narrow electrochemical window for attaining a tetracation state, illustrate the new extended TTF as an outstanding and promising π-electron donor.



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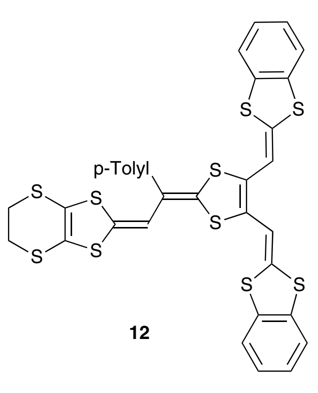

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Initial attempts at forming charge-transfer (CT) materials with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$) has resulted in the isolation of an amorphous powder with a donor–acceptor stoichiometry of 1:1.[16] The conductivity of this material was found to be 2.4×10^{-4} Scm^{-1} by the two-probe compressed pellet method[17] (average of five readings).

In conclusion, we have presented some new TTF materials featuring fused, electroactive and highly planar triaryl fragments. Compound **10** is the highlight in this series, due to its exceptional π-electron donor properties and its ability to be reversibly oxidised to the tetracation species.

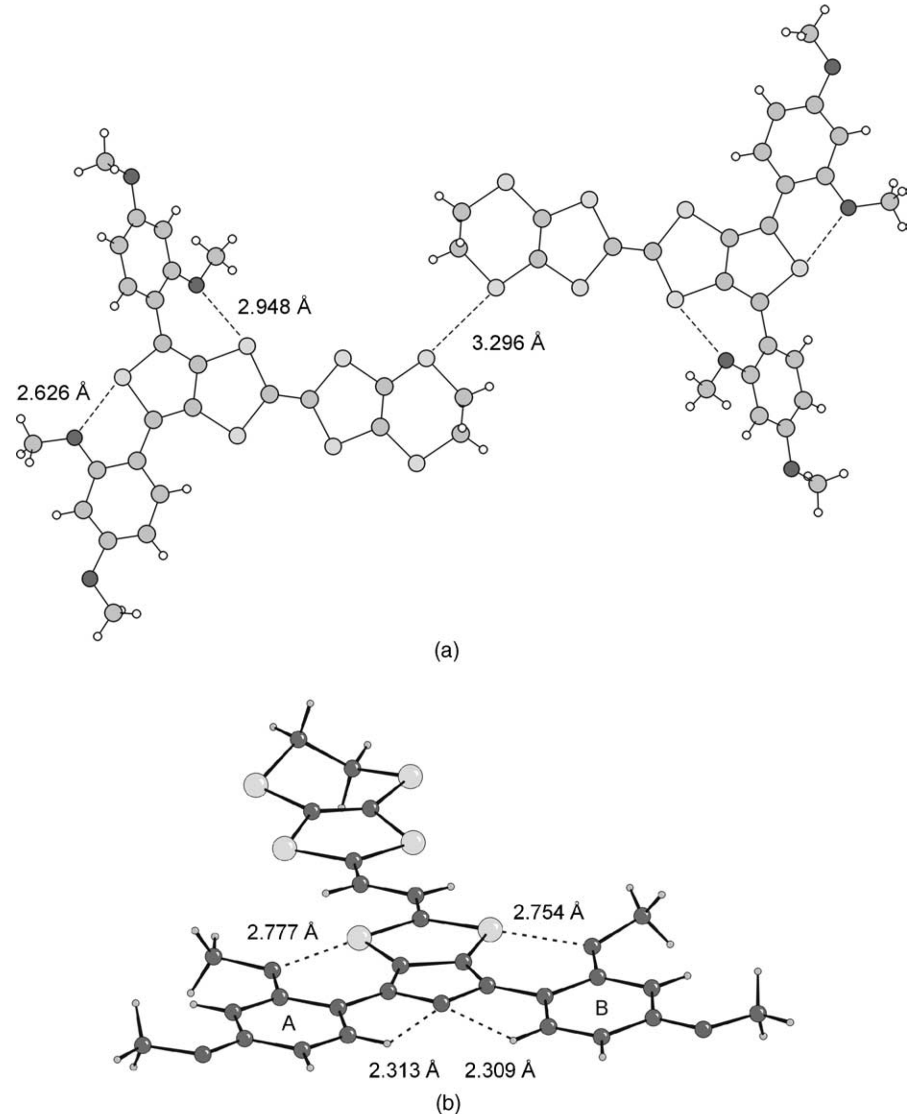

Figure 1. X-ray crystal structures of (a) compound **4** and (b) derivative **10** with the solvent of crystallisation (toluene) omitted.

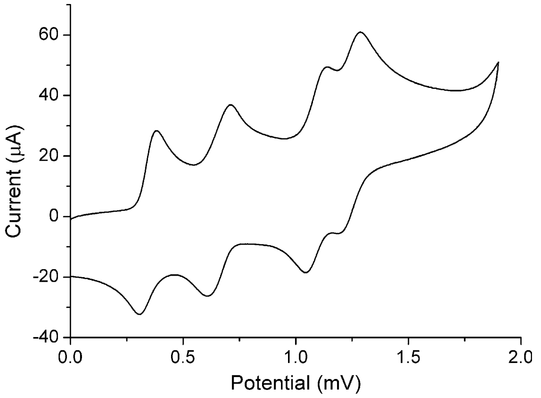

Figure 2. Cyclic voltammogram of compound **10** vs Ag/AgCl reference electrode, using a Au working electrode, Pt counter electrode and Bu_4NPF_6 as the supporting electrolyte.

Acknowledgements

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9. Selected data for compound **10**: Mp, 154–156 °C; MS (APCI) = 632.0; (Found: C, 53.01; H, 3.82; S, 29.87. Calcd for $C_{28}H_{24}O_5S_6$: C, 53.14; H, 3.82; S, 30.40%); ^{1}H NMR ($CDCl_3$, 300 MHz, δ) 7.65 (2H, d, J 8.65), 6.58–6.45 (4H, m), 6.08 (1H, d, J 11.12), 5.83 (1H, d, J 11.13), 3.92 (6H, d, J 7.14), 3.84 (6H, s) 3.30 (4H, s); ^{13}C NMR ($CDCl_3$, 75 MHz, δ) 161.0, 160.9, 156.2, 156.0, 141.2, 139.3, 139.2, 127.6, 127.4, 126.5, 123.1, 122.3, 113.1. 112.2, 112.0, 111.5, 105.7, 105.6, 98.8, 98.7, 55.8, 55.5, 55.3 and 30.2; V_{max} (KBR)/cm^{-1} 1611, 1504, 1287, 1226, 1160, 1030 and 819.
10. Crystallographic data for compound **4**: $C_{26}H_{22}O_4S_7$, monoclinic, space group P12$_1$/n1, $a = 16.286(2)$, $b = 10.6501(7)$, $c = 16.636(1)$ Å, $\alpha = 90°$, $\beta = 111.379(9)°$, $\gamma = 90°$, volume = 2686.9(8) Å^3, $T = 293$ K, $Z = 4$, $\mu = 0.620$ mm^{-1}, 3211 reflections measured and 1808 symmetry-independent with $I > 3\sigma(I)$, full matrix least-squares refinement on F^2, $R_{all} = 0.053$, $wR_{all} = 0.075$. Supplementary data in the form of a CIF has been deposited with the Cambridge Crystallographic Data Centre (CCDC 231107).
11. Close contacts refer to interatomic distances shorter than the sum of the van der Waals radii for the two corresponding atoms.
12. Crystallographic data for compound **10**: $C_{28}H_{24}O_5S_6 \cdot C_7H_8$, triclinic, P-1, $a = 7.7619(1)$, $b = 14.1309(4)$, $c = 15.3911(4)$ Å, $\alpha = 100.642(2)°$, $\beta = 91.195(2)°$, $\gamma = 100.785(2)°$, volume = 1627.11(7) Å^3, $T = 120$ K, $Z = 2$, $D_c = 1.48$ Mg/m^3, $\mu = 0.464$ mm^{-1}, $\theta_{max} = 27.48°$, 36270 measured and 7418 unique ($R_{int} = 0.0653$) reflections, R_1 (obs) = 0.0647 and wR_2 (all data) = 0.1721, $\rho_{max}/\rho_{min} = 2.614/-0.716$ eÅ^{-3}. Supplementary data in the form of a CIF has been deposited with the Cambridge Crystallographic Data Centre (CCDC 228893).
13. Experiments were run in CH_2Cl_2–CH_3CN (1:1) with substrate concentration ca. 10^{-4} M, using a Ag/AgCl reference electrode, Au working electrode, Pt counter electrode and Bu_4NPF_6 (0.1 M) as the supporting electrolyte.
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16. Found C, 51.82; H, 2.42; N, 6.01. Calcd for $C_{40}H_{24}F_4N_4O_5S_6$: C, 52.85; H, 2.66 N, 6.16%); V_{max} (KBr)/cm^{-1} 2190, 1609, 1505, 1438, 1497, 1336, 1191 and 1021.
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