Highly efficient polymer phosphorescent light-emitting devices based on a new polyfluorene derivative as host*

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Several highly efficient iridium-complex polymer light-emitting devices (PLEDs) are fabricated, with a newly synthesized blue conjugated polymer, poly[(9,9-bis(4-(2-ethylhexyloxy)phenyl)-fluorene)-*co*-(3,7-dibenziothiene-S,S-dioxide15)] (PPF-3,7SO15), chosen as host. High luminous efficiencies of 7.4 cd·A^{-1} and 27.4 cd·A^{-1} are achieved in red and green PLEDs, respectively, by optimizing the doping concentrations of red phosphorescent dye iridium bis(1-phenylisoquinoline) (acetylacetonate) (Ir(piq)) and green phosphorescent dye iridium tris(2-(4-tolyl)pyridinato-N, $C^{2'}$) (Ir(mppy)$_3$).Furthermore, highly efficient white PLEDs (WPLEDs) with the Commission Internationale de l'Eclairage (CIE) coordinates of (0.35, 0.38) are successfully produced by carefully controlling the doping concentration of the iridium complex. The obtained WPLEDs show maximal efficiencies of 14.4 cd·A^{-1} and 10.1 lm·W^{-1}, which are comparable to those of incandescent bulbs. Moreover, the electroluminescent spectrum of the white device with an initial luminance of about 1000 cd·m^{-2} is stable, subject to constant applied current stress, indicating that good device stability can be obtained in this system.

Keywords: phosphorescent, polymer light-emitting devices, host, white

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1. Introduction

Organic/polymer light-emitting diodes (OLEDs or PLEDs) have attracted increasing attention due to their potential applications in full-colour flat panel displays and solid-state lighting.[1−5] Owing to the use of phosphorescent materials, the efficiencies of OLEDs have been improved greatly as both singlet and triplet excitons can be harvested for light emission.[6,7] The efficiencies of polymer phosphorescent light-emitting devices are much less than those of molecular devices. A number of efficient devices based on poly(N-vinylcarbazole) (PVK) as host doped with iridium complexes have been reported due to its high triplet energy level.[8−11] However, the devices with PVK as host will degrade significantly during operation and have poor colour stability, which restricts their practical applications. Polyfluorenes (PFs) and their derivatives are good hosts for polymer phosphorescent light-emitting devices, especially for red and green phosphorescent devices.[12−14] The devices in which PFs or their derivatives are used as both host materials and blue emitters have all shown high colour purity and long-time stability.[15−18]

In the present paper, highly efficient polymer phosphorescent light emitting devices are obtained based on poly[(9,9-bis(4-(2-ethylhexyloxy)phenyl)-fluorene)-*co*-(3,7-dibenziothiene-S, S-dioxide15)] (PPF-3, 7SO15) doped with a red phosphorescent dye, a green phosphorescent dye, and their blends. More importantly, the obtained white device has a lower operating voltage and high power efficiency (PE) without an additional electron-transport layer (ETL). An optimized white device shows a peak PE of 10.1 lm·W^{-1}, with the Commission Internationale de l'Eclairage (CIE) coordinates of (0.35, 0.38).

2. Experimental details

The chemical structures of the emitting materials and the energy diagram of the devices are

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shown in Fig. 1. The PPF-3,7SO15, with high efficiency and excellent spectrum stability, was synthesized in our laboratory.[19] The triplet energy level of PPF-3,7SO15 was estimated to be 2.08 eV,

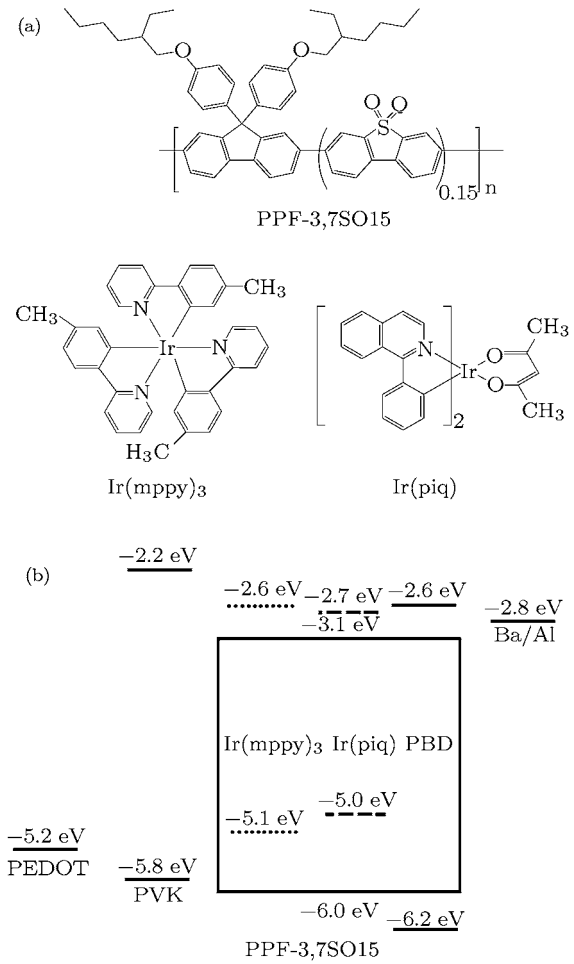


Fig. 1. (a) Chemical structure of the emitting materials and (b) energy diagram of the devices.

much less than 3.0 eV for PVK. Two phosphorescent dopants, iridium bis(1-phenylisoquinoline) (acetylacetonate) (Ir(piq), red emission) and iridium tris(2-(4-tolyl)pyridinato-$N, C^{2'}$) (Ir(mppy)$_3$, green emission) were purchased from America Dyes Sources Inc. All of the devices discussed in this work were fabricated based on the device structure of indium tin oxide (ITO)/PEDOT:PSS (40 nm)/PVK (40 nm)/PPF-3,7SO15:PBD:phosphorescent dopants (70 nm)/Ba (4 nm)/Al (150 nm), where poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) was used as the hole-transporting layer (HTL), and 2-(4-biphenylyl)-5-(4-tert-butylpheny1)-1,3,4-oxadiazole (PBD) was used as the electron-transporting material. Since PPF-3,7SO15 has the highest occupied molecular orbital (HOMO) level at 6.0 eV, a thin layer of PVK was incorporated into the top of the PEDOT:PSS as the hole-injection layer (HIL). Afterwards, the PVK layer was annealed at 120 °C in nitrogen atmosphere for 10 min. The emitting layer containing an appropriate weight ratio of PPF-3,7SO15, PBD, and phosphorescent dopants was spin coated from dimethylbenzene solution, with a thickness of 70 nm determined by a profiler. The spin-cast active layer was annealed 80 °C for 20 min atop a hotplate. Finally, the cathode, comprising two thin layers of barium (4 nm) and aluminum (150 nm), were thermally deposited with a shadow mask at a base pressure of 3×10^{-4} Pa. The weight ratio of PPF-3,7SO15 and PBD was fixed at 70:30, while the concentrations of Ir(mppy)$_3$ and Ir(piq) varied. The fabrication process and the measurement have been described in Ref. [15].

3. Results and discussion

For the red devices and green devices, the best device performances are achieved with doping concentrations of 4 wt% for Ir(piq) (device A) and 2 wt% for Ir(mppy)$_3$ (device B) to the PPF-3,7SO15 and PBD matrix respectively. The maximal luminous efficiencies of devices A and B reach 7.4 cd·A^{-1} and 27.4 cd·A^{-1} respectively, while the maximal luminances of the red device and the green device are observed to be 7310 cd·m^{-2} and 33945 cd·m^{-2} respectively (Fig. 4). Figure 2 shows luminance–voltage (L–V) characteristics for the devices, respectively, with 0.2%, 1%, 2%, and 4% of Ir(piq) and Ir(mppy)$_3$ concentrations by weight. The operating voltages increase monotonically as the Ir(piq) and Ir(mppy)$_3$ concentrations increase. This phenomenon can be explained by the direct charged carrier trap effect.[20] From Fig. 1, we can see that the HOMOs of Ir(piq) and Ir(mppy)$_3$ are both above those of PPF-3,7SO15. Because of the very high concentrations of Ir(piq) and Ir(mppy)$_3$, we believe that the direct hole trapping is more likely to happen when guest dopants are introduced. The increase in the operating voltage with increasing concentration is the evidence for hole trapping in the doping system.

The fact that PPF-3,7SO15 is not only an efficient blue emitter but also a good host for red and the green phosphors makes it suitable for both host material and blue emitter for white PLEDs. Herein, we have fabricated the white devices based on PPF-3,7SO15 serving as host doped with Ir(piq) and Ir(mppy)$_3$ blends. When the weight ratio of PPF-3,7SO15:PBD:Ir(mppy)$_3$:Ir(piq)

is 70:30:0.15:0.16 (device C), a nearly pure white emission with CIE coordinates of (0.35, 0.38) and an excellent colour rendering index (CRI) of 83 is achieved at 12 mA·cm^{-2} (Fig. 3). Spectrum stability is very important for practical lighting applications. Therefore, we have studied the emission colour stabilities at different current densities and under constant current stress with an initial luminance of about 1000 cd·m^{-2}.

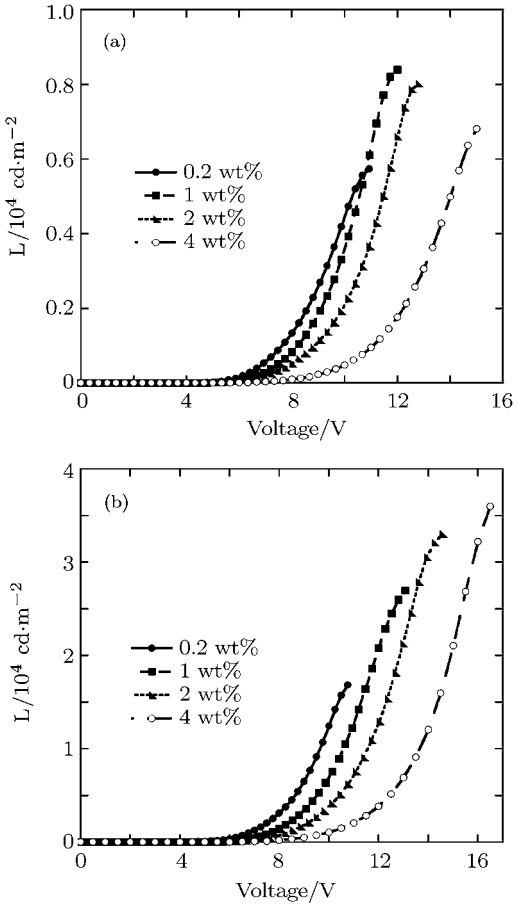


Fig. 2. Luminance–voltage (L–V) characteristics for the devices with different concentrations of (a) Ir(piq) and (b) Ir(mppy)$_3$.

As shown in Fig. 3, there is no obvious change in the electroluminescent (EL) spectrum with variation of the operating time up to 3 h. In most cases, the emitting colour is usually blueshifted at higher luminance or after long operation stress. Dopants and guests each with a smaller energy gap than that of the polymer host can trap charge carriers that will return to the host under high applied voltage or continuous stress, resulting in a shift of the exciton region and the blueshift emitting colour.[19] As a result of the low guest concentration in the obtained white device, blueshift is not obvious at higher luminance or after operation stress.

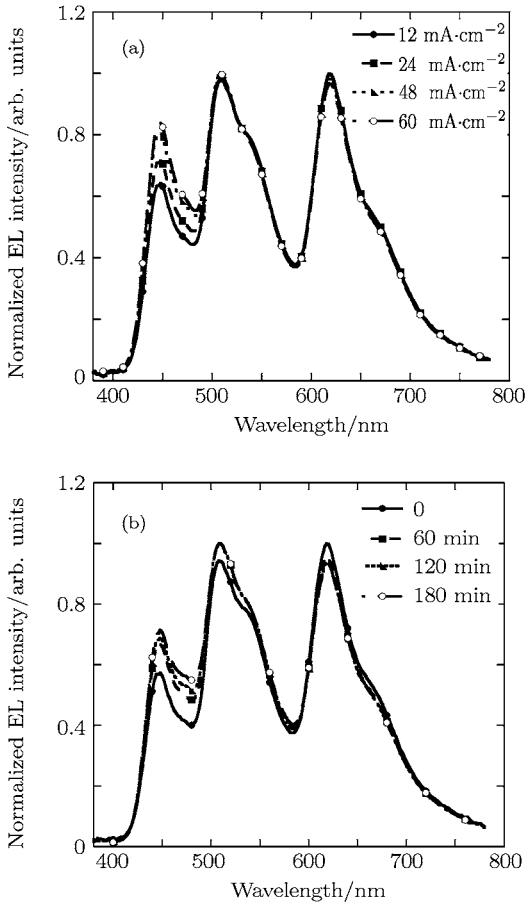


Fig. 3. EL spectra of device C at different current densities (a) and at an initial luminance of about 1000 cd·m^{-2} (b).

Figure 4 displays a typical luminous efficiency–luminance–current density (LE–L–J) of devices A, B, and C. Owing to the low concentrations of Ir(piq) and Ir(mppy)$_3$, the turn-on voltage (V_T), which is defined as the voltage at a luminance of 1 cd·m^2, is only 3.6 V.

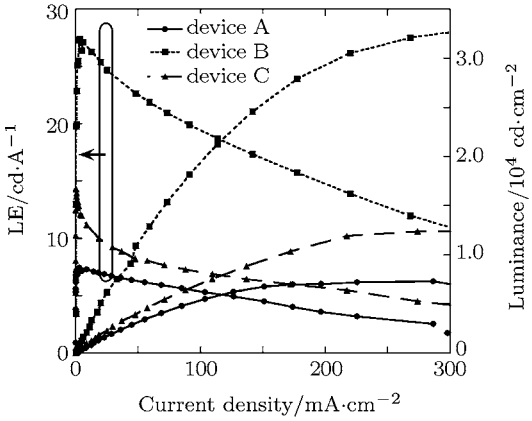


Fig. 4. Curves for luminous efficiency–luminance–current density (LE–L–J) of devices A, B, and C.

Because of the low operating voltage, the maximum PE of the white device achieves 10.1 lm·W^{-1}. The white device has a peak luminous efficiency of 14.4 cd·A^{-1} at a current density of 0.31 mA·cm^2 (4.7 V) with a luminance of 43 cd·cm^2

Figure 5 shows a representative atomic force microscopy (AFM) image of the blend film PPF-3,7SO15:PBD:Ir(piq) (70:30:4 wt) and PPF-3,7SO15:PBD:Ir(mppy)$_3$:Ir(piq) (70:30:0.15:0.16 wt). Very homogeneous films with root-mean-square (RMS) roughnesses of 0.730 nm and 0.602 nm are observed [Figs. 5(b) and 5(c)], which are comparable to that of the neat PPF-3,7SO15 film (0.612 nm) [Fig. 5(a)], indicating that there is no obvious phase separation in the blend; thus the dye has good compatibility with the PPF-3,7SO15 host polymer.

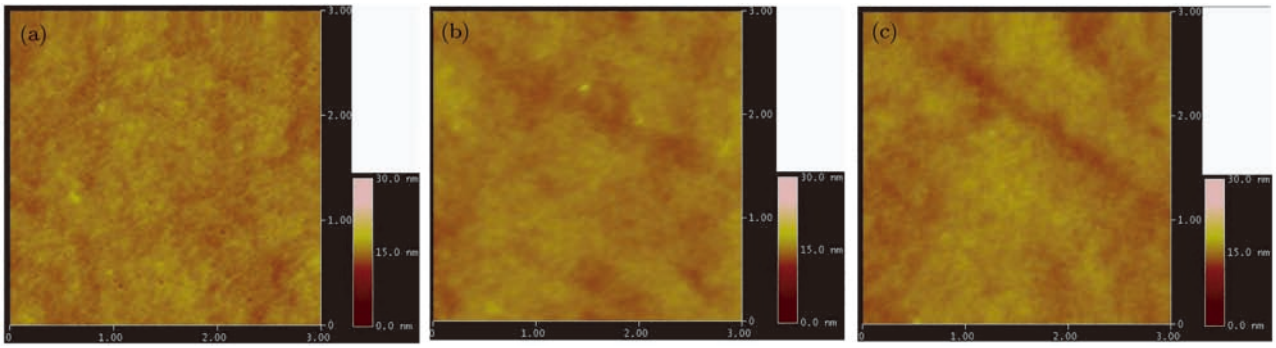


Fig. 5. AFM images of neat PPF-3,7SO15 film (a), blend film of PPF-3,7SO15:PBD:Ir(piq) (70:30:4 wt) (b), and blend film of PPF-3,7SO15:PBD:Ir(mppy)$_3$:Ir(piq) (70:30:0.15:0.16 wt) (c).

4. Conclusions

PPF-3,7SO15 as a good host material is doped with Ir(piq), Ir(mppy)$_3$ and their blends. Several highly efficient polymer phosphorescent light-emitting devices are fabricated. The operating voltages increase monotonically as Ir(piq) and Ir(mppy)$_3$ concentrations increase. The optimized white device has a $V_{\rm T}$ as low as 3.6 V, leading to a peak power efficiency of 10.1 lm·W^{-1}. The white PLEDs each display a high colour quality and an electroluminescent spectrum stability, which makes these devices promising candidates for lighting applications.

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