

## Electroluminescence Based on $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$ Doped Poly N-Vinylcarbazole

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**Abstract:** A novel rare earth complex  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$ , displaying electroluminescent property, was synthesized, and monolayer and double-layer devices were fabricated by doping it into poly N-vinylcarbazole. The characteristics of these optimized devices were investigated, and the emitting mechanism was explained through the energy band diagram. Optimized double-layer devices with a turn-on voltage of 6.5 V were achieved. At the current density of  $68.48 \text{ mA} \cdot \text{cm}^{-2}$ , the maximum brightness and the current efficiency of the device reached  $238.4 \text{ cd} \cdot \text{m}^{-2}$  and  $0.35 \text{ cd} \cdot \text{A}^{-1}$ , respectively.

**Key words:** europium complex; electroluminescence; energy transfer; rare earths

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Organic electroluminescence (OEL) has been extensively studied owing to its potential application in flat panel displays ever since the first double-layer OEL device that has high efficiency and luminescence was fabricated in 1987<sup>[1-4]</sup>. When compared with common smaller organic molecules and polymers, rare earth (RE) complexes exhibit extremely sharp, well-defined spectral lines due to the emissions that originate from the lanthanide metal ions. So the electroluminescence (EL) of RE complexes has been attracting much attention because of the characteristics of excellent color purity and high internal quantum efficiencies, ever since the OEL device using terbium and europium complexes as emitters was demonstrated by Kido et al.<sup>[5,6]</sup>. To synthesize good light-emitting RE complexes, two efficient approaches can be used: (1) selecting suitable ligands for the complexes; (2) intro-

ducing other metal ions into the complexes, which act as bridges for energy transfer from host (PVK) to guest (europium complex)<sup>[7]</sup>. In this article, a novel RE complex  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$ , which was synthesized and used as the emitting material in EL devices was discussed, and the characteristics of the devices were studied.

## 1 Experimental

### 1.1 Synthesis of $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$

$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ , thenoyl-trifluoroacetate (TTA), and 1,10-phenanthroline (phen) of stoichiometric amounts were separately dissolved in 95% of  $\text{C}_2\text{H}_5\text{OH}$ . The pH of TTA solution was adjusted to 7 using  $1 \text{ mol} \cdot \text{L}^{-1}$  NaOH solution. The mixed ligands (TTA and phen) solution was added in drops into the

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$\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$  solution. During this process flesh-colored precipitates appeared. After the mixture was stirred for 2 h, the precipitate was filtered and washed twice using 95%  $\text{C}_2\text{H}_5\text{OH}$  and was then dried in the infrared desiccator.

## 1.2 Fabrication of EL devices

To improve the film-forming and conducting properties of  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$ , poly N-vinylcarbazole (PVK) was introduced as the host material. The indium tin oxide (ITO) glass was cleaned using ultrasonic baths of acetone, isopropyl alcohol, methanol solvents, and deionized water. The light-emitting film was prepared by spin coating the PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  chloroform solution onto the clean dry ITO glass at different weight ratios (1:1, 3:1, 10:1). The layers of  $\text{Alq}_3$ , LiF, and Al were then deposited by vacuum deposition at the rate of 0.05, 0.03, and  $0.2 \text{ nm} \cdot \text{s}^{-1}$  under a pressure of  $3 \times 10^{-3} \text{ Pa}$ , respectively. The thickness of each layer was measured using the quartz oscillating thickness monitor (IL-400). Two kinds of devices were then fabricated: (1) ITO/PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}/\text{Al}$ ; (2) ITO/PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}/\text{Alq}_3/\text{LiF}/\text{Al}$ . The pixel area of the device was  $3 \text{ mm} \times 3 \text{ mm}$ . The photoluminescence (PL) and EL spectra were measured on the Fluolog-3 fluorescent spectrometer and the brightness was measured using the Photo Research PR-650 Spectroradiometer. All the measurements were carried out at room temperature.

## 2 Results and Discussion

### 2.1 PL properties

The PL spectrum of PVK and  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$ -blended film is shown in Fig. 1. The emission peaks at 410, 596 and 618 nm corresponded to PVK,  $^5\text{D}_0 \rightarrow ^7\text{F}_1$ , and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$  ions, respectively. As seen from Fig. 1, the excitation spectra of PVK and their blended film are much alike, and both differ from the excitation spectrum of pure europium complex, which shows that emissions of  $\text{Eu}^{3+}$  ions mainly originate from the excitation of PVK<sup>[8]</sup>. Comparison of the PVK emission spectrum and europium-complex excitation spectrum shows that there is some overlap between them, which indicates that there should be a Förster energy transfer from PVK to the europium complex. The introduction of  $\text{La}^{3+}$  ions into the complex decreases the concentration of  $\text{Eu}^{3+}$  ions, which restrains the concentration quenching of  $\text{Eu}^{3+}$  ions, and then enhances the energy

transfer from the host (PVK) to the guest (europium complex)<sup>[7]</sup>.

### 2.2 Properties of device

Monolayer devices with different weight ratios of PVK to  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  (1:1, 3:1, 10:1) were fabricated. The structure of the devices is: ITO/PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}/\text{Al}$ . The EL spectra of the monolayer devices (Fig. 2) show only the emissions of  $\text{Eu}^{3+}$  ions. Moreover, with the increase of the driven voltage, there is virtually no emission from PVK in the EL spectra of monolayer devices, which is different from the PL spectra (Fig. 1) of the emission layer. Obviously, the EL mechanism of the doped systems is not similar to that of PL. In the EL process, emissions of  $\text{Eu}^{3+}$  ions may occur due to two reasons: one is a Förster energy transfer from PVK to the europium complex<sup>[9,10]</sup>; the other is a direct charge trapping on the europium complex<sup>[11]</sup>. However, no emis-

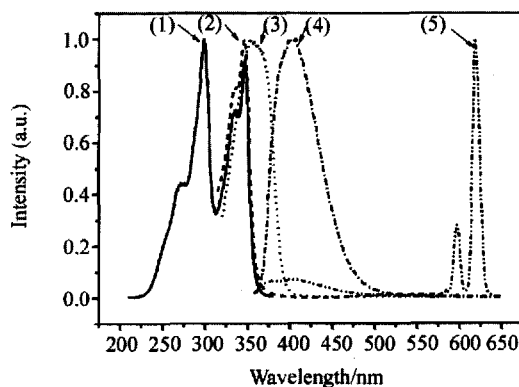


Fig. 1 PL excitation spectra of PVK (1); the blended film of PVK and  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  (2);  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$ (3); PL emission spectra of PVK(4); the blended film of PVK and  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  (5)

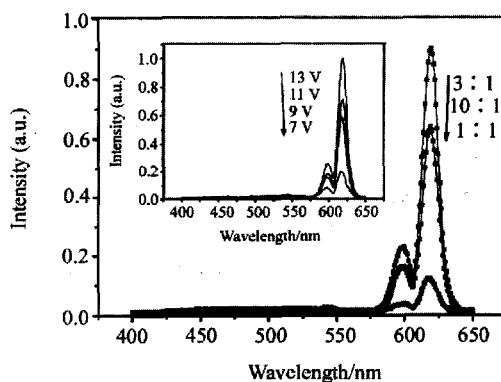


Fig. 2 EL spectra of monolayer device ITO/PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  ( $x:1$ )/Al at 13 V ( $x:1$  is 1:1, 3:1 and 10:1, respectively); the inset shows the EL spectra of monolayer device with a ratio of 3:1 at different driven voltages

sion from PVK is observed in monolayer devices, which indicates that the Förster energy transfer plays only a minor role in the EL process, whereas a direct charge trapping on the europium complex is dominant. In the charge trapping process, PVKs act as hole-transporting materials and europium complexes act as electron-trapping centers. The europium complexes trap electrons and holes, thereby enabling a direct recombination on the europium complexes. Fig.2 also shows that the emitting intensity reaches a maximum when the weight ratio of PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  is 3:1, which can be explained by the fact that the probability of europium complexes trapping the electron-hole pairs increases along with the increase of the europium complex weight ratio before the effect becomes saturated. Moreover, the film-forming property

and carrier-transporting properties of the solution are poor when the weight ratio is lower than 3:1<sup>[12]</sup>.

To equilibrate the carrier injection, double-layer devices with different thicknesses of  $\text{Alq}_3$  as electron transporting layer (ETL) were fabricated. The double-layer devices have the structure ITO/PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  (3:1) (30 nm)/ $\text{Alq}_3$  ( $x$  nm)/LiF (0.3 nm)/Al (150 nm), where  $x$  is 6, 8, and 10 nm, respectively. The EL spectra of double-layer devices show (Fig.3 (a)) that the emission intensity of  $\text{Alq}_3$  is enhanced with the increase in its thickness. In contrast to the devices with the same ETL thicknesses, the emitting intensity of  $\text{Eu}^{3+}$  ions is enhanced with increase in the voltages. Furthermore, the emitting intensity of  $\text{Alq}_3$  (515 nm) is also enhanced relatively.

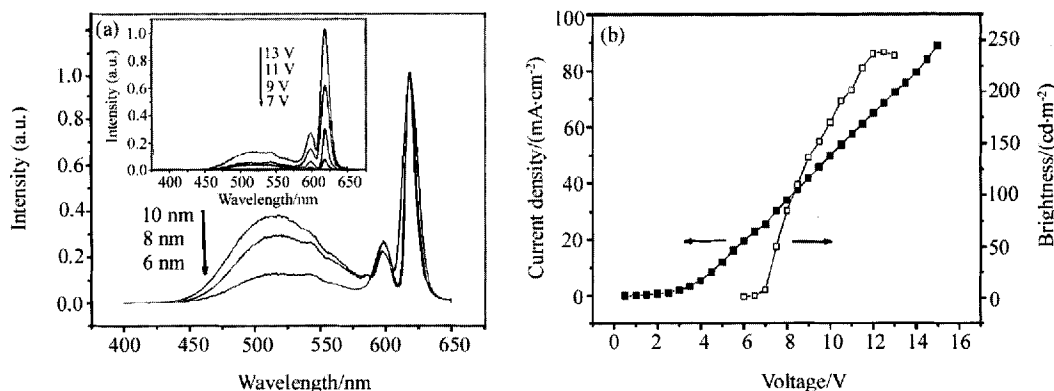


Fig.3 EL spectra of double-layer devices ITO/PVK:  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  (3:1) (30 nm)/ $\text{Alq}_3$  ( $x$  nm)/LiF (0.3 nm) Al (150 nm) at 13 V ( $x$  is 6, 8 and 10 nm, respectively), the inset shows the EL spectra of double-layer device with 6 nm thick  $\text{Alq}_3$  at different driven voltages (a); Current density-voltage-brightness (J-V-B) curves of double-layer device with 6 nm thick  $\text{Alq}_3$  (b)

The EL mechanism can be explained through the energy-band diagram<sup>[13,14]</sup> of the double-layer devices (Fig.4). The 0.5 eV energy band is formed between the highest occupied molecular orbital (HOMO) levels (-6.3 eV) of TTA and PVK (-5.8 eV), which may efficiently block the holes and limit the formation of excitons in the emitting layer. So emission from  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  is clearly observed. As the lowest unoccupied molecular orbital (LUMO) level (-3.1 eV) and the HOMO level (-5.8 eV) of  $\text{Alq}_3$  are in good agreement with the LUMO level (-3.1 eV) of TTA and the HOMO level of  $\text{Eu}^{3+}$  (-5.7 eV), the introduction of  $\text{Alq}_3$  can enhance the brightness of  $\text{Eu}^{3+}$ . Increasing the thickness of  $\text{Alq}_3$ , especially at high operating voltage, changed the compound current around the anode area and cathode area and resulted in the formation of an area of excitons closely transferring to ETL ( $\text{Alq}_3$ )<sup>[15]</sup>. So the emission of  $\text{Alq}_3$  is clearly observed. Considering both the color purity and the emitting intensity of the devices, the optimum

thickness of  $\text{Alq}_3$  is 6 nm. Fig.3(b) shows that the current density and the brightness functioned as the operating voltages. Optimized double-layer devices with a turn-on voltage of 6.5 V were achieved. At the current density of  $68.48 \text{ mA} \cdot \text{cm}^{-2}$ , the maximum brightness and the current efficiency of the device reached 238.4 and  $0.35 \text{ cd} \cdot \text{A}^{-1}$ , respectively.

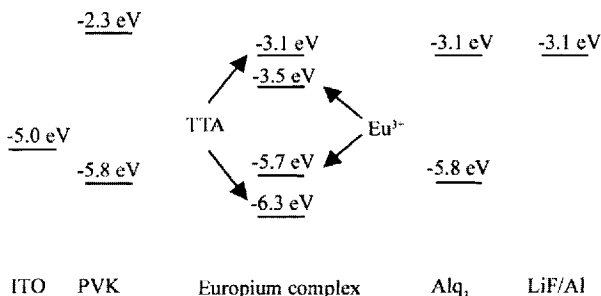


Fig.4 Schematic description of energy-band diagram

### 3 Conclusion

To summarize, a novel europium complex  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  was synthesized and used as the emission material for OEL. The polymer PVK was introduced to improve the film-forming and carrier-transporting properties of the europium complex. By measuring the PL and EL spectra, the emission mechanism was studied, and the optimal conditions for both monolayer (the weight ratio of PVK and  $\text{Eu}_{0.5}\text{La}_{0.5}(\text{TTA})_3\text{phen}$  is 3:1) and double-layer devices (the thickness of ETL is 6 nm) were obtained in this study. Sharp-band red emissions of the optimized double-layer devices with turn-on voltage of 6.5 V were achieved. At the current density of  $68.48 \text{ mA} \cdot \text{cm}^{-2}$ , the maximum brightness and the current efficiency reach  $238.4 \text{ cd} \cdot \text{m}^{-2}$  and  $0.35 \text{ cd} \cdot \text{A}^{-1}$ , respectively.

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### Effects of M-Doping (M = Al or Si) on Electronic Structure of $\text{LaNi}_5$

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**Abstract:** Employing the first principles discrete variational method (DVM), the electronic structures of  $\text{LaNi}_5$  hydrogen storage alloys with Ni replaced by common element M (M = Al or Si) were investigated. The results show that the s electrons of H mainly interact with the s electrons of non-hydride-forming ele-

**Key words:**  $\text{LaNi}_5$ ; electronic structure; first principles; rare earths

ment Ni and M, though there is a larger affinity of La for hydrogen than that of Ni and M in pure metal-hydrogen system. The effect on the electronic structure of Al is very similar to that of Si in the  $\text{LaNi}_5$  alloy because of their similar character.

(See *J. Chin. RE. Soc. (in Chin.)*, 2006, 24(5): 556 for full text)