

PREPARATION AND OPTOELECTRONIC PROPERTIES OF GREEN LIGHT EMITTING TERBIUM COMPLEX

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ABSTRACT: A β -hydroxyketone 5-fluoro-2-hydroxyacetophenone (FHAP) was employed to synthesize the green light emitting terbium complex. The various techniques such as CHN elemental analysis, IR, NMR, UV-visible and photoluminescence (PL) spectroscopy were used to characterize the ligand and complex. In the emission spectra, three peaks at 491 nm, 545 nm and 592 nm observed which were assigned to the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$ and $^5D_4 \rightarrow ^7F_4$ transitions of the terbium(III) metal ion. The electric dipole $^5D_4 \rightarrow ^7F_5$ transition dominated in the emission spectra which was sensitive to the chemical environment of the terbium ion and controlled the green luminescent color of the complex. The CIE color coordinates (x and y) fall in the green region of the chromaticity diagram. The optoelectronic properties demonstrated that the terbium(III) complex can be applied as luminescent component in display devices.

Keywords: β -hydroxyketone, IR, UV-visible, optoelectronic properties.

1. INTRODUCTION

The optoelectronic properties of luminescent lanthanide complexes is highly fascinating because these complexes widely used in display panels [1-2], organic light emitting devices [3] fluoroimmunoassays [4], laser technology and optical telecommunication [5]. The lanthanide ions have unique photophysical properties such as narrow emission bands, large Stoke's shifts, long luminescence decay time and high quantum efficiency due to the transitions of the inner 4f electrons which are shielded from their outer filled 5s and 5p subshells. As a consequence of Laporte forbidden f-f transitions, the lanthanide ions exhibit low absorption which leads to low photoluminescence intensity. In order to solve this problem, the lanthanide ion encapsulated with light harvesting organic ligands which increases the luminescence intensity of the complexes via antenna effect [6]. The role of organic ligand absorbs UV light and then transfers it to the emitting state of the central metal ion via its lower excited triplet state [7]. It is well known that the rare earth ions have strong affinity for hard base such as oxygen and nitrogen donor ligands. So, β -hydroxy ketone having aromatic ring was selected as light harvesting organic chelating agent for the synthesis of terbium complex. The β -hydroxy ketone FHAP (5-fluoro-2-hydroxyacetophenone) was synthesized by Fries rearrangement and employed as main organic ligand to synthesize the terbium complex. The composition and structure of ligand and its terbium complex were analyzed by FT-IR, ¹H-NMR and elemental analysis. The excitation and emission spectra, decay curves and CIE chromaticity coordinates of the complexes were estimated and analyzed in detail to focus on the photoluminescence properties of the complex.

2. Experimental

Lanthanide nitrate [Tb(NO₃)₃.5H₂O] of high purity was purchased from Sigma Aldrich. Other chemicals of analytical grade such as hexane, ether, aluminium chloride and 4-fluorophenylacetate were purchased from the commercial source and used without any purification process. The FHAP ligand was synthesized and purified by the recrystallization process with hexane solvent. The elemental analysis for carbon, hydrogen and nitrogen was carried out on Perkin Elmer 2400 CHN Elemental analyzer. The terbium metal content in the complex was calculated by complexometric titration with EDTA (ethylenediaminetetraacetate) chelating agent. The FT-IR spectra were performed on Nicolet iS50 FT-IR spectrometer with KBr pellets in mid IR (4000-400 cm⁻¹) region. The ¹H-NMR spectra were obtained from Bruker Avance II 400 spectrometer in chloroform and TMS as a reference. The UV- visible absorption spectra of ligand and complexes were recorded on Shimadzu UV-3600 plus UV-visible spectrophotometer referenced to DMSO as the internal standard. The photoluminescence measurements were measured on Hitachi F-7000 fluorescence spectrometer equipped with Xe lamp as irradiation source. The excitation and emission spectra of complexes were recorded in wavelength scan mode at a 240 nm/min scanning speed with 2.5 nm slit width. Also, the luminescence decay curves were measured in time scan mode excited at 370 nm.

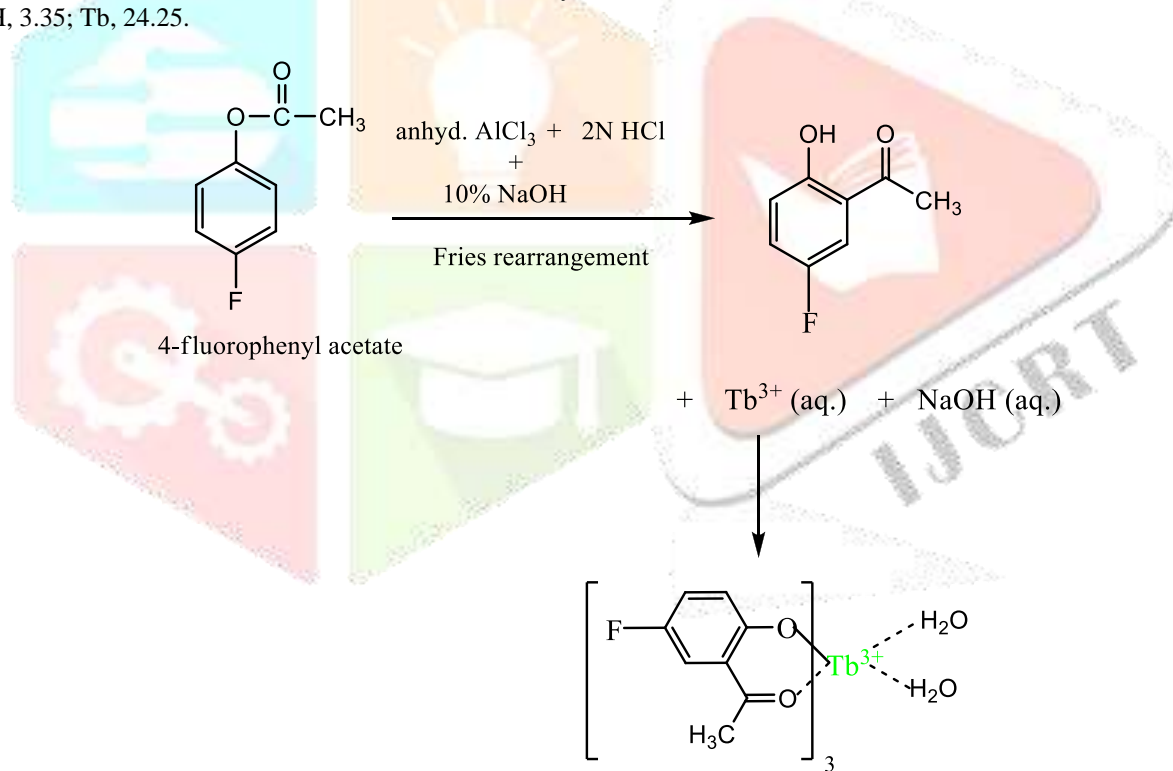
2.1 Synthesis of 5-fluoro-2-hydroxyacetophenone (FHAP) ligand

The FHAP ligand was synthesized by the Fries rearrangement (Scheme 1) and the procedure is described as follows: In a round bottom flask, 4-fluorophenylacetate (76 mL, 0.58 mol) was added to anhydrous aluminium chloride (86 g, 0.64 mol). The reaction mixture heated around 115°C for 2 h on the oil bath and cooled to room temperature. The solid mass was formed to which 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 [8]. 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, $-\text{CH}_3$) ppm. Elemental analysis calculated for $\text{C}_8\text{H}_7\text{O}_2\text{F}$: C, 62.33; H, 4.54; Found C, 62.12; H, 4.50.

2.2 Synthesis of terbium(III) complex

The terbium(III) complex was synthesized by using solution precipitation method. An ethanolic solution of FHAP (0.49 g, 3.2 mmol) and an aqueous solution of terbium nitrate pentahydrate (0.43 g, 1.0 mmol) were mixed under vigorous stirring on the magnetic stirrer. Then, the pH of resulting mixture was set to 6.5 by using 0.05 M sodium hydroxide solution and kept the solution on the magnetic stirrer at about 45°C temperature. After some time, yellow precipitates started to appear. Then stirred the mixture for 2 h and allowed the mixture to stand for half an hour. These precipitates settled down, which were collected and purified by washing with distilled water and ethanol. Finally, precipitates were dried in hot air oven to obtain the yellow solid powder [9].

$\text{Tb}(\text{FHAP})_3(\text{H}_2\text{O})_2$: light yellow solid, yield 72%; IR (KBr): cm^{-1} 3412 (b), 3062 (m), 2989 (m), 1629 (s), 1457 (s), 1422 (s), 1364 (s), 1315 (s), 1248 (s), 1215 (s), 1182 (s), 1058 (s), 965 (m), 912 (m), 858 (m), 805 (m), 736 (s), 676 (s), 423 (m); $^1\text{H-NMR}$ (400 MHz): δ 7.92-7.12 (m, 9H, Ar-H), 2.68 (s, 9H, $-\text{CH}_3$). Elemental analysis calculated for $\text{TbC}_{24}\text{H}_{22}\text{O}_8\text{F}_3$: C, 44.03; H, 3.36; Tb, 23.31; found: C, 43.96; H, 3.35; Tb, 24.25.



Scheme 1. The synthetic route and structures of the FHAP ligand and its terbium(III) complex.

3. Results and discussion

3.1. Elemental analysis

In elemental analysis, the experimental values were found to be in good agreement with the theoretical values, confirming the successful synthesis of ligand and complex. All complexes were yellow solid and stable at room temperature conditions. These complexes exhibited the solubility in chloroform, dichloromethane, DMSO and dimethyl formamide solvents.

3.2 FT- IR and NMR spectral analysis

The most significant infrared bands of FHAP ligand and terbium(III) complex were studied to know the binding sites of the ligand. The binding sites of ligand were mainly affected in coordination process. Therefore, the spectrum of ligand showed some remarkable changes in comparison to spectra of complex. In the spectrum of ligand, the broad band appeared at 3428 cm^{-1} which was associated with the phenolic $-\text{OH}$ stretching vibration. This band merged with another broad band of $-\text{OH}$ stretching vibration of water molecules presents in coordination sphere of the complex. The stretching vibration of $>\text{CO}$ group in the spectrum of ligand noticed at 1650 cm^{-1} which was shifted to lower value in the spectrum of complex indicating the involvement of $>\text{CO}$ group in coordination and acts as binding site of the ligand [10]. This was definitely confirmed by the new bands which appeared in $425\text{--}419\text{ cm}^{-1}$ region, assigned to Tb-O stretching vibrations. From the above discussion, it could be concluded that the $>\text{CO}$ group and phenolic $-\text{OH}$ are the main binding sites of FHAP ligand which directly coordinates to the central Tb(III) ion.

The chemical shifts of the $^1\text{H-NMR}$ spectra were taken in ppm with respect to TMS as a reference. A singlet of phenolic proton observed at 11.91 ppm in the spectrum of FHAP ligand which disappeared in the spectra of complexes, confirming the phenolic group as coordination site. In the spectrum of complex, the signal of aromatic protons moved downfield as compared to the spectrum of ligand due to the extended conjugation in the complexes. Therefore, the NMR and IR studies assured the binding sites of the ligands in the complex.

3.3 UV-visible absorption spectra

Figure 1 displays the UV-visible absorption spectra of FHAP ligand and terbium(III) complex which were measured with 1×10^{-5} mol/L concentration using DMSO as reference. The maximum absorption noticed at 318 nm in the spectrum of FHAP ligand, was attributed to singlet-singlet $\pi\text{-}\pi^*$ absorption of aromatic ring [11] while, the maximum absorption of complex exhibited red shift in comparison to ligand which was also assigned to the $\pi\text{-}\pi^*$ transition of ligand. The shifting of absorption maxima in complexes clearly showed the extended π -conjugation in complexes due to the three molecules of FHAP ligands. These results clearly indicated that FHAP ligand sensitized the metal ion efficiently in which ligand helped in the absorption of energy over a wide range of UV-visible wavelength and finally transferred it to the central metal ion.

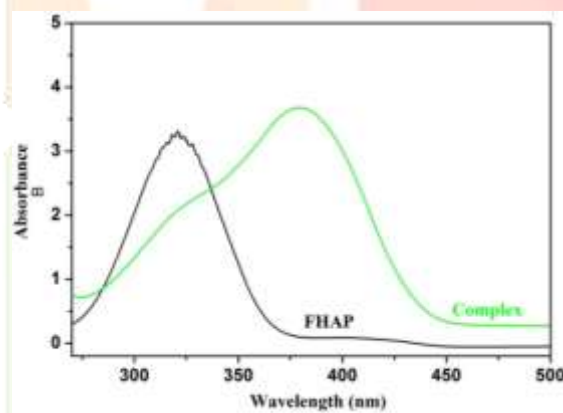


Fig. 1. The UV-visible absorption spectra of FHAP ligand and terbium complex in DMSO solvent.

3.4 Luminescence properties

Excited by 545 nm wavelength, the solid state photoluminescence excitation spectra of C1-C5 Tb(III) complexes were recorded at room temperature as displayed in Fig .2.

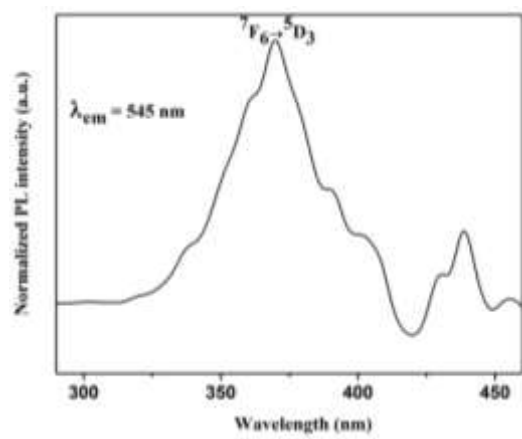


Fig. 2. The photoluminescence excitation spectrum of terbium(III) complex monitored at 545 nm.

The maximum excitation wavelength of the complexes was observed at 370 nm which can be assigned to the π - π^* transition mainly centered at the organic ligand. The excitation maxima of the complexes associated with the ${}^7F_6 \rightarrow {}^5D_3$ electronic transition of the terbium ion.

The emission spectrum of terbium(III) complex displayed the characteristic sharp peaks upon excitation at 370 nm which were assigned to the transition between the excited 5D_4 level and 7F_j ($j = 0-4$) levels of terbium ion as shown in Fig. 3. The emission spectrum of complex manifested three peaks at 491 nm, 545 nm and 592 nm corresponding to the ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$ and ${}^5D_4 \rightarrow {}^7F_4$ transitions of the terbium(III) ion [9]. The ${}^5D_4 \rightarrow {}^7F_5$ transition at 545 nm dominates in the emission spectrum, which is electric dipole transition and sensitive to the local site symmetry of terbium(III) ion. This strongest peak controlled the green luminescence color of the terbium complex. On the other hand, the peak of ${}^5D_4 \rightarrow {}^7F_6$ transition at 491 nm is magnetic dipole transition and insensitive to the local chemical environment around the central rare earth Tb^{3+} ion. The highest intensity of electric dipole transition demonstrated the asymmetric environment around the Tb(III) ion. On the contrary, the peak of ${}^5D_4 \rightarrow {}^7F_4$ transition is forbidden in electric as well as in magnetic dipole.

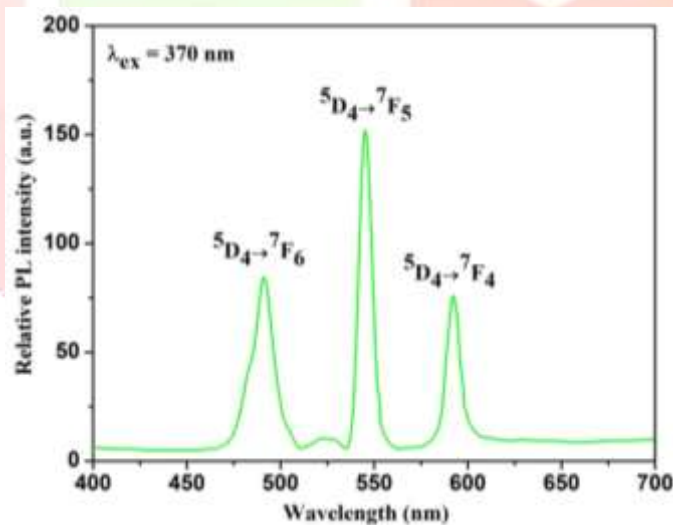


Fig. 3. The solid state emission spectra of terbium(III) complex excited at 370 nm.

On the basis of luminescence emission spectra, the CIE (Commission Internationale de Eclairage) chromaticity coordinates of terbium(III) complex were determined and their values were spotted in the coordinate chromaticity diagram as shown in Fig 4. The color coordinates (0.1424, 0.6493) of the complex located in the green regime of the chromaticity diagram which clearly revealed the candidature of terbium complex as one of the green component in display devices.

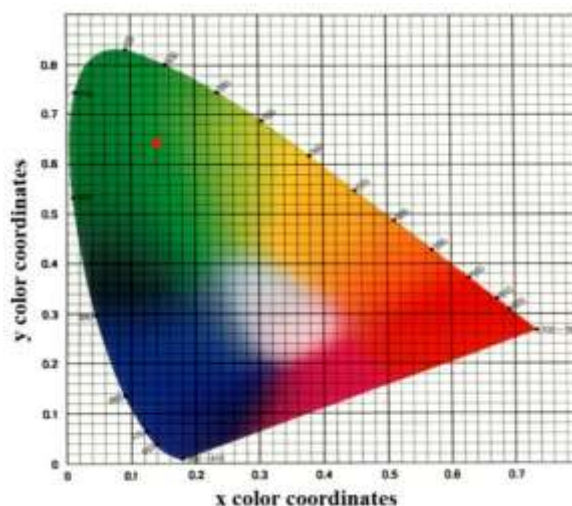


Fig. 4. The CIE color coordinates of terbium(III) complex.

The photoluminescence decay profile of the 5D_4 emitting level of the complex was recorded in solid state, excited with 370 nm wavelength at room temperature as displayed in Fig. 5. The photoluminescence decay time of the complex was calculated by fitting the decay profiles into single exponential function $I=I_0 \exp^{-t/\tau}$ here, I and I_0 are the luminescence intensity at time t and 0 respectively and τ is the radiative decay time. This suggested that only one luminescent centre was present in the complexes.

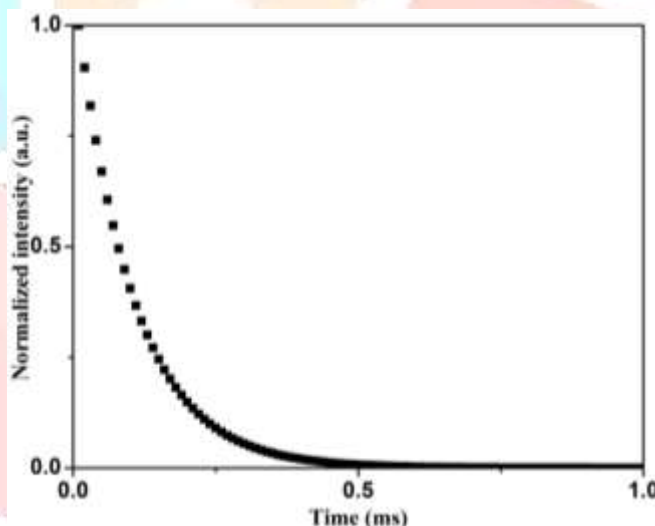


Fig. 5. The photoluminescence decay curve terbium(III) complex.

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