# Supporting Information for:

# Evaluating metal-organic frameworks for natural gas storage

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# 1. Experimental

#### **General information**

Anhydrous dichloromethane and N,N-dimethylformamide were obtained from a Vac anhydrous solvent system. The ligand 5,5'-(9,10-anthracenediyl)-di-isophthalic acid (H<sub>4</sub>adip) was synthesized according to a literature procedure.<sup>1</sup> The AX-21 carbon was purchased from a commercial vendor and activated at 200 °C under vacuum for 24 h prior to use. All other reagents were obtained from commercial vendors and used without further purification. UHP-grade (99.999% purity) helium, nitrogen, and methane were used for all adsorption measurements. Infrared spectra were obtained on a Perkin-Elmer Spectrum 100 Optica FTIR spectrometer furnished with an attenuated total reflectance accessory. Diffraction data were collected with 0.02° steps using a Bruker AXS D8 Advance diffractometer equipped with Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å), a Göbel mirror, a Lynxeye linear position-sensitive detector, and mounting the following optics: fixed divergence slit (0.6 mm), receiving slit (3 mm), and secondary beam Soller slits (2.5°). The generator was set at 40 kV and 40 mA.

#### Low-pressure gas adsorption measurements

Gas adsorption isotherms for pressures in the range 0-1.1 bar were measured using a Micromeritics ASAP 2020 instrument. For standard measurements in ASAP low-pressure glass sample holders, activated samples were transferred under a  $N_2$  atmosphere to preweighed analysis tubes, which were capped with a Transeal. The samples were evacuated on the ASAP until the outgas rate was less than 3 µbar/min. The evacuated analysis tubes containing degassed samples were then carefully transferred to an electronic balance and weighed to determine the mass of sample (typically 100-200 mg). The tube was fitted with an isothermal jacket and transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 3 µbar/min.

Langmuir surface areas and pore volumes were determined by measuring  $N_2$  adsorption isotherms in a 77 K liquid  $N_2$  bath and calculated using the Micromeritics software, assuming a value of 16.2 Å<sup>2</sup> for the molecular cross-sectional area of  $N_2$ .

#### Metal-organic framework synthesis

 $Ni_2(dobdc)$  (Ni-MOF-74, CPO-27-Ni;  $dobdc^{4-} = 2,5$ -dioxido-1,4-benzenedicarboxylate)

The compound Ni<sub>2</sub>(dobdc) was synthesized and activated using a strategy adopted from previous reports.<sup>2</sup> Specifically, H<sub>4</sub>dobdc (1.42 g, 7.2 mmol) and Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (5.23 g, 18 mmol) were combined with 350 mL of anhydrous dimethylformamide (DMF) and 42 mL of anhydrous methanol (MeOH) in a 500 mL Schlenk flask under N<sub>2</sub>. The solution was heated at 120 °C under a positive N<sub>2</sub> pressure with stirring for 18 h. After cooling, the resulting yellow-orange precipitate settled to the bottom of the Schlenk flask, and the reaction solvent was removed via cannula, replaced with fresh DMF, and heated to 100 °C for 5-6 h. The DMF was replaced with fresh DMF two additional times. The DMF was replaced with fresh MeOH, and the mixture was heated to 60 °C for 5-6 h. The MeOH was replaced with fresh MeOH two additional times. The majority of MeOH was then removed via cannula, and the resulting bright

orange compound was activated at 180 °C under vacuum for 24-48 hr to yield 1.5 g of desolvated  $Ni_2$ (dobdc). Note that while the solvent exchanges were conducted under  $N_2$ , anhydrous solvents were not used. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface area to those previously reported (see Figs. S1, S7).

#### *Co*<sub>2</sub>(*dobdc*) (*Co*-*MOF*-74, *CPO*-27-*Co*)

The compound  $Co_2(dobdc)$  was synthesized and activated using a strategy adopted from a previous report.<sup>2a</sup> Specifically, H<sub>4</sub>dobdc (0.964 g, 4.9 mmol) and  $Co(NO_3)_2 \cdot 6H_2O$  (4.754 g, 16.3 mmol) were combined with a 1:1:1 (v/v/v) mixture of DMF:ethanol:H<sub>2</sub>O (400 mL) in a 1 L jar, sparged with N<sub>2</sub> for 1 h, and heated at 100 °C for 24 h. Following the reaction, the resulting redviolet crystals were collected by filtration and washed repeatedly with DMF. The compound was then soaked in DMF at 120 °C for 5-6 h. The DMF was decanted, replaced with fresh DMF, and again heated to 120 °C for 5-6 h. This was repeated one additional time. Then, the DMF was decanted and replaced by MeOH, which was heated to 60 °C for 5-6 h. This was repeated 2 additional times. The final product was collected by filtration and then activated under vacuum at 180 °C for 24-48 h. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported (see Figs. S2, S8).

#### Mg<sub>2</sub>(dobdc) (Mg-MOF-74, CPO-27-Mg)

The compound Mg<sub>2</sub>(dobdc) was synthesized and activated using a strategy adopted from previous reports.<sup>2a,3</sup> Specifically, H<sub>4</sub>dobdc (1.11 g, 5.6 mmol) and Mg(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (4.75 g, 18.6 mmol) were dissolved in a 15:1:1 (v/v/v) mixture of DMF:ethanol:H<sub>2</sub>O (500 mL) and sparged with N<sub>2</sub> for 1 h. The resulting solution was evenly distributed into thirty-eight 20 mL vials, which were sealed with Teflon-lined caps and heated to 120 °C for 8 h. Following the reaction, the resulting yellow microcrystalline material was collected by filtration and washed repeatedly with DMF. The solid was then soaked in DMF at 120 °C for 5-6 h. The DMF was decanted, replaced with fresh DMF, and again heated to 120 °C for 5-6 h. This was repeated one additional time. Then, the DMF was decanted and replaced by MeOH, which was heated to 60 °C for 5-6 h. This was repeated 2-3 additional times, until the DMF C=O stretch (~1650 cm<sup>-1</sup>) was no longer observed in the infrared spectrum. The resulting dark yellow powder was collected by filtration and then activated under vacuum at 180 °C for 24-48 h. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported (see Figs. S3, S9).

#### $Cu_3(btc)_2$ (HKUST-1; $btc^{3-} = 1,3,5$ -benzenetricarboxylate)

The compound HKUST-1 was synthesized and activated using a strategy adopted from a previous report.<sup>4</sup> Specifically,  $Cu(NO_3)_2 \cdot 2.5H_2O$  (2.4 g, 10.3 mmol) was dissolved in 30 mL deionized H<sub>2</sub>O, and 1,3,5-benzenetricarboxylic acid (0.68 g, 3.2 mmol) was dissolved in 30 mL ethanol. The two solutions were combined in a 250 mL one-neck round-bottom flask. DMF

(2 mL) was added, and the flask was sealed with a rubber septum. The reaction mixture was heated at 80 °C for 24 h with stirring. The resulting light blue compound was filtered and washed with H<sub>2</sub>O and EtOH. The product was further suspended in EtOH at 55 °C for 12 h. The EtOH was removed, fresh EtOH was added, and the suspension was again heated at 55 °C for 12 h. The final product was collected by filtration and activated by heating at 150 °C under vacuum for 24 h. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported (see Figs. S4, S10).

## $Cu_2(adip)$ (PCN-14; $adip^{4-} = 5,5'-(9,10-anthracenediyl)-di-isophthalate)$

The compound PCN-14 was synthesized and activated using a strategy adopted from a previous report.<sup>5</sup> Specifically, H<sub>4</sub>adip (0.6 g, 1.2 mmol) and Cu(NO<sub>3</sub>)<sub>2</sub>•2.5H<sub>2</sub>O (2.4 g, 10.3 mmol) were fully dissolved in DMF (180 mL) with 10 drops of HBF<sub>4</sub>. The solution was evenly distributed into twenty-found 20 mL vials, which were sealed with Teflon-lined caps and heated to 75 °C for 24 h. The resulting green powder was collected by filtration and washed with DMF. The product was further suspended in DMF for 12 h at room temperature, then the DMF was exchanged with MeOH. After 6 h, the MeOH was decanted and replaced with fresh MeOH. This was repeated one further time. The final product was collected by filtration and activated by heating at 120 °C under vacuum for 24 h. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported (see Figs. S5, S11-S13).

#### $Zn_4O(bdc)_3$ (MOF-5, IRMOF-1; $bdc^{2-} = 1,4$ -benzenedicarboxylate)

The compound MOF-5 was synthesized and activated using a strategy adopted from a previous report.<sup>6</sup> Specifically, H<sub>2</sub>bdc (0.66 g, 4.0 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (3.6 g, 12.1 mmol), and diethylformamide (100 mL) were combined in a 250 mL Schlenk flask sealed with a rubber septum. The Schlenk flask was heated at 90 °C for 24 h, then placed under N<sub>2</sub>, and the reaction solvent was removed via cannula and replaced with anhydrous DMF at room temperature. The DMF was exchanged with fresh, anhydrous DMF two further times. The DMF was then exchanged with anhydrous dichloromethane (DCM) at room temperature. The DCM was removed via cannula. The resulting clear, cubic crystals were activated by heating at 150 °C under vacuum for 24 h. The successful synthesis and activation of the framework was confirmed by comparing the X-ray powder diffraction pattern and Langmuir surface areas to those previously reported (see Figs. S6, S14).

# 2. Powder X-ray diffraction



**Fig. S1** Powder X-ray diffraction pattern of as-synthesized Ni<sub>2</sub>(dobdc) ( $\lambda = 1.5418$  Å). Calculated peak positions from the crystal structure are shown (blue tick marks).



**Fig. S2** Powder X-ray diffraction pattern of as-synthesized Co<sub>2</sub>(dobdc) ( $\lambda = 1.5418$  Å). Calculated peak positions from the crystal structure are shown (blue tick marks).



**Fig. S3** Powder X-ray diffraction pattern of as-synthesized Mg<sub>2</sub>(dobdc) ( $\lambda = 1.5418$  Å). Calculated peak positions from the crystal structure are shown (blue tick marks).



**Fig. S4** Powder X-ray diffraction pattern of as-synthesized HKUST-1 ( $\lambda = 1.5418$  Å). Calculated peak positions from the crystal structure are shown (blue tick marks).



**Fig. S5** Powder X-ray diffraction pattern of as-synthesized PCN-14 ( $\lambda = 1.5418$  Å). Calculated peak positions from the crystal structure are shown (blue tick marks).



**Fig. S6** Powder X-ray diffraction pattern of as-synthesized MOF-5 ( $\lambda = 1.5418$  Å). The baseline is magnified in the inset to make the peak positions more obvious. Calculated peak positions from the crystal structure are shown (blue tick marks).

![](_page_8_Figure_1.jpeg)

#### 3. Surface areas and pore volumes

**Fig. S7** 77 K N<sub>2</sub> adsorption isotherm for Ni<sub>2</sub>(dobdc) activated at 180 °C in the HPVA highpressure adsorption cell. The calculated Langmuir surface area is 1574 m<sup>2</sup>/g (n<sub>sat</sub> = 16.1 mmol/g), and the total pore volume at  $p/p_0 = 0.9$  is 0.56 cm<sup>3</sup>/g. Here,  $n_{sat}$  is the amount of N<sub>2</sub> adsorbed at saturation (mmol/g), p is the pressure, and p<sub>0</sub> is the saturation pressure of N<sub>2</sub>.

![](_page_8_Figure_4.jpeg)

**Fig. S8** 77 K N<sub>2</sub> adsorption isotherm for Co<sub>2</sub>(dobdc) activated at 180 °C in the HPVA highpressure adsorption cell. The calculated Langmuir surface area is 1433 m<sup>2</sup>/g (n<sub>sat</sub> = 14.7 mmol/g), and the total pore volume at  $p/p_0 = 0.9$  is 0.51 cm<sup>3</sup>/g.

![](_page_9_Figure_1.jpeg)

**Fig. S9** 77 K N<sub>2</sub> adsorption isotherm for Mg<sub>2</sub>(dobdc) activated at 180 °C in an ASAP-2020 lowpressure sample holder (red) and the HPVA high-pressure adsorption cell (blue). The calculated Langmuir surface area is 1957 m<sup>2</sup>/g (n<sub>sat</sub> = 20.1 mmol/g), and the total pore volume at  $p/p_0 = 0.9$ is 0.69 cm<sup>3</sup>/g.

![](_page_9_Figure_3.jpeg)

**Fig. S10** 77 K N<sub>2</sub> adsorption isotherm for HKUST-1 activated at 150 °C in the HPVA highpressure adsorption cell. The calculated Langmuir surface area is 2190 m<sup>2</sup>/g ( $n_{sat} = 22.5 \text{ mmol/g}$ ), and the total pore volume at  $p/p_0 = 0.9$  is 0.77 cm<sup>3</sup>/g.

![](_page_10_Figure_1.jpeg)

**Fig. S11** 77 K N<sub>2</sub> adsorption isotherm for PCN-14 activated at 120 °C in an ASAP-2020 lowpressure sample holder (red) and the HPVA high-pressure adsorption cell (blue). The calculated Langmuir surface area is 2360 m<sup>2</sup>/g (n<sub>sat</sub> = 24.2 mmol/g), and the total pore volume at  $p/p_0 = 0.9$ is 0.83 cm<sup>3</sup>/g. The calculated BET surface area is 1984 m<sup>2</sup>/g.

![](_page_10_Figure_3.jpeg)

**Fig. S12** Plot of  $n \cdot (1-p/p_0)$  vs.  $p/p_0$  to determine the maximum  $p/p_0$  used in the BET linear fit according to the first BET consistency criterion.<sup>7</sup>

![](_page_11_Figure_1.jpeg)

**Fig. S13** Plot of  $p/p_0/(n \cdot (1-p/p_0))$  vs.  $p/p_0$  to determine the BET surface area.<sup>7</sup> The slope of the best fit line for  $p/p_0 < 0.03$  is 0.049, and the y-intercept is 2.9 x 10<sup>-6</sup>, which satisfies the second BET consistency criterion. This results in a saturation capacity of 20.3 mmol/g and a BET surface area of 1984 m<sup>2</sup>/g.

![](_page_11_Figure_3.jpeg)

**Fig. S14** 77 K N<sub>2</sub> adsorption isotherm for MOF-5 activated at 150 °C in the HPVA highpressure adsorption cell. The calculated Langmuir surface area is 3961 m<sup>2</sup>/g (n<sub>sat</sub> = 40.6 mmol/g), and the total pore volume at  $p/p_0 = 0.9$  is 1.4 cm<sup>3</sup>/g.

![](_page_12_Figure_1.jpeg)

**Fig. S15** 77 K N<sub>2</sub> adsorption isotherm for AX-21 activated at 200 °C in the HPVA high-pressure adsorption cell. The calculated Langmuir surface area is 4880 m<sup>2</sup>/g ( $n_{sat} = 50.1 \text{ mmol/g}$ ), and the total pore volume at  $p/p_0 = 0.9$  is 1.64 cm<sup>3</sup>/g.

**Table S1** Summary of gravimetric Langmuir surface area  $(m^2/g)$ , volumetric Langmuir surface area  $(m^2/cm^3)$  pore volume  $(cm^3/g)$ , and crystallographic density  $(g/cm^3)$  for all materials synthesized and evaluated in this work.

	Langmuir surface area (m <sup>2</sup> /g)	Langmuir surface area (m <sup>2</sup> /cm <sup>3</sup> )	Pore volume (cm <sup>3</sup> /g)	Crystallographic density (g/cm <sup>3</sup> )
Ni <sub>2</sub> (dobdc)	1574	1881	0.56	1.195
Co <sub>2</sub> (dobdc)	1433	1681	0.51	1.169
Mg <sub>2</sub> (dobdc)	1957	1779	0.69	0.909
HKUST-1	2190	1929	0.77	0.881
PCN-14	2360	1956	0.83	0.819
MOF-5	3961	2460	1.4	0.621
AX-21 Carbon	4880	2377	1.64	0.487

## 4. High-pressure gas adsorption measurements

High-pressure adsorption isotherms in the range of 0-100 bar were measured on a HPVA-II-100 from Particulate Systems, a Micromeritics company. In a typical measurement, 0.3-0.7 g of activated sample was loaded into a tared 2 mL stainless steel sample holder inside a glove box under a  $N_2$  atmosphere. Prior to connecting the sample holder to the VCR fittings of the complete high-pressure assembly inside the glove box, the sample holder was weighed to determine the sample mass.

The fully assembled sample holder was transferred to an ASAP 2020 low-pressure adsorption instrument, fitted with an isothermal jacket, and evacuated at the material's original activation temperature for at least 1 h. Then, a 77 K N<sub>2</sub> adsorption isotherm was measured. This was used to verify that the high-pressure sample mass was correct and the sample was still of high quality by comparing the resulting Langmuir surface area to the expected value (Figs. S7-S15). Note that a specially designed OCR adapter was used to connect the stainless steel high-pressure adsorption cell directly to the ASAP 2020 analysis port, allowing the measurement of accurate low-pressure isotherms on the exact same samples used for high-pressure measurements in the same sample holders.

The sample holder was then transferred to the HPVA-II-100, connected to the instrument's analysis port via an OCR fitting, and evacuated at room temperature for at least 1 h. The sample holder was placed inside an aluminum recirculating dewar connected to a Julabo FP89-HL isothermal bath filled with Julabo Thermal C2 fluid, for which the temperature stability is  $\pm 0.02$  °C. Note that while the majority of the sample holder is placed inside the temperature bath (analysis zone), there is still a significant volume that is exposed to the air (ambient zone) and is affected by fluctuations in room temperature (Fig. S16). A small upper volume of the sample holder above the analysis port is inside a temperature controlled heated enclosure, along with the gas dosing manifold (manifold zone). While this setup is typical of most volumetric adsorption instruments, it creates challenges in determining the free space (or empty volume) of the sample holder that is in each temperature zone. Accurately determining these volumes is particularly important because nonideality corrections have a significant temperature dependence that can lead to large errors at higher pressures.

For measurements at room temperature, the ambient and analysis zones will be at the same temperature. Since the dosing manifold volume is known accurately from volume calibrations during manufacturing, He can be used to determine the total free space in the sample holder by using the standard method of expanding from the dosing manifold to the evacuated sample holder and recording the change in pressure, assuming He adsorption is negligible. Note that the HPVA-II-100 is equipped with two pressure transducers: 1) a 100,000 torr GE Sensing UNIK5000 series transducer (accuracy of  $\pm 0.04\%$  full scale), and 2) a 1000 torr transducer (accuracy of  $\pm 0.15\%$  reading). The addition of the low-pressure transducer allows the He free space measurement to be performed at lower pressures (0.7-0.8 bar), where He adsorption is negligible for most materials.<sup>8</sup>

For measurements at non-ambient temperatures, it further becomes necessary to determine both the volume of the sample holder that is at ambient temperature and the volume that is at the analysis temperature. Note that there are several approaches to doing this.<sup>9</sup> By default, the commercial HPVA-II-100 software uses He to measure the total volume in both the ambient and analysis temperature zones, with all volumes set to the ambient temperature. Then, the temperature of the analysis zone is changed to the desired analysis temperature, and the resulting change in He pressure is used to calculate the volume that is in the analysis temperature zone. Unfortunately, the pressure changes that result from most temperature changes are relatively small (especially for measurements near ambient temperature), and the 1000 torr transducer is not accurate or stable enough to reliably determine the analysis volume using this method. Indeed, small errors in the pressure readings were found to lead to large errors in the calculated analysis volume, and consequently, large errors in the resulting isotherms, especially at the high pressures where the temperature-dependent nonideality corrections are most significant (Fig. S17).

![](_page_14_Figure_2.jpeg)

**Fig. S16** For the HPVA-II-100 high-pressure instrument, there are three distinct temperature zones on the sample holder: 1) manifold zone inside a heated enclosure that contains both the upper part of the sample of the sample holder (3.5 mL) and the calibrated dosing volume, 2) ambient zone that is the upper portion of the sample holder outside of the constant temperature analysis bath (5-6 mL), and 3) analysis temperature zone that is the lower portion of the sample holder inside the constant temperature bath (4-5 mL).

![](_page_14_Figure_4.jpeg)

**Fig. S17** Using the default analysis routine of the HPVA software can lead to large errors in the free space of the sample holder that is in each temperature zone, causing large errors in the resulting adsorption isotherm, especially at the higher pressures where temperature dependent nonideality corrections are most significant.

An alternative method, which was used here, is to determine the volumes of the ambient and analysis temperatures zones for an empty sample holder. Since the portion of the sample holder containing the sample is always fully immersed in the constant temperature bath and the bath is always placed at the exact same height on the sample holder, the ambient volume will always be constant, regardless of the amount of sample present. On the other hand, the analysis volume will depend on the amount of sample present, but it can be easily determined by subtracting the volume of the sample from the analysis volume of the empty sample holder. Here, the sample volume is determined by subtracting the total free space of the filled sample holder from that of the empty sample holder. The total free spaces of the empty or filled sample holders were determined using ambient temperature He free space measurements, which were repeated 20 times and averaged. The analysis volumes of the empty sample holder were determined by performing He free space measurements at each potential analysis temperature and calculated using the ideal gas law with the measured total empty volume of the sample holder, the ambient temperature, the analysis temperature, the He dose pressure, the He equilibrium pressure, the known dosing manifold volume, and the dosing manifold temperature. It is worth noting that by using this technique, it is only necessary to measure the He free space at ambient temperature for a new sample, and it is not necessary to measure He free space at any other analysis temperatures.

Other approaches to accounting for the different temperature zones are certainly possible, but regardless of the exact method used, it is critical to ensure that background CH<sub>4</sub> adsorption is negligible, or at least properly corrected for, at all relevant pressures and temperatures. To this end, background CH<sub>4</sub> adsorption were measured for a sample holder containing 0.34 mL of glass beads (similar in volume to a typical sample) at -25, 0, 25, 38, 50, 75, 100, and 150 °C. All background measurements were repeated at least 3 times at each temperature. With the exception of at -25 °C, background CH<sub>4</sub> adsorption was less than  $\pm 4$  cm<sup>3</sup><sub>STP</sub> at pressures from 0-100 bar. At 35 bar, the background CH<sub>4</sub> adsorption was less than  $\pm 1$  cm<sup>3</sup><sub>STP</sub>. This relatively low background confirms that all volume and temperature calibrations are accurate, and provides an estimate of the error of a typical measurement, which is inversely proportional to the sample mass used. For instance, the error for a 0.5 g sample can be estimated a  $\pm 2$  cm<sup>3</sup><sub>STP</sub>/g at 35 bar and  $\pm 8$  cm<sup>3</sup><sub>STP</sub>/g at 100 bar.

For the -25 °C background measurements, a significant negative background was observed, which is most likely due to a temperature gradient between the analysis and ambient zones on the sample holder (Fig. S19). This would affect the accuracy of nonideality corrections that assume there is a sharp temperature change between the ambient and analysis temperature. However, the background at -25 °C is consistent across several measurements, and as a result, it was fit with a 3<sup>rd</sup> order polynomial that was used to perform a background correction on all subsequent -25 °C isotherms.

![](_page_16_Figure_1.jpeg)

**Fig. S18** Background CH<sub>4</sub> adsorption isotherms at 0, 25, 38, 50, 75, 100, and 150 °C for the HPVA sample holder containing  $0.34 \text{ cm}^3$  of glass beads.

![](_page_16_Figure_3.jpeg)

**Fig. S19** Background CH<sub>4</sub> adsorption isotherms at -25 °C for the HPVA sample holder containing 0.34 cm<sup>3</sup> of glass beads. The black line represents a 3<sup>rd</sup> order polynomial fit to the background adsorption that was subsequently applied as a correction to all isotherms at -25 °C. The background adsorption is most like the result of a temperature gradient between the ambient and analysis zones on the sample holder.

![](_page_17_Figure_1.jpeg)

Fig. S20 Excess  $CH_4$  adsorption isotherms for  $Ni_2$ (dobdc) at 25 °C from 0 to 100 bar repeated eight times.

# 5. Crystallographic density calculations

Table 52 Summary of crystanographic density calculations.							
	Asymmetric	Total mass of	Ζ	Unit cell	Temp	Density	Crystal
	unit	asymmetric		volume	(°C)	$(g/cm^3)$	structure
		unit (g)		$(\text{\AA}^3)$			ref
Ni <sub>2</sub> (dobdc)	NiC <sub>4</sub> HO <sub>3</sub>	4.657 x 10 <sup>-21</sup>	18	3898.3	22	1.195	10
$Co_2(dobdc)$	CoC <sub>4</sub> HO <sub>3</sub>	4.664 x 10 <sup>-21</sup>	18	3977.3	195	1.173	11
Mg <sub>2</sub> (dobdc)	MgC <sub>4</sub> HO <sub>3</sub>	3.629 x 10 <sup>-21</sup>	18	3992.5	27	0.909	12
HKUST-1	$Cu_{3}C_{18}H_{6}O_{12}$	1.608 x 10 <sup>-20</sup>	16	18247.4	25	0.881	13
PCN-14	$CuC_{15}H_7O_4$	1.882 x 10 <sup>-20</sup>	36	22697.7	-183	0.829	5
MOF-5	$Zn_4C_{24}H_{12}O_{15}$	1.066 x 10 <sup>-20</sup>	8	17153.6	27	0.621	14

 Table S2
 Summary of crystallographic density calculations.

Note that all crystal structures were chosen to be as representative of the state of each metalorganic framework during ambient temperature CH<sub>4</sub> adsorption as possible, but in some cases, there are potentially important differences:

- The unit cell volumes of Ni<sub>2</sub>(dobdc), Co<sub>2</sub>(dobdc), and Mg<sub>2</sub>(dobdc) are all taken from crystal structures of the fully desolvated frameworks. Note that the Co<sub>2</sub>(dobdc) structure, however, was at elevated temperature (195 °C).
- The unit cell volume of HKUST-1 is for the fully desolvated framework at 25 °C.
- The crystal structure of PCN-14 is for the solvated framework at 90 K. All solvent molecules were removed for the calculation, but possible changes in unit cell volume upon desolvation and warming to ambient in temperature are not accounted for.
- The unit cell volume of MOF-5 is for the fully desolvated framework at 27 °C.
- Since the activated carbon AX-21 is not crystalline, its density,  $\rho_{\text{bulk}}$ , was estimated at 0.487 g/cm<sup>3</sup> based on the measured pore volume,  $V_{\text{p}}$ , from 77 K N<sub>2</sub> adsorption (1.64 cm<sup>3</sup>/g) and the skeletal density,  $\rho_{\text{sk}}$ , from a He free space measurement at 25 °C (2.42 g/cm<sup>3</sup>) using the following equation:

$$\rho_{\text{bulk}} = \frac{\rho_{\text{sk}}}{\rho_{\text{sk}}V_{\text{p}} + 1} \tag{1}$$

To the best of our knowledge, this density calculation is the most appropriate for a meaningful comparison with the volumetric uptakes of metal-organic frameworks as it should represent the maximum achievable density of AX-21 in the absence of any packing losses.

![](_page_19_Figure_1.jpeg)

## 6. Excess CH<sub>4</sub> adsorption isotherms

Fig. S21 Excess CH<sub>4</sub> adsorption isotherms for Ni<sub>2</sub>(dobdc).

![](_page_19_Figure_4.jpeg)

Fig. S22 Excess CH<sub>4</sub> adsorption isotherms for Co<sub>2</sub>(dobdc).

![](_page_20_Figure_1.jpeg)

Fig. S23 Excess CH<sub>4</sub> adsorption isotherms for Mg<sub>2</sub>(dobdc).

![](_page_20_Figure_3.jpeg)

Fig. S24 Excess CH<sub>4</sub> adsorption isotherms for HKUST-1.

![](_page_21_Figure_1.jpeg)

Fig. S25 Excess CH<sub>4</sub> adsorption isotherms for PCN-14.

![](_page_21_Figure_3.jpeg)

Fig. S26 Excess CH<sub>4</sub> adsorption isotherms for MOF-5.

![](_page_22_Figure_1.jpeg)

Fig. S27 Excess CH<sub>4</sub> adsorption isotherms for AX-21.

## 7. Isotherm fitting

Prior to fitting the CH<sub>4</sub> adsorption isotherms, experimentally measured excess adsorption  $(n_{ex})$  was converted to total adsorption  $(n_{tot})$  using total pore volumes  $(V_p;$  Table S1), as determined from N<sub>2</sub> isotherms at 77 K ( $P/P_0 = 0.9$ ), and the bulk gas density at each temperature and pressure from the NIST Refprop database (Eqn 2).<sup>15</sup>

$$n_{\rm tot} = n_{\rm ex} + V_{\rm p} \cdot \rho_{\rm bulk} \left( P, T \right) \tag{2}$$

Total CH<sub>4</sub> adsorption isotherms for each material were then fit with either a single- or dualsite Langmuir equation (Eqn 3), where *n* is the total amount adsorbed in mmol/g, *P* is the pressure in bar,  $n_{\text{sat},i}$  is the saturation capacity in mmol/g, and  $b_i$  is the Langmuir parameter in bar<sup>-1</sup> for up to two sites 1 and 2. The Langmuir parameter can be expressed using Eqn 4, where  $S_i$  is the site-specific molar entropy of adsorption in J/mol•K,  $E_i$  is the site-specific binding energy in kJ/mol, *R* is the gas constant in J/mol•K, and *T* is the temperature in K. The fitted parameters for each adsorption isotherm can be found in Table S3. Plots of the total adsorption isotherms with the corresponding single- or dual-site Langmuir fits can be found in Fig. S28-S34. Note that isotherm data at all measured temperatures were fit simultaneously with one set of parameters.

$$n = \frac{n_{\text{sat},1}b_1P}{1+b_1P} + \frac{n_{\text{sat},2}b_2P}{1+b_2P}$$
(3)

$$b_{i} = e^{-S_{i}/R} e^{E_{i} \cdot 1000/RT}$$
(4)

	$Ni_2(dobdc)$	$Co_2(dobdc)$	$Mg_2(dobdc)$	HKUST-1	PCN-14	MOF-5	AX-21
$n_{\text{sat},1} \text{ (mmol/g)}$	7.2	8.5	11.1	16.9	10.4	30.5	28.3
$S_1(-R)$	10.0	9.7	9.6	9.7	9.9	9.2	9.2
$E_1$ (kJ/mol)	21.0	19.7	18.6	17.1	16.2	12.3	10.7
$n_{\text{sat},2} \text{ (mmol/g)}$	4.3	3.7	5.9	-	6.0	-	10.5
$S_2(-R)$	10.0	11.6	11.9	-	9.3	-	9.0
$E_2$ (kJ/mol)	16.1	17.6	16.4	-	18.3	-	16.6

 Table S3
 Single- or dual-site Langmuir parameters for all isotherm fits.

![](_page_24_Figure_1.jpeg)

**Fig. S28** Total CH<sub>4</sub> adsorption isotherms for Ni<sub>2</sub>(dobdc) at -25, 0, 25, 38, 50, 75, 100, and 150 °C and the corresponding dual-site Langmuir fits (black lines). See Table S3 for the dual-site Langmuir parameters.

![](_page_24_Figure_3.jpeg)

Fig. S29 Total CH<sub>4</sub> adsorption isotherms for Co<sub>2</sub>(dobdc) at -25, 25, 38, 50 °C and the corresponding dual-site Langmuir fits (black lines). See Table S3 for the dual-site Langmuir parameters.

![](_page_25_Figure_1.jpeg)

**Fig. S30** Total CH<sub>4</sub> adsorption isotherms for Mg<sub>2</sub>(dobdc) at -25, 25, 38, 50 °C and the corresponding dual-site Langmuir fits (black lines). See Table S3 for the dual-site Langmuir parameters.

![](_page_25_Figure_3.jpeg)

**Fig. S31** Total CH<sub>4</sub> adsorption isotherms for HKUST- at -25, 0, 25, 38, 50, 75, 100, and 150 °C and the corresponding single-site Langmuir fits (black lines). See Table S3 for the single-site Langmuir parameters.

![](_page_26_Figure_1.jpeg)

**Fig. S32** Total CH<sub>4</sub> adsorption isotherms for PCN-14 at 17, 25, 38, 50 °C and the corresponding dual-site Langmuir fits (black lines). See Table S3 for the dual-site Langmuir parameters.

![](_page_26_Figure_3.jpeg)

**Fig. S33** Total CH<sub>4</sub> adsorption isotherms for MOF-5 at -25, 25, 38, 50, 75, 100, and 150 °C and the corresponding single-site Langmuir fits (black lines). See Table S3 for the single-site Langmuir parameters.

![](_page_27_Figure_1.jpeg)

**Fig. S34** Total CH<sub>4</sub> adsorption isotherms for AX-21 at -25, 25, 38, 50 °C and the corresponding dual-site Langmuir fits (black lines). See Table S3 for the dual-site Langmuir parameters.

### 8. Isosteric heats of adsorption

Using the single- and dual-site Langmuir fits, the isosteric heat of adsorption can be calculated for each material as a function of the total amount of  $CH_4$  adsorbed using the Clausius-Clapeyron relation (Eqn 5). The isosteric heat of adsorption for a single-site Langmuir model is constant by definition. For a dual-site Langmuir model, however, it is necessary to derive an expression for the loading dependence of the isosteric heat of adsorption (Eqn 6).<sup>16</sup> Note that, as written, Eqn 6 gives the isosteric heat of adsorption as a function of pressure, rather than the amount adsorbed. To calculate the isosteric heat of adsorption for evenly spaced loadings, Mathematica was used to solve each dual-site Langmuir equation at 25 °C for the pressures that correspond to specific loadings, and these calculated pressures were then used in Eqn 6 to determine the heat of adsorption as a function of CH<sub>4</sub> adsorbed (Fig. 5).

$$-Q_{\rm st} = \mathbf{R}T^2 \left(\frac{\partial \ln P}{\partial T}\right)_n \tag{5}$$

$$-Q_{\rm st} = \frac{E_{\rm l}n_{\rm sat,l}b_{\rm l}(1+b_2P)^2 + E_2n_{\rm sat,2}b_2(1+b_1P)^2}{n_{\rm sat,l}b_{\rm l}(1+b_2P)^2 + n_{\rm sat,2}b_2(1+b_1P)^2}$$
(6)

![](_page_28_Figure_1.jpeg)

## 9. PCN-14 literature comparison

Fig. S35 Comparison of the excess  $CH_4$  adsorption isotherms at 17 °C for PCN-14 as originally reported in Ref. 5 and as measured in this work.

![](_page_28_Figure_4.jpeg)

Fig. S36 Comparison of the total  $CH_4$  adsorption isotherms at 17 °C for PCN-14 as originally reported in Ref. 5 and as measured in this work.

![](_page_29_Figure_1.jpeg)

**Fig. S37** Comparison of the CH<sub>4</sub> isosteric heats of adsorption for PCN-14 as originally reported in Ref. 5 and as measured in this work.

![](_page_30_Figure_1.jpeg)

#### **10.** CH<sub>4</sub> uptake vs. surface area

**Fig. S38** There is a moderate correlation between gravimetric surface area and total gravimetric CH<sub>4</sub> adsorption at 25 °C and 35, 65, and 100 bar for  $M_2$ (dobdc) (M = Ni, Co, Mg), PCN-14, HKUST-1, and AX-21.

![](_page_30_Figure_4.jpeg)

Fig. S39 There is little correlation between volumetric surface area and total volumetric  $CH_4$  adsorption at 25 °C and 35, 65, and 100 bar for  $M_2$ (dobdc) (M = Ni, Co, Mg), PCN-14, HKUST-1, and AX-21.

## **11. Usable CH<sub>4</sub> capacity**

![](_page_31_Figure_2.jpeg)

Fig. S40 The gravimetric usable  $CH_4$  capacity as a function of desorption temperature for adsorption at 25 °C and 35 bar and desorption at 5 bar.

![](_page_31_Figure_4.jpeg)

Fig. S41 The volumetric usable  $CH_4$  capacity as a function of desorption pressure for adsorption at 25 °C and 35 bar and desorption at 25 °C.

![](_page_32_Figure_1.jpeg)

Fig. S42 The gravimetric usable  $CH_4$  capacity as a function of desorption pressure for adsorption at 25 °C and 35 bar and desorption at 25 °C.

![](_page_32_Figure_3.jpeg)

Fig. S43 The volumetric usable  $CH_4$  capacity as a function of desorption temperature for adsorption at -25 °C and 35 bar and desorption at 5 bar.

![](_page_33_Figure_1.jpeg)

**Fig. S44** The volumetric usable  $CH_4$  capacity as a function of desorption pressure for adsorption at -25 °C and 35 bar and desorption at -25 °C and pressures from 5 to 0 bar.

![](_page_33_Figure_3.jpeg)

Fig. S45 The gravimetric usable  $CH_4$  capacity as a function of adsorption pressure for adsorption at 25 °C and pressures from 35 to 95 bar and desorption at 25 °C and 5 bar.

![](_page_34_Figure_1.jpeg)

**Fig. S46** The volumetric usable  $CH_4$  capacity as a function of adsorption pressure for adsorption at 25 °C and pressures from 35 to 95 bar and desorption at 25 °C and 5 bar.

# 12. HKUST-1 pore window adsorption site

![](_page_35_Figure_2.jpeg)

**Fig. S47** View of a CD<sub>4</sub> molecule adsorbed at one octahedral cage window site of HKUST-1 that highlights the close interactions of CD<sub>4</sub> with framework O atoms, which are in the range of 2.7-3.2 Å. Green, gray, red, and light blue spheres represent Cu, C, O, and D atoms, respectively; H atoms have been omitted for clarity. The atomic coordinates are taken from a powder neutron diffraction structure at 4 K with a loading of 1.1 CD<sub>4</sub> per Cu<sup>2+.17</sup>

## 13. Optimal binding enthalpy

Using a single-site Langmuir model, it is possible to calculate the optimal binding enthalpy for maximizing the usable capacity for a given set of adsorption-desorption conditions.<sup>18</sup> In this simple model, it is assumed that the pore surface contains one type of adsorption site with a maximum capacity of  $n_{sat}$ , a binding energy of E, and a molar entropy of adsorption of S. Based on this, the usable capacity can be calculated for different adsorption pressures,  $P_{ads}$ , and temperatures,  $T_{ads}$ , and desorption pressures,  $P_{des}$ , and temperatures,  $T_{des}$  (Eqn 7). Here, adsorption was assumed to be at 35 bar and 25 °C, while desorption was at 5 bar and temperatures ranging from 25 to 145 °C. The usable capacity can then be calculated at different binding energies, assuming a constant S.

For CH<sub>4</sub>, *S* is often assumed to be near -9.5R, however, there is a correlation between adsorption enthalpy and entropy, whereby as the binding energy increases, the entropy also increases.<sup>19</sup> This enthalpy-entropy correlation results in higher optimal binding energies than would otherwise be predicted, but the relationship between desorption temperature and optimal binding enthalpy is unchanged. To illustrate the affects of the enthalpy-entropy correlation, the percentage of the saturation capacity that is usable ( $n_{usable}/n_{sat}$ ) is plotted as a function of binding energy and desorption temperature using a molar entropy of adsorption of -9.5R (Fig. 7) and 10.5R (Fig. S48). The optimal binding energy at each desorption temperature occurs at the maximum of each curve. For example, the optimal binding energies for 25 °C desorption are -17.1 kJ/mol and -19.6 kJ/mol for entropies of -9.5R and -10.5R, respectively.

![](_page_36_Figure_4.jpeg)

**Fig. S48** Assuming a single-site Langmuir isotherm, the percentage of the saturation capacity that is usable is plotted for isosteric heats of adsorption,  $Q_{st}$ , ranging from 10 to 25 kJ/mol and desorption temperatures from 25 to 145 °C, with adsorption at 35 bar, desorption at 5 bar, and a molar entropy of adsorption of -10.5R. As the desorption temperature increases, the optimal  $Q_{st}$  and usable capacity also increase. Note that the higher entropy value leads to higher optimal binding enthalpies (see Fig. 7 for comparison).

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