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Luminescence mechanism and property of white light PVK:MEH-BP-PPV polymer LED prepared by blending

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The white color polymer was prepared by the binary blending technique and the polymer light emitting diode (PLED) with single emission layer was achieved by spin-coating method. By means of Förster energy transfer mechanism, the excitation energy was partially transferred from the blue poly(9-vinylcarbazole) (PVK) to the red poly[2-methoxy-5-{2-etylhexyloxy}1,4-phenylenevinylene-co-(4,4'-biphenylene)] (MEH-BP-PPV), which resulted from poorly miscible effect and partially spectral overlap of polymers. A broad band white light emission with two emission peaks at 400 and 560 nm was obtained. The optimal composition weight ratio of PVK to MEH-BP-PPV for achieving the white line emission was 100 to 5. The CIE coordinates of the emission light were at x = 0.29, y = 0.33 when the PVK:MEH-BP-PPV blend was irradiated by an UV lamp. The turn-on voltage for the white light PVK:MEH-BP-PPV PLED was about 3.5 V, although the luminance was low and needed to be improved.

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1. Introduction

Recently, organic materials have attracted much attention due to their potential applications as conductor, electro-active material for battery and flat panel displays (FPDs). In FPDs technologies, the polymer light emitting diode (PLED) is a new display technique, where a conjugated organic polymer film is sandwiched between anode and cathode in a short distance. With the simple fabrication procedures, the high efficiency PLED could achieve the inexpensive display compared with liquid crystal display (LCD) or organic light emitting diode (OLED). However, the purity and intensity of emission light of PLED are still important factors which will influence their development. Therefore, many projects are executed in order to improve the emission property of PLED by using multilayer structure, confining the conjugation length, adopting the copolymer system or choosing the blend techniques. Among those approaches, the blend method has been widely adopted to prepare white light emitting polymer for back light and lamp applications.

The PLED could be a multilayer or a single layer structure. The fabrication of the multilayer PLED involves a complicated materials engineering which ensures that the solvents used for the successive layers do not dissolve the preceding layer [1,2]. This limits the choice of practical materials, and often precludes the use of the best available materials. Beside, the cost associated with manufacturing increases commensurately with the number of layers. In contrast, the single layer PLED could be achieved with an uniform polymer active layer fabricated by once spin coating, herein the emission color of PLED could be obtained from the blend light emitting polymer by voltage applied. Based on the advantage of single layer PLED, the white light emitting was achieved by colour complement from a binary blend in this study. The host (blue) and guest (red) light emitting materials were the compounds poly(9-vinylcarbazole) (PVK) and poly[2-methoxy-5-{2-etylhexyloxy}1,4-phenylenevinylene-co-(4,4'-biphenylene)] (MEH-BP-PPV), respectively. The I-V property of the white light PVK:MEH-BP-PPV PLED was measured and analyzed. The color tuning behavior and Förster inefficient energy transfer phenomenon of the PVK:MEH-BP-PPV blend polymer will be discussed [3-6].

2. Experimental

In this binary blend system, the donor material of PVK was purchased from Aldrich, and the acceptor material of MEH-BP-PPV from H. W. Sands. The structures of PVK and MEH-BP-PPV polymers are shown in Fig. 1. They were used as received from commercial sources without further purification. The polymer film was prepared by spin-coating the blend solution containing 0.5 wt% of the polymers in tetrahydrofuran (THF) solvent. The dopant in blend polymer was usually controlled to a low doping level. Thus, the composition ratio of PVK/MEH-BP-PPV was altered from 100/10 to 100/1. Furthermore, for preparation the single layer white light PVK:MEH-BP-PPV PLED, a modified water dispersion of poly(3,4-ethylenedioxy-thiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS) (Polysciences, Inc.) was firstly spin-coated on ITO, which was used as a hole injection/transport layer. The chemical structures of PEDOT and PSS are shown in Fig. 1. The PEDOT is not intrinsically conductive because the conjugated carbon chain does not conduct, however, when doped with PSS it becomes a p-type conductor. Thus, the PEDOT:PSS conductive polymer layer improves the hopping ability of holes and reduces the tunneling effect. After the

PEDOT:PSS layer was prepared, the PVK:MEH-BP-PPV emission layer was subsequently spin-coated on PEDOT:PSS. Finally, an Al metal contact was deposited on top of the emission layer by evaporation under pressure of 2.5×10^{-5} Torr.

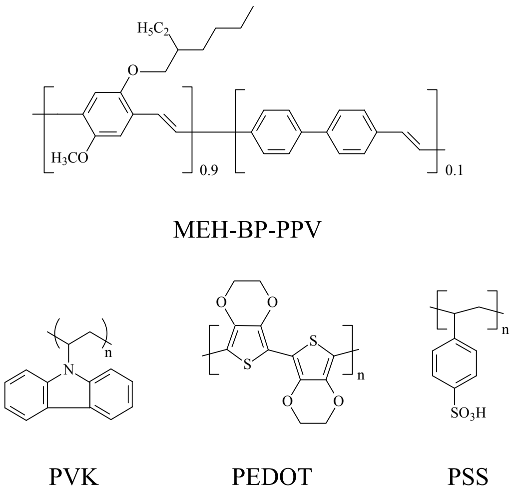
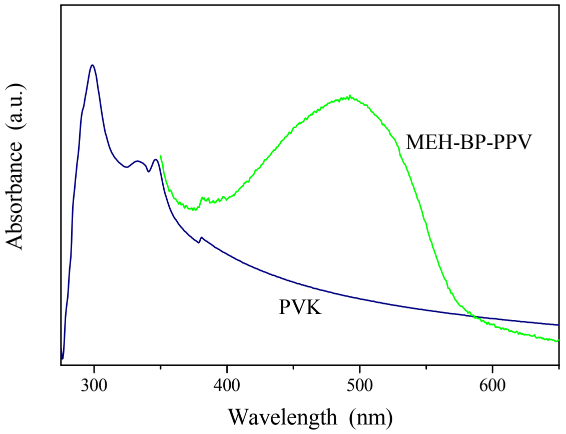


Fig. 1. Chemical structures of MEH-BP-PPV, PVK, PEDOT and PSS polymers.

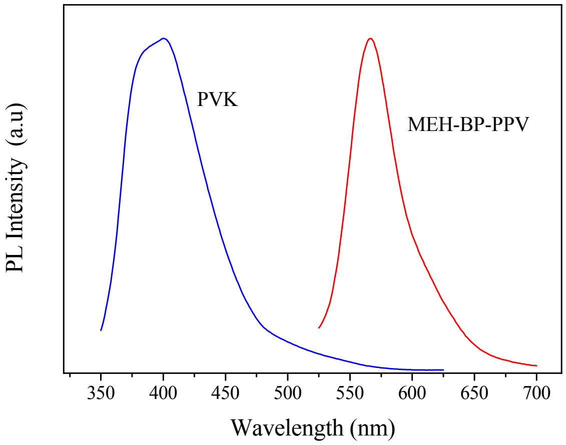
The absorption spectra were measured by a Hitachi spectrophotometer model U-2800, the steady-state photoluminescence (PL) spectra were evaluated using Hitachi F-4500; the excitation wavelength was set at 500 nm for MEH-BP-PPV, and fixed at 340 nm for PVK and PVK:MEH:BP:PPV. The CIE coordinates were measured by Minolta CHROMA meter model CS-100A, and a 6 W UVGL-58 UV lamp with wavelength at 254 nm was used as excitation source. The current-voltage (I-V) property of white light PLED was measured by HP 4155B. Furthermore, the positions of the highest/lowest occupied molecular orbitals (HOMO/LUMO) of PVK and MEH-BP-PPV were measured by cyclic voltammogram (CV) method. It was observed that the LUMO and HOMO energy levels correspond to 2.03 and 5.34 eV for PVK, and to 3.3 and 5.46 eV for MEH-BP-PPV, respectively. In this work, all processes and measurements were carried out in air at room temperature.

3. Results and discussion

The polymer of PVK is a blue wide bandgap material and its emission color is easily tuned by copolymerizing with low bandgap monomer or blending with dyes [2]. In this paper, the PVK blended with the derivative of poly(1,4phenylene-vinylene) (PPV) of MEH-BP-PPV was used for the poorly miscible system to prepare the white emitters of light.



(a) Absorbance of PVK and MEH-BP-PPV



(b) PL intensity of PVK and MEH-BP-PPV

Fig. 2. (a) Absorbance and (b) PL intensity of PVK and MEH-BP-PPV polymers.

Fig. 2(a) shows the UV-visible spectra of PVK and MEH-BP-PPV polymer films. The absorption maxima of PVK and MEH-BP-PPV appear at 300 and 480 nm, respectively. These absorption curves have been attributed to the π-π^* electronic transition of conjugated polymers, which indicates that the electrons in PVK for HOMO-LUMO transition require more energy than in the case of MEH-BP-PPV. The corresponding absorption edges for PVK and MEH-BP-PPV are situated at 375 and 575 nm. Consequently, the optical band gaps for PVK and MEH-BP-PPV were 3.30 and 2.16 eV, respectively. Fig. 2(b) shows the PL spectra of the PVK and MEH-BP-PPV. The carbazole unit in PVK absorbs ultraviolet light and emits light with a broad band ranged between 350 and 550 nm in the blue region. The emission peaks (λ_{max}) of blue PVK and red MEH-BP-PPV are located at 400 and 560 nm, respectively. Obviously, in this poorly miscible blend of PVK and MEH-BP-PPV distributed within the limited region of Förster radius, each material not only emits its own colour, but also partially transfers the excitation energy from the wide bandgap material of PVK to the narrower bandgap material of MEH-BP-PPV. From the emission spectra of Fig. 2(b), seems that the white colour PLED with single emission layer could be obtained by blending the PVK and MEH-BP-PPV polymers.

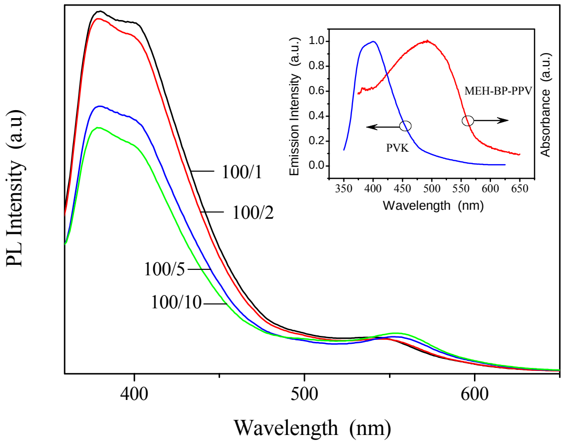


Fig. 3. PL spectra of PVK:MEH-BP-PPV blend polymer for different weight ratios of PVK/MEH-BP-PPV.

The PL spectra of the PVK:MEH-BP-PPV blend polymer film for different weight ratios of PVK to MEH-BP-PPV are shown in Fig. 3. The emission peaks of PVK:MEH-BP-PPV at around 400 and 560 nm were correspondingly referred to the emission of PVK and MEH-BP-PPV. In the meantime, it was observed that the PL intensities of blue emission was diminished and red enhanced with the increase of blending concentration of MEH-BP-PPV, which indicated there was an inefficient energy transfer between PVK and MEH-BP-PPV. The spectra of PVK emission and MEH-BP-PPV absorption exhibited in the insert of Fig. 3 showed that the energy is partially transferred from PVK to MEH-BP-PPV by the Förster mechanism. So, the intensified red and declined blue emissions with the increase concentration of MEH-BP-PPV were examined. In this figure, as the concentration of MEH-BP-PPV was increased, the PL intensity of longer wavelength portion of PVK was quenched by MEH-BP-PPV addition [7], or by partially energy transfer to MEH-BP-PPV. And the concomitant sequentially red shift of the MEH-BP-PPV emission peak was attributed to the reabsorption and radiation migration for the increased MEH-BP-PPV concentration, but not referred to excimers species owing to the PL peak of eximers resulted in a red-shift wavelength longer than 560 nm.

Fig. 4 shows the PL excitation (PLE) spectrum of the PVK:MEH-BP-PPV blend film monitored at 560-nm wavelength. The peaks at 350 and 495 nm arise in that order from the absorption of PVK and MEH-BP-PPV, which coincides with the absorption measurement as displayed in Fig. 2(a). From PLE analysis, it was found that the emission of MEH-BP-PPV in the blend system comes mainly from the absorption of MEH-BP-PPV, along with partially energy transfering from PVK to MEH-BP-PPV via emission-absorption mechanism.

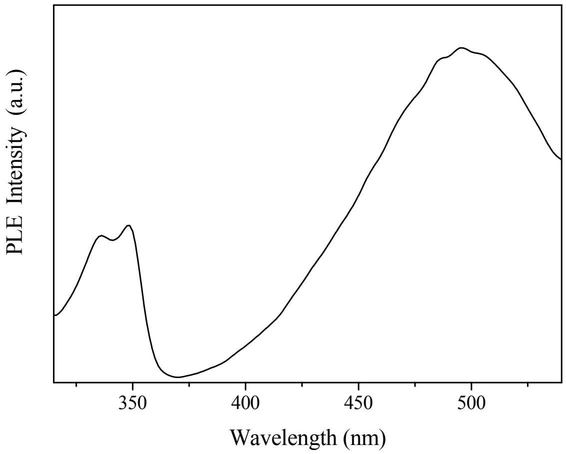


Fig. 4. PLE spectrum of PVK:MEH-BP-PPV blend polymer.

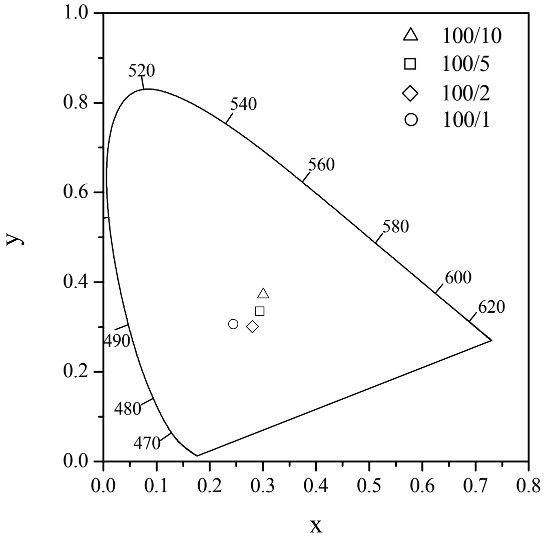


Fig. 5. CIE coordinates chart for PVK:MEH-BP-PPV blend polymer for different weight ratios of PVK/MEH-BP-PPV.

The CIE coordinates chart for the PVK:MEH-BP-PPV blend polymer excited at 254 nm by a 6 W UV lamp and measured with a CS-100A colorimeter is shown in Fig 5, where the concentration ratio of PVK/MEH-BP-PPV was varied from 100/10 to 100/1. As the PVK concentration increases a blue shift phenomenon is observed. This fact is due to the obvious increase in intensity in the blue region. However, although the emission colour varies with composition ratio of blend polymers, it remains in the white light region. The optimal white emission for PVK:MEH-BP-PPV blend film was obtained when the concentration ratio of PVK/MEH-BP-PPV was at 100/5; the CIE coordinates were at x = 0.29, y = 0.33. The current-voltage (I-V) characteristic of white light PLED with structure of ITO glass/ PEDOT:PSS/ PVK:MEH-BP-PPV/Al is shown in Fig. 6, where the concentration ratio of PVK to MEH-BP-PPV was 100 to 5. In this figure, two carrier transfer mechanisms are exhibited, in the low bias region holes and electrons are transferred by the hopping mechanism, and under high bias carriers move by tunneling. The turn-on voltage for the white light PVK/MEH-BP-PPV PLED is about 3.5 V. However, the electroluminescence intensity was still low and must be improved.

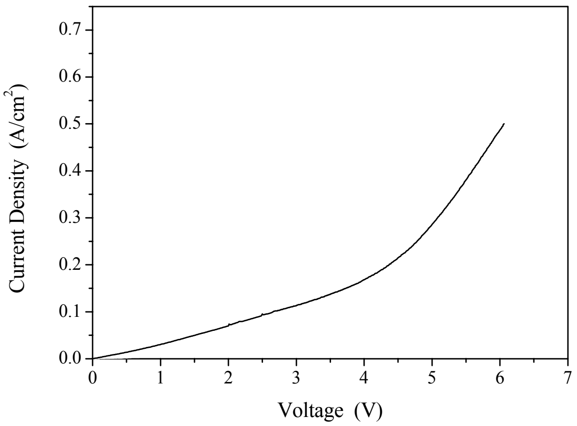


Fig. 6. I-V plot of PVK:MEH-BP-PPV polymer for 5 wt% of MEH-BP-PPV blended.

4. Conclusions

The white emission for PVK blended with MEH-BP-PPV was attributed to poorly miscible property of polymers and to partial spectral overlap between emission of PVK and absorption of MEH-BP-PPV, which were two important factors affecting the energy transfer efficiency of polymers. An inefficient Förster energy transfer was observed from the PLE spectrum of PVK:MEH-BP-PPV film. The optimal luminescence was obtained when the composition weight ratio of PVK/MEH-BP-PPV was 100/5. In these conditions we obtain white colour with CIE coordinates at x = 0.29, y = 0.33. A single layer of white light PVK/MEH-BP-PPV PLED was fabricated, with a low turn-on voltage about 3.5 V.

Acknowledgments

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