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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

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Chihaya Adachi, Marc A. Baldo, and Stephen R. Forrest
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\textsuperscript{3}) iridium(acetylacetonate) [Btp-Ir(acac)] as a red phosphor. A maximum external quantum efficiency of $\eta_{\text{ext}}= (7.0 \pm 0.5)\%$ and power efficiency of $\eta_p = (4.6 \pm 0.5) \text{lm/W}$ are achieved at a current density of $J = 0.01 \text{mA/cm}^2$. At a higher current density of $J = 100 \text{mA/cm}^2$, $\eta_{\text{ext}} = (2.5 \pm 0.3)\%$ and $\eta_p = (0.56 \pm 0.05) \text{lm/W}$ are obtained. The electroluminescence spectrum has a maximum at a wavelength of $\lambda_{\text{max}} = 616 \text{nm}$ with additional intensity peaks at $\lambda_{\text{sub}} = 670$ and $745 \text{nm}$. 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-Ir(acac) leads to a significant improvement in $\eta_{\text{ext}}$ 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,\textsuperscript{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).\textsuperscript{3-6} For example, OLEDs employing the phosphor, fac-tris(2-phenylpyridine)iridium [Ir(ppy)\textsubscript{3}], exhibit green emission with an external quantum efficiency ($\eta_{\text{ext}}$) of $\sim 15\%$.\textsuperscript{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.\textsuperscript{7} Both red-emitting fluorescent and phosphorescent dopants have shown promise for use in OLEDs. While fluorescent dyes, including dicyanomethylene-2-methyl-6-[2-(2,3,6,7-tetra-hydro-1H,5H-benzo[j]quinolinizin-8-yl)-4H-πyan (DCM),\textsuperscript{8,9} and porphyrin derivatives (TPP,\textsuperscript{10} ZnTPP,\textsuperscript{11} and TPC),\textsuperscript{12} have been investigated, their maximum external quantum efficiencies are limited to less than 1%. Furthermore, the red phosphorescent europium complexes (EuL\textsubscript{3})\textsuperscript{13,14} and 2,3,7,8,12,13,17,18-octaethyl-12H,23H-prophine platinum (II) (PtOEP) have been studied.\textsuperscript{3,4} Although EuL\textsubscript{3} complexes show very strong red Eu\textsuperscript{3+} ion emission (with an internal quantum efficiency $\eta_{\text{int}} > 80\%$),\textsuperscript{15} the long lifetime of the Eu\textsuperscript{3+} excited state ($\sim 350 \mu s$) results in pronounced triplet-triplet (T-T) annihilation at high current.\textsuperscript{14} In addition, the high triplet energy of the ligands causes backward energy transfer to the host molecule, leading to $\eta_{\text{ext}} < 1.4\%$.\textsuperscript{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).\textsuperscript{4} However, the relatively long phosphorescence lifetime ($\sim 80 \mu s$) again results in T-T annihilation at high current.\textsuperscript{16}

In this study, we demonstrate red organometallic phosphors characterized by a high quantum efficiency and a short radiative lifetime.\textsuperscript{17} The metal complexes contain cyclometalated benzothienylpyridine ligands, i.e., bis(2-(2′-benzo[4,5-α]thienyl) pyridinato-N,C\textsubscript{3}) iridium (acetyl-acetonate) [btp-Ir(acac)]\textsuperscript{2} and (2-(2′-benzo[4,5-α]thienyl)pyridinato-N,C\textsubscript{3}) platinum (acetylacetonate) [btp(acac)], shown in Fig. 1. The synthesis of btpPt(acac) was prepared by a method analogous to that used\textsuperscript{7} for btp-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\textsuperscript{-6} Torr) thermal evaporation onto pre-cleaned glass substrates as described elsewhere.\textsuperscript{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,\textsuperscript{3} a 65-nm-thick tris(8-hydroxyquinoline)aluminum (Alq\textsubscript{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 HTL, a 25-nm-thick 2,2′,2″-(1,3,5-benzenetriyl)tris[1-phenyl-1H-benzimidazole] (TPBI)\textsuperscript{18} EML doped with $\sim 7\%$ phosphor.
phor, a 50-nm-thick Alq₃ ETL, and the same cathode as in device I.

Figure 2 shows $\eta_{ext}$ and the power efficiency ($\eta_p$) as functions of current density for device I with a btp₂Ir(acac) guest. A maximum $\eta_{ext} = (7.0 \pm 0.5)\%$ and $\eta_p = (4.6 \pm 0.5)$ lm/W, and a luminance of 6.5 cd/m² were obtained at $J = 0.1$ mA/cm². The device showed a gradual decrease of $\eta_{ext}$ with increasing current, which has been previously attributed to T–T annihilation. Nevertheless, at $J = 100$ mA/cm², the device efficiency remained high at $\eta_{ext} = (2.5 \pm 0.3)\%$ and $\eta_p = (0.56 \pm 0.05)$ lm/W. A maximum luminance of 6800 cd/m² was obtained at $J = 690$ mA/m².

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 $\eta_{ext} \approx 7\%$ was obtained with btp₂Ir(acac) in both devices I and II, and PtOEP in device II. Also, the maximum $\eta_p$ of btp₂Ir(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 ~30 nm redshifted relative to btp₂Ir(acac). A pronounced improvement in $\eta_{ext}$ of btp₂Ir(acac) was observed at high current. At $J = 100$ mA/cm², the btp₂Ir(acac) doped device I showed a relatively high $\eta_{ext} = (2.5 \pm 0.5)\%$, compared with PtOEP and Eu(TTA)₃phen doped devices I with $\eta_{ext} = (0.61 \pm 0.05)\%$ and $\eta_{ext} = (0.21 \pm 0.05)\%$, respectively. The roll off in $\eta_{ext}$ with $J$ is consistent with the electrophosphorescent lifetimes, $\tau$, of the several materials employed. As shown

![Image](72x489 to 276x738)

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

**FIG. 2.** External quantum efficiency ($\eta_{ext}$) and power efficiency ($\eta_p$) vs. current density for device I with a btp₂Ir(acac) guest.

<table>
<thead>
<tr>
<th>$\eta_{ext}(%)$</th>
<th>$\eta_p$(lm/W) at $J$(mA/cm²)</th>
<th>TTTA, TTA(acac)</th>
<th>Btp₂Ir(acac)</th>
<th>BtpPt(acac)</th>
<th>PtOEP</th>
<th>Eu(TTA)₃phen</th>
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<td>(2.1)</td>
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<td>2.6</td>
<td>1.9</td>
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<td>(0.54)</td>
<td>(0.25)</td>
<td>(0.083)</td>
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<tr>
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<td>(0.34)</td>
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<td>(0.17)</td>
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<td>(0.010)</td>
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<td>(1.2)</td>
<td>(0.94)</td>
<td>(0.53)</td>
<td>(0.21)</td>
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</table>
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 \( \tau^2 \). This figure of merit of a phosphor is listed in Table I along with the \( \eta_{\text{ext}} \) for the devices tested. The \( \text{btp}_2\text{Ir(acac)} \) lifetime is \( \sim 12 \) times smaller than that of PtOEP, leading to considerably improved high-current performance of the Ir-based compound. The low \( \eta_{\text{ext}} \) of \( \text{btp}_2\text{Ir(acac)} \) is consistent with its low phosphorescence efficiency \((8 \pm 2\% \)\) compared to that of \( \text{btp}_2\text{Ir(acac)} \) \((21 \pm 5\% \)\) 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:Alq3 device \((x = 0.61, 0.39)\) (inset of Fig. 2). Similar to the Eu(TTAA)phen of \((x = 0.68, y = 0.32)\), the \( \text{btp}_2\text{Ir(acac)} \) and \( \text{btpPt(acac)} \) 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 \( \text{btp}_2\text{Ir(acac)} \) 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.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 \( \eta_{\text{ext}} \) 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.

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