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PAPER

Highly-thermostable lanthanide–organic coordination frameworks with *N*-protonated 2,6-dihydroxypyridine-4-carboxylate exhibiting unusual 3-D mixed-connected network topology†

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A series of three-dimensional (3-D) lanthanide–organic frameworks (LnOFs), with the general formula $[\text{Ln}_2(\text{H-L})_3(\text{H}_2\text{O})]_\infty$ (H-L = *N*-protonated 2,6-dihydroxypyridine-4-carboxylate; Ln^{III} = La^{III} for **1**, Pr^{III} for **2**, Nd^{III} for **3**, and Sm^{III} for **4**), have been synthesized under hydrothermal conditions. X-Ray diffraction and energy dispersive X-ray spectroscopy (EDS) analyses reveal that complexes **1–4** are isostructural and exhibit the unique 3-D coordination framework with (4,5,7)-connected network topology, in which the H-L ligands adopt the μ_4 - and μ_5 -bridging fashions. Remarkably, thermogravimetric analysis of the crystalline materials shows their exceptionally high thermal stability (up to 530 °C), which should originate from the dense nature of the packing lattices and the unusual network structures.

Introduction

By virtue of a feasible synthesizing strategy of crystal engineering,¹ a large number of coordination polymers (CPs) based on lanthanide metals,^{2,3} that is, lanthanide–organic frameworks (LnOFs), have been rationally designed and constructed. This flourishing field has paved the way for a sound junction between their attractive network structures⁴ and their potential applications, mainly in magnetism,^{5,6} luminescence,^{7,8} gas adsorption,⁹ catalysis,¹⁰ non-linear optics,¹¹ electroluminescence,¹² and thermostability materials.^{9c,13,14} Basically, these structural patterns and the associated properties rest with the deliberate choice of organic bridging ligands with adjustable binding nature and metal ions/clusters with pre-designed coordination geometry.^{2–14}

In this context, it becomes more crucial and practical to realize some primary laws on the structure–property correlations of such crystalline solids.¹⁵

As is well known, lanthanide metals normally show stronger affinity to *O*-donor ligands and flexible coordination numbers/geometries, compared with the d-block transition metal ions.^{2,3} In this regard, a type of organic ligand with three carboxyl and/or hydroxyl groups arranged in 1,3,5- or *meta*-fashion around the central aromatic group, such as pyridine-2,4,6-tricarboxylic acid (H₃ptc, see Scheme S1, ESI†), 4-hydroxypyridine-2,6-dicarboxylic acid (H₃hpdc),¹⁷ 5-hydroxy-1,3-benzenedicarboxylic acid,¹⁸ and 3,5-dihydroxybenzoic acid,¹⁹ have been widely used to prepare various LnOFs.^{16–19} However, the relevant study on 2,6-dihydroxypyridine-4-carboxylic acid (H₃L, see Scheme S1, ESI†), as a comparable ligand of H₃ptc and H₃hpdc, has received less attention so far, although it may show different binding features to construct novel coordination architectures.

Very recently, we have reported a series of Ln^{III}–H–L coordination frameworks $[\text{Ln}_2(\text{H-L})_3(\text{H}_2\text{O})_4]_\infty$ (Ln = Dy^{III}, Gd^{III}, Tb^{III}, Eu^{III}, and Ho^{III}, H–L = *N*-protonated 2,6-dihydroxypyridine-4-carboxylate), which exhibit the trinodal (3,4,5)-connected net topology and interestingly ferromagnetic behaviors.²⁰ Significantly, the H₃L ligand is present as a negative bivalent H–L style (see Chart 1) in these resulting LnOFs, which results in the different coordination modes and bridging directions of this tecton in comparison with H₃ptc and H₃hpdc, and thus the distinct coordination networks. As part of our ongoing effort on the design and synthesis of LnOFs crystalline materials, we report here four isostructural Ln^{III}–H–L coordination polymers based on lanthanide salts of light rare earth ions, with the general

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† Electronic supplementary information (ESI) available: Chemical structures of H₃L and the related ligands H₃ptc and H₃hpdc (Scheme S1), coordination modes of H–L in **1–4** (Scheme S2), comparison of PXRD patterns for **1–4** (Fig. S1), additional structural figures for **1** and **4** (Figs. S2–S5), TG curve for H₃L (Fig. S6) and **2–4** (Figs. S7–S8), comparison of PXRD patterns at different temperatures for **2–4** (Fig. S9), SEM images of **1** based on the samples treated at different temperatures (Fig. S10), and the emission and excitation fluorescent spectra of **1–4** (Fig. S11) and the H₃L ligand (Fig. S12). CCDC reference numbers 778311, 821513, 832151 and 832152. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ce05465a

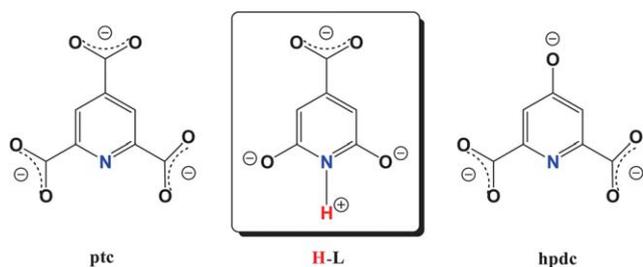


Chart 1

formula $[\text{Ln}_2(\text{H-L})_3(\text{H}_2\text{O})]_\infty$ ($\text{Ln}^{\text{III}} = \text{La}^{\text{III}}$ for **1**, Pr^{III} for **2**, Nd^{III} for **3**, and Sm^{III} for **4**). Of particular importance, the unusual network topology and extremely high thermal stability of such LnOFs materials have also been presented and discussed in detail.

Experimental section

Materials and general methods

All the starting reagents and solvents for synthesis were commercially available and used as received without further purification. Elemental analyses of C, H, and N were performed on a Vario EL III Elemental analyzer. IR spectra were recorded in the range of 4000–400 cm^{-1} on a Bruker Tensor 27 OPUS FT-IR spectrometer with KBr pellets. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer ($\text{Cu-K}\alpha$, $\lambda = 1.54056 \text{ \AA}$) at 40 kV and 100 mA, by using a Cu-target tube and a graphite monochromator. The powder samples were prepared by crushing the single-crystal (**1** and **4**) or microcrystalline (**2** and **3**) products and the intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 3° to 80° with a step size of 0.02° and a scan speed of 8° min^{-1} . Simulation of the PXRD patterns of **1** and **4** was taken by the single-crystal data and diffraction-crystal module of Mercury (Hg). Thermogravimetric and differential thermal analysis (TG-DTA) experiments were carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 1000°C at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. The morphology and composition of these materials were characterized by a JEOL-JSM-6700F field-emission scanning electron microscope (SEM) at an acceleration voltage of 10.0 kV and equipped with an energy dispersive X-ray spectroscopy (EDS). The emission and excitation fluorescent spectra were recorded on an F-7000 (Hitachi) spectrophotometer at room temperature in solid state.

Preparation of LnOFs 1–4

$[\text{La}_2(\text{H-L})_3(\text{H}_2\text{O})]_\infty$ (1**).** A mixture of La_2O_3 (0.3 mmol, 0.0977 g) and 2,6-dihydroxypyridine-4-carboxylic acid (H_3L , 0.3 mmol, 0.0465 g) in distilled water (12 mL) was placed in a 25-mL-capacity stainless steel reactor with a Teflon liner, heated at 140°C for 3 days, and then cooled to room temperature at a rate of 5°C h^{-1} . Light yellow single crystals of **1** suitable for X-ray diffraction were obtained by filter, washed thoroughly with distilled water–ethanol–diethyl ether, and dried in air. Yield: $\sim 40\%$ (based on H_3L). Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{La}_2\text{N}_3\text{O}_{13}$: C,

28.63; H, 1.47; N, 5.56%. Found: C, 28.79; H, 1.38; N, 5.73%. IR (cm^{-1}): 3429(m, br), 3220(m, br), 3089(m), 1631(vs), 1500(w), 1461(s), 1439(s), 1382(m), 1300(s), 1268(w), 1239(m), 1188(m), 1129(w), 1101(w), 1047(w), 994(m), 957(w), 915(w), 885(w), 869(w), 837(m), 777(s), 727(w), 641(w), 617(m), 563(m), 531(w), 450(w), 411(m).

$[\text{Pr}_2(\text{H-L})_3(\text{H}_2\text{O})]_\infty$ (2**).** The same procedure as that for **1** was used with the exception of using Pr_2O_3 (0.3 mmol, 0.0989 g) instead of La_2O_3 , forming light yellow microcrystalline precipitates. Yield: $\sim 50\%$ (based on H_3L). Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{Pr}_2\text{N}_3\text{O}_{13}$: C, 28.48; H, 1.46; N, 5.54%. Found: C, 28.61; H, 1.55; N, 5.67%. IR (cm^{-1}): 3426(m, br), 3220(m), 3214(m), 3092(m), 1631(vs), 1494(m), 1459(s), 1437(s), 1302(m), 1239(m), 1189(m), 1099(w), 1042(w), 994(w), 962(w), 912(w), 886(w), 837(m), 778(m), 688(w), 614(m), 564(m), 516(w), 465(w), 414(m).

$[\text{Nd}_2(\text{H-L})_3(\text{H}_2\text{O})]_\infty$ (3**).** The same procedure as that for **1** was used with the exception of using Nd_2O_3 (0.3 mmol, 0.1009 g) instead of La_2O_3 , forming light yellow microcrystalline precipitates. Yield: $\sim 30\%$ (based on H_3L). Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{Nd}_2\text{N}_3\text{O}_{13}$: C, 28.23; H, 1.45; N, 5.49%. Found: C, 28.34; H, 1.57; N, 5.64%. IR (cm^{-1}): 3444(m, br), 3215(m), 3094(m), 1635(vs), 1500(w), 1458(s), 1438(s), 1381(w), 1300(m), 1271(w), 1240(m), 1191(m), 1131(w), 1103(w), 1046(m), 996(w), 961(w), 917(w), 886(w), 839(m), 778(m), 690(w), 618(m), 567(m), 514(w), 466(w), 417(m).

$[\text{Sm}_2(\text{H-L})_3(\text{H}_2\text{O})]_\infty$ (4**).** The same procedure as that for **1** was used with the exception of using Sm_2O_3 (0.3 mmol, 0.1046 g) instead of La_2O_3 . Light yellow crystals of **4** were obtained in $\sim 30\%$ yield (based on H_3L). Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{Sm}_2\text{N}_3\text{O}_{13}$: C, 27.79; H, 1.43; N, 5.40%. Found: C, 27.94; H, 1.59; N, 5.64%. IR (cm^{-1}): 3451(m, br), 3210(m), 3096(m), 1632(vs), 1441(s), 1381(w), 1300(m), 1239(m), 1192(m), 1102(w), 1046(w), 995(w), 842(m), 777(m), 621(w), 567(m), 409(w), 417(m).

X-Ray data collection and structure determination

Single-crystal X-ray diffraction data for **1** and **4** and their dehydrated phases **1'** and **4'** were collected on a Bruker Smart 1000 CCD area-detector diffractometer at 294(2) K with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by ω scan mode. The program SAINT²¹ was used for integration of the diffraction profiles and a semi-empirical absorption correction was applied by SADABS program.²² The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.²³ Metal ions in each structure were located from the *E*-maps, and the other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . Crystallographic data and structural refinement details for **1** and **4** are summarized in Table 1.

Results and discussion

Synthesis and characterization

A hydrothermal synthesis method²⁴ was used to prepare **1–4** due to the poor solubility of H_3L in common solvents. Suitable single-crystal products cannot be obtained from the reactions of

Table 1 Crystallographic data and structure refinement summary for complexes **1** and **4**

	1	4
Empirical formula	C ₁₈ H ₁₁ La ₂ N ₃ O ₁₃	C ₁₈ H ₁₁ Sm ₂ N ₃ O ₁₃
Formula weight	755.12	778.00
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2/c</i>	<i>P2/c</i>
<i>a</i> /Å	6.6641(2)	6.5605(7)
<i>b</i> /Å	7.7528(3)	7.6743(8)
<i>c</i> /Å	19.6619(7)	19.351(2)
β (°)	109.750(3)	108.709(9)
<i>V</i> /Å ³	956.08(6)	922.79(17)
<i>Z</i>	2	2
<i>D</i> /g cm ⁻³	2.623	2.800
μ /mm ⁻¹	4.496	6.393
Crystal size/mm	0.28 × 0.19 × 0.18	0.28 × 0.21 × 0.19
<i>F</i> (000)	716	736
Range of <i>h, k, l</i>	−6/7, −9/7, −23/18	−7/5, −8/9, −22/22
Reflections collected/unique/observed	3328/1683/1256	3127/1619/1147
Max. & min. transmission	0.4983 & 0.3658	0.3764 & 0.2676
<i>R</i> _{int}	0.0302	0.0400
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0228/0.0304	0.0316/0.0498
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (all data)	0.0386/0.0312	0.0605/0.0527
Largest diff. peak & hole/e Å ⁻³	0.597 & −0.586	0.936 & −0.799

$$^a R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|, \quad ^b wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)]^{1/2}.$$

H₃L with Ln(NO₃)₃ by trial and error. Generally, when lanthanide oxide (Ln₂O₃) was used in the synthetic system, the lanthanide ions will be released more slowly *via in situ* Lewis acid–base reactions with the acidic organic ligands, which may be helpful for the growth of single crystals. Considering this point, Ln₂O₃ were used to react with H₃L under hydrothermal conditions, and well-shaped single crystals for **1** (La^{III}) and **4** (Sm^{III}) were successfully isolated. Unfortunately, only microcrystalline products were obtained for **2** (Pr^{III}) and **3** (Nd^{III}). Nevertheless, it can be concluded that all complexes **1–4** are isomorphous in nature, as confirmed by their uniform PXRD patterns (see Fig. S1, ESI†).

To further clarify the compositions of **2** and **3**, energy dispersive X-ray spectrometry (EDS) measurements were performed on a scanning electron microscope (SEM). The SEM and EDS results of the microcrystalline surfaces of **2** and **3** are depicted in Fig. 1. The mean values for the detected surface atom ratios for **2** and **3** related to C, O, N, and Pr/Nd are 28.28/28.32%, 28.75/28.09%, 5.22/5.05%, and 37.75/38.53%, respectively (selecting different surface sites time after time), which also agree well with the calculated results (C₁₈Pr₂N₃O₁₃/C₁₈Nd₂N₃O₁₃: C, 28.90/28.65; O, 27.81/27.56; N, 5.62/5.57; Pr/Nd, 37.67/38.22%).

Complexes **1–4** are air stable and insoluble in common organic solvents and water. The IR spectra usually show features attributable to each component of the complexes.²⁵ In the IR spectra of **1–4**, the broad peaks centered at *ca.* 3200 cm⁻¹ (3220 cm⁻¹ for **1**, 3220 cm⁻¹ for **2**, 3215 cm⁻¹ for **3**, and 3210 cm⁻¹ for **4**) indicate the O–H stretching vibration of water. In fact, the IR absorption of carboxylate is very complicated due to its coordination diversity.^{25,26} The characteristic bands of carboxylate groups in **1–4** appear at 1631–1635 cm⁻¹ and 1437–1461 cm⁻¹ for antisymmetric and symmetric stretching vibrations, respectively.²⁶ The $\Delta\nu$ [$\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$] values are 170 and 192 cm⁻¹ for **1**, 172 and 194 cm⁻¹ for **2**, 177 and 198 cm⁻¹ for **3**, and 191 cm⁻¹ for **4**. These results indicate that the carboxylate

groups in **1–4** are coordinated to the Ln^{III} ions in the same bridging fashion,²⁶ as observed in the crystal structures (see Scheme S2, ESI†). Also, the absence of the characteristic band at *ca.* 1700 cm⁻¹ confirms the complete deprotonation of carboxyl for the ligands in **1–4**,²⁷ which is in good agreement with their solid state structural features.

Structural description for LnOFs **1** and **4**

[Ln₂(H–L)₃(H₂O)]_∞ [Ln = La (**1**) and Sm (**4**)]. Single-crystal X-ray diffraction of **1** and **4** indicates that they are isostructural and crystallize in space group *P2/c* (see Table 1). Thus, only the crystal structure of **1** is described herein as a representative example. The structure of **1** is a very complicated 3-D coordination network, the asymmetric unit of which contains one La^{III} ion, one and a half H–L ligands, and half a disordered water molecule (see Fig. 2). The La^{III} center is eight-coordinated to three carboxylates and four ionized hydroxyls from different H–L ligands as well as one water molecule, taking a distorted square antiprism geometry.^{16e,28,29} All La–O distances and the bond angles around La^{III} are typical and comparable to those observed in the literature.^{16,17,30} For H–L in the network of **1**, there exist two different types of carboxyl/hydroxyl coordination modes with La^{III} (see Fig. 3 and Scheme S2, ESI†). One is the μ_5 -bridging type that uses all of its four O atoms of H–L (two carboxylate oxygen and two hydroxyl oxygen) to bridge five distinct La^{III} centers by μ_2 - η^1 : η^1 -*syn-syn* bridging carboxylate as well as μ_1 -monodentate/ μ_2 -bidentate bridging hydroxyls (see Fig. 3 and Scheme S2a, ESI†). The other is a μ_4 -bridging type that links four different La^{III} ions by μ_2 - η^1 : η^1 -*syn-syn* bridging carboxylate and two μ_1 -monodentate hydroxyl groups (see Fig. 3 and Scheme S2b, ESI†). Two μ_2 -bridging ionized hydroxyl groups from two different H–L ligands link two La^{III} ions to form a planar four-membered La1–O3B–La1K–O3D ring (see Fig. 4) with the non-bonding La1⋯La1K separation of 4.321(4) Å

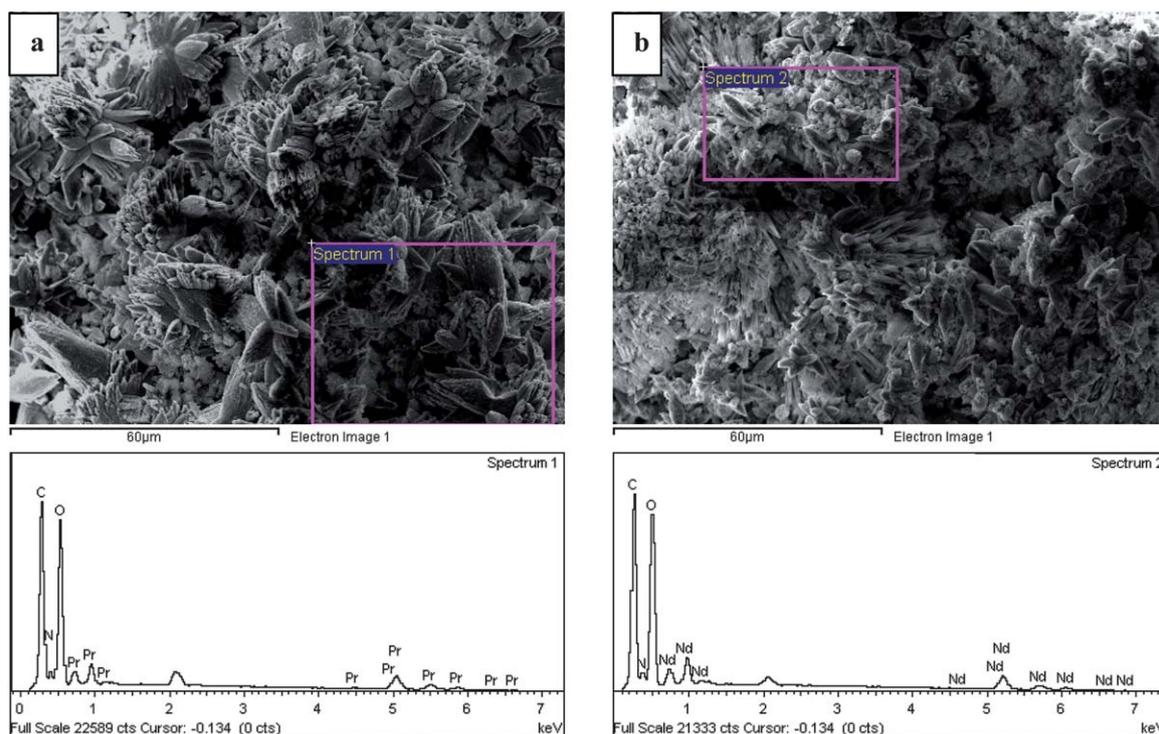


Fig. 1 SEM images and EDS patterns of (a) **2** and (b) **3**.

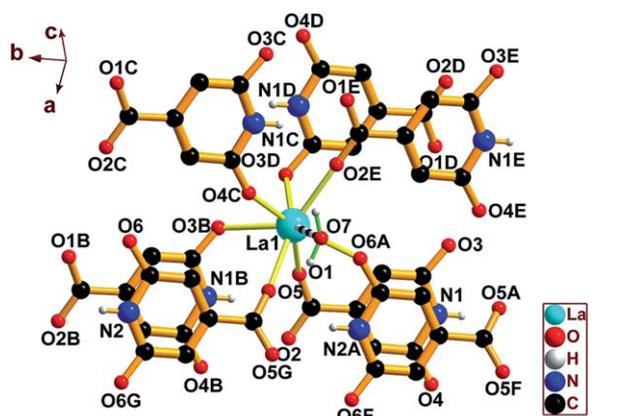


Fig. 2 Local coordination environment of La^{III} in **1**, in which the $\text{La}-\text{O}_{\text{water}}$ bond is shown as striped bond. Symmetry codes: A = $x, y - 1, z$; B = $x, y + 1, z$; C = $x - 1, y + 1, z$; D = $-x + 1, -y - 1, -z$; E = $x - 1, y, z$; F = $-x + 1, y - 1, -z - 1/2$; G = $-x + 1, y, -z - 1/2$.

(B = $x, y + 1, z$; D = $-x + 1, -y - 1, -z$; K = $-x + 1, -y, -z$). The adjacent La^{III} dinuclear subunits are further interlinked through the H-L ligands to afford 1-D motifs along the [100], [010], and [001] directions, respectively (see Fig. S4, ESI †), and then an overall 3-D coordination network (see Fig. 4).

Analysis of network topology provides a possible method in directing the syntheses and describing the resulting crystal structures of new materials, especially those with complicated coordination and/or H-bonding networks.^{4,31} To clearly describe the 3-D structure of **1**, a proper reduction to the underlying topological network is required. In this regard, the μ_5 -H-L and μ_4 -H-L ligands will be regarded as 5-connected and 4-connected

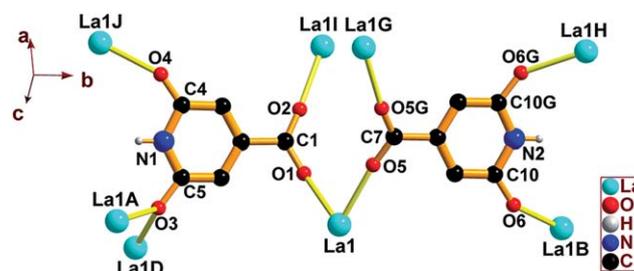


Fig. 3 Coordination modes of the H-L ligands in **1**: μ_2 - η^1 : η^1 -*syn-syn* bridging mode for O1-C1-O2 and O5-C7-O5G carboxylate groups, μ_1 -monodentate mode for O4, O6, and O6G hydroxyl groups, and μ_2 -bridging mode for O3 hydroxyl group. Symmetry codes: A = $x, y - 1, z$; B = $x, y + 1, z$; D = $-x + 1, -y - 1, -z$; G = $-x + 1, y, -z - 1/2$; H = $-x + 1, y + 1, -z - 1/2$; I = $x + 1, y, z$; J = $x + 1, y - 1, z$.

nodes, respectively, in a 2 : 1 chemometrics ratio (see Fig. S5a and Fig. S5b, ESI †). Each La^{III} ion is connected to five μ_5 -H-L plus two μ_4 -H-L ligands and, thus, can be viewed as a 7-connected node (see Fig. S5c, ESI †). As a consequence, the 3-D coordination framework of **1** can be properly assigned to a trinodal (4,5,7)-connected topological net (see Fig. 5) with the point symbol of $(4^4.6^2)(4^8.6^2)(4^{13}.6^8)_2$. A careful examination of the RCSR,⁴⁸ EPINET,^{31a} and TOPOS^{31b} databases reveals that the topological network of **1** is unprecedented so far.

Thermal behavior of LnOFs 1-4

LnOFs **1-4** are air stable and can retain the crystalline integrity at ambient conditions for a long time. The thermal stability of **1-4** was studied by TG-DTA experiments, which is an important

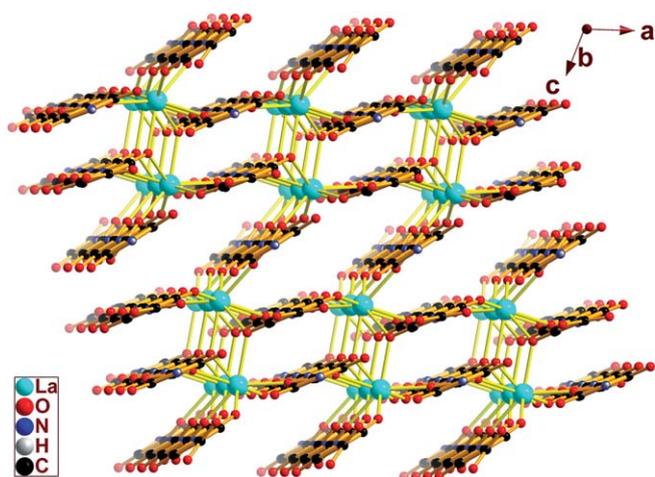


Fig. 4 3-D network of **1** viewed along [010]. For clarity, the disordered water molecules were omitted.

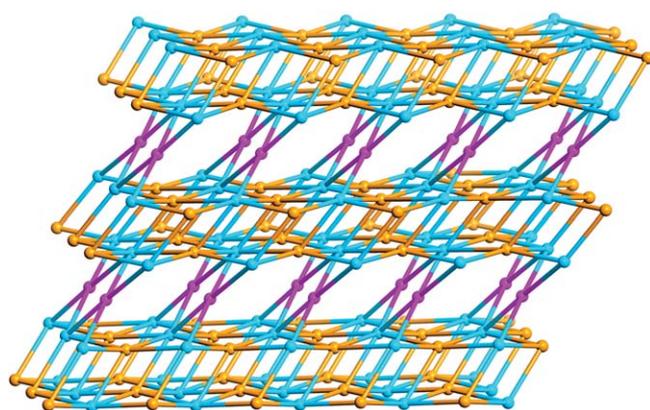


Fig. 5 Schematic representation of the trinodal (4,5,7)-connected topological network of **1** with the point symbol of $(4^4.6^2)(4^8.6^2)_2(4^{13}.6^8)_2$. Color codes: cyan spheres for La^{III} ions; pink spheres for μ_4 -H₃-L ligands; and orange spheres for μ_5 -H₃-L ligands.

parameter for metal-organic frameworks (MOFs) materials.^{9a,13,14} In fact, the experimental results show the similar thermal behaviors of **1–4** due to the isostructural nature of these

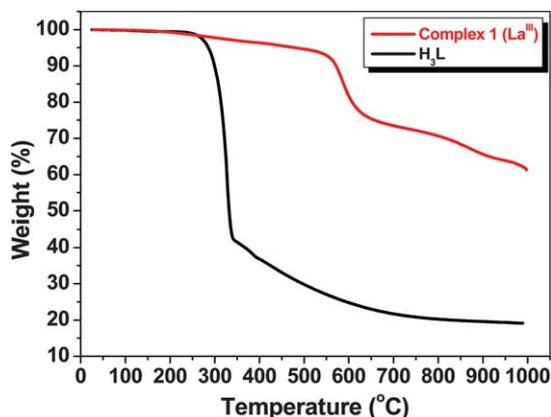


Fig. 6 TG curves for H₃L and **1**.

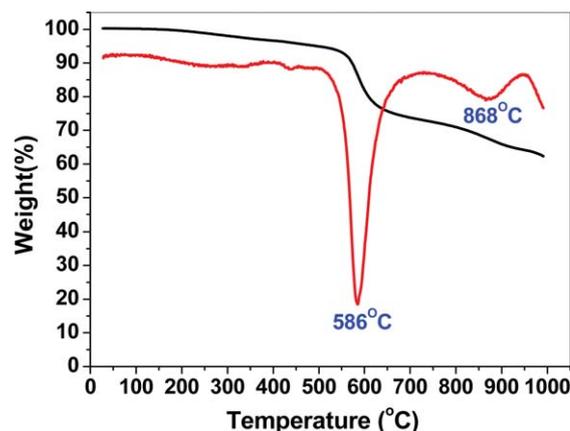


Fig. 7 TG-DTA curves for **1**.

materials (see Fig. 6–10 and Figs. S6–S10, ESI[†]). Thus below, only the thermal properties of **1** will be discussed in detail. For the free H₃L ligand, the sharp weight loss of *ca.* 60%, occurring in the range of 250–350 °C (peaking position: 320 °C), implies the decomposition of ligands (see Fig. 6 and Fig. S6, ESI[†]). The TG curve of **1** (see Fig. 6 and 7) reveals that the first weight loss of 2.62% in 150–370 °C corresponds to the gradual release of water molecule in the crystalline lattice (calcd: 2.39%). With that, the dehydrated solid is robust and thermally stable in a wide temperature region, and then, decomposition of the La–H–L framework occurs upon heating to 530 °C (peaking at 586 and 868 °C), as suggested by a significant weight loss of 33.67% that may correspond to the release of CO₂ (calcd: 34.97%).

To further investigate the heat-resistance of **1**, several freshly ground samples were placed inside a crucible of thermogravimetric analyzer upon a prolonged heating treatment (over 2 h) in air at 100, 200, 300, 400, 500, 510, 520, 530, 540, 600, and 1000 °C, respectively. It is evident that the PXRD patterns of the

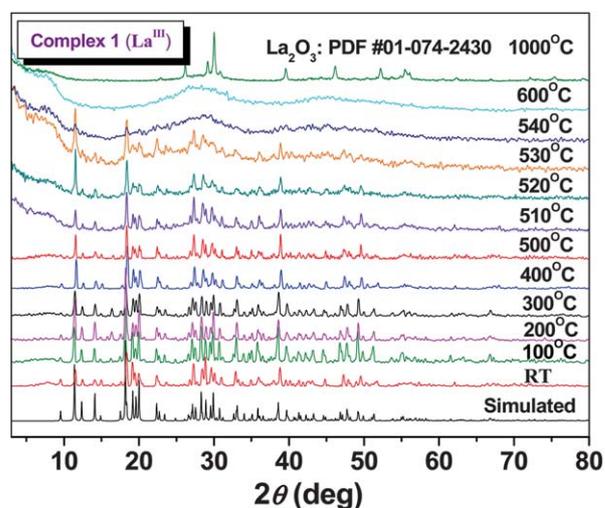


Fig. 8 PXRD patterns of **1**. The bottom is the simulated pattern obtained from single-crystal data. The others are those obtained from the as-synthesized sample and from the samples after a prolonged heating (at least 2 h) in a crucible of thermogravimetric analyzer at different temperatures.

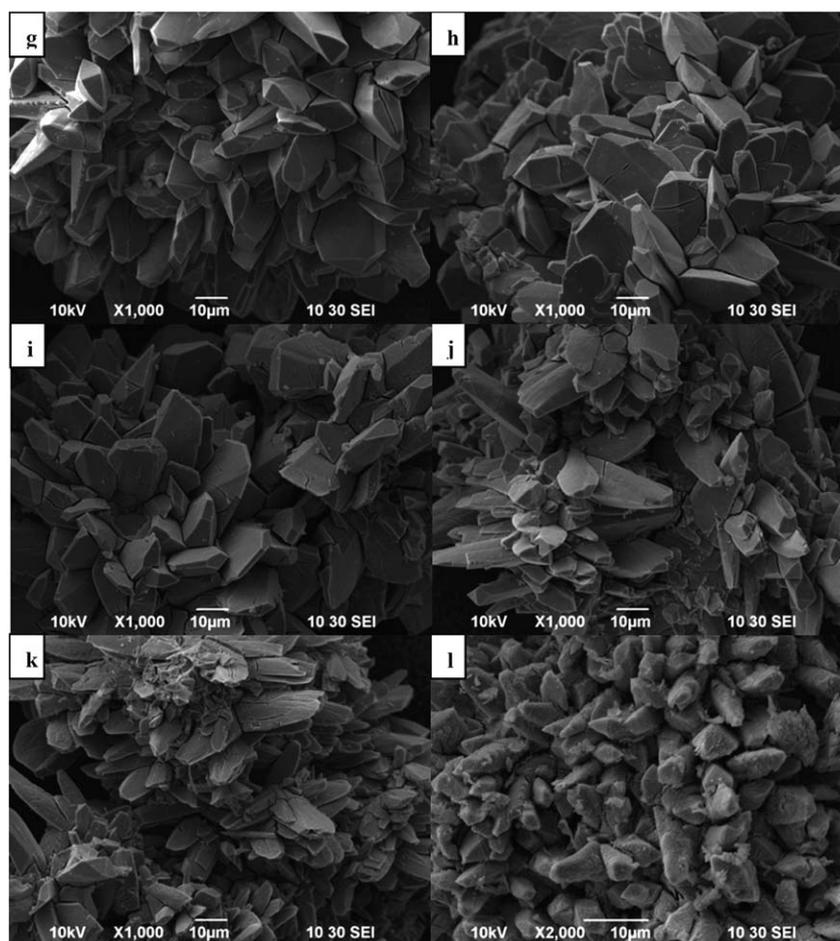


Fig. 9 SEM images of **1** based on the samples prepared at (g) 510, (h) 520, (i) 530, (j) 540, (k) 600, and (l) 1000 °C, respectively, after a prolonged heating (for 2 h) in a crucible of thermogravimetric analyzer.

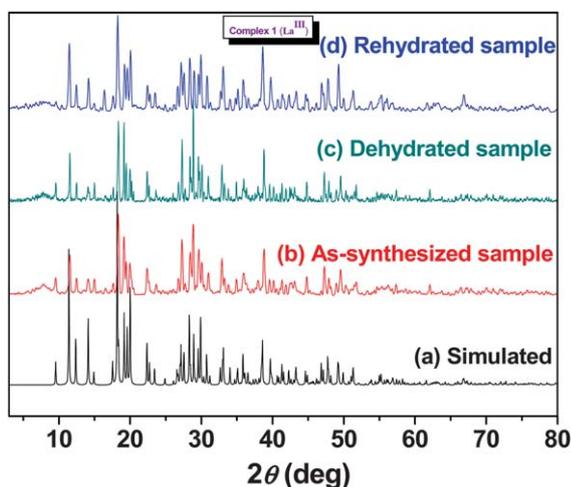


Fig. 10 Comparison of the PXR D patterns of **1**: (a) simulated from single-crystal data, (b) the as-synthesized sample, (c) the dehydrated sample after heating at 500 °C over 8 h, and (d) the rehydrated sample after soaking in distilled water over 24 h.

evacuated solid samples below 530 °C match well the simulated one obtained from single-crystal data and also that of as-synthesized sample prior to thermal treatment (see Fig. 8). The

results indicate that the crystalline lattice of **1** remains intact after removal of the water molecule and the dehydrated LnOF material **1** can be thermally stable up to 530 °C. Notably, the PXR D pattern recorded at 540 °C displays an evident decrease in intensity, but all diffraction peaks still match with those of the simulated one, further supporting the higher thermal stability of **1** and also, validating the maintenance of periodicity of the crystalline lattice. However, the sample becomes amorphous when the temperature is increased to 600 °C, as shown by the absence of sharp diffraction peaks in the PXR D patterns (see Fig. 8 and 9), revealing a completely structural change or collapse.

The surface morphology of the crystalline solids of **1** was characterized by scanning electron microscope (SEM) based on the as-synthesized sample as well as those after the heating treatment (for 2 h) inside a crucible of thermogravimetric analyzer at 100, 200, 300, 400, 500, 510, 520, 530, 540, 600, and 1000 °C, respectively (see Fig. S10, ESI† and Fig. 9). The results show that the morphology will not change significantly after heating at 100, 200, and 300 °C (see Fig. S10b–d, ESI†). When the temperature is increased to 400 °C (see Fig. S10e, ESI†), the block crystals start to split slightly, and beyond 500 °C (see Fig. S10f, ESI†), the crystals tend to further split with more small fragment broken being observed. Continuing to increase the

temperature every other 10 °C till 540 °C (see Fig. 9g–j), the collapse progress of **1** can be tracked in detail. At 540 °C, many small fragments are observed and the surface of these crystals is obviously coarse. At the moment, the surface morphology and crystal structure of **1** are destroyed, being agreement with the results of PXRD experiments (see Fig. 8). When the temperature is further increased to 600 °C (see Fig. 9k), the phenomenon of collapse is more clear. According to the PXRD patterns of the samples of **1–4** at 1000 °C (see Fig. 8 for **1** and Fig. S9 for **2–4**, ESI†), the final products seem to be lanthanide oxide (Ln₂O₃), that is, La₂O₃ (PDF #01-074-2430; Version: PDF.2006.4CA) for **1**, Pr₂O₃ (PDF #01-082-1401; Version: *vide supra*) for **2**, Nd₂O₃ (PDF #00-043-1023; Version: *vide supra*) for **3**, and Sm₂O₃ (PDF #01-070-2642; Version: *vide supra*) for **4**. Additionally, the PXRD patterns at 1000 °C exhibit some very minor peaks that cannot be properly identified.

When a freshly synthesized sample of **1** was placed in a crucible of a thermogravimetric analyzer upon heating at 500 °C for 8 h, the measured weight loss of 2.47% indicates the removal of one water molecule per formula unit (calcd: 2.39%), which is also supported by elemental analysis of the dehydrated solid [La₂(H–L)₃]_∞ [calcd. (found) for C₁₈H₉La₂N₃O₁₂: C, 29.33 (29.17); H, 1.23 (1.17); N, 5.70 (5.61)%]. Further, the PXRD pattern for the dehydrated solid (see Fig. 10) shows no marked change in comparison with the simulated pattern of **1**, indicating the framework of **1** remains unchanged after eliminating the water molecules. Additionally, the crystal structures of the dehydrated samples (**1'** and **4'**), obtained by a heating treatment at 300 °C for 2 h, were determined by single crystal X-ray diffraction analysis (see CIF, ESI†), showing no significant change of the structures. When the evacuated sample of **1** was immersed in distilled water over 24 h, the increase in weight (found: 2.51%) was in good agreement with the gain of one water molecule per formula [La₂(H–L)₃]_∞ (calcd: 2.44%). And also, the rehydrated material displays an essentially identical PXRD pattern with that of the original material [La₂(H–L)₃(H₂O)]_∞ (see Fig. 10). These results evidently demonstrate that the framework integrity of **1** can be fully retained with no loss of crystallinity, after the cycle process of dehydration and rehydration.

One of the main concerns in MOF materials is their thermal stability.^{9a,13,14} In comparison with general decomposition of the organic components in the synthesized MOFs at moderate temperatures (200–350 °C),^{13a} it is quite limited that a MOF material can be thermally stable above 400 °C^{9a,13d,14b,g,h} and even up to around 500^{9a,13b,e,14c,d,h} or 600 °C.^{13a} However, the reasons for this viewpoint are still unspecified so far.^{13a} It is believed that the included solvent molecules (either coordinated directly to metal centers or uncoordinated in the framework channels of the MOF materials) as well as multidentate functionality of organic linkers and rigidity of extended frameworks, may be associated with their thermal stability.^{13a,14b,h} In the connection of organic carboxylate linkers, some robust and thermally stable MOFs have been constructed.^{9a,13,14b,d–j} Furthermore, we found that the introduction of triangular ligands with three carboxyl groups arranged in the *meta*-fashion around the central aromatic/saturated ring can be used to prepare LnOFs with high thermal stability. For example, [Er(btc)]_∞ (btc = 1,3,5-benzenetricarboxylate),^{13b} {[Eu₃(btc)(OH)₆(H₂O)](H₂O)₃]_∞,^{9a} {[Er(ctc)(H₂O)₂](H₂O)_{2.5}]_∞ (ctc = *cis,cis*-

1,3,5-cyclohexanetricarboxylate),^{13c} and [Ln(ctc)]_∞ (Ln = Er^{III} and Tb^{III})^{13a} can be thermally stable to 500 °C, 500 °C, 480 °C, and 600 °C, respectively. Likewise, our present results present a family of unusual examples for LnOFs with higher thermal stability (up to 530 °C) after exclusion of the water molecules. We can tentatively presume that (1) the robust Ln–O_{carboxylate} and Ln–O_{hydroxyl} interactions tighten the backbone of H–L ligands; and (2) the relatively compact packing of coordination frameworks can also accommodate any structural changes caused by heating, that is, the frameworks of these materials are quite dense without residual solvent accessible void according to the PLATON analysis.³² Accordingly, the aforementioned structural features of LnOFs **1–4** enhance the heat-resistance to pyrolysis and, also, play a vital role in their highly-thermostable behaviors (the free H₃L ligand starts to degrade upon heating to only 250 °C, see Fig. 6).

Luminescence properties of LnOFs **1–4**

The solid state photoluminescent spectra for LnOFs **1–4** were measured at room temperature (see Fig. S11†). Upon excitation at 338 nm (for **1** and **2**), 310 nm (for **3**), and 358 nm (for **4**), the maximal emissions appear comparably at 415 nm (for **1** and **4**) or 416 nm (for **2** and **3**). The fluorescent behaviors of **1–4** are very similar to that observed for the free H₃L ligand (see Fig. S12†), which displays the maximal emission at 438 nm upon excitation at 344 nm. Thus, the emission mechanism for LnOFs **1–4** can be properly ascribed to the intraligand π → π* transitions.

Conclusions

Four isostructural 3-D lanthanide–organic frameworks based on 2,6-dihydropyridine-4-carboxylic acid have been successfully prepared under hydrothermal conditions, which show the unusual (4,5,7)-connected topological network. The *N*-protonated H–L ligands in these materials adopt two types of μ₅- and μ₄-bridging coordination modes to extend the lanthanide centers to afford the final 3-D LnOFs. Noticeably, these materials exhibit the exceptional thermal stability (up to 530 °C) and zeolite-like behavior mainly, owing to the dense nature of crystalline lattices and the unique network topology. This work may further enrich the crystal engineering strategy and provide the possibility of controlled preparation of the desired LnOFs materials. Following this line, more efforts on the H–L-based coordination frameworks with other rare earth and/or transition metals are currently made in our lab, for developing new crystalline materials with desired structures and properties.

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