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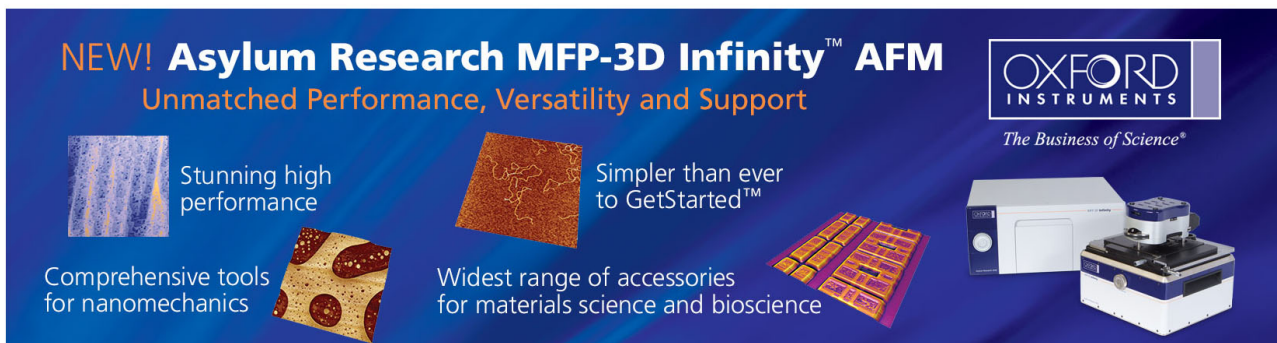Characteristics of an organic light-emitting diode utilizing a phosphorescent, shallow hole trap
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Single-layer triplet white polymer light-emitting diodes incorporating polymer oxides: Effect of charge trapping at phosphorescent dopants

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This paper describes the effects of charge trapping on the device performances of triplet polymer light-emitting diodes (PLEDs) after the cathode contact had been improved through the blending of poly(ethylene glycol) (PEG) into the active layer. The external quantum efficiency (EQE) was enhanced when the dopant tended to trap electrons. In contrast, we observed no EQE enhancement for the device featuring a hole-trapping dopant. Because PEG promoted electron injection, more electrons were trapped in the triplet molecules, thereby enhancing the probability of recombination. Finally, after incorporating PEG, we further achieved white PLEDs exhibiting both high EQE and high power efficiency. © 2009 American Institute of Physics. [DOI: 10.1063/1.3075066]

White organic/polymeric light-emitting diodes (OLEDs/PLEDs) are attracting increasing attention because of their promising applications in solid state lighting and flat-panel displays.[1,2] The advantages of using white OLEDs/PLEDs are their light weight, mechanical flexibility, and low-temperature fabrication. Furthermore, white PLEDs are readily fabricated using simple, low-cost processes, such as spin coating, ink-jet printing, screen printing, and roll-to-roll coating technologies.[3,4] One approach toward the realization of white OLEDs/PLEDs is the use of various singlet dopants having different emission colors.[5] Several devices exhibiting high quantum efficiencies have been developed by harvesting triplet excitons through doping with phosphorescent dyes.[6–9] Although the quantum efficiencies of such doped devices are improved, charge trapping at the dopants usually requires a higher operating voltage[10,11] and leads to a lower power efficiency. As a result, the dopant approach cannot improve the device power efficiency, which is a more practical factor for lighting applications, as much as it improves the quantum efficiency.

Recently, several reports indicated that device performance can be improved substantially by placing a thin layer of polymer oxide (surfactant), such as poly(ethylene glycol) (PEG), on the cathode interface,[12–14] or by blending such materials into the active layer of devices.[15,16] This enhanced device performance is attributed to the chemical interaction between PEG and the Al cathode decreasing the electron injection barrier and contact resistance.[12–16] In this study, we applied this method to achieve efficient phosphorescent PLEDs. We obtained lower operating voltages and higher power efficiencies after blending PEG into the electroluminescent (EL) layer. In addition we developed a white-emitting device after simultaneously doping sky blue and red triplet dopants. More importantly, we observed different enhancement mechanisms, which we attribute to charge trapping phenomena, for devices emitting different colors.

Figure 1 displays the energy levels of the chemicals and the work functions of the electrode materials we used

in this study.[17–22] The PLEDs were prepared on pre-cleaned indium tin oxide -coated glass substrates. Poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) was first spin coated onto the substrates and then baked at 120 °C. The components of the EL layer, namely, poly(vinylcarbazole) (PVK), 1,3-bis[(4-*tert*-butylphenyl)-1,3,4-oxidiazolyl]phenylene (OXD-7),[23] and phosphorescent dopants, were dissolved in 1,2-dichlorobenzene and spin coated on top of the PEDOT:PSS layer; the system was then annealed at 100 °C for 15 min. The triplet dopants were iridium bis[2-(4,6-difluorophenyl) pyridinato-N,C$^{2'}$] picolinate (FIrpic, blue emission) and iridium bis[2-(2'-benzothienyl)pyridinato-N,C$^{3'}$]acetylacetonate [Btp$_2$Ir(acac), red emission].[24] For the preparation of devices containing PEG, the polymer was blended at 10% into the EL layer. The weight ratio of the PVK, OXD-7, triplet dopant, and PEG components of the EL layer was 100:60:10:10. Finally, the cathode, comprising of calcium (Ca: 50 nm) and aluminum (Al: 100 nm), was thermally deposited at a base pressure of ca. 1×10^{-6} torr. The control devices were prepared identically, except that they did not contain PEG. Moreover, these active layers of the devices prepared with and without 10 wt % PEG have the almost identical thickness (about 65 nm), which is confirmed by using Alpha stepper. The electri-
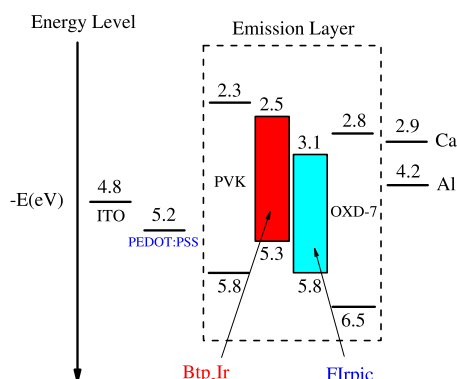

FIG. 1. (Color online) Energy levels and work functions of the chemicals and electrode materials used in this study.

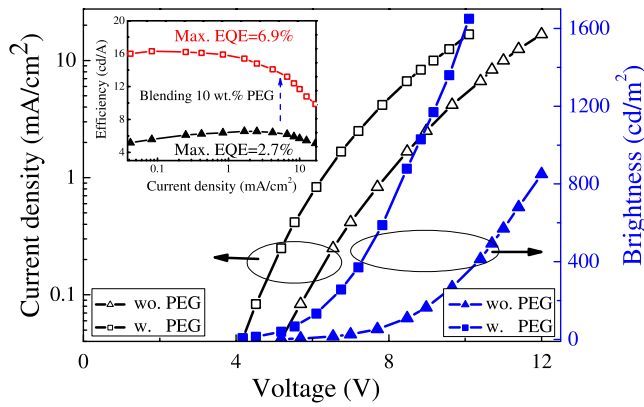a)Author to whom correspondence should be addressed. Electronic mail: fcchen@mail.nctu.edu.tw.

FIG. 2. (Color online) J-B-V curves of the sky-blue phosphorescent PLEDs prepared with and without the addition of PEG. The inset displays plots of the L_E in the presence and absence of PEG.

FIG. 3. (Color online) J-B-V characteristics of red phosphorescent PLEDs prepared with and without the addition of PEG. The inset displays plots of the L_E in the presence and absence of PEG.

cal characteristics were measured using a Keithley 2400 source measure unit; the brightness and the EL spectra were recorded using a PR650 spectrascan colorimeter.

Figure 2 displays the current density-brightness-voltage (J-B-V) curves of the blue phosphorescent PLEDs prepared with and without PEG in the EL layer. The turn-on voltage (V_T), defined for a brightness of 0.1 cd/m^2, was 4.1 V for the control device. The peak luminescence efficiency (L_E) was 6.6 cd/A, corresponding to an external quantum efficiency (EQE) of 2.7% (see the inset to Fig. 2). On the other hand, after the addition of PEG into the EL layer, the value of V_T decreased to 3.3 V and the peak L_E increased to 16.3 cd/A, corresponding to an EQE of 6.9%. The lower value of V_T was probably due to the presence of PEG resulting in a lower injection barrier at the cathode.[16] On the other hand, from the energy levels in Fig. 1, we deduce that FIrpic prefers to trap electrons, rather than holes.[22] Therefore, whereas PEG promoted electron injection, more electrons were trapped in the FIrpic moieties, enhancing the probability of recombination and, therefore, the EQE. In short, the introduction of PEG into the blue device resulted in lower turn-on and operating voltages and a higher EQE. As a result, the power efficiency was significantly enhanced—approximately fourfold (from 3.14 to 12.04 lm/W). This blue device based on single-layer structure exhibits one of the best power efficiencies.

For the PLEDs doped with $Btp_2Ir(acac)$, we observed different device behaviors. Figure 3 displays the J-B-V characteristics of the red devices prepared with and without PEG. The value of V_T of the device with incorporating 10 wt % PEG was 4.3 V, considerably lower than that of the control device (5.6 V). In addition, the PEG device had a lower operating voltage (8.7 V) than the control one (11.6 V) at a brightness of 100 cd/m^2. Unlike the blue devices, however, the peak L_E of the PEG device was 2.4 cd/A, which was comparable to that of the control device. This different behavior probably resulted from the fact that $Btp_2Ir(acac)$ favors hole trapping (Fig. 1), i.e., the improved electron injection occurring after the addition of PEG would not affect the charge balance significantly. In other words, the presence of PEG reduced the contact resistance and the electron injection barrier between the active layer and the cathode, thereby lowering the operating voltage. Note, however, that the power conversion efficiency was still improved (from 1.1 to 1.5 lm/W) because of the lower driving voltage.
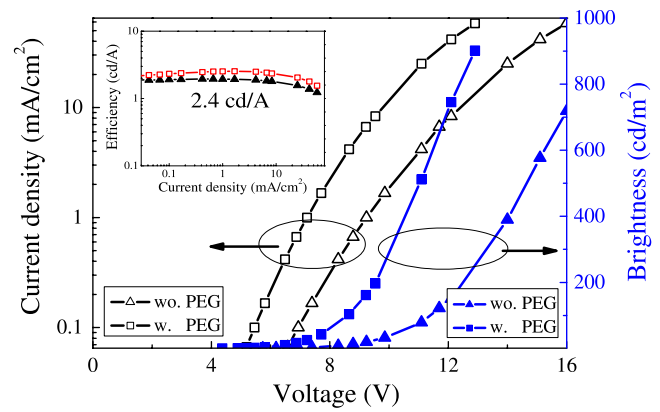
Finally, we fabricated white PLEDs using these two triplet complexes at various dopant ratios. The EL spectra of the white PLEDs were strongly influenced by the dopant concentrations. For the device prepared without PEG, we achieved a pure white emission having Commission Internationale de L'Eclairage (CIE) coordinates of (0.33,0.37) when the FIrpic-to-$Btp_2Ir(acac)$ dopant ratio was 10:0.50 [Fig. 4(a)]. After the addition of PEG, the white PLEDs exhibited different emission patterns in which the intensity of the blue emission was strengthened [Fig. 4(a)]. Because the very high concentration of FIrpic, we believed that the higher possibility of direct charge trapping in FIrpic dopants happened. On the other hand, the red emission should mainly come from the energy transfer process due to the low concentration of $Btp_2Ir(acac)$. Therefore, the change of the energy transfer rate resulted in different emission patterns. To achieve a
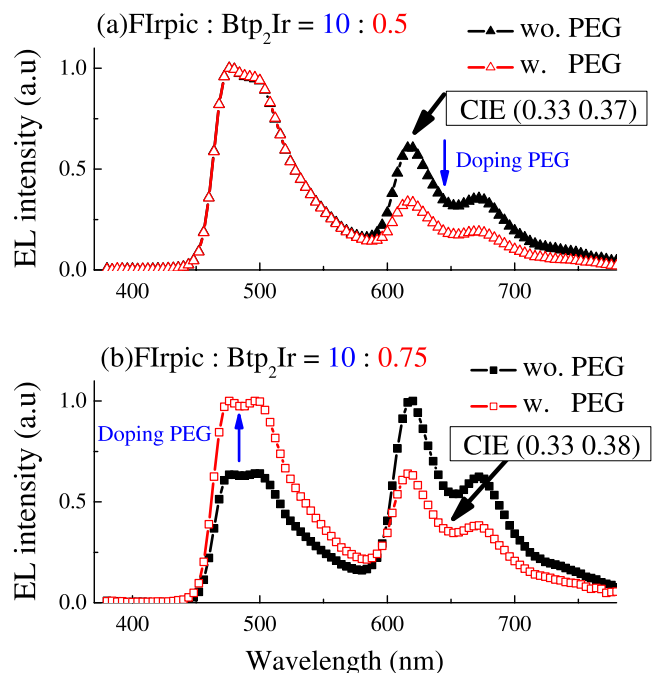

FIG. 4. (Color online) EL spectra of the white PLEDs prepared with and without 10% PEG, observed at a fixed current density of 8.33 mA/cm^2. Dopant weight ratios: (a) FIrpic:$Btp_2Ir(acac) = 10:0.5$ and (b) FIrpic:$Btp_2Ir(acac) = 10:0.75$. (Operating voltage and brightness in each spectrum: ▲, 9.45 V, 317 cd/m^2; △, 9.02 V, 593 cd/m^2; ■, 9.6 V, 280 cd/m^2; □, 9.19 V, 566 cd/m^2.)
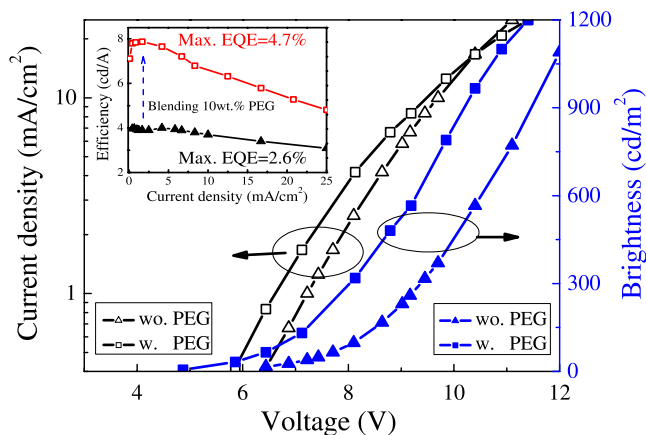
FIG. 5. (Color online) J-B-V curves of the white PLEDs prepared with and without the addition of PEG. The inset displays plots of the L_E of the white devices in the presence and absence of PEG. The FIrpic-to-Btp$_2$Ir(acac) weight ratios of the dopants were 10:0.75 and 10:0.50 for the devices prepared with and without PEG, respectively.

high power efficiency. We suspect that the method presented herein will be a significant one not only for the production of full-color OLED displays but also for the future lighting applications.

white color, we increased the red dopant concentration to an FIrpic-to-Btp$_2$Ir(acac) ratio of 10:0.75; a white emission having a CIE coordinates of (0.33,0.38) was obtained for this PEG-blended device [Fig. 4(b)].

Figure 5 displays the electrical characteristics of the white devices prepared with and without 10% PEG. The white PLEDs incorporating 10% PEG exhibited better performance relative to that of the control device. The peak L_E increased from 4.1 to 7.9 cd/A, corresponding to an EQE of 4.7%. Because of the lower operating voltage and the higher EQE obtained after blending PEG into the EL layer, the power efficiency improved once more from 1.94 to 4.60 lm/W.

In summary, we developed high-performance blue, red, and white triplet PLEDs incorporating a polymer surfactant, PEG, as an additive in the EL layer. We observed that the presence of PEG had different effects on performance of these three devices because of the hole and electron trapping effects of the Ir-based red and blue dopants, respectively. When the triplet dopant in the device tended to trap electrons, the presence of PEG led to a profound enhancement of the device performance. Because of the simple (single-layer) device structure, this approach allows the ready preparation of phosphorescent PLEDs exhibiting both high EQE and

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