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

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ABSTRACT

A series of novel luminescent europium (III) complexes based on fluorinated β-diketone ligand 4,4-difluoro-1-phenyl-1,3-butanedione (DPBD) and auxiliary ligands 2,2-biquinoline (biq) or 1,10-phenanthroline (phen) or neocuproine (neo) or 2,2-bipyridyl (bipy) have been synthesized. The ligand DPBD with their complexes Eu(DPBD)$_3$·(H$_2$O)$_2$ (**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 $^5D_0$–^7F_j (j = 0–3) transition of europium ion with $^5D_0$–$^7F_2$ 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.

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 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 4f^n configuration to the LMCT (ligand to metal charge transfer) [13].

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Table 1
The elemental analytical data of europium (III) complexes **C1–C5**.

Complexes	C (%) found (cal.)	H (%) found (cal.)	N (%) found (cal.)	Eu (%) found (cal.)
DPBD	59.96 (60.60)	3.92 (4.04)	–	–
C1	45.96 (46.21)	2.92 (3.20)	–	19.02 (19.51)
C2	57.46 (57.65)	2.98 (3.30)	2.47 (2.80)	14.90 (15.21)
C3	54.40 (54.60)	3.04 (3.14)	2.90 (3.03)	16.12 (16.46)
C4	55.27 (55.52)	3.32 (3.47)	2.78 (2.94)	15.85 (15.98)
C5	53.21 (53.39)	3.06 (3.22)	2.98 (3.11)	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-phenanthroline were synthesized. We have also explicated the photoluminescence 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)$_3$·H$_2$O (**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 >C=C in spectra of complexes **C1–C5** are red shifted 9–27 cm^{-1} and 11–40 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.

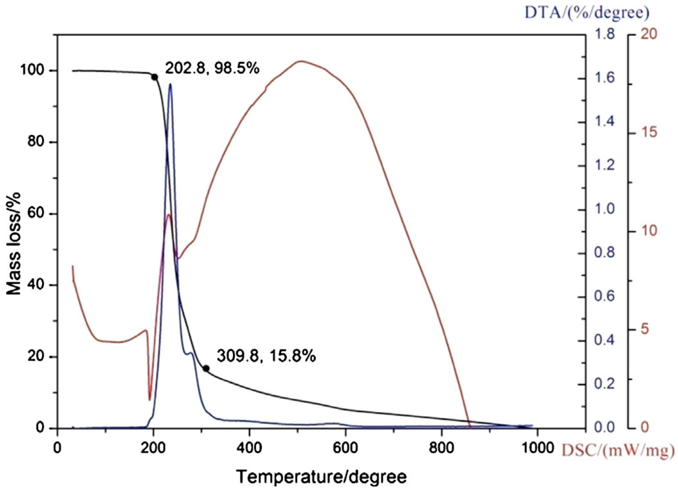

Fig. 1. The TG/DTA-DSC curves of the complex **C5**.

In ^{1}H 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 –CH$_2$ 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.

Complexes	ν(O–H)	ν(C=O)	ν(C=N)	ν(C=C)	ν(C–F)	ν(Eu–N)	ν(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.