Facile Mechanosynthesis of Amorphous Zeolitic Imidazolate Frameworks

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Supporting Information

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SI-1: Synthesis

Synthesis of starting materials

ZIF-1, -3, -4, -8, -zni and nanoZIF-8 were synthesized and evacuated according to previously described procedures.[1-4]

Mechanosynthesis

In all reactions, 100 mg of evacuated ZIF [$Zn(Im)_2$] or [$Zn(mIm)_2$] were placed in a 10 mL stainless steel jar along with one 7 mm diameter stainless steel ball. The ZIF was then ground for 30 min in a Retsch MM400 grinder mill operating at 30 Hz. Pure amorphous products were obtained in each case, as shown in Figure 2 of the manuscript for ZIF-1, -3 and -4 and in Figure S1 for nanoZIF-8. The PXRD trace of bulk crystalline ZIF-8 after milling is shown below.

Whilst exhaustive mechanochemical studies have not been carried out, we did observe that higher frequencies, larger ball sizes and longer reaction times all contributed to more complete amorphization of the samples. Liquid was not necessary to facilitate the amorphization, though no work was carried out on the inhibitory effects of different solvents.

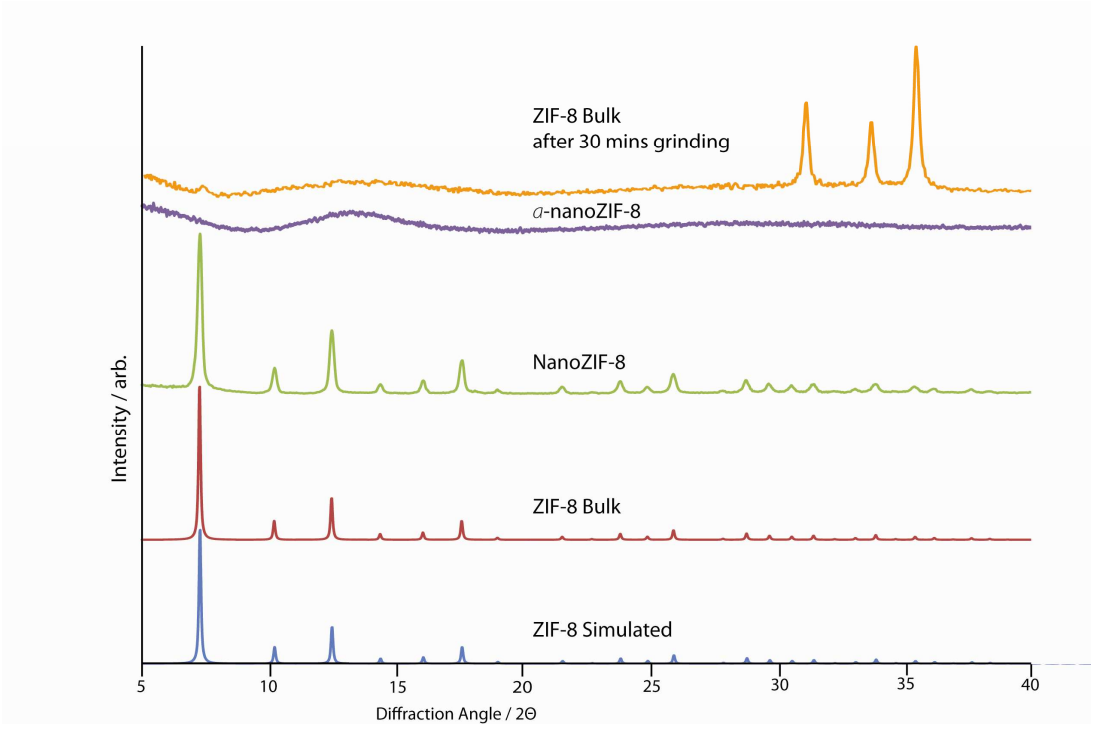

Figure S1 - Uncorrected X-ray diffraction patterns for crystalline ZIF-8, partially amorphized ZIF-8, nanoZIF-8 and amorphous nanoZIF-8, as produced by mechanosynthesis. The bragg peaks in the partially amorphized ZIF-8 sample have been assigned to zinc oxide.

SI-2: Experimental Methods

Powder X-ray Diffraction

Room temperature PXRD data were collected with a Bruker-AXSD8 diffractometer using $CuK\alpha_1$ (λ = 1.540598 Å) radiation and a LynxEye position sensitive detector in Bragg Brentano parafocusing geometry. Analysis of the data was carried out using the X'pert HighScore Plus program.

Gas Pycnometry

Pycnometry on the samples was performed using a Micromeritics Accupyc 1340 helium pycnometer, equipped with a 0.1 cm^3 insert. The typical mass used was 30 mg, the values quoted being the mean and standard deviation from a cycle of 10 measurements.

Scanning Electron Microscopy

Secondary electron image was taken on JEOL 6340F FEGSEM, which is a field-emission scanning electron microscope. The accelerating voltage used was 5 keV and the working distance was 3.8mm.

Transmission Electron Microscopy

Samples for TEM were prepared by ultrasonically dispersing small quantities of the as-synthesized materials in ethanol. Small amounts of this suspension were dropped by pipette onto amorphous holey carbon films supported on standard Cu mesh TEM grids, and the solvent was allowed to evaporate. Bright field images were collected using a JEOL 2000FX TEM operating at 200 keV, maintaining the electron dose as low as possible, consistent with obtaining acceptably sharp images.

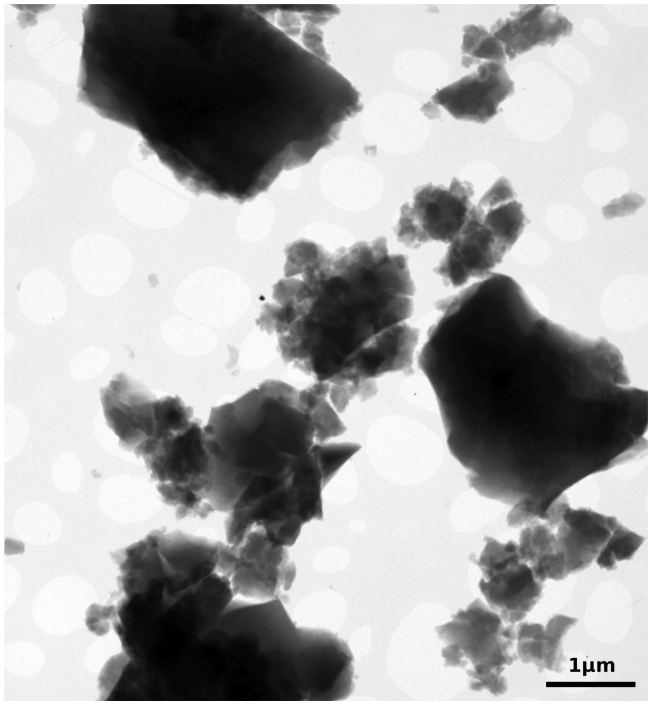

Figure S2a – Bright field TEM image of a typical particle distribution in α_m-ZIF-4.

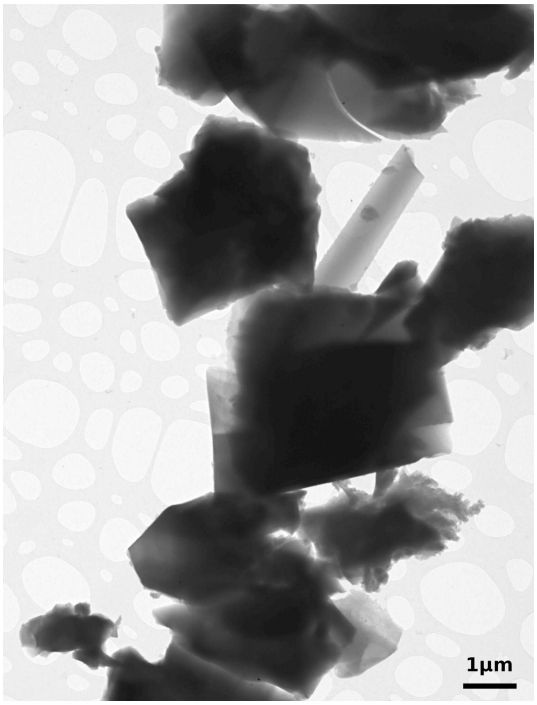

Figure S2b – Bright field TEM image of a typical particle distribution in α_T-ZIF-4. Note the smaller scale bar compared to Fig S2a.

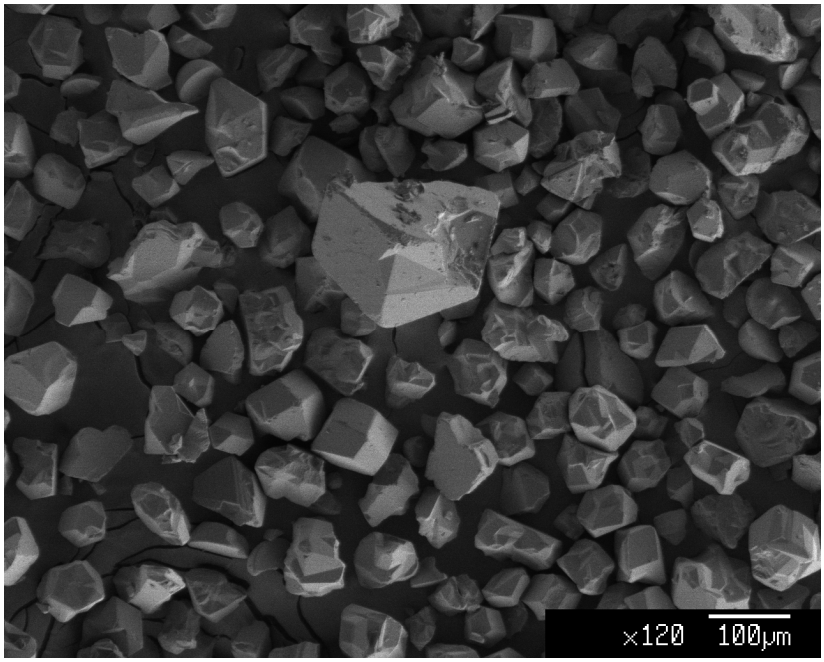

Figure S3a –Secondary electron image of pristine bulk crystalline ZIF-8. Typical sizes of crystallites is about 80 μm across, with some smaller crystallites also present.

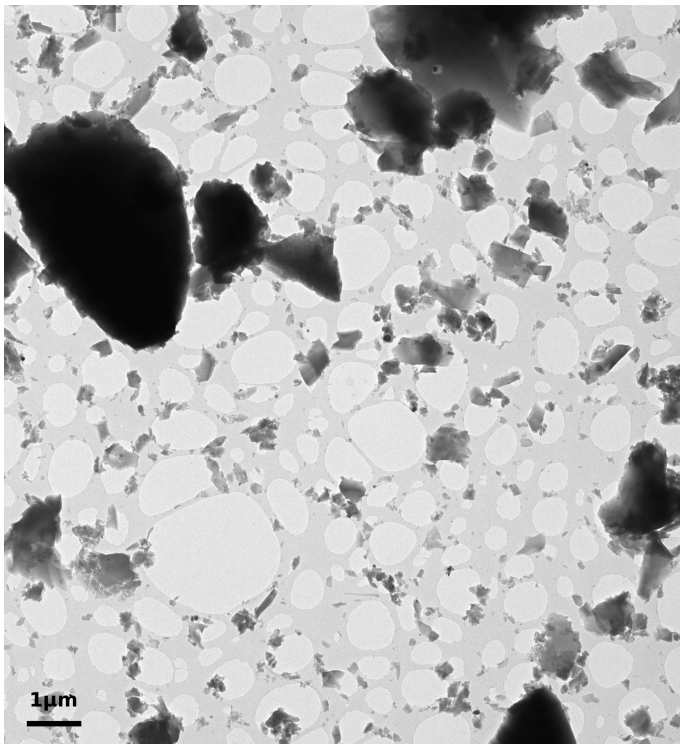

Figure S3b – TEM image of the polycrystalline bulk ZIF-8 sample used for the gas sorption experiment. A small volume of very large particles (up to tens of microns) was found in the sample, which accounts for a significant part of the volume fraction.

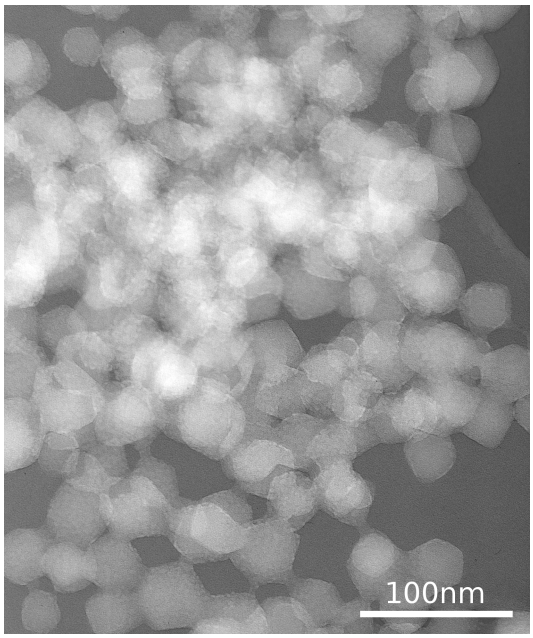

Figure S3c – Bright field TEM image of ZIF-8 nanoparticles, representative of the typical particle size distributions.

X-ray Total Scattering

Ag-source X'pert Pro MPD lab diffractometer (λ = 0.561 Å). Data collection was performed using loaded 1.0 mm diameter capillaries and collection times of approximately 40 hrs.

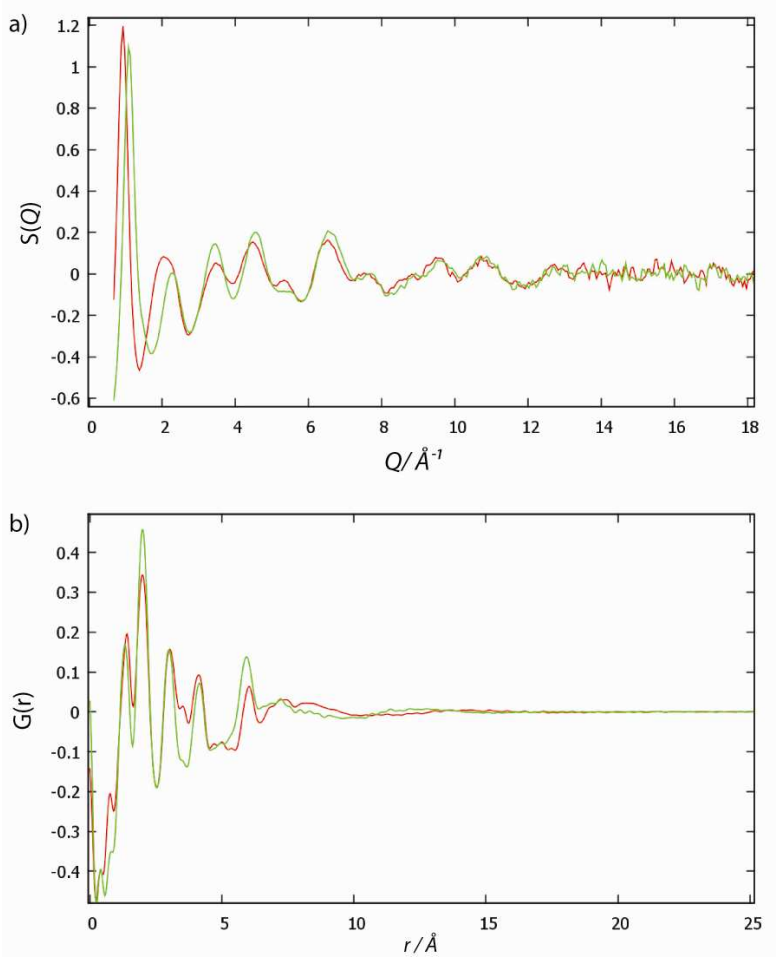

Figure S4 – X-ray total scattering data measured for the a_m-nanoZIF-8 (red), compared to a_m-ZIF-1 (green). (a) X-ray total scattering function *S(Q)*. (b) Pair distribution function *G(r)* calculated *via* Fourier transform of *S(Q)*. The regions of the PDFs below 6 Å look broadly similar, implying a retention of the bridging imidazolate motif (in keeping with that seen for all other *a*-ZIFs). Above this, differences are evident.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed using a TA instruments Q-500 series thermal gravimetric analyser with the sample (30 mg) held on a platinum pan under a continuous flow of dry N_2 gas. The heating rate used was 10 °C min^{-1}. While TGA of ZIF-1, -3, -4 and –8 have been reported previously, here we performed measurements on the evacuated nanoparticles of ZIF-8 (before and after milling).

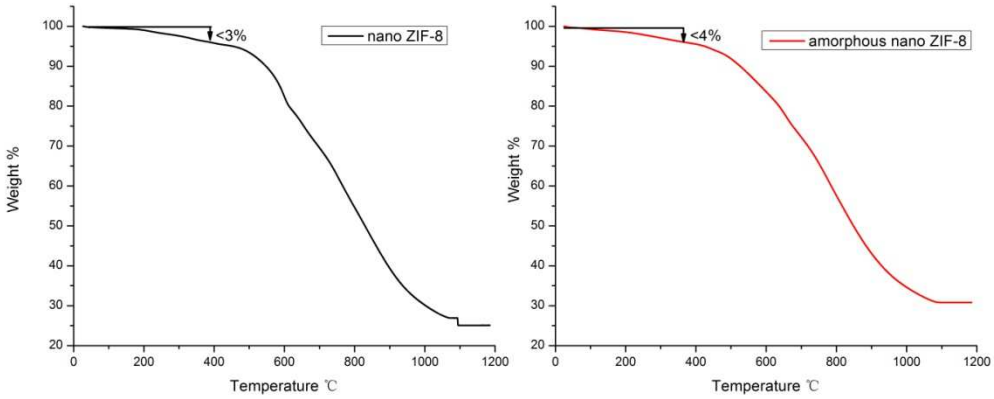

Figure S5 – TGA traces of both nano ZIF-8 and amorphous nano ZIF-8. Their weight loss at 400□ being less than 4%, which illustrates that the samples have been fully evacuated before milling.

SI-3: N_2 Sorption Analysis

Nitrogen sorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 instrument. Samples were outgassed in vacuum for at least 5 hours at approximately 373 K before starting the sorption measurements. ZIF-8 nanoparticles, however, were not heated during outgassing. The surface areas were estimated using the Brunauer – Emmett – Teller (BET) equation for the relative pressure range (P/P_0) of 0.002 to 0.3. The saturation pressure, P_0, corresponds to ca. 103.4 kPa.

Table S1

Sample	Maximum Uptake / cm^3g^{-1}	BET Surface Area / m^2g^{-1}
ZIF-4	260	300
α_m-ZIF-1	21	11
α_m-ZIF-3	41	21
α_m-ZIF-4	22	10
α_T-ZIF-4	1.5	1
ZIF-zni	9	4
ZIF-8 (bulk)	312	1006
nanoZIF-8	1000	1630
α_m-nanoZIF-8	70	56

Table S2

Material	Gate Opening Pressure (kPa)	Solvent Accessible Volume[a]	Crystallographic Density (gcm^{-3})
ZIF-4 [$Zn(Im)_2$]	35	36.8%	1.444
ZIF-8 [$Zn(mIm)_2$]	2[5]	50.30%	0.946

[a]As found using the PLATON program.[6]

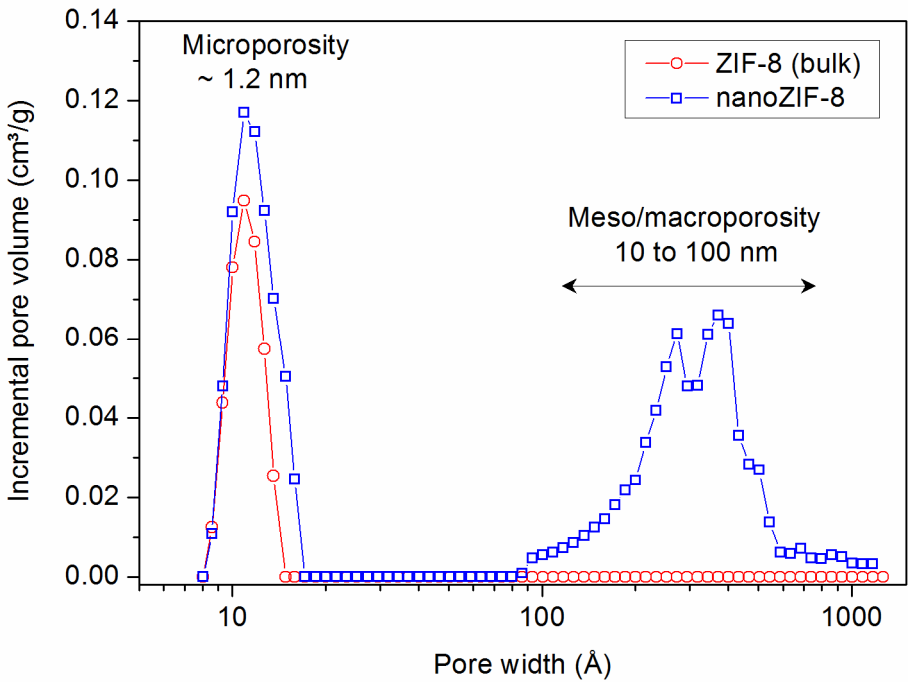

Figure S6 – Pore size distribution determined by density functional theory (DFT) based on the model of N_2 adsorption at 77K on slit pores.[7] Both the bulk and nanoparticles of ZIF-8 are microporous with a characteristic mean pore diameter of 12 Å, consistent with reported crystallographic data.[2, 8] In addition, nanoparticles of ZIF-8 contain also meso-/macro-porosity with diameters ranging from 10 to 100 nm. Because of capillary condensation, features at such length scales found in nanoZIF-8 can lead to the hysteretic response observed during desorption from 100 to 90 kPa (see Figure 4 in manuscript).

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