Lanthanide luminescence based probe for detection of picric acid

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Europium fluorescence is significantly enhanced through ligand sensitization using aromatic benzene mono and di carboxylic acids as ligands in aqueous solution. By optimising metal to ligand ratio and solution pH, it is established that the enhancement is maximum with isophthalic and terephthalic acid. Phosphorescence of isophthalic acid is recorded and its triplet energy level is found to be at 25633 cm^{-1}; just above the fluorescing energy level of Eu^{3+}. On complexation with these ligands though the europium luminescence is enhanced by orders of magnitude, the europium lifetime increased marginally. Addition of picric acid resulted in the quenching of europium luminescence in europium-isophthalic acid complex. Based on this quenching, a fluorimetric method is developed for the estimation of picric acid in aqueous solution. Picric acid in aqueous solution could be estimated down to 0.23 ppm. Common cations and anions found in natural waters did not interfere in the analysis. The precision in measurement is within 5% RSD in the entire range of measurement.

In recent years much attention is focused on the reliable detection of 2,4,6,-trinitrophenol, popularly known as picric acid (PA). PA is highly toxic[1] and is also an explosive[2,3]. It causes cancer[3], affects the respiratory tract, eyes and liver[1,3]. It is not restricted only to military use but finds application in chemical, leather, dye and pharmaceutical industries[3,4,5]. PA is highly soluble in water and resists degradation resulting in its long persistence in water bodies[6]. Hence, it is important to detect and estimate PA in industrial effluents, mine field soil contaminated with explosives, water bodies suspected of PA contamination, forensic and installations of high security. Towards this, a simple and quick method of detecting and estimating PA is required.

Several methods are reported for the detection and quantification of PA based on spectrophotometry[7], high performance liquid chromatography[8], capillary electrophoresis[9], mass spectrometry[10], ion-selective electrodes[11] and fluorimetry[12,13,14,15]. Fluorescence based sensors are recognized for their sensitivity, selectivity, rapid response and compatibility for field analysis[3,16]. Fluorophores based on organic molecules or organic-metal complexes are extensively used as probes/sensors. Picric acid sensing materials reported in recent past are based on triphenyl benzene[16], pyrene[17], 2-arylbenzothiozols[5], anthracene[18], BF$_2$-curcumin[19] etc. He *et al.*[20] and Sohn *et al.*[21] have synthesized sensors based on siloles. In the work of He *et al.* the sensor was prepared by doping hexaphenylsilol into a chitosan film while Sohn *et al.* has prepared a polytetraphynylsiol coated on a suitable substrates such as glass, filter paper etc. Another mode of PA detection is metal organic frame work as reported by Hu *et al.*[22] and Zhou *et al.*[23]. Recently Huang *et al.*[1] has prepared a reduced graphene oxide for the determination of PA. Chakravarty *et al.*[4] has prepared probes based on biomaterials namely scutellarin-hispiduloside and curcumin in aqueous medium. The reported limit of detection using scutellarin-hispiduloside and curcumin are 9.1e^{-8} M and 6.03e^{-8} M, respectively. Ding *et al.*[24] and Zhang *et al.*[25] have reported the detection of PA based on its quenching action on certain micelles that act as fluorophores with detection limits of 1e^{-6} M and 0.5e^{-7} M, respectively. Lu *et al.*[26] has described an optical fibre based method wherein Eu-thenoyltrifluroacetone luminescence quenching is monitored and the reported detection limit is 2e^{-6} M. Of the above mentioned techniques most of sensing materials in general require lengthy and multistep preparation and long analysis time. Lanthanide luminescence finds a variety of application ranging from: as phosphor for fluorescent lamps and televisions[27], study of enzyme activity[28], cell

imaging[29], as bioprobes in time resolved luminescent immunoassays[30], coordination chemistry[31] etc. Lanthanides are known to have low quantum yields and low molar absorptivities[32] in aqueous medium. However, sensitization through suitable ligands is reported to enhance the lanthanide fluorescence by orders of magnitudes[32,33]. Beta-diketones and aromatic carboxylic acid ligands are well known for their lanthanide fluorescence sensitization efficiency in aqueous medium[33].

Presence of nitro groups in aromatic acids is known to quench the lanthanide luminescence[26]. Therefore, PA containing three nitro groups is expected to quench the europium luminescence as well. The present method combines the lanthanide fluorescence enhancement capability of aromatic carboxylic acids with the lanthanide luminescence quenching possibility by PA. For enhancement of Eu^{3+} luminescence, both aromatic monocarboxylic as well as aromatic dicarboxylic acids in aqueous medium were chosen. In the first category, salicyclic acid (SA, pK=2.98), benzoic acid (BA, pK=4.2) and p-anisic acids (PAA, pK=4.5) were chosen as ligands whereas in the second category, phthalic acid (PTA, pK_1= 2.94 pK_2= 5.43), iso-phthalic acid (IPA, pK_1=3.7, pK_2=4.6) and tere-phthalic acid (TPA, pK_1=3.54, pK_2=4.34) were chosen for complexation. Quenching of strongly fluorescent europium-acid complex is monitored by adding different concentrations of picric acid to estimate PA in aqueous solution. The first part of the paper deals with photoluminescence optimization studies carried out to arrive at a suitable Eu^{3+}-aromatic acid system that acts as a probe for PA. The second part of the paper deals with the calibration, lifetime studies, interference studies and figures of merit of the proposed technique such as precision and limit of detection.

Materials and Methods

Europium nitrate was prepared from Eu_2O_3, obtained from Alfa Asear with 99.99% purity. The oxide was dissolved in concentrated nitric acid and then evaporated to near dryness followed by its dissolution in deionized water. A 0.01 M PA stock solution was prepared by dissolving 0.23 g of PA in 100 mL deionized water. PA and all the organic ligands used were from either Sigma Aldrich or Merck. Millpore water with specific conductivity <1 μS cm⁻¹ was used to prepare the stock solutions.

All the photoluminescence (PL) studies were carried out using Edinburgh make FLS-980 system using a 450 W xenon lamp as the excitation source and maintaining

both the excitation as well as the emission slit width at 2 nm and. The phosphorescence of isophthalic acid was recorded at 77 K in presence of gadolinium. For recording PL lifetime measurements, a xenon pulsed lamp with 1 μS pulse width was used. A Lovibond make S-320 pH meter with a gel type electrode was used to adjust the solution pH within ±0.05 units from the desired value. Further, the pH probe was calibrated daily prior to its use.

Results and Discussion

Six different ligands comprising of both aromatic monocarboxylic acids (AMCA) as well as aromatic dicarboxylic acids (ADCA) are chosen for this study. To begin with, optimization studies were carried out on all the six Eu^{3+}-aromatic acid complexes by monitoring Eu^{3+} luminescence as a function of solution pH and M:L ratio in order to find out the maximum enhancement in Eu^{3+} luminescence. A greater enhancement will improve the detection limit of PA, as the analytical method adopted here is based on quenching of Eu^{3+} luminescence. During optimization, the emission intensity of Eu^{3+} was always monitored at its characteristic wavelength at 616 nm. However, for each complex, depending on the ligand, pH of the solution and the M:L ratio, the excitation maximum was found to vary between 235 and 305 nm. Only salicylic acid failed to sensitize Eu^{3+} fluorescence due to strong intramolecular hydrogen bonding existing in the ligand molecule itself and thus preventing it from complexing with Eu^{3+}.

For studying the effect of pH, a fixed M:L ratio of 1:10 was chosen. Fig. 1a shows the variation of luminescence intensity as a function of pH for
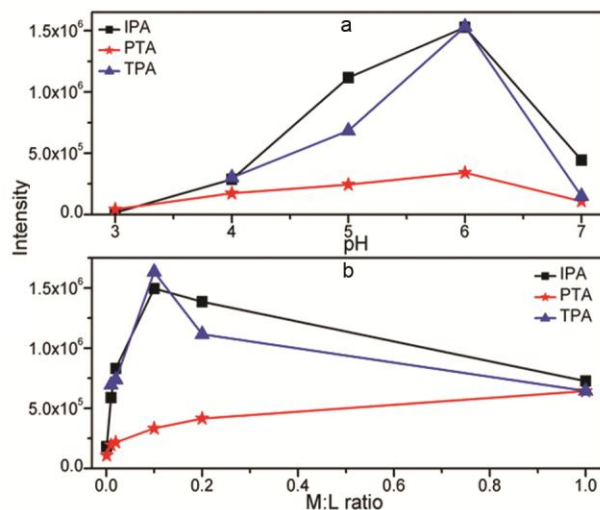

Fig. 1 — Luminescence intensity of Eu^{3+}-ADCA complexes monitored at 616 nm as a function of (a) solution pH at a constant M:L ratio of 1:10 and (b) as a function of M:L ratio at a pH of 6.0

Eu^{3+}-IPA/PTA/TPA systems. The solution pH is varied from 3 to 7 for both Eu^{3+}-IPA and Eu^{3+}-PTA systems, whereas it is varied from 4 to 7 in the case of Eu^{3+}-TPA as in the latter case, precipitation started appearing around pH 3.5. For all these three acids, both the carboxylic acid groups are dissociated more than 90% at pH 6.0 and beyond this pH, the possibility of europium getting hydrolyzed cannot be ruled out. For all the dicarboxylic acid complexes emission intensity is maximum near pH 6.0 (Fig. 1a). Therefore, maintaining the solution pH at 6.0, the M:L ratio of each complex was varied from 1:1000 to 1:1. Fig. 1b shows the effect of M:L ratio on the intensity. Both Eu^{3+}-IPA and Eu^{3+}-TPA complexes exhibit maximum intensity at a M:L ratio of 1:10 whereas for Eu^{3+}-PTA system, the optimum M:L ratio is at 1:1. In the case of PTA, the complexation with europium is expected to be different as both the carboxylic acid groups are ortho to each other and can possibly bind to the same europium ion. Moreover, hydrogen bonding between the two ortho carboxylic groups can also affect the complexation with europium. However, no effort was made to study the complexation pattern of europium with these ligands as it is beyond the scope of this study. In case of Eu^{3+}-TPA, the particular M:L ratio of 10^{-4} M Eu^{3+}: 10^{-1}M TPA was not studied due to the appearance of precipitate. Fig. 2a shows the effect of

pH on the Eu^{3+}-BA and Eu^{3+}-PAA (AMCA complexes) at a M:L ratio of 1:10. The luminescence intensity for both the complexes is maximum at pH 6.0. The influence of M:L ratio at pH 6.0 on the luminescence intensity is shown in Fig. 2b. Benzoic acid at a M:L ratio of 1:10 enhances Eu^{3+} luminescence better than p-anisic acid at pH 6.0. The optimized pH and M:L were used for the rest of the studies with all the ligands chosen here except salicylic acid.

Spectral characteristics

Fig. 3a shows the excitation and emission spectra of uncomplexed Eu^{3+} in aqueous solution whereas Fig. 3b
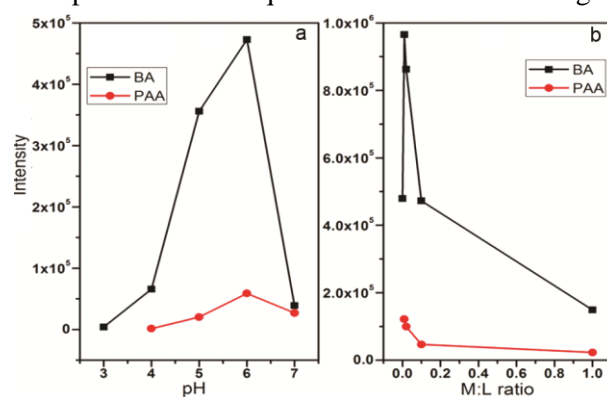

Fig. 2 — Variation of intensity (616 nm) of Eu^{3+}-AMCA complexes (a) as a function of solution pH at a constant M:L ratio of 1:10 and (b) as a function of M:L ratio at the optimum pH of 6.0
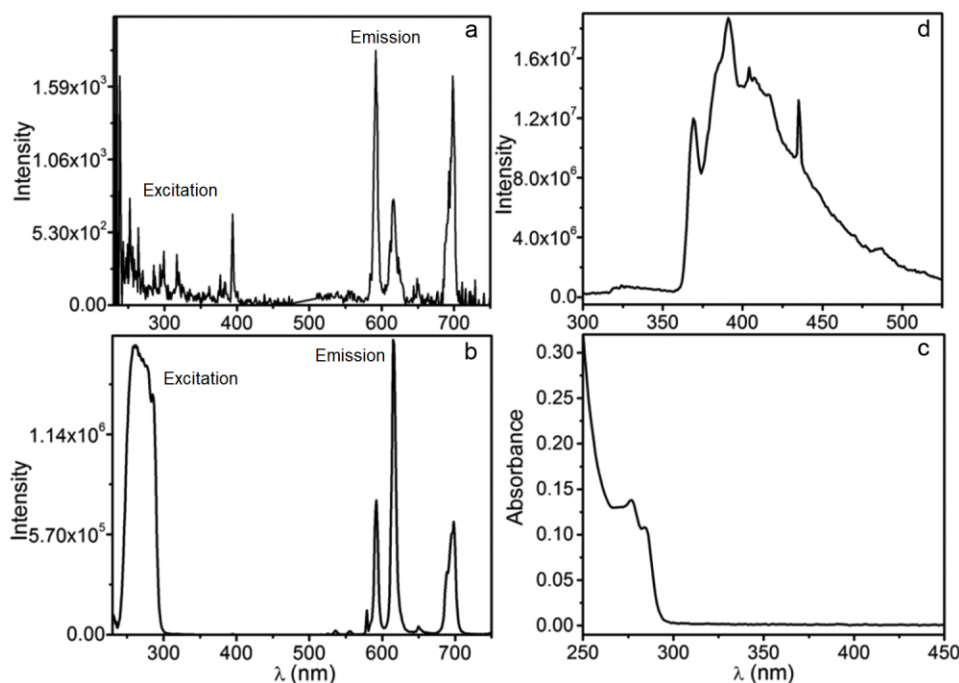

Fig. 3 — (a) Excitation and emission spectra of 10^{-4}M uncomplexed Eu^{3+} in water (λ_{em}= 616 nm, λ_{ex}=394 nm), (b) Excitation and emission spectra of Eu^{3+}-IPA complex containing 10^{-4}M Eu^{3+} and 10^{-3}M IPA at pH 6.0 (λ_{em}= 616 nm, λ_{ex}=259 nm), (c) Absorbance spectrum of isophthalic acid, and (d) Phosphorescence spectra of isophthalic acid recorded at 77 K

shows that of Eu^{3+}-IPA complex. The excitation spectrum was recorded by monitoring the europium emission at 616 nm and the emission spectrum was recorded by exciting at 394 nm and 259 nm for Eu^{3+} and Eu^{3+}-IPA systems, respectively. The absorption spectrum of IPA is shown in Fig. 3c. The excitation spectra of Eu^{3+} and Eu^{3+}-IPA are different from each other though the emission spectra are similar but for the different intensity ratio of 616/592 nm suggesting sensitization of europium luminescence by this dicarboxylic acid ligand. Comparison of luminescence intensities of Eu^{3+} and Eu^{3+}-IPA complex confirms the enhancement of europium luminescence due to sensitization. For europium luminescence sensitization and enhancement, the triplet energy level of the ligand should be above and near to the fluorescing energy level of the Eu^{3+}. Fig. 3d shows the phosphorescence spectrum of IPA. The triplet energy level of isophthalic acid as calculated from the recorded phosphorescence spectrum is at 25633 cm^{-1}. The $^5D_1$ fluorescing energy level of europium is reported[31] to be at 18973 cm^{-1}. Therefore, sensitization of Eu^{3+} luminescence by isophthalic acid is obvious. A similar sensitization and luminescence enhancement of Eu^{3+} is observed with all other ligands studied here though the extent of enhancement is different with different ligands. The Eu^{3+}-IPA emission spectrum exhibits europium peaks at 525, 535, 560, 580, 594, 616, 650 and 698 nm corresponding to $^5D_1 \rightarrow {}^7F_0$, $^5D_1 \rightarrow {}^7F_1$, $^5D_1 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. The $^5D_0 \rightarrow {}^7F_1$ is a magnetic dipole transition whereas $^5D_0 \rightarrow {}^7F_2$ is the induced electric dipole transition, known for its hypersensitivity to the europium environment[31]. The emission from $^5D_1$ excited level, as seen here from Eu^{3+}-IPA complex, is not always observed due to the strong non-radiative transitions from this energy state. The appearance of $^5D_0 \rightarrow {}^7F_0$ transition at 580 nm without splitting indicates the presence of a single Eu^{3+}-acid species in the medium, a fact further confirmed from lifetime measurement studies discussed later. All the emission peaks of Eu^{3+} are observed with all the five Eu^{3+}-acid complexes and for avoiding the repetition their emission spectra are not presented.

The ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ transitions, in terms of their integrated intensities, is known as asymmetry ratio ($R_{21} = I_{5D_0 \rightarrow {}^7F_2}/I_{5D_0 \rightarrow {}^7F_1}$) and it indicates symmetry/asymmetry around europium[34,35]. A higher R_{21} is indicative of a larger deviation from the centro-symmetric geometry. For the uncomplexed Eu^{3+}, the asymmetry ratio was found to be 0.8. Fig. 4a shows the variation of R_{21} for all the three ADCA complexes, as a function of M:L ratio at a solution pH of 6.0. Eu^{3+}- IPA system shows an increase in the symmetric environment around europium, i.e., a decrease in R_{21}, as compared to the other two systems at a M:L ratio of 1:1000. For M:L = 1:10, the R_{21} increases with solution pH for all three complexes (Fig. 4b). The variation of R_{21} of Eu^{3+}-AMCA complexes with respect to M:L ratio and the solution pH are presented in Figs. 5a and 5b, respectively. The asymmetry of Eu^{3+}-AMCA complexes increases with increase in ligand concentration (Fig. 5a). Similarly, as seen with Eu^{3+}-ADCA complexes, the asymmetry increases with increase in solution pH for both the AMCA complexes (Fig. 5b). However, the R_{21} versus pH profile of Eu^{3+}-AMCA systems is different from that observed for the Eu^{3+}-ADCA systems probably due to different mode of complexation depending on the position of carboxylic groups and their extent of dissociation at different pH.
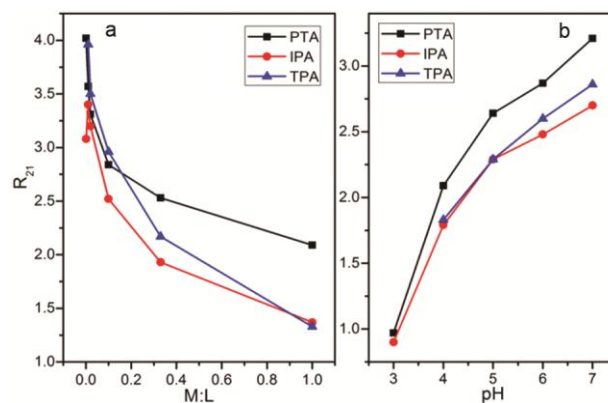

Fig. 4 — (A) Influence of M:L ratio on R_{21} of Eu^{3+}-ADCA complexes at a solution pH of 6.0. (B) Variation of R_{21} of the complexes with respect to pH at a constant M:L ratio of 1:10
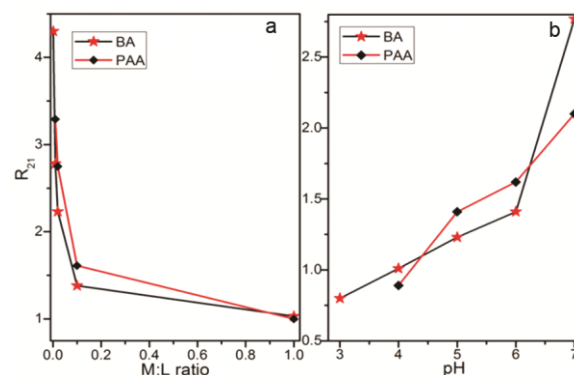

Fig. 5 — Variation of R_{21} of Eu^{3+}-AMCA complexes: (a) as a function of M:L ratio and (b) as a function of pH

Table 1 — Comparison of the few of the techniques reported in the literature

| Technique	LOD (M)	Experimental details	Reference
Luminescence quenching	2×10^{-6}	Static quenching of PA on Eu-theonoyltrifluoroacetone complex immbilized on a chelating resin	26
Fluorescence quenching	1×10^{-6}	Fluorescence quenching of PA on fluorophore/micelle system. Sodium dodecyl sulphate acts as surfuctant, Py-diIM-Py acts as fluorophore	24
Fluorescence quenching	0.5×10^{-7}	Fluorescence quenching of PA on Fluorescent micelle system. Micelle: Cationic cellulose derivative, Fluorophore: (4,7-bis [4- (1,2,2- triphenylvinyl)phenyl] benzo-2,1,3-thiodiazole)	25
Fluorescence quenching	9.1×10^{-8}	Fluorescence quenching of PA on biomaterial Scutellarin-Hisiduloside-glycerol	4
Fluorescence quenching	1×10^{-6}	Fluorescence quenching of PA on Eu^{3+}- isophthalic system	present technique
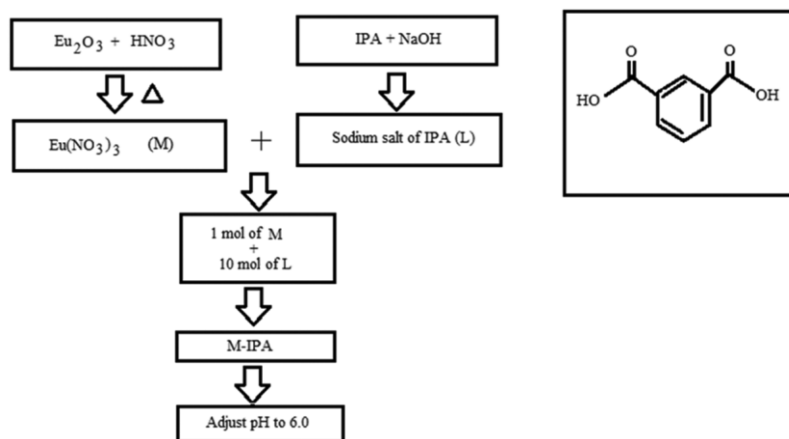
Fig. 6 — Schematic representation of synthesis of the metal-ligand complex with the inset shows the structure of the ligand

Quenching characteristics, selectivity and stability

It is seen that, among the five ligands taken for sensitization of Eu^{3+} luminescence, both IPA as well TPA give nearly the same enhancement (Fig. 1). However, for studying the luminescence quenching behaviour of PA, Eu^{3+}-IPA system is chosen. The sensor preparation is shown schematically in Fig. 6, whereas the inset shows the structure of the ligand (IPA). Based on the optimization studies we arrived at a M:L ratio of 1:10 (10^{-4} M Eu^{3+} and 10^{-3} M IPA) at a solution pH of 6.0. PA concentration was varied from 0 M to $2*10^{-4}$ M. It should be noted here that, the final sample pH after the addition of PA was always maintained at 6.0.

Fig. 7 shows the Eu^{3+} emission spectra of Eu^{3+}-IPA complex in aqueous solution with increasing PA concentration. The inset of Fig. 7 shows the quenching behaviour of PA in a wide concentration range with the linear portion extending up to 10 μM. In this linear region, the following relation I = $-2.49839e^{10}$ [PA] + $1.60869e^{6}$ having R^2=0.99 holds good. Using this mathematical relation and based on the criterion of 3σ for blank, the limit of detection (LOD) for PA turns out to be $1x10^{-6}$ M which corresponds to 0.23 ppm of PA. The detection
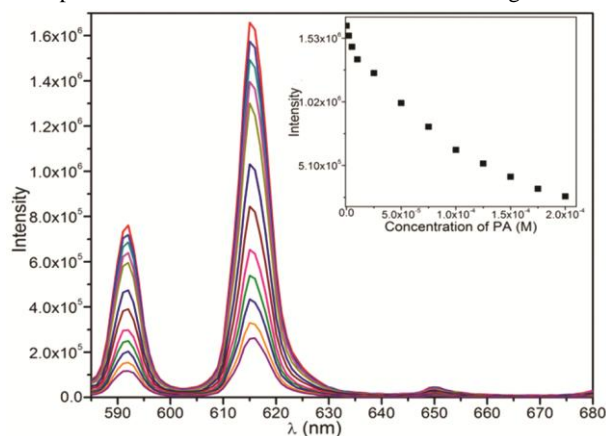

Fig. 7 — Progressive quenching of Eu^{3+} luminescence in Eu^{3+}-IPA system with increasing PA concentration. Concentration of PA (μM) increases in the following order 0, 2, 5, 10, 25, 50, 75, 100, 125, 150, 175 and 200. Inset shows the smooth variation of intensity at 616 nm as a function of concentration of PA

limit observed here is comparable to the values reported by earlier workers.[24,26] Table 1 compares the current technique, with respect to LOD, with some of the techniques reported earlier. All the luminescence measurements in this study were made with 2 nm slit width for both excitation and emission monochromator. The detection limit can be further

lowered by increasing the slit width wherever feasible. Further, a limited interference study was conducted by introducing some of the commonly found cations and anions to find out their effect on the estimation of PA. The ions studied along with minimum tolerable limits as indicated in the parentheses are as follows, Mg^{2+} (50 ppm), K^+(40 ppm), SO_4^{2-} (20 ppm), Na^+(35 ppm), NH_4^+(25 ppm), Cl^- (40 ppm), NO_3^-(30 ppm), CO_3^{2-}(25 ppm) and HCO_3^-(60 ppm). By carrying out experiments on different days with fresh set of reagents, the obtained reproducibility of the results is within 5% RSD. The stability of the aqueous solution containing the Eu^{3+}-IPA complex is good enough for over two hours duration with negligible variation in the signal strength.

Lifetime studies

We also carried out quenching studies on Eu^{3+}-IPA system. In aqueous solution, the lifetime of uncomplexed Eu^{3+} is found to be 110 µs (λ_{ex}=259 nm, λ_{em}=615 nm) and this value is in agreement with the value reported in literature.[31] Complexation of europium with isophthalic acid although increased the europium lifetime, the increase was not dramatic. The life time of Eu^{3+}-IPA complex without the quencher as well as with varying concentrations of PA was also measured. For calculating the quenching constant, the well known Stern Volmer equation[36] $I_0/I = 1 + k_q \tau_0[Q]$ is used. Here, I and I_o are the intensities with and without the quencher, Q is the concentration of quencher (PA), k_q is the bimolecular quenching constant and τ_0 is the excited state lifetime of Eu^{3+} complexed with IPA in absence of quencher. A Plot of variation of (I_0/I) as a function of quencher concentration reveals linearity at low concentrations while showing upward curvature at higher concentrations (Fig. 8). This is suggestive of the fact that either static or both static as well as dynamic quenching processes are operating[4,37]. By measuring τ_0, the bimolecular quenching constant in the linear portion and the non-linear portion of the plot turns out to be 1.4×10^8 M^{-1} $s^{-1}$and 2.87×10^8 M^{-1} s^{-1}, respectively. The lifetime τ_0 is found to be 128 µS (χ^2=1.10) and the value decreased continuously with increasing concentration of PA and reached 122 µS (χ^2=1.03) at a PA concentration of 200 µM. All the corresponding decay curves showed a single exponential fit (with χ^2 lying between 1.03 and 1.15) suggesting the existence of a single species in solution as mentioned earlier considering the $^5D_0 \rightarrow ^7F_0$ emission peak (Fig. 3b).
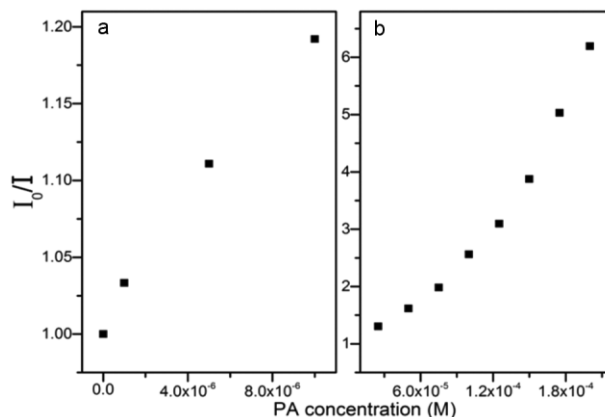

Fig. 8 — Stern Volmer plot of Eu^{3+}-IPA system at (a) lower and (b) higher concentrations of PA
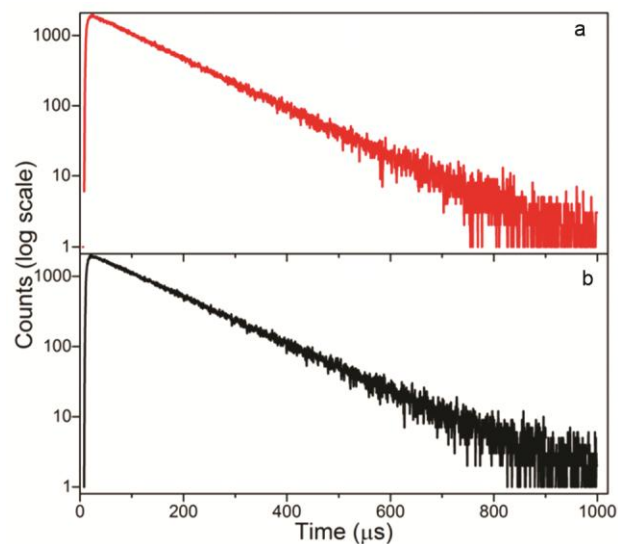

Fig. 9 — Lifetime decay profile of Eu^{3+} complexed IPA (a) in the absence of PA and (b) in the presence of PA (200 µM)

Fig. 9 shows the exponential decay curves of Eu^{3+}-IPA without PA and with PA (200 µM). Using the lifetime data we also calculated the hydration number, i.e., the number of water molecules associated with the metal ion, for both the uncomplexed Eu^{3+} and for Eu^{3+}-IPA, using the relation[33] q($\pm$0.5)= 1.05 * (1/τ_{H2O}) - 0.7. The increase in excited state lifetime of Eu^{3+}-IPA (0.128 mS) compared to that of uncomplexed Eu^{3+} (0.110 ms) is due to the removal of some of the water molecules from the coordination sphere, that otherwise efficiently depopulates the $^5D_0$ state of Eu^{3+} through non-radiative relaxation caused by O-H vibronic oscillations.[31] Substituting τ_{H2O} for Eu^{3+} and Eu^{3+}-IPA, we obtain the corresponding water of hydration as 9 and 7 respectively; effectively implying that two water molecules are removed from the coordination sphere through the complexation of IPA ligand. The

replacement of only two water molecules following the complexation with isophthalic acid suggests that this ligand acts only as monodentate ligand which is expected as both the carboxylic groups are meta-positioned to each other and therefore, it is difficult for both the carboxylic groups to bind with the same europium. The removal of two water molecules did not result in dramatic enhancement of europium lifetime as still there are seven more water molecules that are inbuilt in the europium coordinate sphere which could efficiently quench the europium luminescence.

Conclusions

Europium luminescence is enhanced by orders of magnitude through ligand sensitization. Except salicyclic acid, all the ligands taken in this study, sensitized the europium luminescence. The enhancement is maximum at pH 6.0 with all the ligands since the dissociation of carboxylic acid group(s) increases with increasing solution pH. However, no single M:L ratio gave maximum enhancement for all the ligands. The pattern of variation of asymmetric ratio with respect to pH and M:L ratio is different for AMCA and ADCA complexes probably due to different mode of complexation. The phosphorescence spectrum of isophthalic acid reveals that, its triplet energy level is above the fluorescing energy level of europium enabling europium luminescence sensitization through this acid ligand. The presence of picric acid leads to the quenching of europium luminescence in the Eu^{3+}-IPA complex in aqueous solution. Stern Volmer plot shows linearity when the quencher (PA) concentration is low while the curve bends upwards at higher quencher concentrations indicating static or a combination of static and dynamic quenching. Lifetime studies indicate that, complexation with isophthalic acid removes two water molecules from the inner europium coordination sphere. Picric acid could be estimated at a level of 0.23 ppm in aqueous solution by europium luminescence quenching method.

Acknowledgment

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