Supplementary Information

Covalent organic frameworks with spatially confined guest molecules in nanochannels and their impacts on crystalline structures

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A. Methods

Simulations of powder X-ray diffraction (PXRD) patterns. PXRD simulations were performed using the Reflex Module as implemented in Materials Studio 4.4.\textsuperscript{1} Scanning ranges between 5° and 25° with a step size of 0.02°. Cu Kα\textsubscript{2} radiation was not considered for clarity. For each structure, we adopted previously reported structural parameters in literature for modeling their different configurations. As for the solvent packing structures, an additional line broadening factor was brought in with mean crystallite size setting to 1 × 10\textsuperscript{3} nm for imitating the experimental PXRD spectra.

Molecular Simulations. Molecular mechanics (MM) and molecular dynamics (MD) calculations were performed using Forcite programs implemented in Materials Studio 4.4 and combined force field (vdW-FF plus Dreiding).\textsuperscript{2} The Validation of the Dreiding force field has been proofed.\textsuperscript{3} A cutoff of 1.8 nm was used to calculate the LJ interactions and short-range electrostatic interactions. The long-range electrostatic interactions were evaluated using the particle-mesh Ewald (PME) algorithm,\textsuperscript{4} with an accuracy tolerance of 10\textsuperscript{-5} kcal mol\textsuperscript{-1}. The supercell for calculations was 3 × 3 × 10 and periodic boundary conditions were exerted in three dimensions. Molecular dynamics calculations were performed for simulating actual environment in which each layer stacks in a random direction. For each MD simulation, we started with the equilibrium geometry after 500 steps of conjugated gradient (CG) minimization (cell coordinates and atom positions) followed by 100 ps of NVT dynamics (amounts of substance (N), volume (V) and temperature (T) are conserved) to heat the system to 398 K. Finally, we run NPT dynamics (amounts of substance (N), pressure (P) and temperature (T) are conserved) at 1 atm and 398 K for 2.0 ns. The output structures are unoptimized and periodic. After the MD simulation, the mesitylene molecules were packing
randomly into the individual pores respectively to represent the random population in as-synthesized COF-1 samples. Based on the sum of guest molecules in each pores, we evaluated the overall amount of mesitylene filled in supercell with the average density of mesitylene that surrounded in Connolly surface.\textsuperscript{5}
B. Supplementary Figures

Figure S1. A snapshot randomly captured in NPT ensemble.

Figure S2. A top view of the channel geometry of COF-1 after MD simulation.
Figure S3. A side view of the channel geometry of COF-1 after MD simulation.
Figure S4. Snapshot structures of AA staking COF-1 with mesitylene in the channels with density of (A) 0.2, (B) 0.3, (C) 0.4, (D) 0.5, (E) 0.6, (E) 0.7, (F) 0.8 and (F) 0.9 g cm$^{-3}$, respectively.
C. Supplementary References


