LUMINESCENCE STUDIES OF Eu^{3+}AND UO_2^{2+} COMPLEXED WITH AROMATIC CARBOXYLIC ACIDS IN ACETONITRILE MEDIUM

By

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DECLARATION

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List of Publications

Journals

1. Ligand sensitized luminescence of uranyl by benzoic acid in acetonitrile medium: A new luminescent uranyl benzoate specie, **Satendra Kumar**, S. Maji, M. Joseph and K. Sankaran, Spectrochimica Acta Part A 138 (2015) 509.

2. Spectroscopic investigation of europium benzoate in acetonitrile: Luminescence enhancement and complexation studies, **Satendra Kumar**, S. Maji, M. Joseph and K. Sankaran, Journal of Luminescence 161 (2015) 123.

3. Fluorescence and co-fluorescence of Tb^{3+} and Eu^{3+} in acetronitrile using 2,6-pyridine dicarboxylic acid as ligand, S. Maji , **Satendra Kumar** and K. Sankaran, Spectrochimica Acta Part A 135 (2015) 405.

4. Luminescence of uranyl ion complexed with 2,6-pyridine dicarboxylic acid as ligand in acetonitrile medium: Observation of co-luminescence**,** S. Maji, **Satendra Kumar** and K. Sankaran, ***Radiochimica Acta*** DOI: 10.1515/ract-2016-2718.

5. Luminescence of Uranyl Picolinate in Water and Acetonitrile: A Comparative Study, **Satendra Kumar**, S. Maji, G. Gopakumar, M. Joseph, K. Sundararajan and K. Sankaran, ***communicated***.

Conferences

1. Luminescence spectroscopy of europium benzoate in acetonitrile: Ligand sensitization and complexation studies; **Satendra Kumar**, S. Maji, M Joseph and K. Sankaran, Recent trends in Spectroscopy June 20-21, 2014 held at IIT Madras.

2. Luminescence enhancement of uranyl ion by benzoic acid in acetonitrile; S. Maji, **Satendra Kumar**, M. Joseph and K. Sankaran, Recent trends in Spectroscopy June 20-21, 2014 held at IIT Madras.

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6. Luminescence spectroscopy of uranyl picolinate: Ligand sensitization and complexation studies, **Satendra Kumar**, S. Maji, M Joseph and K. Sankaran, National conference on Luminescence spectroscopy Feb 18-20, 2016 held at Nagpur University, Nagpur.
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2. Ligand sensitized fluorescence of uranyl in its fluoride complex by picolinic acid: An application for trace fluoride ion determination, **Satendra Kumar,** S. Maji and K. Sankaran J. Indian Chem. Soci. 90 (2013) 2075.
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Dedicated to

My Father

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SYNOPSIS

Trace level detection of lanthanides and actinides has become increasingly significant in various process streams, particularly in nuclear industry, such as their extraction from ores and spent nuclear fuels [1]. The lanthanide and actinide ions are known to show characteristic luminescence features, however these metal ions are weakly luminescent species, due to their low molar absorptivities and poor quantum yields in aqueous medium [2]. In order to overcome the low absorptivities of the lanthanides, ligand sensitized luminescence has been employed to sensitize and enhance the luminescence of lanthanide ions [3-6]. Ligands such as β- diketones and aromatic carboxylic acids have been used to enhance the luminescence intensity of these ions in aqueous medium. This ligand sensitized luminescence of lanthanides is further enhanced by using synergistic agents such as trioctyl phosphine oxide (TOPO), organic phosphates [7-8]. The synergistic agent displaces water molecules from the inner coordinating sphere of lanthanide and also provides an insulating layer around the lanthanide complex. As a result, the lanthanide complex is protected from quenching due to –OH oscillators and hence, further enhancement in luminescence is observed.

Ligand sensitized luminescence, which is a popular way to enhance the luminescence of lanthanides, however, is not useful in the case of uranium as most of the ligands do not sensitize the luminescence intensity of uranium. Though, there are plenty of ligands which enhance the luminescence of lanthanides, only a few such as 2,6-pyridine di-carboxylic acid and trimesic acid were reported to enhance the luminescence of uranyl ion (UO_2^{2+}) [9-10]. However, several enhancing reagents such as H_3PO_4, H_2SO_4, $HClO_4$ have been widely used to enhance the luminescence of uranyl ion in aqueous medium [11-12]. These agents make complex with uranyl ion, thereby eliminating water molecules from the inner coordination sphere of uranyl ion and consequently the quenching effects due to water is reduced which results in luminescence enhancement of uranyl ion.

Apart from using synergistic or complexing agents, changing the medium from aqueous to non-aqueous can also be looked upon to reduce the quenching effects of water molecules. In an earlier work from our group, task specific ionic liquids were used as luminescence enhancing agents for the study of Eu^{3+} and Tb^{3+} ion [13-14]. A larger enhancement in luminescence was noticed using ionic liquids over aqueous medium. But, because of highly fluorescing background of ionic liquids in the region 350-550 nm, these ionic liquids were limited to the study of the luminescence in the region above 550 nm and hence only useful for the study of Eu^{3+}. Therefore there is a need to find a fluorescence free medium, alternative to ionic liquids, to study luminescence of lanthanides and actinides. This encouraged us to use a non-aqueous solvent to carry out luminescence studies of lanthanide and actinide ions. Acetonitrile, a weak coordinating solvent is found to be the best, over other solvents in this regard. In this work, luminescence of Eu^{3+} and UO_2^{2+} complexed with some aromatic carboxylic acids has been studied in acetonitrile medium. Earlier from our group it has been shown that aromatic carboxylic acids serve as excellent ligands for the sensitization and enhancement of lanthanide luminescence in the aqueous medium [15-17], which prompted us to use these ligands in acetonitrile medium. In this work, six ligands have been used to examine the Eu^{3+} and UO_2^{2+} luminescence. Ligands used in this study are benzoic acid (BA), *o*- toluic acid (*o*-TA), *m*- toluic acid (*m*-TA), *p*- toluic acid (*p*-TA), pyridine-2-carboxylic acid or picolinic acid (PA), pyridine-2,6- dicarboxylic acid or dipicolinic acid (DPA).

The detailed studies on the luminescence of Eu^{3+} and UO_2^{2+} complexed with aromatic carboxylates in acetonitrile medium are discussed in this thesis. This work opens the possibility for the use of ligand sensitized luminescence for detecting Eu^{3+} and UO_2^{2+} at trace levels. The reason that UO_2^{2+} luminescence is not sensitized by many of the aromatic carboxylate ligands is not fully understood yet. The work carried out in this thesis also elucidates in this direction and corroborates the mechanism of ligand sensitized luminescence of UO_2^{2+} ion. The thesis consists of seven chapters and the brief description of each chapter is given in the following contents.

Chapter 1

This chapter gives an introduction of luminescence of lanthanides, actinides and their complexes, drawn from the literature. It also describes about the fundamental mechanism and applications of ligand sensitized luminescence. Different ligands used in literature to enhance the luminescence of these metal ions are discussed in this chapter. Details of earlier studies on luminescence of these metal ions in non-aqueous medium are given in this chapter to justify the choice of the ligands and solvent chosen in this study.

Chapter 2

In this chapter experimental details are described. In the present work, instruments used for the study include spectrofluorimeter (Edinburgh, model FLS920) and UV-Vis spectrophotometer (Anantes, model AvaSpec-2048). The luminescence spectra and lifetimes were recorded using spectrofluorimeter and the absorbance spectra were recorded using UV-Vis spectrophotometer. Triplet level energies of all the ligands used in this study were determined by recording the phosphorescence spectra of the ligands at liquid nitrogen temperature (77K). Preparation of complexes of Eu^{3+} and UO_2^{2+} in acetonitrile medium is also discussed here.

Chapter 3

This chapter deals with the luminescence studies of Eu^{3+}-benzoate carried out in acetonitrile medium. With benzoate as a ligand, about two orders luminescence enhancement from Eu^{3+} is observed in acetonitrile compared to aqueous medium. In addition, contrary to aqueous medium where Eu^{3+} forms 1:1 and 1:2 complexes with benzoate ion [18], a 1:3 type complex, which is highly luminescent, is formed in acetonitrile medium. Luminescence and UV-visible spectroscopy data are used to determine the stability constant of this ML_3 complex. This chapter also presents the effect of water on the luminescence and absorbance of Eu^{3+}-BA complex in acetonitrile. In order to see the effect of methyl group, Eu^{3+} complexed with ortho, meta and para toluates and its luminescence is also studied and results are compared with Eu^{3+}- BA.

Chapter 4

This chapter describes the luminescence studies of UO_2^{2+} using benzoate and methyl substituted benzoate (*o*-TA, *m*-TA, *p*-TA) as ligands in acetonitrile medium. In aqueous medium, the luminescence of uranyl ion gets quenched by these ligands whereas, its luminescence is found to increase in acetonitrile medium. The detailed studies of the uranyl complexes have been investigated by UV-Vis absorption spectroscopy. In contrary to aqueous medium where uranyl benzoate forms 1:1 and 1:2 species [19-20], spectroscopic data reveal formation of 1:3 complex in acetonitrile medium. Similar to uranyl benzoate, toluates also form 1:3 complex with uranyl in acetonitrile medium. Mechanism of ligand sensitized luminescence in acetonitrile medium has been discussed in this chapter. 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. The effect of methyl groups at different positions of benzoic acid has also been studied. Methyl group presented at ortho position of benzoic acid quenched the uranyl luminescence by non-radiative decay. Luminescence intensity of uranyl complexed with toluates is in the order of *p* toluate > *m* toluate > *o*-toluate.

Chapter 5

This chapter deals with the luminescence studies of Eu^{3+} using picolinic acid (PA) and dipicolinic acid (DPA) as ligands in acetonitrile medium. Similar to aqueous medium, both the ligands are found to sensitize the luminescence of Eu^{3+} in acetonitrile medium also. Lifetime measurements are carried out in order to identify the luminescent species. While, the stoichiometries of the europium complexes with these ligands are found to be similar as in aqueous medium, more luminescence enhancement is observed in acetonitrile compared to aqueous medium. The large enhancement in luminescence intensity is attributed to mainly due to reduction in non-radiative decay channels from outer coordination sphere of Eu^{3+} because of the removal of water. Interestingly, dipicolinic acid exhibits co-luminescence in acetonitrile medium whereas this phenomenon does not occur in aqueous medium. Mechanism of co-luminescence enhancement of Eu^{3+} is also discussed in this chapter.

Chapter 6

This chapter describes the luminescence studies of UO_2^{2+} using picolinic acid as a ligand. In aqueous medium, the uranyl luminescence is quenched when uranyl complexed with picolinic acid. In contrary to aqueous medium, uranyl luminescence was found to be enhanced by picolinic acid in acetonitrile medium. UV-Vis spectroscopy studies reveal the formation of 1:2 type complex of uranyl with picolinate in acetonitrile. This chapter also presents detailed luminescence studies of UO_2^{2+} complexed with dipicolinic acid (DPA) in acetonitrile medium. The enhancement in luminescence intensity because of sensitization by DPA in this medium is found to be one order better than in aqueous medium. With the steady state and life time results, complexation of DPA with uranyl ion are assessed and discussed. The luminescence of UO_2^{2+} complexed with DPA is found to be further enhanced due to co-luminescence, whereas no co-luminescence is observed in case of uranyl complexed with PA in acetonitrile medium. Mechanism of co-luminescence is discussed in this chapter.

Chapter 7

This chapter summarizes the results of the systems studied in the thesis in terms of enhancement factor, detection limits and lifetimes for various Eu^{3+} and UO_2^{2+} complexes in acetonitrile and all above three parameters are compared with that of the aqueous medium. Among all the ligands studied in this work, dipicolinic acid shows the highest enhancement for both of the metal ions, Eu^{3+} and UO_2^{2+} leading to the detection limits of $4x10^{-11}$ M for Eu^{3+} and $1x10^{-9}$ M for UO_2^{2+}.

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LIST OF ABBREVIATIONS

Symbol	**Abbreviation**
BA	Benzoic acid
TA	Toluic acid
PA	Picolinic acid
DPA	Dipicolinic acid
TOPO	Tri-octyl phosphine oxide
TTA	Thenoyl tri-fluoro acetone
UV/Vis	Ultra-Violet/Visible
R	Asymmetry ratio
EF	Enhancement factor
$[Eu^{3+}]$	Concentration of europium
$[UO_2^{2+}]$	Concentration of uranyl
[Ligand]	Concentration of ligand

CHAPTER 1 Introduction

1.1 Luminescence

When a molecule is excited to a higher energy state, it returns to its ground state unless it gets involved in a photochemical reaction and loses its identity. The energy released by the molecule in this de-excitation process may be radiative or non-radiative. Luminescence is the photo physical process in which molecules emit energy radiatively. Depending on the nature of excited states, luminescence can be divided into two categories- the fluorescence and phosphorescence. These processes can be defined as indicated below. The electron in the excited orbital is paired to the second electron in the ground state orbital in case of singlet states while electrons are parallel in triplet states. Therefore, return to the ground state from the singlet excited state is a spin allowed process that occurs rapidly by emission of a photon. This kind of emission which involves the transition between singlet states is known as fluorescence. The lifetimes of fluorescence are typically in nano seconds. Phosphorescence is the emission of light from triplet excited states. Therefore, in case of phosphorescence, transitions to the ground state are forbidden and the emission rates are slow and phosphorescence lifetimes are typically in the range of milliseconds to seconds.

1.2 Lanthanide and Actinide ions

Trivalent lanthanide ions are characterized by their partially filled f orbitals, except lanthanum and lutetium - the former has completely empty and later has completely filled f orbital [1-2]. Lanthanides play a very important role in various fields such as environmental science, biosciences, nuclear industry etc [3-8]. The most stable and predominant oxidation state of all the lanthanides is +3 [1], although some of the lanthanides like cerium can exhibit +4 whereas europium and ytterbium can exhibit +2 oxidation states also [1-2]. The oxidation states besides +3 are also stable because these valance states approach towards stable states like $4f^0$, $4f^7$ and $4f^{14}$ configurations of lanthanides. The 4f valence orbital is well-shielded by the $5s^2$ and $5p^6$ orbital of the lanthanides and thus not directly available for bonding. However, lanthanides interact strongly with negatively charged groups such as polydentate inorganic anions ($[NO_3]^-$, $[SO_4]^{2-}$) because of electrostatic nature of the coordination bonds. The coordination number of lanthanide ions in aqueous medium is generally 8-9 [1-2]. Aqua complex of lanthanide ions in crystalline compounds are generally nine coordinated having tricapped trigonal prism structure [2].

Actinides have similar properties like lanthanides having their partially filled 5f orbitals. All the actinides are radioactive and release energy during their decay processes. Actinides exhibit a variety of oxidation states from +3 to +6. The most stable oxidation states are +6 for uranium, +5 for protactinium and neptunium, +4 for thorium and +3 for other actinides [9-10]. Uranyl ion (UO_2^{2+}) is the most stable form of uranium in aqueous medium. UO_2^{2+} is linear and symmetrical [11]. It behaves as a hard acceptor and form strong complexes with oxygen donor ligands. UO_2^{2+} in aqueous medium is coordinated to five water molecules and has pentagonal bi-pyramidal structure [9]. UO_2^{2+} is generally coordinated to 4-6 ligand sites in aqueous medium [10-11]. The complexes of UO_2^{2+} in aqueous medium are very important for the extraction of uranium in various process streams such as its extraction from ores and spent nuclear fuels [12-14].

1.2.1 Lanthanides luminescence

Trivalent lanthanides are characterized by their luminescence properties having sharp line like spectra, large stokes shift and relatively long luminescence lifetimes [15-16]. The geometry of electronic levels of lanthanides ions in ground state and in excited states is almost same and excitation only involves some rearrangement of electrons within 4f orbitals. The 4f orbitals do not participate much in chemical bonding with ligands since these are deeply buried and surrounded by s and p orbitals and hence, show characteristic sharp luminescence features [9]. The energy levels of f orbital are not degenerate. The non-degeneracy of f orbital arises because of three types of interactions -electronic repulsion between the electrons, spin orbit coupling and the interaction of ions with its environment (ligand field) [9]. Figure 1.1 shows the typical splitting pattern of 4f energy levels of europium ion (Eu^{3+}) as a result of all these interactions. Among these three factors, electronic repulsion is the strong interaction and it causes the splitting between energy levels with the separation of about 10^4 cm^{-1}. Spin orbit coupling is the interaction between electron's spin and the magnetic field generated by the electron's orbit around the nucleus which causes further splitting of energy levels. The spin orbit splitting called as J splitting is in the order of 10^3 cm^{-1}. The effect of environment on the f orbitals are not pronounced as mentioned earlier and ligand field splitting of lanthanides ions is very small being in the range of 10^2 cm^{-1}. The typical energy level diagram for some of the lanthanides, known as Dieke diagram [9] is shown in Figure 1.2.

In aqueous medium, lanthanide ion exists in +3 oxidation state. Due to f-f Laporte forbidden transitions, lanthanide ions have very low molar absorption coefficients (less than 5 $M^{-1}cm^{-1}$). In solutions, generally the decay of lanthanide luminescence is dominantly non-radiative and solvent plays a very important role in the decay processes. The non-radiative decay of lanthanide ion luminescence originates from the fact that an interaction may exist between emitting state of lanthanide ion and vibrational states of the solvent.

Based on their luminescence intensities in solution, luminescent lanthanide ions can be classified into two groups-

a. This group contains Ce, Sm, Eu, Tb, Dy and exhibit fair luminescence. The energy gap between the lowest emitting state and highest non-luminescent state is large and hence these ions are less sensitive to quenching from high energy oscillators of solvent molecules (–OH oscillators in case of water).

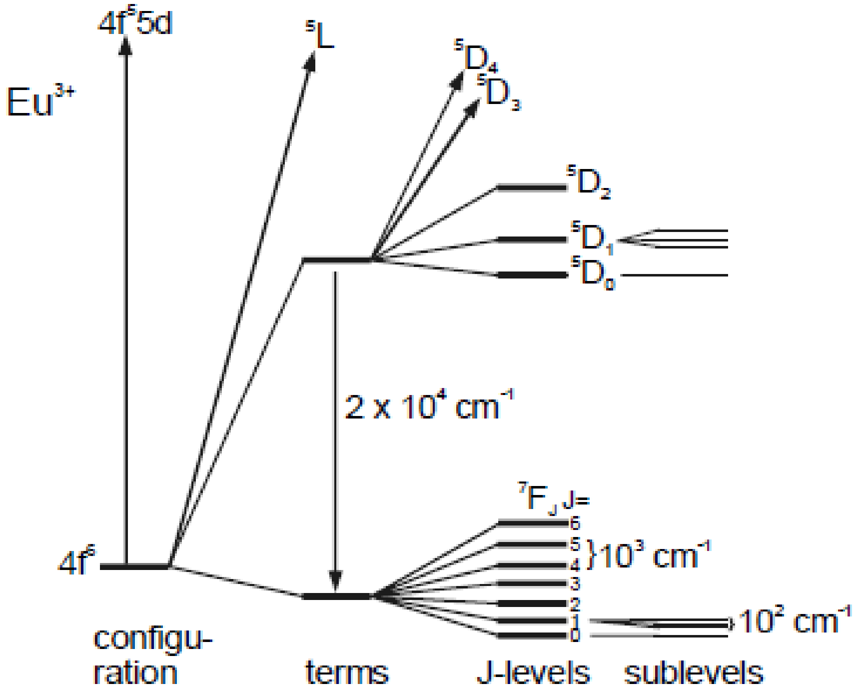

Figure 1.1 Non-degeneracy of 4f orbitals of Eu^{3+} as a result of electronic repulsion, spin orbit coupling and ligand field effect [16].

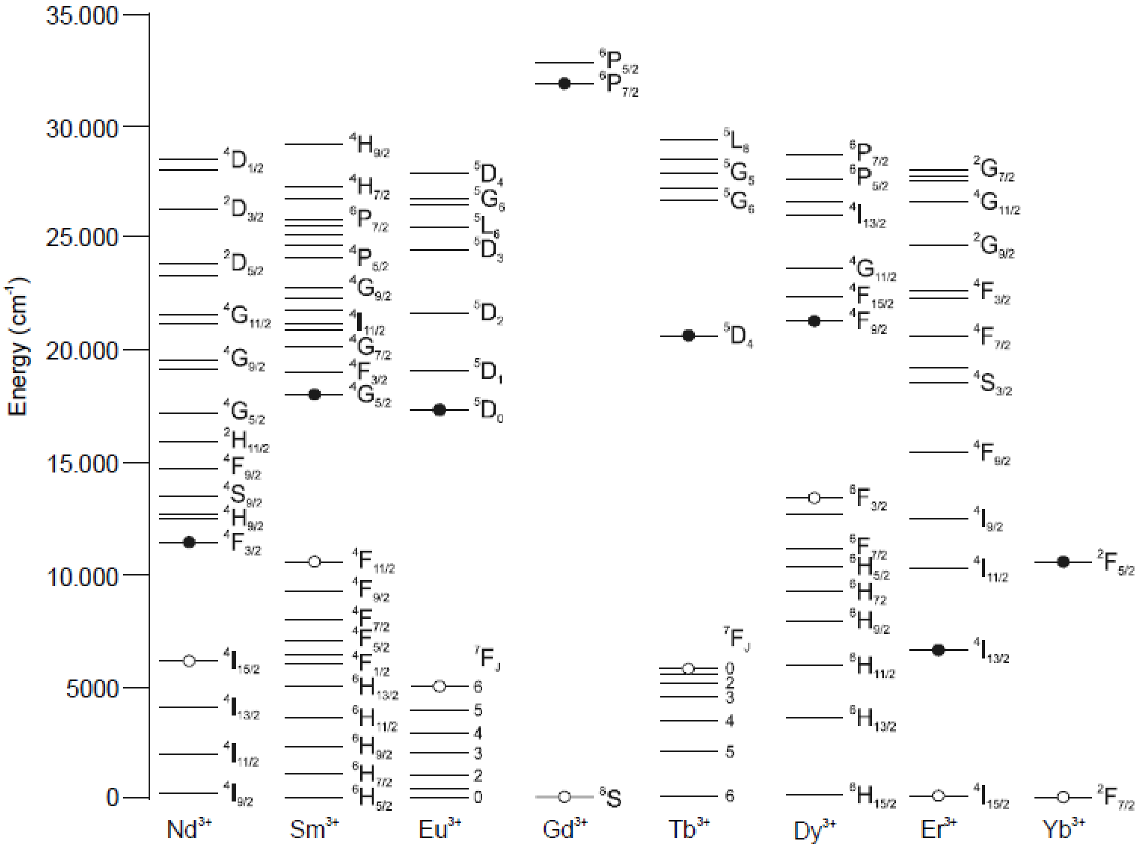

Figure 1.2 Energy levels for some of the lanthanide ions. A filled circle denotes the lowest luminescent level and a white circle denotes highest non-luminescent levels [16].

b. The second group contains Pr, Nd, Pm, Ho, Er, Tm and Yb; the ions of all these elements exhibit poor luminescence. The reason for poor luminescence is due to the fact that there is a small energy gap between highly luminescent and lowest non- luminescent state. This low energy gap makes these lanthanides to couple with vibrational modes of high energy oscillators efficiently and hence, decay non-radiatively.

The other lanthanides like La^{3+} and Lu^{3+} hardly show any luminescence because of either empty 4f orbital or fully filled 4f orbital. The large energy gap between lowest luminescent states to highly non-luminescent state makes Gd^{3+} difficult to be luminescent [Figure 1.2].

1.2.2 Eu^{3+} luminescence

The luminescence of Eu^{3+} is one of the most studied subject among lanthanides [16]. The luminescence of Eu^{3+} originates from the transitions among 4f electronic energy states as mentioned earlier. The electronic configuration of Eu^{3+} is $[Xe]4f^6$ and the spectroscopic term symbol of the ground state is $^7F_{0.}$ The luminescence of Eu^{3+} is characterized by the emission from the energy state $^5D_0$ to many energy states of ^7F level. This results in following transitions:

$^5D_0 \rightarrow {}^7F_0$ (580 nm)

$^5D_0 \rightarrow {}^7F_1$ (592 nm)

$^5D_0 \rightarrow {}^7F_2$ (615 nm)

$^5D_0 \rightarrow {}^7F_3$ (650 nm)

$^5D_0 \rightarrow {}^7F_4$ (700 nm)

The emissive energy level ($^5D_0$) of Eu^{3+} lies 17250 cm^{-1} above the ground level [15]. Among the above transitions, transitions occurring at 592 and 615 nm have strongest luminescence. The transition $^5D_0 \rightarrow ^7F_2$ at 615 nm is an electric dipole allowed transition and known as hypersensitive transition as its intensity depends on the local environment. The transition $^5D_0 \rightarrow ^7F_1$ at 592 nm is a magnetic dipole allowed transition and its intensity hardly changes with the local symmetry of Eu^{3+} ion [15-16]. For the $^5D_0 \rightarrow ^7F_2$ transition luminescence intensity is much more sensitive on complexation compared to other transitions. Intensity of the hypersensitive transition in complexed Eu^{3+} may be several times more as compared to hydrated ion. Because the intensity of this hypersensitive transition is strongly dependent upon the Eu^{3+} ion environment, the ratio of intensities of 615 nm to 592 nm transitions, which is known as asymmetry ratio, can be used to identify coordination structure or local site symmetry of the Eu^{3+} ion.

1.2.3 Actinide luminescence

Most of the actinides like U, Am, Np, Cm, Bk, Cf, Es show luminescence properties in one or more oxidation states [9]. But due to the difficulties in handling and restricted availability of these materials, luminescence studies are more or less restricted only to U, Am and Cm. Due to the larger spin orbit coupling, electronic energy levels of actinides are more packed as compared to lanthanides [17]. Figure 1.3 shows a comparison in the free ion energy levels of trivalent actinides with similar lanthanides. This Figure shows that the energy difference between emitting and highly occupied ground states is small for actinides compared to that of lanthanides. This less energy gap makes actinides more susceptible to non-radiative decay as compared to lanthanides. Uranium is the most studied luminescent element among the actinides [9]; other actinides like Am^{3+} and Cm^{3+} luminescence also have been reported [18-21]. Curium shows the most intense luminescence among all the actinides except uranium and therefore, estimation at a level of 10^{-7} M is possible by luminescence measurements [11]. The luminescence of americium has been carried out in its complex with

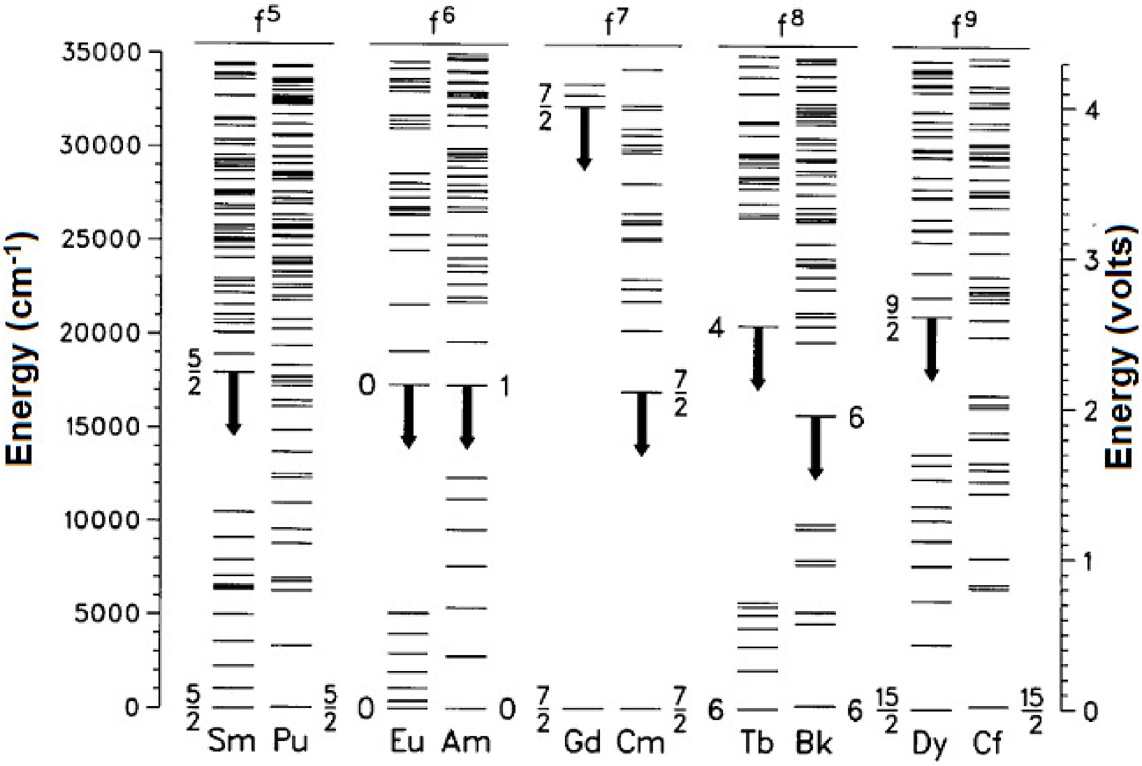

Figure 1.3 Comparison of energy levels of trivalent lanthanides and actinide ions having same number of f electrons [17].

pyromellitic acid and an increase in luminescence lifetime has been observed thereby, its detection could be possible at trace level [21].

1.2.4 UO_2^{2+} luminescence

Urany ion (UO_2^{2+}) is known to exhibit luminescence in solution. The ground state of UO_2^{2+} has a closed shell configuration ($5f^0$). The electronic spectra of UO_2^{2+} salts typically show a ligand-to-metal charge transfer electronic transition centered around 420 nm, with a superimposed vibrational fine structure and a maximum of twelve transitions can be resolved. The corresponding green emission is centered at 520 nm and is a result of deactivation of the excited triplet state [22-24]. The typical energy levels involved in electronic spectra have been shown in Figure 1.4. The ground state of UO_2^{2+} is $^1\Sigma_g$ (S_0). The excited levels involved in electronic spectra are $^1\Phi g$ (S_1), $^3\Delta g$ (T_2), $^3\Phi g$ (T_1). There are a lot of discrepancies regarding luminescence of UO_2^{2+} in terms of phosphorescence or fluorescence [25-28]. Having lifetimes in the range of microseconds and being large atomic number, which can induce spin orbit coupling, lead to inter system crossing to lowest lying triplet levels. Therefore, in maximum reports luminescence of UO_2^{2+} is said to be phosphorescence [25, 29]. Ghosh and co-workers studied the ultrafast dynamics of UO_2^{2+} in solution and they also found the luminescence of UO_2^{2+} to be phosphorescence [29]. The luminescence lifetime of UO_2^{2+} in its carbonate solution is found to be very short (40 ns) and therefore few researchers assign UO_2^{2+} emission as fluorescence [26, 28].

1.3. Ligand sensitized luminescence

Because of low molar absorptivity of the lanthanides and actinides (<10 M^{-1} cm^{-1}) [9], which is an intrinsic property, lanthanide and actinides are poor luminescent elements. The low molar absorptivities of trivalent lanthanide and actinide ions arise from the Laporte forbidden f-f transitions. Therefore, simply by exciting the absorption bands of lanthanides and actinides rarely yield fair luminescence. The alternate way to achieve high luminescence

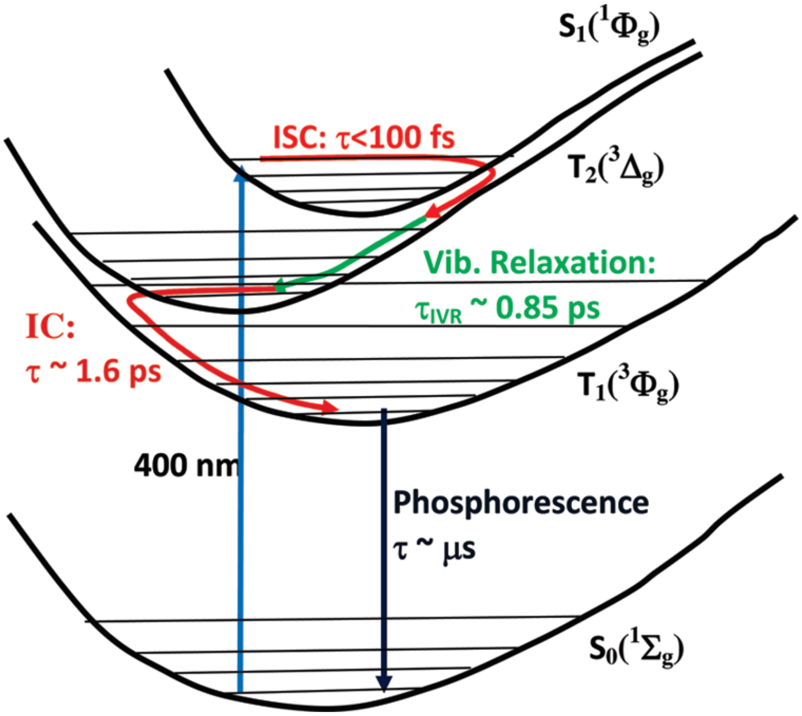

Figure 1.4 Schematic potential energy diagram of UO_2^{2+} showing many electronic levels and excited state relaxation processes [29].

is to bind the metal ion with some organic ligands having high molar extinction coefficient. By this way, luminescence occurs by a transfer of energy from the organic ligand to the metal ion through a three step mechanism namely: absorption of light by the ligand, transfer of the energy to the metal ion and eventually characteristic emission of light by the later [30]. Upon absorbing light, the ligand is first excited to the singlet state. An intersystem crossing then takes place leading to a long lived triplet state from where energy transfer occurs to the excited state of metal ion. This results in an indirect way of excitation of metal ion which then exhibit luminescence and this process is known as 'ligand sensitized luminescence'. The pictorial representation of ligand sensitization luminescence of Eu^{3+} is shown in Figure 1.5 [9].

The other processes such as fluorescence of ligands, quenching of triplet states with molecular oxygen are in competition with energy transfer process to metal ions. The overall quantum yield (ϕ) of sensitized luminescence is thus the product of intersystem quantum yield (ϕ_{ISC}), energy transfer quantum yield (ϕ_{ET}) and the luminescence quantum yield (ϕ_{LUM}):

$$\phi = (\phi_{ISC}) \text{ x } (\phi_{ET}) \text{ x } (\phi_{LUM}) \quad \text{-------------------} \; 1.1$$

The luminescence quantum yield indicates the efficiency of ions to decay radiatively and defined as:

$$\phi_{LUM} = k_{rad}/(k_{rad}+ k_{nrad}) \quad \text{------------------} \; 1.2$$

where k_{rad} and k_{nrad} are the rate constants for radiative and non-radiative decays, respectively.

In order to have efficient ligand sensitized luminescence to occur the following criteria must be considered:

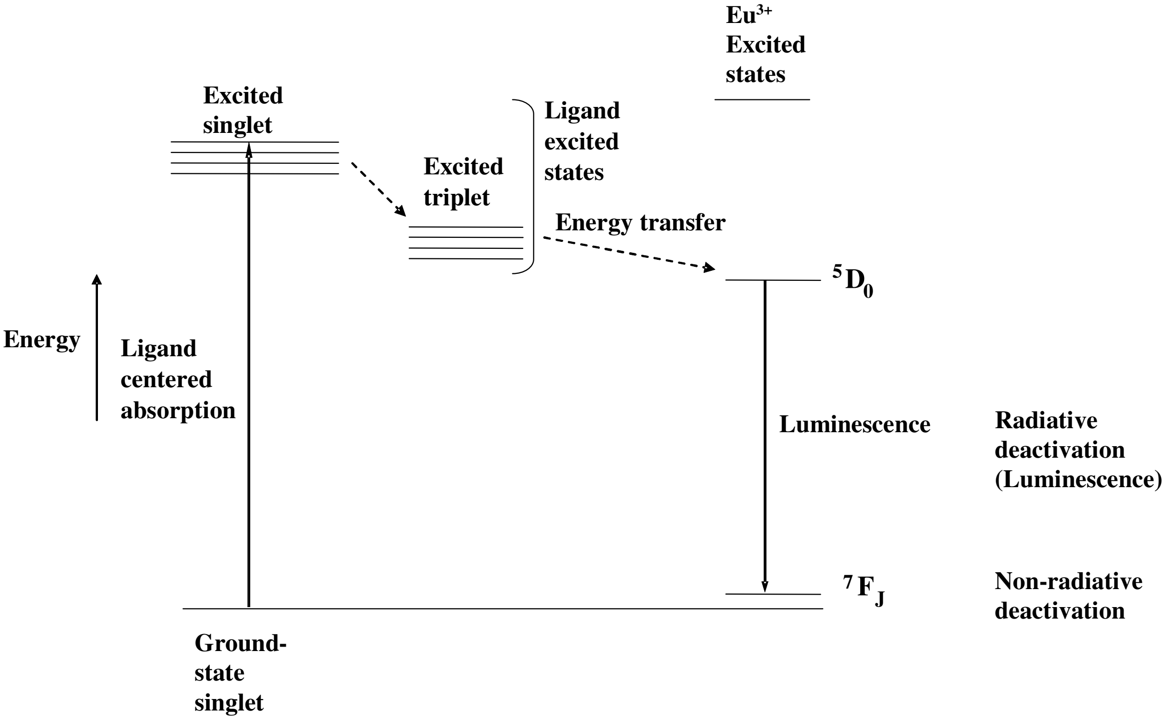

Figure 1.5 Schematic diagram for depicting different processes of ligand sensitized luminescence for Eu^{3+} [9].

1. The ligand should have high molar absorption coefficient
2. The fluorescence or phosphorescence decay of ligand should be minimal
3. The energy of emitting level of metal ion must be just below the triplet energy level of ligand

1.3.1 Luminescence enhancement of Eu^{3+} by different ligands

The sensitization of lanthanide luminescence was first observed by Weissman *et al.* in the year of 1942 [31]. An intense luminescence could be observed for lanthanide complexes containing benzoyl acetone and other acetones as a ligand after excitation to the ligand band. In the year 1961, the mechanism of sensitization from the ligand to lanthanide ion was established by Crosby *et al.* [32] and after that intense research has been carried out by many researchers on luminescence of lanthanide-β-diketone complexes [33-40]. The interaction between Eu^{3+} and diketone ligands can be electrostatic or ionic in nature. The most studied ligand among diketones for Eu^{3+} complexation is thenoyl tri-fluoro acetone (TTA) [39]. Complexation with TTA expels water molecules from the inner coordination sphere of Eu^{3+} in aqueous medium. Generally TTA forms tris complex with Eu^{3+} and hence only six coordination sites are occupied by TTA molecules, thereby quenching by water molecules at remaining three sites is still possible. Removal of these remaining water molecules could be achieved by using trioctyl phosphine oxide which has oxygen as binding site or 1, 10 phenathroline containing two nitrogen sites [39].

Aromatic carboxylic acids have also been used as sensitizing ligand for enhancement of the luminescence of Eu^{3+} [41-49]. The sensitization of Eu^{3+} luminescence by aromatic carboxylate anion was first observed by Tran and co-workers in the year of 1990 [49]. In their work they have shown that the luminescence intensity of Eu^{3+} could be sensitized by 67 times by benzoate ion in an organic phase of crown ether-benzoate system. Later in 1992, Peter and co-workers have used benzoic acid for the enhancement of lanthanide luminescence in aqueous medium [41]. The luminescence intensity of Eu^{3+} was further enhanced by using trioctylphosphine oxide (TOPO) / Triton X-100 as a synergistic agent in aqueous solutions. Different benzene carboxylic acids have been used for the luminescence enhancement of Eu^{3+} in the extensive work carried out by Panigrahi *et al.* [42-45]. The luminescence was further enhanced by an order of magnitude when some of these Eu^{3+} complexes were treated with TOPO and Triton X-100. Furthermore, pyridine based carboxylic acids namely; picolinic acid, nicotinic acid and dipicolinic acid have been studied by Panigrahi for the luminescence enhancement of Eu^{3+} in aqueous medium [44]. However, synergistic enhancement of Eu^{3+} luminescence due to the addition of TOPO/ Triton X-100 was observed only with nicotinic acid. Naphthalene based carboxylic acids have been shown to sensitize the luminescence of Eu^{3+} in the work carried out by Maji *et al.* [48]. The conclusion drawn from all these studies was that if the absorption of the ligand is strong and the energy transfer to the Eu^{3+} is efficient, the resulting lanthanide luminescence due to ligand sensitization would be many orders of magnitude greater than that resulting from the direct excitation of the Eu^{3+}.

1.3.2 Luminescence enhancement of UO_2^{2+} by different ligands

Unlike lanthanide ions, reports on ligand sensitized luminescence studies are scarce in the case of UO_2^{2+}. Most of the ligands do not sensitize the luminescence of UO_2^{2+} in aqueous medium. Out of aromatic carboxylate ligands, only a few such as dipicolinic acid (DPA) and trimesic acid were found to sensitize the luminescence of UO_2^{2+} [50-51]. The luminescence intensity of UO_2^{2+} could be sensitized by about two orders of magnitude using these ligands in aqueous medium. In order to enhance the luminescence of UO_2^{2+} in aqueous medium, luminescence enhancing reagents such as H_3PO_4, H_2SO_4, $HClO_4$ have been widely used [52-53]. These agents make complex with UO_2^{2+}, thereby eliminating water molecules from the primary coordination sphere of UO_2^{2+} leading to reduction in the quenching effects due to water and enhancement of UO_2^{2+} luminescence.

1.3.3 Co-luminescence

It has also been shown that the ligand sensitized luminescence can be further enhanced by the addition of certain non-luminescent metal ions such as La^{3+}, Gd^{3+}, Lu^{3+}, Y^{3+} to the solution of lanthanide complex [54-66]. This phenomenon is known as co-luminescence and it has been shown as an efficient way of improving the sensitivity of the fluorimetric determination of lanthanides. In case of lanthanide complexes with aromatic carboxylic acids, it is believed that the co-luminescence enhancement is due to the formation of poly-nuclear complexes as aromatic carboxylate having more than one binding site can bind together with luminescence ion and other metal ion [58]. Ligands such as benzoic acid, phthalic acid, dipicolinic acid (DPA) etc make luminescent complexes with lanthanides in aqueous medium but do not show co-luminescence. The reason of non-exhibition of co-luminescence with these ligands is due to the fact that formation of poly-nuclear complexes is not possible, as there are no free sites available in these complexes to bind with other metal ions. Co-luminescence enhancement of Eu^{3+} was found to be observed only with certain aromatic ligands, such as trimesic acid, pyromellitic acid and mellitic acid. Eu^{3+} complexes with mellitic acid, pyromellitic acid have free donor sites to bind further with other metal ions and hence there is a possibility to form poly-nuclear complexes leading to co-luminescence. It is to be noted that lanthanide complexes with β-diketones also not have any free ligand site to bind with other metal ion and cannot form poly-nuclear complexes but still exhibit co-luminescence in aqueous medium. Now, it has been established that in lanthanide-β-diketonate complexes, the co-luminescence enhancement is not due to formation of poly-nuclear complexes but is due to inter-molecular energy transfer from other non-luminescent metal complex to luminescent complex [64-66]. UO_2^{2+} complex with trimesic acid also can have free sites to attach with other metal ion and thus exhibit co-luminescence. UO_2^{2+} also exhibited co-luminescence with trimesic acid after the addition of Y^{3+} ion in aqueous medium and formation of poly-nuclear complexes is believed to be responsible for co-luminescence [51].

1.3.4 Application of ligand sensitized luminescence

The large enhancement in lanthanide luminescence intensity through ligand sensitized luminescence finds analytical application in trace metal ion detection [67-70]. Aromatic carboxylate ligands provide a detection of lanthanides at a level up to 10^{-11} M by co-luminescence and synergistic enhancement in aqueous medium. Eu^{3+} ion detection could be pushed to a level of 10^{-13} M by co-luminescence enhancement using TTA as a ligand [33]. Determination of trace amount of Eu^{3+} ion in various matrices has been studied by many researchers [69-70]. A method based on luminescence measurements was developed for the determination of ultra trace amounts of Eu^{3+} (down to 10^{-13} M) in high purity lanthanum, praseodymium and dysprosium oxides. This was based on the enhanced luminescence of Eu^{3+}-thenoyltrifluoroacetone (TTA)-dibenzo-18-crown-6 (DBC)-Triton X-100 [69]. Estimation of Eu^{3+} in a large excess of uranium could be achieved using TTA as a sensitizing ligand and dimethyl sulphoxide (DMSO) as a solvent [70]. Taking advantage of co-luminescence, uranium could be determined at the level of 10^{-9} M using trimesic acid as ligand in aqueous medium [51].

Recently, the use of lanthanide complexes as luminescent probes has been studied extensively [71-75]. Several types of lanthanide complexes have been used as an anion sensor. Wang *et al.* has prepared a luminescent probe of Eu^{3+} with 2-(2-hydroxyphenyl) imidazo[4,5-*f*]-1,10-phenanthroline for fluoride ion sensing where the emission of Eu^{3+} ion was completely quenched by addition of 2 equivalent of fluoride ions in DMSO [71]. Mahajan *et al.* has reported a luminescent probe of lanthanides complexed with tris(fluorinated β-diketonates) which could sense chloride ion effectively [72]. A novel dual-functional ligand, di (2-picolyl) amine (DPA)–β-diketone1,2-bis[4’-(1”,1”,1”,2”,2”-

pentafluoro-3”,5”-pentanedion-5”-yl)benzyl]-4-chlorosulfo-benzene (BPPBCB) has been synthesized by Liu *et al.* and its luminescent probe with Eu^{3+} ion has been used for Cu^{2+} ion sensing [73]. In the work of McMahon and coworkers, a Tb^{3+}-cyclen-based sensor possessing a phenyl iminodiacetate based receptor has been designed and synthesized for the selective detection of Cu^{2+} and Hg^{2+} ions in water [74]. Recently from our group, we have made use of the luminescent complex based on binary ligands fluoride-picolinate with UO_2^{2+} for the estimation of F^- ion in water [75].

Apart from analytical applications and luminescent probes, ligand sensitized luminescence also finds application in fundamental understanding of complexation of lanthanide with different ligands [76-78]. Eu^{3+} ion is good luminescence probe for studying complexation reactions of lanthanides. The complexation of Eu^{3+} with phthalic acid and mandelic acid has been carried out by Jain *et al.* using luminescence [76]. The ratio of the intensities of 616 and 592 nm peaks was used to determine the stability constants of Eu^{3+}-phthalate and Eu^{3+}- mandelate complexes. Klenze *et al.* has studied the complexation of Tb^{3+} and Cm^{3+} with 5- sulpho salicylic acid using time resolved luminescence spectroscopy [78]. The stability constants were determined by quantification of different metal ion through de-convolution of emission spectra.

1.4 Quenching of luminescence

Apart from poor absorption bands of lanthanides and actinides, another factor that is responsible for the poor luminescence in solution is the poor quantum yield and this is due to the competition of luminescence with non-radiative decay channels in solution. In aqueous medium, deactivation of the excited state of the metal ion through vibrational energy transfer to the water molecules strongly competes with the luminescence of metal ions. In other words, the coordination of solvent molecules to the luminescent metal ions leads to reduction of luminescence lifetimes and quantum yields due to the non-radiative depopulation of the luminescent state via vibronic coupling with the vibrational states of high energy solvent oscillators such as –OH, –CH, –NH etc [79].

1.4.1 Quenching of Eu^{3+} luminescence

The energy gap between the excited and ground states of the lanthanide ions plays an important role in luminescence quenching via non-radiative decay processes. The non-radiative deactivation arises by the vibronic coupling between the f electronic states of lanthanides and vibrational levels of high energy oscillators. Energy gap law gives quantitative information about the non-radiative decay processes in lanthanide ions. According to the energy gap law, the smaller the harmonic number of vibrational levels to match the energy gap between the lowest luminescent state and highest non-luminescent state, the more energy will be transferred non-raditively [79]. The harmonic number of vibrational levels of –OH and –OD require to match the energy gap in Eu^{3+} is shown in Figure 1.6. In case of –OH oscillators, the 4th vibrational level matches with energy gap, however if these –OH are replaced by –OD, energy difference requires 5th vibrational level and hence the quenching is less efficient in case of –OD.

Frank condon factor (F) is a measurement of vibronic coupling between the emitting states of lanthanide ions and vibrational level of high energy oscillators. Quantitatively F has been calculated by the following equation [80]:

$$F \quad = [\exp(-\gamma)\, \gamma^{\nu}]/\, \nu! \qquad \text{---------------} \ 1.3$$

where γ is the displacement factor defined as $\gamma = ½\ k\ (q-q^0)^2/\ \hbar\omega$, (q and q^0 are the equilibrium positions in the ν^{th} vibrational states and k is the Boltzmann constant). According to the above equation vibronic coupling decreases rapidly as number of vibrational states increases and therefore vibronic coupling is less efficient in case of –OD ($\nu = 5$) than –OH (ν

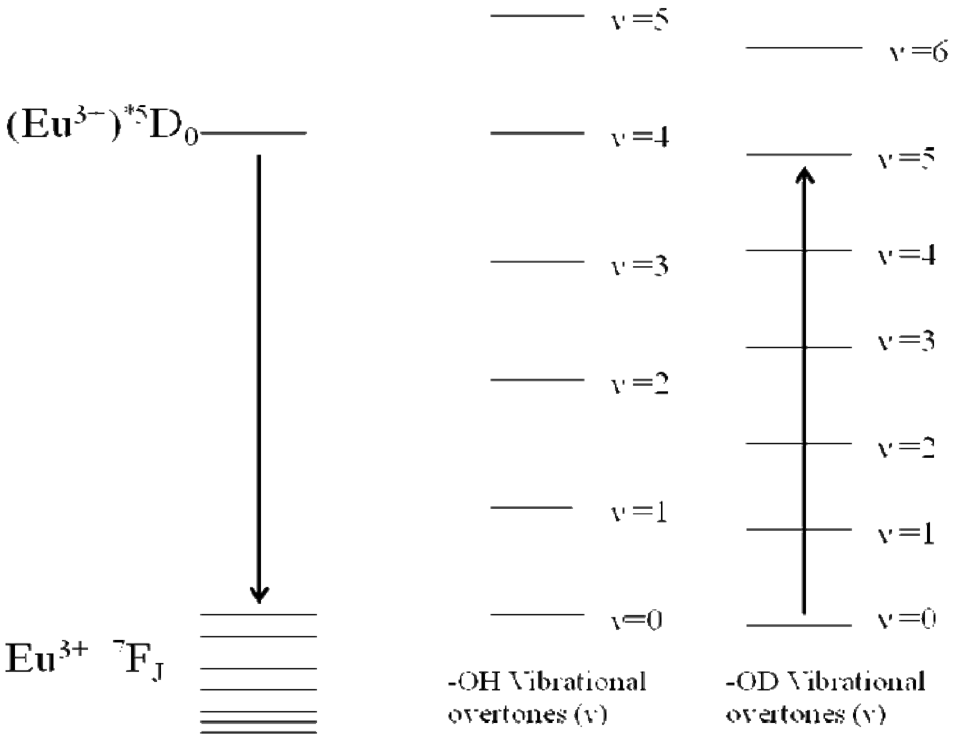

Figure 1.6 Schematic diagram for vibronic quenching of Eu^{3+} by 4 th overtone of –OH oscillator and 5 th overtone of –OD oscillator [79].

= 4). If γ is assumed to be 1, F is calculated as 0.015 and 0.0031 for –OH and –OD oscillators, respectively [80].

1.4.2 Quenching of UO_2^{2+} luminescence

Unlike the lanthanides, where luminescence is very sensitive to high energy oscillators such as –OH, UO_2^{2+} luminescence is less sensitive towards –OH oscillators [81]; hence replacement of –OH by –OD does not increase the lifetime of UO_2^{2+} significantly. Also in case of UO_2^{2+} the quenching by water is very sensitive to the temperature; contrary to this lanthanides luminescence show little dependence on the temperature. Considering all these observations, Moriyasu and co-workers proposed a quenching mechanism for UO_2^{2+} luminescence [81] based on electron transfer in terms of oxidation reduction potentials and interpreted satisfactorily as given below:

$$UO_2^{2+\,*} + H_2O \longrightarrow UO_2^{+} + H^{+} + {}^{\cdot}OH + e^{-} \qquad \text{---------------} \; 1.4$$

$$UO_2^{2+\,*} + H_2O \longrightarrow UO_2H^{2+} + {}^{\cdot}OH + e^{-} \qquad \text{---------------} \; 1.5$$

Since the value of oxidation-reduction potential of water depends on pH of the solution and which is correlated with quenching, this mechanism also explains the variation in quenching rate constant with change in acidity of UO_2^{2+} solution.

1.5 Eu^{3+} and UO_2^{2+} luminescence in non-aqueous medium

Hopkins and co-workers have studied the luminescence of Eu^{3+} and Tb^{3+} in ionic liquid namely, 1-butyl-3-methylimidazolium bromide (BMIBr) and water mixture [82]. The observed spectroscopic properties of $EuBr_3$, $TbCl_3$ salts are affected by the high water content, but also unexpectedly affected by the BMIBr ionic liquid. However, the spectroscopy of Eu^{3+} complexed with pyridine di-carboxylic acid was unaffected by the presence of BMIBr. A spectroscopic investigation of Eu^{3+} dissolved in 1-butyl-3-methylimidazolium $[(CF_3SO_2)_2N]^-$ has been investigated, particularly with respect to the effect of water and added tetrabutylammonium chloride by Billard *et al.* [83]. In the work of Billard *et al.*, similar trends of coordination and spectroscopic properties have been observed for Eu^{3+} in degassed 1-butyl-3-methylimidazolium $[(CF_3SO_2)_2N]^-$ and organic hygroscopic solvents such as acetonitrile or ethanol. The luminescence properties including lifetimes of Eu^{3+}, Sm^{3+}, Nd^{3+} etc. complexed with Tf_2N (Tf_2N = bis-(trifluoromethanesulfonyl)amide) in the ionic liquid bmpyr Tf_2N (bmpyr =1-n-butyl-1-methylpyrrolidinium) was studied by Brandner *et al.* [84]. The luminescence lifetimes in this system was found to be remarkably long as compared to values reported for lanthanides in aqueous. It was also observed that water introduced into the system binds quantitatively with lanthanide ions. The effect of relative water content on the luminescence properties and speciation of Eu^{3+} ions in the binary solvent mixture water/1-butyl-3-methylimidazolium chloride was studied by Samikkanu *et al.* [85]. This study suggested that ionic liquid is a promising medium for luminescent lanthanide compounds due to the low-energy phonon environment of the formed $[LnCl_x]^{3-x}$ complex and to the fact that moderate water contamination does not result in direct binding of water to lanthanides which would result in luminescence quenching. Nockemann and coworkers have studied the Eu^{3+}-tetrakis(2-thenoyltrifluoroacetonate) complex dissolved in the imidazolium ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and acetonitrile [86]. They found that the complex is photochemically more stabilized in the ionic liquid than in acetonitrile. Recently, Devi *et al.* has synthesized task specific ionic liquids and studied the luminescence of Eu^{3+} and terbium complexes [87-88]. In addition to reduction of non-radiative decay channels, a large enhancement due to sensitization could lead the detection of these metal ions at trace levels.

There are few reports available in literature on spectroscopic studies of UO_2^{2+} complexes in non-aqueous medium [89-94]. The main motive of these studies is towards speciation, complex structure and their spectroscopic properties in non-aqueous medium.

Servaes and co-workers have investigated the UO_2^{2+} complexation with nitrate and chloride ions in acetonitrile medium [89-90]. The important conclusions drawn from their studies are that with nitrate ion a tris complex of UO_2^{2+} named UO_2^{2+} nitrato with D_{3h} symmetry and with chloride ion $[UO_2Cl_4]^{2-}$ with D_{4h} symmetry is formed in acetonitrile and there were no evidence of these complexes in aqueous medium. Sornein and co-workers have studied complex formation between UO_2^{2+} and bromide ion in ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][Tf_2N]) and methyl-tributylammonium bis(trifluoromethylsulfonyl)imide ([$MeBu_3N$][Tf_2N]) [91]. The formation of $[UO_2Br_4]^{2-}$ could be evidenced in these ionic liquids. Nockemann and coworkers have studied UO_2^{2+} complexes with chloride, nitrate and acetate ions in ionic liquids and it was concluded that both the cation and weakly coordinated anion have a minor influence on the optical spectra of UO_2^{2+} complexes [93]. The studies carried out by the same researchers on UO_2^{2+} complexed with carboxyl functionalized ionic liquids showed that carboxylate groups remain coordinated to UO_2^{2+} in ionic liquid and acetonitrile medium but not in water [94].

1.6 Properties of acetonitrile as a solvent for luminescence studies

1.6.1 Binding Strength and solubility

The coordination of ligand to metal ion in solution occurs in competition with the solvation of specie involved [95]. More the binding strength of solvent, it will hold the metal ion strongly and will not allow ligand to bind with metal ion efficiently. Therefore, binding strength of solvent always plays an important role in complexation with metal ion. A detailed study on binding strength of Eu^{3+} towards different organic solvents have been examined by Kimura *et al.* by measuring luminescence decay constant and is in the order of - phosphoramide > dimethyl sulphoxide > N-methylformamide ~ N,N-dimethylformamide ~ formamide > N,N-dimethylacetamide > H_2O > pyridine > methanol > ethanol ~ acetone >

tetrahydrofuran ~ acetonitrile [96]. Acetonitrile being a poor coordinating solvent, it is expected to be a good solvent for studying luminescence of metal ligand complexes.

Acetonitrile is a medium polarity solvent and miscible in water and many organic solvents. It dissolves a wide range of ionic and non-polar compounds and therefore it is used as a mobile phase in chromatographic techniques [97-98]. Therefore, it is expected to dissolve the Eu^{3+} and UO_2^{2+} complexes in this solvent.

1.6.2 UV Cut-off region

Luminescence intensity is directly proportional to the intensity of incident light [99]. Therefore solvent should be optically transparent in the wavelength region where the complex absorbs; otherwise it will absorb the light and cause reduction in luminescence intensity by inner filter effect. Aromatic carboxylic acids absorb radiation in the range of 220-300 nm; hence, solvent absorption should be minimum in this region. Acetonitrile is optically transparent above 200 nm and can be used as a solvent for studying luminescence of metal-ligand complexes. Table 1.1 presents the UV cut off wavelength of some organic solvents here. L_0 is the wavelength where the absorbance for 10 mm path length of the solvent exceeds 0.05 absorbance units (relative to water).

1.6.3 Fluorescing nature of solvent

Some solvents exhibit fluorescence upon photo irradiation. In general, organic solvents do not exhibit fluorescence but some ionic liquids having bulky organic groups do show strong fluorescence. Because of this fluorescence background from solvents of bulky ionic liquids, there will be interference in the luminescence of metal ligand complex [93]. Being a small molecule, acetonitrile does not show any fluorescence.

Owing to all these above properties of solvents, acetonirile was chosen as a solvent to study the luminescence of Eu^{3+} and uranium complexes. Acetonitrile (CH_3CN) is a colorless

Table 1.1 UV cut off wavelength of some organic solvents.

Solvent	**Wavelength L_0 (nm)**
Water	190
Acetonitrile	**200**
DMSO	330
DMF	300
Acetone	340
THF	280
Pyridine	345

Table 1.2 Some physical properties of acetonitrile.

Appearance	**Density ($g\ mL^{-1}$)**	**Boiling point (^0C)**	**Water Solubility**	**Refractive index**	**UV Cut-off (nm)**
Colorless liquid	0.786	81.6	Miscible	1.344	200

liquid. It is used as polar organic solvent in organic synthesis [100]. Some important physical properties of acetonitrile are given in Table 1.2 [101].

1.7 Luminescence lifetime and number of coordinated water molecules

The luminescence lifetime is defined as the average time a molecule spends in the excited state before returning to ground state. For lanthanide and actinide ions, luminescence lifetime ranges from nanoseconds to milliseconds. Knowledge of excited state lifetime of a fluorophore is important for quantitative interpretation of numerous luminescence measurements such as quenching, polarization, characterization of luminescent species etc [99]. It is well known that the luminescence lifetimes of lanthanides and actinides in solution are sensitive to the environment of coordinated sphere of ions. In aqueous medium, as already mentioned, the –OH oscillators quenches the luminescence intensity and luminescence lifetime provides indirectly an approximation regarding this quenching process.

The luminescence lifetime of free Eu^{3+} in aqueous medium is around 110 μs [87]. In case of Eu^{3+} complex, water molecules are replaced by ligand molecules and therefore the luminescence lifetime of Eu^{3+} varies with complexation. The sensitivity of lanthanide ions luminescence towards high energy oscillators such as –OH has been studied in detail and it was observed that luminescence lifetime is proportional to number of water molecules attached to inner coordination sphere of lanthanide ions. Based on experiments, following expressions have been derived empirically to calculate number of water molecules coordinated to lanthanide ion (N_{H2O}) [102]:

$$N_{H2O} = q\,[1/\tau\,(H_2O) - 1/\,\tau\,(D_2O)] \quad \text{--------------- } 1.6$$

where q is a constant and depends on the spectroscopy property of lanthanide ions: 1.05 for Eu^{3+} and 4.2 for Tb^{3+}; $\tau\,(H_2O)$ & $\tau\,(D_2O)$ are the luminescence lifetimes (in ms) of Eu^{3+}/ Tb^{3+} in water and heavy water, respectively. In general, ligands are not as effective as –OH oscillators in causing non-radiative de-excitation and hence, the above equation for calculating number of water molecules can be derived directly from the lifetime measurement in water medium alone [30, 103]. Following equation has been derived empirically for Eu^{3+} ion when it is complexed with a ligand:

$$N_{H2O} (\pm 0.5) = 1.05/\tau (H_2O) - 0.70 \quad \text{--------------} \; 1.7$$

The luminescence lifetime of free UO_2^{2+} in aqueous medium is around 1 μs [26]. Like lanthanides, luminescence lifetime of UO_2^{2+} also increases upon complexation. The lifetime of UO_2^{2+} in its complex with DPA and trimisic acid have been reported to be 7 and 10 μs respectively [50-51]. The decay of UO_2^{2+} luminescence show a very little effect on isotopic substitution as solvent is changed from H_2O to D_2O [81]. As discussed earlier, it has been established that electron transfer mechanism rather than energy transfer is responsible for quenching in case of UO_2^{2+} and hence correlation of life-time with number of water molecule present in the inner coordination sphere of UO_2^{2+} is not possible.

1.8 Motivation of the present work

In the recent past, much attention has been paid on complexation of lanthanides and actinides. Fundamental understanding of the complexation of lanthanides and actinides is necessary in various fields such as synthesis of luminescent materials, solvent extraction, analytical detection etc. In view of ligand sensitized luminescence, it also helps in choosing the efficient ligand for complexation and to enhance the luminescence signal of lanthanide ions. There is a lot of scope in the field of ligand sensitized luminescence studies of lanthanides and actinides and many phenomenons have not been understood thoroughly. One such example is co- luminescence enhancement of metal ions. Many aromatic carboxylic acids sensitize the luminescence of metal ions but do not exhibit co-luminescence and mechanism of this phenomenon is therefore sought off. The other unresolved problem is the sensitization of UO_2^{2+} luminescence. In case of uranium, there are only few ligands which sensitize the luminescence of UO_2^{2+} in aqueous medium. Therefore, there is a thirst to understand the basic mechanism related to ligand sensitized luminescence and co-luminescence of lanthanides and actinides. In earlier work from our group, task specific ionic liquids were synthesized and used to study the luminescence of Eu^{3+} and terbium. A large enhancement in luminescence was noticed using these ionic liquids. Because of highly fluorescing background of ionic liquids terbium luminescence could be seen only after applying gating to detector to avoid ionic liquid fluorescence. Therefore, there is a need to find a fluorescence free medium alternative to ionic liquid to study luminescence of lanthanides and actinides. This prompted us to use non-aqueous solvents to study the luminescence of lanthanide and actinide ions. Acetonitrile is found to be the best, over other solvents and all luminescence studies were carried out in this medium. The motivation of the thesis was of two folds as indicated below:

(i) Luminescence studies of Eu^{3+} with aromatic carboxylic acids in acetonitrile medium

Aromatic carboxylic acids have been widely used for sensitizing the luminescence of lanthanides in aqueous medium. The sensitization takes place by energy transfer from triplet level of the ligand to the low lying lanthanide emitting levels as mentioned earlier; as a result these emitting levels are populated indirectly. Though by this way lanthanide can be excited efficiently, the luminescence intensity of lanthanides which originates as a result of radiative decay depends on the nature of the solvent, eventually. Unfortunately, in aqueous medium lanthanide luminescence is very sensitive towards the high energy –OH oscillators. The problem of quenching due to high energy –OH oscillators can be circumvented by using some synergistic agents such as trioctyl phosphine oxide, organic phosphates etc [41-42]. Apart from using synergistic agents, one can think of non-aqueous solvents to get rid of high energy –OH oscillators.

The reason to study Eu^{3+} complexes in acetonitrile is to see the luminescence efficiency of Eu^{3+} compared to aqueous medium. The ligands chosen in this study are of two types; (i) Ligands which replace one or two water molecules from the first coordination sphere of Eu^{3+}. In this case, we may expect luminescence enhancement due to removal of remaining water molecules by acetonitrile molecules. Also, stoichiometry of these complexes might be different from aqueous medium. (ii) Ligands which replace almost all the water molecules from the inner coordination sphere of Eu^{3+}. These ligands do not exhibit co-luminescence in aqueous medium and therefore co-luminescence studies may be also interesting in acetonitrile medium. Though in these complexes water molecules are not present in inner sphere of Eu^{3+}, non-radiative decay originated from bulk of the solvent is expected to reduce.

(ii) Luminescence studies of UO_2^{2+} with aromatic carboxylic acids in acetonitrile medium

As mentioned above although there are plenty of ligands which enhance the luminescence of lanthanides, only few such as 2,6-pyridine di-carboxylic acid and trimesic acid were found to enhance the luminescence of UO_2^{2+} [50-51]. The reason that UO_2^{2+} luminescence is not sensitized by many of aromatic carboxylate ligands is not fully understood yet. It is believed that presence of water molecules at inner coordination sphere of UO_2^{2+} complexes suppresses the sensitized luminescence. The aim of the present work is to examine the possibility of using acetonitrile medium for enhancing the luminescence intensity of UO_2^{2+} through sensitized process. It is also aimed in this work to understand the mechanism the luminescence enhancement of UO_2^{2+}.

With this in view, luminescence of UO_2^{2+} complexes with different aromatic carboxylic acids have been examined in acetonitrile medium. The aromatic carboxylic acids used for UO_2^{2+} complexation are of two type (i) ligands which do not enhance the luminescence of

UO_2^{2+} in aqueous medium; using acetonitrile medium can help in sensitizing the UO_2^{2+} luminescence. (ii) Ligands which sensitize the luminescence of UO_2^{2+} in aqueous medium; Further luminescence enhancement due to removal of bulk water molecules by acetonitrile molecule can be expected.

1.9 Scope of the present work

In this work, luminescence and co-luminescence from Eu^{3+} and UO_2^{2+} complexed with some aromatic carboxylic acids has been studied in acetonitrile medium. Earlier from our group it has been shown that aromatic carboxylic acids serve as excellent ligands for the sensitization and enhancement of lanthanide luminescence in the aqueous medium [41-45], which prompted us to use these ligands in acetonitrile medium. In this work, six ligands have been used to examine the Eu^{3+} and UO_2^{2+} luminescence. Ligands used in this study can be categorized in two classes-

A. Benzoate and methyl substituted benzoates: All of these ligands have been shown to exhibit ligand sensitized luminescence of lanthanides in aqueous medium. But these ligands do not enhance the luminescence of UO_2^{2+} in aqueous medium. Following were the ligands used in this category-

- Benzoic acid (BA)
- *o*- toluic acid (*o*-TA)
- *m*- toluic acid (*m*-TA)
- *p*- toluic acid (*p*-TA)

B. Pyridine based aromatic carboxylates: Following were the ligands used in this category-

- Pyridine -2- carboxylic acid or Picolinic acid (PA)
- Pyridine-2,6- dicarboxylic acid or Dipicolinic acid (DPA)

These two ligands sensitize the luminescence of lanthanides in aqueous medium but luminescence of UO_2^{2+} is sensitized only by dipicolinic acid in aqueous medium.

The outline of thesis is as follows-

Chapter 1: This chapter discusses about the fundamentals of ligand sensitized luminescence, literature on luminescence of Eu^{3+} and UO_2^{2+} in aqueous medium as well as non-aqueous medium.

Chapter 2: This chapter consists of the details of experimental techniques used for the research such as spectrofluorimeter, UV-Vis spectrophotometer. Calculation of triplet level energies of all the ligands by recording the phosphorescence spectra of these ligands at liquid nitrogen temperature is also discussed here.

Chapter 3: This chapter discusses both the luminescence enhancement and characterization of the Eu^{3+} complex using benzoate and methyl substituted benzoate as ligands in acetonitrile medium.

Chapter 4: In this chapter study of UO_2^{2+} luminescence has been carried out in acetonitrile medium using benzoate and methyl substituted benzoate as ligands. A comparison on luminescence studies has been made in water and acetonitrile medium. Mechanism of ligand sensitized luminescence has been presented. Structure of the UO_2^{2+} complexes has been investigated by UV-Vis spectroscopy.

Chapter 5: This chapter describes the detailed luminescence studies of Eu^{3+} using picolinic acid and dipicolinic acid as ligands in acetonitrile medium. Mechanism of co-luminescence enhancement of Eu^{3+} with dipicolinic acid has been discussed.

Chapter 6: This chapter describes the luminescence studies of UO_2^{2+} using picolinic acid and dipicolinic acid as ligands in acetonitrile medium. Structure of the UO_2^{2+} complexes with both the ligands has been presented in this chapter. Mechanism of co-luminescence enhancement of UO_2^{2+} with dipicolinic acid has been discussed.

Chapter 7: This chapter presents a summary of all the works discussed in preceding chapters. This concluding chapter also discusses the future perspectives which stem out from this research work.

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CHAPTER 2 EXPERIMENTAL

2.1 Introduction

This chapter describes the experimental details employed in this study. This will cover experimental aspects of both the luminescence and lifetime measurements of complexes. The details of the instruments used in this study are given in this chapter. The procedure to record the phosphorescence spectra in order to calculate triplet energy of various ligands employed in this study is also presented.

2.2 Spectrofluorimeter

Luminescence measurements were recorded using a FLS920 spectrofluorimeter (Edinburgh Instruments Ltd., UK). It enables to record both steady state and lifetime measurements. Figure 2.1 shows the photograph of the spectrofluorimeter employed for luminescence experiments. It consists of light sources i.e. Xenon lamp (A) for continuous mode luminescence measurements, microsecond Xenon flashlamp (B) for lifetime measurements, excitation monochromator (C), sample chamber (D), emission monochromator (E) and a photomultiplier tube detector (F). The description of each component of the fluorimeter and the data acquisition details are discussed below.

2.2.1 Excitation sources - Xenon lamp and Microsecond flashlamp

The most commonly used excitation source for luminescence measurements is the high-pressure Xenon arc light source. The Edinburgh FLS920 spectrofluorimeter system consists of a 450 W Xenon lamp (Xe900) mounted in an air cooled lamp housing with a built in de-ozoniser filter. The lamp orientation is adjustable in two orthogonal planes for alignment. The ozone free Xe arc lamp emits a continuous radiation from 190 to 2600 nm. The emitted light from the lamp is focused onto the slit of the excitation monochromator using an adjustable lens system.

Lifetime measurements were recorded using a microsecond flash lamp (μF920H) for sample excitation. The μF920H is a pulsed 60 W Xenon microsecond flash lamp producing typically 1.5 μs, high irradiance optical pulses at repetition rates up to 100 Hz. This microsecond flashlamp was operated at a repetition rate of 20-100 Hz for all temporal decay measurements.

2.2.2 Monochromators

The spectrofluorimeter has an excitation monochromator and an emission monochromator. Both the excitation (TMS-X300) and emission (TMS-M300) monochromator used in this fluorimeter are of the Czerny-Turner configuration with 300 mm focal length and a high optical throughput (f/4.2). The standard grating in the instrument has 1800 l/mm. The monochromators have a wavelength accuracy and resolution of ±0.2 nm and 0.05 nm, respectively. The monochromators have computer controlled slits which are adjustable up to 15 mm. For steady state measurements, the band pass for the excitation and emission monochromators were set at 3 nm. Excitation spectrum was recorded by fixing the emission wavelength and scanning the excitation monochromator over the wavelength range of interest. The emission spectrum was recorded by exciting the sample at appropriate excitation wavelength and the emission intensity was recorded as a function of wavelength. In the acquisition of excitation and emission spectrum, the step size of scan was fixed at 1 nm and the dwell time (dwell period at each wavelength) was set at 0.3 s. Suitable long wavelength pass filters 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 falling into the emission monochromator.

2.2.3 Detector

The detector used in the spectrofluorimeter consisted of a red sensitive S900-R (Hamamatsu, Model R928P) photomultiplier tube (PMT). The PMT detection system

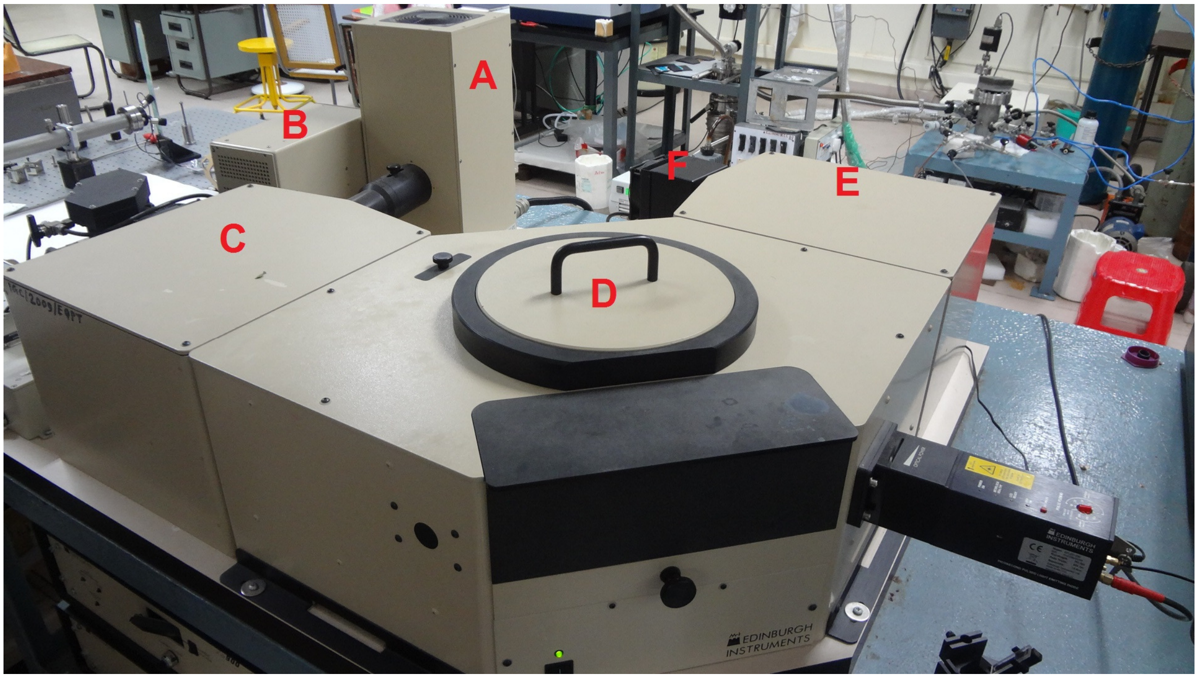


Figure 2.1 Photograph showing the spectrofluorimeter.

A - Xenon arc lamp source

B - Microsecond flashlamp source

C - Excitation monochromator

D - Sample chamber

E - Emission monochromator

F - Detector

operates in a single photon counting mode (as used in lifetime measurements) with very high amplification and very low dark noise level (< 50 cps at -20°C). This photon counting mode uses a pulse height discriminator to separate the signal pulses from the noise pulses, enabling high-precision measurement compared to the analog mode (as used in steady state measurements). The typical response ranges for photomultiplier tube is 160 to 870 nm. The red sensitive detector is operated with a peltier cooled housing at -20 °C to -30 °C and thus the detector was cooled for 30 minutes prior to acquisition to get low dark count rate.

2.2.4 Data acquisition for time resolved luminescence

The spectrometer incorporated single photon counting technology in the form of the PCS900 computer plug-in card. Time resolved single photon counting detection is made using the Multi-Channel Scaling (MCS) mode of the PCS900 card. In this, the photons are counted in a time window, which sweeps across the full time range following each excitation pulse, creating a histogram of counts versus time.

2.2.5 Luminescence lifetime data analysis

Decay curve analysis is crucial for time-resolved luminescence measurements. An exponential decay process is expressed in mathematical form as:

$$R(t) = A + \sum_{i=1}^{n} B_i \, e\,(-t / \tau_i) \quad \text{---------------} \; 2.1$$

In this equation, R(t) is the sample decay model with pre-exponential factors B_i, the characteristic lifetimes τ_i, and an additional background A. The pre-exponential factors B_i are values which include instrumental and sample parameters. The characteristic lifetime τ_i, is the time at which the intensity decreases to 1/e of the intensity at t = 0. The numerical procedure based on Marquardt-Levenberg algorithm produces the best lifetime parameters, along with the standard deviation for each of the fit parameters. The reduced chi-square ($\mathcal{X}^2$) is the fit quality parameter which is obtained by normalizing chi-square by degree of fredom. The $\mathcal{X}^2$ has the theoretical limit of 1.0 for data having a Poisson distribution ($w_k = 1 / \sqrt{F_k}$); w_k is the weighting factor for each data point (F_k). $\mathcal{X}^2$ values close to 1.0 indicate a good fit. Weighted residuals are another important means of determining the goodness of fit. For a good fit, weighted residuals should be randomly distributed around zero among the data channels.

The F900 software offers two fitting routines; 'Tail Fit' and 'Reconvolution Fit'. The two fitting procedure matches the theoretical sample response to the raw data, to obtain the best lifetime data. In the Tail Fit routine, the analysis fit is applied to a channel range when the exciting light pulse has diminished. Tail fit routine is thus used to fit the profile of samples with long decay times. The Reconvolution Fit procedure eliminates both the noise and the effects of the exciting light pulse and thus this is used for the analysis of short lifetime measurements. Since the temporal profile of the pulsed source was around 1.5 μs, lifetimes that were of this order of magnitude were determined after correcting the instrument response function before fitting.

In all cases of lifetime measurements used in this study, single or bi-exponential fit was found to be adequate and tail fit was done using the fit routine. The relative standard deviation in the lifetime values was found to be less than 5%.

2.2.6 Sample holders

The standard sample holder for the spectrofluorimeter consists of a single cuvette holder with filter retainer in 90° emission collection geometry. In all cases studied here, the luminescence measurements were recorded using standard cuvette at room temperature having path length of 2 mm.

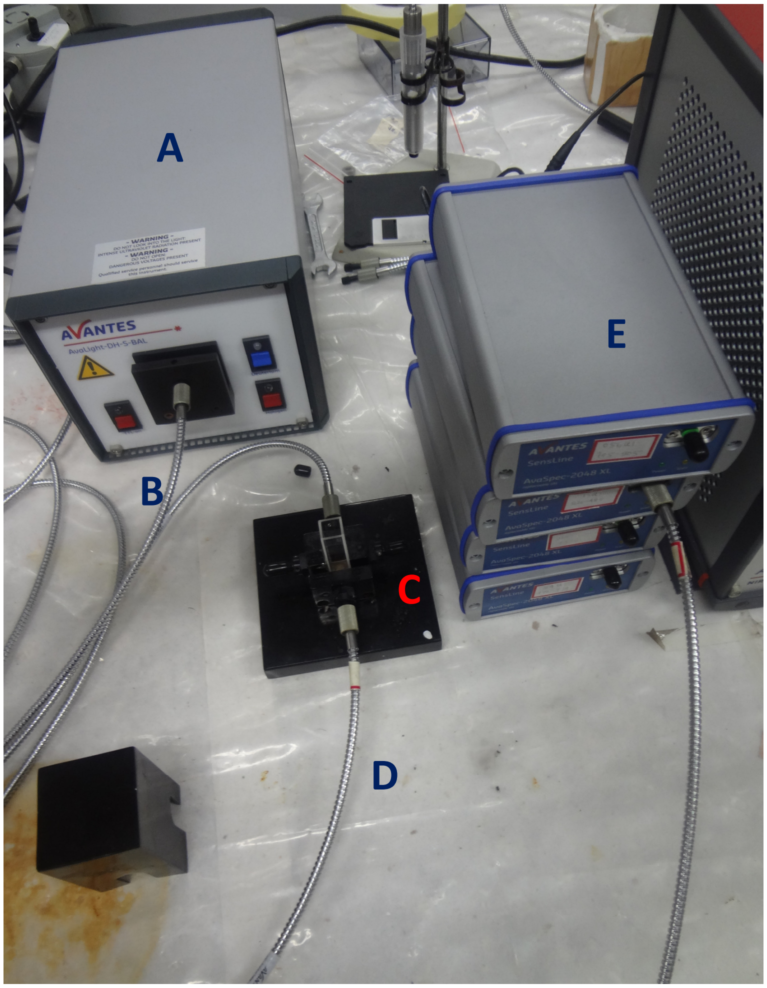


Figure 2.2 Photograph showing the Fibre optic spectrophotometer:

A - Lamp source

B – Fibre optic cable connecting source and sample compartment

C – Cuvette holder

D - Fibre optic cable connecting sample compartment and detector

E – Spectrometer

2.3 Spectrophotometer

UV-Vis absorption spectra were recorded using M/s Avantes fiber optic absorption spectrophotometer, model AvaSpec-2048 with 300 lines per mm grating and 2048 pixel CCD array detector. Figure 2.2 shows the photograph of the spectrophotometer employed in our experiments. It consists of light sources i.e. Deuterium / Tungsten lamp (A), fibre optic cables for transmitting incident light (B), Cuvette holder (C), fibre optic cables for light collection (D) and spectrometer (E). Around 20 spectra were averaged to improve the signal to noise ratio. Cuvette of 10 mm path length was used to record the UV-Vis absorption spectra.

2.4 Phosphorescence spectra of ligands

Phosphorescence is generally not observed in liquid phase at room temperature because radiationless transition occurring via collisions dominates at room temperature [1]. Therefore, in order to avoid radiationless transitions, phosphorescence spectra are observed in a rigid matrix at low temperature [1-2]. Phosphorescence spectra of molecules represent the excited state characteristics and therefore different aromatic carboxylic acid ligands show different phosphorescence emission bands; thus the excited triplet state energies of these ligands can be determined from their phosphorescence spectra. In the present study, the low temperature phosphorescence spectra of the aromatic carboxylic acids were measured in liquid nitrogen atmosphere (77 K) and the triplet state energy of these ligands were determined based on the maximum phosphorescence band.

Liquid nitrogen quartz Dewar was used to record the phosphorescence spectra of ligands. A quartz sample tube containing around 0.5 ml of sample was immersed into the nitrogen dewar containing liquid nitrogen thereby cooling the sample to 77 K. Figure 2.3 (a) shows the pictorial representation of dewar housing and Figure 2.3 (b & c) show the photograph of the liquid nitrogen dewar along with quartz tube employed in experiments for

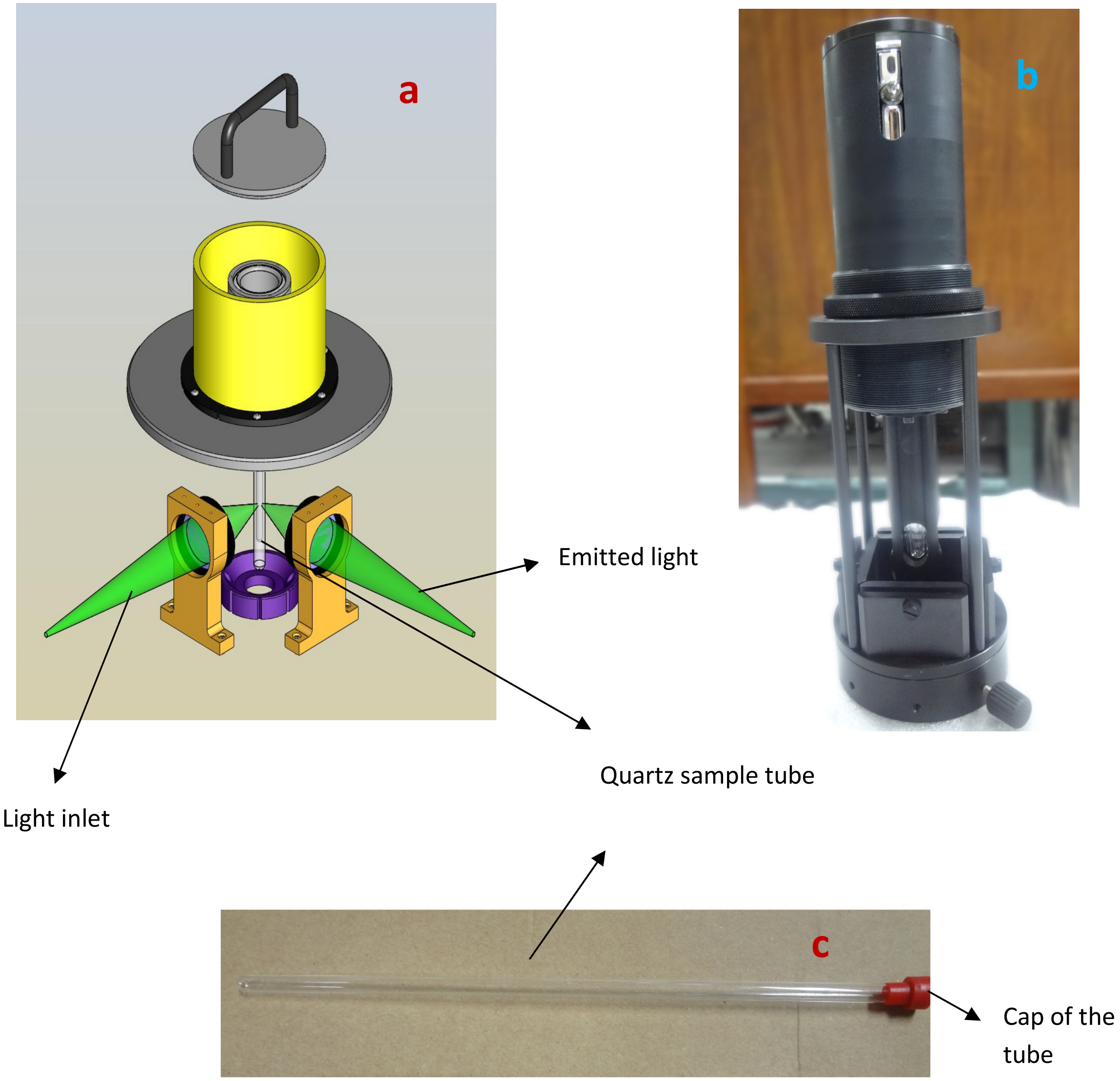


Figure 2.3 (a) The pictorial representation of quartz Dewar housing (b) Photograph of original Dewar (c) Photograph of quartz sample tube.

recording the phosphorescence spectra. Since there may be little variation in triplet energies of pure ligand and ligand complexed with metal ion, gadolinium complexes of these ligands were selected as model complex for recording the phosphorescence spectra. Gadolinium having high energy emitting levels which cannot be sensitized by ligands and also it helps in enhancing the intersystem crossing yield of ligands. For determining the triplet energy, complexes of these ligands with gadolinium were dissolved in acetonitrile. In order to determine triplet energies of ligands in aqueous medium, complexes of these ligands (concentration = $2x10^{-4}$ M) were dissolved in 50:50 mixture of water and ethanol. Aqueous solution of complexes freezes with the introduction of cracks and unclear matrix which results in scattering of light and hence addition of ethanol in aqueous solution helps in making clear rigid matrix at 77 K [3].

Figure 2.4 shows the phosphorescence spectra of benzoic and methyl substituted benzoic acids at 77 K in acetonitrile medium. Similar phosphorescence spectra for pyridine based carboxylic acids in acetonitrile medium are shown in Figure 2.5. Table 2.1 presents the triplet energies of various ligands calculated from the phosphorescence spectra in acetonitrile medium and for comparison triplet energies calculated in aqueous medium are also shown (though spectra in aqueous have not shown). It can be seen from the Table that triplet energies of ligands are slightly higher in aqueous than in acetonitrile medium. The variation in triplet energies in two different solvents may be due to the difference in the hydrogen bond interaction between ligands and solvent. Similar difference was observed for the Pybox ligand studied by Dias *et al.* where the triplet energy was found to be 26200 cm^{-1}, little lower in acetonitrile medium compared to 26700 cm^{-1} in aqueous medium [4]. The energy differences between the triplet energy levels of different carboxylic acids and the lowest emitting energy levels of Eu^{3+} (17250 cm^{-1}) & UO_2^{2+} (22000 cm^{-1}) is calculated and shown in Table 2.2. As all the luminescence experiments of metal-ligand complexes were carried out at

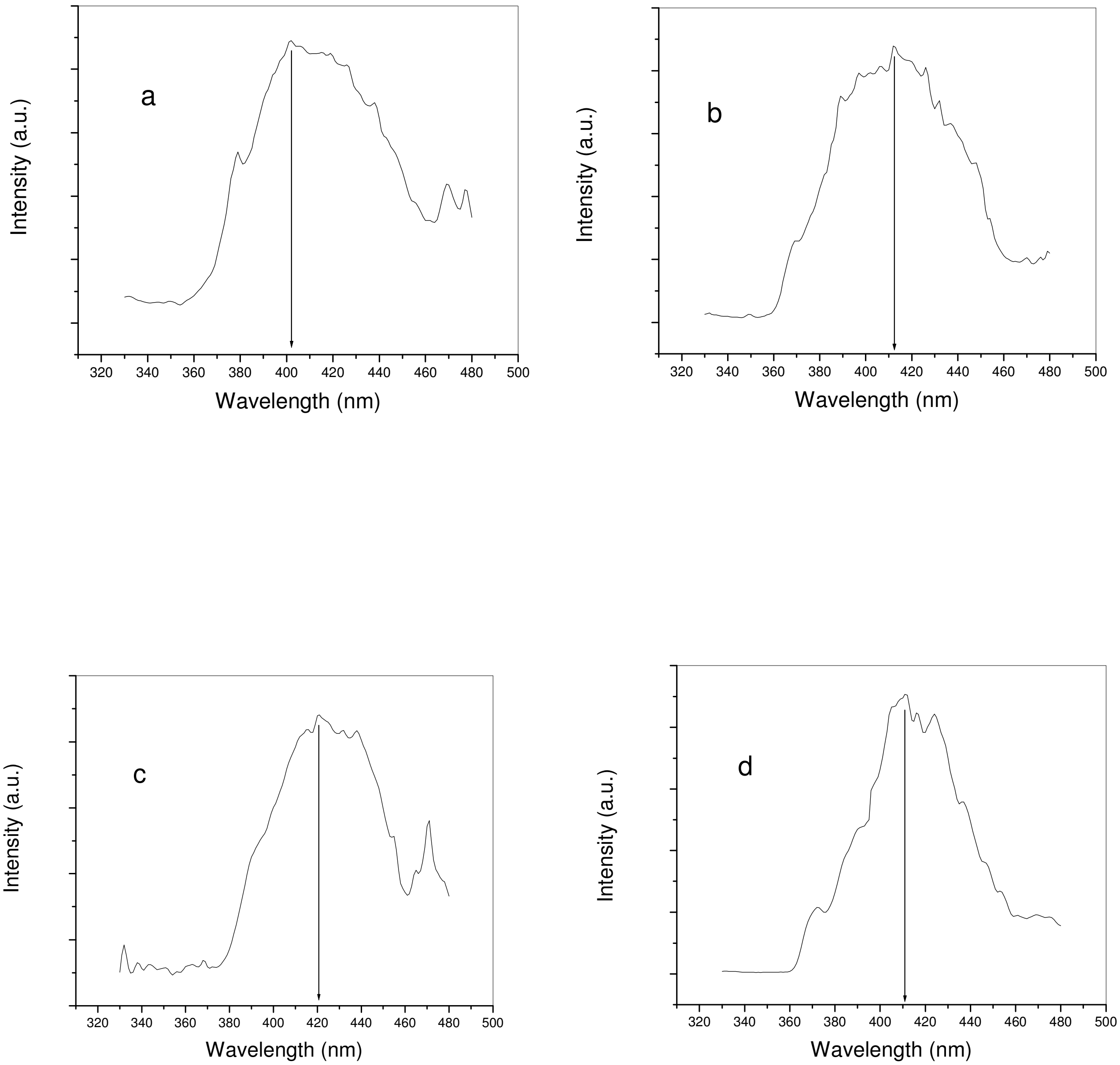
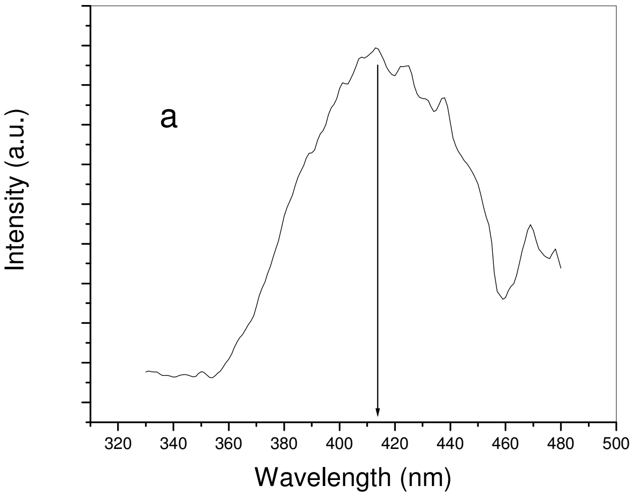


Figure 2.4 Phosphorescence spectra of benzoic acid and methyl substituted benzoic acids measured at 77 K; (a) benzoic acid (b) *o* toluic acid (c) *m* toluic acid (d) *p* toluic acid. Peak wavelengths which were taken for calculating triplet energies are shown by arrow.



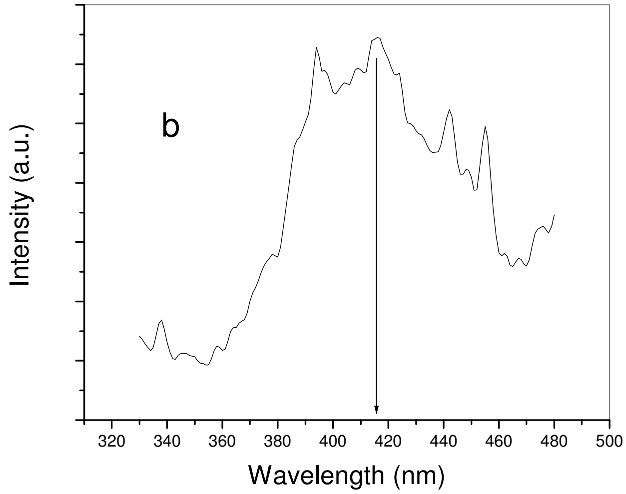


Figure 2.5 Phosphorescence spectra of pyridine based carboxylic acids at 77 K; (a) picolinic acid (b) dipicolinic acid. Peak wavelengths which were taken for calculating triplet energies are shown by arrow.

Table 2.1 The phosphorescence spectra data of different ligands used in this study.

Ligand	**Triplet energy in acetonitrile (cm^{-1})**	**Triplet energy in aqueous (cm^{-1})**
Benzoic acid	24938	25000
o toluic acid	24270	25060
m toluic acid	23810	24330
p toluic acid	24330	24570
Picolinic acid	24213	24570
Dipicolinic acid	24040	24450

Table 2.2 Energy difference between the triplet levels of ligands and lowest emitting level of metal ions.

Ligand	**ΔE (Eu^{3+}) (cm^{-1})**	**ΔE (UO_2^{2+}) (cm^{-1})**
Benzoic acid	7688	2938
o toluic acid	7020	2270
m toluic acid	6560	1810
p toluic acid	7080	2330
Picolinic acid	6963	2213
Dipicolinic acid	6790	2040

room temperature and this energy difference in both cases is very much higher than the room temperature energy i.e. 200 cm^{-1}, the possibility of back energy transfer can be neglected. From these energy differences, it can be concluded that all these ligands can transfer the energy to both the metal ions effectively in acetonitrile medium.

2.5 Reagents and Chemicals

Standard aqueous stock solution of Eu^{3+} and UO_2^{2+} was prepared from their per chlorate solutions. Europium perchlorate was prepared from europium oxide powder (Indian Rare Earth Limited, India, Purity 99.99 %) by dissolving it in perchloric acid (Sigma make) and then evaporated to dryness. The residue was then dissolved in 0.1 M perchloric acid/acetonitrile to get the stock solution of Eu^{3+} in water and acetonitrile, respectively. Uranyl perchlorate solution was prepared from UO_2 powder (Nuclear Fuel Complex, India, Purity 99.9 %). 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 the respective solution of 10^{-1} M UO_2^{2+}. The aqueous solution was acidified with a few drops of 1M perchloric acid.

Stock solutions of ligands (Sigma make) were prepared by dissolving the required amount in water. To ensure dissolution of the ligands, in some cases little amount of NaOH was also added. pH of the aqueous solutions was adjusted to a desired value by the addition of sodium hydroxide / perchloric acid. Ionic strength of the aqueous solutions was adjusted by sodium perchlorate (99.99 % Sigma make). Acetonitrile 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 MΩ) obtained from a Milli-Q (Millipore) system was used for preparing all solutions.

2.6 Preparation of Eu^{3+}-ligand complexes in acetonitrile

Eu^{3+}-ligand complexes were prepared in water at different pH by mixing the required amount of ligands and Eu^{3+} solution from their stocks. The ionic strength of this solution was adjusted to 0.1 M using $NaClO_4$. 5 μL of this solution was then mixed with 0.5 mL of acetonitrile. This resulting solution was transferred to the sample cell and the luminescent spectra recorded.

However to record the absorption spectra of Eu^{3+}-ligand complex in acetonitrile medium, 15 μL of aqueous ligand solution of desired concentration and required amount of Eu^{3+} ion (from acetonitrile stock) were added to 1.5 mL of acetonitrile.

2.7 Preparation of UO_2^{2+} and UO_2^{2+}-ligand complexes in acetonitrile

Aqueous UO_2^{2+} solutions of different concentrations were prepared from the 10^{-1} M UO_2^{2+} (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 UO_2^{2+}-ligand complexes at different pH were prepared by mixing the required amount of ligand and UO_2^{2+} (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, ligand solutions of different concentrations were prepared at desired pH and the ionic strength of the solution was kept constant at 0.1 M. 20 μL of each of these solutions along with desired concentration of UO_2^{2+} (acetonitrile) stock solution was taken in a 2 mL vial and the volume was made up with acetonitrile.

All the above working solutions were mixed thoroughly by shaking manually. In all our above experiments (absorbance and luminescence), in acetonitrile medium, about 1% water was present to begin with.

It must be noted that exactly identical instrument settings such as slit widths, step sizes and dwell times have been used in all the experiments used for comparative studies.

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CHAPTER 3 Luminescence studies on Eu^{3+}-benzoate & Eu^{3+}-toluates systems

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3.1 Introduction

Due to their large molar extinction coefficient and efficient binding nature, aromatic carboxylic acid served as a promising complexing agent for enhancing the luminescence of lanthanides in aqueous medium. Depending on the ligand structure, lanthanides make complexes with these ligands having different stoichiometry [1-4]. As a result of complexation, water molecules from the inner coordination sphere of the metal ion are removed. Generally, due to limited stoichiometry, removal of all the water molecules by mono-dentate ligands such as benzoic acid from the inner coordination sphere of lanthanides is not seen in aqueous medium. Aromatic carboxylic acids such as benzoate and terepthalate replace one water molecule, whereas phthalate replaces two water molecules from the inner coordination sphere of lanthanides [4]. Therefore –OH oscillators of remaining water molecules present in the inner coordination sphere of lanthanides still contribute to non-radiative decay in aqueous medium. These non-radiative decays via vibronic coupling with the vibrational states of –OH oscillators can be reduced when water is replaced by non-aqueous solvent such as ionic liquids [5-12]. Therefore, study of lanthanides luminescence in non-aqueous medium was of particular interest.

There are reports on luminescence studies of lanthanides in ionic liquids and some other non-aqueous medium [10-13]. Lunstroot *et al.* have studied diketonate and dipicolinate complexes of samarium in ionic liquid and acetonitrile medium [10]. High quantum yields of these complexes were observed in these solvents. The studies carried out by Hopkins *et al.* showed that spectroscopy of Eu^{3+}-picolinate complex was unaffected in imidazolium ionic liquids [12]. Recently, Shyamala *et al.* synthesized task specific ionic liquids and studied the luminescence of $Eu^{3+}$and Tb^{3+} in these ionic liquids [11,13]. In her study, different aromatic carboxylates were used as anion counter parts in synthesizing imidazolium cation based ionic liquids and Eu^{3+} and Tb^{3+} were detected at nano molar levels; but no efforts were made to study the complexation of lanthanides in these ionic liquids. Although lanthanide luminescence is widely studied in non-aqueous medium towards basic spectroscopic properties and analytical applications, reports are scarcely available about the complexation behavior.

Lanthanide luminescence sensitized by benzoate ligand in aqueous medium has been studied by Peter *et al.* [14]. They studied the ligand sensitized luminescence of Eu^{3+} using benzoate as a ligand and TOPO as synergistic agent in aqueous solutions and observed three orders enhancement of Eu^{3+} luminescence. This chapter of the thesis describes luminescence studies of Eu^{3+}-benzoate (Eu^{3+}-BA) carried out in acetonitrile medium. Compared to aqueous medium, about four orders of luminescence enhancement is observed for Eu^{3+} in acetonitrile medium with benzoate as a ligand. In addition, contrary to aqueous medium where Eu^{3+} forms 1:1 and 1:2 complexes with benzoate ion [4], a 1:3 type complex, which is highly luminescent, is formed in acetonitrile medium. The stability constant of the complex is determined using luminescence and UV-Vis data. This chapter also presents the effect of water on the luminescence and absorbance of Eu^{3+}-BA complex in acetonitrile. In order to see the effect of methyl group, Eu^{3+} complexed with ortho, meta & para toluates and its luminescence is also studied and the results are compared with Eu^{3+}-BA and presented in this chapter.

3.2 Results and discussion

3.2.1 Luminescence enhancement studies of Eu^{3+}-BA

To begin with, luminescence intensity of complexed Eu^{3+} ($1x10^{-5}$ M) in acetonitrile was measured as a function of BA concentration and pH of the solution. Maximum luminescence intensity was found over $3x10^{-4}$-$7x10^{-4}$ M of BA concentration and at pH 4.5. Therefore, in the luminescence enhancement studies, concentration of BA and pH of the solution was maintained at $5x10^{-4}$ M and 4.5, respectively. The excitation and emission spectra of Eu^{3+} species recorded in different medium are shown in Figure 3.1 and Figure 3.2, respectively. The excitation and emission spectra of Eu^{3+}-BA recorded in acetonitrile are shown in Figure 3.1c and 3.2c, respectively. For comparison, spectra recorded for uncomplexed Eu^{3+} (Figure 3.1a and 3.2a) and Eu^{3+}-BA complex (Figure 3.1b and 3.2b) in aqueous are shown in the same Figure. The uncomplexed Eu^{3+} refers to Eu^{3+}-aqua complex without any ligand. The excitation wavelengths are selected so as to get maximum luminescence intensity. The excitation spectrum of uncomplexed Eu^{3+}, monitoring the strongest emission peak at 592 nm, shows a sharp intense peak at 394 nm and it is due to the $^7F_0$-$^5L_6$ transition. This excitation spectrum agrees well with the absorption spectrum of Eu^{3+} in aqueous medium [15]. The luminescence peak positions at 592 and 615 nm (Figure 3.2) are due to the transitions $^5D_0$ - $^7F_1$ and $^5D_0$ - $^7F_2$, respectively and are well reported in literature [15-17]. Despite the fact that emission spectra shown in Figure 3.2 have similar spectral characteristics (except for relative intensities of the two peaks, which will be discussed later), the excitation spectrum for Eu^{3+}-BA (Figure 3.1b and c) system is entirely different from that observed for the uncomplexed Eu^{3+} (Figure 3.1a), pointing to different absorbing species in these two experiments. The excitation spectrum shown in Figure 3.1c observed for Eu^{3+}-BA in acetonitrile resembles that of Eu^{3+}-BA in aqueous medium (Figure 3.1b). In earlier luminescence studies carried out by Peter *et al.* [14], it has been shown that in aqueous Eu^{3+}-BA system, the benzoate is the absorber, which then sensitizes the luminescence of Eu^{3+}. Therefore, it indicates that in acetonitrile medium also, benzoate sensitizes Eu^{3+} luminescence. Although the concentration of Eu^{3+} in Eu^{3+}-BA complexes in

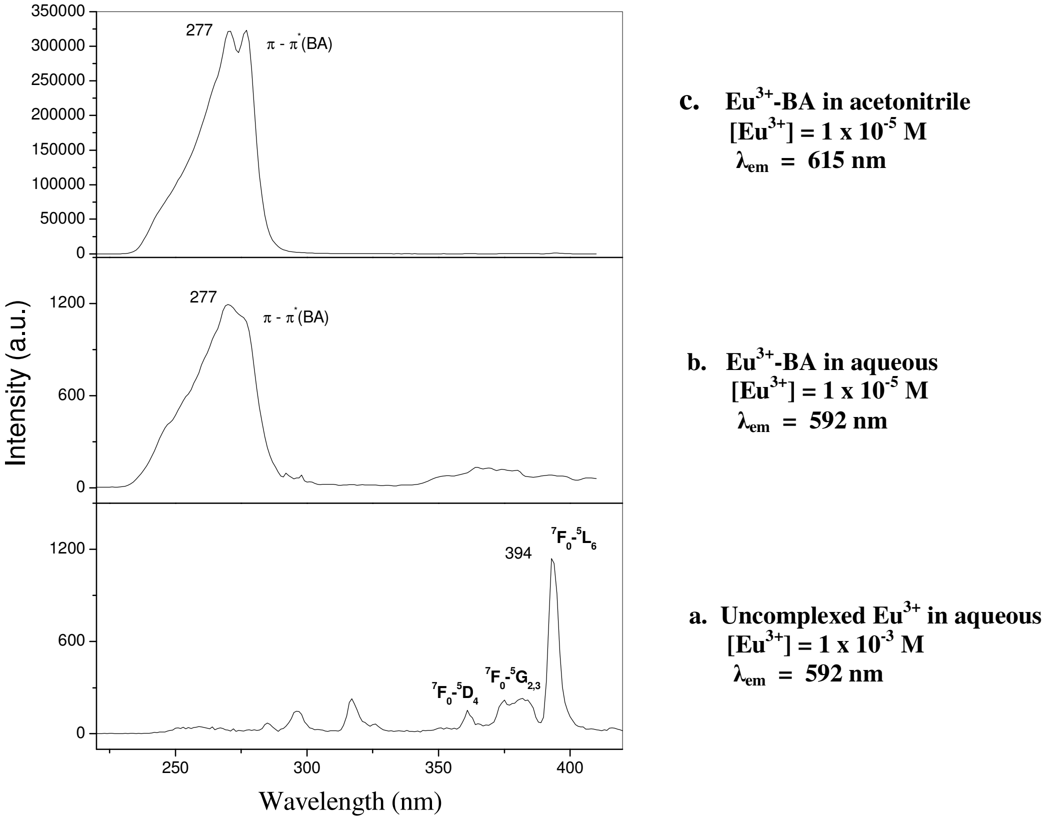

Figure 3.1 Excitation spectra of (a) Uncomplexed Eu^{3+} ($1x10^{-3}$ M) in aqueous (b) Eu^{3+} ($1x10^{-5}$ M)-BA ($5.0x10^{-4}$ M) at pH 6.0 in aqueous (c) Eu^{3+} ($1x10^{-5}$ M)-BA ($5x10^{-4}$ M) at pH 4.5 in acetonitrile. The emission wavelength used to record each of the spectra is shown alongside.

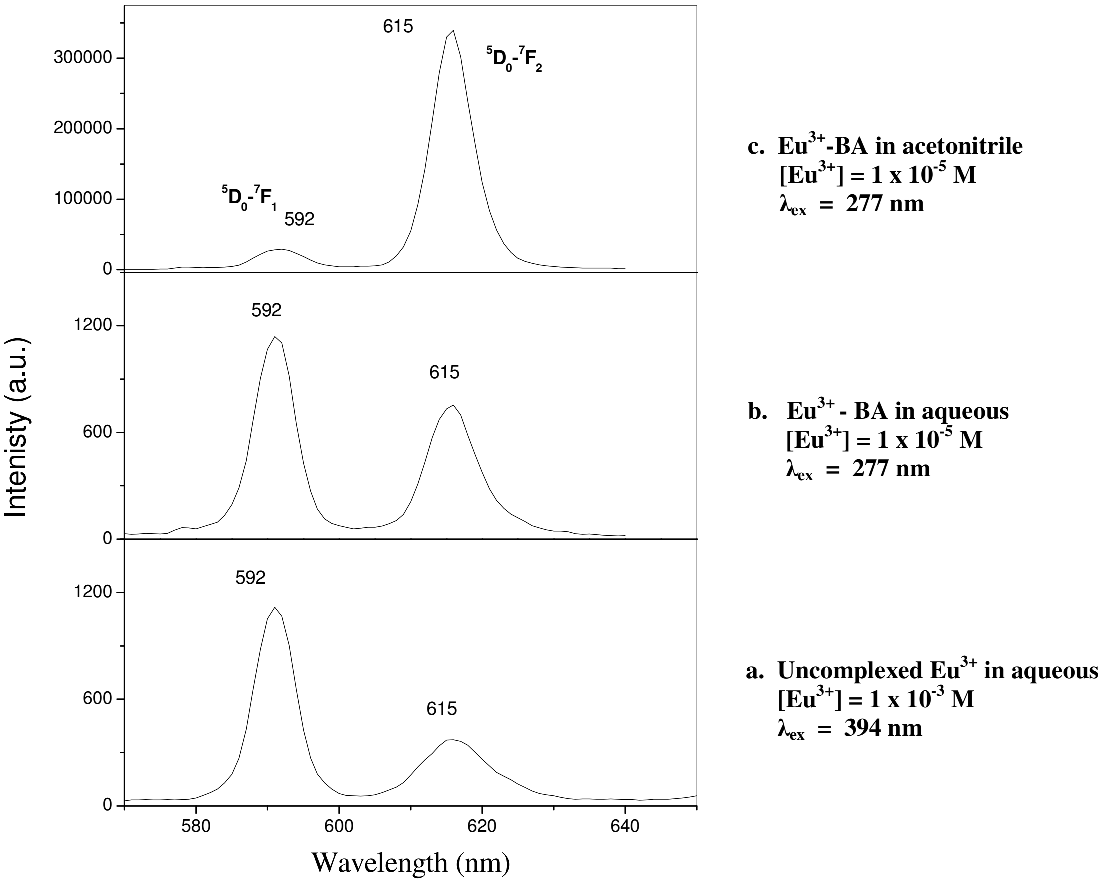

Figure 3.2 Luminescence spectra of (a) Uncomplexed Eu^{3+} (1x10^{-3}M) in aqueous (b) Eu^{3+} (1x10^{-5} M)-BA (5x10^{-4} M) at pH 6.0 in aqueous (c) Eu^{3+} (1x10^{-5} M)-BA (5x10^{-4} M) at pH 4.5 in acetonitrile. The excitation wavelength used to record each of the spectra is shown alongside.

aqueous and acetonitrile medium (Figure 3.2b and Figure 3.2c) is the same, the large intensity for later, reflects a huge enhancement in the luminescence of Eu^{3+}-BA in acetonitrile compared to the same in aqueous medium.

Table 3.1 gives the luminescence enhancement of Eu^{3+} in its complexes. Enhancement factor (EF), given in Table 3.1 is calculated as the ratio of Eu^{3+} concentrations that gave the same luminescence intensity in uncomplexed Eu^{3+} to that of Eu^{3+}-BA complex. The luminescence intensities of the stronger peaks between 592 and 615 nm are used in calculating EF. For example, the EF of Eu^{3+}-BA in aqueous is 100 (Table 3.1), which implies that the Eu^{3+} concentration in the Eu^{3+}-BA in aqueous medium is 100 times smaller than that of uncomplexed Eu^{3+} and show the same Eu^{3+} luminescence intensity as in uncomplexed. The enhancement factor for Eu^{3+}-BA in acetonitrile medium is 32000 which is more than two orders high compared to enhancement factor for Eu^{3+}-BA in water (100). This huge increase in the luminescent enhancement cannot be explained just based on the reduction of non-radiative decay process because acetonitrile is a poor coordinating solvent and hence cannot replace the water from the inner co-ordination sphere. Hence, the enhancement in luminescent intensity should be due to ligand sensitization only.

The measurement of luminescence lifetimes of Eu^{3+} ions in its complexes has been carried out, as this data can provide the extent of non-radiative processes in these complexes. Figure 3.3 shows the decay profile of uncomplexed Eu^{3+} in aqueous (Figure 3.3a) and acetonitrile medium (Figure 3.3b) and which seems to be similar in both solvents. Table 3.1 presents the values of lifetimes of Eu^{3+} luminescence measured for various systems. The luminescence lifetimes of uncomplexed Eu^{3+} in water and acetonitrile are nearly same, namely 110 and 120 μs. This indicates that being a poor coordinating solvent, acetonitrile hardly replace water molecules from the inner coordination sphere of Eu^{3+}. Figure 3.4 shows the decay profile of Eu^{3+}-BA in aqueous (Figure 3.4a) and acetonitrile (Figure 3.4b) medium.

Table 3.1 Lifetime (τ), Enhancement factor (EF) and asymmetry ratio (R) for Eu^{3+} ion in different systems.

Systems	Lifetime (τ) in μs, S.D. = ± 5%	Enhancement factor (EF)	Asymmetry Ratio (R)*
Eu^{3+} (aqueous)	110	1	0.4
Eu^{3+} (acetonitrile)	120	1.1	0.5
Eu^{3+}-BA (aqueous)	118	100	0.8
Eu^{3+}-BA (acetonitrile)	900	32000	13.2

* calculated as the ratio of the areas of the 615 and 592 nm peaks

The lifetime of Eu^{3+}-BA in water is 118 μs, which is comparable to the lifetime of 110 μs for uncomplexed Eu^{3+} in aqueous medium. Even though the benzoate complex in aqueous medium yields significant enhancement of the Eu^{3+} luminescence, only a marginal increase in lifetime upon complexation is observed. The luminescence lifetime of Eu^{3+} in the Eu^{3+}-BA in acetonitrile medium was, on the contrary, considerably longer, 900 μs, clearly indicating strong reduction in the rates of non-radiative processes in the acetonitrile medium. The reduction in nonradiative decay channels is due to removal of water molecules from the inner sphere of Eu^{3+} ion upon complexation.

Information regarding the symmetry for Eu^{3+} nearest surroundings can be obtained from the asymmetry ratio, R (ratio of the integral intensities at 615 nm to that of 592 nm). It has been established for Eu^{3+} that the transition $^5D_0$ - $^7F_1$ (592 nm) is primarily magnetic dipole in nature and weakly dependent on the crystal field effect, while the transition $^5D_0$ - $^7F_2$ (615 nm) is electric dipole in nature and strongly dependent on the crystal field [15]. The extreme sensitivity of the $^5D_0$ - $^7F_2$ peak to the Eu^{3+} coordination environment makes this a hypersensitive transition. The value of R therefore can be used for qualitative comparisons of the degree of distortion of the Eu^{3+} nearest surroundings in various complexes. The values of R calculated for various systems are given in Table 3.1. It can be seen from this Table that the value of R for the uncomplexed Eu^{3+} is the lowest (R=0.4), in agreement with literature [16], increases to 0.8 for Eu^{3+}-BA in aqueous but increases significantly (R=13.2) for the Eu^{3+}-BA complex in acetonitrile medium. Though large values of R are not common for Eu^{3+} - aromatic carboxylate complexes, similar large values of R have been reported in literature for various beta diketonate tris complexes of Eu^{3+} [17-18]. This large R value obtained for Eu^{3+}-BA system in acetonitrile clearly indicates that the coordination environment of Eu^{3+} ion is entirely different from the one expected to be present in aqueous medium. Longer lifetime (900 μs) of Eu^{3+}-BA system in acetonitrile corroborates the fact that a less hydrated

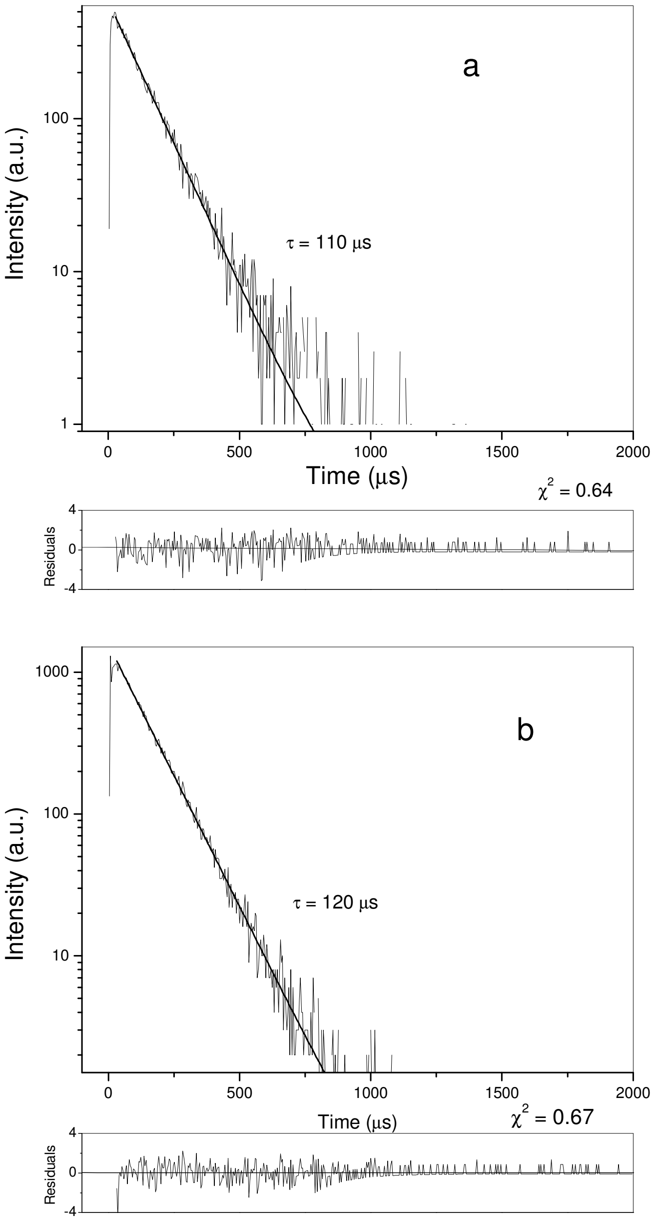

Figure 3.3 Luminescence decay profile of uncomplexed Eu^{3+} in (a) aqueous medium (b) acetonitrile medium. Excitation wavelength = 394 nm; Emission wavelength = 592 nm for both cases.

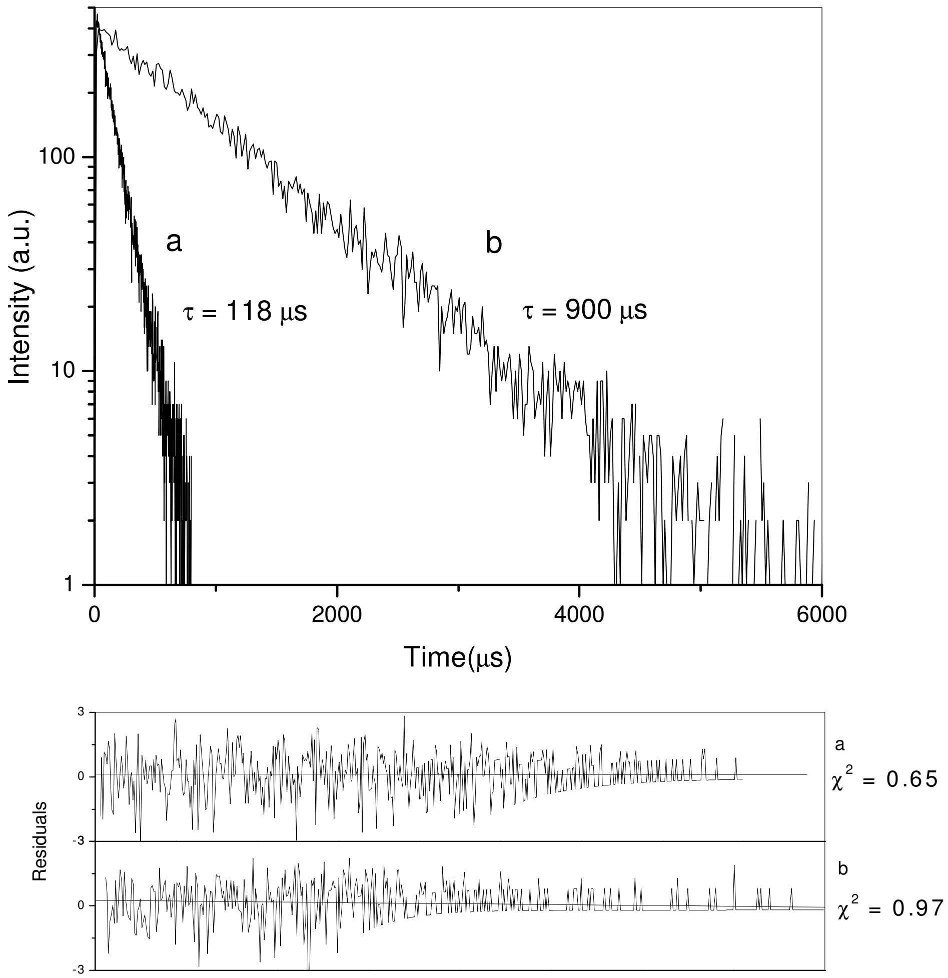

Figure 3.4 Luminescence decay profile of Eu^{3+}-BA in (a) aqueous and (b) acetonitrile medium. Excitation wavelength = 277 nm; Emission wavelength = 615 nm for both cases.

complex is formed by substituting water molecules from the inner coordination sphere of Eu^{3+}.

3.2.2 Complexation studies of Eu^{3+}-BA by UV–Vis spectroscopy

To study the complexation nature of Eu^{3+} with benzoate, absorption spectra were recorded by titration of benzoate with Eu^{3+} ion in acetonitrile. Figure 3.5 shows the absorption spectra of $1x10^{-4}$ M BA with different concentration of Eu^{3+} ion (0.0-$4.66x10^{-5}$ M) in acetonitrile medium at pH 4.5. The absorption spectrum of BA without Eu^{3+} shows maximum at 226 nm in acetonitrile. Complexation of benzoate ion with Eu^{3+} results in increase in absorbance along with a gradual red shift in the absorption maximum (231 nm). It appears that complexation stabilizes the electronic excited state of europium benzoate more compared to that of the ground state, causing red shift in absorption maximum.

The stoichiometry of the Eu^{3+}-BA complex is determined from the absorption spectra (Figure 3.5) by applying mole ratio method [19-21]. The absorbance of Eu^{3+}-BA measured at 231 nm is plotted in Figure 3.6 as a function of mole ratio (Eu^{3+} to benzoate). The intersection of two tangents of the absorbance data occurs at a molar ratio of 0.33, which indicates the formation of ML_3 type complex by Eu^{3+}-BA in acetonitrile. The stability constant of the above complex was calculated from these absorption spectra using the *HypSpec 2009* program [22]. The log β of the ML_3 complex is computed to be 12.55 ± 0.25 (Table 3.2).

3.2.3 Complexation studies of Eu^{3+}-BA by luminescence spectroscopy

Time resolved luminescence spectroscopy is used to obtain stability constant of Eu^{3+} complexes [23-24]. The hyper-sensitive nature of the $^5D_0$ - $^7F_2$ transition can be utilized for studying complexation behavior of Eu^{3+}. The luminescence spectra of solutions having Eu^{3+} concentration of $1x10^{-5}$ M with different metal to ligand ratio in acetonitrile are shown in Figure 3.7 after normalizing to the intensity of 592 nm peak. It can be seen from this Figure

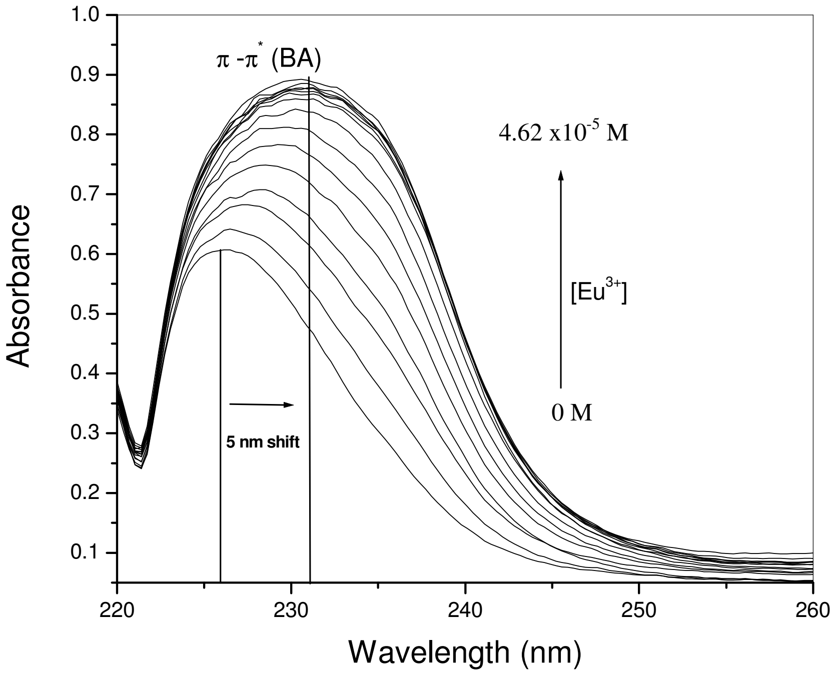

Figure 3.5 Spectrophotometric titration of BA ($1x10^{-4}$ M) at pH 4.5 with a gradual increment of Eu^{3+} ($0.33x10^{-5}$ M) in acetonitrile.

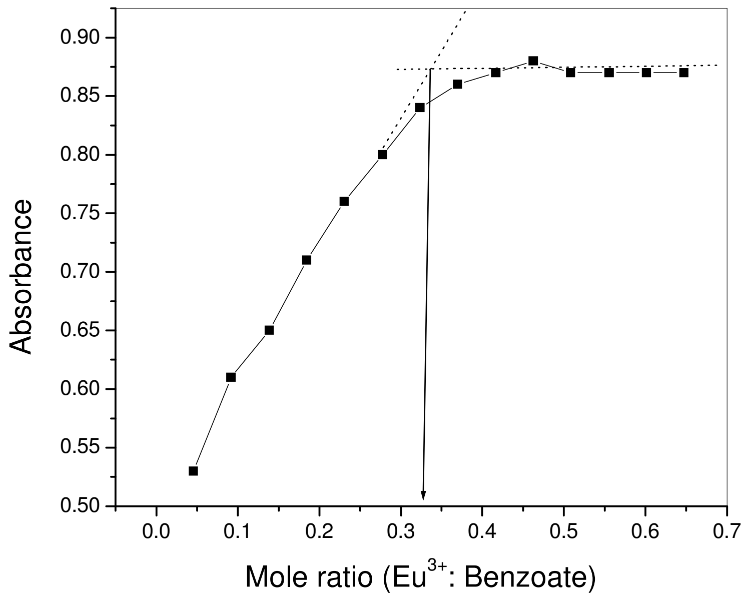

Figure 3.6 Variation of absorbance at 231 nm with the molar ratio of Eu^{3+} (0.33x10^{-5} M-4.62x10^{-5} M) to BA (1x10^{-4} M) in acetonitrile. Intersection of two tangents represents the stoichiometry of the complex.

Table 3.2 Stability constant (log β) of Eu^{3+}-BA complexes in acetonitrile and water medium at 25 °C, I = 0.1 M $NaClO_4$.

Solvent	**Stoichiometry**	**Stability constant**	**Reference**
Acetonitrile	ML_3	12.55 ± 0.25 13.07± 0.08	UV-Vis method (This work) Lumin. Method* (This work)
Water	ML & ML_2	1.84 ± 0.02 & 2.92 ± 0.04	[4]

* Average of values calculated by lifetime and asymmetry ratio data

that intensity of 615 nm peak increases as the BA concentration is increased from $1x10^{-5}$ to $4x10^{-4}$ M. This is due to the fact that complexation with benzoate ion changes the co-ordination geometry of Eu^{3+} ion, making the transition corresponding to 615 nm peak to be more intense. Figure 3.8 shows the ratio of peak areas of 615 to 592 nm (Asymmetry ratio) as a function of BA concentration. The luminescence lifetimes measured for all these solutions are also plotted in the same Figure 3.8. It can be seen from this Figure that both lifetime and asymmetry ratio increases gradually with increasing BA concentration and remains nearly constant above BA concentration of $3x10^{-4}$ M. The value of R increases from 3.7 to 13.2 and lifetime increases from 190 to 900 μs as BA concentration is changed from$1x10^{-5}$ to $4x10^{-4}$ M. The lifetime and asymmetry ratio data obtained from titration were used in the *HypSpec 2009* computation program and the stability constants (log β) are obtained for ML_3 type complex. The values of log β calculated are 12.94 ± 0.08 and 13.20 ±0.05, respectively. Average of these values (13.07) is found to be in good agreement with the log β value (12.55 ± 0.25) obtained by UV-Vis method (Table 3.2) and strongly supports the formation of ML_3 type complex.

Eu^{3+} forms 1:1 and 1:2 complexes in aqueous medium with benzoic acid having stability constant of 1.84 ± 0.02 and 2.92 ± 0.04, respectively [4]. In aqueous medium, the stoichiometry of Eu^{3+}-BA complex is limited up to 1:2 and which might be due to competition of ligand with water molecules towards metal ion, whereas in a poor coordinating (less solvating) solvent such as acetonitrile, more free ligands are made available towards Eu^{3+} ion compared to aqueous medium. Therefore, there is a possibility of forming high stoichiometry complex in acetonitrile compared to aqueous medium; the latter reduces the extent of interaction of metal ion to ligand.

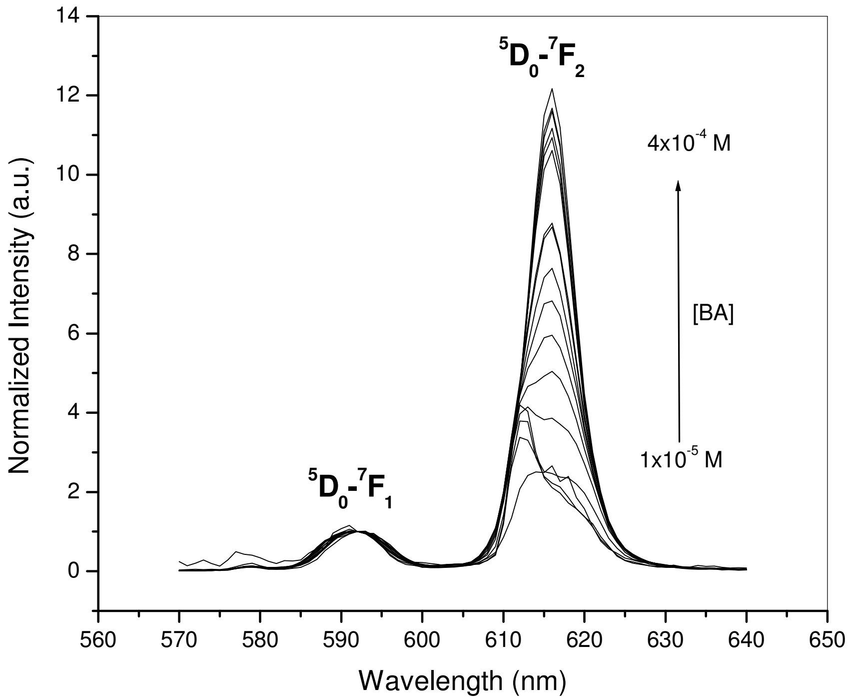

Figure 3.7 Luminescence spectra of Eu^{3+} (1x10^{-5} M)-BA as a function of BA concentration (1x10^{-5} M to 4x10^{-4} M) at pH 4.5 in acetonitrile, λ_{exc} = 277 nm. The spectra have been normalized to the luminescence intensity at 592 nm peak.

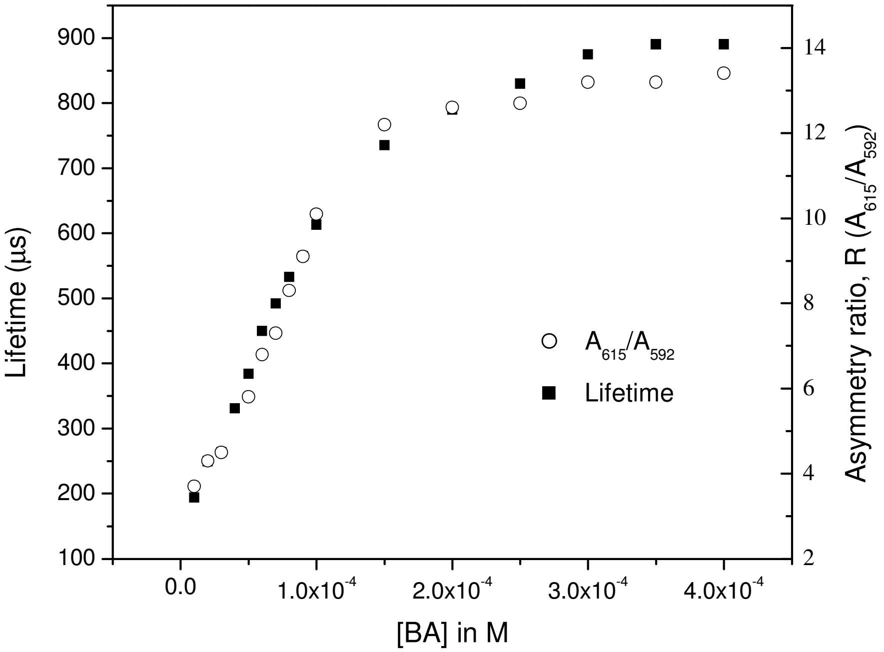

Figure 3.8 Variation of asymmetry ratio (A_{615}/A_{592}) and luminescence lifetime of Eu^{3+} ($1x10^{-5}$ M) with BA in acetonitrile at pH 4.5.

3.2.4 Composition of the complex

The lifetime (τ) can be correlated with number of water molecules (N_{H2O}) present in inner sphere of Eu^{3+} ion by the following formula [25] as discussed earlier in section 1.7:

$$N_{H2O} (\pm 0.5) = 1.05/\tau \ - 0.70 \quad \text{--------------} \ (3.1)$$

The lifetime of Eu^{3+}-BA complex in acetonitrile is 900 μs and using the above formula, number of water molecules coordinated to Eu^{3+} in the above complex is calculated to be nearly zero. This indicates that all the water molecules from the inner coordination sphere of Eu^{3+} are expelled. Therefore, assuming nine coordination number of Eu^{3+} in ML_3 complex, six acetonitrile molecules are coordinated to Eu^{3+} ion and hence, composition of the formed complex is proposed as $Eu(BA)_3(CH_3CN)_6$.

As 1% water is present in our experimental solutions to start with, a preferential solvation of Eu^{3+} ion by water molecules over acetonitrile can be expected as acetonitrile is a poor coordinating medium. Therefore, in ML_3 type complex as suggested by UV-Vis and luminescence spectroscopy in acetonitrile, six water molecules can be expected in the inner sphere of Eu^{3+}. Accordingly by the above formalism (Eq. 3.1), the expected lifetime of Eu^{3+} in Eu^{3+}-BA would be nearly 150 μs. But the observed luminescence lifetime of 900 μs in the ML_3 type complex of Eu^{3+}-BA indicates that water molecules in the inner sphere of Eu^{3+}-BA are getting replaced as more and more benzoate ions are introduced into the system. It appears that apart from complexation, benzoate ions make water molecules to move out from the inner sphere of Eu^{3+}-BA, which helps acetonitrile to bind with Eu^{3+} in place of water molecules. Since water is more polar than acetonitrile, strong interaction of benzoate ions can be responsible for moving out water molecule from the inner Eu^{3+} sites. Thus, it can be summarized that though Eu^{3+} has a strong affinity towards water molecules, a strong interaction with benzoate ion force the water molecules to come out from inner sphere and a less polar solvent, acetonirile, occupies the position in the inner coordinated sphere of Eu^{3+}.

3.2.5 Effect of water on the composition of Eu^{3+}-BA complex

To examine the tolerance limit of water in acetonitrile for making ML_3 type species, since Eu^{3+} does not form ML_3 complex with benzoate in water medium, steady state and lifetime experiments on $Eu^{3+}(1x10^{-5}$ M)-BA$(5x10^{-4}$ M) luminescence in acetonitrile were performed after deliberately adding water to it. It must be noted that in all the experiments in acetonitrile, 1% water was initially present to begin with. The luminescence intensity and lifetime decreases as water content increases in acetonitrile. Figure 3.9 shows the lifetime variation as a function of water content in acetonitrile. Using the Eq. 1, the number of water molecules coordinated to Eu^{3+} ion at different water content is calculated and also plotted in the same Figure. A marked decrease in lifetime (from 900 µs to 260 µs) is observed as water content is increased from 1 to 5%. The number of water molecules coordinated to Eu^{3+} is about 3 for 5% water content in acetonitrile (Figure 3.9) and this indicates that three acetonitrile molecules are removed from the inner sphere of Eu^{3+} ion at this water content. As water content is increased further, more and more acetonitrile molecules are removed and at 30% water content where lifetime is ~156 µs, all six acetonitrile molecules coordinated to Eu^{3+} are replaced by water molecules. At 50% water content the lifetime of Eu^{3+}-BA is 130 µs, indicates formation of ML_2 species. Probably ML and ML_2 species are formed above 50% water content, a situation similar to aqueous medium. UV Visible spectra of Eu^{3+}-BA recorded at different water content in acetonitrile also support the formation of ML and ML_2 species at higher water content. Figure 3.10a and 3.10b shows the variation of absorbance as a function of mole ratio (Eu^{3+} to benzoate) at 20% and 50% water content in acetonitrile, respectively. Presence of one inflection point at a mole ratio of ~ 0.33 in Figure 3.10a and two inflection points, first at a mole ratio of ~ 0.5 and second at mole ratio of ~ 1.0 in Figure 3.10b confirms that ML_3 complex exist even at 20% water content whereas ML and ML_2 complexes are formed when 50% water was present in acetonitrile.

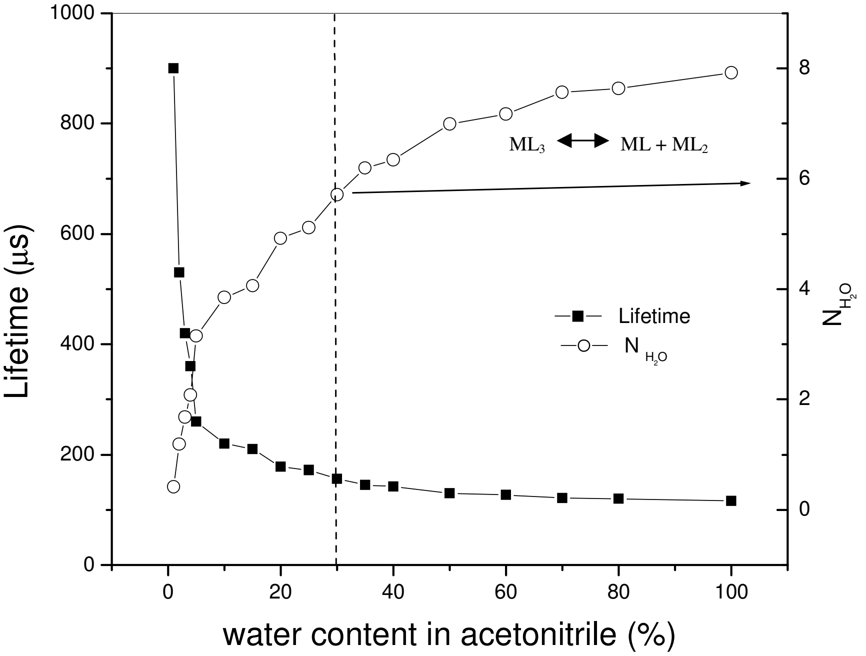

Figure 3.9 Variation of luminescence lifetime of Eu^{3+} and the number of calculated water molecules (N_{H2O}) in Eu^{3+}($1x10^{-5}$ M)-BA ($5x10^{-4}$M) complex as a function of water in acetonitrile. The dotted line indicates the water content 30% above which ML_3 dissociates.

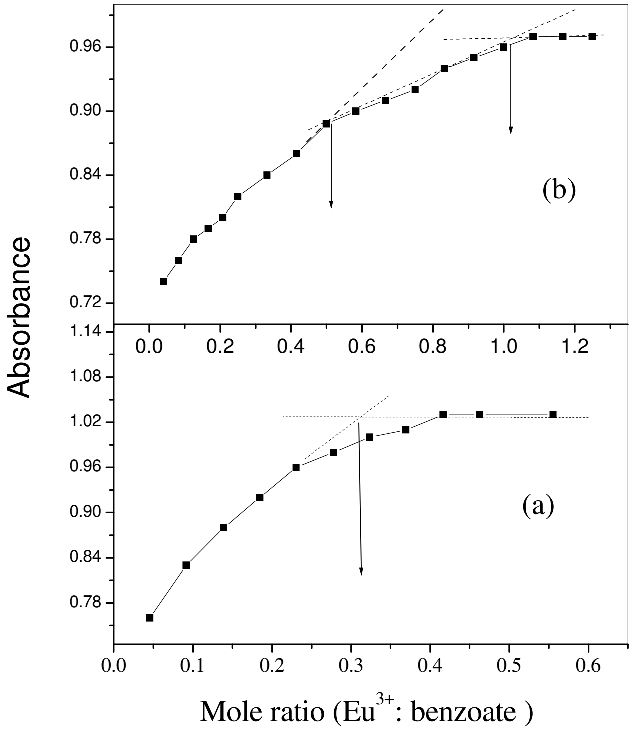

Figure 3.10 Variation of absorbance at 231 nm with the molar ratio of Eu^{3+} to BA ($1x10^{-4}$ M) (a) at 20% water in acetonitrile (b) at 50% water in acetonitrile.

3.2.6 Luminescence of Eu^{3+} complexed with ortho, meta and para toluates

Like benzoic acid, toluic acids (TA) also enhance the luminescence of Eu^{3+} in aqueous medium [26]. Hence, the luminescence of Eu^{3+} ion is also expected to be enhanced by toluic acids in acetonitrile medium. Figure 3.11 shows the luminescence spectra of Eu^{3+} complexed with ortho (*o*), meta (*m*) & para (*p*) TA and compared with that of Eu^{3+}-BA. In case of Eu^{3+}-TA, solution becomes turbid above a TA concentration of $1x10^{-4}$ M which might be due to limited solubility of these ligands in acetonitrile. Therefore, for comparison the luminescence intensity of Eu^{3+}-TA with Eu^{3+}-BA, a concentration of $1x10^{-4}$ M was taken for all the cases. The luminescence intensity of Eu^{3+} complexed with TA is in the order of *p* TA > *m* TA > *o* TA as can be seen from Figure 3.11. It must be noted that methyl acts as electron donating group and therefore one can expect larger luminescence intensity of Eu^{3+} in toluate complexes compared to benzoate. However, with *o* TA the luminescence intensity of Eu^{3+} is found to be least among all. Lifetimes of these complexes were recorded in order to see any quenching effect from –CH oscillators of methyl group. Table 3.3 presents the comparison of luminescence lifetimes for Eu^{3+}-TA and Eu^{3+}-BA at a ligand concentration of $1x10^{-4}$ M. Lifetimes of Eu^{3+} complexed with meta and para TA are 590 and 620 μs respectively and are comparable to the lifetime of Eu^{3+}-BA (610 μs). The lifetime of Eu^{3+}- *o* TA is 530 μs, which is slightly less in comparison to other ligands. It clearly indicates that presence of high energy –CH oscillators at ortho position of carboxylate diminishes the luminescence intensity by non-radiative decay. In case of meta and para TA, –CH oscillators are quite away from carboxylate and hence not much effective in diminishing the luminescence intensity.

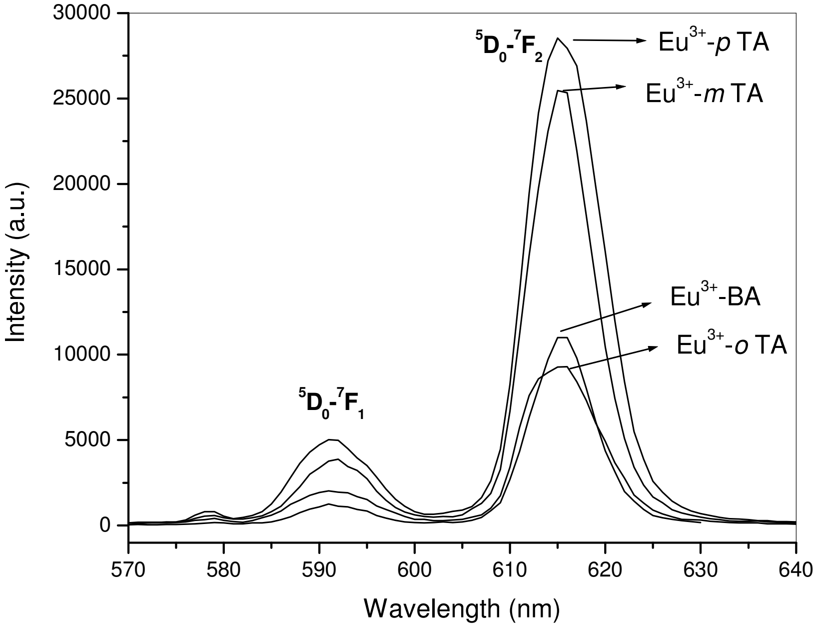

Figure 3.11 Comparison of luminescence intensity of Eu^{3+}-BA and Eu^{3+}-TA in acetonitrile medium; [Eu^{3+}]-1x10^{-6} M, [Ligand]- 1x10^{-4} M, pH-4.5, λ_{exc} = 277 nm for all cases.

Table 3.3 Luminescence lifetimes of Eu^{3+}-BA and Eu^{3+}-TA in acetonitrile medium at pH 4.5; [Eu^{3+}]-1x10^{-6} M, [Ligand]-1x10^{-4} M, Excitation wavelength = 277 nm, Emission wavelength = 615 nm for all cases.

System	**Lifetime (µs)** **RSD = ±5 %**
Eu^{3+}-BA	610
Eu^{3+}-*o* TA	530
Eu^{3+}-*m* TA	590
Eu^{3+}-*p* TA	620

3.2.7 Analytical application of this study

This present study of Eu^{3+} luminescence in acetonitrile medium finds analytical application for detection of europium. The large enhancement of Eu^{3+} luminescence in its complexes with benzoate and methyl substituted benzoates in acetonitrile medium can be used for trace level detection of Eu^{3+} ion. Linearity in the luminescence intensity is seen over the Eu^{3+}concentration range of $5x10^{-9}$ to $1x10^{-5}$ M for Eu^{3+}-BA; $5.0x10^{-8}$ to $1.5x10^{-6}$ M for Eu^{3+}-*o* TA; $2.5x10^{-8}$ to $1.5x10^{-6}$ M for Eu^{3+}-*m* TA; and $2.5x10^{-8}$ to $1.0x10^{-6}$ M for Eu^{3+}-*p* TA. The typical calibration curve for Eu^{3+}-BA is shown in Figure 3.12. The detection limit for Eu^{3+} calculated using the criterion of 3σ(σ - Standard deviation of the blank) is ~ $3x10^{-10}$ M in Eu^{3+}-BA; $1.6x10^{-9}$ M in Eu^{3+}-*o* TA; $4.5x10^{-10}$ M in Eu^{3+}-*m* TA and $1.2x10^{-9}$ M for Eu^{3+}-*p* TA sytems.

3.3 Conclusions

The present study has shown that Eu^{3+} forms 1:3 complex with benzoic acid in acetonitrile medium which is different from that of the aqueous medium, where 1:1 and 1:2 complexes were reported. The number of water molecules coordinated to Eu^{3+} in its inner sphere, as calculated based on luminescence lifetime using the empirical formula is almost zero indicating the coordination of six acetonitrile molecules to the central Eu^{3+} in its 1:3 complex. Consequently, quenching due to –OH oscillators of water molecules decreases sharply resulting in enhancement of luminescence. This enhancement is about two orders of magnitude more than what is observed in aqueous medium, leading to the possibility of detecting Eu^{3+} at levels of 10^{-10} M. Luminescence and UV-visible spectroscopy data are used to determine the stability constant of the ML_3 complex and the results are in good agreement. The influence of water present in acetonitrile on the luminescence is studied and it shows that the Eu^{3+}-BA complex with six acetonitrile molecules present in the inner sphere of Eu^{3+} starts losing its composition as water content of the solvent is more than 1%. While the inner

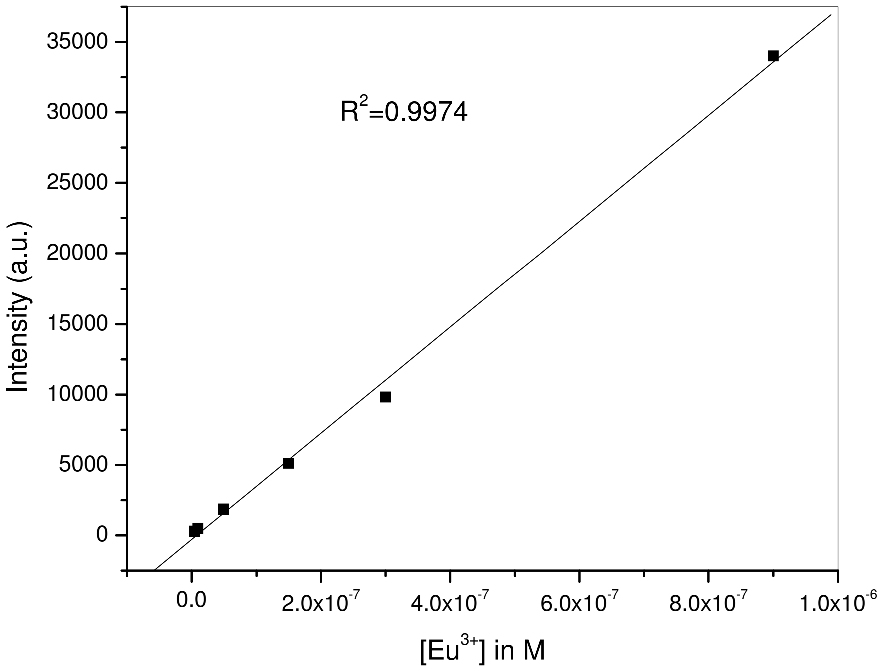

Figure 3.12 Plot of intensity of Eu^{3+} luminescence at 615 nm for Eu^{3+}-BA as a function of Eu^{3+} concentration; [BA] = $5x10^{-4}$ M.

coordinated acetonitrile molecules are replaced by water molecules as water content is increased, ML_3 type complex with different water molecules at the inner sphere still prevails up to 30% (v/v) water content. The effect of methyl groups at different positions of benzoic acid has also been studied. Methyl group occupying the ortho position of benzoic acid quenched the Eu^{3+} luminescence by non-radiative decay. Luminescence intensity of Eu^{3+} complexed with toluates is in the order of *p* TA > *m* TA > *o* TA. Luminescence lifetime data along with mole ratio determined from absorption data suggest implosion of ML_3 complex to ML and ML_2 type complexes beyond 30% (v/v) water content. For effective complexation of Eu^{3+} to BA and its luminescence, acetonitrile should not contain water beyond 1% (v/v).

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CHAPTER 4 Luminescence studies on UO_2^{2+} -benzoate & UO_2^{2+}-toluates systems

4.1 Introduction

Being a hard acceptor, UO_2^{2+} forms strong complexes with oxygen, nitrogen and fluorine donor ligands [1-5]. These complexes find major applications in various fields such as nuclear industry, environmental science etc. In nuclear industry coordination chemistry of UO_2^{2+} plays an important role starting from its nascence from ore to nuclear fuel reprocessing [6-8]. Organic phosphates such as tributyl phosphate (TBP) containing oxygen as donor sites serve the purpose for the extraction of uranium by making strong complex with UO_2^{2+} in the nuclear reprocessing industry. In environmental science, to understand the migration behavior of UO_2^{2+} in environment, many complexes of UO_2^{2+} with ligands such as benzoic acid, nicotinic acids and hydroxyl acids have been studied [9-12].

The coordination of a metal ion to ligand occurs in competition with solvent molecules. Therefore, depending on the nature of solvents, the stoichiometry of the metal-ligand complex may be different in different solvents. In strong coordinating solvent such as aqueous medium, the metal solvation interaction hampers the stoichiometry of metal ligand complex. Though there are many reports available on UO_2^{2+} complexation in aqueous medium [6-12], similar studies in non-aqueous medium are scarcely available. Recently a few studies have been reported in literature on UO_2^{2+} complexation and its luminescence in non-aqueous medium [13-15]. These studies have reported the formation of different species, their structure and spectroscopic properties in acetonitrile and ionic liquid medium. Servaes *et al.* have studied the complexation between UO_2^{2+} and nitrate ion in acetonitrile medium [13]. The important conclusion drawn from their studies is that a tris complex of UO_2^{2+} named uranyl nitrato with D_{3h} symmetry is formed in acetonitrile whereas no evidence of this complex in aqueous medium was observed. Nockemann and coworkers have studied UO_2^{2+} complexes with chloride, nitrate and acetate ions in ionic liquids [15] and it was concluded that both the cation and weakly coordinated anion have minor influence on the optical spectra of UO_2^{2+} complexes. Studies by the same group showed that when UO_2^{2+} is complexed with carboxyl functionalized ionic liquids, carboxylate groups remain coordinated to UO_2^{2+} in both ionic liquid and acetonitrile medium, but not in water [14].

In this chapter luminescence of UO_2^{2+} complexed with benzoate (UO_2^{2+}-BA) and methyl substituted benzoates (toluates) in acetonitrile medium is discussed. Recently, Lutke *et al.* have reported the complexation of uranyl benzoate system in aqueous medium [12]. In their study they observed that luminescence intensity of UO_2^{2+} decreased with the addition of benzoic acid to UO_2^{2+} solution. Furthermore, they had reported that uranyl benzoate specie did not show any luminescence in aqueous medium. Uranyl benzoate complexes with 1:1 & 1:2 stoichiometry could be identified in aqueous medium [12]. In contrary to aqueous medium, uranyl benzoate specie formed in acetonitrile medium exhibited strong luminescence. This encouraged us to study this system thoroughly in acetonitrile medium. The studies on UO_2^{2+} speciation will be discussed in detail in aqueous and acetonitrile medium. Comparative studies on luminescence intensities and lifetimes of UO_2^{2+} and UO_2^{2+}-BA system in water and acetonitrile will also be discussed in this chapter. In order to see the effect of methyl group, luminescence of UO_2^{2+} complexed with ortho, meta & para toluates was also studied and the results are compared with uranl benzoate. This chapter also presents a possible mechanism for UO_2^{2+} luminescence enhancement in acetonitrile.

4.2 Results and discussion

4.2.1 UO_2^{2+} luminescence and decay profile in acetonitrile medium

At the outset, the luminescence spectra of uncomplexed UO_2^{2+} as a function of pH are studied in acetonitrile medium. Figure 4.1 compares the luminescence spectra of $4x10^{-5}$ M UO_2^{2+} solution as a function of pH from 2.4 to 5.0 in acetonitrile medium. For comparison, UO_2^{2+} luminescence in aqueous medium is also shown as dotted lines in the same Figure. The concentration of the UO_2^{2+} used to record the spectra in the aqueous medium is ten times more ($4x10^{-4}$ M) compared to acetonitrile as $4x10^{-5}$ M UO_2^{2+} concentration does not show measurable luminescence intensity in aqueous medium at pH 2.4. At pH 2.4, UO_2^{2+} showed five sharp peaks at 488, 509, 532 & 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 UO_2^{2+} luminescence in acetonitrile. From pH 3.0 onwards the behavior of UO_2^{2+} luminescence in acetonitrile is different from that in aqueous medium. In aqueous medium, the peak positions of UO_2^{2+} do change with pH as many species of UO_2^{2+} such as UO_2OH^+, $UO_2(OH)_2$, $(UO_2)_3(OH)_5^+$ etc. are formed and it is well reported in literature [16-19]. At pH 3.0, new luminescence peaks appeared at 499, 520 & 545 nm along with other peaks of UO_2^{2+} in the acetonitrile medium. These new features in acetonitrile medium could be due to hydrolysis of UO_2^{2+} as small amount of water is always present in the solution. Above pH 3.0, only these new peaks were observed while the peaks due to free UO_2^{2+} start disappearing. Similar features were observed in literature for UO_2OH^+ complex in aqueous medium [16-17]. It must be noted that in acetonitrile, the luminescence peaks positions at 499, 520 & 545 nm are not changing with pH. This implies that only one type of hydroxide is formed and strongly solvated by acetonitrile molecules which help in preventing UO_2^{2+} to polymerize into other higher species. Appearance of these peaks at pH 3.0 suggests that this specie might be UO_2^{2+} specie which exist at this pH in aqueous, namely UO_2OH^+ and this

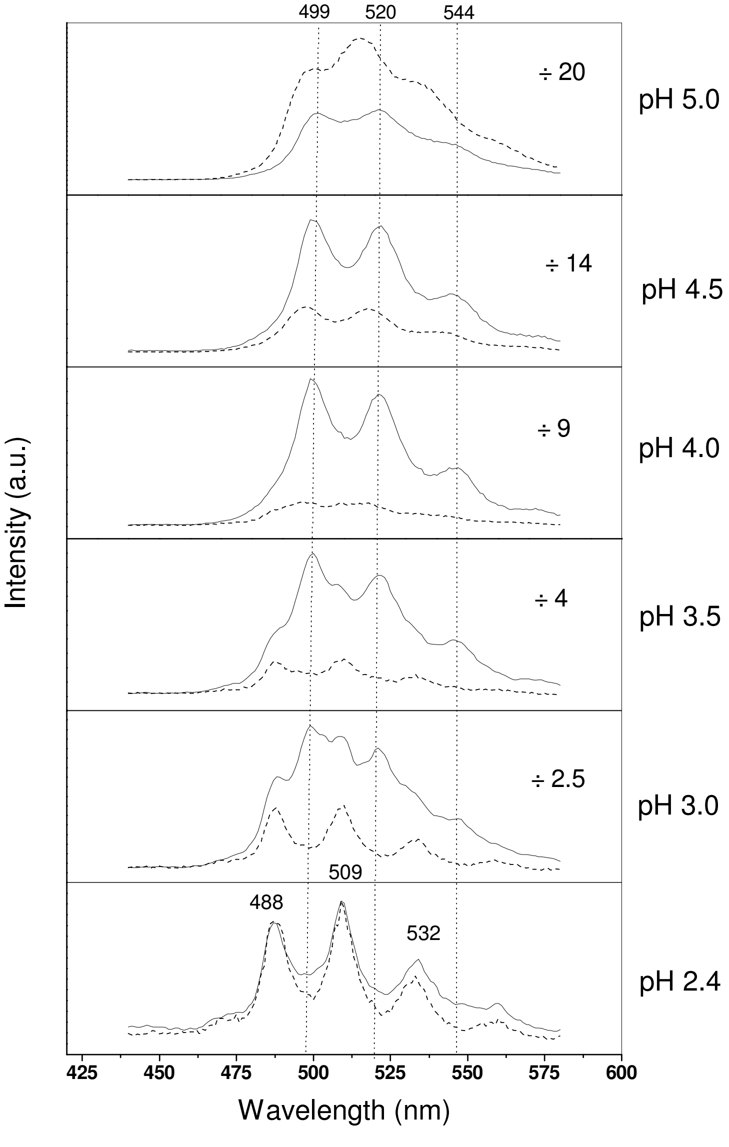

Figure 4.1 Emission spectra of UO_2^{2+} at different pH in water (dashed line); $[UO_2^{2+}] = 4x10^{-4}$ M and in acetonitrile (solid line); $[UO_2^{2+}] = 4x10^{-5}$ M. λ_{ex} = 250 nm for all cases. Intensity scales are same for all cases.

hydroxide specie dominates even at this low pH in acetonitrile medium, which is present in negligible amount in aqueous at the same pH [16]. The luminescence intensity of this specie is found to increase with pH. Figure 4.2A and 4.2B show the luminescence decay profile of UO_2^{2+} in aqueous and acetonitrile medium, respectively at pH 2.4. Table 4.1 compares the lifetimes of UO_2^{2+} at different pH in acetonitrile and aqueous medium. At pH 2.4, the lifetime of UO_2^{2+} is 1.5 μs in aqueous medium which is very well reported in literature for free UO_2^{2+}. The decay profile of UO_2^{2+} is fitted to a mono-exponential decay with lifetime of 20 μs in acetonitrile medium. 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 UO_2^{2+}. This is similar to a behavior seen in the luminescence of lanthanides in acetonitrile medium [20]. Therefore, increase in lifetime from 1.5 to 20 μs when we go from aqueous to acetonitrile medium suggests that the removal of water molecules from the outer sphere of UO_2^{2+} by acetonitrile and not due to the removal of inner sphere water molecules by acetonitrile. Above pH 2.4, bi- exponential decay with lifetimes around 20 and 60 μs indicates that two different species are present in the solution; the first one could be due to free UO_2^{2+} and the second due to hydroxide specie of UO_2^{2+}. Above pH 4.0, only the hydroxide specie is predominant, showing a single decay lifetime of about 60 μs.

4.2.2 UO_2^{2+}-BA luminescence and decay profile in acetonitrile medium

Figure 4.3 shows the luminescence spectra of UO_2^{2+} with different UO_2^{2+} to BA concentration in aqueous medium at pH 3.0. It can be seen from this figure that addition of benzoic acid to UO_2^{2+} solution results in quenching of UO_2^{2+} luminescence. The decrease in luminescence intensity of UO_2^{2+} indicates the complex formation of UO_2^{2+} with benzoate ion and this has been reported in the literature [11-12]. It must be noted that there is no change in positions of emission peaks indicating that the UO_2^{2+}-BA complex formed, does not show

Table 4.1 Lifetimes of UO_2^{2+} species at different pH in water and acetonitrile medium.

pH	In aqueous medium		In acetonitrile medium	
	Lifetimes (μs)	Ref.	Lifetimes (μs)	Ref.
2.4	1.5 1.9 1.3	This work [18] [19]	20	This work
3.0	1.5 1.3 1.8, 32.8	This work [19] [18]	20, 58	
3.5	1.4, 9.0 1.9, 32.8, 8.8	This work [18]	21, 65	
4.0	1.8, 11.0 1.6, 32.8, 9.9	This work [18]	62	
4.5	1.8, 10 2.2, 6.8 1.6, 9.3	This work [19] [18]	60	
5.0	14 12	This work [18]	70	

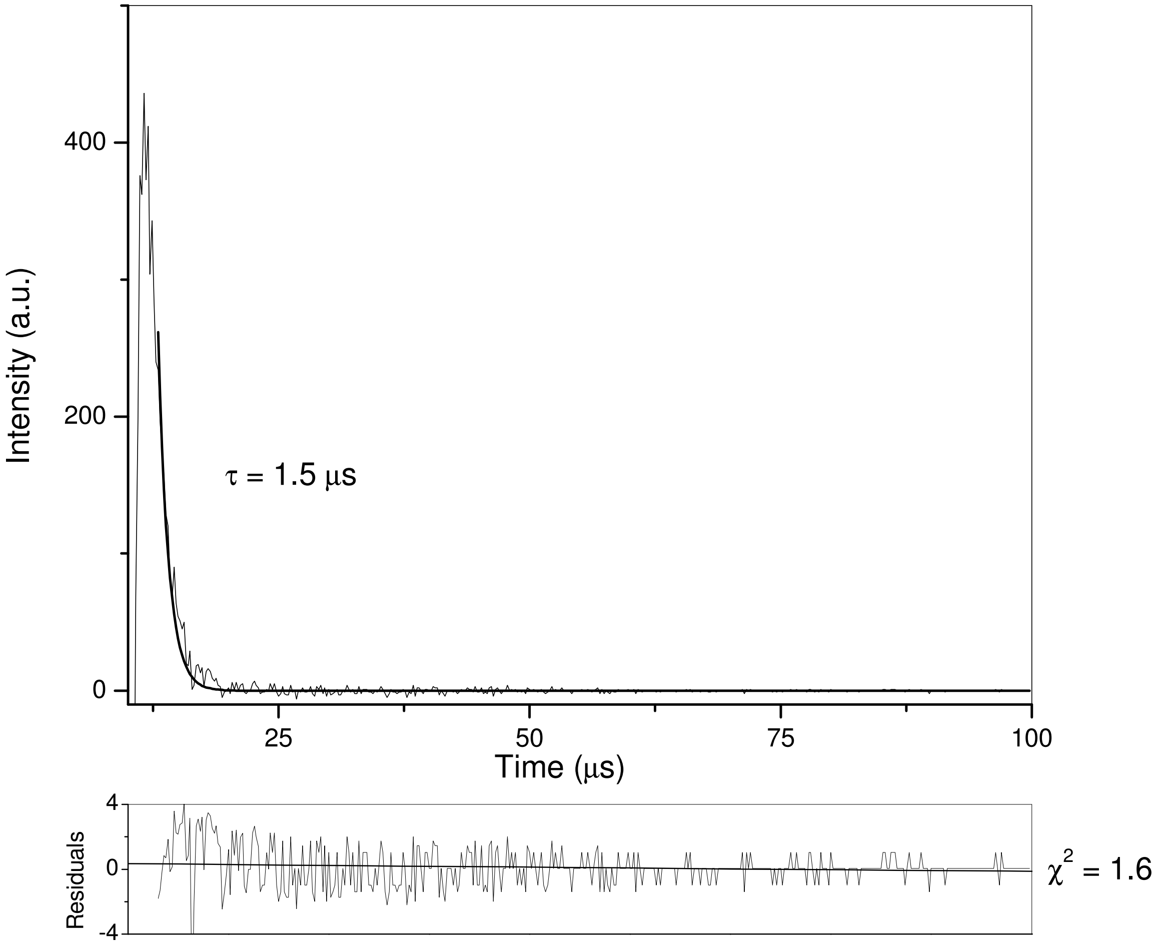

Figure 4.2A Luminescence decay profile of UO_2^{2+} in aqueous medium at pH 2.4; Excitation wavelength = 250 nm, Emission wavelength = 509 nm.

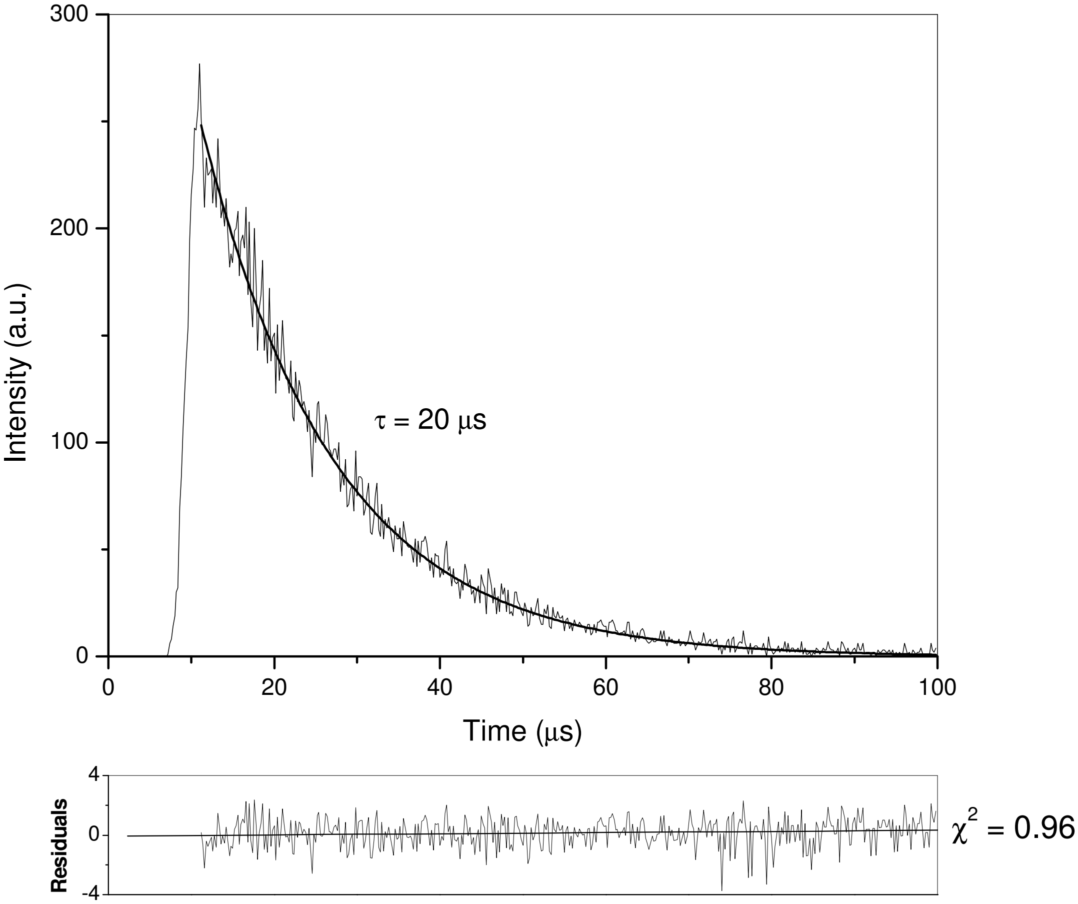

Figure 4.2B Luminescence decay profile of UO_2^{2+} in acetonitrile medium at pH 2.4; Excitation wavelength = 250 nm, Emission wavelength = 509 nm.

any luminescence. The species of UO_2^{2+}-BA formed in aqueous medium were inferred to be 1:1 and 1:2 types according to Lutke *et al.*[11-12].

In acetonitrile, UO_2^{2+} luminescence is found to increase by the addition of benzoate ion. At the outset, UO_2^{2+} luminescence was measured as a function of benzoic acid concentration and pH of the solution. Figure 4.4 shows the variation of luminescence intensity of UO_2^{2+}-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 $1x10^{-4}$ M and hence this concentration was used in all our subsequent experiments. Figure 4.5 shows the variation of luminescence intensity of UO_2^{2+}-BA complex at 481 nm as a function of pH. For the pH range 3.5 to 5.0 the luminescence intensity was almost constant for a given ligand concentration. Therefore, in all our experiments pH of the solution was maintained at 4.5. Figure 4.6 compares the excitation spectra of uncomplexed UO_2^{2+} and UO_2^{2+}-BA complex in acetonitrile medium. The excitation spectrum of the uncomplexed UO_2^{2+} was recorded by monitoring the luminescence at 499 nm, while the spectrum of complexed UO_2^{2+} was recorded by monitoring the luminescence at 481 nm. The excitation spectra for UO_2^{2+}-BA complex display a maxima at 243 nm (Figure 4.6a), which is different from uncomplexed UO_2^{2+} (250 nm), indicating the complexation of UO_2^{2+} with benzoate.

Figure 4.7a & 4.7b shows the UO_2^{2+} luminescence spectra with and without benzoic acid in acetonitrile medium at pH 4.5. The emission spectrum of uncomplexed UO_2^{2+} (Figure 4.7b) shows bands at 499, 520 & 545 nm. However, emission spectrum of UO_2^{2+}-BA complex (Figure 4.7a), shows five well resolved sharp peaks at 462, 481, 501, 522 & 546 nm. Although the luminescence intensities shown in Figure 4.7a & 4.7b for the complexed and uncomplexed UO_2^{2+} are comparable, the concentrations of UO_2^{2+} used to record the spectra are different. Concentration of UO_2^{2+} used to record the spectrum in its complex in acetonitrile medium is $8x10^{-7}$ M. At this concentration, uncomplexed UO_2^{2+} showed no

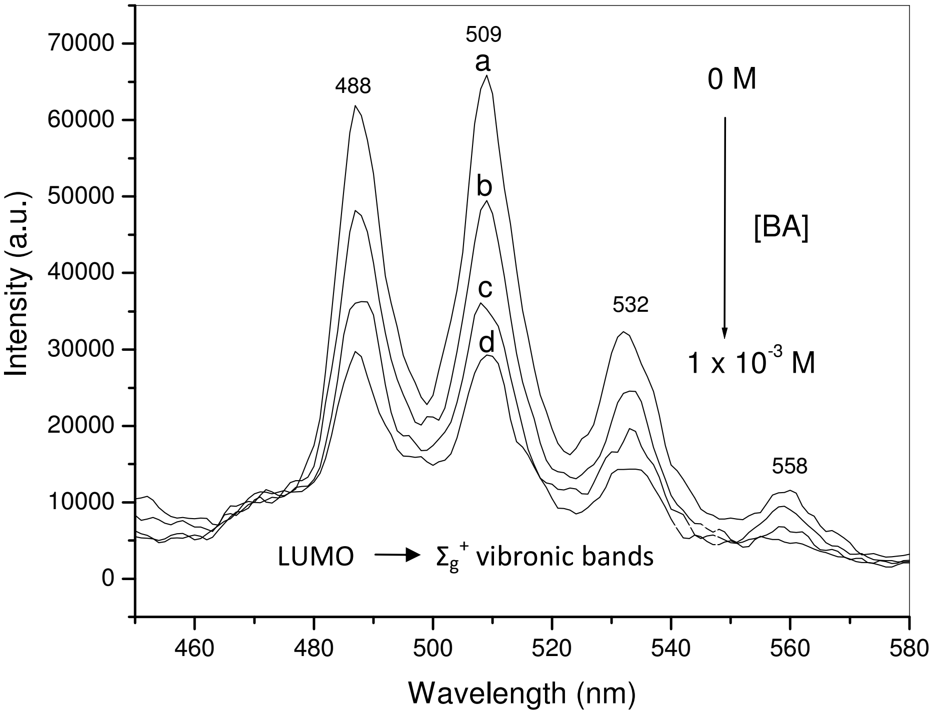

Figure 4.3 Luminescence spectra of UO_2^{2+}-BA complex in aqueous medium as a function of BA concentration at pH 3.0 (a) 0 M ; (b) $1x10^{-4}$ M; (c) $5x10^{-4}$ M; (d) $1x10^{-3}$ M; $[UO_2^{2+}]$ - $4x10^{-4}$ M, λ_{ex} = 250 nm.

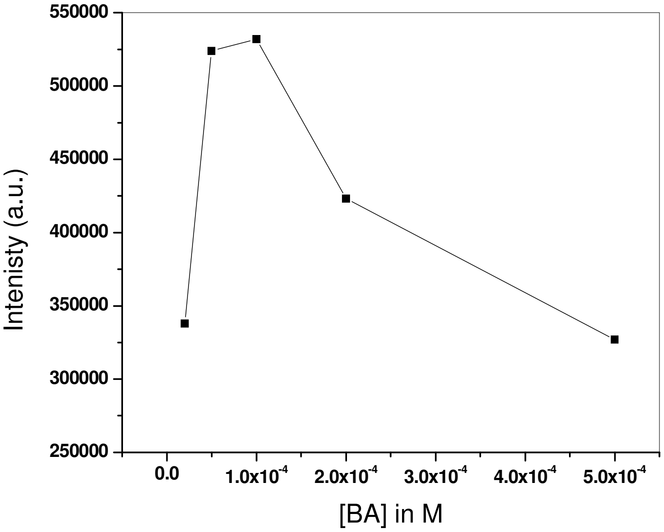

Figure 4.4 Variation of luminescence intensity of UO_2^{2+}-BA complex at 481 nm as a function of the concentration of BA in acetonitrile; pH 4.5, $[UO_2^{2+}] = 8x10^{-7}$ M.

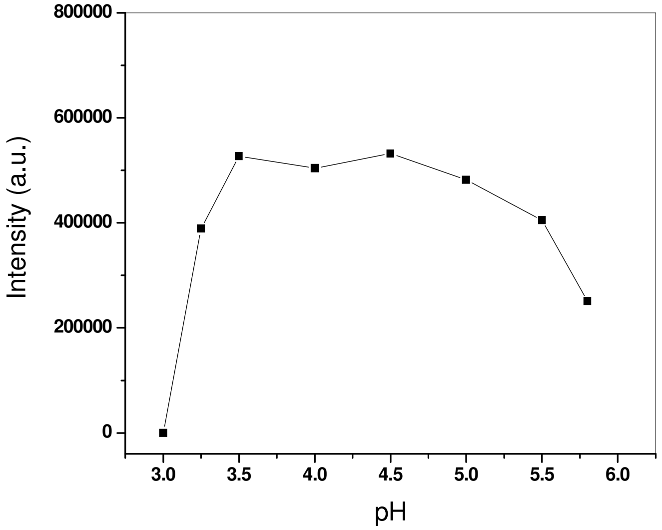

Figure 4.5 Variation of luminescence intensity of UO_2^{2+}-BA complex at 481 nm as a function of pH in acetonitrile; $[UO_2^{2+}] = 8x10^{-7}$ M, $[BA]=1x10^{-4}$ M.

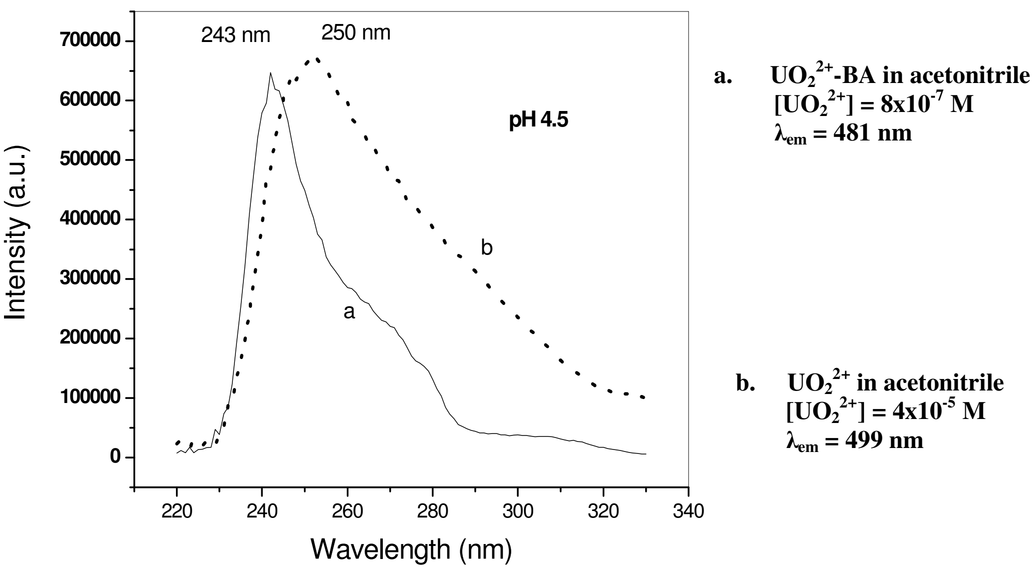

Figure 4.6 Excitaion spectra of (a) UO_2^{2+} (8x10^{-7} M)-BA(1x10^{-4} M) and (b) UO_2^{2+} (4x10^{-5} M) in acetonitrile medium at pH 4.5. The emission wavelength used to record each of the spectra is shown alongside.

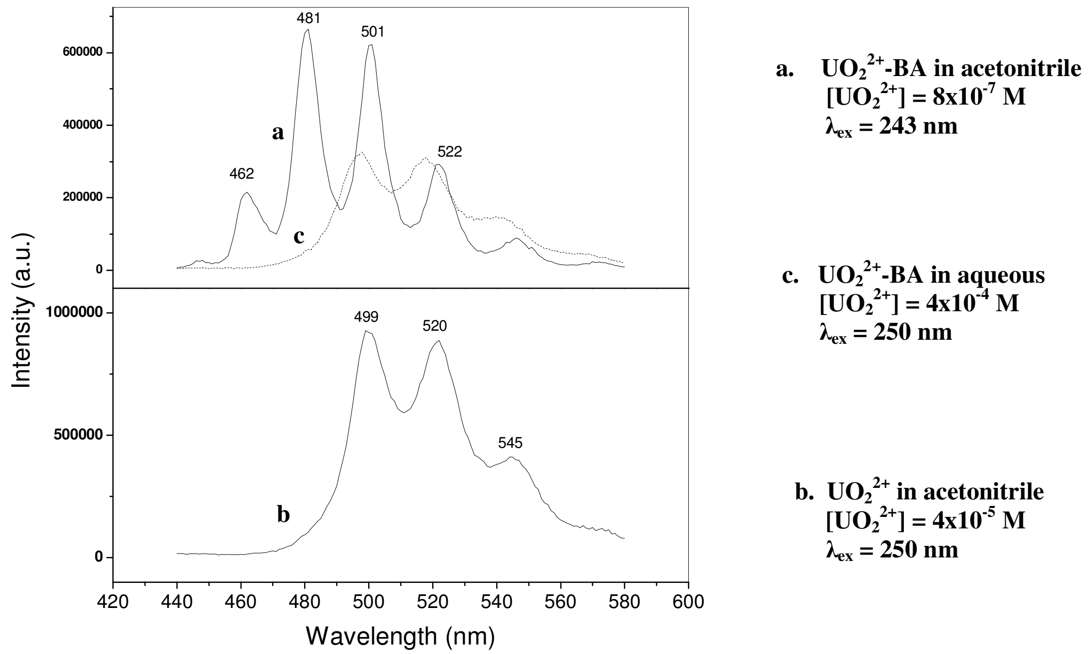

Figure 4.7 Emission spectra of (a) UO_2^{2+}(8x10^{-7} M)-BA(1x10^{-4} M) (b) UO_2^{2+} (4x10^{-5} M) in acetonitrile medium and (c) UO_2^{2+}(4x10^{-4} M)-BA(1x10^{-4} M) in aqueous medium at pH 4.5. The excitation wavelength used to record each of the spectra is shown alongside.

measurable luminescence, and hence to record the spectrum of uncomplexed UO_2^{2+}, a concentration of $4x10^{-5}$ M is used. For comparison, emission spectrum of UO_2^{2+}-BA in aqueous medium is also shown as dotted line (Figure 4.7c) with UO_2^{2+} concentration of $4x10^{-4}$ M, 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 UO_2^{2+} luminescence in acetonitrile. Complexation with benzoate yields more than two orders of enhancement in the luminescence of UO_2^{2+} in acetonitrile medium. The average spacing between the spectral features in the emission spectrum of UO_2^{2+}-BA complex in acetonitrile, which is calculated from the energy difference between two consecutive peaks (481 and 501 nm), is 832 cm^{-1} ($\Delta\lambda$ ~ 20 nm), which is close to a value of 855 cm^{-1} reported for vibrational spacing in the ground electronic state of free UO_2^{2+} [17]. While the spacing between the vibronic features in our spectrum (Figure 4.7a), agrees with that of the reported value for other UO_2^{2+} complexes in aqueous [21-22], each of the features is blue-shifted by 8 nm in acetonitrile medium, compared with that observed for free UO_2^{2+} (Figure 4.1, 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 UO_2^{2+}-trimesic acid complex in aqueous medium [22]. Figure 4.8 shows the decay profile of UO_2^{2+}-BA in acetonitrile medium. The UO_2^{2+}-BA system shows a single exponential decay with a lifetime of 68 μs, which indicates presence of single UO_2^{2+}-BA specie. Complexation of BA to UO_2^{2+} increases its lifetime from 20 to 68 μs in acetonitrile medium. These lifetime results suggest that upon complexation with benzoate ion, water molecules are displaced from the first coordination sphere of the central UO_2^{2+} 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

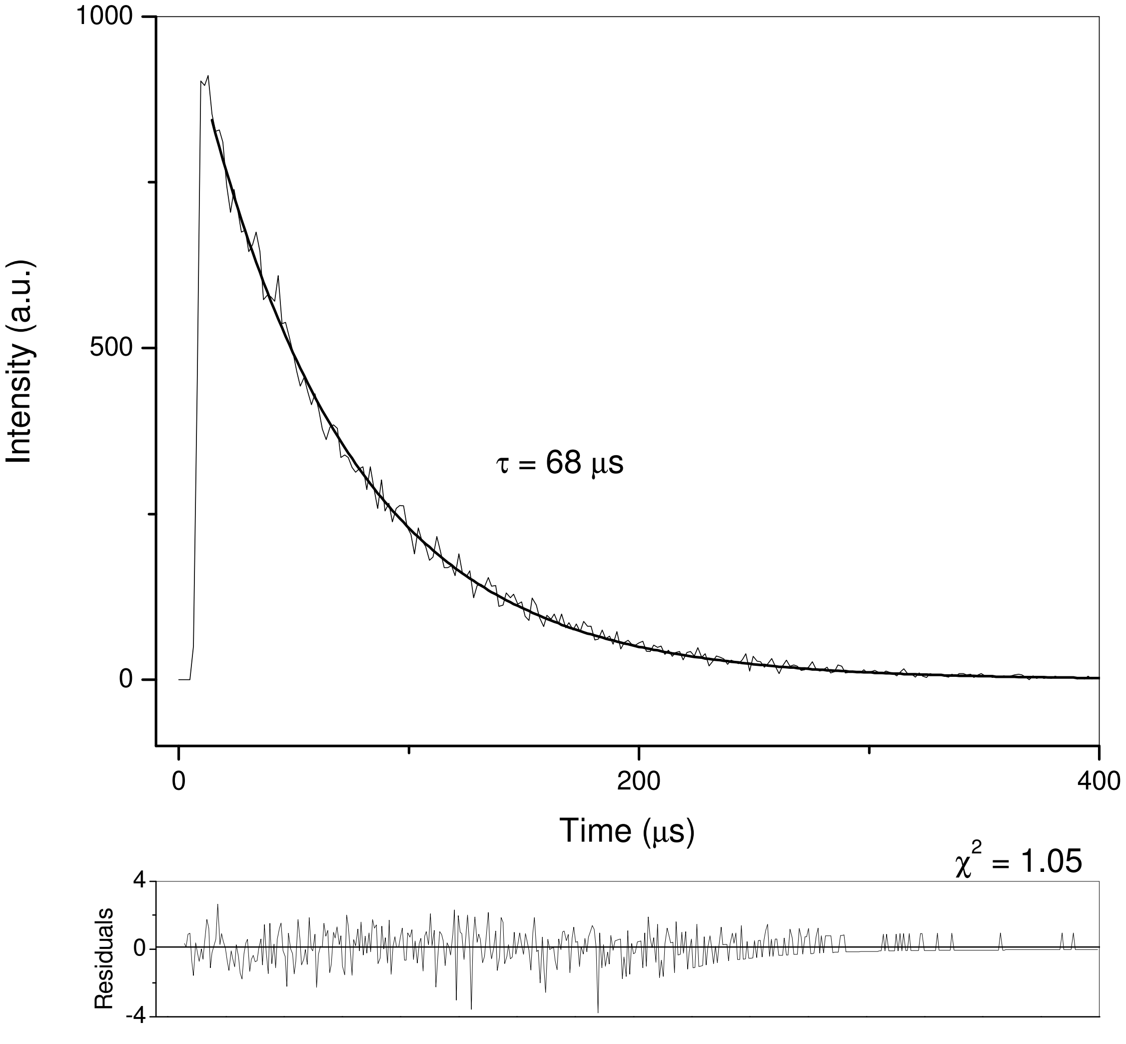

Figure 4.8 Luminescence decay profile of UO_2^{2+}-BA in acetonitrile medium at pH 4.5; Excitation wavelength = 243 nm, Emission wavelength = 481 nm.

luminescence of UO_2^{2+} complexed with DPA [21], TMA [22], malonic acid [23], glycine [24] in aqueous medium. The lifetime of UO_2^{2+} was found to increase from 1.5 μs in aqueous medium to 3, 6.8, 10 and 18 μs due to complexation with glycine, malonic acid, DPA and TMA respectively.

4.2.3 Effect of water on luminescence of UO_2^{2+}-BA in acetonitrile

As benzoic acid did not enhance the luminescence of UO_2^{2+} in aqueous medium, we have examined the tolerance limit of water in acetonitrile and studied the effect of water on UO_2^{2+}-BA luminescence in acetonitrile medium. For these studies, steady state and lifetime experiments were performed after deliberate addition of water to the UO_2^{2+}-BA in acetonitrile. It must be noted that in all the experiments in acetonitrile medium, ~1% water was initially present to begin with. Figure 4.9 illustrates the variation of luminescence intensity of the UO_2^{2+}-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 lifetime decreases exponentially with increase in water content in acetonitrile (Figure 4.10a & 4.10b). This decrease in luminescence intensity as well as lifetime is due to the removal of acetonitrile by water molecules from the outer coordination sphere of the complex, as water can form stronger complex compared to acetonitrile. From the above studies, 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 content relative to acetonitrile. Above 20 % of water, the sharp UO_2^{2+} luminescence features become broader [Figure 4.9 in inset]. Therefore, it can be concluded that above 20 % of water in acetonitrile, hydroxide species of UO_2^{2+} dominates and hence the spectrum is broad and no sensitized luminescence of UO_2^{2+} observed, a situation similar to the one seen in pure aqueous medium.

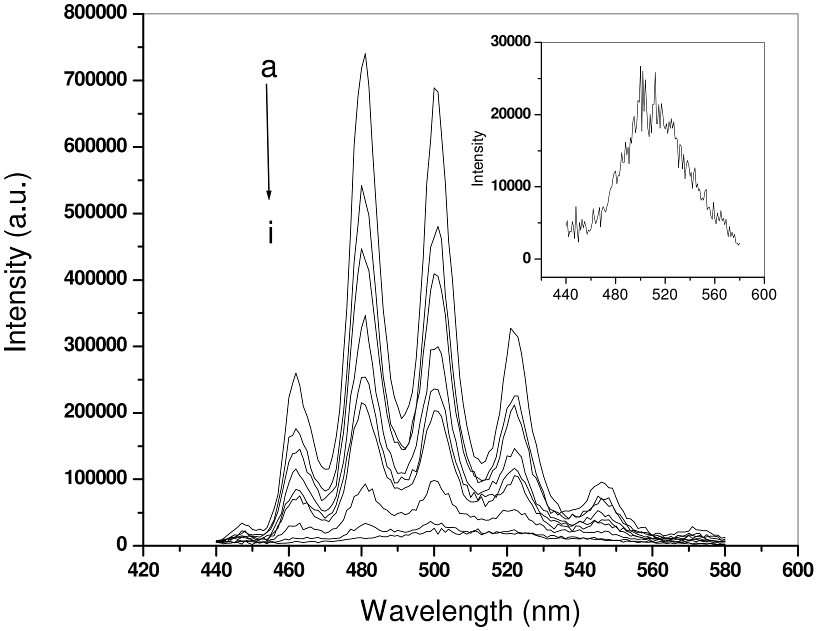

Figure 4.9 Luminescence spectra of UO_2^{2+}-BA complex in acetonitrile as a function of water (a) 1%; (b) 2%; (c) 4%; (d) 6%; (e) 8%; (f) 10%; (g) 15%; (h) 20%; (i) 25% content relative to acetonitrile; $[UO_2^{2+}]$ - $8x10^{-7}$ M, [BA] - $1x10^{-4}$ M, λ_{ex} = 243 nm. For clarity the spectra with 25% water is again shown in inset.

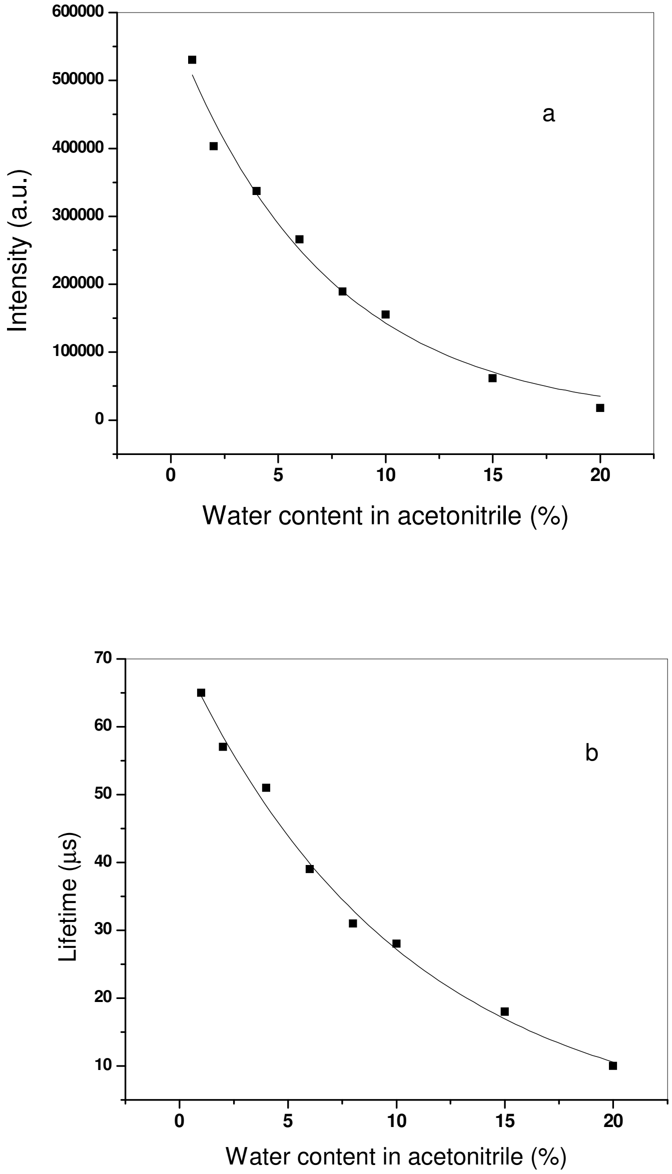

Figure 4.10 Plots showing the UO_2^{2+}-BA (a) intensity at 481 nm and (b) life time as a function of water content relative to acetonitrile; $[UO_2^{2+}]$-$8x10^{-7}$ M, [BA]-$1x10^{-4}$ M.

4.2.4 Structure of the complex

UV-Vis spectroscopy was used to see the possibility of characterizing the UO_2^{2+}-BA specie formed in the acetonitrile which is responsible for luminescence. Figure 4.11a shows the UV-Vis spectrum of UO_2^{2+} ($1x10^{-2}$ M) in acetonitrile. The spectrum exhibited three absorption bands which resembles the absorption of hydrated UO_2^{2+} specie [25]. 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 UO_2^{2+}. The UV-Vis spectra of solutions containing UO_2^{2+} ($2x10^{-3}$ M) with different benzoate concentration in acetonitrile are also shown in Figure 4.11b-4.11d. When UO_2^{2+} to ligand ratio is 1:3 (Figure 4.11c), UV-Vis spectra displayed three intense sharp peaks at 431, 443, 461 nm. Similar sharp peaks were first observed in the spectrum of $CsUO_2(NO_3)_3$, reported by Dieke and Duncan and were named as 'magnetic series' [26]. The absorption bands at this region were also reported in literature for uranyl tris-nitrato, uranyl tris-acetato complexes in ionic liquid medium [15]. The observation of these peaks in our experiment, which is typical for UO_2^{2+} complexes with D_{3h} symmetry [15], is a clear indication of formation of tris complex of UO_2^{2+}. Hence, we believe that the specie formed in acetonitrile medium could be $[UO_2(C_6H_5COO)_3]^-$. It is noted that in aqueous medium two benzoate ligands are coordinated to UO_2^{2+} [12]. A similar observation has been found [14] when UO_2^{2+} betaine complex dissolved in water showed spectrum similar to hydrated UO_2^{2+} indicating betaine ligands are no longer coordinated to UO_2^{2+}, and the same complex exhibited sharp intense peaks as if carboxylate groups of three betaine ligands remain co-ordinated after dissolution in acetonitrile. Luminescence spectra recorded at different UO_2^{2+} to benzoate ratio also supports the formation of this specie. Figure 4.12a-4.12e shows the luminescence spectra of UO_2^{2+}-BA at different UO_2^{2+} to benzoate ratio (1:1-1:5) in acetonitrile medium. The concentration of UO_2^{2+} is $4x10^{-5}$ M and concentration of benzoate is varied from $4x10^{-5}$ M to $2x10^{-4}$ M. It can

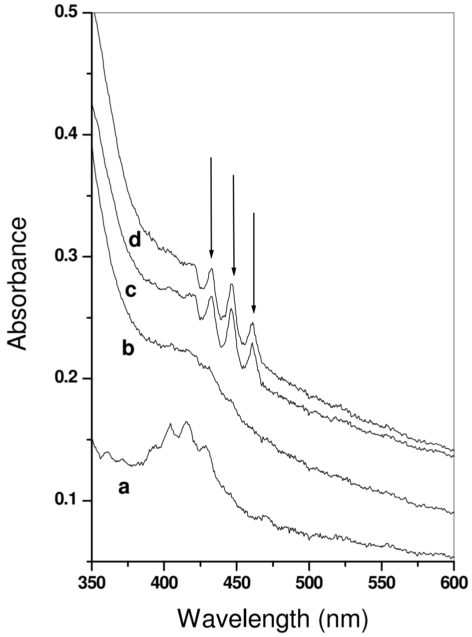

Figure 4.11 UV-Vis absorption spectra of (a) free UO_2^{2+}($1x10^{-2}$ M) and with different UO_2^{2+}($2x10^{-3}$ M) to benzoate ratio (b) 1:2; (c) 1:3; (d) 1:4 in acetonitrile. The three peaks shown by arrow are the characteristic of uranyl tris complex. The plots c & d are offset to Y axis by 0.05 units for clarity.

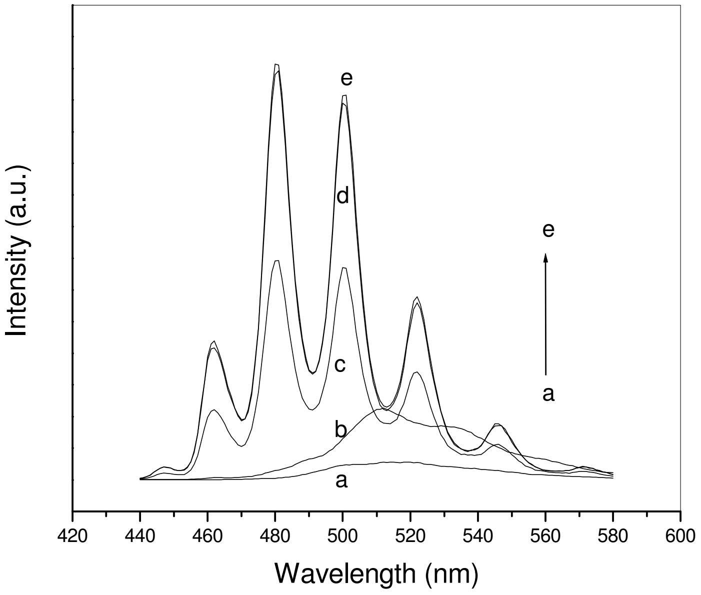

Figure 4.12 Luminescence spectra of UO_2^{2+} ($4x10^{-5}$ M) with different UO_2^{2+} to benzoate ratio in acetonitrile (a) 1:1; (b) 1:2; (c) 1:3; (d) 1:4 ; (e) 1:5; λ_{ex} = 243 nm for all cases.

be seen from Figure 4.12c that sharp features of UO_2^{2+}-BA luminescence originate when the UO_2^{2+} to benzoate ratio reaches 1:3. This observation is found to be consistent with other concentrations of UO_2^{2+} (2×10^{-5} M, 2×10^{-4} M and 2×10^{-3} M) also. For UO_2^{2+} to ligand ratio of 1:4 and above, no definite change in luminescence intensity is observed, thus concentration of $[UO_2(C_6H_5COO)_3]^-$ reached maximum when UO_2^{2+} to ligand ratio is 1:4. Nockmen *et al.* [15] also prepared tris nitrato compound of UO_2^{2+} by mixing 1:4 ratio of UO_2^{2+} 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 Figure 4.13.

4.2.5 Mechanism of ligand sensitization in acetonitrile

The UO_2^{2+} forms complex with benzoic acid in aqueous medium and the triplet energy of benzoic acid is 25641 cm^{-1} [27], while the UO_2^{2+} emitting energy level is about 22000 cm^{-1} [28], hence, one can expect intra-molecular energy transfer from the triplet level of benzoic acid to the excited electronic level of UO_2^{2+} to take place. Therefore, like lanthanides [29], UO_2^{2+} 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 to aqueous UO_2^{2+} solution [12]. Although benzoic acid might be transferring energy from its triplet level to UO_2^{2+}, it appears that the excited UO_2^{2+} are decaying non-radiatively and water molecules which are present in the coordination sphere of UO_2^{2+} 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 UO_2^{2+} 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

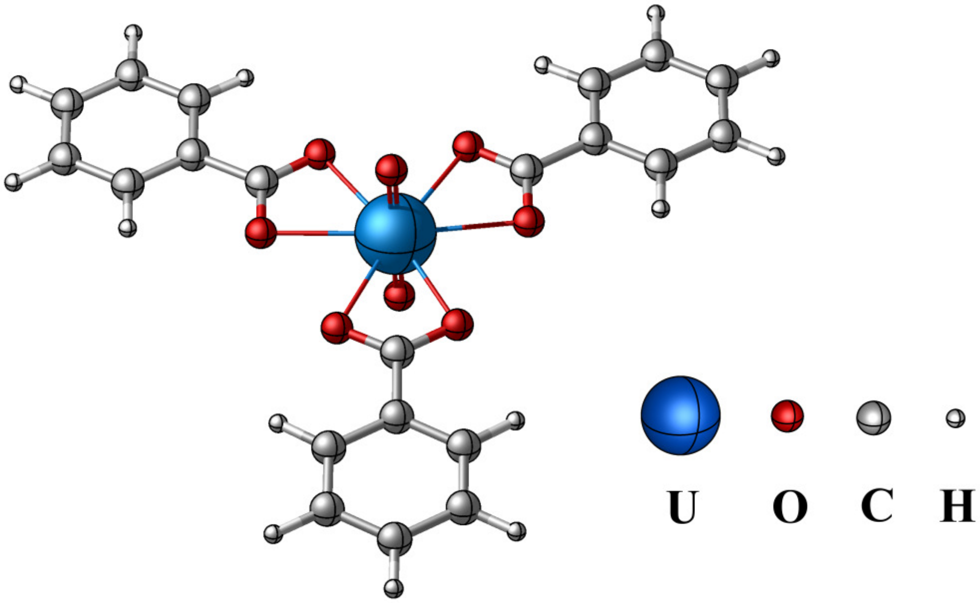

Figure 4.13 Schematic diagram of $[UO_2(C_6H_5COO)_3]^-$ having D_{3h} symmetry. Benzoate moieties are in the plane of the paper.

transfer to higher energy vibrational level of water molecules and thereby replacing one or more water molecule helped in reduction of non-radiative decay. In order to verify the different quenching behavior of Eu^{3+} and UO_2^{2+}, lifetime measurements were carried out in D_2O and values were compared with that of in H_2O. The luminescence lifetime is found to be increased from 110 μs (in H_2O) to 1800 μs for Eu^{3+}, whereas it remains same (1.5 μs) for UO_2^{2+} in D_2O. Therefore, it appears that quenching mechanism of UO_2^{2+}, which is governed by electron transfer, is more detrimental than energy transfer quenching. 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 UO_2^{2+}, 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.

4.2.6 Luminescence of UO_2^{2+} complexed with ortho, meta and para toluates

Like benzoic acid, toluic acids also do not enhance the luminescence of UO_2^{2+} in aqueous medium. In a similar fashion of UO_2^{2+}-benzoate, the luminescence of UO_2^{2+} is found to be enhanced by toluic acids in acetonitrile. Figure 4.14 shows the luminescence spectra of UO_2^{2+} complexed with ortho, meta & para toluates and compared with luminescence spectrum of uranyl benzoate, all in acetonitrile. It must be seen that the luminescence intensity of UO_2^{2+} complexed with toluates is in the order of *p* TA > *m* TA > *o* TA. It is to be noted that methyl acts as electron donating group and therefore one can expect larger luminescence intensity of UO_2^{2+} in toluate complexes compared to benzoate but contrary to this it is not true for UO_2^{2+}- *o* TA system. Lifetimes of these complexes were recorded in order to see this anomalous behavior. Table 4.2 presents the comparison of luminescence lifetimes for uranyl toluates and uranyl benzoate. Lifetimes of UO_2^{2+} complexed with meta

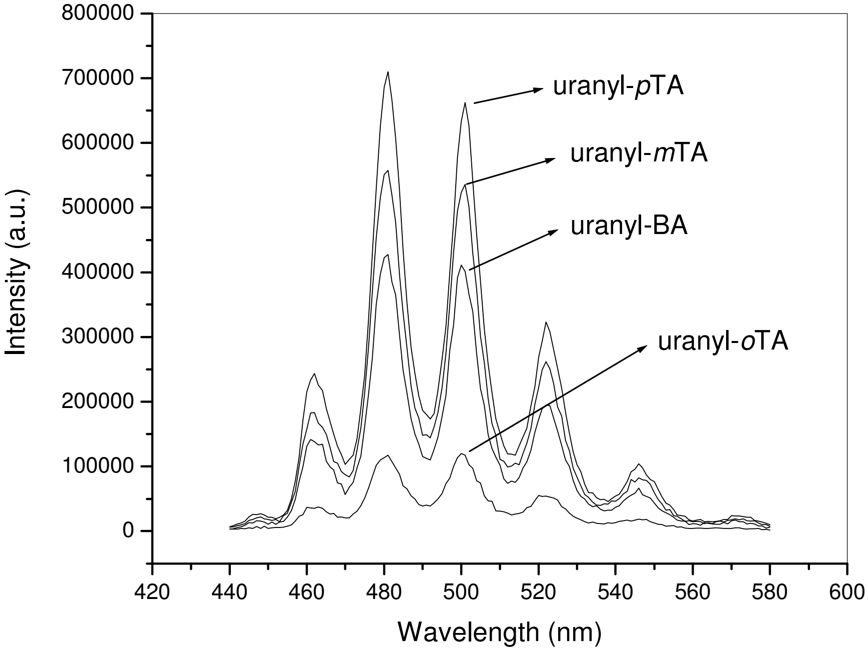

Figure 4.14 Comparison of luminescence intensity of UO_2^{2+}-BA and UO_2^{2+}-TA in acetonitrile medium; [UO_2^{2+}]-8.4 x 10^{-7} M, [Ligand]-1x10^{-4} M; λ_{ex} = 243 nm, 245 nm, 244 nm and 248 nm for UO_2^{2+}-BA, UO_2^{2+}-*o* TA, UO_2^{2+}-m TA, UO_2^{2+}-*p* TA, respectively.

Table 4.2 Luminescence lifetimes of UO_2^{2+}-BA and UO_2^{2+}-TA in acetonitrile medium.

System	Lifetime (μs) RSD = ± 5 %
UO_2^{2+}-BA	**68**
UO_2^{2+}-*o* TA	**15**
UO_2^{2+}-*m* TA	**56**
UO_2^{2+}-*p* TA	**65**

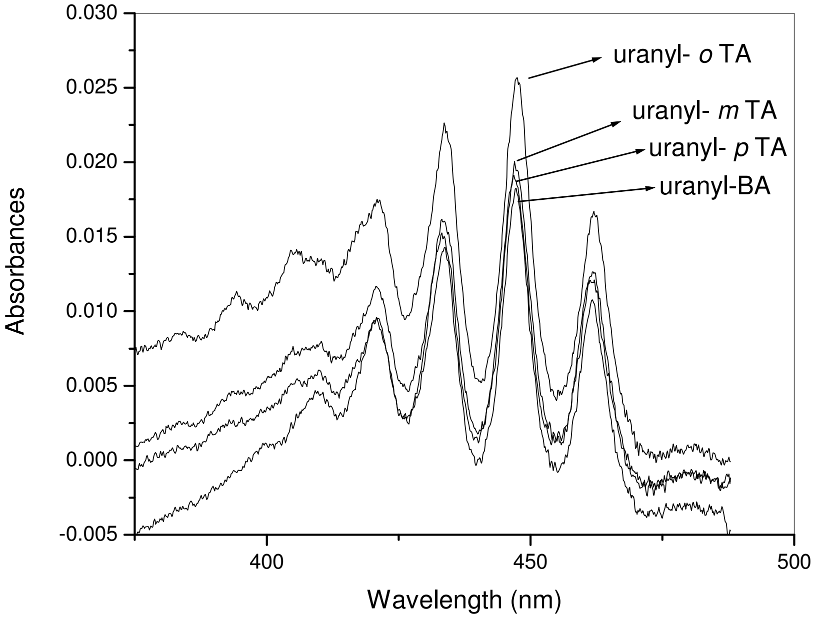

Figure 4.15 Comparison of absorption spectra of UO_2^{2+}-BA and UO_2^{2+}-TA in acetonitrile medium; $[UO_2^{2+}] = 1x10^{-3}$ M, [Ligand] = $4x10^{-3}$ M. All the spectra are blank subtracted.

and para toluate are 56 and 65 μs respectively and are comparable to uranyl benzoate. The lifetime of UO_2^{2+}-*o* TA is 15 μs, which is very less in comparison to other ligands. This indicates that presence of –CH oscillators at ortho position of carboxylate diminish the luminescence intensity sharply by non-radiative decay via collisions. In case of meta and para TA, –CH oscillators are quite away from carboxylate groups and hence not much effective in diminishing the luminescence intensity. Figure 4.15 shows the absorption spectra of UO_2^{2+}-toluates and all these spectra resemble the absorption spectrum of tris complex of UO_2^{2+}. It confirms that like uranyl benzoate, UO_2^{2+} forms tris complexes with toluates also and methyl group situated at different positions in the benzene ring does not interfere in complexation with UO_2^{2+}.

4.2.7 Analytical application of this study

The present study of UO_2^{2+} luminescence in acetonitrile medium finds an analytical application for UO_2^{2+} detection. The large enhancement of UO_2^{2+} luminescence in its complexes with benzoate and methyl substituted benzoates in acetonitrile medium can be used for trace level detection of UO_2^{2+}. Linearity in the luminescence intensity is seen over the UO_2^{2+} concentration range of $6.7x10^{-8}$ to $6.7x10^{-6}$ M for UO_2^{2+}-BA, $2.1x10^{-7}$ to $3.4x10^{-6}$ M for UO_2^{2+}-*o* TA, $8.4x10^{-8}$ to $1.7x10^{-6}$ M for UO_2^{2+}-*m* TA and $8.4x10^{-8}$ to $1.7x10^{-6}$ M for UO_2^{2+}-*p* TA. The typical calibration curve for UO_2^{2+}-BA is shown in Figure 4.16. The detection limit for uranium calculated using the criterion of 3σ is ~ $4.2x10^{-9}$ M in UO_2^{2+}-BA and UO_2^{2+}-*m* TA, $2.1x10^{-8}$ M in UO_2^{2+}-*o* TA and $3.2x10^{-9}$ M for UO_2^{2+}-*p* TA sytems.

4.3 Conclusions

In this work luminescence of UO_2^{2+} complexed with benzoic acid has been studied in acetonitrile and the data was compared with aqueous medium. In acetonitrile, luminescence spectra and especially UV-Vis spectroscopy studies revealed the formation of tri benzoate

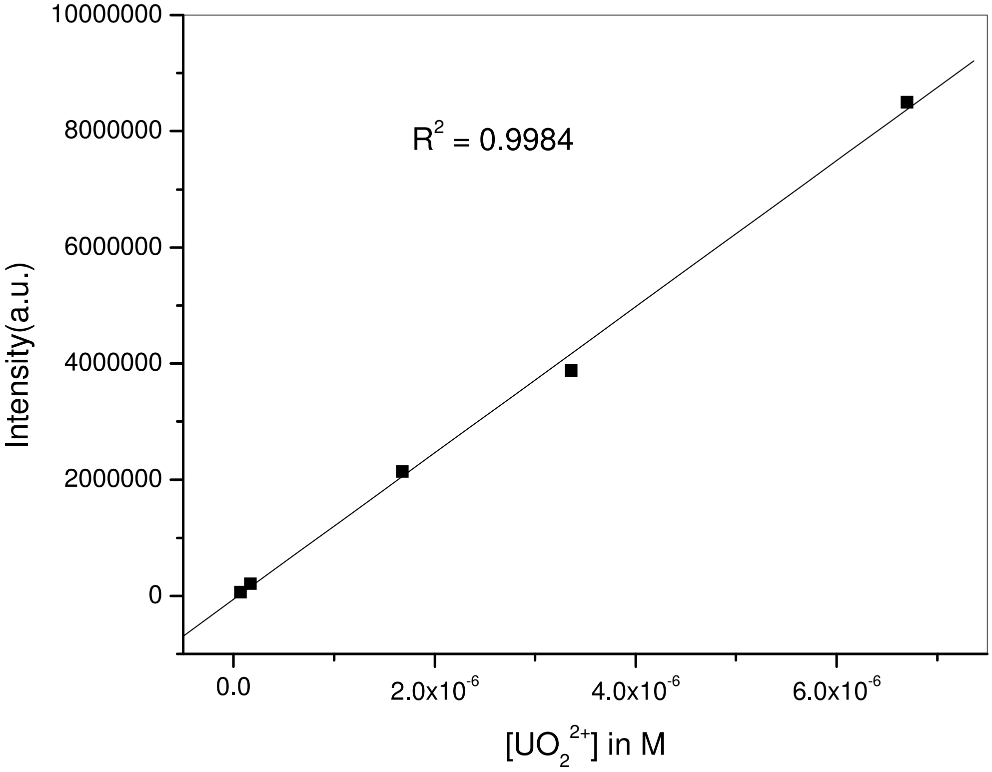

Figure 4.16 Plot of intensity of UO_2^{2+} luminescence at 481 nm in UO_2^{2+}-BA as a function of UO_2^{2+} concentration; [BA] = $1x10^{-4}$ M.

complex of UO_2^{2+} i.e. $[UO_2(C_6H_5COO)_3]^-$ which was highly luminescent. The lifetime of UO_2^{2+} in this complex was 68 μs which was more compared to 20 μs luminescence lifetime for uncomplexed UO_2^{2+} in acetonitrile medium. In contrary to aqueous medium where UO_2^{2+}-BA 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 fade at 20% (v/v) of water content. In the absence of BA, only one type of UO_2^{2+} hydroxide i.e. UO_2OH^+ dominates in this medium. Electron transfer quenching which caused the absence of sensitized luminescence of UO_2^{2+} by benzoic acid in aqueous medium is reduced by the formation of UO_2^{2+} complex coordinated by carboxylate groups of three benzoate and hence the enhancement in luminescence. The effect of methyl groups at different positions of benzoic acid has also been studied. Methyl group presented at ortho position of benzoic acid quenched the UO_2^{2+} luminescence by non-radiative decay. Luminescence intensity of UO_2^{2+} complexed with TA is in the order of *p* TA > *m* TA > *o* TA.

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CHAPTER 5 Luminescence studies on Eu^{3+}-picolinate & Eu^{3+}-dipicolinate systems

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5.1 Introduction

Luminescence of lanthanides sensitized by pyridine based carboxylic acids such as nicotinic acid, picolinic acid (PA) and dipicolinic acid (DPA) have been reported in aqueous medium by Panigrahi [1]. This author has reported that the luminescence intensity of Eu^{3+} and Tb^{3+} could be enhanced by two to three orders of magnitude when complexed with these ligands. To further enhance the luminescence of these lanthanides, a neutral ligand, trioctyl phosphine oxide (TOPO), in triton X-100 micellar medium was added to the complexes of Eu^{3+} and Tb^{3+}. However, the additional luminescence enhancement of these lanthanides, following the addition of TOPO was observed only with nicotinic acid.

Recently, a complexation study of Eu^{3+} with different ligands such as nicotinic acid, iso-nicotinic acid and picolinic acid has been repoted by Rao *et al.* in aqueous medium [2]. In their study, time resolved luminescence measurements indicated the formation of ML_4 complex of Eu^{3+} with picolinic acid, whereas only ML type complexes were formed in case of nicotinate and iso-nicotinate ligands. The complexation of dipicolinic acid with Eu^{3+} is widely studied in literature and it is well known that this ligand forms ML_3 complex with lanthanide ions in aqueous medium [3-4]. Ligands, PA and DPA bind to Eu^{3+} ion in bi-dentate and tri-dentate fashion, respectively, through nitrogen and oxygen donor atoms present in these ligands [2-3]. In case of PA, therefore, 8 coordinating sites of Eu^{3+} are occupied by four PA ligands while the entire coordinating sites of Eu^{3+} are coordinated by three DPA ligands in aqueous medium.

This chapter describes the luminescence study of Eu^{3+} complexed with picolinic and dipicolinic acid in acetonitrile medium. Similar to aqueous medium, both the ligands were found to sensitize the luminescence of Eu^{3+} in acetonitrile medium also. Lifetime measurements were carried out in order to identify the luminescent species. While, the stoichiometries of the Eu^{3+} complexes with these ligands are found to be similar as in aqueous medium, a large luminescence enhancement is observed in acetonitrile compared to aqueous medium. The large enhancement in luminescence intensity is attributed mainly to the reduction of non-radiative decay channels from outer coordination sphere of Eu^{3+}. The luminescence of Eu^{3+} complexed with DPA is found to be further enhanced due to co-luminescence, whereas no co-luminescence is observed in case of Eu^{3+}-PA in acetonitrile medium. Mechanism of co-luminescence enhancement is also discussed in this chapter.

5.2 Results and Discussion

5.2.1 Eu^{3+}-PA system

5.2.1.1 Luminescence studies of Eu^{3+}-PA in acetonitrile medium

At the outset, luminescence intensity of Eu^{3+}-PA in acetonitrile was measured as a function of PA concentration and pH of the solution. Figure 5.1 shows the variation of luminescence intensity of Eu^{3+}-PA complex ($[Eu^{3+}]$-$1x10^{-7}$ M) as a function of PA concentration at pH 4.5. The optimum ligand concentration was found to be $1x10^{-5}$ M and hence, this concentration was used in all our subsequent experiments. Figure 5.2 shows the variation of luminescence intensity of Eu^{3+}-PA complex at 615 nm as a function of pH. Maximum luminescence intensity was found over pH 4.5-5.0 for a given ligand concentration. In all our experiments pH of solutions was maintained at 4.5. The excitation spectra of Eu^{3+}-PA ($[Eu^{3+}]$-$1x10^{-7}$ M) recorded in acetonitrile is shown in Figure 5.3a. For comparison, excitation spectra recorded in aqueous medium for Eu^{3+}($1x10^{-5}$ M) -PA($1x10^{-3}$ M) complex is also shown in the Figure 5.3b. The excitation spectrum shown in Figure 5.3a observed for Eu^{3+}-PA in acetonitrile resembles that of Eu^{3+}-PA in aqueous medium (Figure 5.3b). In earlier luminescence studies carried out by Panigrahi [1], it has been shown that in

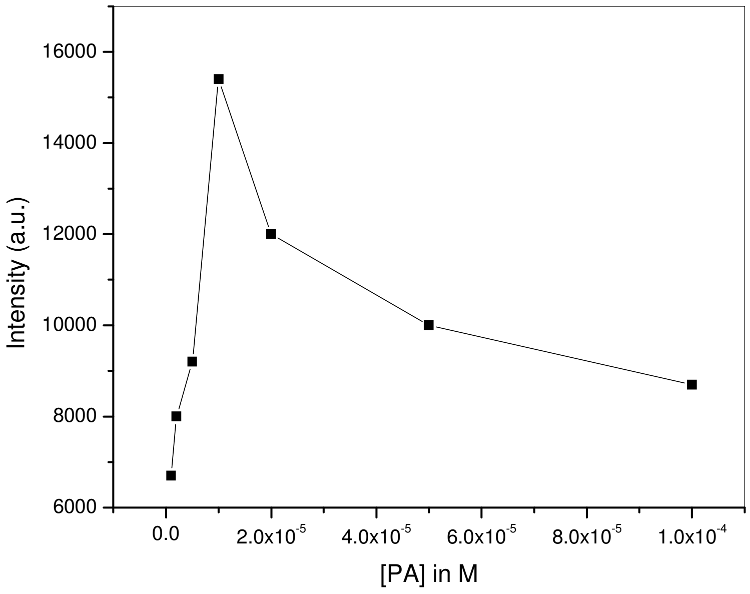


Figure 5.1 Variation of luminescence intensity of Eu^{3+}-PA complex at 615 nm as a function of concentration of PA in acetonitrile; pH 4.5, $[Eu^{3+}] = 1x10^{-7}$ M.

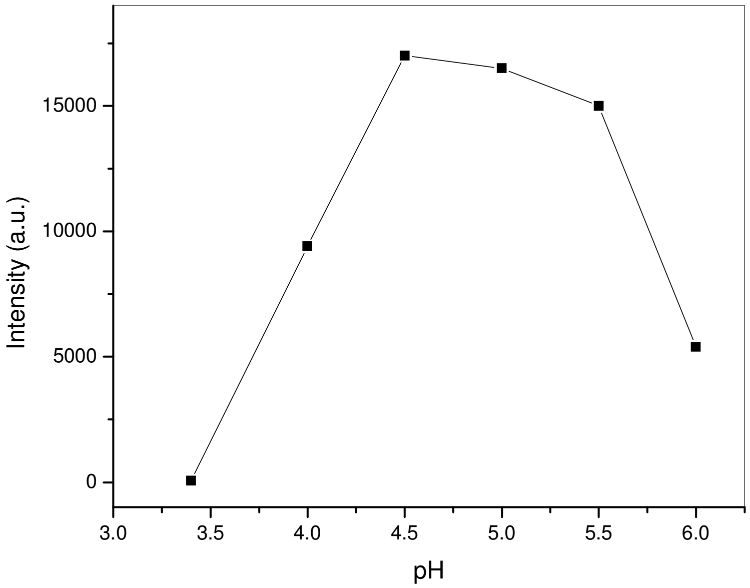


Figure 5.2 Variation of luminescence intensity of Eu^{3+}-PA complex at 615 nm as a function of pH in acetonitrile; $[Eu^{3+}] = 1x10^{-7}$ M, $[PA]=1x10^{-5}$ M.

aqueous Eu^{3+}-PA system, the picolinate is the absorber, which then sensitizes the luminescence of Eu^{3+}. Therefore, it indicates that in acetonitrile too, picolinate sensitizes Eu^{3+} luminescence. Though excitation spectra in both medium resembles, there is an 8 nm red shift in the excitation maxima of Eu^{3+}-PA (275 nm) in aqueous medium compared to acetonitrile medium (267 nm). This shift may be due to inner filter effect arising from the absorption of ligand as PA concentration is 100 times more than that of aqueous medium. Figure 5.4a and 5.4b show the luminescence spectra of Eu^{3+}-PA in acetonitrile and aqueous medium, respectively. The luminescence peak positions in Figure 5.4a and 5.4b are similar, indicating that the features at 592 and 615 nm are due to the $^5D_0$ - $^7F_1$ and $^5D_0$ - $^7F_2$ transitions, respectively. Although the intensity of Eu^{3+} in Eu^{3+}-PA complexes in acetonitrile medium shown in Figure 5.4a is almost double to that is the observed in aqueous medium (Figure 5.4b), the Eu^{3+} concentration in aqueous medium is 100 times more, manifesting that there is a huge enhancement in the luminescence of Eu^{3+}-PA in acetonitrile compared to the same in aqueous medium.

Figure 5.5a and 5.5b show the luminescence decay profiles of Eu^{3+}-PA in aqueous and acetonitrile medium, respectively. The luminescence lifetimes of Eu^{3+}-PA in water is 600 μs whereas it is 1200 μs in acetonitrile medium. Based on the lifetime values, number of inner sphere water molecules is calculated in both the medium using the equation 3.1 (chapter 3). The number of water molecule calculated in the inner sphere of Eu^{3+}-PA is close to one in aqueous medium. It indicates that eight water molecules have been replaced from the inner coordination sphere of Eu^{3+} after complexation with PA. Picolinate is a bi-dentate ligand and hence each PA would replace two water molecules. It indicates that eight water molecules are replaced by PA with a formation of ML_4 type complex in aqueous medium. A similar stoichiometry (1:4) of Eu^{3+}-PA was also observed by Rao *et al.* in aqueous medium [2]. On the other hand, in acetonitrile medium, the number of water molecules coordinated to Eu^{3+} in

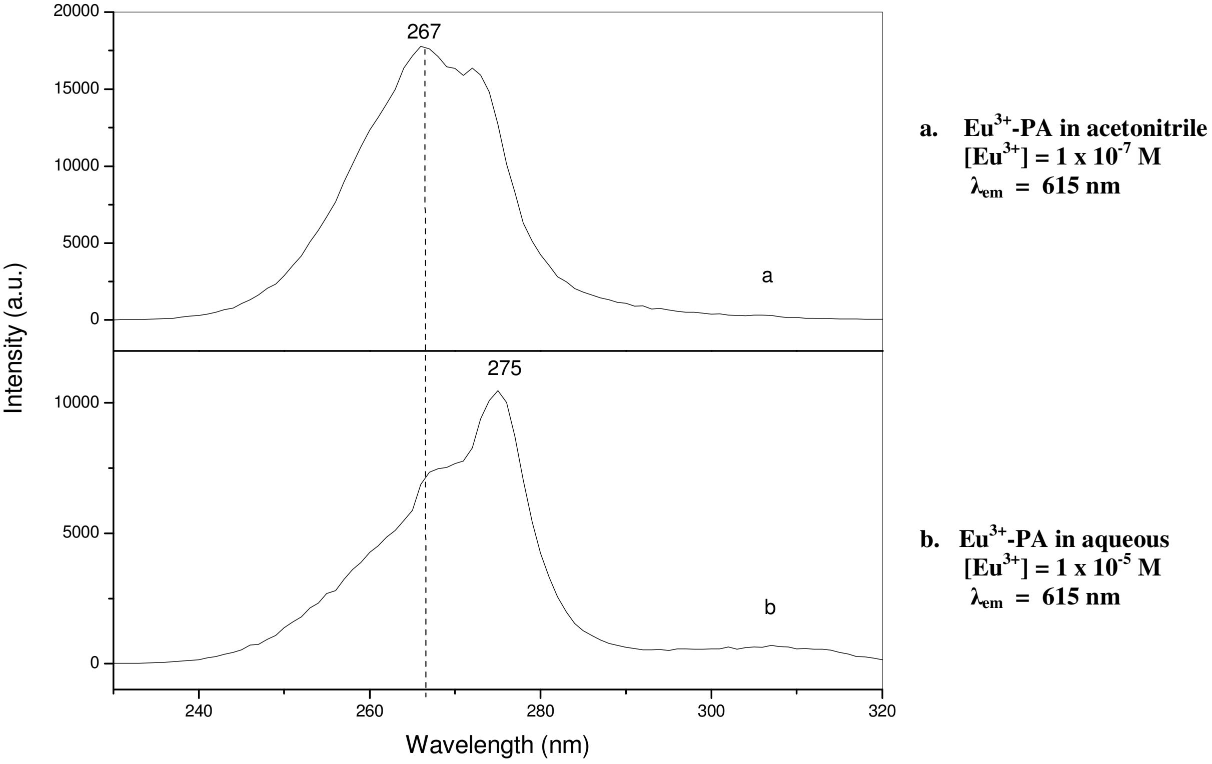
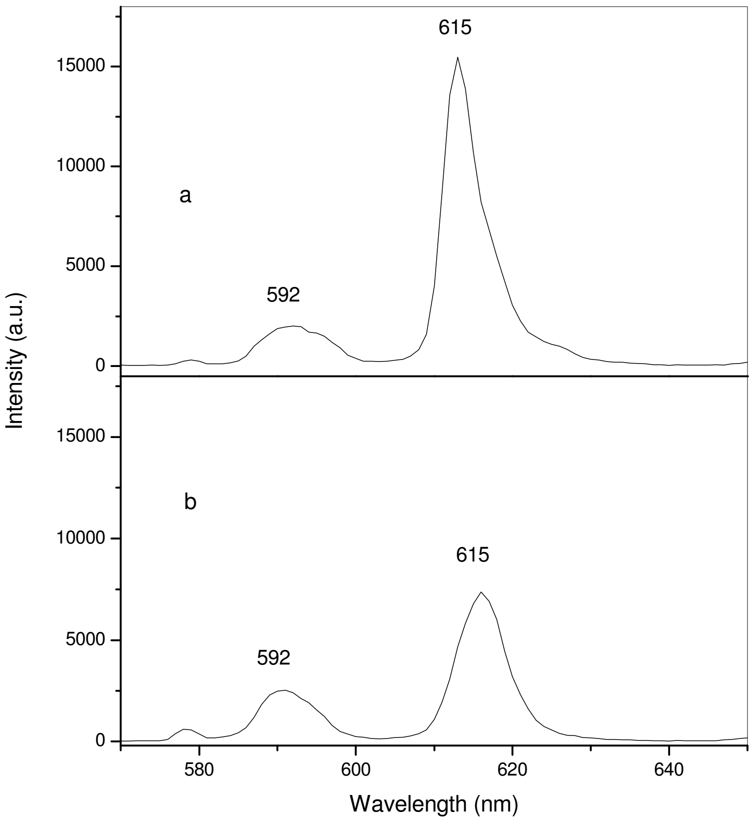


Figure 5.3 Excitation spectra (a) Eu^{3+} ($1x10^{-7}$ M)-PA ($1x10^{-5}$ M) in acetonitrile (b) Eu^{3+} ($1x10^{-5}$ M)-PA ($1x10^{-3}$M) in aqueous medium; pH 4.5. The emission wavelength used to record the spectra is 615 nm.



a. Eu^{3+}-PA in acetonitrile
$[Eu^{3+}] = 1.0 \times 10^{-7}$ M
λ_{ex} = 267 nm

b. Eu^{3+}-PA in aqueous
$[Eu^{3+}] = 1.0 \times 10^{-5}$ M
λ_{ex} = 275 nm

Figure 5.4 Emission spectra (a) Eu^{3+} ($1x10^{-7}$ M)-PA ($1x10^{-5}$ M) in acetonitrile (b) Eu^{3+} ($1x10^{-5}$ M)-PA ($1x10^{-3}$ M) in aqueous medium, pH 4.5. The excitation wavelength used to record each of the spectra is shown alongside.

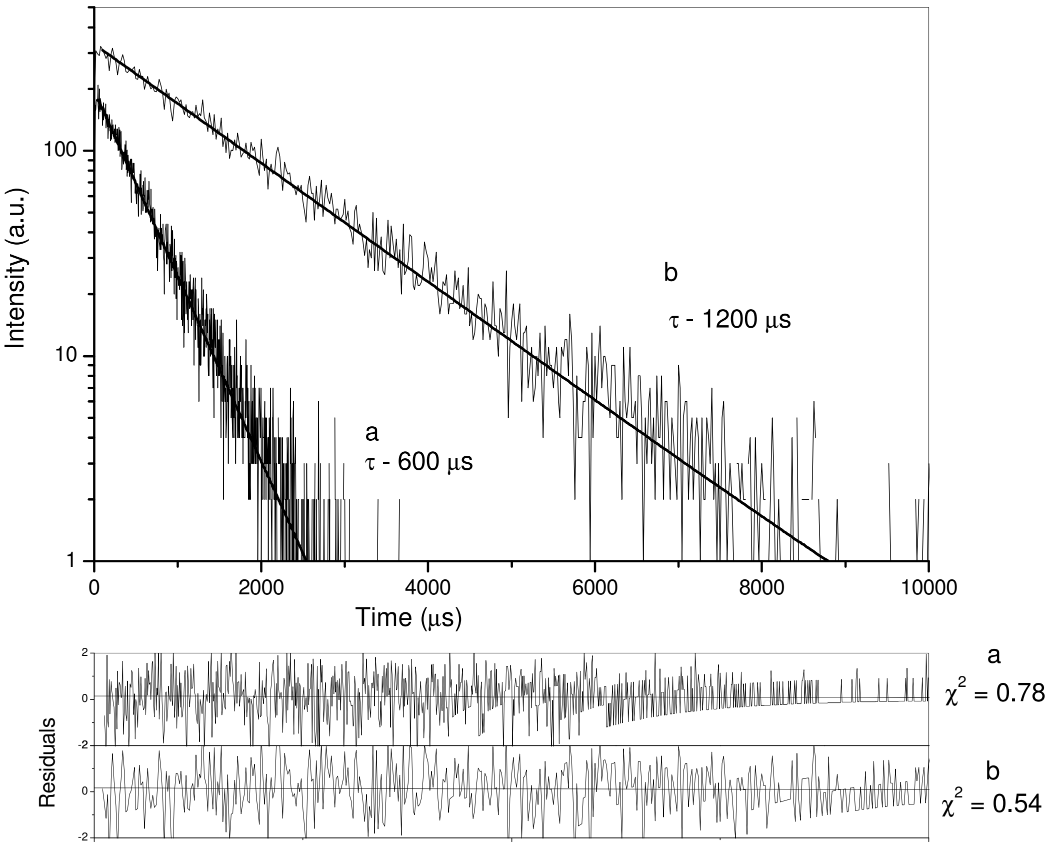


Figure 5.5 Luminescence decay profile of Eu^{3+}-PA in (a) aqueous, Excitation wavelength = 267 nm; Emission wavelength = 615 nm and (b) acetonitrile medium, Excitation wavelength = 275 nm; Emission wavelength = 615 nm.

its Eu^{3+}-PA complex based on lifetime is calculated to be zero. It indicates that in acetonitrile, all the water molecules in the inner sphere of Eu^{3+} are replaced either by PA or acetonitrile.

5.2.1.2 Composition of the Eu^{3+}-PA complex in acetonitrile

In order to find out the stoichiometry of Eu^{3+}-PA in acetonitrile medium, mole ratio method [5-6] was used. In this method, both luminescence lifetimes and intensity of Eu^{3+}-PA were plotted as a function of ratio of PA to Eu^{3+} concentrations as shown in Figure 5.6. It can be seen from this Figure that luminescence lifetime/intensity increases as a function of PA/ Eu^{3+} ratio and above a ratio of 1:4, it becomes nearly constant. It confirms that the stoichiometry of the complex Eu^{3+}-PA in acetonitrile medium is ML_4. Also, at this ratio, a lifetime value of 1200 µs indicates absence of water molecules leading to the fact that out of nine coordination sites of Eu^{3+}, eight sites are coordinated by PA ligand and remaining one is bonded by acetonitrile. The composition of the formed complex is proposed as $Eu(PA)_4(CH_3CN)$.

5.2.1.3 Analytical application of this study

The present study of Eu^{3+} luminescence in acetonitrile medium finds analytical application for detection of europium. The large enhancement of Eu^{3+} luminescence for Eu^{3+}-PA complex in acetonitrile medium can be used for trace detection of Eu^{3+}. Linearity in the luminescence intensity is seen over the Eu^{3+} concentration range of $4x10^{-9}$ to $4x10^{-7}$ M (Figure 5.7). The detection limit calculated using the criterion of 3σ of the noise is $\sim 1.5x10^{-10}$ M.

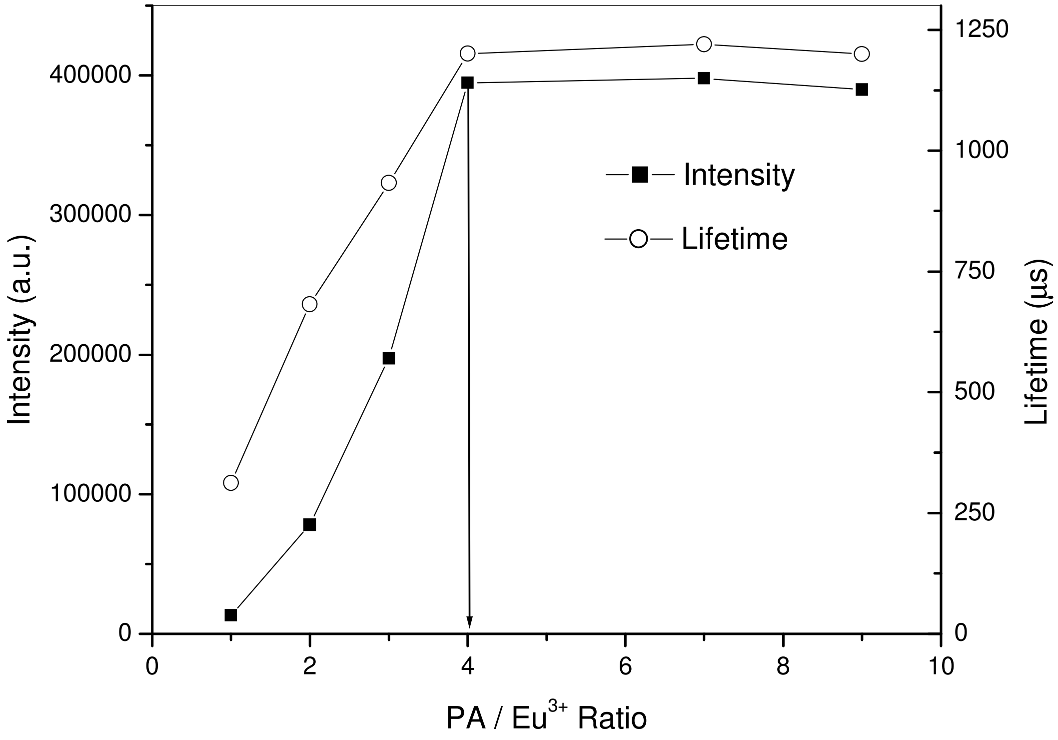


Figure 5.6 Variation of luminescence intensity at 615 nm and lifetime of Eu^{3+} ($1x10^{-5}$ M) with PA in acetonitrile at pH 4.5.

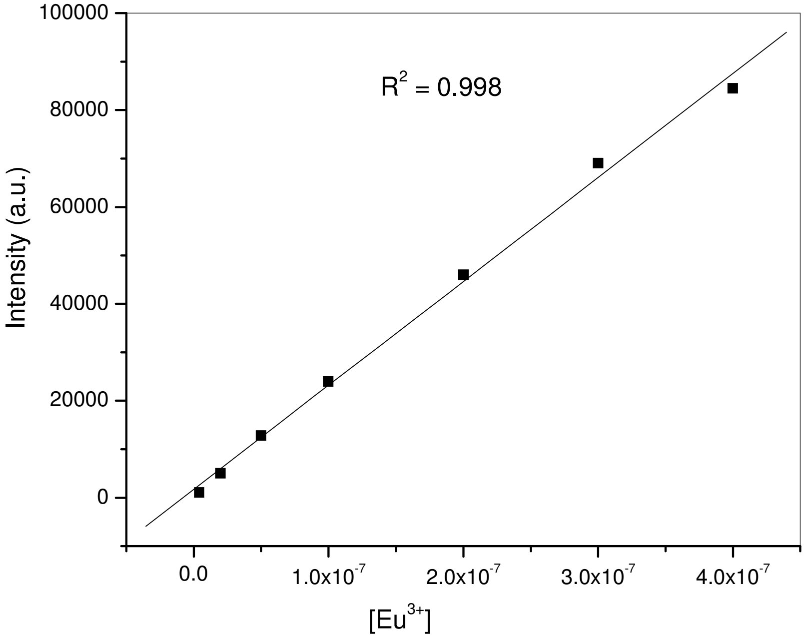


Figure 5.7 Plot of intensity of Eu^{3+} luminescence at 615 nm in Eu^{3+}-PA as a function of Eu^{3+} concentration; [PA] = $1x10^{-5}$ M; pH-4.5.

5.2.2 Eu^{3+}-DPA system

5.2.2.1 Luminescence studies of Eu^{3+}-DPA in acetonitrile medium

To begin with, luminescence intensity of Eu^{3+}-DPA in acetonitrile was measured as a function of DPA concentration and pH of the solution. Figure 5.8 shows the variation of luminescence intensity of Eu^{3+}-DPA complex ($[Eu^{3+}]$-$2.5x10^{-8}$ M), measured at 615 nm as a function of DPA concentration at pH 7.0. The maximum luminescence intensity was observed at a ligand concentration of $1x10^{-4}$ M and hence this concentration was used in all our subsequent experiments. Figure 5.9 shows the variation of luminescence intensity of Eu^{3+}-DPA complex at 615 nm as a function of pH. Maximum luminescence intensity was found at pH 7.0 for a given ligand concentration. Therefore, in all our experiments pH of solutions was maintained at 7.0. Figure 5.10a and 5.10b show the excitation spectra of Eu^{3+}-DPA, recorded in aqueous and acetonitrile medium, respectively by monitoring the luminescence at 615 nm. The excitation maxima of Eu^{3+}-DPA appeared at 279 nm for both the cases, indicating clearly a common absorber, namely DPA and these excitation maxima resembles to Eu^{3+}-DPA system reported earlier in aqueous medium [1]. Figure 5.11a and 5.11b show the luminescence spectra of Eu^{3+}-DPA in aqueous and acetonitrile medium, respectively. Although the concentration of Eu^{3+} in Eu^{3+}-DPA complexes in both of the medium are same ($[Eu^{3+}]$-$2.5x10^{-8}$ M), the luminescence intensity in acetonitrile is 1.5 times more compared to that in aqueous medium. It must be noted that there are no water molecules present at inner coordination sphere of Eu^{3+}-DPA in aqueous medium [3], the enhancement in acetonitrile can be expected to be due to removal of water molecules from the outer sphere of Eu^{3+}-DPA complex.

Figure 5.12 shows the decay profile of Eu^{3+}-DPA in aqueous and acetonitrile medium. The luminescence lifetimes of Eu^{3+}-DPA in aqueous medium is 1460 μs whereas it is 1890

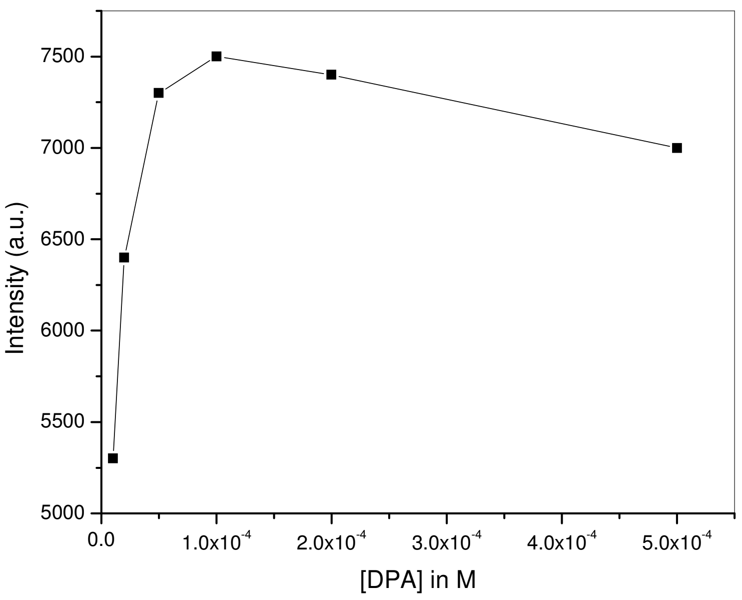


Figure 5.8 Variation of luminescence intensity of Eu^{3+}-DPA complex at 615 nm as a function of the concentration of DPA in acetonitrile; pH 7.0, [Eu^{3+}] = 2.5x10^{-8} M.

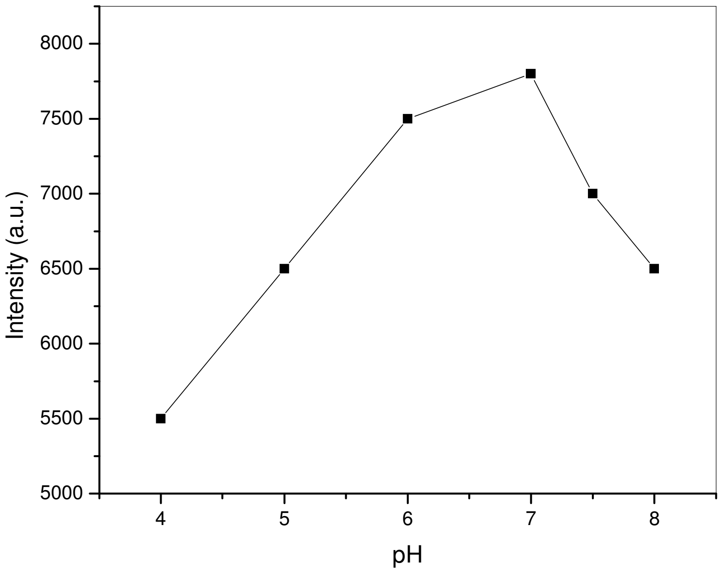
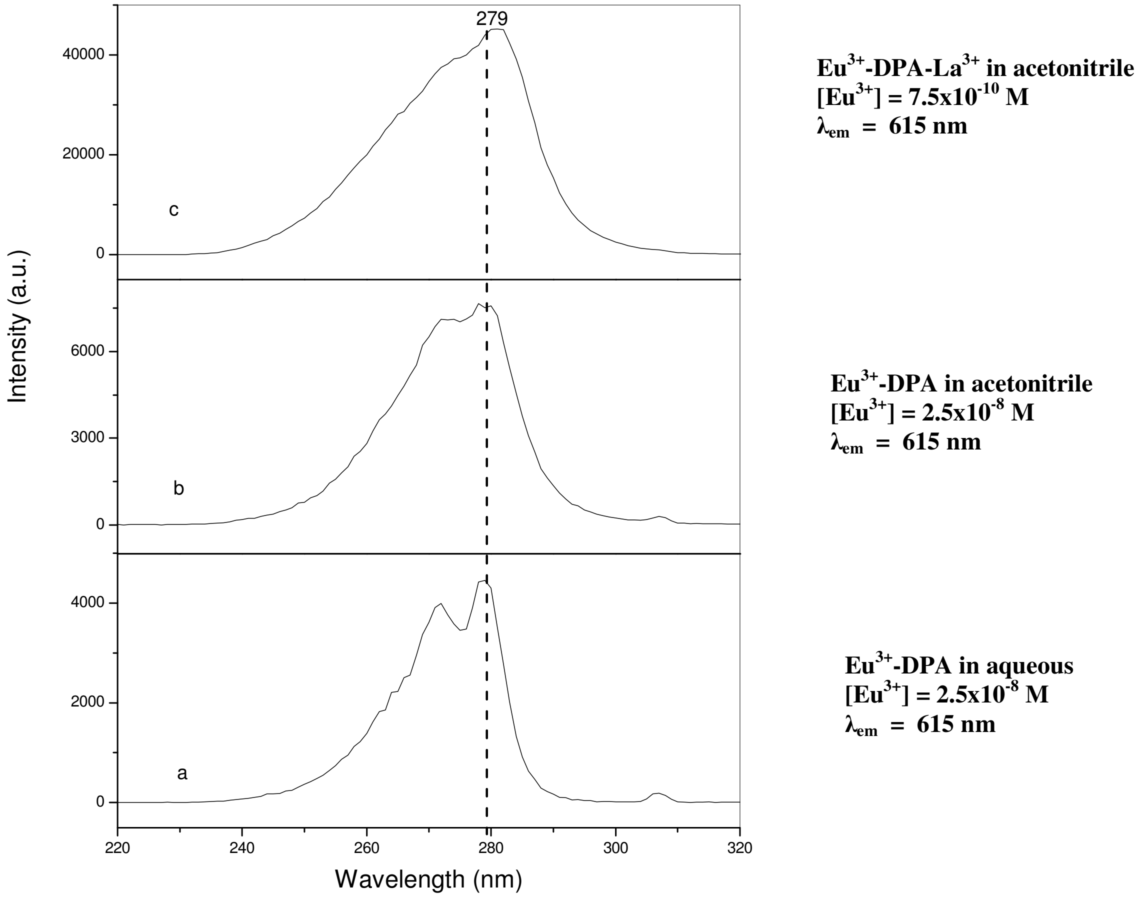


Figure 5.9 Variation of luminescence intensity of Eu^{3+}-DPA complex at 615 nm as a function of pH in acetonitrile; $[Eu^{3+}] = 2.5x10^{-8}$ M, [DPA]=$1x10^{-4}$ M.

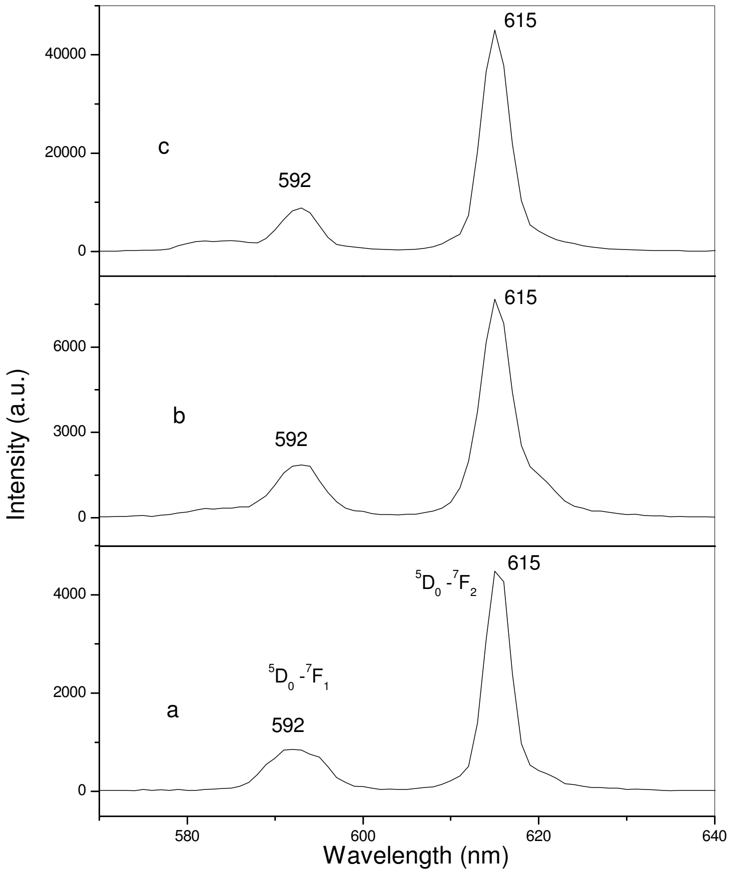


Eu^{3+}-DPA-La^{3+} in acetonitrile
[Eu^{3+}] = 7.5x10^{-10} M
λ_{em} = 615 nm

Eu^{3+}-DPA in acetonitrile
[Eu^{3+}] = 2.5x10^{-8} M
λ_{em} = 615 nm

Eu^{3+}-DPA in aqueous
[Eu^{3+}] = 2.5x10^{-8} M
λ_{em} = 615 nm

Figure 5.10 Excitation spectra of (a) Eu^{3+} (2.5x10^{-8} M)-DPA (1x10^{-4} M) in aqueous; (b) Eu^{3+} (2.5x10^{-8} M)-DPA (1x10^{-4} M) in acetonitrile; (c) Eu^{3+} (7.5x10^{-10} M)-DPA (1x10^{-4} M) -La^{3+}(1x10^{-5} M) in acetonitrile. The emission wavelength used to record the spectra is 615 nm.



Eu^{3+}-DPA-La^{3+} in acetonitrile
[Eu^{3+}] = 7.5x10^{-10} M
λ_{ex} = 279 nm

Eu^{3+}-DPA in acetonitrile
[Eu^{3+}] = 2.5x10^{-8} M
λ_{ex} = 279 nm

Eu^{3+}-DPA in aqueous
[Eu^{3+}] = 2.5x10^{-8} M
λ_{ex} = 279 nm

Figure 5.11 Emission spectra of (a) Eu^{3+} (2.5x10^{-8} M)-DPA (1x10^{-4} M) in aqueous; (b) Eu^{3+} (2.5x10^{-8} M)-DPA (1x10^{-4} M) in acetonitrile; (c) Eu^{3+} (7.5x10^{-10} M)-DPA (1x10^{-4} M) -La^{3+}(1x10^{-5} M) in acetonitrile. The excitation wavelength used to record the spectra is 279 nm.

μs in acetonitrile medium. Based on the lifetime values, number of inner sphere water molecules were calculated in both the mediums. The number of water molecule calculated using equation 3.1 presented in chapter 3, in the inner sphere of Eu^{3+}-DPA is almost zero in both the mediums. The lifetime of DPA complexes of Eu^{3+} got increased from 1460 (in water) to 1890 μs when acetonitrile was used as solvent. Although, in aqueous medium, DPA replaces all the water molecules coordinated to inner sphere of Eu^{3+}, enhancement in luminescence lifetime, when acetonitrile is used as solvent, can be expected due to the reduction of non-radiative decay channels from the bulk of the solvent. Similar observations were reported for Sm^{3+} complexes when solvent was changed from water to imidazolium ionic liquid namely, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [7]. The lifetime of Sm^{3+} was 21 μs when Sm^{3+}-DPA complex was in aqueous medium whereas it was increased to 61 μs when the complex was dissolved in ionic liquid.

5.2.2.2 Composition of the complex

It is well known that Eu^{3+} forms very strong tris complex with DPA in aqueous medium [3]. In order to get the stoichiometry of Eu^{3+}-DPA in acetonitrile medium, the mole ratio method has been used. In this method, both luminescence lifetime as well as intensity of Eu^{3+}-DPA are plotted as a function of ratio of concentrations of DPA to Eu^{3+}. Figure 5.13 shows the plot of luminescence lifetimes/intensity vs. ratio of concentrations of DPA to Eu^{3+}. It can be seen from this Figure that luminescence lifetime/intensity increases as a function of DPA/ Eu^{3+} ratio and reaches maximum at a ratio of DPA to Eu^{3+} 1: 3, and remains nearly constant above this ratio. It confirms the stoichiometry ML_3 for the Eu^{3+}-DPA complex in acetonitrile medium and the complex formed is proposed to be as $Eu(DPA)_3$.

5.2.2.3 Co-luminescence

When La^{3+} was added to Eu^{3+}-DPA complexes in acetonitrile, co-luminescence was observed with enhanced luminescence intensity of Eu^{3+}. The enhancement due to co-

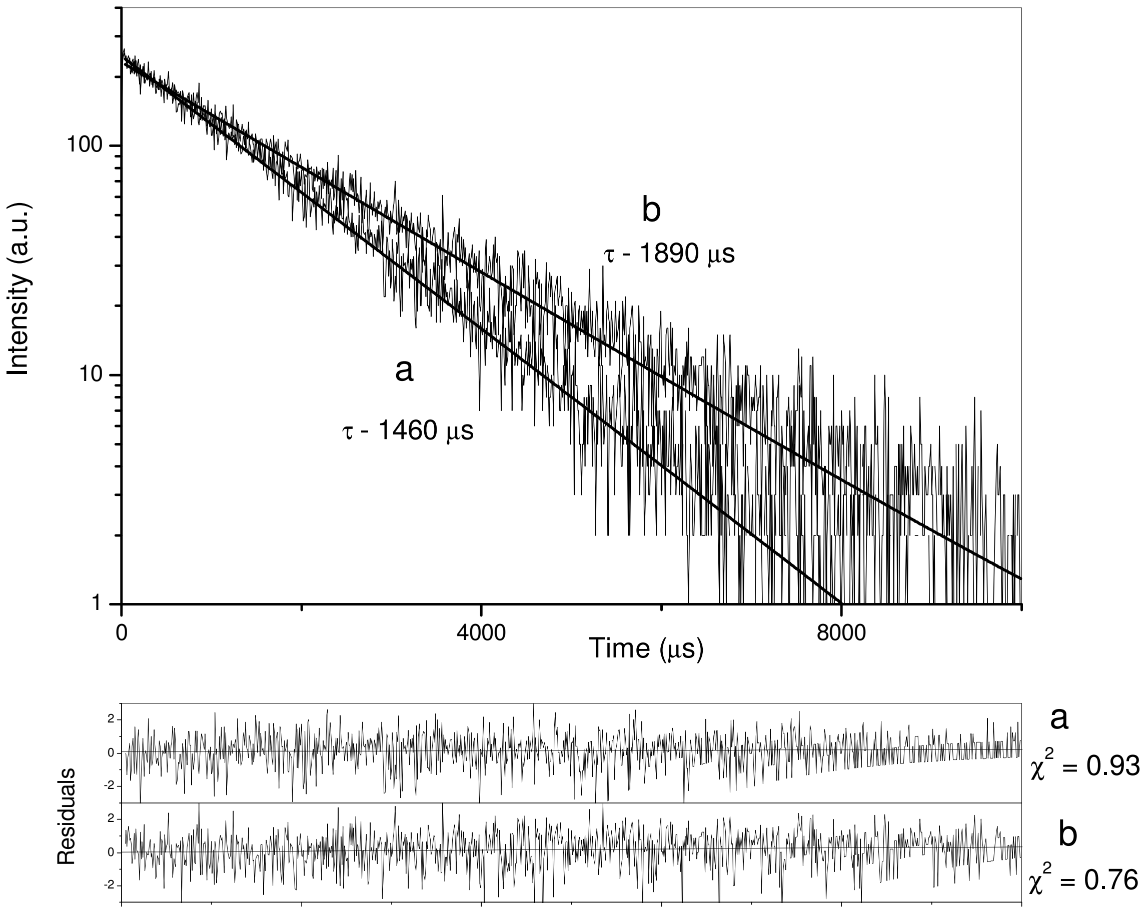


Figure 5.12 Luminescence decay profile of Eu^{3+}-DPA in (a) aqueous and (b) acetonitrile medium. Excitation wavelength = 279 nm; Emission wavelength = 615 nm for both the cases.

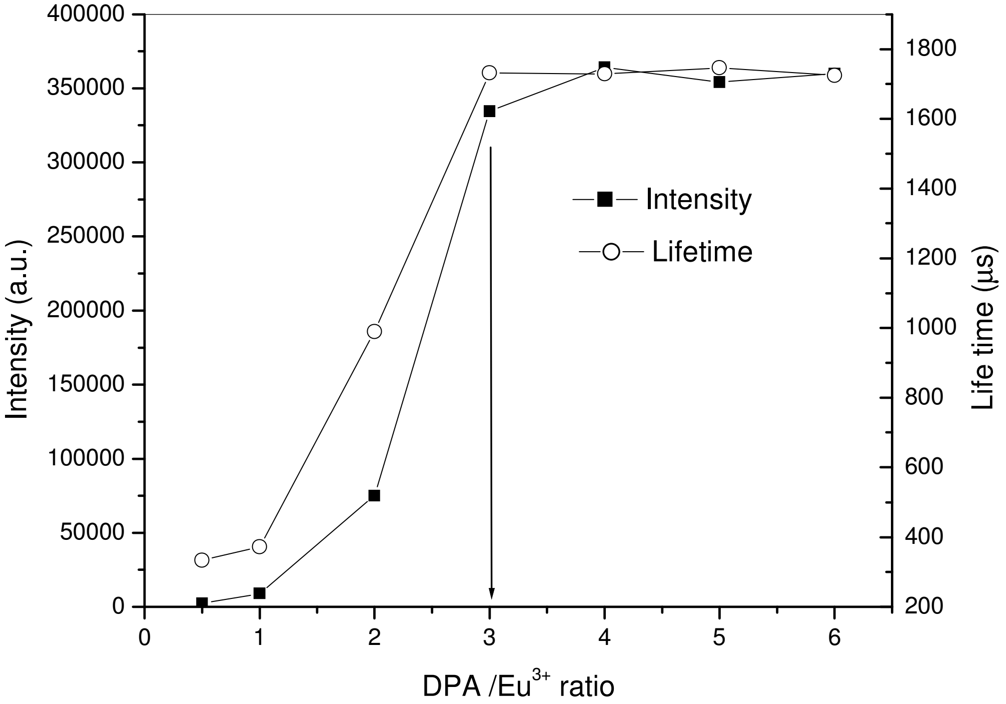


Figure 5.13 Variation of luminescence intensity at 615 nm and lifetime of Eu^{3+} (1x10^{-5} M) with DPA in acetonitrile at pH 4.5.

luminescence was found to be maximum for 1x10^{-5} M of La^{3+} for a fixed concentration of ligand. The luminescence intensity was also observed as a function of time. The result showed that the luminescence intensity reached a maximum after 25 minutes of preparation of the sample and remained constant for more than 1 hour. In all the experiments of co-luminescence, therefore, the luminescence intensity was measured 30 min after the preparation of the sample. Figure 5.10c and 5.11c show the excitation and emission spectra of Eu^{3+}-DPA-La^{3+} system respectively, in acetonitrile medium. The concentration of Eu^{3+} used to record these spectra was 7.5x10^{-10} M and this concentration is much lower than the concentration used to record the spectra of Eu^{3+}-DPA without the La^{3+} (2.5x10^{-8} M, Figure 5.11b). Enhancement in luminescence intensity by the addition of La^{3+} is about 160 times due to co-luminescence. Figure 5.14 shows the luminescence decay profile of Eu^{3+}-DPA-La^{3+} system in acetonitrile medium. This decay profile could be fitted to a mono exponential decay of lifetime 1700 μs indicating single luminescent specie.

In the study of ultra-trace determination of lanthanides by luminescence enhancement, Jenkins *et al.* [8] had reported that the luminescence of Tb^{3+} and Eu^{3+} coordinated to DPA in water was further enhanced by the addition of co-fluorescent ions such as La^{3+}, Y^{3+}, Tb^{3+} and Gd^{3+}. They explained that the most efficient excitation path was through a lanthanide ion excitation rather than the excitation through the absorption band of the ligand DPA. However, in our study we have observed that the luminescence and co-luminescence of Eu^{3+} were maximum only when DPA band was excited in acetonitrile. In fact in our studies, in aqueous medium, Eu^{3+} did not show any co-luminescence with DPA and similar observations were also reported by Panigrahi [1].

5.2.2.4 Analytical application of this study

The present study of Eu^{3+} luminescence in acetonitrile medium finds analytical application for europium detection. The large enhancement of Eu^{3+}-DPA-La^{3+} system in

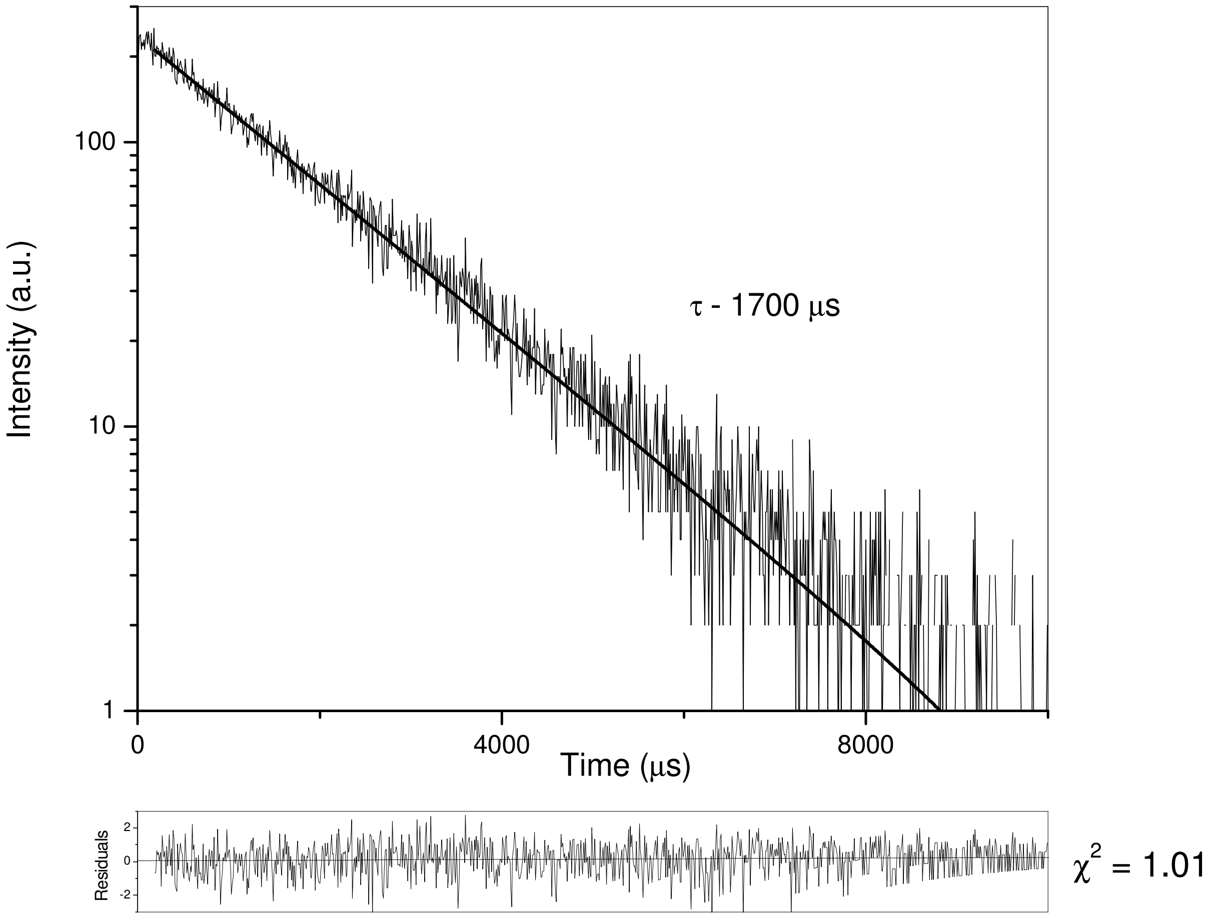


Figure 5.14 Luminescence decay profile of Eu^{3+}-DPA-La^{3+} in acetonitrile medium. Excitation wavelength = 279 nm; Emission wavelength = 615 nm.

acetonitrile medium can be used for trace detection of Eu^{3+}. Under optimal experimental conditions, the luminescence intensity of the co-luminescence systems shows linear relationship in the concentration range of $5x10^{-10}$ to $1x10^{-8}$ M for Eu^{3+} ions (Figure 5.15). The detection limit (3σ) was determined to be $4x10^{-11}$ M for Eu^{3+}. This is the best detection limit for Eu^{3+} among all the ligands studied in this thesis.

5.2.2.5 Co-luminescence mechanism

In case of aromatic carboxylic acids, it is believed that the formation of poly-nuclear complexes is responsible for the co-luminescence [9]. DPA is a tridentate ligand and it forms tris complex with Eu^{3+} resulting in all coordinating sites occupied by Eu^{3+}. Therefore, poly-nuclear complex formation can be ruled out when La^{3+} is added to Eu^{3+}-DPA complex. However, it is possible that co-precipitate of Eu^{3+}-DPA and La^{3+}-DPA complexes are being formed and intermolecular energy transfer can take place from La^{3+}-DPA complex to Eu^{3+}-DPA complex which will lead to an enhancement in luminescence intensity of Eu^{3+}. It must be noted that C≡N oscillators of acetonitrile have low vibrational energy ($V_{C≡N}$ =2253 cm^{-1}) compared to –OH oscilators ($V_{O\text{-}H}$ =3450 cm^{-1}) and hence it is less effective in luminescence quenching. In literature also, it is well reported that O-H vibrations quench the luminescence more effectively than other vibrations like C-H, C=O, S=O etc. [10-12]. The OH vibrations of water molecules present at secondary co-ordination sphere of Eu^{3+} take away the energy transferred by La^{3+}-DPA to Eu^{3+}-DPA complex, non-radiatively, and hence, inhibit further enhancement in luminescence which results in the absence of co-luminescence in aqueous medium. Co-luminescence using methanol as a solvent was also studied and found to be similar to the one seen in aqueous medium.

It is observed that the lifetime of the co-luminescence system has decreased by about 190 μs (from 1890 μs to 1700 μs). Similar trend of reduction in lifetime was also reported for the co-luminescence system of Tb^{3+} where lifetime has decreased from 400 μs (luminescent

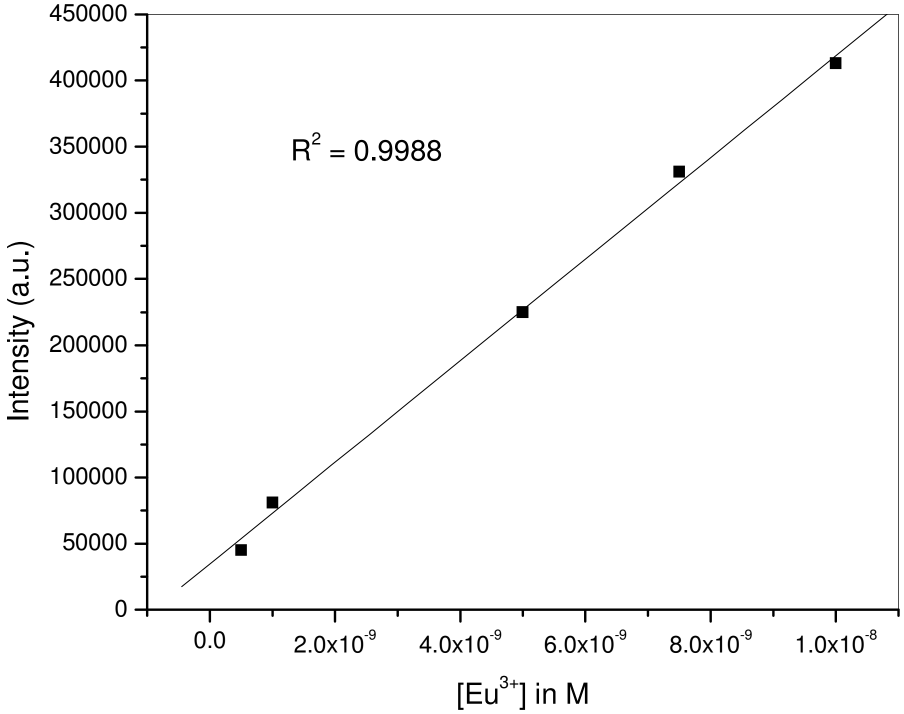


Figure 5.15 Plot of intensity of Eu^{3+} luminescence at 615 nm in Eu^{3+}-DPA-La^{3+} as a function of Eu^{3+} concentration; [DPA] = $1x10^{-4}$ M.

system) to 323 μs [13]. In the present study, formation of tiny particles were not observed to naked eye. But the fact that the co-luminescence intensity is time dependent, suggest the formation of co-precipitate of Eu^{3+}-DPA and La^{3+}-DPA. Acetonitrile, being less polar than water may favor the close proximity between the co-fluorescing specie (La^{3+}-DPA) and the fluorescing specie (Eu^{3+}-DPA). This close proximity results in efficient energy transfer but does not promote increase in lifetime. However, such a process is not possible in aqueous medium where solvation of both ions occur leaving the ions away from each other.

5.3 Conclusions

Luminescence of Eu^{3+} has been studied in its complexes with PA and DPA in acetonitrile medium. The luminescence enhancement of Eu^{3+} in these complexes are found to be more in acetonitrile medium compared to aqueous. The stoichiometries of the Eu^{3+}-PA and Eu^{3+}-DPA complexes in acetonitrile are found to be ML_4 and ML_3, respectively and these stoichiometry are same as that in aqueous medium. Therefore, we believe more luminescence enhancement in acetonitrile is due to the reduction in non-radiative deactivation processes due to removal of water molecules from bulk of the solvent. Co-luminescence enhancement following the addition of La^{3+} to Eu^{3+}-DPA is observed in acetonitrile medium. Intermolecular energy transfer is believed to be responsible for co-luminescence.

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CHAPTER 6 Luminescence studies on UO_2^{2+}-picolinate & UO_2^{2+}-dipicolinate systems

6.1 Introduction

Picolinic acid (PA) has been shown to sensitize the luminescence of lanthanide ions in aqueous medium [1] but no work has been carried out towards the luminescence of UO_2^{2+} complexed with PA in literature. Luminescence of UO_2^{2+} complexed with dipicolinic acid (DPA) in aqueous medium has been carried out by Maji *et al.* [2]. In their study, dipicolinic acid has been shown to efficiently sensitize and enhance the luminescence of UO_2^{2+} in aqueous medium. There are no literatures available on the complexation of picolinic acid with UO_2^{2+} although interaction of picolinic acid with other actinides such as neptunium has been reported in literature [3]. Therefore, in order to understand the luminescence behavior of UO_2^{2+}-PA, a study on complexation of UO_2^{2+}-PA system has been carried out.

In this chapter luminescence of UO_2^{2+} complexed with picolinic acid and dipicolinic acid has been studied in aqueous and acetonitrile medium. In aqueous medium, the UO_2^{2+} luminescence is quenched when it is complexed with picolinic acid. In contrary to aqueous medium, UO_2^{2+} luminescence was found to be enhanced by picolinic acid in acetonitrile medium. Excitation spectra along with lifetime data suggest that enhancement is due to sensitization of UO_2^{2+} luminescence by picolinate ion and reduction of non-radiave decay channels in acetonitrile medium. UV-Vis spectroscopy studies reveal the formation of 1:2 type complex of UO_2^{2+} with picolinate in acetonitrile. This chapter also presents detailed luminescence studies on UO_2^{2+} complexed with DPA in acetonitrile medium. The enhancement in luminescence intensity because of sensitization by DPA in this medium is found to be one order better than in aqueous medium. With the steady state and lifetime results, complexation of DPA with UO_2^{2+} are assessed and discussed. The luminescence of UO_2^{2+} complexed with DPA is found to be further enhanced due to co-luminescence, whereas no co-luminescence is observed in case of UO_2^{2+} complexed with PA in acetonitrile medium. Mechanism of co-luminescence will also be discussed in this chapter.

6.2 Results and Discussion

6.2.1 UO_2^{2+}-PA system

6.2.1.1 Luminescence study of UO_2^{2+}-PA in aqueous medium

Figure 6.1a shows the luminescence spectra of free UO_2^{2+} at a concentration of $2x10^{-4}$ M in aqueous medium at pH 2.8. The well resolved sharp peaks at 488, 509, 532 and 559 nm are due to the different vibrational levels in the ground electronic state of UO_2^{2+} [4]. The effect of PA to UO_2^{2+} luminescence is shown in Figure 6.1b-6.1h. It can be seen from the Figure 6.1 that the addition of PA to UO_2^{2+} solution results in quenching of UO_2^{2+} luminescence. The decrease in luminescence intensity of UO_2^{2+} indicates the complex formation between UO_2^{2+} and picolinate ions and we believe that UO_2^{2+}-PA complex does not show any luminescence as no shift in peak positions of emission spectra are observed.

For a given pH, complex formation of UO_2^{2+}-PA can be described by the following equilibrium with ‘x’ as stoichiometric coefficient:

$$UO_2^{2+} + x\ PA \quad \leftrightarrow \quad UO_2^{2+}(PA)_x \qquad \text{---------------} \ 6.1$$

The equilibrium constant K of the above equilibrium is given by:

$$K = \frac{[UO_2^{2+}(PA)_x]}{[UO_2^{2+}]\,[PA]^x} \qquad \text{----------------} \ 6.2$$

The concentration of the complex can be correlated with the intensity of UO_2^{2+} luminescence as the UO_2^{2+}-PA complex is non-luminescent. To get the stoichiometry of the complex, slope analysis method [5] has been used and it is shown in Figure 6.2. It can be seen from this

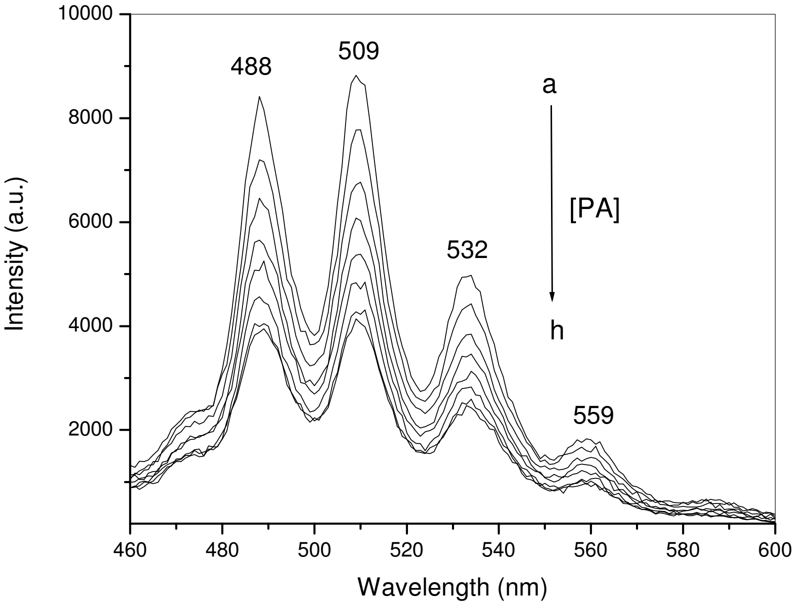

Figure 6.1 Luminescence spectra of UO_2^{2+}-PA complex in water as a function of PA concentration at pH 2.8 (a) 0 M ; (b) $2x10^{-5}$ M; (c) $4x10^{-5}$ M; (d) $6x10^{-5}$ M; (e) $8x10^{-5}$ M; (f) $1x10^{-4}$ M; (g) $1.2x10^{-4}$ M; (h) $1.4x10^{-4}$ M ; $[UO_2^{2+}]$ - $2x10^{-4}$ M, λ_{exc} = 250 nm.

Figure that the log–log plot of [UO_2^{2+} (PA) $_x$]/ [UO_2^{2+}] vs. [PA] gives a straight line with slope 1.10 ± 0.01, which confirms that single complex with stoichiometry 1:1 is formed. The stability constant of this 1:1 complex can be calculated using Stern-Volmer (S-V) equation [6]:

$$I_0 / I = 1 + k_D [Q] \quad \text{--------------} \; 6.3$$

where I_0 and I are the luminescence intensity of the free UO_2^{2+} and the UO_2^{2+}-PA complex respectively, k_D represents the S-V constant, and [Q] is the concentration of quencher i.e concentration of PA. When the change in luminescence intensity of UO_2^{2+} by PA (Figure 6.1) is subjected to the S-V analysis, a linear plot is obtained (Figure 6.3). Stern-Volmer constant can be defined as binding constant since only one complex is present. From this plot the stability constant (log β) of the complex UO_2^{2+}-PA is calculated to be 3.95±0.02. It is to be noted that this log β value is close to the reported value 3.73 of UO_2^{2+} nicotinate [5].

6.2.1.2 Luminescence study of UO_2^{2+}-PA in acetonitrile medium

In contrary to aqueous medium, luminescence of UO_2^{2+} was found to be enhanced by PA in acetonitrile medium. At the outset, UO_2^{2+} luminescence was measured as a function of PA concentration and pH of the solution. Figure 6.4 shows the variation of luminescence intensity of UO_2^{2+}-PA complex as a function of pH. For the pH range 2.5 to 3.0 the luminescence intensity was maximum and almost constant for a given ligand concentration. Therefore, in all our experiments pH of solution was maintained at around 2.8. The optimum acid concentration was determined to be 1×10^{-4} M and hence, this concentration was used in all our subsequent experiments. Figure 6.5 compares the excitation spectra of uncomplexed UO_2^{2+} and UO_2^{2+}-PA complex in acetonitrile medium. The excitation spectrum of the uncomplexed UO_2^{2+} (Figure 6.5a) was recorded by monitoring the luminescence at 509 nm, while the spectrum of complexed UO_2^{2+} (Figure 6.5b) was recorded by monitoring the luminescence at 495 nm. The excitation spectra for UO_2^{2+}-PA complex display a maxima at

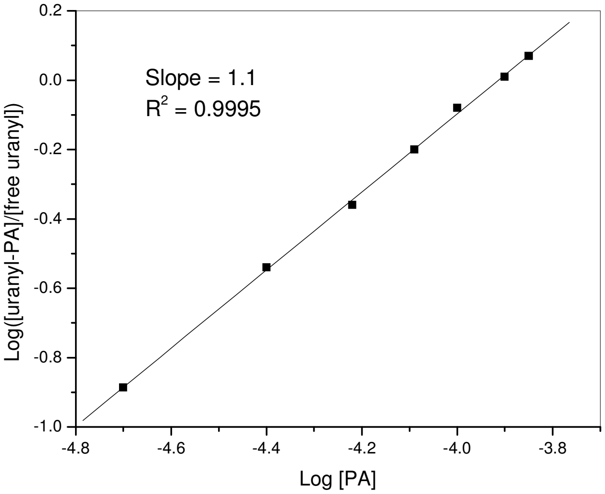

Figure 6.2 Slope analysis of complex formation of UO_2^{2+}-PA in aqueous medium at pH 2.8.

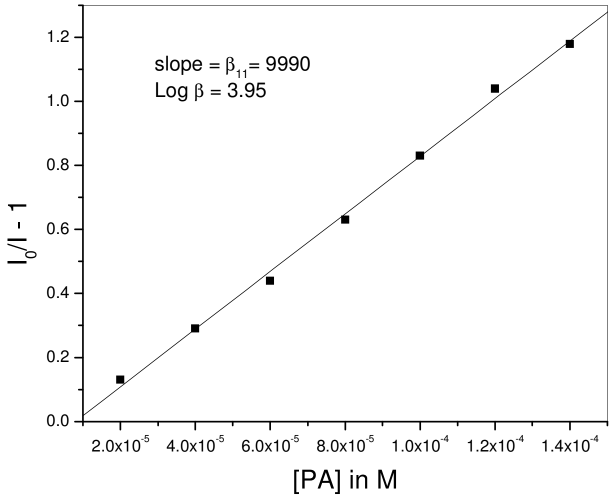

Figure 6.3 Stern-Volmer plot based on static quenching of UO_2^{2+} luminescence by picolinate ion at pH 2.8.

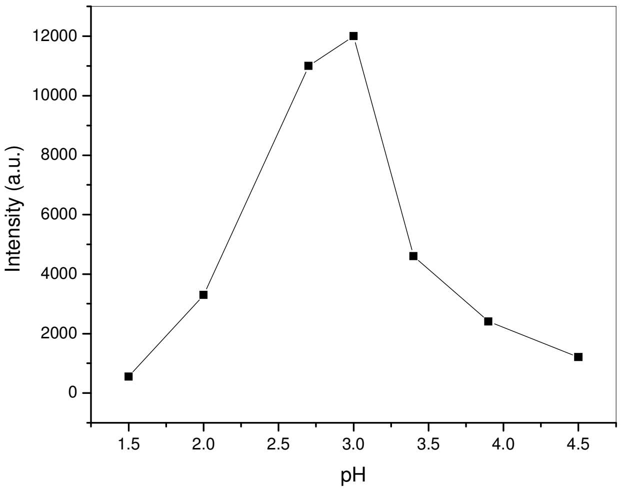

Figure 6.4 Variation of luminescence intensity of UO_2^{2+}-PA complex as a function of pH in acetonitrile; $[UO_2^{2+}] = 8x10^{-7}$ M, $[PA]=1x10^{-4}$ M.

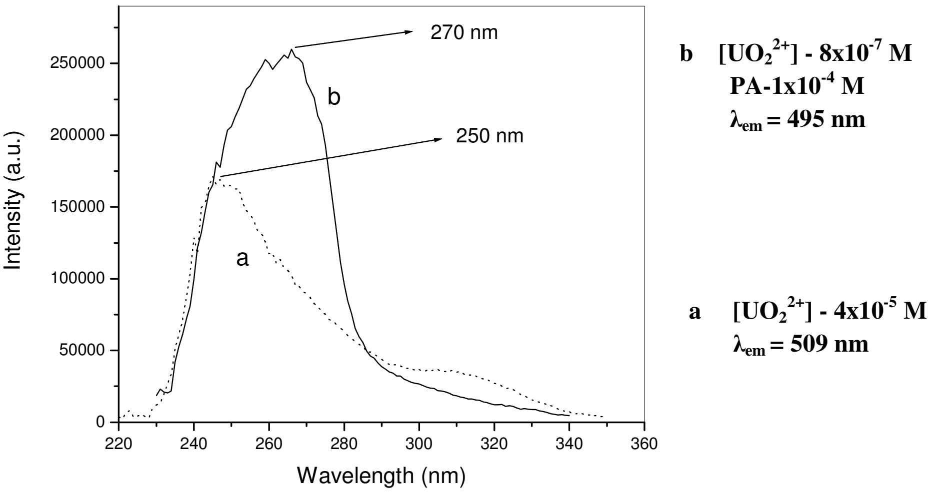

Figure 6.5 Excitation spectra of UO_2^{2+} in aceonitrile (a) without and (b) with PA at pH 2.8; [PA]-$1x10^{-4}$ M. The emission wavelength used to record each of the spectra is shown alongside.

270 nm (Figure 6.5b), which is different from uncomplexed UO_2^{2+} (250 nm), indicating the complexation of UO_2^{2+} with picolinate ion.

Figure 6.6a & 6.6b shows the UO_2^{2+} luminescence spectra without and with PA in acetonitrile medium at pH 2.8. The emission spectrum of uncomplexed UO_2^{2+} (Figure 6.6a) shows bands at 488, 509, 532 & 558 nm, while emission spectrum of UO_2^{2+}-PA complex (Figure 6.6b), shows peaks at 479, 495, 514, 540 & 565 nm. Concentration of UO_2^{2+} used to record the spectrum in its complex in acetonitrile medium was $8x10^{-7}$ M. At this concentration, uncomplexed UO_2^{2+} showed no measurable luminescence, and hence to record the spectrum of uncomplexed UO_2^{2+}, a concentration of $4x10^{-5}$ M was used. The enhancement in luminescence is thus obvious and clearly indicates the role of picolinate ion in sensitizing the UO_2^{2+} luminescence in acetonitrile. Complexation with picolinate yields more than two orders of enhancement in the luminescence of UO_2^{2+} in acetonitrile medium. Nearly 6 nm red-shift in the emission spectrum of UO_2^{2+}-PA complex compared to free UO_2^{2+}, implies that this ligand stabilizes the excited state more than the ground state.

Figure 6.7 shows the decay profile of UO_2^{2+}-PA in acetonitrile medium. This decay profile could be fitted to a single exponential decay with a lifetime of 65 μs, which indicates presence of single UO_2^{2+}-PA specie. The luminescence lifetime of free UO_2^{2+} is 20 μs in acetonitrile medium [7]. These lifetime values suggest that upon complexation with picolinate ion, water molecules are displaced from the first coordination sphere of the central UO_2^{2+} and hence the non-radiative decay, induced by water molecules are suppressed further. Similar enhancements in lifetime were observed in our earlier studies on the luminescence of UO_2^{2+} complexed with benzoic acid in acetonitrile medium. In aqueous medium lignads such as 2-6-pyridinedicarboxylic acid [1], trimesic acid [8], malonic acid [9], glycine [10] have been reported to increase the lifetime of UO_2^{2+} after complexation.

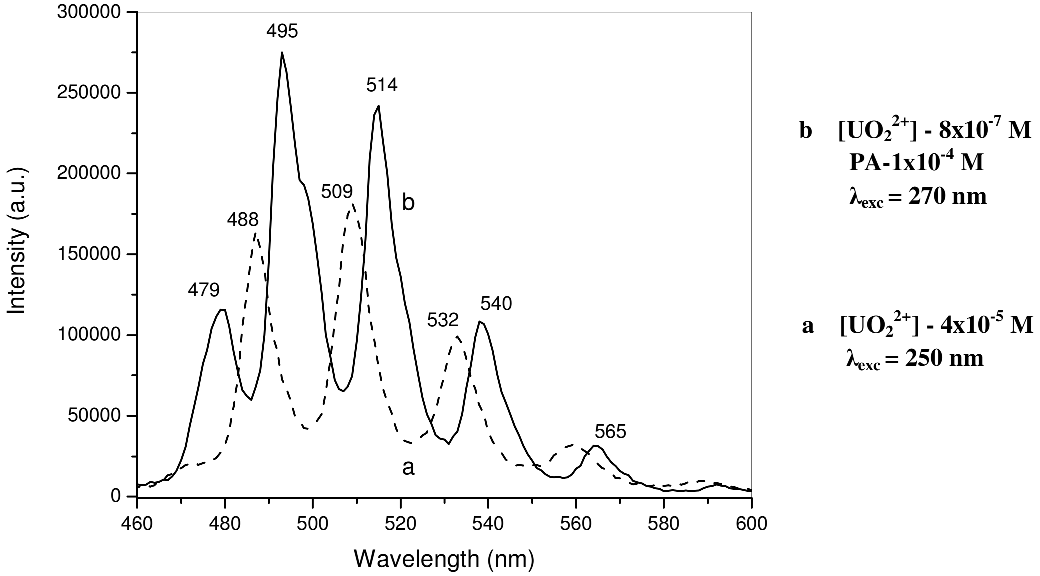

Figure 6.6 Emission spectra of UO_2^{2+} in aceonitrile (a) without and (b) with PA at pH 2.8; [PA]-1x10^{-4} M. The excitation wavelength used to record each of the spectra is shown alongside.

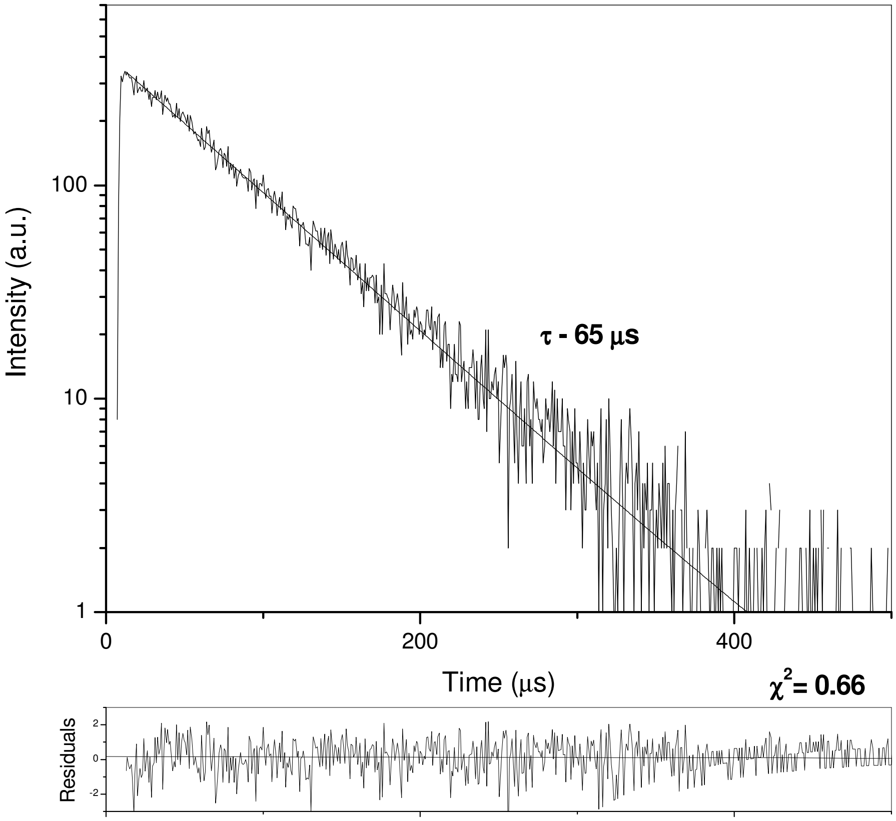

Figure 6.7 Luminescence decay profile of UO_2^{2+}-PA in acetonitrile medium at pH 2.8. Excitation wavelength = 270 nm, Emission wavelength = 495 nm.

6.2.1.3 Effect of water on luminescence of UO_2^{2+}-PA in acetonitrile medium

UO_2^{2+}-PA complex is non-luminescent in aqueous medium whereas it is luminescent in acetonitrile medium, it is necessary to see the nature of quenching by water molecules in acetonitrle medium. With this idea both steady state and lifetime experiments were performed after deliberate addition of water to the UO_2^{2+}-PA complex in acetonitrile medium. Both luminescence intensity and lifetime are decreased with the addition of water to UO_2^{2+}-PA system. It must be noted that in all the experiments in acetonitrile medium 1% water was initially present to begin with. Figure 6.8 illustrates the variation of luminescence intensity and lifetimes of the UO_2^{2+}-PA in acetonitrile medium with addition of water at pH 2.8 in the form of Stern-Volmer plots. These S-V plots were used to see the nature of quenching showed by water. The S-V plot of steady state experiments shows an exponential emergence (Figure 6.8a), whereas S-V plot of lifetime experiments shows linearity (Figure 6.8b). These observations indicate the quenching behavior of water seems to be both dynamic and static in nature. As water is introduced in acetonitrile, non-luminescent 1:1 complex of UO_2^{2+}-PA is formed gradually and is responsible for static quenching. On the other hand, dynamic quenching arises as water can remove acetonitrile molecules from the outer coordination sphere of luminescent complex, which then causes reduction in lifetime of UO_2^{2+}-PA.

6.2.1.4 Structure of the UO_2^{2+}-PA complex in acetonitrile medium

UV-Vis absorption spectroscopy was used to see the possibility of characterizing the UO_2^{2+}-PA specie formed in the acetonitrile medium which showed luminescence. Figure 6.9 shows the measured UV-Vis spectra at a UO_2^{2+} concentration of $2x10^{-3}$ M at pH 2.8 as a function of UO_2^{2+} to PA ratio in aqueous medium. The absorption spectrum of UO_2^{2+} without PA (Figure 6.9a) exhibited three absorption bands at 404, 415, 428 nm and it resembles to the absorption spectrum of free UO_2^{2+} in aqueous medium reported in literature [11]. Complexation of UO_2^{2+} with PA results in increase in absorbance along with a gradual red

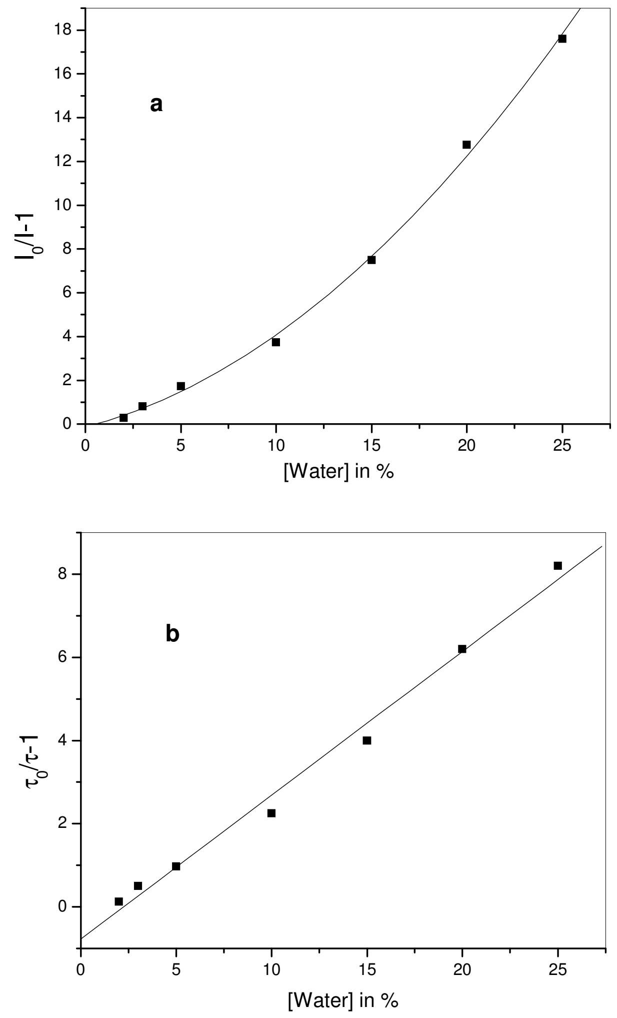

Figure 6.8 Stern-Volmer (a) intensity (b) lifetime plots based on quenching of UO_2^{2+}-PA luminescence in acetonitrile by water at pH 2.8.

shift in the absorption maxima. The shift in absorption spectra is due to the complex formation of UO_2^{2+}-PA in aqueous medium. Similar shift was observed in the absorption spectra of 1:1 complex of uranyl benzoate in aqueous medium [6]. Figure 6.10 shows the UV-Vis spectrum of UO_2^{2+}-PA with different ratio of UO_2^{2+} to PA in acetonitrile medium at pH 2.8. The UV-Vis spectrum of UO_2^{2+} ($2x10^{-3}$ M) without PA (Figure 6.10a) in acetonitrile resembles to the spectrum in aqueous medium (Figure 6.9a). This suggests that being the less coordinating solvent acetonitrile cannot replace the water, which is present in acetonitrile at trace level, from the inner coordination sphere of UO_2^{2+}. An increase in the absorbance with a red shift is observed as UO_2^{2+} to PA ratio is increased (Figure 6.10b-6.10f). When UO_2^{2+} to PA ratio is 1:2 (Figure 6.10c), features at 401, 411, 423, 435 nm in UV-Vis spectra starts originating and these features become much sharper at UO_2^{2+} to PA ratio of $\geq$ 1:3 (Figure 6.10d-6.10f). These absorption bands in acetonitrile are much sharper and more shifted in contrast to that observed for 1:1 type complex of UO_2^{2+}-PA in aqueous medium. In aqueous medium we have examined UV-Vis spectra of UO_2^{2+}-PA up to a ratio of UO_2^{2+} to PA, 1:20 (Figure 6.9g) and even at this high UO_2^{2+} to PA ratio, UV-Vis spectrum does not show sharp features like what were observed in acetonitrile medium at UO_2^{2+} to PA ratio of 1:3. It clearly indicates that the stoichiometric nature of complex in acetonitrile medium is entirely different from aqueous medium. The features observed in the absorption spectra of uranyl picolinate in acetonitrile medium resembles the UV-Vis spectrum of uranyl nitrate solution which was inferred to $UO_2(NO_3)_2$ species of uranyl nitrate in literature [12]. Hence we believe that the specie formed in acetonitrile medium could be that of $UO_2(PA)_2$. The absorption feature of 1:2 complex of uranyl benzoate were also found to be sharper than that of 1:1 type in aqueous medium [6]. Furthermore, the luminescence spectrum shows peaks at 492, 514, 535 and 561 nm (Figure 6.6b) closely matches with the luminescence peaks of single crystal of $UO_2(PA)_2$ reported in literature [13].

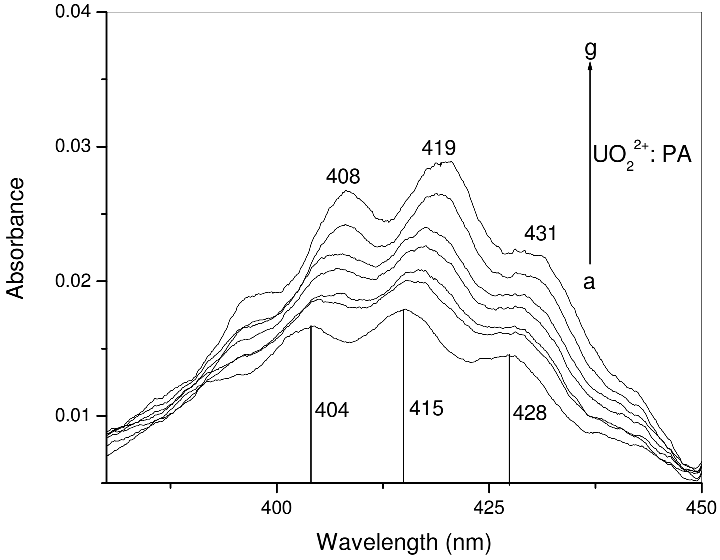

Figure 6.9 UV-Vis absorption spectra of UO_2^{2+} ($2x10^{-3}$ M) with different UO_2^{2+}: PA (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:5; (f) 1:10; (g) 1:20 in aqueous medium at pH 2.8.

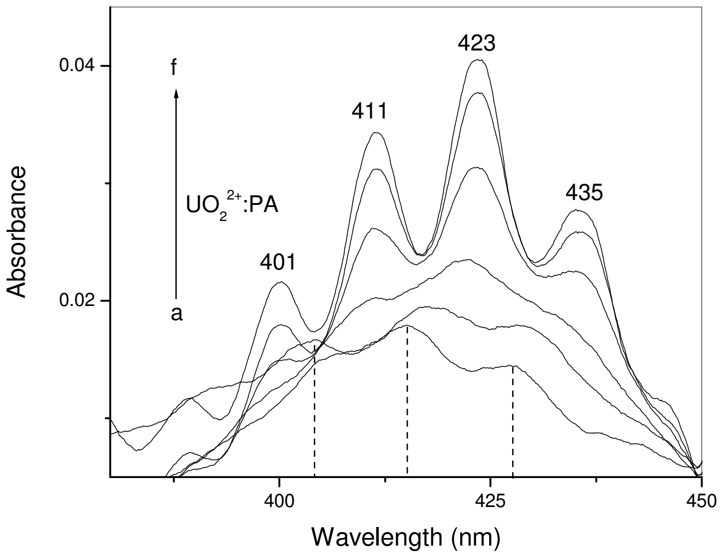

Figure 6.10 UV-Vis absorption spectra of UO_2^{2+} ($2x10^{-3}$ M) with different UO_2^{2+}: PA (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:4; (f) 1:5 in acetonitrile at pH 2.8.

It must be noted that in case of uranyl benzoate, UO_2^{2+} formed tris complex in acetonitrile [7]. The absorption peaks for tris complex occurred at 431, 443, 461 nm and have reported in literature for D_{3h} symmetry compounds [14]. These features were not observed for UO_2^{2+}-PA complex in acetonitrile and hence, formation of tris complex can be ruled out for this system. Like benzoate, where both the oxygen atoms of carboxylate group participate in complexation [6], picolinate also bind with actinyl ions in a bidentate fashion (through N atom of pyridyl and O atom of carboxylate group) and its bidentate complexation with neptunium (V) has been reported in literature [3]. In uranyl benzoate, benzoate acted as bidentate ligand and the benzene ring is away (3 bond away) from the uranium atom and therefore without much steric-hindrance three benzoate moieties could bind with UO_2^{2+}. The presence of nitrogen atom which is one of the donor atom in picolinic acid makes benzene ring closer to uranium atom in order to make complex and hence, only two ligands fit in order to avoid steric hindrance. The proposed structure of the complex $[UO_2\,(PA)_2]^-$ is shown in Figure 6.11.

6.2.1.5 Analytical application of this study

The present study of UO_2^{2+} luminescence in acetonitrile medium finds analytical application for uranium detection. The large enhancement of UO_2^{2+} luminescence of UO_2^{2+}-PA complex in acetonitrile medium can be used for trace level detection of UO_2^{2+}. Linearity in the luminescence intensity is seen over the UO_2^{2+} concentration range of 4.2×10^{-8} to 1.3×10^{-5} M (Figure 6.12) and the detection limit calculated using the criterion of 3σ is ~ 2.5×10^{-9} M.

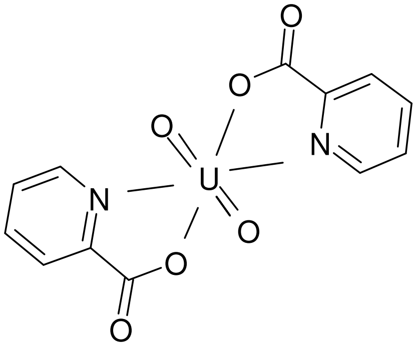

Figure 6.11. Proposed structure of UO_2^{2+}-PA in acetonitrile medium.

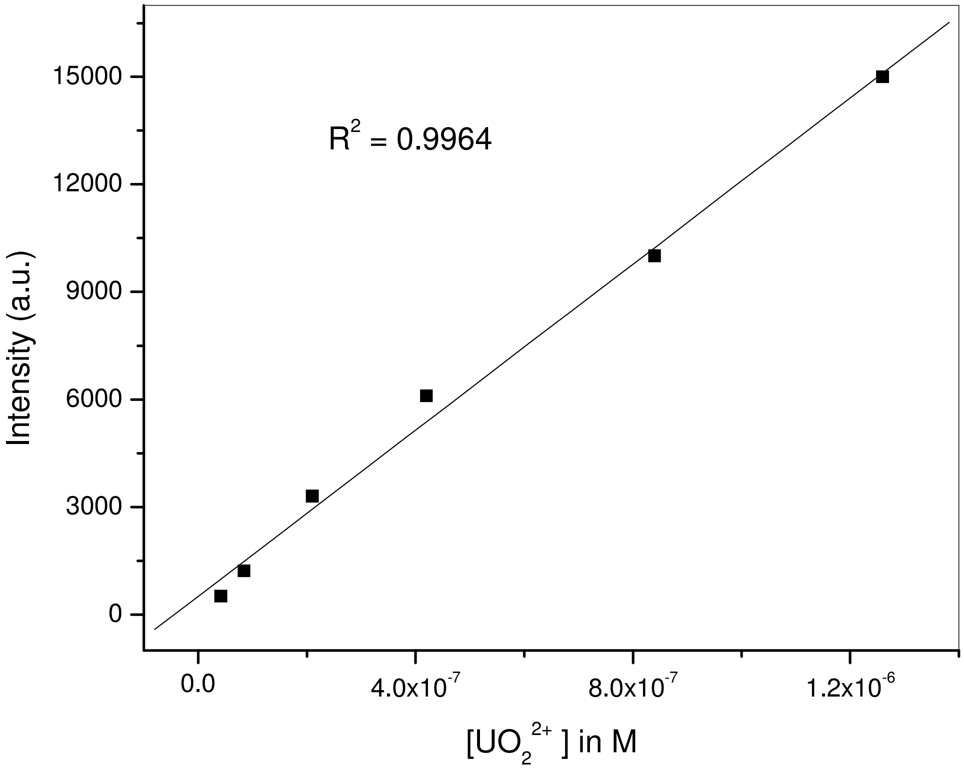

Figure 6.12 Plot of intensity of UO_2^{2+} luminescence at 514 nm in UO_2^{2+}-PA as a function of UO_2^{2+} concentration; [PA] = $1x10^{-4}$ M.

6.2.2 UO_2^{2+}-DPA system

6.2.2.1 Luminescence study of UO_2^{2+}-DPA in acetonitrile medium

At the outset, the luminescence of UO_2^{2+} was recorded in acetonitrile medium as a function of DPA concentration and pH of the solution for a fixed UO_2^{2+} concentration (8.4×10^{-8} M). Figure 6.13 shows the luminescence intensity of UO_2^{2+} measured at 509 nm as a function of DPA concentration at pH 4.0. The maximum and nearly same luminescence intensity is observed for the UO_2^{2+} over the DPA concentration range of 8×10^{-5}-1×10^{-4} M. In all our following experiments DPA concentration was maintained at 1×10^{-4} M. Variation of luminescence intensity measured at 509/514 nm (it is 514 nm at pH 1.0) over the pH 1.0-6.0 is shown in Figure 6.14. The luminescence intensity is found to be highest and almost constant over pH range 2.5-5.0.

Figure 6.15b and 6.16b show the excitation and emission spectra of UO_2^{2+}-DPA recorded in acetonitrile medium at pH 4.0. The UO_2^{2+} concentration was maintained here at 8.4×10^{-8} M. For comparison, the excitation and emission spectra of UO_2^{2+}-DPA recorded in aqueous medium are also shown in the Figure 6.15a and 6.16a respectively. To record these spectra in aqueous medium, the concentration of UO_2^{2+} was maintained at 8.4×10^{-7} M. It is to be noted that the wavelength of the excitation maxima is nearly same in both the medium as seen in the spectra (Figure 6.15a and 6.15b). The emission spectra shown in Figure 6.16b, over the range 460-600 nm, recorded using λ_{ex} of 270 nm, displays well resolved features at 488, 509, 532 and 556 nm. The position of peak maxima matches with that observed in aqueous medium (Figure 6.16a). About 20 times increase in luminescence intensity is found when acetonitrile is used as the solvent compared to aqueous medium. In earlier luminescence studies [2], it has been shown that in the aqueous UO_2^{2+}-DPA system, DPA is the absorber, which then sensitizes the luminescence of UO_2^{2+}. Therefore considering the

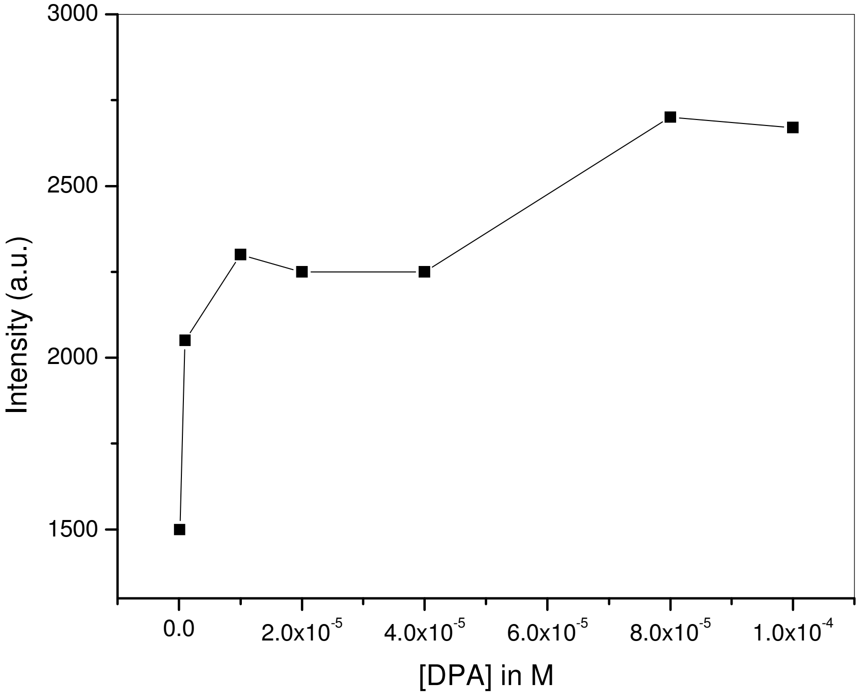

Figure 6.13 Variation of luminescence intensity of UO_2^{2+}-DPA complex as a function of concentration of DPA in acetonitrile medium; pH = 4.0; $[UO_2^{2+}] = 8.4x10^{-8}$ M.

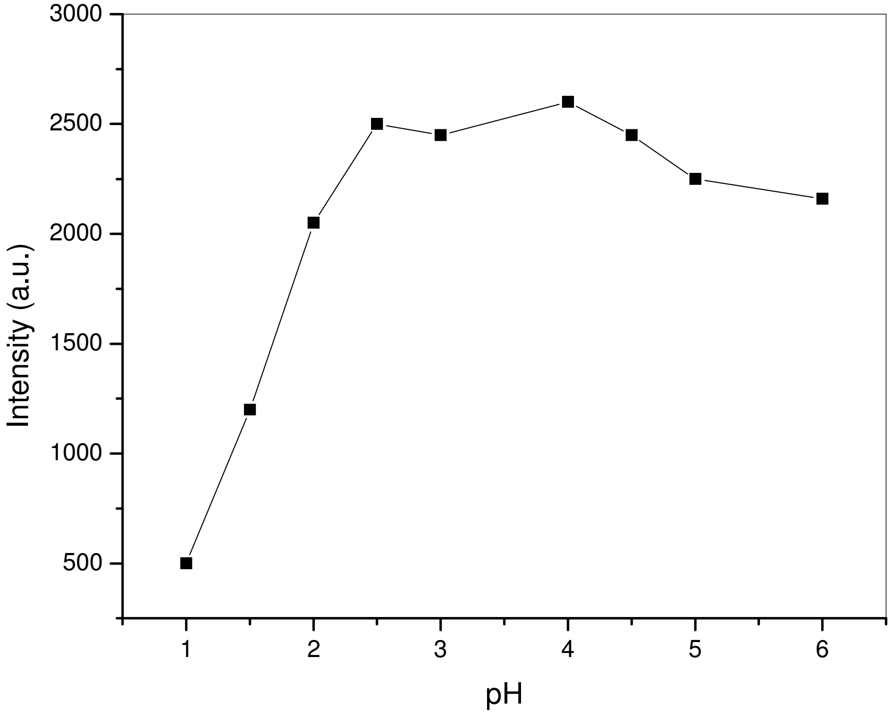

Figure 6.14 Variation of luminescence intensity of UO_2^{2+}-DPA complex as a function of pH in acetonitrile medium; [DPA] = $1x10^{-4}$ M; [UO_2^{2+}] = $8.4x10^{-8}$ M.

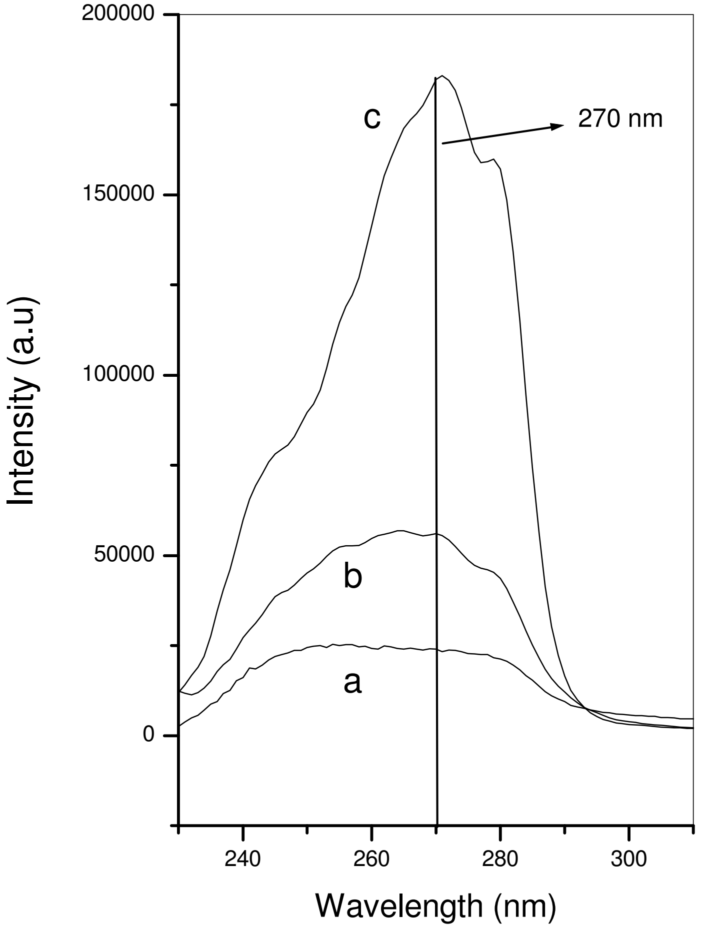

Figure 6.15 Excitation spectra of (a) UO_2^{2+}-DPA in aqueous medium; [UO_2^{2+}] -8.4x10^{-7} M (b) UO_2^{2+}-DPA; [UO_2^{2+}] -8.4x10^{-8} M and (c) UO_2^{2+}-DPA-Y^{3+}; [UO_2^{2+}] -8.4x10^{-8} M, [Y^{3+}]-5x10^{-5} M both in acetonitrile medium at pH 4.0, λ_{em} = 509 nm for a & b whereas 514 nm for c, [DPA] = 1x10^{-4} M for all cases.

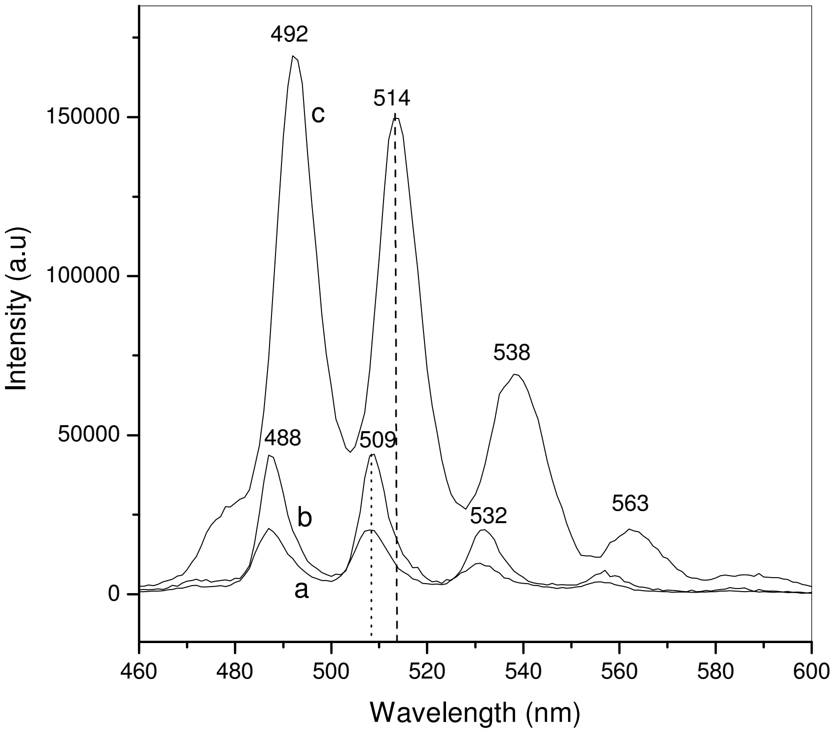

Figure 6.16 Emission spectra of (a) UO_2^{2+}-DPA in aqueous medium ; [UO_2^{2+}] -8.4x10^{-7} M (b) UO_2^{2+}-DPA; [UO_2^{2+}] -8.4x10^{-8} M and (c) UO_2^{2+}-DPA-Y^{3+}; [UO_2^{2+}] -8.4x10^{-8} M, [Y^{3+}]-5x10^{-5} M both in acetonitrile medium at pH 4.0; [DPA] = 1x10^{-4} M, λ_{exc} =270 nm for all cases.

position of excitation maxima and the position of emission peaks it can be inferred that in acetonitrile medium also, DPA sensitizes UO_2^{2+} luminescence.

Luminescence lifetime data has served to determine the extent of non-radiative decay processes and also it indirectly provides the number of luminescent species present in the system. Time resolved luminescence decays of UO_2^{2+}-DPA are recorded over pH 1.0-6.0. The typical decay profile as measured at pH 1.0 and 4.0 are shown in Figure 6.17a and 6.17b, respectively. The luminescence decay profile at pH 1.0 could be fitted with mono-exponential decay whereas over pH 2.0-6.0, the decay profiles are fitted bi-exponentially. Figure 6.18 shows the bar graph of the measured lifetimes over pH 1.0-6.0. In case of bi-exponential decays, one lifetime is shorter and almost constant over pH whereas the other lifetime is much larger than the first one and varies over pH values. The mono-exponential decay at pH 1.0 indicates the presence of single specie whereas bi-exponential decay over pH 2.0-6.0 indicates the presence of two species. At pH 1.0 the lifetime value corresponding to mono exponential decay (Figure 6.17a) is 43 μs and in the pH range 2.0-6.0, the lifetime values corresponding to bi-exponential decay are 63 μs for first specie and 200-280 μs for second specie. This variation of lifetimes corresponding to second specie over pH indicates that there is a change in the environment of the specie with pH of the solution.

6.2.2.2 Effect of water on luminescence lifetime

Above pH 4.0, hydroxide specie of UO_2^{2+} ion is predominant in acetonitrile medium in the absence of DPA [7]. So the specie having longer lifetime over pH 2.0-6.0 can be thought of DPA complex of uranyl hydroxide. In order to check this, water was added to the solution deliberately and the emission intensity as well as lifetimes were measured. The variation of amplitudes of lifetimes corresponding to the two species is shown in Figure 6.19 with addition of water at pH 3.0. It can be seen that the percentage amplitude of the specie having longer decay diminishing very fast and it disappears when water content in

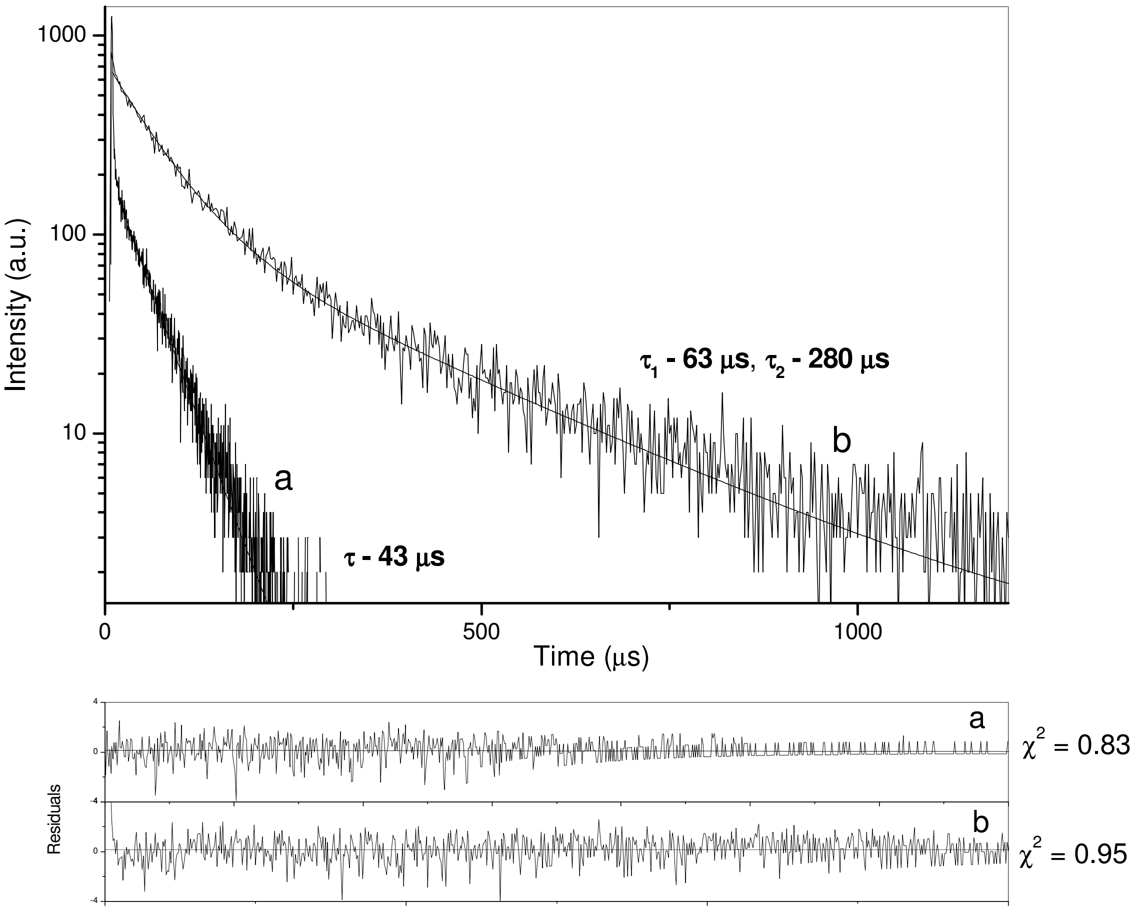

Figure 6.17 Luminescence decay profile of UO$_2^{2+}$-DPA in acetonitrile medium at (a) pH 1.0 ; Excitation wavelength = 270 nm, Emission wavelength = 514 nm (b) pH 4.0; Excitation wavelength = 270 nm, Emission wavelength = 509 nm.

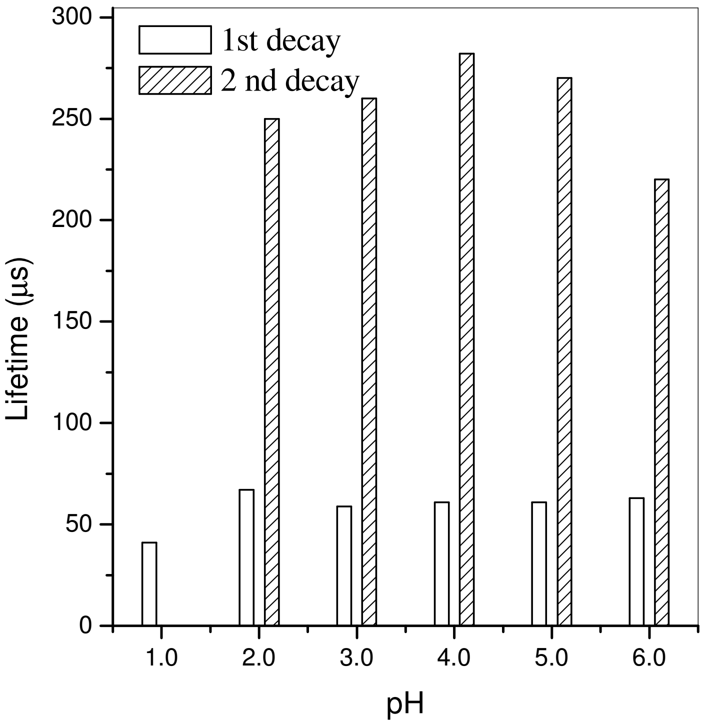

Figure 6.18 Bar graphs showing lifetimes of UO_2^{2+}-DPA as a function of pH; $[UO_2^{2+}] = 8.4x10^{-8}$ M , [DPA] = $1x10^{-4}$ M.

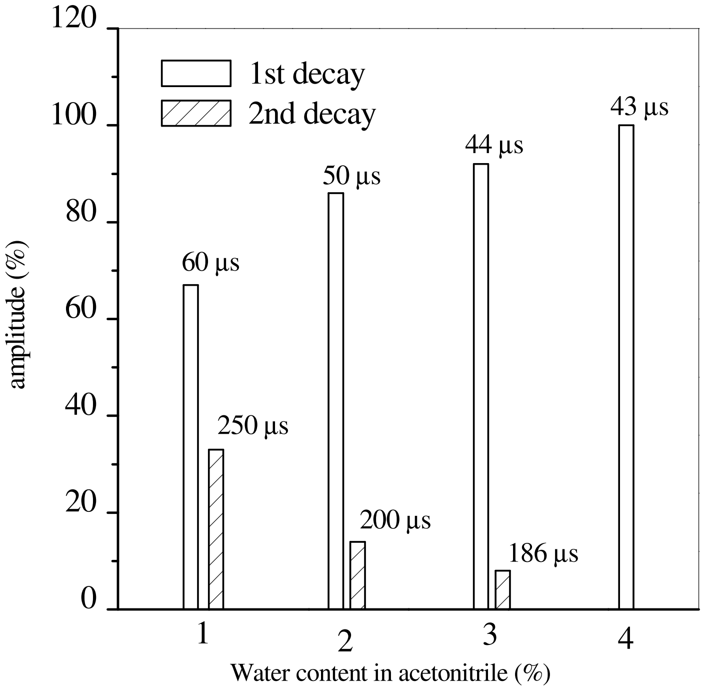

Figure 6.19 Bar graphs showing the variation of amplitude of the lifetime decays as a function of water content relative to acetonitrile at pH 3.0; $[UO_2^{2+}] = 8.4x10^{-8}$ M, [DPA] $= 1x10^{-4}$ M.

acetonitrile is about 4%. Similar experiment was done at pH 5.0 and same results were obtained. Therefore, it can be concluded that the specie having longer decay is not a complex of uranyl hydroxide, rather a sort of UO_2^{2+} complex with DPA. The fact that the second specie of higher lifetime disappears with addition of water, indicates the specie to be weakly formed in acetonitrile medium.

6.2.2.3 Proposed luminescent species

DPA shows versatile structure and it co-ordinates in a variable fashion with many heavy metal ions [15-18]. The reason for this is probably due to the position of the two –COOH groups which are close to N atom. The pK_{a1} and pK_{a2} values of DPA are 1.05 and 2.22 [15], respectively and therefore, at pH 1.0, DPA probably co-ordinates to UO_2^{2+} in a bi-dentate fashion where only one ionized –COOH and N of pyridine participate in complexation similar to the case of UO_2^{2+}-PA system. Furthermore, it should be noted that the peak positions of the emission spectra at pH 1.0 shown in Figure 6.20a are similar to that is found for UO_2^{2+} complexed with PA at pH 2.8 as shown in Figure 6.6b in section 6.2.1.2. The emission spectra recorded at pH 2.0 is shown in Figure 6.20b. It can be seen from this Figure that the peak positions of the emission spectra are blue shifted by 5 nm compared to the peak positions at pH 1.0 (Figure 6.20a). Similar peak positions are observed over pH 2.0 to 6.0. Above pH 1.0, both -COOH groups may ionize and could participate in complexation with UO_2^{2+}. The proposed structure of the complex at pH 1.0 is shown in Figure 6.21a and the observed lifetime of 43 μs is inferred to this specie.

A very strong 1:2 sodium salt of UO_2^{2+}-DPA complex was reported, where the N of pyridine and the two carboxylate oxygen atoms act as donor atoms [19]. It can be expected that similar 1:2 complex is formed over the pH range 2.0-6.0 in the present studies as well. The proposed structure is shown in Figure 6.21b where two DPA molecules coordinate to UO_2^{2+} in a tri-dentate fashion. The observed lifetime of 63 μs in bi-exponential decay is

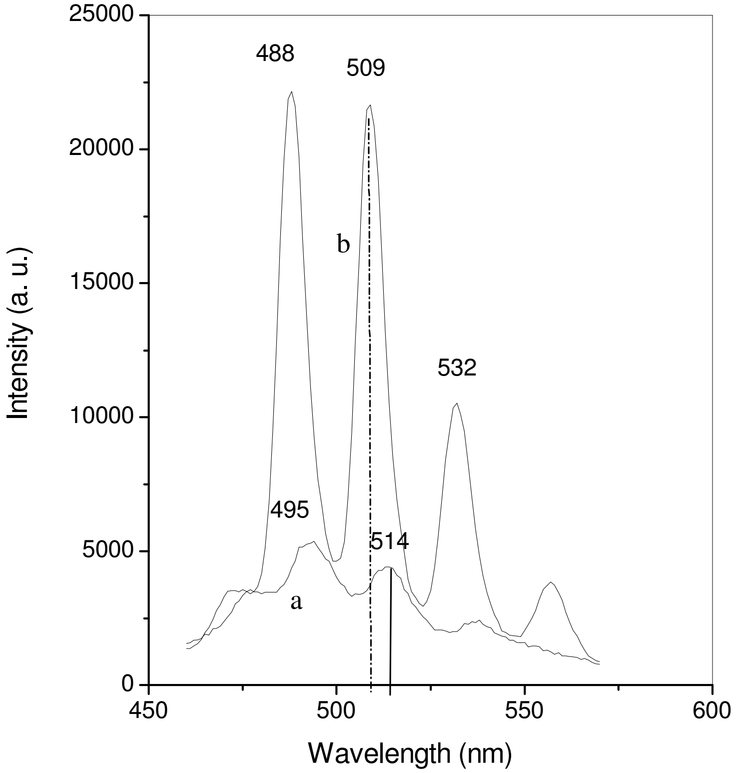

Figure 6.20 Luminescence spectra of UO_2^{2+}-DPA at pH (a) 1.0, (b) 2.0; $[UO_2^{2+}]$ = 8.4×10^{-8} M, [DPA] = 1×10^{-4} M.

believed for this 1:2 type specie of UO_2^{2+}-DPA . The lifetime value of second specie is quite high as compared to first specie. It suggests that non-radiative decay channels associated with higher lifetime specie are less. Hence we believe that more than two DPA molecules may participate in the complexation with UO_2^{2+}. Also the second decay completely fades away when water content in acetonitrile is 4% and above (Figure 6.19). On the basis of these data, the specie corresponds to the second lifetime can be hypothesized that the third DPA molecule display a partial tridentate co-ordination. The mode of co-ordination of the third DPA may be mono-dentate or bi-dentate and by keeping restrictions on coordination number of UO_2^{2+}, we expect third DPA coordination to be mono dentate (Figure 6.21c).

6.2.2.4 Luminescence of UO_2^{2+}-DPA-Y^{3+} complex

In addition to luminescence enhancement due to reduction in non-radiative decay channel as solvent is changed from water to acetonitrile, it is also observed that the addition of Y^{3+} or La^{3+} ion further enhances the luminescence of UO_2^{2+}-DPA. The impurity of uranium was found to be more in standard lanthanum oxide than standard yttrium oxide and hence all the co-luminescence experiments were done by addition of Y^{3+} ion. The luminescence background from yttrium oxide has been taken care by recording the spectra with respect to blank. To optimize the experimental conditions for this co-luminescence process, the luminescence intensity was measured as function of Y^{3+} concentration for a fixed concentration of UO_2^{2+} and DPA. The enhancement due to co-luminescence was found to be maximum at Y^{3+} concentration of $5x10^{-5}$ M. Figure 6.15c & 6.16c show the exciataion and emission spectra of UO_2^{2+}-DPA-Y^{3+} respectively in acetonitrile. About four times luminescence enhancement is found over pH 2.0-5.0 due to the addition of Y^{3+}. It is to be noted that in aqueous medium UO_2^{2+}-DPA does not show co-luminescence. It is in agreement with co-luminescence results presented in Chapter 5 for Eu^{3+} complexed with DPA, where

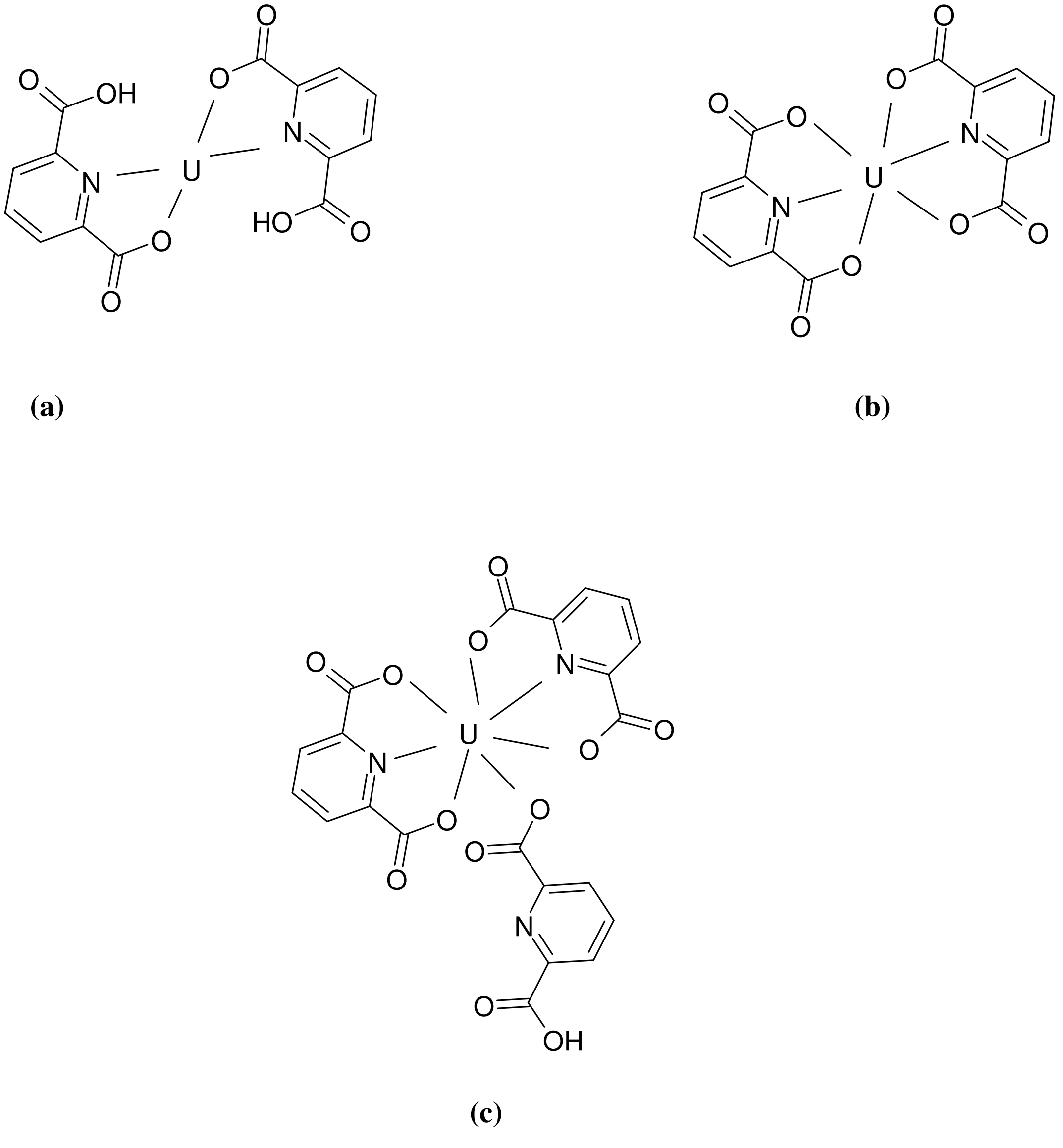

Figure 6.21 Proposed structures of different species of UO_2^{2+}-DPA in acetonitrile medium.

Eu^{3+} show co-luminescence in acetonitrile with the addition of La^{3+} whereas Eu^{3+}-DPA does not show co-luminescence in aqueous medium.

Though the co-luminescence enhancement is not huge, lifetime measurements show interesting results. Figure 6.22 shows the typical time resolved decay profile of UO_2^{2+}-DPA-Y^{3+} in acetonitrile medium at pH 4.0. Figure 6.23 shows the bar graph of measured lifetimes over the pH range 1.0-6.0. Throughout the pH range of 1.0-6.0 studied here two species are found; one is having shorter lifetime (63-82 μs) and other one is nearly 5-6 times longer (290-380 μs). It is to be noted here that at pH 1.0 where single specie is found for UO_2^{2+}-DPA complex but double decays are found for UO_2^{2+}-DPA-Y^{3+} complex. Both the lifetimes varies with pH and remain nearly constant over pH 4.0-6.0 (Figure 6.23). All these data suggest that complxeation behavior of species formed at different pH in co-luminescence solution and without Y^{3+} are certainly different.

6.2.2.5 Proposed mechanism for co-luminescence

Based on the results of emission spectra and lifetimes, the following mechanism is proposed. In case of luminescent complex without Y^{3+} at pH 1.0, only specie with lifetime 43 μs is found (Figure 6.18a) and it co-ordinates with UO_2^{2+} like picolinic acid. At the same pH when Y^{3+} is added to this solution, two species are found with lifetimes 64 μs and 286 μs respectively (Figure 6.24). Addition of Y^{3+} to the luminescence solution result in either a co-precipitate of UO_2^{2+}-DPA and Y^{3+}-DPA complexes or a suspension of the UO_2^{2+}-DPA-Y^{3+} poly-nuclear complex. These two lifetimes point that both the co-precipitate and poly-nuclear complexes i.e. intra and inter molecular species are formed in presence of Y^{3+}. The intra molecular specie (UO_2^{2+}-DPA-Y^{3+}) thus formed shows lifetime of 64 μs. The inter molecular specie i.e. the co-precipitate of UO_2^{2+}-DPA and Y^{3+}-DPA complexes where each UO_2^{2+}-DPA complex is surrounded by many Y^{3+}-DPA complexes show a lifetime of 286 μs. The

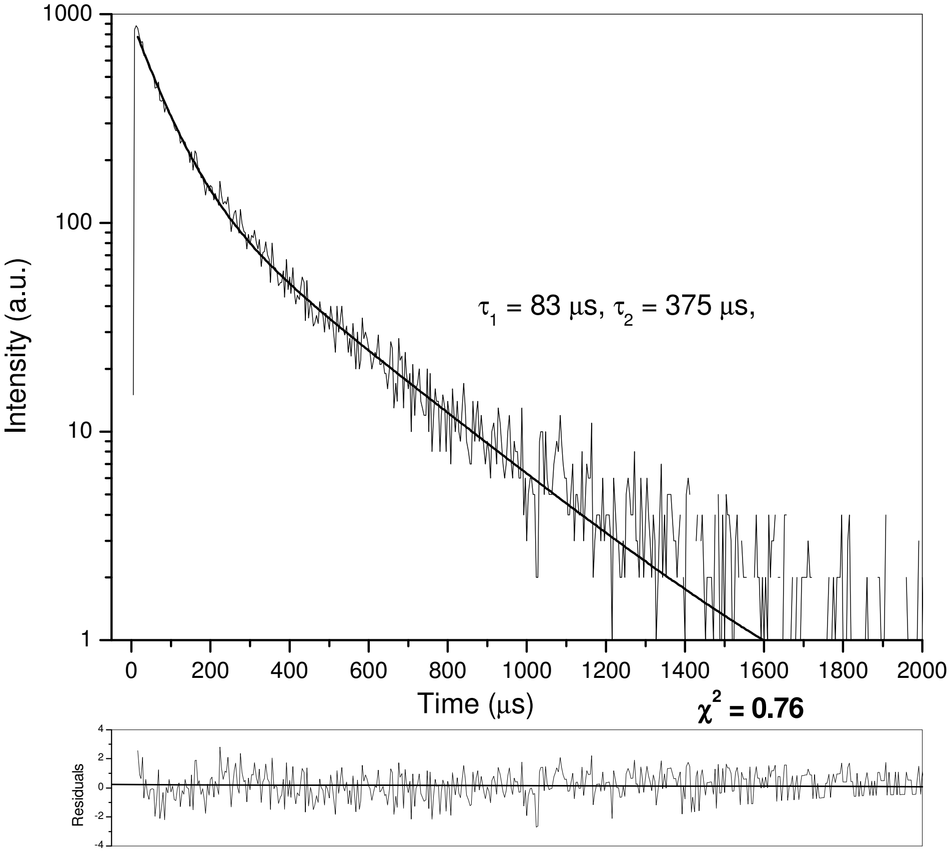

Figure 6.22 Luminescence decay profile of UO_2^{2+}-DPA-Y^{3+} in acetonitrile medium at pH 4.0. Excitation wavelength = 270 nm, Emission wavelength = 514 nm.

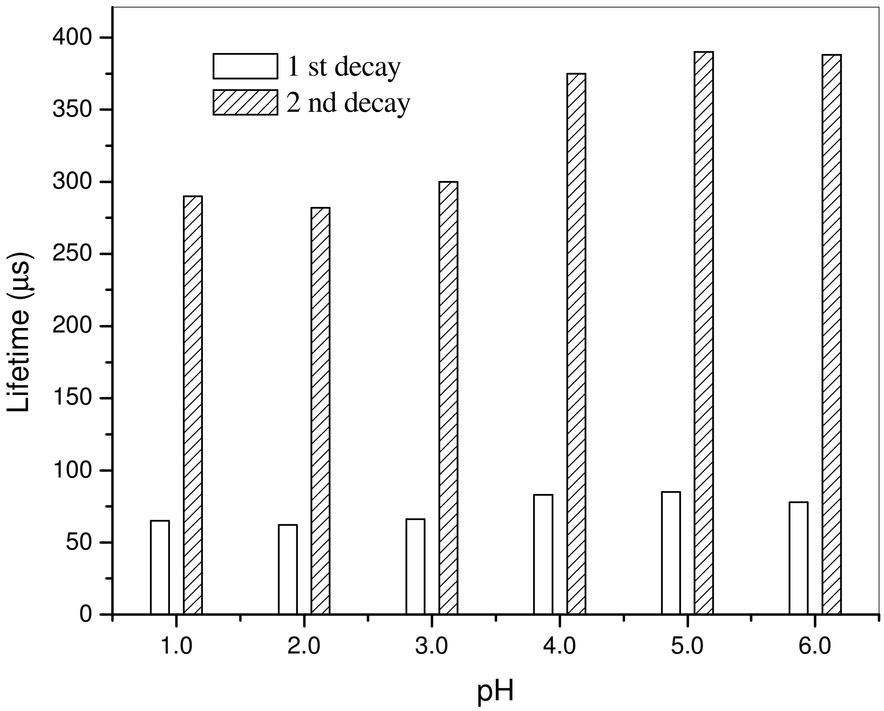

Figure 6.23 Bar graphs showing lifetimes of UO_2^{2+}-DPA-Y^{3+} as a function of pH; [UO_2^{2+}] =8.4x10^{-8} M , [DPA] = 1x10^{-4} M, [Y^{3+}]- 5x10^{-5} M.

surrounding Y^{3+}-DPA molecules can act as an energy insulating sheath which can prevent collision of UO_2^{2+}-DPA with surroundings, thus increasing the lifetime of it and hence, higher lifetime compared to intra molecular specie i.e. UO_2^{2+}-DPA-Y^{3+}. The value of these two lifetimes remains nearly constant over pH 1.0-3.0 and then slowly increases with pH.

6.2.2.6 Analytical application of this study

The present study of co-luminescence of UO_2^{2+}-DPA-Y^{3+} complex in acetonitrile medium finds an analytical application for uranium detection. Linearity in the luminescence intensity is seen over the UO_2^{2+} concentration range of 4.2×10^{-9} M to 4.2×10^{-7} M (Figure 6.24) and the detection limit calculated using the criterion of 3σ is ~ 1.6×10^{-9} M.

6.3 Conclusions

Luminescence of UO_2^{2+} has been studied using PA and DPA as sensitizing ligands. UO_2^{2+} forms 1:1 type non-luminescent complex with PA in aqueous medium which is identified by slope ratio method. In acetonitrile, both the ligands enhance the luminescence of UO_2^{2+} through sensitization and reduction in non-radiative decay channels. UV-Vis spectroscopy showed the stoichiometry of UO_2^{2+}-PA specie to be 1:2 in acetonitrile medium. With DPA as a ligand, lifetime studies indicate the stoichiometry of UO_2^{2+}-DPA species to be 1:2 and higher. Co-luminescence enhancement following the addition of Y^{3+} to UO_2^{2+}-DPA is observed in acetonitrile with formation of both intra and intermolecular complex.

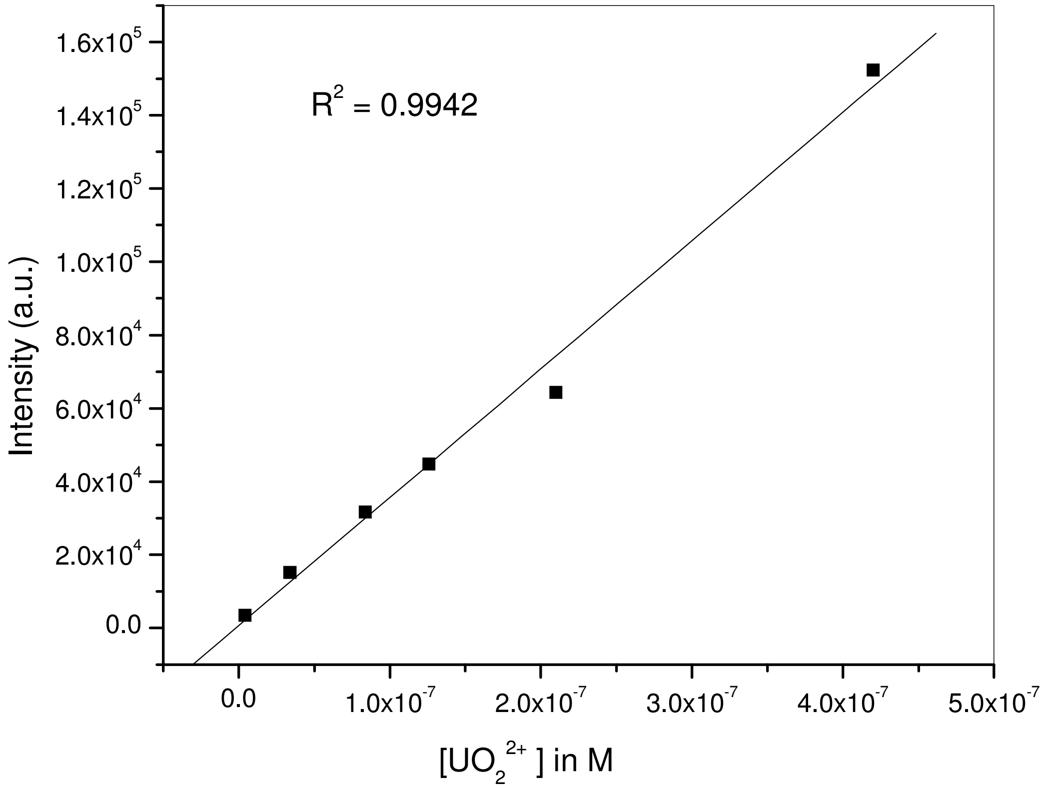

Figure 6.24 Plot of intensity of UO_2^{2+} luminescence at 514 nm in UO_2^{2+}-DPA-Y^{3+} as a function of UO_2^{2+} concentration; [DPA] = $1x10^{-4}$ M.

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CHAPTER 7 Summary and Conclusions

This chapter presents a summary of all the works discussed in preceding chapters. This concluding chapter also discusses the future perspectives which stem out from this research work. This thesis presents the ligand sensitized luminescence of Eu^{3+} and UO_2^{2+} complexed with aromatic carboxylic acids in acetonitrile medium. The aromatic carboxylic acids used are benzoic acid, methyl substituted benzoic acids, picolinic acid and dipicolinic acid. In all the cases, the luminescence intensity of Eu^{3+} and UO_2^{2+} complexed with these ligands is found to be more than that of in aqueous medium. Among all these ligands, only dipicolinic acid exhibits co-luminescence with Eu^{3+} and UO_2^{2+} in acetonitrile medium. In this study, an attempt also has been made to provide the complexation behavior of Eu^{3+} and UO_2^{2+} and an insight into the role of acetonitrile for ligand sensitized luminescence.

The luminescence enhancement found in acetonitrile is presented in terms of enhancement factor. The lifetimes and detection limits of the complexes are also presented. Table 7.1 lists the enhancement factor, detection limits and lifetimes for various Eu^{3+} and UO_2^{2+} complexes studied in this thesis in acetonitrile and all these parameters are compared with aqueous medium. The luminescence enhancement in acetonitrile medium for all the cases is sufficient to push the detection limits to sub-nano molar level. Figure 7.1 and 7.2 compares the enhancement factor graphically for different complexes of Eu^{3+} and UO_2^{2+} respectively. Among all the ligands studied in this work, dipicolinic acid shows the highest enhancement for both, Eu^{3+} and UO_2^{2+}. An enhancement factor of $2.78x10^5$ and $2.0x10^4$ is obtained with this ligand for Eu^{3+} and UO_2^{2+} respectively. When La^{3+} and Y^{3+} are used as

Table 7.1 Enhancement factor, detection limit and lifetime for Eu^{3+} and UO_2^{2+} in different systems.

System	Enhancement factor		Detection limit (M)		Lifetime (μs)	
	Acetonitrile	**Aqueous**	**Acetonitrile**	**Aqueous**	**Acetonitrile**	**Aqueous**
Eu^{3+}-benzoate	32000	100	3.0x10^{-10}	1x10^{-6}-1x10^{-8}	900	115
Eu^{3+}-*o* toluate	15000	71	1.6 x10^{-9}		550	114
Eu^{3+}-*m* toluate	44000	160	4.5 x10^{-10}		700	116
Eu^{3+}-*p* toluate	25000	160	1.2 x10^{-10}		680	118
Eu^{3+}-picolinate	137000	650	1.5 x10^{-10}		1200	600
Eu^{3+}-dipicolinate	278000	170000	6.0 x10^{-11}		1850	1460
[1]Eu^{3+}-dipicolinate-La^{3+}	47400000	-	4.0 x10^{-11}	-	1700	-
UO_2^{2+}-benzoate[2]	2800	-	4.2 x10^{-9}	-	65	~ 1
UO_2^{2+}-*o* toluate[2]	1000		2.1 x10^{-8}		15	~ 1
UO_2^{2+}-*m* toluate[2]	4500		4.2 x10^{-9}		55	~ 1
UO_2^{2+}-*p* toluate[2]	8000		3.2 x10^{-9}		65	~ 1
UO_2^{2+}-picolinate[2]	6000		2.5 x10^{-9}		65	~ 1
UO_2^{2+}-dipicolinate	20000	1000	1.0 x10^{-9}	1.7 x10^{-8}	[3]τ_1 65 τ_2 280	10
[1]UO_2^{2+}-dipicolinate-Y^{3+}	80000	-	1.0 x10^{-9}	-	[3]τ_1 80 τ_2 375	-

[1] - These systems do not show co-luminescence in aqueous medium

[2] - The ligands present in these systems quench the luminescence of UO_2^{2+} in aqueous medium

[3] - at pH 4.0

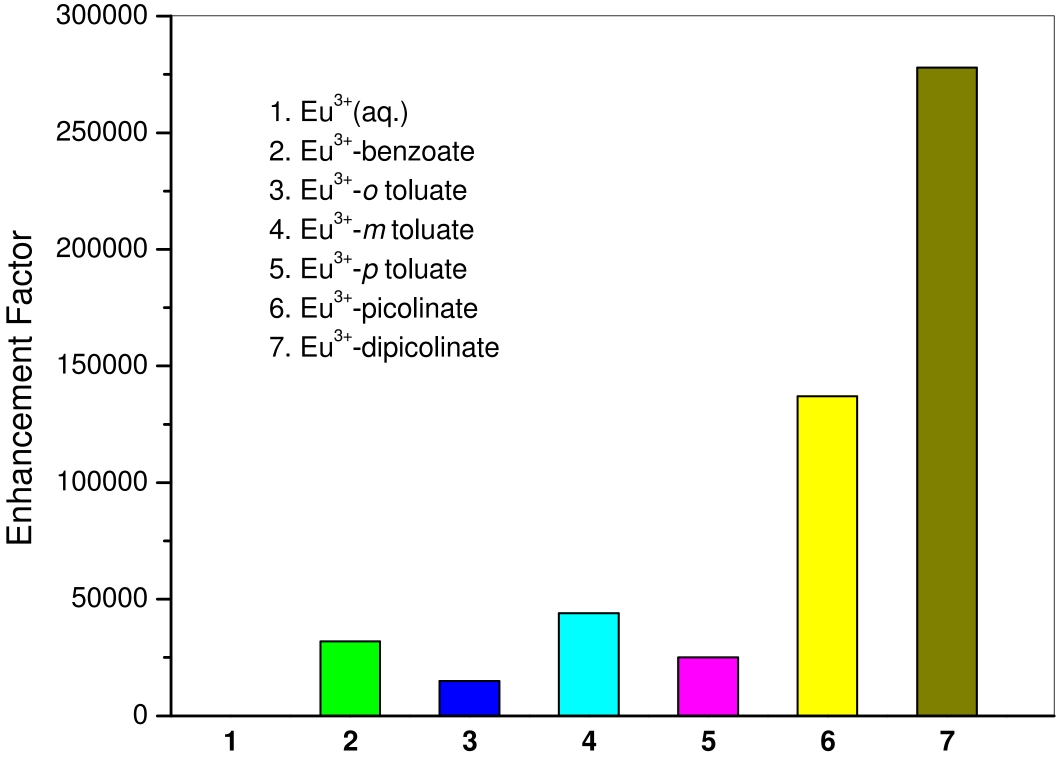

Figure 7.1 Bar graphs showing the enhancement factor for different Eu^{3+} complexes in acetonitrile medium (bars 2-7). For bar 1 (free Eu^{3+}) enhancement factor is 1 and hence not visible in the scale used.

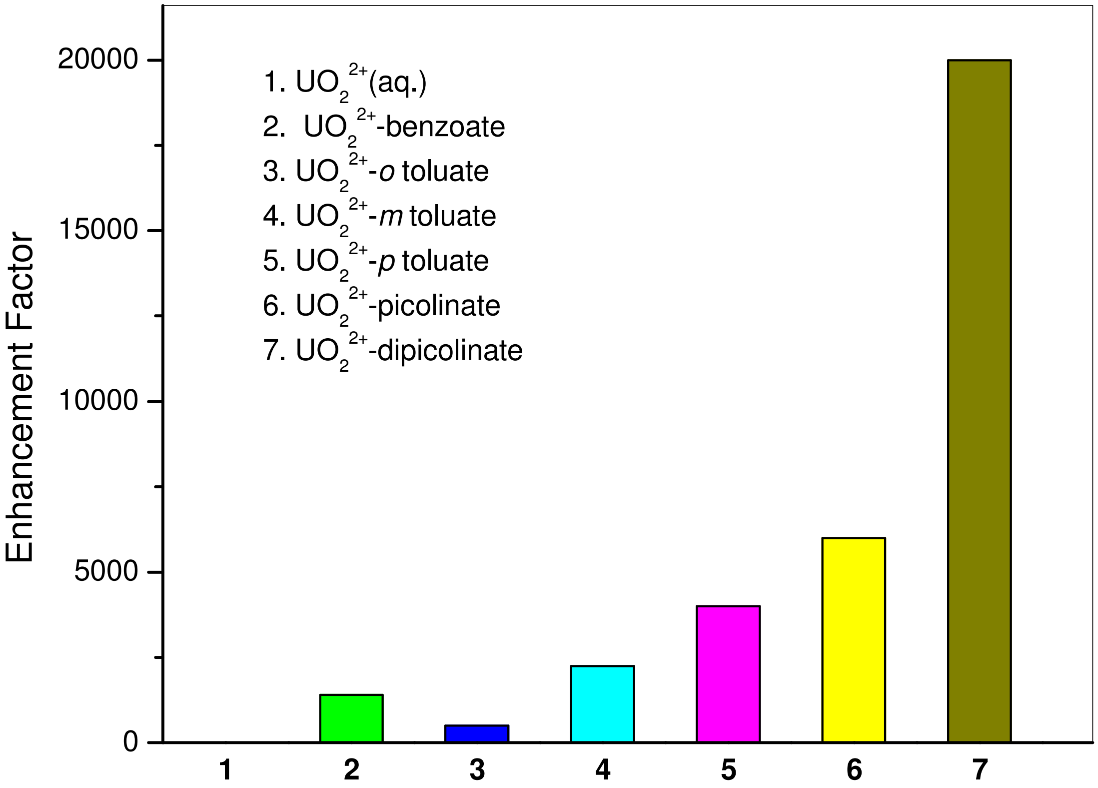

Figure 7.2 Bar graphs showing the enhancement factor for different UO_2^{2+} complexes in acetonitrile medium (bars 2-7). For bar 1 (free UO_2^{2+}), enhancement factor is 1 and hence not visible in the scale used.

co-luminescent ion, the enhancement factor due to co-luminescence reaches the value of $4.74\text{x}10^6$ and $8.0\text{x}10^4$ for Eu^{3+} and UO_2^{2+} respectively. This huge enhancement brings the detection limits to $4\text{x}10^{-11}$ M for Eu^{3+} and $1\text{x}10^{-9}$ M for UO_2^{2+}. These detection limits achieved in acetonitrile medium is much more than that obtained in aqueous medium. Apart from the luminescence intensity enhancement, the lifetimes of Eu^{3+} and UO_2^{2+} in their complexes is also increased substaintialy, though to different extents, relative to that in aqueous medium. Highest lifetime is obtained for dipicolinic acid, whereas lowest lifetime is observed for *o* toluic acid.

The significant contribution of this work is the fundamental understanding of co-ordination chemistry of Eu^{3+} and UO_2^{2+} complexes in acetonitrile medium. Studies carried out in this thesis have shown that Eu^{3+} forms ML_3 complex with benzoic acid and toluic acids in acetonitrile medium whereas in the aqueous medium ML and ML_2 complexes are reported. Due to higher stochiometry in acetonitrile, quenching due to –OH oscillators decreases resulting in luminescence enhancement. However, the studies here on Eu^{3+}-PA and Eu^{3+}-DPA system show that the stoichiometries of the Eu^{3+}-PA and Eu^{3+}-DPA complexes both in acetonitrile and aqueous medium are ML_4 and ML_3, respectively. Though the lifetimes in acetonitrile are higher than that in aqueous medium, the luminescence enhancement of these complexes in acetonitrile is due to the reduction in non-radiative deactivation processes arising by removal of water molecules from outer sphere of these metal ions.

In contrary to aqueous medium, where luminescence of UO_2^{2+} gets quenched with all of the aromatic carboxylic acids studied in this work (except DPA), its luminescence is found to be sensitized in acetonitrile medium with all these liagnds. Uranyl benzoate is reported to form non-luminescent 1:1 and 1:2 species in aqueous medium whereas studies carried out in this work indicate the formation of 1:3 complexes in acetonitrile medium. UV-Vis absorption spectroscopy studies confirmed the formation of tri benzoate complex of UO_2^{2+} i.e.

$[UO_2(C_6H_5COO)_3]^-$ which is responsible for sensitized luminescence. Studies using picolinic acid show that UO_2^{2+} forms 1:1 type non-luminescent complex with PA in aqueous medium as it is identified by slope ratio method. UV-Vis absorption spectroscopy shows that the formed UO_2^{2+}-PA specie is a 1:2 type complex in acetonitrile medium. Luminescence lifetime measurements of UO_2^{2+}-DPA complex show the formation of complexes with a stoichiometry of 1:2 and higher.

The luminescence studies carried out in this thesis also corroborate the mechanism of ligand sensitized luminescence of UO_2^{2+}. The triplet level energies of ligands (discussed in chapter 2) indicate that all the ligands used in my study can transfer energy to UO_2^{2+} and Eu^{3+}. But, the absence of sensitized enhancement in aqueous medium with all the ligands (except dipicolinic acid) indicates that non-radiative deactivation of UO_2^{2+} is so efficient to nullify ligand sensitized enhancement processes. In case of lanthanides, non-radiative deactivation involves the energy transfer to higher energy vibrational level of water molecules and therefore, replacing one or more water molecule helps in reduction of non-radiative decay. Therefore, it appears that non-radiative deactivation of UO_2^{2+} which is governed by electron transfer is more detrimental than energy transfer and hence, just by removing one or two water molecules from the inner coordination sphere of UO_2^{2+} (it happens in most of the UO_2^{2+}-ligand complexes in aqueous medium), ligand sensitized enhancement cannot be achieved. In order to get the sensitized luminescence enhancement, UO_2^{2+} complex must be completely free from water molecules at the inner coordination sites. Hence, in ligand sensitized luminescence, even though energy transfer is the key factor, deactivation process eventually decides the fate of UO_2^{2+} whether to be luminescent or not.

7.1 Scope of future work

This work can be extended to-

- Luminescence studies of UO_2^{2+} ions with poly-carboxylic acids such as ortho, meta, para phthalic acids, trimesic acid, mellitic acid to understand the exact mechanism of liagnd sensitized enhancement in acetonitrile medium.

- Determination of europium and uranium in presence of other ions using these ligands in acetonitrile medium for analytical applications.

- Alternating non-aqueous medium to study the luminescence of Eu^{3+} and UO_2^{2+} complexes.

- Theoretical studies such as DFT calculations to understand the different luminescence behavior and structures of Eu^{3+} and UO_2^{2+} complexes in aqueous and acetonirile medium to support experimental data.