

# Synthesis, Characterization and Photoluminescence of Terbium (III) Complex with the Schiff Base

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**Abstract**—A new terbium (III) complex of the Schiff base (HL) derived from 1-phenyl-3-furyl-4-benzoyl-4, 5-dihydropyrazol-5-one (PFBP) and 2-aminobenzimidazole (2-AB) has been synthesized and investigated by photoluminescence spectroscopy. The molecular structure was characterized by IR spectra, UV spectra and <sup>1</sup>H NMR spectra; moreover, a high performance liquid chromatography-mass spectrometry (HPLC-MS) method was developed for the analysis of synthetic system. The integrated analytical results show that the new ligand coexists in keto-form structure and enol-form structure under the measuring conditions, the keto-form structure may change into the enol-form structure during the coordination process. The photoluminescence spectra show that the complex exhibits the strong green fluorescence.

**Keywords**-Schiff base; terbium (III) complex; HPLC-MS; photoluminescence

## I. INTRODUCTION

The organic rare earth complexes have intensively been studied owing to their good luminescence properties[1-3], bioinorganic sensors[4] and organic electroluminescent devices (OELD)[5-7]. Because of the shielding effect of 5s and 5p electrons, 4f electrons of the rare earth ions do not participate bonding with the ligands directly, the 4f → 4f transitions act as those of free atoms, resulting in very narrow absorption and emission bands. This leads to good luminescent. The complexes of Sm(III), Eu(III) and Tb(III) with β-diketones or other ligands which can absorb and transfer the light energy to the central metals give very strong luminescent intensity due to the increase of absorbability[8].

4-Acyl pyrazolones are good extractants of rare earth ions. In addition, 4-acyl pyrazolones can form a variety of Schiff bases which have been reported to be superior ligands of rare earth ions<sup>[9,10]</sup>. In the hunt for obtaining luminescence and amplifying the scope of 4-acyl pyrazolone derivatives coordinated with rare earth, the synthesis of new rare earth complex of 4-acyl pyrazolone derivatives, terbium (III) complex with the Schiff base derived from 1-phenyl-3-furyl-4-benzoyl-4, 5-dihydropyrazol-5-one and 2-aminobenzimidazole was performed. Their coordination structure and luminescent

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property were studied.

## II. EXPERIMENTAL

### A. Materials and methods

The compound 1-phenyl-3-furyl-5-pyrazolone (PFP) was synthesized according to the literature [11]. The 2-AB was synthesized according to the literature [12].

Terbium was estimated by the titrimetric method using EDTA. LC-MS analysis was performed on a model Agilent 1100 LC-MSD-TRAP. Infrared (IR) spectra were recorded on a Avatar 370 FT-IR spectrometer as KBr pellets. <sup>1</sup>H NMR spectra were recorded on a model AV 300 Bruker nuclear magnetic resonance instrument. Electronic spectra were recorded on a model U-3010 Hitachi spectrophotometer. Photoluminescence were made on a Hitachi F-4500 spectrometer equipped with quartz cuvettes of 1 cm path length.

### B. Synthesis of PFBP

PFP (2.26 g, 0.01mol) was dissolved in hot dioxane (10 mL) in a flask equipped with a stirrer, separating funnel and reflux condenser. Calcium hydroxide (1.48 g, 0.02 mol) was added to this solution, followed by benzoyl chloride (1.40g, 0.01 mol) added dropwise with precaution. After the complete addition, the reaction mixture was refluxed for half an hour and then it was poured into dilute hydrochloric acid (10 mL, 2 M). The flaxen needle shaped crystals (PFBP) thus obtained were separated by filtration and recrystallized from an acidified methanol–water mixture.

### C. Synthesis of the Schiff base (HL)

Anhydrous alcohol (10mL) was added to a 150mL Erlenmeyer flask containing PFBP (3.30g, 0.01mol) equipped with a stirrer, separating funnel and reflux condenser. After heating up the flask to dissolve the PFBP completely, ethyl alcohol solution containing 2-AB (1.33g, 0.01mol) was added dropwise with precaution. Then the reaction mixture was refluxed for four hours. Yellow crystal matter was obtained after filtrating, washing by anhydrous alcohol, recrystallizing two times in acetone and drying.

#### D. Synthesis of terbium complex [ $TbL_2 \cdot 2H_2O$ ]

The HL (0.445 g, 1mmol) dissolved in hot anhydrous alcohol (8 mL) was added dropwise into an anhydrous alcohol of terbium nitrate (0.227 g, 0.50 mmol) with stirring. After the complete addition, NaOH solution ( $v + v = 1 + 4$ ) was added to adjust the pH = 5~6 and the reaction mixture was refluxed for 6 h. The bisque solid matter was obtained after filtrating, washing, recrystallizing two times in acetone and drying in air. Synthetic route was presented in Fig. 1.

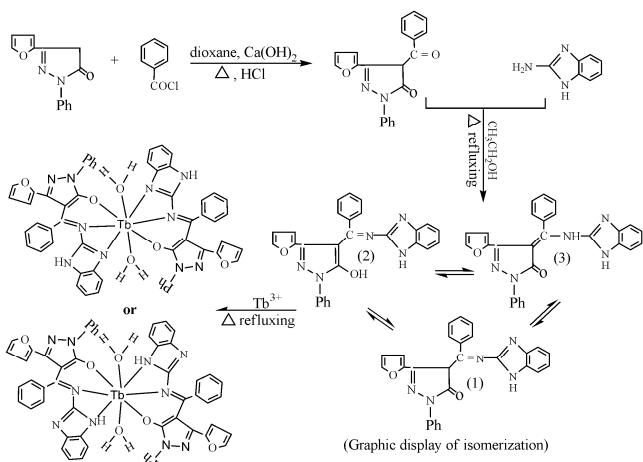


Fig. 1 Synthetic route of terbium complex.

#### E. LC-MS analysis for the reaction system of terbium complex [ $TbL_2 \cdot 2H_2O$ ]

The experiment was carried out with a LC-MSD-Trap system being comprised of a quaternary pump, vacuum degasser, thermostated column compartment. After the base line became stable, samples were injected according to the sequence of initial-term, medium-term and final-term reaction solution. Ion peaks of MS and their intensity data corresponding to the retention time of chromatograms are listed as: t0.78: (+)[M+H] $^+$  = 446.2 (0.8 $\times$ 106), [M+Na] $^+$  = 468.0 (0.3 $\times$ 106), [M-H+2Na] $^+$  = 490.2 (0.1 $\times$ 106), [M+K] $^+$  = 484.4 (0.15 $\times$ 106), [M-H+Na+K] $^+$  = 506.1 (0.1 $\times$ 106), (-)[M-H] $^+$  = 444.0 (0.9 $\times$ 107); t6.50: (+)[M+H] $^+$  = 446.0 (0.3 $\times$ 106), [M+Na] $^+$  = 468.1 (0.6 $\times$ 106), [M-H+2Na] $^+$  = 490.1 (0.2 $\times$ 106), [M+K] $^+$  = 484.2 (0.1 $\times$ 106), (-)[M-H] $^+$  = 444.2 (0.07 $\times$ 104); t7.19: (+)[M+H] $^+$  = 446.0 (0.2 $\times$ 106), [M+Na] $^+$  = 468.1 (0.5 $\times$ 106), [M+K] $^+$  = 484.1 (0.15 $\times$ 105), (-)[M-H] $^+$  = 444.0 (0.1 $\times$ 104); t11.42: (+)[M-2H2O+H] $^+$  = 1048.6 (0.5 $\times$ 105),

[M-2H2O+Na] $^+$  = 1070.4 (0.3 $\times$ 105), [M-2H2O+K] $^+$  = 1086.5 (0.1 $\times$ 105).

### III. RESULTS AND DISCUSSION

#### A. Electronic spectra

The electronic spectra of HL and its terbium complex were recorded in DMF solution of  $1\times 10^{-5}$  mol·L $^{-1}$  and the data are presented in Table 1. The four absorption peaks of HL at ultraviolet region at 209, 222, 236 and 330 nm are assigned to the band of  $\pi-\pi^*$  or  $n-\pi^*$  transitions of aromatic ring, furan ring, benzimidazole ring and two imido groups. Compared with HL, the first peak of terbium complex unchanges basically and the second, the third and the fourth peak exhibit the red shifts in various degrees. These are possibly concerned with the coordination between terbium central ion and two N atoms of imido group and benzimidazole ring of HL, which causes the polarization of C=N bond and effects energy levels of the related conjugated molecular orbitals.

#### B. IR spectra

The characteristic absorption bands data of IR spectra of HL and its terbium complex recorded in the range of 4000-400 cm $^{-1}$  are shown in Table 1. The broad  $\nu_{O-H\cdots N}$  band formed by enolic OH of pyrazolone ring and N atom of imido group was observed at 3528 cm $^{-1}$  for HL, which shows that the HL coexists in keto-form structure and enol-form structure. This inferred conclusion is in accord with the one enduced from LC-MS and  $^1H$  NMR analysis. Compared with HL, H<sub>2</sub>O band appears at 3618 cm $^{-1}$  after formation of terbium complex, which indicates that O atom of H<sub>2</sub>O participates in the coordination process. That the absorption band of  $\nu_{C=O}$  shifts from 1630 cm $^{-1}$  of HL to 1619 cm $^{-1}$  of terbium complex shows that the keto-form structure may change into the enol-form for HL during the coordination process, moreover the vibrational bands of  $\nu_{Tb-O}$  appears at 506 cm $^{-1}$ , which shows that O atom of hydroxyl group of enol-form structure participates in the coordination; That the absorption band of  $\nu_{C=N}$  shifts from 1563 cm $^{-1}$ , 1552 cm $^{-1}$  and 1546 cm $^{-1}$  of HL to 1560 cm $^{-1}$ , 1548 cm $^{-1}$  and 1539 cm $^{-1}$  of terbium complex and the vibrational band of  $\nu_{Tb-N}$  appears at 492 cm $^{-1}$  show that two N atoms of imido group and benzimidazole ring participate in the coordination<sup>[13]</sup>. The analytical results show that the keto-form structure of HL may change into the enol-form structure during the coordination and the ligand bonds with terbium central ion by two O atoms of hydroxyl group of pyrazolone ring and H<sub>2</sub>O and two N atoms of imido group and benzimidazole ring.

TABLE 1 UV SPECTRAL AND IR DATA OF THE LIGAND AND ITS TERBIUM COMPLEX

Complex	UV[nm]					IR[cm $^{-1}$ ]				
	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\lambda_4$	$\nu_{O-H\cdots N}$	$\nu_{C=O} (\nu_{C=C})$	$\nu_{C=N}$	$\nu_{C-O}$	$\nu_{Tb-O}$	$\nu_{Tb-N}$
HL	209	222	236	330	3128	1630	1563 1552 1546	1480		
$TbL_2 \cdot 2H_2O$	209	224	244	342	3618	1619	1560 1548 1539		506	492

#### C. $^1H$ NMR of H

The  $^1H$  NMR spectra of HL was recorded in CDCl $_3$  at room temperature regarding TMS as internal standard. From

Fig.2, The multiplets of 17 protons appearing at the range of  $\delta$  7.112-8.385 are assigned to 17 protons of benzene ring, furan ring and benzimidazole ring. The singlet whose integral area is

good equivalent to one proton appearing at  $\delta$  12.852 corresponds to the proton of  $-\text{NH}$  of benzimidazole ring. Another weak and broad singlet is observed at  $\delta$  13.333 at low field region. It can be assigned to either to OH or NH, in either case it is strongly deshielded because of hydrogen bonding with the other atom (N/O)<sup>[14]</sup>. The sum of its integral area of 0.8800 and the integral area of 0.1150 of weaker singlet at  $\delta$  6.784 perfectly matches with one proton, so the proton appeared at  $\delta$  6.784 is assigned to the proton of methylene of pyrazolone ring, which suggests that HL coexists in keto-form structure and in enol-form structure under the experimental conditions. This conclusion is in accord with the one enduced from IR spectra and LC-MS analysis.

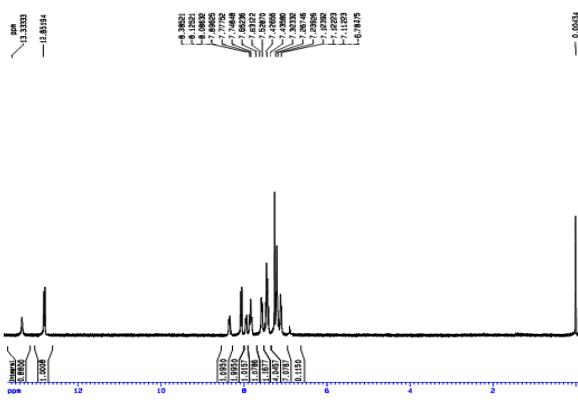


Fig. 2  $^1\text{H}$  NMR of HL

#### D. Analysis of LC-MS testing for synthetical system of terbium complex

From Fig. 2, three absorption peaks appeared at  $t_{0.78}$ ,  $t_{6.50}$  and  $t_{7.19}$  in initial-term reaction system respectively. Under positive ion scanning mode,  $[\text{M}+\text{H}]^+$  of  $m/z$  446 is base peak among ion peaks of MS corresponding with  $t_{0.78}$ , but  $[\text{M}+\text{Na}]^+$  of  $m/z$  468 is base peak among ion peaks of MS corresponding with  $t_{6.50}$  and  $t_{7.19}$ ; Under negative ion scanning mode, very strong  $[\text{M}-\text{H}]^-$  ion peak of  $m/z$  444 appeared under injection volume of 2  $\mu\text{L}$  at  $t_{0.78}$ , but weak signal of this ion peak was observed under injection volume of 20  $\mu\text{L}$  at  $t_{6.50}$  and  $t_{7.19}$ , which results from that the hydroxyl of enol-form structure is easier to lose one proton to form negative ion. The absorption peak corresponding to  $t_{0.78}$  is inferred to be the one corresponding to enol-form structure, but two absorption peaks corresponding to  $t_{6.50}$  and  $t_{7.19}$  are two ones corresponding to two keto-form structures. They may be inferred to be two absorption peaks corresponding to keto-form structure (3) and (1) orderly from the polarity of molecular structure. According to mass spectra data corresponding to the absorption peaks of medium-term reaction system, mass spectra ion peaks corresponding to HL and target product appeared, of which mass spectra ion peaks corresponding to enol-form structure and two keto-form structures of HL were all observed. Three ion peaks are confirmed to be  $[\text{TbL}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O} + \text{H}]^+$ ,  $[\text{TbL}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O} + \text{Na}]^+$  and  $[\text{TbL}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{H}_2\text{O} + \text{K}]^+$  respectively. The varying of absorption peak shape and the data of corresponding mass spectra show that the keto-form structure of HL may change into the enol-form structure during

the formation of terbium complex and O atom of hydroxyl group of pyrazolone ring and N atom (or N atom of  $-\text{NH}$ ) of benzimidazole ring participate in the coordination by losing the proton.

#### E. Photoluminescence studies

The excitation spectra and the emission spectra of the complex in solid and in DMF solution are shown in Fig.3. From Fig.3 it could be seen that the excitation wavelengths of the complex are different between in solid ( $\lambda_{\text{ex}} = 326$  nm) and in DMF solution ( $\lambda_{\text{ex}} = 380$  nm). Three characteristic bands of the central  $\text{Tb}^{3+}$  ion at around 494nm, 545 nm and 590nm were observed and assigned to the  $\text{Tb}^{3+}$  f-f transition of  $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  and  $^5\text{D}_4 \rightarrow ^7\text{F}_4$  respectively. It were showed the relative intensity of the complex at 545 nm is strong either in solid or in DMF solution, this is related to the efficiency of the intramolecular energy transfer between the triplet level of ligand and the emitting level of the ion, which depends on the energy gap between the two levels. Probably the energy gap between the ligand triplet levels and the emitting level of terbium favor to the energy transfer process for terbium.

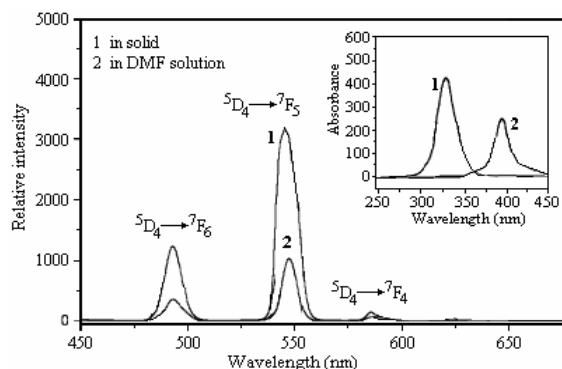


Fig. 3 Photoluminescence spectra of the complex

#### IV. CONCLUSION

A new 4-acyl pyrazolone-based Schiff base ligand and its terbium (III) complex was synthesized in this paper. The results of LC-MS analysis integrating with other characterization means else show that the new ligand coexists in keto-form structure and enol-form structure under the measuring condition, the keto-form structure may change into the enol-form structure during the coordination and the ligand bonds with terbium central ion by two O atom of hydroxyl group of pyrazolone ring and  $\text{H}_2\text{O}$  and N atom of imine group and N atom (or N atom of  $-\text{NH}$ ) of benzimidazole ring by losing the proton. The photoluminescence data show that the complex exhibits three characteristic emission peaks of  $\text{Tb}^{3+}$  ion both in solid and in DMF solution. That the peak's relative intensity at 545 nm is strong suggests that the new ligand can activate efficiently the luminescence of the  $\text{Tb}^{3+}$  ion, making the complex a potential candidate as emitter in photonic systems.

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