Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary data

Mechanochemical Synthesis of Mixed Metal, Mixed Linker, Glass-Forming Metal–Organic Frameworks

Michael F. Thorne,[a] María Laura Ríos Gómez,[a,b] Alice M. Bumstead,[a] Shichun Li,[a,c] and Thomas D. Bennett[a*]

[a] Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS, UK.

[b] Institute of Materials Research (IIM-UNAM). Circuito Exterior, Ciudad Universitaria, Coyoacán, 04510, D. F., México

[c] Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, P. R.China

Email: tdb35@cam.ac.uk

ZIF mechanosynthesis

Table S1: Reagents required for LAG mechanosynthesis of 100% Zn ZIF-62 through 20% Co ZIF-62 with the ligand ratio $(Im)_{1.75}(bIm)_{0.25}$

Sample	ZnO (<100 nm)	$Zn(OAc)_2.2H_2O$	$Co(OAc)_2.4H_2O$	Imidazole	Benzimidazole	DMF
100% Zn ZIF-62	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	-	119.0 mg (1.75 mmol)	30.0 mg (0.25 mmol)	50 µL
1% Co ZIF-62	80.2 mg (0.99 mmol)	-	2.5 mg (0.01 mmol)	119.0 mg (1.75 mmol)	30.0 mg (0.25 mmol)	50 µL
5% Co ZIF-62	77.0 mg (0.95 mmol)	-	12.5 mg (0.05 mmol)	119.0 mg (1.75 mmol)	30.0 mg (0.25 mmol)	50 µL
10% Co ZIF-62	72.9 mg (0.90 mmol)	-	24.9 mg (0.10 mmol)	119.0 mg (1.75 mmol)	30.0 mg (0.25 mmol)	50 µL
20% Co ZIF-62	64.8 mg (0.80 mmol)	-	49.8 mg (0.20 mmol)	119.0 mg (1.75 mmol)	30.0 mg (0.25 mmol)	50 µL

Table S2: Reagents required for LAG mechanosynthesis of ZIF-62 with the ligand ratios $(Im)_{1.80}(bIm)_{0.20}$ through $(Im)_{1.95}(bIm)_{0.05}$

Sample	ZnO (<100 nm)	$Zn(OAc)_2.2H_2O$	Imidazole	Benzimidazole	DMF
$Zn(Im)_{1.80}(bIm)_{0.20}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	122.4 mg (1.80 mmol)	23.6 mg (0.20 mmol)	50 µL
$Zn(Im)_{1.85}(bIm)_{0.15}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	125.8 mg (1.85 mmol)	17.7 mg (0.15 mmol)	50 µL
$Zn(Im)_{1.90}(bIm)_{0.10}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	129.2 mg (1.90 mmol)	11.8 mg (0.10 mmol)	50 µL
$Zn(Im)_{1.95}(bIm)_{0.05}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	132.6 mg (1.95 mmol)	5.9 mg (0.05 mmol)	50 µL

Table S3: Reagents required for LAG mechanosynthesis of ZIF-UC-5 with the ligand ratios $(Im)_{1.75}(ClbIm)_{0.25}$ through $(Im)_{1.95}(ClbIm)_{0.05}$

Sample	ZnO (<100 nm)	$Zn(OAc)_2.2H_2O$	Imidazole	5-Chlorobenzimidazole	DMF
$Zn(Im)_{1.75}(ClbIm)_{0.25}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	119.0 mg (1.75 mmol)	38.3 mg (0.25 mmol)	50 µL
$Zn(Im)_{1.80}(ClbIm)_{0.20}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	122.4 mg (1.80 mmol)	30.6 mg (0.20 mmol)	50 µL
$Zn(Im)_{1.85}(ClbIm)_{0.15}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	125.8 mg (1.85 mmol)	23.0 mg (0.15 mmol)	50 µL
$Zn(Im)_{1.90}(ClbIm)_{0.10}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	129.2 mg (1.90 mmol)	15.3 mg (0.10 mmol)	50 µL
$Zn(Im)_{1.95}(ClbIm)_{0.05}$	80.2 mg (0.99 mmol)	2.2 mg (0.01 mmol)	132.6 mg (1.95 mmol)	7.7 mg (0.05 mmol)	50 µL

Table S4: Reagents used in attempts to produce 100% Co ZIF-62 with the ligand ratio $(Im)_{1.75}(bIm)_{0.25}$

Attempted synthesis	CoO	$Co(OAc)_2.4H_2O$	$CoCO_3$	Imidazole	Benzimidazole	DMF
$Co(Im)_{1.75}(bIm)_{0.25}$	74.18 mg (0.99 mmol)	2.5 mg (0.01 mmol)	-	119.0 mg (1.75 mmol)	30.0 mg (0.25 mmol)	50 µL
$Co(Im)_{1.75}(bIm)_{0.25}$	-	-	118.9 mg (1.00 mmol)	119.0 mg (1.75 mmol)	30.0 mg (0.25 mmol)	50 µL

IPA Solvothermal Synthesis

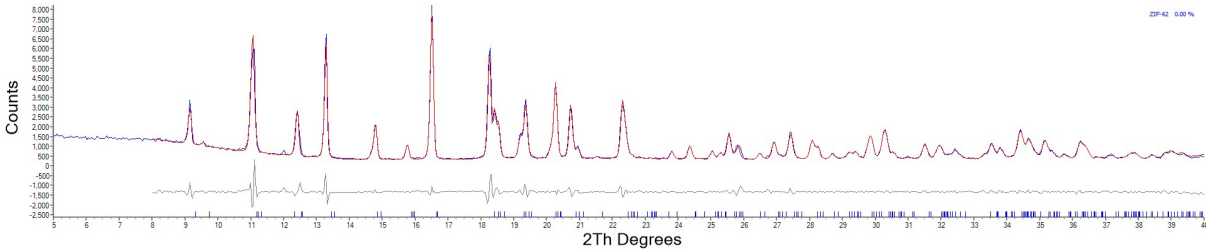

Figure. S1: Pawley refinement of ZIF-62 produced using IPA solvothermal methods. IPA solvothermal ZIF-62 crystalized in the orthorhombic crystal system, and the reflections were consistent with space group *Pbca* (61). Cell parameters were determined from a single-phase designation, using the values for lattice parameters published CIF for ZIF-62 produced solvothermally with DMF.[1] The difference plot (grey) between experimental and simulated is shown.

Table S5: Crystal data and structure refinement for IPA solvothermal ZIF-62

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
8.377	*Pbca*	a = 15.810(3) Å	a = 15.6620(14) Å
		b = 15.606(3) Å	b = 15.6621(13) Å
		c = 18.158(4) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

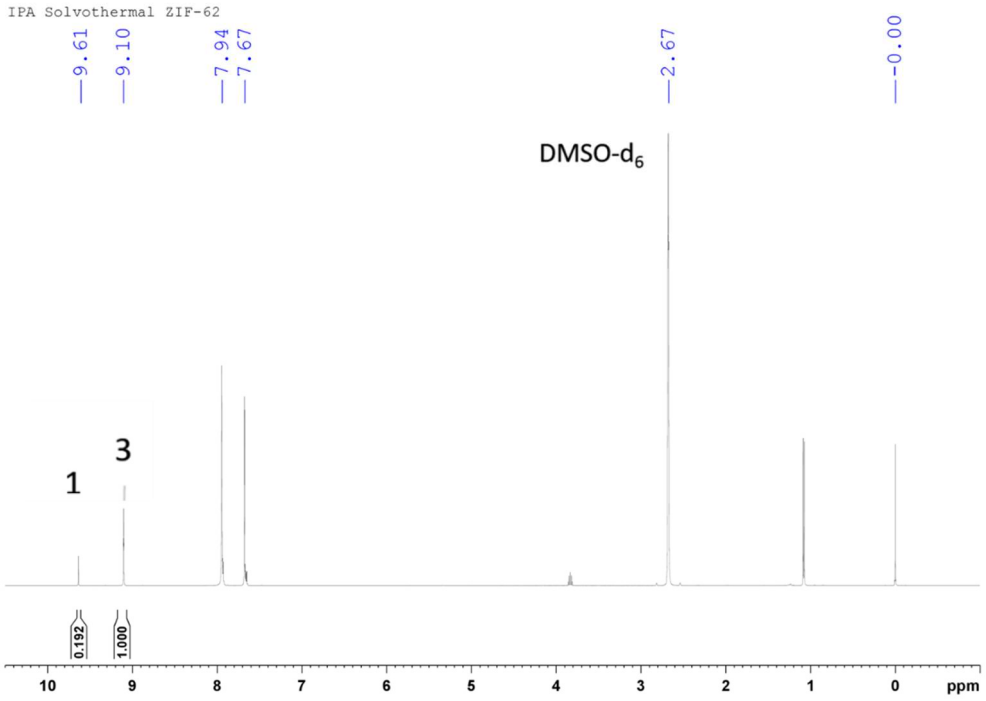

Figure. S2: ^{1}H nuclear magnetic resonance spectra of IPA solvothermally produced ZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d6 (1:5); Me4Si) 9.61 (1H, s, H1), 9.10 (1H, s , H3), 7.94 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

IPA solvothermal ZIF-62 (cag – Orthorhombic)
Experimental and Refinement Details
(CCDC Deposition Number 1959087)

A colourless polyhedral crystal (0.10 × 0.07 × 0.05 mm^3) of ZIF-62 was collected from the mother liquor and placed in a 0.2 mm diameter borosilicate loop. This loop was mounted on a Gemini E Ultra diffractometer from Oxford Diffraction, equipped with an Atlas CCD area detector and operated at 35 kV and 35 mA, to generate Cu Kα radiation (λ = 1.54184 Å) at 293(2) K. A total of 11373 reflections were collected, from which 3732 reflections were unique and 3287 of these were greater than $2\sigma(I)$. Reflections were collected for a θ range from 2.43 to 64.13°. Analysis of the data showed negligible decay during collection. The structure was solved in the orthorhombic *Pbca* space group with $Z = 8$ using the SUPERFLIP method, and the structure was refined using SHELXL both in the WinGX suite version 2018.2.[2–4] Modelling of electron density leaded to the identification of 0.82 IPA molecules in the asymmetric unit, distributed in two slightly different positions with occupancies 0.42 and 0.40. The asymmetric unit is also integrated by two independent Zn and four independent organic linkers. From those four linkers, two are imidazolate in positions with no disorder, a third linker is in a position disordered between 0.462(8) benzimidazolate and 0.538(8) imidazolate, and the fourth linker is disordered between 0.089(10) benzimidazolate and 0.911(10) imidazolate. The third position can contain a maximum of 50% benzimidazolate because the centre of symmetry in this space group would bring the benzimidazolate linkers related by this centre into contact with each other. The benzimidazolate linker at the fourth position is shifted away from the complementary imidazolate position by 63.15°, which results in partial occupancy of sites normally occupied by solvent molecules. The shift happens to avoid a steric clash with one of the two neighbouring imidazolate linkers in totally occupied sites. All non-hydrogen atoms, except the four disordered ones in each benzene ring from benzimidazolate linkers and the ones from the solvent, have been refined anisotropically. All hydrogen atoms, except H15 have been placed in geometrically located positions and their displacement parameters are tied to those of the attached carbon atoms. H15 was fixed in the geometrically equivalent position. The unit cell of ZIF-62 contains 1.72 imidazolate and 0.28 benzimidazolate per Zn. Final full matrix least -50 squares refinement on F^2 converged to $R_1 = 0.0450$ ($F_0 > 4\sigma F_0$) and $wR_2 = 0.1374$ (all data) with GooF = 1.054.

Table S6: Crystal data and structure refinement for IPA solvothermal ZIF-62

Chemical formula	$C_{16.69}\ H_{18.62}\ N_8\ O_{0.83}\ Zn_2$
Formula weight	475.35 g mol^{-1}
Temperature	293(2)
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	*a* = 15.6052(5) Å α = 90° *b* = 15.8374(6) Å β = 90° *c* = 18.1718(5) Å γ = 90°
Volume	4491.1(3)
Density (calculated)	1.405 g cm^{-3}
Absorption coefficient	2.801
F(000)	2151.36
Crystal size	0.10 × 0.07 × 0.05 mm^3
Theta range for data collection	2.431 - 64.131°
Index ranges	-16 <= h <= 18, -18 <= k <= 18, -21 <= l <= 21
Reflections collected	11373
Independent reflections	3732
Completeness to theta = 66.97°	93.35 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3732 / 34 / 251
Goodness-of-fit on F^2	1.054
Final R indices [I>2σ(I)]	R_1 = 0.0450, wR_2 = 0.1313
R indices (all data)	R_1 = 0.0505, wR_2 = 0.1374
Largest diff. peak and hole	0.576 and -0.462 e. $Å^{-3}$

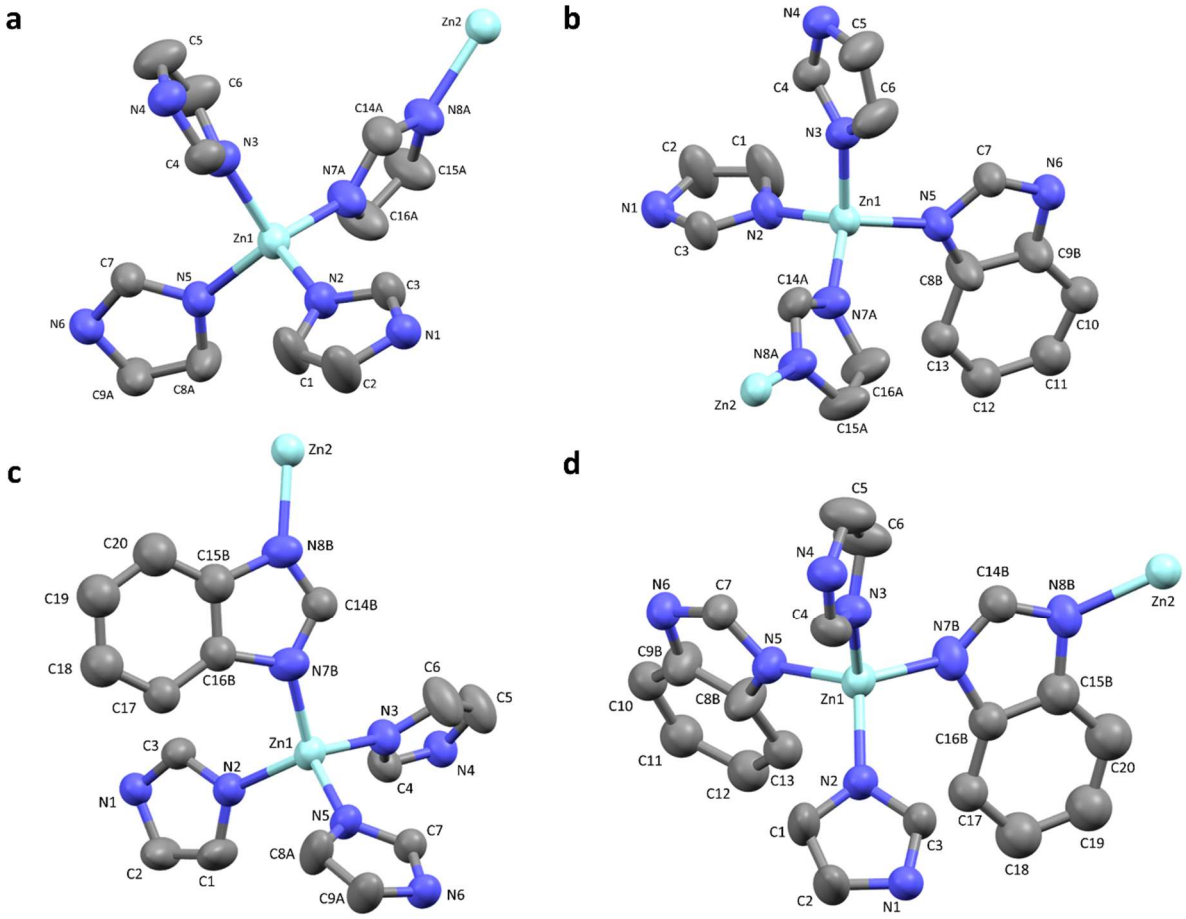

Figure. S3: Graphical representation (thermal ellipsoids) of the four possible configurations for the asymmetric unit of the ZIF-62 produced solvothermally using IPA. Hydrogen atoms and solvent molecules are omitted for clarity. a) Two Zn atoms and four imidazolate linkers. This configuration represents 46% of the coordination environments for Zn atoms. b) Two Zn atoms, three imidazolate linkers and one benzimidazolate. The crystallographic position for benzimidazolate has a maximum occupancy of 50% to prevent the centre of symmetry in *Pbca* group bringing the benzimidazolate linkers related by this centre into contact with each other. c) Two Zn atoms, three imidazolate linkers and one benzimidazolate. The benzimidazolate linker is shifted away from the complementary imidazolate position by 64.13° to avoid clashing with a neighbour imidazolate linker in a totally occupied site. This shift results in partial occupation of solvent molecule sites. d) Two Zn atoms, two imidazolate linkers and two benzimidazolate linkers. All three local configurations: b), c) and d) represent in total the 54% of the coordination environments for Zn atoms in the structure.

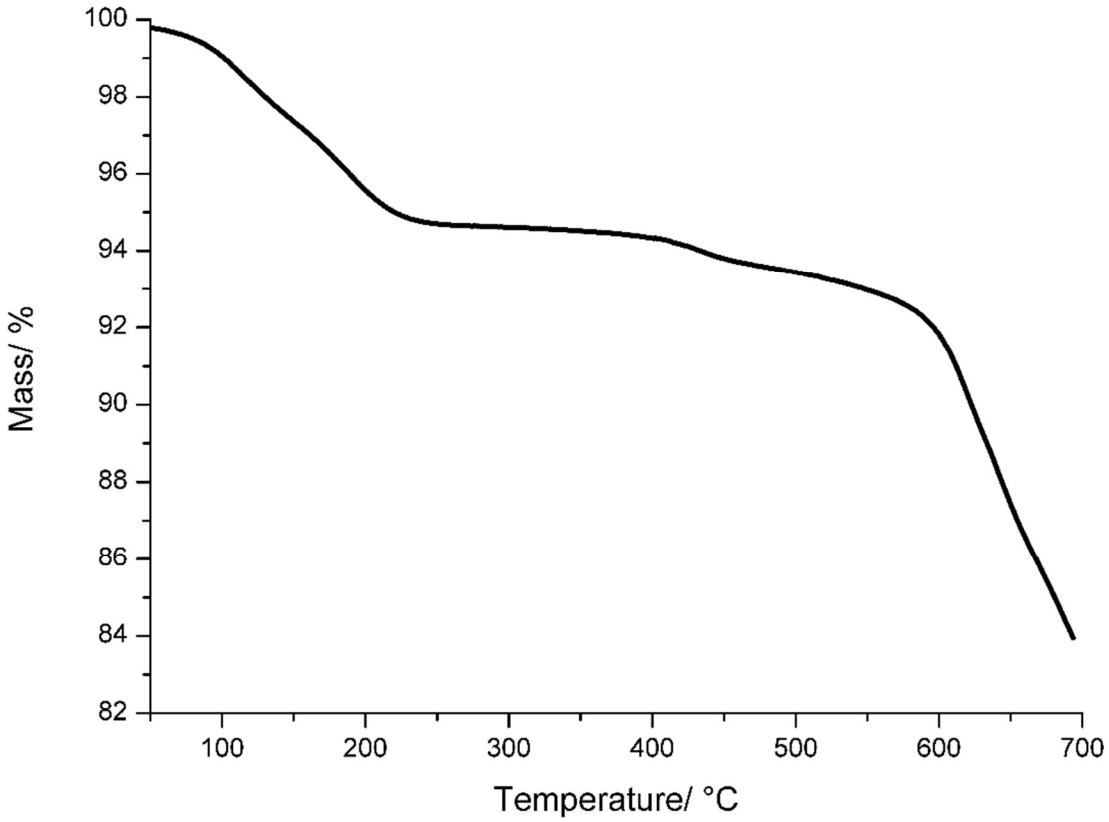

Figure. S4: Thermogravimetric analysis under Ar, of IPA solvothermal ZIF-62. A heating rate of 10 °C min^{-1} was used.

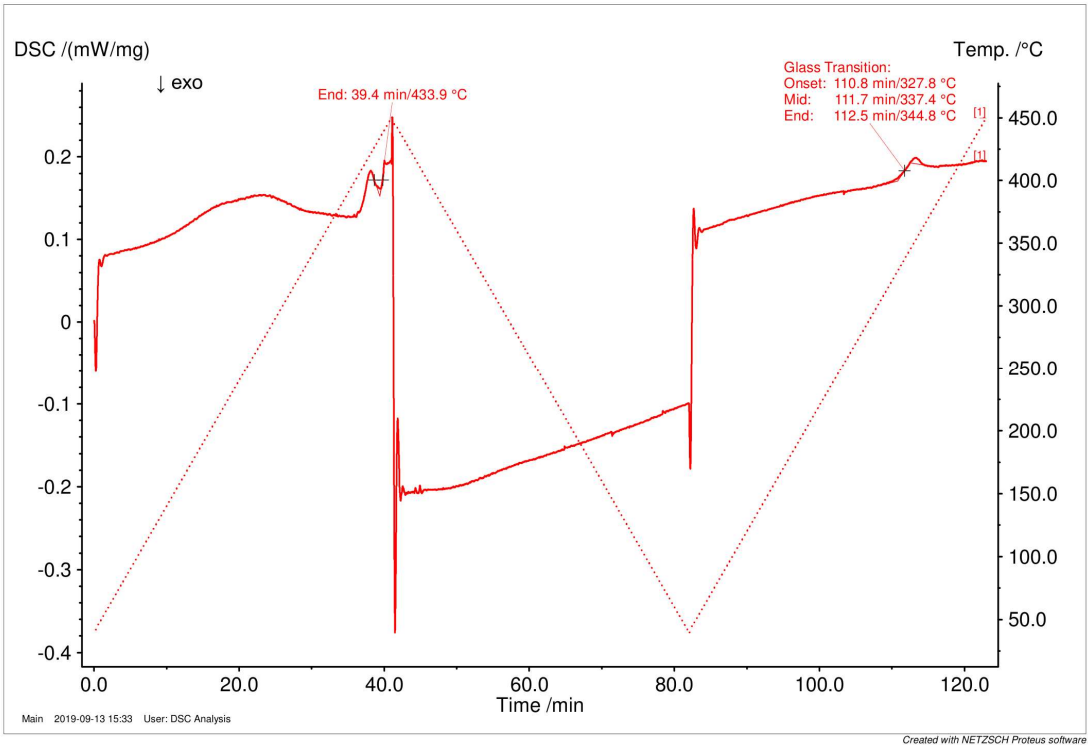

Figure. S5: Differential scanning calorimetry of IPA solvothermal ZIF-62 showing T_m and T_g.

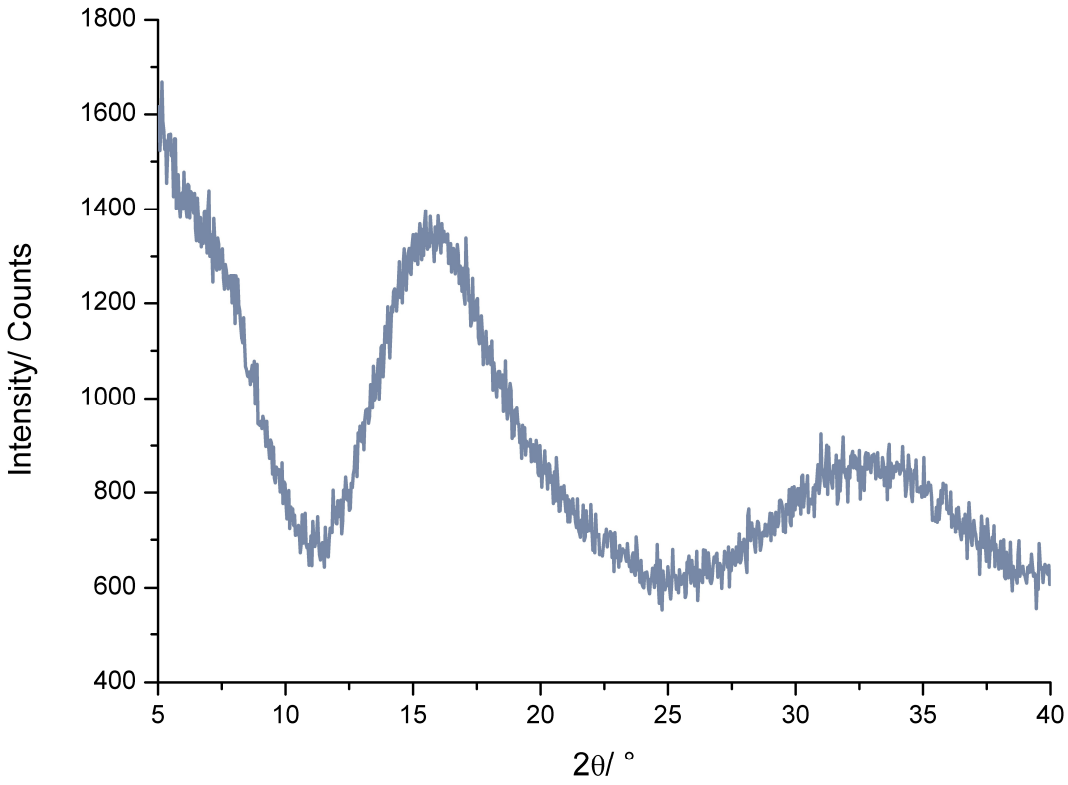

Figure. S6: Room temperature powder X-ray diffraction pattern of IPA solvothermal ZIF-62, after heating to 450°C.

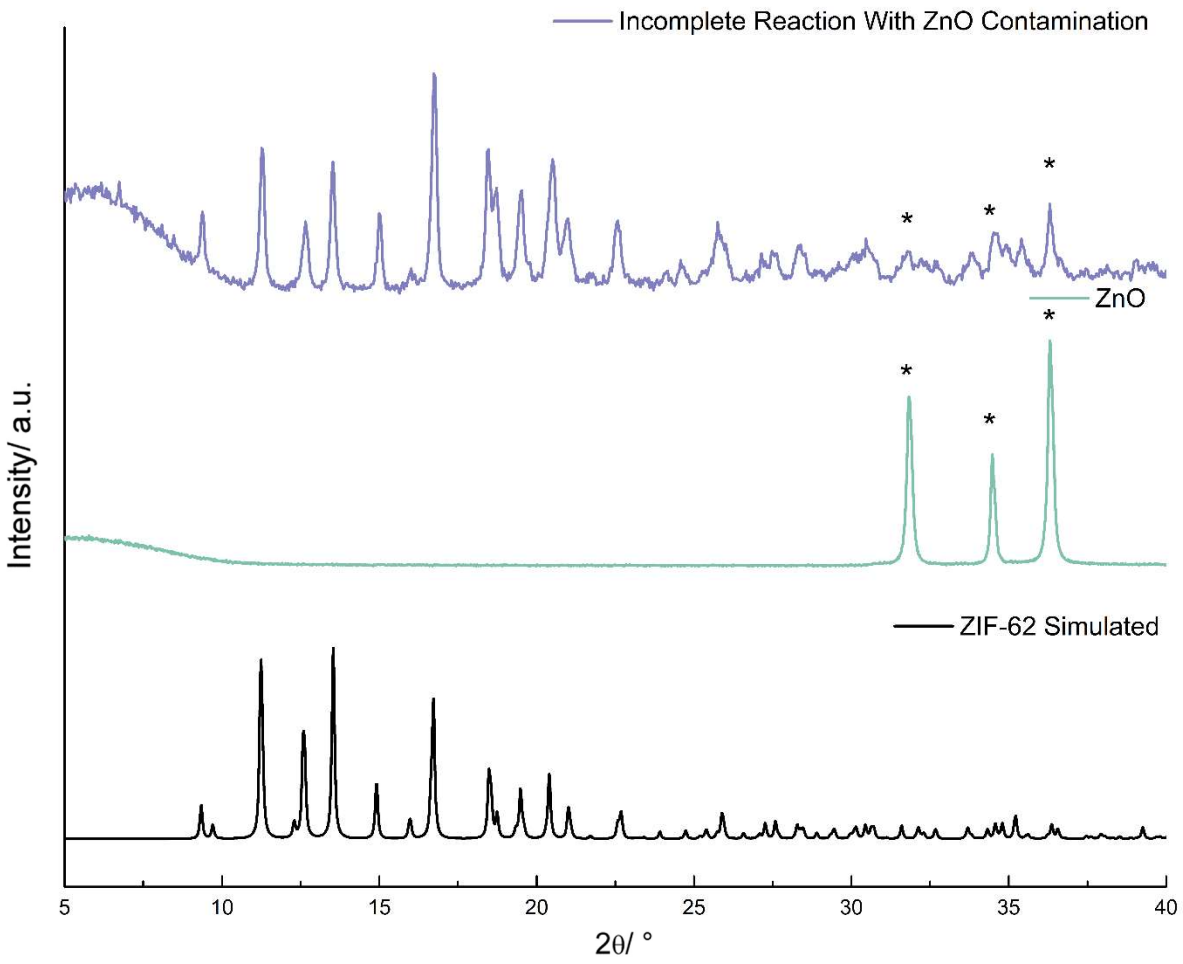

Figure. S7: Powder X-ray diffraction data of a non $Zn(OAc)_2.2H_2O$ catalysed ZIF-62 mechanosynthetic reaction, an experimental ZnO diffraction pattern. ZIF-62 simulated data is also shown using a literature CIF.[1]

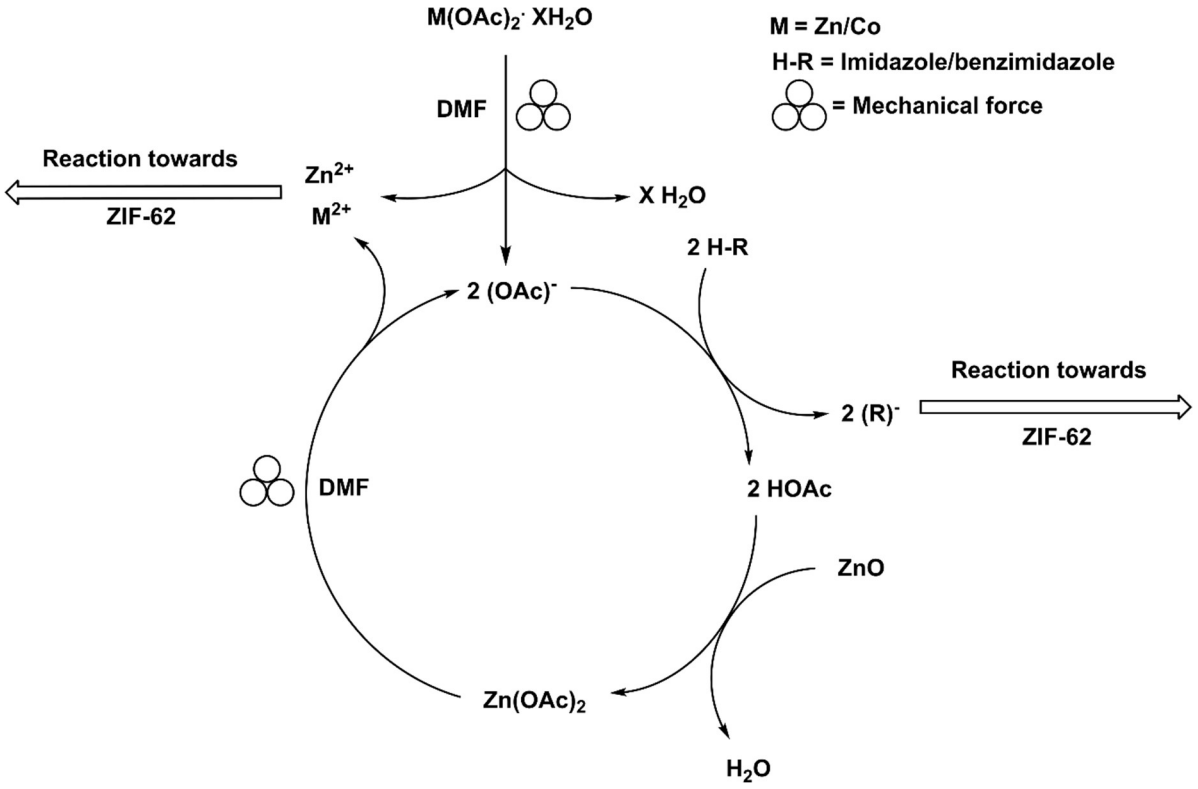

Figure. S8: Proposed catalytic cycle of ZIF-62 mechanosynthesis.

Mixed Metal ZIF-62 Pawley Refinements

Values for lattice parameters were obtained from a literature CIF for DMF solvothermal ZIF-62.[1]

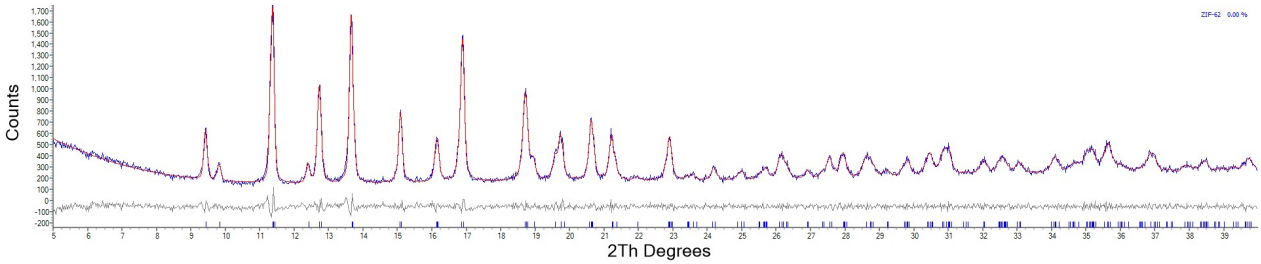

Figure. S9: Pawley refinement of 100% Zn ZIF-62, with difference plot (grey) showing no extra crystalline phases.

Table S7: Crystal data and structure refinement for mechanosynthetic 100% Zn ZIF-62

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.143	*Pbca*	a = 15.460(7) Å	a = 15.6620(14) Å
		b = 15.508(6) Å	b = 15.6621(13) Å
		c = 17.956(6) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

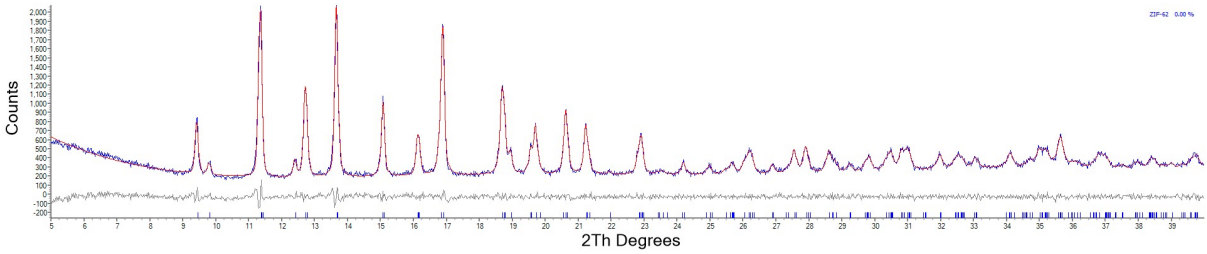

Figure. S10: Pawley refinement of 1% Co ZIF-62, with difference plot (grey) showing no extra crystalline phases.

Table S8: Crystal data and structure refinement for mechanosynthetic 1% Co ZIF-62

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.056	*Pbca*	a = 15.456(5) Å	a = 15.6620(14) Å
		b = 15.494(5) Å	b = 15.6621(13) Å
		c = 17.979(4) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

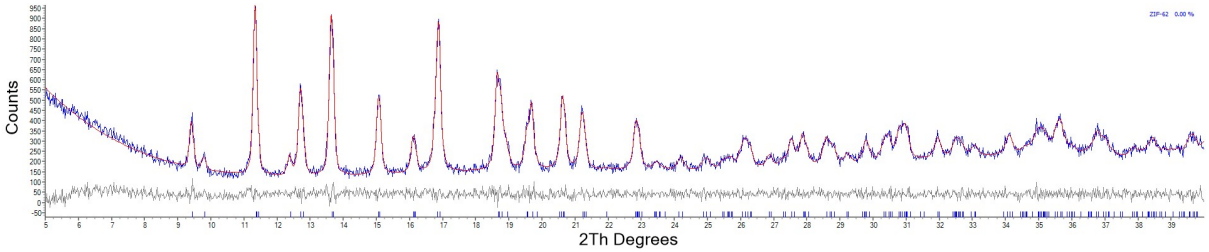

Figure. S11: Pawley refinement of 5% Co ZIF-62, with difference plot (grey) showing no extra crystalline phases.

Table S9: Crystal data and structure refinement for mechanosynthetic 5% Co ZIF-62

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.637	*Pbca*	a = 15.444(9) Å	a = 15.6620(14) Å
		b = 15.525(9) Å	b = 15.6621(13) Å
		c = 17.995(8) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

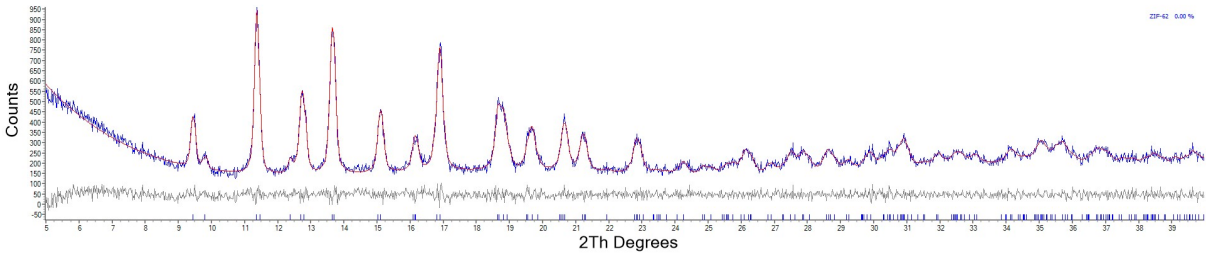

Figure. S12: Pawley refinement of 10% Co ZIF-62, with difference plot (grey) showing no extra crystalline phases.

Table S10: Crystal data and structure refinement for mechanosynthetic 10% Co ZIF-62

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.604	*Pbca*	a = 15.431(11) Å	a = 15.6620(14) Å
		b = 15.573(11) Å	b = 15.6621(13) Å
		c = 18.026(14) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

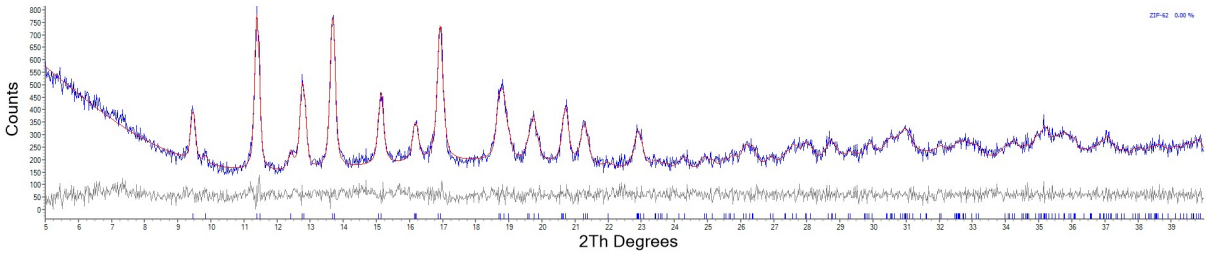

Figure. S13: Pawley refinement of 20% Co ZIF-62, with difference plot (grey) showing no extra crystalline phases.

Table S11: Crystal data and structure refinement for mechanosynthetic 20% Co ZIF-62

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.525	*Pbca*	a = 15.404(13)	a = 15.6620(14) Å
		b = 15.525(15)	b = 15.6621(13) Å
		c = 17.959(17)	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

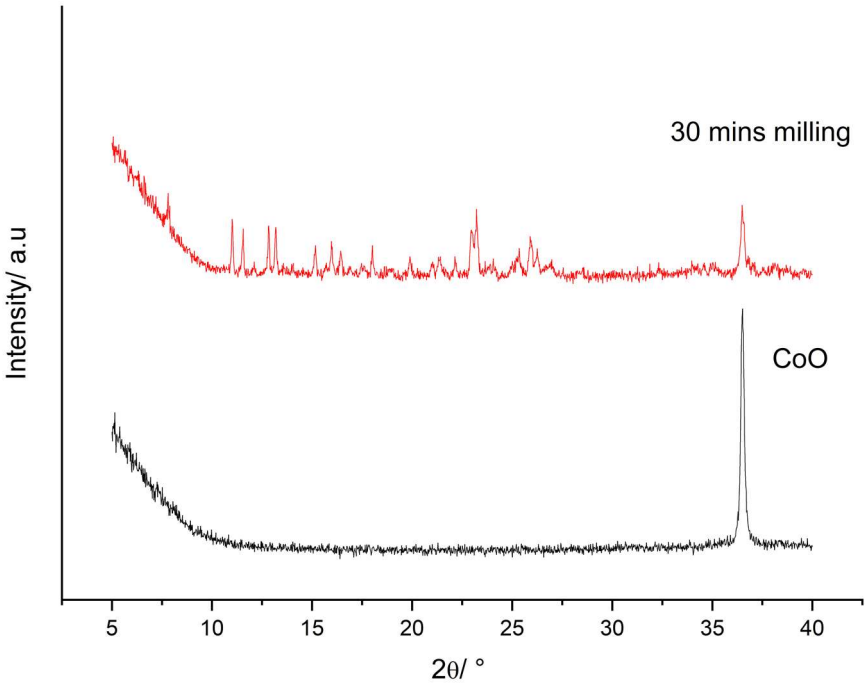

Figure. S14: Failed attempt to produce 100% Co ZIF-62 mechanosynthetically using CoO and $Co(OAc)_2.4H_2O$, showing unreacted CoO and an unknown phase.

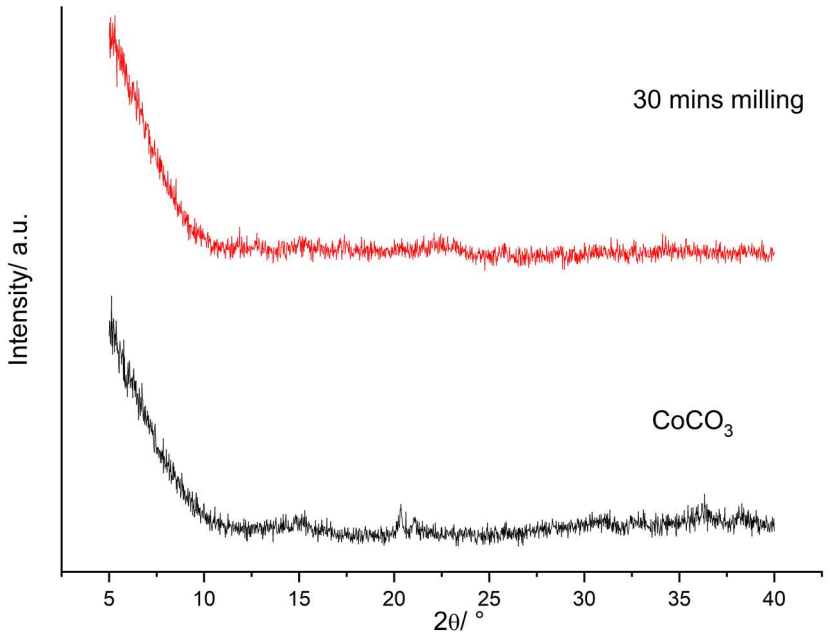

Figure. S15: Failed attempt to produce 100% Co ZIF-62 mechanosynthetically using $CoCO_3$.

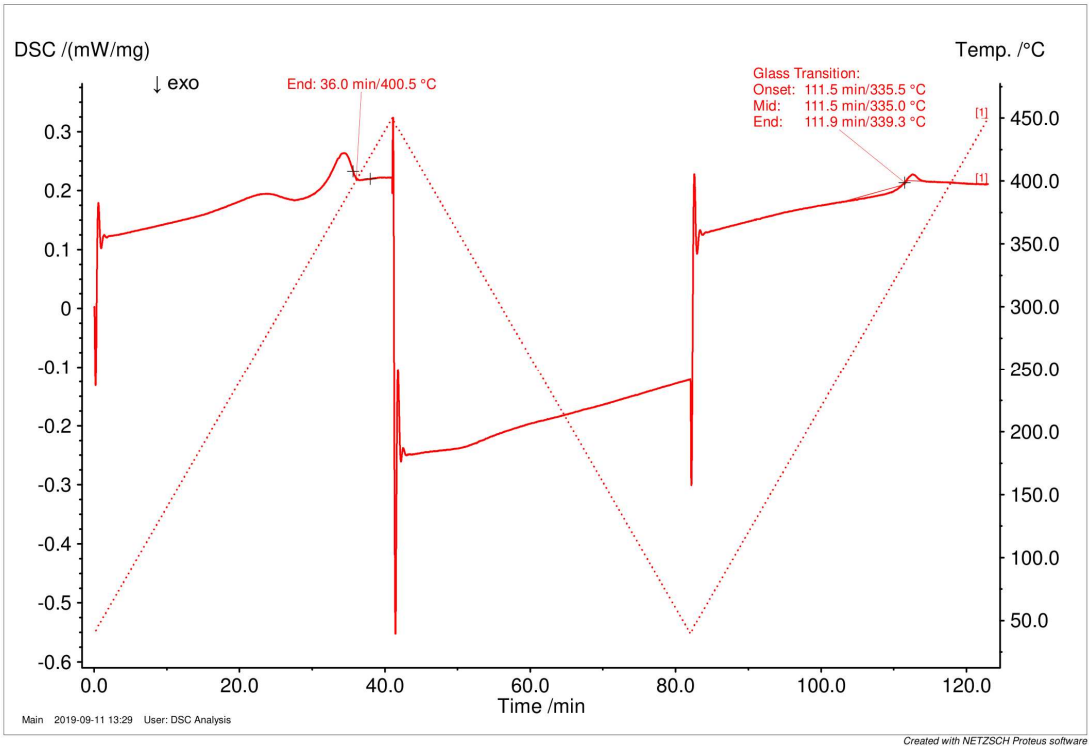

Figure. S16: Differential scanning calorimetry of 100% Zn ZIF-62.

Air TGA of Solvothermal and Mechanochemical ZIF-62

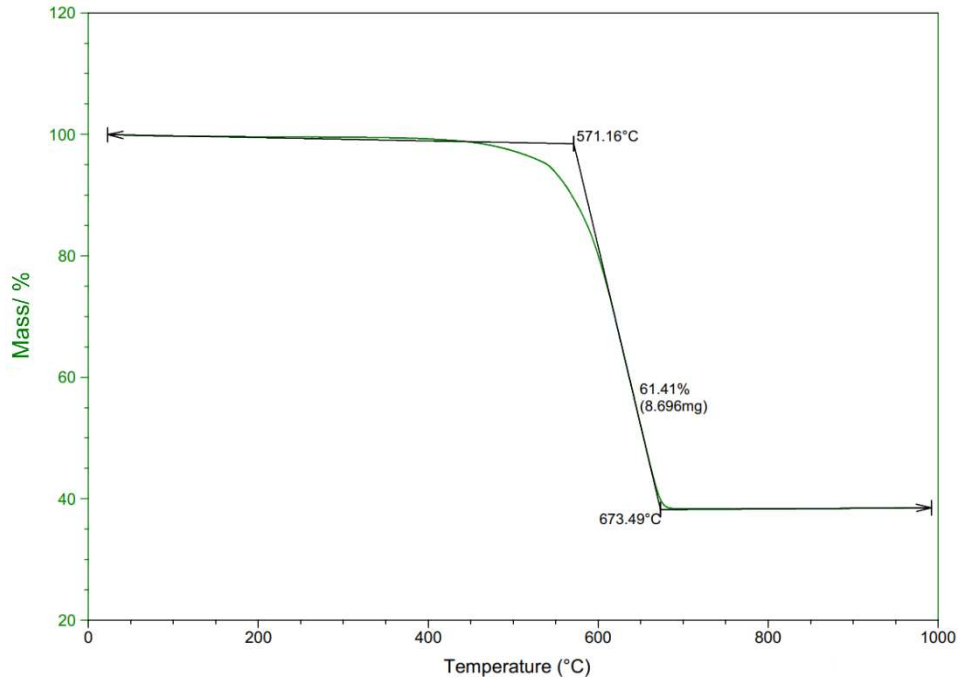

Figure. S17: Thermogravimetric analysis of mechanochemical 100% Zn ZIF-62 under air, using a heating rate of 20 °C min^{-1}.

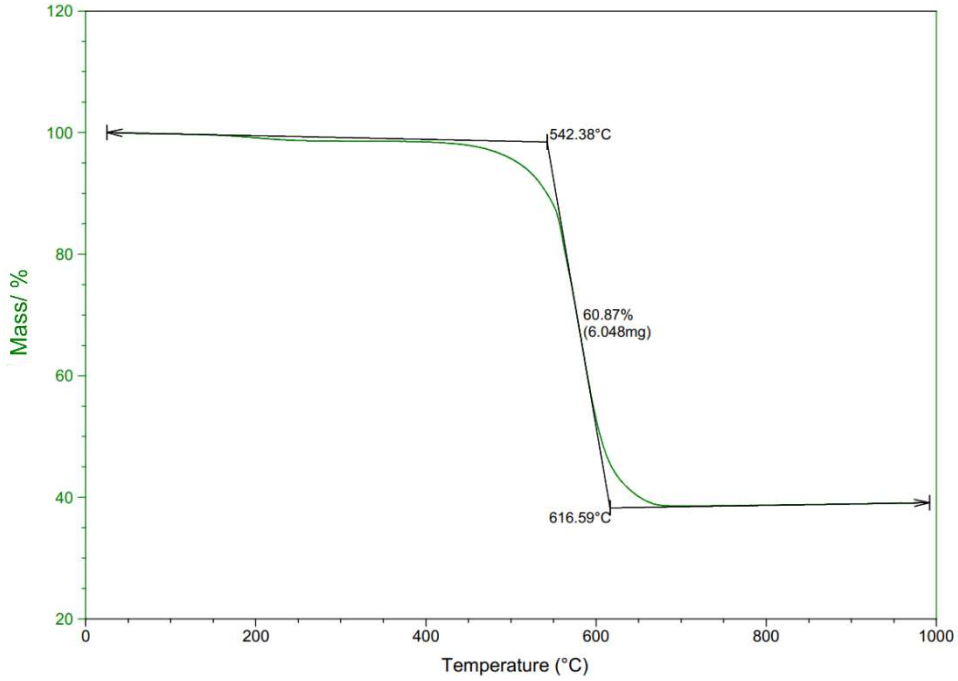

Figure. S18: Thermogravimetric analysis of DMF solvothermal 100% Zn ZIF-62 under air, using a heating rate of 20 °C min^{-1}.

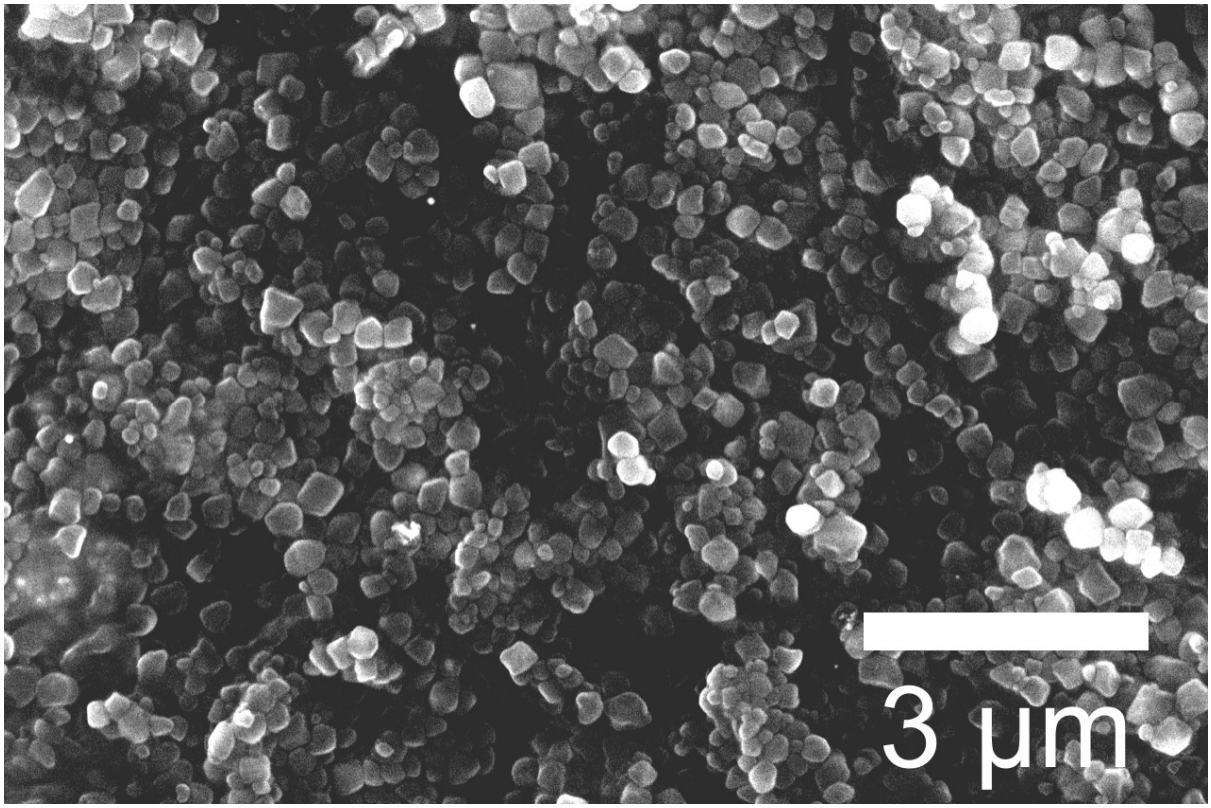

Figure. S19: Scanning electron microscope image of 100% Zn ZIF-62 produced mechanochemically, showing sub micrometre particle sizes.

Mixed Metal ZIF-62 ^{1}H NMR

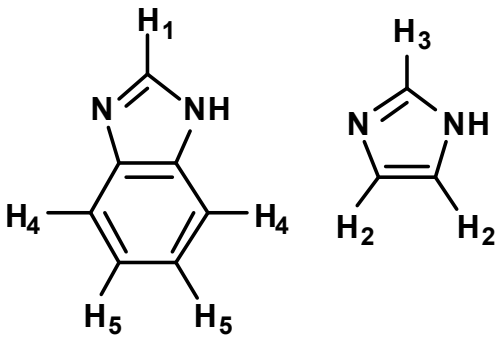

Figure. S20: Structure of imidazole, and benzimidazole. H_1 and H_3 integrations are used to determine linker ratios in crystalline and glass samples.

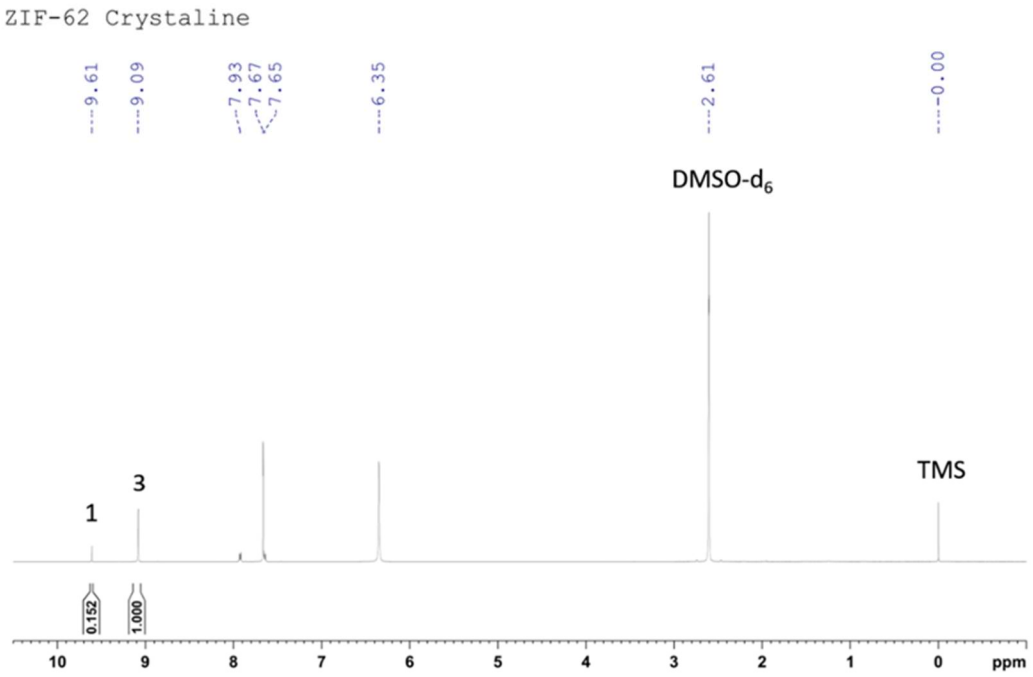

Figure. S21: ^{1}H nuclear magnetic resonance spectra of 100% Zn ZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s , H_3), 7.65 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

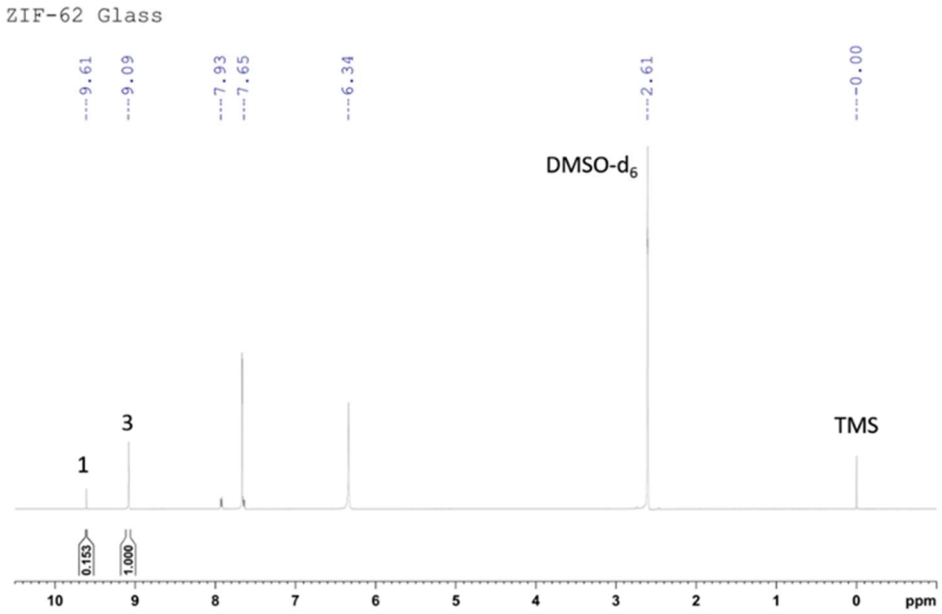

Figure. S22: ^{1}H nuclear magnetic resonance spectra of 100% Zn a_gZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s , H_3), 7.65 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

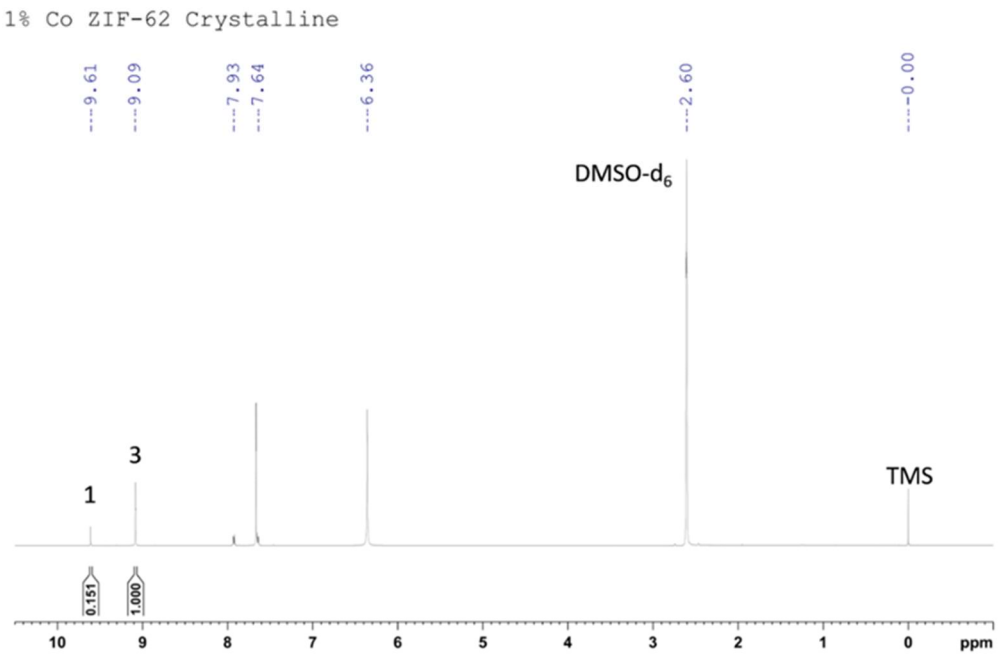

Figure. S23: ^{1}H nuclear magnetic resonance spectra of 1% Co ZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s , H_3), 7.64 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

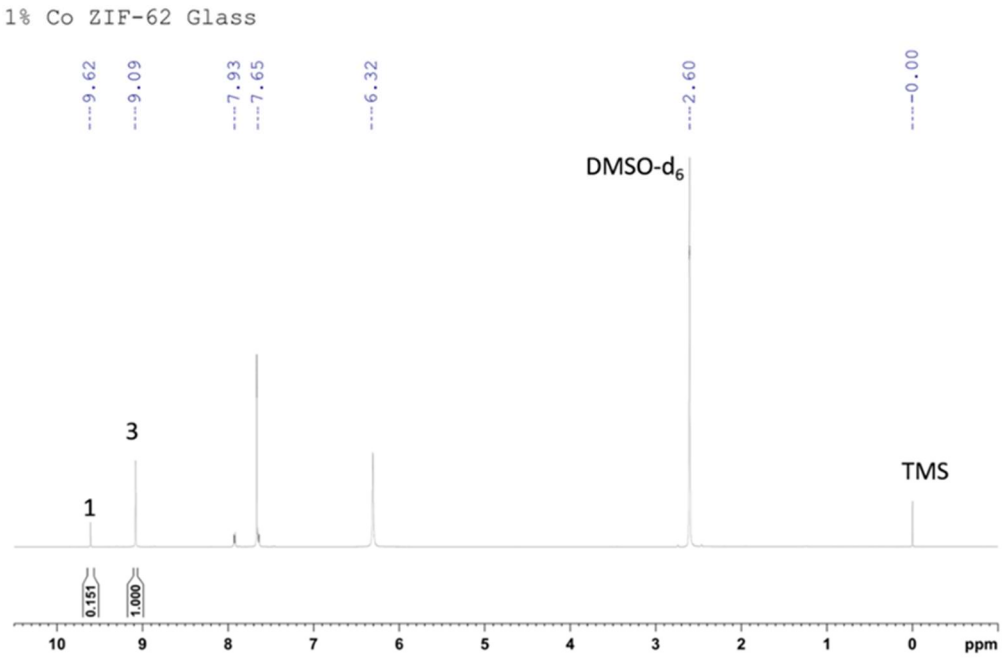

Figure. S24: ^{1}H nuclear magnetic resonance spectra of 1% Co a_gZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.62 (1H, s, H_1), 9.09 (1H, s , H_3), 7.65 (5H, m, aromatic), 2.60 (DMSO), 0.00 (TMS).

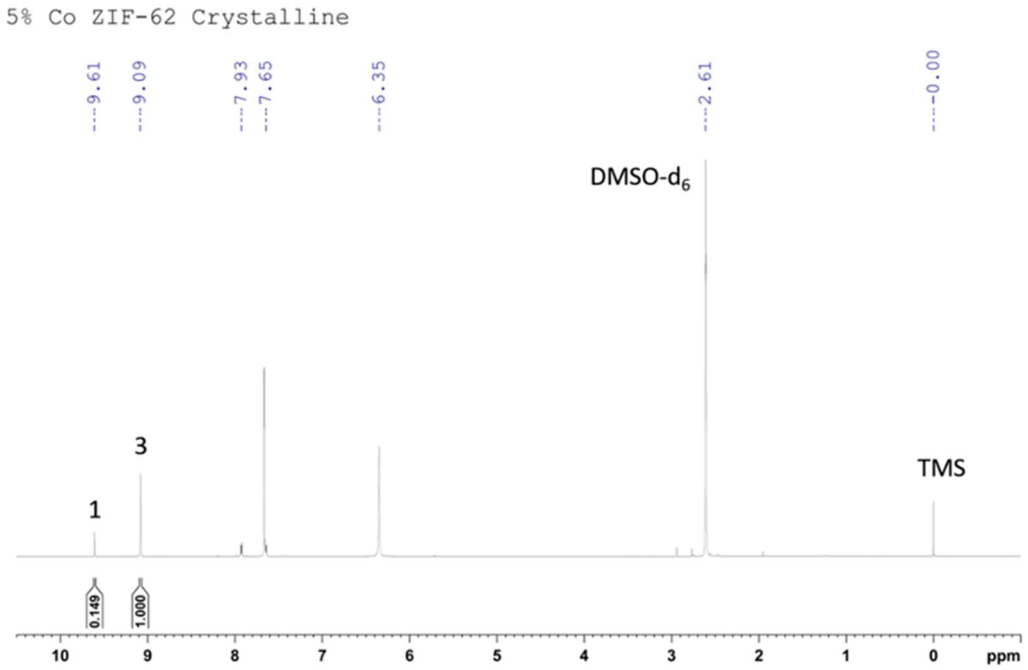

Figure. S25: ^{1}H nuclear magnetic resonance spectra of 5% Co ZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s , H_3), 7.65 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

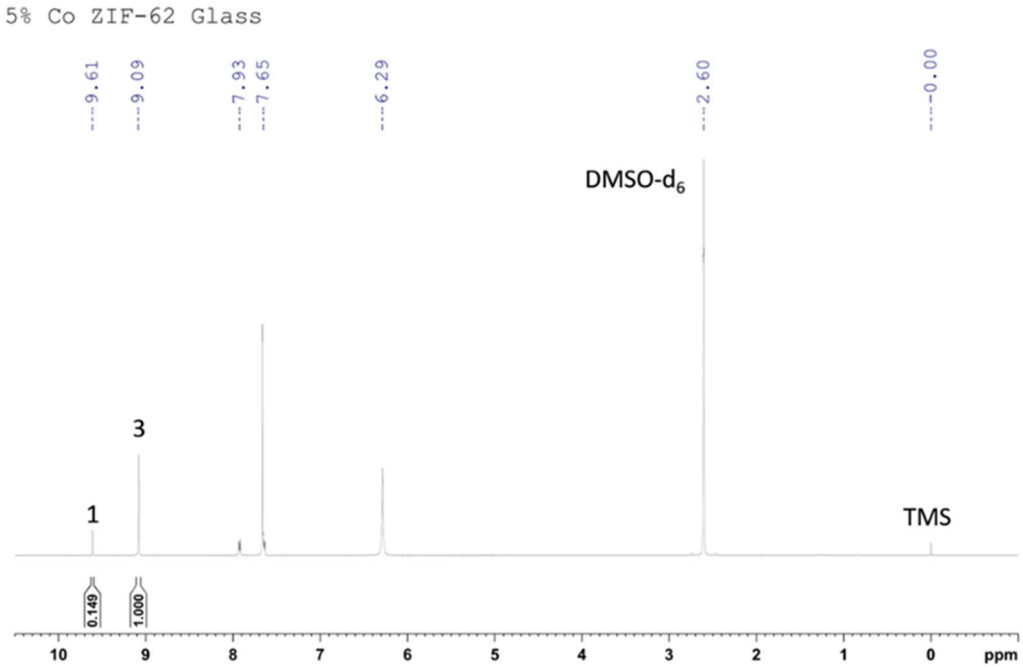

Figure. S26: ^{1}H nuclear magnetic resonance spectra of 5% Co a_gZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s, H_3), 7.65 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

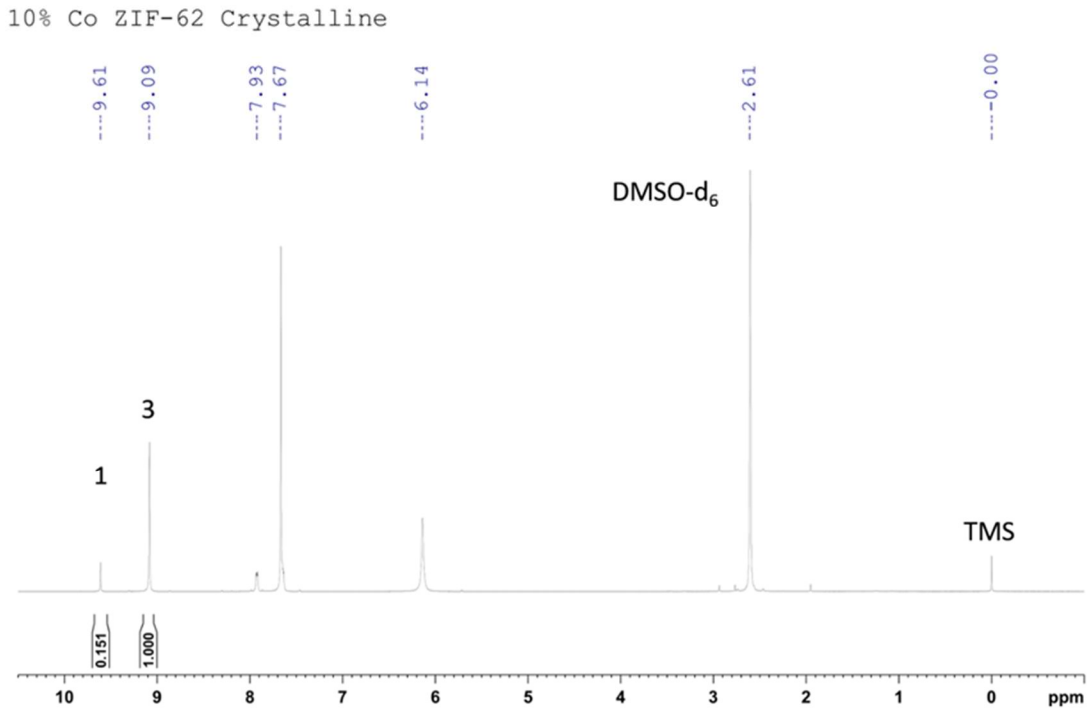

Figure. S27: ^{1}H nuclear magnetic resonance spectra of 10% Co ZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s, H_3), 7.67 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

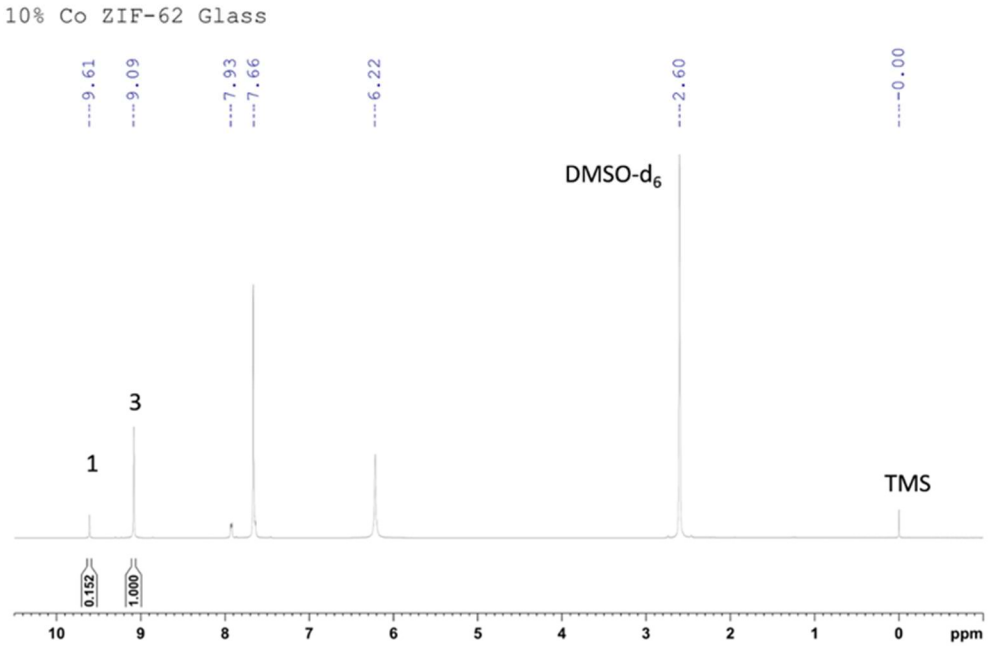

Figure. S28: ^{1}H nuclear magnetic resonance spectra of 10% Co a_gZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s, H_3), 7.66 (5H, m, aromatic), 2.60 (DMSO), 0.00 (TMS).

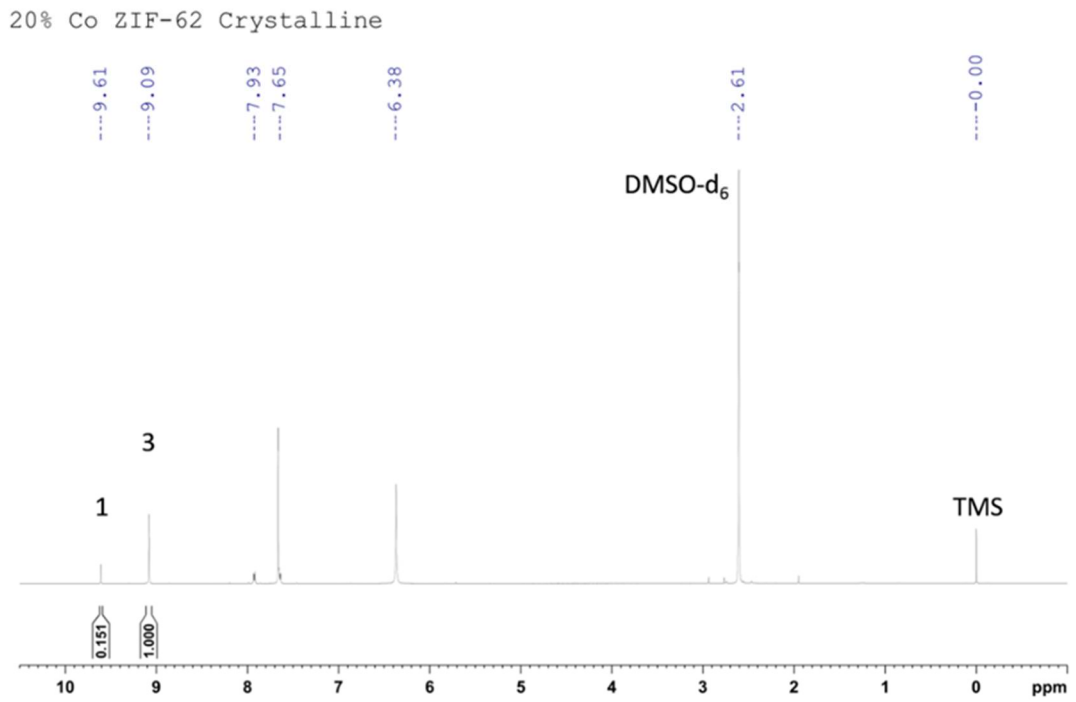

Figure. S29: ^{1}H nuclear magnetic resonance spectra of 20% Co ZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s, H_3), 7.65 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

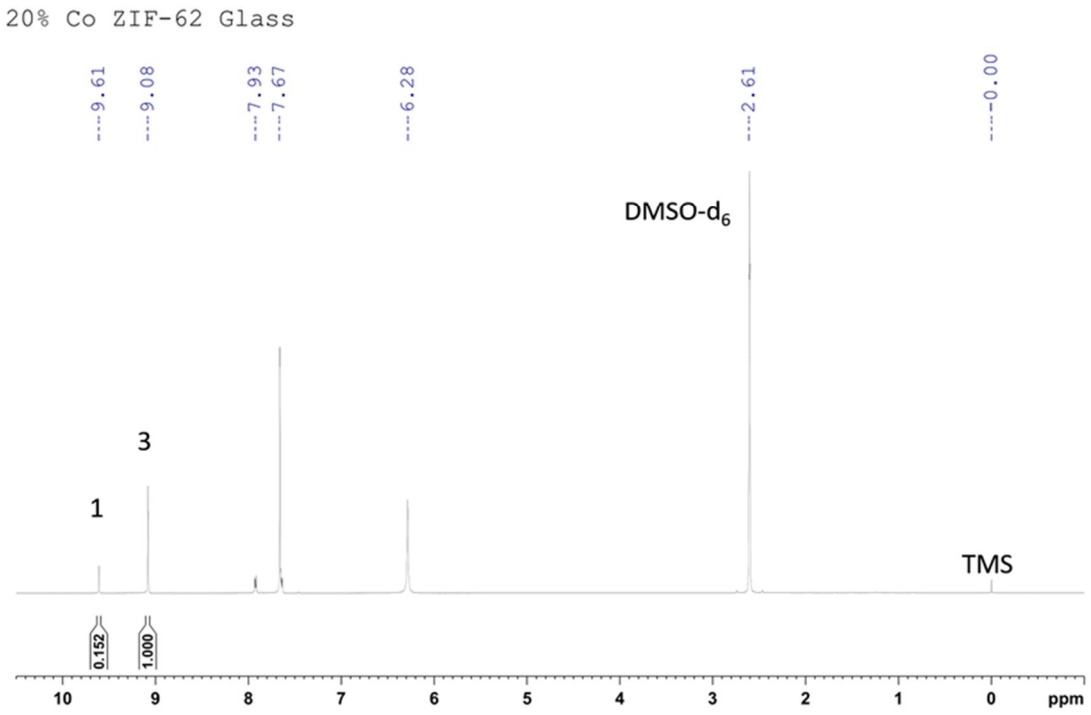

Figure. S30: ^{1}H nuclear magnetic resonance spectra of 20% Co a_gZIF-62. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.61 (1H, s, H_1), 9.09 (1H, s, H_3), 7.67 (5H, m, aromatic), 2.61 (DMSO), 0.00 (TMS).

Mixed Metal ZIF-62 DSC

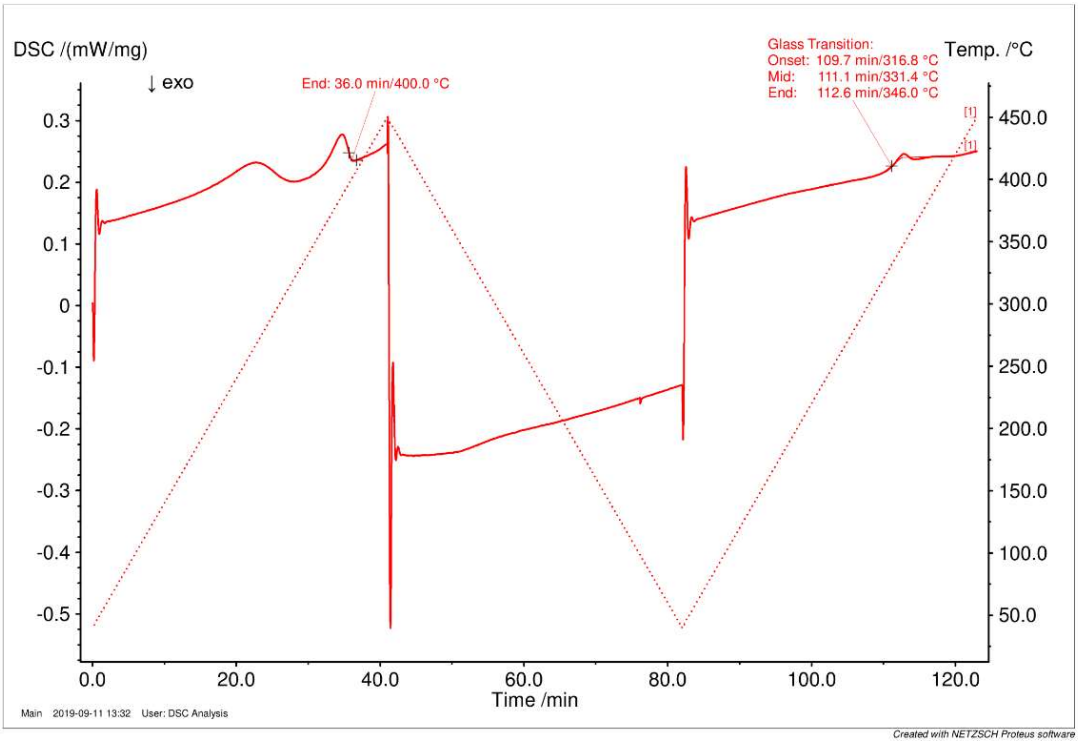

Figure. S31: Differential scanning calorimetry of 1% Co ZIF-62.

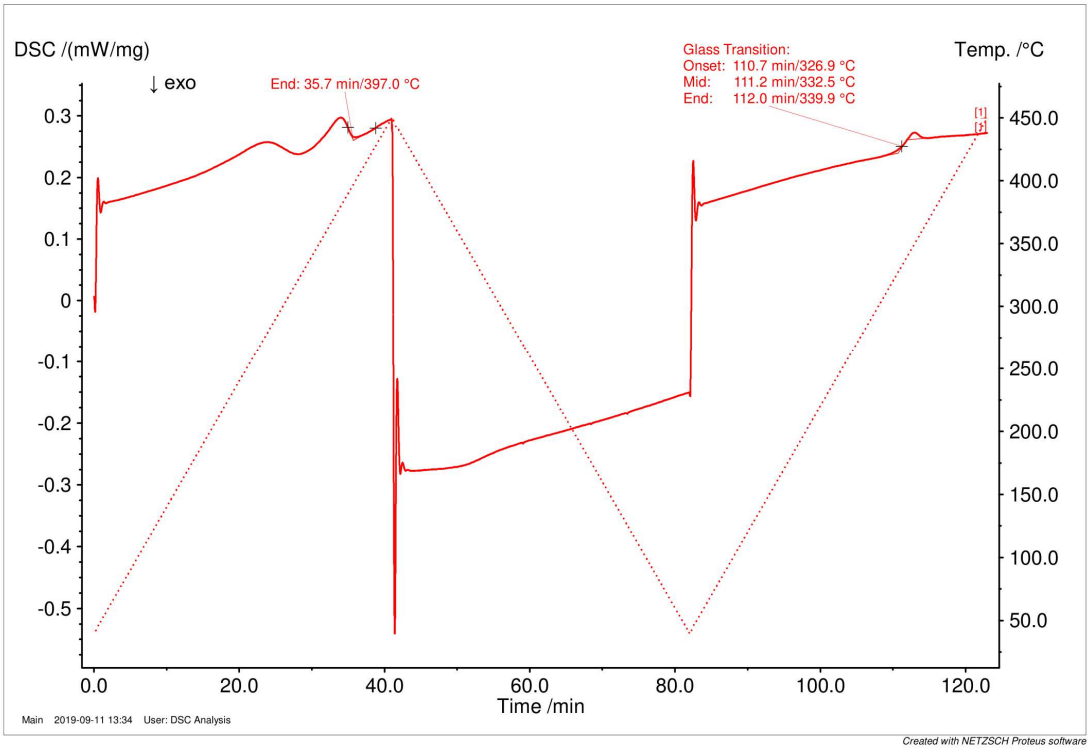

Figure. S32: Differential scanning calorimetry of 5% Co ZIF-62.

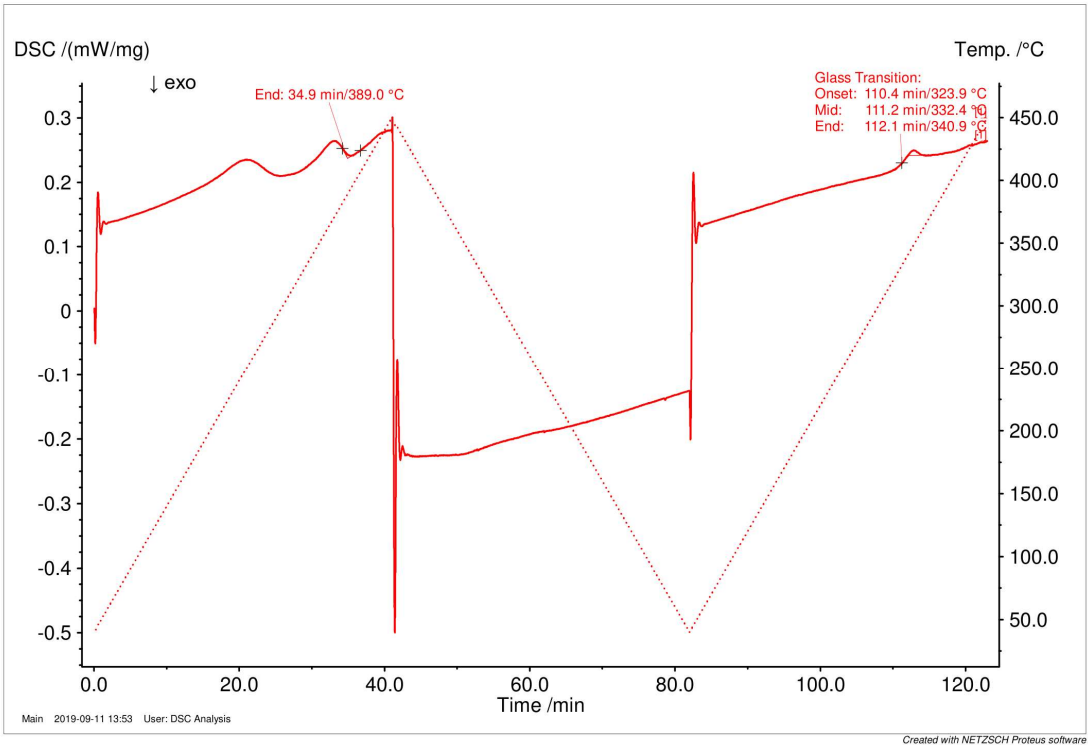

Figure. S33: Differential scanning calorimetry of 10% Co ZIF-62.

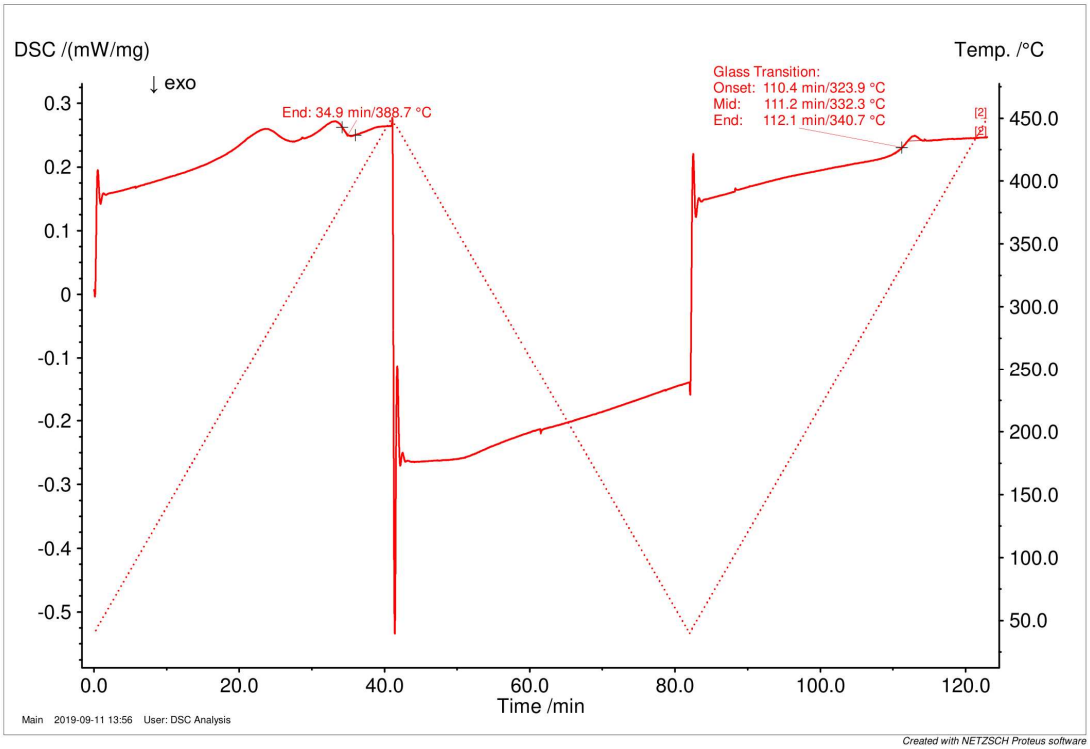

Figure. S34: Differential scanning calorimetry of 20% Co ZIF-62.

Mixed Metal ZIF-62 TGA

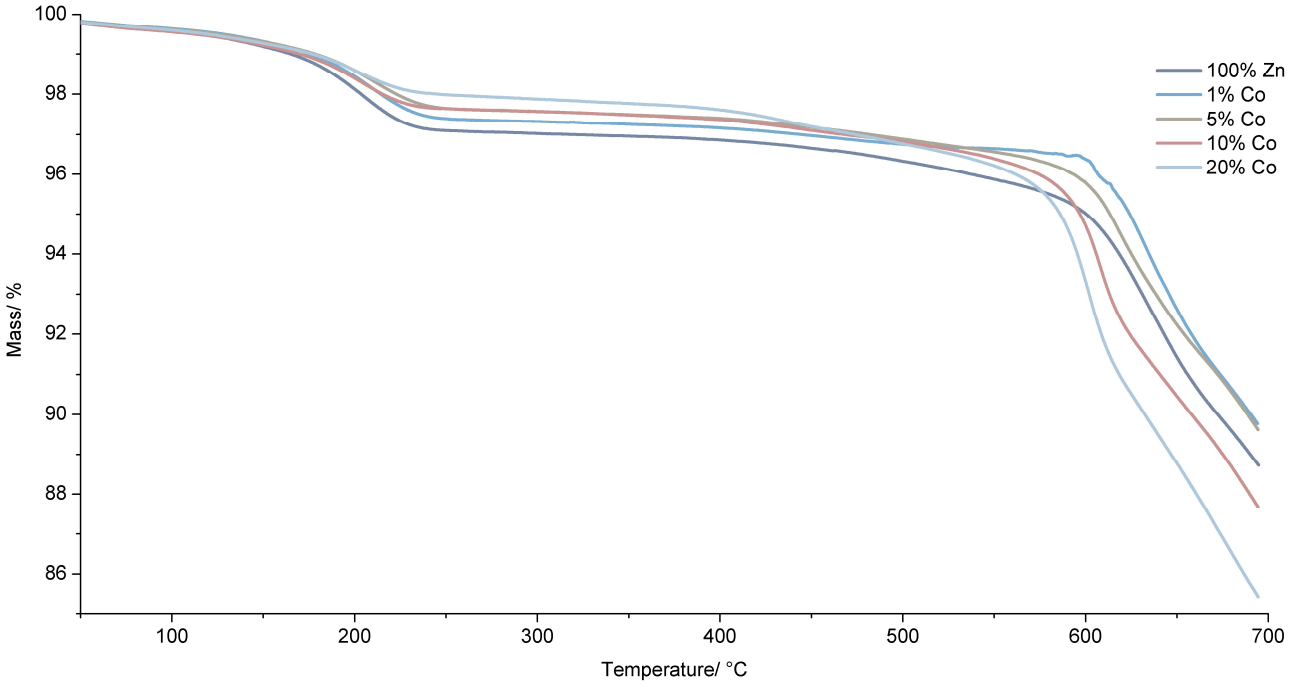

Figure. S35: Thermogravimetric analysis performed on mechanochemically produced Co/Zn ZIF-62 at 10 °C min^{-1} under Ar, showing no mass loss during melting (< 400 °C). Initial mass loss is ascribed to the loss of residual water/solvent.

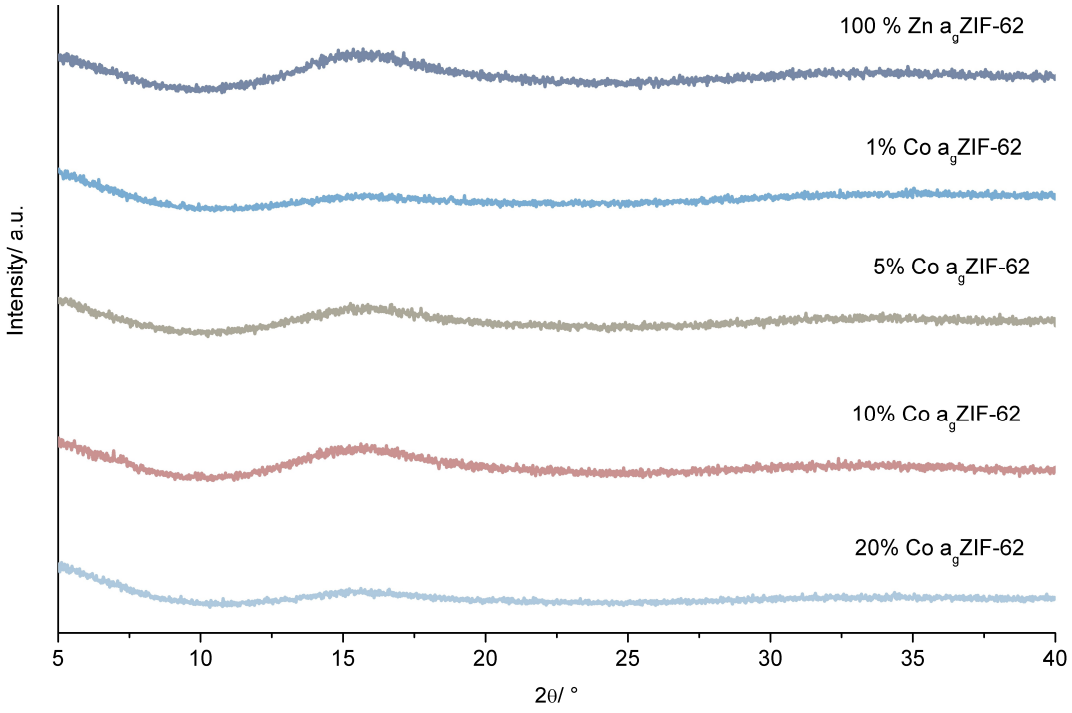

Figure. S36: Powder X-ray diffraction of a_gZIF-62 containing different quantities of Co^{2+} and Zn^{2+}.

SEM-EDX of Co/Zn ZIF-62 glasses

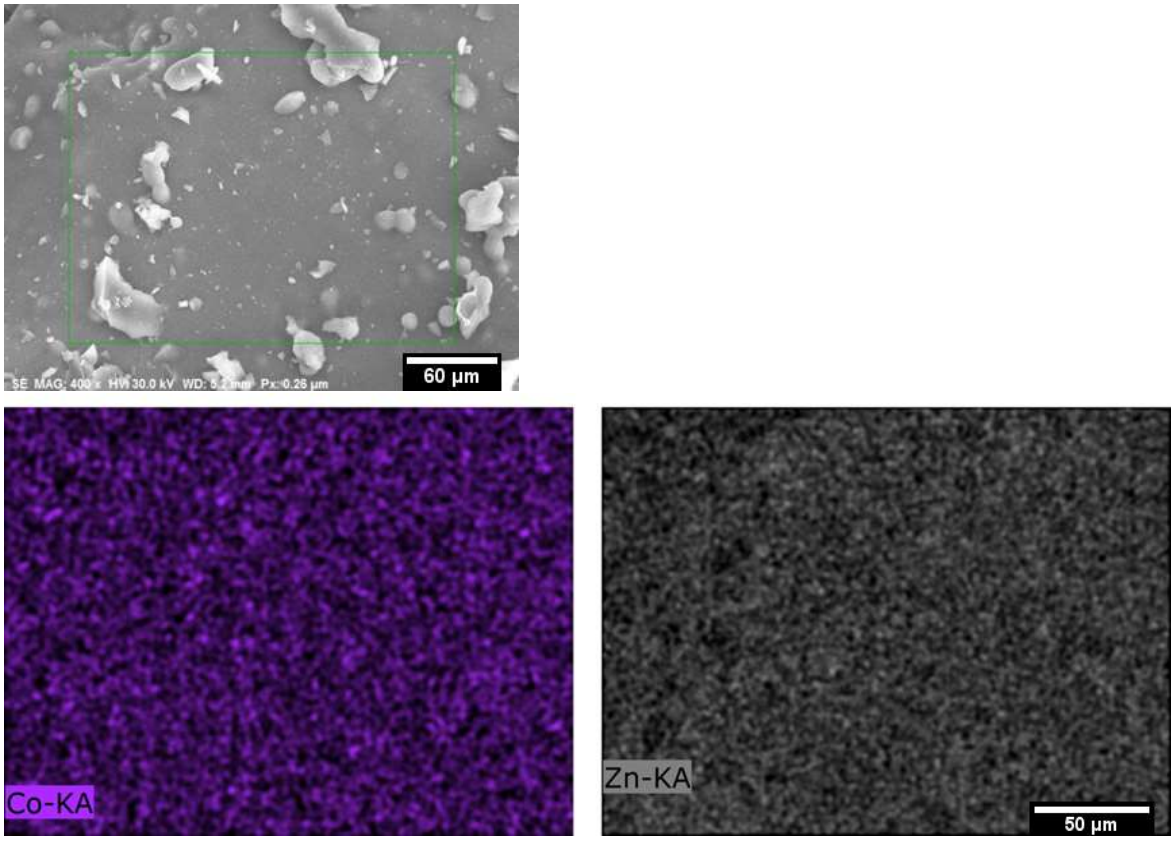

Figure. S37: 1% Co a_gZIF-62 SEM image, and EDX maps for Co and Zn.

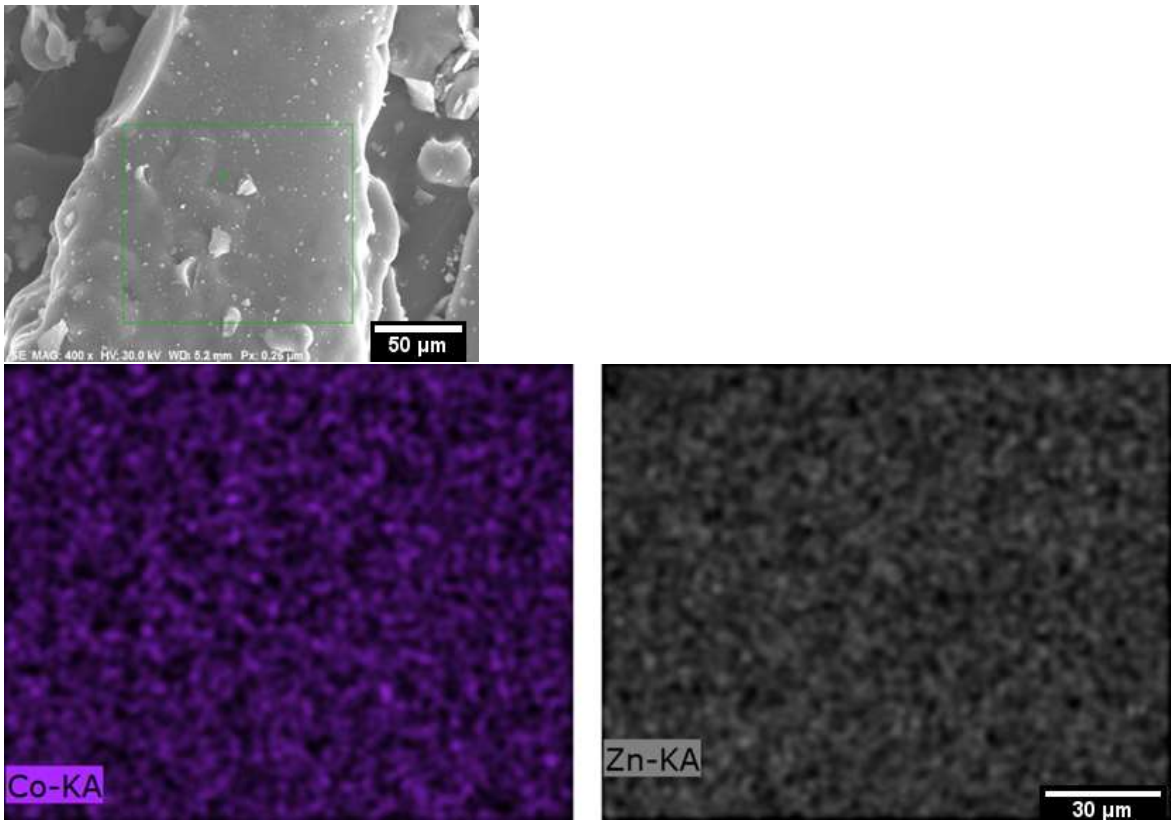

Figure. S38: 5% Co a_gZIF-62 SEM image, and EDX maps for Co and Zn

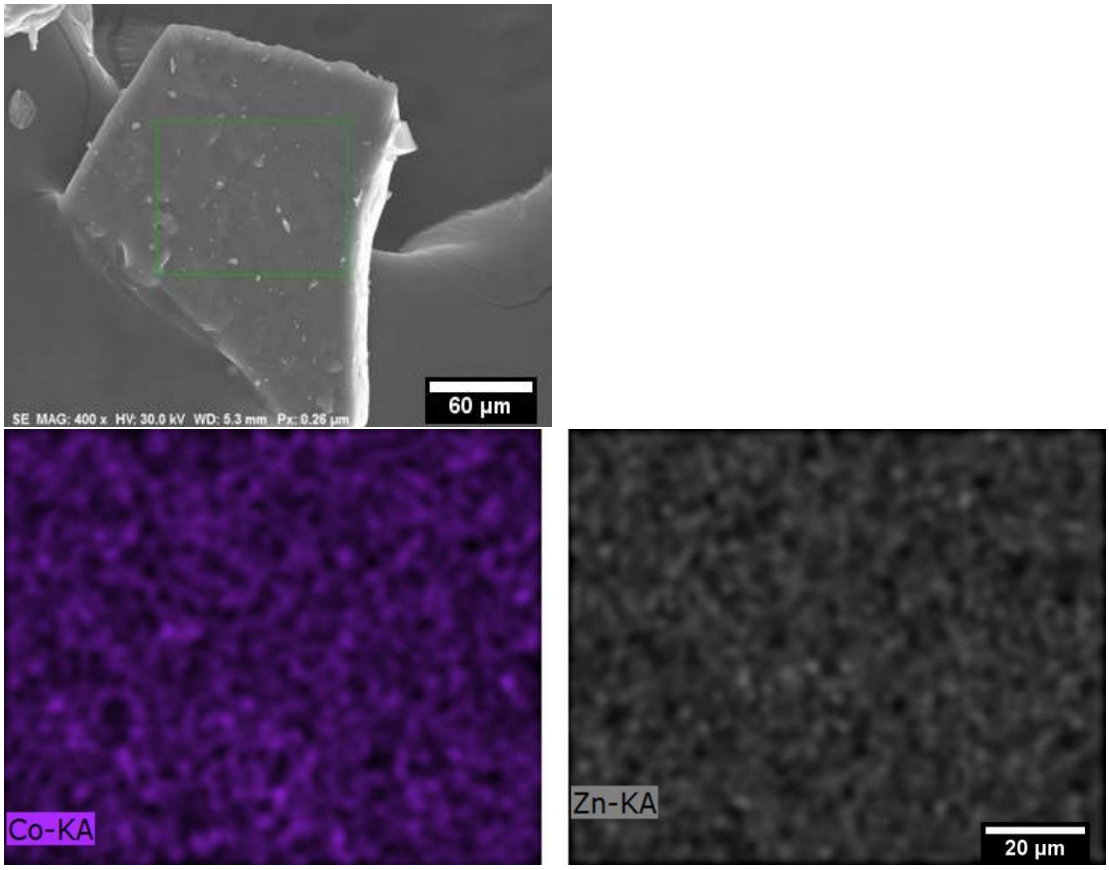

Figure. S39: 10% Co a_gZIF-62 SEM image, and EDX maps for Co and Zn.

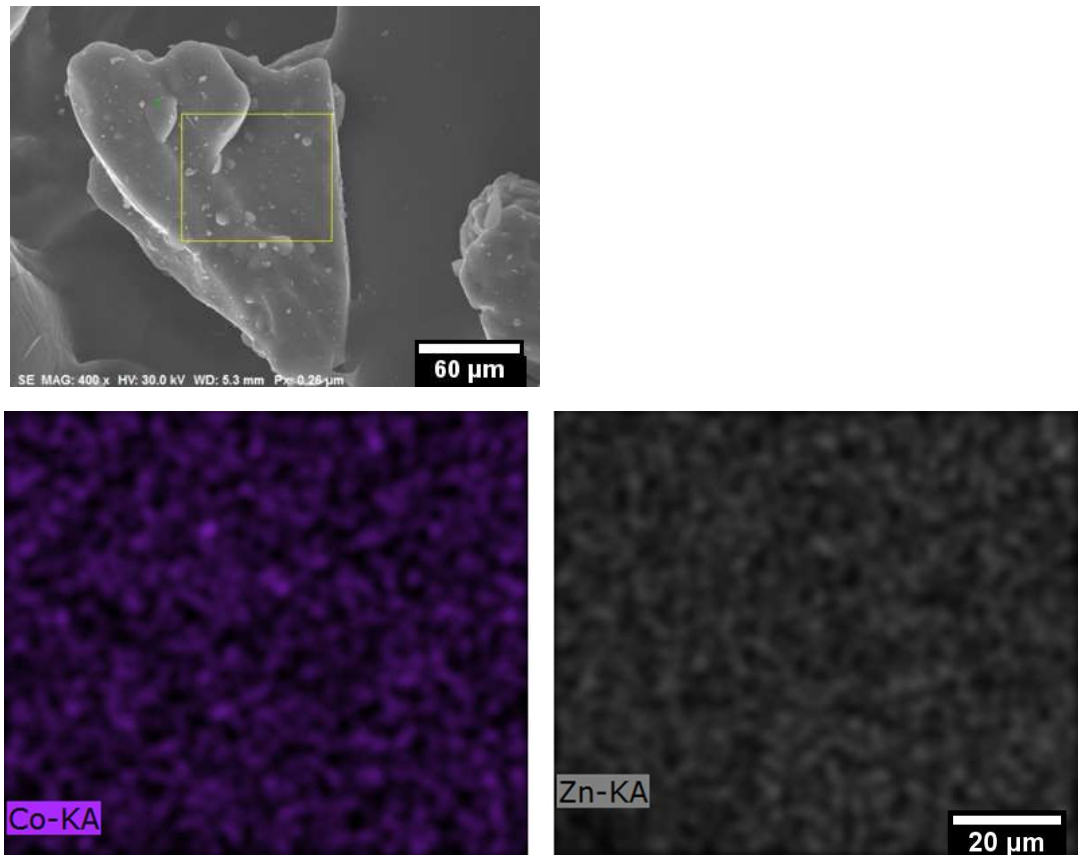

Figure. S40: 20% Co a_gZIF-62 SEM image, and EDX maps for Co and Zn.

Table S8: ICP-AES results, showing Zn and Co ratios of mechanochemically produced Zn/Co ZIF-62 crystalline and glass samples

Sample	Co (PPM)	PPM Zn (PPM)	Co (%)	Zn (%)
1% Co ZIF-62	0.02	2.91	0.73	99.27
1% Co a_gZIF-62	0.02	2.68	0.74	99.26
5% Co ZIF-62	0.15	3.52	4.18	95.82
5% Co a_gZIF-62	0.07	1.65	4.10	95.90
10% Co ZIF-62	0.25	2.90	8.66	91.34
10% Co a_gZIF-62	0.04	0.50	8.58	91.42
20% Co ZIF-62	0.50	2.64	18.80	81.20
20% Co a_gZIF-62	0.32	1.63	19.60	80.40

Table S9: CHN analysis of mechanochemically produced Zn/Co ZIF-62 crystalline and glass samples, and predicted values based upon the shown chemical formulae

Sample	C (%)	H (%)	N (%)
100% Zn ZIF-62	39.5	3.0	25.7
100% Zn a_gZIF-62	39.4	3.0	25.8
1% Co ZIF-62	39.6	3.0	25.6
1% Co a_gZIF-62	39.3	2.9	25.6
5% Co ZIF-62	39.7	2.9	25.5
5% Co a_gZIF-62	39.5	2.9	25.5
10% Co ZIF-62	39.7	2.9	25.4
10% Co a_gZIF-62	39.3	3.1	25.5
20% Co ZIF-62	39.8	3.0	25.5
20% Co a_gZIF-62	39.5	2.9	25.6
Predicted	39.8	3.1	26.4

Optical Images

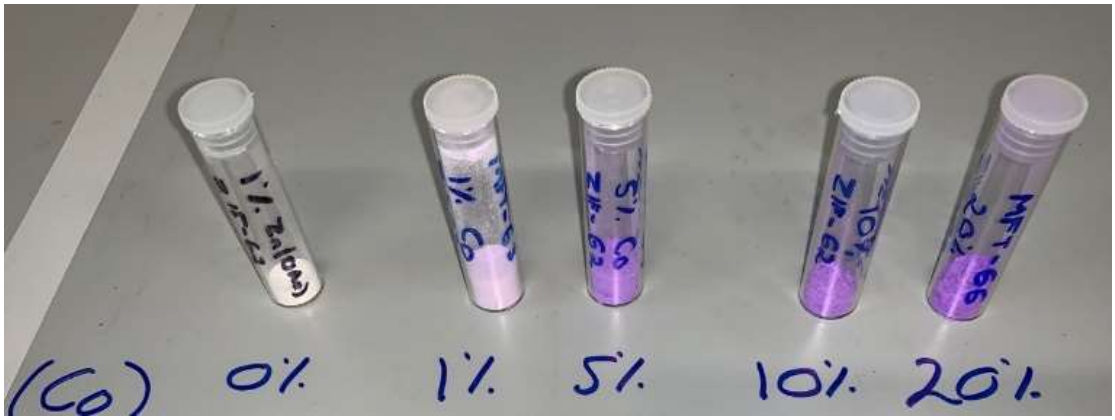

Figure. S41: Photograph of ZIF-62 crystalline samples produced by vibratory ball milling, showing a gradual progression from white through pink to purple ZIF-62 as Co^{2+} content is increased.

Variable Linker Ratio ZIF-62 and ZIF-UC-5 Refinements

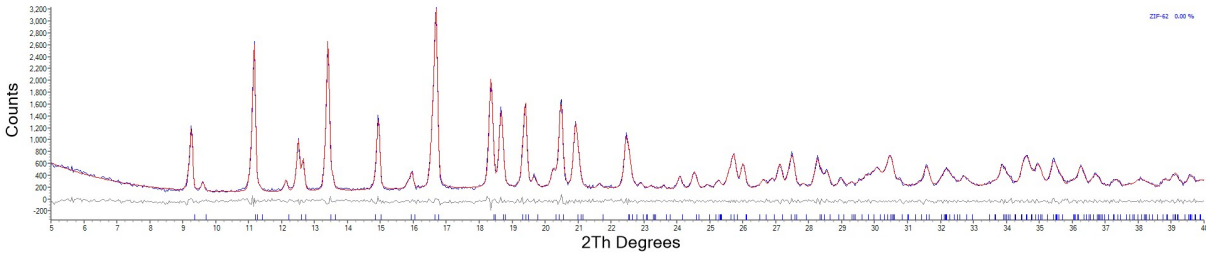

Figure. S42: Pawley refinement of $[Zn(Im)_{1.80}(bIm)_{0.20}]$, with difference plot (grey) showing no extra crystalline phases.

Table S10: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.80}(bIm)_{0.20}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.051	*Pbca*	a = 15.4665(18) Å	a = 15.6620(14) Å
		b = 15.759(2) Å	b = 15.6621(13) Å
		c = 18.204(2) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

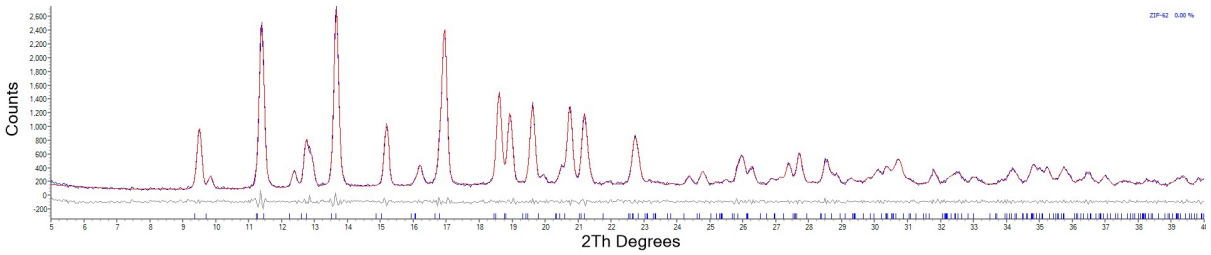

Figure. S43: Pawley refinement of $[Zn(Im)_{1.85}(bIm)_{0.15}]$, with difference plot (grey) showing no extra crystalline phases.

Table S11: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.85}(bIm)_{0.15}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.014	*Pbca*	a = 15.437(2) Å	a = 15.6620(14) Å
		b = 15.744(2) Å	b = 15.6621(13) Å
		c = 18.212(3) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

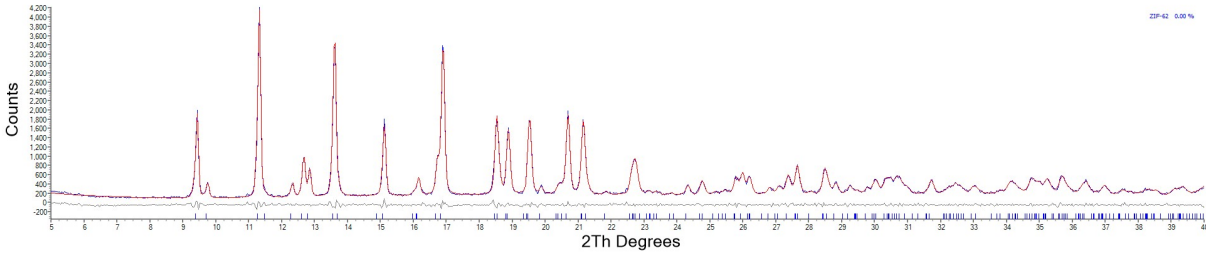

Figure. S44: Pawley refinement of $[Zn(Im)_{1.90}(bIm)_{0.10}]$, with difference plot (grey) showing no extra crystalline phases.

Table S12: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.90}(bIm)_{0.10}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.315	*Pbca*	a = 15.4062(15) Å	a = 15.6620(14) Å
		b = 15.6901(16) Å	b = 15.6621(13) Å
		c = 18.211(2) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

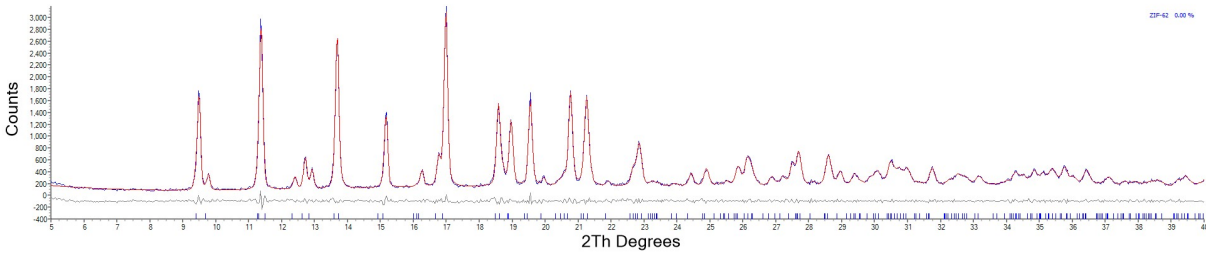

Figure. S45: Pawley refinement of $Zn(Im)_{1.95}(bIm)_{0.05}$, with difference plot (grey) showing no extra crystalline phases.

Table S13: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.90}(bIm)_{0.10}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
6.348	*Pbca*	a = 15.3659(19) Å	a = 15.6620(14) Å
		b = 15.6243(19) Å	b = 15.6621(13) Å
		c = 18.226(3) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

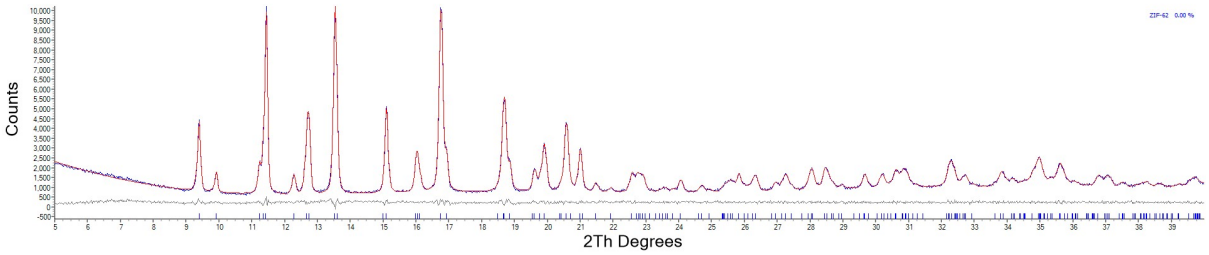

Figure. S46: Pawley refinement of $[Zn(Im)_{1.75}(ClbIm)_{0.25}]$, with difference plot (grey) showing no extra crystalline phases.

Table S14: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.75}(ClbIm)_{0.25}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
3.438	*Pbca*	a = 15.5768(11) Å	a = 15.6620(14) Å
		b = 15.7524(12) Å	b = 15.6621(13) Å
		c = 17.8304(15) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

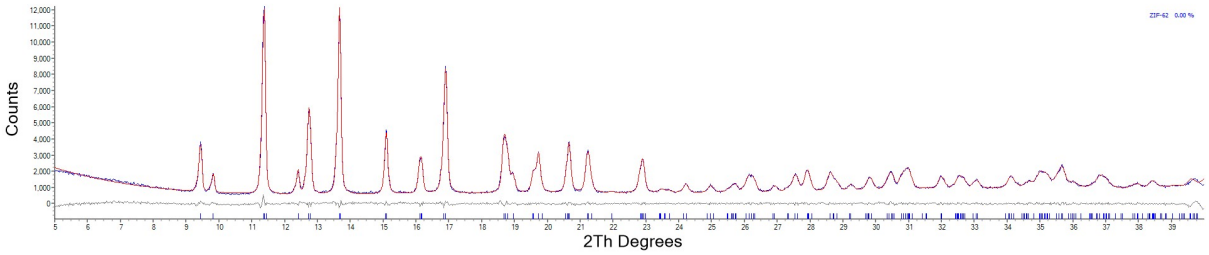

Figure. S47: Pawley refinement of $[Zn(Im)_{1.80}(ClbIm)_{0.20}]$, with difference plot (grey) showing no extra crystalline phases.

Table S15: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.80}(ClbIm)_{0.20}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
4.205	*Pbca*	a = 15.453(2) Å	a = 15.6620(14) Å
		b = 15.527(2) Å	b = 15.6621(13) Å
		c = 17.986(2) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

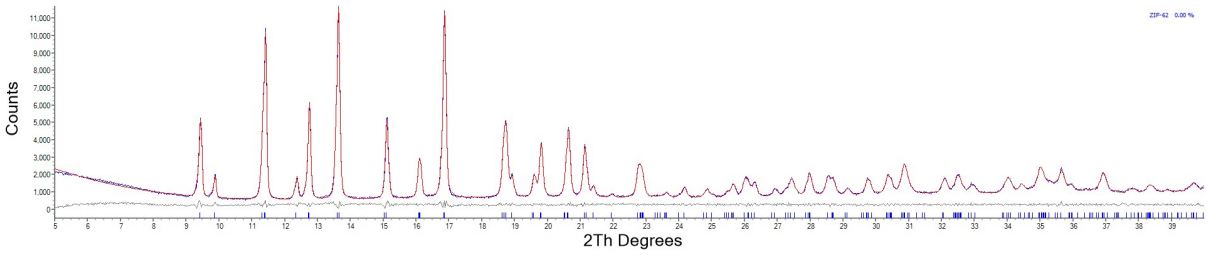

Figure. S48: Pawley refinement of $[Zn(Im)_{1.85}(ClbIm)_{0.15}]$, with difference plot (grey) showing no extra crystalline phases.

Table S16: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.85}(ClbIm)_{0.15}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
3.790	*Pbca*	a = 15.5039(15) Å	a = 15.6620(14) Å
		b = 15.6258(14) Å	b = 15.6621(13) Å
		c = 17.933(2) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

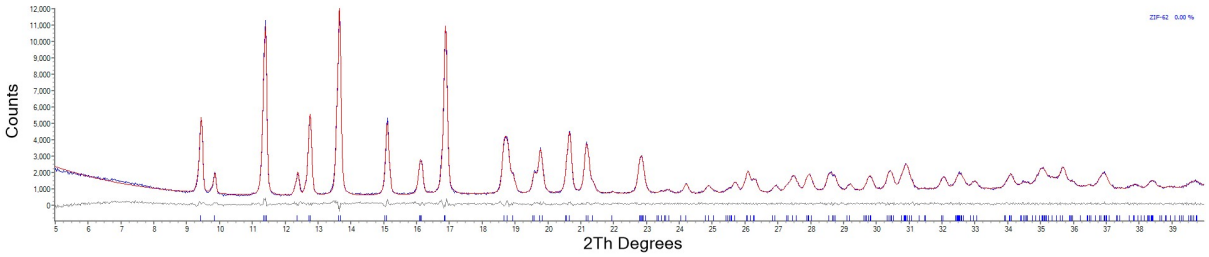

Figure. S49: Pawley refinement of $[Zn(Im)_{1.90}(ClbIm)_{0.10}]$, with difference plot (grey) showing no extra crystalline phases.

Table S17: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.90}(ClbIm)_{0.10}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
3.849	*Pbca*	a = 15.477(2) Å	a = 15.6620(14) Å
		b = 15.5944(19) Å	b = 15.6621(13) Å
		c = 17.965(2) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

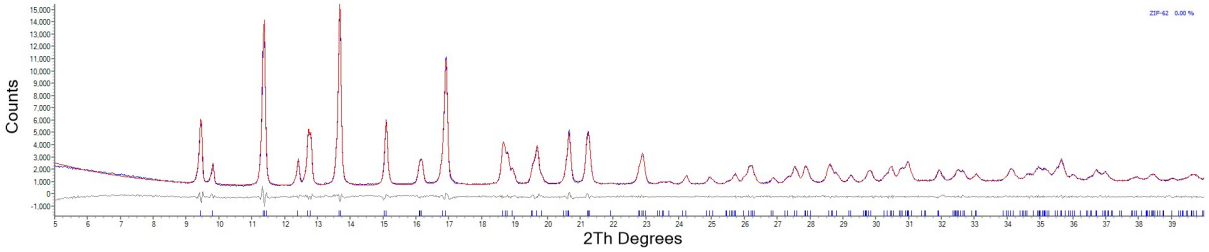

Figure. S50: Pawley refinement of $[Zn(Im)_{1.95}(ClbIm)_{0.05}]$, with difference plot (grey) showing no extra crystalline phases.

Table S18: Crystal data and structure refinement for mechanosynthetic $[Zn(Im)_{1.95}(ClbIm)_{0.05}]$

R_{wp}	Space Group	Lattice Parameters	Lattice Parameters Reported for ZIF-62[1]
4.476	*Pbca*	a = 15.4595(15) Å	a = 15.6620(14) Å
		b = 15.5372(15) Å	b = 15.6621(13) Å
		c = 18.0420(17) Å	c = 18.2073(19) Å
		α = 90 °	α = 90 °
		β = 90 °	β = 90 °
		γ = 90 °	γ = 90 °

ZIF-62 TGA

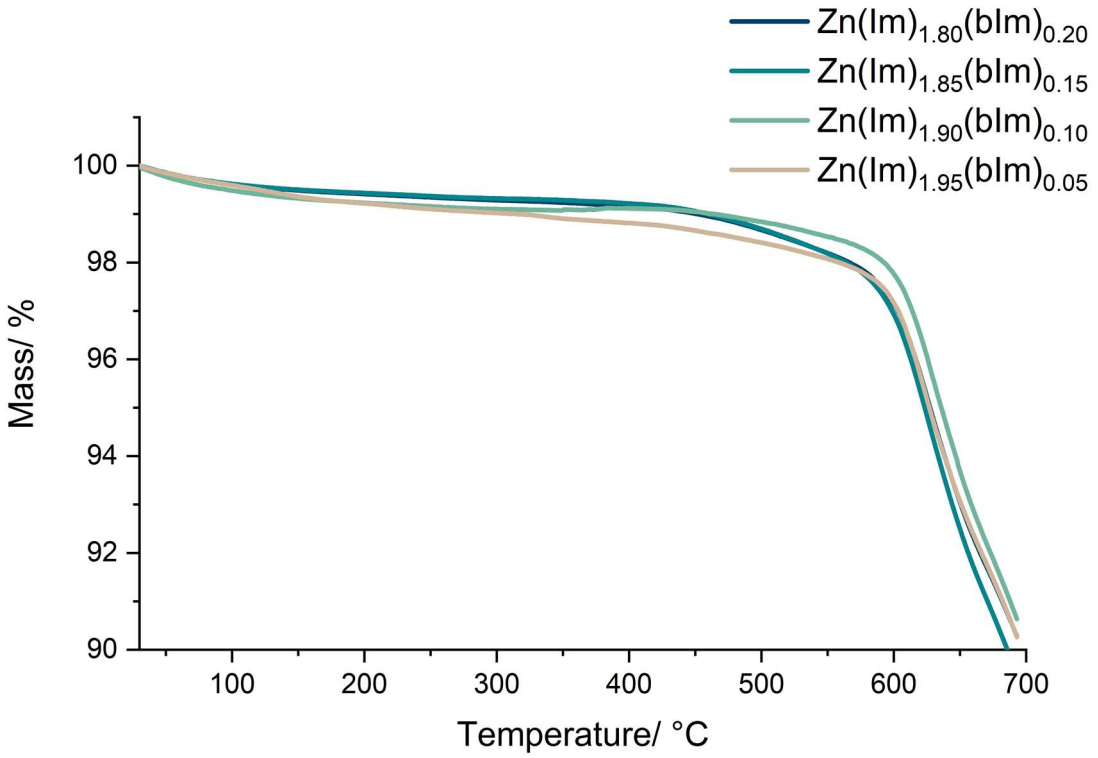

Figure. S51: TGA of ZIF-62 samples with variable linker ratios. The samples were measured under an argon atmosphere with a heating rate of 10 °C min^{-1}.

ZIF-UC-5 TGA

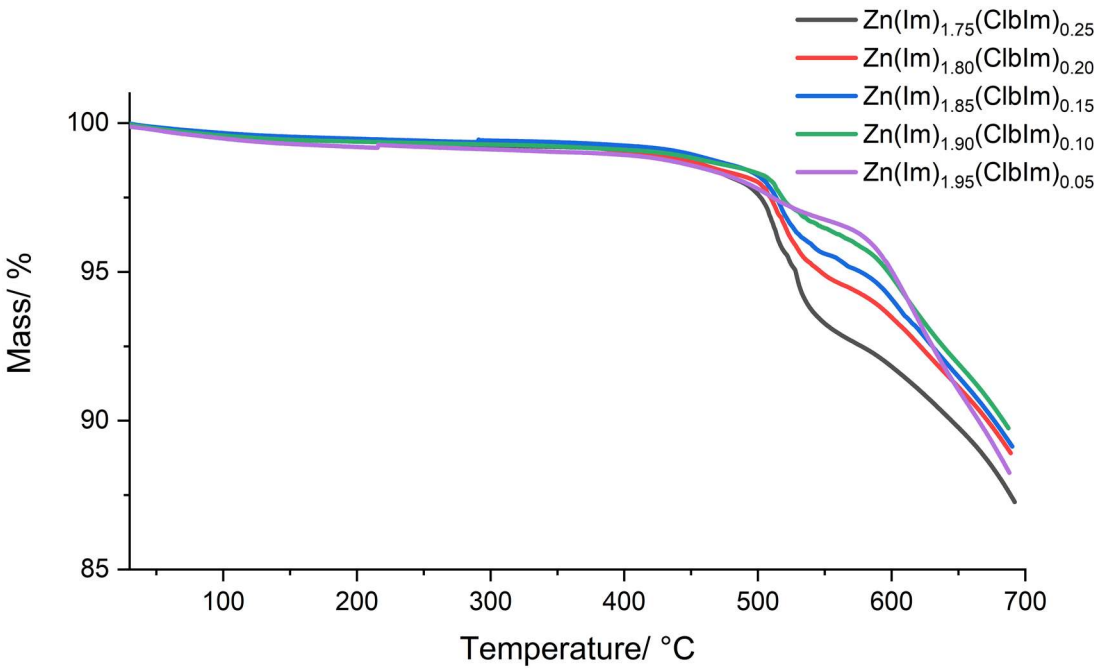

Figure. S52: TGA of ZIF-UC-5 samples with variable linker ratios, showing an increased rate of decomposition as the ClbIm content is increased. The samples were measured under an argon atmosphere with a heating rate of 10 °C min^{-1}.

ZIF-62 DSC

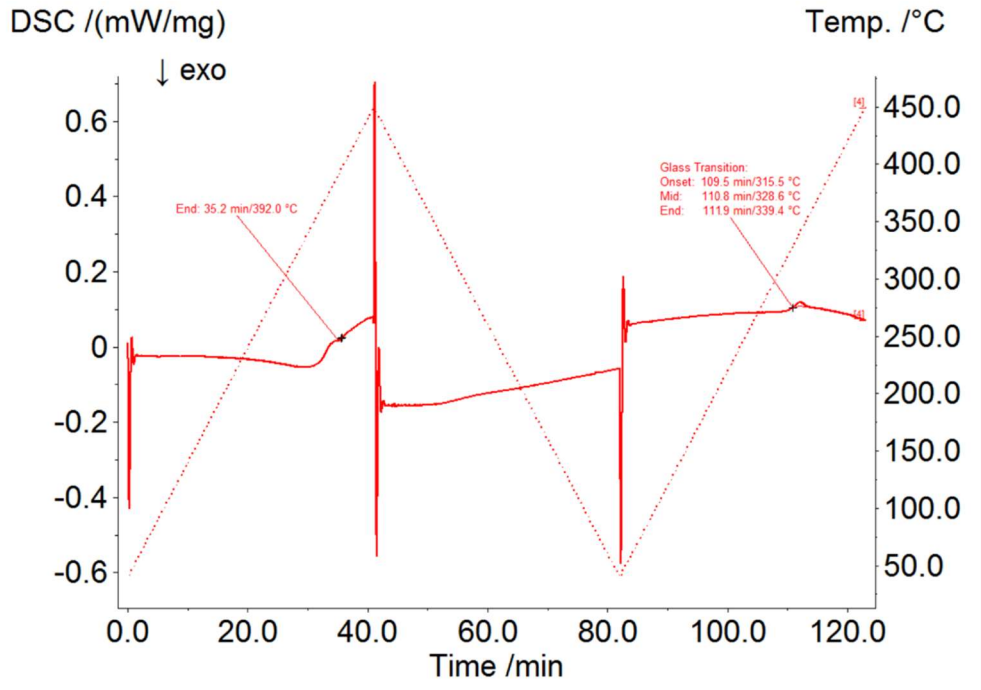

Figure. S52: Differential scanning calorimetry of $[Zn(Im)_{1.80}(bIm)_{0.20}]$.

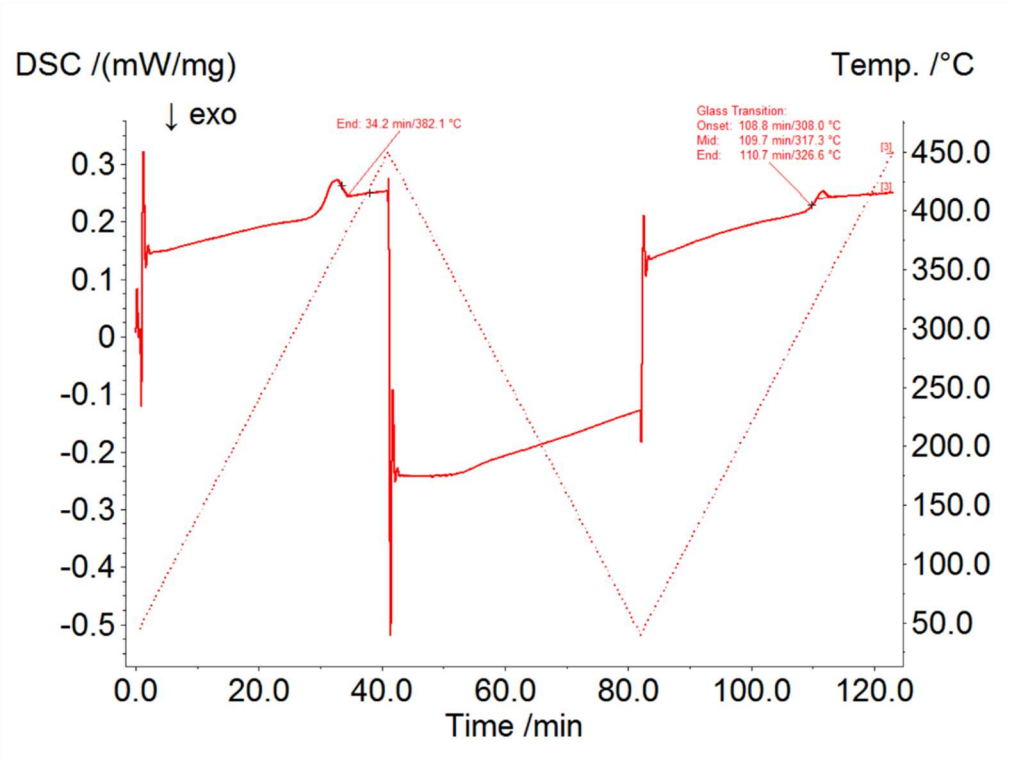

Figure. S53: Differential scanning calorimetry of $[Zn(Im)_{1.85}(bIm)_{0.15}]$.

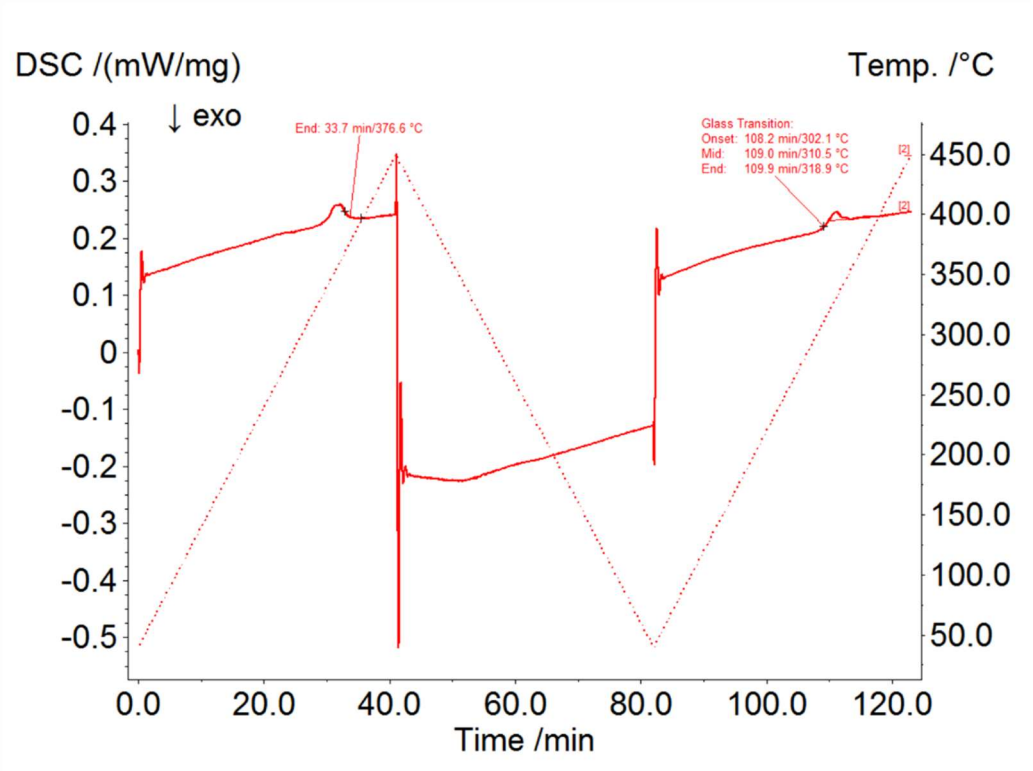

Figure. S54: Differential scanning calorimetry of $[Zn(Im)_{1.90}(bIm)_{0.10}]$.

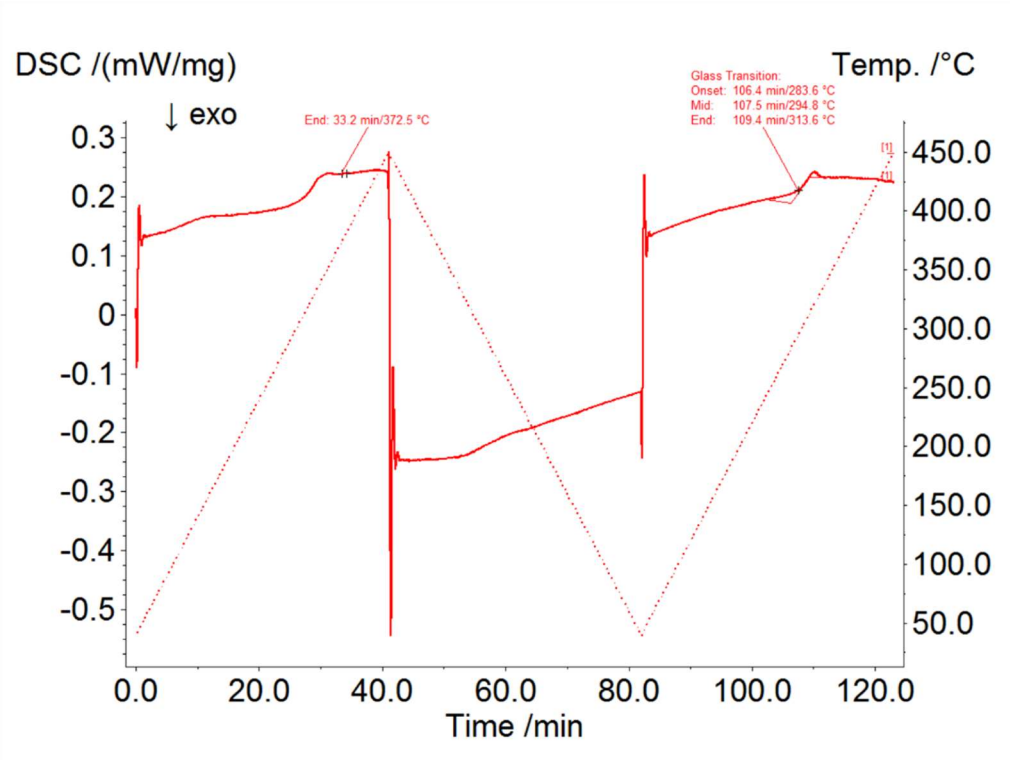

Figure. S55: Differential scanning calorimetry of $[Zn(Im)_{1.95}(bIm)_{0.05}]$.

ZIF-UC-5 DSC

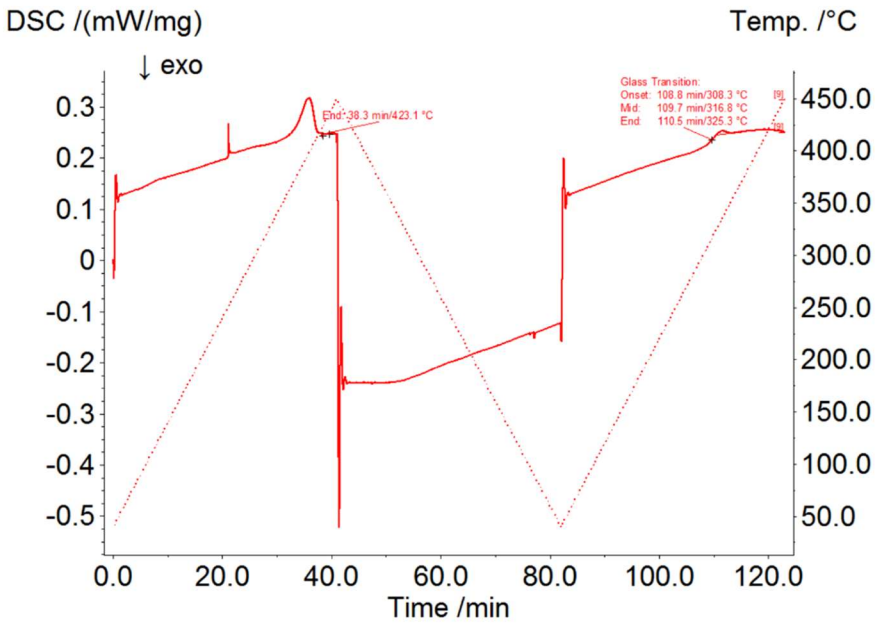

Figure. S56: Differential scanning calorimetry of $[Zn(Im)_{1.75}(ClbIm)_{0.25}]$.

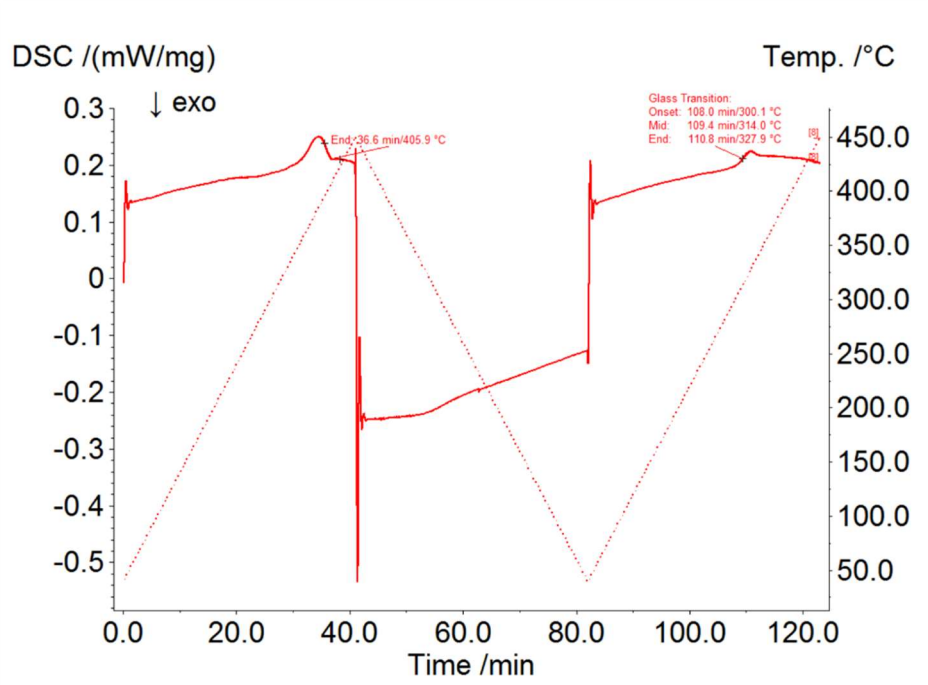

Figure. S57: Differential scanning calorimetry of $[Zn(Im)_{1.80}(ClbIm)_{0.20}]$.

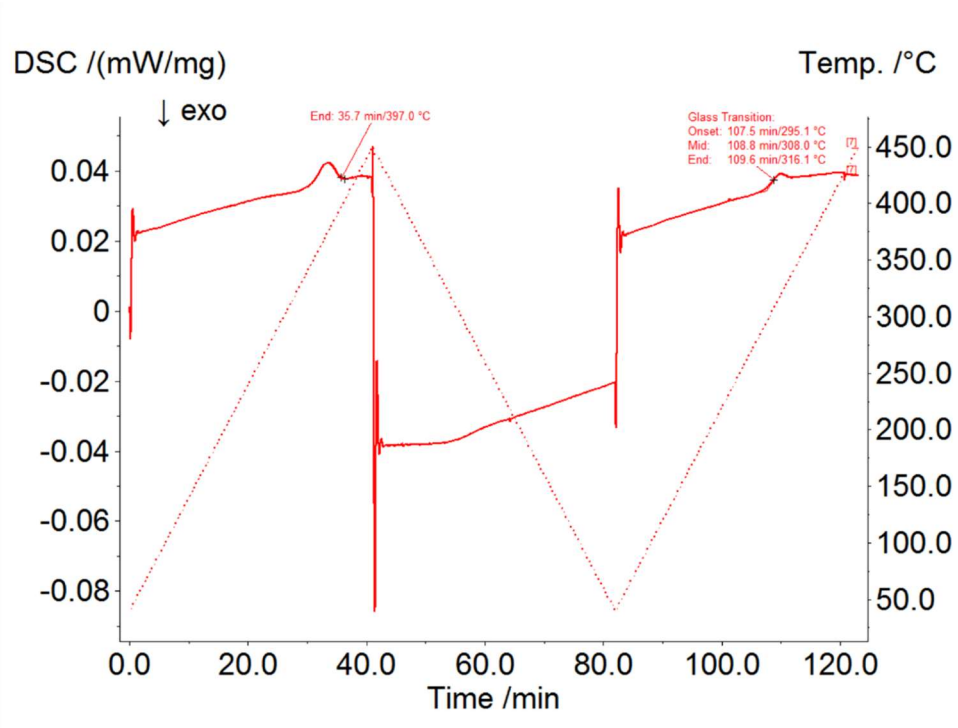

Figure. S58: Differential scanning calorimetry of $[Zn(Im)_{1.85}(ClbIm)_{0.15}]$.

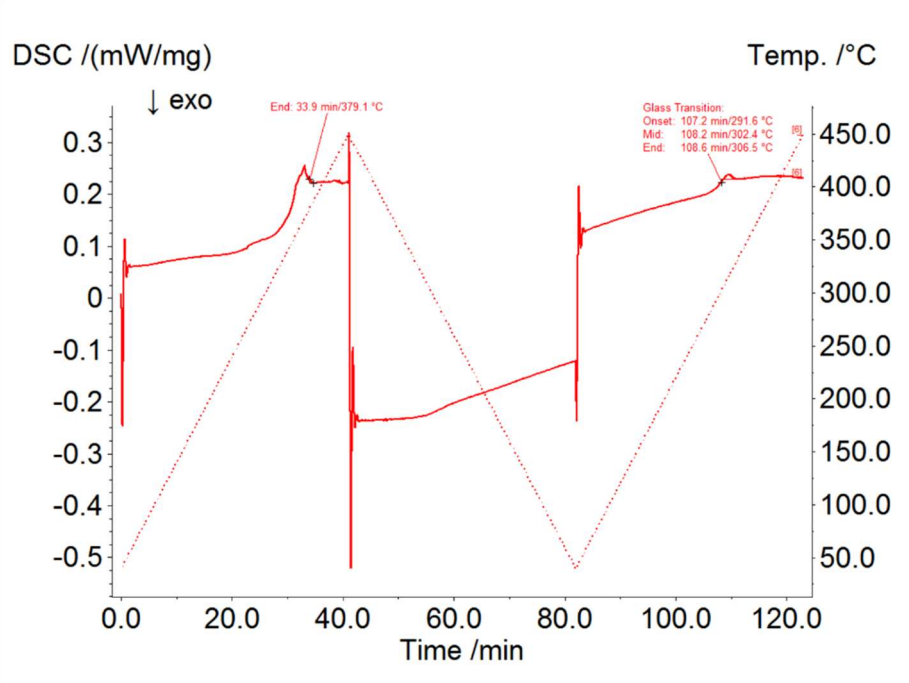

Figure. S59: Differential scanning calorimetry of $[Zn(Im)_{1.90}(ClbIm)_{0.10}]$.

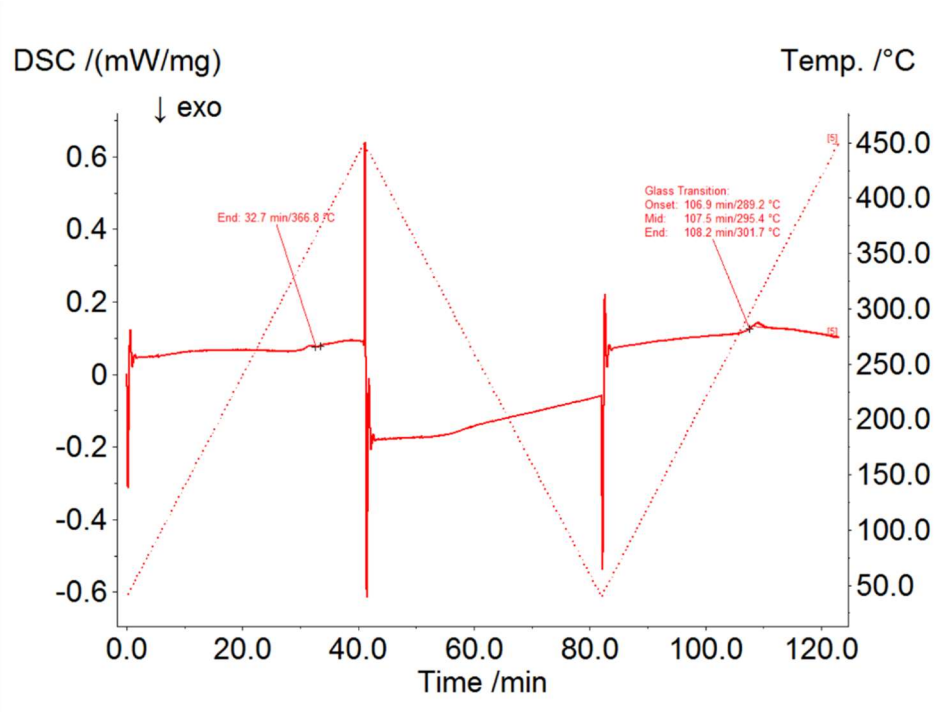

Figure. S60: Differential scanning calorimetry of $[Zn(Im)_{1.95}(ClbIm)_{0.05}]$.

PXRD of ZIF-62 Glasses

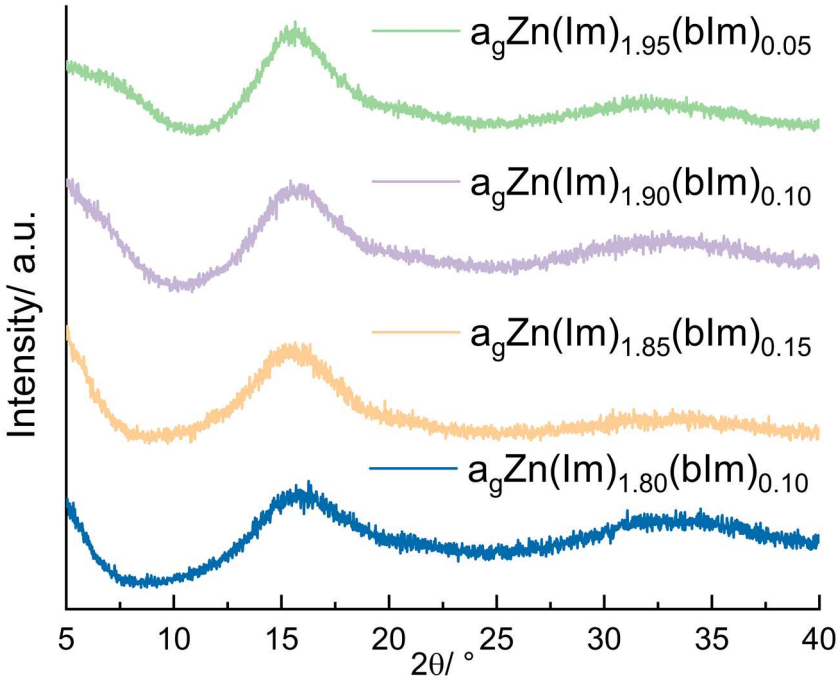

Figure. S61: Powder X-ray diffraction of a_gZIF-62 containing different ratios of Im and bIm.

PXRD of ZIF-UC-5 glasses

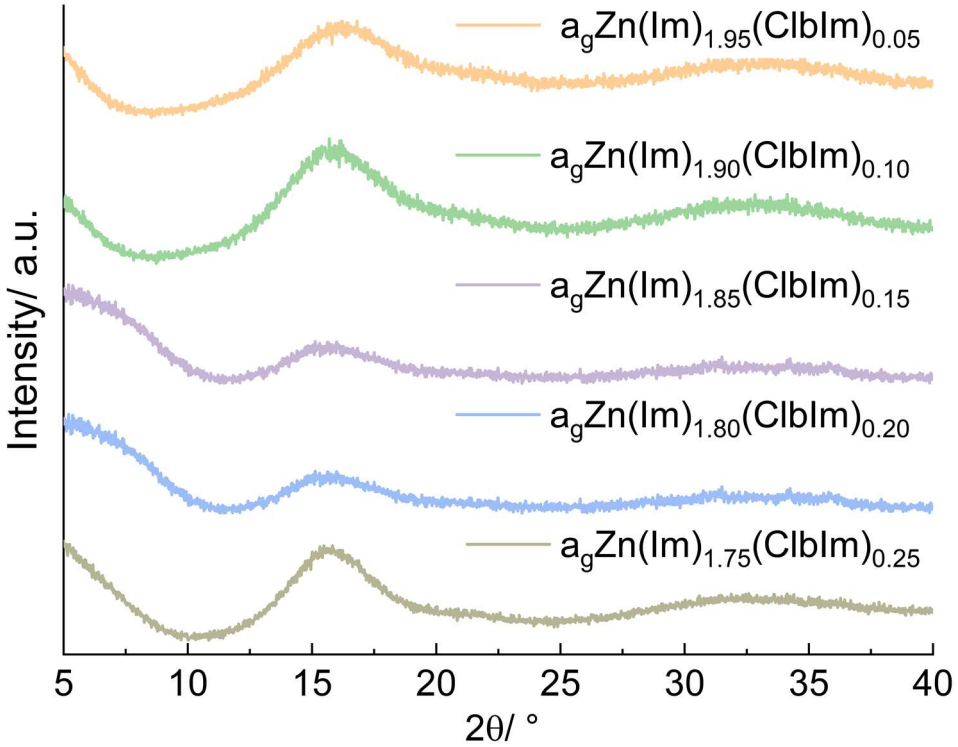

Figure. S62 Powder X-ray diffraction of a_gZIF-UC-5 containing different ratios of Im and ClbIm.

^{1}H NMR ZIF-62

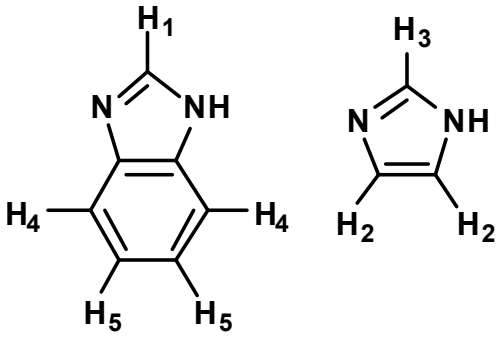

Figure. S63: Structure of imidazole and benzimidazole, with labelled hydrogens. Hydrogens 1 and 3 were used to calculate the linker ratio in ZIF-62 crystals and glasses.

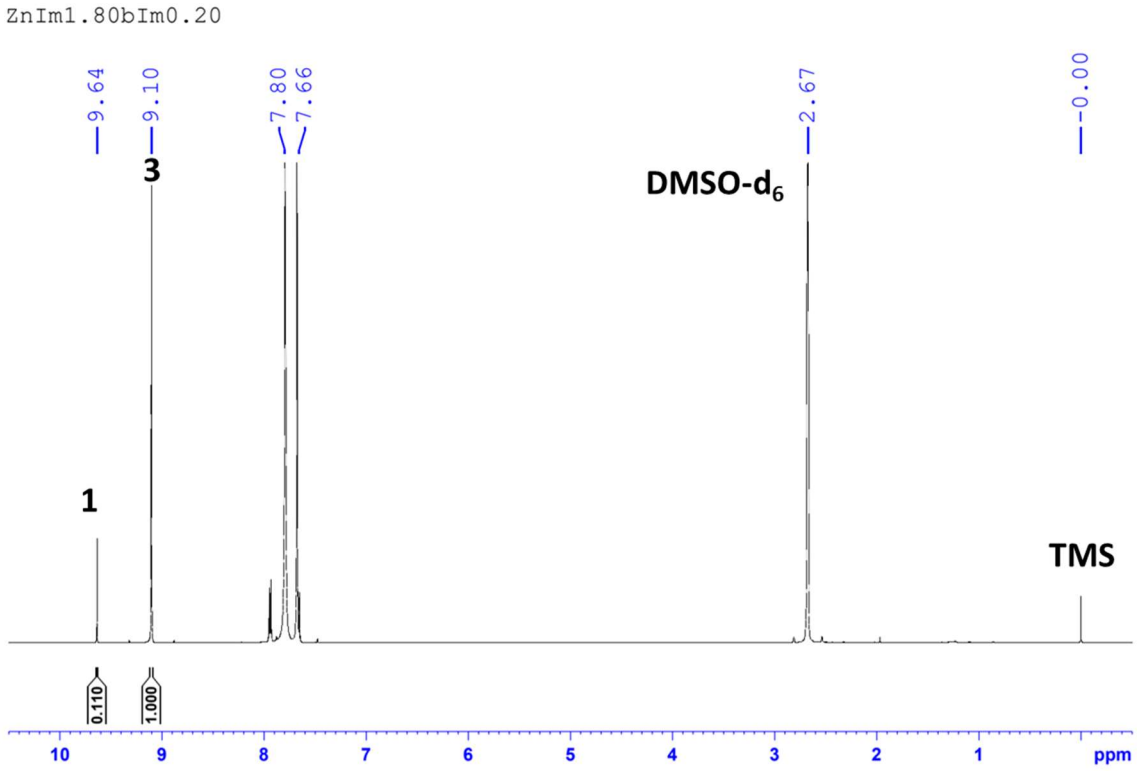

Figure. S64: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.80}(bIm)_{0.20}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.64 (1H, s, H_1), 9.10 (1H, s, H_3), 7.80 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

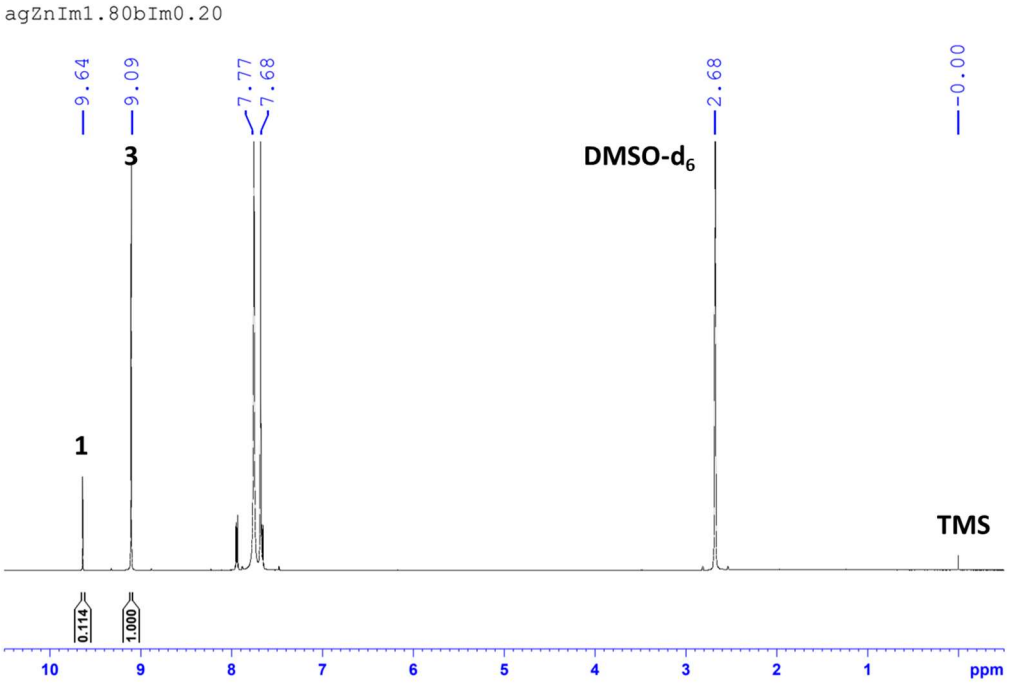

Figure. S65: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.80}(bIm)_{0.20}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.64 (1H, s, H_1), 9.09 (1H, s, H_3), 7.77 (5H, m, aromatic), 2.68 (DMSO), 0.00 (TMS).

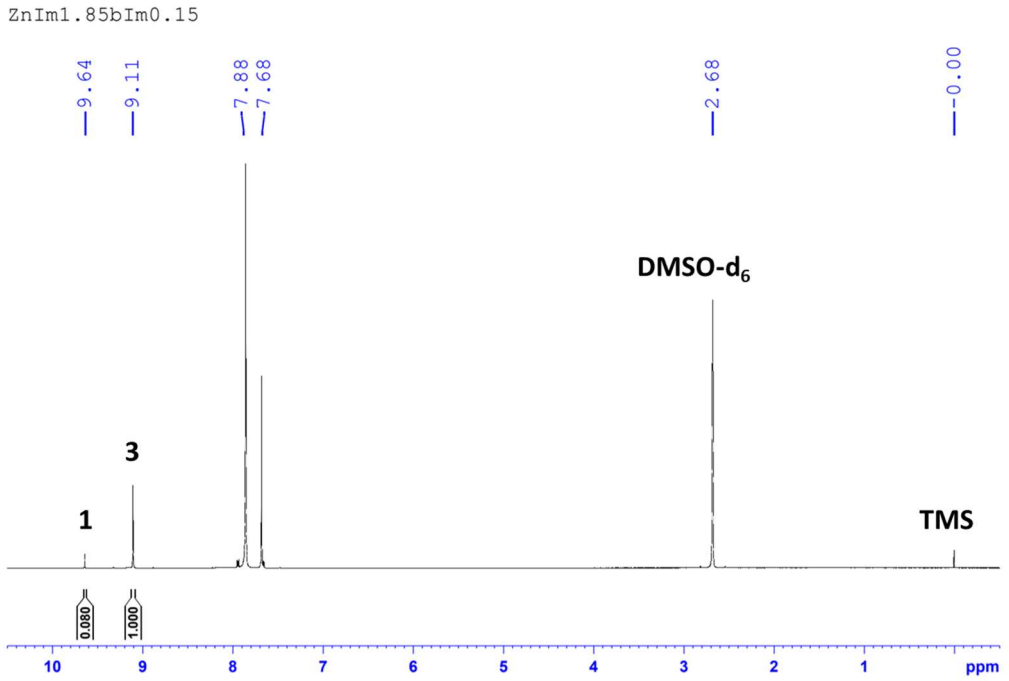

Figure. S66: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.85}(bIm)_{0.15}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.64 (1H, s, H_1), 9.11 (1H, s, H_3), 7.88 (5H, m, aromatic), 2.68 (DMSO), 0.00 (TMS).

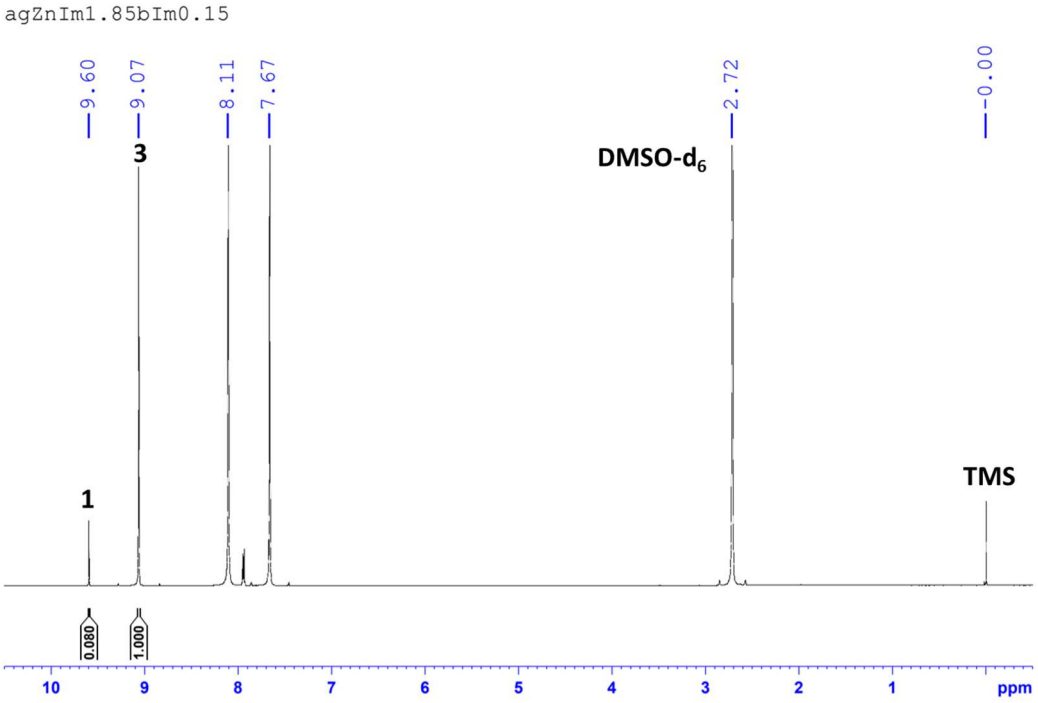

Figure. S67: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.85}(bIm)_{0.15}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.60 (1H, s, H_1), 9.07 (1H, s, H_3), 7.67 (5H, m, aromatic), 2.72 (DMSO), 0.00 (TMS).

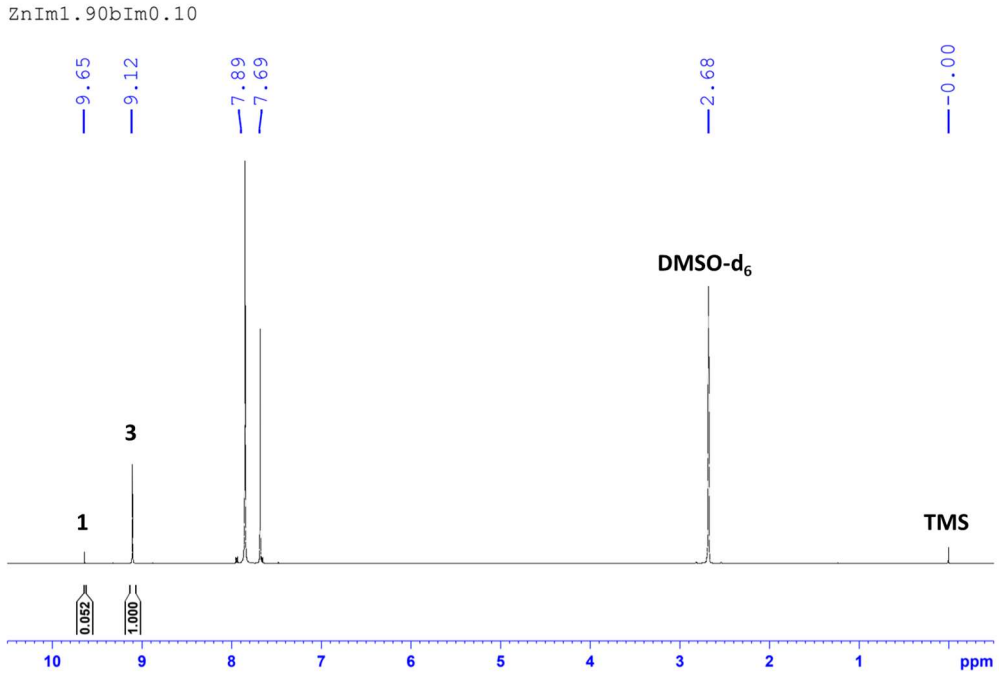

Figure. S68: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.90}(bIm)_{0.10}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.65 (1H, s, H_1), 9.12 (1H, s, H_3), 7.89 (5H, m, aromatic), 2.68 (DMSO), 0.00 (TMS).

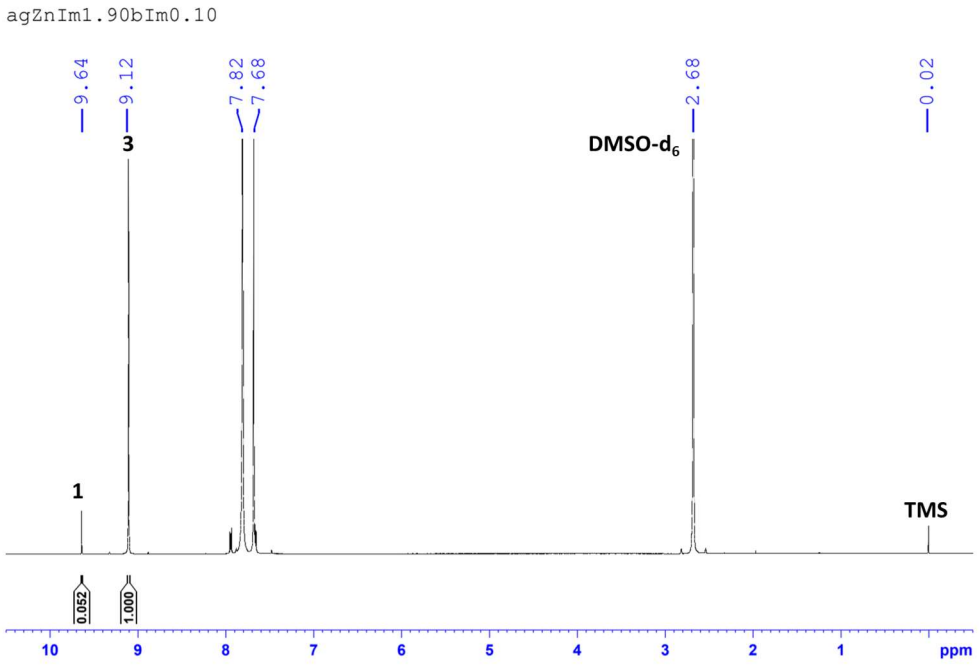

Figure. S69: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.90}(bIm)_{0.10}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.64 (1H, s, H_1), 9.12 (1H, s, H_3), 7.82 (5H, m, aromatic), 2.68 (DMSO), 0.00 (TMS).

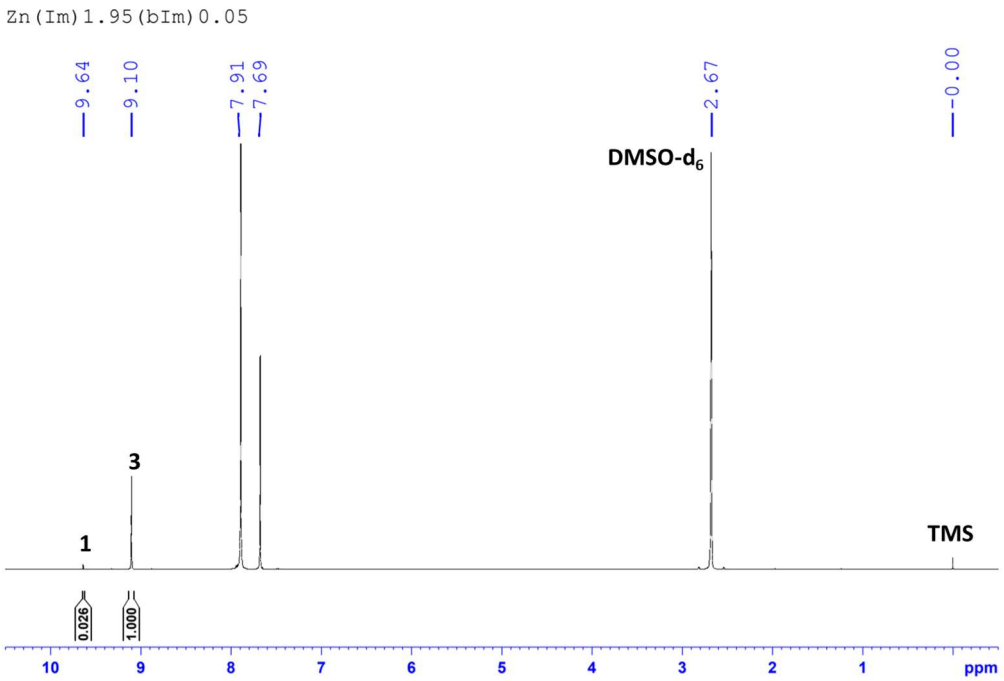

Figure. S70: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.95}(bIm)_{0.05}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.64 (1H, s, H_1), 9.10 (1H, s, H_3), 7.91 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

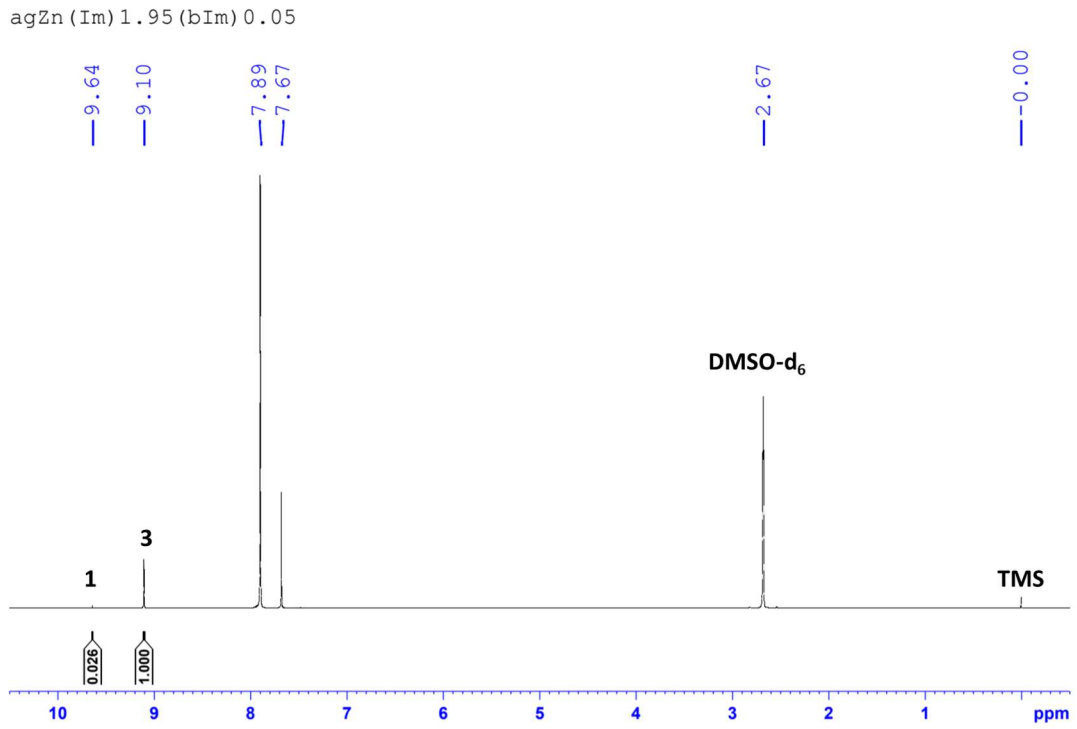

Figure. S71: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.95}(bIm)_{0.05}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.64 (1H, s, H_1), 9.10 (1H, s, H_3), 7.89 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

ZIF-UC-5 NMR

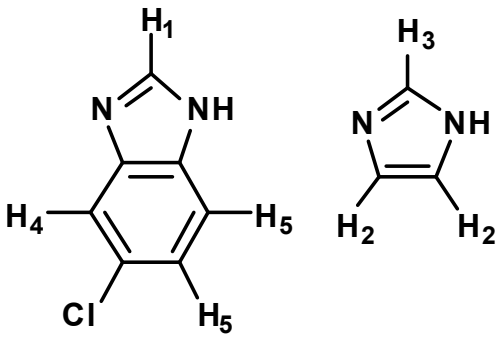

Figure. S72: Structures of imidazole and 5-chlorobenzimidazole, with labelled hydrogens. Hydrogens 1 and 3 were used to calculate the linker ratio in ZIF-UC-5 crystals and glasses.

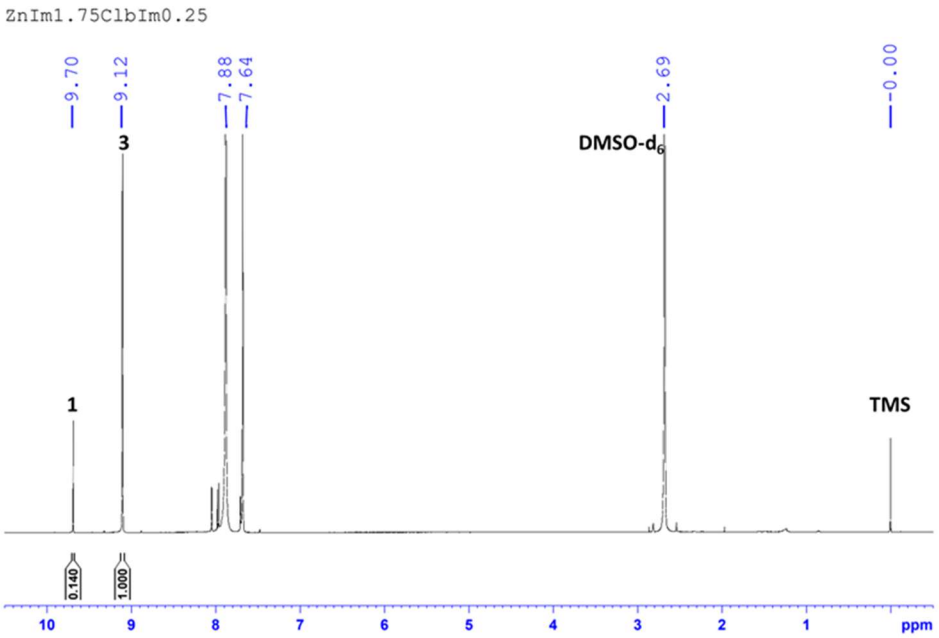

Figure. S73: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.75}(ClbIm)_{0.25}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.70 (1H, s, H_1), 9.12 (1H, s, H_3), 7.88 (5H, m, aromatic), 2.69 (DMSO), 0.00 (TMS).

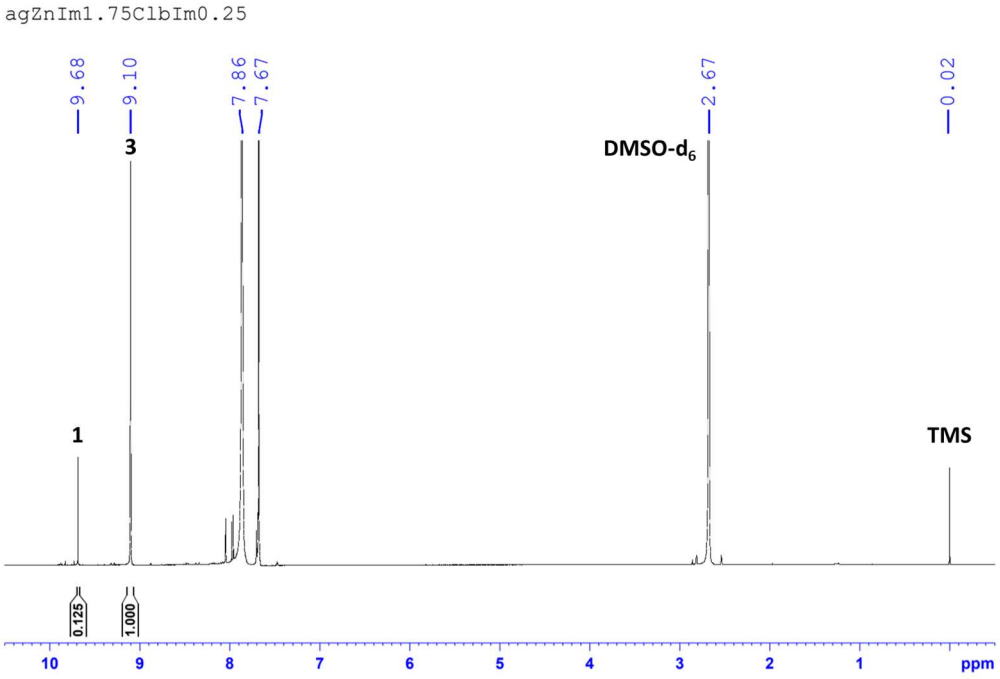

Figure. S74: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.75}(ClbIm)_{0.25}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.68 (1H, s, H_1), 9.10 (1H, s, H_3), 7.86 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

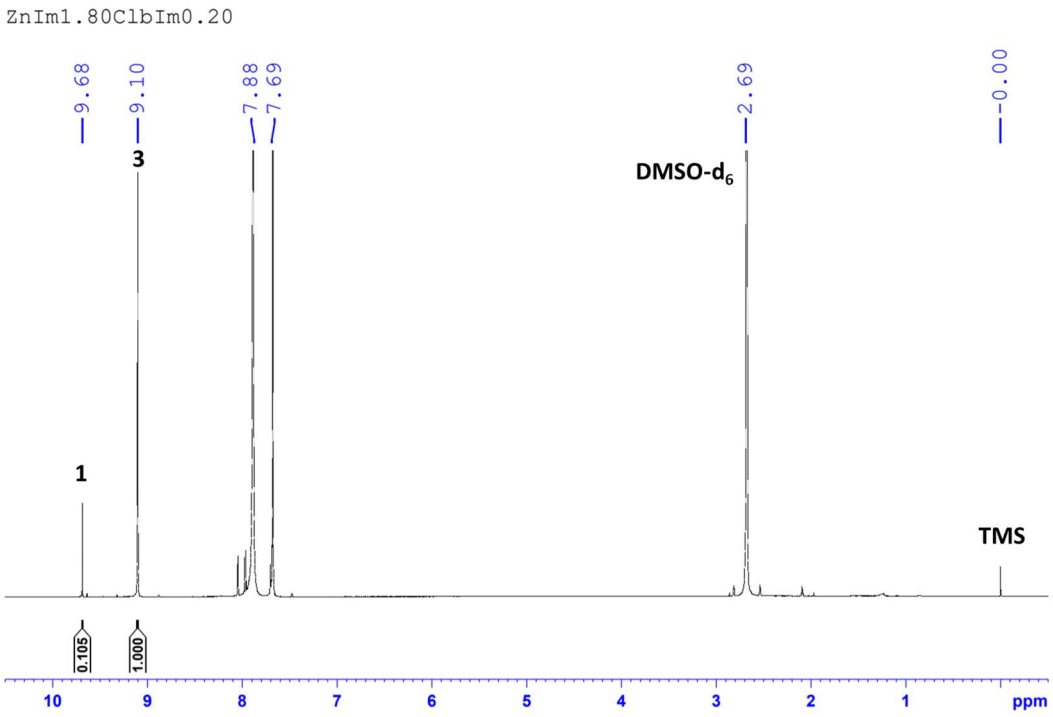

Figure. S75: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.80}(ClbIm)_{0.20}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.68 (1H, s, H_1), 9.10 (1H, s, H_3), 7.88 (5H, m, aromatic), 2.69 (DMSO), 0.00 (TMS).

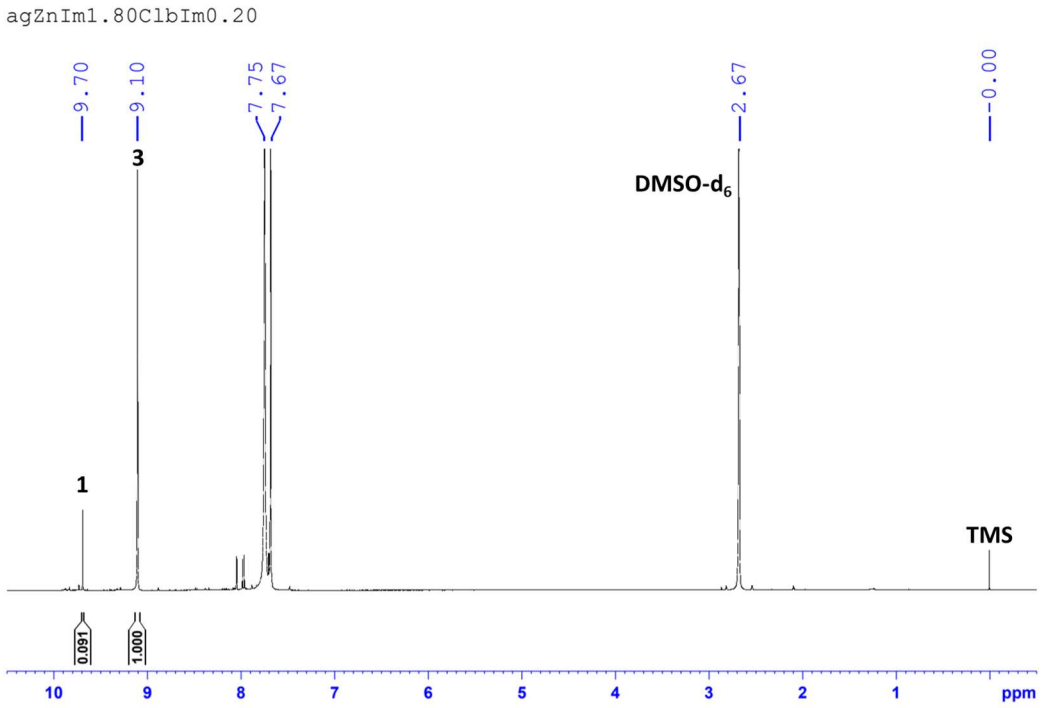

Figure. S76: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.80}(ClbIm)_{0.20}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.70 (1H, s, H_1), 9.10 (1H, s, H_3), 7.75 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

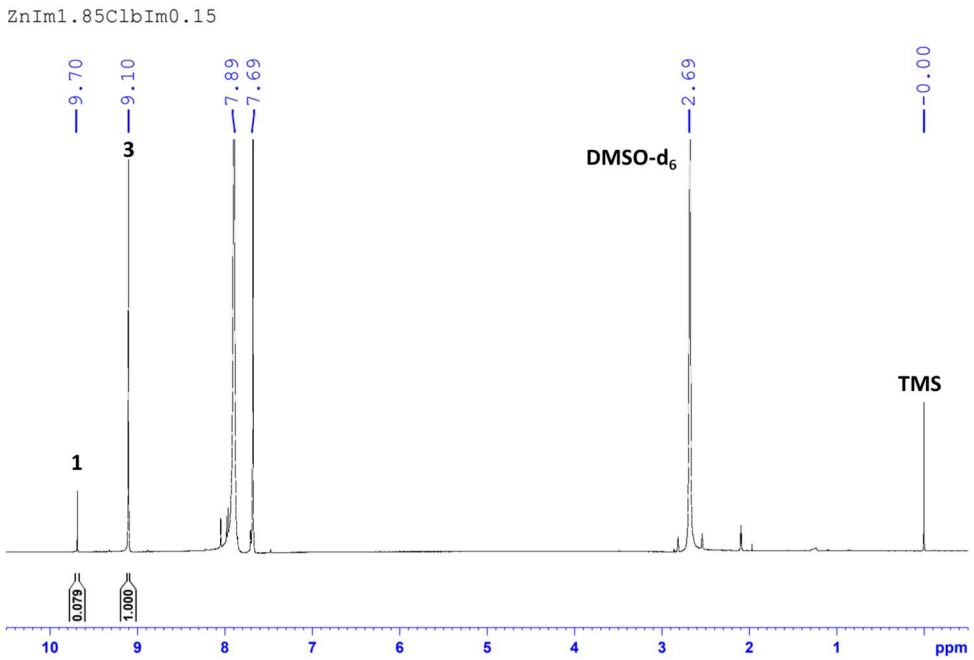

Figure. S79: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.85}(ClbIm)_{0.15}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.70 (1H, s, H_1), 9.10 (1H, s, H_3), 7.89 (5H, m, aromatic), 2.69 (DMSO), 0.00 (TMS).

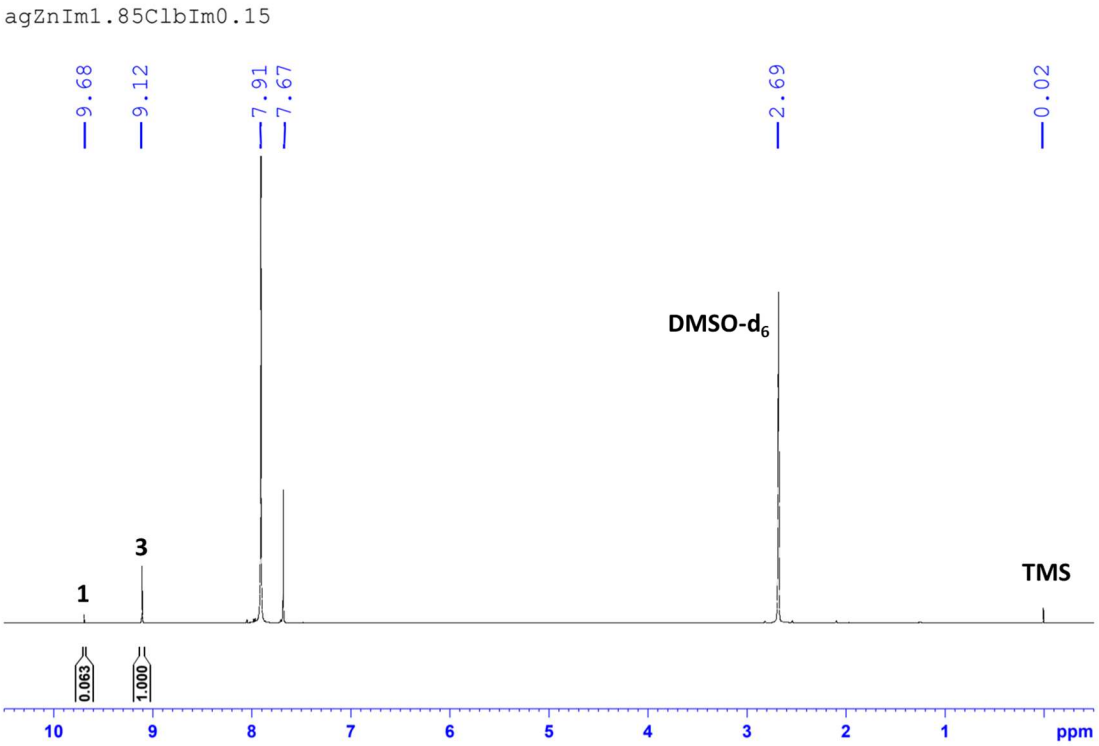

Figure. S80: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.85}(ClbIm)_{0.15}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.68 (1H, s, H_1), 9.12 (1H, s, H_3), 7.91 (5H, m, aromatic), 2.69 (DMSO), 0.00 (TMS).

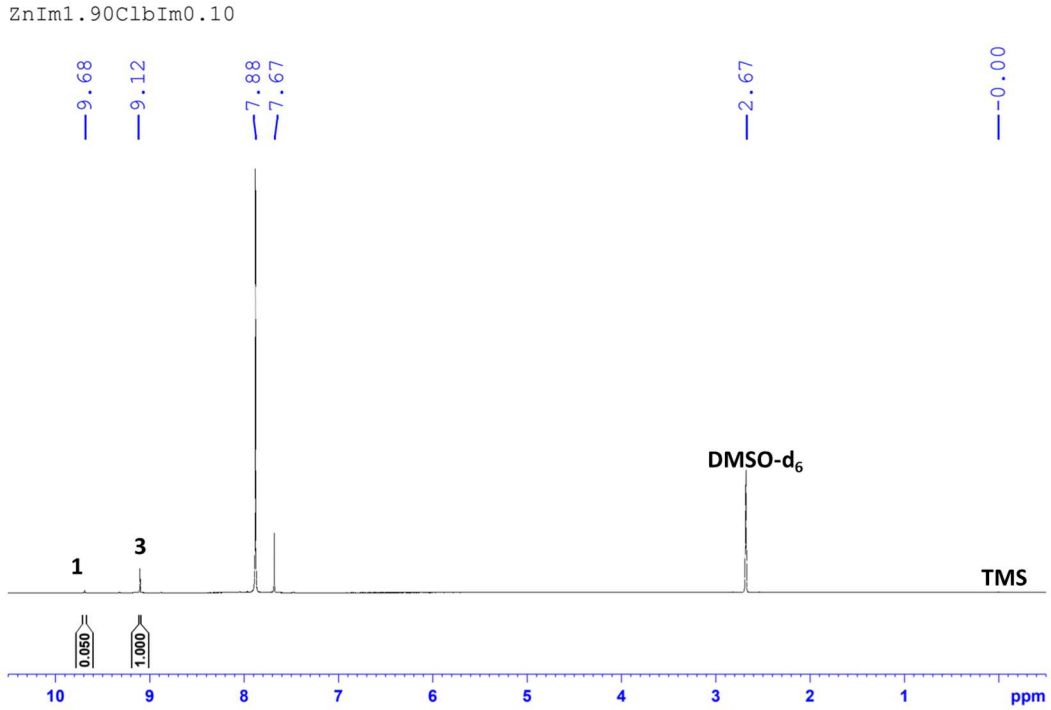

Figure. S81: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.90}(ClbIm)_{0.10}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.68 (1H, s, H_1), 9.12 (1H, s, H_3), 7.88 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

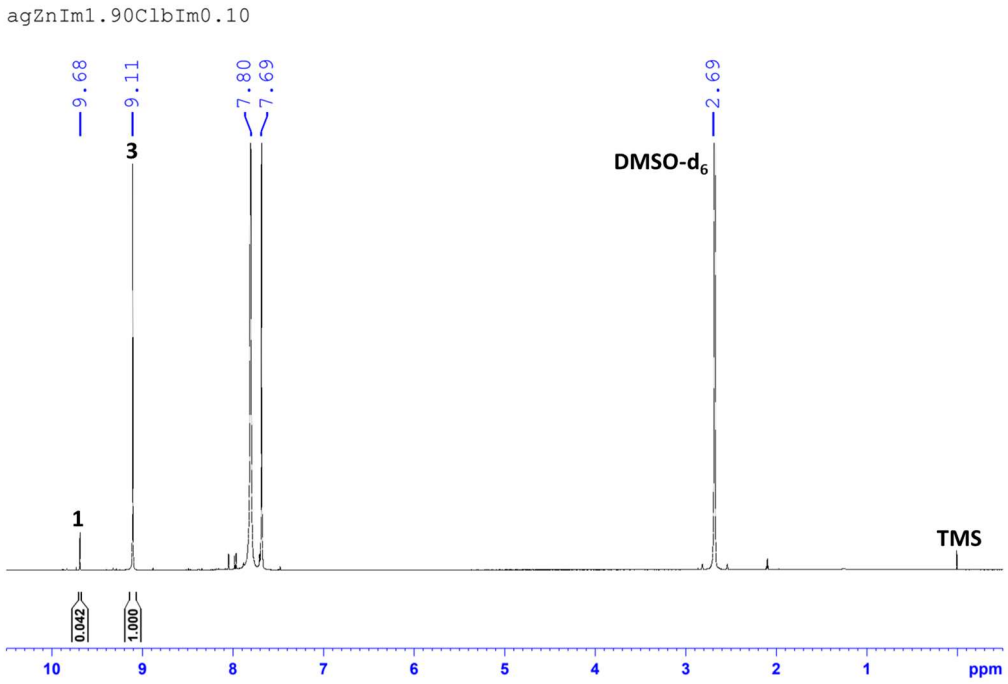

Figure. S82: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.90}(ClbIm)_{0.10}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.68 (1H, s, H_1), 9.11 (1H, s, H_3), 7.80 (5H, m, aromatic), 2.69 (DMSO), 0.00 (TMS).

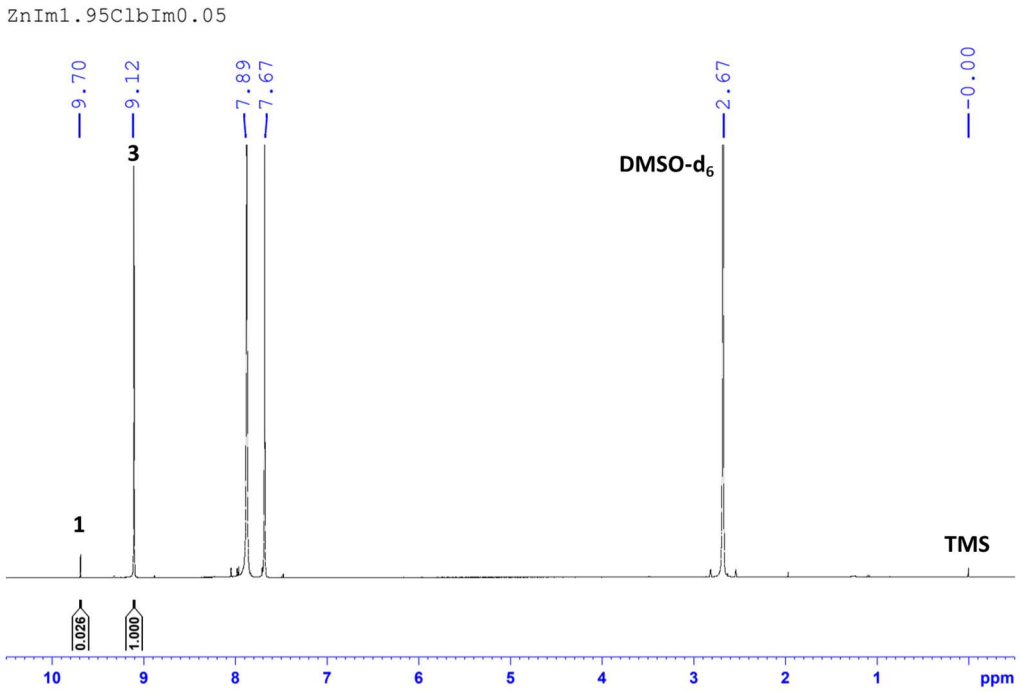

Figure. S83: ^{1}H nuclear magnetic resonance spectra of $[Zn(Im)_{1.95}(ClbIm)_{0.05}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.70 (1H, s, H_1), 9.12 (1H, s, H_3), 7.89 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

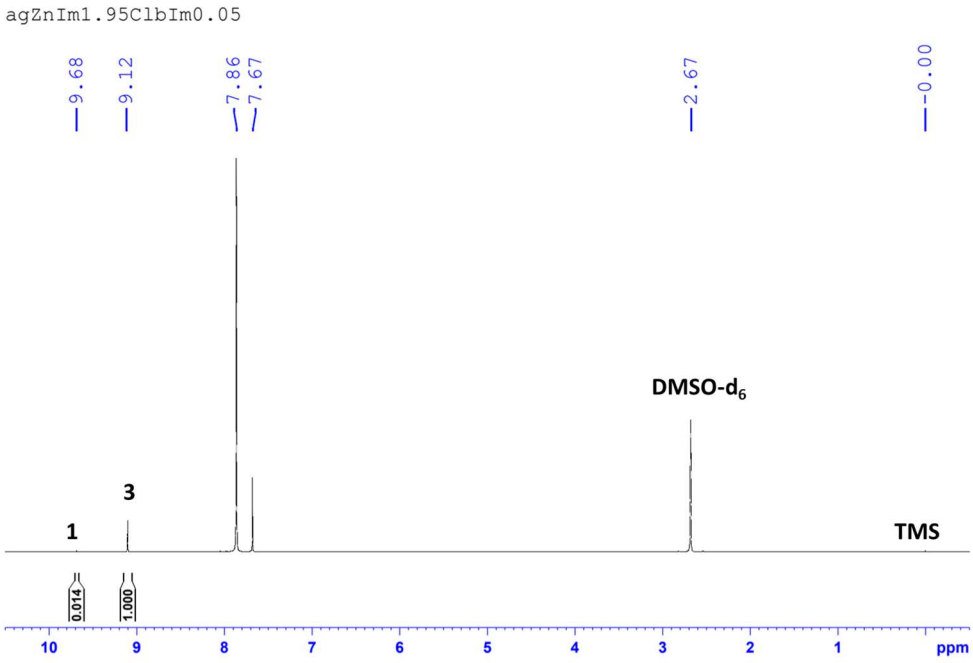

Figure. S84: ^{1}H nuclear magnetic resonance spectra of $[a_gZn(Im)_{1.95}(ClbIm)_{0.05}]$. δH (500 MHz; DCl (35%)/D_2O:DMSO-d_6 (1:5); Me_4Si) 9.68 (1H, s, H_1), 9.12 (1H, s, H_3), 7.86 (5H, m, aromatic), 2.67 (DMSO), 0.00 (TMS).

Table S19: CHN analysis of mechanochemically produced ZIF-62 and ZIF-UC-5 with variable ligand ratios, and predicted values based upon the shown chemical formulae

Sample	C (%)	H (%)	N (%)
$[Zn(Im)_{1.95}(bIm)_{0.05}]$	36.6	2.9	26.8
$[a_gZn(Im)_{1.95}(bIm)_{0.05}]$	36.6	2.9	27.0
Predicted	36.9	3.0	27.7
$[Zn(Im)_{1.90}(bIm)_{0.10}]$	37.4	2.8	26.6
$[a_gZn(Im)_{1.90}(bIm)_{0.10}]$	37.4	2.9	26.8
Predicted	37.6	3.0	27.4
$[Zn(Im)_{1.85}(bIm)_{0.15}]$	38.0	2.8	26.3
$[a_gZn(Im)_{1.85}(bIm)_{0.15}]$	38.1	3.0	26.5
Predicted	38.3	3.0	27.0
$[Zn(Im)_{1.80}(bIm)_{0.20}]$	38.8	2.9	26.0
$[a_gZn(Im)_{1.80}(bIm)_{0.20}]$	38.8	3.0	26.2
Predicted	39.0	3.1	26.8
$[Zn(Im)_{1.95}(ClbIm)_{0.05}]$	36.4	2.8	26.5
$[a_gZn(Im)_{1.95}(ClbIm)_{0.05}]$	35.8	2.9	26.3
Predicted	36.6	3.0	27.5
$[Zn(Im)_{1.90}(ClbIm)_{0.10}]$	36.7	2.9	26.1
$[a_gZn(Im)_{1.90}(ClbIm)_{0.10}]$	36.4	2.9	26.5
Predicted	37.0	2.9	27.0
$[Zn(Im)_{1.85}(ClbIm)_{0.15}]$	37.1	2.8	26.0
$[a_gZn(Im)_{1.85}(ClbIm)_{0.15}]$	36.9	2.8	25.8
Predicted	37.4	2.9	26.4
$[Zn(Im)_{1.80}(ClbIm)_{0.20}]$	37.4	2.8	25.3
$[a_gZn(Im)_{1.80}(ClbIm)_{0.20}]$	36.9	2.6	24.9
Predicted	37.7	2.9	25.9
$[Zn(Im)_{1.75}(ClbIm)_{0.25}]$	37.9	2.8	24.8
$[a_gZn(Im)_{1.75}(ClbIm)_{0.25}]$	37.6	2.7	24.7
Predicted	38.1	2.8	25.4

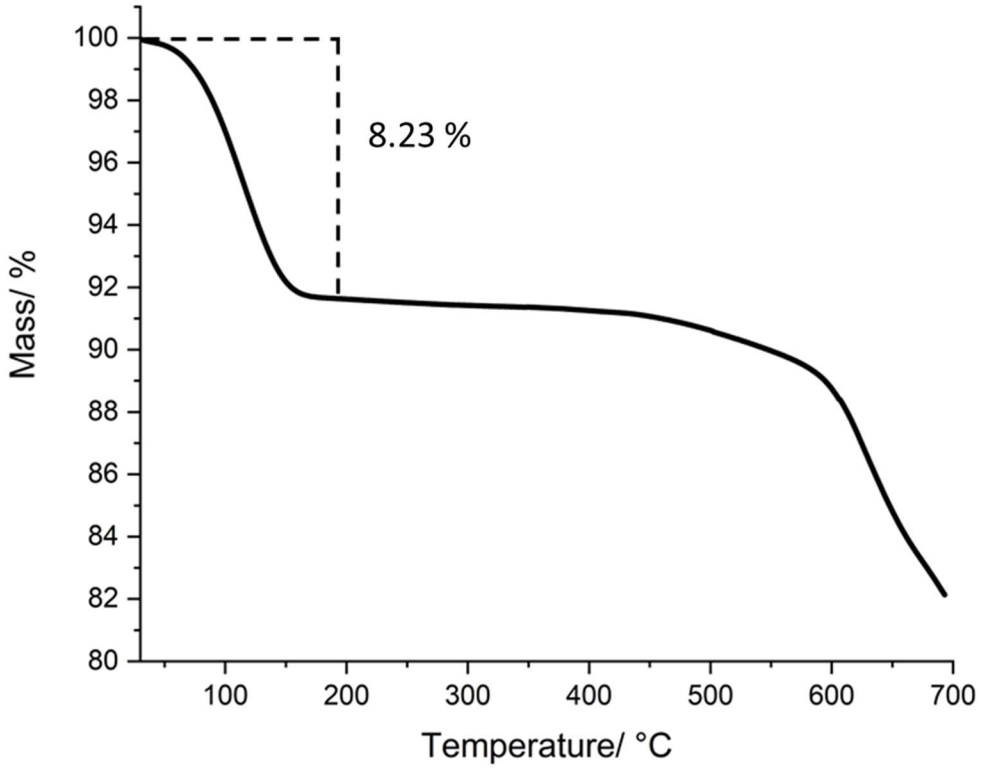

Figure. S84: Resolvated $[Zn(Im)_{1.75}(bIm)_{0.25}]$ showing DCM loss upon heating. The sample was run under an argon atmosphere with a heating rate of 10 °C min^{-1}.

1 R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science.*, 2008, **319**, 939–943.

2 L. Palatinus and G. Chapuis, *J. Appl. Crystallogr.*, 2007, **40**, 786–790.

3 L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.

4 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.