

## Europium complexes as emitters in organic electroluminescent devices

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### Abstract

Using two different trivalent europium ( $\text{Eu}^{3+}$ ) complexes, europium(dibenzoylmethanato)<sub>3</sub>(bathophenanthroline) [ $\text{Eu}(\text{DBM})_3\text{bath}$ ] and europium(dibenzoylmethanato)<sub>3</sub>(monophenanthroline) [ $\text{Eu}(\text{DBM})_3\text{phen}$ ], with different ligands for emission-layer materials, various types of electroluminescent (EL) devices have been fabricated. Combined with a triphenylamine derivative (TPD) and an oxadiazole derivative (OXD7) as hole-transport-layer materials, two-layer- and three-layer-type devices have been fabricated. We find that these two emission-layer materials have similar EL spectra, but their EL performances are different. The EL capability of the Eu complexes and their carrier-transporting characteristics are largely dependent on the ligands. © 1997 Elsevier Science S.A.

**Keywords:** Europium complexes; Organic electroluminescent devices

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### 1. Introduction

Red-light-emitting organic electroluminescent (EL) devices with trivalent europium (Eu) complexes as emitting-layer materials have been demonstrated by Kido et al. [1,2]. The Eu complexes which they used had poor carrier-transport properties and the luminance was low (about  $0.3 \text{ cd m}^{-2}$ ) if only the Eu complex is used as the emitting-layer material. To improve the carrier-transport property and luminance, they codeposited 2-(4-biphenyl)-5-(4-terbutylphenyl)-1,2,3-oxadiazole (PBD) with the complex as emission layer, thus drastically improving the luminance level. A maximum luminance of  $460 \text{ cd m}^{-2}$  was achieved.

In this paper we shall compare the EL performance of two Eu complexes in various EL devices in order to obtain relations between light-emitting properties and carrier-transport characteristics with different ligands.

### 2. Materials and device fabrication

In Fig. 1, the configurations of the EL devices and the molecular structures of the materials used in this study are shown. A conventional hole-transport material, a triphenylamine derivative (TPD), and electron-transport material, an oxadiazole derivative (OXD7), were employed. All of the

organic layers and the top aluminium electrode were fabricated by successive vacuum vapour depositions at  $2 \times 10^{-5}$  torr onto an ITO-coated glass substrate. The thickness of all organic layers was 50 nm. The thickness of the aluminium electrode was 200 nm. The emitting area of the devices was  $2 \text{ mm} \times 2 \text{ mm}$ . The luminance of the EL devices was measured with a Spectra Pritchard photometer, model 1980A, at room temperature under ambient atmosphere. The EL spectra of the two Eu complexes consist of similar sharp emission bands with an emission peak at 614 nm, which corresponds to the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of the trivalent Eu ion.

### 3. Results and discussion

Fig. 2 shows luminance–current density relations in three devices with  $\text{Eu}(\text{DBM})_3\text{phen}$  as the emission-layer material. At the same luminance, the three-layer-type device had the lowest current density. Luminance values at a fixed current density indicate relative EL quantum efficiencies, and thus luminance–current density curves can be conveniently used as measures of EL efficiency [3]. The efficiency of the three-layer-type device was about 50 times higher than that of the  $\text{Eu}(\text{DBM})_3\text{phen}/\text{OXD7}$  device (at  $0.12 \text{ cd m}^{-2}$ ) and about 30 times higher than that of the TPD/ $\text{Eu}(\text{DBM})_3\text{phen}$  device (at  $0.3 \text{ cd m}^{-2}$ ). These facts imply that  $\text{Eu}(\text{DBM})_3\text{phen}$  has poor carrier (both electron and hole) injection/transport capability. So the three-layer-type device combining a hole-

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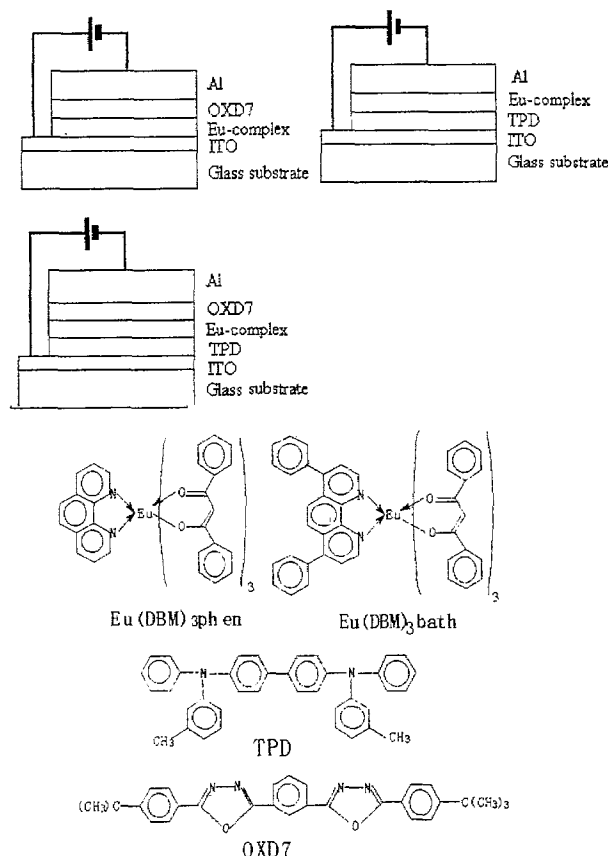


Fig. 1. The configuration of the EL devices and molecular structures of materials used.

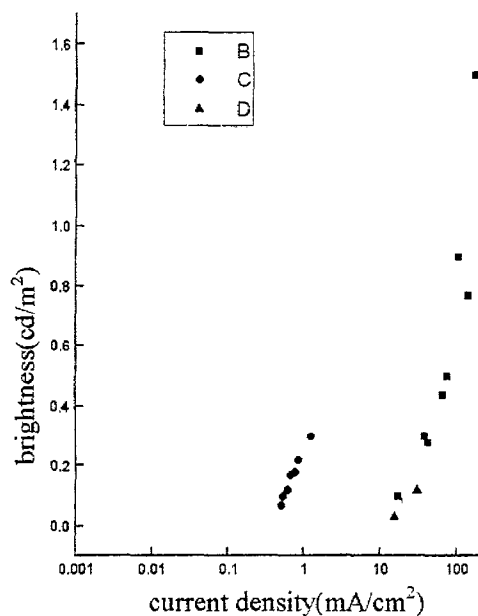


Fig. 2. Luminance-current density relations in (B) the TPD/Eu(DBM)<sub>3</sub>phen device, (C) the TPD/Eu(DBM)<sub>3</sub>phen/OXD7 device and (D) the Eu(DBM)<sub>3</sub>phen/OXD7 device.

transport-layer material and an electron-transport-layer material results in high efficiency [4].

Fig. 3 shows luminance-current density relations in a TPD/Eu(DBM)<sub>3</sub>bath/OXD7 device and a TPD/

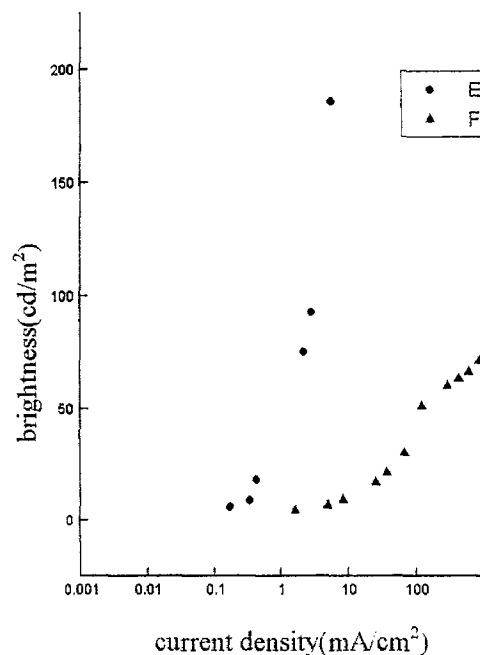


Fig. 3. Luminance-current density relations in (E) the TPD/Eu(DBM)<sub>3</sub>bath/OXD7 device and (F) the TPD/Eu(DBM)<sub>3</sub>bath device.

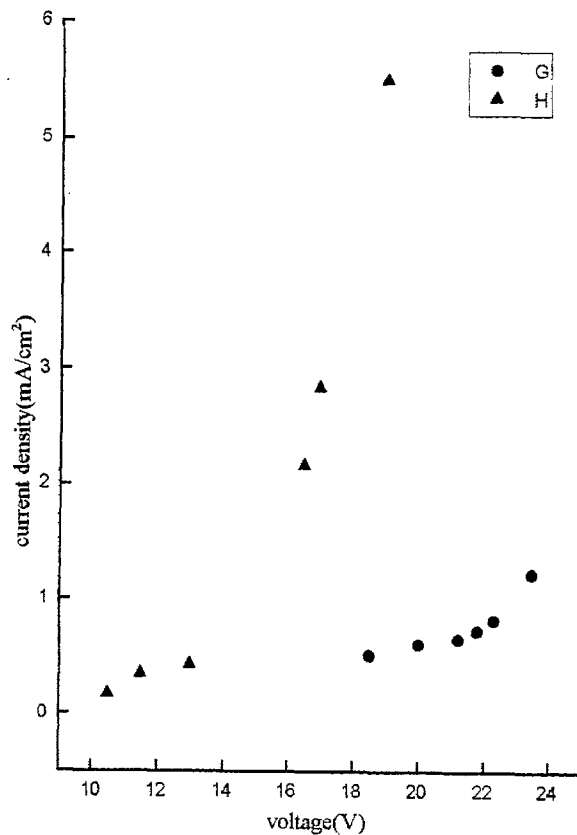


Fig. 4. Current density-voltage relations in (G) the TPD/Eu(DBM)<sub>3</sub>phen/OXD7 device and (H) the TPD/Eu(DBM)<sub>3</sub>bath/OXD7 device.

Eu(DBM)<sub>3</sub>bath device. At a luminance of 9 cd m<sup>-2</sup>, the efficiency of the TPD/Eu(DBM)<sub>3</sub>bath/OXD7 device was about 25 times higher than that of TPD/Eu(DBM)<sub>3</sub>bath device. This means that Eu(DBM)<sub>3</sub>bath exhibits poor hole

blocking and electron injection/transport capability. At a luminance of  $71 \text{ cd m}^{-2}$ , the efficiency of the three-layer-type device was about 400 times higher than that of the TPD/Eu(DBM)<sub>3</sub>bath device. This means that holes were the dominant carriers for current-density improvement. The luminance of the Eu(DBM)<sub>3</sub>bath/OXD7 device was too low to measure, which implies that Eu(DBM)<sub>3</sub>bath has poor hole-injection capability from an ITO electrode. Fig. 4 shows voltage–current density relations in TPD/Eu(DBM)<sub>3</sub>phen/OXD7 and TPD/Eu(DBM)<sub>3</sub>bath/OXD7 devices. At a fixed voltage, the current density of TPP/Eu(DBM)<sub>3</sub>bath/OXD7 was about one order of magnitude higher than that of the TPD/Eu(DBM)<sub>3</sub>phen/OXD7 device. These facts tell us that Eu(DBM)<sub>3</sub>bath has better carrier-transport tendency than Eu(DBM)<sub>3</sub>phen.

In Figs. 2 and 3, we found that the efficiency of the TPD/Eu(DBM)<sub>3</sub>bath/OXD7 device was about two orders of mag-

nitude higher than that of the TPD/Eu(DBM)<sub>3</sub>phen/OXD7 device. This may be attributed to the effect of the two additional phenyls attached to the phenonothroline. The radiationless energy loss of Eu(DBM)<sub>3</sub>bath is lower than that of Eu(DBM)<sub>3</sub>phen, because the Eu(DBM)<sub>3</sub>bath with the two phenyls should have a better insulating effect than Eu(DBM)<sub>3</sub>phen [5].

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