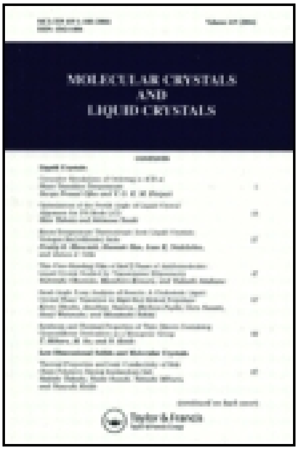

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Optimization of the Organic Lightemitting Diodes with a Red Phosphor

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Version of record first published: 17 Oct 2011

To cite this article: Mi-Youn Yang, Doo Won Gong, Young-Kwan Kim, Jun-Ho Kim, Ja-Ryong Koo, Kum-Hee Lee & Seung-Soo Yoon (2006): Optimization of the Organic Lightemitting Diodes with a Red Phosphor, Molecular Crystals and Liquid Crystals, 462:1, 169-177

To link to this article: http://dx.doi.org/10.1080/07370650601013112

Mol. Cryst. Liq. Cryst., Vol. 462, pp. 169–177, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/07370650601013112

Optimization of the Organic Lightemitting Diodes with a Red Phosphor

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We demonstrate very high efficiency electro phosphorescence in organic light-emitting diodes (OLEDs) employing a phosphorescent molecule doped into a conductive host material. Electrophosphorescent OLEDs were fabricated with bis(2-(2′-benzo[4,5-a]thienyl)pyridinato-N,$C^{3'}$) iridium(acetylacetonate) [$btp_2Ir(acac)$] as a pure red phosphor which has photoluminescence spectrum centered at 615 nm. The device structure was as follows; ITO/2-TNATA/NPB/$btp_2Ir(acac)$ doped in host/BCP/Alq_3/Liq/Al. CBP, BCP and Alq_3 were used as a host, and the concentration of $btp_2Ir(acac)$ was varied from 8 to 11%. The device with 11% $btp_2Ir(acac)$ doped in Alq_3 showed saturated electroluminescence (EL) peak at 615 nm and an efficiency of 4.76 cd/A with an initial brightness of 1100 cd/m^2. The CIE coordinates of the device showed $x = 0.67$, $y = 0.32$ at a current density of 1 mA/cm^2. The photoluminescence spectrum of Alq_3 centered at 510 nm is sufficiently overlap with absorption of dopant, therefore, energy transfer from host to guest is efficient.

Keywords: conductive host; energy transfer; organic light-emitting diodes; red phosphorescent material

This work is fully supported by the Ministry of Commerce, Industry and Energy.

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INTRODUCTION

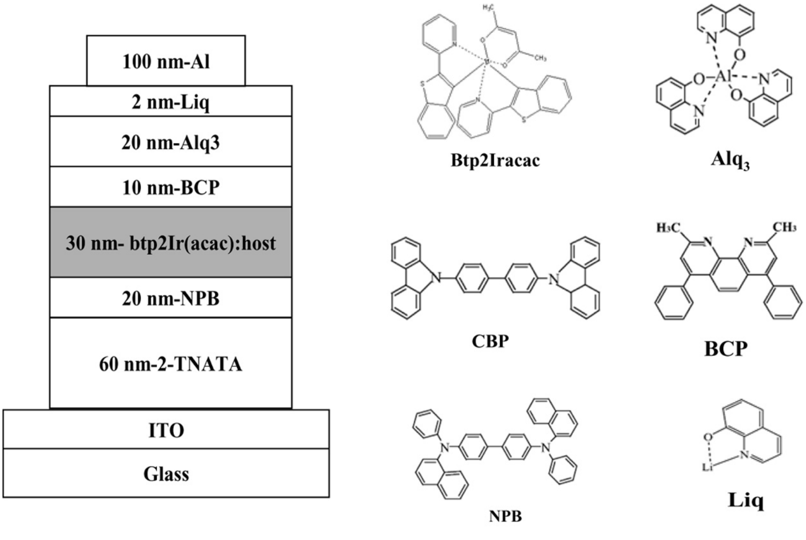
The efficiency of organic light-emitting diodes (OLEDs) has been dramatically improved by the use of heavy metal phosphorescent emitters [1–6]. Heavy-metal complexes which have strong spin-orbit coupling leads to singlet-triplet state mixing and removes the spin-forbidden nature of the radiative relaxation of the triplet state, result in high efficiency electrophosphorescence in OLEDs at room temperature [7–9]. The holes and electrons recombine to form radiative excited states, or excitons. This electrically generated exciton can be either a singlet or a triplet. Both theoretical predictions and experimental measurements give a singlet/triplet ratio for these excitons of 1 to 3. If only singlet is radiative in fluorescent materials, internal quantum efficiency ($\eta_{\rm int}$) is limited to 25%. In contrast, by using high efficiency phosphorescent materials which harvest both singlet and triplet excitons, ($\eta_{\rm int}$) can approach 100%. The iridium complexes developed by Thompson *et al.* [7] containing the 2-phenyl pyridine type cyclometalated ligands, such as $\rm Ir(ppy)_3$, have been extensively studied for the fabrication of green LEDs. The strong emission occurring at $\lambda_{\rm max} = 514\,\rm nm$ is believed to originate from the triplet manifold containing both the intraligand π–π^* and the metal-to-ligand charge transfer (MLCT) characters. It is anticipated that color tuning from green to red can be achieved by lowering the energy gap of either the π–π^* or the MLCT excited states. Ir complexes usually have efficient phosphorescence and short lifetimes, which typically range from 1 to 14 μs [10]. The shorter exciton lifetime makes Ir complexes more attractive candidates than platinum porphyrins, which usually have about one order of magnitude longer lifetime.

In previous report, the $\rm btp_2Ir(acac)$-based device gives saturated red emission with a quantum efficiency of 6.5% and a luminance efficiency of 2.2 lm/W [10]. These $\rm btp_2Ir(acac)$ doped OLEDs show some of the highest efficiencies reported for organic light emitting diodes. The high efficiencies result from efficient trapping and radiative relaxation of the singlet and triplet excitons formed in the electroluminescent process. 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. It has been synthesized and successfully used as the dopant to fabricate high efficiency small-molecule OLEDs [3,10].

In this study, we demonstrate high-efficiency red phosphorescent OLEDs employing $\rm btp_2Ir(acac)$ as a red phosphor doped into several conductive host material. We explore the photophysical and electroluminescent properties and demonstrate energy transfer process of our OLEDs.

EXPERIMENTS

The OLED structure employed in this study is shown in the Figure 1. Organic layers were fabricated by high-vacuum (10^{-6} Torr) thermal evaporation onto a glass substrate precoated with an indium-tin-oxide (ITO) layer with a sheet resistance of $20\,\Omega/\square$. Prior to use, ITO substrates were cleaned in the ultrasonic bath of acetone and methanol consecutively, and then rinsed with the distilled water. The substrate was then transferred into a plasma treatment chamber and exposed to O_2 plasma for 2 min with a power of 125 W under 2×10^{-2} Torr. A 60 nm thick 4,4′,4″-tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA) and 20 nm thick N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (NPB) used as a hole injection layer (HIL) and hole transporting later (HTL), respectively. The light emitting layer was prepared by coevaporating a 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP), tris(8-hydroxyquinoline)-aluminum (Alq_3) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) hosts and the red phosphorescent dopant, $btp_2Ir(acac)$, with both deposition rates being controlled with two independent quartz crystal oscillators. Next, 10-nm-thick BCP as a hole and exciton blocking layer (HBL) and 20 nm thick Alq_3 as an electron transport layer, and



(a) (b)

FIGURE 1 (a) The scheme of the OLEDs and (b) molecular structures of organic materials.

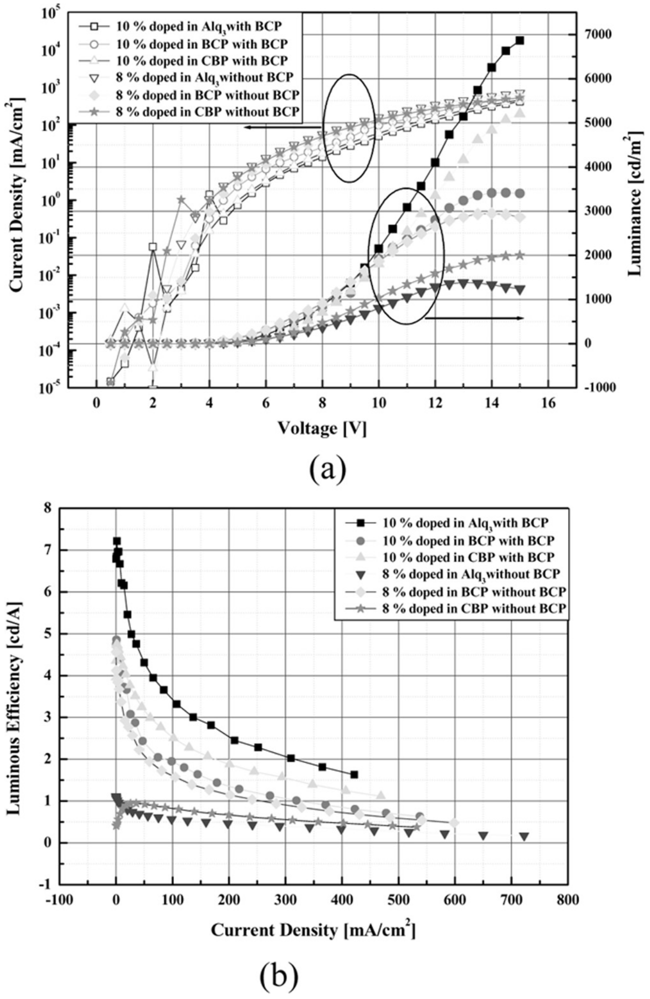
8-hydroxy-quinolinato lithium (Liq) of 20 nm thick as an electron injection layer (EIL) were deposited on the emitter layer. Finally, 100 nm thick Al layer was deposited as a cathode. Current density-voltage-luminance (J-V-L) characteristics were obtained using a Keithley 238 and performed in ambient conditions under the forward DC voltage bias.

RESULTS AND DISCUSSION

The current density–voltage (*J–V*) and Luminance–voltage (*L–V*) characteristics are shown in Figures 2(a), and (b) also shows luminous efficiency as functions of current density for our OLEDs. The device of 10% btp$_2$Ir(acac) doped in Alq$_3$ with BCP indicated that a maximum brightness of 6864 cd/m^2 at $J = 421$ mA/cm^2, and the highest luminous efficiency of 3.3 cd/A at a current density 100 mA/cm^2. While the devices of 10% btp$_2$Ir(acac) doped in CBP or BCP with HBL obtained lower characteristics than the Alq$_3$ host device, maximum brightness of 5204 cd/m^2 and 3416 cd/cm^2, and the luminous efficiency of 2.5 cd/A and 1.9 cd/A at a current density 100 mA/cm^2, respectively. The devices without BCP obtained roll off in brightness below about 3000 cd/cm^2 as increasing current density, and, very low luminous efficiencies were observed. Clearly that without BCP as the hole-blocking, most of the injected holes can penetrate through the device, being wasted without contributing to the light emission.

The devices with BCP host, hole injection from the NPB highest occupied molecular orbital (HOMO) into the BCP host is energetically unfavorable. The large energy difference between the HOMO level of NPB and BCP host of $\sim$1.0 eV prevents hole injection from NPB into BCP. Therefore, the accumulated holes at the NPB/BCP interface recombine with electrons injected from BCP layer, and the exciton formed near the NPB site. As a result, it lead to strong blue NPB emission.

There are two possible mechanisms that occur in host-guest process: The energy transfer from host to dopant or the direct charge-trapping in the dopant and recombination. In the former process, excitons formed in the host migrate to dopant triplet states via the dipole resonance coupling or charge exchange [15,16]. In the latter process, charge carriers are directly trapped by guest and await the arrival of opposite carriers for recombination [17]. In case of the devices with CBP or Alq$_3$ host, direct charge-trapping and the energy transfer from host to guest are possible. However, due to the LUMO level of btp$_2$Ir(acac) is not well aligned with that of the CBP and BCP [12]. Therefore, the most electrons are injected through the host LUMO level, addition to the mismatch between the NPB and CBP or Alq$_3$ HOMO level. As a result,



(a)

(b)

FIGURE 2 The characteristics of OLEDs with various host materials. (a) The current density–voltage (*J*–*V*) and Luminance–voltage (*L*–*V*) curves and (b) luminous efficiency as functions of current density.

the exciton recombination might occur in the host site then transfer to the guest. We expect that the latter energy transfer process occur dominantly.

To investigate the host-guest energy transfer mechanism, we observed the overlap between the absorption spectrum of dopant and the emission spectra of hosts as sown in Figure 3. The btp complexes has been shown that the emission spectra result from mixtures of

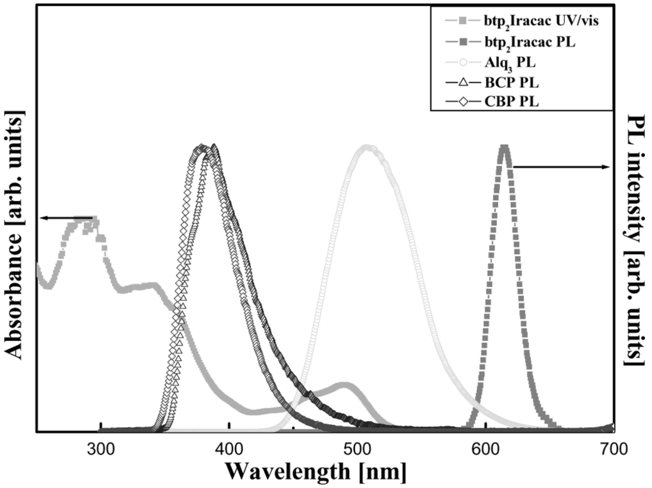


FIGURE 3 The absorption and emission spectra of btp$_2$Ir(acac) and the photoluminance (PL) spectrum of the hosts.

^{3}MLCT and π–π^* transitions [11], and the π–π^* transition level is below the ^{3}MLCT energy [10]. The absorption peak of btp$_2$Ir(acac) at 491 nm correspond to the ligand-centered π–π^* transition. From the moderate overlap between the PL spectrum of Alq$_3$ and the absorption of btp$_2$Ir (acac), we expect that the energy transfer between Alq$_3$ and btp$_2$Ir (acac) is efficient. Although the Alq$_3$ triplet energy level is identical with that of btp$_2$Ir(acac) which is 2.0 eV [13], due to very short triplet lifetime (~5 μs) and strong spin orbit coupling of btp$_2$Ir(acac), the back transfer from btp$_2$Ir(acac) to the Alq$_3$ host can be suppressed. Figure 4 (a) shows the luminance and luminous efficiency of the devices with btp$_2$Ir(acac) doped in Alq$_3$ on concentration. At concentrations of 10%, indicates higher luminance and luminous efficiency, as the concentration of btp$_2$I(racac) was increased, the luminous efficiency of the device decreased due to T-T annihilation [14,18]. As shown at Figure 4 (b), at concentrations 11%, we only observe the electroluminescence (EL) component centered at a wavelength of 615 nm due to the (btp$_2$Iracac) phosphorescence. But, the device with 10% btp$_2$Ir(acac) concentration, an additional green emission at 500 nm due to from Alq$_3$ host fluorescence is also observed. It is suggested that the saturation of the btp$_2$Ir(acac) triplet site with voltage increased.

The Commission Internationale de L'Eclairage (CIE) coordinates for the device with 11% btp$_2$Ir(acac) doped in Alq$_3$ are shown in Figure 5. This device indicated a saturated red emission that has

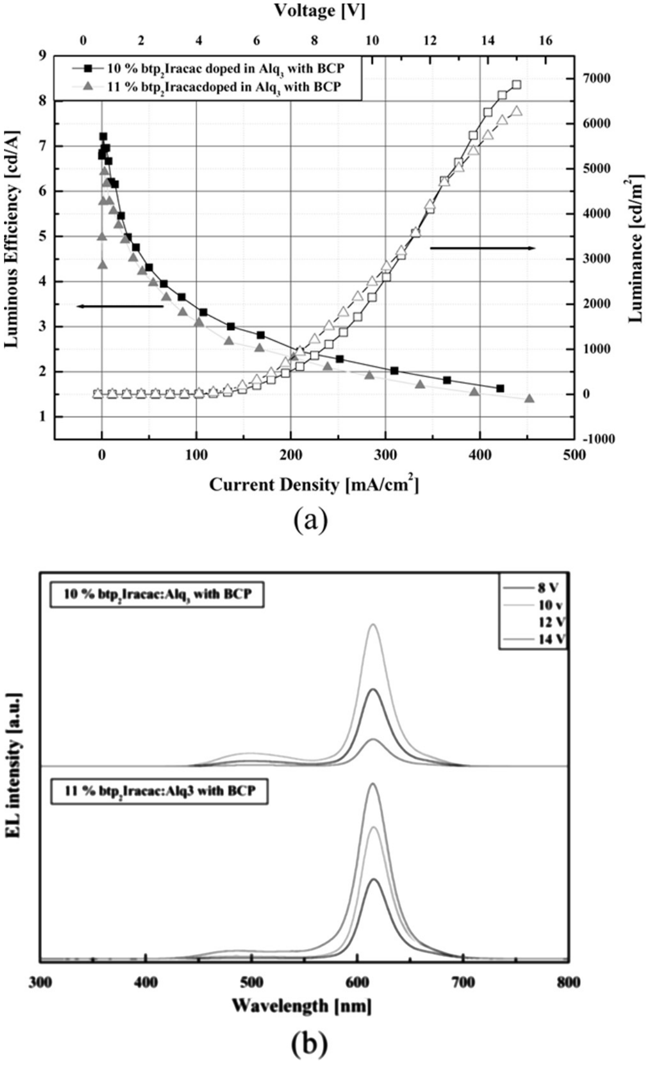


FIGURE 4 The characteristics of OLEDs with btp$_2$Ir(acac) doped in Alq$_3$. (a) Luminance and luminous efficiency curves and (b) electroluminescence (EL) spectrum.

CIE coordinates (x = 0.67, y = 0.32) are independent of current. Even at very high current density (100 mA/cm^2), green emission from Alq$_3$ or blue emission from NPB is negligible, result in completely energy transfer from Alq$_3$ host to btp$_2$Ir(acac).

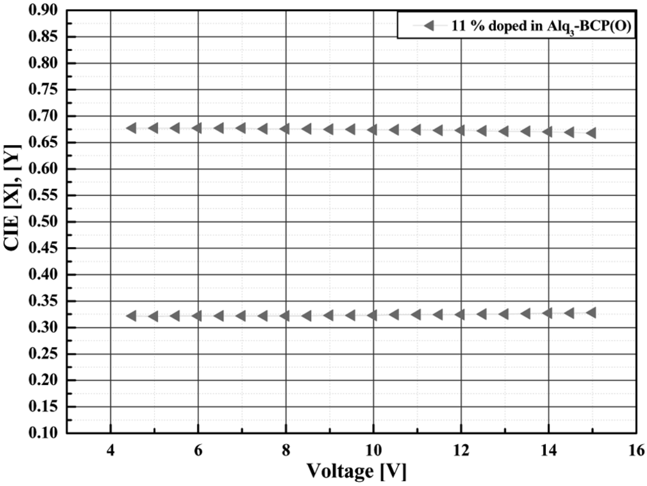


FIGURE 5 The Commission Internationale de L'Eclairage (CIE) coordinates for the device with 11% $btp_2Ir(acac)$ doped in Alq_3.

CONCLUSIONS

High efficiency in a red phosphorescent light-emitting diode was achieved by doping with $btp_2Ir(acac)$ into Alq_3. The photoluminescence spectrum of Alq_3 centered at 510 nm is sufficiently overlap with absorption of dopant ^{3}MLCT and π–π^* states. Therefore, energy transfer from host to guest occurs efficiently. Very short triplet excited state lifetime of $btp_2Ir(acac)$, that can be suppressed back transfer from guest triplet to that of host. The device of 11% $btp_2Ir(acac)$ doped in Alq_3 with BCP hole block layer was obtained saturated red emission, peak at 615 nm, and an efficiency of 4.76 cd/A with an initial brightness of 1100 cd/m^2. The CIE coordinates of the device showed $x = 0.67$, $y = 0.32$ at a current density of 1 mA/cm^2.

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