

# High luminescence quantum yields and long luminescence lifetime from Eu(III) complex containing two crystal water based on a new $\beta$ -diketonate ligand

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## Abstract

New members of family of Eu(III) complex based on the thenoylacetophenone have been synthesized and characterized. The compounds were found for high metal luminescence quantum yields and long luminescence lifetime, especially for compound with two crystal water, corresponding with other compounds containing two crystal water. The result is attributed to high molar absorption coefficients of the Eu(III) complex according to UV–vis and emission spectra. The high molar absorption coefficients balance quenching effect from O–H oscillators of water contained in compound.

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*Keywords:* Synthesized; Thenoylacetophenone; Optical properties; Water

## 1. Introduction

Luminescent rare earth complexes, particularly europium diketonates, have been intensively studied with respect to applications for luminescence and as laser materials [1]. Since the nature of ligands surrounding lanthanoid complexes strongly influence the photophysical properties, such as relative intensity, quantum yield and luminescent life decay, it may be possible to tune them to the desired purpose. The design of molecular ligands with defined architecture is important in order to investigate structure versus properties relationships in lanthanide solid-state framework structures [2], liquid crystalline materials [3], sensors [4] or luminescent label design [5] for specific biomolecule interactions. Ligand design has been based mainly on structure that encapsulates the lanthanide such as macrocycles and cryptands [6], podands [7] or shell-type ligands [8]. In this context, there is also the great majority of works [9] which study the various second ligand of lanthanide to overcome quenching effect attributed to crystal water contained in lanthanide complex for vibrational quenching of O–H oscillators. But there are few considerations

to balance the quenching effect by improving energy transfer ratio and absorption efficiency, resulting from the existence of water. Here, we extend the synthesis of europium complexes based on a new ligand of thenoylacetophenone (TAP). And the optophysical properties of those new compounds were measured and the new ligand in presence of crystal water for complete energy transfers to the europium center and their utilization as red emitters in EL devices were explored. This europium complex appears to be the breakthrough of preparing and using lanthanide complex in water-containing system.

## 2. Experiment

### 2.1. Synthesize TAP and its $\text{Eu}^{3+}$ complexes

Acetyl thiophene was synthesized according to the following procedure. Thiophene (84 g) and acetic anhydride (83.5 g, 95%) were added into three-neck flask and then added phosphate (5.0 g, 85%) under stirring at 50 °C. The mixture was stirred for 3 h at 100–110 °C. Water was added after finishing the reaction and cooling the reactive mixture. Oil layer was washed by the  $\text{Na}_2\text{CO}_3$  aqueous solution and water to pH at 7 and then were dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the  $\text{Na}_2\text{SO}_4$ , the pure product was obtained by distilling under reduced pres-

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sure (0.91 MPa) at 124–136 °C. TAP and its Eu(III) complexes were synthesized by the Claisen condensation method [10] and according to the procedure [10] reported before, respectively. Structure of TAP and its Eu(III) complexes were determined by NMR, IR spectra and element analysis.

## 2.2. Measurement and instrument of optical properties

The absorption spectra were measured with a SHIMADZU UV-2401PC spectrophotometer. The emission spectra of fluorescence and phosphorescence spectra were obtained with SHIMADZU RF-5301PC spectrofluorometer and Perkin-Elmer LS55 luminescence spectrometer, respectively. Luminescence quantum yields were obtained with SHIMADZU UV-2401PC and RF-5301PC spectrofluorometer. Luminescence lifetime was measured with lifetime spectrofluorometer (Fluorolog-3-TAU).

## 3. Results and discussion

### 3.1. Preparation and characterization of ligand and its Eu(III) complex

Here a facile synthetic route of  $\beta$ -diketone ligand with thiophene chromophores and phenyl group which affects the luminescence lifetime and quantum yield of rare earth complexes is developed. The structures of acetyl thiophene and TAP were monitored and identified by NMR as shown in the Fig. 1(a):  $\delta$ 7.69 (a, 1H),  $\delta$ 7.62–7.63 (b, 1H),  $\delta$ 7.10–7.13 (c, 1H),  $\delta$ 2.55 (d, 3H) and Fig. 1(b):  $\delta$ 8.11–8.11 (a, 3H),  $\delta$ 7.60–7.64 (b, 2H),  $\delta$ 7.50.25–7.25 (c, 3H),  $\delta$ 1.25 (d, 2H), respectively.

Reaction of TAP with a metal chloride hexahydrate in a 3:1 ratio in presence of triethylamine leads to formation of  $\text{Eu}(\text{TAP})_3\text{L}$  ( $\text{L} = 2\text{H}_2\text{O}$ , Phen(1,10-phenanthroline)). The solids are soluble in DMSO and slightly soluble in THF and acetone solvents. IR and element analysis were employed to identify the molecular species. The IR spectra of final rare earth complexes in Fig. 2 show C=O group at 1594.83–1611.2  $\text{cm}^{-1}$ , Phen group at 1532.8–1568.14  $\text{cm}^{-1}$  and C=C group at 1494.4  $\text{cm}^{-1}$ . The result of element analysis of the products is shown:  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$ , C, 52.9% (theory 53.3); H, 1.71% (theory

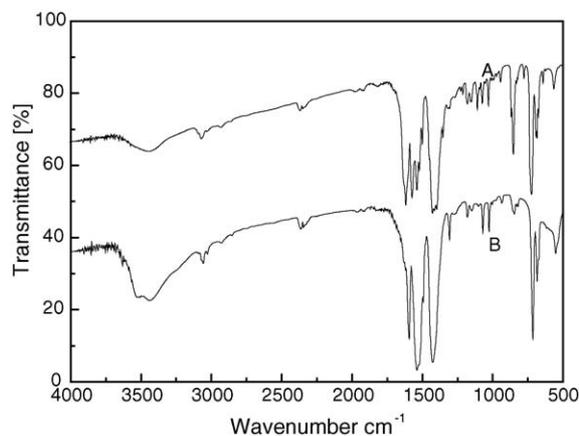


Fig. 2. IR spectra of (A)  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  and  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  complex.

Table 1

Quantum yield and lifetime of the emitting levels in the  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  compounds

Compound	$\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$	$\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$
Lifetime ( $\mu\text{s}$ )	829	868
Quantum yield (%)	61.6	62.0

The values for the Eu compounds are at room temperature.

1.60).  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$ , C, 60.2% (theory 61.2); N, 2.75% (theory 2.70); H, 2.53% (theory 2.40).

### 3.2. Luminescent quantum yields and luminescent lifetime from Eu(III) complexes

The lifetime measurements and luminescent quantum yield  $q$  were made for the  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  compounds. The results are presented in Table 1. The luminescent quantum yield  $q$  for the  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  compounds were obtained following the procedure described in expression 1. The  $q$  value is defined as the ratio between the number of photons emitted by the Eu(III) ion and the number of photons absorbed by the ligands. According to the method

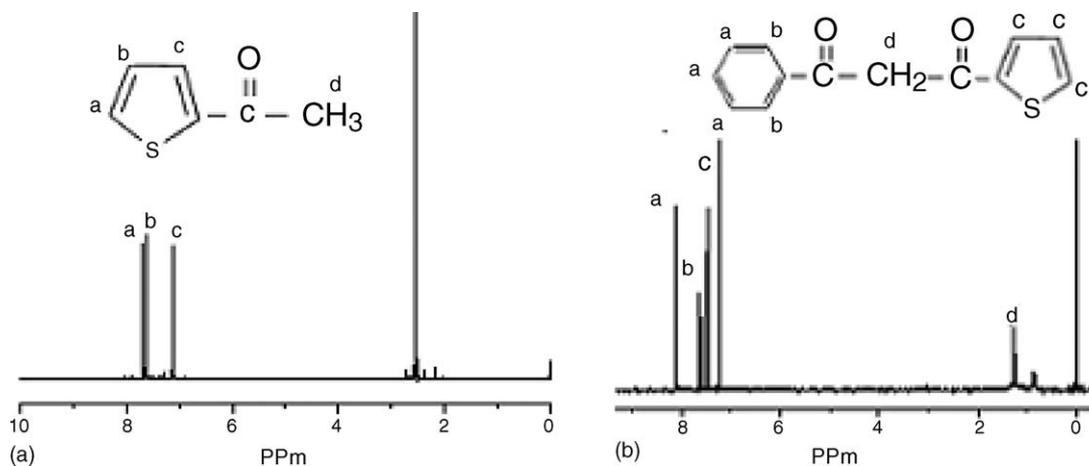


Fig. 1. 400 MHz NMR spectrum of: (a) acetyl thiophene and (b) TAP in  $\text{CDCl}_3$ .

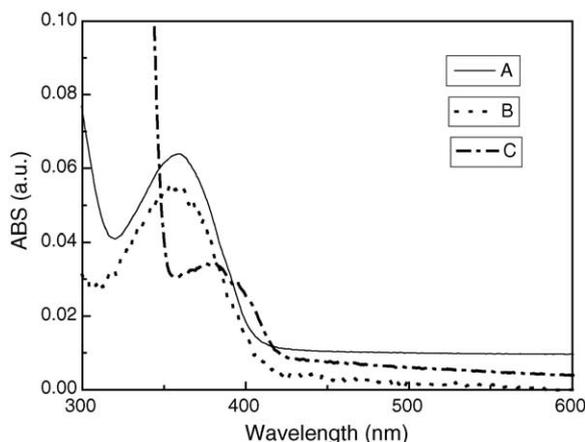


Fig. 3. Absorption spectra of: (A) TAP, (B)  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  and (C)  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  complex in DMSO.

developed by Bril et al. at Philips Research Laboratory [11], the  $q$  value for a given sample can be determined by comparison with standard phosphors, whose quantum yields have been previously determined by absolute measurements. This method provides absolute yield while avoiding absolute measurements, which are in general complicated. The quantum yield  $q_x$  of a sample is thus determined as follows:

$$q_x = \left\{ \frac{1 - R_{st}}{1 - R_x} \right\} \left\{ \frac{\Delta\varphi_{st}}{\Delta\varphi_s} \right\} q_{st} \quad (1)$$

where  $R_{st}$  and  $R_x$  are the amount exciting radiation reflected by the standard and by the sample, respectively, and  $q_{st}$  is the quantum yield of the standard phosphor. The terms  $\Delta\varphi_{st}$  and  $\Delta\varphi_s$  give the integrated photo flux (photons  $\text{s}^{-1}$ ) for the sample and the standard phosphors, respectively. The stand in our case was sodium salicylate, which has a broad emission band with the maximum at 616 nm and  $q = 60\%$  at room temperature [12]. The results show that the method is accurate within 10%, in agreement with the accuracy reported in previous work [11]. The luminescent lifetime and luminescent quantum yield  $q$  for the  $\text{Eu}(\text{III})$  compounds are considerable high, compared with the similar  $\text{Eu}(\text{III})$  complexes with ligand of trifluorothienoyl-acetone (HTTA) and dibenzoylmethane (DBM) [9,12]. This is consistent with emission from a state with a strong triplet character. Especially note was given to the quantum yield and lifetime of  $\text{Eu}(\text{TPA})_3 \cdot 2\text{H}_2\text{O}$  complex different from other rare earth complexes in previous works with the low quantum yield and short lifetime for containing crystal water molecules [9,13,14]. That has almost the same value of quantum yield and lifetime, compared to the second ligand of Phen (no  $\text{H}_2\text{O}$ ).

### 3.3. Absorption and luminescent properties of $\text{Eu}(\text{III})$ complexes

The UV-vis absorption spectra of TAP and its  $\text{Eu}(\text{III})$  complexes were shown in Fig. 3 and exhibited an intense band (ca. 350–390 nm), attributing to  $\pi-\pi^*$  characteristic enol absorption of the enol form  $\beta$ -diketones. It is easily known that the

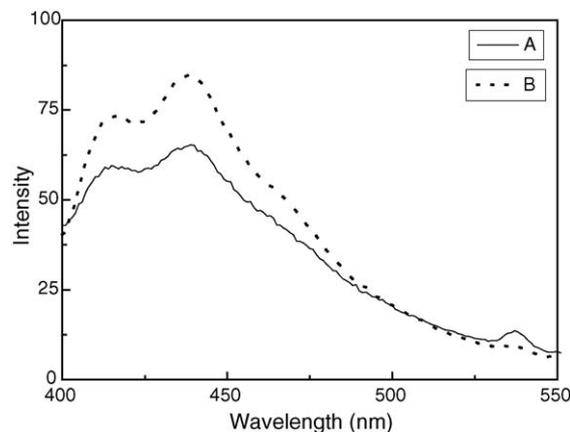


Fig. 4. Ligand luminescent spectra of: (A)  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  and (B)  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  complex in DMSO solution;  $\lambda_{\text{exc}} = 350$ .

ligand  $\pi^*$  energy level of  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  in DMSO had no change, comparing with the ligand of TAP. However, when second ligand of Phen was introduced, the ligand  $\pi^*$  energy level of  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  in DMSO changed, which was confirmed by change of the maximum absorption from 357 to 389 nm.

To investigate the photophysical properties of the energy donor singlet-singlet  $\pi-\pi^*$  state of the ligand, the luminescent properties of the  $\text{Eu}(\text{III})$  complexes was examined. The room-temperature luminescent spectra of  $\text{Eu}(\text{III})$  complexes in DMSO solution exhibits a broad emission band with  $\lambda_{\text{max}} = 438$  nm ( $228310 \text{ cm}^{-1}$ ) (Fig. 4) attributing to ligand  $\pi-\pi^*$  transition, which suggests the lowest  $\pi^*$  (singlet) state not depend on the second ligand of water or Phen.

The ligand phosphorescence was clearly observed in the 77 K luminescent spectra of  $\text{Eu}(\text{III})$  complexes (Fig. 5). As the energy of the ligand-centered triplet state did also not depend significantly on the second ligand of water or Phen, according to the same luminescent band of 497 nm ( $20121 \text{ cm}^{-1}$ ) for the two  $\text{Eu}(\text{III})$  complexes. The luminescent band of 497 nm is assigned to 0-0 transition of the energy of the  $\pi-\pi^*$  level for  $\text{Eu}(\text{III})$  lanthanide ligands of TAP. The energy of this state is higher than and close to the emitting excited state of  $\text{Eu}(\text{III})$  ( $17210 \text{ cm}^{-1}$ )

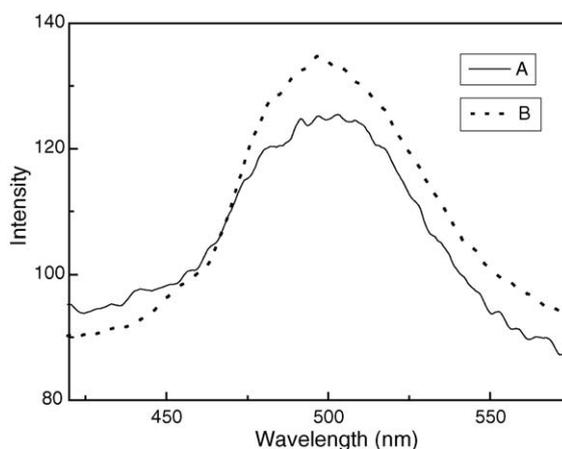


Fig. 5. Luminescent spectra of: (A)  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  and (B)  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  complex in DMSO at 77 K;  $\lambda_{\text{exc}} = 350$  nm.

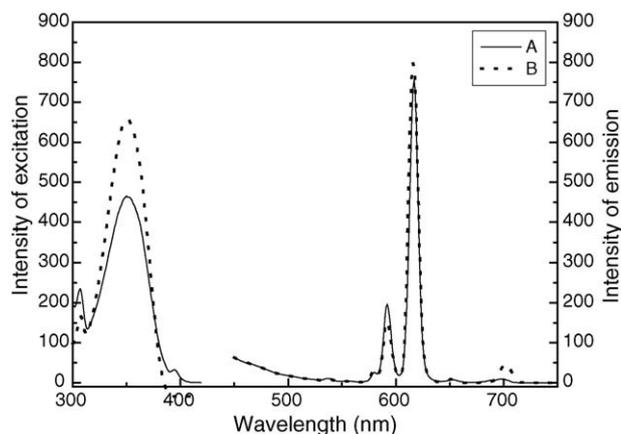


Fig. 6. Excitation and luminescent spectra of (A)  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  and (B)  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  complex in DMSO.

confirming the suitability of the ligand as sensitizer for that lanthanide of Eu(III).

Although the excitation spectra (Fig. 6) of Eu(III) complex was inconsistent to absorption spectra (Fig. 3), they all show a maximum band at around 350 nm, confirming that energy transfer takes place from the ligand to Eu(III) ion. Light excitation (ca. 350 nm) into the ligand  $\pi-\pi^*$  state of Eu(III) complex in DMSO is followed by the strong red luminescence and characteristic of the  $^5\text{D}_0-^7\text{F}_J$  ( $J=0-4$ ) luminescent bands of Eu(III). Eu(III) complexes showed similar luminescent and excitation spectra, suggesting that the 4f state of Eu(III) and excited state of TAP was independent on the second ligand.

In Fig. 7, we show the energy level diagrams of ligand and Eu(III) excited states. For the compounds with water and Phen, the triplet state (2) is same at  $20,121\text{ cm}^{-1}$  that is agreement with the result in luminescent spectra at 77 K. However, the maximal absorption sate of compounds with water and Phen is different, corresponding to the level (4) and (3) as shown in Fig. 7, respectively. It is clear that  $\text{Eu}(\text{TPA})_3 \cdot 2\text{H}_2\text{O}$  complex has higher absorption coefficients, comparing with  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  at excitation bands around 350 nm. So high luminescent quantum yields and long luminescent lifetime from  $\text{Eu}(\text{TPA})_3 \cdot 2\text{H}_2\text{O}$  complex can be obtained, which is different from previous work

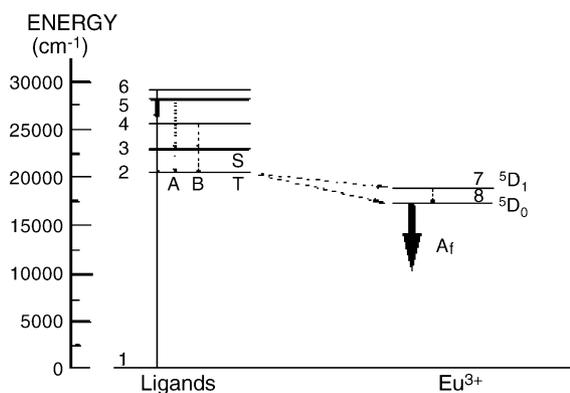


Fig. 7. Simplified energy diagram showing the singlet (3) and triplet (2) state of ligand, the excited state (6) and the maximal absorption sate of  $\text{Eu}(\text{TAP})_3 \cdot 2\text{H}_2\text{O}$  (5) and  $\text{Eu}(\text{TAP})_3 \cdot \text{Phen}$  (4).

that is believed to result from difference of triplet state (2) in [15].

#### 4. Conclusions

Results of this work represent a novel ligand design based on diketonate lanthanide complexes with interesting in luminescent properties. NMR spectroscopy and element analysis had been used to fully confirm the preparation of new Eu(III) complexes. The complexes has long luminescent lifetime and high luminescent quantum yields even in the case of the presence of  $\text{H}_2\text{O}$ . These results indicate that the energy transfer process is efficient in Eu(III) complex with  $\text{H}_2\text{O}$ , resulting from high absorption efficiency and not resulting from change of singlet and triplet energy level, which is confirmed by luminescent (luminescence and phosphorescence) spectra and UV-vis absorption spectra of ligand and its Eu(III) complex. So it can well overcome the problem that strongly luminescence quenching was observed in previous Eu(III) complexes with water for its O–H oscillators. In our systems, the magnitude of the lifetime and the luminescent efficiency of the Eu(III) complexes are higher and longer comparing with previous Eu(III) complex with crystal water molecules, which indicate that such results are attributed to delicate balance between highly energy transfer efficiency and quenching effect from O–H oscillators of water.

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#### References

- [1] H. Lemmetyinen, E. Vuorimaa, A. Jutila, V.M. Mikkala, H. Takalo, J. Kankare, *J. Luminescence* 15 (2000) 341.
- [2] L. Pan, K.M. Adams, H.E. Hernandez, X.T. Wang, C. Zheng, Y. Hattori, K. Kaneko, *J. Am. Chem. Soc.* 125 (2003) 3062.
- [3] K. Binnemans, C. Goerller-Walrand, *Chem. Rev.* 102 (2002) 2302.
- [4] D. Parker, *Coord. Chem. Rev.* 205 (2000) 109.
- [5] P.B. Glover, A. Rodger, P.R. Ashton, M. Kercher, R.M. Williams, L. De Cola, Z. Pikramenou, *J. Am. Chem. Soc.* 125 (2003) 9918.
- [6] D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, J.A.K. Howard, *Chem. Rev.* 102 (2002) 1977.
- [7] N. Marques, A. Sella, J. Takats, *Chem. Rev.* 102 (2002) 2137.
- [8] S.W. Magennis, S. Parsons, Z. Pikramenou, *Chem. Eur. J.* 8 (2002) 5761.
- [9] F.R.G. eSilva, J.F.S. Menezes, G.B. Rocha, S. Alves, H.F. Brito, R.L. Longo, O.L. Malta, *J. Alloys Compd.* 303–304 (2000) 364.
- [10] H.F. Jiu, W. Su, Y.H. Ji, et al., *Chin. J. Chem. Phys.* 17 (2004) 4460.
- [11] A. Bril, W. De Jager-Veenis, *J. Res. Nat. Bureau Stand.* 80A (1976) 401.
- [12] A. Bril, A.W. De Jager-Veenis, *J. Electrochem. Soc.* 123 (1976) 396.
- [13] D.E. Williams, *Acta Crystallogr.* 21 (1966) 340.
- [14] A.P. Bassett, S.W. Magennis, P.B. Glover, D.J. Lewis, N. Spencer, S. Parsons, R.M. Williams, L. De Cola, Z. Pikramenou, *J. Am. Chem. Soc.* 126–130 (2004) 9414.
- [15] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Goncalves e Silva, S. Alves Jr., F.S. Farias Jr., A.V.M. de Andrade, *J. Lumin.* 75 (1997) 255.