

Chapter 9

Electrospun $\text{Eu}(\text{TTA})_3\text{Phen}$ /Polymer Blend Nanofibers for Photoluminescent Smart Fabrics



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Abstract Here, we report an innovative electrospun composite nanofiber having a complex of $\text{Eu}(\text{TTA})_3\text{Phen}$ doped in a matrix of polymer blends prepared by electrospinning for designing smart fabrics. Europium complex $\text{Eu}(\text{TTA})_3\text{Phen}$ contains 2-thenoyltrifluoroacetone (TTA), 1,10-phenanthroline (Phen) and europium. It was synthesized by co-precipitation technique for the preparation of electrospun nanofibers of $\text{Eu}(\text{TTA})_3\text{Phen}$ /polymer blends such as $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PMMA (Polyvinylidene fluoride-Polymethylmethacrylate) and $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PS (Polyvinylidene fluoride-Polystyrene). Nanofibers of $\text{Eu}(\text{TTA})_3\text{Phen}$ /polymer blends were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infra Red (FTIR), X-ray diffraction (XRD) and Photoluminescence (PL). Photoluminescence study of the nanofibers shows red emission which is allocated to the transitions between the first excited state (${}^5\text{D}_0$) and the multiplet states (${}^7\text{F}_{0-4}$). Due to the integration of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex into the polymer matrix and subsequent distortion of the symmetry around the Eu^{3+} ions by the chapping Polymer, the polarization of the Eu^{3+} ions was improved, which increased the probability for electronic dipole allowed transitions. The Judd-Ofelt theory was used to calculate intensity parameters from emission data of $\text{Eu}(\text{TTA})_3\text{Phen}$ /polymers blends. As compared to PS and PMMA, presence of PVDF in both polymer blends generally increases the intensity of hypersensitive transition and perhaps is responsible for enhancement of photoluminescence properties. Electrospun nanofibers of $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PS and $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PMMA can be important candidate for designing photoluminescent smart fabrics.

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9.1 Introduction

There has been an increasing interest in use of europium complex with β -diketones due to their intense emission peaks in the visible and near infrared region when excited by ultraviolet radiation. These photoactive europium complexes are of both essential and technological interest due to their distinguishing luminescence properties such as extremely sharp emission bands, potential high internal quantum efficiency and long lifetime of emission. The trivalent europium ion (Eu^{3+}) exposes strong and intense emission bands due to their f-f-electronics transition and broad range of luminescent lifetime, suitable for various applications, but they have low absorption coefficient, limiting the lighting output. However, these limitations can be improved by forming complexes of the rare-earth ions with organic ligands such as TTA and phen [1].

Chromophores of organic ligands used with europium shows strong absorption bands, so europium complex $\text{Eu}(\text{TTA})_3\text{Phen}$ have ability to absorb much more light than the Eu^{3+} ions. These organic ligands used as an antenna effect in which it absorbs the excitation light and to shift the excitation energy to the higher energy levels of the Eu^{3+} ion, as of the emitting excited levels of Eu^{3+} ion can be populated [2, 3]. Organic ligand in complex such as Phen is a synergic shielding ligand which used to reduce the rate of non-radiative decays and strongly enhance the fluorescence intensity of the complex. Therefore, the key problem related to rare earth complex is to try to find a suitable matrix material to load them. Inorganic solid matrixes are promising host materials due to their good optical, thermal and chemical stability. In fact, many RE complexes have already been encapsulated in or adsorbed on host materials including silica, sol-gels and zeolite. A number of properties make polymers attractive hosts for rare-earth ions, including low cost, ease of fabrication on a wide range of substrates, low dispersion, and broad luminescence bands. Such europium complexes doped in polymers possess enhanced photoluminescence properties with this it shows improved thermal stability and mechanical flexibility [4]. The incorporation of europium complex into organic polymers presents an ideal and multipurpose approach to generate hybrid materials. It has been verified that the polymer-capped $\text{Eu}(\text{TTA})_3\text{Phen}$ complexes possess improved photoluminescence properties and thermal stability, and are mechanically flexible. There is tremendous work going in textile for the fabrication of smart clothes with the use of nanofibers. Nanofibers of photoluminescent materials prepared by electrospinning method are in special demand. One-dimensional (1D) nanofibers are very interesting because of their surface properties, different from bulk materials. The photoactive $\text{Eu}(\text{TTA})_3\text{Phen}$ complexes doped in polymer matrixes presents a class of new materials that shows the properties of both the europium complexes and the polymer matrix materials, useful in a wide range of new technologies. Nanofibers of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex cannot be directly obtained by electrospinning without the use of polymers. Polymer nanofibers do not emit light without lanthanide complexes mixed with polymers. Therefore, there is the need of composites of both categories to have fibers in nanoscale and light emission. Use of polymer not only as a carrier but it helps to

enhance luminescent properties of material. The enhancement of luminescent efficiencies in $\text{Eu}(\text{TTA})_3\text{Phen}$ /Polymer occurs as uniform distribution of the complex units along macromolecular chains of polymers. In present work PS, PMMA, PVDF with their blends are used as matrix material for observing the good coordination between $\text{Eu}(\text{TTA})_3\text{Phen}$ complex and polymer so as to get enhanced luminescent fibers for fabric designing in the textile industries.

9.2 Experimental

9.2.1 Preparation of $\text{Eu}(\text{TTA})_3\text{Phen}$ Complex

$\text{Eu}(\text{TTA})_3\text{Phen}$ complex powder was prepared by simple solution method [5]. TTA (6.63 mmol, 1.4725 g) and phen (2.21 mmol, 0.3979 g) were dissolved in 20 ml of ethanol in flask. This solution neutralized with NaOH solution to obtained pH = 7. In another flask europium chloride salt EuCl_3 (2.21 mmol, 0.5708 g) was dissolved in 10 mL of double distilled water. Prepared solution was poured into the solution of TTA and phen. Finally, prepared solution was heated at 60 °C with continuous stirring for 1 h for obtaining homogenous solution. After 1 h precipitate of solution was formed and it was separated by using filter paper. The color of obtained compound was off-white which was then dried in oven at 80 °C for 2 h.

9.2.2 Preparation of $\text{Eu}(\text{TTA})_3\text{Phen}$ /Polymer Blend Solutions

Preparation of electrospinning solution of $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PS composites, 1 g PVDF and 1 g PS were dissolved in 10 mL THF (tetrahydrofuran) solvent in one flask for obtained mass fraction of 20 wt%. Obtained mixture was magnetically stirred for 12 h till becoming uniform solution. Then 20% of $\text{Eu}(\text{TTA})_3\text{Phen}$ was added to above uniform solution of polymer and again magnetically stirred for 12 h. Now solution is ready for electrospinning process for preparation of nanofibers. The same process was repeated for preparation of electrospinning solution of $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PMMA blend.

9.2.3 Preparation of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer Blend Nanofibers}$

The prepared uniform electrospinning solution of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ blend was firstly filled into a 5 mL plastic syringe for preparation of nanofibers by electrospinning method. For the electrospinning process, prepared solution was fed to the tip using a syringe pump and adjust flow rate of 0.3 mL/h. A positive voltage of 25 kV was applied to the needle of the syringe that containing electrospinning solution. Metallic plate wrapped with aluminum foil and connected with grounded electrode. Distance between needle of the syringe and metallic plate must kept at a distance of 15 cm. The uniform electrospun nanofibers were collected on the conducting aluminum foil. After electrospinning process, collected membranes of nanofibers on aluminum foil were dried in a vacuum oven at 60 °C for 12 h so that to eliminate the residual organic solvent present with nanofibers. Same electrospinning method was repeated for another electrospinning solution of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ polymer blend.

9.3 Results and Discussion

9.3.1 Scanning Electron Microscopy

Surface morphological and structural properties of prepared nanofibers of different composites by electrospinning method can be studied by SEM (scanning electron microscopy). It examines the surface information of the materials and a detailed study of the morphological features like diameter of fibers, their length, and alignment etc. of all the samples had been carried. SEM study of synthesized nanofibers is important since they directly affect the photoluminescence emission intensity of the materials. As compare with nanofibers of pure polymer, diameter of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{polymer}$ blends are found to be smaller, this may be due to effect of increased conductivity of the electrospinning solution as addition of $\text{Eu}(\text{TTA})_3\text{Phen}$ in pure polymer solutions. With addition of $\text{Eu}(\text{TTA})_3\text{Phen}$ in pure polymer complex uniformly distributed along macromolecular chain of the polymers and it helps to increase conductivity of electrospinning solution which results to decrease diameter of nanofibers of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{polymer}$ blends. The presence of europium complex into the polymer matrix can efficiently recover the morphology of the electrospinning fibers. Such $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer}$ blend nanofibers show more photoluminescence intensity as compared to nanofibers of pure $\text{Eu}(\text{TTA})_3\text{Phen}$ complex, Increased in intensity of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer}$ blend nanofibers which may be due to their large surface area and small diameter as they show high aspect ratio that confirmed from their SEM images.

SEM images of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ blend electrospun nanofibers shows diameters in the range of 300 to 700 nm and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ blend

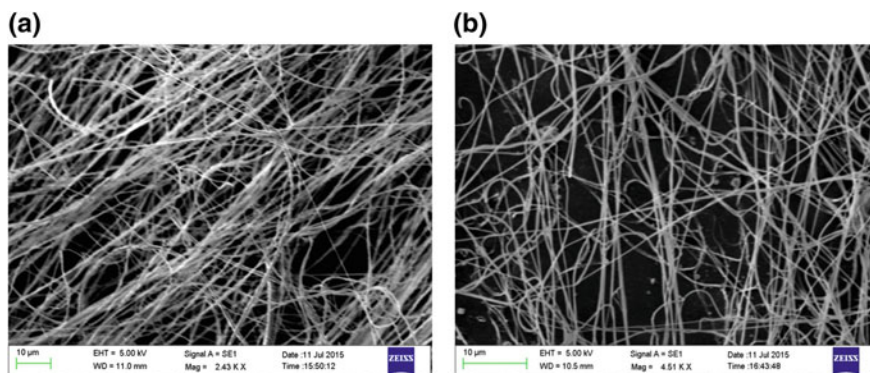


Fig. 9.1 SEM images of **a** $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PS blend and **b** $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PMMA blend nanofibers

electrospun nanofibers shows diameters in the range of 100 to 500 nm as respectively shown in Fig. 9.1a, b. Obtained nanofibers of $\text{Eu}(\text{TTA})_3\text{Phen}$ /polymer blends are aligned in random orientation on the collector, which was occurred by the bending instability of the spinning jet and stationary collector [6, 7].

9.3.2 FTIR Spectroscopy

FTIR spectra of $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PS blend and $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PMMA blend nanofibers are shown in Fig. 9.2. In the spectrum of $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PS blend there are presence of bands of PS and PVDF with europium complex. FTIR spectra shows bands of PS which are shifted from its original position to slightly higher frequencies at 756, 1450, 1492 and 1602 cm^{-1} , shows the vibrations of the benzenoid ring in PS and one extra broad band appeared at 3400 cm^{-1} arises by the vibration of hydroxyl groups of PS [8]. FTIR spectra shows the bands of stretching vibration of the C=O group at 1185 cm^{-1} which are characteristic peak of PVDF, which shows a little shift to the higher frequencies as compared with pure PVDF spectra. These shifting of bands for PS and PVDF in $\text{Eu}(\text{TTA})_3\text{Phen}$ /polymers blends occur due to coordination of europium complex with PS and PVDF polymer matrix [9]. The vibration peaks of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex also get shifted to higher frequencies due to the surrounding polymer matrix. In FTIR spectrum of $\text{Eu}(\text{TTA})_3\text{Phen}$ /PVDF-PMMA polymer blends, there are presence of characteristic bands of PMMA and PVDF at 1724 cm^{-1} and 1185 cm^{-1} respectively, at higher frequency region with some bands of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex [10]. These shifting of bands from its positions, show that the europium complexes are effectively incorporated into polymer blend matrix.

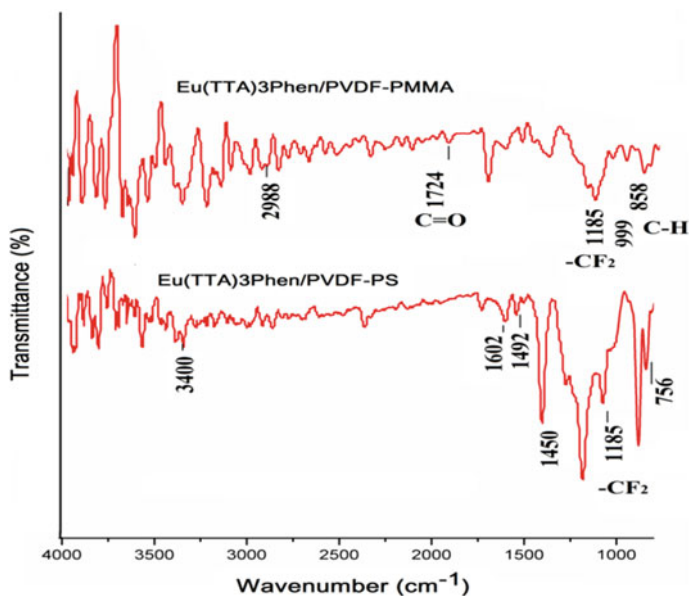


Fig. 9.2 FTIR spectra of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ blend and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ blend nanofibers

9.3.3 X-Ray Diffraction

Figure 9.3 shows X-ray diffraction patterns of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ blend and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ blend nanofibers. In XRD pattern of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer}$ blends, there are diffraction peaks of PMMA, PVDF and PS exist. Diffraction peaks shows the maximum sharp peak intensity for polymer/polymer blends as europium complex $\text{Eu}(\text{TTA})_3\text{Phen}$ doped in polymer blend matrix which results a maximum degree of crystallinity due to increasing degree of ordering of atoms at polymer blend, means that the crystal structure remained constant [11]. X-ray diffraction patterns also shows a sharp peak of europium complex in $\text{Eu}(\text{TTA})_3\text{Phen}/\text{polymer}$ blend, it represented that chemical bonding exist between polymers and europium complex. There are small corresponding diffraction peaks at $2\theta = 15^\circ\text{--}58^\circ$ of europium observed. Presence of all these peaks of europium complex in XRD pattern of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{Polymer}$ blends, indicates the development of a solid solution of $\text{Eu}(\text{TTA})_3\text{Phen}$ in polymer blend matrix.

9.3.4 Photoluminescence

The emission spectra of europium complex $\text{Eu}(\text{TTA})_3\text{Phen}$, $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ blend and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ blend electrospun nanofibers are shown

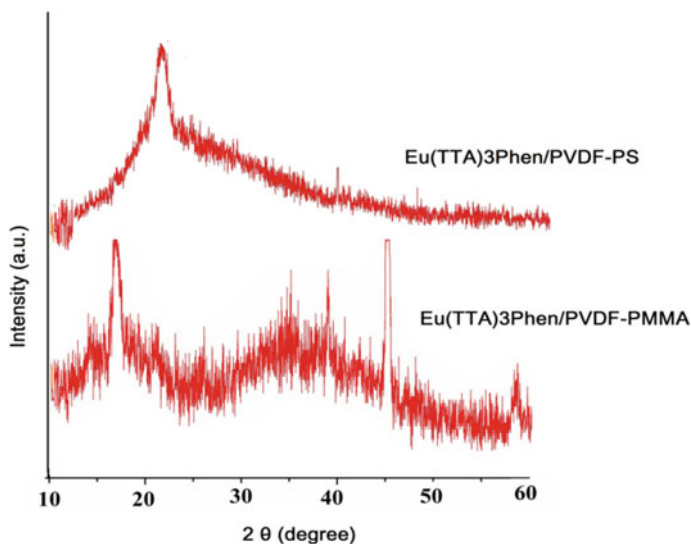


Fig. 9.3 XRD patterns of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ nanofibers

in Fig. 9.4. Under excitation at 354 nm, emission spectrum of $\text{Eu}(\text{TTA})_3\text{Phen}$ was extended from 550 to 655 nm [12]. The emission spectrum shows four emission peaks at 579, 592, 612, 642, 654 nm, for the transitions $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, $^5\text{D}_0 \rightarrow ^7\text{F}_4$ respectively. These transitions can be characteristically the f-f transitions of Eu^{3+} ions in the europium complex. The transition $^5\text{D}_0 \rightarrow ^7\text{F}_1$ is a magnetic dipole transition, it allowed by the Laporte selection rule. The intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition are very weak as it is unaffected by the influence of surrounding material environment. The lower transitions $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^7\text{F}_3$ are forbidden transitions and its intensities not change with external change in surrounding materials. The transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ called as hypersensitive transition and its emission intensity strongly influenced by surrounding polymer matrix as well as local

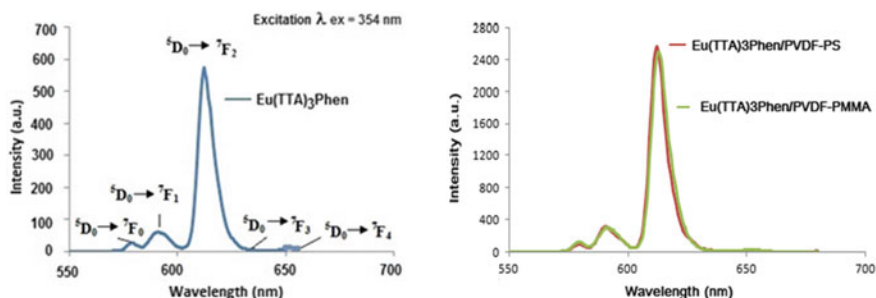


Fig. 9.4 Emission spectra of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex, $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ nanofibers

symmetry of the europium ions of the complex and nature of ligands. The emission spectra of $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PS}$ blend and $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PMMA}$ blend electrospun nanofibers shows much stronger intensity of hypersensitive transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ than hypersensitive transition of $\text{Eu}(\text{TТА})_3\text{Phen}$ complex, indicates that Eu^{3+} ion is in a single site without a center of inversion and presence of surrounding polymer matrix region around the europium complex which influenced the chemical environment around the Eu^{3+} ions due to this, higher probability for the electronic dipole allowed transitions which leads to increased hypersensitive transition rate and varies its intensity [13–19]. Hypersensitive transition are intraconfigurational electric dipole transitions which are initially forbidden by the Laporte selection rule but when a europium ions of europium complex conjugated to a chemical complex of $\text{Eu}(\text{TТА})_3\text{Phen}$, the Eu^{3+} ion commencing is in a coordinating environment and the forbidden transitions changes into partly allowed.

As compare with hypersensitive intensity of $\text{Eu}(\text{TТА})_3\text{Phen}$ complex, intensity of $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PMMA}$ blends are much high, due to the presence of PVDF in both polymer blends. Increased in intensity of $\text{Eu}(\text{TТА})_3\text{Phen}/\text{Polymer}$ blend nanofibers which may be due to their large surface area and small diameter as they show high aspect ratio that confirmed from their SEM images study. The enhancement of luminescent efficiencies in $\text{Eu}(\text{TТА})_3\text{Phen}/\text{Polymer}$ blend occurs as there uniform distribution of the complex units along macromolecular chains of polymer matrix.

The CIE (Commission Internationale de l' Eclairage) color model is used to study emission intensity in terms of intensity of color emitted during transitions. This study used coordinates system. The coordinates of the $\text{Eu}(\text{TТА})_3\text{Phen}$ complex, $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PMMA}$ nanofibers were obtained by color calculator software of CIE using PL emission data of each sample. The CIE coordinates calculated for $\text{Eu}(\text{TТА})_3\text{Phen}$ complex shows red emission in visible region with coordinates $x = 0.61$, $y = 0.32$ shown in Fig. 9.5a.

Figure 9.5b, c show CIE calculated coordinates for $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PMMA}$, respectively. For $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PS}$ CIE coordinates are $x = 0.64$, $y = 0.33$ and for $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PMMA}$ CIE coordinates are $x = 0.64$, $y = 0.34$. As addition of polymers PS and PVDF into pure $\text{Eu}(\text{TТА})_3\text{Phen}$ complex, CIE results shows slightly change in coordinates with position of color in CIE graph. CIE coordinates for $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TТА})_3\text{Phen}/\text{PVDF-PMMA}$ deviated from its original position as in europium complex and it shows good red color saturation. The calculated CIE shows good color saturation for red emission. As europium complex is integrated with polymers matrix, the emission intensity of hypersensitive transitions increased and the CIE color coordinates for its moves towards pure or deep saturated red emission region. The CIE calculated color coordinates for europium complex showed red color region and for europium complex incorporated polymer matrix showed deep saturated red emission region.

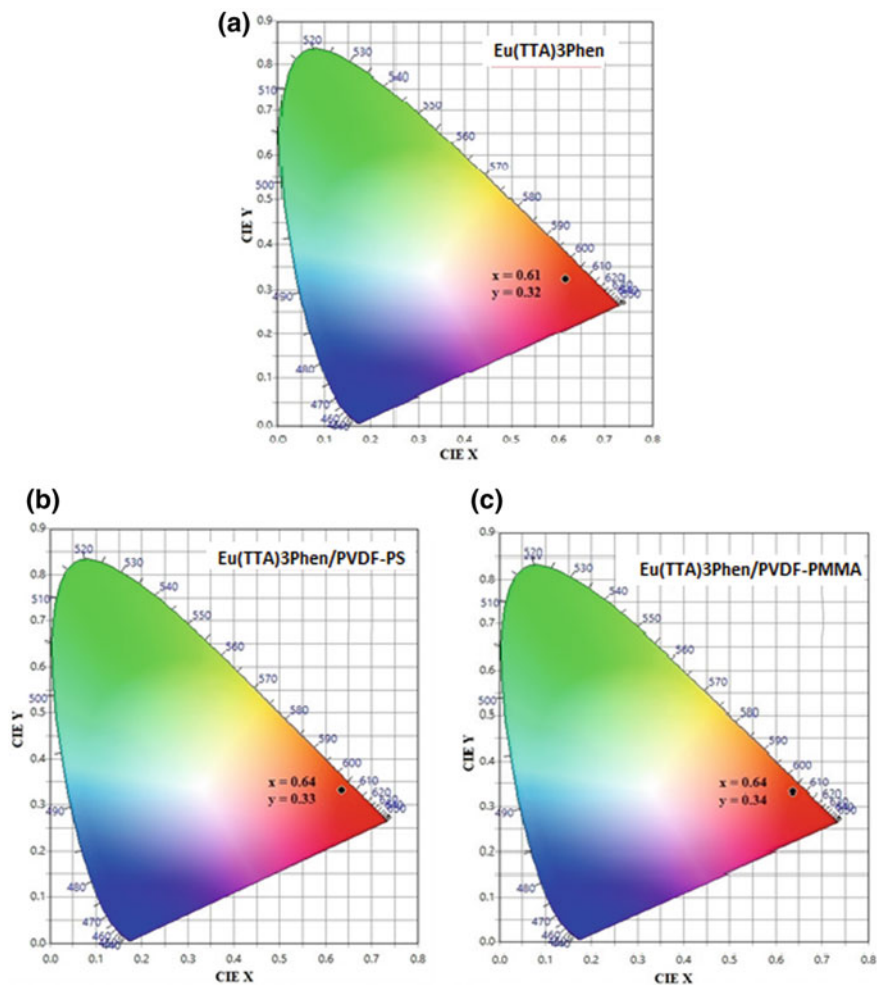


Fig. 9.5 CIE chromaticity coordinates for **a** $\text{Eu}(\text{TTA})_3\text{Phen}$, **b** $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ and **c** $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$

9.4 Conclusion

$\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ blend and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ blend nanofibers with diameters in nano range were prepared by electrospinning process. Due to the addition of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex into the polymer matrix and successive distortion of the symmetry around the Eu^{3+} ions by the chapping Polymer, the polarization of the Eu^{3+} ions was improved, which increased the probability for electronic dipole allowed transitions. As increased in electronic dipole allowed transitions there were

increased in intensity of hypersensitive transition. Addition of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex in polymers generally enhances the luminescent intensity as compared to pure europium complex $\text{Eu}(\text{TTA})_3\text{Phen}$. Polymers like PS, PMMA and PVDF generally increases the luminescent intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ hypersensitive transition of Eu^{3+} ions. As compare with hypersensitive intensity of $\text{Eu}(\text{TTA})_3\text{Phen}$ complex, intensity of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ blends are much high, due to the presence of PVDF in both polymer blends. Nanofibers of $\text{Eu}(\text{TTA})_3\text{Phen}/\text{polymer}$ blends shows large surface area and small diameter as they represents high aspect ratio that confirmed from their SEM images. As $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PS}$ and $\text{Eu}(\text{TTA})_3\text{Phen}/\text{PVDF-PMMA}$ blend nanofibers shows good morphology and excellent luminescent property, it could be applied for the designing of photoluminescent smart fabric.

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