Supporting Information

Uncovering the role of metal–organic framework topology on the capture and reactivity of chemical warfare agents

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Instrumentation

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.

Nitrogen Physisorption Measurements: Nitrogen isotherms were collected on a Micromeritics Tristar II 3020 at 77 K. Samples were activated under vacuum with a Micromeritics Smart VacPrep instrument according to their specified procedures. Pore-size distributions were obtained using DFT calculations with a carbon slit geometry and a N_2 DFT model. For UiO-66 and UiO-66-Defective, pore-size distributions were obtained using DFT calculations with a cylinder geometry and a N_2 Tarazona NLDFT model. Total pore volumes were based on single point adsorption, while micropore and mesopore volumes were calculated using the cumulative pore volume obtained from the pore-size distribution DFT calculations.

Water Vapor Isotherms: Water vapor isotherms were collected on a Micromeritics 3Flex instrument at 298 K. Samples were activated under vacuum using a Micromeritics Smart VacPrep instrument prior to collecting measurements.

Nuclear Magnetic Resonance (NMR). ¹H NMR spectra of samples were obtained using a Bruker Avance III 500 MHz (IMSERC-Northwestern University).

Synthesis of Materials

NU-901,¹ NU-1200,² NU-1008,³ MOF-525,⁴ MOF-808,⁵ NU-1000,⁶ NU-1000-BA,⁶ and NU-1000-Dehyd,⁷ and UiO-66-Defective⁸ were synthesized and activated according to published procedures. UiO-66 was synthesized according to published procedure,⁹ with a few modifications specified below.

UiO-66: 900 mg of terephthalic acid (5.42 mmol), 140 μ L of TEA (1.0 mmol), 128.8 mL of acetic acid (17.5 mmol), and 1260 mL of DMF were dissolved by sonication in a 2-L glass jar until clear, heated at 100°C in an oven for 15 minutes, and cooled completely. 1260 mg of ZrCl₄ (5.41 mmol) was sonicated in 90 mL DMF until dissolved. The ZrCl₄ solution was then added to terephthalic acid solution and heated for 18 hours at 100°C in an oven and cooled completely. After decanting the supernatant, the white powder was collected by centrifugation at 7500 rpm for 5 minutes into six 50-mL centrifuge tubes and soaked three times in a total of 300 mL of DMF for 20 minutes each time. After each soak, the powder was collected by centrifuging at 7500 rpm for 5 minutes. Following this, three acetone washes/soaks were completed with the same methodology, ending with a final overnight acetone wash. The powder was then centrifuged down at 7500 rpm for 5 minutes. This procedure was repeated six times in total. Since separate characterization for each of the six batches indicated similar results, they were combined and used for further experiments.

Breakthrough Measurements

MOF powders were evaluated for total capacity and chemical retention using a small scale microbreakthrough system. Powders were equilibrated at the appropriate temperature and humidity prior to measurements and ~5-30 mg of MOF were loaded into a 4 mm ID fritted glass tube. Liquid sarin (GB) and 2-chloroethyl ethyl sulfide (CEES) were contained within a glass saturator cell with a ceramic wick. An air stream was pushed through the cell and the saturated vapor subsequently was mixed with a diluent stream at rates necessary to achieve concentrations of approximately 900 mg/m³ and 4,000 mg/m³ for GB and CEES, respectively. Materials were tested under dry (~0% RH) conditions for GB and dry and humid (80% RH) conditions for CEES. The effluent stream was monitored continuously using a Fourier Transform infrared detector for GB and a HP5890 gas chromatograph (GC) equipped with a flame ionization detector for CEES. After saturation, the feed was terminated, and the effluent was monitored to detect desorption of the target chemical. The capacity was calculated via mass balance at saturation and after desorption.

Dose-Extraction Tests

Samples for the dose-extraction tests were prepared by placing a measured mass of sorbent in a scintillation vial. The samples were then gently dried at 50°C for 2 hours. A humidification chamber with internal circulation was used to humidify the samples overnight at 50% relative humidity and 25°C. A dose of chemical agent was then delivered to the prepared vials at a ratio of 10 μ L to 10 mg of sorbent. The vials were capped and let stand for 24 hours. Extraction was conducted using acetonitrile (1.5 mL) with the slurry mixture, which was then filtered and transferred to an autosampler vial. Analysis of extract was performed using a GC with a mass spectrometer.

Powder X-ray Diffraction



Figure S1. PXRD of UiO-66-Defective, UiO-66, MOF-525, MOF-808, NU-1200, NU-1008, NU-901, NU-1000-Dehyd, NU-1000-BA, and NU-1000 collected on a STOE STADI P with a CuK α 1 radiation source, $\lambda = 1.54056$ Å.

Nitrogen Isotherms and Pore Size Distributions



Figure S4. A) N₂ isotherm and B) pore size distribution of NU-1000-Dehyd



Figure S7. A) N₂ isotherm and B) pore size distribution of NU-1008



Figure S10. A) N₂ isotherm and B) pore size distribution of UiO-66.



Figure S11. A) N₂ isotherm and B) pore size distribution of UiO-66-Defective.

Breakthrough Curves for GB and CEES



Figure S12. Breakthrough curves for GB for A) NU-901, NU-1008, NU-1000, NU-1000-BA, and NU-1000-Dehyd and B) MOF-808, NU-1200, MOF-525, UiO-66, and UiO-66-Defectives. Curves were plotted on two graphs for clarity.



Figure S13. Breakthrough curves of CEES in dry conditions for A) NU-901, NU-1008, NU-1000, NU-1000-BA, and NU-1000-Dehyd and B) MOF-808, NU-1200, MOF-525, UiO-66, and UiO-66-Defectives. Curves were plotted on two graphs for clarity.



Figure S14. Breakthrough curves of CEES in humid conditions for A) NU-901, NU-1008, NU-1000, NU-1000-BA, and NU-1000-Dehyd and B) MOF-808, NU-1200, MOF-525, UiO-66, and UiO-66-Defectives. Curves were plotted on two graphs for clarity.

Nuclear Magnetic Resonance (NMR)



Figure S15. ¹H NMR spectrum of activated NU-1000. The sample was digested in D_2SO_4 and diluted in DMSO prior to the measurement. Peaks corresponding to the linker 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid are marked with (*) and the peaks corresponding to the benzoate ligand are marked with (#).



Figure S16. ¹H NMR spectrum of activated NU-1200. The sample was digested in 10 wt% NaOD in D₂O and diluted in DMSO prior to the measurement. Peaks corresponding to the linker 4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid are marked with (*) and the peak corresponding to the formate ligand is marked with (#). Integration revealed that there are approximately 2.7 formate ligands per Zr₆ node.

Water Isotherms



Figure S17. Water isotherms of UiO-66 and UiO-66-Defective



Figure S18. Water isotherms for NU-1000, NU-1000-BA, and NU-1000-dehydrated, where A is the full isotherm and B is the lower P/P° region of 0 to 0.5.

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