The electroluminescent investigation of double layer Eu-complex organic electronic luminescence diodes

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Abstract

Double layer organic electronic luminescence diodes (OLEDs) based on europium(dibenzoylmethanato)$_3$monophenanthroline [Eu(DBM)$_3$bath], ITO/N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD)/Eu(DBM)$_3$bath/LiF/Al have been fabricated. With increasing the thickness of hole transporting layer, the maximum EL efficiency was increased, and the EL efficiency of 10 cd/A was achieved when the thickness of TPD layer was 80 nm; however, at high current density, the EL efficiency of all devices was decreased drastically. Besides, the evolution of EL emission spectra with increasing operating voltage was found, the mechanisms of the symmetry around the ion improved and the annihilation of excited state of Eu(DBM)$_3$bath were discussed in explaining this phenomenon.

1. Introduction

Organic electronic luminescence diodes (OLEDs) attracted many researchers attention because of their potential for large-area, flexible light emitting displays, and so on. It has obtained great progress since Tang and VanSlyke demonstrated the high efficiency double layer structure device [1]. Their device consisted of a hole transporting layer and an emitting layer, and the hole transporting layer can both improve the injection of holes and block electrons, thus the efficiency was improved. However, high efficiency pure red emission was still a challenge for OLEDs. Kido [2] first reported the narrow band emission centered at 612 nm of rare earth Eu^{3+} was suitable for red emission of OLEDs, and it has high photoluminescence efficiency which caused by the intercrossing, however, the EL luminescence efficiency was rather low, especially, when it was operated at high current density. Many researchers have studied the mechanism of

the efficiency decline and favor to improve it by changing the emission material [3–5] or optimizing the device structure [6–9]. Our group has successfully fabricated bright pure red emission by mixing with Eu-complex and TPD [6]; at the same time, it was found that the EL efficiency depends on the molecular ratio of the mixing layer and the highest external quantum efficiency was 4.6% [7]. Hu and his coworker [8] improved the device efficiency using the alternate layer of BCP and Eu-complex as emitting layer and obtained an optimal alternate number for obtaining a high EL efficiency, 3 cd/A. Besides, they reported that the efficiency of the emission from Eu(DBM)$_3$TPPO can be improved by increasing the thickness of the Eu(DBM)$_3$TPPO layer. They attributed this effect to the thicker Eu(DBM)$_3$TPPO layer reduced the hole density in this layer, therefore, the quenching of Eu(DBM)$_3$TPPO in the excited state by the holes was lessened [9].

In this paper, we observed the efficiency of the devices with Eu-complexes was improved at low current density with increasing the thickness of TPD layer and the evolution of emission spectra on operating voltage. Using the dependence of EL efficiency on current density and the

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carrier injection characteristic, we discussed the reason of the improved EL efficiency. Besides, the change of emission spectra was mostly due to the annihilation of excited state of $Eu(DBM)_3bath$.

2. Experiments

Fig. 1 shows the materials molecular structures used in this experiment. The devices were based on glasses coated by ITO with a sheet resistance of $100\,\Omega/\square$, which was used as anode, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-bi-phenyl-4,4'-diamine (TPD) was the hole transport layer, 40 nm europium(dibenzoylmethanato)$_3$monophenanthro-line $(Eu(DBM)_3bath)$ was both the electron transport layer and the emitting layer, and the cathode was composed of an ultra-thin LiF layer (1.5 nm) and Al layer (200 nm). All organic layers and cathode layers were deposited by conventional vacuum evaporation at about $5 \times 10^{-4}\,Pa$. The emission area was about $2 \times 4\,mm^2$. The thickness of the films was controlled *in vacuo* with a quartz crystal monitor. The brightness was measured by a 1980A sport photometer, and EL spectra were detected by a charge couple device (CCD) camera. All the measurements were carried out in ambient at room temperature.

3. Results and discussion

The relationship between the luminescence efficiency and current density with different thickness of hole transport-ing layer is shown in Fig. 2. The maximum efficiency of the emission from $Eu(DBM)_3bath$ can be improved from 1.38 to 10 cd/A, through increasing the TPD layer from 10 to 80 nm (see the insert of Fig. 2). Besides, the maximum luminescence efficiency of each device was obtained at

different current density, and with increasing TPD layer, the corresponding current density was decreased. However, at high current density, the efficiency of each device was decreased drastically and the device with thicker hole transport layer did not possess superiority any more. But in Fig. 3, which demonstrated the voltage dependence of efficiency, it can be seen that the luminescence efficiency with thicker TPD layer decreased slowly with increasing the operated voltage. The difference between the two figures can be explained by the *I–V* and *L–V* character-istics, which are shown in Figs. 4 and 5, respectively. The capability of current injection of 10 nm TPD is much worse than that of 20 nm, it is considered that the un-match of the hole and electron transporting layer. Further increasing
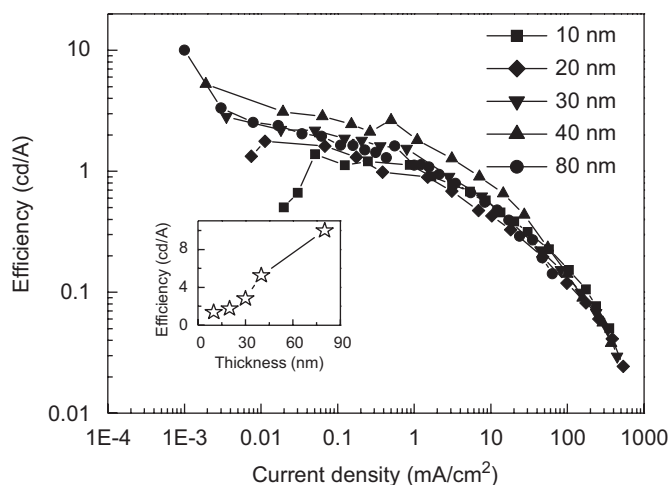

Fig. 2. Relationship between the EL efficiency and current density of $ITO/TPD/Eu(DBM)_3bath/LiF/Al$ cells with different thickness of the TPD layer, and the insert was the maximum luminescence efficiency vs. the thickness of the TPD layer thickness.
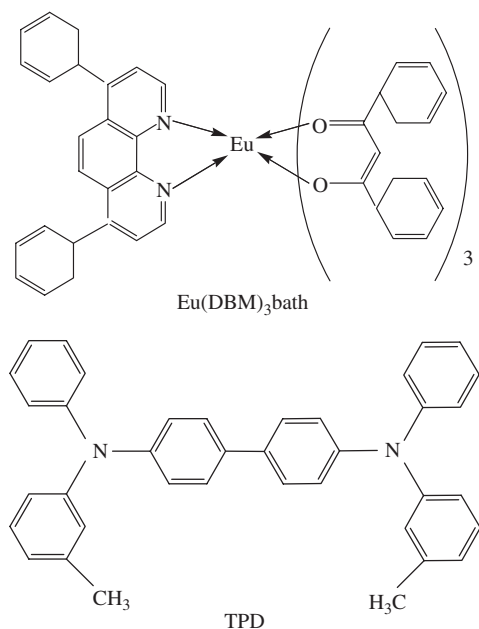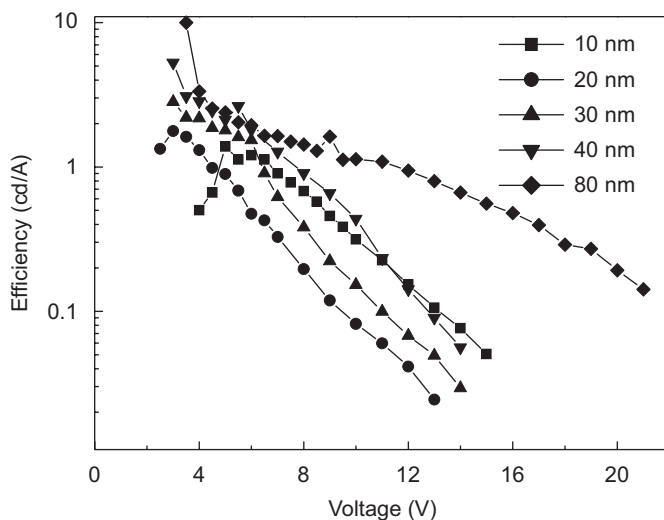

Fig. 1. Molecular structures of materials used.

Fig. 3. Relationship between the EL efficiency and operating voltage of $ITO/TPD/Eu(DBM)_3bath/LiF/Al$ cells with different thickness of the TPD layer.
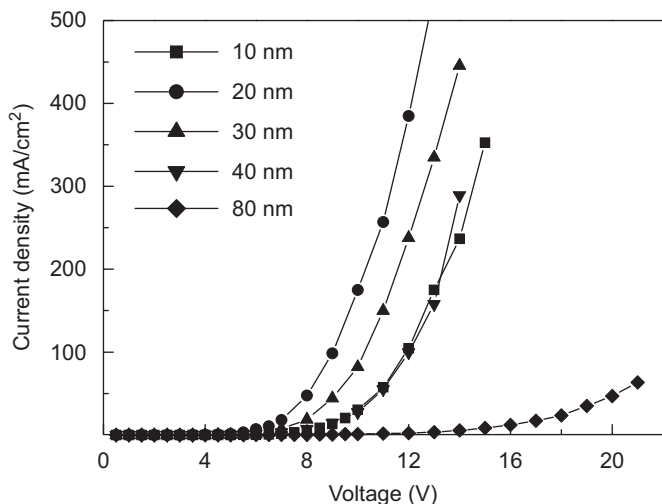
Fig. 4. Current density vs. voltage characteristics of ITO/TPD/Eu(DBM)$_3$bath/LiF/Al cells with different thickness of the TPD layer.
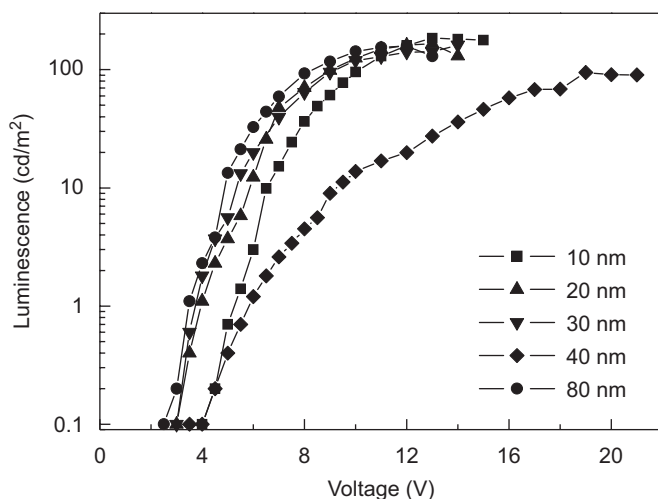

Fig. 5. Luminescence vs. voltage characteristics of ITO/TPD/Eu(DBM)$_3$bath/LiF/Al cells with different thickness of the TPD layer.

hole transporting layer thickness, the current injection of the device is gradually reduced. This should be ascribed to the TPD layer possess high hole mobility, and the change of voltage decreased on this layer caused by the thickness of TPD could be neglected, in other words, the voltage decreased on Eu(DBM)$_3$bath layer was constant, and the electron injection capability of each device was not changed. However, with increasing the thickness of TPD layer, the intensity of electric field across TPD layer was decreased, the hole injection was lessen, which could cause the less of electron injection, responsively, and the current injection was reduced at a certain voltage. From Fig. 5, it can be seen that the luminescence threshold voltage of 10 nm TPD is slightly higher than that of 20–40 nm. The TPD layer possessed double role, hole transporting and electron blocking, when it is too thin, the two functions cannot bring into good play, which would cause the worse

current injection and incompletely recombination of electron, thus its luminescence voltage characteristic is worse. However, for the worst luminescence voltage characteristic one with 80 nm TPD layer, this should be ascribed to the rather low current injection. Although the current injection is rather low, the recombination is available, it can emission from Eu(DBM)$_3$bath at very low current density, therefore, the maximum luminescence efficiency from this device is highest.

Since the luminescence lifetime of lanthanide complexes is generally long, such as Eu, about 200 μs, due to highly prohibited f–f transitions, the probability of quenching by the charge carrier is much higher than that for other organic materials which have shorter fluorescence lifetimes. And the quenching process can be represent by

$$M_1^* + M_2^+ \rightarrow M_1^+ + M_2,$$
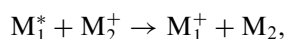
where M_1^* stands for a Eu(DBM)$_3$bath molecule in the excited state, and M_2^+ is a hole in the close vicinity of the M_1^* molecule [8].

The luminescence efficiency of each device decreases with the current density increases in the high current density after reaching the maximum value. This should be partly attributed to the quenching the excited state of the Eu(DBM)$_3$bath by the charge carrier because the concentration of the charge carrier increases with increasing the current. This phenomenon has been proved by C. Adachi [10]. On the other hand, the decreasing of efficiency at high current density could be partly attributed to the decomposing of the materials, which has been mentioned by Hong [7].

The $^5D_0 \rightarrow {}^7F_1$ emission around 590 nm is a pure magnetic dipole (MD) transition, and it is independent of the coordination sphere; however, the strongest $^5D_0 \rightarrow {}^7F_2$ emission centered at 612 nm is an electric dipole (ED) transition, which is sensitive to the nature and symmetry of the coordination environment, and it is an example of a hypersensitive transition. The intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ transition and the $^5D_0 \rightarrow {}^7F_1$ transition (I_{7F2}/I_{7F1}) is a good measure of the nature and symmetry of the first coordination sphere. In a centro-symmetric environment the MD transition of Eu^{3+} is dominating, whereas distortion of the symmetry around the ion causes an intensity enhancement of the $^5D_0 \rightarrow {}^7F_2$ transition [11].

In order to avoid the emission spectrum distorted by the continue current injection, it was measured by a CCD camera. The spectra were shown in Fig. 6. The two spectra were the device with 40 nm TPD layer operated at 8 and 13 V, the operating current density was 7 and 370 mA/cm^2, respectively. When the 590 nm emission intensity was normalized, the emission intensity of $^5D_0 \rightarrow {}^7F_2$ transition was decreased with increasing operating voltage indicated that or the symmetry around the ion was improved or the quenching excited state of Eu(DBM)$_3$bath was serious, or the two mechanisms were both existence.

The emission spectrum of the device that have operated with 100 mA/cm^2 DC current for 10 min was the same with
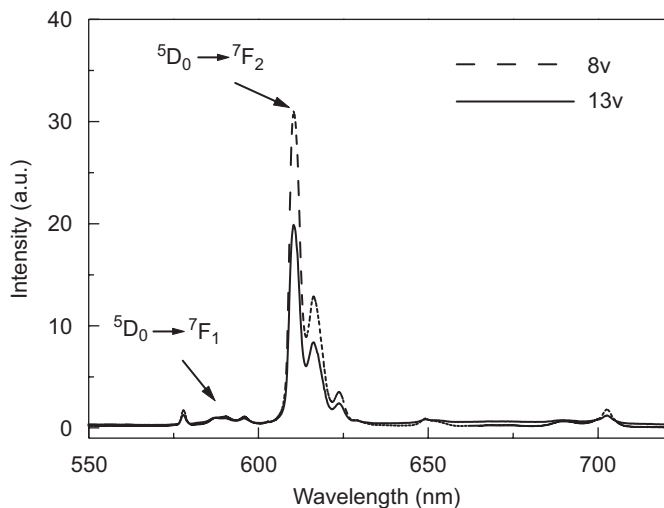
Fig. 6. Electroluminescence spectra of ITO/TPD (40 nm)/Eu(DBM)$_3$bath/ LiF/Al operated at 8 and 13 V.

that of before operated one at the same current density, this phenomenon suggested the decomposing of material in the entire process was in-dominant. Besides, circular measure results showed that the change trend of the first time emission spectra of the device operated with 8 and 13 V was the same with that of the second time measured. This indicated that the emission change of device operated at different current density was reversible, which further confirmed that the decomposing of material had little contribution in the emission change, and this phenomenon was peculiarly owned to the annihilation of excited state of Eu(DBM)$_3$bath at high current density.

The emission spectra of devices with different thickness of TPD layer were also measured at different voltage, and the same change trend was found. This indicated that only increasing the thickness of TPD cannot relax the annihilation of excited state of Eu(DBM)$_3$bath at high current density, therefore, this method cannot decrease the decline of the efficiency with increasing current density.

4. Conclusion

In summary, we have obtained the high electroluminescence efficiency, about 10 cd/A, from at low current density region by increasing the hole transporting layer, which cause the low current density at a certain voltage. Through the comparing of emission spectra, the decomposing of Eu(DBM)$_3$bath was found, which partially have effect on the drastic decreasing of efficiency at high current density. This indicated that only increasing the thickness of hole transporting layer or other function layer cannot solve the problem of decreasing of efficiency at high current density and new mechanism should be found out.

Acknowledgments

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