Effects of Morphology on Energy transfer and Device performance in Phosphorescent Dye Doped Polymer Light Emitting Devices

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Abstract

The effect of morphology on energy transfer and device performance in phosphorescent dye doped polymer light emitting diodes is reported. We selected two host polymers (PVK and PFHP) which have nearly the same potential for the energy transfer to $Ir(ppy)_3$. The PFHP:$Ir(ppy)_3$ film showed sub-micron size aggregation, whereas the PVK:$Ir(ppy)_3$ film showed homogeneous and smooth images. As a result, energy transfer is efficient with high emission efficiency in PVK:$Ir(ppy)_3$ whereas little energy transfer and low quantum efficiency are obtained in PFHP:$Ir(ppy)_3$.

1. Introduction

Singlet and triplet energy transfer in phosphorescent dye doped organic and polymer light emitting diodes (LEDs) represents a topic of considerable interest during the last few years in terms of achieving a high emission efficiency by simultaneously harvesting both the singlet and triplet excitons [1-3]. However, energy transfer in polymer LEDs has been a subject of great controversy [4-5].

In an earlier study, we reported on the excitation energy transfers via the Förster and Dexter mechanism from poly (N-vinylcarbazol) (PVK) and poly(9,9'-di-n-hexyl-2,7-fluorene-alt-1,4(2,5dinhexyloxy) phenylene) (PFHP) to the phosphorescent dye, *fac* -tris(2-phenypyridine) irdium(III) [$Ir(ppy)_3$] [6]. The singlet and triplet emission of each of PVK and PFHP show good spectrum overlap with the singlet and triplet metal-to-ligand charge-transfer absorption of $Ir(ppy)_3$, respectively, so that efficient singlet and triplet energy transfer would be expected from both the polymers. We observed that singlet-singlet and triplet-triplet energy transfer from PVK to $Ir(ppy)_3$ took place efficiently. On the other hand, energy transfers were not found from PFHP to the guest, even though the spectrum overlap requirement for efficient Förster and Dexter energy transfer was satisfied. We inferred that aggregate formation was the reason for this, since energy transfer was not observed in the PL spectra of $Ir(ppy)_3$ (8 wt.%) doped PFHP films whereas it was observed in solutions and diluted film states of the same components.

In this paper, we present the direct evidences of the aggregation formation in $Ir(ppy)_3$ doped PFHP films and homogenous dispersion of the dye in PVK films using atomic force microscopy (AFM) and transmission electron microscopy (TEM) and describe effect of the morphology of polymer films on singlet and triplet energy transfer and device performances.

2. Experimental

$Ir(ppy)_3$ was synthesized according to the literature

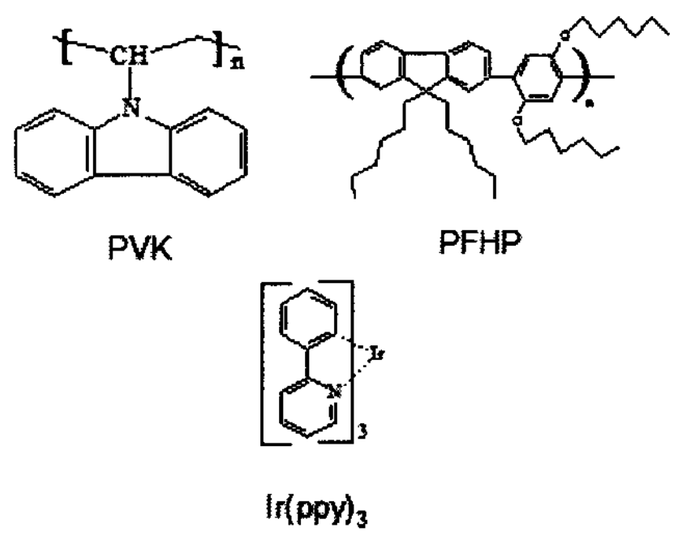

Figure 1. Molecular structures of PVK, PFHP and $Ir(ppy)_3$.

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method [7] and PFHP was synthesized using the Suzuki coupling process. PVK was purchased from Kanto. The thin films for AFM measurements were formed on pre-cleaned silicon substrates. PVK and PFHP were dissolved with the phosphorescent dye (8 wt.% of the host) in 1,2-dichloroethane and *p*-xylene, respectively, at a concentration of 10.8 mg/1 g. These solutions were filtered using a polytetrafluoroethylene (PTFE) syringe filter (Whatman) with a pore size of 0.2 μm. After spin coating (5000 rpm, 10 sec), the solvent was evaporated in a vacuum oven at 100 °C for 1 hour. The AFM system used in this study was a NanoScope III (Digital Instrument, Inc. Santa Barbara, CA).

The TEM instrument used here was a Carl-Zeiss LEO EM-912 equipped with an Omega-type energy filter at an accelerating voltage of 120 kV. Specimens for TEM observation were prepared as follows: the polymer solutions doped with $Ir(ppy)_3$ were cast on an air-cleaved potassium chloride (KCl) surface and then reinforced by the plasma-polymerized osmium tetraoxide. The thin film on KCl was then stripped from the substrate and then transferred to a cupper mesh.

The fabricated devices have the structure of ITO/ PEDOT (40 nm)/ Host-$Ir(ppy)_3$ (30 nm)/TAZ (30 nm)/ Alq_3 (20 nm)/ LiF (0.5 nm)/ Al (200 nm). PEDOT and the emitting layer were spin coated and the rest of the layers were formed by thermal evaporation. PFHP:$Ir(ppy)_3$ film shows the aggregate domains on length scales of 50-200 nm as shown in Figure 2a.

3. Results and Discussion

Figure 2a and b show TEM images of freestanding films (thickness ~20 nm) of PFHP and PVK doped with $Ir(ppy)_3$ (8 wt.% of the hosts). Since the iridium atom has a larger electron scattering cross section, the dark spots are likely to be $Ir(ppy)_3$ aggregates. However, the chemical composition of the aggregated domains has not yet been clarified. On the other hand, the PVK:$Ir(ppy)_3$ film shows a featureless image as displayed in Figure 2b, suggesting that the film is homogeneous, with no phase separation or aggregates. The surface topographies of the films were investigated and are demonstrated in Figure 3. The PFHP:$Ir(ppy)_3$ film shows an aggregated domain with a horizontal size of ~250 nm and a vertical roughness in the range of ±25 nm as shown in Figure 3a. In contrast, the PVK:$Ir(ppy)_3$ film is smooth with height variations in the range of less than ±1 nm as shown in Figure 3b. Figure 3c shows the AFM image of surface of the undoped PFHP film. This film shows a somewhat rough image, typical of a conjugated polymer having rigid backbone [8]. However, this image is significantly different from the PFHP:$Ir(ppy)_3$ film, that has aggregated features. These results indicate that the aggregated domains of the doped PFHP film are induced by the doping process with the phosphorescent dye.

The singlet and triplet energy transfer by the Förster and Dexter mechanism from PFHP or PVK to the phosphorescent dye, $Ir(ppy)_3$ was examined [6]. Both host polymers showed almost the same Förster transfer radius of ~30 Å for $Ir(ppy)_3$. The PL and EL spectra of PVK:$Ir(ppy)_3$ show the green emission from

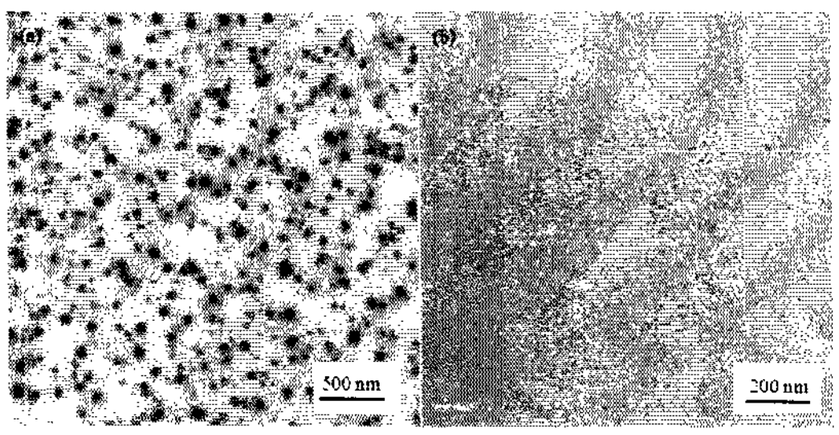

Figure 2. TEM image of films of (a) $Ir(ppy)_3$ (8 wt.%) doped in PFHP shows evidence of aggregation unlike the (b) $Ir(ppy)_3$ film (8 wt.%) doped in PVK.

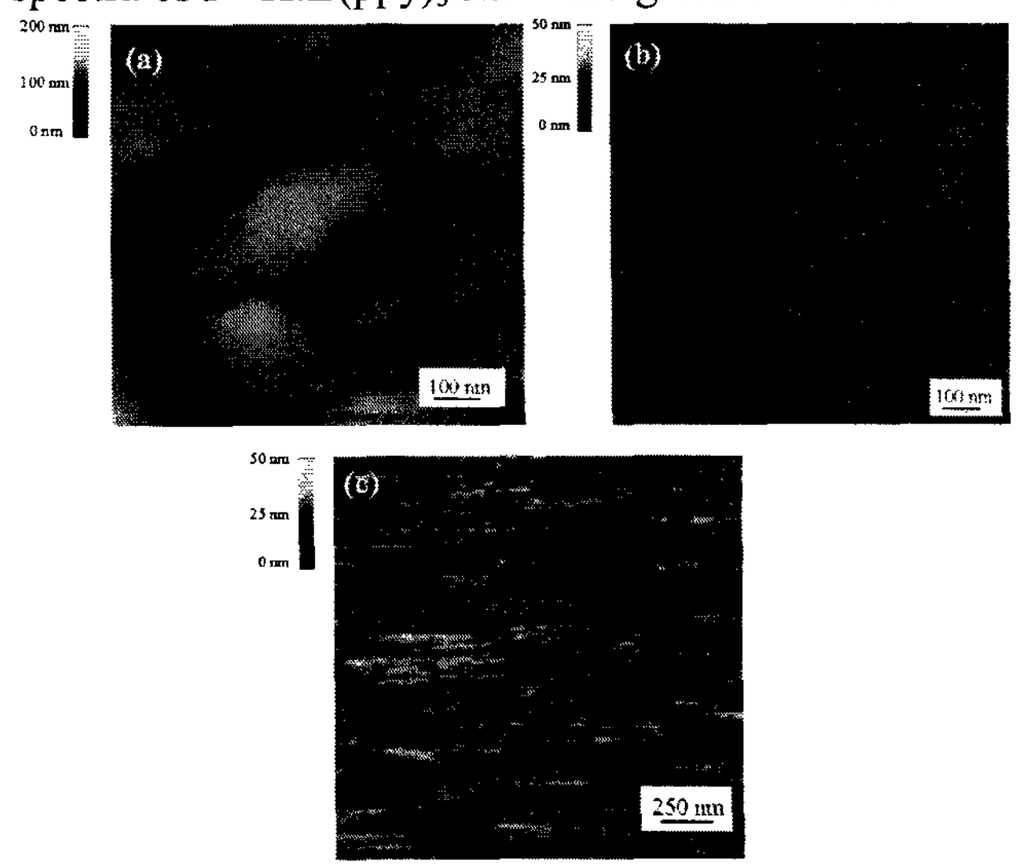

Figure 3. AFM images of the surfaces of (a) PFHP:$Ir(ppy)_3$ (8 wt.%), (b) PVK: $Ir(ppy)_3$ (8 wt.%) and (c) PFHP.

$Ir(ppy)_3$ via energy transfers as shown in Figure 4a and b. The homogeneous dispersion of $Ir(ppy)_3$ in PVK as demonstrated in Figure 2b permits the contact of the dopant molecules with the host polymer, which are in close proximity to one another. Therefore, the homogenous dispersion of dopant molecules in the host polymer along with a good spectrum overlap allows the efficient energy transfers even at the low doping concentration of 1 wt.% in the films.

On the other hand, singlet energy transfer was not observed from PFHP to $Ir(ppy)_3$ as shown in Figure 5a. The photoluminescent (PL) spectra of PFHP:$Ir(ppy)_3$ films show only a blue emission from PFHP at various doping concentrations. Moreover, the triplet energy transfer from PFHP to $Ir(ppy)_3$ did not occur, as evidenced by a transient electroluminescence (EL) study and a decay analysis of the triplet states of the host polymers.[15] Considering the TEM and AFM results shown in Figure 2 and 3, the aggregated domains in the PFHP: $Ir(ppy)_3$ film appear to prevent singlet and triplet energy transfer from PFHP to $Ir(ppy)_3$. Figure 5b shows the EL spectra of PFHP:$Ir(ppy)_3$ at various doping concentrations. The EL spectrum changes with doping concentration and the applied voltage at the same doping concentration (not shown). Most of the light is emitted from PFHP in the EL devices when the doping concentration is lower than 2%.

In contrast, light is mostly emitted from $Ir(ppy)_3$ if the doping is higher than 8%. This fact indicates that the light is emitted by direct charge trapping and recombination on the dye molecules at the high doping concentrations since the singlet and triplet energy transfer do not take place in the PFHP: $Ir(ppy)_3$ film. HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels of the PVK, PFHP and $Ir(ppy)_3$ are aligned favorably for the charge confinement. The HOMO levels of PVK, PFHP and $Ir(ppy)_3$ are 5.9, 5.7 and 5.5 eV and LUMO levels are 2.4, 2.7, and 3.0 eV, respectively, which were measured by ultraviolet photoelectron spectroscopy. However, the charge confinement in the aggregates formed in PFHP:$Ir(ppy)_3$ system is less effective than in the homogeneously doped system of PVK:$Ir(ppy)_3$ as evident from the requirement of high doping concentration for emission from the dopant.

The difference in the morphologies of the phosphorescent dye doped polymer systems corroborates

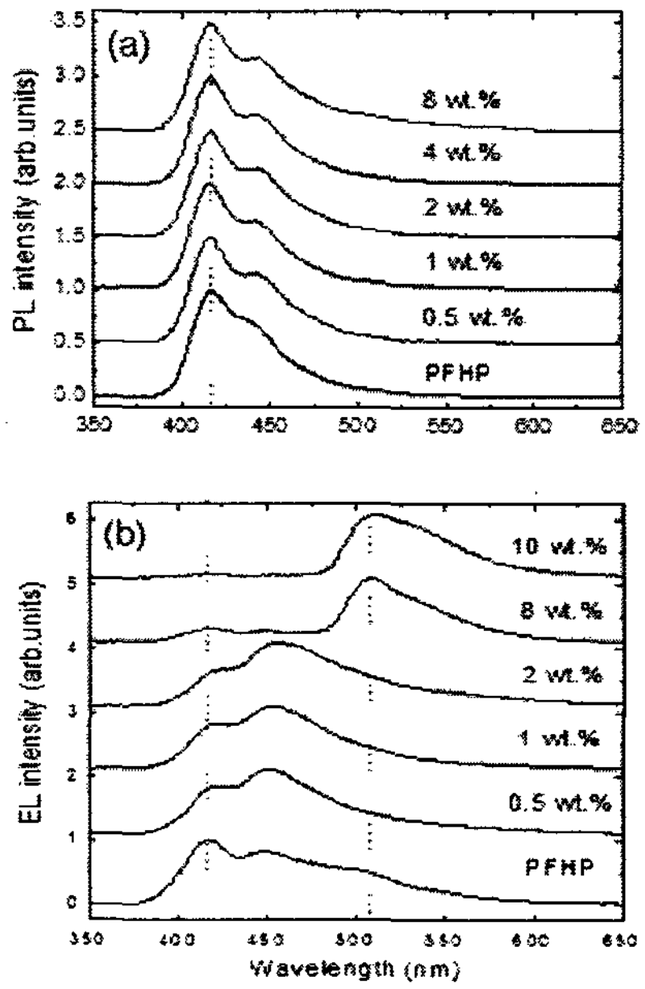

Figure 4. (a) PL spectra of PFHP and $Ir(ppy)_3$ films (0.5, 1, 2, 4, and 8 wt.%) doped with PFHP. (b) The EL spectra were taken from the devices having the structure of ITO/ PEDOT (40 nm)/ PFHP-$Ir(ppy)_3$ (30 nm)/ TAZ (30 nm)/ Alq_3 (20 nm)/ LiF (0.5 nm)/ Al (200 nm).

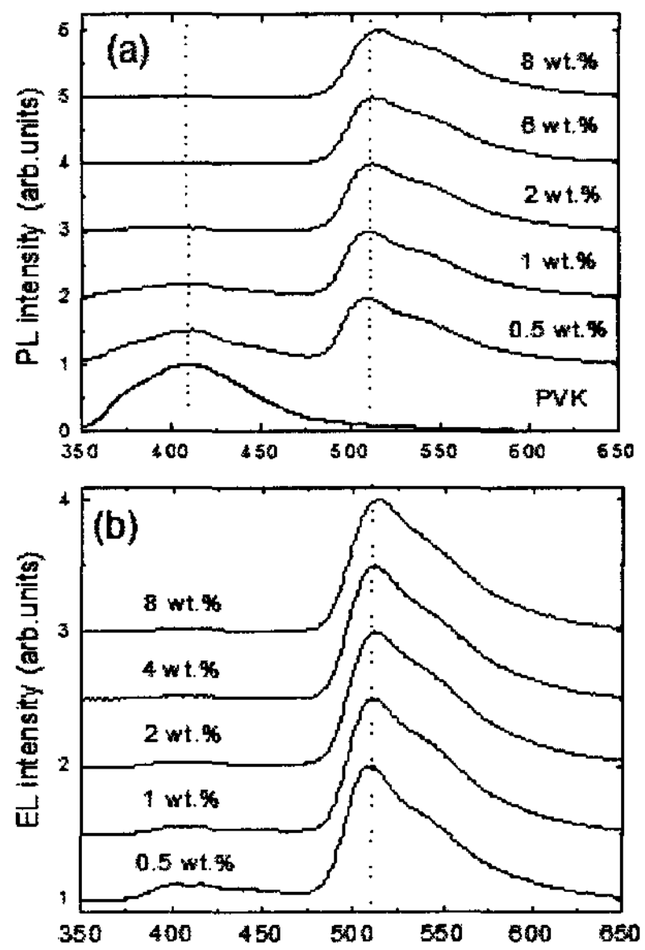

Figure 5. (a) PL spectra of PVK and $Ir(ppy)_3$ films (0, 0.5, 1, 2, 6, and 8 wt.%) doped with PVK. (b) The EL spectra were taken from the devices.

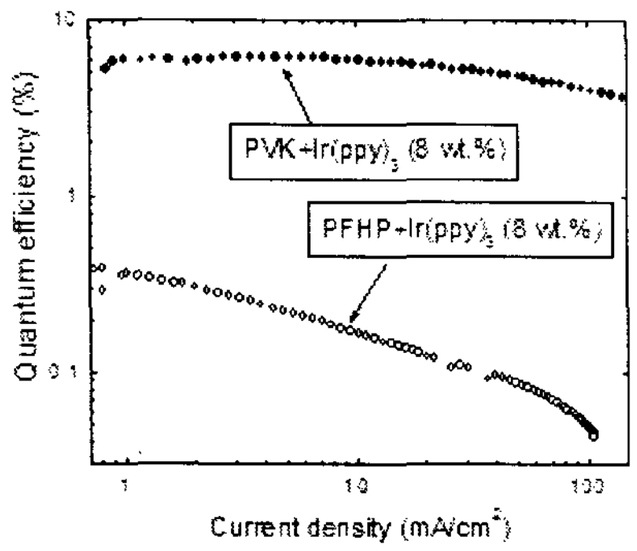

Figure 6. The external quantum efficiency of OLEDs using PVK:Ir(ppy)$_3$ (filled circles) and PFHP: Ir(ppy)$_3$ (opened circles) as a function of the current density.

the device performance significantly. Figure 6 shows the external quantum yields of OLEDs using PVK:Ir(ppy)$_3$ and PFHP:Ir(ppy)$_3$ as the luminescent layers. The maximum external EL efficiency (~6%) of PVK:Ir(ppy)$_3$ device at the current density of 7.4 mA/cm^2 is 15 times higher than that (~0.4%) of PFHP:Ir(ppy)$_3$ at the current density of 0.8 mA/cm^2. Each of the devices, fabricated with undoped PVK or PFHP as a luminescent layer shows the quantum efficiency of ~ 0.1%. Blocking of energy transfer, less efficient charge confinement and concentration quenching effect by the aggregates could contribute to the lower efficiency in the aggregate forming system. Therefore, the homogeneous dispersion of a dopant in a host must be addressed when doping systems for polymer LEDs are selected to utilize energy transfers.

4 Conclusion

In conclusion, we report on the morphology of spin-coated PFHP and PVK films doped with the phosphorescent dye Ir(ppy)$_3$, using TEM and AFM and its effect on singlet and triplet energy transfer. The PFHP:Ir(ppy)$_3$ film showed sub-micron size aggregation, whereas the PVK:Ir(ppy)$_3$ film showed homogeneous and smooth images. These results are consistent with the energy transfer characteristics of the dye doped systems: efficient energy transfers in the homogeneously dispersed PVK:Ir(ppy)$_3$ film and inefficient energy transfers in an aggregate forming PFHP:Ir(ppy)$_3$ system. The formation of aggregates prevents the dopant molecules from being in close proximity with the host molecules, thereby inhibiting the energy transfer processes. In addition, we found that the aggregated domains were induced by doping with Ir(ppy)$_3$ since an undoped PFHP film did not show any evidence of aggregation. It also explains the lower emission efficiency of the PFHP:Ir(ppy)$_3$ LED. Therefore, the homogenous dispersion of dopant with host materials as well as the usual requirements of Förster and Dexter energy transfer must be considered in order to successfully prepare efficient phosphorescent dye doped polymer LEDs.

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