

Effects of Dilution and Charge Trapping on the Performance of a Light-Emitting Diode of Poly(9-vinylcarbazole) Doped with Poly[2-methoxy-5-(2'-ethyl hexyloxy)-1,4-phenylene vinylene]

Xinwen Zhang,¹ Zhaoxin Wu,¹ Dongdong Wang,² Dawei Wang,¹ Xun Hou¹

¹Key Laboratory for Physical Electronics and Devices (Ministry of Education), School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

²School of Science, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

Received 30 August 2009; accepted 10 December 2009

DOI 10.1002/app.31961

Published online 26 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We report the electroluminescence (EL) enhancement of polymer light-emitting diodes made by the dispersion of poly[2-methoxy-5-(2'-ethyl hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) into poly(9-vinylcarbazole) (PVK). From the photoluminescence and EL spectra of the polymer blend films, we found that, because of the dilution effect, interchain interactions in MEH-PPV were reduced markedly. The EL spectrum indicated that the charge-trapping effect contributed to the formation of excitons at the MEH-PPV centers and, thus, strongly enhanced

EL. Because of the balance between increasing trapping centers and suppressing interchain interactions, the best device performance was achieved when the polymer blend contained 12% MEH-PPV and 88% PVK (weight ratio), and this also led to improved color purity of the polymer blend devices. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1213–1217, 2010

Key words: blends; conjugated polymers; charge transfer; diodes; spin coating

INTRODUCTION

Because of their potential applications in flat-panel display technologies, polymer light-emitting diodes (PLEDs) have attracted much interest.^{1–3} Poly(*p*-phenylene vinylene) (PPV) and its derivatives are the most widely studied luminescent polymers. Among PPVs, poly[2-methoxy-5-(2'-ethyl hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) is considered to be one of the most promising light-emitting materials in PLEDs because of its advantages of solubility in common solvents and good performance in charge injection and transport.^{4–7} However, when polymer chains in a solid-state thin film are in contact, the aggregation of polymer chains enhances the interchain exciton formation; these can act as efficient quenching centers.^{8–10} It has been found that interchain excitons lead to a significant reduction in the

luminescence efficiency of conjugated polymers.^{9–12} Therefore, it is important to reduce polymer chain aggregation to develop high-efficiency PLEDs.

Much attention has been focused on the reduction of the aggregation quenching of MEH-PPV to enhance the light intensity and efficiency of PLEDs.^{8–16} It has been shown that the interchain interaction can be reduced by changing the molecular conformation in different solutions,^{14,15} where the film morphology and chain aggregation are controlled by the solvent, the concentration of solution, and the spin-coating conditions.¹⁶ More recently, several groups have found that MEH-PPV blending with an active polymer or inert polymer could reduce interchain interaction effectively^{8–13} by separating the conjugated polymer chains. Polymer blending is, thus, expected to be an efficient approach to improving device performance. It has been reported that the luminescence efficiency of MEH-PPV is enhanced by the dispersion of MEH-PPV into an inert polymer polystyrene^{8–10} and poly(methyl methacrylate).¹¹ However, from a practical point of view, a high-efficiency device cannot use MEH-PPV blends with inert polymers because they will further weaken charge transport and, thus, increase the operational voltage of the devices.¹⁷

Correspondence to: Z. Wu (zhaoxinwu@mail.xjtu.edu.cn).

Contract grant sponsor: Ministry of Science and Technology of China; contract grant number: 2006CB921602.

Contract grant sponsor: Program for New Century Excellent Talents.

Electroluminescence (EL) in doped devices is accomplished in two ways: energy transfer from host molecules to guest molecules and charge trapping by guest molecules.^{18,19} In the second way, the direct recombination of holes and electrons occurs on guest molecules, and their trapping can significantly enhance the external EL quantum efficiency.^{19,20} The essential requirement for efficient carrier trapping is that the guest dopant must have a highest occupied molecular orbital (HOMO) energy higher than that of the host and a lowest unoccupied molecular orbital (LUMO) energy lower than that of the host material.²¹ In this study, we examined the emission properties of polymer blend films formed by the dispersion of MEH-PPV into poly(9-vinylcarbazole) (PVK), where PVK molecules not only supported good charge transport but also served as a solid solution to separate the MEH-PPV chains from each other. The device of MEH-PPV/PVK (12/88) showed a much higher EL efficiency compared to the pure MEH-PPV devices. By analyzing the emission spectra of the polymer blend films and the devices, we found that the suppression of the interchain interaction and the charge-trapping effect were the two main causes for the performance enhancement.

EXPERIMENTAL

The PLED structure we used was indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS; 40 nm)/MEH-PPV/PVK (80 nm)/Ca (20 nm)/Al (120 nm). PEDOT:PSS, MEH-PPV (number-average molecular weight = 150,000–250,000), and PVK (weight-average molecular weight = 1,100,000) were purchased from Alfa Aesar (Beijing, China) and Sigma Aldrich (Beijing, China) respectively. The molecular structures of MEH-PPV and PVK are shown in Figure 1(a).

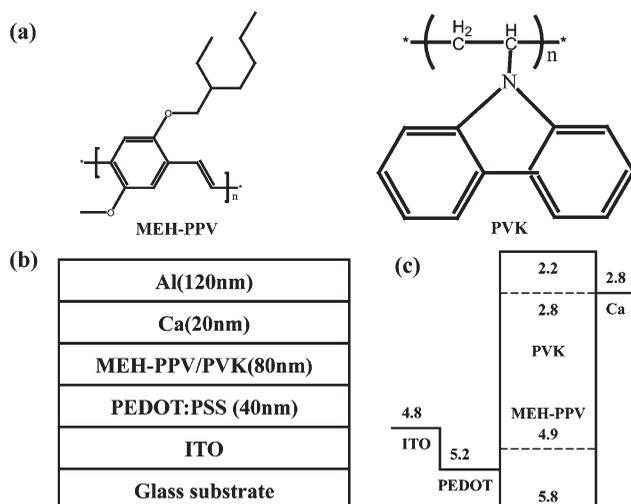


Figure 1 (a) Chemical structure of MEH-PPV and PVK, (b) structure of the device, and (c) energy-level diagram of the device.

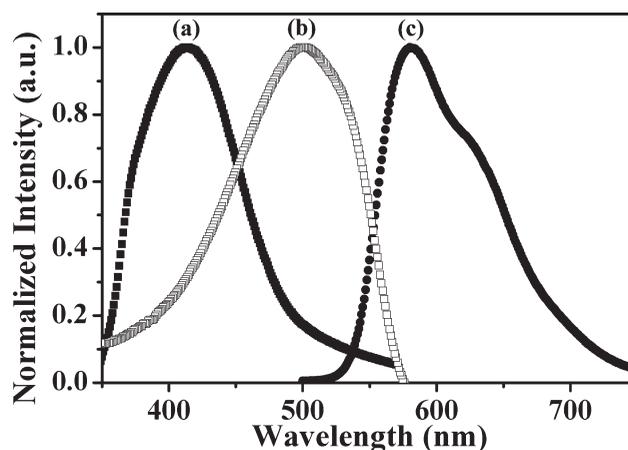


Figure 2 Normalized UV-vis absorption spectrum of MEH-PPV and PL spectra of MEH-PPV and PVK: (a) PL of the PVK film, (b) absorbance of the MEH-PPV film, and (c) PL of the MEH-PPV film.

In the experiment, MEH-PPV and PVK were dissolved in tetrahydrofuran to prepare solutions with concentrations of 6 and 10 mg/mL, respectively. Then, the MEH-PPV and PVK solutions were mixed to form six kinds of blend solutions, in which the weight percentages for MEH-PPV were 0.5, 2, 4, 8, 12, and 16 wt %. PEDOT:PSS was cast onto an ITO substrate at a spin speed of 1000 rpm for 40 s. The PEDOT:PSS layer was baked at 120°C for 1 h. It had a thickness of 40 nm and acted as the hole-injection layer. The polymer blend layer was then prepared on this hole-injection layer by spin coating. The blend film thickness was about 80 nm. The Ca/Al cathode was formed by thermal evaporation under a pressure of 5×10^{-4} Pa. The Al was used as a metallic cap to protect oxidation of the reactive Ca underneath. The thickness of the Ca and the Al layers were approximately 20 and 120 nm, respectively. The active area of the device was 12 mm². Figure 1(b) shows the structure of the devices.

The UV-vis absorption spectrum of the MEH-PPV film was recorded by a spectrophotometer (U-3010, Hitachi, Inc., Tokyo, Japan). The photoluminescence (PL) spectra were obtained by a FluoroMax-4 spectrophotometer from Horiba Jobin-Yvon Inc. (Edison, NJ). The EL spectra of were measured by a Spectra-Scan PR650 was purchased from Photo Research, Inc. (USA). The current devices–voltage–luminance characteristics of the PLEDs were analyzed by a Keithley 2602 source meter was purchased from Keithley Instruments, Inc. (Cleveland, OH). All measurements were carried out at room temperature and atmospheric conditions.

RESULTS AND DISCUSSION

Figure 2 shows the UV-absorption spectrum of MEH-PPV, and the PL spectra of MEH-PPV and

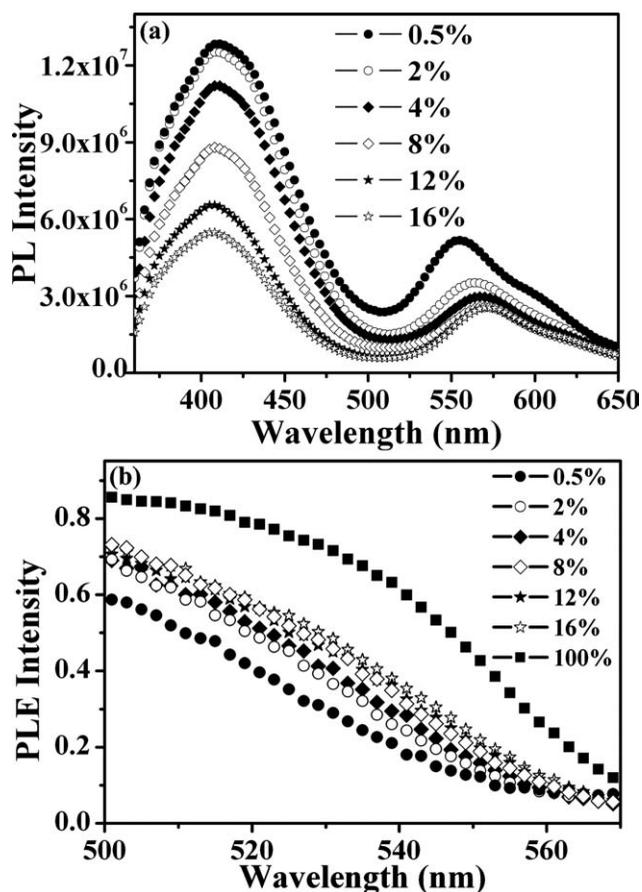


Figure 3 Curves of (a) PL spectra (excited at 335 nm) and (b) PL excitation (PLE) spectra (collected at 620 nm) for MEH-PPV/PVK blend films with different weight ratios.

PVK. Because the PL spectrum of the PVK film had a peak at 414 nm, and the absorption spectrum of the MEH-PPV film had a peak at 500 nm, there was a partial overlap between the emission of PVK and the absorption of MEH-PPV. This fact implied the possibility of Förster energy transfer from the PVK host to the MEH-PPV guest. As also shown in Figure 2, the PL spectrum of the MEH-PPV film showed an emission maximum at 580 nm with a shoulder at approximately 620 nm. It has been reported that this shoulder is mainly due to interchain interaction.^{9,12,16}

The films of MEH-PPV/PVK (0.5, 2, 4, 8, 12, and 16%) were fabricated on the glass substrates and excited by a monochromatic light at 335 nm. The PL spectra of blend films are shown in Figure 3(a). As shown, the spectrum consisted of two components: one was the emission from the PVK host, and the other was from the MEH-PPV guest. The PL intensity due to MEH-PPV only changed slightly as its concentration increased, and the emission from PVK (the left peak) was the main part of the entire spectrum, which suggested that the Förster energy transfer in the blend films from PVK to MEH-PPV was incomplete.^{22,23} As the MEH-PPV contents decreased in the

blends, the emission spectrum consistently blue-shifted from 571 to 554 nm because of the reduced interchain interaction due to dilution effect.²⁴

The interchain interaction in conjugated polymers can be observed through PL excitation spectra.^{8,9,24} The PL excitation spectrum of the blend films with various weight ratios collected with a fixed emission wavelength of 620 nm are shown in Figure 3(b). As shown, the MEH-PPV film showed a strong signal of long-wave excitation compared to the blend films. This suggested that the absorption spectrum of the pure MEH-PPV was redshifted because of the interchain interactions. This long-wave excitation has been attributed to small-gap species, such as interchain species or excimer species.^{8,9} In addition, the relative intensity of the long wavelength decreased when the PVK concentration in the blends increased; this indicated that the interchain interactions between the MEH-PPV chains were reduced upon blending with PVK.^{8,9}

A similar spectra change was also observed in EL. The EL spectra of the devices based on MEH-PPV/PVK with different MEH-PPV/PVK weight ratios are shown in Figure 4. The spectrum of the pure PVK device was measured at a voltage of 14 V, and the others were measured at 10 V. The EL spectrum of the device had a main peak at 584 nm and a shoulder at 620 nm. It is known that the emission at 584 nm originates from single-chain excitons, whereas the shoulder is associated with the interchain interaction.^{9,10} With the decrease in the MEH-PPV concentration, the peak at 584 nm gradually shifted to 560 nm, and the relative intensity of the shoulder at 620 nm decreased from 0.93 to 0.53 as the concentration of MEH-PPV decreased from 100 to 4%, which indicated that the interchain interaction in MEH-PPV was effectively suppressed. In addition, the emission spectra became narrower as the MEH-PPV concentration in the polymer blend films decreased.

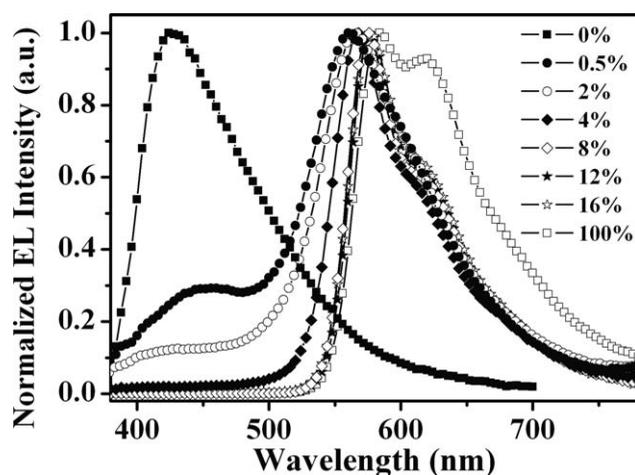


Figure 4 Normalized EL emission spectra of devices based on MEH-PPV/PVK polymer blend films.

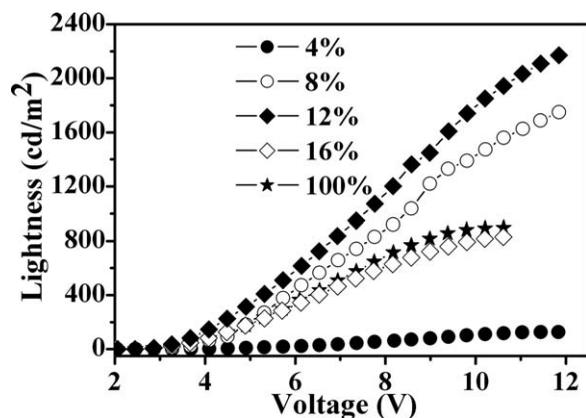


Figure 5 Luminance–voltage characteristics of devices.

As shown in Figure 4, no emission from PVK was detected in the spectra when the concentration of MEH–PPV was greater than 4%. Compared to the PL spectra of the blend films, the emission from the MEH–PPV dominated the entire spectrum, which suggested a new emission mechanism, other than the incomplete Förster energy transfer from PVK to MEH–PPV. We determined this new emission route by checking the energy band of the device [see Fig. 1(c)]. The energy band showed that the LUMO and the HOMO of MEH–PPV were 2.8 and 4.9 eV,²⁵ respectively, which were between the LUMO (2.2 eV) and HOMO (5.8 eV) of PVK.²⁶ Thus, charge-trapping centers were formed in the MEH–PPV/PVK blend films, which could confine electrons and holes and lead to efficient exciton formation in the MEH–PPV and the subsequent radiative decay of these excitons.

Figure 5 shows the luminance–voltage characteristic of the devices based on MEH–PPV/PVK (4, 8, 12, 16, and 100%) blend films. As shown in Figure 5, it was clear that the brightness of the device increased significantly with the concentration of MEH–PPV. At a concentration of 12%, the polymer blend device achieved a maximum brightness of 2170 cd/m², which was much higher than that of the pure MEH–PPV device. The performances of the devices started decreasing when the concentration of MEH–PPV was greater than 12%. From these results, there were two important effects that helped the generation of luminescence in the polymer blend devices, which were the dilution effect and the charge-trapping effect. As we know, the charge density increased with increasing concentration of MEH–PPV. However, the dilution effect decreased with increasing concentration of MEH–PPV. The balance of these two effects determined that the best device performance was achieved when the polymer blend contained 12 wt % MEH–PPV and 88 wt % PVK. The lightness–voltage curves also showed that the polymer blend helped reduce the driving voltage. For example, the turn-on voltage of the device with 12%

MEH–PPV was 2.1 V, which was reduced by 0.4 V from the value for the pure MEH–PPV.

On the basis of this discussion, two factors were responsible for the improvement of the device performance. First, in the polymer blend film, the interchain interactions within the MEH–PPV chains were reduced dramatically by dilution effects. Because interchain species quenches the fluorescence in solid-state films,^{12,27,28} increasing the PVK content in the MEH–PPV/PVK blend films, which effectively reduced the interchain interactions of MEH–PPV, increased the PL and EL emissions from devices. Second, the exciton formation in the MEH–PPV charge-trapping centers was an important luminescent mechanism. Increasing the concentration of MEH–PPV helped to enhance the luminescence intensities. It was these two competing factors that eventually determined the optimal concentration ratio of MEH–PPV.

CONCLUSIONS

In this research, PLEDs were fabricated via the dispersion of MEH–PPV into PVK, which acted as the emitting layer. We have found that, because of the suppression of the interchain interaction of MEH–PPV and the formation of charge-trapping centers, the brightness and the efficiency of the polymer blend devices were improved. The same effect also led to improved color purity in the polymer blend devices. A comparison of the PL and the EL spectra revealed that the EL from the blend film was strongly influenced by the exciton formation due to the charge-trapping effect. Finally, the device made of MEH–PPV/PVK (12/88 w/w) showed the highest EL efficiency and the lowest turn-on voltage.

References

- Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* 1990, 347, 539.
- Braun, D.; Heeger, A. *J Appl Phys Lett* 1991, 58, 1982.
- Parker, I. D. *J Appl Phys* 1994, 75, 1656.
- Nguyen, T. Q.; Martini, I. B.; Liu, J.; Schwartz, B. J. *J Phys Chem B* 2000, 104, 237.
- Gong, X.; Soci, C.; Yang, C. Y.; Heeger, A. J.; Xiao, S. *J Phys D: Appl Phys* 2006, 39, 2048.
- Yamamoto, H.; Wilkinson, J.; Long, J. P.; Bussman, K.; Christodoulides, J. A.; Kafafi, Z. H. *Nano Lett* 2005, 5, 2485.
- Garcia, A.; Yang, R.; Jin, Y.; Walker, B.; Nguyen, T. Q. *Appl Phys Lett* 2007, 91, 153502.
- Marletta, A.; Goncalves, V. C.; Balogh, D. T. *J Lumin* 2006, 116, 87.
- He, G. F.; Li, Y. F.; Liu, J.; Yang, Y. *Appl Phys Lett* 2002, 80, 4247.
- Yan, M.; Rothberg, L. J.; Kwock, E. W.; Miller, T. M. *Phys Rev Lett* 1995, 75, 1992.
- Heller, C. M.; Campbell, I. H.; Laurich, B. K.; Smith, D. L. *Phys Rev B* 1996, 54, 5516.
- Liu, J.; Shi, Y. J.; Yang, Y. *Appl Phys Lett* 2001, 79, 578.
- Lee, R. H.; Lai, H. H. *Eur Polym J* 2007, 43, 715.

14. Nguyen, T. Q.; Doan, V.; Schwartz, B. J. *J Chem Phys* 1999, 110, 4068.
15. Nguyen, T. Q.; Kwong, R. C.; Thompson, M. E.; Schwartz, B. J. *Appl Phys Lett* 2000, 76, 2454.
16. Shi, Y.; Liu, J.; Yang, Y. *J Appl Phys* 2000, 87, 4254.
17. Iyengar, N. A.; Harrison, B.; Duran, R. S.; Schanze, K. S.; Reynolds, J. R. *Macromolecules* 2003, 36, 8978.
18. Shoustikov, A. A.; You, Y.; Thompson, M. E. *IEEE J Sel Top Quantum Electron* 1998, 4, 3.
19. Pschenitzka, F.; Sturm, J. C. *Appl Phys Lett* 2001, 79, 4354.
20. Gong, X.; Robinson, M. R.; Ostrowski, J. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv Mater* 2002, 14, 581.
21. Uchida, M.; Adachi, C.; Koyama, T.; Taniguchi, Y. *J Appl Phys* 1999, 86, 1680.
22. Lee, T. W.; Park, O. O.; Cho, H. N.; Hong, J. M.; Kim, Y. C. *Mol Cryst Liq Cryst* 2001, 371, 435.
23. Yang, S. H.; Chuang, P. S.; Chang, W. K. *J Electron Mater* 2008, 37, 1681.
24. Nguyen, T. Q.; Doan, V.; Schwartz, B. J. *J Chem Phys* 1999, 110, 4068.
25. Xu, D. H.; Deng, Z. B.; Li, X. F.; Chen, Z.; Liang, C. *J Appl Surf Sci* 2007, 253, 3378.
26. Shih, P. I.; Shu, C. F.; Tung, Y. L.; Chi, Y. *Appl Phys Lett* 2006, 88, 251110.
27. Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys Rev Lett* 1994, 73, 744.
28. Antoniadis, H.; Rothberg, L. J.; Papadimitrakopoulos, F.; Yan, M.; Galvin, M. E. *Phys Rev B* 1994, 50, 14911.