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Highly efficient phosphorescent organic light-emitting devices based on Re(CO)$_3$Cl-bathophenanthroline

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Abstract

Highly efficient orange organic electroluminescent devices based on Re(CO)$_3$Cl-bathophenanthroline have been fabricated. A device with 9 wt% shows the highest efficiencies of 13.8 cd A^{-1} (luminance efficiency), 8.69 lm W^{-1} (power efficiency) and 5.24% (external quantum efficiency). Maximum luminance over 4000 cd m^{-2} is obtained. By discussing the mechanisms, it is believed that trapping contributes mostly to these relatively much higher efficiencies.

Organic light-emitting diodes (OLEDs) remain a subject of intense investigation because of their potential applications in flat-panel display and solid-state lighting [1–3]. Phosphorescent OLEDs [4–6] based on phosphorescent heavy-metal complexes have received considerable attention because of their highly efficient emission compared with conventional fluorescent OLEDs, which results from the elimination of the 25% maximum quantum efficiency (QE) limit that is inherent to fluorescent OLEDs. Both singlet and triplet excitons can be harvested for light emission in phosphorescent complexes that makes their internal quantum efficiency theoretically approach 100%. The highly efficient phosphorescence emission is attributed to strong spin–orbit coupling that enhances intersystem crossing and mixes the singlet and triplet states. Among all the transition metal complexes that have been employed as emitters in phosphorescent OLEDs, Ir complexes and Pt complexes have been extensively studied. Recently, Re complexes [7–10] have been attracting more and more attention because they feature high room-temperature (RT) phosphorescent quantum yield, relatively short excited state lifetime and excellent thermal stability. To the best of our knowledge, highest luminance efficiencies of 7.81 cd A^{-1} and 7.15 cd A^{-1} have been achieved according to the works reported by Duan *et al* [10] and Li *et al* [7]. However, these can hardly satisfy expectations for Re complexes; improvement should be achieved in the field. In this paper, we will report phosphorescent OLED based on a Re complex: Re(CO)$_3$Cl-bathophenanthroline (Re-Bphen), which shows a much higher luminance efficiency of 13.8 cd A^{-1} (corresponding to a power efficiency of 7.21 lm W^{-1} and external quantum efficiency (EQE) of 5.24%). The light-emission mechanism has also been discussed.

The molecular structure of Re-Bphen and the device configuration are shown in figure 1. In the devices, 30 nm 4,4′,4′′-tris(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (m-MTDATA), 20 nm N,N′-di(naphthalene-1-yl)-N,N′-diphenyl-benzidine (NPB), 20 nm bathophenanthroline (Bphen) and 20 nm tris(8-hydroxy-quinoline)aluminium (Alq$_3$) are used as a hole injecting layer, hole transporting layer, hole blocking/electron transporting layer and electron transporting layer, respectively. 30 nm Re-Bphen-doped 4,4′-N,N′-dicarbazole-biphenyl (CBP) is an emission layer; the doping concentrations are 3 wt%, 6 wt%, 9 wt% and 12 wt%, respectively. 150 nm LiF/Al is the cathode. Re-Bphen is designed and synthesized by our group and other materials are got commercially. Organic layers were deposited by high-vacuum (4 × 10^{-4} Pa) thermal evaporation onto a cleaned glass substrate precoated with ITO. The LiF layer and Al cathode were vapour deposited at a background pressure of 5 × 10^{-4} Pa and 3 × 10^{-3} Pa, respectively.

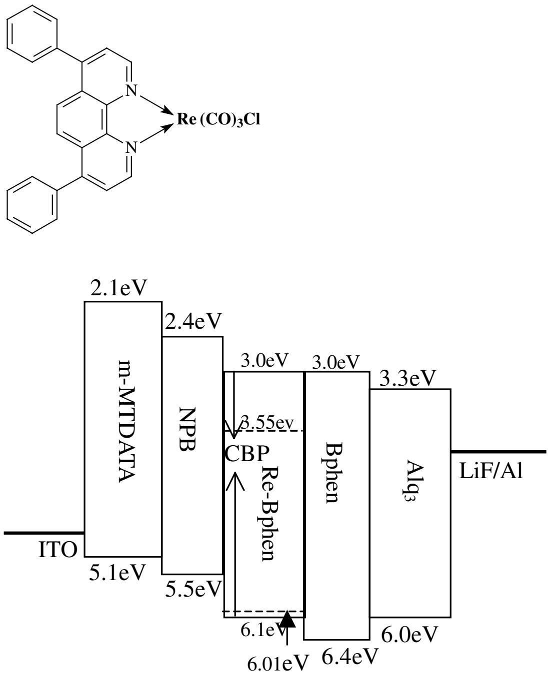


Figure 1. Chemical structure of Re-Bphen and device configuration.

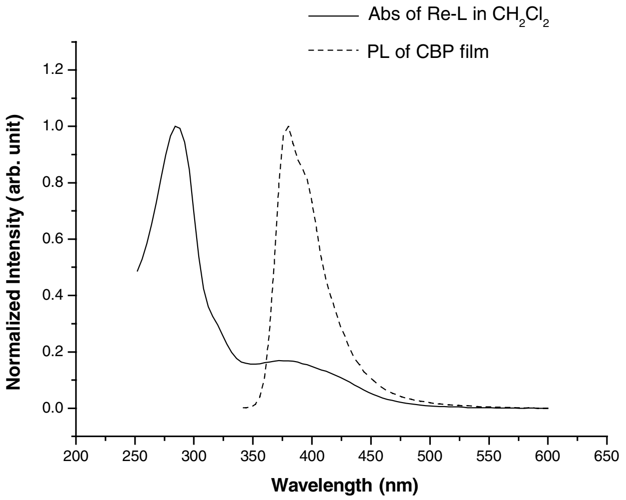


Figure 2. The absorption spectrum of Re-Bphen in CH_2Cl_2 solution and PL spectrum of a CBP film.

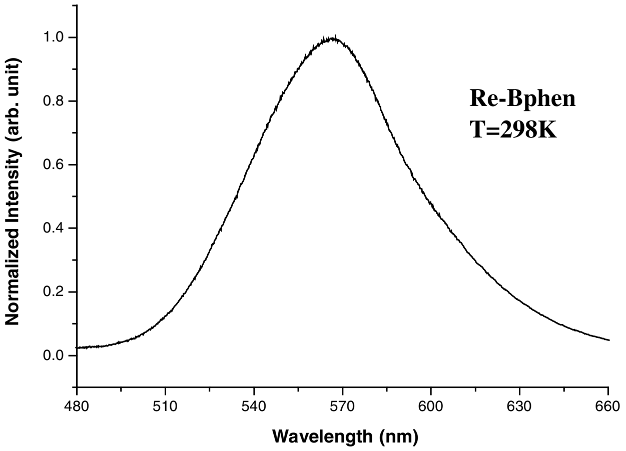


Figure 3. The PL of Re-Bphen at RT.

EL spectra and Commission International De L'Eclairage (CIE) coordination of these devices were measured by a PR650 spectrascan spectrometer. The luminance–current density–voltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage–current source. UV-visible absorption and PL spectra were measured with a UV-1700 UV-visible spectrophotometer and a RF-5301Pc spectrofluorophotometer, respectively. All measurements described above were carried out at room temperature under ambient condition. Cyclic voltammetry was used to estimate Re-Bphen's highest occupied molecule orbit (HOMO) level and lowest unoccupied molecule orbit (LUMO) level, and those of other materials are available from other literatures.

The photoluminescence (PL) spectrum of the CBP film and absorption spectrum of Re-Bphen in CH_2Cl_2 are shown in figure 2. The ultraviolet absorption spectrum of the complex exhibits a strong peak at 284 nm due to intraligand $\pi \rightarrow \pi^*$ transition. The broad absorption band that centres at about 380 nm is assigned to metal-ligand-charge-transfer (MLCT, $d\pi \rightarrow \pi^*$) transition. The sufficient overlap between the PL spectrum of CBP and MLCT absorption bands of Re-Bphen indicates that efficient Förster energy transfer will occur from two paths: (i) between the lowest singlet-excited state (S_1) of the host and S_1 state of the guest from which the exciton will then fast intersystem cross (ISC) to the lowest triplet excited state (T_1) followed with phosphorescence emission; (ii) between the S_1 of the host and the T_1 of the guest; this is also followed by phosphorescence emission.

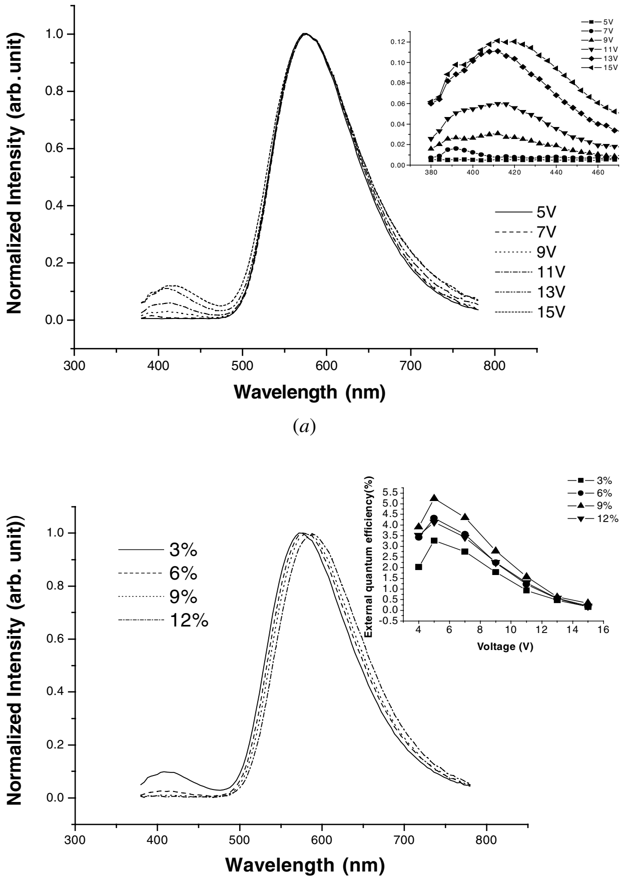
The host material CBP is fluorescent and possesses negligible phosphorescence at room temperature that is due to thermally activated nonradiative processes. Reducing the temperature can slow the rate of phonon-assisted decay and triplet diffusion. Baldo and Forrest [12] obtain the phosphorescence spectra of CBP under 10 K and estimate the energy difference between T_1 and ground state to be 2.6 eV from the highest peak of the spectra. The PL spectrum of Re-Bphen under RT is shown in figure 3. Because of the very fast ISC in the metal-ligand complex, the RT PL of Re-Bphen can be attributed to the emission from T_1 of the material. Thus we can decide the energy difference between T_1 and the ground state of Re-Bphen to be 2.1 eV (corresponding to the peak of PL spectra located at about 580 nm) by the same way. Baldo and Forrest [12] have studied the triplet energy transfer of several kinds of guest–host systems and outlined fundamental principles of the transfer. They found that the guest–host system is most close to resonance when the triplet energy difference is small (T_1 of the host is higher than that of the guest, and the examples for this kind are PtOEP:Alq_3 and Ir$(ppy)_3$:CBP systems with triplet energy differences of 0.1 eV and 0.2 eV, respectively.). That is to say that the triplet energy transfer between the host and guest is efficient under this condition. While for the case of large energy difference (e.g. PtOEP:CBP and PtOEP:TPD with energy differences of 0.4 eV and 0.7 eV, respectively), the triplet excitons are strongly confined within the guest; the system is nonresonant

Table 1. Devices' performances of OLEDs with various Re-Bphen concentrations.

Device	I	II	III	IV
Concentration (wt%)	3%	6%	9%	12%
Maximum luminance (cd m^{-2})	4322 cd m^{-2}	4271 cd m^{-2}	4347 cd m^{-2}	4036 cd m^{-2}
Maximum efficiency (cd A^{-1})	8.3 cd A^{-1} at 5 V	11.5 cd A^{-1} at 5 V	13.8 cd A^{-1} at 5 V	10.8 cd A^{-1} at 5 V
Maximum efficiency (lm W^{-1})	5.22 lm W^{-1} at 5 V	7.25 lm W^{-1} at 5 V	8.69 lm W^{-1} at 5 V	6.80 lm W^{-1} at 5 V
Maximum EQE (%)	3.26%	4.32%	5.24%	4.14%

and triplet energy transfer is not very efficient. As to our Re-Bphen:CBP system, the 0.5 eV triplet energy difference makes us believe that it belongs to the latter situation—the triplet energy transfer will take place, but will not be very efficient.

As is shown by figure 1, the HOMO and LUMO levels of Re-Bphen are −6.01 eV and −3.55 eV, respectively. Both of them locate between the HOMO and LUMO of CBP. Moreover, comparing the host and the guest, there is a more than 0.5 eV difference in the LUMO level. This makes the guest a deep trap for charge carriers (electrons). This is supported by the current density versus voltage (J–V) characteristics of the devices, which is shown in figure 5. From figure 5 we can see that with increasing doping concentrations, the J–V characteristic curves shift gradually to higher voltage, suggesting that the trapping effect of Re-Bphen basically affects the carrier transporting. Cleave *et al* [11] have pointed out that charge trapping might be an important factor in producing high efficiency phosphorescent OLEDs when the guest acts as a deep trap for one or both kinds of charges. By analysing the time-resolved EL of a deep trap phosphorescent guest–host system, they find that trapping seems to dominate the performance of the devices at low currents. By observing the EL spectra of our devices which are shown in figure 4(*a*), we can draw a conclusion similar to their opinion. We choose the EL spectra of a 3 wt% device which are recorded at different drive voltages ranging from 5 V to 15 V by 2 V a step. We observe the spectra at a shorter wavelength within the range from 380 nm to about 480 nm. Compared with the EL spectra at 5 V, the 7 V one shows a small peak at 392 nm which can be attributed to the weak emission from CBP. Then another peak (attributed to the overlap of spectra of CBP and NPB emission) appears at a longer wavelength when voltage increases to 9 V and it becomes stronger and redshifts together with the enhancement of the field until, at last, it goes to 436 nm (the location for the emission peak of NPB). This provides us a proper description of the device's working process: under low drive voltage (5 V, which means low charge and exciton concentrations), trapping on Re-Bphen molecules in CBP is the main source for phosphorescence emission until, at higher voltage, the guest sites are partially filled and some excitons are generated in the host (corresponding to the very weak emission from CBP) rather than directly on the guest. A further increase of the voltage makes the recombination zone move towards the NPB layer, and the emission from it is visible and becomes continually stronger.



(*a*)

(*b*)

Figure 4. The EL spectra of the device with a doping concentration of 3 wt% under different voltages (*a*) and the EL spectra of the devices with different doping concentrations (*b*). Inset of (*a*): amplified EL signal at a short wavelength range from 380 nm–480 nm. Inset of (*b*): EQE versus voltage plots of the devices.

Devices' performances are shown in table 1. The maximum current efficiencies are 8.3 cd A^{-1} (device I), 11.5 cd A^{-1} (device II), 13.8 cd A^{-1} (device III) and 10.8 cd A^{-1} (device IV). They correspond to the maximum power efficiencies of 5.22 lm W^{-1}, 7.25 lm W^{-1}, 8.69 lm W^{-1}, 6.80 lm W^{-1} and EQE of 3.26%, 4.32%, 5.24%, 4.14%, respectively. EQE versus voltage plots of the devices are shown in the inset of figure 4(*b*). For all three kinds of efficiencies, an optimal doping concentration of 9% can be derived from above. Moreover, optimal efficiencies of the devices are all derived at 5 V. As has been discussed before, under this relatively low voltage, trapping plays a dominant role, so we consider that the high efficiency is obtained due to the good charge trapping and exciton confinement abilities of Re-Bphen in CBP. Relatively lower efficiency obtained from device IV is caused by concentration quenching. Maximum luminance of the four devices are 4322 cd m^{-2} (device I), 4271 cd m^{-2} (device II), 4347 cd m^{-2} (device III) and 4036 cd m^{-2} (device IV). Normalized EL spectra

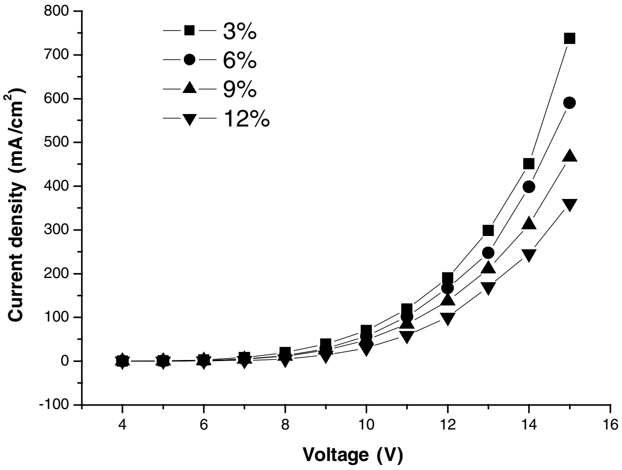


Figure 5. J–V curves of the devices at different doping concentration.

of the devices driven under 10 V have been shown in figure 4(*b*). With increasing doping levels, EL bands exhibit a redshifting trend from 572 nm (device I) to 588 nm (device IV). This concentration-dependent varies within the yellow–orange region and is always considered to be the result of the polarization effect [13]. The weak peaks which appear in the shorter wavelength range of the spectra of device I and device II from 380 nm to 480 nm, however, cannot be observed in those of device III and device IV. This indicates that excitons are effectively confined within Re-Bphen molecules at a higher doping concentration under 10 V.

In conclusion, phosphorescent OLEDs based on Re-Bphen have been fabricated. Devices show highest efficiencies of 13.8 cd A^{-1}, 8.69 lm W^{-1} and 5.24%, respectively. These much higher efficiencies in OLEDs based on Re complexes make us believe that achievement of good performance of this kind of devices is also possible. The mechanism of our devices is also discussed thoroughly.

Acknowledgments

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