

Relative Study of Luminescent Properties with Judd-Ofelt Characterization in Trivalent Europium Complexes Comprising ethyl-(4-fluorobenzoyl) Acetate

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Abstract Five new europium(III) complexes Eu(p-EFBA)₃·(H₂O)₂ (C1), Eu(p-EFBA)₃·neo (C2), Eu(p-EFBA)₃·batho (C3), Eu(p-EFBA)₃·phen (C4), Eu(p-EFBA)₃·bipy (C5) have been synthesized by using ethyl-(4-fluorobenzoyl) acetate (p-EFBA) as β -ketoester ligand and neocuproine (neo), bathophenanthroline (batho), 1,10-phenanthroline (phen) and 2,2-bipyridyl (bipy) as ancillary ligands. The synthesized complexes C1–C5 were characterized by elemental analysis, nuclear magnetic resonance spectroscopy (¹H-NMR), infrared (IR) spectroscopy, thermogravimetric analysis (TG/DTG), UV-visible and photoluminescence (PL) spectroscopy. The relative study of luminescence spectra of complexes with the previously reported complexes of isomeric ligand (ortho and meta substituted ligand) indicate the higher luminescence properties of complexes as an effect of fluorine position on β -ketoester ligand. The para substituted ligand shows a remarkable effect on quantum efficiencies and Judd-Ofelt intensity parameters (Ω_2 , Ω_4) of the complexes. The higher value of intensity parameter Ω_2 associated with hypersensitive ⁵D₀ → ⁷F₂ transition of europium(III) ion revealing highly polarizable ligand field. The purposed energy transfer mechanism of complexes indicates the efficient energy transfer in complexes.

Keywords Luminescence · Infrared spectroscopy · Quantum efficiency · Judd-Ofelt intensity parameters · Energy transfer

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Introduction

The interesting luminescent behaviour of organic rare earth complexes initiate the utilization of these complexes in magnetism [1], sensors [2], fluoroimmunoassays [3], chelates for bioanalysis and imaging [4, 5], catalyst [6], luminescent devices and displays [7]. The synthesis of these metal complexes particularly involves the coordination between organic ligand and trivalent lanthanide ion, owing to smaller molar absorption coefficient inherent with 4f-4f transition of lanthanide ion which is not allowed according to Laporte's rule [8–10]. The organic ligand inserted into the coordination environment of lanthanide ion should be able to harvest energy and effectively transfer it to the resonating level of metal ion. Following this pioneer investigation by Weissman and co-worker [11]; a wide variety of complexes involving organic ligand and Eu(III) and Tb(III) ions as main luminescent centers have been synthesized. Based on the different choices of chromophoric organic ligands, functionalised β -ketoester ligands are found to be best candidate for the synthesis of the complexes. Particularly the fluorination of ligand with low energy C-F oscillators reduces the non-radiative energy losses occur due to vibrational energy of C-H oscillators, resulting higher luminescence of metal complexes [12, 13]. In addition, the fluorination of ligand possesses significant effect on the properties of materials mainly contributed by its small size and highest electronegativity. The thermal stability is also affected by the substitution of fluorine on the ligand resulting longer luminescence life time [14]. Thus the fluorinated ligand provide a fascinating prospect in the synthesis of organic metal complexes which prompt us to synthesize a series of complexes based on organic ligand having different position of substituent fluorine and to study the effect of substituent position on the luminescent properties of these complexes.

The present communication deals with the synthesis of five new europium(III) complexes (C1-C5) by using ethyl-(4-fluorobenzoyl) acetate (p-EFBA) as fluorinated β -ketoester ligand and neocuproine, bathophenanthroline, 1,10-phenanthroline and 2,2-bipyridyl as ancillary ligands. All the synthesized complexes were characterized by elemental analysis, ^1H -NMR, IR, thermogravimetric analysis, UV-visible and photoluminescence spectroscopy. The investigation is made on the basis of fluorine substituent position (ortho, meta and para) on the ligand and its effect on the luminescent properties is studied. The luminescence properties of complexes are compared and effect of different position of fluorine is studied. The calculated quantum efficiencies and intensity parameters of complexes further confirms the obtained results.

Experimental

Materials and Methods

The chemicals and solvent used were of reagent grade and used without further purification. Lanthanide nitrates and ancillary ligands used were purchased from commercially available sources. Elemental analyses (C, H and N) of complexes were performed on Perkin Elmer 2400 CHN elemental analyser. The concentration of Eu(III) ion determined by complexometric titration with ethylenediaminetetraacetate (EDTA). Nuclear magnetic resonance spectra (^1H -NMR) were obtained on a Bruker Avance II 400 NMR spectrometer in deuterated chloroform solution by using tetramethylsilane (TMS) as standard. The Infrared spectra (IR) were carried out with Perkin Elmer Spectrum 400 spectrometer in the range of 4000–400 cm^{-1} using dried KBr disks. Shimadzu-2450 UV-Visible Spectrophotometer was employed to measure the UV-visible absorption spectra of the complexes. Thermogravimetric analyses (TG/DTG) were performed at heating rate of 10 $^{\circ}\text{C}/\text{min}$ on SDT Q600. Luminescent (PL) measurements were recorded with Hitachi F-7000 fluorescence spectrophotometer equipped with a xenon lamp as excitation source. The decay time of complexes were calculated by using software (FL solution of F-7000) of the spectrophotometer.

Synthesis

The synthetic route of ligand (p-EFBA) and corresponding europium(III) complexes C1-C5 shown in Scheme 1.

Synthesis of β -ketoester Ligand

To a solution of 4-fluorobenzoyl chloride and 2, 2-dimethyl-1,3-dioxane-4,6-dione in dry methylene chloride, addition of 4-(dimethylamino) pyridine was done at about 0 $^{\circ}\text{C}$ and the

resulting mixture was stirred at room temperature for one hour. The mixture was washed with water and 1 N HCl and then dried by employing anhydrous sodium sulphate. The resulting product was dissolved with ethanol in toluene and heated on reflux condenser at 90 $^{\circ}\text{C}$ for 24 h. Subsequently solvents were allowed to evaporate at room temperature and product formed was recrystallized with ethanol [15]. Ligand ethyl-(4-fluorobenzoyl) acetate (p-EFBA) was obtained with 56% yield. IR(KBr): cm^{-1} 3670 (b), 2984 (s), 1740 (s), 1692 (s), 1648 (s), 1587 (s), 1443 (s), 1412 (s), 1326 (w), 1275 (s), 1217 (s), 1148 (m), 1030 (s), 876 (s), 591 (m); ^1H NMR (CDCl_3 , 400 MHz): δ 12.54 (s, 1H, enolic OH), 7.46 (m, 4H, Ar-H), 5.64 (s, 1H, C = CH), 3.96 (s, 2H keto CH_2), 3.67 (q, 2H, OCH_2CH_3), 1.32 (t, 3H, OCH_2CH_3) ppm.

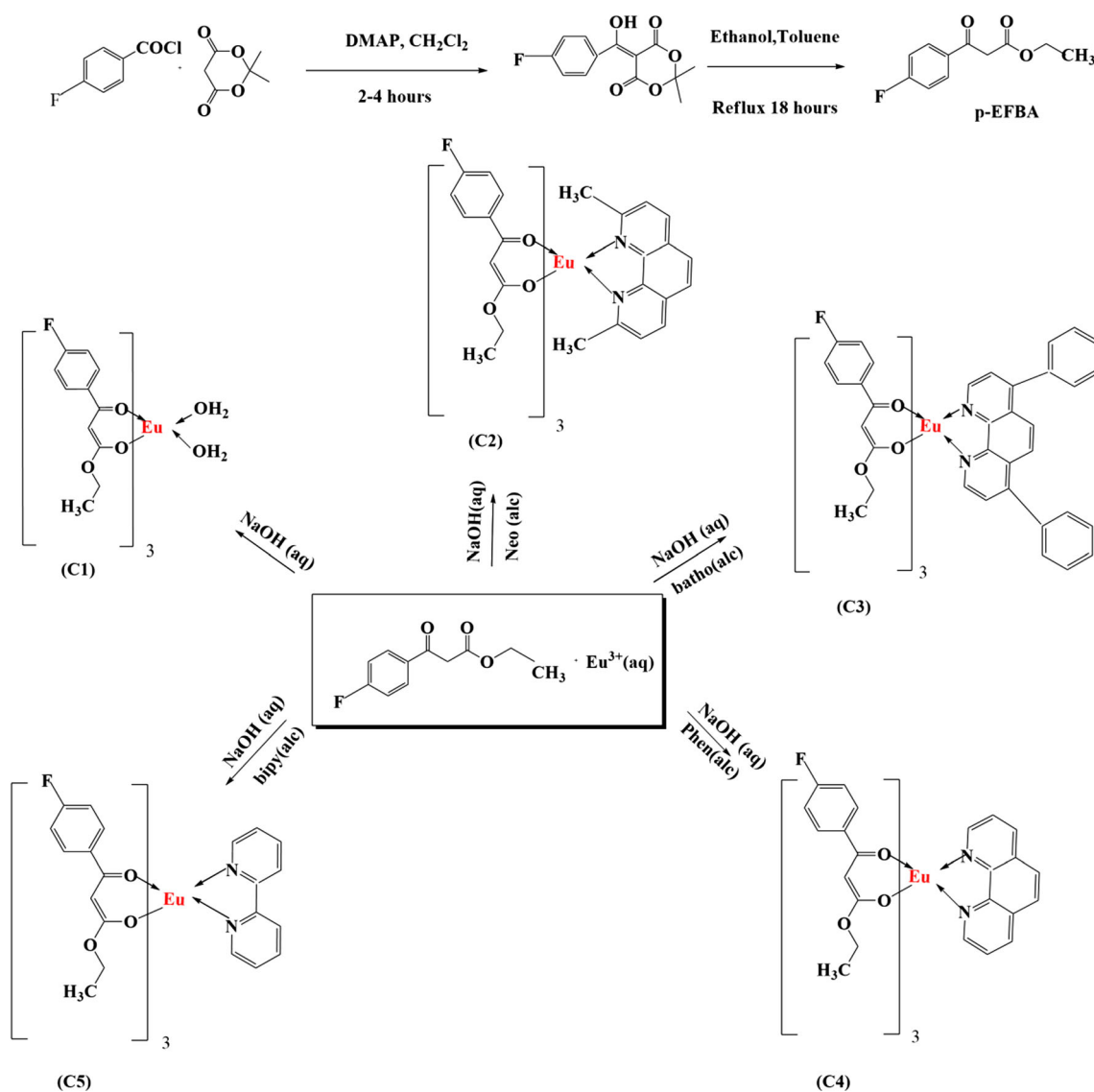
Synthesis of europium(III) Complexes C1-C5

The synthesis of ternary complexes C2-C5 follow the similar procedure as used for the synthesis of binary complex C1 but differed only in addition of 1 mmol ethanolic solution of ancillary ligand (neo batho, phen and bipy) respectively. For the synthesis of complex C1, an ethanolic solution of ligand p-EFBA (3 mmol) was added dropwise to the aqueous solution of europium nitrate (1 mmol) and stirred the mixture on magnetic stirrer. The pH of solution was adjusted (6.5–7) with 0.05 M sodium hydroxide solution, leading to white precipitates in mixture which were collected by filtration. The washing of precipitates with water and ethanol makes complete removal of free ligand from mixture. The white powder of complex C1 was obtained by drying solid residue in vacuum desiccator.

Eu(p-EFBA) $_3$.(H $_2$ O) $_2$ (C1): White powder, yield 79%; IR(KBr): cm^{-1} 3612 (b), 2984 (s), 1733 (s), 1630 (s) 1517 (s), 1480 (s), 1385 (s), 1283 (s), 1215 (s), 1094 (m), 1036 (s), 943 (s), 875 (s), 732 (m), 705 (m), 423 (m); ^1H NMR (CDCl_3 , 400 MHz): δ 7.24 (m, 12H, Ar-H), 4.34 (q, 6H, OCH_2CH_3), 2.69 (s, 3H, C = CH), 1.36 (t, 9H, 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, 48.54; H, 4.13; Eu, 18.19.

Eu(p-EFBA) $_3$.neo (C2): White powder, yield 77%; IR(KBr): cm^{-1} 2984 (s), 2360 (m), 1741 (s), 1628 (s), 1582 (s), 1520 (s), 1478 (s), 1283 (s), 1211 (s), 1171 (s), 1096 (s), 1036 (s), 946 (s), 876 (m), 737 (m), 709 (m), 530 (s), 420 (m); ^1H NMR (CDCl_3 , 400 MHz): δ 8.31 (d, 2H, Ar-H), 7.87 (m, 4H, Ar-H), 7.49 (m, 12H, Ar-H), 4.51 (q, 6H, OCH_2CH_3), 3.49 (s, 6H, Ar-H), 2.61 (s, 3H, C = CH), 1.34 (t, 9H, OCH_2CH_3) ppm; Anal. Cal. For EuC $_{47}$ H $_{42}$ N $_2$ O $_9$ F $_3$: C, 57.36; H, 4.27; N, 2.84; Eu, 15.05; Found: C, 57.21; H, 4.24; N, 2.71; Eu, 14.96.

Eu(p-EFBA) $_3$.batho (C3): White powder, yield 82%; IR(KBr): cm^{-1} 2981 (s), 1738 (s), 1617 (s), 1582 (s), 1518 (s), 1479 (s), 1370 (s), 1279 (s), 1212 (s), 1165 (s), 1096 (s), 1040 (s), 875 (s), 735 (m), 702 (m), 541 (s), 422 (m); ^1H NMR (CDCl_3 , 400 MHz): δ 10.31 (d, 2H, Ar-H), 9.11 (d, 2H, Ar-



Scheme 1 Synthetic route of the ligand and europium(III) complexes C1-C5

H), 8.31 (m, 12H, Ar-H), 7.40 (d, 2H, Ar-H), 6.76 (s, 10H, Ar-H), 4.20 (q, 6H, OCH_2CH_3), 2.52 (s, 3H, $\text{C}=\text{CH}$), 1.39 (t, 9H, OCH_2CH_3) ppm; Anal. Cal. For $\text{EuC}_{57}\text{H}_{46}\text{N}_2\text{O}_9\text{F}_3$: C, 61.76; H, 4.15; N, 2.52; Eu, 13.36; Found: C, 61.57; H, 4.04; N, 2.38; Eu, 13.22.

$\text{Eu}(\text{p-EFBA})_3\text{phen}$ (C4): White powder, yield 81%; IR(KBr): cm^{-1} 2982 (s), 1733 (s), 1624 (s), 1576 (s), 1511 (s), 1481 (s), 1423 (s), 1382 (s), 1311 (s), 1223 (s), 1182 (s), 1092 (s), 1033 (s), 941 (m), 871 (s), 743 (m), 704 (m), 538 (s), 419 (m); ^1H NMR (CDCl_3 , 400 MHz): δ 9.41 (d, 2H, Ar-H), 8.42 (m, 4H, Ar-H), 7.65 (d, 2H, Ar-H), 7.36 (m, 12H, Ar-H), 6.94 (d, 2H, Ar-H), 4.42 (q, 6H, OCH_2CH_3), 2.65 (s, 3H, $\text{C}=\text{CH}$), 1.38 (t, 9H, OCH_2CH_3) ppm; Anal. Cal. For $\text{EuC}_{45}\text{H}_{38}\text{N}_2\text{O}_9\text{F}_3$: C, 56.32; H, 3.97; N, 2.93; Eu, 15.49; Found: C, 56.13; H, 3.76; N, 2.82; Eu, 15.38.

$\text{Eu}(\text{p-EFBA})_3\text{bipy}$ (C5): White powder, yield 79%; IR(KBr): cm^{-1} 2979 (s), 1742 (s), 1622 (s), 1583 (s), 1514

(s), 1483 (s), 1369 (s), 1272 (s), 1215 (s), 1161 (s), 1094 (s), 1036 (s), 942 (s), 876 (s), 732 (m), 708 (m), 529 (s), 428 (m); ^1H NMR (CDCl_3 , 400 MHz): δ 8.55 (d, 2H, Ar-H), 7.98 (d, 2H, Ar-H), 7.56 (m, 4H, Ar-H), 7.30 (m, 12H, Ar-H), 4.31 (q, 6H, OCH_2CH_3), 2.66 (s, 1H, $\text{C}=\text{CH}$), 1.29 (t, 9H, OCH_2CH_3) ppm; Anal. Cal. For $\text{EuC}_{43}\text{H}_{38}\text{N}_2\text{O}_9\text{F}_3$: C, 55.41; H, 4.08; N, 3.01; Eu, 15.89; Found: C, 55.29; H, 3.94; N, 2.91; Eu, 15.71.

Results and Discussion

Composition and Spectroscopic Characterization of Complexes

The elemental analysis data of C, H, N and europium(III) ion of complexes are represented in Table 1. The obtained results are compared with the theoretically calculated values which

Table 1 Elemental analysis data of europium(III) complexes C1-C5

Complexes	C (%) found (cal.)	H (%) found (cal.)	N (%) found (cal.)	Eu (%) found (cal.)
C1	48.54 (48.82)	4.13 (4.19)	-	18.19 (18.24)
C2	57.21 (57.36)	4.24 (4.27)	2.71 (2.84)	14.96 (15.05)
C3	61.57 (61.76)	4.04 (4.15)	2.38 (2.52)	13.22 (13.36)
C4	56.13 (56.32)	3.76 (3.97)	2.82 (2.93)	15.38 (15.49)
C5	55.29 (55.41)	3.94 (4.08)	2.91 (3.01)	15.71 (15.89)

confirms the proposed formulae $\text{Eu}(\text{p-EFBA})_3 \cdot (\text{H}_2\text{O})_2$, $\text{Eu}(\text{p-EFBA})_3 \cdot \text{neo}$, $\text{Eu}(\text{p-EFBA})_3 \cdot \text{batho}$, $\text{Eu}(\text{p-EFBA})_3 \cdot \text{phen}$, $\text{Eu}(\text{p-EFBA})_3 \cdot \text{bipy}$ for complexes C1-C5 respectively.

The infrared spectral data of ligand p-EFBA and corresponding europium(III) complexes C1-C5 are listed in Table 2. In comparing with complexes C2-C5, ligand and complex C1 shows a broad band at 3670 cm^{-1} and 3612 cm^{-1} accredited with vibrational frequency of enolic O-H and absorbed or coordinated water molecule respectively. The absence of band in C2-C5 hinting the coordination of enolic O-H with the europium(III) ion. A shift in vibrational frequencies of $> \text{C}=\text{O}$ and $> \text{C}=\text{C}$ bands in complexes occurs due to extension of π -conjugation in complexes [16]. A strong band at $1576\text{--}1583 \text{ cm}^{-1}$ in complexes C2-C5 assigned to $\text{C}=\text{N}$ bands of coordinating ancillary ligands which are supported by the presence of Eu-N bands in complexes. The binding mode of ligand with europium ion further approved by the appearance of new absorption bands Eu-O at $419\text{--}428 \text{ cm}^{-1}$ in the spectra of complexes C1-C5 [17, 18]. The observation indicates that europium ion coordinated through enolic O-H and $> \text{C}=\text{O}$ group of ligand in complexes.

^1H -NMR spectral analysis of ligand and complexes in the deuterated chloroform solution confirms the bonding mode of ligand with europium(III) ion. In the spectrum of ligand, there is a singlet at 12.54 ppm and 3.96 ppm attributed to enolic O-H and ketonic $-\text{CH}_2$ peak respectively [19]. The coordination of ligand with europium ion is confirmed by the absence of specific proton peak (enolic and ketonic proton) in complexes. Due to paramagnetic behavior of europium ion, a singlet at 5.64 ppm in spectrum of ligand ascribed to methine proton move toward higher field value in spectra of complexes [20].

Table 2 The characteristic IR spectral bands of the ligand p-EFBA and complexes

Complex	$\nu(\text{O-H})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C-F})$	$\nu(\text{Eu-N})$	$\nu(\text{Eu-O})$
p-EFBA	3670 (b)	1692 (s)	-	1587 (s)	1217 (s)	-	-
C1	3612 (b)	1630 (s)	-	1517 (s)	1215 (s)	-	423 (m)
C2	-	1628 (s)	1582 (s)	1520 (s)	1211 (s)	530 (s)	420 (m)
C3	-	1617 (s)	1582 (s)	1518 (s)	1212 (s)	541 (m)	422 (m)
C4	-	1624 (s)	1576 (s)	1511 (s)	1223 (s)	538 (m)	419 (m)
C5	-	1622 (s)	1583 (s)	1514 (s)	1215 (s)	529 (s)	428 (m)

Thermal Behaviour (TG/DTG)

The thermal analysis (TG/DTG) of europium(III) complexes are carried out from ambient temperature to 1070°C under the environment of nitrogen gas along with a heating rate of $10^\circ\text{C min}^{-1}$. Figure 1 depict the decomposition processes of complex $\text{Eu}(\text{p-EFBA})_3 \cdot \text{bipy}$, chosen as representative for all the complexes as an effect of similar pattern followed by them. The TG curve demonstrate the start of decomposition around 235°C and continue upto 507°C with a loss of weight 66.94% (theoretical weight loss 67.34%) indicating the loss of three organic ligand coordinating to europium ion in the complex. The second stage of decomposition occurs in the temperature range of $507^\circ\text{C}\text{--}959^\circ\text{C}$ with a loss of 16.65% weight (theoretical weight loss 16.75%) estimated with the removal of 2,2-bipyridine ligand from complex. The DTG curve of complex also support the decomposition pattern by the presence of peaks at 271°C and 951°C corresponds with the weight losses. Finally remaining product of approximately 14.58% associated with the oxides of europium. The analysis indicate the higher thermal stability of europium complexes.

UV-Visible Absorption Spectra

The UV-visible absorption spectra of ligand (p-EFBA) and its corresponding binary and ternary Eu(III) complexes are shown in Fig. 2. The measurements were made in chloroform solution at room temperature in the range 200–400 nm. The free ligand shows strong absorption at 318 nm. Although the spectral profile of europium(III) complexes were similar to that of ligand but chelating nature of ligand around central metal ion extends the conjugated system as well as electron density around ion which causing the absorption bands of complexes to shift toward higher wavelength [21].

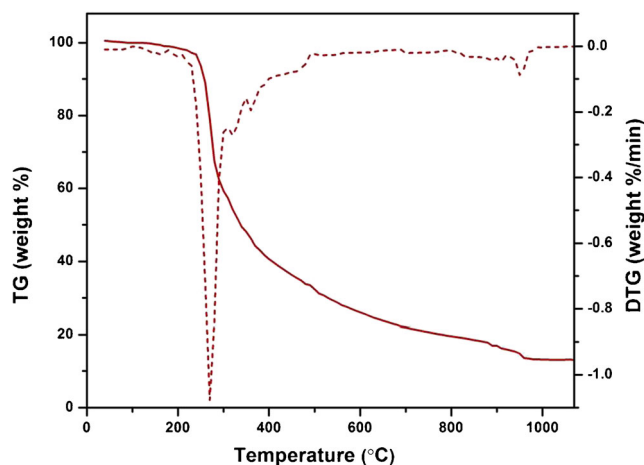


Fig. 1 The TG/DTG curve of complex $\text{Eu}(\text{p-EFBA})_3\cdot\text{bipy}$ recorded under nitrogen atmosphere

Photoluminescence Spectra

Figures 3 and 4 represents the excitation and emission spectra of complexes obtained at room temperature by indexing the intense emission band $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and broad excitation band $^7\text{F}_0 \rightarrow ^5\text{D}_4$ respectively. The excitation spectra of complexes consist of a broad band at 366–369 nm assigned to $\pi \rightarrow \pi^*$ transition of ligand, alongwith a narrow peak at 463 nm (C1–C3, C5) and 466 nm (C4) associated with intraconfigurational $4f\text{-}4f$ transition $^7\text{F}_0 \rightarrow ^5\text{D}_2$ of europium ion [22]. The higher intensity of broad band clearly suggests the role of ligand in energy transfer processes to metal ion.

The emission spectra of europium(III) complexes C1–C5 shows magnificent luminescence behaviour on excitation with UV light. The spectra were measured in 500–700 nm range with slit width of 2.5 nm and voltage of 400PMT in the solid state. Figure 4 displays the characteristic emission peaks

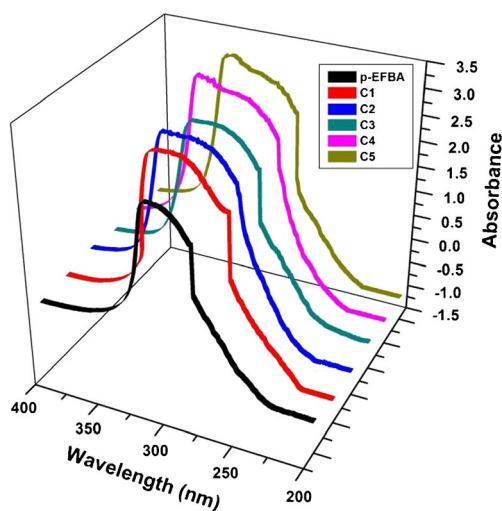


Fig. 2 UV-visible absorption spectra of the ligand p-EFBA and europium(III) complexes C1–C5

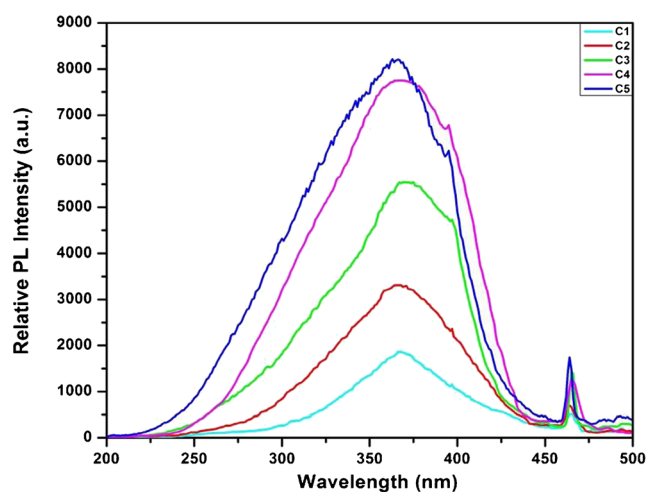


Fig. 3 Excitation spectra of complexes C1–C5 in solid state at room temperature

$^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ of europium ion at 580 nm, 590 nm, 613 nm, 652 nm and 686 nm arise as a result of intraconfigurational transitions from the emitting state ($^5\text{D}_0$) to the low lying multiplet $^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) of central metal ion [23]. The spectra of complexes are devoid of peaks related to free ligand pointing out the efficient sensitization mechanism in complexes. In accordance with the selection rule followed by the forced electric and magnetic dipole transition, the intense emission peak at 612 nm associated with the electric dipole transition and weaker intensity band at 590 nm belongs to magnetic dipole transition [24]. The intensity ratio of these characteristic bands imparts useful information about the coordination environment of central metal ion. The complexes shows a centrosymmetric behaviour around the europium ion with an intensity ratio lower than 0.7 while the value higher than 8 reflects the asymmetric environment possessed by luminescent centre [25]. Thus the higher intensity ratio of studied complexes directs the asymmetric

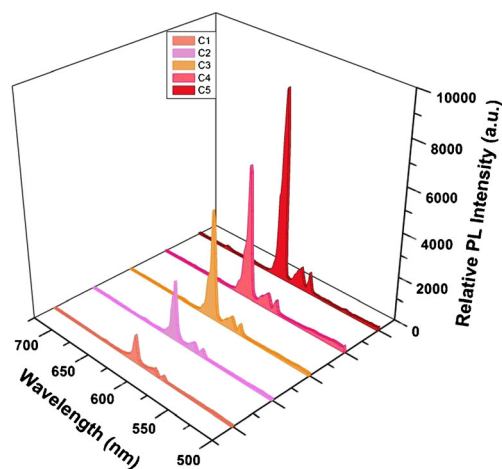


Fig. 4 Emission spectra of complexes C1–C5 in solid state at room temperature

environment around Eu(III) ion which is also pointed by the presence of stark splitting in emissions bands of complexes. The emission spectra also indicate a weak emission band at 535 nm attributed to $^5D_1 \rightarrow ^7F_0$ transition of europium ion. As a result of weak interaction between the ligand field Hamiltonian and central europium ion there is appearance of electric and magnetic forbidden transition $^5D_0 \rightarrow ^7F_0$ in the spectra [26]. Additionally, the spectra also shows the presence of primarily forbidden $^5D_0 \rightarrow ^7F_3$ transition of Eu(III) ion. The complexes shows similar behaviour of emission spectra with an increasing intensity parameter from C1-C5 due to the presence of ancillary ligands in complexes (C2-C5) which restrict the O-H vibrations and thermal quenching resulting enhanced luminescence of complexes. The substitution of ancillary ligands also diminished the non radiative losses of energy and effectively increases the luminescence [27]. Figure 5 clearly displays the higher luminescence properties of complexes from the previously reported complexes of isomeric ligands on the basis of combined effects of electron withdrawing and resonance phenomenon attributed to position of substituent fluorine in the ligand [28]. The photoluminescence data of complexes C1-C5 tabulated in Table 3.

The CIE (Commission Internationale de l'Eclairage) color coordinate diagram are applied to observe the luminescence intensity of organic metal complexes in terms of x and y values. The coordinates (x, y) recorded by employing the emission spectra of complexes and given in Table 3. The coordinates of complexes fall in red region of diagram but due to close proximity between values only C1 and C5 values shown in Fig. 6. The calculated values are comparable with the Society of Motion Picture and Television (SMPTE, x = 0.63, y = 0.34), National Television System committee (NTSC 1987, illuminant red 0.63, 0.34) and European Broadcasting Union (EBU illuminant red 0.64, 0.33) reference color systems. The observed values mark the complexes as worthy candidates in regime of luminescent materials.

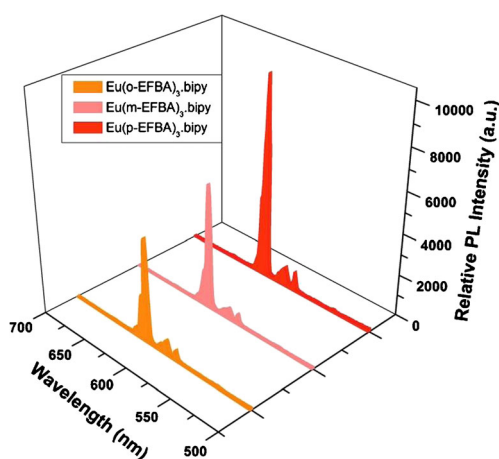


Fig. 5 Relative luminescence of ortho, meta and para derivative complexes of β -ketoester ligand

Luminescence Quantum Efficiency (η) and Judd-Ofelt Parameters

The luminescence quantum efficiency (η) is an important parameter to study the sensitization effect of ligand field on the central metal ion. Hence to calculate quantum efficiencies, an investigation based on luminescence decay time and emission intensity of complexes has been made [29]. The luminescence decay curve of europium(III) complexes C1-C5 are recorded by monitoring the intense emission band $^5D_0 \rightarrow ^7F_2$ at 613 nm and displayed in Fig. 7. Decay curve of all complexes show monoexponential behaviour which is directed by the equation $I = I_0 \exp(-t/\tau)$ where τ is the life time for radiative emission, I_0 and I are the luminescence intensities at time 0 and t respectively, suggesting presence of similar ligand field around europium(III) ion [30]. The obtained results are listed in Table 3. By inverting this luminescence lifetime, total transition rates of radiative (A_{rad}) and nonradiative (A_{nrad}) processes can be calculated according to equation [31]

$$A_{\text{total}} = 1/\tau = A_{\text{rad}} + A_{\text{nrad}} \quad (1)$$

The radiative rate A_{rad} can be calculated by carrying out the sum of individual radiative rate A_{0J} for each emission transition ($^5D_0 \rightarrow ^7F_J$) of europium ion. The individual transition rates can be estimated by the given equation [32]

$$A_{0J} = A_{01}(I_{0J}/I_{01})(\nu_{01}/\nu_{0J}) \quad (2)$$

where A_{01} is the spontaneous emission coefficient for $^5D_0 \rightarrow ^7F_1$ transition having a value found to be 50 s^{-1} [33]. Depending on the independent coordination environment around europium(III) ion for magnetic dipole transition, A_{01} is used as standard to calculate the A_{0J} value for each transition ($J = 0, 2, 3, 4$) of europium ion. ν_{0J} is the energy barycentre and I_{0J} is the integrated emission intensity for different transitions ($^5D_0 \rightarrow ^7F_J$) respectively.

The radiative and nonradiative processes affect the quantum efficiency of complexes as expressed by following equation [34]

$$\eta = A_{\text{rad}}/A_{\text{rad}} + A_{\text{nrad}} \quad (3)$$

The results for efficiency parameters are tabulated in Table 3. The higher quantum efficiency of complexes indicates that ligand acts as good sensitizer for europium ion.

The Judd-Ofelt intensity parameters Ω_λ ($\lambda = 2, 4$) of europium(III) complexes C1-C5 were estimated by making utilisation of calculated radiative transition rate (A_{rad}) and Judd-Ofelt theory which was developed by Judd and Ofelt for the analysis of laporte forbidden 4f-4f electronic transitions [35]. The intensity parameters

Table 3 Photoluminescence data of complexes C1-C5 in solid state

Complexes	CIE Coordinates (x, y)	τ (ms)	A_{total} (s^{-1})	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	η (%)
C1	(0.6301, 0.3691)	0.466	2145	369	1776	6.41	0.18	17.2
C2	(0.6309, 0.3684)	0.570	1754	449	1305	7.49	0.25	25.6
C3	(0.6388, 0.3605)	0.594	1683	531	1152	9.31	0.26	31.6
C4	(0.6318, 0.3674)	0.655	1526	537	989	9.43	0.24	35.2
C5	(0.6436, 0.3558)	1.181	846	597	297	10.7	0.35	69.4
Eu(o-EFBA) ₃ .bipy	(0.6077, 0.3893)	0.668	1156	473	683	8.31	—	40.9
Eu(m-EFBA) ₃ .bipy	(0.6431, 0.3563)	0.760	1305	576	729	10.11	0.25	44.1

Ω_λ for the emissions $^5D_0 \rightarrow ^7F_J$ ($J = 2, 4$) can be calculated by following equation [36]:

$$\Omega_\lambda = 3 \hbar c^3 A_{0j} / 4e^2 \omega^3 \chi \left(\langle 5D_0 | U^{(\lambda)} | 7F_J \rangle \right)^2 \quad (4)$$

Where $\chi = n^2(n^2 + 2)^2/9$ is Lorentz local field correction, n is the refractive index (1.5) and e is the electronic charge (4.80×10^{-10} esu) used. $\langle 5D_0 | U^{(\lambda)} | 7F_J \rangle^2$ are the square reduced matrix elements 0.0032 ($J = 2$) and 0.0023 ($J = 4$) respectively. The Judd-Ofelt intensity parameters for complexes C1-C5 are represented in Table 3.

The intensity parameter for transition $^5D_0 \rightarrow ^7F_2$ (Ω_2) related with the hypersensitive and covalence character of chemical environment around europium(III) ion while Ω_4 associated with the interionic bond distances [37]. The intense emission of transition $^5D_0 \rightarrow ^7F_2$ leads to stronger radiative rates and resulting much higher value of Ω_2 as compared to Ω_4 in all the complexes [38]. A comparative analysis of efficiency and intensity parameters of highly intense complex Eu(p-EFBA)₃.bipy (C5) with the previously reported complexes Eu(o-EFBA)₃.bipy and Eu(m-EFBA)₃.bipy shown in

Table 3 which clearly reveals the effect of fluorine position on the luminescent properties and confirms that para position of fluorine is most significant for the development of highly luminescent complexes [39, 40].

Energy Transfer Mechanism

The purposed intramolecular energy transfer mechanism for highly intense complex C5 is shown in Fig. 8 to describe the sensitization process in complexes. In the sensitization process, first of all ligand gets excited to its singlet state by absorbing energy and then from singlet excited state to triplet excited state by the process of intersystem crossing (ISC). The triplet excited state of ligand transfers energy to the emitting level of europium ion [41]. Hence singlet and triplet excited states (S_1 ; 27,472 cm^{-1} , T_1 ; 22,271 cm^{-1}) of ligand play a significant role in energy transfer and calculated from UV-visible absorbance edge and phosphorescence spectra of corresponding gadolinium complex respectively [42]. The phosphorescence spectrum of complex is displayed in Fig. 9. The singlet and triplet excited states of

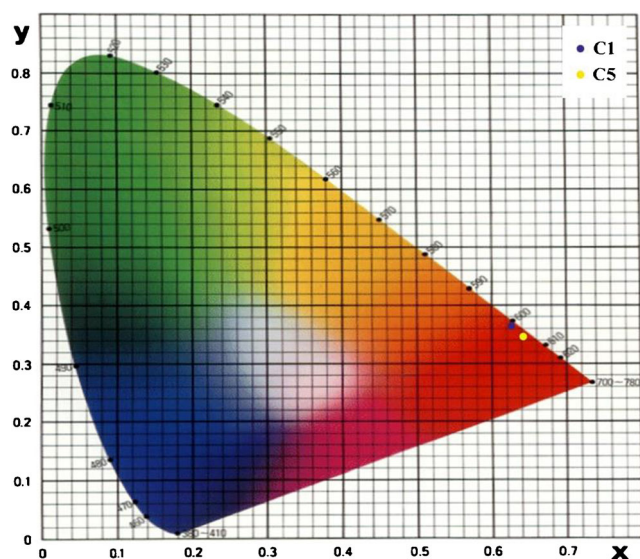
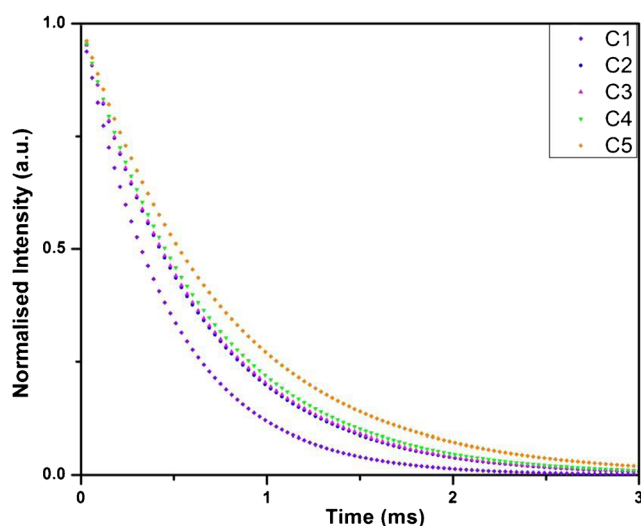
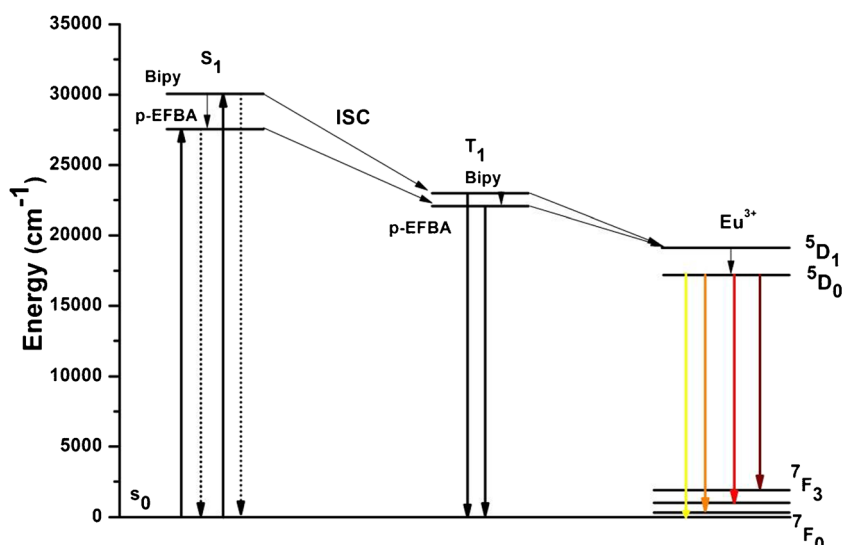
**Fig. 6** CIE color coordinate diagram of europium(III) complexes C1 and C5**Fig. 7** The luminescence decay curve of europium(III) complexes (C1-C5) at room temperature

Fig. 8 The energy transfer mechanism in complex $\text{Eu}(\text{p-EFBA})_3\text{bipy}$ (C5)



ancillary ligand bipy ($29,900\text{ cm}^{-1}$, $22,900\text{ cm}^{-1}$), phen ($31,000\text{ cm}^{-1}$, $22,100\text{ cm}^{-1}$) and batho ($29,000\text{ cm}^{-1}$, $21,000\text{ cm}^{-1}$) are calculated and found to be well matched with the literature [12].

The effective energy transfer in complexes attributed as a result of suitable energy difference between triplet state of ligand to the resonating level of europium(III) ion according to Latva's empirical rule suggesting an optimal energy gap ΔE ($T_1\text{-M}^{3+}$) of the range $2000\text{--}5000\text{ cm}^{-1}$ [43]. The triplet level of ligand tailored to maintain the upper emitting level $^5\text{D}_1$ ($18,691\text{ cm}^{-1}$) and then vibrationally relaxes to the lower emitting level $^5\text{D}_0$ ($17,241\text{ cm}^{-1}$). From this emitting level $^5\text{D}_0$ releases energy to ground $^7\text{F}_j$ levels of europium ion and gives the luminescence [44]. Figure 8 clearly depicts that T_1 state of ancillary ligand first absorb energy and then transfer this energy to the triplet level of p-EFBA, from this level the

energy transmitted to the $^5\text{D}_1$ level of europium ion. This also suggests the role of ancillary ligand in the enhancement of luminescence for complexes. The T_1 levels of phen and batho ligand are lower and may be associated with back energy transfer processes resulting weaker luminescence complexes (C3, C4) compared to complex C5. The Dexter theory [45] and thermal de-excitation theory [46] helps to conclude the energy transfer processes in complexes.

Conclusion

In this study, a series of europium(III) complexes C1-C5 have been synthesized and characterized by elemental analysis, IR, $^1\text{H-NMR}$, UV-visible, TG/DTG and PL spectroscopy. The effect of position of substituent fluorine on the luminescence properties of complexes $\text{Eu}(\text{p-EFBA})_3(\text{H}_2\text{O})_2$ (C1), $\text{Eu}(\text{p-EFBA})_3\text{neo}$ (C2), $\text{Eu}(\text{p-EFBA})_3\text{batho}$ (C3), $\text{Eu}(\text{p-EFBA})_3\text{phen}$ (C4), $\text{Eu}(\text{p-EFBA})_3\text{bipy}$ (C5) was investigated successfully. The enhanced luminescence of complexes from previous reported complexes shows the remarkable effect of substituent position on luminescence properties. The effect of position studied as a combined effect of resonance phenomenon and electron withdrawing nature of substituent attached. The studied complexes show higher intensity and efficiency parameters which pointing the utilisation of complexes in development of excellent luminescent materials.

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Compliance with Ethical Standards

Conflict of Interest The authors indicated no potential conflict of interest.

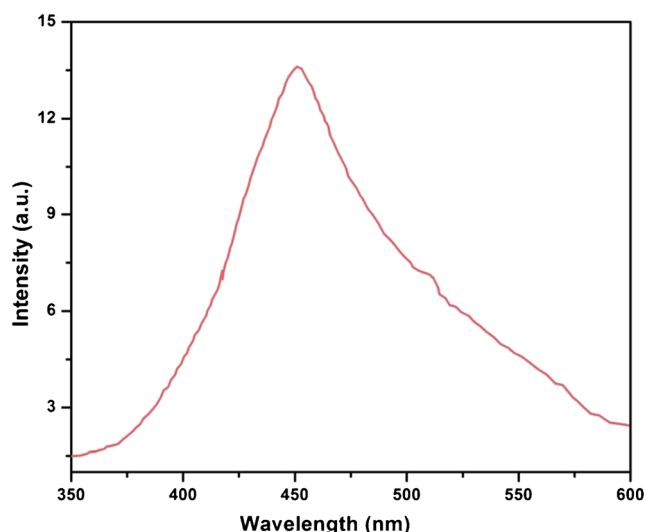


Fig. 9 The phosphorescence spectra of complex $\text{Gd}(\text{p-EFBA})_3(\text{H}_2\text{O})_2$

References

- Liu JQ, Wang YY, Batten SR, Sakiyama H, Ma DY (2012) An unusual self-penetrated metal–organic framework from mixed ligands: synthesis, structure and magnetism. *Inorg Chem Commun* 19:27–30
- Zhu X, Zheng HY, Wei XF, Lin ZY, Guo LH, Qiu B, Chen GN (2013) Metal–organic framework (MOF): a novel sensing platform for biomolecules. *Chem Commun* 13:1276–1278
- Mukkala VM, Helenius M, Hemmila I, Kankare J, Takalo H (1993) Development of luminescent europium(III) and terbium(III) chelates of 2,2':6',2"-terpyridine derivatives for protein labelling. *Helv Chim Acta* 76:1361–1378
- Pandya S, Yu JH, Parker D (2006) Engineering emissive europium and terbium complexes for molecular imaging and sensing. *Dalton Trans* 23:2757–2766
- Bünzli JC, Piguet C (2005) Taking advantage of luminescent lanthanide ions. *Chem Soc Rev* 34:1048–1077
- Shi LX, Wu CD (2011) A nanoporous metal–organic framework with accessible Cu²⁺ sites for the catalytic Henry reaction. *Chem Commun* 10:2928–2930
- Justel T, Nikol H, Ronda C (1998) New developments in the field of luminescent materials for lighting and displays. *Angew Chem Int Ed* 37:3084–3103
- Bekiari V, Lianos P (1998) Strongly luminescent poly(ethyleneglycol)-2,2'-bipyridine lanthanide ion complexes. *Adv Mater* 10:1455–1458
- Gao B, Qiao Z, Chen T (2014) Structure and photoluminescence properties of aromatic carboxylic acid-functionalised polysulfone with Eu(III) and Tb(III). *Mater Chem Phys* 143:1119–1130
- Koen B (2009) Lanthanide-based luminescent hybrid materials. *Chem Rev* 109:4283–4374
- Weissman SI (1942) Intramolecular energy transfer the fluorescence of complexes of europium. *J Chem Phys* 10:214–217
- Raj DBA, Biju S, Reddy MLP (2008) One-, two-, and three-dimensional arrays of Eu³⁺-4,4',5,5'-pentafluoro-1-(naphthalen-2-yl)pentane-1,3-dione complexes: synthesis, crystal structure and photophysical properties. *Inorg Chem* 47:8091–8100
- Yang C, Fu LM, Wang Y, Zhang JP, Wong WT, Ai XC, Qiao YF, Zou BS, Gui LL (2004) A highly luminescent europium complex showing visible-light-sensitized red emission: direct observation of the singlet pathway. *Angew Chem Int Ed* 43:5010–5013
- Martinelli C, Farinola GM, Pinto V, Cardone A (2013) Synthetic aspects and electro-optical properties of fluorinated arylenes/vinylenes for luminescence and photovoltaics. *Materials* 6:1205–1236
- Roh EJ, Keller JM, Olah Z, Ladarola MJ, Jacobson KA (2008) Structure–activity relationships of 1,4-dihydropyridines that act as enhancers of the vanilloid receptor 1 (TRPV1). *Bioorg Med Chem* 16:9349–9358
- Sareen V, Gupta R (1996) Studies in fluorinated 1,3-diketones and related compounds. Part XVIII. Synthesis of some new tris(1,3-diketono)lanthanide complexes. *J Fluor Chem* 76:149–150
- Zhang W, Liu CH, Tang RR, Tang CQ (2009a) Preparation and luminescent properties of a novel carbazole functionalized bis- β -diketone ligand and corresponding Eu(III) and Tb(III) complexes. *Bull Kor Chem Soc* 30:2213–2216
- Arvind M, Sageed K (1986) Studies on bis(p-dimethylaminobenzylidene)benzidine complexes of trivalent lanthanides. *Indian J Chem A* 25:589–594
- Bala M, Kumar S, Taxak VB, Boora P, Khatkar SP (2016) Optical features of efficient europium(III) complexes with β -diketonato and auxiliary ligands and mechanistic investigation of energy transfer process. *J Fluoresc* 26:1813–1823
- 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. *Synth Met* 162: 2063–2068
- An BL, Gong ML, Li MX, Zhang JM (2004) Synthesis, structure and luminescence properties of samarium (III) and dysprosium (III) complexes with a new tridentate organic ligand. *J Mol Struct* 687: 1–6
- Meijuan L, Xiaoping W, Qiang T, Qidan L (2013) Luminescence properties of polymers containing europium complexes with 4-tert-butylbenzoic acid. *J Rare Earths* 31:950–956
- Shao G, Li Y, Feng K, Gan F, Gong M (2012) Diphenyl based β -diketonato europium(III) complexes as red phosphors applied in LED. *Sensors Actuators B Chem* 173:692–697
- Kai J, Parra DF, Brito HF (2008) Polymer matrix sensitizing effect on photoluminescence properties of Eu³⁺- β -diketonato complex doped into poly- β -hydroxybutyrate (PHB) in film form. *J Mater Chem* 18:4549–4554
- Kirby AF, Foster D, Richardson FS (1983) Comparison of 7FJ \leftarrow 5DO emission spectra for Eu(III) in crystalline environments of octahedral, near-octahedral, and trigonal symmetry. *Chem Phys Lett* 95:507–512
- Richardson FS (1982) Terbium(III) and europium(III) ions as luminescent probes and stains for biomolecular systems. *Chem Rev* 82: 541–552
- Wang H, He P, Yan H, Gong M (2011) Synthesis, characteristics and luminescent properties of a new europium(III) organic complex applied in near UV LED. *Sensors Actuators B Chem* 156:6–11
- Pu S, Yang T, Li G, Xu J, Chen B (2006) Substituent position effect on the optoelectronic properties of photochromic diarylethenes. *Tetrahedron Lett* 47:3167–3171
- Werts MHV, Jukes RTF, Verhoeven JW (2002) The emission spectrum and the radiative lifetime of Eu³⁺ in luminescent lanthanide complexes. *Phys Chem Chem Phys* 4:1542–1548
- Brito HF, Malta OL, Souza LR, Menezes JFS, Carvalho CAA (1999) Luminescence of the films of europium (III) with thenoyltrifluoroacetate and macrocyclics. *J Non-Cryst Solids* 247:129–133
- De Sà GF, Malta OL, de Mello DC, Simas AM, Longo RL, Santa-Cruz PA, da Silva Jr EF (2000) Spectroscopic properties and design of highly luminescent lanthanide coordination complexes. *Coord Chem Rev* 196:165–195
- Carlos LD, Messaddeq Y, Brito HF, Ferreira RAS, Bermudez VD, Ribeiro SJL (2000) Full-color phosphors from europium(III)-based organosilicates. *Adv Mater* 12:594–598
- Ferreira R, Pires P, Castro BD, Ferreira RAS, Carlos LD, Pischel U (2004) Zirconium organophosphonates as photoactive and hydrophobic host materials for sensitized luminescence of Eu(III), Tb(III), Sm(III) and Dy(III). *New J Chem* 28:1506–1513
- Stanimirov S, Petkov I (2009) Photophysical properties of novel fluorescent poly(oxyethylene phosphate) tris(β -diketonato) europium (III) complexes. *Spectrochim Acta A Mol Biomol Spectrosc* 72: 1127–1133
- Zhang X, Zhou F, Shi J, Gong M (2009b) Sr_{3.5}Mg_{0.5}Si₃O₈Cl₄: Eu²⁺ bluish–green-emitting phosphor for NUV-based LED. *Mater Lett* 63:852–854
- Teotonio EES, Brito HF, Felinto MCFC, Kodaira CA, Malta OL (2003) Luminescence investigations on Eu(III) thenoyltrifluoroacetate complexes with amide ligands. *J Coord Chem* 56:913–921
- Ferreira RAS, Nobre SS, Granadeiro CM, Nogueira HIS, Carlos LD, Malta OL (2006) A theoretical interpretation of the abnormal ⁵D₀ \rightarrow ⁷F₄ intensity based on the Eu³⁺ local coordination in the Na₉[EuW₁₀O₃₆] \cdot 14H₂O polyoxometalate. *J Lumin* 121:561–567
- Li XP, Chen B, Shen R, Zhong H, Cheng L, Sun J, Zhang J, Zhong H, Tian Y, Du G (2011) Fluorescence quenching of ⁵D_J (J = 1, 2 and

- 3) levels and Judd–Ofelt analysis of Eu^{3+} in NaGdTiO_4 phosphors. *J Phys D Appl Phys* 44:335403–335410
39. Devi R, Dalal M, Bala M, Khatkar SP, Taxak VB, Boora P (2016a) Investigations of luminescent behavior and intramolecular energy transfer mechanism of europium(III) complexes with fluorinated β -ketoester ligand. *J Fluor Chem* 181:36–44
 40. Devi R, Dalal M, Bala M, Khatkar SP, Taxak VB, Boora P (2016b) Synthesis, photoluminescence features with intramolecular energy transfer and Judd–Ofelt analysis of highly efficient europium(III) complexes. *J Mater Sci Mater Electron* 27:12506–12516
 41. Taha ZA, Ajlouni AM, Al-Hassan KA, Hijaki AK, Faiq AB (2011) Syntheses, characterization, biological activity and fluorescence properties of bis-(salicylaldehyde)-1,3-propylenediimine Schiff base ligand and its lanthanide complexes. *Spectrochim Acta A Mol Biomol Spectrosc* 81:317–323
 42. Gawryszewska P, Sokolnicki J, Legendziewicz J (2005) Photophysics and structure of selected lanthanide compounds. *Coord Chem Rev* 249:2489–2509
 43. Latva M, Takalo H, Mikkala VM, Matachescu C, Ubbis JCR, 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
 44. Lee JC, Leong YK, Kim JM, Kang JG (2014) Sensitized luminescence of Eu(III) complexes with Schiff-base and 1,10-phenanthroline: role of Schiff-base as a sensitizer. *Spectrochim Acta A Mol Biomol Spectrosc* 124:256–264
 45. Dexter DL (1953) A theory of sensitized luminescence in solids. *Chem Phys* 21:836–850
 46. Dean CRS, Shephard TM (1975) Evaluation of the intramolecular energy transfer rate constants in crystalline $\text{Eu}(\text{hfaa})_4\text{Bu}^t\text{NH}_3$. *J Chem Soc Faraday Trans 2(71)*:146–155