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Photoacoustic and luminescence properties study on energy transfer and relaxation processes of Tb(III) complexes with benzoic acid

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Abstract

The photoacoustic (PA) amplitude spectra of $Tb(Benz)_3$, $Tb(Benz)_3Phen$ and $Tb(Benz)_3Bpy$ complexes (Benz: benzoic acid; Phen: 1,10-phenanthroline; Bpy: 2,2′-bipyridine) have been measured, and the PA phase data of the different complexes calculated. The PA amplitude spectra combined with the luminescence spectra reflected the variation of the luminescence properties, and the PA phase is directly relative to the relaxation time. The luminescence intensity and the PA phase data increase when the second ligand Bpy is introduced, while they decrease greatly when Phen is added. These results are due to the different intramolecular energy transfer processes. Compared with $Tb(Benz)_3$, the energy gap between Tb^{3+} and Bpy is more suitable for energy transfer, while the energy gap between Tb^{3+} and Phen is so small that the thermally activated Tb^{3+}-to-Phen inverse energy transfer rate increase more. The models of energy transfer and relaxation processes of $Tb(Benz)_3Bpy$ and $Tb(Benz)_3Phen$ are established.

Keywords: Photoacoustic spectroscopy; Phase; Terbium complex; Energy transfer

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1. Introduction

Rare earth complexes with carboxylic acids may be used as structural and functional probes of biological macromolecule systems [1,2]. On the other hand, they are a kind of potential luminescent materials for further application [3]. Tb^{3+} complexes with organic ligands often show strong luminescence due to the efficient energy transfer from the triplet state of ligands to the rare earth ions [4]. So there has been a growing interest in the studies of the luminescence properties of terbium complexes with carboxylic acids.

Photoacoustic spectrum (PAS) is a direct monitor of nonradiative relaxation channel and therefore it is the complement of the fluorescence spectroscopy [5]. Since energy transfer is a nonradiative process, PAS has an advantage to reveal the detail process. In recent works [6–8], PAS has been found to be very suitable for investigating the solid rare earth compounds by providing their PA amplitude or PA phase spectra.

In this paper, the PA and luminescence spectra of the binary and ternary Tb^{3+} complexes with benzoic acid and 1,10-phenanthroline or 2,2′-bipyridine are measured. The PA phase data are calculated. $Tb(Benz)_3Bpy$ shows the lowest PA amplitude, the strongest emission and the biggest PA phase among the title complexes, but in contrast the PA phase of $Tb(Benz)_3Phen$ is the smallest. From the results, the energy transfer mechanism is discussed in detail.

2. Experimental

2.1. The synthesis of rare earth complexes

$Tb(Benz)_3$ was prepared according to [9]. The ternary complexes were synthesized as follows. Excess 1,10-phenanthroline or 2,2′-bipyridine (1 mmol) and sodium benzoate (3 mmol) were dissolved by absolute ethanol and mixed together, then an alcoholic solution of terbium chloride (1 mmol) was added. After heating and stirring, the precipitated complex was filtered off, washed with water and ethanol, dried and then stored over silica–gel drier.

The sample powders were prepared by manual grinding with an agate mortar and pestle. The top of the sample powder loaded into the PA cell was compacted by a flat end metal rod.

2.2. Spectroscopy measurements

The PA measurements were performed on a single-beam PA spectrometer constructed in our lab. A 500 W xenon

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lamp, a CT-30F monochromator, a CH-353 chopper and a PA cell fitted with an ERM-10 electret microphone were used. The output signal of the microphone was fed to a lock-in-amplifier (LI-574A) and was collected on an ac/dc converter and dealt with by computer. The data were normalized for changes in lamp intensity using a carbon black reference.

The luminescence spectra were measured with a Shimadzu RF-5301 PC fluorescence photometer.

3. Results

3.1. Photoacoustic amplitude spectra of the complexes

The PA signal is obtained by detecting the heat generated through the nonradiative transitions by the sample after absorbing the modulated incident light [10]. It reveals the absorption and relaxation information of a sample.

The PA amplitude spectra of the complexes at a frequency of 12 Hz are shown in Fig. 1. The PA signal is only relative to the nonradiative transition processes. Tb^{3+} is a fluorescent ion and the absorption coefficient of the π–π* transitions of ligands is higher than that of f–f transitions of rare earth ions, hence the absorption peaks of Tb^{3+} were covered by the π–π* transition of ligand within 300–350 nm. From the PA amplitude spectra of $Tb(Benz)_3$, we can conclude that the maximum absorption wavelength of Benz is at 303 nm. Compared with the absorption peak of Benz in solution (located at 280 nm), the PA peak shows a significant red shift. This is due to the fact that the π electron conjugated system of the complex is much larger than that of free-base ligand.

In general, the PA signal can be expressed as [11]

$$P = K_1 A_{abs}\left(1 - \eta - \sum_i \gamma_i\right) \qquad (1)$$

where A_{abs} is the absorbance of the sample, K_1 a coefficient which is determined by the thermal properties of the sample and by the spectrometer, η the luminescence efficiency, and γ_i is the conversion efficiencies of the other non-thermal deexcitation channels except the luminescence (such as photochemistry, photoconductivity, etc.). For the title complexes, there are no other non-thermal deexcitation processes generally, so all γ_i may be omitted. Under this condition, Eq. (1) is simplified to

$$P = K_1 A_{abs}(1 - \eta) \qquad (2)$$

It can be inferred from Eq. (2) that as the PA intensity (P) of the sample increases, the luminescence efficiency (η) exhibits a corresponding decrease. For the title compounds, the intensities of PA bands in the region of ligand absorption change significantly, which indicates that the luminescence properties of the Tb(III) complexes vary a lot.

3.2. Luminescence spectra of the complexes

Fig. 2 shows the excitation and emission spectra of Tb(III) complexes with benzoic acid. To study the relaxation process, the excitation wavelength was selected at 303 nm which is the same in the PA spectra. The emission peaks at 489, 545, 586 and 620 nm are, respectively, assigned to $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ of Tb^{3+} ion. Among these transitions, $^5D_4 \rightarrow {}^7F_5$ is the strongest. The emission intensities at 545 nm of the complexes are listed in

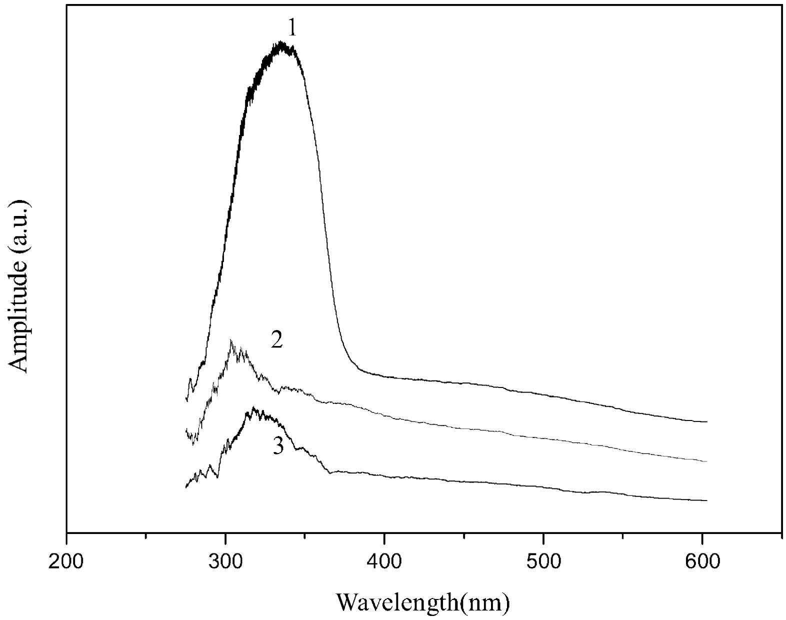

Fig. 1. Amplitude spectra of Tb(III) complexes at a chopping frequency of 12 Hz: (1) $Tb(Benz)_3Phen$; (2) $Tb(Benz)_3$; (3) $Tb(Benz)_3Bpy$.

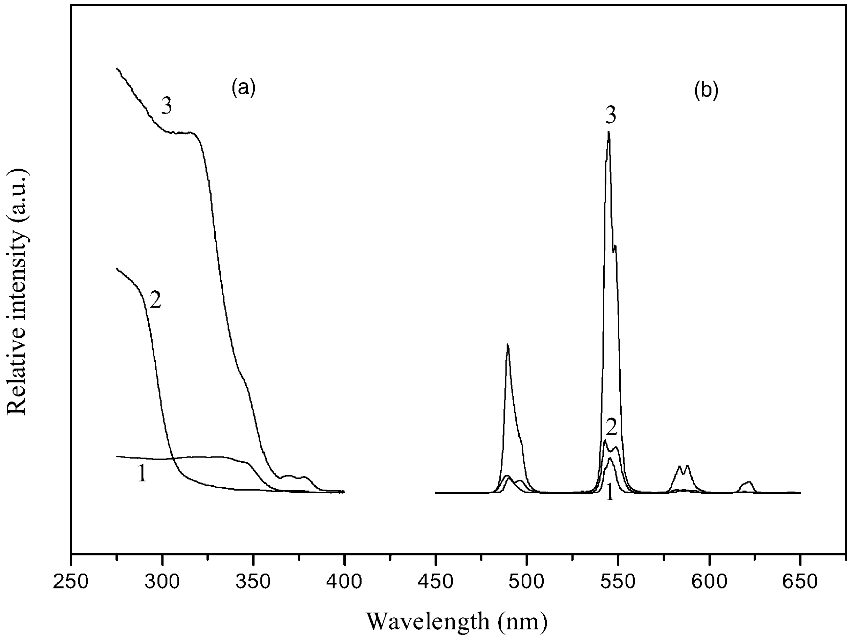

Fig. 2. Luminescence spectra of the complexes of (a) excitation spectra and (b) emission spectra: (1) $Tb(Benz)_3Phen$; (2) $Tb(Benz)_3$; (3) $Tb(Benz)_3Bpy$.

Table 1. Compared with $Tb(Benz)_3$, the addition of a second ligand Bpy makes the emission intensity of Tb^{3+} increase, while the intensity of $Tb(Benz)_3Phen$ decrease. These are consistent with the PAS results.

3.3. Photoacoustic phase spectra of the complexes

Photoacoustic spectra cannot only provide amplitude information, but also provide phase information. PA phase is the time delay that occurs during the process from light absorbed by sample to acoustic signal being detected by microphone. The phase data contain contributions from a number of sources: the geometry of the photoacoustic cell, the response of the detecting system, the optical absorption coefficient, the nonradiative decay paths, etc. [12]. In an actual photoacoustic measurement, many of the non-sample related parameters may be maintained constant and the phase data may therefore be expressed as [13]:

$$\Psi = \tan^{-1}(1 + 2/\beta\mu_s) + \tan^{-1}(\omega\tau) \quad (3)$$

where β is the optical absorption coefficient of the sample, μ_s the thermal diffusion length ($\mu_s = 1/\alpha$, α is the heat diffusion coefficient), $\omega = 2\pi f$ (f is the modulated frequency), and τ is the relaxation time. For Tb(III) complexes with the conjugated π electron ligand, the absorption coefficient is high enough, then the phase data could be only relative to the relaxation time.

$$\Psi = \Psi_0 + \tan^{-1}(\omega\tau) \quad (4)$$

The phase shifts associated with different complexes are best observed by plotting the amplitude versus phase angle at the absorbance peak of the ligand. Such plots are generated by measuring in-phase (I_0) and quadrature (I_{90}) interferograms simultaneously and calculating the interferogram I_ϕ at detection angle from [14]

$$I_\phi = I_0 \cos\phi + I_{90} \sin\phi \quad (5)$$

The PA phase spectra for different complexes at 303 nm are shown in Fig. 3. The phase angle of maximum amplitude is sample's PA phase. The phase data are listed in Table 1. The phase data of $Tb(Benz)_3Phen$ is 3.7° smaller than that of $Tb(Benz)_3$, while the phase data of $Tb(Benz)_3Bpy$ is 3.1° bigger than that of $Tb(Benz)_3$ at 303 nm. According to Eq. (4), the bigger the PA phase is, the longer the relaxation time is. $Tb(Benz)_3Phen$ has the smallest PA phase data, which means the relaxation process in $Tb(Benz)_3Phen$ is very quick.

Table 1
The luminescence properties and the PA phase data of terbium complexes

Matter	λ_{exc} (nm)	λ_{em} (nm)	Relative intensities (a.u.) ($^5D_4 \rightarrow {}^7F_5$)	PA phase data (°)
$Tb(Benz)_3Phen$	303	545	56	109.8
$Tb(Benz)_3$	303	543	87	113.5
$Tb(Benz)_3Bpy$	303	546	592	116.6

4. Discussion

The variation of Tb(III) complexes in photophysical properties (PA amplitude, luminescence and PA phase) are due to the different energy transfer mechanism.

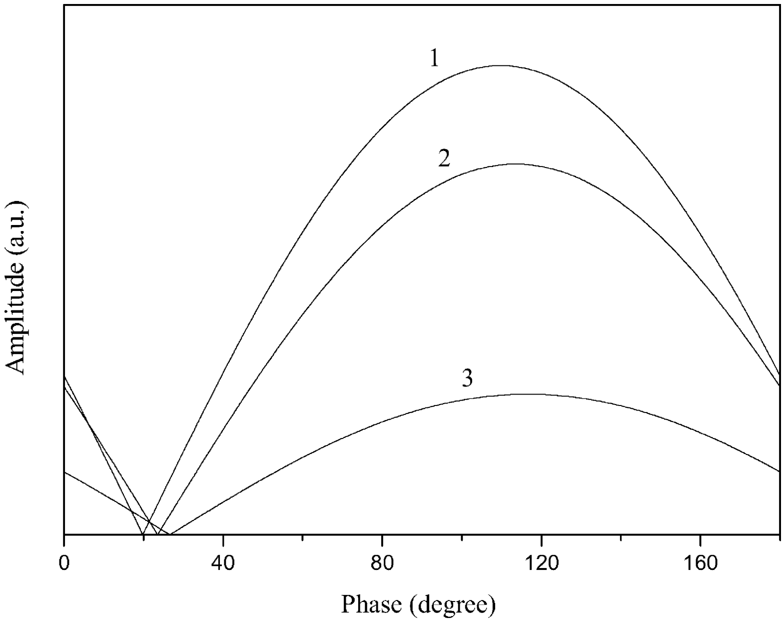

Fig. 3. The PA phase spectra at 303 nm: (1) $Tb(Benz)_3Phen$; (2) $Tb(Benz)_3$; (3) $Tb(Benz)_3Bpy$.

The intramolecular energy transfer efficiency depends mainly on two energy transfer processes [15], one of which is from the lowest triplet level of organic ligand to the resonant energy level by Dexter's resonant exchange interaction theory [16]. The energy transfer rate constant P_{sa} is given by

$$P_{sa} = \left(\frac{2\pi Z^2}{h}\right) \int F_s(E)\xi_a(E)\,dE \tag{6}$$

where $F_s(E)$ represents the observed shape of the emission band of the triplet state of ligand (donor), and $\xi_a(E)$ is the shape of the absorption band of the excited state of central ion (acceptor). Therefore, P_{sa} is decided by the overlap between the triplet state of ligand and the resonance level of lanthanide ion. The other process is the inverse energy transfer by the thermal deexcitation mechanism. The thermal deexcitation rate constant $K(T)$ is given as follows [17]:

$$K(T) = A \exp\left(\frac{-\Delta E}{RT}\right) \tag{7}$$

where ΔE is the energy gap between the ligand triplet state and the resonance level of rare earth ion.

From Eqs. (6) and (7), if the energy gap (ΔE) is too large, although the thermal deexcitation rate constant ($K(T)$) is small, the energy transfer rate constant (P_{sa}) is low due to the diminution in the overlap between donor and acceptor. When the energy gap becomes small, P_{sa} increases, while $K(T)$ increases also. So the suitability of the energy gap between the excited triplet level of ligand and resonance energy level of rare earth ions is critical for efficient energy transfer.

The resonance level of Tb^{3+} is 20,500 cm^{-1}. The lowest triplet level of Benz, Bpy and Phen are 24,800, 22,900 and 22,100 cm^{-1} [18,19], respectively. The energy gap between the lowest triplet level Benz, Bpy or Phen and the resonance level Tb^{3+} are, respectively, 4300, 2400 or 1600 cm^{-1}. For $Tb(Benz)_3Bpy$, the energy gap between Tb^{3+} and Bpy is more suitable for energy transfer from Bpy to Tb^{3+} than that between Tb^{3+} and Benz. Some energy absorbed by Benz may be transferred to Bpy firstly, then transferred to Tb^{3+}. Certainly the thermally activated Tb^{3+}-to-Bpy inverse energy transfer rate also increases. But the rate of energy transfer from Bpy to Tb^{3+} increases more than the inverse energy transfer rate does. Hence the luminescence intensity of $Tb(Benz)_3Bpy$ is higher than that of $Tb(Benz)_3$. Similarly the energy gap between Tb^{3+} and Phen is the most suitable for energy transfer from ligand to Tb^{3+} within these complexes. But the energy gap is so small that the thermally activated Tb^{3+}-to-Phen inverse energy transfer rate increases more. Latva et al. [20] have found that the inverse energy transfer is evident when the energy gap between the $^5D_4$ level of Tb(III) and lowest triplet state energy level of the ligand is less than 1850 cm^{-1}. The fast inverse energy transfer makes the luminescence intensity of $Tb(Benz)_3Phen$ be the lowest among these complexes.

From the above results, the models of energy relaxation processes of $Tb(Benz)_3Bpy$ and $Tb(Benz)_3Phen$ are established (see Fig. 4). Energy can transfer effectively from the ligand to Tb^{3+}, which makes the lifetime of ligand shorter. Therefore, relaxation time (τ) is determined by the lifetime of Tb^{3+} in these complexes. According to Eq. (4) and the phase data, we know the variation of the lifetime of Tb^{3+} in different complexes. The lifetime of Tb^{3+} is shorter in $Tb(Benz)_3Phen$ than in $Tb(Benz)_3$, but it is longer in $Tb(Benz)_3Bpy$. Compared with $Tb(Benz)_3$, the energy gap between Tb^{3+} and Bpy is more suitable for energy transfer, which makes the relaxation process longer. While the energy

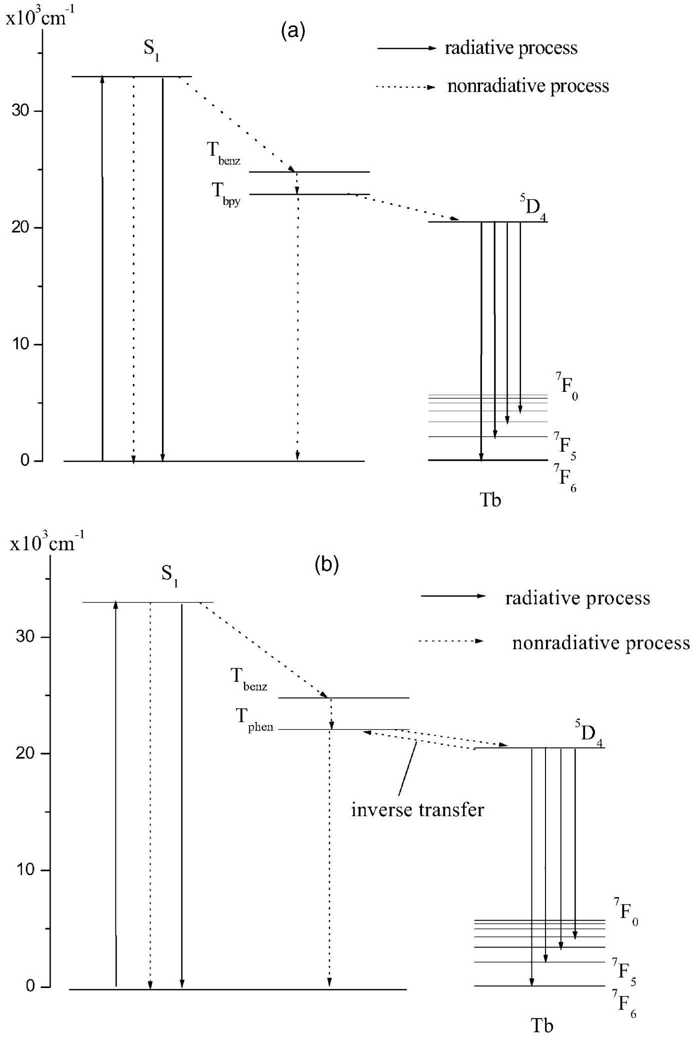

Fig. 4. Models of intramolecular energy transfer and relaxation processes of (a) Tb(Benz)$_3$Bpy and (b) Tb(Benz)$_3$Phen.

gap between Tb^{3+} and Phen is so small that the thermally activated Tb^{3+}-to-Phen inverse energy transfer rate is high, which induces the short lifetime of Tb^{3+} in Tb(Benz)$_3$Phen.

5. Conclusions

The energy transfer and relaxation process of Tb(Benz)$_3$-Phen, Tb(Benz)$_3$ and Tb(Benz)$_3$Bpy are studied by measuring their photoacoustic amplitude spectra and luminescence spectra. The PA phase shifts of the different complexes are calculated. The luminescence intensity of Tb(Benz)$_3$Bpy is higher than that of Tb(Benz)$_3$, and the relaxation process is lower. This is by reason that the energy gap between Tb^{3+} and Bpy is more suitable for energy transfer. For Tb(Benz)$_3$Phen, the energy gap between Tb^{3+} and Phen is so small that the thermally activated Tb-to-Phen inverse energy transfer rate increases more. That makes the relaxation process of Tb(Benz)$_3$Phen be the quickest among those complexes.

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