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The reduced triplet-triplet annihilation of electrophosphorescent device doped by an iridium complex with active hydrogen

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We demonstrate high efficiency electrophosphorescent devices doped by bis(2-phenylbenzimidazole) iridium (III) acetylacetonate [Ir(ppi)₂acac] with active hydrogen. At 100 mA/cm² 2 wt % Ir(ppi)₂acac doped device offers an external quantum efficiency (η_{ext}) of 5.1% and an efficiency roll-off of 28.2%, which decreases for 33.5% and 39.1% compared with that of 2 and 6 wt % fac-tris(2-phenylpyridine) iridium (III) [fac-Ir(ppy)₃] doped reference devices, respectively. 7 wt % Ir(ppi)₂acac doped device behaves a maximum η_{ext} of 13.4% and a η_{ext} of 8.0% at a luminance of 10 000 cd/m². Both the η_{ext} are higher than that of the reference device. The improvement in electroluminescent performance was assumed to be the very short triplet lifetime (3.74 ns) induced by the active hydrogen atom. © 2008 American Institute of Physics. [DOI: 10.1063/1.2998571]

Organic light-emitting devices (OLEDs) are currently an active research area due to their potential applications in flat-panel displays and solid state lightings.^{1–5} Except for fluorescent OLED materials, octahedral 4d⁶ and 5d⁶ metal complexes based phosphorescent (Ph) materials such as the Ir-complexes have attracted much attention on improvement in OLED efficiency because these complexes can provide the close-lying π - π^* and metal to ligand charge transfer states that combine together with the heavy atom effect to enhance the spin-orbit coupling. Finally both singlet and triplet excitons can be used causing nearly unity of internal quantum efficiency.^{5–9} Problems exist in the work processes of PhOLEDs. (1) If lower phosphor concentration was used in the device, host or adjacent layer would also provide emission because the larger distance between the dopant and host exceeds the Dexter energy transfer radius leading to the decline of the EL efficiency.^{1–4,10} (2) The EL efficiency drops badly if the doping concentration rises due to the concentration quenching that resulted from the phosphor aggregate.¹¹ (3) Even though a suitable doping concentration was used, the efficiency roll-off at high drive current could occur due to the well known long triplet (*T*) lifetime (microsecond level) of the phosphors. The efficiency roll-off is caused by the long triplet lifetime of the phosphor that shows inverse proportion with the molecule aggregate, which can be proven by fact that there is a shorter triplet lifetime of the common phosphors in film state than in dilute solution.^{12–14} Many researches based on minishing the molecule aggregate have been reported,^{11,15} but attention paid on strengthening the molecule aggregate has been reported rarely.

In this letter, we employ an Ir-phosphor with active hydrogen but without substitution, bis(2-phenylbenzimidazole)iridium(III) acetylacetonate [Ir(ppi)₂acac]. At 100 mA/cm² 2 wt % Ir(ppi)₂acac doped device offers an external quantum efficiency (η_{ext}) of 5.1% and an efficiency roll-off of 28.2%, which decreases for 33.5% and 39.1% compared to that of 2 and 6 wt % fac-tris(2-phenylpyridine) iridium (III) [fac-Ir(ppy)₃] doped reference devices, respectively. External quantum efficiency was calculated by the formula $\text{EQE} = \pi^* \text{ sum photons/current density}$. The synthesis process is described in Fig. 1.

Absorption spectra were measured with a Shimadzu UV-3101PC UV-visible-near infrared scanning spectrophotometer. The photoluminescent (PL) excited state lifetimes were determined by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:yttrium aluminum garnet laser with a THG 355 nm output. PL spectra were carried out with a Hitachi F-4500 fluorescence spectrophotometer in air. The synthesized Ir-complex was characterized by ¹H NMR and mass data, respectively. The fabrication and EL charac-

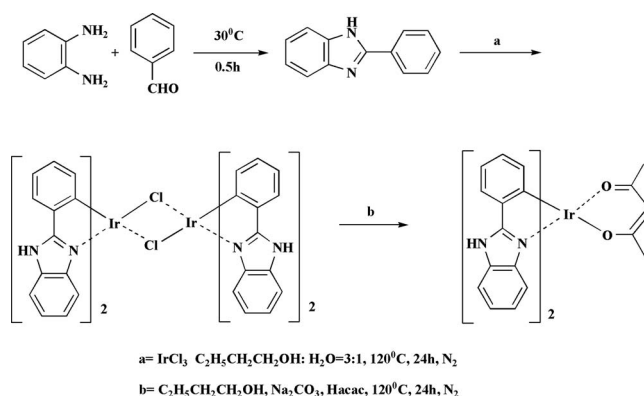


FIG. 1. Synthesis of complex Ir(ppi)₂acac and its chemical structure.

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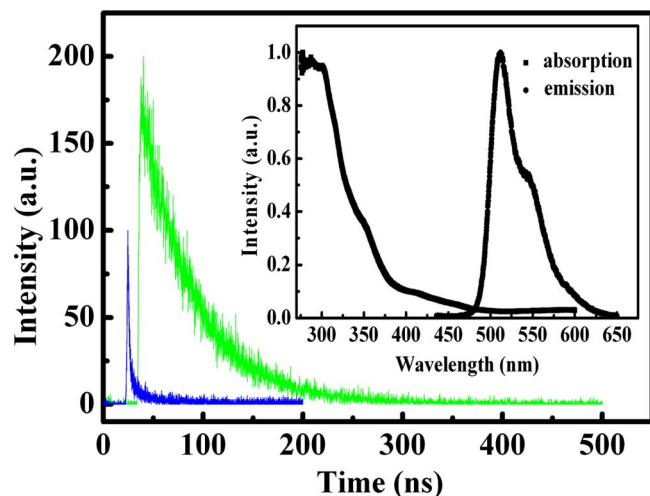


FIG. 2. (Color online) Transient PL decay characteristics of 7 wt % Ir(ppy)₂acac in solid state CBP film (blue) and in solution (green) of CH₂Cl₂; the detected wavelength is 513 nm. Inset: normalized UV-visible and PL spectra of Ir(ppy)₂acac in CH₂Cl₂ solution with the concentration of 10⁻⁵ M under an excited wavelength of 365 nm.

teristics of PhOLED devices were mainly carried out by the previous reported processes in our group.¹⁶ Device structures with indium tin oxide (ITO)/NPB (35 nm)/4,4'-N,N'-dicarbazole-biphenyl (CBP): *x* wt % Ir(ppy)₂acac (30 nm)/BCP (10 nm)/AIQ (20 nm)/LiF (1 nm)/Al (100 nm), here NPB, CBP, and AIQ, denote 4, 4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl, 2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline, and tris-(8-hydroxyquinoline)aluminum, which act as the hole transporting layer (HTL), exciton blocking layer, and electron transporting layer, respectively, and *x* is from 2 to 9. fac-Ir(ppy)₃ doped devices with *x*=2 and 6 were called as reference devices hereafter. The highest occupied molecule orbit and the lowest unoccupied molecule orbit levels of Ir(ppy)₂acac were analyzed by cyclic voltammetry, and the values are 4.9 and 2.5 eV, respectively.

The absorption and PL spectra of Ir(ppy)₂acac in CH₂Cl₂ solutions are described in the inset of Fig. 2; the Ir-complex in CH₂Cl₂ solution offers a 511 nm peak wavelength with a 543 nm shoulder band in PL at room temperature, which displays vibronic progressions that just look like other Ir-complexes reported.^{17,18} Figure 2 indicates the transient PL decay times in solid state film of 7 wt % Ir(ppy)₂acac doped CBP host and in solution, respectively. We observe that the Ir-complex shows a single exponential decay curve, the ex-

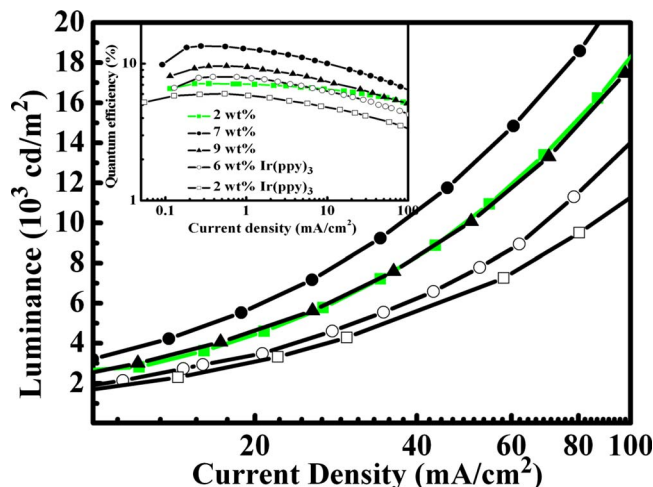


FIG. 3. (Color online) The luminance and current density relationship of the devices [2, 7, and 9 wt % doped Ir(ppy)₂acac and 2, 6 wt % fac-Ir(ppy)₃ doped devices]. Inset: the external quantum efficiencies and the current density characteristics of the devices.

cited state lifetimes in the film and in the solution were fitted to be ~3.73 and ~52 ns, respectively, which are markedly shorter than that (713 ns) of fac-Ir(ppy)₃ complex doped CBP film. We attribute the short excited state lifetimes to the strong interaction between >N-H in imidazole group of one molecule and >C=O in acetylacetonate ligand of another molecule (see Fig. 1); as the two groups coexist together, active hydrogen is familiar in many compounds.^{19,20} Just as the above argument, the active hydrogen would rise the intermolecular interaction of Ir(ppy)₂acac molecules so that the molecule aggregate between the Ir(ppy)₂acac complexes increased, which leads to short triplet lifetime.

EL performances of Ir(ppy)₂acac and fac-Ir(ppy)₃ doped devices with various concentrations are summarized in Table I. It can be seen that the maximum η_{ext} of 7 wt % Ir(ppy)₂acac doped device is 13.4%, which increases by 67.5% than that of 6 wt % fac-Ir(ppy)₃ doped reference device, and at a luminance (*L*) of 10 000 cd/m², 7 wt % Ir(ppy)₂acac doped device still exhibits a η_{ext} of 8.0% that is higher for almost double than that (4.6%) of 6 wt % fac-Ir(ppy)₃ doped reference device.

Suitable phosphor concentration of general fac-Ir(ppy)₃ doped PhOLED devices was well known 6–8 wt %, and the EL efficiency roll-off would occur at the high drive current, but if the doping concentration is lower than this value, the blue emission of NPB would be observed due to the long lifetime triplet (*T*) excitons formed in the emitting layer (EML) diffuse forward to the HTL, which leads to low efficiency.^{1-4,8,11} However, because the triplet lifetime of Ir(ppy)₂acac is too short compared with that of fac-Ir(ppy)₃, the triplet excitons formed in EML emit prior to transport forward to HTL; thus we could expect that lower Ir(ppy)₂acac concentration doped device could also harvest higher η_{ext} . Figure 3 and its insert describe the relations between the *L* and η_{ext} versus current density for 2, 7, and 9 wt % Ir(ppy)₂acac doped devices and 2 and 6 wt % fac-Ir(ppy)₃ doped reference devices. It is noticed that 2 wt % Ir(ppy)₂acac and 6 wt % fac-Ir(ppy)₃ doped devices behave the maximum η_{ext} of 7.1 and 8.0% as well the η_{ext} of 5.1 and 4.3% at 100 mA/cm², respectively, that is, the η_{ext}

TABLE I. EL performances of OLEDs with various Ir(ppy)₂acac and fac-Ir(ppy)₃ concentrations.

Doping concentration (wt %)	η_{ext}^a (%)	η_{ext}^b (%)	η_{ext}^c (%)	<i>L</i> ^d (%)	λ^e (nm)
2	7.1	5.7	5.1	38 920	513
7	13.4	8.0	6.5	55 060	513
9	9.6	5.8	5.1	42 659	513
2[fac-Ir(ppy) ₃]	5.9	3.5	3.4	29 970	507(NPB:449)
6[fac-Ir(ppy) ₃]	8.0	4.6	4.3	48 503	507

^aMaximum external quantum efficiency.

^bExternal quantum efficiency at the luminance of 10 000 cd/m².

^cExternal quantum efficiency at 100 mA/cm².

^dMaximum luminance.

^ePeak wavelength of EL.

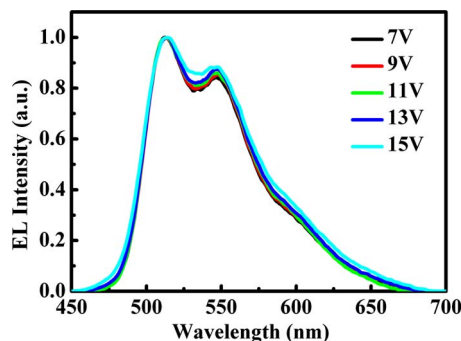


FIG. 4. (Color online) The normalized EL spectra of the 2 wt % Ir(ppy)₂acac doped device from 7 to 15 V.

at 100 mA/cm² was improved by 18.6% and the efficiency roll-off decreased by 39.1% for our device compared to the reference device, although the peak η_{ext} is higher by only 12.7% for the latter than the former. The findings indicate that our 2 wt % new Ir-complex doped device behaves considerably mitigation of the efficiency roll-off.

From Table I and Fig. 3 we also observed that the efficiency roll-off of 2 wt % Ir(ppy)₂acac and 2 wt % fac-Ir(ppy)₃ doped devices are 28.2% and 42.4%, respectively; the reason for decreased efficiency roll-off of Ir(ppy)₂acac doped device could be explained as follows. Triplet excitons would keep at comparative high concentration in the EML because the triplet excitons with short excited state lifetime were not easily diffused into the adjacent NPB layer leading to NPB emission;^{5,11} this can be proved by the EL spectra shown Fig. 4 in which NPB emissions are not observed under any drive bias voltages. On the other hand lower exciton density that resulted from the low doping concentration at higher drive current can also be in favor of mitigation of the *T-T* annihilation; we can conjecture that in the 7 wt % Ir(ppy)₂acac doped device the effects of the short triplet lifetime and the *T-T* annihilation that resulted from the intermolecular aggregation would basically keep a balance, so a maximum η_{ext} of 13.4% was obtained. When the doping concentration increased to 9 wt % η_{ext} descends due to the predominant *T-T* annihilation.

In summary, we have synthesized Ir(ppy)₂acac with active hydrogen that considerably shorten the excited state lifetime of the complex; the EL performances of the Ir(ppy)₂acac doped devices were improved considerably. The fabricated device using much lower concentration such as 2 wt% behaves markedly mitigation of efficiency roll-off at a

100 mA/cm² compared to that of 6 wt % fac-Ir(ppy)₃ doped reference device; we attribute the improvement to the reduced triplet-triplet annihilation. Besides, η_{ext} is higher for 7 wt % Ir(ppy)₂acac doped device (8.0%) than for 6 wt % fac-Ir(ppy)₃ doped reference device (4.6%) at a luminance of 10 000 cd/m². So the short triplet lifetime should be very important for improving EL intensities of either lower or higher concentration phosphor doped devices.

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