

# Synthesis and luminescent properties of ternary complex $\text{Eu}(\text{UVA})_3\text{Phen}$ in nano- $\text{TiO}_2$ \*

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By introducing 2-hydroxy-4-methoxy-benzophenone (UVA) and 1,10-phenanthroline (Phen) as the ligands, the ternary rare earth complex of  $\text{Eu}(\text{UVA})_3\text{Phen}$  is synthesized, and it is characterized by elemental analysis, mass spectra (MS) and infrared (IR) and ultraviolet (UV) spectroscopy. Results show that the Eu(III) in complex emits strong red luminescence when it is excited by UV light, and it has higher sensitized luminescent efficiency and longer lifetime. The organic-inorganic thin film of complex  $\text{Eu}(\text{UVA})_3\text{Phen}$  doped with nano- $\text{TiO}_2$  is prepared, and the nano- $\text{TiO}_2$  is used in the luminescence layer to change the luminescence property of  $\text{Eu}(\text{UVA})_3\text{Phen}$ . It is found that there is an efficient energy transfer process between ligands and metal ions. Moreover, in an indium tin oxide (ITO)/poly(N-vinylcarbazole) (PVK)/ $\text{Eu}(\text{UVA})_3\text{Phen}/\text{Al}$  device,  $\text{Eu}^{3+}$  can be excited by intramolecular ligand-to-metal energy transfer process. The main peak of emission at 613 nm is attributed to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of the  $\text{Eu}^{3+}$ , and this process results in the enhanced red emission.

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Lanthanide complexes are known to give sharp, intense emission lines under ultraviolet (UV) light irradiation. For technological applications, these complexes have to be incorporated into a stable solid matrix. Luminescent rare earth complexes have been intensively studied because of their applications in luminescent and laser materials<sup>[1-5]</sup>. As functional materials, rare earth  $\beta$ -diketone complexes have been widely used in a lot of aspects, such as luminescent materials, organic electroluminescent technology, bioinorganic sensors and luminescent labels in bioaffinity assays. Most of rare earth  $\beta$ -diketone complexes have strong absorption properties in the UV-visible (Vis) region, and have high thermal stability and good solubility in many organic solvents. The rare earth  $\beta$ -diketonate complexes not only display a high luminescent efficiency but also are suitable to be thermally deposited. Organic light emitting diodes (OLEDs) based on tetrakis  $\beta$ -diketonate rare earth complexes as electron transport and emitting layer were developed to obtain pure red OLED devices<sup>[6]</sup>. Ion-exchange studies of the poly[(2-hydroxy-4-methoxybenzophenone)

ethylene] at different electrolyte concentrations, pH values and rates have been carried out for lanthanides (III) metal ions<sup>[7]</sup>. Little attention has been paid to rare earth complexes of europium (Eu) with 2-hydroxy-4-methoxy-benzophenone (UVA) as the ligand, and few discussions have been reported in organic electroluminescence. Besides the synthesis and experimental investigation of the luminescence properties of new lanthanide complexes, our group has successfully developed the photophysical properties of new lanthanide complexes, the position and nature of the ligand excited states in the complex, the ligand-to-lanthanide ion energy transfer rates and the luminescence quantum yields<sup>[8-13]</sup>.

In this paper, we introduce UVA ligand for the enhancement of luminescent properties, and Eu(III) rare earth complex with violet light absorption is designed and synthesized. The  $\text{Eu}(\text{UVA})_3\text{Phen}$  can emit strong red luminescence, and has a higher sensitized luminescent efficiency and a longer lifetime. The complex of  $\text{Eu}(\text{UVA})_3\text{Phen}$  is synthesized, and the nano- $\text{TiO}_2$  is mixed with the rare earth complex to form the luminescence layer.

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It is found that there is an efficient energy transfer process between the complex and the europium ion. The nano-TiO<sub>2</sub> acts as an energy transfer bridge which helps the energy transfer from ligands to Eu<sup>3+</sup>. It shows that it is an effective method to improve the luminescent intensity of lanthanide complex by using electronic characteristics of inorganic semiconductor materials. In a poly(N-vinylcarbazole) (PVK)/Eu(UVA)<sub>3</sub>Phen blend, the red emission of the europium complex is enhanced, and the mechanism of the electroluminescent devices is discussed.

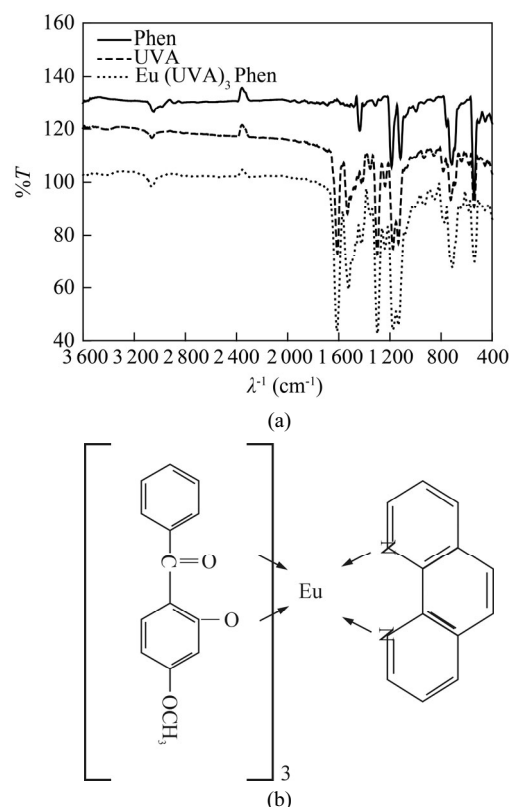
Rare earth complex was prepared as follows. EuCl<sub>3</sub>·6H<sub>2</sub>O (1 mmol) and UVA (3 mmol) were dissolved in 50 mL ethanol. The pH value of the solution was adjusted to be 6–7 by the addition triethylamine. Then, 1,10-Phen in ethanol solution was added to the reaction mixture, and the molar ratio of 1,10-Phen to Eu<sup>3+</sup> is 1:1. The mixture solution was stirred at 50 °C for 6 h. The precipitate was then filtered out, washed with water and ethanol, and dried at room temperature. It was stored in a silica-gel drier<sup>[14,15]</sup>. Nano-TiO<sub>2</sub> was prepared using the chemical vapor deposition (CVD) of TiCl<sub>4</sub>.

The device structure of Eu(UVA)<sub>3</sub>Phen was fabricated according to the method mentioned in Ref.[16]. PVK was dissolved in chloroform with concentration of 10 mg/mL. To improve the performance of the Eu(UVA)<sub>3</sub>Phen thin film, Eu(UVA)<sub>3</sub>Phen was doped into PVK with weight ratio of 1:3. The PVK: Eu(UVA)<sub>3</sub>Phen thin film was fabricated on the top of cleaned indium tin oxide (ITO) coated glass substrate by spin-coating method. 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) and aluminum quinoline(Alq<sub>3</sub>) films were fabricated by thermal evaporation at a rate of about 0.03 nm/s under high vacuum of 2.7×10<sup>-4</sup> Pa.

Elemental analyses were performed on the Perkin-Elmer 240C analytical instrument. Metal contents were determined by ethylene diamine tetraacetic acid (EDTA) complexometry. Mass spectra (MS) were determined using an LDI-1700 mass analyzer. Infrared (IR) spectra were recorded in the range from 4 000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> using a ProStige-21IR spectrophotometer and a KBr pellet. UV-Vis spectra were taken 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 with slit width of 1.5 nm on both excitation and emission sides. Lifetime was measured with a Spex 1934D phosphorimeter using a 450 W flash lamp with pulse width of 3 μs as the excitation source. The electroluminescence spectra were measured on a Fluorolog-3 spectrophotometer made by the American SPEX Company. The luminance was measured by PR-650 spectra scan spectrometer.

IR spectra of Eu(UVA)<sub>3</sub>Phen are shown in Fig.1(a). In the case of Eu(UVA)<sub>3</sub>Phen, the bands at wavenumbers of 1 539 cm<sup>-1</sup> and 730 cm<sup>-1</sup> correspond to stretching vibration of -N=C and ν<sub>C-H</sub> vibration of 1,10-Phen, respectively.

The band in the spectrum of complex at about 1 656 cm<sup>-1</sup> reveals the typical asymmetric vibration of carbonyl group (ν<sub>C=O</sub>), which can be observed at about 1 691 cm<sup>-1</sup> in spectrum of UVA ligand. Mass spectra reveal that *m/z* for a cationic peak is 1 016.2, which is attributed to [M+]. Fig.1(b) shows the chemical structure of the Eu(UVA)<sub>3</sub>Phen.



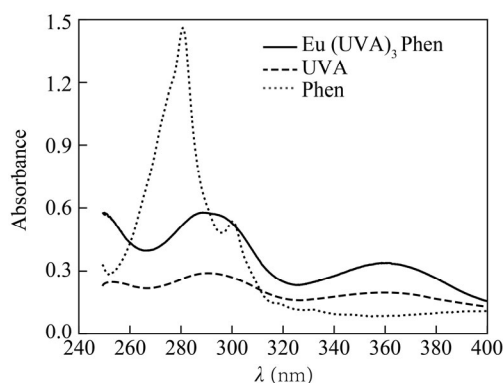
**Fig.1 (a) IR spectra of ligands and Eu(UVA)<sub>3</sub>Phen; (b) Chemical structure of Eu(UVA)<sub>3</sub>Phen**

**Tab.1 The analytical data for the complex of Eu(UVA)<sub>3</sub>Phen**

Complex	Analytically found (calculated) data (%)				
	Eu	C	H	O	N
Eu(UVA) <sub>3</sub> Phen	15.01 (14.96)	63.75 (63.78)	4.31 (4.33)	14.20 (14.17)	2.78 (2.76)

The UV spectra of the UVA ligand, Phen ligand and Eu(UVA)<sub>3</sub>Phen are shown in Fig.2. The complex exhibits the absorption in UV region with the maximum absorption peaks at 280 nm and 358 nm, the maximum absorption peaks for UVA ligand are at 282 nm and 355 nm, and those for 1,10-Phen ligand are at 275 nm and 300 nm. It can be seen that the UV spectrum shifts after introducing the ligands to synthesize complex Eu(UVA)<sub>3</sub>Phen. The result can be explained as after the metal ions are connected with enol form hydroxyl oxygen and enol form carbonyl oxygen atoms in the ligand, the oxygen atom is easier to give unbonded electron to π-electron system, which makes the red shift of the absorption peaks of the UVA ligand. This ability can be

increased with the increase of the positive electricity ability of metal ion.



**Fig.2 UV spectra of ligands and Eu(UVA)<sub>3</sub>Phen**

The complex shows the characteristic line emission of f-f transition arising from metal ions by UV light excitation. The luminescence characteristics of the complex in liquid state are listed in Tab.2. Luminescent spectrum is recorded by monitoring the Eu<sup>3+</sup> luminescence at 613 nm. Luminescence emission spectrum of the Eu(UVA)<sub>3</sub>Phen complex is shown in Fig.3. Five typical Eu<sup>3+</sup> luminescence peaks appear at 583.0 nm, 593.5 nm, 613.0 nm, 656.0 nm and 707.5 nm, which are due to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>3</sub> and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>4</sub> transitions, respectively. The relative intensity of the emission at <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> is stronger than those of the other luminescence emissions. In addition, the complex Eu(UVA)<sub>3</sub>Phen has a long luminescence lifetime of 916 μs.

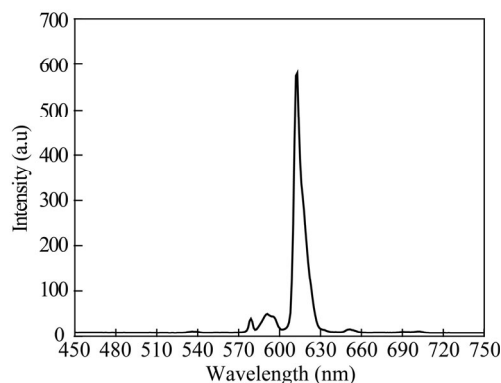
The organic-inorganic film of Eu(UVA)<sub>3</sub>Phen/nano-TiO<sub>2</sub> was fabricated. The nano-TiO<sub>2</sub> was used in the luminescence layer to change the luminescence property of complex Eu(UVA)<sub>3</sub>Phen, Eu(UVA)<sub>3</sub>Phen was doped into nano-TiO<sub>2</sub> with different weight ratios, and the thin film was fabricated on the top of glass substrate. Two kinds of devices with and without nano-TiO<sub>2</sub> were fabricated, and their structures are ITO/Eu(UVA)<sub>3</sub>Phen (50 nm): nano-TiO<sub>2</sub> (10–20 nm) and ITO/Eu(UVA)<sub>3</sub>Phen (50 nm), respectively.

**Tab.2 The luminescence properties of the rare earth complex**

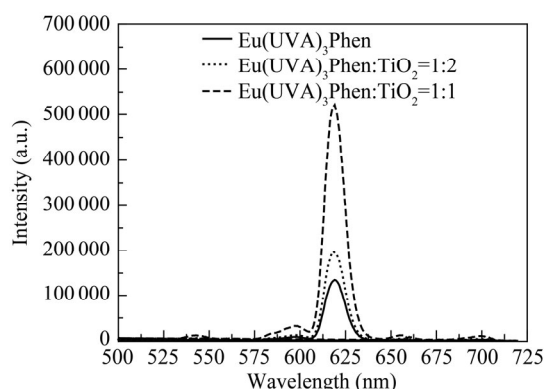
Material	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	Relative intensity (a.u.)	Lifetime (μs)
Eu(UVA) <sub>3</sub> Phen	325	613	1 012	916

In the thin film with nano-TiO<sub>2</sub>, the semiconductor TiO<sub>2</sub> thin film acts as the transporting layer according to its electronic characteristics and energy level. The intensity of the red emission at 613 nm in the thin film with nano-TiO<sub>2</sub> is stronger than that in the thin film without nano-TiO<sub>2</sub>, and the best weight ratio of rare earth complex to nano-TiO<sub>2</sub> is 1:1 as shown in Fig.4. In the two kinds of thin films, the characteristic emissions of Eu<sup>3+</sup> at 594 nm, 613 nm, 655 nm and 690 nm are obtained, and

these emission peaks are ascribed to four energy level transitions of Eu<sup>3+</sup>, i.e., <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub> with J=1, 2, 3 and 4, respectively. The luminescence intensity of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> is the strongest. As shown in Fig.4, the emission of Eu<sup>3+</sup> is enhanced due to the introduction of TiO<sub>2</sub>, which helps the energy transfer from ligands to Eu<sup>3+</sup>. These results demonstrate an efficient energy transfer from ligands to Eu<sup>3+</sup>, which exists in the complex of Eu(UVA)<sub>3</sub>Phen. Finally, most of the energy is given out by the radiation of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition of Eu<sup>3+</sup>.



**Fig.3 Typical emission spectrum of the Eu(UVA)<sub>3</sub>Phen excited at 325 nm**

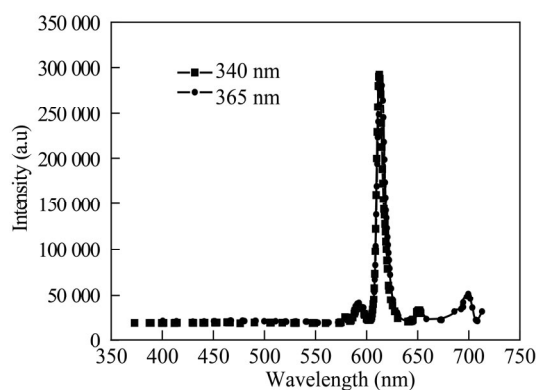


**Fig.4 Typical emission spectra of the Eu(UVA)<sub>3</sub>Phen and Eu(UVA)<sub>3</sub>Phen/nano-TiO<sub>2</sub>**

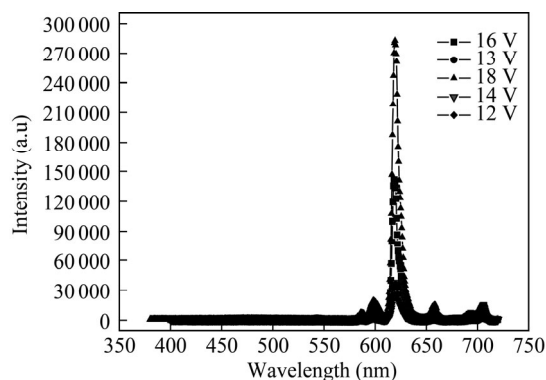
The electroluminescence intensity depending on the driving voltage is obtained by using the time-base spectra. In the device, the electroluminescent intensity sharply increases when the driving voltage is set as 12 V as shown in Fig.5.

Fig.6 shows the electroluminescence spectra of the PVK/Eu(UVA)<sub>3</sub>Phen at various driving voltages. The emission peaks are observed around 579 nm, 590 nm, 613 nm, 653 nm and 699 nm, which are assigned to the 4f transitions of Eu(III), i.e., <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub> with J=0, 1, 2, 3 and 4, respectively. The most intense peak, which is corresponding to the electronic dipole transition <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> of Eu<sup>3+</sup>, is observed at 613 nm. The electroluminescence starts at forward bias of 12 V. Therefore, the enhancement of red emission in an ITO/PVK/Eu(UVA)<sub>3</sub>Phen/Al device

is most likely due to the energy transfer enhancement from organic ligands to  $\text{Eu}^{3+}$ .



**Fig.5 EL spectra of PVK/Eu(UVA)<sub>3</sub>Phen blend with different exciting wavelengths of 340 nm and 365 nm at a driving voltage of 12 V**



**Fig.6 EL spectra of the Eu(UVA)<sub>3</sub>Phen at various driving voltages**

In this paper, we present the synthesis, characteristics, photophysical properties and structure of the new Eu(UVA)<sub>3</sub>Phen complex. The results indicate the complex has a higher sensitized luminescent efficiency and a longer lifetime. A novel thin film with organic-inorganic structure is fabricated, in which nano-TiO<sub>2</sub> is utilized as electron function layer, so the excitation of lanthanide can be carried out in a new route. Thus, it can be expected that nano-TiO<sub>2</sub> material plays an important role in improving luminescent intensity of lanthanide complex. It is suggested that Eu(UVA)<sub>3</sub>Phen can be applied in a new type of electro-luminescence device.

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