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High-efficiency red electrophosphorescence devices

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We demonstrate high-efficiency red electrophosphorescent organic light-emitting devices employing *bis*(2-(2'-benzo[4,5-*a*]thienyl)pyridinato-N,C^{3'}) iridium(acetylacetonate) [Btp₂Ir(acac)] as a red phosphor. A maximum external quantum efficiency of $\eta_{\text{ext}} = (7.0 \pm 0.5)\%$ and power efficiency of $\eta_p = (4.6 \pm 0.5)$ lm/W are achieved at a current density of $J = 0.01$ mA/cm². At a higher current density of $J = 100$ mA/cm², $\eta_{\text{ext}} = (2.5 \pm 0.3)\%$ and $\eta_p = (0.56 \pm 0.05)$ lm/W are obtained. The electroluminescent spectrum has a maximum at a wavelength of $\lambda_{\text{max}} = 616$ nm with additional intensity peaks at $\lambda_{\text{sub}} = 670$ 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 (~ 4 μ s) of Btp₂Ir(acac) leads to a significant improvement in η_{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 ~ 50 μ s. © 2001 American Institute of Physics. [DOI: 10.1063/1.1355007]

Heavy-metal complexes,^{1,2} where strong spin-orbit coupling leads to singlet-triplet state mixing, can result in high-efficiency electrophosphorescence in organic light-emitting devices (OLEDs).^{3–6} For example, OLEDs employing the phosphor, *factris*(2-phenylpyridine)iridium [Ir(ppy)₃], exhibit green emission with an external quantum efficiency (η_{ext}) of $\sim 15\%$.⁶ By designing appropriate ligands for heavy-metal complexes, high-efficiency electrophosphorescence at other emission colors is anticipated for high-performance full-color display applications.⁷ Both red-emitting 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)^{8,9} and porphyrin derivatives (TPP,¹⁰ ZnTPP,¹¹ and TPC¹²), have been investigated, their maximum external quantum efficiencies are limited to less than 1%. Furthermore, the red phosphorescent europium complexes (EuL₃)^{13,14} and 2,3,7,8,12,13,17,18-octaethyl-12H,23H-porphine platinum (II) (PtOEP) have been studied.^{3,4} Although EuL₃ complexes show very strong red Eu³⁺ ion emission (with an internal quantum efficiency $\eta_{\text{int}} > 80\%$),¹⁵ the long lifetime of the Eu³⁺ excited state (~ 350 μ s) results in pronounced triplet-triplet (T-T) annihilation at high current.¹⁴ In addition, the high triplet energy of the ligands causes backward energy transfer to the host molecule, leading to $\eta_{\text{ext}} < 1.4\%$.¹⁴ The highest $\eta_{\text{ext}} = 5.6\%$ for a red phosphor has been achieved with PtOEP doped into 4,4'-N,N'-dicarbazole-biphenyl.

(CBP).⁴ However, the relatively long phosphorescence lifetime (~ 80 μ s) again results in T-T annihilation at high current.¹⁶

In this study, we demonstrate red organometallic phosphors characterized by a high quantum efficiency and a short radiative lifetime.¹⁷ The metal complexes contain cyclometalated benzothienylpyridine ligands, i.e., *bis*(2-(2'-benzo[4,5- α]thienyl)pyridinato-N,C^{3'}) iridium (acetyl-acetonate) [btp₂Ir(acac)]⁷ and (2-(2'-benzo[4,5- α]thienyl)pyridinato-N,C^{3'}) platinum (acetylacetonate) [btpPt(acac)], shown in Fig. 1. The synthesis of btpPt(acac) was prepared by a method analogous to that used⁷ for btp₂Ir(acac). The small π - π^* 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} Torr) thermal evaporation onto pre-cleaned glass substrates as described elsewhere.⁶ Device I is comprised of a 20 $\Omega/\square$ indium tin oxide (ITO) anode, a 50-nm-thick 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl hole transport layer (HTL), a 20-nm-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,⁴ a 65-nm-thick tris(8-hydroxyquinoline)aluminum (Alq₃) 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'-dimethylbiphenyl⁶ HTL, a 25-nm-thick 2,2',2''-(1,3,5-benzenetriyl)tris[1-phenyl-1H-benzimidazole] (TPBI)¹⁸ EML doped with $\sim 7\%$ phos-

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FIG. 1. Device structures I and II. Molecular structure of the btp₂M(acac) phosphors (here *M* = Ir, *n* = 2 and *M* = Pt, *n* = 1).

phor, a 50-nm-thick Alq₃ ETL, and the same cathode as in device I.

Figure 2 shows η_{ext} and the power efficiency (η_p) as functions of current density for device I with a btp₂Ir(acac) guest. A maximum $\eta_{\text{ext}} = (7.0 \pm 0.5)\%$ and $\eta_p = (4.6 \pm 0.5) \text{ lm/W}$, and a luminance of 6.5 cd/m² were obtained at $J = 0.1 \text{ mA/cm}^2$. The device showed a gradual decrease of η_{ext} with increasing current, which has been previously attributed to T–T annihilation.^{14,19} Nevertheless, at $J = 100 \text{ mA/cm}^2$, the device efficiency remained high at $\eta_{\text{ext}} = (2.5 \pm 0.3)\%$ and $\eta_p = (0.56 \pm 0.05) \text{ lm/W}$. A maximum luminance of 6800 cd/m² was obtained at $J = 690 \text{ mA/cm}^2$.

FIG. 2. External quantum efficiency (η_{ext}) and power efficiency (η_p) vs current density for device I with a btp₂Ir(acac) guest.

Table I summarizes the electroluminescence characteristics of btp₂Ir(acac), btpPt(acac), PtOEP and Eu(TTA)₃phen (TTA = thenoyltrifluoroacetone, phen = 1,10-phenanthroline) guests in devices I and II. A maximum $\eta_{\text{ext}} \sim 7\%$ was obtained with btp₂Ir(acac) in both devices I and II, and PtOEP in device II. Also, the maximum η_p of btp₂Ir(acac) was $(4.6 \pm 0.5) \text{ lm/W}$ which is significantly higher than that of PtOEP, since the spectral peak of the latter compound is $\sim 30 \text{ nm}$ redshifted relative to btp₂Ir(acac). A pronounced improvement in η_{ext} of btp₂Ir(acac) was observed at high current. At $J = 100 \text{ mA/cm}^2$, the btp₂Ir(acac) doped device I showed a relatively high $\eta_{\text{ext}} = (2.5 \pm 0.5)\%$, compared with PtOEP and Eu(TTA)₃phen doped devices I with $\eta_{\text{ext}} = (0.61 \pm 0.05)\%$ and $\eta_{\text{ext}} = (0.21 \pm 0.05)\%$, respectively. The roll off in η_{ext} with J is consistent with the electrophosphorescent lifetimes, τ , of the several materials employed. As shown

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

		$\eta_{\text{ext}}(\%)$ [$\eta_p(\text{lm/W})$] at $J(\text{mA/cm}^2)$						$\lambda_{\text{max}}(\text{nm})$	$\tau(\mu\text{s})$	$J_0(\text{mA/cm}^2)$
		$J=0.01$	0.1	1	10	100	1000			
Btp ₂ 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)	616	6.5	27.4
	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)			
BtpPt(acac)	Device I	2.7 (2.5)	2.7 (1.4)	2.6 (0.93)	1.9 (0.54)	1.0 (0.25)	0.37 (0.083)	610	9.3	37.7
	Device II	2.2 (1.7)	2.2 (1.1)	2.1 (0.72)	1.3 (0.34)	0.57 (0.12)	0.02 (0.036)			
PtOEP	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)	650	86.5	6.4
	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)			
Eu(TTA) ₃ 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
	Device II	1.4 (1.2)	1.3 (0.94)	1.2 (0.53)	0.68 (0.21)	0.21 (0.08)	...

FIG. 3. Electroluminescent spectra of device II employing $\text{btp}_2\text{Ir}(\text{acac})$, PtOEP or $\text{btpPt}(\text{acac})$ at a current density of $\bar{J}=1.3 \text{ mA/cm}^2$. Inset: CIE coordinates for $\text{btp}_2\text{Ir}(\text{acac})$ ($x=0.67$, $y=0.33$), $\text{btpPt}(\text{acac})$ ($x=0.67$, $y=0.33$), PtOEP ($x=0.70$, $y=0.30$) and $\text{Eu}(\text{TTA})_3\text{phen}$ ($x=0.68$, $y=0.32$) doped devices and a 2%-DCM2:Alq₃ ($x=0.61$, $y=0.39$) device. The triangles show the NTSC recommended blue, green, and red coordinates.

previously, the characteristic current (J_0) at which η_{ext} falls to 50% its peak value due to T–T annihilation is inversely proportional to τ^2 .^{14,19} This figure of merit of a phosphor is listed in Table I along with τ for the devices tested. The $\text{btp}_2\text{Ir}(\text{acac})$ lifetime is ~ 12 times smaller than that of PtOEP, leading to considerably improved high-current performance of the Ir-based compound. The low η_{ext} of $\text{btpPt}(\text{acac})$ is consistent with its low photoluminescence efficiency $[(8 \pm 2)\%]$ compared with that of $\text{btp}_2\text{Ir}(\text{acac})$ $[(21 \pm 5)\%]$ and PtOEP $[(40 \pm 10)\%]$.

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:Alq₃ device ($x=0.61, y=0.39$) (inset of Fig. 2). Similar to the $\text{Eu}(\text{TTA})_3\text{phen}$ of ($x=0.68, y=0.32$), the $\text{btp}_2\text{Ir}(\text{acac})$ and $\text{btpPt}(\text{acac})$ 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 $\text{btp}_2\text{Ir}(\text{acac})$ 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.²⁰

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

FIG. 4. Electroluminescent spectra of device II with a $\text{btp}_2(\text{acac})$ guest dopant as a function of OLED drive current density.

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