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## Efficient organic light-emitting devices with platinum-complex emissive layer

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We report efficient organic light-emitting devices having a platinum-complex emissive layer with the peak external quantum efficiency of 17.5% and power efficiency of 45 lm W<sup>-1</sup>. Variation in the device performance with platinum-complex layer thickness can be attributed to the interplay between carrier recombination and intermolecular interactions in the layer. Efficient white devices using double platinum-complex layers show the external quantum efficiency of 10%, the Commission Internationale d'Éclairage coordinates of (0.42, 0.41), and color rendering index of 84 at 1000 cd m<sup>-2</sup>. © 2011 American Institute of Physics. [doi:10.1063/1.3541447]

Due to their potential in flat panel display and solid-state lighting applications, organic light-emitting devices (OLEDs) have attracted broad attention since the early work of Tang and Van Slyke.<sup>1</sup> Doping with fluorescent<sup>2</sup> or phosphorescent<sup>3</sup> dye is widely practiced in device fabrication and is a crucial step for tuning emission color, improving efficiency, and prolonging the operating lifetime of the device. On the other hand, nondoped devices utilizing emissive materials with high solid state luminescence efficiency have been actively investigated.<sup>4,5</sup> Meanwhile, the use of dye layers (partial doping layers) instead of mixed host: guest emissive layers has been examined in monochromatic and white OLEDs.<sup>6-12</sup> Recently, Divayana and Sun<sup>8</sup> introduced an OLED structure consisting of a group of sequentially deposited host, and dopant films acting as the emissive layer. In this case, phosphorescent OLEDs with six layers of alternating 5 nm 4-4'-bis(9-carbazolyl)-2,2'-biphenyl and 1 nm fac-tris(2-phenylpyridyl)iridium (III) [Ir(ppy)<sub>3</sub>] showed the peak external quantum efficiency (EQE) of 8.8%. White emitting devices having a dye emissive layer were reported by Tsuji *et al.*,<sup>10</sup> where blue and orange emissions originated from 4,4'-bis[N-1-naphthyl-N-phenyl-amino]biphenyl (NPB) and 1 nm 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran layers, respectively. A maximum luminance of ca. 1000 cd m<sup>-2</sup> was demonstrated from such approach. Selection of an efficient blue emitter and optimization of the thickness and location of the dye layer improved luminous and power efficiencies (PE) of fluorescent white OLEDs to 8.1 cd A<sup>-1</sup> and 4.8 lm W<sup>-1</sup>, respectively.<sup>12</sup> Despite such advances, the efficiency of devices using dye emissive layers lags significantly behind that of OLEDs having host: guest emissive layers.<sup>13-15</sup> In this paper, we report efficient monochromatic (and white) OLEDs having single (double) platinum-complex emissive layer. Variation in the device performance with the platinum-complex layer thickness can be attributed to the interplay between carrier recom-

bination and intermolecular interactions in the layer. In contrast to what is commonly believed, these devices show similar or slightly faster reduction in the EQE with increased current density, compared with devices having a host: guest emissive layer.

The device fabrication and testing followed previously reported protocol.<sup>16</sup> Emissive layers were sandwiched between a 20 nm hole-transporting/electron-blocking 1,3-bis(*N*-carbazolyl)benzene (mCP) layer and 40 nm electron-transporting/hole-blocking 1,3-bis[4-*tert*-butylphenyl-1,3,4-oxadiazolyl]phenylene (OXD-7) layer. Poly[3,4-ethylenedioxythiophene] doped with poly[styrene-sulfonate] (PEDOT:PSS) and NPB functioned as the hole-injection and hole-transporting layers, respectively. Chemical structure of some materials is shown in Ref. 17. Indium-tin-oxide with sheet resistance ca. 20 Ω/□ and cesium fluoride/aluminum (CsF/Al) served as electrodes. Figure 1 shows the schematic energy diagram of devices. Values of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of organic materials, work function of the electrodes are cited based on published literature.<sup>15,16,18</sup> A noticeable mismatch between the LUMO level of mCP and HOMO level of OXD-7 and those of the platinum-complexes allows for the confinement of carrier re-

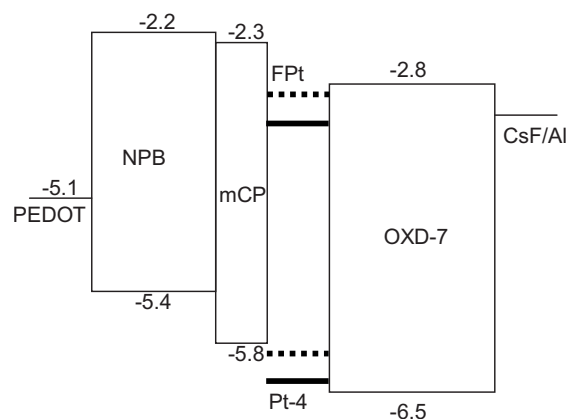


FIG. 1. Energy level diagram of layers used.

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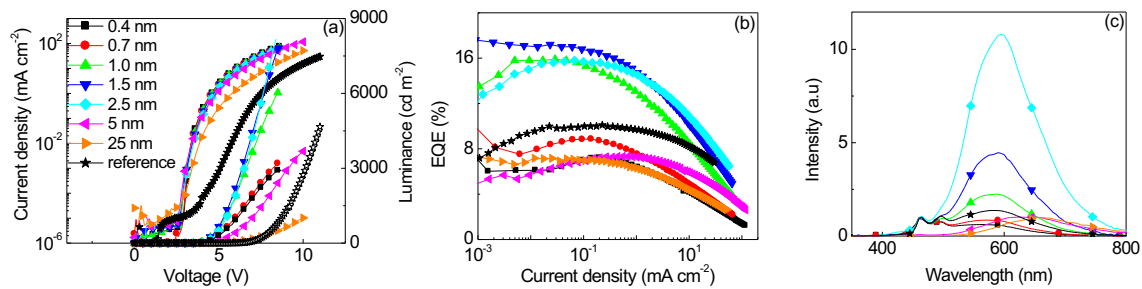


FIG. 2. (Color online) Performance of devices having different thickness FpT layer. (a) Current density-voltage-luminance characteristics, (b) EQE-current density properties, and (c) EL spectra of devices.

combination activity in the platinum-complex layer. In addition, the high triplet state energy of mCP and OXD layers minimizes possible quenching of excited states formed in the emissive layer.

OLEDs incorporating platinum-complexes such as platinum(II)[2-(4',6'-difluorophenyl)pyridinato-N,C<sup>2'</sup>)](2,4-pentanedionato) (FPt), which exhibited a pronounced excimer/aggregate emission in the electroluminescent (EL) spectra, were shown to have high device efficiency.<sup>19–22</sup> This observation suggests that excimer/aggregate formation in these platinum-complex solid films may not work as an effective nonradiative channel. Therefore, such platinum-complexes are particularly suitable to work as a dye emissive layer in light-emitting devices. Figure 2(a) shows current density-voltage-luminance characteristics of devices having FPt emissive layer with different thickness. While devices with a FPt layer thinner than 5 nm show similar current density-voltage properties, the operating voltage shifts to higher values with further increase in FPt layer thickness. Compared with the control mCP: 12% FPt device having identical carrier-transporting layers, the drive voltage of devices with a 25 nm FPt layer is reduced, which can be attributed to good carrier-transporting ability of FPt and elimination of possible carrier-trapping effect of FPt in mCP host. Figure 2(b) shows EQE-current density properties. The EQE of devices increases with increasing FPt layer thickness, reaching a maximum for FPt layer thickness of 1.5–2.5 nm, then decreases with further increase in FPt layer thickness. The peak EQE and PE of devices with a 1.5 nm FPt layer is 17.5% and 45 lm W<sup>-1</sup>, respectively. At the luminance of 1000 cd m<sup>-2</sup>, these efficiencies are 12.8% and 18.7 lm W<sup>-1</sup>, which compare favorably with those of the mCP: 12% FPt device (8.9% and 7.3 lm W<sup>-1</sup>).<sup>19</sup> Table I in Ref. 17 summarizes the device characteristics. The EL spectra of devices shown in Fig. 2(c) display high-energy structured monomer and redshift broad excimer/aggregate emission bands. The intensity of excimer/aggregate emission to that of monomer emission increases with FPt layer thickness, accompanied by a gradual redshift in excimer/aggregate emission band, indicating increased interactions among FPt molecules. The change of relative monomer and excimer/aggregate emission intensities with FPt layer thickness allows a wide-range manipulation of the Commission Internationale d'Éclairage (CIE) coordinates. The CIE coordinates of devices with a 0.4, 1.5, and 5 nm FPt layer are (0.31, 0.36), (0.46, 0.47), and (0.54, 0.41), respectively. Enhanced FPt intermolecular interactions reduce the EQE of devices with a thick FPt layer (>2.5 nm). Cocchi *et al.*<sup>21</sup> report a higher luminescence quantum yield of excimer/aggregate emission for

platinum (II)N<sup>^C^2^N</sup>-[1,3-di(4-methoxy-pyrid-2-yl)-4,6-difluorobenzene] chloride than that of monomer emission. Light-emitting devices based on neat platinum-complex emissive layers show slightly lower efficiency than devices with doped emissive layers. The difference may be attributed to the fact that luminescence quantum yield of platinum-complex neat films is dependent on the chemical structure and packing of such molecule in solid films. The additional emission band in the wavelength range of 400–450 nm can be resolved in the EL spectra of devices. A comparison of the EL spectra among devices with/without a 0.4 nm FPt layer and control mCP: 12% FPt device, as presented in Fig. 2 of the Ref. 17, indicates that the emission comes from carrier-transporting layers as results of carrier leakage and subsequent recombination outside FPt layer. This explains why devices with a 0.4/0.7 nm FPt layer show relatively low EQE. It should be noted that the EQE of the present device represents significant improvement over that of devices having dye emissive layers reported previously.<sup>6–12</sup> One reason for the enhancement is the improved balance of carrier injection/transport and confinement of the carrier recombination zone in the dye layer. Selection of the hole-transporting and electron-transporting materials is important for achieving enhanced device performance.<sup>17</sup>

Two working mechanisms represented in carrier recombination in the dye layer and energy transfer to dye molecules, followed by the formation of excited states in the carrier-transporting layers, prevail in these devices. Significant variation of device EQE with FPt layer thickness in the range of 0.4–2 nm indicates dominance of carrier recombination in FPt layer. All devices with a FPt emissive layer show a roll-off of the EQE with increasing current density, as generally observed in phosphorescent OLEDs.<sup>3</sup> The reduction of the EQE with increasing current density is comparable or slightly faster than that of devices with a host: guest emissive layer. Therefore, our results support that leakage of carriers and excited states outside the emissive layer is the main reason for the roll-off in device efficiency.<sup>17</sup>

The most efficient FPt devices in the present study show an elevated excimer/aggregate emission over monomer emission. In what follows, a blue fluorophore or phosphor is incorporated into the device to compensate for the dominant excimer/aggregate contribution and tune device emission to white. First, 1-(2,5-dimethyl-4-(1-pyrenyl)phenyl)pyrene (DMPPP),<sup>23,24</sup> an efficient singlet blue emitter with high solid state luminescence efficiency, is used. Figure 3(a) shows the EL spectra of devices with an emissive layer structure of DMPPP (1, 2 nm)/mCP (2 nm)/FPt (0.7 nm) at different drive voltages. The mCP interlayer is used to adjust

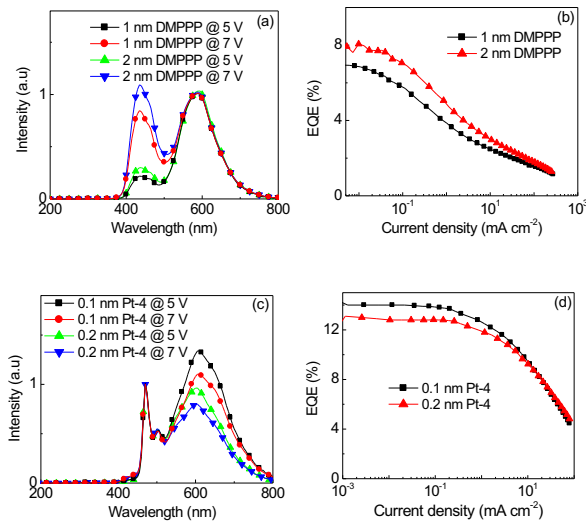


FIG. 3. (Color online) Properties of white-emitting devices. (a) EL spectra, and (b) EQE-current density characteristics of the DMPPP device; (c) EL spectra and (d) EQE-current density properties of the Pt-4 device.

carrier recombination in DMPPP and FPt layers, and to prevent the loss of FPt triplet excited states from transferring energy to the lower energy, nonemissive DMPPP triplet states.<sup>25,26</sup> In this case, the EL spectra exhibit blue emission mainly from DMPPP and yellowish-orange emission from FPt excimer/aggregates. The blue emission intensity from DMPPP is enhanced in devices with a 2 nm DMPPP layer. In this case, the CIE coordinates and CRI of (0.44, 0.41)/65 and (0.34, 0.31)/83 at 5 and 7 V are measured. An increase in DMPPP layer thickness results in a slight improvement in the device EQE, as shown in Fig. 3(b). The peak EQE and PE for devices with a 2 nm DMPPP layer are ca. 8% and 15 lm W<sup>-1</sup>, respectively. In order to improve the efficiency, platinum(II)[1,3-difluoro-4,6-di(2-pyridinyl)benzene] chloride (Pt-4),<sup>16</sup> an efficient blue phosphor, is incorporated in the device structure. Figure 3(c) displays the EL spectra of devices with an emissive layer structure of Pt-4 (0.1 nm, 0.2 nm)/FPt (0.7 nm) at different drive voltages. Light emission from Pt-4 and FPt excimer/aggregate emission, as well as slight emission from the carrier-transporting layers can be seen. The relative Pt-4 to FPt excimer/aggregate emission intensity increases with an increase in drive voltage and thickness of Pt-4 layer. The CIE coordinates and CRI of the Pt-4 (0.1 nm)/FPt (0.7 nm) device are (0.46, 0.41)/85 and (0.44, 0.40)/86, respectively, and a shift to (0.42, 0.41)/84 and (0.40, 0.40)/84 for the Pt-4 (0.2 nm)/FPt (0.7 nm) device is seen at 5 and 7 V, respectively. As shown in Fig. 3(d), the peak EQE and PE of the device having Pt-4 (0.1 nm)/FPt (0.7 nm) emissive layer stack are 14% and 25 lm W<sup>-1</sup>, respectively. These values are higher than those of the Pt-4 (0.2 nm)/FPt (0.7 nm) device (12.8% and 22 lm W<sup>-1</sup>). The EQE

of our devices represents three to four times improvement over those of previously reported white-emitting devices utilizing dye emissive layers,<sup>12</sup> and is comparable with white devices using Pt-4 and FPt as dopants.<sup>27</sup>

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- <sup>1</sup>C.-W. Tang and S. A. Van Slyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- <sup>2</sup>C.-W. Tang, S. A. Van Slyke, and C.-H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
- <sup>3</sup>M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).
- <sup>4</sup>Y. Wang, N. Herron, W. Grushin, D. Lecloux, and V. Petrov, *Appl. Phys. Lett.* **79**, 449 (2001).
- <sup>5</sup>Q.-X. Tong, S.-L. Lai, M.-Y. Chan, K.-H. Lai, J.-X. Tang, H.-L. Kwong, C.-S. Lee, and S.-T. Lee, *Appl. Phys. Lett.* **91**, 153504 (2007).
- <sup>6</sup>T. Mori, K. Miyachi, and T. Mizutani, *J. Phys. D: Appl. Phys.* **28**, 1461 (1995).
- <sup>7</sup>H. Kajii, K. Takahashi, J. S. Kim, and Y. Ohmori, *Jpn. J. Appl. Phys., Part 1* **45**, 3721 (2006).
- <sup>8</sup>Y. Divayana and X.-W. Sun, *Phys. Rev. Lett.* **99**, 143003 (2007).
- <sup>9</sup>J. Wang, J.-S. Yu, L. Li, T. Wang, K. Yuan, and Y.-D. Jing, *Appl. Phys. Lett.* **92**, 133308 (2008).
- <sup>10</sup>T. Tsuji, S. Naka, H. Okada, and H. Onnagawa, *Appl. Phys. Lett.* **81**, 3329 (2002).
- <sup>11</sup>W.-F. Xie, Z.-J. Wu, S.-Y. Liu, and S.-T. Lee, *J. Phys. D: Appl. Phys.* **36**, 2331 (2003).
- <sup>12</sup>H.-S. Yang, Y. Zhao, F.-W. Xie, Y.-W. Shi, W. Hu, Y.-L. Meng, J.-Y. Hou, and S.-Y. Liu, *Semicond. Sci. Technol.* **21**, 1447 (2006).
- <sup>13</sup>J.-H. Jou, M.-H. Wu, C.-P. Wang, Y.-S. Chiu, P.-H. Chiang, N.-C. Hu, and R.-Y. Wang, *Org. Electron.* **8**, 735 (2007).
- <sup>14</sup>C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **90**, 5048 (2001).
- <sup>15</sup>B. W. D'Andrade and S. R. Forrest, *Adv. Mater.* **16**, 1585 (2004).
- <sup>16</sup>X.-H. Yang, Z.-X. Wang, S. Madakuni, J. Li, and G. E. Jabbour, *Adv. Mater.* **20**, 2405 (2008).
- <sup>17</sup>See supplementary material at <http://dx.doi.org/10.1063/1.3541447> for chemical structure of materials, summary of device performance and discussion of the reduction of device EQE with increasing current density.
- <sup>18</sup>D. O'Brien, A. Bleyer, D. G. Lidzey, D. D. C. Bradley, and T. Tsutsui, *J. Appl. Phys.* **82**, 2662 (1997).
- <sup>19</sup>E. L. Williams, K. Haavisto, J. Li, and G. E. Jabbour, *Adv. Mater.* **19**, 197 (2007).
- <sup>20</sup>M. Cocchi, J. Kalinowski, V. Fattori, J. A. G. Williams, and L. Murphy, *Appl. Phys. Lett.* **94**, 073309 (2009).
- <sup>21</sup>M. Cocchi, J. Kalinowski, L. Murphy, J. A. G. Williams, and V. Fattori, *Org. Electron.* **11**, 388 (2010).
- <sup>22</sup>J. Kalinowski, M. Cocchi, V. Fattori, L. Murphy, and J. A. G. Williams, *Org. Electron.* **11**, 724 (2010).
- <sup>23</sup>K.-C. Wu, P.-J. Ku, C.-S. Lin, H.-T. Shih, F.-I. Wu, M.-J. Huang, J.-J. Lin, I.-C. C. Chen, and C.-H. Cheng, *Adv. Funct. Mater.* **18**, 67 (2008).
- <sup>24</sup>S.-H. Lin, F.-I. Wu, and R.-S. Liu, *Chem. Commun. (Cambridge)* **2009**, 6961.
- <sup>25</sup>Y. R. Sun, N. C. Giebink, H. Kano, B. W. Ma, M. E. Thompson, and S. R. Forrest, *Nature (London)* **440**, 908 (2006).
- <sup>26</sup>G. Schwartz, K. Fehse, M. Pfeiffer, K. Walzer, and K. Leo, *Appl. Phys. Lett.* **89**, 083509 (2006).
- <sup>27</sup>X.-H. Yang, Z.-X. Wang, S. Madakuni, J. Li, and G. E. Jabbour, *Appl. Phys. Lett.* **93**, 193305 (2008).