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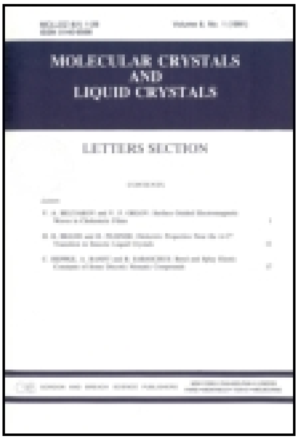

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Fabrication of White Polymer Light Emitting Diode with Single Emitting Layer Using Blends of Polyfluorene Based Polymers

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We synthesized one blue emitting polymer (P1) and two green emitting polymers (P2, P3) based on polyfluorene with wide photoluminescence spectra, and fabricated white polymer light emitting diodes (W1, W2) with single emitting layer through a blend method. The weight ratio of P1 and P2 or P3 was adjusted to achieve white light emission and to balance the light color. In this study, we achieved (575 cd/m^2, 0.68 cd/A) with bluish white emission using W1 (P1 : P2 = 98.0 : 2.0), and (554 cd/m^2, 0.8 cd/A) using W2 (P1 : P3 = 98.0 : 2.0) with greenish white emission. Luminance of devices, which had the donor concentration above 2.0 wt%, decreased on account of high concentration quenching.

Keywords Blend method; polyfluorene; white polymer light emitting diode

Introduction

In recent years, white organic light emitting diodes (WOLEDs) have attracted an increasing attention for various applications such as next generation lighting source, full color display with color filter and backlight for liquid crystal display (LCD) [1–3]. In the fabrication of WOLEDs, various methods have been used to create white light emission, for example, multi-layer structures [4,5], polymer blends [6–9], a small molecular [10] or polymer [1,11] host doped with different color dyes, microcavity structures [12], and single-material active layer with a wide emission spectrum [13,14]. To fabricate WOLEDs based on small molecules, a general approach is sequentially to evaporate multiple layers with a specific emission color for each layer [4,5] or simultaneously to evaporate multi-materials in one layer [10] in a high vacuum, which is a quite complicated technique to realize white light. The WOLED based on light emitting polymer (WPLED), however, often consist of a single active layer easily made by wet processes, including spin-casting, screen printing or ink-jet printing techniques [6,11,15–17], which are expected to reduce the cost in mass production, especially in the production of large-area panel displays and light source.

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Polymers based polyfluorenes (PFs) have not only high photoluminescence (PL) efficiency and high stability of temperature and oxidation, but also simple synthetic process and high quantum efficiency. Moreover, because PFs can be functionalized readily by modifying the C—9 position of the fluorene monomer, they have various merits such as a good solubility in common organic solvents, a simple process for adjustment of PL, etc. Therefore, polymer based PFs are very promising candidates for light emitting materials. [7,18–20]

In this study, we developed one blue emitting polymer (P1) and two green emitting polymers (P2, P3) with wide PL spectra through Suzuki cross coupling. Also, we fabricated two polymer blends (W1, W2) for white light emission. W1 and W2 were produced by mixing P1 and P2, and P1 and P3 with weight ratio from 98.5 : 1.5 to 97.0 : 3.0, respectively. The weight ratio of blue and green polymer was adjusted to achieve white light emission and a balance the light color. Additionally, we fabricated and evaluated WPLEDs with W1 and W2 by various mixing ratio.

Experimental

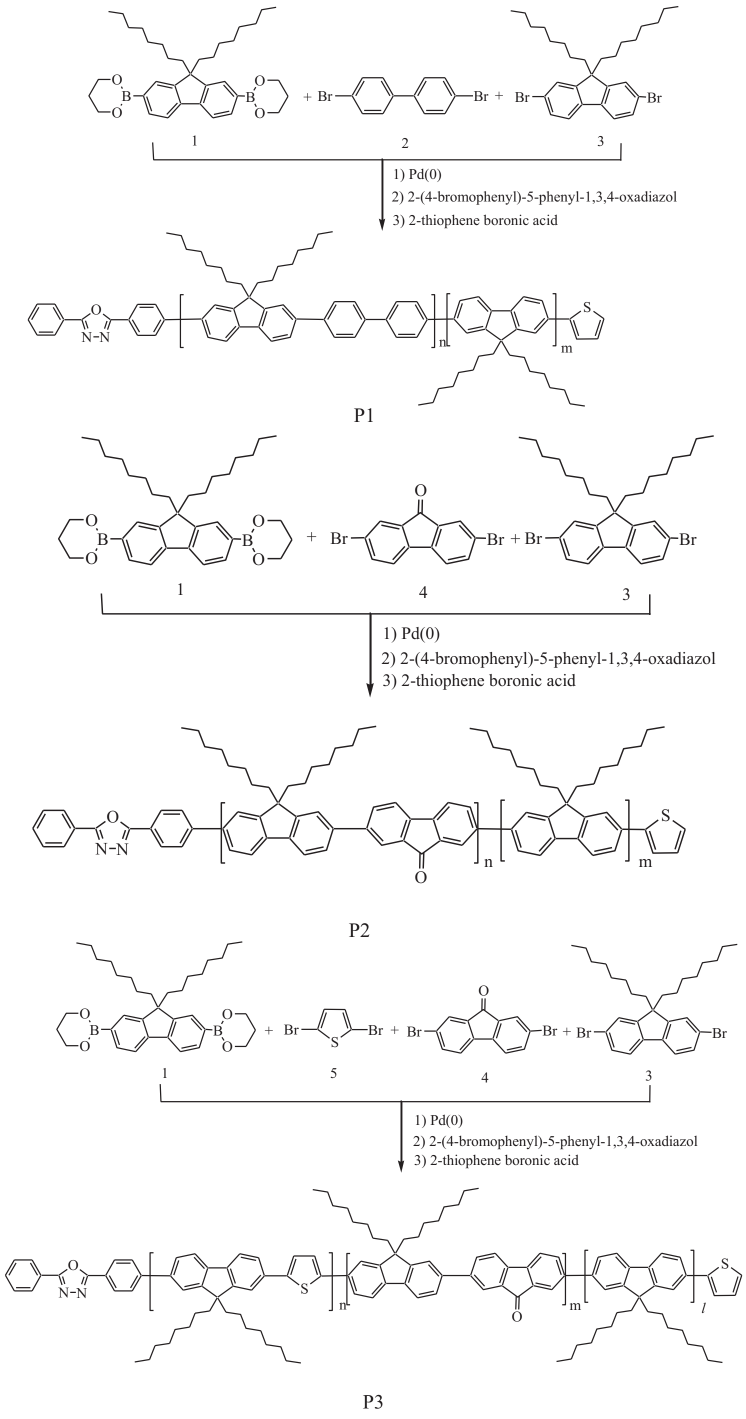
1. Instrumentation

Molecular weight was determined using a Water's alliance 2000 gel permeation chromatography (GPC) instrument calibrated with polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymers were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min using a Setaram, Betsys 24 TG-DTA and Seiko, SSC5200H instruments, respectively. The absorption spectra and the PL spectra of the polymers were measured using an Optizen 3220 UV/Vis spectrophotometer and a spectra pro 2150i spectrometer, respectively. Current density (J) - voltage (V) - luminescence (L) characteristics of WPLEDs were measured with a XANTRAX XLD35–5TP and Minolta CS—100, respectively.

2. Synthesis of Polymers

The synthetic routes of the copolymers were shown in Scheme 1. Solvents were purchased form Aldrich Chemical Company. The monomer, 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **1,** 2,7-dibromo-9,9-dioctylfluorene **3**, 2,7-dibromo-9-fluorenone **4,** 2,5-dibromothiophene **5**, dibromobiphenyl **2** and the two end capping reagents, 2-thiophene boronic acid and 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole, were purchased from Aldrich Chemical Co. and were used without further purification.

2.1. Blue Polymer (P1). The phase transfer catalyst, aliquat 336 (0.70 g), tetrakis (triphenylphosphine)palladium (0.02 g) and 2 M aqueous sodium carbonate (25 mL) were added sequentially to a mixture of 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **1** (2.50 g, 4.47 mmol), 2,7-dibromo-9,9-dioctylfluorene **3** (2.07 g, 3.78 mmol), dibromobiphenyl **2** (0.20 g, 0.65 mmol) in toluene (35 mL) under nitrogen. The solution was stirred vigorously and heated under gentle reflux for 1 hour until a viscous reaction mixture was observed. An additional 10 mL of toluene was added, and the reaction was allowed to continue for further 48 hours. Subsequently, the polymer was capped by adding 0.05 g of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole and heating for 6 hours, followed by adding of 0.15 g of 2-thiophene boronic acid and heating for 6 hours. The reaction mixture was cooled



Scheme 1. Synthetic scheme of polymer.

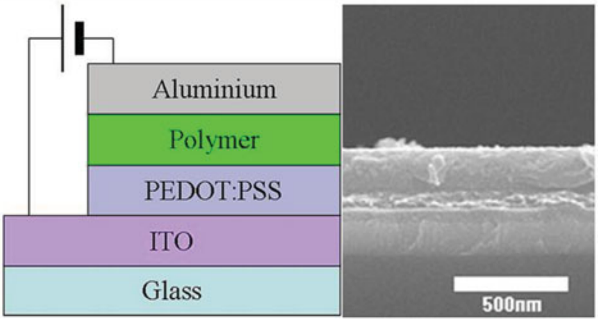


Figure 1. Structure of WPLEDs.

to 50 °C and added slowly to a stirred solution containing 500 mL of methanol and 50 mL of deionized water. The polymer fibers were collected by filtration and washed with methanol. The crude product was dissolved in toluene and reprecipitated with methanol-acetone (1:1). The solid material was washed with acetone for 24 hours in a soxhlet apparatus and dried in a vacuum oven at 60 °C for 24 hours. The polymer weighed 3.11 g (approximately 94% yield).

2.2. Green Polymer (P2). P2 was prepared using a similar procedure used for P1 from 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **1** (2.50 g, 4.47 mmol), 2,7-dibromo-9,9-dioctylfluorene **3** (2.07 g, 3.78 mmol) and 2,7-dibromo-9-fluorenone **4** (0.233 g, 0.69 mmol) in approximately 95% yield.

2.3. Green Polymer (P3). P3 was prepared using a similar procedure used for P1 from 9,9-dioctylfluorene-2,7-bis(trimethyleneborate) **1** (2.50 g, 4.47 mmol), 2,7-dibromo-9,9-dioctylfluorene **3** (2.07 g, 3.78 mmol), 2,7-dibromofluorenone **4** (0.189 g, 0.558 mmol) and 2,5-Dibromothophene **5** (0.135 g, 0.558 mmol) in approximately 95% yield.

3. *Fabrication of WPLEDs*

Patterns of indium tin oxide (ITO) were formed on glass by using photolithography process. The sheet resistance and roughness of the ITO were approximately 11 Ω/□ and 0.608 nm, respectively. Patterned ITO glass was cleaned with acetone, methyl alcohol, 3 % mucasol (Brand Gmbh) solution and Di water in ultrasonic bath. Finally, it was treated with O_2 plasma. The device structure of ITO (150 nm) / poly(styrene sulfonic acid doped poly(ethylene dioxylthiophene) (PEDOT:PSS, BAYTRON P AI4083) (60 nm) / polymer

Table 1. Physical properties of copolymers P1, P2 and P3

	Mw[a]	Mn[a]	PDI[a]	T_g(°C)	T_d[b](°C)
P1	42,048	12,693	3.312	219.9	436.0
P2	28,921	8,240	3.509	216.0	437.2
P3	36,983	14,363	2.574	188.1	437.0

[a] Mw, Mn and PDI of the polymers were determined by GPC using polystyrene standards.
[b] Temperature of 1.6% weight loss measured by TGA in nitrogen.

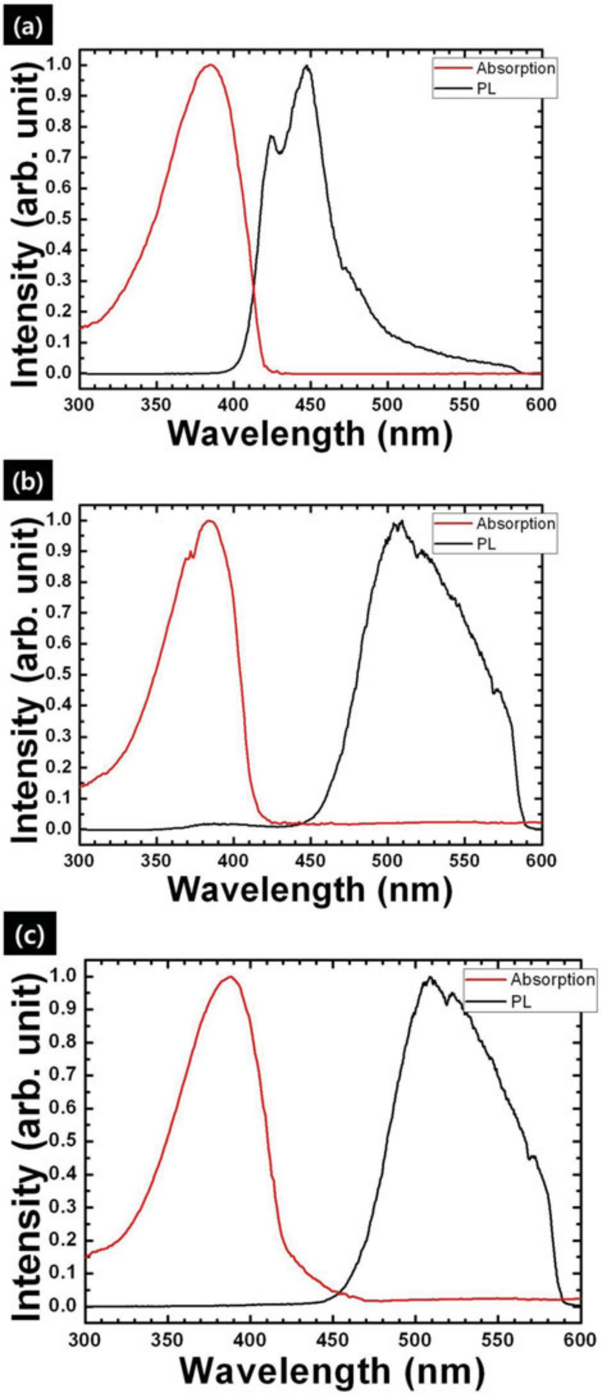


Figure 2. UV-visible absorption and PL spectra of (a) P1, (b) P2 and (c) P3.

blend (80 nm) / aluminum (Al) (160 nm) was employed as shown in Fig. 1. First, for the hole injection layer, PEDOT:PSS filtered with 0.45 um syringe filter was spin-coated on ITO and dried at 100 °C. Then, polymer blend filtered through glass filter with 16 ∼ 40 um pore was spin-coated on the top of PEDOT:PSS. Finally, Al was deposited with a shadow mask by a thermal evaporator under 10^{-5} Torr. The emitting area of device is 3 × 3 mm^2.

Results and Discussion

Table 1 listed the weight-average molecular weight (Mw), number-average molecular weight (Mn), polydispersity index (PDI), glass transition temperature (T_g), and decomposition temperature (T_d). The thermal properties of the polymers were measured by TGA and DSC under a nitrogen atmosphere. The polymers possessed an excellent thermal stability. The T_gs of P1, P2 and P3 were approximately 219.9 °C, 216 °C, and 188.1 °C, all of which were higher than those of the poly(9,9-disubstitutedfluorene) derivatives (∼ 55 °C). The T_ds, as measured by TGA, were all around 467 °C. At lower temperatures, almost no weight loss was observed.

The UV-Vis and PL spectra of polymers, which were measured in methylene chloride at a room temperature, were shown in Fig. 2. The wavelengths of the maximum absorption

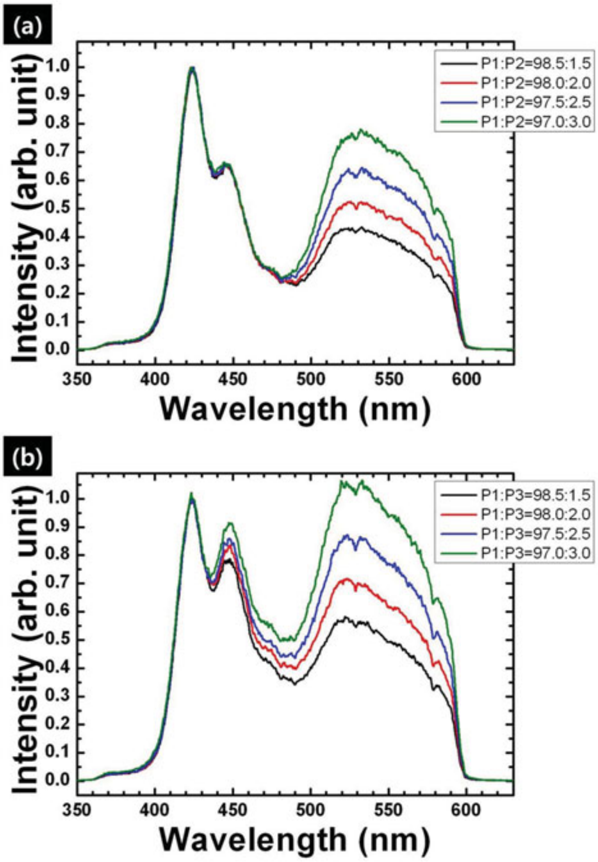


Figure 3. Photoluminescence spectra of (a) W1 and (b) W2.

of P1, P2, and P3 were 385 nm, 384 nm and 388 nm, respectively. These results attributed to π-π^* transition of the conjugated segment. The PL spectra of polymers in thin film were taken under the excitation of the 325 nm line of an He-Cd laser. A thin film of polymers was prepared from a toluene solution by spin-coating it on a quartz plate. Polymer P1 emitted in the blue region with a maximum emission band at 447 nm (shoulder at 423 nm). P2 and P3 showed the green emission at 579 nm and 548 nm.

Figure 3 showed the PL spectra of W1 and W2. We fabricated the two polymer blends, W1 and W2. W1 was produced by mixing P1 and P2 at a mixing weight ratio of 98.5 : 1.5, 98.0 : 2.0, 97.5 : 2.5 and 97.0 : 3.0 in toluene. W2 was produced by mixing P1 and P3 at a mixing weight ratio of 98.5 : 1.5, 98.0 : 2.0, 97.5 : 2.5 and 97.0 : 3.0 in toluene. As shown in Fig. 3, the PL spectra covered a wide range of the visible region. The peaks at the range of 400 ~ 450 were originated from P1, and those of the 500 ~ 600 nm corresponded to the emissions from P2 or P3, respectively. The intensity of each peak could be altered by changing the concentration of the corresponding polymers. As the concentrations of P2 and P3 increased, the peaks around 510 nm went up. These results could be explained with

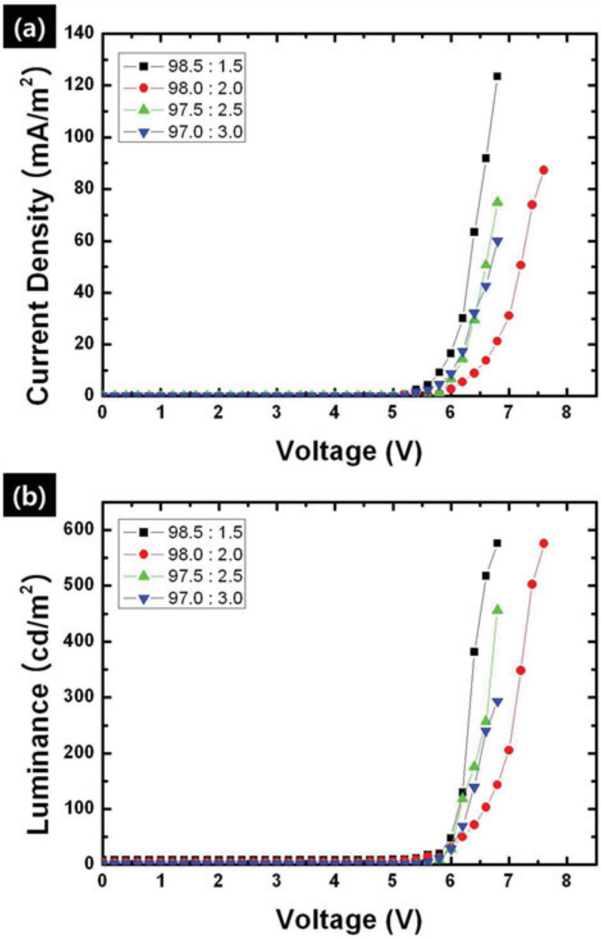


Figure 4. (a) Current density-voltage and (b) luminance-voltage results of WPLEDs using W1.

Förster energy transfer. According to resonance energy transfer theory, an efficient Förster energy transfer requires a large overlap between host emission and acceptor absorption. The small overlap between the emission of P1 and the absorption of P2 or P3 signified low energy transfer efficiency from P1 to P2 or P3. The emission bands from W1 and W2 could cover almost visible spectrum.

The J-V-L characteristics of the devices using W1 and W2 as single emitting layer were shown in Figs. 4 and 5. The maximum luminance and current efficiency of devices based on W1 were (576 cd/m^2, 0.46 cd/A) for 98.5 : 1.5, (575 cd/m^2, 0.68 cd/A) for 98.0 : 2.0, (456 cd/m^2, 0.60 cd/A) for 97.5 : 2.5, and (293 cd/m^2, 0.48 cd/A) for 97.0 : 3.0. In terms of W2 devices, the maximum luminance, current efficiency were (462 cd/m^2, 1.0 cd/A) for 98.5 : 1.5, (554 cd/m^2, 0.8 cd/A) for 98.0 : 2.0, (191 cd/m^2, 0.58 cd/A) for 97.5 : 2.5, and (212 cd/m^2, 0.34 cd/A) for 97.0 : 3.0. The turn-on voltage of W1 device was below 6 V which was lower than that of W2 device. However, W1 device had higher current efficiency than W2 device. As concentration of P2 or P3 increased further above 2.0 wt%, the luminance decreased. It could be due to the concentration quenching of the excited state. Generally, the quenching of donor emission was observed with the decrease of the total blend emission as the relative concentration of the red increased.

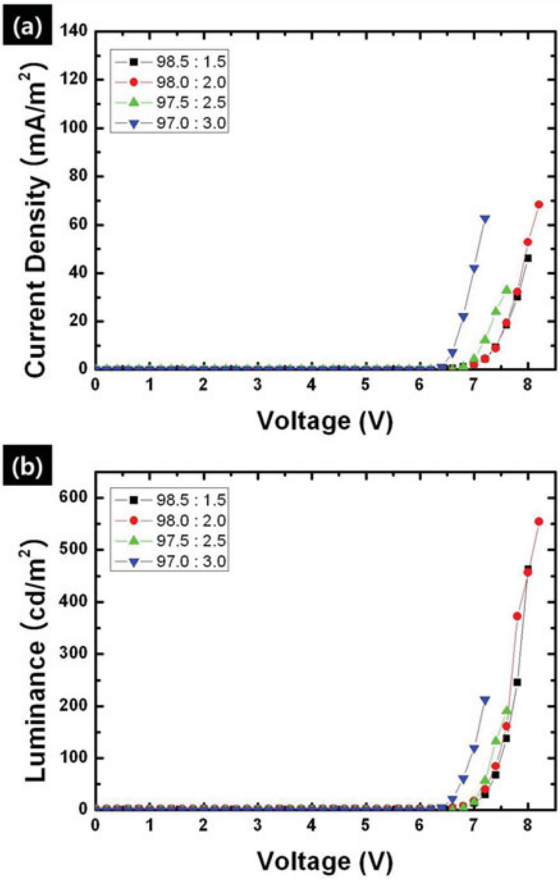


Figure 5. (a) Current density-voltage and (b) luminance-voltage results of WPLEDs using W2.

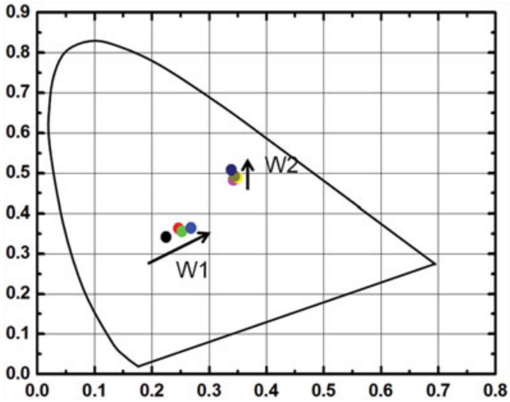


Figure 6. CIE coordinates of WPLEDs using W1 and W2.

Figure 6 showed the 1931 Commission Internationale de l'Enclairage (CIE) coordinates [21] at the maximum luminescence of W1 and W2 devices. As P2 concentration of W1 increased from 1.5 to 3.0, CIE coordinates were changed in bluish white area, (0.225, 0.342), (0.247, 0.363), (0.252, 0.256), (0.269, 0.364). W2 device showed the similar change in greenish white area on the CIE coordinates analysis, (0.343, 0.483), (0.350, 0.488), (0.345, 0.492), (0.339, 0.507). Comparing the results of PL spectra and CIE coordinates, PL spectra by concentration corresponded to CIE coordinates moving to green area. As concentration of P2 and P3 increased in W1 and W2, CIE coordinates shifted to long wave length region, respectively. The CIE coordinate from W1 and W2 could be further tuned by broadening or red-shift of P2 and P3 emission. These results are preliminary, and the optimizations of devices and polymers are required to obtain WPLED with good efficiency and pure white light emission, which are under investigation.

Conclusions

We developed one blue emitting polymer and two green emitting polymers with wide PL spectrum through Suzuki cross coupling, and fabricated WPLEDs with single emitting layer through blend method. The weight ratio of blue and green polymers was adjusted to achieve white light emission and balance the light color. In PL spectra, P1 had narrow blue emitting peak around 448 nm, and P2 and P3 had broad green emitting peaks around 509 nm and 510 nm. Then, we had synthesized blends, W1 and W2 by controlling concentration of P1, P2, and P3 for WPLEDs to adjust white light emission and a balance the light color. The highest luminescence and current efficiency of W1 (P1 : P2 = 98.0 : 2.0) device were 575 cd/m^2, 0.68 cd/A at 7.6 V with bluish white light, and those of W2 (P1 : P3 = 98.0 : 2.0) device were 554 cd/m^2, 0.81 cd/A at 8.2 V with greenish white light. The luminance of W1 and W2 devices was decreased rapidly. It might be caused by the concentration quenching of P2 and P3. This work demonstrates that the polymers based polyfluorene are promising materials in that they can adjust emission wavelength and can be used for the WPLED by solution process.

Acknowledgement

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