Supporting Information

Double-Step CO₂ Sorption and Guest-Induced Single-Crystal-to-Single-Crystal Transformation in a Flexible Porous Framework

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Materials and Measurements. All reagents and solvents were commercially available and were used without further purification. Infrared spectra (IR) were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400–4000 cm⁻¹ region. Elemental analyses (C, H and N) were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu K α , 1.5418 Å). All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment.

Synthesis of [Cu(L)(Me₂NH)]·DMF·H₂O (1). A mixture of Cu(NO₃)₂·3H₂O (24.1 mg, 0.10 mmol) and H₂L (25.9 mg, 0.10 mmol) in DMF (6 mL) was placed in a screw-capped vial (10 mL) and heated at 100 °C for 36 h and then cooled to room temperature at a rate of 10 °C/h. Purple block crystals of 1 were isolated by washing with DMF and dried in air. The yield was 24.1 mg (52.8%, based on H₂L). Anal. Calcd for C₁₈H₂₃CuN₃O₇: C, 47.31; H, 5.07; N, 9.20. Found: C, 47.51; H, 4.78; N, 9.25.

Transformation of 1 to [Cu_2(L)_2(Me_2NH)_2(H_2O)_2] \cdot 5H_2O (1b). 1b was obtained by repeatedly soaking sample of **1** in fresh CH_2Cl_2 solution every 12 hours for 3 days. In order to demonstrate that CH_2Cl_2 -induced transformation of **1** to **1b** occurs in a SC \rightarrow SC fashion, but not *via* dissolution of **1** followed by growth of **1b** in CH_2Cl_2 . Several crystals were carefully selected under an optical

microscope and soaked in fresh CH_2Cl_2 solution. During the transformation from 1 to 1b, except the color changed from original purple to blue, the morphology and size of the crystals did not changed, suggesting the SC \rightarrow SC process. Anal. Calcd for $C_{30}H_{42}Cu_2N_4O_{17}$: C, 42.01; H, 4.94; N, 6.53. Found: C, 42.14; H, 4.85; N, 6.47.

X-ray Single-Crystal Diffraction Analysis. The diffraction data were collected at 296(2) with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and Mo K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were carried out utilizing SADABS routine.¹ The structures were solved by direct methods and refined by full-matrix least-squares refinements based on F^2 with the SHELXTL program.² All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The guest solvents in **1b** are highly disordered and impossible to refine using conventional discrete-atom models, the SQUEEZE³ subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered solvent molecules. Further details of crystal data and structure refinement for **1** and **1b** were summarized in Table S1 and selected bond lengths and angles are given in table S2. The final formulas of **1** and **1b** were determined by combining single-crystal structure, elemental microanalysis and TGA. Crystallographic data for this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC: 1029487 for **1**, 1029488 for **1b**).

References

- 1 Bruker. SADABS, SMART and SAINT, Bruker AXS Inc., Madison, Wisconson, USA, 2002.
- 2 G. M. Sheldrick, Acta Crystallogr. A, 2008, 64: 112-122.
- 3 A. L. Spek, Acta Crystallogr., Sect. A, 1990, 46, C34.

Complex No.	1	1b
Empirical formula	C ₁₈ H ₂₃ CuN ₃ O ₇	$C_{30}H_{42}Cu_2N_4O_{17}$
Formula mass	456.94	857.76
Temperature [K]	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	8.976(4)	10.665(15)
<i>b</i> [Å]	10.699(5)	12.107(16)
<i>c</i> [Å]	11.570(6)	16.77(2)
α [deg]	99.393(8)	80.14(2)
β [deg]	104.513(8)	88.09(2)
γ [deg]	102.434(8)	69.37(2)
V[Å ³]	1022.3(9)	1996(5)
Ζ	2	2
$D_{\text{calcd.}}[g \cdot \text{cm}^{-3}]$	1.478	1.277
μ [mm ⁻¹]	1.112	1.122
GOF on F ²	1.041	1.094
reflns collected/ unique	15767/5055	10534/7208
R _{int}	0.0366	0.0928
Final R ^[a]	$R_1 = 0.0514$	$R_1 = 0.1030$
indices [I>2 σ (I)]	$wR_2 = 0.1565$	$wR_2 = 0.2577$

Table S1. Crystal data and structure refinements for 1 and 1b.

^{*a*} $R_1 = \Sigma ||F_0| - |F_c|) / \Sigma |F_0|; w R_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}$

Table S2. Selected bond lengths [[Å] and angles [°] f	for complexes 1 and 1b.
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Complex 1					
Cu(1)-O(1)	1.954(3)	Cu(2)-O(4)	1.946(2)		
Cu(1)-O(1)#1	1.954(3)	Cu(2)-O(4)#2	1.946(2)		
Cu(1)-N(2)#1	2.008(4)	Cu(2)-N(1)#3	2.029(3)		
Cu(1)-N(2)	2.008(4)	Cu(2)-N(1)#4	2.029(3)		
O(1)-Cu(1)-O(1)#1	180.00(16)	O(4)-Cu(2)-O(4)#2	180		
O(1)-Cu(1)-N(2)#1	89.95(14)	O(4)-Cu(2)-N(1)#3	89.64(10)		
O(1)#1-Cu(1)-N(2)#1	90.05(14)	O(4)#2-Cu(2)-N(1)#3	90.36(10)		
O(1)-Cu(1)-N(2)	90.05(14)	O(4)-Cu(2)-N(1)#4	90.36(10)		
O(1)#1-Cu(1)-N(2)	89.95(14)	O(4)#2-Cu(2)-N(1)#4	89.64(10)		
N(2)#1-Cu(1)-N(2)	180.0(2)	N(1)#3-Cu(2)-N(1)#4	180.00(14)		
Complex 1b					
Cu(1)-O(7)#1	1.937(8)	Cu(2)-O(3)#2	1.972(8)		
Cu(1)-O(1)	1.994(8)	Cu(2)-O(9)#3	1.973(7)		
Cu(1)-N(3)	2.043(11)	Cu(2)-N(1)	2.009(7)		
Cu(1)-N(4)	2.071(10)	Cu(2)-N(2)	2.049(8)		

Cu(1)-O(1W)	2.369(8)	Cu(2)-O(2W)	2.391(11)
O(7)#1-Cu(1)-O(1)	175.9(3)	O(3)#2-Cu(2)-O(9)#3	176.3(4)
O(7)#1-Cu(1)-N(3)	91.9(4)	O(3)#2-Cu(2)-N(1)	90.3(3)
O(1)-Cu(1)-N(3)	89.2(4)	O(9)#3-Cu(2)-N(1)	89.7(3)
O(7)#1-Cu(1)-N(4)	91.2(4)	O(3)#2-Cu(2)-N(2)	88.8(3)
O(1)-Cu(1)-N(4)	86.8(4)	O(9)#3-Cu(2)-N(2)	90.7(3)
N(3)-Cu(1)-N(4)	165.4(4)	N(1)-Cu(2)-N(2)	174.4(3)
O(7)#1-Cu(1)-O(1W)	84.1(3)	O(3)#2-Cu(2)-O(2W)	99.4(4)
O(1)-Cu(1)-O(1W)	99.7(3)	O(9)#3-Cu(2)-O(2W)	84.3(4)
N(3)-Cu(1)-O(1W)	97.7(4)	N(1)-Cu(2)-O(2W)	90.9(4)
N(4)-Cu(1)-O(1W)	96.8(4)	N(2)-Cu(2)-O(2W)	94.7(4)

Symmetry codes: 1, #1 -x+2, -y+2, -z; #2 -x+1, -y, -z+1; #3 -x+1, -y+1, -z+1; #4 x, y-1, z; #5 x, y+1, z; 1b, #1 x, y,

z+1; #2 x+1, y, z; #3 x-1, y, z; #4 x, y, z-1.



Figure S1. The 2D layers of 1 a) and 1b b).



Figure S2. The green dotted lines show the π - π interactions between the neighboring 2D layers in **1**. One of the later is shown in blue and the other in pink.



Figure S3. The hydrogen bonds between the host structure and the guest molecules (O6–N3 = 2.881(7) Å, O6–O1w = 2.874(2) Å).



Figure S4. TGA curves for 1, 1a and 1b.



Figure S5. IR spectra for 1 (black) and 1a (red). The characteristic C=O vibration at 1666 cm⁻¹ of DMF in 1 is absent in 1a, indicating the complete removal of DMF.



Figure S6. PXRD patterns of 1: simulated from the crystals I), as-synthesized sample II), MeOH exchanged-sample III), after gas adsorption sample IV), and resolvated sample V).



Figure S7. Simulated (black) and experimental (red) XRPD patterns for 1b.





Figure S8. View of the π - π interactions between the neighboring 2D layers in 1 (up) and 1b (down). The pink and green dotted lines show the the vertical distance of two phenyl in 1 and 1b, respectively. The vertical distance of two phenyl is 3.381(5) in 1 and 3.399(3) Å in 1b, respectively. The red and green colors present four different layers in 1; The red and pink colors present four different layers in 1b.



Figure S9. The XRD of the samples of 1 and those after soaking in the saturated vapor or liquid CH_3OH/CH_2Cl_2 .



Figure S10. Gas sorption isotherms: N_2 and H_2 at 77 K, and CH_4 at 195 K. Closed symbols and open symbols represent adsorption and desorption isotherms, respectively.