Synthesis, characterization and luminescent properties of Tb(III) doped Eu(III) complex nanoparticles

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Abstract
In recent years, considerable effort has been devoted to the development of transition metal complexes as novel luminescent materials that have potential application in the fluorescent labels for chemistry or biology. Among them, the nanostructured lanthanide complexes have been receiving much attention because of their excellent luminescence properties, which are attributed to the intramolecular energy transfer between the ligands and chelated lanthanide ions and their high solubility in water. This paper presents some results of the synthesis and characterization of the nanoparticles of Eu(III) and Tb(III) complexes with naphthoyl trifluoroacetone and tri-n-octylphosphineoxide. In addition, the influence of the dopant Tb(III) on the photophysical properties of the system of lanthanide complexes of Eu(III) and Tb(III) is also studied.

Keywords: lanthanide complexes, nanoparticles, luminescence, fluorescent labels

Classification number: 4.02

1. Introduction
Various luminescent nanoparticle materials have recently been fabricated and applied in diagnostics, high throughput screening, and bioimaging [1–4]. The use of fluorescent nanoparticle labels in highly sensitive assays is based on their optical properties [5–8]. The lanthanide chelate labels in biological studies contain typically an organic chromophore, which sensitizes to absorb the excitation light and transfer the excitation energy to the lanthanide ions. Consequently, lanthanide chelates exhibit broad excitation spectra owing to the organic ligands and narrow emission spectra resulting from the lanthanide ions. Recently, their application to biological labeling has attracted growing interest due to their high photochemical stability and quantum yield, and their good water solubility, and because they possess a reactive group that allows covalent attachment to biomolecules. The spectral characteristics include a long fluorescence lifetime (sub-microsecond to millisecond range), sharply spiky emission spectra (<10 nm full width at half-maximum, FWHM), large Stockes shifts (>150 nm), and high quantum yield (~1) [9, 10]. In this study, the nanostructured Tb(III) doped Eu(III) complexes with tri-n-octylphosphineoxide and naphthoyl trifluoroacetone ligands were synthesized and their characterization and spectral properties, such as fluorescence intensity, emission spectrum and fluorescence lifetime, were studied in detail.

2. Experimental
2.1. Materials
EuCl₃·6H₂O (99.99%), TbCl₃·6H₂O (99.99%), tri-n-octyl-phosphineoxide (TOPO) and 1-(2-naphthoyl)-3,3,3-trifluoroacetone (NTA) were purchased from Sigma Aldrich. Sodium dodecyl sulfate (SDS), dimethyl sulfoxide
### Table 1. The ratios of Eu(III) complex solution and Tb(III) complex solution.

| Sample | MEu | MTbEu1a | MTbEu2a | MTbEu3a | MTbEu4a |
|---|---|---|---|---|---|
| Ratio Tb/Eu | 100% Eu | 16/1 | 8/1 | 4/1 | 1/1 |

![Figure 1](image1.png)

**Figure 1.** Structure of lanthanide chelates with NTA and TOPO ligands.

(DMSO), dimethyl formamide (DMF) and polyvinylpyrrolidone (PVP) ($M = 40,000 \text{ g mol}^{-1}$) were from Merck. Deionised water was used for the preparation of nanoparticle solutions. All other chemicals were of analytical grade.

### 2.2. Synthesis

Eu(III) complex solution was prepared from 50 mg EuCl$_3$·6H$_2$O, 135 mg TOPO and 125 mg NTA in 40 ml DMSO. Tb(III) complex solution was formed from 60 mg TbCl$_3$·6H$_2$O, 160 mg TOPO and 125 mg NTA in 40 ml DMSO. Eu(III) complex and Tb(III) complex solutions were mixed with the ratios in table 1.

The fabrication of the nanostructured particles of lanthanide complexes was carried out using a vortex mixer (Labino L46, Netherlands). The reaction tube containing 5 ml of water was stirred at 500 rpm and a mixture of 0.25 ml Tb(III) doped Eu(III) complex solution and 0.1 ml SDS 10 mM was rapidly added to the tube using a maximum vortex mixing speed of 2500 rpm. The reactions were carried out at room temperature. A colloidal solution of Tb(III) doped Eu(III) nanoparticles was produced by agglomerating hydrophobic chelates in aqueous solution. After agglomeration, 0.1 ml PVP was added into the solution. A PVP shell was subsequently grown onto the agglomerated nanoparticles (figure 1).

The morphology and size of the nanoparticles were determined by using a field emission scanning electron microscope (FESEM, Hitachi, S-4800). The emission (fluorescence) spectra were recorded on a luminescence spectrophotometer system (Horiba Jobin Yvon IHR 550). Fourier transform infrared (FTIR) spectra of the nanoparticles were measured by using an IMPACT 410-Nicolet (FTIR) spectrometer.

### 3. Results and discussion

In this research, uniform fluorescent nanoparticles were synthesized in one step at room temperature. Figure 2 shows FESEM images of synthesized nanoparticles of Tb(III) doped Eu(III) chelate with TOPO and NTA ligands. Aggregation of nanoparticles is not observed. The obtained nanosized particles were uniform with a mean diameter of 25 nm ± 5 nm and shell thickness of 10 nm.

The FTIR spectra of the synthesized nanoparticles of Tb(III) doped Eu(III) chelates are given in figure 3. A broad band at wavenumber of 3444 cm$^{-1}$ is attributed to the H$_2$O molecule, and the band at 1650 cm$^{-1}$ is related to the C = O group of the ligand. The complexation between Eu(III) and Tb(III) with NTA.TOPO ligands is evidenced by a narrow band located at 1388 cm$^{-1}$, which appeared to prove that Eu(III) or Tb(III) ions may be coordinated to two oxygen atoms of ligands.

![Figure 2](image2.png)

**Figure 2.** FESEM images of the fluorescent nanoparticles of (a) Tb(III) doped Eu(III): NTA.TOPO and (b) Tb(III) doped Eu(III): NTA.TOPO@PVP.
Emission spectra of nanostructured Eu(III) chelates and Tb(III) doped Eu(III) chelates in aqueous solution were measured under excitation of $\lambda_{\text{exc}} = 325$ nm and $\lambda_{\text{exc}} = 370$ nm. It can be seen that the nanoparticle complexes exhibit the characteristic narrow emission peaks of trivalent lanthanide ions. The Eu(III) nanoparticles showed a maximum emission at 616 nm (figure 4). The emission spectra consist of four main peaks at 593, 616, 652 and 702 nm, which correspond to the $5D_0 \rightarrow 7F_n$ transitions of Eu(III) ($5D_0 \rightarrow 7F_1$ at 593 nm, $5D_0 \rightarrow 7F_2$ at 616 nm, $5D_0 \rightarrow 7F_3$ at 652 nm and $5D_4 \rightarrow 7F_4$ at 702 nm).

The influence of the dopant to optical properties of the nanoparticle complexes of Tb(III) doped Eu(III) was investigated. The shape of the spectra of samples of nanoparticle Tb(III) doped Eu(III) chelates is similar in the case of Eu(III) nanoparticles and the emission maximum is not
shifted. However, the fluorescent intensity of nanoparticles in aqueous solution depends strongly on the ratio of Tb(III) in Eu(III) chelates (figure 5).

In the studied range of ratios, the intensity at the peak of 616 nm of sample MTbEu4a with ratio (1:1) is higher than that of MEu. The fluorescence lifetime of nanosized complex samples MTbEu4a, MEu, and MTbEu3a was found to be 587, 566 and 431 µs, respectively (figure 6).

4. Conclusions

The nanostructured particles of Tb(III) doped Eu(III) chelate with TOPO and NTA ligands were successfully synthesized. The uniform nanoparticles can be synthesized at room temperature without rigorous experimental conditions. These nanoparticles Tb(III) doped Eu(III) chelates are stable in aqueous solution, which was obtained by adsorbing PVP on their surface. The aggregation of the nanoparticles is prevented, which is a result of the presence of a protective polymer layer. A nanoparticle size of 25 nm ± 5 nm and a shell thickness of 10 nm were obtained. The nanoparticle complexes exhibit the characteristic narrow emission peaks and maximum emission at 616 nm. The fluorescent intensity of nanoparticles in aqueous solution depends on the ratio of Tb(III) in Eu(III) chelates. The fluorescence lifetime of synthesized nanoparticle chelates was approximately 550 µs.

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