



Effect of doping of calcium fluoride nanoparticles on the photoluminescence properties of europium complexes with benzoic acid derivatives as secondary ligands and 2-aminopyridine as primary ligand



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ABSTRACT

The present article reports the synthesis of three Eu(III) complexes [Eu(BA)₃(2-ap)] (1), [Eu(HBA)₃(2-ap)] (2) and [Eu(ABA)₃(2-ap)] (3) (BA = benzoic acid, HBA = 2-hydroxy benzoic acid, ABA = 2-amino benzoic acid and 2-ap = 2-aminopyridine) carried out in ethanol solution. The complexes were further doped with CaF₂ nanoparticles and a change in the photoluminescence properties was observed. The compositions and structural investigation of the complexes were determined by elemental analysis and Fourier transform infrared spectroscopy (FTIR) which suggest the coordination of ligands with the central Eu(III) ion. The optical properties of the complexes were studied by Ultraviolet Visible absorption spectroscopy (UV–Vis) and photoluminescence studies (PL). The relative PL intensity was enhanced in the Eu(III) complexes doped with CaF₂ nanoparticles as compared to the pure Eu(III) complexes, however the increase in intensity varied in the order of ligands ABA > HBA > BA. The photoluminescence lifetime decay curves also revealed the longer lifetime (τ) and higher quantum efficiency (η) for europium complexes with ABA ligands suggesting the efficient energy transfer and better sensitizing ability of the ligand to europium ion. The morphology of the synthesized compounds were studied by Scanning Electron Microscopy (SEM) revealing spherical morphology with agglomeration of the nanoparticles.

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1. Introduction

The lanthanide coordination compounds have attracted a variety of biological and chemical applications such as white light emitting diodes (WLED) which act as a potential candidate for replacing conventional incandescent and fluorescent lamps [1–5]. These LEDs have long fluorescence lifetime, low energy consumption, high efficiency, reliability and environmental friendly characteristics [6–9]. The emission of light from lanthanide ions arises from f–f transitions resulting in emission bands with extremely narrow bandwidths. Since f–f transitions are laporte forbidden and free Ln³⁺ ion has low extinction coefficient resulting in low luminescence intensity, therefore sensitization of these lanthanide ions is necessary using organic ligands called chromophores [10–12]. These chromophores act as photon collectors, transferring the absorbed energy to the Ln³⁺ ion and exciting it indirectly. The Ln³⁺ ion then relaxes to its electronic ground state accompanied by the emission of light. This effect is called antenna effect and due to these properties, these compounds are also known as light

conversion molecular devices [13–16]. Recently rare earth complexes formed by different carboxylic acid ligands with a conjugated system have gained much attention because of excellent performance of absorbing energy of UV light. These compounds possess not only good luminescent properties but also good ultraviolet durability and chemical stability. The different substituents on the benzoic acid have great influence on the luminescence of the corresponding rare earth complexes [17,18]. In case of aromatic carboxylates complexes of lanthanide ion, the carboxylate group can strongly coordinate the highly oxophilic lanthanide ion and the delocalized aromatic π -electron conjugated system absorbs photons due to $\pi \rightarrow \pi^*$ transitions and efficiently transfer the energy causing the luminescence of lanthanide ion [19,20]. On the other hand, benzoate ligands functionalized with polar substituents like –OH and –NH₂ affect the luminescence of lanthanide ion [21]. The lanthanide aminobenzoates with high quantum yield of luminescence can be utilized for application in molecular electronic devices by coordinating to the Ln³⁺ ion through –NH₂ group as well as COO[–] group. The presence of electron donating amino group affects the excitation energy transfer to the Ln³⁺ ion. The rare earth doped fluorides possess excellent optical properties and good mechanical properties, chemical properties. These fluorides act as

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perfect hosts for rare earth ions due to their low phonon energy (300–400 cm^{-1}) and higher quantum efficiency due to many active transitions [22]. Among the fluorides, calcium fluoride serve as a perfect host for luminescent lanthanide ions as it decreases the quenching of the lanthanide excited states, high transparency in a broad wavelength range and low phonon energy ($\sim 328 \text{ cm}^{-1}$). Recently, the luminescent $\text{CaF}_2:\text{Eu}^{3+}$ nanoparticles sensitized by organic ligands are gaining particular attention as there are very few reports on these nanoparticles.

In this paper, the aim is to examine the influence of benzoic acid derivatives functionalized CaF_2 nanoparticles grafted on the surface of $\text{Eu}(\text{III})$ complexes with benzoic acid, 2-hydroxybenzoic acid, 2-aminobenzoic acid and 2-aminopyridine ligands in ethanol solution. In order to achieve this aim, the structural characterization of the complexes are done using elemental analysis and FTIR spectroscopy and the optical properties are studied by UV–Vis absorption spectroscopy, photoluminescent emission spectroscopy and lifetime decay curves.

2. Experimental

2.1. Materials and measurements

$\text{EuCl}_3(\text{anhy})$, benzoic acid (BA, 99.5% purity), 2-hydroxybenzoic acid (HBA, 99% purity), 2-aminobenzoic acid (ABA, 98% purity), 2-aminopyridine (2-ap, 99% purity) were procured from Sigma Aldrich and used as received without any further purifications. CaCl_2 (99% purity), NH_4F (99% purity) were obtained from CDH and used as received without any further purifications. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5% purity) of analytical grade was used as such without any further purification. The elemental analysis was performed using GmbH Vario EL CHNS Elemental Analyzer. Fourier Transform Infra Red (FTIR) spectra were acquired on a Perkin Elmer Spectrometer in the range of 4000–400 cm^{-1} . Ultraviolet absorption spectra were recorded by Shimadzu UV-1601 spectrometer. Photoluminescence measurements were done on a Perkin Elmer LS55 fluorescence spectrophotometer equipped with a 150 W Xenon lamp as the excitation source and the photoluminescence decay measurements were performed on Horiba Jobin-Yvon FL-3-22 spectrofluorometer.

2.2. Synthesis of europium complexes $[\text{Eu}(\text{BA})_3(2\text{-ap})]$ (**1**), $[\text{Eu}(\text{HBA})_3(2\text{-ap})]$ (**2**) and $[\text{Eu}(\text{ABA})_3(2\text{-ap})]$ (**3**)

The procedure for synthesis of europium (III) complexes is described as: The complex (**1**) was synthesized by taking solution of ligands BA (3 mmol, 0.366 g) and 2-ap (1 mmol, 0.094 g) in anhydrous ethanol solution (15 ml) and the reaction mixture was stirred for half an hour. The pH of the solution was adjusted between 6–7 with dilute NaOH solution (1 mol L^{-1}). An ethanol solution containing EuCl_3 (1 mmol, 0.2582 g) was added slowly dropwise to the ligand solution under stirring and the resulting solution was refluxed for 2 h at 70 °C. The precipitates were filtered, washed several times with ethanol and then dried in a vacuum oven to obtain europium complexes. The complex (**2**) was synthesized using EuCl_3 (1 mmol, 0.2582 g), HBA (3 mmol, 0.414 g) and 2-ap (1 mmol, 0.094 g) and complex (**3**) by taking EuCl_3 (1 mmol, 0.2582 g), ABA (3 mmol, 0.411 g) and 2-ap (1 mmol, 0.094 g) following the similar procedure as mentioned above.

2.3. Synthesis of water-dispersible $\text{CaF}_2:\text{Eu}^{3+}$ nanoparticles

$\text{CaF}_2:\text{Eu}^{3+}$ nanoparticles were synthesized following the procedure as: 1 mmol of EuCl_3 (1 mmol, 0.2582 g) was dissolved in 20 ml dilute ethanol solution and this solution was added

dropwise to the CaCl_2 solution (4.5 mmol, 0.51 g dissolved in 5 ml ethanol solution) under continuous stirring. Another solution containing NH_4F (8 mmol, 0.30 g dissolved in 15 ml ethanol solution) was added dropwise to the above solution and the resulting solution was stirred for 2–3 h at 70 °C with continuous stirring. The white precipitates obtained were collected by centrifugation for 10 min at 9000 rpm.

2.4. Synthesis of organic ligands functionalized $\text{CaF}_2:\text{Eu}^{3+}$ nanoparticles

The $\text{CaF}_2:\text{Eu}^{3+}$ nanoparticles synthesized before were dissolved in 30 ml deionized water to obtain a colloidal solution. Another solution of sodium benzoate (1 mmol, 0.12 g dissolved in 5 ml deionized water) was added dropwise to the above solution to obtain white precipitates which were collected by centrifugation and then dried in vacuum oven. The $\text{CaF}_2:\text{Eu}^{3+}$ nanoparticles functionalized by salicylic acid (1 mmol, 0.138 g) and 2-aminobenzoic acid (1 mmol, 0.13 g) were also prepared by following the same procedure as above.

3. Results and discussion

3.1. Elemental analysis results

The elemental analysis results confirmed the proposed stoichiometry of metal to ligand 1:3 ratio in all the three complexes. The contents of C,H,N in the complexes were determined and these results are listed in Table 1, which shows a good agreement between the experimental and calculated values.

3.2. FTIR spectra

The FTIR spectra of the ligands and the corresponding complexes are shown in Figs. 1(a)–(d) and 2(e–g) respectively. The FTIR spectra reflects the coordination of the ligands with metal ion and revealed noticeable changes in the absorption of complexes as compared to that of free ligands. The ligands BA, HBA and ABA show —C=O stretching vibration at 1698 cm^{-1} , 1661 cm^{-1} and 1676 cm^{-1} respectively and the mode of coordination of COO^- group can be attributed to the difference of stretching vibrations in antisymmetric (ν_{as}) and symmetric (ν_{s}) components in the ftir spectra of the complexes respectively. The difference ($\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$) was found to be 139 cm^{-1} for complex (**1**), which is associated with ideal symmetric bidentate coordination mode of carboxylate group with lanthanide ion. The complex (**2**) and complex (**3**) showed $\Delta\nu$ value of 160 cm^{-1} and 115 cm^{-1} respectively which corresponds to the unidentate coordination mode of COO^- group of ligands HBA and ABA to the metal ion. The free ligand 2-ap shows a broad band at 3459 cm^{-1} corresponding to $\nu(\text{N—H})$ stretching vibration which undergoes downward shift to 3064 cm^{-1} , 3167 cm^{-1} , and 3450 cm^{-1} in complexes (**1**), (**2**) and (**3**) respectively. The $\nu(\text{C=N})$ stretching vibration also undergoes downward shift from 1644 cm^{-1} to 1638, 1634, 1628 cm^{-1} for complexes (**1**), (**2**) and (**3**) respectively. These downward shifts

Table 1
Elemental analysis results of complexes.^a

Complexes	Experimental values (calculated values) %		
	C	H	N
$[\text{Eu}(\text{BA})_3(2\text{-ap})]$	50.89 (50.98)	3.94 (3.92)	4.45 (4.57)
$[\text{Eu}(\text{HBA})_3(2\text{-ap})]$	47.23 (47.27)	3.59 (3.63)	4.26 (4.24)
$[\text{Eu}(\text{ABA})_3(2\text{-ap})]$	47.45 (47.49)	4.06 (4.10)	10.60 (10.65)

^a The values in brackets are the calculated values.

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