Highly-functionalised Tetrathiafulvalene (TTF) Derivatives

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Efficient syntheses are described for a range of new functionalised tetrathiafulvalene donors, notably those substituted with vinylthio and acrylate groups; solution redox properties have been studied by cyclic voltammetry.

Derivatives and analogues of tetrathiafulvalene (TTF) **1** are of great interest as π-electron donors, because at the radical cation stage they are components of organic-metals and -superconductors.[1,2] The most widespread modification to the TTF framework has been the fusion of heterocyclic rings,[3–5] *e.g.* bis(ethylenedithio)-TTF (BEDT-TTF).[4] In contrast, scant attention has been paid to the attachment of *functionalised* substituents to TTF.[6–10] Such derivatives, bearing appropriate functionality, should be interesting donors *per se*, and be valuable units for the synthesis of polymeric TTF systems. In this context, monovinyl-TTF was isolated some years ago and reported to polymerise slowly on standing,[11] whereas tetravinyl-TTF could not be isolated owing to its rapid polymerisation.[7]

Herein we report the efficient synthesis of TTF donors substituted with one, two and four vinylthio groups which are stable materials at room temperature. Moreover, functionalised TTFs prepared *en route* to these compounds offer great synthetic potential as versatile building blocks for new donors: this is exemplified by the preparation of TTF-acrylate and -methacrylate derivatives **5** and **6**.

The synthesis of vinylthio-TTF **4** is shown in Scheme 1. Monolithio-TTF was generated[6] and reacted with elemental sulphur, as described previously;[9] alkylation of the resulting thiolate anion with 2-bromoethanol yielded alcohol **2**. Mesylation of **2**, to yield **3**, followed by treatment with sodium ethoxide, gave vinylthio derivative **4**† (53% overall yield from TTF **1**).

The synthesis of tetra(vinylthio)TTF **11** and di(vinylthio)-ethylenedithioTTF **14** are shown in Scheme 2. Zincate salt **7**[12] reacted with 2-bromoethanol to yield 1,3-dithiole-2-thione

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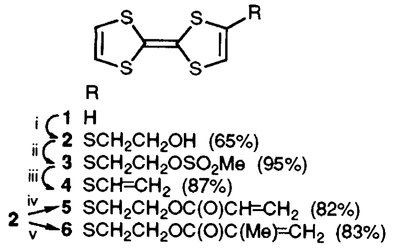
† *Selected spectral data* for **4**: *m/z* (DCI) 263 ($M^+ + 1$); δ_H (250 MHz, $CDCl_3$, Me_4Si) 6.46 (1H, s), 6.32 (2H, s), 6.35, 5.39 and 5.38 (3H, ABX, J_{AX} 16.52, J_{BX} 9.35, $J_{AB} < 1$ Hz); δ_C (500 MHz, $CDCl_3$, Me_4Si) 130.2, 124.5, 123.7, 119.0, 118.9, 115.9, 113.2 and 109.2.

For **5**: *m/z* (DCI) 335 ($M^+ + 1$); δ_H (250 MHz, $CDCl_3$, Me_4Si) 6.45 (1H, s), 6.38 (2H, s), 6.11, 5.86 and 5.82 (3H, ABX, J_{AX} 17.27, J_{BX} 10.35, $J_{AB} < 1$ Hz), 4.35 (2H, t), 3.03 (2H, t); δ_C (500 MHz, $CDCl_3$, Me_4Si) 165.8, 131.5, 127.9, 125.6, 124.3, 119.0, 118.9, 113.4, 109.0, 62.8 and 34.0.

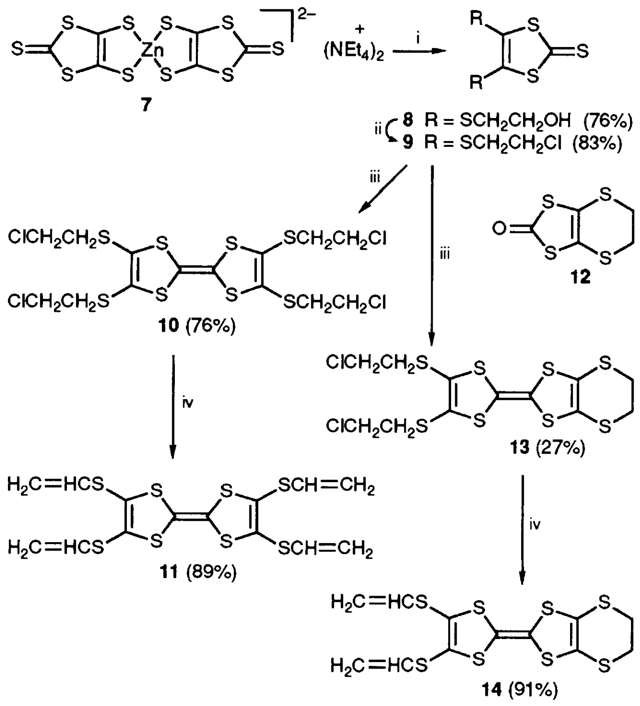
For **6**: *m/z* (DCI) 349 ($M^+ + 1$); δ_H (250 MHz, $CDCl_3$, Me_4Si) 6.44 (1H, s), 6.32 (2H, s), 6.12 and 5.56 (each 1H, AB, $J_{AB} < 1$ Hz), 4.33 (2H, t), 3.02 (2H, t), 1.93 (3H, s); δ_C (500 MHz, $CDCl_3$, Me_4Si) 167.0, 135.8, 126.3, 124.8, 124.3, 119.0, 118.9, 113.4, 109.1, 63.0, 34.0 and 18.2.

For **11**: *m/z* (DCI) 437 ($M^+ + 1$); δ_H (250 MHz, $CDCl_3$, Me_4Si) 6.38, 5.44 and 5.43 (12H, ABX, J_{AX} 16.45, J_{BX} 9.42, $J_{AB} < 1$ Hz); δ_C (500 MHz, $CDCl_3$, Me_4Si) 129.2, 126.0, 117.4 and 111.4.

For **14**: *m/z* (DCI) 411 ($M^+ + 1$); δ_H (250 MHz, $CDCl_3$, Me_4Si) 6.37, 5.43 and 5.42 (6H, ABX, J_{AX} 16.47, J_{BX} 9.45, $J_{AB} < 1$ Hz) and 3.30 (4H, s); δ_C (500 MHz, $CDCl_3$, Me_4Si) 133.1, 129.2, 117.3, 113.9, 113.2, 110.2 and 30.2.



Scheme 1 *Reagents and conditions*: i, (*a*) lithium diisopropylamide (1 equiv.), diethyl ether, −78 °C, 0.5 h; (*b*) elemental sulphur, −78 °C, 8 h; (*c*) $BrCH_2CH_2OH$, −78 → 20 °C, 14 h; ii, $MeSO_2Cl$, Et_3N, dioxane, 20 °C, 2 h; iii, NaOEt, EtOH, 20 °C, 10 h; iv, $CH_2{=}CHC(O)Cl$, Et_3N, dioxane, 20 °C, 2 h; v, $CH_2{=}C(Me)C(O)Cl$, Et_3N, dioxane, 20 °C, 2 h



Scheme 2 *Reagents and conditions*: i, $BrCH_2CH_2OH$, acetone, reflux, 10 h; ii, $SOCl_2$, CH_2Cl_2, 0 °C, 0.5 h, then reflux 1 h; iii, $(EtO)_3P$, 100 °C, 4 h; iv, NaOEt, EtOH, 20 °C, 10 h

derivative **8** which was converted into the dichloride **9**. Self-coupling of **9** proceeded cleanly in the presence of neat triethylphosphite under standard conditions,[3] to afford the tetrafunctionalised TTF system **10**, from which base-induced, fourfold elimination of HCl gave the desired tetra(vinylthio) derivative **11**† (40% overall yield from zincate salt **7**). Di(vinylthio) derivative **14**† was prepared analogously from compound **13**, which was obtained by cross-coupling reaction of thione **9** and ketone **12**.[4] (Self-coupled products in this reaction were separated by column chromatography.)

The synthetic potential of TTF-alcohol **2** was further demonstrated in the efficient formation of acrylate and methacrylate derivatives, **5**† and **6**†, by reaction with acryloyl chloride and methacryloyl chloride, respectively, under basic conditions.

The new vinylthio- and acrylate-substituted TTF derivatives **4**–**6**, **11** and **14** are all air-stable oils which partially crystallise on storage at 0 °C. Their electrochemical redox properties have been studied by cyclic voltammetry and these data are collated in Table 1. Compounds **4**–**6**, **11** and **14** display two, single-electron, redox waves typical of the TTF system. Both waves are reversible for compounds **5**, **6** and **11** [*e.g.* Fig. 1(*a*) for compound **11**] but compound **4** is anomalous in that while the first oxidation wave is reversible, the second oxidation (*i.e.* radical cation → dication) is irreversible on scanning above +1.2 V [Fig. 1(*b*)]. It would, therefore, seem that oxidation involving the vinylthio group of compound **4** occurs at higher potentials, as was suggested previously for the unstable vinyl-TTF.[11] Studies on the polymerisation of these new donors will be reported separately.

Table 1 Cyclic voltammetric data[a]

Donor	$E_1^{\frac{1}{2}}$/V	$E_2^{\frac{1}{2}}$/V
TTF **1**	0.34	0.78
BEDT-TTF	0.59	0.99
4	0.45	0.92
5	0.43	0.83
6	0.43	0.89
11	0.59	0.92
14	0.54	0.91

[a] *Experimental conditions*: donor (*ca.* 1×10^{-5} mol dm^{-3}), electrolyte $Bu_4N^+PF_6^-$ (*ca.* 1×10^{-1} mol dm^{-3}) in dry CH_2Cl_2 under argon, 20 °C, *vs.* Ag/AgCl, Pt electrode, scan rate 100 mV s^{-1} using a BAS 100 Electrochemical Analyser.

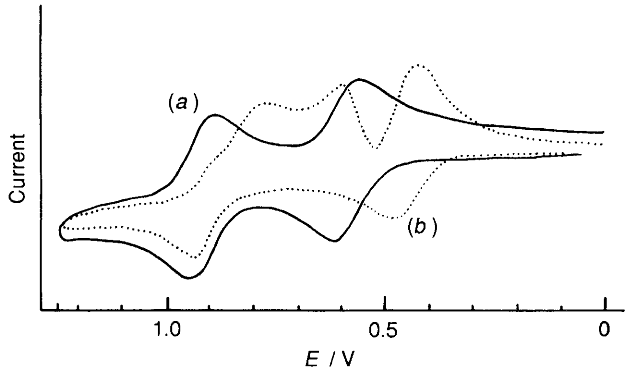


Fig. 1 Cyclic voltammograms of (*a*) donor **11** and (*b*) donor **4**

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