Electronic Supplementary Information

A novel porous metal-organic framework from a new bis(acylhydrazone) ligand capable of reversibly adsorbing/desorbing water and small alcohol molecules

Chun-Li Guo,[a,b] Xiao-Zeng Li,*[a,b] Xing-Mei Zhang,[a] Lu Wang[a] and Li-Na Zhu[a]

[a] Department of Chemistry, School of Science, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China. Tel: +86-022-27403475; Fax: +86-022-27403475; E-mail: lixiaozeng321@tju.edu.cn

[b] State Key laboratory of Crystal Material, (Shandong University), Jinan, 250100, P. R. China

Materials and Measurements. All starting materials and solvents were purchased commercially and were used as received. Elemental analyses of C, H and N were carried out with a Perkin-Elmer 240 Elemental Analyzer. Infrared spectra were obtained from KBr pellets on a BIO-RAD 3000 infrared spectrophotometer in the region of 400 – 4000 cm^{-1}. Thermogravimetric analyses (TGA) were conducted in nitrogen stream using a STA-409PC equipment at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/max 2500v/pc X-ray powder diffractometer (Cu Kα, 1.5418 Å).

Synthesis of $\{[PbL1(H_2O)]_6 \cdot 30H_2O\}_\infty$ (1). A solution of isonicotinyl hydrazide (0.1097 g, 0.8 mmol), $Pb(NO_3)_2$ (0.1325 g, 0.4 mmol) and 2,3-butanedione (0.0344 g, 0.4 mmol) in a mixture solvent of 30 mL distilled water and 40 mL acetonitrile was mixed with triethylamine (0.1 mL). The mixture was stirred for 1 hour to form an orange turbid liquid. The liquid was then filtered and the orange filtrate was stored at room temperature. Orange block crystals suitable for X-ray single crystal diffraction were obtained after 16 days. Yield: 0.0400 g. Anal. Calc. for $C_{32}H_{52}N_{12}O_{16}Pb_2$: C 30.14, H 4.11, N 13.18 %; Found: C 30.27, H 4.24, N 13.10 %. IR (KBr, cm^{-1}): 3412(m), 1648(s), 1604(s), 1572(s), 1354(s), 1311(m),752(m).

Crystallography for 1. The diffraction data were collected with a Rigaku Saturn CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with ω and φ scans. Absorption corrections were carried out utilizing SADBS routine.[1] The structure was solved by the direct methods and refined by full-matrix least-squares refinements based on F^2.[2]

References

1 G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany, 1996.

2 G. M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, 1997.

Table S1 Selected bond lengths (Å) and angles (°) for complex **1**

Bond lengths			
Pb(1)-N(1)A	2.468(7)	Pb(1)-N(4)	2.489(6)
Pb(1)-N(3)	2.490(6)	Pb(1)-O(1)	2.536(6)
Pb(1)-O(2)	2.602(6)	Pb(1)···N(5)B	2.991(8)
Pb(1)···O(10)	3. 02(2)	O(2)-C(6)	1.28(1)
O(1)-C(11)	1.27(1)	N(1)-C(14)	1.34(1)
N(1)-C(15)	1.35(1)	N(2)-N(3)	1.392(9)
N(2)-C(11)	1.33(1)	N(4)-C(7)	1.29(1)
N(3)-C(9)	1.27(1)	N(5)-C(6)	1.33(1)
N(4)-N(5)	1.391(9)	C(7)-C(9)	1.49(1)
C(5)-C(6)	1.49(1)	C(11)-C(12)	1.48(1)
Bond angles			
N(1)A-Pb(1)-N(4)	85.6(2)	N(3)-Pb(1)-O(1)	63.3(2)
N(1)A-Pb(1)-N(3)	78.3(2)	N(1)A-Pb(1)-O(2)	81.7(2)
N(4)-Pb(1)-N(3)	63.3(2)	N(4)-Pb(1)-O(2)	61.9(2)
N(1)A-Pb(1)-O(1)	80.9(2)	N(3)-Pb(1)-O(2)	122.5(2)
N(4)-Pb(1)-O(1)	126.5(2)	O(1)-Pb(1)-O(2)	159.9(2)
N(1)A-Pb(1)-N(5)B	158.0(1)	O(1)-Pb(1)-O(10)	80.6(5)
N(3)-Pb(1)-N(5)B	91.9(2)	N(1)A-Pb(1)-O(10)	83.9(6)
N(4)-Pb(1)-N(5)B	72.4(2)	N(3)-Pb(1)-O(10)	141.6(5)
O(1)-Pb(1)-N(5)B	112.3(2)	N(4)-Pb(1)-O(10)	148.8(5)
O(2)-Pb(1)-N(5)B	87.3(2)	N(5)B-Pb(1)-O(10)	114.8(5)
		O(2)-Pb(1)-O(10)	87.6(5)

Symmetry transformations used to generate equivalent atoms:
A: x-y, x, 2-z ; B: 1-x, 1-y, 1-z

Table S2 Short atom-to-atom distances (Å) (Pb1···N5B weak bonds and π···π interactions) between a pair of the metallomacrocycles in **1**.

Pb1···N5B	2.991(8)	N3···C6B	3.74(1)
O1···C3B	3.45(1)	N4···C6B	3.296(9)
O1···C4B	3.40(1)	N5···N4B	3.69(1)
O2···N4B	3.581(8)	N5···N5B	3.345(8)
O2···C7B	3.408(9)	N6···N2B	3.263(8)
N2···C2B	3.70(1)	N6···C11B	3.642(9)
N2···C3B	3.58(1)	C1···C9B	3.636(8)
N2···C4B	3.68(1)	C1···N3B	3.69(1)
N2···C5B	3.79(1)	C2···N2B	3.43(1)
N3···C1B	3.56(1)	C3···N2B	3.56(1)
N3···C4B	3.504(9)	C3···C11B	3.70(1)
N3···C5B	3.31(1)	C3···C12B	3.58(1)

Symmetry transformation used to generate equivalent atoms:
B: 1-x, 1-y, 1-z

Table S3 H-bonds in the crystal of **1**

D···A	distance (Å)	Symmetry transformation
N2···O3	2.96(1)	y, -x+y, 2-z;
N6···O4	2.86(1)	2/3+x-y, 1/3+x, 4/3-z
O1···O11	2.85(1)	-x+y, -x, z
O2···O5	2.78(1)	
O3···O3	2.83(1)	1/3-x, 2/3-y, 4/3-z
O3···O4	2.89(1)	
O3···O13	2.83(1)	
O4···O5	2.69(1)	1/3-x, 2/3-y, 5/3-z
O5···O7	2.84(1)	
O5···O13	2.79(1)	
O6···O7	2.73(1)	
O6···O7	2.85(1)	x-y, x, 1-z
O6···O11	2.79(1)	
O7···O10	2.86(1)	
O8···O13	2.83(1)	
O11···O13	2.73(1)	

Table S4. Data from the dehydration-rehydration investigation of **1**.[a]

Experiment cycle number	1	2	3
Weight after dehydration (mg)	131.1	131.0	131.4
Weight loss (mg)	24.4	24.5	24.1
Weight loss percentage (%)[b]	15.7	15.8	15.5
Weight after rehydration (mg)	155.3	155.4	155.6
Weight increase (mg)	24.2	24.4	24.2
Percent weight increase (%)[c]	15.6	15.7	15.6

a. For each cycle, the dehydration was performed by heating the sample (originally 155.5 mg) at 100 °C in air for 5 hours, and the rehydration was conducted by sealing the dehydrated sample together with water (in an open beaker) in a glass desiccator at room temperature for 36 hours.

b. Weight loss percentage = (Weight loss (mg) / 155.5 mg) × 100 %.

c. Percent weight increase = (Weight increase (mg) / 155.5 mg) × 100 %.

Table S5. Adsorption/desorption data of **1** for alcohol vapours.[a]

Alcohol	Methanol			Ethanol		
Experiment cycle number	1	2	3	1	2	3
Weight after adsorption (mg)	144.5	144.2	144.9	141.0	140.7	141.1
Weight increase (mg)	18.0	17.7	18.4	14.6	14.3	14.7
Percent weight increase (%)[b]	12.0	11.8	12.3	9.7	9.5	9.8
Weight after desolvation (mg)	126.4	126.5	126.3	126.6	126.3	126.5
Weight loss (mg)	17.7	18.1	18.6	14.4	14.4	14.6
Weight loss percentage (%)[c]	11.8	12.1	12.4	9.6	9.6	9.7

Table S5. (Continued)

Alcohol	Isopropanol			n-butyl alcohol		
Experiment cycle number	1	2	3	1	2	3
Weight after adsorption (mg)	136.5	136.7	136.8	133.3	133.0	133.1
Weight increase (mg)	10.2	10.4	10.5	6.8	6.5	6.6
Percent weight increase (%)[b]	6.8	6.9	6.7	4.5	4.3	4.4
Weight after desolvation (mg)	126.4	126.5	126.3	126.3	126.4	126.6
Weight loss (mg)	10.1	10.2	10.5	7.0	6.6	6.5
Weight loss percentage (%)[c]	6.7	6.8	7.0	4.7	4.4	4.3

a. For each experiment, the original sample of **1** was 150.0 mg, and the completely dehydrated sample was 126.4 mg. The desolvations were performed by heating the samples at 100 °C in air for 5 hours. For each cycle, the vapour adsorption was conducted by sealing the desolvated sample together with the corresponding alcohol (in an open beaker) in a glass desiccator at room temperature for 36 hours. Further extension of the adsorption time did not bring about any weight increase for the samples.

b. Percent weight increase = (Weight increase (mg) / 150.0 mg) × 100 %.

c. Weight loss percentage = (Weight loss (mg) / 150.0 mg) × 100 %.

Fig. S1 Schematic representation of a hexametallomacrocycle interacting with six other hexametallomacrocycles through weak Pb···N_{amide} bonds and π···π interactions in a 3D network of **1** (Solid lines represent moieties of the bridging ligands between Pb nodes and dashed lines represent the inter-metallomacrocycle weak Pb···N_{amide} bonds and π···π interactions. Atoms other than Pb are omitted for clarity).

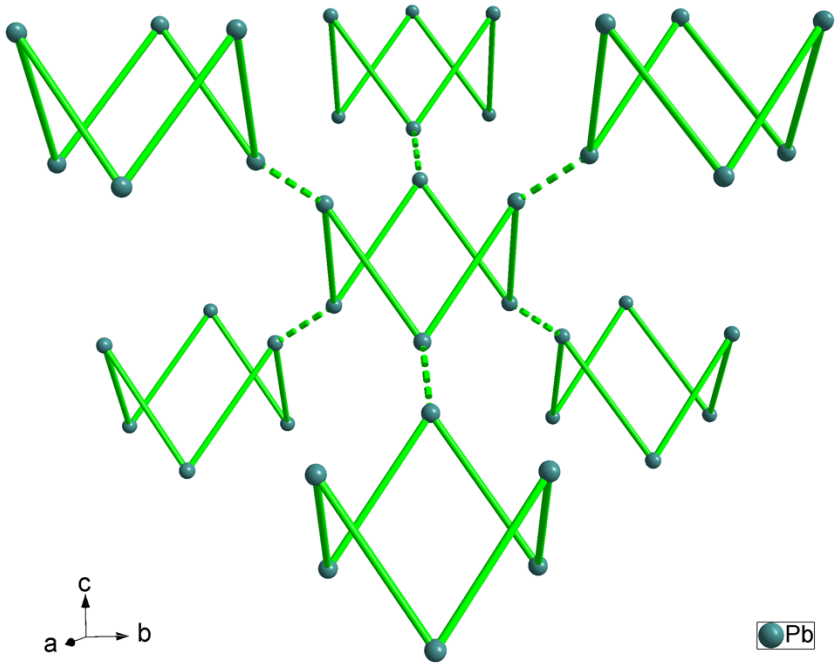

Fig. S2 A 3D network of **1** viewed along *a* (top) and *b* (bottom) directions.

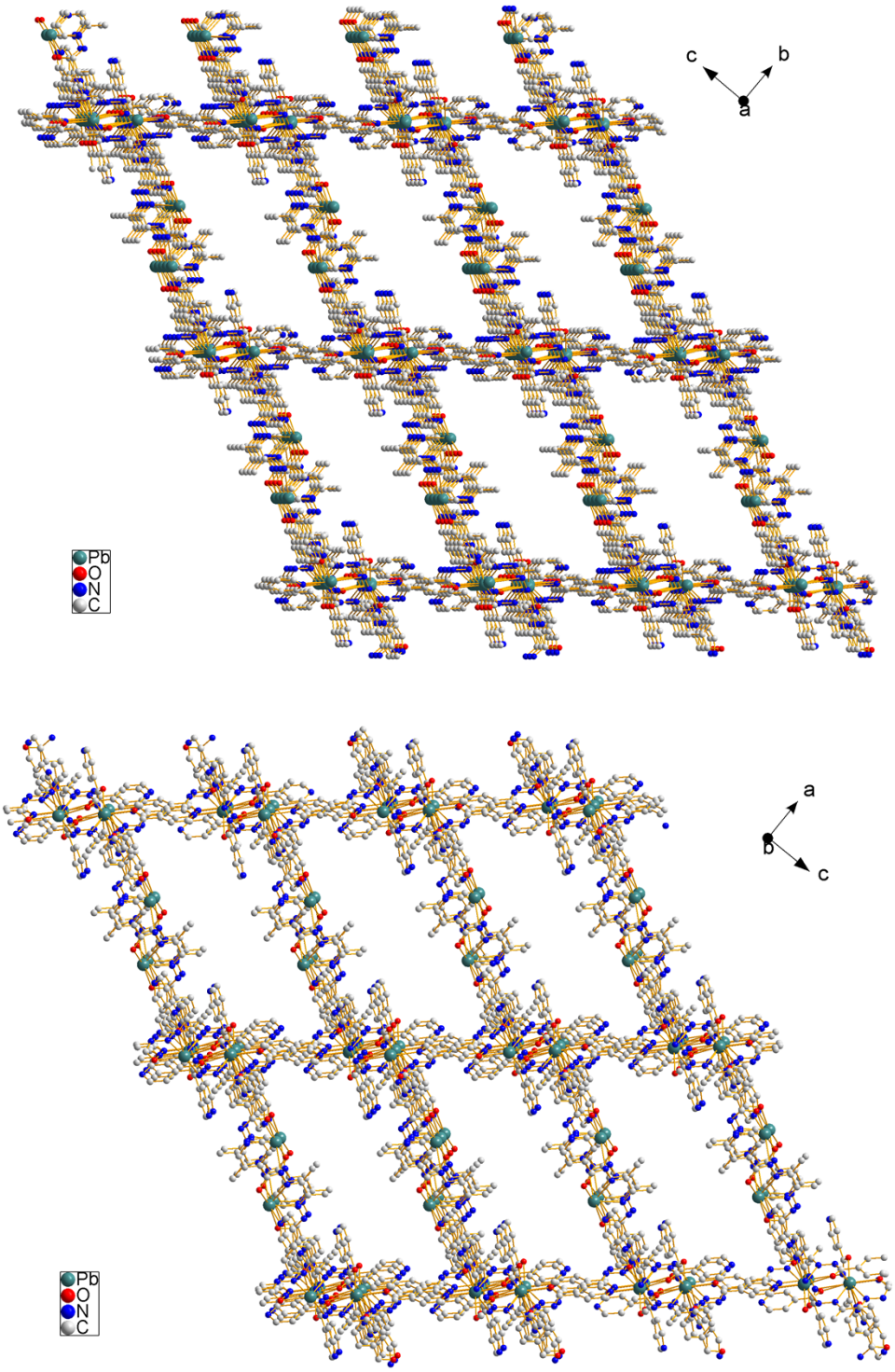

Fig. S3 Schematic representation of a 3D network in **1** formed by hexametallomacrocycles interacting through weak Pb···N_{amide} bonds and π···π interactions (Solid lines represent moieties of the bridging ligands between Pb nodes and dashed lines represent the inter-metallomacrocycle Pb···N_{amide} weak bonds and π···π interactions. Atoms other than Pb are omitted for clarity).

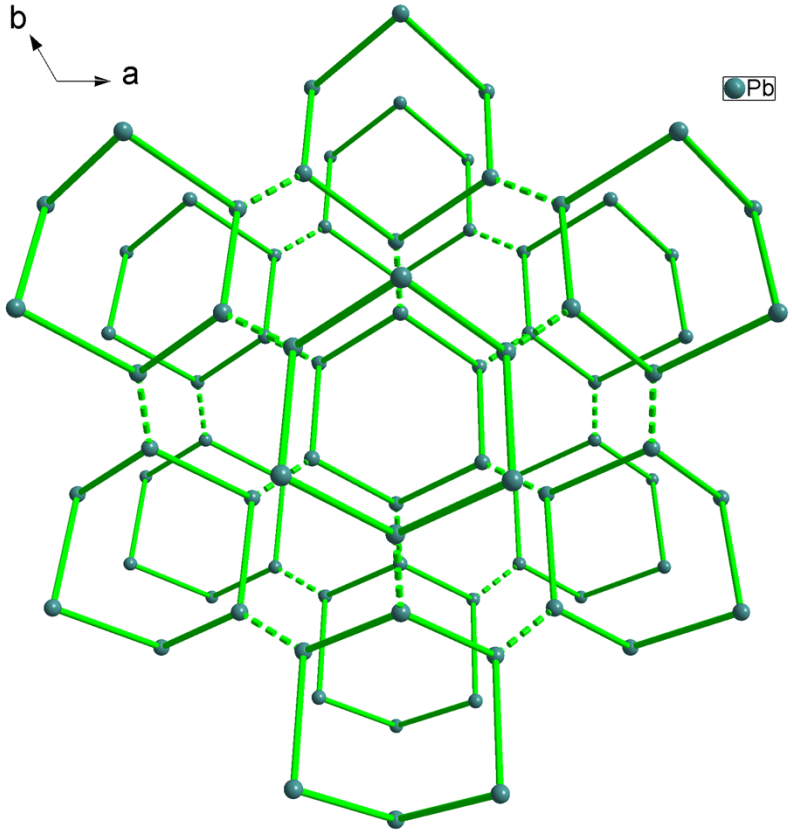

Fig. S4 Plot showing the open channels in the crystal of **1**.

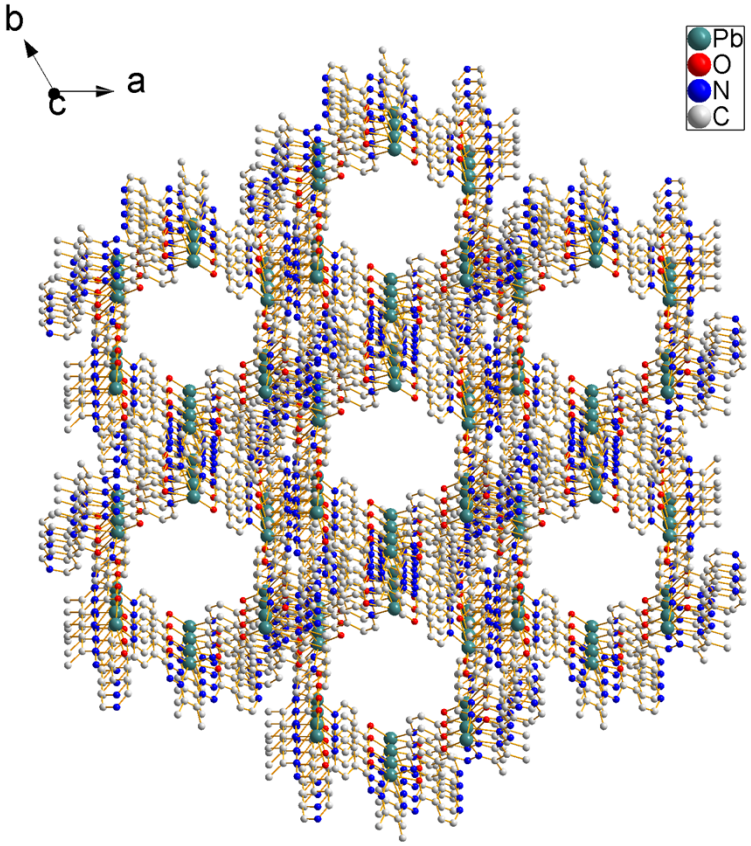

Fig. S5 TG plot of **1**.