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# Spectroscopic investigation of europium benzoate in acetonitrile: Luminescence enhancement and complexation studies

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## ABSTRACT

Luminescence from  $\text{Eu}^{3+}$  complexed with benzoic acid (BA) has been studied using acetonitrile (MeCN) as solvent. More than two orders luminescence enhancement is found as compared to  $\text{Eu}^{3+}$ -BA complex in aqueous medium. The lifetime of  $\text{Eu}^{3+}$  in this complex is 900  $\mu\text{s}$  which is much higher as compared to 118  $\mu\text{s}$  in aqueous medium, suggesting the luminescence enhancement is a result of reduction in non-radiative decay channels in MeCN medium. Luminescence spectroscopy along with UV-vis spectroscopy is used to study the complexation behavior of  $\text{Eu}^{3+}$ -BA in this medium. In contrary to aqueous medium where  $\text{Eu}^{3+}$ -BA forms ML and  $\text{ML}_2$  type species, spectroscopic data reveal formation of only  $\text{ML}_3$  complex with composition  $\text{Eu}(\text{BA})_3(\text{MeCN})_6$  in MeCN medium. Absorbance, luminescence lifetimes and the ratio of areas of 615–592 nm peaks are used in HypSpec computation program to determine the  $\log \beta$  for the  $\text{ML}_3$  complex.

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## 1. Introduction

Trivalent lanthanides are characterized by their luminescent properties having sharp line like spectra and relatively long luminescence lifetimes [1–5]. But, due to small absorption coefficients, lanthanides are poor luminescent species [2–5]. To overcome this drawback, the technique of ligand sensitized luminescence is often used [6–13]. It has been established that in ligand sensitized luminescence firstly ligand absorbs the light and makes a transition to singlet excited level from where it decays to long lived triplet level. The energy transfer takes place via triplet level to the low lying lanthanide emitting levels; as a result these emitting levels are populated indirectly. Though by this way lanthanide can be excited efficiently, eventually solvent plays an important role in deciding the decay of lanthanides radiatively. Unfortunately, in aqueous medium lanthanide luminescence is very tender towards the high energy –OH oscillators [14,15]. The problem of poor quantum yield can be eliminated by using some synergistic agents such as trioctyl phosphine oxide (TOPO), organic phosphates etc. In this process water molecules from the first coordination sphere of lanthanides are replaced by the synergistic agents and there by quenching caused by –OH oscillators is reduced [16–18].

Recent reports show that radiationless decay via vibronic coupling with the vibrational states of –OH oscillators becomes less effective when conventional solvents are replaced by properly designed ionic liquids [19–25]. Alternatively one can think of non-aqueous solvents to get rid of high energy –OH oscillators. Studies on luminescence of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  complexed with 2,6-pyridine dicarboxylic acid and uranyl complexed with benzoic acid in MeCN medium have been carried out recently. Luminescence behavior of the complexes formed in MeCN medium was found to be different from the aqueous medium [26,27]. Benzoic acid does not enhance the luminescence of uranyl ion in aqueous medium but interestingly it did enhance the same by a factor of two when MeCN is used as a solvent. It was also found that stoichiometry of uranyl benzoate complex formed in MeCN was completely different from that of in aqueous medium.

In this work, we report for the first time the luminescence of  $\text{Eu}^{3+}$  complexed with benzoic acid using MeCN as a solvent. Since coordination of lanthanides to ligand in solution occurs in competition with solvent molecules, being a poor coordinating solvent, MeCN can be an ideal choice to study the luminescence and complexation of europium to benzoate ion. Both steady state and lifetime measurements were carried out, which are presented. In addition, absorption spectra were recorded by titration of benzoate with  $\text{Eu}^{3+}$  and the stoichiometry of the complex was determined by a mole ratio method. Contrary to aqueous medium where  $\text{Eu}^{3+}$  forms 1:1 and 1:2 complexes with benzoate ion [28,29], 1:3 type complex with high luminescence intensity was

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formed in MeCN medium. The stability constant of the complex was also determined using luminescence and UV–vis data. Composition of the complex was proposed based on luminescence lifetime data. We also studied the luminescence and absorbance of  $\text{Eu}^{3+}$ –BA complex after deliberate addition of water to MeCN and followed the changes in the  $\text{Eu}^{3+}$  coordination environment and hence the complex.

## 2. Experimental details

### 2.1. Instrumentation

Edinburgh spectrofluorimeter, model FLS920, which has a 450 W xenon lamp source, was used for recording the steady state luminescence spectra. Fused silica cuvette of path length 2 mm was used as a sample cell for recording the luminescence spectra. The band pass of 3 nm was set for each excitation as well as for emission monochromator. A long-wavelength pass filter (UV–39, Shimadzu), with a maximum and uniform transmittance ( $> 85\%$ ) above 400 nm, was placed in front of the emission monochromator, in order to reduce the scatter of the incident beam into the emission monochromator. Spectra were recorded at room temperature with a  $90^\circ$  collection geometry.

Time resolved spectra of the excited states were recorded using the same instrument with a  $\mu\text{s}$ -Xe flash lamp. Luminescence decay times were determined by fitting the observed time resolved luminescence signals to an exponential decay function. A single exponential fit was found to be adequate for the decay processes observed in this study. The  $\chi^2$  values of all the fits ranged between 0.9 and 1.1. The relative standard deviation of the lifetime values was less than 5%.

UV–vis absorption spectra were recorded at room temperature using an Avantes fiber optic spectrophotometer (AvaSpec-3648-USB2) with 300 lines per mm grating. An integration time of 6 ms was used and 20 spectra were averaged to improve the signal to noise ratio. Fused silica cuvette of path length 10 mm was used as a sample cell for recording the absorption spectra.

### 2.2. Reagents

Europium perchlorate was prepared from europium oxide powder (Indian Rare Earth Limited, India) by dissolving it in perchloric acid (Sigma make) and then evaporated to dryness. The residue was then dissolved in 0.1 M perchloric acid/MeCN to get the stock solution of  $\text{Eu}^{3+}$  in water and MeCN. Stock solution of benzoic acid (Fluka make, A.R grade) was prepared by dissolving the required amount in water. To ensure complete dissolution of the acid, required amounts of sodium hydroxide (A.R grade) was added. pH of the aqueous solutions was adjusted by the addition of sodium hydroxide and perchloric acid. Ionic strength of the aqueous solutions was adjusted by sodium perchlorate (99.99% Sigma make). MeCN used was of HPLC grade (Merck, purity  $> 99.8\%$ , water impurity  $< 0.05\%$ ). All chemicals were used as purchased from the supplier. De-ionized water (18 M $\Omega$ ) obtained with a Milli-Q (Millipore) system was used in preparing all solutions.

### 2.3. Preparation of $\text{Eu}^{3+}$ –BA solution in MeCN

Europium benzoate complexes were prepared in water at different pH by mixing the required amount of benzoic acid and  $\text{Eu}^{3+}$  solution from the stocks. The ionic strength of this solution was adjusted to 0.1 M. 5  $\mu\text{L}$  of this solution was then mixed with 0.5 mL of MeCN. This solution was then transferred to the sample cell and the luminescent spectra recorded.

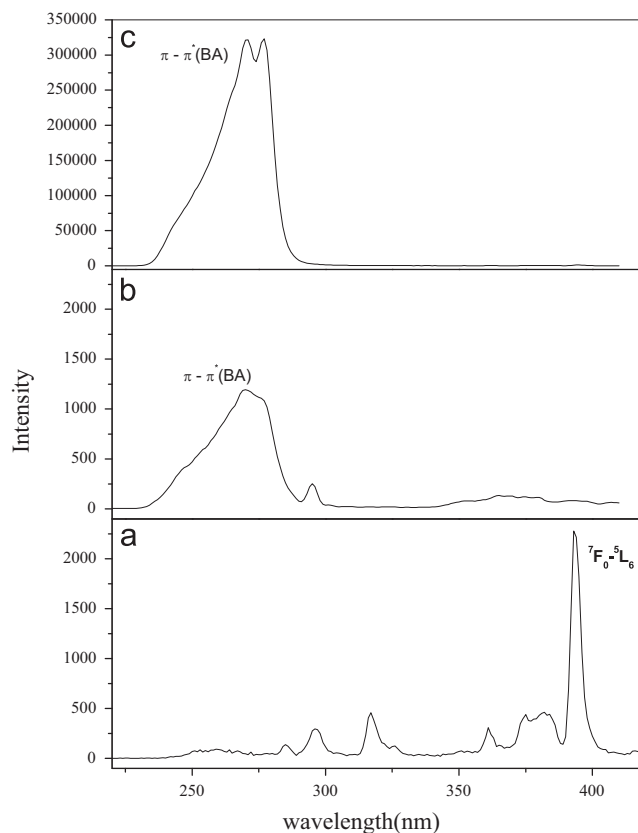
However to record the absorption spectra of  $\text{Eu}^{3+}$ –BA complex in MeCN medium, 15  $\mu\text{L}$  of aqueous benzoate solution of desired concentration (pH 4.5,  $I=0.1$  M  $\text{NaClO}_4$ ) and required amount of  $\text{Eu}^{3+}$  ion (from MeCN stock) were added to 1.5 mL of MeCN solution. Therefore in all the experiments (absorbance and luminescence) which were carried out in MeCN medium, 1% of water was present to begin with.

## 3. Results and discussion

In the following text the term ‘pH in MeCN medium’ implies the aqueous solution of BA/ $\text{Eu}^{3+}$ –BA prepared at a pH, from which 5  $\mu\text{L}$  was taken and dissolved in 0.5 mL of MeCN. Also the terms ‘uncomplexed  $\text{Eu}^{3+}$ ’ and ‘complexed  $\text{Eu}^{3+}$ ’, refer to  $\text{Eu}^{3+}$  species in MeCN/water medium without and with benzoate ion, respectively.

### 3.1. Luminescence enhancement studies of $\text{Eu}^{3+}$ –BA in MeCN

To begin with, luminescence intensity of complexed  $\text{Eu}^{3+}$  in MeCN was measured as a function of BA concentration and pH of the aqueous solution. Maximum luminescence intensity was found over  $3 \times 10^{-4}$ – $7 \times 10^{-4}$  M of BA concentration and pH 4.5. Therefore in the luminescence enhancement studies, concentration of BA and pH of the solution was maintained at  $5 \times 10^{-4}$  M and 4.5, respectively. The excitation and emission spectra of various  $\text{Eu}^{3+}$  ion species recorded in different medium are shown in Figs. 1 and 2 respectively. The excitation and emission spectra of  $\text{Eu}^{3+}$ –BA recorded in MeCN medium are shown in Figs. 1c and 2c, respectively. For comparison, spectra recorded in aqueous medium for uncomplexed  $\text{Eu}^{3+}$  (Figs. 1a and 2a) and  $\text{Eu}^{3+}$ –BA complex



**Fig. 1.** Excitation spectra (a) uncomplexed  $\text{Eu}^{3+}$  ( $2.0 \times 10^{-3}$  M) in water; (b)  $\text{Eu}^{3+}$  ( $1 \times 10^{-5}$  M)–BA ( $5 \times 10^{-4}$  M) at pH 6.0 in water; (c)  $\text{Eu}^{3+}$  ( $1 \times 10^{-5}$  M)–BA ( $5 \times 10^{-4}$  M) at pH 4.5 in MeCN. Spectra were recorded by monitoring the emission at 615 nm for complexed  $\text{Eu}^{3+}$  and 592 nm for uncomplexed  $\text{Eu}^{3+}$ .

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