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We demonstrate high-efficiency red electrophosphorescent organic light-emitting devices employing $bis(2\text{-}(2'\text{-benzo}[4,5\text{-}a]\text{thienyl})\text{pyridinato-N,C}^{3'})$ iridium(acetylacetonate) [Btp$_2$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^2. At a higher current density of $J = 100$ mA/cm^2, $\eta_{ext} = (2.5 \pm 0.3)\%$ 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 (~ 4 μs) of Btp$_2$Ir(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 μs. © *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, fac tris(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 TPC[12]), have been investigated, their maximum external quantum efficiencies are limited to less than 1%. Furthermore, the red phosphorescent europium complexes (EuL$_3$)[13,14] and 2,3,7,8,12,13,17,18-octaethyl-12H,23H-porphine platinum (II) (PtOEP) have been studied.[3,4] Although EuL$_3$ complexes show very strong red Eu^{3+} ion emission (with an internal quantum efficiency $\eta_{int} > 80\%$),[15] the long lifetime of the Eu^{3+} excited state (~ 350 μs) 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 $\eta_{ext} < 1.4\%$.[14] The highest $\eta_{ext} = 5.6\%$ 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 μs) 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., $bis(2\text{-}(2'\text{-benzo}[4,5\text{-}\alpha]\text{thienyl})$ pyridinato-N,C$^{3'}$) iridium (acetyl-acetonate) [btp$_2$Ir(acac)][7] and $(2\text{-}(2'\text{-benzo}[4,5\text{-}\alpha]\text{thienyl})\text{pyridinato-N,C}^{3'})$ platinum (acetylacetonate) [btpt(acac)], shown in Fig. 1. The synthesis of btpPt(acac) was prepared by a method analogous to that used[7] for btp$_2$Ir(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 Ω/□ 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 (Alq$_3$) 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[6] 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-
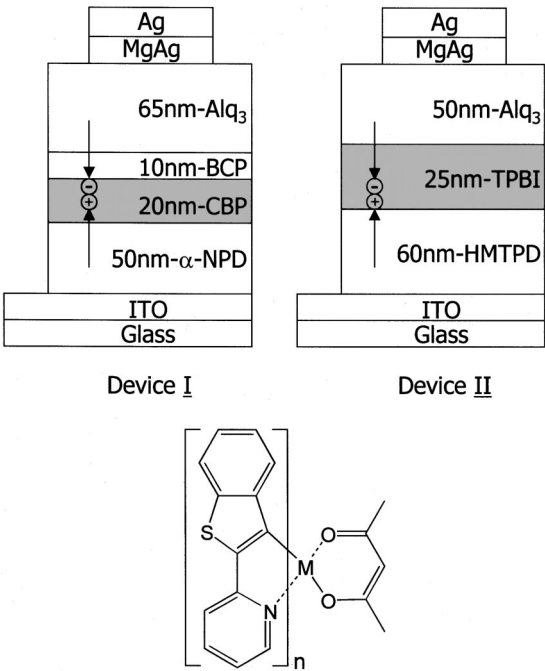

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FIG. 1. Device structures I and II. Molecular structure of the btp$_2$M(acac) phosphors (here $M=$ Ir, $n=2$ and $M=$Pt, $n=1$).
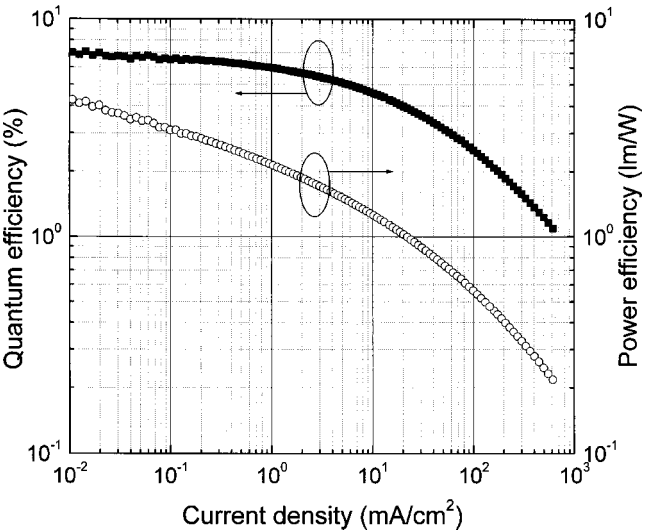

FIG. 2. External quantum efficiency (η_{ext}) and power efficiency (η_p) vs current density for device I with a btp$_2$Ir(acac) guest.

phor, a 50-nm-thick Alq$_3$ 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 btp$_2$Ir(acac) guest. A maximum $\eta_{ext}=(7.0\pm0.5)\%$ and $\eta_p=(4.6\pm0.5)$ lm/W, and a luminance of 6.5 cd/m^2 were obtained at $J=0.1$ 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 $J=100$ mA/cm^2, the device efficiency remained high at $\eta_{ext}=(2.5\pm0.3)\%$ and $\eta_p=(0.56\pm0.05)$ lm/W. A maximum luminance of 6800 cd/m^2 was obtained at $J=690$ mA/m^2.

Table I summarizes the electroluminescence characteristics of btp$_2$Ir(acac), btpPt(acac), PtOEP and Eu(TTA)$_3$phen (TTA = thenoyltrifluoroacetone, phen = 1, 10-phenanthroline) guests in devices I and II. A maximum $\eta_{ext}\sim7\%$ was obtained with btp$_2$Ir(acac) in both devices I and II, and PtOEP in device II. Also, the maximum η_p of btp$_2$Ir(acac) was (4.6 ± 0.5) lm/W which is significantly higher than that of PtOEP, since the spectral peak of the latter compound is $\sim$30 nm redshifted relative to btp$_2$Ir(acac). A pronounced improvement in η_{ext} of btp$_2$Ir(acac) was observed at high current. At $J=100$ mA/cm^2, the btp$_2$Ir(acac) doped device I showed a relatively high $\eta_{ext}=(2.5\pm0.5)\%$, compared with PtOEP and Eu(TTA)$_3$phen doped devices I with $\eta_{ext}=(0.61\pm0.05)\%$ and $\eta_{ext}=(0.21\pm0.05)\%$, 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.

| | | η_{ext}(%) [η_p(lm/W)] at J(mA/cm^2) | | | | | | | | |
		$J=0.01$	0.1	1	10	100	1000	λ_{max}(nm)	$\tau(\mu s)$	J_0(mA/cm^2)
	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
Btp$_2$Ir(acac)								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
	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)		9.3	37.7
BtpPt(acac)								610		
	Device II	2.2 (1.7)	2.2 (1.1)	2.1 (0.72)	1.3 (0.34)	0.57 (0.12)	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)$_3$ 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
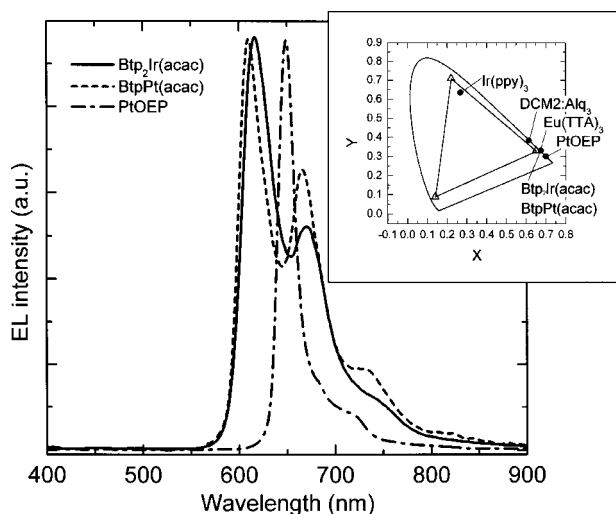
FIG. 3. Electroluminescent spectra of device $\underline{\text{II}}$ employing btp$_2$Ir(acac), PtOEP or btpPt(acac) at a current density of $\bar{J} = 1.3$ mA/cm^2. Inset: CIE coordinates for btp$_2$Ir(acac) ($x = 0.67$, $y = 0.33$), btpPt(acac) ($x = 0.67$, $y = 0.33$), PtOEP ($x = 0.70$, $y = 0.30$) and Eu(TTA)$_3$phen ($x = 0.68$, $y = 0.32$) doped devices and a 2%-DCM2: Alq$_3$ ($x = 0.61$, $y = 0.39$) device. The triangles show the NTSC recommended blue, green, and red coordinates.

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

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 btp$_2$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 η_{ext} of btpPt(acac) is consistent with its low photoluminescence efficiency $[(8 \pm 2)\%]$ compared with that of btp$_2$Ir(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:Alq$_3$ 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$_2$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$_2$Ir(acac) in devices $\underline{\text{I}}$ and $\underline{\text{II}}$ are independent of current (Fig. 4). Even at $J > 100$ 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 μs of the new compounds studied, thereby minimizing T–T annihilation and saturation of the ligand excited state.
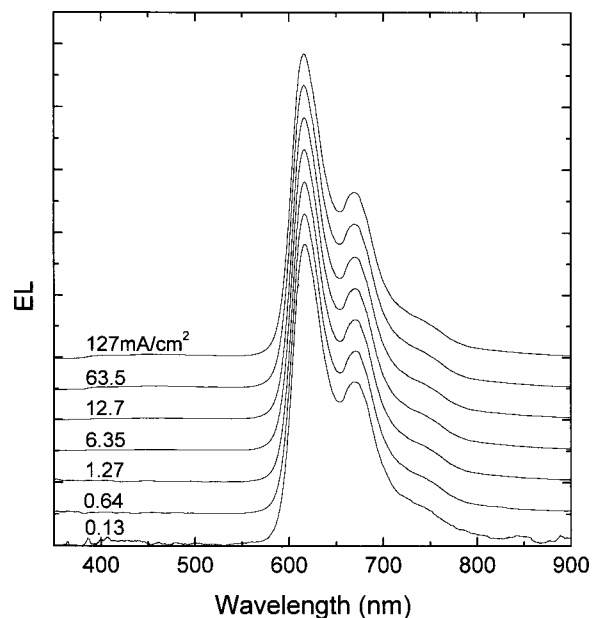
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