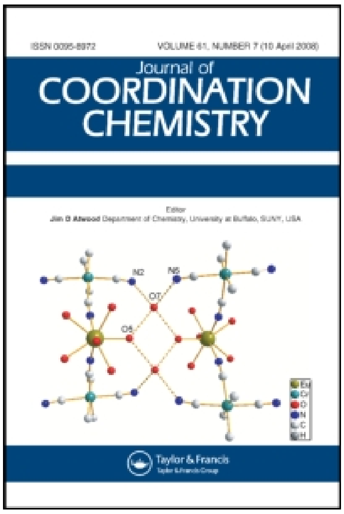

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Three lanthanide coordination polymers with nitrilotriacetic acid: hydrothermal syntheses, crystal structures and fluorescent property

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Three lanthanide coordination polymers with nitrilotriacetic acid: hydrothermal syntheses, crystal structures and fluorescent property

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Hydrothermal reactions of Sm_2O_3, $Gd(ClO_4)_3 \cdot 6H_2O$ and $Tb(ClO_4)_3 \cdot 6H_2O$ with nitrilotriacetic acid, give rise to three lanthanide coordination polymers, $\{[Sm(NTA)(H_2O)_2] \cdot H_2O\}_n$ (**1**), $\{[Gd(NTA)(H_2O)] \cdot H_2O\}_n$ (**2**) and $\{[Tb(NTA)(H_2O)] \cdot H_2O\}_n$ (**3**). Their solid-state structures have been characterized by elemental analysis, and IR spectroscopy. X-ray single-crystal diffraction analyses indicated that **2** and **3** are isomorphous three-dimensional coordination polymers with eight-coordinate Gd(III) (or Tb(III)), while **1** forms a two-dimensional coordination polymer containing nine-coordinate Sm(III). The photophysical properties of **3** have been studied with excitation and emission spectra, which exhibit strong green emission.

Keywords: Lanthanide complexes; Crystal structure; Coordination polymer; Hydrothermal syntheses; Fluorescence

1. Introduction

Lanthanide complexes receive attention because of their interesting photophysical properties, which have potential application in the luminescence probes for chemical or biological macromolecules and the active center for luminescent materials [1–9]. Nitrilotriacetic acid (H_3NTA) is one of the important derivatives of glycine, and is widely used in biochemistry and medicine. Lanthanide complexes with nitrilotriacetate have been studied for a long time. In 1972, Martin concluded that RE · NTA complexes were divided into three group [10, 11]. The first group include La and Ce and the second group Pr, Nd, Sm, Eu, Gd, Tb, while Dy, Ho, Er, Tm, Yb, Lu belong to the third group. Complexes of the different ions with one group were supposed to have identical crystal structures with the complexes obtained under the same experimental conditions.

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In order to study structural transformations in lanthanide series, some multiple dimension polymer structures have been prepared under hydrothermal conditions [10–13], while some monomers have also been prepared under slow evaporation of filtrate [14–18]. Nonetheless, it is still worth investigating the structural diversity of such lanthanide coordination polymers with NTA. Therefore complexes $\{[Sm(NTA)(H_2O)_2]\cdot H_2O\}_n$ (**1**), $\{[Gd(NTA)(H_2O)]\cdot H_2O\}_n$ (**2**) and $\{[Tb(NTA)(H_2O)]\cdot H_2O\}_n$ (**3**), were synthesized by hydrothermal reaction and characterized by X-ray diffraction.

2. Experimental

2.1. *Materials and apparatus*

$Ln(ClO_4)_3\cdot 6H_2O$ (Ln = Gd, Tb) were prepared by reaction of Ln_2O_3 with $HClO_4$; all other chemicals were purchased and used as received without further purification. All solvents were analytical grade. C, H and N data were obtained using an American PE 2400II CHNS/O elemental analyzer. Infrared spectra were measured from KBr pellets using a Nicolet 5DXB system. Excitation and emission spectra for solid **3** were measured with a F-4500 FL Spectrophotometer mode spectrophotometer at room temperature. The single-crystal structure data were collected on a Smart apex CCD with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 293(2) K.

Caution: Perchlorate salts of metal complexes are potentially explosive.

2.2. *Preparation of complexes 1–3*

2.2.1. $\{[Sm(NTA)(H_2O)_2]\cdot H_2O\}_n$ (1). An aqueous mixture (15 mL) containing H_3NTA (0.7 mmol, 0.1337 g), Sm_2O_3 (0.25 mmol), and KOH (0.5 mmol) was placed in a Teflon-lined stainless steel vessel (25 mL). Ethanol (5.0 mL) was added to the mixture. The vessel was sealed and heated to 130°C for 3 days. Upon cooling to room temperature, yellow block crystals of **1** were obtained. Anal. Calcd for $C_6H_{12}NO_9Sm$: C, 18.34; H, 3.05; N, 3.57. Found: C, 18.43; H, 3.12; N, 3.54. IR data: (KBr pellet, cm^{-1}), 3559(m), 3552(s), 2961(w), 2912(w), 1647(s), 1591(s), 1559(s), 1471(m), 1439(m), 1426 (m), 1404(m), 1352(m), 1332(m), 1300(m), 1254(m), 1244(m), 1116(m), 1023(m), 996(m), 970(m), 944(m), 931(m), 912(m), 760(m), 743(m), 644(w), 621(w), 568(w), 549(w), 515(w), 472(w), 412(W).

2.2.2. $\{[Gd(NTA)(H_2O)]\cdot H_2O\}_n$. The procedure was similar to that for **1** except that $Gd(ClO_4)_3\cdot 6H_2O$ was used. Light-pink crystals were obtained. Anal. Calcd for $C_6H_{10}NO_8Gd$: C, 18.90; H, 2.62; N, 3.67. Found: C, 18.84; H, 3.17; N, 3.59. IR data: (KBr pellet, cm^{-1}), 3389(s), 3246(s), 3263(s), 2968(w), 2852(w), 1645(s), 1599(s), 1564(s), 1472(m), 1456.5(w), 1452(w), 1439(s), 1406(m), 1353(w) 1332(w), 1300(w), 1255(w), 1116(m), 1024(w), 997(w), 971(w), 946(w), 932(w), 913(w), 762(m), 744(m), 645(w), 623(w), 569(w), 550(w), 517(w), 471(w), 414(w).

2.2.3. {[Tb(NTA)(H_2O)] · H_2O}$_n$. The procedure was similar to that for **1** except that $Tb(ClO_4)_3 \cdot 6H_2O$ was used. Red crystals were obtained. Anal. Calcd for $C_6H_{10}NO_8Tb$: C, 18.80; H 2.61; N, 3.66. Found: C, 18.74; H, 2.69; N, 3.62. IR data: (KBr pellet, cm^{-1}), 3401(S), 2960(W), 2929(W), 1636(S), 1595(S), 1467(S), 1417(m), 1396(w), 1338(w), 1315(w), 1300(w), 1274(w), 1230(w), 1117(m), 1021(w), 991(w), 970(w), 951(w), 934(w), 915(w), 770(w), 740(m), 674(w), 606(w), 574(w), 501(w), 468(w), 419(w).

2.3. *Crystal structure determination*

The X-ray single crystal data collections for **1**–**3** were performed on a Bruker Smart CCD diffractometer equipped with a graphite monochromator Mo-Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods using the SHELXS-97 program. Refinement on F^2 was performed using SHELXS-97 by full-matrix least-squares with anisotropic parameters for all non-hydrogen atoms. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. Selected bonds and angles are presented in table 2.

3. Result and discussion

3.1. *Spectroscopic properties*

The υ(C–N) of **1**, **2**, and **3** are at 1116, 1116 and 1117 cm^{-1}, undergoing red-shifts 84, 84 and 83 cm^{-1} compared with that of NTA (1200 cm^{-1}), indicating that N atoms of NTA coordinate to Sm(III), Gd(III) and Er(III). For the COOH group, $\nu_{as}(COO^-)$ of NTA at 1725 cm^{-1} disappeared in the complexes, and $\nu_{as}(COO^-)$ at 1620 cm^{-1} of NTA red-shifts to 1591, 1599, 1595, and $\nu_s(COO^-)$ at 1340 $cm^{-1}$of NTA blue-shift to 1404, 1406 and 1417 cm^{-1} in complexes, respectively, confirming that the O atoms of COO^- also coordinate with Sm(III), Gd(III) and Tb(III). There are broad υ(OH) bands of H_2O near 3550 cm^{-1}, showing H_2O in **1**–**3**.

3.2. *Crystal structure of 1–3*

Crystal data of **1**–**3** are listed in table 1, and selected bond distances and angles are listed in the table 2. Single crystal X-ray determination reveals that NTA coordinates to the Sm(III) ion in a tetradentate mode through three oxygen atoms of three different carboxyl groups and a nitrogen atom, forming three five-membered chelate rings. The Sm(III) ion is nine-coordinate, in a capped square antiprism with one site occupied by O4 and four sites occupied by one NTA ligand (O1, O3, O5, and N1), see figure 1. The remaining four sites are carboxyl groups from two different NTA ligands (O5A, O6), and from two different water ligands (O1W, O2W). Four oxygens

Table 1. Summary of crystallographic data for **1**, **2** and **3**.

Parameter	**1**	**2**	**3**
Formula	$C_6H_{12}SmNO_9$	$C_6H_{10}GdNO_8$	$C_6H_{10}TbNO_8$
Formula weight	392.52	381.40	379.04
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*P*212121	*P*212121
a (Å)	8.1058(5)	6.6007(10)	6.5738(4)
b (Å)	13.1221(7)	11.8071(3)	11.8027(6)
c (Å)	20.7734(12)	13.0234(3)	12.9586(9)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å^3)	2209.6(2)	1014.98(4)	1005.44(11)
Z	8	4	4
F(000)	1512	724	712
P_{Calcd} (mg m^{-3})	2.305	2.496	2.504
T (K)	293(2)	293(2)	293(2)
Reflections collected	12667	5064	4686
Independent	2577	1977	1928
Reflections	1.005	1.120	1.203
Goodness-of-fit on F^2	$R_1 = 0.0207$	$R_1 = 0.0182$	$R_1 = 0.0215$
Final R index [$I > 2\sigma(I)$]	$wR_2 = 0.0486$	$wR_2 = 0.0444$	$wR_2 = 0.0587$

(O1, O3, O4, O6) of NTA ligands bond only one Sm atom, while the other two oxygen atoms (O5A, O5) connect two Sm(III) ions. Thus there are two coordination modes between Sm(III) and O, monodentate and bridging coordination. Every four Sm(III) ions are bridged by NTA, resulting in the formation of a two-dimension neutral square grid with a cavity dimension of 11.45×6.024 Å^2, see figure 2.

All coordination and crystal lattice water molecules are involved in the hydrogen bonding network with O3W–H3WB $\cdots$ O1W = 3.096 Å $(x+1/2, y, -z+1/2)$, O1W–H1WA $\cdots$ O3 = 2.748 Å $(x-1/2, -y+3/2, -z)$, O2W–H2WA $\cdots$ O2 = 2.742 Å $(x+1/2, y, -z+1/2)$, O2W–H2WB $\cdots$ O4 = 2.730 Å $(x+1/2, -y+3/2, -z)$. Monodentate carboxyl groups O(2), O(3) and O(4) are also associated with intermolecular hydrogen bonds. The adjacent layers almost perfectly overlap, and are further linked through hydrogen bondings into a three-dimensional network as depicted in figure 3.

Single-crystal X-ray diffraction studies show that $\{[Gd(NTA)(H_2O)] \cdot H_2O\}_n$ (**2**) and $\{[Tb(NTA)(H_2O)] \cdot H_2O\}_n$ (**3**) are isomorphous; discussion of the structure of **2** follows. As shown in figure 4, tetradentate chelated NTA coordinates to Gd(III) by O1, O3, O5, and N1. The other four coordinate sites of Gd(III) are occupied by one water molecule (O7) and three carboxyl oxygen atoms (O2A, O4A, O6A) from three neighboring NTA ligands yielding a distorted square antiprism. The Gd–O bond distances range from 2.293(2) Å to 2.465(2), and the Gd–N bond distance is 2.639(2) Å. The complex can be considered a polymer in which [Gd(NTA)] units are linked by carboxylate bridges from different directions. The structural units are connected by carboxyl O atoms along *a*, *b* and *c* axes forming the three-dimension network structure. The coordinated water molecules protrude from the polymeric layer and hydrogen bond to the oxygen atoms of carboxylate groups from the neighboring layer. The lattice water molecules are intercalated in the 3D channel through hydrogen bonding involving water molecules and carboxylate groups of NTA (figure 5).

Table 2. Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

1					
Sm(1)–O(6)	2.344(2)	Sm(1)–O(2W)	2.428(2)	Sm(1)–O(5)	2.547(2)
Sm(1)–O(1)	2.407(2)	Sm(1)–O(1W)	2.463(3)	Sm(1)–N(1)	2.639(2)
Sm(1)–O(3)	2.409(2)	Sm(1)–O(4)	2.470(2)	Sm(1)–O(5)#1	2.671(2)
O(1)–Sm(1)–O(4)	148.34(8)	O(1)–Sm(1)–N(1)	64.76(7)	O(6)–Sm(1)–O(2W)	85.24(9)
O(6)–Sm(1)–O(3)	138.16(8)	O(5)–Sm(1)–N(1)	63.71(7)	O(1W)–Sm(1)–N(1)	95.53(9)
O(6)–Sm(1)–N(1)	144.68(8)	O(4)–Sm(1)–O(5)#1	50.54(7)	O(3)–Sm(1)–O(4)	87.20(8)
2					
Gd(1)–O(6)#1	2.293(2)	Gd(1)–O(2)#2	2.354(2)	Gd(1)–O(4)#3	2.362(2)
Gd(1)–O(3)	2.3321(18)	Gd(1)–O(5)	2.358(2)	Gd(1)–O(7)	2.416(3)
Gd(1)–O(1)	2.465(2)	Gd(1)–N(1)	2.639(2)		
O(6)#1–Gd(1)–O(5)	156.79(9)	O(1)–Gd(1)–N(1)	64.36(7)	O(3)–Gd(1)–O(5)	88.08(9)
O(2)#2–Gd(1)–O(7)	149.18(9)	O(5)–Gd(1)–N(1)	64.47(8)	O(2)#2–Gd(1)–O(5)	91.65(8)
O(3)–Gd(1)–O(4)#3	144.39(9)	O(2)#2–Gd(1)–N(1)	73.25(8)	O(5)–Gd(1)–O(7)	83.59(11)
3					
Tb(1)–O(1)#1	2.277(4)	Tb(1)–O(2)	2.342(3)	Tb(1)–O(5)#3	2.355(3)
Tb(1)–O(6)	2.310(3)	Tb(1)–O(3)#2	2.343(3)	Tb(1)–O(7)	2.421(3)
Tb(1)–O(4)	2.455(3)				
O(1)#1–Tb(1)–O(2)	156.13(13)	O(5)#3–Tb(1)–O(7)	73.56(12)	O(1)#1–Tb(1)–O(3)#2	91.74(13)
O(3)#2–Tb(1)–O(7)	148.99(10)	O(6)–Tb(1)–O(7)	72.19(12)	O(1)#1–Tb(1)–O(6)	104.25(14)
O(6)–Tb(1)–O(5)#3	143.91(11)	O(6)–Tb(1)–O(4)	73.08(11)	O(2)–Tb(1)–O(3)#2	92.17(12)

Symmetry code: #1: $x+1/2, -y+3/2, -z$; #2: $-x+1/2, y+1/2, z$; #3: $x-1/2, -y+3/2, -z$; #4: $-x+1/2, y-1/2, z$ for **1**; #1: $-x+5/2, -y+1, z+1/2$; #2: $x+1/2, -y+1/2, -z+2$; #3: $x+1, y, z$; #4: $x-1/2, -y+1/2, -z+2$; #5: $-x+5/2, -y+1, z-1/2$; #6: $x-1, y, z$ for **2**; #1: $-x-1/2, -y+1, z-1/2$; #2: $x-1/2, -y+1/2, -z$; #3: $x-1, y, z$; #4: $-x-1/2, -y+1, z+1/2$; #5: $x+1/2, -y+1/2, -z$; #6: $x+1, y, z$ for **3**.

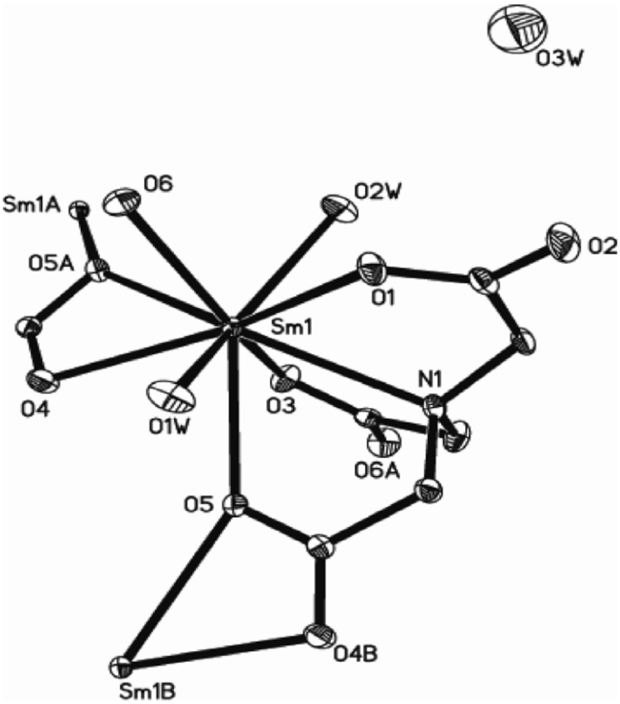

Figure 1. ORTEP view of **1**.

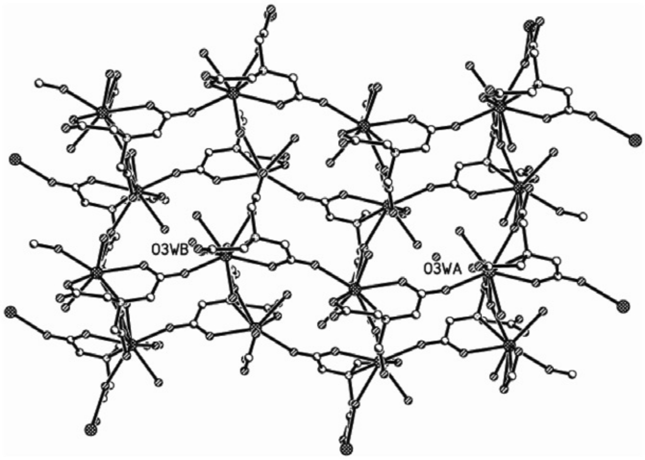

Figure 2. An extended two-dimensional network perspective view of **1**.

According to the classification suggested by Martin and Jacobson, Sm, Tb and Gd fall in the same group and are expected to have similar structures [10, 11]. However, complex **1** is quite different from complexes **2** and **3**. This exception indicates that such a grouping may no longer be appropriate. The structural difference may result from the variation of the lanthanide ion radii, the variable coordination modes of NTA, or different synthetic conditions.

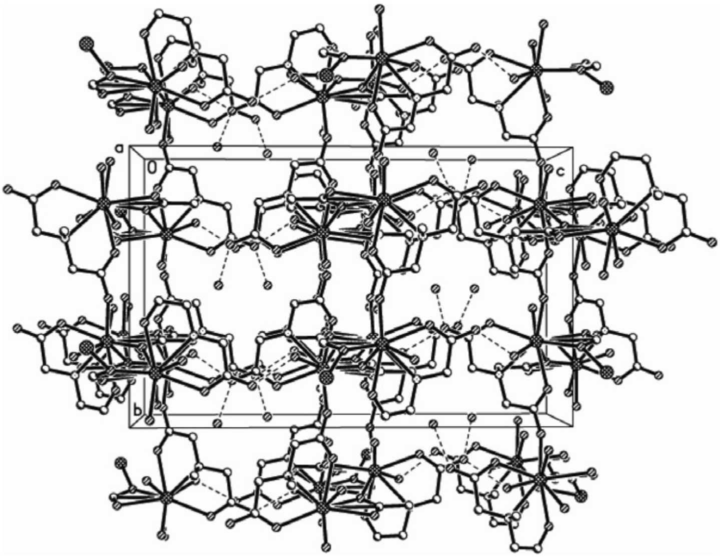

Figure 3. Crystal packing view of complex **1** along the *a* axis.

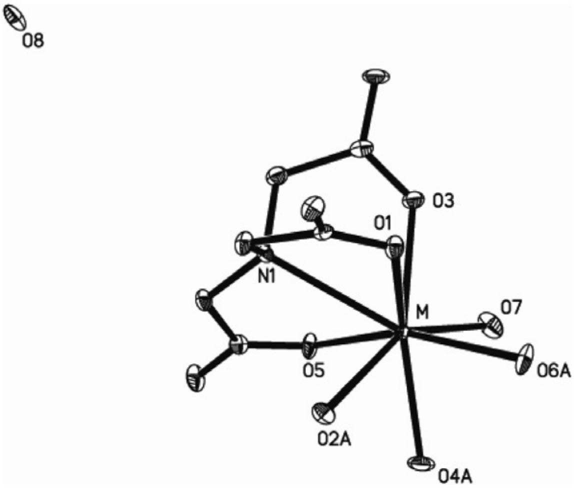

Figure 4. The asymmetric unit of $\{[Gd(NTA)(H_2O)] \cdot H_2O\}_n$ (**2**) (M = Gd) and $\{[Tb(NTA)(H_2O)] \cdot H_2O\}_n$ (**3**) (M = Tb) showing 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

3.3. *Photophysical properties of 3*

The solid-state excitation spectrum of **3** shows effective energy absorption mainly in the ultraviolet region of 230–390 nm under emission of 544 nm. We further measured the corresponding emission spectra by excitation with wavelengths of 340 nm. Figure 6 gives the emission spectrum of **3**, the strong green luminescence with four emission bands are at 491, 545, 583, and 621 nm, corresponding to the characteristic emissions originating from the $^5D_4 \rightarrow {}^7F_j$ $(j = 6, 5, 4, 3)$ transitions of Tb^{3+}. The $^5D_4 \rightarrow {}^7F_5$

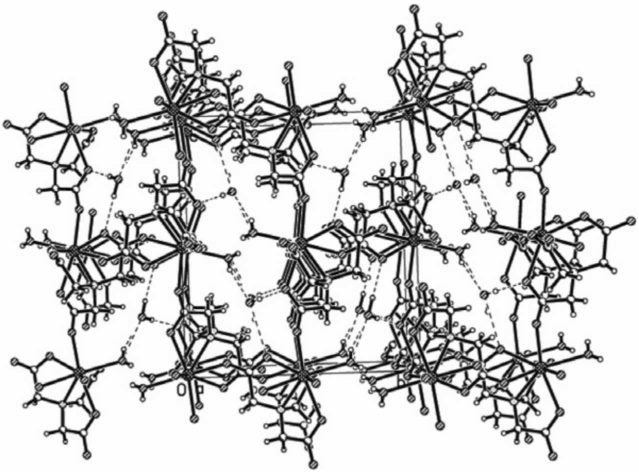

Figure 5. An extended three-dimensional network perspective view of **2** and **3**.

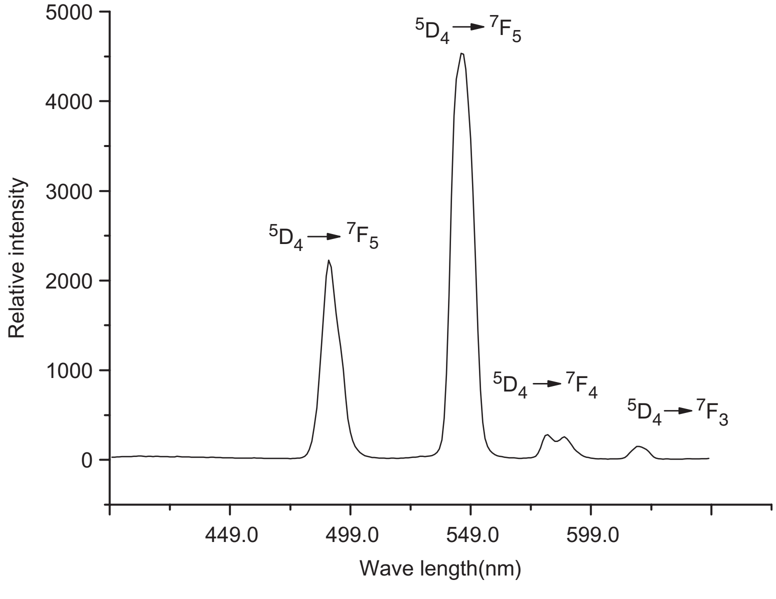

Figure 6. The emission spectrum of $\{[Tb(NTA)(H_2O)]\cdot H_2O\}_n$.

transition exhibits the strongest green emission, and $^5D_4 \rightarrow {}^7F_6$ transition shows the second strongest blue emission.

Supplementary material

Crystallographic data for **1**, **2** and **3** are deposited to the Cambridge Crystallographic Data Centre with deposition numbers CCDC 613064, 614255 and 614256, respectively.

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