Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Relating Structural Disorder and Melting in Complex Mixed Ligand Zeolitic Imidazolate Framework Glasses

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1. X-ray Diffraction

Two members of the ZIF family: ZIF-62 $[Zn(Im)_{1.75}(bIm)_{0.25}]$ and TIF-4 $[Zn(Im)_{1.5}(mbIm)_{0.5}]$, have been previously studied because of their glass forming abilities. They are isomorphous (space group *Pbca*) with a cag network topology. Their unit cell parameters and volumes are similar: a = 15.6620(14) Å, b = 15.6621(13) Å, c = 18.2073(19) Å, V = 4466.2(7) Å^3 for ZIF-62; and a = 15.6251(9) Å, b = 16.3217(9) Å, c = 18.1244(10) Å, V = 4622.2(4) Å^3 for TIF-4. They both undergo a single melting event at T_m = 710K and T_m = 740 K respectively, before decomposition at around 875 K. The glasses formed by melt quenching at T_m, exhibit a T_g at 591 K and 616 k respectively. These previous results support the viability of obtaining a system with three linkers (Im, bIm and mbIm), able to crystallize in *Pbca* space group and able to form melt-quenched glasses.

1.1. Powder diffraction

All powder samples crystalized in the orthorhombic crystal system, and the reflections were consistent with space group *Pbca* (# 61). Pawley refinements were conducted using the software TOPAS (version 5). Cell parameters were determined from a single phase designation, using the ones reported for ZIF-62 by Yaghi[1] (CSD No. 671070) as a starting point. All 3 cell parameters were allowed to vary until convergence. Results are detailed in Table S1.

Table S1: Pawley refinement of powder samples: cell parameters and refinement parameters.

Samples	a (Å)	b (Å)	c (Å)	R_{wp}	Goof
ZIF-UC-**1a**	15.448(3)	15.534(3)	18.023(3)	7.0180	1.3429
ZIF-UC-**1b**	15.427(6)	15.530(6)	17.980(6)	6.2389	1.1778
ZIF-UC-**1c**	15.413(4)	15.527(4)	18.010(4)	6.2224	1.2176
ZIF-UC-**1d**	15.424(6)	15.542(6)	17.946(7)	6.2736	1.1840
ZIF-UC-**1e**	15.397(4)	15.544(4)	18.023(4)	6.3727	1.2585

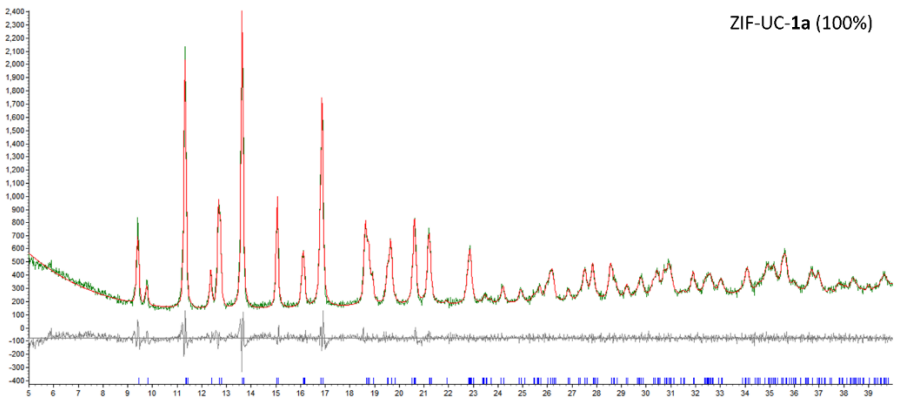

Figure S1. Experimental X-ray diffraction pattern of ZIF-UC-**1a** powder sample (green). Pawley refinement using Topas (red).

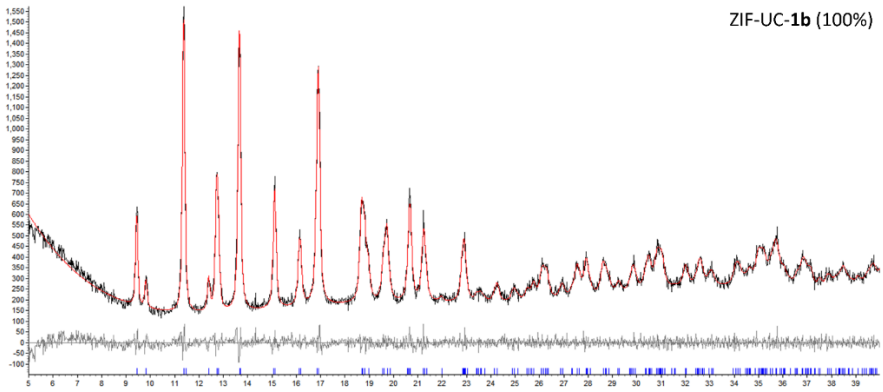

Figure S2. Experimental X-ray diffraction pattern of ZIF-UC-**1b** powder sample (black). Pawley refinement using Topas (red).

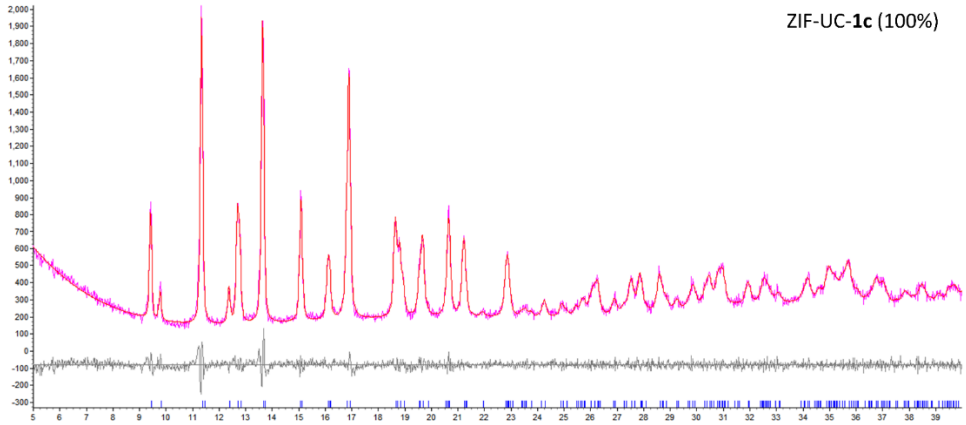

Figure S3. Experimental X-ray diffraction pattern of ZIF-UC-**1c** powder sample (pink). Pawley refinement using Topas (red).

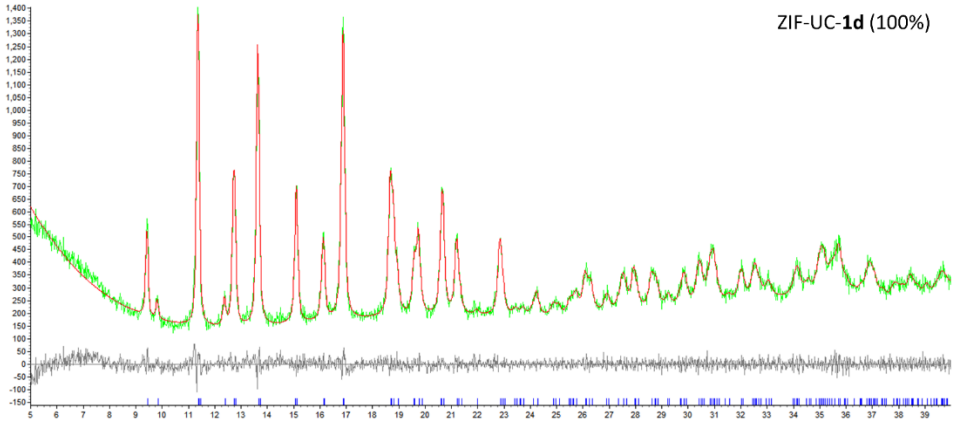

Figure S4. Experimental X-ray diffraction pattern of ZIF-UC-**1d** powder sample (light green). Pawley refinement using Topas (red).

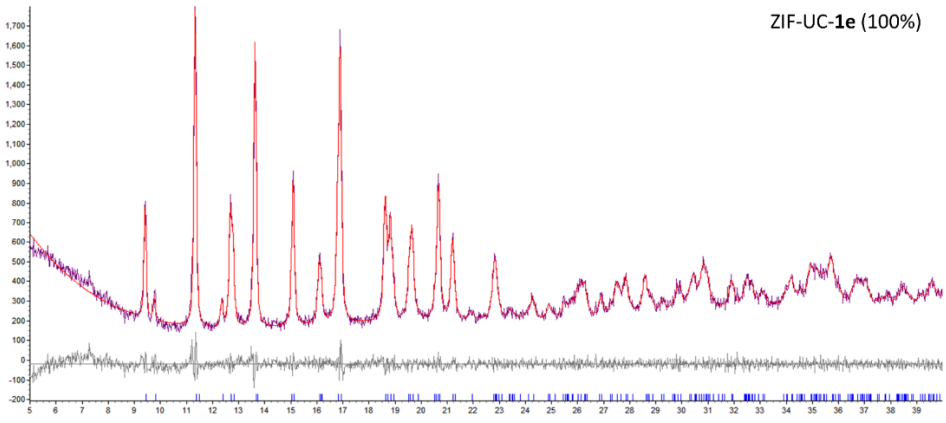

Figure S5. Experimental X-ray diffraction pattern of ZIF-UC-**1e** powder sample (purple). Pawley refinement using Topas (red).

1.2. Single crystal diffraction

ZIF-UC-**1a** (*CAG* – Orthorhombic)
Experimental and Refinement Details for ZIF-UC-**1a**

A colourless polyhedral crystal of size 0.20 x 0.15 x 0.10 mm^3, was placed in a 0.2 mm diameter borosilicate loop and mounted on a Gemini E Ultra diffractometer from Oxford Diffraction equipped with an Atlas CCD area detector and operated at 1200 W power (35 kV, 35 mA) to generate Cu Kα radiation (λ = 1.54184 Å) at 293(2) K. A total of 10797 reflections were collected, of which 3902 were unique and 3145 of these were greater than 2σ(I). The value of θ went from 2.3658° to 64.029°. Analysis of the data showed negligible decay during collection. The structure was solved in the orthorhombic *Pbca* space group with Z = 8 using SUPERFLIP method.[2] Modelling of electron density within the void of the frameworks leads to identification of 0.91 N,N-Diethylformamide (DEF) guest molecules in the asymmetric unit (in addition to 2 independent Zn and 4 independent linkers). From those linkers, 2 are unsubstituted Im with no disorder, the third linker position is disordered between 0.60 Im, 0.23 bIm and 0.17 mbIm and the fourth position is disordered between 0.13 bIm and 0.87 Im. Note that the third position can contain a maximum of 0.5 occupancy for mbIm linkers, because a centre of symmetry in this space group would bring the mbIm linkers related by this centre into contact with each other. In the fourth position, on the other hand, the bIm linker is shifted away from the Im position by 53.7° to avoid sterically clashing with a neighbouring Im linker in a fully occupied position. Such symmetry limitations result in bIm linkers partially occupying the same crystallographic position as DEF molecules. With the exception of the carbon atoms within bIm and mbIm linkers, the nitrogen atoms in the third position and the solvent atoms, all non-hydrogen atoms have been refined anisotropically. All hydrogen atoms have been placed in geometrically located positions and their displacement parameters are tied to those of the attached carbon atoms. Hydrogens atoms for the benzene ring in the third linker position and for the methyl group in the fourth position have not been included because the occupancy is low to provide accurate coordinates. The unit cell of ZIF-UC-**1a** contains 1.74 Im and 0.18 bIm and 0.08 mbIm per zinc. Final full matrix least squares (50 cycles) refinement on F^2 converged to $R1$ = 0.0665 (F >2σF) and wR2 = 0.2121 with GOOF = 1.077. CCDC Deposition Number 1943552.

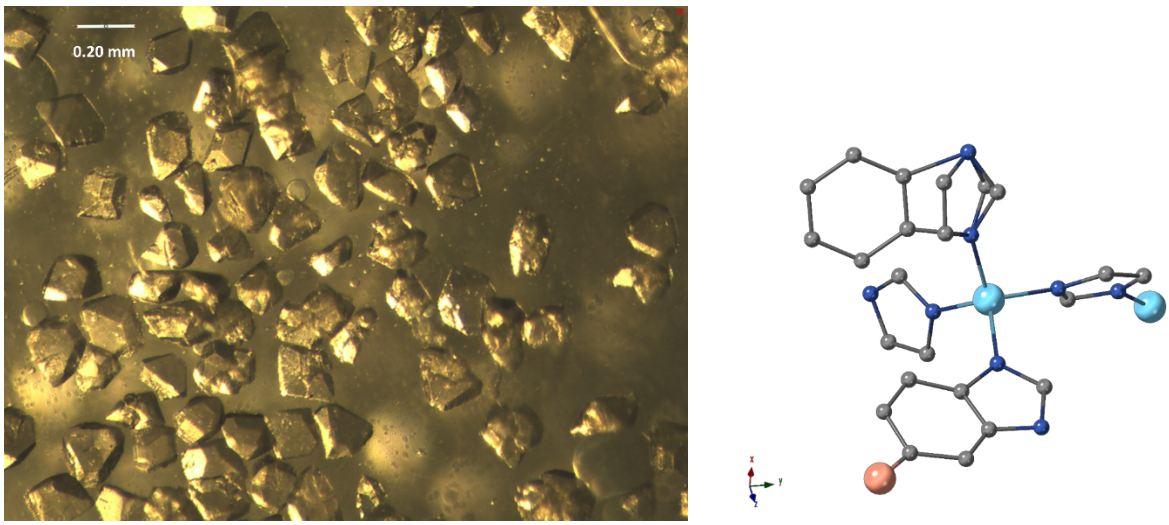

Figure S6. Single crystals of ZIF-UC-**1a**: Optical images (left) and asymmetric unit (right). C- grey, C- dark blue, Zn- light blue. A carbon atom is also coloured orange, which indicates the methyl group. Hydrogen atoms and the solvent are omitted for clarity.

Table S2. Crystal data and structure refinement for ZIF-UC-**1a**.

Chemical formula	$C_{18.84}\ H_{22.06}\ N_{8.92}\ O_{0.92}\ Zn_2$
Formula weight	517.74 g/mol
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	*a* = 15.7365(4) A˚ α = 90°
	b = 16.0434(4) A˚ β = 90°
	c = 18.6754(7) A˚ γ = 90°
Volume	4714.9(2) $Å^3$
Density (calculated)	1.460 g/cm³
Absorption coefficient	2.73
F(000)	2364.64
Crystal size	0.20 x 0.15 x 0.10 mm^3
Theta range for data collection	2.3658 - 64.029°
Index ranges	-16 <= h <= 18, -10 <= k <= 10, -21 <= l <= 21
Reflections collected	10797
Independent reflections	3902
Completeness to theta = 66.9682 °	99.68 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3902 / 22 / 237
Goodness-of-fit on F^2	1.077
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0665, wR2 = 0.2121
R indices (all data)	*R*1 = 0.0771, wR2 = 0.2261
Largest diff. peak and hole	0.845 and -0.439 e. $Å^{-3}$

ZIF-UC-**1f** (*CAG* – Orthorhombic)

Experimental and Refinement Details for ZIF-UC-**1f**

A colourless polyhedral crystal of size 0.15 x 0.12 x 0.10 mm^3, was placed in a 0.2 mm diameter borosilicate loop and mounted on a Gemini E Ultra diffractometer from Oxford Diffraction equipped with an Atlas CCD area detector and operated at 1200 W power (35 kV, 35 mA) to generate Cu Kα radiation (λ = 1.54184 Å) at 293(2) K. A total of 10732 reflections were collected, of which 3844 were unique and 3025 of these were greater than 2σ (I). The varied of θ was from 2.3789° to 64.1320°. Analysis of the data showed negligible decay during collection. The structure was solved in the orthorhombic *Pbca* space group with Z = 8 using SUPERFLIP method.[2] Modelling of electron density within the void of the frameworks leads to identification of 0.88 N,N-Diethylformamide (DEF) guest molecules in the asymmetric unit (in addition to 2 independent Zn and 4 independent linkers). From those linkers, 2 are unsubstituted Im with no disorder, the third linker position is disordered between 0.54 Im, 0.31 bIm and 0.15 mbIm; while the fourth position is disordered between 0.12 mbIm and 0.88 Im. Note that the third position can contain a maximum of 0.5 occupancy for bIm and mbIm linkers, because a centre of symmetry in this space group would bring the linkers related by this centre into contact with each other. In the fourth position, on the other hand, the bIm linker is shifted away from the Im position by by 56.6° to avoid sterically clashing with a neighbouring Im linker in a fully occupied position. Such symmetry limitations result in bIm linkers partially occupying the same crystallographic position as DEF molecules. Carbon atoms within bIm and mbIm linkers (except two) and the solvent atoms were refined isotropically. The rests of non-hydrogen atoms have been refined anisotropically. All hydrogen atoms have been placed in geometrically located positions and their displacement parameters are tied to those of the attached carbon atoms. Hydrogens atoms for the mbIm linker in the fourth position and for the methyl group in the third position have not been included because of the shared electronic density with the solvent molecule (in the first case) and because the occupancy is low to provide accurate coordinates (in the second case). The unit cell of ZIF-UC-**1f** contains 1.71 Im, 0.16 bIm and 0.13 mbIm per zinc. Final full matrix least squares refinement (50 cycles) on F^2 converged to $R1$ = 0.0820 (F >2σF) and wR2 = 0.2416 with GOOF = 1.056. CCDC deposition number 1943553.

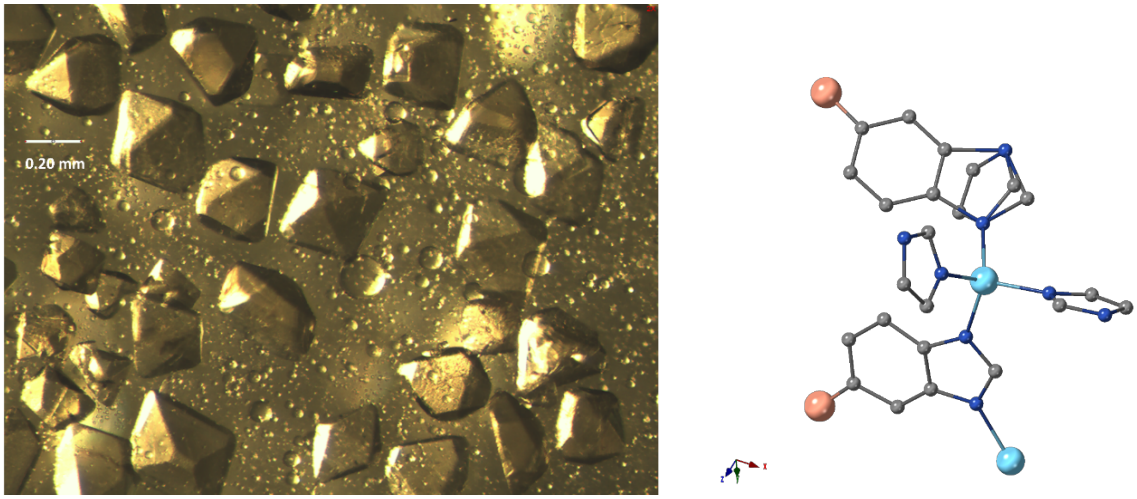

Figure S7. Single crystals of ZIF-UC-**1f**: Optical images (left) and asymmetric unit (right). C- grey, C- dark blue, Zn- light blue. Two carbon atoms are also coloured orange, which indicates the methyl groups. Hydrogen atoms and the solvent are omitted for clarity.

Table S3. Crystal data and structure refinement for ZIF-UC-**1f**.

Chemical formula	$C_{18.98}\ H_{23.37}\ N_{8.88}\ O_{0.88}\ Zn_2$
Formula weight	520.78 g/mol
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	*a* = 15.9807(11) A˚ α = 90°
	b = 18.5721(16) A˚ β = 90°
	c = 15.6944(8) A˚ γ = 90°
Volume	4658.0(6) $Å^3$
Density (calculated)	1.481 g/cm³
Absorption coefficient	2.76
F(000)	2377.52
Crystal size	0.15 x 0.12 x 0.10 mm^3
Theta range for data collection	2.3789 ° - 64.1320 °
Index ranges	-18 <= h <= 16, -21 <= k <= 18, -15 <= l <= 18
Reflections collected	10732
Independent reflections	3844
Completeness to theta = 66.9682 °	99.03 %
Absorption correction	'multi-scan'
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3844 / 19 / 267
Goodness-of-fit on F^2	1.056
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0820 , wR2 = 0.2416
R indices (all data)	*R*1 = 0.0964 , wR2 = 0.2590
Largest diff. peak and hole	0.970 and -0.378 e. $Å^{-3}$

ZIF-UC-**1g** (*CAG* – Orthorhombic)

Experimental and Refinement Details for ZIF-UC-**1g**

A colourless polyhedral crystal of size 0.15 x 0.10 x 0.05 mm^3, was placed in a 0.1 mm diameter borosilicate loop and mounted on a Gemini E Ultra diffractometer from Oxford Diffraction equipped with an Atlas CCD area detector and operated at 1200 W power (35 kV, 35 mA) to generate Cu Kα radiation (λ = 1.54184 Å) at 293(2) K. A total of 10112 reflections were collected, of which 3836 were unique and 3390 of these were greater than 2σ (I). The range of θ was from 2.3801° to 63.9444°. Analysis of the data showed negligible decay during collection. The structure was solved in the orthorhombic *Pbca* space group with Z = 8 using SUPERFLIP method.[2] Modelling of electron density within the void of the frameworks leads to identification of 0.65 N,N-Diethylformamide (DEF) guest molecules in the asymmetric unit (in addition to 2 independent Zn and 4 independent linkers). From those linkers, 2 are unsubstituted Im with no disorder, the third linker position is disordered between 0.52 Im, 0.41 bIm and 0.07 mbIm; the fourth linker position is 0.32 mbIm and 0.68 Im. Note that the third position can contain a maximum of 0.5 occupancy between bIm and mbIm, because a centre of symmetry in this space group would bring non-Im linkers related by this centre into contact with each other. The mbIm linker in the fourth position is shifted away from the imidazole position by 60.7° to avoid sterically clashing with a neighbouring Im linker in a fully occupied position. Such symmetry limitation results in bIm linkers partially occupying the same crystallographic position as DEF molecules. All non-hydrogen atoms were refined anisotropically, except solvent atoms and Carbon atoms from bIm and mbIm benzene rings. All hydrogen atoms have been placed in geometrically located positions and their displacement parameters are tied to those of the attached carbon atoms. Hydrogens atoms for the mbIm linker in the fourth position and for the methyl group in the third position have not been included because of the shared electronic density with the solvent molecule (in the first case) and because the occupancy is low to provide accurate coordinates (in the second case). The unit cell of ZIF-UC-**1g** contains 1.60 Im, 0.21 bIm and 0.19 mbIm per zinc. Final full matrix least squares (50 cycles) refinement on F^2 converged to $R1$ = 0.0785 (F >2σF) and wR2 = 0.2299 with GOOF = 1.175. CCDC deposition number 1943554.

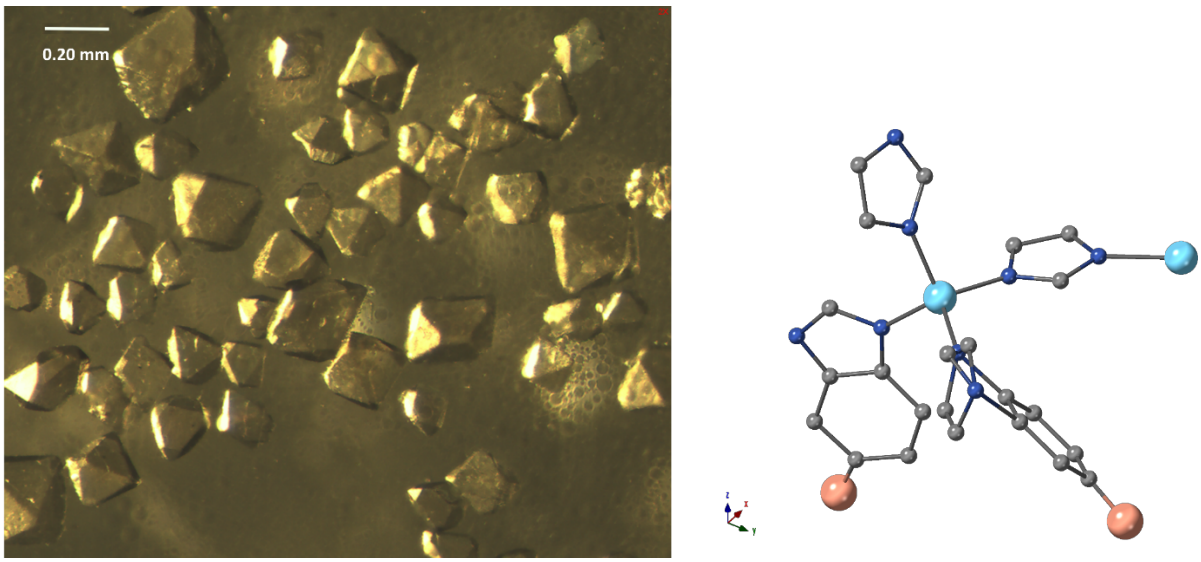

Figure S8. Single crystals of ZIF-UC-**1g**: Optical images (left) and asymmetric unit (right). C- grey, C- dark blue, Zn- light blue. Two carbon atoms are also coloured orange, which indicates the methyl groups. Hydrogen atoms and the solvent are omitted for clarity.

Table S4. Crystal data and structure refinement for ZIF-UC-**1g**.

Chemical formula	$C_{18.78}\ H_{21.46}\ N_{8.65}\ O_{0.65}\ Zn_2$
Formula weight	509.55 g/mol
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	*a* = 15.6574(5) A˚ α = 90°
	b = 15.9532(5) A˚ β = 90°
	c = 18.5634(7) A˚ γ = 90°
Volume	4636.9(3) $Å^3$
Density (calculated)	1.457 g/cm³
Absorption coefficient	2.75
F(000)	2319.76
Crystal size	0.15 x 0.10 x 0.05 mm^3
Theta range for data collection	2.7540 - 63.8120 °
Index ranges	-16 <= h <= 18, -18 <= k <= 18, -13 <= l <= 21
Reflections collected	10112
Independent reflections	3836
Completeness to theta = 66.9682°	99.79 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3836 / 19 / 250
Goodness-of-fit on F^2	1.175
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0785 , wR2 = 0.2299
R indices (all data)	*R*1 = 0.0845 , wR2 = 0.2349
Largest diff. peak and hole	0.961 and -0.556 e. $Å^{-3}$

2. Chemical composition of powder and glass samples

Table S5. Summary of nuclear magnetic resonance results.

Samples	Integration ratio [Im: bIm: mbIm]	Formula	Composition
ZIF-UC-**1a**	1 : 0.10 : 0.05	$Zn\ (Im)_{1.74}\ (bIm)_{0.17}\ (mbIm)_{0.09}$	$Zn_1\ C_{7.13}\ N_4\ H_{6.70}$
a_g ZIF-UC-**1a**	1 : 0.10 : 0.05	$Zn\ (Im)_{1.74}\ (bIm)_{0.17}\ (mbIm)_{0.09}$	$Zn_1\ C_{7.13}\ N_4\ H_{6.70}$
ZIF-UC-**1b**	1 : 0.13 : 0.07	$Zn\ (Im)_{1.66}\ (bIm)_{0.22}\ (mbIm)_{0.12}$	$Zn_1\ C_{7.45}\ N_4\ H_{6.90}$
a_g ZIF-UC-**1b**	1 : 0.13 : 0.07	$Zn\ (Im)_{1.66}\ (bIm)_{0.22}\ (mbIm)_{0.12}$	$Zn_1\ C_{7.45}\ N_4\ H_{6.90}$
ZIF-UC-**1c**	1 : 0.10 : 0.09	$Zn\ (Im)_{1.68}\ (bIm)_{0.17}\ (mbIm)_{0.15}$	$Zn_1\ C_{7.43}\ N_4\ H_{6.94}$
a_g ZIF-UC-**1c**	1 : 0.10 : 0.09	$Zn\ (Im)_{1.68}\ (bIm)_{0.17}\ (mbIm)_{0.15}$	$Zn_1\ C_{7.43}\ N_4\ H_{6.94}$
ZIF-UC-**1d**	1 : 0.17 : 0.09	$Zn\ (Im)_{1.59}\ (bIm)_{0.27}\ (mbIm)_{0.14}$	$Zn_1\ C_{7.79}\ N_4\ H_{7.11}$
a_g ZIF-UC-**1d**	1 : 0.17 : 0.09	$Zn\ (Im)_{1.59}\ (bIm)_{0.27}\ (mbIm)_{0.14}$	$Zn_1\ C_{7.79}\ N_4\ H_{7.11}$
ZIF-UC-**1e**	1 : 0.11 : 0.13	$Zn\ (Im)_{1.61}\ (bIm)_{0.18}\ (mbIm)_{0.21}$	$Zn_1\ C_{7.76}\ N_4\ H_{7.19}$
a_g ZIF-UC-**1e**	1 : 0.11 : 0.13	$Zn\ (Im)_{1.61}\ (bIm)_{0.18}\ (mbIm)_{0.21}$	$Zn_1\ C_{7.76}\ N_4\ H_{7.19}$

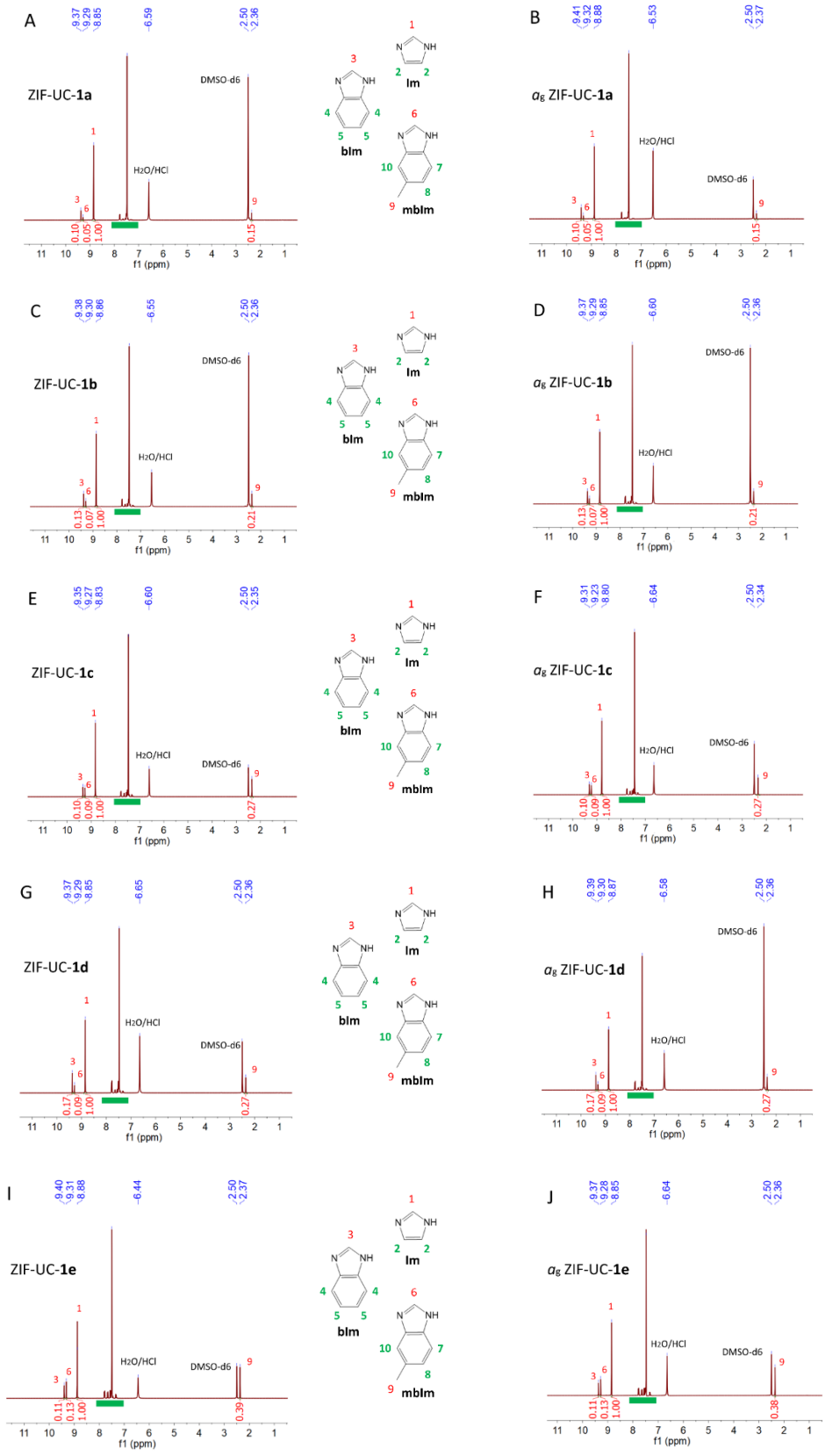

Figure S9. Nuclear magnetic resonance spectra for crystalline and glasses samples. Peaks inside the region highlighted in green correspond to aromatic hydrogen atoms. The DMSO-d6 peak was set to be at 2.500 ppm, according to the values provided in the software MestReNova version 6.0.2-5475.

Table S6. Summary of elemental analysis results. Zn % was indirectly determined from HCN results.

Samples	Weight (mgs)	C %		N %		H %		Zn %	
		exp	*calc*	*exp*	*calc*	*exp*	*calc*	*exp*	*calc*
ZIF-UC-**1a**	0.69	38.15	40.05	24.65	26.2	3.14	3.16	34.06	30.58
a_g ZIF-UC-**1a**	1.00	38.68	40.05	25.61	26.2	3.02	3.16	32.69	30.58
ZIF-UC-**1b**	1.83	39.18	41.07	24.91	25.72	3.11	3.19	32.80	30.02
a_g ZIF-UC-**1b**	2.58	38.96	41.07	24.92	25.72	3.15	3.19	32.97	30.02
ZIF-UC-**1c**	1.71	39.40	41.00	25.09	25.74	3.13	3.21	32.38	30.04
a_g ZIF-UC-**1c**	1.15	39.32	41.00	25.05	25.74	2.99	3.21	32.64	30.04
ZIF-UC-**1d**	1.00	40.18	42.12	24.23	25.22	3.01	3.23	32.58	29.44
a_g ZIF-UC-**1d**	1.47	40.08	42.12	24.31	25.22	2.95	3.23	32.66	29.44
ZIF-UC-**1e**	0.85	40.39	42.01	24.00	25.25	2.91	3.27	32.70	29.47
a_g ZIF-UC-**1e**	1.76	40.55	42.01	24.31	25.25	3.05	3.27	32.09	29.47

3. Differential scanning calorimetry

Each experiment was designed to run three scans with results listed in Table S7. Original scans are shown in Figure S10. Glass transition temperatures were reported as the midpoint of the glass transition interval, while melting temperatures were determined at the offset of the melting peaks.

Table S7. Experimental results from DSC scans.

Samples	Composition	T_g (K)	T_m onset (K)	T_m offset (K)	ΔH_m (J/g)
ZIF-UC-**1a**	Zn $(Im)_{1.74}$ $(bIm)_{0.17}$ $(mbIm)_{0.09}$	588	561	706	16.2
ZIF-UC-**1b**	Zn $(Im)_{1.66}$ $(bIm)_{0.22}$ $(mbIm)_{0.12}$	578	563	691	18.9
ZIF-UC-**1c**	Zn $(Im)_{1.68}$ $(bIm)_{0.17}$ $(mbIm)_{0.15}$	584	575	698	20.8
ZIF-UC-**1d**	Zn $(Im)_{1.59}$ $(bIm)_{0.27}$ $(mbIm)_{0.14}$	583	546	693	21.7
ZIF-UC-**1e**	Zn $(Im)_{1.61}$ $(bIm)_{0.18}$ $(mbIm)_{0.21}$	589	558	703	27.9

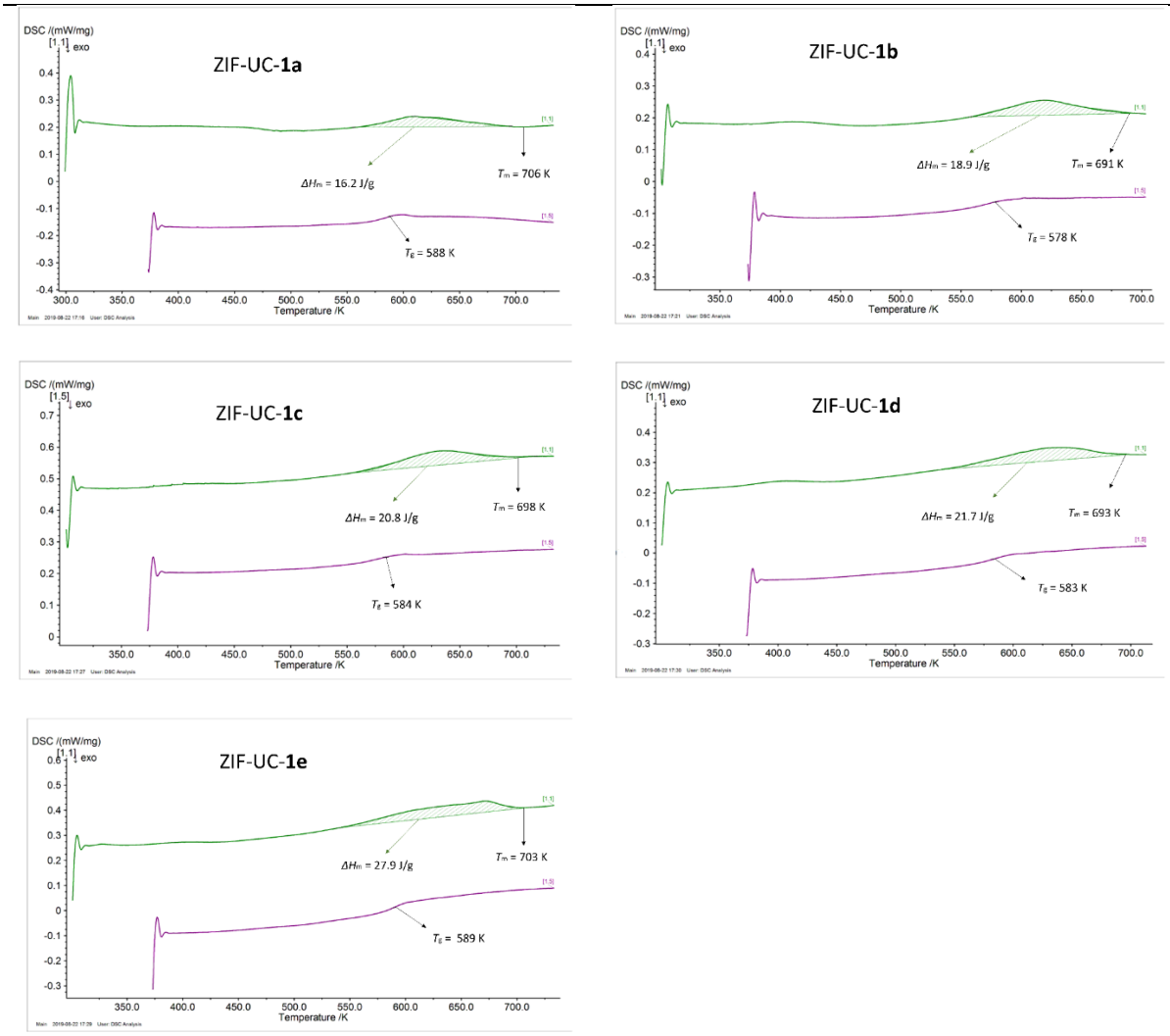

Figure S10. DSC scans. Melting and glass transition temperatures are highlighted, as well as the change in enthalpy of melting. First upscan shown in green and second in purple.

4. Statistical analysis

Table S8. Probabilities for tetrahedral configurations $Zn(Im)_k\,(bIm)_l\,(mbIm)_m$, ($k + l + m = 4$).

			$F_j(k,l,m)$				
k	l	m	ZIF-UC-**1a**	ZIF-UC-**1b**	ZIF-UC-**1c**	ZIF-UC-**1d**	ZIF-UC-**1e**
0	0	4	4.10E-06	1.30E-05	3.16E-05	2.40E-05	1.22E-04
0	1	3	3.10E-05	9.50E-05	1.43E-04	1.85E-04	4.17E-04
0	2	2	8.78E-05	2.61E-04	2.44E-04	5.36E-04	5.36E-04
0	3	1	1.11E-04	3.19E-04	1.84E-04	6.89E-04	3.06E-04
0	4	0	5.22E-05	1.46E-04	5.22E-05	3.32E-04	6.56E-05
1	0	3	3.17E-04	7.17E-04	1.42E-03	1.09E-03	3.73E-03
1	1	2	1.80E-03	3.94E-03	4.82E-03	6.31E-03	9.59E-03
1	2	1	3.39E-03	7.23E-03	5.46E-03	1.22E-02	8.22E-03
1	3	0	2.14E-03	4.42E-03	2.06E-03	7.82E-03	2.35E-03
2	0	2	9.20E-03	1.49E-02	2.38E-02	1.86E-02	4.29E-02
2	1	1	3.47E-02	5.46E-02	5.40E-02	7.17E-02	7.35E-02
2	2	0	3.28E-02	5.00E-02	3.06E-02	6.91E-02	3.15E-02
3	0	1	1.19E-01	1.37E-01	1.78E-01	1.41E-01	2.19E-01
3	1	0	2.24E-01	2.52E-01	2.02E-01	2.71E-01	1.88E-01
4	0	0	5.73E-01	4.75E-01	4.98E-01	3.99E-01	4.20E-01

5. Topological constraint theory (TCT) model for T_g

Based upon the TCT model recently developed by Yang et al., the relation between T_g and the atomic degree of freedom in the ternary system [$Zn(Im_{2-(x+y)}\,bIm_x\,mbIm_y)$] can be written as follows

$$T_g \cdot \left[3 - \frac{2+14\cdot(2-x-y)+(26+\Delta_{bIm})\cdot x+(26+\Delta_{mbIm})\cdot y+\Delta_{ex}}{11+4\cdot(x+y)}\right] = C \quad (1)$$

Where C is treated as a fitting parameter and is constant within a given family of glass. Δ_{bIm} and Δ_{mbIm} denote the constraint changes when an Im is substituted by a bIm or a mbIm due to the constraint differences between them. Δ_{ex} denotes the extra constraint change from special ligand coordination configurations including $Zn(Im)_3(bIm)_1$, $Zn(Im)_3(mbIm)_1$ and $Zn(Im)_2(bIm)_1(mbIm)_1$ which is calculated as:

$$\Delta_{ex} = \Delta_{Im_3bIm_1}\binom{4}{1}\left(\frac{2-x-y}{2}\right)^3\left(\frac{x}{2}\right) + \Delta_{Im_3mbIm_1}\binom{4}{1}\left(\frac{2-x-y}{2}\right)^3\left(\frac{y}{2}\right) + \Delta_{Im_2bIm_1mbIm_1}\binom{4}{2}\binom{2}{1}\left(\frac{2-x-y}{2}\right)^2\left(\frac{x}{2}\right)\left(\frac{y}{2}\right) \quad (2)$$

Here $\Delta_{Im_3bIm_1}$, $\Delta_{Im_3mbIm_1}$ and $\Delta_{Im_2bIm_1mbIm_1}$ denote extra change of constraint due to appearance of one unit of each of the three configurations: $Zn(Im)_3(bIm)_1$, $Zn(Im)_3(mbIm)_1$ and $Zn(Im)_2(bIm)_1(mbIm)_1$. To obtain $\Delta_{Im_3bIm_1}$, $\Delta_{Im_3mbIm_1}$ and $\Delta_{Im_2bIm_1mbIm_1}$, we fit Eq. (1) using experimentally measured T_g of [$Zn(Im_{2-(x+y)}\,bIm_x\,mbIm_y)$] by minimizing the residual sum of squares. The resultant predictions are listed in Table S8 with a root-mean-square-error of 3 K. The values of C, Δ_{bIm}, Δ_{mbIm} $\Delta_{Im_3bIm_1}$, $\Delta_{Im_3mbIm_1}$ and $\Delta_{Im_2bIm_1mbIm_1}$ are 154.4 K, -0.52, -0.51, 0, 0 and -0.10, respectively, indicating that the effects of $Zn(Im)_3(bIm)_1$ and $Zn(Im)_3(mbIm)_1$ on the total atomic constraint can be ignored and the configuration $Zn(Im)_2(bIm)_1(mbIm)_1$ tends to further reduce the atomic constraint in the ternary system. Based on Eq. (1), the compositional dependence of T_g for the ternary system is illustrated in Fig. 4a.

Table S9. Experimental and predicted glass transition temperatures for a system with chemical composition Zn $(Im)_{2-(x+y)}$ $(bIm)_x$ $(mbIm)_y$ using molecular dynamic simulations.

x	y	Experimental T_g (K)	Predicted T_g (K)	Error
0.00	0.00	565	566.27	1.27
0.03	0.00	568	569.21	1.29
0.04	0.00	569	570.80	1.53
0.06	0.00	571	572.91	1.82
0.08	0.00	575	575.01	0.03
0.13	0.00	579	579.41	0.65
0.17	0.00	584	583.49	-0.09
0.19	0.00	586	585.77	-0.31
0.21	0.00	590	587.77	-2.19
0.22	0.00	592	589.27	-2.56
0.25	0.00	595	591.99	-3.01
0.28	0.00	596	594.94	-1.06
0.32	0.00	600	598.82	-1.18
0.36	0.00	602	602.64	0.64
0.44	0.00	607	610.15	3.15
0.25	0.00	591	591.99	0.99
0.00	0.50	616	616.85	0.85
0.17	0.09	588	582.47	-5.53
0.22	0.12	578	584.35	6.35
0.17	0.15	584	582.67	-1.33
0.27	0.14	583	585.98	2.98
0.18	0.21	589	583.72	-5.28

6. Reproducibility of DSC measurements

To estimate the error associated with the determination of T_g, T_m and ΔH_m (J/g), five DSC experiments on sample ZIF-UC-**1a** were performed. Results appear in Table S10 and corresponding DSC scans appears in Fig S11. Glass transition temperatures were reported as the midpoint of the glass transition interval, while melting temperatures were determined at the offset of the melting peaks.

Table S10. Experimental results from DSC scans of sample ZIF-UC-**1a.** Average values and standard deviations were estimated from these 5 measurements.

Samples	T_g (K)	T_m onset (K)	T_m end (K)	ΔH_m (J/g)
ZIF-UC-**1a**	591	553	703	16.2
ZIF-UC-**1a_I**	590	561	706	13.8
ZIF-UC-**1a_II**	588	557	708	19.1
ZIF-UC-**1a_III**	586	543	705	18.1
ZIF-UC-**1a_IV**	585	548	699	17.2
Average	588	552	704	16.9
Std Dev	2	6	3	1.5

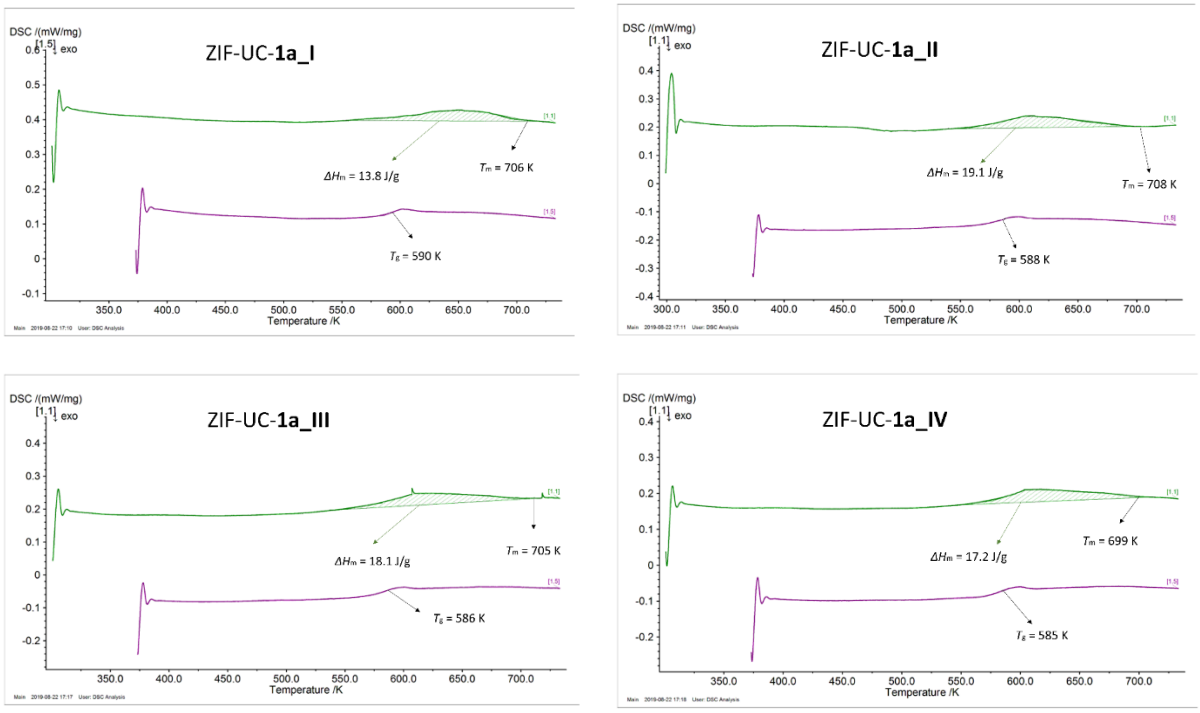

Figure S11. Reproducibility measurements for ZIF-UC-**1a.** The first measurement (ZIF-UC-**1a**), was already reported in Fig. S10.

7. SDT and TGA data

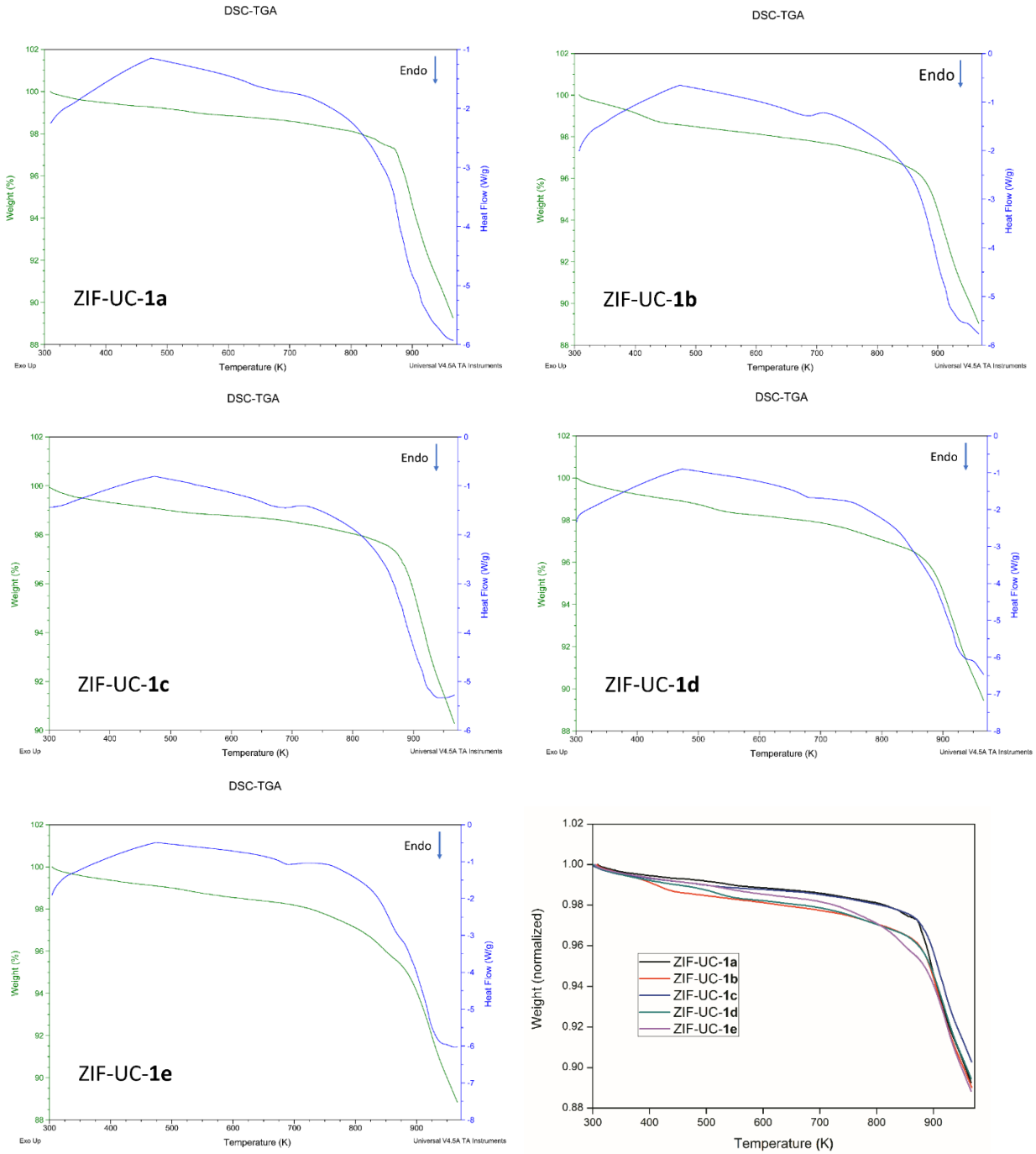

Figure S12. SDT and TGA data.

8. Bulk glass formation

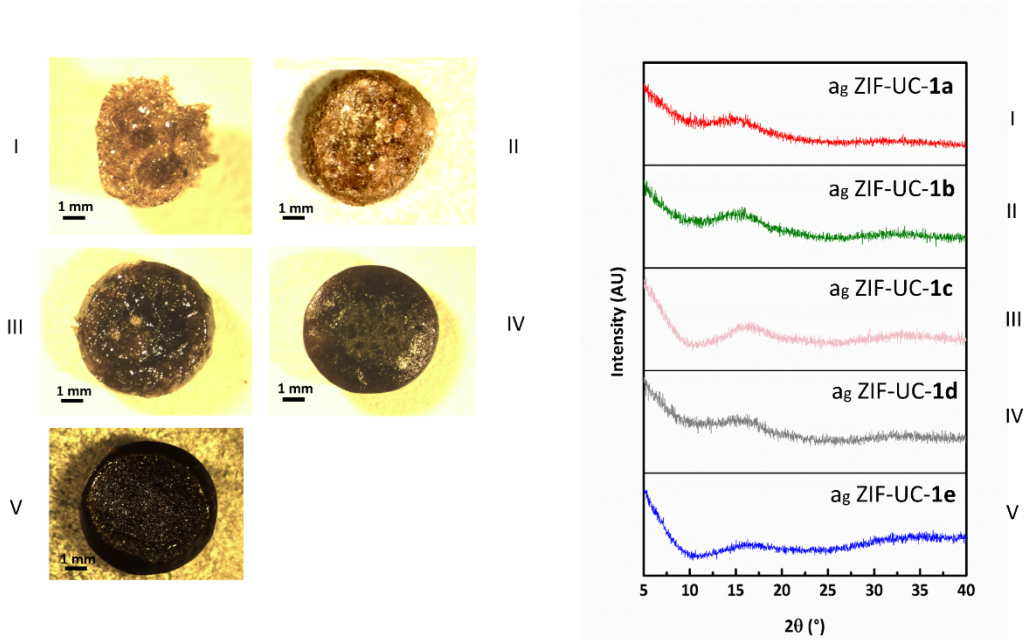

Figure S13. X-ray diffraction patterns of all glass samples with corresponding pictures of the obtained glasses. The colour of the final glass depends of the amount of mbIm and may indicate partial demethylation upon melting.

References

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