

Electronic Supplementary Information

Destruction and reconstruction of the robust [Cu₂(OOCR)₄] unit during crystal structure transformations between two coordination polymers

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Contents

Experimental and computational details

Supplementary illustrations for crystal structures (Fig. S1 and Fig. S2)

Change of coordination bonds in transformation from **1** to **2** (Scheme S1)

Crystal photo (Fig. S3), PXRD patterns (Fig. S4), and TG curves (Fig. S5)

Tables of crystallographic data (Table S1, Table S2, and Table S3)

Experimental details

Materials and general methods. All starting materials and solvents were obtained commercially and used as received. Fourier transform (FT) IR spectra (KBr pellets) were recorded on an AVATAR-370 (Nicolet) spectrometer. Elemental analyses for C, H, and N were taken on a CE-440 (Leemanlabs) analyzer. Thermogravimetric (TG) and differential scanning calorimetric (DSC) experiments were performed on a NETZSCH TG209 (Siemens) thermal analyzer under N₂ atmosphere in 25–750 °C at a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) patterns were carried out on a Rigaku D/max-2500 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a step size of 0.02° in 2θ and a scan speed of 2 °/min. The simulated PXRD patterns were calculated from single-crystal X-ray diffraction data.

Single-crystal X-ray diffraction. X-ray diffraction data for complexes **1** and **2** were collected on a Bruker Apex II CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. In each case, a semi-empirical absorption correction (SADABS) was applied and the SAINT program was used for integration of the diffraction profiles. The structure was solved by direct methods using the SHELXS program of SHELXTL and refined using SHELXL by full-matrix least-squares methods on F^2 (with anisotropic thermal parameters for all non-H atoms). In general, C-bound H atoms were located geometrically and refined as riding, whereas O-bound H atoms (in **2**) were first determined in difference Fourier syntheses and then fixed at the calculated sites. Isotropic displacement parameters of H atoms were derived from their parent atoms. Further crystallographic details, selected bond lengths and angles, and H-bonding geometries are listed in Table S1, Table S2, and Table S3, respectively.

Preparation of [Cu(5-BN)₂]_n (1**).** A mixture of 5-HBN (20 mg, 0.1 mmol) in CH₃OH (5 mL) and CuSO₄·5H₂O (25 mg, 0.1 mmol) in H₂O (5 mL) was vigorously stirred for *ca.*

30 min and then filtrated. The solution was left to stand at room temperature. Green block single crystals of **1** were formed after 3 days and collected in 47% yield (11 mg, based on 5-HBN). Anal. calcd for $C_{12}H_6CuN_2O_4Br_2$: C, 30.96; H, 1.30; N, 6.02%. Found: C, 30.88; H, 1.21; N, 6.11%. IR (cm^{-1}): 1637vs, 1441m, 1392vs, 1290m, 1236w, 1133m, 1025w, 877w, 782m, 745s, 686m, 581w, 495m.

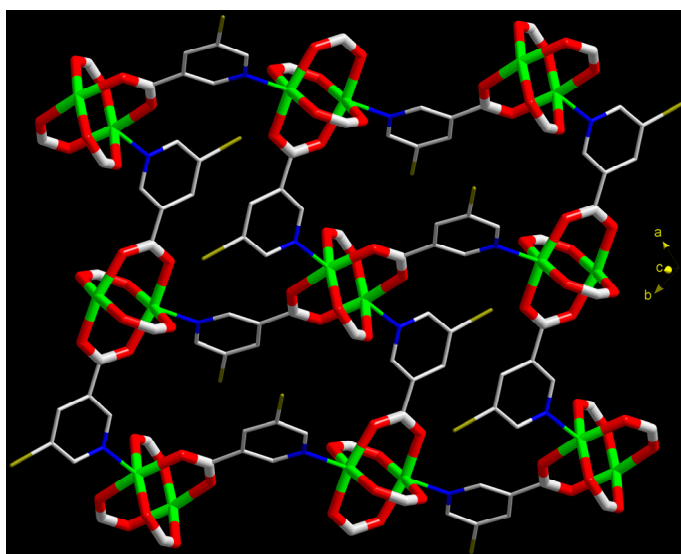
Preparation of $[Cu(5-BN)_2(H_2O)_2]_n$ (2**).** Blue block crystals of **2** were obtained from **1**, *via* a complete single crystal to single crystal (SC–SC) transformation at ambient conditions after a long period of ca. 40–50 days. Anal. calcd for $C_{12}H_{10}CuN_2O_6Br_2$: C, 28.74; H, 2.01; N, 5.59%. Found: C, 28.66; H, 1.93; N, 5.73%. IR (cm^{-1}): 3435b, 1637vs, 1557s, 1439s, 1386vs, 1291m, 1132m, 1095w, 1025w, 957w, 907w, 870w, 781m, 745s, 686m, 584w, 484w.

Computational details

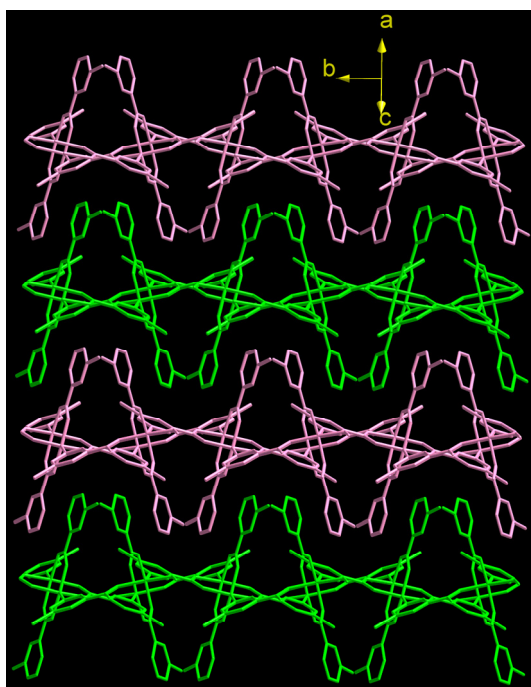
Herein, all calculations were performed with the Vienna Ab-initio Simulation Package (VASP),^{1,2} which is based on an iterative solution of the Kohn-Sham equations by using a plane wave basis set. Exchange-correlation energy was calculated within the generalized gradient approximation (GGA), using the form of the functional proposed by Perdew and Wang,^{3–5} which is usually referred to as Perdew-Wang 91 (PW91). Electron-ion interaction was described by using the projector-augmented wave (PAW) scheme.^{6,7} Reciprocal space of the unit cell was sampled with a $(6 \times 6 \times 4)$ *k*-points grid, generated automatically by using the Monkhorst-Pack method.⁸ Gaussian smearing profile (with a smearing parameter of 0.20 eV) was imposed at the Fermi level and the energy was extrapolated to zero smearing. Geometry optimization was stopped when atomic force is lower than 0.02 eV/Å. For the isolated water molecules, a cubic box was also built with the lattice length of 15 Å. Ground state energies for **1**, **2**, and water were calculated to be –181.67, –211.73, and –14.27 eV, respectively.

References

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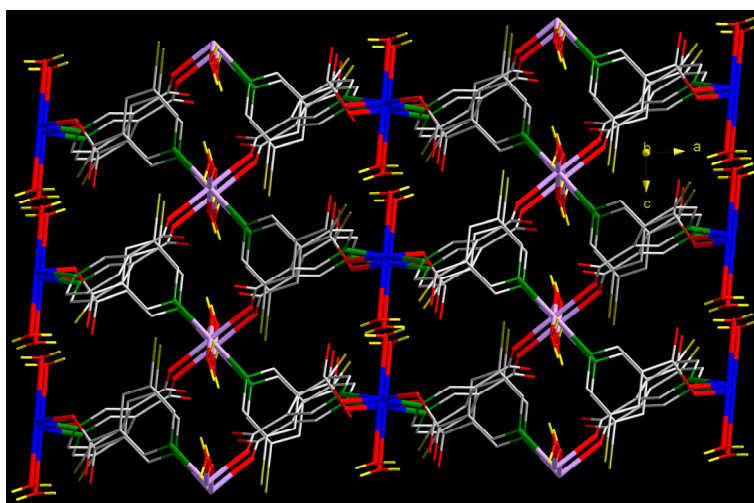


(a)

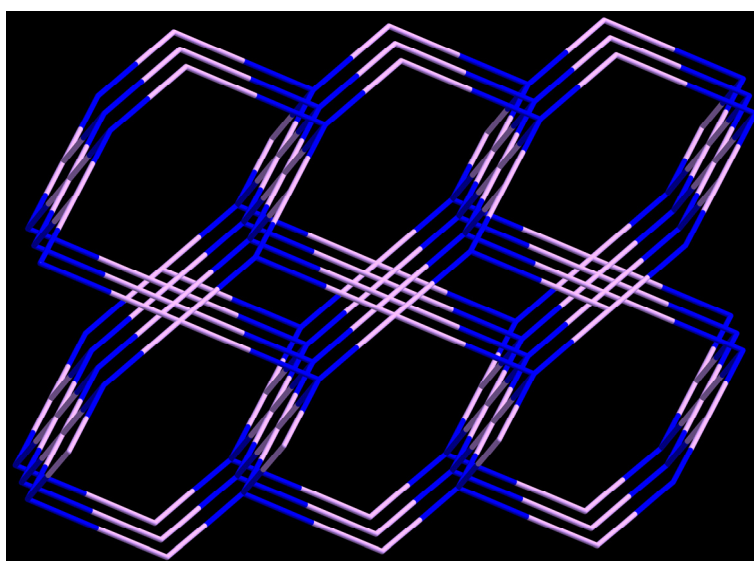


(b)

Fig. S1 Crystal structure of **1**. (a) 2-D layered array (the uncoordinated 5-bromopyridyl segments of 5-BN being omitted for clarity). (b) Packing diagram of the 2-D patterns. The adjacent 5-BN pendants coming from different layers are parallel with the center-to-center and center-to-plane distances of 3.635(2) and 3.461(2) Å, respectively.

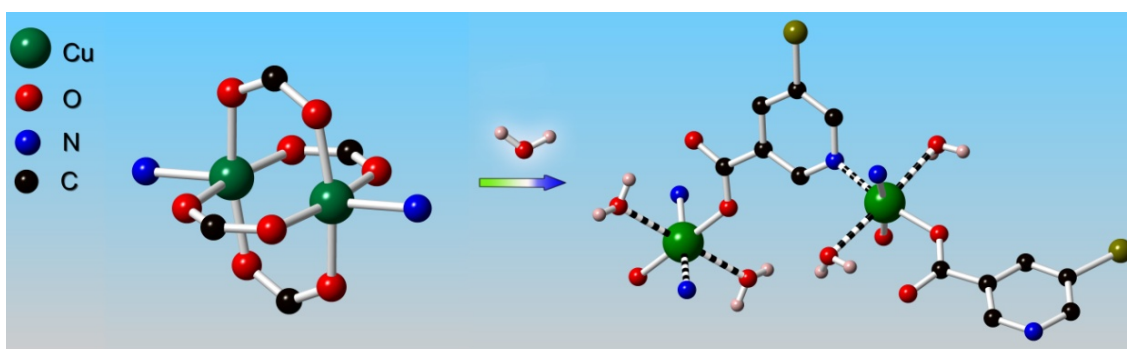


(a)



(b)

Fig. S2 Crystal structure of **2**. (a) 3-D coordination network. (b) Scheme of topological simplification. Cu1 and Cu2 nodes are shown in blue and lavender, respectively.



Scheme S1 Change of coordination bonds in transformation from **1** (left) to **2** (right). The striped lines in **2** represent the newly-formed Cu-N_{pyridyl} and Cu-O_{water} bonds.

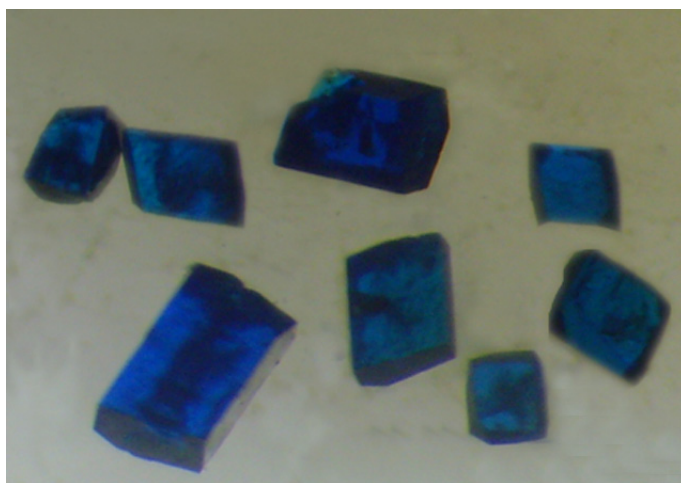


Fig. S3 Crystal photo for **2** synthesized at 5 °C.

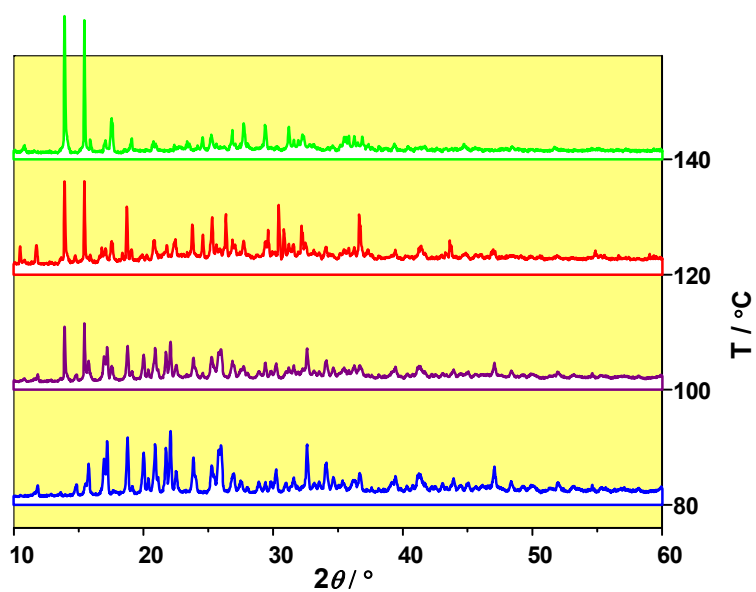


Fig. S4 PXRD patterns for hydrothermal crystalline products at different temperatures.

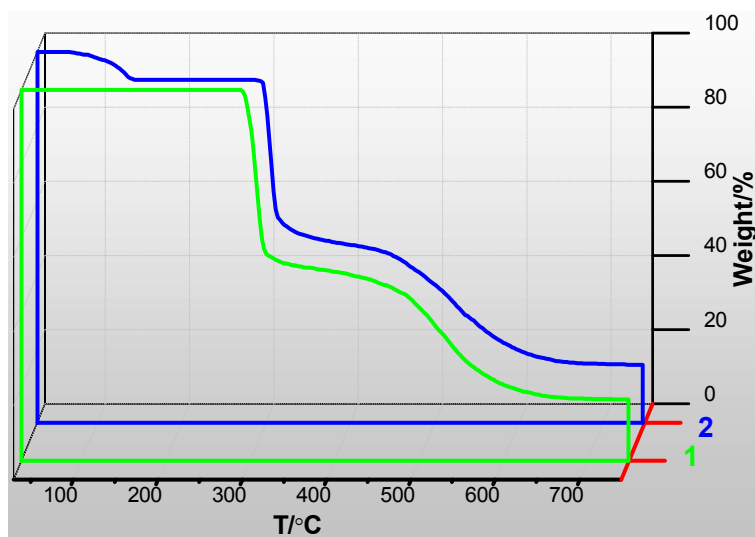


Fig. S5 Thermogravimetric (TG) curves for **1** (green) and **2** (blue).

Table S1 Crystallography data and structural refinement summary for **1** and **2**

	1	2
Chemical formula	C ₁₂ H ₆ CuN ₂ O ₄ Br ₂	C ₁₂ H ₁₀ CuN ₂ O ₆ Br ₂
Formula weight	465.55	501.58
Crystal size (mm ³)	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	11.2259(6)	25.981(3)
<i>b</i> (Å)	11.6460(7)	11.213(1)
<i>c</i> (Å)	12.8181(5)	11.088(1)
β (°)	116.694(3)	93.681(2)
<i>V</i> (Å ³)	1497.2(1)	3223.4(6)
<i>Z</i>	4	8
ρ_{calcd} (g cm ⁻³)	2.065	2.067
μ (mm ⁻¹)	6.810	6.343
No. of reflections measured	7535	8096
No. of independent reflections	2647	2847
<i>F</i> (000)	892	1944
Parameters	190	211
<i>R</i> _{int}	0.0198	0.0205
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2σ(<i>I</i>))	0.0327	0.0244
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.0910	0.0563
Final <i>R</i> _{<i>I</i>} values (all data)	0.0433	0.0290
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1095	0.0584
Goodness of fit on <i>F</i> ²	1.092	1.035
Residuals (e Å ⁻³)*	1.532, -1.155	0.840, -0.742

* In **1**, the peak and hole positions deviate by 0.99 Å from Br2 and 0.87 Å from Br1, respectively.

Table S2 Selective bond lengths (Å) and angles (°) for **1** and **2**

1			
Cu1–O2A	1.976(3)	Cu1–O1B	1.984(3)
Cu1–O4C	1.961(3)	Cu1–O3	1.961(3)
Cu1–N1	2.171(4)		
O4C–Cu1–O3	168.0(1)	O4C–Cu1–O2A	89.3(2)
O3–Cu1–O2A	89.4(2)	O4C–Cu1–O1B	89.2(2)
O3–Cu1–O1B	89.5(2)	O2A–Cu1–O1B	167.7(1)
O4C–Cu1–N1	92.9(2)	O3–Cu1–N1	99.1(2)
O2A–Cu1–N1	92.9(1)	O1B–Cu1–N1	99.3(1)
2			
Cu1–O3	1.961(2)	Cu1–N1	2.071(2)
Cu1–O5	2.390(2)	Cu2–O1	1.964(2)
Cu2–N2C	2.019(2)	Cu2–O6	2.483(2)
O3–Cu1–O3A	92.7(1)	O3–Cu1–N1	170.31(8)
O3–Cu1–N1A	89.03(8)	N1–Cu1–N1A	90.9(1)
O3A–Cu1–O5	99.02(7)	O3–Cu1–O5	84.06(7)
O5–Cu1–N1A	90.64(8)	N1–Cu1–O5	86.26(8)
O5–Cu1–O5A	175.6(1)	O1–Cu2–N2D	87.53(8)
O1–Cu2–O6B	93.18(8)	N2C–Cu2–O6	90.20(9)

Symmetry codes: A = $-x + 1, y - 1/2, -z + 3/2$; B = $x, -y + 3/2, z - 1/2$; C = $-x + 1, -y + 1, -z + 1$ for **1**;
A = $-x + 2, y, -z + 1/2$; B = $-x + 3/2, -y + 3/2, -z + 1$; C = $x - 1/2, y + 1/2, z$; D = $-x + 2, -y + 1, -z + 1$
for **2**.

Table S3 Hydrogen-bonding geometries (Å, °) in crystal structure of **2**

D–H...A	$d_{D...A}$	$d_{H...A}$	$\angle_{D-H...A}$	Symmetry code
O5–H5A...O4 ⁱ	2.847(3)	2.04	159	$i = x, -y + 1, z - 1/2$
O5–H5B...O4 ⁱⁱ	2.767(3)	1.95	160	$ii = -x + 2, y, -z + 1/2$
O6–H6A...O2 ⁱⁱⁱ	2.958(3)	2.24	142	$iii = -x + 3/2, -y + 3/2, -z + 1$
O6–H6B...O2 ^{iv}	3.053(3)	2.22	166	$iv = -x + 3/2, y - 1/2, -z + 1/2$