_____

Supporting Information

Heats of Adsorption of N_2, CO, Ar and CH_4 versus Coverage on the Zr-Based MOF NU-1000: Measurements and DFT Calculations

Graeme O. Vissers[+], Wei Zhang[+], Oscar E. Vilches[#], Wei-Guang Liu[‡], Haoyu S. Yu[‡], Donald G. Truhlar[‡], and Charles T. Campbell[+*]

[+] Department of Chemistry, University of Washington, Seattle WA 98195-1700

[#] Department of Physics, University of Washington, Seattle WA, 98195-1560

[‡] Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431

[*] Corresponding author: charliec@uw.edu

S1. Table of Contents

S2. Gases used

N_2: Praxair, Grade 4.8

CO: Linde, Grade 3.0, 99.9%

Ar: US Airgas, minimum purity 4.8

CH_4: Praxair, Grade 3.7 UH, 99.97%

_____

S3. N$_2$ adsorption isotherm and BET plot on Sample 8 of NU-1000 at 77 K

All our NU-1000 samples were synthesized at Northwestern University and given to us by J. T. Hupp and O. K. Farha, as described in reference #1 of the main text. Sample 8 was accurately measured to have a mass of 10.3 mg before baking it to 75 ˚C.
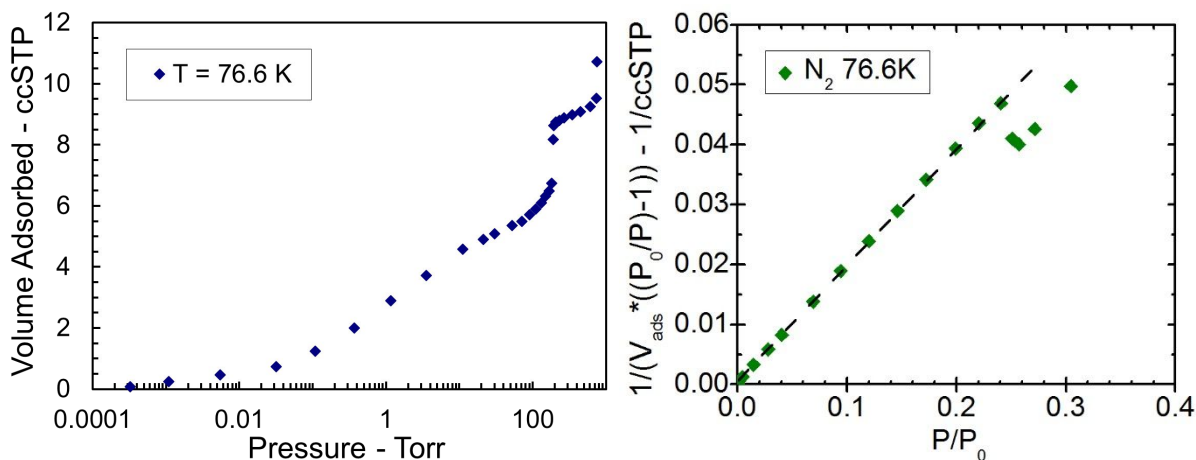

Figure S1. Left: N$_2$ equilibrium adsorption isotherm on Sample 8 of NU-1000 measured at approximately 77 K in the cryocooler system after baking for several hours at 75 ˚C and 10^{-6} Torr. Right: BET plot of this same N$_2$ isotherm. Here, V_{ads} is the volume of gas adsorbed (if measured at STP), P is the pressure and P_0 is the equilibrium vapor pressure of the bulk liquid at the measurement temperature. The BET linearized best-fit equation shown gives V_{ML} = 5.11 ccSTP. This value was used to scale coverages to those of Sample 6 for which V_{ML} = 4.7 ccSTP (i.e., ~8% smaller sample size).

S4. Adsorption isotherms of N$_2$, CO, Ar, and CH$_4$

Two different approaches were used to measure adsorption isotherms of N$_2$, CO, Ar, and CH$_4$ (see Figure S2 – S5). By keeping the temperature constant, a complete N$_2$ isotherm was measured up to the equilibrium vapor pressure of the bulk liquid at the measurement temperature (see Figure S1 left). To map the low-coverage and low-pressure region and check reproducibility after a certain amount was adsorbed, a different approach was also used to measure the isotherms for the four gases. In this approach, the temperature was regularly lowered or raised in approximately 5 K steps by keeping the coverage constant.
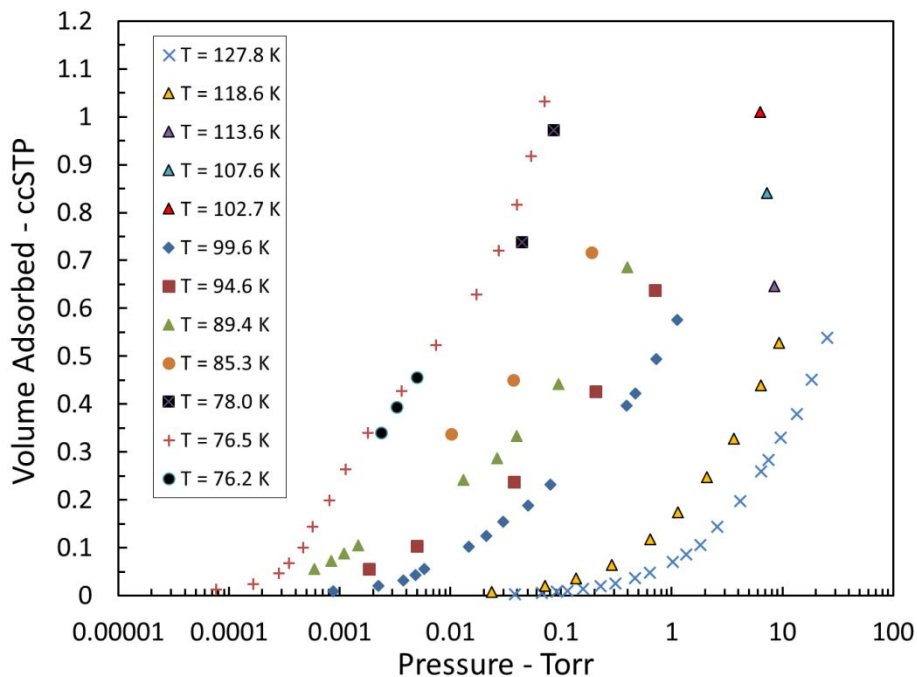
S4(a). N₂ isotherms

Figure S2. The N$_2$ adsorption isotherms on NU-1000 measured at the temperatures indicated in the inset. Only the data above 0.01 Torr and 98 K were used to calculate Q_{st} versus coverage.
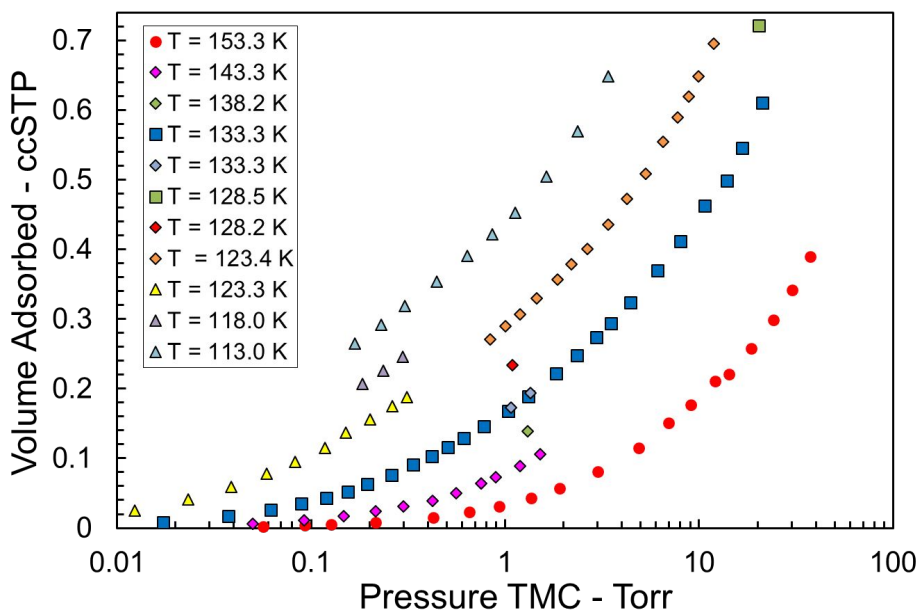
S4(b). CO isotherms

Figure S3. The CO adsorption isotherms on NU-1000 measured at the temperatures indicated in the inset.
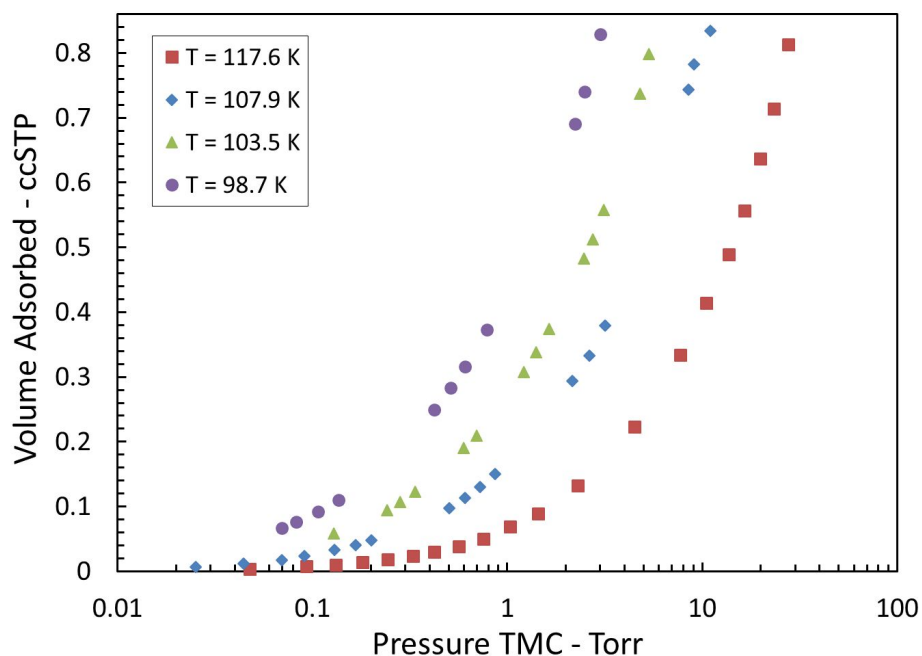
S4(c). Ar isotherms

Figure S4. The Ar adsorption isotherms on NU-1000 measured at the temperatures indicated in the inset.
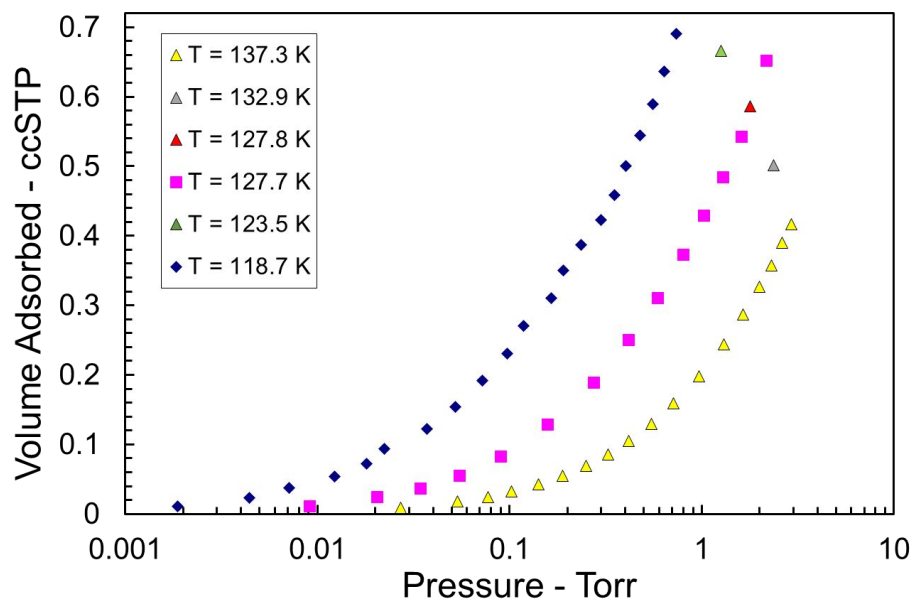
S4(d). CH$_4$ isotherms

Figure S5. The CH$_4$ adsorption isotherms on NU-1000 measured at the temperatures indicated in the inset.