Journal of Materials Physics and Chemistry, 2017, Vol. 5, No. 1, 1-10
Available online at http://pubs.sciepub.com/jmpc/5/1/1
©Science and Education Publishing
DOI:10.12691/jmpc-5-1-1

Structural and Optical Investigation of Novel Europium Hybrid Organic Complex for OLEDs and Solid State Lighting

Dipti Chitnis[1], **N. Thejo Kalyani**[2,*], **S.J. Dhoble**[1]

[1]Department of Physics, RTM Nagpur University, Nagpur-440033, India
[2]Department of Applied Physics, Laxminarayan Institute of Technology, Nagpur-440033, India
*Corresponding author: thejokalyani@rediffmail.com

Abstract We report the design and synthesis of volatile europium β-diketonate Eu(dmh)$_3$phen organic hybrid complex by precipitation technique. A series of complexes were synthesized for different pH values, ranging between 8.0 and 6.0 maintaining stoichiometric ratio. Among all the synthesized complexes, Eu(dmh)$_3$phen with pH 7 exhibits red intense emission at 613 nm with a sharp spectral bandwidth of 5 nm when excited at a wavelength of 372nm,infering that the synthesized complex is pH sensitive. This complex is further assessed for structural, thermal and luminescence behavior in various solvents. X-ray diffractogram reveals its crystalline nature and FTIR confirms the complete formation of the complex revealing the presence of TTA and bipy structure in the metal complex. TGA/DTA exhibits good thermal stability, which is highly essential for fabricating organic light emitting diodes (OLEDs) for solid state lighting. Hypsochromic shift was observed in the optical absorption spectra of Eu(dmh)$_3$phen, when the solvent is changed from basic to acidic media.

Keywords: *biodegradable, europium, solid state lighting, OLEDs*

Cite This Article: Dipti Chitnis, N. Thejo Kalyani, and S.J. Dhoble, “Structural and Optical Investigation of Novel Europium Hybrid Organic Complex for OLEDs and Solid State Lighting.” *Journal of Materials Physics and Chemistry*, vol. 5, no. 1 (2017): 1-10. doi: 10.12691/jmpc-5-1-1.

1. Introduction

Since time immemorial, there is an incredible change in lighting technology, as it plays a significant factor contributing to the quality and productivity of human life. Though fire was used by our primate ancestors 2–6 million years ago, it is still thought of as an exemplary human invention [1]. But till date the so developed technologies face many challenges in order to offer ecofriendly climate and energy efficient solid state lighting (SSL). Billions of people around the world, including the poorest and most vulnerable small holders still depend on fuel based lighting, which is climate hazardous. Hence, there is growing focus on adoption of technology for improvising lighting techniques, with an agenda of green lighting to ensure light for all. For SSL, highly intense and narrow peak emission of the primary colours (RGB) is essential. However, red light emission is considered as the weakest one because the transition corresponding to red light occurs at a comparatively small energy band gap, which is hard to match the energy level of carrier transmission layer [2]. This drawback can be overcome to certain extent by employing europium complexes in view of their high photo luminescent (PL) efficiency and the red-emission ability that are widely exploited in full-color displays. At present, research activity involving the design and construction of novel Eu $^{3+}$ complexes for the light-emitting device is prevalent because of their sharp emission peak at 612 nm [3,4]. β-diketones (1,3-diketones) with rare-earth ions are the most popular and the most intensively investigated rare earth coordination compounds [5]. This popularity is partially due to the fact that many different β-diketones are commercially available and the fact that the synthesis of the corresponding rare-earth complexes is relatively easy [6]. However, the main drive for the intense research activity on the rare-earth β-diketonates was and is still continued due to their potential of being used in several applications [7,8]. Hence, it proposed to design, synthesize and characterize novel europium complex with dmh and phen as ligands by precipitation technique.

2. Experimental

Chemicals of analytical reagents (AR) grade were purchased from Sigma Aldrich and Across organics. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere.

2.1. Reagents and Solvents

Starting materials used for the synthesis of Eu(dmh)$_3$phen complex are europium chloride hexahydrate ($EuCl_3.6H_2O$), [Across chemicals] Purity – 99.99%, M.Wt = 366.40 g/mol.

2,6-Dimethyl-3,5-heptanedione, [pale yellow liquid]($C_9H_{16}O_2$) [Across chemicals] Purity – 99%; M.Wt = 127.13 g/mol. Phen- 1,10 Phenanthroline, ($C_{12}H_8N_2.H_2O$)[Fisher scientific] purity – 99.9%, M.Wt = 198.23 g/mol Ethanol absolute (C_2H_5OH), purity – 99.98%, M.Wt = 46.07 g/mol, chloroform ($CHCl_3$) [Qualigens company] purity – 99.7 %, M.wt.= 119.38, Toulene ($C_6H_5CH_3$), M.wt = 92.14 gm purity - 99.9%, refractive index is 1.493-1.497, b.p (92%) = 110-111°C; Tetra hydro Furan(THF)(C_4H_8O), M.wt = 72.11 gm purity - 99.9%, refractive index at 20°C is 1.407-1.409, boiling range 65-67°C, Acetic acid (CH_3COOH) [sd fine chemicals] purity – 99.5%, M.wt.=60.05, Potassium hydroxide (KOH), purity – 99.9% and double distilled water.

2.2. Structure and Synthesis of Organic Complexes

The chemical structure of dmh, phen, Eu(dmh)$_3$phen are shown in Figure 1(a) (b) and (c), respectively. Synthesis scheme of Eu (dmh)$_3$phen complex is shown in Figure 2 It can be clearly stated that Eu^{3+} is associated with three molecules of dmh and one molecule of phen. Eu^{3+} has 8 co-ordinates (6 with dmh, which are shown to the left of Eu^{3+} while the other two with phen on the right side). For the formation of Eu(dmh)$_3$phen complex, the stichiometry of chemical compounds are taken in 1:3:1 ratio.

2.3. Synthesis Procedure

Step 1: dmh (6.63 mmol= 0.842 gm) and phen (2.21 mmol = 0.438 gm) were dissolved in 20ml ethanol (Sol I).

Step 2: Later, $EuCl_3.6H_2O$ (2.21 mmol = 0.809 gm) was separately dissolved in 10 ml double distilled water in another beaker (Sol II).

Step 3: Both the solutions were mixed and the pH of the resultant solution was found to be in between 0.25 - 0.35. In order to obtain a neutral solution with pH=7, KOH solution is added drop by drop into the resultant solution.

Step 4: The solution thus obtained was heated at 60°C on a hot plate with continuous stirring with a magnetic stirrer for 1 hour.

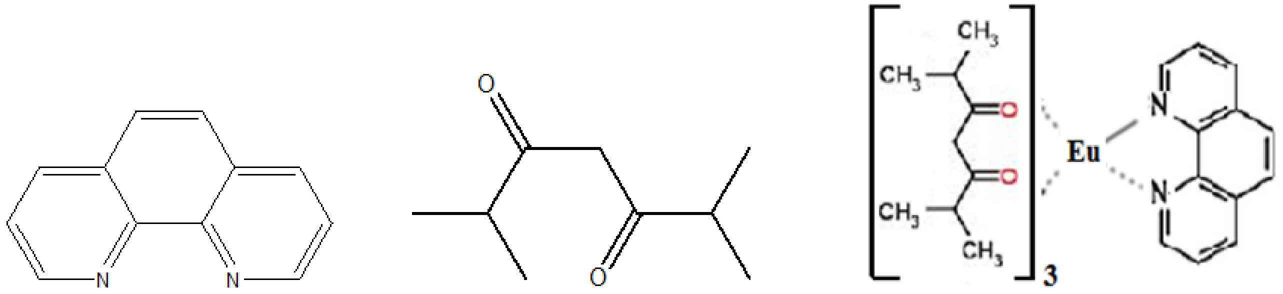
Step 5: The precipitate so obtained was filtered and washed with double distilled water twice or thrice.

Step 6: The complex was dried at room temperature and then eventually in the hot air oven at 80°C for two hours [9].

Similarly, series of complexes were prepared by increasing pH to 8.0 from 7.0 and also by decreasing the pH to 6.0 from 7.0 at an interval of 0.5 pH. Pictorial demonstration of synthesis procedure of Eu(dmh)$_3$phen complex is shown in Figure 3.

3. Result and Discussion

Structural properties of Eu(dmh)$_3$phen are evaluated by wide angle X-ray diffraction on Philips Analytical X' Pert Pro Powder Diffractometer, while Fourier Transform Infrared spectra and thermal properties of the synthesized complexes are explored on Perkin Elmer-Spectrum one and Perkin Elmer Diamond TGA/DTA analyzer, respectively. Optical absorption and emission spectra were carried out on HR 4C 4568 UV –Vis spectro photophotometer and Humamatsu F-4500 spectroflurometer, respectively. Among all the synthesized complexes, maximum photoluminescence intensity was obtained from Eu(dmh)$_3$phen with pH=7.0. Hence this complex is considered for further characterizations such as XRD, TGA/DTA, FTIR, optical absorption spectra in acidic and basic media.



(a) (b) (c)

Figure 1. The chemical structure of (a) 1,10 Phenanthroline (b) 2,6-Dimethyl-3,5-heptanedione (c) Eu(dmh)$_3$phen

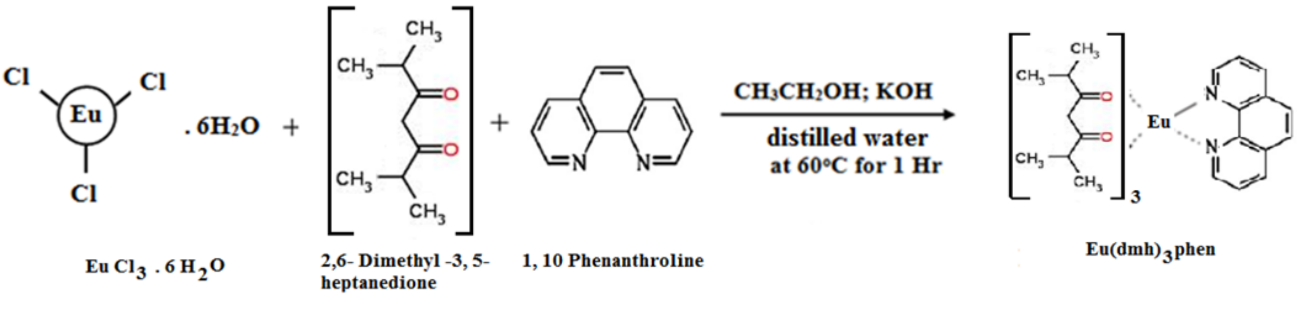


Figure 2. Synthesis route of Eu(dmh)$_3$phen complex by solution technique

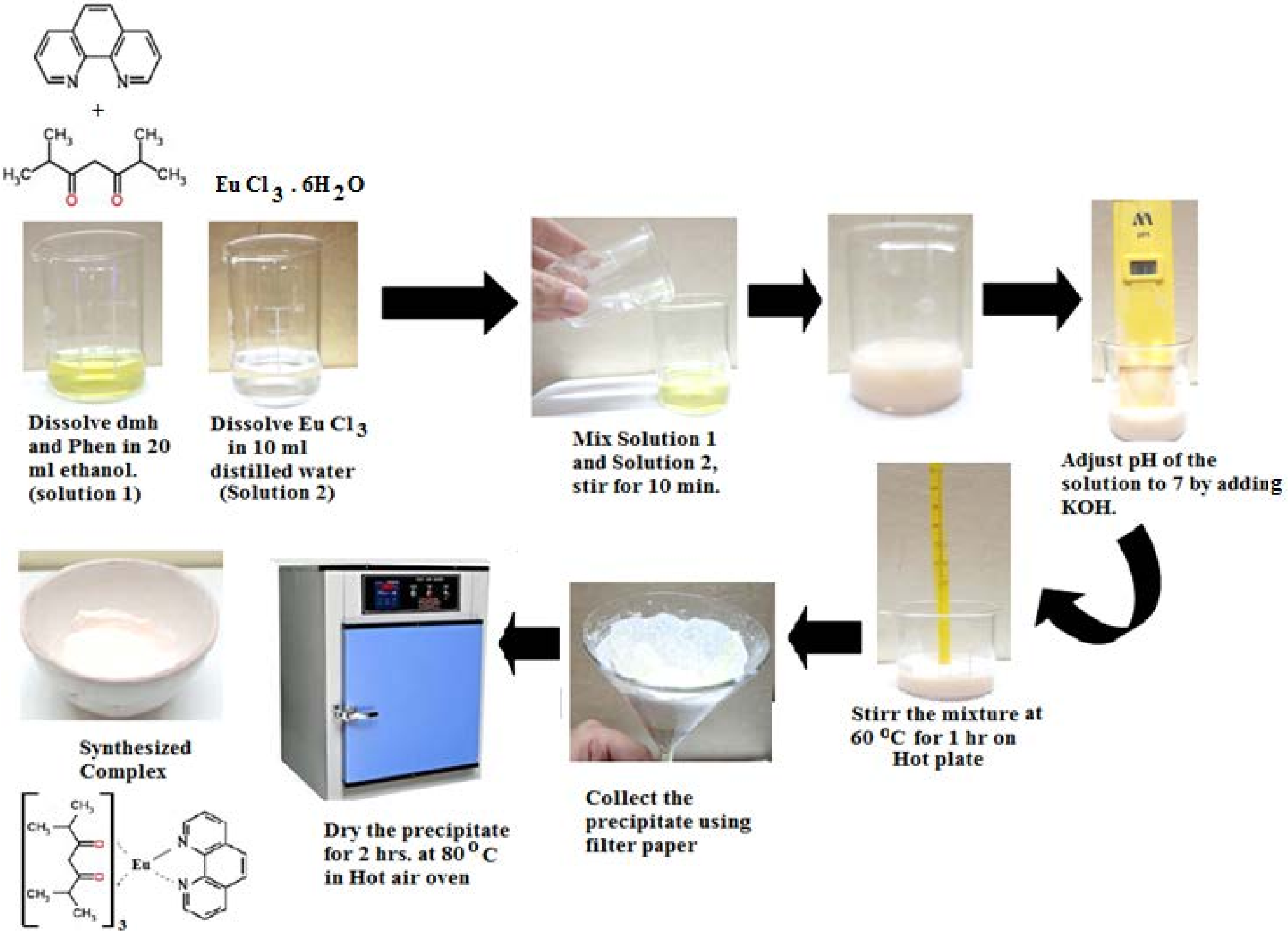


Figure 3. Pictorial demonstration of synthesis procedure of Eu(dmh)$_3$phen complex

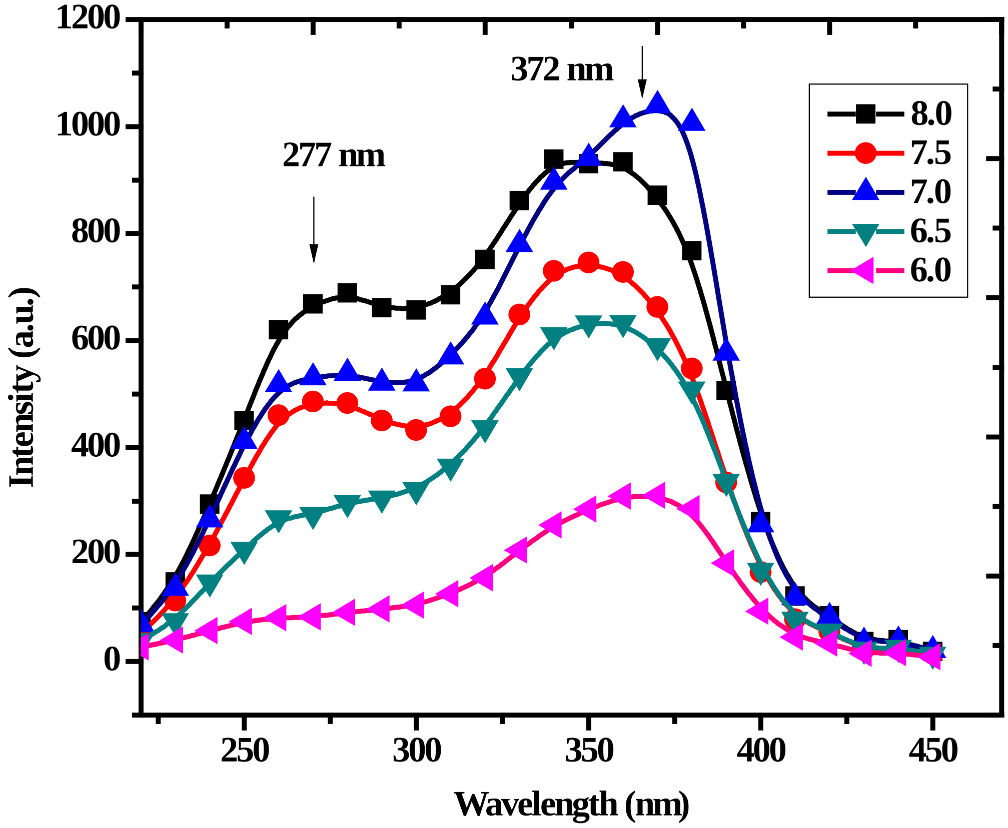


Figure 4. Excitation spectra of Eu(dmh)$_3$phen complex for different values of pH

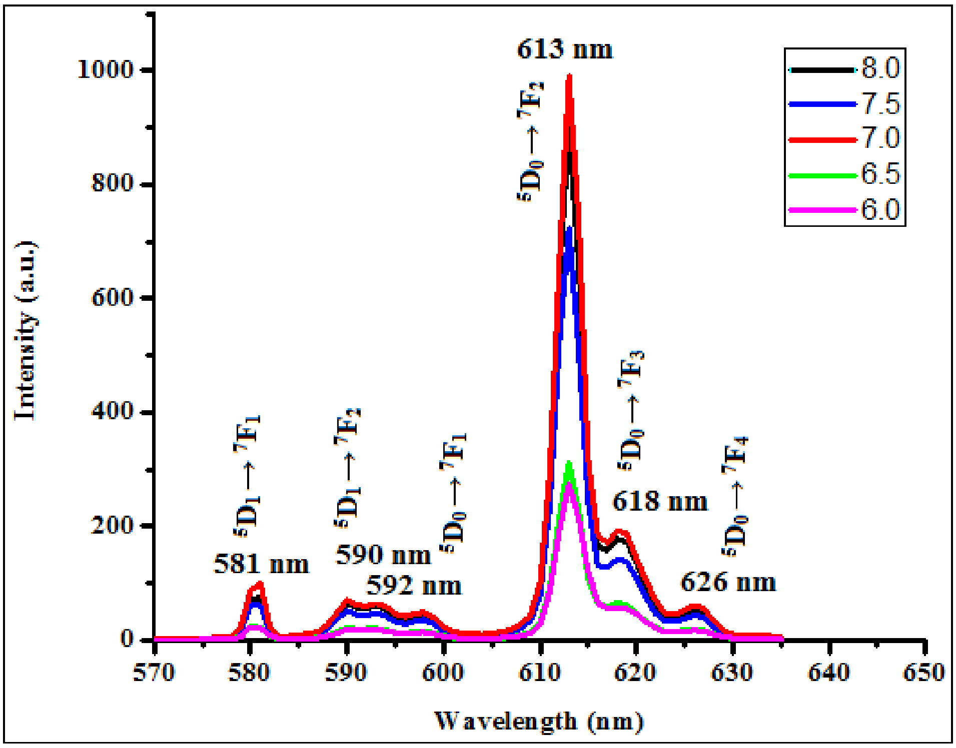


Figure 5. Emission spectra of Eu(dmh)$_3$phen complex for different values of pH

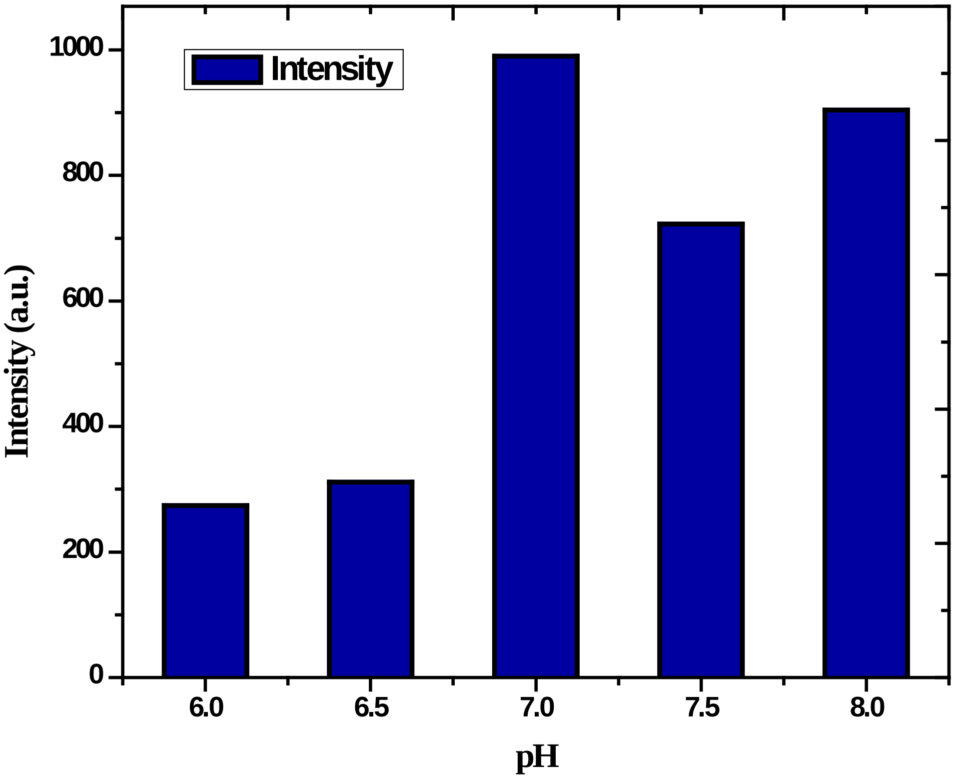


Figure 6. The variation of emission intensity of complex with pH

3.1. Photoluminescence Spectra

The excitation and emission spectrum of Eu(dmh)$_3$phen complexes at pH ranging from 8.0 to 6.0 is shown in Figure 4 and Figure 5, respectively. The complexes were excited in the wavelength range of 250 nm to 500 nm monitoring emission at 613 nm. Variation in intensity of red light emission was observed with change in pH. Emission spectra revealed that Eu(dmh)$_3$phen exhibits a sharp spectral emission centered at 613 nm when excited at 372 nm wavelength. PL emission spectrum also displays weak emission peaks at 581nm, 590 nm and 592 nm 618 nm and 626 nm.

The emission spectra of the Eu(dmh)$_3$phen complex showed the highest intensity at 613 nm, which corresponds to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition. The intensity of the electric dipole transition $^5D_0 \rightarrow {}^7F_2$ transition is much stronger than the magnetic dipole allowed $^5D_0 \rightarrow {}^7F_1$ transition, indicating that Eu^{3+} ions in these systems occupy very low symmetric sites [10]. This hyper sensitive $^5D_0 \rightarrow {}^7F_2$ transition is very sensitive to the intermediate environments around Eu^{3+} ions. The synthesized Eu complex exhibited a synergistic effect in which the ligand could absorb UV light and transfer energy to Eu(III), leading to enhancement of intensity. Variation of emission intensity of complex with Ph is displayed in Figure 6.

3.2. Determination of CIE Co-ordinates for Eu(dmh)₃phen

The CIE chromaticity coordinates of the light emission from these pH dependent phosphors, excited at 372nm are depicted in Figure 7.

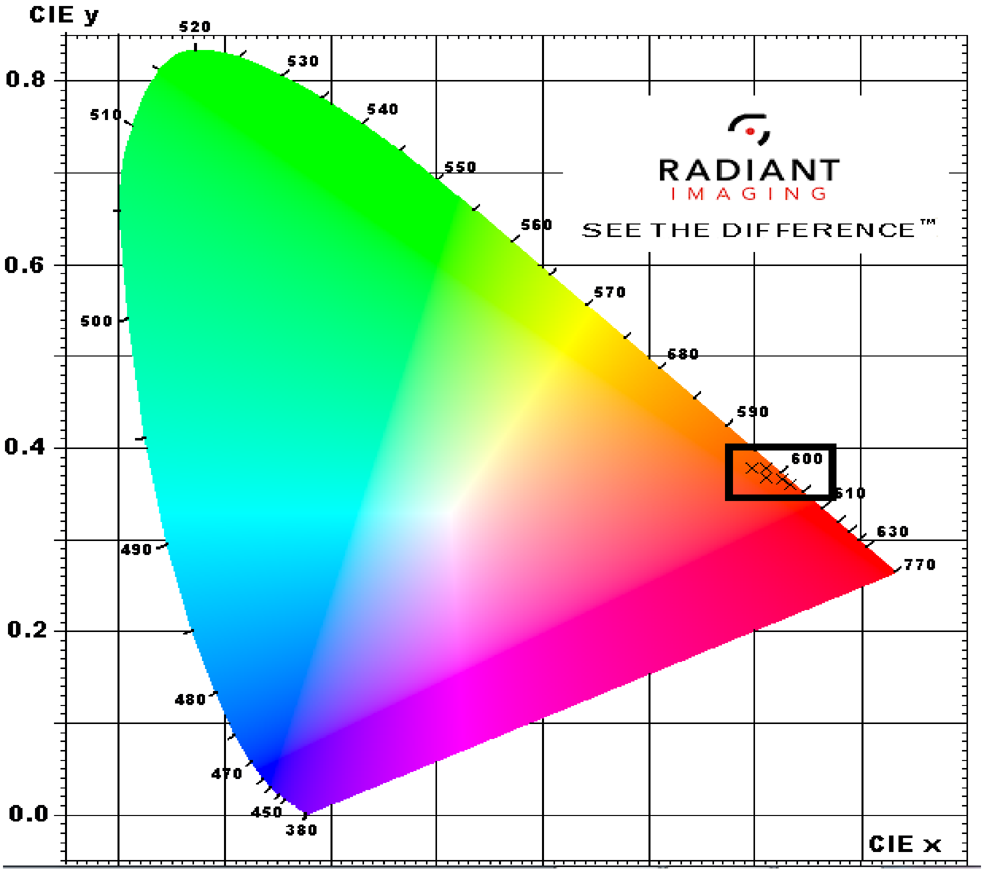


Figure 7. CIE 1931 (x, y) diagram displaying emission color coordinates of Eu(dm)$_3$phen

Table 1. Yield % and X,Y co-ordinate values in CIE system with varying pH value of complex Eu(dmh)$_3$phen

Complex	pH	Yield %	CIE co-ordinates (x, y)	Digital photograph
Eu(dmh)$_3$phen	6.0	62.8%	(0.580, 0.326)	
	6.5	65.0%	(0.577, 0.325)	
	7.0	72.0%	(0.585, 0.327)	
	7.5	70.4%	(0.581, 0.325)	
	8.0	62.1%	(0.582, 0.324)	

The emission colour of the synthesized phosphors with different pH lies in the orange-reddish region with CIE co-ordinates varying from (0.582, 0.324) to (0.580, 0.326). The CIE co-ordinates of Eu(dmh)$_3$phen at pH 6, 6.5, 7, 7.5 and 8 are found to be (0.582, 0.324), (0.581, 0.325), (0.585, 0.327), (0.577, 0.325) and (0.580, 0.326), respectively. Starting from the higher pH value 8.0, it was found that the values of x, y chromaticity co-ordinates increased up to 7.0 pH, whereas with further decrease in the pH, x and y values dropped down till 6.0 pH. However, the largest values of x and y co-ordinates are (0.585, 0.327) corresponding to 7.0 pH. Summary of yield %, CIE co-ordinates and the digital photographs of raw complexes synthesized at different values of pH shown in Table 1.

3.3. Absorption Spectra

The UV-vis absorption spectra for the synthesized volatile complex Eu(dmh)$_3$phen was recorded and analyzed with a UV-vis spectrophotometer with PC interface by first calibrating with a cuvet of chloroform/toluene/THF/acetic acid to get a baseline, later, running a cuvet filled with each of the solutions at different molar concentrations. Different solutions of Eu(dmh)$_3$phen of chloroform, toluene and THF (basic medium) and acetic acid (acidic medium), respectively were prepared with different molar concentrations to study the shift of $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ optical transitions in Eu^{3+} ion and β-diketonate moieties. Figure 8 shows the optical absorption spectra of the electro and photo active solvated Eu(dmh)$_3$phen complex with pH = 7.0 for the molar concentration of 10^{-3}mol/L in various basic and acidic solvents [10].

The absorption spectra of solvated Eu(dmh)$_3$phen exhibits two absorption peaks, one at 249nm and other in the range of 289-330 nm, which may be attributed to the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ optical transitions of the Eu^{3+} ion and β-diketonate moieties, respectively. Intense absorption peaks are reported for the 10^{-3} M solution. Strong absorption peak at 289 nm, 295 nm, 307 nm and 330nm can be observed in UV-vis spectra of Eu(dmh)$_3$phen in chloroform, THF, toluene and acetic acid, which may be due to $n \rightarrow \pi^*$ optical transition. A weak shoulder was accompanied at 249 nm corresponding to $n \rightarrow \pi^*$ transition for all the organic solvents considered in the present study. The optical densities of the excited molecules in THF and toulene were found to be greater as compared to that of in acetic acid, indicating little decomposition of the ligand in acidic conditions [11]. Hypsochromic shift - a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a shorter wavelength (higher frequency) was observed in the optical absorption spectra of Eu(dmh)$_3$phen, when the solvent is changed from acidic to basic media. This effect is also commonly called a blue shift because the blue colour in the visible spectrum has a shorter wavelength than most other colors. Comparative graph of π- π*and n – π* transitions in absorption spectra of Eu(dmh)$_3$phen complex in different solvents is shown in Figure 9.

3.4. X-Ray Diffraction

Figure 10 shows the diffractogram of Eu(dmh)$_3$phen and displays many strong, sharp diffraction peaks inferring the crystalline nature of the synthesized complex . 100% relative intensity corresponds to d-value of 9.82 A^0 at interplanar distance of 8.99A^0.

3.5. Scanning Electron Microscopy (SEM)

The synthesized Eu(TTA)$_3$bipy complex was analyzed with SEM for topological investigations and the digital images for different resolutions are shown in Figure 11. The obtained micrograph demonstrates the agglomeration of the particles with various grain size. The digital images illustrates that the complex exhibits rod like surface morphology having dimensions in micrometer scale and have crystalline nature as displayed in Figure 11(a, b, c). Thus the data from XRD resembles with the SEM analysis, proving crystallinity of the complex.

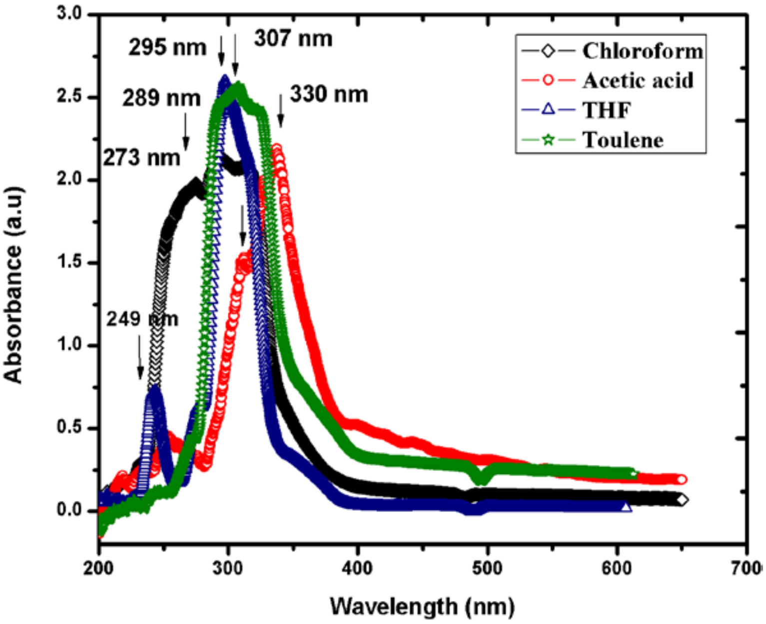


Figure 8. UV-vis spectra of Eu(dmh)$_3$phen in various solvents

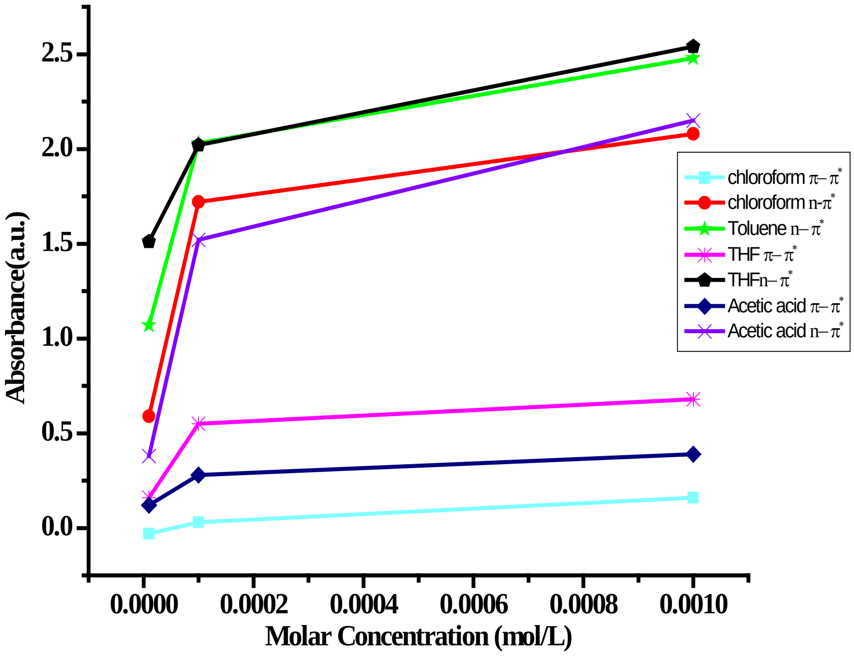


Figure 9. Comparative graph of π- π*and n – π* transitions in absorption spectra of Eu(dmh)$_3$phen complex in different solvents

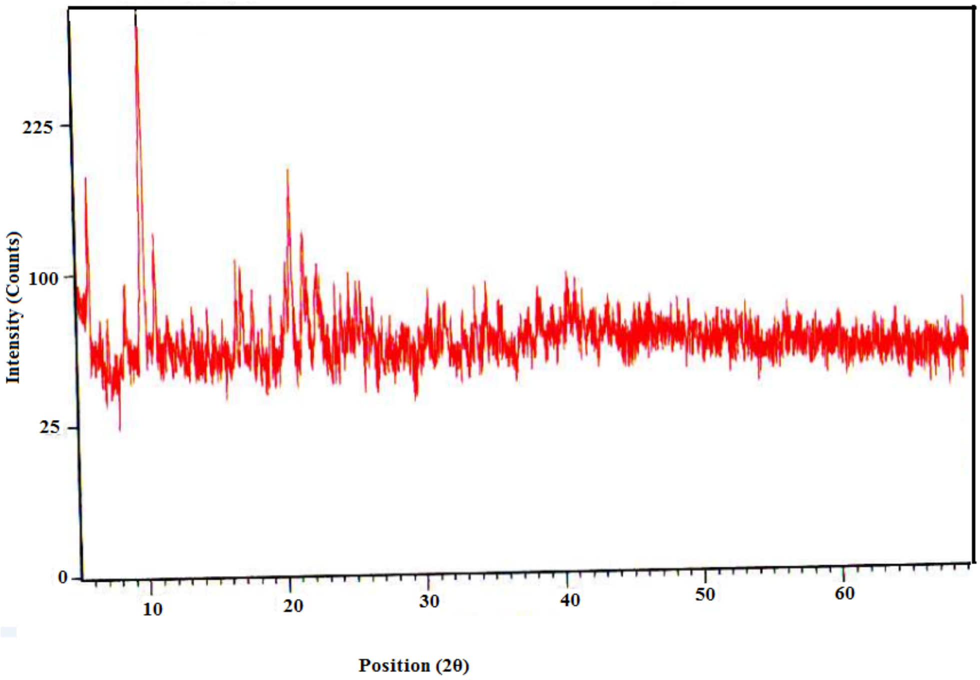
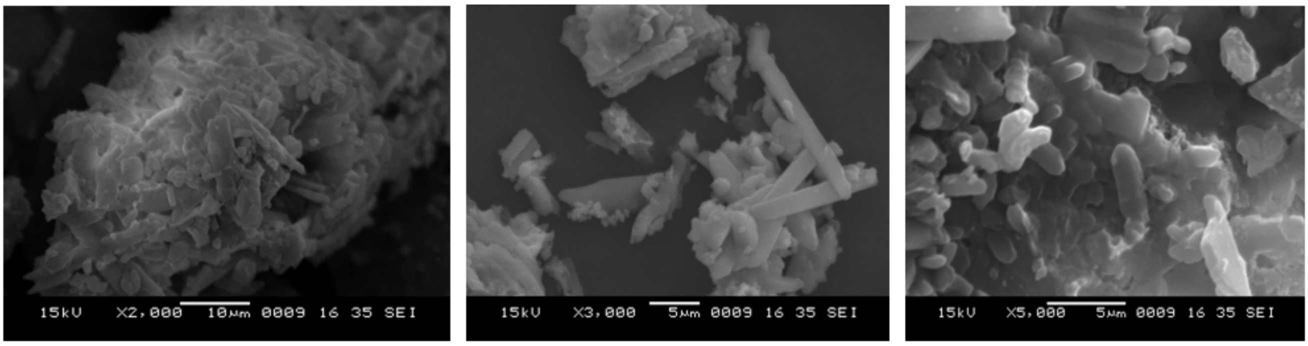


Figure 10. Diffractogram of Eu(dmh)$_3$phen at pH=7.0



(a) (b) (c)

Figure 11. Digital micrographs of Eu(dmh)$_3$phen complex at pH =7.0

3.6. Fourier Transform Infrared (FT-IR) Spectra

The FT-IR spectrum of Eu(dmh)$_3$phen samples measured on KBr pellets in a Perkin Elmer-Spectrum Fourier transform infrared (FT-IR) spectrometer with KBr beam splitters and a resolution of 20cm^{-1} is shown in Figure 12. Spectrum shown here is raw data, without any further correction (smoothing, background). In the case of the polycrystalline samples, scattering due to crystallinity is responsible for the broad background with some asymmetric peaks. Broad background with some asymmetric peaks were observed below 450 cm^{-1}, which may be due to scattering of crystalline nature of the phosphor and hence not recorded.

The absorption bands in the finger print region (1600-1350 cm^{-1}) are generally due to intra molecular phenomena, and are highly specific for each material. They predicts aromatic ring stretching, revealing the presence of C=C group. The aromatic C-H vibration stretch appears at 2800-3000cm^{-1}. The strong and considerable peak at 3146 cm^{-1} predicts the presence of ammonium ion in the complex [12,13]. The aromatic C-C bands emerged about 1500 cm^{-1}. The peak 1965 cm^{-1} owes to the carbonyl group can be observed in the FTIR-spectrum of Eu(dmh)$_3$phen. Strong peaks between 1600-1400 cm^{-1} may be due to the presence of C=N group. The peaks between 700 – 1300 cm^{-1} is indicative of skeletal C-C vibrations. These results confirm the formation of the desired complex and the presence of dmh and phen in the synthesized Eu- β-diketonate Eu(dmh)$_3$phen organic hybrid complex.

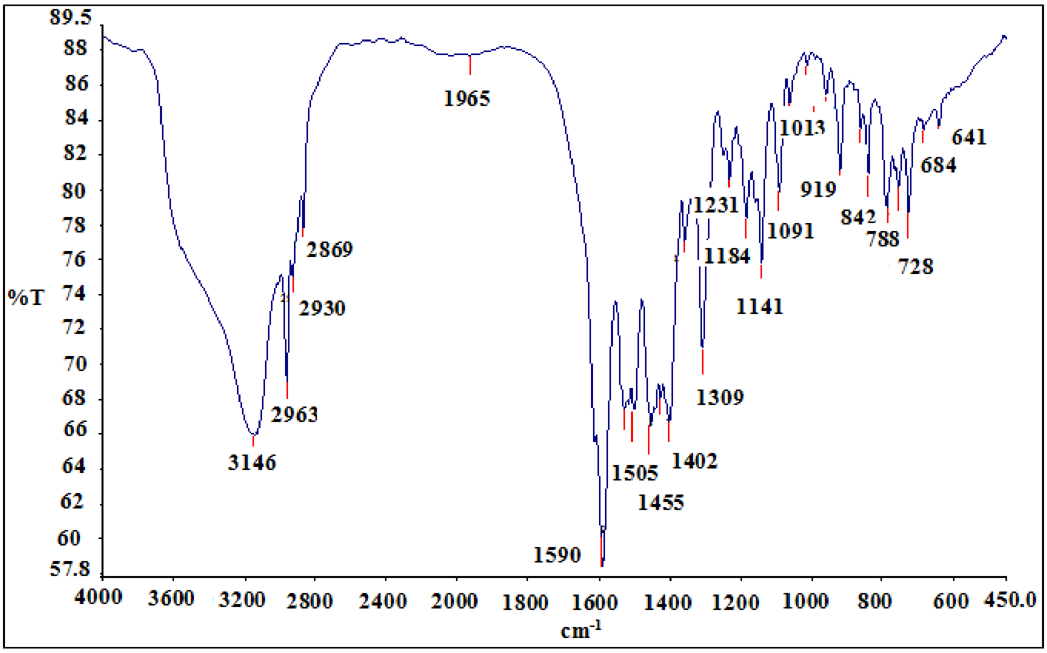


Figure 12. FTIR Spectrum of Eu(dmh)$_3$phen for pH=7.0

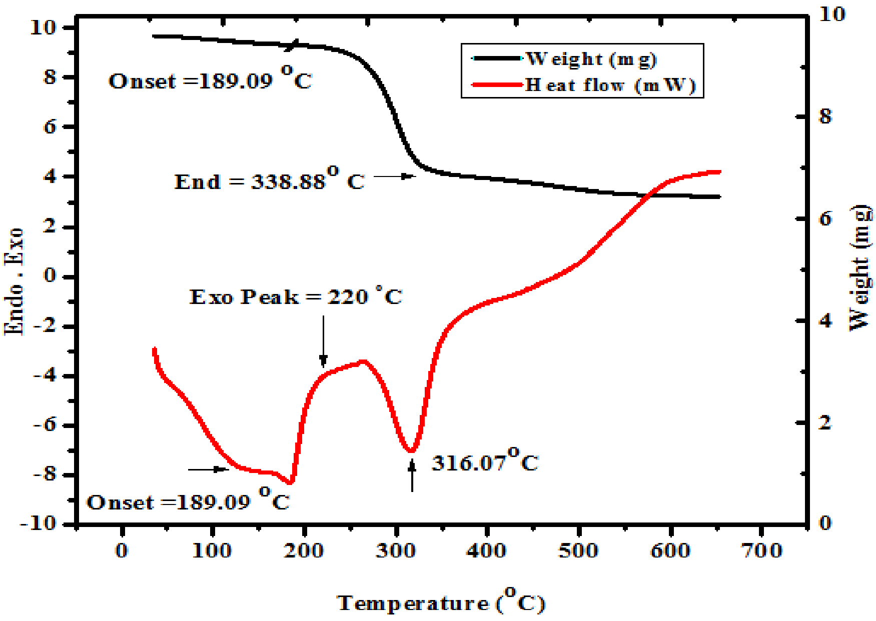


Figure 13. TGA/DTA curve of Eu(dmh)$_3$phen at pH=7.0

3.7. Thermo Gravimetric and Differential Thermal Analysis (TGA/DTA)

To elucidate the thermal properties of Eu(dmh)$_3$phen complex, a TGA/DTA analysis was carried out. The results so obtained are depicted in the thermogram shown in Figure 13. The thermogram revealed no significant loss in the weight of sample until the temperature reached 189.09°C which is denoted as the onset point. Beyond the onset temperature a small decrease in the weight of sample started from 220°C which can be attributed as the melting point of the complex upto the end point temperature 338.88°C. No further loss of weight of the synthesized complex is seen from the TGA data. DTA curve of the complex shows two endothermic peaks at 189.09°C and 316.07°C resulting in the distortion of water molecules and evaporation of residual moisture from the surface of the complex. The exothermic peak at 220°C corresponds to the decomposition process of the residual organic materials. No further exothermic peak is found in the DTA results giving strong thermal stability to the complex which is very important for the fabrication of OLED devices, displays and solid state lighting.

4. Conclusions

Volatile europium β-diketonate Eu(dmh)$_3$phen (Eu: Europium chloride, 2,6-Dimethyl-3,5-heptanedione, 1,10 Phenanthroline)europium(III)complex for different pH values, ranging between 8.0 and 6.0 were synthesized by precipitation method maintaining stichiometric ratio. The effect of pH value on the characteristic photoluminescence spectra (PL) was studied for the synthesized complexes. The UV-vis absorption spectra of solvated Eu(dmh)$_3$phen exhibits two absorption peaks, one at 249nm and other in the range of 289-330 nm, which may be attributed to the $\pi\rightarrow\pi^*$ and the $n\rightarrow\pi^*$ optical transitions of the Eu^{3+} ion and β-diketonate moieties, respectively. Optical densities of the excited molecules in chloroform, THF and toulene were greater as compared to that of in acetic acid, indicating little decomposition of the ligand in acidic conditions. Eu(dmh)$_3$phen exhibits red intense emission at 613 nm with a sharp spectral bandwidth of 5 nm when excited at a wavelength of 372nm with narrow full width at half maxima (FWHM),due to f–f transitions of the central Eu^{3+} ion. Among all synthesized complexes, the complex with pH 7.0 showed maximum peak intensity. However of pH, the position of the emission spectra, corresponding to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition remained at 613 nm as the β-diketonate ligand (dmh) used is same in all complexes. Among all the synthesized complexes, the complex with pH 7.0 showed maximum peak intensity, which may be due to superior intermolecular energy transfer between Eu(III) and β-diketonate ligand. The complex exhibiting maximum intensity was assessed for structural, thermal and luminescence behavior in various solvents. X-ray diffractogram reveals its crystalline nature with 100% relative intensity corresponding to d-value of 9.82A^0 at interplanar distance of 8.99A^0. The calculated grain size of particle at 100% relative intensity was found to be 2.76 nm. FTIR spectra confirms the complete formation of the complex with and the presence of dmh and phen structure in the metal complex. TGA/DTA curve of Eu(dmh)$_3$phen complex reveals that the complex has an ability to maintain its properties unchanged upon heating till 189.09°C. With further increase in temperature, decomposition of the sample was observed. End peak at 338.88°C indicates the final temperature at which the cumulative weight change first reaches its maximum value, corresponding to the complete reaction. Hypsochromic shift was observed in the optical absorption spectra of Eu(dmh)$_3$phen, when the solvent is changed from basic to acidic media. The effect of change in pH value of the complex on the characteristic photoluminescence spectra (PL) was studied for the synthesized complexes. The synthesized Eu complex exhibits synergistic effect in which the ligand could absorb UV light and transfer energy from Eu(III), leading to enhancement of intensity, suggesting a potential application of the complexes as red emitting materials in OLEDs, display devices and solid state lighting.

Acknowledgements

One of the authors (NTK) wishes to thank Rashtrasanth Tukadoji Maharaj Nagpur University for providing financial support to carry out the synthesis and characterization of the synthesized Eu(TTA)$_3$bipy complex under University Research Project Scheme (Sanction letter No. Dev. 2140 dated 16 th Nov. 2015).

References

[1] N. Thejo Kalyani, S.J. Dhoble, “Importance of Eco-friendly OLED Lighting,” *Defect and Diffusion Forum*, Trans Tech Publications, Switzerland 357, (2014), 1-27.

[2] N A.H. Male, Oleg V.Salata, Victor Christou, “Enhanced electroluminescent efficiency from spin-coated europium(III) organic light-emitting device”, *Synth metals* 12, (2002) 7-10.

[3] H Liang, Fang Xie, “Photoluminescence study of a europium (III) complex containing 1, 5-styrylacetylacetone ligands”, *Spectrhema Acta Part A*, 77, (2010) 348-350.

[4] L Zhang, Bin Li, “A series of Eu(III) emitters with a novel triphenylamine-derived beta-diketone ligand,” *J Lumin* 129(11), (2009) 1304-1308.

[5] H Liang, Fang Xie, Xiaojun Ren, Yifa Chen, Biao Chen, Fuquan Guo. “Temperature dependent luminescence of a europium complex incorporated in poly(methyl methacrylate”, *Spectrochem Acta Part A*: *Mol Bimol Spectro;* 116, (2013) 317-320.

[6] Melby, L. R. Rose, N. J. Abramson, E. Caris, J. C. “Synthesis and fluorescence of some trivalent lanthanide complexes,” *J. Am. Chem. Soc*., 86, 5117, (1964).

[7] S Linfang, Li Yanwei, Cao Huaru, Guan Ying, Ma Yongchun, “Synthesis of novel europium complexes and their photoluminescence properties”, *J. Rare Earths*, 30(1), (2012) 17-20.

[8] M. Fernandes, V. de Zea Bermudez, R. A. Sa´ Ferreira, L. D. Carlos, A. Charas, J. Morgado M. M. Silva,M. J. Smith,” Highly Photostable Luminescent Poly(ε-caprolactone)siloxane Biohybrids Doped with Europium Complexes,” *Chem. Mater*., 19(16), (2007). 3892-3901.

[9] N. ThejoKalyani, S.J.Dhoble, “Novel materials for fabrication and encapsulation of OLEDs” *Ren.Sus.Ene. Rev*. 44, (2015) 319-347.

[10] N.Thejo Kalyani, S.J. Dhoble and R.B. Pode. “Optical Properties of Eu$_x$Re$_{(1-x)}$(TTA)$_3$Phen Organic Complexes in Different Solvents” *J. Kor Phys Soc*. 57(4), (2010) 746-751.

[11] K. E, Fukuda .T, Kato .S, Honda .Z, Kamata. N. “pH and concentration dependence of luminescent characteristics in glass-

encapsulated Eu-complex”, *J Sol-Gel Sci Technol*, 50(3), (2009) 409-414.

[12] J.P.Coates, Á Review of sampling Methods For Infrared spectroscopy’in Applied Spectroscopy: a compact Reference for practitioners, eds. J.Workman A.W.Sprinsteen, Academic press New York, (1998) 49-91.

[13] J.P.Coates, ‘Ínto the unknown: the first in the series’, Spectroscopy, 11(5), (1996) 32-39.