Electrochromic properties of a poly(dithienylfuran) derivative featuring a redox-active dithiin unit†


A teraryl monomer containing a 1,4-dithiin-furan central unit has been synthesised and characterised by single crystal X-ray crystallography. The di(thienyl)furan monomer 11 was successfully polymerised electrochemically and shown to possess a lower electrochemical band gap than its terthiophene analogue (1.97 eV cf. 2.11 eV). The electrochromic properties of this polymer proved to be superior to PEDOT, with fast switching and reversible colour transformation at high colour contrast (CE = 212 cm² C⁻¹ cf. 183 cm² C⁻¹ for PEDOT at 95% optical switch).

Introduction

Over the past four decades, organic macromolecules with extended π-conjugation have been employed in many applications such as optical displays, solar cells, organic field-effect transistors, batteries and sensors. Organic electrochromic materials offer key advantages over existing inorganic materials, namely high colouration efficiency, enhanced stability, faster response times, flexibility, a wider colour range and wide absorption characteristics from UV to near IR. Electrochromic materials have the ability to undergo a reversible visible switch upon electrochemical doping. During a redox process, the applied potential breaks and rearranges π-bonds within the material, causing a change in the electronic structure of the molecule, which in turn affects the absorption characteristics of the polymer. These smart materials have the potential to be employed in many applications, such as anti-glare mirrors in cars, smart windows, adaptive camouflage, near-IR telecommunications and displays.

Electrochromic devices can be fabricated from a range of materials, but conjugated polymers excel in the properties outlined above. These simple organic molecules can provide exceptional materials for the fabrication of full-colour electrochromic devices using various processes. The optical and physical properties of organic materials can be fine-tuned through structural modification, such as, the introduction of various substituents; alkyl-chain side groups aid solubility, whilst the presence of electron-withdrawing or donating groups can alter the band gap. Polyheterocyclic polymers such as poly(pyrrrole), polypyridine, polyselenophene and their derivatives have been extensively studied since they possess chemical and electrical stability in both neutral and doped states. The electrical and optical properties of these polymers are highly influenced by the change in electronegativity of the heteroatom.

Polyfurans have not been intensively investigated as an electrochromic material, despite possessing many similar characteristics to thiophene. These furan derivatives are naturally occurring materials and are readily biodegradable. Unfortunately, furans are known to have a high oxidation potential (ca. 2 V), but with band gap engineering via the introduction of electron-rich systems or extension of conjugation, this problem can be overcome.

Bendikov et al. have shown oligofurans to have increased fluorescence, a higher HOMO, better packing, greater rigidity and efficient processability compared to their thiophene analogues. These oligofurans can be used as p-type semiconductors in OFETs, showing similar field effect mobilities to the thiophene analogue, leading to the development of new ‘green’ organic semiconductors. Fréchet et al. have been pursuing this idea and recently revealed a bulk heterojunction solar cell fabricated from furan-containing polymers and PC71BM with a power conversion efficiency of 5%. The incorporation of furan units into a conjugated backbone has been shown to enhance the solubility of mixed thiophene–furan oligomers compared to the all-thiophene analogues. Additionally, the morphological properties of the polymer would differ due to the presence of the smaller, more electronegative oxygen atom in place of the larger sulfur atom.
Recently, we reported two polymers, Polyl and Polyl, which were structurally designed as electrochromic materials (see Fig. 1). Polyl bears a quinoline heterocycle fused to the central thiophene ring of the repeat unit via a 1,4-dithiin bridge. This polymer was found to have superior switching speeds than poly(3,4-ethylenedioxythiophene) (PEDOT) (ΔΤ 44% optical change in 1 s, cf. 2.2 s for PEDOT). The fast switching response of Polyl is a result of the non-planar nature of the repeat units, facilitated by the boat conformation of the non-aromatic dithiin rings. This suggests that the loosely packed polymer allows efficient ingress/egression of ions throughout the film during chemical redox processes and hence improves switching speeds. It is anticipated that the marriage of furan and a dithiin ring within a conjugated polymer would provide interesting chemical and physical properties compared to the all-thiophene analogue. This report describes a general synthetic route to three novel furan monomer units, 7, 8 and 11, together with the successful electropolymerisation of monomer 11 to form Polyl. This polymer is studied further as an electrochromic material.

Results and discussion

Synthesis

Monomers 7, 8 and 11 were prepared according to Scheme 1. Initially, cycloaddition of alkene 1 with 1,3-dithiole-2,4,5-trithione oligomer (DMIT) 2, using a literature-based method, was followed by reduction of the resulting aldehyde 3 to give alcohol 4. The acid-catalysed cyclisation of the alcohol 4 gave the furan derivative 5 in an 87% yield. Thione 5 was further transchalconogated into the corresponding carbonyl derivative 6 in high yield, which was subsequently converted to the dithiolate and alkylated to give bis(ethylthio)dithiino furan 7 or bis(hexylthio)dithiino furan 8. Compound 7 was further functionalised by bromination with N-bromosuccinimide and subsequently used for Stille cross-coupling with stannylated thiophene to form Polyl in 22% yield.

Absorption spectroscopy and electrochemistry of monomers

The electronic absorption spectra for the three monomers were recorded in dichloromethane solution (see Table 1). As expected, the absorption maxima for monomers 7 and 8 are similar given their near identical structures (268 and 267 nm, respectively). However, as anticipated the increase in conjugation length to a teraryl unit in monomer 11 leads to a π−π* transition at 342 nm.

In cyclic voltammery (CV) experiments, the structurally similar monomers 7 and 8 showed one quasi-reversible, anodic oxidation peak at +0.91 and +0.98 V, respectively (see Fig. 2 and Table 1). The CV of di(thienyl)furan monomer 11 revealed two anodic oxidation processes at +0.76 and +1.11 V with the latter being irreversible. The electrochemical HOMO–LUMO gaps of the monomers were calculated from the difference in the onset of the first oxidation and reduction peaks. The increase in the electrochemical HOMO–LUMO gap of monomer 11 is unexpected in comparison to monomer 7 and 8 (2.98 V compared to 2.42 V and 2.37 V respectively). All three monomers retain similar HOMO levels whilst monomer 11 shows the LUMO level to have moved towards vacuum. This rise in LUMO of monomer 11 can be rationalised by the inductive effect of the thiophene ring pushing electron density towards the central furan core and thus making monomer 11 a poor electron acceptor. The spectral and electrochemical properties of all three monomers clearly reveal significant differences when comparing their optical and electrochemical HOMO–LUMO gaps. It can be hypothesised that the 1,4-dithiin side group shows some reductive electroactivity that is independent from the heterocyclic core.

Electropolymerisation

Electrochemical oxidative polymerisation of monomers 7 and 8 was unsuccessful despite continuously cycling over both redox peaks and this is explained later. However, monomer 11 polymerised readily onto a carbon-working electrode during repetitive cycling over the first oxidation peak. The growth trace is displayed in Fig. 3. Once Polyl was deposited on the carbon-working electrode, it was dedoped to neutral by repetitive cycling in a region of no electroactivity (−0.4 to +0.1 V), before its electrochemistry was investigated in monomer-free acetonitrile solution (see Fig. 4). When a polymeric species is formed the conjugation length is increased, giving rise to a new lower
oxidation peak. The oxidation of Poly3 exhibits a large broad reversible wave at +0.63 V, compared to the all-thiophene analogues Poly1 at +0.40 V and Poly2 at +0.60 V. This broad redox wave could be due to the simultaneous oxidation of the 1,4-dithiin and bithiophene units, which are both electroactive. UV-Vis absorption of Poly3 revealed a significant bathochromic shift compared to monomer 11 (474 nm for Poly3 cf. 342 nm for monomer 11, see Fig. 4), a result of the increased effective conjugation length. The onset of the absorption edge for the longest wavelength band is at 650 nm, giving an optical band gap of 1.90 eV. This value corresponds closely to the electrochemical band gap of Poly3 obtained by cyclic voltammetry (1.97 eV, see Table 2).

Interestingly, we have shown the furan-based Poly3 to have both a lower electrochemical and optical band gap when compared to its thiophene analogue Poly2 (see Table 2). Recent reports by Bunz have demonstrated bithiophene rings to twist by 22.6° with respect to one another, whilst bifuran monomers were found to be planar. Their study pointed to steric hindrance between the larger sulfur atom and the 30-hydrogen of the adjacent ring, which was not evident in bifuran due to the smaller oxygen atoms. Additionally, the difference in electronegativity and less aromatic character of the furan ring cf. thiophene contributes to the narrower band gap of Poly3.

X-ray crystallography

The structure of monomer 11 was determined by single crystal X-ray diffraction. In general, dithiin rings are known to adopt a boat conformation, with the degree of bending in the ring expressed as a folding along the S...S vector (see Fig. 5); the hinge angle along the S...S vector is 137° and 133° for the two independent molecules. Monomer 11 retains a high degree of planarity between the adjacent thiophene units bound to the furan core. Two molecular conformers are present within the unit cell – one conformer shows both peripheral thiophene units to be anti to the furan (torsion angles O1–C1–C9–S2 169(2), O1–C4–C5–S1 176(2)), forming close S...S intramolecular contacts with the 1,4-dithiin ring on the furan (S2...S4 3.43, S1...S3 3.33 Å). The other conformer within the unit cell exists with one peripheral thiophene unit in the anti conformation with respect to the furan (O1a–C4a–C5a–S11a = −176(2)°).

Table 1  HOMO and LUMO values are calculated from the onset of the first peak of the corresponding redox wave and referenced to ferrocene, which has a HOMO of −4.8 eV. Electronic absorption spectra all recorded in CH2Cl2

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$E_{\text{ox1}}^a/E_{\text{red}}^b$ (V)</th>
<th>$E_{\text{ox2}}$ (V)</th>
<th>Ered (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>HOMO − LUMO (eV)</th>
<th>UV-Vis $\lambda_{\text{max}}$ (nm)</th>
<th>Optical gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.55/0.48</td>
<td>0.91</td>
<td>−2.07</td>
<td>−5.34</td>
<td>−2.92</td>
<td>2.68</td>
<td>268</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>0.65/0.57</td>
<td>0.98</td>
<td>−2.08</td>
<td>−5.28</td>
<td>−2.91</td>
<td>2.37</td>
<td>267</td>
<td>—</td>
</tr>
<tr>
<td>11</td>
<td>0.76/0.67</td>
<td>1.11</td>
<td>−2.36</td>
<td>−5.43</td>
<td>−2.45</td>
<td>2.98</td>
<td>342</td>
<td>3.07</td>
</tr>
</tbody>
</table>

$^a$ Anodic peak. $^b$ Cathodic peak. $^c$ Quasi-reversible peak. $^d$ Irreversible peak.

Fig. 2  Cyclic voltammograms: (A) oxidations and (B) reductions of monomers 7, 8, 11 in CH2Cl2 solution (glassy carbon working electrode, silver wire pseudoreference, TBAPF6 as the supporting electrolyte (0.1 M), substrate concentration 10−4 M, scan rate 100 mV s−1). The data was referenced to the Fe/Fc+ redox couple.

Fig. 3  Electrochemical growth of monomer 11 using a glassy carbon working electrode, Ag wire pseudo-reference electrode, platinum counter electrode, TBAPF6 as supporting electrolyte (0.1 M), substrate concentration 10−4 M, oxidative voltage sweep ran from 0 to 1 V over 150 cycles. The scan rate was 100 mV s−1.
S11a–S3a = 3.39 Å) and the other to be either in the anti or cis conformation in a 1:1 ratio (O1a–C1a–C9a–S2a = 173(2), O1a–C1a–C9a–S2a = 7(3), S2a–S4a = 3.35 Å for the anti conformation). There is some sign of disorder between the cis and trans conformation for the other thiophene rings but to a much lesser degree and it was not modelled.

Theoretical calculations

The unsuccessful electropolymerisation of monomers 7 and 8 can be explained via molecular modelling calculations. Computational calculations were performed using density functional theory (DFT) at the B3LYP/6-31G* level (Spartan’10) on monomer 7. The HOMO is situated predominantly over the dithiin ring, with a small contribution on the furan ring (Fig. 6). The 1,4-dithiin ring is a better electron donor than the furan fragment and is most likely to donate the first electron upon oxidation. The LUMO resides across the four sulfur atoms and two sp² carbons between the heteroatoms. Examination of the SOMO (the radical cation of monomer 7) reveals that electron spin density is localised within the dithiin ring. To initiate successful radical polymerisation of monomer 7 the system requires electron spin density on either the 2- or 5-position of the furan ring. Thus, it would appear that successful electropolymerisation of monomer 7 (or 8) does not occur at potentials below that which would cause monomer decomposition (>2 V).

Spectroelectrochemistry

The UV-Vis spectroelectrochemical measurements of the neutral Poly3 film deposited on an ITO glass substrate were investigated in monomer-free acetonitrile solution with the same electrolyte concentration as before (see Fig. 7). Spectroelectrochemical studies improve our understanding of transient chemical species generated in situ during redox reactions occurring at the electrode surface.56,57 The spectroelectrochemical plot shows the generation of new absorption waves forming at +0.9 V in the wavelength region of 600–1100 nm alongside the concomitant loss of intensity of the π–π* band at 474 nm. The optical transition observed at ca. 600 nm is evidence of the formation of positively delocalised polaron species within the polymer chain and, upon further oxidation, a broader optical transition near 900–1100 nm represents the

Table 2  Electrochemical and absorption spectroscopy data for thin films of Poly3 compared to the analogous polymer Poly2 and Poly1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{ox1}$ (V)</th>
<th>$E_{ox2}$ (V)</th>
<th>$E_{red}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
<th>UV-Vis $\lambda_{max}$ (nm)</th>
<th>Optical gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly1</td>
<td>+0.40</td>
<td>1.20</td>
<td>−1.87</td>
<td>—</td>
<td>—</td>
<td>1.85</td>
<td>467</td>
<td>1.90</td>
</tr>
<tr>
<td>Poly2</td>
<td>+0.60</td>
<td>0.83</td>
<td>−1.93</td>
<td>−5.30</td>
<td>−3.19</td>
<td>2.11</td>
<td>450</td>
<td>2.00</td>
</tr>
<tr>
<td>Poly3</td>
<td>+0.63$^{a}$+0.22$^{b}$</td>
<td>0.83</td>
<td>−2.14</td>
<td>−5.02</td>
<td>−3.05</td>
<td>1.97</td>
<td>474</td>
<td>1.90</td>
</tr>
</tbody>
</table>

$^a$ Broad quasi-reversible anodic peak. $^b$ Peak onset.
Propagation of doubly charged bipolaron species. These spinless bipolaron species are thermodynamically stable when structurally manipulating the polymer chain from its aromatic structure and adopting the quinoidal polymer form. The bond length between neighbouring heterocycles is contracted when in the quinoidal form, which allows efficient orbital overlap and charge delocalisation.

Additionally, the 1,4-dithiin pendant groups of the conjugated polymer oxidise at lower potentials as illustrated in cyclic voltammograms for monomers 7, 8, 11 and Poly3 (see Fig. 2 and Fig. 4). However, the oxidised 1,4-dithiin rings are not spectroscopically detected due to the weak sulfur n–π* transitions. Fig. 7 (bottom), illustrates the spectro-electrochemical studies of Poly3 in a 2D plot and clearly shows the formation of polarons and bipolarons upon increasing potentials. At higher oxidation potentials (>1.4 V) the spectral profile differs and shows the formation of a new absorption wave at ca. 400 nm. This signifies the polymer morphology has changed and is possibly due to an over population of the bipolaron species, which increases the polymers electrophilicity and susceptibility to nucleophilic attack by water molecules/OH⁻ ions or other nucleophilic impurities that may be present in the investigating medium. Thus, it would result in non-reversible formation of the polymer with shorter conjugation lengths. To overcome such issues, polymer films can be encapsulated into devices or supported with a gel electrolyte coating. Spectroelectrochemical studies have clearly illustrated Poly3 undergoing reversible redox changes at oxidation potentials lower than 1.4 V with different optical responses from visible to the NIR region.

Switching studies

The switching ability of Poly3 was studied by measuring the wavelength at which the greatest absorbance change is experienced when stimulated between two different potentials. The potential switch from 0 to +1.3 V causes a change in the polymeric state from neutral to p-doped. The rate of change in transmittance upon oxidation/reduction provides a direct indication of the switching ability of a material, an important property for display industries. Poly3 was grown on ITO glass and dedoped. The transmittance was monitored at 705 nm as the potential was switched between 0 and +1.3 V (vs. Ag wire) using...
square wave potentiometry, as shown in Fig. 8. The switching characteristics of the polymer were followed over cycles of 10, 5, 2.5, 1.25, 0.5, 0.25 s and the change in transmittance was 83.9, 79.8, 72.9, 62.4, 39.8 and 23.8%, respectively. One reason for this fast optical change is the bent 1,4-dithin ring conformation, a feature of both Poly2 and Poly3, which distorts the π-π stacking and creates an open morphology, thus allowing the efficient flow of counterions into and out of the polymer film. However, Poly3 shows a faster and greater change compared to the analogous terthiophene Poly2 (see Table 3). The single difference being that Poly3 contains one furan to every two thiophene units. It is not clear why, but the subtle incorporation of an oxygen atom, providing a less aromatic furan ring, improves the switching properties compared to the all thiophene analogue.

**Colorimetry**

The CIE colour coordinates of Poly3 electrochemically deposited on ITO were measured in monomer-free acetonitrile solution with the same electrolyte concentration as previously stated. The analysis is reported via the 1931 (Yxy) CIE and 1964 (L*a*b*) CIE representation of colour space as recommended by the “Commission Internationale de L’Eclairage” (CIE). The measurements recorded were using a 10° standard observer and Source C illuminant (overcast daylight, CIE 1964, 6770 K). Y is defined as the luminance of the CIE XYZ tristimulus values, which are assigned to the red, green and blue curves respectively. The L* coordinates represent the brightness of the material ranging from 0–100. A positive a* value represents the redness; whilst the negative a* value represents the greenness of the sample. Complementary, a positive b* is yellow and a negative b* is blue in colour. The polymer film was subjected to constant applied potential at 0 V then +1.3 V for a duration of 90 seconds to achieve the neutral and doped state, whilst the colour coordinates were measured to determine the colour transformation, see Table 4.

The optical change experienced can be seen by the naked eye. Poly3 shows a reversible transition from salmon-red to a beige tan colour (see inset in Fig. 9), whilst the closely related polymer Poly2 shows an optical change from red to yellow.

**Colouration efficiency (chronocoulometry)**

Colouration efficiency (CE) is a parameter, which characterises the ability of the material to change absorbance upon injecting electric charge during oxidation (or reduction). CE is expressed as: \[ \eta = \frac{\Delta OD(\lambda)}{Q_d} \] (1)

\[ \Delta OD = \log\left(\frac{\%T_b(\lambda)}{\%T_c(\lambda)}\right) \] (2)

The optical density at a specific wavelength (\(\lambda_{\text{max}}\)) was determined by using %T values of bleached (%T_b) and coloured films (%T_c) using eqn (2). The colouration efficiency (\(\eta\)) of the material can be calculated by using eqn (1), where \(\Delta OD(\lambda)\) is the change in optical absorbance, and \(Q_d\) is the charge density which causes \(\Delta OD(\lambda)\).

Chronocoulometry studies were performed on neutral state Poly3, electrochemically deposited onto an ITO slide in monomer-free acetonitrile solution. This film was subjected to a low current through the film, leading to a colour transformation over a 30 second interval. Fig. 9 shows the simultaneous measuring of % change in transmittance of the film, and charge flow during a complete switch. The electrochromic film was monitored at \(\lambda_{\text{max}} = 705\) nm as the voltage was pulsed for a 10 second step between the neutral state (0 V) and the oxidised state (+1.3 V), see Fig. 9.

According to eqn (1) and (2), the CE of Poly3 was calculated to be 212 cm² C⁻¹ at 95% of full switch (\(\lambda_{\text{max}} = 705\) nm), which is higher than that of closely packed PEDOT film (183 cm² C⁻¹),

![Fig. 8](image-url)
Table 4  CIE Yxy 1931 and L*a*b* 1964 colour space for Poly3 in the neutral and doped form using 10' standard observer and Source C illuminant

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly3 neutral</td>
<td>55.45</td>
<td>50.56</td>
<td>45.48</td>
<td>0.3660</td>
<td>0.3338</td>
<td>0.3002</td>
<td>76.41</td>
<td>16.21</td>
<td>13.01</td>
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<tr>
<td>Poly3 doped</td>
<td>55.78</td>
<td>57.50</td>
<td>54.84</td>
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<td>0.3420</td>
<td>0.3262</td>
<td>80.46</td>
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Fig. 9 (A): colouration efficiencies (chronocoulometry) experiments of Poly3 film on ITO, switched from fully neutral (0 V) to fully oxidised state (+1.3 V) and back to neutral state, 3 steps for 10 second pulse and transmittance measured at λ<sub>max</sub> = 705 nm. (B) graph shows various % optical changes from which to calculate CEs. Inset: Adobe Photoshop images to represent Poly3's colour switch, images created by conversion of CIE Lab to CIE XYZ coordinates.

but slightly lower than that of PProDOT (285 cm<sup>2</sup> C<sup>-1</sup>).<sup>67</sup> see Fig. 9 and Table 5. Comparatively, Poly1 (possessing large quinoxaline pendant groups) shows superior CE of 381 cm<sup>2</sup> C<sup>-1</sup> at 95% full switch). The incorporation of a furan unit has improved the electrochromic properties compared to its all-thiophene analogue.<sup>51</sup>

Table 5  Colouration efficiencies determined for Poly3 at various % optical changes of complete colour switch

<table>
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<tr>
<th>∆T&lt;sub&gt;uc&lt;/sub&gt; (%)</th>
<th>% Change</th>
<th>T&lt;sub&gt;uc&lt;/sub&gt; (%)</th>
<th>T&lt;sub&gt;uc&lt;/sub&gt; (%)</th>
<th>τ (s)</th>
<th>Q (C)</th>
<th>Q&lt;sub&gt;uc&lt;/sub&gt; (C cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>∆OD&lt;sub&gt;uc&lt;/sub&gt;</th>
<th>η&lt;sub&gt;uc&lt;/sub&gt; (cm&lt;sup&gt;2&lt;/sup&gt; C&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<tr>
<td>40.91</td>
<td>100</td>
<td>45.51</td>
<td>86.42</td>
<td>5.36</td>
<td>3.02  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>1.34  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.279</td>
<td>207.45</td>
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<tr>
<td>38.86</td>
<td>95</td>
<td>45.51</td>
<td>84.37</td>
<td>3.86</td>
<td>2.84  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>1.26  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.268</td>
<td>212.39</td>
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<tr>
<td>36.82</td>
<td>90</td>
<td>45.51</td>
<td>82.33</td>
<td>3.76</td>
<td>2.74  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>1.12  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.257</td>
<td>211.41</td>
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<td>34.77</td>
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<td>45.51</td>
<td>80.28</td>
<td>3.68</td>
<td>2.66  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>1.18  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
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<td>208.51</td>
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<td>32.73</td>
<td>80</td>
<td>45.51</td>
<td>78.24</td>
<td>3.61</td>
<td>2.60  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>1.16  × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.235</td>
<td>203.64</td>
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Conclusions

Three new furan-based monomers were synthesised and characterised by absorption spectroscopy and cyclic voltammetry. Monomer 11 was successfully electropolymerised to form Poly3 and investigated by UV-Vis spectroelectrochemistry and electrochromic switching studies. Poly3 exhibited a lower electrochemical band gap of 1.97 eV and superior switching speeds than its corresponding terthiophene analogue.<sup>54</sup> This is explained by the lower aromaticity of furan systems over thiophene analogues with Poly3 possessing efficient charge delocalisation across the polymer backbone than the previously published analogues.<sup>38</sup> Poly3 showed a reversible optical transformation from a red salmon colour when neutral, to a beige tan colour in the doped form, with a higher colour contrast than PEDOT<sup>69</sup> (212 cm<sup>2</sup> C<sup>-1</sup> cf. 183 cm<sup>2</sup> C<sup>-1</sup> at 95% full switch). The incorporation of a furan unit has improved the electrochromic properties compared to its all-thiophene analogue.<sup>51</sup>

Experimental

General

<sup>1</sup>H and <sup>1</sup>C NMR spectra were recorded on a Bruker Avance AV3 400 or DRX 500 apparatus at either 500.13 and 125.76 MHz or 400.13 and 100.61 MHz, in CDCl<sub>3</sub>. Chemical shifts are given in ppm; all J values are in Hz. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Electron absorption spectra were measured on a Unicam UV 300 spectrophotometer. MS LDI-TOF spectra were run on a Shimadzu Axima-CFR spectrometer (mass range 1–150 000 Da). IR spectra were measured on a Unicam UV 300 spectrophotometer. Melting points were stated otherwise. Anhydrous solvents were obtained from Anhydrous solvents were obtained from Analytical grade reagents were obtained from Sigma-Aldrich and Alfa Aesar and were used without further purification, unless stated otherwise. Anhydrous solvents were obtained from PureSolv solvent purification system.

1<sup>H</sup> and 1<sup>C</sup> NMR spectra were recorded on a Bruker Avance AV3 400 or DRX 500 apparatus at either 500.13 and 125.76 MHz or 400.13 and 100.61 MHz, in CDCl<sub>3</sub>. Chemical shifts are given in ppm; all J values are in Hz. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer. Electron absorption spectra were measured on a Unicam UV 300 spectrophotometer. MS LDI-TOF spectra were run on a Shimadzu Axima-CFR spectrometer (mass range 1–150 000 Da). IR spectra were recorded on a Perkin-Elmer 2400 analyzer. Electron absorption spectra were measured on a Unicam UV 300 spectrophotometer.
X-ray crystallography

Data for 11 were collected on an Enraf Nonius Kappa CCD using Mo-Kα radiation, as φ scans and ω scans to fill the Ewald sphere. Data collection, cell refinement and data reduction were carried out using COLLECT® and DENZO.® The structure solution was obtained by direct methods (SHELXS-97) and a full-matrix least-squares refinement on $F^2$ was performed on all reflections by SHELXL-97 in the OLEX2 environment.\textsuperscript{71}

Crystal structure determination of monomer 11

Crystal data. C$_{16}$H$_{12}$O$_7$S$_6$, $M$ = 412.61, monoclinic, $a = 22.338(3)$, $b = 4.7901(7)$, $c = 17.757(3)$, $\beta = 113.326(7)$°, $U = 1744.7(4)$ Å$^3$, $T = 120$ K, space group $Pc$ (no. 7), $Z = 4$, 11 738 reflections measured, 5748 unique ($R_{int}$ = 0.142) which were used in all calculations. The final $wR(F)$ was 0.265, $R_1$ was 0.12 for 3919 observed data. The CCDC deposition number is: 879413.

Electrochemistry

CV measurements were performed on a CH Instruments 660A electrochemical workstation with CV measurements were performed on a CH Instruments 660A electrochemistry observed data. The CCDC deposition number is: 879413.

Synthesis

Compounds 5 and 6 were prepared using the procedure of Berridge et al.\textsuperscript{72}

6-(Dimethoxymethyl)-2-thioxo-[1,3]dithiole[4,5-b][1,4] dithiene-5-carbaldehyde (3)

To a solution of 4,4-dimethoxybut-2-ynal (4.30 g, 0.034 mol, 3.50 ml) in 500 ml of dry toluene, oligo trithioxo-1,3-dithiole (DMIT) 2 (6.50 g, 0.50 mol) was added and this mixture was refluxed for 2 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using toluene as eluent to give a red-orange solid (7.64 g, 97%). 1H NMR (400 MHz, CDCl$_3$): $\delta_H$ 3.46 (6H, s, $\text{CHO(CH}_3)_2$), 2.92 (4H, t, $J_{2,4} = 7.4$ Hz, (–CH$_2$CH$_2$)$_2$), 2.46 (6H, s, $\text{S(CH}_3)_2$), 7.26 (2H, s, (Ar-H)); 13C NMR (125 MHz): $\delta_C$ 18.4, 21.9, 27.8, 29.2, 30.8, 34.5, 119.3, 128.7, 134.1, 154.7, 181.7 ppm; MS: $m/z$ GC/CI: 248.9 Da; EA Calc: $C$, (38.68%); $H$, (3.25%); S, (51.63%); EA Found: $C$, (39.06%); H (3.23%); S (51.15%); $\rho_{\text{max}}$ ATR-IR/cm$^{-1}$: 3120, 2922, 1537, 1410, 1032, 873 and 842; Mpt: 67–69 °C.

2,3-Bis(methylothio)-[1,4]dithiino[2,3-c]furan (7)

To a cold (−15 °C) mixture of carbonyl derivative 6 (0.333 g, 1.36 mmol) in THF (20 ml) was added sodium methoxide (25%, 4.37 M, 0.22 ml) dropwise. The mixture was stirred for 30 min whilst under nitrogen. Then iodomethane (0.70 ml, 10.8 mmol) was added dropwise and the mixture allowed to reach room temperature and left to stir overnight. The solvent was removed under reduced pressure, and the residue was dissolved in chloroform, filtered and, after removal of the solvent, the crude product was subjected to column chromatography on silica gel using 20% dichloromethane in hexane as eluent. The product was isolated as a yellow crystalline solid (0.245 g, 46%); 1H NMR (400 MHz, CDCl$_3$): $\delta_H$ 2.46 (6H, s, S(CH$_3$)$_2$), 7.26 (2H, s, (Ar-H)); 13C NMR (125 MHz): $\delta_C$ 18.4, 119.2, 128.8, 137.2 ppm. MS: $m/z$ GC/CI: 324.01 Da; EA Calc: $C$, (39.06%); H, (3.25%); S, (51.15%); $\rho_{\text{max}}$ ATR-IR/cm$^{-1}$: 3120, 2922, 1537, 1410, 1032, 873 and 842; Mpt: 67–69 °C.

2,3-Bis(hexythio)-[1,4]dithiino[2,3-c]furan (8)

To a cold (−15 °C) mixture of carbonyl derivative 6 (0.140 g, 53.4 mmol) in dry THF (30 ml) was added sodium methoxide (25%, 4.37 M, 0.52 ml) dropwise. The mixture was stirred for 30 min whilst under constant flow of nitrogen gas. 1-Bromohexane (0.62 ml, 3.2 mmol) was added drop wise and the mixture was allowed to reach room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was treated with chloroform, filtered and after removal of solvent, the crude product was subjected to column chromatography on silica gel using 1% dichloromethane in hexane as eluent. The product was isolated as a yellow oil (0.167 g, 81%); 1H NMR (400 MHz, CDCl$_3$): $\delta_H$ 0.87 (6H, t, $J = 6.6$ Hz, 2 × CH$_3$), 1.26 (8H, m, –CH$_2$CH$_2$), 1.38 (4H, quintet, $J = 7.4$ Hz –CH$_2$(CH$_3$)$_2$), 1.56 (4H, quartet, $J = 7.4$ Hz, –(–CH$_2$(CH$_3$)$_2$)Me)$_2$, 2.92 (4H, t, $J = 7.3$ Hz, (SCH$_2$(CH$_3$)$_2$)Me)$_2$, 7.25 (2H, s, Ar-H); 13C NMR (100 MHz): $\delta_C$ 13.5, 21.9, 27.8, 29.2, 30.8, 34.5, 119.3, 128.7, 136.6 ppm; MS: $m/z$ HRMS/El: theoretical mass: 388.1023, found mass: 388.1021 Da; $\rho_{\text{max}}$ ATR-IR/cm$^{-1}$: 3114, 2954, 2924, 2853, 1500, 1226, 1125, 1032 and 955.

5,7-Dibromo-2,3-bis(methylthio)-[1,4]dithiino[2,3-c]furan (9)

Compound 7 (0.100 g, 4.00 mmol) was dissolved in dichloromethane (20 ml) and treated with N-bromosuccinimide (0.150 g, 0.841 mmol). This mixture was stirred for 4 h at room temperature then quenched with water (50 ml) and the organic phase was separated. The organic layer was further washed with saturated sodium sulfite solution (50 ml), water (50 ml), before drying

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with MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by passing through a plug of silica gel with 10% dichloromethane/hexane eluent to afford a brown semi solid (0.146 g, 91%). This was used immediately further without further purification; ¹H NMR (400 MHz, CDCl₃): δ 7.24 (6H, s, S(CH₃)₂); ¹³C NMR (125 MHz): δ 18.6, 29.7 (traces of hexane), 117.1, 120.8, 127.5 ppm; MS: m/z GC/EI, monoisotopic peak: 404.01 Da.

2.3-Bis(methylthio)-5,7-di(thiophen-2-yl)-1,4-dithiin(2,3-c)furran (11)

Tetrakis(triphenylphosphine) palladium(0) (0.066 g, 0.21 mmol) was added to a mixture of compound 10 (0.3 mL, 8.9 mmol), dissolved in tetrahydrofuran (20 ml). The reaction mixture was refluxed under N₂ for 24 h. The mixture was then cooled, quenched with water (200 ml) and extracted with dichloromethane (3 × 100 ml). The organic phases were combined and dried over MgSO₄ and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel, using 20% dichloromethane in hexane as eluent, to give a yellow crystalline solid (37 mg, 22%); ¹H NMR (500 MHz, CDCl₃): δ 7.12 (1H, d, J = 3.5 Hz, Ar-H), 7.13 (1H, d, J = 3.5 Hz, Ar-H), 7.36 (2H, dd, J = 5.3 Hz, J = 1.0 Hz, Ar-H), 7.42 (2H, dd, J = 3.8 Hz, J = 1.0 Hz, Ar-H); ¹³C NMR (100 MHz): δ 18.2, 114.8, 123.9, 124.0, 125.2, 128.1, 130.7, 141.3 ppm; MS: m/z LDI: 412.0 Da; m/z ATR-IR/cm⁻¹: 3101, 2915, 1466, 1257, 1080, 1045, 1030 and 989. MS: HRMS/EI: theoretical mass: 411.9212, found mass: 411.9213. Mpt: 97–98 °C.

Acknowledgements

We thank the EPSRC and DSTL for providing a research grant to S.K., Miss Patricia Keating for mass spectrometry and Mrs Denise Gilmour for elemental analysis.

Notes and references

58 H. Münstedt, Polymer, 1986, 6, 899.