

RED LIGHT EMITTING EUROPIUM COMPLEX FUNCTIONALIZED WITH HYDROXYKETONE

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ABSTRACT: The luminescent europium was successfully synthesized by using 5-fluoro-2-hydroxyacetophenone (FHAP) hydroxyketone ligand. The composition and structure of the FHAP ligand and its complex were supported by various techniques such as IR, NMR and CHN elemental analysis. The UV-visible and photoluminescence spectroscopy were used to explain the sensitization or antenna effect of the organic ligand. On successful irradiation at 397 nm, the emission spectra of complex showed narrow characteristic peaks at 580 nm, 592 nm, 616 nm and 652 nm corresponding to the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, and $^5D_0 \rightarrow ^7F_3$ electronic transition of the europium ion. Among these peaks, the electric dipole $^5D_0 \rightarrow ^7F_2$ transition noticed the most intense peak which was hypersensitive to the site symmetry of europium ion and associated with the red luminescence of the complex. The CIE color coordinates of the complex fall in the red region of the chromaticity diagram. These results suggested that the light harvesting organic ligand FHAP absorbed the energy and transferred to the metal ion through sensitization process in an effective manner. On the basis of above results, we can conclude that the complex possesses the candidature for light emitting materials and devices.

Keywords: Sensitization, antenna effect, europium ion, IR, photoluminescence.

1. INTRODUCTION

The attractive luminescence properties of rare earth ions made their complexes of great interest for various potential applications like optical material [1], tunable laser [2], luminescence probe for bioanalysis [3], light emitting devices [4-5] and sensory materials [6]. These complexes were distinct by their characteristic features such as long luminescence decay time, extremely narrow emission peaks, high luminescence efficiency and large Stoke's shift. These features are associated with the deeply seated f-orbital of metal ion and antenna effect of the organic moiety. As we know that the f-f transition of the metal ion is parity forbidden according to the Laporte selection rule and rare earth metal ion as associated with low absorption coefficient [7]. But, organic ligands help in the absorption of energy and populate the emitting level of metal ion much more efficiently than by the direct excitation of the central metal ion. In this way, organic ligands act as sensitizer and their effect is antenna effect [8]. To keep the all above facts in mind, the main focus on the exploring of such organic ligands which have large absorption coefficient and high coordination ability to sensitize the rare earth ion. The β -hydroxy ketones with aromatic ring are emerging as good sensitizer and received fascinating prompt to synthesize the highly luminescent metal complex. In addition, the β -hydroxy ketones behave as bidentate and monoanionic ligand which produce stable and neutral complexes with trivalent rare earth ion.

The present communication includes the synthesis of 5-fluoro-2-hydroxyacetophenone (FHAP) ligand. By using FHAP europium(III) complex was synthesized. The complex was characterized by IR, NMR, CHN, UV-visible and photoluminescence spectroscopy. But the authors focused on mainly luminescence properties of europium complex, therefore, to better explicate the luminescence feature, excitation and emission spectra, luminescence decay curves and CIE chromaticity coordinates (x and y) studied in detail.

2. Experimental

The starting material such as aluminium chloride, hexane, ether and 4-fluorophenyl acetate were of analytical grade and purchased from the commercial source. These chemicals were used without any purification process. High purity metal nitrate $[Eu(NO_3)_3 \cdot 5H_2O]$ was purchased from Sigma Aldrich. The FHAP ligand was synthesized and recrystallized three times with hexane. The europium ion in the complexes was estimated by complexometric titration with EDTA (ethylenediaminetetraacetate). The elemental analysis of carbon, hydrogen and nitrogen were carried out on Perkin Elmer 2400 CHN Elemental Analyzer. The Fourier transform infrared spectra (FT-IR) were performed with KBr pellets on Nicolet iS50 FT-IR spectrometer in mid IR ($4000-400\text{ cm}^{-1}$) region. The NMR spectra were measured on Bruker Avance II 400 spectrometer in chloroform solution with TMS (tetramethylsilane) as a reference. The UV-visible absorption spectra were recorded on Shimadzu UV-3600 plus UV-visible spectrometer using DMSO as reference solvent. The photoluminescence studies were carried out on Hitachi F-7000 fluorescence spectrometer. The excitation and emission spectra were determined in wavelength scan mode at a 240 nm/min scanning speed with the xenon lamp as irradiation source and 2.5 nm slit width while luminescence decay curves were obtained in time scan mode and other conditions remained the same.

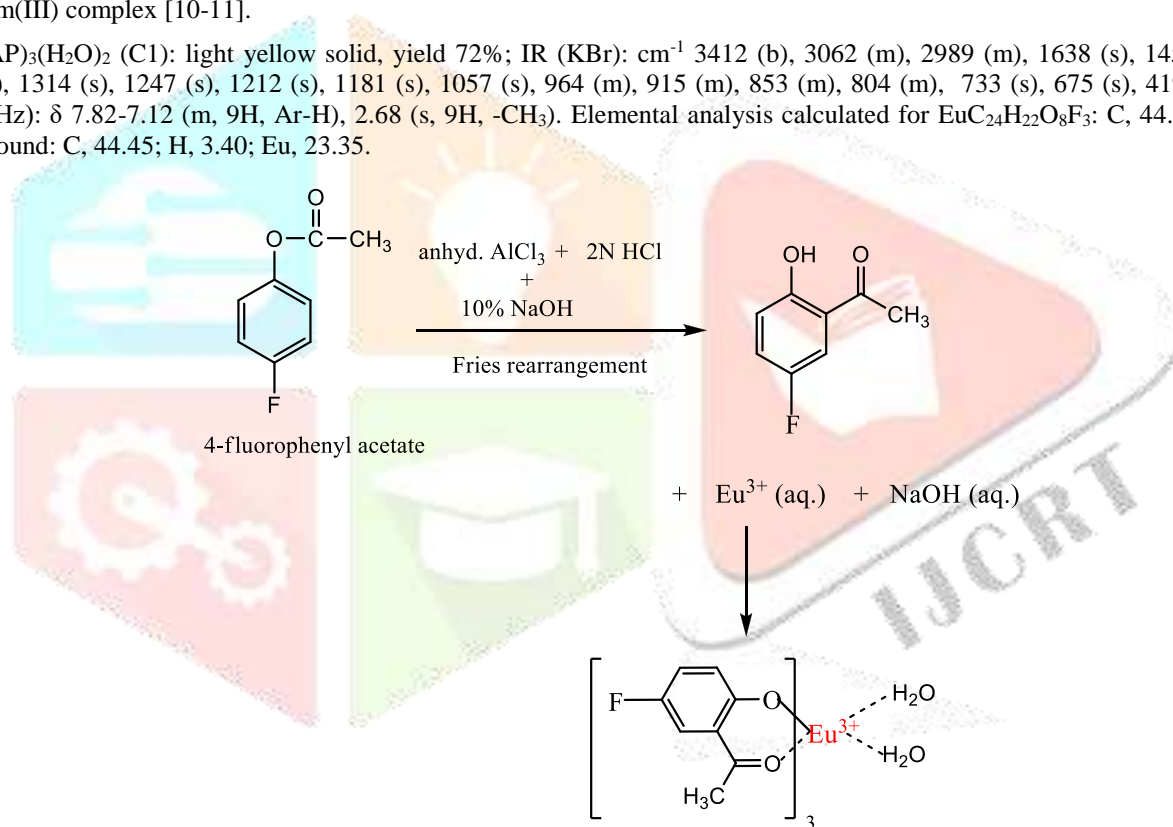
2.1 Synthesis of 2-benzoylacetanilide (BAA) ligand

The Scheme 1 illustrates the synthesis of FHAP ligand. The 4-fluorophenylacetate (76 mL, 0.58 mol) was added to anhydrous aluminium chloride (86 g, 0.64 mol) in a round bottom flask. The reaction mixture heated around 115°C for 2 h on the oil bath and cooled to room temperature. The solid mass was formed and then added 200 mL solution of 2N HCl. The resulting mixture was stirred for 40 minutes. The product was extracted with ether and purified by aqueous 10% NaOH solution. This solution was acidified with dilute HCl and again product was extracted with ether. The final product obtained by evaporation of solvents, which was recrystallized with hexane [9]. IR (KBr): cm^{-1} 3420 (b), 3053 (m), 3002 (m), 1650 (s), 1470 (s), 1428 (s), 1368 (s), 1325 (m), 1283 (s), 1248 (m), 1214 (m), 1179 (m), 1026 (m), 966 (m), 880 (m), 829 (m), 786 (s), 700 (m), 632 (m); $^1\text{H-NMR}$ (400MHz): δ 11.91 (s, 1H, phenolic OH), 7.41-6.92 (m, 3H, Ar-H), 2.62 (s, 3H, -CH₃) ppm. Elemental analysis calculated for C₈H₇O₂F: C, 62.33; H, 4.54; Found C, 62.12; H, 4.50.

2.2 Synthesis of europium(III) complex

A mixture of an aqueous solution of europium nitrate pentahydrate (0.42 g, 1.0 mmol) and an ethanolic solution of FHAP (0.49 g, 3.2 mmol) was stirred on the magnetic stirrer. The pH of resulting mixture was adjusted to 6.5 by using 0.05 M aqueous solution of sodium hydroxide. Then, the precipitates started to appear which were stirred for 2 h at 40°C temperature and then cooled to room temperature. These precipitates were filtered, purified by washing with distilled water and dried in hot air oven to obtain the europium(III) complex [10-11].

Eu(FHAP)₃(H₂O)₂ (C1): light yellow solid, yield 72%; IR (KBr): cm^{-1} 3412 (b), 3062 (m), 2989 (m), 1638 (s), 1456 (s), 1420 (s), 1362 (s), 1314 (s), 1247 (s), 1212 (s), 1181 (s), 1057 (s), 964 (m), 915 (m), 853 (m), 804 (m), 733 (s), 675 (s), 419 (m); $^1\text{H-NMR}$ (400 MHz): δ 7.82-7.12 (m, 9H, Ar-H), 2.68 (s, 9H, -CH₃). Elemental analysis calculated for EuC₂₄H₂₂O₈F₃: C, 44.51; H, 3.40; Eu, 23.49; found: C, 44.45; H, 3.40; Eu, 23.35.



Scheme 1. The synthetic pathway for the synthesis of FHAP ligand and europium(III) complex.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis data of ligand and europium complex showed good agreement between experimental and theoretical values. These results revealed the successful synthesis of FHAP ligand and its corresponding europium(III) complex. The complex was yellow solid and stable under normal atmospheric conditions. The complex was soluble in chloroform, acetone, dichloromethane, DMSO and DMF solvents.

3.2 FT- IR and NMR spectral analysis

In order to know the binding mode of the ligand in complexes, the IR spectrum of free ligand and complexes were compared. The broad absorption band of phenolic –OH group was noticed at 3428 cm^{-1} in the spectrum of FHAP ligand. This band diminished in the spectrum of complex, indicating the phenolic –OH group as coordination site of the ligand. On the other hand, the –OH stretching vibrations of water molecules present in the coordination sphere of the complex was also merged in broad band of phenolic –OH group. It was noticed from the spectra of FHAP ligand and complex that there was no changes in the C-F stretching vibration at 1248 cm^{-1} , suggesting non participation of C-F group in the chelation process due to electronegative behavior of fluorine. In the spectrum of free FHAP ligand, a strong band at 1650 cm^{-1} attributed to $>\text{CO}$ stretching vibration which was shifted to 1638 cm^{-1} value in the spectrum of complex due to the involvement of $>\text{CO}$ group in coordination process [12]. This was also confirmed by the Eu-O stretching vibration at about 419 cm^{-1} region in the spectrum of complex.

In the $^1\text{H-NMR}$ spectrum of FHAP ligand, a singlet of phenolic proton appeared at 11.91 ppm which was not observed in the spectrum of complex, indicating that the ligand coordinated to the metal ion through oxygen atom of the phenolic group [13]. The signal of aromatic protons in the complex shifted to slightly downfield as compared to ligand due to the extended conjugation in the complex. The results of NMR study agreed with the IR results and thus confirmed the binding site of the ligand.

3.3 UV-visible absorption spectra

Figure 1 displays the UV-visible absorption spectra of FHAP ligand and europium complex. These UV-visible spectra were measured with 10^{-5} mol/L concentration in DMSO solvent. In the spectrum of FHAP ligand, the maximum absorption band at 318 nm is assigned to the singlet-singlet $\pi-\pi^*$ absorption of the aromatic ring of ligand [14]. The maximum absorption of complex noticed at about 380 nm, which were red shifted by 62 nm as compared to the spectrum of free FHAP ligand, indicating the extended π -conjugation of the ligands in the complexes. The absorption maxima of the complexes also assigned to the $\pi-\pi^*$ transition of ligand.

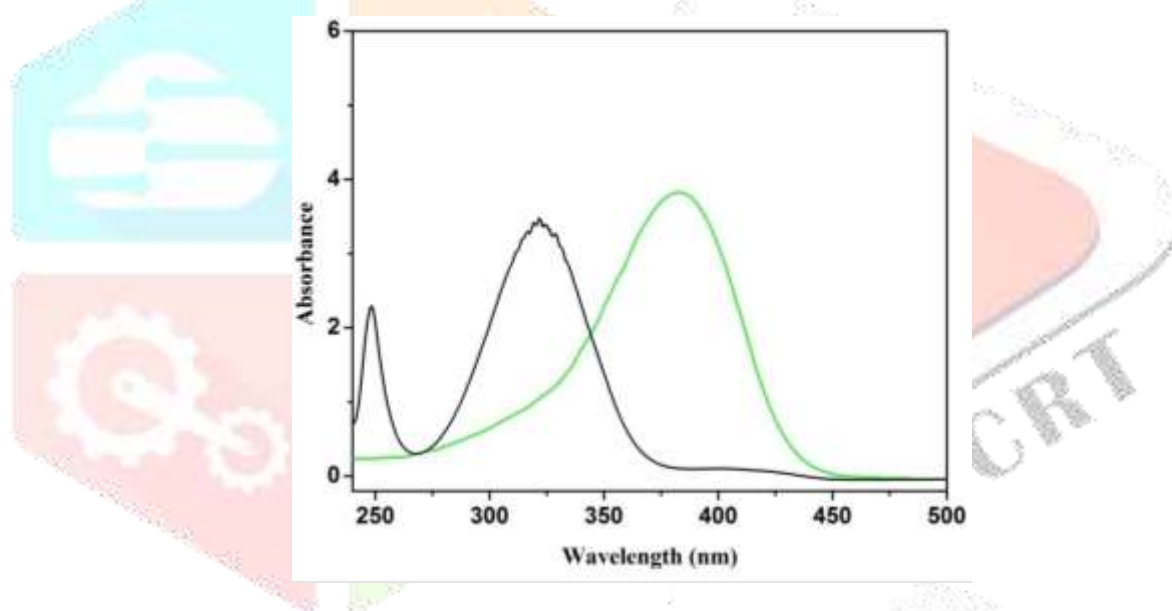


Fig. 1. The UV-visible absorption spectra of FHAP ligand and europium complex in DMSO solvent.

3.4 Photoluminescence behavior

The photoluminescence excitation spectrum of europium(III) complex was recorded in the solid state at room temperature as depicted in Fig. 2. The spectrum exhibited the maxima at 397 nm, which was attributed to the $\pi-\pi^*$ transition of the ligand [15]. The excitation maxima ascribed to $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of europium ion. This indicates the efficient absorption of energy by the ligand, which sensitized the central Eu^{3+} ion by transferring the absorbed energy.

Excited by 397 nm wavelength, the solid state photoluminescence emission spectrum was obtained at room temperature as depicted in Fig. 3. The emission spectra showed narrow characteristic peaks at 538 nm, 580 nm, 592 nm, 616 nm and 652 nm corresponding to the $^5\text{D}_1 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, and $^5\text{D}_0 \rightarrow ^7\text{F}_3$ electronic transition of the europium ion. The most intense peak of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition was an electric dipole transition which was hypersensitive to the site symmetry of europium ion and responsible for the red photoluminescence of the complexes [16]. While medium intense peak of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition was magnetic dipole transition which was insensitive to the local chemical environment of europium ion. It is observed from the emission spectra that the luminescence intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is higher than that of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, suggesting the asymmetric coordination environment around the central europium ion which is devoid of an inversion centre.

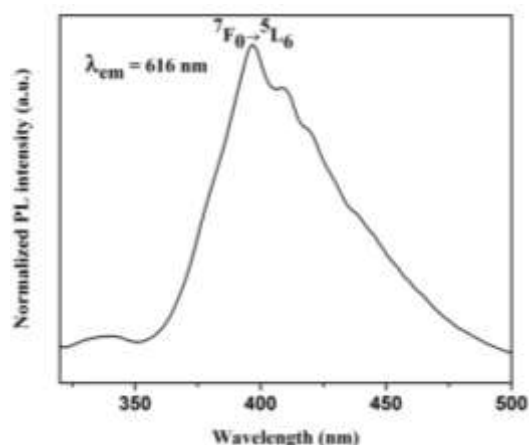


Fig. 2. The solid state excitation spectrum europium(III) complex monitored at 616 nm.

On the other hand, the weak intense $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_3$ transitions are forbidden in both electric as well as in magnetic dipole. In the emission spectra, the single peaks of $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_1$ transition are observed, suggesting the one type of chemical environment around the luminescent centre.

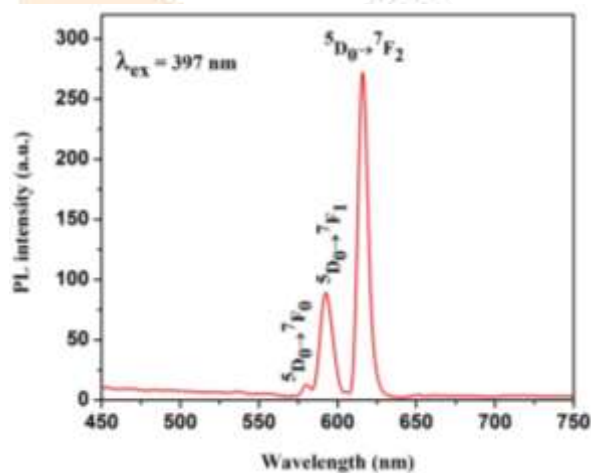


Fig. 3. The solid state luminescence emission spectrum of europium(III) complex excited at 397 nm.

The CIE (Commission Internationale de Eclairage) chromaticity coordinates (x and y) were used to analyze and confirm the luminescence color of the europium complex. These were estimated from their corresponding emission spectrum excited at 397 nm.

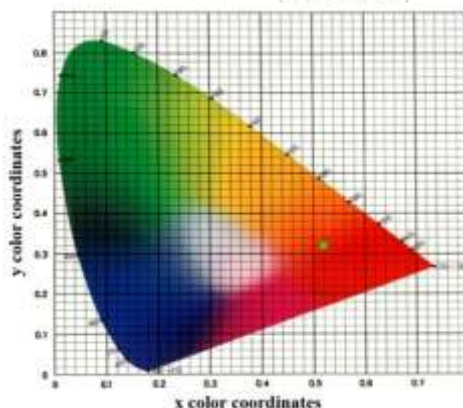


Fig. 4. The CIE color coordinates of europium(III) complex.

The chromaticity coordinates are represented in the form of CIE chromaticity diagram as depicted in Fig. 4. The x and y coordinates (0.5245, 0.3239) located in the red region of chromaticity diagram, indicating that these complexes can be used as red component in display devices.

The luminescence decay curve of the europium(III) complex was obtained in solid state by monitoring the most intense emission (616) and excitation (397nm) peaks as shown in Fig. 5. The luminescence decay time of 5D_0 state of europium ion was measured by fitting the decay curves with a single exponential function ($I=I_0 \exp^{-t/\tau}$), implying the existence of only one luminescent centre in the complex.

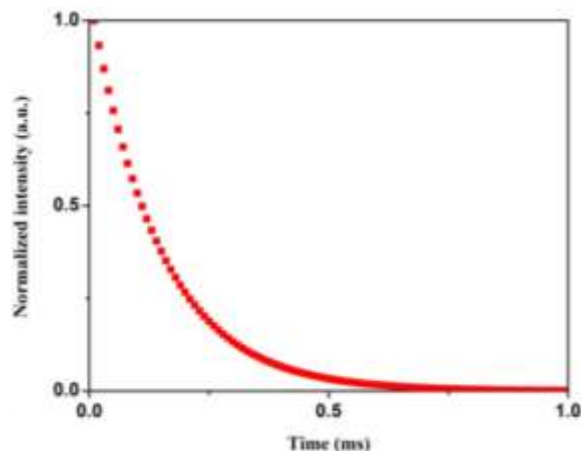


Fig. 5. The photoluminescence decay curve europium(III) complex.

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