

Synthesis Characterization and Fluorescence Property of Terbium(III) Complexes with N-phenylanthranilic Acid

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Abstract: Two binary and ternary complexes of Terbium with N-HPA and Bipy (N-HPA: N-phenylanthranilic acid, Bipy: 2,2'-bipyridine) were synthesized, and its structure was characterised by elemental analysis, UV and IR spectra. The effect of the second ligand on the fluorescence property of the complex was studied. The result proved that the fluorescence intensity of the binary terbium N-HPA complex was rather weak, but the addition of the second ligand Bipy could effectively increase luminescence intensity of terbium ions. The ternary complex of Tb(NPA)₃ (Bipy) (NPA: radical of N-HPA by removal of one H atom) has good fluorescence property. Tb(NPA)₃ (Bipy)₂ is a promising fluorescent material, which widely used in optoelectronics engineering and technology.

1. Introduction

Some of rare earth organic complexes especially composed by Eu³⁺ or Tb³⁺ ions with organic ligands such as β -diketones, carboxylic acids, organic supramolecular macrocycles are of promising luminescent materials[1-2]. These complexes are widely applied in luminescent materials[3,4], fluorescent probe detection[5,6], molecular imaging[7,8], displays[9,10], anti-counterfeit materials [11,12], bioscience[13-14] and other fields. Luminescent material, as we well know, the main component of light display material, is of supporting material in the field of optoelectronics engineering and technology. The optoelectronics engineering and technology plays an more and more important role in current information society. Therefore, it is of practical significance to synthesize highly efficient luminescent material and to study its luminescence mechanism. Since 1942 the luminescence of rare earth organic complex has been discovered by weissman[15], much research on them has been done[16,17]. One of the research directions is to study the effect of organic ligand on luminescence of the complex. Among many organic ligands, carboxylic acid, as mentioned above, has been widely focused on its chemical modification of substituent, and synergy with other ligands. Among carboxylic acid ligands, ligand N-phenylanthranilic acid has been widely studied. According to luminescent mechanism of rare earth organic complex, both ligand structure and energy level matching degree between ligand and rare earth ion are major factors influencing luminescence of the complex, moreover appropriate second ligand can significantly influence the complex luminescence. With the second ligand 2,2'-bipyridine adding, the binary and ternary complexes of Tb-N-phenylanthranilic acid and Tb-N-phenylanthranilic acid and 2,2'-bipyridine were synthesized. Their luminescence properties were studied and compared, which provided some references for the



further study of sensitized luminescence of Terbium N-phenylanthranilic acid complex with second ligand.

2. Experiment

2.1 Instruments and reagents

PE-2400 element analyzer (US PE company); Magna750 Fourier Transform Infrared Spectrometer(KBr tableting, Nicolet, USA); 970CRT Fluorescence Spectrometer(Shanghai analytical instruments factory); UV-757 UV-Vis Spectrophotometer (SHIMADZU Shimadzu, Japan).

Determination of Terbium ion content by EDTA titration with xylenol orange as indicator.

Tb₄O₇(99.9%, China pharmaceutical group Shanghai chemical reagent Co. Ltd.), N-phenylanthranilic acid and triphenylphosphine oxide with analytical purity.

2.2 Preparation of TbCl₃ 6H₂O

First Tb₄O₇ was completely dissolved in proper amount of concentrated hydrochloric acid changing into TbCl₃, second after evaporating excess hydrochloric acid in heating and stirring conditions, adding water, slowly evaporating some water until appropriate amount of solution left, the solution was cooled down, crystallized, filtered and dried, then the hydrated rare earth chloride TbCl₃ 6H₂O was obtained.

2.3 Synthesis of complex

First amount of TbCl₃ 6H₂O and N-phenylanthranilic acid(Mole ratio 1: 3) was dissolved in ethanol respectively, then mixed together. Second the solution pH was adjusted to 6-7 with ammonia water, after stirring for 4-5 hours under heating and refluxing, standing for some time, and some solid powder was obtained. Third after the powder was washed with water and ethanol 3 times respectively, and dried. Finally the white powder precipitation of binary Terbium-N-phenylanthranilic acid complex was obtained. So as to the ternary Terbium-N-phenylanthranilic acid-2,2'-bipyridine (Mole ratio 1:3:1).

3. Results and Discussions

3.1 Structural characterization of the complex

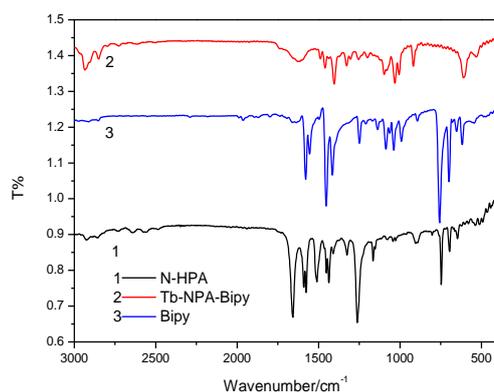
The infrared spectra of the complex Tb(NPA)₃ (Bipy) and ligands were shown in Fig.1. The main IR absorption data of ligands and complex was shown in table 1. After formation of the complex, the characteristic peaks of $\nu_{C=O}$ (1659cm⁻¹) of the original free ligand N-HPA disappear while symmetric stretching vibration of carboxyl $\nu_{as}(COO^-)$ at 1402cm⁻¹ and antisymmetric stretching vibration at peak of carboxyl $\nu_{as}(COO^-)$ at 1633cm⁻¹ appear. Furthermore the stretching vibration (3335cm⁻¹) of N-H from N-HPA presence both in ligand and complex, which indicates that the N atom from amino group does not bond with Tb³⁺. The characteristic absorption peak of δ_{C-H} bond from ligand BIPY moves from 756 cm⁻¹ to 614 cm⁻¹, meanwhile the telescopic vibration absorption peak of Tb-O appears near 540cm⁻¹. The infrared data show that O atom from COO⁻¹ of N-phenylanthranilic acid form coordination bond with Tb³⁺. The element analysis result is showed in Table 2. According elemental analysis, composition of the ternary complex is Tb(NPA)₃(BIPY), composition of the binary complex is Tb(NPA)₃ H₂O. Solubility test showed that Tb(NPA)₃(BIPY) is soluble in chloroform, DMSO and DMF, while insoluble in water, ethanol, ether, cyclohexane, ethyl acetate, methanol and acetone.

Table 1. The main IR spectra date of ligands and complex

| Vibration frequency | ν_{O-H} | $\nu_{C=O}$ | ν_{sCOO-} | ν_{asCOO-} | δ_{C-H} | ν_{Tb-O} |
|-----------------------------|-------------|-------------|---------------|----------------|----------------|--------------|
| N-HPA | 2500-2800 | 1659 | | | | |
| BIPY | | | | | 756 | |
| Tb(NPA) ₃ (BIPY) | - | - | 1402 | 1633 | 614 | 540 |

Table 2. The element analysis result of the complex

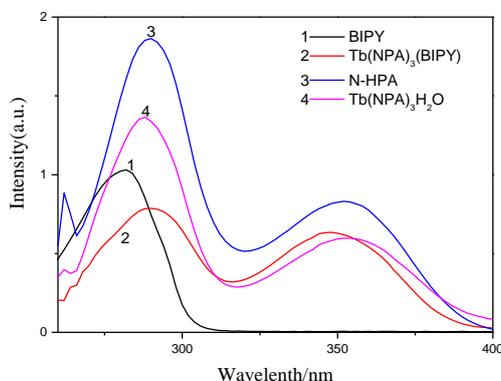
| complex | Elemental Analysis (measured/theoretical) | | | |
|---------------------------------------|---|------------|------------|--------------|
| | C% | H% | N% | Tb% |
| Tb(NPA) ₃ (BIPY) | 61.75(62.03) | 3.11(3.69) | 6.79(7.42) | 16.38(16.75) |
| Tb(NPA) ₃ H ₂ O | 57.29(57.57) | 3.83(3.96) | 5.35(5.16) | 19.37(19.53) |

**Figure.1** Infrared spectra of the complex Tb(NPA)₃ (BIPY) and ligands

3.2 UV spectra of complex

The ligand and the complex were dissolved in chloroform respectively, and the UV absorption spectra were measured in range of 200-400nm.

As shown in figure 2, both the two complexes and the ligand have strong UV absorption, while the shape of the absorption peak of the complex is similar to that of the free ligand N-HPA, the relative intensity of the absorption peaks changes, and the peaks position move slightly. The absorption peaks of the ternary complex are at 288nm and 347nm, the absorption peaks of the binary complex are at 285nm and 353nm while the absorption peaks of ligand N-HPA are at 291nm and 350nm respectively. The energy absorption of the complex in ultraviolet region mainly comes from absorption of ligand N-HPA.

**Figure.2** UV spectra of ligands and complexes

3.3 Fluorescence spectra of complex

As shown in Fig. 3, The maximum excitation wavelength of terbium binary and ternary complex is 358nm and 370nm respectively, using 545nm as monitoring wavelength. The corresponding emission spectra is obtained excited by the maximum excitation wavelength of 358nm and 370nm respectively. As shown in Fig. 4, both complexes have four emission peaks at 490nm, 546nm, 591nm and 619nm with different intensity, which are characteristic emission peaks of Tb^{3+} and attribute to $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$ transitions. Among them, the 545nm green fluorescence emission from transition $^5D_4 \rightarrow ^7F_5$ of Tb^{3+} is the strongest. Obviously stronger is the ternary complex emission intensity than the binary. Furthermore at 546nm the ternary complex emits nearly four times stronger luminescence with narrower peak width than the binary complex, which shows that the second ligand BIPY can greatly enhance fluorescence intensity and significantly improve the fluorescence property of Terbium-N-phenylanthranilic acid complex.

According to the principle of energy transfer[16,17], there exists optimum energy matching between triplet energy level of organic ligand and the lowest excited state energy level of rare earth ion. But the energy gap between triplet energy level (24330 cm^{-1}) of the first ligand of N-HPA[18] and the lowest excited state energy level of Tb^{3+} is rather large, so the energy transfer efficiency between them is not high, moreover the degree of conjugation of ligand N-HPA in Tb-NPA is poor because of steric hindrance of N atom, thus the binary complex has rather weak fluorescence. Meanwhile the lowest triplet energy level 22940 cm^{-1} of the second ligand BIPY [19], matches well with energy level 20454 cm^{-1} of 5D_4 of Tb^{3+} , so the good energy match effectively improves energy transfer efficiency from BIPY to Tb^{3+} and significantly increases the fluorescence intensity of the ternary complex of $Tb(NPA)_3(BIPY)$. As a result the synthesized rare earth complex $Tb(NPA)_3(BIPY)$ with BIPY as the second ligand has excellent luminescence properties.

Another reason is that second ligand can take part or all of the place of solvent molecules involved in the coordination, therefore can form a protective layer around the rare earth complex and effectively reduce energy loss caused by the solvent molecules, prevent fluorescence quenching, therefore improve energy transfer efficiency.

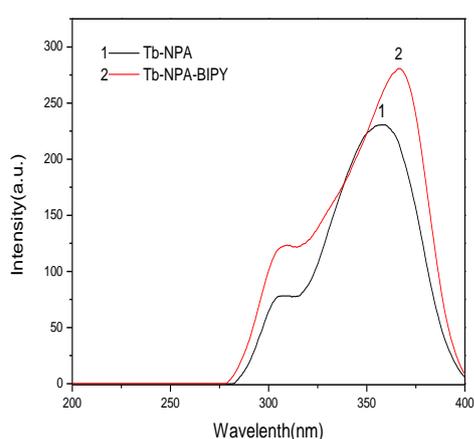


Figure.3 Excitation spectra of complexes (1 binary complex; 2 ternary complex)

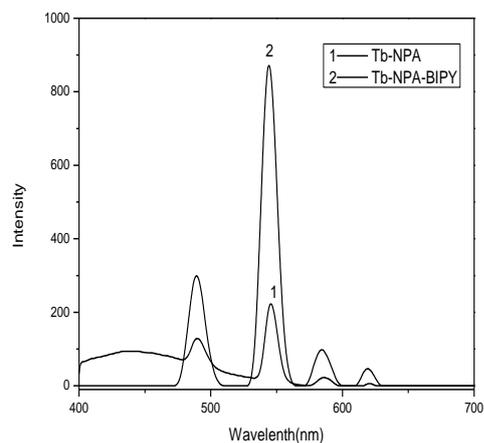


Figure.4 Fluorescence emission spectra of complexes (1 binary complex; 2 ternary complex)

4. Conclusion

The binary complex of N-phenylanthranilic acid with Terbium and the ternary complex of N-phenylanthranilic acid and 2,2'-bipyridine with Terbium were synthesized respectively. The fluorescence intensity of the ternary complex is significant stronger than that of the binary complex, which shows that 2,2'-bipyridine as auxiliary ligand can sensitize Tb^{3+} luminescence, greatly improve

the luminescence of the binary complex of Tb-N-phenylanthranilic acid. The synthesized Tb(NPA)₃(BIPY) complex has good fluorescence properties. So for rare earth binary complex with weak luminescence, the addition of an appropriate second ligand can significantly increase the fluorescence intensity multiply, resulting in excellent fluorescence of the complex.

Acknowledgements

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