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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 $Tb(N\text{-}PA)_3Phen < Tb(N\text{-}PA)_3(H_2O)_2 < Tb(N\text{-}PA)_3Bipy < Tb(N\text{-}PA)_3(TPPO)_2$. The second ligands TPPO and Bipy enhanced the luminescence intensity of the complexes while the Phen quenched it.

Keywords: Tb^{3+}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^{3+} 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 ligand-to-metal ions energy transfer efficiency, and the energy levels of the aromatic carboxylic acids match the $^5D_4$ energy level of Tb^{3+} 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) 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, $Tb(N\text{-}PA)_3(H_2O)_2$ 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_4O_7 (99.99%), *N*-phenylanthranilic acid (*N*-HPA), 1,10-phenanthroline (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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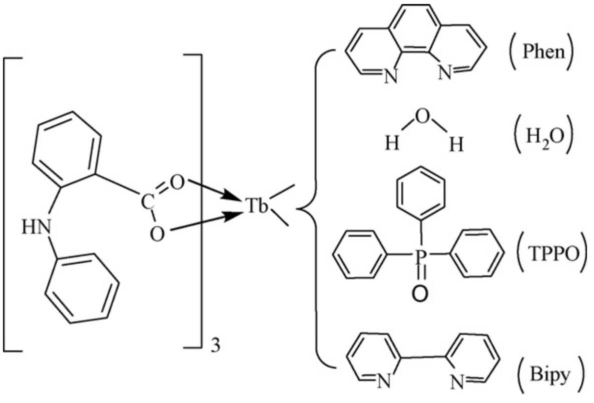

Fig. 1. The structures of Tb(*N*-PA)$_3$Phen, Tb(*N*-PA)$_3$(H_2O)$_2$, Tb(*N*-PA)$_3$ (TPPO)$_2$ and Tb(*N*-PA)$_3$Bipy.

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 among 200–400 nm. The excitation and emission spectra (5×10^{-5} 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 $TbCl_3 \cdot 6H_2O$, *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 gives the characteristic bands of the ligands and the complexes. The infrared spectra for the ligand *N*-HPA and the Tb^{3+} complexes are shown in Fig. 2. It is obviously that the spectra of the Tb^{3+} complexes are similar. The characteristic absorption bands for *N*-HPA at 1661 cm^{-1}($\upsilon_{C=O}$) and 3200–2500 cm^{-1} (υ_{-OH}) disappeared in the Tb^{3+} complexes. The presence of carboxylate groups in the various complexes was definitely confirmed by both the asymmetric stretching bands (υ_{asCOO-}) at about 1550 cm^{-1} and the symmetric stretching (υ_{sCOO-}) at about 1400 cm^{-1}.

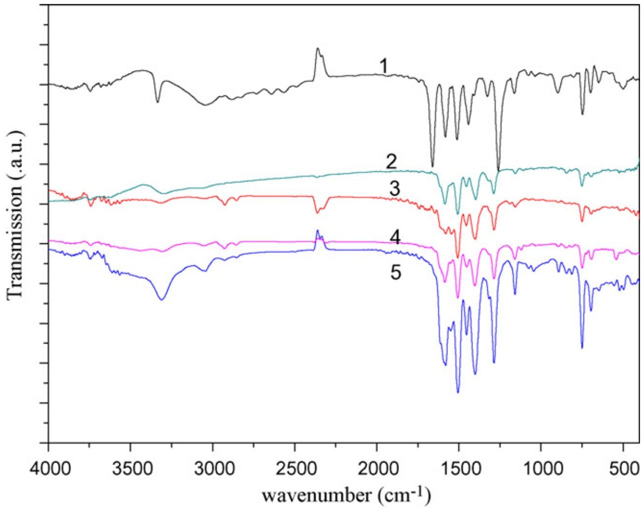

Fig. 2. IR absorption spectra of the Tb(III) complexes and the first ligand: 1, *N*-HPA; 2, Tb(*N*-PA)$_3$Phen; 3, Tb(*N*-PA)$_3$Bipy; 4, Tb(*N*-PA)$_3$(TPPO)$_2$; 5, Tb(*N*-PA)$_3$(H_2O)$_2$.

Table 1 also shows the shift of twisting bending vibrations (δ_{C-H}) of Bipy from 754 cm^{-1} to approximately 749 cm^{-1} for Tb(*N*-PA)$_3$Bipy, which indicated the coordination between Bipy and Tb^{3+}. The twisting bending vibrations (δ_{C-H}) of Phen also shifted from 737 cm^{-1} to 724 cm^{-1} compared to Tb(*N*-PA)$_3$Phen, which suggested Phen was coordinated with Tb^{3+}. The displacement of $\upsilon_{P=O}$ stretching from 1187 cm^{-1}, in free TPPO ligand, to approximately 1159 cm^{-1} 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^{-1} for Tb(*N*-PA)$_3$(H_2O)$_2$ originated from the presence of the O–H stretching vibrations of H_2O 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

Table 1
Attribution of IR main peaks of the ligands and Tb(III) complexes (cm^{-1})

	N-HPA	Tb(*N*-PA)$_3$(H_2O)$_2$	Tb(*N*-PA)$_3$ Bipy	Tb(*N*-PA)$_3$Phen	Tb(*N*-PA)$_3$(TPPO)$_2$	Bipy	Phen	TPPO
$\upsilon_{C=O}$	1661	–	–	–	–	–	–	–
$\upsilon_{-OH(m)}$	3200–2500	–	–	–	–	–	–	–
υ_{asCOO-}	–	1547	1551	1552	1550	–	–	–
υ_{sCOO-}	–	1401	1400	1398	1402	–	–	–
δ_{C-H}	–	–	749	843	–	754	851	–
	–	–	–	724	–	–	737	–
$\upsilon_{P=O}$	–	–	–	–	1159	–	–	1187