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Reduced efficiency roll-off in electrophosphorescent devices by a short-living rhenium emitter with well-matched energy levels

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We demonstrated reduced efficiency roll-off in electrophosphorescent devices based on a rhenium [Re(I)] complex, {9, 9-Di-[9′-(4″-phenoxybutyl)-9′*H*-carbazyl]-9-*H*-4,5-Diazafluorene Re(CO)$_3$Br} (Re-PCDF). The devices based on Re-PCDF exhibited the peak luminance of 7888 cd/m^2 and the maximum efficiency of 7.41 cd/A, respectively. Remarkably, the devices exhibited very small efficiency roll-off with only ca. 28%, which is much better than the reported Re(I) complexes based devices. Such excellent performances could be ascribed to the short luminescent lifetime of Re-PCDF and well-matched energy levels between the singlet host and the triplet emitter. The detailed mechanisms of such small efficiency roll-off were also investigated. © *2010 American Institute of Physics*. [doi:10.1063/1.3531576]

High-efficiency phosphorescent organic light-emitting diodes (PHOLEDs) are increasingly important in recent years as theoretical maximum internal quantum efficiency value of 100% is achievable in those devices.[1,2] Rhenium (Re) complexes, as a class of promising electroluminescent (EL) phosphorescent materials in PHOLEDs have attracted much attention over the past decades due to their high phosphorescence quantum yield at room temperature, relatively short excited state lifetime, excellent thermal and photochemical stabilities and so on.[3–5] Currently, some achievements have been achieved in application of Re(I) complexes as emitters in PHOLEDs. Liu *et al.* reported Re(I)-based PHOLEDs with a maximum current efficiency of 17.6 cd/A.[6] The Re(I)-based PHOLEDs reported by our group reached a peak luminance of 8315 cd/m^2 and a maximum efficiency of 21.8 cd/A.[7] However, the devices' performances based on Re(I) complexes are still unsatisfactory when compared with those of PHOLEDs containing Ir(III) complexes as emitters.[8–11] Especially, it was found that the device efficiency dropped rapidly with an increase in the current density in Re(I)-based PHOLEDs, making them difficult to be used in large area displays and general illuminations. Detailed research suggests that the triplet-triplet (T-T) annihilation,[12–14] electric field induced dissociation of excitons,[15] and triplet-polaron annihilation[12] are responsible for the rapid efficiency roll-off at high current densities. To resolve the efficiency roll-off issue, many tactics were adopted such as mixed emissive host and multilayer device structures,[16,17] fluorescence compensating layer[18] and so on. Common bottlenecks among those approaches mainly include the complexity of device fabrication which is difficult to commercial production. A more effective way employing a short-living Ir(III) complex as emitter to suppress the efficiency roll-off had been realized.[19] To date, there was no report on address the efficiency roll-off issue of PHOLEDs based on Re(I) complexes. 4,5-Diazafluorene derivatives and their complexes have stimulated interests in photoisomerization, biochemical, biomedical applications and so on,[20–22] while they are less studied in OLEDs.[5] In this letter, we demonstrate a neutral Re(I) complex, {9, 9-Di-[9′-(4″-phenoxybutyl) - 9′*H*-carbazyl] - 9-*H* - 4,5-Diazafluorene Re(CO)$_3$Br} (Re-PCDF) as triplet emitter in PHOLEDs. The devices exhibit a peak luminance of 7888 cd/m^2, a maximum efficiency of 7.41 cd/A, and very low efficiency roll-off of only ca. 28%, respectively. Such excellent performances are attributed to the short luminescent lifetime of this Re(I) complex and its well-matched energy levels with the commonly used host material, 4,4′-N,N′-dicarbazole-biphenyl (CBP).

Re-PCDF was synthesized in our laboratory and fully characterized by mass spectroscopy, ^{1}HNMR and elemental analysis. Detailed synthetic procedures will be reported elsewhere. Re-PCDF is sufficiently stable to be sublimed and its chemical structure is depicted in Fig. 2. UV-vis absorption spectra were obtained on a PerkinElmer Lambda 900 spectrophotometer. Photoluminescence (PL) spectra were measured on a PerkinElmer LS 55 fluorescence spectrophotometer. The luminescent lifetime of Re-PCDF in solid state was detected by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:YAG laser with a Third-Harmonic-Generator 355 nm output. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of Re-PCDF were analyzed by cyclic voltammetry. The fabrication and EL characteristics of PHOLEDs were carried out by previously reported processes.[18] The devices have the common structure of indium tin oxide (ITO)/4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenyl-amine (m-MTDATA) (10 nm)/4′-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl(NPB) (20 nm)/CBP:

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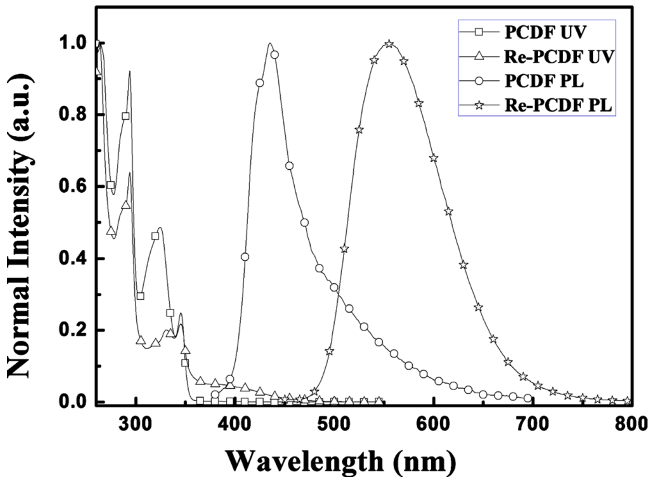

FIG. 1. (Color online) UV-vis absorption and PL spectra of PCDF and Re-PCDF in dichloromethane solution.

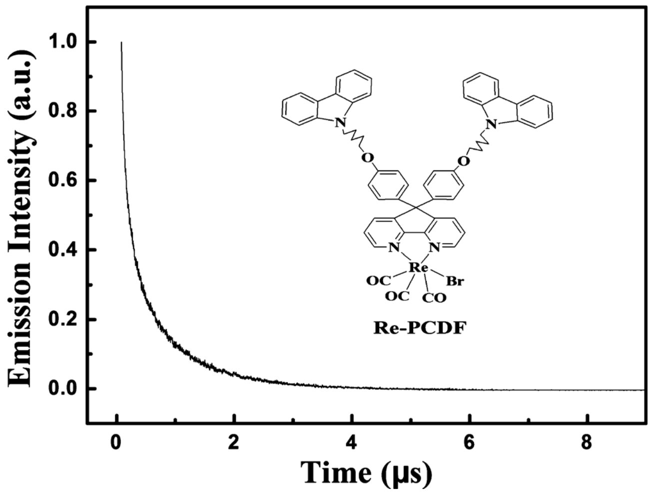

FIG. 2. Emission decay curve of Re-PCDF powder and its chemical structure.

Re-PCDF(30 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (10 nm)/tris(8-hydroxyquinoline)aluminum (Alq_3) (20 nm)/ LiF (1 nm)/Al (150 nm). m-MTDATA, NPB, Bphen, and Alq_3 were used as hole injection layer, hole transporting layer, exciton blocking layer and electron transporting layer, respectively, and LiF/Al as the composite cathode. EL spectra were measured with a Hitachi MPF-4 fluorescence spectrophotometer. The luminance-current-voltage (*L-I-V*) characteristics were measured with a 3645 dc power supply combined with a spot photometer and were recorded simultaneously with measurements.

Both absorption and PL spectra in an ambient dichloromethane solution are shown in Fig. 1. By comparison to the absorption of the free ligand (PCDF), the absorption band located at $\lambda < 350$ nm can be assigned to spin-allowed $^1\pi$-π^* PCDF-centered transitions. The moderately intense absorption bands extending into the visible region from 360 to 500 nm are tentatively assigned to an admixture of metal-to-ligand charge transfer states, $d\pi(\mathrm{Re}) \rightarrow \pi^*(\mathrm{PCDF})$ (^{1}MLCT and ^{3}MLCT). Re-PCDF emits intensively with yellow phosphorescence peaked at 557 nm, which can be assigned to radiative transitions from ^{3}MLCT level.[23] The PL quantum yield of Re-PCDF measured in deaerated dichloromethane is as high as 12% by using quinine sulfate as a reference.[4]

As has been proved, the phosphorescent lifetime is a key factor for T-T annihilation. The luminescence lifetime (τ) is determined by the sum of radiative probability (k_r) and nonradiative probability (k_{nr}), as depicted by the equation $\tau = 1/(k_\mathrm{r} + k_\mathrm{nr})$. The strong steric hindrance of PCDF may distort the coordination geometry, resulting in the asymmetric coordination environment around the Re(I) center and, consequently, the increased k_r. Moreover, the concomitant geometrical changes and the associated skeletal vibrations could also facilitate an efficient nonradiative decay.[24,25] Therefore, the Re-PCDF would exhibit the short luminescent lifetime. The luminescence decay curve of Re-PCDF powder is shown in Fig. 2. According to Fig. 2, the phosphorescence decay of Re-PCDF follows the single exponential equation: $y = A_1 \times \exp(-x/t_1) + y_0$, so its lifetime is 0.09 μs which is short enough to suppress T-T annihilation at high current densities.

The *L-I-V* characteristics of 8 wt % Re-PCDF doped device are plotted in Fig. 3. The device exhibits the peak luminance of 7888 $\mathrm{cd/m^2}$ at 19 V, which is comparable with that of the Re(I)-based PHOLEDs.[6,7] The turn-on voltage of the device is lower than 7 V. The EL spectra of the same device are shown in inset of Fig. 3, which exhibit the identical emission at different voltages. Moreover, the EL spectra do not consist of any other residual emission from host or NPB, indicating complete energy transfer from the singlet host to the triplet emitter upon electrical excitation.

Figure 4 depicts current density vs current efficiency curves of different ratio Re-PCDF doped PHOLEDs. It can be seen that a maximum current efficiency of 7.41 cd/A at 7.7 $\mathrm{mA/cm^2}$ is achieved. Obviously, reduced efficiency roll-off is observed. For those devices, the efficiency roll-off is only ca. 28% at 100 $\mathrm{mA/cm^2}$, which is much better than those of the reported Re(I)-based PHOLEDs.[6,7] The reasons for reduced efficiency roll-off of Re-PCDF doped devices could be explained as follows according to the inset of Fig. 4. It can be found that there exists a potential of only 0.33 eV for hole transfer from CBP to Re-PCDF, so hole transfer from CBP to Re-PCDF is energetically favorable and Re-PCDF can form shallow positive charge traps in the CBP host. Furthermore, the barrier for electron transfer is also as small as 0.02 eV. The positive charges could disperse not

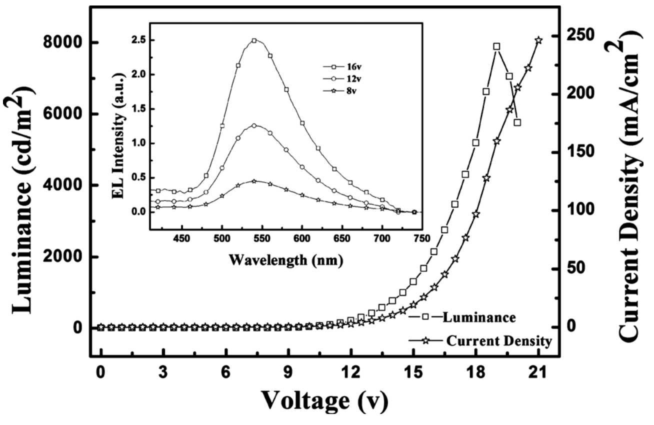

FIG. 3. *L-I-V* characteristics of 8 wt % Re-PCDF doped device. Inset: EL spectra of 8 wt % Re-PCDF doped device.

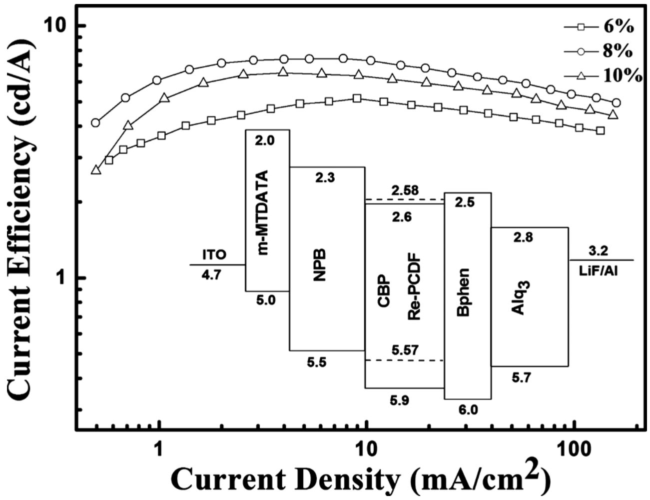

FIG. 4. Current density vs current efficiency curves of different ratio Re-PCDF doped PHOLEDs. Inset: the proposed HOMO and LUMO energy levels diagram.

only on the guest emitter at the interface but also on the host. Therefore, energy transfer from host to guest will also occur in addition to direct carrier recombination on Re-PCDF. The excitons which are formed on the CBP molecule at the recombination zone can be transferred to the guest Re-PCDF molecule located far away from the interface via energy transfer. This will result in low exciton density and uniform distribution of excitons in the whole emitting layer, significantly reducing T-T annihilation.[26,27] As a result, reduced efficiency roll-off at high current densities is achieved.

In summary, high-efficiency PHOLEDs with reduced efficiency roll-off were fabricated with Re-PCDF as a dopant triplet emitter. The 8 wt % Re-PCDF doped device exhibited the peak luminance of 7888 cd/m^2 and the maximum efficiency of 7.41 cd/A, respectively. Remarkably, the reduced efficiency roll-off of only ca. 28% in Re(I)-based PHOLEDs was favorably realized. Such excellent performances were attributed to the short luminescent lifetime of Re-PCDF and well-matched energy levels between the host CBP and the triplet emitter Re-PCDF. Our results indicate that this type of phosphorescent materials is useful for practical applications in flat panel displays and illuminations.

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