



# ELECTROSPUN NANOFIBERS OF EUROPIUM COMPLEX EU(TTA)<sub>3</sub>PHEN/PS-PVDF COMPOSITE FOR PHOTOLUMINESCENT FABRIC DESIGNING

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## ABSTRACT

The synthesis of electrospun nanofibers of europium complex Eu(TTA)<sub>3</sub>phen using electrospinning technique is reported. Europium complex Eu(TTA)<sub>3</sub>phen (TTA=2-thenoyltrifluoroacetone, phen=1,10-phenanthroline) was synthesized by solution technique and then used for the preparation of electrospun nanofibers of Eu(TTA)<sub>3</sub>phen using polymers such as polystyrene (PS) and polyvinylidene fluoride (PVdF) and its combination such as, PS-PVDF as carrier. During the electrospinning process the solution was fed to the tip using syringe pump at a flow rate of 0.3 ml/hr. A positive voltage of 25kV was applied to the polymer solution, the electrospun fibers were typically obtained at a tip-to-collector distance of 15cm. Nanofibers formation of Eu(TTA)<sub>3</sub>phen/polymer was confirmed by SEM. photoluminescence study of the fibers show typical Eu<sup>3+</sup> ion red emission, assigned to the transitions between the first excited state (<sup>5</sup>D<sub>0</sub>) and the multiplet (<sup>7</sup>F<sub>0-4</sub>). Here, we compare the photoluminescence properties of nanofibers of PS, PVDF and its combination. In presence of different polymers and combination of polymers there was change in photoluminescence properties with change in diameter of nanofibers. These light emitting polymer nanofibers may be suitable for photoluminescent fabric designing.

**Keywords:** Electrospun nanofibers, Rare-earths complex, Photoluminescence property, Polymers, Histogram

## 1.Introduction

The trivalent europium ion (Eu<sup>3+</sup>) exhibits strong and intense emission bands based on

their f-f-electronics transition and wide range of luminescent lifetime, suitable for various applications, but they have low absorption coefficient, limiting the lighting output. However, this can be improved by forming complexes of the rare-earth ions with organic ligands. These ligands can act as an antenna to absorb the excitation light and to transfer the excitation energy to the higher energy levels of the Eu<sup>3+</sup> ion, from which the emitting excited levels can be populated. Phen is a synergic shielding ligand which can reduce the rate of non-radiative decays and strongly enhance the fluorescence intensity of the complex, Lunstrook K. et al. [1]. The presence of the ligand surrounding the ion acts as a physical buffer between the rare-earth ions and the other ions Yan et al.[2]. Therefore, Eu(TTA)<sub>3</sub>Phen as a successful lanthanide organic complex has attracted great attention in virtue of the intense emission peaks in the visible and near-infrared region upon UV excitation. However, disadvantages of the pure β-diketone complexes with low processing ability, poor thermal stability and low mechanical strength limit its direct applications in the past. In order to overcome the shortcomings of them, europium complexes are usually incorporated into organic, inorganic or organic/inorganic hybrid matrices, Petoud et al. [3]. The incorporation of europium ligands into organic polymers presents an ideal and versatile approach to generate hybrid materials. It has been proved that the polymer-capped RE complexes possess improved photoluminescence properties and thermal stability, and are mechanically flexible, Werts et al. [4]. The RE complexes incorporated in the polymer matrixes embody a class of new materials that present the

characteristics of both the complexes and the matrix materials, making them applicable in a wide range of new technologies. PVDF (poly vinylidifluoride) is a semicrystalline engineering polymer with very good resistance to chemicals, oxidation, and UV radiation, it is known for its polymorphism crystalline structure and one of the most widely studied polymers due to its non-linearity, piezo- and pyro-electricity. Polystyrene (PS) is a very good electrical insulator, has excellent optical clarity due to the lack of crystallinity, and has good chemical resistance to diluted acids and bases. One-dimensional (1D) nano/micro-fibers have been of great interest owing to their tremendous properties and potential applications in many fields. The polymer optical fibers synthesized by the electrospinning technique possess several advantages, such as extremely high surface-to-volume ratio, tunable porosity, malleability and the ability to control the fiber composition to achieve the desired performances from their properties and functionalities. These fibers are good candidates for many fields, including protective clothing, filtration, electrode materials, optical and chemical sensors, microarray optical ion sensors, defence and security, optical communication and environmental engineering fields. Electrospinning, a spinning technique, is a unique approach using electrostatic forces to produce fine fibers from polymer solutions or melts. The solution used in the electrospinning process has a significant influence on its spin ability. The presence of polymer increases the fluorescent intensity of the  $5D_0 \rightarrow 7F_2$  hypersensitive transition of  $\text{Eu}^{3+}$  ions.  $\text{Eu}(\text{TTA})_3\text{Phen}$  was prepared by solution method.

## 2. Experimental

### 2.1 Synthesis of $\text{Eu}(\text{TTA})_3\text{phen}$

TTA (1.5 mol) and phen (0.5 mol) were dissolved in 20 ml of ethanol in flask and neutralized with NaOH solution by maintaining  $\text{pH}=7$ .  $\text{EuCl}_3$  salt was dissolved in 10 ml of double distilled water in another flask. This solution was poured into the TTA and phen solution. Whole solution was heated at  $60^\circ\text{C}$  with continuous stirring for 1 hour. The precipitate was formed and separated by using filter paper. The color of the compound was pale color which then dried for 2 hours at  $80^\circ\text{C}$  in oven.

### 2.2 Synthesis of solution of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS}$

In the preparation of the electrospinning solution, 1g PS was dissolved in 10 ml THF solvent to give a mass fraction of 20 wt. % and magnetically stirred for 12 hr till uniform. Then 20% of  $\text{Eu}(\text{TTA})_3\text{phen}$  was added to uniform PS solution and magnetically stirred for 12 hr till uniform.

### 2.3 Synthesis of solution $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$

In the preparation of the electrospinning solution, 1g PVDF was dissolved in 10 ml THF solvent to give a mass fraction of 20 wt. % and magnetically stirred for 12 hr till uniform. Then 20% of  $\text{Eu}(\text{TTA})_3\text{phen}$  was added to uniform PVDF solution and magnetically stirred for 12 hr till uniform.

### 2.4 Preparation of solution of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS-PVDF}$

In the preparation of the electrospinning solution, 0.5 g PS and 0.5 g PVDF were dissolved in 10 ml THF (tetrahydrofuran) solvent to give a mass fraction of 20 w% and magnetically stirred for 12 hr till uniform. Then 20% of  $\text{Eu}(\text{TTA})_3\text{phen}$  was added to above solution and magnetically stirred for 12 hr till uniform.

### 2.5 Electrospun nanofibers of $\text{Eu}(\text{TTA})_3\text{PS-PVDF}$

The prepared solution of  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS-PVDF}$  was firstly placed into a 5ml plastic syringe. During the electrospinning process, the solution was fed to the tip using a syringe pump at a flow rate of 0.3 ml/h. A positive voltage of 20 kV was applied to the needle of the syringe containing polymer solution. The grounded electrode was connected to a metallic plate wrapped with aluminium foil kept at a distance of 15 cm from the needle of the syringe. The electrospun nanofibers were collected on the conducting foil (aluminum). After electrospinning, the nonwoven membranes of the fibers were dried in a vacuum oven at  $60^\circ\text{C}$  for 12 hr to remove the residual organic solvent. Same process repeated for  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS}$  and  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$ .

### 3. Results and Discussion

#### 3.1 SEM Study

##### 3.1.1 Morphology of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS}$ nanofibers

SEM image of  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS}$  composite electrospun nanofibers are shown in Fig. 1 along with their histograms to find the average diameter of the fibers. It displays morphologically nanofibrous with uniform in diameter and aligned in random orientation

caused by the bending instability associated with the spinning jet and stationary collector. It shows that the average diameters of the composite nanofibers are smaller about 688 nm, Xiaoping et al. [5]. This may be caused by the increased conductivity of the electrospinning solution due to the addition of  $\text{Eu}(\text{TTA})_3\text{Phen}$ . It shows that the addition of europium complex into the polymer matrix can effectively improve the morphology of the electrospinning fibers.

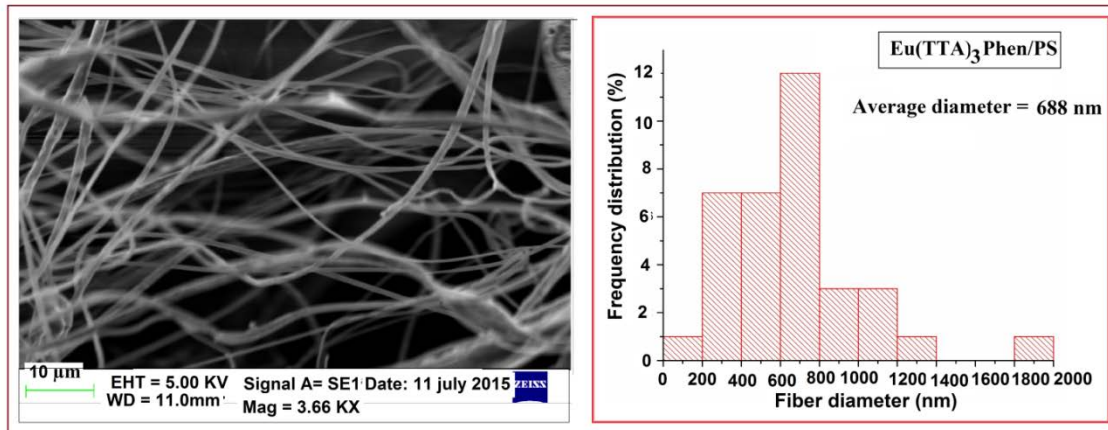


Fig. 1 SEM image and histogram of  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS}$  nanofibers

##### 3.1.2 Morphology of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$ nanofibers

Nanofibers of  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$  composite were prepared by electrospinning process, and the morphologies of which are shown in Fig. 2

Histogram of nanofibers  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$  shows that the average diameters 320.63 nm. This results by increased conductivity of the electrospinning solution due to the addition of  $\text{Eu}(\text{TTA})_3\text{Phen}$  in PVDF polymer.

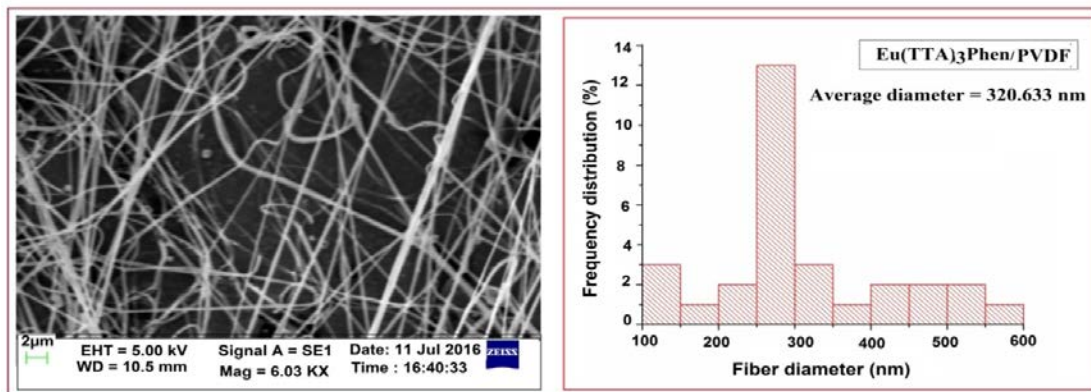


Fig.2 SEM image and histogram of  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$  nanofibers

##### 3.1.3 SEM image of $\text{Eu}(\text{TTA})_3\text{phen}/\text{PS-PVDF}$ nanofibers

Uniform  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS-PVDF}$  composite electrospun nanofibers with diameters in the range of 300 to 700 nm were prepared, and the

morphologies of which are shown in Fig.3. From the study of historiography of nanofibers, the average diameter of the fibers was found to be 691.52 nm.

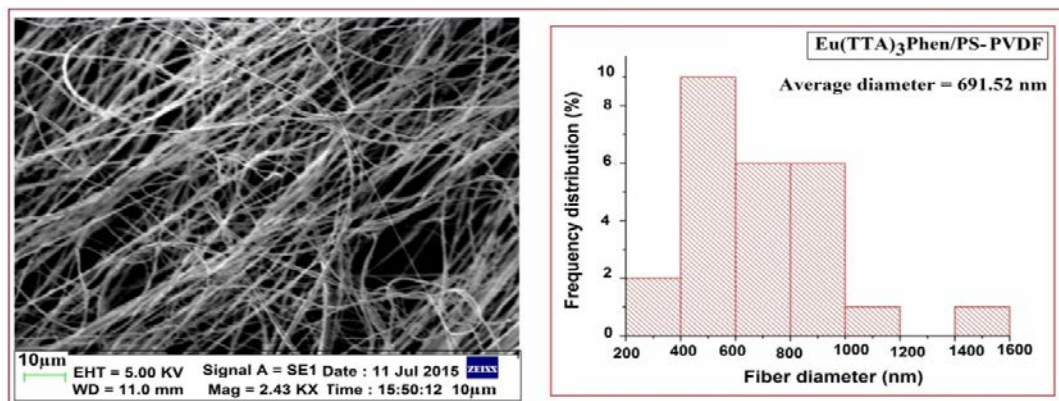


Fig.3 SEM image and histogram of Eu(TTA)<sub>3</sub>Phen/PS- PVDF nanofibers

### 3.2 FT-IR Study

#### 3.2.1 FTIR spectra of Eu(TTA)<sub>3</sub>Phen

Fourier Transform Infrared Spectroscopy (FTIR) provides the information about the vibration and rotation of the chemical bonding and molecular structures of the compound. Fig. 4 shows FTIR spectra of Eu(TTA)<sub>3</sub>Phen powder that clearly represents, the C=O stretching vibrations of TTA in the complex are shifted to lower frequencies, from 1645 cm<sup>-1</sup> of free TTA to 1624 cm<sup>-1</sup> of coordinated TTA, as the intensity of C=O weakens after it coordinates with Eu<sup>3+</sup> ion, same as C=C

stretching vibrations of TTA in the complex are shifted to lower frequencies from 1585 cm<sup>-1</sup> to 1535 cm<sup>-1</sup>. Also, the stretching vibrant peak of the C=N bond in phen shifts from 1614 to 1601 cm<sup>-1</sup> and the peaks of phen at 739 and 851 cm<sup>-1</sup> corresponding to the stretching vibration of C-H bonds shift to 724 and 843 cm<sup>-1</sup>, respectively, that shows phen participated in the coordination. Also presence of peaks at 1306, 1190 and 1140 cm<sup>-1</sup> of C-F in the FT-IR spectrum which indicates phen had coordinated with Eu<sup>3+</sup>, Zhang et al.[6].

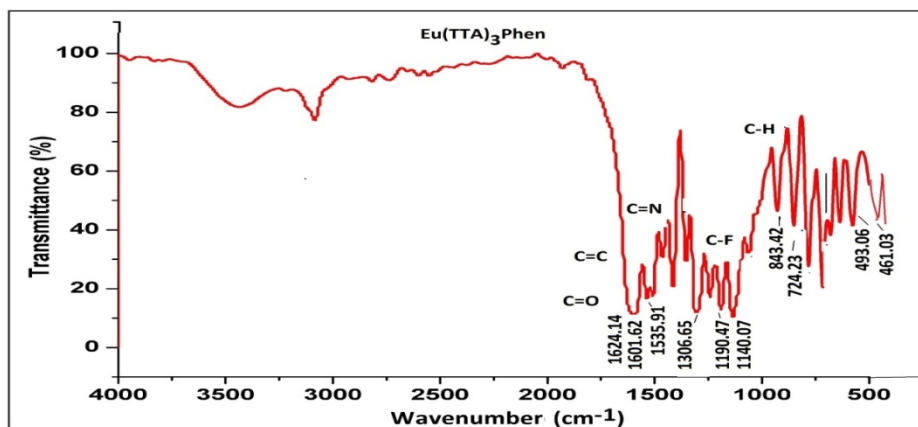


Fig.4 FTIR Spectra of Eu(TTA)<sub>3</sub>Phen Complex

#### 3.2.2 FTIR spectra of Eu(TTA)<sub>3</sub>Phen/PS Nanofibers

Fig.5 shows FTIR spectra of Eu(TTA)<sub>3</sub>Phen/PS and pure PS nanofibers. In FTIR spectra of PS the transmittance bands at 690, 750, 1089, 1447, 1492, and 1602 cm<sup>-1</sup> can be assigned to the vibrations of the benzenoid ring, Hongquan et al. [7]. And the broad band at 3400 cm<sup>-1</sup> is caused by the vibration of its associated hydroxyl groups. The Eu(TTA)<sub>3</sub>Phen/PS

composite nanofibers, characteristic IR peaks of the pure PS slightly shifted to higher frequencies as coordinates with europium complex. Also spectra of Eu(TTA)<sub>3</sub>Phen complex are not in measured range and it shifted to other frequencies. This implies that the vibration of ligands in Eu(TTA)<sub>3</sub>Phen complex may be slowed down by the surrounding PS matrix.



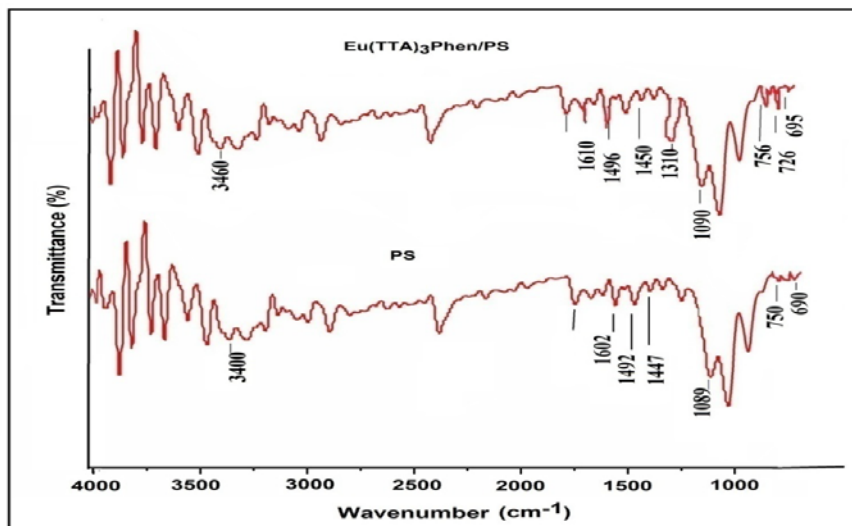


Fig. 5 FTIR spectra of Eu(TTA)<sub>3</sub>Phen/PS Nanofibers

### 3.2.3 FTIR spectra of Eu(TTA)<sub>3</sub>Phen/PVDF Nanofibers

Fig.6 shows FTIR spectra of Eu(TTA)<sub>3</sub>Phen/PVDF and pure PVDF nanofibers. The FTIR spectra of pure PVDF show strong absorption peak which appeared at 1173 cm<sup>-1</sup> is assigned to the symmetrical stretching of -CF<sub>2</sub> groups, as characteristic peak of PVDF. The absorption peak appeared at 1408 cm<sup>-1</sup> was attributed to CH<sub>2</sub> wagging vibration of polymer. In Eu(TTA)<sub>3</sub>Phen/PVDF, the characteristic peak of PVDF at 1173 cm<sup>-1</sup>

shift to the higher frequencies at 1185 cm<sup>-1</sup> and the absorption peak appeared at 1408 cm<sup>-1</sup> shifted to 1414.52 cm<sup>-1</sup>. Other small peaks of europium complex are 492 cm<sup>-1</sup> and 728 cm<sup>-1</sup> also appears at higher frequencies. The characteristic peaks of Eu(TTA)<sub>3</sub>Phen complex and peaks of pure PVDF are slightly shifted to higher frequencies, Betz et al. [8]. This implies that the Eu(TTA)<sub>3</sub>Phen complex effectively incorporated in PVDF polymer matrix and there were changes in its vibration frequencies.

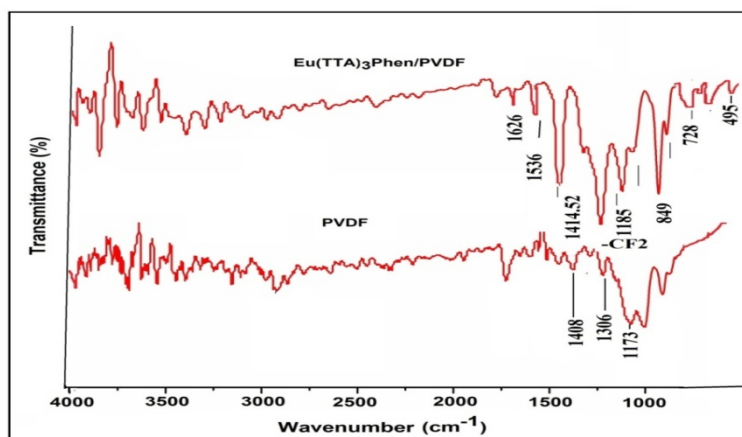


Fig.6 FTIR spectra of Eu(TTA)<sub>3</sub>Phen/PVDF Nanofibers

### 3.2.4 FTIR spectra of Eu(TTA)<sub>3</sub>Phen/PS-PVDF composite Nanofibers

Fig.7 shows combined FTIR spectra of, Eu(TTA)<sub>3</sub>Phen/PS-PVDF composite with PS and PVDF. In spectra of Eu(TTA)<sub>3</sub>Phen/PS-PVDF there are presence of bands of PS which are shifted at 756, 1450, 1492, and 1602 cm<sup>-1</sup> can be assigned to the vibrations of the benzenoid ring and the broad band at 3400 cm<sup>-1</sup>

is caused by the vibration of its associated hydroxyl groups of PS, Hongquan et al [7]. Spectra also shows the band at 1185 cm<sup>-1</sup> which is due to the stretching vibration of the C=O group in PVDF as a characteristic peak of PVDF, Euler et al. [9]. This band shows a little shift to the higher frequencies as compare with pure PVDF spectra. This shifting of bands occurs due to coordination of europium complex with PS and PVDF polymer matrix,

Euler et al. [9]. The vibration peaks of be due to the surrounding polymer matrix. Eu(TTA)3Phen complex also get shifted may

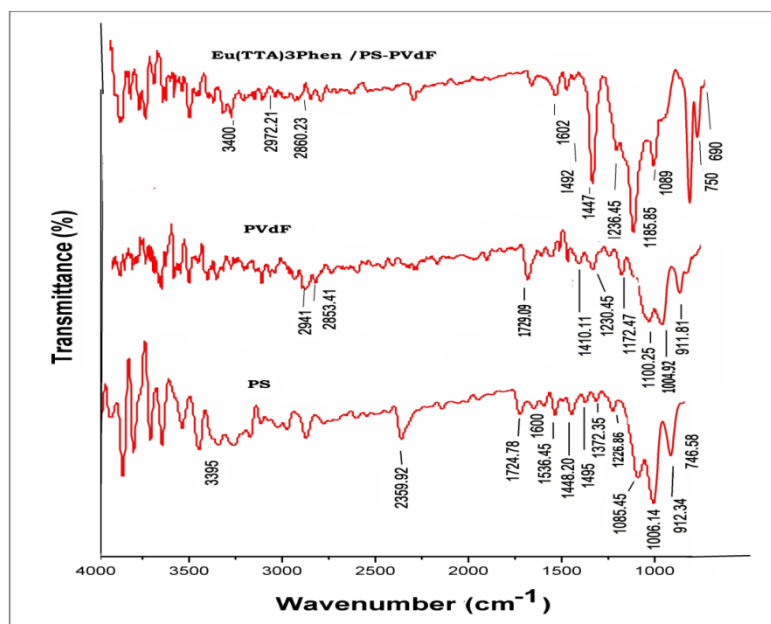


Fig.7 FTIR spectra of Eu(TTA)3Phen/PS-PVDF Composite Nanofibers

### 3.3 Photoluminescence in Eu(TTA)3Phen/Polymer nanofibers

#### 3.3.1. Photoluminescence of Eu(TTA)3Phen complex

The emission spectra of the Eu(TTA)3phen complex are shown in Fig.8. The emission spectrum of Eu(TTA)3Phen was recorded from 550 nm to 655 nm under excitation at 354 nm, Xiaoping et al. [10], Shin Chang et al.[11], Zhang et al. [12]. It can be seen that four emission peaks are centred at 579, 592, 612, 642, 654 nm, and can be assigned to the  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_3$ ,  $^5D_0 \rightarrow ^7F_4$  respectively which can be recognized to the f-f transitions of  $\text{Eu}^{3+}$ . The presence of only one  $^5D_0 \rightarrow ^7F_0$  line indicates that  $\text{Eu}^{3+}$  ion exists in a single chemical environment. The much stronger intensity of  $^5D_0 \rightarrow ^7F_2$  than those of other transitions indicates that  $\text{Eu}^{3+}$  ion is in a single site without a centre of inversion. Amongst these transitions the  $^5D_0 \rightarrow ^7F_1$  is a

magnetic dipole transition. Magnetic dipole transitions are allowed by the Laporte selection rule, but their intensities are weak. The transitions  $^5D_0 \rightarrow ^7F_0$  and  $^7F_3$  are forbidden transitions. These are intraconfigurational electric dipole transitions which are forbidden by the Laporte selection rule. The others are electric dipole transitions. An electric dipole transition is the linear movement of charge, such transition has odd parity, K. Binnemans [13]. It can be seen that the hypersensitive transition intensity of the  $^5D_0 \rightarrow ^7F_2$  is much higher than the others. Intensity of hypersensitivity transition is strongly influenced by the local symmetry of the  $\text{Eu}^{3+}$  ions as well as nature of the ligands. It obeys the selection rules  $|\Delta S|=0$ ,  $|\Delta L| < 2$  and  $|\Delta J| < 2$ , K. Binnemans [13], J. Vuojola and T. Soukka[14]. According to the dynamic coupling mechanism, the  $\text{Eu}^{3+}$  ion is in a highly polarizable chemical environment in this complex.

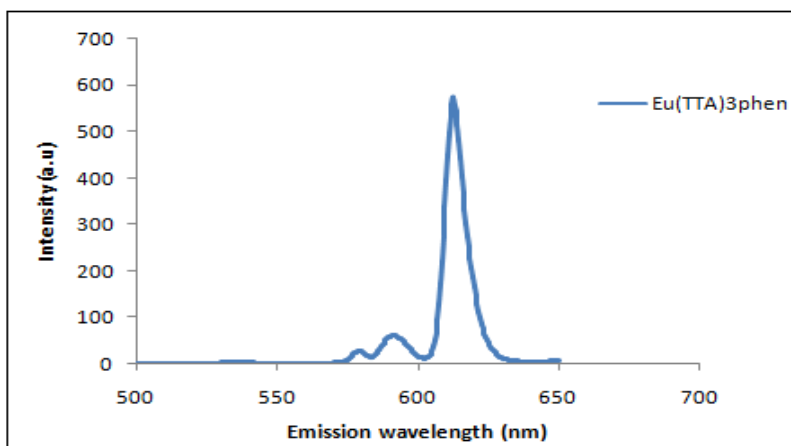


Fig.8 The emission spectra of the Eu(TTA)3Phen complex

### 3.3.2. Photoluminescence of *Eu(TTA)3Phen/PS* and *Eu(TTA)3Phen/PVDF* nanofibers

The emission spectra of the Eu(TTA)3phen/Polymers composites are shown in Fig.9, recorded from 550 nm to 655 nm under excitation at 354 nm. It can be seen that four emission peaks are centered at 579, 592, 612, 652 nm, and assigned to the  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_3$ , respectively. The room-temperature fluorescence spectra of the composite nanofibers were composed of the typical  $\text{Eu}^{3+}$  ion red emission, assigned to the transitions between the first excited state ( $^5D_0$ ) and the multiplet ( $^7F_0-4$ ). The presence of only one  $^5D_0 \rightarrow ^7F_0$  line indicates that  $\text{Eu}^{3+}$  ion exists in a single chemical environment. The much stronger intensity of  $^5D_0 \rightarrow ^7F_2$  than those of other transitions indicates that  $\text{Eu}^{3+}$  ion is in a single site without a center of inversion and it

was the hypersensitive transition having intensity much greater than pure complex. For Eu(TTA)3Phen/PVDF nanofibers, the results shows that, there was suddenly increase in hypersensitive transition intensity due to increase in electric dipole transition as compare to magnetic dipole transition. It may be due to the high surface area of Eu(TTA)3Phen/PVDF nanofibers, so that more emission centers  $\text{Eu}^{3+}$  could be excited. And hence the intensity of Eu(TTA)3Phen/PVDF nanofibers had a significantly increased. As incorporation of PVDF matrix in surrounding complexes organic ligand, the distortion of the symmetry around the  $\text{Eu}^{3+}$  ions occurred and  $\text{Eu}^{3+}$  ions gets polarized, that is the reason of increase of electric dipole allowed transition which increase the hypersensitivity transition and results, enhance the intensity of hypersensitive transition.

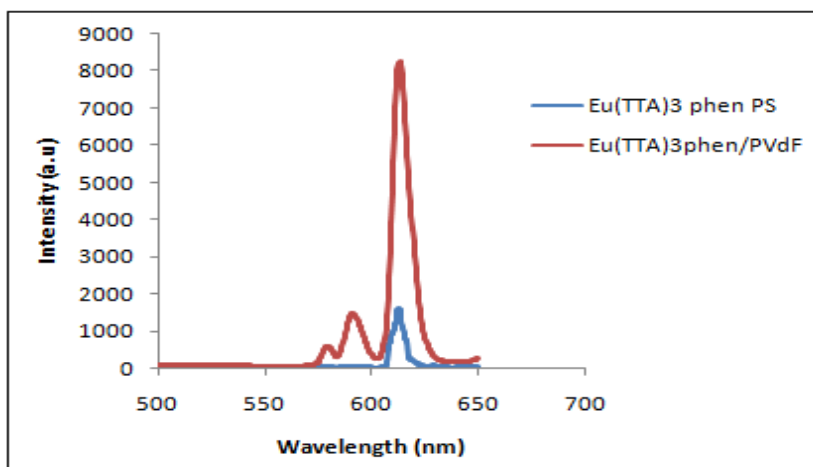


Fig.9 The emission spectra of the Eu(TTA)3Phen/Polymer

### 3.3.3 Photoluminescence of *Eu(TTA)3Phen/PS-PVDF composite*

The emission spectra of the *Eu(TTA)3Phen/PS-PVDF* are shown in Fig.10 recorded from 550 nm to 655 nm under excitation at 354 nm. It can be seen that four emission peaks are centered at 579, 592, 612, 652 nm, and can be assigned to the  $^5D_0 \rightarrow ^7F_0$ ,  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_3$  respectively, which can be known as the f-f transitions of  $\text{Eu}^{3+}$ . A. Zhang et al.[15], D. Chitnis et al.[16]. The much stronger intensity of  $^5D_0 \rightarrow ^7F_2$  than those of other transitions indicates that  $\text{Eu}^{3+}$  ion is in a single site without

a center of inversion and it was the hypersensitive transition having intensity much greater than pure complex. For *Eu(TTA)3Phen/PS-PVDF*, presence of PVDF in *Eu(TTA)3Phen/PS* is the basic reason of higher intensity of hypersensitive transition. Presence of PVDF in europium complex suddenly increase in hypersensitive transition intensity due to increase in electric dipole transition as compare to magnetic dipole transition, increased allowed electric dipole transition lead to increased hypersensitive transition and varied its intensity.

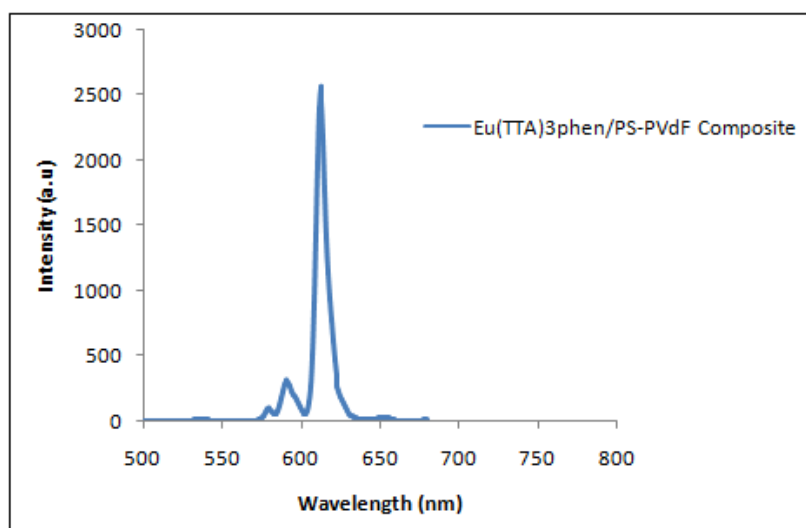


Fig.10 Emission Spectra of *Eu(TTA)3Phen/PS-PVDF* composite

Presence of *Eu(TTA)3Phen* complex in polymers generally enhances the luminescent intensity as compare to pure complex due to uniform distribution of the complex along macromolecular chains of the polymers. As fibers of *Eu(TTA)3Phen/Polymers* are electrospun nanofibers, the luminescent complex get similarly distributed to macromolecular chain of polymers and increased luminescent intensity of materials as compare to bulk material, X. Zhang et al.[17]. Therefore, the above results indicate that the presence of polymers like PS and PVDF generally increases the fluorescent intensity of the  $^5D_0 \rightarrow ^7F_2$  hypersensitive transition of  $\text{Eu}^{3+}$  ions. When the europium complexes are incorporated into the microcavities of the polymers matrix, the complexes exhibit more disordered local environments due to the influence of the surrounding polymer, Y. Tao et al. [18]. Different polymer matrix when used for  $\text{Eu}^{3+}$  ions to be embedded represents the

enhancement in emission intensity as excited nearly at same wavelength. *Eu(TTA)3Phen/PVDF* nanofibers shows more intensity as compared to other samples which may be due to its large surface area as it shows high aspect ratio as confirmed from SEM images. The results infer that PVDF is an effective polymer to improve the luminescence properties of  $\text{Eu}^{3+}$  ions. Including PS, also show good emission intensity, H. Shao et al. [19]. The environment provided by the PVDF polymer matrices and the interactions taking place between their functional groups and surrounded complexes are most probably responsible for the recorded enhancements of the photoluminescence properties. It is expected that nanofibers of *Eu(TTA)3Phen/PVDF* could be applied for the designing of photoluminescent fabric.



**3.4. Judd-Ofelt Analysis**

Judd-Ofelt theory is a useful method for analyzing f-f inner shell electronic transitions and its intensity parameters, Malta et al.[20], D. Carlos et al.[21], B. R. Juud [22]. Judd-Ofelt intensity parameters for transitions are denoted by  $\Omega_\lambda$  ( $\lambda=2, 4$  and  $6$ ) which are obtained from emission data of electronic transitions  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_4$  and  $^5D_0 \rightarrow ^7F_6$  respectively. However, in case of  $\text{Eu}^{3+}$  the pure magnetic dipolar transition display by the  $^5D_0 \rightarrow ^7F_1$  transition makes possible the determination of the intensity parameters from emission spectra since, this transition does not depend on the local ligand field seen by  $\text{Eu}^{3+}$  ions. Therefore this transition used as reference for the whole spectrum. In particular, the electric dipole transition  $^5D_0 \rightarrow ^7F_2$  so called hypersensitive transition is more sensitive to the symmetry and sequence of ligand fields, hence used to find intensity parameters  $\Omega_2$ .

From the emission spectra of the  $\text{Eu}(\text{TTA})_3\text{Phen}$  complex and  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer}$  blends, it determined the experimental intensity parameters  $\Omega_2$  by using the  $^5D_0 \rightarrow ^7F_2$  transition by expressing the emission intensity 'I' in terms of the surface 'S' under the emission curve, Xiaoping et al. [10], D. Carlos et al.[21].

$$I_j = \hbar \omega_{0j} A_{RAD} N(^5D_0) \text{-----} (4.1)$$

Where,  $\hbar \omega_{0j}$  is the transition energy,  $A_{RAD}$  the radiative transition rate, and  $N(^5D_0)$  is the population of the emitting level ( $^5D_0$ ).

$$A_{RAD} = \frac{4e^2 \omega^3}{3\hbar c^3} \chi \sum_\lambda \Omega_\lambda \langle 7F_j | U^{(\lambda)} | 5D_0 \rangle^2 \text{----} (4.2)$$

where  $e$  is the electronic charge,  $\omega$  is the angular frequency of the transition,  $\hbar$  is Planck's constant over  $2\pi$ ,  $c$  is the velocity of light,  $\chi$  is the Lorentz local field correction term and it is given by  $n(n^2+2)/9$ ,  $n$  being the

refraction index and the average value of which is equal to 1.5, Xiaoping et al. [10], and  $\langle 7F_j | U^{(\lambda)} | 5D_0 \rangle^2$  are the squared reduced matrix element whose values are 0.0032 and 0.0023 for  $J = 2$  and  $4$ , respectively, D. Carlos et al.[21], B. R. Juud [22], G. S. Ofelt [24], O. L. Malta et al.[25]. Where  $U(\lambda)$  is a tensor operator of rank  $\lambda$ , and the sum runs over the three values  $2, 4$ , and  $6$  of  $\lambda$ . The value of magnetic dipole allowed  $^5D_0 \rightarrow ^7F_1$   $A_{RAD}(^5D_0 \rightarrow ^7F_1) = 50 \text{ s}^{-1}$ , S. G. Pergamon et al. [23]. The obtained  $\Omega_2$  intensity parameters for samples  $\text{Eu}(\text{TTA})_3\text{Phen}$ ,  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer}$  and  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer}$  composites listed in Table 1. It is noted that the composite nanofibers of  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$  have values of  $\Omega_2$  higher than that of the pure complex, as well as  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS}$  and  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS-PVDF}$  composite suggestive of an increase in the covalency degree in the europium first coordination shell interaction in the sense of the dynamic coupling contribution to the total intensity and the polarization of the ligand field induces stronger europium ligand bonds and an increase in electric dipolar transitions for non-centro-symmetric ligand fields, Xiaoping et al. [10]. And results, relatively stronger hypersensitive behaviour of the  $^5D_0 \rightarrow ^7F_2$  transition under the influence of PVDF matrix. As a consequence, this might also suggest that the ligand effect of TTA in the composites was disturbed by the surrounding PVDF matrix, conferring a more polarized chemical environment of the  $\text{Eu}^{3+}$  ion.

From the results, value of intensity parameters and radiative transition rate for  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF}$ ,  $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PS-PVDF}$  are higher than the pure complex indicating, that when the europium complex are incorporated into the microcavity of PVDF matrix, it increases in the covalency degree which increases the probability for electronic dipole allowed transition.

Table 1. Judd-Ofelt Intensity parameters and Radiative transition rate of samples

Samples	Intensity (I) (a.u.)	$\Omega_2(10^{-20} \text{ cm}^2)$	$A_{\text{RAD}}(S^{-1})$
Eu(TTA) <sub>3</sub> Phen Complex	573.32	6.025	203.54
Eu(TTA) <sub>3</sub> Phen/PS	1603.32	16.84	569.22
Eu(TTA) <sub>3</sub> Phen/PVDF	8253.52	86.737	2930.25
Eu(TTA) <sub>3</sub> Phen/PS-PVDF	2564.62	26.95	910.51

### 3.5 CIE chromaticity coordinates

The CIE color model is a color space model created by the International Commission on Illumination known as the Commission Internationale de l'Éclairage (CIE). CIE coordinates of the Eu(TTA)<sub>3</sub>Phen complex, Eu(TTA)<sub>3</sub>Phen/Polymers and polymer composite were obtained by color calculator

software using PL emission data. The CIE result of Eu(TTA)<sub>3</sub>Phen complex shows red emission with appropriate CIE values with coordinates are  $x = 0.61$ ,  $y = 0.32$  shown in Figure 11 (a). These are near to the National Television System Committee (NTSC) coordinates for pure red emission, B. Rajamouli et al.[26], J. Feng et al.[27].

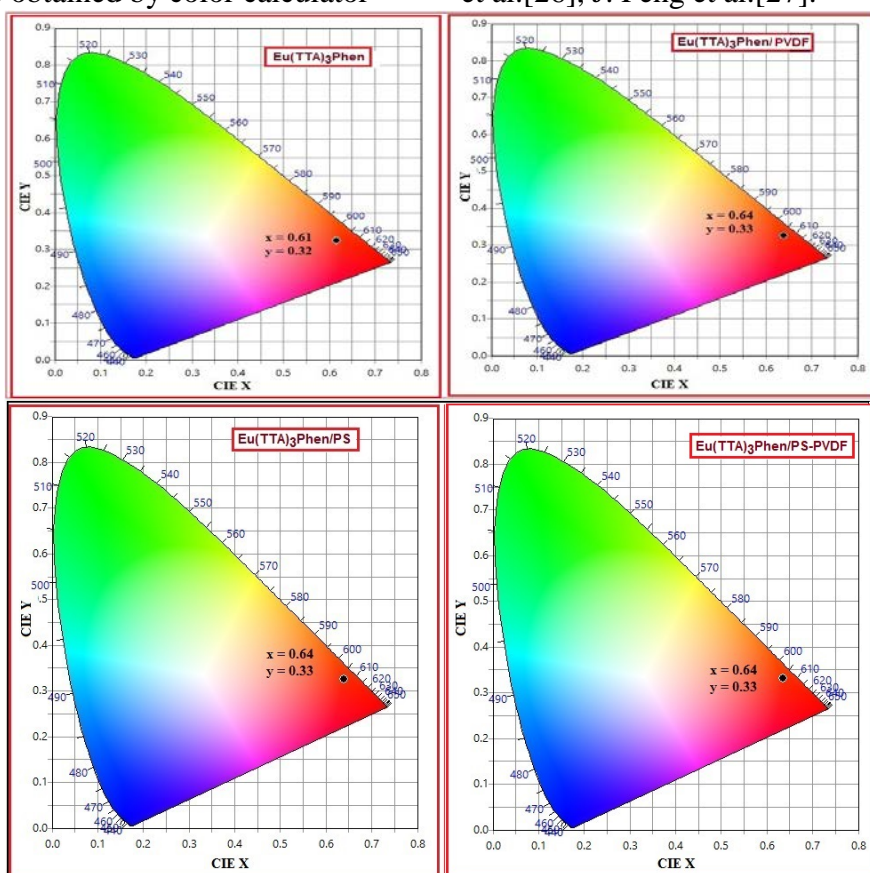


Fig. 11 CIE chromaticity coordinates for (a) Eu(TTA)<sub>3</sub>Phen, (b) Eu(TTA)<sub>3</sub>Phen/PVDF (c) Eu(TTA)<sub>3</sub>Phen/PS and (d) Eu(TTA)<sub>3</sub>Phen/PS-PVDF composite

In presence of polymer into Eu(TTA)<sub>3</sub>Phen complex, CIE coordinates deviated from its original position as in complex and it shows good color saturation. Fig.11 shows CIE chromaticity coordinates for (c) Eu(TTA)<sub>3</sub>Phen/PS (b) Eu(TTA)<sub>3</sub>Phen/PVDF and (d) Eu(TTA)<sub>3</sub>Phen/PS-PVDF. The calculated CIE coordinates for Eu(TTA)<sub>3</sub>Phen/PS are  $x = 0.61$ ,  $y = 0.33$ , and for Eu(TTA)<sub>3</sub>Phen/PVDF are  $x = 0.64$ ,  $y =$

$0.33$ . For Eu(TTA)<sub>3</sub>Phen/PS-PVDF composite,  $x = 0.64$ ,  $y = 0.33$ . The calculated CIE shows good color saturation. It is observed that as europium complex doped polymers matrix, the emission intensity increased and the CIE color coordinates moves towards pure or saturated red emission. The CIE color coordinates of the complex showed red color and the complex incorporated polymer matrix showed saturated red emission.

The most favorable situation is achieved in the case of the Eu(TTA)<sub>3</sub>Phen/ PVDF composite where the dominant 612 nm peak provides photoluminescence emission with a higher level of chromatic purity, thus allowing “deeper” red emission as shown in CIE graph with coordinates (0.64, 0.33). For Eu(TTA)<sub>3</sub>Phen/PS-PVDF peak provides photoluminescence emission with a higher level of chromatic purity with good color saturated red emission as it may be due to presence of PVDF in polymer.

#### 4. Conclusion

Uniform Eu(TTA)<sub>3</sub>phen/polymer composite nanofibers were successfully prepared by electrospinning. The presence of polymers, PS and PVDF in Eu(TTA)<sub>3</sub>phen complex increased the fluorescent intensity of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> hypersensitive transition of Eu<sup>3+</sup> ions in the complex, since the influence of polymer on the coordination ions changes the energy-transfer probabilities of electric dipole transition which increase in luminescent intensity of 612 nm peak. Due to the good morphology and outstanding fluorescent property, these Eu(TTA)<sub>3</sub>phen/PVDF composite nanofibers show potential applications in preparation of various photoluminescent fabrics.

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