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Improved performance of electrophosphorescent devices based on Re(CO)$_3$Cl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine

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Highly efficient orange-yellow organic electroluminescent (EL) devices based on Re(CO)$_3$Cl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine (Re-DPPz) have been fabricated. By incorporating Re-DPPz into EL devices with balanced charge injection and efficient host-to-guest energy transfer, the EL performances were significantly improved comparing with previously reports based on the same complex. For EL device with 7 wt % Re-DPPz doped emissive layer, turn-on voltage of 6 V, maximum efficiency of 6.3 cd/A, and orange-yellow emission with brightness approaching 1000 cd/m^2 were achieved. The mechanism responsible for the significant improvement was discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2167401]

Recently, there has been growing interesting in employment of transition metal complexes as emitters in organic light-emitting diodes (OLEDs),[1–15] since many of them have excellent photoluminescence (PL) properties and potential advantages of achieving a maximum internal quantum efficiency of 100%.[1] Highly efficient OLEDs based on the Ir complexes[1–3] and Pt complexes[7,8] have been extensively studied. Carbonyl bipyridine Re(I) complexes have been found to exhibit intense PL originating from the Re low-lying spin-forbidden excited state,[16,17] recent research results indicate that they can also serve as a new class of electroluminescence (EL) materials.[9–15] However, the previously reported phosphorescent Re(I) complexes as emitters in the OLEDs have many disadvantages, such as saturation of emission sites due to an long lifetime and triplet-triplet annihilation at high concentration, leading to low efficiency.[10–13] Therefore, it is desirable to explore new Re complexes with good career transporting ability, short lifetime, and sterically hindered spacers, which can overcome the problems mentioned earlier. Eu(TTA)$_3$ (DPPz) as a emitter in OLEDs exhibits excellent EL performance, indicating DPPz is a suitable ligand for metal complexes as EL materials.[18] Work by Waterland and Jayaweera shows that the lowest-energy transition for Re-DPPz is metal-to-ligand charge transfer (MLCT) and its lifetime is very short (0.04 μs),[19] besides Re-DPPz possesses a relative large sterically hindered spacer, which make Re-DPPz a promising candidate emitter for OLEDs. Gordon *et al.* reported that the OLEDs based on Re-DPPz are able to exhibit EL behavior. However, the luminance of the OLEDs can only reach 50 cd/m^2 with an efficiency of 0.12 cd/A.[15] The low efficiency may be attributed to device structure, emissive layer fabricating method, or unbalanced charge injection and recombination. It is obvious that phase segregation is inevitable during solution process, especially in the case of high doping concentration which is often required in phosphorescent OLEDs. On the other hand, vacuum vapor deposition is the most appealing technique for making highly efficient and practical devices. In this letter, we redesign the device structure and vacuum deposition is used instead of spin coating to fabricate the emissive layers since Re-DPPz is stable enough to be sublimated. The maximum efficiency and brightness achieved from the devices based on Re-DPPz is drastically improved.

Re-DPPz was prepared according to a literature procedure.[19] The chemical structure is depicted in Fig. 1. The EL devices based on Re-DPPz were fabricated through vacuum deposition of the materials onto a precleaned ITO coated glass substrate (sheet resistance of 20 Ω/sq). Organic and inorganic layers were deposited successively during one vacuum run at 2×10^{-4} Pa. Thermal deposition rates for organic materials, LiF, and Al were ~2, ~1, and ~10 Å/s, respectively. PL, EL spectra, and CIE coordinates were mea-

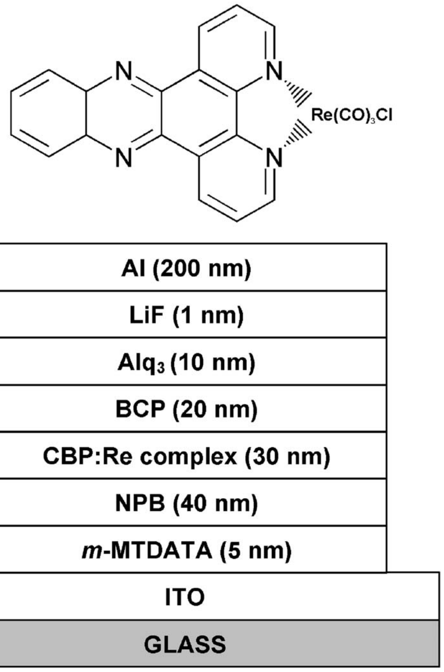

FIG. 1. Chemical structure of Re-DPPz and device configuration.

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TABLE I. Summary of the performance of Re-DPPz-based orange-yellow OLEDs. External quantum efficiency (η_{ext}), maximum luminance ($L_{\max}$), maximum current efficiency (η_c), and maximum power efficiency (η_p) at given current density.

Concentration (wt %)	J (mA/cm^2 V)	η_{ext} (%)	$L_{\max}$ (cd/m^2)	η_c (cd/A)	η_p (lm/W)
5	0.4	1.72	990	5.5	3.1
7	0.3	1.98	970	6.3	4
10	0.2	1.88	920	6.0	3.8
15	0.2	1.76	810	5.6	3.9

sured with a HITACHI MPF-4 fluorescence spectrophotometer. The data of brightness-current-voltage were measured with a 3645 dc power supply combined with a 1980A spot photometer. All measurements were carried out in air at room temperature.

EL devices with structure of indium tin oxide (ITO)/4,4′,4″-tris[3-methylphenyl(phenyl)amino] triphenylamine (*m*-MTDATA) (5 nm)/N,N′-di-1-naphthyl-N,N′-diphenylbenzidine (NPB) (40 nm)/(4,4′-N-N′-dicarbazole) biphenyl (CBP): × wt % Re-DPPz (30 nm)/2,9-dimethy-4,7-diphenyl-1,10-phenanthroline (BCP) (20 nm)/tris (8-hydroxyquinoline)aluminum (Alq_3, 10 nm)/LiF(1 nm)/Al(200 nm) were fabricated as shown in Fig. 1. Re-DPPz doped CBP film with mass ratios ranging over 2%–20% acts as an emissive layer. BCP is utilized as both an electron-transporting layer and a hole-blocking layer to confine exciton decay within the emissive layer. *m*-MTDATA, NPB, and Alq_3 are used as a hole injection layer, a hole-transporting layer, and an electron-transporting layer, respectively. Key parameters of these devices are listed in Table I.

Figure 2 shows the absorption spectrum in CH_2Cl_2 solution, the PL and EL spectra of Re-DPPz as well as the PL spectrum of CBP film. The broad absorption bands that centers at 380 nm for Re-DPPz is assigned to the singlet metal-ligand-charge-transfer (^{1}MLCT). The insufficient overlap between the PL spectrum of CBP and the ^{1}MLCT absorption of Re-DPPz indicates Förster energy transfer is not the dominant process upon electrical or UV excitation. For both EL and PL cases, only emission originating Re-DPPz was observed from 5% to 15% Re-DPPz doped CBP film and no CBP emission was found. The OLEDs based on 5%–15% Re-DPPz in CBP show orange-yellow emission centering at 588 nm that coincides with the PL spectrum shown in Fig. 2.

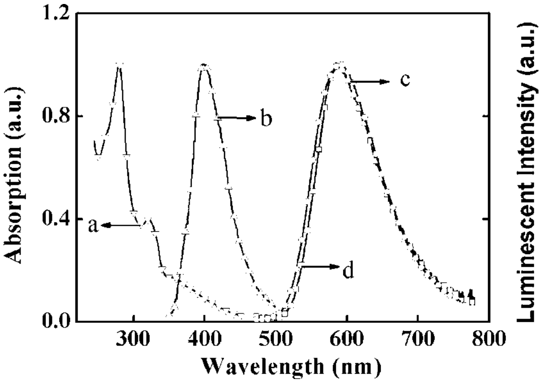

FIG. 2. The absorption spectrum of Re-DPPz in CH_2Cl_2 solution (a), PL spectrum of CBP film (b), PL spectrum of 5% Re-DPPz in CBP (c), and EL spectrum of a 5% Re-DPPz-based device at 8 V (d).

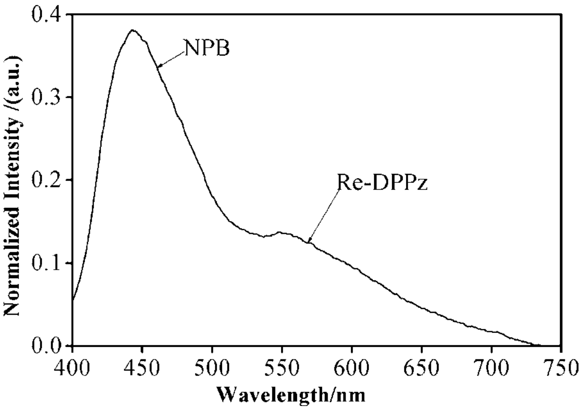

FIG. 3. EL spectrum of 2% Re-DPPz in CBP.

The close resemblance of the EL and PL spectra suggests that Re-DPPz is thermal stable in vacuum and the EL emission comes from the radiative recombination of the same excited state as PL, i.e., the triplet MLCT state. The EL spectra and CIE coordinates ($x=0.530$, $y=0.460$) are independent of the current. Even at very high current densities ($\sim 300\ \text{mA/cm}^2$), blue emission from CBP is negligible, indicating complete Dexter energy transfer from CBP host to Re-DPPz. The absence of site saturation on Re-DPPz emitters should be ascribed to the relatively short decay time. However, when doping concentration decreases to 2%, there exists blue emission centering at around 440 nm, which originates from NPB, showing that Re-DPPz participates in hole transporting in CBP layer and direct charge recombination on Re-DPPz molecules may take place at higher doping concentration. Bluish white EL emission with CIE coordinates $X=0.23$, $Y=0.24$ is observed from the device as shown in Fig. 3. The spectrum consisted of two peaks from NPB and Re-DPPz, respectively. It means that the combination of Re-DPPz and other kinds of blue EL material may result in white OLEDs.

Figure 4 shows the current efficiency versus current density characteristics of Re-DPPz-based devices with various doping concentrations. EL efficiency of the devices decreases slowly at first with increasing current, suggesting that the saturation of the phosphorescence sites is not severe owing to short lifetime of Re-DPPz. The saturation is respon-

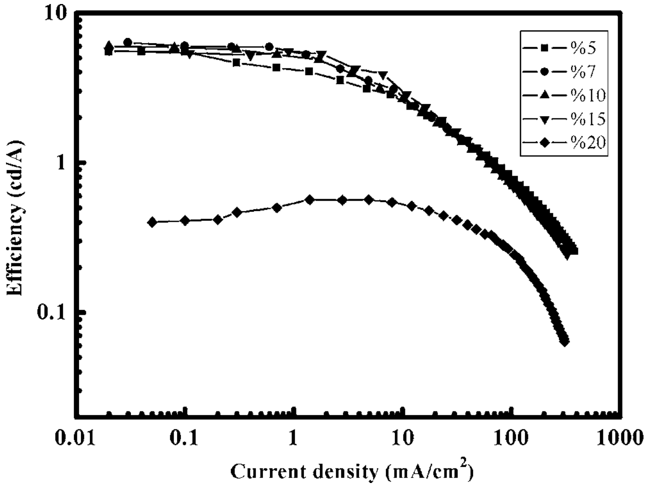

FIG. 4. The efficiency vs current density characteristics of OLEDs based on Re-DPPz doped into CBP.

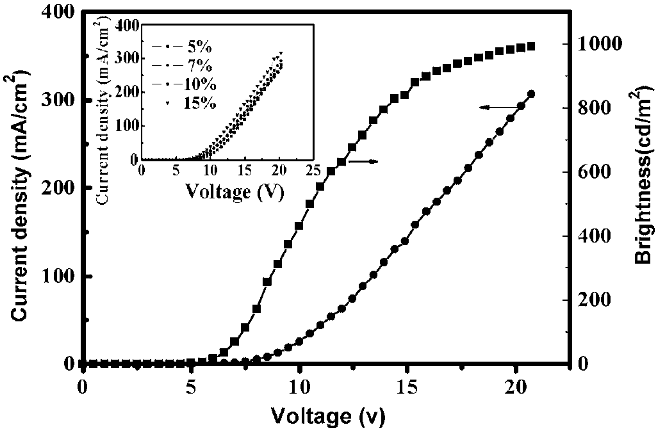

FIG. 5. Current density-brightness-voltage characteristics of a device based on 5% Re-DPPz in CBP. Inset: *I-V* curves for different doping concentration.

sible for the fast decreased EL efficiency at high current density exceeding 10 mA/cm^2. No significant difference in EL efficiencies was observed when increasing the doping concentration from 5% to 15%. At a doping concentration of 20%, concentration quenching results in very low EL efficiency. Previous results for the OLEDs based on Re complexes demonstrate that the optimum concentration is only ~2%.[10,11] The 7% optimum concentration in this letter should be largely attributed to the reduced concentration quenching through introducing a sterically hindered spacer in the phosphor molecule and decreasing its lifetime. It has been shown that a 7% doped device offers the best EL efficiency of 6.3 cd/A at 7.5 V among devices with various doping concentrations. Dexter transfer preserves the total spin of the system and thus allows triplet-triplet energy transfer from donor to acceptor. Here there exists the triplet MLCT emission originating from Re-DPPz. The optimum concentration of 7% is much higher than that of the device based on the fluorescence materials, indicating Dexter transfer occurs here.

Figure 5 shows the current density-brightness-voltage characteristics of a 5 wt % Re-DPPz doped CBP device. Orange-yellow EL emission of Re-DPPz under 6 V bias was observed, and a maximum brightness of ~1000 (990) cd/cm^2 is achieved at 20 V. The EL efficiency of the devices is 55 times higher than that of ITO/PEDOT/PVK:Bu-PBD:TPD:Re-DPPz/Bu-PBD/Al,[15] which is merely 0.12 cd/A. Such improvement is due to the efficient Dexter energy transfer between the CBP host and Re-DPPz as well as high quality of the emissive layer.

The inset of Fig. 5 shows the effect of the doping concentration on the *I-V* characteristics of the OLEDs. The doping concentration exhibits a minor effect on I-V curves, indicating that Re-DPPz molecules in the CBP layer participate in charge carrier-transporting process.

In conclusion, the utilizing structure of ITO/*m*-MTDATA/NPB/CBP:Re-DPPz/BCP/Alq$_3$/LiF/Al fabricated by vacuum deposition, the electrophosphorescent devices based on Re-DPPz with excellent EL performance were demonstrated. The EL efficiency is enhanced by 55 times, compared with previous devices based on the same Re(I) complex. On the other hand, Re-DPPz can also be used as the one source using two kinds of luminescence materials to fabricate highly efficient white OLEDs, and we are in the progress of exploring this possibility.

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[1] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature (London) **395**, 151 (1998).
[2] X. Chen, J. L. Liao, Y. Liang, M. O. Ahmed, H. E. Tseng, and S. A. Chen, J. Am. Chem. Soc. **125**, 636 (2003).
[3] Y. H. Niu, B. Q. Chen, S. Liu, H. Yip, J. Bardecker, A. K. Y. Jen, J. Kavitha, Y. Chi, C. F. Shu, Y. H. Tseng, and C. H. Chien, Appl. Phys. Lett. **85**, 1619 (2004).
[4] F. G. Gao and A. J. Bard, J. Am. Chem. Soc. **122**, 7426 (2000).
[5] X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan, and A. J. Hegeer, Adv. Mater. (Weinheim, Ger.) **14**, 581 (2002).
[6] M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, Appl. Phys. Lett. **79**, 156 (2001).
[7] G. E. Jabbour, J. F. Wang, and N. Peyghambarian, Appl. Phys. Lett. **80**, 2026 (2002).
[8] W. Lu, B. X. Mi, M. C. Chan, Z. Hui, C. M. Che, N. Z. Zhu, and S. T. Lee, J. Am. Chem. Soc. **126**, 4958 (2003).
[9] Y. Q. Li, Y. Wang, Y. Zhang, Y. Wu, and J. C. Shen, Synth. Met. **99**, 257 (1999).
[10] B. Li, M. T. Li, Z. R. Hong, W. L. Li, T. Z. Yu, and H. Z. Wei, Appl. Phys. Lett. **85**, 4786 (2004).
[11] F. Li, M. Zhang, J. Feng, G. Cheng, Z. J. Wu, Y. G. Ma, and S. Y. Liu, Appl. Phys. Lett. **83**, 365 (2003).
[12] V. W. W. Yam, B. Li, Y. Yang, B. W. K. Chu, K. M. C. Wong, and K. K. Cheung, Eur. J. Inorg. Chem. **25**, 4035 (2003).
[13] K. Z. Wang, L. Huang, L. H. Gao, L. P. Jin, and C. H. Huang, Inorg. Chem. **41**, 3353 (2002).
[14] W. K. Chan, P. K. Ng, X. Gong, and S. J. Hou, Appl. Phys. Lett. **75**, 3920 (1999).
[15] G. David, P. J. Walsh, and K. C. Gordon, Chem. Phys. Lett. **383**, 292 (2004).
[16] R. M. Leasure, L. Sacksteder, D. Nesselrodt, G. A. Reitz, J. N. Demas, and B. A. Degraff, Inorg. Chem. **31**, 3722 (1991).
[17] J. Lees, Coord. Chem. Rev. **177**, 3 (1998).
[18] P. P. Sun, J. P. Duan, H. T. Shih, and C. H. Cheng, Appl. Phys. Lett. **81**, 792 (2002).
[19] M. R. Waterland, K. C. Gordon, J. J. McGarvey, and P. Jayaweera, J. Chem. Soc. Dalton Trans. 609 (1998).