EXCITATION AND PHOTOLUMINESCENCE SPECTRA OF THE COORDINATION COMPOUND $[Eu(\mu_2\text{-}OC_2H_5)(btfa)(NO_3)(phen)]_2 \cdot phen$

SPECTRELE DE EXCITARE ŞI DE FOTOLUMINESCENŢĂ ALE COMPUSULUI COORDINATIV [Eu(μ2-OC2H5)(btfa)(NO3)(phen)]2·phen

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This paper presents experimental results on photoluminescence properties of an europium(III) coordination complex under blue-light excitation. The complex $[Eu(\mu_2\text{-}OC_2H_5)(btfa)(NO_3)(phen)]_2 \cdot phen$ {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 Eu^{3+} ion, $^5D_1 \rightarrow {}^7F_j$ and $^5D_0 \rightarrow {}^7F_j$ (j = 0–4). Overall, the photoluminescence spectra suggest that the europium ions are situated in a low-symmetry environment.

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

Acest articol prezintă rezultatele experimentale privind proprietăţile de fotoluminescenţă ale complexului coordinativ cu europiu(III) sub actiunea unui fascicol de lumină 405 nm. Complexul $[Eu(\mu_2\text{-}OC_2H_5)(btfa)(NO_3)(phen)]_2 \cdot phen$ {btfa = benzoil trifluoroacetona, phen = 1,10-fenantrolină} a fost investigat prin înregistrarea spectrelor de emisie şi excitaţie ale probelor sub formă de pulbere la temperatura camerei. Spectrele de emisie reprezintă benzi de luminescenţă înguste, care sunt atribuite tranziţiilor radiative interne ale ionului Eu^{3+}, $^5D_1 \rightarrow {}^7F_j$ şi $^5D_0 \rightarrow {}^7F_j$ (j = 0–4). În ansamblu, spectrele de fotoluminescenţă indică că ionii de europiu(III) sunt situaţi într-un mediu cu simetrie joasă.

***Cuvinte-cheie**: compus coordinativ binuclear; Eu(III); lumina albastră; fotoluminescenţă.*

INTRODUCTION

Europium(III) coordination compounds have garnered substantial attention due to their photoluminescence properties, which have practical and scientific significance [1-4]. These Eu(III)-based complexes exhibit vivid red light emission with exceptional colour purity and quantum yield in the visible spectrum. This feature makes them a valuable tool for spectroscopic investigations into the structural aspects and symmetry surrounding the Eu(III) ion within the ligand matrix [5,6]. This study presents experimental findings concerning a europium(III) coordination complex with the chemical

composition $[Eu(\mu_2\text{-}OC_2H_5)(btfa)(NO_3)(phen)]_2 \cdot phen$, where btfa represents benzoyl trifluoroacetone, and phen denotes 1,10-phenantroline.

EXPERIMENTAL DETAILS

The coordination complex $[Eu(\mu_2\text{-}OC_2H_5)(btfa)(NO_3)(phen)]_2 \cdot phen$ was synthesized as previously described [7]. PL emission spectra were recorded with a resolution of 0.0715 nm using different excitation sources with a 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. The excitation spectra were registered with a 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 emission spectra were corrected to account for instrumental spectral sensitivity [8].

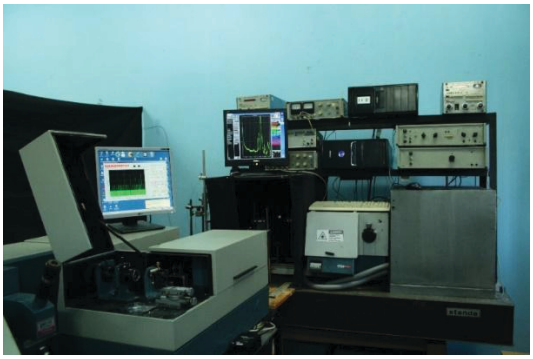


Figure 1. Measurement setup: MDR-23 – single-grating monochromator and, DFS-52 – double-grating monochromator.

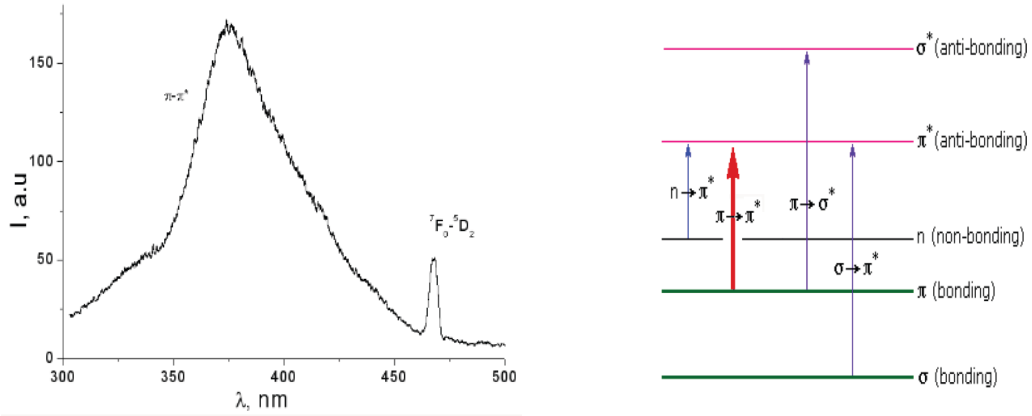
RESULTS AND DISCUSSIONS

The photoluminescence emission spectra were registered at room temperature under excitation of UV laser beam 375 nm or blue-light beam 405 nm. Both the excitation wavelengths were selected within the excitation spectrum of the complex.

The excitation spectrum (Figure 2) shows a broad band between 300 and 460 nm with a maximum at ~375 nm. A sharp, narrow transition at around 464 nm can be attributed to 4f–4f intra-configurational transitions in the Eu^{3+} ion from the $^7F_0$ ground states to the $^5D_2$ state. A weak shoulder at about 395.7 nm is ascribed to transition from the ground state $^7F_0$ to higher states $^5L_6$ [9-10]. The strong broad band in the spectrum with a maximum at 375 nm and a shoulder at ~335 nm can be attributed to the ligand-centered S_0-S_1 (π-π^*) transition of the ligands or with a possible charge transfer (LMCT) [11].

Under UV or blue-light excitation beam the complex exhibits a strong, bright read emission, with the dominant emission band at about 612 nm. These narrow emission bands are ascribed to the internal radiative transitions of the Eu(III) ion, basically from

the fist excited level $^5D_0$ to the ground manifold $^7F_0$. Other very weak transitions, observed at about 540 nm can be ascribed to the radiative transition from the second, short-lived excited state $^5D_1$ to the ground manifold $^7F_0$.



a *b*

Figure 2. (a) Excitation spectrum of the coordination compound; (b) Ilustration of ligand optical transitions.

A wide, very weak emission band can be observed around 450-530 nm, which is associated with the phosphorescence of the ligands matrix (Figures 3,4). A very low intensity of this emission band is a confirmation of high efficiency of the energy transfer from the ligand to the Eu(III) ion. The specific features of the Eu(III) PL emission spectra are their narrow, atomic-like emission bands, along with an ultra-narrow emission band at about 580 nm.

The electric-dipole transition $^5D_0 \rightarrow {}^7F_0$ is a forbidden one, according to ΔJ selection rule of the Judd–Ofelt theory. Its registration in the PL spectrum of the Eu(III) ion is usually associated with J-mixing due to the crystal-field perturbation [12].

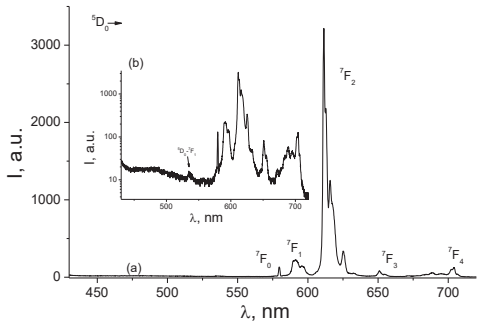


Figure 3. PL spectra of the powder sample measured at 300 K (λ_{ex} = 405 nm).

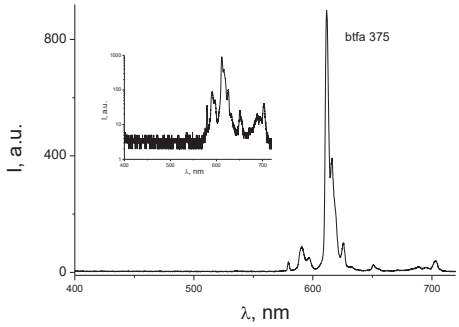
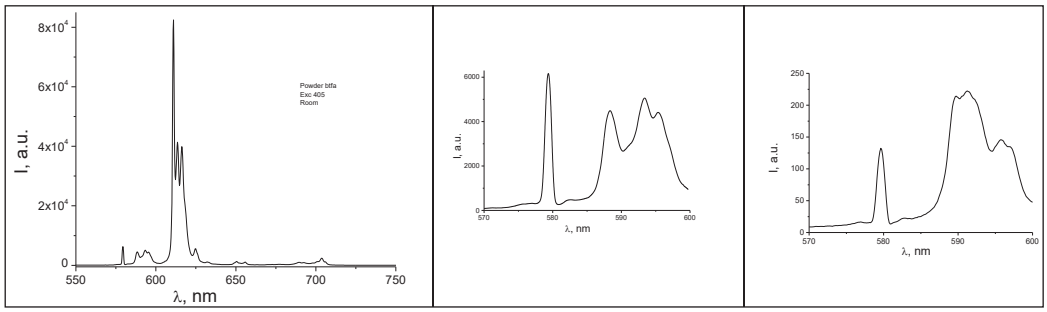


Figure 4. PL spectra of the powder sample measured at 300 K (λ_{ex} = 375 nm).

The dominant emission band of the spectra is related to the electric-dipole allowed transition $^5D_0 \rightarrow {}^7F_2$ at about 612 nm (Figure 5a). This transition is considered a hypersensitive to the symmetry of the Eu^{3+} environment, as far as its pattern depends on the symmetry around the Eu^{3+} ion. The emission band, registered at 585-600 nm refers to the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, which is considered as independent on the site symmetry of the Eu^{3+} ion, and therefore is usually is taken as a reference [5]. The asymmetric parameter R, defined as the ratio of integrated intensity of the electric-dipole transition and of the magnetic-dipole transition, $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$, was found to be equal to 10.6, which indicates on the high polarizability of the ligands around the Eu(III) ion [13].



a *b* *c*

Figure 5. (a,b) PL spectra of the powder sample (λ_{ex} = 405 nm) [7]; (c) Optical transition $^5D_0 \rightarrow {}^7F_{0,1}$ from Figures 3,4.

We noticed a minor difference in the PL emission spectra of the sample under the long-time storage. It is about the change of the relative intensities of the transitions $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ (Figure 5). We attribute these changes to some minor structural changes in the complex.

A very weak emission band at 650 nm is related to the forbidden electric-dipole transition $^5D_0 \rightarrow {}^7F_3$. This transition is forbidden by the Judd–Ofelt theory, and it can only gain intensity because of the J-mixing mechanism [14]. Another weak emission band at ~700 nm is related to the electric-dipole $^5D_0 \rightarrow {}^7F_4$ transition. The overall pattern of the PL spectra depends on the site symmetry around the Eu(III) ion, which is explored for evaluation of the site symmetry of the Eu(III) complexes [6].

The photoluminescence emission of the Eu(III) complex is intricately linked to what is known as the “antenna effect”. This phenomenon involves the transfer of energy from the organic ligand to the Eu(III) ion, as illustrated in Figure 6 [15]. When exposed to blue-light radiation, an organic ligand undergoes excitation, from the singlet ground state S_0 to the first excited singlet state S_1. Following a rapid relaxation process, the energy is transferred from the singlet excited state S_1 to the triplet state T_1 and ultimately to the excited levels $^5D_{0,1}$ of the ion emitting states Eu^{3+} [16,17]. The observation of the $^5D_0 \rightarrow {}^7F_0$ transition signifies the presence of a low-symmetry complex, as this transition is not observed in other symmetries.

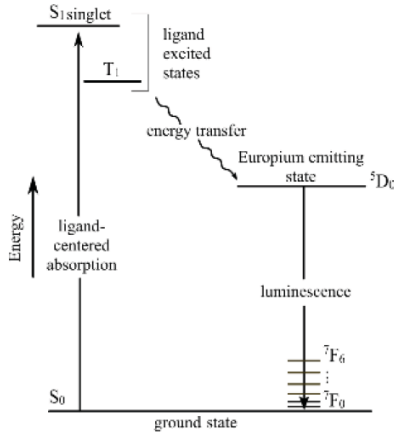


Figure 6. A very schematic illustration of the mechanism of energy transfer from the ligands to the Eu^{3+} ion [17].

CONCLUSIONS

The paper describes experimental results on photoluminescence excitation and emission spectra of the coordination compound $[Eu(\mu_2\text{-}OC_2H_5)(btfa)(NO_3)(phen)]_2 \cdot phen$. Under the blue-light excitation the complex exhibits a strong, bright-red emission with high colour purity. The emission spectra show characteristic metal-centered luminescence bands, which are assigned to internal radiative transitions of the Eu^{3+} ion, $^5D_{0,1} \rightarrow {}^7F_j$ (j = 0–4). Overall, the photoluminescence spectra suggest that the europium ions are situated in a low-symmetry environment. The character of the excitation spectrum of the complex indicates on high efficiency of excitation of the PL emission with cheap blue-light LED sources. The overall specific features on the emission spectra of this compound, along with its PL emission high intensity, indicates on its good potential for practical applications.

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