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# Synthesis and fluorescence properties of ofloxacin rare-earth nanocomplexes

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**Abstract:** Two rare- earth complexes with a high fluorescence activity, namely Terbium (Tb)-Ofloxacin(OFLX)-Phenanthroline(Phen) and Europium(Eu)-OFLX-Phen, were prepared. The coordination forms, structure characteristics, and fluorescence properties of the prepared complexes were studied by powder diffraction, infrared spectroscopy, elemental and thermogravimetric analyses. The results show that Tb (OFLX)<sub>3</sub>Phen and Eu(OFLX)<sub>3</sub>Phen complexes were successfully prepared. The infrared (IR) spectroscopy showed that the ligand of ofloxacin could coordinate with rare-earth Tb (III) or (III) ligands via single and double coordinations. The fluorescence spectra showed that complexes exhibited distinct fluorescence characteristic peaks, which differed from those of ligands. The optimum excitation and emission wavelengths of Tb (OFLX)<sub>3</sub>Phen complex were 275 and 545nm, respectively, while those of Eu (OFLX)<sub>3</sub>Phen were 325 and 614 nm. The fluorescence spectrum revealed that the complex can be used as a fluorescent probe to detect the drug presence. Moreover, the photoluminescence (PL) and electroluminescence (EL) properties of the complexes were studied. The rare-earth complexes formed in this experiment are instrumental in further fluorescent probe applications.

## 1. Introduction

In recent years, rare-earth elements attracted much attention in many fields, such as chemical processes, materials science, life sciences and other fields [1]. According to reports, the rare-earth ions have a good anti-inflammatory, bactericidal, analgesic, anticoagulant, and anti-tumor activity [2]. Due to the antibacterial activity and anti-tumor activity of rare-earth inorganic salts and the complexes, researchers have an increasing interest in the research of rare-earth complexes. It is reported that low doses of rare-earth complexes have inhibitory effects on tumor cells [3]. Rare-earth ions and their derivatives are widely used because of their unique electronic configuration, good luminescence, magnetic properties and catalytic properties [4-6].

As a third-generation quinolone antibiotic, ofloxacin (OFLX) has the characteristics of broad antibacterial spectrum, low toxicity, strong activity, and high efficiency [7-9]. According to the research, quinolones have a wide range of uses in the clinical treatment of various infectious diseases. Currently, OFLX is one of the most widely used quinolone drugs [10-14]. However, the synthesis, structure, spectroscopy and biological activity of ofloxacin complexes still less. In addition, ofloxacin has a large volume effect [15-16].

Quinolones can form complexes with electron-deficient rare-earth ions due to their predominantly alpha-keto acid structure, and the large number of conjugate structure can greatly enhance the stability



of the system. Complexes can absorb some energy when they are irradiated by UV light and transfer through the electronic transition effect to show the unique fluorescence characteristics of rare-earth ions. Therefore, the analytical method of use rare-earth ions as a fluorescent probe to detect quinolone drugs was also received widespread attention. Studies had shown that rare-earth ions as a fluorescent probe is mainly due to its electronic transition characteristics can emit sharp spectrum, the formation of complexes can greatly enhance the fluorescence intensity of rare-earth ions, thus this method shows a good application prospects [17-20]. In view of this, two crystal complexes of Tb(III)-OFLX-Phen and Eu(III)-OFLX-Phen were synthesized and characterized by elemental analysis, infrared (IR) spectroscopy, fluorescence spectra and thermal analysis. The fluorescence of the complexes was measured under normal temperature. This study provided a new measure for monitoring the rational use of medicines.

## 2. Experimental work

### 2.1 Material and methods

Terbium trichloride was purchased from Beijing Fangzheng Rare-earth Technology Co., Ltd. (China), Europium trichloride from Beijing Fangzheng Rare-earth Technology Co., Ltd. (China). Ofloxacin complied with the Chinese Medicine and Biological Products Inspection Standards. Phenanthroline was obtained from Tianjin Kaitong Chemical Reagent Co., Ltd. (China). Ethanol ammonia was from Zibo Hui Peng Industry and Trade Co., Ltd. (China), while chloroform and methanol were purchased from BDH and Sigma-Aldrich and utilized without purification. IR analysis for complexes was performed using a NEXUS-670 Fourier transform infrared spectrometer. The fluorescence analysis for complexes was conducted via a 970CRT fluorescence spectrophotometer.

The devices were fabricated, according to the following method. Here, poly (N-vinylcarbazole) (PVK) was dissolved in chloroform with concentration 10mg/ml. In order to improve the performance of Tb(OFLX)<sub>3</sub>Phen and Eu(OFLX)<sub>3</sub>Phen thin film, Tb(OFLX)<sub>3</sub>Phen and Eu(OFLX)<sub>3</sub>Phen were doped into PVK at weight ratio of 1:3. Indium tin oxide (ITO) coated glass substrates were cleaned consecutively in ultrasonic baths containing acetone, ethanol and DI-water. The PVK: Tb(OFLX)<sub>3</sub>Phen and Eu(OFLX)<sub>3</sub>Phen 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 (Alq3) films were fabricated by thermal evaporation at a rate of about 0.3 °A/s under high vacuum of  $2 \times 10^{-6}$  Torr.

### 2.2 Synthesis

Synthesis of Complex a. (Tb(III)-OFLX-Phen), TbCl<sub>3</sub>·6H<sub>2</sub>O (0.3362 g), OFLX (0.4879 g), and Phen (0.0811 g) were dissolved in 7.5 ml of ethanol solution respectively. The OFLX solution was mixed with Phen, and adjusted pH to 7 with ammonia, then slowly added Tb(III) solution and stirred for 6 h at room temperature with a magnetic stirrer (30r/min). After completion of the reaction, insoluble matter was removed by filtration, and the filtrate was evaporated at low temperature to precipitate crystals.

Synthesis of Complex b. (Eu(III)-OFLX-Phen), EuCl<sub>3</sub> · 6H<sub>2</sub>O (0.3298g), OFLX (0.4879 g), and Phen (0.0811 g) were dissolved in 7.5 ml of ethanol solution, respectively. The OFLX solution was mixed with Phen, and it pH was adjusted pH to 7.5 with ammonia, then slowly added to Eu(III) solution and stirred for 6 h at room temperature with a magnetic stirrer (30r/min). After completion of the reaction, insoluble matter was removed by filtration and the filtrate was evaporated at low temperature to precipitate crystals.

Detection of Complexes. A certain amount of the two complexes were dissolved in ethanol respectively (the concentration for  $1 \times 10^{-4}$ M). The glass rods can be used to accelerate the dissolution. The two complex solution were diluted to the desired  $1 \times 10^{-4}$ M concentration for fluorescence spectral scanning. The FTIR spectra of the samples were recorded by KBr pellet technique. The sample was ground with spectral grade KBr to form a mixture pellet using a hydraulic press. This pellet was used

to record the infrared spectra in the range of 4000–400  $\text{cm}^{-1}$ .

### 3. Results and discussion

The physical properties of complex **a** and complex **b** are relatively stable, they are not easily decomposed in the air but are readily dissolved in organic solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO), being insoluble in chloroform, ether, acetone and other solvents. In this study, the complexes **a** and **b** were determined by the elemental analysis, infrared spectroscopy, thermogravimetric analysis, and fluorescence spectra.

#### 3.1 Elemental Analysis

Elemental analysis (%) (theoretical calculation) for the complex **a** was: C, 50.47 (51.05), H, 5.10 (5.79) and N, 9.26 (9.41). The chemical formula of the complex **a** was  $\text{Tb}(\text{OFLX})_3\text{phen}$ . Elemental analysis (%) (theoretical calculation) for the complex **b** was: C, 51.37(51.27), H, 5.33(5.64) and N, 8.92(9.26). The chemical formula of the complex **b** was  $\text{Eu}(\text{OFLX})_3\text{phen}$ . The molar conductance of the complex **a** and the complex **b** were measured to be less than  $60 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  in DMF solution of  $1 \times 10^{-3} \cdot \text{mol}\cdot\text{L}^{-1}$  at  $30^\circ\text{C}$ .

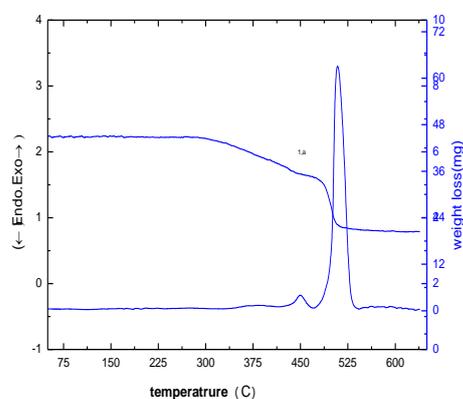
#### 3.2 Infrared (IR) Spectroscopy and XRD spectra Analysis

The infrared data of complex **a** was similar with complex **b**, took the data of complex **a** as an example. Table 1 shows the infrared detection results of  $\text{Tb}(\text{OFLX})_3\text{Phen}$ .

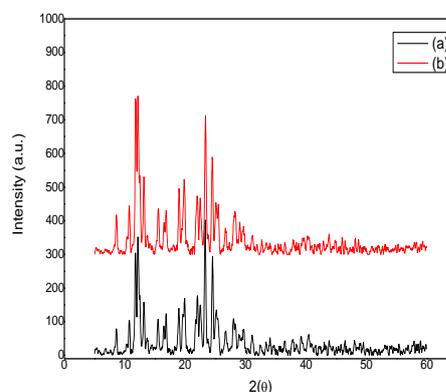
**Table 1.** Infrared (IR) spectra data of  $\text{Tb}(\text{OFLX})_3\text{phen}$

	$\nu(\text{O-H})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta$	$\nu(\text{C=O})$
Ofloxacin	3431(s)	1734(vs)	1734(vs)		1614(vs)
$\text{Tb}(\text{OFLX})_3\text{phen}$	3412(s)	1618vs, 1576s, 1529w	1380(s)	238, 196, 149	1486(vs)

The results show that the absorption peak of ofloxacin at  $1734 \text{ cm}^{-1}$  is  $\nu(\text{COOH})$  stretching vibration peak. The characteristic absorption peak of complex **a** disappeared at  $1734 \text{ cm}^{-1}$  and re-appeared at 1618, 1576, and  $1529 \text{ cm}^{-1}$ . This implies that it belongs to the carboxyl group and corresponds to the  $\nu_{\text{as}}(\text{COO}^-)$  asymmetric stretching vibration absorption peak. In addition, the carboxyl  $\nu_{\text{s}}(\text{COO}^-)$  symmetrical stretching vibration absorption peak was at  $1380 \text{ cm}^{-1}$ . One of the value of  $\Delta = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-) > 200 \text{ cm}^{-1}$ , indicating that the formation of ofloxacin anions, carboxyl and rare-earth ions occurs in a single coordination mode. Other values of  $\Delta$  for 196 and  $149 \text{ cm}^{-1}$  indicate that the ligand carboxyl also exists as a bidentate bit. In addition, the absorption peak of carbonyl  $\nu(\text{C=O})$  of ofloxacin was observed at  $1486 \text{ cm}^{-1}$ , indicating that the ligand carbonyl oxygen atoms and rare-earth ions formed a terbium bond.



**Figure 1.** Thermogravimetric analysis (TGA)



**Figure 2.** XRD patterns of complexes [(a)

of the Tb (OFLX)<sub>3</sub>Phen compound

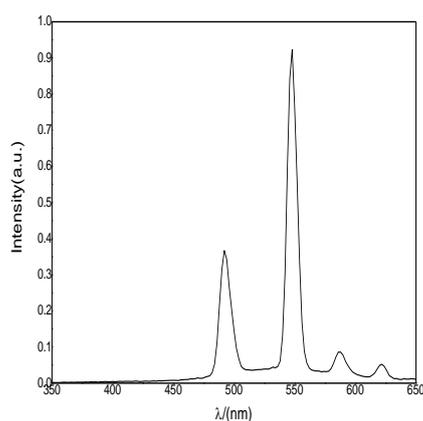
Tb(OFLX)<sub>3</sub>Phen.(b) Eu(OFLX)<sub>3</sub>Phen]

Therefore, ofloxacin and rare-earth ions of terbium formed a stable complex with monolabial and bidentate patterns. Figure 1 shows that the broad and strong absorption peak of complex was observed at 3412 cm<sup>-1</sup> approximately. There was no change in the position of the absorption peak after the complex was formed, which may be the stretching vibration peak of OH of the crystal water.

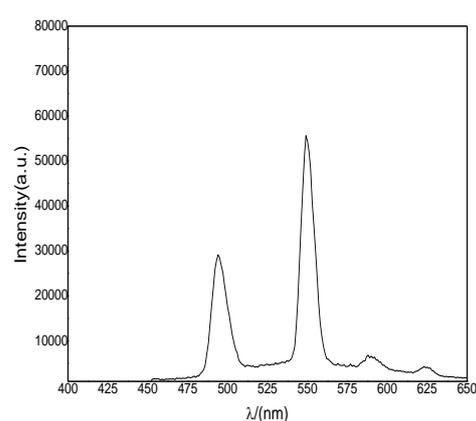
Figure 2 depicts the XRD spectra of Tb(OFLX)<sub>3</sub>Phen and Eu(OFLX)<sub>3</sub>Phen rare-earth organic complexes. The results show that the XRD patterns of rare-earth organic complexes and organic ligands are similar.

### 3.3. Fluorescence Detection

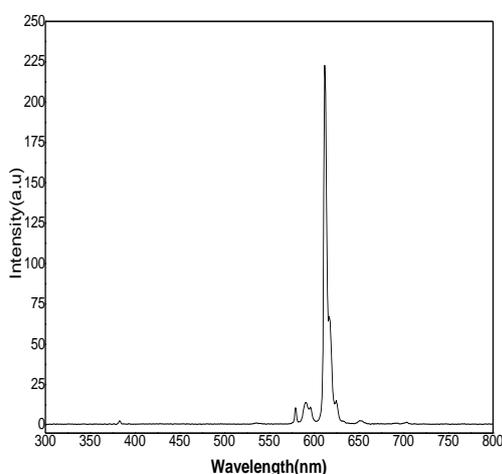
Emission spectra give energy to the sample and obtain linear absorption spectra. When a sample is irradiated with a certain wavelength of light, it partially absorbs the light. There is a change in light intensity before and after irradiation. The absorption spectra, such as molecular and atomic absorption spectra, are recorded. The difference is that the emission spectrum produced by the sample itself is received by the detector. Absorption spectrum is that the spectrum emitted by the light source is absorbed by the sample, and the rest of the spectrum is received by the detector. Absorption spectra have light sources, the source always works, and the light sources, samples and detectors are in a straight line.



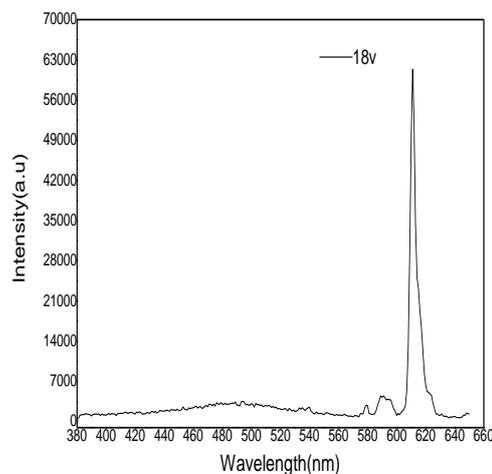
**Figure 3.** Emission (right) spectra of Tb(OFLX)<sub>3</sub>Phen complex.



**Figure 4.** Emission spectra of the thin film of PVK/Tb(OFLX)<sub>3</sub>Phen ( $\lambda_{em}=545$  nm)



**Figure 5.** Typical emission spectrum of Eu (OFLX)<sub>3</sub>Phen



**Figure 6.** Typical emission spectrum of PVK/Eu (OFLX)<sub>3</sub>Phen ( $\lambda_{\text{ex}}=325$  nm)

Rare-earth terbium had no fluorescence peak, while single ofloxacin had a weak fluorescence peak. As seen in figure 2, the best excitation and emission wavelengths of the composite were 275 and 545 nm, respectively. As seen in figure 3, three characteristic peaks of terbium ions were observed at 492, 590, and 638 nm. Figure 4 shows that the excitation spectrum of PVK/Tb (OFLX)<sub>3</sub>Phen has a peak at 545 nm. This implies the energy transfer from PVK to rare-earth complex. Figure 5 depicts a typical emission spectrum of Eu (OFLX)<sub>3</sub>Phen, while a typical emission spectrum of PVK: Eu (OFLX)<sub>3</sub>Phen ( $\lambda_{\text{ex}}=325$  nm) at a driving voltage of 18V is shown in figure 6. There are two main peaks at 614 and 595 nm. The two bands from Eu<sup>3+</sup> ion are corresponding to the transition of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>.

#### 4. Conclusions

Two new crystalline materials Tb(III)-OFLX-Phen and Eu(III)-OFLX-Phen were synthesized successfully under specific conditions. Both complexes were characterized by powder diffraction, infrared, elemental analysis, and thermogravimeter. It was proved the structure of complex was formed successfully with three ligands. In addition, the fluorescence spectra showed that the complex could be used as a fluorescent probe to detect drug content. The experimental results showed that the complex formed in this experiment was not easily decomposed, which allowed its further application in the area of fluorescent probe. The electroluminescence intensity of the combined structural device was strongly improved, as compared to a purely organic structural device.

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