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Enhancement effects of Y(III) ion on Tb(III) fluorescence in Tb(III)–Y(III)–benzoic acid complexes

Wenlian Li, Gui Yu and Shihua Huang
Changchun Institute of Physics, Academia Sinica, 1 Yan An Street, Changchun 130021 (China)

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Abstract

The fluorescence enhancement of Tb(III) due to the addition of the Y(III) ion in complex solution and in solid powder containing benzoic acid was studied. From fluorescence absorption, excitation and emission spectra and lifetime measurements it was concluded that the enhancement effects of the Y(III) ion on the Tb(III) fluorescence were caused by energy transfer from the Y(III) complex to the Tb(III) ion.

1. Introduction

The fluorescence properties of rare earth (RE) –β-diketone chelates and RE–macrocycle complexes and the associated energy transfer have been widely studied [1–4]. An important application of RE complexes was developed by Dew-Horrocks and coworkers, namely RE ions were used as a central probe for the structure of biological macromolecules [5, 6]. Other interesting work has been carried out on the fluorescence or aromatic carboxylic acid complexes of REs [7, 8]. The intermolecular energy transfer between RE complexes has also been examined [9, 10], where the energy donor was the Tb(III) ion and the acceptor was the Eu(III) ion. Although a certain amount of work has been done on the interaction between two RE ions in complex systems, the influence of the Y(III) ion on the Tb(III) emission properties in complexes has not yet been considered. In this paper our focus was on the enhancement of Tb(III) emission by the Y(III) ion in ethanol solution and in solid powder of benzoic acid (BA) complexes.

2. Experimental details

2.1. Materials

The benzoic acid (AR) was not purified before use. Ethanol solutions of Tb(III) ions and other RE ions were obtained by dissolving the corresponding oxides (99.95%) in a minimum amount of 1N HCl with heating, evaporating the excess acid and diluting to the desired volume with absolute ethanol. For a typical run the initial concentrations of the Tb(III) ion and the BA ligand were 1×10^{-3} and 2×10^{-3} M for the solution complexes and 5×10^{-2} and 0.2 M for the solid complexes respectively. To evaluate the fluorescence enhancement of Tb(III) due to the addition of the Y(III) ion, various Y(III) concentrations were used, but the Tb(III):BA ratio was kept fixed at 1:6, *i.e.* a typical solution was adjusted to 1×10^{-3} M in Tb(III) and 6×10^{-3} M in Y(III). All solutions of Tb(III) were adjusted to pH 6.

Solid powders of Tb(III)–Y(III)–BA complexes were prepared by homogeneous precipitation from an ethanol solution of $TbCl_3\cdot6H_2O$ and sodium carboxylate at pH 7.5. The solid powder was filtered out, washed with deionized water and then dried at 50 °C in vacuum.

2.2. Apparatus

Fluorescence excitation and emission spectra were measured on a Hitachi MPF-4 spectrophotometer. The samples were excited at 280 nm for the solution samples and 320 nm for the powder samples. The absorption spectrum of the solution complex was determined with a Shimadzu UV-3000 dual-wavelength double-beam recording spectrophotometer. The fluorescence lifetime of the solid complex was measured by use of a GBM-1000 spectrometer equipped with an MIEFC51 photomultiplier tube, the sample being excited by a pulsed YAG:Nd^{3+} laser (fourth harmonic frequency). The decay time curve was obtained with a 530 boxcar and processed by a microprocessor. The pH values of the solution samples were determined on a PHS-25C pH meter. Phase identification of the powder sample was achieved using a D/MAX-rA X-ray diffractometer employing Cu Kα radiation and operating at 40 kV and 15 mA.

3. Results and discussion

3.1. Solution complexes

Brittain [7] and Shou *et al.* [8] have reported the luminescence properties of Tb(III)–BA complex systems and the intramolecular energy transfer from the aromatic acid to the Tb(III) ion. However, the effect of the Y(III) ion on the fluorescence properties of Tb(III) in Tb(III)–BA complexes has been almost ignored. We have observed the fluorescence enhancement in Tb(III)–BA complexes due to the addition of Y(III). We have measured the dependence of the Tb(III) emission on the pH value in ethanol solution and found that the maximum Tb(III) emission was at pH 6, which is consistent with Shou *et al.*'s result [8]. In order to determine the optimum ligand-to-metal ratio for the Tb(III) emission, the BA:Tb(III) ratio was varied from 1:1 to 12:1. Figure 1 shows the dependence of the Tb(III) emission intensity on the molar ratio in the Tb(III)–BA complex system. It was found that the maximum Tb(III) emission occurred at BA:Tb(III) = 6. Thus the conditions pH 6 and BA:Tb(III) = 6 were chosen for the study of the dependence of the Tb(III) emission intensity on the Y(III) concentration in the $TbY_x(BA)_6$ system ($x = 0$–1.4).

Figure 2 shows the dependence of the Tb(III) fluorescence intensity ln I_{Tb} on the Y(III) concentration ln C_Y. It is seen that the Tb(III) emission intensity increased with increasing Y(III) concentration. Therefore it was demonstrated that the enhanced Tb(III) emission did not result from a change in the BA:Tb(III) ratio (see Fig. 1). It was presumably caused by a complexation between the Y(III) ions and the BA molecules around the Tb(III)–BA complex molecule, because the emission intensity of Tb(III) changed little with varying BA:Tb(III) ratio in the region BA:Tb(III) < 6:1.

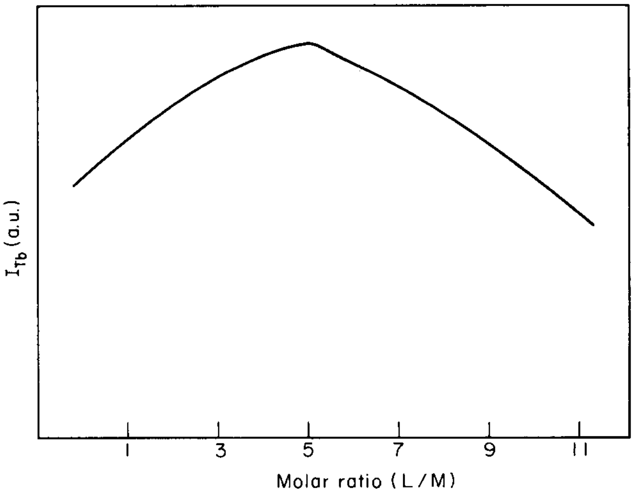

Fig. 1. Dependence of fluorescence intensity of Tb(III) ion on concentration of BA ligand in ethanol solution complexes.

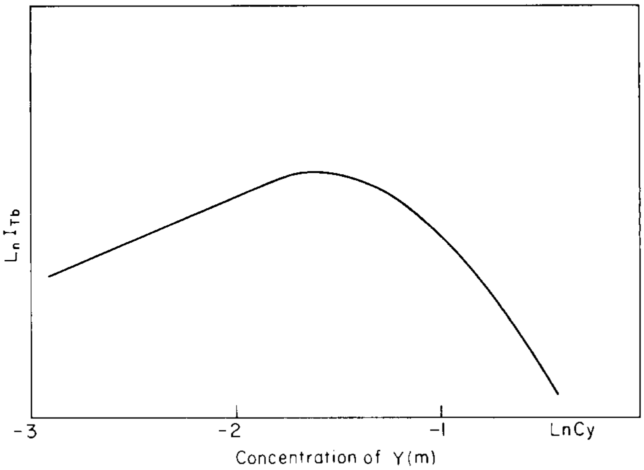

Fig. 2. Dependence of fluorescence intensity of Tb(III) ion on concentration of Y(III) ion in Tb(III)–Y(III)–BA complex solutions.

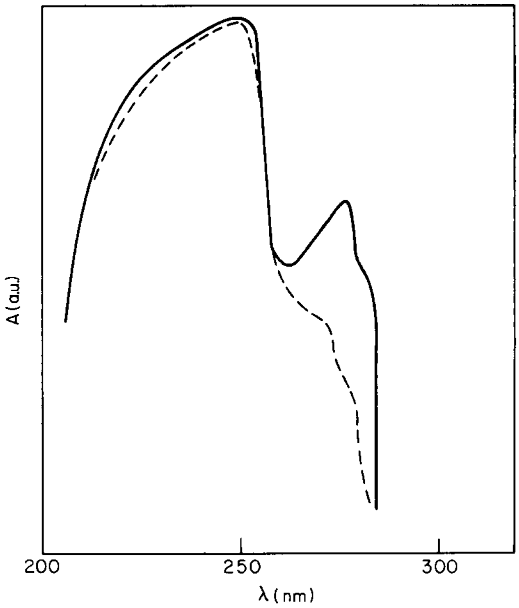

Fig. 3. Relative absorption spectra of Tb(III)–Y(III)–BA (——) and Tb(III)–BA (– – –) complexes.

Figure 3 shows the relative absorption spectra for the Tb(III)–BA and Tb(III)–Y(III)–BA systems in ethanol solutions. It is seen that the absorption intensity in the 265–275 nm band was increased by the addition of the Y(III) ion. This increased absorption was presumably due to a complexation between Y(III) and the BA ligand. The increase in absorption intensity for the Tb(III)–Y(III)–BA complex must be related to the arrangement of the environment of the Tb(III) ion. In other words, the environment of the Tb(III) ion was changed from an irregular state of the free ligand to a regular state of the Y(III)–BA complex, *i.e.* the electron-conjugated surface was larger for the

Y(III)–BA system than for the free BA ligand. Thus we can say that the length of the conjugated Tb(III)–Y(III)–BA system was increased. On the other hand, the excitation band at 270 nm corresponds to the absorption band at 250–270 nm as shown in Fig. 3. Thus an energy transfer from the Y(III)–BA complex to the Tb(III) ion must take place.

In order to understand the transfer process, let us return to Fig. 2, in which the dependence of the Tb(III) emission on the Y(III) concentration in the Tb(III)–Y(III)–BA complex system was shown. With the help of the fluorescence transfer function [11] we obtained the dependence of the acceptor luminescence intensity on the sensitizer concentration under limiting conditions:

$$I_{\mathrm{Tb}} \propto C_{\mathrm{Y}} \qquad (C_{\mathrm{Y}} \text{ very small}) \qquad (1)$$

$$I_{\mathrm{Tb}} \propto \frac{A C_{\mathrm{Y}}^{1-S_{(\mathrm{Y-Y})}/S_{(\mathrm{Y-Tb})}}}{1+A C_{\mathrm{Y}}^{S_{(\mathrm{Y-Y})}/2-S_{(\mathrm{Y-Y})}/S_{(\mathrm{Y-Tb})}}} \qquad (C_{\mathrm{Y}} \text{ larger}) \qquad (2)$$

Here A is a constant related to the transfer and the concentration quenching is considered, $S_{(\mathrm{Y-Y})}$ and $S_{(\mathrm{Y-Tb})}$ are the electronic multiple indexes of the Y(III)–Y(III) and Y(III)–Tb(III) interactions respectively and C_{Y} is the Y(III) concentration. Therefore the intermolecular energy transfer might take place by electronic multiple interaction between the Y(III) complex and the Tb(III) ion. The probable transfer processes may be described as

$$\mathrm{Y(III)\text{–}BA} \xrightarrow{h\nu} \mathrm{Y(III)\text{–}BA^*}$$

$$\mathrm{Y(III)\text{–}BA^* + Tb(III)\text{–}BA} \xrightarrow{\mathrm{ET_1}} \mathrm{Y(III)\text{–}BA + Tb(III)\text{–}BA^*}$$

$$\mathrm{Tb(III)\text{–}BA^*} \xrightarrow{\mathrm{ET_2}} \mathrm{Tb(III)^*\text{–}BA} \xrightarrow{h\nu} \mathrm{Tb(III)}$$

i.e. the Y(III)–BA complex is first excited, then the energy is transferred to the Tb(III) ion through the interaction between the Y(III) complex and the Tb(III) ion, and finally the Tb(III) ion fluoresces.

In addition to the BA ligand, salicylic acid was also chosen as a ligand for studying the enhancement effect of the Y(III) ion on the Tb(III) emission in Tb(III)–Y(III) systems. An increased Tb(III) emission was also observed in the salicylic acid system. Thus it was deduced that the enhancement effect was related to the structure of the organic ligands. However, no fluorescence enhancement effects of Tb(III) by Eu(III) and Sm(III) in ethanol complex systems were observed. This was due to the fact that the lowest excited states of Eu(III) and Sm(III) ions are below the $^5\mathrm{D}_4$ level of the Tb(III) ion and the Tb(III) emission intensities were decreased by Eu(III) and Sm(III) ions.

3.2. *Solid powder complex system*

Isolated powder complexes of Tb(III)–BA and Tb(III)–Y(III)–BA were prepared. The two complex compositions are $\mathrm{Tb(BA)_3}$ and $\mathrm{Tb_{0.5}Y_{0.5}(BA)_3}$ respectively. Figure 4 shows the X-ray diffraction patterns of the two complexes. It is seen that the diffraction lines have very similar intensities for the two complexes. Thus it is confirmed that the two complexes should have the same structure.

Figure 5 shows the excitation and emission spectra of the $\mathrm{Tb(BA)_3}$ and $\mathrm{Tb_{0.5}Y_{0.5}(BA)_3}$ complexes. It is

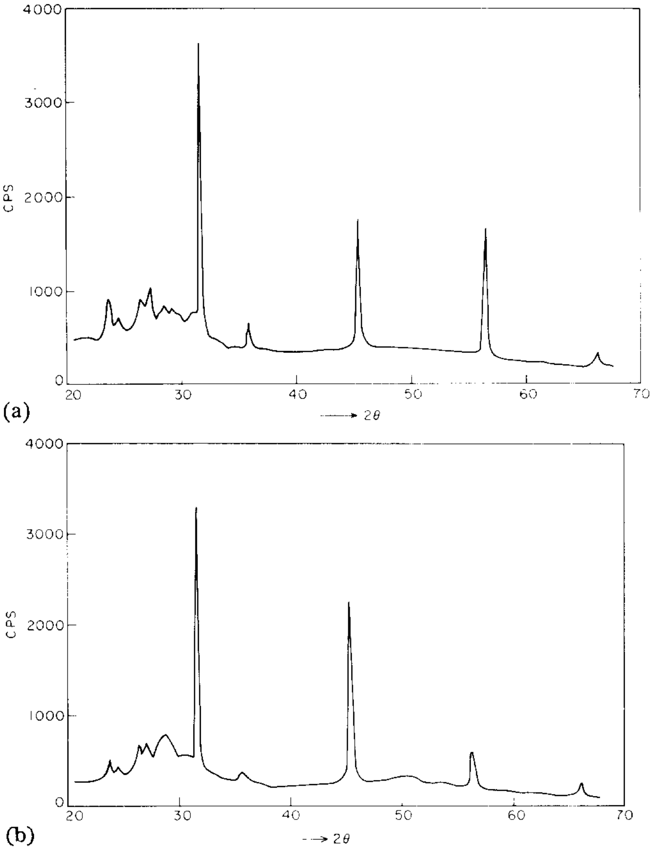

Fig. 4. X-ray diffraction patterns of polycrystalline powders of (a) $\mathrm{Tb(III)(BA)_3}$ and (b) $\mathrm{Tb(III)_{0.5}\text{–}Y(III)_{0.5}(BA)_3}$ complexes.

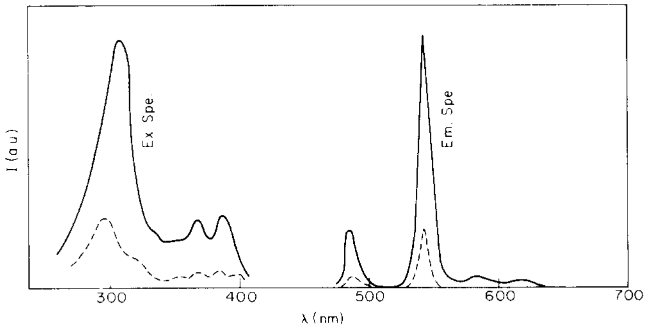

Fig. 5. Excitation and emission spectra of polycrystalline powders of $\mathrm{Tb(III)(BA)_3}$ (– – –) and $\mathrm{Tb(III)_{0.5}\text{–}Y(III)_{0.5}(BA)_3}$ (——) complexes.

seen that the emission intensity of the Tb(III) ion is about three times stronger for $Tb_{0.5}Y_{0.5}(BA)_3$ than for $Tb(BA)_3$. The fluorescence lifetimes of Tb(III) in $Tb(BA)_3$ and $Tb_{0.5}Y_{0.5}(BA)_3$ were measured as 250 and 270 μs respectively. The difference of 20 μs is probably related to an energy transfer from the Y(III) complex to the Tb(III) ion, although the transfer mechanism is not known in detail.

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