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# The study on the effect and mechanism of the second ligands on the luminescence properties of terbium complexes

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#### Abstract

The binary complex of Tb(III) with *N*-phenylanthranilic acid (*N*-HPA) was synthesized, and the ternary complexes were synthesized by introducing 1,10-phenanthroline (Phen), 2,2'-dipyridyl (Bipy), trioctylphosphine oxide (TPPO) as the second ligand, respectively. These complexes were characterized by infrared spectra, UV spectra and fluorescence spectra. The effect and mechanism of different second ligands on the fluorescent intensity of the terbium *N*-phenylanthranilic acid complexes was discussed. It showed that all the complexes exhibited ligand-sensitized green emission. The luminescence intensity increased in the sequence of Tb(*N*-PA)<sub>3</sub>Phen < Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> < Tb(*N*-PA)<sub>3</sub>Bipy < Tb(*N*-PA)<sub>3</sub>(TPPO)<sub>2</sub>. The second ligands TPPO and Bipy enhanced the luminescence intensity of the complexes while the Phen quenched it. © 2007 Elsevier B.V. All rights reserved.

Keywords: Tb3+ complexes; N-Phenylanthranilic acid; Second ligand; Luminescence

## 1. Introduction

Recently, much attention has been paid to the fluorescent rare earth complexes, which not only can be used as probes and sensors for natural and medical science, but also can be used as the active center for electroluminescent devices [1-5].

The luminescence property of lanthanide complexes depends on the central metal ions, the energy level and the structure of the ligands [4–7]. Tb<sup>3+</sup> ion, the complexes of which emit green, is one of the rare earth ions that show the best luminescence property. The ligands called "antennas" absorb and transfer energy to the rare earth ions and consequently increase their luminescence intensity. The aromatic carboxylic acids and β-diketones ligands have attracted intense research interest due to their high ligandto-metal ions energy transfer efficiency, and the energy levels of the aromatic carboxylic acids match the <sup>5</sup>D<sub>4</sub> energy level of Tb<sup>3+</sup> ion better [1–6]. Moreover, in the hydrated complexes the water molecules act as effective luminescence quencher due to O–H oscillators, so substituting the water molecules by a second kind of organic ligands such as 1,10-phenanthroline (Phen)

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and 2,2'-dipyridyl (Bipy) can minimize the contribution of the radiationless processes [7].

In order to improve the luminescence properties of rare earth complexes, the choosing of the second ligands is very important. Though there was some research work, the effect and mechanism of the second ligands on the luminescence properties of terbium complexes still need to be further studied.

In this work,  $\text{Tb}(N\text{-}\text{PA})_3(\text{H}_2\text{O})_2$  and the ternary complexes of terbium *N*-phenylanthranilic acid with the second ligand (Phen, Bipy, TPPO) were synthesized. The spectra property of the complexes was studied. The results indicated that the impact of the second ligands on the fluorescence characteristics of terbium(III) ions due to the energy level and the structure of them.

## 2. Experiments

#### 2.1. Reagents and apparatus

Tb<sub>4</sub>O<sub>7</sub> (99.99%), *N*-phenylanthranilic acid (*N*-HPA), 1,10phenanthroline (Phen), 2,2'-dipyridyl (Bipy), trioctylphosphine oxide (TPPO) and other chemicals were analytical reagent grade and used without further purification.

 $TbCl_3 \cdot 6H_2O$  was prepared by dissolving terbium oxides in hot hydrochloric acid, and evaporating excess hydrochloric acid and water.

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Fig. 1. The structures of  $Tb(N-PA)_3Phen$ ,  $Tb(N-PA)_3(H_2O)_2$ ,  $Tb(N-PA)_3$  (TPPO)<sub>2</sub> and  $Tb(N-PA)_3Bipy$ .

Infrared spectra were recorded in the range of  $4000-400 \text{ cm}^{-1}$  by a prostige-21IR spectrophotometer in KBr flake. UV–vis spectra were performed on a UV-2501PCS double spectrophotometer among 200–400 nm. The excitation and emission spectra ( $5 \times 10^{-5} \text{ mol/L}$  DMF solution) were obtained with a Shimadzu 5301 spectrofluorophotometer equipped with a 150 W xenon lamp as the excitation source, PMT 20 KV, scanning velocity 1200 nm/min. Spectra were recorded using monochromator slit widths of 3 nm on both excitation and emission sides.

## 2.2. Synthesis of the complexes

The ternary Tb(III) complexes were synthesized by mixing the TbCl<sub>3</sub>· $6H_2O$ , *N*-HPA and the second ligand in ratio 1:3:1 (Phen, Bipy), and in ratio 1:3:2 (TPPO) in ethanol under stirring, which was adjusted to pH 6–7 by adding ammonia. The precipitation was then filtered, washed with water and ethanol and dried, then stored in a silica-gel drier.

The binary complex was prepared in similar process except adding the second ligand . The structures of the complexes are shown in Fig. 1.

#### 3. Results and discussion

### 3.1. IR spectra analysis

Table 1

Table 1 gives the characteristic bands of the ligands and the complexes. The infrared spectra for the ligand *N*-HPA and



Fig. 2. IR absorption spectra of the Tb(III) complexes and the first ligand: 1, *N*-HPA; 2, Tb(*N*-PA)<sub>3</sub>Phen; 3, Tb(*N*-PA)<sub>3</sub>Bipy; 4, Tb(*N*-PA)<sub>3</sub>(TPPO)<sub>2</sub>; 5, Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>.

the Tb<sup>3+</sup> complexes are shown in Fig. 2. It is obviously that the spectra of the Tb<sup>3+</sup> complexes are similar. The characteristic absorption bands for *N*-HPA at 1661 cm<sup>-1</sup>( $v_{C=O}$ ) and 3200–2500 cm<sup>-1</sup> ( $v_{-OH}$ ) disappeared in the Tb<sup>3+</sup> complexes. The presence of carboxylate groups in the various complexes was definitely confirmed by both the asymmetric stretching bands ( $v_{asCOO-}$ ) at about 1550 cm<sup>-1</sup> and the symmetric stretching ( $v_{sCOO-}$ ) at about 1400 cm<sup>-1</sup>.

Table 1 also shows the shift of twisting bending vibrations  $(\delta_{C-H})$  of Bipy from 754 cm<sup>-1</sup> to approximately 749 cm<sup>-1</sup> for Tb(*N*-PA)<sub>3</sub>Bipy, which indicated the coordination between Bipy and Tb<sup>3+</sup>. The twisting bending vibrations  $(\delta_{C-H})$  of Phen also shifted from 737 cm<sup>-1</sup> to 724 cm<sup>-1</sup> compared to Tb(*N*-PA)<sub>3</sub>Phen, which suggested Phen was coordinated with Tb<sup>3+</sup>. The displacement of  $\upsilon_{P=O}$  stretching from 1187 cm<sup>-1</sup>, in free TPPO ligand, to approximately 1159 cm<sup>-1</sup> in the complexes, indicating that Tb(III) ion was coordinated with the oxygen atom of P=O. Furthermore, the broad bands at 3100–3500 cm<sup>-1</sup> for Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> originated from the presence of the O–H stretching vibrations of H<sub>2</sub>O molecule.

### 3.2. UV absorption spectra analysis

UV absorption spectra of the ligand *N*-HPA and the complexes in DMF solution are shown in Fig. 3. They all exhibit

Attribution of IR main peaks of the ligands and Tb(III) complexes (cm <sup>-1</sup> )								
	N-HPA	$Tb(N-PA)_3(H_2O)_2$	Tb(N-PA) <sub>3</sub> Bipy	Tb(N-PA) <sub>3</sub> Phen	Tb(N-PA) <sub>3</sub> (TPPO) <sub>2</sub>	Bipy	Phen	TPPO
UC=0	1661	_	_	_	_	_	_	_
$v_{-OH(m)}$	3200-2500	-	-	-	-	-	-	-
$v_{asCOO-}$	-	1547	1551	1552	1550	-	-	-
$v_{sCOO-}$	-	1401	1400	1398	1402	-	-	-
$\delta_{C-H}$	-	-	749	843	-	754	851	-
	_	_	-	724	-	-	737	-
UP=O	-	-	-	-	1159	-	-	1187

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Fig. 3. The UV absorption spectra of the Tb(III) complexes and the first ligand:1, Tb(*N*-PA)<sub>3</sub>(TPPO)<sub>2</sub>; 2, Tb(*N*-PA)<sub>3</sub>Bipy; 3, Tb(*N*-PA)<sub>3</sub>Phen; 4, Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>; 5, *N*-HPA.

domain absorption peaks in the ultraviolet region (200–400 nm). The maximum absorption peaks are listed in Table 2. The results show that UV spectra of the Tb(III) complexes and the ligand *N*-HPA are very similar, and the absorbance of the ternary complexes just a little stronger than that of the binary complex, which implies *N*-phenylanthranilic acid absorbed energy mainly either in binary or ternary complexes.

Furthermore, a red shift (from 291 to 295 nm) is observed comparing Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> with *N*-HPA, which illuminates the formation of more extensive conjugated systems between Tb<sup>3+</sup> and *N*-HPA. The small blue shift of the ternary complexes compared with the binary complex Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> is due to the coordination interaction between lanthanide ions and second ligands, which confirming the second ligands have some impact on the conjugated systems between the Tb<sup>3+</sup> and *N*-HPA. And the blue shift of the Tb(*N*-PA)<sub>3</sub>Phen complex is the greatest, suggesting that when Phen is coordinated to Tb<sup>3+</sup> the  $\pi$ \* orbital of the complex is destabilized and shifted to higher energy. However, this destabilization is not obvious when the second ligands TPPO and Bipy are coordinated.

#### 3.3. Luminescent properties of the complexes

Fig. 4 shows the excitation spectra for the complexes recorded by monitoring the Tb<sup>3+</sup> luminescence at 545 nm in the range of 200–450 nm. The excitation spectra of the four complexes (Tb(N-PA)<sub>3</sub>(TPPO)<sub>2</sub>, Tb(N-PA)<sub>3</sub>Bipy, Tb(N-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and Tb(N-PA)<sub>3</sub>Phen) exhibit similar profile but with different intensity, and with the maximum excitation wavelength of 367, 365, 358 and 359 nm, respectively. Moreover, compared with the excitation band of Tb(N-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, the peak position of the ternary complexes presents red shift, the intensity of the spectra



Fig. 4. The excitation spectra of Tb(III) complexes 1, Tb(*N*-PA)<sub>3</sub>(TPPO)<sub>2</sub>; 2, Tb(*N*-PA)<sub>3</sub>Bipy; 3, Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>; 4, Tb(*N*-PA)<sub>3</sub>Phen.



Fig. 5. The emission spectra of Tb(III) complexes: 1, Tb(*N*-PA)<sub>3</sub>(TPPO)<sub>2</sub>; 2, Tb(*N*-PA)<sub>3</sub>Bipy; 3, Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>; 4, Tb(*N*-PA)<sub>3</sub>Phen.

of  $\text{Tb}(N-\text{PA})_3(\text{TPPO})_2$  and  $\text{Tb}(N-\text{PA})_3\text{Bipy}$  is stronger while the intensity of  $\text{Tb}(N-\text{PA})_3\text{Phen}$  is weaker.

The emission spectra were recorded in the range of 400–700 nm by monitoring the maximum excitation wavelength, as shown in Fig. 5. Note that the Tb<sup>3+</sup> complexes Tb(*N*-PA)<sub>3</sub>(TPPO)<sub>2</sub>, Tb(*N*-PA)<sub>3</sub>Bipy, Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and Tb(*N*-PA)<sub>3</sub>Phen all emitted the typical sharp emission bands at 489, 544, 584 and 621 nm, corresponding to the transitions of the Tb<sup>3+</sup> ion <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>6</sub>, <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>5</sub>, <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>4</sub> and <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>3</sub>, respectively. No emission bands from the ligands were observed, indicating that the ligands transferred the excitation energy efficiently to the Tb<sup>3+</sup> ion.

The intensity of the peaks of the complexes is listed in Table 3. It is obvious that compared with  $Tb(N-PA)_3(H_2O)_2$  the emission intensity of  $Tb(N-PA)_3(TPPO)_2$  and  $Tb(N-PA)_3Bipy$ 

 Table 2

 The domain ultraviolet absorption of Tb(III) complexes

	<i>N</i> -HPA	Tb( <i>N</i> -PA) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	Tb(N-PA) <sub>3</sub> Phen	Tb(N-PA) <sub>3</sub> (TPPO) <sub>2</sub>	Tb(N-PA) <sub>3</sub> Bipy
$\lambda$ (nm)	291.2	295.4	292.4	294.8	294.2

Complexes	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm) (relative intensity)				
		$^{5}D_{4} \rightarrow {}^{7}F_{6}$	$^5D_4 \rightarrow {}^7F_5$	$^5D_4 \rightarrow {}^7F_4$	$^5D_4 \rightarrow {^7F_3}$	
$Tb(N-PA)_3(H_2O)_2$	358	489(106.386)	544(271.525)	584(17.535)	621(7.034)	
Tb(N-PA) <sub>3</sub> Phen	359	489(76.718)	544(197.961)	584(11.999)	621(4.834)	
Tb(N-PA) <sub>3</sub> Bipy	365	489 (133.036)	544(358.338)	584(20.693)	621(8.020)	
$Tb(N-PA)_3(TPPO)_2$	367	489(146.452)	544(391.969)	584(23.102)	621(8.710)	

Table 3 Relative intensity of fluorescence of Tb(III) complexes

is stronger, while that of complex  $Tb(N-PA)_3$ Phen is weaker, which is ascribed to the second ligands.

The result shows that substituting the water molecules with the second ligands TPPO and Bipy intensifies the luminescence of  $Tb(N-PA)_3(H_2O)_2$ , while substituting with Phen weakens it. The quenching effect of Phen is consistent with the report of Wang et al. [8].

The intramolecular energy transfer efficiency from organic ligands to  $RE^{3+}$  ion is the most important factor which influencing the luminescence properties of rare earth complexes [9]. According to the intramolecular energy mechanism [10], the intramolecular energy transfer efficiency depends chiefly on two energy transfer processes: the first one comes from the triplet level of ligands to the emissive energy level of the  $RE^{3+}$  ion by Dexter's resonant energy transfer by a thermal deactivation mechanism. Both energy transfer rate constants depend on the energy differences between the triplet level of the ligands and the resonant emissive energy level of  $RE^{3+}$ .

According to Dexter luminescence theory [11], intramolecular energy transfer efficiency is directly proportional to the overlap between the luminescence spectrum of energy donor (ligand) and the absorption spectrum of energy acceptor ( $Tb^{3+}$ ). As energy gap between the resonance energy level of  $Tb^{3+}$  and the triplet state energy of ligand decreases the overlap increases. Consequently, the intramolecular energy transfer efficiency increases. Thus, ligands with a large energy difference such as *N*-HPA cannot sensitize  $Tb^{3+}$  effectively because the overlap integral is too small to produce effective intramolecular energy transfer.

There also exists an inverse energy transfer process, which affected by temperature [10]. The activation energy is approximately equal to the energy difference between the triplet level of the ligands and the resonant emissive energy level of  $RE^{3+}$  in the inverse energy transfer process, so as energy difference decreases the energy inverse transfer ratio will increases, then the luminescence intensity decreases.

The second ligands TPPO and Bipy, of which the energy level of the triplet state are lower than that of *N*-HPA but higher than the  ${}^{5}D_{4}$  energy level of Tb<sup>3+</sup> ion, work as an energy transfer bridge helping decrease the overlap integral between the Tb<sup>3+</sup> ion and ligands. As a consequence, the energy transfer efficiency increases.

In addition, the water molecules act as effective luminescence quencher due to O–H oscillators. The second ligands can prevent  $Tb^{3+}$  ion from coordinating water around. This shielding effect can reduce considerably radiationless processes [7]. Thus, the luminescence intensity of  $Tb(N-PA)_3(TPPO)_2$ and  $Tb(N-PA)_3Bipy$  is much stronger than  $Tb(N-PA)_3(H_2O)_2$ . Since the energy level of the triplet state of TPPO matches the  ${}^5D_4$  energy level of  $Tb^{3+}$  ion better than Bipy, the luminescence intensity of  $Tb(N-PA)_3(TPPO)_2$  is stronger than  $Tb(N-PA)_3Bipy$ .

However, the second ligand Phen quenched the luminescence of the complex. On one hand, the energy level of the triplet state of Phen  $(22,100 \text{ cm}^{-1})$  is lower than that of Bipy and TPPO [12], and it is too near to the energy level of  ${}^{5}D_{4}(20,400 \text{ cm}^{-1})$  of Tb<sup>3+</sup> ion, which will make the inverse energy transfer  ${}^{5}D_{4} \rightarrow T_{1}$ happen easily. Thus, most of the excitation energy of itself and the energy transferred from the ligand N-HPA is consumed by this to-and-fro energy transfer pattern, which leads to the poor photoluminescence property of the complex Tb(N-PA)<sub>3</sub>Phen. On the other hand, the coordination of N-phenylanthranilic acid with Tb<sup>3+</sup> ion makes the space around very narrow, so Phen with a large conjugate  $\pi$ -bond system may change the distribution of  $\pi$ -electronic density in the complexes even leads to the change of bond strength and distances of "RE-ligand". Thus Phen will destabilize the conjugate system between the *N*-phenylanthranilic acid and  $Tb^{3+}$  ion, which has been confirmed by the result of the UV spectra, thus it will weaken the energy transfer efficiency between N-phenylanthranilic acid and Tb<sup>3+</sup> ion. Hence, Phen quenches the luminescence intensity of the complexes of Tb(III) with N-phenylanthranilic acid and results in the poor luminescence property of the complex Tb(N-PA)<sub>3</sub>Phen.

## 4. Conclusion

A series of Tb<sup>3+</sup> *N*-phenylanthranilic acid complexes were synthesized. It showed that the complexes all emitted ligand-sensitized green emission, and the intensity of the complexes followed the decreasing sequence of Tb(*N*-PA)<sub>3</sub>(TPPO)<sub>2</sub>, Tb(*N*-PA)<sub>3</sub>Bipy, Tb(*N*-PA)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, Tb(*N*-PA)<sub>3</sub>Phen. The introduction of TPPO enhanced the luminescence intensity of the complex while the introduction of Phen weakened it, which was due to the energy level and structure of the second ligands.

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