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Poly(alkyl thiophene-3-carboxylates). Synthesis, properties and electroluminescence studies of polythiophenes containing a carbonyl group directly attached to the ring

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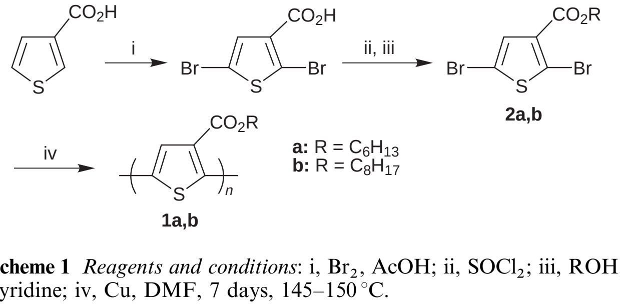
Improved synthetic methodology for poly(3-hexyl- and 3-octyloxycarbonylthiophene-2,5-diyl) (**1a** and **1b**) is reported. $\bar{M}_n = 6700$ and 9400 ($\bar{M}_w/\bar{M}_n = 2.5$ and 3.2), λ_{max} for fluorescence emission = 600 and 610 nm and λ_{max} for electroluminescence = 600 and 615 nm, for **1a** and **1b** respectively. The ^{1}H NMR spectra required that pentads be considered to explain the spectra. That is the four nearest neighbours to a given ring influence the ^{1}H NMR spectrum. Electroluminescence efficiencies of 0.016% and 0.018% were observed for devices made from **1a** and **1b**, respectively. A bilayer device of ITO/poly(3-octylthiophene)/**1b**/Al emitted at 646 nm, the same wavelength where poly(3-octylthiophene) itself emits. The efficiency was low but was an order of magnitude greater than for poly(3-octylthiophene) itself. Regioregular (HH–TT) poly(4,4′-bis(hexyl- and octyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a** and **3b**) were also prepared *via* the Ullmann reaction and $\bar{M}_n = 7900$ and 11000 respectively. Films of **3a** and **3b** were yellow in color and showed $\lambda_{max} = 377$ and 381 nm respectively, about 55–80 nm blue shifted compared with **1a** and **1b**. This is due to the large rotational barrier in the HH dyads which reduces the effective conjugation length in **3a** and **3b**. **3a** and **3b** showed bright fluorescence and electroluminescence with emission of yellow light. Electroluminescence efficiencies were 8.5×10^{-3}% and 4.7×10^{-3}%, respectively.

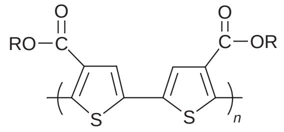
Introduction

Since Burroughes *et al.* first demonstrated the electroluminescent properties of poly(*p*-phenylenevinylene) (PPV),[1] electroluminescent devices based on organic conjugated polymer thin films have attracted much interest. Conjugated polymers show unique optical and electronic properties, while still retaining their polymeric materials properties, in particular ease of processing.[2] We recently reported on the synthesis of soluble poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**) and poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**) from the corresponding dibromo esters, hexyl and octyl 2,5-dibromothiophene-3-carboxylate (**2a** and **2b**), using the Ullmann coupling reaction employing 3 equivalents of copper metal (Scheme 1).[3] In that case the molecular weights, $\bar{M}_n$, were about 3000–4000.

In this paper we report on an improved preparation of **1a** and **1b** and on the properties of these polymers including their electroluminescence behaviour. Further, we report on the preparation and properties of poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**) and poly(4,4′-bis(octyloxycarbonyl[2,2′-bithiophene]-5,5′-diyl) (**3b**), regioregular variations of poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**) and poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**) containing alternating head-to-head (HH) and tail-to-tail (HT) linkages.



Scheme 1 *Reagents and conditions*: i, Br_2, AcOH; ii, $SOCl_2$; iii, ROH, pyridine; iv, Cu, DMF, 7 days, 145–150 °C.



3 a: R = C_6H_{13}
b: R = C_8H_{17}

Results and discussion

Regiorandom poly(3-hexyloxycarbonylthiophene-2,5-diyl) (1a) and poly(3-octyloxycarbonylthiophene-2,5-diyl) (1b)

Our recent report on the synthesis of poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**) and poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**) shown in Scheme 1 involved the reaction of the dibromo esters, hexyl and octyl 2,5-dibromothiophene-3-carboxylate (**2a** and **2b**), with three equivalents of freshly prepared copper powder.[3] We have now found, however, that the use of four equivalents of copper provided **1a** and **1b** with about double the molecular weights (determined by GPC with polystyrene standards) in about 48–50% yield. The polymers prepared this way were free flowing deep red powders. Table 1

Table 1 Molecular weight, polydispersity and degree of polymerization of **1a** and **1b**

Polymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Degree of polymerization
1a (4 equiv. Cu)	6600	2.5	31
1a (3 equiv. Cu)	3000	2.6	14
1b (4 equiv. Cu)	8800	3.4	37
1b (3 equiv. Cu)	3900	2.6	16

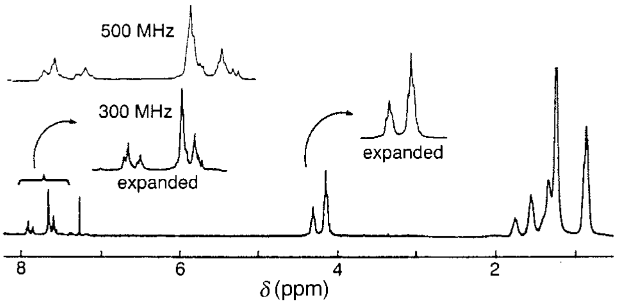


Fig. 1 ^{1}H NMR spectra of poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**).

compares the molecular weights ($\bar{M}_n$), polydispersity ($\bar{M}_w/\bar{M}_n$) and the degree of polymerization. These higher molecular weight polymers had better film forming characteristics than the lower molecular weight materials.

Compounds **1a** and **1b** showed UV–VIS absorption maxima at 410 and 419 nm for THF solutions and at 434 and 460 nm for films cast from toluene. The ^{1}H NMR spectra were quite interesting. At 300 MHz the spectra clearly showed four sets of peaks at $\delta = 7.92$, 7.85, 7.66 and 7.60 for the ring hydrogen [see Fig. 1 for the spectra of poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**)]. However, the 500 MHz ^{1}H NMR spectra showed many more peaks, up to about 12–16 peaks and shoulders (Fig. 1). It is well known in the case of many 3-substituted polythiophenes such as poly(3-alkylthiophenes) that there are four triads to be considered with respect to the ^{1}H NMR spectra[4,5] and so one should expect four peaks for **1a** and **1b**. The observation of many more than four peaks suggests that pentads rather than triads must be considered. This is because of the strongly electron withdrawing character of the ester group which enables it to influence the ^{1}H chemical shift over a greater distance. Fig. 2 shows four pentads based on a single configurational triad. Since there are four possible triads there is a total of 16 pentads. As mentioned above we see peaks or shoulders for 12–16 of them.

The ^{1}H NMR spectra of **1a**/**1b** showed two peaks at $\delta =$ 4.30/4.31 and 4.13/4.14 which are assigned to the CH_2 groups attached to the oxygen in the esters. Based upon the assignments of the CH_2 groups attached to the thiophene rings in poly(3-dodecylthiophene)[4,5] the peaks at 4.30/4.31 and 4.13/4.14 are assigned to the head-to-tail (HT) and head-to-head (HH) dyads, respectively. Furthermore, this assignment was confirmed by preparation of a regioregular version of these polymers containing only the HH and not the HT dyad (*vide infra*). The ratio of the HH : HT dyads was 2.15 : 1 and 2.16 : 1 for **1a** and **1b** respectively. The greater amount of head-to-head dyads is reasonable since it is known in the benzene series that strong electron withdrawing groups activate the *ortho* position in the Ullmann coupling reaction.[6] Thus, in the early stages of the reaction higher concentrations of HH dyads would be formed.

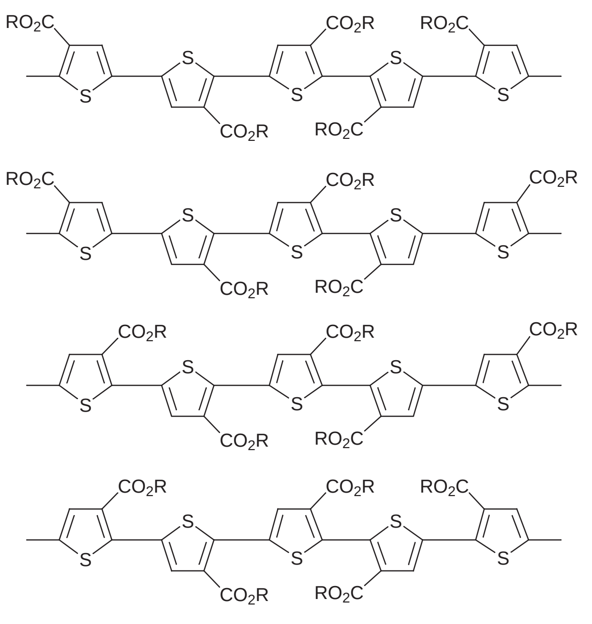


Fig. 2 4 Configurational pentads of **1a** and **1b** with a single central triad.

We have also carried out the coupling reactions of **2a** and **2b** using Rieke nickel[7–9] and, while the molecular weights of **1a** and **1b** obtained by this procedure were low (3300 and 7200 respectively), the ratio of the HH : HT dyads was 0.32 : 1 and 0.31 : 1. In this case it is known that aromatic couplings with Rieke nickel are subject to steric effects and *ortho* substituents hinder the coupling.[7] Thus, in the early stages of this reaction high concentrations of TT dyads would be formed followed by HT dyads. In later stages of the reaction HH coupling would be required and since there is considerable steric hindrance, lower overall molecular weights are observed.

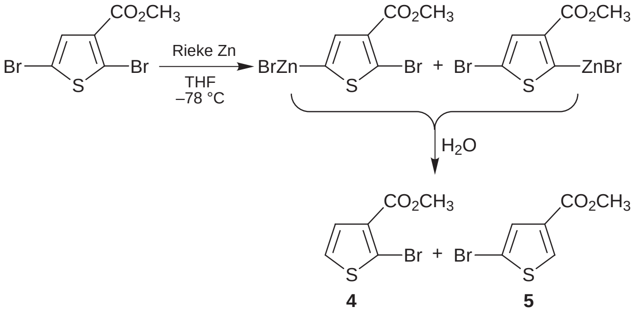
Since fluorescence is a necessary condition for electroluminescence, the fluorescence characteristics of the two polymers **1a** and **1b** from the Ullmann coupling reactions were examined. The fluorescence emission maxima for **1a** in THF solution and as a film were 565 nm and 600 nm respectively while the corresponding THF solution and film emission maxima for **1b** were 560 nm and 610 nm respectively.

Regioregular poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (3a) and poly(4,4′-bis(octyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (3b)

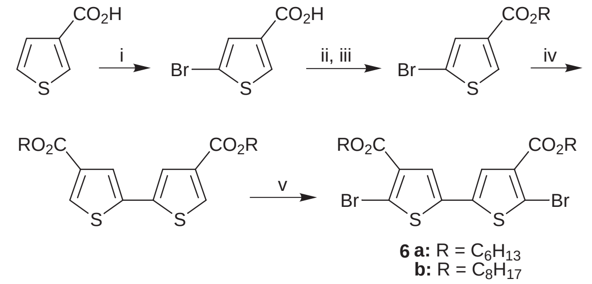
Preparation of regioregular variations of poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**) and poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**) were carried out as follows. Initially an attempt was made to prepare completely head-to-tail (HT) polymer employing Rieke zinc as was done by Rieke in the case of regioregular poly(3-alkylthiophenes).[10–12] To examine the regiochemistry of the reaction of a 2,5-dibromothiophene ester with Rieke zinc, methyl 2,5-dibromothiophene-3-carboxylate was treated with Rieke zinc at −78 °C and the product was quenched with H_2O. Scheme 2 shows this reaction. The ratio of products **5** : **4** was 86 : 14, determined by integration of the ^{1}H NMR spectra, which indicates that the reaction was not completely regioselective and so an alternate regioregular polymer was prepared.

The monomers chosen for these syntheses were dihexyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylate (**6a**) and dioctyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylate (**6b**). The synthesis of these monomers is shown in Scheme 3.

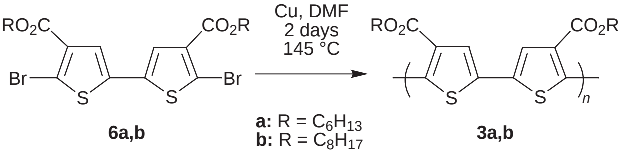
The preparation of the polymers, poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**) and poly(4,4′-bis(octyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3b**), was carried



Scheme 2 Reaction of methyl 2,5-dibromothiophene-3-carboxylate with Rieke zinc.



Scheme 3 *Reagents and conditions*: i, 0.97 equiv. Br_2, AcOH; ii, $SOCl_2$; iii, ROH, pyridine; iv, $NiBr_2$, Zn, PPh_3, DMF, 80 °C, 24 h; v, Br_2, $CHCl_3$.



Scheme 4 Preparation of poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**) and poly(4,4′-bis(octyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3b**).

out *via* the Ullmann reaction using 4 equivalents of copper powder in DMF at 145 °C for 2 days as shown in Scheme 4. Polymers **3a** and **3b** are regioregular, they contain alternating HH and TT linkages and they contain only a single one of the 16 possible pentads described above. This is shown in Fig. 3.

GPC analysis of **3a** and **3b** provided the results shown in Table 2. The molecular weights and average number of thiophene rings in a chain is comparable to what was observed in polymers **1a** and **1b**. The UV–VIS absorption maxima for **3a** and **3b** were 387 nm and 389 nm for THF solutions, respectively, and 377 nm and 381 nm for cast films, respectively. These values are unusual in that the film spectra are somewhat blue shifted compared with the solution spectra. Generally polythiophene film spectra are red shifted compared with solution. These values are also considerably blue shifted relative to the values for **1a** and **1b**, 23–30 nm for the solution spectra and 57–79 nm for the film spectra. This suggests that there is less effective conjugation in **3a** and **3b** than in **1a** and **1b**. The origin of these UV–VIS spectral differences and the shorter conjugation lengths is the result of there being more HH linkages in the regioregular polymers **3a** and **3b** than in **1a** and **1b**. Polymers **3a** and **3b** have 100% HH dyads and essentially no HT dyads while **1a** and **1b** have 68% HH and 32% HT dyads. Similar observations involving regioregular HH–TT poly(dialkylbithiophenes) have been made.[13–15]

We have recently shown by quantum mechanical calculations on dimethyl 2,2′-bithiophene-3,3′-dicarboxylate, dimethyl 2,2′-bithiophene-3,4′-dicarboxylate and dimethyl 2,2′-bithiophene-4,4′-dicarboxylate that the rotational barrier for the model head-to-head dimer is fairly large, 36 kJ mol^{-1} (8.55 kcal mol^{-1}).[16] Furthermore the rotation barriers for the model head-to-tail and tail-to-tail dyads are quite low [0.35 kJ mol^{-1} (0.084 kcal mol^{-1}) for HT and 1.5 kJ mol^{-1} (0.37 kcal mol^{-1}) for TT].[16] This means that in the polymers at the HT and TT linkages the rings will be more coplanar while at the HH linkages the rings will be considerably twisted. The calculations indicate a thiophene–thiophene dihedral angle of 77.4° in the lowest energy conformation of dimethyl 2,2′-bithiophene-3,3′-dicarboxylate. Thus **3a** and **3b** with a greater amount of HH dyads will absorb at shorter wavelengths than **1a** and **1b**. Generally, in most polythiophenes, the UV–VIS absorption shows a significant bathochromic shift in going from solution to the solid state (film);[17] however, in the case of **3a** and **3b**, there is essentially no shift. This is probably due to the large HH rotational barrier[16] which, even in the solid state, can not be overcome to produce a more flattened and conjugated system.[17]

Solid films of polymers **3a** and **3b** showed bright orange fluorescence under UV light, prompting examination of their fluorescence properties. The peak emission wavelengths of polymers **3a** and **3b** were independent of the excitation wavelength, but the intensities were a function of the excitation wavelength. The intensities reached a maximum when the excitation wavelength was about 435 to 475 nm. Using an excitation wavelength between 435 and 475 nm, THF solutions of the two polymers **3a** and **3b** showed emission maxima at 530 and 540 nm, respectively, 20–35 nm shorter than poly(3-hexyl- and 3-octyloxycarbonylthiophene-2,5-diyls) (**1a** and **1b**). Both polymers **3a** and **3b** showed cast film emission at 560 nm, 40–50 nm shorter than **1a** and **1b**. This also suggests that the conjugation lengths are shorter in the regioregular HH–TT polymer even in the excited state as discussed above.

The 300 MHz ^1H NMR spectra of poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**) and poly(4,4′-bis(octyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3b**) showed only one main aromatic hydrogen peak at $\delta = 7.66$ (Fig. 4). It should be recalled that samples of **1a** and **1b** showed up to 16 peaks and shoulders in their ^1H NMR spectra for the 16 different configurational pentads. Since **3a** and **3b** are both made up of only a single pentad (Fig. 3) they show only the single major peak. Furthermore, there is also one major triplet at $\delta = 4.14$ (–O–CH_2–) which corresponds to the HH dyads and a very small peak (about 5%) at $\delta = 4.30$ corresponding to a very small impurity of the HT dyad (or possibly end

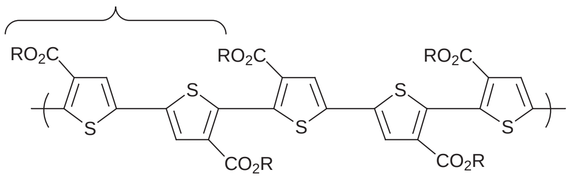


Fig. 3 The single pentad of regioregular polymers **3a** and **3b**.

Table 2 Molecular weight, polydispersity and degree of polymerization of **3a** and **3b**

Polymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Number of thiophene rings
3a	8100	1.8	39
3b	8700	2.0	37

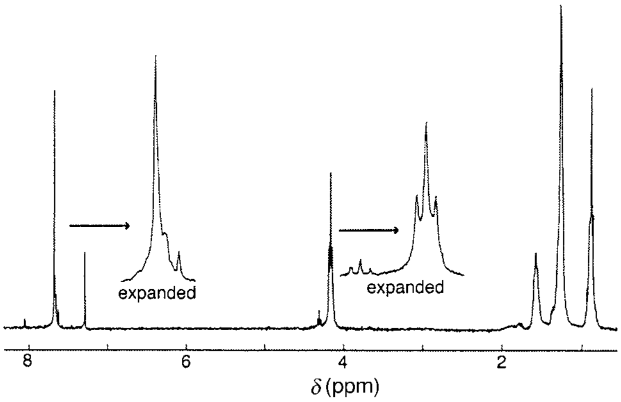


Fig. 4 300 MHz ^1H NMR spectra of poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**).

groups). In the ^{13}C NMR spectra there is a single carbonyl peak at $\delta = 162.2$ (**3a**) and 162.1 (**3b**) and a single peak at $\delta =$ 65.3 (both **3a** and **3b**) which corresponds to the carbon attached to the oxygen ($O{-}CH_2$). These peaks are either split into four peaks or three peaks and a shoulder in **1a** and **1b**[3] and, once again, this attests to the regioregular nature of the polymers **3a** and **3b**.

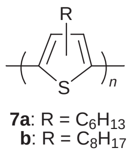
Electroluminescence studies

In the literature, there is very little on the study of electron-withdrawing group substituted polythiophenes for electroluminescent applications. Wudl and Heeger reported on the preparation of poly(3,4-dicyanothiophene) and demonstrated a bilayer polymer LED using it with MEH-PPV as the active polymer. The devices were reported to show a quantum efficiency of 0.1%. Since poly(3,4-dicyanothiophene) is not soluble in common organic solvents, fabrication of devices using this material proved extremely difficult.[18] We have successfully prepared LEDs from **1a**, **1b**, **3a** and **3b** using them as the emitting material.

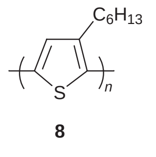
Electroluminescent devices were made by spin-coating the polymer onto ITO (indium-tin oxide) coated glass and then evaporatively depositing a layer of aluminum onto the polymer layer. The electroluminescence spectra were acquired with a Tracor-Northern 1710A Diode Array Spectrometer and the emission efficiencies were measured using a silicon photodiode. The electroluminescence % external efficiency, defined as the number of photons emitted per 100 electrons injected, was calculated as shown in eqn. (1), where π is the correction factor for the flux per unit solid angle leaving the device directly in the forward direction.[19]

$$\text{EL\% external efficiency} = \frac{\text{Light output (watts)} \times \pi}{\text{Device current (amp)} \times \text{Energy of photons}} \times 100\% \qquad (1)$$

Poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**) produced red–orange light with an emission maximum at around 600 nm (Fig. 5). Poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**) displayed an emission maximum at around 615 nm. The electroluminescence efficiencies of **1a** and **1b** were 0.016% and 0.018% respectively, which is hundreds of times higher than non-regioregular poly(3-hexylthiophene) (**7a**) (5×10^{-5}%), non-regioregular poly(3-octylthiophene) (**7b**) (7×10^{-5}%), regioregular poly(3-hexylthiophene) (**8**) (1.5×10^{-4}%)[20] and regioregular poly[4-(octylphenyl)thiophene] (**9**) (2×10^{-4}%).[21] Fig. 6 shows the current–voltage plot for the LED made from poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**) and it can be seen that the turn-on voltage for passage of current is less than 4 V.



7a: R = C_6H_{13}
b: R = C_8H_{17}



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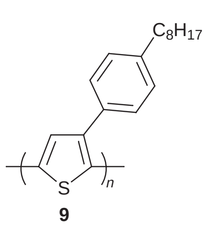

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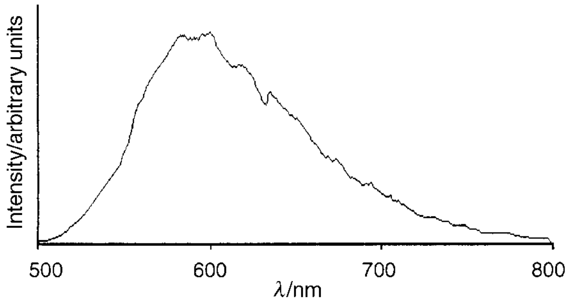

Fig. 5 Electroluminescence from an ITO/poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**)/Al LED.

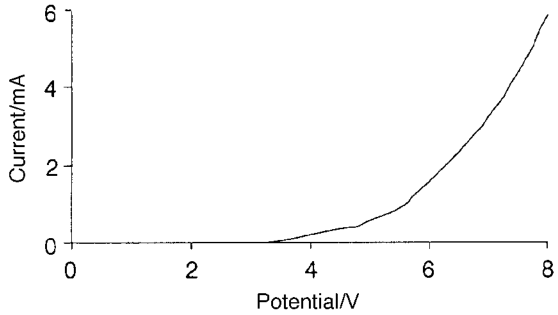

Fig. 6 Current–voltage curve for an ITO/poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**)/Al LED.

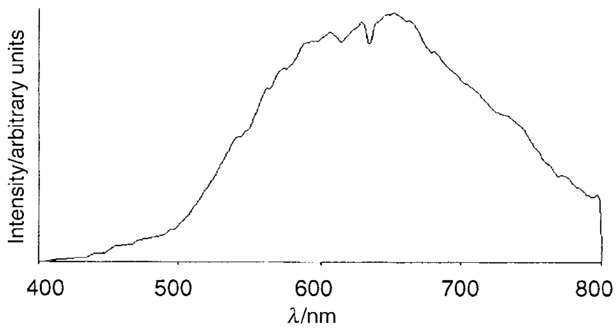

Fig. 7 Electroluminescence from an ITO/poly(octylthiophene)/**1b**/Al LED.

A bilayer device was fabricated consisting of ITO/poly(3-octylthiophene) (**7b**)/**1b**/Al. The electroluminescence emission maximum was at 646 nm (Fig. 7) and the quantum efficiency was 4.5×10^{-4}%. Poly(3-octylthiophene) (**7b**) itself showed its electroluminescence emission at 646 nm, but the efficiency was only 5×10^{-5}%. Thus, in the bilayer device the emission was from **7b** and electroluminescence efficiency was an order of magnitude greater than for poly(3-octylthiophene) (**7b**) itself. Polymer **1b** with an electron-withdrawing ester group directly attached to the ring has a high electron affinity. This affinity reduces the barrier to electron injection, making it easier to inject electrons into the polymer, and consequently causes a higher electroluminescent efficiency in the bilayer device than in a device using poly(3-alkylthiophene) (**7b**) alone. This increased electron affinity also allows **1b** to function as a more efficient electron transporting layer than **7b** alone. Fig. 8 shows the current–voltage plot for the LED made from ITO/poly(octylthiophene)/poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**)/Al and it can be seen that the turn-on voltage for passage of current is about 4–5 V with a sharp increase of the current at about 9 V.

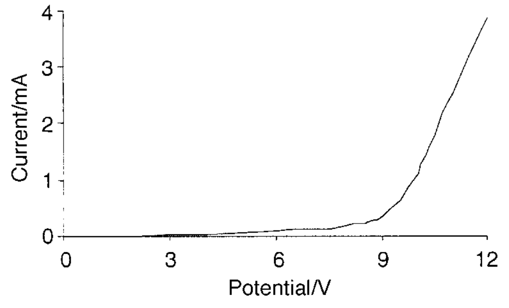

Fig. 8 Current–voltage curve for an ITO/poly(octylthiophene)/**1b**/Al LED.

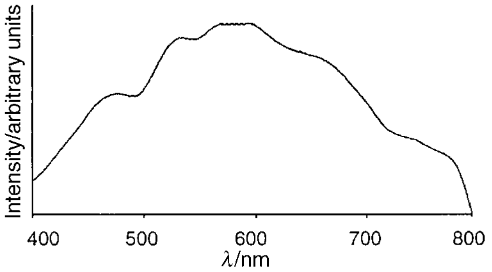

Fig. 9 Electroluminescence from an ITO/poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**)/Al LED.

The bilayer devices were prepared by spin-coating the poly(3-octylthiophene) from toluene solvent, drying the film and then spin-coating the poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**) from THF. The poly(3-octylthiophene) employed was of high molecular weight, was much less soluble in THF than toluene and dissolved in THF only very slowly. Thus, the two layers were separate and discrete, but there may have been a small amount of mixing of the polymers at the interface.

The electroluminescence emission maxima for LEDs made from **3a** and **3b** (ITO/**3a** or **3b**/Al) were at 590 nm and 600 nm for **3a** (Fig. 9) and **3b** and the quantum efficiencies were 8.5×10^{-3}% and 4.7×10^{-3}% for **3a** and **3b** respectively. Thus the regioregular polymers **3a** and **3b** had electroluminescence efficiencies about two to four times lower than those of **1a** and **1b**. Polymers **3a** and **3b** have a homogeneous regioregular structure which at first sight might appear to favour charge transport. However, compared to polymers **1a** and **1b**, the average conjugation length of polymers **3a** and **3b** is shorter owing to increased steric interactions between adjacent thiophene rings causing a larger dihedral angle in the head-to-head dyads. Therefore charge transport is hindered owing to less efficient conjugation along the chains and this might be the cause of the lower electroluminescence efficiency compared with polymers **1a** and **1b**. In addition, there might also be a somewhat higher barrier to charge injection. The devices based on polymers **3a** and **3b** lasted only 20 to 30 min (for both **3a** and **3b** devices, the operating voltage was 14 V), while the devices fabricated from polymers **1a** and **1b** lasted 15 to 25 h before failing (the operating voltages were 20 and 50 V for **1a** and **1b** respectively). The current–voltage curve for an ITO/poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**)/Al LED is shown in Fig. 10 and it can be seen that the turn-on voltage for passage of current is about 7–8 V with a sharp increase of the current at about 12 V. This higher turn on voltage is also consistent with shorter conjugation lengths and the more twisted nature of the polymer backbone compared to **1a**.

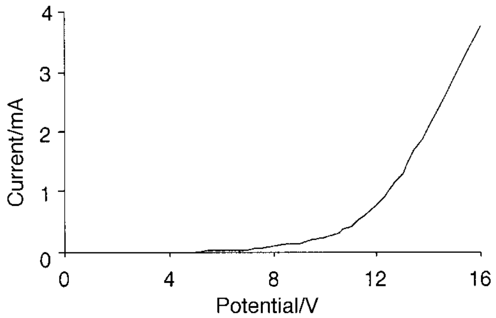

Fig. 10 Current–voltage curve for an ITO/poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a**)/Al LED.

Electrical conductivity studies

Attempts were made to study the electrical conductivity of cast films of polymers **1a** and **1b** by doping with 0.1% solutions of $FeCl_3$, $Cu(ClO_4)_2$, $NOPF_6$ (nitrosonium hexafluorophosphate), $NOBF_4$ (nitrosonium tetrafluoroborate), DDQ (2,3-dichloro-5,6-dicyanobenzo-1,4-quinone) and TCNQ (7,7,8,8-tetracyanoquinodimethane) solutions in nitromethane at room temperature for 10 to 15 min and with I_2 vapour at room temperature for 24 h. No color changes were observed for the polymer films. The conductivity of the films before and after doping was too low to be measured using our instrument ($<10^{-8}$ S cm^{-1}). Thus poly(3-hexyloxycarbonylthiophene-2,5-diyl) (**1a**) and poly(3-octyloxycarbonylthiophene-2,5-diyl) (**1b**) could not be oxidatively p-doped. Attempts were also made to reductively n-dope the polymers. The entire n-type doping procedure was carried out in a dry box. All the solvents were degassed (freeze–thaw) right before use. Polymer films were immersed in a sodium naphthalide solution in THF for 1 to 2 min. The color of the film changed from orange to dark brown–black. The polymer films became insoluble in THF. Obviously, a reaction occurred between the polymer films and the sodium naphthalide. However, the conductivity measurements showed that the film did not conduct ($\sigma = <10^{-8}$ S cm^{-1}).

Experimental

General

300 MHz NMR spectra were obtained on a Bruker MSL-300 spectrometer. ^{1}H NMR spectra were recorded at 300 MHz using TMS ($\delta = 0.00$) as internal reference. ^{13}C NMR spectra were recorded at 75 MHz using $^{13}CDCl_3$ ($\delta = 77.00$) as internal reference. All spectra were taken using $CDCl_3$ as solvent and reported in ppm relative to the internal references. 500 MHz ^{1}H NMR spectra were obtained on a JEOL Eclipse 500 instrument or from the University of Michigan on a Bruker AMX-500 spectrometer. Infrared spectra were recorded on a JASCO FT/IR-410 Fourier Transform Infrared instrument, using KBr pressed pellets (approximately 1 mg of sample in 100 mg of KBr) or neat liquid samples between NaCl plates and are reported in cm^{-1} with a resolution of 4 cm^{-1}. HPLC was performed on a Waters HPLC system, using a Waters Model 501 HPLC pump, a Lambda-Max Model 481 UV–VIS detector ($\lambda = 254$ nm), Maxima 820 Chromatography Software, and an Econosil C18 10U (10 μm) reversed-phase column (250 mm × 4.6 mm). Methanol was used as the eluent with a flow rate of 1.0 mL min^{-1}. Gel permeation chromatography (GPC) was carried out on a Waters GPC system, using a Waters Model 510 HPLC pump, a Model 490 multi-wavelength detector ($\lambda = 254$ nm), Millennium 2010 Software, and a serial combination of 10^3, 10^4, and 10^5 Å Ultrastyragel columns. THF was used as the eluent with a flow rate of 1.0 mL min^{-1}. The calibration curve was established using polystyrene standards with a molecular weight range of 800 to 9×10^5 g mol^{-1}. The molecular weights of polymer in THF were measured relative to the polystyrene standards. UV–VIS spectra were recorded on a Varian Cary 5E UV–VIS–NIR spectrophotometer or a Perkin-Elmer Lambda Array 3840 UV–VIS spectrophotometer. Samples were either polymer–THF solutions or polymer thin films cast on quartz cuvettes from polymer–toluene solutions. Elemental analyses were obtained on a Perkin-Elmer 2400 CHN elemental analyzer or determined by Texas Analytical Laboratories, Stafford, Texas. Melting points were measured using a Thomas-Hoover capillary melting point apparatus and were uncorrected. Fluorescence determinations were performed on a Perkin-Elmer Model 204 fluorescence spectrophotometer. All solvents were purified and dried prior to use according to standard procedures.[22] All monomers were shown to be >99% pure by

HPLC analysis. Cu and Zn powders were prepared by literature procedures.[23] Electroluminescence spectra were recorded using a Tracor-Northern 1710A Diode Array Spectrometer and the emission efficiencies were measured using a silicon photodiode.

Syntheses

Poly(alkyl thiophene-3-carboxylates) prepared by the Ullmann reaction: general procedure. Alkyl 2,5-dibromothiophene-3-carboxylate **2a** or **2b** (27 mmol),[3] 6.86 g (0.108 mol) of Cu powder, and 90 mL of dry DMF were put into a 250 mL one-necked flask in a dry box. The flask was removed from the dry box and equipped with a magnetic stirring bar and an air cooled condenser capped with a drying tube. The polymerization was carried out at 145 °C for 7 days. The mixture then was cooled, diluted with $CHCl_3$ to about 1500 mL, and filtered to remove excess Cu powder. The orange–red organic phase was washed with water (10 × 500 mL) and dried over $MgSO_4$. The $CHCl_3$ was removed with a rotary evaporator and a dark red polymer was obtained. Soxhlet extraction with methanol was performed for 48 hours to remove the low molecular weight material from the bulk polymer. After drying under vacuum at room temperature, a red solid was obtained.

*Poly(3-hexyloxycarbonylthiophene-2,5-diyl) (*__1a__*).*[3] 2.9 g (51%) of polymer **1a** was obtained as a red solid. 300 MHz ^1H NMR ($CDCl_3$) δ 7.93 (br, m), 7.91 (br, m), 7.87 (br, m), 7.85 (br, m), 7.66 (br, m), 7.59 (br, m), 7.58 (br, m), 7.56 (br, m), 4.31 (br, t, $J=7$ Hz), 4.15 (br, t, $J=6$ Hz), 1.76 (br, m), 1.56 (br, m), 1.34 (br, m), 1.24 (br, s), 0.87 (br, m); 500 MHz ^1H NMR ($CDCl_3$) δ 7.93 (br, m), 7.91 (br, m), 7.86 (br, m), 7.85 (br, m), 7.65 (br, m), 7.59 (br, m), 7.57 (br, m), 7.56 (br, m), 4.30 (br, m), 4.14 (br, m), 1.75 (br, m), 1.56 (br, s), 1.39 (br, s), 1.33 (br, s), 1.24 (br, m), 0.87 (br, m); ^{13}C NMR ($CDCl_3$) (^1H decoupled) δ 162.6, 162.5, 162.2, 162.1, 145–123 (at least 14 peaks), 65.5, 65.4, 65.2, 31.5, 28.5, 28.4, 25.7, 22.5, 14.0; IR (KBr) 3088, 2952, 2926, 2856, 1712, 1460, 1398, 1343, 1238, 1140, 987, 849, 770, 664 cm^{-1}; UV–VIS (THF) λ_{max} 410 nm (3.0 eV); film (cast from toluene) λ_{max} 434 nm (2.9 eV); fluorescence emission (THF) λ_{max} 565 nm; film (cast from toluene) λ_{max} 600 nm. GPC analysis of the THF polymer solution indicated that the polymer had a number average molecular weight ($\bar{M}_n$) of 6600 g mol^{-1} with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 2.5.

*Poly(3-octyloxycarbonylthiophene-2,5-diyl) (*__1b__*).*[3] 2.83 g (44%) of polymer was obtained as a red solid. 300 MHz ^1H NMR ($CDCl_3$) δ 7.93 (br, m), 7.91 (br, m), 7.87 (br, m), 7.85 (br, m), 7.66 (br, m), 7.59 (br, m), 4.30 (br, m), 4.14 (br, m), 1.75 (br, m), 1.55 (br, m), 1.22 (br, m), 0.87 (br, m); 500 MHz ^1H NMR ($CDCl_3$) δ 7.93 (br, m), 7.91 (br, m), 7.86 (br, m), 7.85 (br, m), 7.84 (br, m), 7.66 (br, m), 7.59 (br, m), 4.30 (br, m), 4.14 (br, m), 1.75 (br, m), 1.56 (br, m), 1.26 (br, m), 1.23 (br, m), 0.87 (br, m); ^{13}C NMR ($CDCl_3$) (^1H decoupled) δ 162.6, 162.5, 162.3, 162.2, 145–120 (at least 17 peaks), 65.5, 65.4, 65.2, 31.8, 29.2, 28.6, 28.5, 26.0, 22.6, 14.1; IR (KBr) 2962, 2924, 2846, 1712, 1654, 1462, 1400, 1346, 1258, 1198, 1150, 1122, 1095, 1021, 804, 770 cm^{-1}; UV–VIS (THF) λ_{max} 419 nm (3.0 eV); film (cast from toluene) λ_{max} 460 nm (2.7 eV); fluorescence emission (THF) λ_{max} 560 nm; film (cast from toluene) λ_{max} 610 nm. GPC analysis of the THF polymer solution indicated a number average molecular weight ($\bar{M}_n$) of 8800 g mol^{-1} with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 3.4.

Poly(alkyl thiophene-3-carboxylates) prepared by Rieke nickel reaction: general procedure. A 25 mL one-necked flask was charged with NiI_2 (1.563 g, 4.994 mmol), freshly cut lithium (0.080 g, 11 mmol), naphthalene (0.064 g, 0.50 mmol) and THF (10 mL), and the mixture was stirred vigorously at room temperature for 12 h under argon. To the precipitated black nickel powder alkyl 2,5-dibromothiophene-3-carboxylate **2a** or **2b** (2.0 mmol) in THF (5 mL) was added directly *via* a syringe. The mixture was refluxed for 60 h under argon. The reaction mixture was diluted with diethyl ether to 100 mL, and then filtered to remove the metal powder. The dark red organic phase was washed with water (3 × 50 mL) and dried over $MgSO_4$. The ether was removed with a rotary evaporator, and a dark red solid polymer was obtained. The polymer was extracted with methanol in a Soxhlet extractor for 48 h to remove the low molecular weight material and, after drying under vacuum at room temperature, a red solid was obtained.

*Poly(3-hexyloxycarbonylthiophene-2,5-diyl) (*__1a__ *from Rieke Ni).* 0.14 g (33%) of red polymer was obtained; ^1H NMR ($CDCl_3$) δ 8.18 (br, m), 8.04 (br, m), 7.93 (br, m), 7.91 (br, m), 7.90–7.80 (br, m), 7.60 (br, m), 7.59 (br), 7.58 (br, m) (there were also an additional 2 small br multiplet peaks at 7.66 and 7.64), 4.30 (br, m), 4.13 (br, m), 1.75 (br, s), 1.55 (br, s), 1.33 (br, m), 1.25 (br, m), 1.24 (br, m), 0.89 (br, m); ^{13}C NMR ($CDCl_3$) (^1H decoupled) δ 162.6, 162.5, 162.3, 145–120 (at least 11 peaks), 65.6, 65.4, 65.2, 65.1, 65.0, 31.4, 29.7, 28.7, 28.6, 28.4, 25.7, 22.5, 14.0; UV–VIS (THF) λ_{max} 420 nm (3.0 eV); film (cast from toluene) λ_{max} 457 nm (2.7 eV); fluorescence emission (THF) λ_{max} 560 nm; film (cast from toluene) λ_{max} 605 nm. GPC analysis of the THF polymer solution indicated a number average molecular weight ($\bar{M}_n$) of 3300 g mol^{-1} with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 1.9.

*Poly(3-octyloxycarbonylthiophene-2,5-diyl) (*__1b__ *from Rieke Ni).* 0.15 g (32%) of red polymer was obtained; ^1H NMR ($CDCl_3$) δ 8.18 (br, m), 8.03 (br, m), 7.93 (br, m), 7.86 (br, m), 7.66 (br, m), 7.60 (br, m), 4.30 (br, s), 4.13 (br, s), 1.75 (br, s), 1.55 (br, s), 1.27 (br, m), 1.22 (br, m), 0.86 (br, m); ^{13}C NMR ($CDCl_3$) (^1H decoupled) δ 162.6, 162.5, 162.3, 145–120 (at least 17 peaks), 65.6, 65.4, 65.2, 65.0, 31.8, 29.2, 28.6, 28.4, 26.0, 22.6, 14.1; UV–VIS (THF) λ_{max} 426 nm (2.9 eV); film (cast from toluene) λ_{max} 475 nm (2.6 eV); fluorescence emission (THF) λ_{max} 565 nm; film (cast from toluene) λ_{max} 620 nm, shoulder at 670 nm. GPC analysis of the THF polymer solution indicated that this polymer had a number average molecular weight ($\bar{M}_n$) 7200 g mol^{-1} with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 2.1.

Generation of organozinc halides from methyl 2,5-dibromothiophene-3-carboxylate and Rieke zinc. In a dry box, finely cut lithium (0.10 g, 15 mmol) and a catalytic amount (10 mol%) of naphthalene (0.19 g, 1.5 mmol) were weighed into a 50 mL one-necked round bottomed flask equipped with a magnetic stirring bar. The flask was sealed with a septum. Similarly, anhydrous $ZnCl_2$ (0.75 g, 5.5 mmol) was weighed into a 25 mL one-necked round bottomed flask. 7.5 mL of THF were added to the flask with the lithium and naphthalene. The solution was dark green. 12.5 mL of THF were added to the flask with $ZnCl_2$ and this was slowly transferred to the flask with the lithium and naphthalene *via* syringe (about 1.5 h). The reaction mixture was further stirred until the small lithium pieces were consumed and black zinc powder was precipitated out. Methyl 2,5-dibromothiophene-3-carboxylate (1.5 g, 5.0 mmol in 10 mL of THF) was then added *via* syringe to the newly prepared zinc at −78 °C. The mixture was stirred for 1 h at this temperature and allowed to warm up to room temperature. The mixture was then poured into a saturated aqueous NH_4Cl solution (10 mL) and extracted with diethyl ether (3 × 20 mL). The organic phase was washed with saturated NaCl (3 × 20 mL) and dried over $MgSO_4$. The diethyl ether was removed with a rotary evaporator. Naphthalene was removed from the mixture using column chromatography (silica gel, 1 × 8 inch) with ethyl acetate–hexane (1 : 75) as eluent and the resultant products methyl 2-bromothiophene-3-carboxylate (**4**) and methyl 2-bromothiophene-4-carboxylate (**5**) were obtained. ^{1}H NMR ($CDCl_3$) δ 7.99 (d, $J=1.5$ Hz), 7.47 (d, $J=1.5$ Hz), 7.36 (d, $J=5$ Hz), 7.24 (d, $J=5$ Hz), 3.89 (s), 3.86 (s).

2-Bromothiophene-4-carboxylic acid. 2-Bromothiophene-4-carboxylic acid was prepared essentially as described in the literature.[24] A solution of 23 g (0.14 mol) of bromine in 113 mL of glacial acetic acid was slowly added to a stirred solution of 19 g (0.15 mol) of thiophene-3-carboxylic acid in 175 mL of glacial acetic acid at room temperature. The mixture was stirred for 15 minutes and then poured into 1 L of cold water (ice bath). The mixture was filtered and a light yellow solid was obtained. The crude product was recrystallized from 1300 mL of water. 15 g (48%) of product **5** was obtained as white needles: mp 140–141 °C (lit.,[24] 117–118 °C; lit.,[25] 139–140 °C); Anal. Calcd. for $C_5H_3O_2SBr$: C, 29.01; H, 1.46; Found: C, 28.71; H, 1.13%; ^{1}H NMR ($CDCl_3$) δ 10.27 (very br s, 1H), 8.12 (d, $J=1$ Hz, 1H), 7.51 (d, $J=1$ Hz, 1H), ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 166.8, 135.8, 133.1, 130.4, 113.4.

Alkyl 2-bromothiophene-4-carboxylates: general procedure. 8.28 g (40.0 mmol) of 2-bromothiophene-4-carboxylic acid and 100 mL of $SOCl_2$ were refluxed for 6 hours. The excess $SOCl_2$ was removed under vacuum (water aspirator) to produce a light yellow solid. Then, 0.40 mol of ROH and 8 mL of dry pyridine were added to the flask dropwise through an addition funnel. The mixture was stirred for 6 h at 80 °C, cooled, poured into a 250 mL beaker with 60 g of ice and 80 mL of 1 M HCl, and stirred for a while. The solution was washed with diethyl ether (4 × 300 mL) and the organic phase was then washed with saturated $NaHCO_3$ (3 × 300 mL) and dried with K_2CO_3. The ethyl ether was removed with a rotary evaporator and a light yellow crude product was obtained and purified as described below.

Hexyl 2-bromothiophene-3-carboxylate. The crude product was distilled under vacuum to give 6.87 g (59%) of product as a pale yellow liquid; purity (HPLC) about 99%; bp 75–76 °C/0.05 mm Hg. Anal. Calcd. for $C_{11}H_{15}O_2SBr$: C, 45.37; H, 5.19; Found: C, 45.41; H, 5.03%; ^{1}H NMR δ 7.98 (d, $J=1$ Hz, 1H), 7.46 (d, $J=1$ Hz, 1H), 4.25 (t, $J=7$ Hz, 2H), 1.72 (quintet, $J=7$ Hz, 2H), 1.45–1.30 (m, 6H), 0.90 (t, $J=7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 161.6, 134.2, 133.6, 130.2, 112.8, 65.1, 31.4, 28.6, 25.6, 22.5, 14.0; IR (neat) 3108, 2959, 2929, 2858, 1719, 1528, 1467, 1422, 1378, 1227, 1175, 1094, 983, 927, 849, 735, 660 cm^{-1}.

Octyl 2-bromothiophene-3-carboxylate. The crude product was distilled under vacuum to give 8.29 g (65%) of product as a pale yellow liquid; purity (HPLC): >99%; bp 91–94 °C/0.05 mm Hg. Anal. Calcd. for $C_{13}H_{19}O_2SBr$: C, 48.91; H, 6.00; Found: C, 48.74; H, 5.88; ^{1}H NMR δ 7.98 (d, $J=1$ Hz, 1H), 7.46 (d, $J=1$ Hz, 1H), 4.25 (t, $J=7$ Hz, 2H), 1.72 (quintet, $J=7$ Hz, 2H), 1.45–1.30 (m, 10H), 0.88 (t, $J=7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 161.6, 134.2, 133.6, 130.2, 112.8, 65.1, 31.7, 29.2, 28.6, 26.0, 22.6, 14.0; IR (neat) 3109, 2954, 2926, 2855, 1721, 1528, 1467, 1422, 1405, 1378, 1229, 1175, 1095, 983, 959, 923, 849, 735, 660 cm^{-1}.

Dialkyl 2,2′-bithiophene-4,4′-dicarboxylates: general procedure. In a 10 mL one-necked flask were placed 22 mg (0.10 mmol) of $NiBr_2$, 0.20 g (0.76 mmol) of triphenylphosphine, 0.20 g (3.1 mmol) of zinc and 1 mL of DMF under argon and the mixture was stirred at 50 °C for 30 min. The color of the reaction mixture changed from orange to reddish brown and then 2.00 mmol of hexyl or octyl 2-bromothiophene-3-carboxylate in 1 mL of DMF was added *via* a syringe. The mixture was warmed to 80 °C and stirred for 24 h. The reaction mixture was cooled, diluted with $CHCl_3$ to 50 mL, and then filtered to remove the metal powder. The organic phase was washed with water (3 × 30 mL) and dried over $MgSO_4$. The $CHCl_3$ was removed with a rotary evaporator. Cold MeOH was added and the precipitate which formed was filtered to give a brown–yellow crude solid product which was purified as described below.

Dihexyl 2,2′-bithiophene-4,4′-dicarboxylate. The crude product (0.21 g) was purified using column chromatography (silica gel, 1 × 8 inch) with ethyl acetate–hexane (1 : 50) as eluent to give 0.18 g (43%) of a pale yellow solid product; purity (HPLC) >99%; mp 60–61 °C. Anal. Calcd. for $C_{22}H_{30}O_4S_2$: C, 62.53; H, 7.16; Found: C, 62.87; H, 7.22%; ^{1}H NMR δ 8.00 (d, $J=1$ Hz, 1H), 7.58 (d, $J=1$ Hz, 1H), 4.28 (t, $J=7$ Hz, 2H), 1.75 (quintet, $J=7$ Hz, 2H), 1.45–1.30 (m, 6H), 0.91 (t, $J=7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 162.4, 136.9, 134.6, 131.7, 124.6, 65.1, 31.4, 28.6, 25.6, 22.5, 14.0; IR (KBr) 3116, 3096, 3062, 2952, 2928, 2871, 2851, 1704, 1523, 1467, 1428, 1397, 1357, 1224, 1176, 1097, 1038, 984, 964, 908, 868, 844, 775, 751, 622, 467 cm^{-1}; UV–VIS (THF) λ_{max} 243 nm ($\varepsilon = 1.4 \times 10^4$), 303 nm ($\varepsilon = 9.9 \times 10^3$), two shoulders at 297 nm ($\varepsilon = 9.7 \times 10^3$) and 312 nm ($\varepsilon = 9.4 \times 10^3$).

Dioctyl 2,2′-Bithiophene-4,4′-dicarboxylate. The crude product (0.28 g) was purified using column chromatography (silica gel, 1 × 8 inch) with ethyl acetate–hexane (1 : 50) as eluent to give 0.24 g (50%) of a pale yellow solid product; purity (HPLC) >99%; mp 69–70 °C. Anal. Calcd. for $C_{26}H_{38}O_4S_2$: C, 65.24; H, 8.00; Found: C, 64.97; H, 7.78%; ^{1}H NMR δ 8.00 (d, $J=1$ Hz, 1H), 7.58 (d, $J=1$ Hz, 1H), 4.28 (t, $J=7$ Hz, 2H), 1.75 (quintet, $J=7$ Hz, 2H), 1.45–1.30 (m, 10H), 0.89 (t, $J=7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 162.4, 136.9, 134.6, 131.7, 124.6, 65.1, 31.8, 29.2, 28.7, 26.0, 22.6, 14.1; IR (KBr) 3121, 3060, 2953, 2915, 2870, 2847, 1709, 1523, 1475, 1403, 1363, 1228, 1173, 1102, 1035, 1018, 972, 941, 864, 845, 800, 772, 734, 621, 486 cm^{-1}; UV–VIS (THF) λ_{max} 243 nm ($\varepsilon = 1.4 \times 10^4$), 303 nm ($\varepsilon = 9.7 \times 10^3$), two shoulders at 300 nm ($\varepsilon = 9.6 \times 10^3$) and 310 nm ($\varepsilon = 9.3 \times 10^3$).

Dialkyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylates (6a and 6b): general procedure. A solution of 0.144 g (0.90 mmol) of bromine in 6 mL of $CHCl_3$ was added slowly to a stirred solution of 0.300 mmol of dihexyl or dioctyl 2,2′-bithiophene-4,4′-dicarboxylate and 6 mL of $CHCl_3$ in a 25 mL round-bottomed flask at room temperature. The mixture was warmed to 60 °C for an additional 10 h and then poured into 50 mL of cold water (ice bath), stirred for a while and Na_2SO_3 was added to react with excess bromine. The solution was washed with $CHCl_3$ (3 × 50 mL), and the organic phase was then washed with water (3 × 30 mL) followed by saturated NaCl (2 × 50 mL) and dried over $MgSO_4$. The $CHCl_3$ was removed with a rotary evaporator and a light yellow crude solid was obtained and purified as described below.

*Dihexyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylate (**6a**).* The crude product (0.12 g) was purified using column chromatography (silica gel, 1 × 8 inch) with ethyl acetate–hexane (1 : 100) as eluent to give 0.104 g (60%) of a white solid product; purity (HPLC) >99%; mp 87–88 °C. Anal. Calcd. for $C_{22}H_{28}O_4S_2Br_2$: C, 45.53; H, 4.86; Found: C, 45.37; H, 4.82%; ^{1}H NMR δ 7.36 (s, 1H), 4.30 (t, $J=7$ Hz, 2H), 1.76 (quintet, $J=7$ Hz, 2H), 1.45–1.30 (m, 6H), 0.91 (t, $J=7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 161.5, 135.2, 132.2, 125.9, 119.1, 65.5, 31.4, 28.6, 25.7, 22.5, 14.0; IR (KBr) 3095, 3066, 2954, 2927, 2890, 2869, 1729, 1522, 1479, 1423, 1318, 1221, 1159, 1060, 1017, 974, 919, 890, 852, 828, 766, 721, 553, 477, 445 cm^{-1}; UV–VIS (THF) λ_{max} 243 nm ($\varepsilon = 1.6 \times 10^4$), 324 nm ($\varepsilon = 1.4 \times 10^4$).

*Dioctyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylate (***6b***)*. The crude product (0.17 g) was purified using column chromatography (silica gel, 1 × 8 inch) with ethyl acetate–hexane (1 : 100) as eluent to give 0.095 g (50%) of a white product; purity (HPLC) >99%; mp 93–94 °C. Anal. Calcd. for $C_{26}H_{36}O_4S_2Br_2$: C, 49.06; H, 5.70; Found: C, 48.80; H, 5.60%; ^1H NMR 7.36 (s, 1H), 4.30 (t, $J = 7$ Hz, 2H), 1.76 (quintet, $J = 7$ Hz, 2H), 1.50–1.20 (m, 10H), 0.89 (t, $J = 7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) (^1H decoupled) δ 161.5, 135.2, 132.1, 125.9, 119.1, 65.5, 31.8, 29.7, 29.2, 28.6, 26.0, 22.6, 14.1; IR (KBr) 3092, 3062, 2956, 2925, 2892, 2849, 1729, 1521, 1479, 1423, 1382, 1319, 1222, 1159, 1081, 1026, 975, 918, 828, 766, 717, 477 cm^{-1}; UV–VIS (THF) λ_{max} 243 nm ($\varepsilon = 1.6 \times 10^4$), 323 nm ($\varepsilon = 1.4 \times 10^4$).

Poly(4,4′-bis(alkoxycarbonyl)[2,2′-bithiophene]-5,5′-diyl)s (3a and 3b): general procedure. 0.156 mmol of dialkyl 5,5′-dibromo-2,2′-bithiophene-4,4′-dicarboxylate **6a** or **6b**, 40 mg (0.63 mmol) of Cu powder, and 0.5 mL of dry DMF were charged into a 5 mL one-necked flask equipped with a magnetic stirring bar and a long air condenser capped with a drying tube. The mixture was stirred at 145 °C for 2 days, cooled, diluted with $CHCl_3$ to 100 mL, and then filtered to remove excess Cu powder. The organic phase was washed with water (5 × 50 mL) followed by saturated NaCl (2 × 50 mL) and dried over $MgSO_4$. The excess $CHCl_3$ was removed with a rotary evaporator, and a solid yellow–orange compound was obtained. Soxhlet extraction with methanol was carried out for 48 hours to remove the low molecular weight material. After drying under vacuum at room temperature, an orange solid was obtained.

*Poly(4,4′-bis(hexyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (***3a***)*. 30 mg (41%) of an orange solid compound was obtained. Anal. Calcd. for $C_{22}H_{28}O_4S_2$: C, 62.83; H, 6.71; S, 15.25; Found: C, 62.51; H, 6.74; S, 15.20%; 300 MHz ^1H NMR 7.65 (br, s) (there were also three additional small br singlet peaks at 8.04, 7.63, 7.61), 4.14 (br, t, $J = 6$ Hz) (there was also an additional small br triplet peak at 4.29, $J = 7$ Hz), 1.56 (br, m), 1.24 (br, m), 0.86 (br, t, $J = 6$ Hz); 500 MHz ^1H NMR ($CDCl_3$) δ 7.65 (br, s) (there were also two additional small br singlet peaks at 7.64 and 7.63 and two additional small br doublet peaks at 8.03 and 7.61, both with $J = 1$ Hz), 4.14 (br, t, $J = 6$ Hz) (there was also an additional small br triplet peak at 4.29, $J = 8$ Hz), 1.55 (br, t, $J = 6$ Hz), 1.23 (br, m), 0.86 (br, t, $J = 6$ Hz) (there were also four additional small br multiplet peaks at 1.75, 1.34, 0.91, 0.83); ^{13}C NMR ($CDCl_3$) (^1H decoupled) δ 162.2, 138.1, 136.0, 133.0, 126.6, 65.3, 31.5, 28.5, 25.7, 22.6, 14.0; IR (KBr) 3082, 2959, 2926, 2855, 1713, 1465, 1399, 1345, 1218, 1139, 985, 846, 771 cm^{-1}; UV–VIS (THF) λ_{max} 387 nm (3.2 eV); film (cast from toluene) λ_{max} 377 nm (3.3 eV); fluorescence emission: solution (THF) λ_{max} 530 nm; film (cast from toluene) λ_{max} 560 nm. GPC analysis indicated a number average molecular weight ($\bar{M}_n$) of 7900 g mol^{-1} with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 1.6.

*Poly(4,4′-bis(octyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (***3b***)*. 33 mg (44%) of an orange solid compound was obtained. Anal. Calcd. for ($C_{26}H_{36}O_4S_2$): C, 65.51; H, 7.61; S, 13.45; Found: C, 65.26; H, 7.68; S, 13.24%; 300 MHz ^1H NMR δ 7.65 (br, s) (there were also three additional small br singlet peaks at 8.04, 7.63, 7.61), 4.14 (br, t, $J = 6$ Hz) (there was also an additional small br triplet peak at 4.29, $J = 6$ Hz), 1.55 (br, m), 1.23 (br, m), 0.86 (br, t, $J = 5$ Hz); 500 MHz ^1H NMR ($CDCl_3$) δ 7.65 (br, s) (there were also four additional small br singlet peaks at 8.04, 7.64, 7.63, 7.61 and four additional very small br singlet peaks between 7.4–7.6), 4.14 (br, t, $J = 6$ Hz) (there was also an additional small br triplet peak at 4.29, $J = 8$ Hz), 1.55 (br, m), 1.23 (br, m), 0.86 (br, t, $J = 7$ Hz) (there were also three additional small br multiplets at 1.75, 1.43, 0.89); ^{13}C NMR ($CDCl_3$) (^1H decoupled) δ 162.1, 138.0, 136.0, 133.0, 126.5, 65.3, 31.8, 29.3, 28.5, 26.0, 22.6, 14.1; IR (KBr) 2955, 2925, 2855, 1713, 1465, 1398, 1345, 1215, 1132, 978, 846, 767, 673 cm^{-1}; UV–VIS (THF) λ_{max} 389 nm (3.2 eV); film (cast from toluene) λ_{max} 382 nm (3.2 eV); fluorescence emission solution (THF) λ_{max} 540 nm; film (cast from toluene) λ_{max} 560 nm. GPC analysis indicated a number average molecular weight ($\bar{M}_n$) of 11000 g mol^{-1} with a polydispersity ($\bar{M}_w/\bar{M}_n$) of 2.3.

Device fabrication

Sputtered ITO coated glass plates, 300 × 300 × 1.1 mm size, were purchased from Photran Corporation. The ITO film thickness and surface roughness were measured to be 50–60 nm and 2–5 nm respectively. The surface resistivity was specified to be 10 Ω per sq. The glass plates were cut into 25 × 25 × 1.1 mm pieces with a diamond scribe for device fabrication. Substrate preparation and device fabrication steps such as photolithography and metal electrode deposition were performed inside Class 10 and Class 100 clean rooms. Polymer films were cast in an argon filled inert atmosphere glove box.

LED Characterization

Contacts to positive and negative electrodes were formed using conductive silver epoxy paint purchased from Delta Technologies. The contacts were dried for at least 8 h before making measurements. Current–voltage characteristics of devices were measured using a Keithley 236 Current/Voltage Source-Measure unit. A single device of area 1 × 1 mm was used for this purpose. Current–voltage sweeps were collected using the ‘step mode’ with a step height of 0.5 V and a time-period of 2 s. EL spectra were recorded using a Tracor-Northern 1710A diode-array spectrometer using a single device of area 4 × 4 mm. Light intensity measurements were made with a calibrated silicon photodiode attached to a Newport 1830-C power meter. The measured values were multiplied by π to correct for the flux per unit solid angle leaving the device directly in the forward direction. Film thickness was measured using a Tencor-Northern Alpha Step profilometer.

Metal electrode deposition

Thin metal films for the negative electrodes were deposited by vacuum evaporation which was carried out in a Veeco Thermal Evaporator under high vacuum of the order of 1×10^{-6} to 8×10^{-7} torr. Aluminum, purchased from Cerac Metals, Inc., was 99.999% pure.

Conclusions

An improved synthesis of poly(3-hexyl- and 3-octyloxycarbonylthiophene-2,5-diyl) (**1a** and **1b**) has been worked out. It provides material with molecular weights, $\bar{M}_n = 6700$ and 9400 ($\bar{M}_w/\bar{M}_n = 2.5$ and 3.2), $\lambda_{max} = 434$ and 460 nm for films cast from toluene, λ_{max} for fluorescence emission (film) = 600 and 610 nm and for electroluminescence $\lambda_{max} = 600$ and 615 nm, for **1a** and **1b** respectively. The ^1H NMR spectra required that pentads be considered to explain the spectra. That is the four nearest neighbours to a given ring influence the ^1H NMR chemical shift of the hydrogen in that ring. Electroluminescence efficiencies of 0.016% and 0.018% were observed for devices made from **1a** and **1b** respectively. A bilayer device of ITO/poly(3-octylthiophene)/**1b**/Al emitted at 646 nm, where poly(3-octylthiophene) emits. The efficiency was 4.5×10^{-4}% and this was an order of magnitude greater than that for poly(3-octylthiophene) itself (5×10^{-5}%).

Regioregular (HH–TT) poly(4,4′-bis(hexyl- and octyloxycarbonyl)[2,2′-bithiophene]-5,5′-diyl) (**3a** and **3b**) were also prepared *via* the Ullmann reaction and provided material whose molecular weights were $\bar{M}_{\mathrm{n}} = 7900$ and 11000, respectively. Films of **3a** and **3b** were yellow in color and showed $\lambda_{\mathrm{max}} =$ 377 and 381 nm, respectively, about 55–80 nm blue shifted compared with **1a** and **1b**. This is due to the large rotational barrier in the HH dyads. Polymers **3a** and **3b** showed bright fluorescence and electroluminescence at 590 nm and 600 nm, respectively. The electroluminescence efficiencies were 8.5×10^{-3}% and 4.7×10^{-3}% for **3a** and **3b**, respectively. Many of the differences in the behavior of **1a** and **1b** compared with **3a** and **3b** were ascribed to the greater number of head-to-head linkages in the regioregular polymers **3a** and **3b** which gives rise to shorter conjugation lengths.

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