Supplementary Material (ESI) for Chemical Communications

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Supplementary Materials

Selective Gas Sorption Property of an Interdigitated 3-D Metal-Organic Framework with 1-D Channels

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Experimental Section

General Procedures. All other reagents were purchased from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed at the Elemental Analysis Laboratory of the Korean Institute of Basic Science. FT-IR spectra were recorded as KBr pellets on a Varian 1000 FT-IR spectrophotometer, using the reflectance technique (4000-400 cm^{-1}). PXRD data were recorded using a Rigaku D/M 2200T automated diffractometer. Simulated XRD patterns were calculated with the SHELXTL-XPOW program using single-crystal data. Thermogravimetric (TG) analyses were performed under N_2 using an STA-1000 system (Scinco Ltd., Korea). The adsorption isotherms were measured at 195 K for CO_2 and 77 K for N_2 and H_2 using an Autosorb-1 system from Quantachrome and ultra-pure gases (99.999%).

Preparation of 4-aminophenyl-1H-tetrazole (HL)

A mixture of 4-aminobenzonitrile (2.95 g, 25 mmol), NaN_3 (2.15 g, 33 mmol), and $Et_3N\cdot HCl$ (4.54 g, 33 mmol) in toluene (50 mL) was heated to between 95 and 100 °C for 24 h with stirring. After cooling to room temperature, the product was extracted with water (50 mL). To the aqueous layer, 36% HCl was added dropwise to salt out the product. Yield = 3.62 g, 90.0%. Elemental analysis: Calcd. for $C_7H_7N_5$: C, 52.17; H, 4.38; N, 43.45%. Found: C, 51.85; H, 4.27; N, 43.04%. IR (KBr, cm^{-1}): 3484, 3382, 2736, 1619, 1509, 1408, 1313, 1196, 1057, 838. ^{1}H-NMR (DMSO-d_6, δ ppm) 7.67 (d, 2H, Ar$\underline{H}$), 7.68 (d, 2H, Ar$\underline{H}$), 5.80 (s, 2H, NH_2); ^{13}C-NMR (DMSO-d_6, δ ppm) 155.6, 152.4, 129.2, 128.7, 114.5, 114.2, 110.8.

Preparation of $[Cd_3L_4(OH)_2(H_2O)_2]\cdot0.75DMF$ (1)

0.162 g (1.00 mmol) of ligand HL, 0.308 g (1.00 mmol) $Cd(NO_3)_2\cdot3H_2O$, 2 mL *N,N*-dimethylformamide (DMF) and 4 mL water were mixed and stirred for ca. 10 min, then sealed in a Pyrex tube and heated at 100 °C for 5 d. After cooling to room temperature, the block crystals were filtered and washed with both methanol and acetonitrile. Yield = 0.120 g, 42.1% (based on ligand). Elemental analysis. Calcd. for $[Cd_3L_4(OH)_2(H_2O)_2]\cdot0.75DMF$ ($C_{30.25}H_{35.25}N_{20.75}O_{4.75}Cd_3$, fw = 1102.73): C, 32.95; H, 3.22; N, 26.36%. Found: C, 32.87; H, 3.38; N, 25.97%. IR (KBr, cm^{-1}): 3414, 3342, 2927, 1680, 1618, 1449, 1385, 1270, 1163, 1088, 842.

Preparation of $[Cd_3L_4(OH)_2(H_2O)_2]$ (1a)

Method A: After heating a crystal of **1** at 200 °C for about 20 min, a crystal of **1a** was obtained. This crystal was used for single-crystal diffraction analysis.

Method B: After washing with methanol (1 × ~5 mL), and with acetonitrile (3 × ~5 mL), **1** was immersed in acetonitrile (~20 mL), soaked for 3 d, during which time acetonitrile was decanted and freshly replenished every day. The solvent was removed under vacuum at 100 °C overnight, yielding the microporous material **1a**. These crystals were used for the gas sorption study. IR spectra of the frameworks obtained using both methods are identical to each other. IR (KBr): 3446, 3342, 3142, 1619, 1450, 1362, 1272, 1176, 1015, 842 cm^{-1}.

Crystallographic Data Collection and Structural Refinements

The ligand crystal was mounted on a glass capillary and the diffraction data were collected at room temperature with a Siemens Smart CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) using the SMART and SAINT software packages.[1] Empirical absorption corrections were applied by use of the SADABS program. A crystal of MOF-**1**, freshly harvested from the mother liquor, was coated with paratone oil. The diffraction data were measured at 100 K with synchrotron radiation (λ =

0.7000 Å) on a 4AMXW ADSC Quantum-210 detector with a silicon double-crystal monochromator at the Pohang Accelerator Laboratory, Korea. The HKL2000 (*Ver*. 0.98.689)[2] was used for data collection, cell refinement, reduction, and absorption correction. Intensity data for host framework MOF-**1a** were measured with a Siemens Smart CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 173 K using the SMART and SAINT software packages.[1] Empirical absorption corrections were applied by use of the SADABS program.[2] All crystal structures were solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL–PLUS software package.[3]

Crystal Structure Determination for 4-aminophenyl-1H-tetrazole (HL)

$C_7H_7N_5$, fw = 161.18, monoclinic, space group $P2_1/n$, a = 8.214(3), b = 5.632(2), c = 15.202(5) Å, β = 90.539(5)°, V = 703.2(4) Å^3, T = 298(2) K, Z = 4, μ(Mo-$K\alpha$, λ = 0.71073 Å) = 0.104 mm^{-1}, 4149 reflections were collected, of which 1662 were unique [R_{int} = 0.0842]. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were found in subsequent difference Fourier maps and refined with assigned isotropic displacement coefficients U(H) = 1.2U(C, N) of their respective atoms. Two hydrogen sites found around the tetrazole residue, which are involved in the intermolecular hydrogen bonds, suggest that the tetrazole group is in static disorder so that the occupancy factors of both hydrogen sites were assigned the same value, 0.5. Refinement of the structure converged at a final $R1$ = 0.0838, $wR2$ = 0.1922 for 1449 reflections with $I > 2\sigma(I)$, $R1$ = 0.0961, $wR2$ = 0.1976, GOF = 1.295 for all 1662 reflections. The largest difference peak and hole were 0.321 and –0.283 e·Å^{-3}, respectively.

Crystal Data for $[Cd_3L_4(OH)_2(H_2O)_2]\cdot DMF\cdot H_2O$ (1)

$Cd_3C_{31}H_{39}N_{21}O_6$, fw = 1139.03, triclinic, space group P-1, a = 7.1063(6), b = 12.095(1), c = 12.766(1) Å, α = 90.833(2)°, β= 105.945(1)°, γ= 97.704(2)°, V= 1030.8(2) Å^3, T = 173(2) K, Z = 1, μ(synchrotron, λ = 0.70000 Å) = 1.603 mm^{-1}, 5460 reflections were collected, of which 3573 were unique [R_{int} = 0.0107]. The asymmetric unit of MOF-**1** consists of one-and-a-half cadmium ions, two ligand units, a μ_3-OH$^-$ group, a coordinating water molecule, a half-occupied noncoordinating DMF molecule, and a half-occupied noncoordinating water molecule. One Cd(II) ion is in a crystallographic inversion center and the other is in a general position. The solvent DMF molecule is disordered in a crystallographic inversion center. Electron density was found in a difference Fourier map around the disordered DMF site and assigned as a water molecule with a half occupancy. All nonhydrogen atoms except those of the noncoordinating structural solvent molecules were refined anisotropically. The protons attached to the N and O atoms were identified from the difference Fourier map and assigned with isotropic displacement coefficients U(H) = 1.5U of their respective atoms. The other hydrogen atoms except those of the noncoordinating solvent molecules were assigned isotropic displacement coefficients U(H) = 1.2U(C), and their coordinates were allowed to ride on their respective atoms. A noncoordinating DMF molecule was refined with geometry restraints during the least-squares refinement because of its poor refinement behavior. Refinement of the structure converged at a final $R1 = 0.0231$, $wR2 = 0.0592$ for 3394 reflections with $I > 2\sigma(I)$, $R1 = 0.0242$, $wR2 = 0.0599$, GOF = 1.073 for all 3573 reflections. The largest difference peak and hole were 0.788 and –0.802 e·Å^{-3}, respectively.

Crystal Data for [$Cd_3L_4(OH)_2(H_2O)_2$] (1a)

$Cd_3C_{28}H_{30}N_{20}O_4$, fw = 1047.92, triclinic, space group P-1, $a = 6.9889(8)$, $b = 12.076(1)$, $c = 12.814(1)$ Å, $\alpha = 87.184(2)°$, $\beta = 105.317(2)°$, $\gamma = 97.988(2)°$, $V = 1032.9(2)$ Å^3, $T = 173(2)$ K, Z = 1, μ(Mo-$K\alpha$, λ = 0.71073 Å) = 1.588 mm^{-1}, 5306 reflections were collected of which 3562 were unique [$R_{\text{int}} = 0.0133$]. All nonhydrogen atoms were refined anisotropically. The protons attached to the N and O atoms were identified from the difference Fourier map and assigned with isotropic displacement coefficients U(H) = 1.5U of their respective atoms. The other hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C), and their coordinates were allowed to ride on their respective atoms. Refinement of the structure converged at a final $R1 = 0.0251$, $wR2 = 0.0618$ for 3220 reflections with $I > 2\sigma(I)$, $R1 = 0.0293$, $wR2 = 0.0638$, GOF = 1.073 for all 3562 reflections. The largest difference peak and hole, 0.914 and –0.729 e·Å^{-3}, respectively, were observed in the vicinities of the metal centers.

A summary of the crystal and intensity data for the ligand, **1**, and **1a** is given in Table S1. Selected bond lengths and angles for t **1** and **1a** are listed in Table S2, and hydrogen bonds in Table S3. CCDC 656711–656713. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

References

1. SMART and SAINT, *Area Detector Software Package and SAX Area Detector Integration Program*; Bruker Analytical X-ray: Madison, WI, **1997**.

2. Z. Otwinowski, W. Minor in *Methods in Enzymology*, ed. C. W. Carter Jr. and R. M. Sweet, Academic Press, New York, 1997, vol. **276**, part A, pp. 307-326.

3. G. M. Sheldrick, SHELXTL–PLUS, *Crystal Structure Analysis Package*; Bruker Analytical X-ray, Madison, WI, 1997.

Table S1. Crystal data and structure refinement for the ligand, **1**, and **1a**.

Identification code	ligand	**1**	**1a**
Empirical formula	$C_7H_7N_5$	$Cd_3\ C_{31}\ H_{39}\ N_{21}\ O_6$	$Cd_3\ C_{28}\ H_{30}\ N_{20}\ O_4$
Formula weight	161.18	1139.03	1047.92
Temperature	273(2) K	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	P-1	P-1
Unit cell dimensions	a = 8.214(3) Å, α = 90°	a = 7.0163(6) Å, α = 90.833(2)°	a = 6.9889(8) Å, α = 87.184(2)°
	b = 5.632(2) Å, β = 90.539(5)°	b = 12.095(1) Å, β = 105.945(1)°	b = 12.076(1) Å, β = 105.317(2)°
	c = 15.202(5) Å, γ = 90°	c = 12.766(1) Å, γ = 97.704(2)°	c = 12.814(1) Å, γ = 97.988(2)°
Volume	703.2(4) $Å^3$	1030.8(2) $Å^3$	1032.9(2) $Å^3$
Z	4	1	1
Density (calculated)	1.522 Mg/m^3	1.835 Mg/m^3	1.685 Mg/m^3
Absorption coefficient	0.104 mm^{-1}	1.603 mm^{-1}	1.588 mm^{-1}
F(000)	336	564	514
Crystal size	0.15 x 0.15 x 0.05 mm^3	0.50 x 0.12 x 0.12 mm^3	0.33 x 0.23 x 0.12 mm^3
Theta range for data collection	2.68 to 28.11°.	1.66 to 25.00°.	1.65 to 25.00°.
Index ranges	-10<=h<=9, -5<=k<=7, -19<=l<=20	-8<=h<=8, -14<=k<=14, -12<=l<=15	-8<=h<=8, -14<=k<=10, -15<=l<=14
Reflections collected	4149	5460	5306
Independent reflections	1662 [R(int) = 0.0842]	3573 [R(int) = 0.0107]	3562 [R(int) = 0.0133]
Completeness to theta = 25.00°	96.8 %	98.2 %	97.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9948 and 0.9846	0.8309 and 0.5011	0.8323 and 0.6223
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1662 / 0 / 133	3573 / 10 / 291	3562 / 0 / 271
Goodness-of-fit on F^2	1.295	1.073	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0838, wR2 = 0.1922	R1 = 0.0231, wR2 = 0.0592	R1 = 0.0251, wR2 = 0.0618
R indices (all data)	R1 = 0.0961, wR2 = 0.1976	R1 = 0.0242, wR2 = 0.0599	R1 = 0.0293, wR2 = 0.0638
Largest diff. peak and hole	0.321 and -0.283 e.$Å^{-3}$	0.788 and -0.802 e.$Å^{-3}$	0.914 and -0.729 e.$Å^{-3}$

Table S2. Comparison of distances (Å) and angles (°) around the metal centers in **1** and **1a**.

1 (with solvents in channels)		**1a** (without solvents in channels)	
Cd(1)-O(1)	2.273(2)	Cd(1)-O(1)	2.267(2)
Cd(1)-N(7)	2.381(2)	Cd(1)-N(7)	2.367(3)
Cd(1)-N(2)	2.395(2)	Cd(1)-N(2)	2.405(3)
Cd(2)-O(1)	2.266(2)	Cd(2)-O(1)	2.259(2)
Cd(2)-O(1)#2	2.280(2)	Cd(2)-O(1)#2	2.280(2)
Cd(2)-N(8)#2	2.315(2)	Cd(2)-N(8)#2	2.304(3)
Cd(2)-N(3)	2.361(2)	Cd(2)-N(3)	2.361(2)
Cd(2)-O(2)	2.386(2)	Cd(2)-O(2)	2.394(2)
Cd(2)-N(5)#3	2.399(2)	Cd(2)-N(5)#3	2.399(3)
Cd(1)-Cd(2)	3.8960(5)	Cd(1)-Cd(2)	3.8804(5)
Cd(2)-Cd(2)#2	3.3700(4)	Cd(2)-Cd(2)#2	3.3766(5)
O(1)-Cd(1)-O(1)#1	180.0	O(1)#1-Cd(1)-O(1)	180.0
O(1)-Cd(1)-N(7)	86.69(7)	O(1)-Cd(1)-N(7)	87.05(8)
O(1)-Cd(1)-N(7)#1	93.31(7)	O(1)-Cd(1)-N(7)#1	92.95(8)
O(1)-Cd(1)-N(2)	86.90(7)	O(1)-Cd(1)-N(2)	86.52(8)
O(1)-Cd(1)-N(2)#1	93.10(7)	O(1)-Cd(1)-N(2)#1	93.48(8)
N(7)-Cd(1)-N(7)#1	180.0(1)	N(7)#1-Cd(1)-N(7)	180.0
N(7)-Cd(1)-N(2)	85.43(8)	N(7)-Cd(1)-N(2)	85.38(9)
N(7)-Cd(1)-N(2)#1	94.57(8)	N(7)-Cd(1)-N(2)#1	94.62(9)
N(2)-Cd(1)-N(2)#1	180.0(1)	N(2)-Cd(1)-N(2)#1	180.00(4)
O(1)-Cd(2)-O(1)#2	84.31(7)	O(1)-Cd(2)-O(1)#2	83.86(8)
O(1)-Cd(2)-N(8)#2	109.97(8)	O(1)-Cd(2)-N(8)#2	109.70(9)
O(1)#2-Cd(2)-N(8)#2	86.80(8)	O(1)#2-Cd(2)-N(8)#2	86.81(8)
O(1)-Cd(2)-N(3)	85.60(7)	O(1)-Cd(2)-N(3)	85.76(8)
O(1)#2-Cd(2)-N(3)	104.77(8)	O(1)#2-Cd(2)-N(3)	104.02(8)
N(8)#2-Cd(2)-N(3)	161.72(8)	N(8)#2-Cd(2)-N(3)	162.23(9)
O(1)-Cd(2)-O(2)	161.71(8)	O(1)-Cd(2)-O(2)	161.21(8)
O(1)#2-Cd(2)-O(2)	92.20(7)	O(1)#2-Cd(2)-O(2)	91.87(8)
N(8)#2-Cd(2)-O(2)	87.68(8)	N(8)#2-Cd(2)-O(2)	88.25(9)

N(3)-Cd(2)-O(2)	77.92(8)	N(3)-Cd(2)-O(2)	77.51(9)
O(1)-Cd(2)-N(5)#3	97.68(8)	O(1)-Cd(2)-N(5)#3	98.25(9)
O(1)#2-Cd(2)-N(5)#3	167.04(8)	O(1)#2-Cd(2)-N(5)#3	167.50(8)
N(8)#2-Cd(2)-N(5)#3	80.48(9)	N(8)#2-Cd(2)-N(5)#3	80.87(9)
N(3)-Cd(2)-N(5)#3	88.16(8)	N(3)-Cd(2)-N(5)#3	88.45(9)
O(2)-Cd(2)-N(5)#3	89.74(8)	O(2)-Cd(2)-N(5)#3	89.88(9)
Cd(2)-O(1)-Cd(1)	117.89(8)	Cd(2)-O(1)-Cd(1)	118.10(9)
Cd(2)-O(1)-Cd(2)#2	95.69(7)	Cd(2)-O(1)-Cd(2)#2	96.14(8)
Cd(1)-O(1)-Cd(2)#2	117.69(8)	Cd(1)-O(1)-Cd(2)#2	117.14(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y,-z #3 -x,-y-1,-z

Table S3. Comparison of hydrogen bonds (Å and °) for **1** and **1a**.

1

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...N(10)#1	0.76(4)	2.26(4)	2.973(3)	158(4)
O(2)-H(21O)...N(1)#2	0.82(4)	2.01(4)	2.822(3)	169(4)
O(2)-H(22O)...N(4)	0.76(4)	2.20(4)	2.870(3)	148(4)
N(5)-H(51N)...N(9)#3	0.83(4)	2.21(4)	2.945(3)	148(3)
N(5)-H(52N)...N(6)#4	0.88(4)	2.10(4)	2.970(4)	173(3)
N(10)-H(101)...N(1)#6	0.91(4)	2.47(4)	3.230(3)	141(3)
N(10)-H(102)...N(4)#5	0.85(4)	2.48(4)	3.322(4)	170(4)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z+1 #2 x+1,y,z #3 x-1,y-1,z

#4 x,y-1,z #5 -x-1,-y,-z-1 #6 -x,-y,-z-1

1a

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...N(10)#1	0.77(4)	2.23(4)	2.953(4)	157(4)
O(2)-H(21O)...N(1)#2	0.83(4)	2.00(4)	2.825(4)	172(4)
O(2)-H(22O)...N(4)	0.81(4)	2.19(4)	2.870(3)	141(4)
N(5)-H(51N)...N(9)#3	0.84(4)	2.31(4)	2.957(4)	134(3)
N(5)-H(52N)...N(6)#4	0.87(4)	2.12(4)	2.988(4)	175(3)
N(10)-H(101)...N(1)#5	0.82(4)	2.47(4)	3.200(4)	149(4)
N(10)-H(102)...N(4)#6	0.92(4)	2.40(4)	3.306(4)	171(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 x-1,y,z #3 x+1,y+1,z

#4 x,y+1,z #5 -x+2,-y,-z+1 #6 -x+1,-y,-z+1

Table S4. π–π interactions in **1**.

tetrazole moiety	phenyl moiety	interatomic distances (Å)
C(8)	C(13)#1	3.7398(3)
C(8)	C(14)#1	3.6348(3)
N(9)	C(13)#1	3.5799(4)
N(9)	C(14)#1	3.7630(3)

Symmetry transformation used to generate equivalent atoms:

#1 –x+1, -y, -z+1

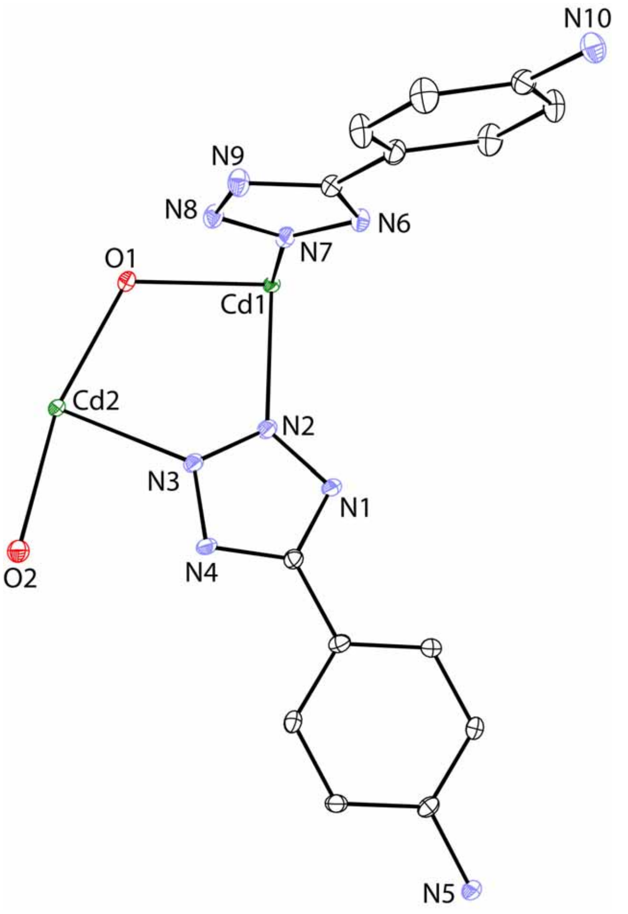

Figure S1. An ORTEP drawing of the asymmetric unit of **1**, where the atoms are represented by 30% probability thermal ellipsoids. Solvent molecules and the hydrogen atoms are omitted for clarity.

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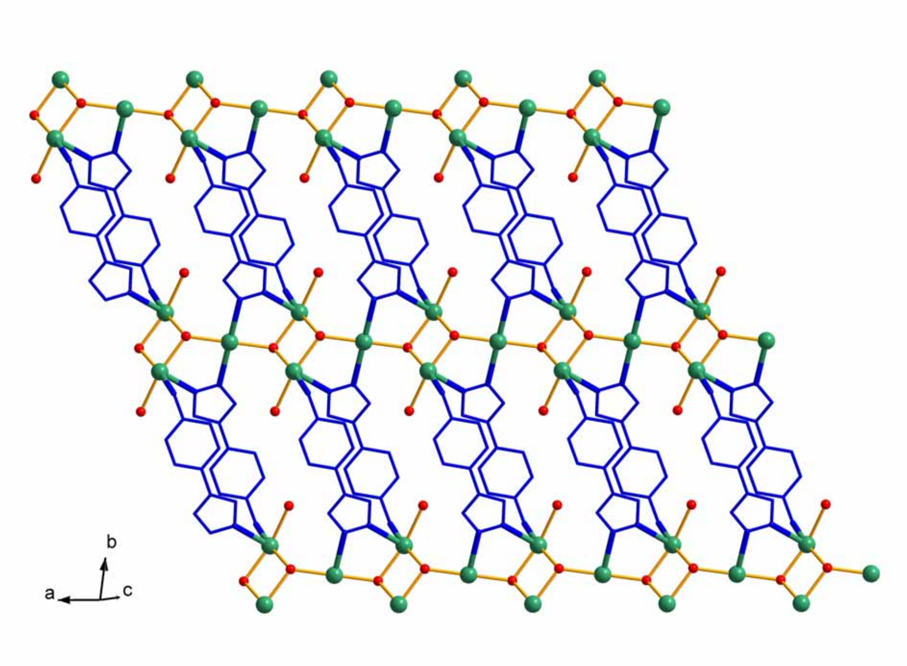


Figure S2. An illustration of a 2-D sheet structure constructed by 1-D chains, $\{[Cd_3(OH)_2]^{4+}\}_n$, and tridentate ligand (blue).

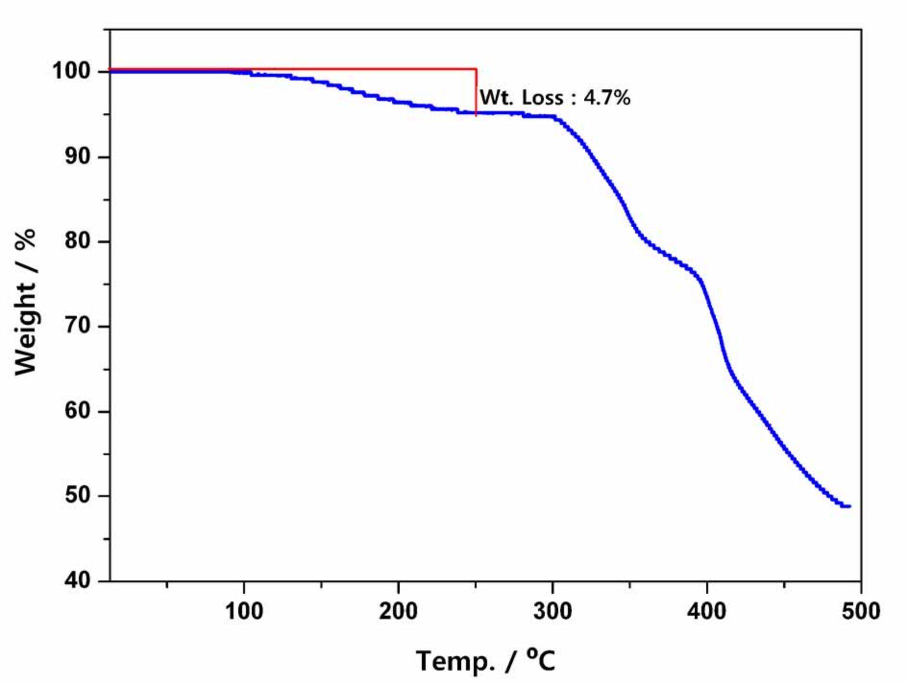
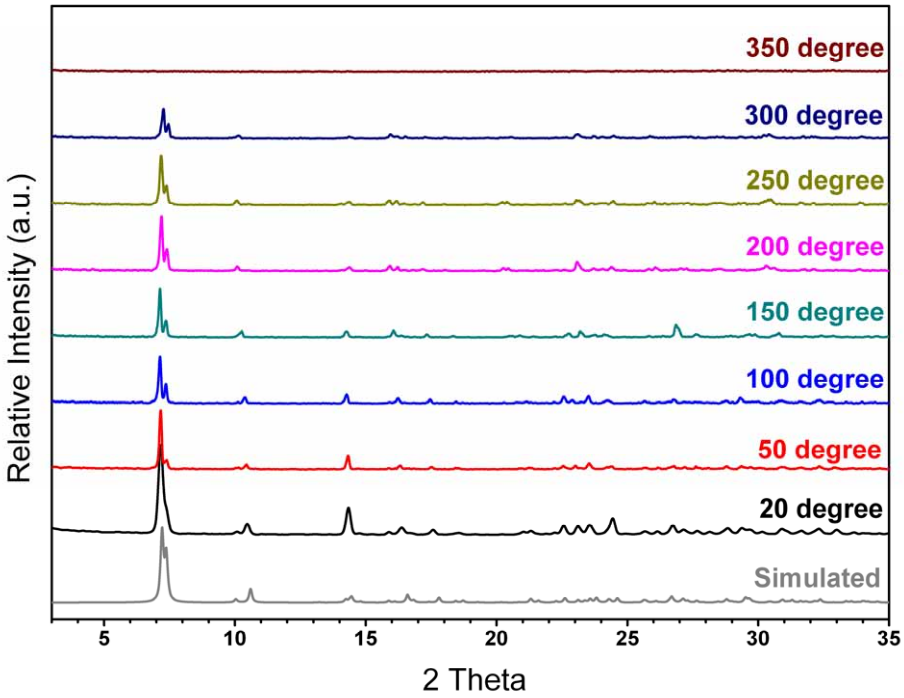


Figure S3. A TGA curve for **1**.



120 Figure S4. Temperature dependent PXRD patterns for **1**.

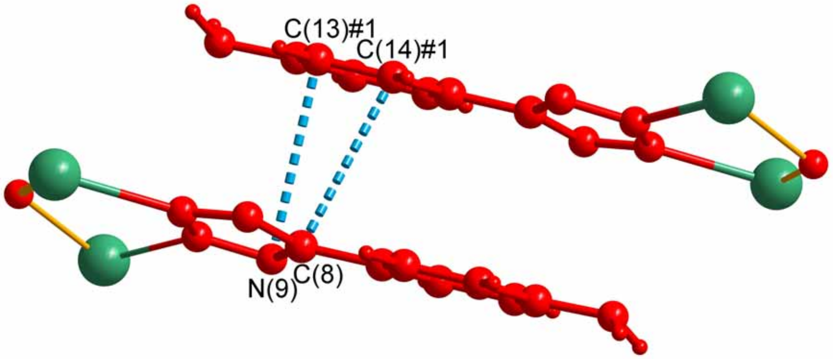


Figure S5. A π–π interaction between the tetrazole and the phenyl group. The closest contacts are represented using the 125 dotted lines in cyan. Symmetry transformation (#1; –x+1, -y, -z+1) was used to generate equivalent atoms.

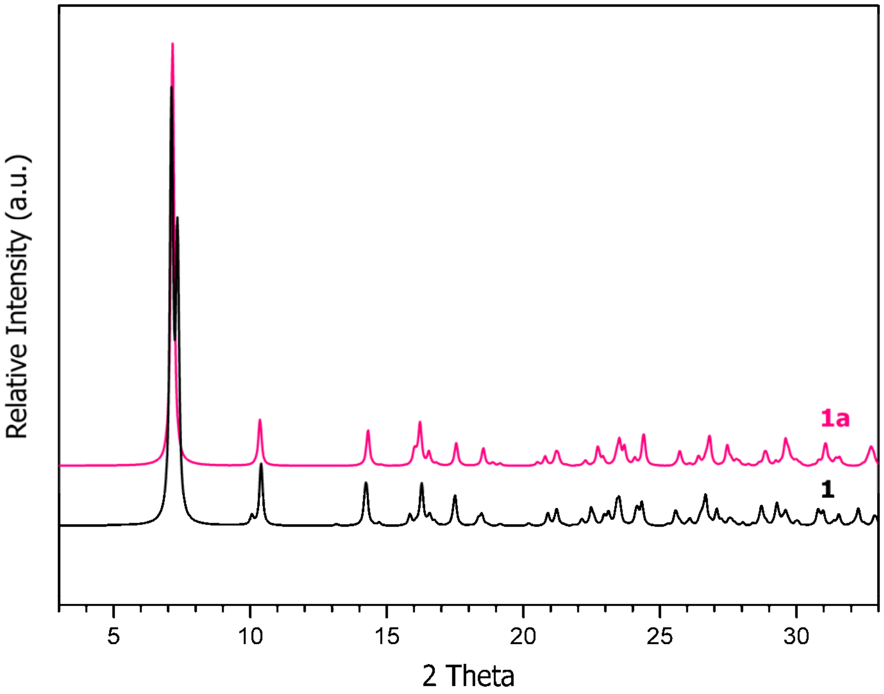


Figure S6. Simulated PXRD patterns for framework **1** and **1a**.

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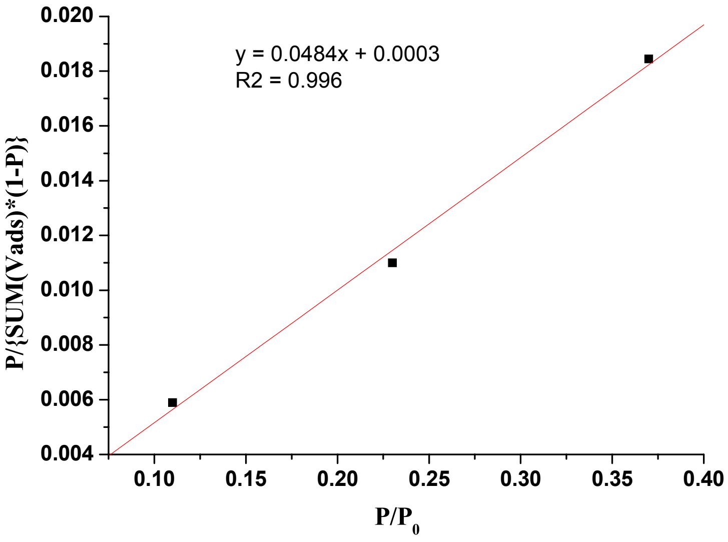
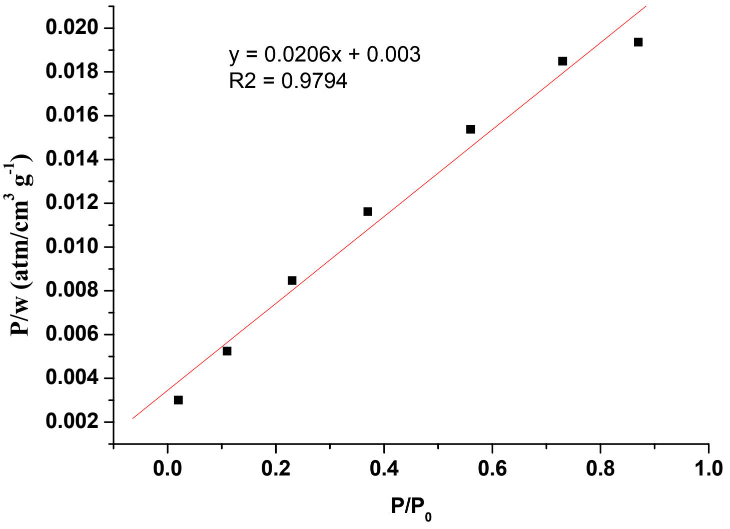


Figure S7. A part of H_2 gas sorption data of **1a** fitted to the BET equation. S_{BET} = 90 m^2/g.



135 Figure S8. H_2 gas sorption data of **1a** fitted to the Langmuir equation. $S_{Langm} = 208\ m^2/g$.

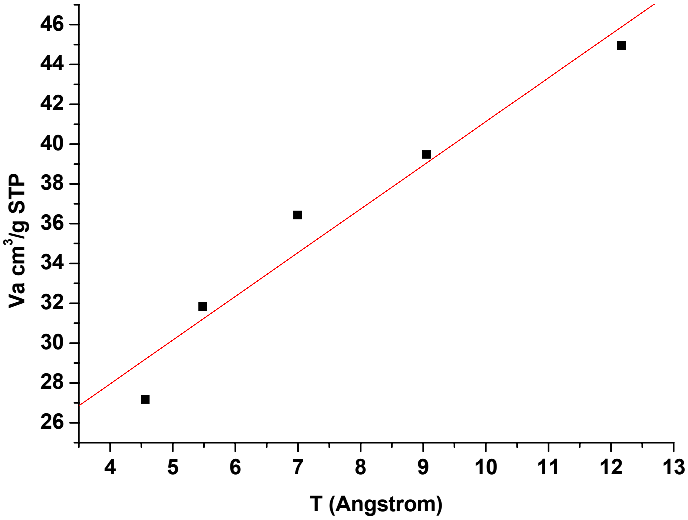


Figure S9. T-plot from hydrogen adsorption isotherm.

$$T = \sqrt{13.99/(0.0340 - \log(\mathrm{P/Po}))}$$

$y = A+Bx$

by fitting we got:

$A = 19.2$ mL/g at STP, $B = 2.2$

$V_{micro} = A \times 2.02 / (22.4 \times 10^3 \times 0.071) = 0.024$ mL/g

$S_{EXT} = 15.47 \times B = 15.47 \times 2.2 = 34.0$ m^2/g

$S_{micro} = S_{Langm} - S_{EXT} = 208 - 34 = 174$ m^2/g

$W_{micro} = \frac{4Vmicro}{Smicro} = 4 \times 0.024 / 174 = 5.5$ Å

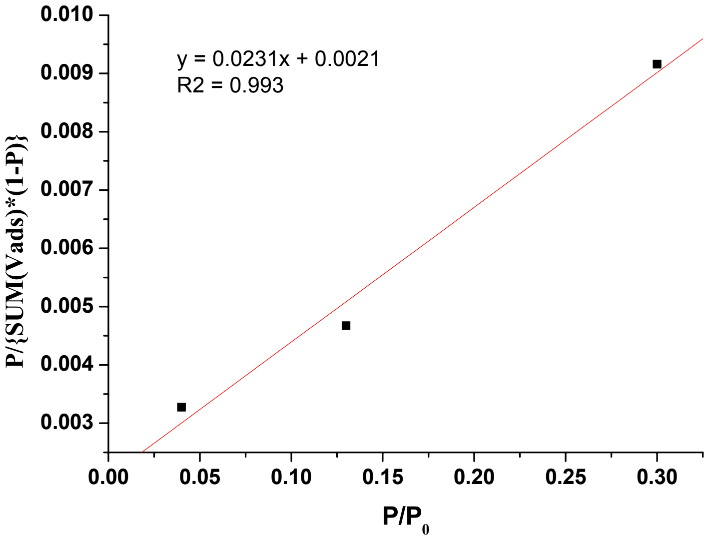
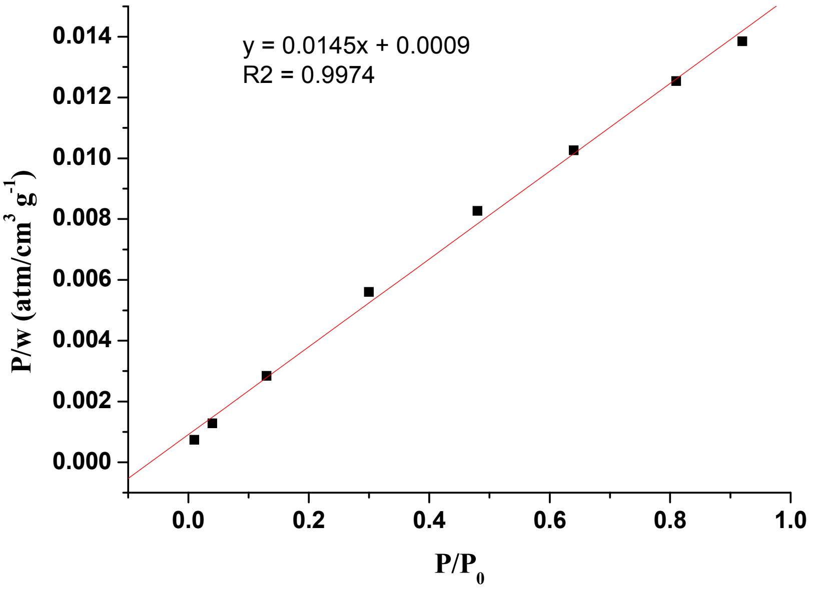


Figure S10. A part of CO_2 gas sorption data of **1a** fitted to the BET equation. $S_{BET} = 210\ m^2/g$.



155 Figure S11. CO_2 gas sorption data of **1a** fitted to the Langmuir equation. $S_{Langm} = 300\ m^2/g$.

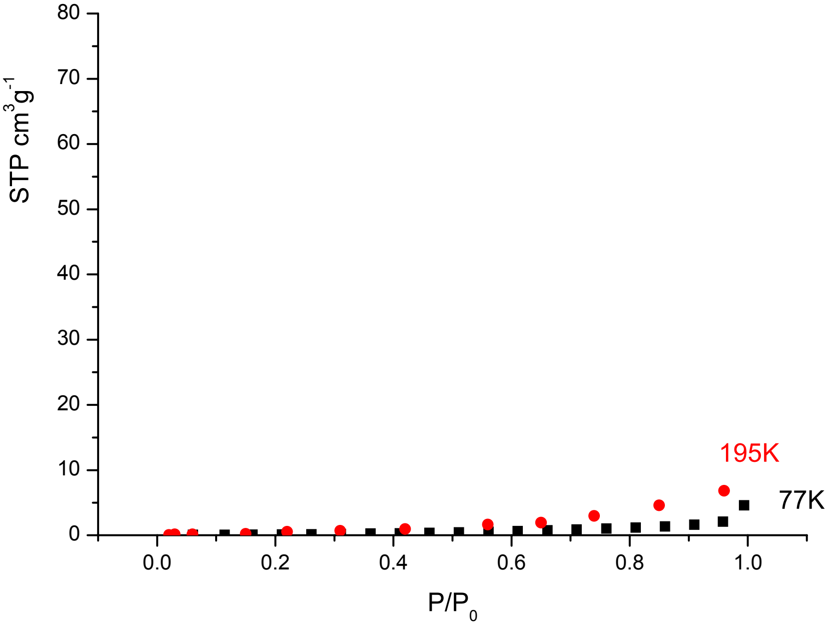


Figure S12. Gas adsorption isotherms of N_2 at 77K (■) and 195K (●).

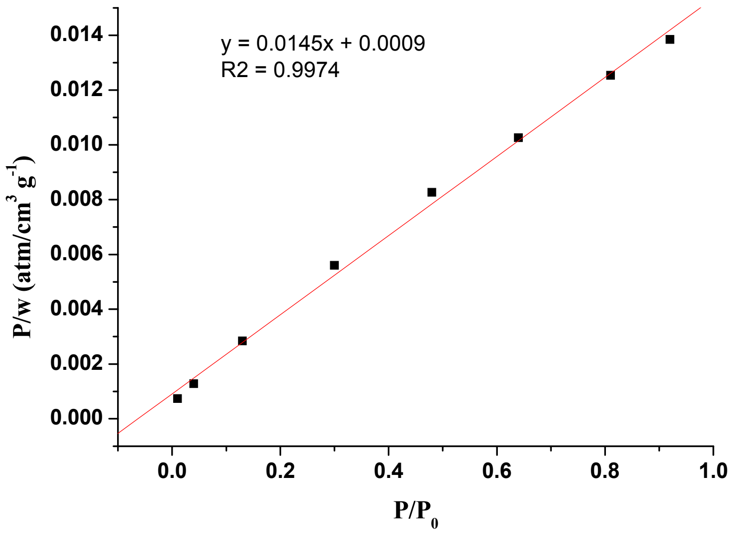


Figure S11. CO_2 gas sorption data of **1a** fitted to the Langmuir equation. S_{Langm} = 300 m^2/g.