Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 138 (2015) 509–516

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

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

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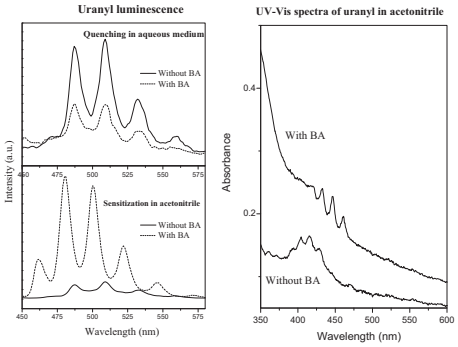
HIGHLIGHTS

- 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 $[UO_2(C_6H_5COO)_3]^-$, which is highly luminescent.
- Acetonitrile plays an important role in the sensitized luminescence by forming tris complex of uranyl.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2014
Received in revised form 18 November 2014
Accepted 20 November 2014
Available online 5 December 2014

Keywords:
Luminescence
Sensitization
Benzoic acid
Uranyl
Acetonitrile

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. $[UO_2(C_6H_5COO)_3]^-$ 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 $[UO_2(C_6H_5COO)_3]^-$ specie in acetonitrile is reported. Mechanism of luminescence enhancement is discussed.

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

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http://dx.doi.org/10.1016/j.saa.2014.11.033
1386-1425/

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 MΩ) 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

fixed to 0.1 M and pH was varied from 2.4 to 5.0. From this solution, 5 μL was taken into 0.5 mL of acetonitrile to get the working solution for recording the luminescence spectrum.

Similarly uranyl–BA complexes at different pH were prepared by mixing the required amount of benzoic acid and 10^{-1} M uranyl (aqueous) stock solution. The ionic strength was adjusted to 0.1 M. 5 μL of this solution was then mixed with 0.5 mL of acetonitrile and the luminescence spectrum recorded.

However to record the absorption spectra, the working solution was prepared as follows. At first, benzoate solutions of concentrations at 4×10^{-1} M, 6×10^{-1} M and 8×10^{-1} M were prepared. The pH of the solutions was adjusted at 5.5 and the ionic strength of the solution was kept constant at 0.1 M. 20 μL of each of these solutions along with 40 μL of 10^{-1} M uranyl (acetonitrile) stock solution was taken in a 2 mL vial and the volume was made up with acetonitrile.

All the working solutions prepared were mixed thoroughly by shaking manually. In all our experiments carried out in acetonitrile medium, about 1% water was present to begin with.

Results and discussion

In the following text the term 'pH in acetonitrile medium' is used. It must be noted that this term implies the pH in aqueous solution of uranyl (not the pH of acetonitrile), from which 5 μL was taken and dissolved in 0.5 mL of acetonitrile. Also the term uncomplexed uranyl and complexed uranyl refer to uranyl specie in acetonitrile/water medium without and with benzoate ion, respectively. The term free uranyl refers to hydrated uranyl ion.

Uranyl luminescence and decay profile in acetonitrile medium

Since uranyl–BA complexes in acetonitrile medium were prepared from aqueous solution of uranyl–BA at different pH, initially we have recorded the luminescence spectra of uncomplexed uranyl ion as a function of pH in acetonitrile medium. Fig. 1 compares the luminescence spectra of 4×10^{-5} M uranyl ion solution as a function of pH from 2.4 to 5.0 in acetonitrile medium. For comparison, uranyl ion luminescence in aqueous medium is also shown as dotted lines in the same figure. The concentration of the uranyl ion used in the aqueous medium is 4×10^{-4} M.

At pH 2.4, uranyl showed five sharp peaks at 470, 488, 509, 532 and 558 nm in acetonitrile medium which is similar to what is observed in aqueous medium (dotted lines) and hence these features are assigned to free uranyl luminescence in acetonitrile. From pH 3.0 onwards the behavior of uranyl luminescence in acetonitrile is different from that in aqueous medium. At pH 3.0, new luminescence peaks appeared at 499, 520 and 545 nm along with the peaks of uranyl ion in the acetonitrile medium. These new features in acetonitrile medium could be due to hydrolysis of uranyl ion as small amount of water is always present in the solution. Similar features were observed in literature for different uranium-hydroxo complexes in aqueous medium [30,31]. Above pH 3.0, only these new peaks were observed while the peaks due to free uranyl ion start disappearing. In aqueous medium, the peak positions of uranyl ion do change with pH and it is well reported [30–33]. This implies that only one type of hydroxide is formed and strongly solvated by acetonitrile molecules which help in preventing uranyl to polymerize into other higher species. Appearance of these peaks at pH 3.0 suggests that this specie might be uranyl hydroxide (UO_2-OH^+) and this hydroxide specie dominates even at this low pH in acetonitrile medium, which is present in negligible amount in water at the same pH. The luminescence intensity of this specie is found to increase with pH.

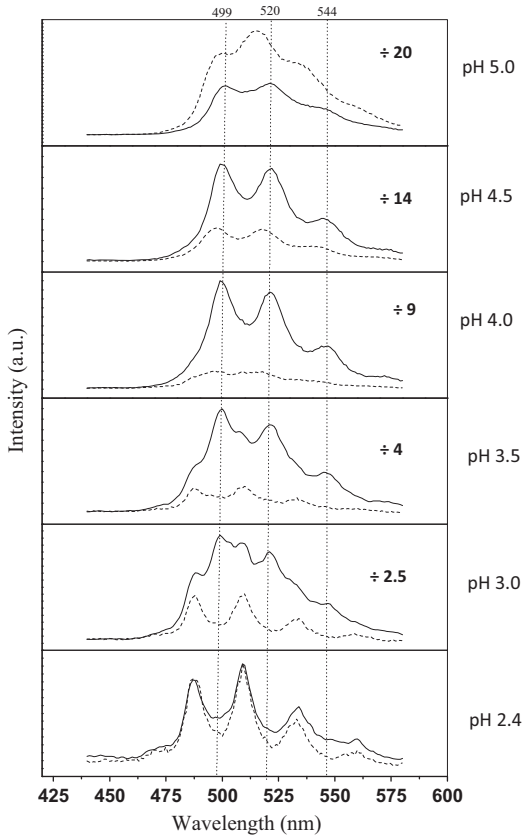

Fig. 1. Emission spectra of uranyl at different pH in water (dashed line); $[UO_2^{2+}] = 4 \times 10^{-4}$ M and in acetonitrile (solid line); $[UO_2^{2+}] = 4 \times 10^{-5}$ M. $\lambda_{ex} = 250$ nm. Ionic strength = 0.1 M.

Table 1 compares the lifetimes of uranyl ion at different pH in acetonitrile and aqueous medium. At pH 2.4 the life time showed single decay of 20 μs in acetonitrile medium which indicates the luminescence life time of free uranyl ion. Since 1% water is present in acetonitrile to begin with and being a weak coordinating solvent, acetonitrile will not bind to the first coordination sphere of uranyl ion which is similar to a situation seen in the luminescence of lanthanides in non-aqueous solvents [34]. Therefore small increase in lifetime from 1.5 to 20 μs when we go from aqueous

Table 1
Lifetimes of uncomplexed uranyl species at different pH in water and acetonitrile medium.

pH	In aqueous medium		In acetonitrile medium	
	Life times[a] (μs)	Refs.	Life times[a] (μs)	Refs.
2.4	1.5	This work	20	This work
	1.9	[28]		
	1.3	[29]		
3.0	1.5	This work	20, 58	
	1.3	[29]		
	1.8, 32.8	[28]		
3.5	1.4, 9.0	This work	21, 65	
	1.9, 32.8, 8.8	[28]		
4.0	1.8, 11.0	This work	62	
	1.6, 32.8, 9.9	[28]		
4.5	1.8, 10	This work	60	
	2.2, 6.8	[29]		
	1.6, 9.3	[28]		
5.0	14	This work	70	
	12	[28]		

[a] ±5% deviation in present study, ionic strength of all the aqueous solutions was 0.1 M.

to acetonitrile medium suggests that the removal of water molecules from the secondary sphere of uranyl ions by acetonitrile and not due to the removal of inner sphere water molecules by acetonitrile. As pH increases the lifetime decays bi exponentially with life times around 20 and 60 μs, indicating that two different species are present in the solution, first one due to free uranyl ion and other one due to hydroxide specie of uranyl. Above pH 4.0, only the hydroxide specie is predominant, showing a single decay lifetime of about 60 μs. The disappearance of first life time 20 μs at pH 4.0 and above is due to the fact that hydroxide formation takes place at higher pH and there may be negligible amount of free uranyl ion to be present. Interestingly, from pH 3.0 to 5.0, no changes in the peak positions of the luminescence spectra as well as in second decay time which is around 60 μs observed, indicating one type of hydroxide specie of uranyl dominates in acetonitrile medium.

Uranyl–BA luminescence and decay profile in acetonitrile medium

Uranyl ion was complexed with benzoic acid and uranyl luminescence was measured as a function of benzoic acid concentration and pH of the solution. Fig. 2 shows the variation of luminescence intensity of uranyl–BA complex, measured at 481 nm as a function of benzoic acid concentration at pH 4.5. The optimum acid concentration was determined to be 1×10^{-4} M and hence this concentration was used in all our subsequent experiments. Fig. 3 shows the variation of luminescence intensity of uranyl–BA complex at 481 nm as a function of pH. For the pH range 3.5–5.0 the luminescence intensity was almost constant for a given ligand concentration. Therefore in all our experiments pH of solutions was maintained at 4.5. Fig. 4 compares the excitation spectra of uncomplexed uranyl ion and uranyl–BA complex in acetonitrile medium. The excitation spectrum of the uncomplexed uranyl was recorded by monitoring the luminescence at 499 nm, while the spectrum of complexed uranyl was recorded by monitoring the luminescence at 481 nm. The excitation spectra for uranyl–BA complex display a maxima at 243 nm (Fig. 4a), which is different from uncomplexed uranyl (250 nm), indicating the complexation of uranyl with benzoate ion.

Fig. 5a and b shows the uranyl luminescence spectra with and without benzoic acid in acetonitrile medium at pH 4.5. The emission spectrum of uncomplexed uranyl ion (Fig. 5b) shows bands

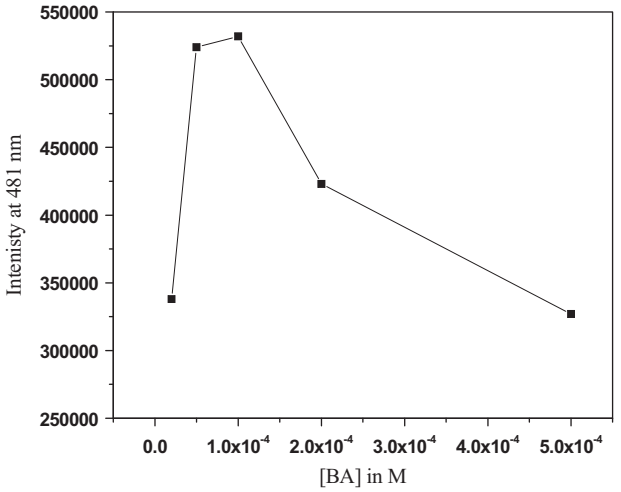

Fig. 2. Variation of luminescence intensity of uranyl–BA complex in acetonitrile with the concentration of BA; pH 4.5, $[UO_2^{2+}] = 8 \times 10^{-7}$ M.

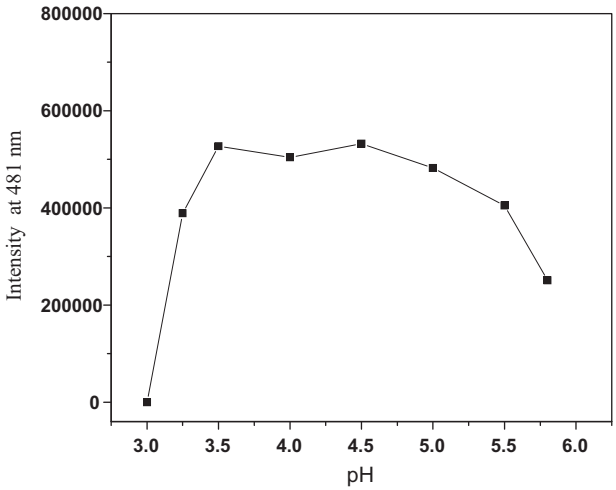

Fig. 3. Variation of luminescence intensity of uranyl–BA complex in acetonitrile with pH of the uranyl solution; $[UO_2^{2+}] = 8 \times 10^{-7}$ M, [BA] = 1×10^{-4} M.

at 499, 520 and 545 nm. However, emission spectrum of uranyl–BA complex (Fig. 5a), shows five well resolved sharp peaks at 462, 481, 501, 522 and 546 nm. Although the luminescence intensities shown in Fig. 5a and b for the complexed and uncomplexed uranyl ion are comparable, the concentrations of uranyl ion used to record the spectra are different. Concentration of uranyl ion used to record the spectrum in its complex in acetonitrile medium was 8×10^{-7} M. At this concentration, uncomplexed uranyl ion showed no measurable luminescence, and hence to record the spectrum of uncomplexed uranyl ion, a concentration of 4×10^{-5} M was used. For comparison, emission spectrum of uranyl–BA in aqueous medium is also shown as dotted line (Fig. 5c), the intensity of which is much lower than the above two spectra. The enhancement in luminescence is thus obvious and clearly indicates the role of benzoate in sensitizing the uranyl luminescence in acetonitrile. Complexation with benzoate yields more than two orders of enhancement in the luminescence of uranyl ion in acetonitrile medium.

The calculated average spacing between the spectral features in the emission spectrum of uranyl–BA complex in acetonitrile is 832 cm^{-1}, which is close to the value of 855 cm^{-1} reported for vibrational spacing in the ground electronic state of free uranyl ion [31]. While the spacing between the vibronic features in our spectrum (Fig. 5a), agrees with that of the reported value for other uranyl complexes in aqueous [22–23], each of the features is blue-shifted by 8 nm in acetonitrile medium, compared with that observed for free uranyl ion (Fig. 1, pH 2.4). We believe that blue-shift in the case of acetonitrile medium stabilizes the ground state more than the excited state without perturbing the shape of the ground state potential, as indicated by the constancy in the vibronic spacing. Similar blue shifting has been observed in the luminescence spectra of uranyl–trimesic acid complex in aqueous medium [23].

The uranyl–BA system shows a single exponential decay with a lifetime of 68 μs, which indicates presence of single uranyl–BA specie. Complexation of BA to uranyl ion increases its lifetime from 20 to 68 μs in acetonitrile medium. These life time results suggest that upon complexation with benzoate ion, water molecules are displaced from the first coordination sphere of the central uranyl ion and hence the non-radiative decay, induced by collisions with water molecules are suppressed further. Similar enhancements in lifetime were observed in earlier studies on the luminescence of uranyl complexed with 2-6-pyridinedicarboxylic acid (PDA) [22],

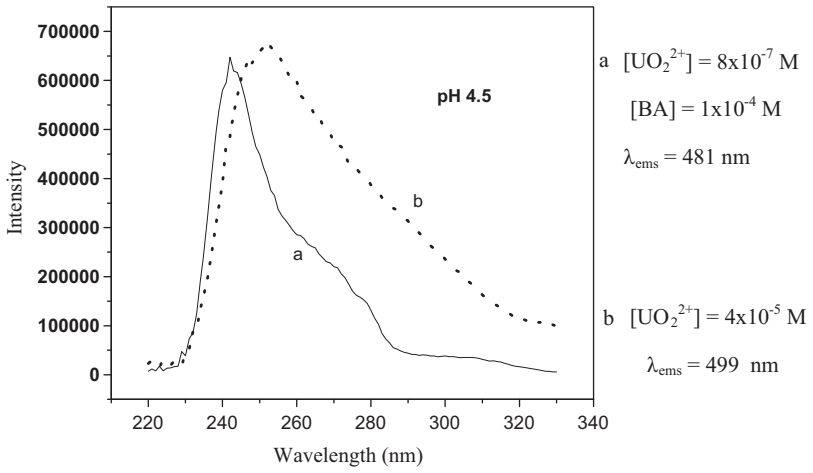

Fig. 4. Excitaion spectra of uranyl in acetonitrile with (a) and without (b) benzoic acid.

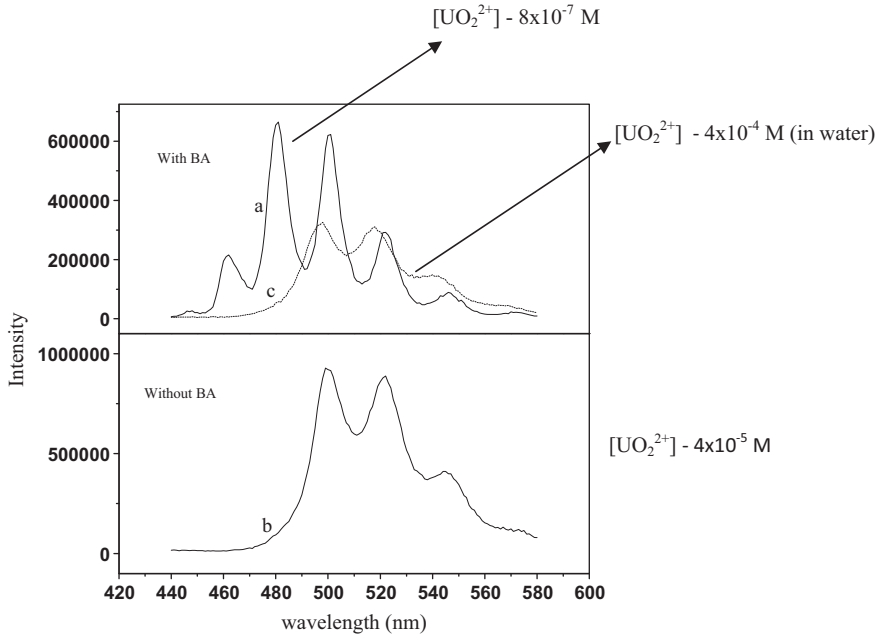

Fig. 5. Emission spectra of uranyl in aceonitrile with (a) and without (b) benzoic acid (1×10^{-4} M) at pH 4.5. Uranyl–BA spectrum in water (c) at pH 4.5 (dashed line).

trimesic acid (TMA) [23], malonic acid [35], glycine [36] in aqueous medium.

Recently Lutke et al. has reported that uranyl forms 1:1 and 1:2 complexes in aqueous medium with benzoic acid [29] and they found that after complexation with benzoic acid, luminescence intensity of uranyl ion decreased with benzoic acid concentration. Furthermore, it was deduced that uranyl benzoate specie shows no luminescence. In contrary to aqueous medium, uranyl benzoate specie formed in acetonitrile medium exhibited strong luminescence through intramolecular energy transfer from benzoate moiety. These observations clearly indicate that luminescence specie of uranyl benzoate formed in acetonitrile is different from that is formed in aqueous medium. The structure of the uranyl–BA specie and the luminescence mechanism will be discussed later.

Effect of water on luminescence of uranyl–BA in acetonitrile

Since benzoic acid did not enhance the luminescence of uranyl in aqueous medium, to examine the tolerance limit of water in acetonitrile, we have studied the effect of water on uranyl–BA luminescence in acetonitrile medium. For these studies, steady state and lifetime experiments were performed after deliberate addition of water to the uranyl–BA in acetonitrile. It must be noted that in all the experiments in acetonitrile medium, 1% water was initially present to begin with. Fig. 6 illustrates the variation of luminescence intensity of the uranyl–BA in acetonitrile with addition of water at pH 4.5. It is clear from the figure that luminescence intensity decreases with the increase in water content in acetonitrile medium. Both, luminescence intensity and life time decreases exponentially with increase in water content in acetonitrile (Fig. 7a and b). This decrease in luminescence intensity as well as life time is due to the removal of acetonitrile by water molecules from the bulk of the complex, as water forms stronger complex compared to acetonitrile. From this it can also be concluded that even though luminescence intensity of the complex decreases, its structure (peak positions) remains intact up to 20% of water relative to acetonitrile. Above 20% of water, the sharp uranyl luminescence features become broader [Fig. 6 in inset]. Therefore it can be

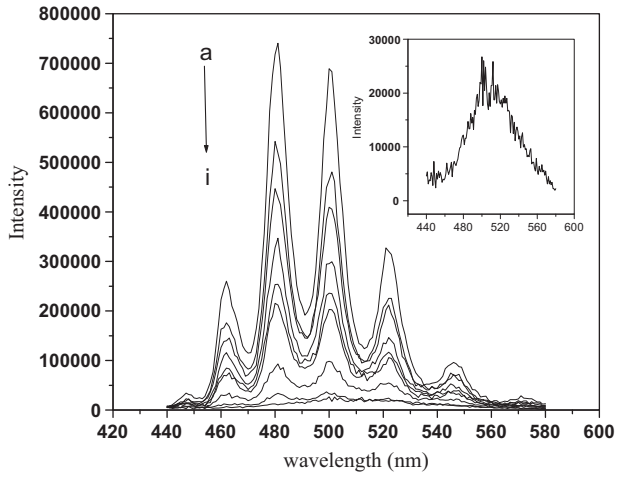

Fig. 6. Luminescence spectra of uranyl–BA complex in acetonitrile as a function of water (a) 1%; (b) 2%; (c) 4%; (d) 6%; (e) 8%; (f) 10%; (g) 15%; (h) 20%; (i) 25% content relative to acetonitrile. $[UO_2^{2+}]$ – 8×10^{-7} M, [BA] – 1×10^{-4} M. For clarity the spectra with 25% water is again shown in inset.

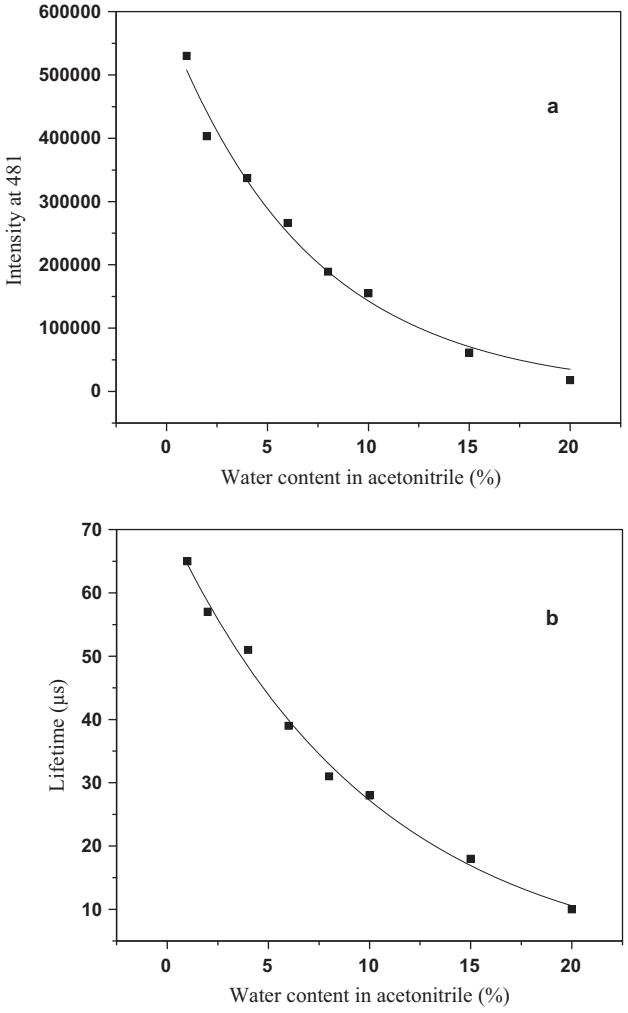

Fig. 7. Plots showing the uranyl–BA (a) intensity and (b) life time as a function of water content relative to acetonitrile; $[UO_2^{2+}]$ – 8×10^{-7} M, [BA] – 1×10^{-4} M.

concluded that above 20% of water in acetonitrile, luminescence from hydroxide specie of uranyl dominates and hence the spectrum is broad and no sensitized luminescence of uranyl observed, a situation similar to the one seen in pure aqueous medium.

Structure of the complex

UV–Vis spectroscopy was used to see the possibility of characterizing the uranyl–BA specie formed in the acetonitrile medium which is responsible for luminescence. Fig. 8a shows the UV–Vis spectrum of uranyl in acetonitrile. The spectrum exhibited three absorption bands which resembles the absorption of hydrated uranyl specie [37]. This suggests that being the less coordinating solvent acetonitrile cannot replace the water, which is present in acetonitrile in trace level, from the inner coordination sphere of uranyl. The UV–Vis spectra of solutions containing uranyl with different benzoate concentration in acetonitrile are also shown in Fig. 8b–d. In acetonitrile medium we observed an increase in the baseline of these spectra and we believe that it could be caused by particles which are not visible to naked eye. The particle formation could be due to limited solubility of complex in acetonitrile medium. When uranyl to ligand ratio is 1:3 (Fig. 8c), UV–Vis spectra displayed three intense sharp peaks at 431, 443 and 461 nm. Similar sharp peaks were first observed in the spectrum of $CsUO_3(NO_3)_3$, reported by Dieke and Duncan and were named as 'magnetic series' [38]. The absorption bands at this region were also reported in literature for uranyl tris nitrato, uranyl tris acetato complexes in ionic liquid medium [26]. The observation of these peaks in our experiment, which is typical for uranyl complexes with D_{3h} symmetry [26], is a clear indication of formation of tris complex of uranyl. Hence we believe that the specie formed in acetonitrile medium could be that of $[UO_2(C_6H_5COO)_3]^-$. It is noted that in aqueous medium two benzoate ligands are coordinated to uranyl ion [29]. A similar observation has been found [25] when uranyl betaine complex dissolved in water showed spectrum similar to hydrated uranyl indicating betaine ligands are no longer

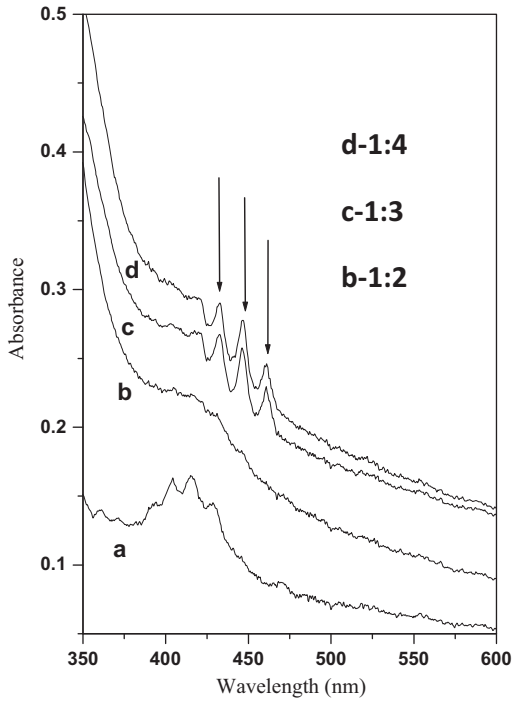

Fig. 8. UV–Vis absorption spectra of (a) uranyl (1×10^{-2} M) and with different uranyl (2×10^{-3} M) to benzoate ratio (b) 1:2; (c) 1:3; (d) 1:4 in acetonitrile. The three peaks shown by arrow are the characteristic of uranyl tris complex. The plots c and d are offset to *Y* axis by 0.05 unit for clarity.

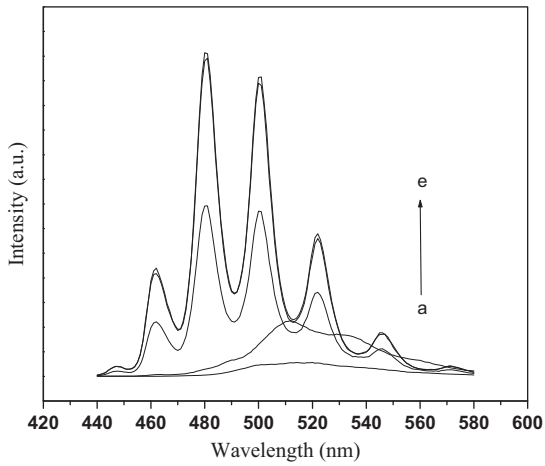

Fig. 9. Luminescence spectra of uranyl (4×10^{-5} M) with different uranyl to benzoate ratio in acetonitrile (a) 1:1; (b) 1:2; (c) 1:3; (d) 1:4; (e) 1:5. λ_{ex} = 243 nm.

coordinated to uranyl ion, and the same complex exhibited sharp, intense peaks as carboxylate groups of three betaine ligands remain co-ordinated after dissolution in acetonitrile.

Luminescence spectra recorded at different uranyl to benzoate ratio also supports the formation of this specie. Fig. 9a–e shows the luminescence spectra of uranyl–BA at different uranyl to benzoate ratio (1:1–1:5) in acetonitrile medium. The concentration of uranyl was 4×10^{-5} M and concentration of benzoate was varied from 4×10^{-5} M to 2×10^{-4} M. It can be seen from Fig. 9c that sharp features of uranyl–BA luminescence originate when the uranyl to benzoate ratio reaches 1:3. This observation is found to be consistent with other concentrations of uranyl (2×10^{-5} M, 2×10^{-4} M and 2×10^{-3} M) also. For uranyl to ligand ratio of 1:4 or above, no change in luminescence intensity was observed, thus concentration of $[UO_2(C_6H_5COO)_3]^-$ reached maximum when uranyl to ligand ratio is 1:4. Nockmen et al. [26] also prepared tris nitrato compound of uranyl by mixing 1:4 ratio of uranyl to nitrate and they also observed that above 1:4 there was no further change in complex structure. The schematic structure of the complex $[UO_2(C_6H_5COO)_3]^-$ is shown in Fig. 10.

Mechanism of ligand sensitization in acetonitrile

Since uranyl forms complex with benzoic acid in aqueous medium and the triplet energy of benzoic acid is 25,641 cm^{-1} [39], while the uranyl emitting level energy is about 22,000 cm^{-1} [40], one can expect intramolecular energy transfer from the triplet level of benzoic acid to the excited electronic level of uranyl ion to take place. Therefore like lanthanides [11], uranyl is also expected to show enhanced luminescence in aqueous medium but this is not the case. In fact luminescence intensity is suppressed after the addition of benzoic acid in aqueous uranyl solution [29]. Although benzoic acid might be transferring energy from its triplet level to uranyl ion, it appears that excited uranyl ions are decaying non-radiatively and water molecules which are present in the coordination sphere of uranyl as well as in bulk are acting as sink in accepting this excess energy by electron transfer mechanism and thus results in ineffective ligand sensitized energy transfer processes. Unlike lanthanide luminescence where coordinating water molecules are only quenchers, in the case of uranyl luminescence, the bulk water molecules in the secondary sphere also act as major quencher. Therefore when solvent is changed from water to acetonitrile, there is reduction of non-radiative decay channels and hence luminescence lifetime is increased from 1.5 to 20 μs. It should be noted that in the case of lanthanides, quenching mechanism involves the energy transfer to higher energy vibrational level of water molecules and thereby replacing one or more water molecule helped in reduction of non-radiative decay. Therefore it appears that electron transfer quenching mechanism is more detrimental than energy transfer quenching and therefore just by removing one or two water molecules from the inner coordination sphere of uranyl as it does in uranyl–BA complexes in aqueous medium, ligand sensitized luminescence could not be achieved. Thus replacing bulk water molecules by acetonitrile and removal of inner coordinated water molecules by three benzoate molecules in a bidentate fashion helped in reducing the non-radiative path ways of excited $[UO_2(C_6H_5COO)_3]^-$ and finally makes it to be luminescent. These results also corroborate that in ligand sensitized luminescence of uranyl, even though energy transfer is the key factor, decay of excited states, which generally depends on solvent molecules, decides the fate of molecule/specie whether to be luminescent or not, eventually.

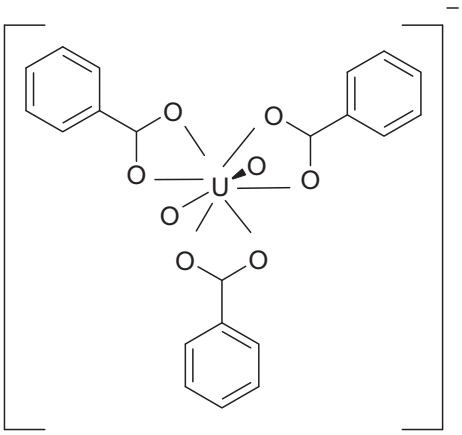

Fig. 10. Schematic diagram for the $[UO_2(C_6H_5COO)_3]^-$ structure having D_{3h} symmetry. Benzoate moieties are in the plane of the paper.

Uranyl–BA luminescence in other solvents

Apart from acetonitrile we have also studied the luminescence of uranyl ion in other medium such as dimethyl sulphoxide, dioxane, tetrahydrofuran, N–N dimethyl sulphoxide, methanol, ethanol, cyclohexane and ether. In none of the above solvents we could get any signature of ligand sensitized luminescence of uranyl. In cyclohexane and ether the complex was not soluble. Other solvents are strong coordinating solvents and competition of solvent molecules with benzoate towards uranyl ion might be the reason for the absence of enhanced luminescence. Thus being polar and less coordinating solvent, acetonitrile seems to be an ideal choice for studying the luminescence of uranyl–BA system.

Analytical application of this study

This present study of uranyl luminescence in acetonitrile medium finds an analytical application for uranyl detection. The large enhancement of uranyl luminescence of uranyl–BA complex in acetonitrile medium can be used for trace level detection of uranyl ion. Linearity in the luminescence intensity is seen over the uranyl concentration range of 6.7×10^{-8} to 6.7×10^{-6} M and the detection limit calculated using the criterion of 3σ is $\sim 4.2 \times 10^{-9}$ M. The detection limit obtained here is only for pure uranium. However in order to apply this method to environmental samples, luminescence quenching studies of uranyl in presence of other foreign ions have to be carried out.

Conclusions

Ligand sensitized luminescence has been demonstrated for uranyl, using BA as the sensitizing ligand in acetonitrile medium. In the absence of BA, only one type of uranyl hydroxide i.e. UO_2OH^+ dominates in this medium, which gives rise to enhanced emission spectrum and lifetime. When BA is present, formation of $[UO_2(C_6H_5COO)_3]^-$ has been reported for the first time for uranyl, which shows a well resolved and enhanced emission spectrum in acetonitrile medium. Electron transfer quenching which caused the absence of sensitized luminescence of uranyl by benzoic acid in aqueous medium is reduced by the formation of uranyl complex coordinated by carboxylate groups of three benzoate and hence the enhancement in luminescence.

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