J Fluoresc (2016) 26:1813–1823
DOI 10.1007/s10895-016-1873-5

ORIGINAL ARTICLE

Optical Features of Efficient Europium(III) Complexes with β-Diketonato and Auxiliary Ligands and Mechanistic Investigation of Energy Transfer Process

Manju Bala[1] · **Satish Kumar**[1] · **V. B. Taxak**[1] · **Priti Boora**[1] · **S. P. Khatkar**[1]

Received: 9 March 2016 / Accepted: 6 July 2016 / Published online: 21 July 2016

Abstract Two new europium (III) complexes have been synthesized with 1,3[bis(4methoxyphenyl)]propane1,3dionato (HBMPD) as main ligand and 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) as an auxiliary ligand. The main ligand HBMPD has been synthesized by ecofriendly microwave approach and complexes by solution precipitation method. The resulting materials are characterized by IR, ^{1}H-NMR, elemental analysis, X-ray diffraction, UV-visible and TG-DTG techniques. The photoluminescence (PL) spectroscopy depicts the detail analysis of photophysical properties of the complexes, their results show that the ligand interact with Eu (III) ion which act as antenna and transfers the absorbed energy to the central europium(III) ion via sensitization process efficiently. As a consequence of this interaction, these materials exhibit excellent luminescent intensity, long decay time (τ), high quantum efficiency (η) and Judd-Ofelt intensity parameter (Ω_2). The CIE coordinates fall under the deep red region, matching well with the NTSC (National Television Standard Committee) standard. Hence, these highly efficient optical materials can be used as a red component in organic light emitting diodes (OLEDs) and full color flat panel displays.

Keywords Optical materials · Ecofriendly microwave approach · Sensitization · Quantum efficiency

Introduction

The optical features of lanthanide ions sensitized with various ligands have attracted the attention of researchers owing to their fascinating properties in many research areas like luminescent materials for organic light emitting diodes (OLEDs), optical fibers, lasers [1–3], chemical and biological sensors [4, 5]. The major interest in exploring the europium complexes is their intriguing luminescent properties such as large stokes shifts, long lifetime and line like emission profile in visible region due to screening of $4f^n$ by 5 s and 5p electrons [6–8]. The 4f-4f intra-configurational forbidden transitions of the europium (III) ion and NH, OH and CH oscillators of the solvent molecules diminish the emission intensity by depopulating the excited state of metal ion by non-radiative decay path, which quench luminescence. In this problem, organic ligands play significant role to sensitize the weak luminescence of europium metal, acting as antennae and also shield the central metal ion from fundamental interaction of NH, OH and CH high energy oscillators of solvents. An organic moiety with magnificent absorption coefficient act as sensitizer or an antenna, which absorbs energy, then reassign the energy from its lowest triplet energy level to the emitting resonance levels of europium(III) ion and hence facilitates the sensitization process [9]. This organic moiety enhances the luminescent intensity of electric dipole $^5D_0 \rightarrow {}^7F_2$ transition by creating asymmetric coordination environment in the complex. The introduction of auxiliary ligand further enhance the luminescence as it restricts the 4f-4f forbidden transition, decrease the loss of energy by non-radiative decay, moreover, confers stability and rigidity to the complex. In aforementioned perspective of ligands, we introduced an electron donating –OCH_3 group in the main organic ligand [10–12] and an auxiliary ligand like bipy or phen having synergistic effect

---

Electronic supplementary material The online version of this article (doi:10.1007/s10895-016-1873-5) contains supplementary material, which is available to authorized users.

✉ S. P. Khatkar
s_khatkar@rediffmail.com

[1] Department of Chemistry, Maharshi Dayanand University, Rohtak, Haryana 124001, India

with main ligand and noticed a dramatically enhanced luminescence. So, the quest of new organic ligand possessing extensive π-conjugation which affirm the complexation with trivalent europium(III) ion, meet with the synthesis of β-diketonato HBMPD ligand.

Here in the present communication, we have synthesized new β-diketonato ligand, namely HBMPD by microwave irradiation and employed this ligand for the synthesis of europium (III) complexes incorporating auxiliary ligands phen or bipy, ensuing to tris[1,3-bis(4-methoxyphenyl)propane-1,3-dionato](bipyridyl) europium(III) (**Eu1**) and tris[1,3-bis(4-methoxyphenyl)propane-1,3-dionato](1,10-phenanthroline) europium(III) (**Eu2**). The spectral, elemental analyses, X-ray, thermal behavior and photophysical studies of these novel Eu (III) complexes are reported. Moreover, the synergistic effect of auxiliary ligands on photophysical properties of these europium complexes is expatiated. On the basis of emission spectra, the CIE color coordinates (x and y), luminescence decay time (τ), radiative decay rate (A_{rad}), nonradiative rate (A_{nrad}), quantum efficiency (η) and Judd-Ofelt intensity parameter (Ω_2) are determined and analyzed. The sensitization process and mechanistic investigation of intramolecular energy transfer in these europium(III) complexes are proposed.

Experimental

Materials

High purity europium nitrate [Eu $(NO_3)_3.5H_2O$; 99.9] and gadolinium nitrate [Gd $(NO_3)_3.5H_2O$; 99.9] were acquired from Sigma Aldrich. The solvents and other chemicals like 2,2′-bipyridyl, 1,10-phenanthroline, 4-methoxyacetophenone, 4-methoxybenzoyl chloride and potassium carbonate were purchased from commercial source and used as received. The ligand HBMPD was synthesized adopting ecofriendly microwave approach and then recrystalized three times with DMSO to obtain ligand of high purity.

Instrumental Measurements

The europium content was enumerated by complexometric titration with disodium ethylenediaminetetraacetate (EDTA) salt. The elemental CHN analyses were performed with Perkin Elmer 2400 CHN Elemental Analyzer. The ^{1}H-NMR spectra of complexes were executed by Bruker Avance II 400 NMR spectrometer in chloroform solvent using tetramethylsilane (TMS) as an internal standard (δ = 0.00 ppm). The infrared spectra were obtained by Shimadzu FT-IR Affinity-1 with KBr pellets in the range of 4000–400 cm^{-1}. The UV-visible absorption spectra were measured on Shimadzu-2450 UV-visible spectrophotometer. The thermal behavior in form of TG-DTG curves were determined by Hitachi STA-7300 thermal system under N_2 atmosphere with a heating rate of 20°C/min. Powder X-ray diffraction patterns were recorded on Rikagu Ultima IV diffractometer of 40 kV tube voltage and 40 mA tube current with CuKα as a radiation source at a scanning rate of 3° min^{-1} in the 2θ angular range of 10–80°. The excitation, emission spectra and decay curves of the complexes were carried out by Hitachi F-7000 fluorescence spectrophotometer equipped with xenon lamp as radiation source in UV-visible range. These measurements were made with the scanning rate of 240 nm/min at 400 PMT and 2.5 nm slit width for excitation and emission process. The decay time values of the complexes were obtained by FL solution software of F-7000 spectrometer under time scan mode.

Synthesis of Ligand

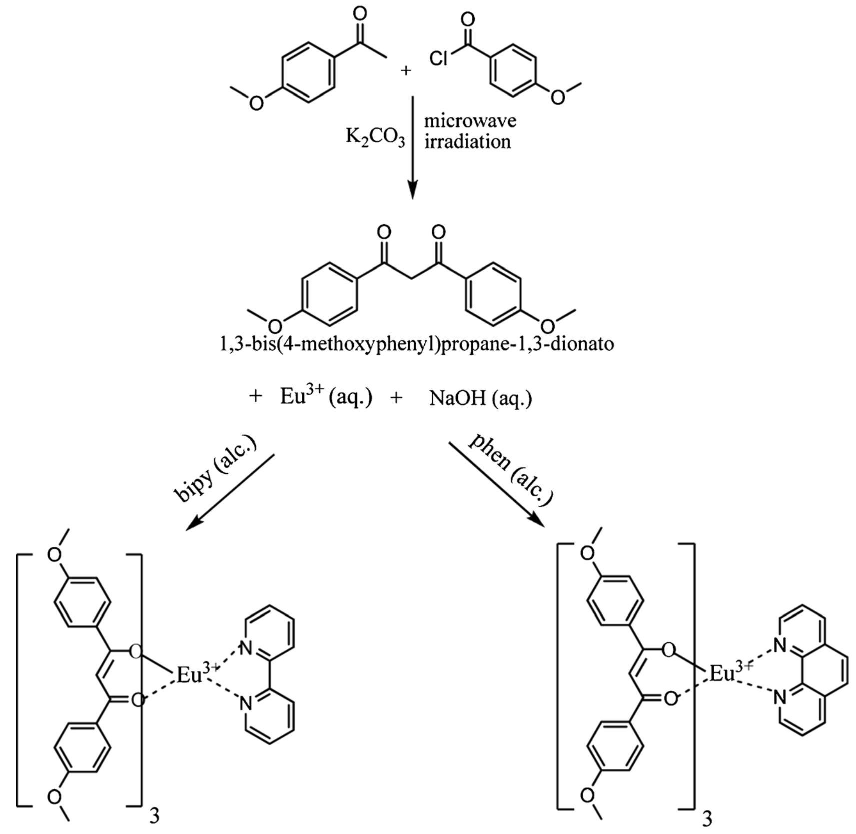
The ligand HBMPD was synthesized adopting microwave irradiation method as illustrated in Scheme 1. To a mixture of 4-methoxybenzoyl chloride (0.68 ml, 5 mmol), 4-methoxyacetophenone (0.75 g, 5 mmol) and potassium carbonate (1.38 g, 10 mmol), a few drops of water were added to make a homogenous mixture. Then resulting mixture was exposed to microwave radiation (300 W) for the 40 s (8 × 5 s). The completion of the reaction was assured by thin layer chromatography (TLC). The reaction mixture was diluted with crushed ice followed by acidification with hydrochloric acid. The solid was separated out and purified by recrystalization process, repeating the process three times in DMSO. The yellow crystalline solid of HBMPD was obtained in 90 % yield with 112°C melting point. IR (KBr): cm^{-1} 3480 (b), 3045 (w), 2949 (w), 1680 (s), 1597 (s), 1490 (s), 1446 (s), 1307 (s), 1251 (s), 1024 (s), 837 (s), 783 (s), 509 (m); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 12.07 (s, 1H, enolic OH), 7.93–6.91 (m, 8H, Ar-H), 6.83 (s, 1H, enol CH), 4.80 (s, 2H, keto-CH_2), 4.62 (s, 6H, OCH_3) ppm. Anal. Calcd for $C_{17}H_{16}O_4$ formula of HBMPD ligand: C, 71.83, H, 5.63; found: C, 71.12; H, 5.21.

Synthesis of Complexes

An ethanolic solution of ligand HBMPD (0.909 g, 3.2 mmol) and bipy (0.15 g, 1.0 mmol) for complex **Eu1** or phen (0.18 g, 1.0 mmol) for complex **Eu2** was slowly added to the aqueous solution of europium nitrate (0.42 g, 1.0 mmol) and the reaction mixture was allowed to stir for 3 h at about 50–55°C temperature on magnetic stirrer. The pH of the resulting mixture was adjusted to 6.5–7.0 by carefully addition of aqueous NaOH solution (0.05 M). The yellow precipitates were collected after filtration and washed with distilled water followed by ethanol to take away the unreacted ligand. The solid was dried at 60° C in hot air oven.

A gadolinium (III) binary complex (**Gd3**) i.e. $[Gd(BMPD)_3(H_2O)_2]$ was also prepared to calculate the lowest triplet level of ligand HBMPD, a similar method was

Scheme 1 The synthetic route of ligand HBMPD and their europium (III) complexes



Eu1 **Eu2**

adopted as in the synthesis of europium complexes using the mixture of HBMPD (0.90 g, 3.2 mmol) in ethanol and aqueous solution of gadolinium nitrate (0.45 g, 1.0 mmol).

[Eu(BMPD)$_3$bipy] (**Eu1**): yellow solid, yield 72 %; IR (KBr): cm^{-1} 3061 (w), 3008 (w), 2948 (w), 1595 (s), 1539 (s), 1481 (s), 1444 (s), 1390 (s), 1247 (s), 1174 (s), 1114 (s), 1026 (s), 837 (s), 516 (w), 460 (w); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.93–7.01 (m, 32H, Ar-H), 4.62 (s, 18H, $-OCH_3$), 3.84 (s, 3H, enol CH). Anal. Calcd for $EuC_{61}H_{53}N_2O_{12}$: C, 63.27; H, 4.58; N, 2.42; Eu, 13.14; found: C, 62.82; H, 4.25; N, 2.16; Eu, 12.96.

[Eu(BMPD)$_3$phen] (**Eu2**): yellow solid, yield 74 %; IR (KBr): cm^{-1} 3049 (w), 3004 (w), 2951 (w), 1595 (s), 1535 (s), 1483 (s), 1442 (s), 1388 (s), 1249 (s), 1174 (s), 1028 (s), 839 (s), 516 (w), 462 (w); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.93–7.0 (m, 32H, Ar-H), 4.62 (s, 18H, $-OCH_3$), 3.84 (s, 3H, enol CH). Anal. Calcd for $EuC_{63}H_{53}N_2O_{12}$: C, 64.01; H, 4.50; N, 2.40; Eu, 12.90; found: C, 63.82; H, 4.15; N, 2.10; Eu, 12.48.

Gd(HBMPD)$_3$(H$_2$O)$_2$ (**Gd3**): yellow solid, yield 64 %; IR (KBr): cm^{-1} 3401 (b), 3068 (w), 3003 (w), 2947 (w), 2837 (w), 1597 (s), 1479 (s), 1375 (s), 1305 (s), 1234 (s), 1180 (s), 1116 (s), 1022 (s), 835 (s), 796 (s), 466 (m); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.93–7.01 (m, 24H, Ar-H), 4.62 (s, 18H, $-OCH_3$), 3.64 (s, 3H, enol CH). Anal. Calcd for $GdC_{51}H_{49}O_{14}$: C, 58.73; H, 4.70; Gd, 15.06; found: C, 58.10; H, 3.98; Gd, 14.62.

Results and Discussion

Elemental and Spectral Analysis

The elements (C, H and N) of ligand HBMPD ligand and their europium complexes are analyzed, results are listed in Table 1. These are in good concordance with values calculated on the basis of proposed molecular formulas. The molecular composition of the complexes conforms to Eu (HBMPD)$_3$bipy (**Eu1**) and Eu(HBMPD)$_3$phen (**Eu2**). These complexes are found to

Table 1 The elemental analytical data of europium (III) complexes **Eu1-Eu2**

Complexes	C(%) found (cal.)	H(%) found (cal.)	N(%) found (cal.)	Eu(%) found (cal.)
HBMPD	71.12 (71.83)	5.21 (5.63)	-	-
Eu1	62.82 (63.27)	4.25 (4.58)	2.16 (2.42)	12.96 (13.14)
Eu2	63.82 (64.01)	4.15 (4.50)	2.10 (2.40)	12.48 (12.90)

Table 2 The IR characteristics bands (cm^{-1}) of ligand and its europium complexes

Complexes	ν(O-H)	ν(C = O)	ν(C = N)	ν(C = C)	ν(Eu-N)	ν(Eu-O)
HBMPD	3480 (b)	1680 (s)	-	1597 (s)	-	-
Eu1	-	1595 (s)	1539 (s)	1481 (s)	516 (m)	460 (w)
Eu2	-	1595 (s)	1535 (s)	1483 (s)	515 (w)	462 (m)

b broad, *s* strong, *m* medium, *w* weak

be highly soluble in DMSO, chloroform and stable under atmospheric condition.

The significant data of FT-IR spectra of HBMPD ligand, **Eu1** and **Eu2** complexes are arranged in Table 2. The binding nature of ligands to the europium (III) ion is assessed by a comparative study of ligand and spectra of complexes. A broad absorption band at 3480 cm^{-1} attributed to the stretching vibration of enolic –OH is absent in the spectra of complexes, proposing the involvement of enolic –OH of ligand in coordination to the Eu (III) ion. The strong absorption bands of ›CO stretch at 1595 cm^{-1} in complexes spectra exhibit a noticeable decrease in the ›CO frequency compared to the spectrum of ligand, suggesting the coordination of ligand to the metal through oxygen atom of ›CO group of ligand, which is further affirmed by visualizing a medium intense band of Eu-O vibration in 460–462 cm^{-1} range. Similarly, the enolic C = C stretching vibration of complexes spectra are red shifted relative to spectrum of ligand, indicating the extension of π-conjugated system in complexes. The IR spectra of complexes only show the intense absorption band in the frequency range 1539–1535 cm^{-1} ascribed to the ›C = N stretch vibration of auxiliary ligands (bipy or phen), ensuring the coordination of bipy or phen ligand to the central metal ion through nitrogen atom. This data is further confirmed by a medium intense band of Eu-N stretching vibration in 516–517 cm^{-1} range. In ^{1}H-NMR spectra, the singlet peaks noticed in spectrum of ligand only at 12.07 ppm and 4.80 ppm are ascertained to enolic –OH and ketonic –CH_2 protons, respectively. These signals disappeared in the spectra of complexes, suggesting that the ligand in enolic form coordinates with the Eu(III) ion. The proton signal of enolic –CH at 6.83 ppm in the spectrum of ligand shifts to upfield at 3.84 ppm in the spectra of complexes, intends the paramagnetism of lanthanide ion [13].

Figure 1 displays the UV-visible absorption spectra of free ligand and their **Eu1** and **Eu2** complexes in DMSO solution (1×10^{-5} mol/L) at room temperature [14, 15]. The UV-absorption profile of europium complexes is similar to the ligand HBMPD absorption profile, proposing that the coordination of europium metal ion does not affect the singlet excited level of ligand in significant way. The maximum absorption at 278 nm and 360 nm is associated with the π-π* transition of organic ligands as the europium ion shows negligible absorption in this range. According to the Beer's Lambert law, the observed values of molar absorption coefficient in **Eu1** and **Eu2** complexes are 1.5×10^3 $Lmol^{-1}$ cm^{-1} and 1.3×10^3 $Lmol^{-1}$ cm^{-1} respectively.

Thermal Analysis and X-Ray Measurements

In order to examine the thermal behavior of **Eu1** and **Eu2** complex, TG-DTG analyses have been carried out in N_2 atmosphere with the range from ambient temperature to 800°C at a heating rate of 20°C/min, resulting traces are depicted in Fig. 2a-2b respectively. The **Eu1** and **Eu2** complexes show initial little mass loss of about 1–3 % which represents the loss of moisture present in complexes and stable about 250°C temperature. Further mass loss upto 700°C temperature corresponds to the removal of three molecule of BMPD ligand and bipy or phen molecules, leaving residue of europium oxides. The TG-DTG curves demonstrate the high thermal stability of complexes, which is quite favourable for the fabrication of OLEDs and other display devices.

The powder X-ray diffraction patterns of Eu^{3+} complexes **Eu1–2** are displayed in Fig. 3. The sharp prominent peaks at 2θ of 12.83, 14.10, 16.39, 20.22, 25.57, 28.11 of **Eu1** and 11.30, 14.10, 16.66, 18.43, 20.22, 28.11 of **Eu2** manifest the crystalline nature of the complexes. The size of particles is estimated with the help of

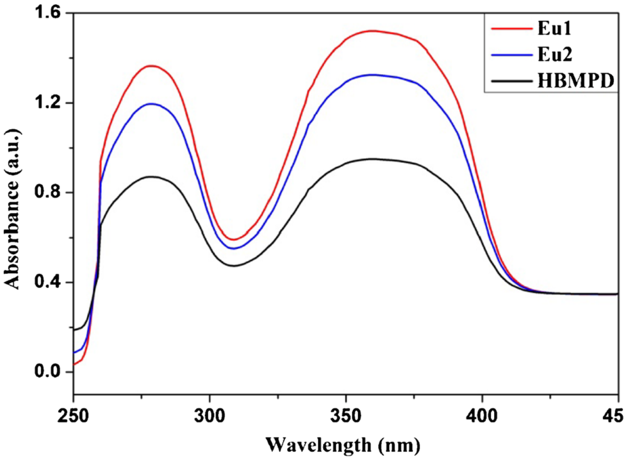


Fig. 1 The UV-visible absorption spectra of HBMPD ligand, **Eu1** and **Eu2** complexes in DMSO solution (1×10^{-5} mol/L)

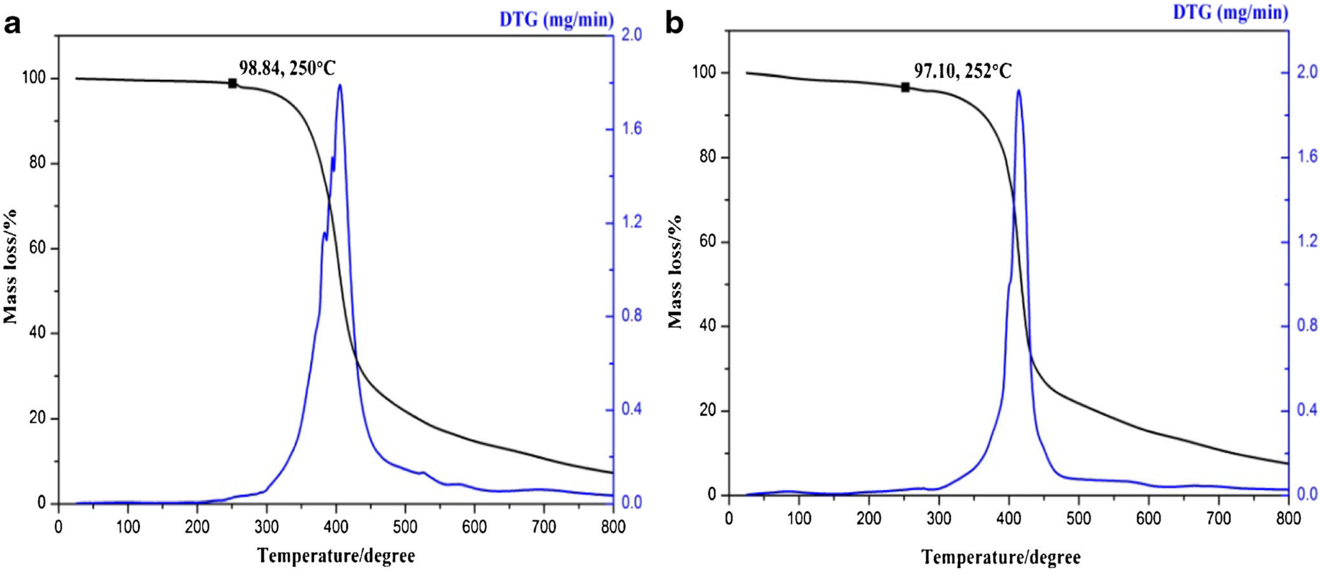


Fig. 2 TG-DTG curves of **Eu1 a** and **Eu2 b** complexes respectively

Scherrer's equation, D = 0.941λ/β cos θ, where D is the average particle size, λ the X-ray wavelength (0.15418 nm) and θ and β are the diffraction angle and full width at half maximum, respectively [16, 17]. The calculated particle size of **Eu1** and **Eu2** complexes from Scherrer's eq. is 36.78 nm and 27.80 nm respectively. The PXRD study designates the crystalline nature and nano range particle size of the complexes.

Optical Features

The emission spectra of **Eu1** and **Eu2** complexes in solid state at 298 K (Fig. 4), being excited at maxima 397 nm of excitation spectra, afford the greatest emission intensity of europium ion. The narrow characteristics emission peaks at 534, 540, 580, 590, 613 and 652 nm associated with the $^5D_{0,1} \rightarrow {}^7F_j$ (where j = 0, 1, 2, 3) transition of europium (III) ion. No ligand based emission peaks are noticed, demonstrating the effective transfer of absorbed energy from ligand to the emitting levels of europium(III) ion. It is well known that the emission peaks of europium ion are highly sensitive to change in symmetry and local chemical environment of the coordination sphere [18–20]. This can be reflected in the intense $^5D_0 \rightarrow {}^7F_2$ electric dipole transition at 613 nm, which is hypersensitive to even slight variation in the coordination environment being amenable for pure red color of the Eu^{3+} ion [21], while the parity-allowed magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ at 592 nm is insensitive to the coordination environment [22]. Hence, the monochromaticity of complexes can be calculated from the intensity ratio of electric dipole transition to magnetic dipole transition (I_2/ I_1 or red/orange) which manifest the low symmetry around Eu (III) ion in coordination sphere [23]. On the basis of data the intensity rations (I_2/I_1) computed are 13.4 (**Eu1**) and 9.3 (**Eu2**), pointing to the non-existence of an inversion center around central europium ion. The emission peaks at 580 nm and 652 nm are weak as their associated transition $^5D_0 \rightarrow {}^7F_{0,\,3}$ are forbidden both in electric as well as in magnetic dipole scheme. We observed one line for $^5D_0 \rightarrow {}^7F_0$ transition and stark splitting of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition in emission spectra due to ligand field around europium(III) ion, suggesting the single chemical environment around europium(III) ion with low symmetry [24, 25]. In addition, rigid auxiliary ligand (bipy or phen) have strong affinity towards lanthanide ions which induced an asymmetry in the complex coordination environment, restricting the thermal vibration as well as f-f forbidden

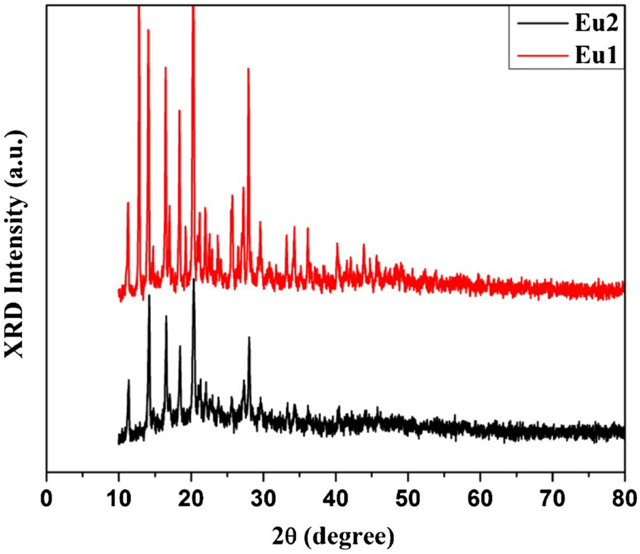
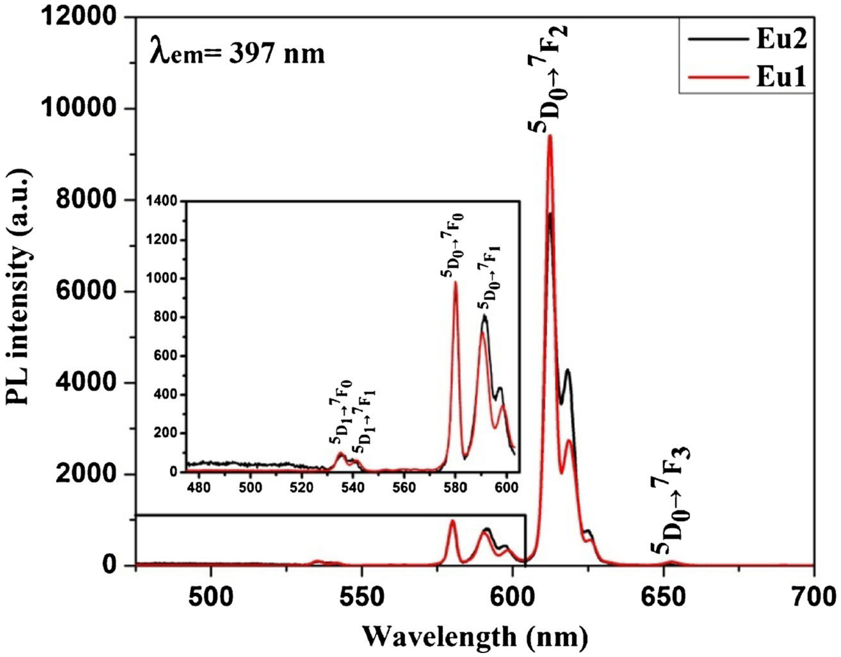


Fig. 3 The Powder XRD patterns for **Eu1** and **Eu2** complexes at room temperature

Fig. 4 Solid state photoluminescence emission spectra of **Eu1** and **Eu2** complexes excited at 397 nm at 298 K



transitions and reducing the non-radiative loss of energy that would enhance the intensity of the complexes [26, 27].

Figure 5 depicts the normalized excitation spectra of europium (III) complexes **Eu1 and Eu2** measured by monitoring the intense $^5D_0 \rightarrow {}^7F_2$ peak of europium ion at 613 nm in solid state at 298 K. The figure displays a broad band from 225 nm to 500 nm, with an excitation maxima 397 nm ($^7F_0 \rightarrow {}^5L_6$) ascribed to the π-π* electronic transition of β-diketonato ligand HBMPD. The excitation spectra also exhibit low intensity peaks in the longer wavelength region at 419 nm and 465 nm corresponding to $^7F_0 \rightarrow {}^5D_{2,3}$ transitions of Eu^{3+} ion respectively.

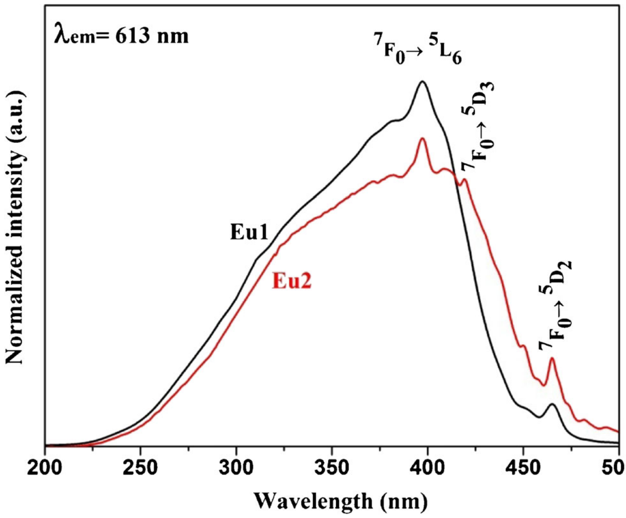


Fig. 5 Solid state photoluminescence excitation spectra of **Eu1** and **Eu2** complexes monitired at 613 nm at 298 K

Figure 6 shows the CIE (Commission Internationale de Eclairage) chromaticity coordinates (x and y) of **Eu1** and **Eu2** complexes estimated from the emission spectra excited at 397 nm and data is tabulated in Table 3. The CIE coordinates for **Eu2** (x = 0.6174 and y = 0.3294) fall in red region which moves to deeper red region in case of **Eu1** (x = 0.6428, y = 0.3454). Also, these values are close to the standard red color values of National Television Standard Committee (NTSC, x = 0.67, y = 0.33), Society of Motion Picture and Television (SMPTE, x = 0.63, y = 0.34) and European Broadcasting Union (EBU, x = 0.64, y = 0.33), which can be explicated on the basis of high intensity rations (I_2/I_1 or red/orange) in complexes.

Luminescence Decay Time (τ), Quantum Efficiency (η) and Judd-Ofelt Analysis

In order to explore the coordination environment around central europium (III) ion in complexes, the luminescence decay time of $^5D_0$ excited level of Eu^{3+} ion in complexes is recorded by monitoring the most intense emission peak ($^5D_0 \rightarrow {}^7F_2$) at 613 nm in solid state (Fig. 7), results are summarised in Table 3. The decay profile of $^5D_0 \rightarrow {}^7F_2$ transition obey single exponential function as $I = I_0\ exp.^{(-t/\tau)}$ where τ is the radiative decay time, I and I_0 are the luminescence intensities at time t and 0, respectively. The results of the decay curves proposed that the europium(III) ion is present in single chemical environment in complexes [28].

The luminescence quantum efficiency of $^5D_0$ excited level of Eu^{3+} ion in **Eu1 and Eu2** complexes are calculated from

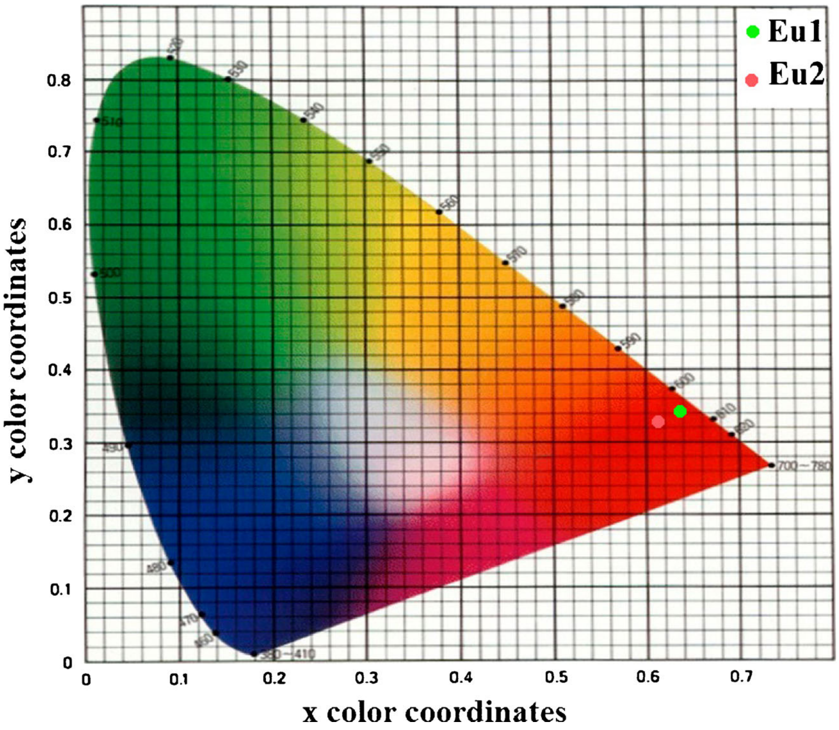


Fig. 6 The CIE chromaticity coordinates of the **Eu1** and **Eu2** complexes

the decay time and emission spectra of complexes using following equations [29].

$$\eta = A_{rad}/A_{rad} + A_{nrad} \tag{1}$$

Here A_{rad} and A_{nrad} represent radiative and non-radiative transitions rates respectively and considering that only these transition are responsible for the depopulation of $^5D_0$ excited level of europium ion. The luminescence decay time is related to radiative and non-radiative transitions according to equation (2).

$$\tau = (A_{rad} + A_{nrad})^{-1} \tag{2}$$

The radiative transition rate (A_{rad}) is determined by the summation of radiative rates A_{0J} for the $^5D_0 \rightarrow {}^7F_{0-3}$ transitions of europium ion. A_{0J} is calculated by applying equation (3) [30–33]

$$A_{0J} = A_{01}(I_{0J}/I_{01})(\nu_{01}/\nu_{0J}) \tag{3}$$

Here, I_{01} and I_{0J} are the integrated intensities; ν_{01} and ν_{0J} are the energy barycenters of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_{0-3}$ transitions respectively. From the emission spectra, it is noticed that $^5D_0 \rightarrow {}^7F_1$ transition does not depend on local chemical environment of Eu^{3+} ion, therefore it may be used as a reference and their value can be calculated to be 50 s^{-1} approximately [34]. The calculated values of A_{rad}, A_{nrad} and η from the above equations are listed in Table 3.

The Judd-Ofelt intensity parameters i.e. Ω_2 and Ω_4 give the information about structural changes around the europium ion in the complexes. Out of these parameters, the Ω_2 is more sensitive to the symmetry and ligand field of the complex which is estimated from the $^5D_0 \rightarrow {}^7F_2$ electronic transition of emission spectra of complexes using equation 3 while Ω_4 is not calculated because $^5D_0 \rightarrow {}^7F_4$ transition is not observed in emission spectra.

$$\Omega_\lambda = 3\hbar c^3 A_{0j}/4e^2\omega^3\chi\left\langle 5_{D0}\middle|U^{(\lambda)}\middle|7_{F_j}\right\rangle^2 \tag{4}$$

Here, ħ is taken as Planck's constant over 2π, c is velocity of light, e is the electronic charge, ω is angular frequency of electronic transition, χ is Lorenz local field correction $[n_0^2\,(n_0^2 + 2)^2/9]$ in which 1.5 average refractive index is used and $\left(5_{D_0}\,\middle|\,U^{(\lambda)}\,\middle|\,7_{F_j}\right)^2$ is taken as 0.0032, representing the square reduced matrix elements [35]. The higher value of Ω_2 intensity

Table 3 The luminescence data of **Eu1** and **Eu2** complexes

Complexes	τ (ms)	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{tot} (s^{-1})	Ω_2(10^{-20} cm^2)	η (%)	CIE coordinates
Eu1	0.70	807.0	621.5	1428.5	15.07	56.5	0.6428, 0.3454
Eu2	0.66	633.5	881.6	1515.1	11.41	41.8	0.6174, 0.3294

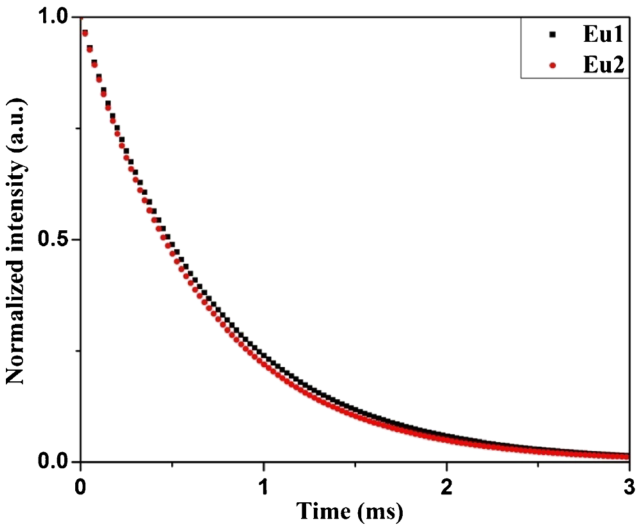


Fig. 7 Luminescence decay curves of **Eu1** and **Eu2** complexes at room temperature in solid state monitored at 613 nm

parameter in **Eu1** as compared to **Eu2** as summarized in Table 3, indicating the highly sensitive nature of $^5D_0 \rightarrow {}^7F_2$ transition and suggesting that the europium ion is presented in highly polarizable chemical environment in these complexes. As a consequence of this, **Eu1** complex possesses higher luminescence intensity than **Eu2** complex which corresponds to the results of emission spectra.

Antenna Effect and Energy Transfer Process

In general, the sensitization process in europium (III) complexes consists of excitation of the organic ligand upto singlet level because the europium(III) ion exhibits very low absorption due to f-f forbidden transition which makes direct excitation of Eu^{3+} ion impossible, therefore the absorption maxima of organic ligand falls in the excitation spectra of complex. First, the energy of excited ligand is transferred from singlet level to triplet level via intersystem crossing (ISC) and then nonradiatively to the ^5D_j manifold, finally to the most emitting $^5D_0$ level of europium(III) ion by internal conversions. Therefore, the effective energy transfer from ligand to Eu^{3+} ion i.e. antenna effect is responsible for intense red emission in the complexes under UV irradiation. The antenna effect of both the complexes (**Eu1** and **Eu2**) depicted in Fig. 8 and Fig. 9 respectively, **Eu1** complex is taken as to describe the antenna effect in detail.

In order to understand the antenna effect, the overlap between the excitation spectrum of **Eu1** complex and absorption spectra of HBMPD and bipy ligands (Fig. 8a) should be considered which suggests that the central europium (III) ion is sensitized by the ligands (HBMPD and bipy) [26, 36–39]. It is also observed that the overlap between **Eu1** complex excitation spectrum and HBMPD absorption spectrum is more than that between **Eu1** complex excitation spectrum and bipy absorption spectrum indicating that the HBMPD ligand is more effective sensitizer than bipy for the europium ion, hence the transfer of intramolecular energy primarily exist between the triplet level of HBMPD ligand and europium ion. Fig. 8b exhibits the overlap between absorption spectrum of europium(III) nitrate and emission spectra of HBMPD as well as bipy ligands, indicating that the both HBMPD and bipy ligands can sensitize the central europium(III) ion [40, 41]. The inset of Fig. 8b depicts the overlap between absorption spectrum of HBMPD and emission of spectrum of bipy,

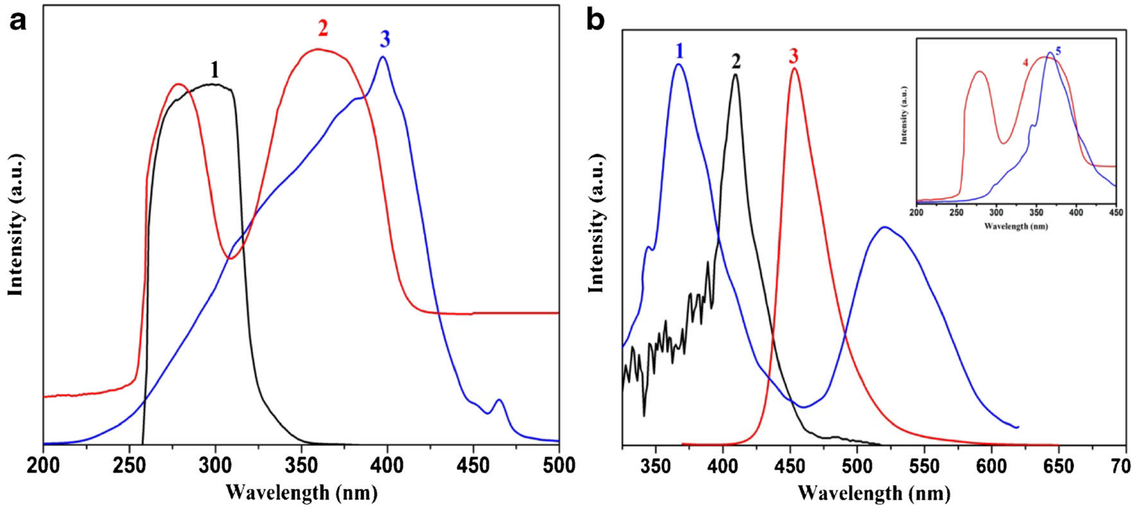


Fig. 8 **a** The absorption spectra of bipy (1) and HBMPD (2); excitation spectrum of **Eu1** monitored at 613 nm (3). **b** The emission spectra of bipy excited at 322 nm (1) and HBMPD excited at 360 nm (3); absorption spectrum of europium(III) nitrate (2). The inset shows the overlap between absorption of HBMPD (4) and emission of bipy spectra (5). All absorption spectra are measured at (1×10^{-5} mol/L) in DMSO. All the spectra are normalized to a constant intensity set at the maximum of the spectra

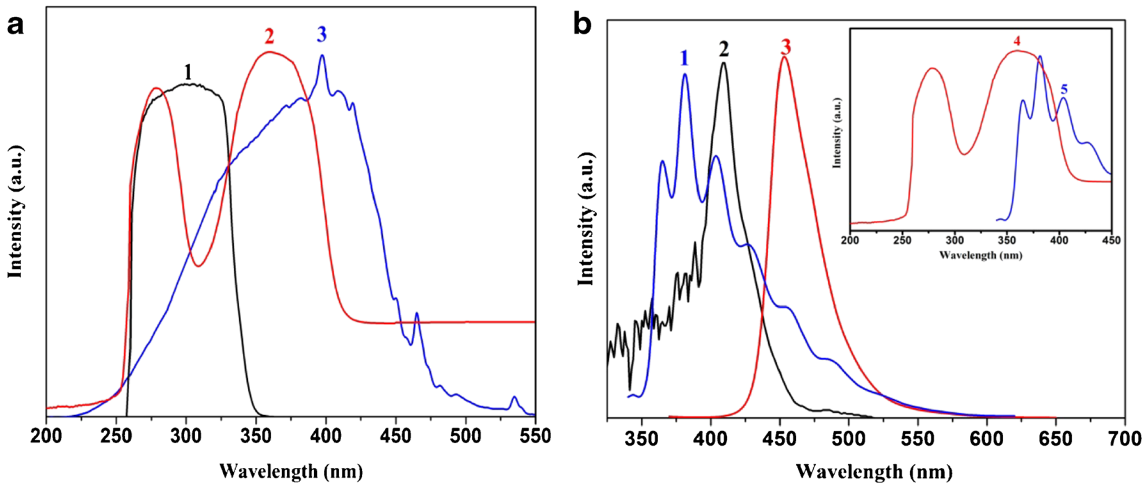


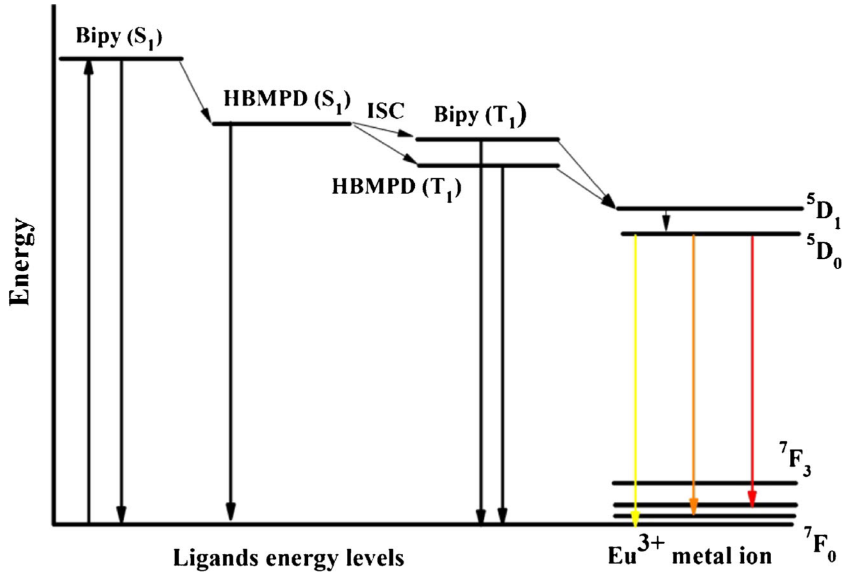
Fig. 9 **a** The absorption spectra of phen (1) and HBMPD (2); excitation spectrum of **Eu2** monitored at 613 nm (3). **b** The emission spectra of phen excited at 322 nm (1) and HBMPD excited at 360 nm (3); absorption spectrum of europium(III) nitrate (2). The inset shows the overlap between absorption of HBMPD (4) and emission of phen spectra (5). All absorption spectra are measured at (1×10^{-3} mol/L) in DMSO. All the spectra are normalized to a constant intensity set at the maximum of the spectra

suggesting that the bipy ligand absorbed the energy firstly which is transferred to the HBMPD ligand as shown in Fig. 10.

The lowest excited singlet (S_1; 23,255 cm^{-1}) and triplet (T_1; 22,538 cm^{-1}) levels of HBMPD ligand are estimated from the UV-visible absorption edge wavelength of spectra and shortest phosphorescence emission wavelength of Gd3 complex (Fig. S1). Similarly, the lowest singlet and triplet levels of bipy (S_1; 29,900 cm^{-1}, T_1; 22,900 cm^{-1}) and phen (S_1; 31,000 cm^{-1}, T_1; 22,100 cm^{-1}) are calculated which match with the literature [42, 43].

To make energy transfer process efficient, the energy gap (ΔE) between emitting level of lanthanides ion (M^{3+}) and ligand triplet level (T_1) should be appropriate i.e. neither too large nor too small according to the Dexter's theory [44]. A large energy gap diminishes the overlapping between the donor and acceptor that decreases the rate of energy transfer while a small energy gap encourages the back energy transfer from metal emitting level to triplet level of ligand. An empirical rule of Latva et al's also suggests that the energy gap ΔE (T_1-M^{3+}) should be in 2000–5000 cm^{-1} range for efficient energy transfer process [45]. The lowest triplet level of HBMPD, bipy and phen are 3812, 4174 and 3374 cm^{-1} respectively above than the emitting level of europium (III) ion (18,726 cm^{-1}) which are well suited for the efficient energy transfer process. From the above discussion the proposed energy transfer process in **Eu1** and **Eu2** complexes is depicted in Fig. 10 and Fig. S2 respectively.

Fig. 10 The proposed energy transfer process in **Eu1** complexes. S_1, lowest excited singlet level; T_1, lowest excited triplet level and ISC, intersystem crossing



Conclusion

In summary, we have successfully synthesized the HBMPD ligand by adopting ecofriendly microwave method and its two new europium (III) complexes. These complexes are characterized by IR, ^{1}H-NMR, elemental analysis and their results clearly demonstrate that the europium(III) ion can be anchored effectively to the ligands molecules through the oxygen atoms of the ›CO group and nitrogen atoms of auxiliary ligands. The TG-DTG analyses indicate the high thermal stability of these materials. The optical properties show that the Eu (III) ion exhibit characteristics intense emission peak at 613 nm in red region and it is present in polarizable chemical environment, acting as only one luminescent center. Furthermore investigation of photophysical properties of these materials clearly reveals that HBMPD ligand acts as sensitizer or antenna and transfers the absorbed energy to the central Eu(III) ion efficiently. It is noteworthy that the N,N donor bidentate auxiliary ligand bipy and phen have synergistic effect with HBMPD ligand which enhance the luminescent features of the complexes. These highly efficient luminescent europium(III) complexes can be employed as excellent emitting material in OLEDs and display devices.

Acknowledgments The present work is financial supported by Council of Science and Industrial Research (CSIR) of India in the form of senior research fellowship (09/382(0155)/2012- EMR-I).

References

1. Koen B (2009) Lanthanide-based luminescent hybrid materials. Chem Rev 109:4283–4374
2. Ken K, Yasuhiro K, Yoshi O (2002) Plastic Optical Fiber Lasers and Amplifiers Containing Lanthanide Complexes. Chem Rev 102: 2347–2356
3. Sebastiaan A, Jos JMH, Van den E, Ilpo M, Maxime AS, Wen TF (2013) Substituted phenanthroline as antennae in luminescent Eu (III) complexes. J Inorg Chem 36:6137–6147
4. Matthew ST, Marlin H, Dalibor S (2007) Cocktails of Tb^{3+} and Eu^{3+} Complexes: A General Platform for the Design of Ratiometric Optical Probes. J Am Chem Soc 129: 7570–7577.
5. Daniel G, Stefan S, Hans GL, Niko H (2013) Six-Color Time-Resolved Förster Resonance Energy Transfer for Ultrasensitive Multiplexed Biosensing. J Am Chem Soc 135:1102–1109
6. Jiang X, Jen AK-Y, Huang D, Phelan GD, Londergan TM, Dalton LR (2002) The effect of ligand conjugation length on europium complex performance in light-emitting diodes. Synth Met 125: 331–336
7. Liang F, Zhou Q, Cheng Y, Wang L, Ma D, Jing X, Wang F (2003) Oxadiazole-Functionalized Europium (III) β-Diketonate Complex for Efficient Red Electroluminescence. Chem Mater 15:1935–1937
8. Fu L, Ferreira RAS, Silva NJO, Fernandes AJ, Ribeiro-Claro P, Goncalves IS, Bermudez VDZ, Carlos LD (2005) Structure–photoluminescence relationship in Eu (III) β-diketonate-based organic–inorganic hybrids Influence of the synthesis method: carboxylic acid solvolysis versus conventionalhydrolysis. J Mater Chem 15:3117–3125
9. de Sá GF, Malta OL, de Mello DC, Simas AM, Longo RL, Santa-Cruz PA, da Silva EF (2000) Spectroscopic properties and design of highly luminescent lanthanide coordination complexes. Coor. Chem Rev 196:165–195
10. Yang L, Gong Z, Nie D, Lou B, Bian Z, Guan M, Huang C, Lee HJ, Baik WP (2006) Promoting near-infrared emission of neodymium complexes by tuning the singlet and triplet energy levels of β-diketonates**.** New J Chem 30:791–796
11. Hernández I. Y.-X Z, Motevalli M, Rendy HCT, Gillina WP, Wyatt PB (2013) Efficient sensitized emission in Yb (III) pentachlorotropolonate complexes. Chem Commun 49: 1933–1935
12. Wang D, Pi Y, Zheng C, Fan L, Hu Y, Wei X (2013) Preparation and photoluminescence of some europium (III) ternary complexes with β-diketone and nitrogen heterocyclic ligands. J. Alloy and Compound 574:54–58
13. Wang D, Zheng C, Fan L, Zheng J, Wei X (2012) Preparation and fluorescent properties of europium (III) complexes with β-diketone ligand and 2, 2-dipyridine or 1, 10-phenanthroline. J. Synt Met 162:2063–2068
14. Shao G, Li Y, Feng K, Gan F, Gong M (2012) Diphenylethyne based β-diketonate europium (III) complexes as red phosphors applied in LED. Sensors Actuat B 173:692–697
15. Taydakov I, Zaitsev B, Krasnoselskiy S, Starikova Z (2011) Synthesis, X-ray structure and luminescent properties of Sm^{3+} ternary complex with novel heterocyclic β-diketone and 1, 10-phenanthroline (Phen). J. Rare Earths 29:719–722
16. Davar F, Hassankhani A, Estarki MRL (2013) Controllable synthesis of metastable tetragonal zirconia nanocrystals using citric acid assisted sol–gel method. Ceram Int 39:2933–2941
17. Mohammadikish M, Davar F, Estarki MRL, Hamidi Z (2013) Synthesis and characterization of hierarchical ZnS architectures based nanoparticles in the presence of thioglycolic acid. Ceram Int 39:3173–3181
18. Francis B, Ambili Raj DB, Reddy MLP (2010) Highly efficient luminescent hybrid materials covalently linking with europium (III) complexes via a novel fluorinated β-diketonate ligand: synthesis, characterization and photophysical properties. Dalton Trans. 39:8084–8092
19. Hasegawa Y, Tsuruoka S-I, Yoshida T, Kawai H, Kawai T (2008) Enhanced Deep-Red Luminescence of Tris (hexafluoroacetylacetonato)samarium(III) Complex with Phenanthroline in Solution by Control of Ligand Coordination. J Phys Chem A 112: 803–807
20. Irfanullah M, Iftikhar K (2010) Hypersensitivity in the Luminescence and 4*f* –4*f* Absorption Properties of Mono- and Dinuclear Eu^{III} and Er^{III} Complexes Based on Fluorinated β -Diketone and Diimine/Bis-Diimine Ligands. J Fluoresc 21:81–93
21. Zucchi G, Murugesan V, Tonfelier D, Aldakov D, Jeon T, Yang F, Thuery P, Ephritikhine M, Geffroy B (2011) Solution, Solid State, And film properties of a structurally characterized highly luminescent molecular europium plastic material excitable with visible light. Inorg Chem 50:4851–4856
22. Wang YB, Zheng XJ, Zhuang WJ, Jin LP (2003) Hydrothermal Synthesis and Characterization of Novel Lanthanide 2,2-Diphenyldicarboxylate Complexes. Eur J Inorg Chem 7:1355–1360
23. Xue FM, Ma Y, LM F, Hao R, Shao GS, Tang MX, Zhang JP, Wang Y (2010) A europium complex with enhanced long-wavelength sensitized luminescent properties. Phys Chem Chem Phys 12:3195–3202
24. Feng R, Jiang F-L, M-Y W, Chen L, Yan C-F, Hong M-C (2010) Structures and Photoluminescent Properties of the Lanthanide Coordination Complexes with Hydroxyquinoline Carboxylate Ligands. Cryst Growth Des 10:2306–2313
25. Li Y-J, Yan B (2010) Photoactive europium(III) centered mesoporous hybrids with 2- thenoyltrifluoroacetone functionalized SBA-16 and organic polymers. Dalton Trans 39:2554–2562

26. 26. Bekiari V, Lianos P (1998) Strongly Luminescent Poly(ethylene glycol)-2,2′-bipyridine Lanthanide Ion Complexes. Adv Mater 10(17): 1455–1458.
27. Wang D, Zheng C, Fan L, Hu Y, Zheng J (2014) Photoluminescence behavior of europium(III) complexes containing 1-(4-tert-butylphenyl)-3-(2-naphthyl)-propane-1,3-dione ligand. Spectrochimica Acta Part A. 117: 245–249.
28. Gago S, Fernandes JA, Rainho JP, Sá Ferreira RA, Pillinger M, Valente AA, Santos TM, Carlos LD, Ribeiro-Carlo PJA, Goncüalves S (2005) Highly Luminescent Tris(β-diketonate)europium(III) Complexes Immobilized in a Functionalized Mesoporous Silica. Chem Mater 17:5077–5084
29. Soares-Santos PCR, Nogueira HIS, Félix V, Drew MGB, Ferreira RAS, Carlos LD, Trindade T (2003) Novel Lanthanide Luminescent Materials Based on Complexes of 3-Hydroxypicolinic Acid and Silica Nanoparticles. Chem Mater 15:100–108
30. Ferreira RAS, Carlos LD, Goncalves RR, Ribeiro SJL, Bermudez VD (2001) Energy-Transfer Mechanisms and Emission Quantum Yields In Eu3 + −Based Siloxane-Poly(oxyethylene) Nanohybrids. Chem Mater 13:2991–2998
31. Teotonio EES, Espínola JGP, Brito HF, Malta OL, Oliveira SF, Foria DLAD, Izumi CMS (2002) Influence of the *N*-[methylpyridyl]acetamide ligands on the photoluminescent properties of Eu(III)-perchlorate complexes. Polyhedron 21:1837–1844
32. Carlos LD, Messaddeq Y, Brito HF, Malta OL, Oliveira SF, Bermudez VD, Ribeiro SJL (2000) Full-Color Phosphors from Europium(III)-Based Organosilicates. Adv Mater 12:594–598
33. Hazenkamp MF, Blasse G (1990) Rare-earth ions adsorbed onto porous glass: luminescence as a characterizing tool. Chem Mater 2:105–110
34. Werts MHV, Jukes RTF, Verhoeven JW (2002) The emission spectrum and the radiative lifetime of Eu^{3+} in luminescent lanthanide complexes. Phys Chem Chem Phys 4:1542–1548
35. Kodaira CA, Claudia A, Brito HF, Felinto MCFC (2003) Luminescence investigation of Eu^{3+} ion in the $RE_2(WO_4)_3$ matrix (RE = La and Gd) produced using the Pechini method. J Solid State Chem 171:401–407
36. Kawa M, Fr chet JMJ (1998) Self-Assembled Lanthanide-Cored Dendrimer Complexes: Enhancement of the Luminescence Properties of Lanthanide Ions through Site-Isolation and Antenna Effects. Chem Mater 10:286–296
37. Carlos LD, Sá Ferreira RA, Rainho JP, Bermudez VDZ (2002) Fine-Tuning of the Chromaticity of the Emission Color of Organic–Inorganic Hybrids Co-Doped with Eu^{III}, Tb^{III}, and Tm^{III}. Adv Funct Mater 12:819–823
38. Okamoto Y, Ueba Y, Dzhanibekov NF, Banks E (1981) Rare earth metal containing polymers. 3. Characterization of ion-containing polymer structures using rare earth metal fluorescence probes. Macromolecules 14:17–22
39. Sabbatini N, Mecati A, Guardigli M, Balzani V, Lehn JM, Zeissel R, Ungaro R (1991) Lanthanide luminescence in supramolecular species. J Lumin 48–49: 463–468
40. Peng CY, Zhang HJ, JB Y, Meng QG, LS F, Li HR, Sun LN, Guo XM (2005) Synthesis, Characterization, and Luminescence Properties of the Ternary Europium Complex Covalently Bonded to Mesoporous SBA-15. J. Phys. Chem. B 109:15278–15287
41. Dang S, Sun LN, Zhang HJ, Guo XM, Li ZF, Feng J, Guo HD (2008) Near-Infrared Luminescence from Sol−Gel Materials Doped with Holmium(III) and Thulium(III) Complexes. J Phys Chem C 112:13240–13247
42. Ambili Raj DB, Francis B, Reddy MLP, Butorac RR, Lynch MV, Cowley H (2010) Highly Luminescent Poly(Methyl Methacrylate)-Incorporated Europium Complex Supported by a Carbazole-Based Fluorinated β-Diketonate Ligand and a 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene Oxide Co-Ligand. Inorg Chem 49:9055–9063
43. Xyu H, Su Q (2003) Photoacoustic and luminescence properties study on energy transfer and relaxation processes of Tb(III) complexes with benzoic acid. J. Photochem. Photobiolog. A 155:73–78
44. Dexter DL (1953) A theory of sensitized luminescence in solids. J Chem Phys 21:836–850
45. Latva M, Takalo H, Mukkala VM, Matachescu C, RodriguezUbis JC, Kankare J (1997) Correlation between the lowest triplet state energy level of the ligand and lanthanide(III) luminescence quantum yield. J. Lumin 75:149–169