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Improved performance of europium-complex electroluminescent devices with metal-mirror microcavity

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Abstract

Eu-complex organic electroluminescent (EL) devices with a double metal-mirror Fabry-Pérot microcavity structure were constructed to increase luminance efficiency and to improve colour purity. By optimizing the device structure, bright pure red EL from the Eu^{3+} ion was obtained. The peak luminance of 1160 cd m^{-2} at 19 V and CIE coordinates of ($x = 0.675$, $y = 0.320$) at 12 V were achieved in the cavity device. The narrow-band emission peak was not changed with increasing detection angle, and the colour saturation of the top 45°-off normal EL emission was even better than that of top normal emission in noncavity devices, overcoming the emission colour blue-shift with increasing detection angle in traditional microcavity devices. It was more important that a significant improvement in EL quantum efficiency at high current density was observed in the cavity device and the increasing mechanism of the EL efficiency was also revealed, which should be mainly ascribed to the shortened lifetime of the excited state of the Eu^{3+} ion.

1. Introduction

Organic light emitting diodes (OLEDs) have been attracting the attention of many researchers because of their potential for application in large area flat displays, and much progress has been achieved, especially since the report on efficient double layer structure OLEDs [1]. However, the bright pure red emission was still an obstacle for the industrialization of OLEDs. Many highly efficient red emitting materials such as fluorescent dyes [2] and phosphorescent materials [3] have been explored, but most of them demonstrated wide-band emission with FWHM (full width at half-maximum) of about 50 nm, which is unsuitable for the red primary colour of a full-colour display. The use of sharp-band trivalent europium (Eu^{3+}) complexes as an emitting layer can not only achieve pure red emission, but, in theory, the EL efficiency is not limited to 1/4 of photoluminescence (PL) efficiency because both the singlet and triplet excitons can be used for the excitation of the rare earth (RE) ion in organic EL devices [4–5]. Thus, the performance improvement of EL devices with RE-complexes, especially Eu-complexes, is a more interesting subject.

Xin *et al* have reported luminance exceeding 2000 cd m^{-2} by optimizing the device structure with tris(dibenzoylmethanato){1-ethyl-2-(*N*-ethyl-carbazole-yl-4)- imidazo[4,5-f]1,10-phenanthroline}europium(III) [$Eu(DBM)_3$-phencarz] as an emitting layer. However, the EL emission was orange–red at high operating voltage because the emission of tris(8-hydroxyquinoline)-aluminium (AlQ) was intensified with

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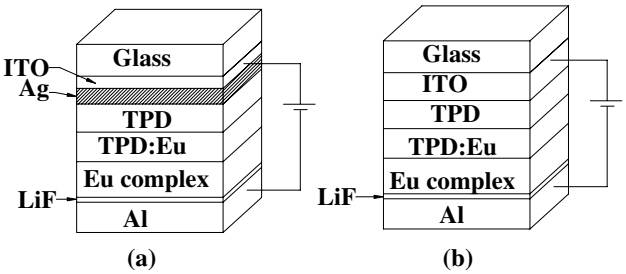

Figure 1. The structures of cavity (*a*) and noncavity (*b*) EL devices based on Eu(DBM)$_3$bath.

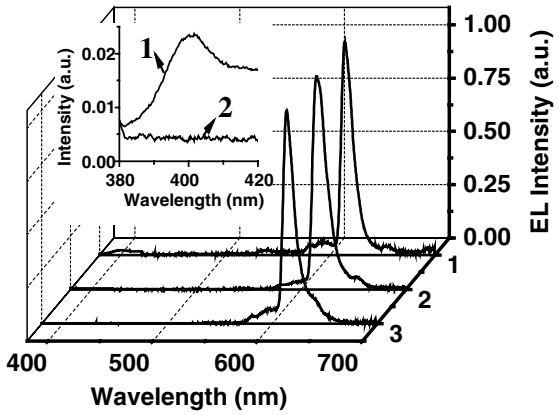

Figure 2. EL spectra of cavity and noncavity devices detected at 12 V. Spectra 1 and 2 represent the top normal emission of cavity and noncavity devices, respectively; spectrum 3 represents the 45°-off top normal emission of the cavity device; curves 1 and 2 in the inset demonstrate the magnified spectra 1 and 2 in the 380–420 nm region, respectively.

increasing operating voltage [6]. Sun *et al* found that in doped emitting layer devices, the EL emission of the host can be observed due to the inefficient energy transfer from host to dopant [7]. Our group has successfully fabricated the triple-layer unclear interfaces device with N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine [TPD]: europium(dibenzoylmethanato)$_3$monophenanthroline [Eu(DBM)$_3$bath] as the emitting layer. Pure red EL from Eu^{3+} was obtained due to the avoidance once of the exciplex emission and higher external EL quantum efficiency (η_{ext}) of 4.6%; however, it was only achieved at low current density of 0.01 mA cm^{-2} [8–9]. What is more important is that the decrease in η_{ext} in Eu-complex devices at high current density was serious in the former devices [6–10]. It is another major handicap to the application of Eu^{3+} complexes in OLEDs besides the monochrome.

In this communication, we designed the OLEDs with a double metal-mirror Fabry-Pérot microcavity structure to overcome the foregoing questions because this structure can enhance the luminance, narrow emission spectra and shorten the decay lifetime [11–13]. Notwithstanding that several groups have studied the Eu-complex microcavity OLEDs with DBRs, and observed the sharply directed emission pattern and the mono-mode emission of 612 nm compared with noncavity devices; they did not confirm the improvement in emission efficiency experimentally [14–15]. However, in this paper, the brightness was improved remarkably and an improvement in η_{ext} at high current density in cavity devices was observed.

2. Experiment details

Microcavity OLEDs and control devices were grown onto the pre-cleaned 100 Ω/□ glass substrates in the same vacuum by high vacuum ($< 5.0 \times 10^{-4}$ Pa) thermal evaporation. The cavity device comprises a 33 nm thickness semitransparent Ag mirror (reflectance is about 80%), N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine [TPD] as the hole transporting layer (HTL), 20 nm of TPD:europium(dibenzoylmethanato)$_3$monophenanthroline-[Eu(DBM)$_3$bath] as the emitting layer, 55 nm of Eu(DBM)$_3$bath as the electron transporting layer (ETL) and a cathode comprising 0.5 nm LiF and 100 nm thickness Al; the configuration is shown in figure 1(*a*). The comparable device (shown in figure 1(*b*)) possesses the same organic layers and cathode. The EL spectra were detected by a Hitach-4000 fluorescence spectrophotometer. The EL luminance–voltage characteristics were measured simultaneously by a dc power supply combined with a spot photometer. The PL decay times were measured by a spectrometer, a photomultiplier, a boxcar averager and the sample was excited by YAG: Nd laser at a wavelength of $\lambda = 355$ nm. For the EL lifetime measurement, an Agilent 8114A 100 V/2 A programmable pulse generator was used to apply rectangular voltage pulses to the devices, and the EL signals were detected by the 50 Ω input resistance of a digital oscilloscope (Aglient Model 54825A, 500 MHz/2 Gs/s) together with a photomultiplier (time resolution ≈ 0.65 ns) located at the top of the devices. All the measurements were carried out at ambient room temperature.

3. Results and discussions

The top normal EL spectra of the cavity and control device operated at 12 V are shown in figure 2 (lines 1 and 2, respectively). It can be seen that the FWHM of top normal emission spectrum of the cavity device was not narrowed as compared with the noncavity device which, was about 5 nm; however, the emissions centred at 405 nm resulted from TPD (seen the inset in figure 2) and at 540 nm due to $^5D_1 \rightarrow {}^7F_{0,1}$ of the Eu^{3+} ion being depressed evidently in the cavity device, which could increase the red colour saturation of the EL. As a result, the CIE coordinates were improved from (0.640, 0.342) in the noncavity device to (0.675, 0.320) in the cavity device, which is much closer to the red recommended by the National Television Standards Committee for a video display. Figure 2 also demonstrates the top 45°-off normal emission spectrum in the cavity device (line 3). It can be seen that the $^5D_0 \rightarrow {}^7F_1$ emission was increased; however, the emission peak centred at 612 nm is not obviously changed and the CIE coordinates were (0.662, 0.328), which is much better than that of top normal emission in the noncavity device. The microcavity devices based on Eu-complexes overcame the defect of traditional cavity device (i.e. the emission peaks were blue-shift with increasing detection angle) [11], which being attributable to the main emission band of $^5D_0 \rightarrow {}^7F_2$ from Eu^{3+} ion is too narrow (about 5 nm) to shift.

Figure 3 shows the dependence of current efficiency on driving current density of the cavity and noncavity devices; it

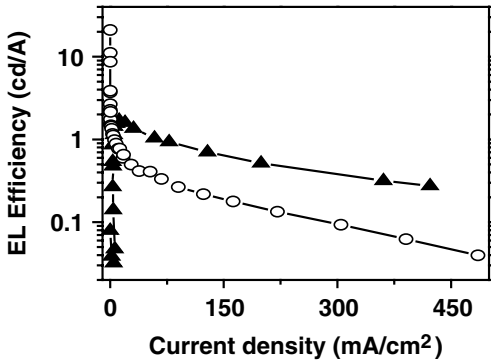

Figure 3. Dependence of the EL efficiency of cavity (▲) and noncavity (○) devices on the current density.

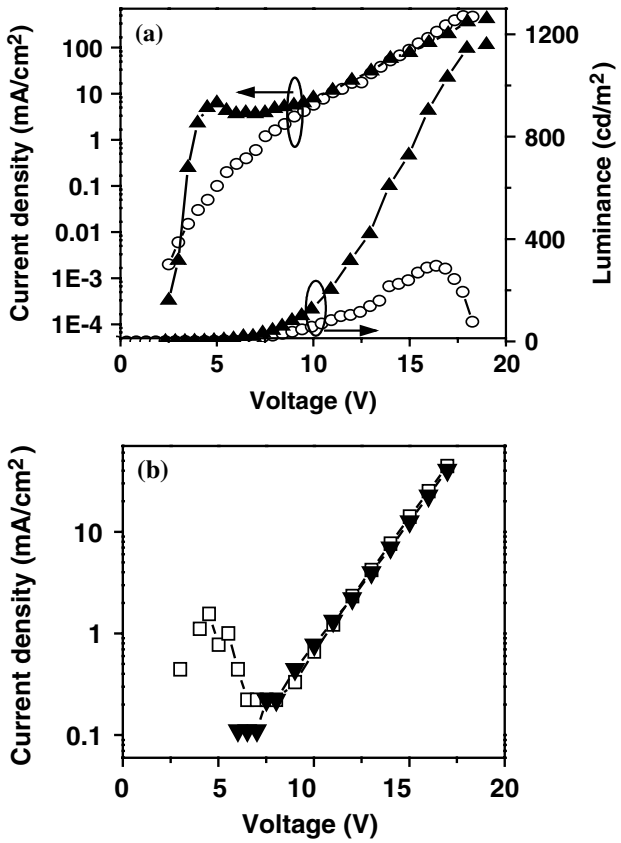

Figure 4. (*a*) Dependence of the current density and luminance of cavity (▲) and noncavity (○) devices on the operating voltage. (*b*) Current density–voltage characteristics of the cavity device measured consecutively; □ and ▼ represent the first and second test, respectively.

can be seen that the maximum current efficiency of 1.7 cd A^{-1} is obtained at $J = 12\,mA\,cm^{-2}$ in the cavity device and 21 cd A^{-1} is obtained at $J = 0.002\,mA\,cm^{-2}$ in the control device, respectively.

Although at lower current density, the efficiency is lower in the cavity device, which is due to the large leakage current [16], as is depicted in the current density–voltage characteristic of figure 4. However, a remarkable improvement in current efficiency at high current density can be observed in the cavity device; that is, at $J = 300\,mA\,cm^{-2}$ the cavity device showed higher efficiency compared with the noncavity device (0.4 cd A^{-1} versus 0.09 cd A^{-1}). And the characteristic current (J_0) at which the current efficiency fell to 50% of its peak value due to the triplet–triplet (T–T) annihilation was $98\,mA\,cm^{-2}$ in the cavity device, even considering the same current efficiency fall (from 1.7 cd A^{-1} dropped to 0.85 cd A^{-1}); in the noncavity device J_0 was $9\,mA\,cm^{-2}$. The current saturation characteristic was considerably improved at larger driving current density, since, for phosphorescent devices, the roll-off of current efficiency with J is consistent with the lifetime (τ) and J_0 is proportional to τ^2 [10]. In theory, the microcavity structure can increase the radiation rate and shorten the emission lifetime [17]. Table 1 lists the PL and EL lifetimes of the excited state of the Eu^{3+} ion of cavity and noncavity devices, respectively. It can be observed that both in the PL and EL measurements, τ was shortened by more than 30 μs. In order to eliminate the effect of the metal cathode on τ, devices using gadolinium(dibenzoylmethanato)$_3$monophenanthroline [Gd(DBM)$_3$bath] as ETL were fabricated, and similar results were observed in PL and EL measurements. Therefore, in the cavity device, the shortened lifetime was caused by the exciton and photon coupled effect [18], which could lead to considerable improvement in η_{ext} at high driving current density.

Table 1. The PL and EL excited state decay times of Eu^{3+} in cavity and noncavity devices using Eu-complex and Gd-complex as the ETL, respectively.

		τ (μs)	
ETL	Structure	PL	EL
Eu(DBM)$_3$bath	Cavity	225 ± 1	157 ± 1
	Noncavity	295 ± 2	197 ± 2
Gd(DBM)$_3$bath	Cavity	203 ± 1	132 ± 1
	Noncavity	280 ± 1	170 ± 1

Figure 4(*a*) shows the dependence of luminance on driving voltage. It is found that in the cavity device a large current existed even if the driving voltage was below the turn-on voltage; this could be caused by the islands on the Ag anode, where short circuit points exist, which can cause leakage current. Figure 4(*b*) demonstrates the comparison of current density–voltage characteristics of the cavity device by repeated measurements. Once the cavity device operated with high voltage, the leakage current at low driving voltage did not exist, which should be ascribed to the high electric field eliminating the short circuit points. In figure 4(*a*), it is also obtained that the maximum luminance of 1160 cd m^{-2} was obtained at 19 V in the cavity device, which is three times larger than that of the noncavity device (370 cd m^{-2} achieved at 16.5 V). The enhancement of the light output should be attributed to the resonant effect of the cavity [11].

4. Summary

In summary, an Eu-complex OLED with microcavity structure was constructed, which can demonstrate high bright and pure red emission. The emission peak was not blue-shifted with the increasing detection angle. What is more important is that, compared with the noncavity device, significant improvement in the current efficiency at high current density was achieved

due to the short lifetime of the excited state caused by the coupled effect of exciton and photon, thereby minimizing the T–T annihilation. The pure red EL with sharp-band emission and high η_{ext} at high current density are very important for achieving red primary colour of full colour displays for OLED, and even for determining electric laser output by the simple microcavity structure based on an Eu-complex.

Acknowledgments

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