

## 两个基于 4-(1*H*-1,2,4-三氮唑)苯甲酸的稀土配位聚合物的合成、晶体结构及荧光性质

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**摘要:** 以 4-(1*H*-1,2,4-三氮唑)苯甲酸为配体, 采用水热法合成了 2 种稀土配位聚合物 [Tb(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**) 和 {[Nd(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O}<sub>n</sub> (**2**) (Htbc=4-(1*H*-1,2,4-三氮唑)苯甲酸)。运用 X-射线单晶衍射法对该配位聚合物进行了结构测定, 并对其进行了元素分析、红外光谱、TG 及荧光光谱表征。单晶结构表明, 配位聚合物 **1** 为三斜晶系, 空间群  $P\bar{1}$ , 配位聚合物 **2** 属于单斜晶系, 空间群为  $P2_1/c$ 。配位聚合物 **1** 和 **2** 均为一维链结构, 均通过非共价键作用形成三维超分子构造。

**关键词:** 稀土配位聚合物; 4-(1*H*-1,2,4-三氮唑)苯甲酸; 晶体结构

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## Two Lanthanide Coordination Polymers Derived from 4-(1*H*-1,2,3-Triazol-1-yl) benzoic Acid: Synthesis, Crystal Structures, and Fluorescence

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**Abstract:** Two lanthanide Coordination Polymers, [Tb(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**) and {[Nd(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O}<sub>n</sub> (**2**) [Htbc=4-(1*H*-1,2,3-triazol-1-yl) benzoic acid], have been synthesized by hydrothermal method and structurally characterized by elemental analyses, FT-IR spectra, and thermal studies, fluorescence spectra, as well as single crystal X-ray diffraction. Structural determination reveals that complex **1** belongs to triclinic system and space group  $P\bar{1}$ . And complex **2** crystallizes in monoclinic system, space group  $P2_1/c$ . Both **1** and **2** possess a one dimensional chain structure constructed from carboxylate O atoms of Htbc ligand bridging the units. Through non-covalent interactions the complex molecules are assembled into 3D supramolecular network structures. CCDC: 957286, **1**; 957287, **2**.

**Key words:** lanthanide coordination polymer; 4-(1*H*-1,2,3-triazol-1-yl) benzoic acid; crystal structure

The design and construction of metal coordination polymers based on metal ions and multifunctional bridging ligands are of interest due to their intriguing topologies and potential applications as functional

materials<sup>[1-5]</sup>. It is well known that the structures of the ligands play a key role in the manipulation of the final structures of their complexes<sup>[6-10]</sup>. Therefore, there are still plenty of publications to design a new ligand

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and study their coordination chemistry<sup>[11-15]</sup>. Admittedly the ligands with carboxylic group are often used to constructing new coordination compounds not only because of their various coordination mode such as monodentate, bidentate chelate and monodentate bridging with metal ions and also their ability to act as hydrogen bond acceptors and donors<sup>[16-18]</sup>. Likewise, the heterocyclic N donor ligands such pyrazole, imidazole, triazole and tetrazole also effective as bridging organic building blocks for coordination compounds with the ability to act as hydrogen bond donors<sup>[19-22]</sup>. In a word, carboxylate O atoms and triazol ring N atoms have good coordination capacities. It can be seen that 4-(1*H*-1,2,3-triazol-1-yl) benzoic acid is a kind of multifunctional ligand.

Encouraged by the previous results, we selected 4-(1*H*-1,2,3-triazol-1-yl) benzoic acid to construct novel lanthanide coordination polymers. There were four coordination complexes which were constructed by another similar ligand 4-(1*H*-1,2,3-triazol-1-ylmethyl) benzoic acid in the literatures<sup>[22-25]</sup>. To the best of our knowledge, only two transition metal complexes which were constructed by 4-(1*H*-1,2,3-triazol-1-yl) benzoic acid were documented<sup>[26-27]</sup>. Herein, we report two coordination complexes [Tb(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**) and {[Nd(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O}<sub>n</sub> (**2**), both of them possess a one dimensional chain structure. For complexes **1** and **2** there is one thing in common that only carboxylate O atoms were coordinated to lanthanide ions but triazol ring N atoms not. Further, their thermal stability and photoluminescent property have been investigated and described.

## 1 Experimental

### 1.1 Materials and apparatus

4-(1*H*-1,2,3-triazol-1-yl) benzoic acid was obtained from Jinan Henghua science and technology Ltd (Jinan, China). The other chemicals were commercially available reagents of analytical grade and used without further purification. Elemental (C, H, N) analyses were performed on Perkin-Elmer 240 element analyzer. The FT-IR spectra were recorded from KBr pellets in the 4 000~400 cm<sup>-1</sup> ranges on a

Nicolet 5DX spectrometer. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C·min<sup>-1</sup> from room temperature to 800 °C under nitrogen atmosphere (All the samples were dried in vacuum at 50 °C for 24 h). Fluorescence spectra were recorded with an F-2500 FL Spectrophotometer analyzer.

### 1.2 Synthesis of [Tb(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**)

A mixture of Tb<sub>2</sub>O<sub>3</sub> (0.045 g, 0.25 mmol), Htbc (0.08 g, 0.5 mmol), HCl (0.2 mL, 0.1 mol·L<sup>-1</sup>) and distilled water (10 mL) was sealed in a 20 ml Teflon-lined stainless steel reactor and then heated to 120 °C for 72 h under autogenous pressure. Then the mixture was slowly cooled to room temperature at a rate of 5 °C·h<sup>-1</sup>, colorless acicular crystals of **1** were obtained and washed with water. Yield: 50%. Calcd. (%) for C<sub>27</sub>H<sub>24</sub>N<sub>9</sub>O<sub>9</sub>Tb (777.47): C 41.7, H 3.1, N 16.2; Found (%): C 41.6, H 3.2, N 16.1. IR (KBr, cm<sup>-1</sup>): 3 130 vs, 2918 m, 2 789 m, 2 511 m, 1 915 m, 1 693 s, 1 606 s, 1 523 s, 1 444 m, 1411 s, 1 261 m, 1 273 s, 1 219 m, 1 155 m, 974 s, 860 m, 773 m.

### 1.3 Synthesis of {[Nd(tbc<sub>3</sub>)(H<sub>2</sub>O)<sub>3</sub>]·H<sub>2</sub>O}<sub>n</sub> (**2**)

A mixture of Nb<sub>2</sub>O<sub>3</sub> (0.045 g, 0.25 mmol), Htbc (0.08 g, 0.5 mmol), HCl (0.2 mL, 0.1 mol·L<sup>-1</sup>) and distilled water (10 mL) was sealed in a 20 mL Teflon-lined stainless steel reactor and then heated to 120 °C for 72 h under autogenous pressure. Then the mixture was slowly cooled to room temperature at a rate of 5 °C·h<sup>-1</sup>, pale purple block-shaped crystals of **2** were obtained and washed with water. Yield: 60%. Calcd. (%) for C<sub>27</sub>H<sub>26</sub>N<sub>9</sub>NdO<sub>10</sub> (780.8): C 41.5, H 3.4, N 16.1; Found(%): C 41.4, H 3.5, N 16.0. IR(KBr, cm<sup>-1</sup>): 3 203 vs, 3 111 s, 1 606 s, 1 554 s, 1 521 s, 1 506 s, 1 400 s, 1 363 m, 1 309 m, 1 276 s, 1 204 m, 1 143 m, 1 051 m, 981 m, 962 m, 858 m, 783 s, 694 m, 671 m, 499 m.

### 1.4 X-ray structure analyses

All the diffraction data for complexes **1** and **2** were collected on a Bruker APEX II Smart CCD diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm) using the  $\omega$ -scan technique. Multi-scan absorption corrections were applied with the SADABS program<sup>[28]</sup>. The structures

were solved by direct methods using the SHELXS-97 program and all the non-hydrogen atoms were refined anisotropically with the full-matrix least-squares on  $F^2$  using the SHELXL-97 program<sup>[29]</sup>. The hydrogen atoms of water molecules were located in the difference Fourier maps and the other hydrogen atoms were

generated geometrically and refined as riding atoms with isotropic thermal factors. Crystallographic data and structure determination summaries for **1** and **2** are given in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC: 957286, **1**; 957287, **2**.

**Table 1** Crystallographic data and structure refinement summary for **1** and **2**

Complex	<b>1</b>	<b>2</b>
Chemical formula	C <sub>27</sub> H <sub>18</sub> N <sub>9</sub> O <sub>9</sub> Tb	C <sub>27</sub> H <sub>26</sub> N <sub>9</sub> NdO <sub>10</sub>
Formula weight	771.47	780.8
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
$a$ / nm	0.593 82(10)	1.324 60(5)
$b$ / nm	1.347 8(2)	0.559 49(3)
$c$ / nm	1.886 8(3)	3.892 3(4)
$\alpha$ / (°)	78.385(2)	90.00
$\beta$ / (°)	86.460(2)	92.448(7)
$\gamma$ / (°)	81.079(2)	90
$V$ / nm <sup>3</sup>	1.460 6(4)	2.881 9(4)
$Z$	2	8
$D_c$ / (g·cm <sup>-3</sup> )	1.768	1.800
$\mu$ / mm <sup>-1</sup>	2.491	1.878
$\theta$ range / (°)	1.56~25.00	2.98~26.00
$F(000)$	720	1 564
Reflections collected	7 260	13 366
Independent reflections ( $R_{int}$ )	4 998 (0.029 6)	5 655 (0.045 4)
Reflections observed ( $I > 2\sigma(I)$ )	4 260	4 643
GOF on $F^2$	1.087	1.086
$R_1$ [ $I > 2\sigma(I)$ ]	0.053 2	0.042 4
$wR_2$ [ $I > 2\sigma(I)$ ]	0.143 4	0.074 5

**Table 2** Selected bond lengths (nm) and angles (°) for **1** and **2**

Complex <b>1</b>					
Tb(2)-O(1)	0.247 5(6)	Tb(2)-O(2)	0.245 9(6)	Tb(2)-O(3)	0.232 0(6)
Tb(2)-O(5)	0.230 6(6)	Tb(2)-O(6) <sup>i</sup>	0.230 7(6)	Tb(2)-O(1w)	0.241 0(6)
Tb(2)-O(2w)	0.243 5(6)	Tb(2)-O(3w)	0.241 8(6)		
O(2)-Tb(2)-O(1)	53.01(19)	O(3)-Tb(2)-O(1)	141.2(2)	O(3)-Tb(2)-O(2)	148.7(2)
O(3)-Tb(2)-O(1W)	128.5(2)	O(3)-Tb(2)-O(2W)	76.5(2)	O(3)-Tb(2)-O(3W)	76.0(2)
O(5)-Tb(2)-O(1)	80.7(2)	O(5)-Tb(2)-O(2)	129.3(2)	O(5)-Tb(2)-O(3)	80.3(2)
O(5)-Tb(2)-O(1W)	71.9(2)	O(5)-Tb(2)-O(2W)	153.1(2)	O(1W)-Tb(2)-O(3W)	140.3(2)
Complex <b>2</b>					
Nd(1)-O(1)	0.235 7(3)	Nd(1)-O(3)	0.244 4(3)	Nd(1)-O(4) <sup>ii</sup>	0.242 2(3)
Nd(1)-O(5)	0.243 7(3)	Nd(1)-O(6) <sup>ii</sup>	0.247 5(3)	Nd(1)-O(1W)	0.250 4(3)
Nd(1)-O(2W)	0.254 1(3)	Nd(1)-O(3W)	0.249 5(3)		

Continued Table 1

O(1)-Nd(1)-O(3)	90.73(13)	O(1)-Nd(1)-O(4) <sup>ii</sup>	74.64(13)	O(1)-Nd(1)-O(5)	142.71(13)
O(3)-Nd(1)-O(3W)	146.37(12)	O(3)-Nd(1)-O(6) <sup>ii</sup>	146.76(13)	O(4) <sup>ii</sup> -Nd(1)-O(5)	141.78(13)
O(4) <sup>ii</sup> -Nd(1)-O(3W)	116.57(13)	O(5)-Nd(1)-O(3)	84.39(12)	O(6) <sup>ii</sup> -Nd(1)-O(3W)	65.45(13)
O(6) <sup>ii</sup> -Nd(1)-O(1W)	132.99(13)	O(1W)-Nd(1)-O(2W)	133.51(12)	O(3W)-Nd(1)-O(2W)	133.56(12)

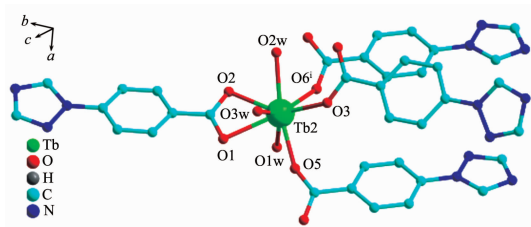
Symmetry transformations used to generate equivalent atoms: **1**:  $i-1+x, y, z$ ; **2**:  $ii x, -1+y, z$ .

## 2 Results and discussion

### 2.1 X-ray Crystallographic Structure

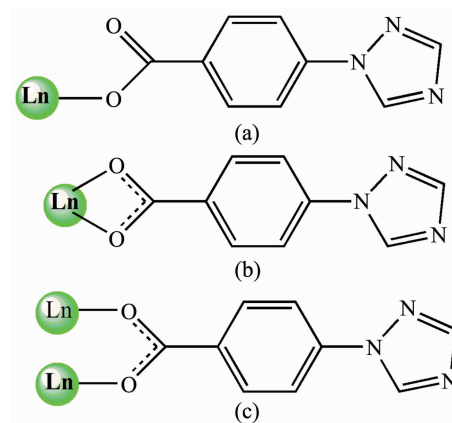
The crystal structure of complex **1** contains one crystallographically independent terbium ion Tb (**1**), three tbc ligands, and three coordinated water molecules in the asymmetrical unit. The Tb<sup>III</sup> ion is eight coordinated by five carboxylic oxygen atoms from four different tbc ligands and three oxygen atoms from three coordinated water molecules (see Fig.1) giving it an distorted trigonal bipyramidal geometry, as indicated by the bond lengths (Table 2). Interestingly, for complex **1** only the carboxylate oxygen atoms of the tbc ligand take part in the coordination with Tb(III) ions, whereas the nitrogen atoms of triazole ring from tbc ligands do not. The Tb-O bond lengths, all of which within the range of those observed for other analogical Tb complexes<sup>[30-31]</sup>, are ranging from 0.230 6(6) to 0.247 5(6) nm. The O-Tb-O bond angles are in the range from 53.01 (19) to 153.1 (2)°, similar to those reported for the Tb(III) complexes<sup>[30-31]</sup>. For complex **1** the tbc ligands adopt three kinds of coordination modes: a monodentate terminal coordination mode (Scheme 1(a)), a bidentate chelate mode (Scheme 1(b)) and a bidentate bridging coordination mode (Scheme 1(c)).

As shown in Fig.2, 1D chain is formed. The two oxygen atoms of carboxylate group from a tbc ligand bridge the two Terbium ions to form a one-

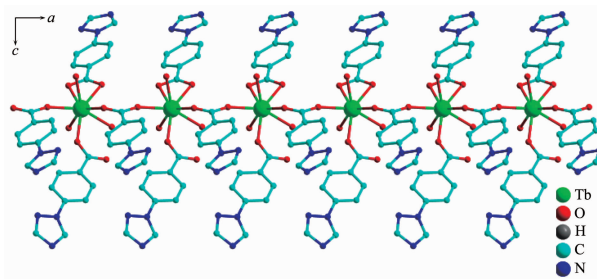


Symmetry code:  $i-1+x, y, z$

Fig.1 Coordination environment of Tb(III)



Scheme 1 Coordination modes of the tbc anions for **1** and **2**



H atoms have been omitted for clarity

Fig.2 A fragment of the polymeric chain of complex **1**

dimensional infinite chain structure via monodentate bridging. The distance of adjacent two Tb ions is about 0.593 82(12) nm, which is shorter than the distances of the nearest adjacent chains with values of about 0.619 3 nm. Furthermore, the adjacent 1D chains are further linked via the weak hydrogen bonds between O atoms from coordinated water molecules (O1w) and tbc ligands (O1, O2) (O1w...O1 0.280 0(8) nm, O1w...O2 0.275 6(9) nm) (see Fig.3, Table 3), forming a larger infinite 1D chains. Then, these larger 1D chains are assembled by hydrogen bonds between N and O atoms from tbc ligands and coordinated water molecules (O3W...N3 0.284 6(12) nm) to give rise to 2D layer supramolecular structure. The adjacent 2D layers are connected by the hydrogen

Table 3 Hydrogen bonding parameters for **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠D-H...A / (°)
Complex <b>1</b>				
O1W-H1WA...O2 <sup>i</sup>	0.085	0.206	0.275 6(9)	138
O1W-H1WB...O1 <sup>ii</sup>	0.085	0.196	0.280 0(8)	170
O3W-H3WA...N6 <sup>iii</sup>	0.085	0.196	0.280 0(9)	170
O3W-H3WB...N3 <sup>iv</sup>	0.085	0.206	0.284 6(12)	154
Complex <b>2</b>				
O2W-H2WA...O4W <sup>v</sup>	0.084(2)	0.186(3)	0.269 3(4)	169(4)
O2W-H2WB...N9 <sup>vi</sup>	0.086(3)	0.205(3)	0.289 5(5)	168(5)
O3W-H3WA...N6 <sup>vii</sup>	0.082(3)	0.207(3)	0.288 9(5)	173(4)
O3W-H3WB...N3 <sup>viii</sup>	0.084(3)	0.200(3)	0.282 5(5)	169(4)
O4W-H4WA...O2 <sup>ix</sup>	0.084(3)	0.216(3)	0.299 2(4)	175(4)
O4W-H4WB...O3	0.085(3)	0.211(3)	0.294 0(4)	167(4)

Symmetry transformations used to generate equivalent atoms: complex **1**: <sup>i</sup> 1-x+1, -y, -z+1; <sup>ii</sup> -x+2, -y, -z+1; <sup>iii</sup> -x+2, -y, -z; <sup>iv</sup> -x+1, -y+1, -z+1. complex **2**: <sup>v</sup> x, y-1, z; <sup>vi</sup> -x+3/2, y-1/2, -z+1/2; <sup>vii</sup> x+1, y-1, z; <sup>viii</sup> -x, -y+1, -z; <sup>ix</sup> -x+1/2, y+1/2, -z+1/2.

bonds between N and O atoms from the ligands, coordinated water molecules (O3W...N6 0.280 0(9) nm) to afford 3D supramolecular network as shown in Fig.3. There are also intra-chain  $\pi$ - $\pi$  stacking interactions to afford 3D supramolecular network. It is found that there are three kinds of  $\pi$ - $\pi$  stacking interactions in complex **1** (see Fig.4): (1) between triazole ring and benzene ring with an average distances of 0.370 7(6) nm; (2) between two benzene rings with an average distances of 0.368 7(5) and 0.389 4(6) nm. (3) between two triazole groups with an average distances of 0.379 2(7) nm.

In the asymmetric unit of **2**, there is one

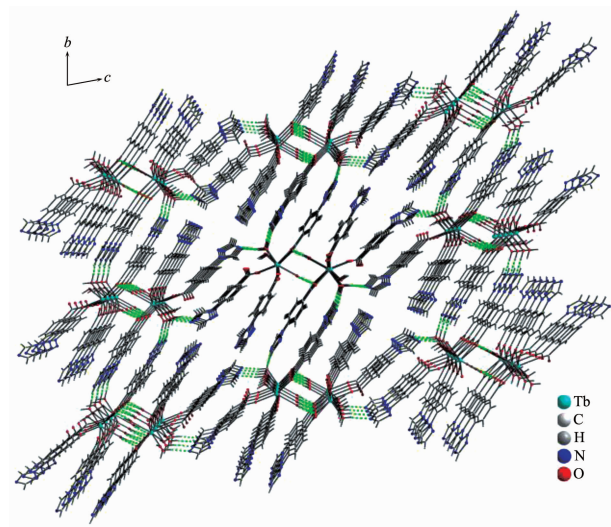
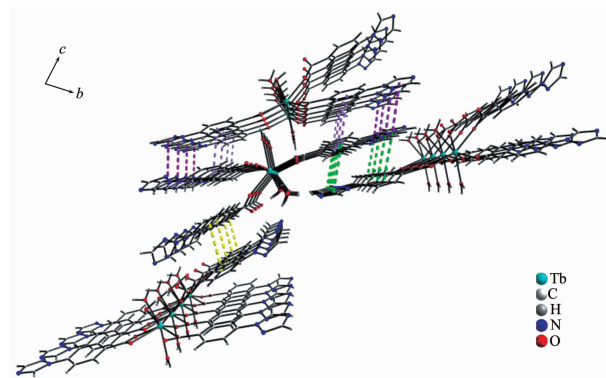


Fig.3 3D supramolecular network of **1** with hydrogen bonds (viewed along *a* axis)

crystallographically independent Nd(III) ion, three the ligands, three coordinated water molecules and one uncoordinated water molecule. The Nd(III) ion is coordinated by eight oxygen atoms from five different the ligands and three water molecules (see Fig.5). The Nd-O bond lengths found to vary from 0.235 7(3) to 0.254 1(3) nm are all in the normal range. The coordination environment of Nd is a distorted trigonal bipyramidal with angles varying from 65.45(13) to 146.76(13)°. Unlike the complex **1**, X-ray diffraction determination reveals that the ligands in complex **2** adopt two kinds of coordination modes: a monodentate terminal coordination mode (Scheme 1 (a)) and a bidentate bridging coordination mode (Scheme 1(c)).



Pink broken line: 0.379 2(7) nm; purple broken line: 0.368 7(5) nm; green broken line: 0.370 7(6) nm; yellow broken line: 0.389 4(6) nm

Fig.4  $\pi$ - $\pi$  stacking interaction between 1D chains in complex **1** in the *bc* plane (viewed along *a* axis)



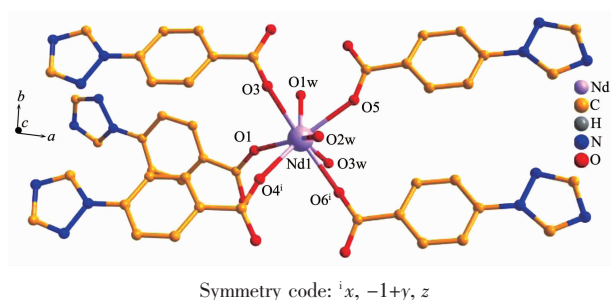


Fig.5 Coordination environment of Nd(III)

Every two adjacent Nd(III) ions are bridged by two carboxylate groups from two the ligands in a syn-anti bridging mode with a Nd...Nd distance of 0.559 49(4) nm. This leads to the construction of a 1D chain along the *b* axis (Fig.6). All the planes of the triazole rings at the symmetric site are parallel to each other. 1D chains are self-associated into layers by hydrogen bonding such as intermolecular O-H...O, O-H...N hydrogen bonds (Table 3). One uncoordinated water molecule in crystal lattice increases the number of hydrogen bonds in the structure. Similarly, the adjacent layers are connected by these abundant hydrogen bonds to afford 3D supramolecular network

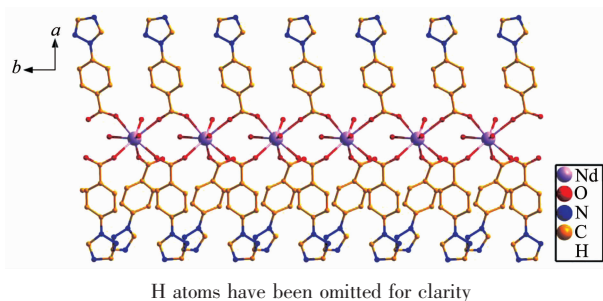
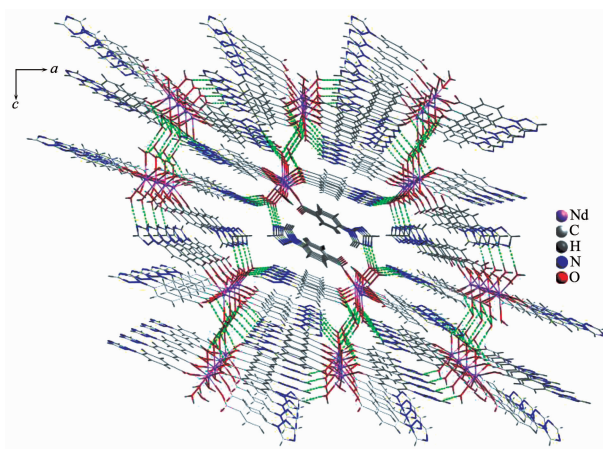
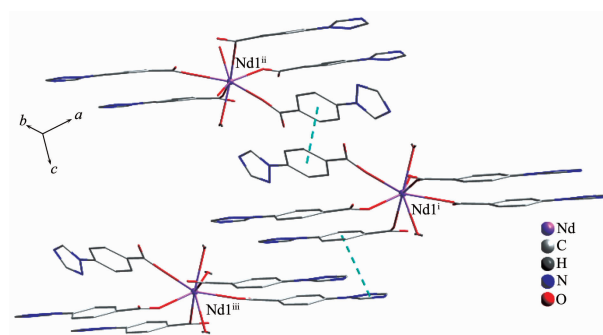


Fig.6 A fragment of the polymeric chain of complex 2

Fig.7 3D supramolecular network of **2** with hydrogen bonds (viewed along *b* axis)

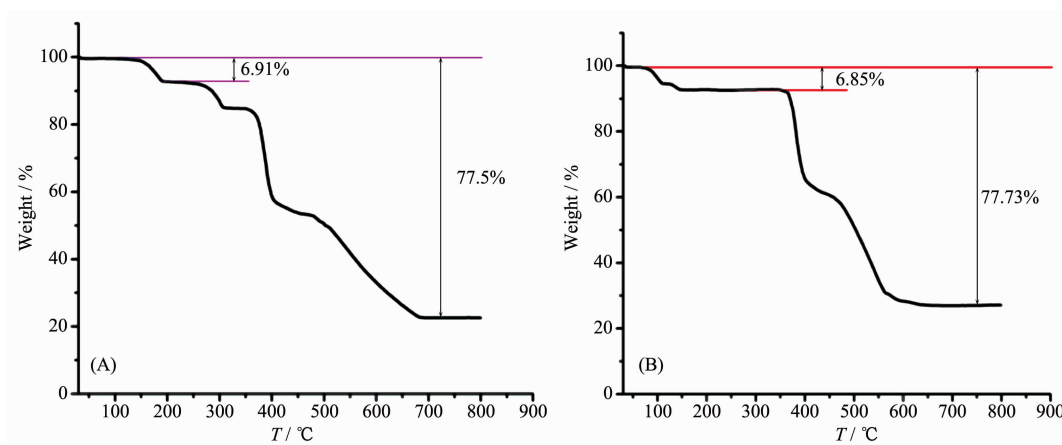
as shown in Fig.7. Moreover, considerable  $\pi$ - $\pi$  stacking interactions which lead to the construction of 3D network are also observed. It is found that there are two kinds of  $\pi$ - $\pi$  stacking interactions in complex **2** (see Fig.8): (1) between triazole ring and benzene ring with an average distances of 0.370 0(3) nm; (2) between two benzene rings with an average distances of 0.369 9(3) nm. All the above interactions come in concert in the formation of a supramolecular structure.

Symmetry code: <sup>i</sup> 0.5+x, 0.5-y, 0.5+z; <sup>ii</sup> 0.5-x, -0.5+y, 0.5-z;  
<sup>iii</sup> -0.5+x, 0.5-y, 0.5+zFig.8 Representation of  $\pi$ - $\pi$  stacking (turquoise broken line) in complex **2**

## 2.2 Thermogravimetric analyse for 1 and 2

To study the thermal stability of complexes **1** and **2**, thermogravimetric analysis (TGA) was performed under nitrogen atmosphere in flowing N<sub>2</sub> with rate of 10 °C·min<sup>-1</sup> in the temperature 30~800 °C. The TGA behavior of complex **1** was shown in Fig.9(A). For complex **1** the first weight loss (6.91%) in the range of 30 ~152 °C corresponds to the loss of three coordinated water molecules (Calcd. 6.95%). Stable framework of molecular formula has formed at the temperature range of 152~260°C with the weight of complex hardly loss. Further heating under increasing temperatures causes the destruction of the 1D-chain structures and the decomposition of the organic ligands. The final residual weight is 23.5% (Calcd. 23.54%) corresponding to Tb<sub>2</sub>O<sub>3</sub>.

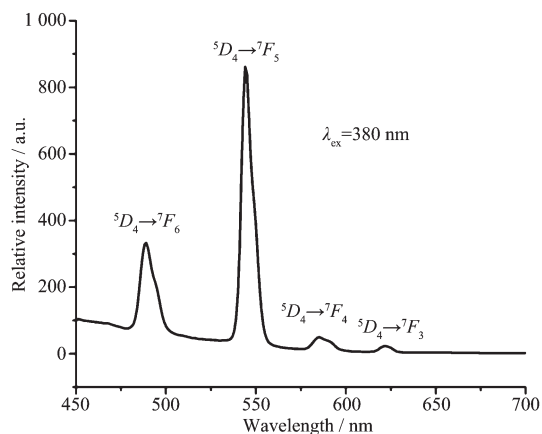
For complex **2**, the sample was dried in vacuum at 50 °C for 24 h before the test of TGA, so it is possible that the vacuum dry give rise to the loss of uncoordinated water. Moreover, it was observed that the transparent sample of complex **2** became opaque


 Fig.9 TGA curves of complex **1** (A) and **2** (B) under a nitrogen atmosphere

after vacuum dry. TGA behavior of complex **2** can further prove the loss of uncoordinated water. TGA studies (see Fig.9(B)) indicated that the first weight loss (6.85%) in the range of 30~160 °C is attributed to the loss of three molecules of coordinated water (Calcd. 6.92%). Further heating under increasing temperatures causes the destruction of the 1D-chain structures and the decomposition of the organic ligands. The final residual weight is 22.27% (Calcd. 21.61%) corresponding to Nd<sub>2</sub>O<sub>3</sub>.

### 2.3 Fluorescent property for **1**

In previous research, lanthanide carboxylate complexes exhibit the characteristic emission of lanthanide ions. The lanthanide(III), especially Eu(III), Tb(III) and Sm(III), can absorb ultraviolet radiation efficiently through an allowed electronic transition to convert excited state  $^5D_4$ , and these excited states are deactivated to the multiplet  $^7F_n$  states radiatively via emission of visible radiation named as luminescence.


 Fig.10 Solid-state emission spectrum for complex **1**

Under the excitation wavelength of 380 nm, the emission spectrum of the topic complex shows four emission peaks: 489, 544, 585, 622 nm, which are attributed to be the characteristic emission  $^5D_4 \rightarrow ^7F_J$  ( $J=6, 5, 4, 3$ ) transition of Tb<sup>3+</sup> ion. Among the  $^5D_4 \rightarrow ^7F_5$  transitions exhibited the strongest green emission, and  $^5D_4 \rightarrow ^7F_6$  transition shows the second strongest blue emission. The emission spectrum for complex **1** is shown in Fig.10.

### 3 Conclusion

In summary, two coordination polymers based on 4-(1*H*-1,2,3-triazol-1-yl) benzoic acid have been obtained under hydrothermal conditions. X-ray diffraction analysis reveals that the coordination modes of the carboxylate ligands and the different choice of the counter ions could promote different topological structures. Moreover, the complex **1** at solid state exhibit strong and characteristic emission of Tb(III) ions in the visible region at room temperature.

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