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Photoacoustic and luminescence spectra study on the effects of chlorine substituent on the energy transfer of Eu(III)–chlorobenzoic acid

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Abstract

The photoacoustic (PA) amplitude spectra of three complexes of Eu(III) combined with chlorobenzoic acid (Eu(*o*-$ClC_6H_4CO_2)_3\cdot H_2O$, Eu(*m*-$ClC_6H_4CO_2)_3\cdot H_2O$ and Eu(*p*-$ClC_6H_4CO_2)_3\cdot H_2O$) have been measured, and the PA phase of the different complexes have been calculated. Both the PA amplitude spectra and the luminescence spectra reflect the variation of the luminescent properties, and the PA phase is directly relative to the relaxation time. Since the relaxation is the process of the intramolecular energy transfer between the ligands and the central ion, the molecular structure of ligand is the important factor to decide the energy gap between the lowest triplet state of ligand and the resonance level of central ion. The effects of chlorine substituent on the molecular structure and energy gap of the complexes have been studied by PA phase and luminescence spectra.

Keywords: Photoacoustic phase; Chlorine substituent; Intramolecular energy transfer

1. Introduction

The great interest in the study of lanthanide complexes is mainly due to their potential practical applications such as laser materials, luminescent labels in the fluorescence analysis and biology system [1–3]. A study of the intramolecular relaxation processes of lanthanide complexes will provide much information on the luminescent properties, the situation of the energy levels and the energy transfer process. If the absorption of excitation energy takes place in ligand instead of central ion, excellent luminescent properties of lanthanide complexes are attributed to the intramolecular energy transfer between the ligands and the central ion [4].

Photoacoustic spectroscopy (PAS) is a recently developed technique. The PA response is generated when optical absorption causes a rapid local heating in the sample under investigation. The subsequent periodic expansion and contraction of the gas in the airtight PA cell generates a pressure wave that is detected with a microphone [5]. PAS is being used extensively in the optical and thermal characterization of many kinds of materials [6]. It can be a direct monitor of energy gaps, non-radiative relaxation processes and the complement of fluorescence spectroscopy [7]. One of the important characteristics of PAS is that it provides information about both amplitude and phase of response of a sample [8]. The PA amplitude signal depends on a combination of the optical absorption properties and the thermal properties of the sample. The phase of the PA signal in response to the incident light is due to a time delay, which is caused by the thermal response of the sample and by the non-radiative relaxation process [9,10].

Lanthanide complexes with aromatic carboxylic acids are frequently used as structural and functional probes in biological systems [11]. PA technique is suitable to the study the intramolecular energy transfer properties of lanthanide complexes. The intramolecular transfer of energy is related with the triplet state of ligand (donor) and the excited state of central ion (acceptor) [12]. Therefore the suitability of the energy gap between the lowest triplet state of ligand and the resonance level of central ion is a critical factor for efficient energy transfer. When a substituent is attached to the ring of ligand at different positions, the molecular structure of ligand and furthermore the energy gap mentioned above will be changed. In this paper, solid complexes: Eu(*o*-$ClC_6H_4CO_2)_3\cdot H_2O$, Eu(*m*-$ClC_6H_4CO_2)_3\cdot H_2O$ and Eu(*p*-$ClC_6H_4CO_2)_3\cdot H_2O$ are

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synthesized. Their PA and luminescence spectra are determined and interpreted.

2. Experimental

2.1. Preparation of complexes

Benzoic acid can combine rare earth ions to form stable complexes. Solid complexes of $Eu(ClC_6H_4CO_2)_3{\cdot}H_2O$ were synthesized according to the procedure given in Ref. [13]. The rare earth oxide was converted to chloride by treatment with concentrated HCl. A solution of the chloride in absolute ethanol was added to a solution of ligand in the same solvent. The precipitation was accomplished by slow addition of aqueous ammonia. The complexes were recrystallized, washed with a little ethanol and the solution was filtered. Products were obtained after dried at room temperature and then stored in desiccator.

The results of the elemental analyses and infrared spectra were consistent with their molecular structures.

2.2. Measurement of spectroscopy

The PA spectra were obtained on a single-beam spectrometer constructed in our laboratory [14]. A 500 W Xenon lamp, a CT-30F monochromator, a CH-353 chopper and a PA cell fitted with an ERM10 electret microphone were used. The output signal of the microphone was fed to a lock-in-amplifier (LI-574A) and was collected on an A/D converter and dealt with by computer. The chopper frequency was set at 12 Hz. The PA spectra were recorded in the region of 300–800 nm, and the amplitude spectra were normalized against the carbon black to account for the variation due to the light source and spectrometer.

3. Results and discussion

3.1. Photoacoustic amplitude spectra of the complexes

The PA amplitude spectra of $Eu(ClC_6H_4CO_2)_3{\cdot}H_2O$ at a frequency of 12 Hz are shown in Fig. 1. The broad band located from 300 to 450 nm were assigned to the π–π^* transition of chlorobenzoic acid. For Eu^{3+} in complexes, only f–f transitions are observed from 300 to 800 nm [15,16]. Since the π–π^* transition of ligand is much stronger than the f–f transition [17], the f–f transition of Eu^{3+} locating at 300–450 nm are covered by the π–π^* transition. In general, the PA signal can be expressed as [18]:

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

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 efficiency 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 process generally, so all γ_i may be omitted. Under this condition, Eq. (1) is simplified to

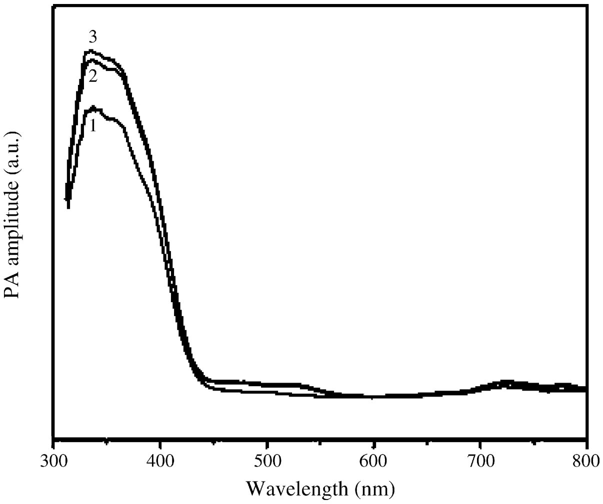

Fig. 1. PA amplitude spectra of Eu(III) complexes at a chopping frequency of 12 Hz: (1) Eu(p-$ClC_6H_4CO_2)_3{\cdot}H_2O$; (2) Eu($m$-$ClC_6H_4CO_2)_3{\cdot}H_2O$; (3) Eu($o$-$ClC_6H_4CO_2)_3{\cdot}H_2O$.

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

As the PA amplitude intensity (P) of the sample increases, the luminescence efficiency (η) exhibits a corresponding decrease. In Fig. 1, the intensities of PA amplitude signals of energy levels of Eu^{3+}, which have fluorescence properties, are quite weak or vanished. For Eu^{3+}, the relaxation of $^5D_0$ cannot be monitored by PA spectroscopy, and the PA signals of $^5D_1$ and $^5D_2$ at 469 and 540 nm are also very small [19].

Because of the similar molecular structures, the PA intensities of three samples at the absorption of ligand approach to each other, especially for the Eu(o-$ClC_6H_4CO_2)_3{\cdot}H_2O$ and Eu(m-$ClC_6H_4CO_2)_3{\cdot}H_2O$. The relative intensities of these samples at 335 nm are shown in Table 1.

3.2. Luminescence spectra of the complexes

Fig. 2 shows the luminescence emission spectra of Eu^{3+} complexes with chlorobenzoic acid. To study the relaxation process, the excitation wavelength was selected at 335 nm, which matches the PA spectra. The emission peaks at 527, 592 and 615 nm are, respectively, assigned to $^5D_1 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} ion [20,21]. Among these transitions, $^5D_0 \rightarrow {}^7F_2$ is the strongest. The relative intensities of three samples show the obvious difference and the trend of rising is contrary to that of PA intensities.

3.3. Photoacoustic phase spectra of the complexes

The photoacoustic phase is the time delay that occurs during the process: from the light absorbed by the sample to the acoustic signal being detected by the 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 non-radiative deexcitation paths, etc. In an actual photoacoustic measurement, many of

Table 1
PA and luminescence relative intensity and PA phase data of complexes

	PA relative intensity (P) (335 nm)	Luminescence relative intensity	PA phase data (°)
Eu(p-$ClC_6H_4CO_2)_3\cdot H_2O$	1.00	1.00	111.8
Eu(m-$ClC_6H_4CO_2)_3\cdot H_2O$	1.17	0.57	117.7
Eu(o-$ClC_6H_4CO_2)_3\cdot H_2O$	1.20	0.22	121.5

the non-sample related parameters may be maintained constant and the phase may therefore be used to provide the information about the non-radiative deexcitation processes. The phase may be expressed as [22].

$$\psi = \tan^{-1}\left(\frac{1+2}{\beta\mu_s}\right) + \tan^{-1}(\omega\tau) \tag{3}$$

where $\omega = 2\pi f$, f is the modulation frequency, and β, μ_s, τ are optical absorption coefficient, thermal diffusion length ($\mu_s = 1/\alpha$, α is the heat diffusion coefficient) and the relaxation time, respectively. For Eu(III) complexes with the conjugated π electron ligand, the absorption coefficient is high enough, then the phase data could be only related with the non-radiative deexcitation processes [23]:

$$\psi = \psi_0 + \tan^{-1}(\omega\tau) \tag{4}$$

The phase shifts associated with different complexes are best observed by the plotting the amplitude versus the phase angle at the absorption peaks of the ligand [24]. Such plots are generated by measuring the in-phase signals (I_0) and quadrature (I_{90}) signals simultaneously under selected modulation frequency and calculating the signal I_ϕ at detecting angle from

$$I_\phi = I_0 \cos\phi + I_{90} \sin\phi \tag{5}$$

Repeat this process by scanning the different values of ϕ from 0 to 180° and then acquire a plot of amplitude versus ϕ. The PA phase spectra for different complexes at 335 nm are shown in Fig. 3. The phase angle of maximum amplitude is sample's PA phase and the data list in Table 1.

The PA phase of the Eu(p-$ClC_6H_4CO_2)_3\cdot H_2O$ is the smallest, which is 5.9° smaller than that of Eu(m-$ClC_6H_4CO_2)_3\cdot H_2O$ and 9.7° smaller than that of Eu(o-$ClC_6H_4CO_2)_3\cdot H_2O$ at 335 nm. According to Eq. (4), the bigger the PA phase is, the longer the relaxation time is.

3.4. Energy transfer and relaxation processes

3.4.1. Models of intramolecular energy transfer and relaxation processes

The variation of Eu(III) complexes in photophysical properties (PA amplitude, luminescence and PA phase) are due to the difference of intramolecular energy transfer.

According to Dexter's theory [25], 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); $\xi_a(E)$ is the shape of the absorption band of the excited state of central ion (acceptor). Therefore, the suitability of the energy gap between the lowest triplet state of ligand and the resonance level of Eu^{3+} is a critical factor for efficient energy transfer.

In the luminescence experiment the excitation wavelength was selected at 335 nm, where the ligands have the strongest absorption. It means that the emission spectra bands of Eu^{3+} are

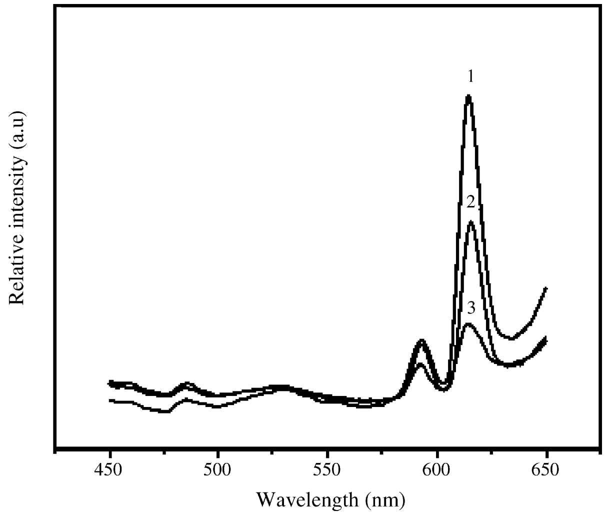

Fig. 2. Luminescence emission spectra of the complexes of: (1) Eu(p-$ClC_6H_4CO_2)_3\cdot H_2O$; (2) Eu($m$-$ClC_6H_4CO_2)_3\cdot H_2O$; (3) Eu($o$-$ClC_6H_4CO_2)_3\cdot H_2O$.

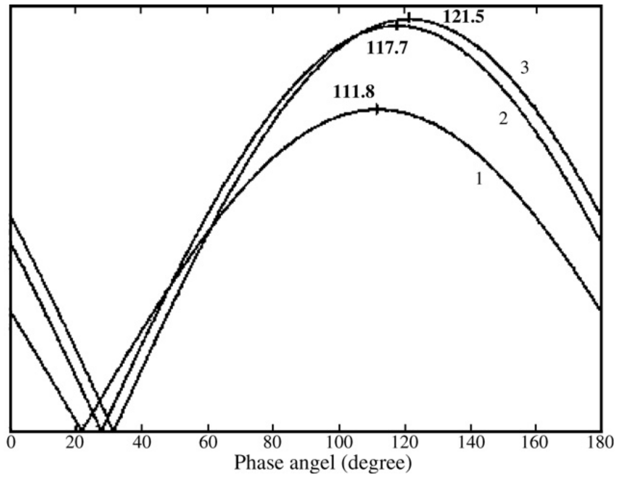

Fig. 3. The variation of the amplitude as a function of phase angle at 335 nm: (1) Eu(p-$ClC_6H_4CO_2)_3\cdot H_2O$; (2) Eu($m$-$ClC_6H_4CO_2)_3\cdot H_2O$; (3) Eu($o$-$ClC_6H_4CO_2)_3\cdot H_2O$.

acquired from the intramolecular energy transfer from donor to acceptor instead of the excitation–deexcitation of Eu^{3+} itself. The effects of different chlorine substituent on the energy levels of the lowest triplet state of ligands are the points to be studied.

The resonance level ($^5D_0$) of Eu^{3+} ion is at 17,300 cm^{-1} [26], and the lowest triplet state (T) of benzoic acid is at 24,800 cm^{-1} [27]. The suitability of energy gap (7500 cm^{-1}) can make the energy transfer from ligand to central ion. But ring substitutent can lead to a change of the energetic disposition of the lowest triplet states [28]. The inductive effects and the conjugative effects of ring substituent react on the energy levels simultaneously. For that chlorine is a kind of strong electron donor, the inductive effects would increase the π–π^* energy. The conjugative effects exceed the inductive effects. So the lowest triplet state of Cl-substituted benzoic acid may lie at a lower energy level than that of unsubstituted compound [29]. In the research about the effects of various ring substituents on the phosphorescence of benzene derivatives, it was reported by Wagner et al. that the triplet state energies are strongly influenced by substituent position [30]. When an electron-donating group, such as chlorine, is attached to the ring of benzoic acid, carbonyl group and the substituent reinforce each other in stabilizing the energy state. However, the effects of the two groups are additive only for 1,4 substitution. So the effect of stabilization from *p*-substitution is remarkable and that from *m*-substitution is only slight. On the other hand, it was also concluded that the slight destabilizations caused by *o*-chlorine should be attributed to some steric hindrance, which makes the energy level a little higher than that of unsubstituted complex.

From the above explanation, a general model of intramolecular energy transfer and relaxation processes of three $Eu(ClC_6H_4CO_2)_3{\cdot}H_2O$ are showed in Fig. 4. The energy levels of lowest triplet states of Eu(*p*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ and Eu(*m*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ are below that of benzoic acid, while that of Eu(*o*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ is above 24,800 cm^{-1}. Especially, the effect of *p*-substituent on energy level is the most remarkable.

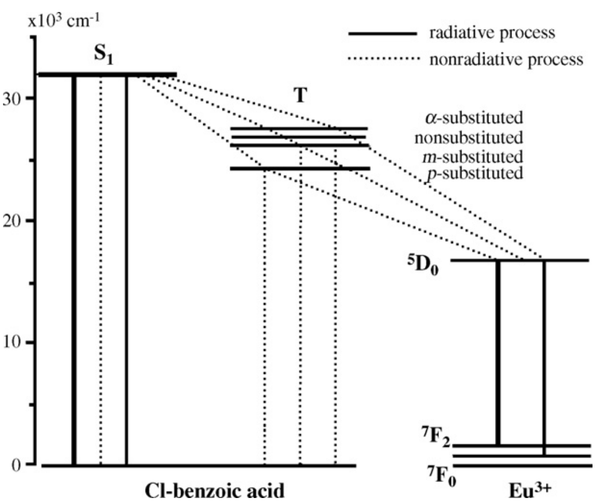

Fig. 4. Models of intramolecular energy transfer processes of Eu(*p*-$ClC_6H_4CO_2)_3{\cdot}H_2O$, Eu(*o*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ and Eu(*m*-$ClC_6H_4CO_2)_3{\cdot}H_2O$.

3.4.2. *Effects of chlorine substituent on the energy transfer and relaxation processes*

The PA phase represents the lifetime of triplet state of ligand. The smaller the phase is, the shorter the lifetime of triplet state of ligand should be. From the models in Fig. 4, the energy gap (7500 cm^{-1}) between the lowest triplet state of benzoic acid and excited state of Eu^{3+} is not most suitable for intramolecular transfer because it is rather big. The *p*-chlorine substitution makes the energy gap much smaller than before, so the energy of Eu(*p*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ may transfer from the lowest triplet state of ligand to the excited state of central ion much more effective and the lifetime of the triplet state becomes shorter. While the *o*-chlorine substitution makes the process more difficult. More energy in this complex may transfer from triplet state to ground state directly instead of to the central ion. The triplet state of Eu(*o*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ is metastable and its lifetime is longer than that of the any other complexes. These inferences also explain why the PA amplitude of Eu(*o*-$C_1C_6H_4CO_2)_3{\cdot}H_2O$ at 335 is the strongest and the luminescence intensity of central ion is the smallest. For Eu(*m*-$ClC_6H_4CO_2)_3{\cdot}H_2O$, because the decrease of triplet state level attributed to *m*-substitution is much smaller than *p*-substitution, the PA phase, the PA amplitude of ligand and the luminescence intensity of central ion of Eu(*m*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ are between those of the other two samples. All of these inferences have been proved by the experimental results mentioned in Figs. 1 and 2 and Table 1.

From the results above, the models of intramolecular energy transfer processes of $Eu(ClC_6H_4CO_2)_3{\cdot}H_2O$ are established. The effects of chlorine substituent on the energy transfer are proved and explained by PA phase and luminescence spectra.

4. Conclusions

The PA amplitude and luminescence spectra of three $Eu(ClC_6H_4CO_2)_3{\cdot}H_2O$ with different chlorine substituents are measured and the PA phase shifts of the different complexes are calculated. The conjugative effects of chlorine substituent and the reinforcing effects between carbonyl group and substituent on benzene ring make the triplet state energy level of each sample different from that of unsubstituted benzoic acid. Because of the best suitability of the energy gap between the lowest triplet state of ligand and the resonance level of Eu^{3+}, the intramolecular energy transfer in Eu(*p*-$ClC_6H_4CO_2)_3{\cdot}H_2O$ can proceed effectively. After the investigations of both photoacoustic and luminescence spectra, the models of intramolecular energy transfer processes are established and applied to explain the effects of chlorine substituent on the energy transfer.

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