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Phenylene-functionalized polythiophene derivatives for light-emitting diodes: their synthesis, characterization and properties†

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The design, synthesis and characterization of a new series of conjugated polymers, poly[(3-(4′-*n*-butylphenyl)thiophene-2,5-diyl)(2,5-dialkoxy-1,4-phenylene)(4-(4′-*n*-butylphenyl)thiophene-2,5-diyl)] are described in this contribution. Three polymers modified by phenyl groups have been successfully synthesized *via* $FeCl_3$-oxiditive polymerization. The well-defined structure of the polymers is fully verified by elemental analysis, FT-IR, and ^1H and ^{13}C NMR spectroscopy. All polymers show good thermal stability and solubility in common organic solvents. The absolute photoluminescence (PL) efficiencies of the polymers in the neat film can be up to 11%. The electrochemical properties of the polymers indicate that their HOMO and LUMO energy levels can be adjusted by means of the aromatic groups both in the side chain and the backbone structure. Yellowish green electroluminescence is achieved from single-layered polymer light-emitting diodes (PLEDs) with the configuration ITO/polymer/Ca or Al.

Introduction

Conjugated polymers exhibit great potential for electronic and photonic applications because they combine the processing and mechanical advantages of polymers with the electronic, optical and physical properties of metals or semiconductors.[1] In particular, enormous efforts have been made toward the development of conjugated polymers as light-emitting materials since the first discovery of electroluminescence (EL) from poly(*p*-phenylenevinylene) (PPV).[2–5] So far, a wide range of conjugated polymer systems, including poly(*p*-phenylenevinylene) (PPV),[4–7] poly(*p*-phenylene) (PPP),[8] polyfluorene (PF),[9–12] polythiophene (PT)[13–15] and their derivatives, have been investigated as active materials in PLEDs.

During the past two decades, intensive studies have been devoted to the synthetic methodology, structure characterization, electrochemical properties, stability, and electrical conductivity of polythiophene derivatives (PTs).[13–18] However, the low PL quantum efficiency in the solid state (typically 1–3%) and poor EL performance of processable polythiophenes (PTs) have limited their application as emissive materials in PLEDs. The low PL efficiency of PTs could be attributed to the intersystem crossing of excitons from the singlet to the triplet state and the intrinsic features of the electronic structure of PTs.[19,20] Therefore, there is still considerable interest in introducing some special functional groups to modify processable polythiophenes to achieve high PL quantum efficiency and balance of charge transporting.

Most recently, it has been demonstrated that the PL efficiency could be significantly increased from a few percent to over 30% by modifying the backbone structure or/and the side chain of thiophene-containing oligomers and polymers.[19–27] The aromatic groups modifications are efficient in improving the PL efficiency, tuning the optical properties and adjusting the HOMO and LUMO energy levels of the resulting polymers.

In this work, we present the design, synthesis, characterization and properties of a series of conjugated polymers, *i.e.*, symmetrically substituted polymers, poly[(3-(4′-*n*-butylphenyl)thiophene-2,5-diyl)(2,5-bis(decyloxy)-1,4-phenylene)[(4-(4′-*n*-butylphenyl)thiophene-2,5-diyl)] (PPTDOPPT, **4a**), poly[(3-(4′-*n*-butylphenyl)thiophene-2,5-diyl)(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)(4-(4′-*n*-butylphenyl)thiophene-2,5-diyl)] (PPTEHOPPT, **4c**),[27] and asymmetrically substituted polymer, poly[(3-(4′-*n*-butylphenyl)thiophene-2,5-diyl)(2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylene)(4-(4′-*n*-butylphenyl)thiophene-2,5-diyl)] (PPTEHMOPPT, **4b**), which are composed of phenylene moieties and phenylene-substituted thiophene moieties along the backbone, to examine the effect of substitution on polymer structure and ultimately their physical, optical, and electrochemical properties.

The pendant phenylene ring at the 3-position of the thiophene ring is expected to act as a molecular bumper to separate the polymer chains and thus reduce the intersystem crossing of excitons. It also allows us to control the connection manner between two adjacent thiophene rings as a defined head-to-head pattern. The head-to-head conformation makes the polymer chains highly twisted. Furthermore, the 4-butylphenyl group on the thiophene ring can activate the thiophene ring more effectively than an alkyl group to yield polymers with higher molecular weights.[28] We also investigate the effect of the phenylene groups on the backbone on improvement of the PL quantum efficiency and the adjustment of the optical properties and the HOMO and LUMO energy levels of the resulting polymers.

Through symmetrically and asymmetrically incorporating long flexible alkoxy side chains onto the phenylene moiety of the polymer backbone, we could examine the effect of the side chain, as well as the symmetry of the repeat unit on the physical and electrical properties of the resulting polymers. Other important effects of these alkoxy side chains are not only to give good solubility to the polymers, which is essential for electroluminescence (EL) materials, but also to improve the PL quantum yields of the desired polymers.[23,25]

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†Electronic supplementary information (ESI) available: experimental details for the preparation of compounds **2**, **3a–c** and **4a–c**. See http://www.rsc.org/suppdata/jm/b1/b103717j/

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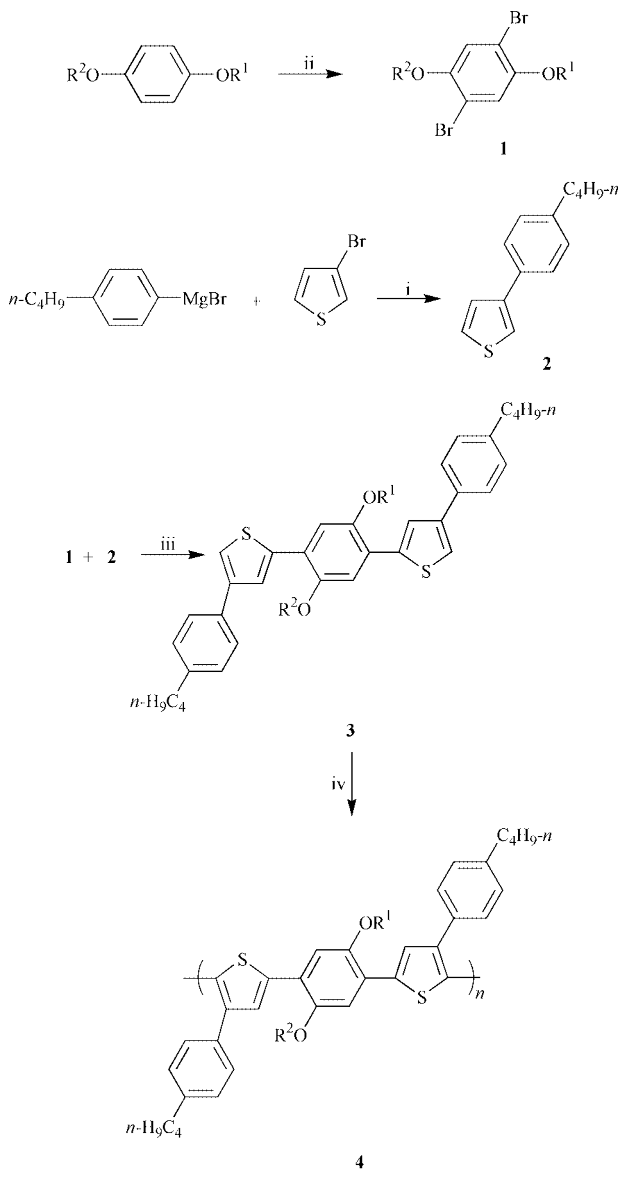

a: $R^1 = R^2 = C_{10}H_{21}$-n; **b**: $R^1 = CH_3$, $R^2 = EH$; **c**: $R^1 = R^2 = EH$

Scheme 1 The synthetic route to the polymers. *Reagents and conditions*: (i) Mg, Ni(dppp)Cl$_2$, THF; (ii) bromine, I$_2$; (iii) n-BuLi, diisopropylamine, ZnCl$_2$, Pd(PPh$_3$)$_4$, THF; (iv) FeCl$_3$, CHCl$_3$, 0 °C–rt.

Results and discussion

Preparation of polymers

The approach to poly[(3-(4′-n-butylphenyl)thiophene-2,5-diyl)-(2,5-dialkoxy-1,4-phenylene)(4-(4′-n-butylphenyl)thiophene-2,5-diyl)] is outlined in Scheme 1.

The starting material, 3-(4-n-butylphenyl)thiophene (**2**), is prepared by the Grignard coupling reaction between 4-n-butylphenylmagnesium bromide and 3-bromothiophene employing Ni(dppp)Cl$_2$ as the catalyst. Alkoxy substituents are introduced onto the benzene ring through the use of the Williamson ether route from hydroquinone for symmetric disubstitution and 4-methoxyphenol for asymmetric substitution.[29] The derivatives with long alkoxy side chains were liable to be selectively brominated with bromine at the 2 and 5 positions of the phenyl ring.

The coupling reaction between an organic halide and excess organic zinc chloride compound is employed to give the monomers according to our previous papers.[23–27] 4-(4-n-Butylphenyl)-2-thienylzinc chloride is prepared by the lithiation of the 3-(4-n-butylphenyl)thiophene and following the transmetallation reaction with anhydrous zinc chloride in THF. The coupling reaction between 4-(4-n-butylphenyl)-2-thienylzinc chloride and 1,4-dialkoxy-2,5-dibromobenzene (**1**) in the presence of tetrakis(triphenylphosphine)palladium(0) gives the monomers (**3**).

The oxidative polymerizations of the monomers using ferric chloride were carried out in dry chloroform. However, the crude polymers should be fully dedoped by ammonium hydroxide in order to avoid the negative effect of FeCl$_3$ residues on the performance of the polymers as emissive materials.[30,31] After fully dedoping and precipitating, the solids collected by filtration were washed with acetone for 2 days and extracted with chloroform in a Soxhlet. After the solvent was evaporated, the polymers were obtained as yellow solids. All the polymers showed good solubility in common organic solvents such as chloroform, THF, toluene and xylene. The structure and the purity of both monomers and polymers were confirmed by ^{1}H and ^{13}C NMR spectroscopes, FT-IR and elemental analyses. The molecular weights were measured by means of gel permeation chromatography (GPC) using THF as eluent and polystyrene as standard. A summary of the molecular weights is listed in Table 1. In comparison with our previous reports,[23,25] this series of polymers has much higher molecular weights, which shows that the phenylene group at the 3-position can activate the thiophene ring more effectively than alkyl groups.

Basic characterization

A comparison between the ^{1}H NMR spectra of monomer **3c** and polymer **4c** is shown in Fig. 1 as representative. In the ^{1}H NMR spectrum of monomer **3c**, the singlet peak at 7.29 ppm is assigned to two protons at the phenylene ring of the backbone. Two other doublet peaks at 7.57 and 7.23 ppm with a coupling constant of 8.07 Hz are consistent with the resonance of the adjacent protons at the phenylene rings of the side chain. In the aromatic region, the remaining two doublet peaks centered at 7.81 and 7.42 ppm with a coupling constant of 1.3 Hz are attributed to the protons on the thiophene rings. Since the coupling constant is much lower than that of the adjacent protons (normally about 5.2 Hz) at the thiophene ring, it demonstrated that the two doublet peaks result from the resonance of the protons at the 3 and 5-positions of the

Table 1 Basic properties of three polymers

Polymers	$M_n \times 10^4$	$M_w \times 10^4$	Polydispersity	T_d/°C)	T_g/°C
4a	8.23	18.0	2.19	350	85
4b	6.85	10.4	1.51	400	135
4c	4.36	7.34	1.68	350	90

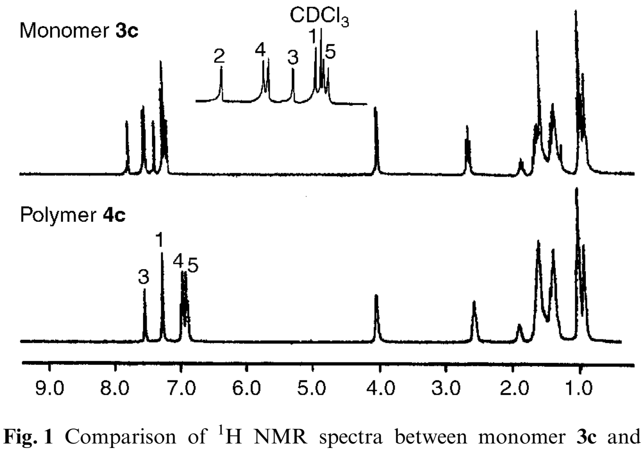

Fig. 1 Comparison of ^{1}H NMR spectra between monomer **3c** and polymer **4c**.

thiophene ring. The low coupling constant is due to the far distant coupling resonance between these two protons. These results prove that we have successfully confined the coupling reaction between the 3-(4-*n*-butylphenyl)thiophene and the substituted 1,4-dibromobenzenes at the 5-positions of the thiophene rings with high selectivity ensuring the high regioregularity of the resulting polymers.

After polymerization, besides the two doublet peaks assigned to the protons on the side chain phenylene, only two singlet peaks are observed, which are attributed to the resonance of the protons at the 3 position of the thiophene ring and on the backbone phenylene respectively. The chemical shift of the proton on the thiophene ring is increased by 0.12 ppm after the polymerization because of the enhancement of π-delocalization. On the contrary, the chemical shifts of the two protons of the *n*-butylphenyl ring decrease. The reason for the phenomenon is that after the polymerization, the thiophene rings have a larger electron donating effect towards the 4-*n*-butylphenyl group. Thus the electron density of the phenyl ring increases and the resonances of these two protons on the *n*-butylphenyl ring shift to higher field. Moreover, because the C_3-H is in an *ortho* position relative to the thiophene rings, it is more affected than the C_5-H, which is *meta* relative to the thiophene ring. Hence, the chemical shift of C_3-H decreases 0.60 ppm, which is larger than that of C_5-H (0.33 ppm).

Compared with the spectrum of the monomer **3c**, the signal corresponding to C_2-H in the monomer completely disappears after the polymerization, which is caused by proton elimination from the 5 and 5′ monomer position during polymerization. The absence of any residue of C_2-H demonstrates that all the polymers have high regioregularity of head-to-head linkage between two adjacent thiophene rings.

The thermal stability of polymers was studied using thermogravimetric analyses (TGA). All the polymers exhibited the onset of degradation above 300 °C with no weight loss at lower temperature. Table 1 also shows the onsets of decomposition (T_d) and glass transition temperatures (T_g) studied by differential scanning calorimetry (DSC). All the polymers have glass transition temperatures higher than 80 °C. The glass transition temperature of polymer **4b** is much higher than that of polymer **4a** and **4c**, which agrees with the fact that the temperature of glass transition decreases as the length of the side chain increases.

Optical properties

The optical properties of the polymers were investigated by absorption and photoluminescence (PL) spectroscopy. Films of the polymers were prepared onto quartz plates or onto micro slides by spin-casting from their solutions in xylene (1.5% w/v). Under ultraviolet light irradiation, the films emitted intense fluorescence of a yellowish green colour. The absorption and photoluminescence spectra of the polymers measured from the films are shown in Fig. 2. There are two peaks in the absorption spectra of the solutions and the films of the polymers. One is due to the $\pi - \pi^*$ transition of delocalized π electrons along the backbone and the other is due to the conjugation of the side chain. The peak wavelengths of the spectra and the $\pi - \pi^*$ band gaps of the polymers estimated from the absorption onset wavelengths are summarized in Table 2. Fig. 2 shows that the absorption maxima of polymer films are about 430–440 nm. According to Andersson *et al.*, the maximal absorption of the film of regioregular poly[3-(4-octylphenyl)thiophene] occurs at 493 nm.[28] Compared with poly[3-(4-octylphenyl)thiophene] the maxima of polymers **4** are blue-shifted up to 50–60 nm. This shift is attributed to the insertion of the phenylene ring into the polythiophene backbone since it induces a larger torsion angle between the thiophene and the phenyl rings and between the two adjacent head-to-head thiophene rings, and therefore lowers the conjugated length. The absorption and PL spectra of polymers **4** are quite similar to those of poly[(4-hexylthiophene-2,5-diyl)(2,5-bis(decyloxy)-1,4-phenylene)(4-hexylthiophene-2,5-diyl).[23,25] It seems that the phenylene group at the side chain might not enhance the conjugation length of the resulting polymers compared with the alkyl groups.

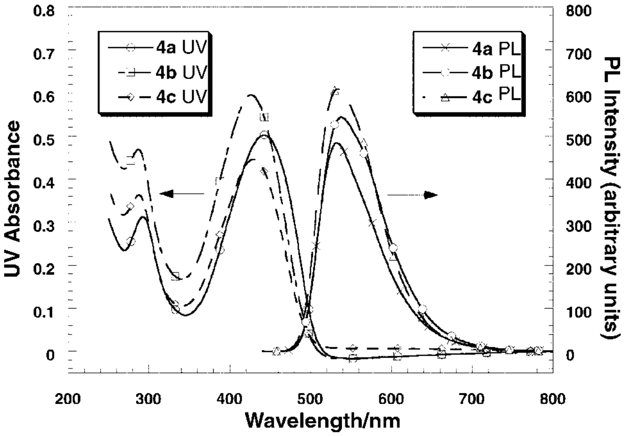

Fig. 2 Spectra of UV-Vis absorption and photoluminescence spectra of the polymer films.

The absorption spectra between the film and the solution of every polymer are quite similar. It is indicative of the lack of polymer interchain interaction even in the film states. The results prove that the insertion of a 4-*n*-butylphenyl group onto the 3-postion of the thiophene ring could obviously separate the polymer chains. It might reduce the opportunities for exciton transfer between chains and thus enhance the PL efficiency of the polymers.

The onsets of absorption, which correspond to an approximation of the band gaps, are calculated to be 2.36 eV for polymer **4a**, 2.35 eV for polymer **4b** and 2.38 eV for **4c**. It is shown that the band gaps of the three polymers are almost the same. The pendant phenyl groups influence the coplanarity of the polymer backbone due to the steric hindrance of the pendant groups. In addition, the phenyl groups conjugated with the polymer backbone may decrease the band gap. These two effects are opposite on the band gap of the polymer. By comparison with the bandgap of poly[(4-hexylthiophene-2,5-diyl)-(2,5-bis(decyloxy)-1,4-phenylene)(4-hexylthiophene-2,5-diyl)], 2.36 eV, and that of poly[(4-cyclohexylthiophene-2,5-diyl)(2,5-bis(decyloxy)-1,4-phenylene)(4-cyclohexylthiophene-2,5-diyl)], 2.48 eV, it indicates that the phenylene group on the side chain does not enhance the conjugation of the whole molecule. However, the phenylene group in the backbone still plays the most important role in the conjugation length.

The absolute PL quantum efficiencies of the polymers in neat films are measured in an integrated sphere at room temperature in air following the procedure described by Greenham *et al.*

Table 2 Optical and electrochemical properties of the polymer films

Polymers		**4a**	**4b**	**4c**
Abs. λ_{max}/nm		442, 292	426, 286	429, 287
Abs. λ_{onset}/nm (band gap/eV)		525 (2.36)	528 (2.35)	522 (2.38)
PL λ_{max}/nm		532	538	533
PL quantum yield (%)		11 ± 2	12 ± 2	11 ± 2
p-doping	E_{onset}/V	0.66	0.64	0.73
	E_{pa}/V	0.79	0.79	0.81
	E_{pc}/V	0.62	0.67	0.74
n-doping	E_{onset}/V	−1.65	−1.64	−1.64
	E_{pc}/V	−1.73	−1.79	−2.09
	E_{pa}/V	−1.64	—	—
Energy levels/eV	HOMO	5.06	5.04	5.13
	LUMO	2.75	2.76	2.79
Band gap/eV		2.31	2.28	2.34

using an argon ion laser line of 358 nm as the excitation source.[32] The results are also shown in Table 2. It shows that the absolute PL quantum efficiencies of the polymer films are over 10%, which are higher than those of normal conjugated polymers based on thiophenes. Although it proves that introducing the phenylene ring onto the polythiophene is a useful approach in increasing the PL quantum efficiency of thiophene-based polymers, the PL quantum efficiencies of polymers **4** are about 60–70% lower than that of poly[(4-hexylthiophene-2,5-diyl)(2,5-bis(decyloxy)-1,4-phenylene)(4-hexylthiophene-2,5-diyl)], and 30% lower than that of poly[(4-cyclohexylthiophene-2,5-diyl)(2,5-bis(decyloxy)-1,4-phenylene)(4-cyclohexylthiophene-2,5-diyl)]. It could be attributed to the change in the supramolecular organization effected by the aromatic groups at the side chain of the thiophene ring.

Electrochemical properties

The redox behavior as well as the HOMO and LUMO energy levels of the polymers were investigated by cyclic voltammetry (CV) in an electrolyte consisting of a solution of 0.10 M tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) in acetonitrile. The cyclic voltammograms of the polymers are displayed in Fig. 3. In the cyclic volatmmogram of polymer **4a**, for example, it shows a reversible p-doping process and a partially reversible n-doping process. On sweeping the polymer anodically, the oxidation process of polymer **4a** onsets at 0.66 V and gives a sharp oxidation peak at 0.79 V. The re-reduction peak appears at 0.62 V. In the cathodic scan, the reduction onsets at -1.57 V. The cathodic peak is at -1.65 V with a corresponding re-oxidation peak at -1.64 V. The electrochemical data of the polymers obtained from their cyclic voltammograms are summarized in Table 2. The p-doping onset potential of polymer **4c** (0.73 V) is 0.13 V higher than that of poly[(4-hexylthiophene-2,5-diyl)(2,5-bis(decyloxy)-1,4-phenylene)(4-hexylthiophene-2,5-diyl)] (0.60 V) reported earlier.[23] The increase of the oxidative potential may be attributed to the electronegativity of the polymer main chain resulting from the phenylene ring attached to the thiophene rings.

The onset potentials of n-doping and p-doping processes can be used to estimate the HOMO and LUMO values of a conjugated polymer. According to the equation reported by Li *et al.* and deLeeuw *et al.*,[34,35] $E_{\mathrm{LUMO}} = [E^{\mathrm{red}}_{(\mathrm{onset}\ vs.\ \mathrm{SCE})} + 4.39\ \mathrm{eV}]$ and $E_{\mathrm{HOMO}} = [E^{\mathrm{ox}}_{(\mathrm{onset}\ vs.\ \mathrm{SCE})} + 4.39\ \mathrm{eV}]$, the LUMO and HOMO energy of the polymers are thus determined and also listed in Table 2. Compared to polymers **4a** and **4b**, the band gap of polymer **4c** is a little larger due to the larger steric hindrance of the two 2-ethylhexyloxy substituents, which is consistent with the conclusion from the absorption and PL spectra.

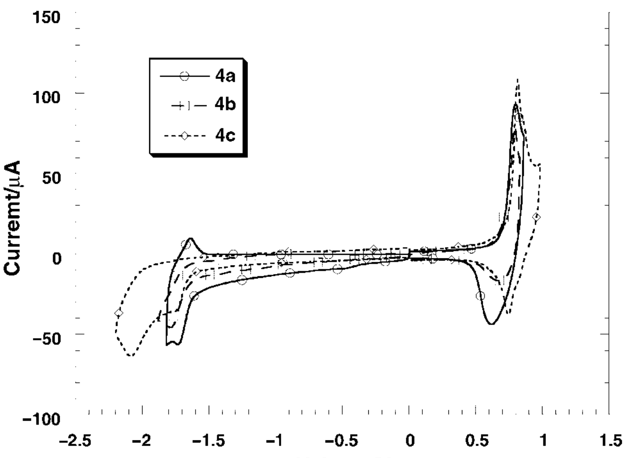

Fig. 3 Cyclic voltammograms for the polymers.

Fabrication of PLEDs

Typical single-layered polymer light-emitting diodes were fabricated using these new polymers as the active materials. Indium-tin-oxide (ITO) coated glass (~20 Ω/□) was used as the substrate. Polymer films were spin-cast on the substrates from their solutions in xylene (2% w/v, 1500 rpm) onto indium-tin-oxide (ITO)-coated glass substrates. The thickness of the films was around 100 nm. A calcium or aluminium layer (100–200 nm) was then deposited on the top of the polymer films under a pressure around 10^{-6} Torr at evaporation rates of 5–8 Å s^{-1}. Diode area was 15 mm^2 defined by the cathode. Device characteristics were measured with a calibrated Si photodiode. All the processes and measurements were carried out in a dry box filled with nitrogen. In forward bias, the ITO electrode was wired as the anode.

The diodes emitted visible light above sufficient voltage under the forward bias. The current–voltage and light intensity–voltage characteristics of a device with the ITO/polymer **4c**/Ca configuration are given in Fig. 4 as a representative example. For polymer **4c**, the turn-on voltage is around 7 V using Ca as the cathode. The current and the light emission both increase rapidly almost at the same voltage. The device of polymer **4c** turns on around 9 V by using Al as the cathode. The fact that changing the cathode material from Al to Ca decreases the turn on voltage may be attributed to the lower work function of Ca and thus the lower energy barrier for electron-injection at the cathode contact. However, a relatively high external EL quantum efficiency of 0.1% is achieved whether using Ca or using Al as cathode. Polymer **4a** and polymer **4b** exhibit similar properties. These results demonstrate the potential of these new polymers as emissive materials in polymer LEDs, although the optimization of polymer chemical structure and of device structure is necessary to improve the performance of PLED devices based on the new series of polymers.

Experimental

See Electronic Supplementary Information† for detailed synthesis procedures, spectroscopic and analytical data for the monomers and polymers prepared in this work.

Conclusions

A series of phenyl-functionalized polythiophene derivatives, poly[3-(4′-n-butylphenyl)thiophene-2,5-diyl)(2,5-dialkoxy-1,4-phenylene)(4-(4′-n-butylphenyl)thiophene-2,5-diyl)], have been synthesized by oxidative polymerization using ferric chloride as oxidant. The structures of the polymers were verified by

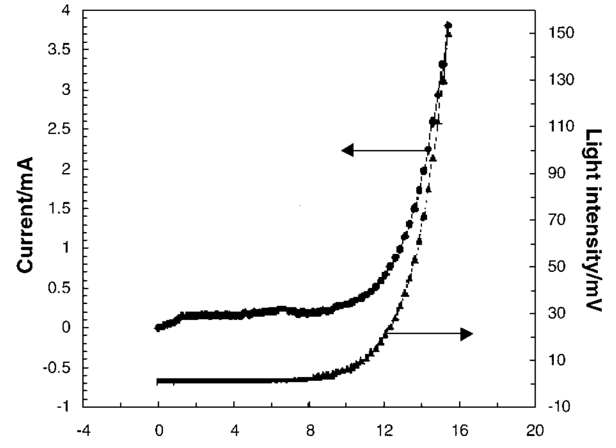

Fig. 4 Current–voltage and luminescence–voltage characteristics of an ITO/polymer **4c**/Ca device.

elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectroscopy. The results reveal that the linkages between the adjacent thiophene rings are predominantly at the 5 and 5′ position because of the high stereo-hindrance of the *n*-butylphenyl group at the 4-position of the thiophene ring. All polymers retain some important advantages of substituted polythiophenes, such as good solubility in common organic solvents; good thermal and environmental stability, while the PL quantum efficiency is increased compared with those of conventional polythiophene materials. The results of the optical and electrochemical investigations demonstrate that inserting a phenyl ring onto the side chain and the backbone of polythiophenes is still an efficient structural modification approach for improving the PL quantum efficiency and adjusting the HOMO and LUMO energy levels of the resulting thiophene-based conjugated polymers although it does not dramatically increase the PL efficiency of the new polymers.

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