

# Synthesis and optical properties of green light emitting Tb(III) complex Tb (CHME)<sub>3</sub>.Bathophen

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## ABSTRACT

The present work reports the synthesis and characterization of Tb(III) complex with  $\beta$ -hydroxyketone 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME) as the main ligand and bathophenanthroline as ancillary ligand by adopting solution precipitation method. The ligand and Tb(III) complex were characterized by elemental analysis, FT-IR, <sup>1</sup>H-NMR and photoluminescence spectroscopy. The emission spectrum of complex upon excitation at  $\lambda_{ex} = 386$  nm exhibit four characteristic peaks attributed to <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>6</sub>, <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub>, <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>4</sub> and <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>3</sub> transitions.

**Keywords:** Tb(III) complex, <sup>1</sup>H-NMR, FT-IR, optical property

## I. INTRODUCTION

The rare earth ion complexes with organic ligands have triggered the interest of researchers owing to their fascinating photoluminescent properties [1-3] due to their large Stokes shift, long luminescence life time and sharp emission in the visible region [4-7]. These complexes are widely explored for applications in full-color flat panel displays [8, 9], laser materials [10, 11] and fabrication of organic light emitting devices [12-14]. Terbium is the important member of the rare earth family, therefore in recent year's great success have been achieved in improving the brightness and electroluminescence efficiencies of OLEDs with Tb(III) ion as luminescent center. The photoluminescent properties of Tb(III) ion are stipulated by spin and parity-forbidden 4f-4f transitions and have extremely low molar extinction coefficients [15, 16] therefore, the direct excitation of Tb(III) ion is quite inefficient. Hence, to improve the process of excitation, an organic ligand or chromophore is required which can chelate the Tb(III) ion and encapsulate it from the solvent molecules.

This organic ligand efficiently transfer the energy to the emitting level of central Tb(III) ion upon excitation with near UV light and the effect is known as antenna effect [17-20]. The literature survey reveals that the  $\beta$ -hydroxyketone and its derivatives acts as a suitable antenna to sensitize the Tb(III) ion efficiently [21-23].

Therefore, to investigate new photoluminescent material, novel terbium(III) complex with  $\beta$ -hydroxyketone 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME) by introducing nitrogen containing ancillary ligand have been synthesized successfully.

## II. EXPERIMENTAL DETAILS

### 2.1 methods and materials

Terbium nitrate pentahydrate [Tb(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O] and bathophenanthroline (bathophen) were purchased from Sigma-Aldrich. Resorcinol, potassium carbonate, 4-chlorobenzylcyanide, dimethyl sulphate were purchased from Hi-Media Pvt. Ltd. The reagent

employed were of analytical grade and used without any further purification. The elemental analysis (C, H, N and O) of the synthesized ligand CHME and its corresponding Tb(III) complex were carried out using thermo scientific flash 2000 elemental analyzer, while the terbium ion in the complex was estimated by complexometric titration with ethylenediaminetetraacetate (EDTA) using xylenol orange as an indicator. <sup>1</sup>H-NMR spectra were recorded on BrukerAvance II 400 spectrometer (400 MHz) in dimethylsulfoxide solution. The Fourier transform infra-red (FT-IR) were recorded on Perkin Elmer spectrum 400 FT-IR spectrometer in the spectral range 4000–400 cm<sup>-1</sup> using KBr discs. The excitation and emission spectra in the UV-Visible region and decay curves were obtained on Hitachi F-7000 fluorescence spectrophotometer equipped with Xe-lamp in solid state at room temperature.

## 2.2 Synthesis

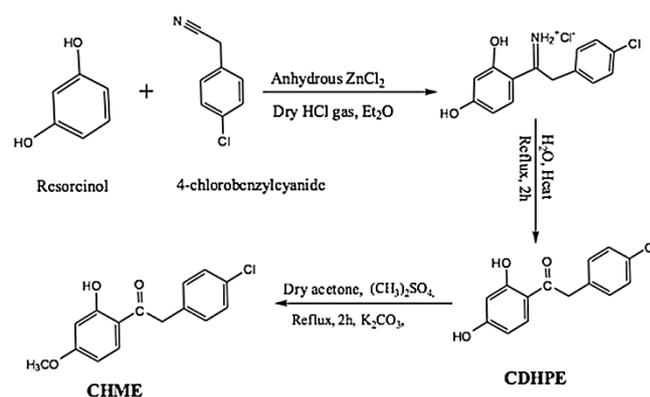
### 2.2.1 Synthesis of ligand 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME)

The ligand was synthesized in two steps by using Houben-Hoesch reaction mechanism between resorcinol and 4-chlorobenzylcyanide [23]. The synthetic route for the ligand CHME is given in Scheme 1.

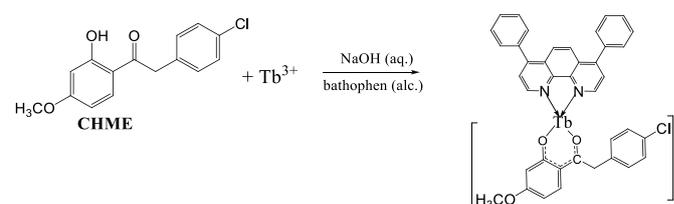
### 2.2.2 Synthesis of complex Tb(CHME)<sub>3</sub>.bathophen

The Tb(III) complex was synthesized as per scheme 2. In an ethanolic solution of CHME (0.82 g, 3 mmol) and bathophen (1 mmol) introduced an aqueous solution of Tb(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O (1 mmol) with constant stirring on magnetic stirrer. The solution was neutralized with 0.05 M NaOH aqueous solution and pH of mixture was adjusted to 7–8. The mixture was stirred for 3h at 35 °C and then allowed to stand for 1 h. During

stirring white precipitates appeared, which were purified by washing with doubly distilled water and then with ethanol to remove the free ligand, after that dried in air and then in vacuum desiccator. Finally, the precipitates were dried at 50 °C in hot air oven to obtain the complex. The complex Tb(CHME)<sub>3</sub>.bathophen was white powder with 87 % yield.



**Scheme 1.** The synthetic route of ligand CHME.



**Scheme 2.** The synthetic route and structure of Tb(CHME)<sub>3</sub>.bathophen complex.

## III. RESULTS AND DISCUSSION

### 3.1. Elemental analysis and solubility

Elemental analysis data for the ligand CHME and its corresponding Tb(III) complex are tabulated in Table 1 which are in accordance with the values calculated from the stoichiometry formula, confirming the composition of the complex.

**Table 1.** Elemental analysis data for ligand CHME and its corresponding Tb(III) complex, Tb(CHME)<sub>3</sub>.bathophen

Complexes	C (%) Found (calc.)	H (%) Found (calc.)	N (%) Found (calc.)	O (%) Found (calc.)	Tb (%) Found (calc.)
CHME	65.18 (65.10)	4.76 (4.73)	---	17.29 (17.34)	---
Tb(CHME) <sub>3</sub> .bathophen	62.76 (62.71)	4.22 (4.19)	2.15 (2.11)	10.76 (10.89)	12.09 (12.02)

The synthesized Tb(III) complex was found to be highly soluble in DMSO, chloroform, dichloromethane, acetone, methanol and ethanol but insoluble in benzene and hexane. The complex was stable under atmospheric condition.

### 3.2 <sup>1</sup>H-NMR and IR spectra

The <sup>1</sup>H-NMR spectra of ligand CHME and its Tb(III) complex were analysed at 400 MHz in DMSO solvent. The spectrum of complex indicates some apparent changes due to the paramagnetism of Tb<sup>3+</sup> ion as compared with those of free ligand CHME. The free ligand exhibits a singlet at  $\delta$  12.61 ppm which was assigned to the phenolic O-H proton. This proton signal of OH band disappeared in the spectrum of Tb(III) complex, indicating that oxygen atom of the phenolic OH coordinated with the Tb(III) ion. The peak of aryl protons of the ligand CHME and ancillary

ligand undergoes slight changes in the spectrum of the complex.

The IR peaks of free ligand CHME and complex were recorded in 4000-400 cm<sup>-1</sup> range and summarized in Table 2. The IR spectrum of free ligand CHME displays characteristic band at 3429 cm<sup>-1</sup> attributed to phenolic O-H stretching which disappeared in the spectrum of Tb(III) ternary complex, indicating that ligand was coordinated with Tb(III) ion through oxygen atom of phenolic group. The spectrum of ligand also displays band at 1633 cm<sup>-1</sup> assigned to C=O stretching vibrations [24, 25] which were red shifted 7cm<sup>-1</sup> in the complex indicating that the phenolic and carbonyl group of ligand CHME participated in coordination with Tb(III) ion. In the spectrum of complex, a new absorption band appeared at 1597 cm<sup>-1</sup> assigned to C=N stretching vibration of the ancillary ligand [26].

**Table 2.** The characteristic IR bands (cm<sup>-1</sup>) of the free ligand CHME and its corresponding Tb(CHME)<sub>3</sub>.bathophen complex

Complexes	$\nu$ (O-H)	$\nu$ (C=O)	$\nu$ (C=N)	$\nu$ (C=C)	$\nu$ (Ph-O)	$\nu$ (Tb-N)	$\nu$ (Tb-O)
CHME	3429	1633	---	1567	1229	---	---
Tb(III) complex	---	1626	1597	1522	1218	544	496

Two new absorption bands in the Tb(III) complex shows at 544 cm<sup>-1</sup> and 496 cm<sup>-1</sup> indicating the presence of Tb-N and Tb-O stretching vibrations respectively [27] as compared with the spectrum of free ligand CHME, confirming that the nitrogen atoms of the respective ancillary ligand was coordinated with Tb(III) ion. Finally, the result of <sup>1</sup>H-NMR and FT-IR spectra indicated that the ligand was coordinated with Tb(III) ion by the oxygen atom of phenolic group and

carbonyl group of the main ligand and nitrogen atoms of the bathophenanthroline.

### 3.3. Optical properties

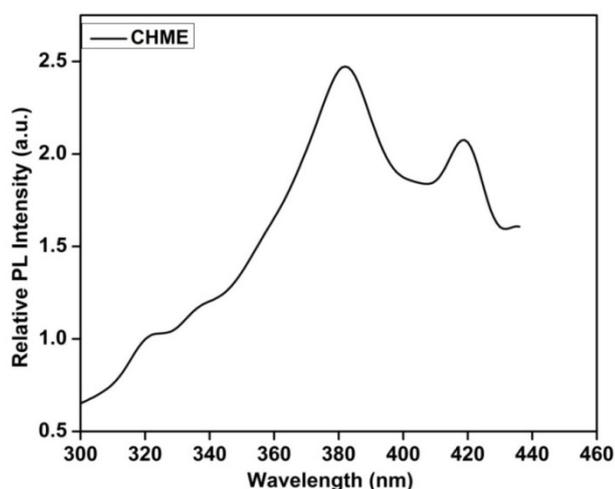
Figure 1 depicts the broad excitation band of ligand CHME centred at 382 nm due to  $\pi$ - $\pi^*$  transition in the

ligand. The photoluminescence data of Tb(III) complex is tabulated in Table 3. The solid state excitation spectrum of complex was investigated by monitoring emission at  $\lambda_{em} = 546$  nm as displayed in Figure 2. The excitation spectrum of Tb(III) complex

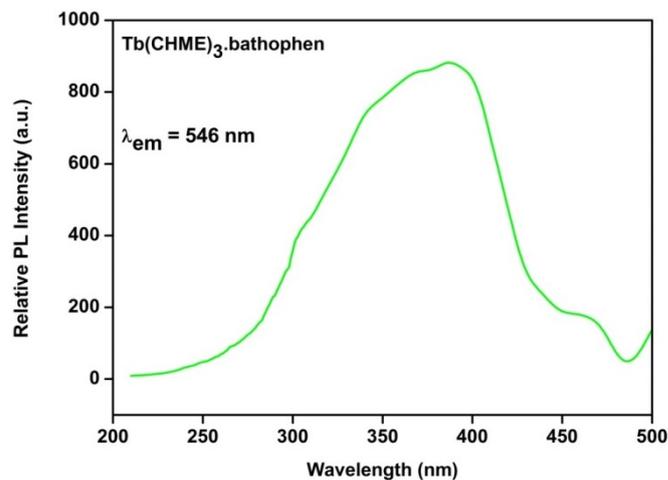
include an intense broad band extending from 250 to 450 nm centred at 386 nm, which was found to be red shifted by 4 nm with incredible enhanced intensity as compared to ligand CHME. This shift in absorbance value is a result of extended  $\pi-\pi^*$  conjugation.

**Table 3.** Photoluminescence data of Tb(CHME)<sub>3</sub>.bathophen.

Tb(CHME) <sub>3</sub> .bathophen	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	Assignment	$\tau$ (ms)	x and y coordinates
		491	$^5D_4 \rightarrow ^7F_6$		
	386	546	$^5D_4 \rightarrow ^7F_5$	2.430	0.2318,
		586	$^5D_4 \rightarrow ^7F_4$		0.4840
		619	$^5D_4 \rightarrow ^7F_3$		



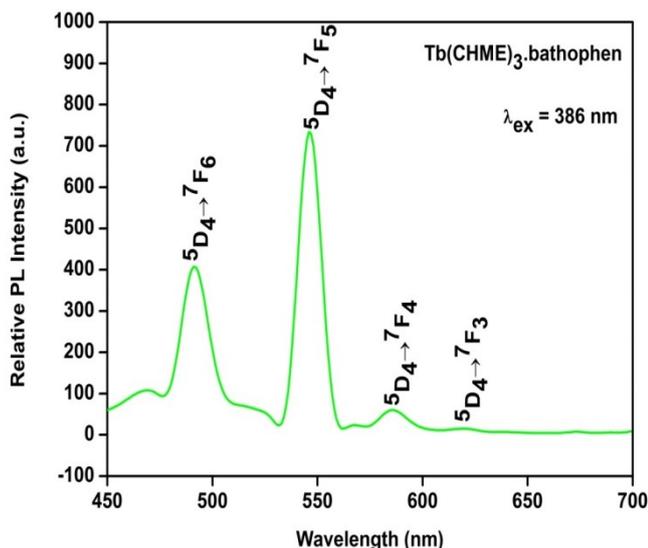
**Figure 1.** Excitation spectrum of CHME in solid state at room temperature.



**Figure 2.** Excitation spectrum of Tb(CHME)<sub>3</sub>.bathophen, monitored at  $\lambda_{em} = 548$  nm in solid

The emission spectrum of complex upon excitation at  $\lambda_{ex} = 386$  nm as shown in Figure 3, exhibit four characteristic peaks of Tb(III) ion at 491 nm, 546 nm, 586 nm and 619 nm attributed to  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$ ,  $^5D_4 \rightarrow ^7F_4$  and  $^5D_4 \rightarrow ^7F_3$  transitions respectively [28, 29]. Among these characteristic transitions, the  $^5D_4 \rightarrow ^7F_5$  transition is electric dipole transition and very sensitive to the coordination environment of the Tb<sup>3+</sup> ion whereas  $^5D_4 \rightarrow ^7F_6$  is magnetic dipole transition which is insensitive to the local structure

environment of central metal ion. In the complex the most intense transition was  $^5D_4 \rightarrow ^7F_5$  as compared to the other transitions which indicated that Tb<sup>3+</sup> ion coordinated in a local site without an inversion center. The intense green emission of these complexes fulfils the requirement of basic green luminescent materials for fabrication of OLEDs.



**Figure 3.** Emission spectra of Tb(CHME)<sub>3</sub>.bathophen in solid state at room temperature, monitored at  $\lambda_{ex} = 386$  nm.

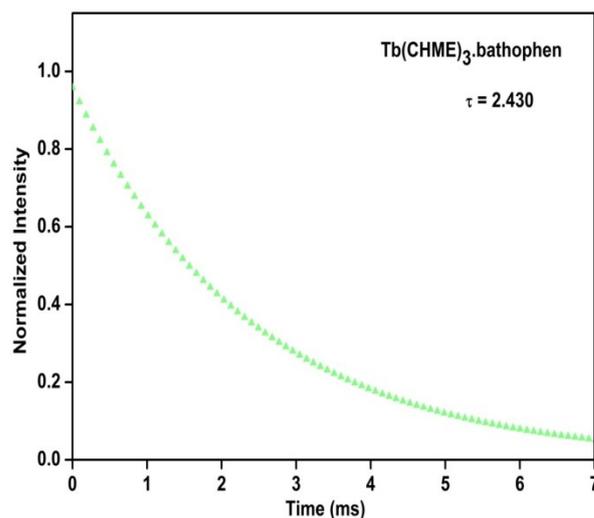
Figure 4 represents the photoluminescence decay curves of <sup>5</sup>D<sub>4</sub> level of these Tb(III) complex monitored at  $\lambda_{em} = 546$  nm under  $\lambda_{ex} = 386$  nm in solid state at room temperature. The lifetime values was calculated by applying the equation  $I = I_0 \exp(-t/\tau)$ , where  $\tau$  is the radiative decay time, I and I<sub>0</sub> are the luminescence intensities at time t and 0, respectively. By fitting single exponential, the lifetime value observed for complex is 2.430 ms. The introduction of nitrogen containing ancillary ligand bathophenanthroline results the longer lifetime.

The CIE color coordinates (x, y) of the Tb(III) complex based on photoluminescence emission spectra are shown in Figure 5 and tabulated in Table 3. The chromaticity coordinate of complex 0.2318, 0.4840 indicates bright green emission of complex in CIE gamut space which clearly reveals the application

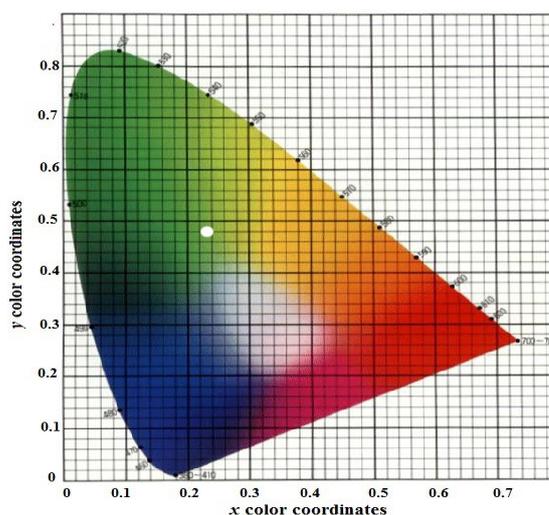
#### IV. CONCLUSION

In this paper, Tb(CHME)<sub>3</sub>.bathophen was synthesized successfully by employing 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one(CHME) as main ligand and bathophenanthroline as ancillary ligand. The structure of the ligand as well as complex was confirmed by elemental analysis, FT-IR, <sup>1</sup>HNMR

of the complex in luminescent materials such as organic light emitting diodes (OLEDs).



**Figure 4.** Luminescence decay profile of complex Tb(CHME)<sub>3</sub>.bathophen in solid state at room temperature, monitored at  $\lambda_{ex} = 386$  nm.



**Figure 5.** CIE color coordinate diagram of Tb(CHME)<sub>3</sub>.bathophen.

and optical properties. The emission spectrum of complex upon excitation at  $\lambda_{ex} = 386$  nm exhibit four characteristic peaks of Tb(III) ion at 491 nm, 546 nm, 586 nm and 619 nm attributed to <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>6</sub>, <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub>, <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>4</sub> and <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>3</sub> transitions respectively. In the complex the most intense transition was <sup>5</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> (electric dipole) as compared to the other transitions which indicated that Tb<sup>3+</sup> ion coordinated

in a local site without an inversion center. The lifetime decay curve of the complex shows the monoexponential behaviour which suggests the presence of single Tb(III) ion luminescent species is present in the chemical environment of the complex and having only one site symmetry. The chromaticity coordinate of complex 0.2318, 0.4840 indicates bright green emission of complex in CIE gamut space.

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