AIP Applied Physics Letters

Very high-efficiency organic light-emitting diodes based on cyclometallated rhenium (I) complex

Xiao Li, Dongyu Zhang, Wenlian Li, Bei Chu, Liangliang Han et al.

Citation: Appl. Phys. Lett. **92**, 083302 (2008); doi: 10.1063/1.2888767

View online: http://dx.doi.org/10.1063/1.2888767

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v92/i8

Published by the American Institute of Physics.

Related Articles

Uniform and refreshable liquid electroluminescent device with a back side reservoir
APL: Org. Electron. Photonics 5, 208 (2012)

Magnetic field dependence of the spin relaxation length in spin light-emitting diodes
Appl. Phys. Lett. 101, 112402 (2012)

Uniform and refreshable liquid electroluminescent device with a back side reservoir
Appl. Phys. Lett. 101, 113302 (2012)

Analytical model for current distribution in large-area organic light emitting diodes with parallel metal grid lines
J. Appl. Phys. 112, 054507 (2012)

Inverted top-emitting blue electrophosphorescent organic light-emitting diodes with high current efficacy
APL: Org. Electron. Photonics 5, 202 (2012)

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: http://apl.aip.org/authors

APPLIED PHYSICS LETTERS **92**, 083302 (2008)

Very high-efficiency organic light-emitting diodes based on cyclometallated rhenium (I) complex

Xiao Li,[1,2] Dongyu Zhang,[1,2] Wenlian Li,[1,2,a)] Bei Chu,[1,2,b)] Liangliang Han,[1,2]
Jianzhuo Zhu,[1,2] Zisheng Su,[1,2] Defeng Bi,[1,2] Dan Wang,[1,2] Dongfang Yang,[1,2] and
Yiren Chen[1,2]
[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China*
[2]*Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China*

(Received 17 December 2007; accepted 7 February 2008; published online 26 February 2008)

A phosphorescent (Ph) cyclometallated rhenium (I) (Re^I) complex was synthesized by reacting 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline with pentacarbonylbromorhenium in refluxing toluene solutions. The precipitates were easily sublimed to obtain a pure electrically neutral carbonyl diamine Re^I complex, (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)$Re(CO)_3Br$. The Re complex was used as an orange emitting dopant in 4,4′-*N*,*N*′-dicarbazole-biphenyl host to fabricate Ph organic light-emitting diodes (PhOLEDs). The maximum electroluminescence (EL) efficiency and luminance of 21.8 cd/A and 8315 cd/cm^2 were harvested, respectively, which were the highest EL results among the PhOLEDs based on Re^I complexes. The improvements of the EL performances could be ascribed to the synergistic effects of together incorporation of two reciprocally repulsive phenyl and methyl groups on the backbone of 1,10-phenanthroline molecule of the ligand. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2888767]

The heavy metal complexes based phosphorescent (Ph) emitting materials have been extensively used to fabricate highly efficient electroluminescent (EL) devices since the pioneering work of Baldo *et al.* in Ph organic light-emitting diodes (PhOLEDs).[1] The PhOLEDs based on Ph materials can significantly improve the EL performances because of the use of both singlet and triplet excitons which is attributed to strong spin-orbital coupling by heavy metal atoms and, therefore, have the potential of achieving an internal quantum efficiency of 100%.[2] In recent years, heavy metal complexes of Os^{II},[3–5] Ir^{III},[6–9] Pt^{II},[10–12] etc., based PhOLEDs have been extensively studied. In addition, Re^I complexes can also serve as a class of phosphor materials of the PhOLEDs,[13–16] because they behave high phosphorescence quantum yield at room temperature (RT) and relatively short excited state lifetime as well as the excellent thermal and photochemical stabilities.[17] Although red, green, and blue emitters of high color purity are required for full color display applications, there is still a great demand for the emitters that emit bright color such as orange emission could be used for multiple color display purposes or a component of the white OLEDs.[18,19] Therefore, we demonstrate an electrically neutral Re^I bipyridyl complex, [(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)$Re(CO)_3Br$] (Re-DDPA), that was used as an orange emitting dopant to fabricate PhOLEDs using 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) as the host. The devices exhibit a maximum current efficiency of 21.8 cd/A and a peak luminance of 8315 cd/m^2, respectively. Such high EL performances may be attributed to the synergistic effects of two repulsive phenyl groups and incorporation of two methyl groups.

Re-DDPA was synthesized by reacting 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline with pentacarbonylbromorhenium in refluxing toluene solutions and the detailed procedures mainly referred to the method of the previous report.[20] The product was thoroughly purified by silica gel column chromatography and then was structurally characterized by ^{1}H-NMR and mass spectroscopy, and the purity was verified by elemental analyses. The chemical structure of the Re complex is depicted in Fig. 3(b). Other materials used are commercially available without further purification prior to use.

The fabricated devices have structures of indium tin oxide (ITO)/*m*-MTDATA (10nm)/NPB (20 nm)/CBP: Re-DDPA (1:x%, 20 nm)/Bphen (10 nm)/Alq_3 (20 nm)/LiF (1 nm)/Al (100 nm). Here, *m*-MTDATA, NPB, Bphen and Alq_3 denote 4,4′,4″-tris[3-methylphenyl (phenyl)amino]triphenylamine, 4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl, 4,7-diphenyl-1,10-phenanthroline, and tris(8-hydroxyquinoline) aluminum, which function as hole injection layer, hole transporting layer, exciton blocking and electron-transporting layers, respectively, as well $x=2-30$. Organic layers were sequentially deposited onto the precleaned ITO glass substrates with a resistance of 20 Ω/sq. The detailed fabrication and measurements were carried out according to previous processes reported in our group.[21] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular (LUMO) levels of Re-DDPA were estimated by cyclic voltammetry on a voltammetric analyzer (CH Instrument, Model 832B), and the HOMO and LUMO levels of other materials were cited from Ref. 22.

The PL and UV-visible absorption spectra of Re-DDPA complex in chloroform solutions are shown in Fig. 1. The pronounced absorption peak in the ultraviolet region is at ~290 nm that can be assigned to spin-allowed π-π^* transition from the cyclometalated ligand. The weaker broad ab-

---

[a)] Author to whom correspondence should be addressed. Electronic mail: wllioel@yahoo.com.cn.
[b)] Electronic mail: beichu@163.com.

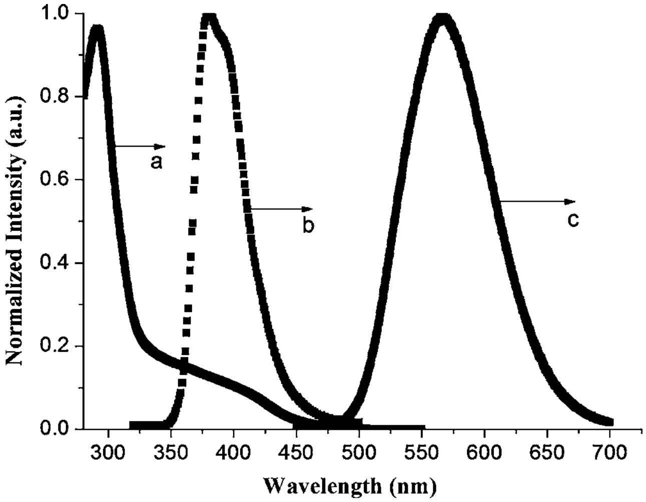

FIG. 1. Absorption spectrum of Re-DDPA (a) and PL spectra of CBP film (b) and Re-DDPA (c).

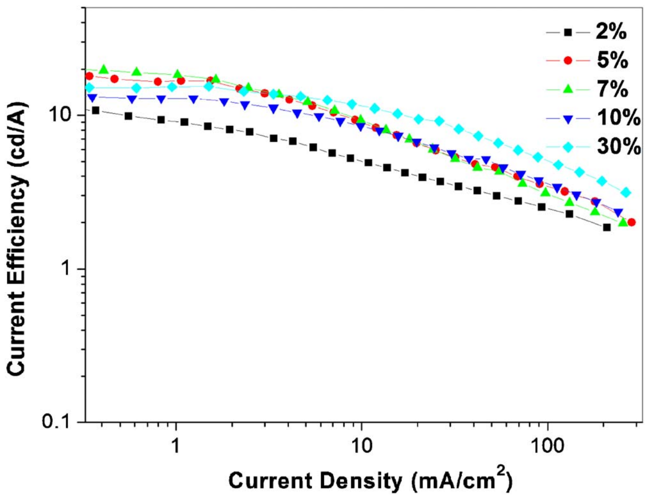

FIG. 2. (Color online) Current efficiency vs current density characteristics of Re-DDPA based devices with various doping concentrations.

sorption bands in the range 350–460 nm are tentatively ascribed to the metal-to-ligand charge transfer (MLCT) transition as well as an intense 566 nm emission at RT under excitation of 360 nm is determined. Obviously, there is a sufficient overlap between PL spectrum of CBP film and MLCT absorption band of the Re-DDPA in chloroform solutions. This indicates that, if Re-DDPA is doped into CBP host, efficient Förster energy transfer from the CBP host to Re-DDPA dopant in the device would occur.

Figure 2 presents the characteristics of current efficiency as a function of current density in various Re-DDPA contents based devices, and a maximum current efficiency of 21.8 cd/A for the 7 wt % Re-DDPA doped device is observed. The value is higher than the highest efficiency of the PhOLED device based on Re complex reported in Ref. 23 by about 1.2 folds. Moreover, it is also interestingly noted that at a current density of 100 mA/cm^2 the 30 wt % Re-DDPA doped device still exhibits a maximum current efficiency of 5.1 cd/A, which shows smaller concentration quenching although the Re complex has a short excited state lifetime of 0.24 μs. The reason may be attributed to the special molecular structure and high electron mobility of the ligand (i.e., DDPA) (Ref. 24) of the Re complex.

Figure 3(a) depicts luminance-current-voltage (*L-I-V*) curves of 30 wt % Re-DDPA doped CBP device. We can see that the device presents a peak luminance of 8315 cd/cm^2 at 17.5 V, which is larger than the highest one of the Re complex based the device previously reported[23] by about 1.3 folds, and the turn-on voltages are lower than 5 V. The inset of Fig. 3(a) indicates EL spectra of the devices with 30 wt % Re-DDPA at a variety of bias voltages from 8 to 18 V. All EL spectra show only identical orange emission bands and their spectral figures are the same as the PL spectrum in Fig. 1. Thinking about the relationship between PL and EL emissions as well as the independence of EL emission spectra on the bias voltage, we conclude that, under electrical excitation, there could be an efficient energy transfer from CBP host to the Re complex emitter. However, comparing the LUMO and HOMO levels of the Re complex with those of CBP host molecule shown in Fig. 4. We note that both the LUMO and HOMO levels of the Re-DDPA molecule locate within those of CBP host molecule. This implies that carrier

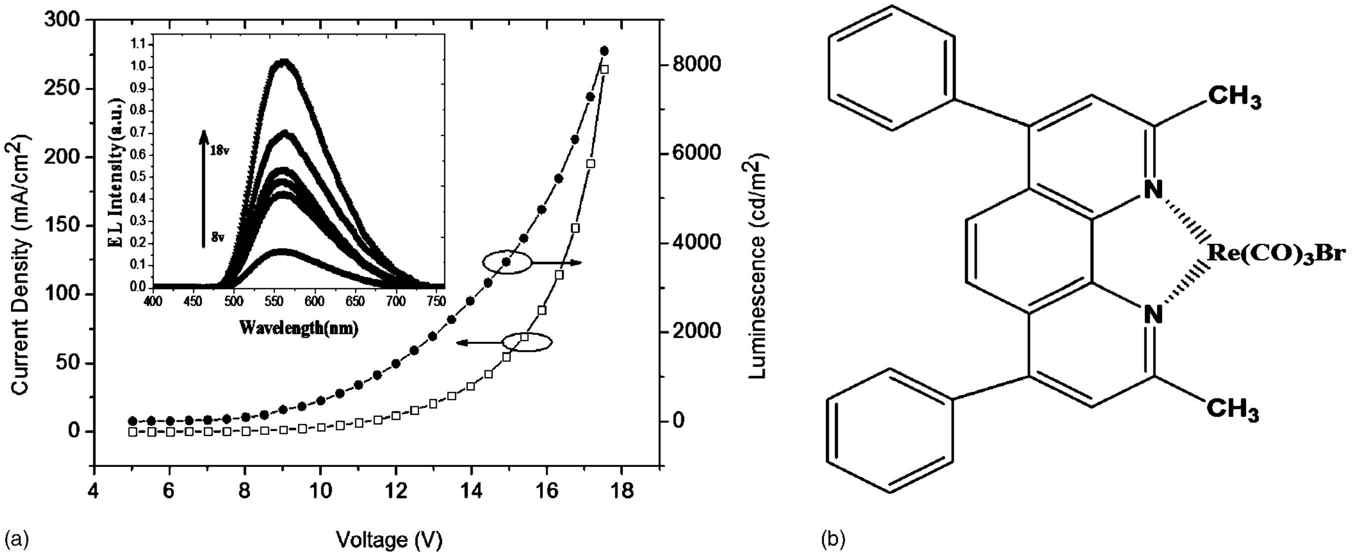

FIG. 3. (a) *L-I-V* curves of the devices based on 30% Re-DDPA in CBP. Inset: EL spectra of the device at different bias voltages. (b) The chemical structure of Re-DDPA.

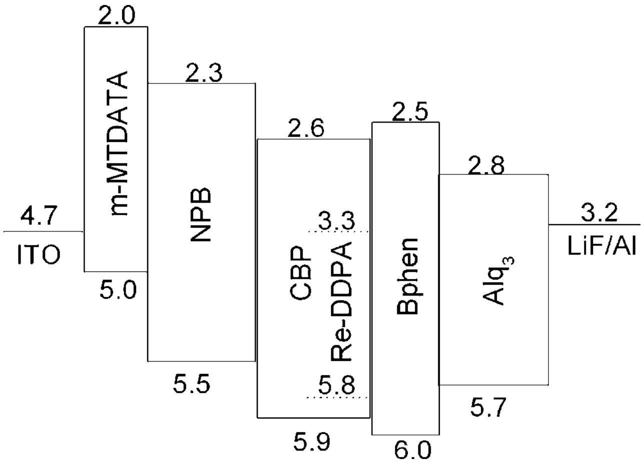

FIG. 4. The schematic energy level diagram of the Re-DDPA based device (the energy level is used as a unit of eV).

trapping at the Re-DDPA molecule in the host also probably occurs.[25] The detailed luminescent mechanism will be published elsewhere.

On basis of the excellent EL properties of the phosphor Re-DDPA, we compare its maximum EL efficiency and luminance with those of the previous three structurally similar Re complexes, (1,10-phenanthroline)Re(C)3Cl (Re-phen), (2,9-dimethyl-1, 10-phenanthroline)Re(CO)$_3$Cl (Re-dmphen),[13] and (bathophenanthroline)Re(CO)$_3$Cl (Re-bath),[26] as listed in Table I. Compared with the complex without substituents on the 1,10-phenanthroline ligand (i.e., Re-phen), incorporation of two methyl groups on 2,9 positions of 1,10-phenanthroline can sterically prevent structural relaxation resulting in nonradiative decay due to the narrowed energy gap between ^{1}MLCT and ^{3}MLCT.[27] In addition, introduction of two phenyl groups on 4,7 positions of 1,10-phenanthroline backbone does not greatly affect the emission wavelength but increases the steric effect which can alleviate self-quenching of the Re-DDPA emitter, as a result the emission intensity increases. Therefore, we can surmise that the synergistic results of together incorporation of two repulsive phenyl and two methyl groups on the backbone of 1,10-phenanthroline molecule as the ligand result in higher performances.

In summary, we synthesized the cyclometallated Re-DDPA complex that was used as a phosphor dopant in CBP host and highly efficient PhOLED device was demonstrated. The 7 wt % Re-DDPA doped device showed a maximum current efficiency of 21.8 cd/A and 30 wt % Re-DDPA doped device offered a peak luminance of 8315 cd/cm^2, and under even a current density of 100 mA/cm^2 the latter device still maintained a current efficiency of 5.1 cd/A. Such excellent performances may be attributed to special molecule structure of Re-DDPA and high electron mobility of the ligand in the Re complex, although the detailed EL mechanisms need to be further understood. We can expect that the Re-DDPA complex could be a potential candidate in construction of simpler white PhOLEDs devices by combining a blue emitter and also become a luminescent sensitizer of the red or infrared emissive EL materials.

TABLE I. Combination of key parameters between Re-phen, Re-dmphen, Re-bath, and Re-DDPA based PhOLEDs.

Triplet emitters	η_c(cd/A)^a	L_{max}(cd/m^2)^b	References
Re-phen	6.67	2769	15
Re-dmphen	7.15	3686	15
Re-bath	13.8	4347	29
Re-DDPA	21.8^c	8315^d	This work

[a] The peak current efficiency.
[b] The maximum luminance.
[c] The maximum current efficiency at 7 wt % doped CBP based device.
[d] The maximum luminance at 30 wt % Re-DDPA doped CBP based device.

[1] M. A. Baldo, D. F. O'Brian, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature (London) **395**, 151 (1998).
[2] C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, J. Appl. Phys. **90**, 5048 (2001).
[3] B. Carlson, G. D. Phelan, W. Kaminsky, L. Dalton, X. Z. Jiang, S. Liu, and A. K.-Y. Jen, J. Am. Chem. Soc. **124**, 14162 (2002).
[4] Y.-L. Tung, S.-W. Lee, Y. Chi, Y.-T. Tao, C.-H. Chien, Y.-M. Cheng, P.-T. Chou, S.-M. Peng, and C.-S. Liu, J. Mater. Chem. **15**, 460 (2005).
[5] X. Jiang, A. K.-Y. Jen, B. Carlson, and L. R. Dalton, Appl. Phys. Lett. **81**, 3125 (2002).
[6] H. Z. Xie, M. W. Liu, O. Y. Wang, X. H. Zhang, C. S. Lee, L. S. Hung, S. T. Lee, P. F. Teng, H. L. Kwong, H. Zheng, and C. M. Che,Adv. Mater. (Weinheim, Ger.) **13**, 1245 (2001).
[7] M. K. Nazeeruddin, R. Humphry-Baker, D. Berner, S. Rivier, L. Zuppiroli, and M. Graetzel, J. Am. Chem. Soc. **125**, 8790 (2003).
[8] Y.-M. You, C.-G. An, D.-S. Lee, J.-J. Kim, and S. Y. Park, J. Mater. Chem. **16**, 4706 (2006).
[9] W.-Y. Wong, G.-J. Zhou, X.-M. Yu, H.-S. Kwok, and Z.-Y. Lin, Adv. Funct. Mater. **17**, 315 (2007).
[10] C.-M. Che, S.-C. Chan, H.-F. Xiang, M. C. W. Chan, Y. Liu, and Y. Wang, Chem. Commun. (Cambridge) **2004**, 1484.
[11] W.-Y. Wong, Z. He, S.-K. So, K.-L. Tong, and Z. Lin, Organometallics **24**, 4079 (2005).
[12] G.-J. Zhou, X.-Z. Wang, W.-Y. Wong, X.-M. Yu, H.-S. Kwok, and Z.-Y. Lin, J. Org. Chem. **692**, 3461 (2007).
[13] F. Li, M. Zhang, G. Cheng, J. Feng, Y. Zhao, Y.-G. Ma, S.-Y. Liu, and J.-C. Shen, Appl. Phys. Lett. **84**, 148 (2004).
[14] K. Z. Wang, L. Huang, L. H. Gao, L. P. Jin, and C. H. Huang, Inorg. Chem. **41**, 3353 (2002).
[15] W. K. Chan, P. K. Ng, X. Gong, and S. J. Hou, Appl. Phys. Lett. **75**, 3920 (1999).
[16] Z. J. Si, J. Li, B. Li, F. F. Zhao, S. Y. Liu, and W. L. Li, Inorg. Chem. **46**, 6155 (2007).
[17] A. J. Lees, Coord. Chem. Rev. **177**, 3 (1998).
[18] F. Li, G. Cheng, Y. Zhao, J. Feng, and S. Y. Liu, Appl. Phys. Lett. **83**, 4716 (2003).
[19] H. A. Al Attar, A. P. Monkman, M. Tavasli, S. Bettington, and M. R. Bryce, Appl. Phys. Lett. **86**, 121101 (2005).
[20] W. K. Chan, C. S. Hui, K. Y. K. Man, K. W. Cheng, H. L. Wong, N. Y. Zhu, and A. B. Djurisic, Coord. Chem. Rev. **249**, 1351 (2005).
[21] G. B. Che, Z. S. Su, W. L. Li, B. Chu, M. T. Li, Z. Z. Hu, and Z. Q. Zhang, Appl. Phys. Lett. **89**, 103511 (2006).
[22] D. Y. Zhang, W. L. Li, B. Chu, J. Z. Zhu, T. L. Li, L. L. Han, D. F. Bi, X. Li, D. Y. Yang, F. Yan, H. H. Liu, and D. Wang, Appl. Phys. Lett. **91**, 183516 (2007).
[23] C. B. Liu, J. Li, B. Li, Z. R. Hong, F. F. Zhao, S. Y. Liu, and W. L. Li, Appl. Phys. Lett. **89**, 243511 (2006).
[24] T. Yasuda, Y. Yamaguchi, D.-C. Zou, and T. Tsutsui, Jpn. J. Appl. Phys., Part 1 **41**, 5626 (2002).
[25] M. Uchida, C. Adachi, T. Koyama, and Y. Taniguchi, J. Appl. Phys. **86**, 1680 (1999).
[26] J. Li, Z. J. Si, C. B. Liu, C. N. Li, F. F. Zhao, Y. Duan, P. Chen, S. Y. Liu, and B. Li, Semicond. Sci. Technol. **22**, 553 (2007).
[27] S.-M. Kuang, D. G. Cuttel, D. R. McMillin, P. E. Fanwick, and R. A. Walton, Inorg. Chem. **41**, 3313 (2002).