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Preparation and Photoluminescence Behaviour of Terbium (III) Complex: Tb (BMPD)₃ biq

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Abstract: The preparation of terbium(III) complex with 1,3-[bis(4-methoxyphenyl)]propane-1,3-dionato (BMPD) as a main ligand and 2,2'-biquinoline (biq) as an ancillary ligand was reported in this communication. The synthesis of BMPD ligand and its terbium (III) complex was supported by means of ¹H-NMR, FT-IR and CHN elemental analysis. The photoluminescence spectroscopy was used to investigate the photoluminescence behaviour of the complex which showed that ligand acts as an antenna and transferred the absorbed energy to the metal ion in an effective manner. In this manner, the complex possessed enhanced luminescent intensity and long decay time (τ). The CIE color coordinates fall under the green region of the chromaticity diagram. Hence, the complex can be used as a luminescent material and found potential application in organic light emitting devices.

Keywords: Photoluminescence behaviour, 2,2'-biquinoline, color coordinates, IR, photoluminescence spectroscopy

I. INTRODUCTION

The synthesis of organic lanthanide complexes attracts the attention of researchers mainly owing to their captivating photophysical properties which find various applications such as luminescence materials [1], electroluminescence devices [2], luminescent probes for development of fluoroimmuno-assays [3], organic light emitting devices (OLEDs) [4] and labels in biological systems [5]. The emission of light originates from the Laporte forbidden intra-configurational 4f-4f transition of the metal ion in the luminescent lanthanide complexes which lead to low intense absorption and emission spectra. Therefore, terbium ion requires coordination with suitable organic chromophore because the absorption of directly excited terbium ion is small [6]. The chelated organic ligand also protects the terbium ion from the solvent molecules and prevents the energy loss through non-radiative processes. The organic ligand absorbs the excitation energy and transfers it to the emitting levels of terbium ion via sensitization processes. In fact, the photoluminescence intensity of complexes is controlled by the efficiency of energy transfer mechanism from ligand to central metal ion. The bidentate β -diketonate ligand possesses strong absorption over a long range of wavelength and has the ability to encapsulate the terbium ion, conferring stability to the complex [7]. These characteristics make the β -diketonate ligand a good class of organic chromophore which meets all the requirements as described above to sensitize the luminescence of terbium ion. Further, the introduction of ancillary ligand increases the luminescence by synergistic effect. In order to obtain highly luminescent complexes, a β -diketonate ligand 1,3-[bis(4-methoxyphenyl)]propane-1,3-dionato (BMPD) and its terbium(III) complex with 2,2'-biquinoline (biq) were synthesized. The synthesized ligand and complex were characterized by various techniques. A detailed investigation of photophysical properties has been done in order to explore the photoluminescence behavior.

II. EXPERIMENTAL

High purity terbium nitrate [Tb(NO₃)₃·5H₂O; 99.9%] and 2,2'-biquinoline ancillary ligands were obtained from Sigma Aldrich. The other chemicals such as 4-methoxyacetophenone, 4-methoxybenzoyl chloride and potassium carbonate were purchased from commercial sources and used as received. The ligand HBMPD was synthesized adopting an ecofriendly microwave approach and then recrystallized three times with DMSO to obtain a ligand of high purity. Double distilled water was used throughout the experiments. The terbium contents of complexes were calculated with ethylenediaminetetraacetate (EDTA) complexometric titration. The elements such as carbon, hydrogen and nitrogen were analyzed by Perkin Elmer 2400 CHN Elemental Analyzer. The IR spectra were recorded on Shimadzu FT-IR Affinity-1 with sample set up as KBr pellets in the 4000-450 cm⁻¹ region. The ¹H-NMR spectra were performed on Bruker Avance II 400 NMR spectrometer using TMS as an internal standard. The ultraviolet absorption studies were carried out with Shimadzu-2450 UV-visible spectrophotometer in DMSO solvent. The solid state luminescence excitation and emission spectra in wavelength-scan function and decay curves in the time-scan function were obtained by Hitachi F-7000 fluorescence spectrophotometer equipped with xenon lamp as an excitation source. In these measurements, the slit widths of 2.5 nm were used with 400 PMT and 240 nm/min.

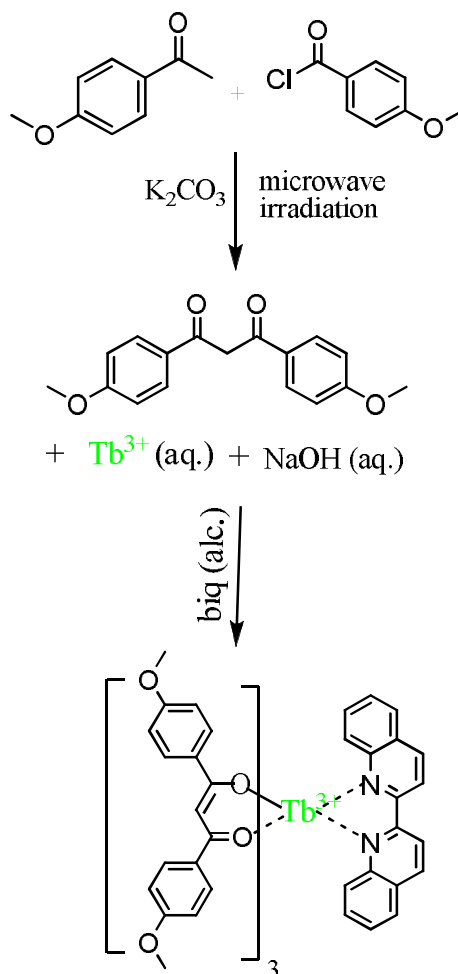
A. Synthesis of ,3-[bis(4-methoxyphenyl)]propane-1,3-dionato (BMPD) ligand

The synthetic route of HBMPD ligand was illustrated in Scheme 1. In a mixture of 4-methoxyacetophenone (0.75 g, 5 mmol), 4-methoxybenzoylchloride (0.68 mL, 5 mmol) and potassium carbonate (1.38 g, 10 mmol), a few drops of water were added to make homogenous mixture. Then resulting mixture was irradiated with microwave radiation for 40 s. The progress of the reaction was examined by TLC (thin layer chromatography). The crushed ice was added to the mixture and acidified with concentrated hydrochloric acid. The solid was separated out and recrystallized three times with DMSO solvent [8]. The HBMPD was obtained as yellow crystalline solid in 90% yield with 112°C melting point. IR (KBr): cm^{-1} 3480 (b), 3045 (w), 2949 (w), 1680 (s), 1597 (s), 1490 (s), 1446 (s), 1307 (s), 1251 (s), 1024 (s), 837 (s), 783 (s), 509 (m); $^1\text{H-NMR}$ (400MHz): δ 12.07 (s, 1H, enolic OH), 7.93-6.91 (m, 8H, Ar-H), 6.83 (s, 1H, enol CH), 4.80 (s, 2H, keto- CH_2), 4.62 (s, 6H, OCH_3) ppm. Anal. Calcd for: C, 71.83, H, 5.63; found: C, 71.62; H, 5.58.

B. Synthesis of terbium(III) complex

The aqueous solution of terbium nitrate pentahydrate (0.43 g, 1.0 mmol), an ethanolic solution of HBMPD ligand (0.909 g, 3.2 mmol) and biq (0.25 g, 1.0 mmol) were slowly mixed on magnetic stirrer. The resulting reaction mixture was stirred for 3 h at 50-60°C temperature. The pH of the mixture was adjusted to 6.0-6.5 with 0.05M aqueous NaOH solution. The slow evaporation formed yellow precipitates of terbium(III) complex which were filtered, washed and dried in hot air oven [9].

$\text{Tb}(\text{BMPD})_3\text{biq}$: yellow solid, yield 72%; IR (KBr): cm^{-1} 3066 (s), 3000 (s), 2959 (s), 1599 (s), 1528 (s), 1490 (s), 1463 (s), 1425 (s), 1381 (s), 1299 (s), 1257 (s), 1225 (s), 1182 (s), 1126 (s), 1020 (s), 846 (s), 789 (s), 514 (s), 469 (s); $^1\text{H-NMR}$ (400MHz): δ 8.43-6.95 (m, 36H, Ar-H), 4.65 (s, 18H, $-\text{OCH}_3$), 3.24 (s, 3H, enol CH). Anal. Calcd for $\text{TbC}_{69}\text{H}_{57}\text{N}_2\text{O}_{12}$: C, 65.50; H, 4.50; N, 2.21; Tb, 12.54; found: C, 65.42; H, 4.42; N, 2.18; Tb, 12.20.



Scheme 1 The synthetic pathway of BMPD ligand alongwith synthetic route of terbium(III) complex.

III. RESULTS AND DISCUSSION

A. Elemental Analysis

The result of elemental analysis of HBMPD ligand and terbium(III) complex indicated that the observed values were closely approaching to calculated values, suggesting that the composition of the complexes was conformed to $Tb(BMPD)_3biq$. The complex showed the solubility in chloroform, dimethylsulphoxide (DMSO), acetone, dichloromethane and dimethylformamide (DMF) solvents.

B. IR and 1H -NMR Spectral Analysis

The IR study revealed the binding mode of ligands to the terbium(III) ion which was assessed by a comparative study of spectra of ligand and complex. In the spectrum of ligand, a broad absorption band of enolic $-OH$ proton appeared at 3480 cm^{-1} , which was disappeared in the spectra of complex, suggesting the coordination of BMPD ligand to the $Tb(III)$ ion through enolic $-OH$ group. The strong absorption band of $>CO$ stretch at 1680 cm^{-1} in spectrum of ligand shifted to 1599 cm^{-1} in spectrum of complex, indicating the coordination of ligand to the metal via oxygen atom of $>CO$ group of ligand [10]. This binding site further confirmed by a medium intense band of $Tb-O$ vibration in $469-466\text{ cm}^{-1}$ range. On the other hand, the enolic $C=C$ stretching vibration were red shifted relative to spectrum of ligand, indicating the extension of π -conjugation in complexes. In the spectrum of complex only, the intense absorption band at 1528 cm^{-1} observed which was ascribed to the $>C=N$ stretch vibration of 2,2'-biquinoline ancillary ligands, ensuring the coordination of ancillary ligands to the central metal ion through nitrogen atom. This data is further confirmed by a medium intense band of $Tb-N$ stretching vibration in 514 cm^{-1} range [85].

The singlet peaks at 12.07 ppm and 4.80 ppm were observed in spectrum of ligand only, assigning to enolic $-OH$ and ketonic $-CH_2$ protons, respectively. These peaks were not present in the spectra of complexes, indicating that the ligand coordinated with the $Tb(III)$ ion in the enolic form [86]. The signal of enolic $=CH$ proton at 6.83 ppm in the spectrum of ligand shifted to high upfield in the spectrum of complex which clearly indicated the paramagnetism of terbium(III) ion.

C. UV-visible spectra

The UV-visible absorption spectra of BMPD ligand and its terbium(III) complex were measured in DMSO solution ($1 \times 10^{-5}\text{ mol/L}$) at room temperature as depicted in Fig. 1. The UV-absorption profile of terbium complexes is almost similar to the HBMPD ligand absorption profile, suggesting that the coordination of terbium metal ion does not affect the singlet excited state of the ligand. In the spectra, the maximum absorption at 360 nm was noticed which was associated with the $\pi-\pi^*$ transition of organic ligands [11].

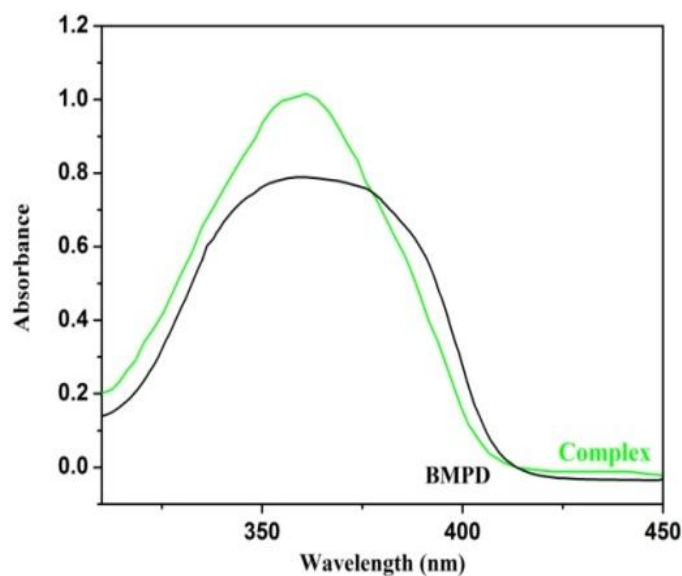


Fig. 1 The UV-visible spectra of BMPD ligand and $Tb(III)$ complex.

D. Photoluminescence Behaviour

Fig. 2 depicts the excitation spectra of terbium(III) complex monitored at 545 nm wavelength. The excitation spectra exhibited a broad band in 280-450 nm region with maxima centered at 362 nm which was associated with the $\pi-\pi^*$ transitions of ligand.

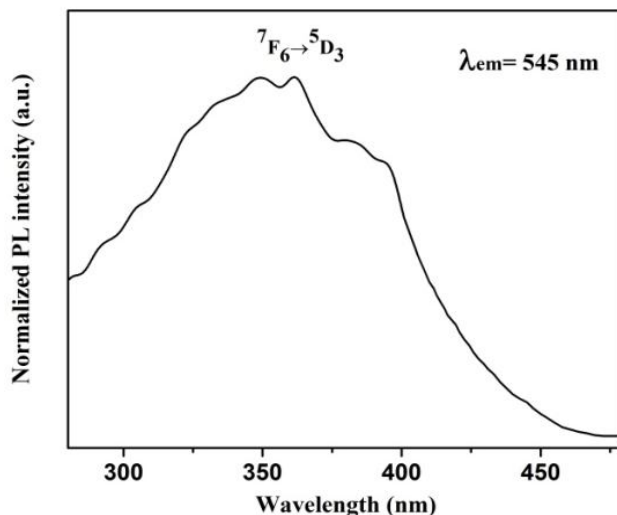


Fig. 2. The solid state excitation spectrum terbium(III) complex monitored at 545 nm.

The strong absorption in 300-400 nm region clearly showed that the ligands played an important role in absorption of energy which transferred to the terbium(III) ion, resulting into characteristic emission bands of Tb(III) ion.

The photoluminescence emission spectra (Fig. 3) of terbium(III) complex exhibited peaks in 400-600 nm region corresponding to the transitions between $^5D_{3,4}$ excited levels and $^7F_{4,6}$ levels of the terbium ion. Three main characteristic bands were observed at 448 nm, 490 nm and 545 nm attributed to $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_6$ (magnetic dipole) and $^5D_4 \rightarrow ^7F_5$ (electric dipole) transitions in the emission spectra respectively. The peak of $^5D_3 \rightarrow ^7F_4$ transition is forbidden in both electric and in magnetic dipole field. The peak of electric dipole transition is highly sensitive to the chemical environment around the terbium ion and directs the green luminescent color of the complexes [9]. While, the peak of magnetic dipole transition is non-sensitive to the coordination environment of terbium ion. The intensity of these transitions is controlled by local symmetry and crystal field of terbium ion. Therefore, a prominent electric dipole transition in the spectra suggests that the terbium(III) ion is located in the asymmetric coordination site of the complex. The 2,2'-biquinoline ancillary ligand also play an important role in the sensitization process which increased the luminescence intensity upto great level by synergistic effect.

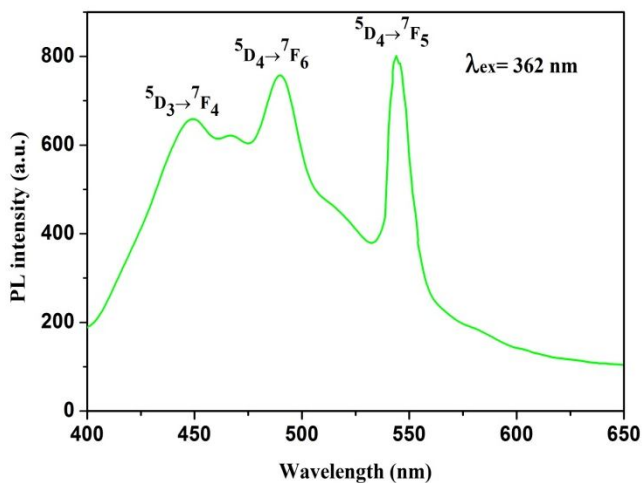


Fig. 3. The solid state luminescence emission spectrum of terbium(III) complex excited at 362 nm.

The Commission Internationale de Eclairage(CIE) color coordinates (x and y) terbium complex was calculated from the emission spectra excited at 362 nm. The value of CIE coordinates found to be $x = 0.1849$; $y = 0.3561$ which were located in green region of chromaticity diagram as depicted in Fig. 4.

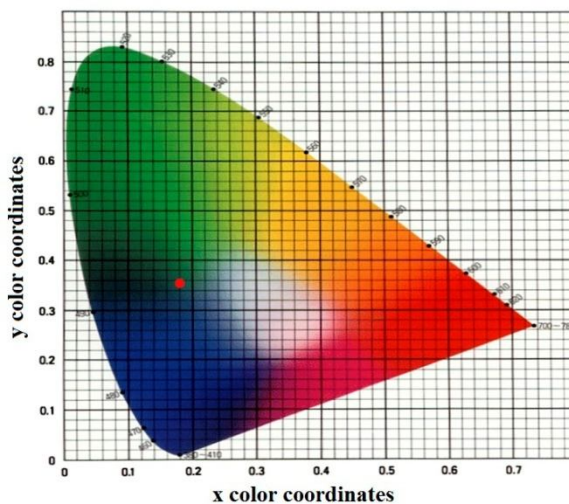


Fig. 4. The CIE chromaticity coordinates of terbium(III) complex.

The decay curves of terbium(III) complex were obtained in order to examine the coordination environment around central terbium(III) ion in the complex as shown in Fig. 5. The luminescence decay time of 5D_4 excited level of terbium ion in complex was estimated from the decay curves by monitoring the most intense emission peak ($^5D_4 \rightarrow ^7F_5$) at 545 nm in solid state. The decay profile of $^5D_4 \rightarrow ^7F_5$ transition obey single exponential function as $I = I_0 \exp(-t/\tau)$ where τ is the radiative decay time, I and I_0 are the luminescence intensities at time t and 0, respectively [90]. The results of the decay curves proposed that the terbium ion is present in single chemical environment in complexes.

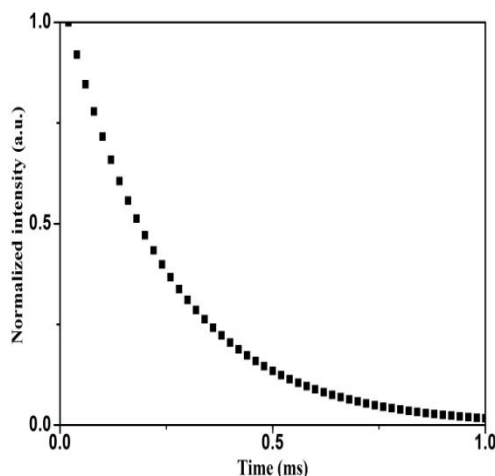


Fig. 5 The luminescence decay curve of the terbium(III) complex.

IV. CONCLUSIONS

In summary, a terbium(III) complex was prepared with BMPD and 2,2'-biquinoline ligands. The complex was characterized by elemental analysis, NMR, IR, UV-visible and photoluminescence (PL) spectroscopy. The results of CHN elemental analysis showed the good agreement between experimental values and calculated values which confirmed the successful synthesis of BMPD ligand and terbium complex. The comparative study of IR spectra of BMPD ligand and terbium complex gave information about the binding sites of the BMPD and 2,2'-biquinoline ligands. Upon excitation at 362 nm, the emission spectra of terbium complexes showed emission peaks at 448 nm ($^5D_3 \rightarrow ^7F_4$), 490 nm ($^5D_4 \rightarrow ^7F_6$) and 545 nm ($^5D_4 \rightarrow ^7F_5$). The intense electric dipole transition ($^5D_4 \rightarrow ^7F_5$) at 545 nm suggested the highly polarizable chemical environment present around the central metal ion and also responsible for the green luminescent color of the complex. The CIE color coordinates of terbium complex fall in the green regime of the CIE chromaticity diagram. The complex can be used as luminescent material and found potential application in display devices.

V. ACKNOWLEDGMENT

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