Journal of Fluorine Chemistry 181 (2016) 36–44

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Investigations of luminescent behavior and intramolecular energy transfer mechanism of europium(III) complexes with fluorinated β-ketoester ligand

Rekha Devi, Manju Bala, S.P. Khatkar, V.B. Taxak, Priti Boora *

Department of Chemistry, Maharshi Dayanand University, Rohtak 124001, India

ARTICLE INFO

Article history:
Received 8 August 2015
Received in revised form 15 October 2015
Accepted 10 November 2015
Available online 14 November 2015

Keywords:
Luminescence
Eu(III) complexes
Sensitization
β-Ketoester

ABSTRACT

A fluorinated β-ketoester ligand, ethyl-(2-fluorobenzoyl) acetate (EFBA) has been employed to synthesized new europium binary and ternary complexes with ancillary ligands neocuproine (neo), bathophenanthroline (batho), 1,10-phenanthroline (phen) and 2,2-bipyridyl (bipy) in high yield by the solution precipitation method. The ligand (EFBA) and the synthesized complexes $Eu(EFBA)_3 \cdot (H_2O)_2$ (C1), $Eu(EFBA)_3 \cdot$neo (C2), $Eu(EFBA)_3 \cdot$batho (C3), $Eu(EFBA)_3 \cdot$phen (C4), $Eu(EFBA)_3 \cdot$bipy (C5) were characterized by elemental analysis, ^{1}H NMR, IR, UV–vis, thermal analysis (TG/DTG) and luminescence spectroscopy. The thermal analysis results show that the complex is stable up to 231 °C temperature which is sufficient for the normal working of OLEDs. The luminescence measurements indicate that π electron rich organic ligand ethyl-(2-fluorobenzoyl) acetate possessing high absorption coefficient acts as a suitable chromophoric moiety for the transfer of energy to the central Eu^{3+} ion by the process of sensitization, this results in strong emissions band in red spectral region attributed to electric dipole $^5D_0 \rightarrow {}^7F_2$ transition of europium ion. The luminescence intensity further enhanced by the introduction of N-containing ancillary ligands neocuproine, bathophenanthroline, 1,10-phenanthroline, and 2,2-bipyridyl in the ternary complexes C2–C5 because these ligands replace the solvent molecule in the coordination sphere and satisfy the coordination number around central europium ion. The sensitization process in europium complexes is investigated through the proposed energy transfer mechanism. The decay curves observations show the similar chemical environment around the europium ion in all the complexes.

1. Introduction

In last decade, the lanthanide ion based complexes have received intensive and greater attention owing to long luminescence life time, large stoke shift and narrow emission bands of lanthanide ion which makes them strong candidates in many applications like luminescent solar concentrators [1], pH sensing [2], MRI contrast agents [3], UV dosimeters [4] and organic light emitting devices (OLEDs) [5–7]. In lanthanide ions the 4f orbitals are well shielded by 5s and 5p orbitals which results in narrow emission bands and long radiative lifetime arising mainly due to the electronic transitions between specific $4f^n$ energy levels [8]. As 4f–4f transitions are laporte forbidden transitions therefore possess low molar absorption coefficient of lanthanide ion resulting in weak luminescence intensity. Hence this mandates the use of organic ligand having high molar absorption coefficient as a chromophore to indirectly sensitize the metal ion by the transfer of energy from triplet excited state of the ligand to the metal ion by the process of sensitization [9–11]. In the sensitization process the ligand get excited by absorbing the energy in its singlet level which further populates the triplet energy level of ligand by the intersystem crossing (ISC) and then transfer the energy to the emitting level of central metal ion, which finally relaxes through radiative and non-radiative transitions. The efficient transfer of energy requires a good overlap between the triplet excited level of ligand and the emitting level of lanthanide ion. As a consequence, β-ketoester ligand with extended π-conjugation fulfils the above conditions and makes them desirable applicant in the field of luminescent materials [12]. However, the complexes with β-ketoester ligand are vaguely investigated in the literature because such ligands contain high energy C–H and O–H oscillators which non-radiatively quench the emitting level of lanthanide ion and lead to diminished luminescence. To overcome this problem, we have selected fluorinated β-ketoester as main sensitizer as it possesses several potential advantages such as C–F bond has low vibrational frequency which

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* Corresponding author. Tel.: +91 9416175000.
E-mail address: pritiboora@gmail.com (P. Boora).

http://dx.doi.org/10.1016/j.jfluchem.2015.11.004
0022-1139/

can decrease the rate of nonradiative deactivation and also reduces the self quenching phenomenon. Moreover, the C–F bond in ligand can change the molecular packing and it also increases the electron mobility of the complex [13–15]. It is further noticed that the fluorine substitution induces heavy atom effect thereby accelerating the spin orbit coupling, which promotes the ISC (intersystem crossing) phenomenon during energy transfer process, resulting into enhanced luminescence [16–18]. Among lanthanide complexes, the complexes containing Eu(III) ion have gained valuable significance for full color flat panel displays due to their peculiar photophysical properties and intense red emission at 613 nm attributed to $^5D_0 \rightarrow {}^7F_2$ transition. For this purpose, a new fluorinated β-ketoester ligand ethyl-(2-fluorobenzoyl) acetate (EFBA) was employed to synthesize new binary and ternary europium complexes. The ternary complexes contain ancillary ligands beside β-ketoester ligand (EFBA) due to liability of rare earth ion to extend its coordination sphere. An ancillary ligand substitutes the water molecules in its coordination sphere and reduces the non-radiative loss which in turn enhances the luminescence properties of metal complexes [19].

In the present communication, we have synthesized five new Eu(III) complexes with fluorine functionalised β-ketoester as primary ligand and neocuproine, bathophenanthroline, 1,10-phenanthroline and 2,2-bipyridyl as N-containing ancillary ligands. The synthesized Eu(III) complexes (C1–C5) were characterized by elemental analysis, ^{1}H NMR, IR, UV–vis, thermogravimetric analysis and luminescence spectroscopy. The result clearly indicates that these ternary complexes possess higher thermodynamic stability, long luminescence life time and strong emission intensity. The energy transfer mechanism was discussed by calculating the singlet and triplet energy levels of ligand which suggest that the ancillary ligands enhance the process of sensitization by the efficient transfer of energy to the europium ion.

2. Results and discussion

2.1. Properties of the complexes

The analytical data of (C, H and N) and the europium ion content of C1–C5 europium(III) complexes are listed in Table 1. The europium ion content of complexes is estimated by the complexometric titration with the help of EDTA using Eriochrome Black T as an indicator. The results obtained are in good agreement with calculated values on the basis of proposed molecular formula. The results clearly reveal that the composition of complexes confirms the formulas Eu(EFBA)$_3$·(H$_2$O)$_2$ (C1), Eu(EFBA)$_3$·neo (C2), Eu(EFBA)$_3$·batho (C3), Eu(EFBA)$_3$·phen (C4), Eu(EFBA)$_3$·bipy (C5), respectively. All the europium (III) complexes are stable in air, non hygroscopic, white color and are highly soluble in CHCl$_3$ and ethanol solvent.

Table 1
Elemental composition data of europium complexes C1-C5.

Complexes	C (%) found (cal.)	H (%) found (cal.)	N (%) found (cal.)	Eu (%) found (cal.)
C1	48.46 (48.82)	3.96 (4.19)	–	18.21 (18.24)
C2	56.87 (57.36)	4.21 (4.27)	2.76 (2.84)	15.44 (15.05)
C3	61.39 (61.76)	4.05 (4.15)	2.45 (2.52)	13.28 (13.36)
C4	56.35 (56.32)	3.92 (3.97)	2.90 (2.93)	15.44 (15.49)
C5	55.39 (55.41)	3.98 (4.08)	3.04 (3.01)	15.84 (15.89)

2.2. ^{1}H NMR spectra

The characteristic ^{1}H NMR spectral data of free ligand and its europium complexes were recorded in CDCl$_3$ solvent. The spectral data of europium complexes as compared to the free ligand, exhibit apparent changes due to the paramagnetism of the europium(III) ion. The spectra of free ligand displays a singlet of enolic proton at δ 12.69 ppm, methine proton at δ 5.86 ppm and keto CH$_2$ proton at δ 4.39 ppm. The purity of the product was confirmed by the absence of specific peaks of keto CH$_2$ proton and enolic proton in the spectra of complexes C1–C5 [21,22]. In the complexes C1–C5, the peak corresponding to methine proton undergoes slightly up-field as compared to free ligand. The chemical shift for aryl protons in ligands (EFBA, ancillary ligand) shows noticeable changes in the NMR spectra of europium complexes.

2.3. IR spectra

The characteristic IR spectral data of ligand EFBA and its europium complexes C1–C5 are tabulated in Table 2.

The IR spectra displays a broad band at 3471 cm^{-1} and 3417 cm^{-1} attributed to enolic O–H stretching vibration of organic ligand EFBA and coordinated water molecule in the complex C1 respectively. The broad band in the spectra of complexes C2–C5 disappears due to coordination of enolic O–H with the europium ion. The spectra of ligand displays a strong bands at 1625 cm^{-1} and 1538 cm^{-1} accredited to >C=O and >C=C which undergoes red shift in the complexes due to the enlarged π-conjugated system of europium complexes [23]. As compared to IR spectra of free ligand and complex C1, the complexes C2–C5 shows a strong stretching vibration band at 1579–1562 cm^{-1} ascribed to C=N bonds of N-containing ancillary ligands like neocuproine, bathophenanthroline, 1,10-phenanthroline and 2,2-bipyridyl. The absorption peaks in the range of 450–490 and 535–542 cm^{-1} in the spectra of europium complexes correspond to new bonds of Eu–O and Eu–N which are absent in the spectra of the ligand [24].

2.4. Thermogravimetric analysis

The thermogravimetric (TG) and differential thermogravimetric (DTG) analysis of europium complexes were conducted at a heating rate of 10 °C min^{-1} from room temperature to 1050 °C temperature under N-atmosphere. The europium complexes C1–C5 show a similar pattern of thermal analysis curve (TG/DTG) hence the thermal analysis curve of complex C3 is taken as analogue for the thermal decomposition of other europium complexes and represented in Fig. 1. The TG curve shows the

Table 2
The characteristic IR data of the ligand EFBA and complexes.

Complex	ν(O–H)	ν(C=O)	ν(C=N)	ν(C=C)	ν(C–F)	ν(Eu–N)	ν(Eu–O)
EFBA	3471 (b)	1625 (s)	–	1538 (s)	1256 (s)	–	–
C1	3417 (b)	1622 (s)	–	1515 (s)	1250 (s)	–	490 (m)
C2	–	1623 (s)	1579 (s)	1514 (s)	1249 (s)	537 (s)	491 (m)
C3	–	1619 (s)	1562 (s)	1514 (s)	1247 (s)	542 (m)	449 (m)
C4	–	1622 (s)	1579 (s)	1505 (s)	1248 (s)	535 (m)	459 (m)
C5	–	1622 (s)	1578 (s)	1515 (s)	1250 (s)	538 (s)	490 (m)

b = broad, s = strong, m = medium.

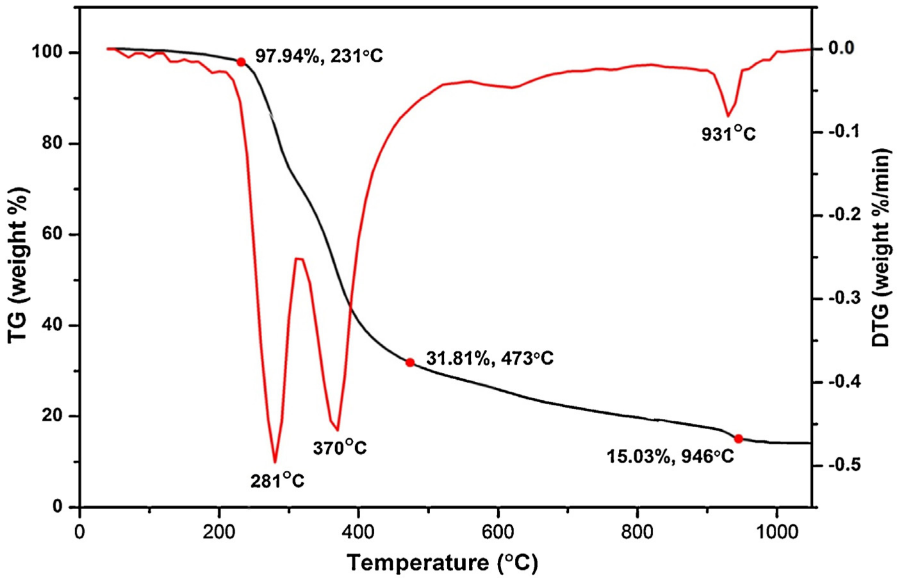


Fig. 1. The TG/DTG curve of complex C3 measured from room temperature to 1050 °C under nitrogen atmosphere.

starting weight loss of approximately 2% from temperature 100–155 °C due to the loss of adsorbed and coordinated water molecules. The first decomposition step occurs from 231 °C to 473 °C accompanied with weight loss of 66.04% due to the elimination of two EFBA molecules and one bathophenanthroline molecule from the europium complex. The second step involves the decomposition of one EFBA molecule started at 473 °C with a weight loss of 17.22% ending at 946 °C. Concordant to these weight losses, the DTG curve of complex exhibit three obvious peaks at 281 °C, 370 °C and 931 °C, respectively. The remaining product approximately 15% corresponds to the formation of europium oxides. The thermal analysis result shows that the europium complexes decomposes at temperature above 150 °C and are thermally stable for the fabrication of light emitting devices.

2.5. Luminescent behavior

2.5.1. UV–vis absorption spectra

UV–vis absorption spectra of the free ligand (EFBA) and the corresponding europium complexes were recorded in chloroform solution ($c = 1 \times 10^{-5}$ M) at room temperature. The spectral profile of Eu(III) complexes are similar to that of free ligand, which demonstrate that the introduction of ligand facilitate the absorption in complexes because Eu(III) ion displays very weak absorption in the selected range due to laporte forbidden transitions [25]. Fig. 2 shows the maximum absorption peak for the ligand EFBA and europium complexes C1–C5 at 310 nm, 317 nm, 319 nm, 315 nm, 318 nm, 316 nm and their corresponding values of extinction coefficient are in range 2.24–2.46×10^5 Lmol^{-1} cm^{-1}, respectively [26]. The bathochromic shift in the absorption value of europium complexes arise mainly due to prominent $\pi \rightarrow \pi^*$ transition of conjugated chromophoric moiety which efficiently transfer the energy to the europium ion [27].

2.5.2. Luminescent spectra

The excitation and emission spectra of binary and ternary Eu(III) complexes in solid state at room temperature are shown in Fig. 3(a)–(e). The excitation spectra of all complexes (C1–C5) monitored at λ_{em} 613 nm illustrates the broad excitation band at 357 nm except for the complex C4 which shows the excitation

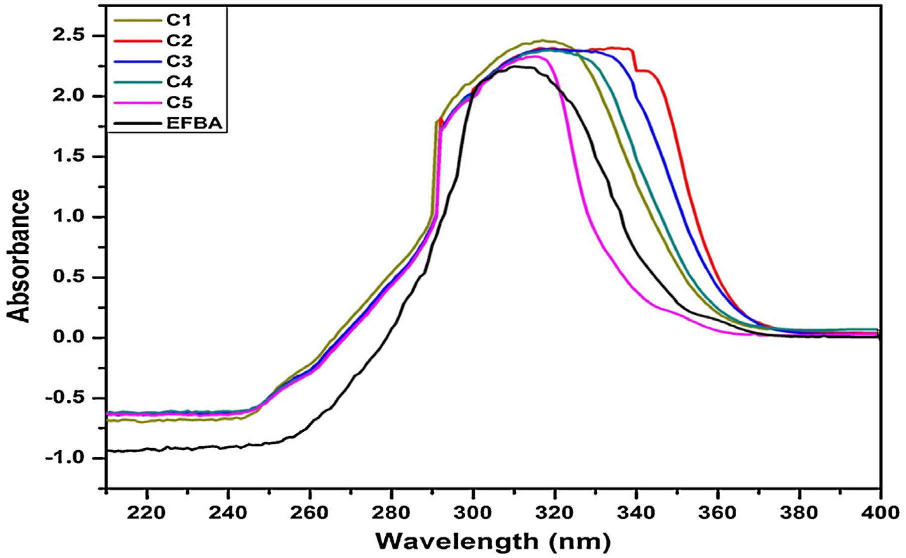


Fig. 2. UV–vis absorption spectra of the ligand EFBA and europium complexes C1–C5 in chloroform solution (1×10^{-5} mol/L).

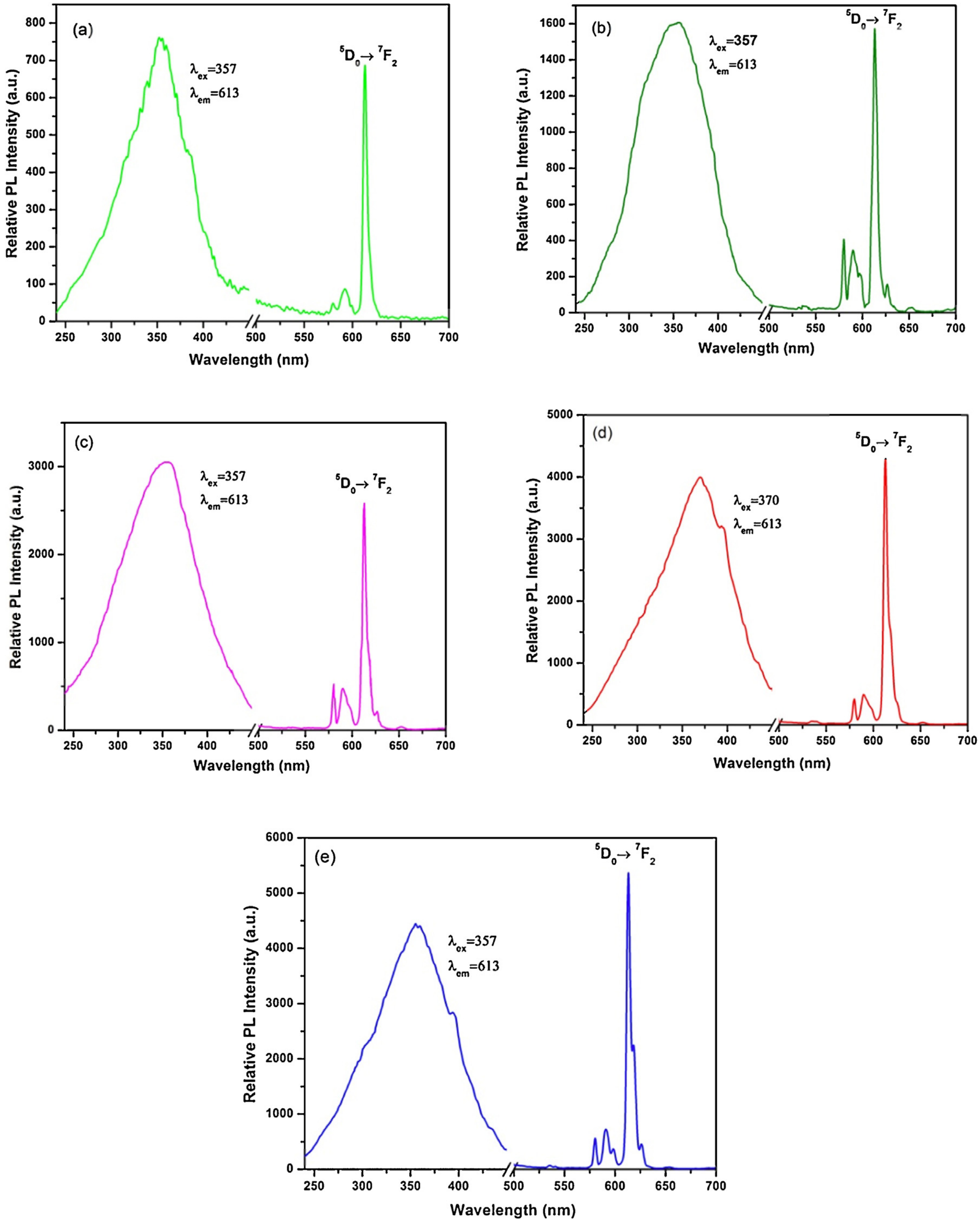


Fig. 3. (a–e) Excitation and emission spectra of complexes C1–C5 in solid state at room temperature.

band at 370 nm. This broad excitation band in the europium complexes ascribed to $\pi \rightarrow \pi^*$ transition of EFBA ligand. The emission spectra of Eu(III) complexes (C1–C5) comprised of many sharp lines in the range 400–700 nm rooting $ʎ_{ex}$ 357 nm (for C4 $ʎ_{ex}$ 370) with 400 PMT voltage set up and 2.5 nm excitation and emission slit width as illustrated in Table 3. The spectra depicts intense emission bands at 580 nm, 590 nm, 613 nm and 652 nm attributed to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ transitions of Eu(III) ion, respectively. Among these transitions the $^5D_0 \rightarrow {}^7F_1$ is magnetic dipole transition insensitive to the local coordination symmetry while $^5D_0 \rightarrow {}^7F_2$ transition is electric dipole allowed which is extremely sensitive to the coordination environment around Eu(III) ion and responsible for the extreme red emission of europium complexes [28]. Further, stark splitting sublevels caused by the external field are shown in $^5D_0 \rightarrow {}^7F_2$ transition which depends on the local symmetry around the luminescent center. The intensity ratio ($I_1/I_2 = {}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$) of electric to magnetic dipole transition lies in range 5–10 and this high intensity ratio reveals that the electric dipole transition has highly asymmetric chemical environment around Eu(III) ion [29,30]. The spectra display $^5D_0 \rightarrow {}^7F_0$ forbidden transition with very low intensity induced by the J-mixing effect [31]. This effect arises due to coupling between the even components of the ligand field Hamiltonian. The intensity

Table 3
Photoluminescence data, color coordinates and decay time of C1–C5 complexes.

Complexes	?$_{ex}$ (cm^{-1}) in nm	?$_{em}$ (cm^{-1}) in nm	Energy transition	Color coordinates (*x*,*y*)	Lifetime (ms)
C1	357 (28,011.21)	580 (17,241.38) 590 (16,949.15) 613 (16,313.21) 652 (15,337.42) 580 (17,241.38)	$^5D_0 \rightarrow {}^7F_0$ $^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_0$	(0.5625, 0.4281)	0.603
C2	357 (28,011.21)	590 (16,949.15) 613 (16,313.21) 652 (15,337.42) 580 (17,241.38)	$^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_0$	(0.6077, 0.3893)	0.615
C3	357 (28,011.21)	590 (16,949.15) 613 (16,313.21) 652 (15,337.42) 580 (17,241.38)	$^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_0$	(0.6210, 0.3766)	0.655
C4	370 (27,027.03)	590 (16,949.15) 613 (16,313.21) 652 (15,337.42) 580 (17,241.38)	$^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$ $^5D_0 \rightarrow {}^7F_0$	(0.6352, 0.3627)	0.668
C5	357 (28,011.21)	590 (16,949.15) 613 (16,313.21) 652 (15,337.42)	$^5D_0 \rightarrow {}^7F_1$ $^5D_0 \rightarrow {}^7F_2$ $^5D_0 \rightarrow {}^7F_3$	(0.6373, 0.3606)	0.865

ratio between the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_2$ transition gives the information about the J-mixing effect and points the interaction between the Eu(III) ion and chemical environment.

The emission of ternary Eu(III) complex containing ancillary ligand is noticed to be highly intense as compared to the binary complex C1 (Fig. 4) due to the quenching caused by the O–H oscillators in the solvent molecule. The result obtained reveals that the ancillary ligand acts as a good sensitizer to effectively transfer the energy to Eu(III) ion [32].

Generally, the color of complexes reported in terms of CIE (Commission Internationale de I' Eclairage) chromaticity coordinates (*x*, *y*). The color coordinates of europium complexes calculated from respective PL spectra are shown in Table 3 and Fig. 5 which depicts that with the introduction of ancillary ligand the coordinates of complexes C2–C5 moves toward optimal red region which can be assigned to reshuffling of emission intensity as compared to complex C1. The CIE color coordinates of the complexes are quiet close to National Television System committee (NTSC, 1987) primary color (0.63, 0.34). These observations prove that these complexes can be used as a red component in white OLEDs.

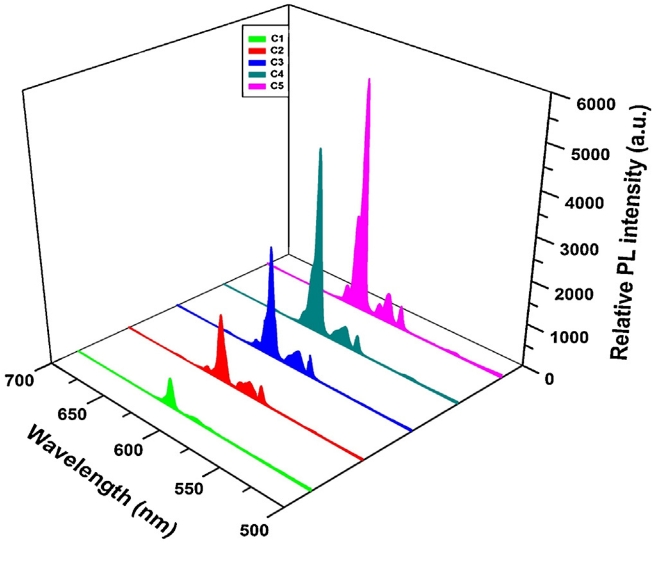


Fig. 4. The emission spectra for complexes C1–C5 in solid state at room temperature excited at 357 nm (for C4 ?$_{ex}$ 370), respectively.

Fig. 6 displays the fluorescence decay profile of $^5D_0$ level of europium(III) complexes (C1–C5) measured by monitoring the emission band of $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm in solid state. The decay time values for the complexes C1–C5 are calculated by the software FL solution for F-7000 spectrophotometer and listed in Table 3. The decay curve obey single exponential function $I = I_0\exp(-t/\tau)$ where τ is the decay time for radiative emission, I_0 and I are the luminescence intensities at time 0 and t respectively. The decay curve clearly reveals the presence of single chemical environment around the central europium ion. The decay time value of all the complexes are comparable (C1; 0.603 ms, C2; 0.615 ms, C3; 0.655 ms, C4; 0.668 ms, C5; 0.865 ms), however slightly longer lifetime for complexes C2–C5 are due to the negligible nonradiative decay and efficient energy transfer from the ancillary ligand to metal ion [33].

The relative quantum efficiency (η) of Eu(III) complexes C1–C5 is calculated by using Rhodamine 6G as a standard compound ($\eta_{std} = 0.5$) in MATLAB software by applying following equation [34]:

$$\eta = \eta_{std}\cdot\frac{I}{I_{std}}\cdot\frac{A_{std}}{A}\cdot\frac{n^2}{n_{std}^2} \qquad (1)$$

η_{std} is the quantum efficiency of the standard compound. A_{std} (0.029) is the absorbance of the standard at the excitation wavelength of 488 nm and A is the absorbance of the complexes with the excitation wavelength of 357 nm for complexes C1–C5 except for C4 (370 nm). Their absorbance values are found to be 0.2877, 0.3405, 0.0897, 0.1103 and 0.75 for complex C1–C5, respectively. I and I_{std} are the integrated intensities of corrected emission spectra of complex and standard compound, respectively. n and n_{std} are the refractive index of the solvent for the complex and standard compound respectively. The europium(III) complexes C1–C5 show the relative quantum efficiency in range 9.06–111.70. This may be the consequence of efficient energy transfer by the ligand and ancillary ligands to the europium(III) ion.

2.5.3. Intramolecular energy transfer mechanism

In order to demonstrate the sensitization pathway in Eu(III) complexes, the proposed mechanism of energy transfer in

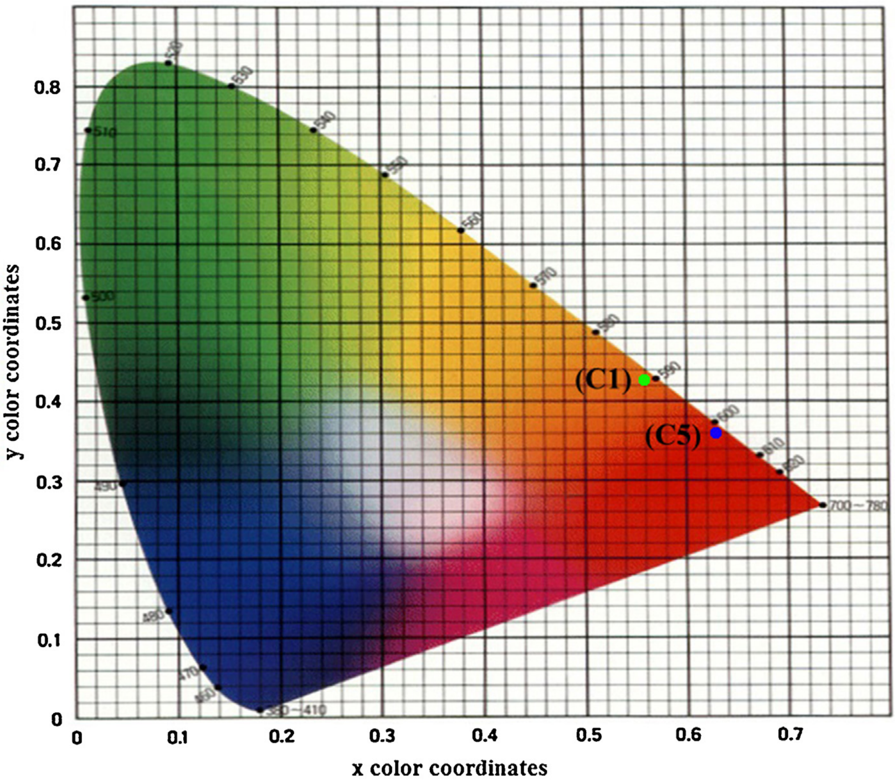


Fig. 5. CIE chromaticity diagram of europium (C1, C5) complexes with ancillary ligand.

europium complexes of distinct skeleton in terms of ancillary ligand (C3–C5) are shown in Figs. S1, S2 and Fig. 7, respectively. The excited singlet and triplet energy levels of ligand EFBA were calculated from the absorbance edge wavelength of UV–vis absorption spectra (Fig. 1) and the shortest wavelength phosphorescence band of the corresponding Gd complex C6 (Fig. S3), respectively [35]. The Gd complexes were selected as a reference complex to determine the energy of triplet level of organic ligand as the energy of lowest emitting level of Gd^{3+} ($^6P_{7/2} \rightarrow {}^8S_{7/2}$) is much higher (32051 cm^{-1}) as compared to the energy of triplet level of EFBA (24154 cm^{-1}) which clearly indicate that Gd^{3+} ion cannot be sensitized by the ligand and tabulated in Table 4, which also involve the energy value of excited singlet (S_1) and triplet (T_1) levels of ancillary ligands batho, phen and bipy as recorded from literature [33].

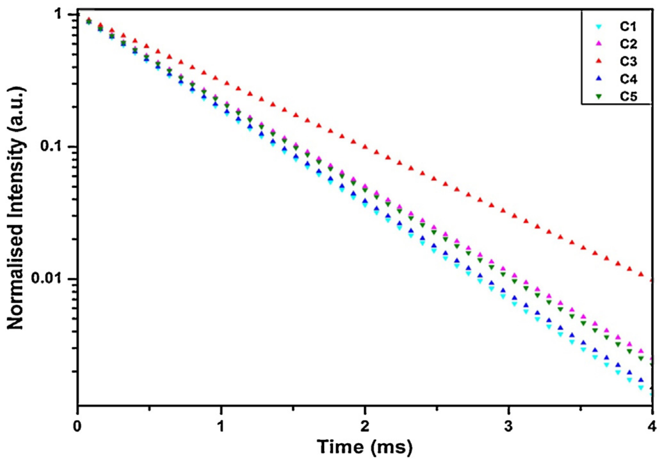


Fig. 6. The luminescence decay curve of europium complexes (C1–C5) at room temperature.

The intersystem crossing (ISC) occurs effectively only with a significant value of energy difference between the singlet and triplet excited levels [ΔE ($S_1 - T_1$)] of ligand. It is clearly revealed by S_1 and T_1 values from the Table 4 that ΔE for ligand EFBA, batho, phen and bipy is 8104 cm^{-1}, 8000 cm^{-1}, 8900 cm^{-1} and 7000 cm^{-1}, respectively which illustrate the efficient intersystem crossing in complexes C3–C5. Latva's empirical rule suggest that the energy gap ΔE ($T_1 - M^{3+}$) should be in range of 2000–5000 cm^{-1} for the effective transfer of energy from triplet excited level of ligand to emitting level of lanthanide ion [36]. The energy gap between triplet energy level of ligand (EFBA, batho, phen and bipy) and emitting level of europium ion is 6913 cm^{-1}, 3759 cm^{-1}, 4859 cm^{-1}, 5659 cm^{-1}, respectively, which indicate that the energy gap between ligand EFBA and Eu^{3+} is not appropriate for the optimal transfer of energy from ligand to Eu^{3+} ion. For the efficient energy transfer, the energy absorbed by EFBA ligand is transferred to the triplet energy level of ancillary ligands first and finally to emitting level of Eu(III) ion which results in higher luminescence intensity of ternary complexes as compared to that of binary complex. This intramolecular energy transfer in Eu^{3+} complexes were supported by the Dexter electron exchange theory and the thermal de-excitation theory. According to Dexter electron exchange theory the process of sensitization is favoured by the appropriate energy difference between the triplet energy level of ligand and emitting level of Eu^{3+} ion which results in higher

Table 4
The excitation energy of EFBA, phen, bipy and batho ligands.

Ligands	Excitation energy in cm^{-1}(eV)	
	Singlet level (S_1)	Triplet level (T_1)
EFBA	32,258 (3.99)	24,154 (2.98)
Phen	31,000 (3.84)	22,100 (2.74)
Bipy	29,900 (3.71)	22,900 (2.83)
Batho	29,000 (3.58)	21,000 (2.59)

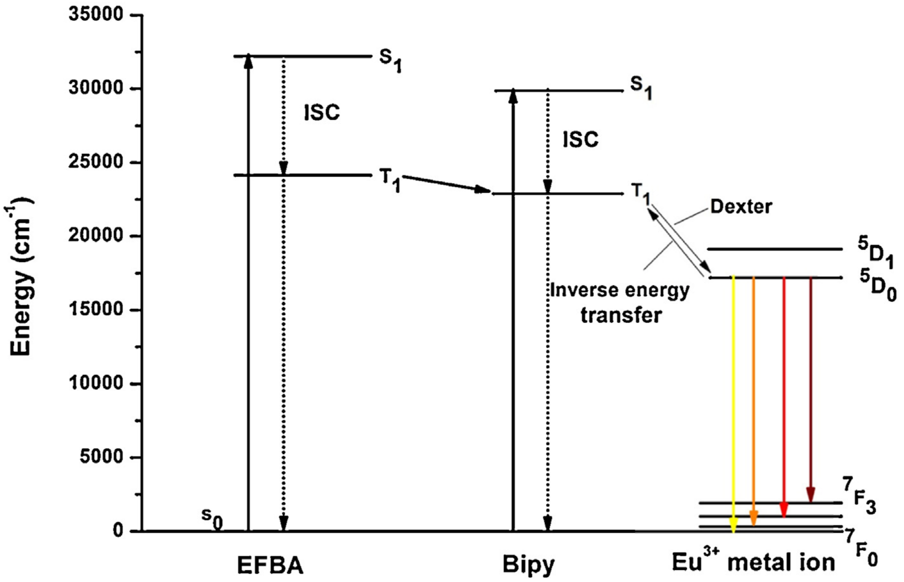


Fig. 7. The schematic energy level diagram and the energy transfer mechanism in Eu(EFBA)$_3$·bipy (C5).

luminescence of complexes [37]. The probability of energy transfer is given as

$$\mathrm{Ps} = \left(\frac{2\pi Z^2}{\mathrm{h}}\right)\int \mathrm{Fs}(E)\cdot\xi s(E)\cdot \mathrm{d}E \qquad (2)$$

where Ps represents the transfer probability constant, Fs(E) is luminescence spectrum of energy donor (ligand), ξs(E) is absorption spectrum of energy acceptor (Eu^{3+}) and 2πZ^2/h is constant relating to mutual distance between Eu^{3+} and coordinating atom.

The thermal de-excitation theory involves the inverse energy transfer from emitting level of Eu(III) ion to the triplet excited level of ligand [38]. The rate of inverse energy transfer is

$$K(T) = \mathrm{A}\cdot e^{-\Delta E/\mathrm{RT}} \qquad (3)$$

where ΔE is the energy difference between the triplet excited level of ligand to emitting level of Eu(III) ion. The lower energy difference between the T_1 of ligand to emitting level of Eu(III) ion facilitate the inverse energy transfer process. Apparently it appears that the energy gap between bipy and Eu(III) ion is much higher as compared to energy gap between batho to Eu(III) ion and phen to Eu(III) ion, therefore it diminished the inverse energy transfer process in complex C5 resulting in high luminescence intensity as compared to complex C3 or C4 in which there is efficient back energy transfer may take place. The above energy transfer mechanism consistent with the luminescent measurements indicating the higher luminescent intensity of ternary complexes C2–C5 as compared to binary complex C1.

3. Conclusion

In summary, the five novel Eu(III) complexes C1–C5 have been synthesized by using a fluorinated β-ketoester as organic ligand and characterized by elemental analysis, IR, ^{1}H NMR, TGA, UV–vis and luminescence spectroscopy. The strong characteristic red emission of Eu^{3+} ion indicates that the ethyl-(2-fluorobenzoyl) acetate (EFBA) ligand acts as a good protector of europium ion from the non radiative losses by the solvent molecules and provides a good sensitization effect for the efficient transfer of energy from ligand to europium ion. The result of emission spectra clearly reveals that the N-containing ancillary ligands neocuproine, bathophenanthroline, 1,10-phenanthroline, and 2,2-bipyridyl have significant effect on the luminescent decay time, chromaticity coordinates and thermal stability of these complexes which makes them as potent material for organic light emitting devices (OLEDs) The energy transfer mechanism also furnishes the utilisation of these europium complexes in the field of development of highly luminescent materials.

4. Experimental

4.1. Starting material

All reagent grade chemicals and solvent employed were commercially available and used as received without further purification. Eu(NO$_3$)$_3$·5H$_2$O and Gd(NO$_3$)$_3$·5H$_2$O with high purity (99.9%) were purchased from Sigma Aldrich.

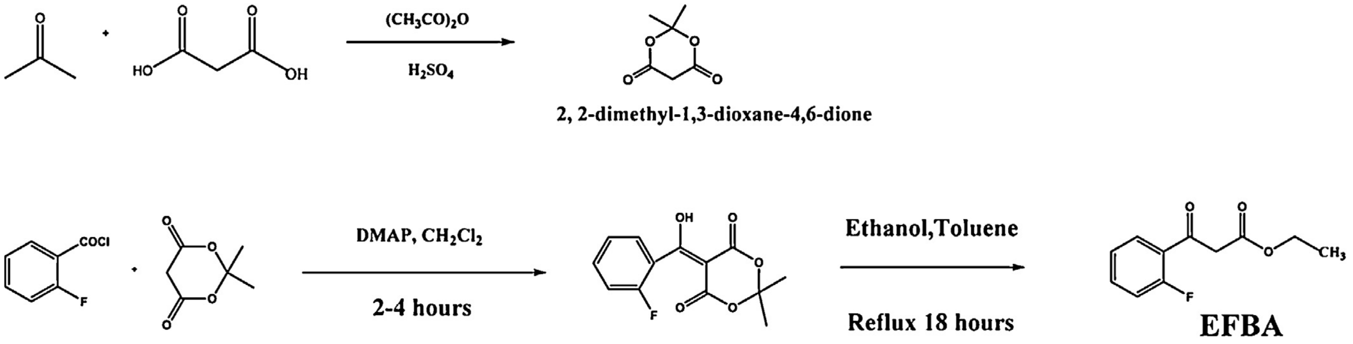
4.2. Physical measurements

All the measurements were carried out at room temperature. The composition of complexes was recorded on Perkin Elmer 2400 CHN elemental analyser. IR spectra were obtained on Perkin Elmer Spectrum 400 spectrometer in dried KBr pellets in the range of 4000–400 cm^{-1}. ^{1}H NMR spectra was obtained in CDCl$_3$ solution on Bruker Avance II 400 NMR spectrometer with tetramethylsilane (TMS) as an internal reference. Luminescence excitation and emission spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer furnished with xenon lamp. The luminescence decay time was recorded by software of the spectrophotometer. Thermal stability of the complexes was measured with SDT Q600 with a heating rate 10 °C/min under nitrogen atmosphere upto 1050 °C. UV–vis absorption spectra of the complexes were recorded with Shimadzu-2450 UV–vis spectrophotometer.

4.3. Synthesis of β-ketoester ligand ethyl-(2-fluorobenzoyl) acetate (EFBA)

The synthesis of ligand EFBA was completed in two steps as given below and illustrated in Scheme 1:

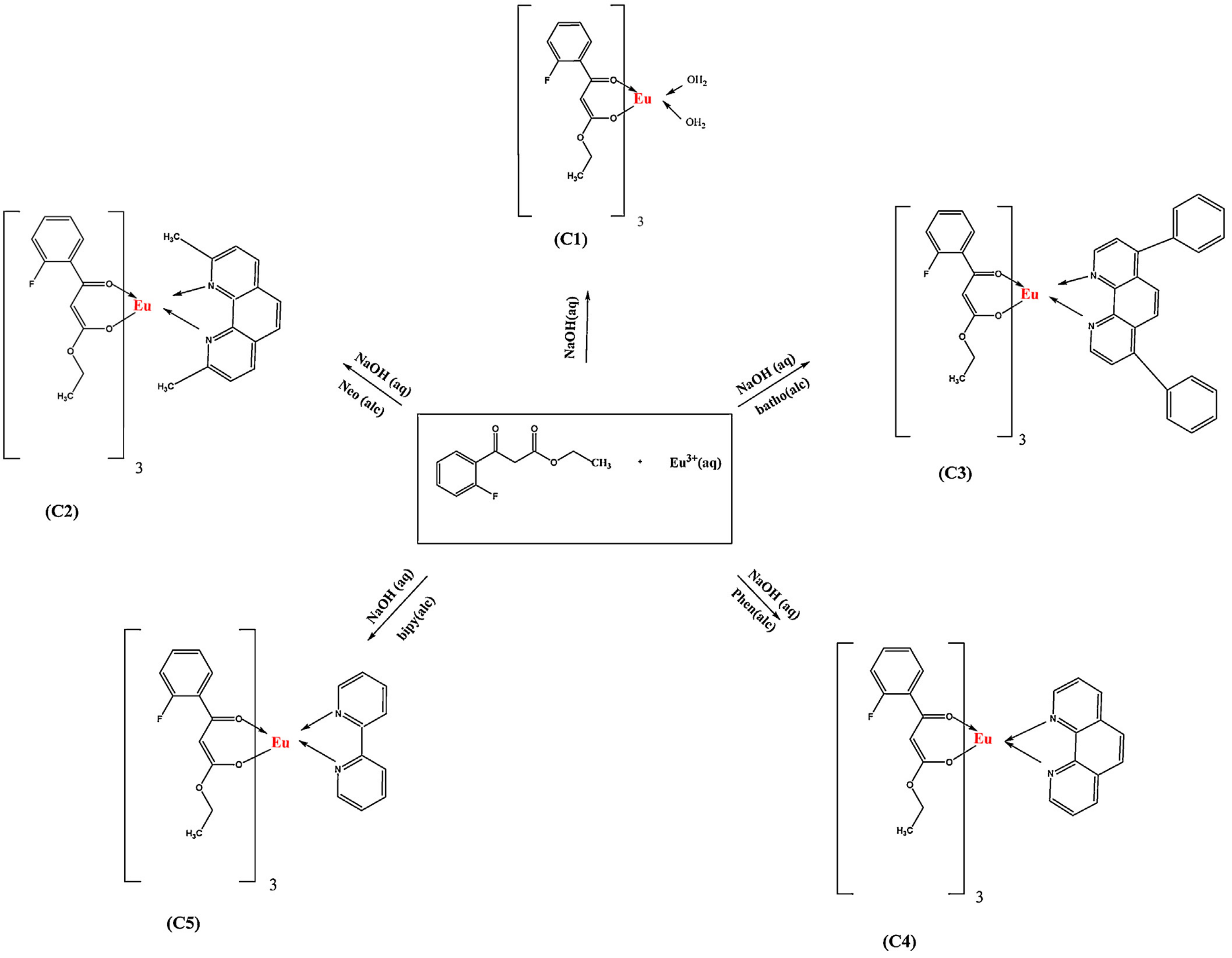
Step 1: 2,2-dimethyl-1,3-dioxane-4,6-dione was prepared by adding a solution of acetone in malonic acid in presence of acid catalyst (H$_2$SO$_4$). Then excess of crushed ice was added and the



Scheme 1. The synthetic route of the ligand EFBA.

reaction mixture was left for 2 h. To the above reaction mixture excess of acetic anhydride was added leading to the formation of product. The product formed was recrystalized with ethanol and used as such for the next step.

Step 2: A mixture is prepared by dissolving 2-fluorobenzoyl chloride and 2,2-dimethyl-1,3-dioxane-4,6-dione in dry methylene chloride (CH_2Cl_2). 4-(Dimethylamino) pyridine was added into the reaction mixture at about 0 °C and stirred for 1 h at room temperature. The resulting mixture was washed with water and then with 1 N HCl and further dried by using anhydrous Na_2SO_4. The product formed was mixed with ethanol in toluene and heated at 90 °C by using reflux condenser for approximately 24 h. The excess ethanol and solvents were removed and progress of reaction was checked by TLC [20]. The final product EFBA was obtained with 52% yield. IR(KBr): cm^{-1} 3471 (b), 3358 (b), 2984 (s), 1743 (s), 1625 (s), 1611 (s), 1538 (s), 1454 (s), 1413 (s), 1328 (s), 1256 (s), 1103 (s), 1028 (s), 812 (s), 765 (m), 594 (m); ^1H NMR ($CDCl_3$, 400 MHz): δ 12.69 (s, 1*H*, enolic OH), 7.36 (m, 4*H*, C_6H_4), 5.86 (s,1*H*, C = CH), 4.39 (s, 2*H* keto CH_2), 4.03 (q, 2*H*, OCH_2CH_3), 1.29 (t, 3*H*, OCH_2CH_3) ppm.



Scheme 2. Synthetic route of the europium complexes C1–C5.

4.4. Synthesis of europium complexes

The synthetic route of binary and ternary europium complexes C1–C5 is demonstrated in Scheme 2. A solution of EFBA (3 mmol) in ethanol was added dropwise to the aqueous solution of europium nitrate (1 mmol) with constant stirring on magnetic stirrer at room temperature. pH of the resulting mixture was set between 6–7 by using dilute NaOH (0.05 M) and white color precipitates were obtained. The resulting precipitates were vaccum filtered along with washing of water and ethanol to remove the unreacted ligand and then dried in vaccum desiccator to obtain the white powder of $Eu(EFBA)_3.(H_2O)_2$ (C1) complex.

$Eu(EFBA)_3{\cdot}(H_2O)_2$ (C1): White powder, yield 79%; IR(KBr): cm^{-1} 3417 (b), 2980 (s), 1740 (s), 1622 (w) 1515 (s), 1406 (s), 1250 (s), 1188 (m), 1028 (s), 917 (s), 848 (s), 797 (s), 766 (s), 747 (s), 673 (m), 624 (m), 490 (m); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.42 (m, 12H, C_6H_4), 2.21 (s, 3*H*, *C* = CH), 4.65 (q, 6*H*, OCH_2CH_3), 1.32 (t, 9*H*, OCH_2CH_3) ppm; Anal. Cal. For $EuC_{33}H_{34}O_{11}F_3$: C, 48.82; H, 4.19; Eu, 18.24; Found: C, 48.46; H, 3.96; Eu, 18.21.

Complexes C2–C5 were prepared by the same procedure as adopted for the synthesis of complex C1 but in addition to the reaction mixture of EFBA (3 mmol) and europium nitrate (1 mmol) there is extra addition of ethanolic solution of neo (1 mmol), batho (1 mmol), phen (1 mmol), and bipy (1 mmol) for the synthesis of ternary europium complexes C2–C5, respectively.

$Eu(EFBA)_3{\cdot}neo$ (C2): White powder, yield 81%; IR(KBr): cm^{-1} 3072 (w), 2979 (s), 1739 (s), 1623 (s), 1579 (s), 1515 (s), 1456 (s), 1362 (m), 1249 (s), 1092 (s), 1029 (s), 917 (s), 849 (m), 795 (m), 766 (m), 674 (m), 563 (s), 537 (s), 491 (m), 443 (m); ^1H NMR ($CDCl_3$,400 MHz): δ 8.21 (d, 2*H*, neo-H), 8.13 (d, 2*H*, neo-H), 7.55 (m, 12H, C_6H_4), 7.27 (d, 2*H*, neo-H), 4.25 (q, 6*H*, OCH_2CH_3), 3.12 (s, 6*H*, neo-H), 2.50 (s, 3*H*, C = CH), 1.27 (t, 9*H*, OCH_2CH_3) ppm; Anal. Cal. For $EuC_{47}H_{42}N_2O_9F_3$: C, 57.36; H, 4.27; N, 2.84; Eu, 15.05; Found: C, 56.87; H, 4.21; N, 2.76; Eu, 15.44.

$Eu(EFBA)_3{\cdot}batho$ (C3): White powder, yield 83%; IR(KBr): cm^{-1} 3062 (w), 2978 (s), 1740 (s), 1619 (s), 1562 (s), 1514 (s), 1430 (s), 1365 (m), 1247 (s), 1092 (s), 1033 (s), 915 (s), 850 (m), 768 (m), 702 (m), 627 (m), 567 (s), 542 (s), 449 (m); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, 2*H*, batho-H), 8.24 (d, 2*H*, batho-H), 8.09 (d, 2*H*, batho-H)), 7.93 (dd, 4*H*, batho-H), 7.40 (m, 12H, C_6H_4), 6.03 (dd, 4*H*, batho-H), 5.72 (t, 2*H*, batho-H), 4.28 (q, 6*H*, OCH_2CH_3), 2.43 (s, 3*H*, *C* = CH), 1.37 (t, 9*H*, OCH_2CH_3) ppm; Anal. Cal. For $EuC_{57}H_{46}N_2O_9F_3$: C, 61.76; H, 4.15; N, 2.52; Eu, 13.36; Found: C, 61.08; H, 3.94; N, 2.74; Eu, 13.28.

$Eu(EFBA)_3{\cdot}phen$ (C4): White powder, yield 82%; IR(KBr): cm^{-1} 3072 (w), 2979 (s), 1735 (s), 1622 (s), 1579 (s), 1505 (s), 1425 (s), 1364 (m), 1248 (s), 1092 (s), 1029 (s), 915 (s), 844 (m), 794 (m), 767 (m), 677 (m), 562 (s), 535 (s), 459 (m), 413 (m);^1H NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, 2*H*, phen-H), 7.91 (s, 2*H*, phen-H), 7.46 (m, 12H, C_6H_4), 7.29 (d, 2*H*, phen-H), 7.10 (dd, 2*H*, phen-H) 4.21 (q, 6*H*, OCH_2CH_3),2.29 (s, 3*H*, C = CH), 1.60 (t, 9*H*, OCH_2CH_3) ppm; Anal. Cal. For $EuC_{45}H_{38}N_2O_9F_3$: C, 56.32; H, 3.97; N, 2.93; Eu, 15.49; Found: C, 56.35; H, 3.92; N, 2.90; Eu, 15.44.

$Eu(EFBA)_3{\cdot}bipy$ (C5): White powder, yield 81%; IR(KBr): cm^{-1} 2980 (s), 1738 (s), 1622 (s), 1578 (s), 1515 (s), 1456 (s), 1363 (m), 1276 (s), 1250 (s), 1093 (s), 1029 (s), 918 (s), 848 (m), 796 (m), 766 (m), 675 (m), 564 (s), 538 (s), 490 (m), 445 (m); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.68 (d, 2*H*, bipy-H), 8.39 (dd, 2*H*, bipy-H), 7.49 (m, 12H, C_6H_4), 7.28 (d, 2*H*, bipy-H), 7.16 (dd, 2*H*, bipy-H), 4.49 (q, 6*H*, OCH_2CH_3), 2.41 (s, 3*H*, C = CH), 1.49 (t, 9*H*, OCH_2CH_3) ppm; Anal. Cal. For $EuC_{43}H_{38}N_2O_9F_3$: C, 55.41; H, 4.08; N, 3.01; Eu, 15.89; Found: C, 55.39; H, 3.98; N, 3.04; Eu, 15.84.

Gadolinium(III) binary complex Gd $(EFBA)_3.(H_2O)_2$ was prepared in order to calculate the triplet energy level of ligand EFBA by adopting the similar procedure as for the europium(III) complexes.

$Gd(EFBA)_3{\cdot}(H_2O)_2$ (C6): White powder, yield 59%; IR(KBr): cm^{-1} 3415 (b), 2982 (s), 1736 (s), 1620 (w) 1517 (s), 1411 (s), 1252 (s), 1184 (m), 1030 (s), 916 (s), 847 (s), 795 (s), 764 (s), 742 (s), 671 (m), 622 (m), 491 (m); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40 (m, 12H, C_6H_4), 2.19 (s, 3*H*, *C* = CH), 4.66 (q, 6*H*, OCH_2CH_3), 1.30 (t, 9*H*, OCH_2CH_3) ppm; Anal. Cal. For $GdC_{33}H_{34}O_{11}F_3$: C, 48.70; H, 4.18; Gd, 18.45; Found: C, 47.88; H, 4.15; Gd, 18.40.

Acknowledgement

One of the authors, Rekha Devi gratefully acknowledge the financial support in the form of junior research fellowship (JRF) from University Grants Commission (UGC), New Delhi, India (Award No: 2121210101).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015.11.004.

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