

Synthetic control of framework zinc purinate crystallisation and properties of a large pore, decorated, mixed-linker RHO-type ZIF

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S1. Synthetic procedures

Synthesis of **1** $Zn(pur)(nim)\cdot xX$ Topology type GME*

Zinc oxide (1 mmol, 81.4 mg, Aldrich), 2-nitroimidazole (1 mmol, 113.1 mg, Alfa Aesar), purine (1 mmol, 120.1 mg, Aldrich) and 15 ml DMF (Aldrich) in a 40 ml Teflon lined steel autoclave were heated at 373 K for 7 days and then cooled to room temperature. This gave a bright orange powder containing structure **1** in in a mixture with unreacted ZnO.

Zinc acetate dihydrate (1 mmol, 219.5 mg, Aldrich), 2-nitroimidazole (1 mmol, 113.1mg, Alfa Aesar), purine (1 mmol, 120.1 mg, Aldrich) and 15 ml N-methylpyrrolidone (NMP) (Aldrich) in a 40 ml Teflon lined steel autoclave were heated at 373 K for 7 days and then cooled to room temperature. A brown powder was obtained, washed with NMP and dried at room temperature, and determined to be pure **1** (289 mg, 81%). Elemental analysis for pure **1** from which solvent had been removed by heating, $Zn(pur)(nim)$, topology type GME, $C_8H_5N_7ZnO_2$: Found % (Calcd. %); C 32.39 (32.31); H 1.69 (1.60); N 33.06 (32.98).

In the formula $Zn(pur)(nim)\cdot xX$, X refers to the solvents (N-methylpyrrolidone, DMF) retained in the channels upon crystallisation and after washing and possibly some adsorbed water adsorbed upon standing. This is observed by TGA (section 5) - the exact amount will vary according to treatment.

Synthesis of **2** $Zn(pur)Br\cdot xDMF$

Zinc bromide (1 mmol, 219.5 mg, Fisons Scientific), 2-nitroimidazole (1 mmol, 113.1 mg, Alfa Aesar), purine (1 mmol, 120.1 mg, Aldrich) and 15 ml DMF (Aldrich) in a 40 ml Teflon lined steel autoclave were heated at 373 K for 7 days and then cooled to room temperature. White crystals were collected from filtration, washed with DMF and dried at room temperature (83.7 mg, 31%). Elemental analysis for as prepared $Zn(pur)Br\cdot 0.125DMF$: $C_{43}H_{31}N_{33}Br_8Zn_8O$. Found % (Calcd %). C 23.64 (23.58); H 1.42 (1.33); N 20.91 (21.11)

Discrepancy of the DMF content compared to the single crystal analysis ($Zn(pur)Br\cdot 0.25$ DMF) is attributed to some loss of DMF from the channels prior to CHN analysis.

Synthesis of **3** $\text{Zn}(\text{pur})(\text{OAc})\cdot x\text{X}$

Zinc acetate dihydrate (1 mmol, 219.5 mg, Aldrich), 2-nitroimidazole (1 mmol, 113.1 mg, Alfa Aesar), purine (1 mmol, 120.1 mg, Aldrich) and 15 ml DMF (Aldrich) in a 40 ml Teflon lined steel autoclave were heated at 373 K for 7 days and then cooled to room temperature. White orange single crystals were obtained from filtration, washing with DMF and drying at room temperature (195 mg, 69%). NMR indicates acetate and DMF are present in the as-prepared material, as well as purine. Elemental analysis of pure sample heated under vacuum to 473 K, estimated as $\text{Zn}(\text{pur})(\text{OAc})\cdot(0.5\text{pur},0.2\text{DMF})$: $\text{C}_{10}\text{H}_{8.6}\text{N}_{6.2}\text{Zn}_1\text{O}_{2.2}$ Found % (Calcd. %). C 37.52 (38.17); H 2.39 (2.73); N 27.51 (27.38), suggesting some purine remains within the channels.

Synthesis of **4** $\text{Zn}_{1.33}(\text{O},\text{OH})_{0.33}(\text{pur})(\text{nim})_{1.167}\cdot x\text{X}$ (Topology type RHO)

Zinc nitrate hexahydrate (1 mmol, 219.5 mg, Aldrich), 2-nitroimidazole (1.05 mmol, 119 mg, Alfa Aesar), purine (1 mmol, 120.1 mg, Aldrich) were dissolved in 15 ml DMF (Aldrich) in a 40 ml Teflon lined steel autoclave. The solution was heated at 373 K for 7 days and then cooled to room temperature. An orange powder was collected by filtration, washed in methanol and dried at room temperature. Single crystals suitable for SXRD were obtained by adding 0.5 ml methanol (Aldrich) to the reaction mixture (277 mg, 87%).

Elemental analysis of **4**, from which the solvent had been removed by heating in vacuum, $\text{Zn}_{1.33}(\text{O},\text{OH})_{0.33}(\text{pur})(\text{nim})_{1.167}$: $\text{C}_{51}\text{H}_{33}\text{N}_{45}\text{Zn}_8\text{O}_{16}$. Found % (Calcd. %); C 29.84 (29.81); H 1.65 (1.70); N 30.91 (30.68).

The water-treated sample was obtained by placing as-synthesized material together with 20 ml of distilled water for four weeks in a plastic bottle without refreshing the liquid followed by filtration, washing with water and drying at ambient temperature.

In the formula $\text{Zn}_{1.33}(\text{O},\text{OH})_{0.33}(\text{pur})(\text{nim})_{1.167}\cdot x\text{X}$, X refers to the solvents (DMF, methanol) retained in the channels upon crystallisation and after washing and possibly some adsorbed water adsorbed upon standing. Their presence is observed by TGA (section 5) - the exact amount will vary according to treatment.

* In structural formulae, *pur* \equiv purinate ($\text{C}_5\text{H}_3\text{N}_4$), *nim* \equiv 2-nitro-imidazolate ($\text{C}_3\text{H}_2\text{N}_3\text{O}_2$) and X refers to unspecified extra framework species

S2. Solution phase NMR

Solution phase NMR was recorded on a Bruker Avance 300 MHz spectrometer. The sample preparation involved digestion of the as prepared material and therefore 4.5 mg of solid were combined with 800 μL of DMSO- d_6 and 150 μL HNO_3 (0.2 M) followed by sonication for ~ 3 min leading to complete dissolution. All structures contain purine, $\delta^1\text{H}$ (300MHz): 8.8 (1H), 9.1 (1H), 9.3 (1H). The presence of 2-nitroimidazole in similar molar amounts to purine in structures **1** and **4** is confirmed by $\delta^1\text{H}$ 7.2 (2H). Small amounts of 2-nitroimidazole in the spectra of dissolved structures **2** and **3** can be explained by incomplete washing or, in the case of structure **3**, residual 2-nitro-imidazole in the pores.

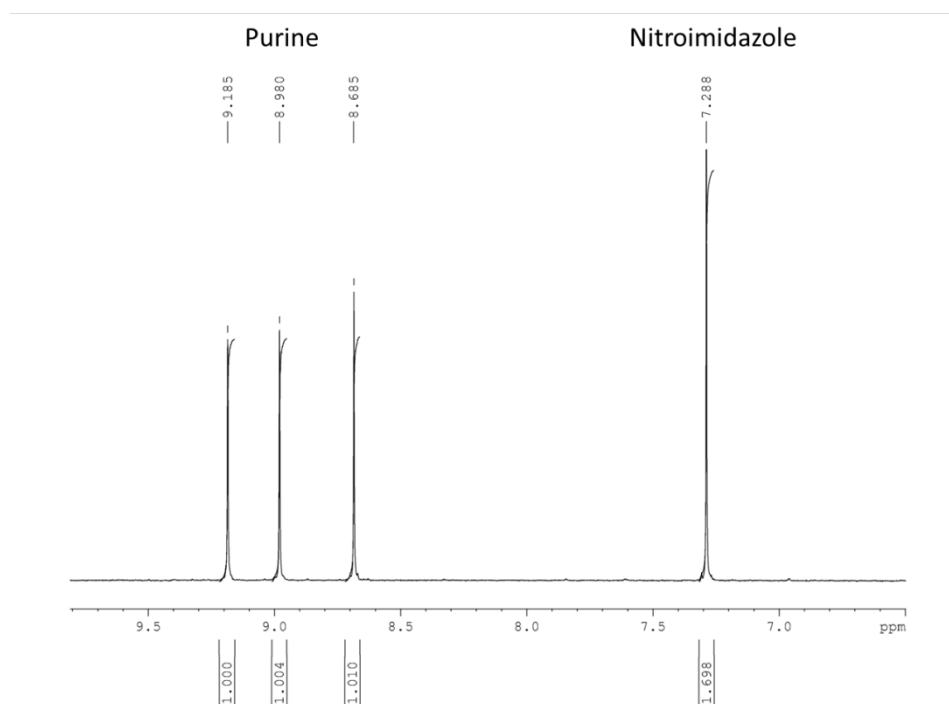


Figure S2.1 ^1H NMR of dissolved structure **1** after heating of as-prepared solid under vacuum at 413 K for 4 h.

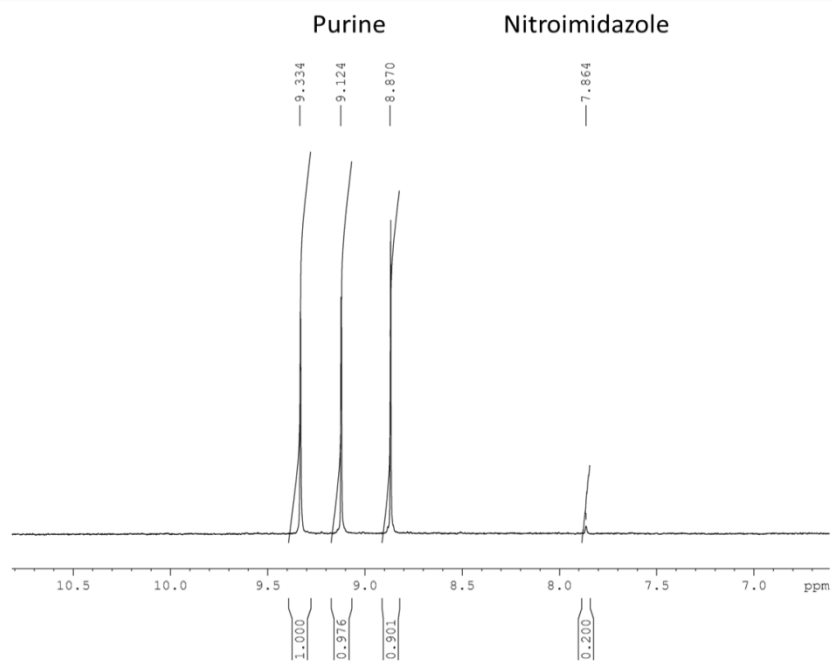


Figure S2.2 ¹H NMR of dissolved structure 2

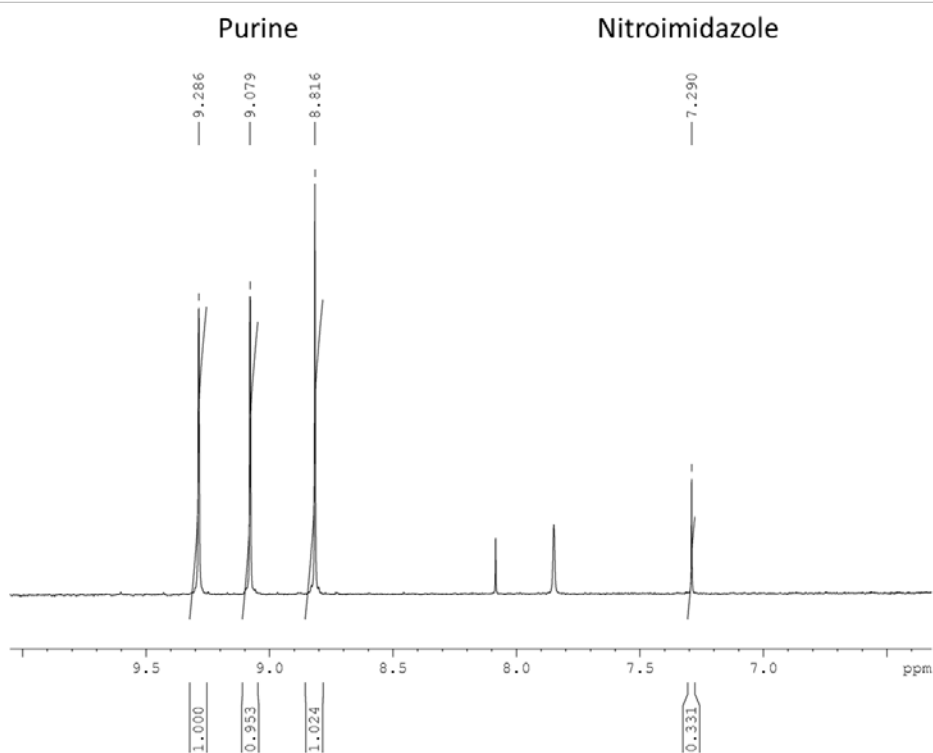


Figure S2.3 ¹H NMR of dissolved as-prepared structure 3, showing residual DMF and 2-nitroimidazole.

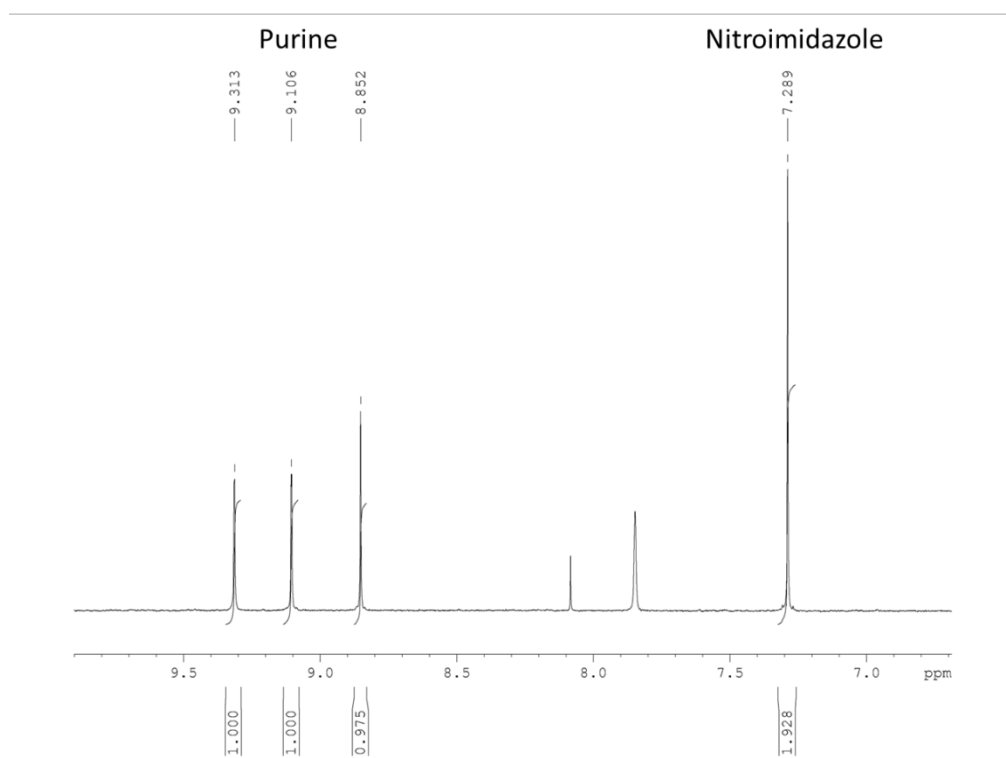


Figure S2.4 ¹H NMR of as prepared structure **4**, heated at 463 K and activated under vacuum at 423 K.

S3. Single crystal XRD data

Data for structure **1** and **4** were collected at 173 K by using a Rigaku MM007 High brilliance RA generator (Cu K α radiation, confocal optics) and Saturn92 CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. H atoms were placed with idealised coordinates, constrained to be a distance of 0.93 Å from their C atom and with fixed U_{iso} values. Structural refinements were performed with full-matrix least-squares based on F2 by using the program SHELXTL.^{S3.1} SADI commands were used to constrain the geometry of the 2-nitroimidazole ligands in structure **1**. All atoms in the pyrimidine moiety of purinate groups in structures **1** and **4** were refined as carbons, although there will be a 50% occupancy by N atoms in the structures. H atoms attached to these C atoms were included with 50% occupancy. Additional scattering was refined as solvent O. In structure **1**, the crystallographically-imposed symmetry results in the two *nim* ligands and the two independent *pur* ligands lying about mirror planes.

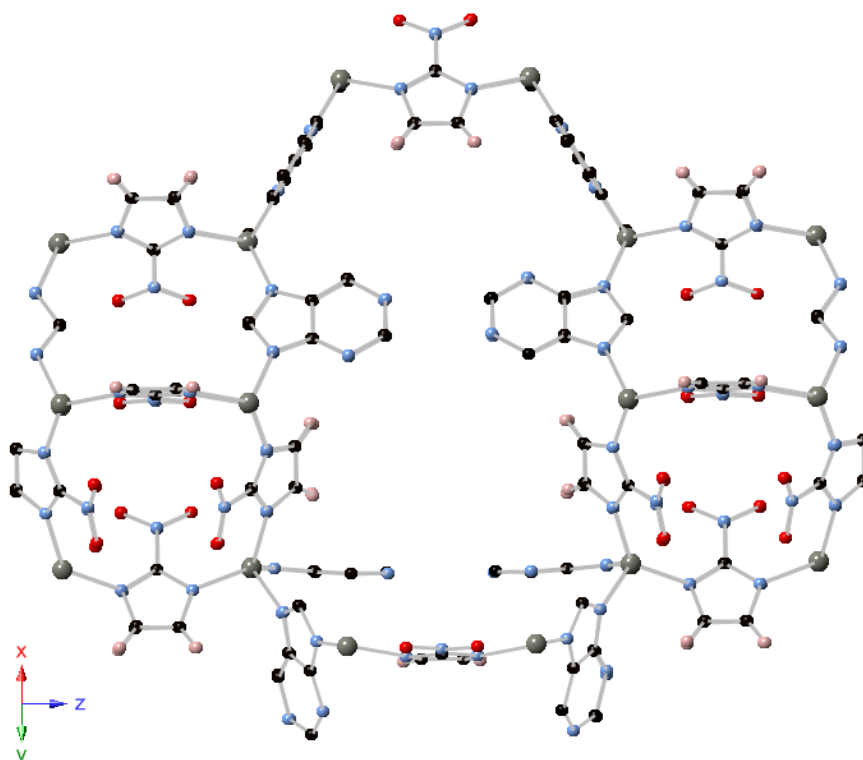


Figure S3.1: Structure **1** viewed perpendicular to channels along c-axis. (Zn, gray; N, blue; C, black; H, pink).

In structure **4**, the crystallographically-imposed symmetry results in positional disorder of C and N atoms in the pyrimidine ring of the purine ligands. Therefore the atoms in the cif have been labelled CN5 and CN6 and H atoms with occupancy 0.5 have been attached.

Also in structure **4**, extra framework Zn atoms and 2-nitroimidazole groups were located by difference Fourier analysis. The zinc atoms were present at 1/3 fractional occupancy and the 2-nitroimidazolate groups, which occupy positions linking two specific Zn positions in 2 symmetry-equivalent configurations, were each refined with 1/24 occupancy. Restraints on carbon/nitrogen- and carbon/carbon-bonds were used to refine distances of the *exo* ligands in structure **4**. Additional scattering was refined as solvent O.

Data for structures **2** and **3** were collected at 93 K by using a Rigaku MM007 High brilliance RA generator (Mo K α radiation, confocal optics) and Mercury CCD system. At least a full hemisphere of data was collected using ω scans. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. H atoms were placed with idealised coordinates, constrained to be a distance of 0.93 Å from their C atom and with fixed U_{iso} values. Structural refinements were performed with full-matrix least-squares based on F2 by using the program SHELXTL.^{S3.1}

Structure **2** was refined hosting DMF in its pores with the fractional occupancies for C, N, O and H set at 0.5. The P2₁/n asymmetric unit has two independent Zn(pur)Br moieties in general positions and a half-occupancy DMF molecule [which happens to lie near the inversion centre at (1/2, 1/2, 1)]

During the refinement of structure **3**, once the framework has been confirmed, residual electron density in the pores could be modelled as an acetate ion. The geometry of the acetate ion was constrained but its position was allowed to refine freely. Although additional species are known to be in the pores from analytical data, it was not possible to fully model all extra framework scattering in the pores.

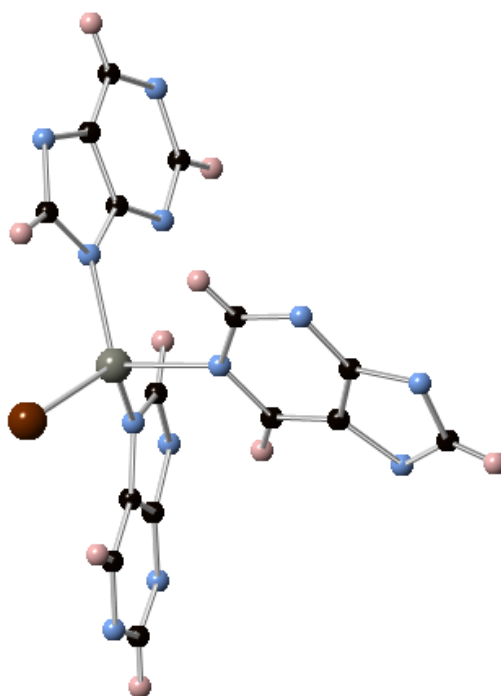


Figure S3.2 Tetrahedral ZnN_3Br environment of structure **2**, showing coordination to two imidazole N atoms, one pyrimidine N of purine and a bromide ion. (Legend same as figure S3.1, with Br brown)

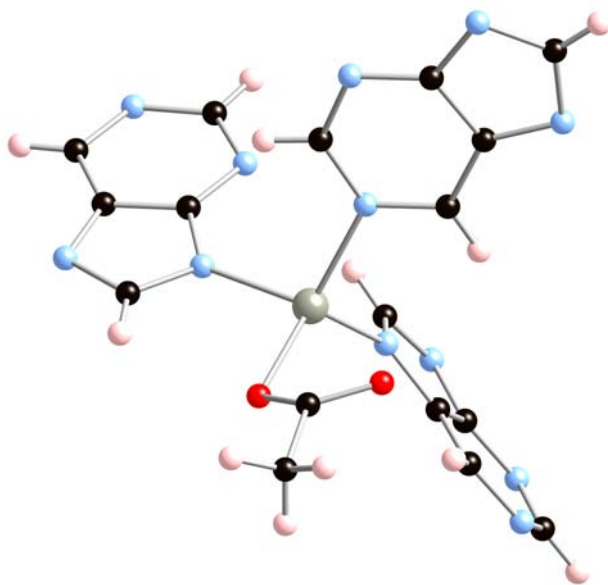


Figure S3.3 Zinc environment of structure **3**, showing coordination of Zn to two imidazole N, one pyrimidine N of purine, and one O atom of an acetate ligand (Zn-O 2.0 Å). A second O atom is at 2.59 Å from the zinc atom. (Key to atom types as above, with O, red),

Table S3.1 Crystallographic details

	Structure 1	Structure 2	Structure 3	Structure 4
Formula Sum*	C ₈ H _{5.5} N ₇ O _{2.25} Zn ₁	C _{11.5} H _{9.5} N _{8.5} O _{0.5} Zn ₂ Br ₂	C ₇ H ₆ N ₄ O ₂ Zn	C _{8.50} H _{6.75} N _{7.5} O _{3.55} Zn _{1.33}
Formula Weight of Unit Cell*	296.6	543.85	243.50	375.9
Calculated Density / g cm ⁻³ *	1.049	1.910	1.498	1.164
Space Group	<i>P</i> 6 ₃ / <i>m m c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>I</i> -4	<i>I</i> <i>m</i> -3 <i>m</i>
<i>a</i> / Å	26.884(10)	13.636(7)	15.02(3)	29.044(6)
<i>b</i> / Å	26.884(10)	10.209(5)	15.02(3)	29.044(6)
<i>c</i> / Å	18.121(10)	14.124(7)	9.570(19)	29.044(6)
α / °	90	90	90	90
β / °	90	91.568(9)	90	90
γ / °	120	90	90	90
<i>V</i> / Å ³	11342(9)	1965.5(17)	2159(7)	24500(9)
<i>Z</i>	24	4	8	48
Crystal Morphology	Prism	Prism	Prism	Prism
Temperature / K	173(2)	93(2)	93(2)	173
Radiation type	Cu K α	Mo K α	Mo K α	Cu K α
Wavelength / Å	1.54178	0.71073	0.71073	1.54178
Unique/Total Reflections	3828/155295	3874/14892	2016/11116	2174/99240
Residual e ⁻ density min/max	-0.892/2.053	-1.132/1.565	-0.976/1.906	-0.943/3.273
R _F	0.2721	0.0640	0.0748	0.1360
R _F [<i>I</i> > 2 σ (<i>I</i>)]	0.2365	0.0561	0.0748	0.1343

Notes:

* Formula sum is that reported in the cif determined on the basis of the refinement and modified by chemical information

(1) Disordered solvent, known to be present in **1**, **3** and **4**, was not observed and is not included in the formula units or formula weights of the unit cells.

(2) The Flack parameter of structure **3** is 0.16(5).

S4. Powder XRD data of as-prepared materials

Laboratory powder XRD data was collected on a Stoe STAD I/P diffractometer using Cu $K_{\alpha 1}$ radiation ($\lambda = 1.540598 \text{ \AA}$). The powders were ground fine, loaded into glass capillaries and data was collected in Debye-Scherrer geometry.

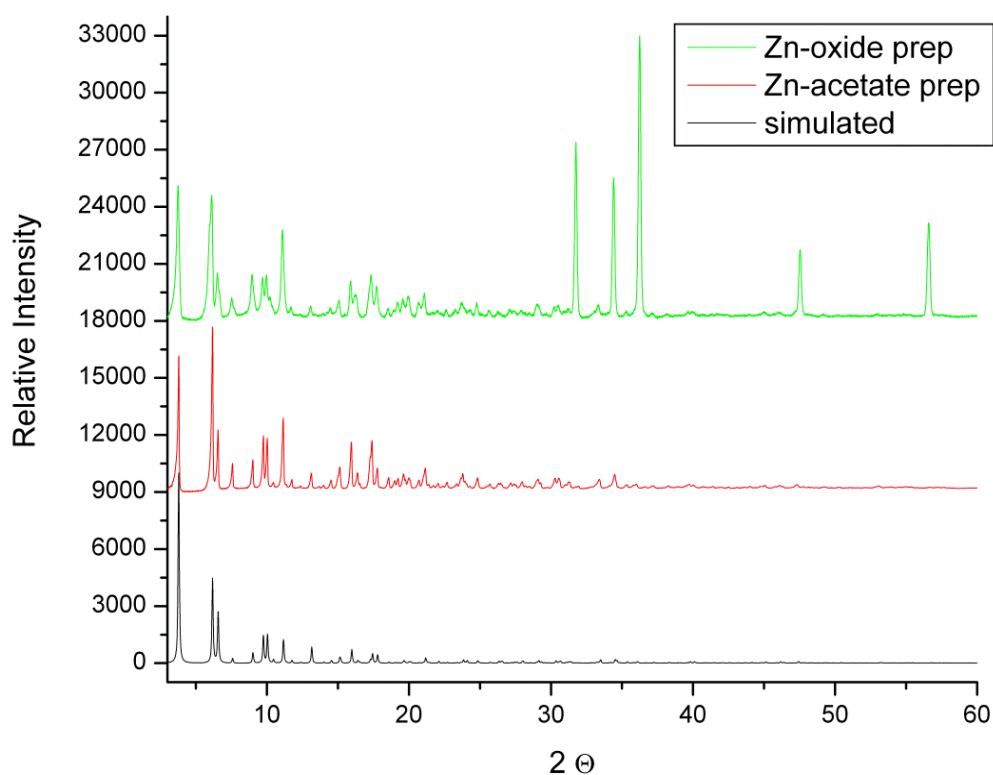


Figure S4.1 Powder X-Ray diffraction patterns of structure **1** $\text{Zn}(\text{pur})(\text{nim})$ (GME) prepared with ZnO (green) and $\text{Zn}(\text{OAc})_2$ (red), compared with a powder XRD pattern simulated using the structure of **1** determined by SXRD (black).

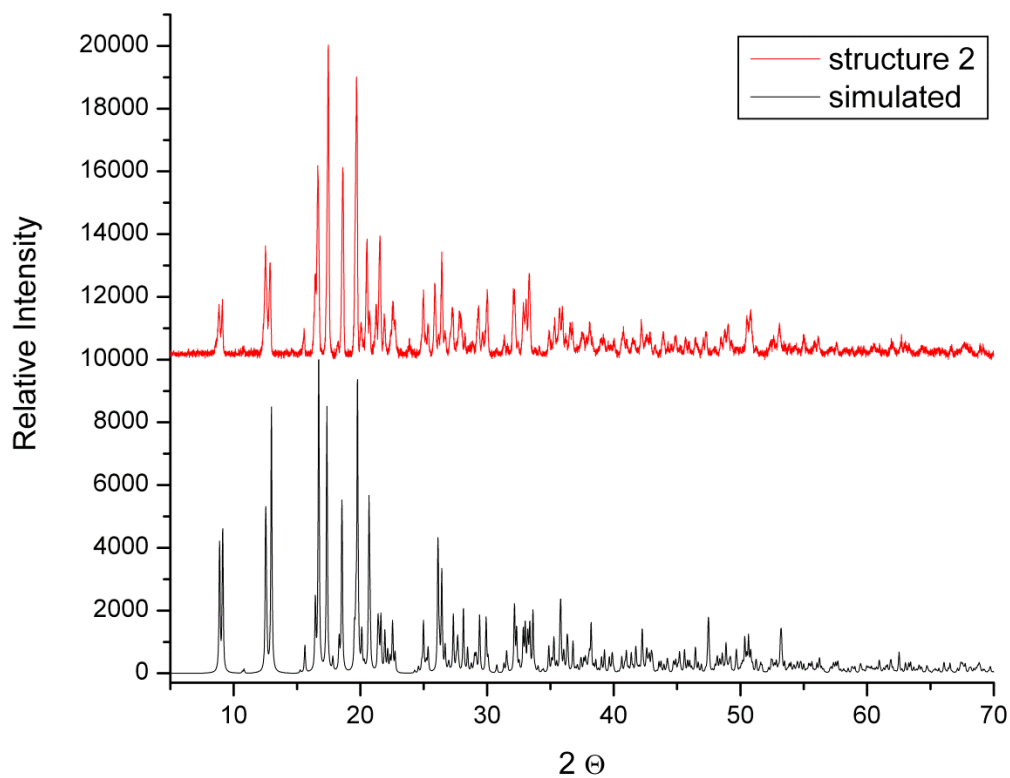


Figure S4.2 Powder X-Ray diffraction pattern of as prepared Zn(*pur*)Br, structure **2** (red) compared with that simulated using the structure determined from single crystal diffraction (black).

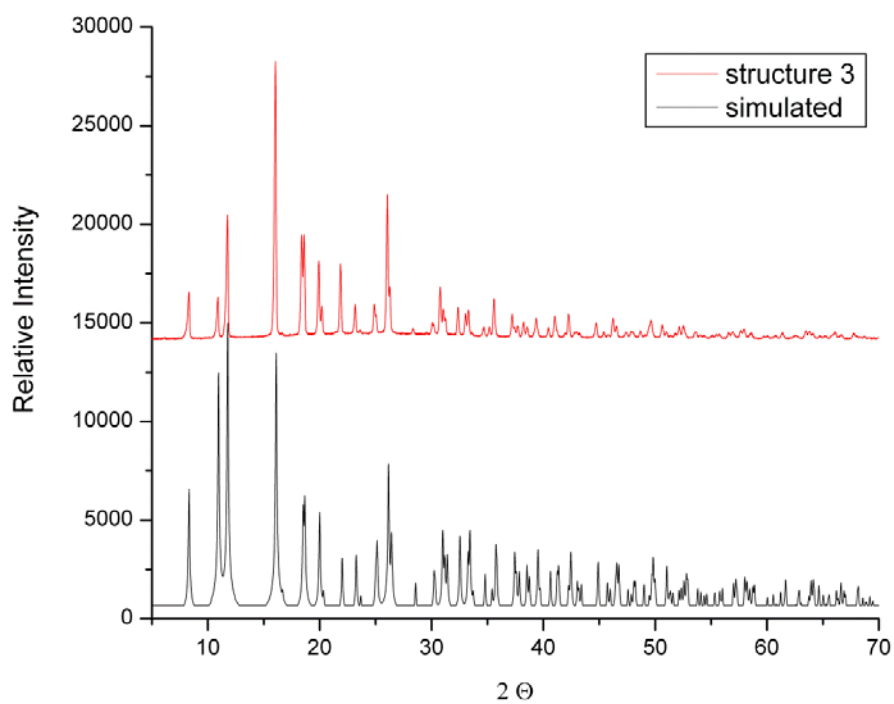


Figure S4.3: Powder X-Ray diffraction pattern of as-prepared Zn(*pur*)OAc.*xX*, structure **3**, (red) compared with that simulated using the structure determined from SXRD (black).

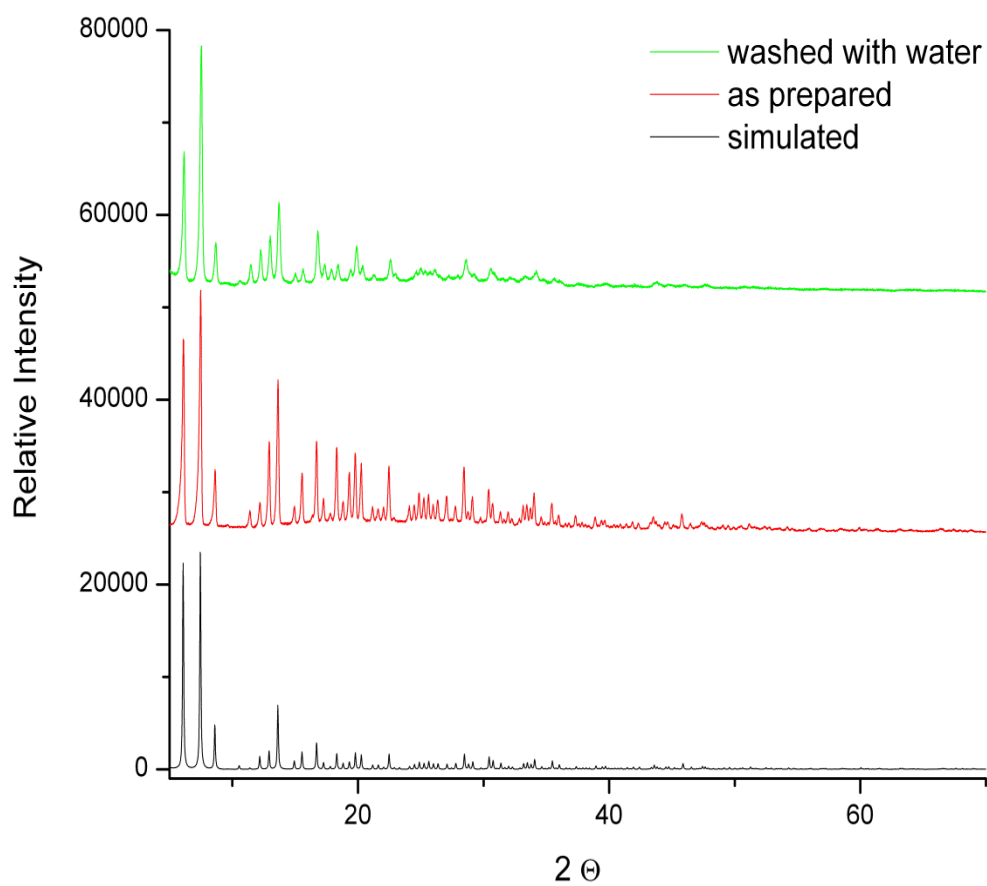


Figure S4.4 Powder X-Ray diffraction pattern of as-prepared $\text{Zn}_{1.33}(\text{O},\text{OH})_{0.33}(\text{pur})(\text{nim})_{1.167}$ (in red) and as-prepared and treated with water (green) compared with that simulated using the structure determined from SXRD on the as-prepared material (black).

S5. Thermogravimetric analysis

TGA data was collected on a Netzsch TG1000M with the sample held in a platinum pan under dry air flow. The temperature range was increased from 293 – 973 K with a heating rate of 5 K/min.

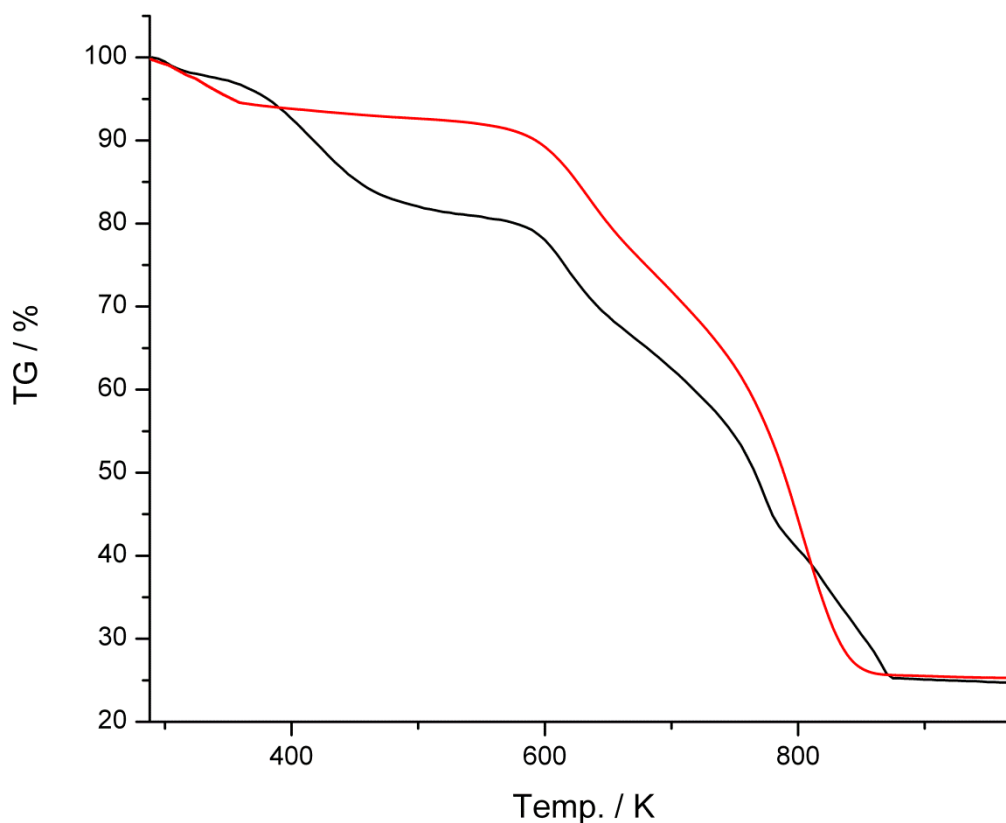


Figure S5.1 TGA of structure **1**, both as-prepared (black) and after heating under vacuum at 473 K (red).

Figure S5.1 show the TGA of structure **1** prepared using zinc acetate. The loss of water and solvent occurs from 293 K and continues up to 333 K (2.5 wt.%) followed by the loss of NMP up to 500 K (17 wt.%). A step at 550 K indicates decomposition. Solvent is therefore lost by heating under vacuum at 473 K.

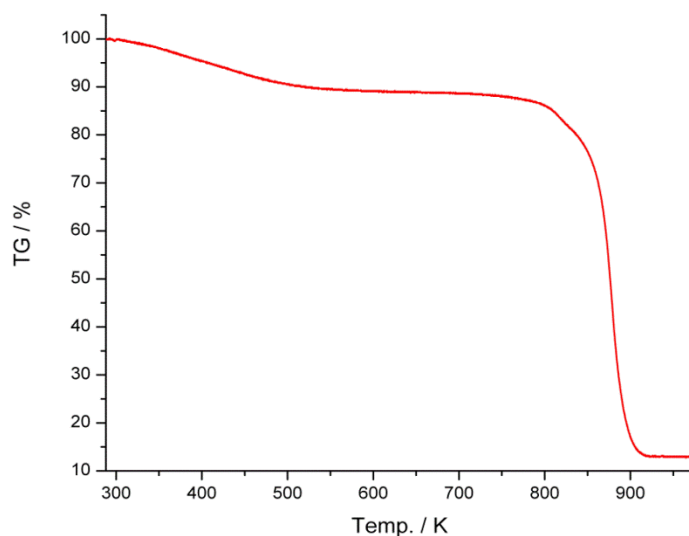


Figure S5.2 TGA of as-prepared structure 2.

Structure 2 shows continuous weight loss from 300 – 550 K which indicates the loss of DMF (10.5 wt.%) with the final decomposition above 750 K.

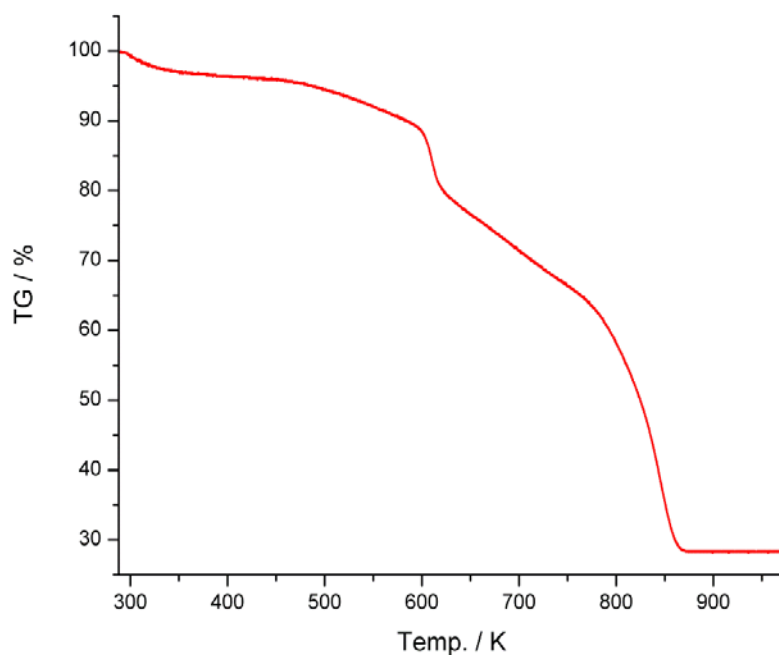


Figure S5.3 TGA of as-prepared structure 3.

The TGA trace of structure 3 shows an initial loss of solvent up to 350 K (3.5 wt.%) followed by loss of weight attributed to included DMF and 2-nitroimidazolate above 450 K. A sharp step at 600 K indicates the decomposition of the structure.

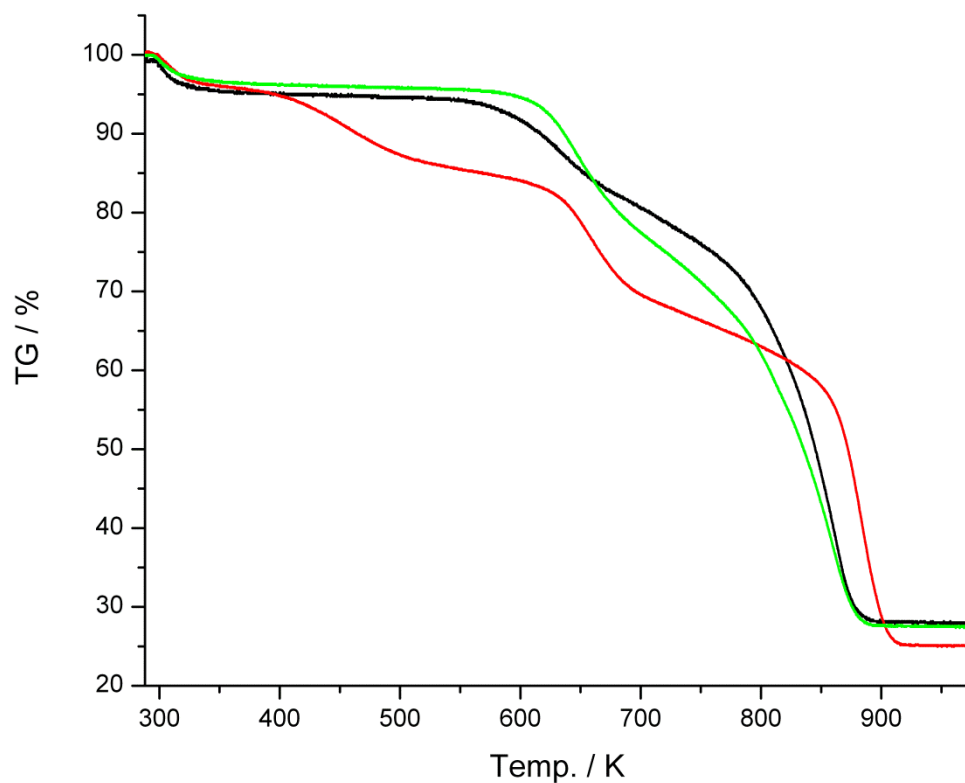


Figure S5.4 TGA of as-prepared structure **4** (red) and the same structure previously heated under vacuum at 500 K (black), showing all the solvent molecules are removed by that heating. The green line shows the TGA on structure **4**, water-treated and heated (463 K, 4 h/ 413 K, 3 h in vacuum).

Figure S5.4 shows the TGA trace of a sample of **4** derived from synthesis in presence of methanol. The initial loss results from to the loss of methanol or water between 300 K and 330 K is followed by loss of DMF up to 550 K. Decomposition starts at around 600 K. Samples heated at 500 K, or water-treated and heated at 413 K, have lost all DMF included in synthesis.

S6. Powder XRD on desolvated structures **1** (GME) and **4** (RHO)

Powder XRD data of desolvated samples of structures **1** and **4** (the latter before and after water treatment) were collected on a Stoe STAD I/P diffractometer using Cu K_{α_1} radiation ($\lambda = 1.540598 \text{ \AA}$). The powders were ground fine, loaded into quartz glass capillaries and heated under a vacuum of 10^{-5} mbar to 413 - 473 K for 4 h to remove solvent before being sealed. Diffraction data were collected in Debye-Scherrer geometry.

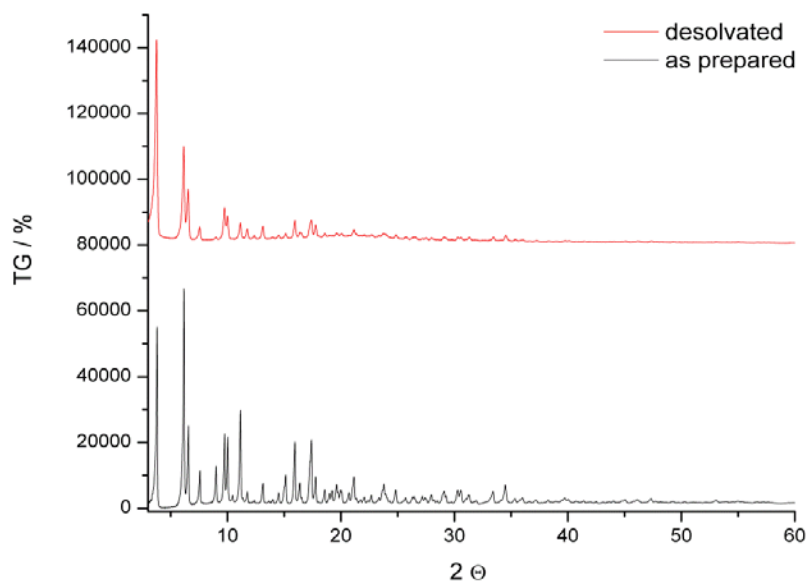


Figure S6.1: Powder X-Ray pattern of structure **1** as-prepared with $\text{Zn}(\text{OAc})_2$ (black) compared with a sample of **1** heated under vacuum at 413 K (red).

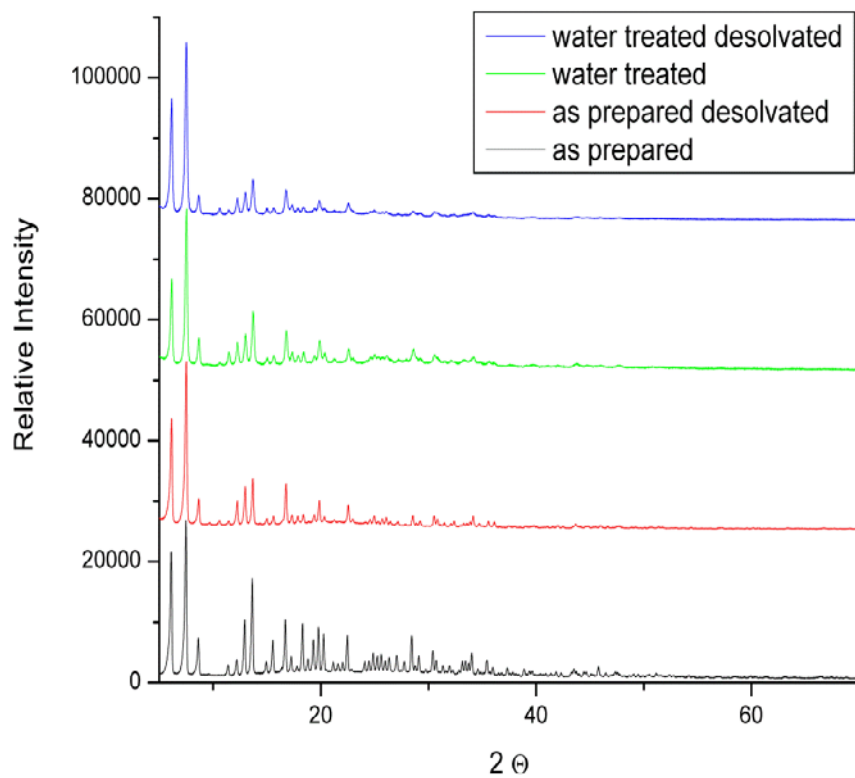


Figure S6.3 PXRD of structure **4**, as prepared (black), as prepared and heated under vacuum at 413 K (red) compared with a sample treated with water (green) and a sample after water treatment and heating under vacuum at 413 K (blue).

S7. Porosity – Nitrogen adsorption

Low pressure gas adsorption (< 0.1 bar) studies were performed on a Micromeritics Tristar II 3020 for N₂ (structure **1** (GME)) and Micromeritics ASAP 2020 volumetric instruments for N₂ (structure **4** RHO). The as prepared structure **1** GME materials have been heated under vacuum to 473 K for 6 h. An activated as-prepared RHO sample was obtained by heating at 463 K for 4 h at ambient pressure followed by 423 K for 3 h under vacuum. The water-treated material was heated under vacuum at 393 K for 2 h (and later showed by TGA not to have residual DMF. All materials show Type I isotherms.

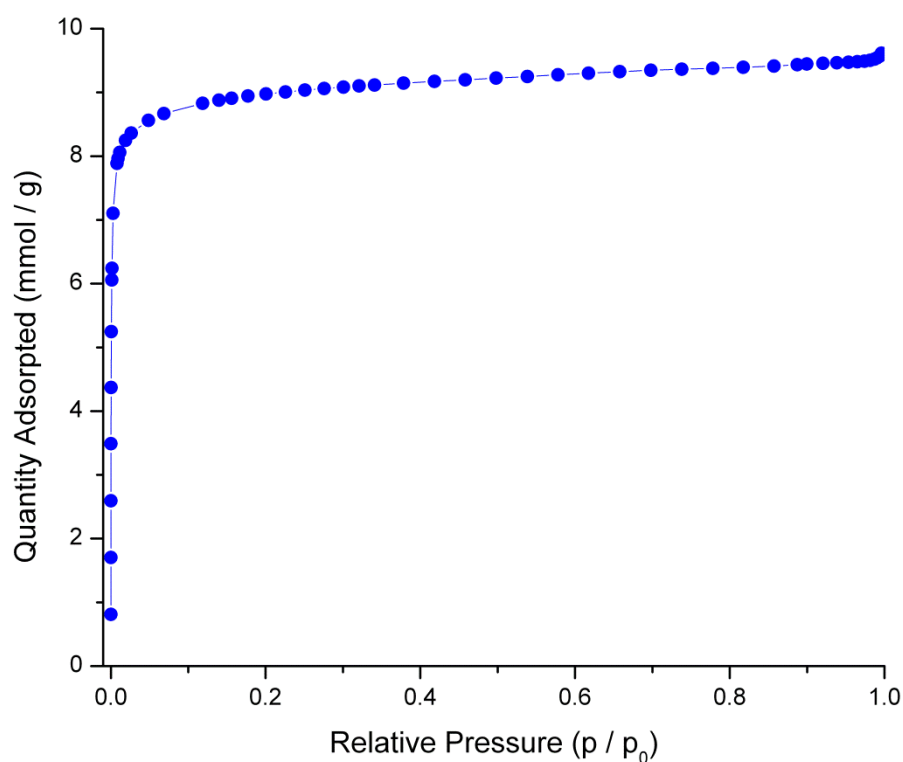


Figure S7.1 Nitrogen adsorption isotherm (at 77 K) for structure **1**, Zn(*pur*)(*nim*) – GME, desolvated at 473K.

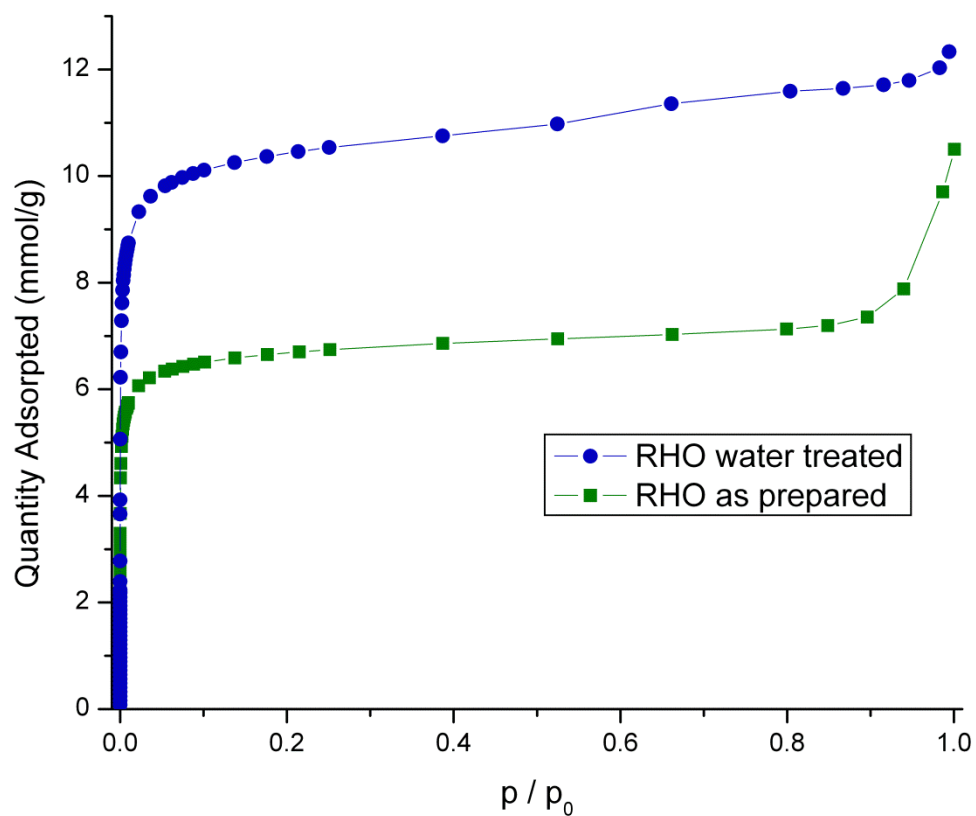


Figure S7.2 Nitrogen adsorption (77 K) for structure $4 \text{Zn}_{1.33}(\text{O},\text{OH})_{0.33}(\text{pur})(\text{nim})_{1.167}$ of as-prepared material heated at 463 K and activated under vacuum at 423 K (green) compared to a sample treated in water and heated under vacuum to 393 K (blue).

S8. Carbon dioxide adsorption (298 K)

Low pressure gas adsorption (< 0.1 bar) studies for CO_2 were performed on a Micromeritics ASAP 2020 instruments with cooler (298 K). Already activated as prepared samples for N_2 adsorption were heated again under vacuum conditions for 2h (363 K) followed by 16 h (473 K). The water treated sample was heated under vacuum for 4 h at 413 K prior to adsorption.

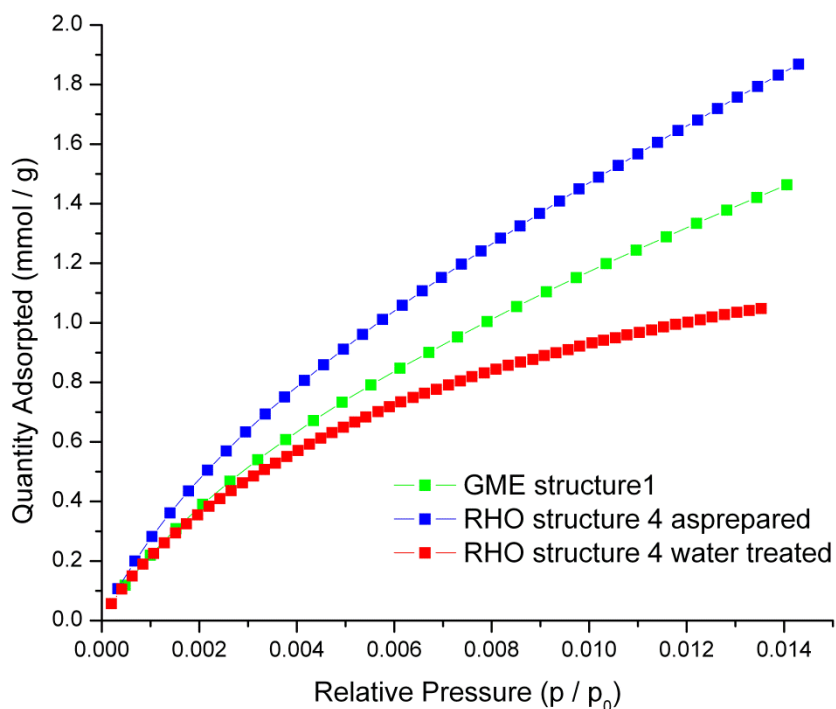


Figure S8.1 Carbon dioxide adsorption (298K) for structure **4** of a as prepared sample heated under vacuum to 473 K (blue), water treated and heated under vacuum to 413 K (red) compared to structure **1** activated under vacuum at 473 K (green).

S9. Modelling of N_2 adsorption isotherms

The adsorption of N_2 was investigated using grand canonical Monte Carlo (GCMC) simulations^{S9.1} implemented in the multipurpose simulation code Music.^{S9.2} We used an atomistic model for all ZIF structures, in which the framework atoms were kept fixed at the crystallographic positions. We used the standard Lennard-Jones (LJ) 12-6 potential to model the interatomic interactions between the framework and N_2 . Apart from the LJ, we included electrostatic interactions between N_2 molecules. The parameters for the framework atoms

were obtained from the UFF force field.^{S9.3} N₂ was modeled using the TraPPE potential with charges placed on each atom and at the centre of mass.^{S9.4} The Lorentz-Berthelot mixing rules were employed to calculate fluid/solid parameters. Interactions beyond 18 Å were neglected. 10⁷ Monte Carlo steps were performed, the first 40% of which were used for equilibration, and the remaining steps were used to calculate the ensemble averages. To calculate the gas-phase fugacity we used the Peng-Robinson equation of state.^{S9.5}

Adsorption Isotherm of N₂ at 77 K on Structure 1

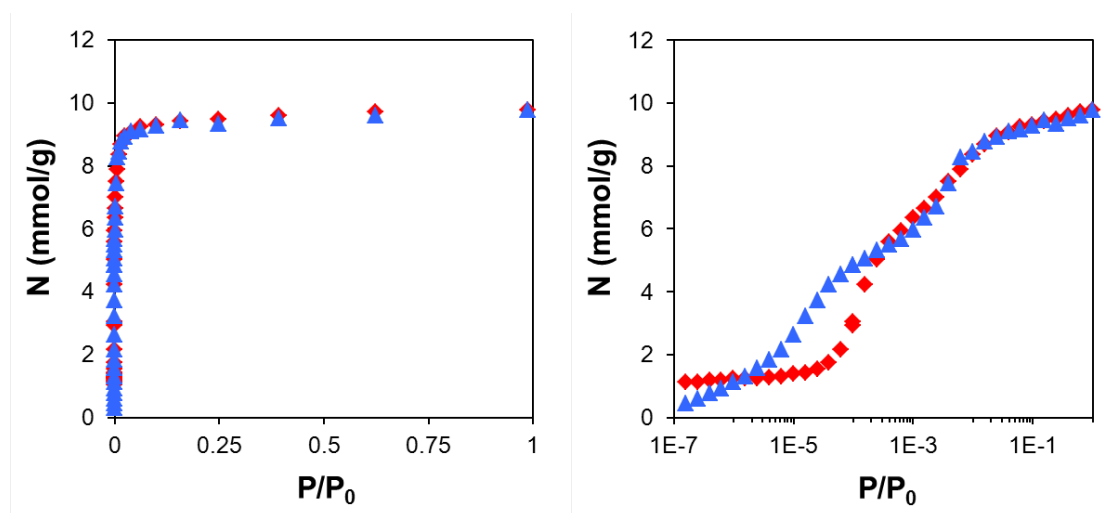


Figure S9.1 Comparison of simulated (red diamonds) and measured (blue triangles) nitrogen adsorption 77 K isotherms for desolvated structure **1**, Zn(*pur*)(*nim*). The sample was heated under vacuum at 473 K for 4 h prior to measurement of the isotherm.

References

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