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We demonstrate that three Ir(III) complexes used as principal dopants in organic electrophosphorescent diodes have very high photoluminescence quantum efficiency (η_{PL}) in a solid-state film. The green emitting complex, fac-tris(2-phenylpyridinato)iridium(III) [$Ir(ppy)_3$], the red-emitting bis[2-(2′-benzothienyl)pyridinato-N,$C^{3\prime}$] (acetylacetonato)iridium(III) [$Btp_2Ir(acac)$], and the blue complex bis[(4,6-difluorophenyl)pyridinato-N,C^2](picolinato)iridium(III) (FIrpic) were prepared as codeposited films of varying concentration with 4,4′-bis(*N*-carbazolyl)-2,2′-biphenyl, a commonly used host material. The maximum η_{PL} values for $Ir(ppy)_3$, $Btp_2Ir(acac)$, and FIrpic were, respectively, 97%±2% (at 1.5 mol%), 51%±1% (at 1.4 mol%), and 78%±1% (at 15 mol%). Furthermore, we also observed that the maximum η_{PL} of FIrpic reached 99%±1% when doped into the high triplet energy host, *m*-bis(*N*-carbazolyl)benzene, at an optimal concentration of 1.2 mol%. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1862777]

The efficiency of organic light-emitting diodes (OLEDs) has been dramatically improved by the use of heavy metal phosphorescent emitters.[1–8] Heavy atom induced spin orbit coupling allows for efficient intersystem crossing from the singlet to the triplet states and therefore can lead to highly efficient OLED devices that are able to utilize both singlet and triplet electrogenerated excited states. Cyclometalated Ir(III) complexes are promising candidates for phosphorescent dopants because they can emit with high efficiency in room temperature from the triplet metal-to-ligand charge-transfer (^{3}MLCT) state.[9,10] An OLED device containing a green emitting Ir(III) complex is reported to have an external EL quantum efficiency (η_{EL}) as high as 19%.[2] Considering losses in efficiency due to light outcoupling from the substrate, it is probable that the internal efficiency (η_{int}) of this green phosphorescent device approaches 100%.[2]

In a previous article, we demonstrated that the photoluminescence (PL) intensity of the green phosphor, *fac*-tris(2-phenylpyridinato)iridium(III) [$Ir(ppy)_3$], showed no temperature dependency from 5 to 300 K when doped in organic hosts.[8,11] This suggests the room temperature rate of thermally activated nonradiative decay processes must be much less than the radiative decay rate. Thus it is implied that, although the room temperature PL efficiency η_{PL} of $Ir(ppy)_3$ in a 2-methyltetrahydrofuran solution is reported in the literature to be ~40%[9] the η_{PL} of $Ir(ppy)_3$ in a solid-state environment should be nearly 100%. Since the emission decay processes in fluid solution markedly differ from those in a rigid solid state, the phosphorescent decay processes of Ir(III) complexes in a practical OLED device configuration should be investigated by measuring the absolute η_{PL} in a solid film. In this study, we determined the absolute η_{PL} of phosphorescent Ir(III) complexes and their dependencies for doping concentrations by using an integrating sphere.[12] We also discuss about the back energy transfer and the triplet exciton confinement in blue phosphorescent system.

Organic films were fabricated at a thickness of 100 nm by conventional thermal vacuum deposition (10^{-3} Pa) on precleaned quartz substrates for measurement of absolute PL quantum efficiency and on silicon substrates for measurement of transient photoluminescence. The doping concentration and film thickness were controlled by two quartz crystal microbalances calibrated for thickness and two thermal evaporating sources. The η_{PL} of the films was measured under N_2 flow using an integrating sphere[12–14] (Labsphere Co., 10 cm diameter) with a 325-nm-cw HeCd laser (Kinmon TK5651) as the excitation source and multichannel spectrometer (Hamamatsu PMA-11) as the optical detector. The system for η_{PL} measurements was calibrated by using a standard light source and it was confirmed that a neat film of tris(8-quinolinolato)aluminum(III) complex, as a standard fluorescent emitter, showed an η_{PL} of 20%±1% in our system.[12] Furthermore, transient photoluminescence was measured using a streak camera (Hamamatsu C4334) with a

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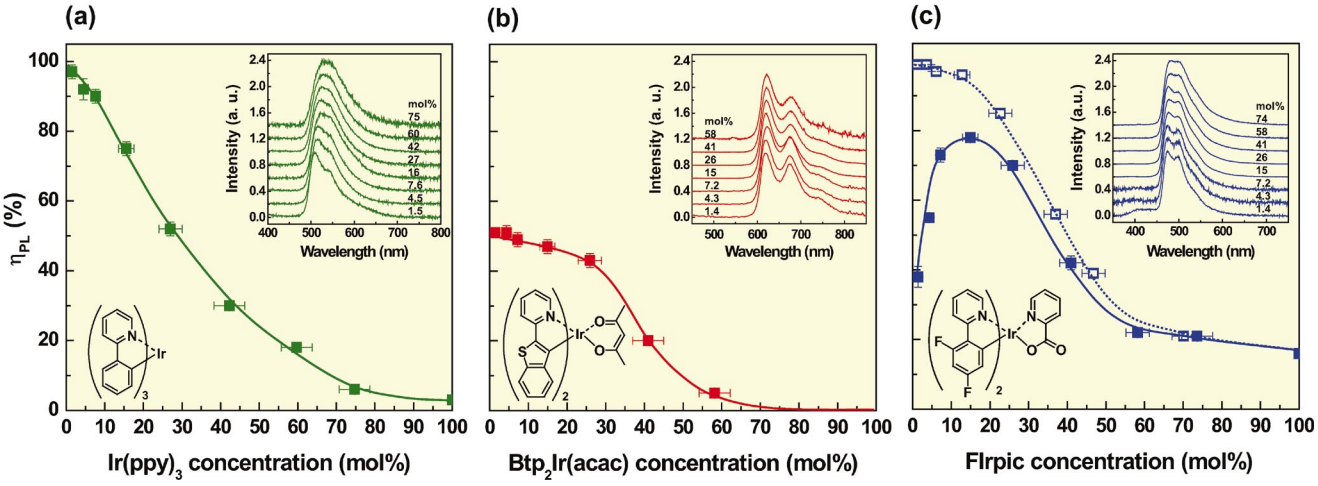

FIG. 1. (Color) PL quantum efficiency η_{PL} vs dopant concentration in (a) Ir(ppy)$_3$:CBP; (b) Btp$_2$Ir(acac):CBP; and (c) FIrpic:CBP (■) and FIrpic:mCP (□). Insets show PL spectra of Ir(III) complex:CBP measured at each dopant concentration (increasing going up on *y* axis): (a) 1.5–75 mol%, (b) 1.4–58 mol%; and (c) 1.4–74 mol%.

N_2 gas laser (MNL 200, Laser Technik Berlin, $\lambda = 337$ nm, pulse width ≈ 500 ps, repetition rate =20 Hz) as the excitation source. The measurements were done under a low pressure ($\approx 10^{-1}$ Pa) in a cryostat.

Figure 1 shows the η_{PL} of the Ir(III) complexes in 4,4′-bis(*N*-carbazolyl)-2,2′-biphenyl (CBP), a conventional host material for emitting layer, as a function of doping percentage. Three Ir(III) complexes were evaluated: Ir(ppy)$_3$ for green, bis[2-(2′-benzothienyl)pyridinato-N,C$^{3\prime}$] (acetylacetonato)iridium(III) [Btp$_2$Ir(acac)] for red, and bis [(4,6-difluorophenyl)pyridinato-N,C^2] (picolinato)iridium(III) (FIrpic) for blue. The doping concentrations of the Ir(III) complexes ranged from 1.2 to 100 mol% (2–100 wt%).

The green phosphorescent Ir(ppy)$_3$:CBP film exhibited an η_{PL} of 97% ± 2% at 1.5 mol% (corresponding to 2 wt%) and 92% ± 3% at 4.5 mol% (6 wt%) [Fig. 1(a)]. At these low doping percentages, it is expected that most of the excitation energy is absorbed by the CBP host which transfers energy with high efficiency to the phosphorescent guest. These results confirm that a dilute concentration of Ir(ppy)$_3$ doped in CBP has a solid state η_{PL} of nearly 100%. This corresponds well to the previous report for a device with a green Ir(III) dopant having an external η_{EL} of 19%.[2] As the concentration of Ir(ppy)$_3$ was increased, significant decreases in η_{PL} were observed resulting in an η_{PL} of less than 3% in the neat film. Additionally, at higher dopant concentrations, the emission peak shifts to a longer wavelength and the full width at half maximum increases [inset of Fig. 1(a)]. These observations clearly demonstrate the existence of self-quenching interactions between Ir(ppy)$_3$ molecules at increased dopant concentrations.

The Btp$_2$Ir(acac):CBP film exhibited a maximum η_{PL} of 51% ± 1% at 1.4 mol% (2 wt%) [Fig. 1(b)]. Despite the fact that η_{PL} also decreased with increasing Btp$_2$Ir(acac) concentration, at a dopant concentration of 26 mol% (33 wt%) the PL intensity was still 90% of its maximum value. This suggests that concentration quenching in the Btp$_2$Ir(acac):CBP film is less effective than observed for the Ir(ppy)$_3$:CBP film. Similar to Ir(ppy)$_3$,[8] the PL intensity of the Btp$_2$Ir(acac):CBP film showed no significant temperature dependence between 5 and 300 K. This result implies that

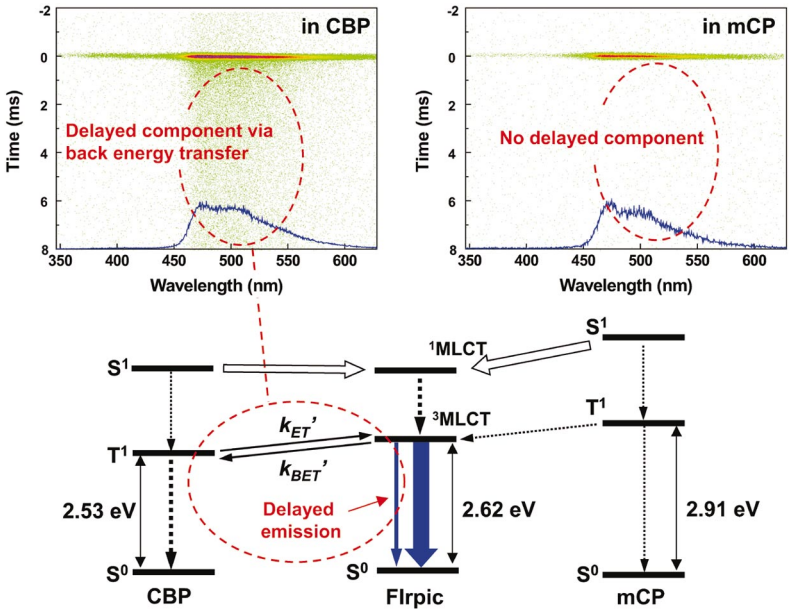

FIG. 2. (Color) Streak images of FIrpic:CBP and FIrpic:mCP films at the 6 wt% doping concentrations (top) and energy levels and energy-transfer schemes for CBP, mCP, and FIrpic (bottom).

$Btp_2Ir(acac)$ has an intrinsic nonradiative decay process that appears to function independently of temperature.

In comparison, the blue phosphorescent FIrpic:CBP films demonstrate very unusual PL characteristics. The η_{PL} increased from $38\% \pm 4\%$ to a maximum of $78\% \pm 1\%$ going from low to intermediate dopant concentration (1.4–15 mol%, corresponding to 2–20 wt%) and then decreased with increasing concentration [Fig. 1(c)]. In contrast to $Ir(ppy)_3$ and $Btp_2Ir(acac)$, FIrpic maintained a rather high η_{PL} of $16\% \pm 1\%$ as a neat film, suggesting that the fluorination on the ppy ligand hinders self-quenching interactions. Since a small amount of emission from the host was observed only at a dopant concentration of 1.4 mol% (2 wt%) [inset of Fig. 1(c)], the increase of η_{PL} at low concentrations can not be attributable to poor energy transfer from CBP to FIrpic but rather to a back energy transfer process from the triplet state of FIrpic to the triplet of CBP. This interaction between FIrpic and CBP has been discussed in a previous publication that describes endothermic energy transfer as a mechanism in a FIrpic:CBP device.[4] Based on the back energy transfer mechanism, more than 40% of the excitation energy in an OLED device comprising 6 wt%-FIrpic:CBP may be nonradiatively wasted through the back energy transfer to the triplet state of CBP.

In order to confirm this potential mechanism for energy loss in blue phosphorescent devices, thin film PL measurements with FIrpic were determined using the high energy host, *m*-bis(*N*-carbazolyl)benzene (mCP). mCP is shown in the literature to have a T_1 energy of 2.91 eV[6] which is considerably higher than that of CBP (T_1 energy =2.53 eV),[4] and should therefore prevent undesired back energy transfer from FIrpic (T_1 energy =2.62 eV).[4] As expected, the η_{PL} of the film of FIrpic in mCP reached $99\% \pm 1\%$ at 1.4 mol% (2 wt%), suggesting that the triplet energy of FIrpic can be completely confined in host materials with a high enough T_1 energy [Fig. 1(c)].

Figure 2 compares streak images for the FIrpic:CBP and FIrpic:mCP films at 6 wt% doping concentrations. In the FIrpic:CBP film, two component decay is observed comprised of a fast decay process and a delayed process. The delayed component is attributed to endothermic back-energy transfer after the triplet energies are migrated between the CBP molecules which have a long excited triplet lifetime. In contrast, no delayed luminescence was observed in the FIrpic:mCP film. These transient PL characteristics are further indications that the triplet energy of FIrpic is sufficiently confined in the FIrpic:mCP film. Blue phosphorescent OLEDs using FIrpic doped into various high energy host materials have been reported, and the highest EL efficiencies η_{EL} values have been limited to about 11%.[6,7] However, the results described here show that blue phosphorescent OLEDs using FIrpic as the dopant can potentially have an external η_{EL} as high as the theoretical limit of 20%. In order to approach this limit, we believe that not only the adequate host material be used, but considerations must be made to other factors such as charge injection balance and confinement, triplet energy diffusion, and interfacial quenching from the adjacent charge transport layers.[8]

In conclusion, the η_{PL} of Ir complexes were measured in solid-state films using an integrating sphere, and the green phosphorescent $Ir(ppy)_3$:CBP film was shown to have an η_{PL} of $97\% \pm 2\%$ (at 1.5 mol%). This value of almost 100% in the solid state is consistent with previous results for temperature dependency of PL and high EL efficiency in a device ($\eta_{EL}=19\%$). Furthermore, the η_{PL} of $Btp_2Ir(acac)$:CBP was $51\% \pm 1\%$ (at 1.4 mol%) and FIrpic:mCP was $99\% \pm 1\%$ (at 1.2 mol%). These results suggest that the η_{EL} of red phosphorescent OLEDs using $Btp_2Ir(acac)$ as the dopant can be as high as 10%, and blue devices using FIrpic can reach the theoretical limit of 20%.

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