

# Synthesis and properties of end-capped sexithiophenes incorporating the ethylene dithiophene unit

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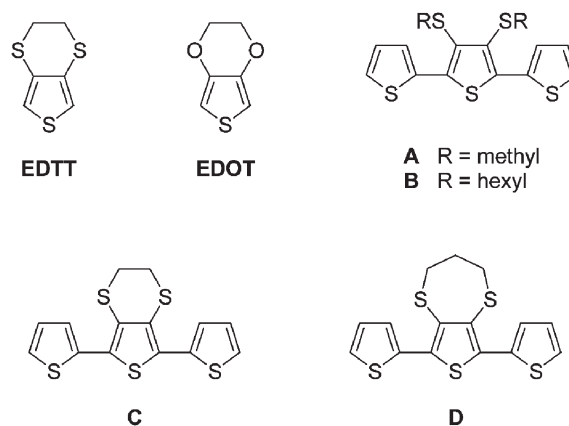
Two new end-capped sexithiophene derivatives (**10a** and **10b**) have been synthesised and characterised by absorption spectroscopy, cyclic voltammetry and UV-vis spectroelectrochemistry. Both oligomers undergo two reversible, sequential oxidation processes (**10a**:  $E_1^{1/2} = +0.61$  V,  $E_2^{1/2} = +0.97$  V; **10b**:  $E_1^{1/2} = +0.70$  V,  $E_2^{1/2} = +0.91$  V vs. Ag/AgCl) and the electronic band gaps of the materials are *ca.* 2.2 eV (solid state). Sexithiophene **10a** has been incorporated as an electron donor material, with C<sub>60</sub> as acceptor, in a bilayer photovoltaic device. The power conversion efficiency is a modest 0.12%, whilst the maximum IPCE at 350 nm gave an external quantum efficiency of *ca.* 12%.

## Introduction

Polythiophene and its many variants have been studied extensively for their use in numerous applications, such as electroluminescence,<sup>1</sup> photovoltaics,<sup>2</sup> field effect transistors,<sup>3</sup> electrochromics<sup>4</sup> and sensors.<sup>5</sup> The electronic properties of these materials rely on the effective conjugation length within the polymers and thereby depend heavily on the degree of planarity in the main chain and the number of undesirable  $\alpha$ - $\beta'$  links between repeat units. Well-defined oligothiophenes are also of high interest as electronic materials<sup>6</sup> and offer several advantages over analogous polymeric materials: (i) monodispersity, (ii) a precise structure with no isomeric impurities, (iii) high chemical stability, (iv) good solubility, (v) direct processability from solution or by vacuum deposition techniques. Moreover, these attributes allow a direct and unequivocal correlation between structure and electronic properties and there is wide coverage in the literature focussing on morphological, electronic and spectroelectrochemical aspects of neutral and charged oligothiophenes.<sup>7</sup>

Recently, we have reported the synthesis, electropolymerisation and characterisation of some 3',4'-bis(alkylsulfanyl)-terthiophenes (**A–D**).<sup>8</sup> Our main interest in this work was the significance of the ethylenedithiophene (EDTT) unit, which is a direct and underexplored analogue of the well-known EDOT unit. Indeed, poly(EDOT) and poly(EDTT) possess very different electronic characteristics, yet the latter has a greater potential for interchain interactions due to the increased number of sulfur atoms in the chain. From this viewpoint, the role of EDTT in polythiophene materials is highly interesting in terms of electronic and charge transport properties, as well as self-assembly and film morphology. To this end, we have synthesised the end-capped sexithiophenes **10a** and **10b** in order to gain a closer understanding of the electronic contribution of the EDTT unit and its effect upon

the structure of the oligomer and morphology of the bulk material.

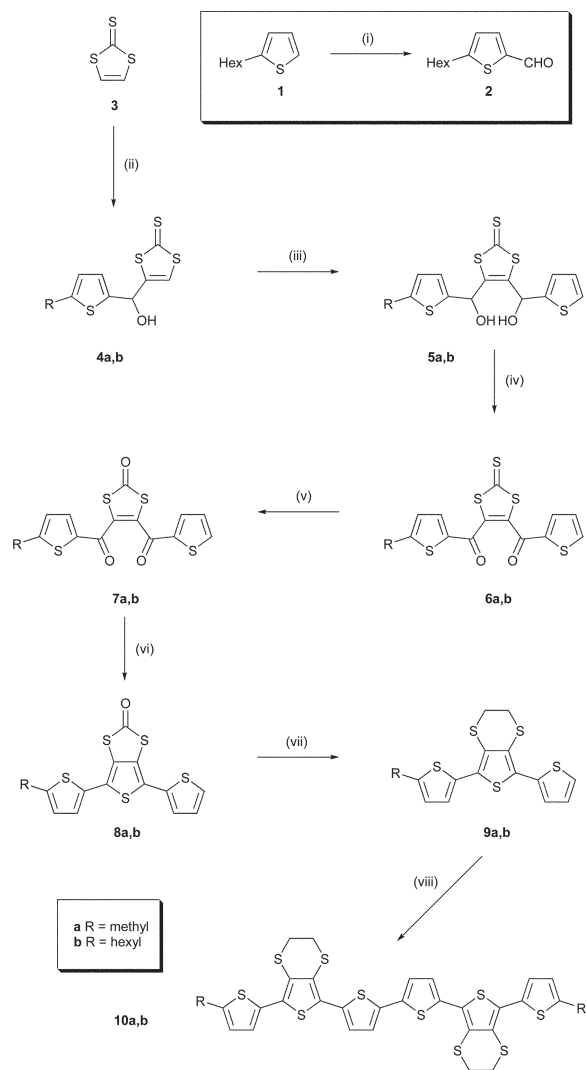


## Results and discussion

### Synthesis

The preparation of alkylterthiophenes **9a** and **9b** (Scheme 1) followed a similar strategy used to prepare terthiophenes **A–D**.<sup>8,9</sup> In this case, vinylene trithiocarbonate **3** was reacted with one equivalent of LDA to obtain the organolithio intermediate, which was subsequently reacted with 5-methylthiophene-2-carbaldehyde and **2** to give the corresponding alcohols **4a** and **4b** as racemic mixtures (91 and 87%, respectively). The aldehyde **2** was prepared simply from 2-hexylthiophene **1** by lithiation with *n*-butyllithium followed by addition of DMF. Further treatment of alcohols **4a,b** with two equivalents of LDA and 2-thiophenecarbaldehyde afforded compounds **5a** and **5b**. 4,5-Bis(2-arylhydroxymethyl)-1,3-dithiole-2-thiones are unstable and undergo various rearrangement pathways,<sup>10</sup> therefore diols **5a** and **5b** were reacted almost immediately with MnO<sub>2</sub> to give the stable diketone products **6a** and **6b** (75% overall yield from **4a,b** in both cases).

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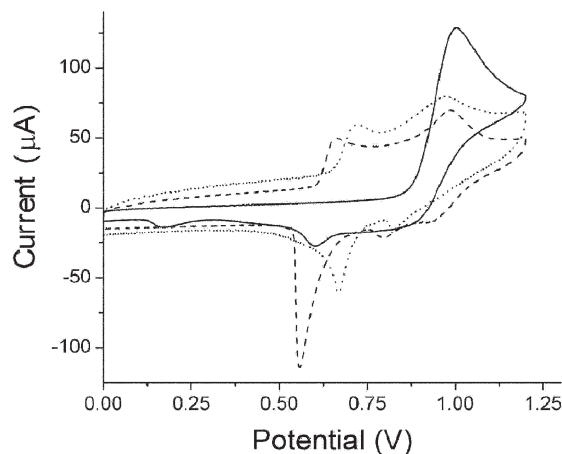


**Scheme 1** Reagents and conditions: (i) *n*-BuLi, THF, 0 °C, 15 min, then DMF; (ii) LDA, THF, -78 °C, 20 min, then **2** or 5-methylthiophene-2-carbaldehyde; (iii) LDA, THF, -78 °C, 20 min, then 2-thiophenecarbaldehyde; (iv) MnO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>; (v) Hg(OAc)<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/AcOH (3:1, v/v); (vi) P<sub>4</sub>S<sub>10</sub>, NaHCO<sub>3</sub>, 1,4-dioxane, 90 °C, 3 h; (vii) NaOEt, THF, then BrCH<sub>2</sub>CH<sub>2</sub>Br; (viii) FeCl<sub>3</sub>, CHCl<sub>3</sub>.

The thiocarbonyl derivatives were converted to their oxone analogues by treatment with mercuric acetate (**7a**, 85%; **7b**, 82%), before these compounds were cyclised to the corresponding thiophenes using phosphorus pentasulfide (**8a**, 69%; **8b**, 75%). Alkylation of the dithiole-one species was accomplished by the action of sodium ethoxide, releasing the dithiolate intermediate, followed by the addition of 1,2-dibromoethane (**9a**, 76%; **9b**, 67%). Finally, the sexithiophene oligomers (**10a** and **10b**) were prepared by reacting the terthiophenes **9a,b** with ferric chloride in chloroform and the materials were isolated in 50 and 40% yields, respectively.

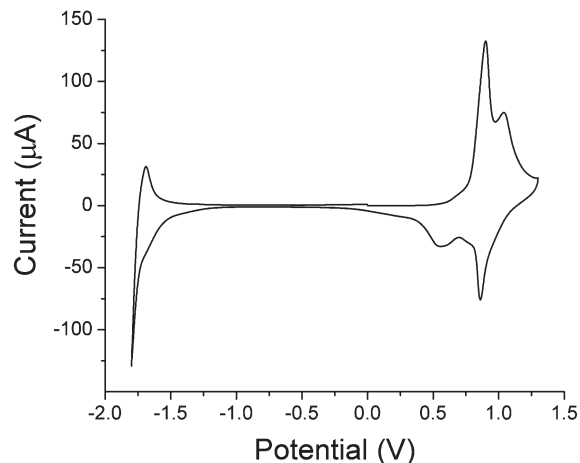
### Electrochemistry

The redox properties of the sexithiophene derivatives have been studied in solution and as thin films on ITO glass. The cyclic voltammogram of compound **9a** shows a single



**Fig. 1** Cyclic voltammograms of compounds **9a** (—), **10a** (---) and **10b** (···) in CH<sub>2</sub>Cl<sub>2</sub> vs. Ag/AgCl reference electrode, Au disk working electrode, TBAPF<sub>6</sub> as the supporting electrolyte (0.1 M), substrate concentration 10<sup>-3</sup> M, scan rate 100 mV s<sup>-1</sup>.

irreversible oxidation wave at +1.00 V (Fig. 1) corresponding to the redox process **9a** → **9a**<sup>+</sup>. A small reduction peak is observed at +0.60 V, which is probably due to the emergence of a dimerised product (**10a**) at the working electrode. In contrast, the sexithiophene derivatives **10a** and **10b** display two sequential quasi-reversible oxidation processes leading to radical cation and dication species, respectively (**10a**:  $E_1^{1/2} = +0.61$  V,  $\Delta E_{a-c} = 100$  mV;  $E_2^{1/2} = +0.97$  V,  $\Delta E_{a-c} = 50$  mV; **10b**:  $E_1^{1/2} = +0.70$  V,  $\Delta E_{a-c} = 50$  mV;  $E_2^{1/2} = +0.91$  V,  $\Delta E_{a-c} = 160$  mV). A film of the methyl substituted sexithiophene was deposited by spin coating onto ITO glass and the solid-state voltammogram of **10a** is depicted in Fig. 2. The reversibility of the redox processes is diminished due to the self-assembly and charge trapping in the solid state. The first oxidation peak is shifted to a more positive value by 0.24 V to +0.90 V, whilst the corresponding reduction process remains unchanged at +0.56 V. The second oxidation wave is less affected in the solid state ( $E_2^{1/2} = +0.95$  V) but the difference between the oxidation and reduction peaks is increased to 170 mV. There was no

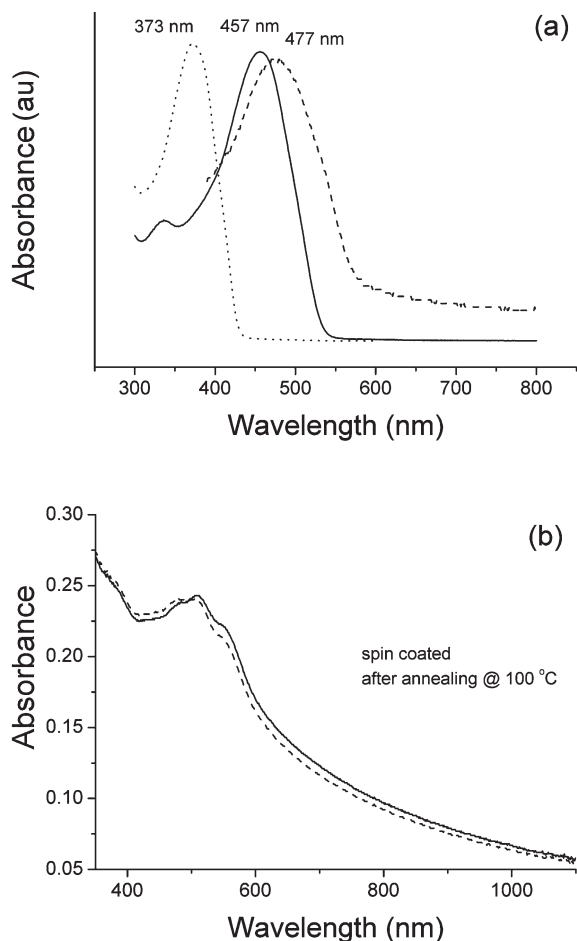


**Fig. 2** Cyclic voltammogram of compound **10a** as a spin-coated film on ITO glass, under identical conditions to those presented in Fig. 1.

evidence of coupling reactions during repetitive cycling experiments, indicating that the alkyl groups are successful in inhibiting any polymerisation processes. In contrast to the solid state CV of dimethyl sexithiophene (DMSxT, which is analogous to **10a** but without the ethylene dithio substituents), **10a** shows good reversibility, although the oxidation peaks of DMSxT are very similar (+0.91 and +1.05 V, vs. Ag/AgCl).<sup>11</sup> In the negative scan, we observed a quasi-reversible reduction wave at -1.74 V ( $\Delta E_{c-a} = 100$  mV). The difference between the onset of the first oxidation and reduction waves gives an estimate of the electrochemical band gap of the material and this was found to be 2.20 eV.

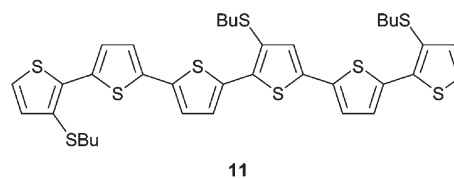
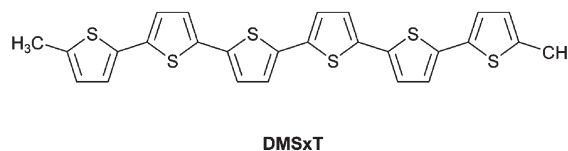
### Absorption studies/spectroelectrochemistry

In contrast to the electrochemical behaviour of the two sexithiophene derivatives, the absorption spectra of the materials in solution are identical. Fig. 3 shows the spectra for compounds **9a** and **10a** in solution (dichloromethane) and for **10a** also in the solid state. The absorption maximum for the terthiophene unit appears at 373 nm, which is slightly higher than that for compound **C** (368 nm)<sup>8</sup> and in the range expected for an additional alkyl group appended to the parent terthiophene. This peak is shifted bathochromically by 84 nm



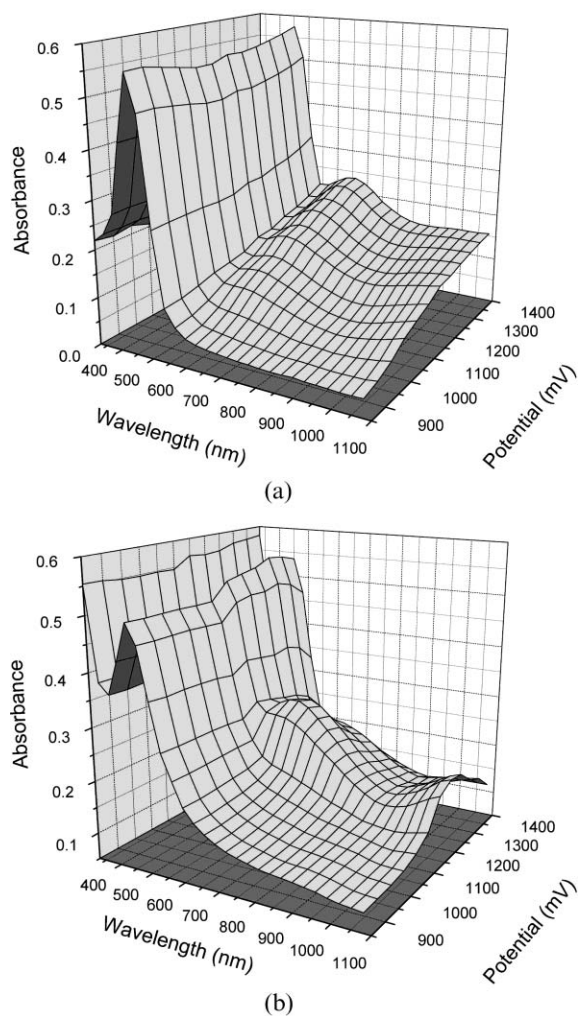
**Fig. 3** Absorption spectra of (a) compounds **9a** (···) and **10a** (—) in dichloromethane solution and **10a** (---) as a film on ITO glass, and (b) compound **10b** as a film on ITO glass.

( $\lambda_{max}$  457 nm) in **10a** due to the elongation of the conjugated chain. In comparison, the absorption maximum for DMSxT in solution is 438 nm<sup>12</sup> and unsubstituted sexithiophene ( $\alpha$ -6T) has a value of 432 nm.<sup>13</sup> The difference in values of  $\lambda_{max}$  between DMSxT and **10a** is due to the electronic contribution of the alkyl sulfanyl groups and this effect is also observed for tris(butylsulfanyl)sexithiophene **11** ( $\lambda_{max}$  449 nm, CHCl<sub>3</sub>).<sup>14</sup>



The optical band gap of the material can be deduced from the longest wavelength absorption edge. The absorption peak for **10a** is particularly sharp for a conjugated system and the band edge (536 nm) equates to a value of  $E_g = 2.3$  eV. In the solid state, the absorption maximum is further shifted to 477 nm ( $E_g = 2.15$  eV), as a function of interchain interactions in the solid.<sup>15</sup> The optical band gaps are in excellent agreement with the electrochemical measurement for  $E_g$ . In the solid-state spectrum of **10b** (Fig. 3(b)), the absorption peak shows greater complexity than that of **10a** (maxima at 481, 510 and 551 nm), indicative of some higher ordering due to the hexyl chains. The spectrum is essentially unchanged after annealing at 100 °C for 1 h. The shoulder of the longest wavelength absorption peak is extremely broad and covers several hundred nm, making it difficult to assign the optical band gap for **10b** in the solid state. The same behaviour is observed for poly(**C**) and poly(**D**).<sup>8</sup>

Spectroelectrochemical (SEC) measurements in acetonitrile were conducted for both sexithiophene derivatives as thin films drop cast on ITO glass (Fig. 4). Here it is worth noting that the drop-cast films gave absorption spectra more reminiscent of the solution state experiments rather than the spin-coated films. Above +0.85 V two additional peaks emerge at 651 and >1100 nm for compound **10a** and these continue to grow up to +1.40 V, which is just beyond the second oxidation process for the material. Since the oxidation of **10a** surpasses the dication threshold, these peaks should be characteristic of the evolution of a bipolaronic species. The oxidation peaks could be sufficiently close together (+0.90 and +1.03 V) to bypass the experimental detection of the intermediate polaron (**10a<sup>+</sup>**). However, in the spectroelectrochemical characterisation of DMSxT, peaks arising at 685 ( $\pi$ -dimer association) and 860 nm (radical cation) were assigned to the signature of DMSxT<sup>+</sup>.<sup>11</sup> Similar conclusions have been made from experiments on methoxyoligothiophene analogues.<sup>16</sup> For compound **10b**, similar absorption peaks are observed for the bipolaron at

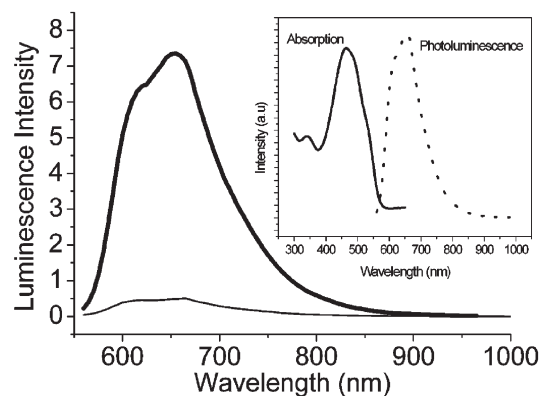


**Fig. 4** UV-vis spectroelectrochemical measurements of (a) **10a** and (b) **10b** on ITO glass.

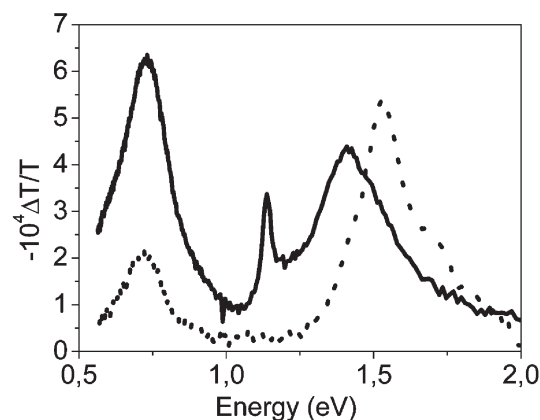
631 and >1100 nm, although above +1.25 V we observed a rapid decrease in peak intensity due to the dissolution of the material into the solvent. Compared to simple oligothiophenes such as DMSxT and **11**, the absorption bands for oligomers **10a** and **10b** at significantly longer wavelengths (860 vs. >1100 nm, corresponding to the polaronic species) indicate a more delocalised charged state and significant electronic contribution from the ethylenedithio units.

#### Photophysical studies and photovoltaic properties

Photoinduced charge transfer between conjugated polymers/oligomers and fullerene is of considerable interest for photovoltaic energy conversion.<sup>17–24</sup> Photoinduced absorption studies have been carried out on photovoltaic devices based on **10a** as a donor, with C<sub>60</sub> as the acceptor. Fig. 5 shows the PL spectrum of pristine **10a** with a maximum at 650 nm (1.9 eV) using an excitation wavelength of 476 nm. It is seen that the relatively strong PL of **10a** is significantly quenched by blending of **10a** with C<sub>60</sub>. This quenching can be related to the photoinduced charge transfer from **10a** excited state to C<sub>60</sub>. Fig. 5 (inset) shows the PL and absorption spectra of **10a** with the onset of absorption at 570 nm.



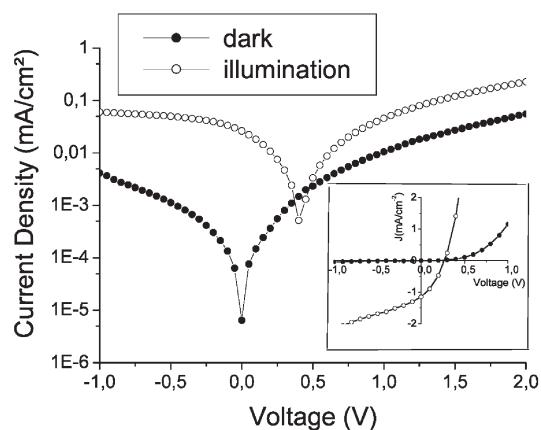
**Fig. 5** Photoluminescence spectra in blends of **10a** and C<sub>60</sub> (—) and **10a** film (---). The electron transfer to C<sub>60</sub> quenches the photoluminescence of **10a**. Inset: Absorption (—) and photoluminescence (···) spectra of pristine **10a**.



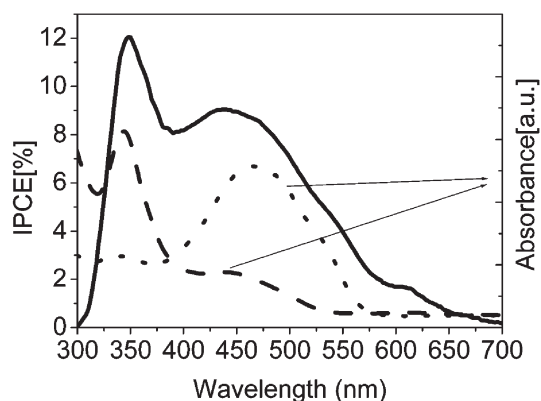
**Fig. 6** Photoinduced absorption spectra of mixed layer **10a**:C<sub>60</sub> (—) and pure **10a** (···) solid films. Excitation at 476 nm, *T* = 18 K.

Fig. 6 displays the photoinduced absorption (PIA) spectrum of pristine **10a** and a co-evaporated film of **10a**:C<sub>60</sub>. The photoinduced absorption spectrum for the pure oligomer exhibits two peaks; these features can be assigned to a charged species (polaronic state) at 0.7 and 1.5 eV. The high energy band at 1.5 eV possibly has an additional contribution from triplet–triplet absorption shifting the spectrum to higher energies. The PIA signals of the co-evaporated film exhibit two peaks at 0.73 and 1.4 eV. These peaks can be attributed to the photoexcited positive polaron species without the additional feature of a triplet. The PIA band centred at 1.12 eV corresponds to the absorption of the C<sub>60</sub><sup>•−</sup> radical anion<sup>22,23</sup> due to intermolecular charge separation, which is necessary for solar energy conversion.<sup>25</sup>

The current–voltage characteristics of a bilayer heterostructure photovoltaic device of ITO|PEDOT:PSS|**10a** (40 nm)|C<sub>60</sub> (60 nm)|Al are displayed in Fig. 7. Diode behaviour with rectification of about 10 is observed. Under white light illumination at 100 mW cm<sup>−2</sup>, through the ITO electrode, an open circuit voltage (*V*<sub>oc</sub>) of 0.27 V and a short circuit current (*I*<sub>sc</sub>) of 1.14 mA cm<sup>−2</sup> have been measured. Using these data, a filling factor (FF) of 0.4 and a power conversion efficiency of 0.12% were calculated. Fig. 8 shows the photocurrent spectrum



**Fig. 7** Logarithmic and linear (inset) representations of the current density–voltage characteristics of a **10a**| $C_{60}$  cell. The empty circles represent data obtained under  $100 \text{ mW cm}^{-2}$  white light illumination while the full circles represent data measured in the dark.



**Fig. 8** IPCE characteristics of the bilayer device using ITO/PEDOT|**10a** (40 nm)| $C_{60}$  (60 nm)|Al (—) is compared with the absorption spectra of **10a** (---) and  $C_{60}$  (···).

of the photovoltaic cell and compares the absorption spectra of pristine **10a** and  $C_{60}$  films. The spectrum shows the maximum incident photon to collected electron (IPCE) at 350 nm with an external quantum efficiency about 12%, which is comparable to other oligomer/ $C_{60}$  blends.<sup>26,27</sup> In order to maximise the photocurrent, further optimisation of the device structure will be necessary.

## Experimental

### General

Melting points were taken using a Stuart Scientific SMP1 Melting Point apparatus and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Unity Innova instrument at 300 and 75 MHz, respectively; chemical shifts are given in ppm; all  $J$  values are in Hz. IR spectra for the characterisation of the compounds were recorded on a ATI Mattson Genesis Series FTIR spectrometer. Mass spectra (EI) and high resolution mass spectra were recorded on Micromass Trio 2000 and Kratos Concept spectrometers, respectively. Elemental analyses were obtained on a Carlo Erba Instruments

EA1108 elemental analyser. Absorption spectra were measured on a Unicam UV 300 spectrophotometer.

All CV and spectroelectrochemical measurements were performed on a CH Instruments 660A Electrochemical Workstation with  $iR$  compensation, using anhydrous  $\text{CH}_2\text{Cl}_2$  or acetonitrile as the solvent, aqueous  $\text{Ag}/\text{AgCl}$  as the reference electrode and platinum wire and gold disk (or ITO glass for SEC) as the counter and working electrodes, respectively. All solutions were degassed ( $\text{Ar}$ ) and, where relevant, contained the substrate in concentrations *ca.*  $10^{-3}$  M, together with  $n\text{-Bu}_4\text{NPF}_6$  (0.1 M) as the supporting electrolyte. Under these conditions, the redox potential for the  $\text{FcH}/\text{FcH}^+$  couple was +0.48 V ( $\text{CH}_2\text{Cl}_2$ , vs.  $\text{Ag}/\text{AgCl}$ ).

The photoluminescence (PL) and photoinduced absorption (PIA) spectra were measured using an excitation  $\text{Ar}^+$  laser at 476 nm. The changes in sample transmission  $\Delta T$  resulting from the mechanically chopped laser pump beam were detected with a Si/InGaAsSb detector and using a lock-in-amplifier (typical chopping frequency was 73 Hz).  $\Delta T$  were corrected for the sample luminescence and normalised by the sample transmission  $T$  to obtain the PIA ( $\Delta T/T$ ) spectrum. PIA and PL measurements of co-evaporated films of **10a** and  $C_{60}$  were carried out at 18 K. Photovoltaic cells were produced as a bilayer heterostructure of **10a**/ $C_{60}$  using thermal evaporation. This active bilayer was deposited on PEDOT:PSS coated ITO substrates. Aluminium (Al) was used as the top electrode. The thickness of the active layer was varied between 40 and 150 nm. Current–voltage characteristics of photovoltaic cells were measured in the dark and under illumination with  $100 \text{ mW cm}^{-2}$  (1.5 AM) from a solar simulator. Incident photon to collected electron (IPCE) was measured with monochromatic light from a Xe lamp and detected by a lock-in-amplifier.

### 5-Hexylthiophene-2-carbaldehyde (**2**)

To a solution of 2-hexylthiophene **1** (6.50 ml, 36.1 mmol) in dry tetrahydrofuran (80 ml), under dry nitrogen at  $0^\circ\text{C}$ , was added butyllithium (2.5 M in hexanes, 18.0 ml, 45.1 mmol). The mixture was allowed to stir for 15 min at which time dimethylformamide (4.21 ml, 54.1 mmol) was added. The mixture was allowed to stir for 30 min whilst warming to room temperature. Ammonium chloride solution (1 M, 100 ml) was added and the product extracted into dichloromethane ( $3 \times 75 \text{ ml}$ ) and dried ( $\text{MgSO}_4$ ). The solvents were removed under reduced pressure and the product isolated by column chromatography (silica, petroleum ether (bp  $40\text{--}60^\circ\text{C}$ )–ethyl acetate, 9:1 v/v) to afford the product as a yellow/orange oil (6.43 g, 90.8%),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ /ppm: 9.85 (1H, s), 7.65 (1H, d,  $J = 3.85$ ), 6.94 (1H, d,  $J = 3.7$ ), 2.90 (2H, t,  $J = 7.1$ ), 1.75 (2H, m), 1.35 (6H, m), 0.95 (3H, t,  $J = 6.9$ ); MS (EI)  $m/z$ : 196 (62%,  $\text{M}^+$ ), 167 (15%), 125 (100%), 97 (43%).

### 4-[Hydroxyl(5-methyl-2-thiophen-2-yl)ethyl][1,3]dithiole-2-thione (**4a**)

A solution of 1,3-dithiole-2-thione **3** (4.78 g, 35.7 mmol) in dry tetrahydrofuran (80 ml) under dry nitrogen was cooled to  $-78^\circ\text{C}$ . Lithium diisopropylamide mono(tetrahydrofuran) (1.5 M in cyclohexanes, 21.9 ml, 32.8 mmol) was added and the mixture allowed to stir for 20 min. A solution of

5-methylthiophene-2-carbaldehyde (4.2 ml, 39.3 mmol) was added and the mixture stirred for a further 10 min. The reaction was left to stir for 1.5 h whilst warming to room temperature. Saturated sodium hydrogencarbonate (150 ml) was added and the organic phase was removed. The aqueous phase was washed with dichloromethane (3 × 50 ml) and the combined organic extracts dried (MgSO<sub>4</sub>). After evaporation of the solvent under vacuum, the product was isolated by column chromatography (silica, petroleum ether (bp 40–60 °C)–dichloromethane, 1:1 v/v, with gradual change to dichloromethane), to afford the product as a red oil (8.42 g, 90.8%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 6.95 (1H, s), 6.90 (1H, d, *J* = 3.4), 6.67 (1H, d, *J* = 3.5), 5.90 (1H, s), 2.90–3.05 (1H, br s), 2.51 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm: 213.8, 150.0, 142.2, 141.3, 126.5, 125.4, 124.3, 124.2, 68.9, 15.8; MS (CI) *m/z*: 261 (M<sup>+</sup> + H, 100%) 243 (4%); FT-IR (KBr): ν/cm<sup>-1</sup>: 3395, 3055, 2913, 1482, 1060, 803; HRMS (EI) *m/z*: calc. for C<sub>9</sub>H<sub>8</sub>OS<sub>4</sub> 259.9458, found 259.9455.

#### 4-[(5-Hexyl-2-thiophen-2-yl)hydroxymethyl][1,3]dithiole-2-thione (4b)

Compound **4b** was prepared as described for **4a** using 1,3-dithiole-2-thione **3** (4.00 g, 29.9 mmol), lithium diisopropylamide mono(tetrahydrofuran) (1.5 M in cyclohexanes, 21.9 ml, 32.8 mmol) and 5-hexylthiophene-2-carbaldehyde **2** (6.43 g, 32.8 mmol) in tetrahydrofuran. The product was obtained as a red oil (8.58 g, 87.1%), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 6.96 (1H, s), 6.94 (1H, d, *J* = 3.7), 6.70 (1H, d, *J* = 3.6), 5.90 (1H, s), 2.94 (1H, s), 2.81 (2H, t, *J* = 7.65), 1.70 (2H, m), 1.36 (6H, m), 0.94 (3H, t, *J* = 6.7 and 6.6); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm: 213.4, 149.6, 148.0, 140.6, 125.9, 123.8, 123.7, 68.7, 31.4, 30.2, 28.7, 22.5, 14.0; MS (CI) *m/z*: 331 (M<sup>+</sup> + H, 100%), 313 (8%); FT-IR (KBr) ν/cm<sup>-1</sup>: 3399, 2953, 2926, 2853, 1463, 1063, 1033, 803; HRMS (EI) *m/z*: calc. for C<sub>14</sub>H<sub>18</sub>OS<sub>4</sub> 330.0240, found 330.0240.

#### 4-[Hydroxy(5-methylthiophen-2-yl)methyl]-5-(hydroxythiophen-2-ylmethyl)[1,3]dithiole-2-thione (5a)

A solution of the alcohol **4a** (8.42 g, 32.4 mmol) in dry tetrahydrofuran (120 ml) under dry nitrogen was cooled to -78 °C. Lithium diisopropylamide mono(tetrahydrofuran) (1.5 M in cyclohexanes, 47.5 ml, 71.3 mmol) was added and the mixture allowed to stir for 20 min. Thiophene-2-carbaldehyde (3.33 ml, 33.6 mmol) was added and the mixture stirred for 10 min. The reaction was stirred for a further 1.5 h whilst warming to room temperature. Saturated sodium hydrogencarbonate (200 ml) was added and the organic phase was removed. The aqueous phase was washed with dichloromethane (3 × 50 ml) and the combined organic extracts dried (MgSO<sub>4</sub>). The solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, dichloromethane then ethyl acetate), to afford the product as a red oil (~11 g).

#### 4-[(5-Hexylthiophen-2-yl)hydroxymethyl]-5-(hydroxythiophen-2-ylmethyl)[1,3]dithiole-2-thione (5b)

The product was obtained using the same conditions as those for **5a** from alcohol **4b** (8.58 g, 26.0 mmol), lithium

diisopropylamide mono(tetrahydrofuran) (1.5 M in cyclohexanes, 38.1 ml, 57.2 mmol) and thiophene-2-carbaldehyde (2.67 ml, 28.6 mmol). The product was obtained as a red oil (~10 g).

#### 4-(5-Methyl-2-thenoyl)-5-(2-thenoyl)[1,3]dithiol-2-one (6a)

To a solution of the diol **5a** (~11 g) in dichloromethane (250 ml), manganese dioxide (10 × excess w/w, ~110 g) was added portionwise and the mixture allowed to stir for approximately 2 min. The mixture was filtered through a silica plug (eluted with dichloromethane) and the solvent removed under reduced pressure. The product was isolated by recrystallisation (dichloromethane–petroleum ether (bp 40–60 °C)) to afford the product as a yellow solid (8.99 g, 75.4% from **4a**), mp 126–128 °C (Found: C, 46.11; H, 2.05; S, 43.78%. Calc. for C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>S<sub>5</sub>: C, 45.63; H, 2.19; S, 43.50%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 7.77 (2H, m), 7.59 (1H, d, *J* = 3.95), 7.15 (1H, t, *J* = 4.0), 6.84 (1H, d, *J* = 3.9) 2.56 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm: 207.8, 176.2, 175.4, 154.8, 144.9, 144.3, 142.5, 140.3, 137.5, 136.7, 135.7, 128.9, 127.9, 16.6; MS (CI) *m/z*: 369 (M<sup>+</sup> + H, 100%), 295 (8%), 265 (17%); FT-IR (KBr): ν/cm<sup>-1</sup>: 3090, 1637, 1522, 1444, 1411, 1351, 1274, 1070.

#### 4-(5-Hexyl-2-thenoyl)-5-(2-thenoyl)[1,3]dithiol-2-one (6b)

The diketone **6b** was prepared as described for **6a** from the diol **5b** (~10 g) in dichloromethane (250 ml) and manganese dioxide (10 × excess w/w, ~100 g). The mixture was filtered through a silica plug (eluted with dichloromethane) and the solvent removed under reduced pressure to afford the product as an orange-red oil (8.50 g, 74.6% from **4b**), <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 7.73 (2H, m), 7.58 (1H, d, *J* = 3.95), 7.14 (1H, t, *J* = 3.95 and 4.0), 6.83 (1H, d, *J* = 3.95), 2.83 (2H, t, *J* = 7.55), 1.68 (2H, m), 1.32 (6H, m), 0.93 (3H, t, *J* = 6.6); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm: 207.8, 176.3, 175.5, 161.0, 145.1, 144.4, 142.6, 140.0, 137.4, 136.5, 135.7, 128.9, 126.7, 31.7, 31.4, 31.1, 28.8, 22.8, 14.3; MS (CI) *m/z*: 439 (M<sup>+</sup> + H, 10%), 365 (13%), 335 (23%); FT-IR (KBr): ν/cm<sup>-1</sup> 3089, 2926, 2854, 1631, 1523, 1444, 1409, 1353, 1272, 1069; HRMS (EI) *m/z*: calc. for C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>S<sub>5</sub> 437.9910, found 437.9906.

#### 4-(5-Methyl-2-thenoyl)-5-(2-thenoyl)[1,3]dithiol-2-one (7a)

To a solution of the diketone **6a** (8.99 g, 24.4 mmol) in dichloromethane–glacial acetic acid (3:1 v/v, 400 ml) was added mercuric acetate (10.90 g, 34.2 mmol). The mixture was stirred at room temperature for 16 h and filtered through a silica plug (eluting with dichloromethane). The organic extract was washed with water (2 × 100 ml), saturated sodium hydrogencarbonate (2 × 100 ml) and dried (MgSO<sub>4</sub>). After evaporation of the solvent, the product was isolated by recrystallisation (dichloromethane–petroleum ether (bp 40–60 °C)) to afford the product as an off white–yellow solid (7.30 g, 84.9%), mp 174–177 °C (Found: C, 47.55; H, 2.24; S, 36.05%. Calc. for C<sub>14</sub>H<sub>8</sub>O<sub>3</sub>S<sub>4</sub>: C, 47.71; H, 2.29; S, 36.38%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 7.76 (1H, d, *J* = 3.8), 7.73 (1H, d, *J* = 4.0), 7.55 (1H, d, *J* = 3.95), 7.14 (1H, t, *J* = 3.9), 6.77 (1H, d, *J* = 3.95), 2.54 (3H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ/ppm: 187.3, 177.8, 177.0, 154.4, 142.7, 140.6, 137.2, 136.6, 136.1, 135.6, 135.5,

128.8, 127.7, 16.5; MS (CI)  $m/z$ : 353 ( $M^+ + H$ , 100%), 295 (15%), 265 (21%); FT-IR (KBr)  $\nu/cm^{-1}$ : 3092, 1670, 1633, 1529, 1441, 1410, 1351, 1278.

#### 4-(5-Methyl-2-thenoyl)-5-(2-thenoyl)[1,3]dithiol-2-one (7b)

The tricarbonyl **7b** was prepared as described for **7a** from the diketone **6b** (8.50 g, 19.4 mmol) in dichloromethane–glacial acetic acid (3:1 v/v, 360 ml) and mercuric acetate (8.66 g, 27.2 mmol). The product was obtained as an orange–red oil (6.74 g, 82.3%),  $^1H$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 7.72 (2H, m), 7.55 (1H, d,  $J = 3.8$ ), 7.1 (1H, t,  $J = 3.85$ ), 6.82 (1H, d,  $J = 4.0$ ) 2.82 (2H, t,  $J = 7.5$  and 7.6), 1.66 (2H, m) 1.33 (6H, m), 0.92 (3H, t,  $J = 6.65$ );  $^{13}C$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 187.3, 177.9, 177.1, 160.6, 142.8, 140.3, 137.1, 136.5, 135.6, 135.5, 129.2, 128.8, 126.6, 31.7, 31.4, 31.1, 28.8, 22.8, 14.3; MS (CI)  $m/z$ : 423 ( $M^+ + H$ , 100%), 367 (9%), 335 (21%); FT-IR (KBr)  $\nu/cm^{-1}$ : 3092, 2927, 2855, 1696, 1633, 1528, 1444, 1409, 1353 1273; HRMS (EI)  $m/z$ : calc. for  $C_{19}H_{18}O_3S_4$  442.0139, found 442.0135.

#### 4-(5-Methyl-2-thiophen-2-yl)-6-thiophen-2-yl-thieno[3,4-*d*][1,3]dithiol-2-one (8a)

A mixture of the tricarbonyl **7a** (4.00 g, 11.4 mmol), sodium hydrogencarbonate (4.8 g, 57.1 mmol) and phosphorus pentasulfide (25.3 g, 56.8 mmol) in 1,4-dioxane (200 ml) was stirred whilst the temperature was raised to 90 °C and maintained for 3 h. The mixture was cooled, water (200 ml) was added (**CAUTION!**  $H_2S$  and  $CO_2$  evolution) and the suspension was allowed to stir overnight. The crude product was filtered, washed with boiling water and dried *in vacuo*. The crude product was redissolved in chloroform, dried ( $MgSO_4$ ), and stirred with decolourising charcoal for 30 min. The mixture was filtered through a silica plug (eluted with chloroform), the solvent reduced in volume and the product precipitated with petroleum ether (bp 40–60 °C). The product was isolated by filtration as an orange solid (2.76 g, 69.0%), mp 138–140 °C (Found: C, 48.04; H, 2.04; S, 45.75%. Calc. for  $C_{14}H_8OS_5$ : C, 47.70; H, 2.29; S, 45.43%);  $^1H$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 7.39 (1H, d,  $J = 5.1$ ) 7.24 (1H, d,  $J = 3.7$ ), 7.13 (1H, t,  $J = 3.7$ ), 7.05 (1H, d,  $J = 3.7$ ), 6.78 (1H, d,  $J = 3.7$ ), 2.56 (3H, s); MS (CI)  $m/z$ : 353 ( $M^+ + H$ , 100%), 324 (8%); FT-IR (KBr)  $\nu/cm^{-1}$ : 2957, 2914, 1707, 1644, 1501.

#### 4-(5-Hexyl-2-thiophen-2-yl)-6-thiophen-2-yl-thieno[3,4-*d*][1,3]dithiol-2-one (8b)

The terthiophene **8b** was prepared as described for **8a** from the tricarbonyl **7b** (6.74 g, 15.9 mmol) in 1,4-dioxane (200 ml), phosphorus pentasulfide (35.5 g, 79.9 mmol) and sodium hydrogencarbonate (6.79 g, 80.8 mmol). The product was obtained as an orange solid (5.02 g, 74.5%), mp 109–111 °C (Found: C, 53.99; H, 4.15; S, 37.58%. Calc. for  $C_{19}H_{18}OS_5$ : C, 53.99; H, 4.29; S, 37.93%);  $^1H$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 7.29 (1H, d,  $J = 5.0$ ), 7.13 (1H, d,  $J = 3.4$ ), 7.03 (1H, t,  $J = 4.4$ ), 6.95 (1H, d,  $J = 3.6$ ), 6.69 (1H, d,  $J = 3.4$ ) 2.76 (2H, t,  $J = 7.6$ ) 1.64 (2H, m), 1.28 (6H, m), 0.85 (3H, t,  $J = 6.3$ ); MS (CI)  $m/z$ : 423 ( $M^+ + H$ , 100%), 391 (32%); FT-IR (KBr)  $\nu/cm^{-1}$ : 2923, 2851, 1717, 1651, 1503.

#### 5-(5-Methylthiophen-2-yl)-7-thiophen-2-yl-2,3-dihydrothieno[3,4-*b*][1,4]dithiine (9a)

To a solution of the terthiophene **8a** (2.6 g, 7.38 mmol) in dry tetrahydrofuran (80 ml) under dry nitrogen was added sodium ethoxide (0.2 M solution in ethanol, 81.3 ml, 16.3 mmol). The reaction was allowed to stir for 30 min at which time 1,2-dibromoethane (0.64 ml, 7.38 mmol) was added and left to stir at room temperature for 16 h. The reaction mixture was filtered through a silica plug and the solvent removed under reduced pressure. The product was isolated by column chromatography (silica, petroleum ether (bp 40–60 °C)–dichloromethane, 4:1 v/v) to afford the product as a yellow solid (1.97 g, 75.8%), mp 102–104 °C (Found: C, 51.00; H, 3.43; S, 45.01%. Calc. for  $C_{15}H_{12}S_5$ : C, 51.10; H, 3.43; S, 45.47%);  $^1H$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 7.34 (2H, m), 7.11 (2H, m), 6.77 (1H, d,  $J = 3.7$ ), 3.29 (4H, s), 2.53 (3H, s);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 141.0, 135.1, 132.5, 128.2, 127.7, 127.1, 126.6, 126.3, 126.0, 125.9, 123.7, 123.1, 28.5, 15.6; MS (EI)  $m/z$ : 352 ( $M^+$ , 49%), 260 (12%); FT-IR (KBr)  $\nu/cm^{-1}$ : 3073, 2912, 1490, 1271.

#### 5-(5-Hexylthiophen-2-yl)-7-thiophen-2-yl-2,3-dihydrothieno[3,4-*b*][1,4]dithiine (9b)

The terthiophene **9b** was prepared as described for **9a** from the terthiophene **8b** (5.02 g, 11.9 mmol) in tetrahydrofuran (100 ml), sodium ethoxide (0.2 M solution in ethanol, 130.8 ml, 26.2 mmol) and 1,2-dibromoethane (1.03 ml, 11.9 mmol). The product was isolated by column chromatography (silica, petroleum ether (bp 40–60 °C)–dichloromethane, 3:1 v/v) to afford the product as a green–orange oil (3.34 g, 66.5%),  $^1H$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 7.35 (2H, m), 7.17 (1H, d,  $J = 3.7$ ) 7.10 (1H, t,  $J = 4.4$ ), 6.79 (1H, d,  $J = 3.5$ ), 3.28 (4H, s), 2.86 (2H, t,  $J = 7.55$ ), 1.74 (2H, m), 1.38 (6H, m), 0.95 (3H, t,  $J = 6.6$ );  $^{13}C$  NMR ( $CDCl_3$ )  $\delta/ppm$ : 147.2, 135.1, 132.3, 128.3, 127.7, 127.1, 126.6, 126.3, 125.9, 124.8, 123.7, 122.9, 31.8, 30.4, 29.1, 28.5, 22.8, 14.4; MS (EI)  $m/z$ : 422 ( $M^+$ , 65%), 351 (72%) 323 (19%); FT-IR (KBr)  $\nu/cm^{-1}$ : 3065, 2924, 2852, 1277; HRMS (EI)  $m/z$ : calc. for  $C_{20}H_{22}S_5$  422.0325, found 422.0325.

#### 5,5'-Dimethyl-3',3''',4',4'''-ethylenedithio-2,2':5',2'':5''',2''':5''',2''':5''',2''''-sexithiophene (10a)

To a solution of the terthiophene **9a** (1.45 g, 4.12 mmol) in anhydrous chloroform (60 ml) under dry nitrogen was added anhydrous iron(III) chloride (0.87 g, 5.36 mmol). The reaction was allowed to stir for 1 h at which time sodium cyanide was added (0.1 M solution in water, 100 ml) and the temperature was raised to 60 °C and maintained at this temperature for 3 h. The aqueous phase was removed (**CAUTION!** cyanide, excess aqueous iron(II) sulfate added to all aqueous washes) and the organic phase was washed with water (4 × 100 ml) and dried ( $MgSO_4$ ). The solvent was reduced in volume and the crude product precipitated with petroleum ether (bp 40–60 °C). The crude product was washed (using Soxhlet apparatus) with methanol and then extracted with chloroform. Once more, the solvent was reduced in volume and the product precipitated with petroleum ether (bp 40–60 °C) to afford the product as a red–deep red solid (0.72 g, 49.8%), mp 223 °C (by DSC)

(Found: C, 51.16; H, 2.78; S, 45.49%. Calc. for C<sub>30</sub>H<sub>22</sub>S<sub>10</sub>: C, 51.25; H, 3.15; S, 45.60%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 7.25 (2H, d, *J* = 3.8), 7.19 (2H, d, *J* = 3.7), 7.14 (2H, d, *J* = 3.5), 6.77 (2H, d, *J* = 3.65), 3.33 (8H, m), 2.52 (6H, s); MS (MALDI TOF) *m/z*: 702 (M<sup>+</sup>, 100%); FT-IR (KBr) *v*/cm<sup>-1</sup>: 3054, 2913, 2872, 1489, 1275, 790.

### 5,5'-Dihexyl-3',3''',4',4'''-ethylenedithio-2,2':5',2'':5'',2''':5''',2''''-sexithiophene (10b)

The sexithiophene **10b** was prepared as described for **10a** from the terthiophene **9b** (1.77 g, 4.19 mmol) in chloroform (30 ml) and anhydrous iron(III) chloride (0.75 g, 4.61 mmol). The crude product was precipitated from solution with petroleum ether (bp 40–60 °C) and washed (using Soxhlet extraction) with methanol and extracted with chloroform. Once again, the solvent was reduced in volume and the product precipitated with petroleum ether (bp 40–60 °C) to afford the product as a red–deep red solid (0.71 g, 40.2%), mp 177 °C (by DSC) (Found: C, 56.68; H, 5.08; S, 37.60%. Calc. for C<sub>30</sub>H<sub>22</sub>S<sub>10</sub>: C, 56.97; H, 5.02; S, 38.01%); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ/ppm: 7.27 (2H, d, *J* = 3.95), 7.20 (2H, d, *J* = 3.8), 7.18 (2H, d, *J* = 3.8), 6.80 (2H, d, *J* = 3.7), 3.35 (8H, m), 2.86 (4H, t, *J* = 7.35), 1.75 (4H, m), 1.37 (12H, m), 0.94 (6H, t, *J* = 6.85); MS (MALDI TOF) *m/z*: 842 (M<sup>+</sup>, 100%); FT-IR (KBr) *v*/cm<sup>-1</sup>: 3056, 2921, 2851, 1274, 1459, 785.

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