

## Synthesis and novel fluorescence phenomenon of terbium(III) complex with N, N', N''-tris (2-benzimidazolmethyl) amine

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A benzimidazole ligand with a tripodal structure, N, N', N''-tris (2-benzimidazolmethyl) amine, and its terbium (III) complex has been synthesized. The complex has been characterized by element analysis, IR spectra, mass spectra, thermal analysis and molar conductivity. The terbium ion is found to coordinate with the nitrogen atoms (=N-) of imidazole ring and the bridgehead nitrogen atom. The fluorescence properties of the complex in aqueous solutions have been studied. Under excitation of UV light, the complex exhibits characteristic fluorescence of terbium ion. The luminescence of terbium complex in aqueous solutions is strongly enhanced by H<sup>+</sup> concentration. This phenomenon makes the new complex favorable for use in fluorescence switches and sensors. The mechanism of the fluorescence enhancement by protonation of the nitrogen atoms (-NH-) of imidazole ring is due to the suppressed photoinduced electron transfer fluorescence quenching on addition of acid.

**Keywords:** Coordination chemistry, Fluorescence, Luminescence, Terbium, Benzimidazoles

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The development of luminescence chemical probes and sensors is the subject of intensive research both in natural and medical sciences. Probes based on europium and terbium ions are of special interest because of the particularly suitable spectroscopic properties of these ions<sup>1,2</sup>. Chemists have realized that it is essential to design the appropriate ligand to optimize luminescent properties of these lanthanide ions by facilitating the well-known light conversion process, i.e., the antenna effect<sup>3-5</sup>. Recently, we have

designed a series of doubly functional ligands having selective ability to coordinate lanthanide ions as well as enhance luminescence, by providing proper conjugate absorption groups suitable for energy transfer that could be used as a luminescent device. In the present work, we have designed and synthesized a new and doubly functional benzimidazole ligand with a tripodal structure, N, N', N''-tris (2-benzimidazolmethyl) amine (L), and have studied the fluorescence properties of terbium(III) complex with the ligand. It is observed that the terbium complex emits intrinsic spectrum of the ion under excitation of ultraviolet light. The results indicate that H<sup>+</sup> strongly enhances the luminescence of terbium complex in aqueous solutions. The mechanism influencing the fluorescence intensity is also discussed.

### Experimental

All the starting materials used herein were of analytical grade and used without further purification. Rare earth nitrates were prepared according to the literature method<sup>6</sup>.

The metal ions were determined by EDTA titration using xylenol orange as an indicator. Combustion analyses were determined using a Vario EL elemental analyzer. The IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument. Conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using 1.0 × 10<sup>-3</sup> mol L<sup>-1</sup> solution in dimethylformamide (DMF) at 25 °C. <sup>1</sup>H NMR spectra were measured on a Mercury plus-400 MHz spectrometer in DMSO-*d*<sub>6</sub> solution, with TMS as internal standard. Mass spectra (fast atom bombardment) were recorded on a VG ZAB-HS mass spectrometer. The thermal behavior was monitored on a WCT-2A thermal analyzer. Fluorescence measurements were made on a Shimadzu RF-540 spectrofluorophotometer equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 10 nm.

To synthesis the ligand, N, N', N''-tris (2-benzimidazolmethyl) amine (L), a mixture of solution of ammonia triacetic acid (1.9114 g, 10 mmol) and δ-phenylenediamine (3.2442 g, 30 mmol) in

ethylene (20 mL) was stirred continuously for 8 h at 160 °C and cooled to room temperature. The obtained white precipitate were filtrated and purified by crystallization with anhydrous ethanol. Yield, 72 %, m.pt.: 274-275 °C. The composition of the ligand was confirmed by elemental analysis and <sup>1</sup>H NMR and IR spectra<sup>7</sup>. Found (Calc.) %: C: 71.02 (70.76); H: 5.23 (5.16); N: 23.93 (24.08).

For synthesis of the complexes, 1.0 mmol Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O in 10 mL ethanol was added dropwise to a solution of (L) (1.0 mmol) in 10 mL ethanol. After stirring for 4 h at room temperature, the precipitate was separated by filtration, and washed several times with ethanol. Further drying in vacuum afforded a grey powder. Yield, 68 %. FAB-MS: *m/z* = 807 (M+1). Found (Calc.) %: C: 35.67 (35.73); H: 3.46 (3.35); N: 17.62 (17.37); Tb: 19.54 (19.73)

## Results and discussion

Analytical data for Tb(III) complex conform to Tb(NO<sub>3</sub>)<sub>3</sub>·L·3H<sub>2</sub>O. The complex is soluble in DMF, DMSO, methanol and water, slightly soluble in ethanol and acetone, insoluble in benzene, diethyl ether and chloroform. Conductivity measurements in 1×10<sup>-3</sup> mol L<sup>-1</sup> DMF solution (87 Λ<sub>m</sub>, S cm<sup>2</sup> mol<sup>-1</sup>) indicate that the complex is 1:1 ionic compound<sup>8</sup>.

The IR spectrum of the free ligand shows bands at 3362 and 1613 cm<sup>-1</sup>, which may be assigned to ν(N-H) and ν(C=N), respectively. In the complex, the band for ν(C=N) is shifted by about 35 cm<sup>-1</sup> (from 1613 to 1578 cm<sup>-1</sup>), indicating that the (=N-) of imidazole ring take part in coordination. The band for ν(N-H) of imidazole ring is not shifted, which indicates that the (N-H) of imidazole ring do not take part in coordination, which is in accordance with the results of mass spectra. The vibration ν(C-N) of ligand at 1248 cm<sup>-1</sup> is shifted to 1232 cm<sup>-1</sup> in the complex, indicating that the bridgehead nitrogen atom of ligand was coordinated to the Tb(III) ion<sup>9,10</sup>. The band corresponding to the ν(O-H) at 3238-3261 cm<sup>-1</sup> shows that the complex contains water molecules, which is in accordance with the results of elemental analyses. The absorption bands assigned to the coordinated nitrates were observed at about 1481 (ν<sub>as</sub>) and 792 (ν<sub>s</sub>) cm<sup>-1</sup> for the complex. The ν<sub>3</sub> (E') free nitrates appear at approximately

1370 cm<sup>-1</sup> in the spectra of the complex<sup>11</sup>, which is in agreement with the results of the conductivity experiments. In addition, the separation of the two highest frequency band |ν<sub>4</sub> - ν<sub>1</sub>| is approximately 186 cm<sup>-1</sup>, indicating that the coordinated NO<sub>3</sub><sup>-</sup> ions in the complexes are bidentate ligands<sup>12</sup>.

The complex is stable in air. DTA and TG curves show that the Tb(III) complex exhibits an endothermic peak at about 81 °C and loses about 6.67 % of its weight at 75-120 °C, which corresponds to the loss of three water molecules (calcd. for 3H<sub>2</sub>O, 6.70 %). This indicates that only lattice water molecules are present in the complex.

The fluorescence characteristics of the terbium complex in aqueous solution were investigated. The ligand having multiple aromatic rings with a rigid planar structure has a strong antenna effect, and hence its terbium complex exhibits very strong fluorescence in the solid state. Under ultraviolet excitation, the emission spectra of Tb(NO<sub>3</sub>)<sub>3</sub>·L·3H<sub>2</sub>O in the solid state and solution are similar to each other and show characteristic emission bands of the Tb(III) ion at about 492, 545, 586 and 620 nm, corresponding 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.

Figure 1 gives the emission spectrum of the terbium complex in aqueous solution. Due to the presence of a scattering signal near 490 nm, the peak height at 545 nm for terbium was used to measure the fluorescence intensities.

Photoinduced electron transfer (PIET) often underlies the mechanism by which the switching or sensing effect occurs. Fluorescent signaling via the PIET strategy is distinguished by its intrinsically supramolecular nature since distinct components perform each one of the necessary functions. The PIET process can be inhibited by conformational changes, local polarity modulations and hydrogen bonding. Such a suppression of the PIET process means that the fluorescence is 'switched on' again. Several researches have reported the enhancement of the fluorescence due to protonation<sup>13-15</sup>.

From Fig. 1 it can be seen that the terbium complex shows very weak fluorescence signal (Fig. 1, curve 1) at 492 and 545 nm when the concentration of H<sup>+</sup> is 0.0 × 10<sup>-4</sup> mol L<sup>-1</sup>. Based on the theory of luminescence, the intensity of the luminescence of Tb<sup>3+</sup> complexes is related to the efficiency of the

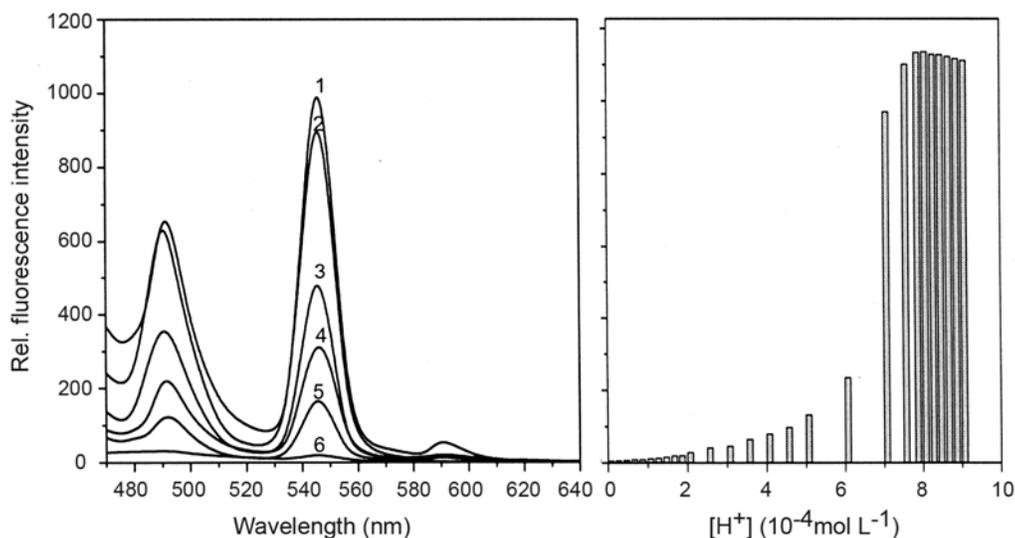


Fig. 1 – Emission spectra of terbium complex in aqueous solution at room temperature. [ $\lambda_{\text{ex}}$ : 385 nm; Conc. of  $\text{HNO}_3$  ( $\text{mol L}^{-1}$ ): 1,  $0.0 \times 10^{-4}$ ; 2,  $2.0 \times 10^{-4}$ ; 3,  $4.5 \times 10^{-4}$ ; 4,  $5.5 \times 10^{-4}$ ; 5,  $7.0 \times 10^{-4}$ ; 6,  $8.0 \times 10^{-4}$ ].

intramolecular energy transfer between the triplet energy level of the ligand and the emitting level of the central ions, which depends on the energy gap between the two levels. It is proposed that in the absence of acids, charge is transferred from the imidazole N-atoms bonding with H atoms donor to the emitting level of terbium, which leads to decrease in the fluorescence.

The fluorescence intensity of the complex increases on addition of  $\text{HNO}_3$ . Protonation of the imidazole nitrogen by strong acid suppress the electron transfer process. The lone pair electrons of the imidazole nitrogen bonding with H atoms are no longer available for PIET due to suppression of the electron transfer process. This makes the energy gap of the lone pair electron of nitrogen atom more favourable for the electron transfer process, leading to fluorescence enhancement. The results demonstrate that the imidazole nitrogen bonding with H atoms is important for the fluorescence enhancement of the switch.

Maximum fluorescence intensity of  $\text{Tb}^{3+}$  is observed when  $\text{HNO}_3$  was  $8.0 \times 10^{-4}$  mol/L. The fluorescence intensity does not increase with further increase in concentration of  $\text{HNO}_3$ .

There is widespread interest in the design of the fluorescent switches and sensors whose properties change upon the addition of the specific analytes<sup>16</sup>. The switches and sensors based on the luminescence property of the lanthanide ions are of special interest

because of the particularly suitable spectroscopic properties of these ions<sup>17</sup>. This system will make it favorable for use in fluorescence switches and sensors. The complex  $[\text{Tb}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$  possesses several attractive sensory feature, and this phenomenon can also be used to determination of trace amount of  $\text{Tb}^{3+}$  in acid. In addition, given that strong terbium luminescence occurs only when acids are present, the complex  $[\text{Tb}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$  could be construed as behaving as a molecular logic gate with  $\text{H}^+$  as the input and delayed terbium luminescence as the signal output. A detailed investigation is being undertaking.

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