

Synthesis and optoelectronic properties of three Eu(III)-dipicolinate complexes based on α -picolinic acid, 2-aminopyridine and 2-hydroxypyridine as secondary ligands

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Abstract We synthesized some Eu(III) complexes $\{[\text{Eu}(\text{dpa})(\alpha\text{-pc})(\text{CH}_3\text{OH})]\cdot 2\text{CH}_3\text{OH}\}$ (**1**), $\{[\text{Eu}(\text{dpa})(2\text{-ap})(\text{CH}_3\text{OH})]\cdot 2\text{CH}_3\text{OH}\}$ (**2**) and $\{[\text{Eu}(\text{dpa})(2\text{-hp})(\text{CH}_3\text{OH})]\cdot 2\text{CH}_3\text{OH}\}$ (**3**) [dpa = dipicolinic acid; α -pc = α -picolinic acid; 2-ap = 2-aminopyridine; 2-hp = 2-hydroxypyridine]. The structural characterization of the complexes were studied by elemental analysis, FTIR spectroscopy, SEM and powder X-ray diffraction studies (XRD) where the elemental analysis and FTIR results indicate the coordination of ligands with the Eu(III) ion. The X-ray diffraction patterns show the crystalline nature of complex (**1**) and amorphous nature of complexes (**2**) and (**3**) and the SEM micrographs also depict different morphologies of the complexes. The thermal properties of the synthesized complexes were studied by TG–DTA technique which indicates good thermal stability of the synthesized complexes. The optical properties were studied using Ultraviolet visible spectroscopy (UV–Vis) and Photoluminescence studies (PL) where photoluminescence measurements indicate that all the three complexes exhibit the characteristic emission bands of Eu(III) ion corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0\text{--}4$) transitions and it has also been observed that the intensity of emission is influenced by the effect of different secondary ligands. The most intense transition and the long radiative lifetime, quantum efficiency of the ${}^5\text{D}_0$ excited level of Eu(III) ion observed for the complex (**2**) with 2-ap as secondary ligand reflects the good sensitizing ability of ligand 2-ap. The optical properties of the obtained complexes can be well utilized for

preparation of rare earth luminescent materials and fluorescence probes.

1 Introduction

The lanthanide complexes attract intense attention due to their superior optical properties and wide variety of potential applications i.e. biomedical assays and imaging, luminescence devices, ionic conductors and sensors [1–3]. The lanthanide based compounds are widely used as luminescent materials due to their extremely narrow emission bands with relatively long excited state lifetimes resulting from intraconfigurational 4f–4f transitions [4–6]. Due to the low molar extinction coefficient of the laporte forbidden f–f transition, the direct photoexcitation of the lanthanide ions becomes difficult [7, 8]. This can be overcome by the introduction of antenna which provides an alternative pathway for energy transfer and enriches the lanthanide emitting level [9–11]. These ligands transfer energy from the excited triplet state of ligand to the lowest emitting level of the lanthanide ion. The lanthanide ion then relaxes to ground state by the emission of energy [12–18]. Among the organic ligands, the pyridine derivatives are important because these can form diversity of coordinating structures including coordination polymers. The pyridine carboxylates act as good candidates due to existence of N and O mixed donor atoms which can coordinate to the metal ion in a bidentate chelating, bidentate bridging and unidentate manner [19, 20]. 2,6-pyridinedicarboxylic acid and α -picolinic acid have been found as promising ligands due to the stability of their Ln(III) complexes, strong fluorescence intensity with long excitation lifetimes [21]. The ligand 2,6-pyridinedicarboxylic acid is water soluble, commercially available having nitrogen and

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oxygen atoms to coordinate with the metal ion. Aminopyridine ligands also act as useful chelating agents for inorganic and organometallic applications and their derivatives can coordinate to the metal ions in a monodentate fashion through the N atom of the ring, however there are several works reported where the amino group also participates in coordination to the metal ion [22–24]. The hydroxypyridine ligands can also coordinate effectively to the metal ion through the N and O donor atoms and are expected to show good luminescent properties.

This article reports the synthesis of three europium complexes with dipicolinic acid (dpa) as a primary ligand and α -picolinic acid (α -pc), 2-aminopyridine (2-ap) and 2-hydroxypyridine (2-hp) as secondary ligands. Their structural, thermal and optical properties have also been studied.

2 Experimental

2.1 Materials and measurements

EuCl₃(anh), dipicolinic acid (dpa, 99 %), α -picolinic acid (α -pc, 99 %), 2-aminopyridine (2-ap, 99 %), 2-hydroxypyridine (2-hp, 97 %) were procured from Sigma Aldrich and used as received without any further purifications. Methanol (CH₃OH, 99.5 %) of analytical grade was used as such without any further purification. The elemental analysis was performed using GmbH Vario EL CHNS Elemental Analyzer. Fourier Transform Infra Red (FTIR) spectra were acquired on a Perkin Elmer Spectrometer in the range of 4,000–400 cm⁻¹. Ultraviolet absorption spectra were recorded by Shimadzu UV-1601 spectrometer. Photoluminescence measurements were done on a Perkin Elmer LS55 fluorescence spectrophotometer equipped with a 150 W Xenon lamp as the excitation source and the photoluminescence decay measurements were performed on Horiba Jobin–Yvon FL-3-22 spectrofluorometer. Thermogravimetry (TG–DTA) data was obtained on Perkin Elmer diamond thermogravimetric analyzer at the heating rate of 10 °C/min under nitrogen atmosphere in the crucibles of Al₂O₃. The X-ray diffraction (XRD) measurements of the powdered samples were carried out by Bruker D8 diffractometer (40 mA–40 kV) using monochromatic Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) over the 2 θ range of 5–80°. The morphology of the synthesized complexes was studied by Scanning Electron Microscopy (SEM) using Carl Zeiss Scanning Electron Microscope.

2.2 Synthesis of europium complexes

The complex (1) was synthesized by taking dpa (1 mmol, 0.1679 g) and α -pc (1 mmol, 0.1231 g) in anhydrous

methanol solution (10 ml) and the reaction mixture was stirred for half an hour. The pH of the solution was adjusted between 6 and 7 with dilute NaOH solution (1 mol L⁻¹). EuCl₃ (1 mmol, 0.2582 g) solution was added slowly dropwise to the ligand solution under stirring and the resulting solution was refluxed for 3–4 h at 70 °C. The white coloured precipitates were filtered, washed with methanol and then dried in a vacuum oven. The complex (2) was synthesized using EuCl₃ (1 mmol, 0.2582 g), dpa (1 mmol, 0.1679 g) and 2-ap (1 mmol, 0.094 g) and complex (3) by taking EuCl₃ (1 mmol, 0.2582 g), dpa (1 mmol, 0.1231 g) and 2-hp (1 mmol, 0.0951 g) following the same procedure as mentioned above.

3 Results and discussion

3.1 Elemental analysis results and solubility of complexes

The contents of C, H, N in the complexes were determined by elemental analysis and the content of Eu was determined by the volumetric titration with EDTA. The results are listed in Table 1. which show a good agreement between the experimental and calculated values. The complexes were found to be soluble in ethanol and water.

3.2 Infrared spectroscopy (FT-IR)

The infrared absorption spectra of the ligands and the complexes are shown in Fig. 1a–d and Fig. 2e–g. The FTIR spectra of the ligands dpa, α -pc and complex (1) showed that the absence of $\nu(\text{C}=\text{O})$ stretching vibration at 1,700 cm⁻¹ in dpa and at 1,605 cm⁻¹ in α -pc suggested the coordination of COO⁻ group of the ligand with rare earth ion. The mode of coordination of COO⁻ group can be attributed to the difference between asymmetric and symmetric vibrations respectively. This difference was found to be 228 cm⁻¹ in the complex which was larger than the ligand α -pc (152 cm⁻¹) and smaller than that of the ligand dpa (242 cm⁻¹) which revealed that the carboxylate group in the ligand dpa is coordinated in a bidentate chelating mode and the ligand α -pc in a unidentate manner. The complex (1) also showed a wide and strong band at 3,392 cm⁻¹ due to $\nu(\text{O}-\text{H})$ stretching vibration. For complex (2), the $\nu(\text{C}=\text{O})$ stretching vibration of COO⁻ group of ligand dpa disappeared and it shifted downward to 1,602 cm⁻¹ in the complex which suggested the coordination of carboxylate group of ligand dpa to the rare earth ion through oxygen atom. The $\nu(\text{N}-\text{H})$ stretching vibration peak at 3,397 cm⁻¹ in ligand 2-ap also migrated to 3,290 cm⁻¹ in the complex which revealed the coordination of N atom of NH₂ group of ligand 2-ap to the rare earth

Table 1 Elemental analysis results of complexes^a

Complexes	Experimental values (calculated values) %			
	C	H	N	Eu
{[Eu(dpa)(α -pc)(CH ₃ OH)]·2CH ₃ OH}	45.75 (45.68)	7.04 (6.9)	4.18 (4.10)	22.32 (22.20)
{[Eu(dpa)(2-ap)(CH ₃ OH)]·2CH ₃ OH}	43.32 (43.21)	6.82 (6.76)	6.94 (6.87)	24.88 (24.80)
{[Eu(dpa)(2-hp)(CH ₃ OH)]·2CH ₃ OH}	43.24 (43.14)	6.66 (6.58)	4.65 (4.57)	24.92 (24.80)

^a The values in brackets are the calculated values

ion. Also, the $\nu(\text{C}=\text{N})$ stretching vibration at $1,487\text{ cm}^{-1}$ in ligand 2-ap shifted to $1,438\text{ cm}^{-1}$ in complex (2) indicating the coordination of N atom to the rare earth ion. In complex (3), the $\nu(\text{C}=\text{O})$ stretching vibration at $1,700\text{ cm}^{-1}$ in dpa disappeared and a new band appeared at $1,606\text{ cm}^{-1}$, the $\nu(\text{O}-\text{H})$ stretching vibration at $2,981\text{ cm}^{-1}$

in ligand 2-hp also shifted downward in the complex and appeared as a wide band at $2,924\text{ cm}^{-1}$. These downward shifts indicated the coordination of N and O atom of the ligand 2-hp to the rare earth ion. In all the three complexes, the $\text{Eu} \leftarrow \text{N}$ bond stretching frequency appeared at 553, 593 and 579 cm^{-1} and the $\text{Eu} \leftarrow \text{O}$ bond appeared at 424, 424 and 433 cm^{-1} for complexes (1), (2) and (3) respectively. These vibrations confirmed the formation of complexes as these could not be observed in the ligand FTIR spectra.

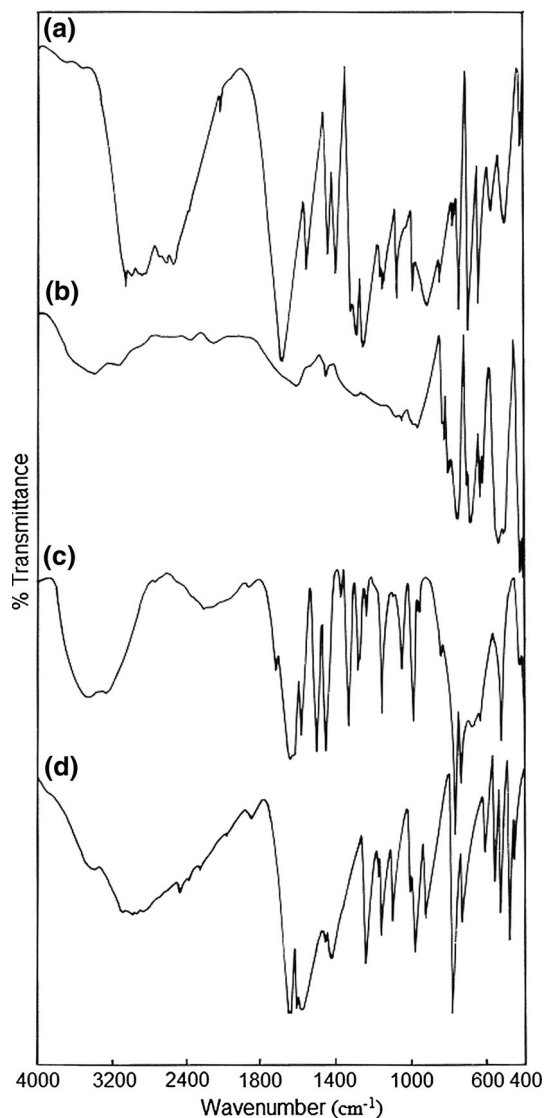


Fig. 1 FT-IR spectra of (a) dpa, (b) α -pc, (c) 2-ap, (d) 2-hp

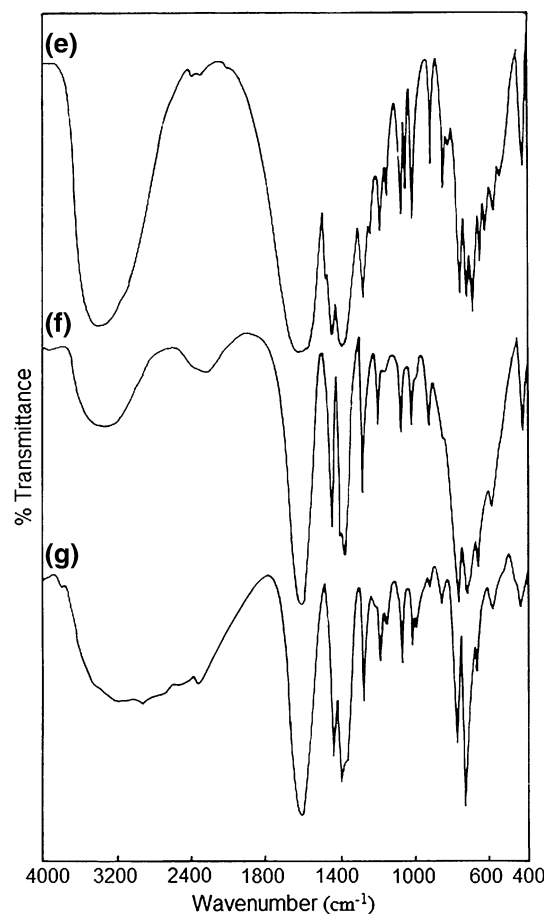


Fig. 2 FT-IR spectra of (e) {[Eu(dpa)(α -pc)(CH₃OH)]·2CH₃OH}, (f) {[Eu(dpa)(2-ap)(CH₃OH)]·2CH₃OH}, (g) {[Eu(dpa)(2-hp)(CH₃OH)]·2CH₃OH}

3.3 Thermogravimetric analysis (TG–DTA)

The TG–DTA curves of the complexes with heating rate of 10 °C/min in N₂ atmosphere using α -Al₂O₃ as reference material are presented in Fig. 3a–c. As shown in Fig. 3a for complex (1), the mass loss observed in the first step of decomposition corresponded to the loss of solvent molecules and showed an endothermic peak at 89 °C. The second degradation occurred due to the loss of coordinated dpa and α -pc ligands and showed an endothermic peak at 469 °C. The thermal degradation continued and finally the complex decomposed through an endothermic effect at 578 °C. In the complex (2) as shown in Fig. 3b, the solvent loss appeared as an endothermic peak at 61 °C accompanied by the loss of coordinated 2-ap ligand through an endothermic effect at 148 °C. The complex finally decomposed through an endothermic peak at 486 °C. Finally, the complex (3) showed three endothermic peaks at 79, 196 and 481 °C due to the solvent loss, release of coordinated 2-hp ligand and final decomposition of the complex respectively.

3.4 UV–Vis absorption studies

The UV–Vis absorption spectra of the ligands and the complexes are recorded in Fig. 4a–c. The ligands dpa and α -pc showed absorption bands at 265 and 269 nm respectively, which could be assigned to $\pi \rightarrow \pi^*$ transitions of the conjugated system of aromatic ring as shown in the

Fig. 4a. In the complex (1), the absorption band observed at 267 nm was due to the overlap of absorption bands of ligands dpa and α -pc respectively and the intensity of this band was higher than that of dpa and lower than α -pc ligand. These observations suggested the formation of new compound by the coordination of ligands dpa and α -pc to the Eu(III) ion. As shown in the Fig. 4b, the ligand 2-ap exhibited mainly two absorption bands at 227 and 259 nm due to $\pi \rightarrow \pi^*$ transitions of conjugated aromatic ring. The absorption bands at 227 and 267 nm in the complex (2) showed the red shift due to the expanded π -conjugated system resulting from the coordination of the ligands 2-ap and dpa to the Eu(III) ion. The band at 227 nm remains unchanged in the complex, however there was change in the intensity of absorption in the complex. In Fig. 4c, two absorption bands at 226 and 300 nm were observed for ligand 2-hp, which were attributed to $\pi \rightarrow \pi^*$ transitions of the ligand and compared with the absorption bands of the ligands 2-hp and dpa, the complex (3) showed red shift in the absorption bands observed at 241 and 304 nm respectively. The intensity of absorption also got influenced after the coordination of Eu(III) ion with the ligands. These results suggested the coordination of Eu(III) ions with the ligands.

3.5 Photoluminescent studies

The room temperature emission spectrum of europium complexes as shown in Fig. 5 showed strong characteristic

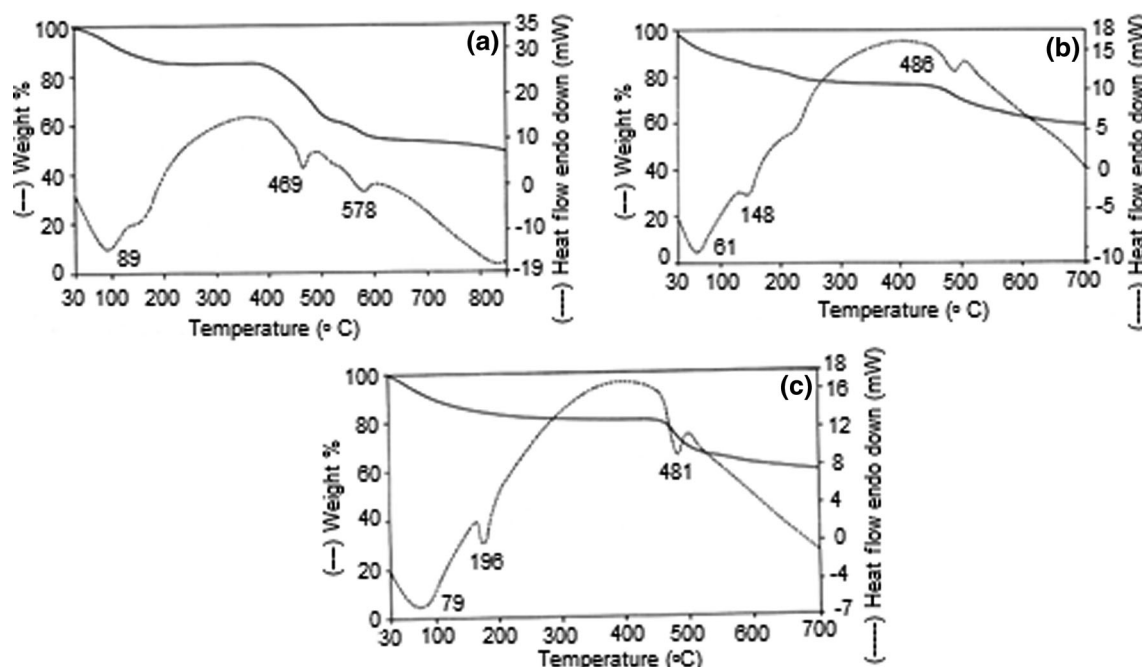


Fig. 3 TG–DTA curves of **a** $\{[Eu(dpa)(\alpha\text{-pc})(CH_3OH)] \cdot 2CH_3OH\}$, **b** $\{[Eu(dpa)(2\text{-ap})(CH_3OH)] \cdot 2CH_3OH\}$, **c** $\{[Eu(dpa)(2\text{-hp})(CH_3OH)] \cdot 2CH_3OH\}$

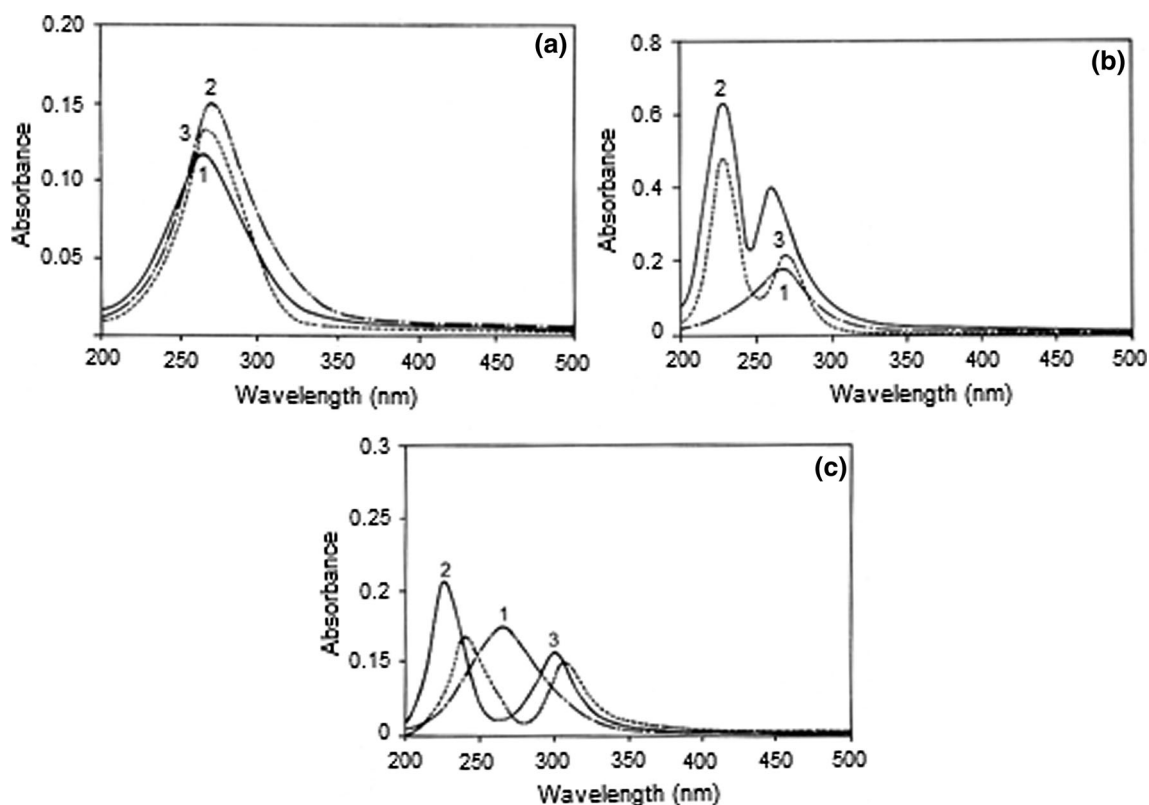


Fig. 4 UV-Vis absorption spectra: **a** dpa (1), α -pc (2), $\{[Eu(dpa)(\alpha\text{-pc})(CH_3OH)] \cdot 2CH_3OH\}$ (3) **b** dpa (1), 2-ap (2), $\{[Eu(dpa)(2\text{-ap})(CH_3OH)] \cdot 2CH_3OH\}$ (3) **c** dpa (1), 2-hp (2), $\{[Eu(dpa)(2\text{-hp})(CH_3OH)] \cdot 2CH_3OH\}$ (3)

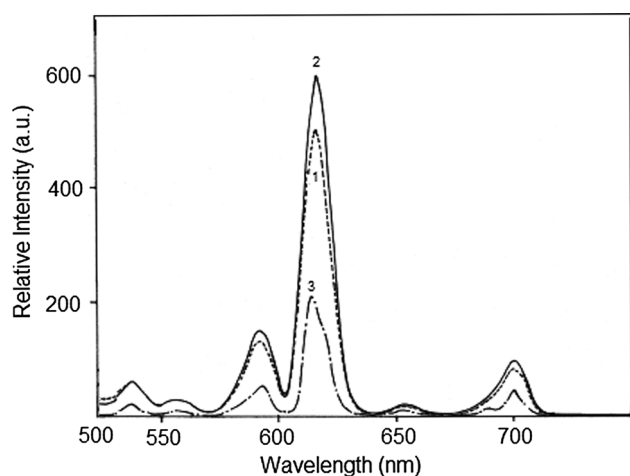


Fig. 5 Luminescent emission spectra of (1) $\{[Eu(dpa)(\alpha\text{-pc})(CH_3OH)] \cdot 2CH_3OH\}$, (2) $\{[Eu(dpa)(2\text{-ap})(CH_3OH)] \cdot 2CH_3OH\}$ and (3) $\{[Eu(dpa)(2\text{-hp})(CH_3OH)] \cdot 2CH_3OH\}$

emission bands of Eu(III) ions in the visible region, which were attributed to the electronic transitions from the excited 5D_0 level to the ground 7F_J ($J = 0-4$) levels of Eu(III) ion. The emission bands at 580 nm ($^5D_0 \rightarrow ^7F_0$) and 650 nm ($^5D_0 \rightarrow ^7F_3$) were very weak since their corresponding transitions were forbidden both in magnetic and

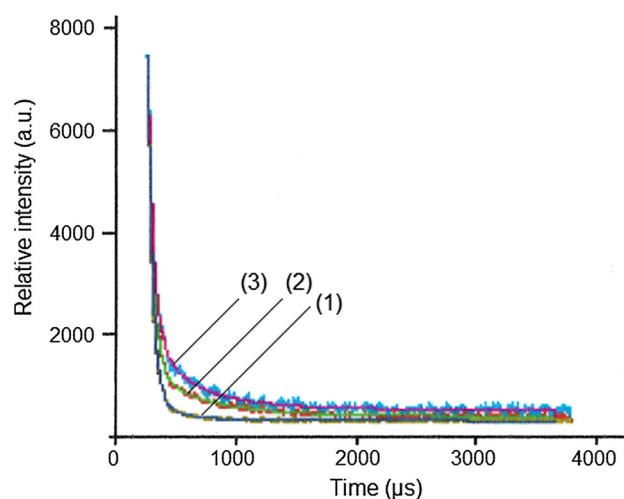


Fig. 6 Photoluminescent lifetime decay measurement of (1) $\{[Eu(dpa)(\alpha\text{-pc})(CH_3OH)] \cdot 2CH_3OH\}$, (2) $\{[Eu(dpa)(2\text{-ap})(CH_3OH)] \cdot 2CH_3OH\}$ and (3) $\{[Eu(dpa)(2\text{-hp})(CH_3OH)] \cdot 2CH_3OH\}$

electric dipole fields. The luminescent intensity of ($^5D_0 \rightarrow ^7F_1$) transition at 592 nm was relatively strong as this is magnetic transition which is independent of the coordinating environment of Eu(III) ion. The strongest emission observed at 615 nm ($^5D_0 \rightarrow ^7F_2$) is an induced

electric dipole transition which is hypersensitive transition and is sensitive to the coordinating environment of Eu(III) ion. This transition is responsible for the brilliant red emission of europium complexes in the visible region. As shown in Fig. 5, the relative luminescent intensity of ${}^5D_0 \rightarrow {}^7F_2$ transition was strongest in complex (2) based on 2-ap as secondary ligand, however the weakest luminescent intensity was observed in complex (3). This could be explained by the non-radiative deactivation of energy of excited state as a result of their interaction with high

frequency oscillators O–H group which act as efficient quencher of lanthanide ion luminescence in 2-hp ligand. These results showed that –NH₂ group in 2-ap ligand can strongly sensitize the luminescence of Eu(III) ion as compared to the 2-pc and 2-hp ligands.

The luminescence decay curves of the complexes were obtained at 298 K by monitoring the ${}^5D_0 \rightarrow {}^7F_2$ transition (615 nm) and are shown in Fig. 6. The decay profiles are monoexponential function indicating the presence of a single chemical environment around Eu(III) ion. The lifetime values were found to be 725, 825 and 675 μ s for complexes (1), (2) and (3) respectively. The longest lifetime of complex (2) can be attributed to the efficient energy transfer and good sensitizing ability of 2-ap ligand while the shortest lifetime for complex (3) is related to the quenching effect of O–H oscillators in 2-hp ligand. According to the emission spectra and the lifetime of the Eu(III) excited state (5D_0), the emission quantum efficiency (η) can be determined which can be calculated as follows:

Table 2 Results of radiative rates (A_r), lifetime (τ) and quantum efficiency (η)

Complexes	A_r (s^{-1})	τ (μ s)	η (%)
{[Eu(dpa)(α -pc)(CH ₃ OH)]·2CH ₃ OH}	320.74	725	21.60
{[Eu(dpa)(2-ap)(CH ₃ OH)]·2CH ₃ OH}	330.95	825	27.30
{[Eu(dpa)(2-hp)(CH ₃ OH)]·2CH ₃ OH}	265.11	675	17.89

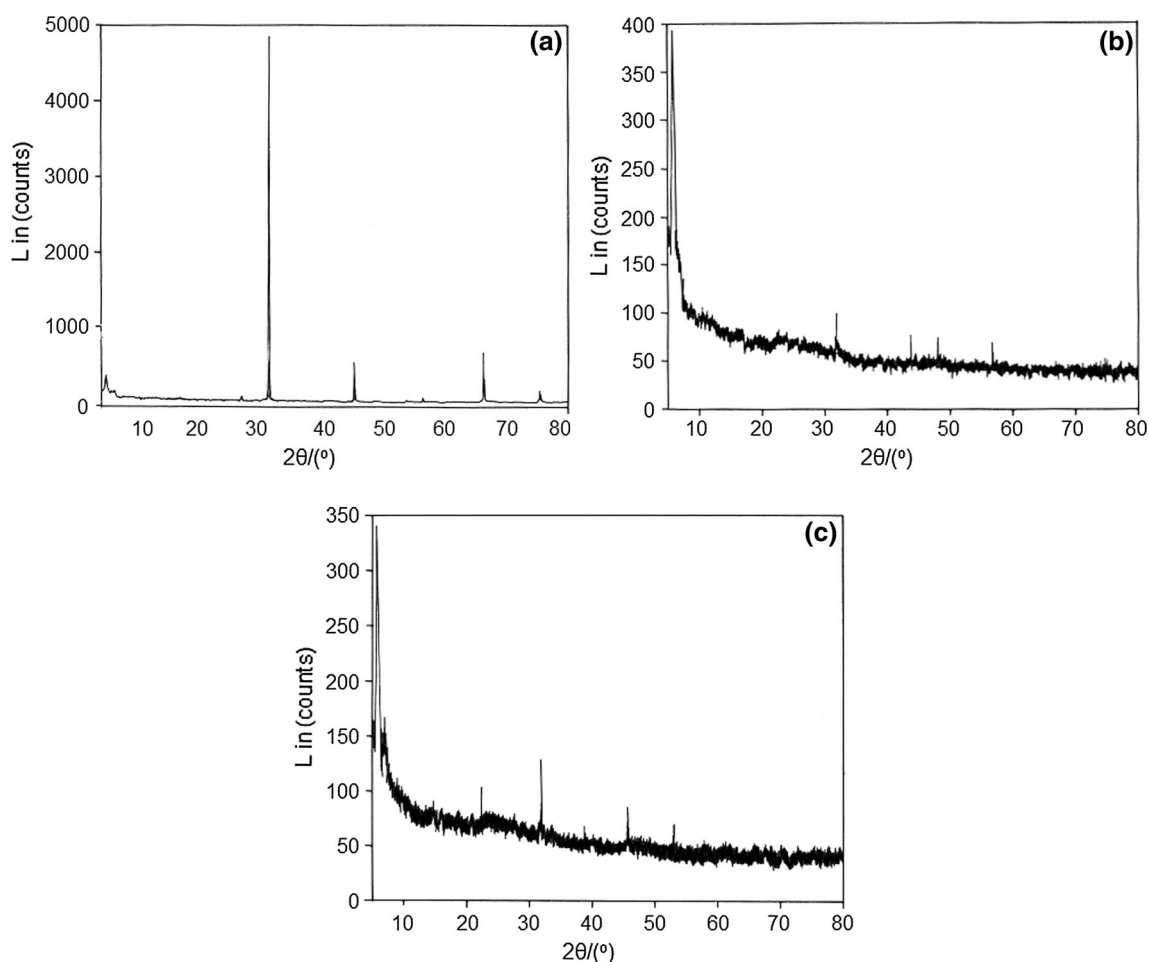


Fig. 7 X-ray diffraction spectra of **a** {[Eu(dpa)(α -pc)(CH₃OH)]·2CH₃OH}, **b** {[Eu(dpa)(2-ap)(CH₃OH)]·2CH₃OH} and **c** {[Eu(dpa)(2-hp)(CH₃OH)]·2CH₃OH}

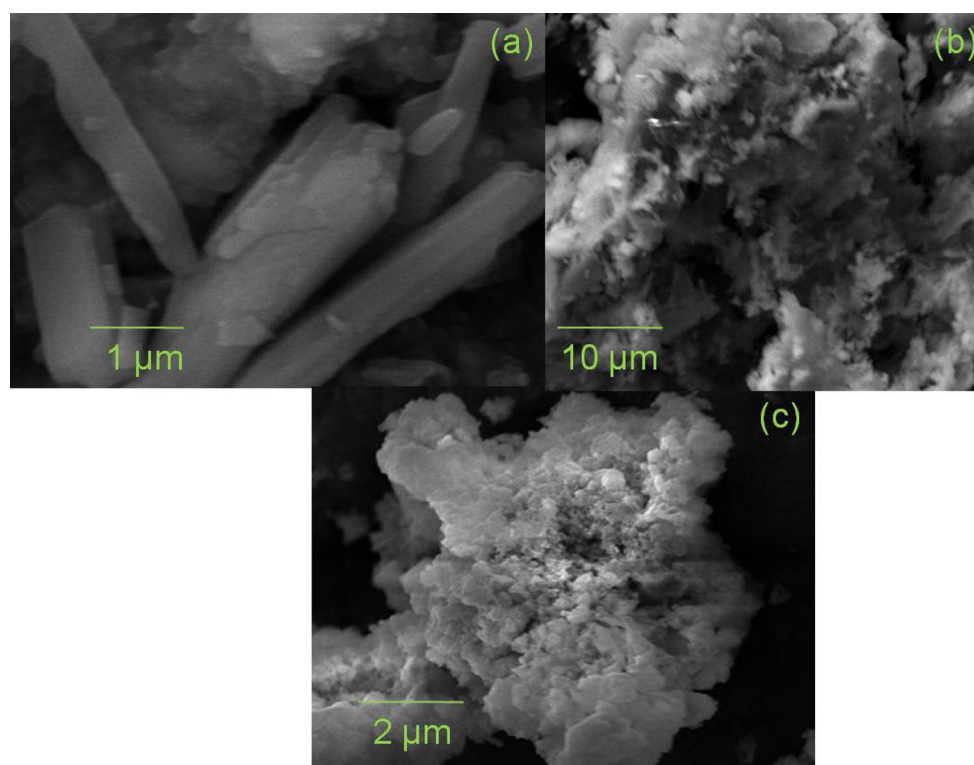


Fig. 8 SEM micrographs of **a**{[Eu(dpa)(α -pc)(CH₃OH)]·2CH₃OH}, **b**{[Eu(dpa)(2-p)(CH₃OH)]·2CH₃OH}, **c**{[Eu(dpa)(2-hp)(CH₃OH)]·2CH₃OH}

$$\eta = A_r / (A_r + A_{nr})$$

where A_r and A_{nr} are the radiative and non radiative transition rates respectively. A_r can be obtained by summing over the radiative rates A_{0J} for $^5D_0 \rightarrow ^7F_J$ transitions ($J = 0-4$) of Eu(III) ion.

$$A_r = \sum A_{0J} = A_{00} + A_{01} + A_{02} + A_{03} + A_{04}$$

The experimental coefficients A_{0J} can be calculated according to the following equation.

$$A_{0J} = A_{01} (I_{0J}/I_{01}) (v_{01}/v_{0J})$$

where A_{01} is Einstein coefficient of radiative emission between 5D_0 and 7F_1 energy levels of Eu(III) ion. Its value in vacuum can be taken as approximately 50 s^{-1} with an average index of refraction 'n' equals to 1.506 ($A_{01} = n^3 A_{01(\text{vac})}$). I_{0J} and I_{01} are the integrated intensities of $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) and $^5D_0 \rightarrow ^7F_1$ transitions of Eu(III) ion and v_{0J} , v_{01} represents the energy barrier of the emission bands of Eu(III), $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions [25, 26]. The lifetime value (τ), radiative rate (A_r) and non radiative rate (A_{nr}) are related by the following equation [27].

$$A_{\text{tot}} = 1/\tau = A_r + A_{nr}$$

On the basis of above calculations, the quantum efficiencies (η) of the complexes are determined and are shown in Table 2. The results reveal that the complex (2) shows high value of lifetime (825 μs) and quantum

efficiency (27.30 %) due to efficient energy transfer from the ligand 2-ap to Eu(III) ion whereas the complex (3) exhibits shortest lifetime owing to the possible quenching by -OH group present in the 2-hp ligand.

3.6 X-ray diffraction and morphological studies

The powder X-ray diffraction patterns of the complexes were recorded in a scanning range of 5–80° with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The complex (1) displayed very sharp and few intense peaks indicating the crystalline nature of complex as shown in Fig. 7a. The diffractograms shown in Fig. 7b, c included weaker diffraction peaks indicating the amorphous nature of the complexes (2) and (3). Figure 8a–c shows the SEM images of the obtained complexes and depicts the distinguishable morphologies of the complexes. The complex (1) showed rod like morphology while the complex (2) displayed agglomerated like structure. The complex (3) indicated sponge like structure containing aggregated particles.

4 Conclusions

In the present paper, three europium complexes based on dpa as primary ligand and α -pc, 2-ap and 2-hp as secondary ligands have been synthesized and characterized using

elemental analysis, FT-IR, TG-DTA, UV-Vis, PL, XRD and SEM. The elemental analysis and FTIR reveals the coordination of the ligands with the rare earth ion. The powder X-ray diffraction studies show the crystalline nature of complex (1) and amorphous nature of complex (2) and complex (3). The SEM micrographs display different morphologies of the obtained complexes. The complexes show the characteristic emission bands of Eu(III) ion in visible region at 580, 592, 615, 650 and 698 nm for $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions respectively. The optical properties of the complexes are influenced by the secondary ligands as studied by the photoluminescence spectra and decay measurements, where the complex (2) with 2-ap as secondary ligand exhibits strongest emission intensity and relatively longer luminescence lifetime, quantum efficiency as compared to the complex (1) and complex (3). The UV-Vis absorption studies show the remarkable changes in the absorption wavelength of complexes, thus indicating the formation of complexes by the coordination of ligands with Eu(III) ion. All the results conclude that the luminescent property of the complexes can be well utilized for the preparation of organic light emitting diodes and fluorescence probes.

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