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Synthesis of Tb$_{0.7}$Eu$_{0.3}$(acac)$_3$ phen organic polymer complex for display devices

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ABSTRACT

Synthesis of volatile Eu(acac)$_3$phen and Tb(acac)$_3$phen complexes by solution technique were reported in this paper. The combination of Eu and Tb complexes, namely Tb$_x$Eu$_{(1-x)}$(acac)$_3$phen (x=0.1,0.3,0.5,0.7,0.9) were also synthesized by maintaining stoichiometric ratio. Optical properties of these synthesized complexes were studied using photoluminescence technique. Eu(acac)$_3$phen exhibits red intense emission at 612 nm with a sharp spectral bandwidth 5 nm when excited at a wavelength of 323nm, while Tb(acac)$_3$ phen shows green emission at 547 nm when excited at 347nm. The emission spectra of Tb$_x$Eu$_{(1-x)}$(acac)$_3$phen reveals that Tb$_{0.7}$Eu$_{0.3}$(acac)$_3$ phen complex exhibits maximum intensity among all the stichiometrically doped complexes. When Tb$_{0.7}$Eu$_{0.3}$(acac)$_3$ phen was molecularly doped in poly methyl Metacrylate (PMMA) to check its compatibility in polymers, enhancement in intensity was observed in these blended films, proving that these complexes can be used as emissive materials for fabricating OLEDs and displays by vacuum deposition as well as solution techniques. Copyright © 2014 VBRI press.

Keywords: Eu/Tb complex synthesis; photoluminescence; iridium complex.

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Introduction

Organic light emitting devices (OLEDs) have undergone a large development since the early discovery of an efficient electroluminescent device **[1-6]**. There is an enormous demand for advanced visual displays in the information age. Portable wireless communication devices, multicolor flat screen. Flat screen displays for computers and televisions are in high demand. The performance of OLED devices is influenced by organic emitting material. Therefore, there is a great interest in the developing OLED technology to produce low power, high luminescence and color flat screen display.

OLED based on organic semiconductor and conjugated polymers are being developed for full color flat panel displays. Organic electroluminescence (EL) devices based on polymeric materials have been reported using conjugated polymer such as polyphylenevinyls **[7]**, polyphenylene **[8]**, polyalkylfluorenes **[9]**, poly alkylyl thiophenea , polyvinylecarvazole etc. Main advantages of polymers are their ease of film formation by costing and no crystallization of films. The organic EL materials based on chelate metal complexes, such as Alq$_3$ **[1]**, Znq$_2$, Eu(TTA)$_3$,Eu(TTA)$_3$ phen **[10-12]** are reported . For achieving the full color displays efficient bright EL of three primary colors, red, green and blue is essential. Consequently, numerous researchers have studied new materials and novel device structure to obtain pure red, green and blue light emission from OLED devices. White light emission is achieved with a combination of these three primary colours. In the present paper we have synthesized green emitting organic material Tb(acac)$_3$phen, red emitting material Eu(acac)$_3$phen [(acac=acetyle acetone),(phen=1,10-phenanthroline) and the combination of Tb and Eu complex Tb$_x$Eu$_{(1-X)}$(acac)$_3$phen. These synthesized materials have been characterized by using photoluminescence techniques. Blended thin films of Tb$_x$Eu$_{(1-X)}$(acac)$_3$ phen in PMMA were made and their optical properties were studied. The **Fig. 1** shows the chemical structure of Eu(acac)$_3$phen and Tb$_x$Eu$_{(1-X)}$(acac)$_3$phen.

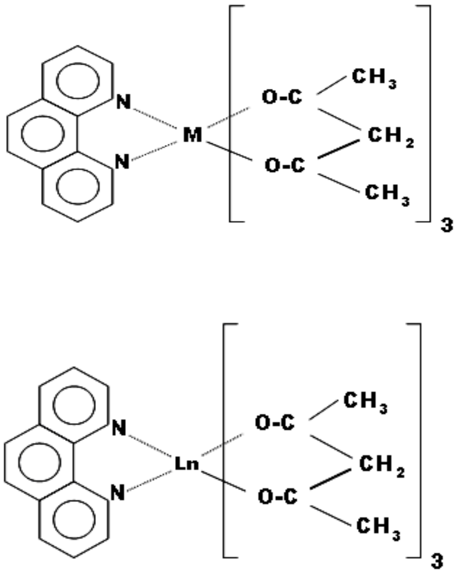

Fig. 1. Chemical structure of Eu(acac)$_3$(phen) and Tb$_x$ Eu$_{(1-X)}$(acac)$_3$ phen. [1:10 phenanthroline acetyl acetone M= Eu, Tb, Ln = Tbx Eu(1-x)].

Experimental

Synthesis of Eu(acac)$_3$ phen,Tb(acac)$_3$ phen and Tb$_x$ Eu$_{(1-X)}$(acac)$_3$phen complexes

A volatile Eu complex Eu(acac)$_3$phen was synthesized by solution technique (precipitation method). The weights of material required are taken by stoichiometric molar calculation. 1 m mole (0.198224gm) of 1:10phenanthroline (phen) and 3 m mole (0.31 ml) of acetyl acetone (acac) were dissolved in 20 ml of ethanol. The pH value of above solution was adjusted to 7 by adding KOH (1N) solution drop wise. 1 m mole (0.35192gm) of Eu_2O_3 (europium oxide) was dissolved in 10 ml dilute HCl and 10 ml of distilled water was added to this solution. The pH value of above solution was adjusted to 7 by adding KOH (1N) solution.

Eu_2O_3 solution was added to the solution of acac and phen drop by drop with continuous stirring tillthe red colored turbid solution was observed. The entire mixture was heated at 60° C with continuous stirring for 1 hour, a pale color precipitate was obtained .The obtained precipitate was filtered and washed with distilled water 4-5 times till the white colored precipitate appears. Then the resulting precipitate was dried for 3-4 hours at 80° C in an oven. Thus a volatile Eu complex Eu(acac)$_3$ phen was formed. Tb(acac)$_3$ phen and Tb$_x$Eu$_{(1-x)}$(acac)$_3$ phen were also synthesized in the same manner.

Blended thin films of Tb$_x$Eu$_{(1-x)}$(acac)$_3$ phen

We have prepared the blended thin films by using binding polymer; poly methyl metacrylate (PMMA) **[13]**. We have chosen PMMA as a model polymer in this study, as these are optically and electronically inert; also have good film forming properties. The blended films of Tb$_{0.7}$Eu0.3(acac)$_3$ in PMMA at 0.1, 0.5, 1, and 5wt% were prepared. The films were made by casting the combination of chloroform and Tb$_{0.7}$Eu0.3(acac)$_3$phen solution on to clean glass or good quality stainless steel plate as substrate and it is allowed to dry for an hour. The so formed film is now prepared from the substrate in order to study its optical characteristics

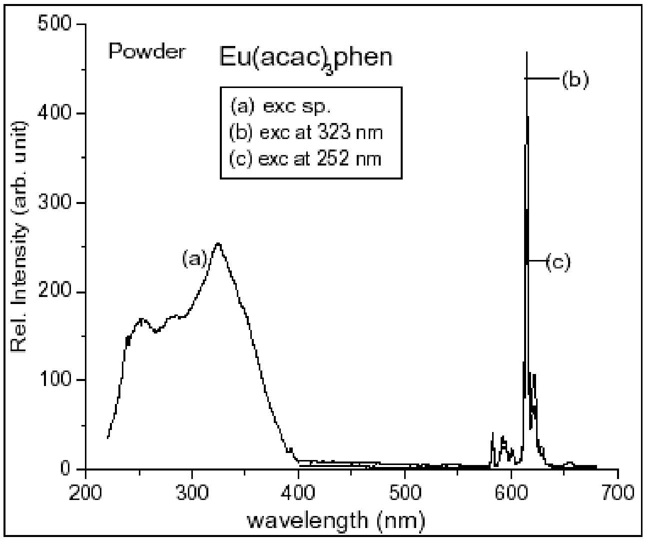

Fig. 2. Excitation and emission spectra of Eu(acac)$_3$phen.

Results and discussion

Photoluminescence spectra

Fig. 2 and **Fig. 3** shows the photoluminescence spectra of Eu(acac)$_3$phen and Tb(acac)$_3$phen, respectively. The excitation spectrum of pure compound Eu(acac)$_3$phen complex exhibits broad excitation band (BEB) between 220nm to 420nm which can be assigned to the π-π* electron transition of ligands and peak at 323nm is observed due to f-f absorption transition ($^7F_0$-$^5D_2$) of Eu^{3+} ion. This transition is weaker than absorption of organic ligand and overlap by BEB which prove that luminescence sensitization via excitation of the ligand is much more efficient than the direct excitation of the Eu^{3+} ion absorption level. The maximum peak was observed at 612nm, when excitation wavelength is 347nm and 252nm. The non-volatitle Eu(acac)$_3$ originates from its high polarity because the co-ordination number of the central metal ion is not saturated by ligands (acac).However Eu(acac)$_3$ phen has the structure of an inner complex salt due to introduction of second ligand (phen) into Eu(acac)$_3$. Therefore, Eu(acac)$_3$ phen has low polarity and it is volatile. The powder of Eu(acac)$_3$ phen exhibits intense PL at 612 nm with a sharp spectral bandwidth 5nm,as shown in **Fig. 2**. The excitation spectra of Tb(acac)$_3$ phen complex exhibits broad excitation band between 200nm to 400nm. The intense PL emission peak was observed at 547nm with shoulder at 490nm **Fig. 3**, exhibiting green -blue emission.

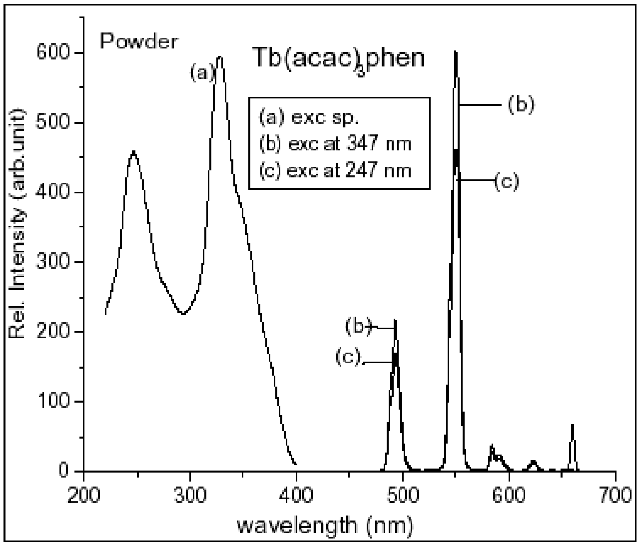

Fig. 3. Excitation and emission spectra of Tb(acac)$_3$phen.

Fig. 4 and **5** show the excitation and emission spectra of Tb$_x$Eu$_{(1-x)(}$acac)$_3$ phen complex at excitation wavelength 247nm and 347nm. The intense PL emission peak was observed at 612nm in the red region of the spectrum with two smaller peaks at 490nm and 550nm. The maximum PL intensity is observed in Tb$_{0.7}$Eu$_{0.3}$(acac)$_3$ phen complex. The Tb$_{0.7}$Eu$_{0.3}$(acac)$_3$ phen complex may be used for white light emission in display devices.

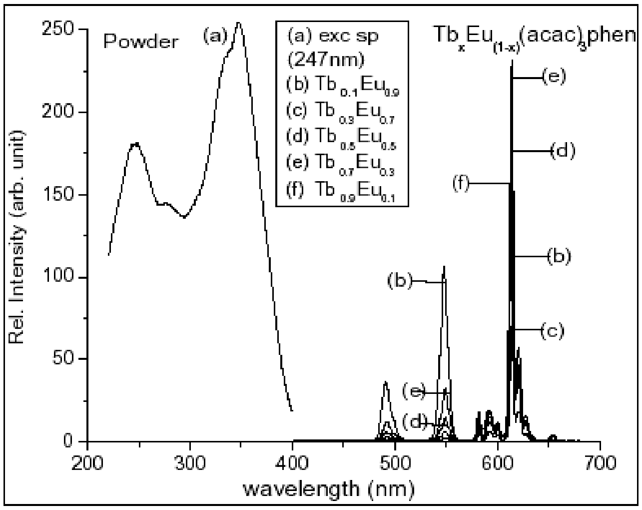

Fig. 4. Excitation and emission spectra of Tb$_x$Eu$_{(1-x)}$(acac)$_3$phen(λ_{exc} = 347 nm).

The **Fig. 6** shows PL spectra of blended films of the Tb$_x$Eu$_{(1-x)}$ (acac)$_3$phen complex and PMMA with excitation peaks at 290nm. Noticeable changes are observed in the emission spectra of Tb$_x$Eu$_{(1-x)}$ (acac)$_3$phen/PMMA blended films when compared with its original powder. At an excitation wavelength of 290 nm, maximum emission peak in blended film for all concentration of Tb$_x$Eu$_{(1-x)}$ (acac)$_3$phen lied at 550nm, indicating that the ligands; acac and Phen play a vital role in the emission peak. Intensity of emitted wavelengths to the corresponding excited wavelengths are shown in **Table 1**.

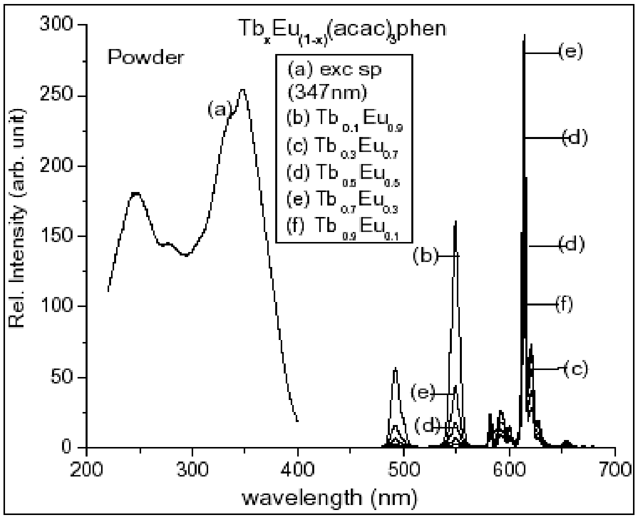

Fig. 5. Excitation and emission spectra of Tb$_x$Eu$_{(1-x)}$(acac)$_3$phen (λ_{exc}=247nm).

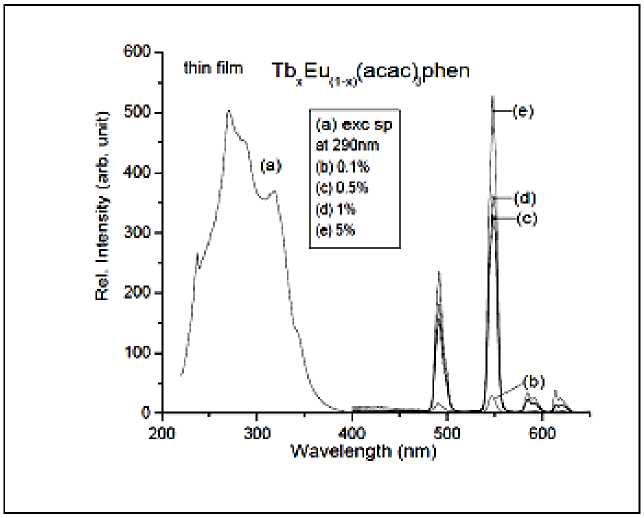

Fig. 6. PL excitation and emission spectra of blended films of Tb$_x$Eu$_{(1-x)}$-(acac)$_3$ phen/PMMA (λ_{exc}=290nm) with different wt %.

Table 1. Excitation, emission wavelength and emission intensity of synthesized complexes.

Material	Excitation wavelength	Emission wavelength	Intensity
Eu(acac)$_3$ phen	252	612	400
	323	612	475
Tb (acac)$_3$ phen	247	490,547	450
	347	490,547	600
Tb$_x$Eu$_{(1-x)(}$acac)$_3$phen	247	490,550,612	225
powder	347	490,550,612	280
Blended film of Tb$_x$Eu$_{(1-x)(}$acac)$_3$phen/PMMA(5%)	290	490,550	535

FTIR analysis

The FT-IR spectrum of $Tb_xEu_{(1-x)}(acac)_3$ phen samples measured on KBr pellets in a Perkin Elmer-LR 64912C Fourier transform infrared (FT-IR) spectrometer with KBr beam splitters and a resolution of 20cm^{-1} is shown in **Fig 7**. Spectrum shown here is raw data, without any further correction (smoothing, background, *etc.*). In the case of the polycrystalline samples, scattering due to crystallinity is responsible for the broad background with some asymmetric peaks. Below 420 cm^{-1} the KBr optic reduces the quality of the spectrum, hence not recorded. The absorption bands in the finger print region (1500-1400 cm^{-1}) are generally due to intramolecular phenomena, and are highly specific for each material. The aromatic C-H vibration stretch appears at 3100-2900cm^{-1}. The aromatic C-C bands appear about 1500 cm^{-1}. The peaks between 1680-2000 cm^{-1} owing to the carbonyl group are completely absent in the FTIR- spectrum of $Tb_xEu_{(1-x)}(acac)_3$phen. New strong peaks between 1600-1400 cm^{-1} due to the C=N group have appeared in the spectrum of $Tb_xEu_{(1-x)}$ $(acac)_3$ phen In addition, the aromatic C-H vibrational bands at 3300-3500 wave numbers are enhanced in $Tb_xEu_{(1-x)}(acac)_3$phen spectrum. These results confirm the formation of the complex.

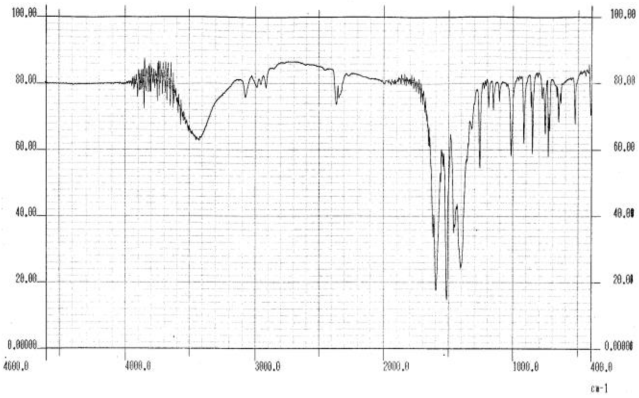

Fig. 7. FTIR spectra of synthesized $Tb_xEu_{(1-x)}(acac)_3$ phen (x=0.7).

Conclusion

Eu complex $Eu(acac)_3$ phen, Tb complex $Tb(acac)_3$ phen and $Tb_xEu_{(1-x)}(acac)_3$ phen (x=0.1,0.3,0.5,0.7,0.9) were synthesized by solution technique. $Eu(acac)_3$phen exhibits red intense emission at 612 nm with a sharp spectral bandwidth 5 nm when excited at a wavelength of 323nm, while $Tb(acac)_3$ phen shows green emission at 547 nm when excited at 347nm. The prepared organic phosphor $Eu(acac)_3$ phen may be useful as a red emitting phosphor and $Tb(acac)_3$ phen phosphor may be useful as a green emitting phosphor for display devices. $Tb_xEu_{(1-x)}(acac)_3$ phen complex at excitation wavelength 247nm and 347nm. The intense PL emission peak was observed at 612nm in the red region of the spectrum with two smaller peaks at 490nm(near blue emission) and 550nm (near green emission). The emission spectra of $Tb_xEu_{(1-x)}(acac)_3$phen reveals that $Tb_{0.7}Eu_{0.3}(acac)_3$ phen complex exhibits maximum intensity among all the stichiometrically doped complexes. When $Tb_{0.7}Eu_{0.3}(acac)_3$ phen was molecularly doped in poly methyl metacrylate (PMMA) to check its compatibility in polymers, enhancement in intensity was observed in these blended films, proving that these complexes can be used as emissive materials for fabricating OLEDs and displays by vacuum deposition as well as solution techniques.

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