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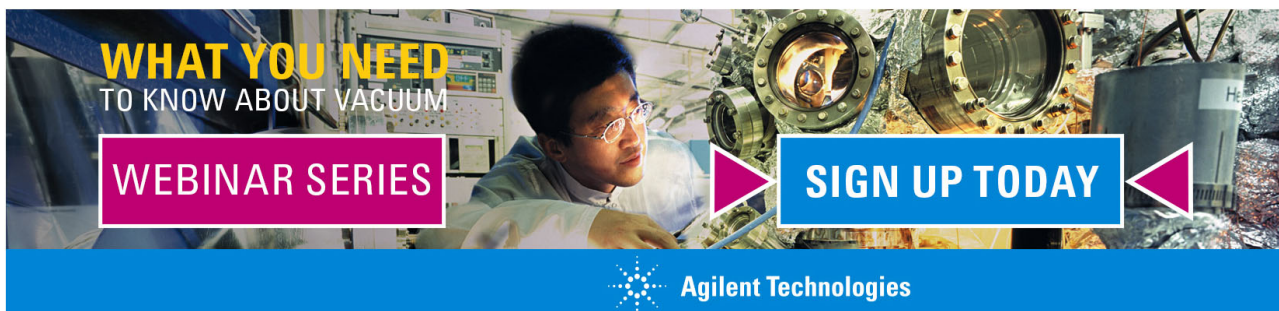
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## High-efficiency turquoise-blue electrophosphorescence from a Pt(II)-pyridyltriazolate complex in a phosphine oxide host

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We demonstrate high-efficiency turquoise-blue electrophosphorescence from bis[3,5-bis(2-pyridyl)-1,2,4-triazolato]platinum(II) [Pt(ftp)<sub>2</sub>] doped in 4-(diphenylphosphoryl)-*N,N*-diphenylaniline(HM-A1). Organic light-emitting diodes (OLEDs) with 5% Pt(ftp)<sub>2</sub>:HM-A1 attain peak power efficiency of 61.2 lm/W, versus 40.8 lm/W for analogous devices employing the standard turquoise-blue phosphor bis[(4,6-difluorophenyl)-pyridinato-*N,C*'](picolinato)iridium(III) (FIrpic). Devices with *x*% Pt(ftp)<sub>2</sub>:HM-A1 exhibit blue emission maxima ( $\lambda_{\text{max}} \sim 480$  nm) with monotonic increase in excimer/monomer intensity ratio at higher doping levels within 1%–10%, causing color shift toward green and less charge balance. This work represents a significant step toward optimizing future white OLEDs from the same phosphor via combination of low-doped and higher-doped or neat films. © 2009 American Institute of Physics. [doi:10.1063/1.3268434]

The organic optoelectronics field has witnessed tremendous progress since Tang and VanSlyke pioneered efficient organic light emitting diodes (OLEDs).<sup>1</sup> Applications that take advantage of the optical and/or semiconducting properties of small organic molecules and conjugated polymers include solid state lighting, OLED displays, photovoltaics, biosensors, etc. In OLEDs, optimizing charge balance and high phosphorescence quantum yields can lead to 100% internal quantum efficiency.<sup>2</sup> Replacing fluorescent emitters with Ir and Pt based phosphorescent metal-organic complexes has led to very high performance OLEDs.<sup>3–5</sup> However, blue OLEDs continue to be the weakest link for lighting and display applications.

Efficient electrophosphorescence dictates that the triplet energy ( $E_{T1}$ ) of the charge transport and host molecules be higher than that of the phosphor. This is particularly important for blue phosphors, in order to avoid exothermic backward or interlayer energy transfer.<sup>6</sup> In green<sup>7</sup> and blue<sup>8</sup> OLEDs based on Ir(III) phenylpyridine complexes better exciton confinement has been demonstrated when *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4''-diamine ( $\alpha$ -NPD) was replaced by 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) as a hole transporting material and exciton blocker ( $E_{T1}$ =2.87 eV for TAPC, 2.29 eV for  $\alpha$ -NPD, 2.42 eV for Ir(ppy)<sub>3</sub>, and 2.7 eV for FIrpic). Several wide-band-gap host molecules have been used for improving the external quantum efficiency (EQE) of blue OLEDs owing to their ambipolarity and/or higher triplet energy ( $E_{T1}$ ). FIrpic doped into 4,4'-bis(carbazol-9-yl)biphenyl (CBP) exhibits a maximum EQE of 6.0%.<sup>9</sup> A higher EQE of 8% was

achieved using 3,5'-*N,N'*-dicarbazole-benzene (mCP) as host<sup>10</sup> ( $E_{T1}$ =2.9 eV), while using 4,4'-bis(9-carbazolyl)-2,2'-dimethyl-biphenyl (CDBP) as host ( $E_{T1}$ =3.0 eV) attained up to 10% EQE.<sup>11</sup> Similar development in electron transporting materials resulting in higher OLED performance has been reported by Tanaka *et al.*<sup>12</sup> wherein tris[3-(3-pyridyl)mesityl]borane (3TPYMB) has higher electron affinity (LUMO=-3.32 eV), higher triplet energy ( $E_{T1}$ =2.95 eV), an order of magnitude higher electron mobility ( $\sim 6 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at  $6.4 \times 10^5$  V cm<sup>-1</sup>), and a higher ionization potential (HOMO=-6.77 eV) versus more common electron transporters.<sup>13</sup> Several phosphine oxide derivatives have also been used as wide-band-gap hosts and/or electron transporters.<sup>14–16</sup>

We report highly efficient light emission from a phosphorescent platinum(II)-pyridyltriazolate complex, bis[3,5-bis(2-pyridyl)-1,2,4-triazolato]platinum(II) [Pt(ftp)<sub>2</sub>],<sup>17,18</sup> doped into the ambipolar host 4-(diphenylphosphoryl)-*N,N*-diphenylaniline (HM-A1,  $E_{T1}$ =2.84 eV).<sup>15</sup> The thickness of the hole transport layer, TAPC, the electron transport layer 2, 8-bis(diphenylphosphoryl) dibenzothiophene (PO15), and the emissive layer were optimized and kept constant while the doping concentration was varied within 1%–10% to fine tune the electroluminescence (EL) efficiency and/or color within the blue-green region. OLEDs with higher Pt(ftp)<sub>2</sub> doping levels exhibit broad, unstructured excimer emissions in the yellow-orange region,<sup>17</sup> which can be mixed with a blue singlet emitter to demonstrate stable, high color rendering index (CRI) white OLEDs.<sup>19</sup>

Devices were fabricated on indium-tin oxide (ITO)-coated glass substrates with a sheet resistance of  $\sim 15$   $\Omega/\square$ , degreased and etched with O<sub>2</sub> plasma immediately prior to thermal evaporation of the organic stack (deposition pressure

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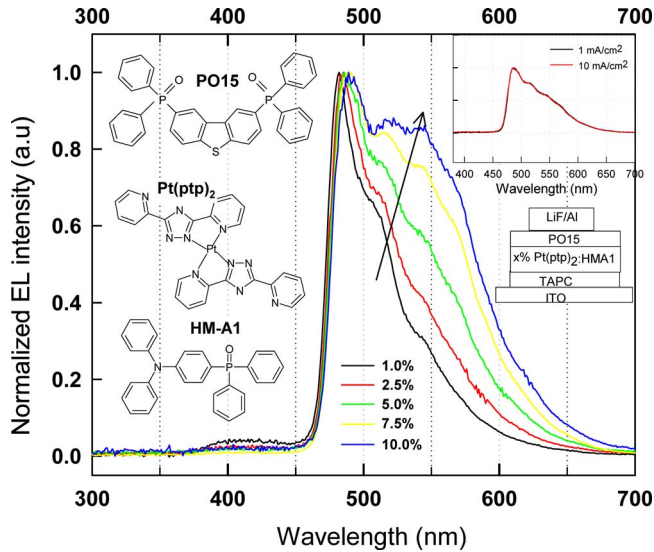


FIG. 1. (Color online) EL spectra vs doping concentrations of Pt(ppy)<sub>2</sub> in HM-A1, recorded at 10 mA/cm<sup>2</sup>. Insets show the chemical structures, EL spectra of a 5% Pt(ppy)<sub>2</sub>:HM-A1 device (demonstrating negligible dependence on current density) and the device structure.

$<3 \times 10^{-7}$  torr). Cathodes of these devices were defined by thermally evaporating LiF/Al. The thickness of each layer was monitored using quartz crystal monitors, which are calibrated *ex situ* with ellipsometry.

The electroluminescence spectra as a function of doping concentration for Pt(ppy)<sub>2</sub> in HM-A1, recorded at 10 mA/cm<sup>2</sup>, are shown in Fig. 1. At low doping concentrations (1% and 2.5%), the structured monomer emission in the blue region ( $\lambda=480$  nm) dominates whereas a progressive increase in the excimer emission (broadening at longer wavelengths) is observed as the doping concentration increases up to 10%. This is due to the stronger Pt(II)···Pt(II) intermolecular interactions caused by stacking of the Pt(II)-bis(pyridyltriazolate) square-planar units.<sup>17</sup> The introduction of some excimer phosphorescence upon increasing Pt(ppy)<sub>2</sub> doping leads to redshifts in the long wavelength edge of the EL spectra, corresponding to a change in Commission Internationale de l'éclairage (CIE) coordinates from (0.19, 0.45) at 1% doping to (0.32, 0.54) at 10% doping, as shown in Table I. The device structure is ITO/350 Å TAPC /150 Å x% Pt(ppy)<sub>2</sub>:HM-A1 /500 Å PO-15 /10 Å LiF/1000 Å Al. The low intensity, broad emission at  $\lambda \sim 420$  nm for the devices

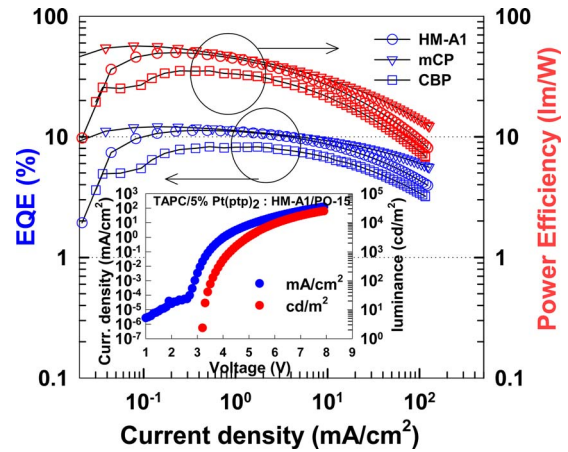


FIG. 2. (Color online) EQE and PE of a 5% Pt(ppy)<sub>2</sub> doped in various hosts as a function of current density. The inset shows a current density-voltage-luminance curve for a typical device with 5% Pt(ppy)<sub>2</sub> doped in HM-A1.

doped at  $<5\%$  is attributed to the host (HM-A1) singlet emission resulting from incomplete energy transfer. There is negligible dependence of the EL profile on current density within the doping concentration studied (e.g., see Fig. 1 inset for the 5% device) and also negligible difference between the EL and PL spectra. (See Ref. 20 for EL versus PL comparison.) This indicates effective charge balance and exciton confinement.

Choice of appropriate host for a particular dopant is essential for achieving high efficiency. The EQE and power efficiency (PE) plots for OLEDs based on 5% Pt(ppy)<sub>2</sub> doped in CBP, mCP, and HM-A1 hosts are shown in Fig. 2. A significant improvement in EQE and PE is achieved by replacing CBP with mCP or HM-A1. We attribute this improvement to the higher triplet energies for mCP and HM-A1, preventing back transfer of triplet excitons from the Pt(ppy)<sub>2</sub> ( $E_{T1}=2.58$  eV, estimated from the shortest-wavelength vibronic peak in the EL spectra). The peak EQE and PE for devices using HM-A1 as host are  $(11.8 \pm 0.6)\%$  and  $(61.2 \pm 5.9)$  lm/W, respectively, compared to  $(8.2 \pm 0.9)\%$  and  $(35.2 \pm 6.6)$  lm/W for devices with CBP as host. Devices with mCP versus HM-A1 host were comparable at  $J \sim 1$  mA/cm<sup>2</sup>. The inset of Fig. 2 shows a typical *J-L-V* (current density-luminance-voltage) curve for the representative device ITO/350 Å TAPC /150 Å 5% Pt(ppy)<sub>2</sub>:HM-A1 /500 Å PO-15 /LiF/Al.

TABLE I. OLED parameters vs doping concentrations of Pt(ppy)<sub>2</sub> in HM-A1. The values reported are an average  $\pm$  standard deviation of eight devices and the numbers in parentheses are the best pixel data.

Doping concentration (%)	1 mA cm <sup>-2</sup>						$\lambda_{\max}$ (nm)	CIE(x,y)
	Voltage (V)	Luminance (cd m <sup>-2</sup> )	EQE <sub>peak</sub> (%)	EQE <sub>1000</sub> (%)	PE <sub>peak</sub> (lm W <sup>-1</sup> )	PE <sub>1000</sub> (lm W <sup>-1</sup> )		
1% Pt(ppy) <sub>2</sub>	3.94 $\pm$ 0.01	358.1 $\pm$ 6.0	11.5 $\pm$ 1.1 (12.4)	8.4 $\pm$ 0.3 (9.0)	37.7 $\pm$ 6.8 (44.5)	21.0 $\pm$ 0.8 (22.3)	482	(0.19,0.45)
2.5% Pt(ppy) <sub>2</sub>	4.13 $\pm$ 0.01	568.5 $\pm$ 7.5	12.0 $\pm$ 0.4 (12.6)	9.7 $\pm$ 0.1 (9.9)	59.9 $\pm$ 3.5 (65.6)	38.6 $\pm$ 0.7 (39.5)	483	(0.22,0.49)
5% Pt(ppy) <sub>2</sub>	3.96 $\pm$ 0.03	568.4 $\pm$ 11.2	11.8 $\pm$ 0.6 (13.1)	10.6 $\pm$ 0.2 (10.8)	61.2 $\pm$ 5.9 (70.6)	40.3 $\pm$ 1.2 (41.6)	486	(0.26,0.51)
7.5% Pt(ppy) <sub>2</sub>	3.93 $\pm$ 0.04	550.2 $\pm$ 6.0	11.5 $\pm$ 0.2 (12.6)	10.4 $\pm$ 0.1 (10.5)	57.8 $\pm$ 2.2 (68.1)	40.2 $\pm$ 0.7 (41.1)	488	(0.29,0.53)
10% Pt(ppy) <sub>2</sub>	3.98 $\pm$ 0.03	510.9 $\pm$ 21.4	11.1 $\pm$ 0.7 (11.6)	9.4 $\pm$ 0.5 (9.9)	58.1 $\pm$ 3.6 (60.8)	35.2 $\pm$ 2.2 (37.9)	490	(0.32,0.54)
5% FIrpic (Control)	4.02 $\pm$ 0.02	431.5 $\pm$ 12	16.7 $\pm$ 0.4 (17.6)	15.4 $\pm$ 0.4 (16.0)	40.8 $\pm$ 1.7 (42.8)	29.4 $\pm$ 0.8 (30.7)	474	(0.16,0.30)

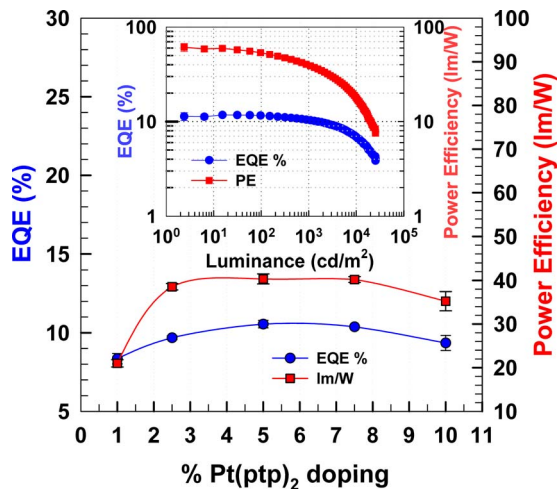


FIG. 3. (Color online) EQE and PE vs doping concentration in HM-A1 at 1000  $\text{cd/m}^2$ . The inset shows EQE and PE vs luminance for the 5% device.

The EQE and PE of OLEDs with variable doping levels of the phosphor in the host HM-A1 at 1000  $\text{cd/m}^2$  are shown in Fig. 3. At very low doping concentration (1%), the lower efficiency is due to incomplete energy transfer from the host to the dopant. Furthermore, the luminance (Table I) is significantly lower for the 1% device at similar current density and operating voltage. The PE and EQE stay essentially constant for a range of doping concentrations (2.5%–7.5%) while the EL color shifts toward the green region as the doping level is increased. We attribute the marginal drop in efficiency at 10% doping to possible participation of the phosphorescent dopant in charge transport, which perturbs the hole/electron transport within the emissive layer, leading to poorer charge balance; direct trapping on dopant and bimolecular quenching of monomer emission also become significant at such conditions. We note that peak EQE and PE values usually occur at very low current densities and low luminance and are susceptible to high standard deviations, whereas values at 1000  $\text{cd/m}^2$  are more reliable and technologically relevant.<sup>21</sup>

In summary, we have demonstrated high efficiency blue phosphorescent OLEDs using a Pt(II)-pyridyltriazolate phosphorescent complex in combination with phosphine oxide based host and electron transporting materials. Better balance of charge carriers and exciton confinement in such devices has led to maximum PE of 61.2  $\text{lm/W}$ , compared to 40.8  $\text{lm/W}$  for analogous FIrpic-based devices that, interestingly, exhibit higher EQE. This is partly attributed to the greater green contribution in the Pt(php)<sub>2</sub>-based devices. Exhaustive optimizations of FIrpic-based OLEDs with different device structures reported elsewhere attained progressively improved efficiencies within 6–50  $\text{lm/W}$ ,<sup>8–12,14–16,22,23</sup> so the higher power efficiency of the Pt(php)<sub>2</sub>-based devices herein will likely stimulate further work on this phosphor and its congeners. The fine color tunability of the blue EL by changing the Pt(php)<sub>2</sub> doping concentration demonstrated herein concomitant with the coarse tuning to other colors that we reported elsewhere<sup>17</sup> warrant further investigation for multiple lighting and display applications. For example, the find-

ings of this work can be useful in designing high-efficiency *warm white* OLEDs because a 5%-doped layer of Pt(php)<sub>2</sub> exhibits sufficient blue-green intensity (monomer emission) to attain white EL upon combination with broad yellow-red excimer/extended-excimer emission from a highly doped ( $\geq 30\%$ ) or neat emissive layer of the same phosphor, as such unoptimized devices attained as high as 82 CRI.<sup>18</sup>

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