Supporting Information

Reversible Pressure-Induced Amorphization of a Zeolitic Imidazolate Framework (ZIF-4)

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SI-1: Single Crystal Diffraction Experiment Details

General Procedures

High-pressure experiments were carried out with a modified Merrill-Bassett diamond anvil cell (DAC) equipped with 600 μm culet diamonds and a tungsten gasket.[1] The single crystal sample and a chip of ruby (as a pressure calibrant) were loaded into the DAC with a 4:1 mixture of methanol and ethanol as a hydrostatic medium. The ruby fluorescence method was utilised to measure the pressure.[2] Pore volume and solvent content were calculated from the refined structural models using the SQUEEZE algorithm within PLATON and void analysis carried out in MERCURY using a probe radius and grid spacing of 1.2 and 1.0 Å respectively.[3, 4]

Data Collection, Reduction and Refinement

A sphere of data was collected on a crystal of ZIF-4 $[Zn(Im)_2]$ at ambient temperature and pressure in order to provide data for comparison with the high pressure studies. Diffraction data were collected on a single crystal on a Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). These data were integrated using the program SAINT,[5] while the absorption correction was carried out using the program SADABS.[6] Refinement was carried out against $|F|^2$ using all data[7] starting from the ambient temperature coordinates of Tian *et al.*, (2007).[8]

High pressure diffraction data were also collected at room temperature, for pressures up to 0.56 GPa, on a Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected in ω-scans in eight

settings of 2θ and ϕ with a frame and step size of 40 seconds and 0.3° respectively. This data collection strategy was based on that described by Dawson *et al.*[9] The data were integrated using the program SAINT[5] using 'dynamic masks' to avoid integration of regions of the detector shaded by the body of the pressure cell. Absorption corrections for the DAC and sample were carried out with the programs SHADE and SADABS respectively.[10] At 0.56 GPa the sample underwent a phase transition that resulted in a rapid degradation of the quality of the data. In order to elucidate the structure of the high-pressure phase and collect data to higher pressure, data were then collected on station I19 at the DIAMOND light source on a Crystal Logic four circle goniometer equipped with a Rigaku Saturn 724 CCD detector (λ = 0.6889 Å). Data were collected using ω-scans with a frame time and step size of one second and 0.5° respectively. Data were collected from 0.9 up to a final pressure of 7.6 GPa.

Refinements of [Zn(Im)$_2$] were carried out against $|F|^2$ using all data. Because of the low completeness of the data-sets, all intra-imidazolate distances were restrained to the values observed from our ambient pressure structure for all C and N atoms, within 0.01 standard deviations. Thermal similarity restraints were applied to all non-hydrogen atoms. Torsion angles were refined freely. H-atoms attached to carbon atoms were placed geometrically and not refined.

The structure of ZIF-4-I at 0.9 GPa was solved starting from the ZIF-4 coordinates transformed onto the ZIF-4-I unit cell, and then refined incrementally using the 1,2 and 1,3 restraints obtained from the ambient pressure structure until the refinement converged. As a consequence of the reduced data quality, all non-hydrogen atoms were refined with isotropic atomic displacement parameters. Only Zn atoms were refined anisotropically. Furthermore, structural data could only be extracted to 3.2 GPa. On increasing pressure to 4.3 GPa the sample became almost completely polycrystalline, though unit cell determination was still possible to 5.1 GPa. On increasing pressure to 6.5 GPa, the sample became amorphous and no Bragg diffraction from the sample could be observed. Listings of crystal structure and refinement data are given in Table S1.

Table S1. Crystallographic Data and Refinement Details

P [GPa]	0	0.13	0.56	0.99[a]	2.06[a]	3.21[a]	4.39[b]	5.01[b]
a [Å]	15.402(7)	15.3486(14)	17.735(9)	17.608(5)	17.4068(18)	17.450(5)	17.563(8)	17.4606
b [Å]	15.459(7)	15.1069(17)	14.457(8)	14.411(5)	14.0783(17)	13.912(5)	13.825(8)	13.6274
c [Å]	18.408(8)	18.3430(19)	14.829(9)	14.703(5)	14.5050(17)	14.118(5)	13.882(8)	13.8185
B (degrees)	90	90	100.25(5)	100.90(2)	101.853(9)	102.18(3)	102.36(5)	102.104
V [Å^3]	4383(3)	4253.2(8)	3741(4)	3663.3(19)	3478.8(7)	3350.1(18)	3293(3)	3214.925
Space Group	$Pbca$	$Pbca$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	P1 $2_1/c$ 1	P1 $2_1/c$ 1
$P_{experimental}$ [gcm^{-3}]	1.431	1.475	1.676	1.712	1.803	1.872	1.905	
Collected reflns	31533	11913	1251	1857	2252	926	750	
Unique reflns	4503	2025	1212	948	870	835	651	
R_{int}	0.1375	0.1810	0.1369	0.1609	0.1675	0.1879	0.2201	
GOF	0.9798	0.8034	1.2976	1.0741	1.1616	1.0450	1.0606	
R^1 [I>2σ(I)]	0.0763	0.0559	0.1369	0.1336	0.1528	0.1513	0.1752	
R^2 [I>2σ(I)]	0.1590	0.0946	0.1206	0.2972	0.2865	0.2836	0.3686	

[a] Data collected at DIAMOND light source

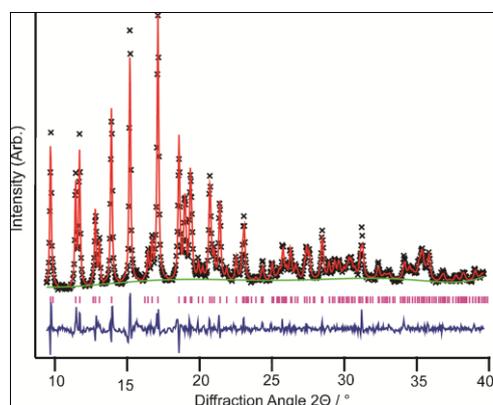[b] Rapid deterioration in data quality above 3.2 GPa.

Figure S0: A Rietveld refinement of X-ray powder diffraction data of ZIF-4 obtained one week after return of a bulk sample to ambient pressure from 8 GPa and measured using a Bruker-AXS D8 diffractometer (λ = 1.541 Å).

SI-2: Powder Diffraction Experimental Details

X-ray powder diffraction data were collected at the Swiss Light Source Materials Science (X04SA) powder diffraction station (λ = 0.729852 Å).[11] Prior to data collection, the samples were gently ground using a mortar and pestle. The samples were mixed with synthetic quartz, which was used as an internal pressure standard. For the high pressure powder X-ray diffraction experiments, a gas-membrane Boehler-type diamond anvil cell [12] equipped with 500 µm diamond culets and an opening angle of 85 ° was used. For each data collection, the sample was loaded into a 150 µm hole of a 250 µm thick stainless steel gasket, which was pre-indented to 120 µm. After adding the pressure medium (4:1 methanol-ethanol or Daphne oil 7474 [13]) to the sample/quartz mixture contained in the gasket hole, the DAC was closed. The DAC was attached to the gas line and mounted to the diffractometer using a custom-made holder. Data collection was performed using the 1-dimensional MYTHEN silicon solid state high resolution detector.[14] To obtain better counting statistics, the DAC was rotated twice by ± 20° with an acquisition time of 400 seconds per 20°, giving four measurements in total. The working photon wavelength and the 2θ zero offset were calibrated using a silicon standard (NIST 640C). Data were collected for several pressure points per sample using steps of 0.01-0.05 GPa. After every high pressure run, the pressure was released from the DAC and a diffraction pattern was recorded at ambient pressure, the sample remaining inside the cell. The raw data were processed and merged using in-house software. Initial Rietveld fitting of the four ambient pressure data sets were consistent with the presence, or absence of solvent (Figure S1). The pressure-dependant lattice parameters were extracted from Le Bail fits to the diffraction data within the GSAS program [15] (Tables S2 – S5). At some pressures, two or more phases were found to co-exist, and all sets of lattice parameters are included where this occurs.

For the capilliary experiments, two ZIF4 samples (solvent containing and solvent free) were mounted in 0.5 mm Lindemann capillaries. Diffraction data were recorded at nominal 0.8 Å over 120° in 2θ using the 1-dimensional MYTHEN silicon solid state high resolution detector. Whole PD patterns at room temperature over 120° in 2θ were collected from ZIF-4 samples, containing solvent and evacuated. The working photon wavelength and the 2θ zero offset were calibrated by recording the diffraction pattern from a silicon standard (NIST 640C) and performing a Le Bail refinement with an in-house refinement program optimized for the MS-PD beamline optics and detectors (Table S-6). Pawley refinement, structure solution, and Rietveld refinement were performed using the TOPAS V3.0 software (Bruker AXS, Karlsruhe, Germany).
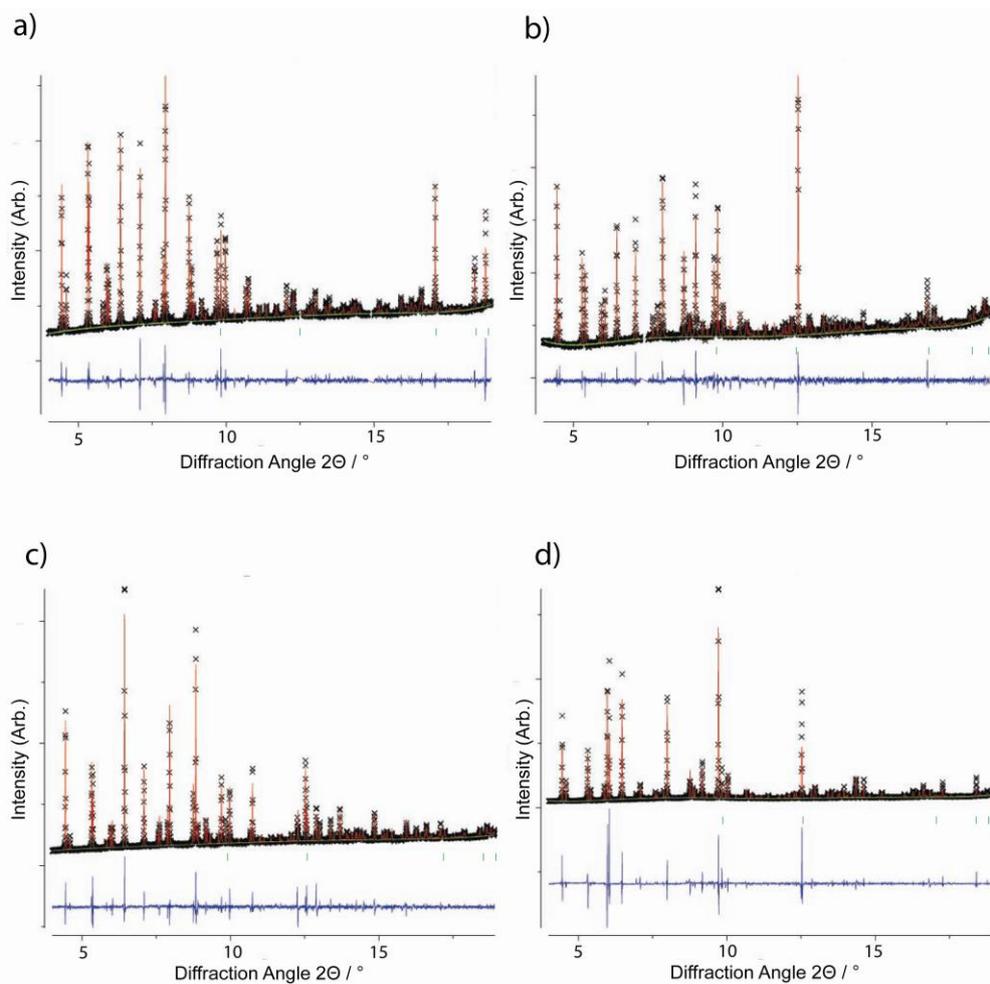
Figure S1: Rietveld fits to the ZIF-4 diffraction data at 0 GPa over the range 4° < 2Θ < 19°. (a) Experiment A starting structure; R_p = 5.73 %, R_w = 9.66 %. (b) Experiment B starting structure; R_p = 5.17 %, R_w = 8.52 %. (c) Experiment C starting structure; R_p = 7.91 %, R_w = 13.24 %. (d) Experiment D starting structure; R_p = 11.25 %, R_w = 16.51 %. Black crosses indicate experimental data points, the red line indicates the fit, with the blue difference plots included for each experiment. The green ticks indicate SiO_2 peak positions.

Table S-2: Parameters gained from the Le Bail fits to the PXRD data for the experiment using ZIF-4 (guest containing) in methanol:ethanol – Measurement A. No measurement was taken on return to ambient pressure, though the PXRD pattern in figure 2 illustrates that recrystallisation does indeed take place.

P/ GPa	V(SiO$_2$) / Å^3	A / Å	B / Å	C / Å	β	V / Å^3
0.00	113.052(3)	15.50267(27)	15.57121(23)	18.15492(25)	90	4382.51(78)
0.12	112.625(0)	15.06245(13)	14.99334(12)	18.23511(15)	90	4118.15(48)
0.12	112.625(0)	17.4848(11)	14.50315(72)	14.69788(13)	99.908(2)	3671.57(12)
0.66	111.083(1)	15.23810(15)	14.97242(17)	18.00543(19)	90	4107.96(54)
0.66	111.083(1)	24.46150(17)	10.59734(11)	15.17675(17)	90	3934.22(46)
0.66	111.083(1)	17.55716(75)	14.39554(13)	14.72947(37)	100.155(2)	3664.22(26)
2.02	107.787(0)	17.49723(19)	14.55440(33)	14.54226(14)	100.363(9)	3642.95(42)
2.02	107.787(0)	24.46142(20)	9.77430(67)	15.00481(12)	90	3587.55(36)
4.53	103.390(3)	Amorphous				

Table S-3: Parameters gained from the Le Bail fits to the PXRD data for the experiment using ZIF-4 (guest containing) in DO – Measurement B.

P/ GPa	V(SiO$_2$) / Å^3	a / Å	b / Å	c / Å	β	V / Å^3
0.00	113.035(2)	15.40520(32)	15.48887(34)	18.39867(27)	90	4390.09(10)
0.02	112.901(2)	15.40271(91)	15.48542(89)	18.39050(67)	90	4386.46(26)
0.13	112.579(5)	15.38737(19)	15.32172(19)	18.33196(17)	90	4321.00(10)
0.21	112.349(1)	15.38096(13)	15.170565(12)	18.27325(10)	90	4263.85(37)
0.32	112.025(1)	15.36770(12)	15.12853(12)	18.23111(10)	90	4238.56(34)
0.32	112.025(1)	17.45463(16)	14.48022(42)	14.672030(96)	99.763(7)	3748.86(23)
0.32	112.025(1)	24.47192(26)	10.6203(11)	15.22060(18)	90	3955.72(64)
0.40	111.792(3)	17.65007(13)	14.329805(20)	14.834985(17)	99.855(9)	3696.74(53)
0.40	111.792(3)	24.46643(30)	10.62032(84)	15.22240(16)	90	3955.41(58)
0.87	110.532(5)	17.59444(12)	14.49266(54)	14.66297(66)	100.227(5)	3679.56(20)
0.87	110.532(5)	24.45878(24)	10.61926(59)	15.228240(17)	90	3955.29(44)
2.61	106.535(7)	17.23102(53)	13.88137(50)	14.31469(32)	101.301(2)	3357.54(52)
6.43	100.317(7)	Amorphous				
0.02	112.922(1)	15.39691(67)	15.48530(73)	5.40502(89)	90	4383.42(66)

Table S-4: Parameters gained from the Le Bail fits to the PXRD data for the experiment using ZIF-4 (evacuated) in methanol:ethanol – Measurement C.

P/ GPa	V(SiO$_2$) / Å^3	A / Å	B / Å	C / Å	β	V / Å^3
0.00	113.004(4)	15.50545(17)	15.57297(19)	18.16954(27)	90	4387.33(66)
0.03	112.897(5)	15.55898(46)	15.48474(57)	18.18536(92)	90	4381.34(24)
0.06	112.798(6)	15.57967(97)	15.36413(92)	18.14771(96)	90	4343.98(28)
0.25	112.239(8)	15.13973(99)	14.97930(11)	18.19706(12)	90	4126.78(39)
0.25	112.239(8)	24.56460(18)	10.58477(55)	15.12291(11)	90	3929.52(33)
0.77	110.799(3)	15.09455(57)	14.87382(46)	18.20568(27)	90	4087.42(45)
0.77	110.799(3)	24.43499 (32)	10.68014(10)	14.81810(13)	90	3867.07(56)
1.49	108.990(3)	15.07460(97)	14.86277(18)	17.861770(28)	90	4001.94(62)
1.49	108.990(3)	24.42765(41)	10.53856(12)	14.62327(18)	90	3764.50(78)
4.54	103.079(9)	Amorphous				
0.01	113.091(2)	15.38751(78)	15.32355(95)	18.41562(11)	90	4342.24(30)

Table S-5: Parameters gained from the Le Bail fits to the PXRD data for the experiment using ZIF-4 (evacuated) in DO – Measurement D.

P/ GPa	V(SiO$_2$) / Å^3	a / Å	b / Å	c / Å	β	V / Å^3
0.00	113.024(5)	15.44731(16)	15.45873(20)	18.22822(30)	90	4352.82(72)
0.05	112.809(4)	15.38621(63)	15.27615(65)	18.18421(65)	90	4274.05(20)
0.06	112.781(3)	15.32645(98)	15.20365(82)	18.18686(97)	90	4237.87(26)
0.09	112.695(3)	15.31787(76)	15.19104(72)	18.14693(86)	90	4222.69(24)
0.10	112.672(3)	15.21941(88)	15.10350(68)	18.16058(81)	90	4174.51(29)
0.13	112.589(2)	15.16399(333)	15.05299(35)	18.20088(42)	90	4154.59(20)
0.17	112.483(2)	Excessive Peak Broadening				
0.35	111.945(2)	14.81726(12)	14.64988(22)	17.96118(19)	90	3898.35(54)
0.35	111.945(2)	24.33917(47)	10.42224(13)	14.69513(28)	90	3727.69(92)
0.98	110.240(2)	Amorphous				
0.03	112.882(5)	15.35619(40)	15.46790(48)	18.37117(35)	90	4363.67(42)

Table S-6: Parameters gained from the Le Bail fits to the PXRD data for the PXRD capilliary experiment under ambient conditions. ZIF-4 with solvent refers to an evacuated sample re-emerged in small molecule PTF and then dried.

Evacuated ZIF-4	$a/Å$	$b/Å$	$c/Å$	$V/Å^3$
	15.39494(78)	15.44783(47)	18.08425(56)	4300.77
With Solvent	$a/Å$	$b/Å$	$c/Å$	$V/Å^3$
	15.40809(37)	15.45133(33)	18.40454(09)	4381.67

Table S-7: Unit cell parameters for single crystal samples of ZIF-4 in a DAC.

Evacuated ZIF-4	$a/Å$	$b/Å$	$c/Å$	$V/Å^3$
Large Molecule PTF	15.487(2)	15.505(2)	18.205(3)	4371.49
Evacuated ZIF-4	$a/Å$	$b/Å$	$c/Å$	$V/Å^3$
Small Molecule PTF	15.473(2)	15.499(4)	18.203(1)	4365.371

SI-3: Bulk Moduli Determination

Equations of state were fitted to P-V data using the EOS-FIT v5.2 program by Ross Angel, where a sufficient quantity of data points permitted.[16]
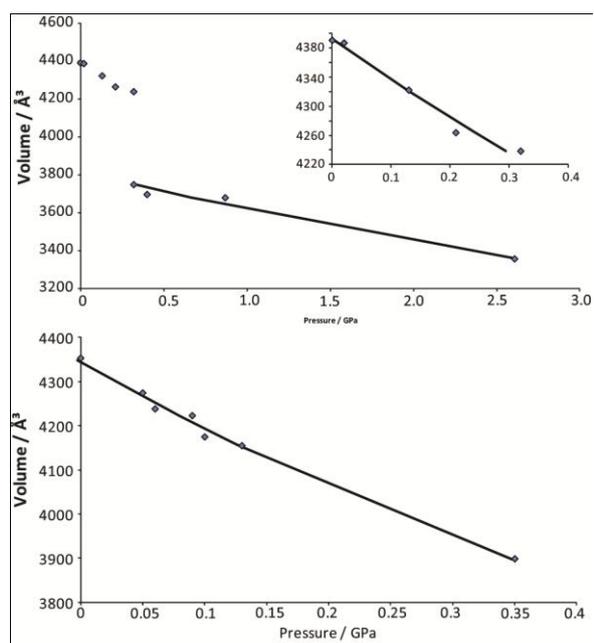

Figure S2: Pressure-dependant lattice volume of ZIF-4 and accompanying equation of state (using DO as a hydrostatic medium). (Top) ZIF-4 containing guest solvent molecules, measurement B (inset being an expansion of the low pressure range). (Bottom) An evacuated sample of ZIF-4, measurement D.

Table S8: Parameters from the second-order Birch Murnaghan equations of state.

	P-range (GPa)	Number of Data points used	V_0 /$Å^3$	K_0 / GPa	K'	Max ΔP	R_w / %
ZIF-4 WS in DO LP	0.00 – 0.32	5	4392.513	7.68(76)	4	0.032	10.53
ZIF-4 WS in DO HP	0.32 –2.61	4	3748.86	15.32(2.08)	4	0.21	9.85
ZIF-4 SF in DO LP	0.00 – 0.35	7	4348.148	2.56(10)	4	0.013	5.00
ZIF-4 WS in Meth:Eth HP [a]	0.56 – 3.2	4	3854.342	16.45(0.47)	4	0.044	1.56

[a] From single crystal experiment.

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