

[https://doi.org/10.52326/jes.utm.2024.31\(2\).03](https://doi.org/10.52326/jes.utm.2024.31(2).03)

UDC 544.228:535.37:546.661



Eu³⁺ AS A LUMINESCENT PROBE FOR LOCAL SITE SYMMETRY IN Eu(III) COORDINATION COMPOUNDS

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Received: 04. 25. 2024

Accepted: 05. 22. 2024

Abstract. The paper deals with the use of tripositive ion Eu³⁺ as a luminescent probe for the evaluation of the local site symmetry in coordination compounds with europium(III) content. The energy levels of the Eu³⁺ multiplets in the ligand matrix may be split by the crystal field into a maximum number of 2J+1 components, depending on the site symmetry of the Eu³⁺ ion. Analysis of photoluminescence spectra provides information on the local site symmetry of the compound. The topic is discussed with reference to literature data as well as own experimental results obtained in the Laboratory of Optoelectronics "A. Andries" of the Institute of Applied Physics. This work gives a deeper insight into the spectral characteristics of Eu³⁺ ions in ligand matrices and can be a guiding support for investigation of photoluminescence in Eu(III) complexes.

Keywords: Trivalent lanthanide, electronic transitions, local symmetry, biomedicine, fluorescent probe.

Rezumat. În lucrare se examinează utilizarea ionului tripozitiv Eu³⁺ în calitate de sondă luminescentă pentru evaluarea simetriei locale în compușii coordinați cu europiu(III). Nivelele energetice multiplu ale ionului Eu³⁺ în matricea ligandului se pot despica în câmpul cristalin într-un număr de maxim 2J+1 componente, în dependență de simetria locală în jurul ionului Eu³⁺. Analiza spectrelor de fotoluminescență oferă informații despre simetria locală în jurul ionului Eu³⁺. Subiectul este examinat cu referire la date din literatură, precum și pe baza rezultatelor experimentale proprii, obținute în Laboratorul de Optoelectronică „A. Andries” al Institutului de Fizică Aplicată. Această lucrare oferă delatii practice despre caracteristicilor spectrale ale ionilor Eu³⁺ în matricele de liganzi și poate fi un ghid pentru investigarea fotoluminescenței în complexe Eu(III).

Cuvinte-cheie: Lantanide trivalente, tranziții electronice, simetrie locală, biomedicină, sondă fluorescentă.

1. Introduction

Ln(III) coordination compounds have been extensively studied over the years because of high potential in experimental applications and research [1-3]. Among the Ln(III) coordination compounds the Eu(III) complexes occupies a special role [4]. They emit in the visible range, usually exhibit bright-red luminescence, and are characterised by high quantum yield [5]. But when Eu^{3+} ions are incorporated in inorganic matrices, for example the ZBLA or PIGLZ glasses, strong green, blue, and ultraviolet emissions were registered, in addition to the red emission of Eu^{3+} [6,7].

Due to their photochemical stability, time-stable luminescence with narrow emission bands, low level of degradation and toxicity in comparison with organic fluorophores, Eu^{3+} compounds are widely applied in optoelectronics and photonics, sensor technology, LEDs, etc. [8]. The unique peculiarities of the Eu^{3+} ions place it as a powerful spectroscopic tool to study structure or follow processes and mechanisms in such applications as biomedicine, photonics, environment monitoring systems, and structural engineering. Europium(III) coordination compounds can be also excellent materials for biochemical or biomedical applications, for example, in nuclear medicine for diagnostic imaging, targeted therapy and as fluorescent probes [7,9]. Some of the Ln(III) complexes are attractive as luminescent materials for *in vitro* and *in vivo* imaging [10] or can be used as biosensors, contrast agents in medical research, etc. Particularly Dy^{3+} based complexes can be used as contrast agents for magnetic resonance diagnosis [11-13]. An advantage of the europium(III) complexes is that they emit in the visible spectrum, with intensities easily observable with the naked eye.

When incorporating the Eu(III) ion in a matrix of ligands, the spherical symmetry of the ion, it has in a free state, is perturbed. Under the influence of the asymmetric ligand electric field the spectroscopic levels of the free ion splits into components, depending on the local symmetry around the Eu^{3+} ion [9]. Since the character of the photoluminescence (PL) emission spectrum is determined by the local site symmetry around the Eu^{3+} ion, it can provide useful information on the local site symmetry of the respective coordination complex. In the following we will discuss some aspects in interpretation of PL emission spectra of Eu^{3+} based complexes, with an example of $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{NO})_3(\text{phen})]_2 \cdot \text{phen}$ compound.

2. Materials and sample preparation

Used reagents and the synthesis process of the complex $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{NO})_3(\text{phen})]_2 \cdot \text{phen}$ were described in detail in Moldovan Patent MD 4677 B1 [13], as well as in [5]. The synthesized compound shows high stability in air, solubility in monoatomic alcohols, in such organic compounds as ether, dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO).

3. Experimental characterization

Low-resolution PL emission spectra (0.0715 nm) were recorded with a single-grating monochromator MDR-23 (LOMO, Sankt-Petersburg). High-resolution (2 cm^{-1}) PL emission spectra were registered with a double-grating spectrophotometer DFS-52 (LOMO) and a Hamamatsu photomultiplier module H8259-01 in a photon counting mode. PL spectra were registered with a Thorlabs laser diode L375P70MLD (375 nm) or collimated laser diode module CPS405 (405 nm) as an excitation source. For the PL time decay measurements, a pulsed nitrogen laser at 337 nm with a repetition rate of 10 Hz and a pulse width of 10 ns was used [5].

4. Results and Discussion

4.1 Photoluminescent properties of the europium(III) coordination compounds

An example of PL emission spectrum for Eu(III) coordination compound – $[\text{Eu}(\mu_2\text{OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2 \cdot \text{phen}$ is represented in Figure 1. The PL emission spectra of the powder samples were registered at room temperature under excitation of the laser beam at 375 nm, selected as close to the maximum absorption of the studied compound.

The PL emission spectrum can be characterized by atomic-like emission bands with multiple splitting, and with an ultra-narrow emission band at ca. 580 nm (Figure 1).

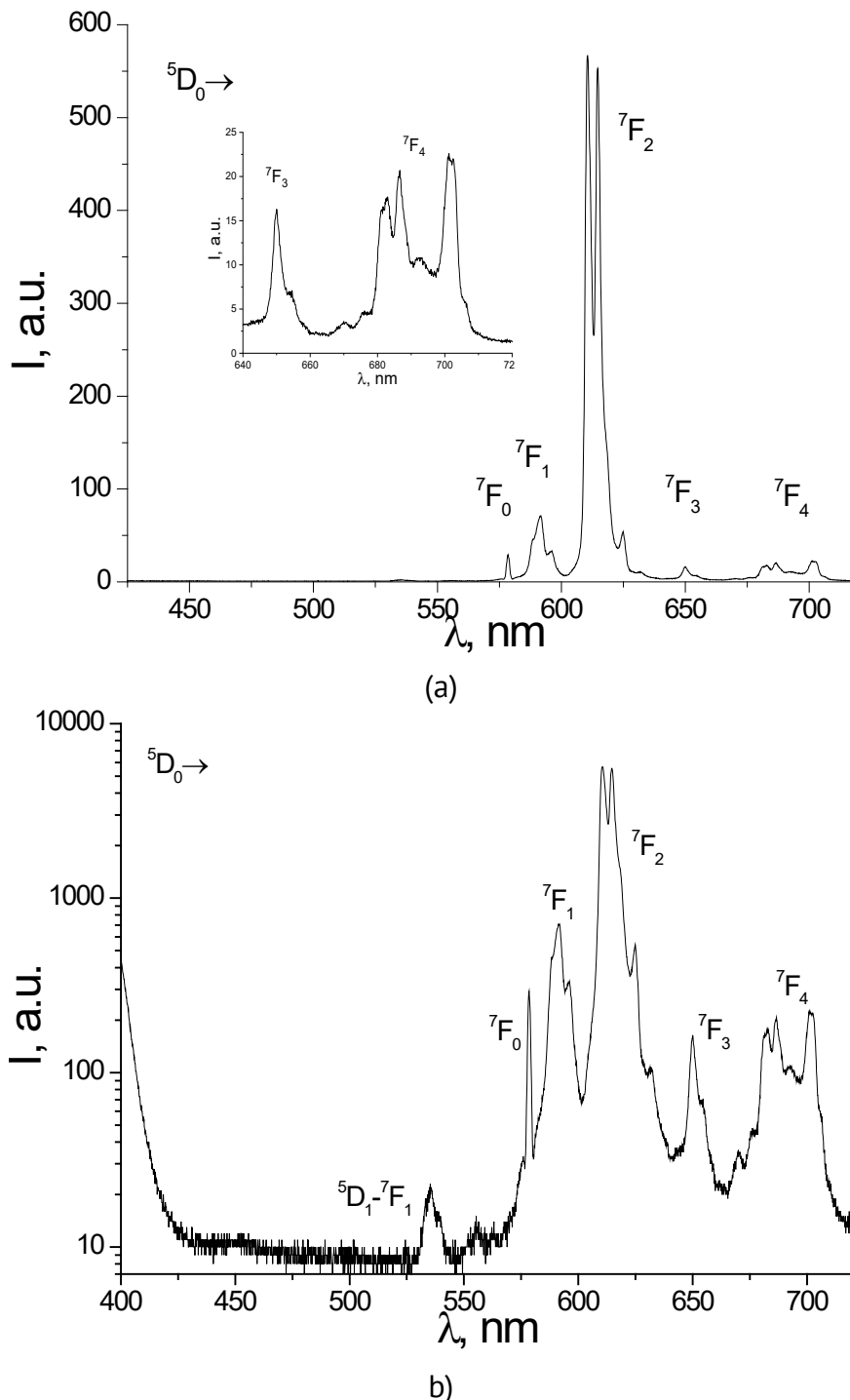


Figure 1. Low-resolution PL emission spectrum of the powder sample $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2 \cdot \text{phen}$ measured at 300 K under excitation 375 nm: a) linear and b) logarithmic scale.

This band is found only in the Eu(III) complexes, where the site symmetry of the Eu^{3+} ion belongs to low symmetries C_s , C_v and C_{nv} [7]. All the transitions, except one at about 580 nm, exhibit a fine structure determined by the interaction of the ligand field with the Eu^{3+} ion, which can split the 7F_J level into at most $2J+1$ sublevels. The metal-centered luminescence bands are determined by 4f-4f radiative transitions of the Eu^{3+} ion, ${}^5D_1 \rightarrow {}^7F_J$ and ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0 - 4$). The major emission bands are related to the transitions from the first excited metastable 5D_0 level to the 7F_J ($J = 0 - 4$) manifold, Figure 1.

The splitting character of the PL emission bands is determined basically by the site symmetry around the Eu^{3+} ion [7,15,16]. The maximum numbers of ligand-field (or Stark) sublevels depend on the point group of symmetry, and Stark-level splitting for specific crystal field symmetry is a function of the total angular momentum J , Table 1 [12,17,18]. In the case of inorganic Eu^{3+} compounds the PL emission can originate from higher excited states, 5D_2 and 5D_3 , which may result in rather complicated luminescence spectra [7,19].

The ${}^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole (MD) transition, and it is considered to be independent on the local site symmetry, and therefore it commonly is taken as a reference. The MD transition can split at most in 3 sublevels for low site symmetry of the Eu^{3+} ion.

Table 1

Stark-level splitting for specific crystal field symmetries as a function of the total angular momentum J [17]

Local Symmetry	Triclinic (C_1, C_i)	Monoclinic (C_s, C_2, C_{2h})	Rhombic (C_{2v}, D_2, D_{2h})
$J = 0$	1	1	1
$J = 1$	3	3	3
$J = 2$	5	5	5
$J = 3$	7	7	7

The example given in Figure 1 for the binuclear complex $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})_2 \cdot \text{phen}]$ shows at least 4 components for the MD transition, which means more than the maximum number of components, which can be registered in the case of mononuclear Eu^{3+} compound. This feature in the PL spectrum suggests a binuclear Eu(III) complex.

The ${}^5D_0 \rightarrow {}^7F_2$ transition is an electric-dipole transition (ED), which is considered to be “hypersensitive transition” to the local site symmetry environment [15]. To compare the intensities of the transition ${}^5D_0 \rightarrow {}^7F_2$ in different Eu(III) compounds the asymmetry ratio R is used, which is defined as the ratio of integrated intensities of ED transition ${}^5D_0 \rightarrow {}^7F_2$ and that of the MD transition ${}^5D_0 \rightarrow {}^7F_1$. The factor R is used in many cases to derive information on the local site symmetry of the Eu(III) ion. It should be noted however, that care should be taken when using the ratio R for deriving information on the local site symmetry. P. Tanner [20] had shown that R factor may vary strongly, depending on the specific crystallographic or “spectroscopic” site symmetry of the Eu^{3+} ion.

The mechanism of PL in Ln(III) complexes is determined by so-called “antenna effect”, which means the excitation energy transfer from the ligand matrix to the Ln(III) ion, Figure 2.

This imply that illumination of the complex by a UV or near-UV light beam leads to the electron excitation from the ground singlet state S_0 to the excited singlet state S_1 . Following the excitation, the electron rapidly relaxes ($\sim 10^{-12} - 10^{-14}$ s) to lower states through vibrational relaxation and internal conversion. After intersystem crossing and change in the

spin, the electron can reach the triplet state T_1 , Figure 2. The energy transfer takes place between the ligand excited state and the excited states of the Eu³⁺ ion.

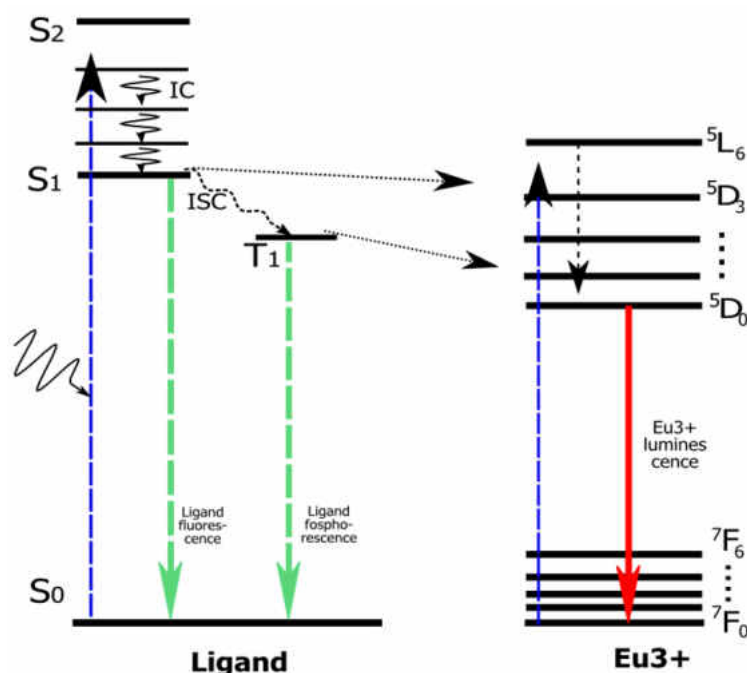


Figure 2. A simplified illustration on the mechanism of energy transfer in Ln coordination compounds: S_0 and S_1 – the singlet ground and excited states; IC – internal conversion; ISC – intersystem crossing; T_1 – the triplet state (adapted from [21]).

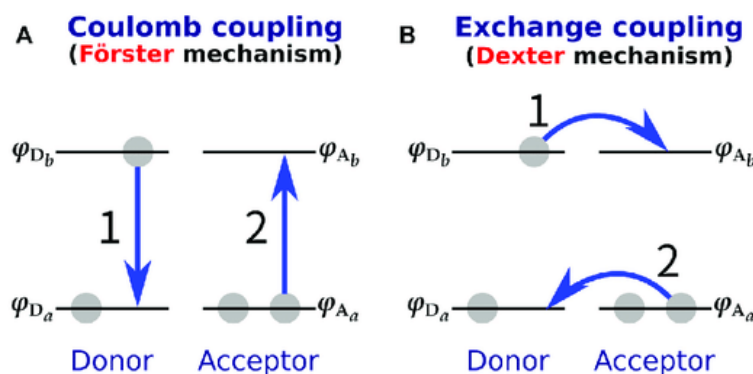


Figure 3. Förster-type (A) and Dexter-type (B) EET mechanisms in which the order of the electronic transitions that take place are shown by indices 1 and 2 [22].

Commonly, the mechanism of energy transfer is treated in the framework of Förster and Dexter-type models, Figure 3. The Förster-type model implies non-radiative energy transfer triggered by Coulomb coupling between donor and acceptor, typically at long-range distance about 10-100 Å. The Dexter-type model supposes transfer of excitation at short-range distance, typically less than 10 Å [15].

4.2 Eu(III) as a luminescent probe for local site symmetry

Incorporation of Eu³⁺ in various organic or inorganic matrices provides advanced materials with high PL quantum yield and attractive optical properties in the visible range of the spectrum. On the other side, the presence of the Eu³⁺ ion in the matrix can be useful as a luminescent probe to study the local symmetry around the Eu³⁺ ion [22,23].

The luminescence spectrum of rare earth Eu^{3+} ions appear as a set of narrow bands (Figure 1) associated with transitions within the shielded f-shell. This shielding strongly attenuates the influence of the crystalline field of the matrix on the f-shell electrons. For these reasons, the Eu^{3+} bands only slightly change their spectral position in various dielectric matrices. The emission bands in the PL spectrum of the binuclear complex $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2\cdot\text{phen}$ (Figures 1 and 4) are determined by radiative transitions between the ${}^5\text{D}_{0,1}$ and ${}^7\text{F}_J$ ($J = 0 - 4$) levels of the Eu^{3+} ion [24].

Because the band intensities and the splitting character in the PL spectra of Eu^{3+} ions depend on the local symmetry of the ion in the matrix, the Eu^{3+} ion can be exploited as a luminescent probe. P. Tanner presents a comprehensive examination of this and other aspects in interpretation of the Eu^{3+} PL spectra in his tutorial review [20].

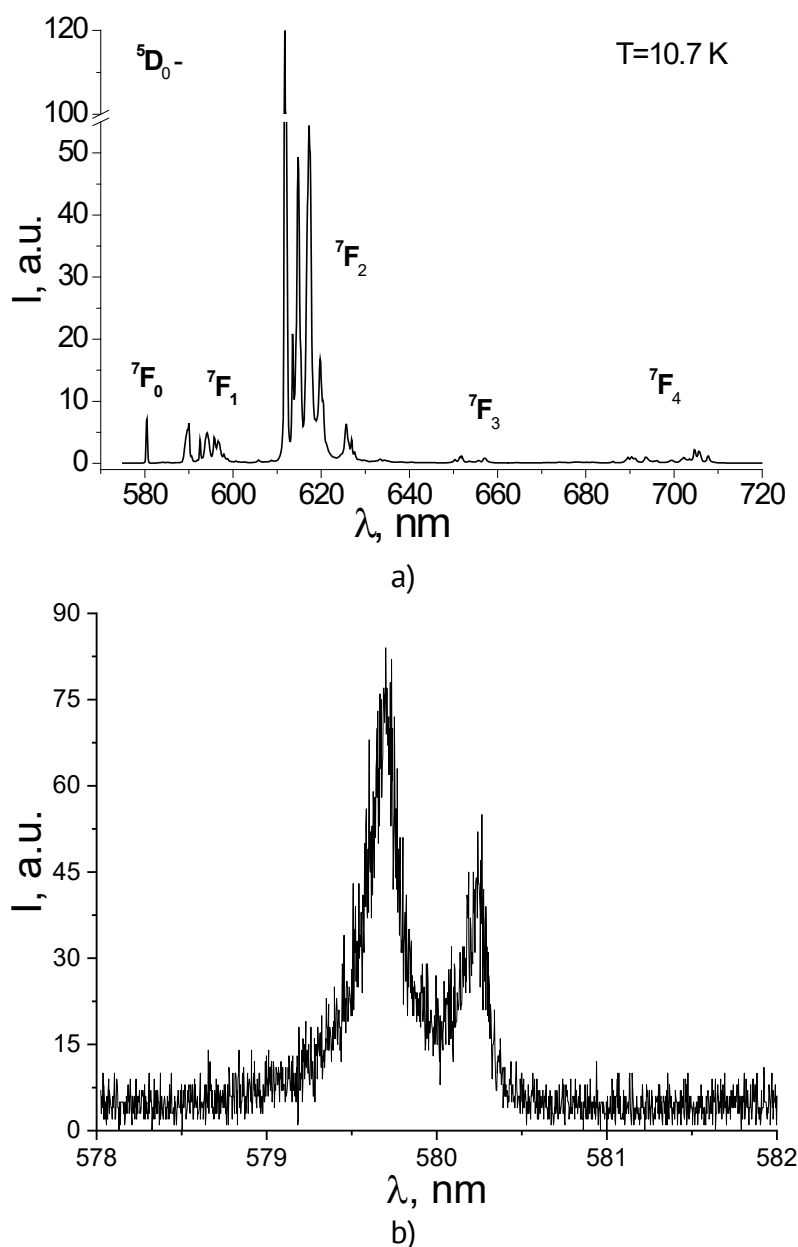


Figure 4. Low-resolution PL spectrum of the binuclear complex $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2\cdot\text{phen}$ at 10.7 K [5] (a) and high-resolution spectrum of PL emission band ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ($\lambda_{\text{exc}} = 405 \text{ nm}$) (b).

Detailed information can be obtained from analysis of high-resolution PL spectra in the framework of group theory. This can provide information not only on local site symmetry of the Eu(III) ion, but also on the number of chemically different metal-ions sites in the studied material and about the total formal charge of the ligating groups directly bonded onto the Eu(III) ion [9,24].

One of the very interesting features of the PL emission spectra of Eu(III) coordination compounds is represented by the ultra-narrow transition at about 580 nm (Figure 4). This transition implies the participation of two non-degenerate energy levels, ⁵D₀ and ⁷F₀, which are not split by the crystal-field. Because of this, the number of components of this transition can be used for determination of the presence of non-equivalent sites in a host matrix of the coordination compound [25]. Consequently, band splitting or asymmetry in the band of the ⁵D₀→⁷F₀ transition represents an indication of a possible existence of different emitting species in the Eu(III) complex [7,15,16,26,27].

Again, we have to be careful when drawing conclusions based on the character of ⁵D₀→⁷F₀ transition. For example, registration of two components of the ⁵D₀→⁷F₀ transition does not necessarily indicate on a bi-nuclear coordination complex. Two or more components can be registered because of other reasons, for example because of defects, isomers, or because of vibronic contributions. Detailed reviews on the major aspects in interpretation of PL spectra of tri-positive europium related to the site symmetry in Eu(III) complexes are presented by K. Binnemans [7] and P. Tanner [15].

Optical transitions registered in the emission spectra of Eu(III) coordination compounds arise from the ⁵D₁ and ⁵D₀ excited states to the ⁷F_J levels, ⁵D₀→⁷F_J, (J = 0 – 6). An example of the PL emission spectrum of a binuclear coordination compound is represented in Figure 4 for the complex [Eu(μ₂-OC₂H₅)(btfa)(NO₃)(phen)]₂·phen. In the low-resolution spectrum of the complex (Figure 4a), we can hardly distinguish the presence of two components for the transition ⁵D₀→⁷F₀.

In order to verify the number of components in the ⁵D₀→⁷F₀ transition, the PL emission spectrum was registered with high resolution (2 cm⁻¹). The high-resolution spectrum (Figure 4b) of the complex reveals two components of this band, which suggests the existence of two different surrounding neighbourhoods for the Eu³⁺ ion in the matrix. Further, one can observe that the magnetic-dipole transition ⁵D₀→⁷F₁ is composed of at least 5 components, while the electric-dipole transition ⁵D₀→⁷F₂ reveals at least 8 components, which again points to existing of two different emitting sites of the Eu³⁺ ion in the matrix of the support the [Eu(μ₂-OC₂H₅)(btfa)(NO₃)(phen)]₂·phen complex. The other two emission bands in this spectrum, ⁵D₀→⁷F₃ and ⁵D₀→⁷F₄ are very weak, and therefore we do not examine them in detail.

The limited number of optical transitions for Eu(III) complexes compared to other Ln(III) coordination compounds makes it easier to interpret the measured photoluminescence emission spectra [28].

Another example of binuclear compound is Eu₂O₃. The measured PL emission spectrum of such a complex (powder sample) is represented in Figure 5 a,b. Because of the binuclear character of the compound, we can observe the band ⁵D₀→⁷F₀ to contain two major components (Figure 5b), and the band ⁵D₀→⁷F₁ to be composed of at least 4 major components, and the electric-dipole transition splits into at least 8 components.

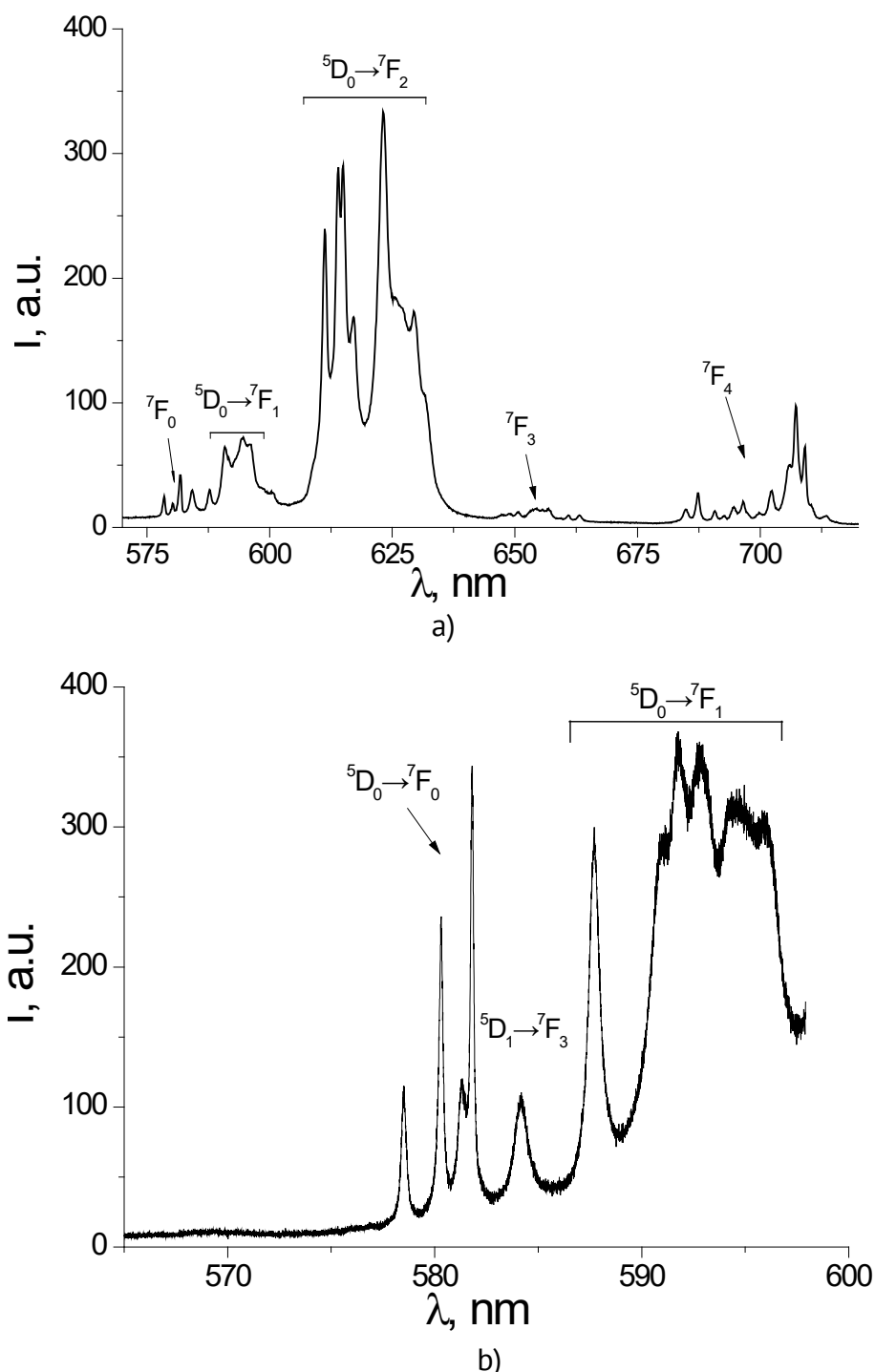


Figure 5. PL spectra of powder sample Eu_2O_3 under the excitation of 405 nm laser beam: a) low-resolution spectrum 570-720 nm; b) high-resolution spectrum, ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions.

Complementary information on the local symmetry around of the Eu(III) in the coordination compound we can get from the PL time relaxation characteristics. Figure 6 [5] illustrates a PL decay profile of the binuclear compound $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2 \cdot \text{phen}$, registered at room temperature.

A theoretical approach to the PL relaxation kinetics for an ensemble of emitters, showing non-single exponential photoluminescence decay, is presented in a recent paper [24]. In the case of Eu(III) coordination complexes, when the PL decay profile exhibits a bi-exponential character, such feature commonly is attributed to the luminescence from two

different emitting Eu³⁺ sites [29]. The average lifetime of the ⁵D₀ excited state evaluated from the PL decay curve of the bi-exponential decay (see Figure 6), can be assumed to be equal to the observed luminescence lifetime [30], and can be used for estimation of the intrinsic quantum yield of the Eu(III) complex [5].

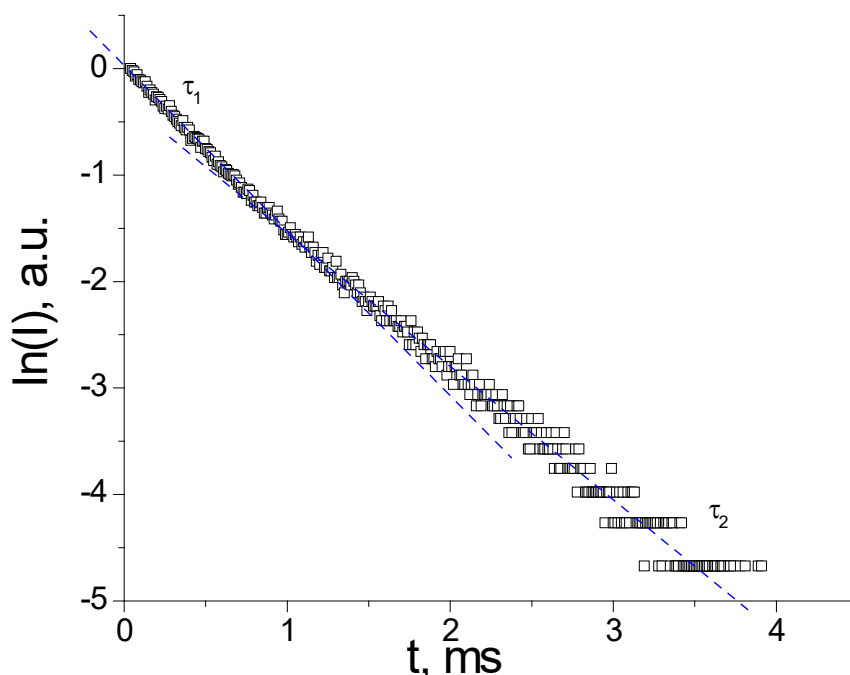


Figure 6. PL decay profile in powder sample at 300 K measured at 612 nm. A pulsed nitrogen laser was used ($\lambda = 337$ nm, repetition rate - 10 Hz, pulse width - 10 ns) [5].

5. Conclusion

Tripositive europium ions Eu³⁺ can serve as luminescent probe, for evaluation of the symmetry of the first coordination sphere of a trivalent lanthanide ion Eu³⁺. We discuss some aspects on the use of tripositive ion Eu³⁺ for evaluation of local symmetry features of the europium(III) coordination compounds. Origin of the distinct emission can be assigned to the site symmetries of Eu³⁺ centres. The report brings the main hints in analysis of the photoluminescence spectra, when drawing conclusions on the structural features of the compound. The paper is based on own experimental results in correspondence with the relevant examples from the literature.

Of course, more detailed information on local structure around the Eu(III) ion can be obtained from analysis of high-resolution PL spectra in the framework of group theory. This refers not only on local site symmetry of the Eu(III) ion, but also the number of chemically different metal-ion sites in the studied material and the total formal charge of the ligating groups directly bonded onto the Eu(III) ion. The final assignment of the point group symmetry can be made on the basis of additional XRD measurements.

The Eu(III) ion easily replaces some metal ions in materials of biomedical importance. For example, the Eu(III) ion is very suitable for replacing Ca(II) ion due to the same spherical ions with non-directional chemical bonding; similar ionic radius and hydration number. Thus, the chemical and structural properties of Ca ion sites in biologically important materials can be tested by analysing the spectroscopic response of Eu(III) ions placed in these sites.

This work gives a deeper insight into the spectral characteristics of Eu^{3+} ions in ligand matrices and can be a guiding support for investigation of photoluminescence in $\text{Eu}(\text{III})$ complexes. The results obtained can be useful to researchers and engineers who use the spectroscopic response of Eu^{3+} ion materials for investigations of the structure and processes that take place in practical applications such as biomedicine, photonics, environmental monitoring, etc.

Acknowledgements: This research is part of the master program work, as well as part of the work funded by the Ministry of Education and Research of the Republic of Moldova (subprogram 011201). The authors are grateful to Dr. V. Verlan for stimulating discussions.

Conflict of interests: The authors declare no conflict of interest.

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Citation: Ghenea, V.; Culeac, I.; Buzdugan, A. Eu³⁺ as a luminescent probe for local site symmetry in Eu(III) coordination compounds. *Journal of Engineering Science* 2024, XXXI (2), pp. 28-38. [https://doi.org/10.52326/jes.utm.2024.31\(2\).03](https://doi.org/10.52326/jes.utm.2024.31(2).03).

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