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Triphenylamine-functionalized rhenium (I) complex as a highly efficient yellow-green emitter in electrophosphorescent devices

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A complex (3-ethyl-2-(4′-triphenylamino)imidazo[4,5-*f*] 1,10-phenanthroline) $Re(CO)_3Br$ functionalized by a hole-transport group triphenylamine was used to fabricate organic light-emitting devices (OLEDs). A current efficiency up to 17.6 cd/A corresponding to a power efficiency of 9.2 ml/W and a peak brightness as high as 6500 cd/m^2 were obtained. These results represent the best values reported for OLEDs based on rhenium complexes. Enhanced carrier injection capability of Re complex and efficient charge-trapping formation followed by triplet exciton confinement in the emissive layer make for the outstanding electrophosphorescent performances. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2408638]

Organic light-emitting devices (OLEDs) have experienced dramatic advances since early successful demonstrations of luminescence from electrophosphorescent materials incorporating heavy metal complexes.[1] These triplet emitters have the potential of achieving an internal quantum efficiency of 100%, which is three times higher than that of electroluminescent (EL) devices based on fluorescent materials.[2,3] In recent years, tricarbonyl di-imine rhenium complexes as a new class of EL materials have been explored due to their highly desirable properties including relatively short excited state lifetime, intense phosphorescence emission, and high stability.[4] Li *et al.* presented efficient devices based on (2,9-dimethyl-1,10-phenanthroline) $Re(CO)_3Cl$ doped into 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) with a high current efficiency of 7.15 cd/A.[5] Yellow electrophosphorescence devices with power efficiency of 1.6 lm/W were reported by utilizing energy transfer from BePP$_2$ (PP=2-(2-hydroxyphenyl)-pyridine) to (Bu^{t}bpy)Re(CO)$_3$Cl (Bu^{t}bpy=4,4′-bi(*tert*-butyl)-2,2′-bipyridine).[6] In addition, white eletrophosphorescence from the mixing of yellow emission from (4,4′-dimethyl-2,2′-bipyridine)Re(CO)$_3$Cl and blue emission from *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) was also reported.[7] All of the above achievements indicate that rhenium complexes have emerged as promising candidates for OLED applications. However, in order to meet the requirement for practical application, the device performance should be further improved. It has been demonstrated that the introduction of carrier transporting groups into emissive materials can enhance the device performance. Niu *et al.* reported highly efficient electrophosphorescent devices based on a trifunctional platinum complex.[8] In their work, a maximum luminous efficiency of 1.2 cd/A and a luminance of 1065 cd/m^2 were obtained. Gong *et al.* also showed the application of funtionalized rhenium complexes as emitter in EL devices, but the maximum brightness of device was only 730 cd/m^2.[9] Herein, we report high-efficiency elecrophos-

phorescent devices fabricated by doping Re-TPIP into CBP. These devices emit strong yellow-green light with an emission maximum at 552 nm. The peak brightness in excess of 6480 cd/m^2 at 16 V, maximum current efficiency up to 17.6 cd/A, corresponding to the power efficiency of 9.2 lm/W at 6 V were achieved. These values are the best reported for devices employing rhenium complexes as emitters so far.

Ligand 3-ethyl-2-(4′-triphenylamino)imidazo[4, 5-*f*] 1,10-phenanthroline (TPIP) and corresponding complex Re-TPIP were synthesized separately according to literature procedures.[10,11] Figure 1 depicts chemical structure of Re-TPIP and device configuration. The phosphorescent lifetime of Re-TPIP measured in solid film state at room temperature is 0.2 μs. The devices have the structure of indium tin oxide, /4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) (30 nm)/NPB (20 nm)/CBP:*x* wt. % Re-
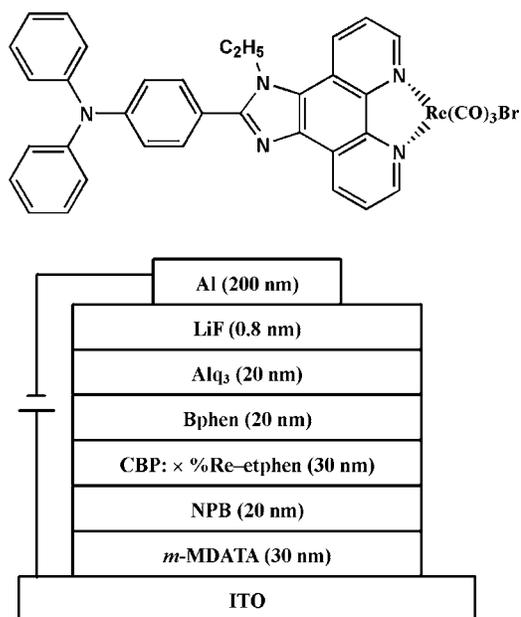

FIG. 1. Chemical structure of Re-TPIP and device configuration.

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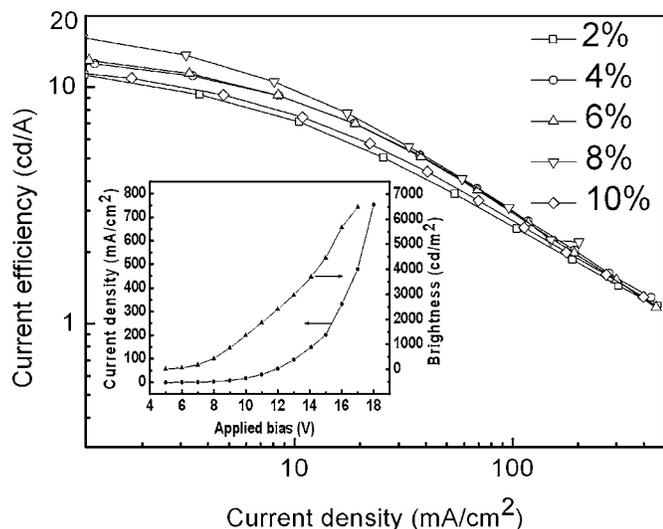[b]Electronic mail: syliu@mail.jlu.edu.cn

FIG. 2. Dependence of current efficiency on current density at different concentrations of Re-TPIP in CBP. Inset: Current density-brightness–voltage-characteristics of a device based on 8 wt. % Re-TPIP in CBP.

TABLE I. Device performance of OLEDs based on Re-etphen.

Concentration (%)	η_{max} [a]	η_2 [b]	η_3 [c]	η	η_{max} [e]	B_{max} [f]
2	11.7	2.6	1.3	11.4	6.2	5476
4	12.5	3.0	1.4	12.5	6.1	5558
6	13.0	3.0	1.4	12.7	6.5	5339
8	17.6	3.0	1.6	16.8	9.2	6483
10	12.0	2.8	1.3	11.8	6.2	5172

[a]Maximum current efficiency (cd/A).
[b]Current efficiency at 100 mA/cm^2 (cd/A).
[c]Current efficiency at 400 mA/cm^2 (cd/A).
[d]Current efficiency at 100 cd/m^2 (cd/A).
[e]Maximum power efficiency (lm/W).
[f]Maximum brightness (cd/m^2).

TPIP (30 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (20 nm)/tris(8-hydroxyquinoline) aluminum (Alq$_3$) (20 nm)/LiF (0.8 nm)/Al (200 nm). *m*-MTDATA was used as the hole injection material and NPB was employed as the hole transporter. Bphen, Alq$_3$, and LiF/Al were used as the hole blocker, the electron transporter, and the cathode, respectively. Re-TPIP was doped into the host material CBP with mass ratios of 2–10 wt. %, and acted as light-emitting layer. Vacuum vapor deposition was used to fabricate the emissive layers since Re-TPIP is stable enough to be sublimed. The pressure of the chamber is below 3×10^{-4} Pa. UV-vis absorption spectra were recorded using Shimadzu UV-3000 spectrophotometer. PL spectra was measured with a RF-5301Pc spectrofluorophotometer. EL spectra and Commission Internationale De L'Eclairage coordination of these devices were measured by a PR650 spectra scan spectrometer. The luminance-current density-voltage characteristics were recorded simultaneously with the measurement of EL spectra by combining the spectrometer with a Keithley model 2400 programable voltage-current source. Fluorescence lifetime was obtained with a 266 nm light generated from the fourth-harmonic-generator pumped, which using the pulsed Nd:YAG (yttrium aluminum garnet) laser as the excitation source. The Nd:YAG laser was with a linewidth of 1.0 cm^{-1}, pulse duration of 10 ns, and repetition frequency of 10 Hz. A rhodamine 6G dye pumped by the same Nd:YAG laser was used as the frequency-selective excitation source. All measurements were carried out in air at room temperature.

Figure 2 presents the effect of doping levels on current efficiency of EL devices based on Re-TPIP. Benefiting from the short lifetime of Re complex, all devices exhibited a gradual decrease in current efficiency with increasing current density. Table I shows the key characteristics of these devices. The turn-on voltage of all four devices is lower than 5 V. The efficiencies at the benchmark luminance of 100 cd/m^2 are almost equal to the maximum efficiency. Even at high current density of 100 mA/cm^2, the devices can maintain 20% of the maximum efficiency. The maximum efficiency as high as 17.6 cd/A corresponding to the power efficiency of 9.2 ml/W, and the peak brightness up to

6480 cd/cm^2 were obtained. To date, this is a significant improvement in performance over the devices using rhenium complexes as emitters. As in the case of other rhenium complexes-based phosphorescent OLEDs, the device performance shows a strong dependence on the doping concentration. When Re-TPIP was blended with CBP in a mass ratio of 8 wt. %, the device demonstrated the best performance. The inset of Fig. 2 shows the current-density-brightness-voltage characteristics of the optimized device. The device demonstrates a peak brightness of 6480 cd/m^2, a maximum current efficiency of 17.6 cd/A, and a current efficiency of 9.7 cd/A at luminance of 1000 cd/m^2. Even at a high luminance of 3000 cd/m^2 with current density of 100 mA/cm^2, the current efficiency of this device remained as high as 3.0 cd/A. These values are greatly improved compared with the previous reports on OLED incorporating rhenium complexes. We thought the introduction of a triphenylamine moiety in Re-TPIP molecule can improve the carrier's injection ability of complex and, consequently, contribute to the improved performances. In addition, efficient exciton formation on the Re-TPIP molecules by direct charge trapping and confinement within the emissive layer is also responsible for the excellent performances. This can be inferred from the following analysis of the PL spectra, EL spectra of Re-TPIP doped films in CBP, and the current density-voltage characteristics of the devices based on Re-TPIP with different doping levels.

The absorption spectrum of Re-TPIP in chloroform solution, PL spectrum of CBP are plotted in Fig. 3. The broad weak absorption band that centers at 375 nm is typical for spin-allowed metal ($d\pi$) to ligand (π^*) charge-transfer (^{1}MLCT) transition. There exists a partial overlap between
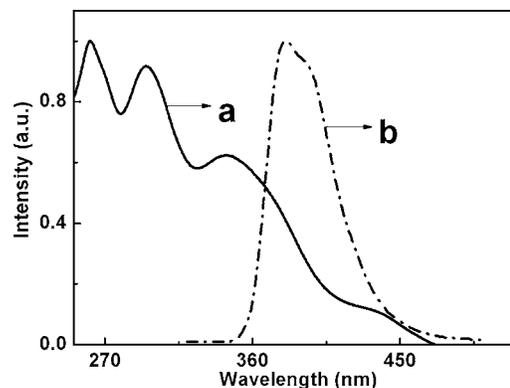

FIG. 3. Absorption spectrum of Re-TPIP in CH$_2$Cl$_2$ solution (a) and PL spectrum of CBP film (b).
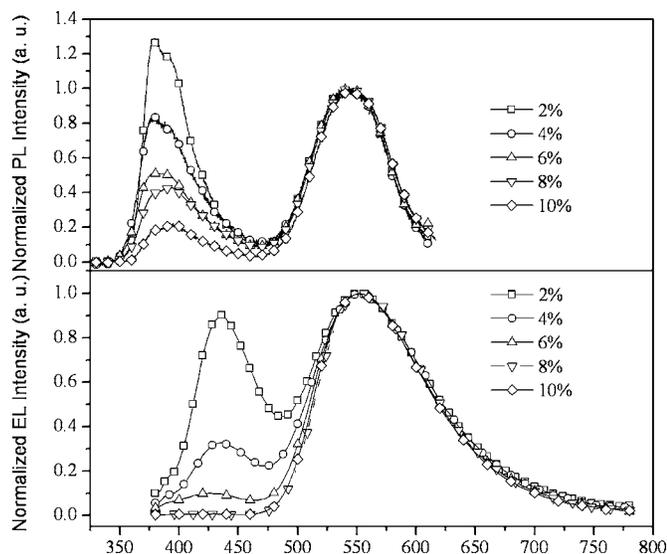
FIG. 4. PL and EL (16 V) spectra of Re-TPIP with various concentrations in CBP.

the fluorescence spectrum of CBP and the absorption spectrum of Re-TPIP. Consequently, as shown by the PL spectra of Re-TPIP doped films in CBP (Fig. 4), the emission from the host cannot be completely quenched even with more than 10 wt. % of Re-TPIP. This implies that the Förster energy transfer from the singlet-excited state in the host (CBP) to the ^{1}MLCT state of the guest (Re-TPIP) occurs only at a moderate level. In a sharp contrast to the PL spectra, the EL spectra show no CBP emission even at very low dopant concentration, as displayed in Fig. 4. However, at lower concentrations, an additional dim blue emission originating from NPB is observed except the strong Re-TPIP emission. The significant differences between the EL and PL spectra of Re-TPIP doped films in CBP indicate that direct charge trapping is the dominating role in the EL process, which is further supported by the current-density versus voltage (*J-V*) characteristics of the EL devices based on Re-TPIP with different doping levels. As illustrated in Fig. 5, with increasing doping concentrations, the *J-V* characteristic curves shift gradually to higher voltage, suggesting that the trapping effect of the rhenium complex basically decreases the carrier transport mobility. So, the electrons and holes in the emissive layer
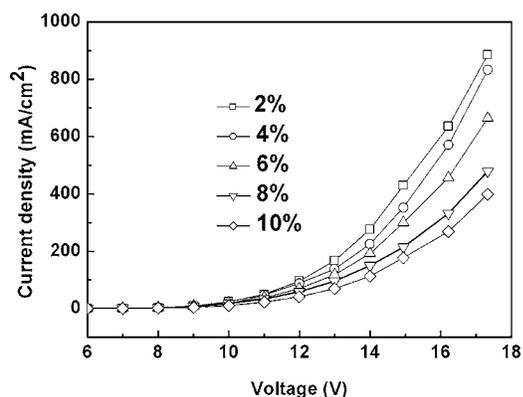
can be trapped by the Re-TPIP molecules directly, followed by subsequent exciton formation and light emission originating from the Re complex. The existence of a triphenylamine moiety in complex can facilitate carrier injection and, consequently, leads to efficient exciton formation on the Re-TPIP molecules and efficient electrophosphorescence. As the dopant concentration is low, accumulated holes in NBP layer meet the electrons injected from the opposite direction to form the excitons, resulting in NPB emission in addition to exciton formation at Re-TPIP. With increase of doping levels, more and more electrons can be intercepted and trapped by Re-TPIP and the contribution from NPB decreased. At Re-TPIP concentrations higher than 6 wt. %, no electrons were injected into NPB layer, so the NPB emission has gone. Another important feature in our devices is that white EL emission (Commission International de L'Eclairage chromaticity coordinates at $X=0.32$, $Y=0.36$) with the maximum current efficiency of 1.1 cd/A, and the brightness of 5500 cd/m^2 is observed from the device with 2 wt. % Re-TPIP in CBP at 16 V, suggesting that the combination of Re-TPIP and blue emitters may result in efficient white OLEDs. The work on improving the efficiency of white OLEDs based on Re-TPIP and other blue emitters is currently in progress.

In summary, we have demonstrated high-efficiency electrophosphorescent devices employing Re-TPIP as an emitter. The devices exhibited a maximum current efficiency up to 17.6 cd/A, corresponding to a power efficiency of 9.2 ml/W, and a peak brightness as high as 6500 cd/m^2. High efficiency can be maintained even at high current densities. These performances are the best reported for devices employing Re(I) complexes as emitters so far. Enhanced charge injection, efficient charge trapping followed by triplet-exciton confinement within the light-emitting layer should be responsible for such an outstanding performance. The emissive colors from Re-TPIP and NPB complement each other resulting in white EL emission with $X=0.32$, $Y=0.36$, suggesting that the combination of Re-TPIP and any other blue emitters may give rise to efficient white OLEDs.

FIG. 5. Current-density vs voltage characteristics of the EL devices based on Re-TPIP with different concentrations.

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