

## The fabrication of europium complex electroluminescence using BCP as hole blocking layer

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### Abstract

A bright and highly monochromatic red organic electroluminescent device based on a poly(*N*-vinylcarbazole) host was made. The device structure consists of poly(*N*-vinylcarbazole) dispersed with a europium complex as an emitting layer and a hole blocking layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP). The EL cell exhibited just characteristic emission of europium ion.

**Keywords** : Rare earth complex, Europium, Red electroluminescence

### 1. Introduction

Organic electroluminescence (OEL) is currently the focus of substantial research effort due to potential applications in the flat-panel display industry[1,2]. One of the requirements for full-colour displays is narrow emission characteristics in the blue, green and red areas of the visible spectrum. For this reason, lanthanide ions are of great interest, since their emissions result from well-defined *f-f* electronic transitions which are relatively insensitive to perturbations in their chemical environment. This allows tailoring of the physical properties of the emitter molecule by variation of the ligand structure without altering the colour of the emission. Lanthanide complexes have further advantages over light-emitting polymers in that triplet excited states can be harnessed negating the 25% maximum theoretical efficiency that

exists for LEDs where it is assumed that emission can only occur from singlet states. Europium complexes are of particular interest due to the sharp red emission which they exhibit. Devices using europium complexes as emitting layers have typically been fabricated by vacuum deposition and so are dependent on materials having the desired volatility. More and more studies are now investigating the use of europium complexes[3,4] as dopants in films formed by spin-coating, but the EL spectra of these devices were composed of two parts, one is a wide band originating from europium ions, so the EL emission is not pure red colour.

In this paper, we used 2,9-dimethyl-4,7-diphenyl -1, 10-phenanthroline (BCP) as a hole-blocking material vacuum-deposited on top of the Eu-containing emission layer, the pure red EL emission was enhanced remarkably.

## 2. Experimental

Tris-(4,4,4-Trifluoro-1-(2-naphthyl)-1,3-butane dione)(4,7-Diphenyl-1,10-phenanthroline) europium was prepared by a standard literature method. PVK was used as a hole-transporting host. Eu(TNB)<sub>3</sub>bath was used as emitter materials. The hole blocking material BCP was used to confine the injected holes in the emitter layer. The chemical structures of the materials used are shown in Fig. 1. In order to study the roles of BCP, two types of EL devices, A and B were fabricated and classified by the contents of Eu(TNB)<sub>3</sub>bath. The two device structures are as follows:

Device A: ITO/PVK: Eu(TNB)<sub>3</sub>bath/Al

Device B: ITO/PVK: Eu(TNB)<sub>3</sub>bath/BCP/Al

The ITO-coated PET substrates with a surface resistance of 55 Ω/sq were cleaned in an ultra-sonic bath of isopropyl alcohol and de-ionized water in turn. The PVK:Eu(TNB)<sub>3</sub>bath layer was deposited on the substrate by spin-coating at 1000 rpm from chloroform solution in a typical weight ratio (1%, 5% and 10%). The thickness of PVK:Eu(TNB)<sub>3</sub>bath layer was about 100 nm. BCP was deposited by vacuum evaporation at a pressure below 310–3 Pa. A 150 nm thick Al was deposited on the organic layer as the top electrode at the same vacuum pressure, the deposition rate was maintained to be 10 Å/s. The area of EL devices was 4 mm × 4 mm.

## 3. Results and discussion

Fig 2 shows the photoluminescence (PL) spectra of PVK:Eu(TNB)<sub>3</sub>bath spin-coating solid films. In film, very strong emissions of Eu<sup>3+</sup> ions dominated the emission spectra of PVK:Eu(TNB)<sub>3</sub>bath thin films, and the emission of PVK was hardly visible in the spectra. From Fig.2 we observe that, as the concentration of PVK increased, the intensities of Eu ion

emissions decreases, showing fluorescent quenching effect of PVK to the Eu complex. When the weight ratio of PVK and Eu(TNB)<sub>3</sub>bath reaches about 10 wt%, further increase of Eu(TNB)<sub>3</sub>bath results in no distinct changes in the emission spectra.

Since the excitons in the doped PVK film are trapped by the guest molecules and result in strong emission of europium ions, we expect that EL of europium ions can be observed if a large number of excitons is formed by recombination of electrons and holes in PVK:Eu layer. So we fabricated two types of organic EL devices with structures of ITO/PVK: Eu(TNB)<sub>3</sub>bath/Al and ITO/PVK: Eu(TNB)<sub>3</sub>bath/BCP/Al, respectively. Red emission can be observed in the dark room in the first device and bright red emission from the latter device.

The EL efficiency is low in the single-layer devices, one of reasons is the unbalance between holes and electrons in the exciton recombination zone. PVK is a good hole-transporting material, so the recombination zone is away from the cathode, thus, reducing the quenching of the excitations by the electrode. For obtaining high efficiency pure red EL emissions, we used low electron mobility material BCP as a hole blocking layer which may limit electron injection and transfer. Fig.3 shows the device energy level structure. The HOMO (highest occupied molecular orbital) level and LUMO (lowest unoccupied molecular orbital) of each layer are listed. In the double-layer device, most electrons will be transferred into the PVK:Eu layer due to similar LUMO level for PVK:Eu and BCP. But holes can not move to BCP layer freely from PVK:Eu because of an energy barrier of 0.3 eV between the HOMOs of PVK and BCP. Therefore, most electrons combine with holes inside the PVK:Eu layer.

Fig.4 show the double-layer device EL spectrum. The EL spectra are predominantly the emission from the host material Eu(TNB)<sub>3</sub>bath.

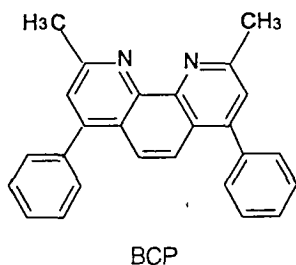
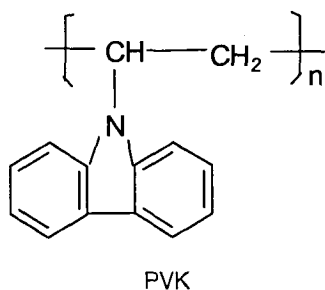
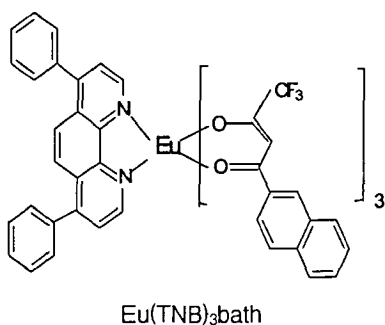


Fig. 1 Molecular structures of the materials used in LEDs.

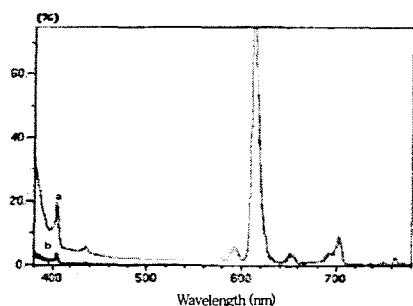


Fig. 2 The PL spectra of PVK:Eu(TNB)<sub>3</sub>bath spin-coating solid films, doping concentration : a 1 wt%; b 5 wt% and c 10 wt%.

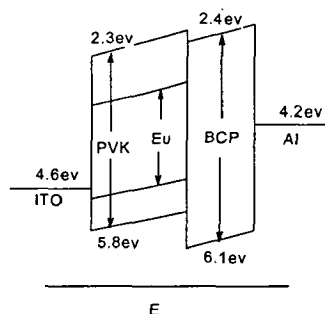


Fig. 3 The device energy level structure.

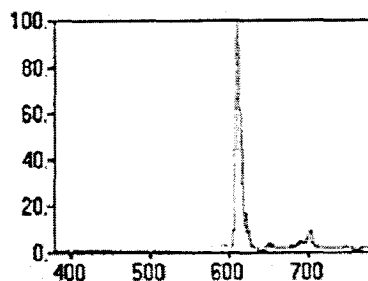


Fig. 4 The EL spectra of double layer device: ITO/PVK: Eu(TNB)<sub>3</sub>bath/BCP/Al.

#### 4. Conclusions

A bright and highly monochromatic red organic electroluminescent device based on PVK host was fabricated. The introduction of hole blocking layer improves the EL performance due to the increase of recombination probability of holes and electrons.

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