Z. SI<sup>1,2</sup> J. LI<sup>3</sup> B. LI<sup>1,2,x</sup> Z. HONG<sup>1,2</sup> S. LU<sup>1,2</sup> S. LIU<sup>3,x</sup> W. LI<sup>1,2</sup>

# High performance yellow light-emitting organic electrophosphorescent devices based on Re(I) complex

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## Received: 11 December 2006/Accepted: 28 February 2007 Published online: 5 June 2007 • © Springer-Verlag 2007

**ABSTRACT** Yellow organic light-emitting devices (OLEDs) with (2,3-diphenylpyrazino [2,3-f] [1,10] phenanthroline) Re(CO)<sub>3</sub>Br (Re-Dppp) doped CBP as emissive layer were studied. It is found experimentally that Re-Dppp based yellow OLEDs possess high electroluminescent efficiency and brightness: a maximum brightness of 6249 cd/m<sup>2</sup> at 15 V and a highest current efficiency of 14.2 cd/A with a brightness of 180 cd/m<sup>2</sup> occurring at 1.3 mA/cm<sup>2</sup> are achieved, which indicate that Re(I) complexes have a potential application in commercialized PMOLEDs.

PACS 85.60.Jb; 33.50.Dq; 33.50.-j; 42.79.Kr; 85.30.De

## 1 Introduction

Organic light-emitting devices (OLEDs) have attracted considerable interest in recent years as one of the best flat panel display technologies that is capable of meeting the most stringent demands of future display applications [1-3]. In order to realize the full potential of this display technology, the passive matrix OLEDs (PMOLEDs) have been extensively studied [4-6] and successively applied in commercial production [7,8] due to their advantages, such as low cost and simple fabrication techniques. Unlike the devices based on fluorescent materials that can only make use of singlet excitons and whose internal efficiency is limited to about 25%, phosphorescent materials, regarded as the ideal materials used in PMOLEDs, can harvest both singlet and triplet excitons and endow OLEDs with the potential of reaching an internal efficiency of 100% [9]. But the emission site saturation and/or triplet-triplet (T-T) annihilation of phosphorescent materials make the device efficiency rapidly roll off at higher current density [10-12]. As a result, the peak efficiency of electrophosphorescence usually occurs at low current densities ( $J < 0.1 \text{ mA/cm}^2$ ), which holds back the development of PMOLEDs based on phosphorescent materials. So it is urgent to obtain novel phosphors with high emission efficiency and brightness at higher current density. In this paper, we report the synthesis of a readily sublimable, charge neutral carbonyl diimine Re(I) complex Re-Dppp (Dppp = 2, 3-diphenylpyrazino [2,3-f] [1, 10] phenanthroline). The device based on 1% Re-Dppp exhibits the maximum brightness of 6249 cd/m<sup>2</sup> at 15 V, and possesses the peak efficiency of 7.3 cd/A when the brightness is 155 cd/m<sup>2</sup>. As the doping concentration is 10%, the brightness of 4778 cd/m<sup>2</sup> is recorded at 14 V, and the highest efficiency of 14.2 cd/A appears as the brightness is 180 cd/m<sup>2</sup>.

#### 2 Experimental details

The ligand of Dppp was conveniently synthesized by the condensation of 5,6-diamino-1,10-phenanthroline and benzil in refluxing acetic acid [13]. Dppp and Re(CO)<sub>5</sub>Br were refluxed in toluene to prepare the target complex of Re-Dppp [14]. The molecular structure of Re-Dppp and the device fabrication are shown in Scheme 1. Both ligand and complex were characterized by <sup>1</sup>H NMR, IR, and elemental analysis. A PerkinElmer thermal analyzer was used to study the stability of Re-Dppp under N2 atmosphere. It was found that Re-Dppp did not decompose even if the temperature was higher than 320 °C. Therefore, Re-Dppp is stable enough to be sublimated to construct OLEDs. The excited-state lifetime of Re-Dppp in dilute degassed  $CH_2Cl_2$  solution is 0.2 µs, which was detected by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:YAG laser with a THG 355 nm output. The room-temperature luminescence quantum yield of Re-Dppp was measured with quinine sulfate in sulfuric acid aqueous solution ( $\varphi = 0.546$ ) acting as the reference, and calculated to be  $1.45 \times 10^{-2}$  [15]. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels were measured to be -3.7and -6.2 eV respectively by cyclic voltammetry on a voltammetric analyzer (CH Instruments, Model 620B). They are, together with the HOMO and LUMO levels of other materials used in OLEDs [10], presented in the inset of Fig. 2.

### 3 Results and discussion

The absorption and photoluminescence (PL) spectra of Re-Dppp in degassed CH<sub>2</sub>Cl<sub>2</sub>, along with the PL spectrum of CBP film and the electroluminescent (EL) spectrum of the device based on 16% Re-Dppp at 13 V, are presented in Fig. 1. The absorption band range from 200 to 360 nm for Re-Dppp is attributed to the spin-allowed ligand-centered

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SCHEME 1 The molecular structure of Re-Dppp and the device configuration



FIGURE 1 The absorption spectrum of Re-Dppp (a), the PL spectra of CBP (b) and Re-Dppp (c), and the EL spectra of the device based on 16% Re-Dppp at 13 V (d)

transitions. The lower-energy band extending into the visible region from 360 to 504 nm, which is tentatively assigned to the metal-to-ligand charge transfer (MLCT)  $[d\pi(\text{Re}) \rightarrow \pi^*(\text{ligand})]$  transitions, largely overlaps with the PL spectrum of CBP with  $\lambda_{\text{max}}$  located at 380 nm. This demonstrates that Förster energy transfer probably exists in the process of UV or electrical excitation. When excited with 365 nm radiation, an intense PL spectrum of Re-Dppp centered at 582 nm from <sup>3</sup>MLCT transitions was observed. Owing to the difference between the electron-induced and photo-induced excited states, [16] the EL spectrum centered at 570 nm observed from 16% Re-Dppp doped device shows broader halfwidth at the half-maximum wavelength and a small blue-shift (~ 14 nm) compared to the PL spectrum.



Current density (mA/cm<sup>2</sup>)

FIGURE 2 The current efficiency versus current density characteristics of Re-Dppp based devices with various doping concentrations. *Inset*: The energy level diagram of the electrophosphorescence device

Re-Dppp is incorporated into a multi-layered device structure ITO/m-MTDATAwith the general of (30 nm)/ NPB(20 nm)/Re-Dppp:CBP  $(30 \text{ nm}, \times [\text{wt}]\%)$ / Bphen  $(20 \text{ nm})/\text{Alq}_3$  (20 nm)/LiF(0.8 nm)/Al(200 nm) as shown in the inset of Fig. 2. The m-MTDATA is used as the hole-injection layer, NPB is the hole-transporting and electron-blocking layer, while Bphen and Alq<sub>3</sub> are employed as the exciton-blocking layer and the electron-transporting layer, respectively. Re-Dppp doped CBP is chosen as the light-emitting layer, and ITO and LiF/Al are the anode and cathode, respectively. Key parameters of these devices are listed in Table 1.

The device efficiency versus current density characteristics of devices based on Re-Dppp are presented in Fig. 2. As can be seen, the efficiency increases slowly at first with the increase of the current density, suggesting that the effect of T-T annihilation on efficiency is neglectable in the low current density range due to the existence of the sterically hindered spacer of phenyl groups in the phosphor molecule and the shorter lifetime of  $0.2 \,\mu s$ . The T-T annihilation induced by the light-emitting site saturation should be responsible for the fast decrease of the EL efficiency at high current density exceeding  $100 \text{ mA/cm}^2$ . As a result, the optimum current density is higher than  $1.0 \text{ mA/cm}^2$  which is one magnitude order higher than that of the traditional electrophosphorescent devices [9]. It is found that a 10% doped device offers the highest EL efficiency of 14.2 cd/A at  $1.3 \text{ mA/cm}^2$  which is comparable to the best for the devices based on Re(I) complexes [17]. The efficiency still remains as 10.0 cd/A with a brightness of  $1500 \text{ cd/m}^2$  at 14.3 mA/cm. The optimum concentration of the device is 10% which is much higher than that of the device based on the fluorescence materials, indicating that Dexter transfer should occur during the EL process [18].

Figure 3 presents the current density–luminance–voltage (I-J-V) characteristics of the device based on 1% Re-Dppp in CBP. The device has a lower onset voltage of 4.5 V

Conc. <sup>a</sup> (×[wt.]%)	$100 \text{ cd}/\text{m}^2$	$\frac{\eta_c (cd/A)^b}{1000 cd/m^2}$	$2000 \text{ cd}/\text{m}^2$	$\eta_{\rm mzx}^{\rm c}({\rm cd}/{\rm A})$	$I^{\rm d}({\rm mA/cm^2})$	$L_{\rm max}^{\rm e}$ (cd/m <sup>2</sup> )
1	7.13	4.92	3.75	7.26	2.13	6249
3	8.33	5.64	4.00	8.48	0.90	5519
7	9.81	8.22	6.68	9.87	0.83	3785
10	12.76	10.77	8.59	14.20	1.30	4778
16	7.30	6.49	5.49	7.81	2.39	4697

**TABLE 1**EL performan-<br/>ces of OLEDs with various<br/>Re-Dppp concentrations

<sup>a</sup> Doping concentration.<sup>b</sup> Device efficiency at given brightness. <sup>c</sup> Peak efficiency. <sup>d</sup> Current density at which peak efficiency appears. <sup>e</sup> Maximum brightness



**FIGURE 3** I-J-V characteristics of the devices based on 1% Re-Dppp in CBP. *Inset:* I-V curves for different doping concentration



FIGURE 4  $\;$  EL spectra of the devices based on Re-Dppp with various doping concentrations at 13 V  $\;$ 

at a brightness of  $1 \text{ cd/m}^2$ , and gives off the characteristic <sup>3</sup>MLCT emission of Re-Dppp at 560 nm with the maximum brightness of 6249 cd/m<sup>2</sup> at 15 V. As can be seen from the *I*-*V* characteristics of the devices based on various doping concentrations presented in the inset of Fig. 3, the current density at a given voltage increases with the increase of the doping concentration, indicating that Re-Dppp molecules doped in the CBP emissive layer can facilitate the electron-injecting from Bphen layer into CBP layer, which is in accordance with the energy level diagram of the device presented in the inset of

Fig. 2. The LUMO level of Re-Dppp (-3.7 eV) is lower than that of CBP (-2.0 eV), which meets the requirement for efficient electron trapping [18]. So the electrons in the Bphen layer driven by the applied bias can be easily transported into the CBP layer and trapped directly by Re-Dppp molecules to recombine with the holes from the NPB layer.

The EL spectra of the devices with various doping concentrations at 13 V are shown in Fig. 4. As can be seen, the minor emission band centered at ca. 430 nm, which maybe originating from NPB, [20] disappears when the doping concentration rises by 7%. The other band, which is attributed to the <sup>3</sup>MLCT emission of the Re-Dppp, shows a red-shift from 560 nm to 570 nm with an increase of the doping concentration from 1 to 16%, which should be attributed to the interaction of dopant molecules [21]. The 10% doped device demonstrates yellow emission with a maximum efficiency of 14.2 cd/A and a luminance of  $180 \text{ cd/m}^2$  at  $1.3 \text{ mA/cm}^2$ . The quality of the yellow emission remains almost unchanged in the current density range of  $1.3-130 \text{ mA/cm}^2$ , as shown by the small variations in the CIE coordinates (0.459, 0.523)-(0.454, 0.522). All data demonstrated above indicate that the performance of the Re-Dppp based OLEDs is among the best reported for devices based on Re(I) complexes, even if the current density is one magnitude order higher than the traditional optimum value.

#### 4 Conclusion

In summary, a novel phosphor of Re-Dppp with a lifetime of 0.2  $\mu$ s in a degassed solution was successfully synthesized and utilized in electrophosphorescent devices. With a maximum brightness of 6249 cd/m<sup>2</sup> appearing at 15 V, these devices possess the highest efficiency of 14.2 cd/A when the current density is one magnitude higher than that for traditional devices, demonstrating that Re(I) complexes have potential application in commercialized PMOLEDs. It also indicates that with the help of molecular engineering and optimal architectures, to purposely design novel phosphorescent materials is an efficient way to further improve device performance, and we are in the progress of exploring these possibilities.

ACKNOWLEDGEMENTS The authors gratefully thank the financial supports of the One Hundred Talents Project from the Chinese Academy of Sciences and the NSFC (grant No. 20571071).

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