Novel three-dimensional Ln-Ag 4d-4f heteropentametallic helix-based microporous metal-organic frameworks with unprecedented (3,4,5,6)-connected topology constructed from isonicotinate ligand

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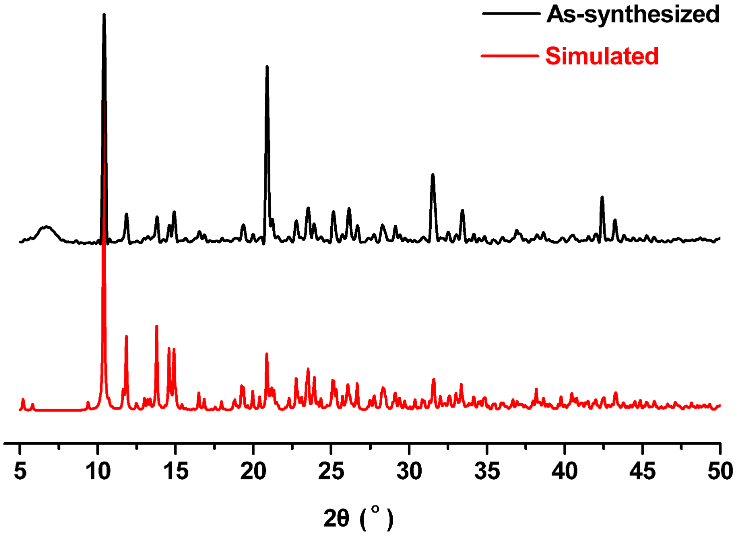

Fig. S1 Powder X-ray diffraction data of complex **1**.

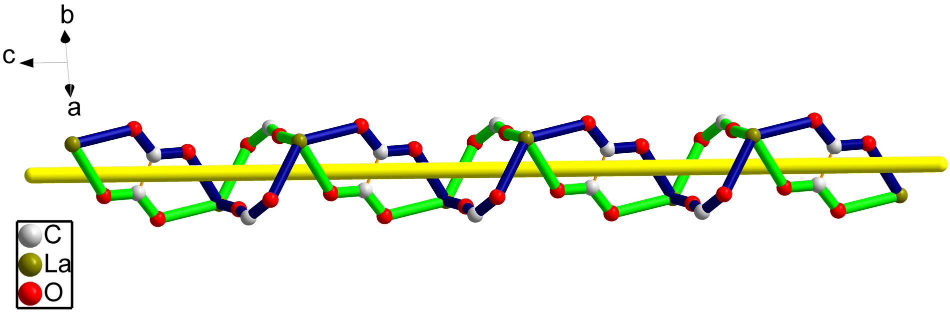

Fig. S2 1D zig-zag chain by the linkage of oxalate ligand and La(III) ions.

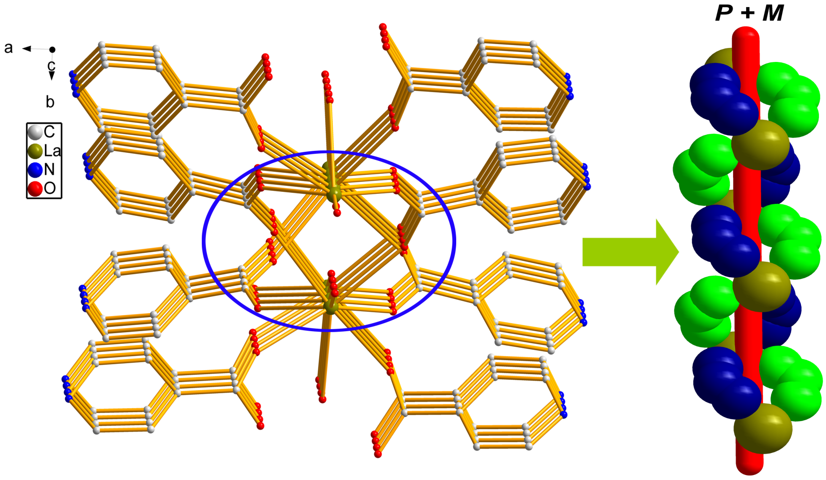

Fig. S3 The bi-strand helical chain through connecting the adjacent La1 ions with a pitch of 8.3694(5) Å.

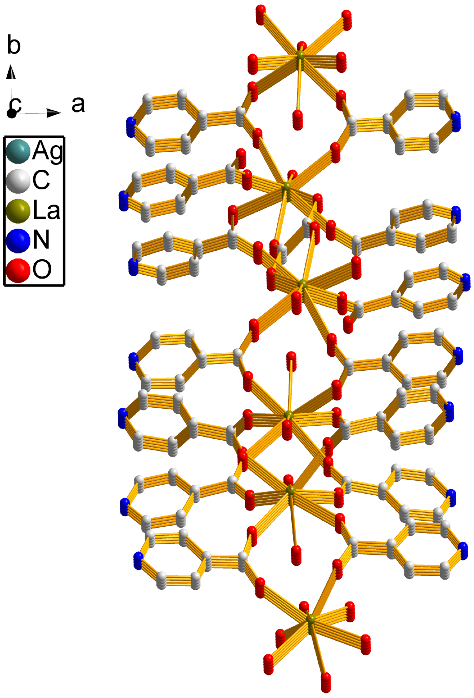

Fig. S4 The 2D paddle-wheel structure of complex **1** in view of *c* axis.

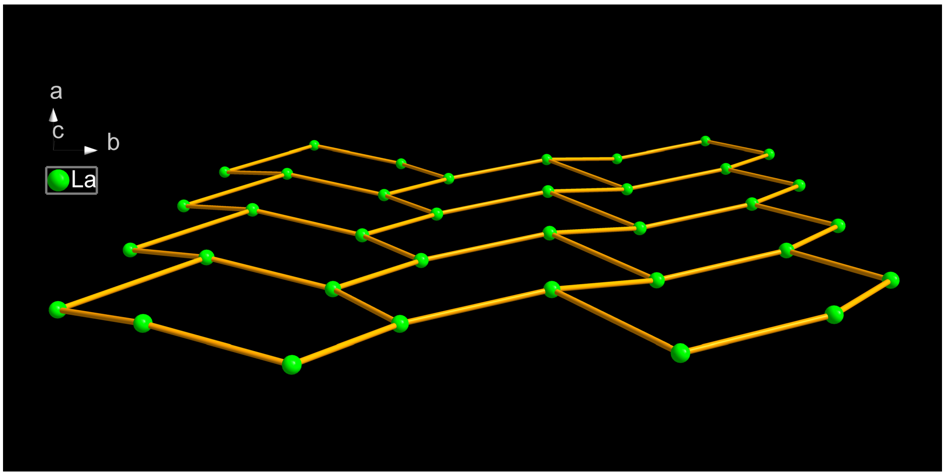

Fig. S5 Schematic illustration of the 2D chair-like layer, all organic ligands are represented as the bridging bonds.

TG analysis

The TGA was performed in air atmosphere from 50 to 800 °C at a heating rate of 10 °C/min, as can be seen in Fig. S6. The title compound undergoes three steps of weight loss. The water molecules are gradually lost in the temperature range of 50-150 °C, a weight loss of 2.02 % was observed for **1**, corresponding to the release of lattice water molecules (calculated 1.69 %). From the temperature range of 150-340 °C the coordinated water molecules and the anions are gradually lost (calcd, 11.74 %, found, 9.86 %). The consecutive weight loss from 350 to 650 °C for compounds **1** is probably caused by the decomposition of the frameworks, resulting in the collapse of structure.

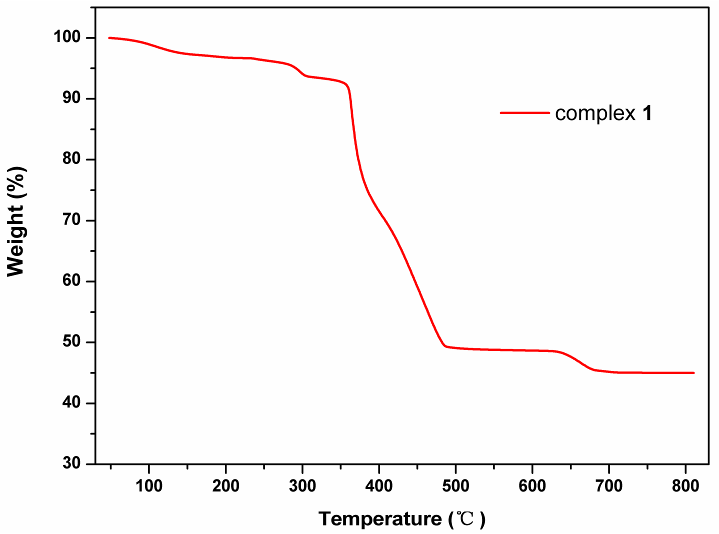

Fig. S6 TG curve of complex **1**.

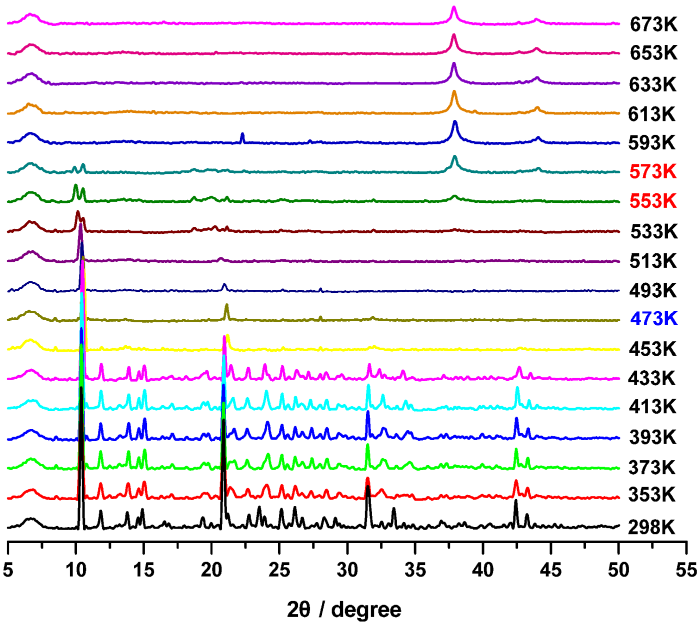

Fig. S7 Variable-temperature PXRD patterns of complex **1**.

Fig. S8 The luminescence spectra of **1**.

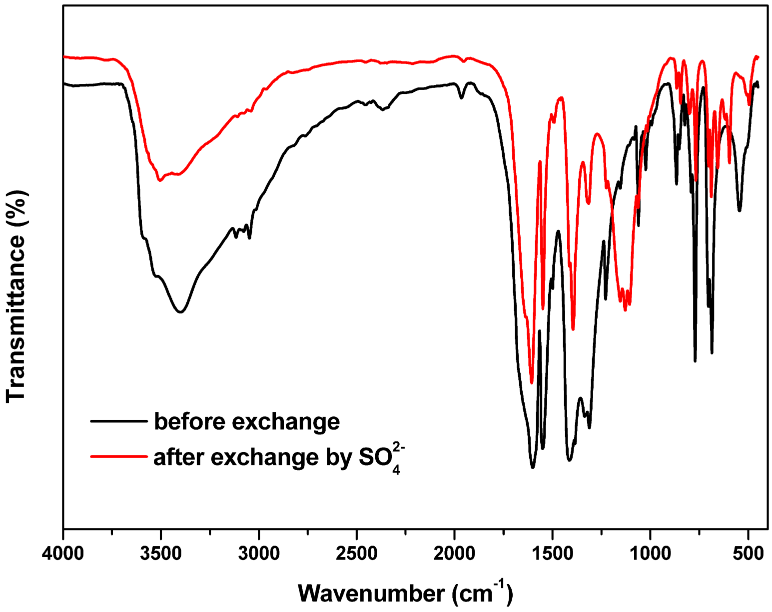

Fig. S9 The IR spectra of complex 1 as-synthesized and after exchange by SO_4^{2-}.

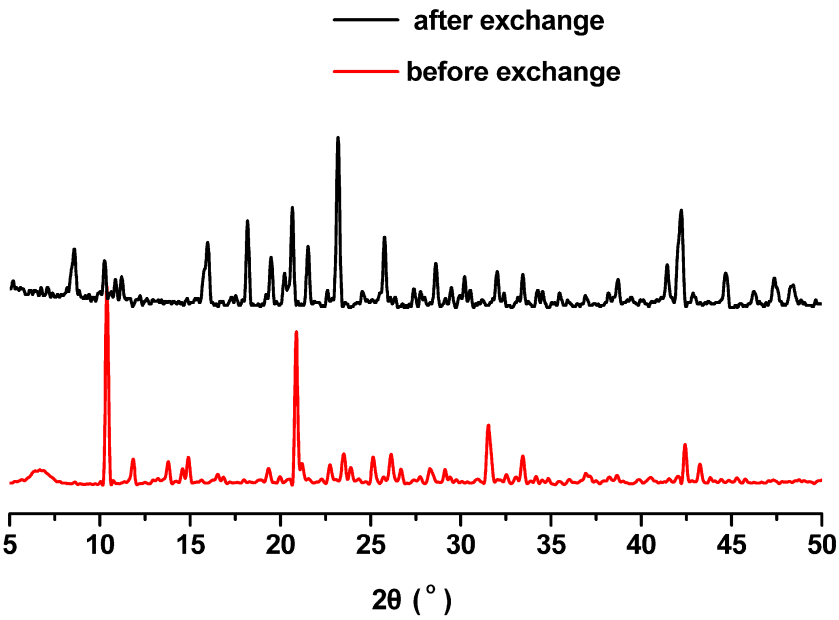

Fig. S10 PXRD patterns of **1** with as-synthesized (red line) and after anion exchanged (black line).

Experimental section

Physical Measurements

All chemicals employed were commercially available and used as received without further purificaion. The C, H and N microanalysis were carried out with Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000-400 cm^{-1} ranges on a Nicolet 5DX spectrometer. Thermogravimetric analyses were performed on Perkin-Elmer TGA7 analyzer with a heating rate of 10 °C/min in flowing air atmosphere. Fluorescence spectroscopy data were recorded on HITACHI F-4500 spectrophotometer analyzer. In the measurements of emission and excitation spectra the pass width is 5.0 nm. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer or Rigaku D/M-2200T automated diffractometer for Cu Kα radiation (λ = 1.54056 Å), with a scan speed of 4° min^{-1} and a step size of 0.02° in 2θ range of 5°-50°.

$\{[Ln_2Ag_3(ina)_6(ox)_{0.5}(\mu_2\text{-}OH_2)(H_2O)_{2.5}]\cdot 1.5H_2O\cdot 2NO_3\}_n$ (1)

Yield: 65% based on La. Anal. Calcd for $C_{74}H_{68}Ag_6La_4N_{16}O_{50}$: C, 27.89; H, 2.13; N, 7.03 %. Found: C, 28.08; H, 2.19; N, 7.09 %. IR frequencies (KBr, cm^{-1}, Figure 5). After SO_4^{2-} exchanged, elemental analysis found: C, 28.13 %; H, 2.15 %; N, 7.10 %, which is identical to the result of partially selective anion exchanged properties.

X-Ray Crystallographic Measurements

Data collections were performed at 298 K on a Bruker Smart ApexII diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for complexes **1**. Absorption corrections were applied by using the multi-scan program *SADABS*. Structural solutions and full-matrix least-square refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages, respectively.[1] All the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically (C—H = 0.93 or 0.96 Å), the water hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Selected bond distances are listed in Table S1. Hydrogen-bonding data for complex **1** are listed in Table S2.

IR spectroscopy

The strong and abroad absorption bands in the range of 3050-3550 cm^{-1} in **1** are ascribed to the characteristic vibration of OH^{-}. The strong vibrations appearing around 1590 and 1410 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the carboxylate groups, respectively.[2] The absence of strong bands around 1700 cm^{-1} indicates that all the ligands are deprotonated.

Table S1 Selected bond distances (Å) and angles (°) for **1**.

Compound **1**			
La(1)—O(1)#7	2.468(3)	Ag(2)—N(4)#2	2.137(4)
La(1)—O(2)#8	2.494(3)	Ag(2)—N(5)	2.134(4)
La(1)—O(3)	2.515(3)	Ag(2)—O(6W)	2.530(8)
La(1)—O(4)#6	2.455(3)	Ag(3)—N(3)#2	2.198(4)
La(1)—O(5)	2.452(3)	Ag(3)—N(6)	2.196(4)
La(1)—O(8)	2.526(4)	O(1)#7—La(1)—O(2)#8	74.84(11)
La(1)—O(3W)	2.697(3)	O(2)#8—La(1)—O(3)	138.13(11)
La(1)—O(3W)#9	2.888(4)	O(3)—La(1)—O(8)	75.55(11)
La(1)—O(4W)	2.601(4)	O(4)#6—La(1)—O(4W)	138.38(11)
La(2)—O(6)	2.450(3)	O(5)—La(1)—O(8)	88.78(12)
La(2)—O(7)	2.461(3)	O(6)—La(2)—O(19)	74.47(11)
La(2)—O(9)	2.442(3)	O(7)—La(2)—O(19)	125.48(12)
La(2)—O(11)	2.446(3)	O(9)—La(2)—O(19)	72.11(12)
La(2)—O(12)#10	2.507(3)	O(11)—La(2)—O(19)	81.35(12)
La(2)—O(19)	2.557(3)	O(12)#10—La(2)—O(19)	133.24(11)
La(2)—O(20)#5	2.555(3)	N(1)—Ag(1)—N(2)	176.81(18)
La(2)—O(5W)	2.596(3)	N(5)—Ag(2)—N(4)#2	167.12(19)
Ag(1)—N(1)	2.151(4)	N(5)—Ag(2)—O(6W)	100.5(2)
Ag(1)—N(2)	2.166(4)	N(4)#2—Ag(2)—O(6W)	89.5(2)
		N(6)—Ag(3)—N(3)#2	168.88(19)

Symmetry codes : #2 x+1,y,z ; #5 -x+1,-y+1,-z ; #6 x,-y+3/2,z+1/2 ; #7 x-1,y,z ; #8 x-1,-y+3/2,z+1/2 ; #9 x,-y+3/2,z-1/2 ; #10 -x+1,-y+1,-z+1.

Table S2 Hydrogen bonding parameters (Å and °) of **1**

compound	D—H···A	d(D—H)	d(H···A)	d(D···A)	∠(DHA)
1	O(1W)—H(1W)···O(4W)#4	0.85	2.52	3.057(14)	121.8
	O(2W)—H(3W)···O(5W)	0.86	2.29	3.087(6)	154.8
	O(2W)—H(3W)···O(6)	0.86	2.57	3.086(5)	119.6
	O(2W)—H(4W)···O(1)#12	0.87	2.26	2.910(5)	132.2
	O(2W)—H(4W)···O(4W)#4	0.87	2.39	3.128(6)	143.6
	O(3W)—H(6W)···O(4)#4	0.82	2.07	2.742(5)	137.8
	O(3W)—H(5W)···O(2W)	0.82	1.98	2.719(6)	149.7
	O(3W)—H(5W)···O(5)	0.82	2.51	2.957(5)	115.0
	O(4W)—H(7W)···O(10)	0.82	1.98	2.801(5)	177.8
	O(4W)—H(8W)···O(1W)#1	0.82	2.33	3.057(14)	148.3
	O(5W)—H(10W)···O(20)#4	0.82	2.08	2.859(5)	157.9
	O(5W)—H(9W)···O(10)#4	0.82	2.06	2.877(5)	175.4
	O(6W)—H(11W)···O(15)#13	0.83	1.94	2.662(11)	145.3
	O(6W)—H(11W)···O(13)#13	0.83	2.25	3.007(13)	152.2
	O(6W)—H(11W)···N(8)#13	0.83	2.36	3.190(16)	173.9

Symmetry codes : **For 1**, #1 x,y,z-1 ; #4 x,y,z+1 ; #12 x-1,y,z+1 ; #13 x+1,y,z-1.

Reference

1 (a) Sheldrick, G. M. *SHELXS 97*, *Program for Crystal Structure Solution*, University of Göttingen: Göttingen Germany, 1997; (b) Sheldrick, G. M. *SHELXL 97*, *Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

2 L. J. Bellamy, The Infrared Spectra of Complex Molecules; Wiley: New York, 1958.