

New lanthanide coordination polymers of 1,2,4,5-benzenetetracarboxylic acid and 4,4'-bipyridine with 1D channels

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Abstract

Three new lanthanide coordination polymers with 1,2,4,5-benzenetetracarboxylic acid, $\text{Pr}_2(\text{betc})_2(4,4'\text{-bpyH}_2) \cdot 0.25\text{H}_2\text{O}$ (**1**), $\text{Ln}_2(\text{betc})_2(4,4'\text{-bpyH}_2)$ ($\text{Ln} = \text{Eu}$ (**2**), Gd (**3**)) were hydrothermally prepared. The crystallographic data of **1–3** show that they are isostructural, and possess 3D framework with 1D rhomboid channels, where the 4,4'-bipyridine molecules exist steadily via hydrogen bonds. Meanwhile, a supramolecular structure of $(4,4'\text{-bpyH}_2)_2(\text{betc})$ (**4**) was also obtained by hydrothermal reaction. The results of **1–4** indicate that 4,4'-bipyridine molecule acting as a template plays an important role in the formation of complexes **1–3**, and thus has a synergistic action in the construction of 3D framework with large channels.

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1. Introduction

The design and synthesis of new metal-organic frameworks with large pores are a continuing challenge for coordination polymers and attract much attention not only because of their intriguing frameworks, but also because of their potential applications as functional materials [1]. With the aim of investigating the coordination polymers with large channels and cavities, coordination polymers comprising of transition metal and lanthanide ions have been studied extensively. Based on the previous works reported in the literature, polycarboxylic acids have proved good organic connectors, and recently we devoted our interests to the syntheses of lanthanide coordination polymers with polycarboxylic acid [2]. Coordination polymers with 1,2,4,5-benzenetetracarboxylic acid (H_4betc) have been widely studied owing to their rich coordination modes coordinating to

metal ions through complete or partial deprotonation of their carboxyl groups [3]. However compared with the d-block transition metal coordination polymers, less lanthanide coordination polymers with H_4betc are reported due to the high coordination numbers of lanthanide ions as nodes in the construction of coordination polymers and thus the difficulties in controlling the structures of the products [4]. As is well known, it is important to prevent interpenetration when we want to generate stable structures with large and potentially useful channels. In this case, introduction of guest molecules into the host structure and then producing expected noninterpenetrating structure are an effective method [5]. Therefore, we selected 1,2,4,5-benzenetetracarboxylic acid as organic connector and 4,4'-bipyridine (4,4'-bpy) as template to synthesize lanthanide coordination polymers by hydrothermal reaction, three new lanthanide complexes $\text{Pr}_2(\text{betc})_2(4,4'\text{-bpyH}_2) \cdot 0.25\text{H}_2\text{O}$ (**1**), $\text{Ln}_2(\text{betc})_2(4,4'\text{-bpyH}_2)$ ($\text{Ln} = \text{Eu}$ (**2**), Gd (**3**)) with large channels were obtained, and a supramolecular compound $(4,4'\text{-bpyH}_2)_2(\text{betc})$ (**4**) was formed hydrothermally.

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2. Experimental

2.1. Materials

$\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving their oxides in hydrochloric acid, respectively, and then dried. 1,2,4,5-benzenetetracarboxylic acid and 4,4'-bipyridine were purchased from Aldrich and used without further purification. While all the other reagents were commercially available and used as received.

2.2. Instrumentation

Elemental analyses were performed on an Elementar Vario EL analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique.

The excitation light source was YAG-Nd laser which emits at 1.064 μm , and the excitation wavelength was 355 nm. The sample was placed in a Dewar and cooled with liquid nitrogen. The fluorescence was collected at right angles through a Spex 1403 monochromator with a photomultiplier tube, then averaged by Boxcar integrator and finally data were transferred to a computer.

2.3. X-ray crystallographic study

The single crystal X-ray data collections for compounds **1–4** were performed on a Bruker Smart 1000 CCD diffractometer, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least square on $|F|^2$ using the SHELXTL-97

program [6]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement.

2.4. Syntheses

2.4.1. $\text{Pr}_2(\text{betc})_2(4,4'\text{-bpyH}_2) \cdot 0.25\text{H}_2\text{O}$ (**1**)

The mixture of $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ (0.071 g, 0.2 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.038 g, 0.15 mmol), 4,4'-bipyridine (0.031 g, 0.2 mmol), H_2O (10 ml) and aqueous solution of NaOH (0.25 ml, 0.16 mmol) was sealed in a 23 ml stainless-steel reactor with Teflon liner and heated to 170 $^\circ\text{C}$ for 72 h, then slowly cooled to room temperature. The products were filtered, washed by ethanol and dried in air. Then light green transparent block crystals of **1** were easily obtained in 67.1% (47.5 mg) yield. Anal. Calcd for $\text{C}_{30}\text{H}_{15}\text{N}_2\text{O}_{17}\text{Pr}_2$: C, 37.64; H, 1.58; N, 2.93. Found: C, 37.89; H, 1.79; N, 2.60. IR data (KBr pellet, ν/cm^{-1}): 446(m), 517(m), 581(m), 799(s), 870(m), 1134(s), 1294(s), 1361(s), 1384(s), 1430(s), 1490(s), 1553 (s), 1630 (s), 3431(s).

2.4.2. $\text{Eu}_2(\text{betc})_2(4,4'\text{-bpyH}_2)$ (**2**)

Synthesis of **2** was similar to **1**. The products were filtered and washed by ethanol, then dried in air. Colorless block crystals of **2** were easily obtained in 53.8% (25.8 mg) yield. Anal. Calcd for $\text{C}_{30}\text{H}_{14}\text{Eu}_2\text{N}_2\text{O}_{16}$: C, 37.45; H, 1.47; N, 2.91. Found: C, 37.42; H, 1.37; N, 2.71. IR data (KBr pellet, ν/cm^{-1}): 443(m), 520(m), 581(m), 799(s), 870(m), 1133(s), 1294(s), 1359(s), 1386(s), 1434(s), 1491(s), 1557 (s), 1633 (s), 3428(s).

Table 1
Crystal data for **1–4**

Complexes	1	2	3	4
Empirical formula	$\text{C}_{30}\text{H}_{15}\text{N}_2\text{O}_{16.5}\text{Pr}_2$	$\text{C}_{30}\text{Eu}_2\text{H}_{14}\text{N}_2\text{O}_{16}$	$\text{C}_{30}\text{Gd}_2\text{H}_{14}\text{N}_2\text{O}_{16}$	$\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_8$
FW	957.26	962.35	972.93	566.52
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (\AA)	7.396(2)	7.283(3)	7.255(3)	7.568(8)
<i>b</i> (\AA)	10.066(3)	9.935(4)	9.910(4)	9.831(8)
<i>c</i> (\AA)	11.205(3)	11.082(5)	11.050(4)	10.266(9)
α (deg)	101.871(5)	102.576(6)	102.585(6)	63.954(11)
β (deg)	106.130(5)	105.764(7)	105.721(6)	71.700(12)
γ (deg)	109.589(4)	109.146(5)	109.010(6)	75.526(13)
<i>Z</i>	1	1	1	1
<i>V</i> (\AA^3)	712.7(4)	686.3(5)	680.9(5)	645.9(10)
ρ_{calcd} ($\text{g}\cdot\text{cm}^{-3}$)	2.230	2.329	2.373	1.457
Temp. (K)	293(2)	293(2)	293(2)	293(2)
μ , (mm^{-1})	3.472	4.621	4.922	0.108
Reflections collected total, independent	4118, 2886	3895, 2737	3930, 2749	3328, 2237
R_{int}	0.0272	0.0226	0.0299	0.0307
λ (Mo K α) (\AA)	0.71073	0.71073	0.71073	0.71073
R_1 , wR_2 [$I > 2\sigma(I)$]	0.0306, 0.0626	0.0245, 0.0599	0.0319, 0.0598	0.0625, 0.1729

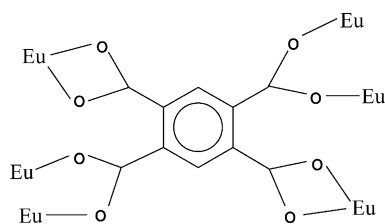
Table 2
Selected bond lengths (Å) and bond angles (deg) for **2**

Eu(1)–O(1)	2.625(3)	Eu(1)–O(5)#3	2.412(3)
Eu(1)–O(2)	2.462(3)	Eu(1)–O(6)	2.508(3)
Eu(1)–O(3)#1	2.394(3)	Eu(1)–O(7)#5	2.452(3)
Eu(1)–O(4)#4	2.416(3)	Eu(1)–O(7)#2	2.405(3)
Eu(1)–O(5)	2.566(3)		
O(1)–Eu(1)–O(2)	51.35(10)	O(3)#1–Eu(1)–O(6)	117.92(11)
O(1)–Eu(1)–O(3)#1	66.95(10)	O(3)#1–Eu(1)–O(7)#2	76.23(10)
		O(3)#1–Eu(1)–O(7)#5	75.43(10)
O(1)–Eu(1)–O(4)#4	137.57(11)	O(4)#4–Eu(1)–O(5)	72.77(9)
O(1)–Eu(1)–O(5)	93.64(9)	O(4)#4–Eu(1)–O(5)#3	69.67(10)
O(1)–Eu(1)–O(5)#3	68.15(10)	O(4)#4–Eu(1)–O(6)	73.61(11)
O(1)–Eu(1)–O(6)	128.48(10)	O(4)#4–Eu(1)–O(7)#2	75.36(10)
O(1)–Eu(1)–O(7)#2	88.99(10)	O(4)#4–Eu(1)–O(7)#5	72.31(10)
O(1)–Eu(1)–O(7)#5	141.78(9)	O(5)–Eu(1)–O(5)#3	65.51(12)
O(2)–Eu(1)–O(3)#1	76.70(10)	O(5)–Eu(1)–O(6)	51.23(9)
O(2)–Eu(1)–O(4)#4	140.82(10)		
O(2)–Eu(1)–O(5)	68.32(10)	O(5)–Eu(1)–O(7)#2	135.03(10)
O(2)–Eu(1)–O(5)#3	97.54(10)	O(5)–Eu(1)–O(7)#5	122.12(9)
O(2)–Eu(1)–O(6)	78.70(10)	O(5)#3–Eu(1)–O(6)	113.34(10)
O(2)–Eu(1)–O(7)#2	138.46(10)	O(5)#3–Eu(1)–O(7)#2	74.13(10)
O(2)–Eu(1)–O(7)#5	126.25(10)	O(5)#3–Eu(1)–O(7)#5	135.91(10)
O(3)#1–Eu(1)–O(4)#4	141.25(10)	O(6)–Eu(1)–O(7)#2	142.39(10)
O(3)#1–Eu(1)–O(5)	144.69(10)	O(6)–Eu(1)–O(7)#5	75.30(10)
O(3)#1–Eu(1)–O(6)	125.76(11)	O(7)#2–Eu(1)–O(7)#5	75.42(11)

Symmetry codes: #1 $-x+2, -y+1, -z+2$; #2 $x, y-1, z$; #3 $-x+1, -y+1, -z+1$; #4 $x, y, z-1$; #5 $-x+2, -y+2, -z+1$.

2.4.3. $Gd_2(betc)_2(4,4'-bpyH_2)$ (**3**)

Synthesis of **3** was similar to **1**. The products were filtered and washed by ethanol, then dried in air. Colorless transparent block crystals of **3** were obtained in 61.5% (59.8 mg) yield. Anal. Calcd for $C_{30}H_{14}Gd_2N_2O_{16}$: C, 36.97; H, 1.45; N, 2.90. Found: C, 36.51; H, 1.18; N, 3.18. IR data (KBr pallet, ν/cm^{-1}): 451(m), 521(m), 581(m), 799(s), 872(m), 1132(s), 1294(s), 1358(s), 1385(s), 1436(s), 1490(s), 1559 (s), 1636 (s), 3427(s).



(a) octadentate coordination mode

2.4.4. $(4,4'-bpyH_2)_2(betc)$ (**4**)

The mixture of $YbCl_3 \cdot 7H_2O$ (0.077 g, 0.2 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.051 g, 0.2 mmol), 4,4'-bipyridine (0.031 g, 0.2 mmol), H_2O (10 ml) and aqueous solution of NaOH (0.81 ml, 0.53 mmol) was sealed in a 23 ml stainless-steel reactor with Teflon liner and heated to 170 °C for 72 h, then slowly cooled to room temperature. The products were filtered, washed by ethanol and dried in air. Then colorless transparent block crystals of **4** were easily obtained in 37.4% (42.5 mg) yield. Anal. Calcd for $C_{30}H_{22}N_4O_8$: C, 63.60; H, 3.91; N, 9.89. Found: C, 64.05; H, 3.74; N, 10.07.

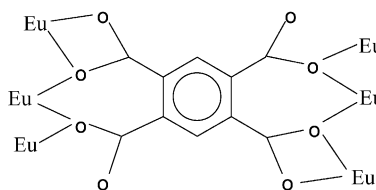
3. Results and discussion

3.1. Descriptions of structures of **1–4**

Crystal data for **1–4** are shown in Table 1. The crystallographic data of **1–3** show that they are isostructural, and herein only compounds **2** and **4** will be described in detail. The selected bond lengths (Å) and bond angles (deg) of **2** are listed in Table 2. In **2**, carboxyl groups of 1,2,4,5-benzenetetracarboxylic acid are all deprotonated and two types of coordination modes, the octadentate and the decadentate, are presented in Scheme 1.

In an asymmetrical unit of **1**, Eu^{3+} ion displays one type of coordination environment (Fig. 1). From Fig. 1, Eu^{3+} ion is coordinated by nine carboxyl oxygen atoms consisting of four oxygen atoms (O1, O2, O3A, O4B) from three octadentate $betc^{4-}$ ligands and five oxygen atoms (O5A, O7B, O7C, O5, O6) from three decadentate $betc^{4-}$ ligands. The average distance of $Eu-O(\text{carboxyl})$ is 2.471 Å.

Viewed along a axis, $betc^{4-}$ ligands connect Eu^{3+} ions into (4, 4) nets parallel to bc plane, which are further linked by $betc^{4-}$ ligands along a axis through coordination bonds producing a 3D architecture with 1D rhomboid channels (Fig. 2). In the 3D framework, Eu^{3+} ions locate at the vertexes of the rhombus; while two octadentate $betc^{4-}$ ligands parallel to ac plane act as a pair of sides of the rhombus and the other two sides of the rhombus are formed by decadentate $betc^{4-}$ ligands, generating rhomboid channels with the dimensions of approximately 12.253×9.729 Å. In the 1D channels, 4,4'-bipyridine molecules



(b) decadentate coordination mode

Scheme 1. The coordination modes of 1,2,4,5-benzenetetracarboxylate ligand in **2**.

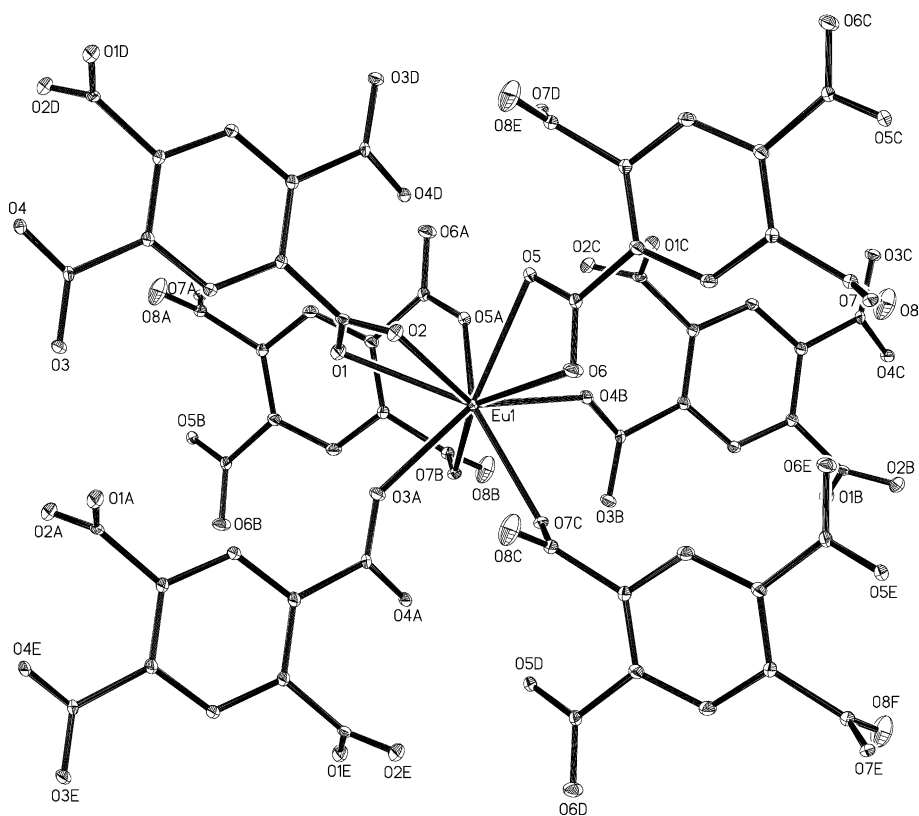


Fig. 1. The coordination environment of Eu^{3+} in **2**.

occupy the cavities through hydrogen bonds between hydrogen atoms of protonated 4,4'-bipyridine molecules and coordinated carboxyl oxygen atoms of betc^{4-} ligands ($\text{N}\cdots\text{O}$: 2.670 Å, $\text{N-H}\cdots\text{O}$: 166.49°). The two pyridyl rings of each 4,4'-bipyridine molecule lie in the same plane,

and all the 4,4'-bpy molecules in the channels are parallel to each other, shown as in Fig. 3.

We also wanted to obtain Yb^{3+} analogue of the title coordination polymers with H_4betc and 4,4'-bipyridine ligands under similar reaction conditions. But we failed to

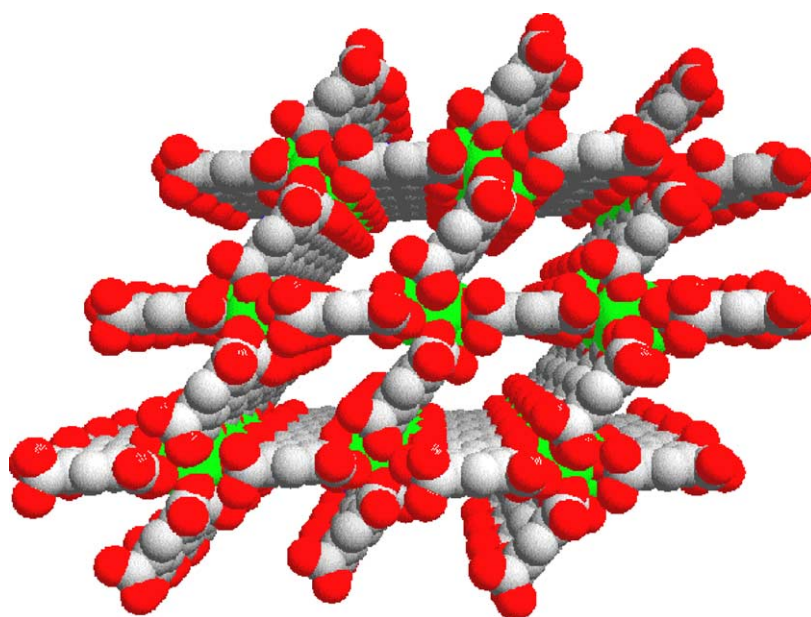


Fig. 2. The space filling diagram of **2** with 1D large channel along *a* axis.

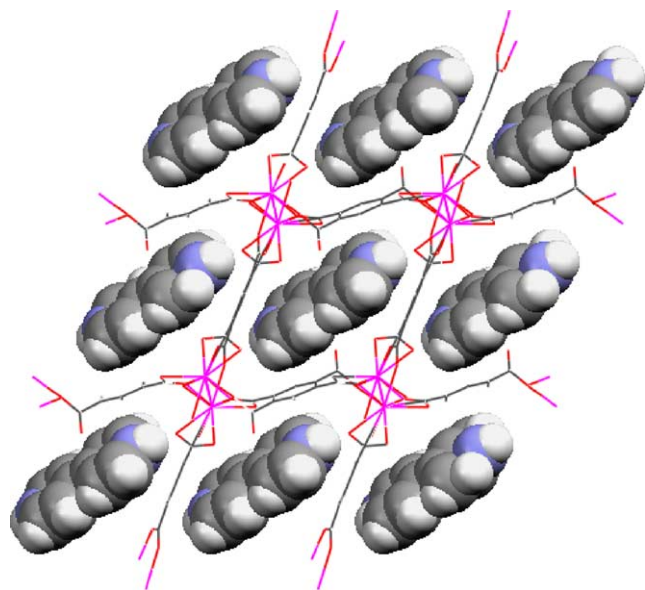


Fig. 3. The 3D structure of **3** with the 4,4'-bpy molecules in the 1D rhomboid channels.

obtain them. While a supramolecular compound composed of betc^{4-} and 4,4'-bpy molecules with a formula $(4,4'\text{-bpyH}_2)_2(\text{betc})$ (**4**) was obtained. The selected bond lengths (Å) and bond angles (deg) of **4** are listed in Table 3. In **4**, the carboxyl groups of H_4betc are all deprotonated, while the nitrogen atoms of 4,4'-bpy molecules are protonated, then 1D ladder-like chains of **4** are generated through strong $\text{N-H}\cdots\text{O}$ and weak $\text{C10B-H10B}\cdots\text{O2AB}$ hydrogen bonds between betc^{4-} and 4,4'-bpy H_2^+ (see Fig. 4). The hydrogen bonds of **4** are listed in Table 4, which is similar to those of $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3 \cdot 1.5(4,4'\text{-bpy})$ [7] and $[(\text{C}_{10}\text{H}_9\text{N}_2)^+]_2 \cdot [(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}]$ [8]. In the ladder-like structure of Fig. 4, the betc^{4-} molecules act as the rungs and the adjacent 4,4'-bpy molecules are all parallel to each other with the shortest distance of 3.617 Å. Similarly, the 4,4'-bpy molecules from two adjacent 1D chains are also parallel to each other viewed along a axis, with the shortest distance of 3.5 Å, which lead to 2D supramolecular structure. At the same time, these 2D structures are assembled through the $\text{C2E-H2AE}\cdots\text{O4AC}$ hydrogen bonds (see Table 4) between oxygen atoms of betc^{4-} and hydrogen atoms of protonated 4,4'-bpy into a 3D supramolecular structure. From the structure of **4**, it has been seen that the formation of $[(4,4'\text{-bpyH}_2)_2(\text{betc})]$ (**4**) is attributed to the high symmetry of betc^{4-} molecules and the linear configuration of 4,4'-bpy molecule. And the hydrogen bonds and π - π interactions lead to the 3D supramolecular structure. Comparing **4** with the reported supramolecular structures forming by H_4betc and 4,4'-bpy [8,9], we can see that H_4betc in compound **4** are all deprotonated, while the other three are partly deprotonated. Thus there are no hydrogen bonds among H_4betc molecules in compound **4**, which is completely different from $[4,4'\text{-bpyH}_2][\text{H}_3\text{betc}]_2$ [9]. On the otherhand, nitrogen atoms of each 4,4'-bpy molecule in compound **4**

Table 3
Selected bond lengths (Å) and bond angles (deg) for **4**

N(1)–C(5)	1.331(6)	C(9)–C(10)	1.372(7)
N(1)–C(1)	1.335(6)	C(11)–C(12)	1.402(6)
N(1)–H(1)	0.8600	C(11)–C(13)#1	1.405(6)
N(2)–C(6)	1.340(6)	C(11)–H(11)	0.9300
C(1)–C(2)	1.378(7)	C(12)–C(13)	1.403(6)
C(1)–H(1A)	0.9300	C(12)–C(14)	1.501(6)
C(2)–C(3)	1.393(6)	C(13)–C(11)#1	1.405(6)
C(3)–C(4)	1.392(6)	C(13)–C(15)	1.519(6)
C(3)–C(8)	1.493(6)	C(14)–O(2)	1.219(5)
C(4)–C(5)	1.368(6)	C(14)–O(1)	1.314(5)
C(6)–C(7)	1.375(6)	C(15)–O(4)	1.226(5)
C(7)–C(8)	1.398(6)	C(15)–O(3)	1.285(5)
C(8)–C(9)	1.403(6)		
C(5)–N(1)–C(1)	119.8(4)	N(1)–C(5)–C(4)	120.9(4)
C(5)–N(1)–H(1)	120.1	N(2)–C(6)–C(7)	122.4(4)
C(1)–N(1)–H(1)	120.1	C(6)–C(7)–C(8)	120.3(4)
C(10)–N(2)–C(6)	118.2(4)	C(7)–C(8)–C(9)	116.3(4)
C(10)–N(2)–H(2)	120.9	C(7)–C(8)–C(3)	122.5(4)
C(6)–N(2)–H(2)	120.9	C(9)–C(8)–C(3)	121.2(4)
N(1)–C(1)–C(2)	122.0(4)	C(10)–C(9)–C(8)	120.0(4)
C(1)–C(2)–C(3)	119.4(4)	N(2)–C(10)–C(9)	122.7(5)
C(4)–C(3)–C(2)	116.8(4)	C(12)–C(11)–C(13)#1	120.0(4)
C(4)–C(3)–C(8)	121.7(4)	C(11)–C(12)–C(13)	120.3(4)
C(2)–C(3)–C(8)	121.5(4)	C(11)–C(12)–C(14)	118.9(4)
C(5)–C(4)–C(3)	121.1(4)	C(13)–C(12)–C(14)	120.7(4)
C(12)–C(13)–C(11)#1	119.8(4)	O(1)–C(14)–C(12)	115.4(4)
C(12)–C(13)–C(15)	121.3(4)	O(4)–C(15)–O(3)	125.5(4)
C(11)#1–C(13)–C(15)	118.9(4)	O(4)–C(15)–C(13)	121.2(4)
O(2)–C(14)–O(1)	124.6(4)	O(3)–C(15)–C(13)	113.4(4)
O(2)–C(14)–C(12)	120.0(4)		

Symmetry codes: #1 $-x, -y, -z+1$.

are all protonated, but in the supramolecular structure of $[(\text{C}_{10}\text{H}_9\text{N}_2)^+]_2 \cdot [(\text{C}_{10}\text{H}_4\text{O}_8)^{2-}]$, they are partly protonated, and thus form hydrogen bonds with partly deprotonated $\text{H}_2\text{betc}^{2-}$ ions.

From the crystallographic data of **1–3**, the average bond lengths of Pr–O, Eu–O and Gd–O are 2.530, 2.471 and 2.458 Å, respectively, and the separations of Pr \cdots Pr, Eu \cdots Eu and Gd \cdots Gd are 3.945, 3.842 and 3.821 Å, respectively. The results show the effect of lanthanide contraction on the structures of **1–3**. Moreover, in the rhomboid channels of **2** and **3**, only 4,4'-bipyridine molecules are held. While besides 4,4'-bipyridine molecules, water molecules are also held in the rhomboid channels of **1**, which results from the larger ionic radius of Pr $^{3+}$ than that of Eu $^{3+}$ and Gd $^{3+}$ ions. That is to say, the dimensions of rhomboid channels of **1–3** decrease with the decreasing of ionic radii from Pr $^{3+}$, Eu $^{3+}$ to Gd $^{3+}$ ions (12.294×10.184 Å for **1**, 12.253×9.729 Å for **2**, and 12.219×9.709 Å for **3**). It seems that the dimensions of 4,4'-bipyridine molecule in the 1D channels are a perfect

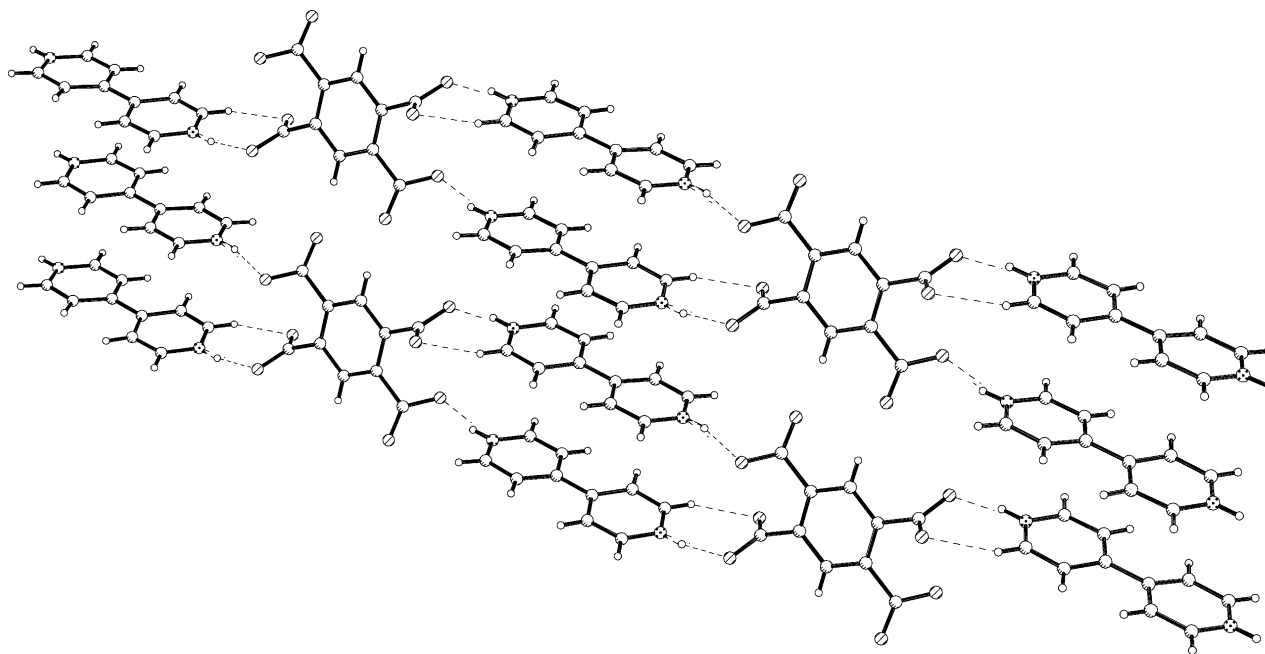


Fig. 4. The 2D supramolecular structure of **4** formed by hydrogen bonds between betc⁴⁻ and 4,4'-bpy molecules and π - π interactions of 4,4'-bpy molecules.

Table 4

Hydrogen bonding geometry (Å and deg) for **4**

D-H	d(D-H)	d(H \cdots A)	\angle (DHA)	d(D \cdots A)	A
N1-H1	0.860	1.712	164.31	2.551	O3 [-x, -y+1, -z]
N2-H2	0.860	1.769	168.34	2.617	O1 [x, y, z+1]
C10D-H10D	0.930	2.463	129.2	3.135	O2AC [x, y, z]
C2E-H2AE	0.930	2.417	160.3	3.308	O4AC [x, y, z]

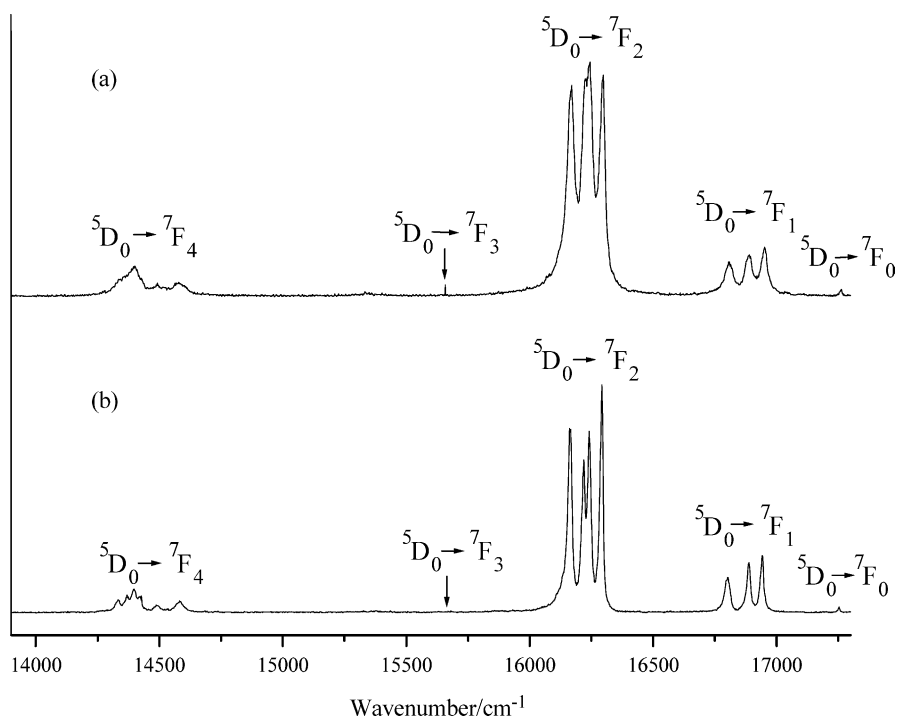


Fig. 5. Emission spectra of **2** corresponding to $^5D_0 \rightarrow ^7F_J$ ($J=0\sim 4$) transitions at 298 K (a) and 77 K (b), $\lambda_{exc}=355$ nm.

match for the dimensions of the rhomboid channels. Therefore, we can see that the dimensions of the channels are closely related to the ionic radii of Ln^{3+} ions, and thus we did not obtain the ytterbium coordination polymer with rhomboid channels under similar reaction conditions due to the smaller ionic radius of Yb^{3+} ion. So we conclude that 4,4'-bipyridine molecule as a template takes a synergistic action for the formation of lanthanide coordination polymers with H_4betc and 4,4'-bpy and contributes to the stability of 3D framework structure with channels.

3.2. Photophysical properties of **2**

The complex **2** emits intensively red fluorescence when it is irradiated by UV light. Fig. 5 shows its high-resolution emission spectrum corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0-4$) transitions in the range of 13,900–17,300 cm^{-1} excited with 355 nm at 298 and 77 K. The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is the induced electronic dipole transition which is greatly affected by the coordination environment, while the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is the magnetic dipole transition which is much less sensitive to the environment. The intensity ratio of $^5\text{D}_0 \rightarrow ^7\text{F}_2 / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ is 5.74, which displays that the Eu^{3+} ions are not in an inversion center. From Fig. 5, the emission peaks are overlapped in the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, and the only one peak of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition, as well as the three peaks in $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition indicate that the europium ions in **2** are located at the same chemical environment [10]. This is in good agreement with the result of single-crystal X-ray diffraction. It can be concluded that there is one type of Pr^{3+} , Eu^{3+} , and Gd^{3+} ion site in the complexes **1**, **2** and **3**, respectively. Comparing the emission spectra of **2** at 77 K with that at 298 K, the low temperature emission spectrum of **2** shows the expected bathchromic shift and line-narrowing.

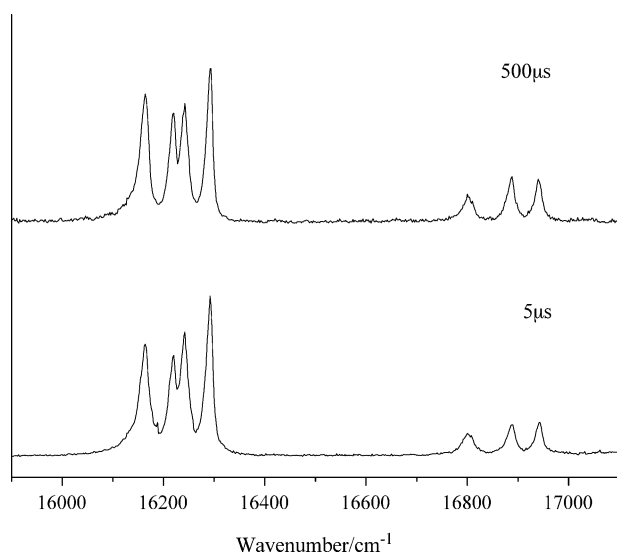


Fig. 6. The time-resolved spectra of **2** in the range of 17,100–15,900 cm^{-1} at 77 K, $\lambda_{\text{exc}} = 355$ nm.

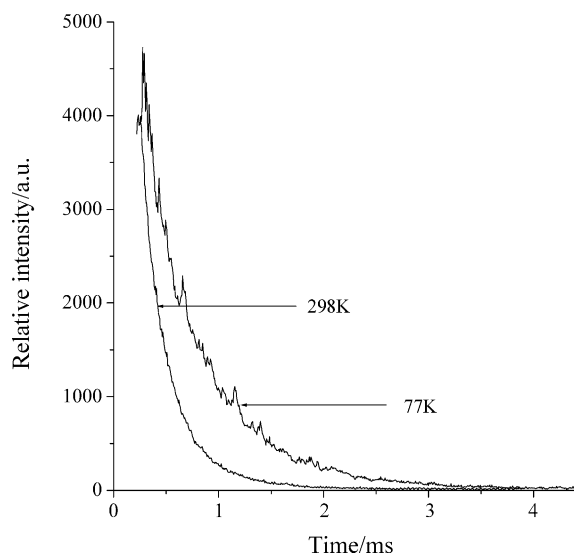


Fig. 7. The decay curves of **2** at 77 and 298 K, analyzing wave number: 16,292 cm^{-1} at 77 K, 16,241 cm^{-1} at 298 K.

The time-resolved spectra of the complex **2** in the range of 17,100–15,900 cm^{-1} (corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$) at 77 K were recorded and are shown in Fig. 6. From Fig. 6, it can be seen that no significant change in the relative intensities, positions and shapes of the emission peaks takes place as the delay time varies, displaying a single $\text{Eu}(\text{III})$ ion site in **2**. The decay curve of **2** (Fig. 7) shows that the luminescence lifetimes of **2** are 565 μs at 77 K and 308 μs at 298 K, which shows that the lower-temperature lifetime is longer than the higher one due to the thermal deactivation at higher temperature.

4. Conclusions

Three new lanthanide coordination polymers (lanthanides: **Pr(1)**, **Eu(2)** and **Gd(3)**) with 1,2,4,5-benzenetetracarboxylic acid and 4,4'-bipyridine were successfully synthesized under hydrothermal conditions, and they are isostructural and display 3D structures with 1D rhomboid channels where 4,4'-bipyridine molecules are encapsulated. However, no ytterbium analogue was obtained and only a supramolecular compound $(4,4'\text{-bpyH}_2)_2(\text{betc})$ was formed under similar reaction conditions. This indicates that 4,4'-bipyridine molecule acting as a template plays a crucial role in the formation of complexes **1–3**, and also shows that due to lanthanide contraction, the radius of Yb^{3+} ion is smaller than that of Pr^{3+} , Eu^{3+} and Gd^{3+} ions, and consequently ytterbium coordination polymer with proper dimensions of channels to accommodate 4,4'-bipyridine molecules can not be obtained via similar reaction conditions.

5. Supplementary material

CCDC Nos. 244702–244705 contain the supplementary crystallographic data for this paper. These data can be

obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

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