

Enhanced electroluminescence using polystyrene as a matrix

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Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) blends with polystyrene (PS) were used as emitting layers in polymer light-emitting diodes. Studies of photoluminescence and electroluminescence (EL) of the blends indicate that interchain interactions were tremendously suppressed due to the dilution effect. The device of MEH-PPV/PS (50/50) shows much higher EL efficiency compared to pure MEH-PPV devices. Since there is neither energy transfer nor charge transfer involved in MEH-PPV/PS blends, the observed efficiency enhancement is mainly attributed to the suppressed interchain species, which are responsible for the low photoluminescence yields. In addition, the addition of PS into MEH-PPV improves the thermal stability of polymer thin films and reduces the sensitivity of device performance to processing conditions. © 2002 American Institute of Physics. [DOI: 10.1063/1.1480098]

Polymer light-emitting diodes (PLEDs) have attracted intense research activities for their promising applications in flat-panel displays.¹⁻³ Aggregation quenching of the excited state is a main reason for low quantum luminescence yields of conjugated polymers.^{4,5} Block copolymers and polymer blends, which separate the chromophores on the polymer chains, are used as emitting materials and demonstrated as an efficient method to improve device performance.⁵⁻⁸ For most polymer blends reported to date, the observed enhancement of electroluminescence (EL) efficiency has been mainly attributed to effective energy transfer from the host to the guest. In our previous study, an "active" polymer, i.e., poly(9,9-dioctylfluorene) (PF), has been used as a host to construct blends with poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV).⁹ Several factors, including suppressed interchain interactions, effective energy transfer, and reduced self-absorption, have been found to be responsible for the enhanced EL efficiency. Among them, due to the Stoke shift in conjugated polymers, the reduction in self absorption is believed to play only a minor contribution to the observed efficiency enhancement. Since forming blends is an effective method to fabricate high-performance PLEDs (high EL efficiency, well-defined emission color, and processing insensitivity), it is very important to fully understand the mechanisms, i.e., which one, suppressed interchain interactions, or effective energy transfer, plays the major contribution to the observed efficiency enhancement.

In this letter, instead of "active" polymers, an "inert" polymer-polystyrene (PS), was chosen as the matrix polymer to form blends with MEH-PPV. Those systems involve neither energy transfer nor charge transfer, thus providing an

approach to study the mechanism of PLED using polymer blends. Similar performance enhancement can be observed when the active polymer matrix is replaced by the inert polymer, thus revealing that the performance enhancement mainly benefits from the suppressed interchain interactions [enhanced photoluminescence (PL) efficiency] because the guest chromophore is diluted by the host.

MEH-PPV and polystyrene were dissolved in *p*-xylene separately. The two solutions were then mixed at different ratios to give the appropriate weight percentages. The device structure used was ITO/PEDOT/polymer film/Ca/Al. The detailed device fabrication process can be found elsewhere.^{9,10} UV-visible absorption spectra were recorded with an HP 8453 spectrophotometer. Photoluminescence emission and excitation (PLE) spectra were measured using a Jobin Yvon Spex Fluorolog-3 double-grating spectrofluorometer.

Figure 1 shows PL emission spectra of a pure MEH-PPV film and MEH-PPV/PS blends. As can be seen, the emission spectra of the MEH-PPV/PS blends show strong concentration dependence. The pure MEH-PPV film is characterized with two main peaks at 590 and 625 nm, respectively. As the MEH-PPV contents decrease in blends, the peak intensity at 625 nm is dramatically reduced and the emission spectrum consistently blueshifts. The MEH-PPV/PS system with a MEH-PPV concentration less than 20% shows a main emission peak at 572 nm with a much weaker red shoulder. The efficiency of the blend film also increased. The PL efficiency of the 20/80 (MEH-PPV/PS) films increases by 40%, and doubled in 50/50 films.

It is well accepted that the emission peak at 590 nm originates from single-chain excitons (also termed intrachain excitons), while those peaks or shoulders appearing at longer wavelengths, such as 625 and 680 nm, are associated with interchain interactions.^{5,10} The presence of interchain interactions in conjugated polymers can be evidenced by measur-

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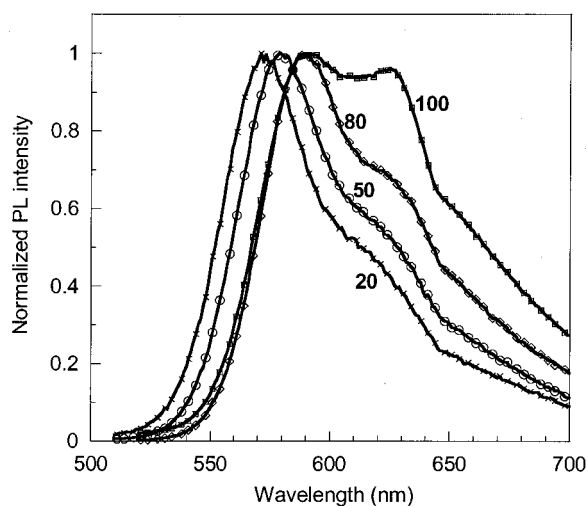


FIG. 1. Normalized photoluminescence spectra of pure MEH-PPV and blends with PS. Numbers shown in the plot correspond to the weight percentage of MEH-PPV.

ing PL excitation spectra.¹¹ Figure 2 shows excitation spectra collected with a fixed emission wavelength at 625 nm, which is related to the emission from interchain species, of a pure MEH-PPV film as well as its blends with PS. As can be seen, the pure MEH-PPV film shows a clear signature of red-edge excitation (redshifted excitation spectrum and a tail appearing at longer wavelength) compared to the blends, indicating the presence of smaller gap species, i.e., the interchain species. In addition, the intensity of the long-wavelength tail decreases when reducing the MEH-PPV concentration in the blends, indicating that interchain interactions between and among MEH-PPV chains have been dramatically suppressed upon blending with PS—so-called “dilution” effects.

A similar phenomenon, i.e., blending emissive polymers with inert polymers, can dramatically suppress interchain interactions, has also been reported by other groups. For example, Yan and his co-workers⁵ studied the photophysics of MEH-PPV blends with PS. The transient photoinduced absorption, the stimulated emission, and the picosecond PL dynamics of highly diluted MEH-PPV/PS blends (solid state

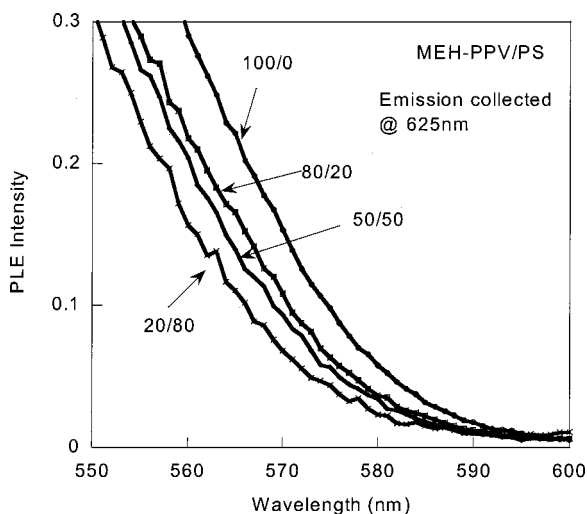


FIG. 2. Excitation spectra of pure MEH-PPV and its blends with PS collected at 625 nm.

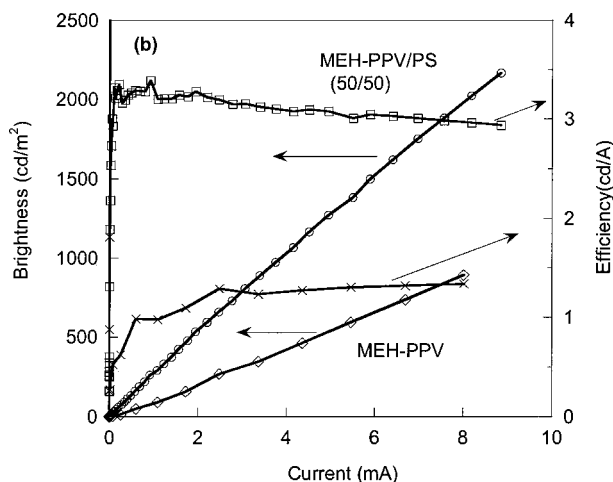
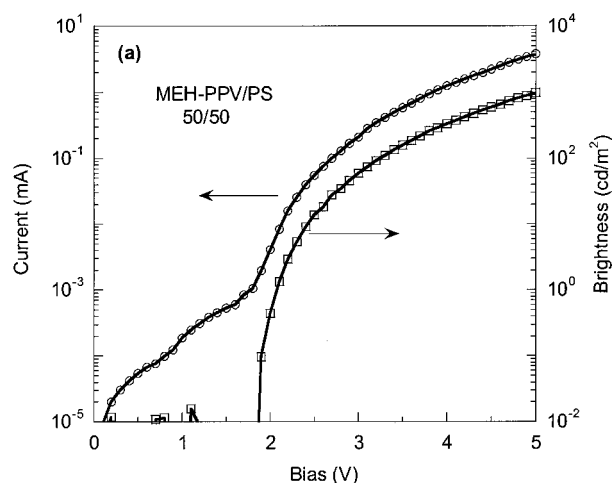


FIG. 3. Current vs voltage curve of a MEH-PPV/PS (50/50) device (a) and brightness-current-efficiency curves of the MEH-PPV/PS (50/50) device and a pure MEH-PPV device (b).

films) are very similar to those observed in diluted MEH-PPV solutions in chlorobenzene. The observed simple exponential decay law indicates interchain interactions in pure MEH-PPV are highly reduced by dilution of MEH-PPV in blends.

A similar spectra change can also be observed in electroluminescence. With the decrease of MEH-PPV concentration, the peak at 630 nm was compressed considerably and the spectrum blueshifted. And the full width at half maximum (FWHM) of the spectra changed from 110 nm for pure MEH-PPV to 60 nm for the MEH-PPV/PS (20/80). The narrower EL output is an advantage in full-color display application because it is important for the individual red, green, and blue light to be as narrow as possible to get saturated colors.

It has been well documented that interchain interactions in pure MEH-PPV films either largely decay nonemissively at ambient temperature or have very low quantum efficiency, thus resulting in much lower photoluminescence quantum yields for thin films compared to that in diluted solutions.⁵ The reduction in interchain species improves the PL efficiency. For example, the relative PL efficiency of the MEH-PPV (80%)/PS film was found to increase by about 40% with respect to that of the pure MEH-PPV film.

As shown in Fig. 3(a), the device fabricated from the

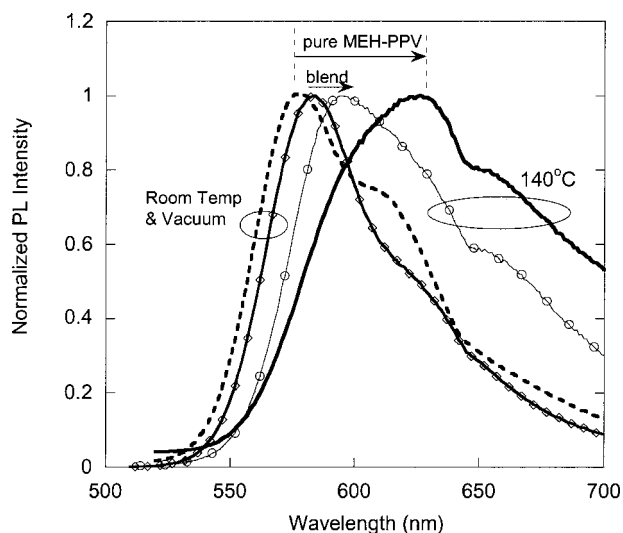


FIG. 4. PL spectra of pure MEH-PPV films and MEH-PPV/PS (50/50) films annealed at room temperature in vacuum and 140 °C, respectively. Dashed and solid curves are pure MEH-PPV film annealed at room temperature and 140 °C, respectively. The diamond (\diamond) and circle (\circ) are 50/50 blend films annealed at room temperature and 140 °C, respectively.

MEH-PPV/PS (50/50) blend has an onset voltage for charge injection of about 1.6 V and a turn-on voltage of about 1.8 V, which are similar to pure MEH-PPV devices. More important, the efficiency at 1000 cd/m² is about 3.2 mcd/A, which is much higher than that of the pure MEH-PPV device (1.4 cd/A) [Fig. 3(b)]. Since neither energy transfer nor charge transfer is involved in MEH-PPV/PS blends, the results indicate that the major contribution to the enhancement of EL efficiency in MEH-PPV-based blends mainly comes from the enhancement of the PL efficiency as a result of the suppressed interchain interactions. However, further decreasing the MEH-PPV concentration will lower the EL efficiency due to the poorer charge injection (unbalanced charge injection) and transport capability.

In addition to efficiency enhancement, another advantage of using blends is the reduced sensitivity of device performance to processing. It has been demonstrated that the PL and EL spectra of MEH-PPV films are highly sensitive to processing, such as annealing temperatures.¹² For example, as shown in Fig. 4, a dramatic difference has been found in PL spectra of MEH-PPV films annealed at room temperature under vacuum and 140 °C, respectively. This is attributed to the aggregation of MEH-PPV chains upon annealing. On the other hand, because the glass transition temperature (T_g) of PS (about 96 °C) is higher than T_g of MEH-PPV (about 75 °C), the relaxation and aggregation of

MEH-PPV chains is retarded by the more-rigid PS host. As a result, PL spectra of MEH-PPV/PS films are much less sensitive to the annealing conditions. (The 0-0 transition peak shifts by 50 nm for the pure MEH-PPV film, and 13 nm for the blend film, respectively.)

In summary, conjugated polymer MEH-PPV blends with an inert polymer—PS—were studied. The PL and EL spectra show strong composition dependence. Evidenced by the PLE measurement, the addition of PS into MEH-PPV can dramatically suppress the formation of interchain interactions (emissive species which largely decay nonradiatively and/or have very low quantum yields). In addition, the EL efficiency is enhanced from about 1.4 cd/A for pure MEH-PPV devices to 3.2 cd/A for the MEH-PPV/PS (50/50) blend. Since there is neither energy transfer nor charge transfer involved in MEH-PPV/PS blends, the efficiency enhancement is mainly attributed to the suppressed interchain interactions and enhanced PL efficiency. Furthermore, adding PS into MEH-PPV also improves the thermal stability of polymer thin films and reduces the sensitivity to processing conditions. Another benefit from constructing PLEDs with MEH-PPV blends with PS is that the fabrication cost can be dramatically reduced by using less-expensive polymer matrices without significant sacrifice of device performance.

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