

Eu³⁺, Yb³⁺ and Eu³⁺-Yb³⁺ Complexes with Salicylic Acid and 1,10-Phenanthroline: Synthesis, Photoluminescent Properties and Energy Transfer

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Abstract This paper reports the synthesis of mononuclear Eu³⁺, Yb³⁺ and binuclear Eu³⁺-Yb³⁺ complexes by solution technique, maintaining the stoichiometric ratios of salicylic acid (sal) and 1,10-phenanthroline (phen) as ligands and their structural, optical and morphological properties were demonstrated. The FTIR absorption spectra indicates that sal and phen are coordinated to the rare earth ion through the chemical bonds formed between oxygen and nitrogen atoms of the ligands and rare earth ion. The UV–vis absorption spectra of the complexes reflect the absorption spectra of the ligands and there is no significant change in the wavelength and band profiles between the spectra of the ligands and that of complexes except a slight red shift. The photoluminescent emission spectra of the complexes in visible and near-infrared (NIR) region was recorded and indicated the emission quenching in complex (2) due to the energy transfer from Eu³⁺ ion to Yb³⁺ ion. The morphological properties of the complexes as characterized by SEM revealed different morphologies of mononuclear and binuclear complexes.

Keywords Rare earth complex · Photoluminescence · Energy transfer · Near infrared · Salicylic acid · 1,10-phenanthroline

Introduction

The metal organic frameworks (MOF's) have been intensively studied in recent years due to their unique photophysical properties and potential applications in

the next generation of full color flat panel displays [1–4], probes and labels in a variety of biological and chemical applications [5, 6], components in optical telecommunications and novel optoelectronic devices [7–9]. Among the rare earth complexes, the photoluminescent properties of europium complexes are particular and attractive in the visible region, however the absorption and emission cross section of europium complexes is small due to spin and parity forbidden f-f transitions [10–12], thus requiring the use of organic chromophores that possess a reasonably large molar absorption cross section ($\epsilon=10^4\text{--}10^5\text{ M}^{-1}\text{ cm}^{-1}$) to indirectly excite the metal centre and sensitize the luminescence. Among the trivalent lanthanide ions, Eu(III) is one of the most emissive, having 4f⁶ configuration with ⁷F₀ as the ground state and long lived ⁵D₀ excited state. The emission spectra of Eu(III) ion consists of sharp and narrow peaks corresponding to the characteristic ⁵D₀ → ⁷F_J (J=0–4) transitions. The most intense peaks are due to ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ transitions located around 592 and 615 nm respectively where the most intense transition at 615 nm is hypersensitive transition which is sensitive to the metal ion environment. Recently, the luminescent materials with the emissions in the near- infrared region such as Sm(III), Dy(III), Pr(III), Ho(III), Yb(III), Nd(III) and Er(III) have gained much interest due to their applications in telecommunication network as optical signal amplifier, probes for bioassays because human tissue is relatively transparent to near infrared light at 1000 nm [13–15]. Yb³⁺ ion is usually a prime candidate to be chosen due to its luminescent efficiency close to 100 % and relatively simple electronic structure of two energy level manifolds: the ²F_{7/2} ground state and ²F_{5/2} excited state around at 10,000 cm⁻¹ in

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the NIR region. [16, 17]. The rare earth ion couples such as $\text{RE}^{3+}\text{-Yb}^{3+}$ can be efficiently utilized for near infrared (NIR) quantum cutting (QC) materials. The energy gap of ${}^5\text{D}_2 - {}^7\text{F}_0$ transition in Eu^{3+} is approximately twice as large as that of ${}^2\text{F}_{5/2} - {}^2\text{F}_{7/2}$ transition in Yb^{3+} which facilitates the energy transfer between Eu^{3+} ion to Yb^{3+} ion [18, 19]. However, to our knowledge the mixed rare earth complexes showing energy transfer from one rare earth ion to other have been less studied.

In this work, we report the synthesis of mononuclear Eu^{3+} , Yb^{3+} and dinuclear $\text{Eu}^{3+}\text{-Yb}^{3+}$ complexes with salicylic acid and 1,10-phenanthroline. The structural characterizations, photoluminescence emissions in the visible and NIR region, mean decay lifetimes and morphologies properties of the complexes have been evaluated. The emission spectra of the complexes show an efficient energy transfer mechanism between Eu^{3+} ion and Yb^{3+} ion. We expect that these rare earth ion couples can be efficiently utilized in optoelectronic devices and quantum cutting materials.

Experimental

Materials and Methods

EuCl_3 (anh), YbCl_3 (anh), salicylic acid (sal, 99 %), 1,10-phenanthroline (phen, 99.5 %) were procured from Sigma Aldrich and used as received without any further purifications. Ethanol (CH_3OH , 99.9 %) 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 $4000\text{--}400\text{ cm}^{-1}$. Ultraviolet absorption spectra ($1 \times 10^{-5}\text{ mol L}^{-1}$, ethanol solution) were recorded by Shimadzu UV-1601 spectrometer. Photoluminescence measurements were done on a Perkin Elmer LS55 fluorescence spectrophotometer equipped with a 150W Xenon lamp as the excitation source. Photoluminescence decay measurements were performed on Horiba Jobin-Yvon FL-3-22 spectrofluorometer. The morphology of the synthesized complexes was studied by

Table 1 Elemental analysis results of complexes ^(a)

Complexes	Experimental values (calculated values)		
	% C	% H	% N
$[\text{Eu}(\text{sal})_3(\text{phen})]$	53.11 (53.09)	3.51 (3.48)	3.72 (3.75)
$[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$	52.31 (52.34)	3.45 (3.43)	3.68 (3.70)
$[\text{Yb}(\text{sal})_3(\text{phen})]$	51.64 (51.62)	3.42 (3.39)	3.63 (3.65)

^(a) The values in brackets are the calculated ones

Scanning Electron Microscopy (SEM) using Carl Zeiss Scanning Electron Microscope.

Synthesis of Complexes $[\text{Eu}(\text{sal})_3(\text{phen})]$ (1) and $[\text{Yb}(\text{sal})_3(\text{phen})]$ (3)

The complex (1) was synthesized by taking sal (1.5 mmol) and phen (0.5 mmol) in anhydrous ethanol 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}). EuCl_3 (1 mmol) solution was added slowly dropwise to the ligand solution under stirring and the resulting solution was refluxed for 3–4 h at $70\text{ }^\circ\text{C}$ with continuous stirring. The white coloured precipitates were filtered, washed with ethanol and then dried in a vacuum oven. The complex (3) was synthesized using YbCl_3 (0.5 mmol), sal (1.5 mmol) and phen (0.5 mmol) by following the same procedure as above and the white colored precipitated complex was filtered, washed with ethanol and dried in vacuum.

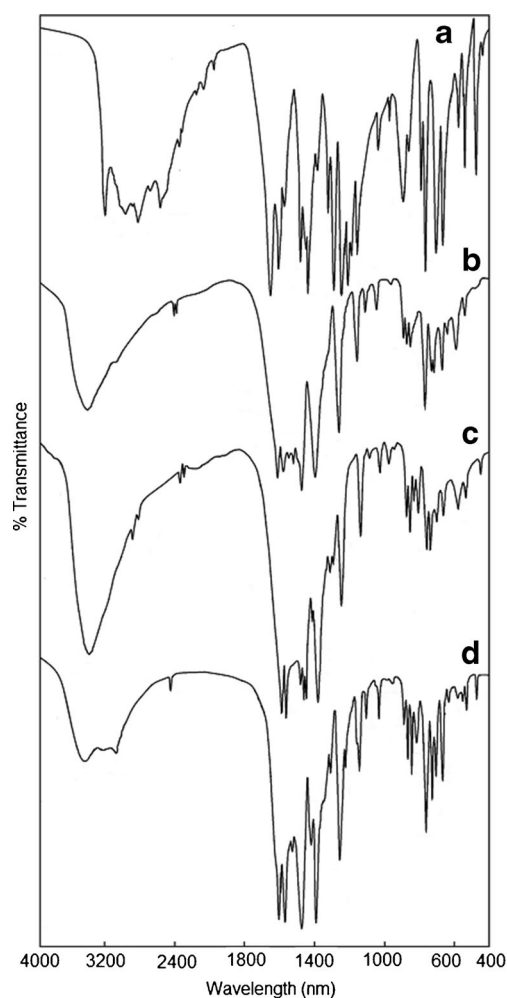


Fig. 1 FTIR spectra of: (a) sal (b) $[\text{Eu}(\text{sal})_3(\text{phen})]$; (c) $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$; (d) $[\text{Yb}(\text{sal})_3(\text{phen})]$

Synthesis of Complex $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$ (2)

The complex was synthesized by the taking sal (1.5 mmol), phen (0.5 mmol) in anhydrous ethanol solution (10 ml) and the reaction mixture was stirred for half an hour. EuCl_3 (0.5 mmol) and YbCl_3 (0.5 mmol) solutions in ethanol were mixed and stirred for half an hour. The ligands solutions and rare earth chlorides solutions were mixed and the pH of the solution was adjusted between 6 and 7 with dilute NaOH solution (1 mol L^{-1}). The resulting mixture was refluxed for 3 h at 70°C with continuous stirring. The white coloured precipitates were filtered, washed with ethanol and then dried in a vacuum oven.

Results and Discussion

Compositions of Title Complexes

The elemental analysis data of C,H,N are listed in Table 1, which shows a good agreement between the experimental and calculated ones.

FTIR Studies

The FTIR spectra of the complexes under study and the ligand sal are shown in Fig. 1. The characteristic band at 1661 cm^{-1} as observed in the Fig. 1a was attributed to the $\nu_{\text{C=O}}$ stretch of the carboxylate group of ligand SA. This band disappeared

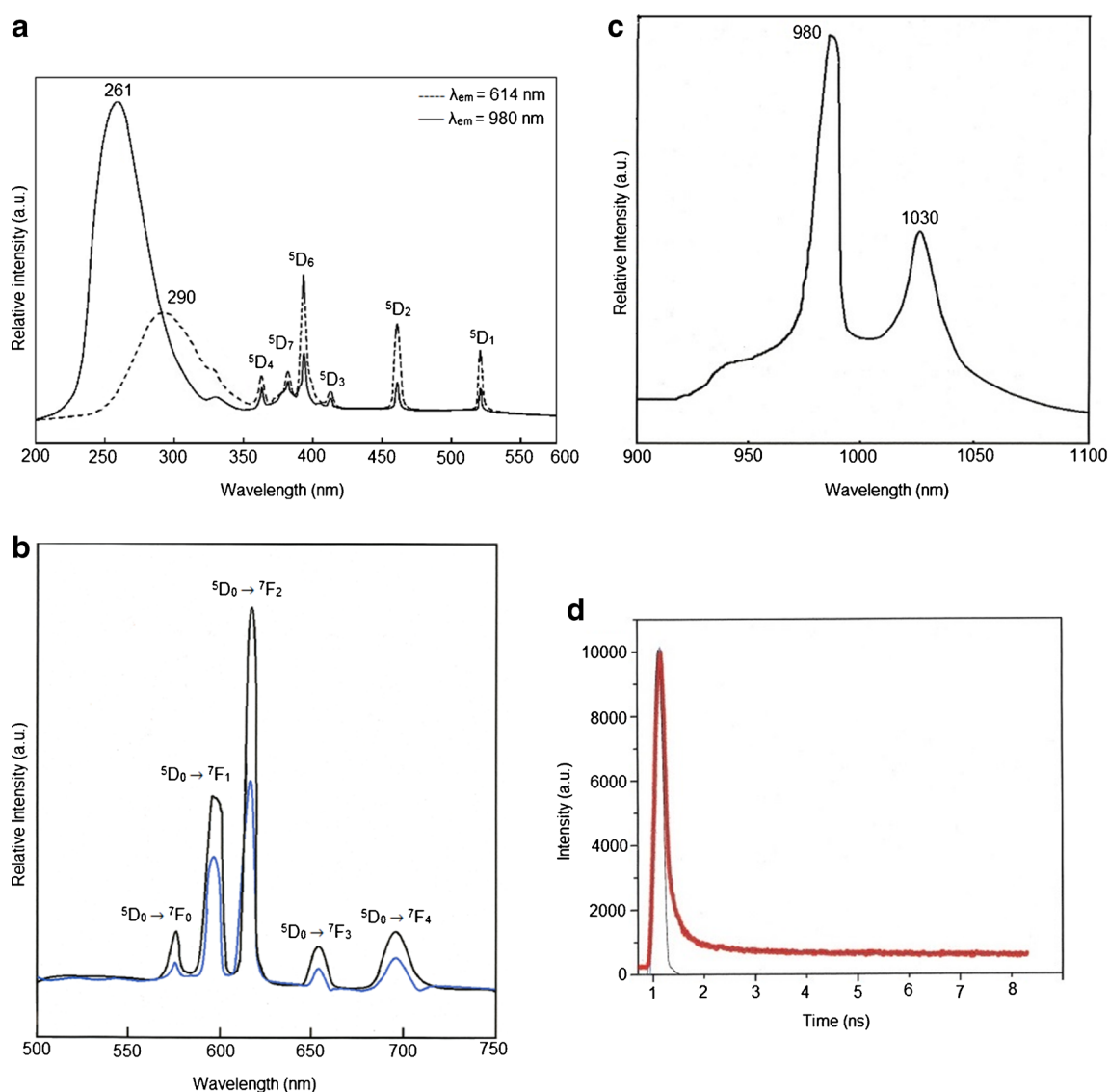


Fig. 2 **a** Photoluminescent excitation spectra of Eu^{3+} emission monitored at 614 nm and Yb^{3+} emission monitored at 980 nm of $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$. **b** Room temperature photoluminescent emission spectra of (A) $[\text{Eu}(\text{sal})_3(\text{phen})]$; (B) $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$ excited at

384 nm. **c** Room temperature photoluminescent emission spectra of $[\text{Yb}(\text{sal})_3(\text{phen})]$ excited at 384 nm. **d** Decay curve of Eu^{3+} , $^5\text{D}_0$ excited state (excitation wavelength : 384 nm; emission wavelength : 614 nm) of $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$

and shifted downward to 1601, 1599 and 1596 cm^{-1} in the complexes (1),(2) and (3) respectively which suggested that the coordinate bonds were formed between oxygen atom of carboxylic group and rare earth ion. The broad band observed at 3421, 3426 and 3425 cm^{-1} due to the $\nu_{\text{O-H}}$ stretching vibration revealed the coordination of hydroxyl group to the rare earth ion. The free isolated C = N group absorbs at 1589 cm^{-1} in phen as reported in literature also shifted towards lower wavenumber at 1560, 1576 and 1575 cm^{-1} in the complexes (1), (2) and (3) respectively. The C-H stretching vibration of phen ring at 739 cm^{-1} , 853 cm^{-1} also disappeared and new bands appeared at 730 cm^{-1} , 843 cm^{-1} in complex (1), 738 cm^{-1} , 844 cm^{-1} in complex (2) and 729 cm^{-1} , 845 cm^{-1} in complex (3) respectively. These shifts prove that a coordination between N atoms of phen and rare earth ion had taken place. The characteristic $\nu_{(\text{Eu-N})}$ and $\nu_{(\text{Eu-O})}$ peaks at 530 and 457 cm^{-1} seen in Fig. 1b–d further confirms the formation of complexes.

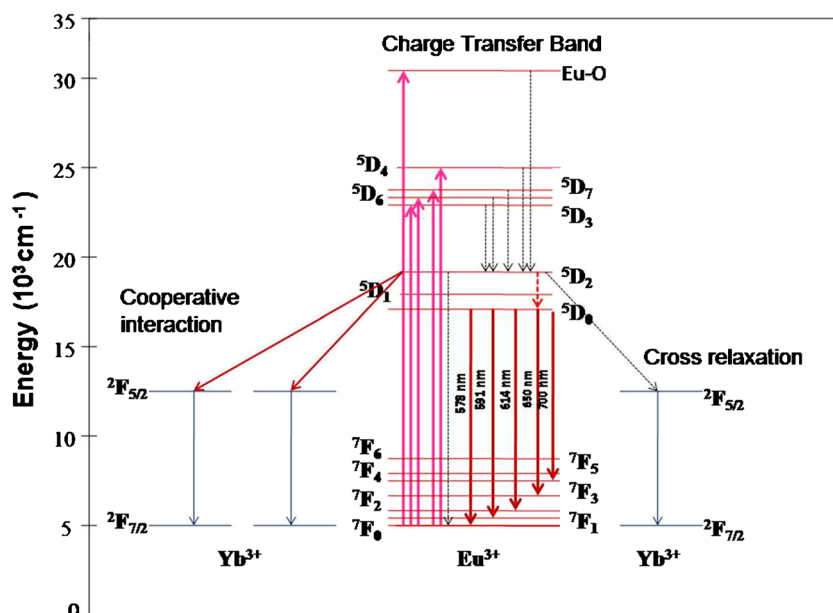
Photoluminescence Studies

The room temperature excitation spectra of complex (2) was shown in Fig. 2a and was obtained by monitoring the longest emission wavelength of Eu^{3+} ion at 614 nm and Yb^{3+} ion at 980 nm. At 614 nm emission of Eu^{3+} ions, the excitation spectra of the complex exhibited a broad band at 290 nm attributable to the ligand to metal charge transfer (CT) transitions caused by the interaction between the organic ligands and the Eu^{3+} ions. The strong absorption band centered at 261 nm corresponded to the ligand to metal charge transfer transitions of Yb^{3+} ions. The presence of relatively strong CT absorption band in the excitation spectrum of Yb^{3+} ions reveals the energy transfer

from Eu^{3+} ions to Yb^{3+} ions [20]. The excitation spectrum also showed the sharp 4f-4f transitions of Eu^{3+} from the ${}^7\text{F}_0$ ground state to ${}^5\text{D}_{3,4,6,7,1,2}$ excited states. The difference in energy between the ${}^5\text{D}_2$ - ${}^7\text{F}_0$ transition of Eu^{3+} ions is twice the energy difference between ${}^2\text{F}_{5/2}$ - ${}^2\text{F}_{7/2}$ transition of Yb^{3+} ions, which means that the ${}^5\text{D}_2$ excited state of Eu^{3+} ion can simultaneously transfer energy to two nearby Yb^{3+} ions and hence the Yb^{3+} ions can emit two infrared photons. This absorption is followed by rapid multi-phonon assisted relaxation from the populated ${}^5\text{D}_2$ energy levels to the metastable energy levels of Eu^{3+} ions. This process is called cooperative energy transfer process and is responsible for the energy transfer from Eu^{3+} ions to Yb^{3+} ions as shown in the Fig. 3 [21].

The photoluminescent emission spectra of the complexes (1–3) in the visible region 550 to 700 nm and near infrared region from 900 to 1100 nm is shown in Fig. 2b and c. The emission spectra obtained by the excitation at 384 nm, we observed that the complexes (1) and (2) showed characteristic narrow emission peaks corresponding to the ${}^5\text{D}_0$ - ${}^7\text{F}_j$ ($J=0-4$) transitions of Eu^{3+} ions. The emission peaks were well resolved and it was observed that the peak at 578 and 650 nm were weak since their corresponding transitions ${}^5\text{D}_0$ - ${}^7\text{F}_0$ and ${}^5\text{D}_0$ - ${}^7\text{F}_3$ were forbidden in magnetic and electric dipole fields. The peak at 591 nm was relatively strong and corresponded to ${}^5\text{D}_0$ - ${}^7\text{F}_1$ magnetic transition, the strongest emission observed at 614 nm (${}^5\text{D}_0$ - ${}^7\text{F}_2$) was an induced electric dipole transition sensitive to the coordination environment of Eu^{3+} ion. This transition was responsible for the red emission of the europium complexes. We also observed a change in intensity of peaks which was stronger in complex (1) as compared to complex (2). The decrease in intensity of all the emission peaks in complex (2) can be considered due to the energy transfer from Eu^{3+} ions to Yb^{3+}

Fig. 3 Schematic energy level diagram of complex $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$ illustrating the cooperative energy transfer process from Eu^{3+} ion excited state (${}^5\text{D}_0$) to Yb^{3+} ion energy levels (${}^2\text{F}_{5/2}$), solid arrows show radiative transitions and dotted arrows show non-radiative transitions



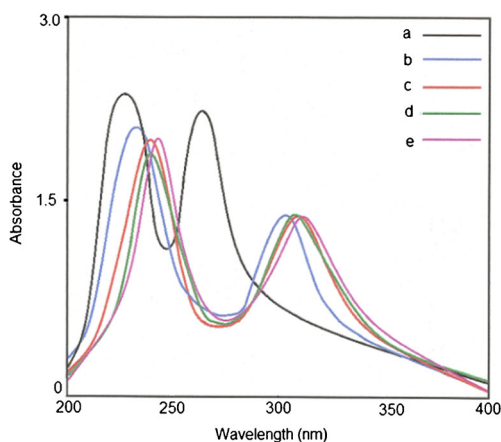


Fig. 4 UV-vis absorption spectra of (a) phen; (b) sal; (c) $[\text{Eu}(\text{sal})_3(\text{phen})]$; (d) $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$; (e) $[\text{Yb}(\text{sal})_3(\text{phen})]$

ions in the complexes. The Fig. 2c shows the emission spectrum of complex (3) which exhibited near infrared emission peaks at 980 and 1030 nm associated with the transition of Yb^{3+} from ${}^2\text{F}_{5/2}$ level to ${}^2\text{F}_{7/2}$ energy level. To further study the energy transfer from Eu^{3+} to Yb^{3+} , the luminescence decay curve of ${}^5\text{D}_0$ excited state of Eu^{3+} at 394 nm and emission monitored at 614 nm for Eu^{3+} - Yb^{3+} complex is shown in Fig. 2d. The decay curve shows the lifetime quenching of Eu^{3+} emission due to the energy transfer from Eu^{3+} to Yb^{3+} with mean lifetime of 461 ps.

UV-vis Absorption Studies

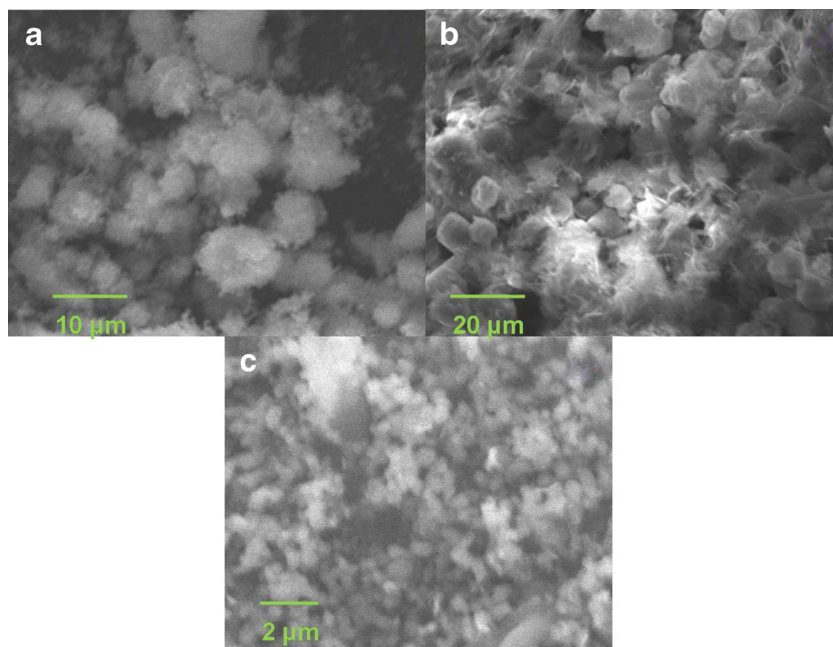
The UV-vis absorption spectra of the ligands and their corresponding complexes in ethanol solution (1×10^{-5} mol/L) are shown in Fig. 4. It was observed that

the absorption bands appearing at 234 nm, 302 nm and at 229 nm, 262 nm were assigned to the $\pi \rightarrow \pi^*$ transitions of aromatic ring of sal and phen respectively. The band profiles of the complexes were attributed to the organic ligands and were dominated by the absorption of phen which indicated that the fluorescence properties of the complexes were mainly determined by the energy transfer from phen to the rare earth ion. A slight red shift was observed and two main absorption bands observed at about 238 and 305 nm in the complexes revealed that both salicylic acid and phen took part in formation of the complexes and due to the formation of large conjugated chelate rings in the complexes, the main absorption bands shifted to longer wavelengths compared with the corresponding ligands. The results suggested that the ligands were successfully coordinated to the rare earth ion.

Morphological Studies

The Fig. 5 demonstrates the morphologies of the prepared complexes, which revealed the different microstructures for three complexes. Figure 5a showed the agglomerated spherical shape structure with narrow distribution while the corresponding Yb^{3+} complex showed a dense distribution of agglomerated particles as shown in Fig. 5c. Figure 5b depicted highly uniform and well dispersed mixed spherical and rod shape like particles. The results revealed that the mixed rare earth complex presented distinguishable morphology from the corresponding Eu^{3+} and Yb^{3+} complexes.

Fig. 5 SEM micrographs of (a) $[\text{Eu}(\text{sal})_3(\text{phen})]$; (b) $[\text{Eu}_{0.5}\text{Yb}_{0.5}(\text{sal})_3(\text{phen})]$; (c) $[\text{Yb}(\text{sal})_3(\text{phen})]$



Conclusions

In summary, the mononuclear Eu^{3+} , Yb^{3+} and binuclear Eu^{3+} - Yb^{3+} complexes can be synthesized by the solution technique. A study of excitation, emission and decay measurements reveals the efficient energy transfer from Eu^{3+} to Yb^{3+} by cooperative energy transfer process, which leads to Eu^{3+} emission quenching and occurrence of near infrared emission at 980 and 1030 nm. Further, the decay measurements also indicates the effective energy transfer between the two rare earth ions. The morphological studies of the synthesized complexes also demonstrated the distinguishable morphology of binuclear complex than the mononuclear complexes. These mononuclear complexes can act as potential candidates for application in optoelectronic devices in visible and near infrared region and dinuclear complexes can be utilized in photovoltaics.

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