Electronic supplementary information

Syntheses, structures, gas adsorption and reversible iodine adsorption of two porous Cu(II)-organic frameworks constructed by a new macrocycle-based tetracarboxylate

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Table S1a Selected bond distances (Å) and angles (°) for **1**.

Cu(1)-N(1)	2.107(2)	Cu(1)-N(2)	2.020(2)
Cu(1)-O(4)$^{\#2}$	2.717(1)	N(2)-Cu(1)-N(1)$^{\#1}$	93.72(9)
N(2)-Cu(1)-N(1)	86.28(9)	N1-Cu(1)-O4$^{\#2}$	95.79(2)
N2-Cu(1)-O4$^{\#2}$	97.88(2)	N1-Cu(1)-O4$^{\#3}$	84.21(2)
N2-Cu(1)-O4$^{\#3}$	82.12(1)		

Table S1b Hydrogen bonds for **1** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1)-H(1)...O(3)$^{\#4}$	0.82	1.84	2.582(3)	150.6
N(2)-H(2A)...O(3)$^{\#3}$	0.84(3)	2.08(3)	2.887(3)	160(3)
N(2)-H(2A)...O(4)$^{\#3}$	0.84(3)	2.64(3)	3.156(3)	120.6(2)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1, -y, -z+2; $^{\#2}$ 1-x+y, 1-x, z; $^{\#3}$ x-y, x-1, -z+2; $^{\#4}$ y+1/3, -x+y+2/3, -z+5/3.

Table S2a Selected bond distances (Å) and angles (°) for **2**.

Cu(1)-N(1)	1.986(8)	Cu(1)-N(2)	2.081(8)
Cu(1)-O(1)$^{\#2}$	2.725(2)	N(1)-Cu(1)-N(2)$^{\#1}$	92.95(3)
N(1)-Cu(1)-N(2)	87.05(3)	N1-Cu(1)-O1$^{\#2}$	80.28(2)
N2-Cu(1)-O1$^{\#2}$	84.35(2)	N1-Cu(1)-O1$^{\#3}$	99.72(2)
N2-Cu(1)-O1$^{\#3}$	95.65(2)		

Table S2b Hydrogen bonds for **1** (Å and °).

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(3)-H(3A)...O(2)$^{\#4}$	0.82	1.80	2.593(11)	163.6

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+2, -y, -z; $^{\#2}$ -1/2+x, 1/2-y, -1/2+z; $^{\#3}$ 5/2-x, -1/2+y, 1/2-z; $^{\#4}$ x-1/2, -y+1/2, z+1/2.

Synthesis of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. $HC1O_4$ (27 g) was added slowly to a mixed cold solution (400 mL acetone and 17.6 g ethylenediamine). The intermediate product of perchloric salt was obtained as a white precipitate which was washed with cold acetone and dried. Yield: 70%. In a 500 mL beaker, 25 g intermediate perchloric salt and 250 mL methanol were added. The mixture was stirred fully, and then 9.5 g $NaBH_4$ and 8.25 g NaOH were added alternately in one hour. The mixture was refluxed with stirring for another 0.5 h, and transferred to a solution of NaOH (25 g) in H_2O (500 mL) after cooling to room temperature. The precipitate formed (white) was filtered off, washed with water to pH ≈ 7 and dried in air. Yield: 63%.

Synthesis of 5-bromomethyl dimethyl isphthalate. A solution of 5-methyl dimethyl isphthalate (8.32 g), N-bromosuccinimide (8.54 g), and benzoyl peroxide (500 mg) in $CC1_4$ (200 mL) was refluxed for 3h. After the solution cooling, the precipitate (succinimide) was separated and washed with $CC1_4$. The filtrate was washed with H_2O, dried with $MgSO_4$, and evaporated. Light yellow crystals of 5-bromomethyl dimethyl isphthalate were obtained. Yield: 42%.

Synthesis of H_4L. In a 500 mL flask 5-bromomethyl dimethyl isphthalate (5.72 g, 20 mmol), 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (4.81 g, 10 mmol), K_2CO_3 (11.06 g, 80 mmol) and 300 mL CH_3CN were added. The mixture was refluxed with stirring for 26 h, and then the solvent was evaporated. An aqueous solution of NaOH (6.40 g in 20 mL H_2O) and 300 mL THF were added. Hydrolysis proceeded for another 10 hours. Then THF was evaporated and 100 mL water was added into it. After filtering and cooling down to room temperature, the resulting water phase was acidified to pH ≈ 2 with diluted HCl solution. Finally, the obtained off-white solid product 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- 1,8-*N*,*N′*-dimethylene-isop-hthalic acid (H_4L) was collected by filtration, washed with water and dried in air (Scheme S1). Yield: 33%.

Scheme S1 The synthetic route of the H_4L ligand.

Fig. S1 The 3D supramolecular architecture of **1** along the b axis furnished via hydrogen-bonding interactions (H-bonds: orange dots).

Fig. S2 Coordination sphere surrounding Cu(II) ion in **2**. Symmetry codes: $^{\#1}$ 2-x, -y, -z; $^{\#2}$ -1/2+x, 1/2-y, -1/2+z; $^{\#3}$ 5/2-x, -1/2+y, 1/2-z.