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A multicomponent rhenium-based triplet emitter for organic electroluminescence

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Abstract

A novel Re complex functionalized by a hole-transport and an electron-transport groups was utilized to fabricate organic light-emitting devices (OLEDs). A current efficiency up to 8.2 cd A^{-1} corresponding to a power efficiency of 4.6 ml W^{-1} and a peak brightness as high as 5500 cd m^{-2} were obtained. These results represent the best values reported for OLEDs based on rhenium complexes. Short lifetime, enhanced carrier injection capability of Re complex, and efficient charge-trapping followed by exciton confinement in the emissive layer should be responsible for the outstanding electrophosphorescent performances.

1. Introduction

Currently, research on organic light-emitting devices (OLEDs) has focused on the improvement in electroluminscent (EL) performances such as efficiency and stability by exploring novel materials and optimizing device architectures [1,2]. Reasonable device structure offers balanced charge injection and transport, which ensure the exciton formation occurring in the emissive layer. An efficient way to harvest exciton energy for light emission is guest–host system, in which exciton can form either on the host sites and then activate the guest, or directly on the guest molecules by charge trapping. Efficient exciton formation and confinement in the emissive layer can make for efficient electroluminescence [3]. Application of phosphorescent complexes incorporating heavy metal ions opens the way to high EL efficiency up to 100%, three times higher than the fluorescent dyes, by utilizing both singlet and triplet excitons [4]. So far, great success has been achieved in application of iridium complexes as emitters in OLEDs [5,6]. However, due to the long exciton decay time of phosphorescent complexes, nonradiative relaxation of triplet excitons, i.e. triplet–triplet annihilation dramatically decrease the EL efficiency with increasing current density. It is favorable to use phosphorescent materials with short lifetime for high EL efficiency at high currents. Re(I) complexes possess the merits such as intense phosphorescence emission, high stability and short phosphorescent lifetime less than 1 μs [7], thus providing the opportunity to use them for highly efficient OLEDs. Li et al. presented efficient devices based on (2,9-dimethyl-1,10-phenanthroline)Re- $(CO)_3Cl$ (dmphen-Re) doped into 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) with a high current efficiency up to 7.15 cd A^{-1} [8]. Wang et al. achieved yellow electrophosphorescence devices with power efficiency of 1.6 lm W^{-1} by utilizing energy transfer from $BePP_2$ (PP = 2-2(hydroxyphenyl)-pyridine) to (Bu^tbpy) $Re(CO)_3Cl$ (Bu^tbpy = 4,4′-bi(*tert*-butyl) 2,2′-bipyridine) [9]. In addition, white eletrophosphorescence

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from the mixing of yellow emission from (4,4′-dimethyl-2,2′-bipyridine)Re(CO)$_3$Cl (Dmbpy-Re) and blue emission from *N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) was also reported [10]. All of the above achievements indicate that rhenium complexes have emerged as promising candidates for OLED applications. Additionally, it has been shown that the introduction of charge transporting groups into emissive molecules can also improve the device performance [11,12]. Gong and Gordon groups reported the application of funtionalized rhenium(I) complexes as emitters in EL devices, showing much space for further enhancement on EL performances [13,14]. Nevertheless, to date, efficient rhenium(I) complexes used for OLEDs are few and further improvement in performance is desired. Therefore, it is crucial to design novel functionalized Re(I) complexes suitable for OLEDs applications.

In this letter, we wish to report the synthesis, photoluminescent (PL) and EL properties of a novel multicomponent Re(I) complex prepared by introducing a triphenylamine and an oxadiazole moieties in the framework of 1,10-phenanthroline molecule. Thus, the hole transporting, electron transporting, and luminescent functional groups are incorporated into a single molecule. The devices based on the developed Re(I) complex emit strong yellowish–green light with a peak emission at ~554 nm. The maximum luminance exceeding 5500 cd m^{-2} at 17 V, maximum current efficiency up to 8.2 cd A^{-1} corresponding to the power efficiency of 4.3 lm W^{-1} at 6 V were obtained. To our knowledge, these results represent the best values reported for devices with Re-complexes as emitters so far.

2. Experimental details

Fig. 1 outlines the synthetic protocol for the Re-complex. First, 2,4′-triphenylamino)-imidazo[4,5-*f*]1,10-phenanthroline (TPIP) and 2-(4-(4-bromo-butyloxy)phenyl)-5-phenyl-1,3,4-oxadiazole (BOXD) were synthesized separately according to literature procedures [15,16]. And then, TPIP reacts with BOXD to afford OXD-TPIP in the presence of sodium hydride. Finally, Re-complex (Re-OXD-TPIP) was synthesized by direct complexation of OXD-TPIP with Re(CO)$_5$Br according to the conventional literature method [17]. The synthetic details are in the supplement. The identity of ligand OXD-TPIP was verified by single crystal X-ray diffraction analysis. A perspective drawing of the structure of OXD-TPIP with atomic numbering is shown in Fig. 2. The purity and composition of Re-OXD-TPIP were confirmed by ^{1}HNMR and positive-ion FAB-MS.

To investigate the EL properties of Re-OXD-TIPP, the devices with various doping concentrations were fabricated using Re-OXD-TPIP as an emitting dopant and CBP as the host. Vacuum vapor deposition was used to fabricate the emissive layers since Re-OXD-TPIP is stable enough to be sublimed. The EL devices are composed of indium tin oxide (ITO)/4,4′,4′′-*tris*[3-methylphenyl(phenyl) amino] triphenylamine (*m*-MTDATA) (30 nm)/*N*,*N*′-di-1-naphthyl-*N*,*N*′-diphenylbenzidine (NPB) (20 nm)/CBP: *x* wt.% Re-OXD-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 hole-injection material and NPB was employed as the hole-transporter. Bphen, Alq$_3$ and LiF/Al were used

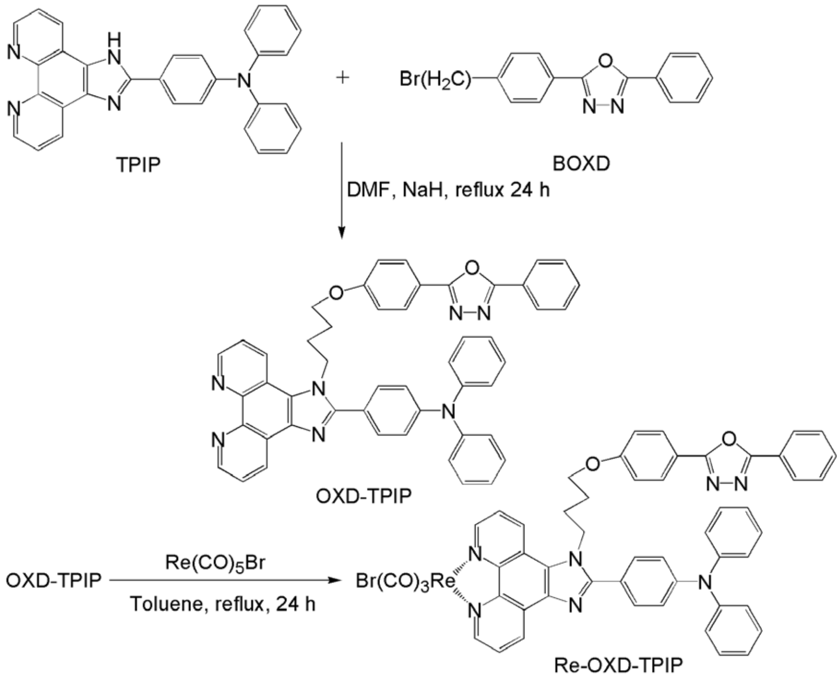

Fig. 1. The synthetic route to Re-OXD-TPIP.

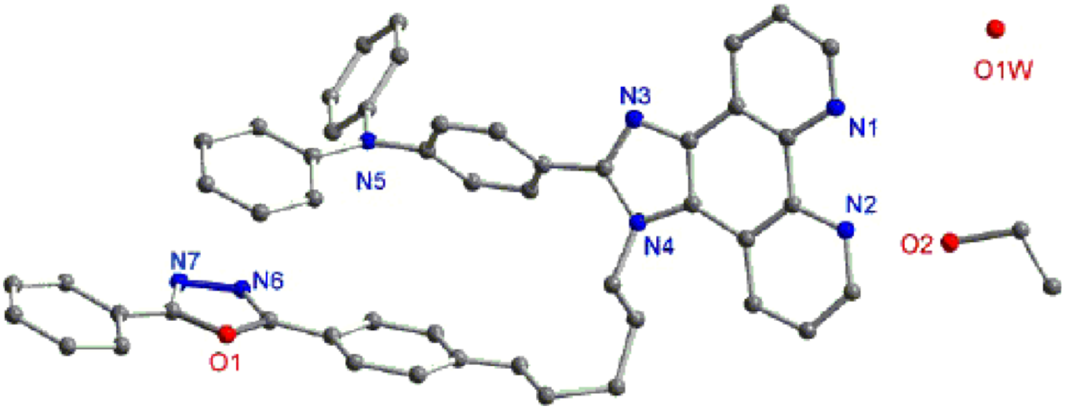

Fig. 2. A perspective drawing of OXD-TPIP with atomic numbering scheme. Thermal ellipsoids at the 10% probability level.

as the hole blocker, the electron transporter and the cathode, respectively. Re-OXD-TPIP was doped into the host material CBP with mass ratios of 2–10 wt.%, and acted as light-emitting layer. The pressure of the chamber is below 3×10^{-4} Pa. UV–vis absorption spectra were recorded using Shimadzu UV-3000 spectrophotometer. PL spectra were measured with a RF-5301Pc spectrofluorophotometer. EL spectra and Commission Internationale 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 EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage–current source. All measurements were carried out in air at room temperature.

3. Results and discussion

Fig. 3 shows the current efficiency versus current density characteristics of the EL devices based on Re-OXD-TPIP with various doping concentrations. Benefiting from the short triplet lifetime of Re-OXD-TPIP in solid state (0.16 μs), a very slow decrease of the current efficiency with an increase of current density was observed for each device. The efficiencies at the benchmark luminance of 100 cd m^{-2} are almost equal to the maximum efficiency, as summarized in Table 1. Thanks to the improvement of the carrier's injection ability by introducing a triphenylamine and an oxadizaole moieties in Re-OXD-TPIP molecules, the turn-on voltage of all four devices is lower than 5 V. As in the case of other phosphorescent OLEDs, the device performance

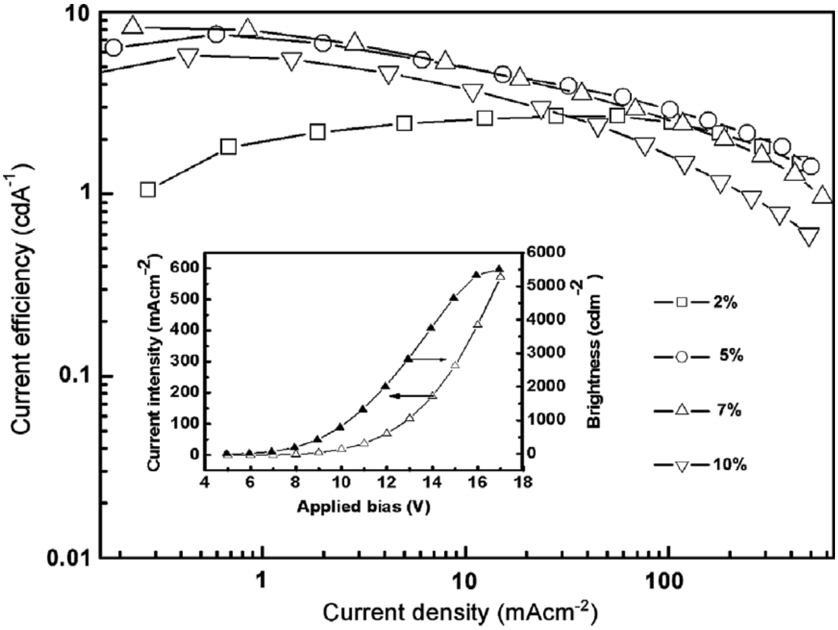

Fig. 3. Dependence of current efficiency on current density at different concentrations of Re-OXD-TPIP in CBP at 6 V. Inset: Current density–brightness–voltage characteristics of a device based on 7 wt.% Re-OXD-TPIP in CBP.

Table 1
EL device performances of Re-OXD-TPIP with different concentrations

Concentration (wt.%)	$\eta_{\max}$[a]	η[b]	η[c]	η[d]	$\eta_{\max}$[e]	$B_{\max}$[f]
2	1.4	0.7	0.6	1.1	0.6	2906
5	7.5	2.9	1.7	6.7	3.4	5682
7	8.2	2.6	1.3	7.5	4.3	5510
10	5.5	1.7	0.7	5.3	2.6	2920

[a] Maximum current efficiency (cd A^{-1}).
[b] Current efficiency at 100 $mAcm^{-2}$ (cd A^{-1}).
[c] Current efficiency at 400 $mAcm^{-2}$ (cd A^{-1}).
[d] Current efficiency at 100 cd m^{-2} (cd A^{-1}).
[e] Maximum power efficiency (lm W^{-1}).
[f] Maximum brightness (cd m^{-2}).

shows a strong dependence on the doping concentration. Comparison of performance of these four devices suggests that the device with 7 wt.% Re-OXD-TPIP in CBP offers the highest device efficiency. The inset of Fig. 3 shows the current density–brightness–voltage characteristics of the optimized device. A maximum brightness of 5505 cd m^{-2} at a current density of $J = 572$ mA cm^{-2} with voltage of 17 V and a maximum current efficiency of 8.2 cd A^{-1} at a current of 0.23 mA cm^{-2} with the luminance of 18 cd m^{-2} were achieved. A luminance of 1000 cd m^{-2} corresponding to current efficiency of 3.6 cd A^{-1} was observed. Even at a high luminance of 2500 cd m^{-2} and high current density of 100 mA cm^{-2}, the current efficiency of this device remained as high as 2.6 cd A^{-1}. These values demonstrated the device stability under continuous operation is improved compared to the previous reports with rhenium(I) complexes as emitters in OLEDs [7–10]. We believe that the relatively short lifetime of Re-OXD-TPIP is an important factor to improve the EL performances. Another main factor to enhance the device performances is efficient exciton formation on the Re-OXD-TPIP molecules by direct charge-trapping and confinement within the emissive layer. This can be inferred from the following analysis of the PL spectra, EL spectra of Re-OXD-TPIP doped films in CBP, and the energy levels of the guest and the host.

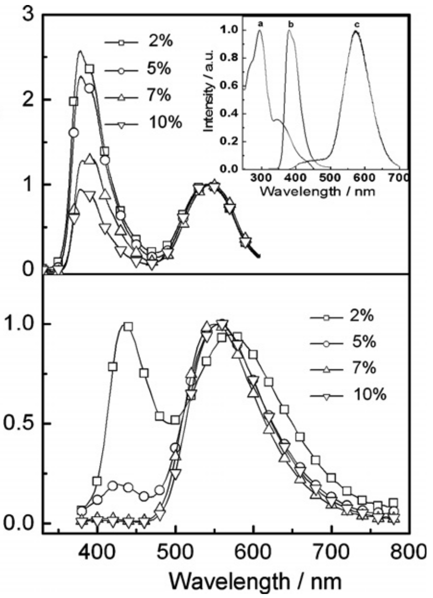

Fig. 4. PL and EL (17 V) spectra of Re-OXD-TPIP with various concentrations in CBP. Inset: Absorption spectrum for Re-OXD-TPIP in chloroform solution (a), PL spectra of CBP flim (b) and of Re-OXD-TPIP (c).

The inset of Fig. 4 plotted the absorption spectrum of Re-OXD-TPIP in chloroform solution, PL spectra of CBP and Re-OXD-TPIP. Two strong absorption bands around 295 and 345 nm can be assigned to spin-allowed $\pi - \pi*$ transitions on the ligand OXD-TPIP. The weak broad absorption band that centers at 437 nm are attributed to the spin-allowed metal(dπ) to ligand ($\pi*$) charge-transfer (^{1}MLCT) transition. There exists a partial overlap between the fluorescence spectrum of CBP and the absorption spectrum of Re-OXD-TPIP. Consequently, as shown by the PL spectra of Re-OXD-TPIP doped films in CBP (Fig. 4a), the emission from the host (CBP) can not be completely quenched even with more than 10 wt.% of Re-OXD-TPIP. This implies Förster energy transfer from the singlet-excited state in the host (CBP) to the ^{1}MLCT state of the guest (Re-OXD-TPIP) occurs only at a moderate level. In a sharp contrast to the PL spectra, no CBP emission from the OLEDs was observed even at dopant concentration of 2 wt.%, as displayed in Fig. 4b. The significant differences between the EL and PL spectra of Re-OXD-TPIP doped films in CBP indicate that direct charge-trapping dominates the EL process. Fig. 5 shows the proposed energy level diagram of the EL device. The highest occupied molecular orbital (HOMO) energy level of Re-OXD-TPIP was determined to be 5.8 eV, by cyclic voltammetry. The lowest unoccupied molecular orbital (LUMO) energy level was calculated to be 3.1 eV according to the absorption band edge of Re-OXD-TPIP. Other data are based on references [18–21]. The energy levels of Re-complex lie between the band gap of CBP, which meets the requirement for efficient carrier trapping [22]. So charge carriers in the emissive layer can be directly trapped by the Re-complex and await the arrival of opposite carrier for recombination to form excitons. The existence of a triphenylamine and an oxadiazole moieties in complex can facilitate carrier

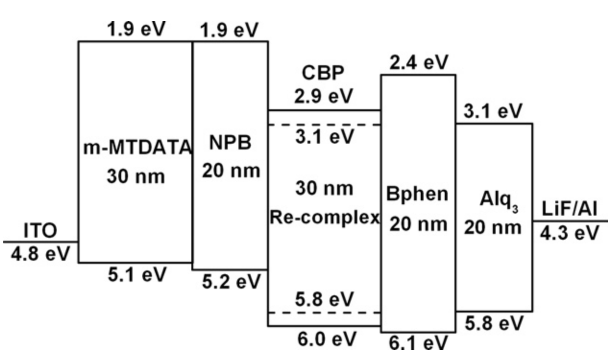

Fig. 5. The energy level diagram of electrophosphorescence device.

injection, and consequently, leads to efficient exciton formation on the Re-OXD-TPIP molecules and efficient electrophosphorescence. Furthermore, an additional dim blue emission originating from NPB was observed at concentration of 2 wt.% and 5 wt.% except the strong Re-OXD-TPIP emission and vanished when the concentration is higher than 7 wt.%. This is the result of charge trapping. Since hole injection from the NPB HOMO into the CBP HOMO is energetically unfavourable, so when the dopant concentration is low, accumulated holes in NBP layer can recombine with the electrons injected from the emissive layer, resulting in NPB emission in addition to exciton formation at Re-OXD-TPIP. With increasing doping concentrations, more and more electrons can be intercepted and trapped by Re-OXD-TPIP and the contribution from NPB decreased. At Re-OXD-TPIP concentrations higher than 5 wt.%, no electrons were injected into NPB layer, so the NPB emission disappeared. Another important feature in our devices is that white EL emission (Commission International de L'Eclairage chromaticity coordinates at $X = 0.33$, $Y = 0.33$) with the maximum current efficiency of 1.4 cd A^{-1} is observed from the device with 2 wt.% Re-OXD-TPIP in CBP at 17 V, suggesting that the combination of Re-OXD-TPIP and a blue emitter may result in pure white OLEDs. The work on improving the efficiency of white OLEDs based on Re-OXD-TPIP and other blue emitters is currently in progress.

4. Conclusions

In summary, we designed and synthesized a novel Re(I) complex for OLEDs application. The EL device based on Re-OXD-TPIP showed typical ^{3}MLCT emission centering at 554 nm, a peak brightness of 5510 cd m^{-2}, and a high current efficiency of 8.2 cd A^{-1} corresponding to a power efficiency of 4.3 lm W^{-1}. The present results indicate that molecular engineering is an effective method to enhance the EL performance of organic metal complexes. The emissive colors from Re-OXD-TPIP and NPB complement each other to result in white EL emission with $X = 0.33$, $Y = 0.33$ in a low concentration of 2 wt.%, suggesting that the combination of Re-OXD-TPIP and other blue emitters may give rise to efficient white OLEDs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2006.12.044.

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