Metal-Organic Frameworks Constructed from Flexible V-shaped Ligand: Adjust the Topology, Interpenetration and Porosity via Solvent System

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1. Materials and methods

The reagents and solvents employed were commercially available and used as received.

Single-crystal X-ray crystallographic studies. X-ray crystallographic data of **1-3** were collected at room temperature using epoxy-coated crystals mounted on glass fiber. All measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[1] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The distribution of peaks in the channels of **1** and **2** was chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining water molecule was removed by the SQUEEZE routine in PLATON.[2]

Comment on X-ray refinement special details for compound 1.

The restraints SIMU (similar Uij values for adjoining atoms) and DELU (rigid-bond) were applied to the Uij values of atoms with the default esd. (SIMU Cu1 O2; DELU DELU 0.001 Cu1 O2 O3 O4 O5 C15; DELU 0.001 N3' C17' N3 C15 N3 C17; DELU 0.001 N3' C15 O5 C15'; DELU 0.01 N17 N17'). However, some atoms went to non-positive-definite and were further restrained with a soft restraint to be approximately isotropic with the ISOR restraint with default esd. (ISOR 0.001 N17 N17'). The coordinated disordered DMF molecules were restrained to have similar geometries to one another without limiting torsion angles with a combination of SADI restraints.

SADI N3 C16 N3' C16'

SADI N3 C17 N3' C17'

SADI C15' N3' C15 N3
SADI C15' O5 C15 O5

Comment on X-ray refinement special details for compound 3.

The restraints SIMU (similar Uij values for adjoining atoms) and DELU (rigid-bond) were applied to the Uij values of all O atoms with the default esd. (SIMU 0.01 O; DELU 0.01 O). The DFIX restraint was applied to the distance of H: with a distance of 2.12 Ang. for H3C-H1WA and 2.20 Ang. for H3C-H3.

IR absorption spectra of the compounds were recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr).

2. Synthesis procedures

2.1 Synthesis of $[Cu(L)(DMF)\cdot xH_2O]_n$ ***(1)***. A mixture of $Cu(NO_3)_2{\cdot}3H_2O$(0.5 mmol, 0.121 g), H_2L (0.5 mmol, 0.129 g), and DMF/H_2O (3:4, v/v) (7 mL) was stirred for 15 min in air, then transferred and sealed in a 25ml Parr Teflon-lined stainless steel vessel, heated to 95 °C for 3 days and then cooled to room temperature at a rate of 10 °C per/h. The resulting green prism crystals were filtered, washed, and dried in air, yield 80% based on Cu. IR (KBr, cm^{-1}): 3390(w), 1593(m), 1520(s), 1389(s), 1323(s), 1247(m), 1172(s), 845(w), 777(m), 697(w), 667(m), 628(w), 480(w).

2.2 Synthesis of $[Cu_2(L)_2(H_2O)_2\,xH_2O]_n$ ***(2)***. A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.5 mmol, 0.121 g), H_2L (0.5 mmol, 0.129 g), and DMF/CH_3CN/H_2O (1:3:4, v/v) (8 mL) was stirred for 15 min in air, then transferred and sealed in a 25ml Parr Teflon-lined stainless steel vessel, heated to 95 °C for 3 days and then cooled to room temperature at a rate of 10 °C per/h. The resulting green block crystals were filtered, washed, and dried in air, yield 75% based on Cu. IR (KBr, cm^{-1}): 3391(w), 1594(m), 1523(s), 1390(s), 1326(s), 1248(m), 1174(s), 845(w), 778(m), 698(w), 668(m), 628(w), 484(w).

2.3 Synthesis of $[Cu(L)(H_2O)\cdot H_2O]_n$ ***(3)***. A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.5 mmol, 0.121 g), H_2L (0.5 mmol, 0.129 g), and CH_3CN/H_2O (5:3, v/v) (8 mL) was stirred for 15 min in air, then transferred and sealed in a 25ml Parr Teflon-lined stainless steel vessel, heated to 95 °C for 3 days and then cooled to room temperature at a rate of 10

^{o}C per/h. The resulting black block crystals were filtered, washed, and dried in air, yield 45% based on Cu. IR (KBr, cm^{-1}): 3390(w), 1593(m), 1522(s), 1390(s), 1323(s), 1248(m), 1173(s), 845(w), 778(m), 698(w), 667(m), 628(w), 481(w).

3. Additional figures and tables

Table S1. Crystal and Structure Refinement Data for Compounds **1**–**3**

Compound	**1**	**2**	**3**
Formula	$C_{17}H_{21}CuN_2O_{7.5}$	$C_{28}H_{27}Cu_2N_2O_{14}$	$C_{14}H_{13}CuNO_6$
Formula Weight	436.87	742.53	354.80
Crystal System	orthorhombic	tetragonal	tetragonal
Space group	Fddd	I4(1)22	I4(1)/a
a (Å)	16.6727(11)	16.6307(8)	17.924(3)
b (Å)	30.982(2)	16.6307(8)	17.924(3)
c (Å)	33.554(2)	16.3071(16)	17.225(6)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
V (Å^3)	17332.4(19)	4510.2(6)	5534(3)
Z	32	4	16
D_c (g cm^{-3})	1.339	1.093	1.703
μ(Mo) Ka)(mm^{-1})	1.047	0.993	1.609
F(000)	7274.0	1414.0	2896.0
R(int)	0.0611	0.0496	0.0767
Observed data	3200	1703	1802
R1, wR2 [I> 2$\sigma(I)$]	0.0618, 0.1667	0.0358, 0.1023	0.0557, 0.1745
S	1.061	1.066	1.063
Min. and Max. Resdens (e·Å^{-3})	-1.035, 0.752	-0.235, 0.653	-0.804, 1.701
Absolute structure parameter	/	0.01(1)	/

Table S2. Selected Bond Distances and Angles for Compounds **1-3**.

Compound **1**

Cu1-O1	1.952(3)	Cu2-O1	1.959(3)
Cu3-O1	1.965(3)	Cu4-O1	1.966(3)
Cu5-O1	2.159(3)		
O1-Cu1-O2	168.42(14)	O1-Cu1-O3	87.14(14)
O2-Cu1-O3	91.58(15)	O1-Cu1-O4	90.73(14)
O2-Cu1-O4	88.26(14)	O3-Cu1-O4	168.55(14)
O1-Cu1-O5	99.02(13)	O2-Cu1-O5	92.52(13)
O3-Cu1-O5	91.52(13)	O4-Cu1-O5	99.92(13)

Compound **2**

Cu1-O1	1.934(2)	Cu1-O2	2.165(5)
Cu1-O3	1.998(3)	Cu1- Cu1	2.6281(12)
O1-Cu1-O1	170.3(2)	O1-Cu1-O2	94.86(10)
O1-Cu1-O3	88.72(10)	O1-Cu1-O3	88.72(10)
O1-Cu1-O3	90.06(10)	O2-Cu1-O3	97.18(10)
O1-Cu1-Cu1	85.14(10)	O2-Cu1-Cu1	180.00(13)
O3-Cu1-Cu1	82.82(10)		

Compound **3**

Cu1-O1	1.959(4)	Cu1-O2	1.963(4)
Cu1-O3	2.182(6)	Cu1-O4	1.953(4)
Cu1-O5	1.944(4)	Cu1- Cu1	2.6008(14)
O1-Cu1-O2	90.38(18)	O1-Cu1-O3	96.6(2)
O2-Cu1-O3	97.0(2)	O4-Cu1-O3	93.9(2)
O5-Cu1-O3	93.7(2)	O1-Cu1-Cu1	83.88(14)
O2-Cu1-Cu1	88.18(12)	O3-Cu1-Cu1	174.8(2)
O4-Cu1-Cu1	85.78(14)	O5-Cu1-Cu1	81.06(12)

Table S3 The Comparison of Compounds **1-3**.

	1	**2**	**3**
The dihedral angle (°)	54.92(16)/55.09 (12)	52.77(11)	43.78(22)
The C···N_{core}···C angle (°)	131.16(7)/133.41(7)	129.70(5)	128.88(13)
The configurations for extension of L^{2-} and SBUs	up-up-down-down	up-down-up-down	up-up-down-down
Angle between up and up (or down and down) (°)	79.88(5)	/	99.67(1)
Angle between up and down (°)	100.12(5)	96.19(1)/84.06(1)	80.33(1)
Topology	lvt	dia	lvt
Interpenetrated number	3	3	5
Solvent accessible volume	~27%	~47%	none

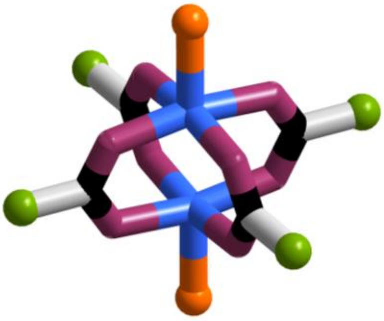

Figure S1. Dinuclear copper paddlewheel $Cu_2(CO_2)_4$

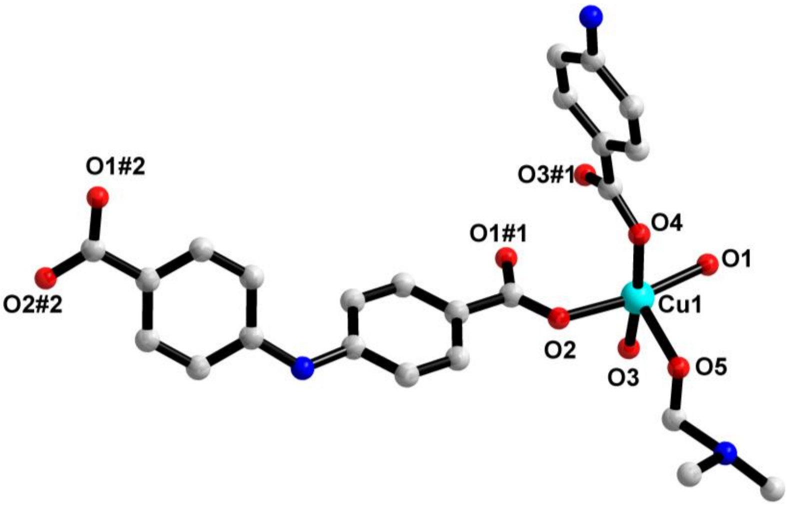

Figure S2. Coordination environment of the Cu(II) ion in **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: (#1) 1-*x*, 1-*y*, -*z*; (#2) 1.75-*x*, *y*, -0.25-*z*.

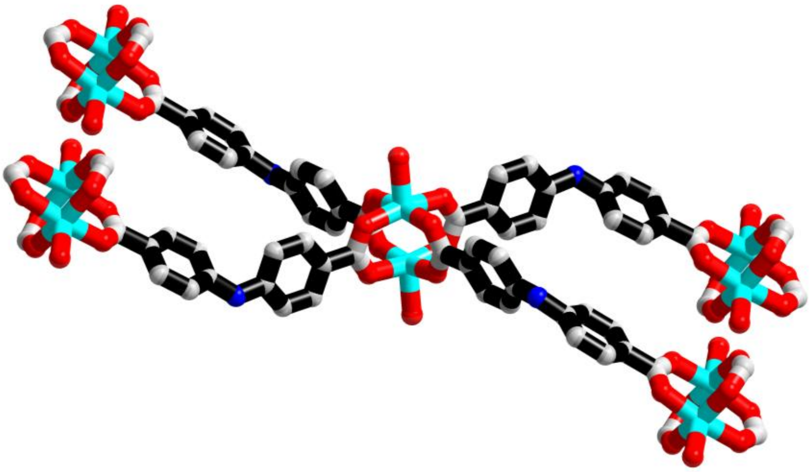

Figure S3. L^{2-} assembly with SBUs in **1** showing the way: up-up-down-down

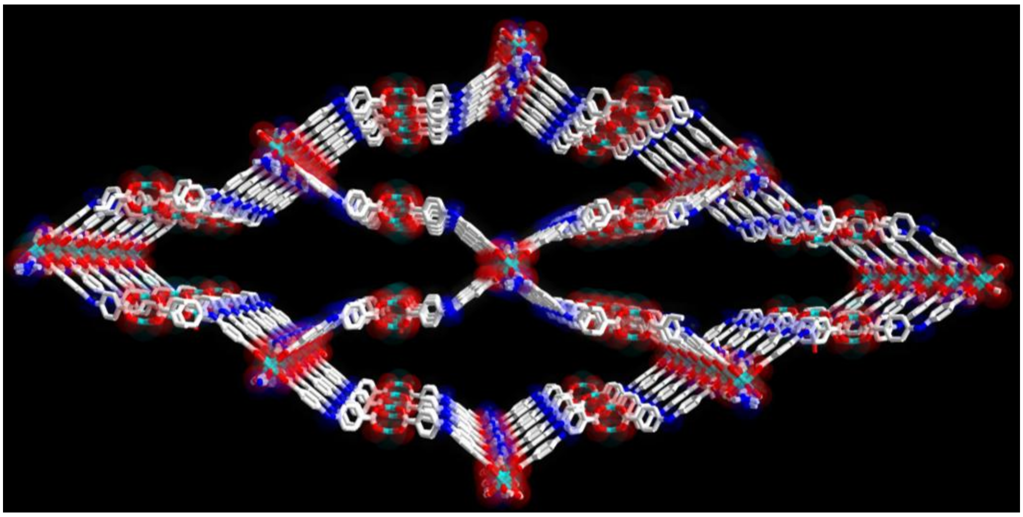

Figure S4. The 3D framework of a single net in **1**

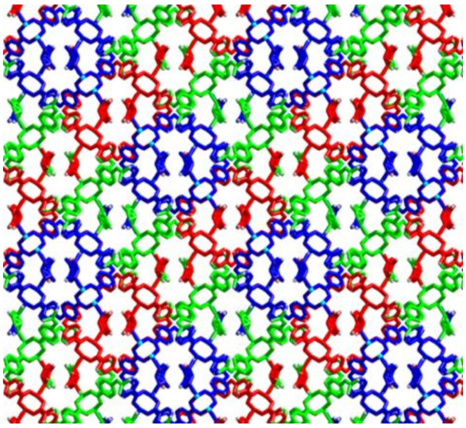

Figure S5. The three-fold interpenetrated framework in **1**

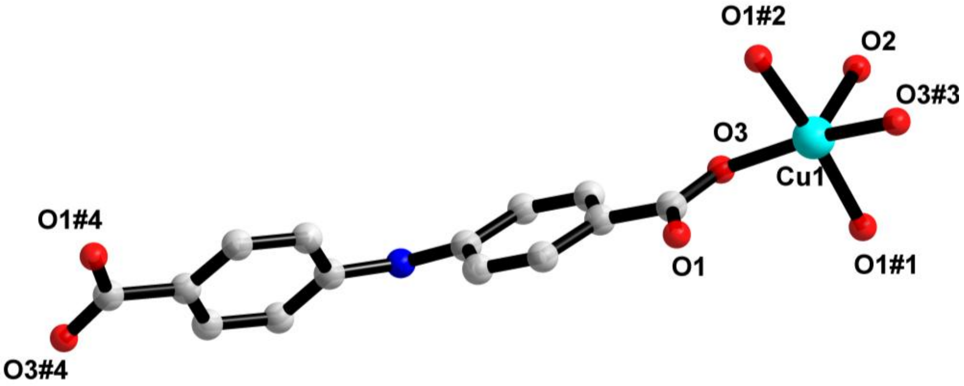

Figure S6. Coordination environment of the Cu(II) ion in **2**. The hydrogen atoms are omitted for clarity. Symmetry codes: (#1) 1-*y*, 1-*x*, -*z*; (#2) 1-*x*, 1-*y*, *z*; (#3) *y*, *x*, -*z*; (#4) 1.5-*x*, *y*, 0.75-*z*.

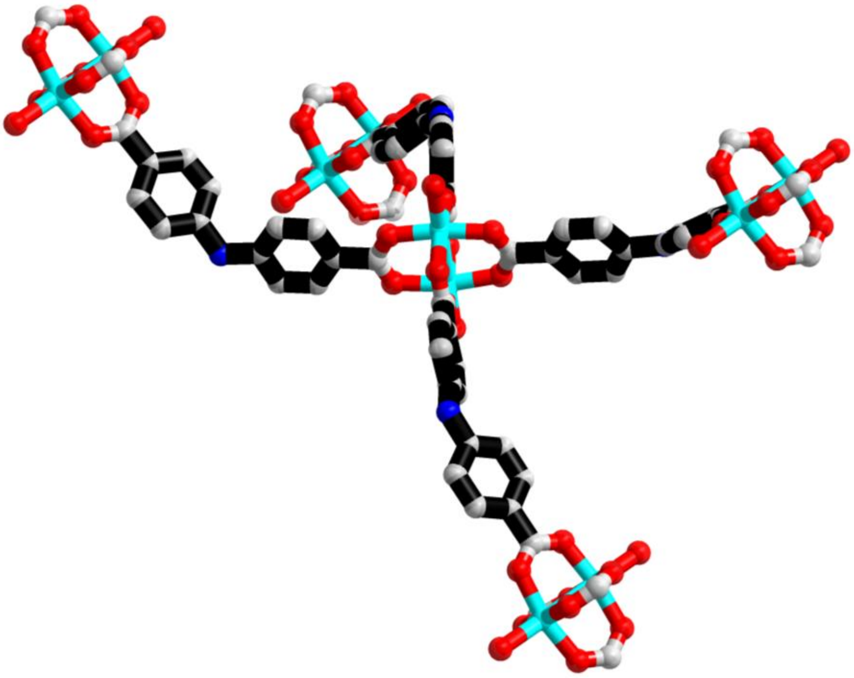

Figure S7. L^{2-} assembly with SBUs in **2** showing the way: up-down-up-down

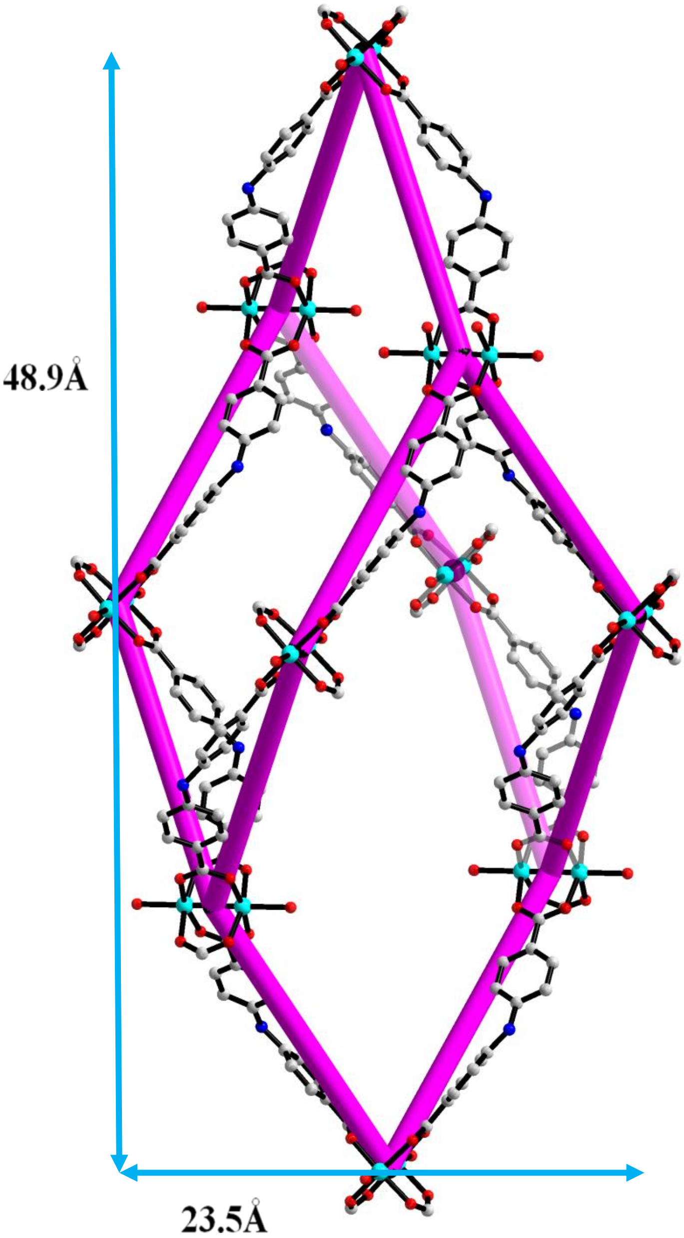

Figure S8. The diamond structure in **2**

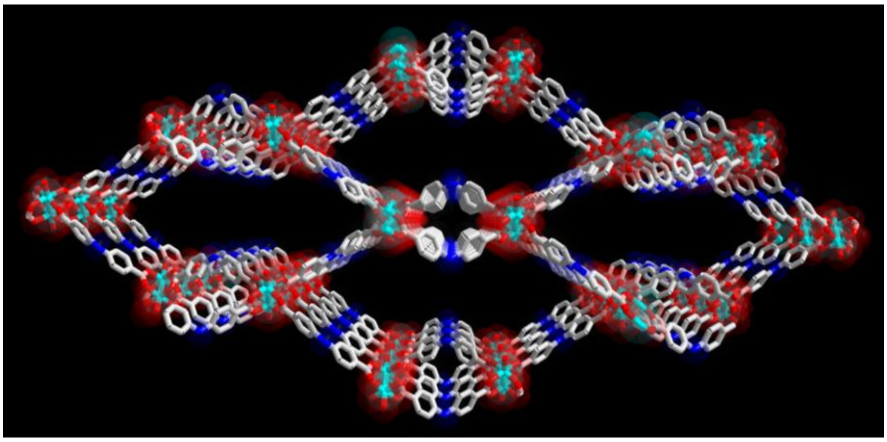

Figure S9. The 3D framework of a single net in **2**

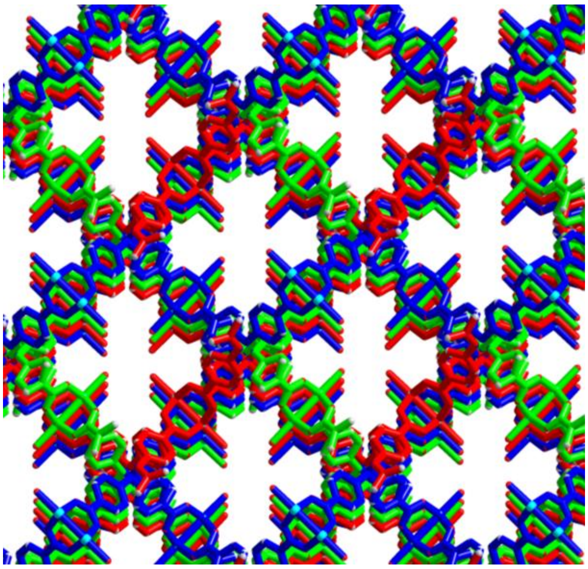

Figure S10. The three-fold interpenetrated net in **2**

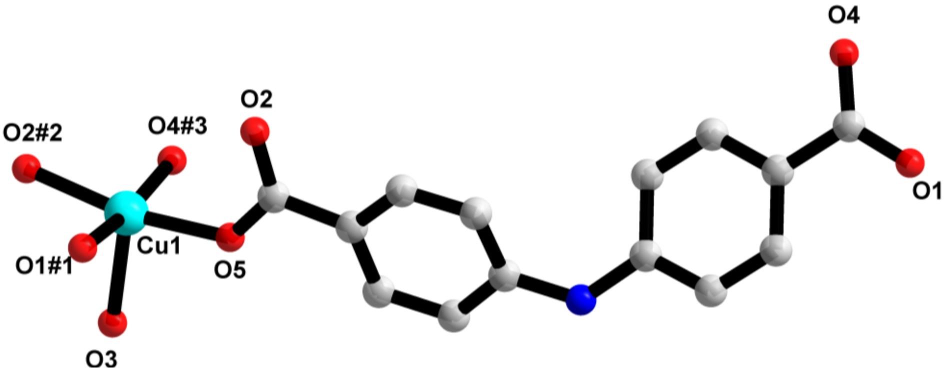

Figure S11. Coordination environment of the Cu(II) ion in **3**. The hydrogen atoms and solvent molecules are omitted for clarity. Symmetry codes: (#1) 0.25-*y*, -0.25+*x*, -0.25+*z*; (#2) -*x*, 1-*y*, 1-*z*; (#3) -0.25+*y*, 1.25-*x*, 1.25-*z*.

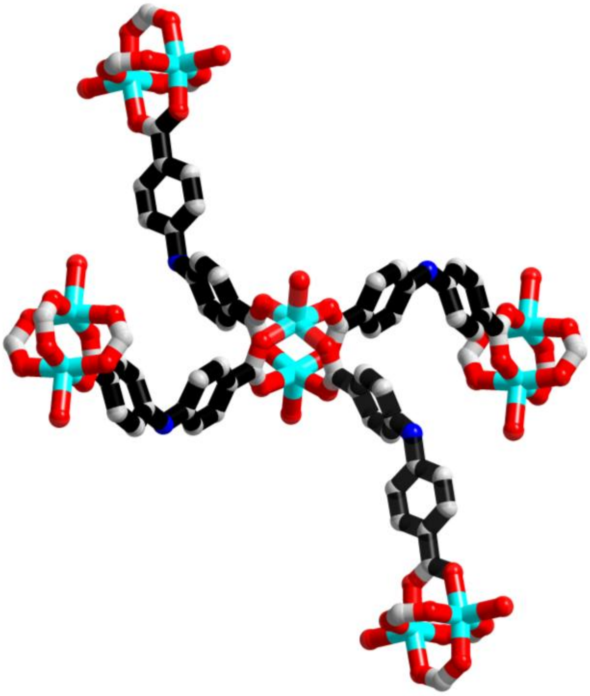

Figure S12. L^{2-} assembly with SBUs in **3** showing the way: up-up-down-down

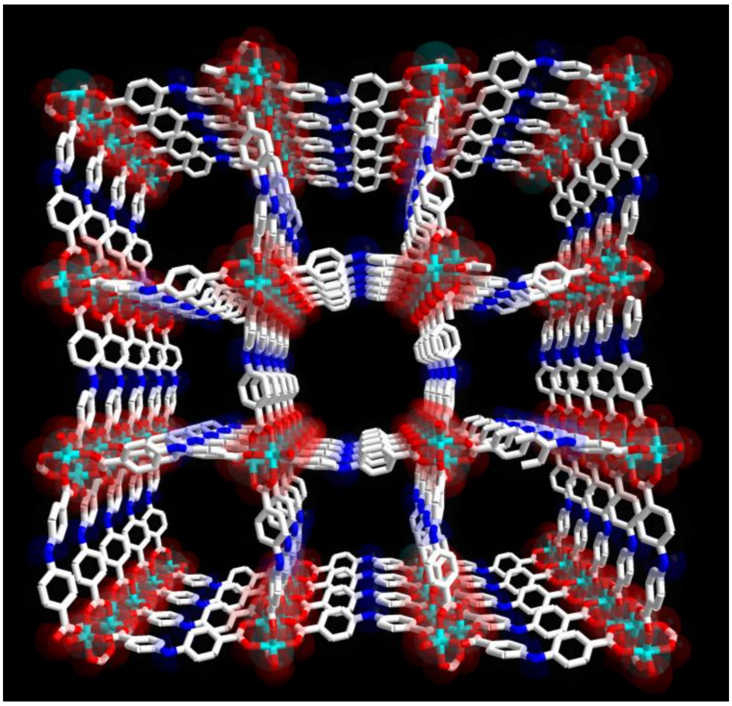

Figure S13. The 3D framework of a single net in **3**

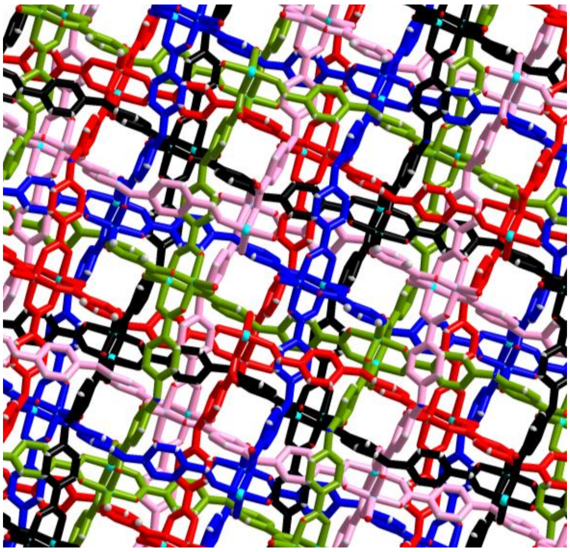

Figure S14. The five-fold interpenetrated framework in **3**

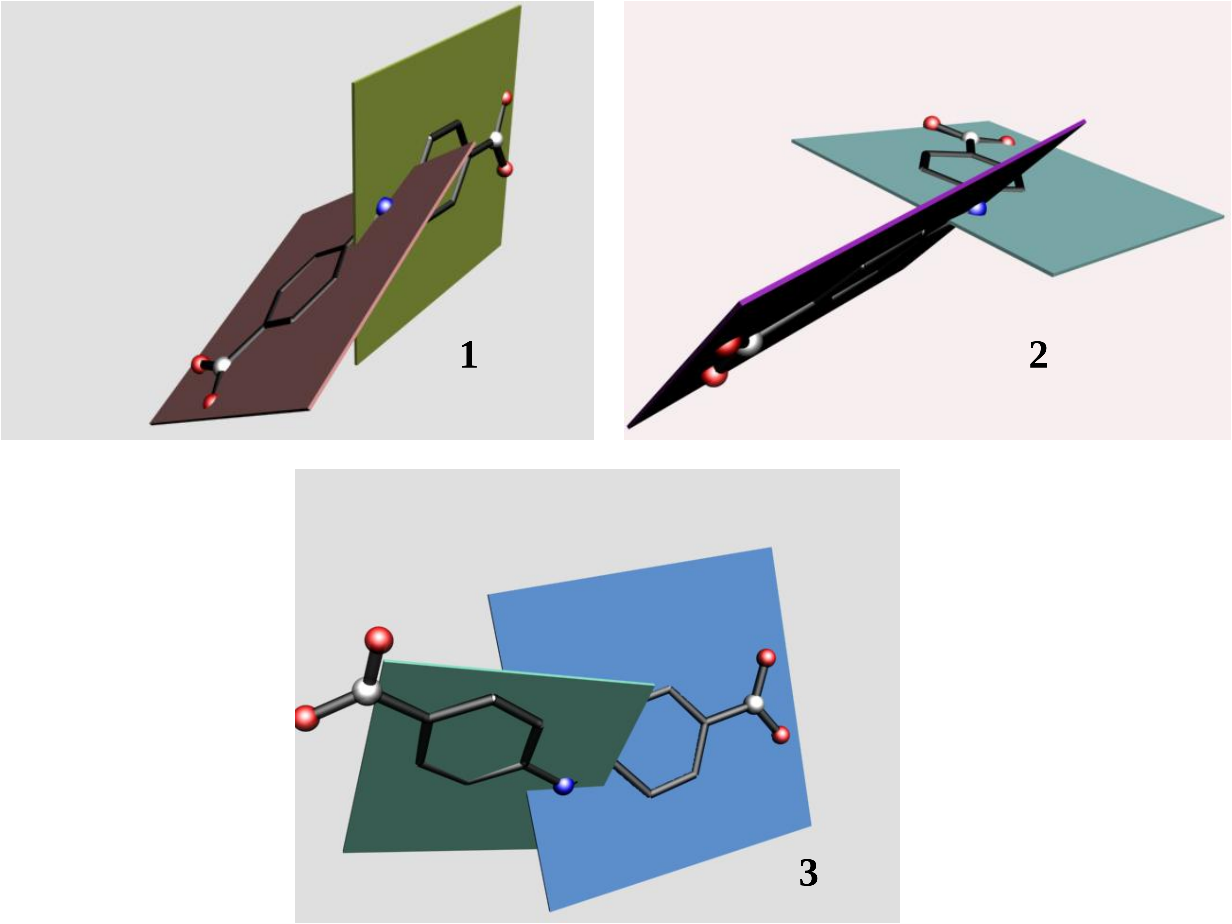

Figure S15. The configurations of L^{2-} in **1**, **2**, and **3**: the dihedral angles are 54.92(16) ^{o} / 55.09(12) ^{o}, 52.77(11) ^{o}, and 43.78(22) ^{o}, respectively; the C···N_{core}···C angles are 131.16 (7) ^{o} / 133.41(7) ^{o}, 129.70(5) ^{o}, and 128.88(13) ^{o}, respectively.

Reference

[1] Bruker **2000**, SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL (Version 6.1), and SADABS (Version 2.03); Bruker AXS Inc.: Madison, WI.

[2] Platon Program: A. L. Spek, *Acta Cryst. Sect.* A. 1990, **46**, 194.