

Effect of *meta*-linkages on the photoluminescence and electroluminescence properties of light-emitting polyfluorene alternating copolymers†

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Alternating copolymers poly[9,9-dihexylfluorene-*alt*-(1,3-phenylene)_x(1,4-phenylene)_{1-x}] ($x = 0, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0$) were prepared, and the absorption spectra showed the expected hypsochromic shift with increasing *meta* linkages. In the solution photoluminescence (PL) emission spectra, all but the all-*meta* polymer ($x = 1$) showed a spectrum similar to the all-*para* polymer, indicating rapid intrachain energy transfer to *para*-linked segments. Similar spectra were observed from thin films in which inter-chain energy transfer is also available. Annealing of the thin films in air above the T_g of the polymer for several hours led to an increase in long wavelength emission, but the increase was smaller for the polymers containing more *meta* linkages. IR experiments confirmed the formation of fluorenone defects during the annealing process. For those polymers with high *meta*-linkage incorporation (*i.e.* 75% and 100% *meta*) the long wavelength emission is suppressed. This suggests that when the conjugation length of the polymer is reduced then energy transfer to fluorenone defects is less likely, due to lower exciton delocalisation and mobility. The long wavelength emission was more prominent in the electroluminescence (EL) spectra of devices prepared from the polymer, and, while initially less intense in the high *meta* linkages polymers, became dominant even for the all-*meta* linked polymer after a few minutes of operation. In summary, the *meta* linkages had a beneficial effect in suppressing the undesirable long wavelength emission in both the PL and EL output.

Introduction

Polyfluorenes are a promising class of materials for blue-emitting polymer LEDs due to their high oxidative and thermal stability.^{1,2} However, a major disadvantage of devices based on polyfluorenes is the growth of an additional, long-wavelength emission during device operation under certain circumstances.³ This emission detrimentally alters the emission colour to green, or even white. There has been much debate in the literature as to the origin of this additional emission band. It has been attributed to the formation of excimers after exciton formation in devices, or due to energy migration along and between chains to impurity defects. These defects are believed to be carbonyl groups, fluorene-9-ones, formed when the C9 of the fluorene has only been singly alkylated (the monoalkylated fluorene cannot be completely separated during synthesis).⁴⁻⁶ The monoalkylated group is thermally oxidised upon annealing or during device operation to the fluorenone group.⁷⁻¹² Evidence for the fluorenone hypothesis arises from IR spectroscopy and the observation that the long wavelength emission was only observed when the thin

films were annealed in air, rather than an inert atmosphere. However, several groups have reported that the long-wavelength emission seems to disappear when bulky or dendritic side groups are attached to the polymer to prevent the polymer chains packing together closely,¹³⁻¹⁶ or alkyl spacer groups are inserted between the aromatic units to prepare what are termed rod-coil polymers.¹⁷ These results seem to suggest that excimer formation is also relevant to polyfluorene photophysics.

For an excimer to form there must be no interruption in the conjugation length of the pair of chains on which the excimer resides.¹⁸ With shorter conjugation lengths two identical segments are far less likely to couple as shown in Fig. 1. This method may also help to decrease the contribution of fluorene-9-ones to the emission spectra due to charge migration being reduced through the polymer.

The extent of electron delocalisation and degree of order in the polymer are obviously important for high conductivity in conjugated polymers through their influence on the band gap

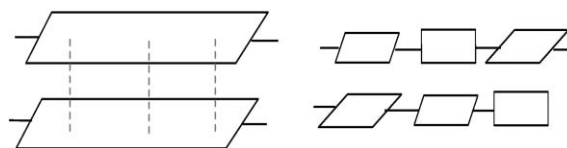


Fig. 1 Diagram to show how shorter conjugation lengths (right) reduce the likelihood of excimer formation between chains (left).

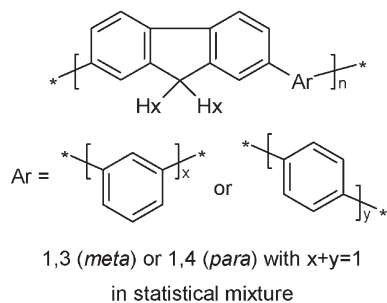
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and the extent of intermolecular charge transport. The extent of delocalisation for the alternating copolymer poly[(1,4-phenylene)-2,7-(9,9-dihexylfluorene)] has not been studied; however, the effective conjugation length for the similar polymer poly(2,7-9,9-dioctylfluorene) has been discussed.¹⁹ Clearly, the introduction of *meta* linkages will influence both the electron delocalisation and the degree of order of fluorene-based and other light-emitting polymers. This has been investigated previously for poly(9,9-dihexylfluorene-*alt*-1,3-phenylenevinylene),^{20–25} poly(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)^{26–32} and fluorene-pyridine copolymers.³³ Theoretical studies on *meta* linked phenylene polymers suggest that these groups interrupt the conjugation by introducing kinks into the chain which lead to a helical conformation.³⁴ It is possible that this would prevent the close contact between chains necessary for excimer formation. A recent study on PPVs concluded that there was considerable excited state localisation to a chain segment defined by the *meta*-linkages in the polymer.³⁵ This would lead to reduced rates of energy transfer to quenching sites and hence a higher photoluminescence efficiency in LEDs.

In the present paper we present a study of the effects of introducing *meta* linkages to interrupt the conjugation in polyfluorene-based alternating copolymers. The alternating copolymer poly[2,7-(9,9-dihexylfluorene)-*co-alt*-(1,4-phenylene)] was synthesised by Suzuki coupling,³⁶ and different amounts of *meta*-linkages were introduced by varying the feed ratio of 1,3-dibromobenzene to 1,4-dibromobenzene in the synthesis.



Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker AV-300 in deuterated chloroform solutions, operating at 299.998 MHz for ¹H and 75.45 MHz for ¹³C. Infra-red spectra were recorded as KBr discs or as thin films of neat polymer on NaCl plates, on either a Perkin Elmer Paragon 1000 or a Nicolet Avatar 360 FTIR spectrometer. Molecular weights were recorded on a Polymer Laboratories Gel Permeation Chromatography 120 Integrated GPC system with Polymer Laboratories gel 5 μm mixed column relative to polystyrene standards. Absorption spectra were recorded either in THF or as a thin film on a quartz substrate using a Varian Cary 300 Bio UV-vis machine. Photoluminescence spectra were recorded either as a dilute solution in THF or as a thin film on quartz substrates with a Fluoromax 2 from JY Horiba Group. DSC thermograms were recorded on a Netzsch DSC 204 Phoenix instrument.

Synthesis

All starting materials were obtained from Aldrich or Lancaster, were reagent grade and used without further drying or purification except where stated otherwise. Tetrahydrofuran was distilled over sodium and benzophenone under an inert atmosphere. 9,9-Dihexylfluorene, 2,7-dibromo-9,9-dihexylfluorene, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene and tetrakis(triphenylphosphine)palladium(0) were prepared by literature procedures.³⁷

General procedure for Suzuki coupling of polymers. The aryl dibromide and boronic ester were placed in a round bottomed flask which was then flushed with argon. To this toluene fresh from the still and degassed tetraethylammonium hydroxide solution were added by syringe. This was then stirred for a further ten minutes before the catalyst was quickly added. The mixture was then refluxed under argon for 6 hours with vigorous stirring. Once cool the reaction mixture was then poured into methanol and the precipitate collected by filtration. The crude product was then washed with methanol, dilute hydrochloric acid and then methanol again. Purification was achieved by washing the polymer with acetone in a Soxhlett apparatus to remove any catalyst residues, tetraethylammonium hydroxide or oligomers.

P1: poly(9,9-dihexylfluorene-*alt*-(1,4-phenylene)). A yellow powder was obtained (0.34 g, 97%). ¹H NMR δ (ppm) 7.5–7.75 (m, 10H), 1.4 (m, 4H), 0.95–1.1 (m, 12H), 0.75 (t, 6H). ¹³C NMR δ (ppm) 152.21, 140.90, 140.57, 140.01, 127.99, 126.37, 121.88, 120.51, 55.72, 40.88, 31.90, 30.16, 24.25, 23.01, 14.43. Anal. Calcd for [(C₆H₁₃)₂(C₁₃H₆)(C₆H₄)_n]: C, 91.12; H, 8.88. Found: C, 90.83; H, 8.91%. IR 2923 cm⁻¹, 2851 cm⁻¹, 1460 cm⁻¹, 808 cm⁻¹.

P2: poly[9,9-dihexylfluorene-*alt*-(1,3-phenylene)_x(1,4-phenylene)_{1-x}] (x = 0.05). 0.26 g, 54%. ¹H NMR δ (ppm) 7.9 (s, 1H), 7.8 (m, 78H), 7.65–7.5 (m, 115H) 2.0 (m, 80H), 1.0 (m, 240H), 0.7 (m, 200H). ¹³C NMR δ (ppm) 152.21, 140.91, 140.57, 140.01, 127.99, 126.38, 121.88, 120.52, 55.72, 40.90, 31.91, 30.16, 24.28, 23.02, 14.44. Anal. Calcd for [(C₆H₁₃)₂(C₁₃H₆)(C₆H₄)_n]: C, 90.91; H, 8.94. Found: C, 89.21; H, 9.56%.

P3: poly[9,9-dihexylfluorene-*alt*-(1,3-phenylene)_x(1,4-phenylene)_{1-x}] (x = 0.1). 0.81 g, 95%. ¹H NMR δ (ppm) 7.96 (m, 10H), 7.8–7.86 (m,), 7.64–7.72 (m,) 1.4 (m, 4H), 0.95–1.1 (m, 24 H), 0.75 (t, 6H). ¹³C NMR δ (ppm) 162.57, 152.20, 140.89, 140.56, 140.00, 129.19, 128.63, 127.98, 127.60, 126.36, 121.87, 120.51, 55.71, 40.89, 31.89, 30.15, 24.25, 23.00, 14.42. Anal. Calcd for [(C₆H₁₃)₂(C₁₃H₆)(C₆H₄)_n]: C, 91.12; H, 8.88. Found: C, 91.04; H, 8.58%.

P4: poly[9,9-dihexylfluorene-*alt*-(1,3-phenylene)_x(1,4-phenylene)_{1-x}] (x = 0.25). 0.29 g, 64%. ¹H NMR δ (ppm) 7.9 (s, 1H), 7.75 (m, 14), 7.65–7.55 (m, 25) 2 (m, 16H), 1.05 (m, 48 H), 0.7 (m, 40H). ¹³C NMR δ (ppm) 152.19, 140.89, 140.55, 140.00, 127.98, 126.65, 126.36, 122.11, 121.87, 120.51, 55.70, 40.91, 31.89, 30.15, 24.25, 23.01, 14.43. Anal. Calcd for

Table 1 GPC and spectroscopic data for synthesized polymers

Polymer	<i>para</i>	<i>meta</i> (<i>x</i>)	M_n	M_w	PD	Absorption λ_{\max}/nm (THF)	Emission λ_{\max}/nm (THF λ_{exc} 335 nm)
P1	1	0	11210	18520	1.652	368	409
P2	0.95	0.05	12500	35290	2.823	368	408
P3	0.9	0.1	24640	94500	3.835	368	408
P4	0.75	0.25	6200	19460	3.139	363	407
P5	0.5	0.5	8602	12780	1.486	353	405
P6	0.25	0.75	19140	36730	1.919	345	401
P7	0	1	3222	16130	5.006	341	385

$[(C_6H_{13})_2(C_{13}H_6)(C_6H_4)]_n$; C, 91.12; H, 8.88. Found: C, 90.75; H, 8.89%.

P5: poly[9,9-dihexylfluorene-*alt*-(1,3-phenylene) $_x$ (1,4-phenylene) $_{1-x}$] ($x = 0.5$). 0.24 g, 57%. ^1H NMR δ (ppm) 7.9 (s, 1H), 7.75 (m, 6H), 7.7–7.4 (m, 13 H), 2.0 (m, 8H), 1.0 (m, 24H), 0.7 (m, 20H). ^{13}C NMR δ (ppm) 127.98, 121.87, 120.51, 31.90, 23.01, 14.43. Anal. Calcd for $[(C_6H_{13})_2(C_{13}H_6)(C_6H_4)]_n$: C, 91.12; H, 8.88. Found: C, 90.82; H, 8.92%.

P6: poly[9,9-dihexylfluorene-*alt*-(1,3-phenylene) $_x$ (1,4-phenylene) $_{1-x}$] ($x = 0.75$). 0.34 g, 81%. ^1H NMR δ (ppm) 7.9 (s, 3H), 7.8 (m, 10H), 7.65–7.5 (m, 27H) 2.0 (m, 16H), 1.05 (m, 48H), 0.7 (m, 40H). ^{13}C NMR δ (ppm) 152.19, 142.75, 140.63, 140.57, 140.03, 129.66, 127.99, 126.65, 122.12, 121.88, 120.50, 55.79, 40.93, 31.90, 30.16, 24.27, 23.01, 14.43. Anal. Calcd for $[(C_6H_{13})_2(C_{13}H_6)(C_6H_4)]_n$: C, 91.12; H, 8.88. Found: C, 90.80; H, 8.76%.

P7: Poly(9,9-dihexylfluorene-*alt*-(1,3-phenylene)). 0.47 g, 73%. ^1H NMR δ (ppm) 7.9 (s, 1H), 7.75 (d, 2H), 7.65–7.5 (m, 7 H), 2.0 (m, 4H), 1.0 (m, 12H), 0.75 (m, 10H). ^{13}C NMR δ (ppm) 152.20, 142.76, 140.64, 140.58, 129.67, 127.62, 126.66, 122.14, 120.51, 55.80, 40.94, 31.91, 30.17, 24.27, 23.01, 14.43. Anal. Calcd for $[(C_6H_{13})_2(C_{13}H_6)(C_6H_4)]_n$: C, 91.12; H, 8.88. Found: C, 90.805; H, 8.96%.

Results and discussion

Some difficulty was experienced initially in obtaining satisfactorily high molecular weights, which was overcome by modifying the procedure,³⁷ including the use of an organic base, tetraethylammonium hydroxide (Et_4NOH). Using this base had the additional advantage of increasing the rate of the reaction, requiring only a few hours to obtain high molecular weights rather than the 48 h previously required. The preparation could easily be altered to produce statistical copolymers with varying percentages of *meta* linkages to introduce conjugation breaks without significantly altering the structure of the polymer. Polymers with 0, 5, 10, 25, 50, 75 and 100% *meta*-substituted monomers were synthesized, since it was expected that a small percentage of *meta* linkages would greatly decrease the contribution from excimers. The singlet peak from the *meta*-phenylene H(2) is clearly visible at δ 7.9 ppm allowing confirmation of the relative quantities of *meta* linkages by ^1H NMR. For **P2**, **P3** and **P4** this peak was clearly visible, but the ratio of *meta*- to *para*-linked phenylene could not be measured with great precision. Within these

limitations, the NMR ratio vs. feed ratio plot was linear within error. There was no discernible trend to lower molecular weights with increasing amounts of *meta* links (Table 1) but the all-*meta* linked polymer **P7** had a much lower molecular weight and a higher polydispersity (Table 1) than the others.

Absorption and emission spectra in solution

The absorbance spectra show a shift to shorter wavelength as the number of *meta*-links increases (Fig. 2 and Table 1). The photoluminescence spectra (Fig. 3) of the dilute solutions show a $\lambda_{\max}^{\text{em}}$ of 422 nm for the all-*para* polymer **P1** corresponding

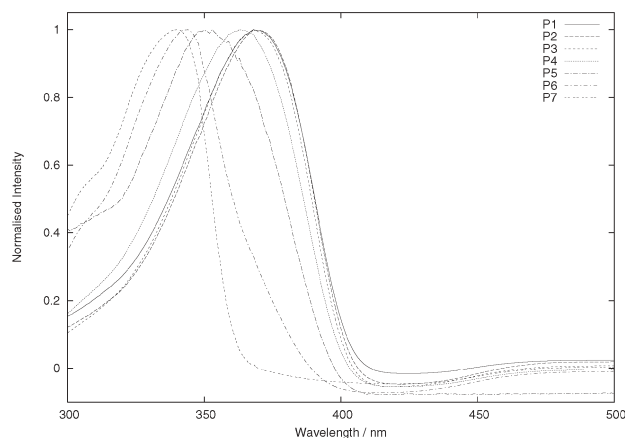


Fig. 2 Solution absorption spectra (THF) of varying *meta* link content polymer **P1–P7** (for details of polymer labelling see Table 1).

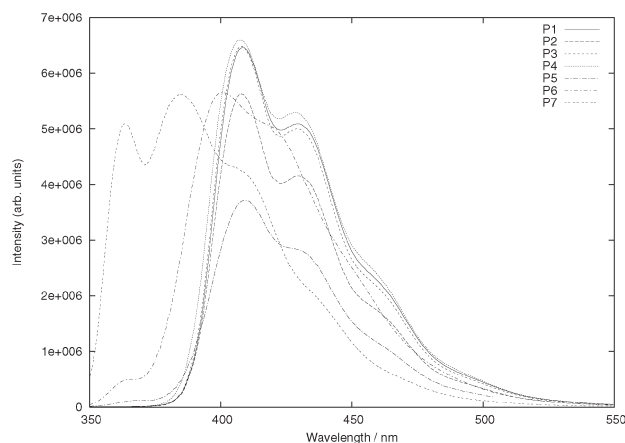


Fig. 3 Solution photoluminescence ($\lambda_{\text{exc}} = 335$ nm) spectra in THF of varying *meta* link content polymers **P1–P7**.

to the blue emission with vibronic structure expected of polyfluorenes. The introduction of *meta*-linkages induces a small hypsochromic shift in the emission and slight changes in the intensity of the vibronic peaks due to greater overlap between the excitation wavelength and the absorption maximum. The small shift in the emission as the number of *meta* links increases is due to energy transfer from short to longer conjugated segments within a chain. Only with the all-*meta* polymer do we observe a big shift in the emission maximum. This particular observation is quite similar to that reported for water-soluble copolymers containing *meta*-links,³⁸ and indicates that Förster energy transfer occurs from shorter conjugation length regions of the chain to more conjugated regions with lower energy. No long-wavelength emission (>500 nm) is observed in the photoluminescence spectra which is in accordance with the polymer chains being well separated in solution, minimizing the formation of excimers.

Thin film emission and the effect of annealing in air

Thin films of all of the polymers give photoluminescence spectra which are very similar to those of the dilute solutions with no obvious long wavelength emission (Fig. 4). However, after the films had been annealed for 24 h at 150 °C (above 127 °C, the T_g of the polymer) long wavelength emission appeared above 500 nm (Fig. 5). After further annealing at this temperature under air a well-defined peak emerged with $\lambda_{\text{max}}^{\text{em}}$ 540 nm. For those polymers with only a small quantity of *meta*-incorporation the spectra closely resemble the all-*para*-linked polymer **P1**. In these cases, the long wavelength emission can be seen to grow in after only one hour's annealing time. For those polymers with high *meta*-linkage incorporation (*i.e.* 75% and 100% *meta*) the relative intensity of this emission band is considerably less than the others after 24 h, as shown in Fig. 5. Under an inert atmosphere the long wavelength peak only began to appear after 72 h of annealing.

The long wavelength emission observed on heating could be due to excimer or fluorenone formation as mentioned in the Introduction. To distinguish between these two possibilities we measured the IR spectra of the polymers during annealing. A thin film of the all-*para* polymer (**P1**) was spin coated onto a

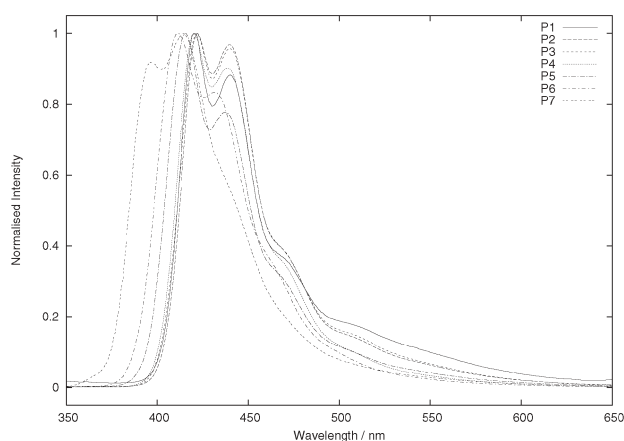


Fig. 4 PL spectra ($\lambda_{\text{ex}} = 335$ nm) of thin films of varying *meta* link content polymers **P1–P7**.

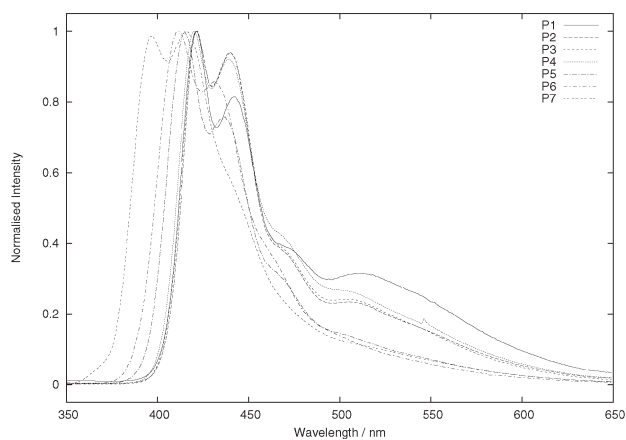


Fig. 5 PL spectra ($\lambda_{\text{ex}} = 335$ nm) of thin films of varying *meta* link content polymers **P1–P7** annealed in air at 150 °C for 1 day.

salt plate used in IR spectroscopy. The IR spectrum for the pristine film was recorded and showed no carbonyl stretching frequency, as anticipated. The film was then annealed in air for 24 h, as done for the measurement of the photoluminescence spectra. Over this period, and beyond, a peak at 1740 cm^{-1} emerges which can be attributed to the $\nu(\text{C}=\text{O})$ stretching frequency of a fluorenone group (Fig. 6). Samples annealed under an argon atmosphere at 150 °C for the same periods of time did not display this peak. This implies that carbonyl moieties are indeed formed in the presence of oxygen.

The long-wavelength emission peak has an emission maximum at 510 nm for shorter annealing periods and a 540 nm band which emerges after annealing for 5 days or longer. This raises the question that the long wavelength peak observed may in fact be superposition of a broad emission at 510 nm and a more dominant peak at 540 nm. Previous work on polyfluorenes¹⁹ argues that both fluorenone emission and excimer formation are promoted in films which have been annealed. In addition, this group report a quickly-forming emission peak due to fluorenones for polymers end-capped with 2-bromofluorene and a slow forming peak due to excimers for those end capped with 2-bromo-9,9-dihexylfluorene. This

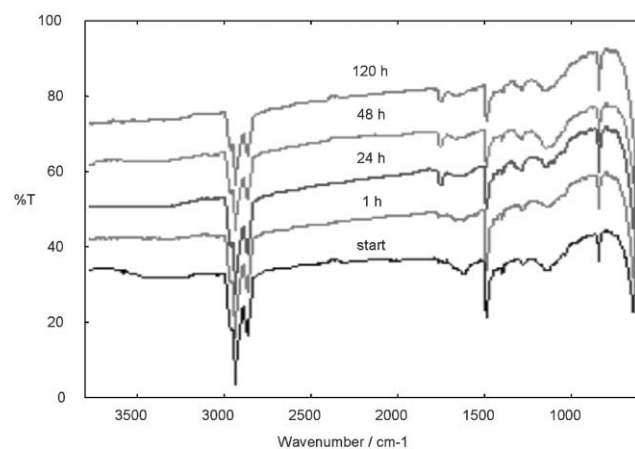


Fig. 6 FTIR spectra of a thin film of **P1** after annealing in air at 150 °C showing the appearance of the fluorenone peak at 1740 cm^{-1} .

would suggest that carbonyl formation occurs quickly relative to the conformational changes required for excimer formation, even when heated above T_g .

After annealing thin films of all the polymers for 5 days and then leaving the films exposed to air for several days the thin film spectra no longer showed any resemblance to that of a polyfluorene spectrum. Indeed, the only observable emission is from the long wavelength region. The polymer film can be washed off the substrate with THF, and a solution photoluminescence spectra of the same sample is now a reversion to emission from polyfluorene. This appears to be consistent with the excimer hypothesis, *i.e.* the polymer chains are being aligned during the annealing process which promotes the subsequent formation of excimers in the film at low temperature. When the films are washed off the substrate excimer formation is no longer observed as the molecules are too far apart in solution. However, an alternative explanation is that sufficiently rapid Förster energy transfer to the fluorenone groups is only possible in the solid state, since both interchain and intrachain energy transfer are possible.

Electroluminescence

All of the polymers were then tested under LED device conditions in order to obtain electroluminescence data. Unfortunately, although the devices had external quantum efficiencies of approximately 0.05%, comparable to literature results for polyfluorenes, the turn-on voltages were very high. Electroluminescence (EL) spectra showed a large peak at $\lambda_{\text{max}}^{\text{em}} = 540 \text{ nm}$ (Fig. 7), which has the effect of making the devices appear white to the naked eye. The long wavelength peak is found to be more dominant in EL than in PL. A possible explanation is that charge carriers are trapped efficiently by the low energy fluorenone sites. Another explanation is that the calcium in EL devices can catalytically oxidise the fluorene to fluorenone, increasing the number of fluorenone defects or the rate at which they are generated.¹¹ **P6** and **P7**, which have shorter conjugation lengths, show considerably less of this green emission. One possible explanation is that the incorporation of conjugation breaks impedes hole

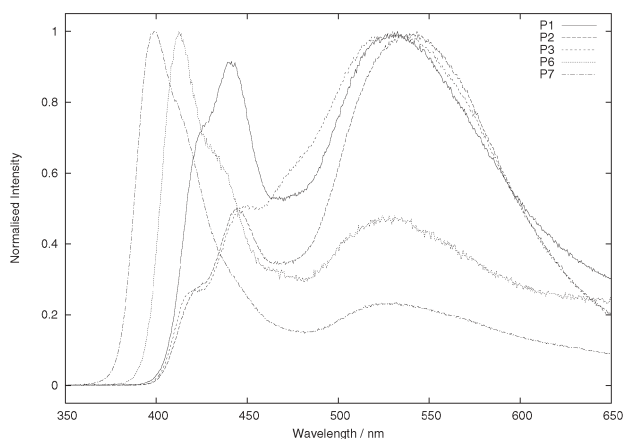


Fig. 7 Initial electroluminescence spectra of varying *meta* link content polymers **P1–3**, **P6–P7**.

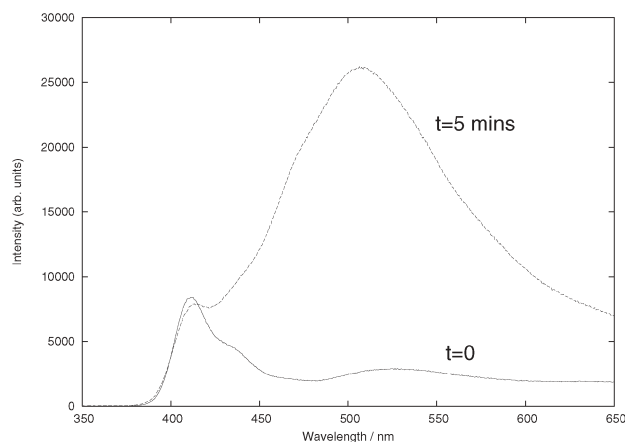


Fig. 8 EL spectra of 100% *meta*-linked polymer **P7** taken when device first operated ($t = 0$) and after 5 minutes of operation ($t = 5 \text{ min}$).

and electron motion along the chains to the fluorenone sites. Despite this, EL spectra of devices using any of the polymers taken after five minutes of operation show much more green emission than when first tested (*e.g.* **P7** in Fig. 8). Clearly, fluorenone production is promoted during operation of the device due to heating caused by the high internal resistance of the materials (as shown by the high turn-on voltages).

Conclusions

The major finding in this work is that the introduction of *meta* linkages has a positive effect on the stability of the polymers to the development of long wavelength emission characteristic of fluorenone groups. This suggests that if the conjugation length of the polymer is reduced and kinks are introduced in the polymer chain then exciton delocalisation and mobility, as well as charge mobility under EL conditions, are reduced as proposed recently.³⁵

The optimum incorporation of *meta* linkages, in terms of the colour of emission and molecular weight, is achieved by incorporating 75% *meta* linkages. Full incorporation of *meta* linkages leads to a regioregular alternating copolymer which also successfully suppresses the long wavelength emission band. However, the emission colour is significantly shifted towards the ultraviolet relative to the original *para* linked polyfluorene. Secondly, a *meta* linkage incorporates a kink onto the polymer backbone which appears to be detrimental to achieving high molecular weights.

Our IR experiments have shown that extensive annealing of thin films in air leads to exclusive long wavelength emission in the PL spectra arising from fluorenone groups. The effect of *meta* linkages in suppressing fluorenone emission may be that the conjugation breaks along the polymer backbone reduce the charge transport rate in the polymer and the exciton cannot migrate to the fluorenone.

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