

Supporting Information for

An amine-functionalized metal organic framework for preferential CO₂ adsorption at low pressures

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Crystallographic details of the structure of **1** at 173K, has been deposited at CCDC with the following reference number:

CCDC 734994

Experimental

Single crystal data collection: Single crystals were mounted by freezing to the tip of a glass capillary using Paratone oil. Experiments were conducted at 173K on a Nonius kappa diffractometer with a graphite monochromated Mo K α radiation (λ = 0.71073 Å) and equipped with a CCD detector. The intensity data collection was performed in the ω - ϕ scanning mode with the goniometer and detector angular settings optimized using the program COSMOS. The unit cell and the orientation matrix were refined using the entire data set of reflections. The diffraction spots were measured in full with a high accuracy, scaled, corrected for Lorentz-polarization correction, and integrated using HKL Denzo and Scalepack (Otwinowski & Minor 1997). Absorption effects were empirically corrected by using SADABS. Full-matrix least-squares refinement on F² was carried out using SHELXL97. The crystallographic data and conditions for structure analysis are listed below.

The solvent water molecules were disordered and hence could not be refined anisotropically and their hydrogens could not be located. All the hydrogens were fixed by placing them in a riding mode. Also, the presence of disorder on one of the amine groups attached to the triazolate ligand (N4 and N4') makes the overall hydrogen count different from the one presented in the formula. The occupancies of disordered water molecules were freely floated and they refined to ~ 0.25 with acceptable thermal parameters.

Crystallographic data for 1: $\text{Zn}_2(\text{C}_2\text{O}_4)(\text{C}_2\text{N}_4\text{H}_3)_2 \cdot (\text{H}_2\text{O})_{0.5}$, Mr = 393.951, orthorhombic, Pbc_a, a = 13.838(3), b = 12.784(3), c = 16.885(3) Å, V = 2987.0(10) Å³, Z = 8, λ = 0.71073 Å, T = 173(2)K, R₁(obs) = 0.0504, R_w(obs) = 0.1204; GOF = 1.113. Reflections measured = 8998; unique reflections = 3040; observed reflections = 2386. These data have been submitted to the Cambridge Crystallographic Database with reference numbers CCDC-734994 (173K, 1) and are available free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Thermal analysis (TGA-DSC) data were recorded on a Netzsch STA 449C apparatus with a heating rate of 5°C /min in the temperature range of 25 to 450°C under N₂ atmosphere.

Synthesis of 1. Cube shaped colorless crystals of **1** were obtained from the reaction of a mixture containing 0.1g of $\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2$, 0.1g of $\text{H}_2\text{C}_2\text{O}_4$ and 0.4g of 3-amino-1,2,4-triazole, 3mL of methanol and 0.5mL of water at 180°C for 2 days (Yield: ~60% based on Zinc). Precise control of the solvent ratios was crucial for the formation of **1** as a pure phase. Changes in the metal/ligand ratios resulted in other competing phases, some of which would be reported elsewhere. Observed CHN % values (calcd. within brackets): C= 18.52 (18.31); H= 1.76 (1.70); N=28.63 (28.46).

Figures

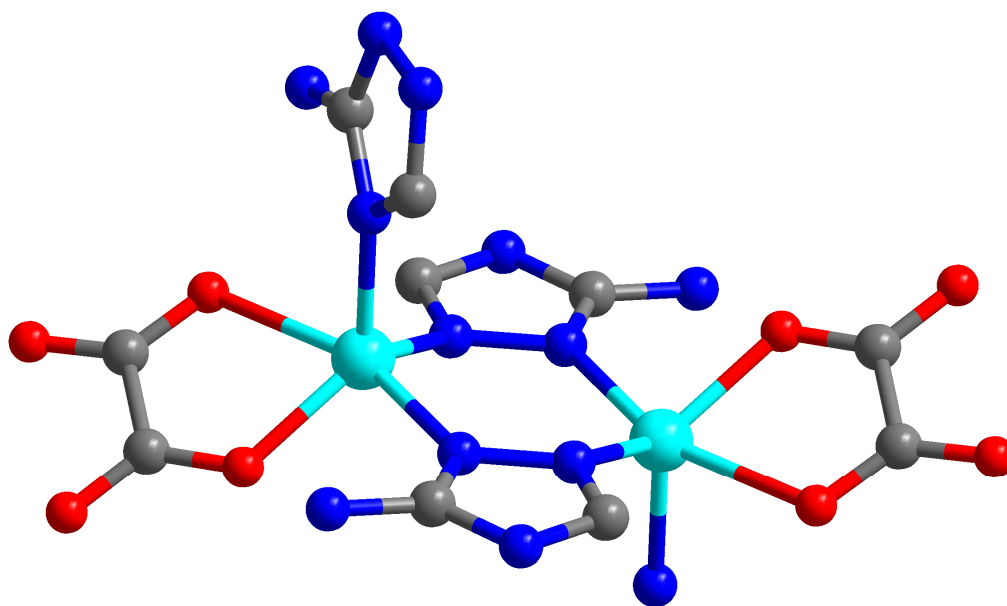


Figure S1. Basic building unit of **1**. The zinc dimers are made up of distorted square pyramidal Zn centers. Color scheme: Zn- cyan; N- blue; O- red; C- grey.

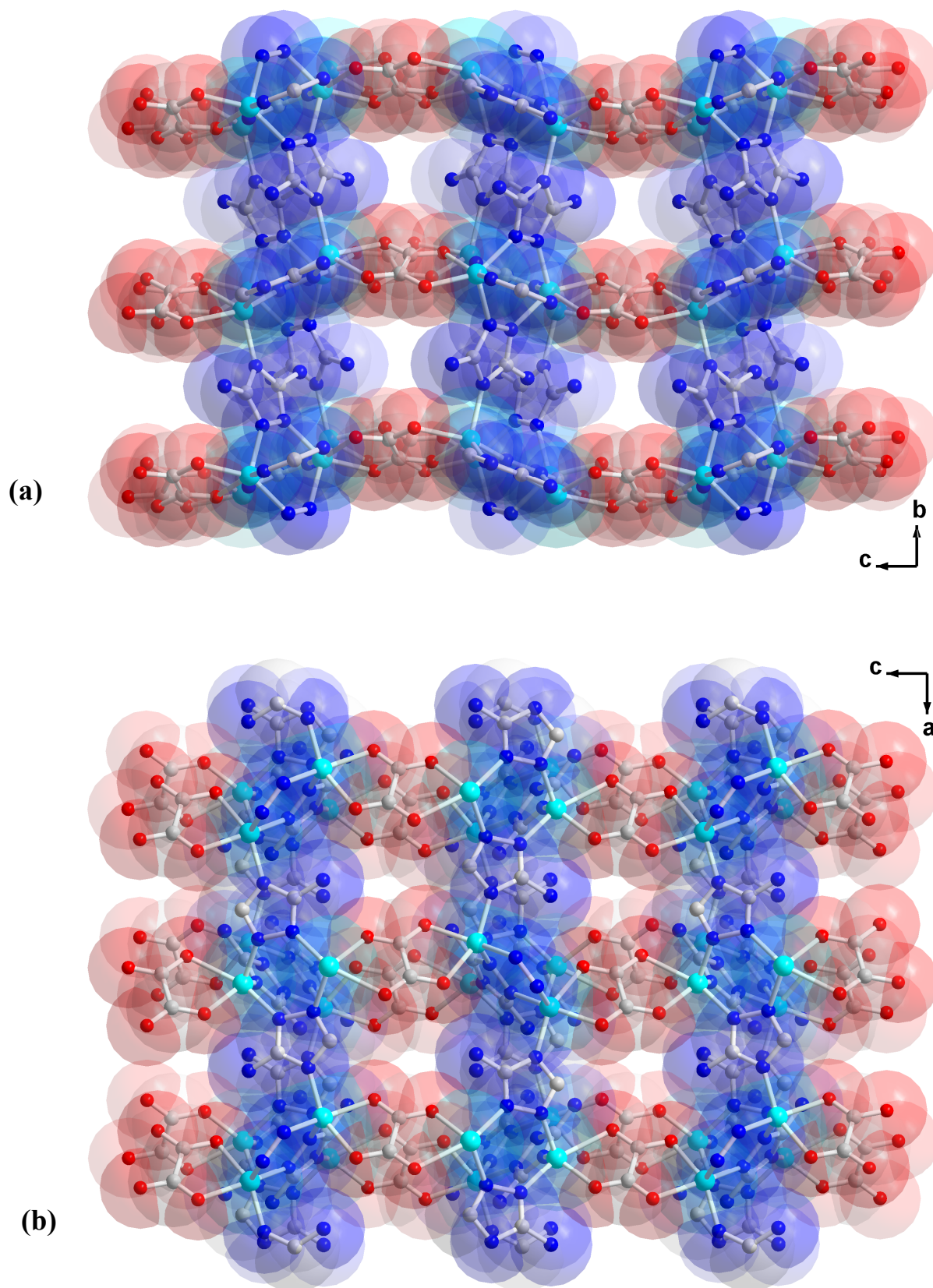


Figure S2. Structure of 1, (a) showing the channels present along the a-axis ($3.5 \times 4.0 \text{ \AA}$). (b) the channels present along the b-axis ($3.9 \times 2.1 \text{ \AA}$). Note: the small slit shaped channels cross-linking these two channels along the c-axis have not been shown.

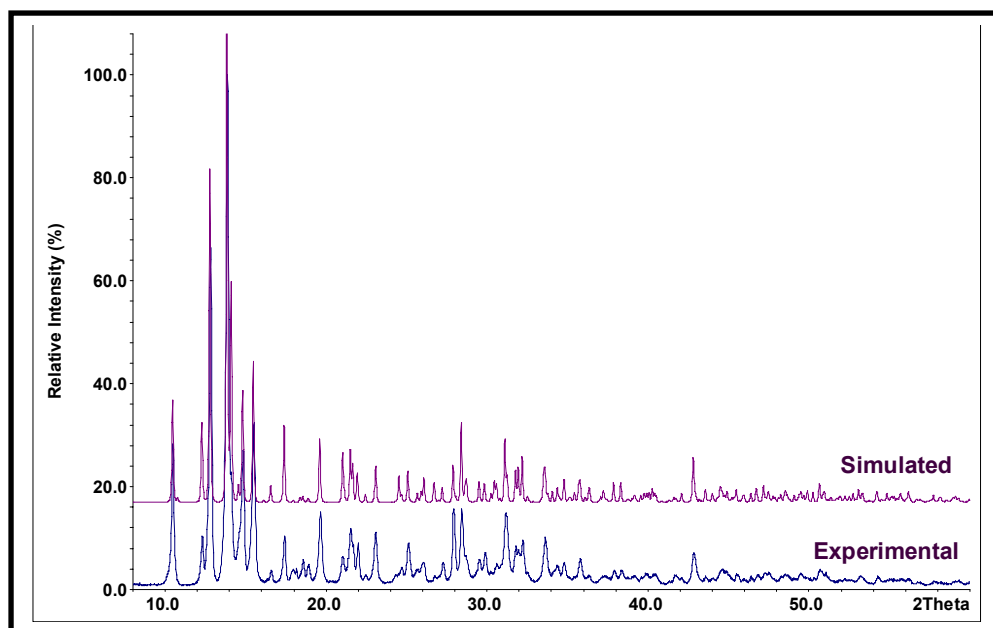


Figure S3. Comparison of the PXRD patterns of the as made **1** with the pattern simulated from the single crystal XRD data.

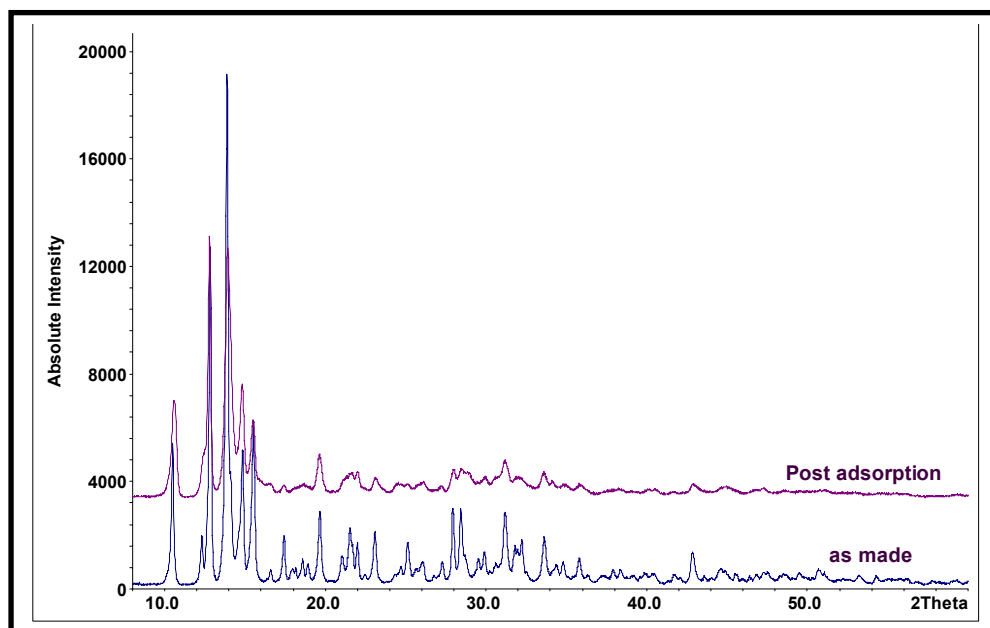


Figure S4. Comparison of the PXRD pattern of as made **1** with a sample which has been activated by soaking in acetone and has been subjected to 8 cycles each involving evacuation at 100°C at 10^{-3} torr for ~16hrs, during the gas adsorption experiments (CO₂, N₂, H₂, Ar).

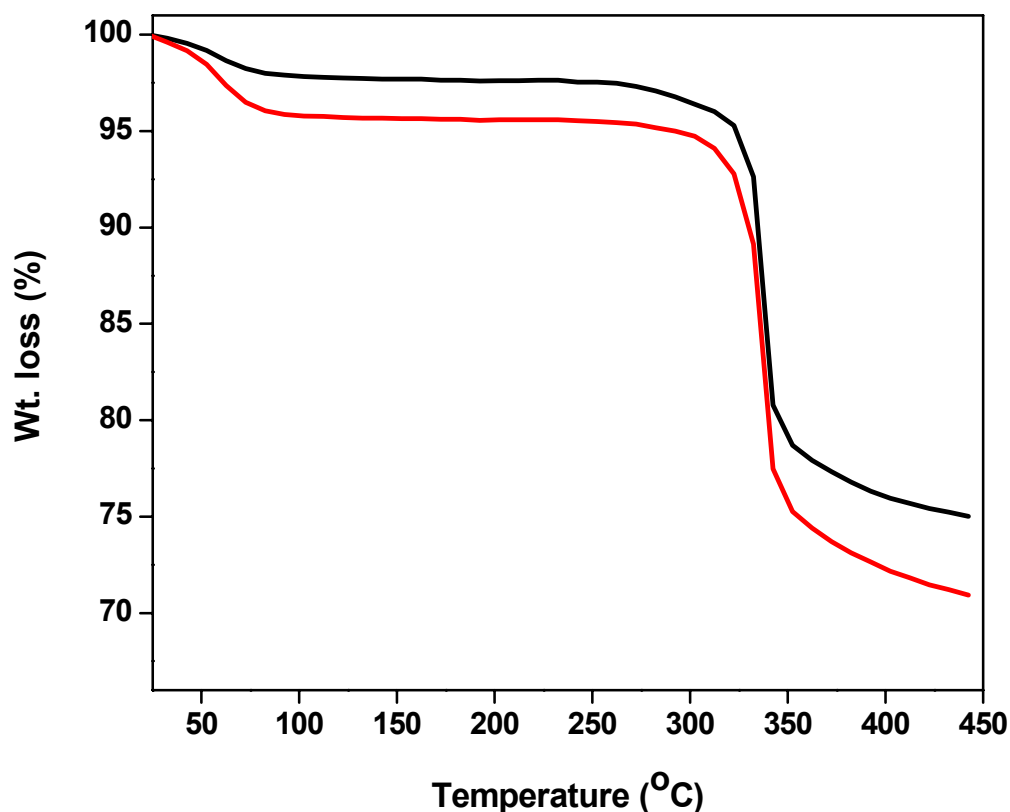


Figure S5. Black: TGA curve of **1**, showing solvent loss (30-130°C) and framework decomposition starting at 300°C. The amount of solvent (0.5 moles per fu) calculated from the weight loss (2.3%) matches with that observed from single crystal XRD (2.3%) and CHN analysis; however PLATON suggests free solvent accessible void capable of accommodating 3 water molecules per fu. This could mean that the as made form of **1** could have methanol solvent molecules along with water, which leave the structure under ambient conditions, leaving **1** partially solvated.

Red: TGA curve of the post adsorption phase of **1**, this indicates that the post adsorption sample is stable up to 300°C after all these heat treatments (100 °C at 10⁻³ torr) and desolvation it has been subjected to during the adsorption experiments. This post adsorption sample was left standing under ambient conditions before being analyzed with the tga. Note that the weight loss due to the solvent (3.8%) is higher than that observed for the as made **1** (2.2%), indicating that the as made **1** is partially solvated -most likely due to loss of solvent methanol molecules.

Adsorption Measurements

The adsorption isotherms for CO₂ (99.998%), N₂ (99.999%), Ar (99.999%) and H₂ (99.999%) were conducted using an Accelerated Surface Area & Porosimetry System (ASAP) 2020 supplied by Micromeritics Instruments Inc. In a general procedure, the dry sample (~100 mg) was loaded into the glass analysis tube. The sample was heated under vacuum (~10⁻⁶ mbar) in two stages, initially to 60 °C at 1 °C min⁻¹ for 2 hrs then to 100 °C at 1 °C min⁻¹ for 12 hrs. After this the outgas rate was less than 2 μbar hr⁻¹. The sample was then backfilled with N₂ before being transferred to the analysis port where it was evacuated for at least a further 240 min before the analysis was started.

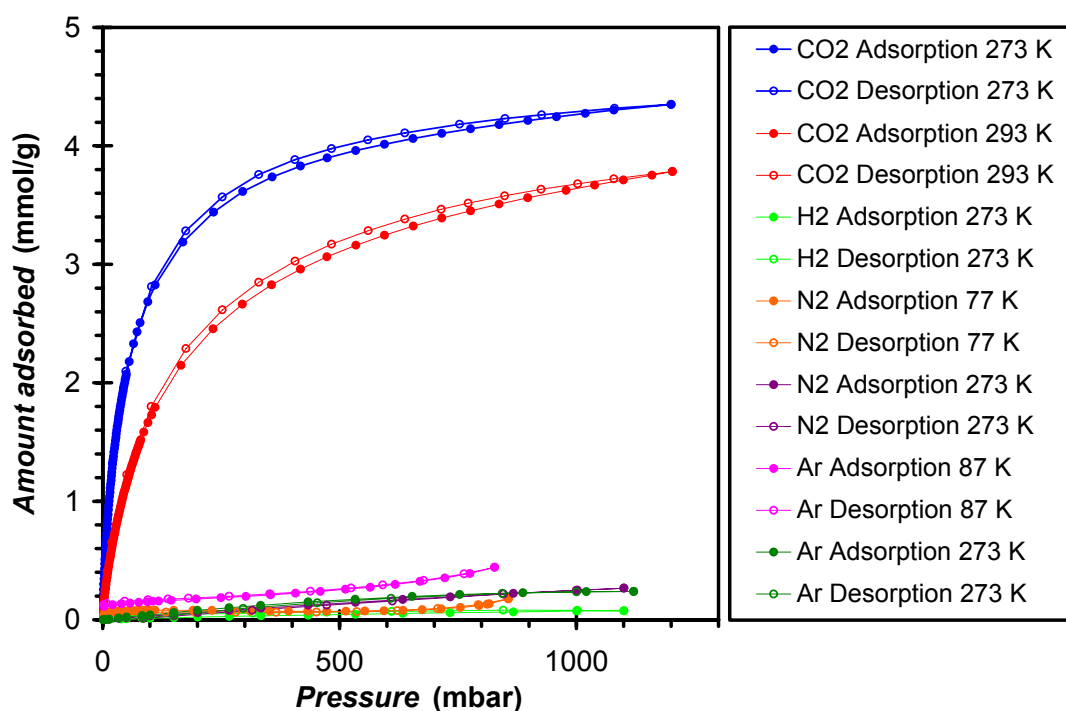


Figure S6. Sorption isotherms of CO₂, H₂, N₂ and Ar in **1**.

Determining the Enthalpy of Adsorption

To allow extrapolation between adsorption points the adsorption branches of the 273.37 and 293.46 K CO₂ isotherms were fitted via least-squares regression to the Virial model (equation 1).¹⁻⁷

$$\ln(n/p) = A_0 + A_1n + A_2n^2 \dots \text{ (equation 1)}$$

Only equivalent adsorption values were fitted on both isotherms. The Virial plot and parameters are shown in figure S7 and table S1 respectively. The isosteric enthalpies of adsorption at zero loading were calculated from the A_0 parameters determined

using equation 1 for adsorption data at 273.37 and 293.46 K. The enthalpies of adsorption of CO₂ for specific surface coverage's were calculated using the van't Hoff isochore.

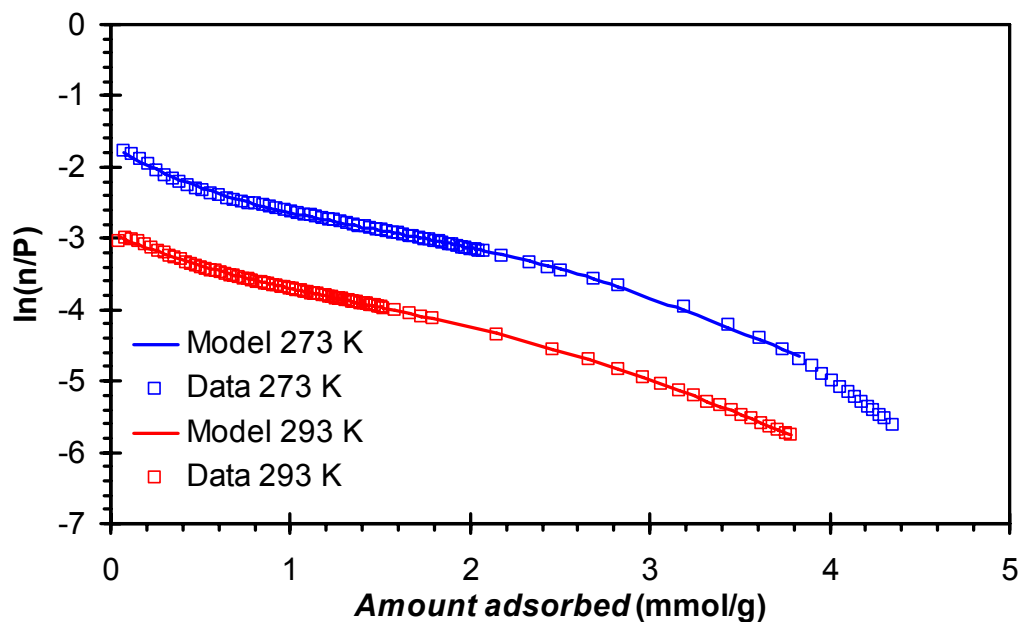


Figure S7. Virial plots

Table S1: Summary of the fitted Virial parameters

Virial Parameter	77.35 K	87.29 K
A_0	-1.69629	-2.92501
A_1	-1.52391	-1.10619
A_2	0.80444	0.46615
A_3	-0.24685	-0.14860
A_4	0.02299	0.01327

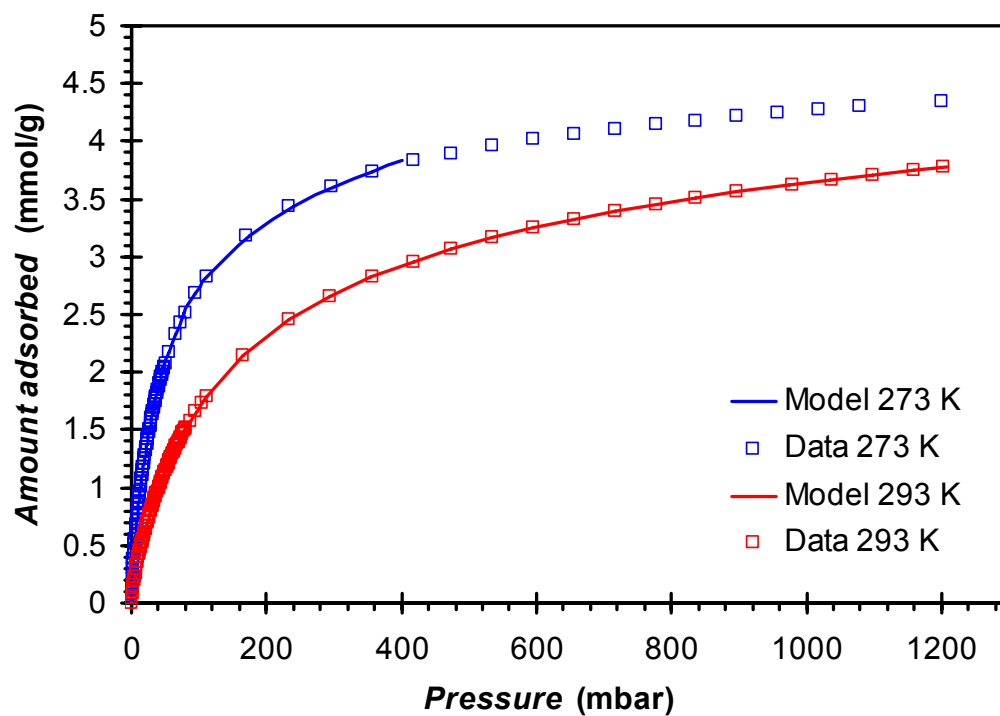


Figure S8. CO₂ sorption isotherms for 273 and 293 K showing the data and fit from the Virial model.

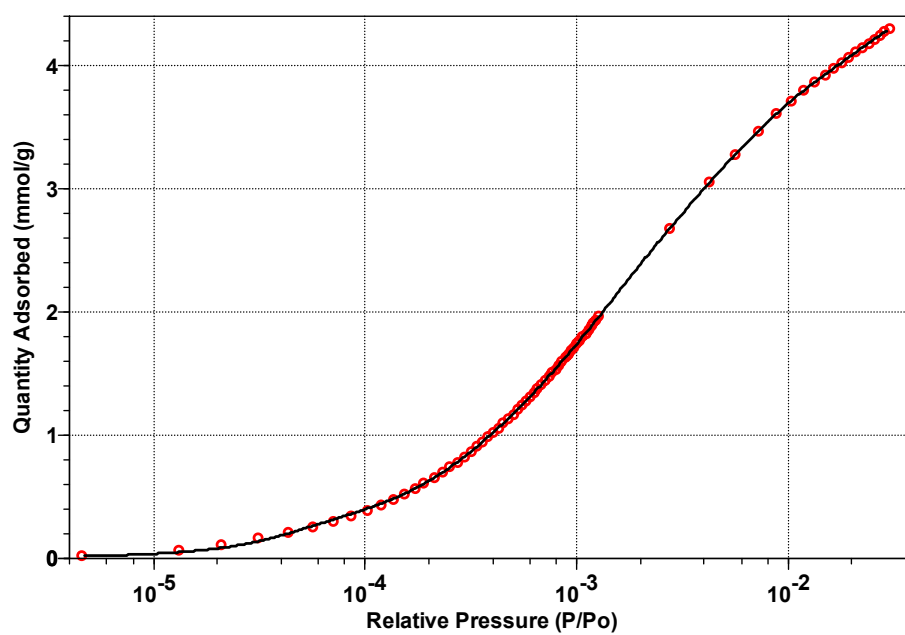


Figure S9. Experimentally determined 273 K CO₂ adsorption isotherm for 1, and fitted DFT model

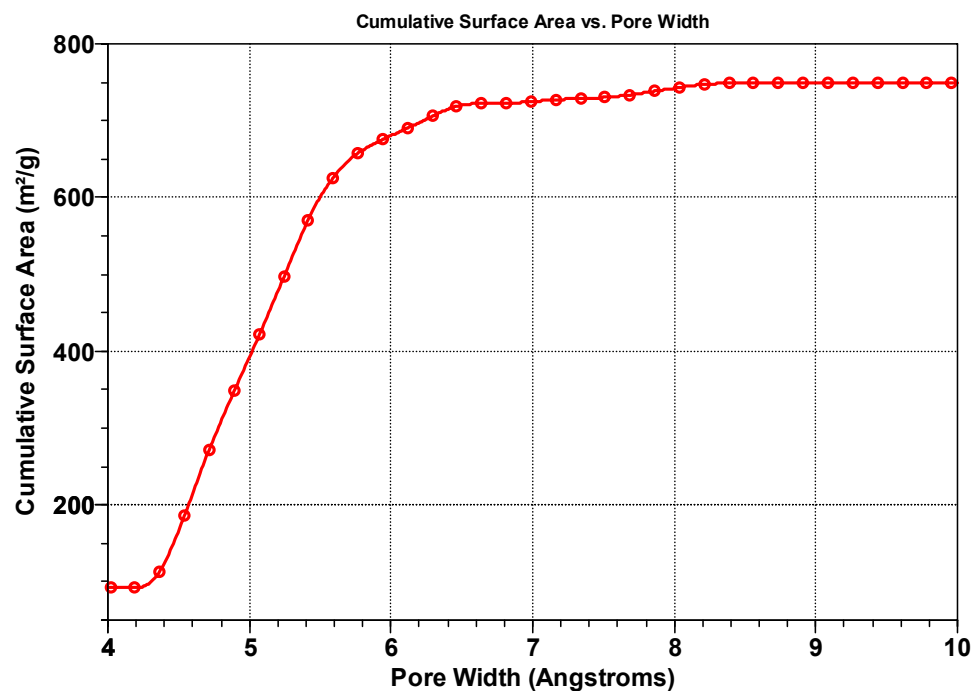


Figure S10. Cumulative surface area as a function of pore width calculated from the adsorption branch of 273 K CO₂ using the Density Functional Model.

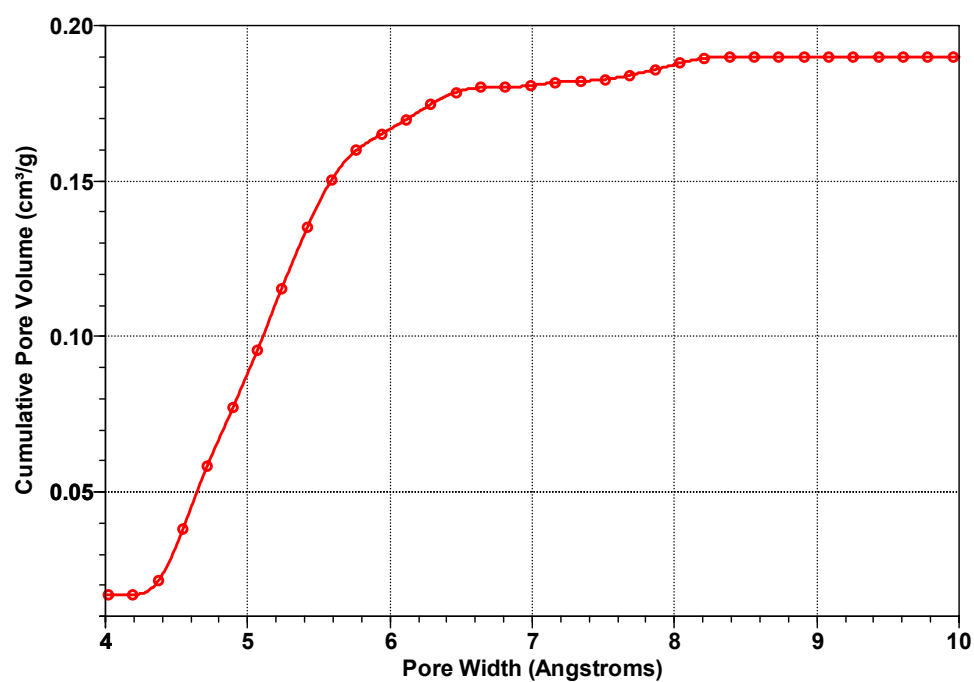


Figure S11. Cumulative pore volume as a function of pore width calculated from the adsorption branch of 273 K CO₂ using the Density Functional Model.

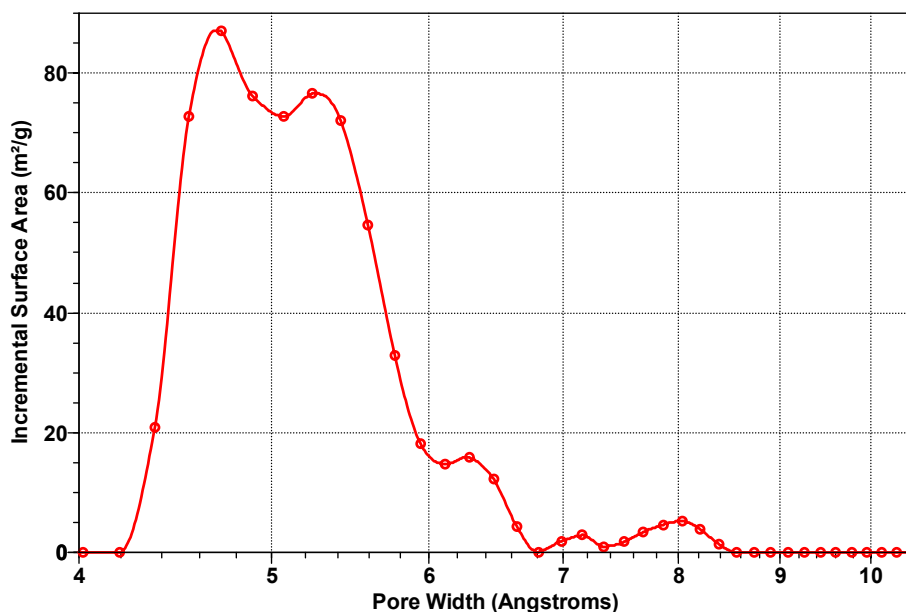


Figure S12. Incremental surface area as a function of pore width calculated from the adsorption branch of 273 K CO₂ using the Density Functional Model.

References

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