

Supplementary Material (ESI) for Energy & Environmental Science

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Carbon Capture in Metal-Organic Frameworks – A Comparative Study

J.M. Simmons,^a H. Wu,^{a,b} W. Zhou,^{a,b} T. Yildirim^{a,c}

^a *NIST Center for Neutron Research, National Institute of Standards and Technology
E-mail: jason.simmons@nist.gov*

^b *Department of Materials Science and Engineering, University of Maryland*

^c *Department of Materials Science and Engineering, University of Pennsylvania*

Section I: Temperature dependent CO₂ isotherms for each MOF.

Section II: Ideal Adsorbed Solution Theory (IAST) Calculated Selectivity

- a) Application of IAST as outlined in Myers and Prausnitz *AIChE J.*, 1965, **11**, 121
- b) CO₂ selectivity against CH₄ and N₂ at 280K
- c) Comparison between CO₂ and CH₄ isotherms at 280K and 300K.
- d) Comparison between CO₂ and N₂ isotherms between 280K and 310K.

Section III: Alternative isosteric heat of adsorption plot showing CO₂-CO₂ interactions at high uptakes.

Section IV: Diffraction characterisation of ZIF-8 sample

Section I: Temperature dependent CO₂ sorption isotherms. Figures S1 and S2 are the same as Figures 2a and 2b in the main text.

Figure S1

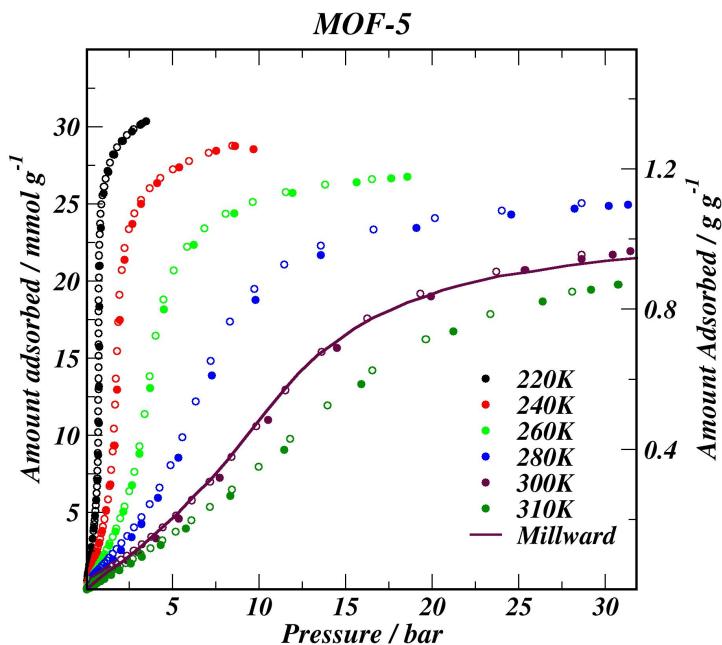


Figure S2

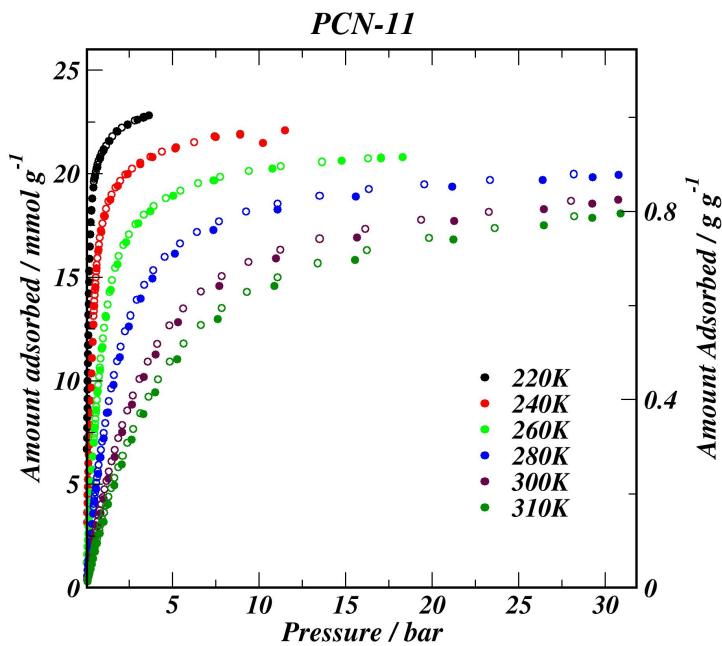


Figure S3

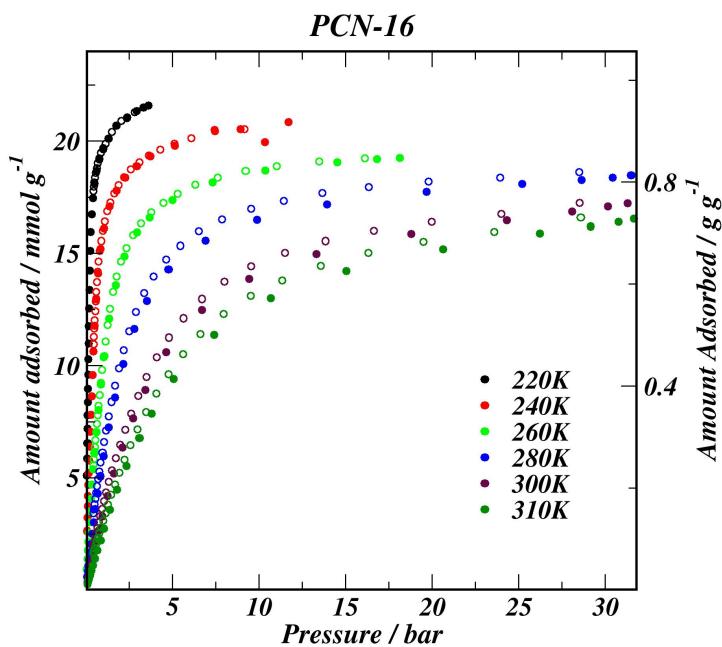


Figure S4

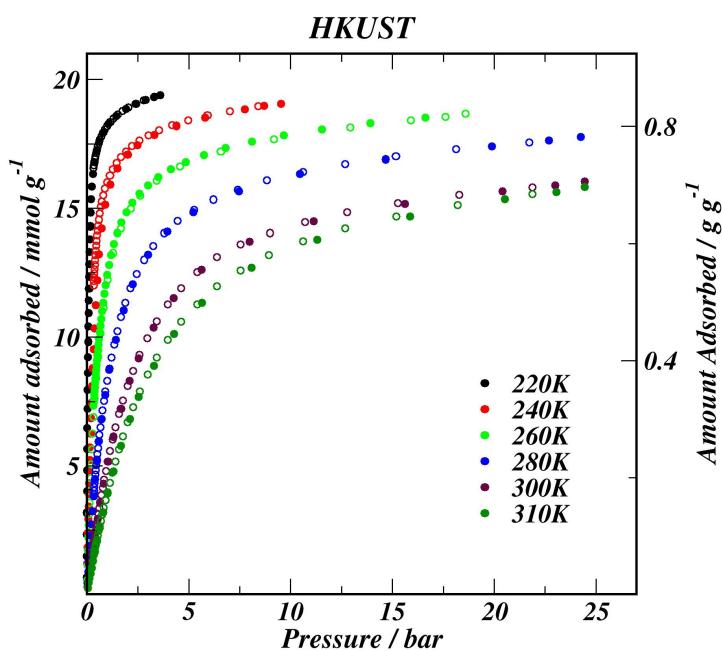


Figure S5

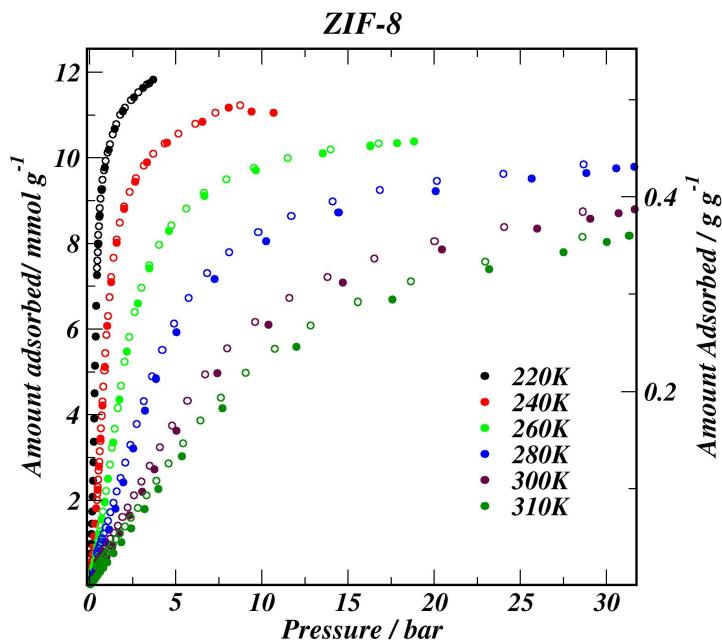


Figure S6

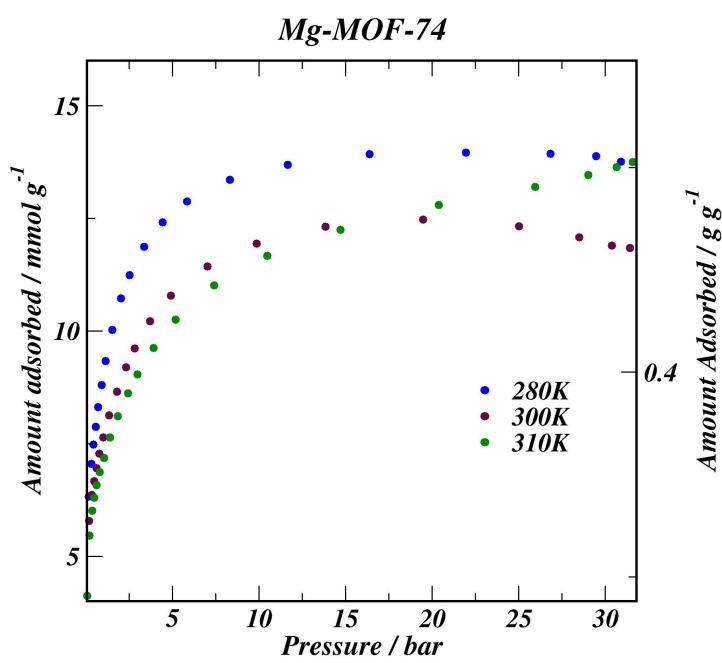
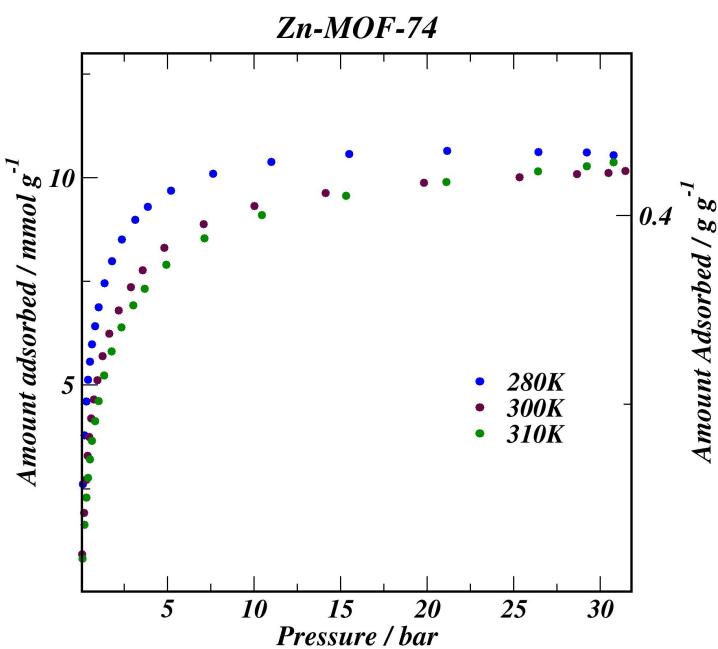


Figure S7



Section II: Ideal Adsorbed Solution Theory (IAST) Calculated Selectivity**IIa)** Application of IAST theory.

The IAST theory is fully explained in the original paper by Alan Myers and John Prausnitz in 1965 (*A/ChE J.* **11**, 121, hereafter “Myers”). Below, we briefly outline the process to obtain the selectivities based on single component excess adsorption isotherms. Though the theory is commonly expressed in terms of absolute isotherms, the corrections at the pressures and temperatures we consider are sufficiently small (<0.24mmol/g at 6 bar) that they fall within the ~5% experimental error and are thus negligible. We also assume that the gas-gas and gas-substrate interactions are sufficiently ideal to warrant using IAST rather than refinements of the theory to account for non-ideality (non unity activity constants). Ultimately, IAST gives an estimate of the real selectivity, with a typical accuracy of ~10%.

The theory consists of a series of equations (Eqs. 19, 28, and 36-42 in Myers, with i, j representing different gases):

$$\begin{aligned}\pi_i^o(P_i^o) &= \frac{RT}{A} \int_{\rho=0}^{P_i^o} \frac{n_i^o(\rho)}{\rho} d\rho \\ Py_i &= P_i^o x_i \\ \pi_i^o &= \pi_j^o \\ \sum x_i &= 1 \\ \sum y_i &= 1 \\ s_{i,j} &= \frac{P_2^o}{P_1^o}\end{aligned}$$

In the first equation n is the experimentally measured gas uptake as a function of pressure ρ , A is the available surface area (assumed to be the same for all gases), π^o is the so-called spreading pressure, and P^o is the equilibrium pressure of the single-component gas corresponding to π^o . The variable x_i and y_i are the adsorbed and gas phase mole fractions of gas i , respectively. For a two component gas mixture, there are seven equations and nine unknowns.

The first equation is a definition of the spreading pressure for a single component gas adsorbate, while the second equation relates the amount of adsorbed component i to the gas phase component for a given total pressure of the simulated multi-component gas stream. The spreading pressure is numerically calculated from the experimentally measured excess isotherms. Though many groups choose to use an analytic isotherm model, there are a number of potential sources of error depending on the choice of model (see E. Richter et al., *Chem. Eng. Sci.* 1989, **44**, 1609 and A.L. Myers, *A/ChE J.* 1973, **19**, 666) and thus we have opted to use numerical techniques which yield equivalent results (M.M. Benjamin, *Environ Sci. Technol.*, 2009, **43**, 2530). The third equation is the statement of equilibrium, analogous to the

statement that all pressures or temperatures must be equalized for equilibrium to be attained. The final equation yields the $i:j$ gas selectivity.

To obtain solutions for the two-component mixtures assumed in this work, we must define two of the variables, namely the gas phase CO_2 concentration, y_1 , (0.5 for CO_2/CH_4 mixtures; 0.2 for CO_2/N_2 mixtures) and the total pressure, P , of the simulated mixed gas. Rather than determine the selectivity for a single fixed pressure, we utilize the relation (Eq. 46 in

Myers) $x_1 = \frac{P_2^o - P}{P_2^o - P_1^o} \Big|_{\pi}$, and $x_2 = \frac{P - P_1^o}{P_2^o - P_1^o} \Big|_{\pi}$. These equations permit the total mixed gas pressure, P , to be calculated for the experimental range of P_i . For a $1:m$ mixture of gases (1:1 for CO_2/CH_4 , 1:4 for CO_2/N_2), it can be shown that $P(\pi) = \frac{(m+1)P_1^o P_2^o}{P_2^o + mP_1^o}$, where $\pi = \pi_1^o = \pi_2^o$.

The process is as follows:

1. Obtain the spreading pressures, $\pi(P_i)$, from the experimental isotherms for each gas.
2. Use the equilibrium condition ($\pi = \pi_1^o = \pi_2^o$), we invert the above and extract $P_1^o(\pi)$, $P_2^o(\pi)$ and $P(\pi)$.
3. Last, the selectivity, $s_{1,2}$, is calculated as a function of $P(\pi)$. It is the selectivity that is plotted in Figure 5 in the main text and below.

IIb) Calculated Selectivity at 280-290K

Figure S8

Calculated CO_2 to CH_4 selectivity at 280K for Mg-MOF-74.

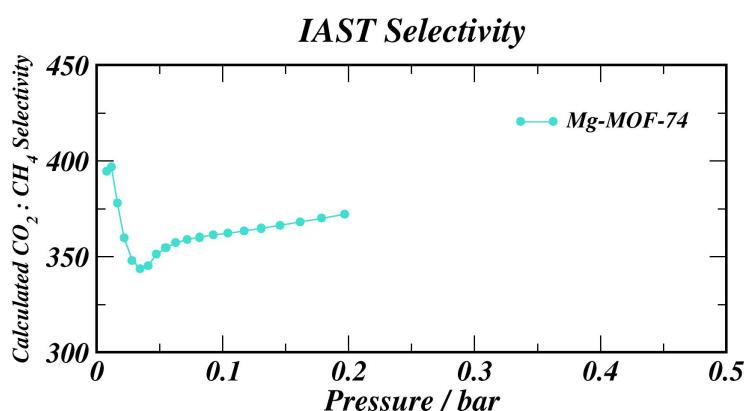


Figure S9

Calculated CO₂ to CH₄ selectivity at 280K for all MOFs except Mg-MOF-74 (figure above).

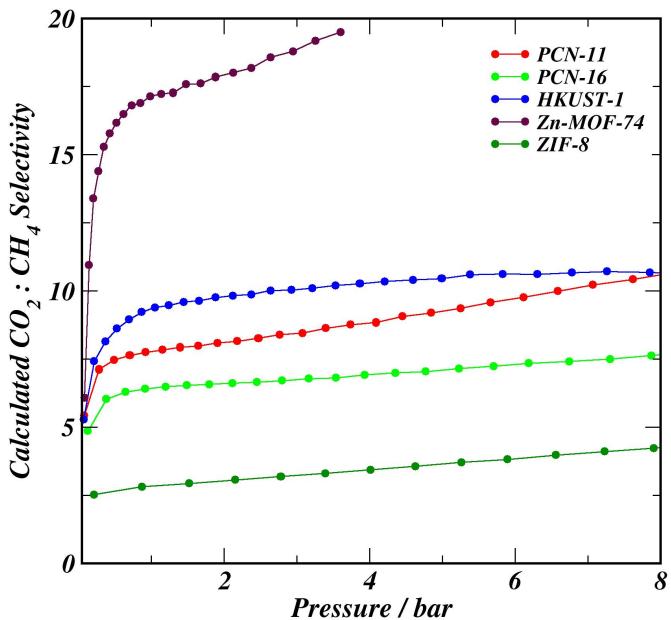
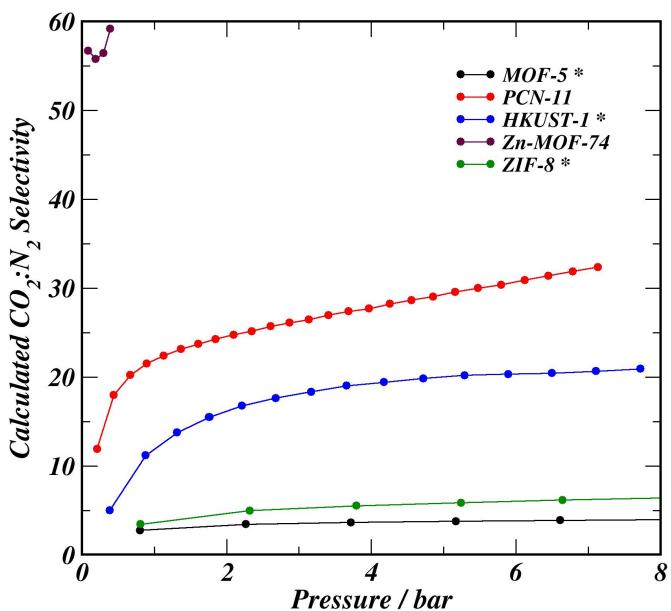


Figure S10

Calculated CO₂ to N₂ selectivity at 280-290K. Samples marked by an asterisk (*) were measured at 290K. Nitrogen adsorption in Mg-MOF-74 was too low to allow the determination of selectivity based on the experimental isotherms



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IIc) Comparison of CO₂ and CH₄ isotherms near room temperature. In each graph, black refers to CO₂ sorption and red shows CH₄ sorption. Open symbols are data collected at 280K, closed symbols at 300K.

Figure S11

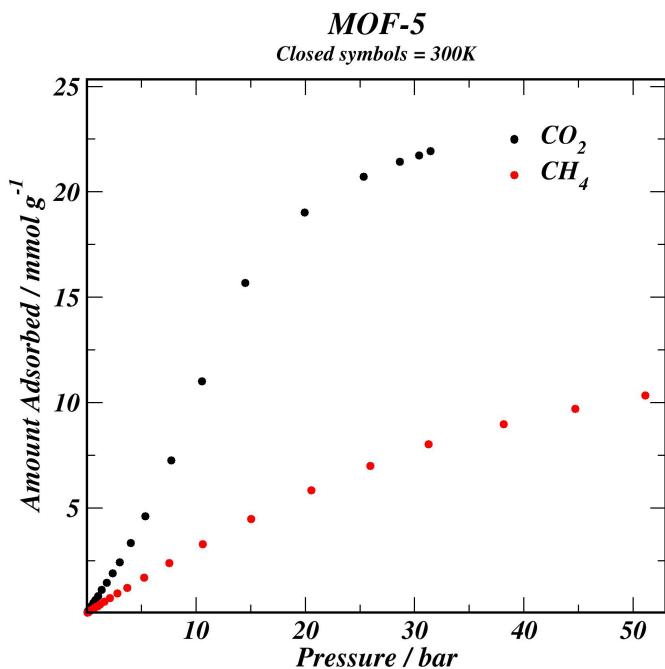


Figure S12

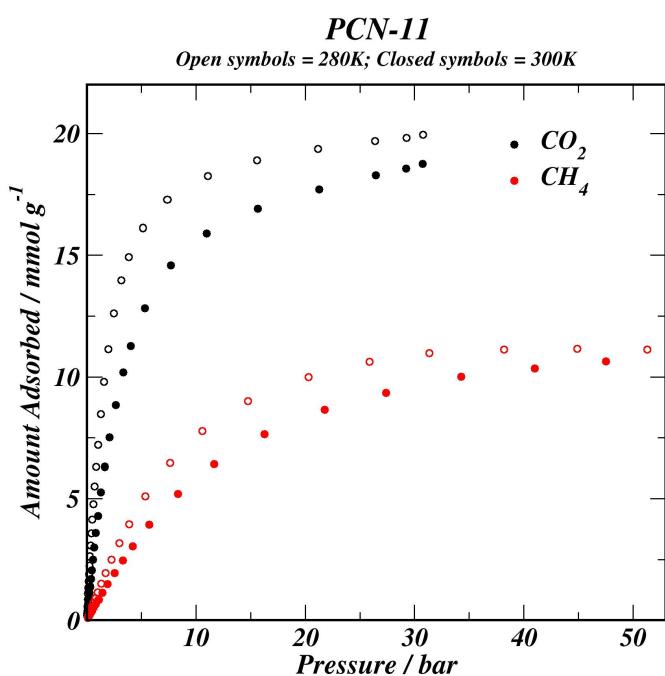


Figure S13

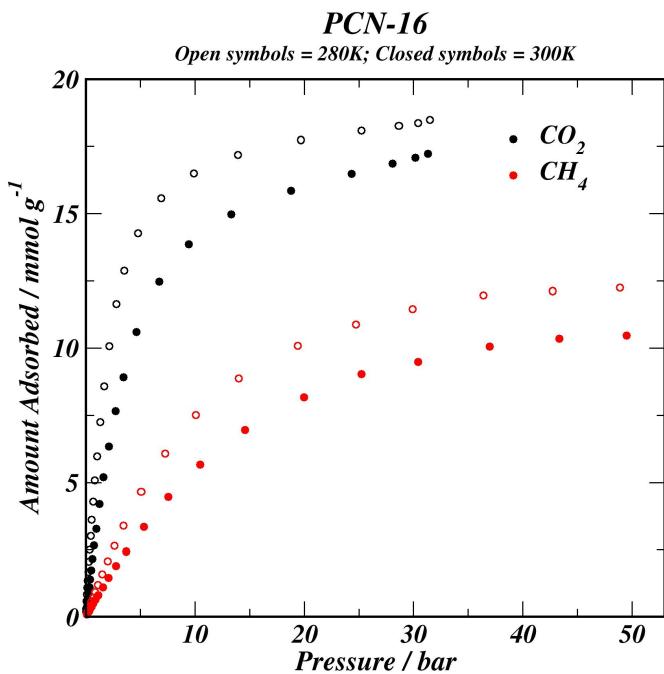


Figure S14

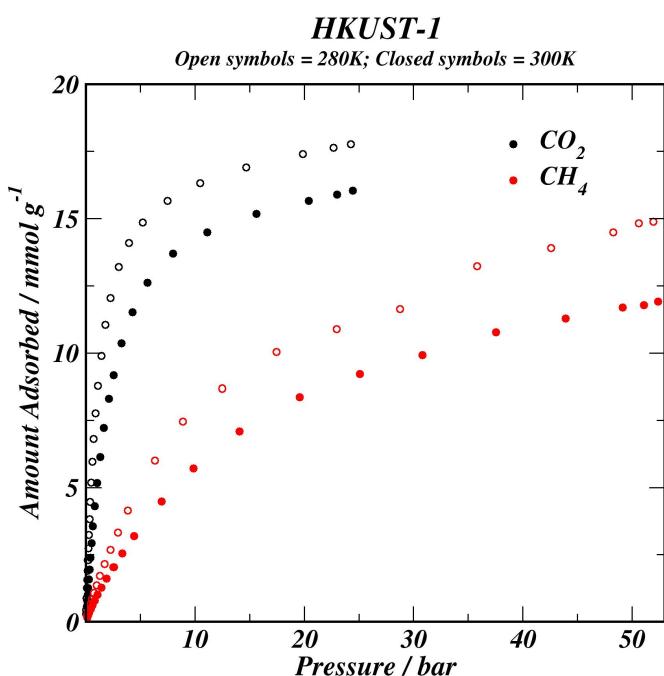


Figure S15

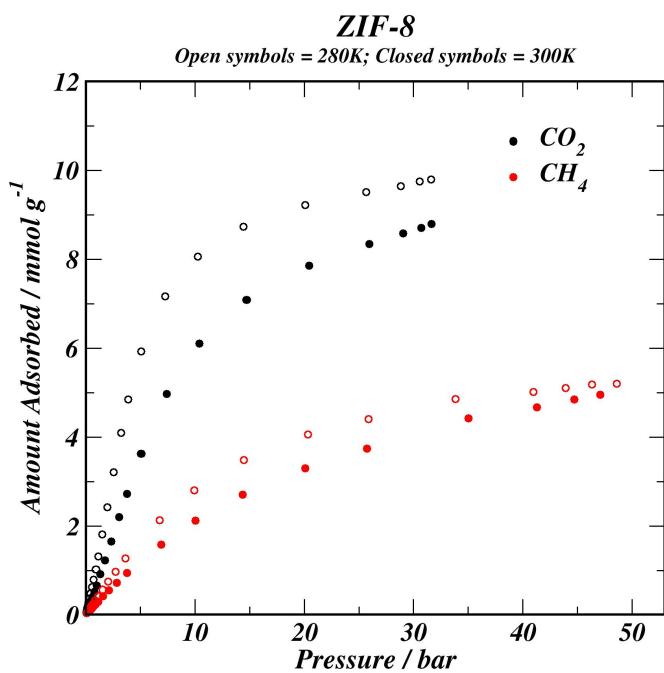


Figure S16

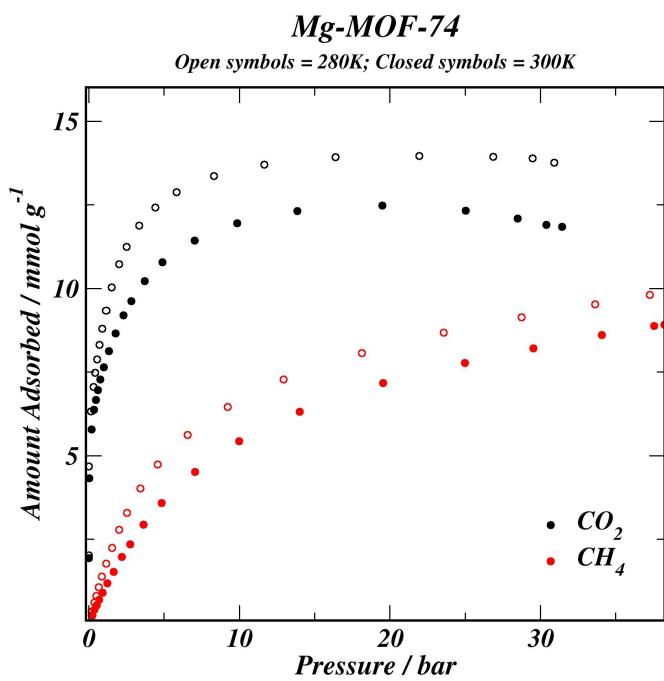
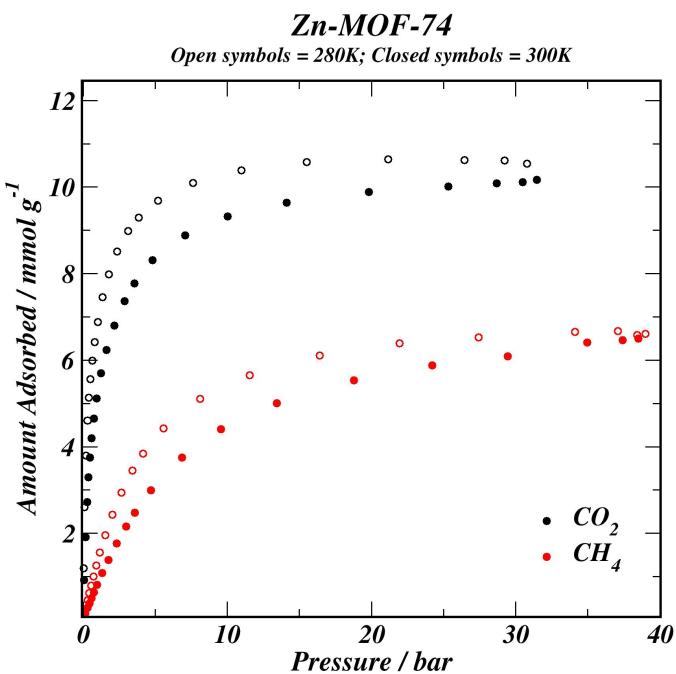


Figure S17



II(d) Comparison of CO₂ and N₂ isotherms near room temperature. In each graph, black refers to CO₂ sorption and red shows N₂ sorption. Open symbols are data collected at 280K or 290K, closed symbols at 300K or 310K as indicated on each graph.

Figure S18
– MOF5

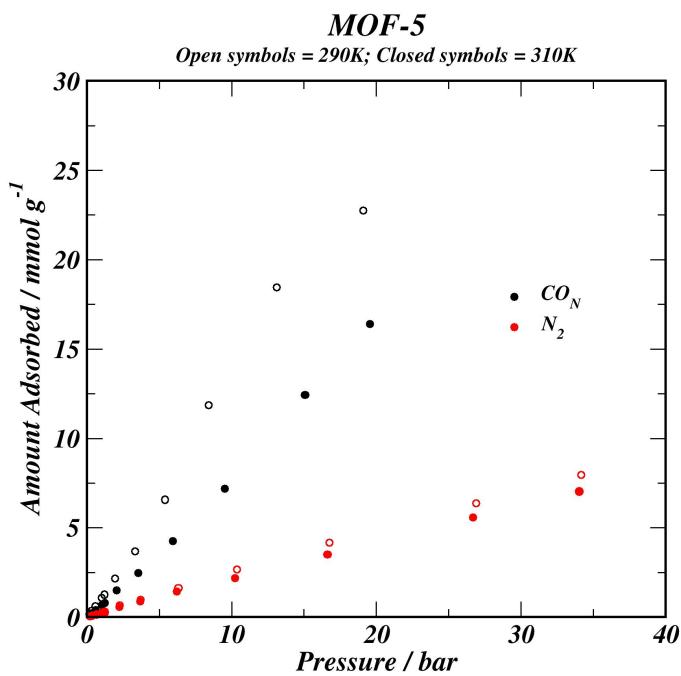


Figure S19
– PCN11

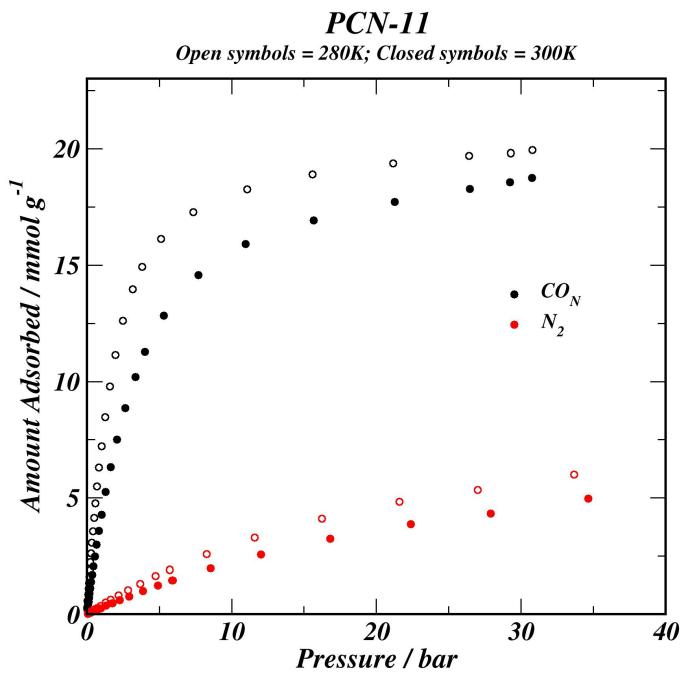


Figure S20
– HKUST-1

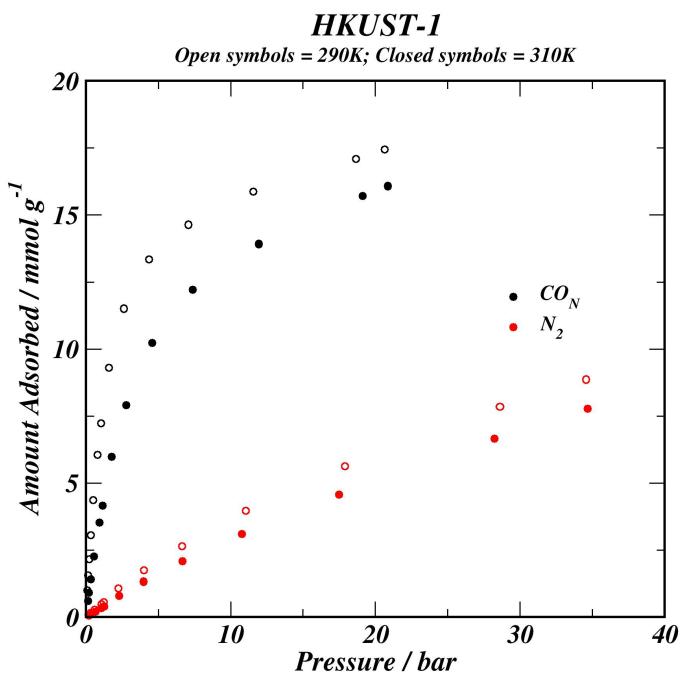


Figure S21 –
Zn-MOF-74

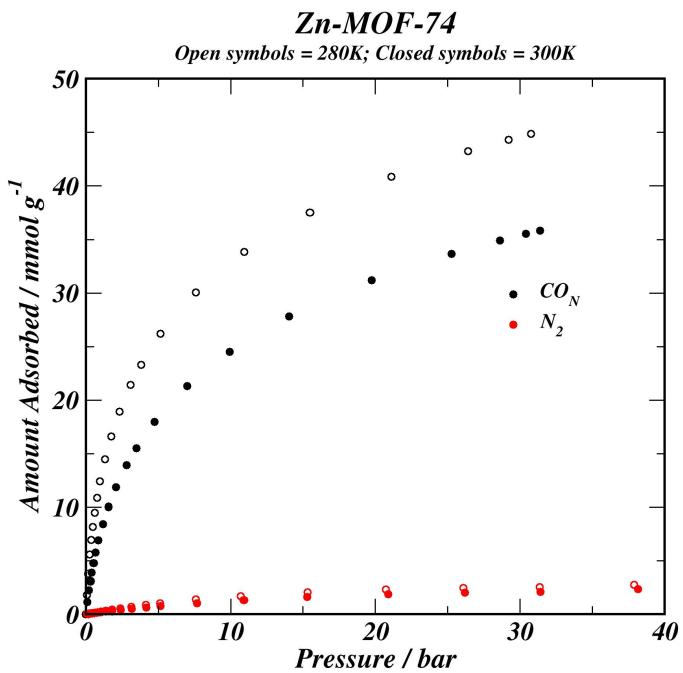
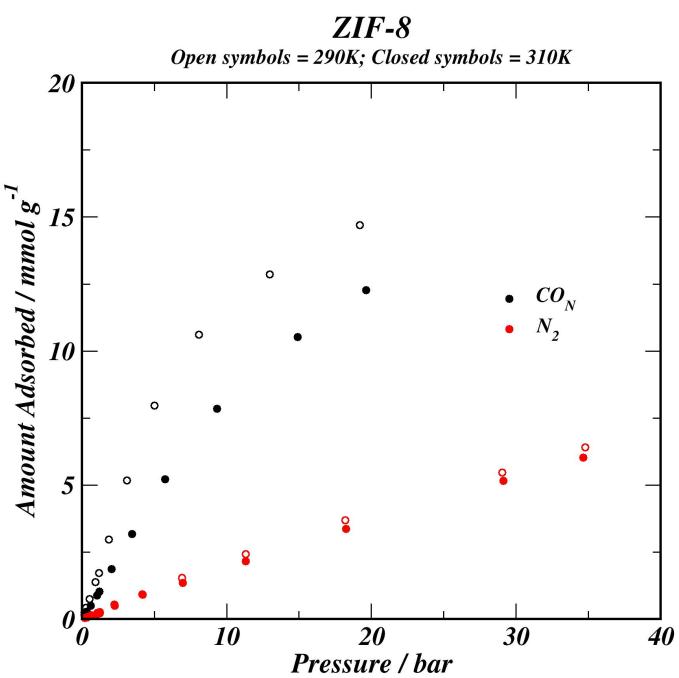


Figure S22
– ZIF8



Section III: Isosteric heat of adsorption as a function of gas uptake, and scaled to the saturation capacity. Figure S23 is the same as was presented (Fig. 3) in the main text. Figure S24 has been scaled by the total amount adsorbed at 220K (N_{max}) in order to show the commonality in the curves at high loading where CO_2 - CO_2 interactions become comparable or larger than the CO_2 -MOF interactions, evidenced by the similar slope as a function of loading.

Figure S23

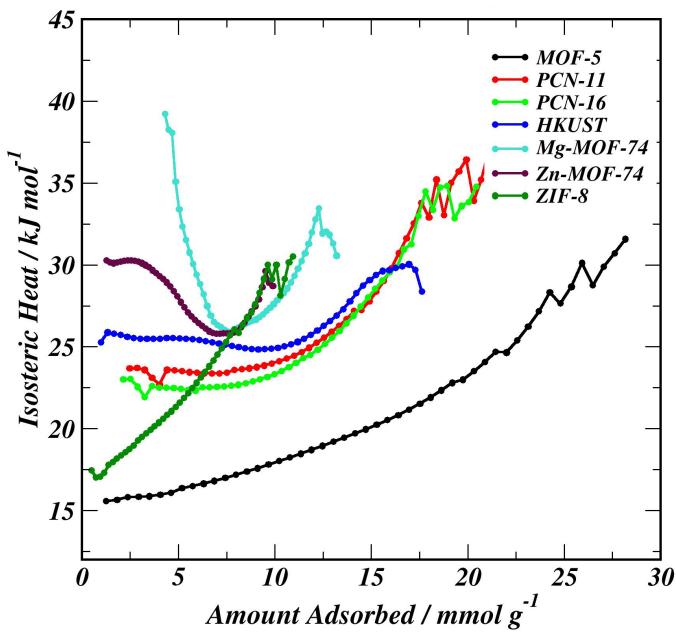
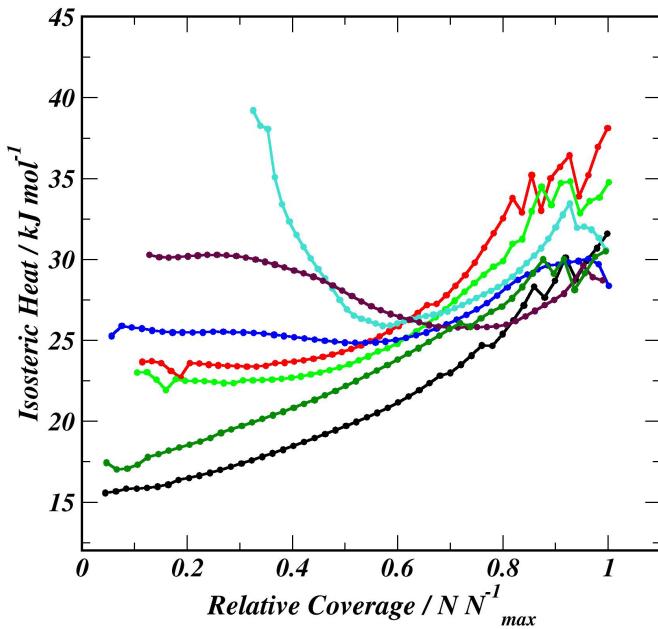


Figure S24



Section IV: Diffraction characterisation of the ZIF-8 sample.

Note: diffraction characterisation of the other MOF samples are included in the references to our earlier work as indicated in the main text.

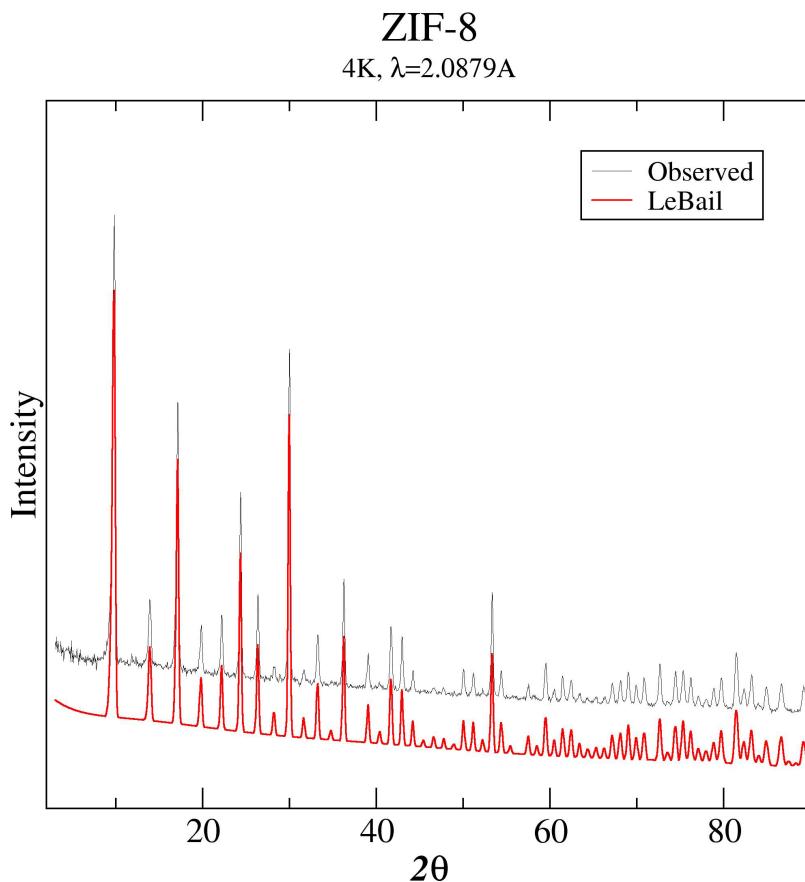


Figure S25

The ZIF-8 sample consists of a 1:1 mixture of Co and Zn atoms but is isostructural to the pure Zn-derived ZIF-8. Observed and calculated diffraction spectra for the ZIF-8 sample, using $\lambda=2.0879\text{\AA}$. The LeBail pattern is generated from the previously published *I4-3m* crystal structure. The lattice parameter of the sample is $16.9962(3)\text{\AA}$, as compared to 16.9910\AA published by Park, et al., (PNAS **103**, 10186 (2006), reference 20 in text), consistent with the slightly larger Co atomic radius.