

Rapid quantification of mass transfer barriers in metal–organic framework crystals

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I. Instrumentation

Sample Activation: Prior to N₂ isotherms and *n*-hexane measurements, NU-1000 and MOF-808 were thermally activated under dynamic vacuum at 120 °C and UiO-66 was activated at 100 °C until outgas rates of ≤ 0.02 Torr/s were achieved using a Micromeritics Smart VacPrep.

Nitrogen Physisorption Measurements: N₂ isotherms were collected at 77 K using a Micromeritics ASAP2420. Pore size distribution analysis was performed using DFT calculations with a carbon slit geometry and a N₂ DFT model.

Powder X-ray Diffraction (PXRD): PXRD measurements were collected on a STOE STADI P with a CuK α 1 radiation source ($\lambda = 1.54056$ Å) at the IMSERC X-ray Facility at Northwestern University

Scanning Electron Microscopy (SEM): SEM images were obtained using a FEI Quanta 650 at the EPIC facility (NUANCE Center-Northwestern University). The samples were coated with 9 nm of osmium using an SPF Osmium Coater (NUANCE Center-Northwestern University) prior to imaging.

n-Hexane Isotherms: *n*-Hexane isotherms were collected on a Micromeritics 3Flex surface analyzer fitted with a vapor source container. Samples were maintained at 25 °C using a Micromeritics ISO Controller Temperature Control Device. Prior to using the *n*-hexane (99+%, Acros Organics), the probe was degassed through a series of freeze-pump-thaw cycles on the instrument.

II. Mathematical basis

The summarized details here are described in detail by Brandani.^{1,2} We first consider a mass balance for the dosing cell, valve assembly, and uptake cell. The mass balance on the valve assembly is:

$$\frac{dn}{dt} \cong \bar{\chi}(P_d - P_u) \quad (1)$$

Where n is the number of moles, $\bar{\chi}$ is the valve coefficient, P_d is the dosing pressure and P_u is the uptake pressure. This holds in the limit of small pressure changes.

The mass balance on the uptake volume includes the free volume of the uptake cell ϵV_u and volume of the solid V_s .

$$V_s \frac{d\bar{q}}{dt} + \epsilon V_u \frac{dc}{dt} = \frac{dn}{dt} \quad (2)$$

The mass balance of the dosing cell includes the dosing cell volume V_d , the dosing cell temperature T_d , and assume an ideal gas R_{IG} .

$$\frac{dn}{dt} = - \frac{V_d}{R_{IG}T_d} \frac{dP_d}{dt} \quad (3)$$

We can make draw a mass balance around the solid assuming a spherical particle according to Fickian diffusion where q is the adsorbed phase.

$$\frac{dq}{dt} = D \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (4)$$

And

$$\frac{d\bar{q}}{dt} = \frac{3D}{R} \left(\frac{\partial q}{\partial r} \right)_{r=R} + \frac{3}{R} k_{LDF} (q^* - \bar{q}) \quad (5)$$

Where the first term on the right-hand side corresponds to intracrystalline diffusion and the second term on the right-hand side corresponds to a linear driving force. We assume that the adsorbed and gas phases are in equilibrium and invoke spherical symmetry in the particles.

The key assumptions used, which are explained in depth in Brandani's work,^{1,2} are:

- 1) The system is isothermal.
- 2) The system is linear.
- 3) There are no external or bed mass transfer resistances.

III. MOF Syntheses

All MOF syntheses (NU-1000,³ MOF-808,⁴ and UiO-66⁵) were made according to previously published procedures.

NU-1000: In a 5-L glass bottle, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (19.4 g, 60 mmol) and benzoic acid (400 g, 3.2 mol) were added to 1.2 L of *N,N*-dimethylformamide (DMF) and sonicated until dissolved. 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzic acid (H_4TBAPy) (8 g, 12 mmol) was added to 400 mL of DMF in a 1 L glass bottle. Both solutions were placed in a 100 °C oven for 1 hour. After cooling to room temperature, the H_4TBAPy solution and 8 mL of trifluoroacetic acid were added to the Zr-solution, sonicated for 10 minutes, then placed in a 120 °C oven for 18 hours. The yellow product was collected by centrifugation and washed three times with DMF. Following this, the MOF was placed in a 5-L glass bottle with 2.6 L of DMF and 100 mL of 8 M HCl and heated in a 100 °C oven for 18 hours. The acid-washed MOF was collected by centrifugation and washed three times with DMF. The acid wash procedure was repeated once more and the final MOF was once again collected by centrifugations, washed three times with DMF, and three times with acetone, soaking for 1 hour in between washes. The MOF was placed in fresh acetone overnight, collected by centrifugation, and dried in an 80 °C vacuum oven for 1 hour. The NU-1000 was activated under dynamic vacuum at 120 °C until the degas rates were below 0.02 Torr/s.

MOF-808: In a 100 mL round-bottom flask, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1.932 g, 6.0 mmol), trimesic acid (420 mg, 2.0 mmol), formic acid (20 mL), deionized water (20 mL), and HCl (12 M, 200 μL) were added. The mixture was heated on an aluminum heating block at 110 °C for 18 hours while stirring at 300 rpm. After, the MOF was collected by centrifugation, washed three times with water (soaking for 30 minutes after each wash), and placed into a clean 100 mL round-bottom flask with 40 mL of 1 M HCl. This mixture was heated overnight on an aluminum heating block at 90 °C. The MOF was collected by centrifugation, washed three times with water followed by three ethanol washes, soaking for 1 hour between each wash. After soaking the MOF in ethanol overnight, MOF-808 was collected by centrifugation, dried in an 80 °C vacuum oven for 1 hour, and activated under dynamic vacuum at 120 °C until the degas rates were below 0.02 Torr/s.

UiO-66: In a 2-L glass bottle, terephthalic acid (0.9 g, 5.42 mmol), 140 μL triethylamine, 128.8 mL acetic acid, and 1.26 L of DMF were added and sonicated until dissolved. The solution was heated at 100 °C for 15 minutes and then allowed to cool completely. While heating the linker solution, ZrCl_4 (1.26 g, 5.41 mmol) was sonicated in 90 mL of DMF until dissolved. The Zr solution was added to the linker solution and placed in a 100 °C oven for 18 hours. Majority of the supernatant was first decanted before collecting the MOF by centrifugation. The MOF was washed with DMF and acetone three times, soaking 1 hour in between each wash. After soaking in fresh acetone overnight, UiO-66 was isolated by centrifugation, dried for 1 hour in an 80 °C vacuum oven, and activated under dynamic vacuum at 100 °C until degas rates of < 0.02 Torr/s were reached.

IV. MOF Characterization

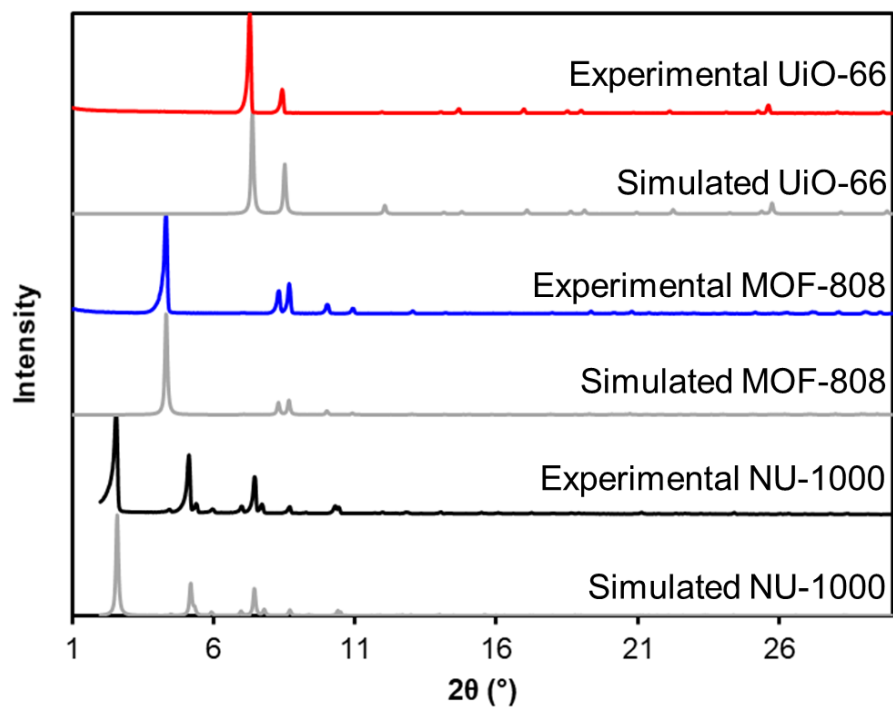


Figure S1. Simulated and experimental PXRD patterns of NU-1000, MOF-808, and UiO-66.

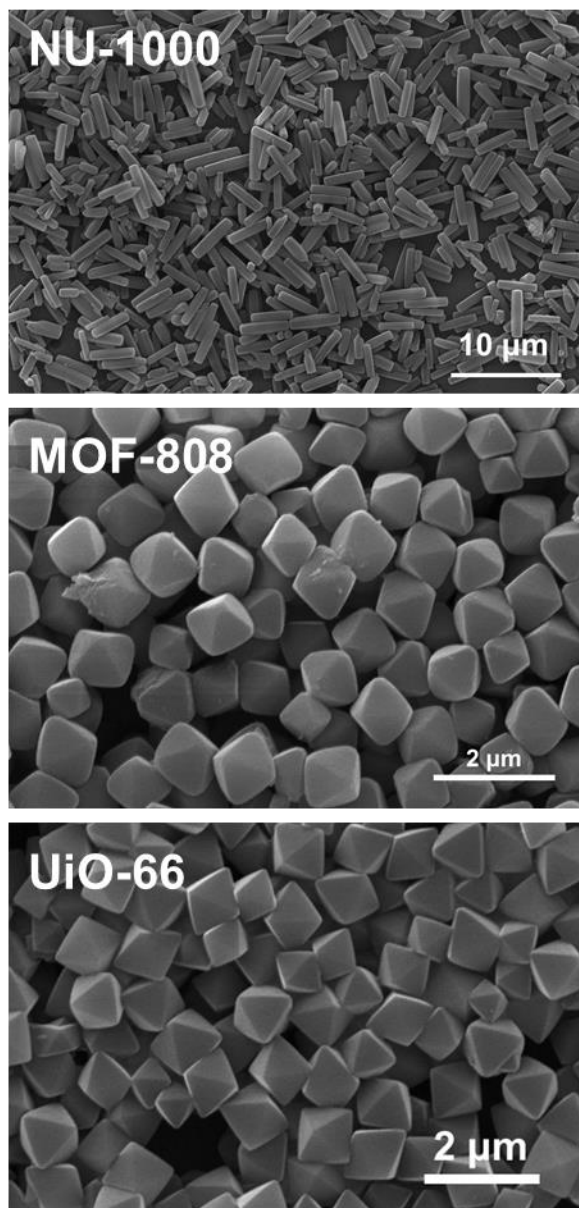


Figure S2. SEM of NU-1000 (average length = 4 μm , particle radius is 2 μm), MOF-808 (average length = 1 μm , particle radius is 0.5 μm), and UiO-66 (average length = 1 μm , particle radius is 0.5 μm).

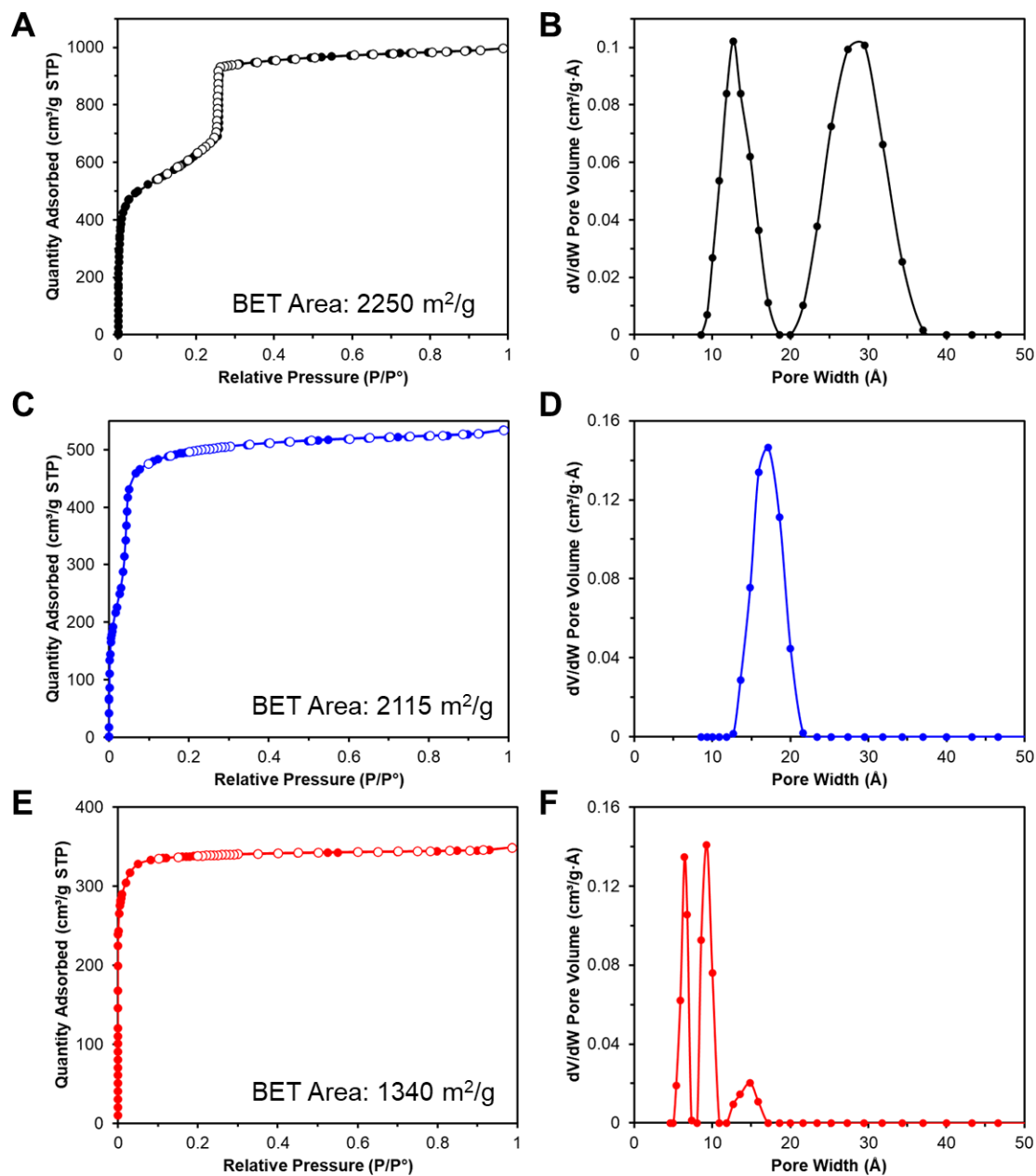
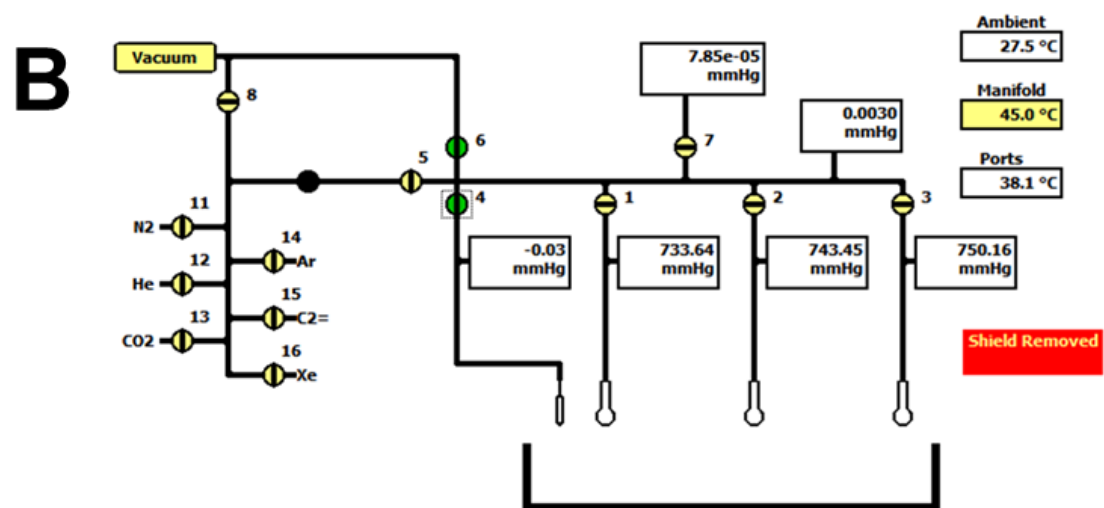
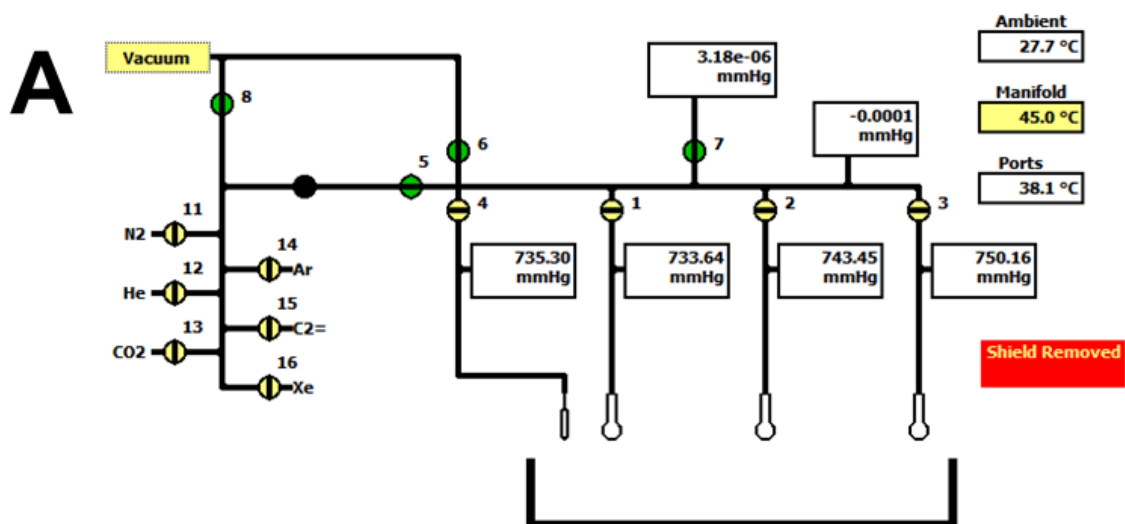
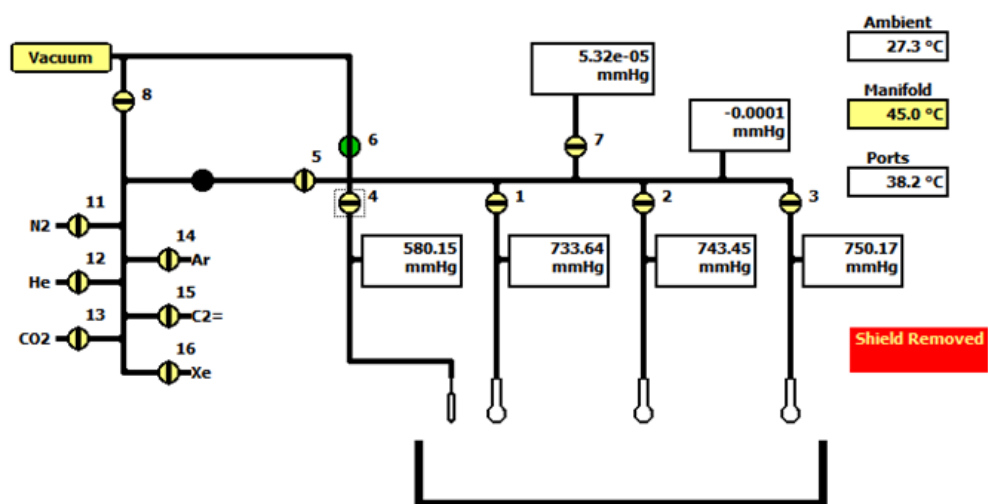


Figure S3. Nitrogen isotherms collected at 77 K with closed markers representing adsorption and open markers desorption for A) NU-1000, C) MOF-808, and E) UiO-66. Pore size distribution of B) NU-1000, D) MOF-808, and F) UiO-66.

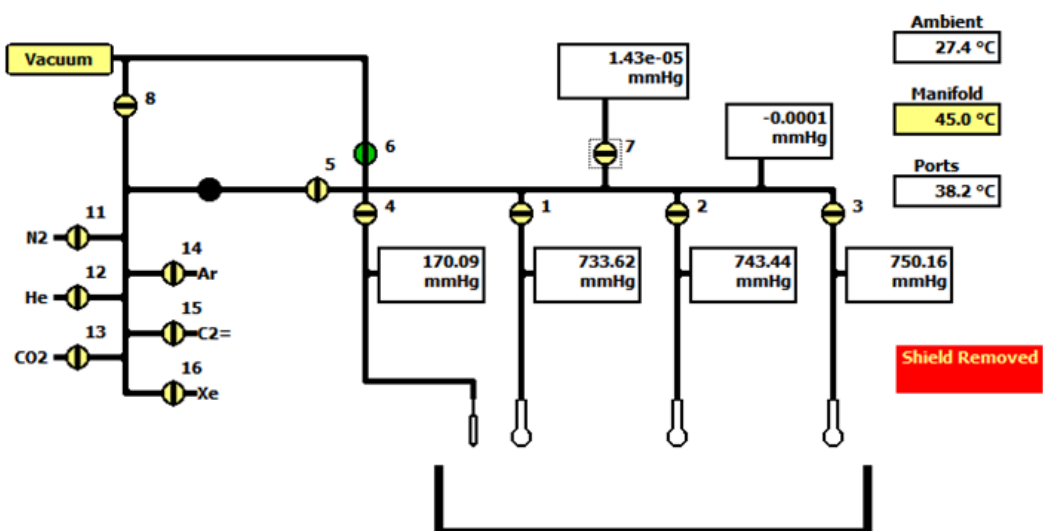
V. 3Flex Vapor Isotherm Setup



C



D



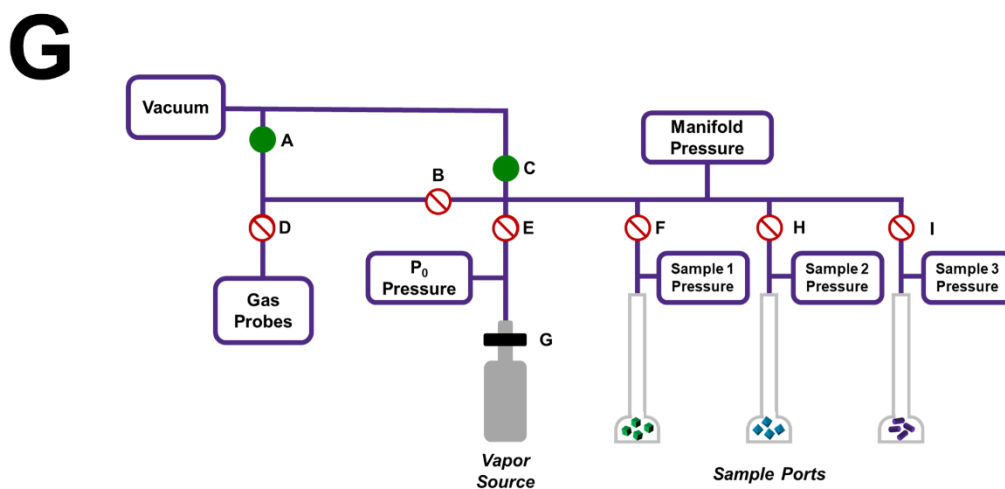
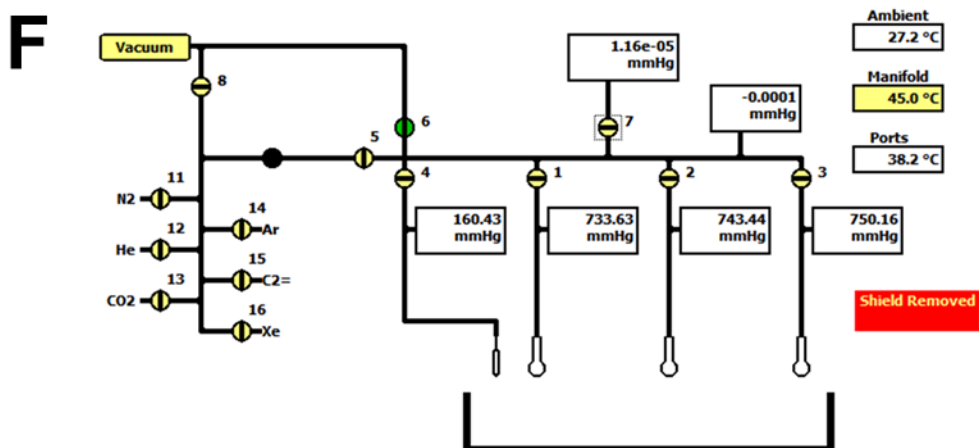
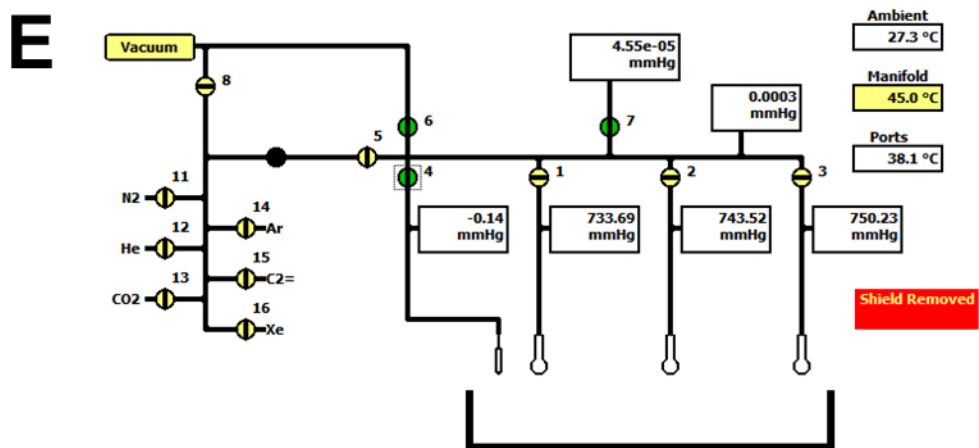


Figure S4. 3Flex instrument schematic for vapor purification (A-F) and a simplified cartoon depiction of the instrument schematic (G).

- A) Schematic after vapor source installation with close-off valve on vapor source container closed.
- B) With close-off valve on vapor source still closed, open valve 4 on the instrument to clear the headspace of the vapor reservoir.
- C) Close valve 4, then open close-off valve of vapor source container.
- D) Submerge vapor source container in liquid nitrogen until the pressure stabilizes. For the first freeze cycle, it will not reach zero. In this example, the pressure dropped until 170 Torr (reading from valve 4)
- E) Once the pressure of the vapor container is stabilized, open valve 4 to expose the container to vacuum, while ensuring that the reservoir is still submerged in liquid nitrogen. Leave valve 4 open until pressures of 10^{-4} – 10^{-5} Torr (reading from valve 7) are achieved.
- F) Close valve 4 and submerge the vapor source container in water to thaw. If the pressure reading is not close to the calculated saturation pressure at room temperature, this is indicative of residual impurities. If impurities remain, repeat steps B through F for additional cycle(s).
- G) Simplified depiction of instrument schematic

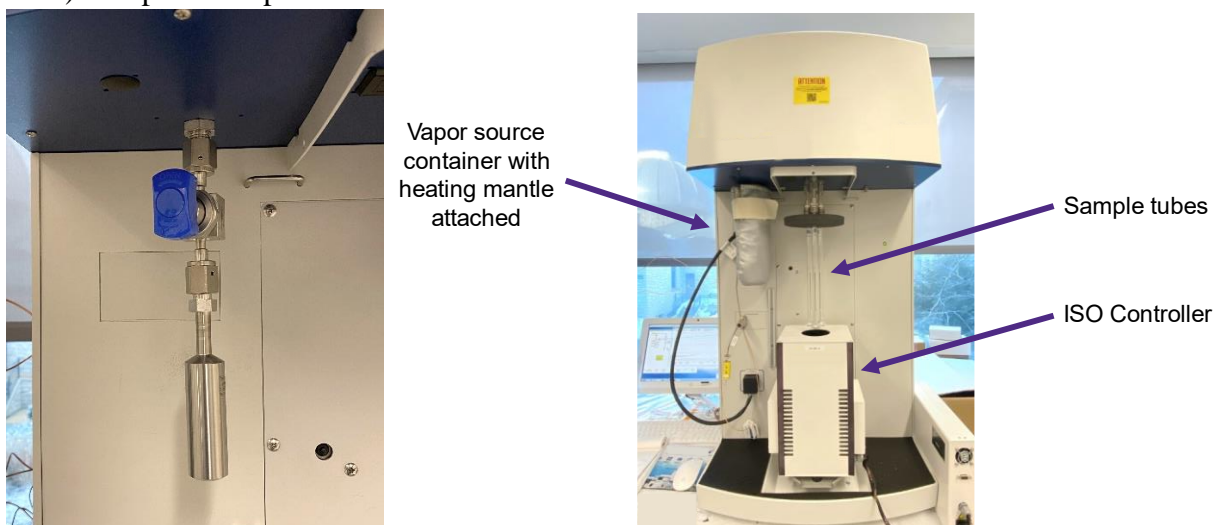


Figure S5. 3Flex setup. Left) installed vapor source container with the close-off valve open. Right) final vapor isotherm collection setup.

Free Space Measurements: Free space, or void/dead space, measurements determine the empty volume in the sample tube, unoccupied by the sample. The quantity adsorbed of a probe (n_{adsorbed}) is calculated from the difference between the quantity dosed (n_{dosed}) and the quantity of the probe remaining in the gas/vapor phase in the sample tube (n_{residual}) (equation 6). The quantity dosed is determined by the change in pressure in the instrument manifold before and after the dose is delivered. n_{residual} is calculated using the free space volume. Other values used in these measurements include the manifold volume, or dosing volume (V_D) and the sample volume (V_S).

$$n_{\text{adsorbed}} = n_{\text{dosed}} - n_{\text{residual}} \quad (6)$$

The Micromeritics 3Flex analyzer can be programmed to automatically measure the free space prior to analysis. As these measurements are performed with the sample in the sample tubes, a gas such as helium, which does not adsorb into the material, is used. The free space is measured using gas laws under two temperatures since a temperature gradient may exist. First, it's measured under ambient conditions, which the top of the sample holder will be subjected to during analysis. Finally, it's measured at the analysis temperature, which the sample will experience. These two values are used to determine the void space more accurately at the analysis temperature using a compressibility correction.

VI. *n*-Hexane Isotherms

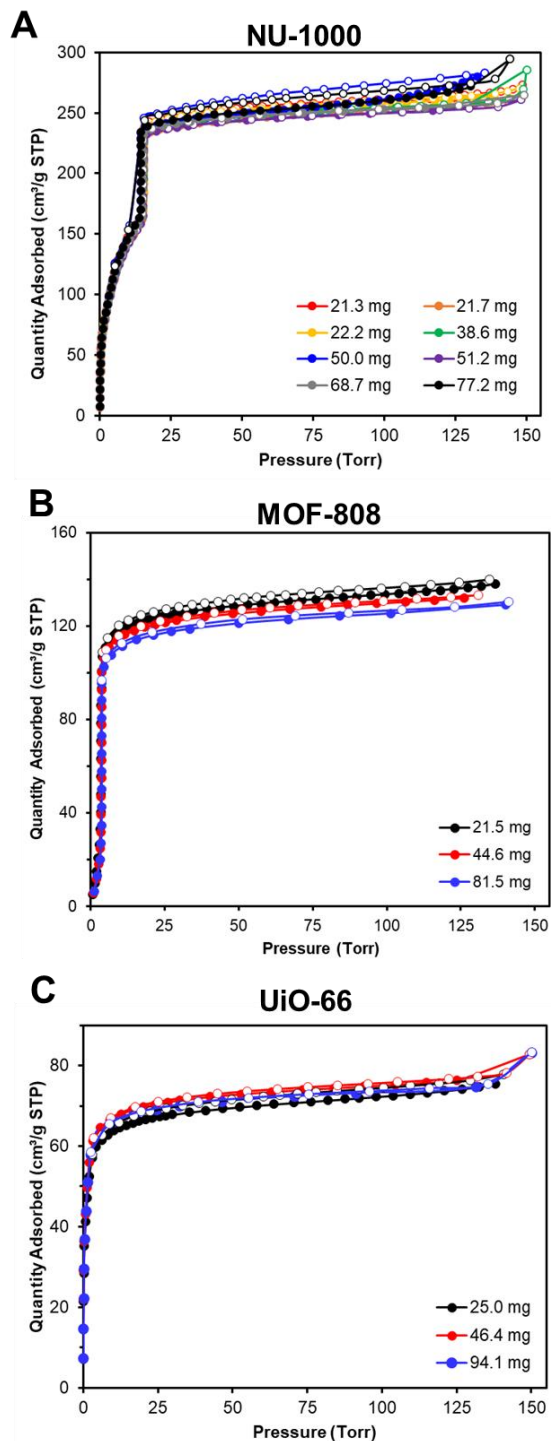


Figure S6. Overlaid *n*-hexane isotherms for A) NU-1000, B) MOF-808, and C) UiO-66 samples at 298 K. Closed markers represent adsorption and open represent desorption.

VII. Mass Transfer Fittings

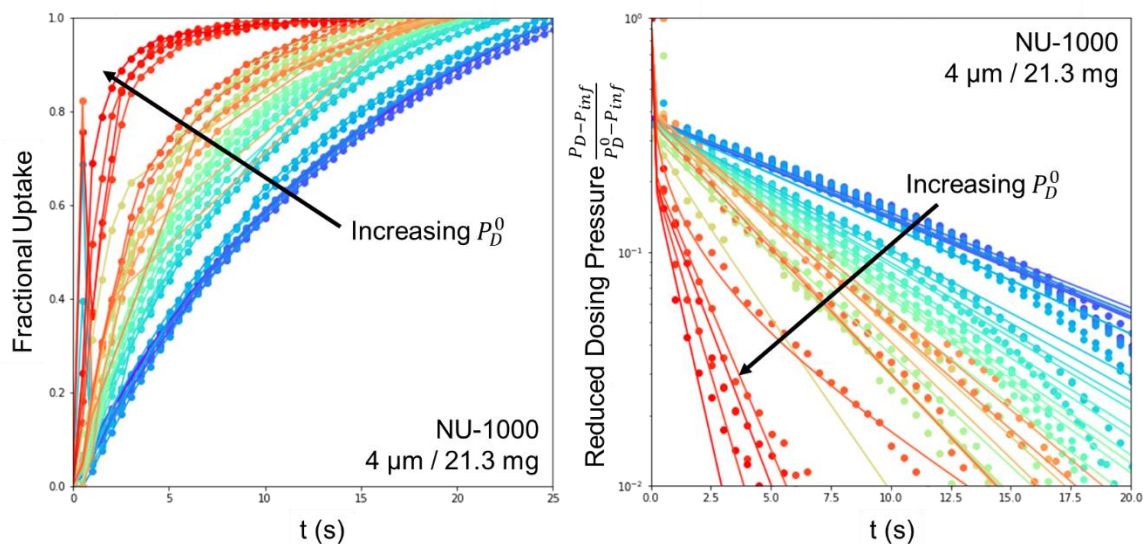


Figure S7. Left) Fractional uptake versus time of n -hexane in NU-1000 and their corresponding dosing pressures (21.3 mg). Sharp jumps at early times, as seen in the light green trace, correspond to instrument errors in the transient data collection. As illustrated by the reproducibility of these results, however, the precision of the results is not impacted by these fluctuations. Right) Reduced dosing pressures versus time.

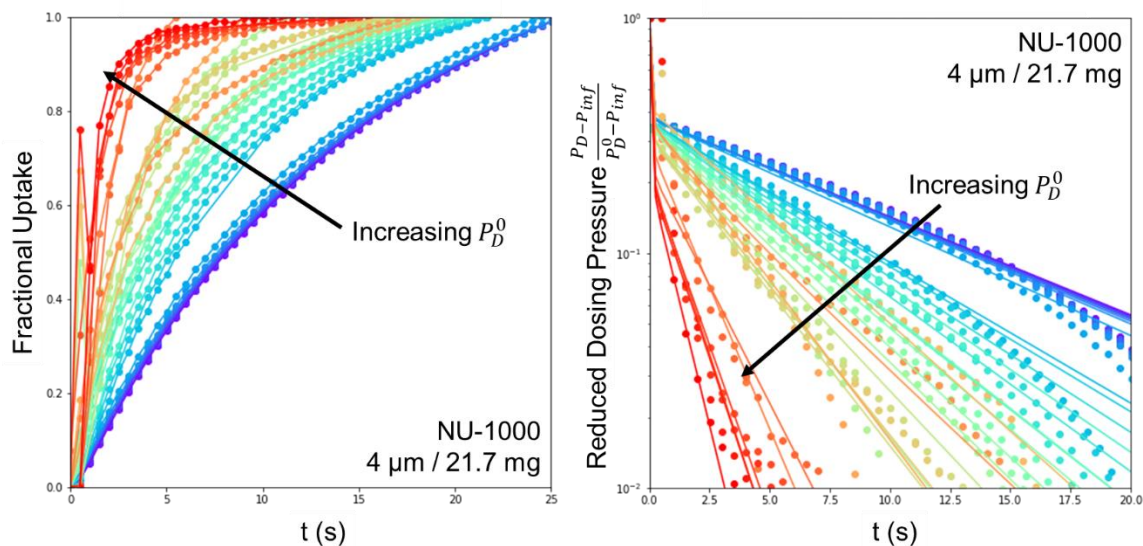


Figure S8. Left) Fractional uptake versus time of n -hexane in NU-1000 and their corresponding dosing pressures (21.7 mg). Right) Reduced dosing pressures versus time.

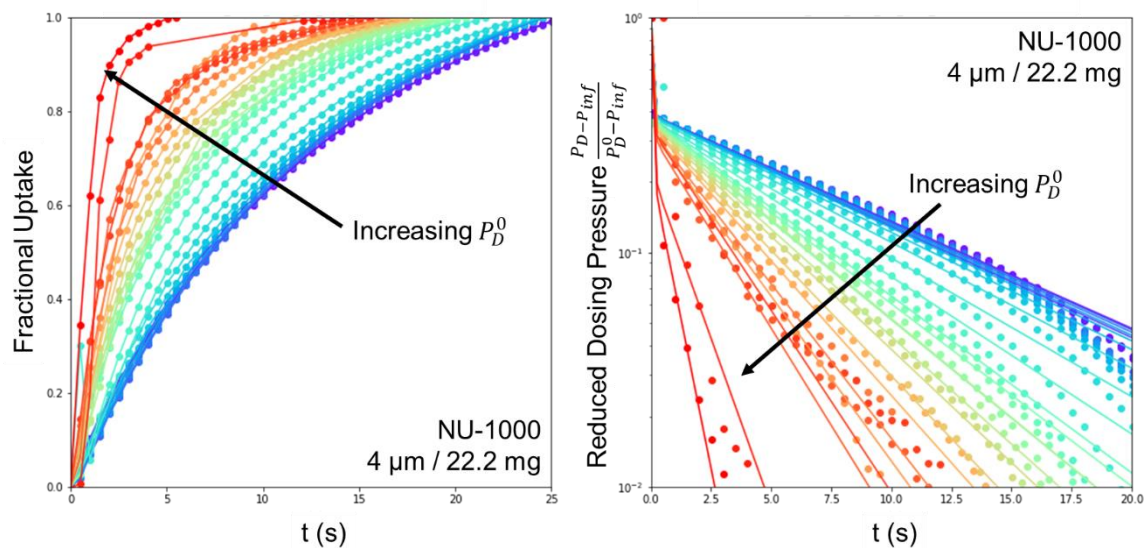


Figure S9. Left) Fractional uptake versus time of *n*-hexane in NU-1000 and their corresponding dosing pressures (22.2 mg). Right) Reduced dosing pressures versus time.

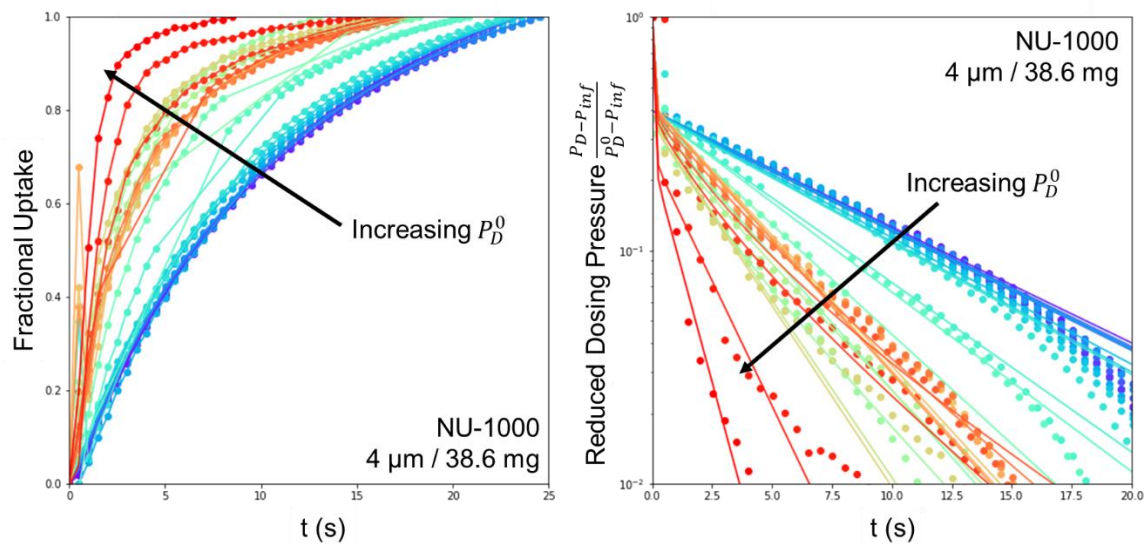


Figure S10. Left) Fractional uptake versus time of *n*-hexane in NU-1000 and their corresponding dosing pressures (38.6 mg). Right) Reduced dosing pressures versus time.

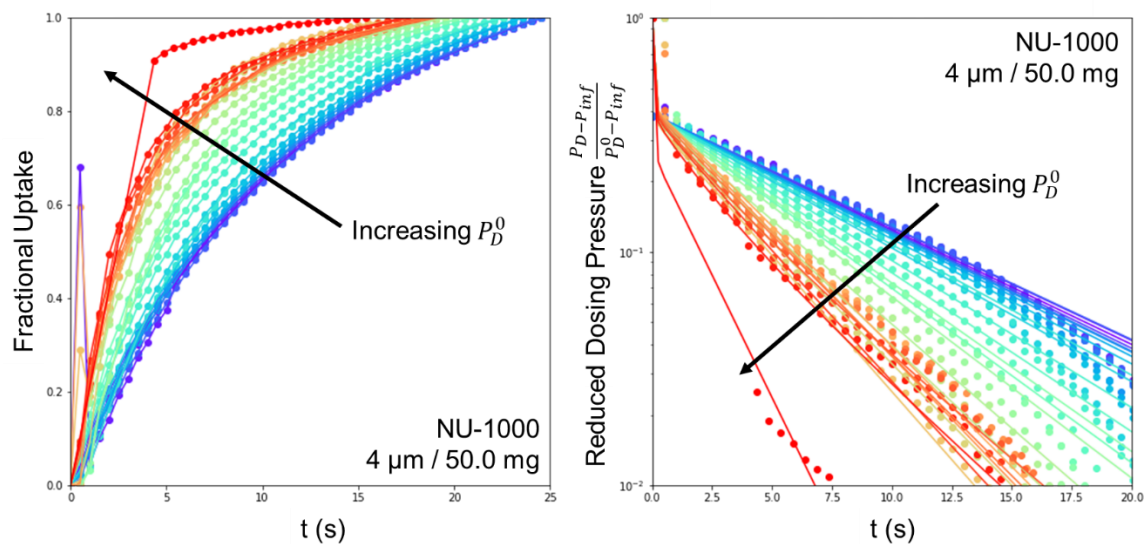


Figure S11. Left) Fractional uptake versus time of *n*-hexane in NU-1000 and their corresponding dosing pressures (50.0 mg). Right) Reduced dosing pressures versus time.

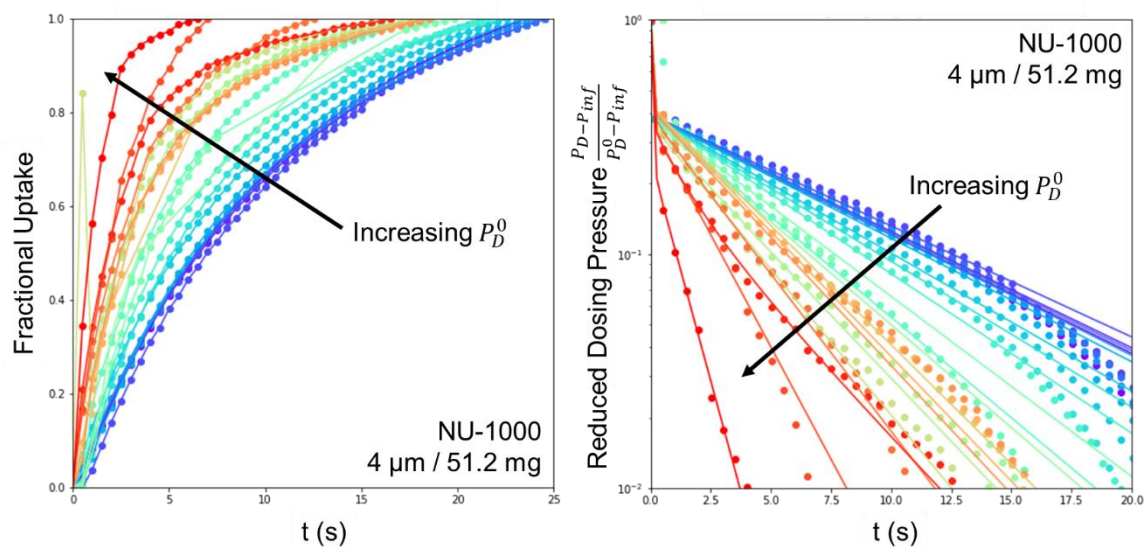


Figure S12. Left) Fractional uptake versus time of *n*-hexane in NU-1000 and their corresponding dosing pressures (51.2 mg). Right) Reduced dosing pressures versus time.

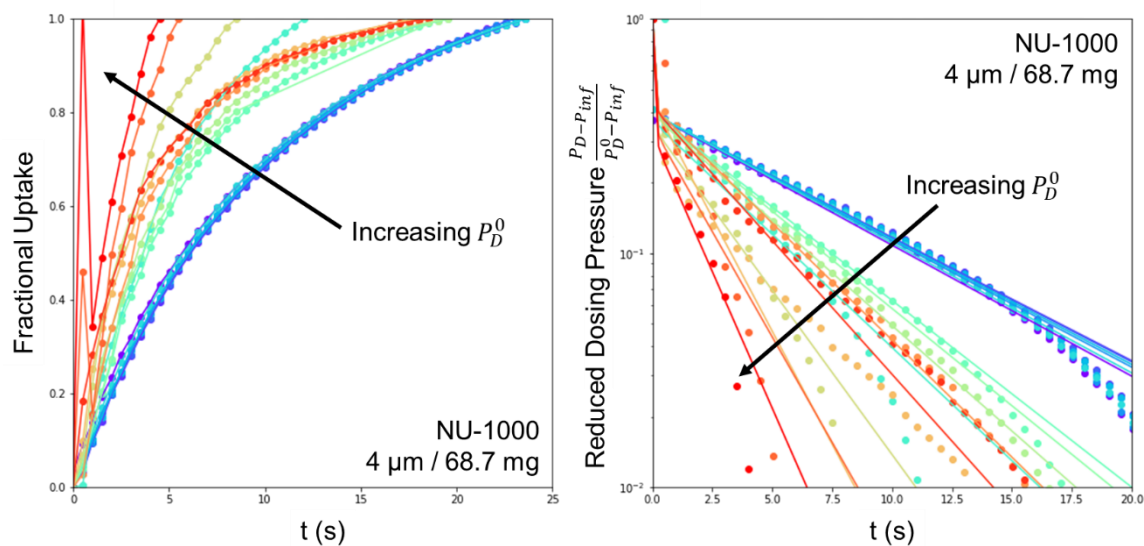


Figure S13. Left) Fractional uptake versus time of *n*-hexane in NU-1000 and their corresponding dosing pressures (68.7 mg). Right) Reduced dosing pressures versus time.

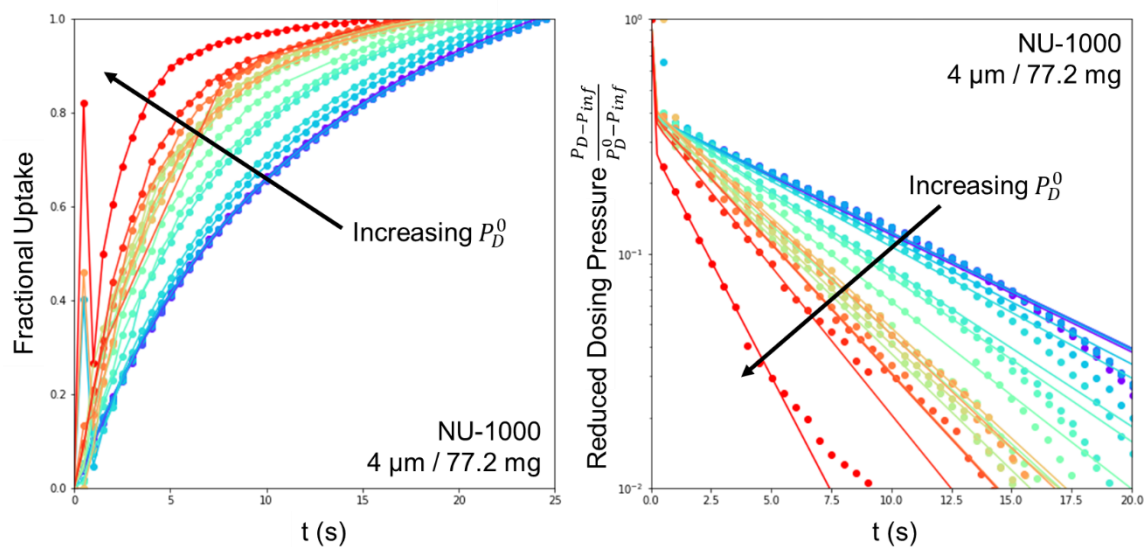


Figure S14. Left) Fractional uptake versus time of *n*-hexane in NU-1000 and their corresponding dosing pressures (77.2 mg). Right) Reduced dosing pressures versus time.

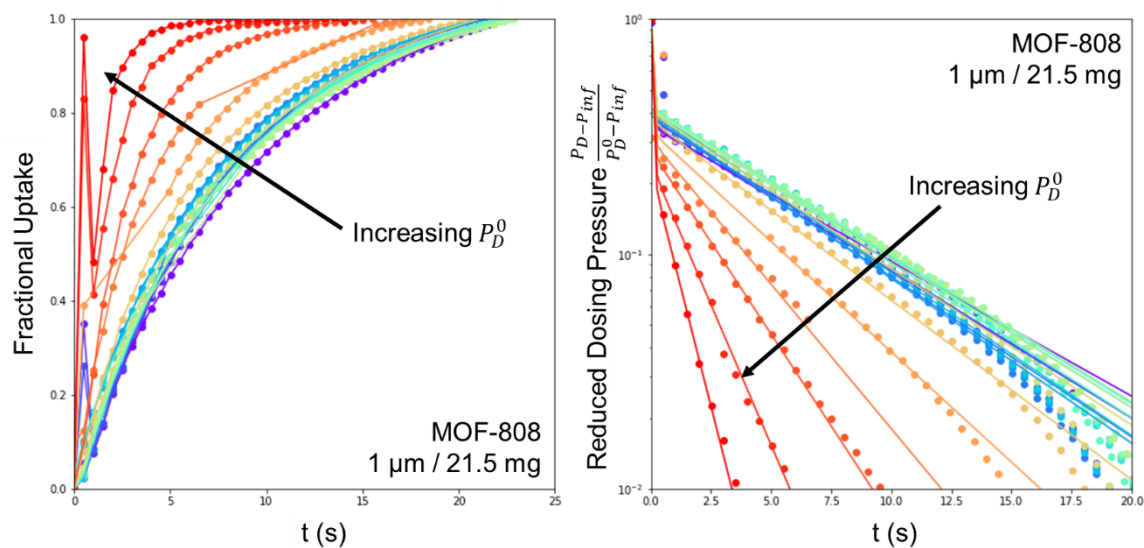


Figure S15. Left) Fractional uptake versus time of *n*-hexane in MOF-808 and their corresponding dosing pressures (21.5 mg). Right) Reduced dosing pressures versus time.

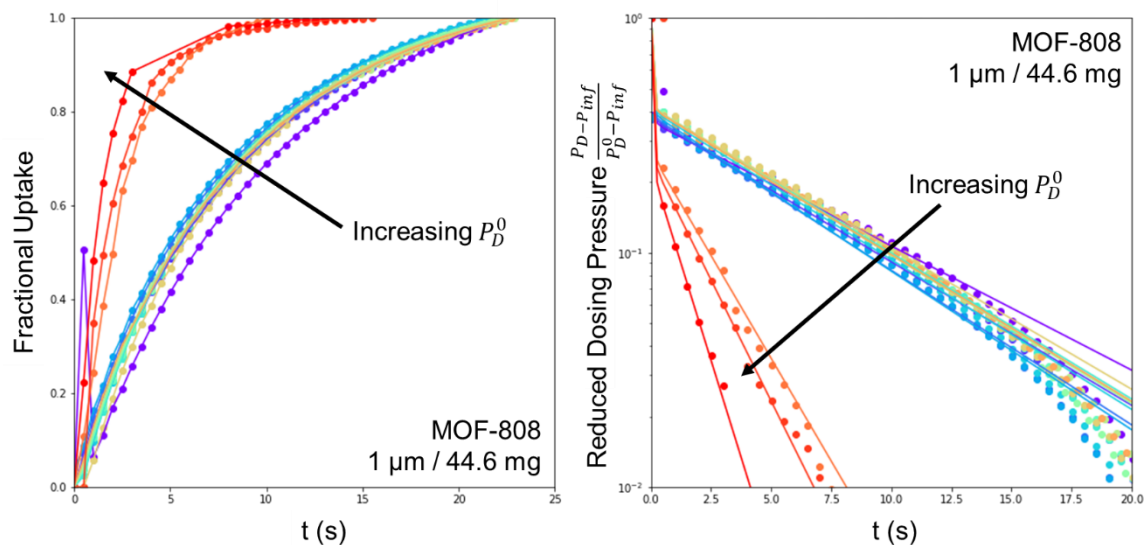


Figure S16. Left) Fractional uptake versus time of *n*-hexane in MOF-808 and their corresponding dosing pressures (44.6 mg). Right) Reduced dosing pressures versus time.

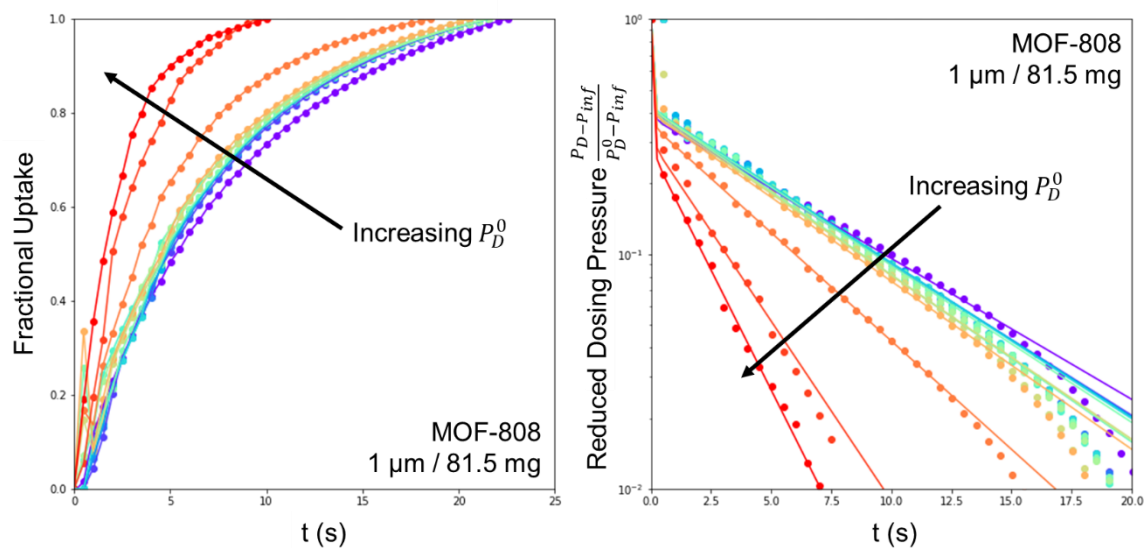


Figure S17. Left) Fractional uptake versus time of *n*-hexane in MOF-808 and their corresponding dosing pressures (81.5 mg). Right) Reduced dosing pressures versus time.

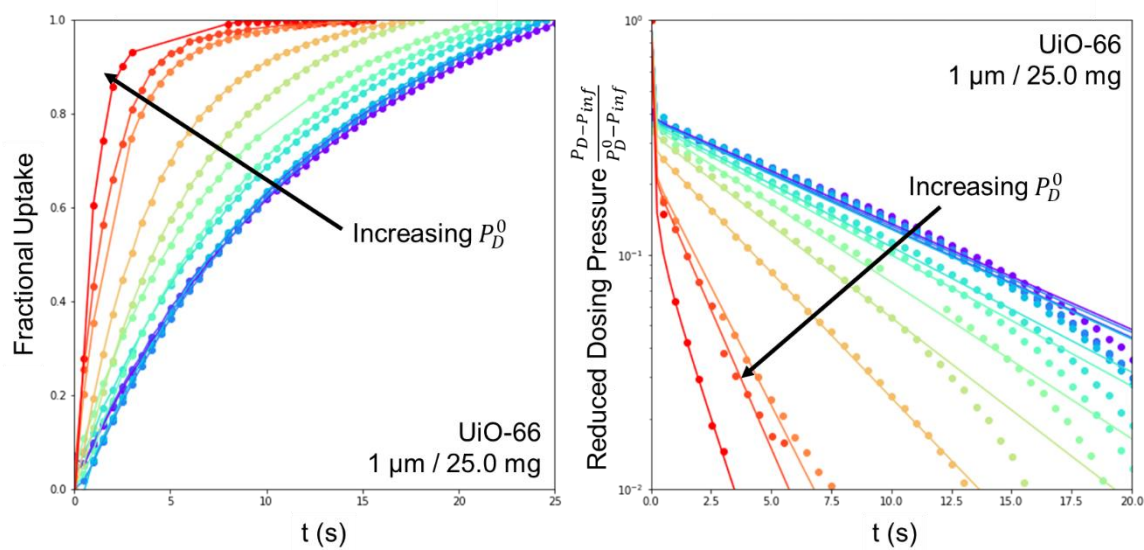


Figure S18. Left) Fractional uptake versus time of *n*-hexane in UiO-66 and their corresponding dosing pressures (25.0 mg). Right) Reduced dosing pressures versus time.

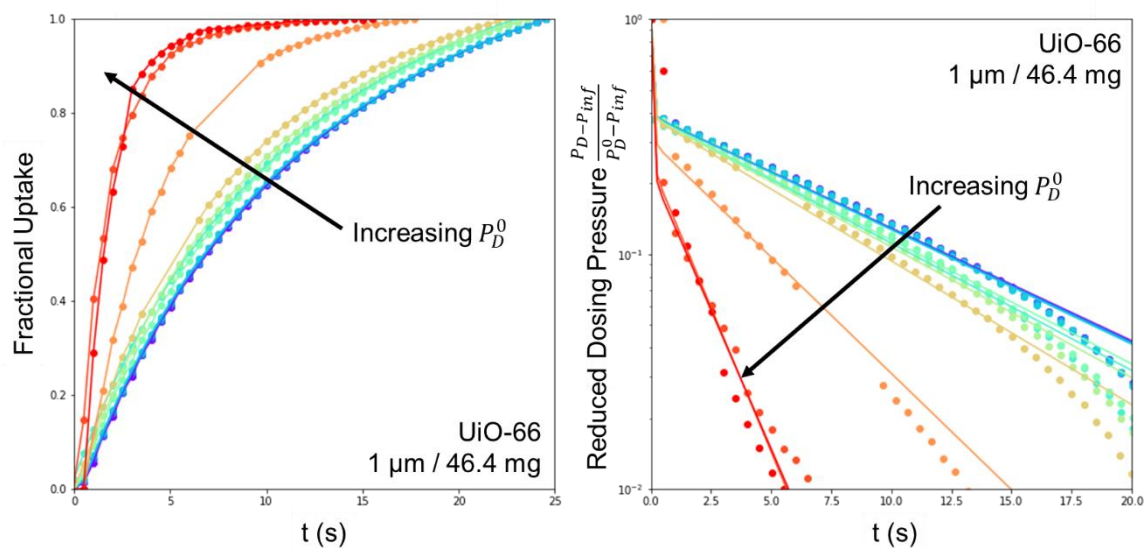


Figure S19. Left) Fractional uptake versus time of n -hexane in UiO-66 and their corresponding dosing pressures (46.4 mg). Right) Reduced dosing pressures versus time.

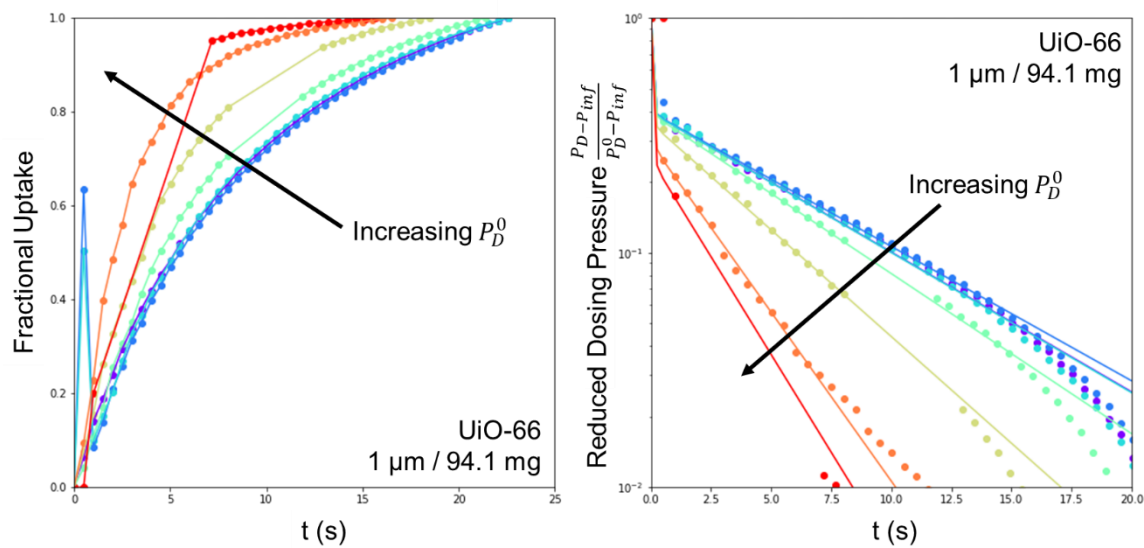


Figure S20. Left) Fractional uptake versus time of n -hexane in UiO-66 and their corresponding dosing pressures (94.1 mg). Right) Reduced dosing pressures versus time.

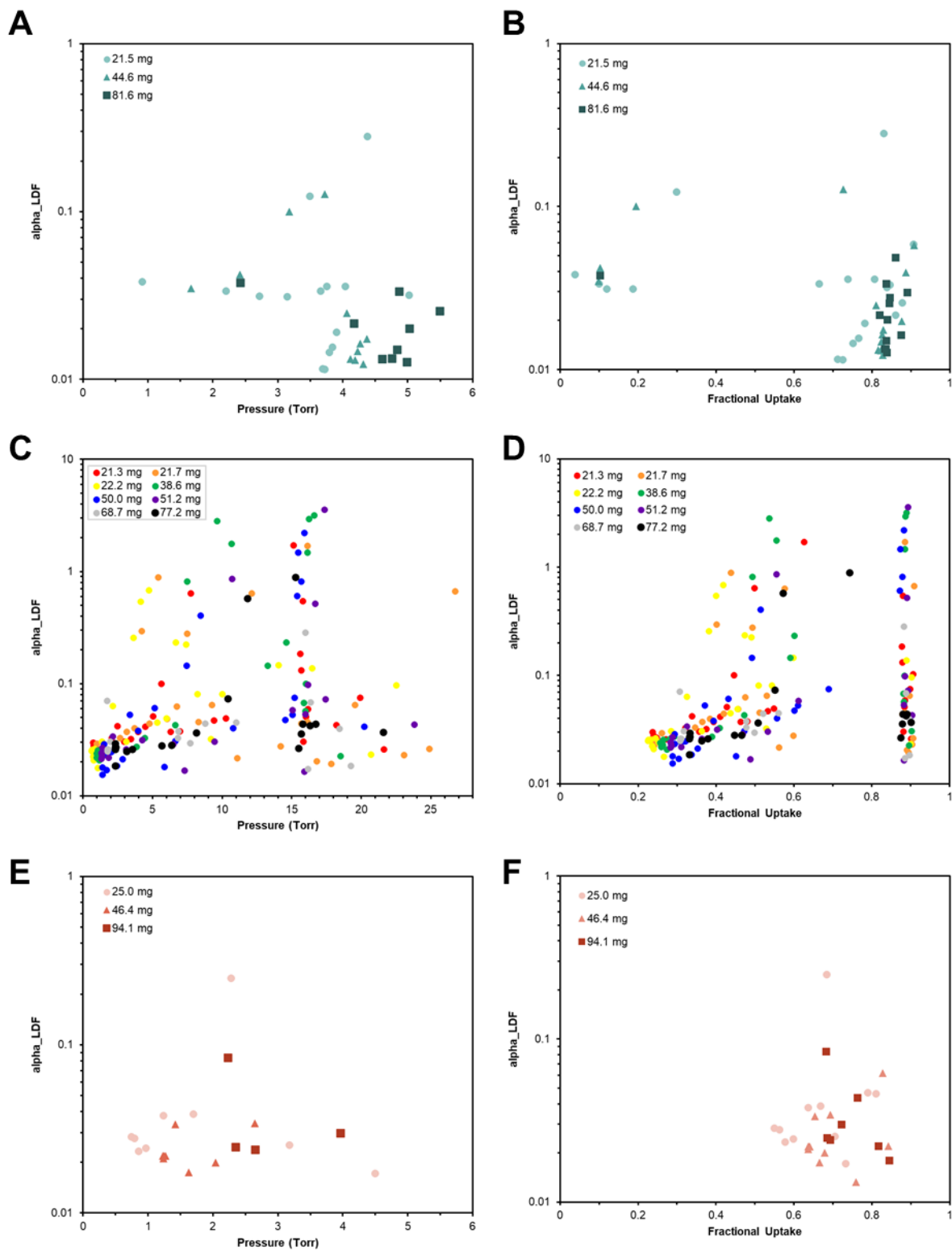


Figure S21. α_{LDF} as a function of pressure for A) MOF-808, C) NU-1000, and E) UiO-66. α_{LDF} as a function of pressure as a function of fractional uptake for B) MOF-808, D) NU-1000, and F) UiO-66.

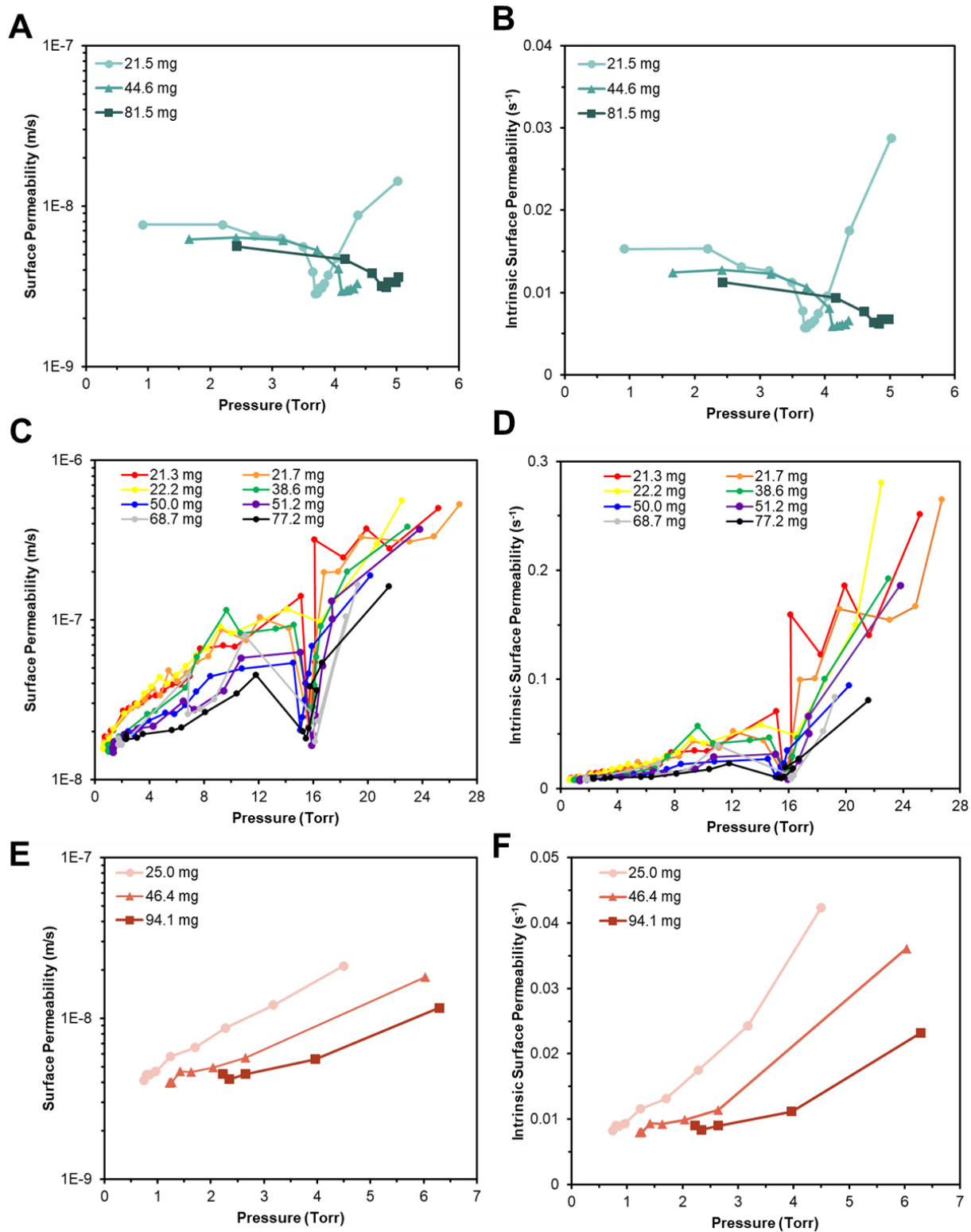


Figure S22. Surface permeability as a function of pressure for A) MOF-808, C) NU-1000, and E) UiO-66. Intrinsic surface permeability as a function of pressure for B) MOF-808, D) NU-1000, and F) UiO-66.

VIII. References

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