

Fluorescent Property of the Gd^{3+} -Doped Terbium Complexes and Crystal Structure of $[Tb(TPTZ)(H_2O)_6]Cl_3 \cdot 3H_2O$

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Received: 20 May 2009 / Accepted: 7 February 2010 / Published online: 3 March 2010
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Abstract The complex of $Tb(TPTZ)Cl_3 \cdot 3H_2O$ was synthesized by adding the ethyl alcohol solution of $TbCl_3$ (1 mmol) to the solution of 2,4,6-tris-(2-pyridyl)-s-triazine (TPTZ, 1 mmol) with constant stirring. The solution which had been filtered was kept at the room temperature for 4 weeks, and then a kind of transparent crystal was formed. Besides, nine kinds of solid complexes in the different molar proportion of terbium to gadolinium had been synthesized by adopting the similar method mentioned above. It was inferred from the elemental analysis and rare earth complexometry that the composition of these complexes is $(Tb_xGd_y)(TPTZ)Cl_3 \cdot 3H_2O$ ($x : y = 0.9 : 0.1, 0.8 : 0.2, 0.7 : 0.3, 0.6 : 0.4, 0.5 : 0.5, 0.4 : 0.6, 0.3 : 0.7, 0.2 : 0.8, 0.1 : 0.9$). The absorption spectra and photoluminescence of the complexes were determined in dimethylsulfoxide (DMF), which showed that the excitation of the complexes is mostly ligand based. The triplet state energy level of TPTZ was measured, indicating that the lowest excitation state energy level of Tb (III) and the triplet state energy level of TPTZ match well each other. The fluorescent data indicated that the fluorescent emission intensity of Tb^{3+} ions would be enhanced in the

complexes after terbium was doped with Gd^{3+} ion. When $x : y$ was 0.5 : 0.5, the fluorescent emission intensity was the largest. The result obtained by testing the X-ray diffraction of the monocrystal revealed that the molecular formula of the mono-crystal complex is $[Tb(TPTZ)(H_2O)_6]Cl_3 \cdot 3H_2O$. The number of metal ion coordinates is nine, and the tridentate TPTZ and six water molecules are bonded with terbium respectively. Besides, it also revealed that the monocrystal belongs to the monoclinic system, and space group Cc with the following unit cell parameters is $a = 1.4785$ (3) nm, $b = 1.0547$ (2) nm, $c = 1.7385$ (4) nm, $\beta = 94.42$ (3)°, $V = 2.7028$ (9) nm³ and $Z = 4$.

Keywords Gd^{3+} -doped terbium complexes ·
2,4,6-tris-(2-pyridyl)-s-triazine · Fluorescent lifetime ·
Crystal structure

Introduction

The rare earth complexes have wide application in fluorescent display phosphorescence, laser, electroluminescence optical devices and the probes of chemical and biological molecules, because the characteristics of the rare earth complexes are high fluorescent efficiency, very sharp emission bands and excellent monochromatocity [1, 2]. The rare earth ion shows weak light absorption and fluorescence emission, and its fluorescent lifetime is quite short. However, the organic rare earth complexes, especially those containing ligands with aromatic rings are capable of giving off strong fluorescence because their light absorption and energy transition are both excellent [3–5]. In addition to the organic ligands, the doped rare earth complexes which are synthesized by adding some cheap inertia rare earth ions to them, have advantages of low cost and good fluorescent property [6–8]. 2,4,6-tris-(2-

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pyridyl)-s-triazine(TPTZ) is a nearly planar molecule, there are three different “coordination sites” in this molecule, and the complexation ability of TPTZ partly depends upon the size of the metal ions [9]. Generally TPTZ is a tridentate ligand which coordinates with rare earth and forms a 1:1 metal/ ligand complex [10–14]. The study of the complexes of rare earth and TPTZ was first reported by Mr. Durham and others in 1969 [15]. In order to study the effect of the doped ions on the fluorescent property of the complexes when the two kinds of rare earth ions exist in the same system, we studied the effect of Gd^{3+} , an inertia rare earth ion, on the fluorescent property of the terbium complex and we obtained the crystal structure of $[Tb(TPTZ)(H_2O)_6]Cl_3 \cdot 3H_2O$. Besides, in this research paper, the results obtained by our work were as follows: some solid complexes of different molar proportional $TbCl_3:GdCl_3$ with TPTZ were synthesized; their absorption spectra in DMF solution and emission spectra in solid were studied; the crystal structure of $[Tb(TPTZ)(H_2O)_6]Cl_3 \cdot 3H_2O$ was also determined and investigated.

Experimental section

Chemical reagents and instruments

Rare earth oxides Tb_4O_7 and Gd_2O_3 were 99.99% of purity and 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ) was 99% of purity. Absolute ethyl alcohol, hydrochloric acid and all other solvents commercially available were analytical purity.

Elemental analyses of C, H and N were performed by PE-2400 elemental analyzer and EDTA titration was used to determine the concentration of total rare earth ions. The contents of terbium and gadolinium were measured by a Varian 725-1 s plasma emission spectrum. The molar conductivity of the complexes was determined in the DMF solution of concentration $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ at the room temperature with DDS-11A conductometer and DJS-

1 platinum black electrode. The thermo-gram and thermogravimetric analysis were performed by a DTG-50 instrument with the rising temperature at $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. A Nicolet Nexus 670 FT-IR spectrometer using KBr (neat) was used to obtain the IR spectral data. Absorption spectra were recorded on a Tu-1901 spectrophotometer, using DMF as the solvent. Excitation and emission spectra of the complexes were studied with a Hitachi F-3010 fluorescence spectrophotometer in DMF solution. Those of the solid state complexes were measured using a Shimadzu RF-5301PC fluorescence spectra-photometer at the room temperature, and the excitation and emission slits were all 3.0 nm. Fluorescence lifetime of the complexes and triplet state energy level of TPTZ were carried out on an Edinburgh FLS920 phosphorimeter. The data of crystal diffraction was collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda=0.071073 \text{ nm}$) at a temperature of 113 K.

Synthesis of the complexes

Preparation of gadolinium chloride $GdCl_3$ was carried out by the reaction of gadolinium oxide with dilute solution of HCl. $TbCl_3$ was prepared by the reaction of Tb_4O_7 with dilute solution of HCl and H_2O_2 . The rare earth chloride was dissolved in absolute ethyl alcohol and then transferred into 100 ml volumetric flask. The absolute ethyl alcohol was poured to the volumetric flask until the solution reached the calibration marked on the neck of the flask. Thus the spare solution of $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ RECl}_3$ was obtained.

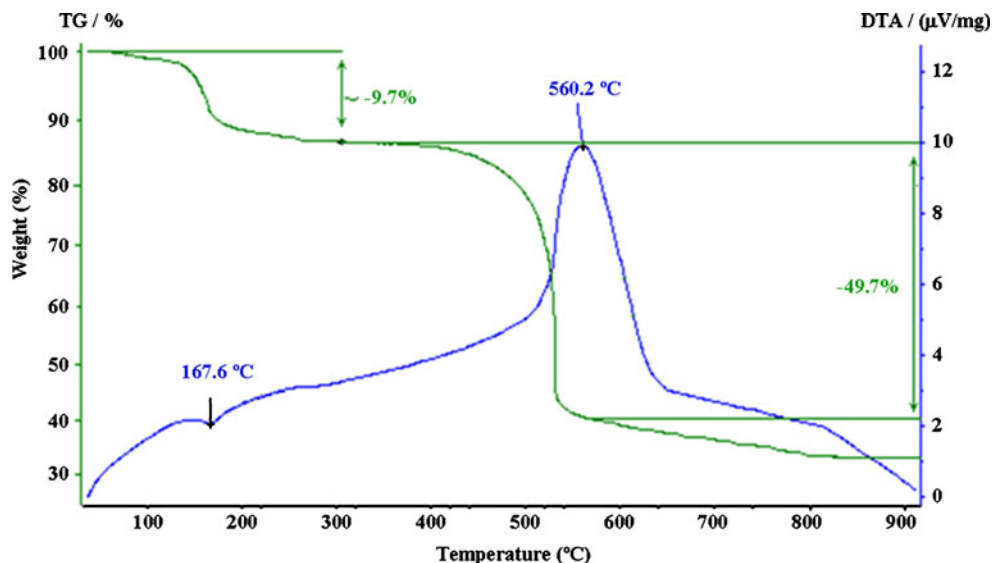
The complex of TPTZ and terbium was prepared by the reaction of $TbCl_3$ with TPTZ as 1:1 ratio in absolute ethyl alcohol. The mixture was heated and stirred for 2 h in bath in the state of reflux then it was cooled down to the room temperature, and the precipitate was filtered and washed with deionized water and ethyl alcohol. The product $Tb(TPTZ)Cl_3 \cdot 3H_2O$ was dried under infrared lamp and kept in a drier. The filtrate solution was collected and the suitable crystals were formed from the filtrate

Table 1 Composition analysis and molar conductivities ($S \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) of the complexes

Complexes	C(%)	H(%)	N(%)	Re(%)	λ_m
Tb (TPTZ) $Cl_3 \cdot 3H_2O$	34.18(34.19)	3.17(2.85)	13.15(13.30)	24.74(25.17)	80
$Tb_{0.9}Gd_{0.1}(TPTZ)Cl_3 \cdot 3H_2O$	33.88(34.20)	3.04(2.85)	13.05(13.30)	24.81(25.13)	80
$Tb_{0.8}Gd_{0.2}(TPTZ)Cl_3 \cdot 3H_2O$	34.06(34.21)	2.97(2.85)	12.93(13.30)	24.78(25.10)	85
$Tb_{0.7}Gd_{0.3}(TPTZ)Cl_3 \cdot 3H_2O$	34.38(34.22)	3.11(2.85)	13.29(13.31)	24.61(25.08)	80
$Tb_{0.6}Gd_{0.4}(TPTZ)Cl_3 \cdot 3H_2O$	34.57(34.23)	3.24(2.85)	13.21(13.31)	24.74(25.06)	85
$Tb_{0.5}Gd_{0.5}(TPTZ)Cl_3 \cdot 3H_2O$	34.26(34.24)	3.14(2.85)	13.25(13.32)	24.71(25.05)	80
$Tb_{0.4}Gd_{0.6}(TPTZ)Cl_3 \cdot 3H_2O$	34.01(34.25)	2.88(2.85)	12.87(13.32)	24.72(25.04)	84
$Tb_{0.3}Gd_{0.7}(TPTZ)Cl_3 \cdot 3H_2O$	33.86(34.26)	3.08(2.85)	13.00(13.32)	24.77(25.02)	80
$Tb_{0.2}Gd_{0.8}(TPTZ)Cl_3 \cdot 3H_2O$	34.16(34.27)	3.00(2.86)	12.90(13.33)	24.61(25.00)	85
$Tb_{0.1}Gd_{0.9}(TPTZ)Cl_3 \cdot 3H_2O$	33.90(34.27)	3.14(2.86)	13.25(13.33)	24.71(24.98)	80

(Calcd.)

Fig. 1 TG-DTA curves of $[\text{Tb}(\text{TPTZ})(\text{H}_2\text{O})_6]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$



solution which had been kept for 4 weeks at the room temperature.

According to the composition of the complex $(\text{Tb}_x\text{Gd}_y)(\text{TPTZ})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, other nine hetero-nuclear rare earth complexes were synthesized by using the above means. The molar ratio of Tb^{3+} to Gd^{3+} is $x : y = 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.3:0.7, 0.2:0.8, 0.1:0.9$ respectively. All the products were white precipitates.

Results and discussion

The compositions of the complexes and analysis of thermostability

The results of elemental analyses of C, H, N and rare earth titration were given in Table 1. The molar conductivity was also shown in Table 1. The contents of terbium and gadolinium in $\text{Tb}_{0.9}\text{Gd}_{0.1}(\text{TPTZ})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tb}_{0.7}\text{Gd}_{0.3}(\text{TPTZ})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ were measured by a Varian 725-1 S plasma emission spectrum: %: 22.47 (22.62)

terbium,2.43 (2.49) gadolinium and 17.32 (17.62) terbium,7.56 (7.47) gadolinium, respectively. It was inferred from the analytic results that the composition of the complexes is $(\text{Tb}_x\text{Gd}_y)(\text{TPTZ})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ($x : y = 1.0:0.0, 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.3:0.7, 0.2:0.8, 0.1:0.9$). The molar conductivity varied from 75 to 85 $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. The result showed that they were all electrolytes of 1:1 in DMF solution [16]. The complex-bounded may be $[(\text{Tb}_x\text{Gd}_y)(\text{TPTZ})(\text{H}_2\text{O})_3 \text{Cl}_2]\text{Cl}$.

Thermo-gram and thermo-gravimetric analysis of the complex $\text{Tb}(\text{TPTZ})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ were performed in Fig. 1. The temperature of thermal absorption of the complex was at 167.6 °C and 9.7% of gravimetric loss appeared. This showed that there were three complex-bounded water

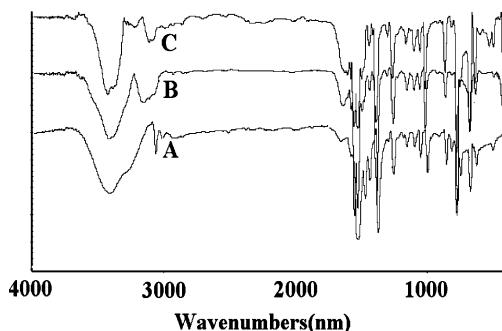


Fig. 2 IR spectra of TPTZ(A), $[\text{Tb}(\text{TPTZ})(\text{H}_2\text{O})_3 \text{Cl}_2]\text{Cl}$ (B) and $[\text{Tb}_{0.9}\text{Gd}_{0.1}(\text{TPTZ})(\text{H}_2\text{O})_3 \text{Cl}_2]\text{Cl}$ (C)

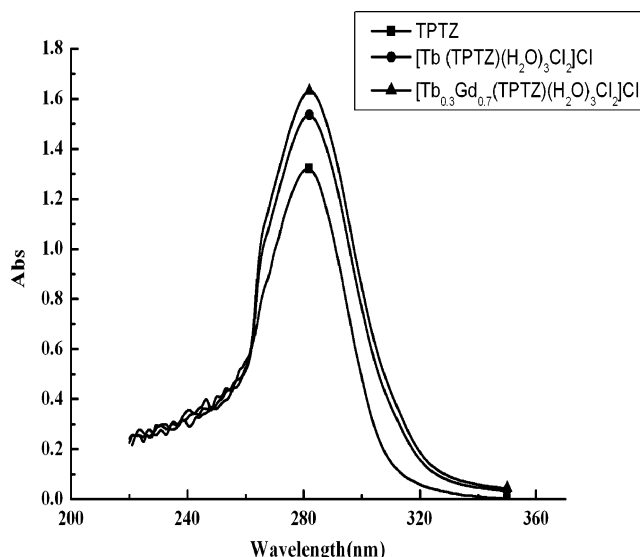


Fig. 3 Absorption spectra of TPTZ, $[\text{Tb}(\text{TPTZ})(\text{H}_2\text{O})_3 \text{Cl}_2]\text{Cl}$ and $[\text{Tb}_{0.3}\text{Gd}_{0.7}(\text{TPTZ})(\text{H}_2\text{O})_3 \text{Cl}_2]\text{Cl}$ in DMF

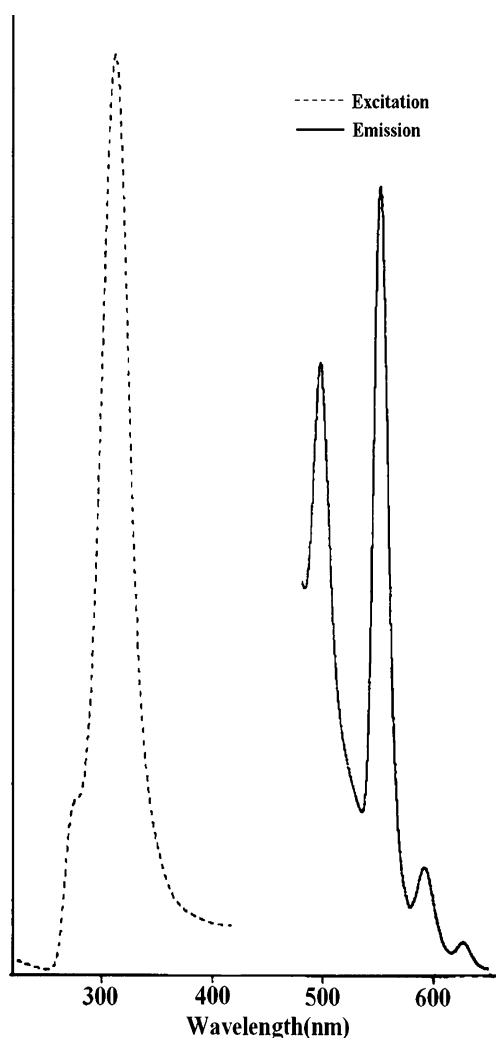


Fig. 4 Excitation and emission spectra of $[\text{Tb}_{0.9}\text{Gd}_{0.1}(\text{TPTZ})(\text{H}_2\text{O})_3\text{Cl}_2]\text{Cl}$ in DMF

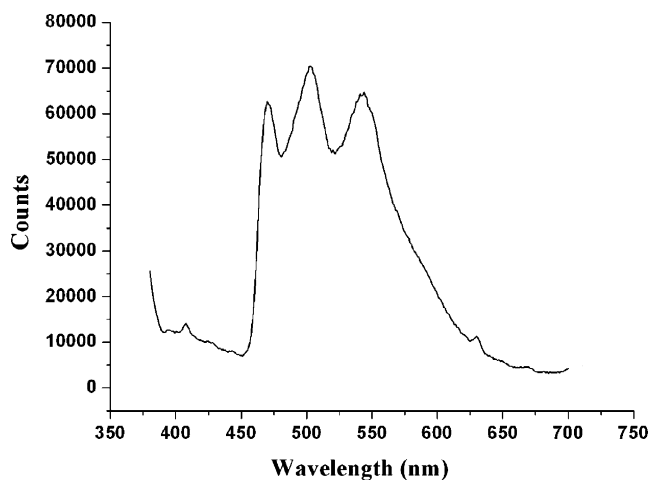


Fig. 5 Phosphorescence spectrum of $\text{Gd}(\text{TPTZ})\text{Cl}_3$ in ethanol

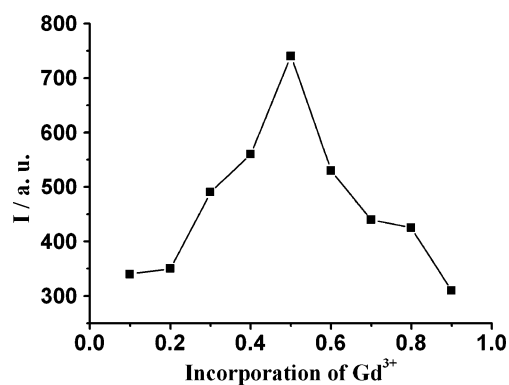


Fig. 6 Emission intensity of Tb^{3+} (${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$) the complexes versus content of Gd^{3+} ions

molecules in the complex. The temperature of the thermal diffusion of the complex was 560.2°C , which showed that the complexes were stable below 560°C .

IR spectra studies

The IR spectra of the complexes was shown in Fig. 2, it is assumed that all of them have similar coordination structures. In the IR spectra of TPTZ ligand, the peak at 1369 cm^{-1} was attributed to breathing vibration of center ring and the peak at 994 cm^{-1} was attributed to bending vibration of pyridyl ring. In the IR spectra of rare earth complexes, the two peaks shifted by $11\text{--}14$ and $14\text{--}16\text{ cm}^{-1}$ respectively indicating that center ring nitrogen atom and pyridyl nitrogen atom were coordinated with the metal ion [17].

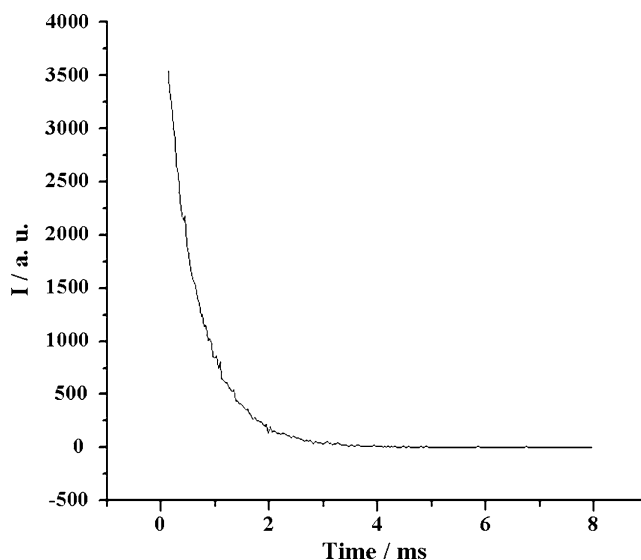


Fig. 7 Decay curve of $[\text{Tb}_{0.5}\text{Gd}_{0.5}(\text{TPTZ})(\text{H}_2\text{O})_3\text{Cl}_2]\text{Cl}$

Absorption spectra

The absorption spectra of TPTZ and the complexes were determined using DMF as a standard sample. The absorption spectra of the complexes are all similar, independent of the central lanthanide metal. The absorption spectra of TPTZ, Tb(TPTZ) $\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Tb}_{0.3}\text{Gd}_{0.7}(\text{TPTZ})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ were shown in Fig. 3. It indicated that the absorption of TPTZ is in the range of 255–320 nm and the complexes are in the range of 255–330 nm. The absorption peaks exhibited a maximum at 282 nm for TPTZ and the complexes revealed a maximum absorption peak at 281 nm. Comparing the absorption spectra of the complexes and TPTZ, we can see a blue-shift of the major $\pi-\pi^*$ electronic transitions (from 282 nm to 281 nm). The maximum peak of complex has not greatly changed in comparison with that of free TPTZ, therefore it showed that the conjugating TPTZ does not greatly affect the absorptions of the complexes [18, 19].

The excitation and emission spectra of the complexes were studied in DMF solutions. The spectra of the complexes are similar and the spectra of $\text{Tb}_{0.9}\text{Gd}_{0.1}(\text{TPTZ})\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ was shown in Fig. 4. The excitation wavelengths match the absorption spectra of the ligand. It is clear that the excitation of these complexes is mostly ligand based [14]. The maximum emission of the terbium complexes was observed when the complexes were excited at 309 nm, suggesting that ligand to Tb^{3+} energy transfer is mainly mediated by the TPTZ ligand.

Phosphorescence properties of ligand

The phosphorescence spectrum of the complex of gadolinium with TPTZ was measured with an exciting wavelength

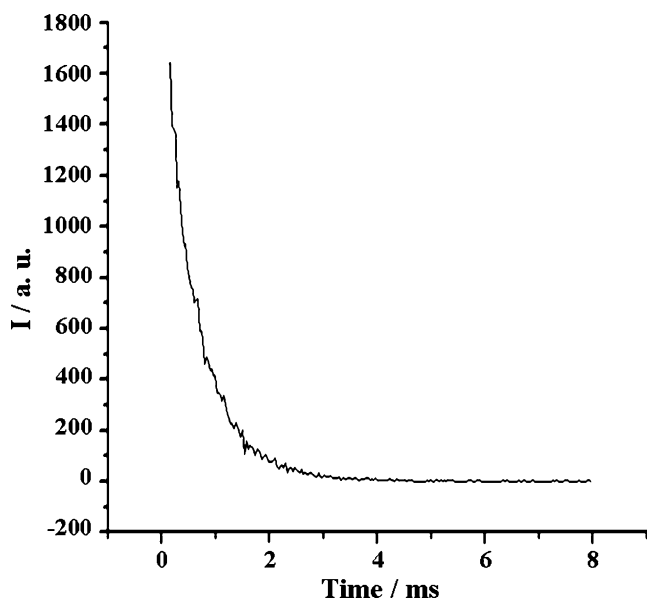


Fig. 8 Decay curve of $[\text{Tb}(\text{TPTZ})(\text{H}_2\text{O})_3 \text{Cl}_2]\text{Cl}$

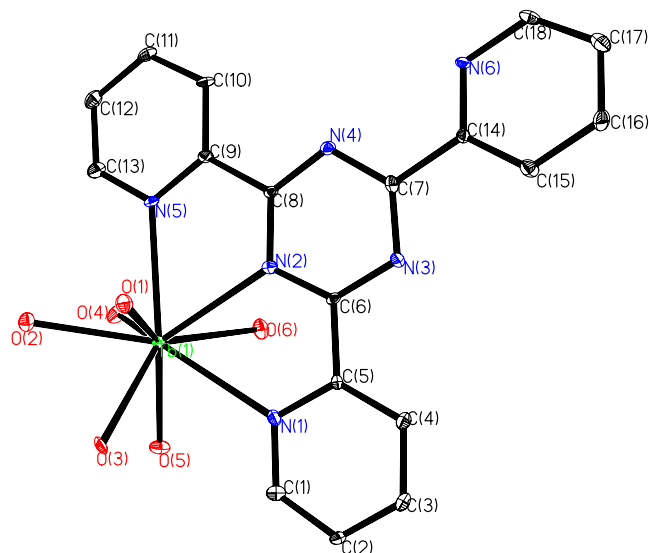


Fig. 9 The structure of $[\text{Tb}(\text{TPTZ})(\text{H}_2\text{O})_6]^{3+}$ cation in crystal of $[\text{Tb}(\text{TPTZ})(\text{H}_2\text{O})_6] \cdot \text{Cl}_3 \cdot 3\text{H}_2\text{O}$

of 360 nm in ethanol at 77 K. As shown in Fig. 5, the first emission peak of the complex shows at 470 nm, from which the obtained triplet state energy level of TPTZ is approximately 21277 cm^{-1} . It is higher than $^5\text{D}_4$ of Tb (III) ion (20430 cm^{-1}) [20].

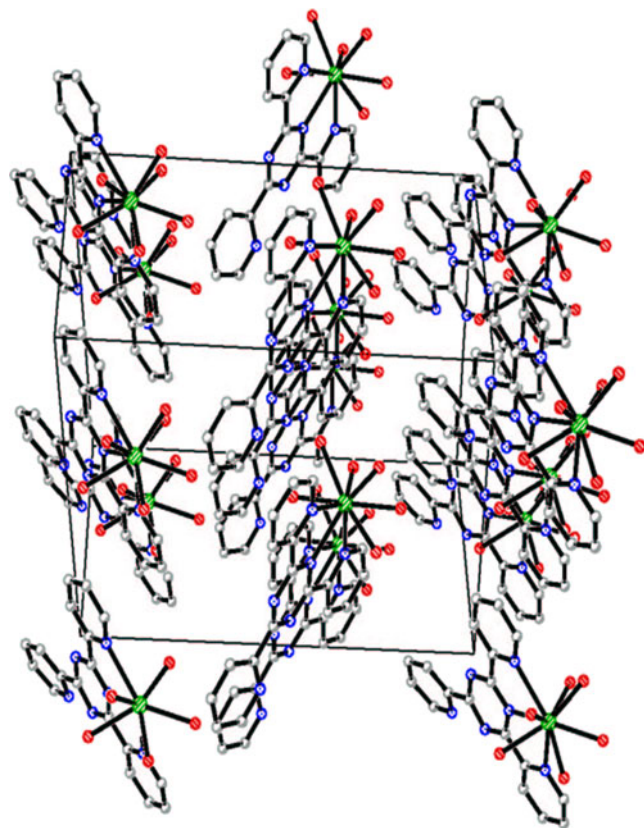


Fig. 10 Packing diagram of $[\text{Tb}(\text{TPTZ})(\text{H}_2\text{O})_6] \cdot \text{Cl}_3 \cdot 3\text{H}_2\text{O}$

Table 2 Crystallographic data and structural refinement parameters

C ₁₈ H ₃₀ Cl ₃ N ₆ O ₉ Tb	
Formula weight	739.75
Crystal system	Monoclinic
Space group	Cc
a /nm	1.4785(3)
b /nm	1.0547(2)
c /nm	1.7385(4)
β/(°)	94.42(3)
V /nm ³	2.7028(9)
Z	4
D _c / [g.cm ⁻³]	1.818
F(000)	1472
Crystal size/mm ³	0.12×0.10×0.10
Temperature /K	113
Index range (h, k, l)	-19/19,-13/12,-22/22
θrange/(°)	2.70–27.86
Wavelength /nm	0.071073
Tot., uniq.data, R(int)	9589, 5384, 0.0354
R, wR ₂	0.0305, 0.0734
Goodness-of-fit	1.056

Fluorescence spectra

At the room temperature, under the condition of the entrance and the exit slits are both 3 nm wide, by taking the fluorescence emission wavelength of terbium, i.e., 545 nm, as the monitoring wavelength, the excited spectra of the complexes in the solid state was tested and considered to be wide band peaks, of which the best excited wavelength was 343 nm. The complexes were excited with an optimum

exciting wavelength of 343 nm then we obtained the feature fluorescent spectra which belong to the transition $^5D_4 \rightarrow ^7F_j$ ($j=6\sim 3$). There are four groups of emission peaks for the complexes, and the strongest emission band $^5D_4 \rightarrow ^7F_5$ is super-sensitive transition. The changes of fluorescent emission intensity of $^5D_4 \rightarrow ^7F_5$ transitions with the increase of Gd³⁺ in the complexes of different molar proportion of terbium to gadolinium [(Tb_xGd_y)(TPTZ)Cl₃·3H₂O] were given in Fig. 6. The results indicated that the fluorescent intensity data are very different. These complexes showed stronger emission. According to the energy transfer and intramolecular energy mechanism [21, 22], the energy difference ΔE between the lowest triple state energy levels of TPTZ (21277 cm⁻¹) and the resonance energy level of Tb³⁺ (5D_4 , 20430 cm⁻¹) is 847 cm⁻¹. It can be predicted that the triplet state energy of TPTZ is more suitable for the sensitization of Tb³⁺ ion.

The influences of different mole ratio (x) Tb-Gd in complexes on the fluorescent intensity was obvious. When x was from 0.9 to 0.3 (the mole number of Tb³⁺ ion is decreased), the fluorescent intensity increased. Especially when x was 0.5, the intensity of the complex [(Tb_{0.5}Gd_{0.5})(TPTZ)Cl₂(H₂O)₃]Cl was the strongest among the nine complexes. The fluorescent intensity data of complexes increased from 308.8 au in complex {[Tb_{0.9}Gd_{0.1}(TPTZ)(H₂O)₃Cl₂]Cl} to 735.17 au in complex {[Tb_{0.5}Gd_{0.5}(TPTZ)(H₂O)₃Cl₂]Cl}, then decreased to 335.3 au in complex {[Tb_{0.1}Gd_{0.9}(TPTZ)(H₂O)₃Cl₂]Cl}. The results showed that if some of terbium ions in the complexes were substituted by gadolinium ions, the emission of Tb³⁺ ion would be enhanced. When x < 0.3, the concentration of Tb³⁺ ion was very low, so their intensity decreased obviously.

The luminescence decay curves of Tb³⁺ ($^5D_4 \rightarrow ^7F_5$ at 545 nm) in complexes [(Tb(TPTZ)Cl₂(H₂O)₃]Cl and [(Tb_{0.5}Gd_{0.5})

Table 3 Selected bond lengths (nm) and bond angles(°) for the title complex

Tb(1)-O(2)	2.368(4)	Tb(1)-O(3)	2.427(4)	Tb(1)-N(2)	2.572(4)
Tb(1)-O(5)	2.383(4)	Tb(1)-O(4)	2.444(4)	Tb(1)-N(5)	2.619(4)
Tb(1)-O(1)	2.423(4)	Tb(1)-O(6)	2.486(4)	Tb(1)-N(1)	2.648(5)
O(2)-Tb(1)-O(5)	98.02(13)	O(1)-Tb(1)-O(6)	137.87(12)	O(3)-Tb(1)-N(5)	138.57(14)
O(2)-Tb(1)-O(1)	74.21(13)	O(3)-Tb(1)-O(6)	135.88(13)	O(4)-Tb(1)-N(5)	73.36(15)
O(5)-Tb(1)-O(1)	136.81(13)	O(4)-Tb(1)-O(6)	69.49(14)	O(6)-Tb(1)-N(5)	84.85(13)
O(2)-Tb(1)-O(3)	73.83(13)	O(2)-Tb(1)-N(2)	130.88(13)	N(2)-Tb(1)-N(5)	62.41(14)
O(5)-Tb(1)-O(3)	69.55(13)	O(5)-Tb(1)-N(2)	131.09(14)	O(2)-Tb(1)-N(1)	145.45(14)
O(1)-Tb(1)-O(3)	67.49(13)	O(1)-Tb(1)-N(2)	69.18(13)	O(5)-Tb(1)-N(1)	77.55(14)
O(2)-Tb(1)-O(4)	68.85(14)	O(3)-Tb(1)-N(2)	118.10(14)	O(1)-Tb(1)-N(1)	85.72(14)
O(5)-Tb(1)-O(4)	72.98(14)	O(4)-Tb(1)-N(2)	120.37(14)	O(3)-Tb(1)-N(1)	72.56(14)
O(1)-Tb(1)-O(4)	135.83(14)	O(6)-Tb(1)-N(2)	68.69(13)	O(4)-Tb(1)-N(1)	138.17(14)
O(3)-Tb(1)-O(4)	121.53(14)	O(2)-Tb(1)-N(5)	77.99(13)	O(6)-Tb(1)-N(1)	74.74(14)
O(2)-Tb(1)-O(6)	137.93(13)	O(5)-Tb(1)-N(5)	145.14(15)	N(2)-Tb(1)-N(1)	62.15(14)
O(5)-Tb(1)-O(6)	75.14(13)	O(1)-Tb(1)-N(5)	76.05(14)	N(5)-Tb(1)-N(1)	124.55(13)

(TPTZ)Cl₂(H₂O)₃]Cl were obtained at room temperature. The lifetime of Tb³⁺ ⁵D₄ excited level in the complexes were determined to be 643.4 μs and 651.4 μs respectively which was shown in Figs. 7 and 8. The lifetime of [(Tb_{0.5}Gd_{0.5})(TPTZ)Cl₂(H₂O)₃]Cl was longer than that of [(Tb(TPTZ)Cl₂(H₂O)₃]Cl. It was clear that the luminescence of Tb³⁺ in the complexes showed simple decay behavior.

Crystal structure

The crystal of [Tb(TPTZ)(H₂O)₆]Cl₃·3H₂O was formed from the filtered solution of synthesizing the complex of Tb(TPTZ)Cl₂(H₂O)₃]Cl, which was kept for 4 weeks at the room temperature. The crystal structure and unit cell packing diagram of the complex [Tb(TPTZ)(H₂O)₆]Cl₃·3H₂O were shown in Figs. 9 and 10 respectively. There are more water molecules in the crystal complex comparing with the precipitate complexes, since more deionized water was added to the filtrate solution in which the crystal was made. The crystal system belongs to monoclinic system and space group Cc with unit cell parameters is *a*=1.4785 (3) nm, *b*=1.0547 (2) nm, *c*=1.7385 (4) nm, β=94.42 (3)°, *V*=2.7028 (9) nm³ and *Z*=4.

The analysis of the crystal structure indicated that the coordinate number of the central metal ion was nine—three nitrogen atoms from the tridentate TPTZ and six oxygen atoms from six water molecules. Crystallographic data was listed in Table 2. The data of selected bond lengths and bond angles were given in Table 3. The six Tb–O bond lengths [2.3684(4)~2.486(4) nm] were different, and they were shorter than that of Tb–N [2.572(4)~2.648(5) nm]. This showed that the symmetries of the water molecules combined with terbium ion is lower and the distance of water molecules to terbium ion is shorter than that of TPTZ to terbium ion in the crystal.

Conclusions

In this work the ten new solid complexes [(Tb_{*x*}Gd_{*y*})(TPTZ)Cl₂(H₂O)₃]Cl were synthesized. The absorption spectra and photoluminescence of the complexes were determined in dimethylsulfoxide (DMF). The triplet state energy level of TPTZ and the crystal structure of [Tb(TPTZ)(H₂O)₆]Cl₃·3H₂O were measured. It was observed that Gd³⁺ ion could enhance the fluorescence emission of Tb³⁺ ion. When the complex is [(Tb_{0.5}Gd_{0.5})(TPTZ)Cl₃·3H₂O] the intensity was the strongest among the nine doped complexes. The excitation of the complexes is mostly ligand based and the lowest excitation state energy level of Tb (III) and the triplet state energy level of TPTZ match well each other. These complexes showed stronger emission under ultraviolet light. The hetero-nuclear complexes have longer fluorescent lifetime than homo-nuclear complex (terbium complex).

Acknowledgements The research work is supported by the National Natural Science Foundation of China (20461002), “Chunhui Plan” Foundation of MOE (Z2004-2-15029) and Natural Science Foundation of Inner Mongolia (200711020203).

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