

Improving the performance of polymer light-emitting diodes using polymer solid solutions

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Optical and electronic properties of conjugated polymers can be modified significantly by arranging the polymer chains differently. For example, it is well known that polymer solutions of lower concentrations have different photoluminescence spectra from solutions of higher concentrations. In this manuscript, we demonstrated that such effects can also be achieved in solid states, i.e., in *polymer solid solutions* consisting of a narrower band-gap material—poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV) with a wider band-gap polymer—poly(9,9-dioctylfluorene). At very low MEH-PPV concentrations, emission spectra of these solid solutions are similar to the photoluminescence spectrum of a diluted MEH-PPV solution in an ordinary organic solvent, suggesting the absence of a significant amount of interchain species. In addition, the electroluminescence efficiency is significantly enhanced. Furthermore, the full width at half maximum (FWHM) is dramatically reduced at lower MEH-PPV concentrations, as a result of suppressed interchain interactions. This approach is particularly important for the application to display technology, in which well-defined narrow FWHM emission spectra of red, green, and blue colors are required. © 2001 American Institute of Physics. [DOI: 10.1063/1.1389324]

Due to their potential use in display technology,^{1–3} polymer light-emitting diodes (PLEDs) have attracted strong attention.⁴ Although conjugated polymers have often been considered as amorphous semiconductors, the detailed arrangement of polymer main chains and its side groups, known as the polymer morphology or conformation in the literature,^{5–8} plays an important role in controlling the electronic characteristics of the polymer thin films. Recently, a systematic study in controlling the optical as well as electrical properties of PLEDs by controlling the morphology of—poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV), i.e., using different solvents, different concentrations of polymer solutions, and different spin coating conditions, revealed many insights regarding the correlation between the polymer chain aggregations and the device performance.^{5,6}

One of the major drawbacks for PLEDs being used in displays is that the emission spectra of the light-emitting polymers are usually very broad due to the formation of interchain emissive species. This problem can be resolved by isolating polymer chains. In some circumstances, reducing the interchain interactions can also enhance the photoluminescence (PL) efficiency. It is well known that a diluted MEH-PPV solution has much higher PL efficiency than the polymer thin films coated from the same solution. This has been attributed to the formation of a less emissive interchain species, which quenches the fluorescence in solid state films.^{9–11} Several groups have found that the incorporation of extremely bulky side groups onto the polymer backbones can effectively reduce interchain couplings.^{12,13} However, devices based on these materials have shown very poor charge

injection and transport, thereby offsetting the overall performance of PLEDs. Yan *et al.*¹⁴ reported that interchain interactions are inhibited by blending MEH-PPV with an inert polymer—polystyrene. However, from a practical point of view, high performance PLEDs can not use polymer blends with inert polymers, since they will deteriorate the electrical properties of the thin film.

In this manuscript, a different approach is proposed. Instead of using inert polymers, a luminescent polymer, poly(9,9-dioctylfluorene) (PF) is used as the host material and blended with MEH-PPV. In this solid state polymer solution, PF molecules serve as the media separating the MEH-PPV chains from each other, as well as conducting the electricity. At optimized MEH-PPV to PF ratio, efficient energy transfer from PF to MEH-PPV can be achieved. It is found that the best device performance is achieved when the solid solution contains 4% of MEH-PPV and 96% of PF.

PF and MEH-PPV were dissolved in p-xylene, separately. The two solutions were then mixed in different ratios to give the appropriate weight percentages. Nominal MEH-PPV concentrations are specified as the wt % in PF host. The fabrication of thin films and devices can be found elsewhere.^{5,6}

The same sample was used for UV-visible absorption and PL measurements. UV-visible absorption spectra were recorded by a HP 8453 spectrophotometer. For PL measurements, the emission spectra and excitation spectra were measured using a Jobin Yvon Spex Fluorolog-3 double-grating spectrofluorometer. Excitation wavelength for pure PF and PF/MEH-PPV thin films was fixed at 370 nm. For pure MEH-PPV thin films, the excitation wavelength was set at 490 nm. Atomic force microscopy (AFM) was used to study the surface characteristics of the polymer thin films. AFM studies were performed with a Nanoscope IIIa Multimode

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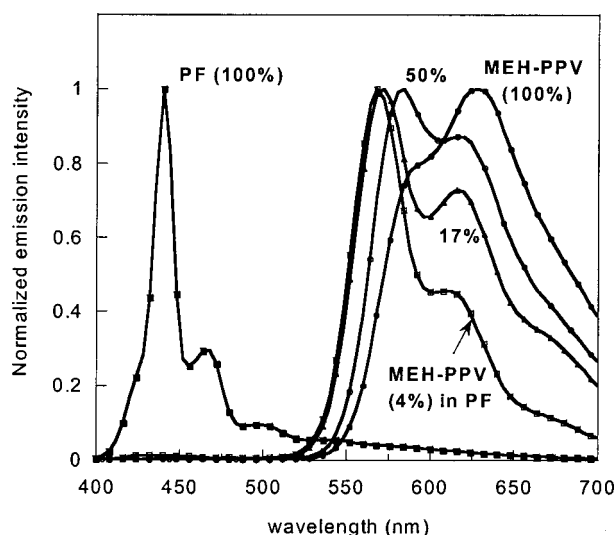


FIG. 1. Normalized PL emission spectra of films of pure MEH-PPV, PF, and MEH-PPV/PF solid solutions are shown. 50%, 17%, and 4% correspond to weight concentrations of MEH-PPV in MEH-PPV/PF solid solutions.

scanning probe microscope (*Digital Instruments*). Height (not shown in this letter) and phase images were recorded in tapping mode simultaneously. Device characterization can be found in our previous papers.^{5,6}

Figure 1 shows the PL emission spectra of pure PF film, MEH-PPV film, and MEH-PPV/PF solid solutions. The emission spectra of the MEH-PPV/PF blends show strong concentration dependence. The pure MEH-PPV film has a reddish emission with a main peak at 630 nm, which has been assigned to an excimer species.⁵ As the MEH-PPV contents decrease, the emission spectrum consistently shifts to the blue. At 4% MEH-PPV, the emission spectrum of the film shows a strong yellowish emission peak at 570 nm, which has previously been assigned to the single chain exciton of MEH-PPV.⁵ Further decrease of the MEH-PPV contents (e.g., to as low as 1% MEH-PPV/PF) does not change the shape of the emission spectrum. This indicates that the MEH-PPV chains are effectively isolated by the PF molecules and interchain interactions are significantly reduced. In addition, the emission spectrum of this 4% MEH-PPV/PF solid solution closely resembles the PL spectrum of a diluted MEH-PPV solution in a regular organic solvent. This suggests that either no exciplex species is formed between the MEH-PPV and PF molecules or, if the exciplex is formed, the exciplex is nonemissive. On the other hand, the absorption spectrum of the blend can be obtained by overlapping the weighted spectra of the two components, indicating no significant π - π overlapping between the two species in the ground states. These observations are consistent with the fact that the shape of the excitation spectrum of the blend resembles its absorption spectrum, and it is independent of the emission wavelength (Fig. 2). At MEH-PPV% \geq 4%, no emission from PF can be detected, suggesting efficient energy transfer from the PF host molecules to MEH-PPV molecules.

AFM phase images of blend polymers reflect differences in the properties of their constituents, thereby allowing surface compositional mapping in polymer blends.¹⁵ Figure 3 shows AFM phase images of two polymer films—17% and

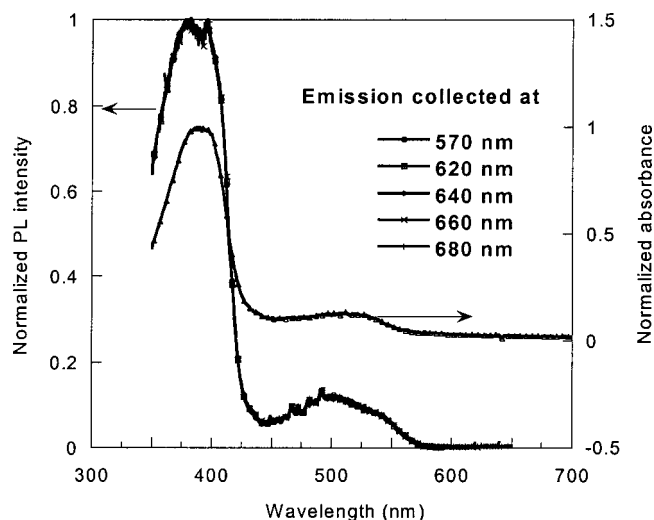


FIG. 2. Normalized UV-visible absorption spectrum and normalized excitation spectra of a 4% MEH-PPV/PF solid solution collected at different emission wavelengths are shown.

4% MEH-PPV/PF solid solutions. The contrast covers phase angle variation in the 50° range. As can be seen, phase separation occurs in the 17% MEH-PPV/PF solid solution. The minor phase, i.e., the MEH-PPV component, is dispersed within the PF matrix as it aggregates with a feature size about 30 nm in width. In addition, the emission spectrum differs remarkably from that of the diluted solution, thereby implying the presence of interchain interactions. In contrast, a uniform, homogenous phase image is observed for 4% MEH-PPV/PF solid solution. The MEH-PPV molecules are well “dissolved” by the PF host, providing little evidence for significant aggregates, which is consistent with the conclusion based on the emission and excitation spectra.

Luminescence-current-efficiency curves are shown in Fig. 4. As can be seen, the efficiency increases as decreasing the concentration of MEH-PPV component in solid solutions. At a current of 3 mA, the luminescence and efficiency of the device (4% MEH-PPV/PF solid solution) is 967 cd/m² and 3.9 cd/A, respectively. This is 70% higher than that of the pure MEH-PPV device (560 cd/m² and 2.2 cd/A, respectively). In addition, the emission peaks become narrower as the MEH-PPV concentrations in polymer solid solutions decrease. For example, as shown in Fig. 1, the full width at half maximum (FWHM) is only 40 nm for the 4% MEH-PPV/PF device in contrast with more than 110 nm for the pure MEH-PPV device.

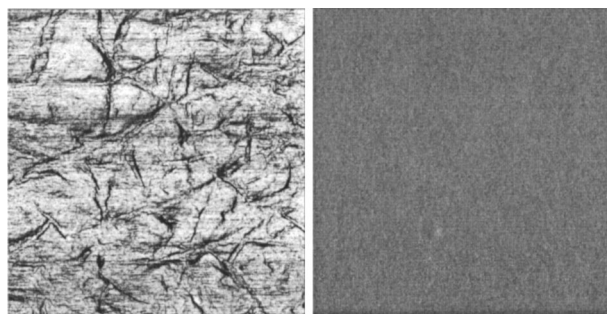


FIG. 3. AFM phase images of films of (left-hand side) 17% and (right-hand side) 4% MEH-PPV/PF solid solutions are shown. Both scans are 3 μ m \times 3 μ m. The contrast covers phase angle variation in the 50° range.

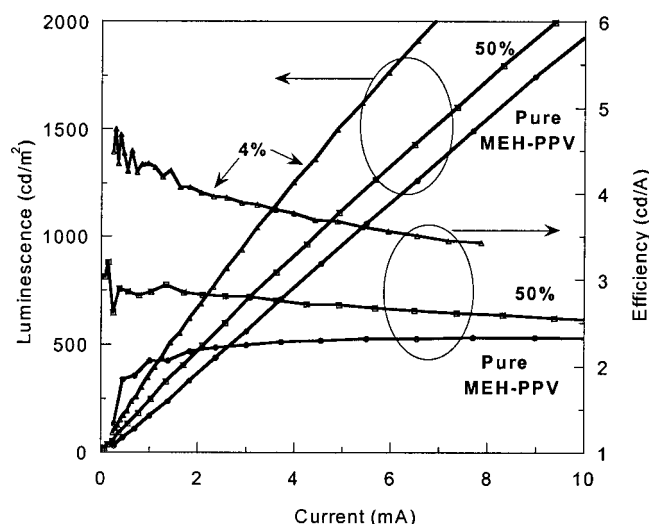


FIG. 4. Luminescence-current-efficiency curves of devices based on the pure MEH-PPV and 4% and 50% MEH-PPV/PF solid solutions are shown.

The improved device performance—enhanced electroluminescence efficiency and reduced FWHM benefits mainly from three sources. The first is suppressed interchain interactions. In solid solutions with very low MEH-PPV concentrations, the interchain interactions within the MEH-PPV chains are reduced dramatically by dilution effects. The second is effective energy transfer from PF to MEH-PPV. As shown in Fig. 1, no emission from PF can be observed in 4% MEH-PPV/PF solid solution indicating energy is effectively transferred from PF matrix to MEH-PPV. As the concentration of MEH-PPV in PF decrease to 1% emission from PF can be observed revealing that the energy transfer is not complete. Since both PF and MEH-PPV make contributions, emission colors can be tuned by varying the concentration. For example, a white color emission with the *Commission International de L'Eclairage* coordinates (0.3578 and 0.3045) can be obtained by using 0.2% MEH-PPV/PF solid solution. The third is the reduction in self-absorption. The absorption intensity in the MEH-PPV emission region (mainly within 550–700 nm) is decreased as the MEH-PPV concentrations in solid solution decrease. As a result of reduced self-absorption, more emitted photons can traverse the polymer film and encounter the detector, thus increasing the efficiency reading.

In summary, polymer solid solutions are formed by blending MEH-PPV with PF. At very low MEH-PPV con-

centrations, emission spectra of solid solutions are consistent with the PL spectrum of a diluted MEH-PPV solution. The absence of MEH-PPV aggregates observed with AFM indicates that the MEH-PPV chains are isolated, thus suppressing the formation of interchain interactions. Because of the inhibition of the interchain interactions, the effective energy transfer and the reduction in self-absorption, device performance is significantly enhanced. In addition, the FWHM of emission bands is dramatically reduced. For the pure MEH-PPV device, the FWHM is more than 110 nm, while the FWHM of the 4% MEH-PPV/PF solid solution is only 40 nm. These results show a promising approach of the fabrication of high performance polymer light-emitting diodes with desired (and controllable) narrow emission peaks for display applications.

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