

Letter

# Organic electroluminescent devices using europium complex as an electron-transport emitting layer

C.J. Liang<sup>a,\*</sup>, Z.R. Hong<sup>a</sup>, X.Y. Liu<sup>a</sup>, D.X. Zhao<sup>a</sup>, D. Zhao<sup>a</sup>, W.L. Li<sup>a,1</sup>, J.B. Peng<sup>b</sup>, J.Q. Yu<sup>b</sup>, C.S. Lee<sup>c</sup>, S.T. Lee<sup>c</sup>

<sup>a</sup>Changchun Institute of Physics, Chinese Academy of Sciences, Changchun, People's Republic of China

<sup>b</sup>Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun, People's Republic of China

<sup>c</sup>Department of Physics and Material Science, City University of Hong Kong, Hong Kong

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## Abstract

Organic electroluminescent (EL) devices with europium complex  $\text{Eu}(\text{DBM})_3$  bath as electron transport emitting layer were fabricated. The devices showed bright red and white EL emissions when PVK and NPB, respectively, were used as the hole transport layer. This imply that  $\text{Eu}(\text{DBM})_3$  bath has excellent electron injection and transport properties besides its luminescent performance. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Rare earth complex; Electroluminescence; Flat panel display; Europium complex

## 1. Introduction

Electroluminescence from thin films of molecular and polymer materials are of great interest because of their potential to enable low-cost, full-color, flat panel display and other emissive devices. By selection of the appropriate emitting layer, the emitting color could be changed through out the visible region. Based on polymer and some metal-chelate complexes, such as  $\text{Alq}_3$  and  $\text{GaMq}_2\text{cl}$ , high performance green and blue EL devices were demonstrated [1–5]. White light was attained applying multilayer or polymer blend structures that contain green, blue and red emissive element [6,7]. Red light-emitting device is not fully explored comparing with the color of blue and green.

There are two advantages in fabricating EL devices using rare earth complexes. (1) Theoretically, the upper limit of inner quantum efficiency is near 100%, which is four times higher than that of the devices using other materials. (2) The sharp emission bands of rare earth ions is very suitable for full-color display. Therefore, to fabricate EL devices using rare earth complex is a subject of interest. The organic EL devices using Tb and Eu complexes as emitters have been demonstrated by Kido et al. [8] and other research groups [9,10]. However, the rare earth complexes used in those

devices don't show effective carrier injection and transport property. Therefore doping of the rare earth complexes in a host material or an additional electron transport layer is needed.

In this letter, the Eu complex  $\text{Eu}(\text{DBM})_3$  bath is used as electron transport emitting layer and two double-layer EL devices are fabricated. One uses PVK as hole-transport layer, the other uses NPB. Bright red and white light was observed in the devices, respectively.

## 2. Experimental

Fig. 1 shows the chemical structures of the materials used and the architectures of the EL devices. The substrate is an indium-tin-oxide (ITO) coated glass with a sheet resistance of  $150 \Omega/\square$ . The substrates are cleaned by ultrasonication first in alcohol then in acetone and last in chloroform. Except for the PVK layer, which is coated on the substrate by spin coating, other organic layers and cathode layer ( $\text{Mg}_{0.9}\text{Ag}_{0.1}$ ) are deposited by conventional vapor vacuum deposition at a pressure of  $10^{-5}$  Torr. The layer thickness is controlled *in vacuo* with a quartz crystal monitor. The emission area is  $10 \text{ mm}^2$ . Photoluminescence (PL) and EL are measured with a Hitachi 4000 fluorescence spectrophotometer, and the brightness is measured by a 1980A spot photometer.

\* Corresponding author.

<sup>1</sup> E-mail address: pjblwl@public.cc.jl.cn

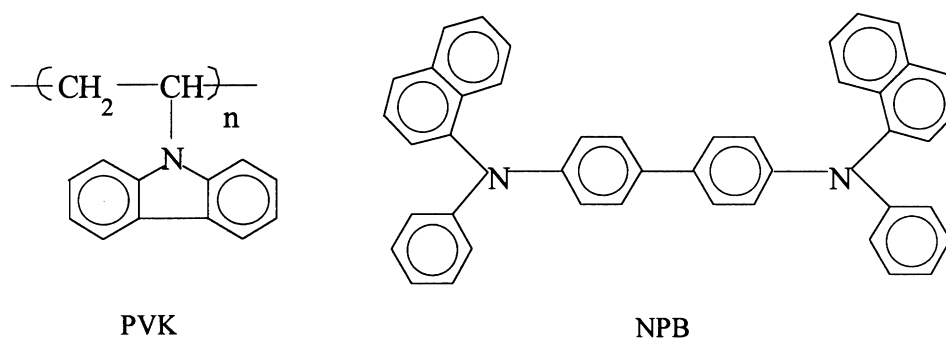
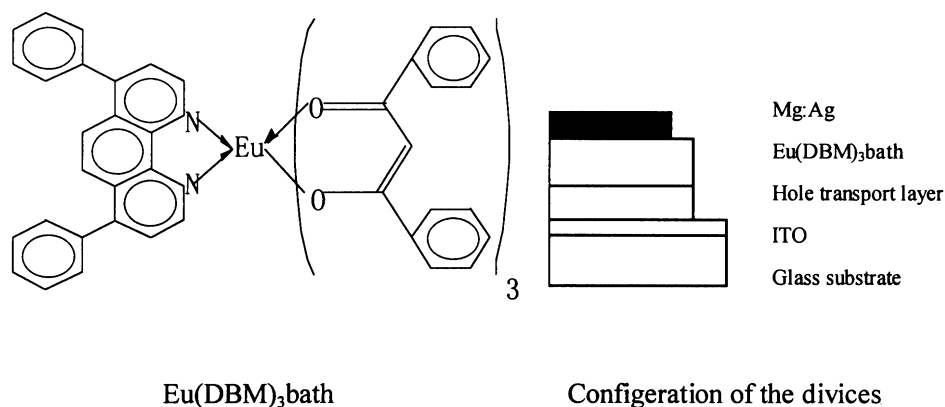


Fig. 1. The molecular structure of the materials and configuration of the devices.

### 3. Results and discussion

Fig. 2 shows the EL spectrum of device A: ITO/PVK(100 nm)/ $\text{Eu}(\text{DBM})_3$  bath(50 nm)/Mg:Ag, which is identical with the PL spectrum of  $\text{Eu}(\text{DBM})_3$  bath thin film. The sharp spectra bands are the characteristic emission of  $\text{Eu}^{3+}$  ion. The main emission peak at 615 nm responds to  $^5\text{D}_0$ – $^7\text{F}_2$  transition of  $\text{Eu}^{3+}$  ion. So this device emits highly monochromatic red light. EL starts at forward bias of 4 V and a luminance of  $400 \text{ cd/m}^2$  is obtained at 15 V.

Generally, in lanthanide metal complexes, a central metal ion is excited through the excitation of the ligand. Thus the EL process of device A can be understood as following. Under EL operation, electrons are injected into  $\text{Eu}(\text{DBM})_3$  bath layer from Mg:Ag cathode, while holes are transported into this layer through PVK. Then excitation of the ligands is realized by combination of the electrons and holes. Afterwards the excited energy at the ligand is transferred to the central ions through the ligand's triplet energy level [11] and finally the emission of the  $\text{Eu}^{3+}$  ions are observed.

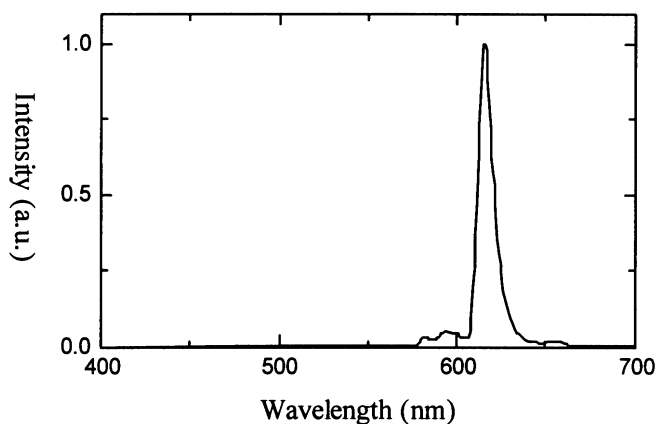


Fig. 2. The EL spectrum of device A: ITO/PVK(100 nm)/ $\text{Eu}(\text{DBM})_3$  bath(50 nm)/Mg:Ag.

When NPB is employed as the hole transport layer, device B: ITO/NPB(50 nm)/Eu(DBM)<sub>3</sub> bath(50 nm)/Mg:Ag is fabricated. The emitting color of device B is significantly different from that of device A. Fig. 3 shows the EL spectrum of device B. In addition to the sharp emission bands of Eu<sup>3+</sup>, a broad band with a peak at 483 nm appears. White light emits out from this device. Fig. 4 shows the CIE (Commission Internationale de l'Eclairage) coordinate of the emitting light. A, B and C represent the emitting color at voltage of 3, 5 and 7 V, respectively. So the emitting color changes with increasing of the driving voltage. In the range of 4–6 V, the CIE coordinates of emitting color locate near the center of the white region. The inset of Fig. 3 shows the brightness–current–voltage behavior of device B. In this device, EL can be observed at a lower voltage of 2.2 V, indicating the excellent electron injection and transport property of Eu(DBM)<sub>3</sub> bath layer. A luminance of 550 cd/m<sup>2</sup> is obtained at about 9 V. At the current density of 4.4 mA/cm<sup>2</sup>, the luminance efficiency reaches 0.4 lm/W.

Fig. 3 also shows the PL spectrum of NPB thin film. The PL spectrum of NPB peaks at 440 nm, indicating that the wide EL band at 483 nm does not originate from NPB layer. It could be due to the emission of exciplex formed at the interface between NPB and Eu(DBM)<sub>3</sub> bath layer. The emission of exciplex, which features new broad structureless band, is a primary phenomenon in multi-layer organic thin films [12–14]. Koji Itano et al. [15] reported exciplex formation at the interface of Alq<sub>3</sub> and the hole-transport material with lower ionization potentials (IPs). This rule is applicable to our above result, i.e. exciplex forms at the interface of Eu(DBM)<sub>3</sub> bath and NPB (IPs = 5.2 eV) layer, but not at the interface between Eu(DBM)<sub>3</sub> bath and PVK (IPs = 6.1 eV) layer. The detailed mechanism needs further investigation.

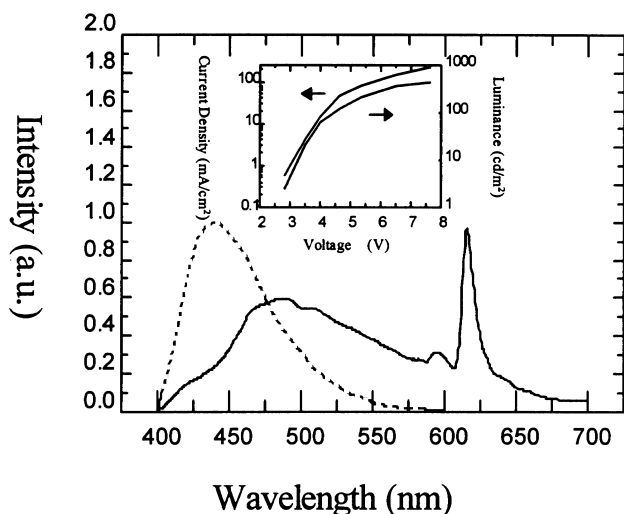


Fig. 3. The EL spectrum of device B: ITO/NPB(50 nm)/Eu(DBM)<sub>3</sub> bath(50 nm)/Mg:Ag at 5 V (—); the PL spectrum of NPB thin film (....); inset: current–voltage–luminance characteristic.

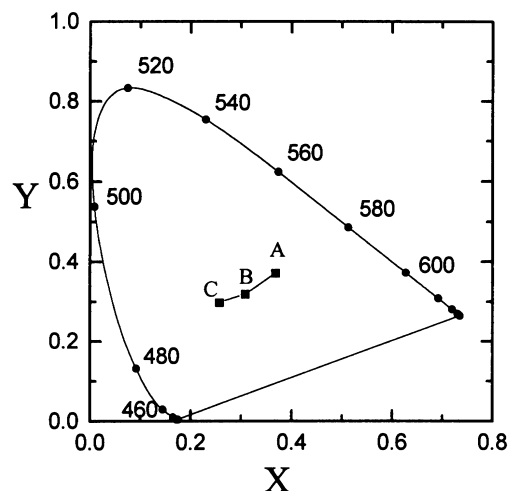


Fig. 4. The CIE coordinate of the emitting color at 3 (A), 5 (B) and 7 V (C).

#### 4. Conclusions

Like Alq<sub>3</sub>, the complex Eu(DBM)<sub>3</sub> bath shows excellent electron injection, transport and luminescent properties. Thus the intensive emission from the rare earth ion can be obtained with only double-layer structure. This is a more convenient way to fabricate various useful organic EL devices using Eu complex.

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