

INSIGHTS INTO THE LUMINESCENCE PROPERTIES OF A DINUCLEAR Eu^{3+} COORDINATION COMPLEX

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Abstract: We report the photoluminescent (PL) properties of a dinuclear Eu(III) complex when subjected to UV excitation. The PL spectra of coordination compound $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2\text{phen}$ were investigated on powder samples at room temperature (btfa stands for benzoyl trifluoro acetone and phen denotes 1,10-phenanthroline). The emission spectra revealed distinctive metal-centred luminescence bands, attributed to internal radiative transitions of the Eu^{3+} ion, specifically ${}^5D_1 \rightarrow {}^7F_j$ and ${}^5D_0 \rightarrow {}^7F_j$ ($j = 0 - 4$). The radiative transition between the non-degenerate states ${}^5D_0 \rightarrow {}^7F_0$ splits into two components. The character of the photoluminescence spectra suggests the europium ions are located in a low-symmetry environment. The actual assignment of the point group symmetry can be made on the basis of XRD measurements. Understanding of the luminescent behaviour will help in development of new Eu(III) coordination compounds, for potential biomedical applications or pure scientific inquiries.

Keywords: Eu(III) ; coordination compound; UV light; PL.

Introduction

The luminescent properties of europium(III) coordination compounds have garnered significant attention, primarily for their utility in practical biomedical applications and fundamental scientific inquiries [1]. These complexes, exhibit vibrant red luminescence characterized by remarkable colour purity and high quantum yield within the visible spectrum. They can be used as spectroscopic probes for structural properties and local symmetry around the Eu(III) ion within the ligand framework [3]. Despite the extensive exploration in this domain, there persists a concerted effort to engineer novel Eu(III) complexes tailored for biomedical and biochemical applications. This study unveils experimental findings on photoluminescence properties of a novel europium(III) coordination complex $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2\text{phen}$. Possible applications of this complex could pertain to the realm of biological systems, facilitating early disease diagnosis and unravelling cellular processes, holding promise for biomedical endeavours.

Experimental details

The synthesis of the $[\text{Eu}(\mu_2\text{-OC}_2\text{H}_5)(\text{btfa})(\text{NO}_3)(\text{phen})]_2\text{phen}$ coordination complex followed previously outlined procedures [2]. Photoluminescence (PL) emission spectra were collected with a resolution 0.125 nm, employing diverse excitation sources. Commonly a Hamamatsu photomultiplier module H9319-12, operating in photon counting mode, and a MDR-23 single grating monochromator were utilized for low-resolution spectra acquisition. Alternatively, for high resolution (2 cm^{-1}) PL emission spectra measurements we employed a double grating spectrophotometer DFS-52. PL excitation was conducted using a Thorlabs laser diode at 375 nm (70 mW power) L375P70MLD.

Photoluminescence spectrum of Eu complex

The photoluminescence spectra of the powdered samples were recorded at room temperature employing the excitation source emitting at 375 nm, aligning closely with the compound's peak absorption wavelength. The PL emission spectra display (Figure 1) characteristic luminescence bands originating from the Eu^{3+} ions internal radiative transitions, specifically ${}^5\text{D}_1 \rightarrow {}^7\text{F}_j$ ($j = 0-3$) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ (where j ranges from 0 to 4). The primary emission bands stem from the radiative transitions between the first excited ${}^5\text{D}_0$ level and the ${}^7\text{F}_j$ (where j ranges from 0 to 4) manifold [3].

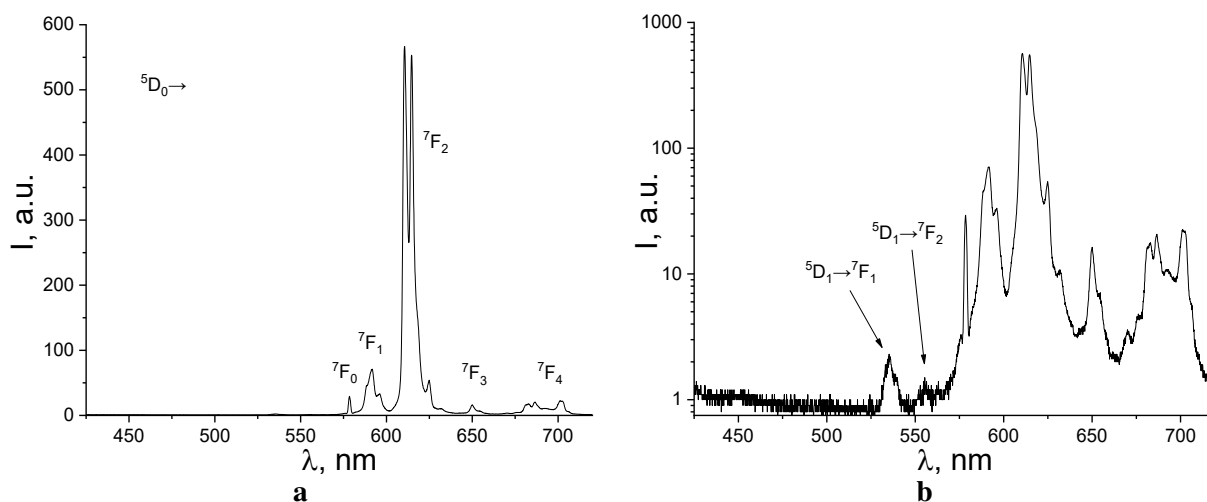


Figure 1. PL emission spectrum of the powder sample: (a) linear scale; (b) logarithmic scale.

The dominant emission band in the luminescence spectrum is determined by the electric dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ of the Eu^{3+} ion, that occurs at about 612 nm which is well-known to be hypersensitive to the local symmetry of the lanthanide ion. The distinct red colour of the compound emission is related to this specific transition.

The intricate structure of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is distinctly discernible, primarily dictated by the molecular electric field generated by the influence of the ligand on the degenerate ${}^7\text{F}_2$ level of the Eu^{3+} ion, as outlined in reference [4].

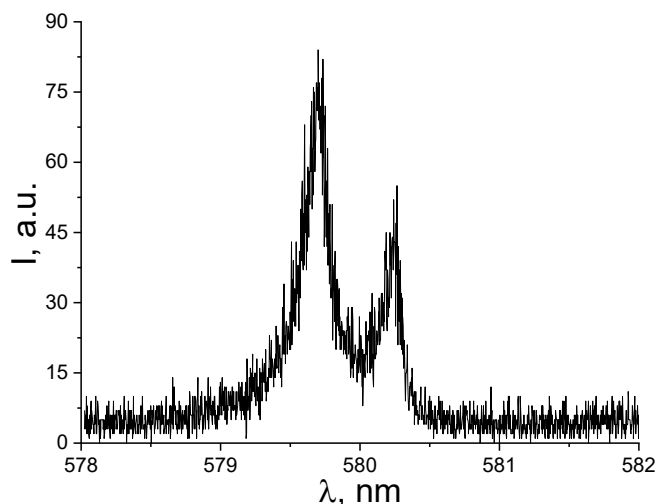


Figure 2. High-resolution PL emission spectrum of the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$.

The ultra-narrow emission band at ca 580 nm is determined by transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, which is forbidden according to the standard Judd–Ofelt theory [3]. Registration of more than one component in the spectrum of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ band suggests that more than one emitting site is present in the $\text{Eu}(\text{III})$ complex. This however, does not allow to determine the exact number of Eu^{3+} sites.

In order to verify the number of components in the ${}^5D_0 \rightarrow {}^7F_0$ transition (Figure 1), the PL emission spectrum was registered with high resolution (2 cm^{-1}). The high-resolution spectrum of the ${}^5D_0 \rightarrow {}^7F_0$ transition, confirms the presence of two components in this band, which supports the model of dinuclear complex.

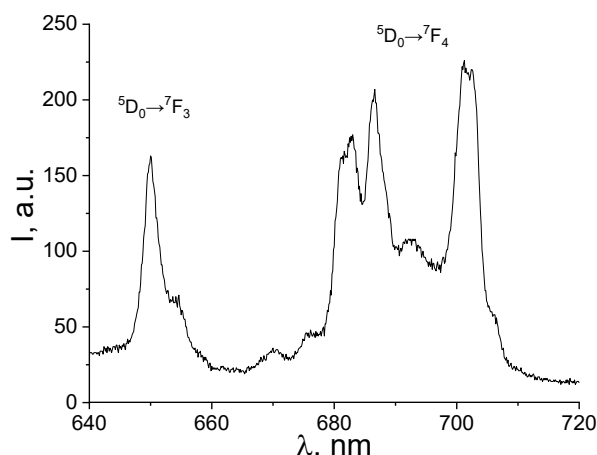


Figure 3. PL emission spectrum of the transitions ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$, under excitation 375 nm.

Notably, the electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ exhibits significantly greater intensity compared to the magnetic dipole transition ${}^5D_0 \rightarrow {}^7F_1$. This feature presumes the non-centrosymmetric placement of the Eu^{3+} . The multiplicity of components observed in the transitions ${}^5D_0 \rightarrow {}^7F_j$ (where j spans from 0 to 4) is intricately linked to the symmetry of the crystal field surrounding the $\text{Eu}(\text{III})$ ion [3].

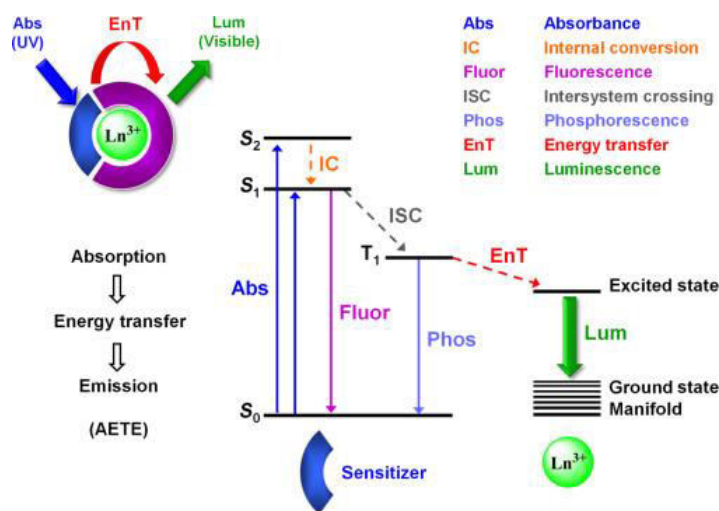


Figure 4. Jablonski diagram of energy transfer mechanism [5].

The energy transfer mechanism in lanthanide compounds during photoluminescence, involving transfer of absorbed energy from organic ligands to $\text{Eu}(\text{III})$ ions, is commonly referred to as the "antenna effect". Essentially, when exposed to UV or near-UV radiation, the organic ligands undergo excitation from their ground singlet state (S_0) to the first excited singlet state (S_1) (Figure 4). Subsequently, the excitation energy shifts from the S_1 state, through intersystem crossing to the triplet state (T_1), and ultimately to the Eu^{3+} ion, leading to the radiative emission from the states 5D_0 and 5D_1 . Notably, the detection of the transition ${}^5D_0 \rightarrow {}^7F_0$ may be an indicator of a low symmetry complex, as far as this particular transition is typically not observable in other symmetries except C_{nv} , C_n or C_s symmetries [4].

Conclusion

The studied complex exhibits strong luminescence under UV excitation (375 nm), which indicates on its good potential for practical applications. For instance, these applications could pertain to the realm of biological systems, facilitating early disease diagnosis and also some unravelling cellular processes. The straightforwardness and affordability of the excitation method rely on employing a cost-effective laser.

The character of PL emission spectra indicates on the existence of two Eu^{3+} emitting centres in the dinuclear coordination compound. The actual assignment of the structural properties of the complex can be made on the basis of XRD measurements.

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