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Improved performance of electroluminescent devices based on an europium complex

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Electroluminescent (EL) devices using an europium complex $\text{Eu}(\text{DBM})_3$ bath as the electron-transport emitting layer were fabricated. The quenching effect of the metal cathode and the unstable nature of the Eu complex under EL operation markedly influence the EL efficiency. By keeping the emitting area far from the metal cathode and partly doping the $\text{Eu}(\text{DBM})_3$ bath layer with a hole-transport material, the EL performance was significantly improved. Sharp-band red emissions with turn-on voltage of 3 V, brightness of 820 cd/m^2 , and external quantum efficiency of 1% were achieved. © 2000 American Institute of Physics. [S0003-6951(00)04101-2]

There are advantages in fabricating electroluminescent (EL) devices using rare earth complexes. Theoretically, the upper limit of inner quantum efficiency can reach 100%, which is four times higher than that of the devices using other fluorescent materials. The sharp emission bands of rare earth ions are very suitable for full-color display. Therefore, to fabricate EL devices using rare earth complex is a subject of interest. Achievements on this subject have been made by several groups.¹⁻³ The brightness of 460 cd/m^2 for red emission and 920 cd/m^2 for green emission had been obtained. However, comparing with their excellent photoluminescence (PL) properties and the potential advantages mentioned above, the performance of rare earth complexes in organic EL devices is not satisfying. The efficiency and the brightness are not as high as expected, and no information concerning the aging process of these devices is found in literatures so far. There is a need to understand in detail the reasons that prevent the devices with rare earth complexes from better performance and to think out ways to overcome it.

In this letter, an Eu complex $\text{Eu}(\text{DBM})_3$ bath is used to fabricate red emissive devices. Two aspects are found to evidently influence the device efficiency and eventually effect the brightness, the degradation property and even emitting color of the device. One is the quenching effect of the metal cathode on the emission of Eu^{3+} ions. The other is the unstable nature of the Eu complex under EL operation. Partly doping of the $\text{Eu}(\text{DBM})_3$ bath layer with the hole-transport material results in the increase of EL efficiency and improvement of overall properties of the device.

The molecular structures of the materials and the device configurations are shown in Fig. 1. $\text{Eu}(\text{DBM})_3$ bath was shown to have excellent electron-transport property in an

earlier study.⁴ The PL spectrum of $\text{Eu}(\text{DBM})_3$ bath shows characteristic emission of Eu^{3+} ions (see Fig. 1). The widely used material TPD is the hole-transport layer. Also a non-fluorescent gadolinium complex $\text{Gd}(\text{acetylacetonato})_3$ (monophenanthroline) $[\text{Gd}(\text{AcA})_3\text{phen}]$ is used to act as spacer layer in this letter. All of the organic layers and cathode layer ($\text{Mg}_{0.9}\text{Ag}_{0.1}$) are deposited by conventional vapor vacuum deposition at a pressure of 10^{-7} Torr. The layer thickness is controlled *in vacuo* with a quartz crystal monitor. The emission area is 10 mm^2 . PL and EL are measured with a Hitachi 4000 fluorescence spectrophotometer, and the brightness is measured by a 1980A spot photometer. EL efficiency is estimated from measurement of the brightness and assumption of a Lambertian emitting surface.

At first, we fabricated the double-layer device with

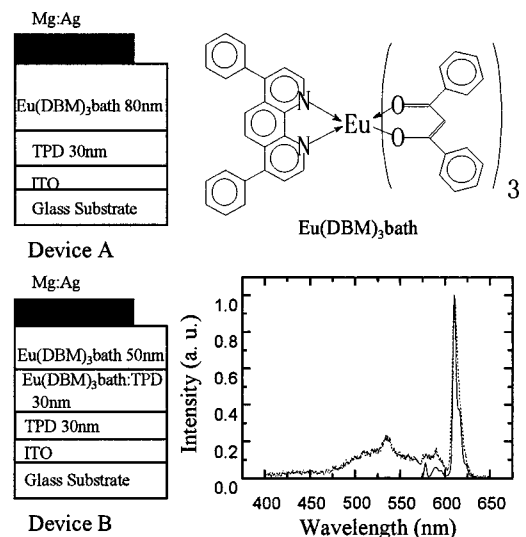


FIG. 1. The molecular structure and device configurations; the PL spectrum of $\text{Eu}(\text{DBM})_3$ bath film (solid line); the EL spectrum of the double-layer device (dotted line); the EL spectrum of the device B is the same as the PL spectrum of the Eu complex.

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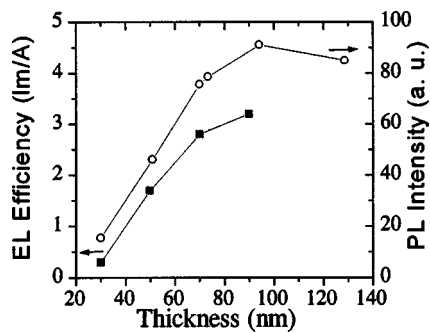


FIG. 2. EL efficiency as a function of the thickness of $\text{Eu}(\text{DBM})_3$ bath layer in double-layer device (solid square); PL intensity as a function of the total thickness of $\text{Eu}(\text{DBM})_3$ bath and $\text{Gd}(\text{AcA})_3\text{phen}$ layers (open circle).

structure of ITO/TPD/ $\text{Eu}(\text{DBM})_3$ bath/Mg:Ag. EL spectrum of the device is also shown in Fig. 1. Apart from the strong sharp emission bands of Eu^{3+} ions, a broad band with a peak at 530 nm appears at the left side of the spectrum. It makes the emitting color become orange-red, not pure red. This broad band is thought to be the result of exciplex formation at the interface of $\text{Eu}(\text{DBM})_3$ bath and TPD layer.

The EL efficiency of the device is sensitive to the thickness of the $\text{Eu}(\text{DBM})_3$ bath layer as shown in Fig. 2. At a constant current density of 1.0 mA/cm^2 , by thickening the $\text{Eu}(\text{DBM})_3$ bath layer from 30 to 90 nm the EL efficiency enhanced from 0.3 to 3.2 lm/A , about 10 times higher. It is believed that the emissions occur in a narrow area at the interface of $\text{Eu}(\text{DBM})_3$ bath and TPD layer. So thickening the $\text{Eu}(\text{DBM})_3$ bath layer actually changes the distance between the emitting area and the Mg:Ag cathode. Thus, the EL efficiency degradation could be interpreted by quenching effect of the metal cathode on the emission of Eu^{3+} ions. This is further confirmed in PL study. A series of samples with structure of glass/Mg:Ag(150 nm)/ $\text{Gd}(\text{AcA})_3\text{phen}$ (different thickness)/ $\text{Eu}(\text{DBM})_3$ bath (30 nm) are prepared. The thickness of $\text{Eu}(\text{DBM})_3$ bath and Mg:Ag layers are same for all of the samples. The spacer layer $\text{Gd}(\text{AcA})_3\text{phen}$ controls the distance between $\text{Eu}(\text{DBM})_3$ bath and the metal film. Under excitation of 350 nm-wavelength ultraviolet (UV) light, the PL intensity (in this case, it also represent the relative PL efficiency) of the $\text{Eu}(\text{DBM})_3$ bath layer in these samples shows sensitive dependency to the spacer layer thickness and this is also shown in Fig. 2. The EL efficiency and the PL intensity show similar tendency when the distance between the metal film and the excited Eu^{3+} ions is changed. This indicates that the proximity of the metal film is correlated with the efficiency decrease in both EL and PL cases.

The presence of a metal film alters the radiative decay rate of an emitter via interference effects, and opens up an efficient nonradiative decay channel via energy transfer to the metal film.⁵⁻⁷ The quantum efficiency for luminescence q is given by $q = k_r / (k_r + k_{nr} + k_{tr})$, where k_r is the radiative decay rate, k_{nr} is the nonradiative decay rate of the material, and k_{tr} is the rate constant for energy transfer to the metal film. k_r of Eu^{3+} ions is much smaller than that of most other emitting dipole such as Alq_3 because of its longer lifetime (about several hundred μs , but the lifetime of exciton for Alq_3 is only about 20 ns⁸). So quantum efficiency can be more easily reduced when even a small k_{tr} appears. We sup-

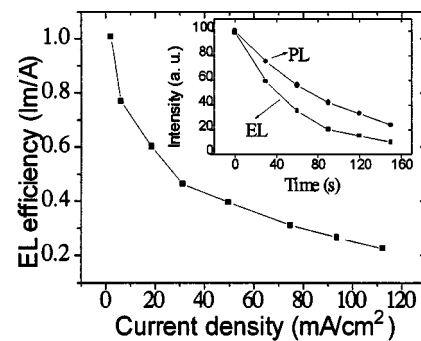


FIG. 3. Efficiency-current characteristics of device A; the inset shows PL and EL intensity quickly decrease under constant current density of 100 mA/cm^2 .

pose the quenching effect of the metal film is more severe in the Eu complex based EL device than in the one based on other materials, such as Alq_3 .

So keeping the emitting area far away from the metal cathode is especially important for Eu complex based EL devices. However, excessive increase of the $\text{Eu}(\text{DBM})_3$ bath layer would result in higher drive voltage. A thickness of 80 nm will be proper for $\text{Eu}(\text{DBM})_3$ bath in the double-layer device when both EL efficiency and drive voltage are considered.

Therefore, device A (shown in Fig. 1) was fabricated and the degradation property of this double-layer device have been tested. It is found that, under certain current for a period of time, not only EL intensity of the device but also PL intensity of the emitting layer decrease, and in a similar manner (see the inset of Fig. 3). The higher the drive current is the more quickly the PL and EL efficiency decrease. This shows the Eu complex is very unstable and may easily lose its luminescent ability in this double-layer device. Therefore, the aging process develops quickly, the EL efficiency quickly drops when the current density is increased (Fig. 3), and it is impossible to drive the EL device to high brightness.

If the deterioration of the Eu complex mainly occurs in the emitting area, the efficiency decrease could be very severe in this double-layer structure, because it is usually believed the emitting area is in a narrow region at the interface between the organic layers and thus it contains only a small amount of $\text{Eu}(\text{DBM})_3$ bath molecules. We suppose the situation will be better if the emitting area is enlarged and contains more $\text{Eu}(\text{DBM})_3$ bath molecules. So we explored a device structure which contains a TPD codeposited $\text{Eu}(\text{DBM})_3$ bath layer with a thickness of about 30 nm as shown in device B in Fig. 1. The weight ratio of TPD to $\text{Eu}(\text{DBM})_3$ bath is 1:3. TPD is used to introduce holes to deeper places in $\text{Eu}(\text{DBM})_3$ bath layer and thus to broaden the emitting region.

The quantum efficiency is further increased about four times in device B compared with device A. As a result, the general performance of device B is significantly improved. This is shown in Table I. We note the lifetime is obtained when the brightness drops to half the initial value by driving the device in argon atmosphere under constant current density.

Due to the excellent electron-transport property of $\text{Eu}(\text{DBM})_3$ bath, the turn-on voltage of the device is about 3

TABLE I. Data comparison between devices A and B.

	Device A	Device B
Turn on voltage	3 V	3 V
Maximum brightness	150 cd/m ² at 18 V	820 cd/m ² at 18 V
Luminescence efficiency at brightness of 100 cd/m ²	0.02 lm/w	0.40 lm/w
Lifetime at the initial brightness of 40 cd/m ²	18 h	200 h
Emitting color	orange-red	pure red

V, which is lower than that reported in earlier studies^{1,3,9} even though they applied additional electron-transport materials. From Table I we notice 20 times higher luminescent efficiency, about 10 times longer lifetime, and much higher brightness is obtained in device B. Moreover, no exciplex emission band appears in the EL spectrum and the emitting color is pure red. When the current density decreases to 0.6 mA/cm² the EL efficiency reaches 1.0 lm/w. The corresponding quantum efficiency is about 1.0%. This is comparable with the Alq₃ based device reported by Tang and Vanslyke.¹⁰

In conclusion, the quenching effect of the MgAg cathode on the emission of Eu³⁺ ions evidently influences the emitting efficiency of the Eu complex in EL devices, and the unstable property of the Eu complex is another factor which is responsible for the low efficiency. By keeping the emitting area far from the metal mirror, and by partly doping the Eu(DBM)₃ bath layer with TPD, these destructive effect can be partly reduced, and a much better EL performance can be achieved. If the EL stability of the rare earth complex is

improved, it is possible to fully realize the potential advantages of the material.

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