

Structural change of supramolecular coordination polymers of itaconic acid and 1,10-phenanthroline along lanthanide series

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Abstract

Five new supramolecular lanthanide coordination polymers with three different structures, $\{[La_2(IA)_3(phen)_2] \cdot 2H_2O\}_n$ (**1**), $\{[Ln(IA)_{1.5}(phen)] \cdot xH_2O\}_n$ [$x = 1$, Ln = Eu (**2**); $x = 0.25$, Ln = Dy (**3**)], and $[Ln(IA)_{1.5}(phen)]_n$ [Ln = Er (**4**); Yb (**5**)], were prepared by hydro- and solvothermal reactions of lanthanide chlorides with itaconic acid (H_2IA) and 1,10-phenanthroline (phen), and structurally characterized by single crystal X-ray diffraction. **1** Comprises 1-D double-chains that are further assembled to a 3-D supramolecular structure via hydrogen bonds and π - π stacks between phen molecules. **2** and **3** have 2-D infinite networks which are further constructed to form 3-D supramolecular architectures with 1-D channels by π - π aromatic interactions. **4** and **5** have 2-D layer structures consisting of three types of rings which are further architected to form 3-D supramolecular structures by C-H...O hydrogen bonds. The H_2IA ligands are all completely deprotonated and exhibit tetra-, penta-, and hexadentate coordination modes in the titled complexes. The high-resolution emission spectrum of **2** shows only one Eu^{3+} ion site in **2**, which is in agreement with the result of X-ray diffraction. And the magnetic property and the thermal stability of **2** were also investigated.

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1. Introduction

The construction of one-, two-, and three-dimensional coordination polymers has been a field of rapid growth in supramolecular and materials chemistry due to their structural characteristics, such as manifold coordination modes, intriguing architecture, and porosity, and also to their physicochemical characteristics and potential applications as functional materials [1–4]. The successful creation of high-dimensional supramolecular

structures by employing coordination bonds, hydrogen bonds, aromatic π - π stacking interactions, etc., is of great interest in inorganic–organic hybrid materials with variable dimensionality and different coordination frameworks.

In general, the synthetic strategy for metal–organic frameworks (MOFs) polymers includes two essential factors: one is the metal ions including diverse electronic properties and coordination geometries; the other is organic ligands with versatile functions and topologies. Thus far, the assembly of metal–organic networks has centred on using organic ligands with functional groups, such as diphosphonates, bipyridine and polyacids, to link d-block metals such as Zn(II) [5–11], Cu(II)

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[12–16], and Co(II) [17–21] to construct microporous compounds, while the analogous chemistry of lanthanide ions is still lacking in scope [22–27]. Lanthanide ions have larger radii, higher coordination numbers than transition metals so that their structures are intriguing, and they have unique luminescent properties and specific magnetic properties, which attract our interest [28–34].

Succinic acid (SCA) as a representative of flexible dicarboxylic acids has been widely used to construct metal-organic frameworks [20,21,35–44]. However, the studies of SCA with non-coordinated groups such as methylene or phenylene group have never been reported so far. One methylene group is introduced to SA, which makes symmetric SCA ligand asymmetric and thus induces different conformations of the SCA bridging modes due to geometrical constraints and finally makes structures of the complexes diverse.

Considering the high coordination number of lanthanide ions, ancillary ligands can be employed to occupy some coordination sites and prevent the interpenetration of frameworks. Phen is a good ligand for lanthanide ions and can construct supramolecular structure via C–H···O and (or) C–H···N hydrogen bonds and π – π aromatic interactions [32–34], thus increasing the thermal stability of MOFs [34]. In addition, phen can enhance the luminescent properties of lanthanide complexes due to the antenna effect of 1,10-phenanthroline.

In the present work, we used lanthanide chlorides, H₂IA and phen to synthesize new lanthanide supramolecular coordination polymers by hydro- and solvothermal techniques and presented their supramolecular architectures and structural changes along the lanthanide series.

2. Experimental

2.1. Chemicals and measurements

Lanthanide chlorides (LnCl₃ · nH₂O) were prepared by dissolving their oxides in dilute hydrochloric acid, respectively, and the solvent was evaporated to dryness, the content of lanthanides and water in lanthanide chlorides was determined with EDTA titration. All the other reagents were commercially available and used without further purification. Elemental analyses were performed with an Elementar Vario EL analyzer. Thermogravimetric analyses were performed with a TGA: 951 thermogravimetric analyzer. The magnetic susceptibilities were obtained on crystal sample using an oxford Mag-Lab System 2000 magnetometer. The experimental susceptibilities were corrected for the sample holder and the diamagnetism contributions estimated from Pascal's constants. The excitation light source was YAG: Nd

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

2.2. Synthesis

2.2.1. $\{[La_2(IA)_3(phen)_2] \cdot 2H_2O\}_n$ (**1**)

Complex **1** was first prepared by mixing lanthanum chloride, itaconic acid, 1,10-phenanthroline, sodium hydroxide, and deionized water in the following ratios: 1:1.5:1:2.9:139. The resulting gel was aged at 120 °C for 72 h in a 25-ml Teflon-lined stainless reactor under autogeneous pressure, then cooled at 5 °C/2 h to 100 °C, followed by slow cooling to room temperature. Colourless stick-like crystals of **1** were collected by filtration, washed thoroughly with water and ethanol, and air-dried to give 0.010 g (9.4%). Calc. for C₃₉H₃₂La₂N₄O₁₄ (1058.5): C, 44.3; H, 3.1; N, 5.3. Found: C, 43.8; H, 2.8; N, 5.1%.

2.2.2. $\{[Eu(IA)_{1.5}(phen)] \cdot H_2O\}_n$ (**2**)

Complex **2** was first prepared by mixing europium chlorides, itaconic acid, 1,10-phenanthroline, sodium hydroxide, xylene, and deionized water in the following ratios: 1:1.5:1:2.4:9.4:139. The resulting gel was aged at 140 °C for 72 h in a 25-ml Teflon-lined stainless reactor under autogeneous pressure, then cooled at 10 °C/2 h to 100 °C, followed by slow cooling to room temperature. Colourless stick-like tiny crystals of **2** were obtained by filtration, washed thoroughly with water and ethanol, and air-dried to give a yield of 73.7% (0.079 g). Calc. for C_{19.5}H₁₆EuN₂O₇ (542.3): C, 43.2; H, 3.0; N, 5.2. Found: C, 43.4; H, 2.8; N, 5.2%.

2.2.3. $\{[Dy(IA)_{1.5}(phen)] \cdot 0.25H_2O\}_n$ (**3**) and $[Ln(IA)_{1.5}(phen)]_n$ [Ln = Er (**4**), Yb (**5**)]

The syntheses of complexes **3–5** were followed by the similar procedure as described for **1**. Colourless tiny crystals of **3** were obtained with a yield of 56.5% (0.061 g). Calc. for C_{19.5}H_{14.5}DyN₂O_{6.25} (**3**; 539.3): C, 43.4; H, 2.7; N, 5.2. Found: C, 43.8; H, 2.6; N, 5.1%. Pink crystals of **4** were obtained with a yield of 67.6% (0.073 g). Calc. for C_{19.5}H₁₄ErN₂O₆ (**4**; 539.6): C, 43.4; H, 2.6; N, 5.2. Found: C, 43.0; H, 2.7; N, 5.0%. And colourless crystals of **5** were obtained with a yield of 79.8% (0.087 g). Calc. for C_{19.5}H₁₄YbN₂O₆ (**5**; 545.4): C, 42.9; H, 2.6; N, 5.1. Found: C, 42.6; H, 2.6; N, 5.2%.

2.3. X-ray crystallographic study

The single-crystal X-ray data of **1–5** were collected using a Bruker SMART 1000 CCD area detector

diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections were applied to all the five complexes using the SADABS program. The structures were solved by direct methods using the program SHELXS-97 [45] and refined by full-matrix least squares on F^2 using SHELXL-97 [46]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. In complex **2**, lattice water oxygen atoms O7 and O8 are disordered; in complexes **2** and **3**, the itaconate carbon atoms C19, C20 and C21 are disordered; in complexes **4** and **5**, the itaconate carbon atom C20 is disordered.

3. Results and discussion

3.1. Description of the structures

Crystal data of the title complexes are listed in Table 1 and selected bond lengths of **1–5** are listed in Table 2. The H₂IA ligands are all completely deprotonated and afford seven types of coordination modes (Scheme 1(a)–(f)). X-ray single crystal diffraction studies reveal that **2** and **3**, **4** and **5** are isostructural, respectively. So only the structures of **1**, **2**, and **4** will be discussed in detail.

3.1.1. $\{[La_2(IA)_3(phen)_2] \cdot 2H_2O\}_n$ (**1**)

In the crystal structure of **1**, $\{[La_2(IA)_3(phen)_2] \cdot 2H_2O\}_n$, the IA ligands exhibit tetra-, penta-, and hexadentate coordination modes (Scheme 1(a)–(c)) in the ratio of 1:3:2. In the three coordination modes, the four

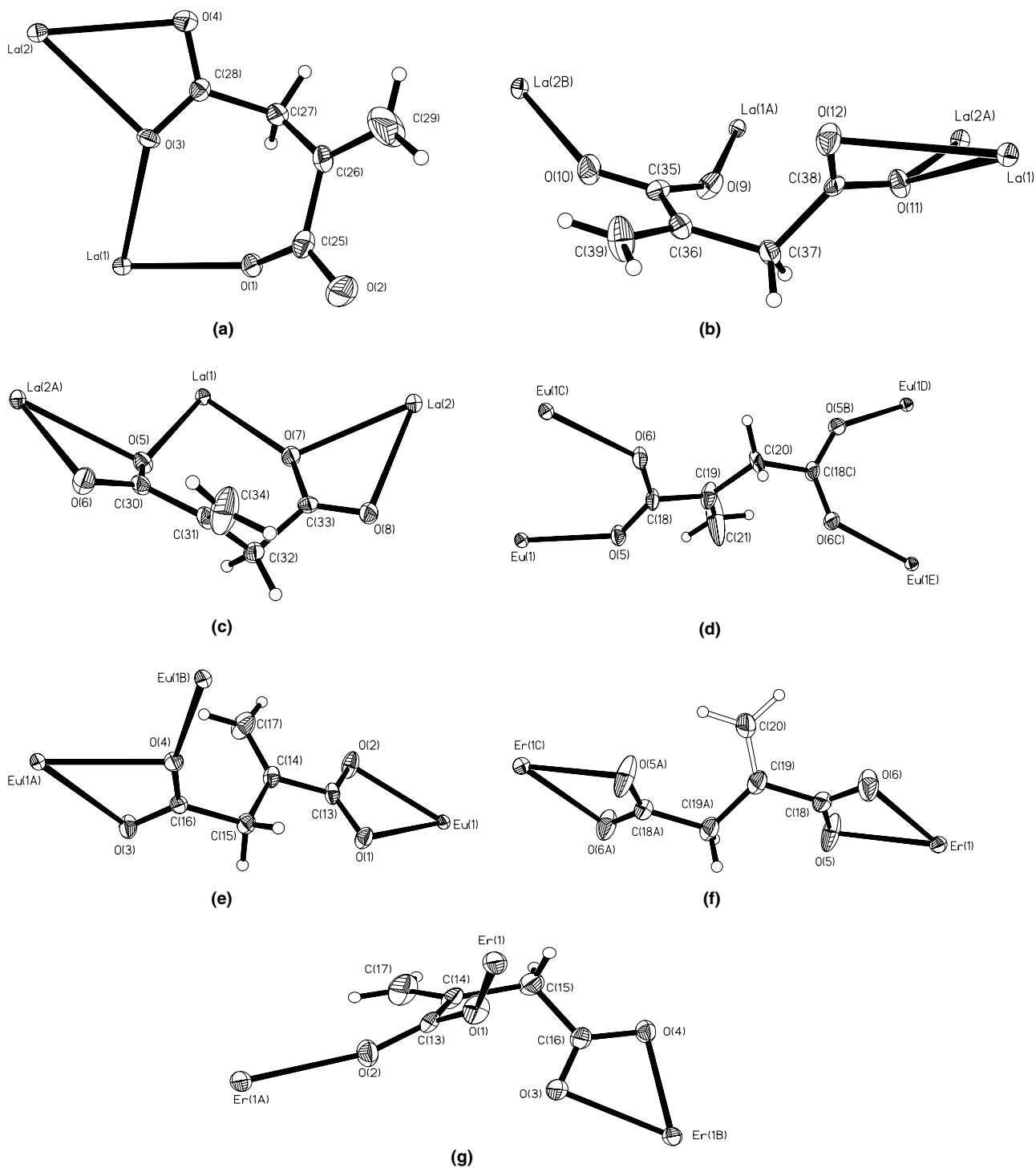
Table 2
Selected bond lengths (Å) for **1–5**

1			
La(1)–O(1)	2.429(5)	La(2)–O(3)	2.718(6)
La(1)–O(3)	2.576(5)	La(2)–O(4)	2.608(5)
La(1)–O(5)	2.544(5)	La(2)–O(5)#1	2.769(5)
La(1)–O(7)	2.520(6)	La(2)–O(6)#1	2.554(5)
La(1)–O(9)#1	2.447(5)	La(2)–O(7)	2.730(5)
La(1)–O(11)	2.673(5)	La(2)–O(8)	2.644(5)
La(1)–O(12)	2.669(5)	La(2)–O(10)#2	2.485(5)
La(1)–N(1)	2.742(6)	La(2)–O(11)#1	2.502(5)
La(1)–N(2)	2.750(6)	La(2)–N(3)	2.752(6)
		La(2)–N(4)	2.714(6)
2		3	
Eu(1)–O(1)	2.467(3)	Dy(1)–O(1)	2.427(4)
Eu(1)–O(2)	2.462(3)	Dy(1)–O(2)	2.424(4)
Eu(1)–O(3)#5	2.475(3)	Dy(1)–O(3)#5	2.436(4)
Eu(1)–O(4)#4	2.364(3)	Dy(1)–O(4)#4	2.321(3)
Eu(1)–O(4)#5	2.591(3)	Dy(1)–O(4)#5	2.565(3)
Eu(1)–O(5)	2.349(3)	Dy(1)–O(5)	2.311(4)
Eu(1)–O(6)#3	2.362(3)	Dy(1)–O(6)#3	2.329(4)
Eu(1)–N(1)	2.638(4)	Dy(1)–N(1)	2.608(5)
Eu(1)–N(2)	2.601(3)	Dy(1)–N(2)	2.561(5)
4		5	
Er(1)–O(1)	2.247(4)	Yb(1)–O(1)	2.194(5)
Er(1)–O(2)#4	2.210(4)	Yb(1)–O(2)#4	2.165(5)
Er(1)–O(3)#6	2.341(4)	Yb(1)–O(3)#6	2.305(5)
Er(1)–O(4)#6	2.392(4)	Yb(1)–O(4)#6	2.353(6)
Er(1)–O(5)	2.410(4)	Yb(1)–O(5)	2.375(6)
Er(1)–O(6)	2.365(4)	Yb(1)–O(6)	2.321(6)
Er(1)–N(1)	2.512(4)	Yb(1)–N(1)	2.458(6)
Er(1)–N(2)	2.506(5)	Yb(1)–N(2)	2.459(6)

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

Table 1
Crystal data for **1–5**

Complex	1	2	3	4	5
Empirical formula	C ₃₉ H ₃₂ N ₄ O ₁₄ La ₂	C _{19.5} H ₁₆ N ₂ O ₇ Eu	C _{19.5} H _{14.5} N ₂ O _{6.25} Dy	C _{19.5} H ₁₄ N ₂ O ₆ Er	C _{19.5} H ₁₄ N ₂ O ₆ Yb
Formula weight	1058.51	542.30	539.33	539.59	545.37
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Crystal size (mm \times mm \times mm)	0.22 \times 0.12 \times 0.10	0.18 \times 0.14 \times 0.12	0.14 \times 0.12 \times 0.08	0.24 \times 0.12 \times 0.10	0.20 \times 0.16 \times 0.12
<i>a</i> (Å)	20.782(6)	25.187(8)	24.979(9)	7.858(3)	7.727(3)
<i>b</i> (Å)	13.550(4)	9.408(3)	9.337(3)	10.063(4)	9.948(3)
<i>c</i> (Å)	13.942(4)	18.387(5)	18.293(7)	12.705(5)	12.592(4)
α (°)	90	90	90	106.507(6)	106.230(5)
β (°)	98.879(5)	110.369(4)	110.583(5)	93.049(6)	92.866(5)
γ (°)	90	90	90	105.376(6)	105.602(5)
<i>V</i> (Å ³)	3879(2)	4085(2)	3994(2)	919.7(6)	886.8(5)
<i>Z</i>	4	8	8	2	2
θ Range (°)	1.8–26.42	2.33–26.41	1.74–25.01	1.69–26.42	2.23–26.39
μ (mm ⁻¹)	2.248	3.114	3.781	4.603	5.315
Goodness-of-fit on F^2	1.052	1.014	1.158	1.121	1.128
Number of data collected	11 024	11 457	8250	5297	4926
Number of unique data	5337	4189	3519	3715	3508
<i>R</i> _{int}	0.0360	0.0412	0.0313	0.0231	0.0332
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0280, 0.0643	0.0305, 0.0607	0.0255, 0.0581	0.0255, 0.0594	0.0419, 0.1240
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0339, 0.0663	0.0461, 0.0652	0.0378, 0.0778	0.0334, 0.0799	0.0441, 0.1263



Scheme 1. The seven crystallographically established coordination modes of the IA ligands.

carbon atoms in IA (not including that of methylene group) are not coplanar. The separations between the head and tail carbon atoms are 3.306, 3.426 and 3.433 Å for modes a, b and c, respectively. In an asymmetric unit of **1**, there are two types of environment for La³⁺ ions with La···La separation of 4.526 Å, as shown

in Fig. 1. La1 is nine coordinated with seven oxygen atoms (O1, O3, O5, O7, O9A, O11, and O12) from one tetradentate, two pentadentate and one hexadentate IA ligands and two nitrogen atoms (N1, N2) from one phen molecule. La2 is ten coordinated with eight oxygen atoms (O3, O4, O5A, O6A, O7, O8, O10B, and O11A)

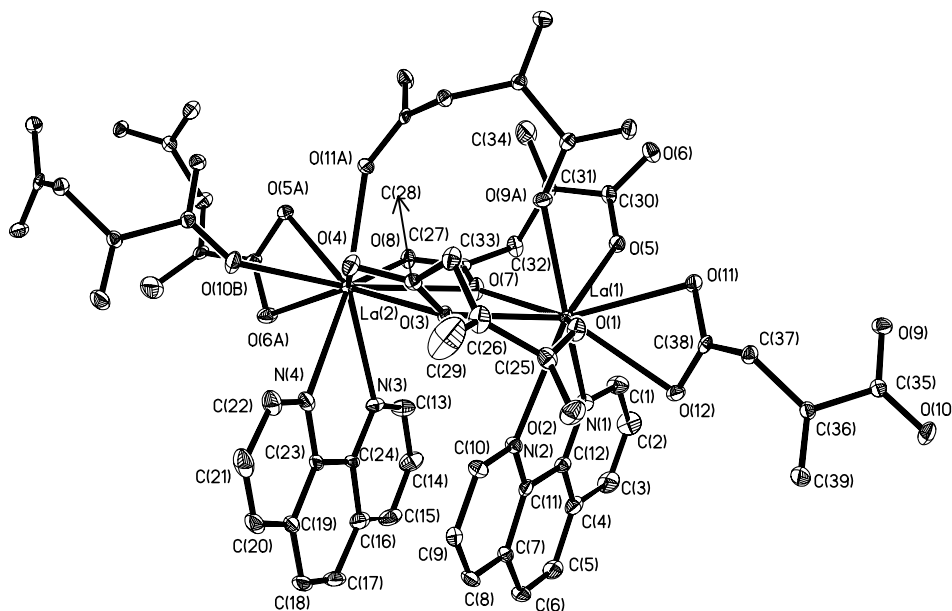


Fig. 1. Coordination environment of the two La(III) ions in **1** with thermal ellipsoids at 20% probability. All the hydrogen atoms are omitted for clarity.

from two tetradentate, one pentadentate and two hexadentate IA ligands and two nitrogen atoms (N3, N4) from one phen molecule. The double-chain of **1** can be viewed as composed of $[\text{La}_2(\text{IA})_3(\text{phen})_2]$ building blocks, as shown in Fig. 2. The two La(III) ions in an asymmetric unit are linked by tetradentate and hexadentate IA ligands, then the building blocks are connected by pentadentate IA ligands to form two sub-chains, depicted as A and B in Fig. 2. A and B are further connected by pentadentate and hexadentate IA ligands to form a double-chain. In the double-chain, all the La(III) ions are distributed in the two planes, respectively. The phen molecules locate at both sides of the double-chain as wings. Face to face π - π stacks exist between phen molecules of two neighbouring double-chains with the nearest distance of ca. 3.0 Å. The H_2IA molecules are all completely deprotonated, but one oxygen atom (O2) of the tetradentate IA ligand remains uncoordinated (see Fig. 1). These uncoordinated oxygen atoms in **1**

form $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds with hydrogen atoms of adjacent phen molecules ($\text{C}\cdots\text{O}$ distance 3.585 Å). While lattice water molecules form three kinds of hydrogen bonds: hydrogen bonds are formed by lattice water molecules with the coordinated carboxylate oxygen atoms ($\text{O}\cdots\text{O}$ distance 2.802–3.001 Å), with the uncoordinated carboxylate oxygen atoms ($\text{O}\cdots\text{O}$ distance 2.815 Å) and with the $\text{H}-\text{C}$ of phen molecules ($\text{C}\cdots\text{O}$ distance 3.183–3.359 Å). It is these hydrogen bonds and π - π interactions of aromatic rings that generate the 3-D supramolecular structure in **1**.

3.1.2. $\{[\text{Eu}(\text{IA})_{1.5}(\text{phen})] \cdot \text{H}_2\text{O}\}_n$ (**2**)

In the crystal structure of **2**, the IA ligands exhibit tetra- and pentadentate coordination modes (Scheme 1(d) and (e)) in the ratio of 1:2. The carbon atoms (not including that of methylene group) in modes d and e are coplanar and the carbon chain lengths are 3.874 and 3.859 Å, respectively. The asymmetric unit of **2** consists of one

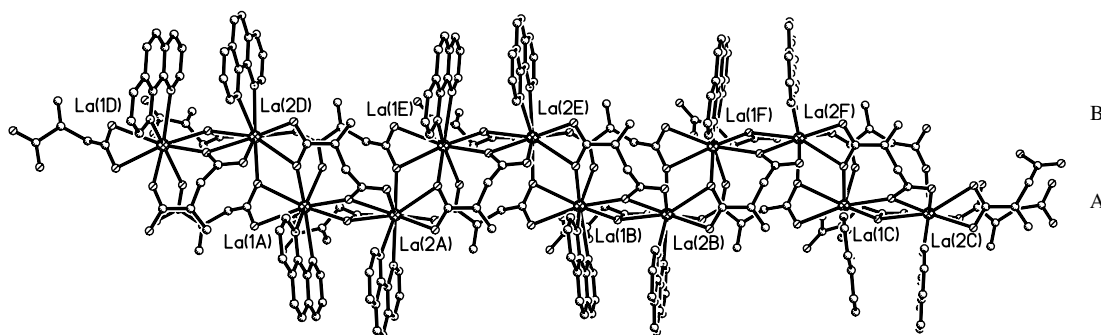


Fig. 2. The 1-D double-chain structure of **1** along the *a*-axis. All the hydrogen atoms are omitted for clarity.

europium(III) ion, which is coordinated to nine atoms: seven oxygen atoms (O1, O2, O3A, O4A, O4B, O5, and O6A) from five IA ligands and two nitrogen atoms (N1, N2) from one phen molecule (see Fig. 3). Two EuO_7N_2 polyhedra share their edge to form a $\text{Eu}_2\text{O}_{12}\text{N}_4$ dimeric unit. The 1-D channel structure of **2** (Fig. 4) can be viewed as composed of the $\text{Eu}_2\text{O}_{12}\text{N}_4$ dimeric units which are linked by carboxylate groups of tetradentate and pentadentate IA ligands through bridging and chelating-bridging coordination modes of IA, respectively, and the distance between the two Eu(III) ions in the dimeric unit is 3.964 Å. Along the [0 0 1] direction, every two $\text{Eu}_2\text{O}_{12}\text{N}_4$ blocks are joined by a tetradentate IA ligand; while along the [0 1 0] direction, every two $\text{Eu}_2\text{O}_{12}\text{N}_4$ blocks are joined by two pentadentate IA ligands, giving rise to a 2-D double-layer structure containing regular grids with dimensions of 10.05×9.41 Å based on the Eu–Eu distance along the *a*-axis, as shown in Fig. 4. All the Eu(III) ions in the 2-D network are distributed in two perfectly parallel planes and the distance between the two Eu(III) ions planes is ca. 3.47 Å. A 3-D supramolecular structure is formed by the π – π stacks between parallel phen molecules of adjacent 2-D layers with the distance of ca. 3.46 Å. It is something worthy to note that the structure of **2** along *c*-axis is composed of A and B parts, part A is 1-D hydrophilic channels with dimensions of 3.96×9.41 Å, in which water mole-

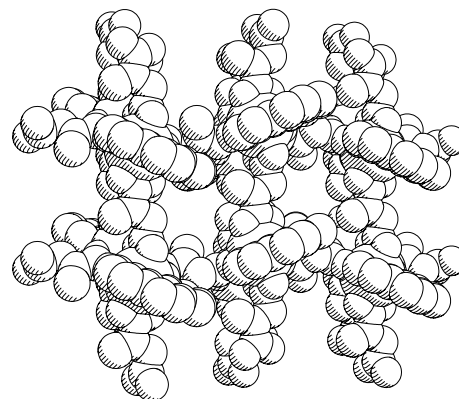


Fig. 4. Spacing-filling model of **2** along *a*-axis. All the hydrogen atoms and lattice water molecules are omitted for clarity.

cules are encased, and part B is hydrophobic phen molecule layers, as shown in Fig. 5, which is rarely seen.

3.1.3. $[\text{Er}(\text{IA})_{1.5}(\text{phen})]_n$ (**4**)

In the crystal structure of **4**, the IA ligands exhibit two sorts of tetradentate coordination modes (Scheme 1(f) and (g)). The carbon atoms (not including that of methylene group) in IA in mode f are coplanar, but the carbon atoms (not including that of methylene group) in mode g are not coplanar. The carbon chain

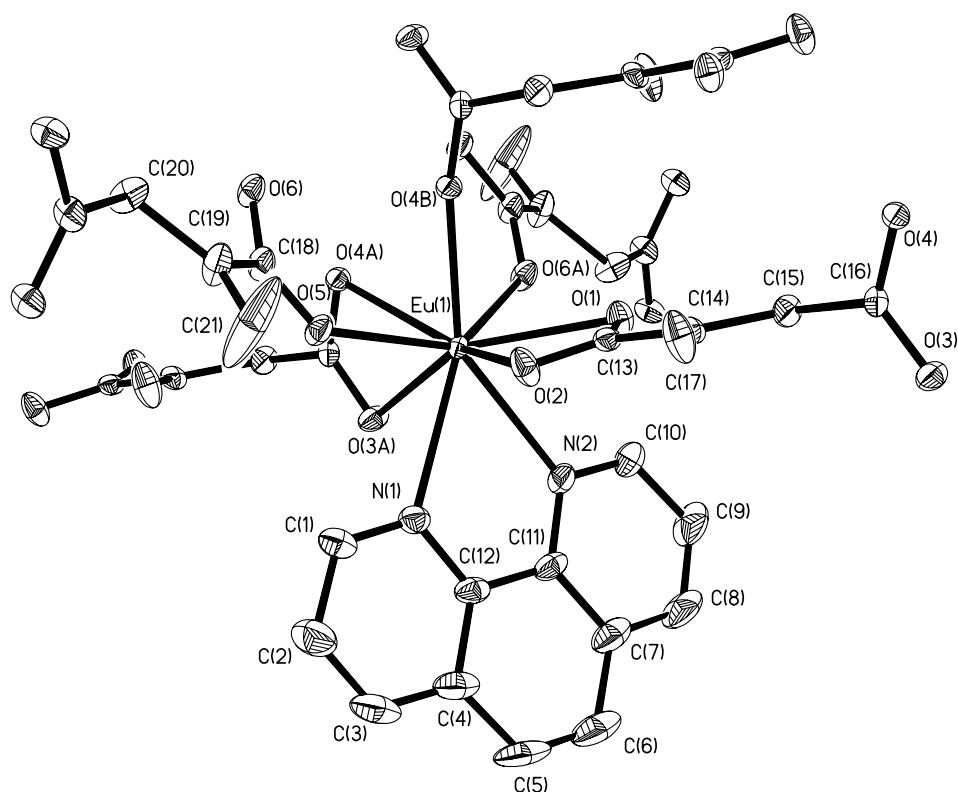


Fig. 3. Coordination environment of the Eu(III) ion in **2** with thermal ellipsoids at 30% probability. All the hydrogen atoms are omitted for clarity.

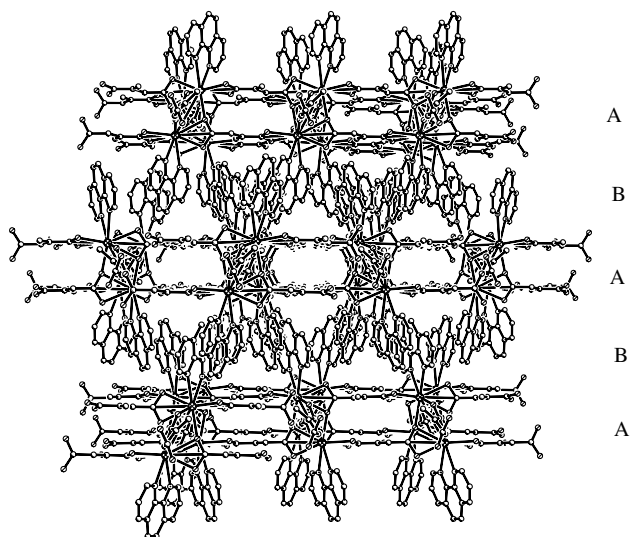


Fig. 5. Packing diagram of **2** along *c*-axis. All the hydrogen atoms and lattice water molecules are omitted for clarity.

of the IA ligand in mode f is 3.868 Å, much longer than 3.131 Å, that in mode g. The asymmetric unit of **4** consists of one Er(III) ion which is coordinated to eight atoms: six oxygen atoms (O1, O2A, O3A, O4A, O5, and O6) from four IA ligands and two nitrogen atoms (N1, N2) from one phen molecule (Fig. 6). As shown in Fig. 7, every Er(III) ion is bridged by four IA ligands with five adjacent Er(III) ions, which results in a 2-D infinite network with three types of rings: 8-membered ring (A), 14-membered ring (B), and 28-membered ring (C). The size of the largest ring is 7.86 × 9.20 Å based on the Er–Er separation and every ring is shared by four

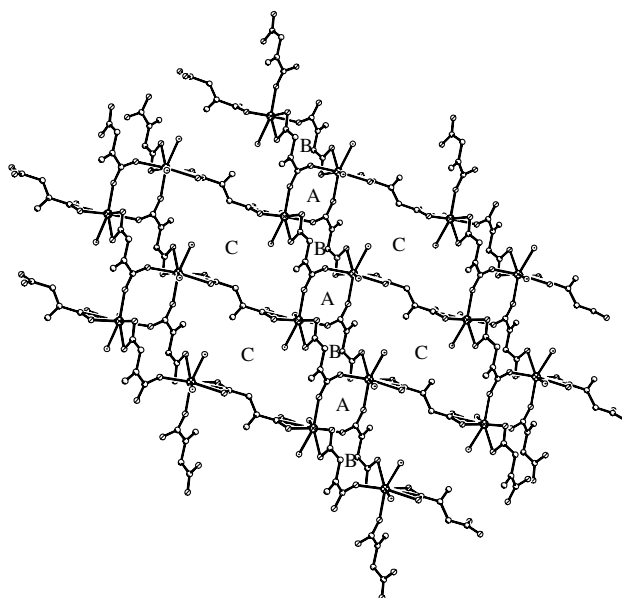


Fig. 7. 2-D framework of **4** along the *b*-axis. Carbon atoms of phen molecules and all the hydrogen atoms are omitted for clarity.

other rings. All the phen molecules are parallel, and the average distance between two adjacent phen molecules is 3.66 Å, and thus weak π – π aromatic interactions exist between the phen molecules in **4**. The carboxylate oxygen atoms form C–H···O hydrogen bonds with the C–H of phen molecules (C···O distance 3.412 Å), which contribute to the 3-D supramolecular structure.

The formation and the structural characteristics of the supramolecular architecture of the titled complexes give rise to the following views: (1) It is interesting to ob-

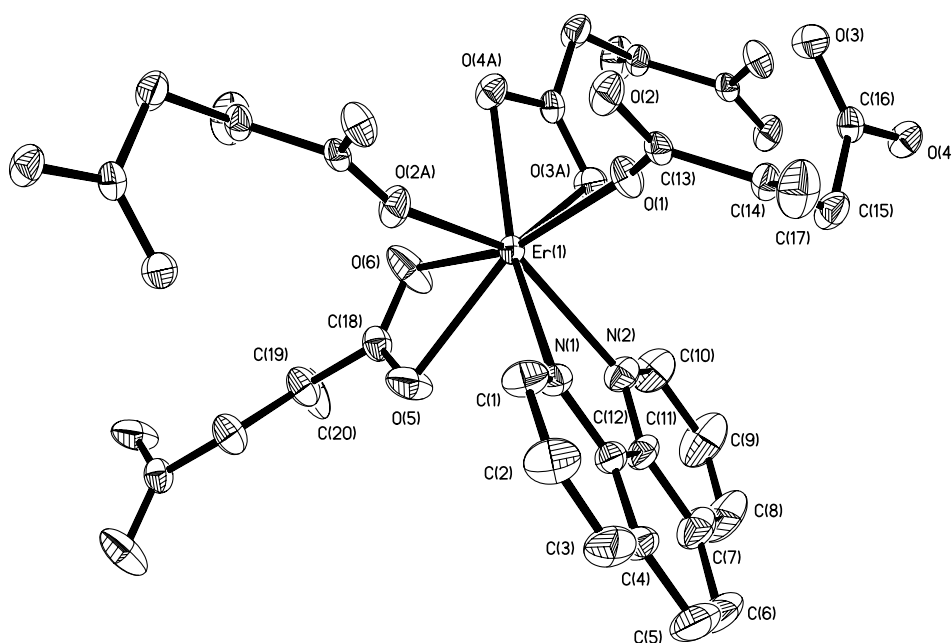


Fig. 6. Coordination environment of the Er(III) ion in **4** with thermal ellipsoids at 30% probability. All the hydrogen atoms are omitted for clarity.

Table 3

The coordination number, coordination mode and average bond length (Å) of Ln–O and Ln–N in **1–5**

Complex	Coordination number	Coordination mode (IA)	The average bond length (Å)	
			Ln–O	Ln–N
1	9,10	tetra-, penta- and hexadentate	2.589	2.739
2	9	tetra- and pentadentate	2.439	2.620
3	9	tetra- and pentadentate	2.402	2.585
4	8	tetradentate	2.329	2.509
5	8	tetradentate	2.285	2.459

serve the effect of lanthanide contraction and methylene substitution of SCA on the coordination modes of IA and thus the structures of the title compounds. The complex **1** has 1-D chain framework constructed by coordination bonds, the complexes **2** and **3** have 2-D double-layer frameworks with regular rhomboid grids, while the complexes **4** and **5** have 2-D single-layer frameworks with three kinds of rings. In **2** and **3**, IA ions (see Scheme 1(d) and (e)) linearly link Eu(III) ions or Dy(III) ions to form a microporous structure, in which lattice water molecules are enclathrated. For **1**, carbon chains of IA ligand are twisted to link two La³⁺ ions of an asymmetric unit, and the two carboxylate groups in a IA ligand link the same La(III) ion to form a 7-number ring (see Scheme 1(a) and (c)); and for **4** and **5** the three sorts of rings are interpenetrated to form 3-D supramolecular network when 2-D framework is further constructed by hydrogen bonds and π – π stackings. Therefore, **1**, **4** and **5** fail to be assembled to microporous structures. (2) The coordination modes, the coordination numbers and the mean Ln–O and Ln–N bond lengths of the titled complexes are given in Table 3.

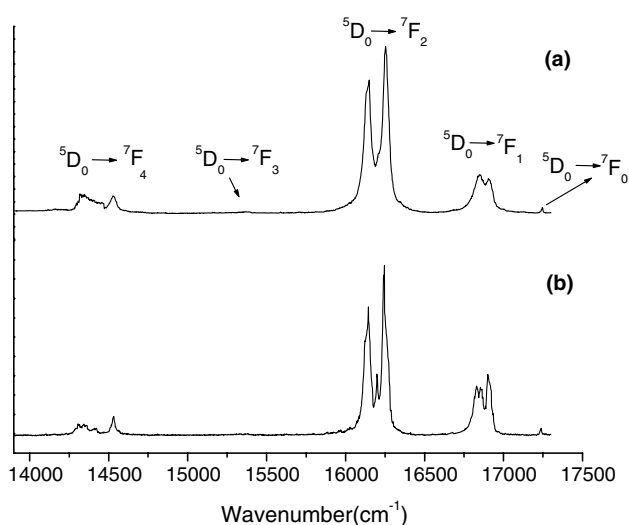


Fig. 8. Emission spectra of **2** corresponding to the $^5D_0 \rightarrow ^7F_J$ ($J = 0-4$) transitions, $\lambda_{exc} = 355$ nm: (a) 293 K; (b) 77 K.

Table 3 shows that the coordination numbers and the average Ln–O and Ln–N bond distances decrease with the increasing lanthanide atomic number. Meanwhile, the variation of coordination modes shows lanthanide contraction over the series. In addition, the lattice water molecules in the channels of **3** are much less than that of **2** because of lanthanide contraction, too. (3) Phen as coligand is vital to the formation of 3-D supramolecular architecture in the titled complexes. The 1-D metal-organic framework of **1** and the 2-D frameworks of **2**, **3**, **4** and **5** are assembled to 3-D supramolecular architecture through π – π stacks between phen molecules and hydrogen bonds. The effect of phen on the supramolecular architectures may be high interest for the design of supramolecular compounds.

3.2. Photophysical properties of $\{[Eu(IA)_{1.5}(phen)] \cdot H_2O\}_n$

Emission spectra and emission lifetimes were measured by the excitation at 355 nm at 293 and 77 K. Emission spectra of **2** are shown in Fig. 8. It is well-known that the $^5D_0 \rightarrow ^7F_2$ transition induced by the electric dipole is hypersensitive to the coordination environment of the Eu(III) ion, while the $^5D_0 \rightarrow ^7F_1$ transition is a magnetic dipole one which is fairly insensitive to the environment of the Eu(III) ion. The intensity ratio $I(^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1)$ is ca. 2.60, which indicates that the Eu(III) ion in **2** is not located at the centre of inversion and symmetry of Eu(III) ion site is low [47]. Comparing emission spectrum of **2** at 77 K with that at 293 K, the low-temperature spectrum shows the expected bathochromic shift and line-narrowing.

Luminescence lifetimes of **2** are 1021 μ s at 293 K and 1298 μ s at 77 K, longer than those of $[Eu(atpt)_{1.5}(phen)(H_2O)]_n$ (atpt = 2-aminoterephthalate), 533 μ s at 293 K and 688 μ s at 77 K [34]. It can be explained by considering the fact that lattice water molecules in **2** partially quench the luminescence and decrease the τ value through vibronic coupling with the vibrational states of the O–H oscillators [48], while more efficient non-radiative deactivations take place for the coordinated water molecules in $[Eu(atpt)_{1.5}(phen)(H_2O)]_n$.

3.3. Magnetic property of **2**

The variable temperature magnetic susceptibility of **2** was measured in the range of 2–303 K. The temperature dependence of the magnetic susceptibility of **2** is shown in Fig. 9, where χ_M is the molar magnetic susceptibility per Eu(III) unit. The χ_M^{-1} value decreases as the temperature decreases at the beginning, reaching a minimum of 152 $cm^{-3} mol$ at 59–64 K, and then increases on further cooling. The observed $\chi_M T$ at room temperature is 1.4 $cm^3 mol^{-1} K$, similar to the value of 1.5 for one Eu(III) ion calculated by van Vleck equation allowing for

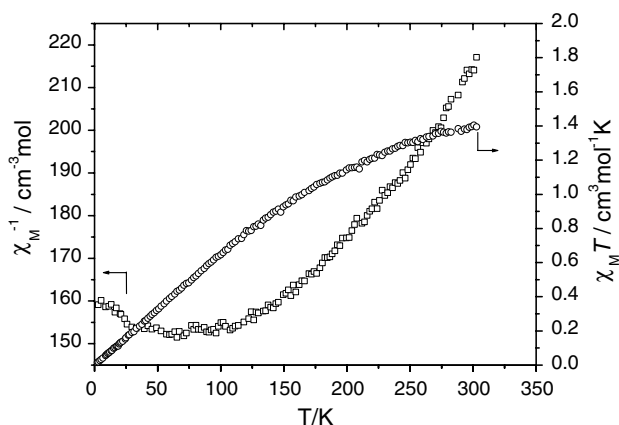


Fig. 9. Plot of the temperature dependence of $\chi_M T$ (○) and χ_M^{-1} (□) for **2** (per Eu^{3+} unit).

population of the lower excited state of 7F_J (Eu^{3+}) in **2** at 293 K. As the temperature was lowered, $\chi_M T$ decreased continuously, which should be attributed to the depopulation of the Stark levels for the $\text{Eu}(\text{III})$ ion. At the lowest temperature, $\chi_M T$ is close to zero, indicating a $J = 0$ ground state of the $\text{Eu}(\text{III})$ ion (7F_0).

3.4. Thermogravimetric analyses

TG curve of **2** shows that the first weight loss of 3.1% from 235 to 311 °C corresponds to the loss of one lattice water molecule per $[\text{Eu}(\text{IA})_{1.5}(\text{phen})] \cdot \text{H}_2\text{O}$ molecule (Calc. 3.3%). Increasing temperature led to the further decomposition of **2** at 351 °C, and the final pyrolysis was completed at 600 °C, as indicated by a significant weight loss of 63.6% with Eu_2O_3 (Calc. 64.2%) obtained.

4. Supplementary material

CCDC Nos. 242407–242411 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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