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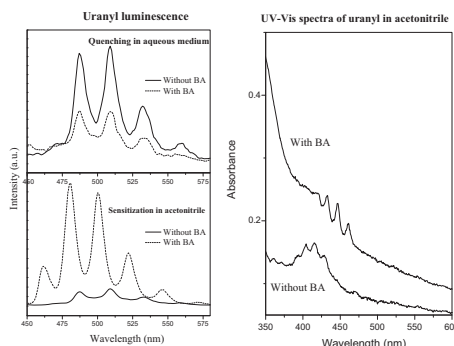
Ligand sensitized luminescence of uranyl by benzoic acid in acetonitrile medium: A new luminescent uranyl benzoate specie

Satendra Kumar^a, S. Maji^a, M. Joseph^b, K. Sankaran^{a,*}^a Materials Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India^b Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

HIGHLIGHTS

- Uranyl luminescence is sensitized by benzoic acid in acetonitrile medium.
- UV–Vis and luminescence spectroscopy is used to characterize uranyl benzoate at different uranyl to benzoate ratio.
- The specie formed is $[\text{UO}_2(\text{C}_6\text{H}_5\text{COO})_3]^-$, which is highly luminescent.
- Acetonitrile plays an important role in the sensitized luminescence by forming tris complex of uranyl.

GRAPHICAL ABSTRACT



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ABSTRACT

Benzoic acid (BA) is shown to sensitize and enhance the luminescence of uranyl ion in acetonitrile medium. Luminescence spectra and especially UV–Vis spectroscopy studies reveal the formation of tri benzoate complex of uranyl i.e. $[\text{UO}_2(\text{C}_6\text{H}_5\text{COO})_3]^-$ which is highly luminescent. In particular, three sharp bands at 431, 443, 461 nm of absorption spectra provides evidence for tri benzoate specie of uranyl in acetonitrile medium. The luminescence lifetime of uranyl in this complex is 68 μs which is much more compared to the lifetime of uncomplexed uranyl (20 μs) in acetonitrile medium. In contrary to aqueous medium where uranyl benzoate forms 1:1 and 1:2 species, spectroscopic data reveal formation of 1:3 complex in acetonitrile medium. Addition of water to acetonitrile results in decrease of luminescence intensity of this specie and the luminescence features implode at 20% (v/v) of water content. For the first time, to the best of our knowledge, the existence of $[\text{UO}_2(\text{C}_6\text{H}_5\text{COO})_3]^-$ specie in acetonitrile is reported. Mechanism of luminescence enhancement is discussed.

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Introduction

In luminescence spectroscopy, absorption coefficient and quantum yield are the two important factors which decide the luminescence behavior of any molecule/specie. In order to have a strong

luminescence, the molecule/specie must have high absorption coefficient and quantum yields. In electronic spectroscopy, after the excitation, the molecule will release the excess energy, photo physically, in the form of two decay channels: radiative and non-radiative. Solvent plays an important role in the decay of excited state of the molecules [1,2].

Lanthanides and actinides are known to be weak luminescent elements in aqueous medium because of their low molar

* Corresponding author.

E-mail address: ksran@igcar.gov.in (K. Sankaran).

absorption coefficient and poor quantum yields [3,4]. The low absorption coefficient arises from the forbidden d–d or f–f transitions. In aqueous medium, the luminescence of the lanthanide and actinide ions is highly quenched by the water molecules. It is reported that in the case of lanthanides, the O–H oscillators of water molecules take the excess energy and cause the molecule to de-excite through non-radiative processes [3,5,6], where as in the case of uranyl ion the electron transfer mechanism is responsible for quenching in aqueous medium [7]. Methods to enhance the luminescence of lanthanides and actinides in aqueous solutions are therefore required. In the case of lanthanides, ligand sensitized luminescence has been widely used to enhance the luminescence intensity and hence the determination of lanthanides in trace level have been reported [8–15]. In ligand sensitized luminescence, ligand absorbs the light and then transfers the energy to the metal ions which results in enhancement in luminescence intensities. According to the theory of “Antenna Effect”, the luminescence intensity of complexes of metal ions is decided by the efficiency of the energy transfer from the ligand to the coordinated metal ion, which in turn dependent on the energy level matching between the triplet state of the ligand and the lowest excited state of metal ion [5,6].

In order to enhance the luminescence of uranyl ion in aqueous medium, luminescence enhancing reagents such as H_3PO_4 , H_2SO_4 , HClO_4 have been widely used [16–18]. These agents make complex with uranyl ion, thereby eliminating water molecules from the primary coordination sphere of uranyl ion and consequently reducing the quenching effects due to water and hence results in enhancement of uranyl ion luminescence. It has also been observed that the luminescence lifetime of uranyl ion increases from 2 μs (uncomplexed) to 10–230 μs (complexed) with the above mentioned agents [16–18]. Luminescence measurements of lanthanides and actinides at low temperature (Cryo-TRLFS) have also been reported in literature [19–21]. As a consequence of reducing quenching effects at low temperature, an increase in luminescence life time of uranyl has been observed at low temperatures [20,21]. The other method to enhance the uranyl luminescence is by ligand sensitized luminescence, a method well established for lanthanides. Although there are plenty of ligands which enhance the luminescence of lanthanides, only a few such as 2–6, pyridine dicarboxylic acid and trimesic acid were found to enhance the luminescence of uranyl ion [22–23].

Recently uranyl luminescence has been studied in non-aqueous medium [24–26]. These studies have reported the formation of different species, their structure and their spectroscopic properties in acetonitrile and ionic liquid medium. The aim of the present work is to examine the possibility of using non-aqueous medium for enhancing the luminescence intensity of uranyl ion for trace level detection. In our earlier work we have reported large enhancement of lanthanide luminescence intensity in acetonitrile compared to aqueous medium [27]. In this work, luminescence and ligand (benzoic acid) sensitized luminescence of uranyl ion has been studied in acetonitrile medium. While earlier works involved luminescence of different uranyl species in acetonitrile medium [24–26], no work has been reported on the ligand sensitized luminescence. It should be noted that in aqueous medium, benzoic acid does not enhance the uranyl luminescence although it forms 1:1 and 1:2 complexes with uranyl ion [28,29]. The luminescence of uranyl ion is found to be enhanced by benzoate in acetonitrile medium and the enhancement is due to sensitization of uranyl by benzoate ions. UV–Vis spectroscopy has been utilized to characterize the uranyl–BA specie in acetonitrile. Mechanism for uranyl luminescence enhancement in acetonitrile is discussed. To the best of our knowledge, this is the first report on ligand sensitized luminescence of uranyl in acetonitrile medium and characterization of the complex of uranyl–BA system.

Experimental details

Instrumentation

All luminescence spectra were recorded using Edinburgh spectrofluorimeter, model FLS920, with a 450 W xenon lamp as the excitation source. 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 both the excitation and emission monochromators. 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, to reduce the scatter of the incident beam into the emission monochromator. Spectra were recorded at room temperature with a 90° collection geometry. All spectra were blank subtracted; a blank spectrum was recorded using identical experimental conditions without the uranyl ion in the solution. All spectra were also corrected for instrument response.

Time resolved spectra are recorded using a μs -Xe flash lamp. Luminescence life times were determined by fitting the observed time resolved luminescence signals to an exponential decay function. A single or double exponential fit was found to be adequate for the decay processes observed in this study. The χ^2 values of all the fits ranged between 0.9 and 1.1. Since the temporal profile of the pulsed source was around 1.5 μs , lifetimes that were of this order of magnitude were obtained after correcting the instrument response function before fitting. However for systems which displayed lifetimes of the order of 20 μs or longer, the lifetimes were extracted through a tail-fit, where the data points in the decay profile extending to long temporal regions were used for the fitting. The relative standard deviation of the lifetime values was less than 5%.

UV–Vis absorption spectra were recorded using Avantes fiber optic spectrophotometer, model 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.

Reagents

Uranyl perchlorate solution was prepared from UO_2 powder (Nuclear Fuel Complex, India). Towards this, first uranium dioxide was dissolved in nitric acid and the solution was evaporated to dryness. Subsequently, the uranyl nitrate residue was then dissolved in perchloric acid and evaporated to dryness until the white fumes of perchloric acid disappear and finally yellow residue of uranyl perchlorate was obtained. This residue was then dissolved in acetonitrile or water to get a stock solution of 10^{-1} M uranyl. The aqueous solution was acidified with a few drops of 1 M perchloric acid. Stock solution of benzoic acid (Fluka make, AR grade) was prepared by dissolving the required amount in water. To ensure complete dissolution of the acid, small amount of sodium hydroxide was added. The pH of the solutions was adjusted by the addition of sodium hydroxide (AR grade)/perchloric acid (Sigma make). Ionic strength of the solution was adjusted using sodium perchlorate (99.99%, Sigma make). Acetonitrile used in our study was of Merck HPLC grade (purity > 99.8%). All chemicals were used as purchased from the supplier. De-ionized water (18 M Ω) obtained with a Milli-Q (Millipore) system was used for preparing the solutions.

Preparation of uranyl and uranyl–benzoate solution in acetonitrile

Aqueous uranyl solutions of different concentrations (4×10^{-3} M to 8×10^{-5} M) were prepared from the 10^{-1} M uranyl (aqueous) stock solution. The ionic strength of these solutions was

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