Supporting Information for:

High-Pressure Methane Storage and Selective Gas Adsorption in a Cyclohexane-Functionalized Porous Organic Cage

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Experimental Procedure

General Considerations. All reagents were obtained from commercial vendors and used without purification. (1R,2R)-(-)-1,2-diaminocyclohexane was purchased from SigmaAldrich. 1,3,5-triformylbenzene was purchased from Combi-Blocks. Dichloromethane (DCM) was obtained as needed from a solvent drying system.

Synthesis of CC3β

The cage was synthesized using a strategy adapted from previous reports. A 1L Schlenk flask equipped with N_2 line and stir bar was charged with 2.5914 g (22.69 mmol) (1*R*,2*R*)-(-)-1,2-diaminocyclohexane, 2.4706 g (15.24 mmol) triformylbenzene, and 750 mL freshly distilled DCM. The vessel was capped with a septum and the atmosphere was purged with N_2 for 1 hour. The purge needle was removed and the clear pale-yellow solution was allowed to stir under an N_2 atmosphere for 3 days. After synthesis, three methods were explored for storage. A portion of the solution was evacuated to dryness, yielding an off-white crumbly powder which was stored inside a glove box. A portion of the solution was transferred to a smaller vessel and purged with N_2 to dryness to allow for an air-free slow evaporation, yielding a flaky off-white solid which was stored inside a glove box. The remainder was preserved in solution under N_2 until needed.

High-Pressure Methane Procedure

High-pressure isotherms were collected on a Sieverts' apparatus (PCT-Pro-2000 from Hy-Energy Scientific Instruments) using ultrahigh purity gases. Total adsorption was calculated using NIST Thermochemical Properties of CH₄ and the pore volume of each material, as determined via 77 K N₂ adsorption experiments.

Density Measurement

High-pressure methane gravimetric uptake was converted to volumetric uptake using three densities: the crystallographic density of the CC3 β cage, the tap density of the activated cage, and a solvent-compacted density. The tap density of the activated cage was obtained by filling a tared, graduated glass tube with cage and gently tapping it until it was sufficiently settled. Density was calculated using the mass of the cage in the tube and the volume measured by from the graduation marks. Solvent-compacted density was calculated by adding DCM to the top of the tap density sample and letting it evaporate under flowing nitrogen. After complete activation of the sample using a Micromeritics Smart VacPrep, the volume was again determined from the graduation marks, yielding the density.

Powder X-ray Diffraction Data

Powder X-ray diffraction patterns were taken at room temperature on a Rigaku MiniFlex powder diffractometer.



Figure S1. Powder X-ray diffraction patterns for the as-synthesized and activated cage as compared to the simulated pattern of the CC3 β polymorph.¹

Nuclear Magnetic Resonance Spectra



Figure S2. NMR Spectrum of the activated cage.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) and TGA-combustion were performed using a TA Q5000 SA. For the TGA, the sample was heated to 600 °C at a ramp rate of 2 °C/min under a flow of N₂. For the TGA-combustion, the sample was heated to 150 °C with a ramp rate of 10 °C/min under a flow of N₂ to remove all solvent from the sample, and was subsequently cooled to 100 °C. The gas was switched from N₂ to O₂ and the sample was heated to 600 °C with a ramp rate of 3 °C/min to combust the sample.



Figure S3. TGA (top) and TGA-Combustion (bottom) plots for the cage. The blue trace represents weight percent. The red trace represents temperature. The black line denotes the change in gas from N_2 to O_2 .

Gas Adsorption Procedure

Low-pressure 77 K N₂ gas adsorption measurements were obtained with a Micromeritics Tristar gas adsorption analyzer. Both flow and vacuum degassing were investigated. For flow activated samples, the Tristar tubes were purged with N2 on a Micromeritics SmartPrep system after being heated in an oven to remove water. After cooling, the tubes were sealed without exposure to air, weighed, and brought into the glove box. The cage was loaded into the tube, sealed, and degassed at room temperature overnight on the SmartPrep before measuring. For the vacuum activated samples, the Tristar tubes were evacuated on a Smart VacPrep system after being heated in an oven to remove water. After cooling and evacuating the air, the sealed tube was backfilled with N₂ and weighed. The loading and activation procedure was the same as for the flow activated samples, using the Smart VacPrep instead of the SmartPrep. Once fully activated, the tubes were weighed to determine an accurate mass of the samples. N2 adsorption isotherm measurements were surveyed from 25 °C to 300 °C in increments of 25 °C. Once maximum surface area was achieved, new samples were then loaded and heated to their optimal temperature. Surface areas were measured via N₂ isotherm in a 77 K liquid nitrogen bath and calculated using the Micromeritics software. All other isotherms were obtained using a Micromeritics 3Flex, submerging the sample in a temperature controlled bath.

Isotherm Fitting

The adsorption isotherms were fit with single- or dual-site Langmuir-Freundlich model (Eq. 1), where *n* is the absolute amount adsorbed in mmol/g, *P* is the pressure in bar, $q_{sat,1}$ is the saturation capacity in mmol/g, b_1 is the Langmuir parameter in bar⁻¹, and v_1 is the Freundlich parameter for two sites, 1 and 2. The parameters used to fit the adsorption isotherms can be found in Tables S1-S9. Plots of the adsorption isotherms along with their fits are presented in Figures S7-S15.

$$n = \frac{q_{sat,1}b_1v_1}{1+b_1P^{v_1}} + \frac{q_{sat,2}b_2v_2}{1+b_2P^{v_2}} \tag{1}$$

The isosteric heats of adsorption, -Qst, were calculated through the use of the Clausius-Clapeyron equation (Eq. 2) for each gas using the single- or dual-site Langmuir-Freundlich fits for each material at 298 K, 308 K, and 318 K. *P* represents pressure, *n* is the amount adsorbed, *T* is the temperature, R is the universal gas constant, and C is a constant. The slope of $(\ln P)_n$ as a function of 1/T was used to obtain the isosteric heats of adsorption for each gas, shown in Figure S16 and Table S10.

$$\ln P = -\frac{Q_{st}}{R} \left(\frac{1}{T}\right) + C \tag{2}$$

N₂ Full Isotherms



Figure S5. N_2 uptake of the flow activated cage at optimal degas temperature. Solid stars denote adsorption and outlines denote desorption.



Figure S6. N_2 uptake of the vacuum activated cage at optimal degas temperature. Solid stars denote adsorption and outlines denote desorption.

N₂ Isotherms



Figure S7. Pure component isotherm data for N_2 . The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S1.

Table	S1
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	298 K	308K	318 K	
q _{sat,1}	0.444	0.289	0.215	
b 1	0.352	0.447	0.504	
V 1	1.212	1.312	1.376	

O₂ Isotherms



Figure S8. Pure component isotherm data for O₂. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S2.

Table	S2
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	298 K	308K	318 K	
q _{sat,1}	0.556	0.356	11.863	
b1	0.334	0.440	0.008	
\mathbf{V}_1	1.223	1.295	0.991	

Ar Isotherms



Figure S9. Pure component adsorption isotherm data for Argon. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S3.

Table S3				
	298 K	308K	318 K	
q _{sat,1}	1.677	0.746	0.419	
b_1	0.120	0.199	0.318	
V 1	1.089	1.165	1.284	

CO Isotherms



Figure S10. Pure component isotherm data for CO. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S4.

Table S4				
	298 K	308K	318 K	
q _{sat,1}	1.411	49.976	13.531	
b ₁	0.156	0.0002	0.0008	
\mathbf{v}_1	1.040	0.147	0.073	
q _{sat,2}	-	0.683	0.428	
b ₂	-	0.268	0.328	
V 2	-	1.131	1.177	

CH4 Isotherms

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Figure S11. Pure component isotherm data for Methane. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S5.

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	298 K	308K	318 K	
q _{sat,1}	1.878	1.582	1.429	
b_1	0.426	0.390	0.332	
V 1	1.005	1.038	1.054	

CO₂ Isotherms

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Figure S12. Pure component isotherm data for CO₂. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S6.

Table S6				
	298 K	308K	318 K	
q _{sat,1}	3.026	3.695	1.661	
b ₁	0.223	0.105	0.432	
V 1	1.036	1.023	1.090	
q _{sat,2}	0.873	0.990	0.457	
b ₂	3.452	2.074	3.069	
V 2	0.990	0.982	1.056	
$\begin{array}{c} q_{sat,1} \\ b_1 \\ V_1 \\ q_{sat,2} \\ b_2 \\ V_2 \end{array}$	3.026 0.223 1.036 0.873 3.452 0.990	3.695 0.105 1.023 0.990 2.074 0.982	1.001 0.432 1.090 0.457 3.069 1.056	

C₂H₄ Isotherms



Figure S13. Pure component isotherm data for Ethylene. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S7.

Table S/				
	298 K	308K	318 K	
q _{sat,1}	2.281	2.003	1.774	
b ₁	0.647	0.598	0.520	
V 1	0.944	0.984	1.016	
q _{sat,2}	0.940	0.877	0.859	
b ₂	8.297	5.783	3.882	
V 2	0.988	0.989	0.985	

C₂H₆ Isotherms

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Figure S14. Pure component isotherm data for Ethane. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S8.

Table S8				
	298 K	308K	318 K	
q _{sat,1}	3.174	2.286	1.777	
b_1	0.436	0.510	0.556	
V 1	0.839	0.899	0.956	
q _{sat,2}	0.848	0.814	0.777	
b ₂	18.687	12.567	8.719	
V 2	0.988	0.993	1.001	

C₂H₂ Isotherms



Figure S15. Pure component isotherm data for Acetylene. The black symbols refer to 298 K, red for 308 K, and blue for 318 K. The closed symbols show adsorption data while the open symbols show desorption. The black lines are the respective Langmuir-Freundlich fits using the parameters in Table S9.

Table S9				
	298 K	308K	318 K	
q _{sat,1}	1.245	1.728	2.358	
b ₁	40.529	14.494	5.456	
V 1	1.571	1.421	1.257	
q _{sat,2}	2.117	1.522	0.261	
b ₂	0.732	0.468	0.674	
V 2	0.903	1.243	3.234	
qsat,3	0.519	0.347	0.140	
b ₃	28.853	24.122	30.908	
V 3	1.0166	0.975	0.968	

Isosteric Heats of Adsorption



References

1. Little, M. A.; Chong, S. Y.; Schmidtmann, M.; Hasell, T.; Cooper, E. I. Guest control of structure in porous organic cages. *Chem. Commun.* **2014**, *50*, 9465-9568.