Supporting Information

Pressure-induced oversaturation and phase transition in zeolitic imidazolate frameworks with remarkable mechanical stability

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1. Synthesis and characterisation of ZIF-7

Synthesis: All chemicals employed were commercially available (Sigma-Aldrich and Acros Organics), with purity of 98 % or above, and were used as received. ZIF-7 sample was prepared following the procedure described in our previous work:¹ zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O, o.75 g, 2.52 mmol) and benzimidazole (HPhIm, o.25 g, 2.05 mmol) were first dissolved in fresh dimethylformamide (DMF, 75 ml). The resultant solution was then poured and sealed into a 100 ml teflon-lined Parr Bomb. The Parr Bomb was heated at 400 K for 48 hours. After naturally cooling to room temperature, white platy crystals were isolated after the mother liquor was removed. The average yield was around o.34 g, 97.15 % based on HPhIm.

Characterisation: The ZIF-7 crystal structure was confirmed by X-ray powder diffraction (XRPD) using Bruker D8 Advance X-ray diffractometer equipped with a Sol-X detector, parallel sollerslits, an incident beam monochromator with CuK α_1 radiation ($\lambda = 1.5406$ Å) and pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. The sample was prepared for analysis by gently grinding the product obtained in an agate mortar and then depositing on a flat-plate sample holder using ethanol. Diffraction data were collected at room temperature in the range of 6-45° (2 θ), in θ :2 θ mode and step-scan with $\Delta 2\theta = 0.02^{\circ}$, for 2 seconds per step. The XRPD pattern of ZIF-7 was compared with the simulated pattern from the model given by Yaghi *et al.*, 2006.²

Because $Zn(NO_3)_2 \bullet 6H_2O$ were excess in the synthesis recipe, zinc oxide (ZnO) impurity was found in the product, with an average weight percentage of probably less than 1% wt.



Figure SI 1. The simulated and experimental XRPD patterns of ZIF-7.

2. Production and characterisation of ZIF-7-II

Production: ZIF-7-II sample was produced by heating as-synthesised ZIF-7 at 400 K in air for 24 hours.

Characterisation: The ZIF-7-II crystal structure was confirmed using the previously-described XRPD instrument. The sample was prepared for analysis by gently grinding the product obtained in an agate mortar and then depositing on a flat-plate sample holder with high vacuum grease. Diffraction data were collected at room temperature in the range of 3-50° (2 θ), in θ :2 θ mode and step-scan with Δ 2 θ = 0.02°, for 2 seconds per step. The XRPD pattern collected was compared with the one we used for structure solution of ZIF-7-II in our previous work.¹



Figure SI 2. The experimental XRPD patterns of ZIF-7-II.

3. High-pressure x-ray powder diffraction on ZIF-7

High-pressure x-ray powder diffraction (HP-XRPD) experiment was conducted at the Materials Science powder diffraction station (Xo4SA), Swiss Light Source ($\lambda = 0.708498$ Å).³ Before data collection, the samples were gently ground in an agate mortar. A gas-membrane Boehler-type diamond anvil cell (DAC) equipped with 500 µm diamond culets and an opening angle of 80° was used to produce high pressures. For each data collection, the sample was loaded into a 50-75 µm hole of a 200-300 µm thick stainless steel gasket. Synthetic quartz was added into the samples as the internal pressure standard. After adding the pressure-transmitting fluid (DMF, 1:1 fluorinert FC770-FC75 or 4:1 methanol-ethanol) to the sample/quartz mixture in the gasket hole, the DAC was closed.

Data collection was performed using a 1D MYTHEN II micro-strip detector.⁴ To obtain better counting statistics, during data collection, the DAC was rotated by ±5°; the detector was moved in 8 positions as far apart as 1° to cover small gaps and bad channels within it, the 8 acquisitions were subsequently merged with a locally developed routine. The working photon wavelength was calibrated using a silicon standard (NIST 64oC). Data were collected using pressure step of 0.01 GPa in the range of 0 to 1 GPa; for high pressures above 1 GPa, the pressure step size varies from 0.1 to 1 GPa. After each high pressure experiment, the pressure was released from the DAC gradually. Data were collected at several pressure points and a diffraction pattern was recorded at ambient pressure. The raw data were processed and merged using inhouse software.

4. Pawley fitting⁵

In order to trace the unit cell behaviour of ZIF-7 under various pressures, Pawley fitting of the HP-XRPD data was carried out using Topas Academic 4.1.⁶ ZIF-7 unit cell given by Yaghi *et al.*, 2006² were converted from hexagonal to trigonal setting using the transformation matrix (2/3, 1/3, 2/3; 1/3, -1/3, 2/3; -1/3, -2/3, 2/3); the cell parameters obtained was used in triclinic setting as the starting point of the Pawley fitting of the first dataset in each experiment. The starting model of each following Pawley fitting was the calculated result from the previous dataset in the sequence.

Rietveld refinement of the quartz structure was incorporated to calculate the actual pressures in the gasket. The initial quartz structural model was obtained from the ICSD database. Considering the presence of ZnO impurity, only diffraction data in the 2θ range of $3-24^{\circ}$ were used for Pawley fitting and Rietveld refinement. ZnO peaks in this 2θ range were excluded. Background was reduced manually to minimise its influence and was described by a shifted Chebyschev function. The 2θ zero offset was calibrated and fixed for each experiment. Peak shape was modeled with pseudo-Voigt functions. Spherical harmonics were used for preferred orientation correction in the Rietveld refinement of the quartz structure. Pawley fitting and Rietveld refinement was carried out on each successive diffraction pattern until the ZIF-7 peaks had almost disappeared at which point Pawley fitting consistently diverged.

The actual pressures in the gasket were calculated according to the function:7

 $c/a = 1.10006 (4) + 0.00280 (3) p + 0.000022 (3) p^{2}$

where *a* and *c* is the cell parameters of quartz, *p* is in GPa.

5. Rietveld refinement of ZIF-7-IV structure⁸

The low-symmetry ZIF-7-IV structure was modelled by Rietveld refinement starting from the ZIF-7 rhombohedral structure using the data collected at p = 0.40 GPa in Experiment A. The refinement started from the previous result from Pawley fitting. Raw data in the 2θ range of $3-14^{\circ}$ (i.e. with a resolution of 2.9068) were used. Rietveld refinement of the quartz structure was incorporated. The background was described by a shifted Chebyschev function. Peak shape was modeled with a Pseudo-Voigt function. Spherical harmonics were used for preferred orientation correction. In ZIF-7-IV structure, benzimidazolate ligands were treated as rigid bodies using Cartesian coordinates to reduce the number of variables. Dummy atoms were added to define the origins of rigid bodies. Distance restraints were set between zinc and the coordinating nitrogen atoms. Angle, flatten and "Anti-bump" restraints were set between zinc and surrounding carbon and nitrogen atoms with reasonable weight factors. Single isotropic thermal factors

were set for the ligands and zinc element respectively. The DMF solvent molecule was defined as a rigid body described by Z-matrix with thermal parameters, occupancy of all atoms constrained.



Figure SI 3. The observed and calculated XRPD patterns of ZIF-7-IV, p = 0.40 GPa.

6. Bulk moduli calculation

The second-order Birch-Murnaghan equation of state:9

$$p(V) = \frac{3K_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (K_0' - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}$$

where *p* is the pressure of measurement, V_o is the initial volume, V is the volume of measurement, K_o is the bulk modulus, and K_o' is the derivative of the bulk modulus with respect to pressure, here $K_o' = 4$.

7. Results from high-pressure X-ray powder diffraction

a) Experiment A



Figure SI 4. The evolution of the unit cell volume of ZIF-7 (DMF) as a function of hydrostatic pressure between 0 and 1.01 GPa (using DMF as PTF).



Figure SI 5. Ferroelastic spontaneous strains in ZIF-7 as a function of hydrostatic pressure between 0 and 1.01 GPa (using DMF as PTF). b is the critical pressure of ZIF-7 to ZIF-7-IV phase transition. Angle strain = $(\alpha - \gamma)$; cell strain = 3(a-c)/(a+b+c).

b) Experiment B



Figure SI 6. The evolution of the unit cell volume of ZIF-7 (DMF) as functions of hydrostatic pressure between 0 and 1.5 GPa (using 1:1 fluorinert FC770:FC75 as PTF).



Figure SI 7. Ferroelastic spontaneous angle strain in ZIF-7 as a function of hydrostatic pressure between o and 0.24 GPa (using 1:1 fluorinert FC770:FC75 as PTF). b is the critical pressure of ZIF-7 to ZIF-7-IV phase transition.



Figure SI 8. Diffraction data of as-synthesised ZIF-7 in 1:1 fluorinert FC770:FC75. SiO₂ standard peak is indicated by *.



c) Experiment C

Figure SI 9. The evolution of the unit cell volume of ZIF-7 as a function of hydrostatic pressure between o and 4.28 GPa (using 4:1 methanol:ethanol as PTF).



Figure SI 10. Diffraction data of ZIF-7 in 4:1 methanol: ethanol. SiO₂ standard peak is indicated by *.

d) Experiment D



Figure SI 11. Diffraction data of ZIF-7-II in 1:1 fluorinert FC770:FC75. SiO₂ standard peak is indicated by *.

8. High-pressure single-crystal X-ray diffraction on ZIF-9

X-ray diffraction data sets were collected on a Bruker APEX II diffractometer with graphitemonochromated Mo K α radiation (λ = 0.71073 Å). Data were collected in ω -scans in twelve settings of 2 θ and ϕ with a frame and step size of 40 seconds and 0.3° respectively. The data were integrated using the program SAINT using "dynamic masks" to avoid integration of regions of the detector shaded by the body of the pressure cell.¹⁰ Absorption corrections for the DAC and sample were carried out with the programs SHADE¹¹ and SADABS¹² respectively.

Structural refinement was carried out against $|F|^2$ using the program CRYSTALS,¹³ starting from ambient temperature coordinates reported in the literature.² All 1,2 and 1,3 distances on the imidazolate ions were restrained to the values observed from our ambient pressure structure. Similarity restraints were applied to Co-N distances while all torsion angles were refined freely. H-atoms attached to carbon were placed geometrically and not refined. Thermal similarity restraints were applied to all non-hydrogen atoms.

The solvent content was calculated using the SQUEEZE algorithm within PLATON.¹⁴ The data are only 81% complete, which although is very good for pressure work, could still cause vast discrepancies in the output which is very sensitive to missing data (particularly strong low angle reflections).



Figure SI 12. (a) The unit cell of ZIF-9. CoN₄ tetrahedra: purple, C: black, N: dark blue, H atoms are omitted for clarity. (b) A crystal of ZIF-9 in a DAC surrounded by a methanol-based PTF.

Pressure	a (Å)	c (Å)	V (Å3)	Electron count	
(GPa)	u (A)	τ (Α)	V (^{N3})	Liection coont	
0	23.0110(8)	15.7647(7)	7229.2(5)	590	15 DMF
0.91	22.4424(18)	15.8063(19)	6894.4(11)		
1.78	21.926(3)	15.704(4)	6538(2)	624	15 DMF + 2 MeOH
2.74	21.607(3)	15.608(4)	6310(2)	585	15 DMF
3.54	21.363(5)	15.438(6)	6102(3)	555	14 DMF
4.14	21.0956	15.3536	5917.3		
4.67	21.0109	15.253	5831.4		
5.27	20.8532	15.1892	5720.2		

 Table SI 1. Crystallographic and pore data for ZIF-9 as a function of pressure.



Figure SI 13. The evolution of the unit cell volume of ZIF-9 as a function of hydrostatic pressure, completed with EoS fit.

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