Applied Physics Letters

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Citation: Appl. Phys. Lett. **89**, 223524 (2006); doi: 10.1063/1.2400112
View online: http://dx.doi.org/10.1063/1.2400112
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v89/i22
Published by the American Institute of Physics.

APPLIED PHYSICS LETTERS **89**, 223524 (2006)

Improved electroluminescent performances of europium-complex based devices by doping into electron-transporting/hole-blocking host

Q. Xin, W. L. Li,[a] G. B. Che, W. M. Su, X. Y. Sun, B. Chu, and B. Li
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 and Graduate School of Chinese Academy of Sciences, 100049 Beijing People's Republic of China

(Received 24 June 2006; accepted 23 October 2006; published online 1 December 2006)

High-efficiency, pure red organic light-emitting devices were fabricated by doping a europium-complex Eu(DBM)$_3$pyzphen (DBM=dibenzoylmethane, pyzphen=pyrazino[2,3-*f*][1,10]phenanthroline) into 4,7-diphenyl-1,10-phenanthroline as emission layer. A maximum current efficiency of 5.1 cd/A at the current density of 1.2 mA/cm^2 and a maximum luminance of 1400 cd/m^2 were obtained from a 25 wt % Eu(DBM)$_3$pyzphen doped device. High efficiencies were maintained at high current densities and high luminance. For example, at the current density of 10 mA/cm^2, the efficiency reached 3.8 cd/A. It means that the efficiency roll-off, a major obstacle to the development of Eu-complex ogranic light-emitting devices, was greatly alleviated. The mechanisms behind the improvement are discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2400112]

Among various materials used in organic light-emitting devices (OLEDs),[1,2] europium (Eu) complexes have attracted much attention because their sharp red emission band is suitable for fabrication of pure red and full color OLEDs.[3] With the shortcomings of most Eu complexes such as poor film-forming and inefficient carrier-transporting ability overcame by doping techniques, the serious efficiency roll-off and impure emission color at high current densities have been the main obstacles to the development of Eu-complex OLEDs.[4–9]

The emission layer (EML) of Eu-complex OLEDs is generally composed of a Eu-complex dopant and a carrier-transporting host. 4,4-*N*,*N*-dicarbazole-biphenyl (CBP) is a typical host material.[4,5] The exciton formation zone of CBP host devices extends over 30 nm and an additional hole-blocking layer is needed to confine excitons. Furthermore, the emission of CBP could not be eliminated absolutely due to the inefficient energy transfer between the CBP and Eu complex. *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) has been demonstrated to be an excellent host for Eu complexes.[7,8] High efficiency was obtained at low current densities, but the efficiency significantly decreased at high current densities. Using 2-(4′-biphenyl)-5-(4″-tert-butylphenyl)-1,3,4-oxadiazole (PBD) as the host of Eu-complex devices had also been proposed.[9] However, it is hard to achieve a long operating lifetime for the instability of the material.

4,7-diphenyl-1,10-phenanthroline (BPhen) has shown excellent electron-transporting/hole-blocking ability, but the low glass transition temperature (T_g) limited its applications to be generalized. Codeposition of BPhen with other electron transport materials is an efficient method to overcome the defect of instability.[10] In this letter, we used BPhen as host and doped it with Eu(DBM)$_3$pyzphen (DBM=dibenzoylmethane, pyzphen=pyrazino[2,3-*f*][1,10]-phenanthroline). The 25 wt % Eu(DBM)$_3$pyzphen doped device showed high efficiency, high stability, weak efficiency roll-off, and pure red light. Furthermore, the structure of using electron-transporting materials as host, which needs no hole-blocking layer, is promising for commercial production of OLEDs.

The energy level diagram of the device and the chemical structures of the materials are shown in Fig. 1. The energy levels were estimated from the results of cyclic voltammetry and absorption spectra. Eu(DBM)$_3$pyzphen was synthesized according to the literature,[11] and other materials were commercially purchased without further purification. Organic materials were evaporated onto precleaned and plasma-treated indium tin oxide (ITO) glass substrate (25 Ω/□) in vacuum at 5×10^{-4} Pa. The emitting area of the device was defined as 10 mm^2 by cathode mask. All measurements were carried out in atmosphere at room temperature with the methods reported in previous letter of our group.[12]

Figure 2(a) shows the efficiency-current (η_c-J) and luminance-current-voltage (L-J-V) characteristics of a device

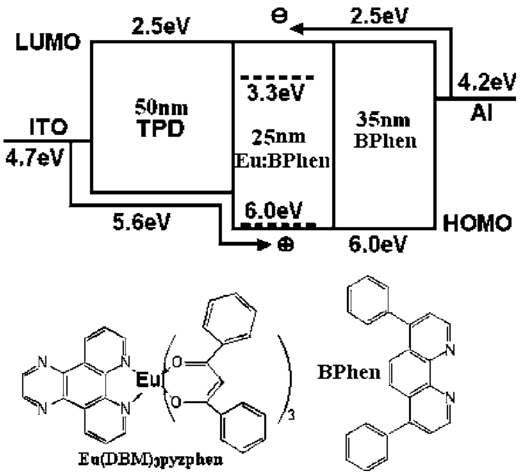

FIG. 1. Energy level diagram of the electroluminesent (EL) device [the highest occupied molecular orbital and lowest unoccupied molecular orbital levels of Eu(DBM)$_3$pyzphen are shown with dashed line] and chemical structures of Eu(DBM)$_3$pyzphen and BPhen.

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[a] Electronic mail: wllioel@yahoo.com.cn

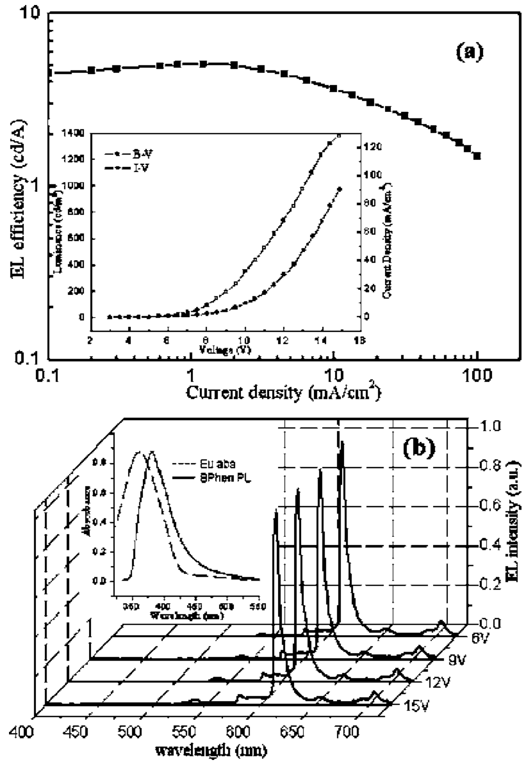

FIG. 2. (a) η_c-J and L-V-J (inset) characteristics of the 25 wt % Eu(DBM)$_3$pyzphen doped BPhen device. (b) EL spectra of the device at 6, 9, 12, and 15 V. PL spectra of BPhen and absorption spectra of Eu(DBM)$_3$pyzphen (inset).

with the structure of ITO/TPD (50 nm)/ Eu(DBM)$_3$pyzphen : BPhen (25 wt %, 25 nm)/BPhen (35 nm)/LiF (1 nm)/Al (100 nm). The concentration of Eu(DBM)$_3$pyzphen in BPhen had been optimized. A maximum current efficiency of 5.1 cd/A, corresponding to an external quantum efficiency of 2.4%, was observed at the current density of 1.2 mA/cm^2. The maximum luminance reached 1400 cd/m^2. It is fascinating that the device maintained high efficiencies at high luminance and current densities. For example, at the luminance of 100 cd/m^2, the efficiency reached 4.7 cd/A, and at the current density of 10 mA/cm^2, the efficiency obtained 3.8 cd/A. The efficiency roll-off in this device is much smaller than that of Eu-complex OLEDs reported previously.[4–9] Emission spectra of the device are insensitive to voltage, as shown in Fig. 2(b). The color coordinates were (0.66, 0.33), (0.66, 0.34), and (0.65, 0.34) at the brightness of 100, 800, and 1400 cd/m^2, respectively.

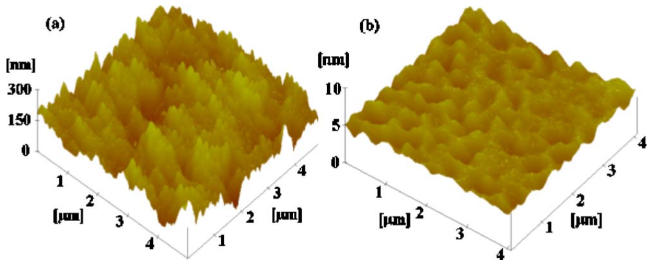

FIG. 3. AFM images of (a) a 250 nm pure Eu(DBM)$_3$pyzphen film and (b) a 250 nm Eu(DBM)$_3$pyzphen : BPhen (25 wt %) film.

Devices of Eu(DBM)$_3$pyzphen doped into typical hosts such as CBP, TPD, and PBD were fabricated for comparison. The device with neat Eu(DBM)$_3$pyzphen as EML was also fabricated. Concentrations of Eu(DBM)$_3$pyzphen in these devices were optimized respectively. We list the performances of these devices in Table I. It can be seen that the neat Eu(DBM)$_3$pyzphen EML device exhibited very poor performances, which would attribute to the poor film-forming ability of the Eu(DBM)$_3$pyzphen. As is shown in atomic force microscopy (AFM) images of Fig. 3, the neat Eu(DBM)$_3$pyzphen film is full of needle crystal and appears inhomogeneous. When Eu(DBM)$_3$pyzphen was doped into BPhen, the doping film looks much more continuous and homogeneous. The root-mean-square roughness (σ_{rms}) of the neat film was roughly 13.0 nm but only 2.4 nm of that in Eu(DBM)$_3$pyzphen : BPhen (25 wt %) film, i.e., doping Eu(DBM)$_3$pyzphen into BPhen could form a better contact with the carrier-transporting layer, which may improve the device stability.

In order to have an estimate of the efficiency roll-off degrees in different devices, we define the efficiency roll-off parameter (ERP) as

$$\mathrm{ERP} = \{\eta_c(\mathrm{max}) - \eta_c(10\ \mathrm{mA/cm^2})\}/\eta_c(\mathrm{max}),$$

where η_c(max) and η_c(10 mA/cm^2) are the maximum efficiency and the efficiency at the current density of 10 mA/cm^2, respectively. The ERP values are listed in Table I.

The data in Table I show that BPhen host device achieved higher efficiency, longer lifetime, purer color, and smaller efficiency roll-off than the other devices. One impor-

TABLE I. Performances of Eu(DBM)$_3$ pyzphen-based OLEDs.

Device structure	L max (cd/m^2)	η_c max (cd/A)	η_c at 10 mA/cm^2 (cd/A)	ERP[a]	CIE[b] (x,y)	T[c] (h)
TPD(50 nm)/Eu(25 nm)/BPhen(35 nm)	26	0.6				
TPD(50 nm)/Eu : TPD(17%, 25 nm)/BPhen(35 nm)	747	2.3	1.1	0.52	(0.65, 0.33)	69
TPD(50 nm)/Eu : PBD(20%, 25 nm)/BPhen(35 nm)	946	3.9	2.1	0.46	(0.63, 0.34)	41
TPD(50 nm)/Eu : CBP(10%, 25 nm)/BPhen(35 nm)	994	3.2	1.4	0.56	(0.61, 0.34)	57
TPD(50 nm)/Eu : CBP(10%, 25 nm)/BCP(20 nm) /Alq(15 nm)	1082	3.0	1.2	0.60	(0.59, 0.34)	52
TPD(50 nm)/Eu : BPhen(25%, 25 nm)/BPhen(35 nm)	1395	5.1	3.8	0.25	(0.66, 0.33)	135

[a] Efficiency roll-off parameter.

[b] Color coordinates at a luminance of 100 cd/m^2.

[c] Half-decay lifetime at a initial luminance of 300 cd/m^2; the devices were encapsulated in atmosphere without segregated water and oxygen.

tant reason for the improvement is that BPhen has excellent electron-transporting properties. The electron mobility of BPhen was reported to be of the order of 10^{-4} cm^2/V s, almost one order of magnitude larger than that of other electron transport materials.[13] Thus using BPhen as EML host might facilitate keeping charge balance and improve the efficiency of devices. On the other hand, holes injected into the EML were found to be quenchers of luminance and sources leading to poor stability.[7,8] In BPhen host device, the hole injection barrier at the TPD/BPhen interface is high enough to prevent the excess holes injecting into EML.

Figure 2(b) (inset) shows the PL spectra of BPhen film and the absorption spectra of $Eu(DBM)_3$pyzphen film. The large overlap between them implies that the Föster energy transfer from BPhen to $Eu(DBM)_3$pyzphen is efficient. The emission of BPhen could be quenched absolutely by $Eu(DBM)_3$pyzphen and a pure red emission was obtained. The analysis of the triplet energy levels and phosphorescent lifetime proved that Dexter energy transfer from BPhen to $Eu(DBM)_3$pyzphen also took place. As a result, the *T*-*T* annihilation of hosts, a main factor leading to efficiency roll-off,[4] might be alleviated. The Föster and Dexter energy transfers between BPhen and $Eu(DBM)_3$pyzphen will be demonstrated in detail in another paper.

In conclusion, we have fabricated an excellent rare-earth OLED by doping $Eu(DBM)_3$pyzphen into BPhen. The performances of the device were comprehensively improved, especially that the efficiency roll-off at high current densities was greatly alleviated. With the stability of BPhen improved by coevaporation of $Eu(DBM)_3$pyzphen and balanced charges injection, the lifetime of our device has also been improved.

The authors are grateful to the National Nature Science Foundation of China (Grant No. 90201012) for financial support.

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