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Study of the effect of ligands on the fluorescence properties of terbium ternary complexes

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Abstract

Four ternary complexes of Tb(III) were synthesized by introducing the first ligand (L_1) (*N*-phenylanthranilic acid (N-HPA), α-furoic acid (FURA)) and the second ligand (L_2) (1,10-phenanthroline (Phen), 2,2′-dipyridyl (Bipy)), respectively. These complexes were characterized by elemental analysis, infrared spectra, XRD, UV spectra and fluorescence spectra. The effect of L_1 and L_2 on the fluorescence properties of terbium complexes was discussed. It showed that all the complexes exhibited ligand-sensitized green emission. The fluorescent intensity increased in the sequence of $Tb(FURA)_3Bipy < Tb(N\text{-}PA)_3Phen < Tb(FURA)_3Phen < Tb(N\text{-}PA)_3Bipy$. It indicated that L_1 affected fluorescence properties of the complexes differently when the corresponding L_2 altered. Meanwhile, the influence of L_2 on the luminescence properties of the complexes also depends on L_1. The results showed that L_1 and L_2 affected each other and worked together as a whole. The matching of L_1, L_2 and Tb^{3+} ion is very important to the luminescence properties of Tb(III) ternary complexes.

Keywords: Tb^{3+} complexes; *N*-Phenylanthranilic acid; α-Furoic acid; Ligand; Fluorescence

1. Introduction

Recently, considerable of studies have been focused on the design and assembly of fluorescent rare-earth complexes [1–4], which have application in luminescent probe, electroluminescent devices [5] and polymer fiber laser [6]. The ligands are usually called “antennas” absorb and transfer energy to the rare-earth ions and consequently increase their luminescence intensity [7].

Tb^{3+} ion, the complexes of which emit green light, is one of the rare-earth ions that show the best luminescence property. The aromatic carboxylic acids whose energy levels match the $^5D_4$ energy level of Tb^{3+} better have attracted intense research interest [1,2,4]. Moreover, introducing a second kind of organic ligand such as 1,10-phenanthroline (Phen) or 2,2′-dipyridyl (Bipy) can improve the luminescence properties of Tb^{3+} complexes [8,9]. In order to improve the luminescence properties of rare-earth complexes, the choosing of ligands is very important. Though much work has been done, the effect the ligands on the luminescence properties of rare-earth complexes still needs to be further studied. What’s more, interaction between the first ligand (L_1) and second ligand (L_2) were always omitted when choosing the ligands.

N-Phenylanthranilic acid (N-HPA) [9] and α-furoic acid (FURA) [10,11] are two carboxylic acids of which the rare-earth complexes exhibit good luminescence properties.

In this work, four ternary complexes of terbium with L_1 (*N*-phenylanthranilic acid, α-furoic acid) and L_2 (Phen, Bipy) were synthesized. The spectra property of the complexes was studied. The effect of the ligands on the fluorescence properties of terbium complexes was studied. The results indicated that the impact between L_1 and L_2 should not be omitted.

2. Experiments

2.1. Reagents and apparatus

Tb_4O_7 (99.99%), *N*-phenylanthranilic acid, α-furoic acid, 1,10-phenanthroline, 2,2′-dipyridyl and other chemicals were analytical reagent grade and used without further purification.

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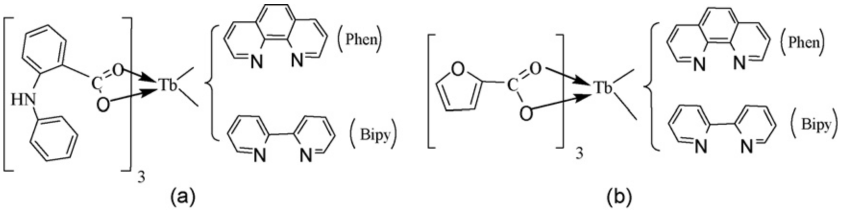

Fig. 1. The structures of the complexes. (a) Tb(N-PA)$_3$Phen and Tb(N-PA)$_3$Bipy; (b) Tb(FURA)$_3$Phen and Tb(FURA)$_3$Bipy.

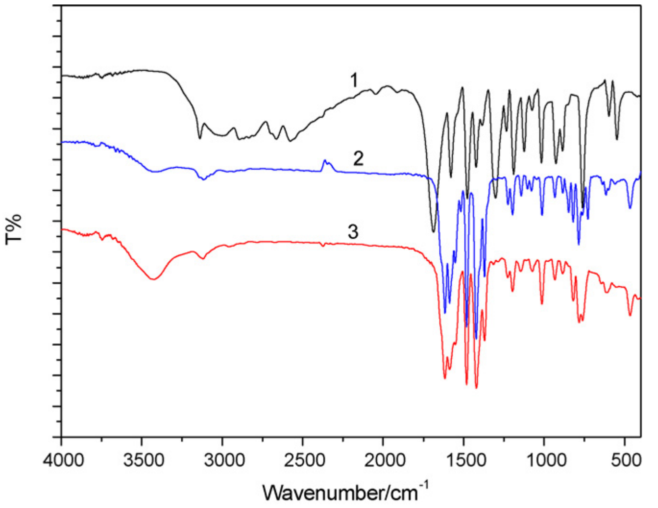

Fig. 2. IR absorption spectra of the Tb(III) complexes and the first ligand. (1) FURA; (2) Tb(FURA)$_3$Phen; (3) Tb(FURA)$_3$Bipy.

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

Elemental analyses were carried out by the PerkinElmer 240C analytical instrument. Infrared spectra were recorded in the range of 4000–400 cm^{-1} by a prostige-21IR spectrophotometer in KBr flake. X-ray diffraction (XRD) analysis were carried out using a D/MAX 2500VB2+/PC, Cu Kα radiation ($\lambda = 1.54056$ Å, $V = 40$ kV, $I = 200.0$ Ma and $\lambda = 1.54056$ Å) at 40 kV and 200 mA, scanning angle (2θ) from 3° to 40° with step scan of 0.04° every second. 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 Tb(III) complexes were synthesized by mixing the $TbCl_3 \cdot 6H_2O$, L_1 (N-HPA or FURA) and L_2 (Phen or Bipy) in ratio 1:3:1 in ethanol under stirring, with the pH of the solution adjusted to 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 structures of the complexes are shown in Fig. 1.

Table 1
Elemental analysis of the complexes

Complexes	Analytically found (calculated) (%)		
	C	H	N
Tb(FURA)$_3$Bipy	45.96 (46.32)	2.76 (2.64)	4.22 (4.32)
Tb(FURA)$_3$Phen	47.89 (48.23)	2.71 (2.55)	4.02 (4.17)
Tb(N-PA)$_3$Phen	62.47 (62.77)	4.24 (3.93)	6.79 (7.18)
Tb(N-PA)$_3$Bipy	62.05 (61.83)	4.19 (4.02)	7.50 (7.36)

3. Results and discussion

3.1. *Compositions of the complexes*

The compositions of the complexes were confirmed by elemental analysis. The results are listed in Table 1. The results of the elemental analysis are close to the calculated values.

3.2. *IR spectra analysis*

Table 2 gives the characteristic bands of the ligands and the complexes. The infrared spectra for the ligand N-HPA and the Tb^{3+} complexes can be seen in paper [9]. The spectra for the ligand FURA and the corresponding Tb^{3+} complexes are shown in Fig. 2. It is obviously that the spectra of the Tb^{3+} complexes with the same L_1 are similar. The characteristic absorption bands for FURA 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

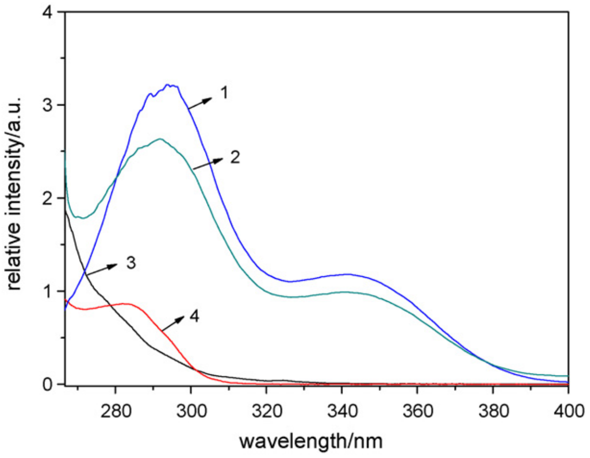

Fig. 3. The UV absorption spectra of the Tb(III) complexes. (1) Tb(N-PA)$_3$Bipy; (2)Tb(N-PA)$_3$Phen; (3) Tb(FURA)$_3$Phen; (4) Tb(FURA)$_3$Bipy.

Table 2
Attribution of IR main peaks of the ligands and Tb(III) complexes (cm^{-1})

	N-HPA	$Tb(N\text{-}PA)_3Bipy$	$Tb(N\text{-}PA)_3Phen$	FURA	$Tb(FURA)_3Bipy$	$Tb(FURA)_3Phen$	Phen	Bipy
$\upsilon_{C=O}$	1661			1683				
$\upsilon_{\text{–OH(m)}}$	3200–2500			3200–2500				
υ_{asCOO-}		1551	1552		1585	1589		
υ_{sCOO-}		1400	1398		1419	1424		
$\delta_{C\text{–}H}$		749	843		738	847	851	754
			724			723	737	

by both the asymmetric stretching bands (υ_{asCOO-}) at about 1585 cm^{-1} and the symmetric stretching (υ_{sCOO-}) at about 1420 cm^{-1}.

Table 2 also shows the shift of twisting bending vibrations ($\delta_{C\text{–}H}$) of Bipy from 754 cm^{-1} to approximately 738 cm^{-1} for $Tb(FURA)_3Bipy$, which indicates the coordination between Bipy and Tb^{3+}. The twisting bending vibrations ($\delta_{C\text{–}H}$) of Phen also shift from 737 cm^{-1} to 723 cm^{-1} comparing $Tb(FURA)_3Phen$ with free Phen, which suggests Phen have been coordinated with Tb^{3+}.

3.3. UV absorption spectra analysis

UV absorption spectra of the complexes in DMF solution (5×10^{-5} mol/L) are shown in Fig. 3. They all exhibit domain absorption peaks in the ultraviolet region (200–400 nm). The results show that UV spectra of the Tb(III) complexes with the same L_1 are similar, that is, the spectra of $Tb(FURA)_3Phen$ are similar to that of $Tb(FURA)_3Bipy$, and the complexes of N-HPA are also similar to each other. It implies that most of the energy absorbed comes from L_1 [9].

Furthermore, comparing with the absorption of the complex with Bipy, the absorption of complex with Phen (with the same L_1) is stronger in the far UV region (<280 nm) but weaker in the near UV region (>280 nm). It implies that the L_2 also works as energy absorber and impacts the absorption of the complexes.

The results also show that comparing with the complexes of FURA, the complexes of N-HPA exhibit a wider absorption region and with stronger intensity, which implies that *N*-phenylanthranilic acid absorbs more energy than furoic acid as most of the energy is absorbed by L_1.

3.4. XRD analysis

The XRD patterns of the complexes are shown in Fig. 4. It can be seen that the patterns of the four complexes are different from each other. The main peaks of the complexes all show up between 3° and 30° (2θ). The XRD patterns of the $Tb(FURA)_3Phen$ and $Tb(FURA)_3Bipy$ show that they are crystal, while the patterns of the complexes with N-HPA show that they are amorphous. It implies that L_1 mainly determines the crystal style of the complexes while L_2 also has some impact on it.

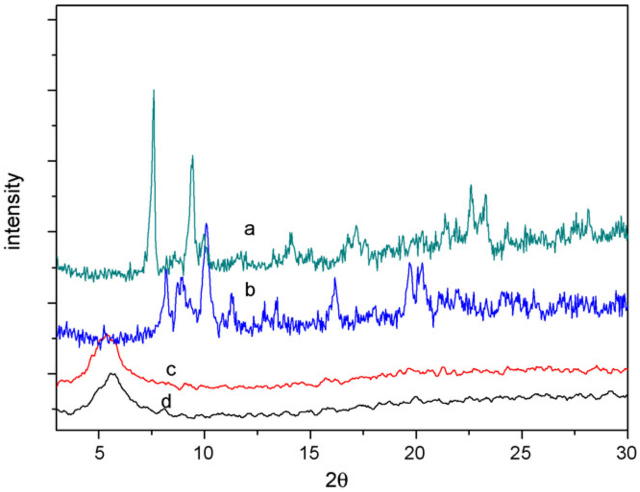

Fig. 4. XRD pattern. (a) $Tb(FURA)_3Phen$; (b) $Tb(FURA)_3Bipy$; (c) $Tb(N\text{-}PA)_3Phen$; (d) $Tb(N\text{-}PA)_3Bipy$.

3.5. Luminescent properties of the complexes

The excitation spectra for the complexes were recorded under the same condition by monitoring the Tb^{3+} luminescence at 545 nm in the range of 200–450 nm. The emission spectra were recorded in the range of 400–700 nm by monitoring the maximum excitation wavelength. Relative intensity of fluorescence of Tb(III) complexes are listed in Table 3. The results show that they all emit the typical sharp emission bands corresponding to the transitions of the Tb^{3+} ion $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$,

Table 3
Relative fluorescence intensity of the complexes

Complexes	λ_{ex} (nm)	λ_{em} (nm) (relative intensity)			
		$^5D_4 \rightarrow {}^7F_6$	$^5D_4 \rightarrow {}^7F_5$	$^5D_4 \rightarrow {}^7F_4$	$^5D_4 \rightarrow {}^7F_3$
$Tb(N\text{-}PA)_3Bipy$	365	489 (133.036)	544 (358.338)	584 (20.693)	621 (8.020)
$Tb(FURA)_3Phen$	292	489 (92.816)	545 (199.506)	585 (29.896)	621 (6.520)
$Tb(N\text{-}PA)_3Phen$	359	489 (76.718)	544 (197.961)	584 (11.999)	621 (4.834)
$Tb(FURA)_3Bipy$	270	489 (38.760)	544 (102.665)	583 (7.283)	621 (3.504)

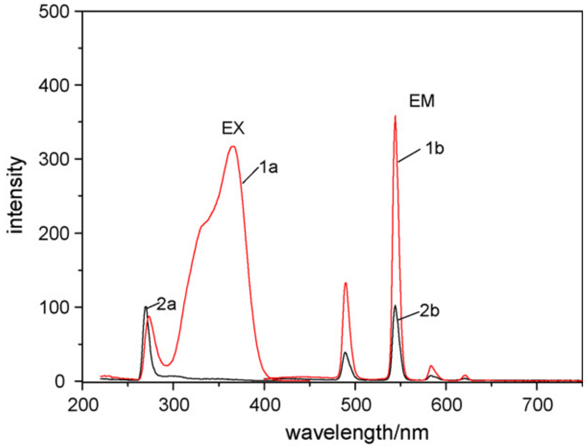

Fig. 5. The excitation spectra of Tb(III) complexes (EX) (1a, $Tb(N\text{-}PA)_3Bipy$; 2a, $Tb(FURA)_3Bipy$) and emission spectra (EM) (1b, $Tb(N\text{-}PA)_3$ Bipy; 2b, $Tb(FURA)_3Bipy$).

respectively. The intensity of the emission at $^5D_4 \rightarrow {}^7F_5$ increases in the sequence of $Tb(FURA)_3Bipy < Tb(N\text{-}PA)_3Phen < Tb(FURA)_3Phen < Tb(N\text{-}PA)_3Bipy$.

The intensity integration proportion of emission peaks for the four complexes are shown in Table 4. Note that data of all the complexes are similar, except for that of the complex $Tb(FURA)_3Phen$.

3.5.1. *The influence of L_1 on fluorescence properties of the complexes*

The luminescence spectra of the complexes with L_2 Bipy are shown in Fig. 5. It is obvious that comparing with $Tb(FURA)_3Bipy$, the emission intensity of $Tb(N\text{-}PA)_3Bipy$ is much stronger, which is ascribed to the change of L_1. The luminescence spectra of the complexes with L_2 Phen are shown in Fig. 6. In comparison with $Tb(N\text{-}PA)_3Phen$, the emission intensity of $Tb(FURA)_3Phen$ is a little stronger, above all, the intensity integration proportion of emission peaks of the complex $Tb(FURA)_3Phen$ are alternated, which can be seen from Table 3.

3.5.2. *The influence of L_2 on the fluorescence properties of complexes*

The luminescence spectra of the complexes with L_1 FURA are shown in Fig. 7. It is obvious that comparing with $Tb(FURA)_3Phen$, the emission intensity of $Tb(FURA)_3Bipy$ is much weaker, that is, the substitution of L_2 Phen with Bipy weakens the luminescence. The luminescence spectra of the complexes with L_1 N-HPA are shown in Fig. 8. It can be seen that the substitution of L_2 Phen with Bipy enhances the luminescence of the complex with N-HPA, which is reverse to the result of the complexes with FURA.

Table 4
Intensity integration proportion of emission peaks for the four complexes

Complexes	Transitions (%)			
	$^5D_4 \rightarrow {}^7F_6$	$^5D_4 \rightarrow {}^7F_5$	$^5D_4 \rightarrow {}^7F_4$	$^5D_4 \rightarrow {}^7F_3$
$Tb(N\text{-}PA)_3Bipy$	25.6	68.9	4.0	1.5
$Tb(FURA)_3Bipy$	25.5	67.4	4.8	2.3
$Tb(FURA)_3Phen$	28.2	60.7	9.1	2.0
$Tb(N\text{-}PA)_3Phen$	26.3	67.9	4.1	1.7

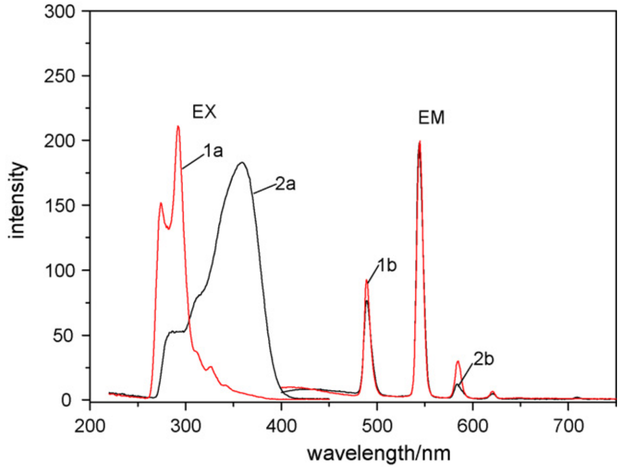

Fig. 6. The excitation spectra of Tb(III) complexes (EX) (1a, $Tb(N\text{-}PA)_3Phen$; 2a, $Tb(FURA)_3Phen$) and emission spectra (EM) (1b, $Tb(N\text{-}PA)_3Phen$; 2b, $Tb(FURA)_3Phen$).

The results show that the influence of L_2 on the luminescence properties is affected by L_1. Sometimes, L_2 even has the opposite effect when L_1 alternates.

3.5.3. *The discussion of the influence of the ligands on the complexes*

The results show that both L_1 and L_2 absorb and transfer energy to Tb^{3+}. And the luminescence properties of terbium complexes are influenced by the interaction between the ligands. It indicates that luminescence properties of the complexes depend on the co-effect of L_1 and L_2.

The intramolecular energy transfer efficiency from organic ligands to RE^{3+} is the most important factor which influencing the luminescence properties of rare-earth complexes [12]. According to the intramolecular energy mechanism [13,14], the

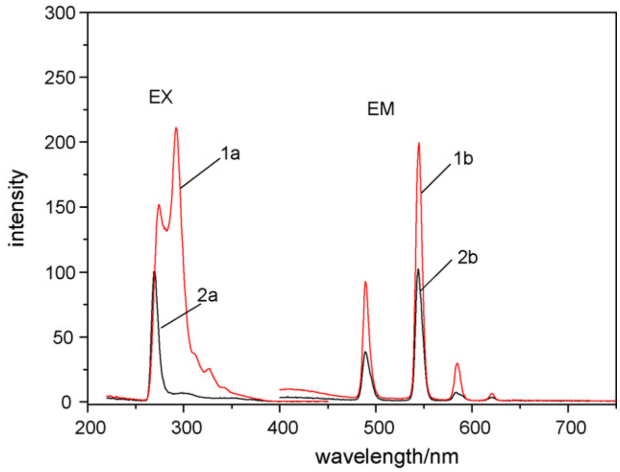

Fig. 7. The excitation spectra (EX) (1a, $Tb(FURA)_3Phen$; 2a, $Tb(FURA)_3Bipy$) and emission spectra (EM) (1b, $Tb(FURA)_3Phen$; 2b, $Tb(FURA)_3Bipy$).

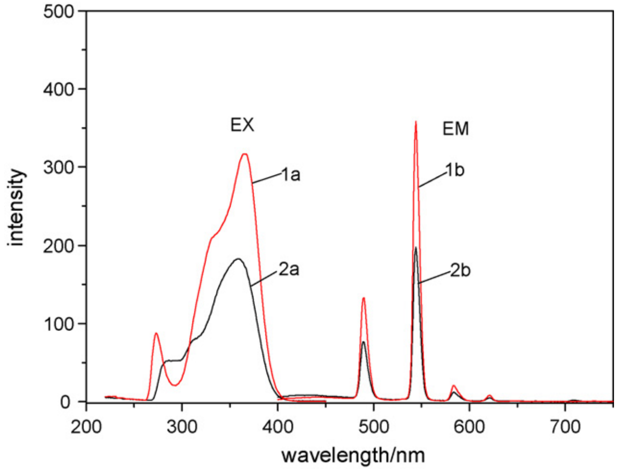

Fig. 8. The excitation spectra (EX) (1a, Tb(N-PA)$_3$Bipy; 2a, Tb(N-PA)$_3$Phen) and emission spectra (EM) (1b, Tb(N-PA)$_3$Bipy; 2b, Tb(N-PA)$_3$Phen).

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+} 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 RE^{3+}.

The L$_2$ Bipy and Phen, of which the energy level of the triplet state are lower than that of N-HPA and FURA but higher than the $^5D_4$ energy level of Tb^{3+}, can work as an energy transfer bridge helping the energy transfer efficiently from the ligands to Tb^{3+} ion. However, the L$_2$ Phen quenched the luminescence of the complex Tb(N-PA)$_3$Phen but enhanced the luminescence of the complex Tb(FURA)$_3$Phen, comparing with the corresponding complexes of Bipy, respectively. The mechanism can be explained on two sides as followed.

On the one hand, it is due to the different energy level of L$_2$. The energy level of the triplet state of Phen (22,100 cm^{-1}) is lower than that of Bipy (22,913 cm^{-1}), and it is too near the energy level of $^5D_4$ (20,400 cm^{-1}) of Tb^{3+}, which will make the inverse energy transfer $^5D_4 \rightarrow T_1$ happen easily [9]. Thus, most of the excitation energy of itself and the energy transferred from L$_1$ N-HPA is consumed by this to-and-fro energy transfer pattern. Considering the energy level of L$_2$, it is obviously that Bipy fits Tb^{3+} better, which will make the energy transfer more efficiency.

On the other hand, it can be ascribed to steric hindrance effect. Phen has a large conjugate π-bond system, while Bipy has a smaller conjugate system and can twisting one of its rings with its middle bond. Under the steric hindrance, Phen with a large conjugate π-bond system may change the distribution of π-electronic density in the complexes and even leads to the change of bond strength and distances of "RE-ligand". While without the steric hindrance effect, the interaction between the Phen and Tb^{3+} will increase the π-electronic density and thus enhance the energy transfer efficiency. However, Bipy with a smaller system contributes less to the enhancement of the conjugate system, and the twisting of the middle bond will consume much of energy absorbed, which will weaken the transfer efficiency. While under steric hindrance effect, the twisting of the Bipy will be limited and the energy will be saved and efficiently transferred to the Tb^{3+}. Because N-HPA has a big conjugate system, the coordination of *N*-phenylanthranilic acid with Tb^{3+} will create steric hindrance effect. As a consequence, it increases the energy transfer efficiency between Bipy and Tb^{3+} but weaken the energy transfer efficiency between Phen and Tb^{3+}.

To the complex Tb(N-PA)$_3$Phen, both of the fact of the steric hindrance and the fact of energy level decrease the energy transfer efficiency, which results in the poor luminescence properties of the complex [9]. To the complex Tb(FURA)$_3$Bipy, with the disappearance of the steric hindrance, Bipy with a smaller system contributes less to the enhancement of the conjugate system, and the twisting of the middle bond will consume much of energy absorbed, and at this time the fact of energy level is less important, so the energy transfer efficiency decreased and leads to the weakest luminescence intensity. To the complex Tb(FURA)$_3$Phen, as the steric hindrance disappears, large conjugate π-bond system of Phen will increase energy transfer efficiency, but the fact of the energy level decreases it, hence, Tb(FURA)$_3$Phen exhibits strong fluorescence intensity. To the complex Tb(N-PA)$_3$Bipy, the fact of steric hindrance effect and the fact of the energy transfer both increase the energy transfer efficiency between the ligands and the Tb^{3+}, as a consequence, the fluorescence intensity of Tb(N-PA)$_3$Bipy is the strongest.

UV absorption ability of the N-HPA is much better than that of FURA, as a result, the luminescence intensity of the complexes of N-HPA is stronger than that of the complexes of FURA in total.

The big change of the intensity integration proportion of emission peaks of the complex Tb(FURA)$_3$Phen is due to special environment which changes the coordination field when FURA and Phen both exist, and the mechanism needs to be further studied.

4. Conclusion

Four ternary complexes of Tb(III) were synthesized by introducing *N*-phenylanthranilic acid and furoic acid (α-FURA) as the first ligand, and 1,10-phenanthroline, 2,2′-dipyridyl as the second ligand, respectively.

1. The complexes with same L$_1$ had similar structure.
2. L$_1$ mainly influenced the absorption intensity and absorption region, and L$_2$ had some effect on the absorption. UV absorption of the complexes was a result of the co-effect of L$_1$ and L$_2$.
3. The complexes of α-furoic acid were crystal but the complexes of *N*-phenylanthranilic acid were amorphous.
4. The complexes exhibited ligand-sensitized green emission, and the intensity of the complexes increased in the sequence of Tb(FURA)$_3$Bipy < Tb(N-PA)$_3$Phen < Tb(FURA)$_3$Phen < Tb(N-PA)$_3$Bipy. The luminescence property of the complexes was a result of the co-effect of L$_1$ and the L$_2$.

In all, the impact between L_1 and L_2 should not be omitted. And the matching of L_1, L_2 and the rare-earth ion is very important to the design of rare-earth complex with good luminescence property.

Acknowledgments

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