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Synthesis and electroluminescent property of ternary complexes Eu(TTA)$_3$M

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ABSTRACT

Three kinds of rare earth ternary complexes of Eu^{3+} with HTTA and M (M = 5-NO$_2$Phen, 2,2′-Dipy and TPPO) have been synthesized and characterized using various spectral techniques such as elemental analysis, TGA-DTA, IR, UV and fluorescent. Results show that the complexes of Eu(III) emit strong red luminescence when excited by UV light. The complex Eu(TTA)$_3$5NO$_2$Phen posses the highest sensitized luminescent efficiency and the longest lifetime in the studied complexes. TG curves indicate that Eu(TTA)$_3$5NO$_2$Phen is most stable. In device ITO/PVK/Eu(TTA)$_3$5NO$_2$Phen/Al, Eu^{3+} may be excited by intramolecular energy transfer from ligands as observed by electroluminescence. The main emitting peak at 614 nm can be attributed to the transition of $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ion, and this process results in the enhancement of red emission from electroluminescence device.

1. Introduction

The rare earth metals are unique elements, which fascinating luminescent properties lead to an outstanding role in light conversion technologies. Stable complexes of luminescent trivalent lanthanide ions are of great interest owing to their broad applications in biochemistry, material chemistry, medicine and so forth [1–4]. Many rare-earth complexes have been developed as the emitters in organic photoluminescence and electroluminescence devices [5–9]. The most useful lanthanide Eu^{3+} ion has unusual spectroscopic characteristics, including millisecond lifetime, very sharp emission bands and large Stokes shifts. In this regard, many research groups have extensively studied various Eu(III) complexes for the purpose of achieving desirable luminescent properties [10–14]. However, the quantum efficiency of most of these lanthanide complexes is still low. Generally, the Eu^{3+} ion shows very weak absorption in the visible region and often require the application of strongly absorbing “antennae” for light harvesting to obtain efficient photoluminescence. This may be mostly due to inefficiency of the energy transfer, particularly, triplet–triplet transfer in these lanthanide complexes. One of the most important problems in this field is a selection of suitable ligands, which would provide high efficiency of emission of the metal ions [15]. The rare-earth β-diketonate complexes not only display a high luminescent efficiency but also are suitable to be thermally deposited. For this reason, as a way to obtain pure red OLED devices and to use triplet excited states, OLEDs based on tetrakis β-diketonate RE complexes as electron transport and emitting layer were developed [16,17].

In this paper, we introduced three different second ligands for the enhancement of luminescent properties, and three kinds of Eu(III) rare-earth complexes with violet light absorption have been designed and synthesized. The luminescence properties of the complexes are influenced by the interaction among the different second ligands. The result shows that electron transitions of lanthanides can be manipulated by designing ligands. The luminescence of lanthanide (III) complexes can be realized and enhanced by designing ligands coordinate to lanthanide (III) ions. The intramolecular energy transfer efficient from organic ligands to Eu^{3+} is the most important factor which influencing the luminescence properties of rare-earth complexes.

In the three Eu(III) complexes, Eu(TTA)$_3$5NO$_2$Phen has the highest sensitized luminescent efficiency and the longest lifetime. In PVK/Eu(TTA)$_3$5NO$_2$Phen blend, the red emission of europium complex is enhanced and PVK emission is quenched. Therefore, EL devices of high red light EL efficiency are obtained.

2. Experimental

2.1. Synthesis of the complexes

Rare-earth complexes were prepared as follows: EuCL$_3$6H$_2$O(1 mmol) and HTTA (3 mmol) were dissolved in 50 mL ethanol. The pH value of the solution was adjusted to 6–7 by the addition triethylamine. Then, 5-NO$_2$ Phenanthroline (or 2,2′-Dipy, TPPO) in ethanol solution was added to the reaction mixture, the molar ratio of 5-

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Table 1
DTA-TG peaks of complexes.

	Melting point T_{m1} (°C)	Weight loss (%)	Decompose temperature (°C) T_{m2} (°C)	Weight loss (%)	RE_2O_3 (%) Analytically found (calculated)
$Eu(TTA)_3Dipy$	223	0.00	496	65.8	17.8 (18.1)
$Eu(TTA)_35NO_2Phen$	242	0.00	501	79.7	17.1 (16.9)
$Eu(TTA)_3(TPPO)_2$	220	0.00	482	70.1	13.1 (12.8)

NO_2 Phenanthroline (2,2′-Dipy) to Eu^{3+} ion being 1:1 (TPPO to Eu^{3+} ion being 2:1). The mixture solution was stirred at 50 °C for 5 h. The precipitate was filtered, washed with water and ethanol, dried at room temperature, and then stored in a silica-gel drier [18].

2.2. Electroluminescence device preparation

The device structure of the complex $Eu(TTA)_3M$ was fabricated according to the literature method [19]. Poly(*N*-vinylcar-bazole) (PVK) was dissolved in chloroform with a concentration of 10 mg/ml. In order to improve the performance of $Eu(TTA)_3M$ thin film, $Eu(TTA)_3M$ was doped into PVK at weight ratio of 1:3. The PVK: $Eu(TTA)_3M$ thin film was fabricated on the top of cleaned ITO coated glass substrate by spin-coating method. 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and aluminum quinoline(Alq_3) films were fabricated by thermal evaporation at a rate of about 0.3 Å/s under high vacuum of 2×10^{-6} Torr.

Table 2
The results of analytical data of complexes.

Complex	Eu (%)	Analytically found (calculated) (%)		
		C	H	N
$Eu(TTA)_3Dipy$	15.59 (15.64)	42.05 (41.99)	2.11(2.06)	2.90 (2.88)
$Eu(TTA)_35NO_2Phen$	14.55 (14.60)	41.48 (41.51)	1.89 (1.83)	4.10 (4.04)
$Eu(TTA)_3(TPPO)_2$	11.10 (11.08)	52.53 (52.49)	3.10 (3.06)	

2.3. Measurements

Elemental analyses were performed with a PerkinElmer 2400 elemental analyzer; Metal contents were determined by EDTA complexometry(previous version:

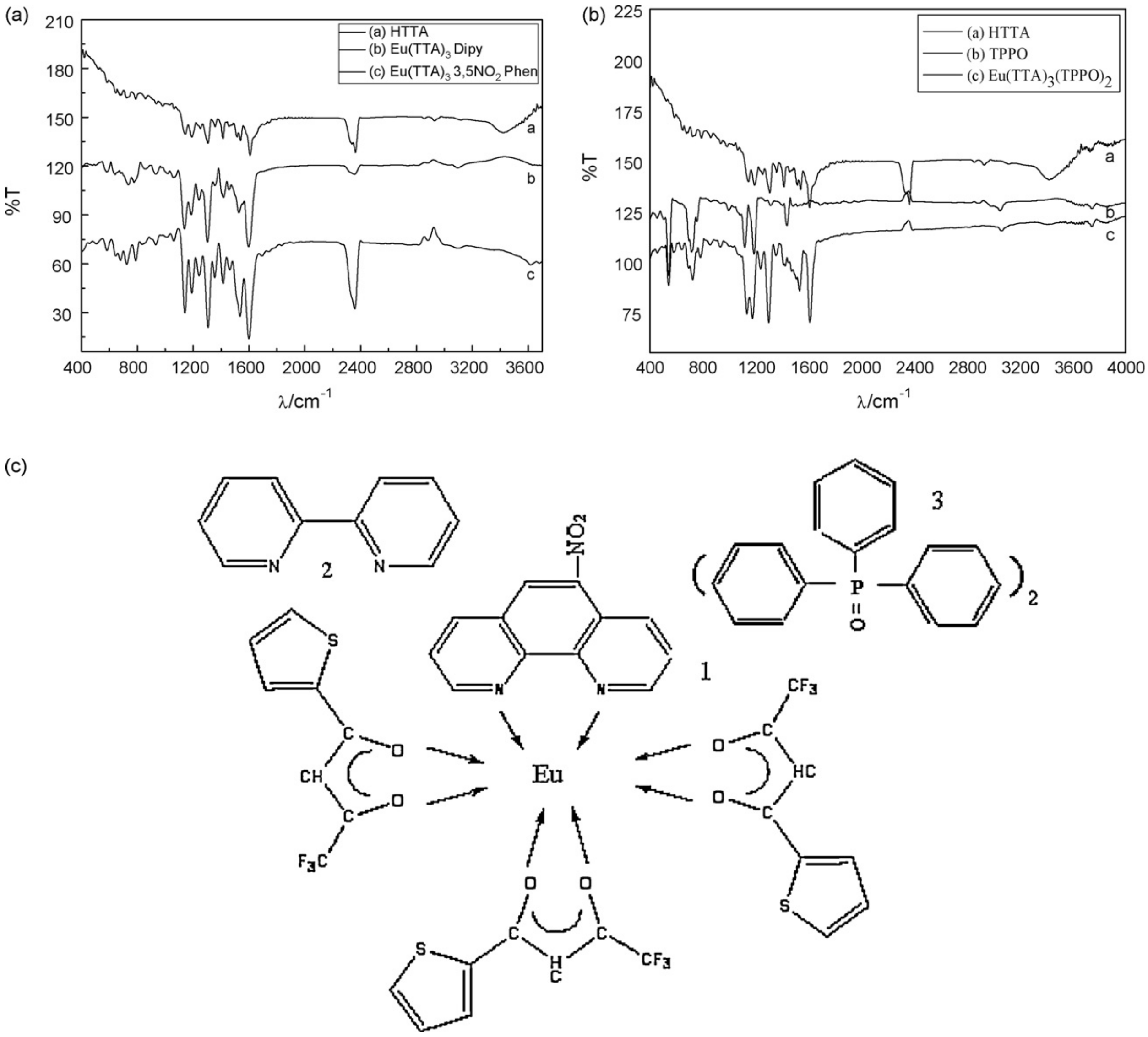

Fig. 1. (a) and (b) Infrared spectra of ligands and complexes (λ = 400–4000 nm) (c) Chemical structures of the complexes with various neutral ligands.

elemental analyses were performed on a PerkinElmer 240C analytical instrument); DTA-TG curves were obtained on a TGA-DTA 1700- PerkinElmer with sample amount of 3.6 ± 0.2 mg; Infrared spectra used to identify synthesized materials were obtained with a prostige-21IR spectrophotometer in the range of 4000–400 cm^{-1} (previous version: infrared spectra were recorded in the range of 4000–400 cm^{-1} by a prostige-21IR spectrophotometer in KBr flake); UV–vis spectra were performed on a UV-2501PCS double spectrophotometer; The excitation and emission spectra were recorded on a Shimadzu 5301 spectrofluorophotometer equipped with a 150 W xenon lamp as the excitation source. Spectra were recorded using monochromator slit widths of 1.5 mm on both excitation and emission sides; lifetimes were measured with a Spex 1934D phosphorimeter using a 450 W flash lamp as the excitation source (pulse width = 3 μs). The EL spectra were measured on a fluorolog-3 spectrophotometer of the American SPEX Company. The luminance was measured by PR-650 spectra-scan spectrometer.

3. Results and discussion

3.1. DTA-TG analysis

In order to examine the thermal stability of the complexes, thermal gravimetric (TG) and differential thermal analyses (DTA) are carried out between 30 and 900 °C in the static atmosphere of air. DTA-TG plots of three complexes show significantly different patterns. DTA-TG peaks of three complexes are listed in Table 1. Table 1 shows the complex $Eu(TTA)_3 5NO_2Phen$ with an endothermic peak around 242 °C and about weight 79.7% of loss at 348–850 °C, in which TG curve shows that $Eu(TTA)_3 5NO_2Phen$ is more stable than $Eu(TTA)_3Dipy$ and $Eu(TTA)_3(TPPO)_2$ in the air. Therefore, the complex is well suited for the use as the emission materials.

3.2. IR spectra analysis

Infrared spectra of ligands and complexes are shown in Fig. 1. For $Eu(TTA)_3Dipy$ (in Fig. 1a), the bands at around 1506 and 759 cm^{-1} are corresponded to stretching vibration of –N=C and rC-H vibration of 2,2′-Dipy, respectively. The peak at about 520 cm^{-1} reveals the presence of O → RE, which cannot be observed in the ligands. In addition, typical asymmetric vibrations of the carbonyl group in HTTA are detected at about 1601 and 1539 cm^{-1}. In the case of $Eu(TTA)_3 5NO_2Phen$, the bands at wavenumber 1539, 2438and 730 cm^{-1} are corresponded to stretching vibration of –N=C, –N=O, and rC-H vibration of $5NO_2$-Phen, respectively. In addition, typical asymmetric vibration of the carbonyl group in HTTA are detected at about 1605 and 1549 cm^{-1}.

In Fig. 1(b), $Eu(TTA)_3(TPPO)_2$ typical vibration are listed: 1650(s, C=O), 1250 –1150(s, C=F), 1125(s, P=O). The elemental analysis data of the europium complexes are listed in Table 2. The results of elemental analysis indicate that the composition of the complexes conforms to $Eu(TTA)_3Dipy$, $Eu(TTA)_3 5NO_2Phen$ and $Eu(TTA)_3$ $(TPPO)_2$, respectively. Fig. 1(c) shows the chemical structures of the complexes with various neutral ligands.

3.3. UV absorption spectra and fluorescence properties

UV spectra of the complexes $Eu(TTA)_3 5NO_2Phen$ and $Eu(TTA)_3Dipy$ are shown in Fig. 2. All of the complexes exhibit absorption in the ultraviolet region with the maximal absorption of $Eu(TTA)_3 5NO_2Phen$ at 273 and 342 nm {$Eu(TTA)_3Dipy$ at 305 and 335 nm}. For $Eu(TTA)_3(TPPO)_2$, the maximal absorption peaks are located at 285 and 353 nm.

The solid complexes have characteristics line emission of f–f transition of metal ions when they are excited by UV light. The fluorescence characteristics of the complexes in liquid state are listed in Table 3. Fluorescent spectra are recorded by monitoring the Eu^{3+} luminescence at 614 nm. Fluorescence emission spectrum of the $Eu(TTA)_3 5NO_2Phen$ complex is shown in Fig. 3. Five typical Eu^{3+} luminescence peaks appear at 583.0, 593.5, 614.0, 656.0 and 707.5 nm, which are due to $^5D_0 \to {}^7F_0$, $^5D_0 \to {}^7F_1$, $^5D_0 \to {}^7F_2$, $^5D_0 \to {}^7F_3$ and $^5D_0 \to {}^7F_4$, respectively, the relative intensity of $^5D_0 \to {}^7F_2$ is stronger than other luminescence emissions. The emission peak positions of $Eu(TTA)_3 5NO_2Phen$ are basically same as those of $Eu(TTA)_3Dipy$ and $Eu(TTA)_3(TPPO)_2$, indicating that there is a typical Eu^{3+} luminescence emission. More importantly, the $Eu(TTA)_3 5NO_2Phen$ complex shows also the longest lifetime in Table 3 (about 865 μs).

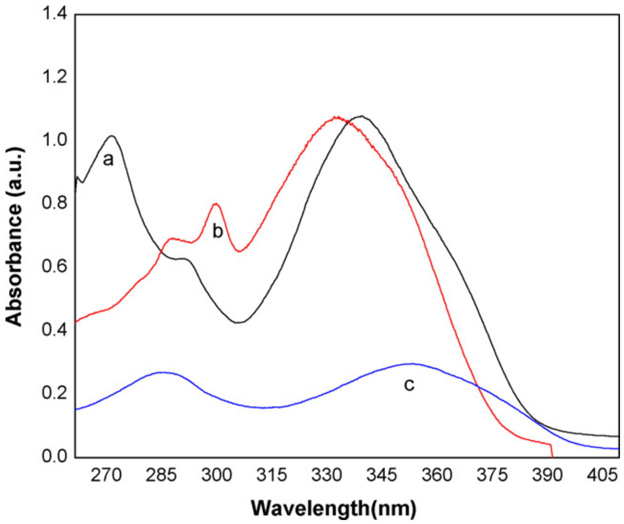

Fig. 2. UV spectra of complexes: (a) $Eu(TTA)_3 5NO_2Phen$, (b)$Eu(TTA)_3Dipy$ and (c) $Eu(TTA)_3(TPPO)_2$.

Table 3
The luminescence properties of rare-earth complexes.

Matter	λ_{ex} (nm)	$Eu(TTA)_3M$ λ_{em} (nm)	Relative intensities (a.u.)	Lifetimes (μs)
$Eu(TTA)_3Dipy$	386	614	802	612
$Eu(TTA)_3(TPPO)_2$	383	614	653	436
$Eu(TTA)_3 5NO_2Phen$	385	614	968	865

3.4. Electroluminescence

Fig. 4 shows absorption spectra of PVK and PVK/$Eu(TTA)_3Dipy$. Obviously, the emission of PVK in the PVK/$Eu(TTA)_3Dipy$ blend

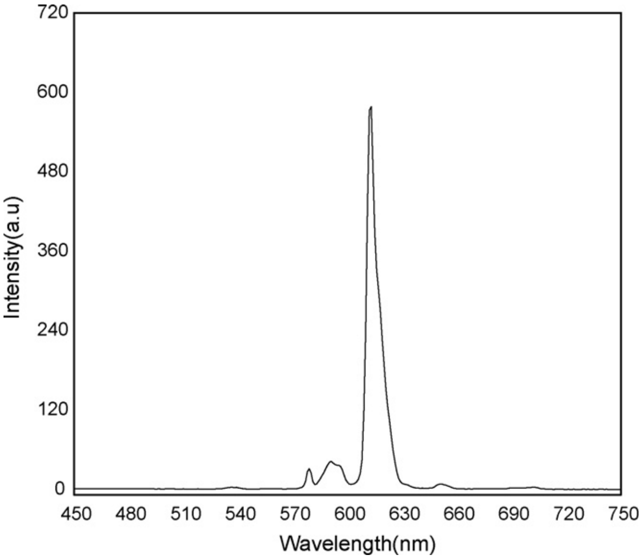

Fig. 3. Typical emission spectra of $Eu(TTA)_3 5NO_2Phen$ complex excited at 385 nm.

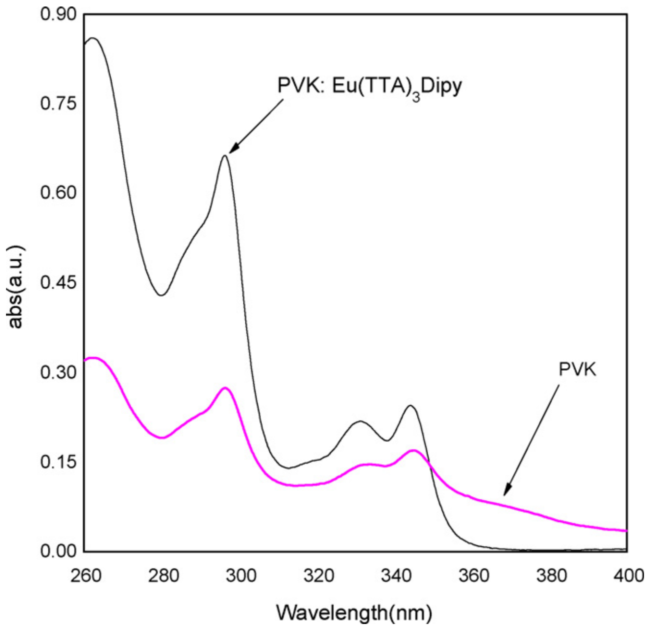

Fig. 4. Absorption spectra of PVK and PVK/Eu(TTA)$_3$Dipy blend.

is stronger than that of PVK alone. Moreover, the Eu^{3+} emission in the PVK/Eu(TTA)$_3$Dipy blend is also stronger than that of the Eu(TTA)$_3$Dipy complex.

Fig. 5 shows electroluminescence spectrum of PVK/Eu(TTA)$_3$5NO$_2$Phen and PVK/Eu(TTA)$_3$Dipy(at a driving voltage of 14 V). The intensity of the red emission at 614 nm in device I{ITO/PVK/Eu(TTA)$_3$5NO$_2$Phen/Al} is stronger than the device II{ITO/PVK/Eu(TTA)$_3$Dipy/Al}.The intensity of the device III{ITO/PVK/Eu(TTA)$_3$ -(TPPO)$_2$/Al}is almost invisible in the electroluminescence spectrum. The emission peaks are observed around 579, 590, 614, 653, and 699 nm, which are assigned to the 4f transitions of Eu(III) ($^5D_0 \rightarrow {}^7F_i$: $i = 0$; 1; 2; 3; 4), respectively. The most intense peaks corresponding to the electronic dipole transition ($^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ion) were observed at 614 nm. The electroluminescence starts at forward bias of 12 V, the brightness of the device is strengthened with the increase of the bias voltage.

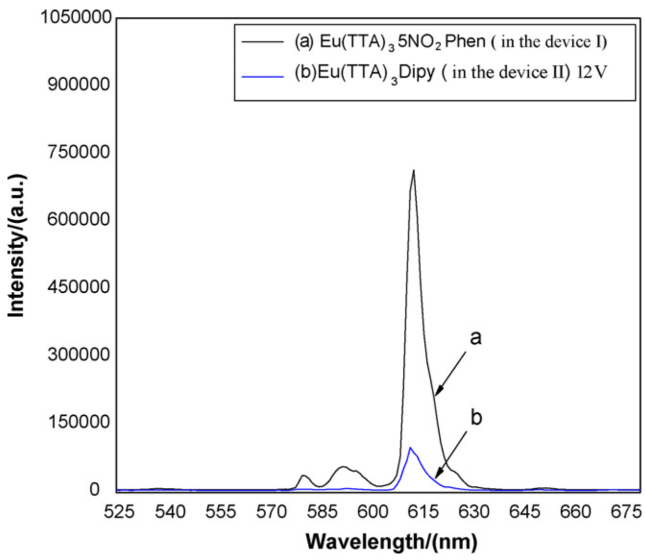

Fig. 5. EL spectra of complexes Eu(TTA)$_3$5NO$_2$Phen and Eu(TTA)$_3$Dipy in device I and device II (at a driving voltage of 12 V).

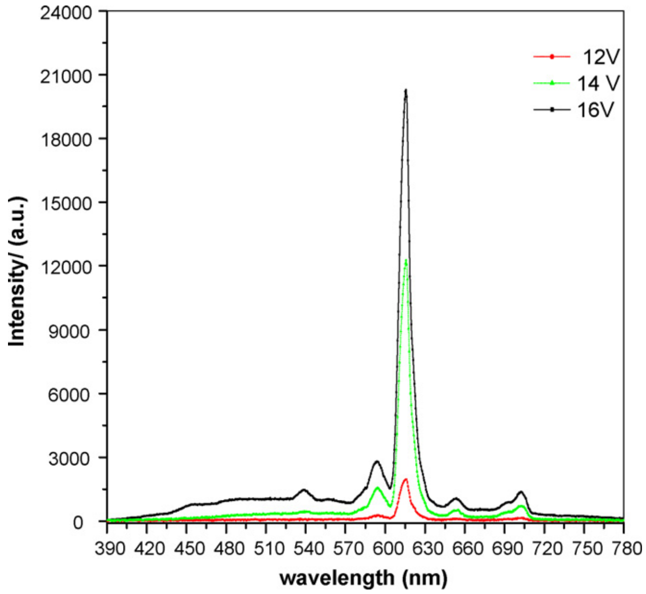

Fig. 6. EL spectra of complexes Eu(TTA)$_3$Dipy at a driving voltage of 12 V.

Fig. 6 is electroluminescent spectrum of the complex Eu(TTA)$_3$Dipy at a driving voltage of 12 V. The electroluminescence intensity dependence on the driving voltage is obtained by using the time-base spectra. In the structural device, electroluminescence intensity sharply increases when the driving voltage of 12 V.

Fig. 7 is current–voltage curves for the complex Eu(TTA)$_3$5NO$_2$Phen of structure devices at 8 V. It is found that the Eu(TTA)$_3$5NO$_2$Phen structural device effectively improves the electroluminescence intensity of lanthanide ions. As shown in Fig. 7, the electron current in the Eu(TTA)$_3$5NO$_2$Phen device sharply increases when the driving voltage goes beyond 16 V.

The luminescence properties of the complexes are influenced by the interaction among the ligands. Electron transitions of lanthanides can be manipulated by designing ligands. The luminescence of lanthanide (III) complexes can be realized and enhanced by designing ligands coordinate to lanthanide (III) ions. In this paper, we introduced different ligands for the enhancement of the lumi-

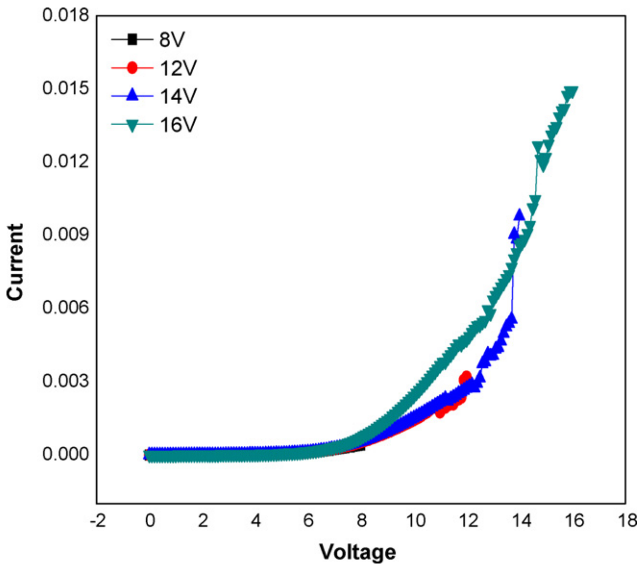

Fig. 7. Current–voltage curves for the complex Eu(TTA)$_3$5NO$_2$Phen at various driving voltages.

nescent properties. In conclusion, we designed and synthesized three kinds of rare-earth complexes with violet light absorption. The intramolecular energy transfer effectively from organic ligands to Eu^{3+} is the most important factor which influencing the luminescence properties of rare-earth complexes. The intramolecular energy transfer effectively depends chiefly on two energy transfer processes: the first one comes from the triplet level of ligands to the emissive energy level of the Eu^{3+} by Dexter's resonant energy transfer interaction; the second one is just an inverse energy transfer by a thermal deactivation mechanism. Both energy transfer rate constant depend on the energy differences between the triplet level of the ligands and the resonant emissive energy level of Eu^{3+}.

4. Conclusions

According to the data and discussion above, we have successfully prepared three kinds of Eu(III) complexes by using the UV absorption reagents as ligands. TG curve prove the complexes are stable, ranging from ambient temperature to 200 °C in air. The study of luminescence properties shows that the complex $Eu(TTA)_3 5NO_2$ Phen has the highest sensitized luminescent efficiency and the longest lifetime than $Eu(TTA)_3$Dipy and $Eu(TTA)_3(TPPO)_2$. The present study shows great promise for the design of a new type electroluminescence device configuration.

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