New vinylogous tetrathiafulvalene π-electron donors with lower oxidation potentials

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The efficient synthesis of three new vinylogous TTF and three new 1,3-dithiole-2-thione derivatives is described; cyclic voltammetry establishes that the new donors have significantly lower solution oxidation potentials than BEDT–TTF.

Among the organic donors, much work has been done on the tetrathiafulvalenes (TTF) **1** in the race for new organic conductors and/or superconductors.[1] Modification of the basic TTF framework leading to new functionalized π-donors has been intensively studied,[2] notably, bis(ethylenedithiol)tetrathiafulvalene (BEDT–TTF) **2** has produced organic superconductors with T_c values as high as 12.8 K.[3] The synthesis of new π-donors related to TTF is central to the understanding of the solid-state properties of this fascinating class of materials. In particular, derivatives with lower oxidation potentials than the parent compounds TTF and BEDT–TTF are prime targets, an interesting type of such derivatives involves insertion of a conjugated spacer between two 1,3-dithiole rings, *i.e.* the so-called vinylogous TTF **3**.[4] The synthesis of such extended TTFs reported in the literature is mainly based on the Wittig–Horner reaction of a (1,3-dithiol-2-yl)phosphonium salt with an appropriate aldehyde.[4] Herein we report an alternative route to the new vinylogous **7** as well as new 1,3-dithiole-2-thiones **8** *via* base catalysed ring opening of 4-(1,4-dithiafulven-6-yl)-1,2,3-thiadiazole; this route seems to have been overlooked as an entry into the preparation of such vinylogous derivatives.[5]

The synthesis of the new donors is outlined in Scheme 1. The key starting material, 4-formyl-1,2,3-thiadiazole **4**, was prepared by the Hurd–Mori reaction,[6] while the (1,3-dithiol-2-yl)phosphonium salts **5** were synthesized by a well-established four-step reaction[7] from the corresponding readily available 1,3-dithiole-2-thiones.[8]

Equimolar amounts of **4** and **5** were condensed in dry acetonitrile in the presence of triethylamine at room temperature under nitrogen, which afforded **6** in 80–85% yield. Treatment of **6** with base (NaH 80% mineral dispersion) in neat acetonitrile at ambient temperature under nitrogen gave the corresponding novel vinylogous TTF derivatives **7a**–**c** in 40–70% yield after purification (route A).† However, when carbon disulfide was added, the NaH catalysed ring opening of **6** afforded new 1,3-dithiole-2-thione **8** in 70–85% yield (route B).‡ Compounds **8** are important synthetic building blocks for the construction of new types of (1,4-dithiafulven-6-yl)-substituted TTF derivatives. The target molecules **7a** and **7b** are very insoluble in

organic solvents, nevertheless, the solubility of **7** can be improved by changing the R group, and indeed, **7c** (R = SMe) is very soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, THF, MeCN. Molecular ion peaks of all new donors could not be obtained using EI, CI or FAB mass spectra, however, the field desorption mass spectra of **7** were successfully recorded.

The mechanism of the base catalysed ring opening of 4-substituted 1,2,3-thiadiazole is briefly outlined in Scheme 2.[9]

Base catalysed decomposition of **6** afforded alkyne **I** and subsequently **II**. It is proposed that 1,3-addition of **I** to the thioketene **II** affords **7**,[9a] however, when CS_2 is added, 1,3-addition of **I** to CS_2 affords **8** in a similar manner.

The electrochemical properties of **7** were investigated by cyclic voltammetry. All new vinylogous derivatives **7a**–**c**
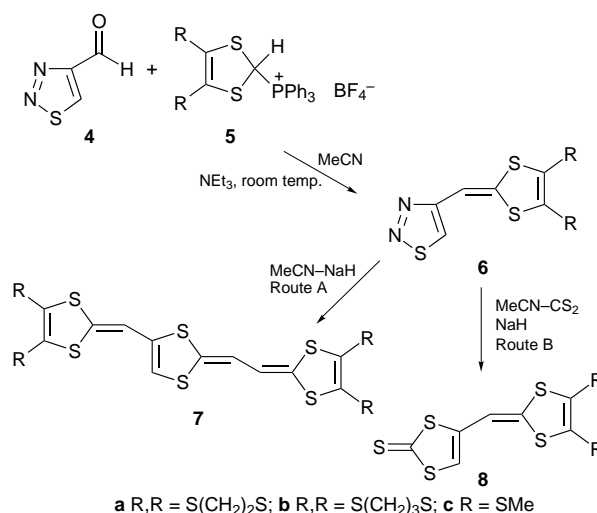
Scheme 1 Synthesis of novel vinylogous TTF and 1,3-dithiole-2-thione derivatives

TTF **1**

BEDT–TTF **2**

Vinylogous TTFs **3**

a R,R = S(CH₂)₂S
b R,R = S(CH₂)₃S
c R = SMe
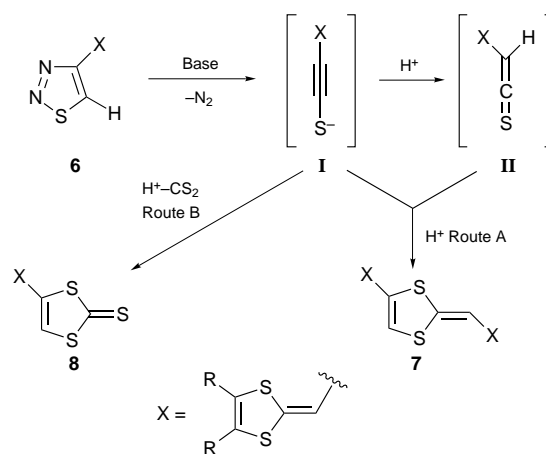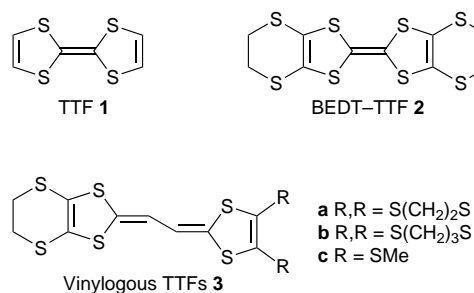
Scheme 2 Mechanism for the formation of **7** and **8**

undergo two reversible, single-electron oxidations, *e.g.* Fig. 1 shows the cyclic voltammogram of compound **7b** recorded at 50 mV s^{-1}. Very similar results were obtained for the other donors. In order to compare the $E_1^{1/2}$ and $E_2^{1/2}$ values of **7** with those of the related vinylogous **3**, we have also synthesized the known donors **3a–c** according to the method described in the literature.[4] Table 1 shows the redox potentials of **7** along with TTF **1**, BEDT–TTF **2** and **3**.

From Table 1, two important consequences of enlarging the conjugated π-system are observed: (i), both the first and second oxidation potentials of **7** are lower in comparison with **1**, **2** and **3**, obviously demonstrating that **7** is a more efficient electron donor than BEDT–TTF as expected from the calculated ionization potentials, and (ii) the difference between the two redox waves $\Delta E^{1/2}$ is reduced in the vinylogues derivatives, evidence of reduced intramolecular Coulombic repulsion in the dication state, suggesting that there is scope for obtaining molecular conductors or magnets based upon entirely new π-electron donors.

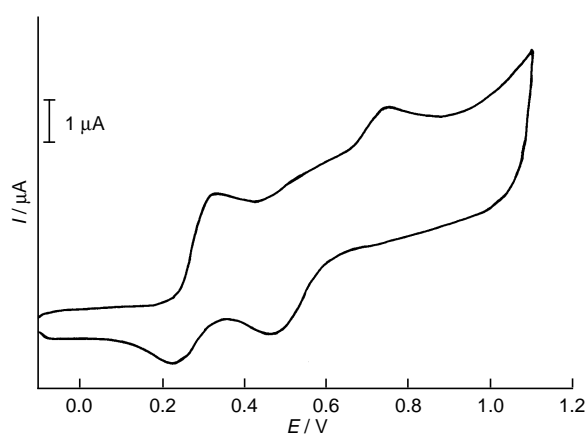As expected from these results, all new donors **7** behave as good precursors for organic metals, and thus further experiments are underway to prepare charge transfer complexes based on the novel donors.

Footnotes

† New compounds **7a–c** have been characterized and presented satisfactory spectra data. *Selected data* for **7a**: yellow solid (yield 40% after purified by chromatography through a short column of silica gel using carbon disulfide as eluent); mp > 270 °C; ^{1}H NMR (200 MHz, CS$_2$–CDCl$_3$, Me$_4$Si) δ_H: 3.12–3.30 (m, 8 H, SCH$_2$), 5.80–6.80 (m, 4 H, alkenyl hydrogens); ν_{max} (KBr)/cm^{-1} 2920(CH$_2$), 1642, 1528, 1505 (C=C); MS (FD) 524.1 (M$^+$); λ_{max}(CH$_2$Cl$_2$) 404 nm (ε = 4.3 × 10^4). For **7b**: Orange microcrystals (yield 72% after recrystallization from CS$_2$–CHCl$_3$); mp 218–220 °C; ^{1}H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ_H: 2.40 (m, 4 H, CH$_2$), 2.65 (m, 8 H, SCH$_2$), 5.64–5.90 (m, 4 H, CH); ν_{max} (KBr)/cm^{-1} 2908 (CH$_2$), 1493 (C=C); MS(FD) 552 (M$^+$); λ_{max}(CH$_2$Cl$_2$) 410 nm (ε = 5.4 × 10^4). For **7c**: (yield 70% after recrystallization from dichloromethane–light petroleum (30–60 °C); mp 46–48 °C; ^{1}H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ_H: 2.41 (s, 12 H, SCH$_3$), 5.74–6.01 (m, 4 H, CH); ν_{max}(KBr)/cm^{-1} 2916 (CH$_2$), 1490, 1425 (C=C), 1022 (C–S); MS (FD) 528 (M$^+$); λ_{max}(CH$_2$Cl$_2$) 412 nm (ε = 4.9 × 10^4).

‡ *Selected data* for **8a**: red plates (yield 83% after recrystallization from chloroform–hexane), mp 190 °C; ^{1}H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ_H: 3.36 (s, 4 H, SCH$_2$), 6.26 (s, 1 H, CH), 6.39 (s, 1 H, CH); MS (EI) 338 (M$^+$, 100%), 310 (M$^+$ −28, 20.3%), 262 (M$^+$ −76, 25.6%), 234 (M$^+$ −104, 43.2%). For **8b**: yellow needles (yield 80% after recrystallization from chloroform–light petroleum (60–90 °C); mp 184–186 °C; ^{1}H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ_H: 2.41 (m, 2 H, CH$_2$), 2.72 (m, 4 H, SCH$_2$), 6.16 (s, 1 H, CH), 6.58 (s, 1 H, CH); MS (EI) 352 (M$^+$, 100%), 276 (M$^+$ −76, 24.5%), 244 (M$^+$ −108, 9.3%), 229 (M$^+$ −123, 15.4%). For **8c**: slightly oily crystals [yield 70% after chromatography on silica gel GF254 with CH$_2$Cl$_2$–light petroleum (30–60 °C) (1 : 1) as eluent]; ^{1}H NMR (200 MHz, CDCl$_3$, Me$_4$Si) δ_H: 2.43 (s, 6 H, SCH$_3$), 6.22 (s, 1 H, CH), 6.80 (s, 1 H, CH); MS (EI) 340 (M$^+$, 100%), 246 (M$^+$ −94, 40.7%).

Fig. 1 Cyclic voltammogram of **7b** range from 0.0 to 1.2 V

Table 1 Cyclic voltammetric data for donors **1**, **2**, **3** and **7**[a]

Compound	$E_1^{1/2}$/V	$E_2^{1/2}$/V	$\Delta E^{1/2}$/V
1	0.36	0.80	0.44
2	0.46	0.96	0.50
3a	0.42	0.77	0.35
3b	0.49	0.71	0.22
3c	0.45	0.72	0.27
7a	0.41	0.62	0.21
7b	0.29	0.60	0.31
7c	0.30	0.61	0.31

[a] Experimental conditions: donors (*ca.* 1.0 × 10^{-4} mol dm^{-3}), supporting electrolyte Et$_4$N$^+$ClO4$^-$ (*ca.* 1.0 × 10^{-1} mol dm^{-3}) in dry dichloromethane, indicating electrode Pt, reference electrode SCE, scan rate 50 mV s^{-1} using EG & G Parc Model 175 electrochemical analythesis meter.

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