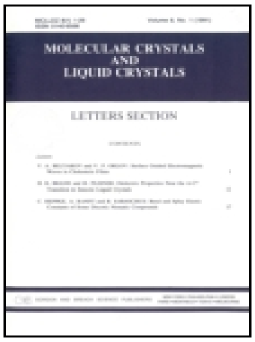
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Synthesis, Structures, and Properties of 3D Lanthanide (III) Coordination Polymers Based on 5-Nitroisophthalic Acid

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A three lanthanide-based coordination compounds of $[Sm_4(NIPH)_5(ox)(H_2O)_5](H_2O)_4$ ***(1)****,* $[Eu_4(NIPH)_5(oba)(H_2O)_5](H_2O)$ ***(2)*** *and* $[Eu_2(NIPH)_3(H_2O)_{14}](H_2NIPH)(H_2O)_6$ ***(3)*** *(*H_2NIPH *= 5-nitroisophthalic acid, ox = oxalic acid,* H_2oba *= 4,4′-oxydibenzoic acid) were synthesized by hydrothermal reaction and characterized by single-crystal X-ray diffraction. These compounds contain an -Ln-O-C-O-Ln- zigzag chain, which connect to each other through the oxygen atoms of the* H_2NIPH *ligands to form a wave-like layer. These layers are bridged by oxalate or* H_2NIPH *ligands to generate three-dimensional coordination framework. Within these compounds, porous structure with one-dimensional channels which were filled with isolated organic ligands or lattice water molecules are also observed. Fascinatingly, these lattice water molecules display unprecedented water morphology and play important roles in the stabilizing the whole network. In addition, these compounds show strong photoluminescence at room temperature, respectively, and may be good candidates for potential luminescence materials.*

Keywords Fluorescence; water cluster; 5-nitroisophthalic acid

Introduction

A great deal of effort has been invested in the design and synthesis of coordination polymers due to their intriguing network topologies and promising applications in fields such as catalysis, ion exchange, gas storage, selective adsorption and separation, optics, and magnetic devices [1, 2]. Up to now, numerous one-, two-, and three-dimensional (1D, 2D, and 3D) coordination polymers have been synthesized by the choice of appropriate metal ions and versatile bridging organic ligands [3, 4]. As compared with the fruitful reports of transition metal coordination polymers, the assembly of lanthanide coordination networks

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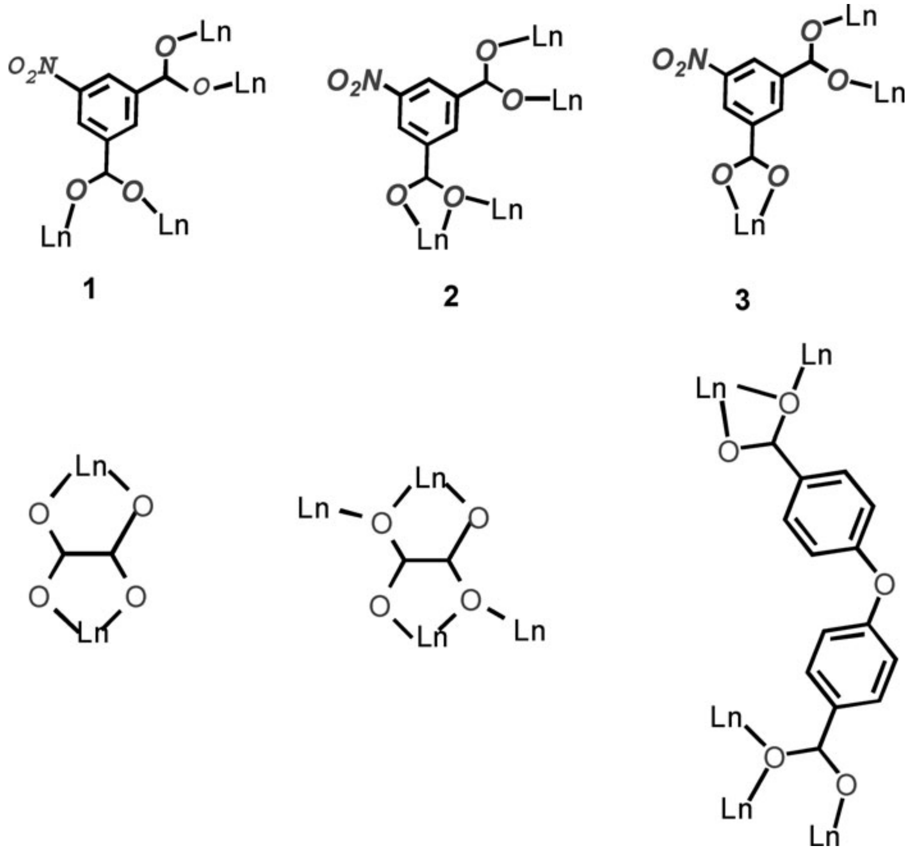
has had an upsurge of interest in recent years [5]. For the variable coordination numbers and special chemical characteristics of lanthanide ions, they can be used to construct fascinating network topologies, in particular, some reported lanthanide coordination polymers exhibit interesting magnetism and luminescence properties arising from 4f electrons [6].

Considering that the lanthanide ions have high affinities for hard donor atoms like oxygen of carboxylic groups, benzenepolycarboxylate ligands are often employed to link the nodes of the single metal ions or metal-carboxylate clusters in lanthanide-organic frameworks [5–7]. For example, the use of 1,4-benzenedicarboxylate has led to a series of lanthanide metalorganic frameworks with novel optical properties [5a, 8]. To construct novel architectures, various functional groups such as amine, sulfonate, nitro and hydroxyl groups have been attached to benzene-polycarboxylate ligands [9–11]. Recently, we have systematically studied supramolecular lanthanide frameworks based on 5-nitroisophthalic acid (H_2NIPH) [11d]. The H_2NIPH is a versatile ligand for the construction of coordination polymers based on the following three points: (i) its two carboxylates groups may be completely or partially deprotonated, resulting in rich coordination modes and formation of the lanthanide clusters, which may act as secondary building units to construct frameworks with novel structural features; (ii) its nitro group can also act as electron donor towards the aromatic ring and easily form lone pair interactions, which is often useful for the formation of stable frameworks; and (iii) its chemical and thermal stabilities are very good [12, 13]. In this work, we used 5-nitroisophthalic acid (H_2NIPH) as the bridge ligand, oxalic acid (ox) and 4,4′-oxydibenzoic acid (H_2oba) as the ancillary ligand to construct novel lanthanide coordination 3D networks under hydrothermal conditions. The synthesis, crystal structures, and properties of eight lanthanide coordination polymers $[Sm_4(NIHPH)_5(ox)(H_2O)_5](H_2O)_4$ **(1),** $[Eu_4(NIHPH)_5(oba)(H_2O)_5](H_2O)$ **(2),** $[Eu_2(NIPH)_3(H_2O)_4](H_2NIPH)(H_2O)_6$ **(3)** will be presented (Scheme 1).

Experimental

Materials and Physical Measurement

All the salts were obtained from commercial sources and used without further purification. Elemental (C, H, N) analyses were performed on a Pekin-Elmer 2400 element analyzer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400–4000 cm^{-1} range using a Nicolet Avatar 360 FT-IR spectrophotometer. Fluorescence spectra were recorded with F-2500 FL Spectrophotometer analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a NETZSCH TGA thermogravimetric analyzer with a heating rate of 10°C/min between 20°C and 1000°C under a dry N_2 atmosphere. Powder XRD investigations were carried out on a Bruker D8-advance X-ray diffractometer with Cu Kα radiation. Single crystal diffraction was carried out on Bruker Apex II Smart X-ray diffractometer. Crystal structure determination: Single crystal X-ray diffraction data collections of **1-3** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo $K\alpha$ radiation ($\lambda = 0.71073$). Data collection and reduction were performed using the Apex II software. Multi-scan absorption corrections were applied for all the data sets using the APEX II program. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package. All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized position and refined using a riding model. Hydrogen atoms on water molecules were located from difference Fourier maps and were refined using riding model, hydrogen atoms of free



Scheme 1. The coordination modes of H_2NIPH, oba, and ox in **1-3.**

water molecules are not located in different Fourier maps but added in the formula. The crystallographic data for **1-3** are shown in Table 1. CCDC number: 866331, 866335, and 872045.

Synthesis of [$Sm_4(NIHPH)_5(ox)(H_2O)_5](H_2O)_4$ (1)

The reagents of H_2NIPH (4.2 mg, 0.2 mmol), Sm_2O_3(3.5 mg, 0.1 mmol), Oxalate (9 mg, 0.1 mmol), one drop of nitric acid, and 2 ml water were placed in a thick Pyrex tube. The sealed tube was heated at 145°C for 6 days to yield light yellow block-shaped crystals. The crystals were washed with ethanol, dried, and stored under vacuum (67% yield based on Sm). Elemental analysis. $C_{42}H_{33}N_5O_{43}Sm_4$: calcd. C, 26.59, H, 1.75, N, 3.69%; Found: C, 26.56, H, 1.70, N, 3.63%. IR: 3316, 3102, 1623, 1256, 1313, 1216, 1116, 853,579, 417.

Synthesis of [$Eu_4(NIHPH)_5(oba)(H_2O)_5](H_2O)$ (2)

The reagents of H_2NIPH (2.1 mg, 0.1 mmol), Eu_2O_3 (3.5 mg, 0.1 mmol), OBA (2.6 mg, 0.1 mmol), one drop of nitric acid, and 2 ml water were placed in a thick Pyrex tube. The sealed tube was heated at 145°C for 6 days to yield light yellow block-shaped crystals. The crystals were washed with ethanol, dried, and stored under vacuum (57% yield based on Eu). Elemental analysis. $C_{54}H_{36}Eu_4N_5O_{41}$: calcd. C, 32.13, H, 1.80, N, 3.47%; Found: C,

Table 1. Crystallographic data and structure refinement details for compounds **1-3**

Complexes	1	2	3
Empirical formula	C42H33N5O43Sm4	C54H36Eu4N5O41	C32H32Eu2N4O34
Formula weight	1897.13	2018.72	1320.54
Temperature	293(2)	296	293(2)
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P-1	P-1	Pna21
a (Å)	13.091(5)	11.7582(4)	14.283(3)
b (Å)	14.660(6)	13.2750(4)	16.456(4)
c (Å)	16.058(6)	21.1653(7)	18.724(4)
α (°)	78.177(4)	97.98	90
β (°)	74.622(4)	91.35	90
γ (°)	74.340(4)	110.61	90
Volume(Å^3)	2832(2)	3053.03(17)	4400.9(17)
Z	2	2	4
D_{calc}mg/m^{-3}	2.225	2.196	1.993
μ	4.210	4.171	2.942
$F_{(000)}$	1824	1950	2600
GOF on F^2	1.025	0.995	1.121
R_1	0.0238	0.0238	0.0273
wR_2	0.0536	0.0552	0.0731
R_1 (all data)	0.0284	0.0294	0.0307
wR_2 (all data)	0.0557	0.0578	0.0751

$^aR_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\Sigma w(|F^2{}_o| - |F^2{}_c|)^2/\sum w(|F^2{}_o|^2)]^{1/2}$.

32.16, H, 1.80, N, 3.43%. IR: 3306, 3002, 1652, 1242, 1309, 1218, 1143, 921, 833, 623, 512, 420.

Synthesis of [Eu_2(NIPH)$_3$(H_2O)$_4$](H_2NIPH)(H_2O)$_6$ (3)

The reagents of H_2NIPH (4.3 mg, 0.2 mmol), Eu_2O_3 (3.5 mg, 0.1 mmol), one drop of nitric acid, and 2 ml water were placed in a thick Pyrex tube. The sealed tube was heated at 145°C for 6 days to yield light yellow block-shaped crystals. The crystals were washed with ethanol, dried, and stored under vacuum (49% yield based on Eu). Elemental analysis. $C_{32}H_{32}Eu_2N_4O_{34}$: calcd. C, 29.11, H, 2.44, N, 4.24%; Found: C, 29.16, H, 2.40, N, 4.23%. IR: 3326, 3109, 1645, 1242, 1306, 1218, 1124, 945, 845, 623, 424.

Results and Discussion

Crystal Structures of 1

[Sm_4(NIPH)$_5$(ox)(H_2O)$_5$](H_2O)$_4$ (**1**). Structure determination shows that compound **1** crystallizes in the monoclinic space group P-1 with a 3D framework. The asymmetric unit of **1** contains four unique Sm(III) ion, five NIPH ligands, one oxalate ligand, five coordinated water molecules and four lattice water molecules. As shown in Fig. 1a, Sm1, Sm2, Sm3, and Sm4 are eight coordinated. Both Sm1 and Sm4 atoms are coordinated to six oxygen atoms from five NIPH ligands, one oxygen from oxalate ligand and one coordinated water oxygen atom. Sm2 ion can be described as a bicapped trigonal prism coordination geometry, four oxygen atoms deriving from four NIPH ligands, two oxygen atoms from half of an oxalate ligand and two oxygen atom deriving from terminal water molecule. But Sm3 coordinated to five oxygen atoms from five NIPH ligands, two oxygen atoms from half of an oxalate ligand, one oxygen atom deriving from terminal water molecule. The bond lengths of Sm-O are ranging from 2.28 to 2.58Å. As shown in Fig. 1d, the ligand contributes its carboxylate groups to link two adjacent Sm(III) ions to form an infinite –Sm-O-C-O-Sm- zigzag chain along b axial. And then adjacent chains are further bridged by the oxalate and NIPH ligand along c axial to form a 2D layers. Taking the nearest metal pair as a node, the 2D layer can be simplified to a (6,3) topology (Fig. 1b). And the adjacent layers finally connect to each other via the NIPH ligands in another direction to generate a 3D framework (Fig. 1c). Within this structure, the oxalate ligand displays chelating-bridging coordination mode and coordinate to four Sm(III) atoms.

Crystal Structures of 2

[$Eu_4(NIPH)_5(oba)(H_2O)_5](H_2O)$**(2)**. Structure determination shows that compound **2** crystallizes in the triclinic space group P-1 with a 3D framework. The asymmetric unit of **2** contains four unique Eu(III) ion, five NIPH ligands, one oba ligand, five coordinated water

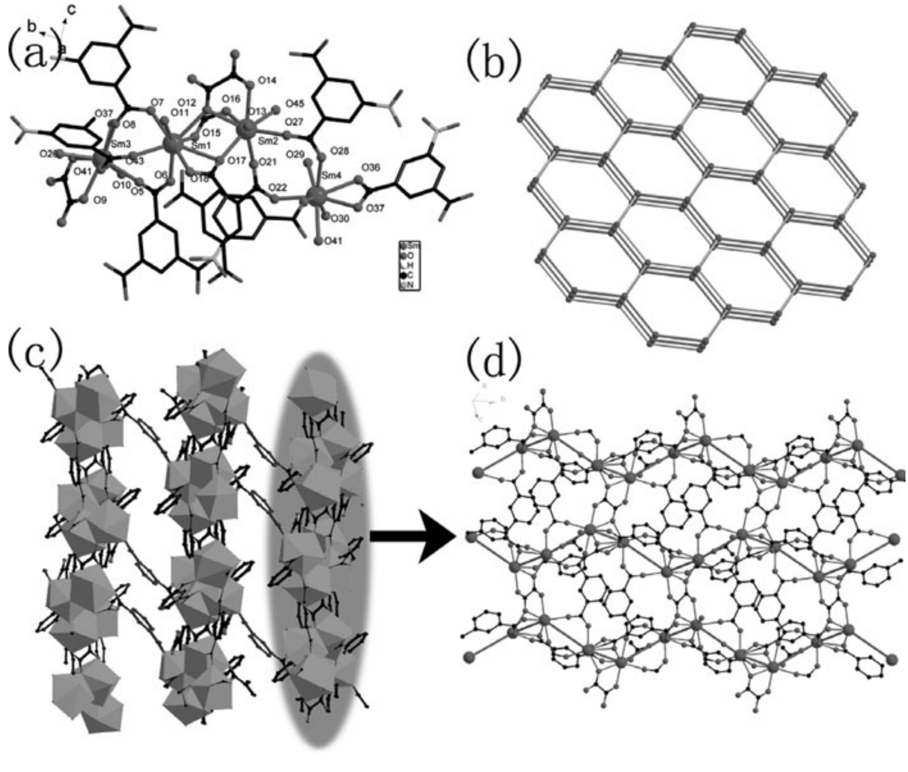


Figure 1. (a) View of the asymmetric unit of structure **1**. (b) **hms** topology of 3D structure of **1**. (c) Three-dimensional framework in **1**. (d) View of a two-dimensional layer (All H atoms were omitted for clarity; N atoms were represented as turquoise, C as black, O as red, and Sm as pink spheres.).

molecules, and one lattice water molecule. As shown in Fig. 2a, Eu1, Eu3, and Eu4 are eight coordinated, while Eu2 is seven coordinated. Eu1 and Eu4 atom are coordinated to six oxygen atoms from five H_2NIPH ligands, two oxygen atoms from coordinated water. Eu2 is seven coordinated to oxygen atoms from seven different carboxylate groups of NIPH ligand. But Eu3 is coordinated to seven oxygen atoms from five H_2NIPH ligands and one coordinated water molecule. 1D metal chains are formed by linking the adjacent Eu(III) atoms with the carboxylate groups along a axis. And the chains are further extended by the H_2NIPH and oba ligand into 2D layer structure along ab plane (Fig. 2b). Furthermore, the linkage of H_2NIPH ligand between the layers plays an important role in the formation of the 3D network (Fig. 2c). A clear insight into the 3D network is shown in Fig. 2c, two NIPH ligands which point to the different direction are held together by weak interactions into a pair of bridge. Strong π-π stacking interactions and lone pair-π interactions play important roles in the formation of the pairs of NIPH with plane-plane distance of 3.32Å and Nitro-oxygen-Cg distance is 3.41 Å (Cg is the ring compose of C39, C40, C41, C42, C43, and C44). It is noteworthy that the oba ligand displays (k1-μ2)-(k2-μ2)-μ5 (Scheme 1) coordination mode and formation of the lanthanide clusters, which may act as secondary building units to construct frameworks into novel structural features. According to our

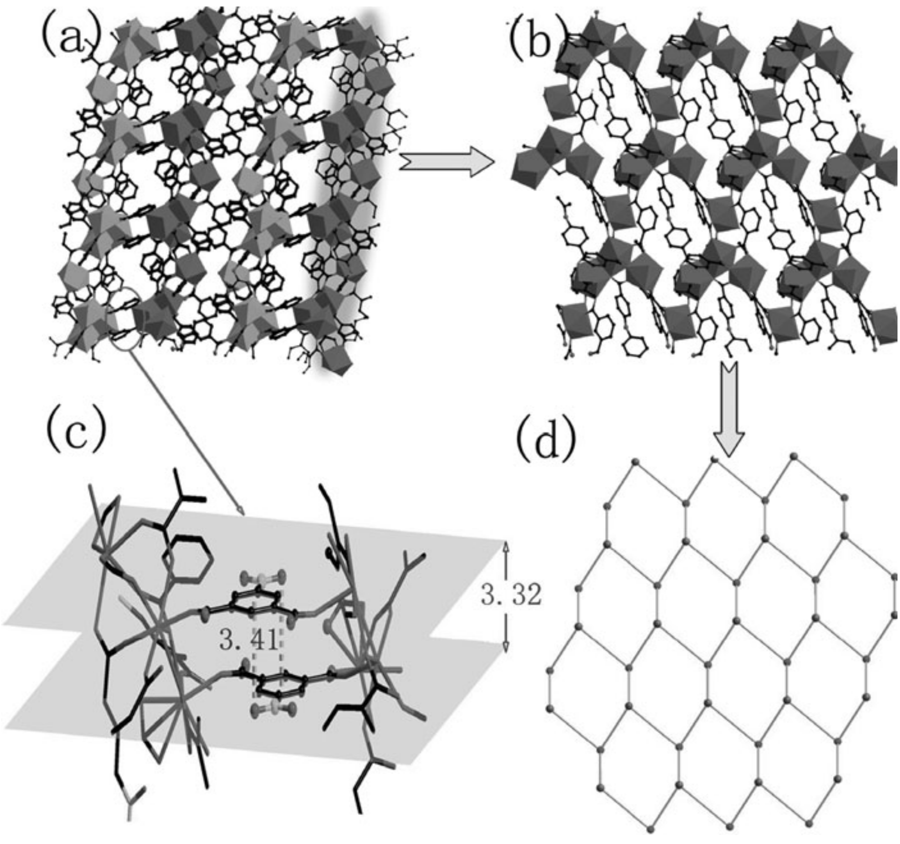


Figure 2. (a) Three-dimensional framework in **2**. (b) View of a two-dimensional layer structure. (c) Showing the 3D framework which were formed by linking adjacent layers by pairs of NIPH ligand. (d) View of the 2D 4-connected (6, 3) topological network in **2** (view Eu1, Eu2, and Eu3 as one node).

investigation in Cambridge Crystallographic Data Centre the μ5-oba coordination modes as that observed in **2** has not been observed for the metal-OBA coordination polymers. The maximal coordination number of oba reported before is μ_4-OBA.

Crystal Structures of 3

[$Eu_2(NIPH)_3(H_2O)_4$](H_2NIPH)(H_2O)$_6$ **(3)**. The asymmetric unit of **3** consists of a binuclear unit, [$Eu_2(INPH)_4(H_2O)_4$]. There are two Eu(III) ions and they are both eight-coordinate with oxygen atoms (Fig. 3a). Both Eu1 and Eu2 are bonded to six oxygen atoms from five NIPH ligands and two oxygen atoms from two water molecules. Four carboxylate groups bridging pairs of Eu atoms at the bottom of the prism geometry and other two carboxylate groups link the Eu(III) atom at the different sides along the axis direction, resulting in similar coordination environment. The NIPH anions in **3** adopt two coordination modes, labeled 1 and 3 (Scheme 1), the bridging ligand NIPH orients in two directions and linking the Eu(III) ions to form a square grid with a dimension of 9.3×10.8 Å^2. Adjacent grids

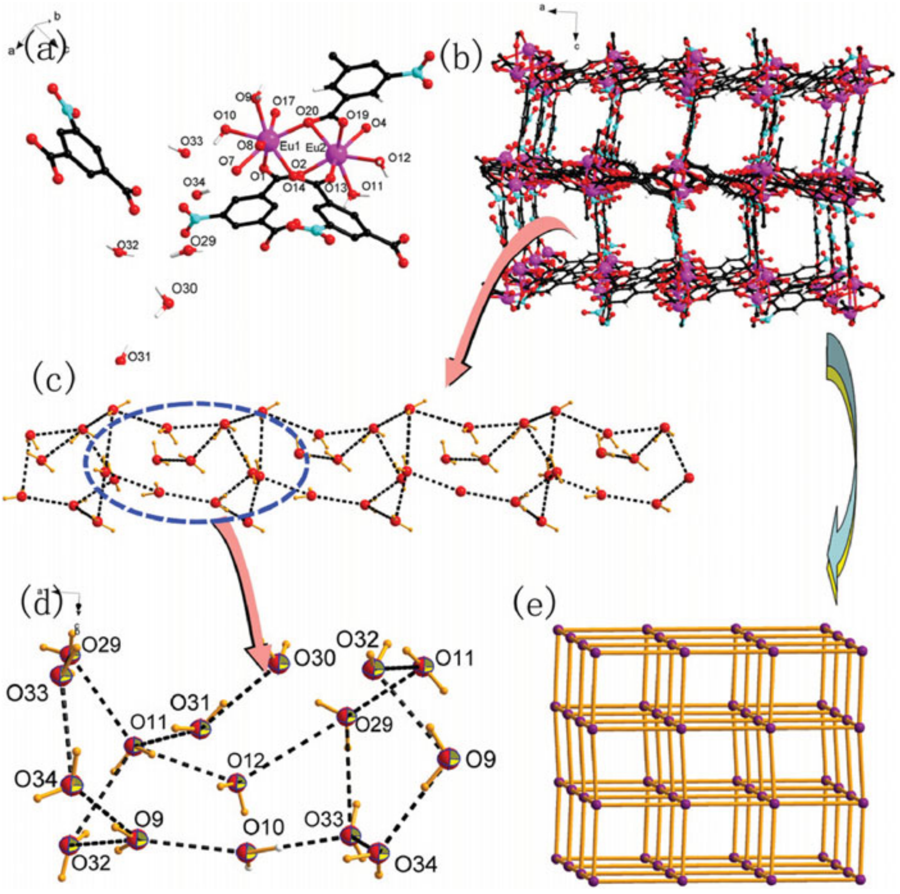


Figure 3. (a) The coordination environment of the center Eu(III) atom. (b) 1D porous structure of **3**. (c) 1D water chains filled in the channel of **3**. (d) Detail of the lattice water cluster. (e) The **pcu** network (view the pair of Eu atoms as one node).

are linked through the chelating-bridging tridentate carboxylate group of the NIPH anion that adopt coordination modes 1. The Eu···Eu distance between adjacent grids is 10.89Å (view of the pair of Eu as one node). In this fashion, compound **3** forms a 3D open framework with 1D square channels with **pcu** topology network (Fig. 3d). However, the channels are partially occupied by free H_2NIPH ligand and lattice water molecules and the oxygen atoms from coordinated water molecules are oriented toward the channel center. In addition, the lattice water molecules are enchased in the cavities through O-H···O hydrogen bonds. Interestingly, the resulting supramolecular architectures are formed through several kinds of weak interactions. It is noteworthy that in spite of the dense arrangement of the network, crystallographically unique uncoordinated water molecules are distributed, which are involved in strong hydrogen bonds of O-H···O with the coordinated water molecules. As shown in Fig. 3d, two six-membered water rings and one seven-member ring are joined together by strong hydrogen bonds. And these units are further connected through O32-H32B···O9 and O9-H9c···O34 hydrogen bonds into a water tape along *a* axis. Within this water morphology, the bonds length rang from 2.658 to 3.393Å and the angle range from 115.6° to 176.4°, which is longer than that observed in the ice II phase 2.77-2.84 Å [14].

Although all of the compounds are based on the H_2NIPH ligand and a lanthanide, their coordination frameworks are quite different. As the increasing of H_2NIPH ligand, 3D networks with 1D channel that accommodate the coordinated and guests organic and water molecules were obtained. To the best of our knowledge, **3** is the limited examples of porous structures of H_2NIPH in lanthanide system. Within these structure, auxiliary ligand oxalate and oba ligand play an important role in the formation of 3D network. As far as we know, it is the first time that the oxalate linked four metal ions in Eu system and no example of coordination mode with single oxygen atoms bridging two metal ((k1-μ2)-(k2-μ2)-μ5-model) of oba ligand has been reported prior to this work [15–17].

Thermal Analysis

All of the compounds are stable under ambient conditions. To study the thermal behavior of the compounds, TGA of **1-3** were carried out from 20 to 1000°C at the heating rate of 10°C /min in N_2 atmosphere. The TGA curves show that there are two or three main events of weight loss as showed in Figure S1. For complex **1**, the TGA indicates that **1** loses of 12.9% of total weight in the 50–210°C temperature range, corresponding to the removal of the night water molecules and oxalate (calcd.13.2%). When the temperature holds on rising, the products lose 65% of the total weight in the 250–650°C temperature range, corresponding to the removal of five NIPH ligands. Compound **2** loses 5.4% of the total weight in the 20–110°C temperature range, corresponding to the removal of six water molecules, when the temperature holds on rising, the products loses 65% of the total weight in the 250–650°C temperature range, corresponding to the removal of the H_2NIPH ligands and oba ligands. Complex **3** loses 13.3% of the total weight in 20–110°C temperature range, which corresponding to the remove of ten water molecules, and then lose 60% at the 250–650°C temperature range, corresponding to the removal of the H_2NIPH ligands.

Fluorescence Properties and PXRD Measurement

Taking into account the excellent luminescent properties of Eu(III) ion, the luminescence of **3** was investigated, recorded under excitation at 349 nm. As shown in Fig. 4, the emission spectrum of **3** consists of four bands of 571, 593, 615, and 663 nm. These two main peaks typically correspond to the characteristic transition of $^5D_0$-^7F_J (J = 0-4) of Eu(III) ions via a ligand-to-metal energy mechanism. The most intense emission at 615 nm is attributed to $^5D_0$-$^7F_2$ transition induced by the electric dipole, suggesting that the interactions between the complex and its local environment are strong [18] and that the ligand is favorable for the sensitization of red luminescence for Eu(III) ions under the experimental conditions used [19]. The medium strong emission at 593 nm and 663 nm are corresponding to the magnetic dipole induced $^5D_0$-$^7F_1$ transition and the electric dipole induced $^5D_0$-$^7F_4$ transition, respectively. The presence of the $^5D_0$-$^7F_0$ transition at 571 nm indicates that the Eu(III) in **3** occupies sites with low symmetry and possess a noncentro symmetric coordination environment [20]. As is well known, the intense ratio of $^5D_0$-$^7F_2$/$^5D_0$-$^7F_1$ was widely used as a measurement of the symmetry of the rare earth. The intense ratio of $^5D_0$-$^7F_2$/$^5D_0$-$^7F_1$ is about 2.26, much higher than 0.67, a typical value for a centrosymmetric Eu^{3+} center, which testifies the low site symmetry of Eu(III) in as well. Moreover, the emission spectrums of 615 exhibit plenty of small splittings, which is useful for confirming the local site symmetry of the lanthanide ions [21]. As shown in Fig. 4, the splittings for the $^5D_0$-^7F_J transition are relatively clear with the exception of the $^5D_0$-$^7F_3$ transition. Additional, it is noted that the $^5D_0$-$^7F_0$ transition of Eu(III) ions only arises in a limited number of site symmetries. According to the coordination number of the europium ions and the splittings, it can be concluded that the central ions could be Cs or C2 symmetry, which is in agreement with the single-crystal X-ray analysis [22].

Simulated and experimental powder X-ray diffraction (PXRD) patterns of **1-3** are shown in Figure S**2**. All the peaks in the recorded curves approximately match those in the simulated curves generated from single-crystal diffraction data, which confirms the phase purity of the as-prepared products.

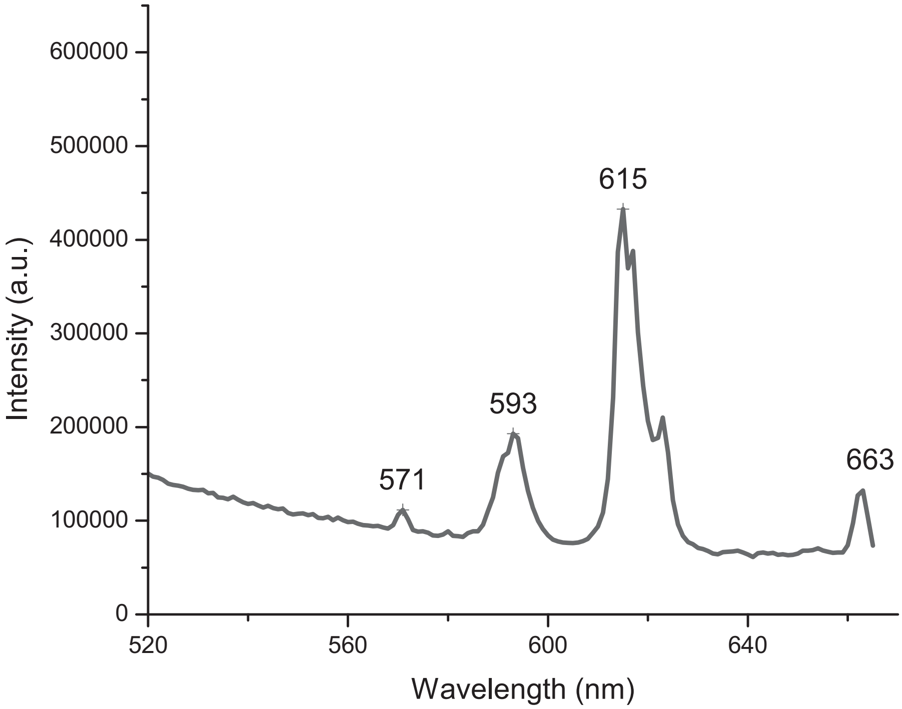


Figure 4. The luminescence curves of **3**.

Conclusions

In summary, we have obtained three 3D lanthanide-metal coordination polymers based on the 5-nitroisophthalic acid (H_2NIPH) linker and adding oba and oxalate as the second ligands. Single-crystal X-ray diffraction analysis revealed that these polymers formed eight coordination numbers with lanthanide atoms, and different coordination modes of the organic bridge ligand could promote different topologies structures. **1** is 3D frameworks with **hms** topology, **2** is 2D 4-connected (6,3) topological network and **3** is 3D frameworks with **pcu** topology network. The **3** is constructed from dinuclear and **1**, **2** are constructed from tetranuclear lanthanide building blocks, respectively. 1D open channels enchased with free organic and lattice water molecules are observed in **3**. The synthesis method and the oxalate and oba ligand play important roles in governing the molecular frameworks.

Supplementary Material

CCDC: 866331, 866335, and 872045 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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