Supplementary Material (ESI) for Chemical Communications

Supporting Information

Stepwise and Hysteretic Sorption N_2, O_2, CO_2, and H_2 Gases in a Porous Metal-Organic Framework $[Zn_2(BPnDC)_2(bpy)]$

Hye Jeong Park and Myunghyun Paik Suh*

Contribution from the Department of Chemistry, Seoul National University, Seoul 151-747, Republic of Korea

E-mail: mpsuh@snu.ac.kr

General Methods. All chemicals and solvents used in the syntheses were of reagents grade and used without further purification, except that purchased anhydrous methanol was further dehydrated by using the activated molecular sieves prior to use. Infrared spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Elemental analyses were performed with a Perkin-Elmer 2400 Series II CHN analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under N_2 at a scan rate of 5 ^{o}C/min, using TGA Q50 and DSC Q10 of TA instruments, respectively. High-resolution powder X-ray diffraction (PXRD) was measured with a synchrotron radiation source (λ = 1.22152 Å, scan speed = 0.01^{o}/sec, step size = 0.01^{o} in 2θ) at Beamline 11A1 RXS, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The temperature dependent PXRD data were recorded on a Bruker Small-Angle X-Ray Scattering (SAXS) with General Area Detector Diffraction System (GADDS) at National Instrumentation Center for Environmental Management (40 kV and 45 mA for Cu Kα (λ = 1.5406 Å), exposure time = 180 sec, step size = 0.02^{o} in 2θ).

{[Zn_2(BPnDC)$_2$(bpy)]•2DEF•2MeOH}$_n$ (1). H_2BPnDC (0.054 g, 2.0 x 10^{-4} mol) and bpy (0.016 g, 1.1 x 10^{-4} mol) were dissolved in DEF (6 mL), and $Zn(NO_3)_2$•$6H_2O$ (0.080 g, 2.7 x 10^{-4} mol) was dissolved in MeOH (3 mL). The solutions were mixed in a glass bottle, which was then tightly capped with silicone stopper and aluminum seal, and then heated at 80 ºC for 24 h. On cooling to room temperature, colorless rod-shaped crystals formed, which were filtered, and washed briefly with MeOH. Yield: 0.080 g (67%). FT-IR for **1** (Nujol mull): ν_{O-H}, 3608, 3468; $\nu_{C=O(DEF)}$, 1670; $\nu_{C=O(BPnDC)}$, 1658; $\nu_{C=C(aromatic)}$, 1607; $\nu_{O-C=O(carboxylate)}$, 1558 cm^{-1}. Anal. Calcd for $Zn_2C_{52}H_{54}O_{14}N_4$: C, 57.31; H, 4.99; N, 5.14. Found: C, 56.63; H, 4.52; N, 5.10.

{[Zn_2(BPnDC)$_2$(bpy)]•6MeOH}$_n$ (1m). Crystals of **1** were immersed in anhydrous MeOH for 12 h, and the solvent was decanted. Fresh anhydrous MeOH was replenished and the crystals were immersed for another 12 h to exchange all DEF guest molecules with MeOH. FT-IR for **1m** (Nujol mull): ν_{O-H},

3369; $\nu_{C=O(BPnDC)}$, 1659; $\nu_{C=C(aromatic)}$, 1607; $\nu_{O-C=O(carboxylate)}$, 1557 cm^{-1}. Anal. Calcd for $Zn_2C_{46}H_{48}O_{16}N_2$: C, 54.40; H, 4.76; N, 2.76. Found: C, 53.90; H, 4.58; N, 2.83.

$[Zn_2(BPnDC)_2(bpy)]_n$ (SNU-9). 1m was heated in a Schlenk tube at 60 ^oC under vacuum for 1.5 h. FT-IR (Nujol mull): $\nu_{C=O(BPnDC)}$, 1667; $\nu_{C=C(aromatic)}$, 1609; $\nu_{O-C=O(carboxylate)}$, 1588 cm^{-1}. Anal. Calcd for $Zn_2C_{40}H_{24}O_{10}N_2$: C, 58.35; H, 2.94; N, 3.40. Found: C, 57.70; H, 2.71; N, 3.39.

Low-Pressure Gas Sorption Measurements. The gas adsorption-desorption experiments were performed using an automated micropore gas analyzer Autosorb-1 or Autosorb-3B (Quantachrome Instruments). All gases used were of 99.999% purity. Sample was predesolvated by heating **1m** in a Schlenk tube at 60 °C under vacuum for 2 h, and the measured amount of the dried solid was introduced to the gas sorption apparatus and then activated at 60 ^oC under vacuum for 1 h. The N_2 and O_2 gas sorption isotherms were monitored at 77 K and 87 K, and the H_2 gas isotherm was measured at 77 K. The CO_2 and CH_4 gas sorption isotherms were measured at 195 K and 273 K at each equilibrium pressure by the static volumetric method. After each gas sorption measurement, sample weight was measured again precisely. Surface area and total pore volume were determined from the N_2 gas adsorption isotherm at 77 K. For estimation of multipoint BET (Brunauer-Emmett-Teller) and Langmuir surface area from the N_2 adsorption data, the data were taken in the range P = 0.040 – 0.16 atm and P = 0.029 – 0.31 atm, respectively.

High-Pressure Gas Sorption Measurements. High pressure gas sorption isotherms were measured by the gravimetric method using a Rubotherm MSB (magnetic suspension balance) apparatus. All gases used were of 99.999 % purity. The H_2 sorption isotherms were measured at 77 K. The CO_2 and CH_4 sorption isotherms were measured at 298 K. Sample was prepared by heating **1m** in a Schlenk tube at 60 °C under vacuum for 2 h, and the measured amount of the dried solid was introduced into the gas sorption apparatus and then activated at 60 ^oC under vacuum for 12 h. Prior to gas sorption measurement, the He isotherm (up to 90 bar) was measured at 298 K to obtain volume of the framework skeleton. The excess sorption isotherms were measured and the data were corrected for buoyancy by

multiplying the volume of the framework skeleton by the density of corresponding gas at each pressure and temperature.[S1] The total amount of H_2 adsorption was estimated by using the densities of the framework skeleton and the crystal.[S2] In the conversion of gravimetric data (wt%) to volumetric ones (gL^{-1}), the crystallographic density of desolvated sample of **1m** (d = 1.106 g/cm^3) was applied.

X-ray Crystallography. Diffraction data of **1** and **1m** were collected at 100 K on a ADSC Quantum 210 CCD diffractometer with synchrotron radiation (λ = 0.79998 for **1** and 82655 for **1m**) at Macromolecular Crystallography II 6C1, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The crystals were coated with Paraton oil to prevent the loss of guest molecules. The diffraction data were collected using a phi scan method through a total of 360° rotation. The raw data were processed and scaled using the program HKL2000. The crystal structure was solved by direct methods[S3] and refined by full-matrix least-squares refinement using the *SHELXL-97* computer program.[S4] The positions of all non-H atoms were refined with anisotropic displacement factors. The H atoms were positioned geometrically using a riding model. The densities of the disordered guest molecules in **1** and **1m** were flattened by using the *SQUEEZE* option of PLATON.[S5] CCDC-726043 (**1**) and 726044 (**1m**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References:

[S1] NIST chemistry webbook (thermophysical properties of fluid systems); http://webbook.nist.gov/chemistry/fluid.

[S2] M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 16876.

[S3] Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112-122.

[S4] Sheldrick, G. M. *SHELEX97*, Program for the crystal structure refinement; University of Göttingen: Göttingen, Germany, **1997**.

[S5] Spek, A. L. *PLATON A Multipurpose Crystallographic Tool*; Utrecht University, Utrecht, The Netherlands, **2007**.

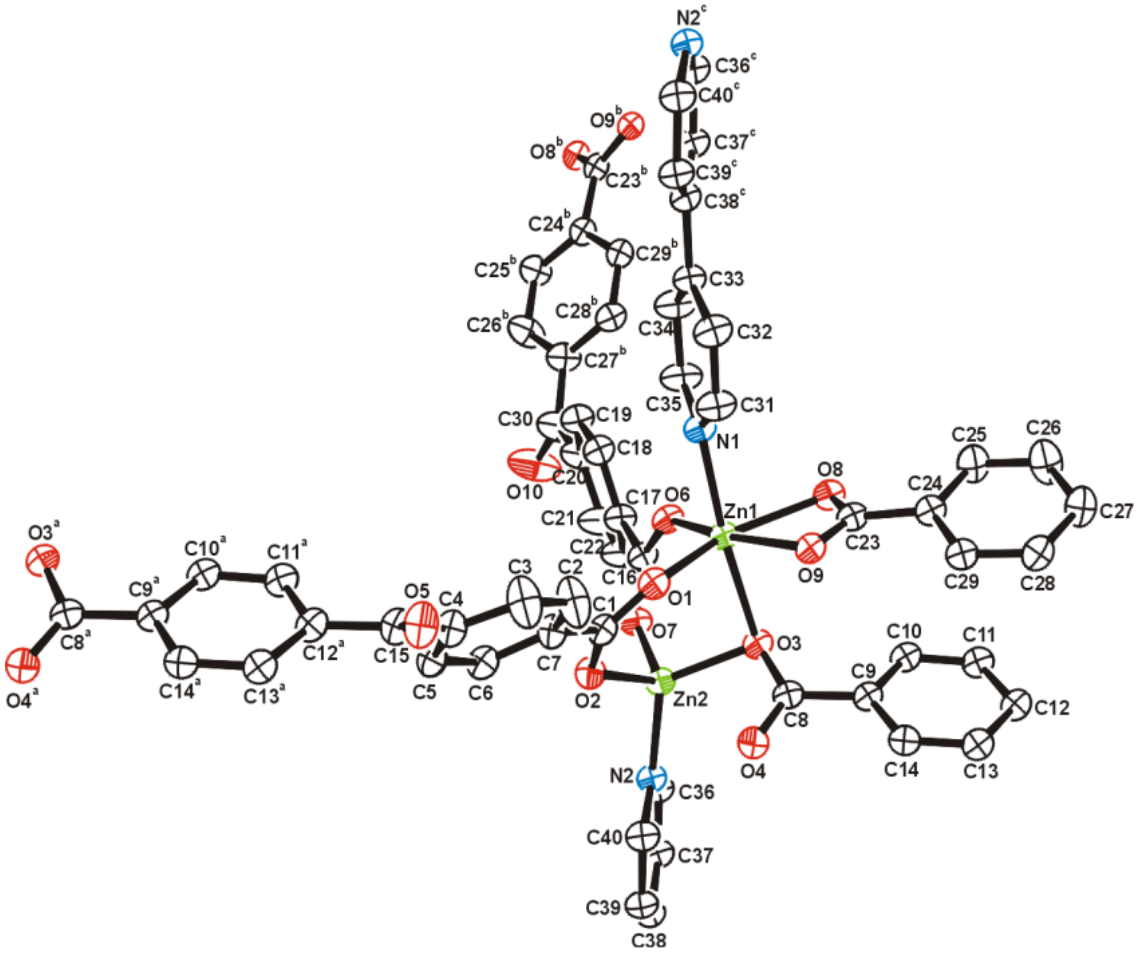

Figure S1. An ORTEP drawing of **1**, showing the coordination environment of two independent Zn^{II} ions. Thermal ellipsoids are drawn with 30% probability. Symmetry transformation: *a*, x+1/2, y+1/2, *z*; *b*, x, -y, z-1/2; *c*, x+1/2, y-1/2, z.

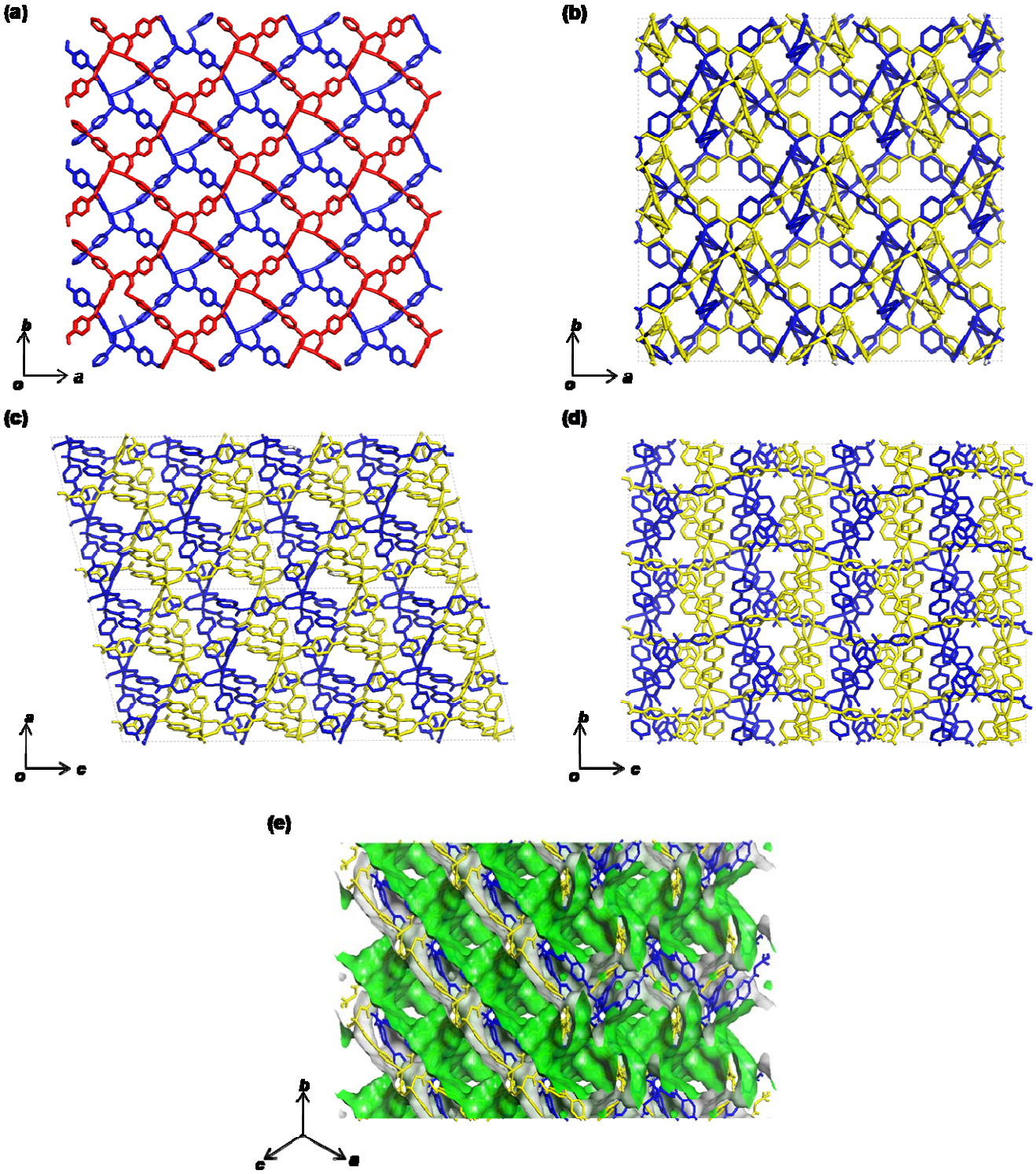

Figure S2. X-ray structure of **1**. (a) View seen on the *ab* plane, showing the 2D layers are repeated in the staggered manner with the ••ABABAB•• sequence. (b) Doubly interpenetrated 3D structure seen on the *ab* plane, (c) on the *ac* plane, and (d) on the *bc* plane. Blue and yellow colors represent each framework of the doubly interpenetrated structure. (e) A view showing the 3D curved channels. The accessible surface in the channels is represented by green color.

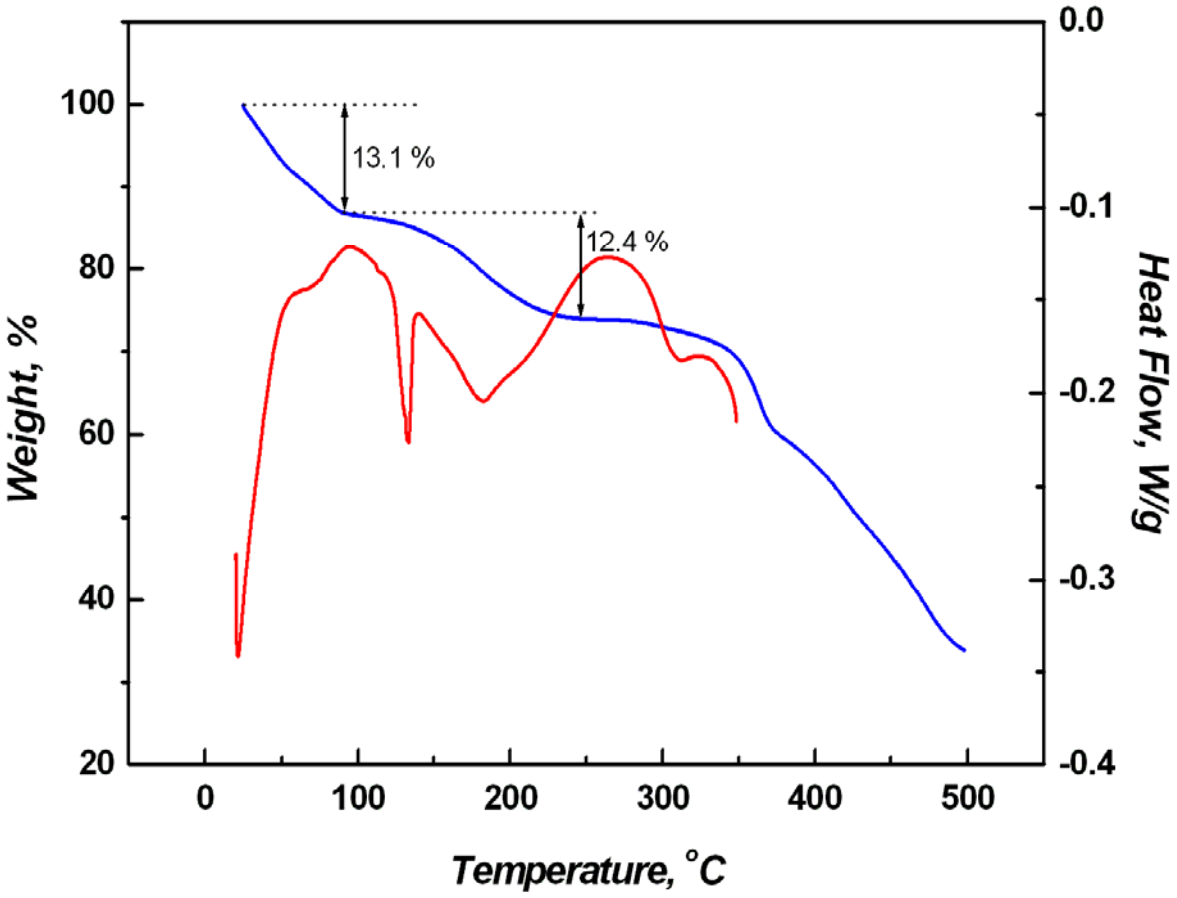

Figure S3. TGA/DSC trace for **1**.

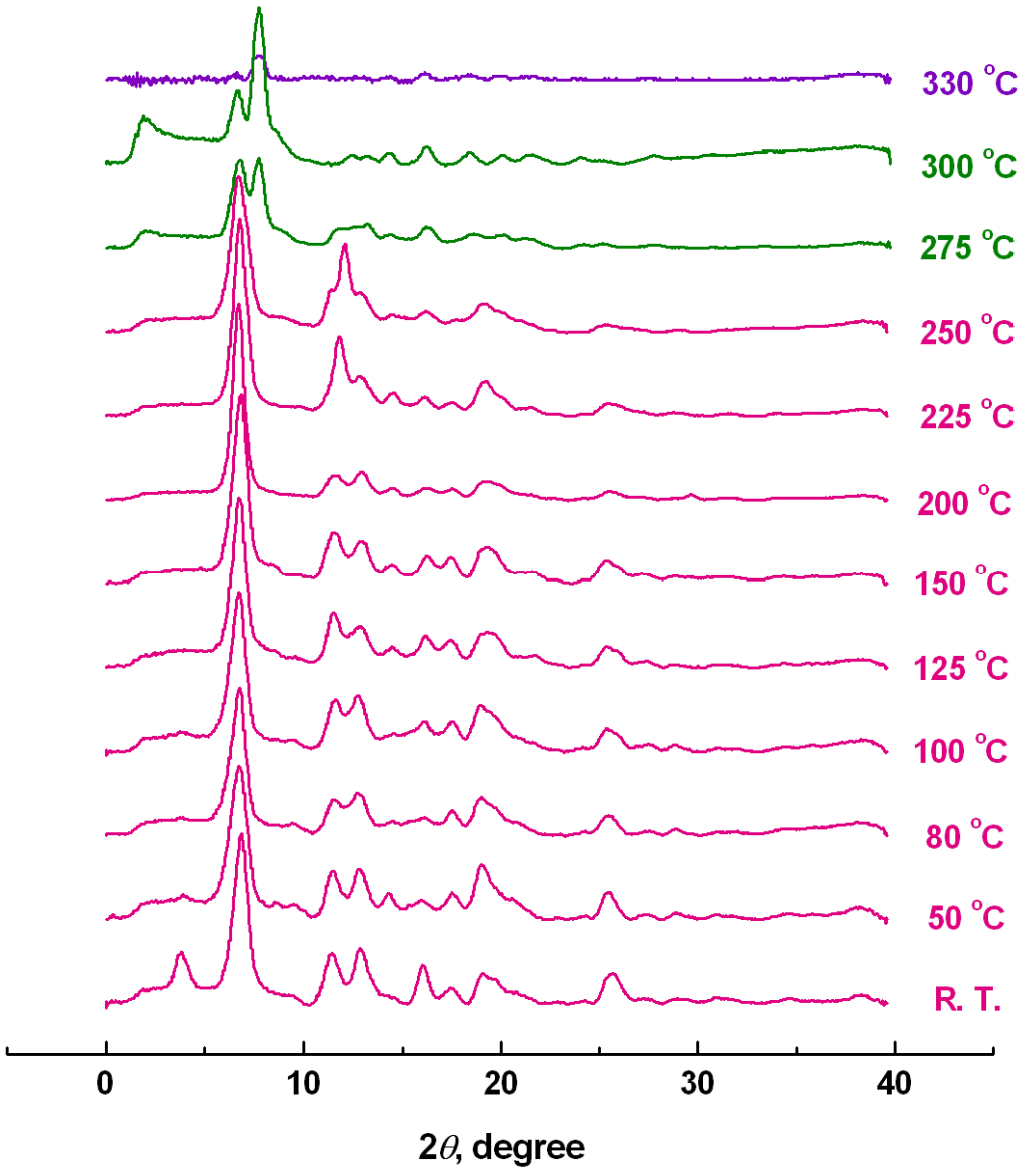

Figure S4. The temperature dependent PXRD patterns of **1** (from R.T. to 330 °C).

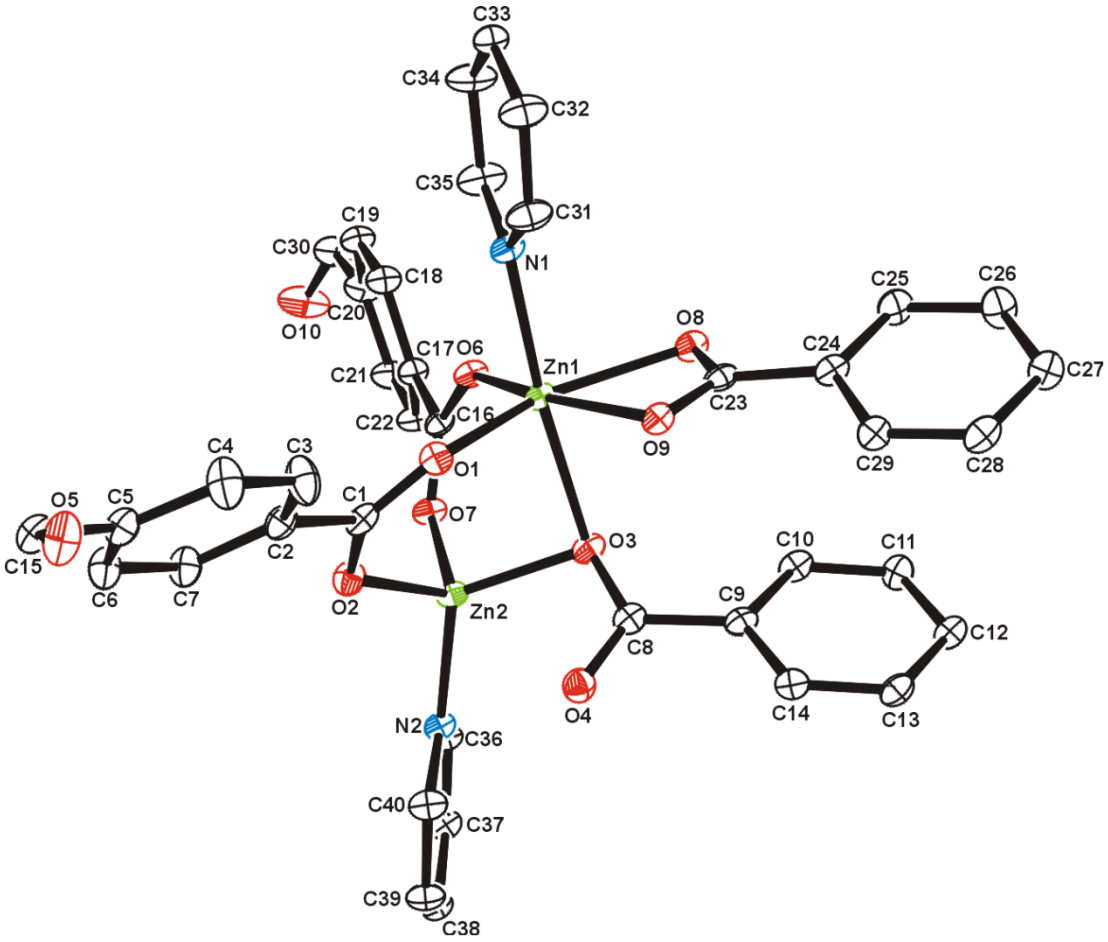

Figure S5. An ORTEP drawing of the asymmetric unit of **1m**. Thermal ellipsoids are drawn with 30% probability.

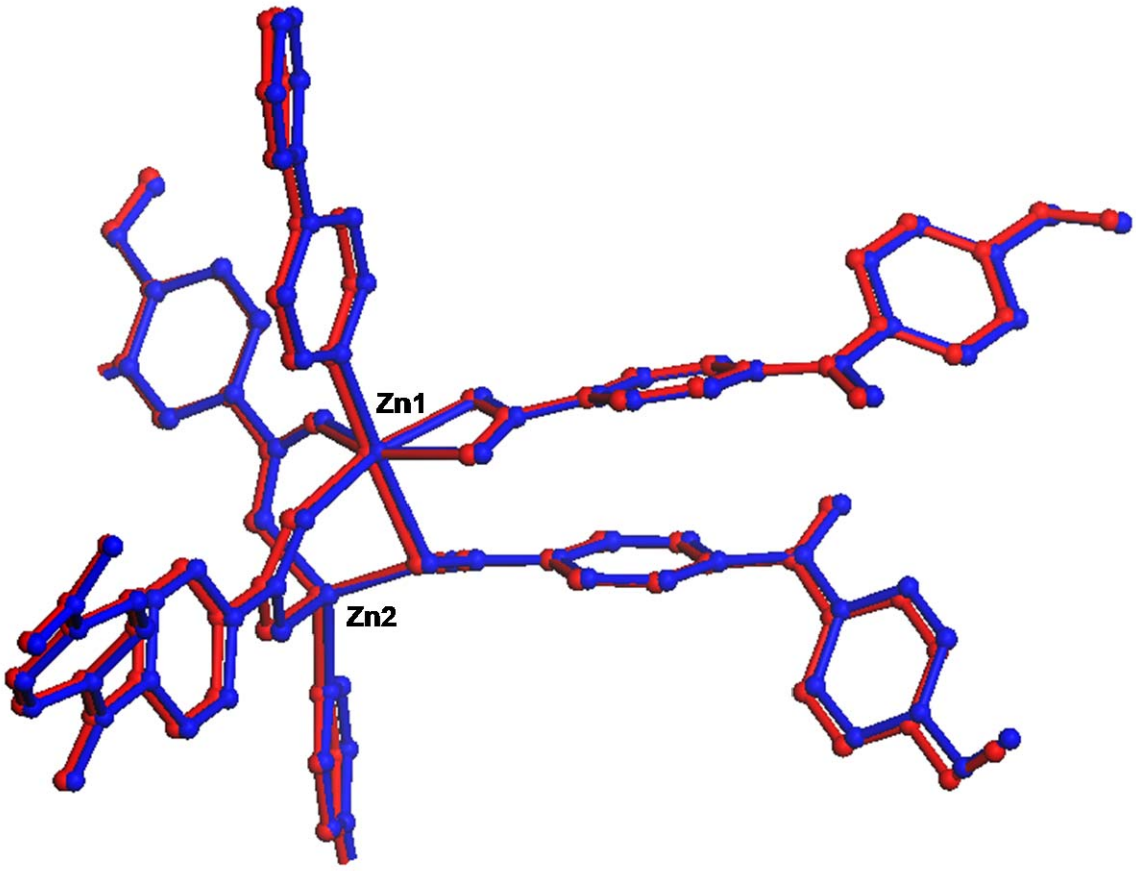

Figure S6. Comparison of the crystallographic asymmetric units of **1** (red) and **1m** (blue) by superimposition.

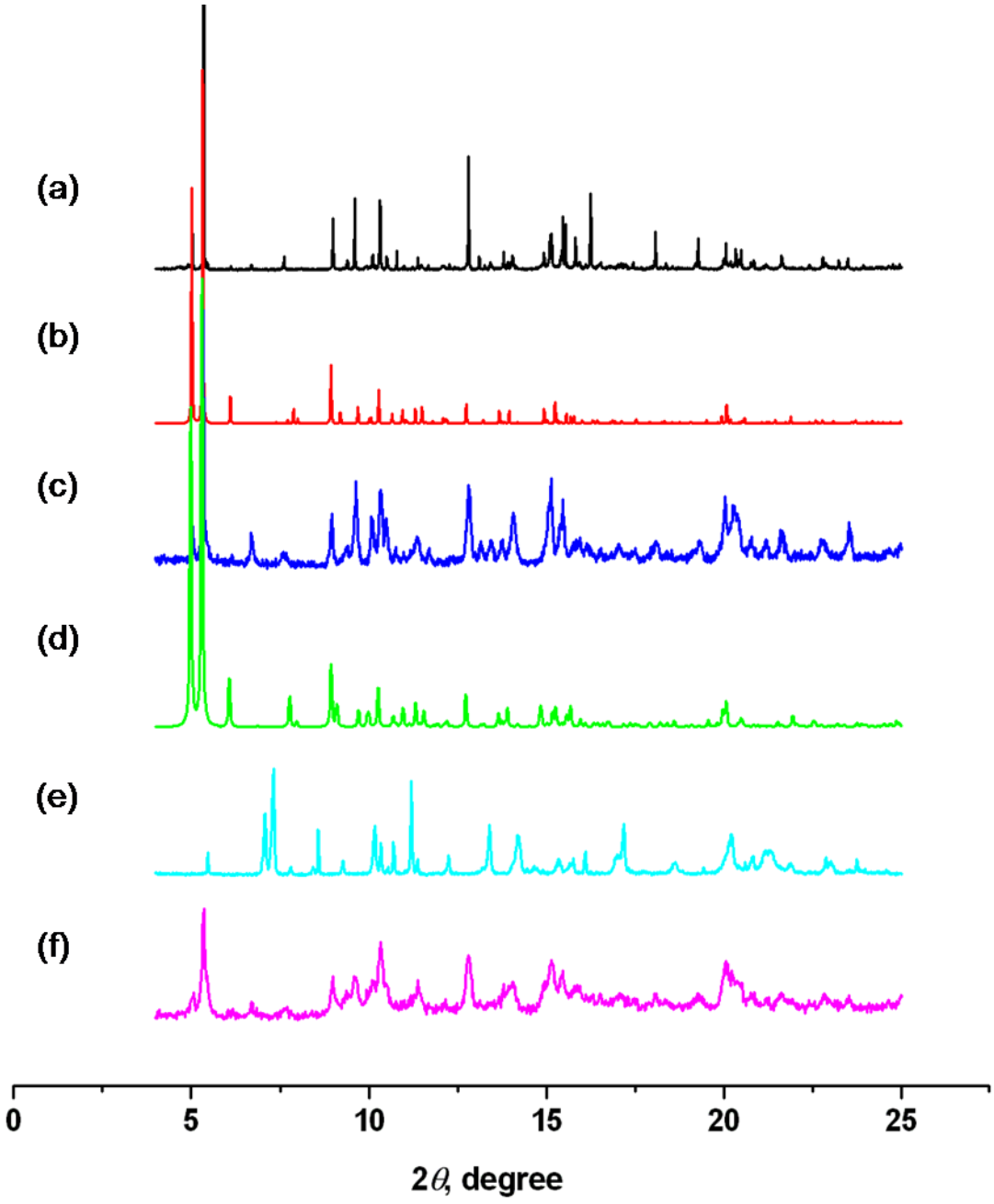

Figure S7. The synchrotron (λ = 1.22152 Å) PXRD patterns measured at room temperature of (a) **1** as-synthesized, (b) the simulated from single-crystal X-ray data of **1**, (c) guest-exchanged solid with MeOH (**1m**), (d) the simulated from single-crystal X-ray data of **1m**, (e) **SNU-9** prepared by drying **1m** at 60 ^{o}C under vacuum for 1.5 h, and (f) a solid resulting after exposure of the sample of (e) to MeOH vapor for 6 h.

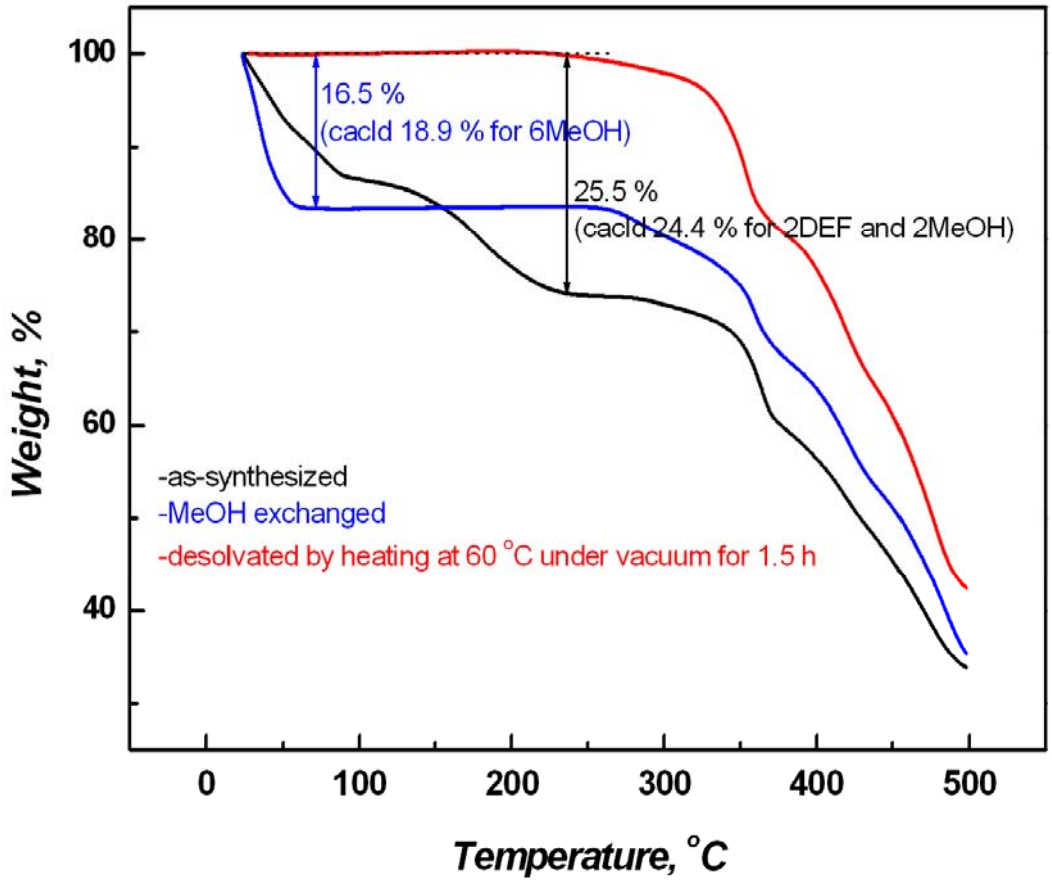

Figure S8. TGA traces for **1**, **1m**, and **SNU-9**.

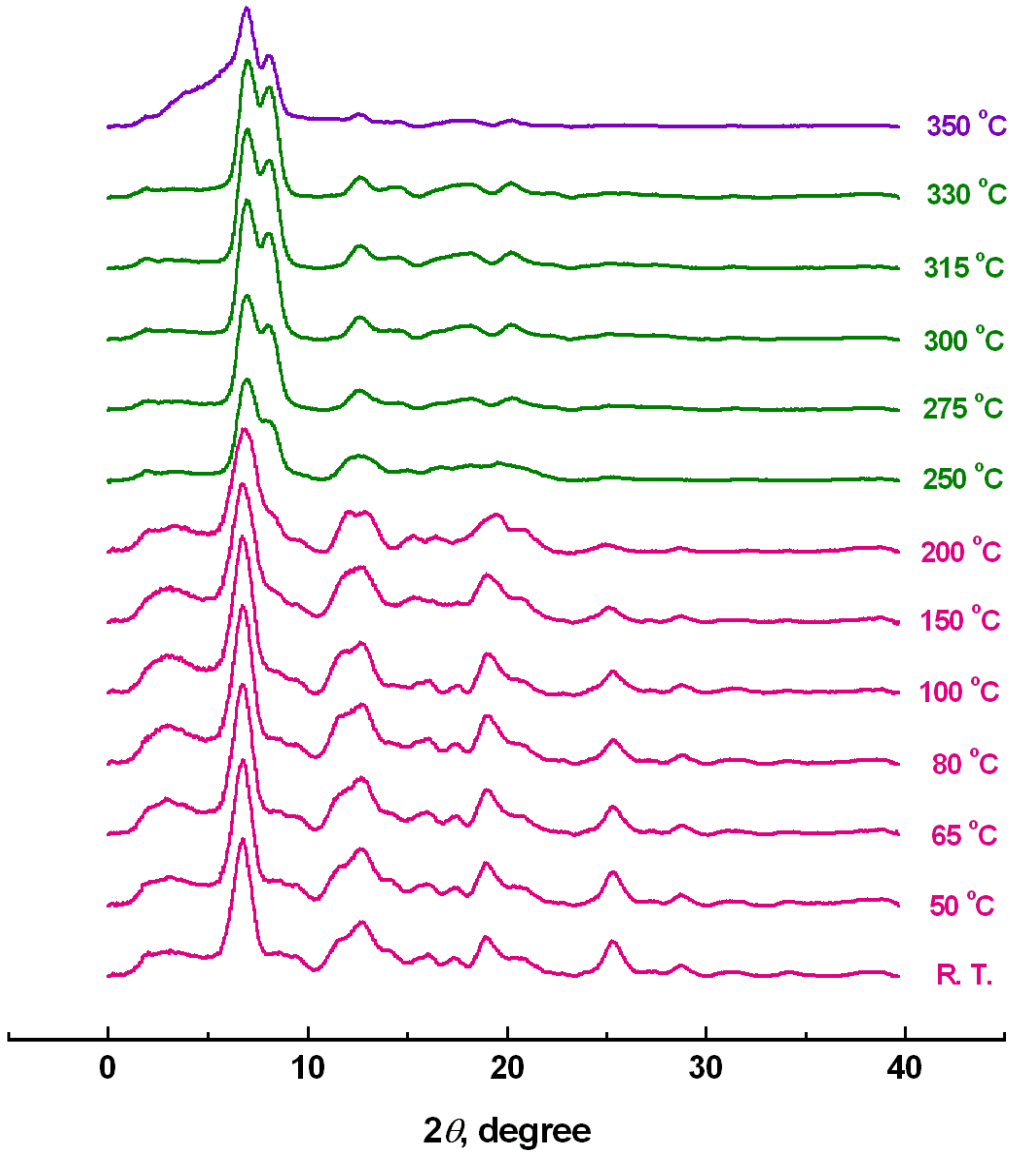

Figure S9. The temperature dependent PXRD patterns of **1m** (from R.T. to 350 °C).

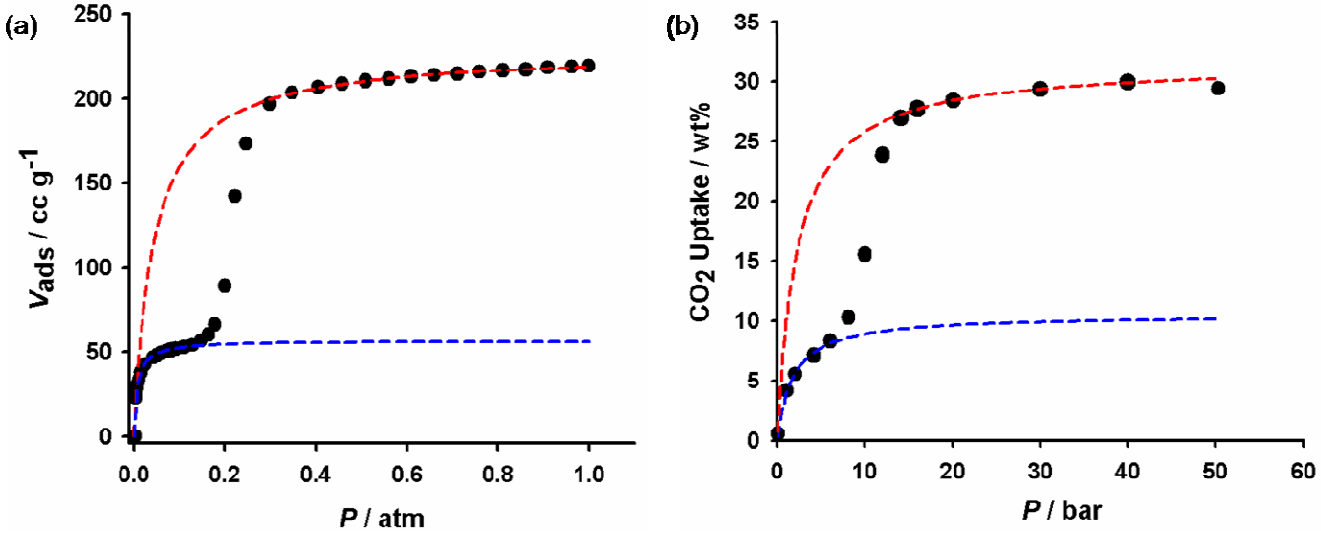

Figure S10. Langmuir fits for two-step CO_2 adsorption isotherms. (a) At 195 K measured up to 1 atm. The blue dashed lines is the fit of the first step adsorption ($P < 0.15$ atm) and the red dashed line is the fit for the second step adsorption ($P > 0.4$ atm). (b) At 298 K measured under high pressures. Langmuir fits for the first step (0 – 6 bar) and the second step (14 – 50 bar) adsorptions are indicated by blue and red dashed lines, respectively.

Table S1. Crystallographic Data for **1** and **1m** [Squeezed Data]

	1	**1m**
formula	$Zn_2C_{40}H_{24}N_2O_{10}$	$Zn_2C_{40}H_{24}N_2O_{10}$
crystal system	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
fw	823.40	823.40
a, Å	21.687 (4)	21.536(4)
b, Å	17.754(4)	18.048(4)
c, Å	26.041(5)	26.298(5)
β, deg	103.95(3)	104.55(3)
V, Å^3	9731(3)	9894(3)
Z	8	8
ρ_{calcd}, g/cm^3	1.124	1.106
temp, K	100	100
λ, Å	0.79998	0.82655
μ, mm^{-1}	1.033	1.016
GOF (F^2)	1.073	1.047
F(000)	3344	3344
reflections collected	13520	11988
independent reflections	7644 [*R*(int) = 0.0308]	6139 [*R*(int) = 0.0222]
independent reflections [$I > 2\sigma(I)$]	6426	5783
completeness to θ_{max}, %	93.0	98.6
data refined/parameters/restraints	7644 / 487 / 0	6139 / 487 / 0
θ range for data collection, deg	1.81 – 27.95	2.10 – 26.09
diffraction limits (*h*, *k*, *l*)	$-25 \le h \le 24$,	$-22 \le h \le 22$,
	$-20 \le k \le 20$,	$-19 \le k \le 19$,
	$-30 \le l \le 30$	$-27 \le l \le 27$
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R_1, wR_2 [$I > 2\sigma(I)$]	0.0606,[a] 0.1811[b]	0.0470,[a] 0.1390[c]
R_1, wR_2 (all data)	0.0660,[a] 0.1860[b]	0.0484,[a] 0.1405[c]
largest peak, hole, eÅ^{-3}	0.563, -1.326	0.515, -0.944

[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 $w = 1/[\sigma^2(F_o^2) + (0.1361P)^2 + (4.5286)P]$, $P = (F_o^2 + 2F_c^2)/3$ for **1**. [c] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0955P)^2 + (28.14)P]$, $P = (F_o^2 + 2F_c^2)/3$ for **1m**.

Table S2. Gas adsorption data of **SNU-9** for N_2, O_2, H_2, CO_2, and CH_4 gases

gas	T (K)	P (bar)	surface area (m^2g^{-1})[a,b]	pore volume (cm^3g^{-1})	mmol of gas/ g of host	wt% gas	Gas adsorbed/ volume of host[c] (gL^{-1})
N_2	77	0.9	1040[a], 820[b]	0.367	11.7	32.7	362
	87	0.9			10.7	30.9	333
O_2	77	0.2			16.1	51.4	569
	87	0.6			12.3	39.2	434
H_2	77	1.0			1.21	0.24	2.65
	77	90			18.0	3.63[d], 6.23[e]	40.2[d], 68.9[e]
CO_2	195	1.0			9.78	43.0	476
CO_2	273	1.0			1.25	5.49	60.7
CO_2	298	40			6.79	29.9	331
CH_4	195	1.0			1.34	2.13	23.6
CH_4	298	65			2.12	3.40	37.6

[a]Langmuir surface area. [b]BET surface area. [c]The values are calculated by mass of adsorbed gas/g x density of sample (density: 1106 gL^{-1}), assuming that the cell volumes of **1m** is retained in its desolvated solid (**SNU-9**). [d]Excess adsorption capacity. [e]Total adsorption capacity at 77 K and 90 bar, which is estimated by using the densities of the framework skeleton and the crystal.

Table S3. Adsorption and Desorption Data for N_2 Uptake in **SNU-9**.

N_2 at 77 K				N_2 at 87 K			
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}
9.55E-05	49.7855	0.907	261.9705	1.24E-04	46.3819	0.911	240.5665
2.72E-04	53.0846	0.846	259.8361	2.34E-04	53.0727	0.848	238.7471
4.31E-04	54.0982	0.790	257.9181	3.89E-04	56.0678	0.789	237.1361
4.19E-04	54.1176	0.740	256.5229	5.46E-04	57.7366	0.740	235.1784
7.54E-04	56.4436	0.690	255.0048	5.39E-04	57.7304	0.689	233.4313
7.06E-04	56.3916	0.640	253.5282	9.68E-04	60.0225	0.640	231.6440
7.07E-04	56.4141	0.589	252.2194	8.98E-04	59.9013	0.590	229.6057
7.99E-04	56.7383	0.540	250.5070	8.92E-04	59.8440	0.539	227.8361
8.94E-04	59.1410	0.490	248.7533	9.05E-04	59.8718	0.490	225.7938
9.97E-04	61.3595	0.449	240.8723	0.00137	61.2974	0.441	223.3943
0.00208	93.7683	0.390	238.9938	0.00208	62.7026	0.390	221.1590
0.00300	116.8044	0.340	236.9656	0.00300	64.1974	0.340	219.3520
0.00403	129.3198	0.287	237.0282	0.00408	67.0053	0.291	216.7423
0.00508	133.5181	0.241	234.3062	0.00504	75.0753	0.240	213.9233
0.00614	135.6396	0.191	231.3559	0.00675	99.0423	0.191	210.6537
0.00709	137.1000	0.141	227.9590	0.00703	99.4463	0.141	206.8031
0.00821	138.5216	0.0935	222.3454	0.00819	107.5678	0.0926	201.9269
0.00902	139.4802	0.0459	214.2934	0.00903	109.9304	0.0449	194.7427
0.0114	141.2648	0.0113	199.4185	0.0102	114.3692	0.0145	185.0365
0.0194	147.6458	0.00858	197.0229	0.0142	121.7612	0.00787	180.5150
0.0291	177.0418	0.00482	192.4282	0.0252	128.2859	0.00495	177.6462
0.0402	198.5136	0.00452	191.8700	0.0410	133.1537		
0.0508	206.6132			0.0502	135.2793		
0.0608	210.4551			0.0602	137.3670		
0.0697	212.7374			0.0703	139.3599		
0.0802	214.8749			0.0797	141.6714		
0.0909	216.6449			0.0894	146.3811		
0.109	219.4260			0.0992	153.8322		
0.156	224.6652			0.151	188.7300		
0.208	228.0260			0.208	201.0264		
0.259	231.0780			0.253	206.8678		
0.309	233.8070			0.304	212.1524		
0.359	236.3022			0.358	215.4608		
0.410	238.4009			0.408	218.8123		
0.460	240.3533			0.459	221.3062		
0.510	242.4269			0.509	223.9789		
0.560	244.3643			0.559	226.0978		
0.610	246.0665			0.610	228.1379		
0.660	247.8775			0.659	230.4894		
0.710	249.6291			0.710	232.1859		
0.760	251.4515			0.760	233.9780		
0.808	254.2736			0.810	235.8630		
0.857	258.0013			0.856	239.1586		
0.907	261.9705			0.911	240.5665		

Table S4. Adsorption and Desorption Data for O_2 Uptake in **SNU-9**.

O_2 at 77 K				O_2 at 87 K			
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}
2.46E-04	117.6581	0.202	360.0414	1.43E-04	54.1418	0.608	274.5440
2.47E-04	117.6432	0.171	351.9674	1.94E-04	57.7678	0.546	271.2242
4.50E-04	120.2000	0.139	350.0674	2.96E-04	61.2308	0.491	268.1718
4.42E-04	120.1877	0.115	347.7599	4.11E-04	64.2890	0.440	265.2004
5.53E-04	122.8299	0.0905	345.0432	5.67E-04	67.2449	0.391	262.1207
5.98E-04	125.6687	0.0651	342.3868	7.42E-04	69.2643	0.340	258.9326
7.35E-04	130.5974	0.0510	331.5436	7.39E-04	69.2533	0.292	255.2599
8.28E-04	133.4286	0.0262	325.7022	0.00103	71.4771	0.241	251.5546
9.60E-04	136.2749	0.0109	318.8832	0.00101	71.4132	0.192	247.7189
0.00111	138.7863	0.00890	317.4449	0.00103	71.4123	0.142	243.2608
0.00206	146.8480	0.00717	315.8013	0.00217	76.7581	0.0933	237.8269
0.00306	150.7973	0.00616	314.5555	0.00303	97.6696	0.0459	229.6308
0.00416	153.3982	0.00514	312.8176	0.00404	116.4837	0.0126	213.8326
0.00500	154.9013	0.00469	312.2899	0.00504	122.3515	0.0101	210.7119
0.00601	156.4084			0.00675	128.2621	0.00552	200.8974
0.00711	157.9238			0.00707	128.9903	0.00468	197.7784
0.00819	159.3907			0.00847	132.1304		
0.00900	160.4286			0.00942	133.8088		
0.0116	161.8793			0.0109	135.8996		
0.0137	168.1643			0.0161	141.6974		
0.0168	190.6828			0.0255	147.9427		
0.0204	226.4335			0.0501	151.2568		
0.0266	265.2141			0.0594	170.2000		
0.0395	299.6172			0.0695	188.7841		
0.0523	313.0449			0.0798	204.0441		
0.0692	322.1361			0.0904	213.8894		
0.0915	328.5388			0.101	221.4401		
0.107	332.1321			0.154	237.9476		
0.131	336.6106			0.204	244.8780		
0.155	341.8022			0.256	250.0418		
0.176	350.6828			0.308	254.2229		
0.202	360.0414			0.358	257.9352		
				0.409	261.2150		
				0.458	264.5185		
				0.509	267.6498		
				0.559	270.7388		
				0.608	274.5440		

Table S5. Adsorption and Desorption Data for CO_2 and CH_4 Uptake in **SNU-9** at 195 K.

CO_2 at 195 K				CH_4 at 195 K			
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}
0.00129	0.0954	0.999	219.0053	3.13E-04	0.0030	0.999	29.7557
0.00378	23.1009	0.939	218.6605	4.12E-04	0.0084	0.937	29.7754
0.00438	24.8262	0.889	218.1372	5.13E-04	0.0136	0.888	29.7523
0.00507	25.9035	0.839	217.3474	6.13E-04	0.0187	0.838	29.5936
0.00689	28.7304	0.789	216.8664	7.13E-04	0.0239	0.788	29.4650
0.00707	28.8800	0.739	216.2852	8.13E-04	0.0289	0.738	29.3724
0.00868	31.1939	0.690	215.2694	9.12E-04	0.0341	0.689	29.1694
0.00934	31.8725	0.639	214.4816	0.00101	0.0400	0.639	28.9044
0.0109	33.5155	0.589	213.8480	0.00227	0.1344	0.589	28.6961
0.0159	38.0164	0.540	212.7967	0.00319	0.2102	0.539	28.4171
0.0257	42.7382	0.490	211.7204	0.00423	0.3099	0.490	28.0508
0.0418	46.4954	0.440	210.6859	0.00515	0.4333	0.440	27.6394
0.0509	47.8322	0.391	209.3181	0.00609	0.5809	0.389	27.2257
0.0606	49.3424	0.341	207.6460	0.00710	0.7413	0.341	26.6302
0.0715	50.3033	0.291	205.7970	0.00886	1.0411	0.290	26.0424
0.0820	51.0243	0.242	203.5503	0.00975	1.1149	0.241	25.3325
0.0920	51.6799	0.216	202.0010	0.0125	1.3024	0.192	24.4052
0.110	52.8671	0.191	200.3832	0.0172	1.5989	0.143	23.2959
0.129	54.3352	0.167	198.3546	0.0219	1.9150	0.0939	21.8627
0.147	56.5740	0.142	195.9928	0.0312	2.4046	0.0468	19.9533
0.164	60.1595	0.118	193.1631	0.0364	2.7370	0.0103	17.2450
0.178	66.2431	0.0943	189.5845	0.0411	3.0982	0.0074	16.8302
0.200	89.1257	0.0715	184.7247	0.0501	3.6794	0.00516	16.3900
0.223	142.0793	0.0500	177.6375	0.0556	4.1400		
0.247	173.2220	0.0385	171.4789	0.0609	4.5353		
0.299	196.8437	0.0298	164.1757	0.0700	5.1145		
0.347	203.2651	0.0212	149.6776	0.0753	5.6183		
0.405	206.4984	0.0185	137.1411	0.0809	6.0166		
0.457	208.7536	0.0154	111.1391	0.0899	6.6037		
0.509	210.2638	0.0121	70.8750	0.0951	7.1226		
0.560	211.3428			0.107	7.9658		
0.609	212.7701			0.130	9.1481		
0.660	213.8053			0.153	10.6185		
0.711	214.5211			0.178	12.0744		
0.759	215.6924			0.206	13.1979		
0.810	216.5283			0.231	14.2095		
0.861	216.9572			0.256	15.2268		

0.909	218.0770
0.961	218.6743
0.999	219.0053

0.281	16.1385
0.307	17.0221
0.352	18.7068
0.405	19.8367
0.451	21.5579
0.505	22.6459
0.556	23.6390
0.606	24.5117
0.657	25.3341
0.706	26.1729
0.757	26.9993
0.807	27.7536
0.856	28.5971
0.909	29.0302
0.958	29.5357
0.999	29.7557

Table S6. High Pressure CO_2 and CH_4 Uptake in **SNU-9** at 298 K.

CO_2 at 298 K				CH_4 at 298 K			
P / bar	Excess wt%	*P* / bar	Excess wt%	*P* / bar	Excess wt%	*P* / bar	Excess wt%
1.08	4.1479	45.24	30.2210	1.02	0.6870	59.59	3.3777
2.06	5.5374	34.76	29.8683	2.11	1.0097	50.14	3.3134
4.18	7.1697	24.74	29.3608	5.04	1.4862	40.01	3.1976
6.06	8.3248	24.79	29.1735	10.00	1.8618	29.75	2.9816
8.11	10.3304	15.02	27.5867	15.16	2.0892	19.77	2.7041
10.02	15.6187	10.00	26.1515	20.12	2.2270	9.89	2.0937
12.01	23.9394	7.49	24.7191	25.08	2.3884	4.95	1.5469
14.10	26.9833	5.00	22.2746	30.02	2.5312	1.98	1.0341
16.00	27.7542	3.50	19.6724	35.06	2.6493		
20.06	28.4119	1.99	14.4544	40.11	2.7890		
29.96	29.3432	0.97	6.7236	44.97	2.8765		
39.97	29.9514			49.97	2.9796		
50.28	29.4223			54.23	3.1692		
				60.05	3.2314		
				64.97	3.4098		

Table S7. High Pressure H_2 Uptake in **SNU-9** at 77 K.

P / bar	Excess adsorbed / wt%	*P* / bar	Excess adsorbed / wt%
0.98	0.45447	80.77	3.50850
0.98	0.45690	80.78	3.50365
2.03	0.61862	80.80	3.49880
2.03	0.61712	70.81	3.42711
5.08	0.85862	70.85	3.43439
5.08	0.85992	70.86	3.43439
10.03	1.11170	60.17	3.43215
10.03	1.11461	60.18	3.42972
15.02	1.32568	60.20	3.43215
15.03	1.32660	50.64	3.09214
20.06	2.16794	50.68	3.09214
20.06	2.16886	39.95	2.94854
25.09	2.37677	39.96	2.95000
25.1	2.37696	39.97	2.94806
30.06	2.56733	29.58	2.71799
30.07	2.56432	29.59	2.71314
35.09	2.71647	29.60	2.71556
35.09	2.71293	19.95	2.30852
40.00	2.86519	19.96	2.30609
40.00	2.86873	19.97	2.31094
45.23	3.01567	15.08	2.06905
45.24	3.01660	15.09	2.06421
49.91	3.13347	15.09	2.06905
49.92	3.13328	10.03	1.82630
55.09	3.24525	10.03	1.82873
55.09	3.24636	10.03	1.82630
60.23	3.36426	4.80	1.08992
60.24	3.36854	4.80	1.08750
65.08	3.44932	4.80	1.09720
65.09	3.45179	2.02	0.36345
69.96	3.49293	2.02	0.36345
69.96	3.49490	2.02	0.36345
75.35	3.54314		
75.35	3.54923		
80.06	3.59954		
80.06	3.59858		
84.93	3.63138		
84.93	3.63328		
90.24	3.63792		
90.24	3.63072		