

Pressure-Induced Amorphization and Porosity Modification in a Metal-Organic Framework

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Supplemental Information

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CONTENTS

<i>In-situ High Pressure X-ray Diffraction</i>	S3
<i>Figure S1</i> Rietveld fit to the ZIF-8 diffraction data (pristine sample) at 0 GPa	S3
<i>Figure S2</i> Diffraction data collected for ZIF-8 upon compression without fluid and in Fluorinert.	S4
<i>Table S1</i> Parameters from Le Bail fits to variable pressure powder diffraction data.....	S4
<i>Table S2</i> Parameters from Birch-Murnaghan equations of state fit to the variable pressure data.....	S4
<i>Sorption Behavior of Pressure-Treated Samples</i>	S5
<i>Figure S3</i> Nitrogen sorption isotherms for untreated and pressure-treated sample of ZIF-8: logarithmic-scale plot and linear-scale plot.....	S5
<i>Table S3</i> Parameters for calculations of the total pore volume, Langmuir and BET surface areas.	S7
<i>Figure S4</i> Pore size distributions using the BJH method on the adsorption branch of the nitrogen isotherms...	S7

In-situ High Pressure X-ray Diffraction

The ZIF-8 (Basolite™ Z1200) was obtained from Sigma-Aldrich and gently stirred in non-penetrating fluid to disperse lumps. The sample was mixed with NaCl powder (~5%) which was used as an internal pressure standard.¹ This was loaded into the 300 μm diameter hole in a stainless steel foil gasket of 250 μm thickness pre-indented to 100 μm thickness within a membrane-driven diamond anvil cell (DAC, Diacell Bragg-G) equipped with 600 μm culet anvils. Fluorinert (FC75) was used as the pressure transmitting medium (hydrostatic limit: 1.2 GPa) or the sample was packed into the cell and compressed without fluid. *In-situ* high-pressure diffraction data were collected using the monochromatic X-rays (0.60511 \AA , 100 μm diameter beam size) available at the 1-BM beamline at the Advanced Photon Source, Argonne National Laboratory in combination with a MAR-345 imaging plate detector. Data were collected with 36 s exposures (2 min per image) as the pressure was varied in the range 0.0-1.2 GPa. Broadening of the diffraction peaks under non-hydrostatic conditions prevented the reliable fitting of the lattice parameters for data collected without fluid. The raw images were processed within Fit-2D, refining the sample-to-detector distance and tilt of the detector relative to the beam based on data obtained for a LaB_6 standard.² The pressure-dependent lattice parameters were extracted from Le Bail fits to the diffraction data within GSAS.³ Rietveld fitting of the ambient pressure data by a model based on the published structure⁴ (removing guest molecules and refining lattice parameters) provided excellent agreement. The excellent fit of the guest-less structural model to the data is consistent with the supplied sample being relatively guest-free, with only heating at 100°C (with vacuum) recommended to "activate" or evacuate the pore network. Equations of state were fit to the P-V data using the EOS-FIT v5.2 program by R. J. Angel. The 3rd-order Birch-Murnaghan equation of state provided the best fit to the data.

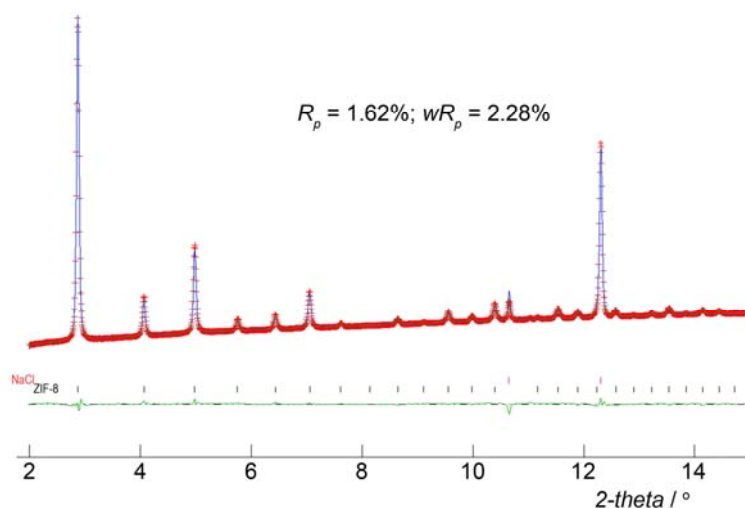


Figure S1. Rietveld fit to the ZIF-8 diffraction data (pristine sample) at 0 GPa.

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- (3) (a) Larson, A. C.; Dreele, R. B. V., General Structure Analysis System (GSAS) 2000, Los Alamos National Laboratory Report, LAUR 86-748; (b) Toby, B. H., *J. Appl. Crystallogr.* **2001**, 34, 210-213.
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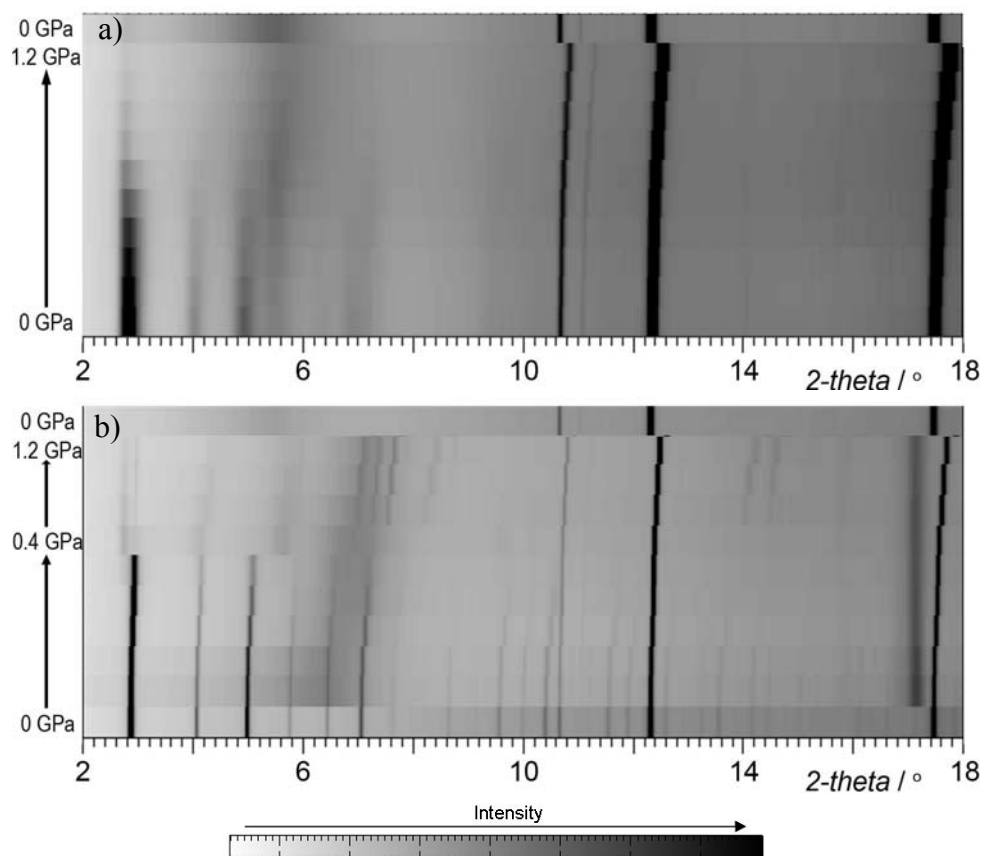


Figure S2. Diffraction data collected for ZIF-8 upon compression without fluid (a) and in Fluorinert (b). The sharp peaks at 10.8, 12.3 and 17.5° are from the sodium chloride pressure marker.

Table S1. Parameters from Le Bail fits to variable pressure powder diffraction data.

P / GPa	$V(\text{NaCl}) / \text{\AA}^3$	$a / \text{\AA}$	$V / \text{\AA}^3$
0.000	179.2061(20)	17.00825(20)	4920.16(10)
0.025	179.0152(19)	16.98421(22)	4899.33(11)
0.064	178.7210(23)	16.94979(29)	4869.60(14)
0.192	177.7832(24)	16.8260(4)	4763.70(18)
0.294	177.0535(25)	16.7127(5)	4668.11(26)
0.340	176.7289(35)	16.6471(12)	4613.3(6)

Table S2. Parameters from Birch-Murnaghan equations of state fit to the variable pressure data.

	P-range	No. data	$V_0 / \text{\AA}^3$	K_0 / GPa	K'	$\text{Max } \Delta P$	$R_w / \%$	χ^2
2 nd -Order	0.00-0.34	6	4928.4(75)	4.85(23)	4	-0.026	5.8	5.46
3 rd -Order	0.00-0.34	6	4918.2(27)	6.52(35)	-4.6(14)	-0.002	0.63	0.09

Sorption Behavior of Pressure-Treated Samples

Bulk samples (~60 mg) were prepared using a hydraulic pellet press with a 10 mm diameter die. The sample, obtained from Sigma-Aldrich, was gently stirred in non-penetrating fluid to disperse lumps before evenly distributing in the die. The press was subjected to loads of 2¼, 4½, 6¾ and 9 ton for ~3 min before recovering the sample.

Nitrogen sorption experiments were measured at -196°C with a Quantachrome Autosorb-1C volumetric gas sorption instrument. Samples were pre-treated in an oven at 130°C for 1 h before outgassing under a high vacuum ($\sim 10^{-7}$ Torr); initially at 30°C for 2 h, and then at 300°C for 5 h immediately prior to the measurements. Outgas tests were rigorously employed to ensure a consistently thorough treatment before each sample was transferred from the outgassing to the measurement port. The same desorption protocols were applied for all samples. Surface area (Langmuir and BET), total pore volume, and pore distribution (BJH, absorption) calculations were performed with the Quantachrome ASWIN program. Although the earliest sorption measurements on ZIF-8 used pre-treatment involving exchange of DMF guests by more volatile methanol, this is not indicated for the material supplied by Sigma-Aldrich which does not contain such non-volatile guests.

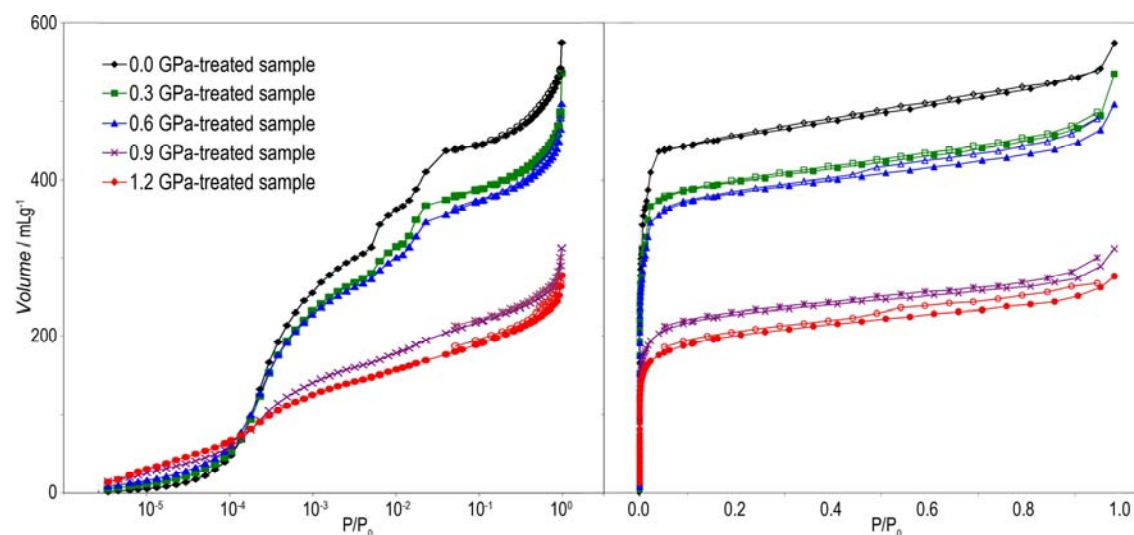


Figure S3. Nitrogen sorption and desorption isotherms for untreated and pressure-treated samples of ZIF-8: logarithmic-scale plot (left) and linear-scale plot (right).

Data for adsorption (5×10^{-6} to $0.95 P/P_0$) and desorption (0.95 to $0.05 P/P_0$) of nitrogen were collected in at least duplicate for the untreated sample and each of the pressure treatments. The data collection protocol was carefully optimized to ensure sufficient data points in the regions of interest, and to account for the relatively slow uptake kinetics in this system by using maximal equilibration times. For the as supplied ZIF-8, the nitrogen sorption is generally consistent with previous reports, but some subtle differences were evident. Here, the multi-step features in the logarithmic-scale plot are somewhat pronounced and clearly show three-steps. This suggests a constricted micro-pore network, with the narrowest channels (first-step, major component) similar in diameter to the adsorbate molecules which fill first and hinder the filling of the larger micro-pore sections (2nd and 3rd steps, minor components). This is further exemplified by the continued gradual uptake of nitrogen beyond the micropore region ($> 0.05 P/P_0$) as would be expected for the slow diffusion kinetics through the narrowest regions. These subtle differences between the commercially available material and previously reported sorption data for highly (typically single) crystalline research samples are not unexpected given the different synthetic procedures and processing involved, particularly in light of the present results. Importantly however, the surface area calculations are in good agreement.

The retention of porosity for the pressure-treated samples of ZIF-8 is clearly indicated by the retention of the Type-I isotherm behavior consistent with microporosity. Several modifications are apparent from the isotherm data:

- Total uptake is reduced with increasing pre-treatment pressure up to the thoroughly amorphized samples (0.9 & 1.2 GPa) which show similar behavior.
- The second- and third-step features are initially significantly reduced upon treatment up to 0.6 GPa, and essentially eliminated upon further pressure-treatment.

The retention of subtle step features for samples treated to above the 0.34 GPa reflects the distribution of pressures generated under the non-hydrostatic pressure-treatment which results in a distribution of amorphized and crystalline portions of the sample. At higher pressures, the remaining crystalline component, and step-like sorption features, are greatly diminished. While the reduction in uptake upon amorphization indicates a decrease in pore volume and surface area (Table S3), the changes in the step features suggest a homogenization of the dimensions or further constriction of the pore network to a point where parts (in this case the minor, wider sections) of the micro-pore network become inaccessible. This is consistent with analyses of pore size distributions using the BJH method and the

adsorption branch of the isotherms (Figure S4), which suggest a gradual loss (or blockage) of the larger diameter pore volumes upon increasing pressure treatment.

Table S3. Parameters for calculations of the total pore volume (at $P/P_o \sim 0.09$), Langmuir and BET surface areas.

Sample	BET				Langmuir		Total Pore Volume
Load /ton	Area /m ² g ⁻¹	Correlation Coefficient	Y-Int	C	Area /m ² g ⁻¹	Correlation Coefficient	/mLg ⁻¹
0	1774	0.99958	0.00042	4693	1980	0.99992	0.687
2¼	1551	0.99951	0.00058	3867	1728	0.99994	0.599
4½	1495	0.99961	0.00154	930	1667	0.99998	0.575
6¾	872	0.99987	0.00510	782	972	0.99994	0.302
9	758	0.99994	0.00599	767	845	0.99985	0.292

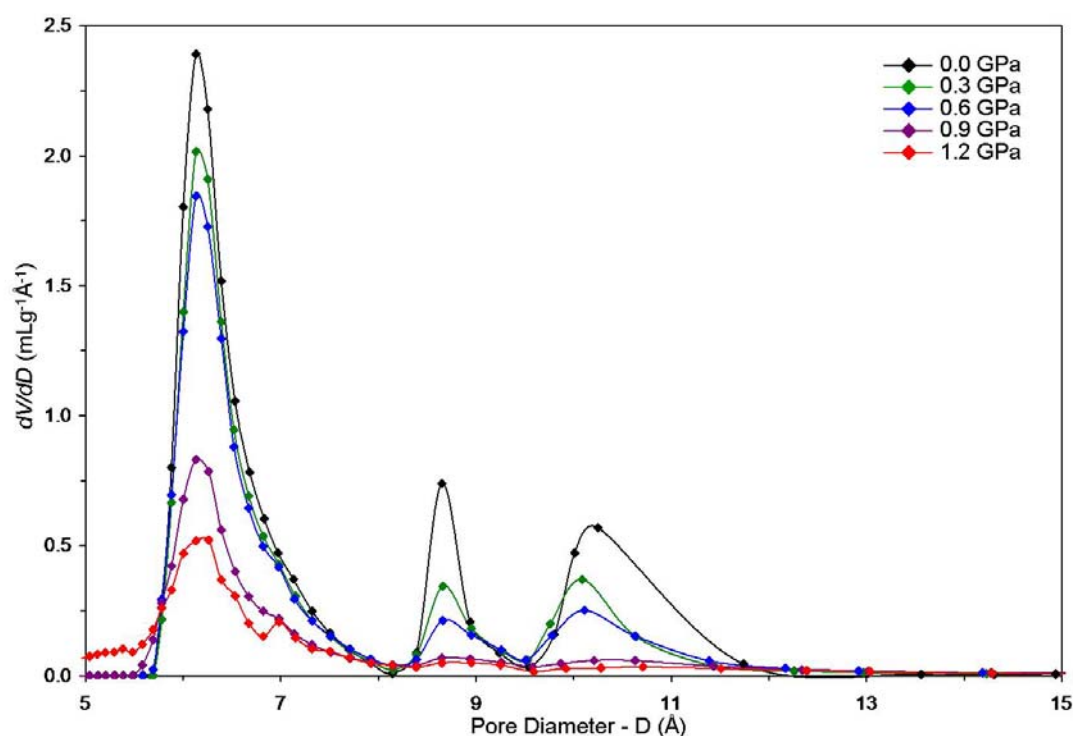


Figure S4. Pore size distributions using the BJH (Barret-Joyner-Halenda) method on the adsorption branch of the nitrogen isotherms.