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Preparation and Characterization of White Polymer Light Emitting Diodes Using PVK:PFO:MDMO-PPV Emission Layer

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White polymer light emitting diodes (WPLEDs) with a glass/ITO/PEDOT:PSS/PVK:PFO:MDMO-PPV/TPBI/LiF/Al structure were fabricated to investigate the effects of the doping concentration of MDMO-PPV emission materials. The PVK, PFO and MDMO-PPV conjugated polymers as host and guest emission materials were spin coated at various concentrations of MDMO-PPV ranging from 15.0 to 30.0 vol%. As the concentration of MDMO-PPV increased from 15.0 to 30.0 vol%, the luminance and current efficiency values were decreased clearly, which are attributable to the quenching effect at a high doping concentration. The maximum luminance and current efficiency were 2280 cd/m² and 3.83 cd/A, respectively for a WPLED with 15.0 vol% of MDMO-PPV. The average CIE color coordinates were about $x = 0.33$, $y = 0.37$ at 15 V, showing a white emission color.

Keywords Current efficiency; luminance; MDMO-PPV; PFO; PVK; white polymer light emitting diode

Introduction

Organic light emitting materials and processing techniques have attracted considerable attention for developing high efficient organic light emitting diodes (OLEDs) because of their promising applications in next-generation displays and lighting sources. Recently, white polymer LEDs (WPLEDs) have been considered to be foundation for the next generation large and flexible lighting sources since they have advantages of allowing inexpensive solution processes, such as spin coating, ink-jet printing, and spray coating [1–3]. For the applications of WPLEDs, the light quantum efficiency should be improved through the optimization of the carrier (electron and hole) recombination process by means of introducing new device structure as well as the new organic materials into the emission layer [4]. Generally, the single host blended system in WPLEDs shows lower efficiency and brightness compared with the host and guest compound system [5]. The light emission and energy transfer can take place from both the host and the guest materials, the combined effect of which results in a high efficiency of the light emission. The performance of a WPLED is controlled mainly by the optimization of the organic materials and the device structure as well as by the surface

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modification of the film layers. The white light emissions can be basically realized by a sequential deposition in order to form a multi-layer device, in which each layer gives a single color emission of red, green and blue light. However, one of the common methods is to blend a blue and orange based fluorescence materials in the single layer because it has rather simple structure [6, 7].

In this report, we focus on the effects of doping concentrations of MDMO-PPV guest material in the single white emission layer for the optimization of host and guest material system.

For this, we prepared fluorescence blended multi-layer WPLEDs with glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] (PEDOT:PSS)/poly-Vinylcarbazole (PVK):poly(9,9-dioctylfluorenyl-2,7-diyl (PFO):poly[2-methoxy-5-3 (3',7'-dimethyloctyloxy)-1-4-phenylenevinylene] (MDMO-PPV)/2,2',2''(1,3,5benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBI)/lithium fluoride (LiF)/aluminum (Al) structures. The optical and electrical properties of the devices at various concentrations of the MDMO-PPV in the PVK:PFO:MDMO-PPV emission layer were investigated.

Experimental

Patterned ITO/glass substrates of the size 1×1 inch square were used as substrates to prepare WPLEDs with glass/ITO/PEDOT:PSS/PVK:PFO:MDMO-PPV/TPBI/LiF/Al structure. The substrates were cleaned ultrasonically with acetone, isopropyl alcohol (IPA), and deionized water. The remaining solvent was removed by soft baking for 10 min at 100°C . A heat treatment for the ITO/glass substrate was carried out at 130°C for 10 min in a vacuum oven. The PEDOT:PSS was used for the hole transport layer [8]. The PVK [9], PFO [10] and MDMO-PPV [11] conjugated polymers were introduced as the host and guest materials in the emission layer. The emission layer of the WPLED was fabricated by blending various concentrations of MDMO-PPV into the fixed PVK host and PFO guest materials with concentrations of PVK:PFO = 100:70 vol%. The starting PVK, PFO and MDMO-PPV polymer materials were dissolved with 1.0, 0.5 and 0.1 vol% with monochlorobenzene, separately for the precursor solutions. Following this, the prepared solution of PVK and PFO was mixed with the MDMO-PPV guest materials in various concentrations ranging from 15.0 to 30.0 vol%. The PVK, PFO and MDMO-PPV mixed solution was spin coated onto the PEDOT:PSS/ITO/glass substrate at a rotation speed of 5000 rpm for 30 sec. To improve the quantum efficiency through effective hole blocking from the emission layer, the TPBI was thermally evaporated onto the emission layer. LiF was used as an electron injection layer and an aluminum cathode electrode (LiF/Al) was deposited by thermal evaporation in a vacuum chamber with a base pressure of 5×10^{-8} Torr.

Figure 1 shows (a) the energy band diagram and (b) the chemical structures of consisting polymer materials for the WPLEDs. The electrical properties of the devices were investigated using a POLARONIX M6100 I-L-V test system. The absorption spectra of the host and guest materials were measured by UV (ultra violet)-visible and a photoluminescence (PL) spectrometer. The morphology and roughness of the emission film layers were analyzed by atomic force microscopy (AFM). The measurements of the optical properties, such as luminance, emission spectrum, and Commission Internationale de l'Eclairage (CIE) color coordinates were measured and evaluated using a CS-1000 spectro-radiometer in a dark room.

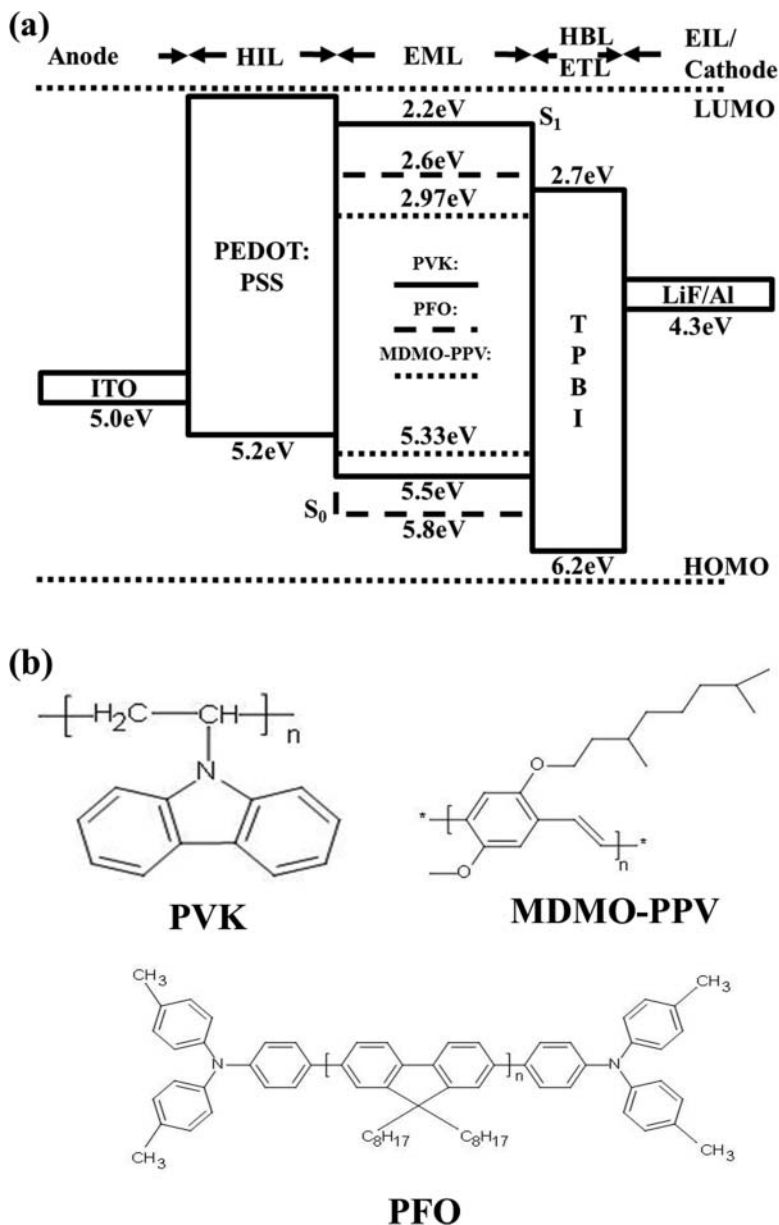


Figure 1. (a) Energy band diagram and (b) chemical structures of the consisting polymer materials for the WPLEDs.

Results and Discussion

As shown in the energy band diagram of Figure 1. (a), the energy band gap (S₁ and S₀ energy states) in PVK host is larger than those of PFO and MDMO-PPV fluorescence guests, which emit blue and orange based colors, respectively, by the energy transition from the PVK host to the guest materials. For a high efficient energy transfer, it is necessary

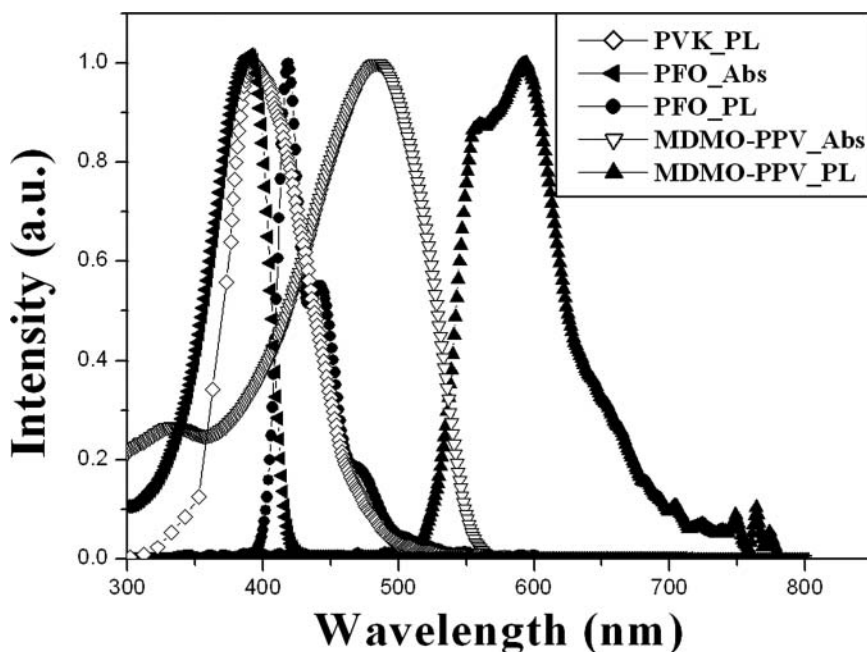


Figure 2. UV-visible absorption and PL emission spectra of the PVK host, PFO and MDMO-PPV guest materials.

to broaden the spectra overlap between the host and guest materials in the UV-visible and PL spectrum measurement. In order to confirm the spectral overlap between the host and the guest materials, the absorption and emission spectra of the consisting materials such as PVK, PFO and MDMO-PPV were investigated [12].

Figure 2 shows the normalized PL spectrum of PVK host, and the absorption and emission spectra of the PFO and MDMO-PPV guest materials. The absorption spectrum of PFO showed good overlap with the emission PL of PVK at a wavelength of around 390 nm. In the same way, the absorption spectrum of MDMO-PPV showed excellent overlap with the emission PL of PFO, suggesting highly effective energy transfer from the PVK host to the PFO and MDMO-PPV guest materials. Considering the results of each PL spectrum of the emission materials, we can expect that the WPLEDs using PVK, PFO and MDMO-PPV material system can lead a effective energy transfer in the emission layer. It is generally explained that the light efficiency can be improved by increments of the energy transfer speed coefficient, $k_{H^* \rightarrow G}$ from the Dexter energy transfer equation [13]. As a consequence, in order to increase the $k_{H^* \rightarrow G}$ value, it is desirable to increase the intensities of the PL emission peaks as well as to spectral overlap among these organic materials. Therefore, it may be concluded that a wide overlap between the PL emission spectrum of PVK and absorption spectrum of PFO and MDMO-PPV in this experiment contributes to improving of the light efficiency.

Figure 3 shows the surface morphologies and the mean roughness (Ra) values of the PVK:PFO:MDMO-PPV film layer at various MDMO-PPV concentrations. The Ra value increased from 2.269 to 4.101 nm with increase of the MDMO-PPV concentrations, suggesting that the film layer changed into rough film surface when the precursor solution

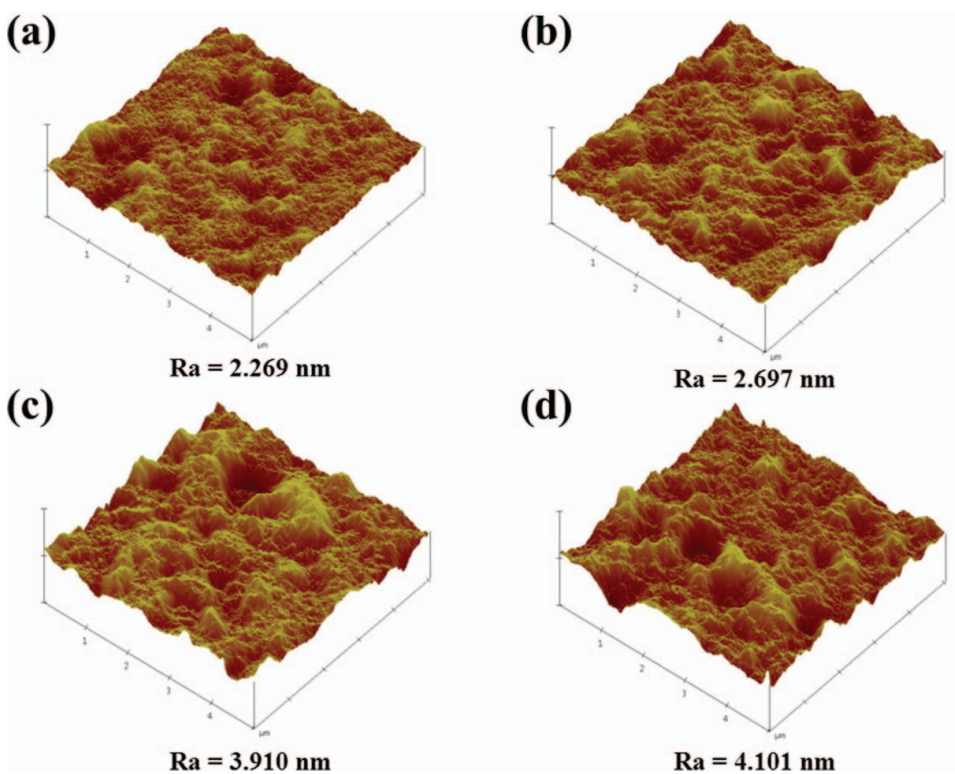


Figure 3. AFM surface images of the PVK:PFO:MDMO-PPV emission film layer at various MDMO-PPV concentrations: (a) 15.0, (b) 20.0, (c) 25.0 and (d) 30.0 vol%.

was spin coated at higher concentrations. It is reasonable to say that a rougher emission layer may have influence on a decrease in the luminance of the devices.

Figure 4 shows the UV-visible absorption spectra of the PVK:PFO:MDMO-PPV emission films coated on PEDOT:PSS/ITO/glass substrates as a function of wavelengths at different MDMO-PPV concentrations. The maximum intensity of the absorption peaks of MDMO-PPV is shown at around 580 nm for the device with 15.0 vol% of MDMO-PPV and tends to shift to larger wavelength with increasing the MDMO-PPV concentration. At high concentration, the organic materials may change their absorption and emission spectrum or, in some cases, exhibit a new emission due to the formation of aggregations, excimers or exciplexes [14]. In addition, the absorption intensities decreased slightly with MDMO-PPV concentration increased from 15.0 to 30.0 vol%, indicating that the maximum intensity occurs for the sample with a 15.0 vol% of MDMO-PPV concentration.

Figure 5 represents the luminance values as a function of input voltages (L-V) for the WPLEDs at different MDMO-PPV concentrations. It was observed clearly that the luminance was decreased from 2280 to 1230 cd/m^2 as the MDMO-PPV concentration increased from 15 to 30.0 vol%. The drop in the luminance and the absorption intensity in figure 3 are attributed to accelerated self quenching effect at higher doping concentration of guest material, which leads to decay the carrier recombination, as reported by Lamansky, S. et al. [15].

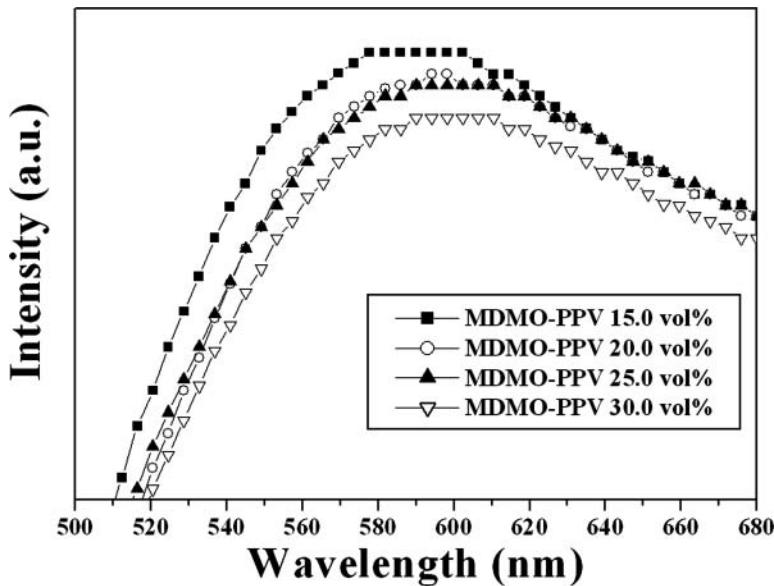


Figure 4. UV-visible absorption spectra of PVK:PFO:MDMO-PPV emission films coated on PE-DOT:PSS/ITO/glass substrates as a function of wavelengths at various MDMO-PPV concentrations.

The current efficiency, η , can be calculated easily by the equation $\eta = L/J$ if the current density-voltage and the luminance-voltage relationships are known, where L (cd/m^2) is the luminance intensity, and J (mA/m^2) is the current density. The current efficiencies of the devices obtained from various MDMO-PPV concentrations are shown in Figure 6.

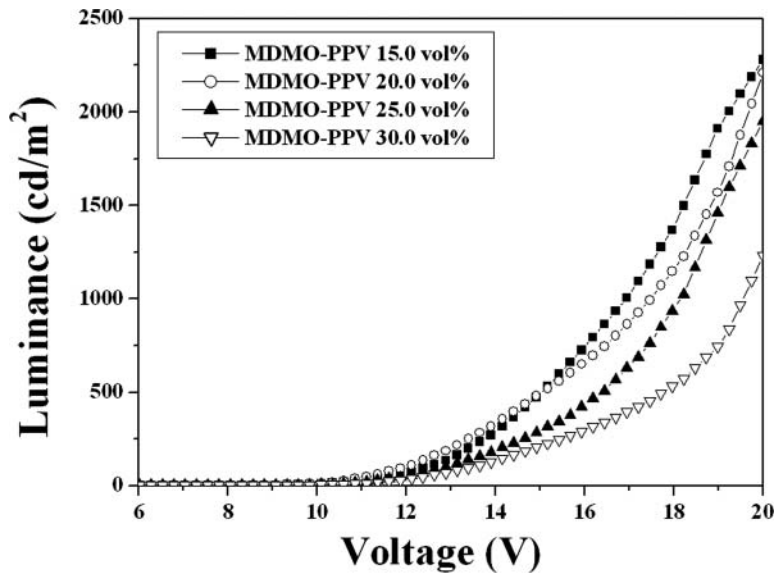


Figure 5. Luminance *versus* voltage (L-V) curves for the WPLEDs at various MDMO-PPV doping concentrations.

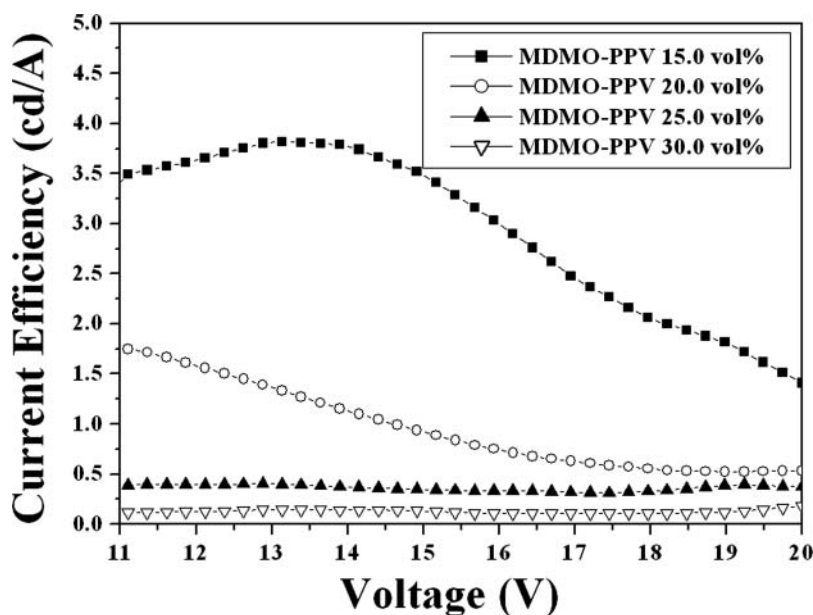


Figure 6. Current efficiency *versus* voltage (η -V) curves for the WPLEDs at various concentrations of MDMO-PPV guest material.

The maximum current efficiency was found to be about 3.83 cd/A at a current density of 3.79 mA/cm² for the WPLED with 15.0 vol% of MDMO-PPV concentration. In addition, the power efficiency was about 0.23 lm/W at the maximum luminance. However, in the case of the sample with MDMO-PPV concentration of above 20.0 vol%, the current efficiency was decreased, which is ascribed to a decay quenching effect as mentioned previously. The CIE color coordinates for the WPLED with 20.0 vol% of MDMO-PPV was about $x = 0.33$ and $y = 0.37$ at 15V, showing a white color. The current density, luminance, maximum current efficiency, maximum power efficiency and CIE color coordinates as a function of MDMO-PPV concentrations for the WPLEDs are summarized in Table 1.

Table 1. The characteristics of the WPLEDs at various MDMO-PPV concentrations

MDMO-PPV Concentration (vol%)	Current Density (mA/cm ²)	Luminance (cd/m ²)	Max. Current Efficiency (cd/A)	Max. Power Efficiency (lm/W)	CIE Color Coordinator (x, y)
15.0	162	2280	3.83	0.23	0.32, 0.41
20.0	413	2210	1.17	0.09	0.33, 0.37
25.0	523	1950	0.38	0.06	0.40, 0.41
30.0	679	1230	0.14	0.03	0.43, 0.44

Conclusions

The PVK, PFO and MDMO-PPV as the host and guest emission materials were spin coated onto PEDOT:PSS/ITO/glass substrates for the fabrication of white polymer light emitting diodes (WPLEDs). We investigated the dependence of MDMO-PPV doping concentrations on the optical and electrical properties of the WPLEDs. The MDMO-PPV fluorescent guest material was doped with ranging from 15.0 to 30.0 vol% into a fixed host and guest materials with the concentration of PVK:PFO = 100:70 vol%. The maximum luminance and the current efficiency of the WPLEDs with 15.0 vol% of MDMO-PPV concentration were found to be 2280 cd/m² and 3.83 cd/A, respectively. The Ra value increased as the MDMO-PPV concentration increased from 15.0 to 30.0 vol%, indicating a rough film surface at the higher doping concentrations. The drop in the luminance can be attributed to increasing self quenching and to rough film surface at higher doping concentration.

Acknowledgment

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