# **Supplementary Information**

## Glassy behaviour of mechanically amorphised ZIF-62 isomorphs

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#### **Experimental Procedures**

**Materials.** Imidazole (99.5%), 5-chlorobenzimidazole (98%), ZnO (< 100 nm), dimethyl sulfoxide (DMSO)-d6 (99.9 atom % D, contains 1% (v/v) tetramethylsilane (TMS)) and D<sub>2</sub>O (35% DCl) were purchased from Sigma Aldrich. Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (98%) and benzimidazole (99%) were purchased from Fisher Scientific. *N*,*N*-dimethylformamide DMF (99.8%) and dichloromethane (DCM) (99.9% stabilised with amylene) were purchased from Acros Organics. All materials were used without further purification.

**Synthesis Conditions.** Mechanosynthetic reactions were performed in a Retsch MM400 vibratory ball mill, using a 10 ml stainless steel jar and 2 x 10 mm diameter stainless steel grinding media (spherical, 4.03 g each). All metal salts and organic compounds were added (Table S1), along with 50  $\mu$ L of DMF. These reactions were run for 30 minutes at 30 Hz unless stated otherwise. Post synthesis, samples were washed with DMF (3 x 10 ml) and DCM (10 ml). Then, solvent exchange was performed by submerging ZIF samples in DCM (10 ml) for 24 hours. After vacuum filtration, samples were evacuated for 5 hours at 180 °C under dynamic vacuum.

*Ex situ* Kinetics Study. The mechanosynthetic reaction for  $a_m$ ZIFs as described above was performed using various intervals of time to produce materials for the *ex situ* kinetics study. To take each measurement in the kinetics study, an entire fresh mechanosynthetic reaction was run for a given time interval. After the given time interval, all powder was extracted from the ball mill jar and was washed with DMF (3 x 10 ml) and DCM (10 ml) to stop any further reaction. Powder X-ray diffraction (PXRD) was then performed on the washed material.

**Powder X-ray Diffraction.** PXRD of crystalline and glass samples was performed on a Bruker D8 Advanced diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å), between 5-40 20° at room temperature.

Crystalline material PXRD patterns were analysed by Pawley refinements using TOPAS academic (V.6) software.<sup>2</sup> Thompson-Cox-Hastings pseudo-Voigt peaks shapes were used along with a simple axial divergence correction. The lattice parameters, namely *a*,*b*, and *c* were refined against the values obtained from the CIF in the 2 $\theta$  range of 5–40°. The zero-point error was also refined.

**Nuclear Magnetic Resonance Spectroscopy.** Hydrogen nuclear magnetic resonance (<sup>1</sup>H NMR) samples were prepared by digesting the ZIF (5-10 mg) in a solution of DMSO-d<sub>6</sub> (1.0 ml, 0.03% TMS), D<sub>2</sub>O (0.2 ml, 35% DCl). Glass samples required sonication for 5 minutes to allow for complete dissolution. Samples were measured in a Bruker Advance III HD 500 MHz spectrometer. Spectra were calibrated using TMS as a standard. The data were processed using TopSpin V 4.0.7.<sup>3</sup>

**Differential Scanning Calorimetry.** Differential scanning calorimetry (DSC) measurements were conducted on a NETSCH DSC 214 Polyma instrument. ~5-10 mg of activated sample was loaded into an aluminium crucible (30  $\mu$ L), with a pierced lid. An empty aluminium crucible was used as a reference. Under argon gas, the sample was heated to an initial temperature of 40 °C. Then the sample was heated to 450 °C at a rate of 10 °C min<sup>-1</sup>. This was followed by cooling back to 40 °C at 10 °C min<sup>-1</sup>. A second up scan to 450 °C at 10 °C min<sup>-1</sup> was then performed.

Further DSC experiments on  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$ , specifically 5 heating and cooling cycles from 30 °C to 450 °C back to 30 °C at a rate of 10 °C min<sup>-1</sup> were performed under an argon atmosphere.

Additionally heating and cooling cycles to various different maximum temperatures: 350 °C, 375 °C, 400 °C, 425 °C, 450 °C and 475 °C were performed on separate  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  samples, at a rate of 10 °C min<sup>-1</sup> were performed under an argon atmosphere.

**Thermogravimetric Analysis.** Thermogravimetric analysis (TGA) was conducted on a TA instruments SDT-Q600, under an argon atmosphere using a heating rate of 10 °C min<sup>-1</sup>. Between 10-15 mg of evacuated sample were used for each run.

Samples used for DMF content determination were heated at a heating rate of 20 °C min<sup>-1</sup> up to 400 °C after a 20minute equilibration time at 30 °C. Between 10-15 mg of unevacuated sample were used for each run.

**DMF Content Determination.** For determination of the DMF content in variable linker ZIF-62 samples, mechanosynthetic reactions as per previous reports were conducted.<sup>1</sup> After synthesis, the materials were washed

with DMF (3 x 10 ml) and DCM (10 ml) then dried at 60  $^{\circ}$ C for 1 hour to remove residual DCM on the surface of particles while leaving DMF in the pores of the materials.

**Thermomechanical Analysis.** Thermomechanical analysis (TMA) was performed using a TA instruments TMA Q400. Firstly, a glassy sample (10 mg) was pressed into a 5 mm diameter circular pellet, by applying 2 tonnes of pressure for 1 minute. This pellet was the transferred to the TMA instrument. TMA was conducted on the glassy pellet using a static force measurement of 10 mN. A heating rate of 10 °C min<sup>-1</sup> was used from 40 °C to 400 °C after an initial equilibration at 40 °C for 20 minutes.

**He Pycnometry.** He pycnometric measurements were performed on a Micromeritics AccuPyc 1340 with a 1 cm<sup>3</sup> insert. Between 100-200 mg of sample was used per measurement, and 10 volume measurements were performed per sample. All samples were evacuated at 180 °C under dynamic vacuum for 5 hours prior to measurement.

**CO<sub>2</sub> Gas Sorption.** Porosity measurements were performed on a Micromeritics ASAP 2020 surface area and porosity analyser. Samples of ca. 100 mg were degassed by heating under vacuum at 100 °C for 12 hours, prior to analysis using carbon dioxide gas at 273 K. Maximum gas uptake, pore volume and pore size were determined using the Micromeritics MicroActive software. Pore widths were calculated using DFT with a slit geometry and the CO<sub>2</sub> @ 273-Carbpm, NLDFT model. Pore volumes were determined using the Horvath-Kawazoe model.

**Scanning Electron Microscopy.** Scanning electron microscopy (SEM) images were collected with a high-resolution scanning electron microscope (FEI Nova Nano SEM 450, accelerating voltage 15 kV). All samples were prepared by dispersing the material onto a double sided adhesive conductive carbon tape that was attached to a flat aluminium sample holder and were coated with a platinum layer of 15 nm.

**Total Scattering.** X-ray total scattering data were collected at Diamond Light Source UK, beamline 115-1, on beamtimes EE20038-9 and EE20038-10. Samples were ground into a fine powder and placed into borosilicate capillaries with 0.150 cm outer (0.117 cm<sup>2</sup> inner) radii. Data scans were 10 minutes in length. Empty capillary and background total scattering data were corrected for in data processing. Sample data were processed to a  $Q_{max}$  of 19 Å<sup>-1</sup> ( $\lambda$  = 0.161669 Å, 76.69 keV). Data were processed using GudrunX to obtain the D(r) by applying a Fourier transform to the total scattering data.

**Variable Temperature Total Scattering.** X-ray total scattering performed at variable temperature was conducted as above, at temperatures up to 400 °C with a heating rate of 10 °C min<sup>-1</sup> with scan times of 10 minutes. A TGA scan was performed with the same heating schedule as the VT total scattering experiments to ensure no major mass loss during the heat treatment.

**PDFgui.** PDF refinements were conducted using PDFgui.<sup>4</sup> Prior to refining data, modifications to a literature CIF were conducted, namely the removal of solvent molecules and H atoms to improve the refinement. These are valid modifications as the  $[Zn(Im)_{1.65}(bIm)_{0.35}]$  formulation has been evacuated to remove solvent, and H atoms weakly scatter X-rays, therefore contribute little to the D(r). Further modifications to the CIF include eliminating the variable occupancy of the bIm linker and fixing the asymmetric unit to be  $[Zn_2(Im)_3(bIm)_1]$ . This was done to eliminate the issue of variable occupancy in the CIF, and to simplify the study of the local Zn-Im<sub>3</sub>bIm<sub>1</sub> unit. From this calculated D(r), a refinement can be performed against experimental data for crystalline  $[Zn(Im)_{1.65}(bIm)_{0.35}]$  after 15 minutes of grinding. This was done by refining the phase scale factor, unit cell parameters, thermal parameters of each element, and the low r peak sharpening parameter.

Sample	ZnO (< 100 nm)	$Zn(OAc)_2.2H_2O$	ImH	blmH	5-ClbImH
[Zn(Im) <sub>1.70</sub> (bIm) <sub>0.30</sub> ]	80.2 mg	2.2 mg	115.6 mg	35.4 mg	-
	(0.99 mmol)	(0.01 mmol)	(1.70 mmol)	(0.30 mmol)	
a <sub>m</sub> [Zn(Im) <sub>1.65</sub> (bIm) <sub>0.35</sub> ]	80.2 mg	2.2 mg	112.2 mg	41.3 mg	-
	(0.99 mmol)	(0.01 mmol)	(1.65 mmol)	(0.35 mmol)	
a <sub>m</sub> [Zn(Im) <sub>1.50</sub> (bIm) <sub>0.50</sub> ]	80.2 mg	2.2 mg	102.2 mg	59.0 mg	-
	(0.99 mmol)	(0.01 mmol)	(1.50 mmol)	(0.5 mmol)	
a <sub>m</sub> [Zn(Im) <sub>1.0</sub> (bIm) <sub>1.0</sub> ]	80.2 mg	2.2 mg	68 mg	118 mg	-
	(0.99 mmol)	(0.01 mmol)	(1.00 mmol)	(1.00 mmol)	
a <sub>m</sub> [Zn(Im) <sub>1.70</sub> (ClbIm) <sub>0.30</sub> ]	80.2 mg	2.2 mg	115.6 mg	-	45.9 mg
	(0.99 mmol)	(0.01 mmol)	(1.70 mmol)		(0.30 mmol)
a <sub>m</sub> [Zn(Im) <sub>1.65</sub> (ClbIm) <sub>0.35</sub> ]	80.2 mg	2.2 mg	112.2 mg	-	53.6 mg
	(0.99 mmol)	(0.01 mmol)	(1.65 mmol)		(0.35 mmol)

Table S1: Reagents used to synthesise various ZIFs mechanosynthetically.

### **Supplementary Data**



Fig. S1: Top, <sup>1</sup>H nuclear magnetic resonance spectra of  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$ .  $\delta$ H (500 MHz; DCI (35%)/D<sub>2</sub>O:DMSO-d<sub>6</sub> (1:5); Me<sub>4</sub>Si) 9.64 (1H, s, H<sub>a</sub>), 9.10 (1H, s, H<sub>b</sub>), 7.65 (DCI/D<sub>2</sub>O), 2.69 (DMSO), 0.00 (TMS). Bottom, portion of the spectra in which Im and bIm linker ratios are determined.



Fig. S2: TGA upscan of  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  to 700 °C at 10 °C min<sup>-1</sup> performed under an argon atmosphere, showing an initial mass loss between 450 °C and 600 °C, with major onset of decompositions at 600 °C. TGA trace (black), and derivative of weight loss with respect to temperature (blue).



Fig. S3: (a) DSC upscan of unevacuated  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  showing surface solvent loss, and solvent loss from pores. (b) DSC trace of evacuated  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  at 10 °C min<sup>-1</sup> performed under an argon atmosphere. DSC heat flow trace in blue, and temperature shown by a red dashed line.



Fig. S4: TMA scan of  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$ , showing a softening of the glassy material. Dimension change in black, and coefficient of thermal expansion in blue.



Fig. S5: Optical image of  $a_g[Zn(Im)_{1.65}(bIm)_{0.35}]$ , showing evidence of flow above  $T_{g1}$  as well as thermal stress-induced striations.



Fig. S6: TGA upscan of  $[Zn(Im)_{1.70}(bIm)_{0.30}]$  to 700 °C at 10 °C min<sup>-1</sup> performed under an argon atmosphere. TGA trace (black), and derivative of weight loss with respect to temperature (blue).





Fig. S7: Top, <sup>1</sup>H nuclear magnetic resonance spectra of  $[Zn(Im)_{1.70}(bIm)_{0.30}]$ .  $\delta$ H (500 MHz; DCl (35%)/D<sub>2</sub>O:DMSO-d<sub>6</sub> (1:5); Me<sub>4</sub>Si) 9.64 (1H, s, H<sub>a</sub>), 9.03 (1H, s, H<sub>b</sub>), 7.65 (DCl/D<sub>2</sub>O), 2.75 (DMSO), 0.00 (TMS). Bottom, portion of the spectra in which Im and bIm linker ratios are determined.



Fig. S8: PXRD of  $a_g[Zn(Im)_{1.70}(bIm)_{0.30}]$  after melt-quenching the crystalline phase, crystalline [Zn(Im)\_{1.70}(bIm)\_{0.30}] after 30 minutes of mechanosynthesis, ZnO and simulated ZIF-62.



Fig. S9: Full DSC trace of  $[Zn(Im)_{1.70}(bIm)_{0.30}]$  at 10 °C min<sup>-1</sup> performed under an argon atmosphere, showing a  $T_m$ , an event which is not present in the  $a_m$ ZIF samples, and upon second heating a  $T_g$ . DSC heat flow trace in blue, and temperature shown in red dotted lines.

R <sub>wp</sub> (%)	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62 <sup>5</sup>
7.256	Pbca	a = 15.7313(16) Å	a = 15.346313 Å
		b = 16.1793(19) Å	<i>b</i> = 15.787006 Å
		<i>c</i> = 18.0589(19) Å	<i>c</i> = 18.162491 Å
		$\alpha = 90$ °	$\alpha = 90$ °
		$\beta = 90$ °	$\beta = 90$ °
		$\gamma = 90$ °	$\gamma = 90$ °

Table S2: Pawley refinement details of crystalline [Zn(Im)<sub>1.70</sub>(bIm)<sub>0.35</sub>] after 30 minutes of mechanosynthesis.



Fig. S10: Pawley refinement of  $[Zn(Im)_{1.70}(bIm)_{0.30}]$  after 30 minutes of mechanosynthesis.



Fig. S11: Left: volume of  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  measured over 10 cycles using He pycnometry, where the sample mass was 0.1856 g. Right: volume of  $a_g[Zn(Im)_{1.65}(bIm)_{0.35}]$  measured over 10 cycles using He pycnometry, where the sample mass was 0.1060 g.



Fig. S12: Left:  $CO_2$  adsorption isotherms for  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$ . Right:  $CO_2$  adsorption isotherm for  $a_g[Zn(Im)_{1.65}(bIm)_{0.35}]$  showing an almost identical response.



Fig. S13: Scanning electron micrographs of: (a)  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  showing nanometre particle size and (b)  $a_g[Zn(Im)_{1.65}(bIm)_{0.35}]$  showing clear evidence particle agglomeration to far above 10 µm particle size, and flow between particles.



Figure S14: 5 DSC heating cycles on  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$ , performed under an argon atmosphere to 450 °C at 10 °C min<sup>-1</sup>. Showing a change in  $T_g$  upon a first and second heating scan, with no subsequent changes in  $T_g$  upon multiple heating scans.



Figure S15: DSC heating upscan 2 of  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  after an initial heat treatment of various maximum temperatures. Specifically: 350 °C, 375 °C, 400 °C, 425 °C, 450 °C and 475 °C. Showing the increase in  $T_{g2}$  after heating to various maximum temperatures in upscan 1.

These DSC experiments show that  $T_{g2}$  is only dependent on maximum temperature on upscan 1. Here, heating scans with lower maximum temperatures (such as 350 °C) result in minimal particle agglomeration and liquidous flow, and therefore smaller T<sub>g</sub> changes. Increasing the maximum scan temperatures, causes a greater extent of particle agglomeration, and hence a higher T<sub>g2</sub>.



Fig. S16: Extended linker ratio series showing production of amorphous materials with formulations  $[Zn(Im)_{1.5}(bIm)_{0.5}]$  and  $[Zn(Im)_{1.0}(bIm)_{1.0}]$ . The sample of  $[Zn(Im)_{1.0}(bIm)_{1.0}]$  contains trace ZnO marked with asterisks. Attempts to produce higher blm content materials yielded incomplete reactions, with substantial amounts of ZnO present. Also, Bragg reflections assigned to ZIF-7 [Zn(bIm)\_2] were observed. Simulated ZIF-7 pattern was obtained from a literature CIF.<sup>6</sup>



Fig. S17: Top, <sup>1</sup>H nuclear magnetic resonance spectra of  $a_m[Zn(Im)_{1.50} (bIm)_{0.50}]$ .  $\delta H$  (500 MHz; DCI (35%)/D<sub>2</sub>O:DMSO-d<sub>6</sub> (1:5); Me<sub>4</sub>Si) 9.57 (1H, s, H<sub>a</sub>), 9.03 (1H, s, H<sub>b</sub>), 7.67 (DCI/D<sub>2</sub>O), 2.74 (DMSO), 0.00 (TMS). Bottom, portion of the spectra in which Im and bIm linker ratios are determined.



Fig. S18: Top, <sup>1</sup>H nuclear magnetic resonance spectra of  $a_m[Zn(Im)_{1.0} (bIm)_{1.0}]$ .  $\delta H$  (500 MHz; DCl (35%)/D<sub>2</sub>O:DMSO-d6 (1:5); Me<sub>4</sub>Si) 9.57 (1H, s, Ha), 9.04 (1H, s, Hb), 7.65 (DCl/D<sub>2</sub>O), 2.75 (DMSO), 0.00 (TMS). Bottom, portion of the spectra in which Im and bIm linker ratios are determined.



Fig. S19: TGA of  $a_m[Zn(Im)_{1.5}(bIm)_{0.5}]$  performed under an argon atmosphere at 10 °C min<sup>-1</sup>. TGA trace (black), and derivative of weight loss with respect to temperature (blue).



Fig. S20: TGA of  $a_m[Zn(Im)_{1.0}(bIm)_{1.0}]$  performed under an argon atmosphere at 10 °C min<sup>-1</sup>. TGA trace (black), and derivative of weight loss with respect to temperature (blue).



Fig. S21: DSC of a<sub>m</sub>[Zn(Im)<sub>1.5</sub>(bIm)<sub>0.5</sub>] performed under an argon atmosphere with a heating/cooling rate of 10 °C min<sup>-1</sup>.



Fig. S22: DSC of a<sub>m</sub>[Zn(Im)<sub>1.0</sub>(bIm)<sub>1.0</sub>] performed under an argon atmosphere with a heating/cooling rate of 10 °C min<sup>-1</sup>.



Fig. S23: TMA scan of  $a_m[Zn(Im)_{1.5}(bIm)_{0.5}]$ , showing a softening of the glassy material at 349.6 °C. Dimension change in black, and coefficient of thermal expansion in blue.



Fig. S24: TMA scan of  $a_m[Zn(Im)_{1.0}(bIm)_{1.0}]$ , showing a softening of the glassy material at 370.4 °C. Dimension change in black, and coefficient of thermal expansion in blue.



Fig. S25: *Ex situ* kinetics study of  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  mechanosynthesis, showing production of crystalline ZIF-62 after 1 minute, with full conversion from ZnO after 5 minutes. After 20 minutes the peak intensity reduced, followed by complete amorphisation after 22 minutes. Amorphous patterns have been scaled to emphasise diffuse scattering.

R <sub>wp</sub> (%)	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62 <sup>5</sup>
6.797	Pbca	<i>a</i> = 15.5640(17) Å	<i>a</i> = 15.6620(14) Å
		<i>b</i> = 15.8058(19) Å	<i>b</i> = 15.6621(13) Å
		<i>c</i> = 18.257(2) Å	<i>c</i> = 18.2073(19) Å
		<i>α</i> = 90 °	<i>α</i> = 90 °
		<i>θ</i> = 90 °	<i>b</i> = 90 °
		γ = 90 °	γ = 90 °

Table S3: Pawley refinement details of crystalline  $[Zn(Im)_{1.65}(bIm)_{0.35}]$  after 15 minutes of grinding.



Fig. S26: Pawley refinement of  $[Zn(Im)_{1.65}(bIm)_{0.35}]$ , after 15 minutes of mechanosynthesis.



Fig. S27:  $Zn_4$  and  $Zn_8$  rings in crystalline ZIF-62 showing pore occupancy by blm rings pointing into a  $Zn_8$  ring and away from a  $Zn_4$  ring. Red regions are occluded space where a DMF molecule could occupy. Reproduced from a literature CIF.<sup>1</sup>



Fig. S28: TGA of solvated crystalline ZIF-62 with the formulation formula  $[Zn(Im)_{1.65}(bIm)_{0.35}]$  (after 15 minutes of mechanosynthesis), and  $[Zn(Im)_{1.75}(bIm)_{0.25}]$ . Showing an increase in the DMF solvent content in formulation of ZIF-62 with less bIm. Scans were conducted at 20 °C min<sup>-1</sup> under an argon atmosphere. From this the DMF lost per mol of Zn can be calculated.  $[Zn(Im)_{1.65}(bIm)_{0.35}]$  lost 19.74 g mol<sup>-1</sup>, and  $[Zn(Im)_{1.75}(bIm)_{0.25}]$  lost 26.51 g mol<sup>-1</sup>.



Fig. S29: Full DSC trace of crystalline [Zn(Im)<sub>1.65</sub>(bIm)<sub>0.35</sub>] at 10 °C min<sup>-1</sup> performed under an argon atmosphere, showing a  $T_m$ , an event which is not present in the  $a_m$ ZIF samples, and upon second heating a  $T_g$ . DSC heat flow trace in blue, and temperature shown in red dotted lines.



Fig. S30: S(Q) for ZIF-62, [Zn(Im)<sub>1.65</sub>(bIm)<sub>0.35</sub>], after 15 minutes of mechanosynthesis with a  $Q_{max}$  = 19 Å <sup>-1</sup>.



Fig. S31: D(r) for ZIF-62,  $[Zn(Im)_{1.65}(bIm)_{0.35}]$  after 15 minutes of mechanosynthesis, correlations between 1 and 7 Å correspond to the local structure of the Zn-Im-Zn secondary building unit, whilst correlations beyond 7 Å correspond to long range order associated with the crystalline structure as expected.



Fig. S32: TGA scan of  $a_m[Zn(Im)_{1.65}(bIm)_{0.35}]$  using the heating profile used during VT PDF, indicating negligible, ~1%, mass loss by the end of the heating scan.



Fig. S33: VT PDF S(Q) data for  $a_m$  [Zn(Im)<sub>1.65</sub>(bIm)<sub>0.35</sub>], from room temperature, up to the liquid state at 400 °C, then back to room temperature. Data were processed up to a  $Q_{max}$  of 22 Å<sup>-1</sup>, and show no sharp features at low Q indicating the retention of the amorphous state throughout the heating scan. Primed temperatures are scans conducted on the cooling scan.



Fig. S34: Zn coordination environment of ZIF-62, highlighting the modifications applied to a literature CIF in order to calculate D(r) and partial PDFs.<sup>1</sup> Zn tetrahedra in purple, nitrogen in blue and carbon in black. Structure refinement against experimental data for D(r) of ZIF-62 crystalline,  $[Zn(Im)_{1.65}(bIm)_{0.35}]$  after 15 minutes of mechanosynthesis.  $\chi^2$ : 68.9736 red.  $\chi^2$ : 0.171576 R<sub>w</sub>: 0.325875. Blue = experimental data, red = calculated and green = difference plot.



Fig. S35: Unit cell, viewed down the *a* axis, of crystalline ZIF-62 after refinement against PDF data. Zn tetrahedra in grey, nitrogen in blue and carbon in black.



Fig. S36:  $g_{ij}(r)$  of ZIF-62 showing individual correlations which contribute to the overall D(r). These  $g_{ij}(r)$  were calculated from the refinement above, and therefore their peak intensties are weighted to reflect their contributions to the overall G(r).



Fig. S37: PXRD of as synthesised a<sub>m</sub>ZIF-UC-5 materials with different linker ratios, experimental ZnO pattern, and simulated crystalline ZIF-UC-5 for reference.<sup>7</sup>



Fig. S38: Top, <sup>1</sup>H nuclear magnetic resonance spectra of  $a_m[Zn(Im)_{1.65}(ClbIm)_{0.35}]$ .  $\delta$ H (500 MHz; DCl (35%)/D<sub>2</sub>O:DMSO-d<sub>6</sub> (1:5); Me<sub>4</sub>Si) 9.68 (1H, s, H<sub>a</sub>), 9.10 (1H, s, H<sub>b</sub>), 7.77 (DCl/D<sub>2</sub>O), 2.68 (DMSO), 0.00 (TMS). Bottom, highlighted portion of the spectra in which Im and ClbIm linker ratios are determined.



Fig. S39: Top, <sup>1</sup>H nuclear magnetic resonance spectra of  $a_m[Zn(Im)_{1.70}(ClbIm)_{0.30}]$ .  $\delta$ H (500 MHz; DCI (35%)/D<sub>2</sub>O:DMSO-d<sub>6</sub> (1:5); Me<sub>4</sub>Si) 9.68 (1H, s, H<sub>a</sub>), 9.10 (1H, s, H<sub>b</sub>), 7.73 (DCI/D<sub>2</sub>O), 2.67 (DMSO), 0.00 (TMS). Bottom, highlighter portion of the spectra in which Im and ClbIm linker ratios are determined.

R <sub>wp</sub> (%)	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-UC-57
9.371	Pbca	a = 15.7313(16) Å	<i>a</i> = 15.7260(8) Å
		b = 16.1793(19) Å	<i>b</i> = 16.0184(11) Å
		<i>c</i> = 18.0589(19) Å	<i>c</i> = 18.1617(10) Å
		$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
		$\beta$ = 90 °	$\beta$ = 90 °
		$\gamma = 90$ °	$\gamma = 90$ °

Table S4: Pawley refinement details of crystalline  $[Zn(Im)_{1.65}(ClbIm)_{0.35}]$  after 15 minutes of mechanosynthesis.



Fig. S40: Pawley refinement of  $[{\sf Zn}({\sf Im})_{1.65}({\sf ClbIm})_{0.35}]$  , after 15 minutes of mechanosynthesis.



Fig. S41: ZIF-UC-5 mechanosynthesis showing production of crystalline ZIF-UC-5 during synthesis, with the formula  $[Zn(Im)_{1.65}(ClbIm)_{0.35}]$ , followed by amorphisation after 30 minutes. Notably the rate of crystalline ZIF-UC-5 production is slower than ZIF-62, with no evidence of ZIF formation after 1 minute of grinding.



Fig. S42: TGA upscan of  $a_m[Zn(Im)_{1.65}(ClbIm)_{0.35}]$  to 700 °C at 10 C min<sup>-1</sup> performed under an argon atmosphere, showing a small mass loss between 400 °C and 500 °C, with major onset of decompositions at over 500 °C. TGA trace (black), and derivative of weight loss with respect to temperature (blue).



Fig. S43: Full DSC trace of  $a_m[Zn(Im)_{1.65}(ClbIm)_{0.35}]$  at 10 °C min<sup>-1</sup> performed under an argon atmosphere. DSC heat flow trace in blue, and temperature shown as a red dashed line.



Fig. S44: TGA upscan of  $a_m[Zn(Im)_{1.70}(ClbIm)_{0.30}]$  to 700 C at 10 °C min<sup>-1</sup> performed under an argon atmosphere, showing a small mass loss between 400 °C and 500 °C, with major onset of decompositions at over 500 °C. TGA trace (black), and derivative of weight loss with respect to temperature (blue).



Fig. S45: Full DSC trace of  $a_m[Zn(Im)_{1.70}(ClbIm)_{0.30}]$  at 10 °C min<sup>-1</sup> performed under an argon atmosphere. DSC heat flow trace in blue, and temperature shown as a red dashed line.



Fig. S46: ZIF-UC-5 composition versus  $T_m$  offsets and  $T_g$  values for ZIF-UC-5 x = 0.05 through 0.25 data points are from literature.<sup>1</sup> Showing an initial  $T_g$  for  $a_m$ ZIF-UC-5 with x = 0.30 and 0.35, and the same materials after thermal treatment to give the same thermal history of melt-quenched ZIF glasses.



Fig. S47: TMA scan of  $a_m[Zn(Im)_{1.65}(ClbIm)_{0.35}]$  showing a  $T_s = 332$  °C, performed under argon using a heating rate of 10 °C min<sup>-1</sup> with an applied force of 10 mN. The sample pellet had an initial thickness of 0.5732 mm.



Fig. S48: S(Q) for crystalline ZIF-UC-5, [Zn(Im)<sub>1.65</sub>(ClbIm)<sub>0.35</sub>] produced after 15 minutes of mechanosynthesis with a  $Q_{max}$  = 19 Å <sup>-1</sup>.



Fig. S49: D(r) for crystalline ZIF-UC-5 [Zn(Im)<sub>1.65</sub>(ClbIm)<sub>0.35</sub>] produced after 15 minutes of mechanosynthesis. The correlations between 1 and 7 Å correspond to the local structure of the Zn-Im-Zn secondary building unit, whilst correlations beyond 7 Å correspond to long range order associated with the crystalline structure as expected.



Fig. S50: S(Q) for  $a_m ZIF-UC-5$ ,  $a_m [Zn(Im)_{1.65}(ClbIm)_{0.35}]$  produced after 30 minutes of mechanosynthesis with a  $Q_{max} = 19$  Å <sup>-1</sup>.



Fig. S51: D(r) of  $a_m[Zn(Im)_{1.65}(ClbIm)_{0.35}]$  produced after 30 minutes of mechanosynthesis, showing no long range order due to the amorphous nature of the material, and the local order of an Zn-Im-Zn bonding unit.

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