

## PHOTOLUMINESCENCE PROPERTIES OF COORDINATION COMPOUND $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{BTFA})(\text{NO}_3)(\text{PHEN})]_2 \cdot \text{PHEN}$

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**Abstract:** This study presents experimental results on photoluminescence properties of europium(III) coordination complex under blue-light excitation. The complex,  $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2\text{phen}$  {btfa = benzoyl trifluoroacetone, phen = 1,10-phenantroline}, was investigated by registering the emission and excitation spectra of powder samples at room temperature. The emission spectra show metal-centered luminescence bands, which are assigned to internal radiative transitions of the  $\text{Eu}^{3+}$  ion,  ${}^5\text{D}_1 \rightarrow {}^7\text{F}_j$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $j = 0-4$ ). Overall, the photoluminescence spectra suggest that the europium ions are situated in a low-symmetry environment.

**Keywords:** dinuclear coordination compound; europium(III); blue light; photoluminescence.

### Introduction

Photoluminescence properties of europium(III) coordination compounds have been extensively studied due to their usefulness in both practical applications and scientific research [1-4]. Eu(III)-based complexes emit bright-red light with high colour purity and quantum yield in the visible range, making them attractive for use as a spectroscopic tool in investigating the structural properties and symmetry around the Eu(III) ion in the ligand matrix [5,6]. Despite the considerable research in this field, efforts are still being made to develop new Eu(III) complexes that are water-soluble and suitable for practical applications in medicine and biochemistry. The current study presents experimental results on an europium(III) coordination complex with chemical composition  $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2 \cdot \text{phen}$ , where btfa stands for benzoyl trifluoroacetone, and phen represents 1,10-phenantroline.

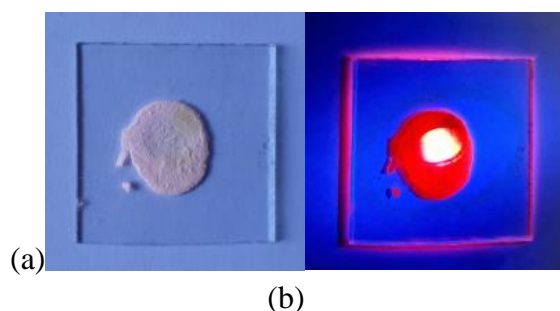
### Experimental details

The coordination complex  $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2 \cdot \text{phen}$  was synthesized as previously described [7,8]. PL emission spectra were recorded with a resolution of 0.0715 nm using different excitation sources with an MDR-23 single emission monochromator and a Hamamatsu photomultiplier module H9319-12 in a photon counting mode. PL spectra were registered with a Thorlabs LD (405 nm, 4.5 mW) as an excitation source. A pulsed nitrogen laser at 337 nm with a repetition rate of 10 Hz and a pulse width of 10 ns was used for the PL time decay measurements. The excitation spectra were registered with an MDR-23 monochromator as an excitation source and a double grating spectrometer DFS-52 for collecting the PL emission. A halogen lamp OSRAM (64623 HLX 12V 100W) was used as a light excitation source. The PL time decay was recorded with a resolution of 50  $\mu\text{s}$  using a counting unit C8855-01 connected to a PC. The emission spectra were corrected to account for instrumental spectral sensitivity.

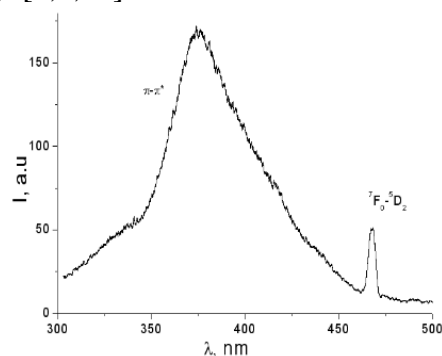
### PL spectra of coordination compound

The  $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2 \cdot \text{phen}$  complex displays a bright-red luminescence when illuminated with blue-light (405 nm), with the dominant emission band observed at around 612 nm (Figure 1). The excitation spectrum of the complex was measured at 300 K while monitoring the

$^5D_0 \rightarrow ^7F_2$  transition of  $\text{Eu}^{3+}$  at 612 nm (Figure 2). The excitation spectrum of the complex exhibits a broad band between 300 and 500 nm, with a peak maximum at 376 nm and a shoulder at 335 nm, which are attributed to the  $\pi-\pi^*$  transitions of the ligands. The sharp peak observed at 468 nm is attributed to the intra-configurational 4f-4f transitions in the  $\text{Eu}^{3+}$  ion, specifically the  $^5D_2 \rightarrow ^7F_0$  transition. Previous studies have reported similar findings [7,9,10].

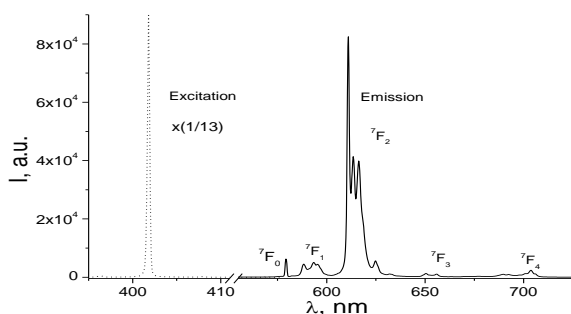


**Figure 1. Illustration of the sample (a) under day light illumination, and (b) under blue-light 405 nm illumination.**

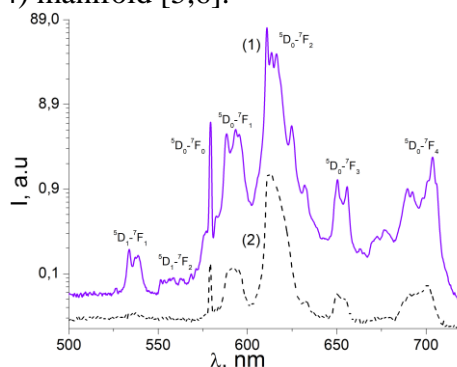


**Figure 2. Low-resolution excitation spectrum of the complex at 300 K for the  $^5D_0 \rightarrow ^7F_2$  transition at 612 nm.**

At room temperature the PL emission spectra of the powder samples were registered using an excitation source at 405 nm, which closely corresponds to the maximum absorption of the compound, as illustrated in Figure 3. The PL emission spectra (shown in Figure 4) display characteristic luminescence bands originating from the  $\text{Eu}^{3+}$  ion's internal radiative transitions, specifically  $^5D_0 \rightarrow ^7F_j$  ( $j = 0-3$ ) and  $^5D_0 \rightarrow ^7F_j$  ( $j = 0-4$ ). The main emission bands originate from the radiative transitions between the first excited  $^5D_0$  level and the  $^7F_j$  ( $j = 0-4$ ) manifold [5,6].

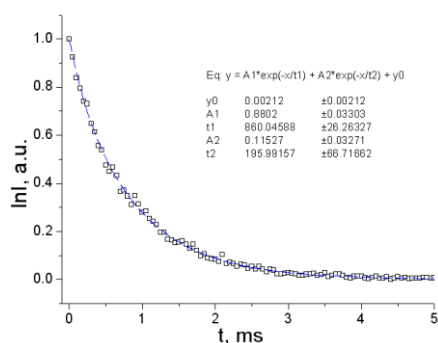


**Figure 3. Low resolution PL spectra of the powder sample measured at 300 K under excitation 405 nm: (a) excitation (dotted) line and (b) emission (solid line) spectrum.**

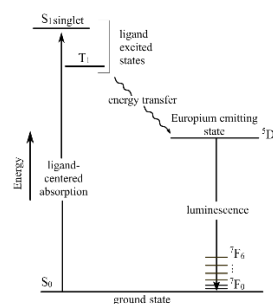


**Figure 4. Low resolution PL spectrum at 300 K: (1) PL spectrum of powder sample at 300 K; (2) PL spectrum of solution sample under excitation of LD 405 nm.**

The most prominent transition in the luminescence spectrum of the complex is the electric dipole transition  $^5D_0 \rightarrow ^7F_2$ , which is located at approximately 612 nm and is hypersensitive to the site symmetry of the  $\text{Eu}^{3+}$  ion [5]. It is this transition that determine a specific bright-red colour of the  $\text{Eu}^{3+}$  ion emission. The fine structure of the transition  $^5D_0 \rightarrow ^7F_2$  is well resolved, and it is determined by the influence of molecular electric field of the ligand on the degenerated level  $^7F_2$  of the  $\text{Eu}^{3+}$  ion, as stated in references [11-12]. One can observe at least six components of this transition. We can also observe several weak emission components, from the second excited state  $^5D_1$  to the  $^7F_j$  ( $j=0-2$ ) manifold (Figure 5).



**Figure 5. PL decay profile in powder sample at 300 K measured at 612 nm under pulsed excitation at 337 nm.**



**Figure 6. A simplified illustration of the energy transfer mechanism [15].**

The electric dipole transition  ${}^5D_0 \rightarrow {}^7F_2$  is much more intense than the magnetic dipole transition  ${}^5D_0 \rightarrow {}^7F_1$ , suggesting that the  $\text{Eu}^{3+}$  ion is located in a non-centrosymmetric environment [6]. The number of components in the transitions  ${}^5D_0 \rightarrow {}^7F_j$  ( $j=0-4$ ) is related to the crystal field symmetry around the  $\text{Eu}(\text{III})$  ion [5]. The photoluminescence decay profile measured at 612 nm for the powder sample at 300 K can be approximated by an exponential function (Figure 5).

The mechanism of energy transfer from organic ligand to the  $\text{Eu}(\text{III})$  ion is known as “antenna effect” and is depicted in Figure 6 [5,15]. In short, under near-UV radiation organic ligand is excited from the ground singlet state  $S_0$  to the first excited singlet state  $S_1$ . The excitation energy is transferred from the excited singlet state  $S_1$  to the triplet state  $T_1$  and finally to the  $\text{Eu}^{3+}$  ion emitting states  ${}^5D_{0,1}$  [12-14]. The observation of the transition  ${}^5D_0 \rightarrow {}^7F_0$  is an indicative of a low symmetry complex, as this transition is not observable in other symmetries [12-14].

## Conclusion

The complex exhibits strong luminescence under blue-light excitation (405 nm), which makes it attractive for practical applications. These applications could be, for example, in the domain of biological systems to enable the early diagnosis of diseases and the deciphering of cellular processes. The simplicity and accessibility of the excitation method is based on the use of a low-cost laser.

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