



Short Communication

Pure red organic light-emitting diode based on a europium complex

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ABSTRACT

A hole-blocking layer, 4,7-diphenyl-1,10-phenanthroline (Bphen), was introduced between the emission layer (EML) and the electron-transporting layer (ETL) for a europium complex based organic red light-emitting device. Such a structure helps to reduce hole leakage from the EML into the ETL, resulting in improved purity of emissive light. Optimum Bphen thickness of around 10 nm was observed to produce a current efficiency of 3.1 cd/A and brightness of 465.2 cd/m² at 14 V. With 10 nm Bphen layer, the red emission spectrum shows excellent color saturation with Commission Internationale De L'Eclairage coordinates of (0.64, 0.33) at 7 V.

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1. Introduction

Organic light-emitting devices (OLEDs) have been developed for full-color, flat panel displays alternative to liquid crystal-based ones, since the pioneering works by Tang and VanSlyke [1]. At present, the development of high-performance red emission is still much in demand compared with green and blue emission. In red OLEDs, fluorescent organic molecules and polymers, and phosphorescent organic molecules with heavy metals have been widely used [2–4]. However, the emission spectra of these materials are broad resulting in poor luminescent purity, which is not suitable for actual display applications. Europium (Eu) complexes, which exhibit red emission corresponding to the ⁵Do → ⁷F₂ transition of Eu³⁺ ions, are attractive because of their pure red emission with a peak of 612 nm and a half bandwidth of 3 nm [5–11]. It is well known that rare-earth (RE) complexes are expected to show high electroluminescence (EL) efficiency since both singlet and triplet excitons are involved in the luminescence process. Previously, much progress in EL performances has been achieved by several groups [12–23]. However, the properties of Eu complex based OLEDs are still not very satisfying; for example, significant decrease of efficiency is observed at high current density because of triplet–triplet annihilation and the emission from Eu³⁺ ions is usually accompanied by the luminescence from the host or electron-transporting material.

In this paper, we report a high purity red OLED using a 4,7-diphenyl-1,10-phenanthroline (Bphen) hole-blocking layer (HBL) between the light-emitting layer (EML) and the electron-transporting layer (ETL). In order to investigate the effect of Bphen on device performance and find out the optimized thickness of it, we have fabricated four devices with the structure of indium–tin-oxide (ITO)/4,4',4''-tris(3-methylphenyl-amino)-triphenylamine (m-MTDA-TA)/N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB)/4,4'-N,N'-dicarbazole-biphenyl (CBP): 2% Eu complex/Bphen (Xnm)/tri(8-hydroxyquinoline) aluminum (Alq₃: 30-Xnm)/LiF/Al, where X = 0, 5, 10 and 15 nm for device A, B, C, D, respectively. The total thickness of ETL layer was maintained at 30 nm. By analyzing the EL spectra and characteristics of these devices, we found out that the emission of the ETL (Alq₃) could be eliminated by 10 nm Bphen. The used Eu complex is 3-ethyl-2-(2-fluorophenyl)imidazo[4,5-f]1,10-phenanthroline (EFPPI). The chemical structure of the Eu complex and the structure of the devices are shown in Fig. 1.

2. Experiments

The OLEDs were grown on ITO-coated glass substrates. Prior to organic-film deposition, the ITO-coated substrates were degreased with detergent solution and solvents, then dried in an oven, and finally treated in an ultraviolet–ozone chamber before being loaded into a vacuum evaporation system with pressure of under 4×10^{-6} Torr. First, a 30 nm thick m-MTDA layer was evaporated followed by a 20 nm thick hole-transporting layer of NPB.

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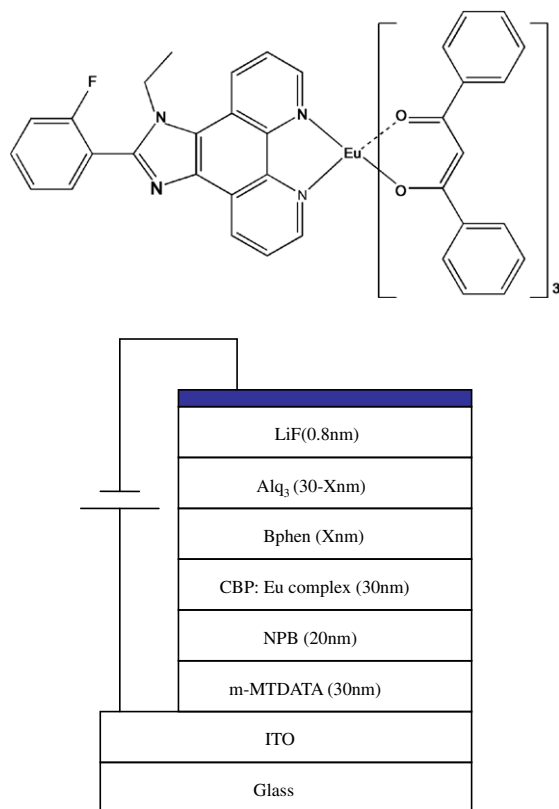


Fig. 1. Chemical structure of the used Eu complex and the structure of devices.

Then a Eu complex doped CBP layer was grown. For the subsequent layers, four different device architectures were fabricated (see Fig. 1). Device A has a structure comprising 30 nm thick Alq₃. Device B corresponds to device A with an additional 5 nm thick Bphen (HBL). For device C and device D, the thicknesses of Bphen are 10 and 15 nm, respectively. For all the devices, the total thickness of Bphen layer and Alq₃ layer was maintained at 30 nm. All organic materials were thermally evaporated at a rate of about 0.1–0.2 nm/s. The top cathode is identical for all devices. It consists of a 0.8 nm thick LiF layer followed by an aluminum layer. The EL spectra and CIE coordinates of the devices were measured by using a PR650 spectroscan spectrometer. The efficiency–luminance–current characteristics were measured with a programmable Keithley 2400 voltage–current source. All measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

The normalized EL spectra corresponding to the four device architectures are shown in Fig. 2. For all the four devices, a narrow red emission at a peak wavelength of 612 nm was observed. From the EL spectra of devices A and B, we can also see that besides the main emissive peak at 612 nm, assigned to ⁵Do → ⁷F₂ transition, a minor green emissive peak at around 520 nm in the EL spectrum becomes visible, which we have attributed to the emission of Alq₃. The emission of Alq₃ may be due to hole-escaping into the Alq₃ layer, which greatly lowered the color purity of the devices. It is clearly that when the thickness of Bphen increases from 0 to 15 nm, the emission from Alq₃ decreases greatly. For devices C and D, we can hardly see light emission from Alq₃. This can be explained by the energy level diagram of the devices shown in Fig. 3.

Bphen has a deeper HOMO level than that of CBP, preventing efficiently the migration of holes out of the luminescent layer.

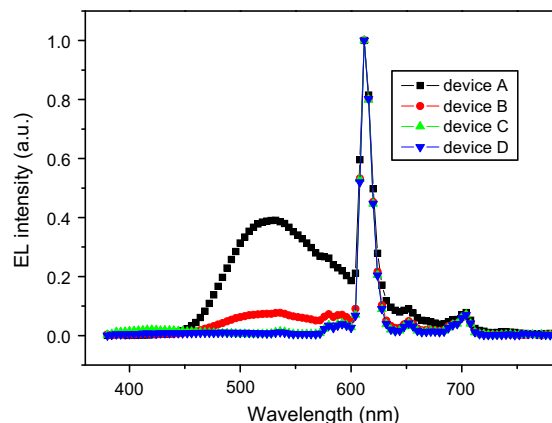


Fig. 2. Normalized EL spectra of the four devices at 9 V.

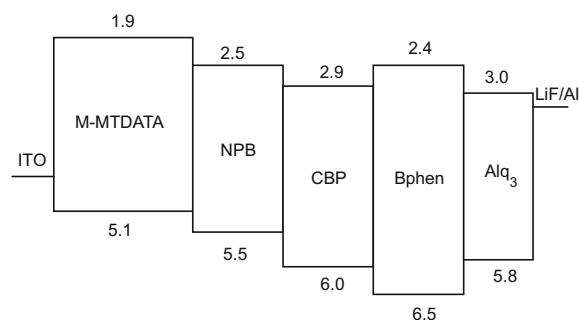


Fig. 3. Schematic energy level diagram of the EL devices.

Table 1
CIE coordinates of the devices A–D as a function of driving voltage.

Devices	Driving voltages			
	5 V	7 V	9 V	11 V
A	(0.494, 0.429)	(0.454, 0.461)	(0.410, 0.489)	(0.369, 0.511)
B	(0.609, 0.355)	(0.591, 0.368)	(0.539, 0.396)	(0.457, 0.437)
C	(0.643, 0.330)	(0.645, 0.328)	0.615, 0.319)	0.554, 0.218)
D	(0.638, 0.332)	(0.647, 0.331)	(0.627, 0.328)	(0.582, 0.321)

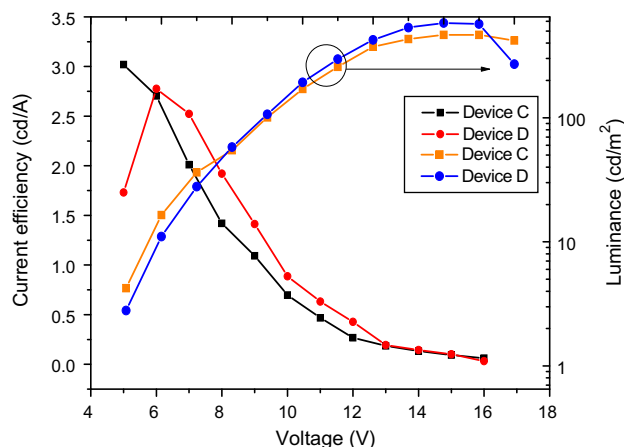


Fig. 4. Current efficiency–luminance–voltage characteristics of devices C and D.

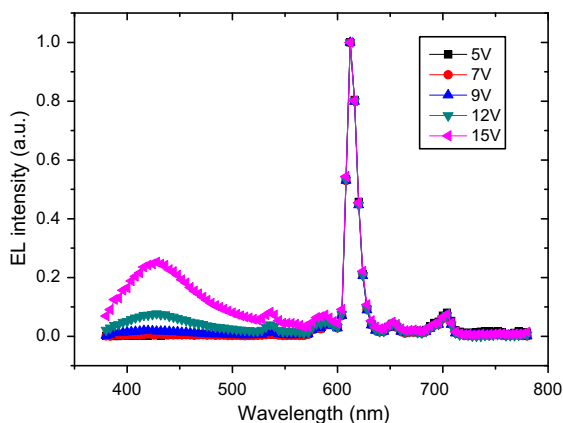


Fig. 5. Normalized EL spectra of device C under different biases.

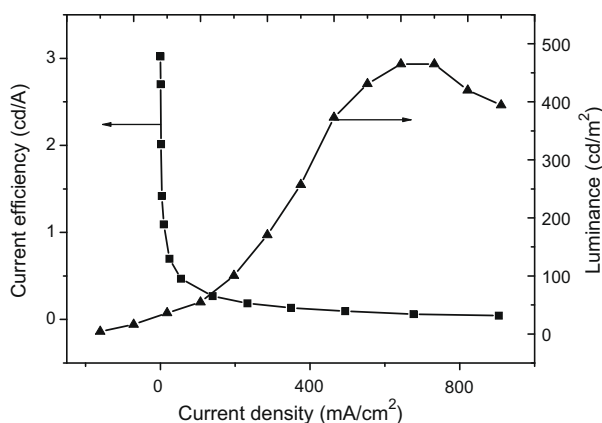


Fig. 6. Current efficiency–luminance–current density characteristics of device C.

With the thickness of Bphen increasing, less holes can migrate into the ETL (Alq_3) and so more holes will be blocked in the interface between the EML and HBL; thus when the electrons are injected into EML, the excitons will be formed in the EML and then recombine. Table 1 summarizes the CIE coordinates of the four devices as a function of driving voltage. We can see that devices C and D have approximately the same color saturation at (0.64, 0.33). The introduction of the hole-blocking layer clearly improves the purity of emissive light. Next, we compared the current efficiency–luminance–voltage characteristics of devices C and D. From Fig. 4, we can see that the performances of these two devices do not have much difference and 10 nm Bphen is enough for our purpose.

Additionally, it is noteworthy in Table 1 that the coordinates of device C change from (0.615, 0.319) at 9 V to (0.554, 0.218) at 11 V, indicating that the emission color shifts from red to magenta. This phenomenon can be explained by Fig. 5 which gives out the normalized EL spectra of device C under different biases. We can observe in Fig. 5 that with increasing voltage the emission at around 440 nm becomes stronger, which can be attributed to

emission from NPB. While the applied voltage becomes larger, more electrons may transverse the CBP layer and reach the NPB layer, and then recombine with the holes there, which leads to stronger emission of NPB.

Fig. 6 shows the current efficiency–luminance–current density characteristics of device C. We can see that device C has the maximum luminance of 465.2 cd/m^2 and the highest efficiency of 3.1 cd/A . As seen in Fig. 6, the EL current efficiency decreased greatly with increasing current density, which may be owing to triplet–triplet annihilation [5].

4. Conclusion

In our experiments, we have introduced a HBL (Bphen) between the EML and the ETL. With the hole-blocking structure, the color purity has largely been improved. The optimum device, which has 10 nm thick Bphen layer, shows excellent pure red emission with a CIE of (0.64, 0.33) at 7 V. The maximum luminance and current efficiency of this device are 465.2 cd/m^2 and 3.1 cd/A , respectively.

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