

Characterization of white electroluminescent devices fabricated using conjugated polymer blends

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We report the characterization of white light emitting devices fabricated using conjugated polymer blends. Blue emissive poly[9,9-bis(4'-n-octyloxyphenyl)fluorene-2,7-diyl-co-10-(2'-ethylhexyl)phenothiazine-3,7-diyl] [poly(BOPF-co-PTZ)] and red emissive poly(2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene) (MEH-PPV) were used in the blends. The inefficient energy transfer between these blue and red light emitting polymers (previously deduced from the photoluminescence (PL) spectra of the blend films) enables the production of white light emission through control of the blend ratio. The PL and electroluminescence (EL) emission spectra of the blend systems were found to vary with the blend ratio. The EL devices were fabricated in the indium tin oxide [poly(3,4-ethylenedioxy-thiophene)-poly(styrenesulfonate)] (ITO/PEDOT-PSS)blend/LiF/Al configuration, and white light emission was obtained for one of the tested blend ratios.

I. INTRODUCTION

Conjugated polymers have attracted much research interest in science and technology in the past few decades as electro-active materials for diverse applications that include transistors,¹⁻³ photovoltaic devices,⁴ nonlinear optical devices,⁵ and polymer light-emitting diodes (PLEDs).⁶⁻¹⁰ In particular, their use in electroluminescence applications has been extensively studied to realize thin, efficient, and stable displays with a wide viewing angle and fast response. Organic electroluminescence (EL) applications such as automotive, mobile, and television displays continue to make progress toward commercial production. Poly(fluorene)s (PFs)¹¹⁻¹⁵ and poly(1,4-phenylenevinylene)s (PPVs)¹⁶⁻²⁰ are promising candidates for PLEDs. PPV derivatives are normally green and red emitting materials; the introduction of electron-donating or electron-withdrawing groups into these derivatives can be used to vary their emitting color.

Although PFs are blue emitting materials, color tuning of these materials is easily obtained by copolymerization with low band gap comonomers.¹⁵

White light emitting diodes have attracted significant research interest due to their applications in full color displays combined with a color filter, in backlights for liquid crystal displays, and in meeting various other lighting requirements. White light emission requires the mixing of two complementary colors or three primary colors. Various methods and challenges for generating white light have been reported. The doping method has been widely used to obtain white light. In small molecule devices, a red light emitting material is co-deposited with blue and/or green light emitting materials.²¹⁻²³ Kido et al. have reported that solution-processed polymer devices using composites of blue (B), green (G), and red (R) emitting dyes and poly(vinylcarbazole) emit white light.²⁴ In both vacuum-deposited small molecule devices and solution-processed polymer devices, control of the energy transfer between the red, green, and blue dyes is essential and usually requires the introduction of very low levels of doping controls.

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Recently, we found that there is inefficient energy transfer between PF and PPV derivatives.²⁵ Therefore, it is possible to obtain white light emission from a blend of PF and PPV derivatives by controlling the blend ratio. In this study, we fabricated white light emitting diodes using polymer blends composed of two emission components. A highly efficient blue light emitting PF copolymer, poly[9,9-bis(4'-*n*-octyloxyphenyl)fluorene-2,7-diyl-co-10-(2-ethylhexyl)phenothiazine-3,7-diyl] [poly-(BOPF-co-PTZ)], and a well known red light emitting PPV derivative, poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV), were used in the blends. The synthetic routes of the polymers used in the blend system are shown in Fig. 1.

II. EXPERIMENTAL

A. Synthesis of poly(84BOPF-co-16PTZ)

Poly(84BOPF-co-16PTZ) was synthesized using nickel (0) mediated polymerization. The feed ratio of phenothiazine monomer was 10 mol% of the total amount of monomer, and the total amount of reactant was 1.8 mmol. Each Schlenk tube containing 5 mL of dimethylformimide (DMF), bis(1,5-cyclooctadienyl) nickel(0), 2,2'-dipyridyl, and 1,5-cyclooctadiene (the last three in a molar ratio of 1:1:1) was kept under argon at 80 °C for 30 min. Five milliliters of anhydrous toluene was then added to the mixture. The polymerization was maintained at 80 °C for 72 h, and then 0.1 g of 9-bromoanthracene was dissolved in toluene and added to the reaction mixture for end-capping. When the reaction had

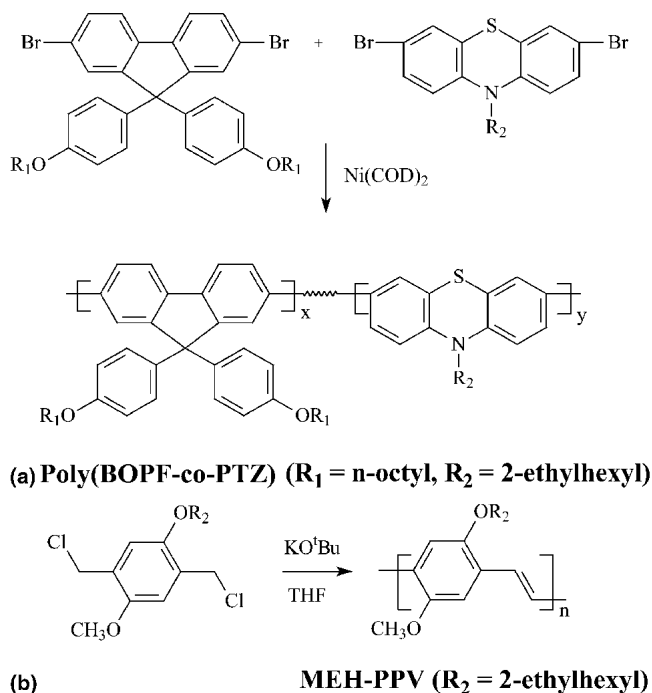


FIG. 1. Synthetic schemes for the (a) poly(BOPF-co-PTZ) and (b) MEH-PPV.

finished, the polymer was precipitated from an equivalent mixture of concentrated HCl, methanol, and acetone. The isolated polymer was dissolved in chloroform and precipitated in methanol. The resulting polymer was dissolved in toluene and purified using silica gel column chromatography with toluene as the eluent. Finally, the polymer was purified by Soxhlet extraction with methanol and dried in vacuum. The polymer yield was 59% after purification. The actual composition of the copolymer was determined by elemental analysis; the proportion of phenothiazine in the copolymer was found to be 16%, so this copolymer is poly(84BOPF-co-16PTZ).

B. Synthesis of MEH-PPV

A solution of 2,5-bis(chloromethyl)-4-(2-ethylhexyloxy)benzene (1.0 g, 3 mmol) in dry tetrahydrofuran (THF) was degassed at room temperature. To the stirred solution a degassed solution of 95% potassium *tert*-butoxide (2.12 g, 19 mmol) in dry THF (80 mL) was added dropwise during 20 min at 20 °C. The reaction mixture became red and viscous during the addition. The highly viscous reaction mixture was stirred at 20 °C under an atmosphere of argon for 16 h, after which it was evaporated to 2/3 of its initial volume and poured into methanol (50 mL) with stirring. The resulting red precipitate was filtered, washed with distilled water, dissolved in the minimum quantity of THF (~100 mL), and then reprecipitated by pouring into methanol (500 mL); the precipitate was then dried in vacuo at 20 °C to afford MEH-PPV. The polymer yield was 60% after purification.

C. Fabrication and characterization of the EL devices

The absorption spectra were measured using a Hitachi spectrophotometer model U-3501, and the steady-state photoluminescence spectra were recorded on a Spex FL3-11. The ionization potentials of the polymer films were measured with a low-energy photo-electron spectroscope (Riken-Keiki AC-2). The polymer films were prepared by spin-casting blend solutions containing 1% of the polymers by weight in chlorobenzene. Uniform and pinhole-free films with a thickness around 80 nm were easily obtained from the polymer solution. For the double layer device, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxy-thiophene)] doped with poly(styrene sulfonate) (Bayer AG, Leverkusen, Germany) was used as the hole-injection/transport layer. To improve the electron injection, we deposited a thin LiF layer (~0.5 nm) onto the polymer film and then deposited the aluminum electrode (~100 nm) using the thermal evaporator at a pressure of 10^{-6} Torr. The device performance was studied by measuring its current-voltage-EL (I-V-L) characteristics, EL spectra, and Commission Internationale d'Eclairage (CIE) coordinates. The I-V-L

characteristics were measured with a Keithley 236 (Keithley Instruments, Inc., Cleveland, Ohio) source-measure unit and a Keithley 2000 multimeter equipped with a photomultiplier tube (PMT) through an ARC 275 (Acton Research Corp, Acton, Massachusetts) monochromator. The external quantum efficiency of the EL, defined as the ratio of the emitted photons to the injected charges, was calculated from the EL intensity measured with the calibrated Si photodiode. All processes and measurements described above were carried out in air at room temperature.

III. RESULTS AND DISCUSSION

Figure 2 shows the ultraviolet (UV)-visible absorption spectrum of each polymer used in the polymer blends. Poly(84BOPF-co-16PTZ) and MEH-PPV exhibit absorption maxima at 371 and 512 nm, respectively. Optical band gaps were obtained from the absorption edges of each polymer. The blue light emitting poly(84BOPF-co-16PTZ) has a wider band gap (2.82 eV) than MEH-PPV (2.10 eV). To determine the highest occupied molecular orbital (HOMO) levels of the polymers, their ionization potentials were measured using photoemission spectroscopy. The measured ionization potentials of poly(84BOPF-co-PTZ) and MEH-PPV were 5.40 and 4.90 eV, respectively. The lowest unoccupied molecular orbital (LUMO) levels of the poly(84BOPF-co-16PTZ) and MEH-PPV thin films were estimated to be 2.58 and 2.80 eV, respectively. Poly(84BOPF-co-16PTZ) and MEH-PPV thin films exhibit photoluminescence (PL) maxima at 482 nm (greenish blue) and 575 nm (orange red), respectively, as shown in Fig. 2.

Several polymer blend systems with different blend ratios were prepared from these two polymers. We prepared several blend systems containing 0.5 to 3.0% red emitting MEH-PPV in the blue emitting PF copolymer

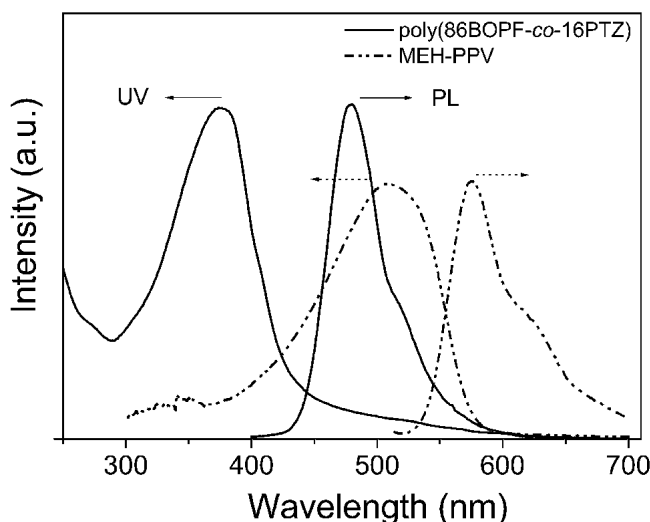


FIG. 2. UV-visible absorption and PL emission spectra of the individual polymer films.

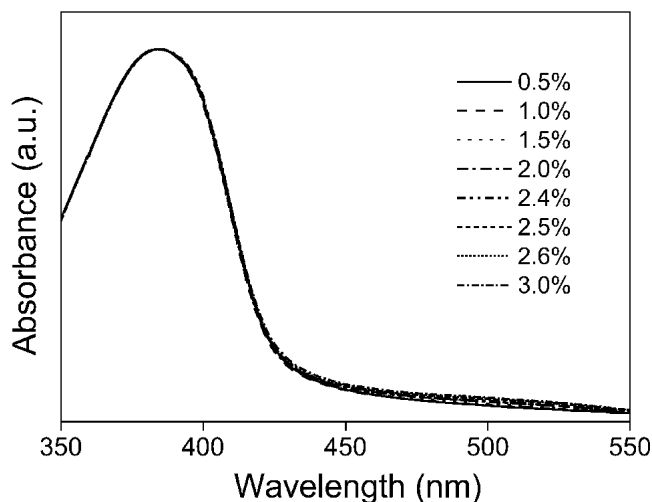


FIG. 3. UV-visible absorption spectra of the thin films of the polymer blends with different blend ratios.

host. Figure 3 shows the UV-visible absorption spectra of the blend systems. Their absorption spectra are almost the same as that of the host PF derivative; only weak absorption due to MEH-PPV was observed, suggesting that most of the absorption was due to the PF copolymer.

Figure 4 shows the PL spectra of the polymer blends. As the ratio of MEH-PPV increases, the intensity of the emission band near 560 nm increases. In the polymer blend containing 2.5% MEH-PPV, the intensities of the two emission bands at 490 and 560 nm are comparable. Considering that the spectral overlaps of poly(BOPF-co-PTZ) and MEH-PPV are large enough to produce Förster energy transfer between the polymers, this inefficient energy transfer is likely to be due to a phase separation of the polymer blends, which should be investigated further. In fact, this inefficient energy transfer enables the production of white light emission through control of the blend ratio. Properties of the poly(84BOPF-co-16PTZ) and MEH-PPV are summarized in Table 1. EL devices were fabricated in the (ITO/PEDOT-PSS)blend/LiF/Al configuration. Figure 5 shows the EL spectra of the EL devices fabricated using the polymer blend systems. As in the PL spectra, as the MEH-PPV ratio in the blend system increases the intensity of the emission band at 560 nm increases. The two emission bands in the EL spectra of the EL device using a polymer blend containing 2.5% MEH-PPV are of comparable intensity, and this device exhibits an efficient white light emission.

One of the major problems of white EL devices is that the emission color varies with the voltage or current that is applied. This variation of the emission color lessens the color purity of such EL devices. To investigate the devices' stability of emission, we measured the voltage dependence of the EL spectra of the devices using 2.5% blend system. As shown in Fig. 6, the devices exhibit EL

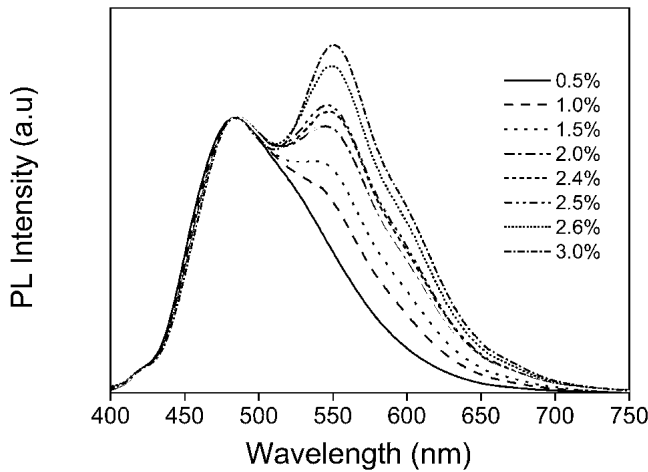


FIG. 4. PL emission spectra of the thin films of the polymer blends with different blend ratios.

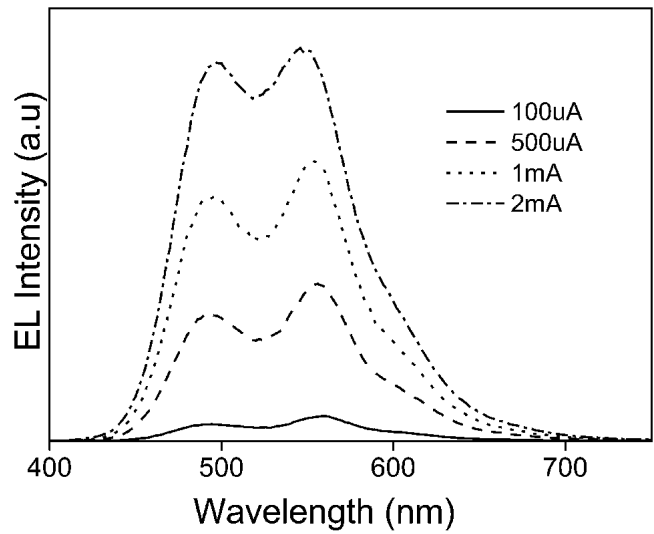


FIG. 6. Current versus EL spectra of the devices using 2.5% MEH-PPV.

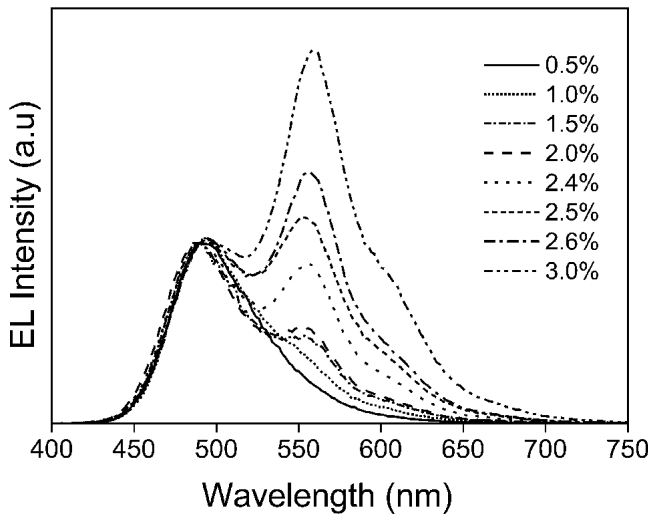


FIG. 5. EL spectra of the devices with ITO/PEDOT/blend/LiF/Al configurations using polymer blends with different blend ratios.

spectra that are stable to variation of the applied current. Among all the EL devices tested in this experiment, the device using the 2.5% MEH-PPV blend system exhibited the CIE coordinates (0.32, 0.49) closest to the standard CIE coordinates for white light emission (0.33, 0.33).

Figure 7 shows the current-voltage and luminance-voltage characteristics of the EL devices. The forward current was found to increase with increasing forward bias voltage, and the curve has the same characteristics as those of a typical diode. There was little difference between the I-V-L characteristics of the devices, and light emission from the devices was observed at an applied voltage of less than 10 V. The maximum brightness of the devices ranged from 1580 to 2640 cd/m^2 with external quantum efficiencies of 0.3 to 0.40%. The CIE coordinates measured at 100 cd/m^2 brightness and other device characteristics are summarized in Table II.

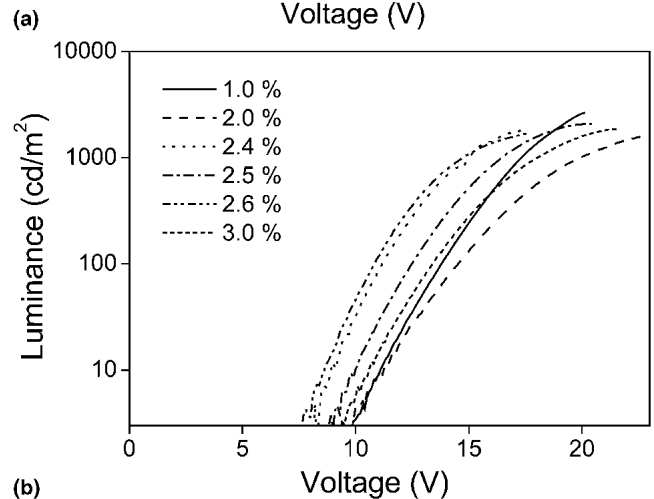
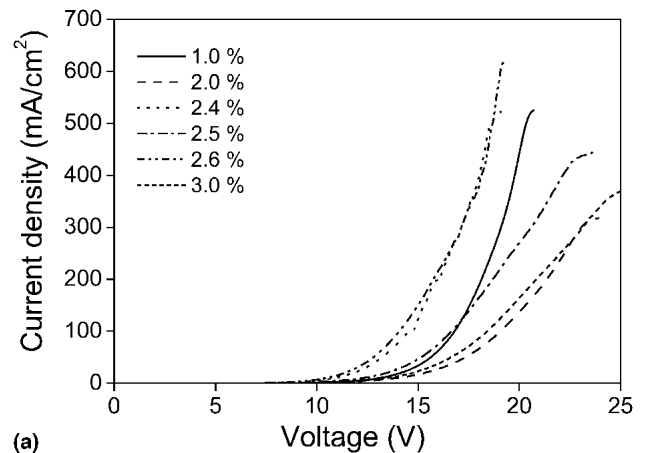


FIG. 7. (a) I-V and (b) L-V curves of the EL devices with ITO/PEDOT/blend/LiF/Al configurations.

The CIE coordinates of the EL devices using the polymer blends can be further tuned by changing the blend ratio. Our results for the EL devices using the above polymer blends are preliminary, so optimizations of

TABLE I. Summary of the properties of the polymers used in the blends.

Polymer	Poly(84BOPF-co-16PTZ)	MEH-PPV
Average M_w	31,500	147,000
PDI	1.7	4.8
UV max (nm) ^a	371	512
PL max (nm) ^a	482	575
Optical band gap (eV)	2.82	2.10
HOMO level (eV) ^b	5.40	4.90
LUMO level (eV)	2.58	2.80

^aMeasured for thin films on fused quartz plates.

^bDetermined by photoemission spectroscopy using Riken Keiki AC-2. PDI, polydispersity index; PL, photoluminescence; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbitals.

TABLE II. Summary of the device characteristics.

Polymers ^a	$V_{\text{turn-on}}$ (V)	Luminance (cd/m ²)	Efficiency (%)	Power efficiency (lm/W)	CIE coordinates ^b (x,y)
Blend 1.0%	9.9	2640	0.31	0.15	(0.19, 0.45)
Blend 2.0%	9.9	1580	0.34	0.16	(0.23, 0.42)
Blend 2.4%	8.2	1800	0.31	0.22	(0.28, 0.46)
Blend 2.5%	9.0	2080	0.39	0.24	(0.32, 0.49)
Blend 2.6%	7.7	1670	0.30	0.22	(0.32, 0.51)
Blend 3.0%	9.4	1860	0.40	0.25	(0.36, 0.51)

^aThe percentage indicates the wt% of MEH-PPV in the blend system.

^bThe CIE coordinates were measured at 100 cd/m² brightness.

the device and the blend ratio are needed to obtain high efficiency white light emission, which are under investigation.

IV. CONCLUSIONS

Blends of light emitting polymers were prepared to produce white light emission. EL devices using polymer blends of poly(84BOPF-co-16PTZ) and MEH-PPV were found to exhibit current- and voltage-independent stable white light emission. A polymer blend contained 2.5% MEH-PPV was found to exhibit an EL spectrum that is closer to the standard white than those of the devices using other blend ratios. A maximum brightness of 2080 cd/m², an external quantum efficiency of 0.39%, and CIE coordinates of (0.32, 0.49) at 100 cd/m² were obtained with the device. We suggest that inefficient energy transfer between blue light emitting PF derivatives and low band gap PPV derivatives can be taken advantage of to produce efficient white light emitting diodes.

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