

## 研究简报

稀土配合物  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  的红光二极管李 斌<sup>\*·1,2</sup> 马东阁<sup>2</sup> 张洪杰<sup>2</sup><sup>(1)</sup> 东北师范大学化学学院, 长春 130024)<sup>(2)</sup> 中国科学院长春应用化学研究所, 长春 130022)

关键词: 发光二极管 稀土配合物 多层结构

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Red Light-Emitting Diodes Based on Rare Earth Complex  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$ LI Bin<sup>\*·1,2</sup> MA Dong-Ge<sup>2</sup> ZHANG Hong-Jie<sup>2</sup><sup>(1)</sup> Faculty of Chemistry, Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun 130024)<sup>(2)</sup> Changchun Institute of Applied chemistry, Chinese Academy of Sciences, Changchun 130022)

A thin film electroluminescence cell with the structure of ITO/PPV/PVK:  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$ : PBD/Alq<sub>3</sub>/Al has been fabricated. Red emission with a very sharp spectral band at 614nm was observed and a maximum luminance of 20cd · m<sup>-2</sup> at 36V was obtained from the spin-coated device. The full width at half maximum of luminescent spectrum is less than 10nm.

Keywords: light emitting diode rare earth complex multilayer structure

## 0 Introduction

Organic electroluminescent (EL) devices have become one of the most important subjects because of their potential application as large-area flat-panel displays since Tang and Van Slyke first reported bright organic EL at low voltages<sup>[1,2]</sup>. 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 the subject of interest<sup>[3]</sup>. Achievements on this subject have been made by several groups<sup>[3-6]</sup>. We also reported green thin-film electroluminescent devices based on monohexadecyl phthalate terbium<sup>[7]</sup>. In this paper, complex  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  which was shown to have excellent photoluminescence properties in early study<sup>[8]</sup> is used to fabricate red emissive device. The long hydrocarbon chain of the complex may improve the film quality. Due to the introduction of the PPV layer and the Alq<sub>3</sub> layer, the injection of the holes and electrons into the emissive layer was increased.

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resulting in the higher recombination of the holes and electrons and the higher luminance. A red monochromatic light was obtained around 614nm, corresponding to  $\text{Eu}^{3+}$  characteristic emission.

## 1 Experimental

The device structure is shown in Fig. 1. tetrakis 1-(2-thenoyl)-3, 3, 3-trifluoroacetate europium N-hexadecyl pyridinium  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  used as the emissive center in the study was synthesized in our laboratory.  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  can be dissolved in chloroform. The device is fabricated on patterned indium-tin-oxide (ITO) coated glass substrate. The device structure of ITO/poly(*p*-phenylenevinylene) (PPV)/poly(N-vinylcarbazole) (PVK): 1, 3, 4-oxadiazole derivative (PBD):  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$ /tris (8-hydroxyquinoline) aluminum ( $\text{Alq}_3$ )/Al was employed, in which hole-transporting layer PPV was obtained by heating treatment the precursor at 220°C in nitrogen for 2h. Due to the poor film-forming property and the poor carrier transport property of the Eu complex itself, it was blend with an electron-transporting material PBD and a hole-transporting material PVK, which has also very good film-forming properties as the emissive layer. Thus, the injection of electrons and holes in the emissive layer will be greatly enhanced, and a high-quality film can be obtained. The emissive layer was spun-casting on PPV from a chloroform solution of PVK, PBD and  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  with a weight ratio of 20mg: 6mg: 2mg in 1ml chloroform.  $\text{Alq}_3$  was deposited by vacuum evaporation on the emissive layer. Finally, an electron injecting electrode Al was deposited on top by vacuum evaporation at a pressure below  $7 \times 10^{-4}\text{Pa}$ .

The EL and the photoluminescent (PL) spectra

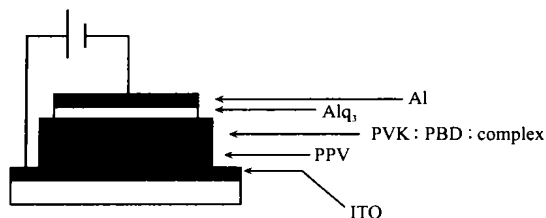


Fig. 1 Device structure

were measured with a SPEX FL-2T2 spectrophotometer. The luminance was measured with a calibrated ST-900 luminance meter.

## 2 Results and Discussions

The PL spectrum of the thin film of PVK: PBD:  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  blends used as emissive layer in our devices is shown in Fig. 2. It is found that only an extremely sharp emission bandwidth at 612nm was observed. This demonstrates that the strongest emission originates from the  $^5D_0$  to  $^7F_2$  transition of the  $\text{Eu}^{3+}$  of  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  in the blend. The EL spectrum of ITO/PPV/PVK: PBD:  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$ / $\text{Alq}_3$ /Al device is also shown in Fig. 2. It is found that a bright red electroluminescence with an extremely sharp emission bandwidth at 614nm was obtained from the device when operated in a continuous dc mode (biased ITO positive). As shown in Fig. 2, the EL spectrum is coincident with the PL spectrum of the blend film. This demonstrates that the electroluminescence also arises from the  $\text{Eu}^{3+}$  ion of  $\text{Eu}(\text{TTA})_4\text{C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}$  in the blend emissive layer. PPV and  $\text{Alq}_3$  only play a role of transporting holes and electrons into the emissive layer, respectively. The excitation mechanism

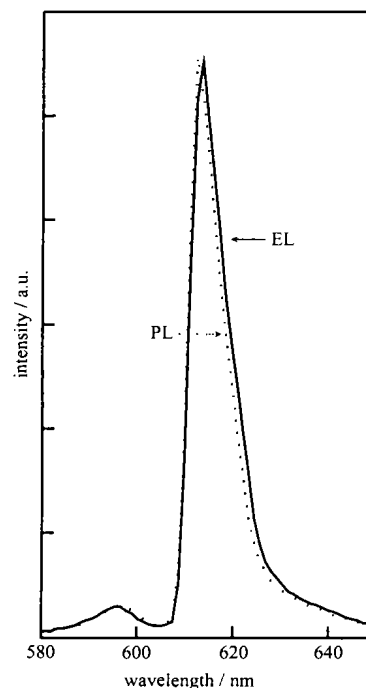


Fig. 2 PL spectrum of complex and EL spectrum of cell

can be explained in terms of energy transfer. In the condition of a forward bias, holes injected from ITO through PPV and electrons injected from Al through Alq<sub>3</sub> migrate in the film of PVK:PBD:Eu(TTA)<sub>4</sub>C<sub>5</sub>H<sub>5</sub>NC<sub>16</sub>H<sub>33</sub>. They meet to form excitons, then the energy of excitons caused by radiative decay is transferred to the ligand, and finally to the central Eu ion. In fact, the trivalent Eu ions are excited via intramolecular energy transfer from the triplet excited states of the ligands<sup>[9]</sup>.

Fig. 3 shows current-voltage and luminance-voltage characteristics of the EL device. The forward bias current can be obtained when the ITO electrode is positively biased and the Al electrode negatively. The current increases when the forward bias voltage increases, and the reverse current remains small when the ITO electrode is negatively biased and the Al electrode positively. The luminance increases with increasing the forward bias voltage. Luminescence starts at 23V and the maximum luminance of 20cd · m<sup>-2</sup> is achieved at 36V.

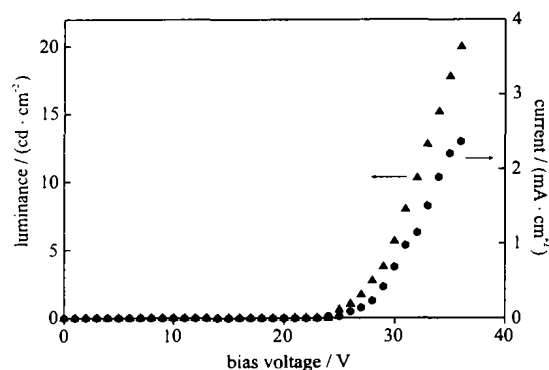


Fig. 3 Current-voltage and luminance-voltage characteristic curves of EL cell

### 3 Conclusions

We have succeeded in fabricating bright red EL device using a soluble trivalent Eu complex as an emitter. The emitting layer, which consists of PVK (= host material and hole transporting materials), Eu(TTA)<sub>4</sub>C<sub>5</sub>H<sub>5</sub>NC<sub>16</sub>H<sub>33</sub> (= dopant) and PBD (= electron-transporting material), was formed by spin-casting method. Red emission with a very sharp spectral band at 614nm was observed and a maximum luminance of 20cd · m<sup>-2</sup> was obtained from the device. The brightness is not as high as expected. It is likely that the charge carrier mobility of Eu-TTA complex is lower than that of Eu-DBM<sup>[3]</sup>.

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