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Synthesis, photoluminescent features and intramolecular energy transfer mechanism of europium (III) complexes with fluorinate β -diketone ligand and auxiliary ligands



Manju Bala, Satish Kumar, V.B. Taxak, Priti Boora, S.P. Khatkar*

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

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ABSTRACT

A series of novel luminescent europium (III) complexes based on fluorinated β -diketone ligand 4,4difluoro-1-phenyl-1,3-butanedione (DPBD) and auxiliary ligands 2,2-biquinoline (biq) or 1,10phenanthroline (phen) or neocuproine (neo) or 2,2-bipyridyl (bipy) have been synthesized. The ligand DPBD with their complexes $Eu(DPBD)_3$ ·(H₂O)₂ (C1), $Eu(DPBD)_3$ ·biq (C2), $Eu(DPBD)_3$ ·phen (C3), Eu(DPBD)₃-neo (C4) and Eu(DPBD)₃-bipy (C5) were confirmed by elemental analysis, infrared (IR) and proton nuclear magnetic resonance (NMR) spectroscopy. The crystalline nature, photoluminescence and thermal behavior were investigated by powder X-ray diffraction (XRD), photoluminescence (PL) spectroscopy and TG/DTA-DSC respectively. The emission spectra of complexes showed the characteristics sharp bands in solid state corresponding to ${}^{5}D_{0}-{}^{7}F_{i}$ (j = 0-3) transition of europium ion with ${}^{5}D_{0}-{}^{7}F_{2}$ as the most intense transition. The emission spectra, energy transfer mechanism, luminescence decay time and relative quantum efficiency clearly reveals that these photophysical properties are greatly influenced by the π -conjugated system, stability of the complexes and the efficient energy transfer from DPBD ligand to emitting level of Eu^{3+} ion. The complex $Eu(DPBD)_3$ bipy (C5) exhibited highest quantum efficiency, luminescence intensity bearing good CIE color coordinates (x = 0.64 and y = 0.34) matching the NTSC (National Television Standard Committee) standard values for the pure red color and longest lifetime which makes it a promising red-emitting component for display devices.

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1. Introduction

The brightly electroluminescent europium complexes reported by Weismann (1942) and its devices by Kido (1991) opened new vistas in the field of luminescence [1,2] since then the luminescence properties of europium complexes have been intensively investigated. These europium complexes established a group of materials with enormous potential application in material science like sensory material [3], luminescent materials [4], light emitting diodes [5], laser materials and optical fiber [6]. The scrutiny of β -diketonato based europium complexes has surpassed the other europium complexes in last decades owing to the intriguing luminescent features such as high efficiency with long fluorescence life time and sharp emission bands in visible region having FWHM (Full Width at Half Maxima) in the range of 4–10 nm [7–9]. The 4f-4f photoluminescence intensity is the consequence of a harmony between

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absorption by the ligand, rate of energy transfer from ligand to central metal ion, radiative emission rates and non-radiative decays. The 4f-4f intra-configurational forbidden transition leads to feeble intensity of absorption and emission spectra. In order to overcome this disadvantage, a chelating organic chromophore with magnificent absorption coefficient is employed. So, β-diketone with extended π -conjugation system fulfill above necessity making them highly luminescent materials. In electroluminescent complexes the efficient energy transfer and high absorption coefficient can be accomplished by selection of appropriate ionizable organic chelating moiety which can coordinate to metal ion constituting an eight, nine or twelve coordinated neutral complex. Among 8-12 possible coordination sites of central metal ion, six coordinative sites are engaged with the three bidentate β -diketones in coordination sphere. Rest of coordination environment is occupied by water or solvent molecules or second auxiliary ligand. But C-H, O-H and N-H stretching vibration in complexes decrease the photoluminescence intensity by vibronic quenching [10,11] via back energy transfer to the ligand-localized electronic state [12] or by the exchange from the 4fⁿ configuration to the LMCT (ligand to metal charge transfer) [13].

^{*} Corresponding author. Tel.: +91 9813805666. *E-mail address:* s_khatkar@rediffmail.com (S.P. Khatkar).

Table I			
The elemental analytica	al data of europium	(III) complexes	C1-C5

Table 1

			-	
Complexes	C (%) found (cal.)	H (%) found (cal.)	N (%) found (cal.)	Eu (%) found (cal.)
DPBD C1 C2 C3 C4 C5	59.96 (60.60) 45.96 (46.21) 57.46 (57.65) 54.40 (54.60) 55.27 (55.52) 53.21 (53.39)	3.92 (4.04) 2.92 (3.20) 2.98 (3.30) 3.04 (3.14) 3.32 (3.47) 3.06 (3.22)	- 2.47 (2.80) 2.90 (3.03) 2.78 (2.94) 2.98 (3.11)	- 19.02 (19.51) 14.90 (15.21) 16.12 (16.46) 15.85 (15.98) 16.78 (16.90)

The loss of energy from the C–H bonds vibration decrease the emission intensity so the substitution of C–H bonds in a β -diketone moiety with lower energy C–F oscillators could decrease the back energy transfer loss and improve the emission intensity of central metal ion. It is well known that the spacing between the vibrational level of C–F oscillators lower the vibration energy of organic ligand and decrease the energy loss caused by vibration of organic ligand. The fluorine substituents on the ligand enhance the spin-orbit coupling via heavy atom effect confirmingly promoting the intersystem crossing (ISC) [14–17]. To achieve the above objective, a new β -diketonate ligand DPBD was synthesized by an ecofriendly microwave method which embodied with fluorinated alkyl group as well as conjugated phenyl group employing as 'antenna' for europium ion to effectively photosensitize its emission [18].

In the present report, with the purpose of growing novel photoluminescent materials, a series of europium (III) binary and ternary complexes by using fluorinated ligand and auxiliary ligand like 2,2-bipyridyl, 2,2-biquinoline, neocuproine and 1,10-phenan-throline were synthesized. We have also explicated the photo-luminescence governing study such as excitation spectra, emission spectra, UV-vis absorption spectra, decay time of emitting metal levels and CIE color coordinates in detail. The meticulous study of sensitization process in these luminescent complexes elucidated through proposed energy transfer mechanism.

2. Results and discussion

2.1. Composition and spectroscopic studies of the complexes

The elemental analytical data of Carbon, Hydrogen, Nitrogen of ligand DPBD, their synthesized complexes and Eu(III) content in complexes **C1–C5** are tabulated in Table 1. The results show that the calculated and experimental values are close to each other, indicating that the composition of the complexes is consistent to $Eu(DPBD)_3$ ·H₂O (**C1**), $Eu(DPBD)_3$ ·biq (**C2**), $Eu(DPBD)_3$ ·phen (**C3**), $Eu(DPBD)_3$ ·neo (**C4**) and $Eu(DPBD)_3$ ·bipy (**C5**).

The significant IR frequencies of ligand DPBD and complexes **C1–C5** are summarized in Table 2. Some distinct changes in ligand spectra are observed in comparison to spectra of complexes. The broad bands at 3430 cm^{-1} and 3421 cm^{-1} are detected which is assigned to the stretching vibration of enolic –OH in ligand DPBD and water molecules present in coordination sphere of the **C1** complex respectively. The strong absorption bands of C=O and



Fig. 1. The TG/DTA-DSC curves of the complex C5.

C=C in spectra of complexes **C1-C5** are red shifted $9-27 \text{ cm}^{-1}$ and $11-40 \text{ cm}^{-1}$ respectively in comparison to the free ligand DPBD ensuing the extended π -conjugated system in complexes [20]. The absorption bands at 1571–1560 cm⁻¹ in the complex spectra are attributed to C=N stretching vibration of auxiliary ligands having coordination through nitrogen which is not reflected in free ligand DPBD spectra. There are no marked changes in C-F stretching vibration at 1270–1269 cm⁻¹ in the spectra of complexes and ligand, indicating that it is not involved in coordination. Two new absorption bands appeared in the complexes spectra only at 536–522 cm⁻¹ and 428 cm⁻¹ assigned to the stretching vibration of Eu–N and Eu–O respectively. The above IR study clearly reveals that the ligand DPBD and auxiliary ligands are coordinated to the central europium (III) ion via C=O, enolic –OH of ligand and N–N groups of auxiliary ligands.

In ¹H NMR, two peaks of ligand spectra show obvious changes relative to spectra of complexes due to paramagnetism of europium (III) ion. The proton signal of enolic –OH at 15.01 ppm and keto –CH₂ protons peak at 4.22 ppm are missing from complexes spectra indicating that the enolic –OH involved in coordination. The enolic –CH proton of ligand exhibits a singlet at 6.35 ppm which is shifted to upfield at 3.20–2.80 ppm in complexes, signifying the paramagnetism of lanthanide ion [21]. The multiplet of benzene protons in ligand is moved toward higher field in the spectra of complexes.

2.2. Thermal behavior and powder X-ray study

The thermal behavior of europium complexes are perceived by TG/DTA-DSC curves which is analyzed at a heating rate of 30 °C min⁻¹ under nitrogen environment. The complexes **C1–C5** show a similar pattern of decomposition temperature and mass loss percentage, therefore complex **C5** is depicted as representative of other complexes in Fig. 1. The TGA curves show three important

Table 2

The IR characteristics bands (cm⁻¹) of ligand and its europium complexes.

_	, , e	Ĩ	1				
Complexes	ν(O-H)	ν(C=O)	ν(C=N)	ν(C=C)	ν(C-F)	ν(Eu–N)	v(Eu-O)
DPBD	3430 (b)	1635 (s)	-	1542 (s)	1270 (s)	-	_
C1	3421 (b)	1626 (s)		1529 (s)	1269 (s)	-	428 (m)
C2	-	1622 (s)	1562 (s)	1525 (s)	1269 (s)	522 (s)	428 (m)
C3	-	1625 (s)	1560 (s)	1531 (s)	1271 (s)	530 (m)	428 (w)
C4	-	1608 (s)	1571 (s)	1502 (s)	1269 (s)	536 (s)	428 (m)
C5	-	1620 (s)	1565 (s)	1517 (s)	1270 (s)	532 (s)	428 (m)

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

consecutive mass loss steps in the 0-1100 °C temperature range. The first mass loss observed at 202.8 °C due to loss of moisture present in complex. The second mass loss step appear from 202.8 °C to 309.8 °C with the 82.7% weight loss due to expelling of three DPBD and one 2,2'-bipyridyl molecules from the coordination sphere of complex. At last step, the product of previous step may be oxide of europium, which dissociate completely up to 1000 °C. In DSC curve, an endothermic peak is observed at 194 °C where no weight loss observed, corresponds to melting point of the complex. In addition, there are two exothermic peaks at 232 °C and 511 °C in DSC attributed to the release of three ligands with one auxiliary ligand and decomposition of the europium oxides respectively. In TGA curve, two exothermic peaks at 232 °C and 280 °C indicate the removal of three ligand and one 2,2'-bipyridyl molecules respectively. The results of TG/DTA-DSC analysis suggested that the all europium complexes exhibited good thermal stability.

In order to know the crystalline nature of ligands and complexes, the powder XRD pattern of ligand as well as complexes C1-C5 are investigated as depicted in Fig. 2. The characteristics peaks of **C2–C5** appeared in the range of $10-80^{\circ}$ at 2θ whereas a regular pattern was obtained for **C1**, clearly indicating the crystalline nature of **C2–C5** and amorphous nature of **C1**, which may be the results of water molecules present in coordination sphere of C1. The diffraction angles, diffraction intensity in XRD pattern of the complexes are different from those of ligand DPBD, bipy and phen which infer the formation of new crystalline complexes. The particle size can be estimated with the help of Scherrer's equation $D = 0.941\lambda/\beta \cos \theta$ where D is the average particle size, λ the X-ray wavelength (0.15406 nm), θ is diffraction angle and β is full width at half maxima (FWHM in radian). Therefore the particle sizes of C2-C5 are 64.5 nm, 63.9 nm, 67.8 nm and 54.8 nm respectively. The above powder X-ray diffraction study confirms the formation of nano-crystalline complexes.

2.3. UV-vis analysis

Fig. 3 illustrates the UV–vis absorption spectra of ligand DPBD, one of auxiliary ligand 1,10-phenanthroline, europium metal ion and their complexes **C1–C5** in ethanol solution (10^{-5} mol/L) at room temperature. The absorption maxima of free ligand (35,460.99 cm⁻¹) and that of the complexes (35714.29–35460.99 cm⁻¹) approach to nearly same value, indicating that







Fig. 3. The UV-vis absorption spectra of europium metal ion, 1,10-phenanthroline, ligand DPBD and C1-C5 complexes in ethanol solution.

the coordination of europium ion doesn't affect the energy of singlet excited state of ligand DPBD significantly [22]. The europium metal ion and 1,10-phenanthroline exhibit absorption at lower range 41666.67–37037.04 cm⁻¹ which is assigned to the π - π * transitions of ligand only. In addition, 1,10-phenanthroline shows absorption at 38,461.54 cm⁻¹, suggesting that the formation of Eu–N affects the absorption noticeably shifting it toward higher wavelength in complexes as a consequence of extended conjugation.

2.4. Photoluminescent features

The excitation spectra of ligand DPBD as well as their complexes **C1–C5** by monitoring ${}^5D_0 - {}^7F_2$ transition ($\lambda_{em} = 16,313.21 \text{ cm}^{-1}$) is displayed in Fig. 4. All the spectra of complexes exhibit a broad band from 40,000.00 cm⁻¹ to 22,222.22 cm⁻¹ and a weak band at 21,551.72 cm⁻¹ ascribed to the $\pi - \pi^*$ transition of coordinated ligand DPBD and absorption of central europium ion respectively. The red shifting of ligand maxima (28,901.73 cm⁻¹) is noticed in complexes (27,027.03–26,525.20 cm⁻¹) which explain the efficient sensitization phenomenon between β -diketone ligand and metal ion in which the ligand DPBD act as an 'antenna'.

The emission spectra of complexes **C1–C5** are recorded at $\lambda_{ex} = 26,881.72-26,525.20 \text{ cm}^{-1}$ with 400 PMT, depicted in Fig. 5.



Fig. 4. The excitation spectra of ligand DPBD and their europium complexes C1–C5 in solid state at room temperature monitored at 613 nm.



Fig. 5. The emission spectra of C1-C5 complexes at room temperature in solid state.

The pertinent data of photoluminescence are arranged in Table 3. The spectra comprise of characteristics narrow emission at 17,241.38 cm⁻¹, 16,920.47 cm⁻¹ and 16,313.21 cm⁻¹ due to ${}^{5}D_{0}-{}^{7}F_{0}$, ${}^{5}D_{0}-{}^{7}F_{1}$, and ${}^{5}D_{0}-{}^{7}F_{2}$ transition of europium ion. The low intensity emission peak at 17,241.38 cm⁻¹ due to ${}^{5}D_{0}-{}^{7}F_{0}$ transition being a one-order perturbation is forbidden in electric as well as magnetic dipole transition in accordance to theory of Judd-Ofelt [23-25]. The emission peak of slightly higher intensity at 16,920.47 cm⁻¹ due to ${}^{5}D_{0}-{}^{7}F_{1}$ transition is magnetic dipole transition being independent on local chemical environment can be employed as an internal standard to infer the differences in ligands [25–27]. The most intense peak at 16,313.21 cm⁻¹ due to ${}^{5}D_{0}-{}^{7}F_{2}$ transition being electric dipole transition depends on highly polarizable coordination environment around the europium ion possessing very low value of full width at half maxima (FWHM) i.e. 6.9 nm, 6.5 nm, 5.6 nm, 3.9 nm and 3.6 nm corresponding to the complexes C1-C5, leading to intense pure red emission. The excellent intensity of ${}^{5}D_{0}-{}^{7}F_{2}$ transition as compared to ${}^{5}D_{0}-{}^{7}F_{1}$ transition points to the lack of an inversion symmetry in the coordination environment of europium ion

Table 3			
The luminescence	data	of complexes	C1-C5.

[26–28]. The luminescent intensity ratio $(I_1/I_2 = {}^5D_0 - {}^7F_2/{}^5D_0 - {}^7F_1)$ of electric to magnetic dipole transitions show the symmetry of the coordination sphere as well as monochromaticity properties of metal complexes, their values are found to be in the range 7.0-10.73, being the highest for complex C5. Fig. 5 clearly shows that the luminescence intensity of complexes C2-C5 possessing auxiliary ligands is greater than complex $Eu(DPBD)_3 \cdot (H_2O)_2$ (C1) owning to the quenched O-H vibrations in coordination sphere, which is consequence of stability and extended π conjugation of auxiliary ligands in C2-C5 complexes which lower the energy level of ligands, constituting the efficient way of energy transfer from ligand to the emitting level of metal ion [29]. The order of emission intensity expounded by the nature of auxiliary ligands, the ligands with same framework i.e. bipyridyl and biquinoline possessing steric effect, makes the biquinoline complex lowest and bipyridyl complex highest intense among the ternary complexes. On the other hand, among 1,10phenanthroline and neocuproine auxiliary ligands which have the similar framework, the electron releasing effect of two methyl groups in neocuproine makes the complex to emit at higher intensity than phenanthroline complex. In addition, these auxiliary ligands have high affinity toward lanthanide ions [30], therefore their company anticipates 4f-4f forbidden transitions by inducing an asymmetric coordination environment around metal ion which increase the intensity of the complexes.

Fig. 6 depicts the emission color of the complexes **C1–C5** calculated from their PL spectra and assured by *Commission Internationale de Eclairage* (CIE) diagram, enlisted in Table 3. The color coordinates of the all complexes **C1**, x = 0.5018 and y = 0.2742; **C2**, x = 0.5234 and y = 0.2886; **C3**, x = 0.5668 and y = 0.3128; **C4**, x = 0.6173 and y = 0.3304 and **C5**, x = 0.6465, y = 0.3424 dropped in red region, with a spectacular shift toward pure red color with increasing intensity. The color coordinates are close to the standard red color of NTSC (x = 0.67, y = 0.33), SMPTE (x = 0.63, y = 0.34) and EBU (x = 0.64, y = 0.33) as a consequence of higher red/orange ratio. The above results of CIE indicate that complexes **C1–C5** are promising candidate of red component in OLEDs.

The luminescence decay profile of ${}^{5}D_{0}$ level of metal ion corresponding to **C1–C5** complexes is investigated by monitoring the emission at 613 nm (Fig. 7). The decay time values of **C1–C5** are calculated by the FL solution software of F-7000 spectrometer, tabulated in Table 3. The decay curves for these complexes obey a single exponential decay law which can be represented 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, suggesting that only single chemical environment around the europium(III) [31]. These results show that the complexes **C2–C5** having auxiliary ligands present longer lifetime relative to **C1**

Complexes	λ_{ex} (nm) in cm ⁻¹	λ_{em} (nm) in cm ⁻¹	Transition assignments	x and y color coordinates	τ (ms)
C1	26,525.20 (377)	17,241.38 (580)	${}^{5}D_{0}-{}^{7}F_{0}$	0.5018, 0.2742	0.22
		16,920.47 (591)	${}^{5}D_{0}-{}^{7}F_{1}$		
		16,313.21 (613)	${}^{5}D_{0}-{}^{7}F_{2}$		
C2	27,027.03 (370)	17,241.38 (580)	${}^{5}D_{0}-{}^{7}F_{0}$	0.5234, 0.2886	0.25
		16,920.47 (591)	${}^{5}D_{0}-{}^{7}F_{1}$		
		16,313.21 (613)	${}^{5}D_{0}-{}^{7}F_{2}$		
C3	27,027.03 (370)	17,241.38 (580)	${}^{5}D_{0}-{}^{7}F_{0}$	0.5668, 0.3128	0.28
		16,920.47 (591)	${}^{5}D_{0}-{}^{7}F_{1}$		
		16,313.21 (613)	${}^{5}D_{0}-{}^{7}F_{2}$		
C4	26,525.20 (377)	17,241.38 (580)	${}^{5}D_{0}-{}^{7}F_{0}$	0.6173, 0.3304	0.33
		16,920.47 (591)	${}^{5}D_{0}-{}^{7}F_{1}$		
		16,313.21 (613)	${}^{5}D_{0}-{}^{7}F_{2}$		
C5	26,881.72 (372)	17,241.38 (580)	${}^{5}D_{0}-{}^{7}F_{0}$	0.6465, 0.3424	0.39
		16,920.47 (591)	${}^{5}D_{0}-{}^{7}F_{1}$		
		16.313.21 (613)	${}^{5}D_{0} - {}^{7}F_{2}$		



Fig. 6. CIE coordinates of the europium complexes C1-C5.



Fig. 7. The luminescence decay profile of C1–C5 complexes monitoring at 613 nm in powder form.

because auxiliary ligands enhance the luminescence stability of the complexes.

The relative quantum efficiency (η) of europium complexes **C1–C5** is estimated by assigning Rhodamine 6G as a reference compound. The relative quantum efficiency of europium complexes is calculated by MATLAB software having Rhodamine 6G compound as reference and assuming their quantum efficiency value as 100. The relative quantum efficiency of complexes **C1–C5** is in the range 146.62–457.68 which is calculated according to the relation [32]

$$\eta = \eta_{\text{std}} \cdot \frac{I}{I_{\text{std}}} \cdot \frac{A_{\text{std}}}{A} \cdot \frac{n^2}{n_{\text{std}}^2} \tag{1}$$

 η is relative quantum efficiencies of the complex, η_{std} (0.5) is quantum efficiencies of the reference compound, *A* and *A*_{std} (0.029) are the absorbance's at the excitation wavelength of the complex and the reference compound, *I* and *I*_{std} are the integrated intensities of corrected emission spectra of the complex and the



Fig. 8. The proposed energy transfer mechanism in Eu(DPBD)₃.phen (C3).

reference, n and n_{std} represent the refractive index of solvent for complex and reference respectively. The relative quantum efficiency is highest for **C5** which may be the effect of energy transfer by the ligand and auxiliary ligand bipy.

In order to elucidate the energy transfer mechanism in photoluminescence process of the complexes, the proposed mechanism of energy transfer in C3 and C5 complexes of two different frameworks among auxiliary ligands are shown in Fig. 8 and Fig. S1 respectively. In the ligand DPBD, the energy of lowest excited singlet state and triplet state are estimated from the edge wavelength of UV-vis absorption spectra (Fig. 3) and the lower emission edge wavelength of phosphorescence spectra of C6 complex (Fig. S2) respectively [33,34] because the triplet energy level of ligand DPBD (32,154 cm⁻¹) approximately equals to lowest excited state $({}^{6}P_{7/2})$ of Gd³⁺ ion so the absorbed energy of ligand can't be transferred to gadolinium ion, hence the triplet state of the ligand is obtained from the phosphorescence spectra. The singlet and triplet excited states of phen as well as bipy are obtained from literature [35]. The respective S_1 and T_1 values of DPBD ligand, auxiliary ligands phen and bipy are listed in Table 4.

In complexes, the efficiency of energy transfer mainly depends on two mechanisms; in first the energy transfer takes place from lowest excited triplet level of DPBD ligand to resonance energy level of metal ion as proposed by Dexter's electron exchange interaction theory [36]. According to this theory, more suitable the energy gap between triplet level of ligand and emitting level of europium ion, more efficient is the energy transfer influencing the luminescence intensity. The transfer probability constant (Ps) is given as

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

where *Fs* (*E*) corresponds to the shape of emission band of triplet state of ligand (energy donor) and ξs (*E*) is shape of absorption spectrum of metal ion (energy acceptor), $2\pi Z^2/h$ term is constant.

 Table 4

 The excited state energy of DPBD, bipy and phen ligands.

Ligands	Excited state	Excitation energy	
		cm^{-1}	eV
DPBD	Singlet (S1)	32,154	3.98
	Triplet (T ₁)	25,125	3.11
Bipy	Singlet (S ₁)	29,900	3.71
	Triplet (T ₁)	22,900	2.83
Phen	Singlet (S ₁)	31,000	3.84
	Triplet (T_1)	22,100	2.74

The second is the thermal de-excitation mechanism dealing with the inverse transfer of energy from metal to ligand which is represented thermal de-excitation constant K(T) [37] as shown below

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

where ΔE is the energy difference between ligand lowest excited triplet level and resonance energy level of metal ion. Therefore, efficient energy transfer decided by the appropriate value of *Ps* and *K*(*T*).

The intersystem crossing (ISC) is effective only when energy gap $\Delta E(S_1 - T_1)$ is appropriated, therefore the ΔE values for DPBD. phen and bipy in ISC process is 7029 cm^{-1} , 8900 cm^{-1} , 7000 cm^{-1} respectively which indicated the efficiency of intersystem crossing in corresponding complexes C3 and C5. An empirical rule of Latva et al's implies that $\Delta E (T_1 - M^{3+})$ should be in 2000– 5000 cm⁻¹ range for an optimal energy transfer from ligand lowest triplet level to metal resonance level [38]. The values of ΔE (T_1-M^{3+}) are found to be approx 7625 cm⁻¹, 5400 cm⁻¹, 4600 cm⁻¹ for DPBD, bipy and phen respectively. The energy gap between DPBD ligand and Eu³⁺ is not desirable for efficient energy transfer so the absorbed energy of the DPBD ligand may be transmitted to auxiliary ligands first and then finally to the Eu³⁺ ion ensuing higher luminescence intensity of ternary complexes C2-C5 as compared to binary complex C1. At the same time, inverse energy transfer process also determines the effectiveness of entire energy transfer mechanism. The slow inverse energy transfer process constitutes an efficient energy transfer mechanism in complex. It is observed that the energy gap between europium ion and bipy is more than that between europium ion and phen which diminished the rate of inverse energy transfer process more in bipy complex leading to higher luminescence intensity as compared to phen complex. The above analyses indicate that auxiliary ligands facilitate the sensitization process which is also noticed in photoluminescence study.

3. Conclusion

In summary, a series of five novel europium(III) C1-C5 complexes have been synthesized and characterized by elemental analysis, ¹H NMR, IR, UV-vis absorption, powder XRD, TG/ DTA-DSC and photoluminescence (PL) spectroscopy. The difference between ligand and complexes IR spectra show that the binding of ligand DPBD to the metal ion through oxygen atoms of enol form of ligand. The characteristics peaks of europium (III) ion in emission spectra and luminescence decay curves of the complexes reveal that Eu³⁺ ion is located in a polarizable chemical environment which is acting as only one luminescent center. All photoluminescent features of the complexes reveal that the europium ion is sensitized efficiently by the primary ligand and auxiliary ligands as shown in proposed energy transfer mechanism. These complexes possess significant impacts on photophysical properties by the introduction of the auxiliary ligands. These results demonstrate that the luminescence properties enhanced effectively by the addition of auxiliary ligands as the π -conjugation system, stability of the complexes increases and the efficient transfer of energy from ligand to metal occurs. The series of crystalline europium complexes C1-C5 exhibiting excellent photoluminescent properties such as high luminescence intensity with longer life time as well as good CIE chromaticity coordinates and high thermal stability are promising red-emitting component for OLEDs having potential application in display devices.

4. Experimental

4.1. Starting materials and instrumentation

All starting materials were purchased from commercial source of analytical grade and used without further purification. The lanthanide nitrates ($Eu(NO_3)_3 \cdot 5H_2O$ and $Gd(NO_3)_3 \cdot 5H_2O$) were acquired from Sigma–Aldrich. The synthesized DPBD ligand was recrystalized three timed with ethanol before the complexation.

The europium content was ascertained by complexometric titration with EDTA (ethylenediaminetetraacetate). Carbon, hydrogen and nitrogen were executed by Perkin Elmer 2400 CHN Elemental Analyzer. Infrared spectra (4000–400 cm⁻¹) were performed with KBr pellets on Perkin Elmer Spectrum 400 spectrometer. ¹H NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer in CDCl₃ solution with TMS as internal standard. UV-vis absorption spectra were measured on Shimadzu-2450 UV-vis spectrophotometer. Thermogravimetric analyses were carried out by using SDT Q600 up to 1100 °C with a heating rate of 20 °C/min under nitrogen atmosphere. Powder X-ray diffraction (XRD) pattern were determined by Rikagu Ultima IV diffractometer with CuKa radiation at 40 kV tube voltage and 40 mA tube current. Fluorescence and phosphorescence measurements were made on Hitachi F-7000 fluorescence spectrophotometer equipped with a xenon lamp as the excitation source. The decay time values of the complexes were calculated by software of the spectrophotometer (FL solution for F-7000).

4.2. Synthesis of ligand

The ligand DPBD was synthesized and their synthetic route is illustrated in Scheme 1. To a solution of acetophenone (0.21 mL, 1.80 mmol) and dry THF (60 mL) added sodium hydride (0.70 g, 2.90 mmol), the resulting mixture was stirred at room temperature for 15 min. Then added methyl-difluoroacetate (0.59 g, 5.40 mmol) and stirred the solution for 12 h at room temperature. The reaction mixture was evaporated till the solid residue was obtained. The residue was dissolved in dichloromethane (15 mL) then acidified with hydrochloric acid (0.5 M) and washed with water [19]. The solid residue was recrystalized from ethanol. The DPBD was obtained as dark brown solid in 62% yield with 47-51 °C melting point. IR (KBr): cm⁻¹ 3430 (b), 3080 (m), 2998 (m), 2890 (w), 1635 (s), 1542 (s), 1480 (s), 1360 (s), 1270 (s), 785 (s), 705 (s); ¹H NMR (400 MHz, CDCl₃): δ 15.01 (s, 1H, enolic OH), 7.45–7.22 (m, 5H, Ar-H), 6.65 (t, 1H, CHF₂), 6.35 (s, 1H, enol CH), 4.22 (s, 2H, keto-CH₂) ppm.

4.3. Synthesis of complexes

The synthesis of europium (III) complexes was accomplished by a general procedure (Scheme 1): An alcoholic solution of DPBD (0.63 g, 3.2 mmol) was added to the aqueous solution of (0.42 g, 1.0 mmol) europium nitrate pentahydrate with constant stirring on magnetic stirrer. Then the resulting mixture was treated with 0.05 M aqueous NaOH to adjust the pH 6.5–7.0. After stirring for 4 h at a temperature of 50 °C, a white solid was filtered, purified by washing with distil water and then with ethanol to remove the free ligand. The solid was dried at 40 °C to obtain the powder Eu(DPBD)₃·H₂O (**C1**) complex.

Eu(DPBD)₃·H₂O (**C1**): white solid, yield 72%; IR (KBr): cm⁻¹ 3421 (b), 3068 (m), 2983 (m), 2879 (w), 1626 (s), 1560 (s), 1529 (s), 1467 (s), 1352 (s), 1269 (s), 1109 (s), 767 (s), 704 (s), 530 (s), 428 (m); ¹H NMR (400 MHz, CDCl₃): δ 6.90 (m, 6H, Ar–H), 6.50 (t, 3H, CHF₂), 6.35 (m, 9H, Ar–H), 3.20 (s, 3H, enol CH). Anal. Calcd for



4,4-difluoro-1-phenyl-1,3-butanedione (DPBD)



Scheme 1. The synthetic route of ligand DPBD and its europium (III) complexes.

 $EuC_{30}H_{25}O_8F_6;$ C, 46.21; H, 3.20; Eu, 19.51; found: C, 45.94; H, 2.92; Eu, 19.02.

Similarly, the complexes **C2–C5** were prepared with the same process as adopted in the synthesis of complex **C1**, but the mixture of DPBD (0.63 g, 3.2 mmol), biq (0.25 g, 1.0 mmol) and europium nitrate (0.42 g, 1.0 mmol) was used for complex **C2**, the mixture of DPBD (0.63 g, 3.2 mmol), phen (0.18 g, 1.0 mmol) and europium nitrate (0.42 g, 1.0 mmol) for complex **C3**, the mixture of DPBD (0.63 g, 3.2 mmol), neo (0.20 g, 1.0 mmol) and europium nitrate (0.42 g, 1.0 mmol) for complex **C4** and the mixture of DPBD (0.63 g, 3.2 mmol), bipy (0.15 g, 1.0 mmol) and europium nitrate (0.42 g, 1.0 mmol) for complex **C4** and the mixture of DPBD (0.63 g, 3.2 mmol), bipy (0.15 g, 1.0 mmol) and europium nitrate (0.42 g, 1.0 mmol) for complex **C5** were used to synthesized the europium(III) ternary complexes.

Eu(DPBD)₃·biq (**C2**): white solid, yield 70%; IR (KBr): cm⁻¹ 3062 (m), 2978 (m), 2880 (w), 1622 (s), 1562 (s), 1525 (s), 1452 (s), 1352 (s), 1269 (s), 1109 (s), 765 (s), 700 (s), 522 (s), 428 (m); ¹H NMR (400 MHz, CDCl₃): δ 7.90 (m, 6H, Ar–H), 7.20 (m, 6H, Ar–H), 6.82 (m, 6H, Ar–H), 6.44 (t, 3H, CHF₂), 6.30 (m, 9H, Ar–H), 3.08 (s, 3H, enol CH). Anal. Calcd for EuC₄₈H₃₃N₂O₆F₆: C, 57.65; H, 3.30; N, 2.80; Eu, 15.21; found: C, 57.46; H, 2.98; N, 2.47; Eu, 14.90.

Eu(DPBD)₃·phen (**C3**): white solid, yield 74%; IR (KBr): cm⁻¹ 3057 (m), 2887 (w), 1625 (s), 1560 (s), 1531 (s), 1467 (s), 1350 (s), 1271 (s), 1111 (s), 769 (s), 704 (s), 530 (m), 429 (w); ¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 2H, Ar–H), 7.70 (m, 6H, Ar– H), 6.88 (m, 6H, Ar–H), 6.48 (t, 3H, CHF₂), 6.32 (m, 9H, Ar–H), 2.98 (s, 3H, enol CH). Anal. Calcd for EuC₄₂H₂₉N₂O₆F₆: C, 54.60; H, 3.14; N, 3.03; Eu, 16.46; found: C, 54.40; H, 3.04; N, 2.90; Eu, 16.12.

$$\begin{split} & \text{Eu}(\text{DPBD})_{3} \cdot \text{neo} \ (\textbf{C4}): \ \text{white solid, yield 70\%; IR (KBr): } cm^{-1} \\ & 3051 \ (s), 2989 \ (m), 2723 \ (w), 1608 \ (s), 1571 \ (s), 1502 \ (s), 1473 \ (s), \\ & 1355 \ (s), 1269 \ (s), 1105 \ (s), 763 \ (s), 700 \ (s), 536 \ (s), 428 \ (m); \ ^{1}\text{H} \\ & \text{NMR} \ (400 \ \text{MHz}, \text{CDCl}_{3}): \\ & \delta \ 7.88 \ (s, 2H, Ar-H), 7.46 \ (m, 4H, Ar-H), \\ & 6.85 \ (m, 6H, Ar-H), 6.45 \ (t, 3H, \text{CHF}_{2}), 6.28 \ (m, 9H, Ar-H), 2.92 \ (s, \\ & 3H, \text{enol CH}), 2.45 \ (s, 6H, \text{CH}_{3}). \ \text{Anal. Calcd for EuC}_{44}H_{33}N_2O_6F_6: \ C, \\ & 55.52; \ H, 3.47; \ N, 2.94; \ Eu, 15.98; \ found: \ C, 55.27; \ H, 3.32; \ N, 2.78; \\ & Eu, 15.85. \end{split}$$

Eu(DPBD)₃·bipy (**C5**): white solid, yield 70%; IR (KBr): cm⁻¹ 3064 (m), 2968 (w), 1620 (s), 1565 (s), 1517 (s), 1471 (s), 1352 (s), 1270 (s), 1105 (s), 767 (s), 704 (s), 532 (s), 428 (m); ¹H NMR (400 MHz, CDCl₃): δ 8.10 (m, 4H, Ar–H), 7.40 (m, 4H, Ar–H), 6.80 (m, 6H, Ar–H), 6.50 (t, 3H, CHF₂), 6.36 (m, 9H, Ar–H), 3.00 (s, 3H, enol CH). Anal. Calcd for EuC₄₀H₂₉N₂O₆F₆: C, 53.39; H, 3.22; N, 3.11; Eu, 16.90; found: C, 53.21; H, 3.06; N, 2.98; Eu, 16.78.

In order to calculate the lowest triplet state of ligand DPBD, a gadolinium (III) binary complex $Gd(DPBD)_3 \cdot (H_2O)_2$ was also prepared in similar way, as adopted in the synthesis of europium complexes using the mixture of DPBD (0.63 g, 3.2 mmol) in ethanol and aqueous solution of gadolinium nitrate (0.45 g, 1.0 mmol).

 $\begin{array}{l} Gd(DPBD)_{3} \cdot (H_2O)_2 \; (\textbf{C6}): \mbox{ white solid, yield 62\%; IR (KBr): } cm^{-1} \\ 3429 \; (b), 3070 \; (m), 2985 \; (m), 2875 \; (w), 1618 \; (s), 1564 \; (s), 1528 \; (s), \\ 1468 \; (s), 1352 \; (s), 1269 \; (s), 1107 \; (s), 768 \; (s), 702 \; (s), 530 \; (s), 428 \\ (m); \; ^1H \; NMR \; (400 \; MHz, CDCl_3): \; \delta \; 6.87 \; (m, 6H, Ar-H), \; 6.47 \; (t, 3H, CHF_2), \; 6.38 \; (m, 9H, Ar-H), \; 3.03 \; (s, 3H, enol \; CH). \; Anal. \; Calcd \; for \; GdC_{30}H_{25}O_8F_6: C, 45.91; H, 3.18; \; Gd, 20.0; \; found: C, 45.84; H, 3.01; \; Gd, 19.62. \\ \end{array}$

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015. 06.011.

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