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# Optical properties of a tetradentate bis(β-diketonate) europium(III) complex

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#### Abstract

Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O, an europium complex chelated with bis( $\beta$ -diketone), was synthesized. Its properties have been investigated by absorption spectrum, emission spectrum and luminescence lifetime measurement. The complex displays strong red luminescence upon irradiation at the ligand band around 355 nm, which indicates that the bis- $\beta$ -diketonate ligand BPOPB is an efficient sensitizer. The Judd–Ofelt parameters obtained from the emission spectrum of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O have been used to calculate the total spontaneous emission probabilities (*A*), the radiative lifetime ( $\tau_{rad}$ ), the fluorescence branching ratio ( $\beta$ ) and the stimulated emission cross-sections ( $\sigma$ ). The luminescence lifetimes are determined to be 402 and 169 µs for Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O and Eu(DBM)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, respectively. The relationship between the structures of rare-earth complexes and luminescence lifetimes was analyzed. The radiative properties reveal that Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O is potential to be an efficient luminescent material. © 2007 Elsevier B.V. All rights reserved.

Keywords:  $bis(\beta$ -Diketonate) Europium(III) complex; Luminescence; Radiative properties; Judd–Ofelt theory

#### 1. Introduction

In recent years, optical properties of lanthanide ion complexes continue to be an active area of research. Luminescence of lanthanide ions usually originates from the forbidden character of their intra-4f electronic transitions, which results in long lifetimes of the excited states of lanthanide ions but unfortunately result in low absorption coefficients [1–3]. For this reason, the design of efficient lanthanide complexes has become an important research goal, working with many different classes of ligands, such as amidic ligands [4],  $\beta$ diketones [5,6], etc. In the efficient lanthanide complexes, the excited state of a luminescent lanthanide(III) ion is generally populated by energy transfer from the triplet state of the ligand (the sensitizer). One approach to increase the luminescence output signal is to introduce ligands with multiple binding sites [5,7]. 1,3-bis(3-phenyl-3-oxopropanoyl)benzene (BPOPB), a bis-( $\beta$ -diketonate) ligand, was chosen for the formation of dinuclear lanthanide complexes. Ligand BPOPB bears two benzoyl  $\beta$ -diketonate sites joined by a 1,3-phenylene spacer unit. The 1,3-phenylene spacer is ideal for formation of helicate metal complexes. At the same time, dinuclear lanthanide diketonate complexes have received scant attention. Eu<sup>3+</sup> is a well-known rare-earth ion with high red fluorescence intensity at 613 nm ( ${}^5D_0 \rightarrow {}^7F_2$ ) and has attracted a lot of attention because of its potential applications in optoelectronics.

It is generally believed that Judd–Ofelt theory can be used to provide insight into the nature of the chemical bonding presented in the rare-earth complexes because the intensity parameter  $\Omega_2$ is sensitive to the changes of the chemical properties and the ligand field around the rare-earth ion centers. At the same time,

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Judd–Ofelt theory can be used to estimate quantitatively the optical properties of rare-earth ions [8–10].

Due to these reasons, in this work,  $Eu_2(BPOPB)_3H_2O$ , an europium complex chelated with  $bis(\beta$ -diketone), was synthesized and its emission spectrum, luminescence lifetime were measured. The relationship between the structures of rareearth complexes and luminescence lifetimes was analyzed. The radiative properties, such as transition probabilities, emission cross-section, fluorescence branching ratios and radiative lifetime were calculated and analyzed according to the Judd–Ofelt analysis based on the emission spectrum.

## 2. Experimental

The ligand, 3-bis(3-phenyl-3-oxopropanoyl)benzene, was obtained by the Claisen condensation following a modification of the reported preparation [7]. A solution of dimethyl isophthalate (0.02 mol) and acetophenone (0.01 mol) in freshly distilled tetrahydrofuran (60 ml) was added to NaH (0.06 mol) at 0–5 °C. The mixture was stirred at this temperature for 2 h and for a further 2 h at room temperature. The product was recrystallized from a mixture solvent of chloroform and petroleum ether (1:1). C<sub>24</sub>H<sub>18</sub>O<sub>4</sub> found: C, 77.7; H, 4.81%, requires C, 77.8; H, 4.86%. Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O was prepared by reacting BPOPB with EuCl<sub>3</sub> (2:3) in ethanol. The mixture was washed with CHCl<sub>3</sub>, methanol, H<sub>2</sub>O and ether and dried under vacuum to give the desired product (Found: C, 60.4; H, 3.25%. C<sub>72</sub>H<sub>48</sub>O<sub>12</sub>Eu<sub>2</sub>·H<sub>2</sub>O requires C, 60.6; H, 3.53%).

Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. UV–vis absorption spectrum was recorded at room temperature with a Shimadzu UV-2401PC. The emission spectrum was analyzed with a 44 W monochromator equipped with a Hamamatsu R456 photomultiplier. The luminescence decay curve was recorded by a Tektronix TDS2024 oscilloscope interfaced with a computer.

## 3. Results and discussions

## 3.1. Absorption of Eu chelates in DMSO

Fig. 1 shows the absorption spectrum of  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O in DMSO at room temperature. The spectrum exhibited intense band with  $\lambda_{max} = 360$  nm ( $\varepsilon = 1.4 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) for Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O, which was attributed to singlet–singlet  $\pi \rightarrow \pi^*$  of the ligand absorption. As it is known that the absorption spectrum of BPOPB exhibited intense bands with  $\lambda_{max} = 357$  nm, the red shift shows the formation of the coordinating bond between Eu<sup>3+</sup> and BPOPB [11].

#### 3.2. Emission spectrum of $Eu_2(BPOPB)_3H_2O$

The emission spectrum of  $Eu_2(BPOPB)_3H_2O$  is shown in Fig. 2.

The emission spectrum was recorded from 570 to 720 nm under excitation at 355 nm which is close to the maximum absorption of  $Eu_2(BPOPB)_3H_2O$ . As seen from Fig. 3, the



Fig. 1. Absorption spectrum of  $1.0\times 10^{-5}\,mol\,dm^{-3}\,\,Eu_2(BPOPB)_3H_2O$  in DMSO.



Fig. 2. Emission spectrum of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O.



Fig. 3. The most possible energy transfer mechanism for  $Eu_2(BPOPB)_3H_2O$ . ISC: intersystem crossing and ET: intramolecular energy transfer.

$\mathbf{I} = \mathbf{I} + $						
Emission transition	$\nu$ (cm <sup>-1</sup> )	$A_{\rm ed}  ({\rm s}^{-1})$	$A_{\rm md}~({\rm s}^{-1})$	$A(s^{-1})$	β (%)	$\sigma~(10^{-22}\mathrm{cm}^2)$
${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{0}$	17271	0	0	0	0	0
${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	16920	0	66.50	66.50	6.88	5.60
${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	16313	846.63	0	846.63	87.65	175.30
${}^{5}D_{0} \rightarrow {}^{7}F_{3}$	15337	0	0	0	0	0
$^{5}D_{0} \rightarrow ^{7}F_{4}$	14205	52.82	0	52.82	5.47	8.61
$A_{\rm T}  ({\rm s}^{-1})$				965.95		

Table 1 Radiative properties of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O

Radiative lifetime  $\tau_{rad}$  (ms) = 1.035.

effective absorption populates the excited singlet  $S_1$  from the ground singlet state  $S_0$  in the ligand of BPOPB. Competing with the fast intersystem crossing (ISC) conversion are organic fluorescence and non-radiative deactivation of  $S_1$ . Intramolecular energy transfers (ET) from ligands lead to a population of  ${}^5D_1$  level (lifetime <4 µs [12]) and long-lived metastable  ${}^5D_0$  level of the Eu<sup>3+</sup> ion giving a rise of the Eu<sup>3+</sup> emission to the ground multiplet  ${}^7F_J$  (J=0-4). Therefore, five emission peaks are centered at 581, 595, 613, 652, 703 nm, and can be assigned to the  ${}^5D_0 \rightarrow {}^7F_0$ ,  ${}^5D_0 \rightarrow {}^7F_1$ ,  ${}^5D_0 \rightarrow {}^7F_2$ ,  ${}^5D_0 \rightarrow {}^7F_3$ , and  ${}^5D_0 \rightarrow {}^7F_4$ , respectively.

#### 3.3. Judd–Ofelt analysis

It is well-known that the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2,4,6}$  transitions of Eu<sup>3+</sup> are allowed by induced electric dipole mechanisms due to selection rules. According to the Judd–Ofelt theory, the spontaneous emission probability of an electric dipole transition between initial *J* manifold  $|(S, L) J\rangle$  to terminal manifold  $|(S', L') J'\rangle$  is given by:

$$A_{\rm ed} = A[(S, L)J; (S', L')J'] = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} S_{\rm ed}$$
  
=  $\frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \sum_{t=2,4,6} \Omega_t |\langle (S, L)J \| \mathbf{U}^{(t)} \| (S', L')J' \rangle|^2$  (1)

where *h* is the Plank's constant, *m* is the mass of the electron, *c* is the velocity of light, *n* is the refractive index of the medium,  $\nu$  is the wavenumber of the transition, *J* is the total angular momentum of the ground state and the  $||\mathbf{U}^{(t)}||^2$  are the squared reduced matrix elements of the rank t = 2,4,6. The squared reduced matrix elements  $\langle {}^{5}\mathbf{D}_{0}||\mathbf{U}^{(2)}||^{7}\mathbf{F}_{2} \rangle = 0.0032$  and  $\langle {}^{5}\mathbf{D}_{0}||\mathbf{U}^{(2)}||^{7}\mathbf{F}_{4} \rangle = 0.0023$  in Eq. (1) were taken from ref. [13].

It is well-known that the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  of Eu<sup>3+</sup> ion is a magnetic dipole transition which is independent of the environment and can be used as a reference. The spontaneous emission probability of magnetic dipole transition  $A_{md}$  is [14]:

$$A_{\rm md} = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} n^3 S_{\rm md}$$
(2)

 $S_{\rm md}$  refers to the strength of the magnetic dipole line strength of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, which is a constant and independent of the medium.

Due to selection rules and the unique nature of transition intensities of  $\text{Eu}^{3+}$  ion, any one of the  $||\mathbf{U}^{(t)}||^2$  parameters decided the intensities of the transition since the remaining two are zero [14]. With the help of Eqs. (1) and (2) and inserting the  $||\mathbf{U}^{(t)}||^2$ 

of Eu<sup>3+</sup> ion into Eq. (1), the  $\Omega_t$  can be determined from the ratios of intensities of  ${}^5D_0 \rightarrow {}^7F_{2,4,6}$  transitions to the intensity of  ${}^5D_0 \rightarrow {}^7F_1$  transition as follows:

$$\frac{\int I_J(\nu) d\nu}{\int I_{md}(\nu) d\nu} = \frac{A_J}{A_{md}} = \frac{e^2}{S_{md}} \frac{\nu_J^3}{\nu_{md}^3} \frac{(n^2 + 2)^2}{9n^2} \Omega_t \|\mathbf{U}^{(t)}\|^2$$
(3)

Using Eq. (3), the Judd–Ofelt parameters have been determined and the values of  $\Omega_2$  and  $\Omega_4$  are  $19.25 \times 10^{-20}$  and  $2.51 \times 10^{-20}$  cm<sup>2</sup>, respectively. The  $\Omega_6$  intensity parameter was not determined because the  ${}^5D_0 \rightarrow {}^7F_6$  transition could not be experimentally detected. This indicates that the  $\Omega_6$  is not important here.

## 3.4. Radiative properties of $Eu_2(BPOPB)_3H_2O$

After the Judd–Ofelt parameters have been determined, the radiative properties, such as spontaneous transition probability of electric dipole transition  $A_{ed}$  and magnetic dipole transition  $A_{md}$ , the total transition probability  $A_{T}$ , the fluorescence branching ratio  $\beta$ , the stimulated emission cross-section  $\sigma$  and the radiative lifetime  $\tau_{rad}$ , can be calculated with the obtained emission spectrum and are presented in Table 1.

The luminescence decay curve of  $Eu_2(BPOPB)_3H_2O$  monitored at 613 nm, which was shown in Fig. 4, was fitted to a single



Fig. 4. The decay curve of (a):  $Eu_2(BPOPB)_3H_2O$  and (b):  $Eu(DBM)_3(H_2O_2)$  (solid: experiment decay curve and dotted: fitting decay curve).

exponential of the form:

$$I(t) = I(0) \exp\left(\frac{-t}{\tau}\right) \tag{4}$$

where I(t) is the intensity at time t after the excitation flash, I(0) is the initial intensity at t = 0 and  $\tau$  is the luminescence lifetime. In our case there is only one type of chromophore BPOPB, thereby single exponential decay function is used to extract the lifetime, which is about 402 µs.

As the energy gap between  ${}^5D_0$  and  ${}^7F_J$  levels is very large (~12,300 cm<sup>-1</sup>), non-radiative decay due to multiphonon relaxation is negligible. The difference between predicted and experimental lifetimes may be due to Eu<sup>3+</sup> ion–Eu<sup>3+</sup> ion interaction.

The non-radiative decay rates in the present Eu chelate are estimated using the following expression [14,15]

$$W_{\rm nr} = \frac{1}{\tau_{\rm exp}} - A_{\rm rad} \tag{5}$$

The non-radiative decay rate for  ${}^{5}D_{0}$  of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O is 1522 s<sup>-1</sup>.

#### 4. Discussions

#### 4.1. Emission spectrum of $Eu_2(BPOPB)_3H_2O$

It is well-known that  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup> ion is a hypersensitive one ( $\Delta J = 2$ ) and its intensity is very sensitive to the local environment in which the Eu<sup>3+</sup> ion is located. Therefore, the emission spectrum can provide some information about the microstructure.

The presence of only one  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  line indicates that the Eu<sup>3+</sup> ion occupies only a single site and a single chemical environment exists around it [16]. Compared to those of other transitions, the much stronger intensity of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  indicates that the ligand field surrounding the Eu ion is highly polarizable and the Eu<sup>3+</sup> ion is in a site without a center of inversion [17], and this will be discussed further in the following sections.

The emission spectrum was recorded under excitation at 355 nm, which matches the corresponding absorption spectrum, confirming that energy transfer takes place from the ligand to the Eu(III) ion. Indeed, the energy of the ligand-centered triplet state is 20,408 cm<sup>-1</sup> [7], which is around 3000 cm<sup>-1</sup> above the <sup>5</sup>D<sub>0</sub> level of Eu<sup>3+</sup>, confirming the suitability of the ligand BPOPB as a sensitizer for Eu<sup>3+</sup>.

### 4.2. Judd–Ofelt analysis

The large value of  $\Omega_2$  indicates the asymmetric environment of Eu<sup>3+</sup> and the presence of covalent bonding between the Eu<sup>3+</sup> ions and the surrounding ligands. The much stronger hypersensitive transition  ${}^5D_0 \rightarrow {}^7F_2$  accounts for such  $\Omega_2$ values. These results show, in spite of having three symmetric BPOPB ligands, Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O has no center of symmetry due to one coordinated water. The asymmetry of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O is confirmed by the splitting of  ${}^5D_0 \rightarrow {}^7F_1$  transition into two components (Fig. 2), though the high-energy component has not been well-resolved. At the same time, the  $\beta$ -diketonates are expected to have covalency in the compounds.

## 4.3. Radiative properties of $Eu_2(BPOPB)_3H_2O$

In our previous study, the lifetime of  $Eu(DBM)_3(H_2O)_2$ was found to be 169 µs (Fig. 4). The luminescence lifetime of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O is much longer than that of  $Eu(DBM)_3(H_2O)_2$ . The energy of the triplet state of BPOPB and DBM are almost the same, the triplet state differences are not significant. Therefore, the much longer luminescence lifetime of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O is attributed to the effect of an additional Eu<sup>3+</sup> lumophor in the dinuclear complexes, which enhances its luminescence efficiency. At the same time, Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O only has one water molecule in the inner coordination sphere of  $Eu^{3+}$ , less than  $Eu(DBM)_3(H_2O)_2$ , which decreases the non-radiative dissipation of energy on the high-energy O-H vibrations too. The non-radiative decay rates can be calculated using Eq. (5), and the values for  ${}^{5}D_{0}$ of Eu(DBM)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O are 6006 and  $1522 \text{ s}^{-1}$ , respectively. From these results, it is clear that nonradiative decay rate of Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O is much smaller than that of  $Eu(DBM)_3(H_2O)_2$ .

The luminescence lifetime of the transition involved is an important parameter in consideration of the pumping requirement for the threshold of laser action and the luminescence lifetime of  $Eu_2(BPOPB)_3H_2O$  is comparable with those of europium laser glasses [18]. At the same time, the decay curve can be fit with a single exponential, which indicates that there is only one site symmetry from the  $Eu^{3+}$  ion [16].

From Table 1, the transition  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  showed the highest  $\beta$  value. It has already established that an emission level with  $\beta$  value near 50% becomes a potential laser emission transition [19]. The stimulated emission cross-section of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is  $175.3 \times 10^{-22}$  cm<sup>2</sup> which is much higher than Eu<sup>3+</sup> doped tellurite glass and fluorophosphates glass [20]. In addition to that, the luminescence lifetime of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is comparable with those of europium laser glasses. All these showed that Eu<sub>2</sub>(BPOPB)<sub>3</sub>H<sub>2</sub>O can be considered as an efficient luminescent material.

## 5. Conclusion

In conclusion,  $Eu_2(BPOPB)_3H_2O$ , an europium complex chelated with  $bis(\beta$ -diketone), was synthesized. It displays strong red luminescence upon irradiation at the ligand band around 355 nm, confirming the suitability of the ligand BPOPB as a sensitizer for  $Eu^{3+}$ . The Judd–Ofelt parameters,  $\Omega_2$  and  $\Omega_4$  were obtained from the emission spectrum of  $Eu_2(BPOPB)_3H_2O$ . The relationship between the structures of rare-earth complexes and luminescence lifetimes was analyzed. The evaluation of the radiative properties of  $Eu_2(BPOPB)_3H_2O$ showed that it has potential to be an efficient luminescent material. The optical properties of  $Eu_2(BPOPB)_3H_2O$  can be improved, suggesting  $H_2O$  is substituted by synergetic ligands, which have lower vibrational frequencies, such as Phen, TOPO, TPPO, etc. This work is undergoing.

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