Supporting Information

Selective CO_2 adsorption in a flexible non-interpenetrated metal-organic framework

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Experimental Details

General Method. All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. Tetrakis[4-(carboxyphenyl)oxamethyl]methane (H_4TCM) was prepared according to the method previously reported.[S1] Infrared spectra were recorded with a PerkinElmer Spectrum One FT-IR spectrophotometer. UV/vis diffuse reflectance spectra were recorded with a PerkinElmer Lambda 35 UV/vis spectrophotometer. Elemental analyses were performed with a PerkinElmer 2400 Series II CHN Analyzer. NMR spectra were measured on a Bruker Avance DPX-300. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed under N_2 (g) at a scan rate of 5 °Cmin^{-1}, using a TGA Q50 and a DSC Q10 of TA instruments, respectively. Powder X-ray diffraction data were recorded on a Mac Science M18XHF-22 diffractometer at 50 kV and 100 mA for Cu Kα (λ = 1.54050 Å), with a scan speed 5 ºmin^{-1} and a step size of 0.02º in 2θ.

$[Cu_2(TCM)(H_2O)_2]$·7DMF·3(1,4-dioxane)·MeOH (SNU-21). H_4TCM (0.033 g, 0.054 mmol) was dissolved in a mixture of DMF (3 mL) and 1,4-dioxane (3mL), and mixed with MeOH (1 mL) solution of $Cu(NO_3)_2$·$2.5H_2O$ (0.025 g, 0.11 mmol). Aqueous HCl (35%) was added (1-2 drops) to the mixture. The solution was heated in a glass serum bottle at 80 °C for 24 h, and then cooled to room temperature. Bluish-green prismatic crystals formed, which were filtered, and washed briefly with the DMF, 1,4-doxane and MeOH mixture (3:3:1, v/v). Yield: 40 mg (47%). Anal. Calcd for $Cu_2C_{67}H_{105}N_7O_{28}$: C, 50.81; H, 6.68; N, 6.19. Found: C, 50.25; H, 6.38; N, 6.04. FT-IR (Nujol mull): $\nu_{OH(water)}$, 3410 (m, br); $\nu_{C=O(guest\ DMF)}$, 1677 (br); $\nu_{O\text{-}C=O}$, 1605, 1571 (s) cm^{-1}. UV/vis (diffuse reflectance spectrum, λ_{max}): 711 nm.

$[Cu_2(TCM)]_n$ (SNU-21H). The crystals of **SNU-21** were heated at 180 °C under vacuum for 12 h. The color of **SNU-21H** changed from bluish-green to light green. Anal. Calcd for $Cu_2C_{33}H_{24}O_{12}$: C, 53.59; H, 3.27; N, 0.00. Found: C, 52.31; H, 3.28; N, 0.08. FT-IR (Nujol mull): $\nu_{O\text{-}C=O}$, 1605(s), 1564(s) cm^{-1}. UV/vis (diffuse reflectance spectrum, λ_{max}): 723 nm.

$[Cu_2(TCM)]_n$ (SNU-21S) Prepared by Supercritical CO_2 Drying Method. The crystals of **SNU-21** as synthesized were placed in the supercritical dryer together with the solvent (DMF, 1,4-dioxane and MeOH), and the drying chamber was sealed. The temperature and pressure of the chamber were raised to 45 °C and 200 bar with CO_2, above the critical point (31 °C and 73 atm). The chamber was vented with the rate of 15 mL/min, and then filled with CO_2 again. The cycle of refilling with CO_2, pressurizing, and venting was repeated for 6 h. After drying, the closed container with the dried crystals was transferred to a glove bag, and the sample was manipulated in a glove bag to prevent it from the exposure to air. Anal. Calcd for $Cu_2C_{33}H_{24}O_{12}$: C, 53.59; H, 3.27; N, 0.00. Found: C, 52.70; H, 3.19; N, 0.31. FT-IR (Nujol mull): 1606 (s); $\nu_{O\text{-}C=O}$, 1565 (s) cm^{-1}. UV/vis (diffuse reflectance spectrum, λ_{max}): 698 nm.

X-ray Crystallography. Diffraction data for **SNU-21** was collected with an Enraf Nonius Kappa CCD diffractometer (Mo Kα, λ = 0.71073 Å, graphite monochromator). Preliminary orientation matrixes and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. The frames were integrated and corrected for the Lorentz and polarization effects using *DENZO*.[S2] The scaling and global refinement of the crystal parameters were performed by using *SCALEPACK*.[S2] No absorption correction was made. The crystal structures were solved by the direct method[S3] and refined by full-matrix least-squares refinement using the SHELXL-97 computer program.[S4] The positions of all of the non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically and refined using a riding model. The identity and number of the guest molecules (7DMF, 3(1,4-dioxane), and MeOH) in **SNU-21** were determined based on the IR, EA, NMR, and TGA data. The electron densities of the disordered guest molecules were flattened by using the SQUEEZE option of *PLATON*.[S5] The crystallographic data and selected bond distances and angles are summarized in Table S1 and Table S2.

Low Pressure Gas Sorption Measurements. The gas adsorption–desorption experiments were performed using an automated micropore gas analyzer, an Autosorb-3B (Quantachrome Instruments).

$[Cu_2(TCM)]_n$ (**SNU-21H**) was predesolvated by heating **SNU-21H** in a Schlenk tube at 180 °C under vacuum for 12 h. The measured amount of the pre-dried solid was introduced to the gas sorption apparatus and then activated at 180 °C under vacuum for 2 h, and then the gas sorption was measured. Between the experiments with various gases, the out-gassing procedure was repeated for ca. 1 h. For $[Cu_2(TCM)]_n$ (**SNU-21S**), the gas sorption isotherms were measured without activation procedure. All of the gases used were of 99.999% purity. The N_2 and O_2 gas sorption isotherms were monitored at 77 K by using liquid nitrogen, and the H_2 gas sorption isotherms were monitored at 77 K and 87 K at each equilibrium pressure by the static volumetric method. The adsorption isotherms for the CO_2 and CH_4 gases were measured at 195 K, 273 K, and 298 K.

Estimation of Isosteric Heats of H_2 Adsorption. The isosteric heats of H_2 adsorption for **SNU-21H** and **SNU-21S** were estimated from the H_2 sorption data measured at 77 K and 87 K. A virial-type expression was used (eq 1), which is composed of parameters a_i and b_i, which are independent of temperature.[S6] In eq. 1, P is the pressure in atm, N is the amount of adsorbed H_2 gas in mgg^{-1}, T is the temperature in K, a_i and b_i are the virial coefficients, and m and n represent the number of coefficients required to adequately describe the isotherms. An equation was fit using the R statistical software package.[S7]

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad \textbf{(1)}$$

The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression:

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad \textbf{(2)}$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

Estimation of Isosteric Heats of CO_2 and CH_4 Adsorption. Gas adsorption data at 195 K, 273 K, and 298 K were fit to Langmuir-Freundlich equation (eq 3), and then heat of adsorption was calculated by using Clausius-Clapeyron equation (eq 4) at each gas loading point.[S6]

$$N = \frac{N_m b P^{1/t}}{1 + b P^{1/t}} \qquad \textbf{(3)}$$

$$\frac{\partial(\ln P)}{\partial(1/T)} = -\frac{Q_{st}}{R} \qquad \textbf{(4)}$$

High Pressure Gas Sorption Measurements. High-pressure sorption isotherms for H_2, CO_2, and CH_4 gases were measured on a Rubotherm MSB (magnetic suspension balance) apparatus by the gravimetric method. All of the gases used were of 99.999% purity and the trace of moisture was removed by drying trap (model 500) filled with 5 Å molecular sieves, which was purchased from the Chromatography Research Supplies (CRS). A measured amount of **SNU-21S,** which was prepared by supercritical CO_2 drying method, was introduced to the apparatus and activated by evacuation at room temperature. To obtain the excess adsorption isotherm, all the data were corrected for buoyancy of the system and the sample. The buoyancy correction of the sample was made by multiplying the volume of the framework skeleton by the density of corresponding gas at each pressure and temperature.[S8] The sample density used for buoyancy correction was determined from the He displacement isotherm (up to 90 bars) measured at 298 K. The total amount of gas adsorbed was calculated using the following equation:[S9]

$$C_{\text{total}} = C_{\text{excess}} + (V_{\text{pore}} \times d_{gas} \times 100) \qquad \textbf{(5)}$$

where C_{total} is the total adsorbed amount (wt%), C_{excess} is the excess adsorbed amount (wt%) on the surface, V_{pore} is the pore volume (cm^3g^{-1}) calculated from the gas sorption, and d_{gas} is the density of the compressed gas as a function of temperature and pressure (gcm^{-3}).[S8]

Gas Cycling Experiments. The CO_2 gas cycling experiments were performed on a TGA Q50. Prior to gas cycling, **SNU-21H** was reactivated at 180 °C for 2 h and **SNU-21S** was reactivated at 30 °C for 1 h, followed by cooling to 25 °C under a nitrogen atmosphere. A flow of 15% (v/v) CO_2 mixture in N_2 was applied followed by a stream of pure N_2 (99.9999%). The flow rates for pure N_2 gas and CO_2 mixture gas are 60 mL min^{-1} and 40 mL min^{-1}, respectively.

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(S2) Z. Otwinowsky, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode. Methods in Enzymology*; C. W. Cater, R. M. Sweet, Eds., Academic Press, New York, 1996, **276**, 307.

(S3) G. M. Sheldrick, *Acta Crystallogr*. 1990, **A46**, 467.

(S4) G. M. Sheldrick, *SHELXL97, Program for the crystal structure refinement*; University of Göettingen: Göettingen, Germany, 1997.

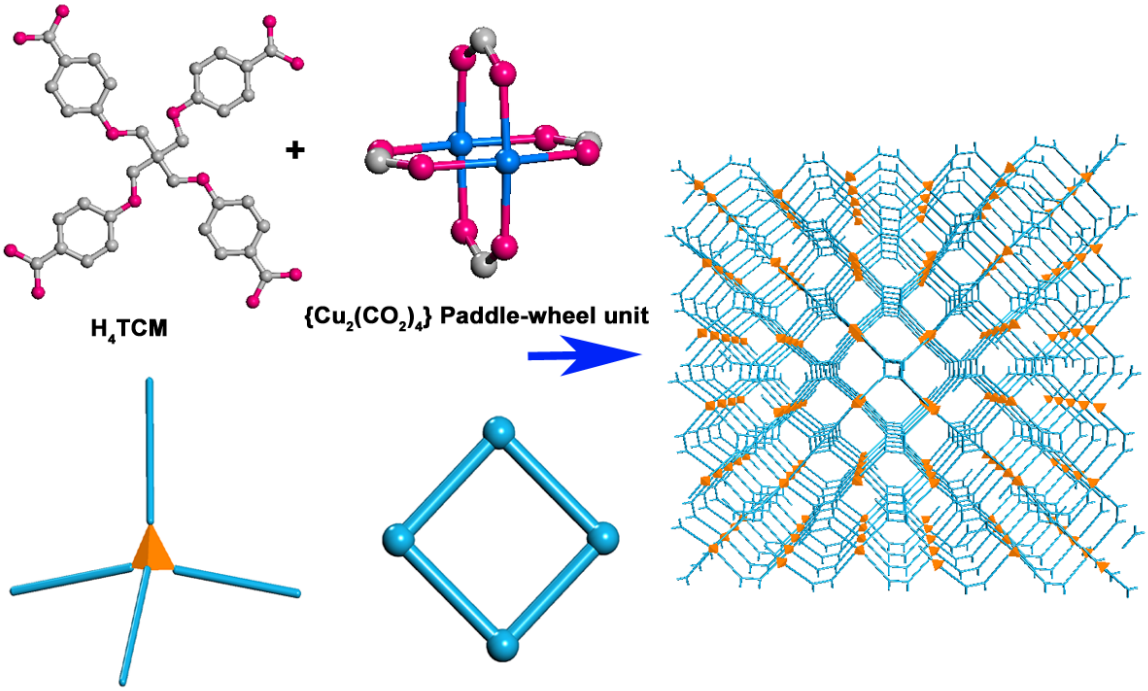
(S5) P.v.d. Sluis, A. L. Speck, *Acta Crystallogr.*, *Sect A* 1990, **46**, 194.

(S6) (*a*) M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.* 2006, **128**, 16876; (*b*) Czepirski and J. Jagiello, *Chem. En. Sci.* 1989, **44**, 797.

(S7) The software package area available online at http://www.r-project.org.

(S8) NIST chemistry webbook (thermophysical properties of fluid systems): http://webbook.nist.gov/chemistry/fluid/.)

(S9) (*a*) H. Furukawa, M. A. Miller and O. M. Yaghi, *J. Mater. Chem.* 2007, **17**, 3197; (*b*) A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.* 2005, **127**, 17998; (*e*) S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Am. Chem. Soc*. 2007, **129**, 14176.1



Scheme S1. Synthetic strategy for construction of PtS-type net from a tetrahedral organic building block and a paddle-wheel SBU.

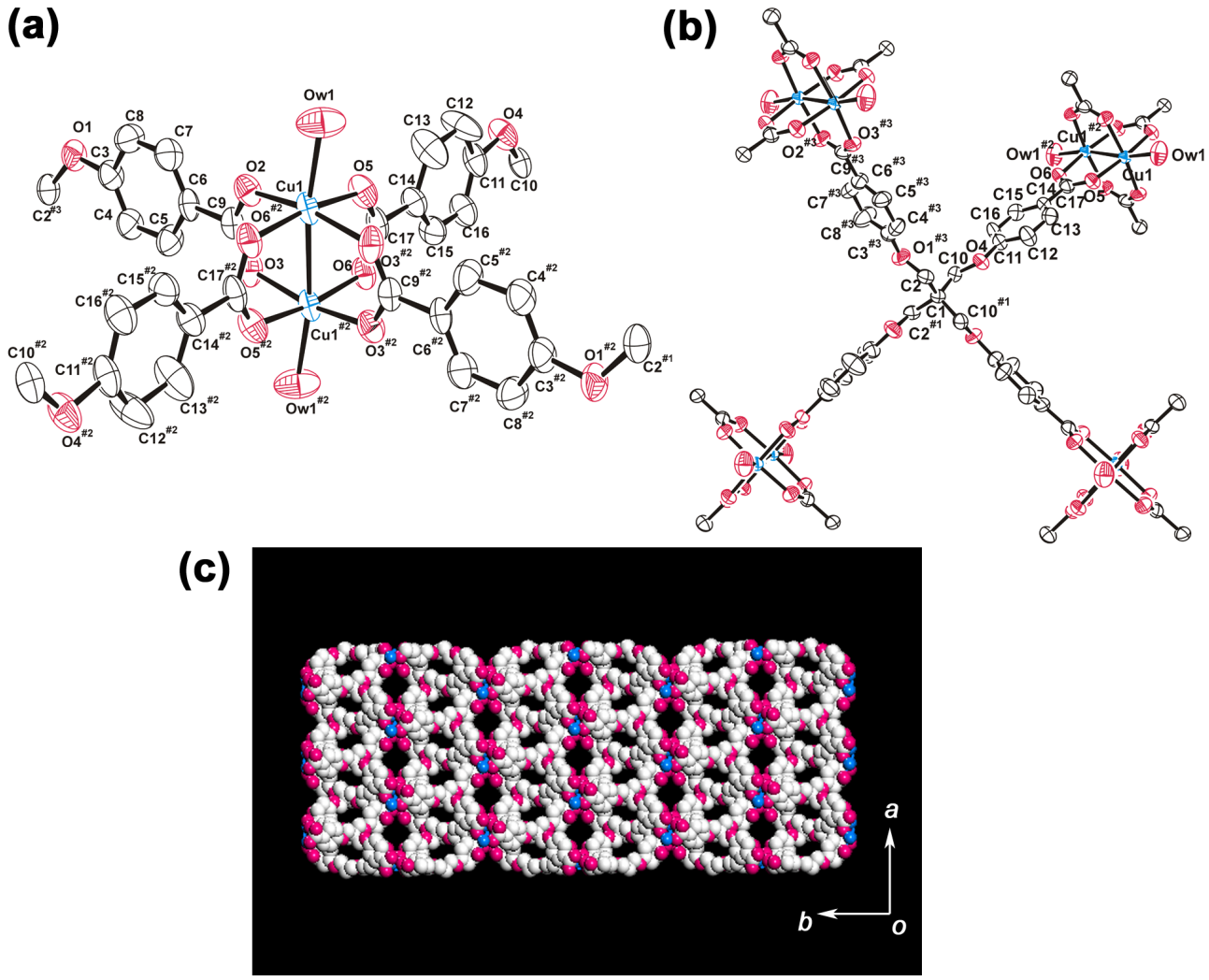


Fig. S1 The X-ray crystal structure of $\{[Cu_2(TCM)(H_2O)_2]\cdot 7DMF\cdot 3(1,4\text{-dioxane})\cdot MeOH\}_n$ (**SNU-21**) (a) An ORTEP drawing with atomic numbering scheme (thermal ellipsoids at 30% probability). Symmetry operation: #1, x+1/2, y-1/2, z; #2, -x+2, -y+1, -z; #3, -x+3/2, -y+3/2, -z. (b) An ORTEP drawing with an atomic numbering scheme (thermal ellipsoids at 30% probability). The hydrogen atoms of coordinated water molecules were not located. Hydrogen atoms are omitted for clarity. Symmetry operations: #1, -x+2, y, -z+1; #2, -x+2, -y+1, -z; #3, -x+3/2, -y+3/2, -z. (c) A view seen on *ab* plane. Color code: Cu, blue; C, white; O, red.

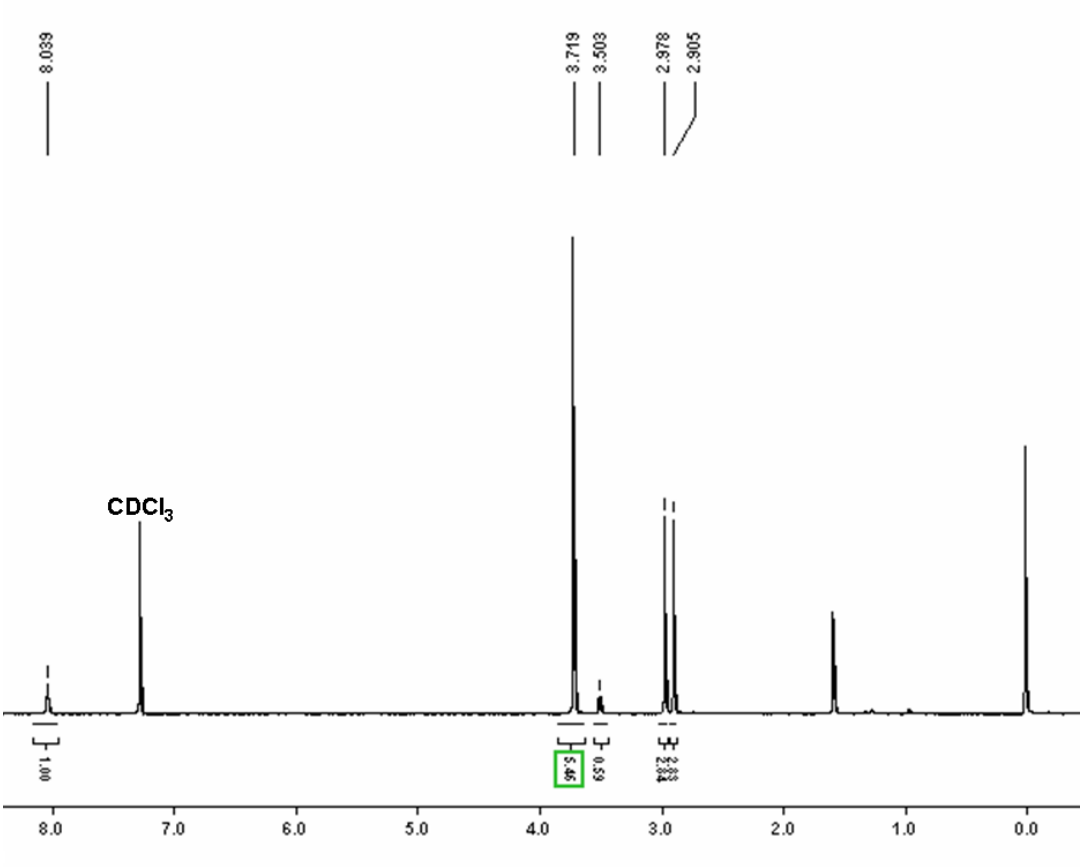


Fig. S2 ^{1}H-NMR spectrum of $CDCl_3$ after the immersion of $\{[Cu_2(TCM)(H_2O)_2]\cdot 7DMF\cdot 3(1,4\text{-dioxane})\cdot MeOH\}_n$ (**SNU-21**) for 24 h. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.04, 3.72, 3.50, 2.91, 2.98. The spectrum was measured to identify the number of guest solvent molecules in **SNU-21**.

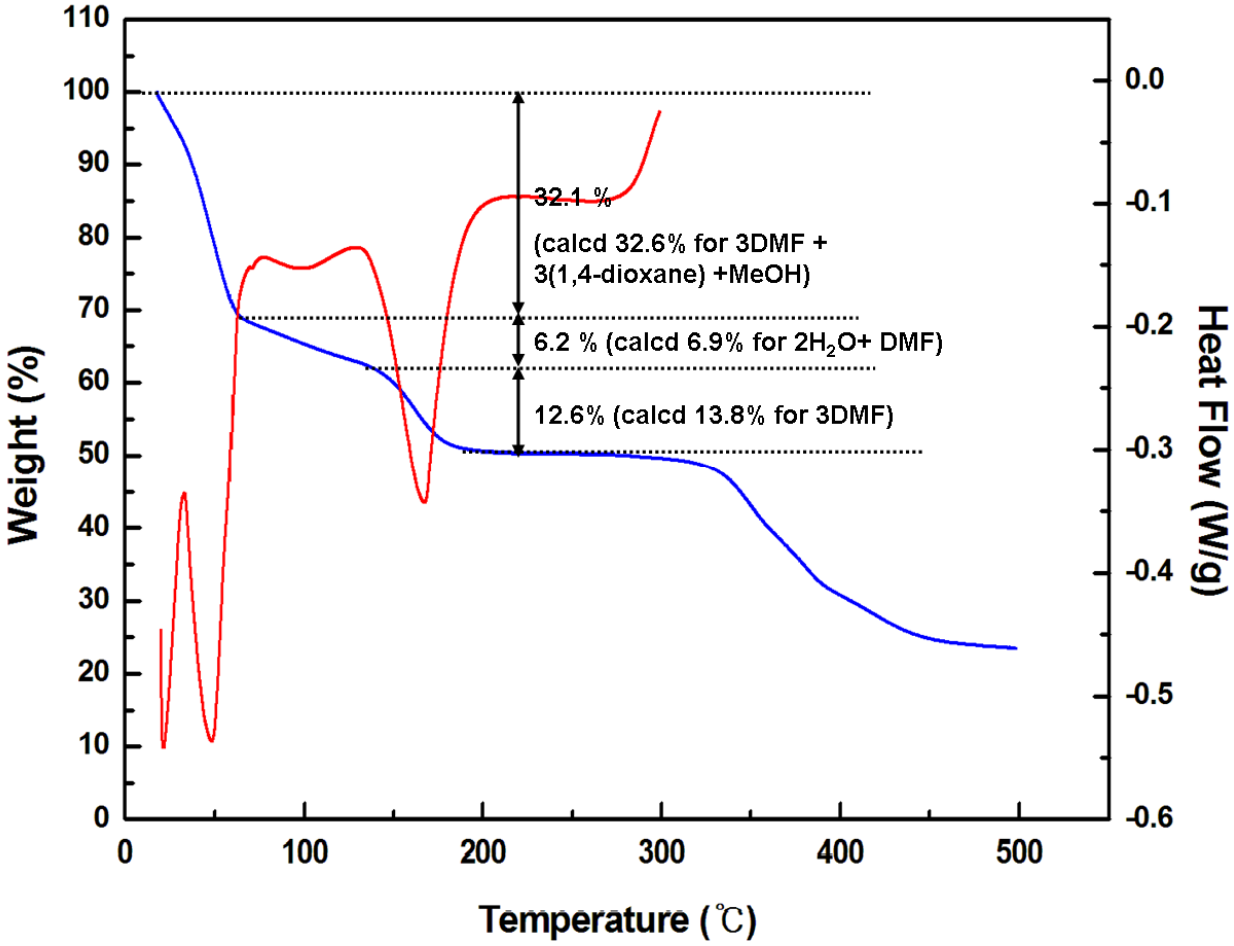


Fig. S3 TGA/DSC traces for $\{[Cu_2(TCM)(H_2O)_2]\cdot 7DMF\cdot 3(1,4\text{-dioxane})\cdot MeOH\}_n$ (**SNU-21**). Thermogravimetric analysis revealed 32.1% weight loss at 25-70 °C, corresponding to the loss of three DMF, three 1,4-dioxane, and one MeOH guest molecules (calcd 32.6%) per formula unit, followed by an additional weight loss of 18.8% at 70-300 °C, corresponding to four DMF guests and two coordinated H_2O molecules (calcd 20.7%).

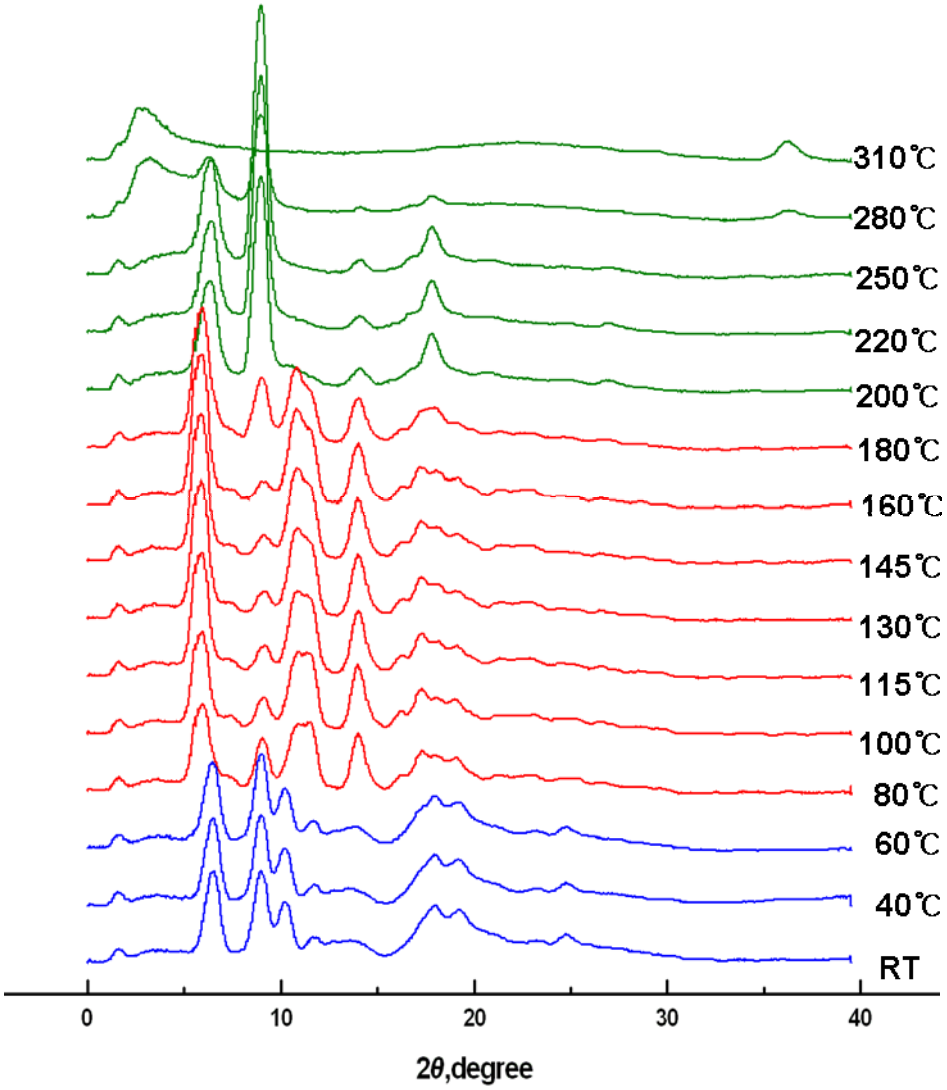


Fig. S4 The PXRD patterns of **SNU-21** measured at various temperatures (from R.T. to 300 ^{o}C).

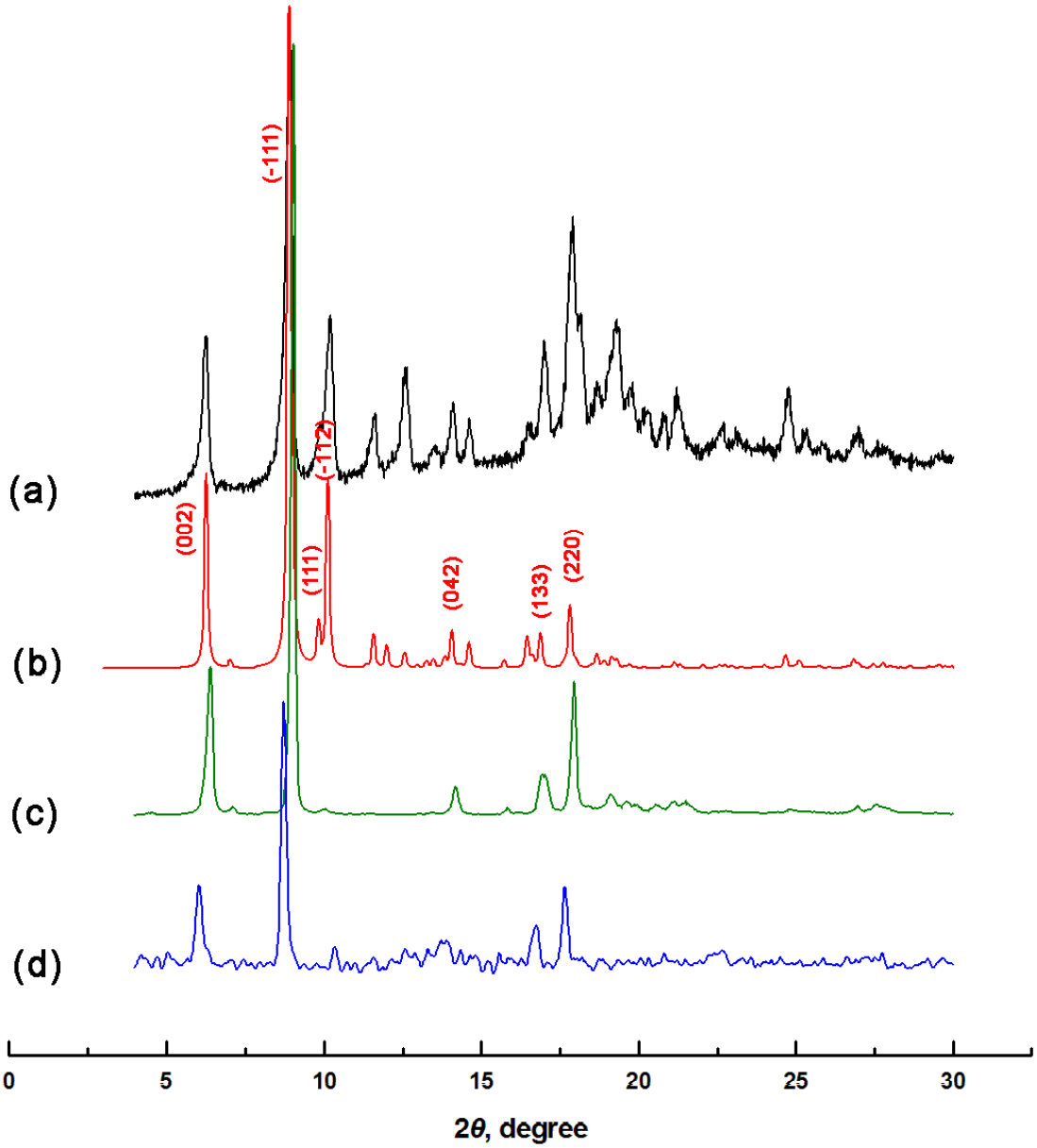


Fig. S5 The PXRD patterns, for (a) original solid **SNU-21**, (b) simulated pattern based on the single-crystal X-ray data of **SNU-21**, (c) desolvated solid **SNU-21H** prepared by heating **SNU-21** at 180 °C under vacuum for 12 h, (d) desolvated solid **SNU-21S** prepared by supercritical CO_2 drying method.

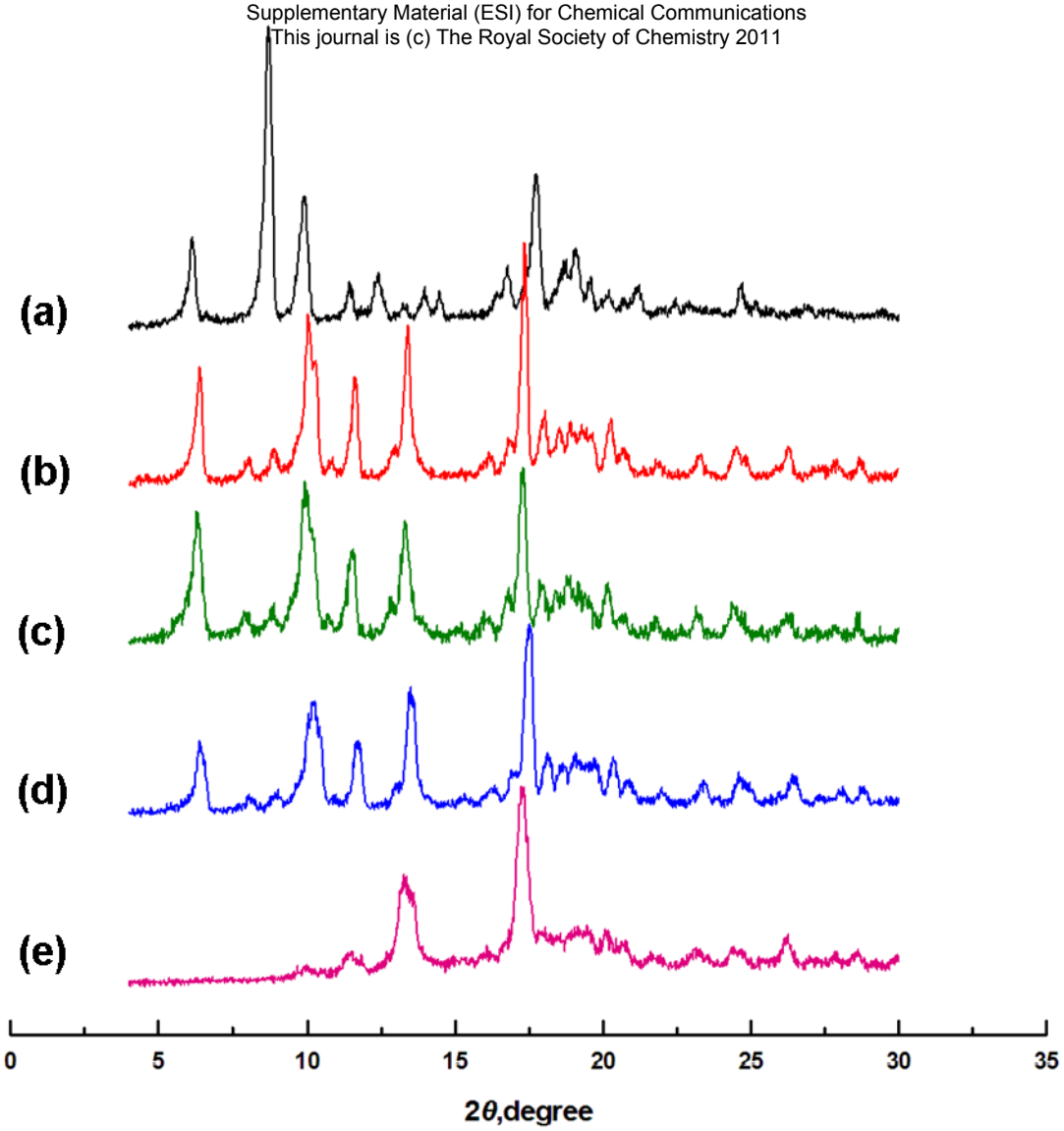


Fig. S6 The PXRD patterns of **SNU-21** on exposure to air. (a) as-synthesized, (b) exposure to air for 1 day, (c) exposure to air for 3 days, (d) exposure to air for 5 days, (e) exposure to air for 7days. When solid **SNU-21** was exposed to air for 1 day, the PXRD pattern of **SNU-21** was changed, indicating that the network structure alters due to the loss of guest solvent molecules

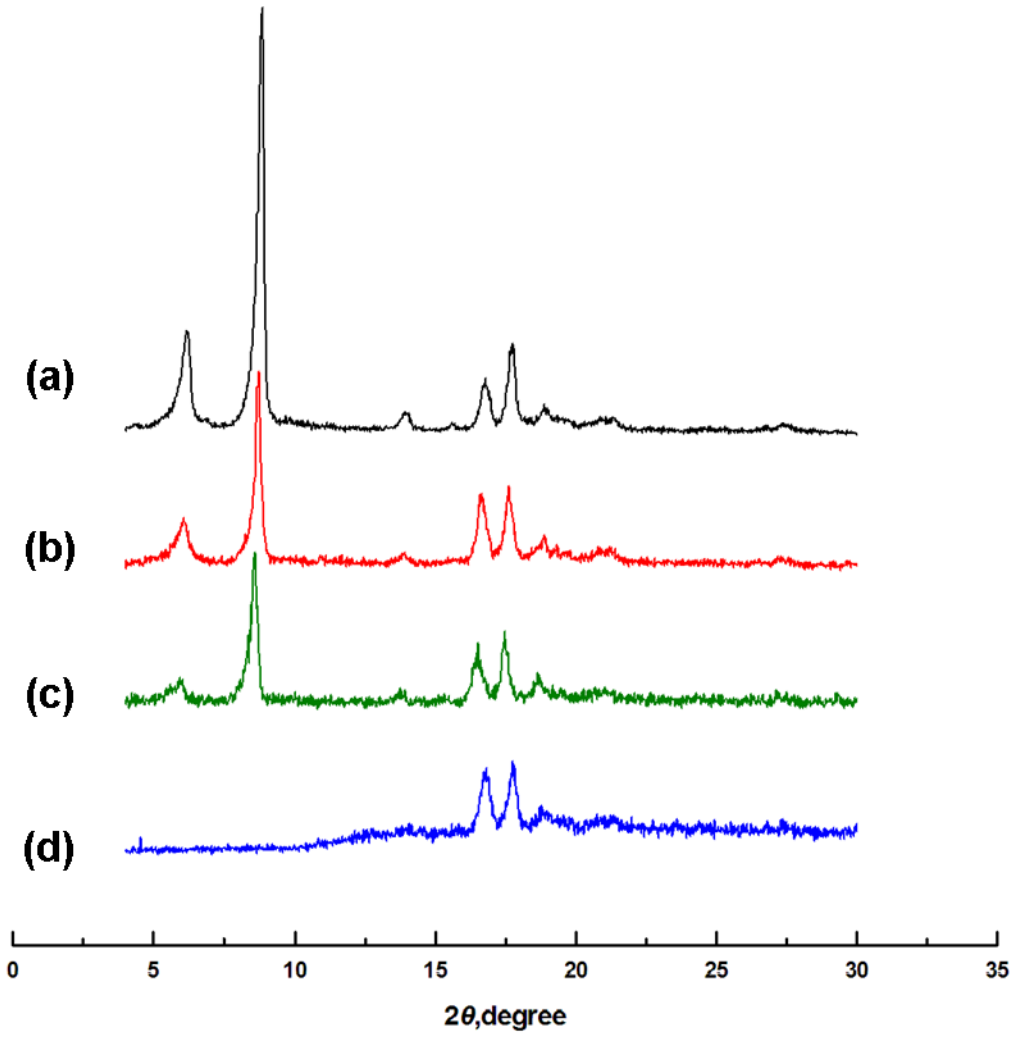


Fig. S7 The PXRD patterns of **SNU-21H.** (a) as prepared by drying **SNU-21** at 180 °C under vacuum for 12 h, (b) after exposure to air for 1 day, (c) after exposure to air for 5 days, (d) after exposure to air for 7 days.

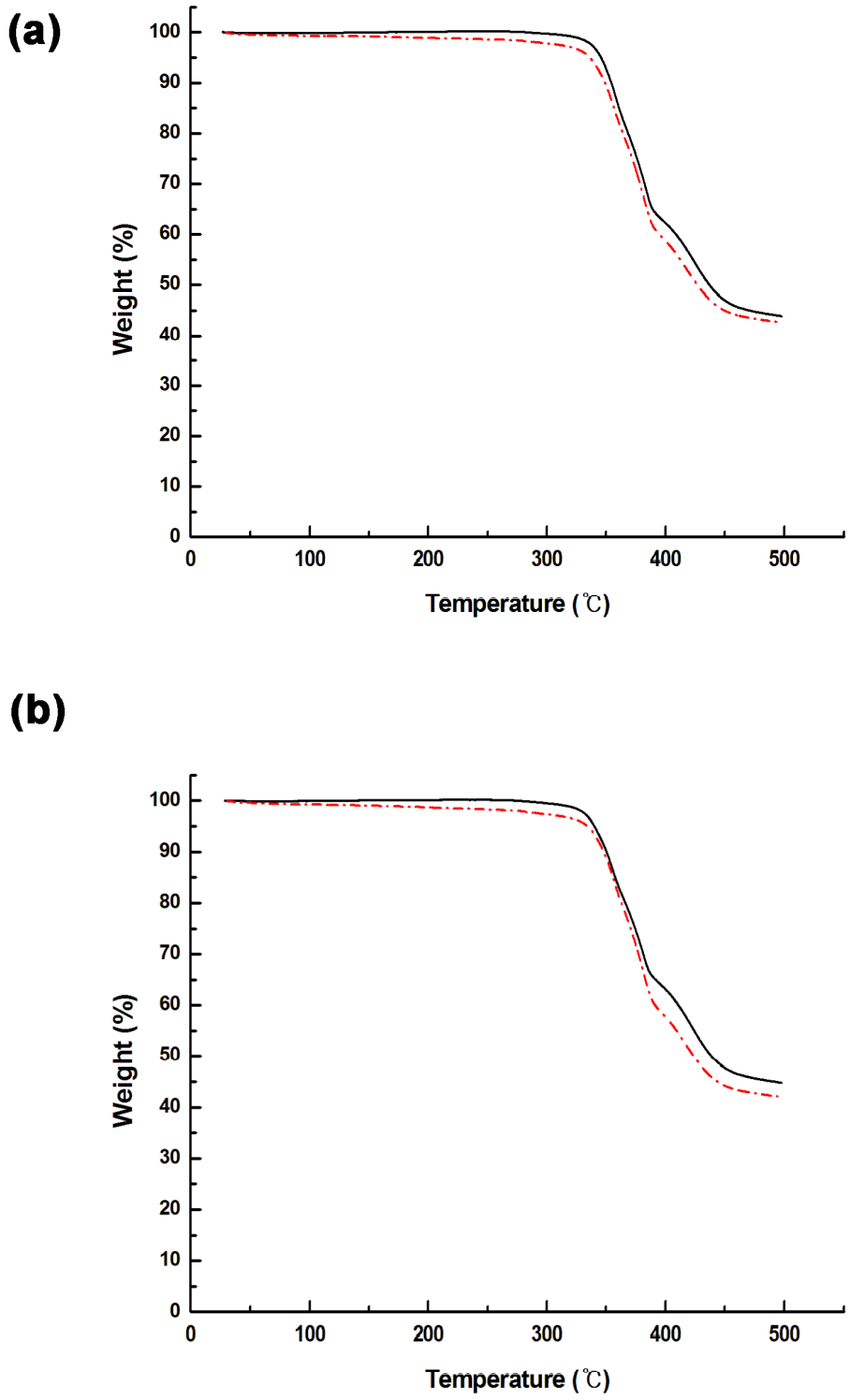


Fig. S8 TGA traces for **SNU-21H** (solid line) and **SNU-21S** (dashed line), (a) before the gas sorption measurement, (b) after the gas sorption measurements.

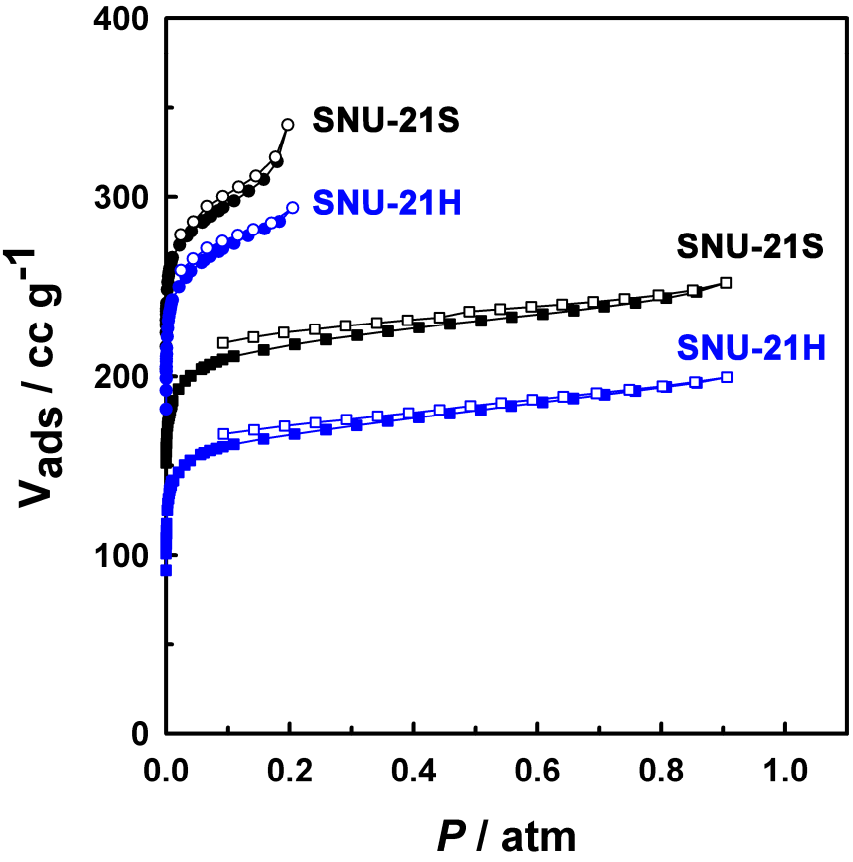


Fig. S9 N_2 (square) and O_2 (circle) sorption isotherms for **SNU-21H** (blue) and **SNU-21S** (black) at 77 K.

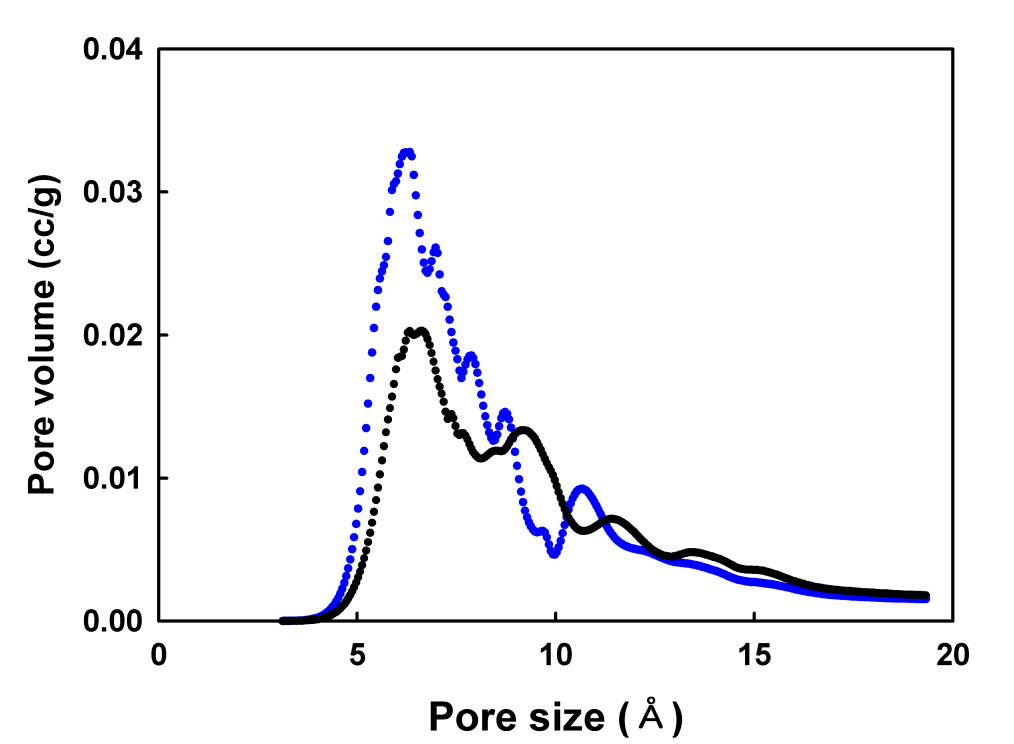


Fig. S10 Pore size distributions of **SNU-21H** (blue) and **SNU-21S** (black) obtained by the Horvath-Kawazoe (HK) method.

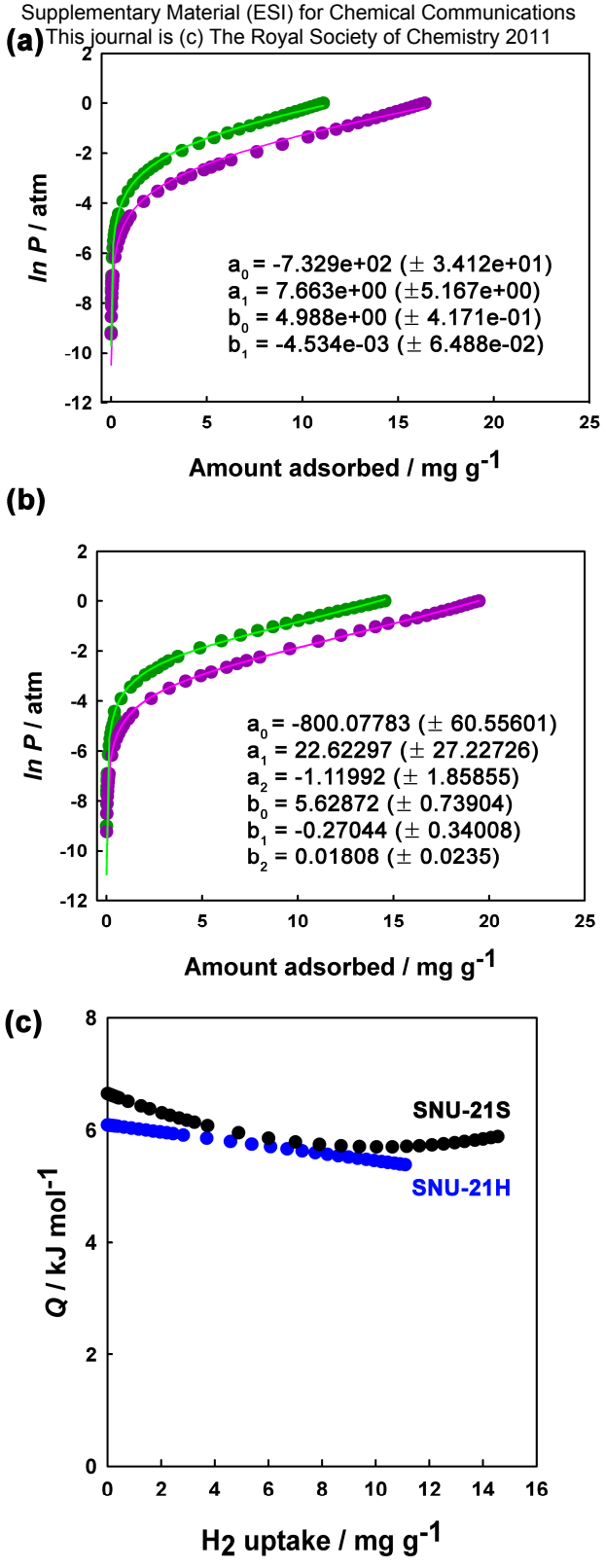


Fig. S11 Virial fit for the H_2 adsorption isotherms measured at 77 K (red) and 87 K (green). (a) **SNU-21H**, (b) **SNU-21S**, (c) Isosteric heats of H_2 adsorption for **SNU-21H** and **SNU-21S**.

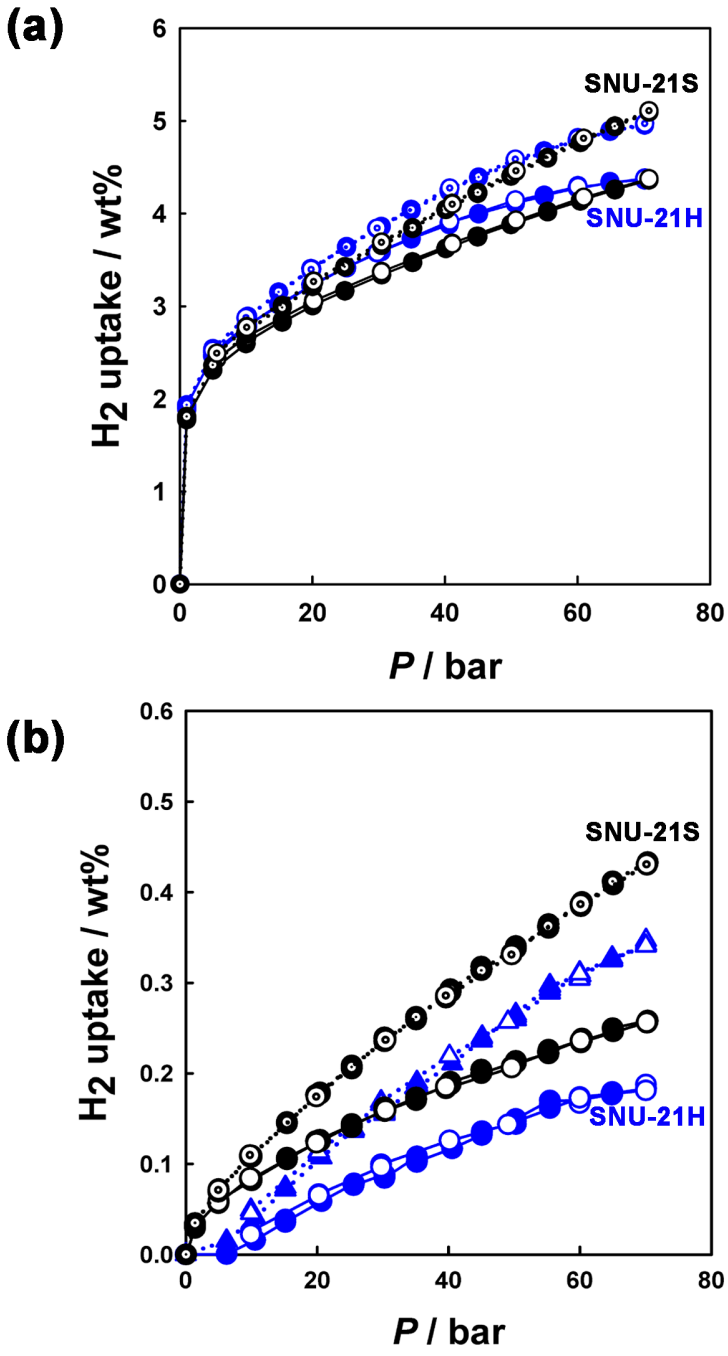


Fig. S12 High pressure H_2 gas adsorption isotherms, (a) at 77 K, (b) at 298 K. Excess amount, solid line; total amount, dashed line.

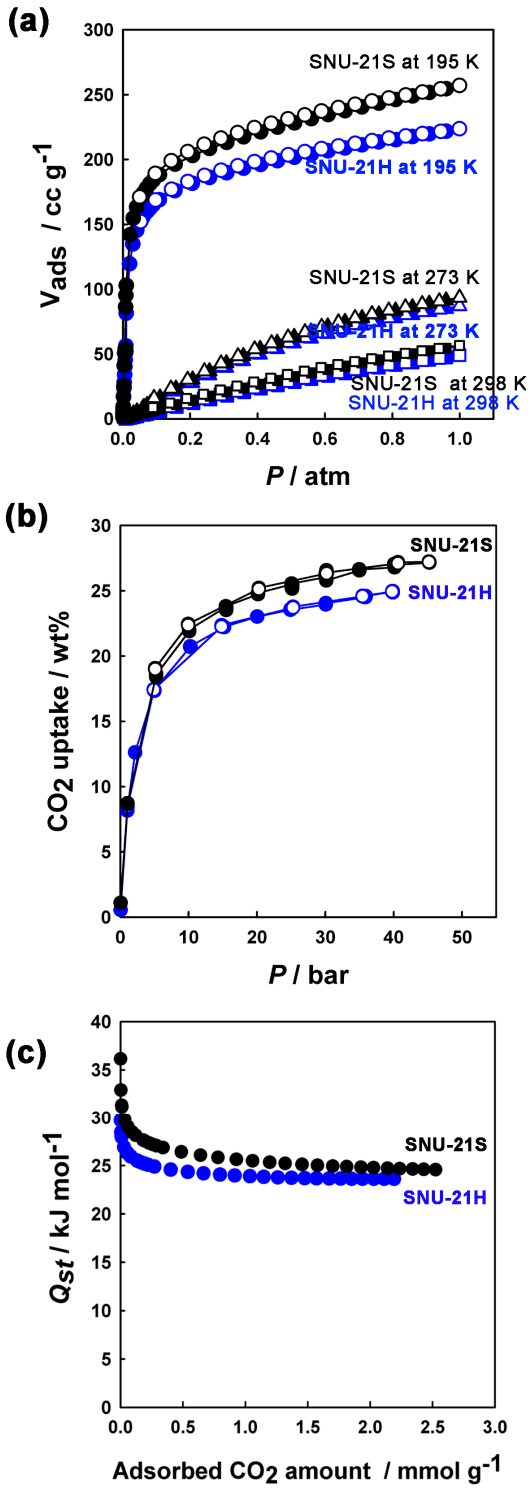


Fig. S13 The CO_2 sorption isotherms of **SNU-21H** (blue) and **SNU-21S** (black). (a) At 195 K (circle), 273 K (triangle), and 298 K (square) measured up to 1 atm. (b) At 298 K and high pressures. (c) Isosteric heats of CO_2 adsorption calculated by Clausius-Clapeyron equation.

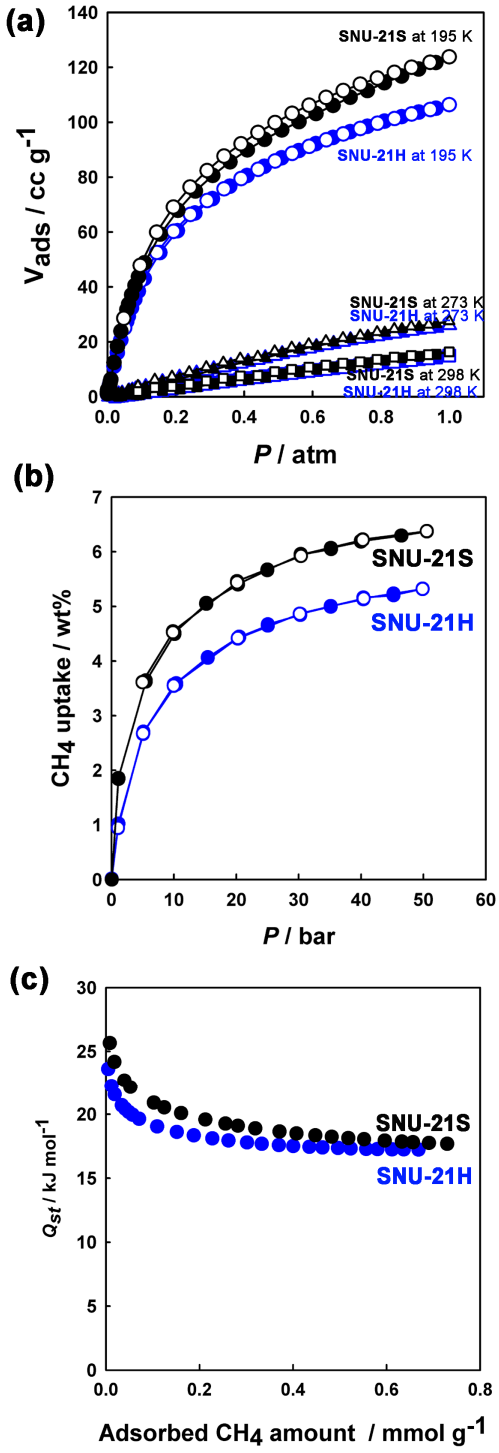


Fig. S14 The CH_4 sorption isotherms of **SNU-21H** (blue) and **SNU-21S** (black). (a) At 195 K (circle), 273 K (triangle), and 298 K (square) measured up to 1 atm. (b) At 298 K and high pressures. (c) Isosteric heats of CH_4 adsorption calculated by Clausius-Clapeyron equation.

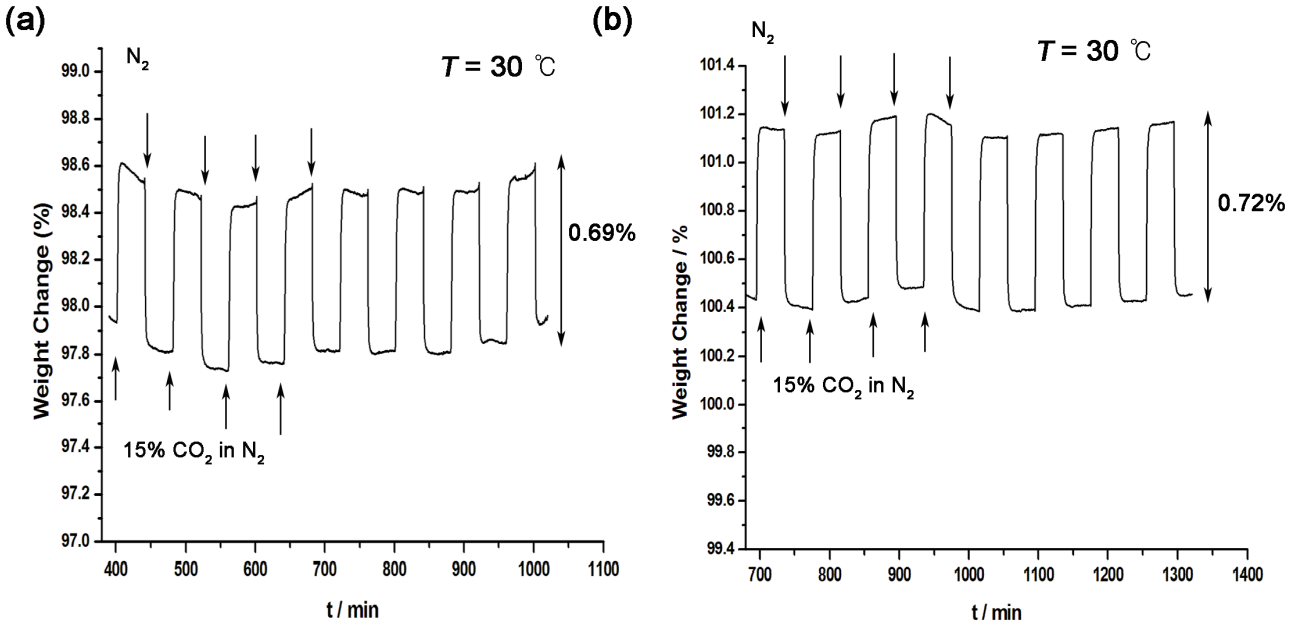


Fig. S15 Gas cycling experiments for (a) **SNU-21H**, and (b) **SNU-21S** at 30 °C. A stream of 15% CO_2 in N_2 was applied, followed by a flow of pure N_2.

Table S1. Crystallographic Data for **SNU-21** [squeezed data].

Compound	**SNU-21**
formula	$Cu_2C_{33}H_{28}O_{14}$
crystal system	*Monoclinic*
space group	*C2/c*
fw	775.67
a, Å	10.7765(9)
b, Å	28.1439(13)
c, Å	28.487(2)
β, deg	98.706(2)
V, Å^3	8540.5(11)
Z	4
ρ_{calcd}, g cm^{-3}	0.603
temp , K	293(2)
λ, Å	0.71073
μ, mm^{-1}	0.525
goodness-of-fit (F^2)	0.772
F(000)	1568
reflections collected	14034
independent reflections	8700 [*R*(int) = 0.0592]
completeness to θ_{max}, %	96.4
data/parameters/restraints	8700/217/0
θ range for data collection, deg	1.45 – 27.47
diffraction limits (*h*, *k*, *l*)	$-13 \le h \le 13$, $-36 \le k \le 27$, $-36 \le l \le 36$
refinement method	Full-matrix least squares on F^2
R_1, wR_2 [$I>2\sigma(I)$]	0.0794[a], 0.2084[b]
R_1, wR_2 (all data)	0.1512[a], 0.2297[b]
largest peak, hole, eÅ^{-3}	0.793, -0.683

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1225\ P)^2 + (0.0000)P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Bond Distances (Å) and Angles (deg) for **SNU-21**[a].

Cu(1)-O(2)	1.987(4)	Cu(1)#2-O(3)	1.966(3)
Cu(1)-O(5)	1.969(4)	Cu(1)#2-O(6)	1.984(4)
Cu(1)-O(3)#2	1.966(3)	Cu(1)-O(6)#2	1.984(4)
Cu(1)-Ow(1)	2.232(4)	Cu(1)-Cu(1)#2	2.625(1)
C(1)-C(10)	1.545(6)	C(1)-C(10)#1	1.545(6)
C(1)-C(2)#1	1.553(6)	C(1)-C(2)	1.553(6)
C(5)-C(6)	1.329(7)	C(5)-C(4)	1.455(7)
C(5)-H(5)	0.9300	C(6)-C(7)	1.367(9)
C(6)-C(9)	1.488(7)	C(7)-C(8)	1.515(9)
C(7)-H(7)	0.9300	C(8)-C(3)	1.399(8)
C(8)-H(8)	0.9300	C(9)-O(3)	1.299(6)
C(9)-O(2)	1.262(6)	C(10)-O(4)	1.433(6)
C(10)-H(10A)	0.9700	C(10)-H(10B)	0.9700
C(15)-C(16)	1.393(7)	C(15)-C(14)	1.408(7)
C(15)-H(15)	0.9300	O(5)-C(17)	1.280(6)
O(6)-C(17)	1.244(6)	C(2)-O(1)#3	1.434(6)
C(2)-H(2A)	0.9700	C(2)-H(2B)	0.9700
C(3)-C(4)	1.323(7)	C(3)-O(1)	1.374(6)
C(4)-H(4)	0.9300	C(11)-C(16)	1.370(7)
C(11)-O(4)	1.386(6)	C(11)-C(12)	1.401(7)
C(12)-C(13)	1.449(7)	C(12)-H(12)	0.9300
C(13)-C(14)	1.349(7)	C(13)-H(13)	0.9300
C(14)-C(17)	1.491(7)	C(16)-H(16)	0.9300
O(1)-C(2)#3	1.434(6)		

O(3)#2-Cu(1)-O(5)	88.84(14)	O(3)#2-Cu(1)-O(6)#2	90.46(15)
O(5)-Cu(1)-O(6)#2	168.76(16)	O(3)#2-Cu(1)-O2	168.58(17)
O(5)-Cu(1)-O(2)	89.85(15)	O(6)#2-Cu(1)-O(2)	88.62(15)
O(3)#2-Cu(1)-Ow(1)	101.41(18)	O(5)-Cu(1)-Ow(1)	99.56(16)
O(6)#2-Cu(1)-Ow(1)	91.58(17)	O(2)-Cu(1)-Ow(1)	89.99(18)

O(3)#2-Cu(1)-Cu(1)#2	87.13(13)	O(5)-Cu(1)-Cu(1)#2	85.40(12)
O(6)#2-Cu(1)-Cu(1)#2	83.37(13)	O(2)-Cu(1)-Cu(1)#2	81.46(13)
Ow(1)-Cu(1)-Cu(1)#1	170.14(14)	C(10)-C(1)-C(10)#1	111.1(5)
C(10)-C(1)-C(2)#1	107.1(3)	C(10)#1-C(1)-C(2)#1	108.8(3)
C(10)-C(1)-C(2)	108.8(3)	C(10)#1-C(1)-C(2)	107.1(3)
C(2)#1-C(1)-C(2)	113.9(5)	C(6)-C(5)-C(4)	121.9(6)
C(6)-C(5)-H(5)	119.0	C(4)-C(5)-H(5)	119.0
C(5)-C(6)-C(7)	118.1(6)	C(5)-C(6)-C(9)	124.7(6)
C(7)-C(6)-C(9)	117.2(6)	C(6)-C(7)-C(8)	123.2(6)
C(6)-C(7)-H(7)	118.4	C(8)-C(7)-H(7)	118.4
C(3)-C(8)-C(7)	113.3(6)	C(3)-C(8)-H(8)	123.4
C(7)-C(8)-H(8)	123.4	O(3)-C(9)-O(2)	127.1(5)
O(3)-C(9)-C(6)	116.3(6)	O(2)-C(9)-C(6)	116.5(6)
O(4)-C(10)-C(1)	105.9(4)	O(4)-C(10)-H(10A)	110.5
C(1)-C(10)-H(10A)	110.5	O(4)-C(10)-H(10B)	110.5
C(1)-C(10)-H(10B)	110.5	H(10A)-C(10)-H(10B)	108.7
C(16)-C(15)-C(14)	123.5(6)	C(16)-C(15)-H(15)	118.2
C(14)-C(15)-H(15)	118.2	C(9)-O(2)-Cu(1)	124.5(4)
C(9)-O(3)-Cu(1)#2	119.7(4)	C(17)-O(5)-Cu(1)	121.9(4)
C(17)-O(6)-Cu(1)#2	124.4(4)	O(1)#3-C(2)-C(1)	105.3(4)
O(1)#3-C(2)-H(2A)	110.7	C(1)-C(2)-H(2A)	110.7
O(1)#3-C(2)-H(2B)	110.7	C(1)-C(2)-H(2B)	110.7
H(2A)-C(2)-H(2B)	108.8	C(4)-C(3)-O(1)	127.1(6)
C(4)-C(3)-C(8)	123.2(6)	O(1)-C(3)-C(8)	109.5(6)
C(3)-C(4)-C(5)	120.0(6)	C(3)-C(4)-C(H4)	120.0
C(5)-C(4)-H(4)	120.0	C(16)-C(11)-O(4)	125.9(5)
C(16)-C(11)-C(12)	124.2(6)	O(4)-C(11)-C(12)	109.7(6)
C(11)-C(12)-C(13)	115.9(6)	C(11)-C(12)-H(12)	122.0
C(13)-C(12)-H(12)	122.0	C(14)-C(13)-C(12)	122.0(6)
C(14)-C(13)-H(13)	119.0	C(12)-C(13)-H(13)	119.0

C(13)-C(14)-C(15)	117.9(6)	C(13)-C(14)-C(17)	122.1(6)
C(15)-C(14)-C(17)	119.8(6)	C(11)-C(16)-C(15)	116.3(6)
C(11)-C(16)-H(16)	121.9	C(15)-C(16)-H(16)	121.9
O(6)-C(17)-O(5)	124.9(6)	O(6)-C(17)-C(14)	119.0(6)
O(5)-C(17)-C(14)	116.0(6)	C(3)-O(1)-C(2)#3	116.5(5)
C(11)-O(4)-C(10)	115.9(5)		

[a] Symmetry transformation used to generate equivalent atoms: #1, -x+2, y, -z+1/2; #2, -x+2, -y+1, -z; #3, -x+3/2, -y+3/2, -z

Table S3. Comparison of Gas Adsorption Data of **SNU-21H** and **SNU-21S**

Gas	*T* (K)	*P* (bar)	surface area		Pore volume		Adsorption capacity			
			(m^2g^{-1})		(cm^3g^{-1})		wt% gas		mmol of gas/g host	
			SNU-21H	**SNU-21S**	**SNU-21H**	**SNU-21S**	**SNU-21H**	**SNU-21S**	**SNU-21H**	**SNU-21S**
N_2	77	0.9	695	905	0.25	0.31	24.9	31.5	8.91	11.3
O_2	77	0.2					42.0	48.6	13.1	15.2
H_2	77	1.0					1.64	1.95	8.13	9.66
		70					4.36	4.37	21.6	21.7
							(4.95)	(5.10)	(24.6)	(25.3)
	87	1.0					1.11	1.46	5.51	7.22
	298	70					0.18	0.26	0.89	1.29
							(0.34)	(0.43)	(1.68)	(2.13)
CO_2	195	1.0	934	1908	0.33	0.68	45.9	50.5	10.4	11.5
	273	1.0					17.1	18.4	3.88	4.17
	298	1.0					9.65	11.1	2.19	2.52
		45					24.9	27.2	5.66	6.18
CH_4	195	1.0					7.62	8.86	4.75	5.53
	273	1.0					1.87	1.97	1.17	1.23
	298	1.0					1.07	1.17	0.67	0.73
		50					5.32	6.38	3.31	3.98

Table S4. The N_2 and O_2 Adsorption and Desorption Data of **SNU-21H** and **SNU-21S.**

N_2 at 77 K for **SNU-21H**		N_2 at 77 K for **SNU-21S**		O_2 at 77 K for **SNU-21H**		O_2 at 77 K for **SNU-21S**	
P / P_0[a]	V_{ads} /cc g^{-1}	P / P_0[a]	V_{ads} /cc g^{-1}	P / P_0[a]	V_{ads} /cc g^{-1}	P / P_0[a]	V_{ads} /cc g^{-1}
1.10E-04	91.7036	1.78E-04	151.4398	4.46E-04	181.6421	4.46E-04	203.9469
2.26E-04	101.0453	2.66E-04	154.2471	9.59E-04	192.1317	9.61E-04	216.3098
4.08E-04	106.064	3.74E-04	157.3715	1.48E-03	198.8282	1.48E-03	224.0363
4.42E-04	107.8577	5.15E-04	160.2783	2.00E-03	202.6711	2.00E-03	228.4093
5.40E-04	109.8929	6.48E-04	162.267	2.54E-03	205.0508	2.52E-03	231.1687
6.49E-04	111.9478	6.38E-04	162.286	3.04E-03	208.0574	3.05E-03	234.3911
7.65E-04	113.9714	9.66E-04	165.1168	3.57E-03	209.5384	3.57E-03	236.1317
9.07E-04	115.9063	9.34E-04	165.0812	4.09E-03	210.8709	4.09E-03	237.6183
1.07E-03	117.611	9.43E-04	165.0914	4.60E-03	212.0946	4.60E-03	239.285
1.04E-03	117.6385	1.38E-03	167.6543	5.12E-03	215.4601	5.13E-03	240.578
2.14E-03	125.147	2.50E-03	172.0222	1.03E-02	221.8104	1.03E-02	248.1156
3.18E-03	129.0681	3.16E-03	173.8082	1.55E-02	226.6355	1.55E-02	252.2097
4.33E-03	131.4593	4.36E-03	176.1195	2.06E-02	230.787	2.09E-02	255.4745
5.39E-03	134.4431	5.26E-03	177.6756	2.58E-02	233.216	2.57E-02	257.6351
6.32E-03	136.1599	6.29E-03	179.3289	3.10E-02	235.6299	3.15E-02	259.6929
7.44E-03	137.5085	7.34E-03	180.9692	3.63E-02	237.5084	3.61E-02	261.2285
8.55E-03	138.85	8.85E-03	183.1878	4.15E-02	239.516	4.15E-02	262.8192
9.41E-03	140.8912	9.71E-03	184.2136	4.64E-02	240.9964	4.74E-02	264.291
1.23E-02	141.706	1.12E-02	186.4	5.20E-02	242.4575	5.31E-02	265.7782
2.12E-02	146.1923	2.12E-02	192.876	1.08E-01	249.6736	1.12E-01	272.8508
3.13E-02	150.322	3.22E-02	197.4398	1.67E-01	254.8058	1.74E-01	277.8206
4.09E-02	152.8428	4.15E-02	200.2063	1.66E-01	255.4057	1.71E-01	277.8985
5.84E-02	156.0783	5.99E-02	203.8937	2.07E-01	258.3752	2.12E-01	280.6862
6.42E-02	157.064	6.41E-02	204.8742	2.97E-01	263.1662	3.02E-01	285.6606
7.41E-02	158.2992	7.41E-02	206.3936	3.18E-01	264.4316	3.20E-01	286.7581
8.49E-02	159.4415	8.43E-02	207.853	3.65E-01	266.5552	3.68E-01	289.0598
9.54E-02	160.4615	9.51E-02	209.2244	4.35E-01	269.2059	4.37E-01	292.1479
1.14E-01	161.8607	1.14E-01	210.9719	4.29E-01	269.3762	4.31E-01	292.162

1.64E-01	164.7816	1.66E-01	214.4964	4.71E-01	270.8983	4.72E-01	293.9966
2.17E-01	167.5555	2.17E-01	217.6371	5.63E-01	273.699	5.64E-01	297.8018
2.69E-01	170.0648	2.69E-01	220.324	6.82E-01	278.091	6.87E-01	303.1942
3.21E-01	172.4415	3.22E-01	222.6873	8.16E-01	281.8988	8.11E-01	309.6956
3.73E-01	174.7772	3.74E-01	224.9195	9.43E-01	286.1301	9.23E-01	319.7641
4.26E-01	176.9283	4.26E-01	227.0665	1.05E+00	293.8846	1.01E+00	340.4617
4.78E-01	179.1577	4.78E-01	229.0457	8.74E-01	285.2969	9.08E-01	322.1176
5.30E-01	181.228	5.31E-01	230.8475	7.24E-01	281.5608	7.44E-01	311.6411
5.82E-01	183.425	5.83E-01	232.8163	5.94E-01	278.4072	6.01E-01	305.3952
6.35E-01	185.4948	6.35E-01	234.5728	4.66E-01	275.0514	4.69E-01	300.082
6.86E-01	187.6541	6.87E-01	236.4878	3.41E-01	271.0452	3.41E-01	294.705
7.39E-01	189.7074	7.38E-01	238.6348	2.26E-01	265.181	2.29E-01	285.9381
7.91E-01	191.7799	7.91E-01	240.8896	1.25E-01	258.6467	1.22E-01	278.5766
8.43E-01	194.0324	8.43E-01	243.4516				
8.95E-01	196.4049	8.94E-01	246.914				
9.45E-01	199.4912	9.44E-01	252.0167				
8.91E-01	196.7134	8.87E-01	247.7973				
8.36E-01	194.461	8.29E-01	245.0611				
7.81E-01	192.4742	7.72E-01	243.0131				
7.25E-01	190.5291	7.20E-01	241.3905				
6.69E-01	188.6676	6.67E-01	239.9412				
6.17E-01	186.8566	6.15E-01	238.6498				
5.65E-01	185.181	5.63E-01	237.2977				
5.13E-01	183.3651	5.11E-01	235.9091				
4.61E-01	181.3074	4.61E-01	232.6082				
4.09E-01	179.4547	4.07E-01	231.0729				
3.56E-01	177.6915	3.55E-01	229.5118				
3.04E-01	175.8014	3.02E-01	227.9701				
2.52E-01	173.9764	2.51E-01	226.0914				
2.00E-01	172.0816	1.98E-01	224.2				
1.48E-01	169.9758	1.47E-01	221.6534				

9.62E-02	167.6462	9.56E-02	218.4255
1.10E-04	91.7036	1.78E-04	151.4398

[a] P_o values of N_2 and O_2 are 0.9588 and 0.1945 atm, respectively.

Table S5. The H_2 Adsorption and Desorption Data of **SNU-21H** and **SNU-21S.**

H_2 at 77 K of SNU-21H		H_2 at 77 K of SNU-21S		H_2 at 87 K of SNU-21H		H_2 at 87 K of SNU-21S	
P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}
9.83E-05	0.0285	9.86E-05	0.0433	1.06E-04	0.0213	1.24E-04	0.0068
1.97E-04	0.1442	2.04E-04	0.2168	1.96E-04	0.0533	2.03E-04	0.0403
2.97E-04	0.2563	3.03E-04	0.3723	3.39E-04	0.105	2.95E-04	0.0891
4.21E-04	0.3989	4.04E-04	0.5217	4.02E-04	0.1263	4.40E-04	0.1713
4.97E-04	0.4848	5.03E-04	0.6732	5.37E-04	0.1756	5.05E-04	0.2014
6.23E-04	0.626	6.04E-04	0.824	6.01E-04	0.1981	5.95E-04	0.2435
6.98E-04	0.7101	7.05E-04	0.9824	7.38E-04	0.2477	7.51E-04	0.3233
8.22E-04	0.8497	8.03E-04	1.123	8.01E-04	0.2693	8.00E-04	0.3494
8.98E-04	0.9342	9.07E-04	1.2759	9.37E-04	0.3179	9.41E-04	0.4251
1.02E-03	1.0743	1.00E-03	1.419	1.00E-03	0.3409	1.00E-03	0.4553
2.14E-03	2.2651	2.08E-03	3.014	2.06E-03	0.7266	2.16E-03	1.0819
3.09E-03	3.2726	3.09E-03	4.4699	3.04E-03	1.0822	3.05E-03	1.5592
4.10E-03	4.3484	4.11E-03	5.9343	4.01E-03	1.4312	4.02E-03	2.0771
5.15E-03	5.4467	5.02E-03	7.2084	5.06E-03	1.8094	5.04E-03	2.6064
6.15E-03	6.4553	6.11E-03	8.6274	6.03E-03	2.1571	6.15E-03	3.1857
7.09E-03	7.4386	7.04E-03	9.9218	7.04E-03	2.5154	7.09E-03	3.6693
8.74E-03	9.0349	8.83E-03	12.3113	8.53E-03	3.0335	8.58E-03	4.4333
9.22E-03	9.5155	9.30E-03	12.9365	9.36E-03	3.3278	9.35E-03	4.8174
1.09E-02	11.1348	1.12E-02	15.217	1.18E-02	4.2337	1.20E-02	4.5628
1.96E-02	18.9088	2.02E-02	25.9707	1.98E-02	6.8637	2.00E-02	8.5384
2.94E-02	27.0676	3.04E-02	36.4538	2.92E-02	9.8847	3.19E-02	13.9438
3.95E-02	34.6953	4.03E-02	45.9629	3.91E-02	12.9608	4.00E-02	17.5028
4.96E-02	41.7313	5.01E-02	54.7643	4.91E-02	15.98	5.18E-02	22.4998

5.67E-02	46.297	5.80E-02	60.7846	5.92E-02	18.92	5.99E-02	25.9665
6.93E-02	53.8942	7.02E-02	69.7629	6.93E-02	21.7787	6.94E-02	29.6907
7.72E-02	57.9588	8.10E-02	75.7738	7.94E-02	24.5412	7.98E-02	32.9171
8.68E-02	62.5321	9.17E-02	81.3403	8.94E-02	27.2141	9.05E-02	36.0218
1.03E-01	69.6022	1.06E-01	88.9982	1.07E-01	31.4363	1.08E-01	41.4608
1.42E-01	84.6102	1.48E-01	106.4548	1.50E-01	41.1096	1.53E-01	54.2891
1.92E-01	99.4703	1.98E-01	123.0606	1.99E-01	50.9728	2.03E-01	66.729
2.57E-01	114.4294	2.51E-01	136.3176	2.50E-01	59.75	2.54E-01	77.8728
3.00E-01	122.5714	3.03E-01	147.2376	3.01E-01	67.5937	3.04E-01	87.7986
3.51E-01	130.7008	3.54E-01	156.2041	3.53E-01	74.4492	3.55E-01	96.7389
4.02E-01	137.5417	4.05E-01	163.505	4.03E-01	80.6461	4.06E-01	104.3683
4.54E-01	143.4448	4.52E-01	173.7778	4.54E-01	86.0673	4.57E-01	111.4946
5.04E-01	148.9731	5.06E-01	180.5072	5.04E-01	91.1569	5.06E-01	118.0104
5.55E-01	153.7159	5.57E-01	186.0009	5.55E-01	95.6582	5.57E-01	123.9489
6.06E-01	157.9967	6.08E-01	190.8014	6.06E-01	99.8288	6.07E-01	129.2466
6.56E-01	161.9761	6.59E-01	194.9308	6.56E-01	103.6143	6.58E-01	134.4213
7.07E-01	165.6354	7.08E-01	199.0317	7.06E-01	107.2363	7.08E-01	139.1918
7.57E-01	169.0231	7.58E-01	202.6959	7.57E-01	110.4264	7.58E-01	143.8068
8.08E-01	172.0373	8.09E-01	205.7371	8.07E-01	113.4489	8.08E-01	147.8914
8.57E-01	174.9505	8.59E-01	208.8955	8.57E-01	116.1151	8.58E-01	152.1624
9.08E-01	177.5868	9.09E-01	211.4389	9.07E-01	118.8618	9.09E-01	155.5724
9.59E-01	180.0253	9.60E-01	214.2113	9.58E-01	121.2066	9.59E-01	158.8815
9.99E-01	182.1709	9.99E-01	216.4615	9.99E-01	123.3214	9.99E-01	161.69
9.45E-01	179.6761	9.45E-01	213.6543	9.44E-01	120.5742	9.45E-01	158.0434
8.91E-01	177.1739	8.90E-01	210.8887	8.91E-01	117.9651	8.91E-01	154.4516
8.41E-01	174.6805	8.40E-01	208.2208	8.41E-01	115.2994	8.41E-01	150.805
7.92E-01	171.8613	7.91E-01	204.8815	7.91E-01	112.5038	7.91E-01	146.762
7.43E-01	168.7577	7.41E-01	201.4615	7.42E-01	109.5132	7.42E-01	142.2742
6.92E-01	165.7912	6.91E-01	197.8398	6.92E-01	106.2212	6.91E-01	137.819
6.43E-01	162.394	6.41E-01	193.8489	6.42E-01	102.7022	6.42E-01	133.1199
5.93E-01	158.7082	5.92E-01	189.7738	5.93E-01	98.9525	5.92E-01	128.1308

5.44E-01	154.589	5.42E-01	184.818	5.43E-01	94.8626	5.42E-01	122.7439
4.94E-01	150.0712	4.92E-01	179.7136	4.94E-01	90.4744	4.93E-01	116.828
4.46E-01	144.9239	4.44E-01	173.5086	4.44E-01	85.4462	4.44E-01	110.1982
3.96E-01	139.4379	3.93E-01	167.5181	3.92E-01	81.083	3.93E-01	103.3778
3.47E-01	133.0931	3.44E-01	159.7068	3.45E-01	75.2874	3.44E-01	95.7131
2.98E-01	125.5709	2.96E-01	150.7946	2.96E-01	68.5712	2.95E-01	87.1792
2.51E-01	116.6876	2.47E-01	140.0756	2.47E-01	60.9547	2.46E-01	77.1109
2.03E-01	106.3684	1.99E-01	127.4416	1.98E-01	52.4346	1.96E-01	66.4127
1.57E-01	93.8396	1.51E-01	111.6946	1.50E-01	42.7069	1.47E-01	54.0081
9.83E-02	72.1992	9.31E-02	86.1792	1.01E-01	31.5582	9.84E-02	39.6369

Table S6. The CO_2 Adsorption and Desorption Data of **SNU-21H**.

CO_2 at 195 K of SNU-21H		CO_2 at 273 K of SNU-21H		CO_2 at 298 K of SNU-21H	
P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}
1.04E-04	1.1765	6.04E-03	0.0308	7.12E-03	0.0261
1.94E-04	2.0884	7.23E-03	0.2059	9.37E-03	0.1543
3.12E-04	3.2282	9.30E-03	0.453	1.01E-02	0.1884
4.02E-04	4.0766	1.01E-02	0.5794	1.31E-02	0.1061
5.01E-04	4.9795	1.28E-02	0.7315	2.23E-02	0.6165
6.14E-04	6.0231	2.12E-02	1.9313	3.27E-02	1.2371
7.02E-04	6.8614	3.15E-02	3.4286	4.25E-02	1.829
8.13E-04	7.8988	4.16E-02	4.8756	6.14E-02	2.9935
9.01E-04	8.7252	5.96E-02	7.529	6.31E-02	3.106
1.09E-03	9.5232	6.25E-02	7.9557	7.27E-02	3.6961
2.06E-03	16.8482	7.17E-02	9.28	8.27E-02	4.3414
3.25E-03	23.6091	8.18E-02	10.7627	9.27E-02	4.9793
4.06E-03	28.0723	9.18E-02	12.2335	1.11E-01	6.083
5.10E-03	34.035	1.10E-01	14.7708	1.60E-01	8.9995
6.14E-03	40.1629	1.57E-01	21.0802	2.10E-01	12.0774

7.06E-03	45.2875	2.06E-01	27.6	2.60E-01	14.9033
8.07E-03	50.7659	2.57E-01	33.5848	3.10E-01	17.8403
9.17E-03	56.2588	3.07E-01	39.3361	3.60E-01	20.486
1.00E-02	81.4586	3.57E-01	44.4892	4.09E-01	23.2368
2.00E-02	119.4987	4.07E-01	49.437	4.60E-01	25.7004
2.94E-02	134.8271	4.58E-01	53.8241	5.10E-01	28.2474
4.10E-02	145.215	5.08E-01	58.1139	5.59E-01	30.6788
5.40E-02	152.7366	5.58E-01	61.8485	6.10E-01	33.0617
6.00E-02	155.5186	6.08E-01	65.5191	6.60E-01	35.1947
7.16E-02	159.7682	6.58E-01	68.8119	7.09E-01	37.4567
8.02E-02	162.4016	7.09E-01	72.0259	7.60E-01	39.4988
9.02E-02	165.0356	7.59E-01	74.7372	8.10E-01	41.4793
1.08E-01	168.8348	8.09E-01	77.5491	8.60E-01	43.4338
1.54E-01	175.9715	8.59E-01	79.9929	9.09E-01	45.463
2.06E-01	181.5968	9.09E-01	82.4306	9.60E-01	47.3439
2.57E-01	186.0824	9.59E-01	84.6716	9.99E-01	49.1065
3.08E-01	189.7036	9.99E-01	86.8027	9.40E-01	46.9168
3.58E-01	193.1083	9.40E-01	84.2425	8.89E-01	45.2984
4.09E-01	196.119	8.90E-01	82.2633	8.39E-01	43.6019
4.59E-01	198.9242	8.40E-01	79.9436	7.89E-01	42.0113
5.09E-01	201.6421	7.90E-01	77.6202	7.40E-01	40.0281
5.60E-01	203.9847	7.40E-01	75.032	6.89E-01	38.1907
6.09E-01	206.5511	6.91E-01	72.2578	6.40E-01	35.9708
6.60E-01	208.8485	6.41E-01	69.1779	5.90E-01	33.8619
7.09E-01	211.2008	5.91E-01	66.0229	5.40E-01	31.5404
7.60E-01	213.5048	5.42E-01	62.4026	4.90E-01	29.1938
8.10E-01	215.2369	4.92E-01	58.6019	4.40E-01	26.6421
8.59E-01	217.6121	4.42E-01	54.4118	3.90E-01	24.1646
9.10E-01	219.667	3.92E-01	50.0943	3.40E-01	21.5064
9.60E-01	221.7366	3.43E-01	45.2175	2.90E-01	18.7846
9.99E-01	223.6935	2.93E-01	40.0546	2.40E-01	15.8

9.44E-01	221.6019	2.49E-01	34.3288	1.90E-01	12.8019
8.89E-01	219.8678	1.93E-01	28.2535	1.40E-01	9.6838
8.39E-01	218.1337	1.43E-01	21.6318	9.02E-02	6.5589
7.89E-01	216.424	9.31E-02	14.6866		
7.40E-01	214.3925				
6.90E-01	212.4311				
6.40E-01	210.3127				
5.90E-01	208.2125				
5.40E-01	205.9507				
4.91E-01	203.5099				
4.40E-01	201.0102				
3.91E-01	198.215				
3.41E-01	195.0925				
2.92E-01	191.5923				
2.42E-01	187.5968				
1.93E-01	182.9288				
1.44E-01	176.9868				
9.69E-02	168.7092				
5.28E-02	152.0788				

Table S7. The CO_2 Adsorption and Desorption Data of SNU-21S

CO_2 at 195 K of SNU-21S		CO_2 at 273 K of SNU-21S		CO_2 at 298 K of SNU-21S	
P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}
1.08E-04	1.414	5.05E-03	0.0855	6.13E-03	0.0045
1.95E-04	2.2623	6.00E-03	0.2042	7.13E-03	0.0596
2.94E-04	3.1508	7.08E-03	0.3523	9.41E-03	0.2099
4.14E-04	4.2178	9.15E-03	0.6349	1.01E-02	0.2392
5.05E-04	5.0035	1.00E-02	0.772	1.29E-02	0.7362
6.00E-04	5.8339	1.29E-02	1.0867	2.25E-02	1.3192
6.98E-04	6.6916	2.18E-02	2.4642	3.22E-02	2.0569
8.13E-04	7.7369	3.15E-02	3.9999	4.23E-02	2.7026
9.03E-04	8.5509	4.18E-02	5.646	6.10E-02	4.0563
1.09E-03	9.2861	6.00E-02	8.4904	6.26E-02	4.3332
2.05E-03	17.1403	6.25E-02	9.0302	7.22E-02	5.1099
3.02E-03	25.4342	7.18E-02	10.5317	8.21E-02	5.7902
4.02E-03	41.0648	8.18E-02	12.1393	9.22E-02	6.4169
5.04E-03	50.5192	9.18E-02	13.7608	1.11E-01	7.6193
8.73E-03	52.0369	1.10E-01	16.4671	1.60E-01	10.9146
7.06E-03	53.8865	1.57E-01	23.2086	2.09E-01	14.3678
8.02E-03	86.215	2.07E-01	30.2211	2.60E-01	17.4804
9.10E-03	95.244	2.57E-01	36.6462	3.09E-01	20.7946
1.01E-02	102.8186	3.07E-01	42.8744	3.60E-01	23.7055
2.17E-02	141.912	3.58E-01	48.3956	4.09E-01	26.7716
3.09E-02	154.7561	4.08E-01	53.8083	4.60E-01	29.5393
4.07E-02	163.1378	4.58E-01	58.6159	5.09E-01	32.5828
5.52E-02	171.416	5.08E-01	63.1876	5.60E-01	35.3593
6.09E-02	173.9772	5.58E-01	67.2439	6.09E-01	38.0907
6.99E-02	177.67	6.08E-01	71.2486	6.60E-01	40.5844
8.00E-02	181.205	6.59E-01	74.6962	7.09E-01	43.1389
9.07E-02	184.0679	7.10E-01	77.629	7.59E-01	45.4104
1.09E-01	188.2177	7.60E-01	80.4973	8.09E-01	47.9217

1.55E-01	196.6683	8.09E-01	83.4536	8.59E-01	50.1047
2.07E-01	202.9113	8.60E-01	86.0544	9.09E-01	52.4324
2.57E-01	208.4892	9.09E-01	88.7668	9.59E-01	54.4224
3.08E-01	213.1042	9.59E-01	91.2245	9.99E-01	56.5476
3.58E-01	217.3495	9.99E-01	93.4509	9.38E-01	54.2175
4.09E-01	221.2124	9.99E-01	93.4509	8.88E-01	52.5029
4.59E-01	224.881	9.39E-01	90.6183	8.38E-01	50.4645
5.09E-01	228.2063	8.89E-01	88.4382	7.88E-01	48.446
5.60E-01	231.3992	8.39E-01	85.9294	7.38E-01	46.3552
6.10E-01	234.4987	7.89E-01	83.4745	6.88E-01	44.1796
6.60E-01	237.5484	7.39E-01	80.6438	6.39E-01	41.8121
7.10E-01	240.455	6.89E-01	77.7003	5.88E-01	39.5189
7.60E-01	243.3488	6.40E-01	74.3441	5.38E-01	36.7416
8.10E-01	246.1855	5.90E-01	70.8542	4.88E-01	34.1414
8.60E-01	248.9409	5.41E-01	66.7885	4.39E-01	31.272
9.10E-01	251.662	4.90E-01	62.7646	3.89E-01	28.4283
9.60E-01	254.4973	4.41E-01	58.2465	3.39E-01	25.2931
9.99E-01	257.0484	3.91E-01	53.5575	2.89E-01	22.2608
9.43E-01	254.418	3.42E-01	48.2731	2.39E-01	18.905
8.89E-01	252.0061	2.92E-01	42.7409	1.89E-01	15.6269
8.40E-01	249.6667	2.42E-01	36.6078	1.39E-01	12.1903
7.89E-01	247.3441	1.92E-01	30.1726	8.92E-02	8.63
7.39E-01	245.0175	1.43E-01	23.1624		
6.90E-01	242.5645	9.23E-02	15.9824		
6.40E-01	239.9194				
5.90E-01	237.2305				
5.40E-01	234.2796				
4.90E-01	231.2231				
4.40E-01	227.9247				
3.91E-01	224.4583				
3.41E-01	220.6626				

2.91E-01	216.0777		
2.42E-01	211.6559		
1.92E-01	206.0182		
1.44E-01	198.9926		
9.61E-02	189.1929		
5.02E-02	171.035		

Table S8. The CH_4 Adsorption and Desorption Data of **SNU-21H**.

CH_4 at 195 K of SNU-21H		CH_4 at 273 K of SNU-21H		CH_4 at 298 K of SNU-21H	
P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}
1.04E-04	0.9	5.01E-03	0.0208	2.28E-02	0.1059
2.10E-04	1.4942	6.08E-03	0.0496	3.27E-02	0.2641
3.14E-04	1.8342	7.01E-03	0.0744	4.28E-02	0.4213
4.09E-04	2.0149	9.11E-03	0.1471	6.18E-02	0.7683
5.37E-04	2.1247	9.88E-03	0.1703	6.29E-02	0.7563
6.22E-04	2.1507	2.30E-02	0.3437	7.27E-02	0.9153
7.06E-04	2.1635	3.31E-02	0.8095	8.26E-02	1.0885
8.20E-04	2.1964	4.33E-02	1.1173	9.22E-02	1.268
9.08E-04	2.2338	6.17E-02	1.8294	1.12E-01	1.592
1.15E-03	2.078	6.32E-02	1.9069	1.61E-01	2.4542
2.14E-03	2.5064	7.28E-02	2.2156	2.11E-01	3.3962
3.18E-03	2.9594	8.29E-02	2.6132	2.61E-01	4.206
4.24E-03	3.3767	9.30E-02	2.862	3.11E-01	5.0961
5.31E-03	3.7703	1.12E-01	3.4797	3.61E-01	5.8682
6.15E-03	4.0385	1.61E-01	5.2826	4.11E-01	6.7572
7.05E-03	4.5121	2.11E-01	6.9145	4.61E-01	7.4647
8.07E-03	5.0539	2.61E-01	8.4165	5.11E-01	8.2829
9.11E-03	5.6144	3.11E-01	9.9995	5.61E-01	8.9701
1.01E-02	6.1738	3.61E-01	11.203	6.11E-01	9.7426

1.92E-02	11.079	4.11E-01	12.6764	6.61E-01	10.3647
2.91E-02	16.0052	4.61E-01	13.9816	7.11E-01	11.111
3.93E-02	20.6205	5.11E-01	15.5263	7.61E-01	11.7198
5.65E-02	27.3712	5.62E-01	16.8319	8.10E-01	12.463
6.14E-02	29.2707	6.11E-01	18.1127	8.61E-01	13.0005
7.05E-02	32.3498	6.61E-01	19.2257	9.11E-01	13.6983
8.03E-02	35.4693	7.11E-01	20.5808	9.61E-01	14.2613
9.04E-02	38.4485	7.61E-01	21.4446	9.99E-01	14.9616
1.08E-01	43.047	8.11E-01	22.4959	9.99E-01	14.9616
1.54E-01	52.4703	8.61E-01	23.3671	9.38E-01	14.0027
2.05E-01	60.4372	9.12E-01	24.458	8.88E-01	13.3764
2.56E-01	66.9268	9.61E-01	25.1154	8.38E-01	12.7564
3.07E-01	72.1012	9.99E-01	26.1004	7.88E-01	12.1254
3.58E-01	76.6706	9.39E-01	24.8201	7.38E-01	11.4423
4.08E-01	80.5521	8.89E-01	23.9729	6.88E-01	10.7696
4.59E-01	83.9441	8.39E-01	22.9793	6.38E-01	10.0839
5.09E-01	87.0036	7.89E-01	22.0278	5.88E-01	9.389
5.59E-01	89.6594	7.39E-01	21.0665	5.39E-01	8.6612
6.10E-01	92.1667	6.89E-01	19.9745	4.88E-01	7.9082
6.60E-01	94.4453	6.39E-01	18.7376	4.38E-01	7.1446
7.10E-01	96.5592	5.89E-01	17.555	3.88E-01	6.3527
7.60E-01	98.5094	5.40E-01	16.2749	3.39E-01	5.5248
8.10E-01	100.3665	4.89E-01	14.8569	2.88E-01	4.6946
8.60E-01	102.0137	4.39E-01	13.4076	2.38E-01	3.8398
9.10E-01	103.6568	3.89E-01	12.0387	1.88E-01	2.972
9.61E-01	105.0544	3.40E-01	10.6877	1.39E-01	2.0684
9.99E-01	106.3609	2.89E-01	9.3133	8.84E-02	1.1979
9.44E-01	104.5897	2.40E-01	7.7759	9.99E-01	14.9616
8.89E-01	102.9629	1.89E-01	6.2115	9.38E-01	14.0027
8.39E-01	101.3208	1.40E-01	4.4969	8.88E-01	13.3764
7.90E-01	99.603	8.98E-02	2.7835	8.38E-01	12.7564

7.39E-01	97.7016	9.39E-01	24.8201	7.88E-01	12.1254
6.90E-01	95.7031	8.89E-01	23.9729	7.38E-01	11.4423
6.40E-01	93.546	8.39E-01	22.9793	6.88E-01	10.7696
5.90E-01	91.1881	7.89E-01	22.0278	6.38E-01	10.0839
5.40E-01	88.6456	7.39E-01	21.0665	5.88E-01	9.389
4.90E-01	85.8561	6.89E-01	19.9745	5.39E-01	8.6612
4.41E-01	82.8282	6.39E-01	18.7376	4.88E-01	7.9082
3.91E-01	79.454	5.89E-01	17.555	4.38E-01	7.1446
3.41E-01	75.7087	5.40E-01	16.2749	3.88E-01	6.3527
2.92E-01	71.4011	4.89E-01	14.8569	3.39E-01	5.5248
2.43E-01	66.3691	4.39E-01	13.4076	2.88E-01	4.6946
1.93E-01	60.2247	3.89E-01	12.0387	2.38E-01	3.8398
1.45E-01	52.5221	3.40E-01	10.6877	1.88E-01	2.972
9.68E-02	42.2032	2.89E-01	9.3133	1.39E-01	2.0684
5.06E-02	25.0546	2.40E-01	7.7759	8.84E-02	1.1979
7.61E-03	4.9846	1.89E-01	6.2115		
4.31E-03	3.4029	1.40E-01	4.4969		
2.51E-03	2.6662	8.98E-02	2.7835		
9.21E-04	2.2253				

Table S9. The CH_4 Adsorption and Desorption Data of **SNU-21S**.

CH_4 at 195 K of SNU-21S		CH_4 at 273 K of SNU-21S		CH_4 at 298 K of SNU-21S	
P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}	P / atm	V_{ads} /cc g^{-1}
1.17E-04	1.0472	1.00E-02	0.0108	3.27E-02	0.1853
2.25E-04	1.7337	1.25E-02	0.1332	4.21E-02	0.4034
2.99E-04	2.0141	2.28E-02	0.5866	6.05E-02	0.9489
4.07E-04	2.2616	3.20E-02	0.9798	6.20E-02	0.9159
5.41E-04	2.4222	4.23E-02	1.4473	7.23E-02	0.8832
6.20E-04	2.4392	6.07E-02	2.3076	8.27E-02	0.8033

7.31E-04	2.4713	6.20E-02	2.3037	9.29E-02	0.7039
8.24E-04	2.4745	7.20E-02	2.4331	1.11E-01	1.1743
9.27E-04	2.4808	8.28E-02	2.5231	1.61E-01	2.2913
1.21E-03	2.1489	9.26E-02	2.594	2.12E-01	2.7942
2.22E-03	2.5595	1.11E-01	3.3526	2.62E-01	3.5974
3.30E-03	2.8519	1.60E-01	5.3175	3.11E-01	4.7603
4.34E-03	3.1153	2.11E-01	6.5283	3.61E-01	5.7254
5.05E-03	3.5768	2.61E-01	8.0364	4.12E-01	6.3211
6.48E-03	4.0038	3.11E-01	9.8878	4.62E-01	7.1533
7.16E-03	4.4251	3.61E-01	11.5146	5.11E-01	8.3088
8.13E-03	5.0358	4.12E-01	12.7853	5.61E-01	9.1245
9.17E-03	5.6806	4.61E-01	14.1476	6.12E-01	10.0245
1.02E-02	6.3167	5.11E-01	15.8388	6.61E-01	10.8145
1.94E-02	12.4126	5.61E-01	17.1548	7.11E-01	11.6038
2.94E-02	18.3608	6.11E-01	18.4653	7.62E-01	12.3587
3.97E-02	23.8151	6.61E-01	19.7431	8.12E-01	13.3464
5.70E-02	31.7193	7.11E-01	20.954	8.61E-01	14.169
6.18E-02	33.6685	7.62E-01	22.0578	9.12E-01	14.6997
7.09E-02	37.071	8.11E-01	23.3425	9.61E-01	15.4675
8.08E-02	40.5092	8.61E-01	24.6296	9.99E-01	16.3381
9.09E-02	43.7018	9.11E-01	25.387	9.39E-01	15.3334
1.09E-01	48.7594	9.61E-01	26.4319	8.88E-01	15.0173
1.55E-01	59.2465	9.99E-01	27.5239	8.38E-01	14.4267
2.06E-01	67.9019	9.39E-01	26.1873	7.88E-01	13.6303
2.57E-01	74.8972	8.88E-01	25.6048	7.39E-01	12.7529
3.08E-01	80.6223	8.39E-01	24.6622	6.88E-01	12.1946
3.59E-01	85.5639	7.89E-01	23.5472	6.39E-01	11.4696
4.09E-01	89.9153	7.39E-01	22.329	5.89E-01	10.7561
4.59E-01	93.7547	6.89E-01	21.3987	5.39E-01	9.956
5.10E-01	97.1277	6.39E-01	20.2846	4.88E-01	9.1042
5.60E-01	100.1942	5.89E-01	19.1274	4.40E-01	7.7653

6.10E-01	103.1297	5.39E-01	17.8891	3.88E-01	7.5956
6.60E-01	106.1445	4.89E-01	16.5745	3.39E-01	6.7161
7.10E-01	109.0511	4.40E-01	14.5645	2.89E-01	5.7253
7.60E-01	111.5457	3.89E-01	13.8901	2.39E-01	4.5432
8.10E-01	114.3555	3.39E-01	12.4196	1.89E-01	3.7032
8.60E-01	116.8152	2.89E-01	10.8054	1.38E-01	3.2989
9.10E-01	119.3683	2.39E-01	8.9372	8.89E-02	1.8784
9.60E-01	121.7137	1.89E-01	7.3431	9.39E-01	15.3334
9.99E-01	123.8018	1.38E-01	6.184	8.88E-01	15.0173
9.43E-01	121.7708	8.93E-02	3.9054	8.38E-01	14.4267
8.89E-01	119.998	9.39E-01	26.1873	7.88E-01	13.6303
8.39E-01	118.1566	8.88E-01	25.6048	7.39E-01	12.7529
7.89E-01	116.078	8.39E-01	24.6622	6.88E-01	12.1946
7.39E-01	113.8878	7.89E-01	23.5472	6.39E-01	11.4696
6.89E-01	111.5007	7.39E-01	22.329	5.89E-01	10.7561
6.40E-01	109.0121	6.89E-01	21.3987	5.39E-01	9.956
5.90E-01	106.1546	6.39E-01	20.2846	4.88E-01	9.1042
5.40E-01	103.2211	5.89E-01	19.1274	4.40E-01	7.7653
4.90E-01	99.8212	5.39E-01	17.8891	3.88E-01	7.5956
4.40E-01	96.2265	4.89E-01	16.5745	3.39E-01	6.7161
3.91E-01	92.1358	4.40E-01	14.5645	2.89E-01	5.7253
3.41E-01	87.6445	3.89E-01	13.8901	2.39E-01	4.5432
2.92E-01	82.375	3.39E-01	12.4196	1.89E-01	3.7032
2.42E-01	76.3521	2.89E-01	10.8054	1.38E-01	3.2989
1.93E-01	69.0739	2.39E-01	8.9372	8.89E-02	1.8784
1.44E-01	59.9548	1.89E-01	7.3431		
9.61E-02	47.8084	1.38E-01	6.184		
4.78E-02	28.5675	8.93E-02	3.9054		

Table S10. The High Pressure H_2 Uptake in **SNU-21H** and **SNU-21S** at 77 K and 298 K.

H_2 at 77 K of SNU-21H		H_2 at 77 K of SNU-21S		H_2 at 298 K of SNU-21H		H_2 at 298 K of SNU-21S	
P / bar	Excess wt%	*P* / bar	Excess wt%	*P* / bar	Excess wt%	*P* / bar	Excess wt%
0.0400	0.0000	0.0400	0.0000	0.0000	0.0000	0.0500	0.0000
1.0500	1.9135	1.0600	1.7934	6.2300	4.1736e-4	1.4400	0.0291
4.9600	2.4626	4.9800	2.3141	10.5600	0.0158	5.0000	0.0594
10.2400	2.7874	9.9800	2.5937	15.1600	0.0387	10.0200	0.0816
14.9200	3.0140	15.4600	2.8261	20.6600	0.0586	15.4100	0.1068
19.9300	3.2249	20.0400	3.0046	25.5800	0.0780	20.4400	0.1251
25.1700	3.4201	24.8900	3.1667	30.2500	0.0885	25.2600	0.1423
30.3900	3.5892	30.4800	3.3378	35.1800	0.1025	30.2500	0.1590
34.8900	3.7298	35.1000	3.4776	40.5400	0.1170	35.0400	0.1730
40.6400	3.8959	40.2000	3.6232	45.0400	0.1349	40.3000	0.1877
45.0700	3.9992	44.9600	3.7550	50.2300	0.1473	44.9900	0.2000
50.6000	4.1062	49.9500	3.8799	55.4300	0.1620	50.2500	0.2123
54.9700	4.1964	55.4900	4.0224	60.0600	0.1707	55.1500	0.2243
60.0000	4.2751	60.4300	4.1327	64.8300	0.1763	60.2900	0.2372
64.8800	4.3387	65.6100	4.2594	70.0400	0.1829	64.9700	0.2498
70.1200	4.3609	70.7700	4.3753	59.9400	0.1675	70.3000	0.2583
60.0100	4.2858	60.9000	4.1767	49.0500	0.1436	60.0800	0.2363
50.6200	4.1453	50.6900	3.9201	40.1500	0.1260	49.6300	0.2076
40.7200	3.9149	41.1000	3.6705	29.7400	0.0996	39.6000	0.1856
29.7600	3.5778	30.4200	3.3733	20.2400	0.0655	30.4200	0.1594
19.8100	3.2207	20.2000	3.0565	9.9300	0.0257	19.8800	0.1233
9.9800	2.7843	10.0600	2.6720			9.7900	0.0827
4.9800	2.4844	5.6000	2.4359			4.9700	0.0583

Table S11. The High Pressure CO_2 Uptake in **SNU-21H** and **SNU-21S** at 298 K.

CO_2 at 298 K of SNU-21H		CO_2 at 298 K of SNU-21S	
P / bar	Excess wt%	*P* / bar	Excess wt%
0.0400	0.5508	0.0500	1.0992
1.0200	8.1671	1.0600	8.6546
2.1600	12.6256	5.2300	18.5612
4.9800	17.3367	10.0800	21.8947
10.2300	20.7431	15.4400	23.8123
15.1900	22.2030	20.1400	24.7310
30.0500	24.0350	25.0600	25.5450
35.8300	24.5018	30.0700	26.0328
39.7600	24.9355	34.9500	26.6320
35.4300	24.5770	40.1100	26.7851
25.2600	23.7693	45.1400	27.2020
14.8100	22.2446	40.6000	27.1005
1.0500	8.4811	30.1800	26.3854
		20.2700	25.1378
		9.9100	22.4581
		5.1100	18.9987

Table S12. The High Pressure CH_4 Uptake in **SNU-21H** and **SNU-21S** at 298 K.

CH_4 at 298 K of SNU-21H		CH_4 at 298 K of SNU-21S	
P / bar	Excess wt%	*P* / bar	Excess wt%
0.0400	0.0190	0.0500	0.0000
1.1200	1.0200	1.1200	1.8416
5.1100	2.6986	5.4900	3.6272
10.3700	3.5681	10.1000	4.4941
15.4300	4.0653	15.1700	5.0494
20.4700	4.4410	20.2700	5.3991
25.0600	4.6716	24.9800	5.6718
30.2700	4.8425	30.2900	5.9352
35.1300	5.0046	35.1700	6.0677
40.3700	5.1303	39.9800	6.1847
45.1800	5.2048	46.4500	6.2952
49.8800	5.3231	50.5400	6.3754
40.4300	5.1428	40.2700	6.2172
30.1700	4.8675	30.3500	5.9456
20.2400	4.4212	20.1200	5.4378
9.9800	3.5676	9.8500	4.5451
5.0500	2.6748	4.9700	3.6107
1.0400	0.9436		