



## OPTICAL PROPERTIES OF $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$ IN POLYSTYRENE

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**Abstract-** Europium  $\beta$ -diketonate complexes  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$ , (Eu: Europium, Re=Y/Tb Y: Yttrium, Tb: Terbium TTA: Thenoyl Trifluoro-Acetone, Phen: 1-10 Phenanthroline;  $x=0.5$ ) were dispersed in Polystyrene (PS) matrix. The resulting systems were studied using optical absorption spectroscopy and photoluminescence (PL) measurements. Absorption spectra of all the complexes have two absorption peaks at 280 and 360nm attributed to  $n-\pi$  &  $\pi-\pi^*$  transition of  $\beta$  diketonate ligand TTA. The composites formed by the three complexes  $\text{Eu}(\text{TTA})_3\text{Phen}$ ,  $\text{Eu}_{0.5}\text{Tb}_{0.5}(\text{TTA})_3\text{Phen}$ ,  $\text{Eu}_{0.5}\text{Y}_{0.5}(\text{TTA})_3\text{Phen}$  show large differences in their luminescence spectra when doped in polymer(PS). The difference between the PL properties may be attributed to different interactions between the chelate molecules and polymer. Thus these complexes can easily be made into flexible films when blended with polymers, making fabrication of OLEDs possible by solution techniques.

**Keywords-**  $\beta$ -diketonate, PS, Matrix, luminescence, ligand

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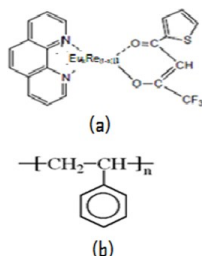
### Introduction

The trivalent rare earth or lanthanide ions are known for their unique optical properties such as line-like emission spectra and long luminescence lifetimes. Because of their intrinsically low absorption cross sections, the indirect excitation of lanthanide ions via an antenna chromophore has been studied in detail for europium ( $\text{Eu}^{3+}$ ) and terbium ( $\text{Tb}^{3+}$ ) luminescence[1,2]. The transfer of the excitation energy to the lanthanide ion is generally considered to take place through the triplet state of the antenna chromophore via an electron-exchange mechanism[3]. The emission spectra of trivalent lanthanide ions contain line like transitions. If one of these transitions dominate the emission spectrum, a very pure emission color is observed. The emission wavelength depends on the lanthanide ions but shows only limited dependence on the local environment of the lanthanide ions[4], provided that a suitable ligand coordinates to the lanthanide ion & ultraviolet emission can be observed for gadolinium(III), blue emission for thulium(III), green emission for terbium(III), red emission for europium(III)[5], and near-infrared emission for neodymium(III), erbium

(III), and ytterbium(III). Because the absorption coefficients of the lanthanide ions are very small, stronger light absorption can be achieved in molecular complexes by ligand absorption, and the excitation energy is transferred from the ligands to the lanthanide ions, which transform it into electromagnetic radiation. This phenomenon is called co-fluorescence or enhanced luminescence [6-8].

In the present work, we have considered one such phenomenon (LB films) as polymer thin films has growing importance in integrated optic technology. We have chosen polystyrene (PS) as model polymer in this study as it is optically and electronically inert, also has good film forming properties with a high glass transition temperature of about 100°C respectively. PS is a common polymer, which have its physical, chemical and optical properties extensively investigated. Moreover, this polymer is stable in air with a high formability, and has no absorption and fluorescence in the visible region. The molecular structure of  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  and PS are shown in fig.1(a) and (b) respectively. Polystyrene is a lightweight cellular plastic foam material composed of

carbon and hydrogen atoms. The polystyrene when undergoes glass transition, becomes flexible rather than rigid. PS is a transparent polymer, having good film forming properties with a high glass transition temperature. Hence the synthesized  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  complexes are doped in PS.



**Fig.1-** Molecular structure of a)  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  and b) Polystyrene

## Experimental

### Reagents and samples:

Europium Chloride ( $\text{EuCl}_3$ , 99.5%, M.Wt = 258.32 g / mol. ), 2-Thenoyl Trifluoro Acetone ( $\text{C}_8\text{H}_5\text{F}_3\text{O}_2\text{S}$ , 99.5% ,M.Wt = 222.19 g / mol, b.p =  $96^\circ\text{--}98^\circ\text{C}$ , at 8 mm Hg, m.p =  $40^\circ\text{--}44^\circ\text{C}$ ), 1-10 Phenanthroline ( $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$ , 99.5%,M.Wt = 198.22 g / mol, m.p=  $100^\circ\text{--}104^\circ\text{C}$ ), Ethanol Absolute ( $\text{C}_2\text{H}_5\text{OH}$ , 99.98% , M.Wt = 46.07 g / mol), Potassium hydroxide (KOH,99.98%),distilled Water,  $[-\text{CH}_2\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3-]_n$ , Chloroform ( $\text{CHCl}_3$ , 99.5% ) ,all purchased from standard company were used.

Volatile  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  complexes ( $x = 0.4, 0.5$ ) were synthesized by maintaining stichiometric ratio through the steps [9]:

**Step 1:** 6.63 m mol (1.4731 gm) of TTA and 2.21 m mol (0.4381 gm) of Phen were dissolved in 20 ml of ethanol.

**Step 2:** PH value of the dissolved solution was noted using pH-meter. It was found to be in between 5 to 6. We need a solution whose pH value is exactly 7. So, in order to increase its pH value, added KOH solution drop by drop till its pH value raises to 7.

**Step 3:** 2.21 m mol (0.5709 gm) of  $\text{EuCl}_3$  ,(0.2157 gm) of  $\text{YCl}_3$ , (0.2931 gm) of  $\text{TbCl}_3$  was dissolved in 10 ml of distilled water.

**Step 4:** The solution obtained in step 1 and the one obtained in step 3 (i.e.,  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  solution) are mixed.

**Step 5:** Mixed solution was stirred continuously for 1 hour at a temperature of  $60^\circ\text{C}$  on a heating mantle with a magnetic stirrer. (Pale yellow precipitate was observed while stirring).

**Step 6:** With the help of filter paper, precipitate (pale yellow) was collected. This precipitate was washed with ethanol and distilled water so as to purify the precipitate. The precipitate can be purified by recrystallization also.

**Step 7:** This precipitate was dried for 2 hrs at  $80^\circ\text{C}$  in an oven.

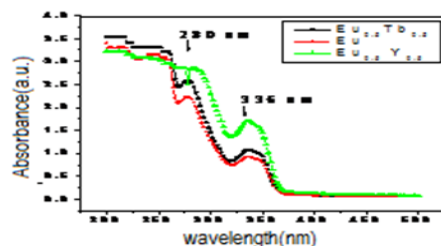
### Preparation and characterization of Blended Films

Commercially available polymer PS was used for making blended films of the synthesized complexes. Polymer (PS) matrix was prepared by dissolving 0.5 grams of polymer (PS) in 15 ml of chloroform at room temperature with vigorous stirring for 15 minutes at room temperature. Later 0.05 gms of the synthesized complex of pure Eu ( $\text{TTA})_3\text{Phen}$  or  $\text{Eu}_{0.5}\text{Tb}_{0.5}(\text{TTA})_3\text{Phen}$  or  $\text{Eu}_{0.5}\text{Y}_{0.5}(\text{TTA})_3\text{Phen}$  taken individually was dissolved in the same solvent in

another beaker by wt. % (In this case it is 10%). Now the complex solution is mixed with PS matrix at room temperature under vigorous stirring for 15 minutes so as to obtain homogeneous mixture. The resulting homogeneous mixture was poured on to a good quality stainless steel substrate to spread it up. The solvent was allowed to evaporate in air for 2 to 3 hrs at room temperature and then pilled up from the substrate. Later the samples were placed in vacuum dry oven at room temperature overnight to remove any residual solvent left if any. Blended films so obtained were homogeneous and showed excellent optical transparency. No visible phase separation was detected. Absorption and Photo luminescence measurements were made on SPECORD 50 at RTM Nagpur university and Humamatsu F-4500 at NEERI, Nagpur respectively.

## Results and discussion

Fig.2 shows the absorption spectra of  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  blended films in PS at room temperature. Absorbance spectra of blended films in PS are characterized by a strong absorbance peak centered at 336 nm with a shoulder at 280 nm. These peaks are attributed to  $n\text{-}\pi^*$  and  $\pi\text{-}\pi^*$  transitions. For all the doped complexes the absorption peak was found to be same because the ligand used is same in all the cases.

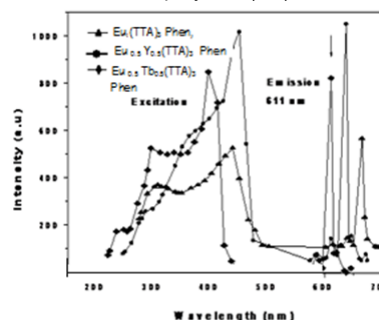


**Fig. 2-** A Absorption Spectra of  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  complexes in PS.

As the absorption wavelength is the characteristic of aromatic group of  $\beta$ -diketonate (TTA), there was no accountable shift in  $\lambda_{\text{max}}$  except the change in the optical density.

### Emission spectra of $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$

Luminescent properties of all the systems were investigated by emission spectroscopy using Hamamatsu F-4500 at NEERI, Nagpur. Fig.5 shows the comparative emission spectra of  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  complex in PS solid matrix.  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  is an electro active and photo active complex made of small molecules that can interact with the polymer (PS) in the excited state.



**Fig. 3-** PL Spectra of  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  and the complex in and PS.

Hence careful consideration is essential to interpret the PL spectra. The  ${}^5D_0 \rightarrow {}^7F_2$  emission bands of  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  in solid state/PS showed a sharp red emission at 611 nm, with two shoulders at 571 nm and 642 nm, suggesting a potential application of  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  in OLED red emitting material. The complex doped in PS have same profile which have sharp peak at 611nm. Fluorescence enhancement factor F, a factor of luminescence enhancement expressing the efficiency of energy transfer [17] is the ratio of the luminescent intensity of the film that contains the Eu complex to that of which does not in this paper.

### Conclusion

Europium  $\beta$ -diketonate complexes  $\text{Eu}_x\text{Re}_{(1-x)}(\text{TTA})_3\text{Phen}$  were dispersed in Polystyrene (PS) matrices. The resulting systems were studied using optical absorption spectroscopy and photoluminescence (PL) techniques. Absorption spectra of all the complexes have two absorption peaks at 280 and 360 nm attributed to  $n-\pi$  &  $\pi-\pi^*$  transition of  $\beta$  diketonate ligand TTA. The composites formed by the three complexes  $\text{Eu}(\text{TTA})_3\text{Phen}$ ,  $\text{Eu}_{0.5}\text{Tb}_{0.5}(\text{TTA})_3\text{Phen}$ ,  $\text{Eu}_{0.5}\text{Y}_{0.5}(\text{TTA})_3\text{Phen}$  show large differences in their luminescence spectra when doped in polymer(PS). The difference between the PL properties may be attributed to different interactions between the chelate and polymer. Thus these complexes can easily be made into flexible films when blended with polymers; furthermore they can be used to fabricate OLED devices by solution techniques

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