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https://hdl.handle.net/2324/19448

出版情報: Applied Physics Letters. 78 (11), pp.1622-1624, 2001-03-12. American Institute of Physics バージョン:

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## High-efficiency red electrophosphorescence devices

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(Received 1 December 2000; accepted for publication 16 January 2001)

We demonstrate high-efficiency red electrophosphorescent organic light-emitting devices employing bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-N,C<sup>3'</sup>) iridium(acetylacetonate) [Btp<sub>2</sub>Ir(acac)] as a red phosphor. A maximum external quantum efficiency of  $\eta_{ext} = (7.0 \pm 0.5)$ % and power efficiency of  $\eta_p = (4.6 \pm 0.5)$  lm/W are achieved at a current density of J = 0.01 mA/cm<sup>2</sup>. At a higher current density of J = 100 mA/cm<sup>2</sup>,  $\eta_{ext} = (2.5 \pm 0.3)$ % and  $\eta_p = (0.56 \pm 0.05)$  lm/W are obtained. The electroluminescent spectrum has a maximum at a wavelength of  $\lambda_{max} = 616$  nm with additional intensity peaks at  $\lambda_{sub} = 670$  and 745 nm. The Commission Internationale de L'Eclairage coordinates of (x = 0.68, y = 0.32) are close to meeting video display standards. The short phosphorescence lifetime ( $\sim 4 \mu s$ ) of Btp<sub>2</sub>Ir(acac) leads to a significant improvement in  $\eta_{ext}$  at high currents as compared to the previously reported red phosphor, 2,3,7,8,12,13,17,18-octaethyl-12H, 23H-prophine platinum (II) PtOEP with a lifetime of  $\sim 50 \mu s$ . © 2001 American Institute of *Physics*. [DOI: 10.1063/1.1355007]

Heavy-metal complexes,<sup>1,2</sup> where strong spin-orbit coupling leads to singlet-triplet state mixing, can result in highefficiency electrophosphorescence in organic light-emitting devices (OLEDs).<sup>3-6</sup> For example, OLEDs employing the phosphor, factris(2-phenylpyridine)iridium [Ir(ppy)<sub>3</sub>], exhibit green emission with an external quantum efficiency  $(\eta_{ext})$  of ~15%.<sup>6</sup> By designing appropriate ligands for heavy-metal complexes, high-efficiency electrophosphorescence at other emission colors is anticipated for highperformance full-color display applications.<sup>7</sup> Both redemitting fluorescent and phosphorescent dopants have shown promise for use in OLEDs. While fluorescent dyes, including 4-dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetra-hydro-1H, 5H-benzo[ij]quinolizin-8-yl)-4H-pyran (DCM2)<sup>8,9</sup> and porphyrin derivatives (TPP,<sup>10</sup> ZnTPP,<sup>11</sup> and TPC<sup>12</sup>), have been investigated, their maximum external quantum efficiencies are limited to less than 1%. Furthermore, the red phosphocomplexes  $(EuL_3)^{13,14}$ europium rescent and 2,3,7,8,12,13,17,18-octaethyl-12H,23H-porphine platinum (II) (PtOEP) have been studied.<sup>3,4</sup> Although EuL<sub>3</sub> complexes show very strong red Eu<sup>3+</sup> ion emission (with an internal quantum efficiency  $\eta_{int} > 80\%$ ),<sup>15</sup> the long lifetime of the  $Eu^{3+}$  excited state (~350 µs) results in pronounced triplet– triplet (T-T) annihilation at high current.<sup>14</sup> In addition, the high triplet energy of the ligands causes backward energy transfer to the host molecule, leading to  $\eta_{ext} < 1.4\%$ .<sup>14</sup> The highest  $\eta_{ext} = 5.6\%$  for a red phosphor has been achieved with PtOEP doped into 4,4'-N,N'-dicarbazole-biphenyl. (CBP).<sup>4</sup> However, the relatively long phosphorescence lifetime ( ${\sim}80~\mu s)$  again results in T–T annihilation at high current.<sup>16</sup>

In this study, we demonstrate red organometallic phosphors characterized by a high quantum efficiency and a short radiative lifetime.<sup>17</sup> The metal complexes contain cyclometalated benzothienylpyridine ligands, i.e.,  $bis(2-(2'-benzo[4,5-\alpha]thienyl)$  pyridinato-N,C<sup>3'</sup>) iridium (acetyl-acetonate)  $[btp_2Ir(acac)]^7$  and (2-(2'-benzo[4,5- $\alpha$ ]thienyl)pyridinato-N,C<sup>3'</sup>) platinum (acetylacetonate) [btpt(acac)], shown in Fig. 1. The synthesis of btpPt(acac) was prepared by a method analogous to that used<sup>7</sup> for btp<sub>2</sub>Ir(acac). The small  $\pi - \pi^*$  transition energy of the btp ligand relative to other ligands used in heavy-metal phosphors leads to a low-energy triplet excited state, giving strong red phosphorescence. OLEDs employing these phosphors were grown by high vacuum  $(10^{-6} \text{ Torr})$  thermal evaporation onto pre-cleaned glass substrates as described elsewhere.<sup>6</sup> Device I is comprised of a 20  $\Omega/\Box$  indium tin oxide (ITO) anode, a 50-nm-thick 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl hole transport layer (HTL), a 20nm-thick light-emitting layer (EML) consisting of a conductive CBP host doped with  $\sim 7\%$  of the guest phosphor, a 10-nm-thick 2,9-dimethyl-4,7-diphenyl-phenanthroline hole and exciton blocking layer,<sup>4</sup> a 65-nm-thick tris(8hydroxyquinoline)aluminum (Alq<sub>3</sub>) electron transport layer (ETL), and a cathode comprised of a 100-nm-thick (10:1) MgAg layer, with a further 20 nm Ag deposited as a protective cap (Fig. 1). Device II has the ITO anode, a 60-nm-thick 4,4'-bis[N,N'-(3-tolyl)amino]-3,3'-dimethylbiphenyl<sup>6</sup> HTL, a 25-nm-thick 2,2',2"-(1,3,5-benzenetriyl)tris[1-phenyl-1*H*-benzimidazole] (TPBI)<sup>18</sup> EML doped with  $\sim$ 7% phos-

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FIG. 1. Device structures I and II. Molecular structure of the  $btp_2M(acac)$  phosphors (here M = Ir, n = 2 and M = Pt, n = 1).

phor, a 50-nm-thick Alq<sub>3</sub> ETL, and the same cathode as in device  $\underline{I}$ .

Figure 2 shows  $\eta_{\text{ext}}$  and the power efficiency ( $\eta_p$ ) as functions of current density for device I with a btp<sub>2</sub>Ir(acac) guest. A maximum  $\eta_{\text{ext}} = (7.0 \pm 0.5)\%$  and  $\eta_p = (4.6 \pm 0.5)$  lm/W, and a luminance of 6.5 cd/m<sup>2</sup> were obtained at J = 0.1 mA/cm<sup>2</sup>. The device showed a gradual decrease of  $\eta_{\text{ext}}$  with increasing current, which has been previously attributed to T–T annihilation.<sup>14,19</sup> Nevertheless, at J= 100 mA/cm<sup>2</sup>, the device efficiency remained high at  $\eta_{\text{ext}}$ = (2.5±0.3)% and  $\eta_p = (0.56\pm0.05)$  lm/W. A maximum luminance of 6800 cd/m<sup>2</sup> was obtained at J = 690 mA/m<sup>2</sup>.



FIG. 2. External quantum efficiency ( $\eta_{ext}$ ) and power efficiency ( $\eta_p$ ) vs current density for device <u>I</u> with a btp<sub>2</sub>Ir(acac) guest.

Table I summarizes the electroluminescence characteristics of btp<sub>2</sub>Ir(acac), btpPt(acac), PtOEP and Eu(TTA)<sub>3</sub>phen (TTA = thenoyltrifluoroacetone, phen = 1, 10-phenanthroline) guests in devices I and II. A maximum  $\eta_{ext} \sim 7\%$  was obtained with btp<sub>2</sub>Ir(acac) in both devices I and II, and PtOEP in device II. Also, the maximum  $\eta_p$  of btp<sub>2</sub>Ir(acac) was  $(4.6\pm0.5)$  lm/W which is significantly higher than that of PtOEP, since the spectral peak of the latter compound is  $\sim 30$ nm redshifted relative to btp<sub>2</sub>Ir(acac). A pronounced improvement in  $\eta_{\text{ext}}$  of btp<sub>2</sub>Ir(acac) was observed at high current. At  $J = 100 \text{ mA/cm}^2$ , the btp<sub>2</sub>Ir(acac) doped device <u>I</u> showed a relatively high  $\eta_{\text{ext}} = (2.5 \pm 0.5)\%$ , compared with PtOEP and Eu(TTA)<sub>3</sub>phen doped devices <u>I</u> with  $\eta_{ext} = (0.61$  $\pm 0.05$ )% and  $\eta_{\text{ext}} = (0.21 \pm 0.05)$ %, respectively. The roll off in  $\eta_{\text{ext}}$  with J is consistent with the electrophosphorescent lifetimes,  $\tau$ , of the several materials employed. As shown

TABLE I. Red electrophosphorescent OLED characteristics. External quantum efficiency ( $\eta_{ext}$ ), and power efficiency ( $\eta_p$ ) are given as functions of current density. Peak wavelength ( $\lambda_{max}$ ) in electroluminescent spectrum. Transient electrophosphorescent time ( $\tau$ ) under electrical pulse excitation with pulse width of 500 ns. The characteristic current ( $J_0$ ) of triplet–triplet annihilation.

$\eta_{\text{ext}}(\%)$ [ $\eta_{\text{p}}(\text{Im/W})$ ] at $J(\text{mA/cm}^2)$										
		$J\!=\!0.01$	0.1	1	10	100	1000	$\lambda_{\text{max}}(nm)$	$ au(\mu s)$	$J_0(\text{mA/cm}^2)$
Btp <sub>2</sub> Ir(acac)	Device I	7.0 (4.6)	6.7 (3.1)	6.0 (2.1)	4.4 (1.3)	2.5 (0.56)	0.69 (0.16)		6.5	27.4
								616		
	Device II	6.9 (5.7)	6.8 (3.6)	5.9 (2.5)	3.7 (1.4)	1.6 (0.57)	0.53 (0.14)		4.0	11.0
BtpPt(acac)	Device I	2.7	2.7 (1.4)	2.6 (0.93)	1.9 (0.54)	1.0 (0.25)	0.37		9.3	37.7
		(2.5)	(1.1)	(0.95)	(0.51)	(0.23)	(0.005)	610		
	Device II	2.2 (1.7)	2.2 (1.1)	2.1 (0.72)	1.3 (0.34)	0.57 (0.12)	0.0.2 (0.036)		5.6	14.5
	Device I	5.2 (1.3)	5.2 (1.1)	4.1 (0.64)	2.1 (0.25)	0.67 (0.066)	0.18 (0.015)		86.5	6.4
PtOEP								650		
	Device II	6.9 (1.4)	6.9 (1.0)	4.3 (0.53)	1.9 (0.17)	0.5 (0.039)	0.10 (0.010)		49.6	2.6
Eu(TTA) <sub>3</sub> phen	Device I	1.4 (1.2)	1.3 (0.94)	1.2 (0.53)	0.68 (0.21)	0.21 (0.08)		614	350	3.6

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FIG. 3. Electroluminescent spectra of device II employing btp<sub>2</sub>Ir(acac), PtOEP or btpPt(acac) at a current density of  $J=1.3 \text{ mA/cm}^2$ . Inset: CIE coordinates for btp<sub>2</sub>Ir(acac) (x=0.67, y=0.33), btpPt(acac) (x=0.67, y=0.33), PtOEP (x=0.70, y=0.30) and Eu(TTA)<sub>3</sub>phen (x=0.68, y=0.32) doped devices and a 2%-DCM2: Alq<sub>3</sub> (x=0.61, y=0.39) device. The triangles show the NTSC recommended blue, green, and red coordinates.

previously, the characteristic current ( $J_0$ ) at which  $\eta_{\text{ext}}$  falls to 50% its peak value due to T–T annihilation is inversely proportional to  $\tau^{2,14,19}$  This figure of merit of a phosphor is listed in Table I along with  $\tau$  for the devices tested. The btp<sub>2</sub>Ir(acac) lifetime is ~12 times smaller than that of PtOEP, leading to considerably improved high-current performance of the Ir-based compound. The low  $\eta_{\text{ext}}$  of btpPt(acac) is consistent with its low photoluminescence efficiency  $[(8\pm2)\%]$  compared with that of btp<sub>2</sub>Ir(acac)  $[(21\pm5)\%]$  and PtOEP  $[(40\pm10)\%]$ .

The EL spectra originating from the triplet-excited states of the phosphors shown in Fig. 3 are coincident with those of the phosphors in a dilute solution. The Commission Internationale de L'Eclairage (CIE) coordinates for the four devices are compared with a fluorescent 2%-DCM2:Alq<sub>3</sub> device (x = 0.61,0.39) (inset of Fig. 2). Similar to the  $Eu(TTA)_3$  phen of (x=0.68, y=0.32), the btp<sub>2</sub>Ir(acac) and btpPt(acac) doped devices demonstrate a saturated red emission (x=0.67, y=0.33) which is close to the National Television Standards Committee recommended red for a video display. Furthermore, the EL spectra and CIE coordinates of btp<sub>2</sub>Ir(acac) in devices I and II are independent of current (Fig. 4). Even at  $J > 100 \text{ mA/cm}^2$ , blue emission from either the CBP or TPBI host is negligible, indicating complete energy transfer under the excitation conditions used: a direct consequence of the short phosphor lifetime of this compound.<sup>20</sup>

In summary, we demonstrated high-efficiency, highbrightness red phosphorescent OLEDs employing benzothienylpyridine (btp) as a ligand in iridium and platinum complexes. Significant improvements in  $\eta_{ext}$  as compared with PtOEP were achieved due to the short phosphorescence lifetimes of <10  $\mu$ s of the new compounds studied, thereby minimizing T–T annihilation and saturation of the ligand excited state.



FIG. 4. Electroluminescent spectra of device  $\underline{II}$  with a btp<sub>2</sub>(acac) guest dopant as a function of OLED drive current density.

This work was funded by Universal Display Corporation, the Defense Advanced Research Projects Agency, and the Air Force Office of Scientific Research.

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