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Optical and electroluminescent properties of polyfluorene copolymers and their blends

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Abstract

Light emitting properties of several polyfluorene (PF) copolymers (**P1**–**P4**) and their blends have been investigated. Light emitting diodes were fabricated with the configuration of ITO/PEDOT:PSS/polymer/Ca/Al. The EL peak wavelengths were 421 nm (violet), 505, 513 nm (green) and 570 nm (yellow) for PF copolymers and 510, 535 nm (green) for **P1/P2** and **P1/P3** blends, respectively. Förster energy transfer in the photoluminescence and electroluminescence of the polymer blends **P1/P2** and **P1/P3** was studied. The LED using the polymer blend **P1/P2** showed a turn-on voltage of 2.5 V and a brightness of 5×10^4 cd/m^2 at 7 V. The highest external quantum efficiency was observed to be 3.71% at 5 V. Upon addition of 20 wt% of the green emitter **P2** to the violet emitter **P1**, the device efficiency increased from 1.18 to 3.71%.

Keywords: Light emitting diode; Electroluminescence; Blending

1. Introduction

The discovery of electroluminescence (EL) in conjugated polymers has provided a new impetus to the development of large-area, flexible and colorful displays with lower power consumption and other applications [1–5]. Polymer light-emitting diodes (PLEDs) offer potential advantages of low turn-on and operating voltages and light weight. They can be flexible in their fabrication procedure. The range of colors available from PLEDs now spans the entire visible spectrum. Recently fluorene-based polymers have been introduced as a prospective emitting layer for PLEDs [6,7]. These materials display extremely high photoluminescence (PL) efficiencies both in solution and in solid films, with emission wavelengths potentially over the whole visible spectral region [8–11]. These polymers are stable above their melting points, permitting melt processing not possible for many conjugated polymers. The optical and electrical properties of polyfluorene have also been modified through copolymerization of fluorene monomers with other molecular subunits [9]. Their photostability and thermal stability are also found to be better than those of PPVs [12–13].

Tuning the emission color of PLEDs has been achieved by changing the main-chain molecular structure [14–16], changing the side-chain molecular structure [17], blending a light-emitting polymer with another polymer [18,19] or an inorganic molecule [20] and by using multi-layer architectures [21]. Polymer blending provides a simple, low-cost, and often very effective way to obtain new chromophores for use in LEDs. By selecting different luminescent polymers for blending and by controlling the content of the target chromophore in the blend, one may obtain different emission colors with reasonable quantum efficiency [22,23]. In all PL and EL studies of conjugated polymer blends, Förster energy transfer [18,24] has been significant. Basic requirements for the Förster type energy transfer are adequate spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor and uniform mixing of the two species on a nanometer scale.

In a paper to be published [25], we have studied optical properties of blends of two polyfluorene copolymers. We

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now extend this work to additional polyfluorene systems covering a wider range of structure. In this study, we investigate the light emitting properties of several polyfluorene copolymer systems (Fig. 1): poly[(9,9-dioctylfluorenyl-2,7-diyl)-*alt-co*-(9-hexyl-3,6-carbazole)] (**P1**), poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-*alt-co*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene}] (**P2**), poly[(9,9-dioctyl-2,7-bis(2-cyanovinylenefluorenyl-ene))-*alt-co*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene}] (**P3**) and poly[(9,9-dioctylfluorenyl-2,7-divinylenefluorenylene)-*alt-co*-(9,10-anthracene)] (**P4**) and some of the blends. Polyfluorene copolymer systems have advantages, often possessing the properties of two monomers, conferring ready tuning of optical properties. Double-layer LEDs have been fabricated using these copolymers and their blends (**P1/P2** and **P1/P3**). Förster energy transfer in the photoluminescence and electroluminescence of the blends was studied. The devices based on the **P1/P2** blend showed enhanced external quantum efficiency and higher brightness compared to pure copolymers and the other blend system.

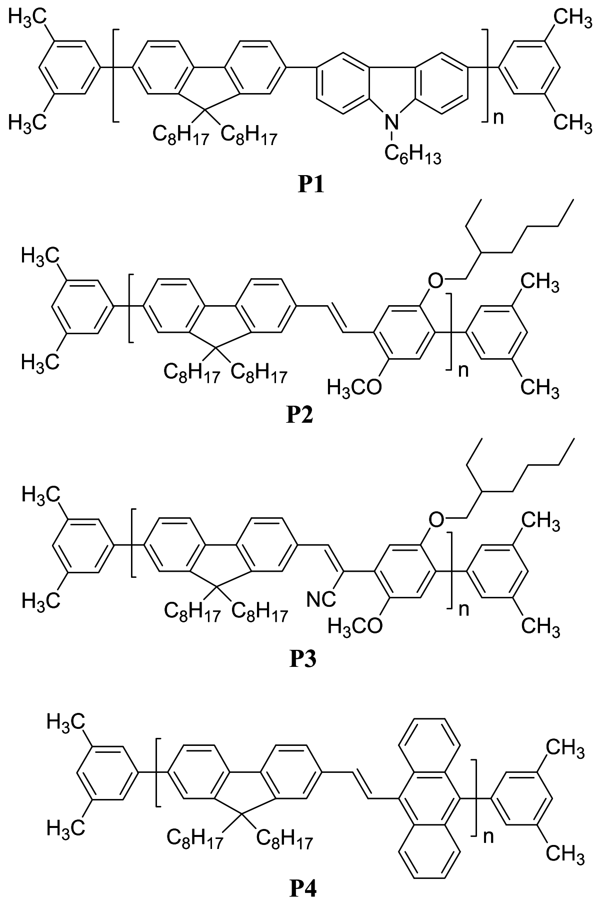

Fig. 1. Chemical structures of polymers **P1**–**P4**.

2. Experimental

2.1. Materials

Chloroform (Aldrich) was used without further purification as were the light emitting polyfluorene copolymers (**P1–P4**) (American Dye Source, Inc) used. Poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) was obtained from Bayer Co. Molecular weights as supplied by the manufacturer are in the range 1.7×10^4 (**P3**) to 1.6×10^4 (**P2**,**P4**).

2.2. Preparation of blends and thin films

P1/P2 and **P1/P3** blends were made by mixing in chloroform at different weight ratios, namely 8:2, 5:5 and 3:7. All polymer solutions (10 mg/mL) were filtered through 0.2 μm Millex-FGS Filters (Millipore Co.). Thin films for optical absorption and photoluminescence measurements were spin-cast onto glass slides. All the films were dried in vacuum at room temperature for 1 h to remove residual solvent.

2.3. Absorption and photoluminescence spectroscopy

Optical absorption spectra were taken on a Hitachi U-3010 UV–vis spectrophotometer. PL spectra were recorded on a Perkin–Elmer LS 50B luminescence spectrometer using a xenon discharge lamp for excitation.

2.4. Fabrication and characterization of PLEDs

Double-layer PLEDs with the configuration ITO/PEDOT: PSS/polymer/Ca/Al were fabricated on ITO-coated glass slides cleaned in ultrasonic baths of water and acetone. A hole injection layer of PEDOT:PSS was spin-coated on top of the ITO and dried at 100 °C for 1 h under vacuum. A 100 nm layer of copolymers and their blends were spin-coated from their chloroform solutions onto the PEDOT:PSS layer under nitrogen. A 400 nm thick calcium electron-injecting cathode was deposited on the polymer film through a mask by vacuum evaporation at a pressure less than 2×10^{-6} Torr resulting in an active area of 6 mm^2, followed by a protective coating of aluminum. The devices were characterized using a system described previously [26].

3. Results and discussion

3.1. Optical absorbance and PL spectra of the copolymers

Fig. 2 shows the UV–vis absorption spectra of the copolymers in chloroform and in the thin films coated onto the glass slides. Polymers, **P1–P4**, in the solid state showed absorption maxima at 365, 454, 425 and 454 nm,

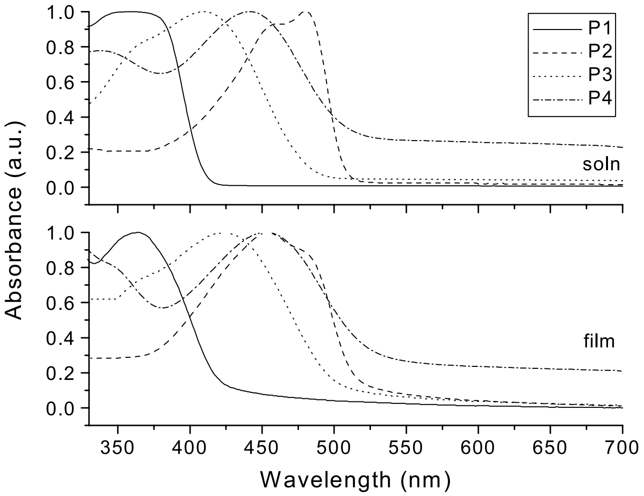

Fig. 2. UV–vis spectra of the copolymers in chloroform and in solid state.

respectively. From the onsets of the absorption spectra, the band gaps of polymers **P1**–**P4** were calculated to be 2.94, 2.39, 2.46 and 2.35 eV, respectively. The blue-shifted UV–vis maximum wavelength of **P3** compared to that of **P2** is due to the presence of the electron-withdrawing CN group in the alternating copolymer system. The absorption and emission maxima and the band-gap of the copolymers are summarized in Table 1. With the introduction of a carbazole unit into the main chain, the absorption spectra are blue shifted ($\lambda_{max}=385$ nm for poly(9,9-dioctylfluorene)) to shorter wavelengths due to the interruption of the main chain conjugation by the presence of this moiety [27]. Incorporating this different unit into the fluorene backbone has substantial effect on the extent of conjugation, resulting in modified electronic transitions and shifts in the absorption peaks [28–32].

The photoluminescence spectra for copolymer **P1**–**P4** solutions and for films under excitation wavelength of 370 nm are shown in Fig. 3(a). The peak wavelengths are listed in Table 1. The PL spectra of all polymer films showed a red shift and some broadening of the emission bands in comparison to their solution spectra. The red shifts in PL are due to intermolecular interactions in the films. Their vibronic features remained unchanged. It was concluded that, in contrast with the other copolymers studied, **P1** exhibits distinct 0–0, 0–1 and 0–2 vibronic transitions. Absorption spectra of fluorene/carbazole copolymers are affected by the side chain on the carbazole unit. In the case of 2-ethylhexyl [33], ethyl [34] and octyl [27] derivatives, the absorption maxima have been observed at 343, 383 and 370 nm, respectively. However, in PL spectra only changes of a few nanometers have been observed (428, 424 and 419 nm). Absorption and PL maximum of **P2** in the film state has been reported in the literature to be at 422 and 592 nm, respectively [29].

3.2. Electroluminescent properties of the copolymers

Fig. 3(b) shows the EL spectra of the ITO/PEDOT:PSS/polymer/Ca/Al devices. The EL spectra of polymers **P1**–**P4** are almost identical to their respective PL spectra, which indicates that these outputs originate from the same radiative decay process of the singlet exciton [35]. The EL peak wavelengths are listed in Table 2. Fig. 4 shows the current density–voltage–luminance (*J*–*V*–*L*) characteristics of the ITO/PEDOT:PSS/polymer/Ca/Al devices. The current density and luminance increase exponentially with increasing forward bias voltage above the turn-on voltage, and all devices exhibit robust diode characteristics. The turn-on voltage for the devices using polymers **P1**–**P4** were found to be 3, 2.5, 3.5 and 2.5 V, respectively. The maximum brightness of single component **P1**–**P4** devices

Table 1
Optical properties of copolymers

Sample	λ_{max}^{Abs} (nm)[a]	λ_{max}^{Abs} (nm)[b]	λ_{max}^{PL} (nm)[a]	λ_{max}^{PL} (nm)[b]	E_g (eV)[c]
P1	**365**[d]	**365**	443, **418**	443, **426**	2.94
P2	458, **480**	480, **454**	**504**	**528**	2.39
P3	370, **410**	365, **425**	536, **502**	**550**	2.46
P4	**442**	**454**	**556**	**558**	2.35

[a] Measured in chloroform solution.
[b] Films cast from chloroform solution.
[c] Band-gap estimated from the onset wavelength of the optical absorption.
[d] Bold data indicate the major peaks.

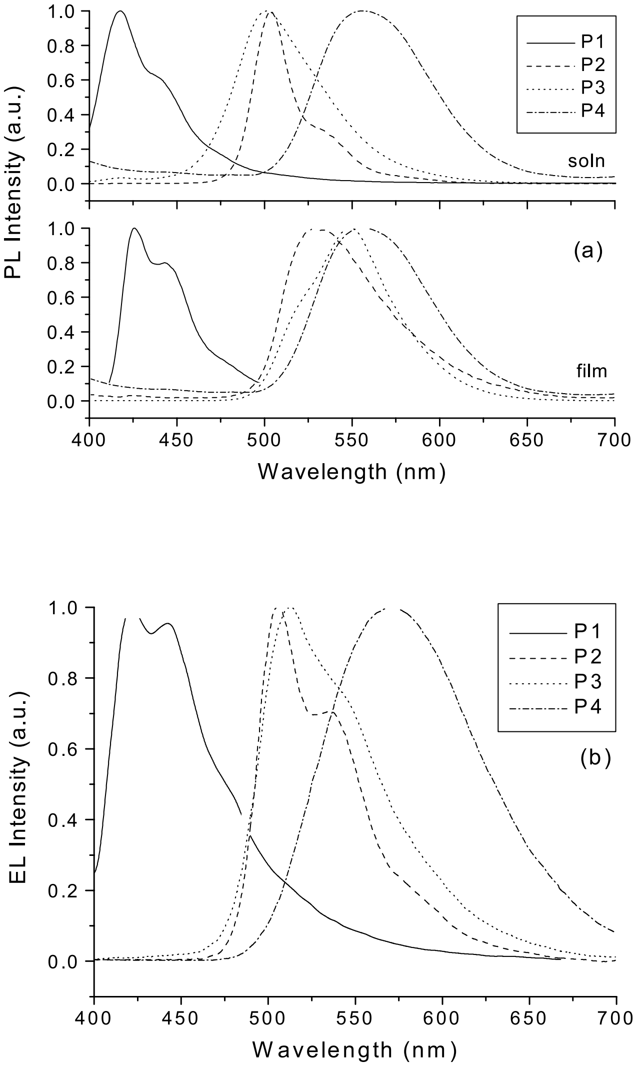

Fig. 3. PL and EL spectra of the copolymers.

are 1.9×10^4 cd/m^2, 1.6×10^4 cd/m^2, 1×10^3 cd/m^2 and 1.3×10^3 cd/m^2. The maximum reported brightness of a **P2** based LED was reported 127 cd/m^2 [29] using a different device configuration. The turn-on voltage for the **P1** device using Al as a cathode material was observed to be greater than 3 V [36].

Table 2
Summary of the characteristics of the ITO/PEDOT:PSS/polymer/Ca/Al devices

Sample	$\lambda_{\max}^{\mathrm{EL}}$ (nm)	Turn-on voltage (V)	Efficiency (η_{ext}, %)
P1	**421**, 443	3	1.18
P2	**505**, 538	2.5	1.86
P3	**513**, 540	3.5	0.21
P4	**570**	2.5	0.05
P2:**P1** (2:8)	**505**, 542	2.5	3.71
P2:**P1** (5:5)	**510**, 542	2.5	1.13
P2:**P1** (7:3)	**510**, 542	2.5	2.06
P3:**P1** (2:8)	513, **535**	3.5	0.005
P3:**P1** (5:5)	513, **535**	5.5	0.002
P3:**P1** (7:3)	513, **535**	4	0.138

Bold data indicate the major peaks.

3.3. Optical properties of polymer blends P1/P2 and P1/P3

To facilitate Förster energy transfer in blending or copolymer systems, the emission peak of the donor with the higher band gap must overlap with the absorption peak of acceptor with the lower band gap. It can be seen from Fig. 5 that the PL spectrum of **P1** overlaps with a major portion of the absorption spectra of both **P2** and **P3**. Thus Förster intermolecular energy transfer from **P1** to **P2** or **P3** is expected to be efficient in these blends.

Fig. 6(a) shows the normalized photoluminescence spectra of the **P1/P2** blend in chloroform and in the thin films. Polymer **P1** has been used as a donor material due to its higher band gap and hole transporting capability. The PL spectra of the **P1/P2** blend solutions show a combination of emissions from each polymer (Fig. 6(a)). These results indicate that Förster energy transfer from the high band gap

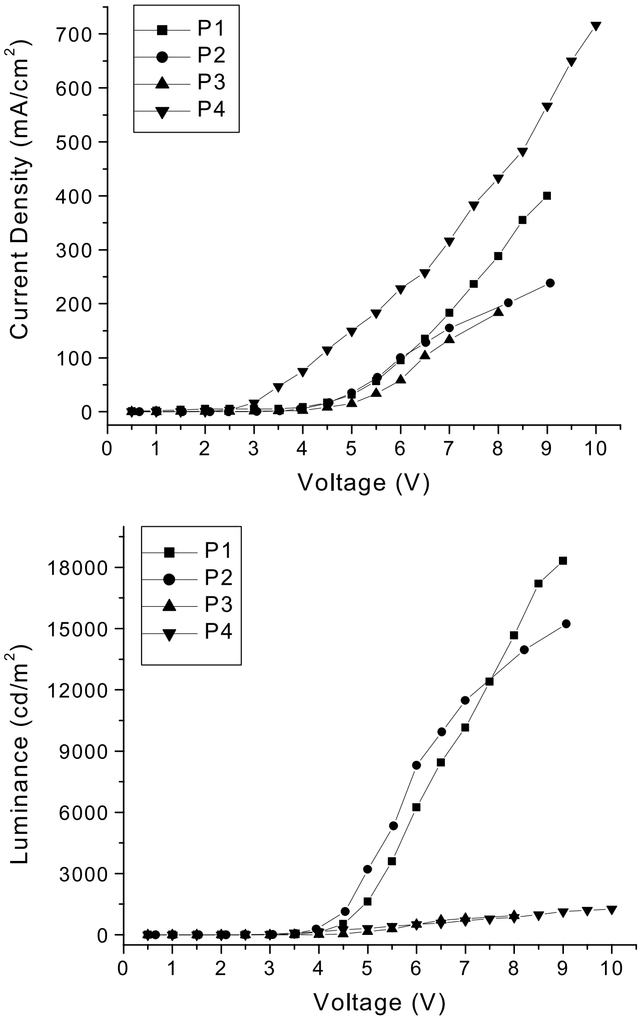

Fig. 4. *J–V* and *L–V* characteristics for the copolymer LEDs.

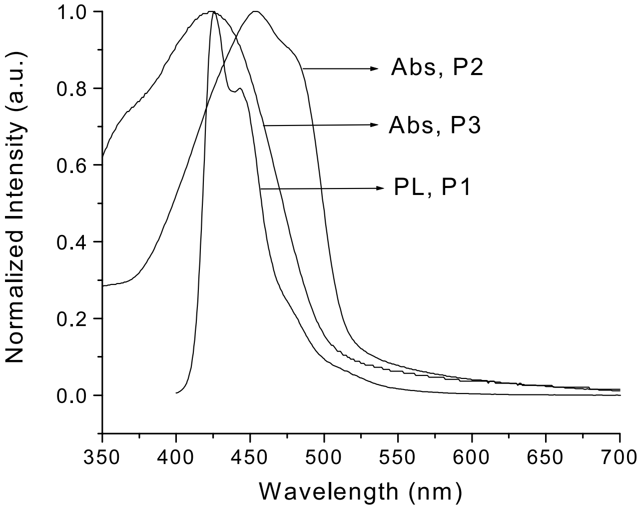

Fig. 5. Normalized absorption spectra of **P2**, **P3** and PL spectrum of **P1**.

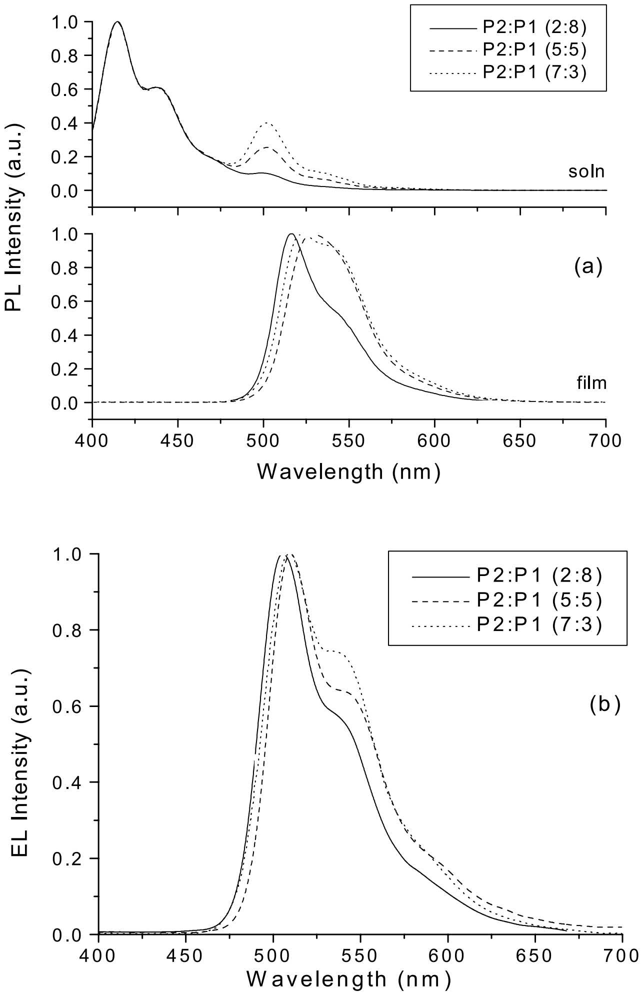

Fig. 6. Normalized PL in chloroform and in the solid-state and EL spectra of **P1/P2** blends.

polymer **P1** to the lower band-gap polymer **P2** as expected cannot occur in very dilute solution. In the case of **P1/P3** blend solution, only blue emission was observed (Fig. 7(a)). In the solid state, the blends display only green emission at around 520 nm with the characteristics of the copolymer **P2** or **P3**, indicating energy transfer take place from **P1** to **P2** or **P3**.

*3.4. Electroluminescent properties of **P1/P2** and **P1/P3** blends*

EL spectra of the devices prepared from the **P1/P2** and **P1/P3** blends are shown in Figs. 6(b) and 7(b), respectively. From the **P1/P2** blend, most of the emission was detected in the emission band of **P2**, indicating a substantially complete energy transfer from **P1** to **P2**. Comparing the EL spectrum of **P3** with those of the **P1/P3** blend, the emission maxima were shifted from 513 to 535 nm. Some broadening of the emission band was also observed in the **P1/P3** blend (Fig. 7(b)). These changes in the EL spectra may be attributed to

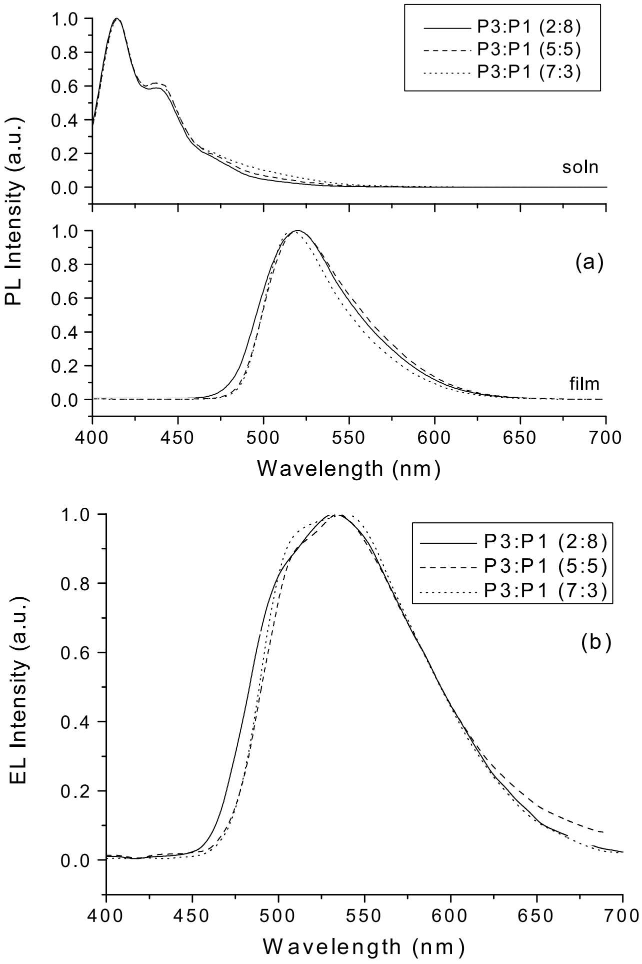

Fig. 7. The normalized PL (in chloroform and in the solid-state) and EL spectra of **P1/P3** blends.

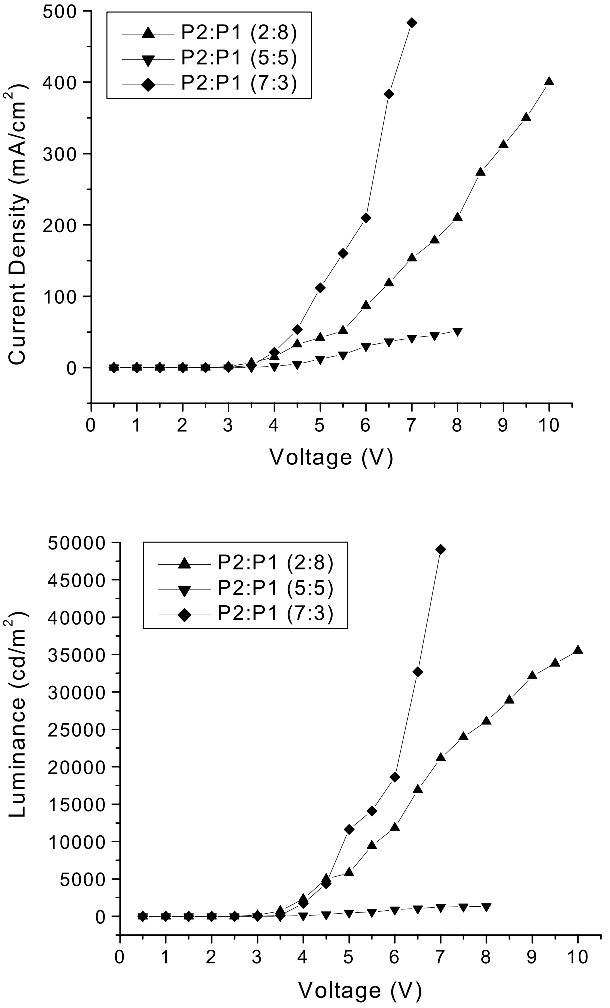

Fig. 8. *J–V* and *L–V* characteristics for the **P1/P2** blend LEDs.

the incomplete energy transfer from **P1** to **P3** as a result of their domain structure.

Figs. 8 and 9 show the *J–V* and *L–V* plots for the devices using **P1/P2** and **P1/P3** blends. The turn-on voltages were about 2.5–5.5 V and the maximum brightness of all devices was in the range 15–5×10^4 cd/m^2. The **P1/P2** blend device had the highest performance with a maximum brightness of 5×10^4 cd/m^2 at 7 V. The external quantum efficiencies of the blends and copolymers are listed in Table 2. The lower quantum efficiency of the 5:5 compositions is due to the formation of a different nanoscopic structure [37]. The maximum external quantum efficiency of the **P1/P2** blend device was 3.71% at 5.5 V. We conclude that the **P1/P2** blend is a good candidate for use as a green-emitting layer in PLEDs. These results also suggest that the **P1/P2** blend facilitates balanced electron and hole injection. More than an order of magnitude enhancement in the maximum brightness is found in the blend devices compared to those using pure copolymers. The turn-on voltages of the **P1/P3** blend, 2:8, 5:5, 7:3, devices are 3.5, 5.5 and 4 V with external quantum efficiencies of 0.005, 0.002 and 0.138%, respectively. The very reduced efficiencies are in large part due to an unbalanced charge carrier injection in the blend.

4. Conclusion

The emission colors of the fluorene copolymers can be tuned from violet to yellow by adjusting their molecular structure. PL studies showed that efficient Förster energy transfer from the higher band-gap polymer (**P1**) to the lower band-gap polymer (**P2** or **P3**) can be achieved in the solid state due to intermolecular interactions whereas in dilute solution, energy transfer was not observed. Only a green emission was obtained in the solid-state PL and EL of the blends, suggesting a complete Förster energy transfer process in the blends. The LEDs of copolymer blends (**P1/P2**) exhibit significantly better performance than the device using **P1** or **P2** because of energy transfer. Studies of other blend combinations are under way.

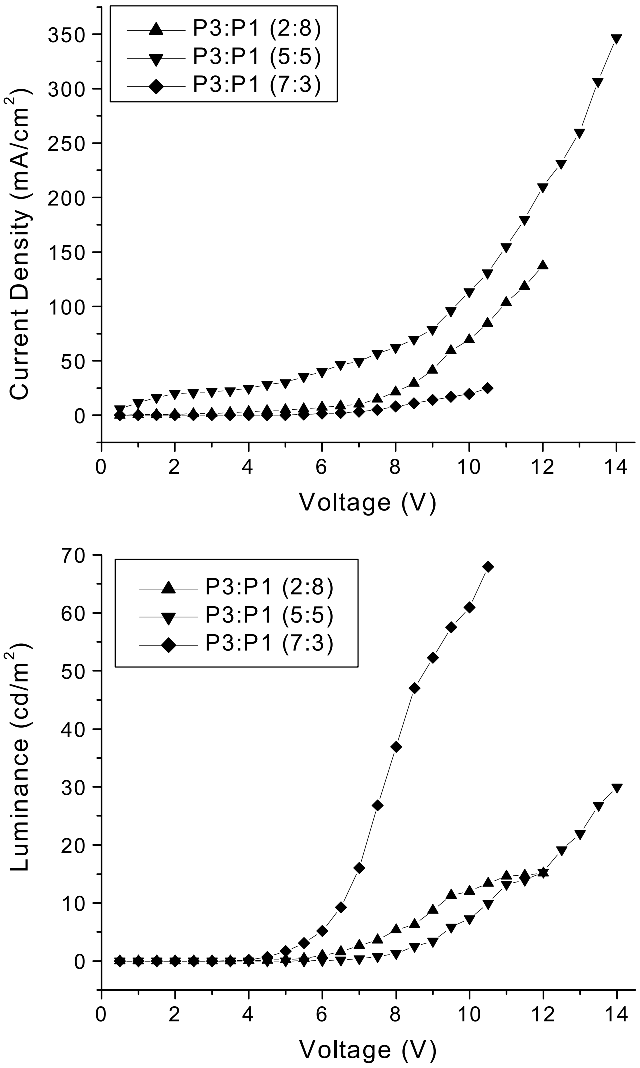

Fig. 9. *J–V* and *L–V* characteristics for the **P1/P3** blend LEDs.

Acknowledgements

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