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Description	

## Organic light-emitting devices with saturated red emission using 6,13-diphenylpentacene

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Organic electroluminescent devices with saturated red emission were developed using 6,13-diphenylpentacene (DPP) doped into tris(8-hydroxyquinolato) aluminum III ( $\text{Alq}_3$ ). DPP exhibits a narrow emission spectrum giving rise to a saturated red peak, centered around 625 nm, with excellent chromaticity coordinates ( $x=0.63$  and  $y=0.34$ ) in accordance with the Commission Internationale de l'Eclairage. An absolute photoluminescence (PL) quantum yield ( $\phi_{\text{PL}}$ ) of  $\sim 30\%$  was measured for a composite film of 0.55 mol % of DPP doped into  $\text{Alq}_3$ . An electroluminescence (EL) quantum efficiency of 1.3% at 100  $\text{A/m}^2$ , close to the estimated theoretical limit (1.5%), was measured for an unoptimized device structure that consists of an active emissive layer sandwiched between hole- and electron-transport layers. In addition, the EL quantum efficiency is constant or stable over a wide range of current densities (1–1000  $\text{A/m}^2$ ) or luminance values (1–1000  $\text{cd/m}^2$ ). [DOI: 10.1063/1.1362259]

Displays based on organic light-emitting devices (OLEDs) have become very promising competitors and potential replacements of liquid-crystal displays (LCDs) due to their wide viewing angle, bright self-emission, and ease of color tunability and processability. Although efficient blue and green OLEDs have been demonstrated,<sup>1–3</sup> there has been a lack of devices that exhibit both saturated red emission and high, stable electroluminescence (EL) quantum efficiency over a wide range of current densities. Many laser dyes have been utilized as emitting centers.<sup>2,4–10</sup> However, most of these dyes exhibit broad, orange-red emission and many lack photochemical stability. Using an additional dopant which acts as an intermediary for more efficient energy transfer from host to emitting guest molecules can lead to better color chromaticity and improved device performance.<sup>8,9</sup> Sharp red emission was demonstrated using rare-earth complexes, however, devices based on them yielded poor EL quantum efficiency.<sup>11–15</sup> Saturated red EL was achieved using phosphorescent porphines such as tetraphenylporphine (TPP), tetraphenylchlorin (TPC), and derivatives of platinum (II) porphines (PtOEP, PtOx, and PtDPP).<sup>16–20</sup> The use of phosphorescent emitters increases the theoretical limit of the EL quantum efficiency by taking advantage of the higher production ratio of triplet to singlet excitons (3:1). PtOEP and PtOx-based devices show improved quantum efficiencies of 2.2% and 1.1%, respectively, at 100  $\text{A/m}^2$ .<sup>19,20</sup> These enhanced EL quantum efficiencies decline quite rapidly with increasing current densities due to triplet–triplet exciton annihilation. A similar problem was observed when a phosphorescent sensitizer was used to excite a highly fluorescent dye.<sup>21</sup> This is a real disadvantage, especially for passive matrix displays which would be required to operate at high current densities in order to achieve the desired brightness for certain applications. We have synthesized 6,13-

diphenylpentacene (DPP), a fluorescent dye, which exhibits a narrow emission in the visible red region with excellent color chromaticity coordinates ( $x=0.63$  and  $y=0.34$ ). DPP shows a strong absorption in the 500–620 nm region, which overlaps well with the emission spectrum of the host used in the present study, tris(8-hydroxyquinolato) aluminum III ( $\text{Alq}_3$ ). This spectral overlap is necessary for efficient energy transfer from the host to the guest molecules. Devices based on an emitting layer that consists of 0.55 mol % DPP doped into  $\text{Alq}_3$ , yielded an EL quantum efficiency of 1.3%, which is stable and does not decrease over a wide current density range ( $<1\text{--}1000$   $\text{A/m}^2$ ).

Tris(8-hydroxyquinolato) aluminum III, obtained from TCI America, was used as both the host and electron transporter. *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), purchased from H.W. Sands Corp., was used as the hole transporter. The guest molecule, 6,13-diphenylpentacene, was synthesized<sup>22</sup> and characterized by elemental analysis,  $^1\text{H-NMR}$ , IR, absorption, and fluorescence spectroscopies. All materials were purified by vacuum train sublimation prior to use.

Precleaned glass substrates patterned with indium–tin–oxide (ITO) stripes, provided by Planar America (340 nm thick with a sheet resistance  $\leq 10$   $\Omega/\text{sq}$ ), were treated in an oxygen plasma prior to introduction to the vacuum deposition chamber. Organic layers were prepared by consecutive vapor deposition followed by a cocondensation of Mg and Ag vapors, which formed the layer of MgAg alloy used as the cathode. The active emitting layers of the devices were prepared by codeposition of the host and guest materials evaporated from separate resistive heating furnaces. A shadow mask forming metal stripes perpendicular to the ITO stripes was used during the metal deposition. The thickness of each of the layers was measured using a quartz-crystal microbalance.

The photoluminescence (PL) and EL spectra were measured inside a glovebox purged with dry nitrogen. The excitation laser beam (325 nm line of a He:Cd laser) was brought

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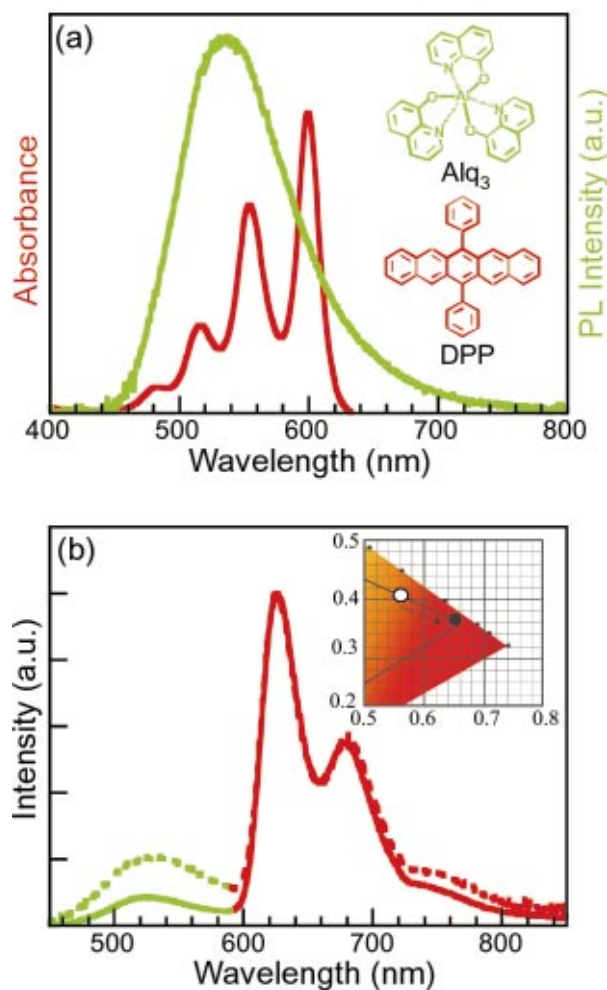


FIG. 1. (Color) Absorbance spectrum of DPP in a toluene solution (red) and the PL spectrum of an Alq<sub>3</sub> film (green). The structures of the materials are also shown. (b) PL (dashed) and EL (solid) spectra based on a 0.55 mol % DPP:Alq<sub>3</sub> film. The color gamut with CIE coordinates for red CRT phosphors and coordinates for the PL (open circle) and EL (filled circle) of 0.55 mol % DPP:Alq<sub>3</sub> emissive layers are shown in the inset (b).

into the glovebox through an optical fiber. The luminescence was collected and brought out through another optical fiber. The absolute PL quantum efficiency ( $\phi_{\text{PL}}$ ) of composite films of DPP doped into Alq<sub>3</sub> was measured using an integrating sphere.<sup>23</sup> Voltage–current–luminance measurements were performed with a Keithley 238 high-current-source measure unit and a Minolta LS110 luminance meter.<sup>24</sup>

Figure 1(a) shows the absorbance spectrum of DPP and the fluorescence of Alq<sub>3</sub>. Good spectral overlap is noted. The maximum  $\phi_{\text{PL}}$  of composite films of DPP and Alq<sub>3</sub> was found to be  $\sim 30\%$  (0.55 mol % DPP:Alq<sub>3</sub>). Doping at DPP concentrations  $>1$  mol % leads to a lowering of the  $\phi_{\text{PL}}$  due to self-quenching caused by aggregation. Figure 1(b) depicts the PL spectrum of a film that consists of 0.55 mol % DPP doped into Alq<sub>3</sub>. The EL spectrum of a device based on the same active emissive layer is shown for comparison. An emission peak centered at 625 nm, corresponding to the emission of DPP in solution, dominates both the PL and EL spectra signaling good energy transfer from host to guest. A small contribution from Alq<sub>3</sub> is observed in both spectra. The contribution of Alq<sub>3</sub> decreases as the concentration of DPP is increased from 0.26 to 1.2 mol % DPP (not shown).<sup>25</sup> At a given DPP concentration, the contribution of the host is

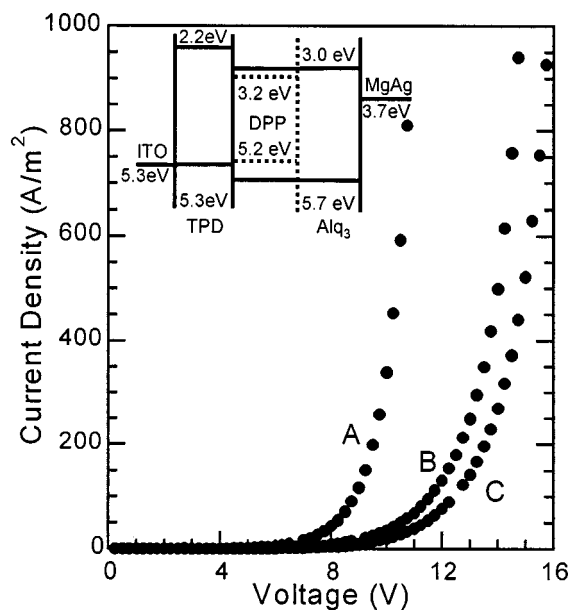


FIG. 2.  $J$ – $V$  characteristics of devices where the emitting layers consist of Alq<sub>3</sub> doped with increasing concentrations of DPP: (A) 0 mol %, (B) 0.55 mol %, and (C) 1.2 mol %. The inset shows the energy-level diagram for the neat organic films, ITO and MgAg, with the device structure used in this study.

always found to be larger in the PL than in the EL spectra, which has a strong effect on the color chromaticity coordinates. The reduction in the contribution of the host dramatically improves the purity of the emission color, with the color coordinates shifting from  $[(x=0.56, y=0.39); \text{PL}]$  to  $[(x=0.63, y=0.34); \text{EL}]$  [see the inset in Fig. 1(b)]. The reduction in the host contribution in the EL spectrum also suggests that energy transfer from the host to the guest molecules cannot be the only operative EL mechanism. Another possible mechanism may be direct carrier recombination<sup>26</sup> on DPP. Figure 2 shows the  $J$ – $V$  characteristics of three devices, where the current densities decrease as a function of increasing DPP concentration, suggesting that DPP acts as a carrier trap.<sup>27</sup> A comparison of the energy levels of DPP relative to those of Alq<sub>3</sub> (inset, Fig. 2) provides further insight into the role that DPP plays as a carrier trap. Ultraviolet photoemission spectroscopy (UPS) measurements were performed on neat films of DPP and Alq<sub>3</sub>. An ionization potential ( $I_p$ ) of 5.2 eV was determined for DPP. An electron affinity ( $E_a$ ) of 3.2 eV was estimated using the measured optical band gap ( $E_g=2.0$  eV), extrapolated from the absorbance spectrum of DPP. Comparing these energy levels to those of Alq<sub>3</sub> ( $I_p=5.7$  eV,  $E_a\sim 3.0$  eV based on  $E_g=2.7$  eV),<sup>28</sup> and assuming that Alq<sub>3</sub> and DPP have a common vacuum level and similar exciton binding energies, it is clear that DPP can act as a hole and possibly a shallow electron trap when doped into Alq<sub>3</sub>.

The maximum theoretical external EL quantum efficiency ( $\eta_{\text{EL}}$ ) of devices using the optimum dopant concentration has been estimated using  $\eta_{\text{EL}} = \alpha \gamma \eta_r \phi_{\text{PL}}$ ,<sup>29</sup> where  $\alpha$  is the light output coupling factor given by  $\alpha = 1/(2n^2)$  ( $n$  is the refractive index of the emissive medium;  $n=1.7$  for Alq<sub>3</sub><sup>30</sup>),  $\gamma$  is the probability of carrier recombination,  $\eta_r$  is the production efficiency of a singlet or triplet exciton, and  $\phi_{\text{PL}}$  is the absolute PL quantum yield of the emitter. Using

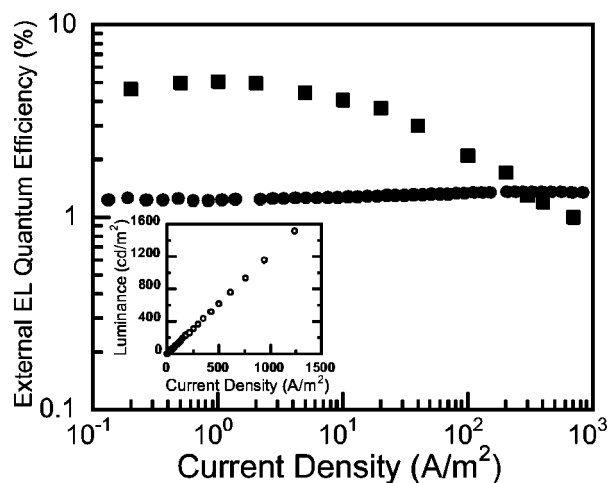


FIG. 3. External EL quantum efficiency as a function of current density for devices with an emissive layer containing 0.55 mol % DPP:Alq<sub>3</sub> (filled circles), and 6% PtOEP:CBP (filled squares). Luminance as a function of the current density for the 0.55 mol % DPP:Alq<sub>3</sub>-based device is shown in the inset.

the measured  $\phi_{\text{PL}} \sim 30\%$ , and assuming  $\alpha = 0.20$ ,  $\gamma = 1.0$ , and  $\eta_r = 0.25$ , a theoretical limit of  $\eta_{\text{EL}} = 1.5\%$  is estimated. The measured  $\eta_{\text{EL}}$  peaks at 1.4% (0.25 mol % DPP), decreases to 1.3% (0.55 mol % DPP), and drops below 1.0% as the DPP concentration increases from 0.8 to 1.2 mol %. The 0.55 mol % DPP:Alq<sub>3</sub> device showed a maximum luminance yield of 1.2 cd/A and a luminance power efficiency of 0.33 lm/W at 100 A/m<sup>2</sup>. The luminance as a function of current density for this device is shown in the inset of Fig. 3.

The external EL quantum efficiencies as a function of current density for devices based on 0.55 mol % DPP:Alq<sub>3</sub>, and the red phosphorescent emitter PtOEP (6%) doped into CBP,<sup>19</sup> are depicted in Fig. 3. A  $\eta_{\text{EL}} > 1.2\%$  is measured at low current densities for the device with the DPP-doped emitting layer. The  $\eta_{\text{EL}}$  increases slightly as a function of current density and reaches 1.3% at 100 A/m<sup>2</sup>, where it is maintained as the current density increases to 1000 A/m<sup>2</sup>. All of the devices based on DPP exhibit similar stability of  $\eta_{\text{EL}}$  over a wide range of current densities ( $< 1\text{--}1000$  A/m<sup>2</sup>). This is in contrast to what is observed in electrophosphorescent devices (see Fig. 3), where a very high  $\eta_{\text{EL}}$  occurs at low current densities or luminance values before a rapid decline takes place as the current density increases ( $< 1$  A/m<sup>2</sup>).<sup>19</sup> A high population of long-lived triplet states results in triplet-triplet exciton annihilation, which leads to the decline of the EL quantum efficiency of the electrophosphorescent devices at high current densities.<sup>31</sup>

In conclusion, we have prepared and spectroscopically characterized the fluorescent dye, 6,13-diphenylpentacene, and incorporated it as the red emitter in OLEDs. EL quantum efficiencies (1.3%–1.4%) close to the estimated theoretical limit (1.5%) were achieved and remained constant at high current densities. The combination of stable device efficiency over a wide range of current densities and a saturated red color, make DPP-based devices ideal for passive and active display applications. We are currently optimizing the device structure and developing pentacene derivatives with higher  $\phi_{\text{PL}}$ .

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