

由 5-磺基水杨酸组装的镧系金属有机骨架配合物的合成及结构

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摘要: 在水热条件下, 合成了 6 个新的镧系金属配位聚合物, $\text{Ln}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$ ($\text{Ln}=\text{Er}(\text{III})$ (**1**), $\text{Yb}(\text{III})$ (**2**)), $[\text{La}_2(\text{SSA})_2(\text{phen})_2(\text{H}_2\text{O})_4 \cdot (\text{phen}) \cdot (\text{H}_2\text{O})_{1.33}]_n$ (**3**) 和 $[\text{Ln}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})]_n$ ($\text{Ln}=\text{Nd}(\text{III})$ (**4**), $\text{Sm}(\text{III})$ (**5**), $\text{Eu}(\text{III})$ (**6**)), $\text{SSA}=5$ -磺基水杨酸, $\text{phen}=\text{邻二氮杂菲}$, $\text{bpdo}=4,4'$ -联吡啶氮氧化物, 并测定了它们的结构。化合物 **1** 和 **2** 都具有蝶状双核中心, 这个双核中心进一步通过氢键和 $\pi-\pi$ 相互作用形成三维骨架。化合物 **3** 在 a 方向形成一维梯状链, 而氢键和 $\pi-\pi$ 堆积作用在这一结构的形成中起着重要作用。化合物 **4~6** 由相互穿插的单螺旋链形成三维骨架结构。此外, 对这 6 个化合物进行了热稳定性和荧光性质的研究。固态化合物 **3** 受激发下, 发射较强的蓝色荧光。

关键词: 镧系元素; 5-磺基水杨酸; 邻二氮杂菲; 4,4'-联吡啶氮氧化物; 荧光性质; 金属有机骨架

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Syntheses and Structures of Lanthanide Metal-organic Frameworks Mainly Assembled by 5-Sulfosalicylic Acid

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Abstract: Six new lanthanide metal coordination polymers, $\text{Ln}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$ ($\text{Ln}=\text{Er}(\text{III})$ (**1**) and $\text{Yb}(\text{III})$ (**2**)), $[\text{La}_2(\text{SSA})_2(\text{phen})_2(\text{H}_2\text{O})_4 \cdot (\text{phen}) \cdot (\text{H}_2\text{O})_{1.33}]_n$ (**3**) and $[\text{Ln}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})]_n$ ($\text{Ln}=\text{Nd}(\text{III})$ (**4**), $\text{Sm}(\text{III})$ (**5**), $\text{Eu}(\text{III})$ (**6**)), $\text{SSA}=5$ -sulfosalicylic acid, $\text{phen}=\text{phenanthroline}$ and $\text{bpdo}=4,4'$ -bipyridine- N,N' -dioxide, were synthesized under hydrothermal conditions and structurally characterized. Compounds **1** and **2** are isostructural with the butterfly-like binuclear cores, which are further connected by hydrogen bonds and $\pi-\pi$ interactions to generate a 3D coordination network. Compound **3** exhibits a 1D infinite ladder-like chain along a -axis, where the hydrogen bonds and $\pi-\pi$ stacking interaction play important roles in the formation of the coordination network. Compounds **4~6** possess 3D frameworks with interweaving single-helical chains. In addition, the thermal stabilities and fluorescent properties of the six compounds are studied as well. Compound **3** displays intense blue emission in solid state when excited. CCDC: 612600, **1**; 612602, **2**; 612601, **3**; 653354, **4**; 653355, **5**; 653356, **6**.

Key words: lanthanide; 5-sulfosalicylic acid; phenanthroline; 4,4'-bipyridine- N,N' -dioxide; fluorescent property;
metal-organic framework

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0 Introduction

Recently, much effort has been dedicated into the area of inorganic-organic hybrid compounds^[1] not only because of their fascinating structural diversities, but also because of their versatile potential applications as functional materials, such as magnetism, catalysis, and porous materials^[2,3]. Now, it's known that the weak intermolecular interactions in these compounds, for example hydrogen bonds and π - π stacking, play vital roles in the formation and stabilization of the coordination architectures^[4].

5-Sulfosalicylic acid (SSA, Scheme 1) is a simple but interesting compound, as it possesses three potential coordinating groups that exhibit various coordinating models in different complexes^[5]. Additionally, SSA and its derivatives have been found to have great fluorescent potential not only in solution but also in solid state. Some of the functional derivatives from SSA have been reported recently^[6]. However, lanthanide metal coordination polymers containing SSA are much less studied up to date^[7]. Owing to their high coordination numbers, special fluorescent and magnetic properties, lanthanide metal coordination complexes have attracted considerable attentions^[8]. It is interesting to assemble on purpose certain lanthanide metal coordination polymers with new architectures and feasible fluorescent properties. Up to now, several this kind of coordination polymers have been reported, which feature 2D layers. These layers are further interlinked via hydrogen bonds resulting in 3D architecture^[9]. In addition to SSA, phenanthroline (phen) and 4,4'-bipyridine-*N,N'*-dioxide (bpdo) (Scheme 1) are also proper ligands for lanthanide ions and able to

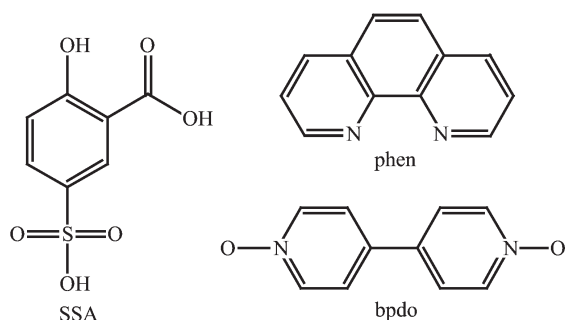
construct coordination networks via various interactions^[10]. Therefore, we selectively choose phen and bpdo as secondary ligands, while SSA as the primary one, to construct lanthanide metal coordination compounds. In this paper, we report the syntheses, structural characterization and photoluminescent properties of six new compounds $\text{Ln}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$ ($\text{Ln}=\text{Er}(\text{III})$ (**1**) and $\text{Yb}(\text{III})$ (**2**)), $[\text{La}_2(\text{SSA})_2(\text{phen})_2(\text{H}_2\text{O})_4 \cdot (\text{phen}) \cdot (\text{H}_2\text{O})_{1.33}]_n$ (**3**) and $[\text{Ln}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})]_n$ ($\text{Ln}=\text{Nd}(\text{III})$ (**4**), $\text{Sm}(\text{III})$ (**5**), $\text{Eu}(\text{III})$ (**6**)).

1 Experimental section

The reagents and solvents were commercially available and used as received without further purification. C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The IR spectra were recorded by KBr disc method on a Bruker Vector 22 spectrophotometer in 4 000 ~400 cm^{-1} region. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer. Thermogravimetric analyses were performed on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$ between ambient temperature and 800 $^\circ\text{C}$. Powder X-ray diffraction patterns were recorded on a RigakuD/max-RA rotating anode X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation ($\lambda=0.1542 \text{ nm}$) at room temperature.

1.1 Synthesis of $\text{Ln}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$ ($\text{Ln}=\text{Er}(\text{III})$ (**1**) and $\text{Yb}(\text{III})$ (**2**))

A mixture of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln}=\text{Er}(\text{III})$ or $\text{Yb}(\text{III})$, 0.25 mmol), SSA (0.054 0 g, 0.25 mmol), NaOH (0.010 0 g, 0.25 mmol) and H_2O (3.0 mL) was heated at 120 $^\circ\text{C}$ for 3 days. Then, ligand phen (0.046 0 g, 0.25 mmol) was added to the resulting solution and heated at 120 $^\circ\text{C}$ for 36 h. After the reactant mixture was slowly cooled down to room temperature, the crystals were obtained. Yield: 40% (based on Er) for **1**; 30% (based on Yb) for **2**. Anal. Calcd for $\text{Er}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$ (%): C 48.94, H 2.78, N 7.36. Found (%): C 48.99, H 2.69, N 7.41. Anal. Calcd for $\text{Yb}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$ (%): C 48.57, H 2.76, N 7.31. Found: C 48.65, H 2.64, N 7.28.



Scheme 1

1.2 Synthesis of $[\text{La}_2(\text{SSA})_2(\text{phen})_2(\text{H}_2\text{O})_4 \cdot (\text{phen}) \cdot (\text{H}_2\text{O})_{1.33}]_n$ (**3**)

The synthesis was similar to that described for **1** except using $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ (0.094 0 g, 0.25 mmol) instead of $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$. Colorless crystals of **3** were obtained (yield: 48% based on La). Anal. Calcd for $\text{La}_2(\text{SSA})_2(\text{phen})_2(\text{H}_2\text{O})_4 \cdot (\text{phen}) \cdot (\text{H}_2\text{O})_{1.33}$ (%), **3**: C 44.66, H 3.05, N 6.25. Found (%): C 44.71, H 2.94, N 6.27.

1.3 Synthesis of $[\text{Ln}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})]_n$ ($\text{Ln}=\text{Nd(III)}$ (**4**), Sm(III) (**5**), Eu(III) (**6**))

The compounds were synthesized by the same method, as follows: A mixture of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln}=\text{Nd(III)}$, Sm(III) and Eu(III) , 0.25 mmol), SSA (0.054 0 g, 0.25 mmol), NaOH (0.010 0 g, 0.25 mmol), bpdo (47.0 mg, 0.25 mmol) and H_2O (5.0 mL) was heated at 160 °C for 3 days. After the reactant mixture was slowly cooled down to room temperature, the crystals were obtained. Yield: 55% (based on Nd) for **4**; 65% (based on Sm) for **5** and 40% (based on Eu) for **6**. Anal. Calcd for $\text{Nd}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})$ (%), **4**: C 29.44, H 2.26, N 2.86. Found (%): C 29.57, H 2.75, N 2.93. Anal. Calcd for $\text{Sm}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})$ (%), **5**: C 29.08, H 2.24,

N 2.83. Found (%): C 29.15, H 2.11, N 2.94. Anal. Calcd for $\text{Eu}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})$ (%), **6**: C 28.99, H 2.23, N 2.82. Found (%): C 29.05, H 2.12, N 2.93.

1.4 Crystal structure determination

Intensity data for the six compounds were collected at 293(2) K on a Siemens SMART-CCD diffractometer with graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively. The structures were solved by direct methods using SHELXS-97 and were refined by full matrix least-squares methods using SHELXL-97. Anisotropic displacement parameters were refined for all non-hydrogen atoms except for the disordered ones. The hydrogen atoms except for those of water molecules were generated geometrically and refined using a riding model. Crystallographic data and other pertinent information for **1**~**6** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. Hydrogen bonds of compound **2** and **3** are listed in Table 3.

CCDC: 612600, **1**; 612602, **2**; 612601, **3**; 653354, **4**; 653355, **5**; 653356, **6**.

Table 1 Crystal data and structure refinement information for compounds **1**~**6**

Compound	1	2	3	4	5	6
Empirical formula	$\text{Er}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$	$\text{Yb}_2(\text{SSA})_2(\text{phen})_4(\text{H}_2\text{O})_2$	$\text{La}_2(\text{SSA})_2(\text{phen})_2(\text{H}_2\text{O})_4 \cdot (\text{phen}) \cdot (\text{H}_2\text{O})_{1.33}$	$\text{Nd}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})$	$\text{Sm}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})$	$\text{Eu}(\text{SSA})(\text{bpdo})_{0.5}(\text{H}_2\text{O}) \cdot (\text{H}_2\text{O})$
Formula weight	1 521.68	1 533.24	1 344.77	489.52	495.63	497.24
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / nm	1.456 7(4)	1.455 0(3)	0.999 9(2)	0.929 8(2)	0.928 4(2)	0.926 8(2)
b / nm	1.320 8(3)	1.316 5(3)	2.433 4(5)	0.760 4(1)	0.757 2(2)	0.756 2(2)
c / nm	1.521 8(4)	1.520 1(4)	2.008 7(4)	2.011 5(3)	2.012 4(4)	2.010 3(5)
$\beta / (^\circ)$	92.00(1)	91.87(1)	102.26(1)	101.336(4)	101.043(4)	101.067(4)
V / nm^3	2.926 2(13)	2.910 2(12)	4.776 0(17)	1.394 5(4)	1.388 6(5)	1.382 7(6)
Z	2	2	4	4	4	4
μ / mm^{-1}	2.995	3.341	1.938	3.927	4.433	4.741
Reflections collected	15 144	15 319	25 498	7 314	7 132	7 146
Unique reflections	5 692	5 719	9 350	2 742	2 723	2 701
Obs. reflections [$I > 2\sigma(I)$]	4 933	4 578	6 966	2 136	2 352	2 313
R_{int}	0.089	0.046	0.054	0.072	0.057	0.045
R_1 [$I > 2\sigma(I)$]	0.035 8	0.030 5	0.041 1	0.053 0	0.029 5	0.039 7
wR_2 [$I > 2\sigma(I)$]	0.089 6	0.053 6	0.068 1	0.094 0	0.064 8	0.078 8
Goodness-of-fit	1.01	0.90	0.97	1.05	0.93	1.08

Table 2 Selected bond lengths (nm) and bond angles (°) for compounds **1**, **3** and **4**^a

Compound 1					
Er1-O1	0.234 0(3)	Er1-N3	0.255 0(4)	Er1-O7	0.233 1(3)
Er1-N4	0.246 9(4)	Er1-N1	0.252 8(3)	Er1-O2 ^{#1}	0.229 8(3)
Er1-N2	0.250 0(4)	Er1-O3 ^{#1}	0.218 7(3)		
O1-Er1-O7	74.4(1)	O7-Er1-N4	73.6(1)	O1-Er1-N1	76.4(1)
O2 ^{#1} -Er1-O7	80.5(1)	O1-Er1-N2	133.9(1)	N1-Er1-N2	65.0(1)
O1-Er1-N3	72.8(1)	N1-Er1-N3	76.5 (1)	O1-Er1-N4	117.2(1)
N1-Er1-N4	130.8(1)				
Compound 3					
La1-O2	0.247 4(3)	La2-O1	0.259 6(3)	La1-O3	0.240 0(3)
La2-O2	0.262 4(3)	La1-O7	0.271 2(3)	La2-O8	0.248 2(3)
La1-O8	0.261 8(3)	La2-O9	0.237 0(3)	La1-O13	0.252 0(3)
La2-O15	0.256 9(3)	La1-O14	0.269 4(3)	La2-O16	0.256 6(3)
La1-N3	0.272 3(4)	La2-N1	0.272 0(4)	La1-N4	0.270 9(4)
La2-N2	0.272 8(4)	La1-O4 ^{#1}	0.245 4(3)	La2-O12 ^{#1}	0.247 1(3)
O2-La1-O3	68.6(1)	O1-La2-O2	49.4(1)	O2-La1-O7	109.9(1)
O1-La2-O8	107.8(1)	O2-La1-O8	63.1(1)	O1-La2-O9	146.4(1)
O2-La1-O13	82.0(1)	O1-La2-O15	72.5(1)	O2-La1-O14	119.6(1)
O1-La2-O16	129.3(1)	O2-La1-N3	74.2(1)	O1-La2-N1	69.5(1)
O2-La1-N4	126.0(1)	O1-La2-N2	115.5(1)		
Compound 4					
Nd1-O4	0.251 6(6)	Nd1-O2 ^{#1}	0.243 5(5)	Nd1-O7	0.261 0(5)
Nd1-O6 ^{#2}	0.249 9(5)	Nd1-O8	0.249 5(6)	Nd1-O7 ^{#2}	0.262 9(6)
Nd1-O1 ^{#1}	0.255 4(6)	Nd1-O2 ^{#3}	0.238 5(5)	Nd1-O3 ^{#3}	0.234 5(5)
O4-Nd1-O7	69.1(2)	O7-Nd1-O7 ^{#2}	130.4(2)	O4-Nd1-O8	133.8(2)
O2 ^{#3} -Nd1-O7	137.5(2)	O1 ^{#1} -Nd1-O4	127.7(2)	O3 ^{#3} -Nd1-O7	80.7(2)
O2 ^{#1} -Nd1-O4	80.2(2)	O1 ^{#1} -Nd1-O8	72.2(2)	O4-Nd1-O6 ^{#2}	146.2(2)
O2 ^{#1} -Nd1-O8	90.3(2)	O4-Nd1-O7 ^{#2}	80.9(2)	O6 ^{#2} -Nd1-O8	72.7(2)
O2 ^{#3} -Nd1-O4	74.9(2)	O7 ^{#2} -Nd1-O8	140.0(2)		

^aSymmetry codes: (**1**)^{#1} -x, -y, 2-z; (**3**)^{#1} 1+x, y, z; ^{#2} -1+x, y, z; (**4**)^{#1} -1+x, y, z; ^{#2} -x, 1/2+y, 1/2-z; ^{#3} 1-x, 1/2+y, 1/2-z.**Table 3** Distances and angles of hydrogen bonding for compounds **2** and **3**^a

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠(D-H...A) / (°)
Compound 2				
O(7)-H(7A)···O6 ^{#1}	0.085	0.200	0.271 8(4)	141
O(7)-H(7C)···O2 ^{#2}	0.085	0.211	0.270 4(4)	126
Compound 3				
O(13)-H(13C)···O5 ^{#1}	0.085	0.216	0.281 9(5)	134
O(14)-H(14A)···O10 ^{#2}	0.085	0.237	0.301 6(4)	133
O(14)-H(14B)···O9 ^{#3}	0.085	0.220	0.293 3(4)	145
O(15)-H(15B)···O11 ^{#4}	0.085	0.246	0.305 6(6)	128
O(15)-H(15D)···N5 ^{#5}	0.085	0.205	0.284 0(7)	154
O(16)-H(16B)···O6 ^{#6}	0.085	0.248	0.297 2(4)	118

Continued Table 3

O(16)-H(16C)···O3 ^{#7}	0.085	0.215	0.280 6(4)	134
O(17)-H(17F)···O14 ^{#7}	0.085	0.221	0.305 5(6)	180

^aSymmetry codes: (2) ^{#1} 1/2-x, 1/2+y, -1/2-z; ^{#2} 1-x, 1-y, -z; (3) ^{#1} 1+x, y, z; ^{#2} -1+x, 3/2-y, -1/2+z; ^{#3} x, 3/2-y, -1/2+z;

^{#4} -1+x, y, z; ^{#5} x, 1+y, z; ^{#6} 1+x, 3/2-y, 1/2+z; ^{#7} x, 3/2-y, 1/2+z.

2 Results and discussion

The reaction temperatures and synthesis procedures for compounds **1**~**6** are not identical, although all of them were prepared under hydrothermal conditions. The variation of their preparation conditions depends on the secondary ligands (phen and bpdo) used in the constructions of metal-organic frameworks. For compounds **1**~**6**, both the center metal ions and the secondary ligands exert important influence on the resulting coordination architectures. Therefore, the diverse structures were experimentally observed as follows.

2.1 Crystal structures of compounds **1** and **2**

Compounds **1** and **2** are isostructural, hence only the structure of **2** was discussed in detail. As shown in Fig.1a, the ytterbium(III) ion is eight-coordinated by two carboxylate and one phenol oxygen atoms from two SSA ligands, one oxygen atoms from aqua molecule and four nitrogen atoms from two chelating phen ligands. The distances of Yb-O range from 0.215 9 to 0.231 5 nm, and those of Yb-N are from 0.245 6 to 0.252 7 nm. In compound **2**, two metal atoms are linked by two SSA ligands to form a butterfly-like core (Fig.1a), in which the dihedral angle between the phen rings around the same Yb(III) ion is 50.6° and the nearest distance between the two Yb(III) ions is 0.527 4 nm. The intriguing feature of compound **2** is that the hydrogen bonding and π - π interactions play important roles in the structural orientating (Fig.1b). As depicted in Fig.1b, the butterfly-like core (building block) connects with four adjacent building blocks via hydrogen bonds O(7)-H(7A)···O6^{#1} to form a 3D architecture. Besides, the adjacent building blocks in compound **2** are stacked in an inverse fashion through strong offset π - π interactions with a face-to-face separation of *ca.* 0.349 5 nm, which is also responsible for the formation of the 3D network.

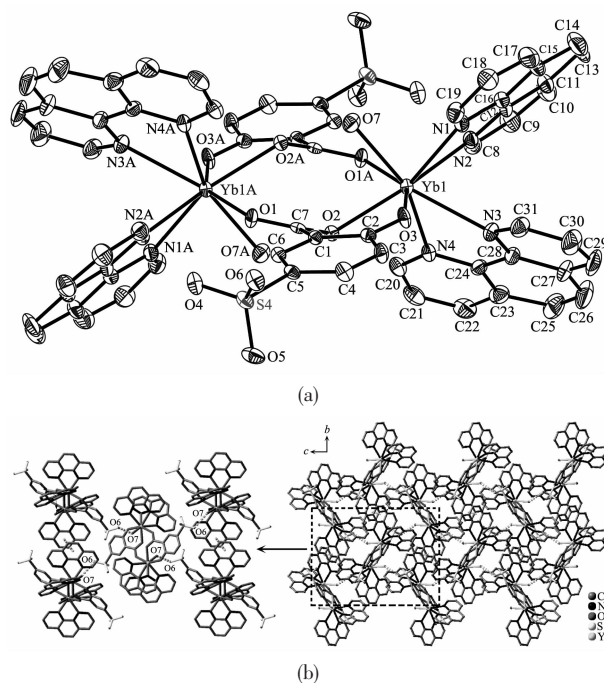


Fig.1 (a) Coordination environment of Yb(III) metal in compound **2**; (b) Crystal structure of compound **2**, viewed along the *a*-axis (right) and showing hydrogen bonds and π - π interactions (dashed lines, left)

2.2 Crystal structure of compound **3**

As depicted in Fig.2a, there are two types of lanthanum(III) ions in the asymmetrical unit of compound **3**. Each La(III) ion is nine-coordinated and surrounded by three oxygen atoms from two carboxylate groups, one oxygen atom from a phenol group, one oxygen atom from sulfonate group, two oxygen atoms from coordinating water molecules, and two nitrogen atoms from one phen molecule. The La-O and La-N distances are in the range from 0.237 0 to 0.271 2 nm and from 0.270 9 to 0.272 8 nm respectively, which are comparable to the reported data [11]. It is noteworthy that there exist three independent phen ligands in the basic cell unit (Fig.2a): one of them, to which N5 belongs, is free, while the other two phen ligands coordinate to different lanthanum (III) ions with the dihedral angle of 7.2°. The

SSA ligand functions as a three-armed connector to link two La(III) centers with the shortest La \cdots La separation of 0.434 8 nm, so that results in the formation of 1D infinite ladder-like chain along the *a*-axis (Fig.2b). In addition, the chelating phen ligands coordinate to each La(III) ion on the same side of the ladder plane to form a 1D chain with Π -shaped pattern along *a*-axis (Fig.2b, bottom left). The 1D chains and adjacent uncoordinated phen rings are further interconnected by strong

hydrogen bonds O(16)–H(16C) \cdots O3^{#7}, O(16)–H(16B) \cdots O6^{#6}, O(14)–H(14B) \cdots O9^{#3}, O(14)–H(14A) \cdots O10^{#2}, O(15)–H(15D) \cdots N5^{#5} (Fig. 2b, top left) to generate a 2D network in the *ac* plane. Furthermore, the 2D architectures were stacked by multiple π - π overlapping interactions between phen rings to form a 3D network (Fig.2b, bottom left and right). The relevant data of the π - π overlapping interactions are summarized in Table 4.

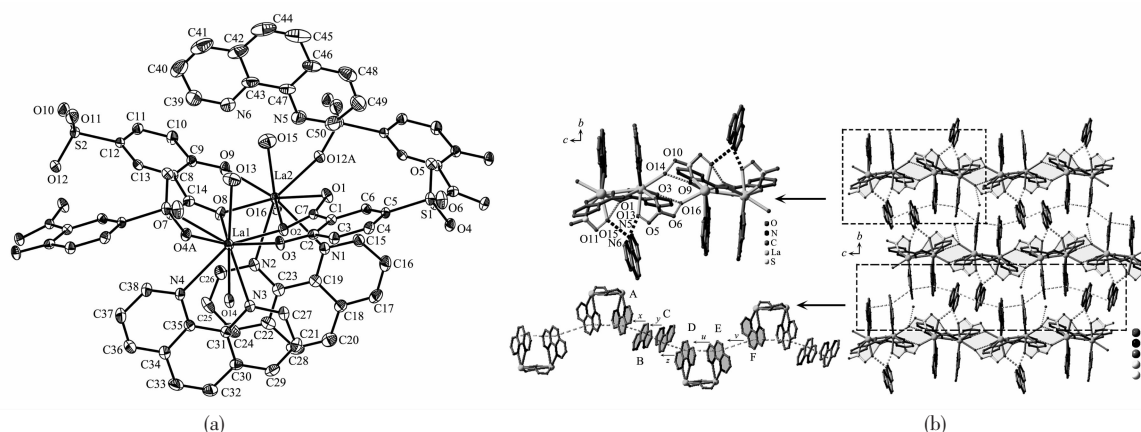


Fig.2 (a) Coordination environment of La(III) metal in compound **3**; (b) Crystal structure of compound **3**, viewed along the *a*-axis (right) and showing hydrogen bonding (top left) and π - π stacking interactions (bottom left)

Table 4 Parameters for the π - π overlapping interactions in compound **3**

	A \cdots B	B \cdots C	C \cdots D	D \cdots E	E \cdots F
$\alpha / (^{\circ})$	16.21(8)	0.00(13)	16.21(8)	7.23(6)	0.00(9)
D_{CP} / nm	0.346	0.352	0.360	0.353	0.323

^aA, B, C, D, E, F denote different phen rings in the Fig.2b; α is the dihedral angle between two different phen rings;

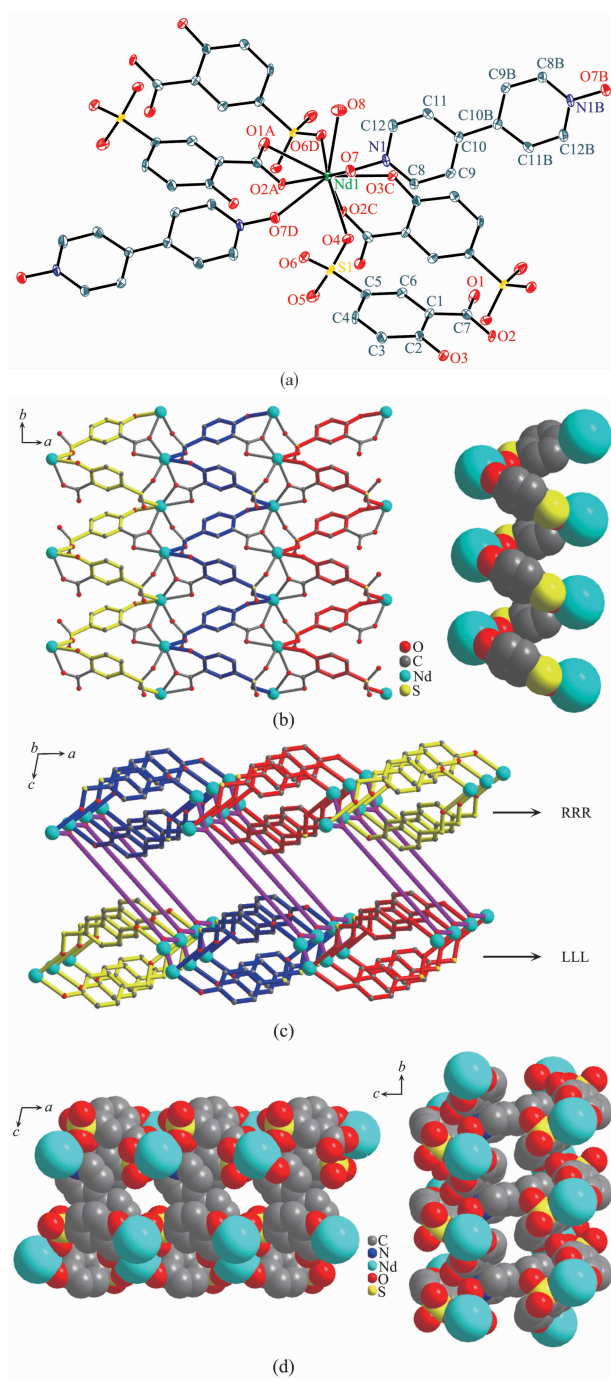
D_{CP} is the distance from the center of the second phen ring to the plane of the first phen ring.

2.3 Crystal structures of compounds 4~6

Compounds **4**~**6** are isostructural, hence only the structure of **4** was discussed in detail. The coordination environment of the Nd(III) ion of **4** is shown in Fig.3a. Each Nd(III) ion is nine-coordinated. Six oxygen atoms belong to four different SSA ligands, another two oxygen atoms belong to two bpdo ligands and the last one is from the coordinating water molecule. The distances of Nd–O range from 0.234 5(5) to 0.262 9(6) nm, and the longest two Nd–O separations are 0.261 0(5) and 0.262 9(6) nm, which result from the Nd(1)–O(7) and Nd(1)–O(7D) bonds by bpdo ligands.

Interestingly, the bridging SSA group connects the two adjacent metal ions into a helical chain with a pitch of 0.760 4(1) nm along the *b*-axis. These helical chains

are further linked by SO₃[−] and COO[−] groups from SSA ligands to form an infinite two-dimensional layer structure in the *ab* plane, as shown in Fig.3b. It is noteworthy that all the helices in one layer exhibit the same helicity. To our best knowledge, this type of helices assembled by SSA ligand has never been reported. Moreover, these 2D chiral layers are alternately arranged in a left- and right-handed manner (Fig.3c). The adjacent layers are supported by the second rigid pillaring spacer to give a 3D centric framework, which has small channels along *b*-axis and *a*-axis to host the free water molecules (Fig.3d). Despite the van der Waals radii of the surface atoms, a calculation by PALTON indicates the volume of these channels is about 8% of the total cell volume.



Hydrogen atoms, coordinating and free water molecules were omitted for clarity

Fig.3 (a) Coordination environment of the Nd(III) ions in compound **4**; (b) Crystal structure of compound **4**, viewed toward *ab*-plane (left); and the space-filling model for a helical stereo view of compound **4** (right); (c) 3D Frameworks of compound **4**, showing its chiral layers and microspores; R and L show the opposite chiralities of the helical chains; (d) Space-filling model of compound **4**, showing the channels along the *b*- and *a*-axis

2.4 XRD patterns and thermogravimetric analyses

The measured XRD patterns of compounds **1**~**6** closely match the ones simulated from their single-crystal diffraction data, indicating that the single phase of these compounds is formed.

To study the thermal stabilities of compounds **1**~**6**, thermogravimetric analysis (TGA) was performed under N_2 atmosphere. In the case of compound **1**, the weight loss of 2.36% below 209 °C (Calcd. 2.35%) corresponds to the loss of one coordinating water molecule. And above 209 °C, the framework structures begin to collapse. Compound **2** has the similar decomposition behavior compared with compound **1** when heated. For compound **3**, the preliminary weight loss attributed to the gradual release of free aqua ligands is above 160 °C, as there exist much more stronger hydrogen bonding interactions between free water molecules, coordinating water molecules and sulfonate groups. The weight loss of 7.17% below 255 °C (Calcd 7.14%) is attributed to one and one third free water molecules and four coordinating water molecules in compound **3**. The main framework in compound **3** began to collapse at *ca.* 260 °C. The TGA curves of compounds **4**~**6** also exhibit the identical steps of weight loss, therefore **4** is used as a model compound. The weight loss of 3.45% below 200 °C (Calcd 3.68%) corresponds to the loss of one free water molecule per formula, and the following weight loss of 3.99% between 200 and 410 °C (Calcd 3.68%) is attributed to one coordinating water molecule in compound **4**. Then at *ca.* 420 °C, the main framework of compound **4** began to collapse.

2.5 Photo luminescent properties

The emission spectra of these compounds in solid state are investigated at room temperature. No intense photoluminescent emissions for compounds **1**, **2**, **4**, **5** and **6** were observed. However, excitation at 340 nm leads to strong blue-fluorescent emission bands at 421 and 535 nm in compound **3**, as illustrated in Fig.4. Given the presence of un-coordinating phen molecules in compound **3**, the first emission band (at around 421 nm) resembles the π - π^* transition (385 and 403 nm) observed for phen in solid state. As La^{3+} has no 4*f* electron and no excited states below the triplet state of

the ligand, the energy absorbed by SSA and phen cannot transfer to La^{3+} ^[12]. Therefore, the second emission band (at around 535 nm) is most probably assigned to the ligand-to-ligand charge transfer (LLCT).

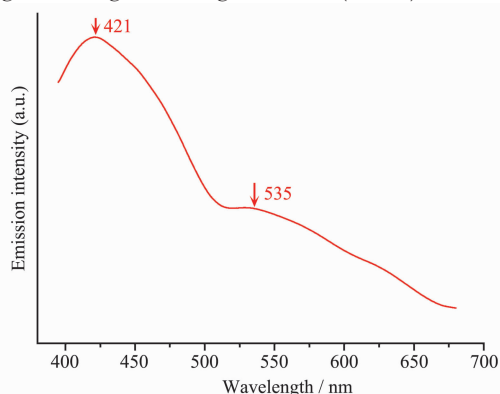


Fig.4 Solid-state emission spectrum of compound **3** at room temperature

In summary, the hydrothermal preparations, crystal structures and luminescent properties of six new rare-earth metal coordination polymers are reported. Due to their different metal centers (Er(III) , Yb(III) , La(III) , Nd(III) , Sm(III) , and Eu(III)) and secondary ligands (phen and bpdo), these compounds exhibit structural diversity in crystals. Compounds **1** and **2** feature the butterfly-like binuclear cores. Compound **3** features a new 1D infinite ladder-like chain, while compounds **4**~**6** exhibit 3D frameworks with interweaving single-helical chains. In addition, compound **3** presents intense blue emission in its solid state when excited.

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