The development of an electropolymerisable unit for TTF-thiophene fused monomers

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A novel poly(terthiophene) species provides the first example of an annelated TTF-thiophene derivative which can be polymerised electrochemically.

In general, the electropolymerisation of a conducting polymer is of particular interest for the following reasons: (i) the process is relatively cheap and can be performed on a small scale; (ii) the 'clean' reaction proceeds in the absence of a catalyst or other chemical reagents; (iii) the electrochemistry of the polymer can be investigated almost immediately and (iv) the electronic bandgap of the polymer can be measured by cyclic voltammetry and is usually comparable to the optical bandgap measured by UV–VIS spectroscopy.

Although we have recently prepared polymer **1** using chemical coupling methods,[1] the electropolymerisation of thiophene units bearing fused **2**[2] or covalently attached[2,3] TTFs
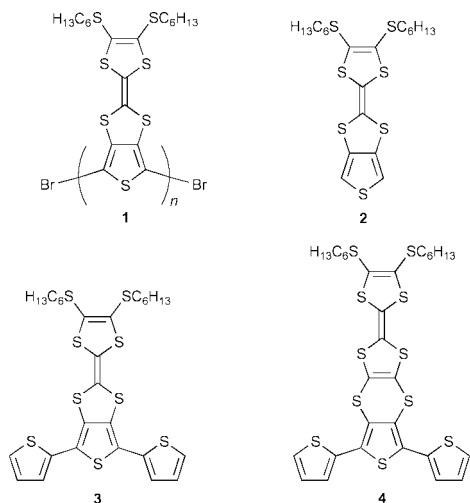
has so far eluded the field. The consensus of opinion points towards the fulvalene acting as a radical scavenger which, together with some degree of intramolecular coulombic repulsion between charged oxidised intermediates, renders the thiophene moiety inert to oxidative coupling reactions. The electrosynthesis of polythiophenes, linked to TTF units *via* saturated spacer groups, has been well established by the group of Roncali,[4] yet the successful electropolymerisation of conjugated TTF-thiophene monomers remains a challenge. In response to this, we have prepared compounds **3** and **4**, which are terthiophene analogues of **2**. The propensity towards electropolymerisation for these derivatives should be improved by the increased donor ability of the thiophene functionality (the oxidation potential of oligothiophenes decreases with an extension of the chain length).

The target compounds were prepared using standard phosphite-mediated cross-coupling reactions of 1,3-dithiole-2-chalcogenones (Scheme 1).[5] Thus, terthiophenes **5**[6] and **6**[7] were

† New address: Department of Chemistry, University of Manchester.
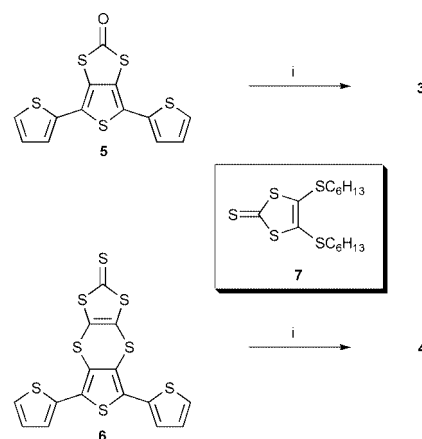
Scheme 1 *Reagents and conditions*: i, P(OEt)$_3$, **7**, 120 °C, 6 h.

reacted with dithiole **7**[8] in the presence of triethyl phosphite at 120 °C, to afford compounds **3** and **4** (30–40% yield in both cases).‡

The electrochemical behaviour of compounds **2**–**4** is summarised in Table 1.§ All three compounds show two sequential reversible oxidation waves corresponding to the formation of the TTF radical cation and dication, respectively. It is noteworthy that the oxidation values for the two terthiophene derivatives are almost identical, thereby indicating that any inductive effect due to the 1,4-dithiin ring is negligible. However, each oxidation of the TTF moiety in **2** is shifted to a more positive value by *ca.* 100 mV, compared to derivatives **3** and **4**. The electronic effect of the fused thiophene ring upon the TTF unit can be explained by a σ electron-withdrawing effect in **2**, which is reduced by a counter-active π-resonance effect of the two peripheral thiophene rings in **3** and **4**.

The high value for the irreversible oxidation of the thiophene ring in **2** (E_3 = +2.18 V)[9] is unfavourable for electropolymerisation, however, the corresponding oxidation processes for compounds **3** and **4** are reduced to +1.55 and +1.52 V, respectively. These values are relatively high for terthiophene derivatives in general and are probably due to an electron withdrawing effect of the TTF dication. For electropolymerisation experiments, repetitive scanning over the range 0.0 to +1.6 V was performed, using a Ag/AgCl reference electrode and a gold disk working electrode in a dichloromethane–hexane (2:1) solution containing tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. As we have observed previously,[9] monomer **2** failed to polymerise; however, we were quite surprised to discover different electrochemical reactivities

Table 1 Cyclic voltammetric data for compounds **2**–**4**

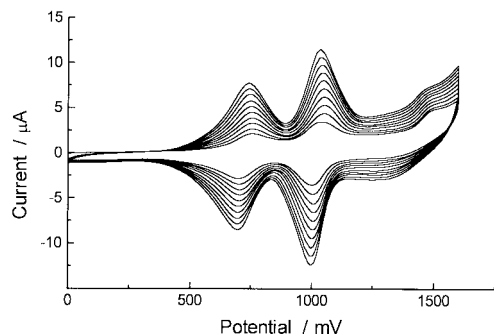| Compound	$E_1^{\frac{1}{2}}$/V	$E_2^{\frac{1}{2}}$/V	E_3/V[a]
2	+0.74	+1.10	+2.18
3	+0.64	+1.02	+1.55
4	+0.64	+0.99	+1.52

[a] Irreversible peaks.

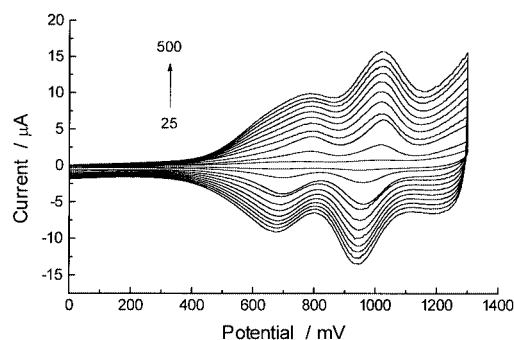**Fig. 1** Electropolymerisation of **4** in dichloromethane–hexane (2:1).

Fig. 2 Cyclic voltammograms of poly(**4**) in monomer-free acetonitrile solution at scan rates of 25, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV s^{-1}.

Fig. 3 Electronic absorption spectra of compound **4** in dichloromethane (-----), oxidised poly(**4**) on ITO glass (······) and neutral poly(**4**) on ITO glass (——).

for compounds **3** and **4**, despite the close similarity in redox potentials. Although, in the case of **3**, we observed the formation of a red film on the surface of the electrode, cyclic voltammetry clearly showed that this was not of polymeric nature. Conversely, reproducible films of poly(**4**) were obtained under identical conditions; a typical trace showing polymer growth over 10 cycles can be seen in Fig. 1. The proportionally higher increase in current between scans for $E_2^{\frac{1}{2}}$, compared to the first oxidation wave, has been seen previously in poly(bithiophenes) linked to TTF units *via* saturated spacer groups.[4c] This type of behaviour shows that the second oxidation of the TTF species develops independently of charge-transport through the film, which is not the case for $E_1^{\frac{1}{2}}$.

Fig. 2 features cyclic voltammograms of poly(**4**) at various scan rates (25–500 mV s^{-1}) in monomer-free acetonitrile solution. The relationship between the maximum peak current and the scan rate (100–500 mV s^{-1}) is linear with a high correlation coefficient ($r > 0.996$). This behaviour is typical of an electroactive polymer attached to an electrode surface and exemplifies the stability of poly(**4**) towards p-doping up to +1.3 V. At higher potentials the CV behaviour becomes ambiguous. Although the polymer does not appear to decompose or break down in the range −1.5 to +2.0 V, the CVs obtained within these limits are poorly defined and irreproducible.

Poly(**4**) was prepared on ITO glass and the electronic spectrum of the film was recorded. Two broad peaks are observed at $\lambda_{max} = 459$ and 833 nm (λ_{max} for compound **4** in dichloromethane is at 344 nm, Fig. 3). The latter peak indicates that the as-grown polymer remains in the oxidised state, however, since doped polythiophene and TTF$^{\bullet+}$ species absorb in this region, the identity of the oxidised species is uncertain. Rinsing the polymer film thoroughly with hydrazine had no effect on the electronic spectrum of poly(**4**), showing that the polymer is quite stable in the doped state. However, after repetitive cycling of the polymer film over the range −0.3 to 0.0 V for 2 h, we were able to obtain the electronic spectrum of the neutral polymer (Fig. 3). A broad band is observed ($\lambda_{max} = 449$ nm),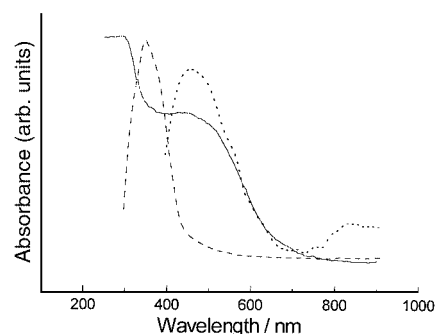 extending to *ca.* 736 nm, which is typical behaviour for a polythiophene system. The absence of a second peak above 800 nm confirms the neutral state of poly(**4**) and the optical bandgap of the neutral polymer (1.69 eV) was found to be somewhat higher than the bandgap determined electrochemically (1.39 V).

In summary, we have presented a logical strategy towards the design of a polymerisable fused TTF-thiophene derivative. Beginning with a monomer unit **2** which has been acknowledged as being *a priori* for the formation of a regiospecific TTF-thiophene polymer,[10] we have highlighted the problems which arise from unfavourable interactions between the two redox units towards electropolymerisation. On one hand, the use of a terthiophene building-block is essential for a low oxidation value of the polymerisable moiety. Secondly, since **3** cannot be polymerised electrochemically, the incorporation of a fused 1,4-dithiin bridging unit in **4** presumably ensures a favourable spin density distribution in the radical trication for polymerisation to take place. We conclude that, in order to understand the nature of poly(**4**) at higher and lower potentials, a detailed spectroelectrochemical investigation would be extremely worthwhile.

Notes and references

‡ Satisfactory elemental analysis, mass spectra and ^{1}H NMR spectra were obtained for all new compounds.
§ Data were obtained in dichloromethane *vs.* Ag/AgCl reference electrode, Au working electrode, Pt counter electrode at 20 °C using 0.1 M NBu$^n_4$PF$_6$ supporting electrolyte, 10^{-3} M substrate and 100 mV s^{-1} scan rate with *iR* compensation.

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4 For example, see: (*a*) C. Thobie-Gautier, A. Gorgues, M. Jubault and J. Roncali, *Macromolecules*, 1993, **26**, 4094; (*b*) L. Huchet, S. Akoudad, E. Levillain, J. Roncali, A. Emge and P. Bäuerle, *J. Phys. Chem. B*, 1998, **102**, 7776; (*c*) L. Huchet, S. Akoudad and J. Roncali, *Adv. Mater.*, 1998, **10**, 541; (*d*) J. Roncali, *J. Mater. Chem.*, 1999, **9**, 1875.
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6 The synthesis of compound **5** directly from the trithiocarbonate derivative and mercury(II) acetate is inefficient (20% yield); an improved method for the preparation of **5** will be reported elsewhere.
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