Supporting Information

"Concentration-driven Evolution of Crystal Structure, Pore Characteristics, and Hydrogen Storage Capacity of MOF-5s: Experimental and Computational Studies"

Seung Jae Yang, Jung Hyun Cho, Kunsil Lee, Taehoon Kim, Chong Rae Park*

Carbon Nanomaterials Design Laboratory, Global Research Laboratory, Research Institute of Advanced Materials, and Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

e-mail : crpark@snu.ac.kr

Computational details for Monte Carlo simulations

Machinery and forcefield parameter

The adsorption of hydrogen gas onto the MOF-5 structures was modeled, at fixed pressures, by a Monte Carlo (MC) simulation. The Lennard-Jones (LJ) potential was used to model interatomic interactions between MOF-5 framework and adsorbates. The Lorentz-Berthelot (LB) mixing rules were employed to calculate the adsorbate/framework energies and distances. The cutoff distance was 12.8 Å, and the spline width was 1.0 Å. The LJ forcefield parameters developed by Snurr[1] were utilized and are given in Table S1.

$$V(r) = D_0\left[\left(\frac{R_0}{r}\right)^{12} - 2\left(\frac{R_0}{r}\right)^{6}\right]$$

MC simulations were carried out using the metropolitan algorithm[2]. For every point on the isotherm, 10^6 Monte Carlo steps, for each of the equilibrium and production calculations, were performed. A larger number of steps were required for equilibration at high adsorption levels.

Table S1. LJ forcefield parameters used in this work

	R_0 (Å)	D_0 (kcal/mol)
N-N	3.72	0.07
N-C	3.81	0.08
N-H	3.45	0.03
N-O	3.56	0.08
N-Zn	4.13	0.06

N_2 adsorption simulation

N_2 adsorption isotherm obtained by MC simulation is absolute adsorption. So, the excess adsorption was modeled by introducing the Peng-Robinson equation of state, designed specifically for the liquefaction of gases (Figure S1). N_2 adsorption isotherms were analyzed by the BET equation.

Excess adsorption (grey area) was calculated by subtracting from the absolute adsorption by MC simulation to free gases (white area). The amount of free gases in white area was determined from total pore volume and nitrogen density of Peng-Robinson (PR) equation at each temperature.

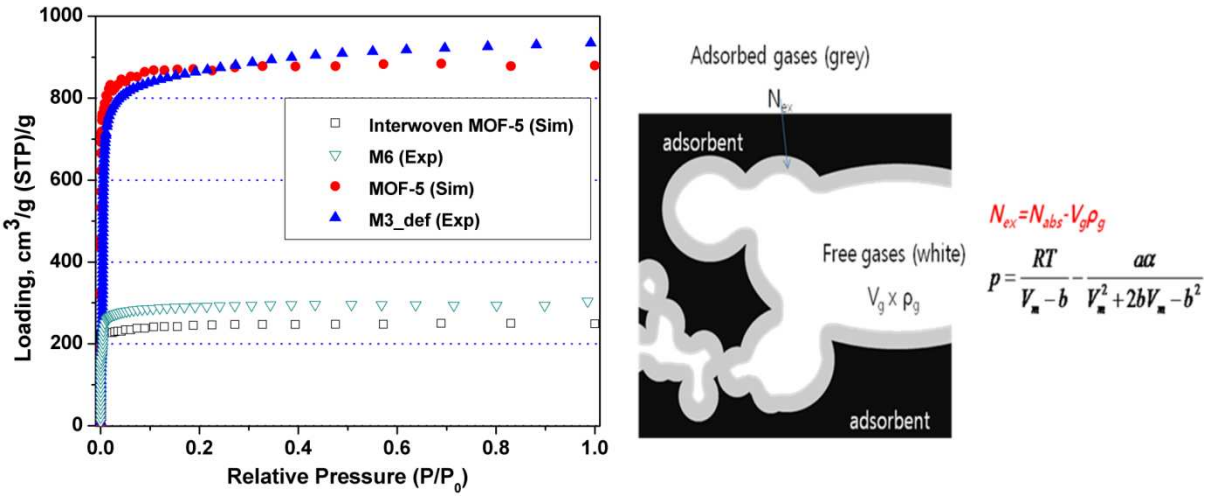

Figure S1. N_2 excess adsorption isotherms of interwoven and MOF-5 with experimental data (left side), and determination of excess adsorption using PR EOS (right side).

Calculation of specific surface area

The BET equation is given by

$$V = \frac{cv_m x}{(1-x)\left[1+(c-1)x\right]} \qquad \text{(S1)}$$

where x is P/P_0, v is the volume of nitrogen adsorbed/gram of MOF at STP, v_m is the

monolayer capacity, and c is the heat of adsorption. The BET equation can be rewritten in the form:

$$\frac{x}{v(1-x)} = \frac{x}{v(P_0 - P)} = \frac{1}{v_m} + \frac{(c-1)x}{v_m c} \qquad \text{(S2)}$$

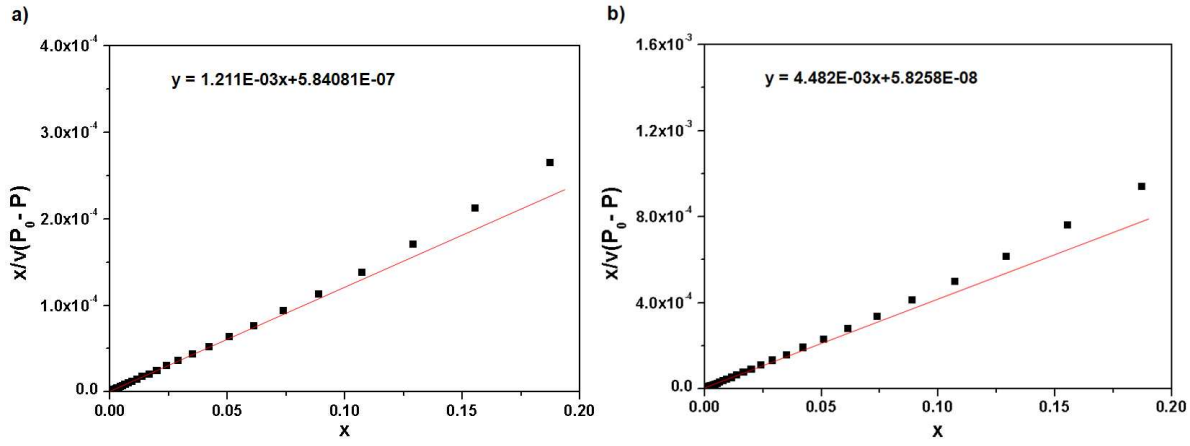

Figure S2. A plot of $x/v(P_0-P)$ vs. x for (a) MOF-5 and (b) interwoven_MOF-5.

The linear fits in Figure S2 yielded monolayer capacities, v_m, of (a) 825 and (b) 223 cm^3(STP)/g.

The surface area, A, was calculated from the equation

$$A = v_m \sigma_0 N_{av}, \qquad \text{(S3)}$$

where σ_0 is the cross-sectional area of nitrogen at liquid density (16.2 Å) and N_{av} = Avogadro's number.

The BET surface areas, A, of (a) MOF-5 and (b) interwoven_MOF-5 were 3596 and 972 m^2/g, respectively.

Nitrogen adsorption isotherms (Semilogarithmic plot)

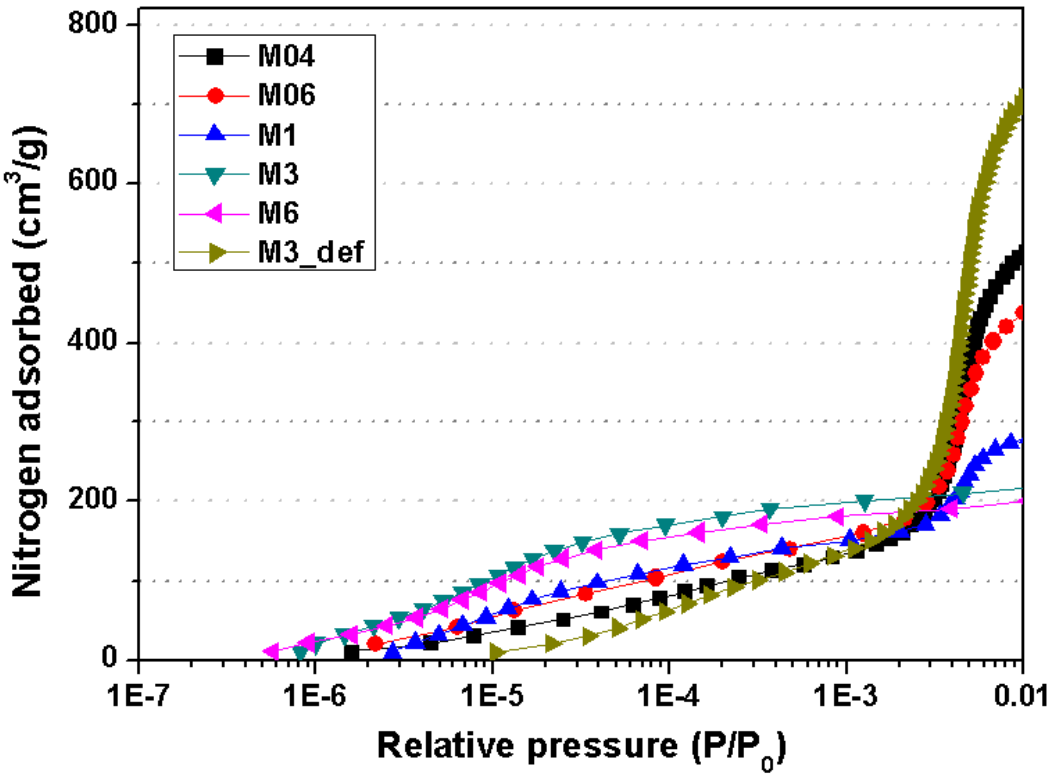

Figure S3. Semilogarithmic plots of the experimental nitrogen adsorption isotherms of the products.

Pore size (diameter) determination

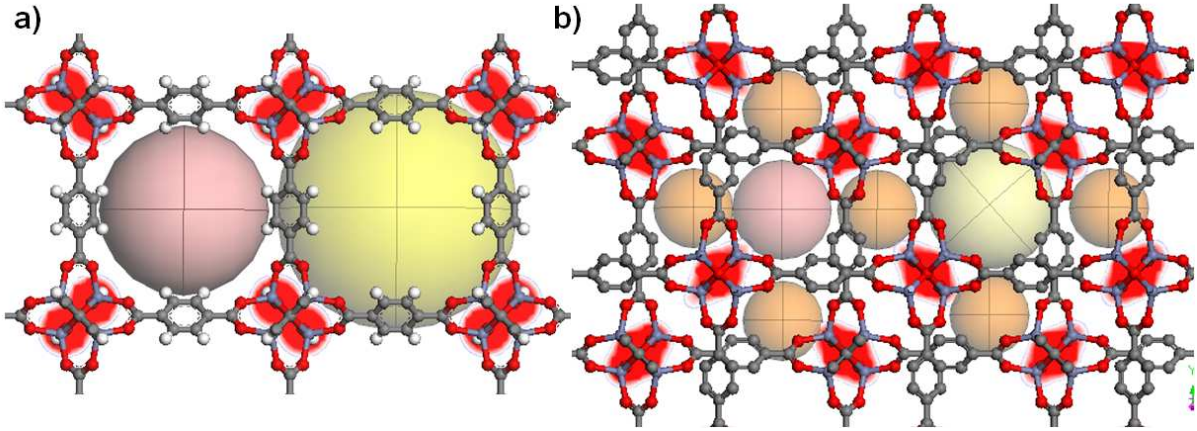

Figure S4. Geometrical pore size determination of the (a) MOF-5 and (b) interwoven_MOF-5.

Effective pore diameters were estimated from the excluded van der Waals radii of zinc, carbon, oxygen, and hydrogen in the frameworks. The red color contour map in Figure S4 represents a projection of the excluded volume occupied by atoms in the framework. The obtained pore sizes were as follows,

MOF-5: Two distinct pore sizes centered at 1.2 nm and 0.8 nm;

Interwoven MOF-5: Single pore size distributed across the range 0.4–0.6 nm.

(Previous studies reported pore diameters for IRMOF-5 of 1.4, 1.0 nm, based on the atom-to-atom distance between the framework and the center of each pore.)

In estimating pore sizes, we excluded micropores smaller than 4 Å because the kinetic diameter of nitrogen gas is 3.68 Å.

Hydrogen adsorption isotherms at 87 K (liquid argon temperature)

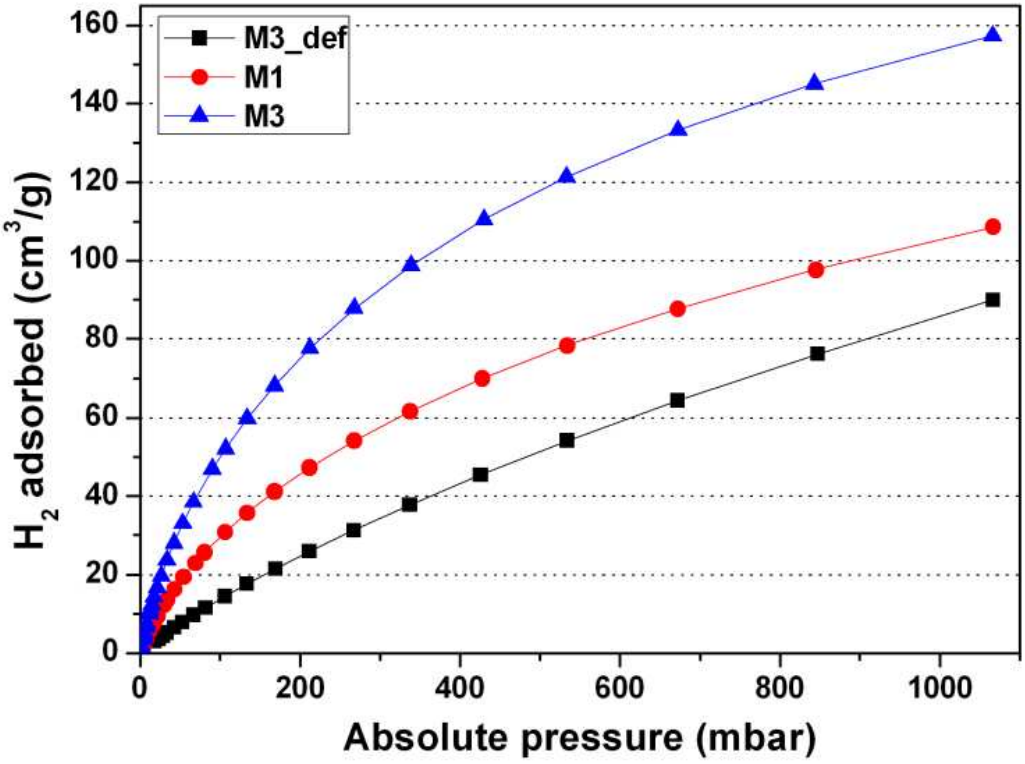

Figure S5. Hydrogen adsorption isotherms of the products at 87 K

(1) Walton, K. S.; Snurr, R. Q. *J. Am. Chem. Soc.* **2007**, *129*, 8552.

(2) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; 2nd ed.; Academic Press: San Diego, 2002.