Supporting Information for

A High Connectivity Metal-Organic Framework with Exceptional Hydrogen and Methane Uptake Capacities

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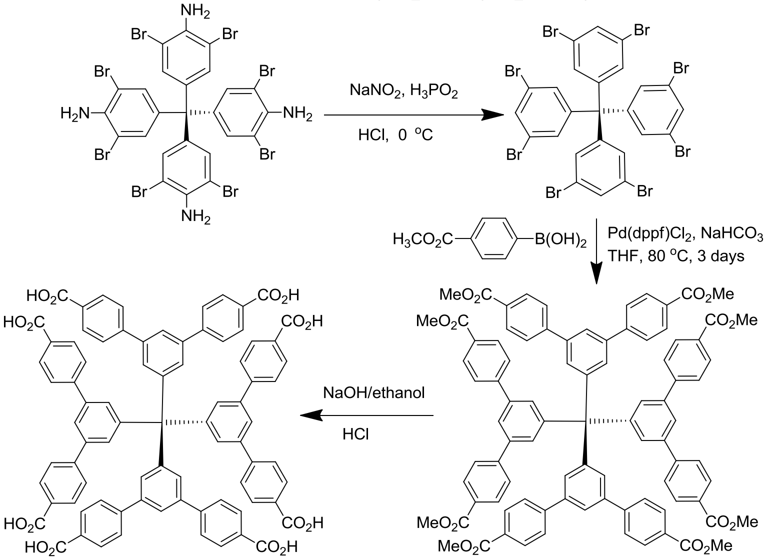
1. Materials and Methods.

All chemicals were purchased from Aldrich and Fisher, unless otherwise noted, and used without further purification. ^{1}H-NMR spectra were recorded on a Bruker NMR 400 DRX Spectrometer at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of deuterated chloroform or methanol. Mass Spectrometric analyses were conducted using positive-ion electrospray ionization on a Bruker BioTOF mass spectrometer. Powder X-ray diffraction (PXRD) analyses were carried out on a Bruker SMART APEX II Diffractometer using Cu radiation. The PXRD patterns were processed with the APEX II package using PILOT plug-in. UV-Vis absorption spectra were obtained using a Shimadzu UV-2401 PC UV-Vis Spectrophotometer. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 equipped with a platinum pan, and all samples were heated at a rate of 5 °C per minute under air. Nitrogen adsorption experiments were performed with a Quantachrome Autosorb-1C. Tetra(4-amino-3,5-dibromo)phenylmethane was made by following the literarure.[1]

2. Procedures for Ligand Synthesis and Crystal Growth.

2.1. Synthesis of tetrakis{3,5-bis[(4-carboxyl)phenyl]phenyl}methane.



To an ice-water cooled and stirred solution of tetrakis[(4-amino-3,5-dibromo)phenyl]methane (3.8 g, 3.7 mmol) in a mixture of 28 mL of acetic acid, 12 mL of H_2O and 3.2 mL of concentrated HCl was added dropwise a solution of $NaNO_2$ (1.25 g, 18.1 mmol) in 4 mL of H_2O. The reaction mixture was stirred for 30 min and was then added to a 32 mL of solution of 50% H_3PO_2 cooled at 0 ^{o}C. After being stirred for 8 h at 0 ^{o}C, the reaction mixture was extracted with ethyl acetate (3×50 mL). Upon being dried over $MgSO_4$ and removal of the solvent, 2.0 g (yield: 55%) of tetrakis(3,5-dibromophenyl)methane was obtained. ^{1}H-NMR ($CDCl_3$): 7.62 (s, 4H), 7.13 (8H).

A solution of tetra(3,5-dibromo)phenylmethane (200 mg, 0.21 mmol) and 4-(methoxycarbonyl)phenylboronic acid (378 mg, 2.1 mmol) in tetrahydrofuran (10 mL) was degassed for 15 min. A N_2 purged, saturated aqueous solution of $NaHCO_3$ (9 mL) and dichloro[1, 1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloromethane adduct (Pd(dppf)Cl_2, 10 mg, 0.014 mmol) were added to this solution. The reaction vessel was sealed and the reaction mixture was stirred at 80 ^{o}C for 3 days. After cooling to room temperature, the mixture was extracted with chloroform and brine. The organic layer was separated and washed with brine, then dried over $MgSO_4$. The crude product was then purified by silica gel column chromatography with hexanes/ethyl acetate (1:1 v/v) as the eluent to afford tetrakis[3,5-bis(methyl 4-benzoate)phenyl]methane. Yield: (120 mg, 39 %). ^{1}H NMR ($CDCl_3$): 8.05 (d, 16H), 7.74-7.78 (m, 12H), 7.56 (d, 16H), 3.91 (s, 24H).

A solution of tetrakis[3,5-bis(methyl 4-benzoate)phenyl]methane (120 mg, 0.086 mmol) in THF (5 mL), ethanol (5 mL), and 6 M aqueous NaOH (3 mL) was stirred at 70 ^{o}C overnight. The solution was cooled to room temperature and acidified to a pH of 1 and extracted with ethyl acetate/H_2O. The organic layer was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to give a solid of tetrakis{3,5-bis[(4-carboxyl)phenyl]phenyl}methane (**L**-H_8). Yield: (100 mg, 91%).^{1}H NMR (MeOD): 8.03 (d, 16H), 7.95 (s, 4H), 7.86 (s, 8H), 7.69 (d, 16H). MS (EI) for $[M+Na]^+$: 1303.32 calcd; 1303.40 found.

2.2.Synthesis of $[Cu_2(L\text{-}H_4)\cdot(H_2O)_2]\cdot18DMF\cdot5H_2O$ (1)

A mixture of **L**-H_8 (10 mg, 0.008 mmol) and $Cu(NO_3)_2\cdot2.5H_2O$ (20 mg, 0.09 mmol) was dissolved in a solvent mixture of DMF/H_2O (1.5 mL/0.5 mL) in a screw-capped vial. After addition of 0.5mL of NH_3 (3M, aq.), the vial was capped and placed in an oven at 100°C for two days. Blue crystals (9.3 mg, 40.7%) were obtained after filtration.

2.3.Synthesis of $\{[Zn_3(\mu_3\text{-}OH)(H_2O)]_4(L)(L\text{-}H_2)_2\}\cdot45DMF\cdot44H_2O$ (2)

A mixture of **L**-H_8 (10 mg, 0.008 mmol) and $Zn(NO_3)_2\cdot6H_2O$ (20 mg, 0.07 mmol) was dissolved in a solvent mixture of DMF/H_2O (6 mL/2 mL) in a screw-capped vial. After addition of 0.1mL of HCl (3M, aq.), the vial was capped and placed in an oven at 80°C for two days. Colorless crystals (10.5 mg, 53.2%) were obtained after filtration.

3. X-ray Structure Determination

All crystallographic measurements were made on a Bruker SMART Apex II CCD-based X-ray diffractometer system equipped with Cu–target X-ray tube and operated at 1600 watts. The frames were integrated with the Bruker SAINT$^©$ build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. All of the structures were solved by direct methods and refined to convergence by least squares method on F^2 using the SHELXTL software suit. All non-hydrogen atoms are refined anisotropically. SQUEEZE subroutine of the PLATON software suit was applied to remove the scattering from the highly disordered solvent molecules. The resulting new HKL4 files were used to further refine the structures. Datasets for **1** and **2** were collected to $2\theta = 85^{o}$ and 80^{o} respectively, with >98% completeness. Restraints (SIMU and DELU) on displacement parameters of **1** and **2** are applied, and all the phenyl rings are constrained to ideal six-membered rings.

Table S1. X-Ray crystallographic data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	C81 H28 Cu2 O18	C34.71 H20 O8 Zn1.71
Formula weight	1416.11	677.14
Temperature (K)	296(2)	296(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	Orthorhombic	Tetragonal
Space group	Pban	I-42d
Unit cell dimensions	a = 28.532(3) Å	a = 36.3615(3) Å
	b = 33.426(3) Å	b = 36.3615(3) Å
	c = 16.0881(14) Å	c = 34.7679(6) Å
	α = 90°	α = 90°
	β = 90°	β = 90°
	γ = 90°	γ = 90°
Volume ($Å^3$)	15343(2)	45968.7(10)
Z	4	28
Density (calcd. g/cm^3)	0.613	0.685
Absorption coeff. (mm^{-1})	0.618	0.996
F(000)	2864	9624
Crystal size(mm)	0.60×0.30 ×0.10	0.50×0.40 ×0.30
Crystal color & shape	blue	colorless
θ range data collection	2.04 to 44.39°.	3.00 to 39.97°
Limiting indices	$-20 < h < 25$	$-21 < h < 21$
	$-30 < k < 26$	$0 < k < 30$
	$-14 < l < 11$	$0 < l < 28$
Reflections collected	31034	6873
Independent reflections	5918 [R(int) = 0.0545]	6873 [R(int) = 0.0000]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Data/restraints/parameters	5918 / 66 / 346	6873 / 506 / 604
Goodness-of-fit on F^2	1.000	0.954
Final R indices [$I>2\sigma(I)$][a,b]	R1 = 0.0677	R1 = 0.0388
	wR2 = 0.1800	wR2 = 0.0933
R indices (all data)	R1 = 0.1096	R1 = 0.0478
	wR2 = 0.1924	wR2 = 0.0966

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_W(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

4. Quantitative determination of solvent molecules in 1 and 2

To minimize the experimental error, each sample was treated in exactly the same way for both ^{1}H NMR and TGA experiments. Fresh crystals were harvested by quick filtration, and briefly dried on filter paper under air for 5 min. The sample was then loaded into screw-capped vial or the sample tray in TGA. To the weighted sample in the crew-capped vial, 0.75 mL CD_3OD was added. 10 μL mesitylene (Mes) was then added as an internal standard. After soaking overnight, the ^{1}HNMR spectrum was taken. Since the DMF or DEF is miscible in CD_3OD, and its exact amount was determined by calibrating against the internal standard. The total amounts of the solvents were obtained by TGA, the amount of water molecules was calculated by subtracting DMF or DEF from the total solvent amount.

4.1 $[Cu_2(L\text{-}H_4)\cdot(H_2O)_2]\cdot 18DMF\cdot 5H_2O$ (1)

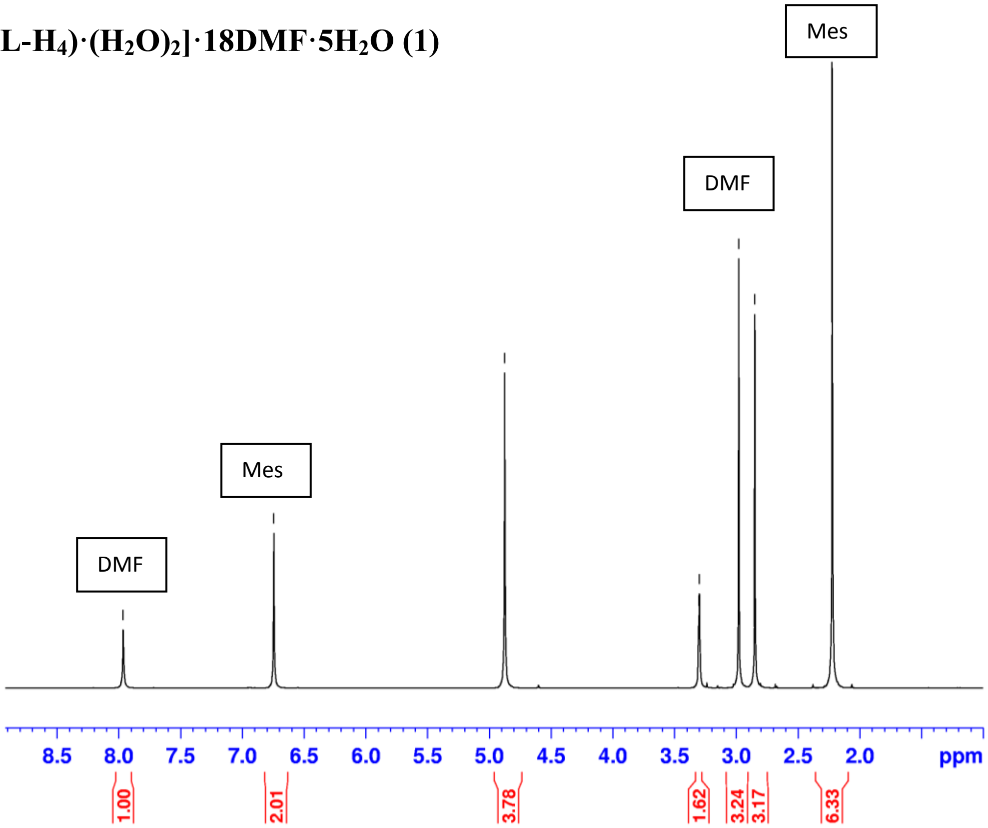
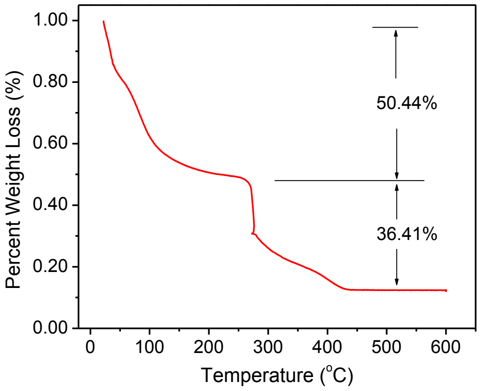


Figure S1. ^{1}H-NMR spectroscopic determination of solvent content in **1**, mesitylene (Mes) was added as an internal standard.



$W_{crystal}$(mg)	16.42
$W_{mesitylene}$(mg)	8.6
W_{DMF} (mg) (From NMR)	7.55
W_{DMF} %	46.0
W_{DMF+H_2O}% (From TGA)	50.4
W_{H_2O}%	4.4
Formula: $[Cu_2(\mathbf{L}\text{-}H_4)\cdot(H_2O)_2]\cdot 18DMF\cdot 5H_2O$	

Figure S2. Thermogravimetric analysis (TGA) curve for **1**. The sample was heated to 600 °C at a heating rate of 5 °C/min (Temperature was then held at 200 °C for 6 hrs).

4.2 {[$Zn_3(\mu_3\text{-}OH)(H_2O)]_4(L)_2(L\text{-}H_4)$}·45DMF·44$H_2O$ (2)

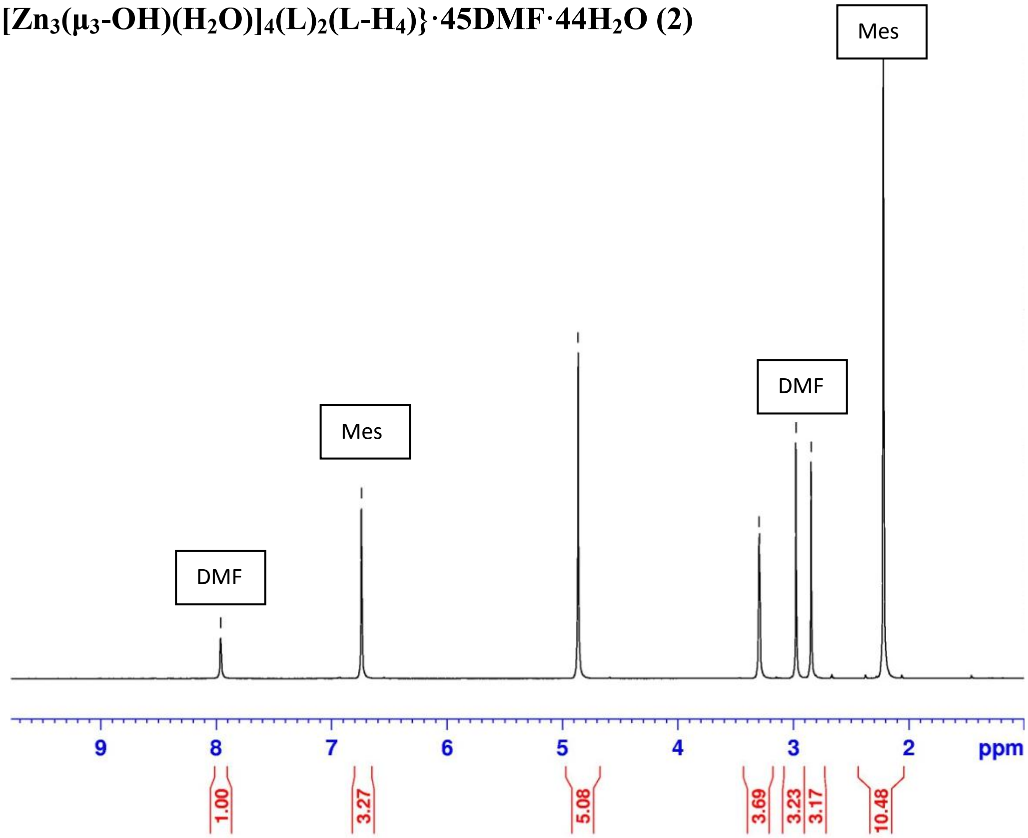


Figure S3. ^{1}H-NMR spectroscopic determination of solvent content in **2**, mesitylene (Mes) was added as an internal standard.

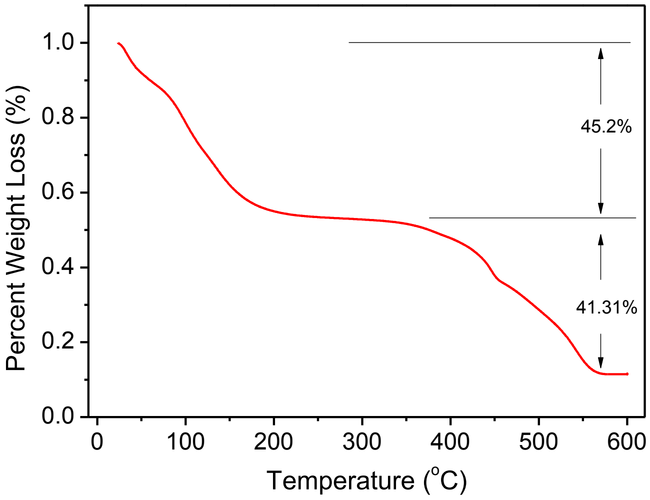


Figure S4. Thermogravimetric analysis (TGA) curve for **2**. The sample was heated to 600 °C at a heating rate of 5 °C/min.

$W_{crystal}$(mg)	6.72
$W_{mesitylene}$(mg)	4.3
W_{DMF} (mg) (From NMR)	2.4
W_{DMF} %	36.0
W_{DMF+H_2O}% (From TGA)	45.2
W_{H_2O}%	9.2
Formula: {[$Zn_3(\mu_3\text{-}OH)(H_2O)]_4$**(L)**(**L**-$H_2)_2$}·45DMF·44$H_2O$	

5. High pressure hydrogen and methane uptake measurements

The high pressure volumetric gas analysis was performed by HPVA-100 (Micromeritics, GA) using H_2 and CH_4 of ultra-high purity (99.999%) from GTS-Welco. The sample was activated as described previously.[2] A typical setup for freeze-drying and high pressure measurement is shown below.

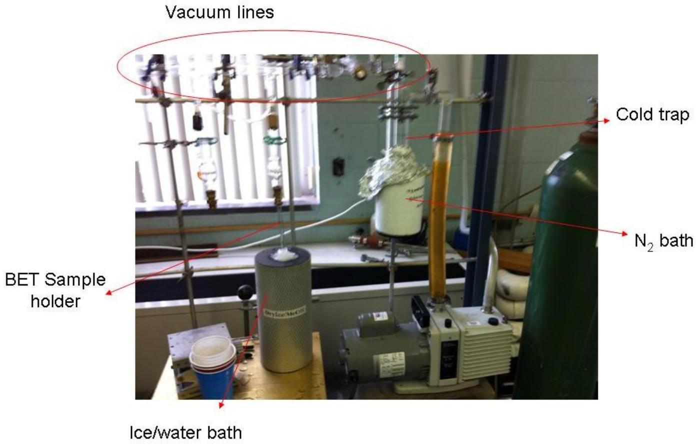


Figure S5. High pressure measurement set up.

Freeze-dried sample was transferred to the high pressure sample cell and evacuated at room temperature for 24 hrs, followed by heating at 60 and 90 °C under vacuum for 36 and 12 hours, respectively, before high pressure CH_4 and H_2 adsorption experiments were carried out.

The total gas uptake capacity was calculated using the following equation:

$$C_{tot} = C_{exc} + \frac{100 \times d_g V_{pore}}{1 + d_g V_{pore}} \qquad (1)$$

Where C_{tot} is the total adsorption capacity (wt%), C_{exc} is the excess adsorption in wt%, d_g is the density of the compressed gas (H_2 and CH_4) in g/cm^3 at the measuring temperature and pressure (data obtained from NIST website[3]), V_{pore} is the pore volume in cm^3/g obtained from nitrogen sorption measurement.

Volumetric uptake capacity was calculated using the following equation:

$$V(STP)/V = \frac{d \times 22.4 \times 1000 \times C}{100 \times MW_{gas}} \qquad (2)$$

Where C is the adsorption capacity in wt% (either excess capacity or total capacity), d is the crystal density calculated from single crystal data (assuming the crystal density is the packing density), and MW_{gas} is the molecular weight of gas molecule.

6. Analysis of isosteric heat of adsorption

The isosteric heat of adsorption Q_{st} was determined by virial method using the following equation:

$$\ln(p) = \ln(n) + \frac{1}{T}\sum_{i=0}^{m} a_i n^i + \sum_{j=0}^{n} b_j n^j \qquad (3)$$

Here, p is the pressure expressed in mbar, n is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_j are virial coefficients, and m and n represent the numbers of coefficients required to well fit the isotherms. The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following equation:

$$Q_{st} = -R\sum_{i=0}^{m} a_i n^i \qquad (4)$$

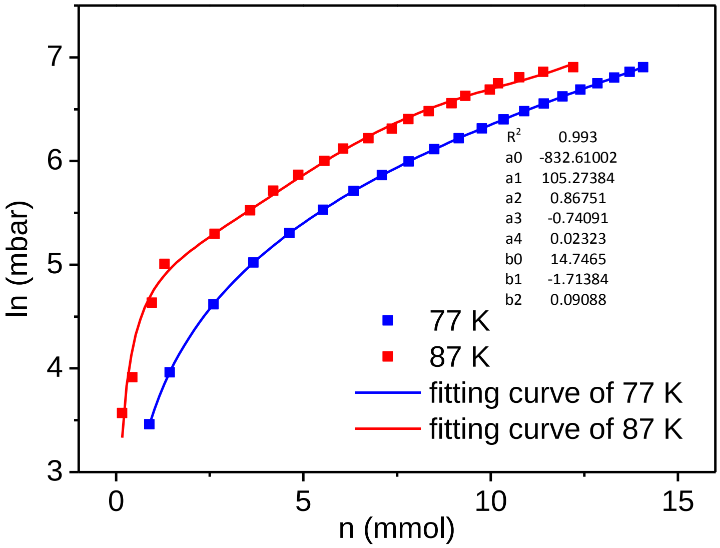


Figure S6. Virial fitting of hydrogen adsorption data for **2** at 77 K and 87 K.

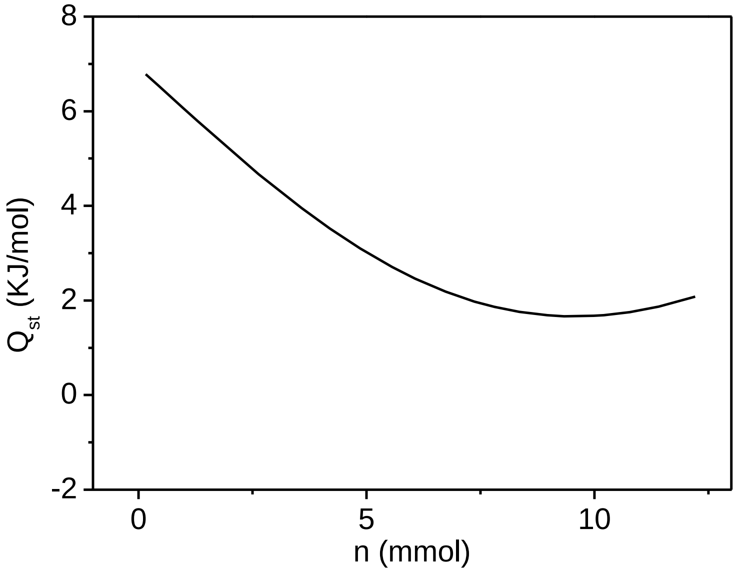


Figure S7. Plot of the isoteric heat of adsorption of **2**.

7. Computational methods.

All the GCMC simulations were performed by the Sorption program, Adsorption Locator module and Metropolis method in the Materials Studio modeling 5.0 packages.[4]

The standard universal force field (UFF) was used in GCMC simulations to describe the framework and methane interaction and the methane and methane interaction. Both the CH_4 molecules and the framework were treated as rigid bodies. One unit cell of **2** was chosen as the simulation box, 5×10^5 steps were used for equilibration and an additional 1×10^5 steps were used to calculate the ensemble average of methane adsorption sites and thermodynamic properties. Atomic partial charges of **2** derived from QEq method and QEq_neutral1.0 parameter setting were included in the simulation to account for electrostatic interactions. The long-range electrostatic interactions were treated using the Ewald summation method. Automated temperature control in the annealing cycles (the temperature cycles to be performed in the simulated annealing run) and 1.5×10^4 steps per cycle were employed in the Adsorption Locator module.

First-principles calculations based on density-functional theory were performed using the CASTEP module in MS.[5] Vanderbilt-type ultrasoft pseudopotentials and the local-density approximation (LDA) with the Perdew-Zunger exchange correlation was used in the DFT calculation. The semi-empirical dispersion correction was implemented in the calculation with OBS correction scheme.[7] Generalized gradient approximation (GGA) was not used here because it severely underestimates the binding energy between open metal sites and methane molecules.[6] A cutoff energy of 300 eV and a *gamma*-point *k* sampling were used in the calculation in order for the total energy to converge within 0.5 meV/atom in less than 50 steps. A primitive cell of **2** was used as the simulation box and then CH_4 molecules, whose structure have been optimized, were introduced into the framework guided by GCMC results. The binding energy was calculated using the following equation:

$$E_b = \frac{\left[E\left(\mathrm{MOF}\right)+E\left(n\mathrm{CH}_4\right)-E\left(\mathrm{MOF}+n\mathrm{CH}_4\right)\right]}{n} \qquad (5)$$

Where $E(\mathrm{MOF})$ is the total energy of a primitive cell of **2** without methane adsorption, $E(\mathrm{MOF}+n\mathrm{CH}_4)$ is the total energy of a primitive cell of **2** with *n* methane molecules adsorbed onto the framework. To obtain the CH_4 binding energies, CH_4 molecules placed in a simulation box with the same dimensions were also relaxed as a reference, the total energy is $E(n\mathrm{CH}_4)$.

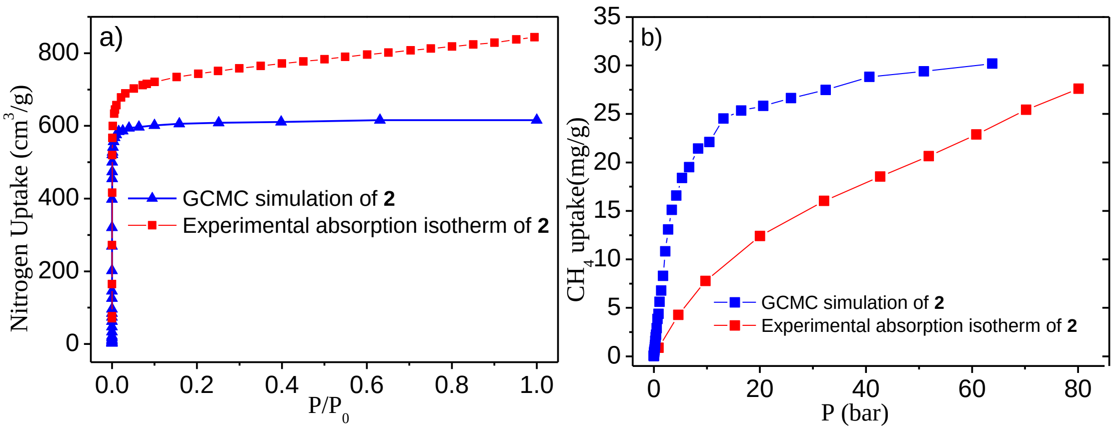
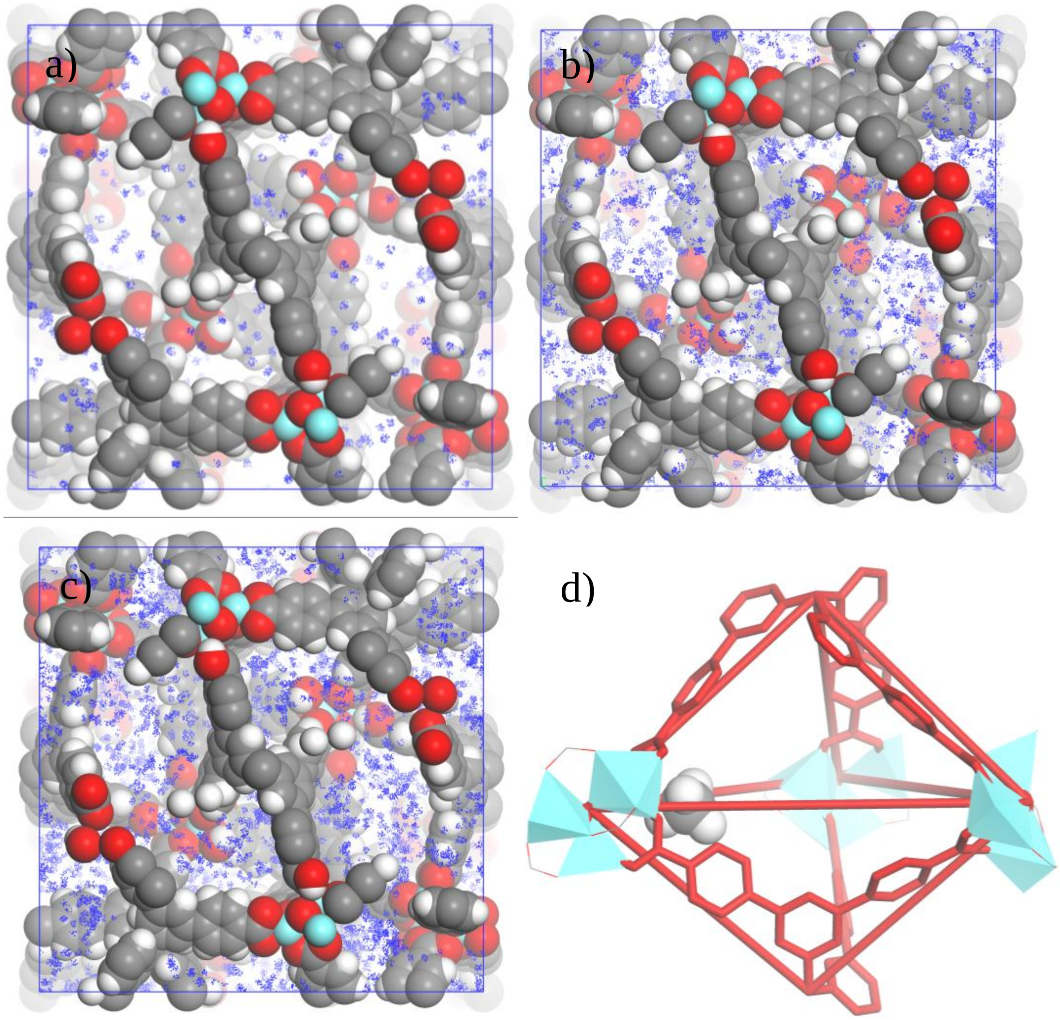


Figure S8. Comparision between experimental data and GCMC simulation of N_2 (a) and CH_4 (b) adsorption isotherms of **2**.



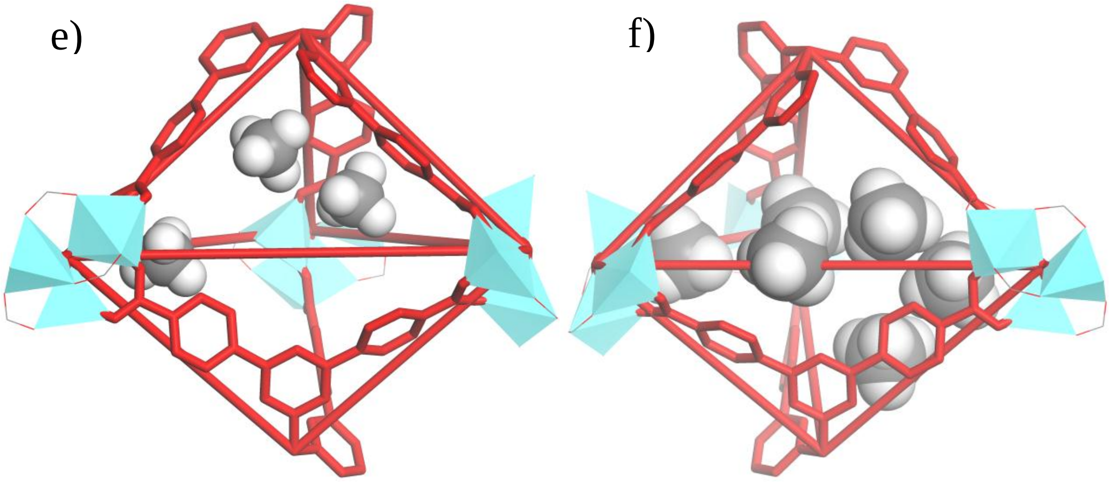


Figure S9. Probability distribution of the CH_4 in MOF **2** from GCMC simulations at 298 K and a) at 0.1 bar; b) at 1 bar; c) at 10 bar. Preferential CH_4 locations in **2** d) at 0.1 bar; e) at 1 bar; f) at 10 bar (methane molecules are shown in space-filling model for clarity).

Table S2. Summary of dye uptake by **1** and **2**.

Framework	Crystal Weight(mg)	Absorption(baseline corrected)	Concentration(μM)	Solvent Weight Loss (%)	wt% Dye/Framework
1	3.38	0.115	4.3	50.4	5.3
2	5.84	0.018	0.9	45.2	0.58

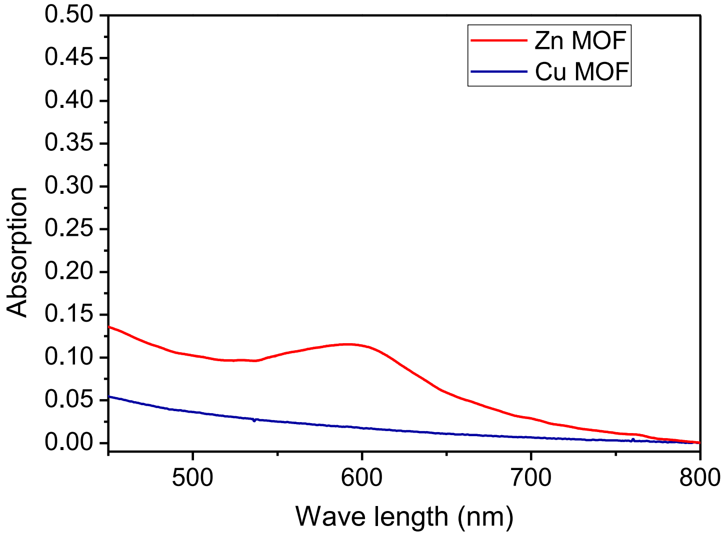


Figure S10. Normalized UV-Vis Absorption spectra of digested **1** and **2** loaded with Brilliant Blue R-250.

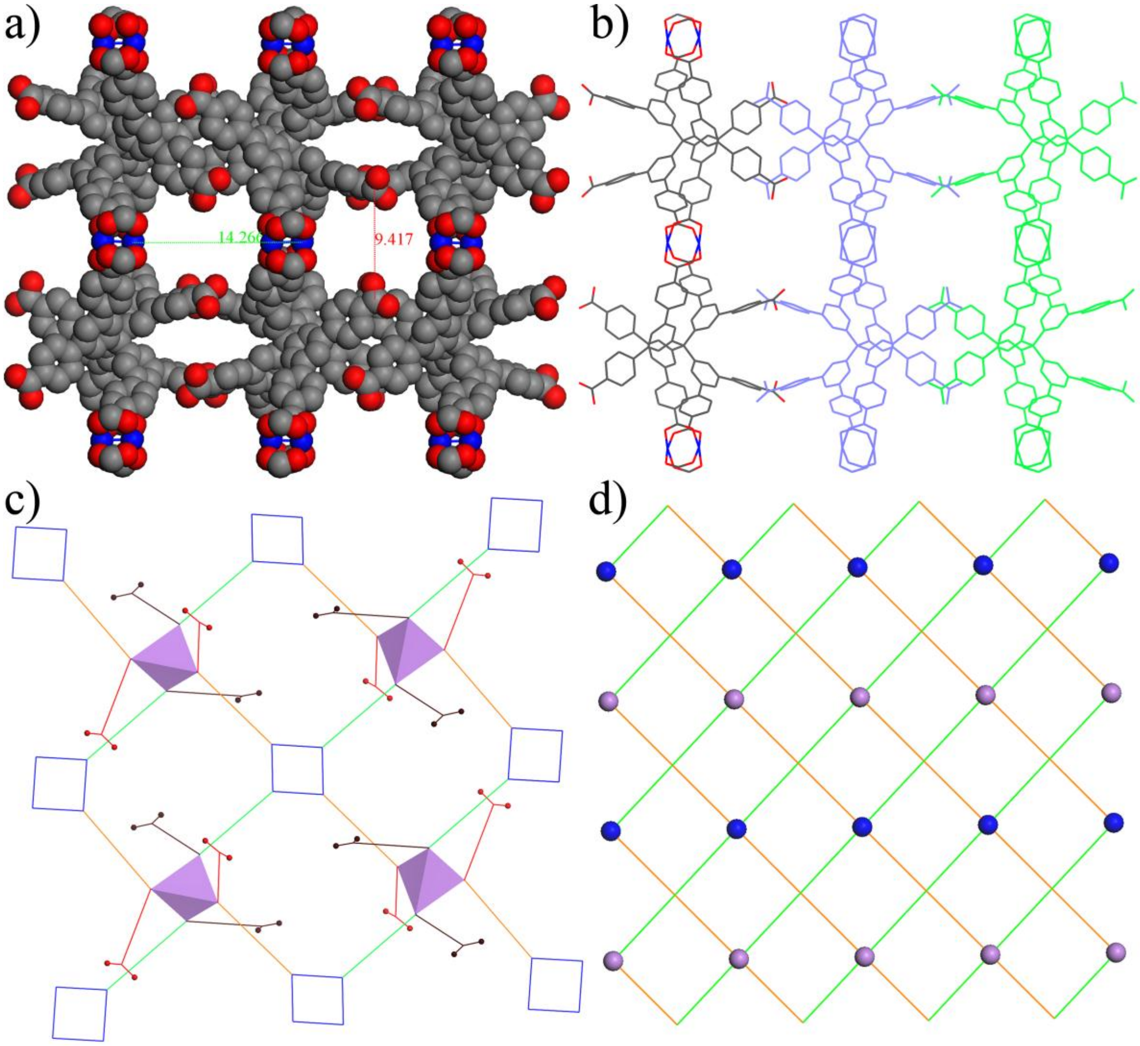


Figure S11. a) Space filling model of **1** showing the largest pore size in **1**. b) Side view of the 2D layer structure along the *c* axis. c) Schematic representation of the octacaboxylate ligand **L** (purple tetrahedra) and copper paddle wheels (blue squares). d) Simplified network connectivity showing the **sql** plane topology for **1** (organic ligand node: purple; $[Cu_2(O_2CR)_4]$ paddlewheel node: blue).

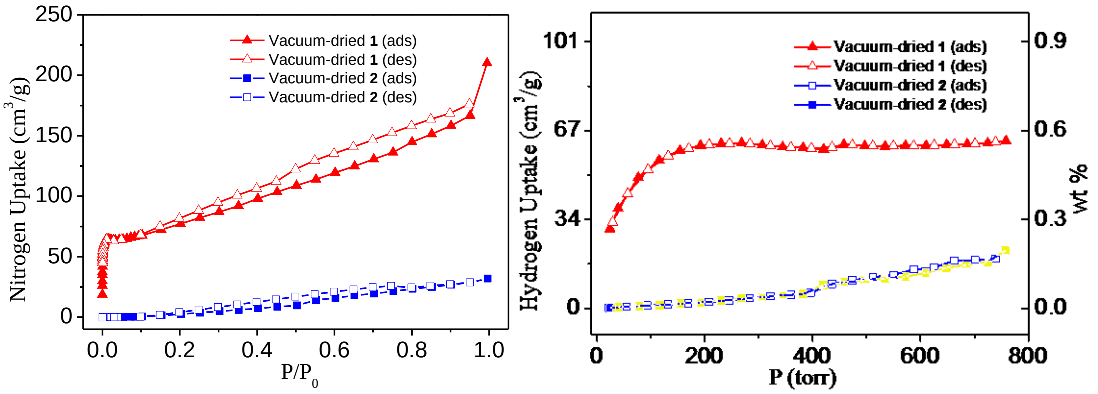


Figure S12. Nitrogen and hydrogen isotherms of vacuum-dried **1** and **2**.

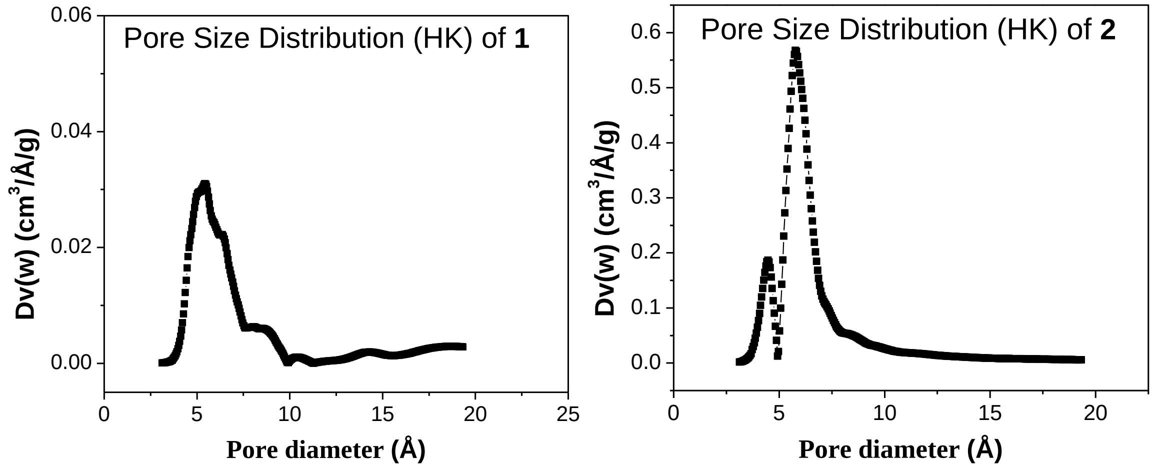
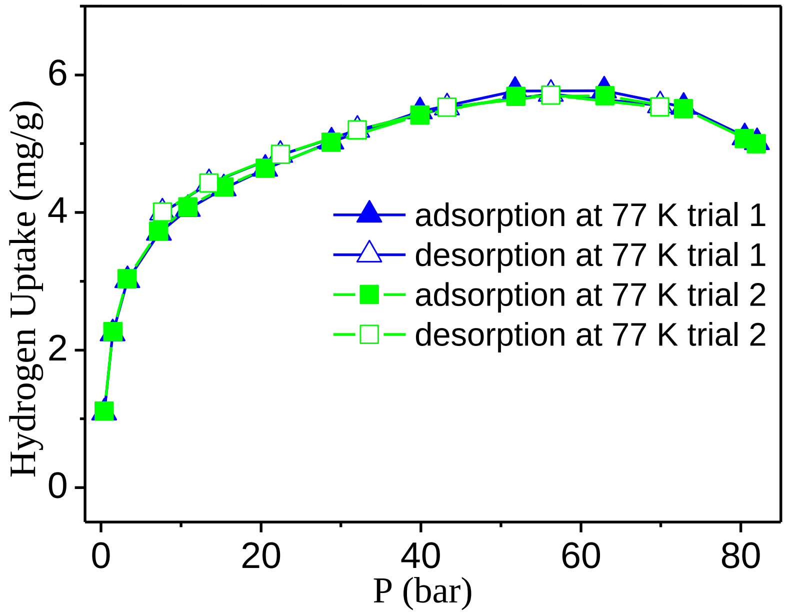


Figure S13. HK method pore size distribution of **1** and **2**.



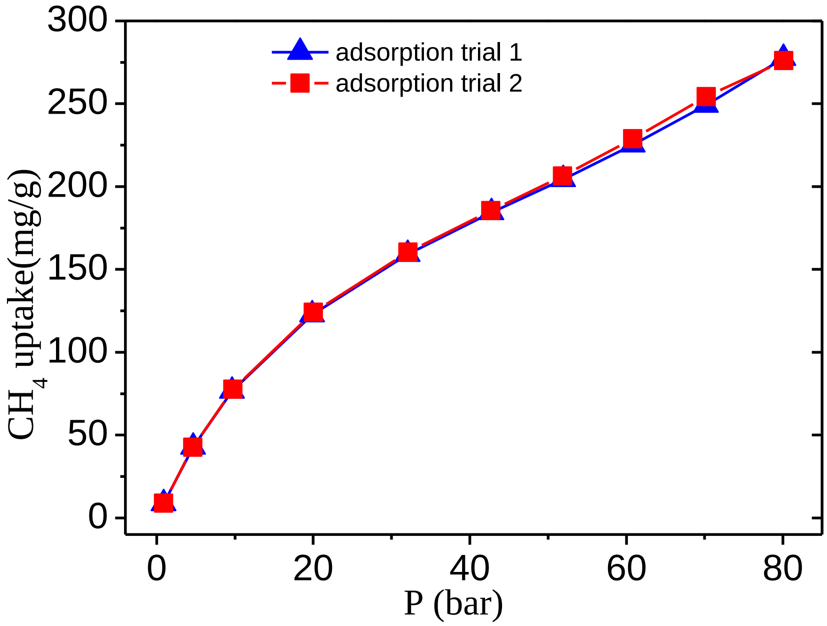


Figure S14. Plots of the first and second cycles of high-pressure hydrogen and methane uptake by **2** at 77 K and 298 K, respectively, showing good reproducibility and high stability of **2**.

References:

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