

SYNTHESIS OF TERBIUM(III) COMPLEX BASED ON HYDROXY KETONE AND ITS OPTICAL FEATURES

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ABSTRACT: Synthesis and optical features of terbium complex with 2-hydroxy-4-methoxybenzophenone (HMBP) ligand has been reported in this communication. The HMBP ligand and its complex were analyzed by various techniques such as ¹H-NMR, IR, CHN elemental analysis and UV-visible spectroscopy. The optical features of the terbium(III) complex was investigated by photoluminescence (PL) spectroscopy. The excitation and emission spectra, CIE color coordinates and luminescence decay curve were deeply analyzed in order to examine the optical properties of the complex in detail. The results demonstrated that the luminescent terbium complex could be a potential component in light emitting materials.

Keywords: Optical features, IR, UV-visible, light emitting materials.

1. INTRODUCTION

The luminescent metal complexes based on organic ligands have been widely studied for its narrow emission bands, long luminescence life time and broad Stoke's shift which find wide range of application in large flat panel display [1-3], in biomedical as a luminescence probe for analyses [4], in chemical sensing [5] and contrast agent for magnetic resonance imaging in biological field [6]. The f-f transitions are Laporte and spin forbidden transitions which are the consequence of weak induced electronic dipole and magnetic dipole, therefore direct excitation of metal ion is not possible. To overcome this problem, an organic moiety with high absorption coefficient is introduced which transfers sufficient energy for excitation to the central metal ion [7]. Among the numerous organic moieties, the hydroxy ketone derivatives are used as a main organic ligand, which saturate the liganacy of central metal ion and act as bridge to obtain the efficient energy transfer for the excitation of metal ion that results in strong absorption over a wide range and sensitize the luminescence of central metal ion.

In this report, the synthesis and optical features of terbium(III) complex with HMBP ligand have been studied. The terbium(III) complex was characterized by means of elemental analysis, ¹H-NMR, infrared (IR), UV-visible and photoluminescence (PL) spectrophotometer. The optical properties were investigated which clearly indicated that the HMBP ligand absorbed the energy over a wide range of wavelength and transferred to the central metal ion effectively via sensitization process.

2. Experimental

The commercially available chemicals employed in this work were reagent grade and used without further purification. The ligand HMBP was synthesized and recrystallized three times in ethanol. The terbium nitrate (Tb(NO₃)₃·5H₂O) was used from Sigma Aldrich chemicals. The ligand HMBP was synthesized adopting ecofriendly microwave approach and then recrystallized three times with DMSO to obtain ligand of high purity. Double distilled water was used through the experiments.

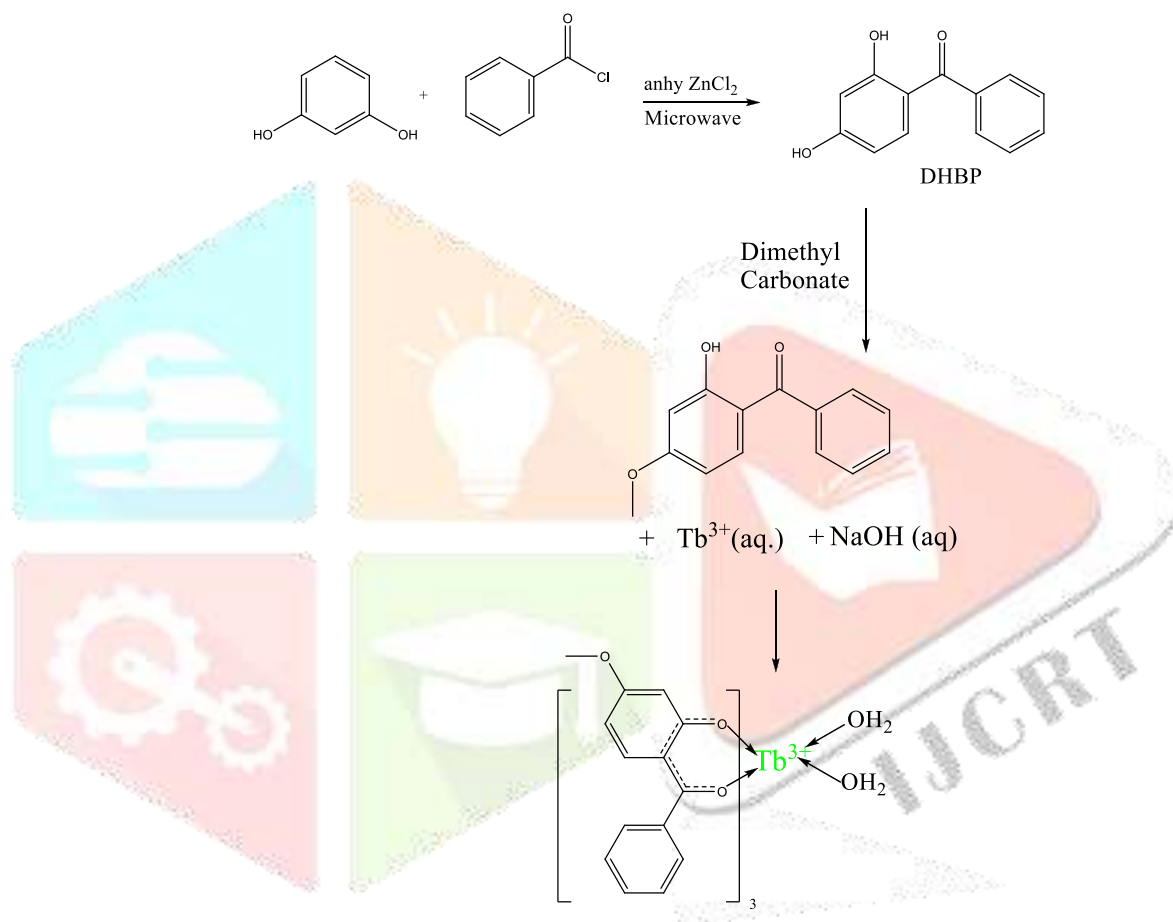
2.1 Synthesis of HMBP ligand

The synthesis of HMBP ligand was divided into two steps. In the first step, 2,4-dihydroxybenzophenone (DHBP) was synthesized as described. To the mixture of resorcinol and benzoyl chloride added anhydrous zinc chloride in the 1:1 ratio at the temperature 50-55°C in solvent free condition under microwave irradiation for the 55 seconds. Zinc chloride catalyzed the Friedal-Craft acylation reaction. The pale yellow powder obtained was recrystallized three times with ethanol. The yield and melting point of the resulting product was found to be 70% and 145°C respectively [8]. In the second step, 2-hydroxy-4-methoxybenzophenone (HMBP) ligand was synthesized from dimethyl carbonate and 2,4-dihydroxybenzophenone using microwave irradiation procedure as described above (Scheme 1). The solid residue was recrystallized from ethanol. HMBP was obtained as a light yellow solid with yield 52% and melting point to be noted 65°C; IR (KBr):cm⁻¹ 3431 (b), 3174 (w), 3068 (w), 2945 (w), 2841 (w), 2727 (w), 1636 (s), 1589 (m), 1506 (s), 1434 (s), 1386 (s), 1262 (m), 1101 (m), 1024 (m), 911 (m), 816 (m), 709 (m), 602 (m); ¹H-NMR (400 MHz): δ 12.34 (s, 1H, OH), 7.62 (d, 1H, Ar-H), 7.61 (m, 2H, Ar-H), 7.57 (m, 2H, Ar-H), 7.46 (m, 1H, Ar-H), 6.60 (d, 1H, Ar-H), 6.55 (s, 1H, Ar-H), 3.82 (s, 3H, OCH₃). Anal. Cal. for C₁₄H₁₂O₃: C, 73.68; H, 5.26; Found C, 73.06; H, 5.01.

2.2 Synthesis of terbium(III) complex

The aqueous solution of terbium nitrate (0.43 g, 1.0 mmol) added to the alcoholic solution of HMBP (0.73 g, 3.2 mmol) under constant stirring. The resulting mixture was stirred at 55-60°C for 3 h on the magnetic stirrer. The pH of the solution was adjusted to 6.5-7.0 with the 0.05 M sodium hydroxide solution. The yellow precipitates of complex appeared which were collected by vacuum filtration. These precipitates were washed with ethanol and then distilled water and finally dried in the hot air oven to obtain the complex [9].

Tb(HMBP)₃(H₂O)₂ (C1): yellow powder, yield 82%; IR (KBr):cm⁻¹ 3057 (w), 2999 (w), 2837 (w), 1598 (s), 1566 (s), 1514 (s), 1460 (m), 1442 (s), 1411 (m), 1358 (s), 1252 (s), 1212 (m), 1163 (m), 1110 (m), 1026 (m), 972 (m), 839 (m), 787 (m), 751 (m), 663 (m), (w); ¹H-NMR (400 MHz): δ 8.20 (d, 3H, Ar-H), 8.10-7.48 (m, 12H, Ar-H), 7.35 (d, 3H, Ar-H), 7.04 (s, 3H, Ar-H), 6.58 (m, 3H, Ar-H), 3.81 (s, 9H, OCH₃); Anal. Cal. for TbC₄₂H₃₇O₁₁: C, 57.53; H, 4.22; Tb, 18.15; Found C, 57.45; H, 4.20; Tb, 18.10.



Scheme 1. The synthetic pathway of HMBP ligand and its terbium(III) complex.

3. Results and discussion

3.1. Elemental analysis

The results of elemental analysis of carbon, hydrogen and nitrogen of HMBP ligand and their complex confirmed the composition of ligand and its terbium complex. The experimental values of elemental analysis closely approached to the calculated values.

3.2 FT- IR and NMR spectral analysis

The comparison of IR spectral data of ligand and terbium complex showed that the >CO stretching frequency of the complex was red shifted in comparison to free HMBP ligand, which was the result of coordination through keto group. The IR spectrum of free HMBP ligand showed a broad band of phenolic -OH at 3431 cm⁻¹ which disappeared in corresponding spectrum of complex, indicating the involvement of the phenolic -OH group in complexation. This is further confirmed by the shifting of Ph-O vibration to lower value in spectrum of complex as compared to the spectrum of ligand. This was also supported by the appearance of bands at 463 cm⁻¹ region in the spectrum of complex only, which were assigned to the coordinated Tb-O stretching vibrations of metal-oxygen bond [10].

The $^1\text{H-NMR}$ spectrum of terbium(III) complex in comparison to the spectrum of HMBP ligand showed shifting of aryl protons signal to the lower magnetic field whereas the $-\text{OH}$ proton signal disappeared in the spectrum of complex. These spectroscopic studies indicated that the coordination of ligand to the central metal ion through phenolic $-\text{OH}$ group and keto group of the HMBP ligand.

3.3 UV-visible absorption spectra

Figure 1 displays the UV-visible absorption spectrum of free HMBP ligands and terbium complex with 10^{-5} mol/L concentration in DMSO solution. These spectra were recorded in 250-500 nm range at room temperature. The strong absorption bands appeared at 288 nm and 325 nm in the spectrum of the ligand which were attributed to the $\pi-\pi^*$ transition. The absorption band of 325 nm was red shifted in the complex, indicating the extended π -conjugation in the complex. The maximum absorption in the complex also assigned to the $\pi-\pi^*$ transition of the ligand [11] because metal exhibited very low absorption coefficient in UV region.

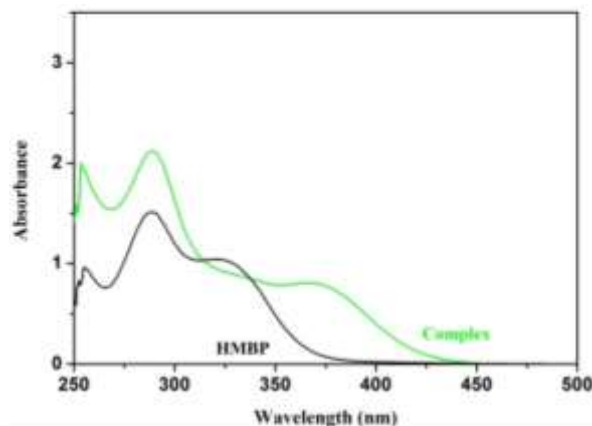


Fig. 1. The UV-visible absorption spectra of HMBP ligand and terbium complex in DMSO solvent.

3.4 Luminescence properties

The solid state excitation spectrum of the complexes was measured at the emission maximum wavelength (545 nm) at room temperature as depicted in Fig. 2. The spectrum showed a broad band in 280-420 nm range with maxima at 370 nm which is attributed to the $\pi-\pi^*$ transition of coordinated HMBP ligand. The maximum of the spectrum was assigned to the $^7\text{F}_6 \rightarrow ^5\text{D}_3$ transition of the terbium ion.

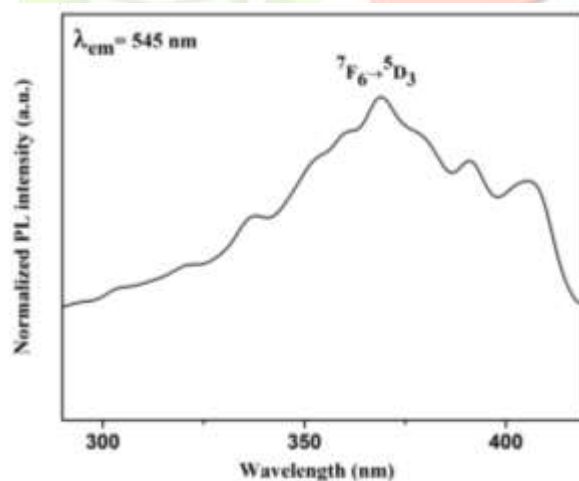


Fig. 2. The solid state excitation spectrum terbium(III) complex monitored at 545 nm.

The characteristic emission bands of terbium complexes were observed at 481 nm, 545 nm and 624 nm, which are associated with $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$ and $^5\text{D}_4 \rightarrow ^7\text{F}_4$ transitions of the Tb^{3+} ion as shown in Fig. 3 [9]. Among the above mentioned transitions, the most intense $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition at 545 nm is induced electric dipole transition which is highly sensitive to the coordinated environment present around the terbium ion while $^5\text{D}_4 \rightarrow ^7\text{F}_6$ transition at 481 nm is magnetic dipole transition which is non-sensitive to the environment of the metal ion.

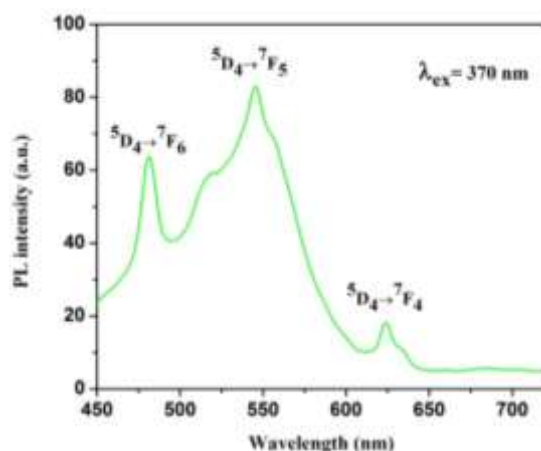


Fig. 3. The solid state luminescence emission spectrum of terbium(III) complex excited at 362 nm.

On the basis of the emission spectrum, the CIE (Commission Internationale de Eclairage) color coordinates (x and y) of the terbium(III) complexes were calculated and their values found to be 0.3112, 0.5730. The color coordinates of the complexes are displayed in the chromaticity diagram as presented in Fig. 4. The color coordinates of the complexes fall in the light green region of the chromaticity diagram.

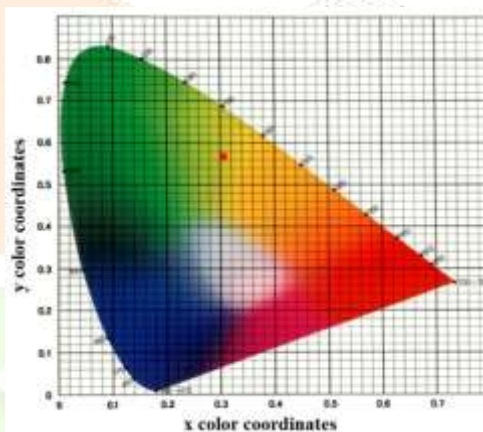


Fig. 4. The CIE color coordinates of terbium(III) complex.

Figure 5 displays the luminescence decay curves of the complexes which were recorded by monitoring the most intense peak of 545 nm, in order to analyze the luminescence decay time and nature of the coordination environment around the luminescent center. The values of decay time were estimated by fitting these curves into single exponential function, indicating the presence of one site symmetry in the complexes [82].

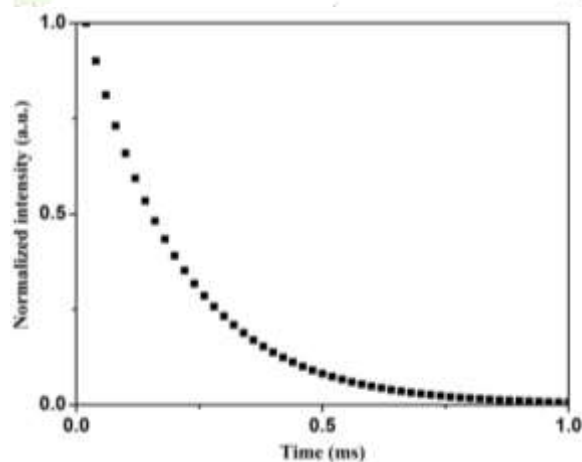


Fig. 5. The photoluminescence decay curve terbium(III) complex.

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