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Photoluminescence behavior of europium (III) complexes containing 1-(4-tert-butylphenyl)-3-(2-naphthyl)-propane-1,3-dione ligand



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HIGHLIGHTS

- Synthesis of europium (III) complexes with β-diketone ligand and 2,2dipyridine or 1.10-phenanthroline.
- Photoluminescence properties of europium (III) complexes.
- Analysis of the intensity parameters
 (Ω_t), the lifetime (τ) and the luminescent quantum yield (η).

G R A P H I C A L A B S T R A C T



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ABSTRACT

Three novel europium complexes with 1-(4-*tert*-butylphenyl)-3-(2-naphthyl)-propane-1,3-dione (TNPD) and 2,2-dipyridine (Bipy) or 1,10-phenan-throline (Phen) were synthesized and confirmed by FT-IR, ¹H NMR, UV-vis absorption and elemental analysis. Photoluminescence behavior of complexes Eu(TNPD)₃, Eu(TNPD)₃·Bipy and Eu(TNPD)₃·Phen were investigated in detail. Their emission spectra exhibited the characteristic emission bands that arise from the ${}^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transitions of the europium ion in solid state. Meanwhile, the results of their lifetime decay curves indicated that only one chemical environment existed around the europium ion. The intrinsic luminescence quantum efficiency (η) and the experimental intensity parameters (Ω_t) of europium complexes were determined according to the emission spectra and luminescence decay curves in solid state. The complex Eu(TNPD)₃·Phen showed much longer lifetime (τ) and higher luminescence quantum efficiency (η) than complexes Eu(TNPD)₃ and Eu(TNPD)₃·Bipy.

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Introduction

Europium (III) complexes with β -diketone ligands have been attracted attention in last decades due to their long fluorescence lifetime and narrow emission bands in the visible region [1,2]. These spectroscopic properties have been utilized in material science such as electroluminescent materials [3], sensory materials [4], laser materials and optical fibers [5]. The β -diketone is one of the important "antenna" ligands. As light conversion materials,

ultraviolet light is firstly absorbed by β -diketone ligands, and then the absorbed energy is transferred from the lowest triplet state energy level of the ligand to the resonance level of europium ions and makes them send out their characteristic light [6]. Recently, the design, synthesis and photoluminescence properties of many new europium complexes with β -diketone ligands have been reported [7–9].

With the purpose of developing novel optical materials, three new europium (III) complexes with 1-(4-*tert*-butyl-phenyl)-3-(2-naphthyl)-propane-1,3-dione (TNPD) and 2,2-dipyridine (Bipy) or 1,10-phenanthroline (Phen) were synthesized. Their structures were confirmed by elemental analysis, FT-IR, ¹H NMR, UV-vis

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absorption and ESI-MS spectroscopy. Their photoluminescence properties have also been investigated by photoluminescent spectroscopy. In addition, according to their photoluminescence spectra and lifetime measurement, the Judd–Ofelt intensity parameters (Ω_t), radiative (A_{rad}), nonradiative (A_{nrad}) rates and the photoluminescent quantum efficiency (η) were calculated and analyzed.

Experimental

Apparatus and measurements

Europium trichloride ethanol solution was obtained by dissolving Eu_2O_3 in concentrated hydrochloric acid. Other chemicals were of analytical grade and used without further purification. The europium content was determined by the complexometric titration with EDTA. Elemental analysis (C, H, N) was performed on a Perkin–Elmer 2400 elemental analyzer. Infrared spectra were recorded on a Nicolet FTIR 5700 spectrophotometer with KBr pellets. ¹H NMR spectra were measured on an Avance IIITM 300 MHz NB Digital NMR spectrometer in CDCl₃ solution with TMS as internal standard. Electrospray ionization mass spectra (ESI-MS) were determined with a Finnigan LCQ Advantage Max spectrometer. Emission spectra and fluorescence lifetimes were measured on a Varian Cary Eclipse fluorescence spectrometer. The UV–vis spectra were obtained with Hitachi U-3010 spectrometer.

Synthesis of β -diketone ligand

1-(4-tert-Butylphenyl)-3-(2-naphthyl)-propane-1,3-dione (TNPD): the mixture of 2-acetylnaphthalene (6.80 g, 0.04 mol), ethyl 4-tert-butylbenzoate (7.68 g, 0.04 mol), NaNH₂ (1.95 g, 0.05 mol) and toluene (50 ml) was heated to 80 °C under stirring and maintained for 6 h. The reaction mixture was cooled to room temperature and acidified with dilute hydrochloric acid, and then extracted with toluene. The toluene layer was washed with a saturated NaHCO₃ solution, dried over anhydrous MgSO₄ and the solvent removed by evaporation. The solid residue was recrystallized from ethanol to obtain β-diketone TNPD. Pale yellow crystals, yield 65%, mp 122–123 °C; IR (KBr): v 3500(w), 3082(w), 2962(s), 2860(w), 1628(s), 1598(m), 1528(s), 1499(m), 1460(m), 1365(m), 1297(m), 1266(m), 1192(s), 1110(s), 1013(s), 910(s), 845(s), 792(s), 756(s) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.37 (s, 9H, C(CH₃)₃), 4.70 (s, 0.14H, keto CH₂), 7.00 (s, 1H, enol CH), 7.52-7.59 (m, 4H, Ar-H), 7.95-8.00 (m, 6H, Ar-H), 8.55 (s, 1H, Ar-H), 17.10 (br s, 1H, enol OH) ppm; ESI-MS: *m*/*z* 331.05 [M + 1]⁺; Anal. Calcd. for C₂₃H₂₂O₂: C, 83.60; H, 6.71; Found C, 83.70; H, 6.69.

Synthesis of complexes

Eu(TNPD)₃ (**C1**): to a solution of TNPD (0.99 g, 3 mmol) in 30 ml ethanol, 1 N aqueous NaOH (0.12 g, 3 mmol) was added followed by an ethanol solution containing 1 mmol EuCl₃. The reaction mixture was stirred at 60 °C for 5 h and yellow precipitate was formed. The product was purified by washing for several times with deionized water and ethanol and dried in vacuum at 80 °C for 48 h to obtain the complex **C1**. Yield: 73%. IR ν (KBr): 3056(m), 2962(s), 2867(m), 1600(s), 1524(s), 1498(s), 1463(s), 1416(s), 1392(s), 1363(s), 1344(s), 1299(s), 1269(s), 1194(s), 789(s), 756(s), 472(m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.37 (s, 27H, C(CH₃)₃), 3.05 (s, 3H, C=CH), 6.42 (d, 6H, Ar-H, *J* = 7.8 Hz), 6.60 (d, 6H, Ar-H, *J* = 7.5 Hz), 7.72–7.80 (m, 18H, Ar-H), 8.51 (s, 3H, Ar-H) ppm; Anal. Calcd. for EuC₆₉H₆₃O₆: C, 72.68; H, 5.57; Eu,13.33; Found C, 72.42; H, 5.50; Eu, 13.51.

Eu(TNPD)₃·Bipy (**C2**): same procedure as for Eu(TNPD)₃ (**C1**), but the reaction mixture with TNPD (0.99 g, 3 mmol), Bipy (0.13 g, 1 mmol) and 1 mmol EuCl₃. The complex **C2** was obtained as a yellow power, yield 70%. IR *v* (KBr): 3056(m), 2962(s), 2867(m), 1599(s), 1548(s), 1523(s), 1498(s), 1441(s), 1421(s), 1391(s), 1362(s), 1344(s), 1298(s), 1269(s), 1193(s), 1122(s), 788(s), 757(s), 506(m), 473(m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.38 (s, 27H, C(CH₃)₃), 2.95 (s, 3H, C=CH), 6.21 (d, 6H, Ar–H, *J* = 7.8 Hz), 6.35 (d, 6H, Ar–H, *J* = 7.8 Hz), 7.51–7.58 (m, 18H, Ar–H), 8.48 (s, 3H, Ar–H), 8.28 (br, 2H, Bipy-H), 9.55 (br, 2H, Bipy-H), 10.13 (d, 2H, Bipy-H, *J* = 7.5 Hz), 12.01 (d, 2H, Bipy-H, *J* = 7.8 Hz) ppm; Anal. Calcd. for EuC₇₉H₇₁N₂O₆: C,73.19; H, 5.52; N, 2.16; Eu, 11.72; Found C, 73.45; H, 5.46; N, 2.18; Eu, 11.85.

Eu(TNPD)₃·Phen (**C3**): same procedure as for Eu(TNPD)₃ (**C1**), but the reaction mixture with TNPD (0.99 g, 3 mmol), Phen (0.18 g, 1 mmol) and 1 mmol EuCl₃. The complex**C3** was obtained as a yellow power, yield 75%. IR *v* (KBr): 3054(m), 2962(s), 2867(m), 1599(s), 1548(s), 1521(s), 1497(s), 1442(s), 1422(s), 1396(s), 1363(s), 1345(s), 1297(s), 1269(s), 1192(s), 1120(s), 841(m), 788(s), 757(s), 730(m), 505(m), 473(m) cm⁻¹; ¹H NMR (300 MHz, CDCl₃): *δ* 1.35 (s, 27H, C(CH₃)₃), 2.98 (s, 3H, C=CH), 6.02 (d, 6H, Ar–H, *J* = 8.1 Hz), 6.16 (d, 6H, Ar–H, *J* = 7.8 Hz), 7.39– 7.46 (m, 18H, Ar–H), 8.42 (s, 3H, Ar–H), 8.93 (br, 2H, Phen-H), 10.39 (br, 2H, Phen-H), 10.81 (br, 2H, Phen-H), 10.98 (br, 2H, Phen-H) ppm; Anal. Calcd. for EuC₈₁H₇₁N₂O₆: C, 73.68; H, 5.42; N, 2.12; Eu, 11.51; Found C, 73.51; H, 5.38; N, 2.16; Eu, 11.67.

Results and discussion

Synthesis

Scheme 1 presents the synthetic routes for β -diketone ligand and europium complexes. The β -diketone TNPD was synthesized by Claisen reaction, which is one of the most widely used methods for the synthesis of β -diketone. Europium (III) complexes **C1–C3** were prepared by reacting the β -diketone ligand with EuCl₃ and 2,2-dipyridine or 1,10-phenanthroline according to the method of Ref. [10].

IR spectra

Compared to the IR spectrum of the free ligand TNPD, the IR spectra of the complexes C1-C3 exhibit apparent changes. The characteristic, strong bands of the ligand TNPD and europium complexes are summarized in Table 1. The absorption bands in the regions of 1600–1599 cm^{-1} and 1524–1521 cm^{-1} in complexes which are the characteristics of β -diketonate coordinated with europium ion. Since the C=O bonds were converted into the vibrating structure of the C=O \rightarrow Eu bond and C–O–Eu bond, their stretching frequencies were red-shifted 4–29 cm⁻¹ with respect to those of the free ligand [11,12]. Further information on the IR spectroscopy for complexes is given by the disappearance of corresponding O-H vibration band which exists in the free ligand due to the keto-enol tautomerism of the β -diketone. In addition, there are new medium absorption peaks at about 506 cm^{-1} and 473 cm⁻¹, which are due to the new bonds of the Eu–N and Eu–O in complexes, respectively [13,14].

¹H NMR spectra

The characteristic ¹H NMR spectral data of the free ligands and complexes are listed in Table 2. From Table 2, the free ligand TNPD showed a singlet for the methine proton at δ 7.00 ppm, the keto-CH₂ proton at δ 4.70 ppm and the enolic proton at δ 17.10 ppm. The keto-CH₂ proton and enolic proton signals were not observed



Scheme 1. The synthetic routes of β -diketone and its complexes.

Table 1

The characteristic IR data of the ligand TNPD and complexes.

Complex v (O-H) v (C=O) v (C=N) v (C=O) v (Eu-O) TNPD 3500(w) 1628(s) - 1528(s) - - C1 - 1600(s) - 1524(s) - 472(m)							
TNPD 3500(w) 1628(s) - 1528(s) - - C1 - 1600(s) - 1524(s) - 472(m)	Complex	v (O—H)	v (C=O)	v (C=N)	v (C=C)	v (Eu—N)	v (Eu—O)
C2 – 1599(s) 1548(s) 1523(s) 506(m) 473(m) C3 – 1599(s) 1548(s) 1521(s) 505(m) 473(m)	TNPD C1 C2 C3	3500(w) - -	1628(s) 1600(s) 1599(s) 1599(s)	- - 1548(s) 1548(s)	1528(s) 1524(s) 1523(s) 1521(s)	- 506(m) 505(m)	- 472(m) 473(m) 473(m)

 Table 2

 Comparison of proton chemical shifts (ppm) for the ligands and complexes.

Compound	$\delta_{\rm keto-CH2}$	$\delta_{C=C-H}$	δ_{O-H}	$\delta_{\mathrm{Bipy-H}}$	$\delta_{\text{Phen-H}}$
TNPD	4.70	7.00	17.10	-	-
Bipy ^a	-	-	-	7.22-8.70	-
Phen ^a	-	-	-	-	7.63-9.19
C1	-	3.05	-	-	-
C2	-	2.95	-	8.28-12.01	-
C3	-	2.98	-	-	8.93-10.98

^a Ref. [18].

the in ¹H NMR spectra of complexes **C1–C3**. But their methine protons exhibited a single peak at δ = 2.95–3.05 ppm and displayed much larger shift to high-field with respect to the ligand, which due to paramagnetism of the europium ion [15,16]. In addition, the signals for aryl protons of β -diketone also shifted to high-field in the europium (III) complexes. However, the proton signals of coordinated Bipy or Phen have been found to shift remarkably to lower fields compared with the free Bipy or Phen, which assigned to the electron-withdrawing inductive effect of coordination. This result was in agreement with the literature [17].

UV-vis spectra

Fig. 1 gave the UV–vis absorption spectra of the ligand TNPD and the europium complexes (**C1–C3**) in chloroform $(1 \times 10^{-5}$ mol/L). It can be seen that the maximum absorption peak (λ_{max}) of TNPD is at 368 nm, which was attributed to TNPD-enol isomer absorption band, and the λ_{max} of complexes **C1–C3** were red-shifted to around 377, 379, 380 nm, respectively. The results indicated the ligand TNPD was coordinated to the europium ion acting as enol form. Therefore, the obvious bathochromic effect for the europium complexes most probably arise from the intense π – π * transition of the conjugated chromophore due to the chelation between the europium ion and organic ligands.



Fig. 1. UV-vis absorption spectra of the ligand TNPD and complexes C1,C2 and C3 in chloroform solution (1 \times 10 $^{-5}$ mol/L).



Fig. 2. The emission spectra for complexes C1, C2 and C3 in the solid state at room temperature, excited around 398, 405 and 407 nm, respectively.

Photoluminescence properties

Fig. 2 presents the photoluminescence spectra of the europium complexes C1, C2 and C3 in the solid state at room temperature. Their emission spectra displayed the characteristic emission lines for Eu³⁺: ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ (580 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (591 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (612 nm), ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ (653 nm), and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ (702 nm). The hypersensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is very intense, pointing to a highly polarizable chemical environment around the Eu³⁺ ion, and is responsible for the brilliant-red emission color of these complexes. The very weak emissions bands at about 580 nm and 653 nm in these spectra were due to the forbidden transition for ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ and ${}^5D_0 \rightarrow {}^7F_3$ both in magnetic and electric dipole schemes. It was well-known that the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is a parity-allowed magnetic dipole transition and is nonsensitive to the local structure environment, while the ${}^5D_0 \rightarrow {}^7F_2$ transition is an induced electric dipole transition and is a very sensitive to the condition environment [19]. In addition, the photoluminescence intensity of europium complex C3 is much higher than that of complexes C1 and C2 corresponded to the coordination of the "antenna" ligands to the europium ion, which causes an efficient energy transfer from the ligands to central the Eu³⁺ ion [20]. 1,10-Phenanthroline is a ligand which has high affinity toward various lanthanide ions, especially toward Eu³⁺ ion. The asymmetry of the complex C3 is increased and prevented the 4f-4f transition because the secondary ligand Phen participates in the coordination. This is helpful for the photoluminescence intensity of the complex **C3**.

The decay curves of ${}^{5}D_{0}$ level for complexes **C1**, **C2** and **C3** were investigated by monitoring the emission of 613 nm, 613 nm and 612 nm, respectively (Fig. 3). It was found that the decay curves for these complexes fitted approximately a single exponential decay law, indicating only one chemical microenvironment around where the Eu³⁺ ion existed [21]. The lifetime values (τ) for the emission of complexes **C1–C3** are listed in Table 3, which were determined from fittings of the decay curves. The results showed that the lifetime value of the complex **C3** presented longer lifetime than that of complexes **C1** and **C2**, suggesting that the introduction of the secondary ligand Phen can enhance the photoluminescence stability of the overall coordination system.

According to the emission spectra and lifetimes of complexes **C1–C3**, the luminescent quantum efficiency (η) for the emitting ⁵D₀ level can be determined. The quantum efficiency, η expresses how well the radiative processes (characterized by the rate constantA_{rad}) compete with non-radiative processes (overall rate constant A_{nrad}) [19].

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}} \tag{1}$$

Assuming that only non-radiative and radiative processes are essentially involved in the depopulation of ${}^{5}D_{0}$ state, non-radiative and radiative processes influence the experimental luminescence lifetime (τ) by the following equation:

$$A_{tot} = \frac{1}{\tau} = A_{rad} + A_{nrad} \tag{2}$$

Here A_{rad} can be calculated by summing over the radiative rates A_{0J} for each ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ transition $(\sum_{J}A_{0J})$ of the europium ion. And A_{0J} is obtained according to the equation as follows [22]:

$$A_{0J} = A_{01} \frac{I_{0J}}{I_{01}} \frac{v_{01}}{v_{0J}}$$
(3)

where I_{0J} is the area under the curve related to the ${}^5D_0 \rightarrow {}^7F_J$ transitions (J = 1, 2 and 4) obtained from the spectral data, and v_{0J} is energy barycenter of transition. The ${}^5D_0 \rightarrow {}^7F_1$ transition does not depend on the local ligand field seen by europium ion and, thus, may be used as a reference, the value of A_{01} is estimated to be $\sim 50 \text{ s}^{-1}$ [23].

The obtained radiative decay rates A_{rad} , the non-radiative decay rates A_{nrad} and the luminescence quantum efficiency η are also presented in Table 3. From Table 3, complex **C3** presented a longer life-



Fig. 3. The luminescence decay curves for complexes C1, C2 and C3 in the powder monitored at 613, 613 and 612 nm, respectively.

Table 3 Experimental intensity parameters and lifetimes of the ${}^{5}D_{0}$ emitting level for complexes C1–C3.

Complex	τ (ms)	A_{tot} (s ⁻¹)	A_{rad} (s ⁻¹)	A_{nrad} (s ⁻¹)	$\Omega_2 (10^{-20}{ m cm}^2)$	$\Omega_4 (10^{-20}{ m cm}^2)$	η (%)
C1	0.017	58,823	516	58,307	12.6	1.8	0.8
C2	0.063	15,873	1074	14,799	30.3	0.8	6.8
C3	0.366	2732	1370	1362	38.5	2.1	50.1

time τ (0.366 ms) and higher luminescence quantum efficiency η (50.1%), which was in agreement with the results from their luminescence emission intensity. The results showed that the introduction of the secondary ligand Phen in europium complex could effectively increase their quantum efficiency. Moreover, the luminescence quantum efficiency of complex Eu(TNPD)₃. Phen is much higher than that of some corresponding dibenzoylmethane (DBM) europium complexes, such as Eu(DBM)₃·Phen (η = 31.3%) [24], Eu(4-methoxy-DBM)₃·Phen (η = 38.8%) [9], europium complex with 1,3,5-tris(2,2-dibenzoylethyl) benzene and Phen ($\eta = 28.0\%$) [25], which due to the introduction of the naphthyl nucleus into the βdiketone to extend π -conjugate system of ligand. The mechanism is that the triplet energy level of ligand gradually decreased with increasing of the conjugate system, the energy level of TNPD ligand perfectly matches the ⁵D₀ energy level of the europium ion and its complexes display the higher luminescence quantum efficiency.

Judd-Ofelt analysis

The Judd–Ofelt theory is useful tool for analyzing 4f–4f inner shell electronic transitions. Interaction parameters of ligand fields are given by the Judd–Ofelt Ω_t (t = 2, 4, and 6), in which Ω_2 is more sensitive to the symmetry and sequence of ligand fields [24]. The Judd–Ofelt intensity parameters Ω_t (t = 2, 4) can be determined from the emission spectra (Fig. 2) using the ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_4$ electronic transitions of the Eu³⁺ ion and they are calculated according to the following equation [26]:

$$\Omega_{t} = \frac{3hc^{3}A_{0J}}{4e^{2}\omega^{3}\chi\langle^{5}D_{0}||U^{(t)}||^{7}F_{J}\rangle^{2}}$$
(4)

where $\chi = n_0^2 (n_0^2 + 2)^2 / 9$ is a Lorentz local field correction and an average index of refraction equal to 1.5 was used. The squared reduced matrix elements are $\langle {}^5D_0 \| U^{(2)} \|^7 F_2 \rangle^2 = 0.0032$ and

$$\langle {}^{5}D_{0} \| U^{(4)} \| F_{4} \rangle^{2} = 0.0023.$$

The experimental intensity parameters Ω_2 and Ω_4 are listed in Table 3. From Table 3, the highest value of the Ω_2 parameters $(38.5 \times 10^{-20} \text{ cm}^2)$ was found for the complex **C3**, which indicated the highest hypersensitive behavior of the ${}^5D_0 \rightarrow {}^7F_2$ transition, which reflected the most polarizable chemical environment of the europium ion. Also are noted that the higher value for the Ω_4 parameter was obtained to the complex **C3**, suggesting that steric factors prevent the Phen ligand from getting closer to the europium ion [27].

Conclusions

In this work, three novel Eu (III) complexes **C1**, **C2** and **C3** have been designed, synthesized and characterized by FT-IR, ¹H NMR, ESI-MS, UV–vis absorption, elemental analysis and photoluminescence spectroscopy. The emission spectra for all complexes displayed the characteristic emission lines for europium ion in solid state. The results of their emission spectra and lifetime decay curves indicated that there was one luminescence center in these complexes, and the europium ion was located in a polarizable chemical environment. Based on the emission spectra and lifetime of the ⁵D₀ emitting level in solid state, experimental intensity parameters (Ω_2 and Ω_4), the radiative decay rate A_{rad} , the nonradiative rates A_{nrad} , the lifetime (τ) and the quantum yield (η) were calculated and the complex **C3** exhibited a longer lifetime τ (0.366 ms) and higher luminescence quantum efficiency η (50.1%). These results demonstrated that the secondary ligand Phen could improve the luminescence properties of the Eu (III) complex with β -diketone.

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