

Synthesis and electroluminescent properties of a carbazole-functionalized europium(III) complex

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Abstract

A novel europium(III) complex, tris(dibenzoylmethanate){1-[9-hexyl-9H-carbazole]-2-(2-pyridyl)-benzimidazole}europium(III) [Eu(DBM)₃(CAR-PyBM)] functionalized by a carbazole fragment, was synthesized and used as emitting material in organic electroluminescent (EL) devices. Compared with the device based on an unfunctional Eu(III) complex, [Eu(DBM)₃HPyBM] (HPyBM = 2-(2-pyridyl)benzimidazole), the EL performances of the device using [Eu(DBM)₃(CAR-PyBM)] as an emitter was significantly enhanced due to the improvement of hole-transporting ability. The maximum efficiency and luminance of red emission achieved from the device with the configuration of ITO/*N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD, 50 nm)/[Eu(DBM)₃(CAR-PyBM)] (30 nm)/1,3,5-tris-(*N*-phenylbenzimidazol-2-yl)benzene (TPBI, 20 nm)/LiF (1.5 nm)/Al were 4.2 cd/A and 200 cd/m², respectively.

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention since the initial works by Tang and Vanslyke [1] and Friend et al. [2] due to their potential applications in the next generation of full-color flat-panel displays [3,4]. Lanthanide complexes, especially europium and terbium complexes [5–14], are of great interest in the electroluminescent (EL) field, because they can emit highly monochromatic light owing to the electronic transitions of the central ions that give sharp narrow spectral characteristic; furthermore, it can offer 100% quantum efficiency theoretically since this kind of transition is not restricted by the spin inhibition rule [10]. However, there is a key problem with OLEDs containing these Eu(III) complexes, that is low EL efficiency of Eu(III) complexes when incorporated into OLEDs on account of the poor carrier

transporting ability reported so far [12,15–17]. Therefore, several groups have devoted to the application of Eu(III) complexes as red emitters in OLEDs and higher brightness more than 1500 cd/m² has been achieved by doping Eu(III) complexes with charge-carrier transporting materials as emitting layer [17–20]. However, doping usually leads to phase separation when the device undergoes operation, and the emission from electron or hole-transporting materials often appears. Therefore, in general, more efficient method to solve this problem is to introduce the charge-carrier transporting group into the complex by molecular design. Wang et al. [12] synthesized a new terbium complex containing oxadiazole-functionalized β -diketone ligand with a light output of 100 cd/m² with an external quantum efficiency as high as 1.1% at 15 V. Liang et al. [21] reported a highly efficient double-layer EL device with current efficiency 1.7 cd/A using an oxadiazole-functionalized Eu(III) complex. Xin et al. [22] designed a carbazole-functionalized Eu(III) complex, and high power efficiency of 2.7 lm/W at 5 V was obtained. The results demonstrate

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that incorporation of functional groups into the Eu(III) complexes can significantly improve the devices performances.

In order to explore highly efficient red OLED materials, herein we report a novel carbazole-functionalized Eu(III) complex $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$. The chemical structure is depicted in Fig. 2. DBM was chosen as the first ligand due to its relatively high photoluminescence (PL) and EL efficiency in Eu(III) complexes. 2-(2-pyridyl)-benzimidazole (PyBM) was selected as the second ligand since it is thought to enhance the electron transport of the material [23]. In order to improve the hole-transporting property of the Eu(III) complex, carbazole fragment was incorporated into PyBM. The PL and EL properties of this new functionalized europium complex, $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$, were investigated.

2. Experimental details

2.1. Synthesis

2.1.1. 9-(6-bromo-hexyl)-9H-carbazole

A mixture of carbazole (5.0 g, 0.03 mol), 1,6-dibromohexane (7.3 g, 0.03 mol), and K_2CO_3 (12.5 g, 0.06 mol) in *N,N'*-dimethylformamide (DMF) (20 mL) was stirred at room temperature for 15 h and was then poured into water. After extraction with CH_2Cl_2 , the solvent was then evaporated. The resulting residue was purified by chromatography to give 3.0 g of product. Yield: 30%. Mp: 51 °C. ^1H NMR (CDCl_3 , ppm): δ 1.38–1.55 (m, 4H), 1.78–1.92 (m, 4H), 3.36 (t, 2H), 4.32 (t, 2H), 7.25 (t, 2H), 7.41 (d, 2H), 7.47 (t, 2H), 8.10 (d, 2H). EI-MS: m/z : 331 (M^+).

2.1.2. 1-[9-hexyl-9H-carbazole]-2-(2-pyridyl)-benzimidazole

A mixture of 9-(6-bromo-hexyl)-9H-carbazole (1.67 g, 0.005 mol), 2-(2-pyridyl)benzimidazole (0.98 g, 0.005 mol), NaOH (0.22 g, 0.0055 mol) and DMF (30 mL) was stirred and heated at 120 °C for 15 h under N_2 . It was subsequently poured into ice water (50 mL), after extraction with CH_2Cl_2 (3 \times 30 mL). The organic layer was washed with water and dried over anhydrous Na_2SO_4 . The solvent was then evaporated, the resulting residue was purified by silica gel column chromatography to give 1.78 g of product. Yield: 80%. Mp: 50 °C. ^1H NMR (CDCl_3 , ppm): δ 1.27–1.39 (m, 4H), 1.68–1.85 (m, 4H), 4.25–4.29 (t, 2H), 4.77–4.81 (t, 2H), 7.27 (t, 2H), 7.31 (t, 2H), 7.32 (t, 2H), 7.35 (d, 2H), 7.37 (d, 2H), 7.45 (d, 2H), 8.10 (d, 1H), 8.17 (t, 1H), 8.29 (t, 1H), 8.501(d, 1H). EI-MS: m/z : 444 (M^+).

2.1.3. $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$

$[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ was synthesized according to the conventional method [22,23]. Elemental analysis for $\text{C}_{75}\text{H}_{61}\text{N}_4\text{O}_6\text{Eu}$. Calcd: C, 71.14; H, 4.85; N, 4.42. Found: C, 71.76; H, 4.11; N, 3.94. The synthesized complex was readily soluble in common organic solvents such as CHCl_3

and can be thermally evaporated, which is in favor of the fabrication of OLEDs.

2.2. Fabrication of EL devices

The EL devices with $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ as the emitting layer were fabricated onto a pre-cleaned ITO-coated glass substrate (sheet resistance of 20 Ω /square). The organic layers were sequentially deposited at a rate in the range of 1–3 $\text{\AA}/\text{s}$ in high vacuum ($< 5 \times 10^{-4}$ Pa). At last, LiF layer and Al layer were deposited at a rate of 0.05 and 0.8–1.0 nm/s, respectively, under the same condition. The thickness of the deposited layer and the evaporation speed of the individual materials were monitored with quartz crystal monitors. The active device area was 10 mm².

2.3. Instruments and physical characterization

The UV-visible absorption spectrum was obtained on a shi-madzu-UV-3101 scanning spectrophotometer. ^1H NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer with chemical shifts reported relative to tetramethylsilane. EI mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. The PL and EL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The luminance–current density and luminance–voltage curves were obtained from a source meter (Keithley 2400) and an optical meter (Newport 1835-C) equipped with a silicon photodiode (Newport 818ST).

3. Results and discussion

The absorption and PL spectra of $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ in CHCl_3 solution are shown in Fig. 1. The bands at 294 and 326 nm are attributed to the absorption of

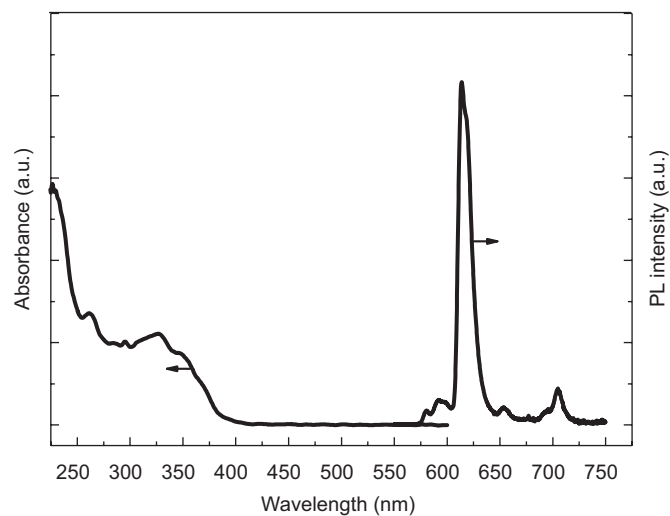


Fig. 1. Absorption and PL spectra of $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ in CHCl_3 solution (concentration = 10^{-5} M).

carbazole fragment. The absorption peak located at 348 nm is associated with the $\pi-\pi^*$ transition of DBM ligand. The PL spectrum exhibits five sharp characteristic emission peaks at 579, 592, 612, 652 and 703 nm corresponding to the $^5D_0 \rightarrow ^7F_J$ ($J=0-4$) transition of Eu(III) ion, respectively.

The configuration of the EL devices and chemical structure of the complex $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ are shown in Fig. 2. TPD was used as the hole transporting layer, $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ was the emitting layer, whereas TPBI was used to act as electron transporting layer. The use of TPBI as the electron transporting layer effectively confined the charge recombination area to be the $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ layer, presumably due to the low HOMO and thus hole-blocking ability of TPBI [24].

The EL spectra of the device at different bias voltage are shown in Fig. 3. The close resemblance of the EL and PL spectra suggests that the EL emission originated from the Eu(III) ion in $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$. The EL spectra exhibit extremely sharp emission centered at 612 nm with the half peak bandwidth of 10 nm and the Commission International de L'Eclairage (CIE) coordinates ($x=0.67$, $y=0.32$), indicating that $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ is a pure saturated red-emission material. The EL spectra and CIE coordinates are independent of the voltage. Even at very high voltage ($\sim 17\text{V}$), blue emission from TPD is negligible, which could confirm that the recombination of electrons and holes were successfully confined to the

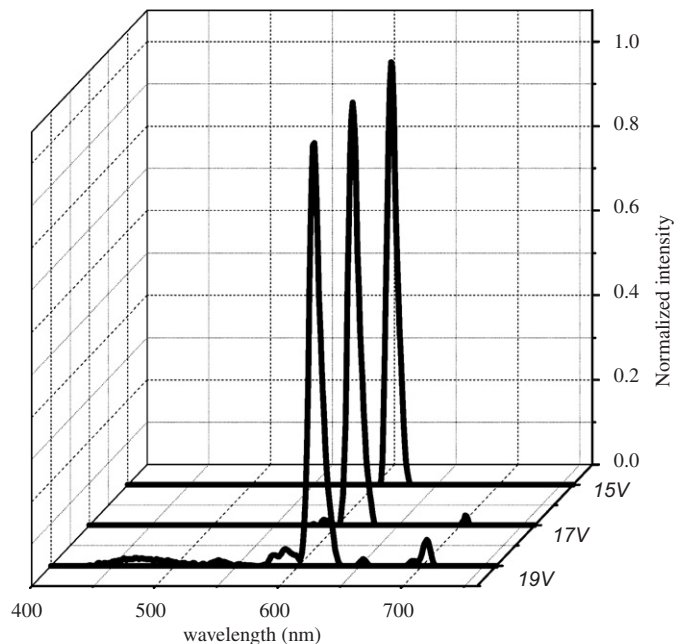


Fig. 3. Normalized EL spectra of the same device at applied voltage 15, 17, 19 V.

Eu(III) complex layer. However, when the bias voltage increases to 19 V, there exists a weak blue emission centering at around 473 nm, which originates from TPD, but the emission is too weak to affect the purity of the color.

Fig. 4 illustrates the typical current–luminance–voltage characteristics of the three-layer device based on $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$. The current increased when the forward bias voltage increased, and the reverse current remained small when the ITO electrode was applied a negative bias voltage and the Al electrode a positive bias. It can be found that pure red emission was observed at 9 V. The luminance of the device increases with increasing bias voltage, because the recombination efficiency increases as the more charge carriers are injected from the anode and cathode, respectively. In our experiment, no exciplex emission was observed at bias voltage range from 9 to 21 V. The reason may be the balanced charge-carrier injection and transport, leading to efficient recombination in emitting layer. The maximum luminance of the three-layer EL device is about 200 cd/m^2 at a driving voltage of 20 V. The maximum current efficiency is about 4.2 cd/A at 0.5 mA/cm^2 and decreased with increasing voltage, as shown in the inset of Fig. 4. Compared with the previously reported device based on $[\text{Eu}(\text{DBM})_3\text{HPyBM}]$ [15], which is merely 1.14 cd/m^2 at 23 V, the luminance level of $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ is dramatically improved due to the second ligand incorporating a carbazole fragment.

The OLEDs based on $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$ with different thicknesses (30, 40, 50 and 60 nm) of the TPD layer were also fabricated, when the thicknesses of the TPD layer were thinner, the hole's mobility is about one-order larger than the electron's, so the hole will easily penetrate

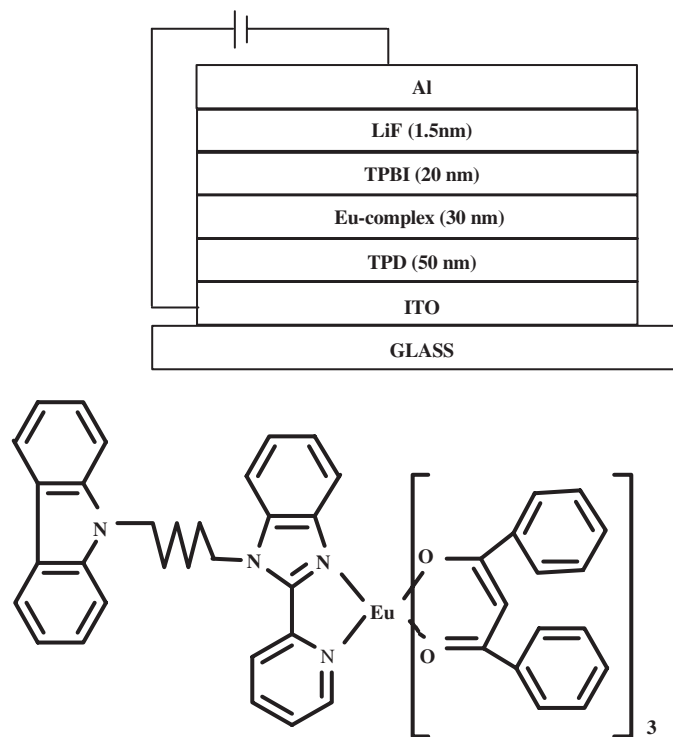


Fig. 2. The configuration of the EL devices and chemical structure of the complex $[\text{Eu}(\text{DBM})_3(\text{CAR-PyBM})]$.

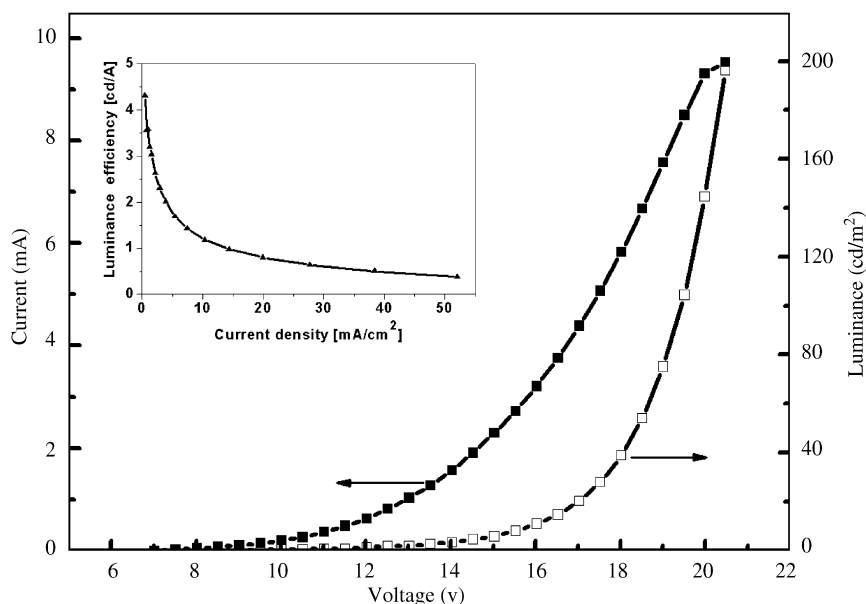


Fig. 4. Luminance–current–voltage characteristics of the three-layer device. Inset: EL efficiency–voltage curve for the device.

the TPD layer and charge build up on the layers' surface between the complex and TPD. So with the increase of bias voltage, the spectrum shows the emission of TPD gradually. If the TPD layer is too thick, it may also cause imbalance of holes and electron and lead to the low efficiency. It was found that when the thickness of TPD was 50 nm, the highest efficiency was obtained.

4. Conclusions

We have synthesized a novel Eu(III) complex containing carbazole-functionalized second ligand. A bright red emission with the maximum luminance of 200 cd/m^2 and current efficiency of 4.2 cd/A was obtained from the device with the structure of ITO/TPD (50 nm)/[Eu(DBM)₃(CAR–PyBM)] (30 nm)/TPBi (20 nm)/LiF (1.5 nm)/Al. By the comparison in the performance of the device based on [Eu(DBM)₃HPyBM] and the device based on [Eu(DBM)₃(CAR–PyBM)], we found that the introduction of the carbazole fragment is helpful for balancing injection, transport, and recombination of charge carriers in Eu(III) complex and increasing luminance and efficiency of OLEDs. Our results demonstrate that the EL performance based on lanthanide complex can be effectively improved by chemical modification on the second ligand.

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