Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supplementary Information for

# Tunable Hydrocarbon Adsorption Based on a Zeolitic Imidazolate Framework in the Sodalite Topology

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**General Experimental Condition:**

4,5,6,7-Tetrahydrobenzimidazole was synthesized as described in reference 1.[i] Reagents were purchased from Sigma-Aldrich and used as received. Unless otherwise specified, diffraction measurements were conducted on either a Bruker Endeavor D8 or a Panalytical XPert Pro diffraction system using Cu Kα radiation with an energy discriminating detector (D8) or a nickel foil and silicon strip detector (Panalytical). For non-ambient measurements, the Panalytical diffraction system with an Anton Parr, HTK-16N environmental diffraction cell was utilized. The sample was heated using a Platinum heating strip, and for in situ activation, the sample cell was evacuated using an Edwards T75 pumping station operating at a pressure of $5\times10^{-4}$ Torr. NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer.

**Synthesis of EMM-36-100**: 100 mg (0.82 mmol) of 4,5,6,7-tetrahydrobenzimidazole was dissolved in 10 mL of ethanol and 0.1 mL of concentrated ammonium hydroxide. To this solution, 100 mg of zinc acetate dihydrate (0.455 mmol) was added as a solid and the suspension stirred for 16 hours at 60 °C. The solids were then filtered and washed with ethanol and dried at 100 °C under air. Samples of EMM-36 comprising benzimidazole were synthesized in an analogous fashion using equal molar substitutions of $4_H$-BIM for BIM.

**Gas Adsorption and Microcalorimetry**

Adsorption isotherm measurements were performed with the Autosorb-iQ and Autosorb-1C volumetric adsorption analyzers from Quantachrome Instr (Anton Paar) using research-grade gases. For the microcalorimetric measurements a custom cell has been connected to the Tian-Calvet type SENSYS microcalorimeter from Setaram. The measured heat flow signal after each successive dose of gas was integrated to obtain the enthalpy change simultaneously with the amount of gas adsorbed in the volumetric measurement. With the dual-cell (sample and reference) the calorimeter measures the isosteric enthalpy of adsorption (isosteric heat) directly. The measurements have been validated by comparisons with the Clapeyron-Clausius equation[ii] [iii] [iv]. When a phase change occurs in the material, the measured enthalpy includes not only enthalpy change due to adsorption, but also enthalpy change due to a phase transition. For the narrow-to-large pore type phase transition in ZIF-7 and EMM-36 this change is endothermic, resulting in an overall lower enthalpy (less negative).[v] [vi]

**DFT Calculations**

DFT calculations were performed using plane-wave CASTEP code (version 2018), PBE functional [vii]with Tkatchenko-Scheffler [viii]dispersion corrections, gamma-point, 517 eV cutoff, ultrasoft pseudopotentials, and 2e-6 eV/atom convergence tolerance. The predicted unit cell dimensions of 23.45 x 23.45 x 15.37 Å compare very well with the experimental values of 23.57 x 23.57 x 15.24 A.

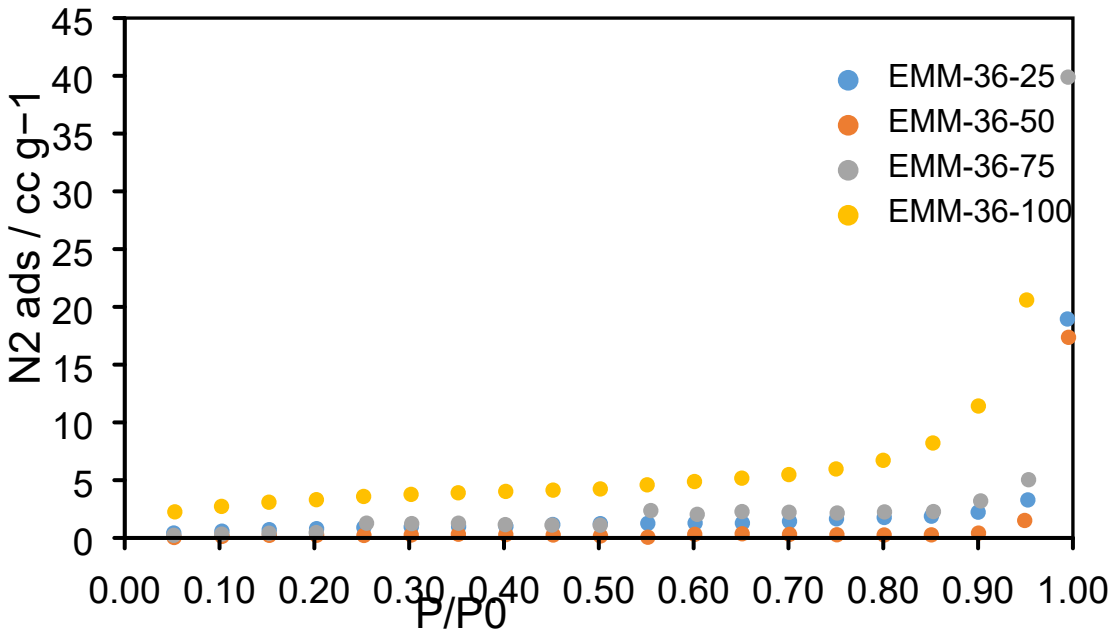


Figure S1. Nitrogen adsorption isotherms conducted on EMM-36 samples at 77 K.

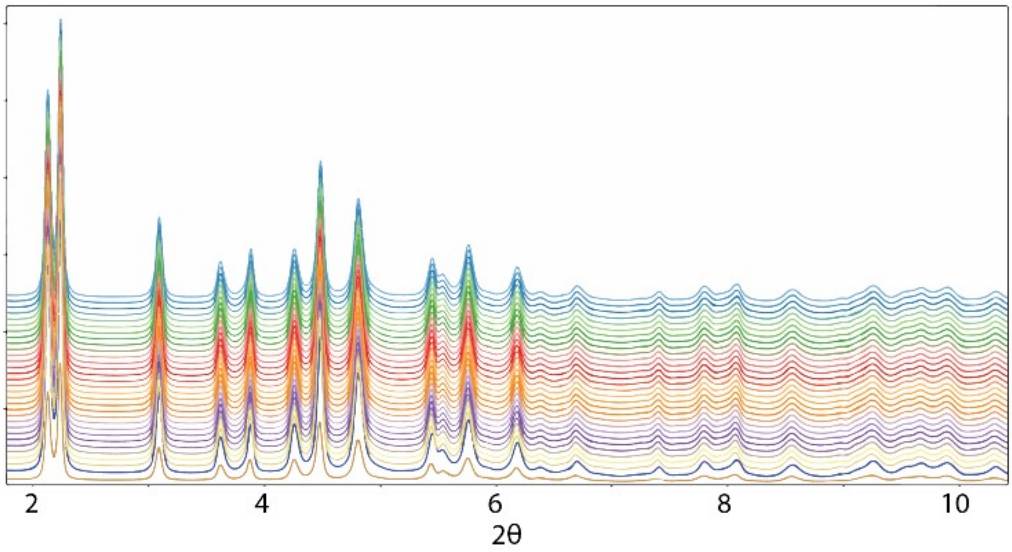


Figure S2 X-ray diffraction patterns taken of EMM-36-100 from temperatures of 150 K (bottom) to 80 K (top) under flowing helium conducted at the Advanced Photon Source at sector 17 BM. λ = 0.45425 Å.

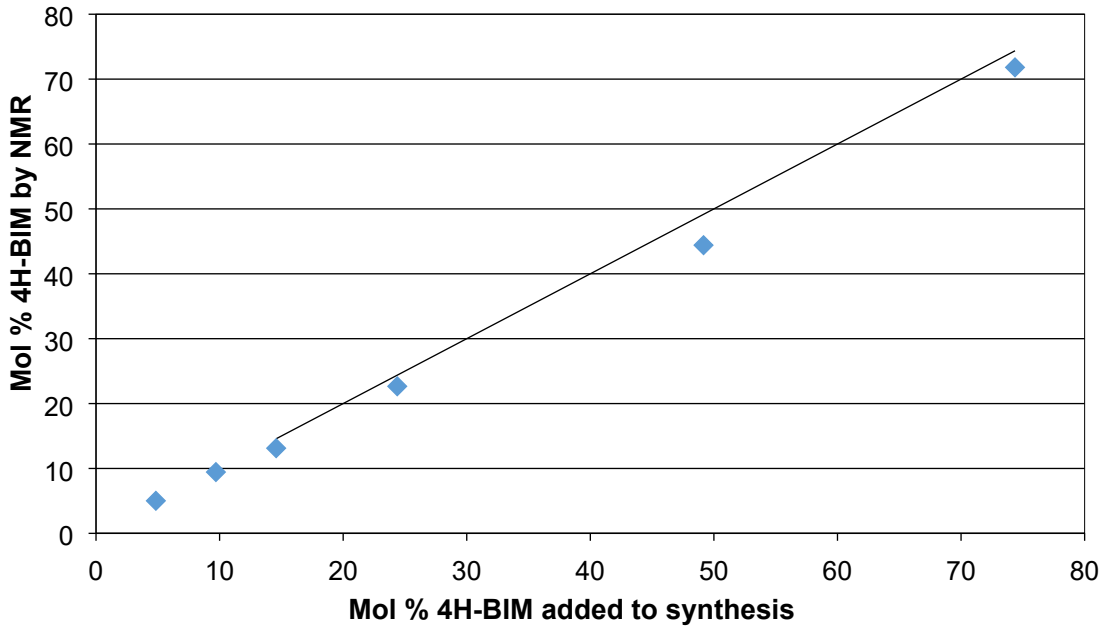


Figure S3. Plot of the mol% of $H_4$-BIM in EMM-36 materials prepared using a mixed-linker approach as determined by solution-state $^1$H NMR spectroscopy performed on the digested material (digestion performed by suspending the material in dimethyl sulfoxide-$d_6$ and adding 1 drop of conc. DCl solution).

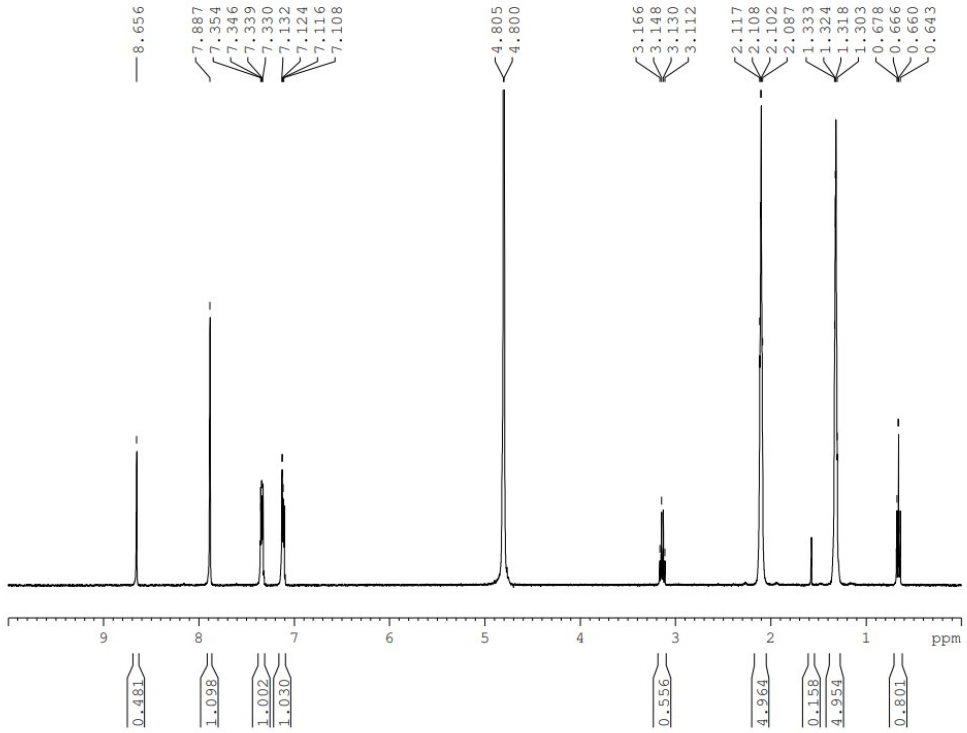


Figure S 4. NMR of EMM-36-75 dissolved in a mixture of DCl and $D_2O$

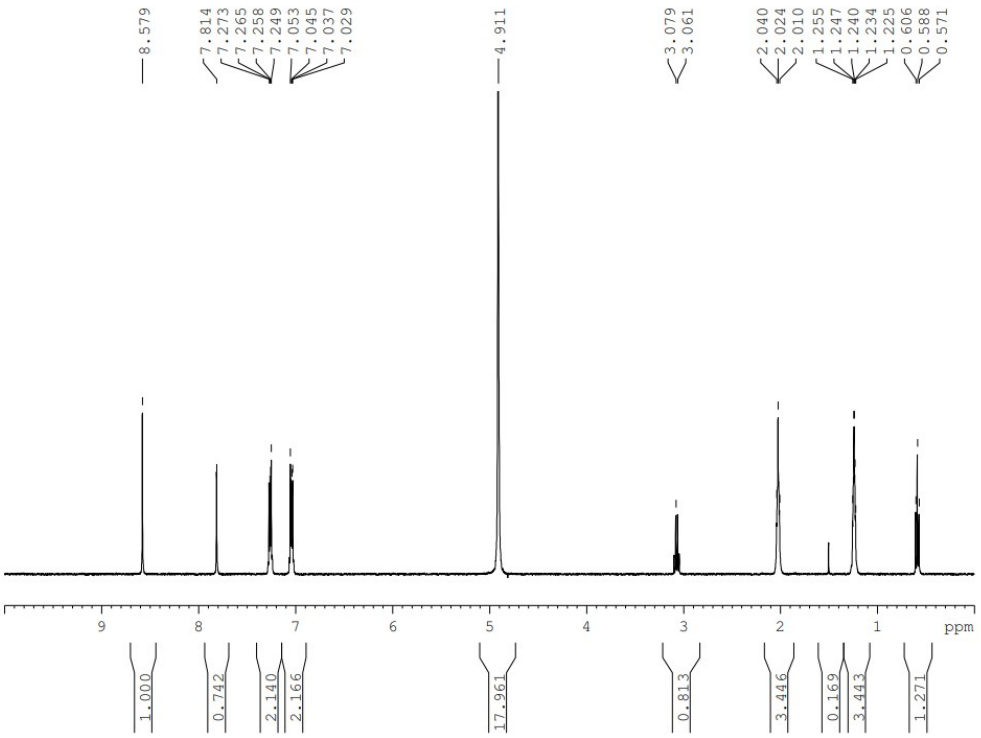


Figure S 5. NMR of EMM-36-50 dissolved in a mixture of DCl and $D_2O$

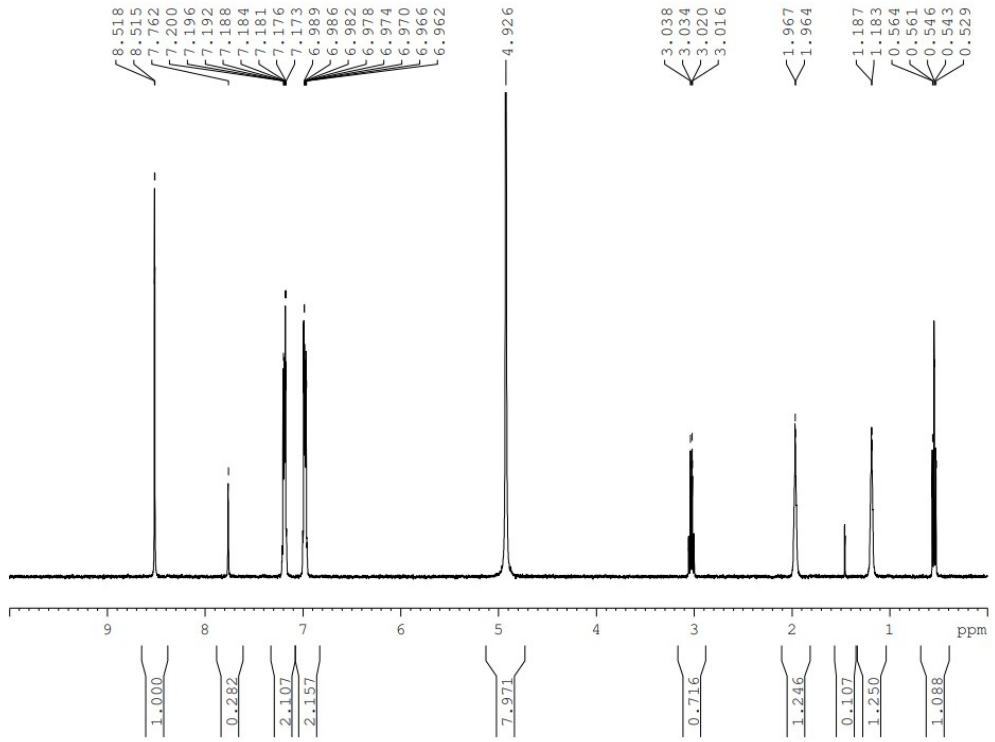


Figure S 6. NMR of EMM-36-25 dissolved in a mixture of DCl and $D_2O$

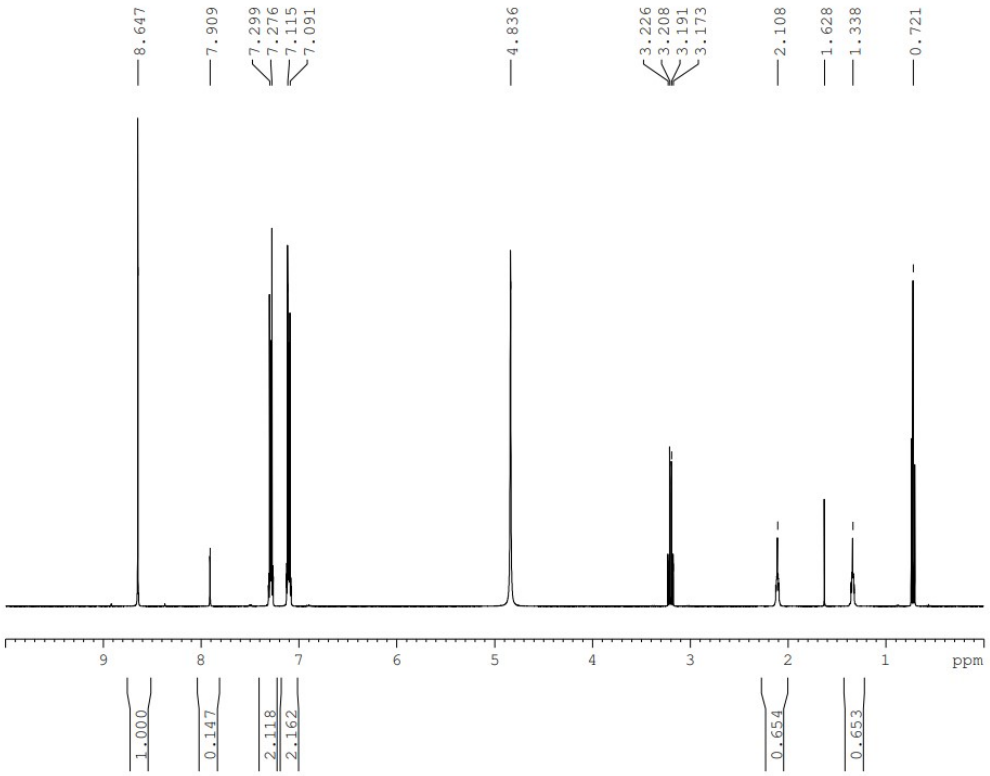


Figure S 7 NMR of EMM-36-15 dissolved in a mixture of DCl and $D_2O$

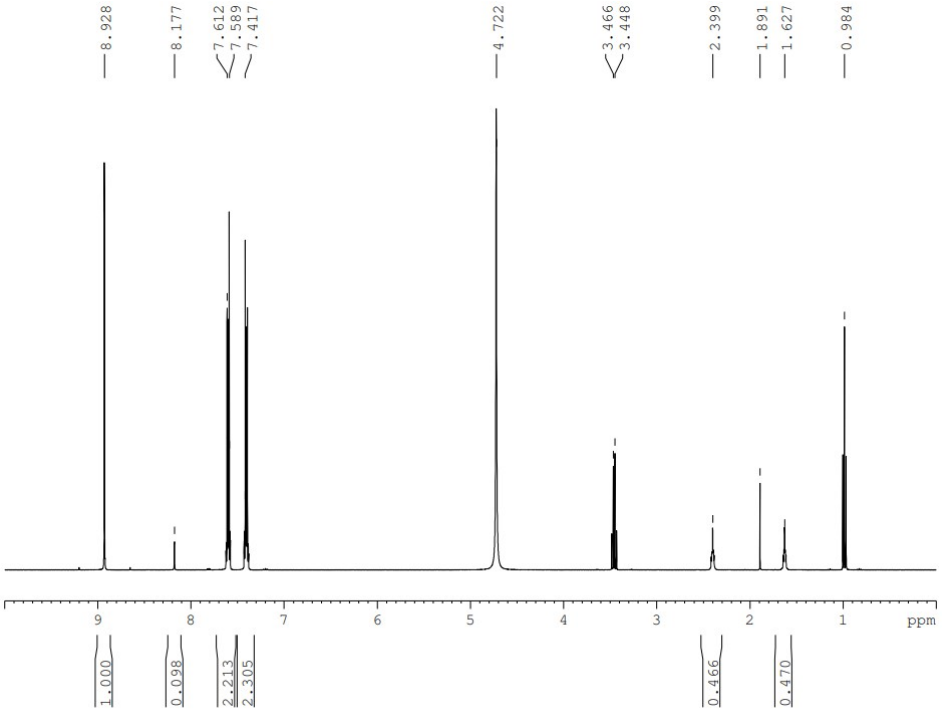


Figure S 8 NMR of EMM-36-10 dissolved in a mixture of DCl and $D_2O$

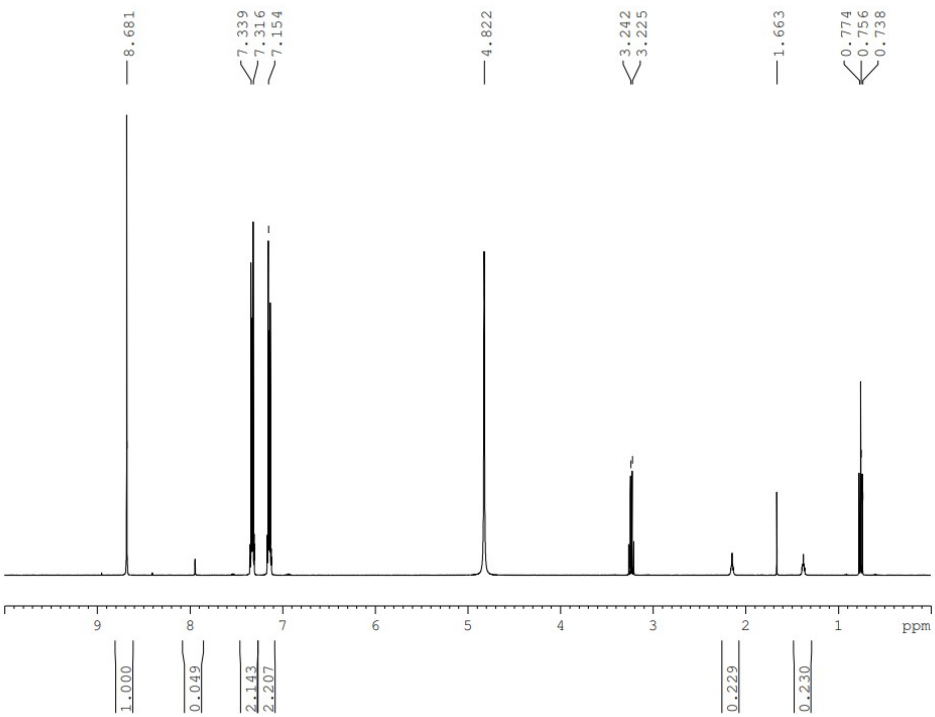


Figure S 9 NMR of EMM-36-5 dissolved in a mixture of DCl and $D_2O$

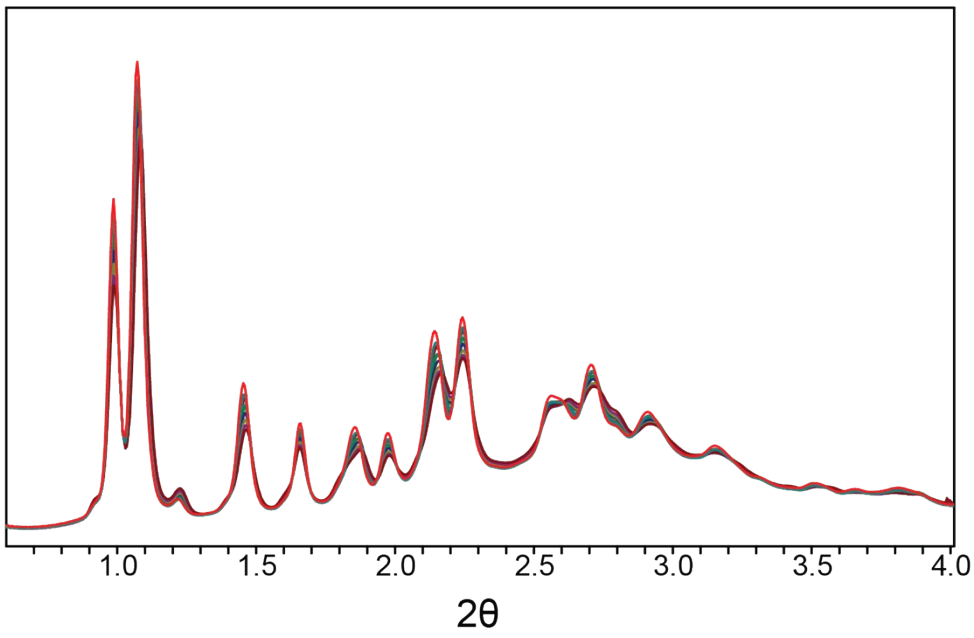


Figure S10. Powder X-ray diffraction patterns collected on EMM-36-22 under a vacuum of $<10^{-5}$ torr and the Advanced Photon Source on the sector 11 ID-B beamline at a wavelength of 0.21150 Å. Temperatures range from 301 K to 203 K.

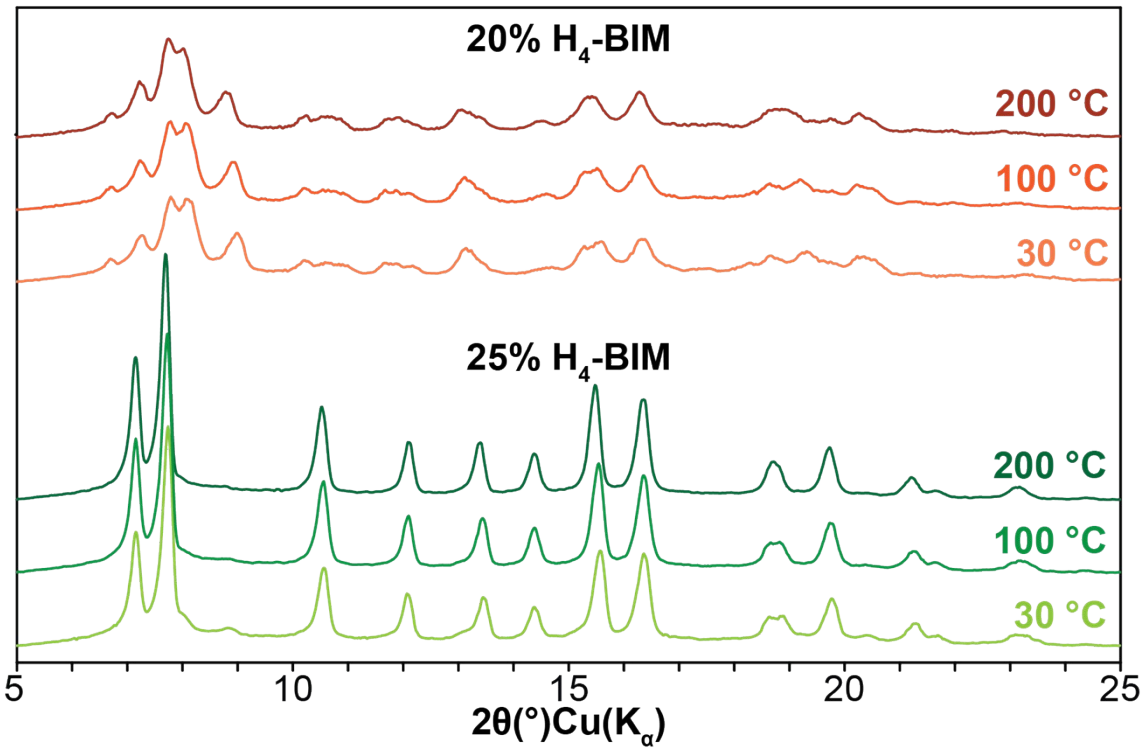


Figure S11. Powder X-ray diffraction patterns of EMM-36-20 (top three traces) and EMM-36-25 (bottom three traces) at 30, 100, and 200 °C. All diffraction patterns were collected under an atmosphere of $N_2$.

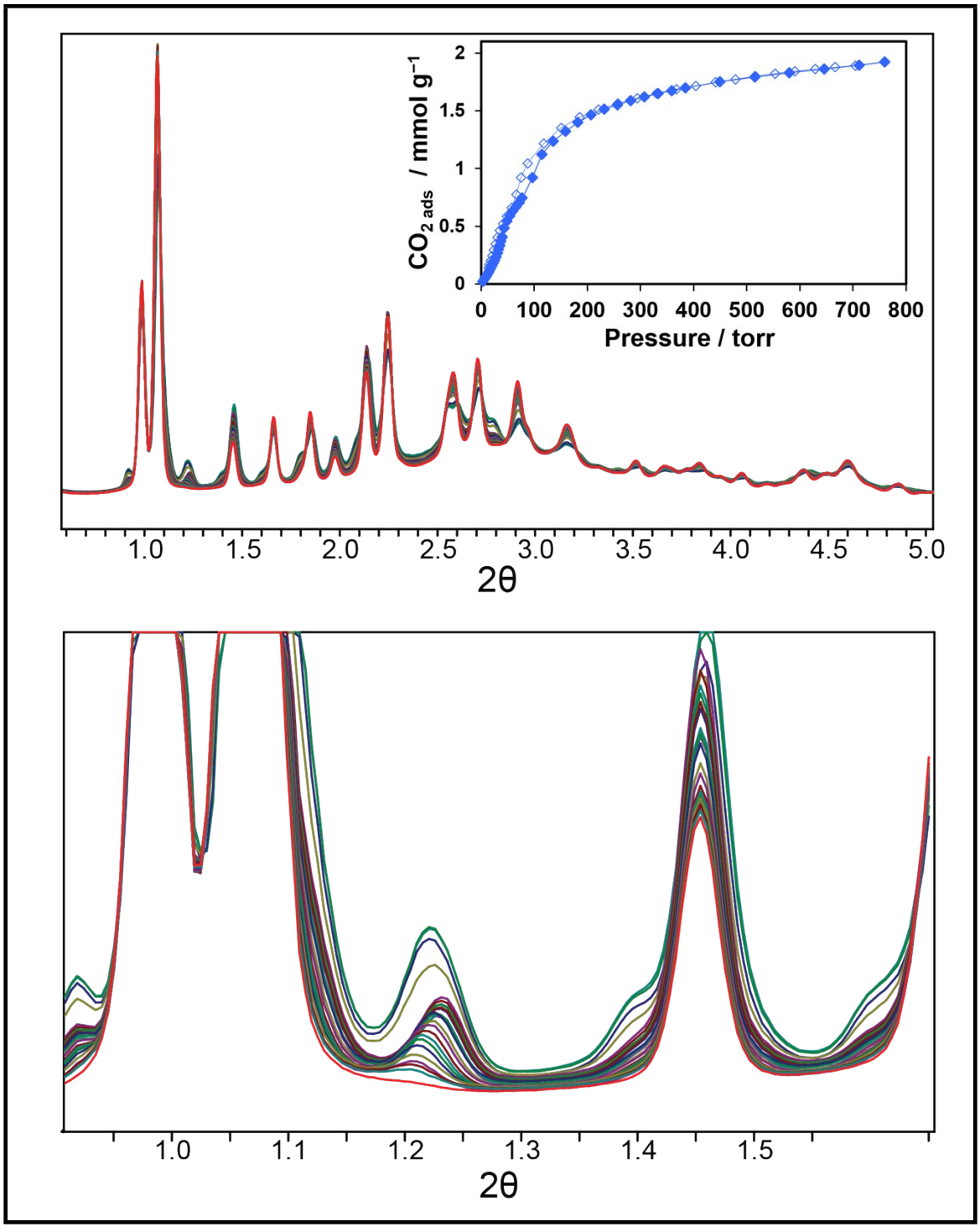


Figure S12. Powder X-ray diffraction patterns collected on EMM-36-25 at 301 K as a function of $CO_2$ pressure. Measurements were conducted at the Advanced Photon Source on sector 11-ID-B at a wavelength of 0.21150 Å. At a vacuum of $<10^{-5}$, an intense peak at 1.25 ° 2θ is observed, which decreases and shifts to higher angles as $CO_2$ is introduced into the system. This represents the first phase transition, which is followed by shifting of these peaks back to higher 2θ as the second phase transition occurs. Inset: Isotherm of EMM-36-25 at 301K

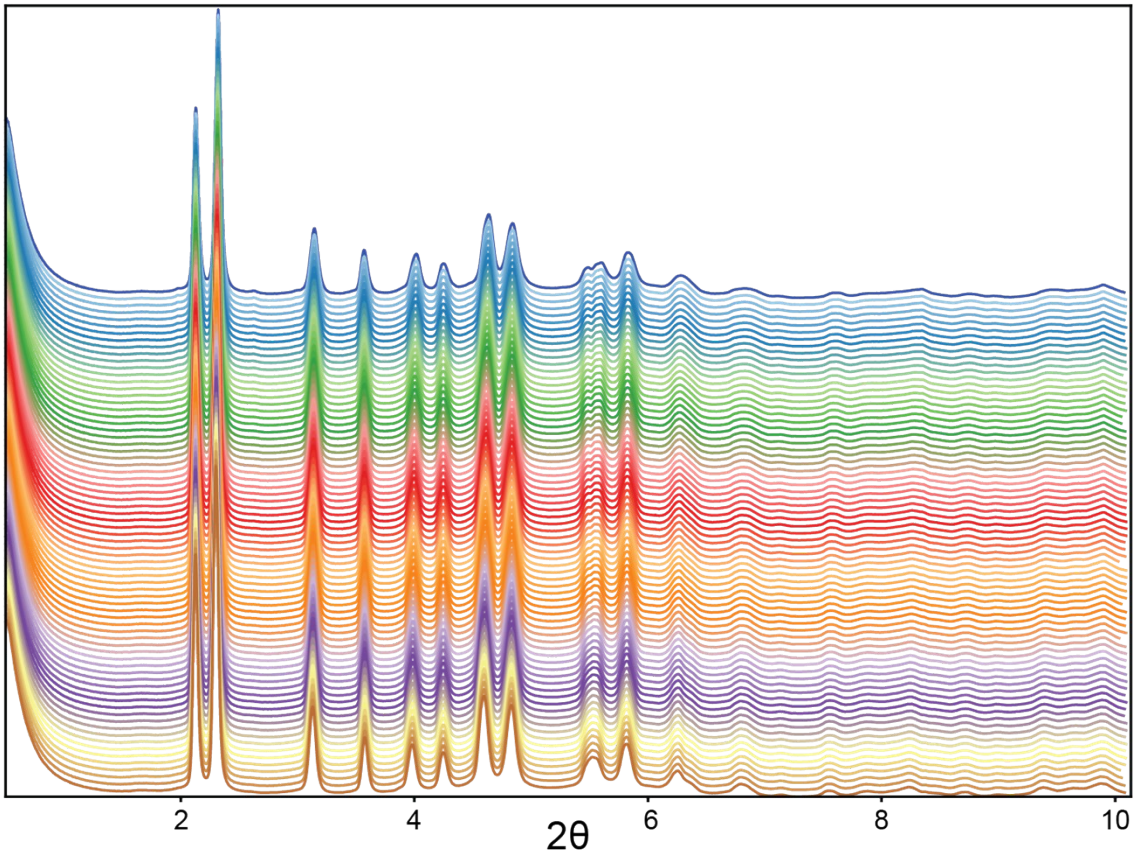


Figure S13. X-ray diffraction patterns collected on EMM-36-30 scanning a range of temperatures from 295 K (bottom) to 180 K (top). Samples collected at the Advanced Photon Source at sector 17-BM at a wavelength of 0.42425 Å.

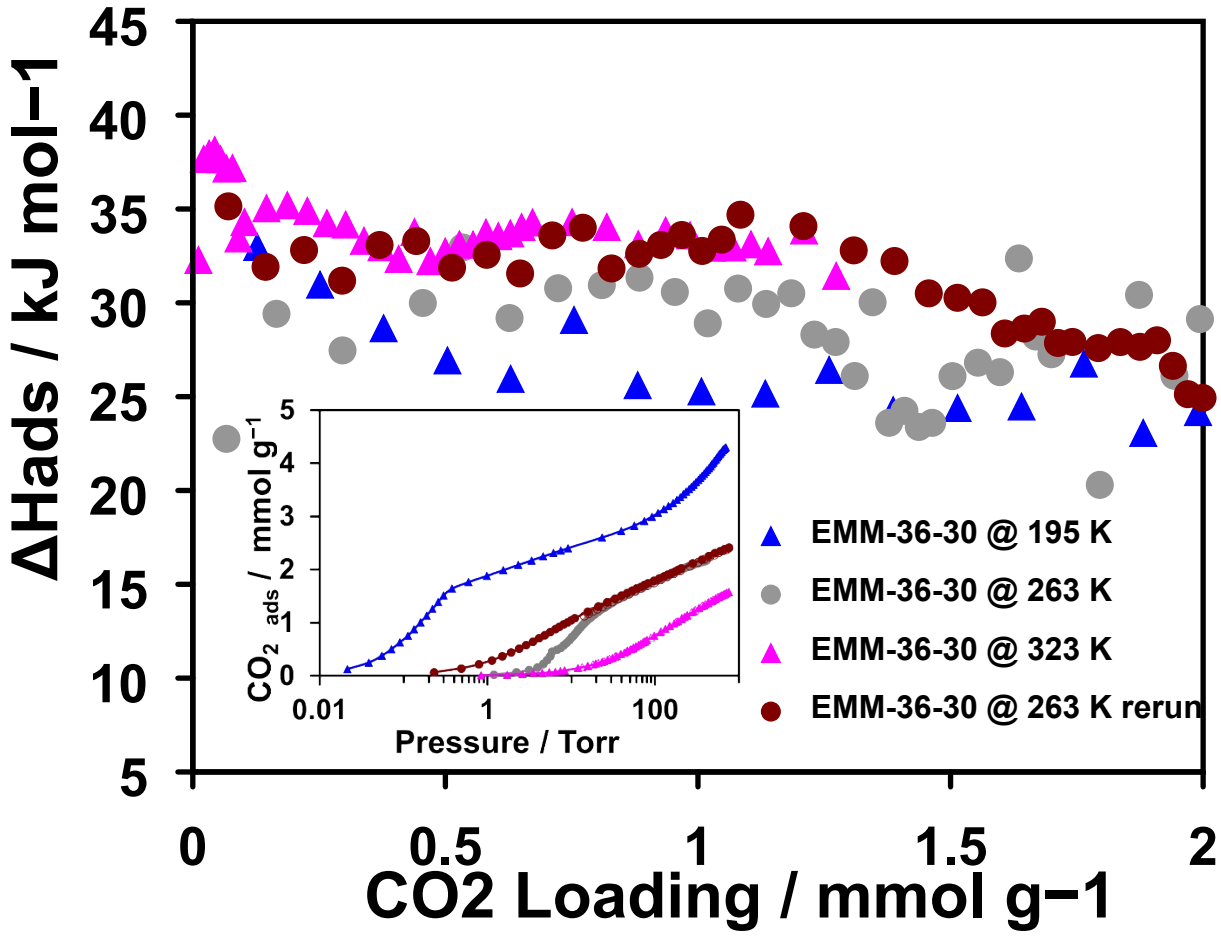


Figure S14. Microcalorimetrically measured enthalpies of $CO_2$ on EMM-36-30. Inset: isotherms of EMM-36-30 at 195, 263, and 323 K. The isotherms were chronologically collected in that order. The brown squares (and brown isotherm) represent the $CO_2$ isotherm conducted at 263 K after measuring the isotherm at 323 K

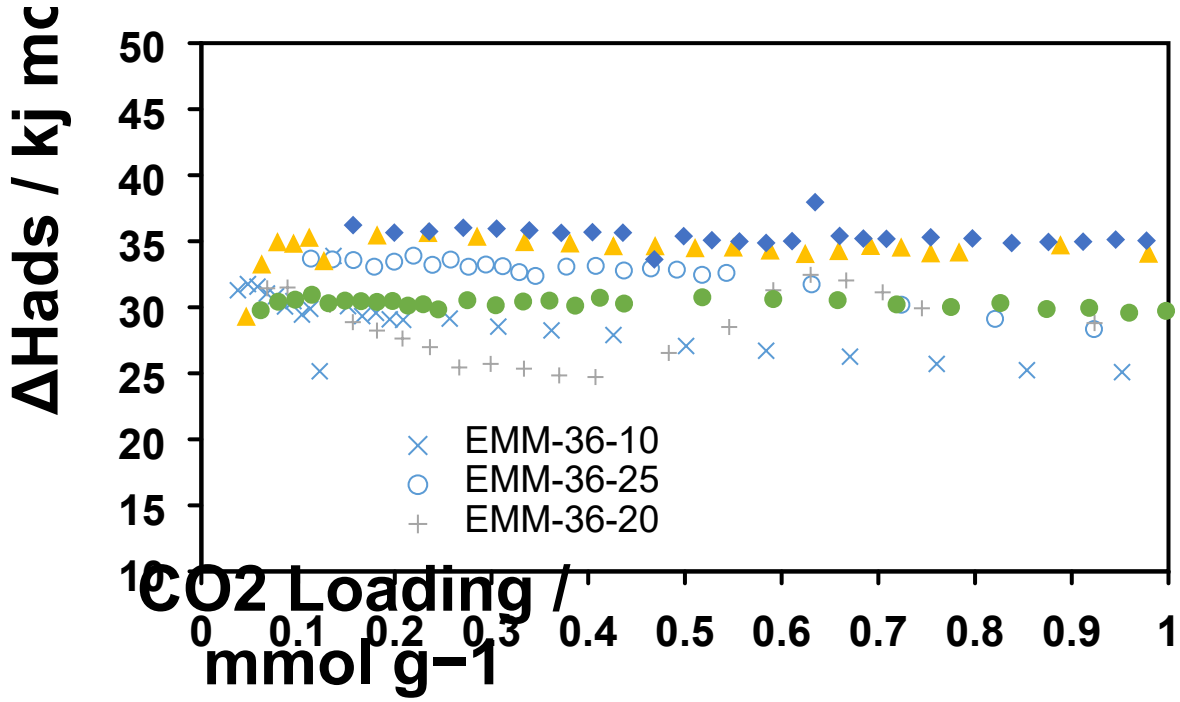


Figure S15. Heat of adsorption of $CO_2$ onto EMM-36 samples measured at 301 K.

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