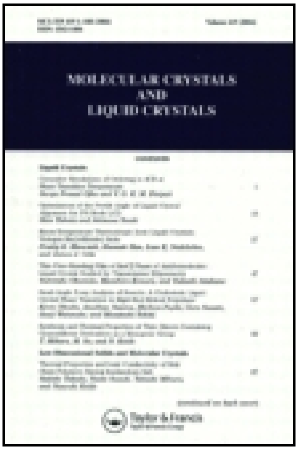

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White Polymeric Light-Emitting Diodes Based on Doping of an Orange Ir Complex in a Fluorene Blue Polymer Host

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A series of white polymer light-emitting devices has been fabricated by using a spiropolyfluorene (SF) blue polymer with an orange Ir complex as a blend system. A SF single polymer host and mixed co-host with CBP (4,4-N,N-dicarbazolebiphenyl) or PBD (2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) are investigated to get high efficiency white OLEDs. A good color coordination of (0.34, 0.36) with a good current efficiency of 1.52 cd/A at 2% doped condition in a CBP mixed co-host system is reported.

Keywords: mixed host; orange Ir complex; spiopolyfluorene; white organic light-emitting diode

INTRODUCTION

White organic light-emitting diodes (WOLEDs) are of increasing interest owing to potential applications such as backlights of LCD, full color active matrix displays, and even lighting sources. So far, there have been many methods to achieve white light emission from small molecule- or polymer-based OLEDs, several techniques are used. For small molecular based devices, WOLEDs made by vacuum deposition process have shown quite high efficiencies with complicate structures. This approach is somewhat difficult to achieve low cost

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mass-production for large area display and lighting applications. For polymer-based devices, WOLEDs fabricated by spin-coating or ink jet printing have advantages for simple and less expensive manufacturing process and can be easily applied to large-area applications. Therefore, many blending systems as soluble processed WOLEDs have been reported [1–6]. Among them, phosphorescent dye doping approach is intensively studying to harvest both singlet and triplet excitons. In previous works, conjugated polymers selected as triplet host materials, typically polyfluorene or other polymers have had low triplet energy states compared to most green phosphorescent dopants, which results relatively low efficiency [7,8]. In contrast, phosphorescent dye doped OLEDs fabricated by non-conjugated polymer host such as poly (9-vinylcarbazole) (PVK) can have good efficiencies [9,10]. However, the PVK-based electrophosphorescent device showed a high operation voltage due to the large hole injection barrier and inferior charge transport property of PVK compared to most conjugated polymers.

To overcome these shortcomings, we have investigated device performances of WOLEDs fabricated by a conjugated SF polymer host with a narrow band gap triplet dopant. A fluorescent SF polymer was chosen as a blue color material and phosphorescent host. The narrow band gap dopant, $Ir(2\text{-}phq)_2(acac)$(Bis(2-phenylquinoline)(acetylacetonate)iridium(III)) was used as an orange emitting material.

EXPERIMENTAL

Devices were fabricated as following procedures. The sheet resistance of ITO substrates used for our work was about 12 Ω/n with 1500 Å thickness. The ITO substrates of 2 × 2 cm were cleaned by sonification in acetone and isopropylalcohol (IPA) in sequence. Then, substrates were washed in deionized (DI) water and dried in high-pressure nitrogen. Finally, UV ozone treatment was done in a chamber.

The structure of ITO/PEDOT:PSS/BFE/polymer blend/BAlq/Alq_3/LiF/Al was employed for WOLED devices. The PEDOT:PSS was spin-coated on the ITO substrates pretreated with UV ozone. Samples were dried at 180°C for 10 min on a hot plate in order to remove water from the polymer layer. The BFE polymer supplied by Dow was spun on the PEDOT:PSS layer as a polymer hole transport layer. Samples were dried again at 180°C for 30 min on a hot plate to remove the solvent. A blue SF polymer supplied by Merck Corporation and $Ir(2\text{-}phq)_2(acac)$ were dissolved in a toluene solvent in various weight/-weight (w/w)% concentrations. The small molecular co-host materials, CBP or PBD, were as mixed in a SF and Ir complex blend system.

Finally, a blend solution for a white emissive layer was spin coated on a BFE layer and baked on hot plate at 120°C for 60 min. The process was carried out in a glove box. Later, BAlq (50 Å) and Alq_3 (200Å) were deposited sequentially in organic chamber and LiF (10 Å) and Al (1000 Å) were deposited in a metal chamber system without breaking the vacuum. The emission area of devices was 2 × 2 mm. The current density-voltage (I-V) and luminance-voltage (L-V) characteristics of WOLEDs were measured with a Keithley SMU 238 and Minolta CS-100A. Electroluminescence (EL) spectra and CIE color coordinate were obtained using a Photo-research PR-650.

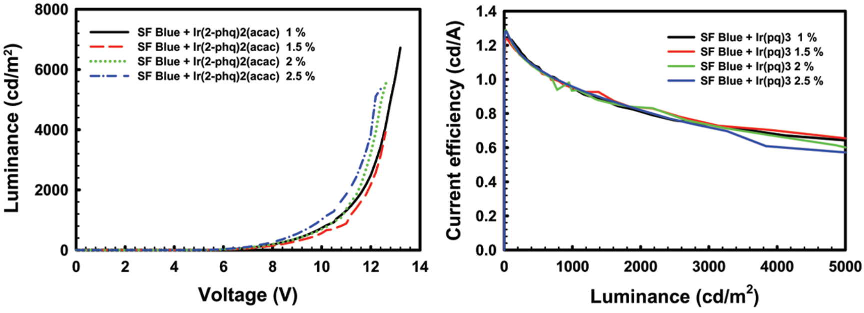
RESULTS AND DISCUSSION

Various WOLED devices are fabricated using a SF blue single host system or a spiropolyfluorene/small molecule co-host system with 1.0, 1.5, 2.0, and 2.5 wt% of $Ir(2\text{–}phq)_2(acac)$ dopant concentrations. The small molecular host materials, CBP or PBD, are added about 1/3 of total weight. Table 1 shows emitting layer compositions for several devices.

Figure 1 shows device characteristics of (a) luminance versus voltage and (b) current efficiency versus luminescence with different doping concentrations in a SF single host system. The current efficiency at 1000 cd/m^2 are 0.94 cd/A and 0.28 lm/W in device 1, 0.93 cd/A and 0.26 lm/W in device 2, 0.93 cd/A and 0.28 lm/W in device 3, 0.96 cd/A and 0.30 lm/W in device 4. The maximum efficiencies of these devices are 1.25 cd/A and 0.66 lm/W, 1.24 cd/A and 0.64 lm/W, 1.29 cd/A and 0.72 lm/W, 1.28 cd/A and 0.71 lm/W in device 1–4, respectively. In a SF single host system, 2 wt% doped device shows the best performance with a maximum current efficiency of 1.29 cd/A. White color coordinates at 1000 cd/m^2 are (0.27, 0.31), (0.29, 0.32), (0.33, 0.34), (0.35, 0.35) in device 1–4, respectively. White color coordinates shift toward reddish white region with increasing

TABLE1 Emitting Layer Compositions in Device 1–6

WOLED devices	Emitting layer composition
1	SF Blue + $Ir(2\text{-}phq)_2(acac)$ 1 wt %
2	SF Blue + $Ir(2\text{-}phq)_2(acac)$ 1.5 wt %
3	SF Blue + $Ir(2\text{-}phq)_2(acac)$ 2 wt %
4	SF Blue + $Ir(2\text{-}phq)_2(acac)$ 2.5 wt %
5	(SF Blue:CBP = 2:1) + $Ir(2\text{-}phq)_2(acac)$ wt %
6	(SF Blue:PBD = 2:1) + $Ir(2\text{-}phq)_2(acac)$ 2 wt %

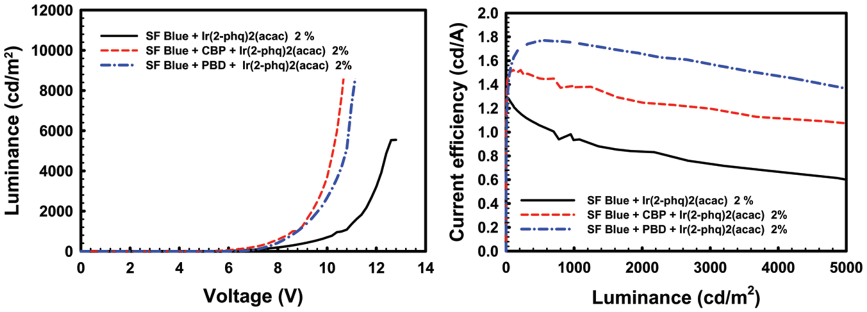


(a) (b)

FIGURE 1 Luminance versus voltage characteristics (a) and current efficiency versus luminescence characteristics (b) of device 1 ~ 4.

doping concentration. Since best results are obtained for the doping concentration of 2 wt % of Ir(2-phq)$_2$(acac), this value is fixed for subsequent measurements. White color point (0.33, 0.34) obtained by a 2% doped device is very close to values of standard white light sources such as D65- and C-light.

After fixing doping concentration, the mixed host system is investigated with CBP and PBD materials to enhance device performance. Usually mixed host system resulted in the improvement of device efficiency and lifetime as charge carriers move via less energy barrier host and more stable material [11]. Figure 2 shows (a) luminance versus voltage and (b) current efficiency versus luminescence characteristics of two mixed host devices. When CBP or PBD is added in the



(a) (b)

FIGURE 2 Luminance versus voltage characteristics (a) and current efficiency versus luminescence characteristics (b) of device 1, 5, 6.

SF blue host system, luminance versus voltage characteristics are significantly improved compared to a SF single host device. Driving voltage to reach 1000 cd/m^2 are improved about 2.0 V by adding a CBP or PBD small molecular host. Driving voltage values of 10.6, 8.6 and 8.8 V in device 1, 5 and 6 were obtained, respectively. Power efficiencies and current efficiencies in mixed host system devices are also significantly improved. The device 5, mixed co-host device [SF blue/CBP(2/1, w/w)] shows a current efficiency of 1.39 cd/A and 0.51 lm/W at 1000 cd/m^2. The maximum efficiency values are 1.52 cd/A and 0.83 lm/W. A current efficiency of 1.75 cd/A and a power efficiency of 0.63 lm/W at 1000 cd/m^2 are obtained in device 6, SF blue/PBD (2/1, w/w) co-host device. The maximum efficiency values are 1.77 cd/A and 0.72 lm/W. A good white color of (0.34, 0.36) at 1000 cd/m^2 is observed in a CBP mixed device. The PBD mixed device, Device 6, shows a good current efficiency, but its color coordinates of white is poor, (0.21, 0.29) at 1000 cd/m^2. Furthermore, color coordinates are not located in white region and strongly dependent on luminescent conditions.

In order to know energy transfer mechanism and variation of color coordinates, electroluminescence spectra and color variation are investigated as a function of driving voltage. The color coordinates are changed from green region to blue region with voltage increase as shown Figure 3. Among the materials used in this study, there were no any green light emitting materials in an emitting layer or in nearby emitting layers. Electroluminescent spectra are investigated to know green emission sources. As shown in Figure 4, a new strong peak is observed at 480$\sim$490 nm, which is almost corresponding to a second strong peak of the SF host polymer. However, this peak intensity is significantly increased in a SF polymer host with 2% Ir(2-phq)$_2$(acac) doping concentration. In addition, this peak intensity can be reduced when the CBP or PBD small molecule host is mixed to the polymer host as shown Figure 4. Photoluminescence spectra of SF polymer and BAlq are investigated in solid film state. Three films using SF polymer, BAlq, and 1:1 mixture of these two materials were fabricated to know the green emission mechanism. Figure 5 shows photoluminescence spectra of these films. The second peak around at 480$\sim$490 nm is increased when BAlq is mixed in a SF polymer. This peak is also shifted slightly to 480 nm region when the BAlq is mixed.

On the basis of above spectral analysis, the origin of green emission could be understood by the emission of BAlq at the emissive layer interface. At low driving voltage condition, emitting zone must be located at the interface region between an emissive layer and hole blocking layer. With increasing driving voltage, emission zone is

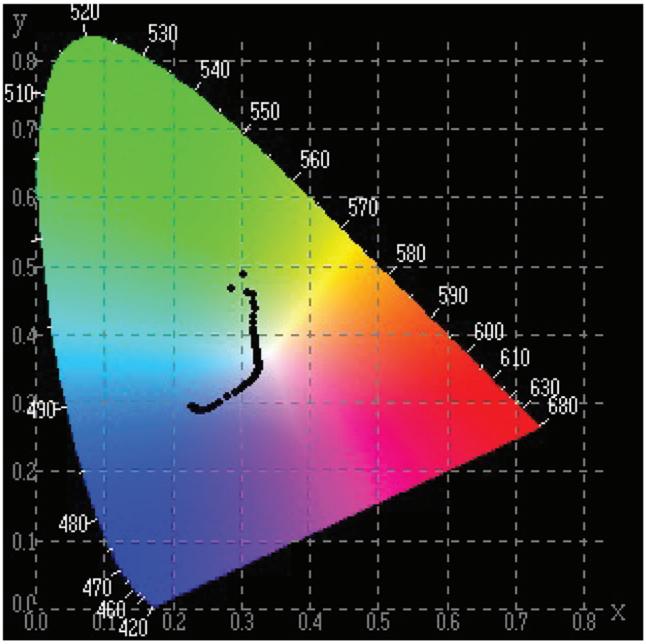
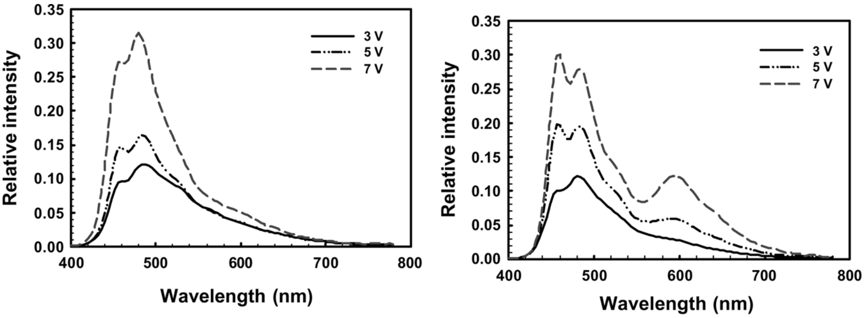


FIGURE 3 Color variation with increasing driving voltage in device 3.

shifted toward the emission layer. Reduction of 480 ~ 490 peak intensity at mixed host system can be explained that the emission zone is shifted to the emission layer due to enhancement of the electron transporting capability by CBP and PBD materials. In case



(a) (b)

FIGURE 4 Electroluminescent spectra of device 2 and 5; (a) device 2 (b) device 5.

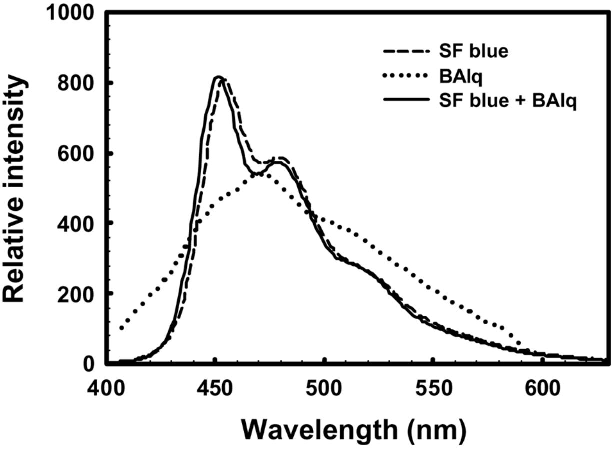


FIGURE 5 Photoluminescent spectra of SF polymer film, BAlq film, and mixture film of SF polymer and BAlq.

of PBD mixed device, BAlq emission peak is almost disappeared due to fast electron transporting ability. As shown in Figure 4, the orange color peak is relatively low in a SF single host system compared to the CBP mixed host system. The SF polymer used in the present study may not be a right host material for orange $Ir(2\text{-}phq)_2(acac)$ material. Some energy quenching by the polymer host may exist in our system. Energy quenching by the SF polymer seems to be reduced by the addition of CBP or PBD.

CONCLUSIONS

A series of white polymer light-emitting devices has been fabricated by using a $SP/Ir(pq)_3$ blend system. Small molecular co-host materials such as CBP and PBD significantly improve the device efficiency. At 2 % doping concentration, good color coordinates with good efficiency values are exhibited in white devices. In a SF blue/CBP co-host system, a good current efficiency of 1.52 cd/A and good color coordinates of (0.34, 0.36) at 1000 cd/m^2 are obtained. In conclusion, we propose a simple blending approach to fabricate good WOLED devices.

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