Supporting Information

Size-Dependent Mechanical Properties of a Metal-Organic Framework: Increase in Flexibility of ZIF-8 by Crystal Downsizing

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1) Synthesis of micro- and nano-dimensional ZIF-8 crystals

**Materials:** 2-methylimidazole and Zn(NO$_3$)$_2$ • 6H$_2$O were purchased from Acros Organics and Sigma Aldrich, respectively, and used without further purification. Micro-sized crystals of ZIF-8 were grown *via* solvothermal reaction as described previously,$^1$ with the exception that a Teflon-lined steel bomb was used as the reaction vessel. Nano-sized crystals were grown *via* an established aqueous solution method.$^2$

2) Powder X-ray diffraction (PXRD) measurements

PXRD data were obtained on a Bruker D500 X-ray diffractometer using Cu Kα$_1$ radiation ($λ = 1.54056$ Å) (scan type: locked coupled; scan mode: continuous; step size: 0.02°; scan time: 2s/step). The samples were mounted on glass slides.
Figure S1. Comparison of ZIF-8 PXRD patterns: simulated pattern from X-ray single crystal data\textsuperscript{1} (blue), micro- (red), and nano-sized (green).

3) Atomic Force Microscopy (AFM) imaging and nanoindentation measurements

Micro-sized ZIF-8 crystals ranging from 50-150 μm were glued directly onto a glass slide using a double-sided tape to ensure a stationary sample during force measurements. Nano-sized crystalline samples were suspended in methanol (791 mg in 1 mL), then drop-casted on a freshly cleaved atomically flat mica substrate (V-1 grade, SPI Supplies, Westchester, PA) and solvent was allowed to evaporate. All AFM studies were conducted using a Molecular Force Probe 3D AFM (Asylum Research, Santa Barbara, CA). AFM images and nanoindentation measurements were collected at room
temperature and pressure using Si$_3$N$_4$ probes (Mikromasch, San Jose, CA, NSC35) with a nominal spring constant of 5.4 N/m and a typical tip radius of 8 nm. Actual spring constants were determined using a built-in thermal noise method.$^3$ Topographic images were collected using an intermittent contact mode (AC mode) or a contact mode at a typical scan rate of 1 Hz.

AFM nanoindentation experiments were performed by recording force versus vertical piezo displacement curves to determine Young's modulus values of individual micro- and nano-sized ZIF-8 crystals. The Young's modulus was determined by fitting the loading force versus indentation depth approach data to the Johnson-Kendall-Roberts (JKR) contact model.$^4$ Here, the Young's modulus and Poisson's ratio of the AFM probe was assumed to be 290 GPa and 0.25, respectively. The Poisson ratio of the ZIF-8 crystals was assumed to be 0.40.$^6$ The JKR model was selected due to overlap between the approach and retract contact region data, confirming purely elastic nanoindentation, and the presence of the adhesion force between the AFM tip and ZIF-8 samples. The
acquisition of the force plots and corresponding data analysis were carried out as reported in our previous work.\textsuperscript{5,7-9}

4) Thermal gravimetric analysis (TGA)

As-synthesized micro- and nano-dimensional ZIF-8 samples were air dried for several days according to the literature.\textsuperscript{1,2} The samples were then immersed in methanol and left to air dry for 1 hour to imitate our AFM sample preparation procedure. Samples were run on a Perkin Elmer TGA 7 thermal gravimetric analyzer with samples held in aluminum pans in a continuous flow of nitrogen. Samples were heated at a constant rate of 5 °C/min from 30-600 °C for both experiments.
Figure S2. TGA curve of micro-dimensional ZIF-8 powder sample after dispersing in methanol.

Ending at ~490 °C, the micro sample exhibits a weight loss step of 11% corresponding to the removal of guest molecules (trace DMF, methanol). The curve is consistent with that reported for micrometer-sized ZIF-8 crystals, though our weight loss percentage is lower due to solvent exchange with methanol.\textsuperscript{1} We note that guest molecules are expected to leave the narrow porous system of ZIF-8 slowly; this will cause some molecules to decompose at high temperature prior to their escape from the pores.\textsuperscript{1}
Figure S3. TGA curve of nano-dimensional ZIF-8 powder sample after dispersing in methanol.

Though it is unclear why the nano-dimensional ZIF-8 sample exhibits a ~0.5% weight gain from 30-120 °C, a long plateau was shown in the range of 200-400 °C which indicates relatively high thermal stability of the sample. Both the slight weight gain and the plateau were also observed in a previous TGA trace on nanocrystals of ZIF-8. At ~400-600 °C, a significant drop in weight (~14%) was observed, also corresponding to a weight loss step that was previously reported. Overall, after ramping both micro- and
nano-dimensional samples up to 600 °C, the weight loss was in the range of 12-14%, rendering the solvent volume inside the micro- and nano-samples used in our AFM study to be comparable. We also note that the effect of pore occupancy on the mechanical properties of ZIF-8 is negligible.10
5) References