

Supporting Information

High Methane Storage Capacity in Aluminum Metal-Organic Frameworks

Felipe Gándara, Hiroyasu Furukawa, Seungkyu Lee, and Omar M. Yaghi*

Department of Chemistry, University of California-Berkeley, Materials Sciences Division,
Lawrence Berkeley National Laboratory, and Kavli Energy NanoSciences Institute at
Berkeley, Berkeley, California 94720, United States

*To whom correspondence should be addressed: Email, yaghi@berkeley.edu

Table of Contents

Section S1 Syntheses of Materials	S2
Section S2 Single Crystal X-ray Diffraction Analyses	S5
Section S3 Powder X-ray diffraction patterns	S8
Section S4 Thermal Gravimetric Analyses	S10
Section S5 Gas Adsorption	S11
Section S6 Complete Reference 9.....	S19
Section S7 References.....	S20

Section S1 Syntheses of Materials

Methods:

Chemicals used in this work. *N,N*-Dimethylformamide (DMF), formic acid (purity > 98%) was obtained from EMD Millipore Chemicals; anhydrous acetone was obtained from Acros Organics; Aluminum nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, purity $\geq 98\%$] was obtained from Sigma-Aldrich Co. 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid, H_3BTB , was obtained from TCI America. Nitric acid (70%) was obtained from Sigma-Aldrich.

Analytical techniques. Single-crystal X-ray diffraction (SXRD) data were collected on a Bruker D8-Venture diffractometer equipped with Mo- ($\lambda = 0.71073 \text{ \AA}$) and Cu-target ($\lambda = 1.54184 \text{ \AA}$) micro-focus X-ray tubes and a PHOTON 100 CMOS detector. Additional data was collected using synchrotron radiation in the beamline 11.3.1 of the Advanced Light Source, LBNL. Powder X-ray diffraction patterns (PXRD) were recorded using a Bruker D8 Advance diffractometer (Göbel-mirror monochromated Cu $K\alpha$ radiation $\lambda = 1.54056 \text{ \AA}$). Elemental microanalyses (EA) were performed in the Microanalytical Laboratory of the College of Chemistry at UC Berkeley, using a Perkin Elmer 2400 Series II CHNS elemental analyzer. Thermal gravimetric analysis (TGA) curves were recorded in-house on a TA Q500 thermal analysis system under N_2 flow. Low-pressure gas (N_2 and CH_4) adsorption isotherms were recorded in-house on a Quantachrome Autosorb-1 volumetric gas adsorption analyzer. High-pressure methane adsorption isotherms for MOF-519 and MOF-520 equilibrium gas adsorption isotherms were measured using the static volumetric method in an HPA-100 from the VTI Corporation (currently Particulate Systems). Ultra-high-purity grade N_2 , CH_4 , and He (99.999% purity) gases were used throughout the gas adsorption experiments. A liquid nitrogen bath was used for the measurements at 77 K. A water circulator was used for adsorption measurements at 273, 283, and 298 K.

Synthesis and Characterization of MOFs:

Synthesis and activation of MOF-519. 109 mg of H₃BTB were dissolved in 9 mL of anhydrous DMF. A freshly prepared 0.2 M stock solution of aluminum nitrate in DMF (0.675 mL) was added, followed by the addition of 0.675 mL of nitric acid. The Teflon vessel was then sealed and placed in a stainless steel Parr autoclave. The autoclave was placed in an oven preheated at 150 °C, and kept in the oven for 72 hours. After that, it was cooled down to room temperature. A white product was obtained, which was separated from the mother liquid by centrifugation at 4400 rpm for 10 minutes. The solid was then washed with 10 mL of anhydrous DMF and centrifuged two times. Then it was immersed in 12 mL of anhydrous acetone. The acetone was exchanged five times over a period of 48 hours. The solid was then transferred to a cellulose extraction thimble which was placed in a Tousimis supercritical point dryer, and immersed in liquid CO₂. The CO₂ was replaced five times over a period of 4 hours. The CO₂ was taken to supercritical conditions and it was slowly bled overnight. E.A.: Found (wt%): C: 59.98; H: 3.92; N: < 0.2. Calculated for [Al₈(OH)₈(BTB)₄(H₂BTB)₄]·22H₂O = C: 61.32; H: 4.10; N: 0.0. The amount of water included in the calculated formula corresponds to a 9.3 wt%, which is consistent with the 9% mass loss at $T = 100$ °C observed in the TGA curve of this sample (see Figure S3).

For the obtaining of a single-crystal of MOF-519, 10.9 mg of H₃BTB were dissolved in 0.45 mL of anhydrous DMF. A freshly prepared 0.065 M stock solution of aluminum nitrate in DMF (0.2 mL) was added, followed by the addition of 0.150 mL of nitric acid. The Teflon vessel was then sealed and placed in a stainless steel Parr autoclave. The autoclave was placed in an oven preheated at 150 °C, and kept in the oven for 72 hours. After that, it was cooled down to room temperature.

Synthesis and activation of MOF-520. H₃BTB (75 mg) was dissolved in 2 mL of DMF. A freshly prepared 0.02 M stock solution of aluminum nitrate in DMF (2 mL) was added,

followed by the addition of 13 mL of DMF and 1.4 mL of formic acid. The 20-mL vial was placed in an oven preheated at 130 °C, and kept in the oven for 72 hours. After that, it was cooled down to room temperature. The obtained single crystals were washed with 20 mL of DMF three times. Then it was immersed in 20 mL of acetone. The acetone was exchanged five times over a period of 48 hours. The single crystals were then transferred to a cellulose extraction thimble which was placed in a Tousimis supercritical point dryer, and immersed in liquid CO₂. The CO₂ was replaced five times over a period of 4 hours. The CO₂ was taken to supercritical conditions and it was slowly bled overnight. Finally, the single crystals were fully activated by heating at 120 °C under vacuum at 30 mTorr for 3 hours E.A.: Found (wt%): C: 59.20; H: 3.20; N: < 0.2. Calculated for Al₈(OH)₈(OOCH)₄(BTB)₄ = C: 58.81; H: 3.14; N: 0.0.

Section S2 Single Crystal X-ray Diffraction Analyses

MOF-519. A crystal of MOF-519 was collected at the beamline 24-ID-C at Advanced Photon Source (Argonne National Laboratory). A crystal of $0.04 \times 0.02 \times 0.02$ mm of dimensions was selected, and data was collected with wavelength = 0.8903 \AA , to a maximum resolution of 1.0 \AA . All the tested specimens were found to be twinned. The structure was solved in the tetragonal space group $P4_22_12$ using direct methods as implemented in SIR2008.¹ Full-matrix least-squares refinements on F^2 were carried out using ShelXL² and OLEX2.³ After location of all the framework atoms in the difference Fourier maps, the squeeze routine in PLATON⁴ was run and additional refinements were carried out. The framework atoms were refined anisotropically, while the atoms belonging to the dangling H₂BTB molecules were kept isotropic because they exhibited large ADP parameters, which we attribute to the different rotational degrees of freedom for these molecules. The limited resolution and the low diffracting quality of the specimens resulted in the presence of A alerts in the checkcif file regarding to the value of $\sin\theta/\lambda$ being smaller than 0.55 and to the presence of isotropic atoms in the asymmetric units, as explained above.

Table S1. Crystal data and structure refinement for MOF-519.

Identification code	MOF-519	
Empirical formula	$C_{216} H_{60} Al_8 O_{56}$	
Formula weight	3766.48	
Temperature	293(2) K	
Wavelength	0.89030 Å	
Crystal system	Tetragonal	
Space group	$P4_22_12$	
Unit cell dimensions	$a = 19.2800(10)$ Å	$\alpha = 90^\circ$.
	$b = 19.2800(10)$ Å	$\beta = 90^\circ$.
	$c = 36.0300(10)$ Å	$\gamma = 90^\circ$.
Volume	$13393.0(11)$ Å ³	
Z	2	
Density (calculated)	0.934 Mg/m ³	
Absorption coefficient	0.168 mm ⁻¹	
F(000)	3816	
Crystal size	$0.04 \times 0.02 \times 0.02$ mm ³	
Theta range for data collection	1.94 to 26.40°.	
Index ranges	$-19 \leq h \leq 19$, $-18 \leq k \leq 19$, $-35 \leq l \leq 35$	
Reflections collected	41675	
Independent reflections	6936 [R(int) = 0.1712]	
Completeness to theta = 26.40°	99.2%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6936 / 12 / 369	
Goodness-of-fit on F ²	1.057	
Final R indices [I > 2sigma(I)]	R1 = 0.1112, wR2 = 0.2792	
R indices (all data)	R1 = 0.1222, wR2 = 0.2892	
Absolute structure parameter	0.0(11)	
Largest diff. peak and hole	0.535 and -0.772 e·Å ⁻³	

MOF-520. An acetone-exchanged crystal of MOF-520 was collected at the beamline 11.3.1 at Advanced Light Source (Lawrence Berkeley National Laboratory). A crystal of $0.1 \times 0.06 \times 0.04$ mm of dimensions was selected, and data was collected with wavelength = 0.95403 \AA , to a maximum resolution of 0.9 \AA . The structure was solved in the tetragonal space group $P4_22_12$ using direct methods as implemented in Shelx. Full-matrix least-squares refinements on F^2 were carried out using ShelXL and OLEX2. Initially, a Flack parameter of 0.5 was found, which indicates the presence of both enantiomers in the crystal. In the final refinement, the BASF parameter was refined resulting in a value of 0.38(0.17).

Table S2. Crystal data and structure refinement for MOF-520.

Identification code	MOF-520	
Empirical formula	$\text{C}_{115} \text{H}_{76} \text{Al}_8 \text{O}_{41}$	
Formula weight	2329.59	
Temperature	100 K	
Crystal system	Tetragonal	
Space group	$P4_22_12$	
Unit cell dimensions	$a = 18.878(4) \text{ \AA}$	$\alpha = 90^\circ$.
	$b = 18.878(4) \text{ \AA}$	$\beta = 90^\circ$.
	$c = 37.043(8) \text{ \AA}$	$\gamma = 90^\circ$.
Z	2	
Density (calculated)	0.586 Mg/m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	2396.0	
Crystal size	$0.08 \times 0.03 \times 0.02 \text{ mm}^3$	
Radiation	0.95403 \AA	
2Θ range for data collection	5.292 to 64.06°	
Index ranges	$-18 \leq h \leq 20, -17 \leq k \leq 20, -41 \leq l \leq 40,$	
Reflections collected	45424	
Independent reflections	9440 [Rint = 0.0829, Rsigma = 0.0667]	
Data/restraints/parameters	9440/0/372	
Goodness-of-fit on F^2	1.173	
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0887, wR2 = 0.2547	
Final R indexes [all data]	R1 = 0.1055, wR2 = 0.2734	
Largest diff. peak/hole	$1.00/-0.52 \text{ e} \cdot \text{\AA}^{-3}$	
Flack parameter	0.4(2)	

Section S3 Powder X-ray diffraction patterns

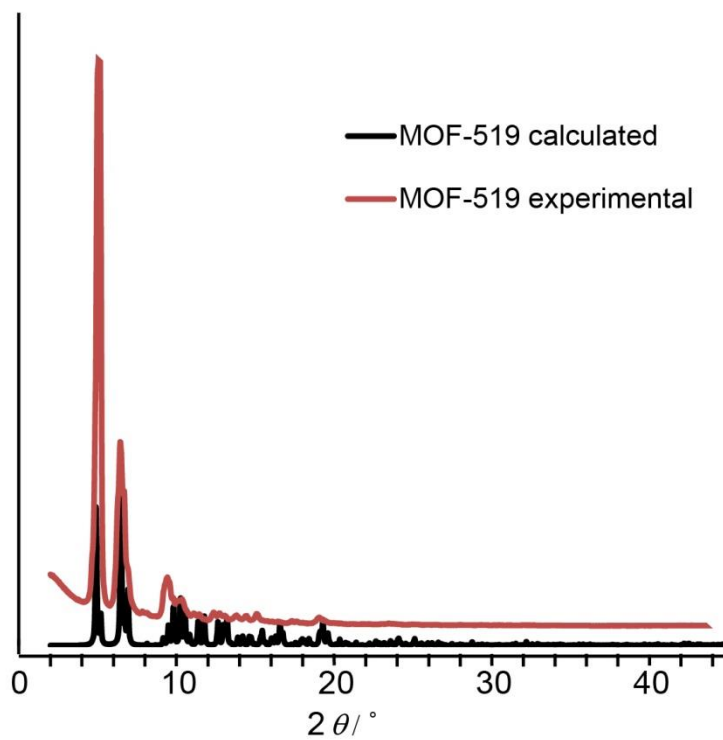


Figure S1. Comparison of the experimental (red) powder diffraction pattern of MOF-519 with the one calculated from the single crystal structure (black).

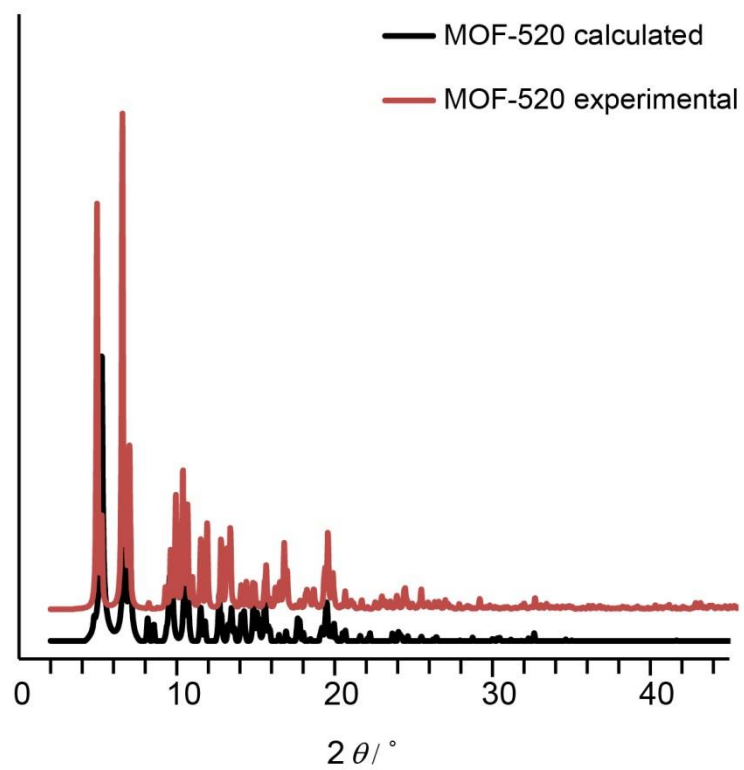


Figure S2. Comparison of the experimental (red) powder diffraction pattern of MOF-520 with the one calculated from the single crystal structure (black).

Section S4 Thermal Gravimetric Analyses

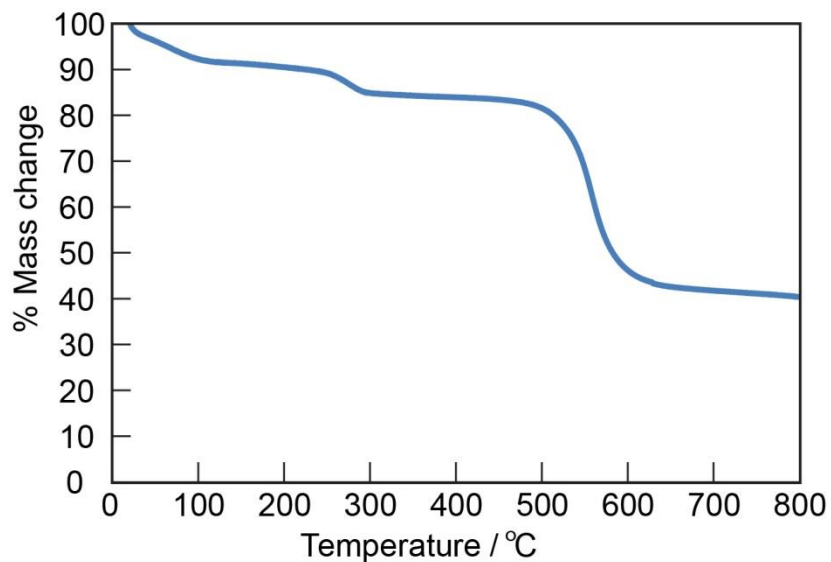


Figure S3. TGA curve of MOF-519 under N₂ flow.

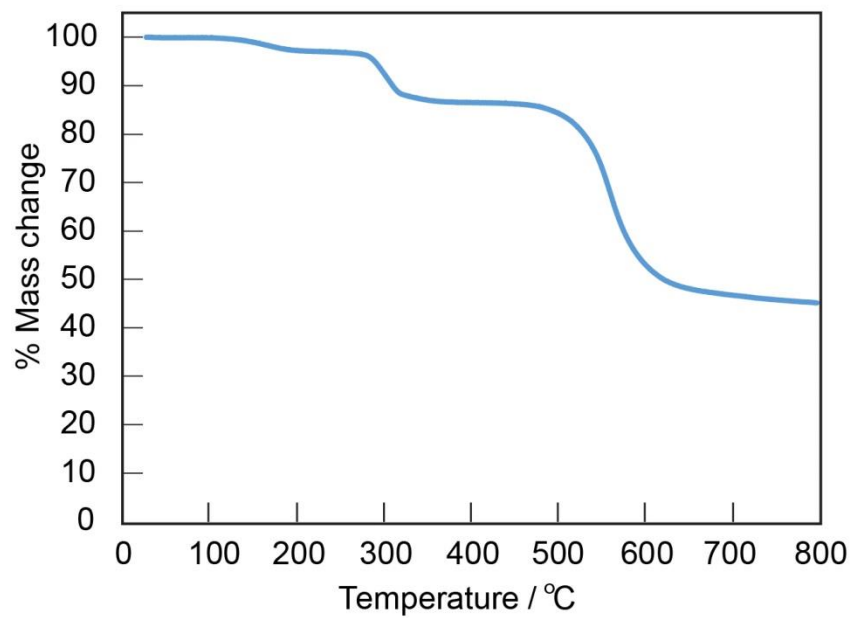


Figure S4. TGA curve of MOF-520 under N₂ flow.

Section S5 Gas Adsorption

Low-pressure N₂ and methane adsorption measurements. In the case of MOF-519, we include two independent measurements carried out with two different sample batches that were prepared under the same conditions. The measurements were performed 22 months apart.

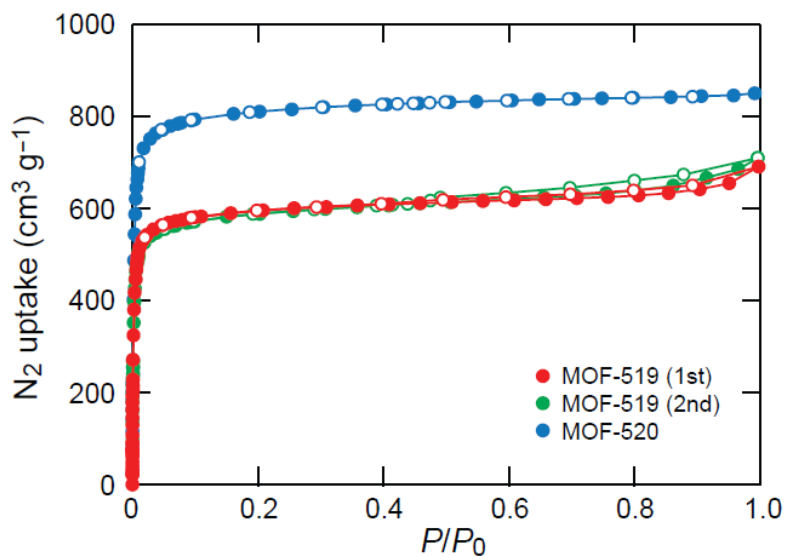


Figure S5. N₂ isotherms of two sample batches of MOF-519 measured at 77 K, where materials were prepared independently but under the same procedure, and of MOF-520.

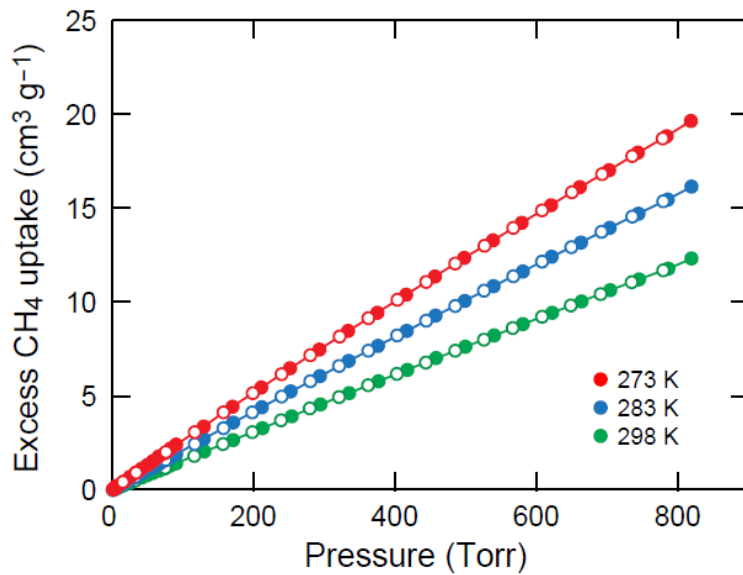


Figure S6. Excess methane isotherms of MOF-519 for sample batch 2, at 273 (red), 283 (blue), and 298 K (green), respectively.

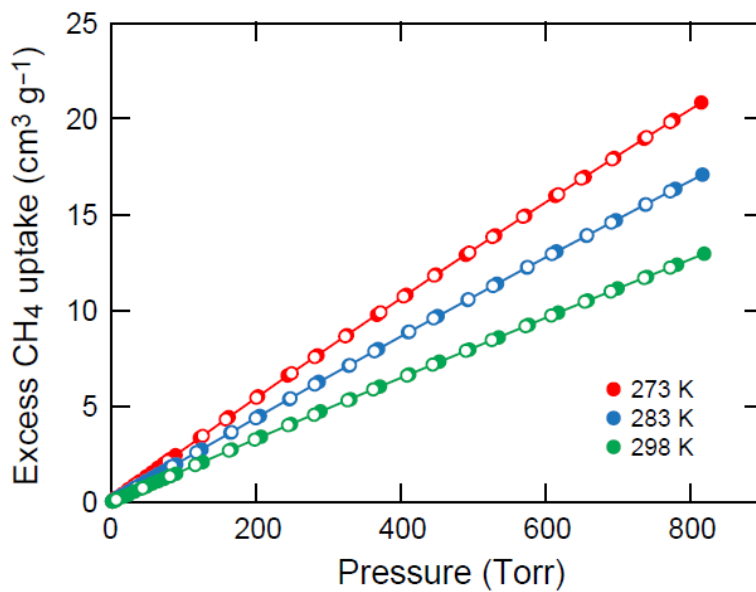


Figure S7. Excess methane isotherms of MOF-520 at 273 (red), 283 (blue), and 298 K (green), respectively.

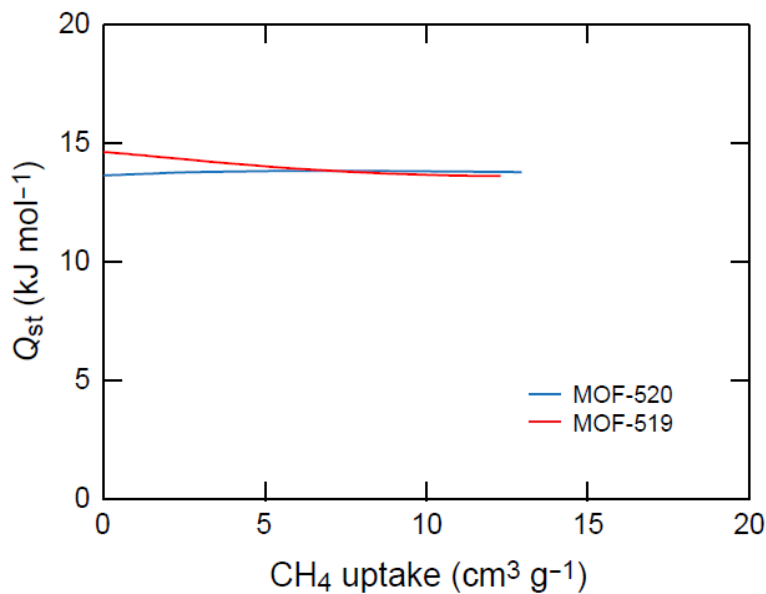


Figure S8. Isosteric heats of adsorption (Q_{st}) for methane in MOF-519 (red) and 520 (blue) calculated from fits of their 273, 283, and 298 K isotherms.

High-pressure methane adsorption measurements. High-pressure methane adsorption isotherms for MOF-519 and 520 equilibrium gas adsorption isotherms were measured using the static volumetric method in an HPA-100 from the VTI Corporation (currently Particulate Systems). Ultra-high-purity grade CH₄ and He (99.999% purity) gases were used throughout the high-pressure adsorption experiments. A water circulator was used for adsorption measurements at 298 K. In the case of MOF-519, we include two independent measurements carried out with two different sample batches that were prepared under the same conditions. The measurements were performed 22 months apart.

Estimation of total methane uptake. The total methane uptake was estimated using a simple equation, since it is not possible to estimate experimentally: (total uptake) = (excess uptake) + (bulk density of methane) × (pore volume). The dual-site Langmuir model [$V_1 \times K_1P/(1 + K_1P) + V_2 \times K_2P/(1 + K_2P)$] was used to estimate the methane uptake up to 250 bar, where V_1 , V_2 , K_1 , and K_2 are parameters and P is pressure.

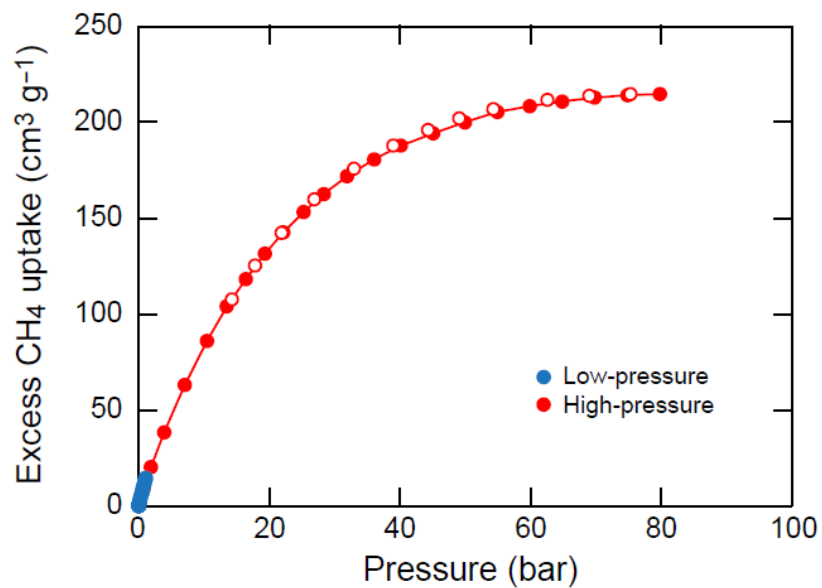


Figure S9. Excess methane isotherm of MOF-519 batch 1 at 298 K (red). Low-pressure isotherm (blue) was overlaid for comparison.

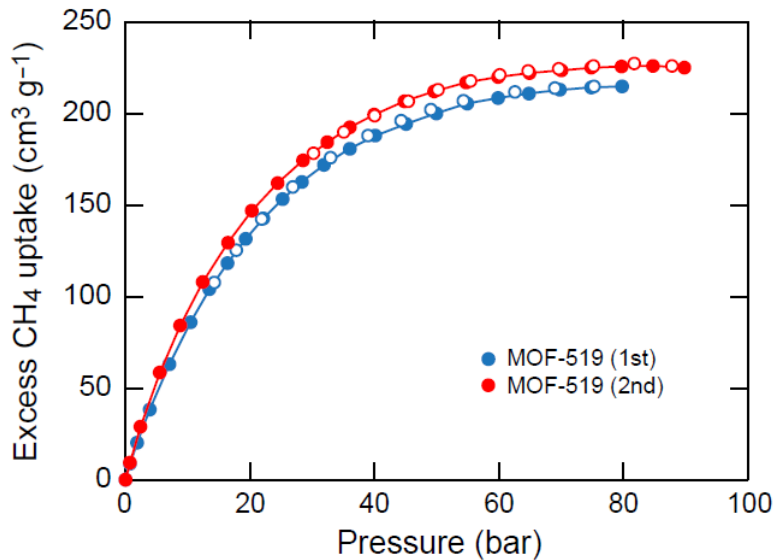


Figure S10. Excess methane isotherms of MOF-519 measured at 298 K, where materials were prepared independently but under the same procedure.

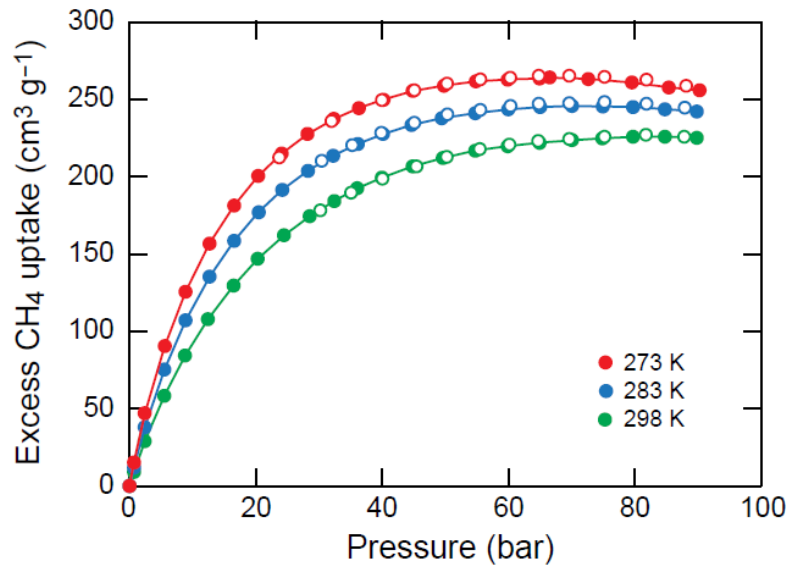


Figure S11. Excess methane isotherms of sample batch 2 of MOF-519 measured at 273 K (red), 283 K (blue), and 298 K (green).

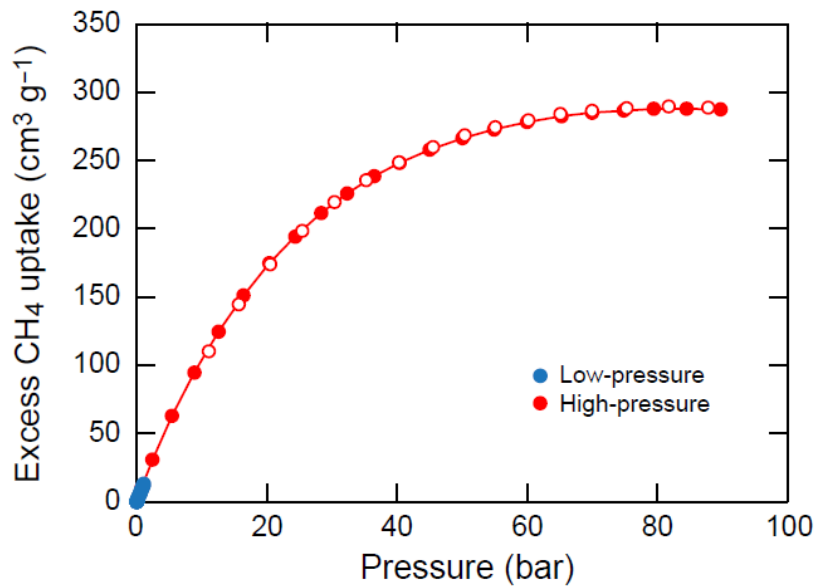


Figure S12. Excess methane isotherm of MOF-520 at 298 K (red). Low-pressure isotherm (blue) was overlaid for comparison.

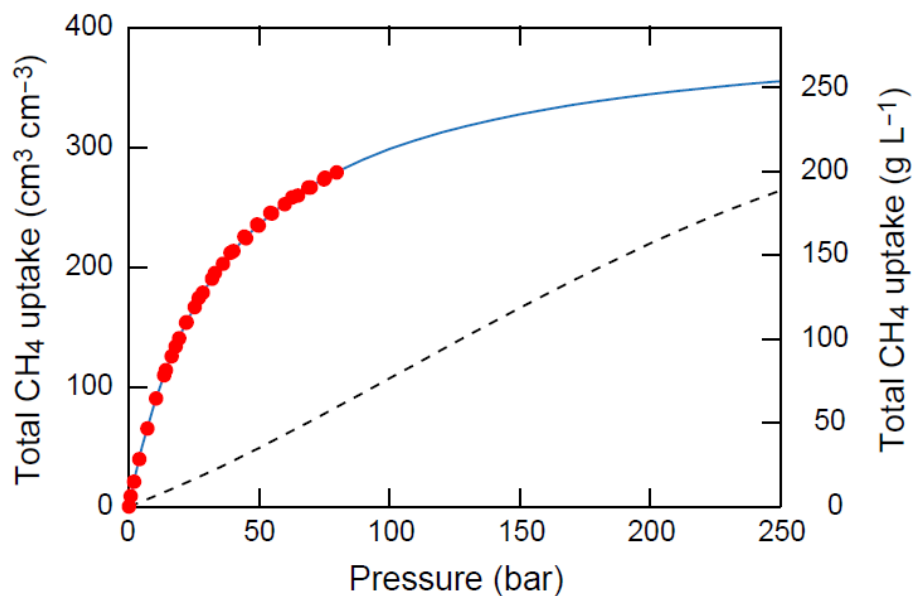


Figure S13. Total methane isotherm of sample batch 1 of MOF-519 (red circles) at 298 K and calculated isotherm from the dual site Langmuir model (blue). Bulk density of methane is overlaid (broken curve).

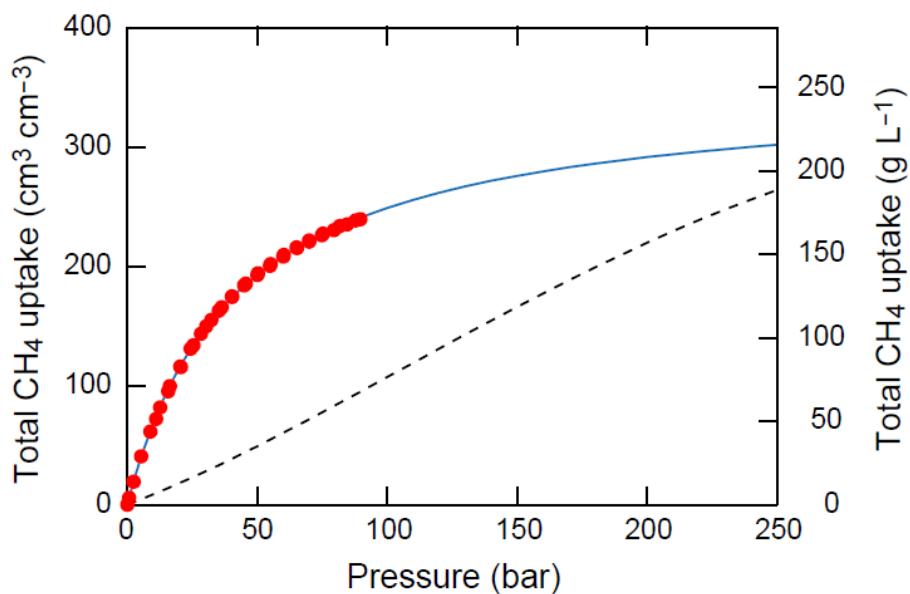


Figure S14. Total methane isotherm of MOF-520 (red circles) at 298 K and calculated isotherm from the dual site Langmuir model (blue). Bulk density of methane is overlaid (broken curve).

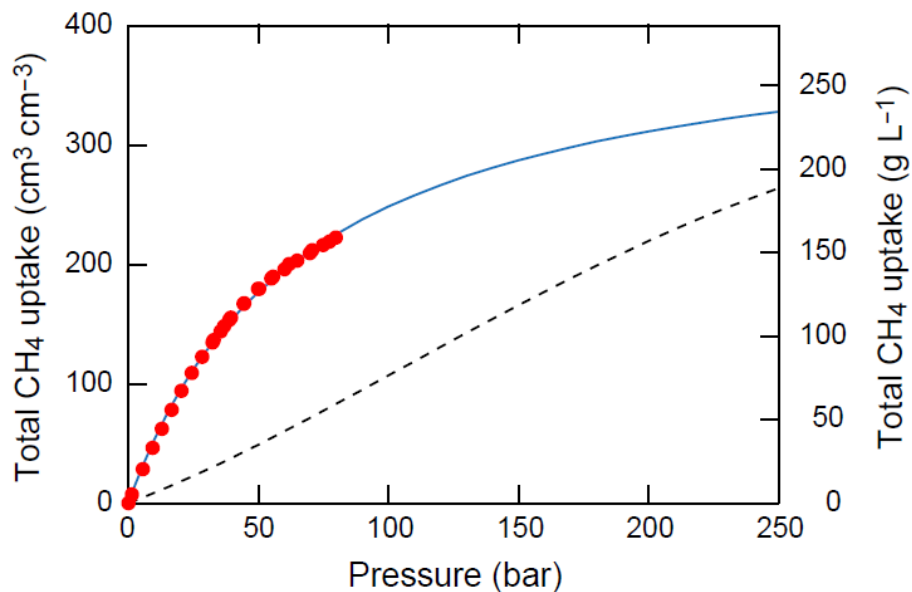


Figure S15. Total methane isotherm of MOF-5 (red circles, data from Ref. 9) at 298 K and calculated isotherm from the dual site Langmuir model (blue). Bulk density of methane is overlaid (broken curve).

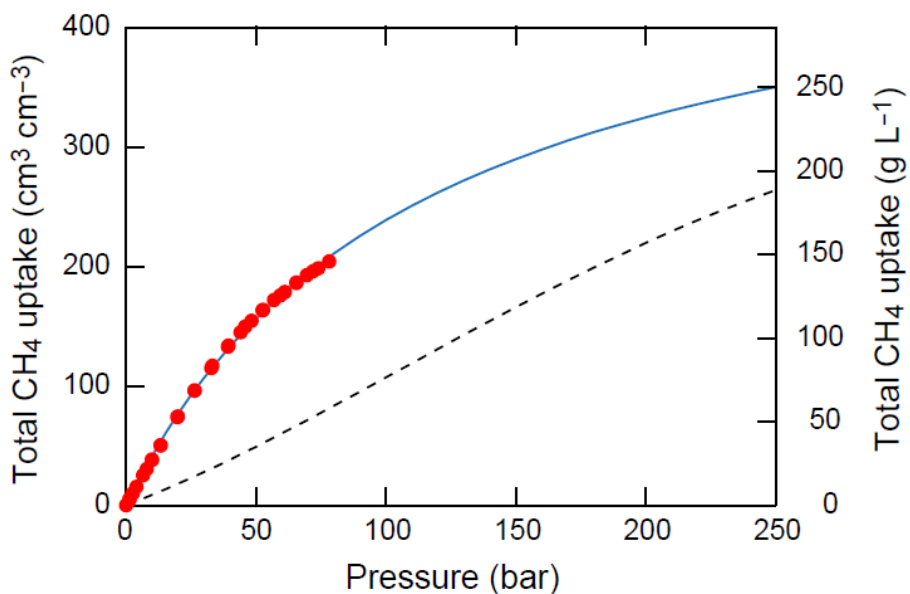


Figure S16. Total methane isotherm of MOF-177 (red circles, data from Ref. 9) at 298 K and calculated isotherm from the dual site Langmuir model (blue). Bulk density of methane is overlaid (broken curve).

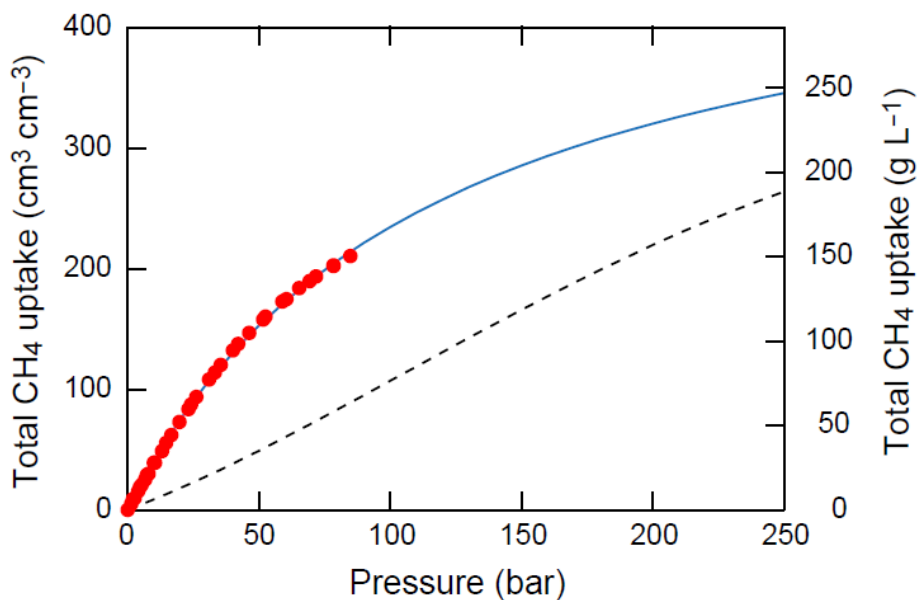


Figure S17. Total methane isotherm of MOF-205 (red circles, data from Ref. 9) at 298 K and calculated isotherm from the dual site Langmuir model (blue). Bulk density of methane is overlaid (broken curve).

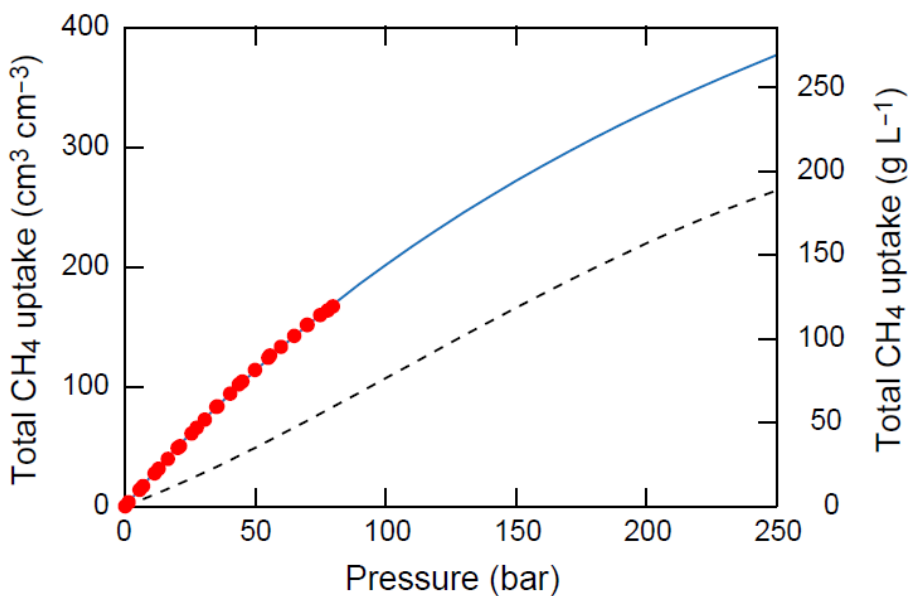


Figure S18. Total methane isotherm of MOF-210 (red circles, data from Ref. 9) at 298 K and calculated isotherm from the dual site Langmuir model (blue). Bulk density of methane is overlaid (broken curve).

Section S6 Complete Reference 9

Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. O.; Snurr, R. Q.; O'Keeffe, M.; Kim, J.; Yaghi, O. M. *Science*, **2010**, *239*, 424-428.

Section S7 References

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- (1) (a) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R., SIR2004: an improved tool for crystal structure determination and refinement. *Journal of Applied Crystallography* **2005**, *38*, 381. (b) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Spagna, R., SIR2011: a new package for crystal structure determination and refinement. *Journal of Applied Crystallography* **2012**, *45*, 357.
- (2) Sheldrick, G. M., A short history of SHELX. *Acta Crystallographica Section A* **2008**, *64*, 112.
- (3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *Journal of Applied Crystallography* **2009**, *42*, 339.
- (4) Spek, A., Structure validation in chemical crystallography. *Acta Crystallographica Section D-Biological Crystallography* **2009**, *65*, 148.