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Adachi, Chihaya

Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University

Baldo, Marc.A.

Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University

Forrest, Stephen R.

Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering and the Princeton Materials Institute, Princeton University

Lamansky, Sergey

Department of Chemistry, University of Southern California

他

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High-efficiency red electrophosphorescence devices

Chihaya Adachi, Marc A. Baldo, and Stephen R. Forrest^{a)}

Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544

Sergey Lamansky and Mark E. Thompson

Department of Chemistry, University of Southern California, Los Angeles, California 90089

Raymond C. Kwong

Universal Display Corporation, 375 Phillips Boulevard, Ewing, New Jersey 08618

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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) [btpt(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 Ω/\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-

^{a)}Electronic mail: forrest@ee.princeton.edu

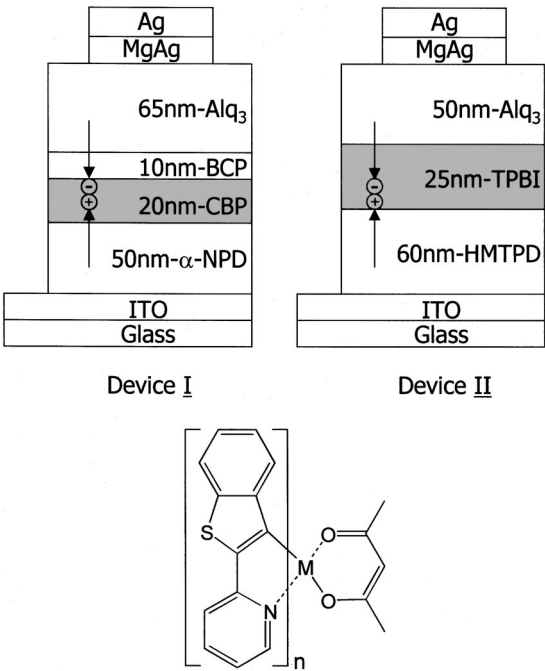


FIG. 1. Device structures I and II. Molecular structure of the btp₂M(acac) phosphors (here *M* = Ir, *n* = 2 and *M* = Pt, *n* = 1).

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 $J = 690 \text{ mA/cm}^2$.

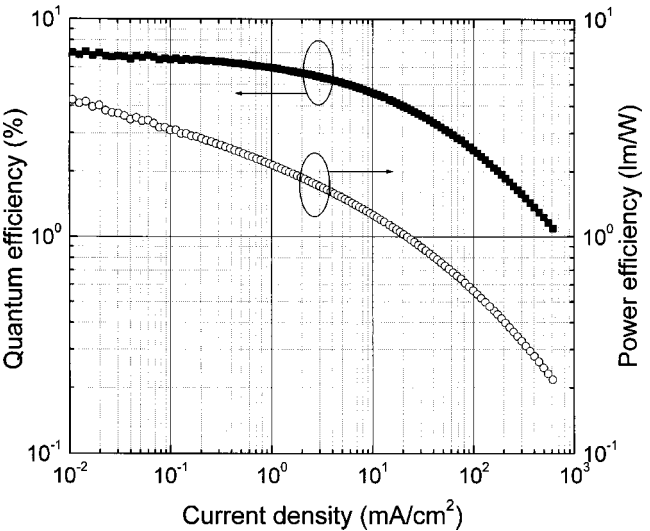


FIG. 2. External quantum efficiency (η_{ext}) and power efficiency (η_p) vs current density for device I with a btp₂Ir(acac) guest.

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)	...			

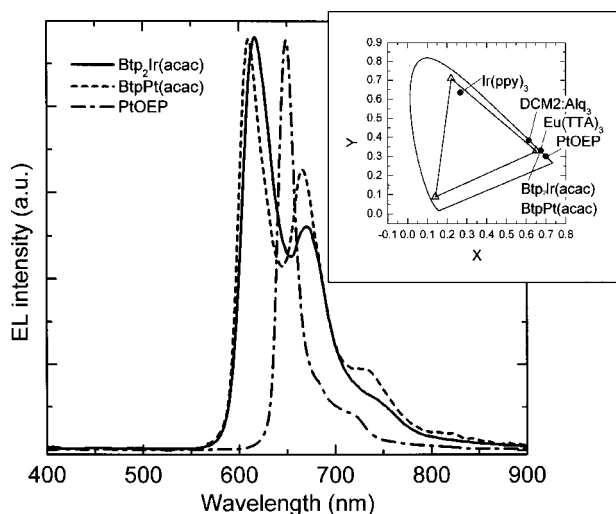


FIG. 3. Electroluminescent spectra of device II employing $\text{btp}_2\text{Ir}(\text{acac})$, PtOEP or $\text{btpPt}(\text{acac})$ at a current density of $\bar{J}=1.3 \text{ mA/cm}^2$. Inset: CIE coordinates for $\text{btp}_2\text{Ir}(\text{acac})$ ($x=0.67$, $y=0.33$), $\text{btpPt}(\text{acac})$ ($x=0.67$, $y=0.33$), 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.

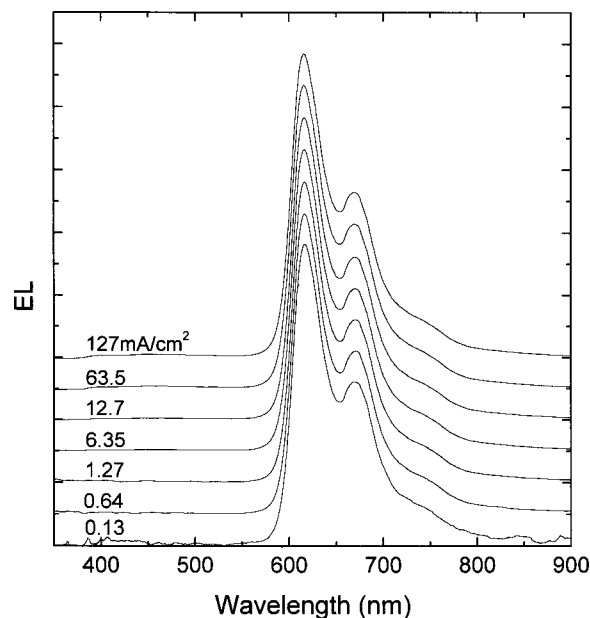


FIG. 4. Electroluminescent spectra of device II with a $\text{btp}_2(\text{acac})$ guest dopant as a function of OLED drive current density.

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