

## Efficient white-light-emitting diodes based on poly( N -vinylcarbazole) doped with blue fluorescent and orange phosphorescent materials

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# Efficient white-light-emitting diodes based on poly(*N*-vinylcarbazole) doped with blue fluorescent and orange phosphorescent materials

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We have fabricated polymer white-light-emitting devices possessing a single emitting layer containing a hole-transporting host polymer, poly(*N*-vinylcarbazole), and an electron-transporting auxiliary, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, doped with a blue-light-emitting amino-substituted distyrylarylene fluorescent dye and an orange-light-emitting osmium phosphor. The doubly doped device exhibited an intense white emission having Commission Internationale de l'Éclairage coordinates of (0.33, 0.34), a high external quantum efficiency of 6.12% (13.2 cd/A), and a maximum brightness of 11 306 cd/m<sup>2</sup>. The color coordinates remained unchanged over a range of operating voltages, even at luminance as high as  $1 \times 10^4$  cd/m<sup>2</sup>. © 2006 American Institute of Physics. [DOI: 10.1063/1.2214141]

White organic light-emitting diodes (WOLEDs) have attracted considerable attention because of their potential applications in solid-state lighting and in back panel lighting for liquid crystal displays.<sup>1,2</sup> Among these devices, white OLEDs based on polymers (PLEDs) are of particular interest because they can be fabricated through spin casting—a potentially less expensive process than high-vacuum deposition,<sup>3–5</sup> which is used commonly for small molecules. Various approaches toward realizing white PLEDs have been described.<sup>6–12</sup> Single emissive layers of dye-doped polymers can be tailored, through suitable control of the doping level, to generate a composed white emission.<sup>6–9</sup> This use of single-layer polymer blends results in devices having simple structures and, therefore, it is an attractive option for low-cost, large-area fabrication.

Because they can harvest both singlet and triplet excitons, electroluminescent (EL) devices based on phosphorescent dyes often exhibit higher quantum efficiencies than those based on fluorescent dyes. Indeed, typical electrophosphorescent devices were prepared through doping of iridium complexes into polymeric hosts such as poly(*N*-vinylcarbazole) (PVK).<sup>13</sup> Although many green- and red-emitting phosphorescent materials have been synthesized,<sup>14,15</sup> authentic blue-emitting phosphors for OLEDs are notably rare; furthermore, blue-emitting phosphors demand a host material possessing a wide band gap to prevent backward energy transfer from the dopant to the host, thereby creating a hurdle for the design of white PLEDs.<sup>16</sup> On the other hand, the combined use of blue fluorescent and orange phosphorescent dyes may provide a suitable solution to these problems and affording white PLEDs with high efficiency and excellent stability.

In this letter, we report the fabrication of white PLEDs through the doping of blue fluorescent and orange phosphorescent dyes into a PVK host polymer blended with 30 wt % of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD),<sup>13</sup> for which PVK has a reasonable film-forming abil-

ity, a high glass-transition temperature, a wide energy gap, and a high hole mobility.<sup>17</sup> Moreover, 4,4'-bis[2-{4-(*N,N*-diphenylamino)phenyl}vinyl]biphenyl (DPAVBi) was selected because of its intense blue fluorescence and impressive performance when applied to OLEDs.<sup>18</sup> In addition, we employed the osmium complex [Os(bpftz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>] [Os(bpftz), where bpftz is 3-trifluoromethyl-5-(4-*tert*-butyl-2-pyridyl)triazolate] as the complementary phosphorescent dye. This triazolate based complex Os(bpftz) showed intense orange luminescence in degassed CH<sub>2</sub>Cl<sub>2</sub> solution ( $\lambda_{\max}$  = 603 nm) and had an exceedingly short emission lifetime ( $\tau$  = 972 ns).<sup>19</sup> Because triplet excitons tend to relax more slowly and are easily affected by the triplet-triplet annihilation, phosphors that exhibit short triplet lifetimes are most desired to minimize these problems. Furthermore, for their application to light-emitting devices, it is imperative that all materials should be of ultrahigh chemical purity. Both of our selected emitting dyes, DPAVBi and Os(bpftz), can be purified readily through a process of recrystallization followed by sublimation. They disperse well into the PVK host, forming good films when spin coated, as is evident from our atomic force microscopy (AFM) measurements (*vide infra*).

Figure 1 illustrates the structural drawings of relevant materials that were used in this study. The device configura-

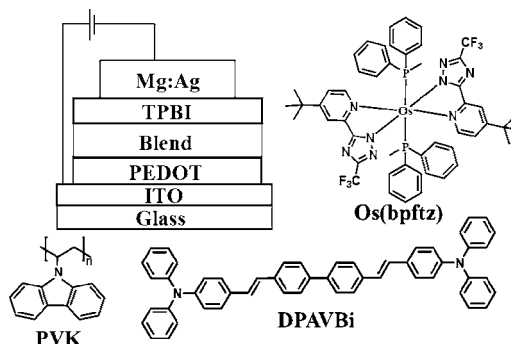


FIG. 1. Chemical structures of PVK, DPAVBi, and Os(bpftz) and a schematic illustration of the device configuration used in this study.

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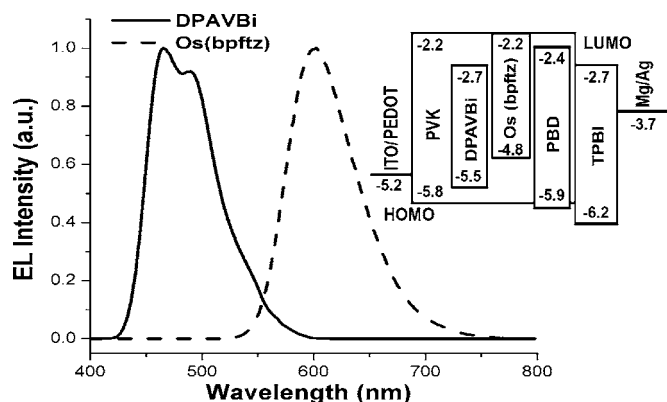


FIG. 2. EL spectra of devices formed using DPAVBi (1 mol %) or Os(bpftz) (0.1 mol %): PVK-PBD as the emitting layer. Inset: energy level diagram for the devices having the configuration ITO/PEDOT/Blend/TPBI/Mg:Ag.

tion consists of indium tin oxide (ITO)/poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) (35 nm)/polymer blend (50–70 nm)/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) (30 nm)/Mg:Ag (100 nm)/Ag (100 nm); the fabrication and characterization of this white-light EL device were conducted using procedures similar to those reported in literature.<sup>20</sup> Figure 2 displays EL spectra of devices fabricated using DPAVBi and Os(bpftz)-doped PVK-PBD as the emitting layers, for which the doping concentrations were 1.0 and 0.1 mol % (relative to PVK monomer units), respectively. The EL spectrum of the DPAVBi-doped device exhibited a maximum intensity at 465 nm that is associated with blue emission from the DPAVBi dopant; its maximum external quantum efficiency ( $\eta_{\text{ext}}$ ) was 2.29% (3.90 cd/A). For the Os(bpftz)-doped device, we observed an orange emission (peak maximum at 602 nm) with the  $\eta_{\text{ext}}$  data being as high as 18.7% (45.0 cd/A).

Figure 3 presents the photoluminescence (PL) and EL spectra of the white-light-emitting device incorporating an emitting layer comprising 1 mol % DPAVBi and 0.04 mol % Os(bpftz) in the PVK-PBD host. In the PL spectrum, the efficient energy transfer from the excited host to dyes results in a combination of blue emission from DPAVBi and orange emission from Os(bpftz), respectively. The intensity of the

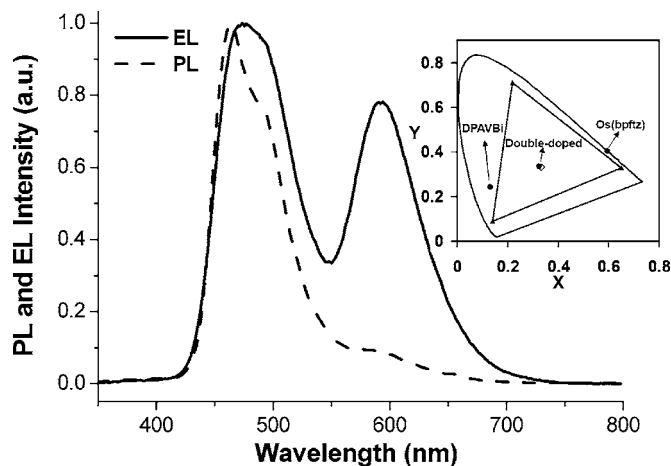


FIG. 3. PL (excited at 300 nm) and EL spectra of the doubly doped device at an applied voltage of 9 V. Inset: CIE color coordinates of the EL emissions from the DPAVBi-doped, Os(bpftz)-doped, and doubly doped devices.

former overwhelms that of the latter, owing to the remarkably low doping concentration of Os(bpftz). In contrast, the EL spectrum of this blend exhibits two well balanced components of blue and orange emissions. We attribute the dramatic differences observed in the PL and EL spectra to a charge trapping effect.<sup>21,22</sup> According to the energy level diagram (inset of Fig. 2), Os(bpftz) can serve as an effective site for direct charge trapping, giving orange emission from the triplet state of Os(bpftz), which is the main factor responsible for the observed EL. Consequently, the EL spectrum displays a dual emission comprising both blue fluorescence from DPAVBi and orange phosphorescence from Os(bpftz), resulting in an apparent white color. The inset of Fig. 3 displays the Commission Internationale de l'Eclairage (CIE) coordinates of the blended device together with those of the blue- (DPAVBi doped) and orange-emitting [Os(bpftz) doped] devices. According to the CIE diagram, the emissions of the blue- and orange-emitting devices are located at (0.13, 0.24) and (0.58, 0.41), respectively, while that of the doubly doped device occurs precisely at the central white region (0.33, 0.34). It is noted that the blue component in the EL spectrum is slightly redshifted and broadened when compared with the PL spectrum. This may be due to the spectral overlap of each individual blue and orange emissions. In addition, the exciplex formation in the emitting layer may also induce the bathochromic shift in emission profiles.<sup>23,24</sup>

The main drawback for the display or illumination applications of white PLEDs formed using dye-doped polymers as an active layer is their color instability. Gratifyingly, the CIE coordinates of this white-light-emitting device change only slightly from (0.33, 0.34) at 9.0 V (2.95 mA/cm<sup>2</sup>, 366 cd/m<sup>2</sup>) to (0.33, 0.32) at 15.0 V (125 mA/cm<sup>2</sup>, 9124 cd/m<sup>2</sup>), i.e., these coordinates are quite insensitive to current density and brightness, and maintain very close to the pure white CIE coordinates of (0.33, 0.33). This remarkable color stability is attributed to the short triplet excited lifetime of Os(bpftz) (ca. 1.0  $\mu$ s), which may prevent saturation of the lightly doped orange phosphor and suppress unwanted triplet-triplet annihilation under a high excitation density. Another possible factor of color instability is the phase separation in the polymer blend.<sup>12,25</sup> Remarkably, the AFM image indicates that no phase separation occurred in our doubly doped PVK film, for which the root-mean-square surface roughnesses of the PVK-PBD blend and doubly doped films were 0.23 and 0.29 nm, respectively. These AFM data confirm the existence of very little, if any, phase separation or dye aggregation occurred within the blended PVK system; therefore, our white PLED exhibits high color stability.

Figure 4 displays a comparison between the device characteristics of the blue and white PLEDs. The current density-voltage (*I*-*V*) characteristics shifted to higher voltages after introducing Os(bpftz) into the blue-emitting (DPAVBi doped) device [Fig. 4(a)] because Os(bpftz) provides effective trapping sites for holes when doped into PVK. This result is consistent with the direct charge trapping mechanism that we proposed earlier. Figure 4(b) displays the luminance-voltage (*L*-*V*) characteristics of the blue and white PLEDs, giving luminances of 5451 and 11 306 cd/m<sup>2</sup> at 16 V, respectively. According to the plots of external quantum efficiency and luminance efficiency (*LE*) versus current density (Fig. 5), the maximum values of  $\eta_{\text{ext}}$  and *LE* of the blue-emitting device were 2.29% and 3.90 cd/A, respectively. The introduction of the orange phosphor Os(bpftz) into the

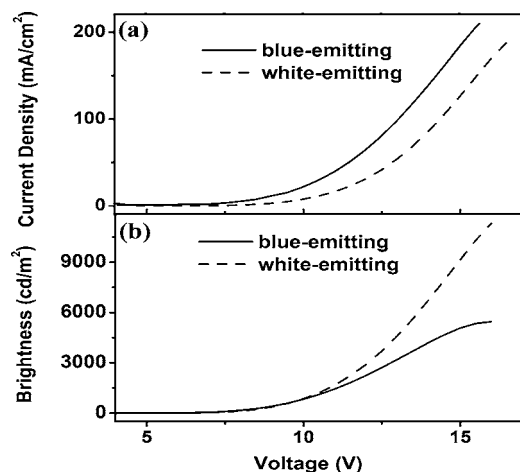


FIG. 4. Plots of (a) current density and (b) luminance as functions of the applied voltage for both the blue and white PLEDs.

blue-light-emitting (DPAVBi doped) device resulted in the white PLED with further improved efficiency; the maximum values of  $\eta_{\text{ext}}$  and  $LE$  are as high as 6.12% and 13.2 cd/A at a current density of 0.92 mA/cm<sup>2</sup> and a brightness of 122 cd/m<sup>2</sup>, respectively. When we increased the luminance of our white PLED up to  $1 \times 10^3$  cd/m<sup>2</sup> (at ca. 11 mA/cm<sup>2</sup>), the corresponding EL efficiency remained above 11 cd/A. The performance of this white-light-emitting device is among the best reported to date for WOLEDs based on a single emitting layer of polymer blends.<sup>6,7,11,25</sup>

In summary, we have fabricated a highly efficient, color-stable white-electrophosphorescent device through incorporation of a blue fluorescent dye and an orange osmium phosphor into a nonconjugated polymer blend (PVK-PBD). This doubly doped device exhibited a pure white-light emission having CIE coordinates of (0.33, 0.34), a high external quantum efficiency of 6.12% (13.2 cd/A), and a maximum

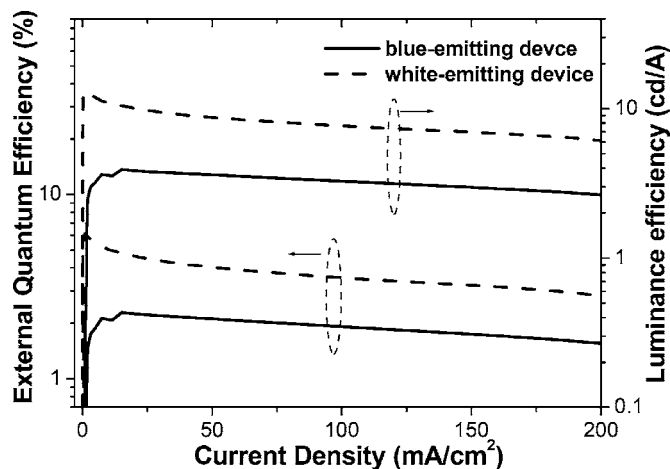


FIG. 5. Plots of external quantum efficiency and luminance efficiency as functions of current density for both the blue and white PLEDs.

brightness of 11 306 cd/m<sup>2</sup>. Even when the brightness was increased up to  $1 \times 10^4$  cd/m<sup>2</sup>, we observed only a slight shifting in the CIE coordinates from (0.33, 0.34) to (0.33, 0.32). The quantum efficiency of this white PLED is higher than those of previously reported devices containing dual phosphorescent dopants.<sup>6</sup> Moreover, our present approach should be valuable for solid-state lighting applications because of the simple device architecture and the promise of low-cost manufacturability.

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