

X-ray radiation-induced amorphization of metal-organic frameworks

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Supplementary information

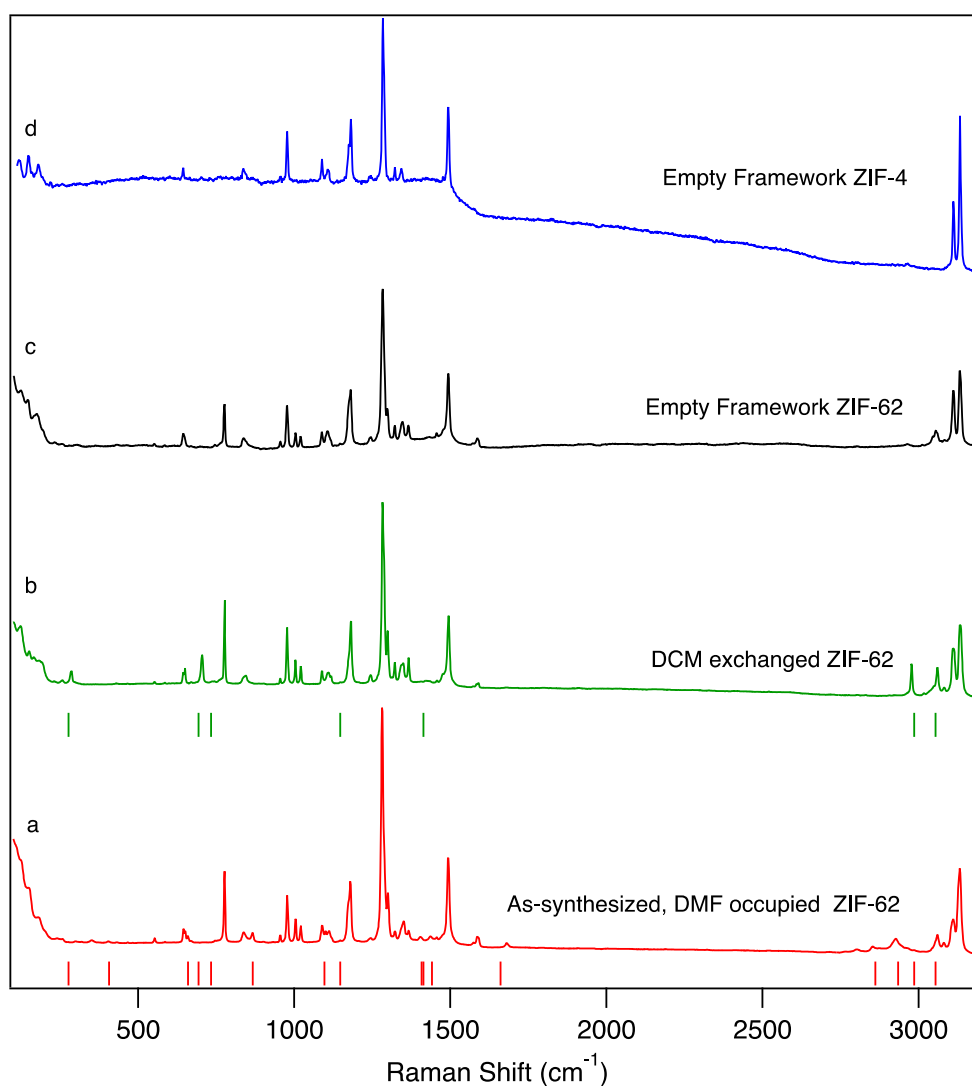
Synthesis

1.2 g $Zn(NO_3)_2 \cdot 6H_2O$ (4.03 mmol), and 0.9 g imidazole (13.2 mmol) (ZIF-4), and 1.515 g $Zn(NO_3)_2 \cdot 6H_2O$ (8 mmol), 7.35 g imidazole (108 mmol), and 1.418 g benzimidazole (12 mmol) (ZIF-62) were dissolved in 75 ml of dimethylformamide (DMF) and transferred into a 100 ml glass jar. The jars were sealed tightly and heated to 140 °C for 48 h in an oven. The precipitated crystalline ZIF powders were filtered off and soaked in dichloromethane for solvent exchange during 24 hours. Finally, the solvent exchanged powders were desolvated in a vacuum oven at 10^{-3} mbar and 150 °C. Raman spectra of the as-synthesized and solvent-exchanged, and desolvated phases are shown in

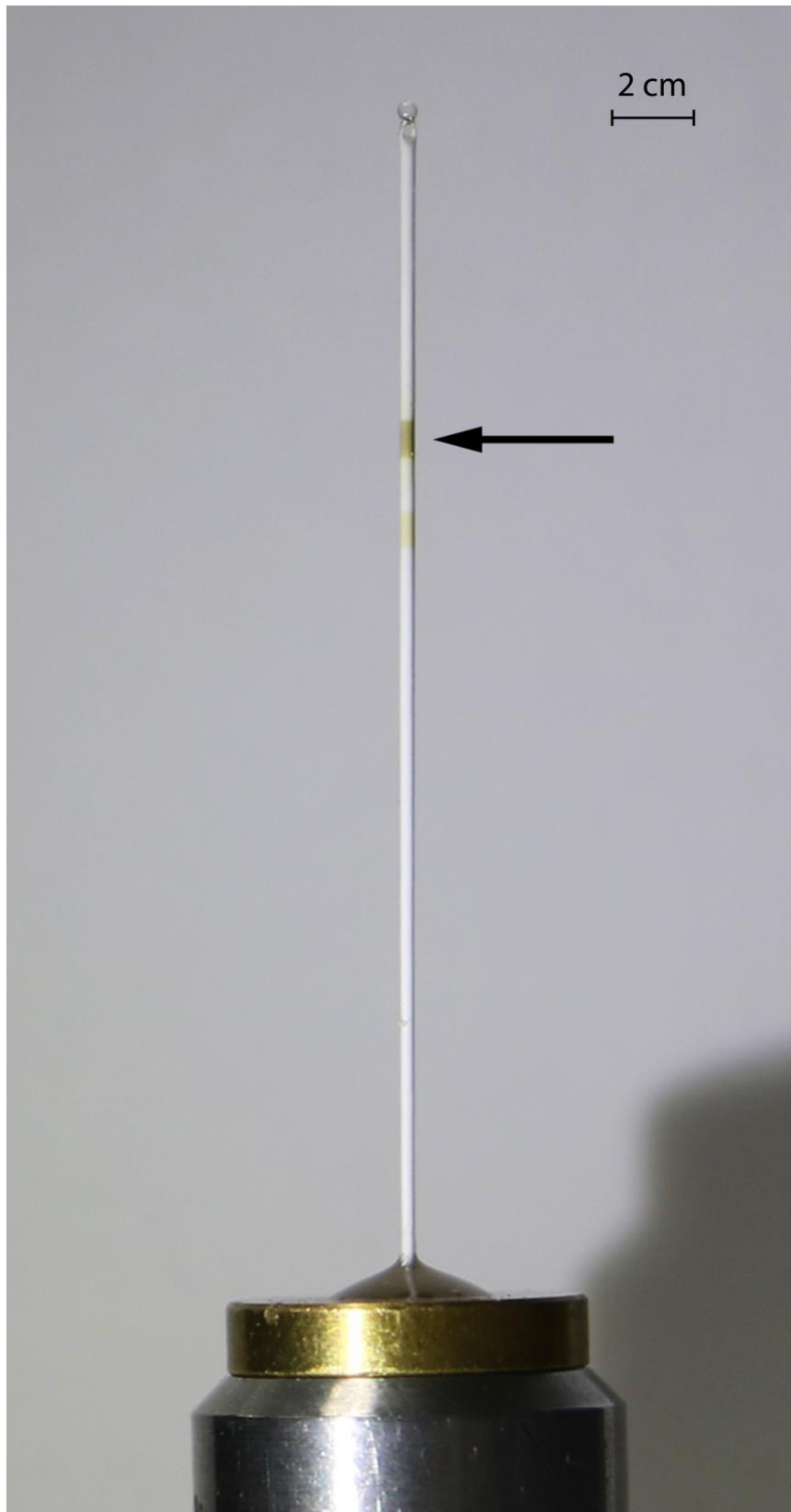
Supplementary Figure 1. The resulting compositions are $Zn(Im)_{1.8}(blm)_{0.2}$ for ZIF-62, and $Zn(Im)_2$ for ZIF-4 as determined by high-performance liquid chromatography (HPLC). **ZIF-zni** was recrystallized by heating a capillary loaded with ZIF-4 for 1 h to 400 °C in air.

Structural Refinements

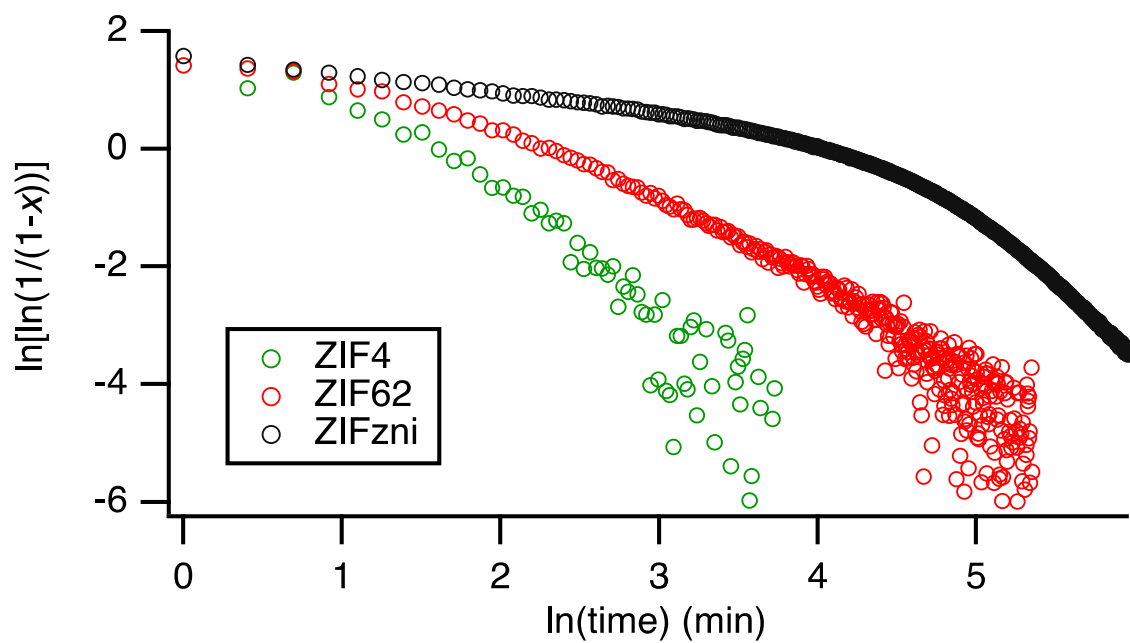
Sequential Rietveld refinements were performed using TOPAS-Academic Version 6. The instrumental contribution to peak shapes was determined separately using a NAC ($Na_2Al_2Ca_3F_{14}$) standard. Structural models of ZIF-4, ZIF-62 and ZIF-zni were taken from the CSD database. An initial refinement against the first measurement of each sequence was performed to refine an aberration correction stemming from the MYTHEN detector, and a spherical harmonic preferred-orientation correction to match observed peak intensities as close as possible. These parameters were from then on held fixed, and only a 5th order Chebyshev polynomial, the unit cell dimensions, and a Lorentzian contribution to strain-related peak broadening were refined over the 2θ -range from 3° to 9° for ZIF-4 and ZIF-62, and from 2° to 8° for ZIF-zni.



Supplementary Figure 1. Raman spectra of ZIF-62 at various stages of preparation. a) ZIF-62, as synthesised, DMF occupied. b) ZIF-62 after solvent exchange (DCM for DMF). c) desolvated ZIF-62, as used for XRD experiments. d) desolvated ZIF-4, as used for XRD experiments. Tick marks underneath a) and c) indicate reference positions of Raman modes of DCM and DMF, respectively.

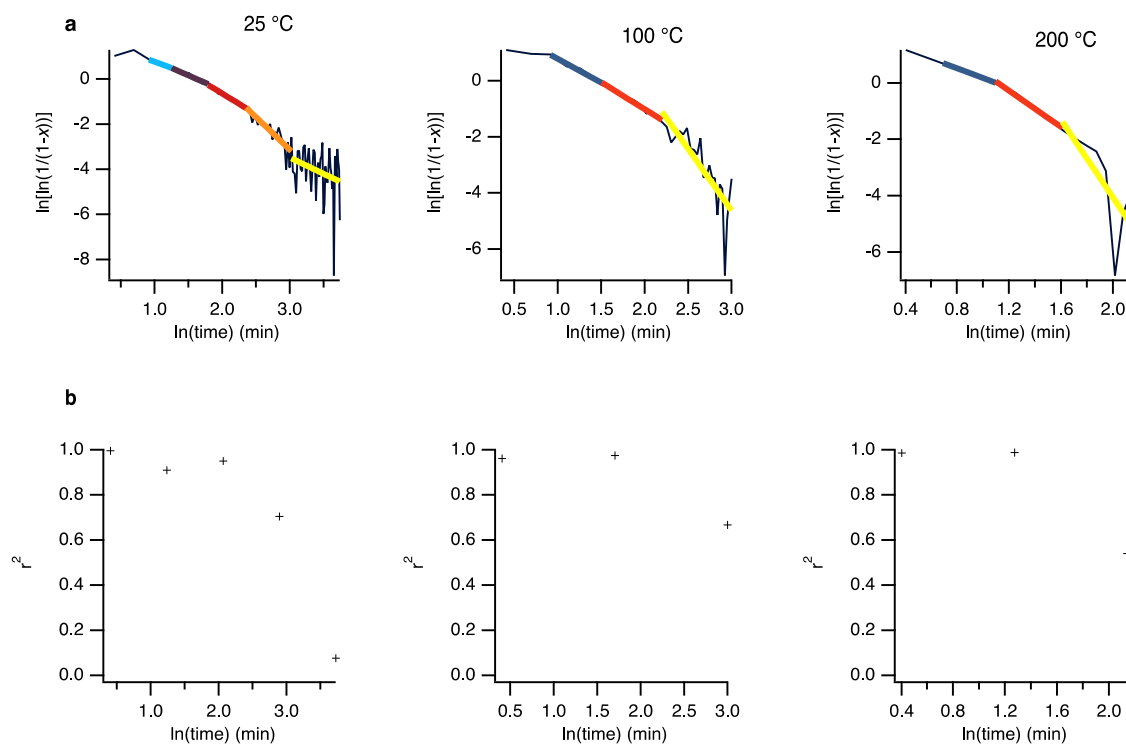


Supplementary Figure 2. Image of the capillary used for synchrotron experiments at the SLS MS-beamline. White material is pristine ZIF-4, while darkened section is where the beam hit the capillary and the X-ray induced amorphisation occurred.



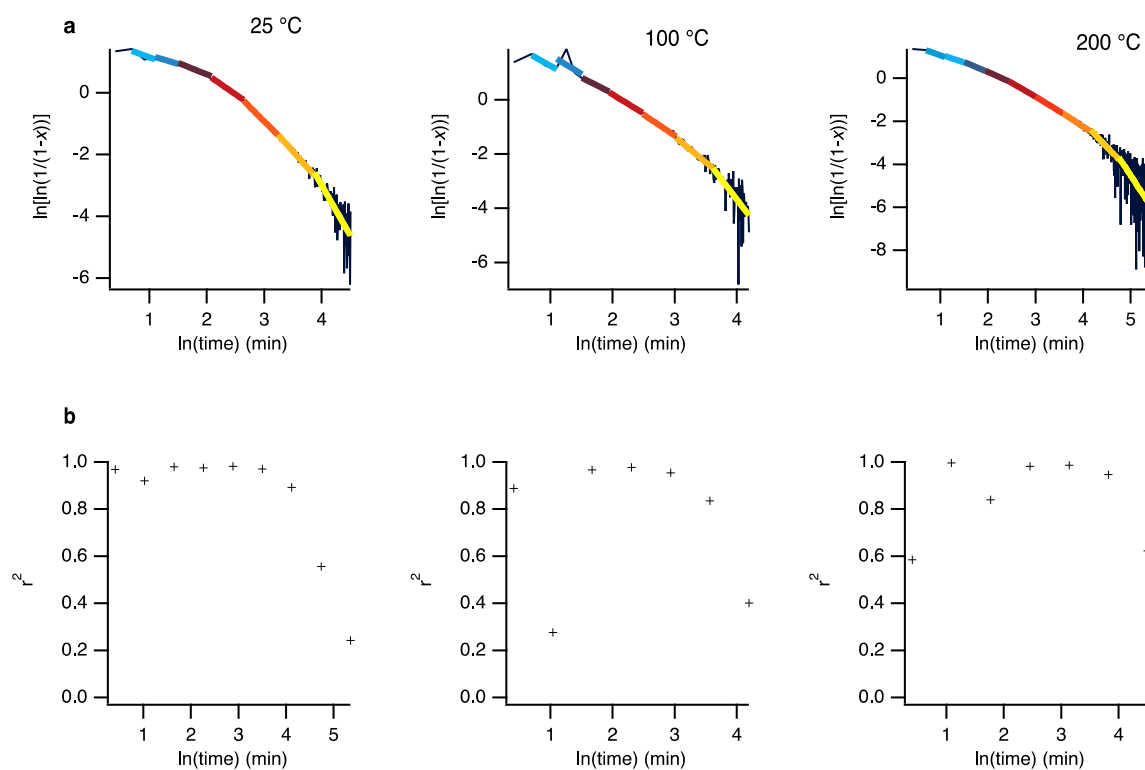
Supplementary Figure 3. Avrami plot of the amorphisation of ZIF-4, ZIF-62, and ZIF-zni.

ZIF-4

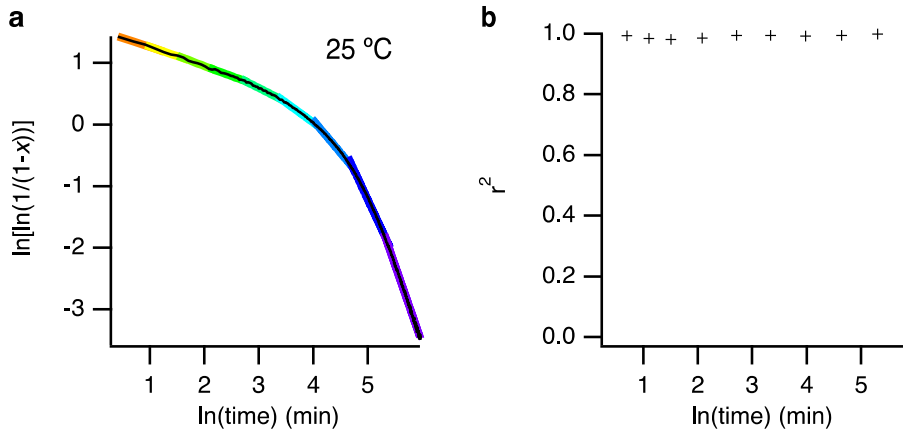


Supplementary Figure 4. a) Avrami plots of the amorphisation process of ZIF-4 at various temperatures and linear fits to segments in colour b) r^2 values of linear fit.

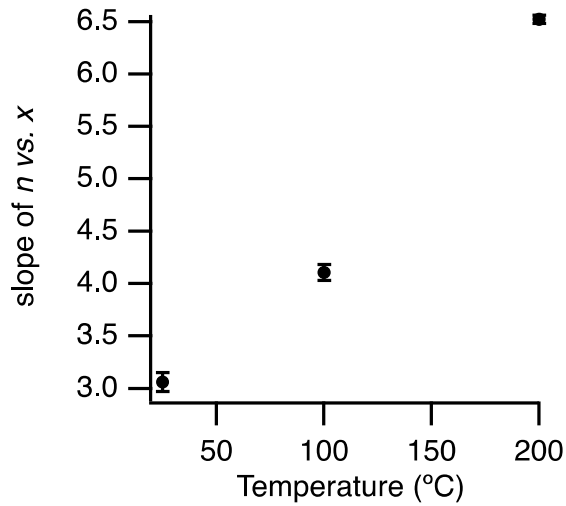
ZIF-62



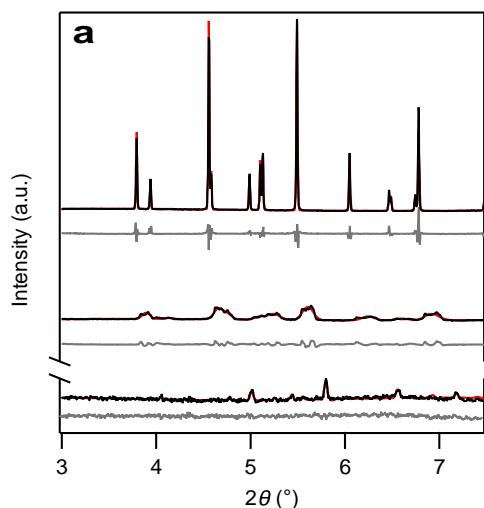
Supplementary Figure 5. a) Avrami plots of the amorphisation process of ZIF-62 at various temperatures and linear fits to segments in colour b) r^2 values of linear fits.



Supplementary Figure 6. a) Avrami plots of the amorphisation process of ZIF-zni at ambient temperature and linear fits to segments in colour b) r^2 values of linear fits.

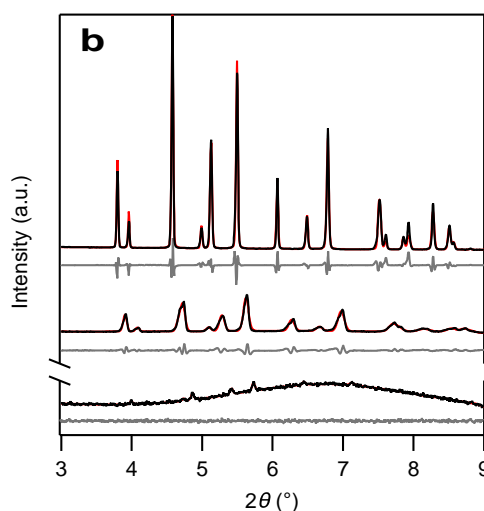


Supplementary Figure 7. Slopes of plots of the Avrami exponent n versus transformed fraction x , as a function of temperature in ZIF-4.



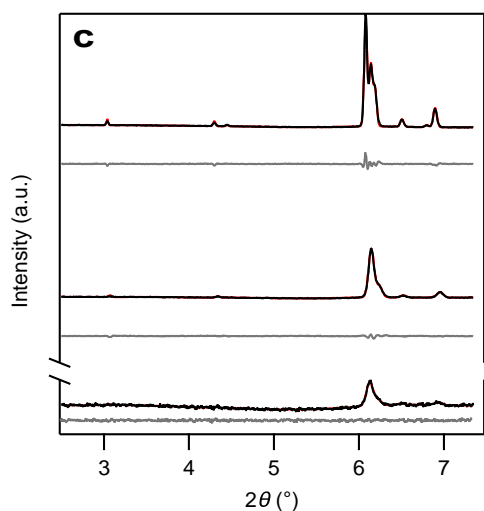
ZIF-62

<i>a</i>	e.s.d.	<i>b</i>	e.s.d.	<i>c</i>	e.s.d.	Volume	e.s.d.
15.6910	0.0009	15.7316	0.0007	18.1942	0.0010	4491.14	0.40
15.1579	0.0036	15.4431	0.0020	17.6441	0.0041	4130.23	1.46
14.7826	0.0069	15.2132	0.0043	17.1176	0.0072	3849.57	2.66



ZIF-4

<i>a</i>	e.s.d.	<i>b</i>	e.s.d.	<i>c</i>	e.s.d.	Volume	e.s.d.
15.3900	0.0019	15.4050	0.0021	17.9124	0.0009	4246.73	0.80
14.7297	0.0048	14.9529	0.0039	16.6747	0.0058	3672.65	1.99
14.4571	0.0048	14.7666	0.0024	16.1235	0.0046	3442.06	1.60



ZIF-zni

<i>a</i>	e.s.d.	<i>c</i>	e.s.d.	Volume	e.s.d.
23.6528	0.0003	12.4986	0.0002	6992.41	0.08
23.4001	0.0018	12.5021	0.0017	6845.70	0.52
23.4710	0.0220	12.5677	0.0233	6923.40	6.73

Supplementary Figure 8. Representative Rietveld fits and unit cell dimensions of progressively amorphised ZIF-62 (a), ZIF-4 (b), and ZIF-zni (c). For each phase, the observed (black), calculated (red), and difference (grey) patterns are given for the initial measurement (top), the measurement at 50 % remaining crystallinity (centre), and the close-to-final measurement (bottom), respectively. The resulting unit cell dimensions are given on the right in the same order, including the estimated standard deviations (e.s.d.'s). All measurements were performed at ambient temperature.