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WHITE ELECTROLUMINESCENT DEVICES USING POLYMER BLENDS

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White light-emitting devices were fabricated using the blends of blue, green, red emissive polymers of poly[9,9-(2'-ethylhexyl)fluorene] (PEHF), poly(9,9-dioctyl-fluorene-2,7-vinylene) (POFV), poly(2-(3',7'-dimethyloctyloxy)-5-methoxy-1, 4-phenylene-1-cyanovinylene) (CN-PPV) and poly(2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene) (MEH-PPV). Inefficient energy transfers between the blue polymer and the green or the red polymer, which was observed in PL spectra of the blend films, provides a good advantage to get a white light emission due to better blend ratio controllability. The EL devices were fabricated with ITO/PEDOT/blend/Ca/Al configuration and good white light-emission was obtained for a certain blend ratio. The light-emission was observable from 4 V and the maximum brightness of $400 \, \text{cd/m}^2$ was obtained with the device.

Keywords: electroluminescence; polymers blends; white light-emitting

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1. INTRODUCTION

Conjugated polymers have attracted much research interest in science and technology in the past few decades as electro-active materials for diverse applications such as batteries, molecular electronic devices, and light emitting diodes (LEDs), etc. Especially, electroluminescence has been studied extensively in order to realize thin, efficient and stable displays with wide viewing angle and fast response. The applications such as automotive, mobile and television displays continue to make progress toward a commercial stage of organic EL. Poly(fluorene)s (PFs) and poly(1,4-phenylenevinylene)s (PPVs) are promising candidates for polymer light emitting diodes (PLED) [1–3]. PPV derivatives are normally green and red emitting materials and introduction of electron-donating or electron-withdrawing group can change emitting color. Although PFs are blue emitting materials, color tuning is easily obtained by copolymerization with low band gap comonomer [4,5] or blend with dyes [6].

White EL materials attract much attention because these applications include full color displays using color filters as well as LCD back light applications. Several approaches have been done to obtain white LEDs. The doping method has been widely used to obtain white light. For small molecule device, red emitting material is co-deposited with blue and/or green emitting materials [7]. In solution processed polymer devices, Kido et al. reported composites of blue(B), green(G), and red(R) emitting dyes and poly(vinylcarbazole) emitted white light [8]. In both vacuum deposited small molecule devices and solution processed polymer devices, control of energy transfer between red, green and blue dyes is essential and it usually needs very low level doping controls.

Recently, we have studied color tuning and energy transfer phenomena between poly(fluorene) (PF) and low band gap materials. Composites or blends of PF and green and/or red emitting dyes exhibited green or red emission from blue emitting PF [9]. From this study, we found that there is an inefficient energy transfer between poly(9,9-bis(2-ethylhexyl)fluorine-2,7-diyl) (PEHF) and poly(1,4-phenylenevinylene) (PPV) derivatives. Therefore, there is an opportunity to obtain white light emission from the blend of PF and PPV derivatives in controllable blend ratio. In this study, poly(9,9-dioctylfluorene-2,7-vinylene) (POFV), which is a new class of bluish green light emitting material, poly(2-(3',7'-dimethyloctyloxy)-5-methoxy-1,4-phenylene-1-cyanovinylene) (CN-PPV), and poly(2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene) (MEH-PPV) have been used for the blends of PF and PPV derivatives. In this paper, the fabrication of white light emitting devices using polymer blends of PF and PPV derivatives will be described.

2. EXPERIMENTAL

Poly[9,9-(2'-ethylhexyl)fluorene] (PEHF) [10], CN-PPV [11] and MEH-PPV [12] were prepared in a similar way to the previous papers, and POFV was supplied by Hanwha Chemical R&D Center. The polymer structures used in the blend system are shown in Figure 1. The absorption spectra were measured by a Hitachi spectrophotometer model U-3501 and steady-state photoluminescence spectra were recorded on a Spex FL3-11. The polymer film was prepared by spin casting the 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(3,4ethylenedioxy-thiophene)] doped with poly(styrene sulfonate) (PSS) (Bayer AG, Germany) was used as a hole-injection/transport layer. Metal contact (Ca) was deposited on the top of the polymer film through a mask by vacuum evaporation at pressure below 4×10^{-6} Torr, yielding active areas of 4 mm². In the case of Ca cathode (~50 nm), an additional encapsulating layer of Al (~200 nm) was thermally evaporated. For the measurements of device characteristics, current-voltage (I-V) changes were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818-SL). Bright and 1931 CIE chromaticity of the EL devices were recorded by a PR-650 SpectraScan colorimeter. All processes and measurements mentioned above were carried out in air at room temperature.

FIGURE 1 Polymer structures used in the polymer blends.

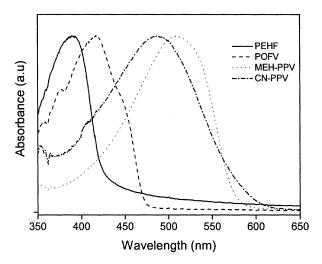


FIGURE 2 UV-visible spectra of the individual polymer films.

3. RESULTS AND DISCUSSION

Figure 2 shows the UV-visible absorption spectra of the each polymer used in the polymer blends. PEHF, POFV, CN-PPV and MEH-PPV show the absorption maxima at 390, 418, 488 and 512 nm, respectively. Optical band gaps were obtained from absorption edges of the each polymer. Blue

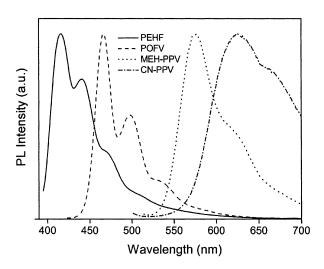


FIGURE 3 PL spectra of the individual polymer films.

	$\lambda_{ m max}(m nm)^a$		Band gap	HOMO ^b	
Polymers	UV absorption	PL emission	(eV)	(eV)	
PEHF	390	416	2.90	5.8	
POFV	418	466	2.60	5.7	
CN-PPV	488	625	2.04	5.7	
MEH-PPV	512	575	2.10	4.9	

TABLE 1 Summary of Spectroscopic Results of the Polymers

light-emitting PEHF shows most wide band gap $(2.90\,\mathrm{eV})$ among the polymers, and the measured band gaps of POFV, CN-PPV and MEH-PPV are 2.60, 2.04 and $2.10\,\mathrm{eV}$, respectively. To determine HOMO levels of the polymers, ionization potentials were measured by photo-emission spectroscopy. The measured ionization potentials of PEHF, POFV, CN-PPV and MEH-PPV were 5.8, 5.7, 5.7, and $4.9\,\mathrm{eV}$, respectively.

Figure 3 shows the PL spectra of the polymers. PEHF, POFV, MEH-PPV and CN-PPV show the peak PL maxima at 416 (blue), 466(blue-green), 575 (orange-red) and 645 nm (red), respectively. All the spectroscopic results of the polymer films are summarized in Table 1.

Four different polymer blends of blend 1 (PEHF:POFV:CN-PPV = 95:4:1), blend 2 (PEHF:POFV:CN-PPV = 90:8:2), blend 3 (PEHF:POFV:MEH-PPV = 95:4:1) and blend 4 (PEHF:POFV:MEH-PPV = 90:8:2), were prepared

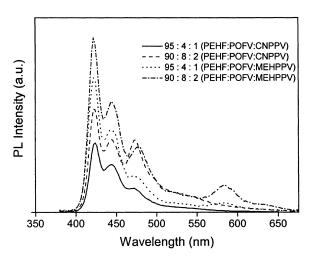


FIGURE 4 PL spectra of the polymer blends.

^aMeasured in the thin films onto fused quartz plates.

^bDetermined by photo emission spectroscopy using Ricken Keiki AC-2.

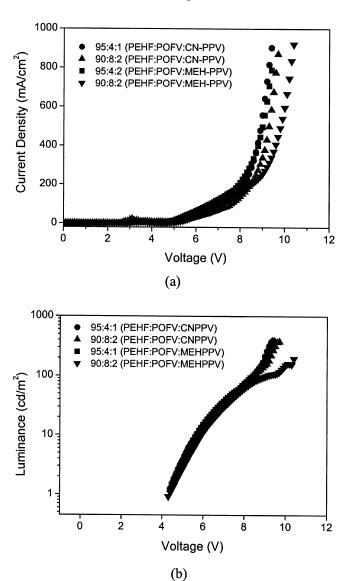


FIGURE 5 I-V (a) and L-V (b) curves of the EL devices with ITO/PEDOT/blend/Ca/Al configuration.

with above polymers in order to get white-light emitting diodes. Figure 4 shows the PL spectra of the polymer blends. All PL spectra show the emission of PEHF and the emissions of POFV, CN-PPV and MEH-PPV are hardly

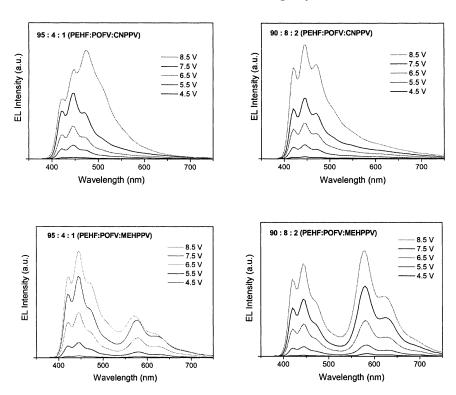


FIGURE 6 Voltage dependent EL spectra of the devices with ITO/PEDOT/blend/Ca/Al configuration.

observed. Considering that the spectral overlaps of PEHF and POFV are good enough to take forster energy transfer between them, this inefficient energy transfer is attributed to a phase separation of polymer blends, which should be investigated further. In fact, this inefficient energy transfer provides a good advantage to get a whit light emission due to better blend ratio controllability.

EL devices were fabricated with ITO/PEDOT/blend/Ca/Al configuration. Figure 5 shows the current-voltage and luminance-voltage characteristics of the EL devices. Forward current increases with increasing forward bias voltage and the curve shows a typical diode characteristics. There was little difference in I-V-L characteristics of the devices and the light-emissions were observable from $4\,\mathrm{V}$. The maximum brightness of the devices ranged from $200\text{--}400\,\mathrm{cd/m^2}$ with luminous efficiencies of $0.023\text{--}0.034\,\mathrm{lm/W}$.

Figure 6 shows the voltage dependence EL spectra of the devices. One of the major problems in white EL device is voltage dependence color

Polymers	$V_{ m turn-on} \ (V)$	Luminance (cd/m²)	Efficiency (lm/W)	CIE coordinate ^a (x,y)
Blend 1	3.3	400	0.023	(0.18,0.14)
Blend 2	3.3	380	0.030	(0.20, 0.17)
Blend 3	3.1	320	0.027	(0.25, 0.20)
Blend 4	3.3	200	0.034	(0.33, 0.28)

TABLE 2 Summary of the Device Characteristics

change, which deteriorate color purity of the EL devices. As shown in Figure 6, EL spectra of the devices using blend 1 and blend 2 were slightly changed by increasing voltage, but the devices using blend 3 and blend 4 showed stable EL spectra against changing applied voltage. In EL spectra of the devices using blend 1 and blend 2, red emission from CN-PPV is very weak, but devices using blend 3 and blend 4, the red emission from MEH-PPV significantly comes out. This difference between CN-PPV and MEH-PPV might be investigated further in terms of phase separation and electronic property. Especially the EL devices using blend 4 showed most good CIE coordinate (0.33,0.28) among the devices, which is the closest value to the best CIE coordinates of a white light emission, (0.33,0.33). One of the major problems in white EL device is a color change with applied voltages which deteriorate color purity of the EL devices. The devices using blend 3 and blend 4 showed stable EL spectra against changing applied voltages. The CIE coordinate measured at 100 cd/m² brightness and other device characteristics are summarized in Table 2. The CIE coordinates of EL devices using the polymer blends can be further tuned by changing blend ratio. The results of the EL devices from the above polymer blends were preliminary and the optimizations of device and blend ratio is needed to obtain white light emission with a good efficiency, which are under investigation.

4. CONCLUSION

Light-emitting polymer blends were prepared in order to get a white light emission. The white EL devices using polymer blend of PF, POFV, MEH-PPV showed less voltage dependence on EL spectra with good CIE coordinates of (0.33,0.28) at $100 \, \text{cd/m}^2$. We suggested that inefficient energy transfer between PFs and low band gap PPV derivatives could be used to get efficient white light-emitting diodes with better blend controllability.

^aMeasured at 100 cd/m² brightness.

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