



Lanthanide-organic frameworks constructed from multi-functional ligands: Syntheses, structures, near-infrared and visible photoluminescence properties

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ABSTRACT

A series of multi-functional ligands supported lanthanide-organic frameworks, formulated as $[Ln(HL_1)(H_2L_2)_{0.5}(H_4L_2)_{0.5}(H_2O)] \cdot (H_2O)_{1.5} \cdot \{Ln = La (1), Pr (2), Nd (3), Sm (4), Eu (5); H_3L_1 = 5\text{-Sulfosalicylic acid}; H_4L_2 = N,N'\text{-piperazine (bis-methylene phosphonic acid)}\}$, have been synthesized by hydrothermal reactions. Single crystal X-ray diffractions and powder XRD patterns confirm they are isostructural. They feature 3D framework structures based on extension of a “zigzag” inorganic chain by organic linkers. Moreover, the photoluminescence properties of **5** and **3** have been investigated, and they show strong solid-state emissions in the visible and near-infrared (IR) regions at room temperature.

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1. Introduction

Porous metal-organic frameworks (MOF) have received extensive research attentions due to their potential applications as functional materials [1–4]. Among the reported MOFs, metal phosphonate frameworks showed special attractive properties in adsorption, ion exchange, electro-optical, catalysis and proton conductivity [5–7]. Most of the reported metal phosphonates displayed open framework architectures. Combining with the good thermal and chemical stabilities of M–O–P bonds that phosphonate ligands made with many metal ions [8], metal phosphonates have been seen as promising microporous materials. Trivalent lanthanide ions are fascinating luminescence sources for their high color purity and relatively long lifetimes of the excited states arising from transitions within the partially filled 4-*f* shell of the Ln (III) ions. Eu (III) and Tb (III) compounds show strong luminescence in the visible region, making them to be good candidates for fluoroimmunoassays and structural probes [9–11]. More recently, many research interests have been focused on designing complexes containing lanthanide ions that show emissions in the near-infrared (IR) region (800–1600 nm), such as

Nd (III) Er (III), which show unprecedented applications in areas such as luminescence bioassays, laser materials, and optical amplifiers [12–15]. Therefore, compounds containing both the advantages of metal phosphonates and the benign luminescence properties of Ln (III) ions can be used as multi-functional materials. However, due to their low solubility and poor crystallinity, the reported structurally definite lanthanide phosphonates is still limited [16–38]. Until now, there are two methods available to solve these problems: (a) modifying the organic moieties of the phosphonic acid with other polar functional groups, such as hydroxyl, amino, carboxylate, sulfonate and crown ether; (b) adding a second ligand containing functional groups such as carboxylate, sulfonate, or oxalate [23–38]. A readily prepared diposphonic acid {N,N'-piperazine (bis-methylene phosphonic acid)} has been found to be a good candidate ligand for yielding porous metal-organic frameworks [39–41]. As part of our interest in investigating lanthanide phosphonates, we choose 5-sulfosalicylic acid, which contains three kinds of functional groups simultaneously (sulfonate, carboxylate, and phenol hydroxyl groups), as a second ligand. Five lanthanide sulfonate–carboxylate–phosphonates, formulated as $[Ln(HL_1)(H_2L_2)_{0.5}(H_4L_2)_{0.5}(H_2O)] \cdot (H_2O)_{1.5} (Ln = La, Pr, Nd, Sm, Eu)$ have been prepared by hydrothermal reactions. They feature 3D metal-organic frameworks based on extension of a “zigzag” inorganic chain via organic ligands. Herein, we report the synthetic process,

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structure characterization and photoluminescence properties of them.

2. Experimental section

2.1. Materials and general methods

All chemicals including 5-sulfosalicylic acid dihydrate ($\text{H}_3\text{L}_1 \cdot 2\text{H}_2\text{O}$) were obtained from commercial sources and used without further purification. $\text{N,N}'$ -piperazine (bis-methylene phosphonic acid) hydrochloride ($\text{H}_4\text{L}_2 \cdot \text{HCl}$) was synthesized by a literature method [8]. Elemental analyses of C, H and N were determined using a Vario MICRO EL III elemental analyzer. Infrared spectra were recorded on PerkinElmer Spectrum One instrument as KBr pellets in the range of 4000–400 cm^{-1} . Thermogravimetric analysis (TGA) was recorded with a NETZSCH STA 449C unit at a heating rate of 10 $^\circ\text{C min}^{-1}$ under nitrogen atmosphere. X-ray powder diffraction patterns of **1–5** were collected on a RIGUKU DMAX2 500PC diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) under ambient conditions. Solid-state luminescent spectra in the visible and near-infrared region were measured at room temperature with an Edinburgh FLS920 fluorescence spectrometer.

2.2. Syntheses of compounds 1–5

2.2.1. Synthesis of $[\text{La}(\text{HL}_1)(\text{H}_2\text{L}_2)_{0.5}(\text{H}_4\text{L}_2)_{0.5}(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_{1.5}$ (**1**)

A mixture of $\text{LaCl}_3 \cdot (0.45 \text{ mmol})$, H_3L_1 (0.3 mmol) and $\text{H}_4\text{L}_2 \cdot \text{HCl}$ (0.4 mmol) in deionized water (10 ml) was stirred. Then 0.5 M NaOH was added drop-wise until the pH value rose to ca. 3.5. After 0.5 h of stirring, it was sealed in a 23 ml Teflon-lined stainless autoclave, and heated at 135 $^\circ\text{C}$ for 100 h, then slowly cooled down to room temperature at a rate of 2 $^\circ\text{C h}^{-1}$. Colorless crystals were recovered by filtration, washed repeatedly with distilled water, and air dried. Yield: 55% (based on H_3L_1 ligand). Calcd for $\text{C}_{13}\text{H}_{24}\text{La}_1\text{N}_2\text{O}_{14.5}\text{P}_2\text{S}_1$: C 23.19, H 3.59, N 4.16; found: C 22.97, H 3.51, N 4.15. IR (KBr (cm^{-1})): 3438 (m, br), 3276 (w), 3060

(m), 1623 (m), 1584 (s), 1478 (m), 1337 (w), 1256 (s), 1223 (vs), 1127 (vs), 1031 (vs), 906 (m), 675 (w), 597 (m).

2.2.2. Synthesis of $[\text{Pr}(\text{HL}_1)(\text{H}_2\text{L}_2)_{0.5}(\text{H}_4\text{L}_2)_{0.5}(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_{1.5}$ (**2**)

The synthetic process was the same as that of compound **1** by using PrCl_3 (0.4 mmol), H_3L_1 (0.3 mmol) and $\text{H}_4\text{L}_2 \cdot \text{HCl}$ (0.3 mmol). Light-green crystals were collected. Yield: 28% (based on H_3L_1 ligand). Calcd for $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_{14.5}\text{P}_2\text{Pr}_1\text{S}_1$: C 23.12, H 3.58, N 4.15; found: C 23.21, H 3.46, N 4.09. IR (KBr (cm^{-1})): 3436 (m, br), 3284 (w, br), 3061 (m), 1623 (m), 1584 (s), 1477 (m), 1338 (w), 1256 (s), 1213 (vs), 1126 (vs), 1031 (vs), 905 (m), 674 (w), 575 (m).

2.2.3. Synthesis of $[\text{Nd}(\text{HL}_1)(\text{H}_2\text{L}_2)_{0.5}(\text{H}_4\text{L}_2)_{0.5}(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_{1.5}$ (**3**)

The synthetic process was the same as that of compound **1** by using NdCl_3 (0.4 mmol), H_3L_1 (0.3 mmol) and $\text{H}_4\text{L}_2 \cdot \text{HCl}$ (0.4 mmol). Light-purple crystals were harvested. Yield: 60% (based on H_3L_1 ligand). Calcd for $\text{C}_{13}\text{H}_{24}\text{N}_2\text{Nd}_1\text{O}_{14.5}\text{P}_2\text{S}_1$: C 23.01, H 3.56, N 4.13; found: C 22.92, H 3.45, N 4.06. IR (KBr (cm^{-1})): 3437 (m, br), 3061 (m), 1623 (m), 1585 (s), 1479 (m), 1337 (w), 1256 (s), 1212 (vs), 1127 (vs), 1032 (vs), 906 (w), 675 (w), 576 (m).

2.2.4. Synthesis of $[\text{Sm}(\text{HL}_1)(\text{H}_2\text{L}_2)_{0.5}(\text{H}_4\text{L}_2)_{0.5}(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_{1.5}$ (**4**)

The synthetic process was the same as that of compound **1** by using SmCl_3 (0.3 mmol), H_3L_1 (0.3 mmol) and $\text{H}_4\text{L}_2 \cdot \text{HCl}$ (0.3 mmol). Light-yellow crystals were harvested. Yield: 40% (based on H_3L_1 ligand). Calcd for $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_{14.5}\text{P}_2\text{S}_1\text{Sm}_1$: C 22.80, H 3.53, N 4.09; found: C 22.87, H 3.37, N 4.06. IR (KBr (cm^{-1})): 3439 (m, br), 3062 (m), 1624 (m), 1587 (s), 1479 (m), 1333 (w), 1256 (s), 1225 (vs), 1128 (vs), 1033 (vs), 898 (w), 675 (w), 577 (m).

2.2.5. Synthesis of $[\text{Eu}(\text{HL}_1)(\text{H}_2\text{L}_2)_{0.5}(\text{H}_4\text{L}_2)_{0.5}(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_{1.5}$ (**5**)

The synthetic process was the same as that of compound **1** by using EuCl_3 (0.3 mmol), H_3L_1 (0.3 mmol) and $\text{H}_4\text{L}_2 \cdot \text{HCl}$ (0.4 mmol). Colorless crystals were harvested. Yield: 62% (based on H_3L_1 ligand). Calcd for $\text{C}_{13}\text{H}_{24}\text{Eu}_1\text{N}_2\text{O}_{14.5}\text{P}_2\text{S}_1$: C 22.75, H 3.52, N 4.08; found: C 23.03, H 3.34, N 4.07. IR (KBr (cm^{-1})): 3437 (m, br), 3063 (m), 1625 (m), 1587 (s), 1479 (m), 1336 (w), 1258 (s), 1215 (vs), 1155 (vs), 1033 (vs), 897 (w), 675 (w), 578 (m).

Table 1

Crystallographic data for compounds **1–5**.

	1	2	3	4	5
Empirical formula	$\text{C}_{52}\text{H}_{96}\text{La}_4\text{N}_8\text{O}_{58}\text{P}_8\text{S}_4$	$\text{C}_{52}\text{H}_{96}\text{Nd}_4\text{N}_8\text{O}_{58}\text{P}_8\text{Pr}_4\text{S}_4$	$\text{C}_{52}\text{H}_{96}\text{Nd}_4\text{N}_8\text{O}_{58}\text{P}_8\text{S}_4$	$\text{C}_{52}\text{H}_{96}\text{Nd}_4\text{N}_8\text{O}_{58}\text{P}_8\text{S}_4\text{Sm}_4$	$\text{C}_{52}\text{H}_{96}\text{Eu}_4\text{N}_8\text{O}_{58}\text{P}_8\text{S}_4$
Formula weight	2693.01	2701.01	2714.33	2738.77	2745.21
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
A (\AA)	22.0735(9)	22.038(5)	22.017(5)	21.9372(15)	21.9438(11)
B (\AA)	8.7489(3)	8.7018(18)	8.6870(18)	8.6546(4)	8.6446(4)
C (\AA)	23.1978(11)	23.130(5)	23.106(5)	23.0491(17)	23.0146(13)
α (deg)	90	90	90	90	90
β (deg)	98.749(3)	98.678(2)	98.628(2)	98.753(5)	98.649(2)
γ (deg)	90	90	90	90	90
V (\AA^3)	4427.8(3)	4384.9(17)	4369.4(17)	4325.1(5)	4316.1(4)
Z	2	2	2	2	2
D_c (g cm^{-3})	2.020	2.046	2.063	2.103	2.112
μ (mm^{-1})	2.245	2.541	2.696	3.038	3.230
F(000)	2680	2696	2704	2720	2728
Reflections collected/unique	14447/4617	16481/5023	16269/4894	15740/4918	14424/4905
R_{int}	0.0344	0.0306	0.0270	0.0260	0.0190
GOF on F^2	1.003	1.001	1.007	1.002	1.004
R_1 ($1 > 2\sigma(I)$) ^a	0.0565	0.0259	0.0267	0.0245	0.0249
wR_2 ($1 > 2\sigma(I)$) ^b	0.1287	0.0549	0.0569	0.0689	0.0569
R_1 (all data) ^a	0.0951	0.0306	0.0294	0.0292	0.0266
wR_2 (all data) ^b	0.2433	0.0598	0.0588	0.0883	0.0587
$\Delta\rho_{min/max}$ (e \AA^{-3})	2.359/−2.703	1.035/−0.657	1.120/−0.646	1.210/−1.176	1.275/−0.865

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$.

^b $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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

Compound 1			
La(1)–O(9)#1	2.433(9)	La(1)–O(10)	2.457(9)
La(1)–O(7)	2.463(10)	La(1)–O(12)#1	2.475(9)
La(1)–O(4)	2.540(10)	La(1)–O(2)#2	2.585(10)
La(1)–O(1)#2	2.730(12)	La(1)–O(13)	2.779(10)
La(1)–O(13)#3	2.780(10)		
Compound 2			
Pr(1)–O(7)	2.380(2)	Pr(1)–O(8)#1	2.406(2)
Pr(1)–O(10)	2.415(2)	Pr(1)–O(12)#2	2.441(2)
Pr(1)–O(4)	2.500(2)	Pr(1)–O(1)#3	2.520(2)
Pr(1)–O(2)#3	2.700(2)	Pr(1)–O(13)	2.765(2)
Pr(1)–O(13)#2	2.770(2)		
Compound 3			
Nd(1)–O(10)	2.366(2)	Nd(1)–O(11)#1	2.397(2)
Nd(1)–O(8)#1	2.399(2)	Nd(1)–O(7)	2.428(2)
Nd(1)–O(4)	2.480(2)	Nd(1)–O(1)#2	2.501(2)
Nd(1)–O(2)#2	2.689(2)	Nd(1)–O(13)#1	2.757(2)
Nd(1)–O(13)	2.763(2)		
Compound 4			
Sm(1)–O(10)	2.336(2)	Sm(1)–O(11)#1	2.361(2)
Sm(1)–O(7)	2.366(3)	Sm(1)–O(9)#2	2.399(2)
Sm(1)–O(5)#3	2.444(3)	Sm(1)–O(2)	2.472(3)
Sm(1)–O(1)	2.661(3)	Sm(1)–O(13)#1	2.722(3)
Sm(1)–O(13)	2.769(3)		
Compound 5			
Eu(1)–O(10)	2.3195(19)	Eu(1)–O(11)#1	2.353(2)
Eu(1)–O(9)#1	2.360(2)	Eu(1)–O(8)	2.391(2)
Eu(1)–O(4)	2.434(2)	Eu(1)–O(1)#2	2.453(2)
Eu(1)–O(2)#2	2.662(2)	Eu(1)–O(13)	2.709(2)
Eu(1)–O(13)#3	2.769(2)	P(1)–O(8)	1.490(2)
P(1)–O(9)	1.495(2)	P(1)–O(7)	1.584(2)
P(2)–O(11)	1.505(2)	P(2)–O(10)	1.516(2)
P(2)–O(12)	1.524(2)	O(3)–H(3A)...O(1)	2.542
N(1)–H(1A)...O(12)#3	2.610	N(2)–H(2A)...O(5)	2.904
O(7)–H(7B)...O(5)	2.616	O(13)–H(13C)...O(12)	3.153
O(13)–H(13D)...O(14)	2.866	O(14)–H(14A)...O(7)#4	3.061
O(14)–H(14B)...O(6)	2.793		

Symmetry codes: for **1** (#1) $-x+1/2, y+1/2, -z+1/2$; (#2) $-x, y, -z+1/2$; (#3) $-x+1/2, y-1/2, -z+1/2$. **2** (#1) $-x+1/2, y+1/2, -z+1/2$; (#2) $-x+1/2, y-1/2, -z+1/2$; (#3) $-x, y, -z+1/2$. **3** (#1) $-x+1/2, y+1/2, -z+1/2$; (#2) $-x, y, -z+1/2$. **4** (#1) $-x+1/2, y+1/2, -z+1/2$; (#2) $-x+1/2, y-1/2, -z+1/2$; (#3) $-x, y, -z+1/2$. **5** (#1) $-x+1/2, y-1/2, -z+1/2$; (#2) $-x, y, -z+1/2$; (#3) $-x+1/2, y+1/2, -z+1/2$; (#4) $x, y-1, z$.

2.3. X-ray crystallographic study

Crystal structure determination for compounds **2–5** were performed on a Rigaku Mercury CCD-based diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Crystal structure determination for compound **1** was performed on a Rigaku SCXmini CCD-based diffractometer. The intensity data sets were collected with the ω -scan technique and reduced by Crystal Clear software. The structure was solved by direct methods and successive Fourier difference syntheses, and refined by full-matrix least-squares on F^2 (SHELXTL Version 5.1) [42]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were refined by a riding-mode with isotropic thermal parameters fixed at 1.2-times that of the mother atoms. Crystallographic data and structure determination summaries are listed in Table 1. Selected bond lengths for compounds **1–5** are listed in Table 2.

3. Results and discussion

3.1. Crystal structure description

Single-crystal X-ray diffractions, powder X-ray diffractions (Figures S1, S2), elemental analyses and IR spectroscopic studies (Figures S3, S4) performed on complexes **1–5** reveal that they are isostructural. Therefore, compound **5** is selected and described here representatively to illustrate their detailed structures. As shown in Fig. 1, the asymmetric unit of **5** consists of one crystallographically independent Eu (III) ion, one HL_1^- ligand, one half occupied H_2L_2^- and one half occupied H_4L_2 ligands (both H_2L_2^- and H_4L_2 are centrosymmetric in the crystal structure). Eu (III) is nine-coordinated with an O_9 donor set, and the coordination geometry can be depicted as a slightly distorted monocapped square antiprism (Fig. 2). Two of the oxygen atoms come from two symmetry-related μ - H_2O molecules, one from a sulfonate group, two from a chelating carboxylate group and four from four phosphonate groups of four different phosphonate ligands. The Eu–O distances range from 2.320(1) to 2.769(2) Å, with an average value of about 2.495(5) Å. Detailed coordination modes of the ligands are shown in Scheme 1. HL_1^- ligand

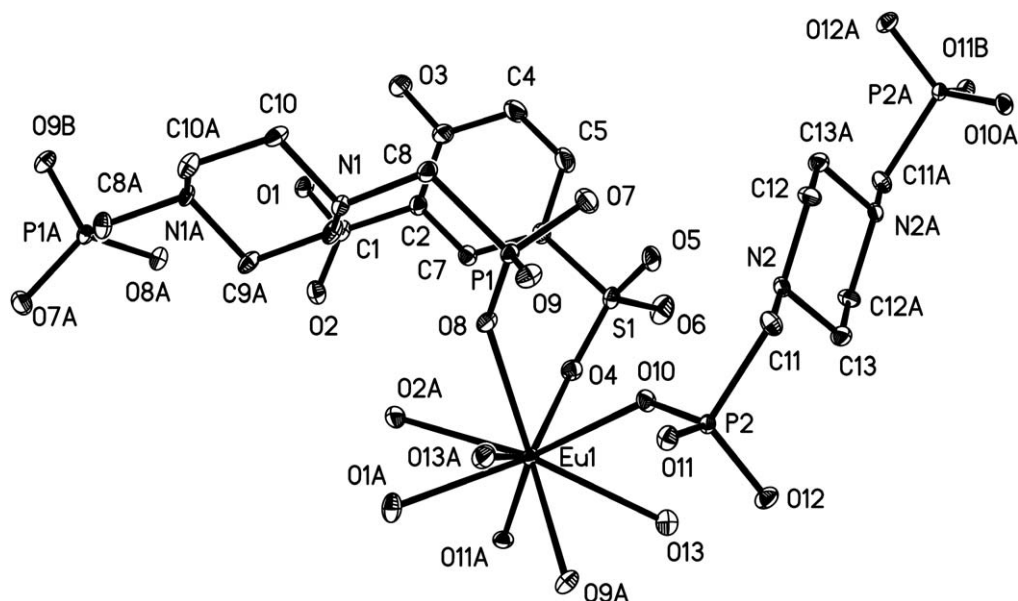


Fig. 1. ORTEP drawing of **5** with 30% probability displacement ellipsoids. Hydrogen atoms and lattice water molecules are omitted for clarity.

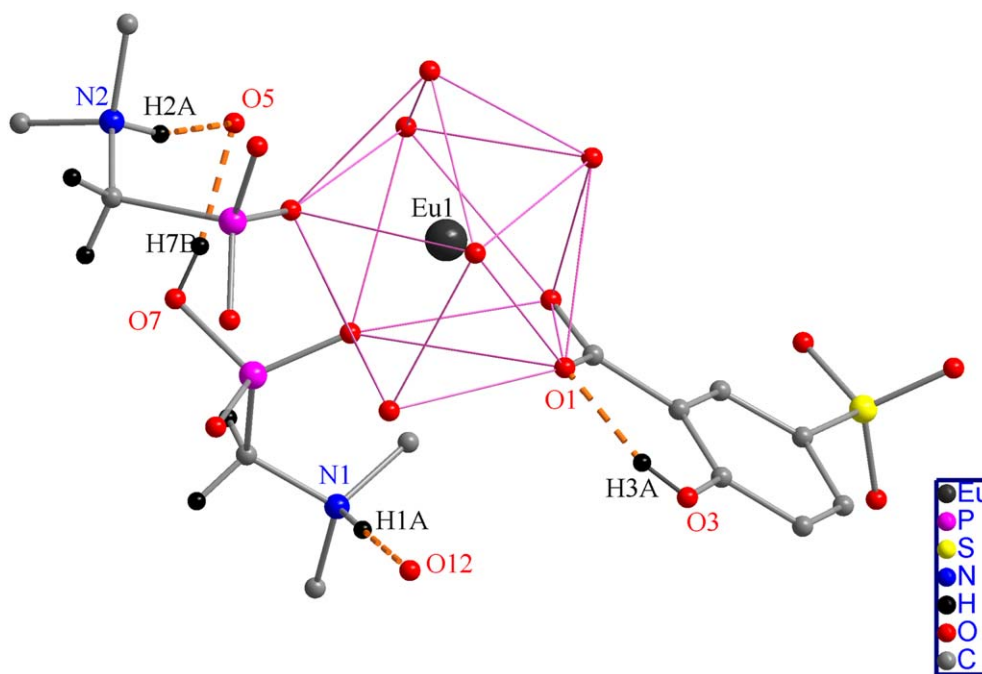
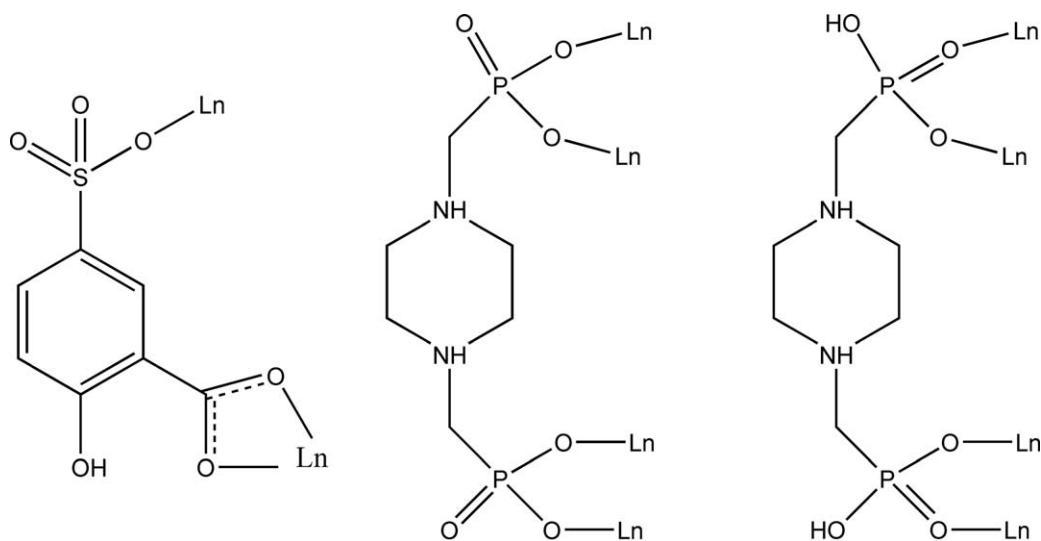


Fig. 2. View of the hydrogen bonds and the EuO_9 polyhedron in **5**.



Scheme 1. Coordination modes of the ligands observed in the crystal structure of compounds **1–5**.

coordinates to Eu (III) by one sulfonate group oxygen atom and two chelating carboxylate oxygen atoms, while the phenol hydroxyl group is free of coordination and protonated to form intra-molecular hydrogen bond with neighboring carboxylate oxygen atom (Fig. 2). Interestingly, Eu (III) is bridged by $\mu\text{-H}_2\text{O}$ and RPO_3H along b -axis forming a “zigzag” chain $\{[\text{Eu}(\mu\text{-H}_2\text{O})(\text{RPO}_3\text{H})_2]_n\}$ (Fig. 3), and adjacent chains are further linked by HL_1^- and H_4L_2 ligands along a -axis (Fig. 4) and by H_2L_2^- ligands along c -axis (Fig. 5). Therefore, each chain is surrounded by four neighboring chains and the overall structure of **5** is 3D polymeric framework (Fig. 6). The distance between adjacent Eu (III) ions within the “zigzag” chain is $5.033(1)\text{Å}$, while the shortest Eu–Eu distances between neighboring chains are $8.406(1)\text{Å}$ (along a -axis) and $11.665(5)\text{Å}$ (along c -axis). Considering the overall charge balance requirements, all the tertiary N atoms and

one of the RPO_3 group must be protonated. Additional evidences can also be found from hydrogen bonds (Fig. 2). Detailed hydrogen bond parameters are listed in Table 2. Evidences for the location of the P–O–H moiety: (a) O(7) is not coordinated to the metal center; (b) P(1)–O(7) bond length is $1.584(2)\text{Å}$, significantly longer than those of the other five P–O bonds ($1.490(2)$ – $1.524(2)$); (c) strong hydrogen bond interaction with oxygen atom from the sulfonate group (O(7)...O(5) = 2.616Å).

3.2. Vibrational spectroscopic study and thermogravimetric analysis

The FT-IR spectra of these compounds (see Figures S3, S4) exhibit very similar absorption bands, in good agreement with the single crystal structure analysis. The absorption bands in the

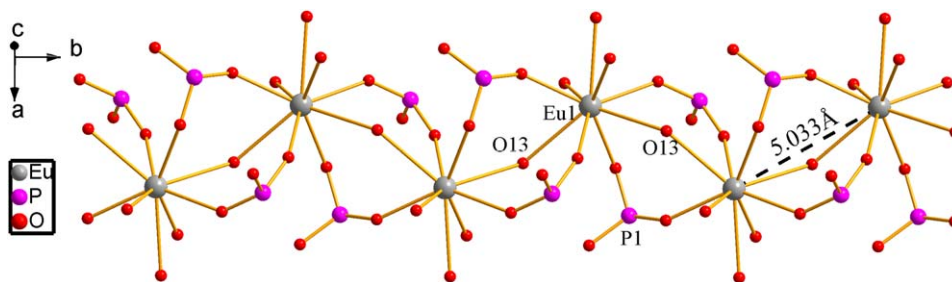


Fig. 3. RPO_3H and $\mu\text{-H}_2\text{O}$ bridged "zigzag" chain $[\text{Eu}(\mu\text{-H}_2\text{O})(\text{RPO}_3\text{H})_2]_n$ extending along b -axis.

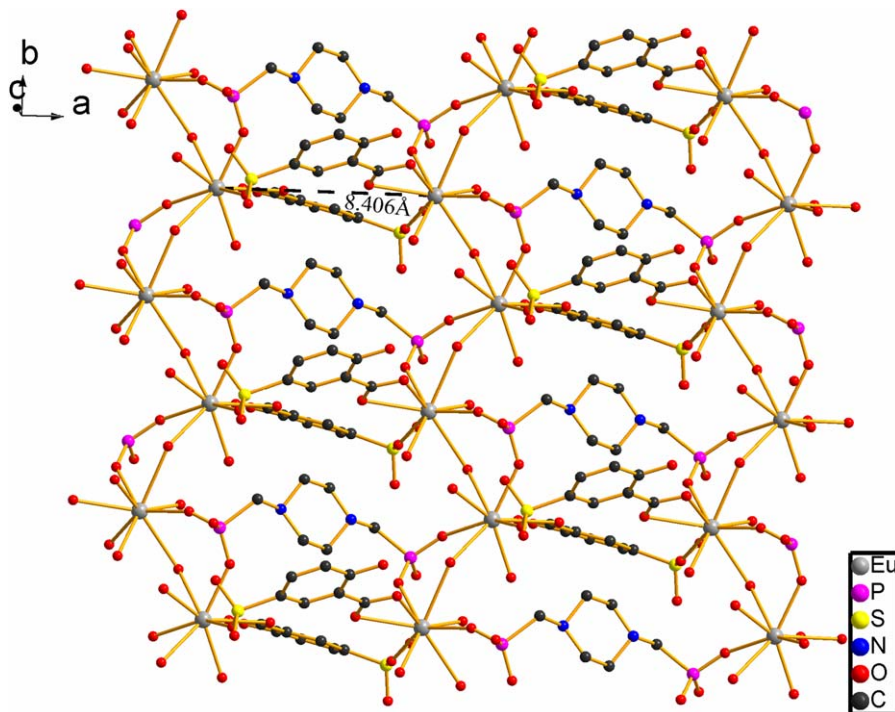


Fig. 4. Linkage of adjacent $[\text{Eu}(\mu\text{-H}_2\text{O})(\text{RPO}_3\text{H})_2]_n$ chains by HL_2^- and H_4L_2 ligands along a -axis into 2D layer.

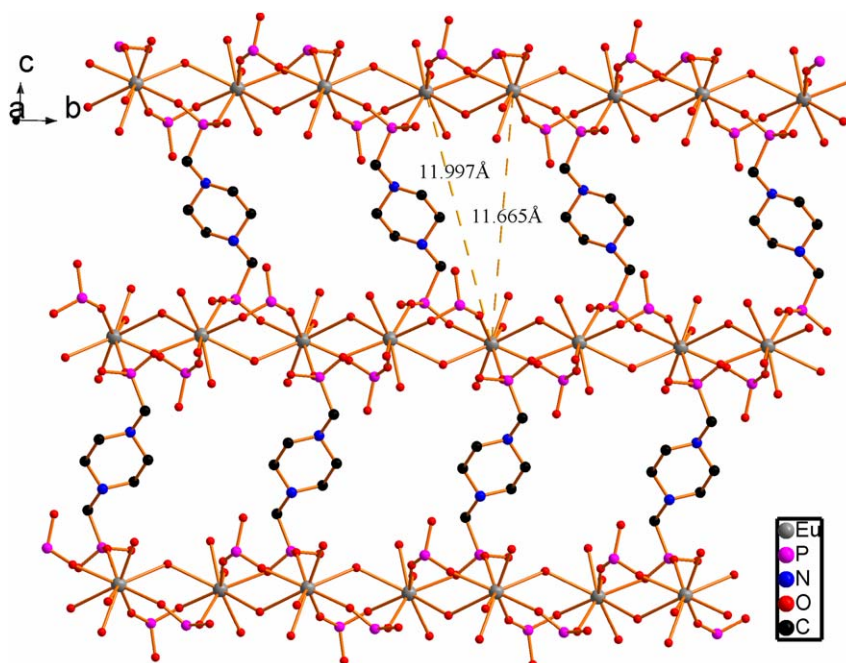


Fig. 5. Linkage of adjacent $[\text{Eu}(\mu\text{-H}_2\text{O})(\text{RPO}_3\text{H})_2]_n$ chains by H_2L_2^- ligands along c -axis into 2D layer.

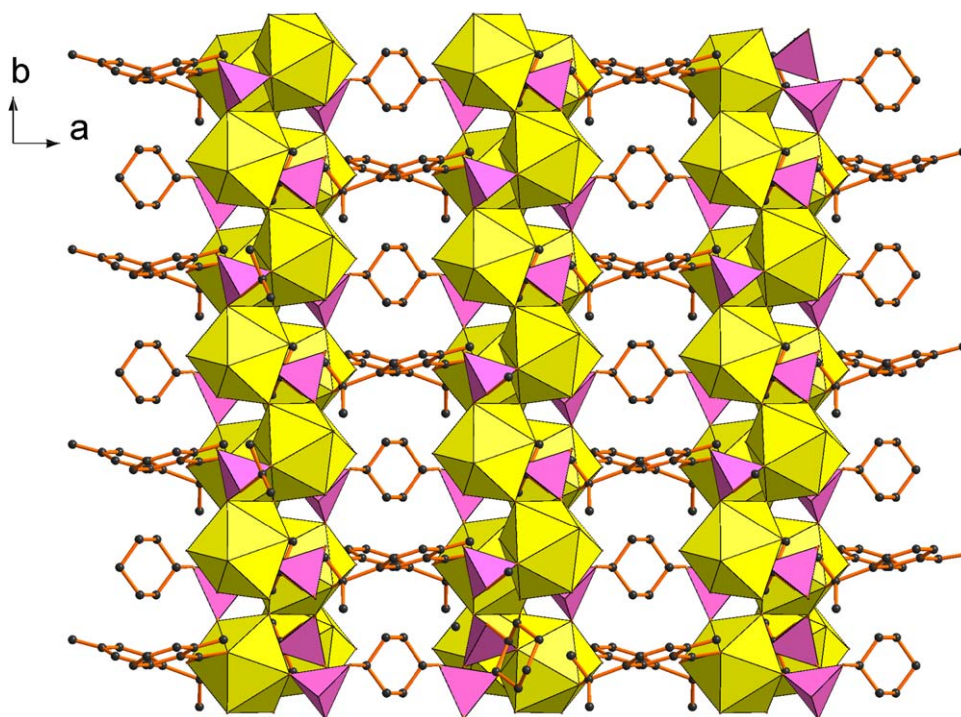


Fig. 6. View the 3D framework structure of **5** along *c*-axis. EuO_9 are represented as yellow polyhedra; PCO_3 are represented as pink tetrahedra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

range of $3280\text{--}3640\text{ cm}^{-1}$ are due to the presence of intermolecular hydrogen bonds of the phenol hydroxyl groups, intra-molecular hydrogen bonds of the $(\text{CH}_2)_3\text{NH}^+$ groups and the $\text{CH}_2\text{PO}_3\text{H}^-$ groups and water molecules in the structure. The strong peaks at 1624 cm^{-1} for all the compounds are attributed to the asymmetric stretching vibration of the carboxylic groups, while the symmetric stretching vibration peaks appear at 1479 cm^{-1} . The difference between ν_{as} and ν_{s} is about 145 cm^{-1} , which is significantly smaller than 200 cm^{-1} , indicating the chelating mode of the carboxylic groups [43]. As compared to the coordinated carboxylate group, the ν_{as} and ν_{s} difference of the protonated carboxylate group in the free ligand was observed to be ca. 205 cm^{-1} (see Figure S3). The strong absorptions in the region $1030\text{--}1260\text{ cm}^{-1}$ for all the complexes are the typical stretching vibration of the sulfonate groups ($\nu_{\text{O}=\text{S}=\text{O}}$).

The thermal stabilities of compounds **3**, **4** and **5** were examined by thermogravimetric analysis in an N_2 atmosphere from 40 to 1000°C . Their TGA curves display two main steps of weight losses (Figure S5). The weight losses from 70 to 180°C were observed to be about 5.6% (**3**), 4.5% (**4**) and 5.0% (**5**), corresponding to the release of the lattice water molecules and parts of the coordinated water molecules. The second step covers a temperature range of $180\text{--}360^\circ\text{C}$, during which the curves showed stable plateau and no weight losses happened. Upon further heating, a sharp drop in weight was observed in the temperature range of $366\text{--}403^\circ\text{C}$, which represented the partial combustion of the ligands. The observed weight losses are 26.9% (**3**), 25.6% (**4**) and 23.7% (**5**). Then the compounds continued to decompose slowly above this temperature and complete decomposition were not achieved until above 1000°C , which has also been observed in other lanthanide phosphonates [33]. It can also prove the unusual thermal stability of the M–O–P bonds. The total weight losses in the range of $40\text{--}1000^\circ\text{C}$ are about 49% (**3**), 48.5% (**4**) and 51.4% (**5**), and the final residues are not identified.

3.3. Photoluminescence properties

Considering the well-known luminescent properties of Eu (III) in the visible region and Nd (III) in the near-infrared region, the solid-state luminescent spectra of compounds **5** and **3** were measured at room temperature. As shown in Fig. 7, compound **5** exhibits very strong and characteristic emission spectrum of Eu (III) ions upon the excitation at 394 nm . The emission bands occurring at 587 (m) , 613 (vs) , 651 (w) , 698 nm (s) can be assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($J = 1, 2, 3, 4$). It is well-known that the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu (III) ion is electric-dipole (ED) and very sensitive to site symmetry, while the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is magnetic-dipole (MD) and insensitive to site symmetry [44]. The intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is about 4 times stronger than that of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, indicating the absence of an inversion center at the Eu (III) site, in good consistency with the result of the single crystal X-ray diffraction analysis. In addition, the triple splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition has also suggested the low symmetry site of the Eu (III) ion. Another interesting characteristic feature of **5** is the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition, which has the second strongest intensity in the visible region. And this indicates the hypersensitivity to the low site symmetry in the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition rather than the $^5\text{D}_0 \rightarrow ^7\text{F}_3$ transition [45]. Under the excitation at 310 nm , compound **3** displays the characteristic emission bands for neodymium (III) ion: a middle emission band at 892 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$), a strong emission band at 1059 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$), and a weak band at 1349 nm ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$) in the near-infrared region (Fig. 8). They are in agreement with the previously reported emission spectra of Nd (III) compounds [30,34,46]. The luminescence decay curve of **5** was recorded at room temperature. The decay curve is well consistent to a single-exponential function ($I = I_0 \exp(-t/\tau)$), indicating the occupation of the same local environment of the Eu (III) site in the structure, namely, there is only one Eu (III) ion in the asymmetric unit [47,48]. The corresponding lifetime for **5** is about 0.57 ms (determined by monitoring the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition line).

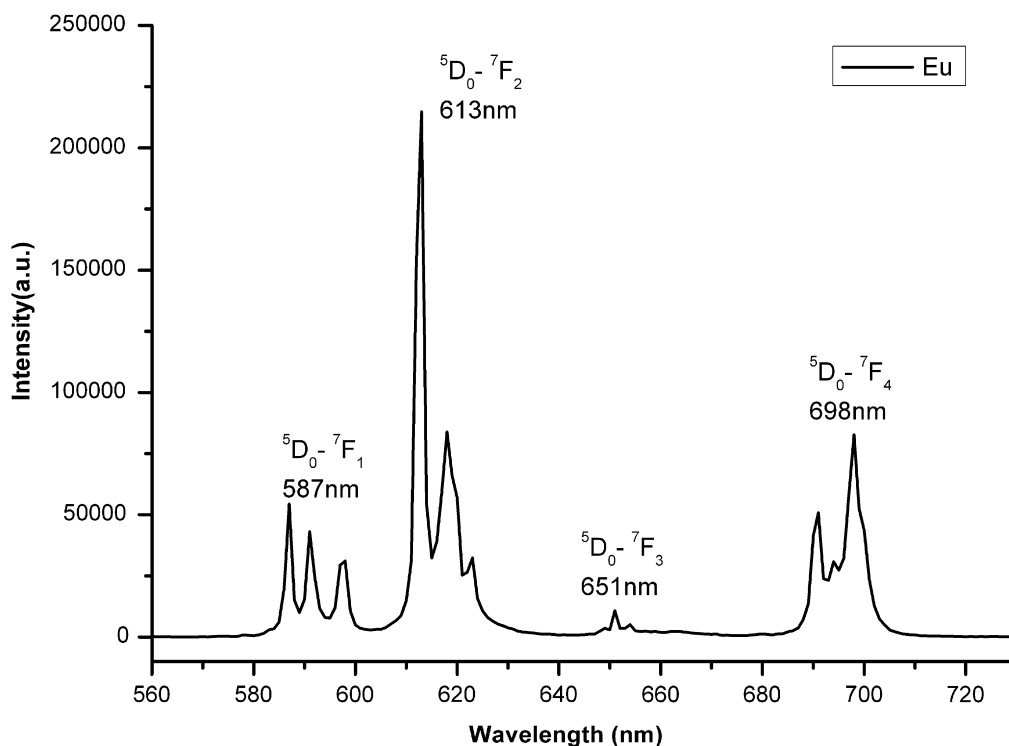


Fig. 7. Solid-state emission spectrum for **5** at room temperature (excitation at 394 nm).

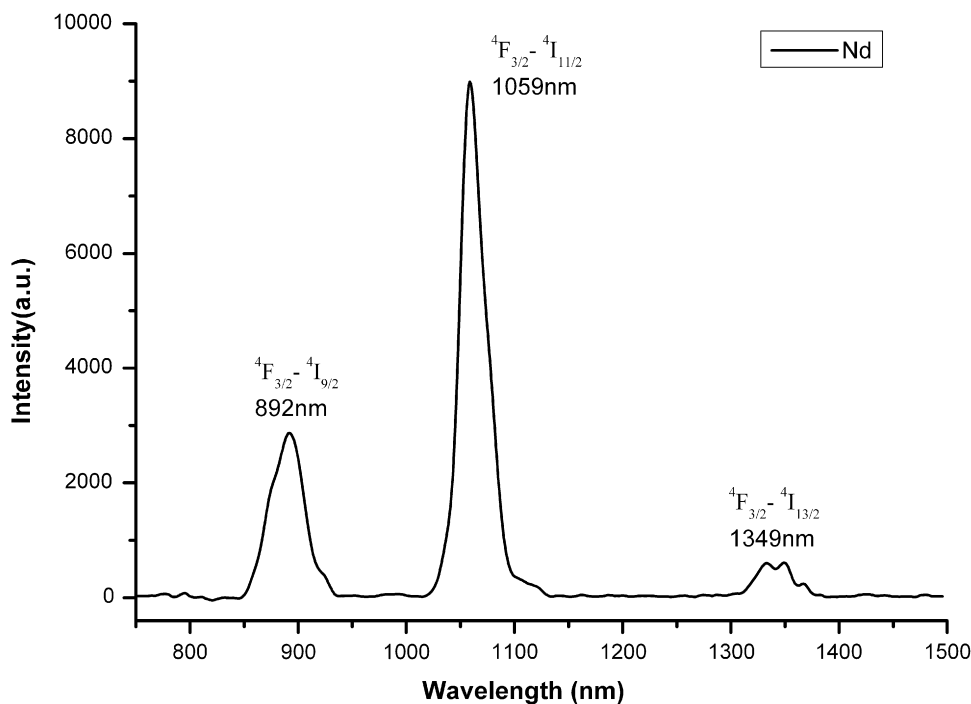


Fig. 8. Solid-state emission spectrum for **3** at room temperature (excitation at 310 nm).

4. Conclusions

Five lanthanide-organic framework architectures have been synthesized by the synergistic coordination of 5-sulfosalicylic acid and *N,N'*-piperazine (bis-methylene phosphonic acid) with *Ln* (III) ions under hydrothermal conditions. They represent an unusual kind of multi-functional ligands supported 3D lanthanide coordination polymers. There are four kinds of functional groups in

the structure, namely, phosphonate, sulfonate, carboxylate and phenol hydroxyl groups. It is undoubtedly that it can provide an enlightening idea in preparing multi-functional materials. Compounds **5** and **3** exhibited strong solid-state emissions in the visible and near-infrared region at room temperature. The results proved that **3** may be used as fluorescent probes and near-IR emitters, while **5** can be a good candidate for red light emitting luminescent materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.06.015.

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