



# Spectra, energy levels, and energy transition of lanthanide complexes with cinnamic acid and its derivatives



Kaining Zhou, Zhongshan Feng, Jun Shen, Bing Wu, Xiaobing Luo, Sha Jiang, Li Li, Xianju Zhou \*

College of Science, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

## ARTICLE INFO

### Article history:

Received 16 June 2015

Received in revised form 15 December 2015

Accepted 11 January 2016

Available online 12 January 2016

### Keywords:

Cinnamic acid

Lanthanide complex

Luminescence

Energy level

Triplet-state

## ABSTRACT

High resolution spectra and luminescent lifetimes of 6 europium(III)-cinnamic acid complex  $\{[Eu_2L_6(DMF)(H_2O)] \cdot nDMF \cdot H_2O\}_m$  ( $L =$  cinnamic acid **I**, 4-methyl-cinnamic acid **II**, 4-chloro-cinnamic acid **III**, 4-methoxy-cinnamic acid **IV**, 4-hydroxy-cinnamic acid **V**, 4-nitro-cinnamic acid **VI**;  $DMF = N, N$ -dimethylformamide,  $C_3H_7NO$ ) were recorded from 8 K to room temperature. The energy levels of  $Eu^{3+}$  in these 6 complexes are obtained from the spectra analysis. It is found that the energy levels of the central  $Eu^{3+}$  ions are influenced by the nephelauxetic effect, while the triplet state of ligand is lowered by the  $p-\pi$  conjugation effect of the para-substituted functional groups. The best energy matching between the ligand triplet state and the central ion excited state is found in complex **I**. While the other complexes show poorer matching because the gap of  $^5D_0$  and triplet state contracts.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

The study of lanthanide complexes with organic ligands is constantly attracting research interest, due to the potential application of biosensor, electronic luminescent materials and anti-cancer drugs [1–10]. The choice of the ligands is very critical for the structure and properties of the complexes. And cinnamic acid has similar structure with benzoic acid except for one more  $C=C$ . Therefore, cinnamic acid with the half-rigid structure is feasible to act as ligands for metal-organic complex. These compounds are interesting in a wide range of applications [11–14]. Ga-Lai Law et al. have synthesized fifteen dipolar polymeric lanthanide complexes with trans-cinnamic acid as ligands. Strong second harmonic generation nonlinear optical activity has been observed in these compounds [15]. Cinnamic acid and its derivatives are also introduced to lanthanide complex polymer nanoparticles, and effective energy transfer is revealed from the ligand to the central metal ions. The fluorescent functional materials might be useful as bio-probe [16].

The synthesis, crystal structure of cinnamic acid europium complexes along with the rough optical properties at room temperature have been reported in our previous work [17,18]. The corresponding formulae and the coordination information of these complexes are summarized in Table 1. The coordination environment of the central  $Eu^{3+}$  ions which is published in ref. 17 could also be found in the Supporting information as Fig. S1. In this work, high resolution emission and excitation spectra of these complexes at various temperatures from 8–300 K have been recorded and analyzed carefully. Energy levels of  $Eu^{3+}$  ion

in these complexes were obtained based on the spectra. The factors which influence the energy levels are investigated as well. The relationship between ligand design and the transition energy for the central europium ion in the crystals was studied. Furthermore, energy transition from the ligand to central metal ions was discussed. Results show that the para-substituted group with different Hammett substituent constant  $\sigma_p$  could efficiently modulate the excitation band and triplet state of the complexes, and impact the energy transition within the complexes.

## 2. Experimental

Synthesis of the complexes could be found in our previous work [17, 18]. The fine powders of these complexes were measured by powder X-ray diffraction on an X-ray Diffractometer (XD-2, Beijing Purkinje General Instrument Co. Ltd.) with  $Cu-K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 36 kV and 20 mA. The scan rate was  $2^\circ/\text{min}$  and the scan range was between  $10^\circ$  and  $80^\circ$ . The results of the powder X-ray diffraction are shown in Fig. S2 in the Supporting information. The FT-IR spectra of the complexes were recorded in the region of  $4000\text{--}400 \text{ cm}^{-1}$  on an FT-IR spectrometer (Perkin Elmer spectrum 65) by the KBr pelleting technique. The FT-IR spectra and the corresponding assignments are shown in Fig. S3 and Table S1 respectively. The TG curves of the complexes (see Fig. S4 in the Supporting information) were recorded on a TA thermogravimetric system. Samples of about 7 mg were used in platinum crucibles, heated at a rate of  $20^\circ\text{C}/\text{min}$  in  $N_2$  flowing at a rate of 20 mL/min at ambient pressure. Absorption spectra of the lanthanide complexes and the corresponding ligand in ethanol solution at a concentration of  $10^{-4} \text{ M}$  were measured on a double-beam spectrometer (TU 1901,

\* Corresponding author.

E-mail address: [zhouxj@cqupt.edu.cn](mailto:zhouxj@cqupt.edu.cn) (X. Zhou).

**Table 1**  
Structure information of the complexes.

Complex	Para-substituent	Formula of complex	Space group	Z <sup>a</sup>	Site sym. <sup>b</sup>	No. sites <sup>c</sup>	C. N. <sup>d</sup>
II	CH <sub>3</sub>	{[Eu <sub>2</sub> (C <sub>10</sub> H <sub>9</sub> O <sub>2</sub> ) <sub>6</sub> (DMF)(H <sub>2</sub> O)]·2DMF·H <sub>2</sub> O} <sub>n</sub>	P $\bar{1}$ (no. 2)	2	C <sub>1</sub>	2	9
III	Cl	{[Eu <sub>2</sub> (C <sub>9</sub> H <sub>6</sub> ClO <sub>2</sub> ) <sub>6</sub> (DMF)(H <sub>2</sub> O)]·2DMF·H <sub>2</sub> O} <sub>n</sub>	P $\bar{1}$ (no. 2)	2	C <sub>1</sub>	2	9
VI	NO <sub>2</sub>	Eu <sub>2</sub> (C <sub>9</sub> H <sub>6</sub> NO <sub>4</sub> ) <sub>6</sub> (DMF) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ·2DMF	P $\bar{1}$ (no. 2)	2	C <sub>1</sub>	1	9
I	H	Eu <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>6</sub> (DMF) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	–	–	–	–	–
IV	OCH <sub>3</sub>	Eu <sub>2</sub> (C <sub>10</sub> H <sub>9</sub> O <sub>3</sub> ) <sub>6</sub> (DMF) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	–	–	–	–	–
V	OH	Eu <sub>2</sub> (C <sub>9</sub> H <sub>7</sub> O <sub>3</sub> ) <sub>6</sub> (DMF) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	–	–	–	–	–

<sup>a</sup> Number of Eu<sup>3+</sup> in the Bravais cell.

<sup>b</sup> Site symmetry of Eu<sup>3+</sup>.

<sup>c</sup> Number of distinct Eu<sup>3+</sup> sites.

<sup>d</sup> Total coordination number of Eu<sup>3+</sup>.

Purkinje General Instrument Co. Ltd.) with quartz liquid sample cell. The emission and excitation spectra of the powder samples were recorded at different temperatures, by a spectrophotometer (FLSP 920, Edinburgh Instruments) equipped with a 450 W xenon lamp and PMT detector (R9287 PMT, Shimadzu). The luminescence lifetime experiments were carried out on the same instrument with pulsed xenon lamp. A closed cycle refrigerator system (CCS 150, Janis), and temperature controller (9700, Scientific Instruments) were utilized to control the sample temperature.

### 3. Results and discussion

#### 3.1. Excitation and emission spectra

From our previous work, the crystal structure of these complexes was found to be one dimensional zigzag chain or dimer. The coordination environment of europium(III) was alike, which could be described as distorted monocapped square antiprism [17,18]. Fig. 1 presents the excitation spectra of two representative complexes from 8 K to room temperature. It is shown that the complexes bear both indirect and direct excitations. Indirect excitation is the ligand to metal charge transfer band (LMCT) from 280–400 nm, overlapping with ligand absorption. Direct excitation is the characteristic f–f transition of europium(III). The detailed assignments of the excitation spectra are labeled in the figure. The shape and the position of the spectra profiles do not show dramatic change with temperature. The excitation intensity increases as temperature lowers; it illustrates that the thermal population is excluded in this case and the non-radiative relaxation decreases at low temperature. The ligand excitation band overlapped with LMCT band sees a blue shift as temperature decreases.

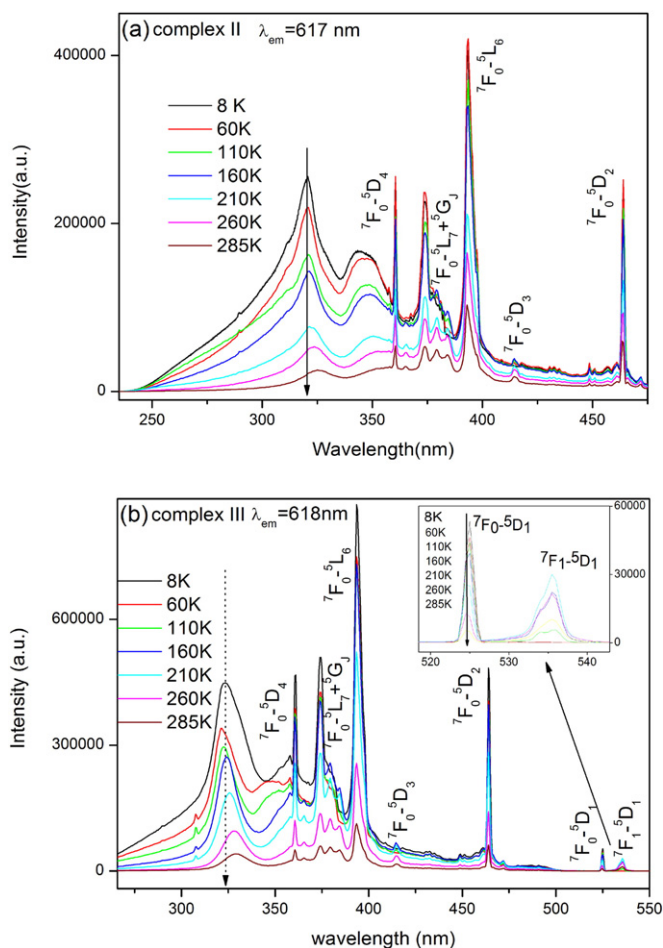
In order to investigate the effect of the para-substituted functional group, excitation spectra of these six complexes at 8 K are compared as shown in Fig. 2. The characteristic f–f transitions of Eu<sup>3+</sup> central ions do not show obvious change except for the intensity because of shielding effect of f-orbital. However, the shape and position of the broad LMCT and ligand excitation band show a sensitive response to the para-substituted groups. First, the intensities of the LMCT band in complexes II (x = CH<sub>3</sub>) and IV (x = OCH<sub>3</sub>) are much weaker than others, with integral area of this broad band being only 1/3 of complex I. Second, the broad band shifts with the electronic effect of the ligand. This phenomenon should be related to the electronic effect of substituted groups, which will be discussed later.

In the emission spectrum shown in Fig. 3, europium intra-configurational transitions of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> (J = 0, 1, 2, 3, 4) are observed. The strongest emission transition is the forced electric dipole allowed transition <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub>. The transition of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>3</sub> is very weak. From the single crystal X-ray diffraction data as reported in our previous work [17,18], there are two non-equal crystal Eu<sup>3+</sup> ions due to different coordination environments. However, due to the low resolution of the spectrum at room temperature, splitting of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub> transition

originating from two different coordination Eu<sup>3+</sup> ions was not observed in refs. [17,18]. In this study, splitting of this transition, at 579.8 and 579.9 nm is recorded at a low temperature of 8 K in complex I, as shown in the inset of Fig. 3(a). But the splitting gap is very narrow, the energy difference between these two peaks is only 3 cm<sup>-1</sup>, which implies that the difference between these two coordination environments of europium ion is relatively small [19].

#### 3.2. Energy levels of Eu<sup>3+</sup> in the complexes

In our previous work, the rough optical properties were studied by the spectra recorded at room temperature. But the energy levels and



**Fig. 1.** Representative excitation spectra at various temperatures of complex II (a) and complex III (b).

Download English Version:

<https://daneshyari.com/en/article/1229140>

Download Persian Version:

<https://daneshyari.com/article/1229140>

[Daneshyari.com](https://daneshyari.com)