Electronic Supplementary Information for

Non-interpenetrated IRMOF-8: synthesis, activation, and gas sorption

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S1. Experimental Procedures

Starting reagents. Zinc nitrate hexahydrate (Fisher Scientific, ACS grade), naphthalene-2,6-dicarboxylic acid (H₂ndc, TCI, >98%), dichloromethane (Fisher Scientific, >99.9%), and dimethylformamide (DMF, Fisher Scientific, >99.5%) were used as-received without further purification. Diethylformamide (DEF, TCI, >99.0%) was purified by storing over activated carbon for ~1 month and subsequently passing through a column containing silica gel. DEF was used within one month of purification in this manner.

Zinc nitrate tetrahydrate, Zn(NO_3)_2 \cdot 4H_2O. Zinc nitrate hexahydrate (~25 g) was placed in a Schlenk flask and exposed to dynamic vacuum (10⁻² Torr) for 24 h, collected, and stored in a desiccator. Water content was assessed periodically by thermogravimetric analysis and maintained at a mol ratio below 4.5:1 H₂O:Zn.

IRMOF-8-HT. A mixture of 0.21 g (0.80 mmol) $Zn(NO_3)_2$ •4H₂O and 0.050 g (0.23 mmol) H₂ndc was dissolved in 10 mL DEF by sonication in a 20 mL scintillation vial. The solution was then incubated at 85 °C for ~36 h, after which time pale yellow crystal clusters formed. The vial was cooled to room temperature, and the solid was rinsed three times over 24 h with fresh DMF and subsequently four times over two days with CH₂Cl₂. The solid was finally dried under reduced pressure (10⁻² Torr) and stored in a N₂ glovebox until analysis. Materials made with DMF were produced identically, but replacing DEF with an equal volume of DMF. The yield of the dry, activated sample is 33%, based on H₂ndc.

IRMOF-8-RT. A procedure modified from a previous preparation¹ was used. A mixture of 2.18 g (8.83 mmol) $Zn(NO_3)_2 \cdot 4H_2O$ and 0.240 g H_2ndc (1.11 mmol) was dissolved in 200 mL DEF by sonication in a 400 mL jar. Ten microscope slides were placed upright in a home-built holder

in solution to afford additional sites for crystal growth and simplify collection of strongly adherent crystals. The solution was incubated at room temperature for 7 days, after which time ~100 μ m diameter clear, truncated cubic crystals had grown on the slides and walls of the jar. The crystals were collected and rinsed four times with fresh DMF over 24 h. The material was activated using supercritical CO₂² with a flow-through apparatus (see below) and stored in a N₂ glovebox until analysis. The average yield as determined from six preparations of the dry, activated sample is 20%, based on H₂ndc.

Supercritical CO₂ activation. Samples were activated by a modification³ of the method detailed in a previous report.⁴

Powder X-ray diffraction. Powder X-ray diffraction data were collected with a Bruker D8 Advance diffractometer having a Bragg-Brentano geometry. The Cu-K α (1.5406 Å) X-ray radiation source was operated at 40 V and 40 mA. Samples were ground in a mortar and pestle and evenly dispersed on a low-background quartz plate with a cavity depth of 0.3 mm (The Gem Dugout) in a N₂ glovebox. Samples were then transferred to the diffractometer and analyzed under ambient conditions and low relative humidity (<25%). Stability of the analyte under measurement conditions was confirmed by comparing rapid (0.1 sec./step) scans obtained immediately after exposure of the analyte to ambient conditions and comparing them with data obtained with slower, higher resolution scans (2-3 sec/step).

Gas sorption measurements. Sorption experiments were carried out using an Autosorb 1C (Quantachrome Instruments, Boynton Beach, Florida, USA). He (99.999%, used to determine void volumes), N_2 (99.999%), Ar (99.999%), and H_2 (99.999%) were purchased from Cryogenic Gases and used as received. For N_2 and Ar measurements, a glass sample cell was charged with 20 mg sample and analyzed at 77 and 87 K, respectively. For analysis of H_2 uptake, 103 mg of sample was added to a glass sample cell. A glass rod of diameter slightly smaller than the inner diameter of the sample cell was inserted into the cell to minimize dead volume. The sample was then analyzed at 77 and 87 K.

Thermogravimetric Analysis. A TA Instruments Q50 TGA was used to obtain thermogravimetric data. Activated analyte (5 mg) was heated and analyzed in a platinum pan under a dry nitrogen atmosphere.





Fig. S1. Thermogravimetric analysis of IRMOF-8-HT under a N_2 atmosphere after solvent removal.

Section S3. Powder X-ray diffraction data



Fig. S2. PXRD pattern of IRMOF-8-RT immediately before and after evacuation.



Fig. S3. PXRD pattern of IRMOF-8-HT compared with the simulated diffractograms of IRMOF-8 and a hypothetical model of interpenetrated IRMOF-8⁵ (based on the interpenetration mode of IRMOF-9).

Section S4. Gas sorption data



Fig. S4. Determination of BET plot range for a) IRMOF-8-HT and b) IRMOF-8-RT based on consistency criteria.⁶



Fig. S5. a) BET plot for a) IRMOF-8-HT and b) IRMOF-8-RT. The maximum points were chosen by the consistency criteria (see Fig. S4). For IRMOF-8-RT, points at P/P_0 values below 0.05 resulted in poorer fits to the data.



Fig. S6. NLDFT model of Ar isotherm for IRMOF-8-RT based on a kernel for zeolites and silica with cylindrical pores. Inset shows poor fitting between 0.02 and 0.08 P/P₀, yielding some uncertainty in the pore size distribution (see Fig. 2b in the main text, inset). No more accurate NLDFT model was available.



Fig. S7. Langmuir-Freundlich fits of IRMOF-8-RT H₂ sorption data at 77 and 87 K.

Henry's Law Constants ($k_{\rm H}$) were determined for IRMOF-8-RT H₂ sorption based on the method of Cole and co-workers.⁷ The constants are 12.82 and 4.36 mmol g⁻¹ bar⁻¹ for H₂ sorption at 77 and 87 K, respectively. To compare the value at 77 K with other zinc-based MCPs, $k_{\rm H}$ was calculated similarly for MOF-5, MOF-177, and IRMOF-8 based on previously published H₂ sorption data obtained at 77 K.⁸ The values of $k_{\rm H}$ MOF-5 and MOF-177 are 12.58 and 10.24 mmol g⁻¹ bar⁻¹, respectively, as would be expected for materials having chemistries and surface areas similar to those of IRMOF-8-RT. For previously published IRMOF-8, $k_{\rm H}$ is equal to 94.63 mmol g⁻¹ bar⁻¹ (at 77 K), a higher value likely attributable to interpenetration in that material.

Section S5. Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Section S6. References

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