



Investigation on the formation of highly luminescent β -diketone-Ln(III)-EDTA water-soluble complexes

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ABSTRACT

Three new β -diketone-Ln-EDTA (β -diketone = TTA, BTFA, ACAC; Ln = Eu^{3+} and Tb^{3+}) water-soluble complexes were prepared, and their photophysical properties were investigated in aqueous solutions and compared with the Eu-EDTA complex. A very strong red and green luminescence was observed by the addition of ligands to the aqueous solutions of the Eu-EDTA and Tb-EDTA complexes, respectively, due to the formation of water-soluble β -diketone-Ln-EDTA complexes. To confirm the formation and stoichiometry of the new β -diketone-Ln-EDTA complex, the Judd-Ofelt intensity parameters Ω_2 for Eu^{3+} complexes and the band width at half height ($\Delta\lambda$) for Tb^{3+} complexes were used. The dependence of these parameters on the addition of the β -diketone strongly suggests that only one β -diketonate ligand is in the first coordination sphere of the β -diketone-Ln-EDTA complexes. These new Eu^{3+} and Tb^{3+} systems may act as red and green optical markers for bioassay or bioimaging.

1. Introduction

In the last few decades, special attention has been devoted to the development of water-soluble trivalent lanthanide (Ln^{3+}) complexes exhibiting strong emission intensities due to their potential application as time-resolved luminescence probes for the imaging analysis of cells and tissues [1], sensors [2,3], bimodal contrast agents for magnetic resonance [4], biosensors, and fluoroimmunoassays [5,6]. The intraconfigurational 4–4 f transitions of Ln^{3+} ions are responsible for the unique spectroscopic properties such as narrow emission and absorption bands and long-lasting emitting states of the lanthanide compounds. Although these electronic transitions are forbidden, organic ligands can indirectly cause excitation to overcome the very low molar absorption coefficients (in the range $0.1\text{--}10\text{ mol}^{-1}\text{cm}^{-1}$) so that highly powerful and focalized sources of excitation such as lasers may not be needed. Additionally, organic ligands must saturate the coordination sphere of the metal ion to prevent coordination of water molecules resulting in efficient luminescent quenching via multiphonon coupling. In many neutral lanthanide complexes, polar moiety of the donor atoms containing the organic ligand is directed at the inner coordination sphere whereas the non-polar moieties are exposed to interactions with

the solvent medium. Furthermore, aromatic groups in organic ligands are essential for their action as efficient luminescence sensitizers operating via the *antenna effect* [7]. Consequently, development of highly luminescent water-soluble lanthanide complexes is a challenging research topic [8–12].

The Ln-EDTA complexes are highly stable in both solid and aqueous solutions. Moreover, X-ray structural data indicate that lanthanide ions are not completely situated inside the cavity formed by the coordinated EDTA ligand [13]. Further, two or three water molecules may saturate the first coordination sphere of the lanthanide ion. The water molecules may be substituted by different types of organic ligands, resulting in new water-soluble ternary coordination compounds. A series of anionic lanthanide complexes based on aminopolycarboxylate ligands such as EDTA and 4-(arylethynyl)pyridine and their derivatives have been widely investigated as promising label systems for time-resolved spectroscopy [14,15]. When these ligands are functionalized with a reactive coupled group, which serves as the binding site for the coupling of a biomolecule, they may act as excellent candidates for use as luminescent markers in aqueous solution for immunological assays [16–20]. We have investigated the luminescent properties of lanthanide-EDTA complexes bonded on silica gel and magnetic nanoparticle surfaces

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sensitized by β -diketonate ligands [21,22].

In this work, we have investigated systematically the photoluminescent properties and formation of β -diketonate–Eu–EDTA (where the β -diketonate is TTA or BTFA) and ACAC–Tb–EDTA complexes in aqueous solution. The experimental intensity parameters (Ω_λ) of the Eu^{3+} compounds were determined and correlated with different β -diketonate: Eu-EDTA molar ratios. For ACAC–Tb–EDTA complex, a similar correlation was performed using the full width at half maximum ($\Delta\lambda$) for the emission band assigned to the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition.

2. Experimental section

2.1. Materials

Sodium hydroxide (NaOH, ACS reagent, 97.0%), hydrochloric acid (HCl, ACS, 37%), ethylenediaminetetraacetic acid (EDTA, ACS, 99.4%), 2-thenoyltrifluoroacetone (tta, 99%), benzoyltrifluoroacetone (BTFA 99%), acetylacetone (ACAC, 99%), europium oxide (Eu_2O_3 , 99.9%), and terbium oxide (Tb_4O_7 , 99.9%) were purchased from Sigma-Aldrich and used without any previous treatment. Water solvent was deionized to 18 M Ω (Milli-Q, Millipore).

2.2. Ln-EDTA complexes and β -diketonate ligand solutions

First, the lanthanide chlorides ($\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$) were prepared by reacting Eu_2O_3 (2 g, 5.68×10^{-3} mol) or Tb_4O_7 (2 g, 2.67×10^{-3} mol) with concentrated hydrochloric acid, according to [22]. The resulting solution was filtered and heated to obtain a fine white powder.

Stock aqueous solutions of Ln–EDTA complexes at 6.60×10^{-3} mol/L were prepared by reacting EDTA and standardized LnCl_3 solutions (Ln: Eu or Tb). Therefore, 0.1228 g (3.30×10^{-4} mol) of EDTA was dissolved in an aqueous solution by adding NaOH (1 mol/L) drop by drop until complete dissolution. An aqueous solution of EuCl_3 (3.30×10^{-4} mol) or TbCl_3 (3.30×10^{-4} mol) was added to the resulting solution. The pH of the Ln–EDTA complex solution was adjusted to approximately 12 using an aqueous solution of NaOH to ensure that all carboxylate groups were deprotonated. It is worth mentioning that, even in a basic solution, no precipitate of $\text{Ln}(\text{OH})_3$ was observed indicating that all Ln^{3+} ions were coordinated by the EDTA ligand.

To investigate the formation of Ln–EDTA– β -diketonate complexes, a stock solution 1.8×10^{-1} mol/L of β -diketonate ligands (where the β -diketonate is TTA, BTFA, and ACAC) were also prepared by mixing aqueous solutions of the β -diketonate and NaOH in a one-to-one molar ratio. Ln–EDTA and β -diketonate aqueous solutions were mixed in different molar ratios. In this case, to a fixed volume (3 mL) of the stock aqueous solution of the Ln–EDTA complex, different volumes of the aqueous solution of the β -diketonate ligand were added, and the final

volume was adjusted with deionized water to 3.33 mL. Fig. 1 shows the luminescent β -diketonate–Ln–EDTA ternary complex formed from the preformed EDTA complex and β -diketonate ligands.

2.3. Instrumentation

The photoluminescence spectra of Ln (III)-EDTA- β -diketonate complexes in aqueous solutions were recorded at room temperature using a Cary eclipse fluorescence spectrophotometer using a Xe flash lamp as source. This equipment was controlled by the Cary Eclipse software.

3. Results and discussion

The Eu-EDTA complex solution exhibits very weak red emission on excitation with UV radiation. As mentioned above, absence of aromatic chromophoric groups in the EDTA ligand structure and the coordination of water molecules to Ln^{3+} ions play a vital role in this spectroscopic behavior. On the other hand, a very strong red luminescence has been observed by addition of TTA or BTFA ligand to the Eu–EDTA complex solution due to the formation of water-soluble β -diketonate–Eu–EDTA complexes. A similar increase in luminescence intensity has been observed for Tb–EDTA on addition of ACAC ligand solution, resulting in water-soluble ACAC–Tb–EDTA complex that exhibits a very strong green emission. The luminescence sensitization in these complexes is a result of the well-known *antenna effect* [7]. This intramolecular ligand-to-metal energy transfer is largely dependent on the relative energy positions of the triplet (T_1) donor states of β -diketonate ligands and excited acceptor energy levels of the Ln^{3+} ions.

The excitation spectra for Eu–EDTA, TTA–Eu–EDTA and BTFA–Eu–EDTA complexes in diluted solutions were recorded at room temperature (Fig. 2) in the spectral range of 340–590 nm under emission monitored at 616 nm that corresponds to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ hypersensitive transition. Fig. 2a shows the excitation spectrum for the Eu-EDTA complex in aqueous solutions at 6.6×10^{-3} mol/L that presents only the characteristic narrow absorption bands owing to the intraconfigurational ${}^7\text{F}_0 \rightarrow {}^{2\text{S}+1}\text{L}_J$ and ${}^7\text{F}_1 \rightarrow {}^{2\text{S}+1}\text{L}_J$ transitions (in nm): ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$ (365 nm), ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$ (385 nm), ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ (394 nm), ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ (464 nm), and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ (525 nm).

On the other hand, the excitation spectra for all solutions with different β -diketonate to Ln–EDTA (where the β -diketonate is TTA or BTFA) molar ratio exhibit an intense broader absorption band in the spectral range 350–450 nm, which may be ascribed to the $\text{S}_0 \rightarrow \text{S}_1$ intraligand transition (Fig. 2b and c). The absorption bands assigned to intraconfigurational ${}^7\text{F}_0 \rightarrow {}^{2\text{S}+1}\text{L}_J$ transitions are also observed, but their intensities are significantly lower than those from TTA and BTFA ligands. This result suggests the formation of water-soluble β -diketonate–Eu–EDTA complexes. However, the spectral profiles change when

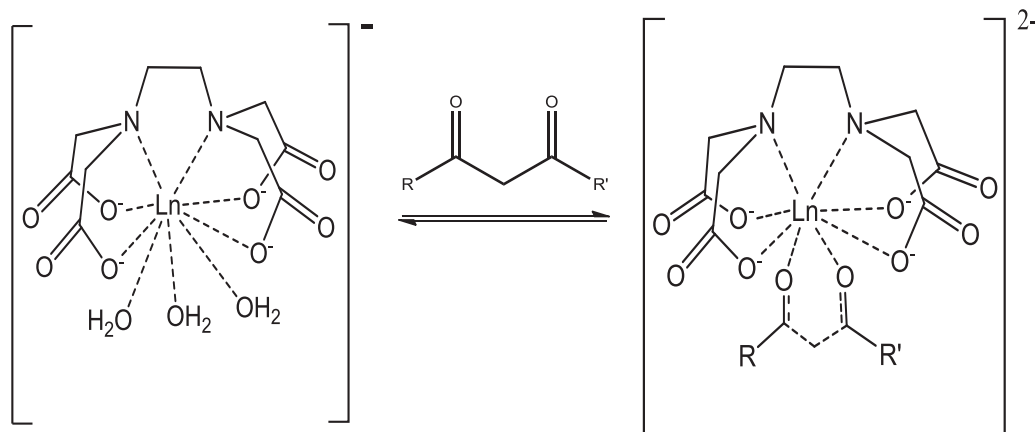


Fig. 1. Scheme showing a proposed structure of the lanthanide ternary β -diketonate–Ln(III)–EDTA complexes.

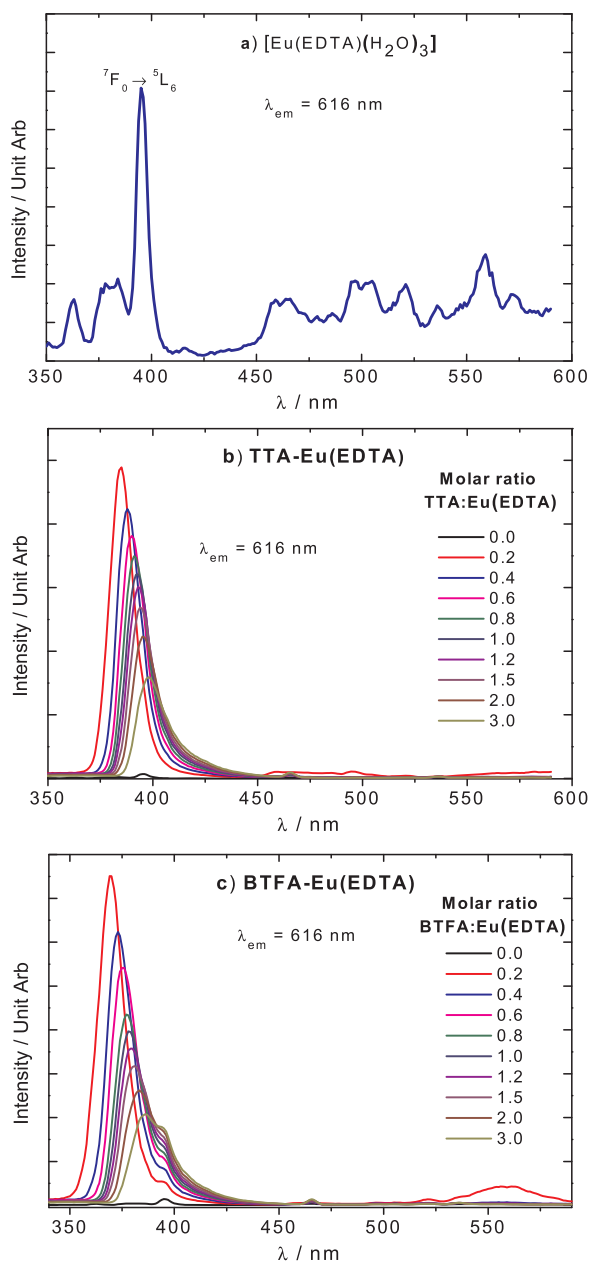


Fig. 2. (a) Excitation spectrum for the aqueous solution of the Eu–EDTA precursor complex (6.0×10^{-3} mol/L) and excitation spectra for aqueous solutions in different molar ratios, (b) TTA to Eu–EDTA precursor complex, and (c) BTFA to Eu–EDTA precursor complex. All spectra were recorded with emission monitored on the hypersensitive ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of the Eu(III) ion.

the β -diketone to Eu–EDTA molar ratio increases from 0.2 to 3. For the solutions presenting the molar ratio of 0.2 (diketone to Eu–EDTA), the excitation spectra are mainly dominated by the β -diketonate broad absorption bands, with maxima at 385 nm (for TTA, Fig. 2b) and 370 nm (for BTFA, Fig. 2c). The molar absorption coefficients of ligand bands for Eu complexes were determined: Eu(EDTA)(TTA), $\epsilon = 9.484 \times 10^3$ L mol $^{-1}$ cm $^{-1}$ and Eu(EDTA)(BTFA), $\epsilon = 7.010 \times 10^3$ L mol $^{-1}$ cm $^{-1}$. Interestingly, when this molar ratio increases, the excitation maxima are gradually redshifted, and their intensities are drastically reduced. This optical behavior may be explained due to the changes in sample composition in solution as the free β -diketonate ligand in the β -diketone–Ln–EDTA complex gradually increases in molar ratio from 0.2 to 3. As a result, the free β -diketonate ligand exerts a competitive effect through the radiation introduced in the system which

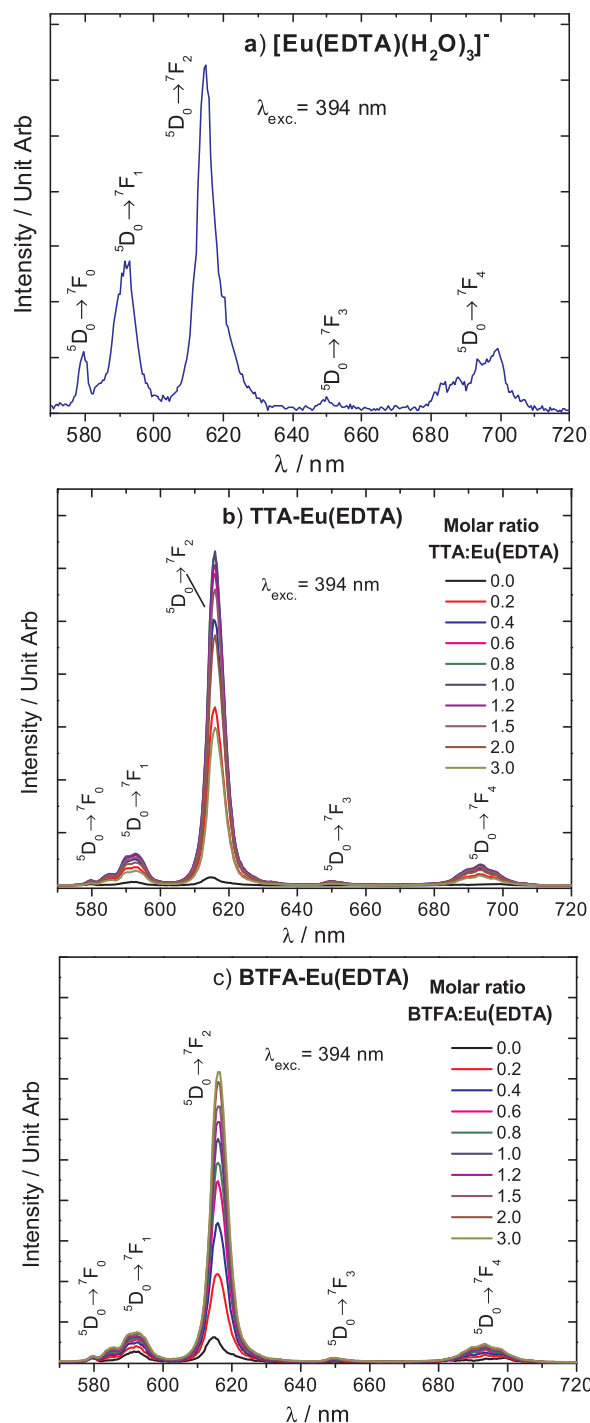


Fig. 3. (a) Emission spectrum for the aqueous solution of the Eu–EDTA precursor complex and emission spectra for aqueous solutions with different molar ratios, (b) TTA to Eu–EDTA precursor complex, and (c) BTFA to Eu–EDTA precursor complex. All spectra were recorded with excitation monitored on the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition of the Eu(III) ion.

is unable to transfer the excited energies to the Eu^{3+} ions. However, the increase of the complex concentration and molar absorption coefficient ligands in solution may also contribute for the observed behavior.

Fig. 3 displays the emission spectra for different β -diketone to Eu–EDTA (where the β -diketone is TTA or BTFA) molar ratios in aqueous solutions, recorded at room temperature in the spectral range from 570 to 720 nm, under excitation monitored at 394 nm (${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition). All emission spectra are characterized by the narrow bands assigned to the intraconfigurational ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions (where $J = 0$,

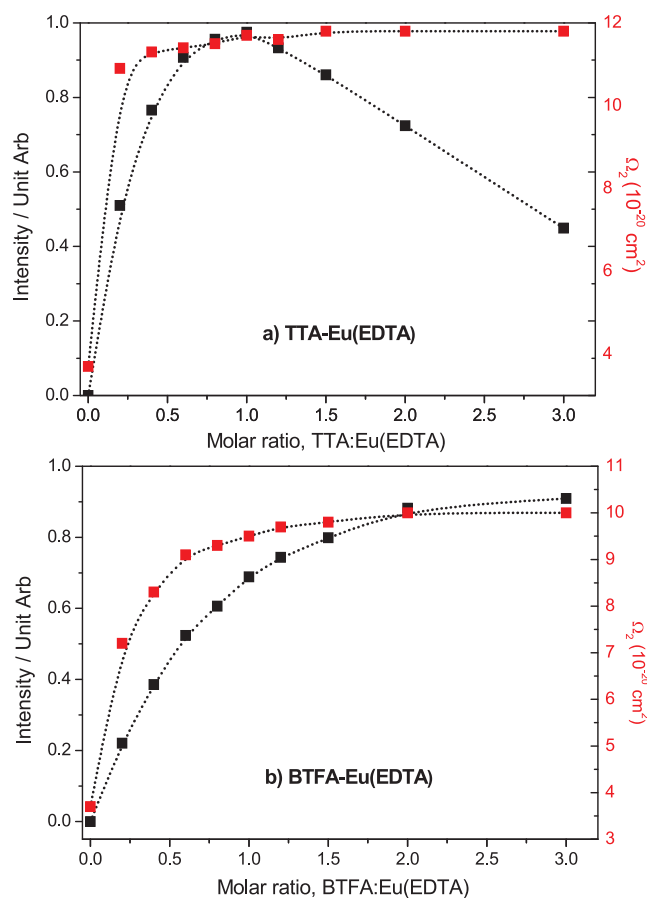


Fig. 4. Relationship between luminescence intensities (black) of the band assigned to the hypersensitive ${}^5D_0 \rightarrow {}^7F_2$ transition of the Eu(III) ion and intensity parameters Ω_2 (red) with respect to molar ratios (a) TTA to Eu-EDTA and (b) BTFA to Eu-EDTA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

1, 2, 3, and 4) of the Eu^{3+} ion. It is interesting to observe that the photoluminescent spectra for aqueous solutions containing TTA or BTFA ligands show both spectral profiles and relative intensities of the emission bands quite different from those for the Eu-EDTA system (insert Fig. 3a), even for lower β -diketone to Eu-EDTA (where the β -diketone is TTA or BTFA) molar ratios (Fig. 3a and b). These spectral data suggest coordination of β -diketonate ligands to the Eu^{3+} , leading to the ternary β -diketone-Ln-EDTA complexes in aqueous solution. Furthermore, a comparison between the emission spectra of the TTA-Eu-EDTA and BTFA-Eu-EDTA systems reveals that they exhibit similar profiles, indicating that these ternary complexes present similar chemical environments around the Eu^{3+} ion.

Fig. 4 shows how luminescence intensities depend on β -diketone to Ln-EDTA (where the β -diketone is TTA or BTFA) molar ratios and explains the photoluminescent behavior of aqueous solutions of the ternary complexes. For the system containing TTA ligand (Fig. 4a), the photoluminescence intensity reaches the maximum at the TTA to Ln-EDTA molar ratio around 1. Thereafter, emission intensity decreases linearly due to the excess, uncoordinated TTA ligand which absorbs radiation but does not act as luminescence sensitizer for Eu^{3+} ions. Consequently, the luminescence intensities decrease at higher TTA to Eu-EDTA molar ratios.

For the aqueous solutions with BTFA ligand (Fig. 4b), the photoluminescence intensity against the BTFA to Eu-EDTA molar ratio curve exhibits a different behavior. The curve shows a tendency to saturation only for the BTFA to Eu-EDTA molar ratio higher than 2.0. Although saturation is expected around the BTFA to Eu-EDTA molar ratio close to

1, factors such as the complex formation constant (K) and the molar absorptivity of the ligands must be included in defining the profile of the intensity of luminescence curve. Thus, it is necessary to use a more appropriate tool to confirm the stoichiometry of the new complexes formed. It is well known that the photoluminescent properties of lanthanide ions are highly dependent on their coordination environment. For Eu^{3+} complexes, small changes in the coordination geometry of the ion can result in significant changes in the intensities of the ${}^5D_0 \rightarrow {}^7F_J$ transitions, mainly for the emission band assigned to the ${}^5D_0 \rightarrow {}^7F_2$ transition.

Thus, Judd–Ofelt intensity parameters Ω_λ ($\lambda = 2, 4, 6$) may be used as an elegant tool to confirm the formation and stoichiometry of the β -diketonate-Eu-EDTA complexes in aqueous solutions. Experimental values of the intensity parameters (Ω_λ) may be determined from the emission spectra, using the ratios of the ${}^5D_0 \rightarrow {}^7F_J$ peaks ($J = 2, 4, 6$), with the ${}^5D_0 \rightarrow {}^7F_1$ intensity as an internal reference [23].

The dependence of Ω_2 intensity parameter for the aqueous solutions on the β -diketonate to Eu-EDTA molar ratio is shown in the Fig. 4. It is clear the lowest value of $\Omega_2 = 3 \times 10^{-20} \text{ cm}^2$ was found for the solution of the Eu-EDTA precursor complex without the diketonate ligands. As the β -diketonate to Eu-EDTA molar ratio increases, the intensity parameter values show asymptotic behavior, reaching maxima values ($\Omega_2 = 12 \times 10^{-20} \text{ cm}^2$ for TTA-Eu-EDTA and $\Omega_2 = 10 \times 10^{-20} \text{ cm}^2$ for BTFA-Eu-EDTA systems) when the β -diketonate quantities are approximately equivalent to the initial quantity of the precursor complex in solution. These luminescence results prove that water molecules were substituted by one β -diketonate molecule in the first coordination sphere of the Eu^{3+} ion.

The luminescence decay curves for Eu-complexes in solutions were recorded in water and deuterated water and the lifetime decay of the 5D_0 emitting level in these complexes were determined, as following: Eu(EDTA)(TTA), $\tau(\text{H}_2\text{O}) = 0.426 \text{ ms}$ and $\tau(\text{D}_2\text{O}) = 0.627 \text{ ms}$; Eu(EDTA)(BTFA), $\tau(\text{H}_2\text{O}) = 0.373 \text{ ms}$ and $\tau(\text{D}_2\text{O}) = 0.676 \text{ ms}$. Based on the Horrocks' formula [24] the number of water molecule coordinated to the lanthanide ion were determined, suggesting that there is no water molecule coordinated to the Eu ion in the Eu(EDTA)(TTA), $q = 0.5$. On the other hand, the $q = 0.98$ value for the solution with BTFA ligand suggests that one water molecule is coordinated to the Eu^{3+} ion, which is in agreement with the Eu(EDTA)(BTFA)(H_2O) formula.

The values of non-radiative (A_{nrad}) and radiative (A_{rad}) rates and, luminescence quantum efficiency (η) values for Eu-complexes in aqueous solutions were determined according with the procedure reported in the literature [23]: [Eu(EDTA)(H_2O) $_3$] ($A_{\text{nrad}} = 2854 \text{ s}^{-1}$; $A_{\text{rad}} = 213 \text{ s}^{-1}$ and $\eta = 7\%$); [Eu(EDTA)(BTFA)(H_2O)] ($A_{\text{nrad}} = 2297 \text{ s}^{-1}$; $A_{\text{rad}} = 384 \text{ s}^{-1}$ and $\eta = 14\%$) and [Eu(EDTA)(TTA)] ($A_{\text{nrad}} = 1899 \text{ s}^{-1}$; $A_{\text{rad}} = 454 \text{ s}^{-1}$ and $\eta = 20\%$). According with the results, the increase of η values reflect a decreasing and an increasing of the non-radiative and radiative rates of the luminescent materials, respectively, when water molecules are substituted by chelating β -diketonate ligands.

The photoluminescent properties of the Tb-EDTA precursor and ACAC-Tb-EDTA complexes in aqueous solution were also investigated. ACAC, instead of TTA and BTFA, was chosen as the ligand based on its ability to sensitize the luminescence of Tb^{3+} ion. The molar absorption coefficients of ligand bands for Tb complex, $\epsilon = 4.076 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Fig. 5a shows the excitation spectrum of the Tb-EDTA precursor complex in aqueous solution $6.6 \times 10^{-3} \text{ mol/L}$ recorded under emission monitored at 545 nm in the interval 250–530 nm. This spectrum shows characteristic narrow emission bands from intraconfigurational- $4f^8$ of the Tb^{3+} ion as follows: ${}^7F_6 \rightarrow {}^5L_6$ (339 nm), ${}^7F_6 \rightarrow {}^5L_9$ (350 nm), ${}^7F_6 \rightarrow {}^5L_{10}$ (369 nm), ${}^7F_6 \rightarrow {}^5G_6$ (376 nm), ${}^7F_6 \rightarrow {}^5D_3$ (380 nm) and ${}^7F_6 \rightarrow {}^5D_4$ (488 nm). For aqueous solutions with ACAC to Eu-EDTA molar ratios from 0.2 to 1.5 (Fig. 5b), a broad absorption band with maximum around 330 nm is observed, which may be attributed to the ACAC ligand's luminescence sensitization of the Tb^{3+} ion. Narrow bands from

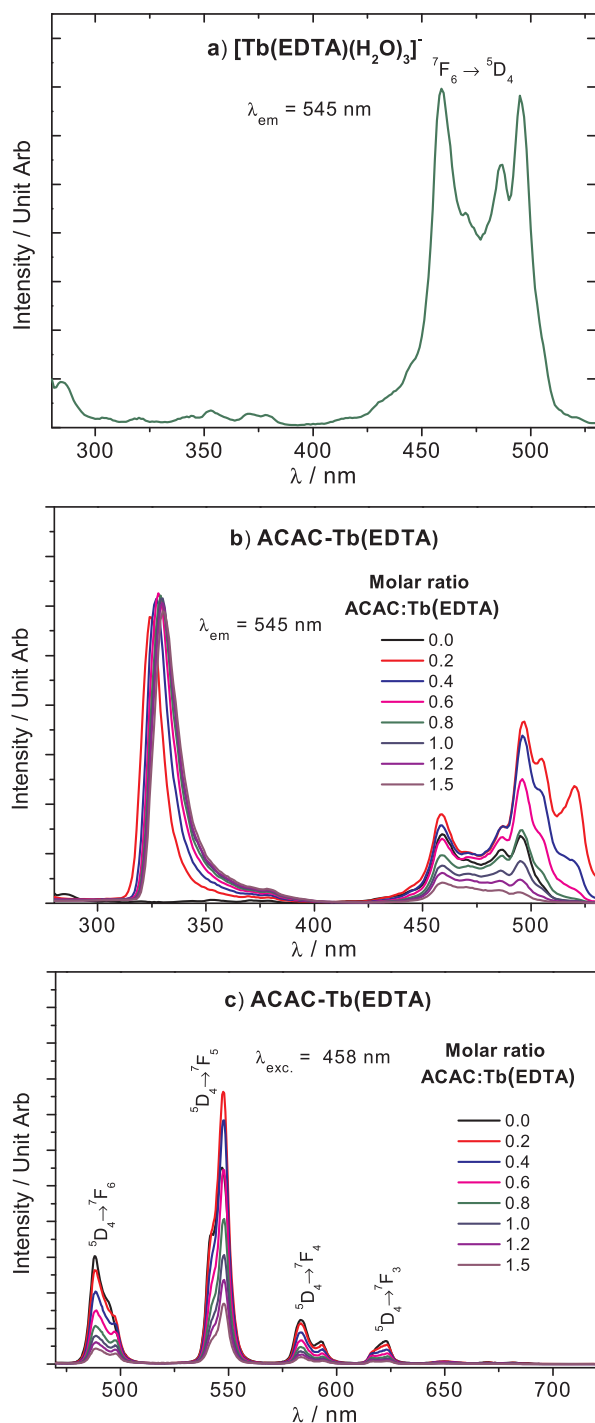


Fig. 5. (a) Excitation spectrum for the aqueous solution of the Tb-EDTA precursor complex, (b) Excitation spectra for aqueous solutions with different ACAC to Tb-EDTA molar ratios. All excitation spectra were recorded with emission monitored on $^5D_4 \rightarrow ^7F_5$ transition of the Tb(III) ion. (c) Emission spectra for aqueous solutions with different ACAC to Tb-EDTA molar ratios, recorded with excitation monitored on $S_0 \rightarrow S_1$ transition of the ACAC ligand.

the intraconfigurational transitions are also observed but with lower intensities. These results suggest coordination of the ACAC ligand to the Tb^{3+} ion, resulting in the ACAC-Tb-EDTA ternary complex.

The photoluminescent spectra of the aqueous solutions at different ACAC to Tb-EDTA molar ratios from 0.0 to 1.5 were recorded under excitation monitored at 458 nm that corresponds to the intraligand transition $S_0 \rightarrow S_1$ transition (Fig. 5b). These spectra present bands that are assigned to the $^5D_4 \rightarrow ^7F_6$ (488 nm), $^5D_4 \rightarrow ^7F_5$ (547 nm) $^5D_4 \rightarrow ^7F_4$

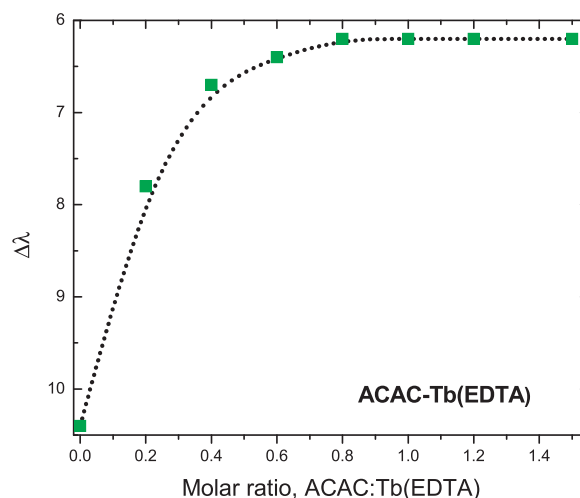


Fig. 6. Relationship between the full width at half maximum ($\Delta\lambda$) of the emission band assigned to the $^5D_4 \rightarrow ^7F_5$ transition of the Tb(III) ion with respect to the ACAC to Tb-EDTA molar ratio.

(584 nm), $^5D_4 \rightarrow ^7F_3$ (623 nm), $^5D_4 \rightarrow ^7F_2$ (650 nm) $^5D_4 \rightarrow ^7F_1$ (670 nm) and $^5D_4 \rightarrow ^7F_0$ (681 nm) transitions. The emission intensities of the $^5D_4 \rightarrow ^7F_J$ transitions exhibit a more complex behavior than those ones for Eu^{3+} systems. On the other hand, Tb^{3+} ion neither presents hypersensitive transitions nor internal relaxation for determination of the Ω_λ like the transitions $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ in the Eu^{3+} ion, respectively. Therefore, experimental determination of intensities parameters for Tb^{3+} ion is quite difficult. In this context, formation of the ACAC-Tb-EDTA complex in aqueous solution at different ACAC to Tb-EDTA molar ratios was investigated considering the full width at half maximum ($\Delta\lambda$) band assigned to the $^5D_4 \rightarrow ^7F_5$ transition at 547 nm, which is a background free and independent of concentration parameter. Just as the Ω_2 intensity parameter for the aqueous solutions depended on the β -diketone to Eu-EDTA molar ratio (Fig. 4), $\Delta\lambda$ against the ACAC to Tb-EDTA molar ratio curve (Fig. 6) shows a saturation profile when the molar ratio is close to 1, indicating that only one ACAC ligand is coordinated to the Tb^{3+} ion in the ternary complex.

4. Conclusions

Ternary β -diketone-Eu-EDTA complexes in the aqueous solution from the precursor Eu-EDTA complex have been systematically investigated through photoluminescent data. The water-soluble β -diketone-Eu-EDTA showed high luminescence intensities, even for dilute solutions, due to the efficient intermolecular energy transfers from the β -diketonate ligands to the lanthanide ions. Further, the Judd-Ofelt Ω_2 intensity parameter (for Eu^{3+} systems) and the band width at half height ($\Delta\lambda$) for the band assigned to the $^5D_4 \rightarrow ^7F_5$ (548 nm) transition (for Tb^{3+} complexes) strongly suggest the coordination of only one β -diketonate ligand in the first coordination sphere of the β -diketone-Ln-EDTA complexes. These new Eu^{3+} and Tb^{3+} systems may act as red and green optical markers in bioassays or bioimaging.

Acknowledgments

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