

## Photoluminescence Enhancement from $\text{Eu}^{3+}$ in presence of Ligands PPIA and TOPO

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**Abstract:** In the present work, study on the photoluminescence behavior of  $\text{Eu}^{3+}$  in presence of the ligands Phenyl phosphinic acid and Trioctylphosphine oxide have been carried out. Enhancement of photoluminescence intensity as well as yield by more than an order of magnitude in presence of Phenyl phosphinic acid and further enhancement by a factor of 1.1 with the addition of Trioctylphosphine oxide is observed. Quantitative analysis of the PL enhancement and the factors responsible for the enhancement is discussed.

**Keywords:** Energy transfer, Ligand Sensitization, Optical Material, Photoluminescence, Rare Earth.

### I. Introduction

The Rare earths (REs) are an important class of optical materials that possess diverse applications viz. in the areas of lasers, biochemistry, material science etc. [1]. They are in general extensively studied as luminescent materials due to their long-lived lifetimes, narrow emission bands, hypersensitivity to coordination environment etc. Although the RE ions show sharp and narrow emissions, they usually possess very low absorption cross-section [2]. Since the luminescence intensity is not only proportional to the luminescence quantum yield but also on the amount of light absorbed, weak absorption of RE ions results in weak luminescence. The probability of spectroscopic transitions of RE ions depends strongly on the symmetry around the RE ions as well and it is reported that higher is the symmetry less is the probability of transitions [3]. Hence, to obtain efficient luminescence, it is necessary either to enhance the absorbance of RE-host system or to change the symmetry around the RE ions. This can be accomplished by a variety of techniques, among which ligand sensitization is a very effective one. Moreover, the ligands can prevent the clustering of dopant ions, isolate the metal ions from the deactivating groups, reduce hydroxyl quenching by dopant ion encapsulation, and also efficiently transfer energy from ligand to RE ions [4]. The luminescence of RE-ligand complexes is of great interest due to their high emission efficiency. In these complexes the energy transfer is observed between ligand (donor) molecules and the RE (acceptor) ions. As a result, the emission from a given complexed ion shows greater efficiency than that of uncomplexed ions. Attention has also been drawn recently by molecular lanthanide coordination complexes due to their potential as phosphors in thin film electroluminescence displays [5].

In the present work, a study on photoluminescence (PL) of  $\text{Eu}^{3+}$  in presence of ligands phenyl phosphinic acid (PPIA) and Trioctylphosphine oxide (TOPO) have been carried out.  $\text{Eu}^{3+}$  is one of the most potential RE ions that is used exclusively as phosphor and in lighting technology. It has the simplest energy level structure among all the RE ions and provides sharp fluorescence spectrum in the visible range. Its ground state  $^7F_0$  is non-degenerate and it has well spaced  $^7F_J$  ( $J=0$  to 6) and  $^5D_J$  ( $J=0$  to 4) excited states for which it is used as efficient optical probe. PPIA is a bidentate ligand with a benzene ring linked to pentavalent phosphorous atom which is attached to an oxygen atom by a double bond, an H atom and a functional group OH by single bonds. The ligand PPIA is selected for the present study since the emission maxima of PPIA considerably overlaps the absorption maxima of  $\text{Eu}^{3+}$  ions. TOPO is a neutral ligand and can help to enhance the luminescence of REs in complex formation by minimizing the collision between RE and water molecules because of its hydrophobic nature [6]. There have been reports of using PPIA as sensitizing ligand for  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions in water medium as well [4].

### II. Experimental

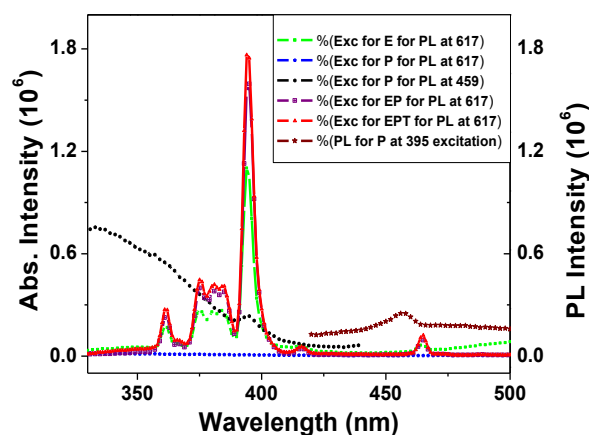
At first the stock solution of  $5 \times 10^{-2}$  M PPIA (Aldrich, 99%) (Solution 1) was prepared by dissolving PPIA in methanol (Merck,  $\geq 99\%$ ) and was magnetically stirred for 15 minutes (Sample P). The stock solution of  $10^{-2}$  M TOPO (Aldrich, 99%) (Solution 2) was prepared by dissolving TOPO in methanol and then stirring magnetically for 10 minutes. To solution 2,  $10^{-2}$  M Europium Chloride (Aldrich, 99.9%) was added and further stirred for 10 minutes. The resultant mixture was mixed with solution 1 and further stirred for 1hr at  $40^\circ\text{C}$  to prepare the final Eu-PPIA-TOPO homogeneous complex (sample EPT). To prepare the sample E,  $10^{-2}$  M Europium Chloride was first dissolved in methanol and then magnetically stirred for 15 minutes. The sample EP was prepared by combining the stock solutions of PPIA and Europium and then magnetically stirring for 10

minutes. The concentration of Europium Chloride and PPIA was kept at  $10^{-2}$  M and  $5 \times 10^{-2}$  M respectively for the sample EP.

Room temperature PL spectra and PL excitation spectra for the as prepared samples were recorded by Fluoromax 4P spectrofluorimeter with spectral resolution 1 nm using the excitation wavelengths at 395nm. For the PL recording, solutions were taken in a 1cm path length quartz cell and 150 watt CW xenon lamp was used as the excitation source. The emission was collected at  $90^\circ$  with respect to the excitation beam. Band passes for the excitation and emission monochromators were set at 3 nm for all the samples.

### III. Results And Discussions

Fig. 1 shows the excitation spectra for samples E, P, EP and EPT with emission wavelength fixed at 617 nm. An additional excitation spectrum for sample P that corresponds to the PL maxima at 459 nm is also shown in the figure. PL spectrum of the PPIA singly doped sample is also incorporated in the figure that clearly shows the considerable overlapping of PPIA PL maxima (around 459 nm) with absorption maxima of Europium doped



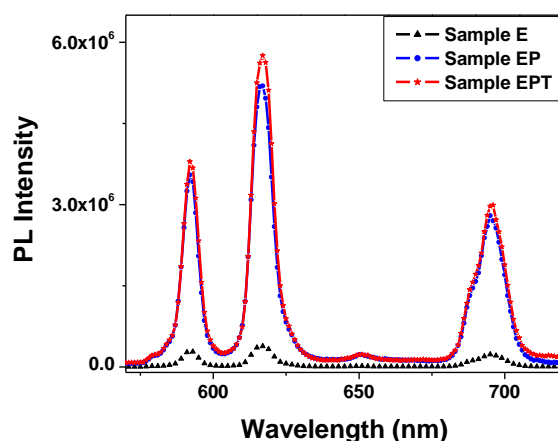
**Figure 1:** Excitation spectra for samples E, P, EP, EPT and PL spectrum for sample P.

samples (around 465 nm). Four absorption maxima at wavelengths 361 nm, 375 nm, 395 nm and 465 nm respectively corresponding to  $\text{Eu}^{3+}$  transitions were observed for the samples E, EP and EPT; with the peak at 395 nm with  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  transition having the maximum absorbance. Based on these results obtained from the excitation spectra, excitation wavelength of 395 nm was selected for recording the emission spectra for the samples. Comparison of the absorption intensities of  $\text{Eu}^{3+}$  (refer Fig.1) also shows that the intensity increases by 1.45 times when PPIA is added to sample E which further enhanced by 1.10 times when TOPO was added to sample EP. The increase in absorbance with the addition of PPIA is attributed to the contribution of PPIA to the overall absorbance of the co-doped samples, since the excitation spectra for sample P (for PL maxima fixed at 450 nm) also reveals an absorption peak around 395 nm.

Fig. 2 depicts the PL spectra for the samples E, EP, and EPT respectively under 395 nm excitation. Three prominent PL maxima at peak wavelengths 592 nm, 617 nm and 695 nm corresponding to  $\text{Eu}^{3+}$  transitions  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  were observed for all the samples with the peak at 617nm showing the maximum intensity. From the observed PL spectra, the PL peak intensity, quantum yield (in comparison to sample E) and full width at half maximum (FWHM) were calculated and are shown in Table I. The areas under the PL maxima were considered for the determination of the yield. An increase in PL peak intensity upto 13.48 times for sample EP in comparison to sample E and a further enhancement for sample EPT by 1.11 times in comparison to EP was observed for the peak at 617nm. For the same PL peak, the corresponding enhancement in yield upto 13.77 times for sample EP in comparison to E and 1.10 times for EPT in comparison to EP was observed. The results indicate a significant enhancement of the PL efficiency of the samples doped with PPIA and TOPO in comparison to the  $\text{Eu}^{3+}$  singly doped sample. A small or no change in FWHM of the PL spectra is observed on the addition of the ligands. The peak at 617 nm arising due to the transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  is an electric dipolar transition and hypersensitive one. The intensity of this hypersensitive transition is strongly dependent on the ligand environment of  $\text{Eu}^{3+}$ , while  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  is magnetic dipolar transition and to first order approximation is independent of environment. M.F. Belian *et al.* [7] reported that if the ratio between intensity of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$  is less than unity, it indicates that  $\text{Eu}^{3+}$  ions occupy low symmetric environment around them. This parameter is known as asymmetry ratio and is used to quantify the change in environment around the RE ions. In the present case the asymmetry ratio is found to

be decreased from 0.79 for sample E to 0.66 for sample EPT (shown in Table II). The result indicates a considerable change in  $\text{Eu}^{3+}$  environment with the addition of the ligands PPIA and TOPO to the samples.

The ligands enhance the PL of RE ions by a variety of processes. In the present case an enhancement of PL intensity, yield as well as absorption intensity with the addition of ligands PPIA and TOPO were observed. The increase in absorption intensity for the ligand PPIA co-doped samples is attributed to the overlapping of absorption maxima for both  $\text{Eu}^{3+}$  and PPIA at 395 nm (refer Fig. 1).



**Figure 2:** PL spectra for samples E, EP and EPT under 395 nm excitation.

**TABLE I:** Comparison of PL intensities, quantum yields and FWHMs for sample E, EP and EPT

PL peak Positions (nm)	PL Intensity (AU)		
	E	EP	EPT
592	$2.99 \times 10^5$	$3.54 \times 10^6$	$3.79 \times 10^6$
617	$3.84 \times 10^5$	$5.18 \times 10^6$	$5.75 \times 10^6$
695	$2.30 \times 10^5$	$2.79 \times 10^6$	$2.98 \times 10^6$
Yield			
592	$2.36 \times 10^6$	$2.94 \times 10^7$	$3.08 \times 10^7$
617	$3.82 \times 10^6$	$5.26 \times 10^7$	$5.77 \times 10^7$
695	$2.98 \times 10^6$	$3.66 \times 10^7$	$4.07 \times 10^7$
FWHM (nm)			
592	7	7	7
617	9	8	9
695	12	12	13

The enhancement of the PL intensity and yield for the ligand co-doped samples in the present study is attributed to the overlapping of absorption maxima for  $\text{Eu}^{3+}$  and PPIA at 395 nm as well as the absorption of the emitted energy from PPIA at 459 nm by  $\text{Eu}^{3+}$ . This is evident from the excitation spectra for sample P shown in Fig.1 which shows a maximum at 395 nm for emission wavelength fixed at 459 nm. So, when sample EP is excited at 395 nm, both  $\text{Eu}^{3+}$  and PPIA absorbs a considerable amount of energy (since both corresponds a strong absorption at 395 nm). The ligand PPIA then emits around 459 nm. This emitted energy is again absorbed by the  $\text{Eu}^{3+}$  (because of the presence of absorption maximum at 465 nm). So the enhancement of PL for samples EP in comparison to sample E is attributed to the overlapping of the emission peak of PPIA and absorption peak of  $\text{Eu}^{3+}$ . The enhancement of the PL in the sample EPT arises due to the hydrophobic nature of

**TABLE II:** Asymmetry ratios for samples E, EP and EPT

Sample	PL intensity (AU)		Asymmetry Ratio
	${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$	${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$	
E	$2.99 \times 10^5$	$3.84 \times 10^5$	0.79
EP	$3.54 \times 10^6$	$5.18 \times 10^6$	0.68
EPT	$3.79 \times 10^6$	$5.75 \times 10^6$	0.66

the ligand TOPO. It is believed that the O–H oscillators of water molecules in aqueous medium absorb a large amount of the excited energy and cause the molecule to de-excite through non-radiative processes which is detrimental for the efficient PL [8]. This de-excitation can be effectively reduced by the incorporation of ligands with lanthanides in aqueous medium. In the present case, ligand TOPO acts as the repellent for water, OH group quenchers from the co-ordination sphere and thus isolates the central Europium ion from them [9]. This results in the minimization of non radiative decay of Eu<sup>3+</sup> and hence enhances the resultant PL.

#### IV. Conclusions

In this work, the effect of organic ligands PPIA and TOPO on the PL behaviour of Eu<sup>3+</sup> in methanol have been studied. The intensities as well as yield of the ligand co-doped samples in comparison to the Eu<sup>3+</sup> singly doped samples are quantified. Significant enhancement of both intensity as well as yield by the addition of ligands was observed. This enhancement is attributed to the efficient energy transfer from PPIA to Eu<sup>3+</sup> ions and the encapsulation of metal ions by the ligand TOPO in the studied medium. The result is very significant as the Eu<sup>3+</sup> in aqueous medium are used extensively as structural probes in fluorescence studies due to its ability to fluoresce in solutions at room temperature. The study can be further extended to different host media viz. glasses, crystals etc. and other ligand- RE combinations.

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