Electronic Supplementary Information for

Significant enhancement of water vapour uptake at lower pressure by amine-functionalization of UiO-67

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Table of Contents

Section S1 General Procedures

4-Iodobenzoic acid was purchased from Tokyo Chemical Industry (TCI) CO., Ltd. Copper powder and zirconium chloride ($ZrCl_4$) were purchased from Sigma-Aldrich. Iron powder was purchased from Alfa Aesar. Nitric acid fuming (nitric acid 93 %) was purchased from Matsunoen Chemicals Ltd. Sulfuric acid fuming (free SO_3 20-23 %) was purchased from Uni-Chem. *N*,*N*-dimethylformamide (DMF), methanol (MeOH), sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), magnesium sulfate ($MgSO_4$), ethyl acetate (EA), acetic acid (AcOH), sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), tetrahydrofuran (THF), lithium hydroxide monohydrate ($LiOH \cdot H_2O$) and acetone were purchased from Daejung Chemicals & Metals Co., Ltd. All starting materials were used without further purification.

Elemental analyses were carried out on an EA 1110 CHN analyzer (CE instrument) at Seoul National University - National Center for Inter-University Research Facilities (NCIRF). IR spectra were recorded on a JASCO FT/IR-4100 spectrophotometer with samples prepared as KBr pellets. ^{1}H-NMR spectra of digested MOF crystals in HF/DMSO and $NaOD/D_2O$ were obtained on a Bruker 400 MHz NMR spectrometer. Powder X-ray diffraction data were collected on a Bruker D8-Advance diffractometer at Seoul National University - NCIRF. A radiation from Cu Kα X-ray source (operated at 40 kV and 40 mA) was filtered using Ge 111 monochromator to give Cu Kα1 radiation (λ = 1.5406Å) for data collection. The samples were loaded on silicon sample holder and the diffraction was recorded in the 2θ range of 3-60°. Thermogravimetric analyses (TGA) were carried out using a Scinco TGA-S1000 thermal analysis system with a heating rate of 5 ºC/min in air.

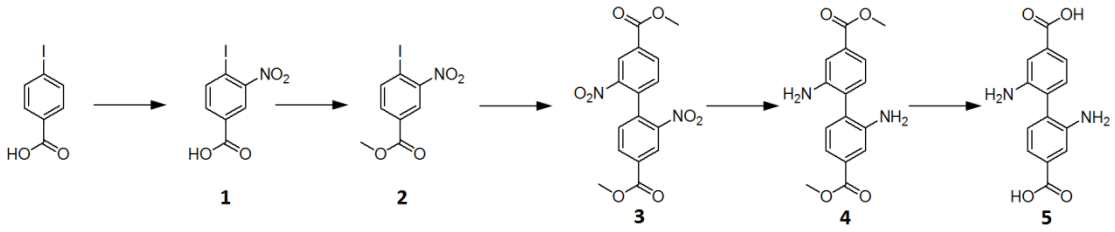
N_2, CO_2 and CH_4 adsorption isotherms at pressures up to 1 bar were measured by standard volumetric procedures on a BELSORP-mini (BEL-Japan, INC.) instrument. Before measuring, each sample was dried and fully degassed at 150 ºC for 6 h under vacuum ($< 1.0 \times 10^{-3}$torr). The dead volume of the sample cell was automatically measured using helium gas. Pressure equilibrium points were also collected automatically by the equipment. Each sample's weight was measured without exposing it to air. Using nitrogen isotherm points below $P/P_0 = 0.20$, BET surface areas were determined by the equation provided by the manufacturer. For CO_2 adsorption measurements, sample cells were maintained at 253 K in an ice/acetone bath, at 273

K in an ice/water bath, or at 298 K in a water bath. The isosteric heats of adsorption were calculated using a virial equation; zero-coverage values were regarded as each MOF's heat of adsorption.

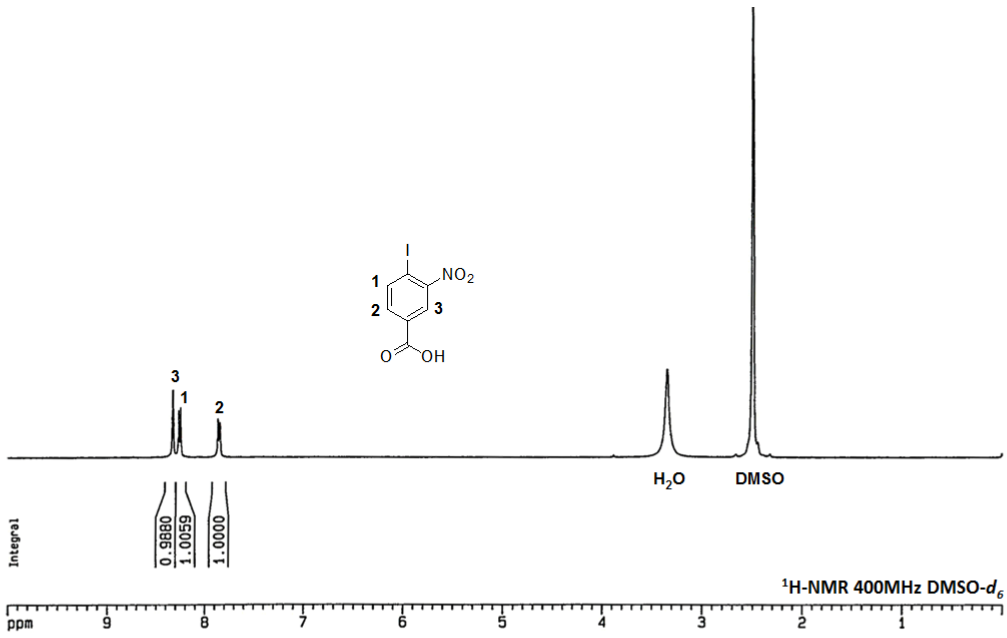
Water vapour adsorption isotherms were measured at 298 K using the standard volumetric procedure on a BELSORP-max (BEL-Japan, INC.) instrument. The samples were filtered and then dried under low vacuum (~10^{-3}Torr) on the Schlenk line before they were loaded into the sample tube of the gas adsorption analyser. The dried samples (ca. 100 mg) were further evacuated at 200 °C (< 1.0×10^{-3} Torr) for 6 h prior to measurement. The dead volume of the sample cell was automatically measured using helium gas. The instrument also collected pressure equilibrium points automatically. After each measurement, the weight of the samples was measured by a microbalance. Adsorption/desorption cycle took about 70 h (P_0 = 3.169 kPa).

Section S2 Syntheses of Materials

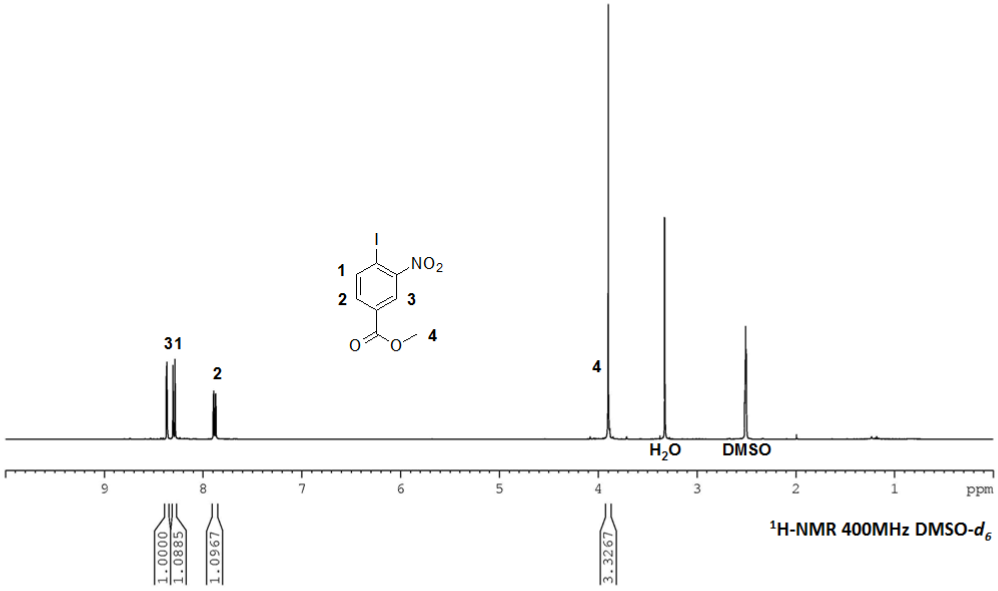
Syntheses of 2,2'-Diaminobiphenyl-4,4'-dicarboxylic acid



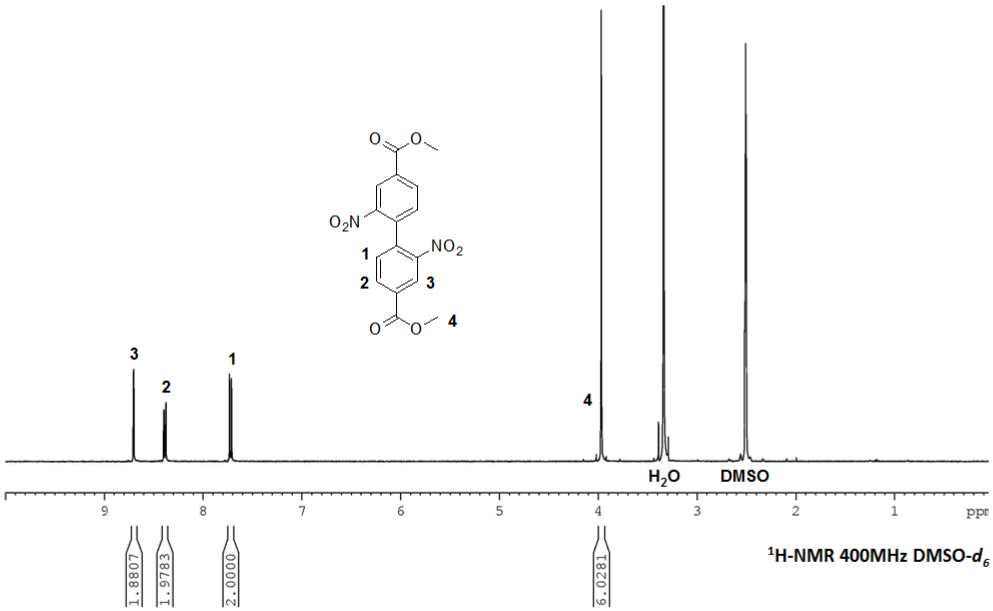
4-Iodo-3-nitrobenzoic acid (1, nitration). A mixture of 4-iodobenzoic acid (25 g, 100 mmol), fuming H_2SO_4 (100 mL), and fuming HNO_3 (75 mL) was stirred for 24 h at 90 °C. The solution was cooled to room temperature and poured into crushed ice (~ 1500 mL). The precipitate was collected, washed with water, and then dried under vacuum to give a yellow solid (27 g, 91.4 %): ^{1}H-NMR (DMSO-d_6, 400 MHz) δ 13.73 (s, 1H), 8.33 (s, 1H), 8.25 (d, 1H, J = 8.0 Hz), 7.54 (d, 1H, J = 8.0Hz); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 165.7, 153.8, 142.5, 133.9, 132.6, 125.6, 94.6; FT-IR (KBr, 4000-400 cm^{-1}) 3422 (br), 3091 (m), 2851 (br), 2656 (w), 2579 (w), 1701 (vs), 1598 (s), 1557 (m), 1535 (vs), 1473 (w), 1422 (m), 1350 (m), 1313 (m), 1253 (m), 1162 (w), 1125 (w), 1023 (m), 907 (w), 845 (w), 807 (w), 769 (w), 742 (w), 713 (w), 656 (w), 601 (w), 538 (w).



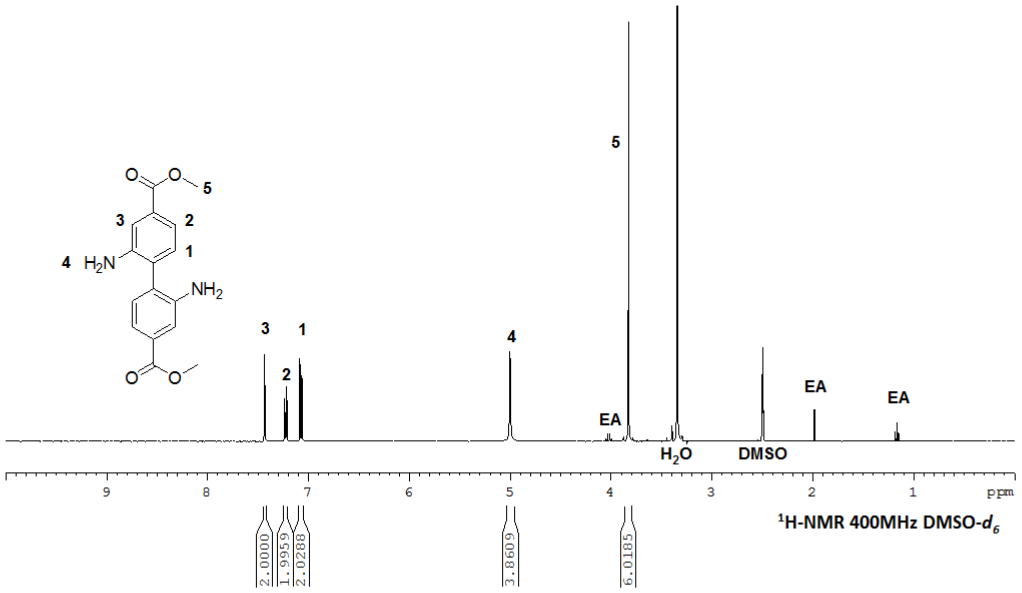
Methyl-4-iodo-3-nitrobenzoate (2, esterification). A mixture of **1** (27 g, 92 mmol) and a catalytic amount of H_2SO_4 (30 mL) in methanol (400 mL) was refluxed for 12 h. After the mixture was quenched with 3M aqueous NaOH solution (200 mL), the precipitated light yellow crystals were collected and washed with water. The product was dried under vacuum to give a light yellow solid (26 g, 91.6 %): ^{1}H-NMR (DMSO-d_6, 400 MHz) δ 8.36 (s, 1H), 8.28 (d, 1H, J = 8.0 Hz), 7.87 (d, 1H, J = 8.0Hz), 3.90 (s, 3H);^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.8, 153.9, 142.6, 133.7, 131.2, 125.5, 95.3, 53.3; FT-IR (KBr, 4000-400 cm^{-1}) 3420 (br), 3088 (w), 2955 (w), 1717 (vs), 1596 (m), 1561 (w), 1533 (s), 1439 (m), 1355 (m), 1286 (s), 1247 (s), 1198 (w), 1152 (w), 1124 (m), 1106 (w), 1022 (m), 975 (w), 911 (w), 884 (w), 842 (w), 821 (m), 766 (m), 741 (m), 724 (m), 687 (w), 655 (w), 593 (w), 549 (w), 497 (w), 464 (w).



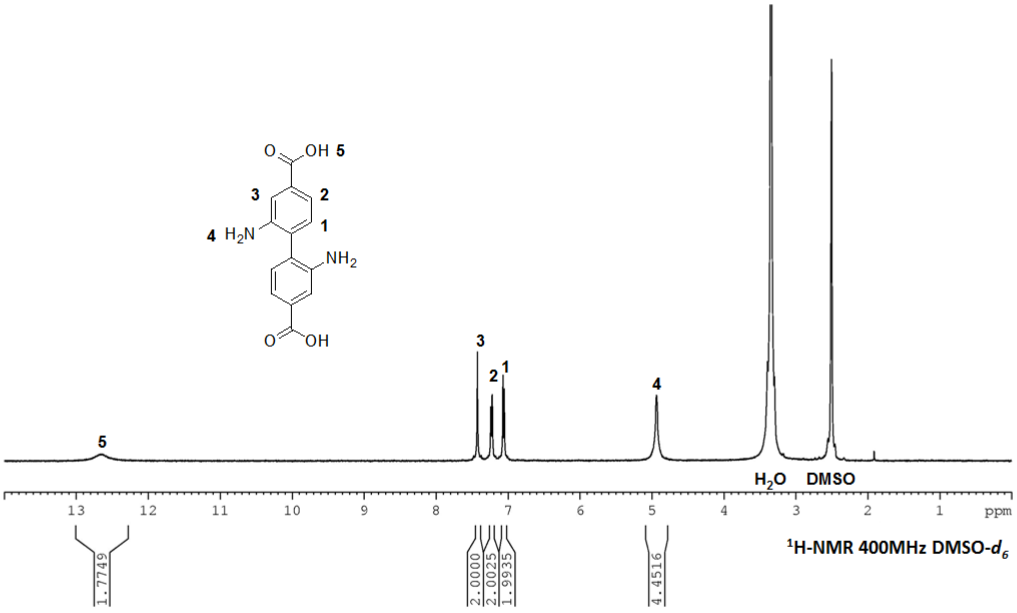
Dimethyl-2,2'-dinitrobiphenyl-4,4'-dicarboxylate (3, Ullmann coupling). A mixture of **2** (26 g, 85 mmol) and freshly activated copper powder (21.5 g, 4 eq) in DMF (250 mL) was refluxed for 20 h under argon atmosphere. The mixture was cooled down to room temperature, filtered over celite, and washed with fresh DMF (30 mL × 2) to remove the residue. DMF solution was quenched with 5% $Na_2S_2O_3 \cdot 5H_2O$ aqueous solution and water (1000mL), and this mixture was extracted with ethyl acetate (100 mL × 9). Then, the organic phase was washed with brine (200 mL x 3), dried over $MgSO_4$, filtered and evaporated. The product was dried under vacuum to give a ivory powder (14.3 g, 93.5 %): ^{1}H-NMR (DMSO-d_6, 400 MHz) δ 8.70 (s, 2H), 8.38 (d, 2H, J = 8.0 Hz), 7.71 (d, 2H, J = 8.0Hz), 3.96 (s, 6H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 164.7, 147.1, 137.4, 134.6, 132.5, 131.6, 125.5, 53.5; FT-IR (KBr, 4000-400 cm^{-1}) 3432(w), 3092(w), 2956(w), 2852(w), 1726(vs), 1618(m), 1561(w), 1528(vs), 1483(m), 1438(m), 1345(s), 1310(s), 1287(s), 1256(s), 1197(w), 1158(w), 1118, 1007(w), 967(w), 935(w), 917(w), 906(w), 862(w), 823(w), 769(m), 756(m), 725(w), 696(w), 676(w), 604(w), 560(w), 484(w), 415(w).



Dimethyl-2,2'-diaminobiphenyl-4,4'-dicarboxylate (4, reduction). A solution of 3 (10.0 g, 28 mmol) in acetic acid (300 mL) was added to Fe powder (47.5 g, 850 mmol). The mixture was stirred for 20 h at room temperature under argon atmosphere. The solution was filtered over celite and evaporated. The residue was dissolved in ethyl acetate and H_2O. The organic layer was washed by conc. $NaHCO_3$ (aq) and brine, dried over $MgSO_4$, and filtered. The solvent was removed by rotary evaporation, yielding yellow powder (7.4 g, 89 %): ^{1}H-NMR (DMSO-d_6, 400 MHz) δ 7.45 (s, 2H), 7.23 (d, 2H, J = 8.0 Hz), 7.08 (d, 2H, J = 8.0Hz), 5.00 (s, 4H), 3.84 (s, 6H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 167.0, 146.1, 131.3, 130.1, 128.1, 117.7, 116.3, 52.4; FT-IR (KBr, 4000-400 cm^{-1}) 3451(m), 3359(m), 3233(w), 2951(w), 1701(vs), 1617(m), 1566(m), 1515(w), 1493(w), 1438(m), 1419(m), 1309(s), 1241(vs), 1117(m), 1000(m), 894(w), 766(m), 484(w), 427(w), 414(w).



2,2'-Diaminobiphenyl-4,4'-dicarboxylic acid (5, hydrolysis). A mixture of **4** (7.2 g, 24 mmol), 0.6 M $LiOH \cdot H_2O$ (aq) (300 mL), THF (300 mL), and MeOH (150 mL) was stirred for 20 h at room temperature. The reaction mixture was concentrated. The residue was acidified with conc. AcOH. The precipitate was filtered, washed with H_2O, and dried under vacuum to give an yellow solid (6.2 g, 95 %): ^{1}H-NMR (DMSO-d_6, 400 MHz) δ 12.68(br, 2H), 7.42 (s, 2H), 7.23 (d, 2H, J = 8.0 Hz), 7.06 (d, 2H, J = 8.0Hz), 4.94 (s, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 168.1, 145.9, 131.2, 131.1, 127.9, 118.0, 116.6; FT-IR (KBr, 4000-400 cm^{-1}) 3434(w), 3398(w), 3298(w), 3197(w), 2955(m), 2924(m), 2855(m), 2642(w), 2542(w), 1686(vs), 1619(m), 1559(m), 1438(s), 1299(s), 1247(m), 1160(w), 1121(w), 1002(w), 928(w), 887(w), 833(w), 761(m), 662(w), 594(w), 565(w), 470(w), 413(w).



Syntheses of MOFs

UiO-67. A solid mixture of H_2BPDC (85 mg, 0.35 mmol), benzoic acid (1.28 g, 10.5 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol) was dissolved in DMF (20 mL) in a 20 mL vial. The vial was capped and heated in an isothermal oven at 120 °C for 48 h to give octahedral-shaped crystals. The reaction mixture was allowed to cool naturally to room temperature. The obtained crystals were washed with DMF (20 mL x 5) and soaked in fresh DMF over the course of 24 h. Finally, the crystals were washed with acetone (20 mL x 5). Yield: 71 mg, 57% based on 1 mol of H_2BPDC. Elemental analysis calculated (%) for the evacuated crystals, $[Zr_6O_4(OH)_4(BPDC)_{5.1}(benzoate)_{1.2}(formate)_{0.6}] \equiv C_{80.4}H_{51.4}O_{32}Zr_6$, Calcd.: C, 46.50; H, 2.49; N, 0.00. Found (%): C, 46.47; H, 2.27; N, 0.00. FT-IR (KBr, 4,000-400 cm^{-1}): 3428 (br, s), 1601 (vs), 1538 (s), 1406 (s), 1386 (vs), 1263 (w), 1108 (w), 851 (w), 798 (m), 769 (m), 656 (m).

UiO-67-$(NH_2)_2$**.** A solid mixture of H_2BPDC-$(NH_2)_2$ (95 mg, 0.35 mmol), benzoic acid (1.71 g, 14.0 mmol), and $ZrCl_4$ (82 mg, 0.35 mmol) was dissolved in a mixture of DMF (20 mL) in a 20 mL vial. The vial was capped and heated in an isothermal oven at 120 °C for 48 h to give a yellow crystalline powder. The reaction mixture was allowed to cool naturally to room temperature and the crystals were washed with DMF (20 mL x 5) and soaked in fresh DMF over the course of 24 h. Finally, the crystalline powder was washed with acetone (20 mL x 5). Yield: 25 mg, 35.5 % based on 1 mol of H_2BPDC-$(NH_2)_2$. Elemental microanalysis for the framework of UiO-67-$(NH_2)_2$, $[Zr_6O_4(OH)_4(BPDC\text{-}(NH_2)_2)_{4.1}(benzoate)_{0.6}(formate)_{3.2}]\bullet 7H_2O \equiv C_{64.8}H_{65.2}N_{8.2}O_{39}Zr_6$, Calcd. (%): C, 36.54; H, 3.09; N, 5.39. Found (%): C, 36.64; H, 3.40; N, 5.22. FT-IR (KBr, 4,000-400 cm^{-1}): 3361 (br, s), 3227 (br, s), 1670 (m), 1597 (s), 1545 (s), 1408 (s), 1283 (m), 1141 (w), 1003 (w), 905 (w), 776 (m), 652 (m).

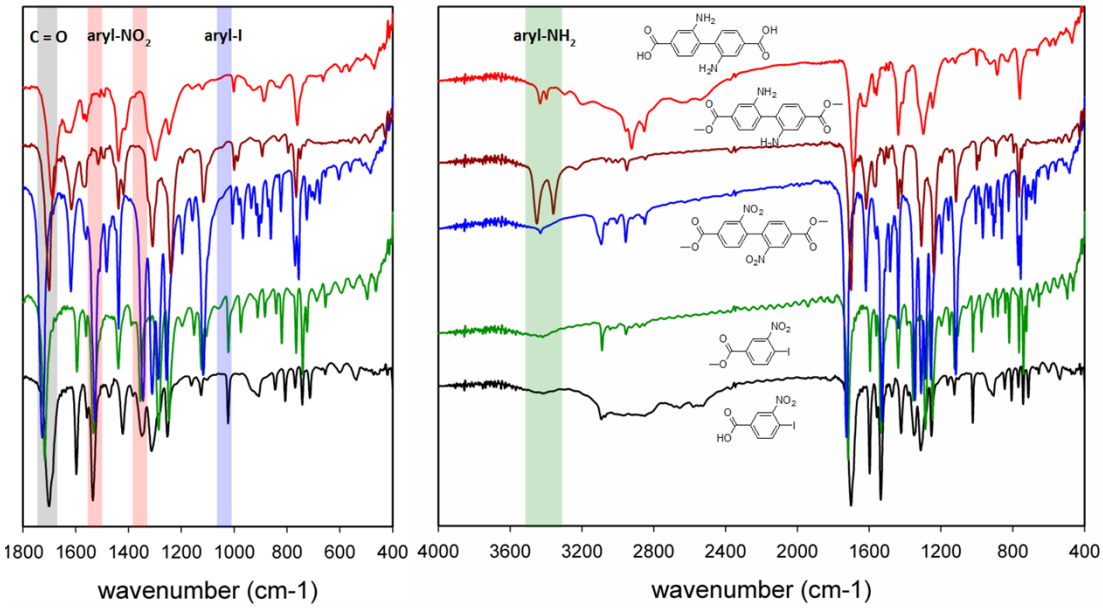


Fig. S1 Comparison of the IR spectra of synthesized organic molecules: **1** (black), **2** (green), **3** (blue), **4** (brown), and **5** (red). Absorption frequencies of characteristic groups (cm^{-1}): aryl-I (1100- 1000), aryl-NO_2 (1400-1300, near 1550), carbonyl (1730-1715), aryl-NH_2 (3500-3250).

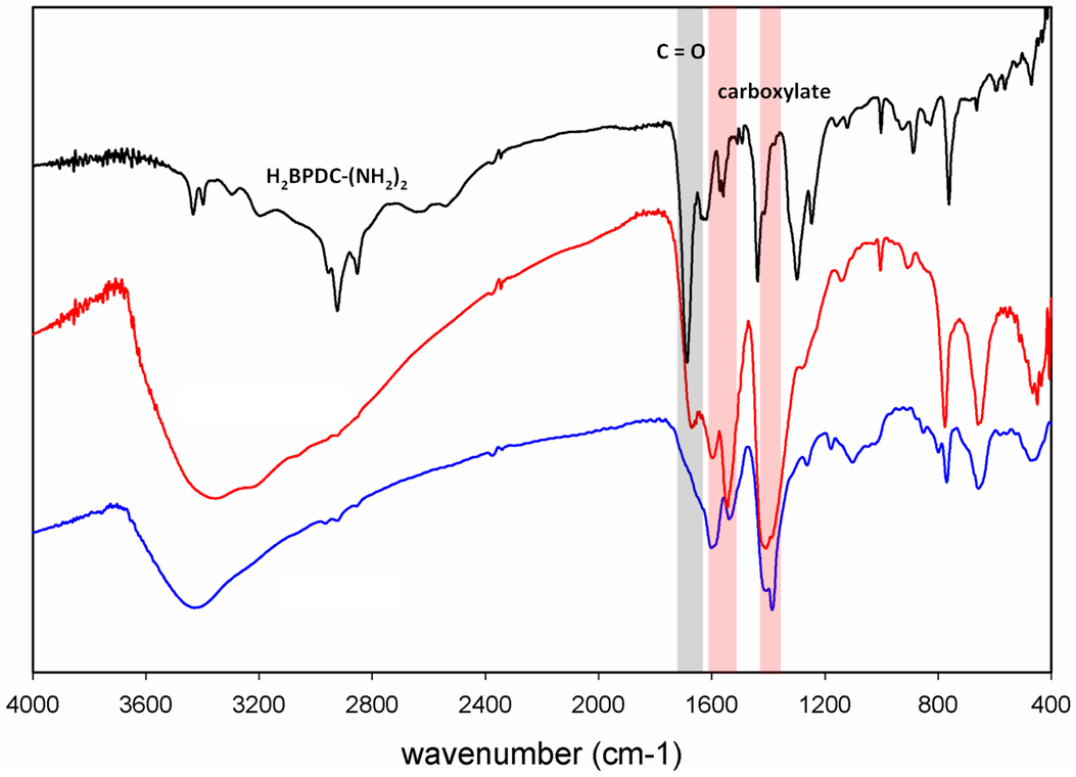


Fig. S2 Comparison of the IR spectra of activated UiO-67 (blue), UiO-67-$(NH_2)_2$ (red), and H_2BPDC-$(NH_2)_2$ (black). Absorption frequencies of characteristic groups (cm^{-1}): carbonyl (1730-1715), carboxylate (1650-1550, near 1400).

Section S3 Powder X-ray Diffraction Patterns

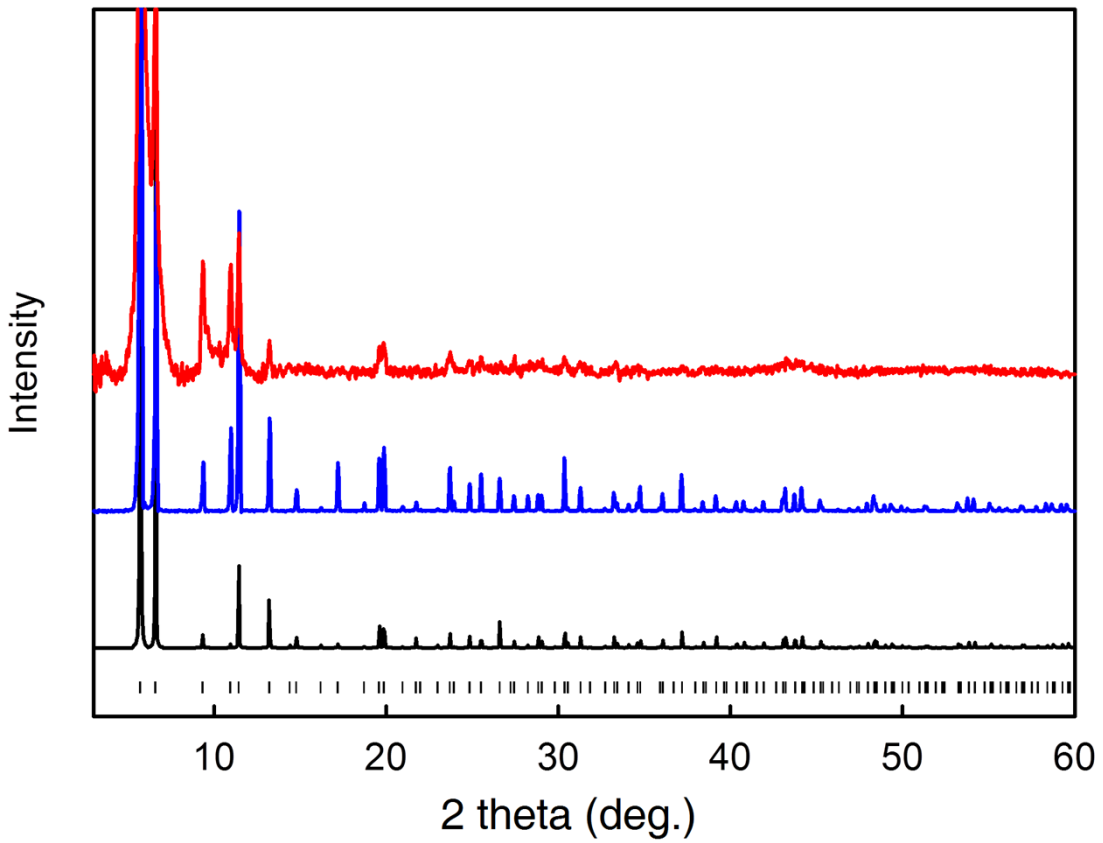


Fig. S3 PXRD patterns: simulated (black) and measured for UiO-67 (blue); measured for UiO-67-$(NH_2)_2$ (red).

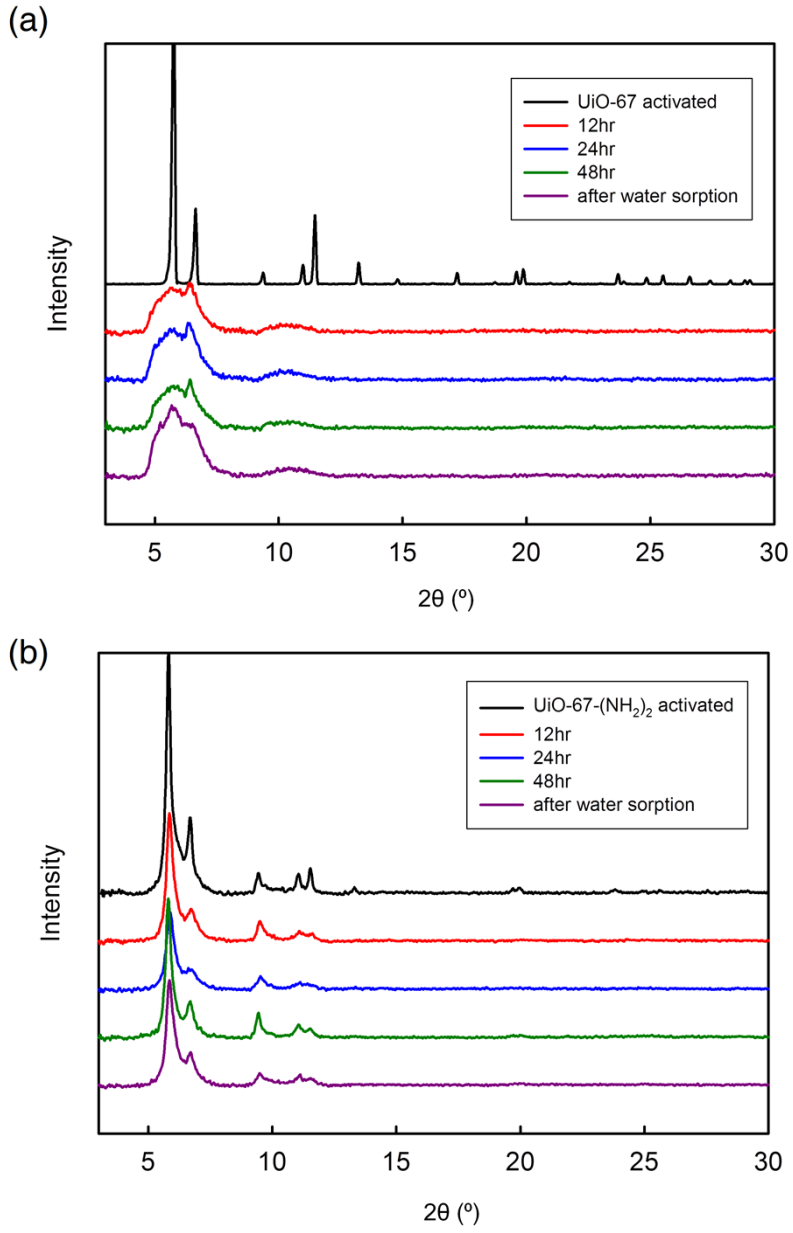


Fig. S4 Comparison of the PXRD patterns before and after water vapor adsorption/desorption of (a) UiO-67 and (b) UiO-67-$(NH_2)_2$ samples. The samples noted with times were exposed to water vapour.

Section S4 Single Crystal X-ray Diffraction Analysis

The X-ray data set for UiO-67 was collected on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The initial structures were obtained by direct methods using SHELXS-97, and refined by subsequent refinement processes using SHELXL-97.[S1] During the refinement an O atom coordinated to Zr1 exhibited an elongated thermal ellipsoid and was divided into two O atoms, O1O (oxo) and O1H (hydroxo) with a half occupancy, respectively. Another O atom (O1w) was considered as a water molecule that formed a hydrogen bond with O1H. The H atoms attached respectively to O1H and O1w were included ideal geometries using DFIX commands in SHELXL. Their bond lengths were fixed at 0.84 Å, and the interatomic distances for the three symmetry-related H atoms at O1w were also fixed at 1.33 Å. As O1w sit on a 3-fold axis, the site occupancy factor of the water H atom was set to 2/3. The 4 C atoms in the disordered benzene ring were made to be located at the same plane with a FLAT command. Before the final stage of the refinement, the diffuse electron densities in the pore were removed by applying SQUEEZE in PLATON.[S2] All non-H atoms were refined anisotropically. The H atoms of BPDC were generated in ideal positions and refined with a riding model. Final crystal and refinement results are listed in Table S1. The oxo (μ_3-O) and hydroxo (μ_3-OH) oxygen atoms could be distinguished as follows. The Zr-O(μ_3-O) and Zr-O(μ_3-OH) bond lengths were found to be 2.051(1) Å and 2.243(1) Å, respectively, which are in good agreement with those found in corresponding molecular complexes: 2.035(2)–2.107(2) Å for Zr–O(μ_3-O) and 2.298(2)–2.331(2) Å for Zr–O(μ_3-OH).[S3] The displacement from the mean plane defined by three bonded Zr ions to the μ_3-O and μ_3-OH oxygen atoms were 0.386(5) and 0.987(3) Å, respectively. A water molecule was found to be engaged in a hydrogen bond with the observed O(water)…O(μ_3-OH) distance being 2.772 (7) Å. A similar hydrogen-bonded water molecule was observed in the crystal structure of water-adsorbed MOF-801, suggesting that the μ^3-OH group is a primary water adsorption site.[S4]

S1 G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112.

S2 A. L. Spek, *Acta Cryst*., 2009, **D65**, 148.

S3 M. Puchberger, F. R. Kogler, M. Jupa, S. Gross, H. Fric, G. Kickelbick and U. Schubert, *Eur. J. Inorg. Chem*., 2006, 3283.

S4 H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson, and O. M. Yaghi, *J. Am. Chem. Soc*., 2014, **136**, 4369.

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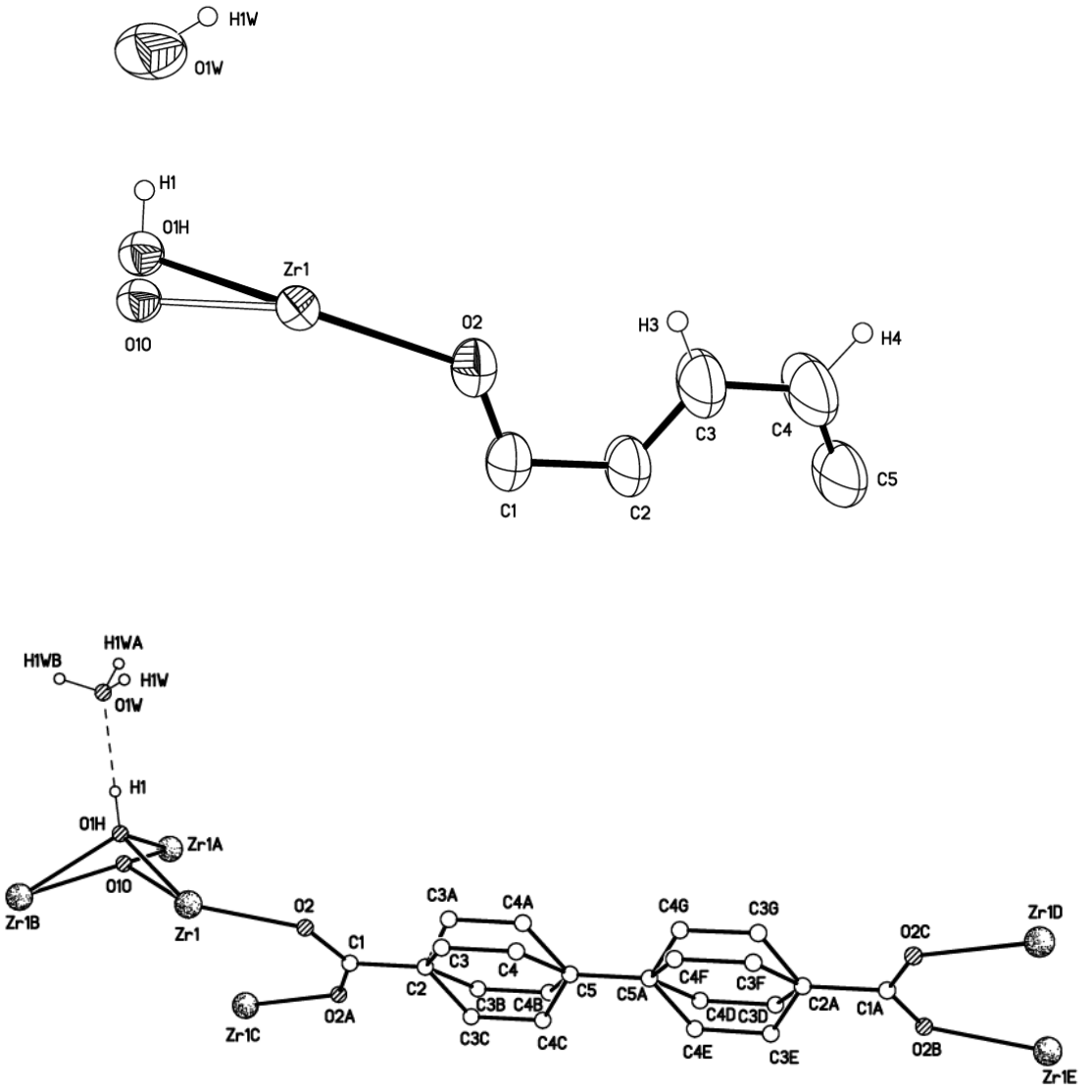

Fig. S5 (Top) Asymmetric unit of UiO-67 complex is shown in an ORTEP diagram with 50% probability. The O atoms (O1O and O1H) are disordered with a half occupancy factor, respectively. (Bottom) A fragment of UiO-67 is displayed with ball-and-stick models, showing the disorder of the BPDC linker adopting two orientations. The water molecule (O1w) sits on a 3-fold axis and is engaged in a hydrogen bond with μ_3-OH.

Table S1 Crystallographic data table for UiO-67 (SQUEEZE applied).

Empirical formula	C84 H60 O36 Zr6	
	$Zr_6O_4(OH)_4(BPDC)_6 \cdot (H_2O)_4$	
Formula weight	2192.64	
Temperature	100(2) K	
Wavelength	0.67000 Å	
Crystal system	Cubic	
Space group	*F m* -3 *m* (No. 225, Z = 192)	
Unit cell dimensions	*a* = 26.783(3) Å	α= 90°.
	b = 26.783(3) Å	β= 90°.
	c = 26.783(3) Å	γ = 90°.
Volume	19212(4) $Å^3$	
Z	4	
Density (calculated)	0.758 g/cm^3 for $Zr_6O_4(OH)_4(BPDC)_6 \cdot (H_2O)_4$	
(Calculated density of the empty framework, $Zr_6O_4(OH)_4(BPDC)_6$ = 0.733 g/cm^3)		
Absorption coefficient	1.736 mm^{-1}	
F(000)	4368	
Crystal size	0.10 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.03 to 33.58°.	
Index ranges	2<=h<=44, 0<=k<=31, 0<=l<=30	
Reflections collected	3827	
Independent reflections	2222 [R(int) = 0.0176]	
Completeness to theta = 33.58°	97.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2222 / 6 / 54	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1845	
R indices (all data)	R1 = 0.0529, wR2 = 0.1890	
Largest diff. peak and hole	0.024 and -0.024 $e.Å^{-3}$	

Section S5 ^{1}H-NMR Spectrums of Digested MOFs

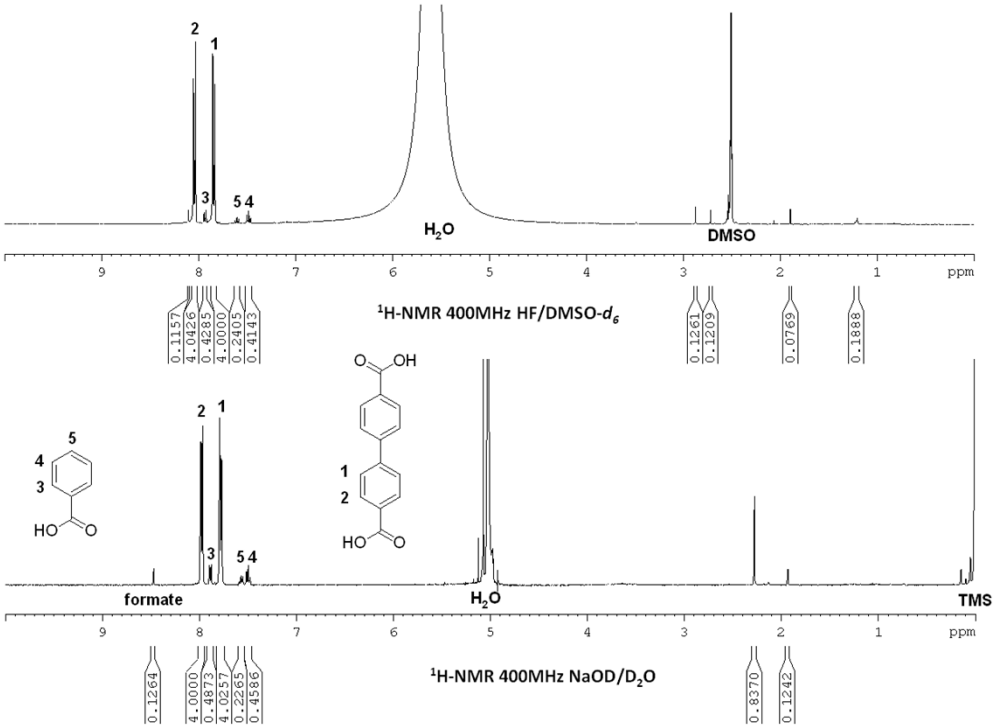

Fig. S6 ^{1}H-NMR spectrum measured for the activated UiO-67 digested in HF/DMSO (top) and NaOD/D_2O (bottom) solutions, resulting in a proposed formula of $Zr_6O_4(OH)_4(BPDC)_{5.1}$ $(benzoate)_{1.2}(formate)_{0.6}$ based on the integration ratios of the proton signals.

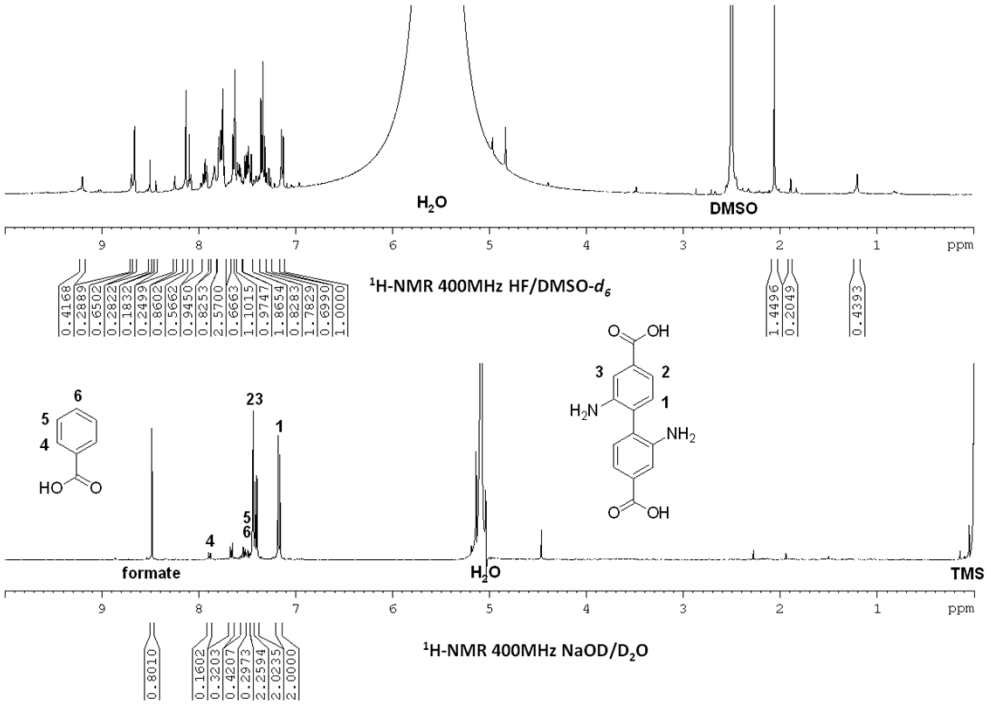

Fig. S7 ^{1}H-NMR spectrum measured for the activated UiO-67-$(NH_2)_2$ dissolved in HF/DMSO (top) and NaOD/D_2O (bottom) solutions, resulting in a proposed formula of $Zr_6O_4(OH)_4$(BPDC-$(NH_2)_2)_{4.1}$(benzoate)$_{0.6}$(formate)$_{3.2}$ based on the integration ratios of the proton signals. The spectrum of UiO-67-$(NH_2)_2$ dissolved in HF/DMSO solution, could not distinguished as each of the peaks found were too complicated. This result was thought to be a side reaction by HF and mediated by Zr ions.

Section S6 Thermogravimetric Analyses

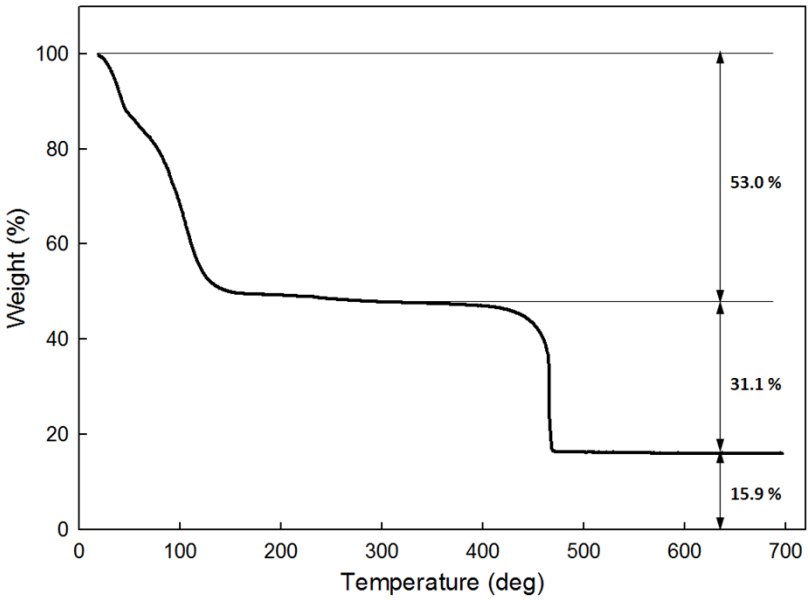

Fig. S8 TGA thermogram for the as-synthesized UiO-67.

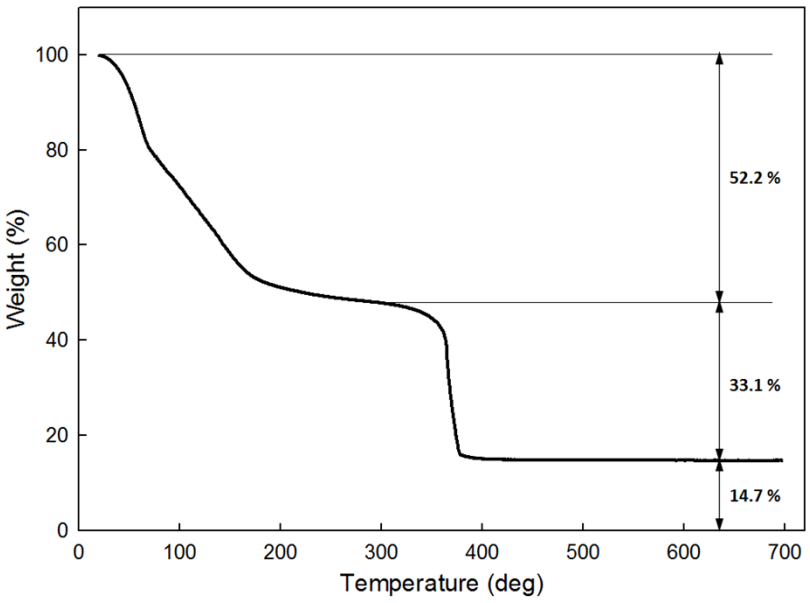

Fig. S9 TGA thermogram for the as-synthesized UiO-67-$(NH_2)_2$.

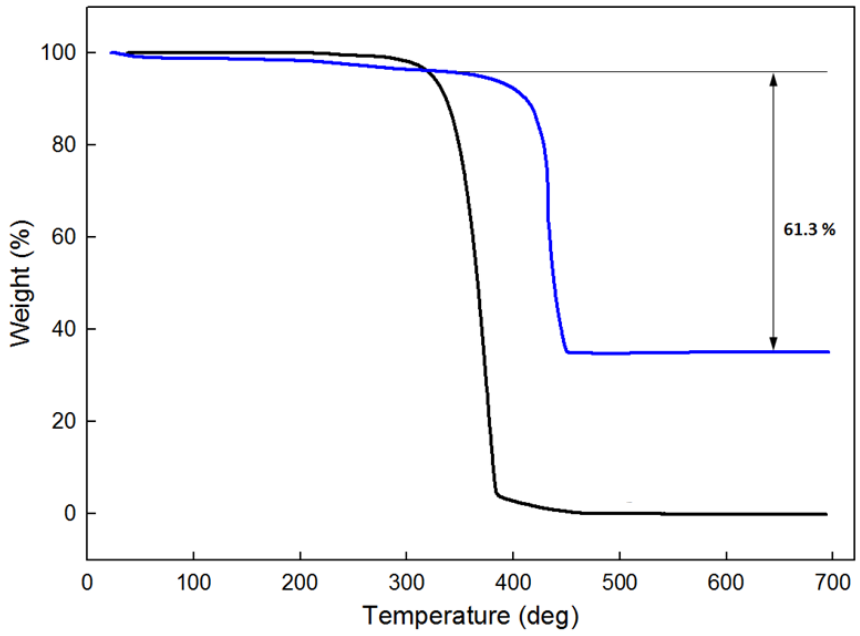

Fig. S10 TGA thermograms for the activated UiO-67 (blue) and H_2BPDC ligand (black).

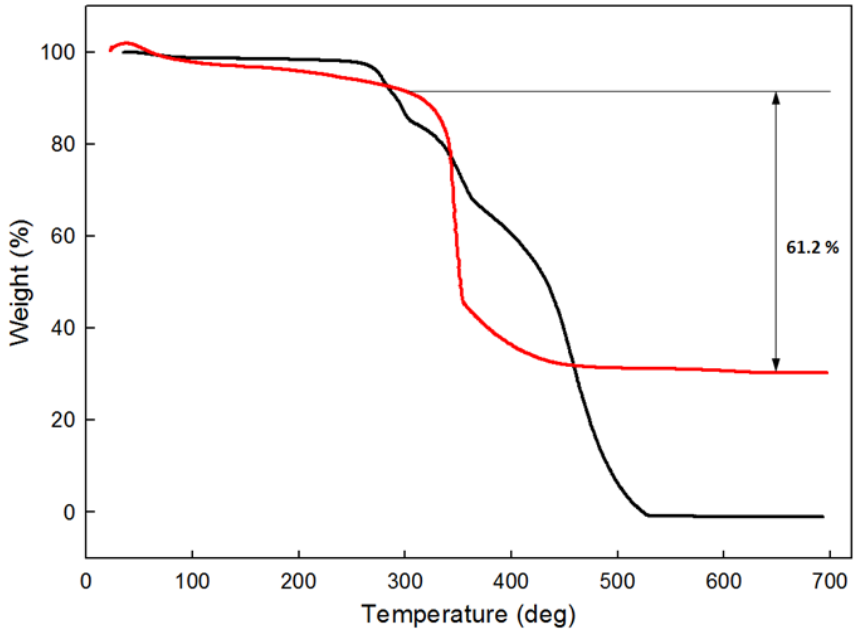

Fig. S11 TGA thermograms for the activated UiO-67-$(NH_2)_2$ (red) and H_2BPDC-$(NH_2)_2$ ligand (black).

Section S7 Gas Adsorption Analyses

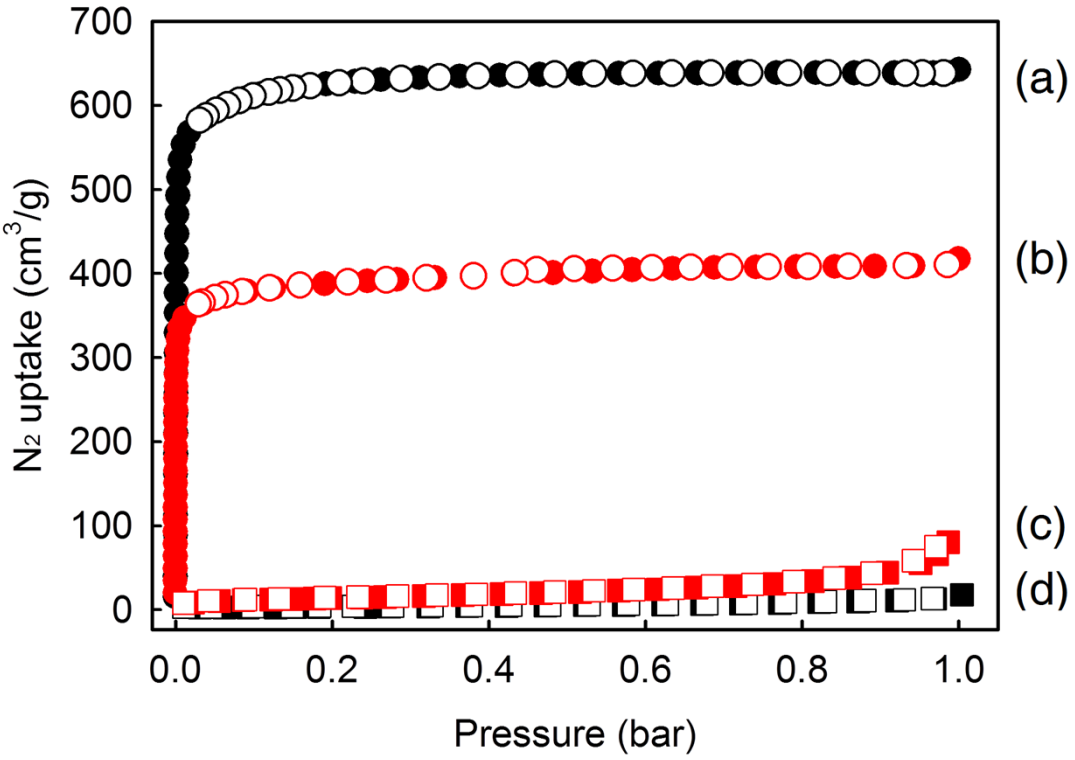

Fig. S12 N_2 adsorption isotherms for UiO-67 (black) and UiO-67-$(NH_2)_2$ (red) measured at 77 K: (a) activated UiO-67, (b) activated UiO-67-$(NH_2)_2$, (c) UiO-67-$(NH_2)_2$ after a water sorption measurements, and (d) UiO-67 after a water sorption measurements.

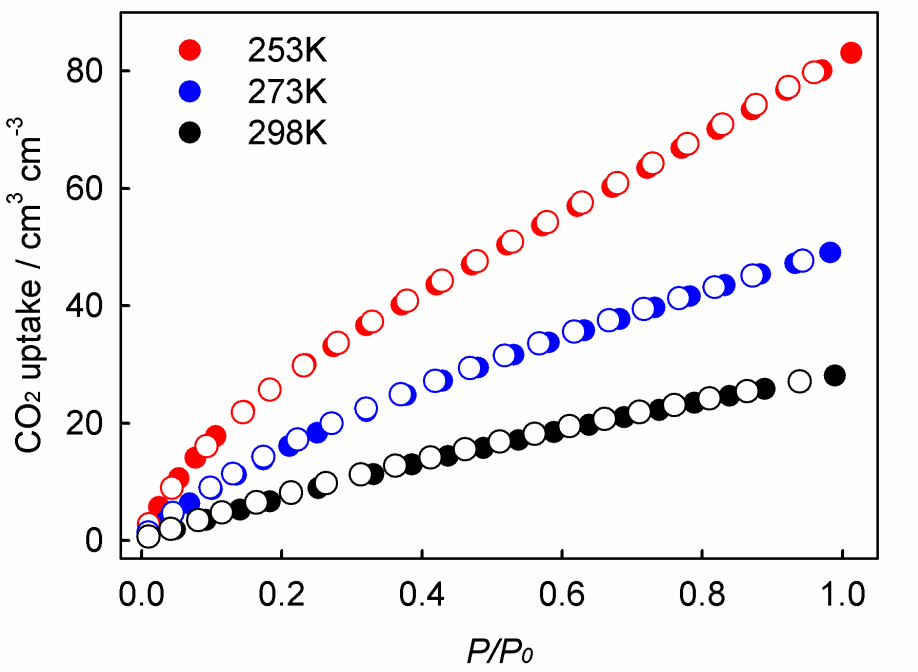

Fig. S13 CO_2 gas isotherms for UiO-67 measured at 253 (red), 273 (blue), and 298 K (black).

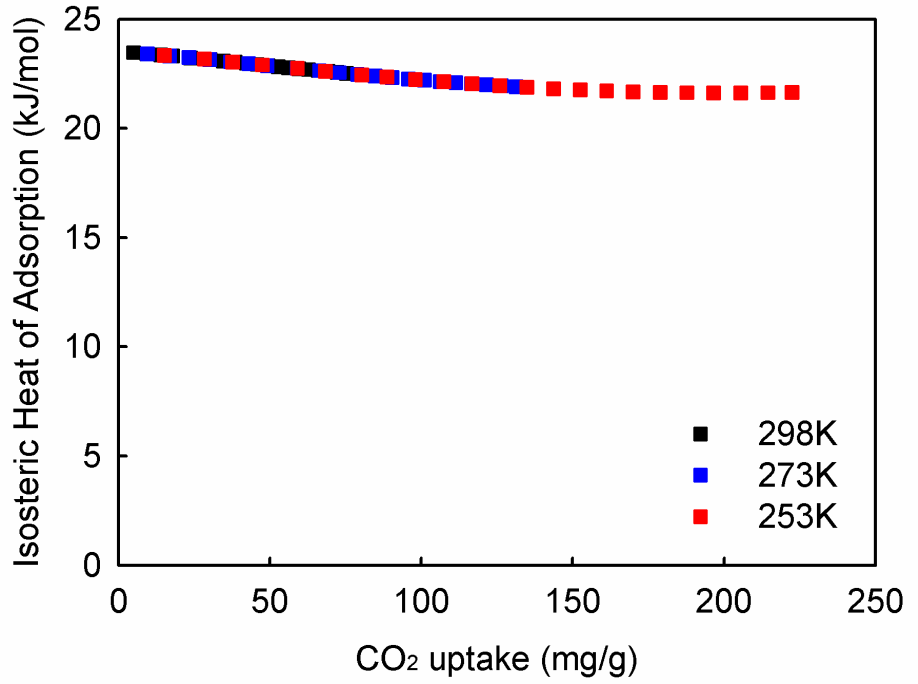

Fig. S14 Plot for isosteric heat of CO_2 adsorption of UiO-67 (23.42 kJ/mol).

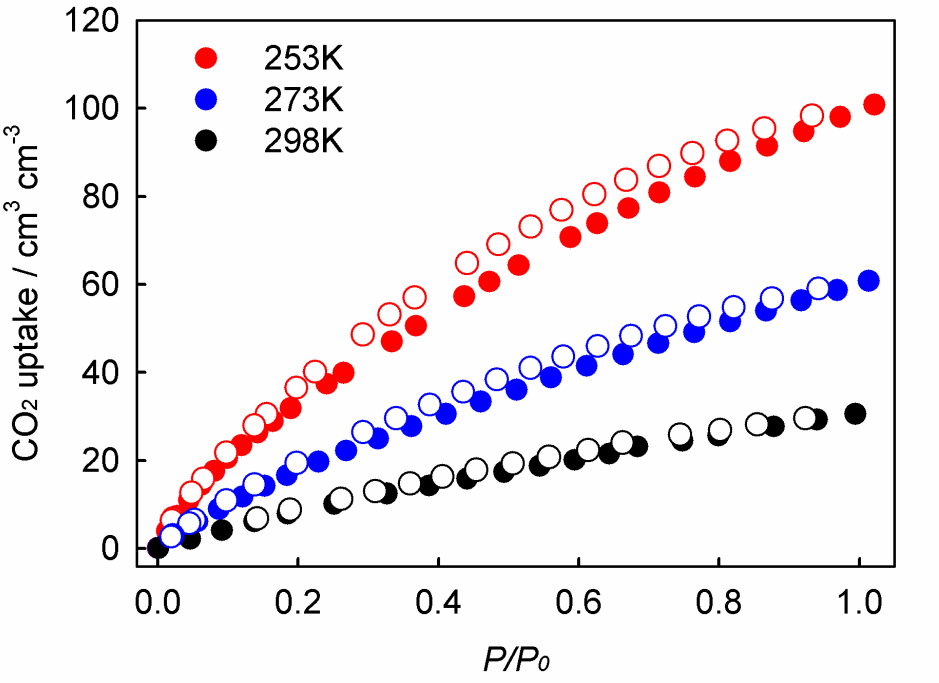

Fig. S15 CO_2 gas isotherms for UiO-67-$(NH_2)_2$ measured at 253 (red), 273 (blue), and 298 K (black).

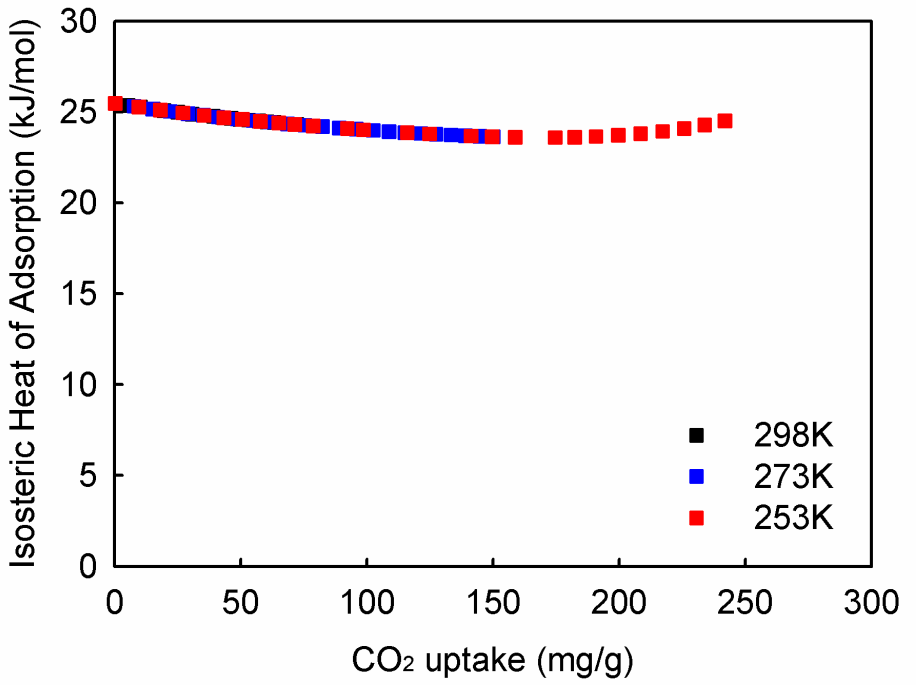

Fig. S16 Plot for isosteric heat of CO_2 adsorption of UiO-67-$(NH_2)_2$ (25.48 kJ/mol).

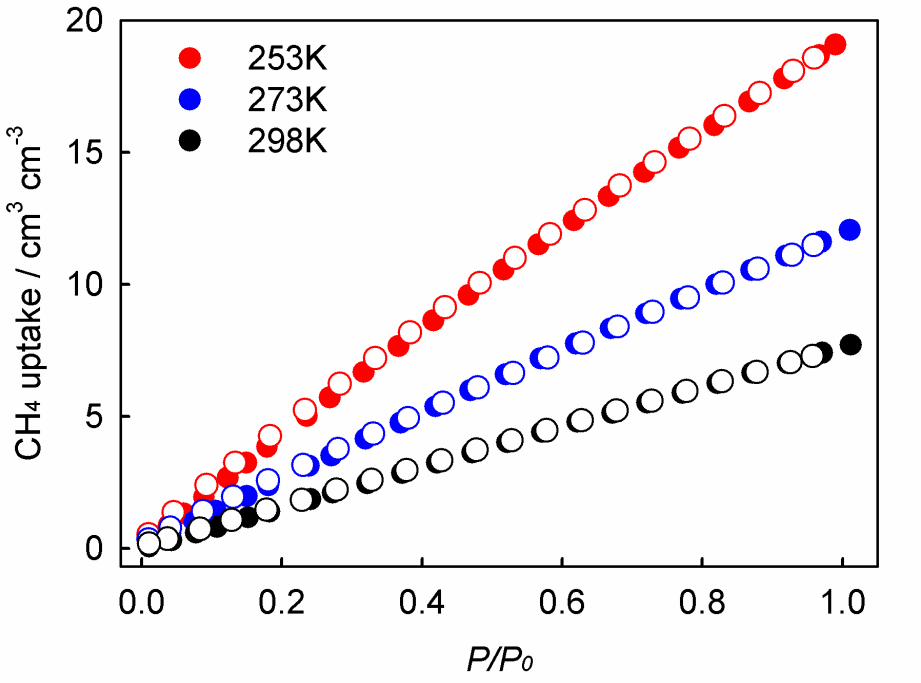

Fig. S17 CH_4 gas isotherms for UiO-67 measured at 253 (red), 273 (blue), and 298 K (black).

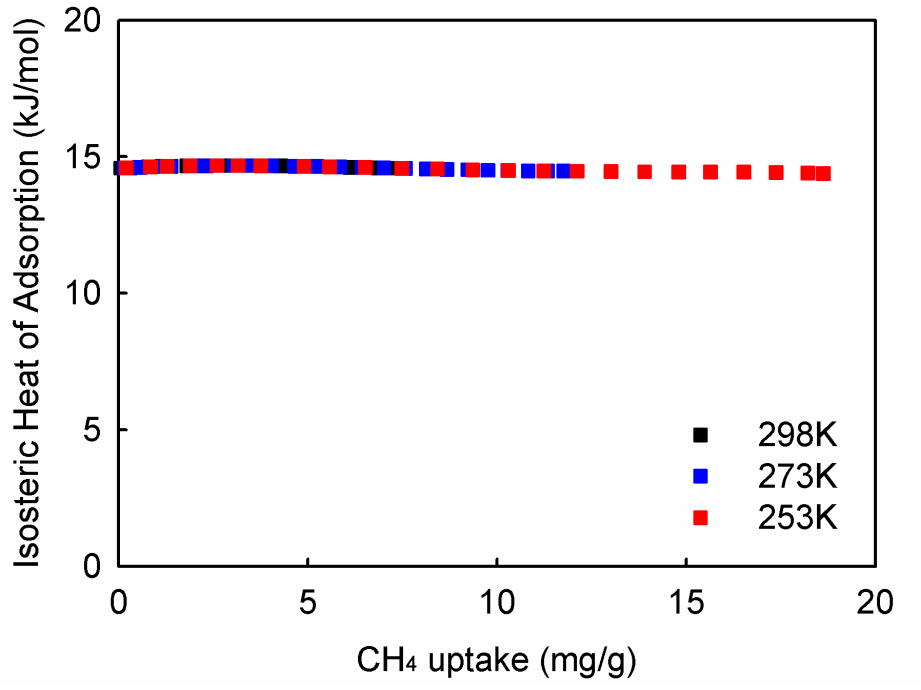

Fig. S18 Plot for isosteric heat of CH_4 adsorption of UiO-67 (14.58 kJ/mol).

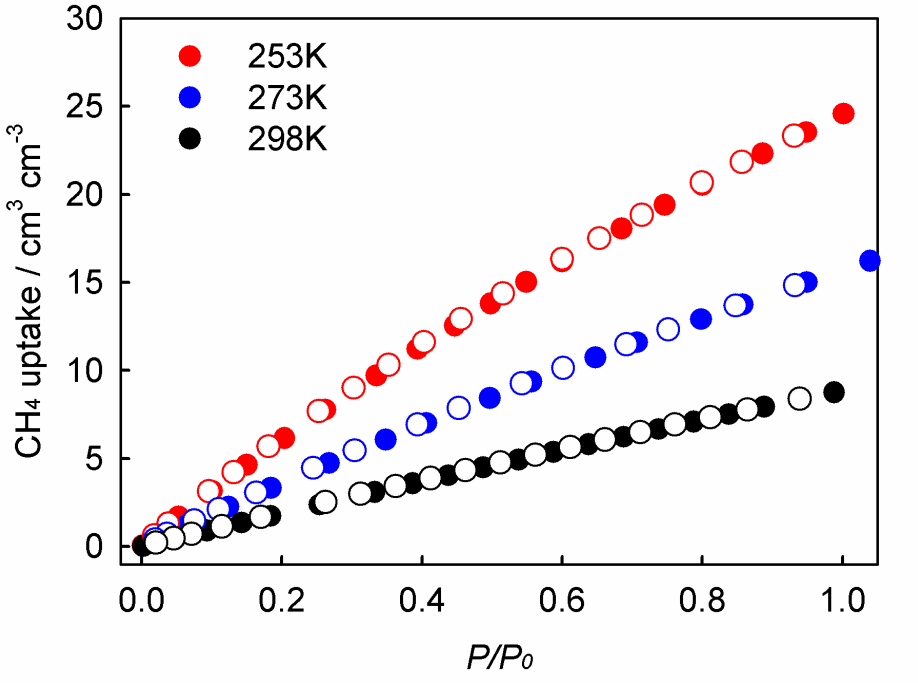

Fig. S19 CH_4 gas isotherms for UiO-67-$(NH_2)_2$ measured at 253 (red), 273 (blue), and 298 K (black).

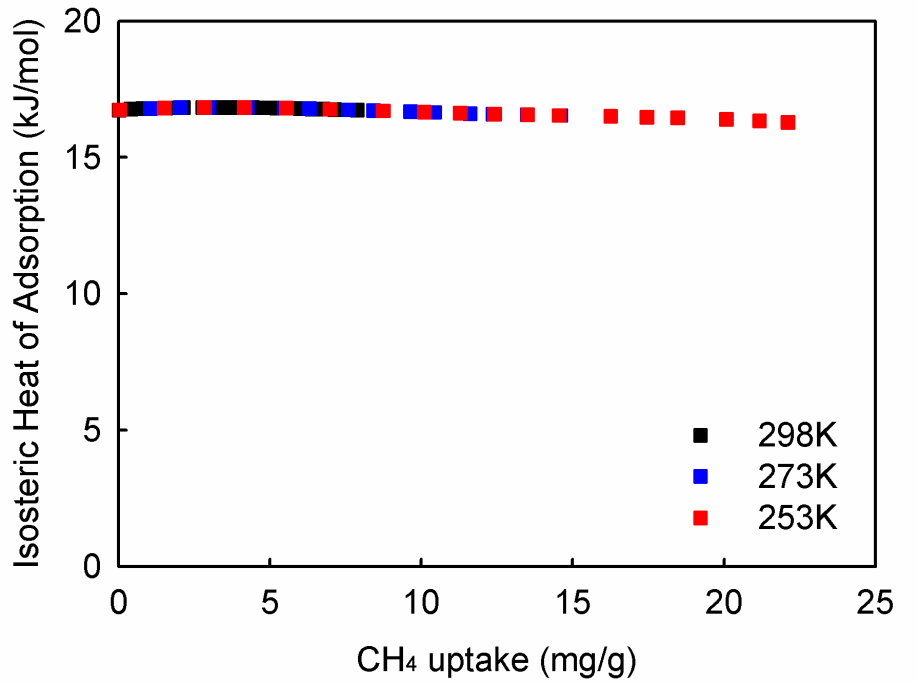

Fig. S20 Plot for isosteric heat of CH_4 adsorption of UiO-67-$(NH_2)_2$ (16.74 kJ/mol).

Section S8 Surface Area Calculations

The crystal structure of UiO-67 was edited by the Visualizer utility of *Materials Studio* 6.1.0™ (Accelrys Software Inc.).[S5] The BPDC was made to be ordered after reducing the space group symmetry from *Fm*-3*m* (No. 225) to *F*23 (No. 196). After generating H atoms at the BPDC carbon atoms, and setting the aromatic C–C and carboxylate C–O bonds to delocalized double bonds, the crystal structure was optimized using a Forcite routine that conducts Molecular Mechanics calculations with the Universal force-fields. During the geometry optimization, the positions of the Zr clusters were fixed and the unit cell parameters were not allowed to be changed. The ordered model structures are displayed in Figure S21.

Using the geometry-optimized models, solvent accessible surface areas were calculated with the following parameters for the 'Atom Volumes & Surface' tool.

Grid resolution: Fine; Grid interval: 0.25 Å; vdW scale factor: 1.0000

Max solvent radius: 1.82 Å; Initial solvent radius: 1.82 Å

The unit of the calculated surface areas can be converted to m2/g by the following equation.

SA_{acc} = (Surface Area)/f.w.

= (accessible solvent surface in m^2)/(Z × f.w. / N_A), where Z is the number of asymmetric unit in the unit cell, and N_A is the Avogadro's number.

UiO-67	**UiO-67-$(NH_2)_2$**
vdW Surface	**vdW Surface**
Occupied Volume: 5365.65 Å³	Occupied Volume: 5676.04 Å³
Free Volume: 13846.58 Å³	Free Volume: 13536.19 Å³
Surface Area: 5155.00 Å²	Surface Area: 5319.06 Å²
Accessible Solvent Surface @1.82	**Accessible Solvent Surface @1.82**
Occupied Volume: 14541.24 Å³	Occupied Volume: 15243.29 Å³
Free Volume: 4670.98 Å³	Free Volume: 3968.93 Å³
Surface Area: 4112.06 Å²	Surface Area: 3869.52 Å²

The solvent accessible surfaces are displayed in Figure S21.

S5 Materials Studio v6.1, Accelrys Inc., San Diego, CA, 2012. Materials Studio 6.1.0™ (Accelrys Software Inc.).

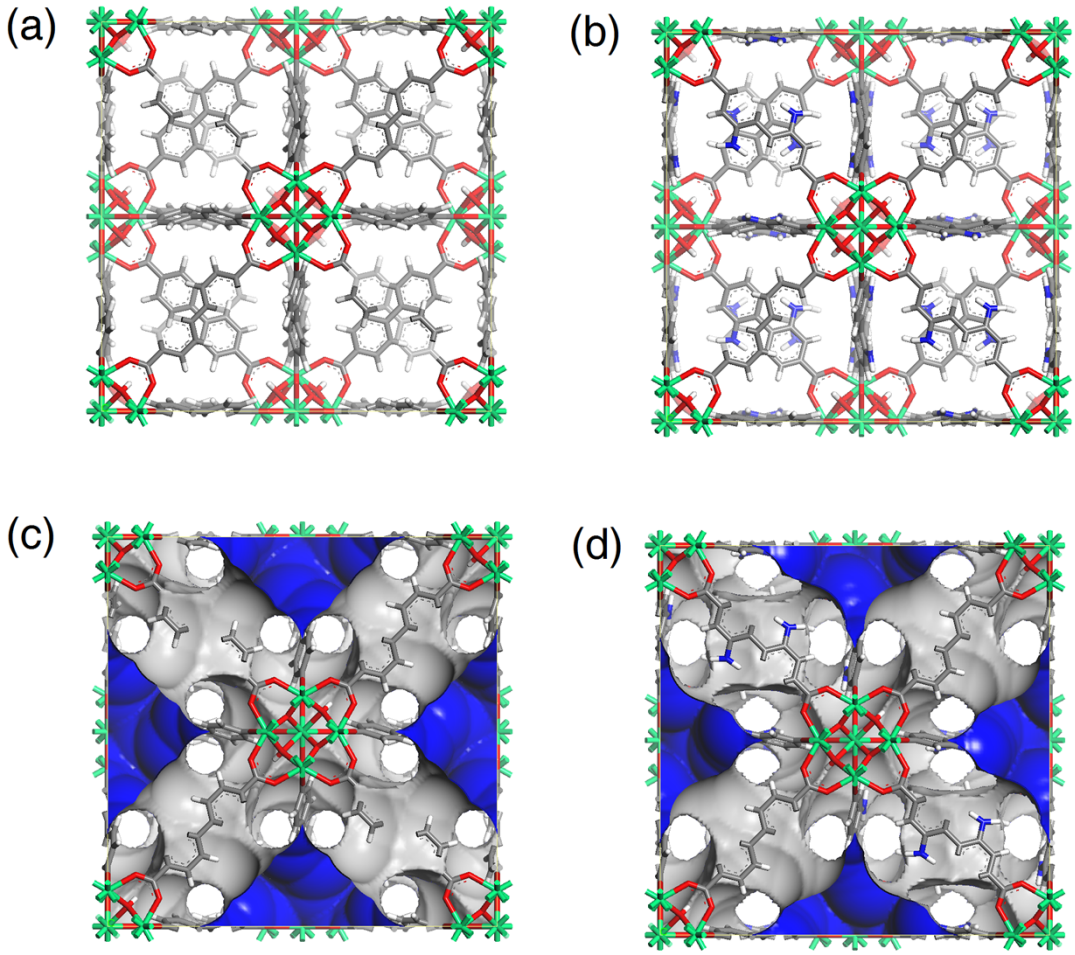

Fig. S21 Geometry optimized structures of (a) UiO-67 and (b) UiO-67-$(NH_2)_2$, and solvent accessible surfaces of (a) UiO-67 and (b) UiO-67-$(NH_2)_2$.