Electronic Supplementary Information

A zeolitic imidazolate framework with conformational variety: Conformational polymorphs *versus* frameworks with static conformational disorder

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Table S1 Relative total energies, crystal and structural data (at -273 °C) for the three conformational [Zn(dcim)$_2$]-SOD polymorphs as obtained by DFT.

	I	**II**	**III**
energy[a] **/ kJ·mol^{-1}**	39.8	28.9	15.9
crystal system	cubic	cubic	trigonal
space group	$Im\bar{3}m$	$I\bar{4}3m$	$R\bar{3}$
***a* / Å**	17.2941	16.8188	22.7695
***c* / Å**	-	-	15.6524
***V* / Å^3**	5172.42	4757.59	7027.79
Z	12	12	18
a_{rhom}[b] **/ Å**	14.9771	14.5655	14.1435
α_{rhom}[b] **/ °**	109.47	109.47	107.21
V_{rhom}[b] **/ Å^3**	2586.22	2378.80	2342.5
Z_{rhom}[b]	6	6	6
ρ / g·cm^{-3}	1.299	1.413	1.435
***d*(Zn−N) / Å**	2.002	2.011	1.996 − 2.013
∢(N−Zn−N) / °	104.78 − 119.32	101.99 − 113.34	102.98 – 119.57
***d*(Zn···Zn) / Å**	6.114	5.946	5.865; 6.082
∢(Zn−*dcim*−Zn) / °	147.86	138.55	135.23; 143.78
$d(Cl\cdots Cl)_{min}$[c] **/ Å**	4.259	3.682	3.630
prim. cavity diameter[d] **/ Å**	9.037	8.184	6.650
sec. cavity diameter[d] **/ Å**	5.839	5.783	5.328 (6R-A); 4.224 (6R-B)
free window diameter[e] **/ Å**	4.275	3.852	3.821 (6R-A); 2.890 (6R-B)
Void system[f] **/ %**	39.7 (1.4)	34.8 (1.4)	31.7 (1.4)
	36.8 (1.7)	31.9 (1.7)	27.5 (1.7)

[a]given relative to the most stable [Zn(dcim)$_2$]-lcs polymorph; [b]rhombohedral (reduced) cell; [c]*inter*-linker distances; [d]estimated as the largest including sphere with considering van der Waals radii of Cl atoms (1.75 Å); [e]estimated as the largest circle fitting in the 6R windows with considering van der Waals radii of Cl atoms; [f]according to a VOID/MERCURY calculation using probe radii of 1.4 and 1.7 Å (approximate kinetic diameters for H_2O and Ar respectively).

Table S2 Atomic co-ordinates, statistical occupancy factors and displacement parameters obtained by Rietveld refinement for **1**.

atom	Wyckoff position	*x*	*y*	*z*	sof	B_{iso} (Å^2)
Zn	18f	0.06958(8)	0.39768(8)	0.65656(14)	1	6.3(1)
N11	18f	0.02461	0.34308	0.55451	1	9.84(9)
C11	18f	-0.00303	0.36371	0.49394	1	9.84(9)
H11	18f	-0.00859	0.40136	0.49984	1	9.84(9)
N21	18f	-0.02180	0.32415	0.42400	1	9.84(9)
C21	18f	0.02317	0.28642	0.52123	1	9.84(9)
C31	18f	-0.00503	0.27500	0.44069	1	9.84(9)
Cl11	18f	0.05349	0.24176	0.57574	1	9.84(9)
Cl21	18f	-0.01777	0.21348	0.36762	1	9.84(9)
N12	18f	0.07842	0.48699	0.63275	1	9.84(9)
C12	18f	0.05409	0.52320	0.67150	1	9.84(9)
H12	18f	0.02168	0.50606	0.71481	1	9.84(9)
N22	18f	0.08163	0.58688	0.64096	1	9.84(9)
C22	18f	0.12478	0.53034	0.57380	1	9.84(9)
C32	18f	0.12688	0.59175	0.57881	1	9.84(9)
Cl12	18f	0.16953	0.50719	0.50761	1	9.84(9)
Cl22	18f	0.17612	0.66423	0.52115	1	9.84(9)

Table S3 Atomic co-ordinates, statistical occupancy factors and displacement parameters obtained by Rietveld refinement for **1**-**DMF**.

atom	Wyckoff position	*x*	*y*	*z*	sof	B_{iso} (Å^2)
Zn	18f	-0.0697(2)	-0.40728(2)	0.3201(4)	1	4.25(14)
N11	18f	-0.0310	-0.3531	0.4190	1	4.53(11)
C11	18f	-0.0066	-0.3730	0.4853	1	4.53(11)
H11	18f	-0.0124	-0.4157	0.4894	1	4.53(11)
N21	18f	0.0268	-0.3247	0.5453	1	4.53(11)
C21	18f	-0.0117	-0.2892	0.4379	1	4.53(11)
C31	18f	0.0229	-0.2721	0.5154	1	4.53(11)
Cl11	18f	-0.0278	-0.2372	0.3720	1	4.53(11)
Cl21	18f	0.0562	-0.1952	0.5691	1	4.53(11)
N12	18f	-0.1565	-0.4124	0.2967	1	4.53(11)
C12	18f	-0.1929	-0.3893	0.3380	1	4.53(11)
H12	18f	-0.1767	-0.3592	0.3837	1	4.53(11)
N22	18f	-0.2557	-0.4152	0.3052	1	4.53(11)
C22	18f	-0.1986	-0.4548	0.2368	1	4.53(11)

C32	18f	-0.2585	-0.4564	0.2419	1	4.53(11)
Cl12	18f	-0.1781	-0.4997	0.1637	1	4.53(11)
Cl22	18f	-0.3288	-0.5044	0.1770	1	4.53(11)
N13	18f	0.3206	0.1620	-0.3531	0.503	10.7(5)
C13	18f	0.2676	0.1677	-0.3968	0.503	10.7(5)
H13	18f	0.2900	0.2139	-0.4355	0.503	10.7(5)
H23	18f	0.2308	0.1680	-0.3510	0.503	10.7(5)
H33	18f	0.2406	0.1254	-0.4410	0.503	10.7(5)
C23	18f	0.3727	0.1621	-0.4065	0.503	10.7(5)
H43	18f	0.3501	0.1178	-0.4494	0.503	10.7(5)
H53	18f	0.4123	0.1612.	-0.3667	0.503	10.7(5)
H63	18f	0.3965	0.2080	-0.4470	0,503	10.7(5)
O13	18f	0.2813	0.1602	-0.2193	0.503	10.7(5)
H73	18f	0.3617	0.1515	-0.2344	0.503	10.7(5)
C33	18f	0.3227	0.1574	-0.2649	0.503	10.7(5)
N14	18f	0.0018	0.0080	-0.9242	0.120	10.7(5)
C14	18f	-0.0623	-0.0159	-0.9673	0.120	10.7(5)
H14	18f	-0.1049	-0.0439	-0.9227	0.120	10.7 (5)
H24	18f	-0.0671	-0.0503	-1.0201	0.120	10.7(5)
H34	18f	-0.0646	0.0272	-0.9944	0.120	10.7(5)
C24	18f	0.0625	0.0409	-0.9760	0.120	10.7(5)
H44	18f	0.0510	0.0431	-1.0452	0.120	10.7(5)
H54	18f	0.0902	0.0134	-0.9701	0.120	10.7(5)
H64	18f	0.0935	0.0928	-0.9534	0.120	10.7(5)
O14	18f	-0.0422	-0.0212	-0.7903	0.120	10.7(5)
H74	18f	0.0551	0.0206	-0.8071	0.120	10.7(5)
C34	18f	0.0069	0.0027	-0.8365	0.120	10.7(5)
N15	18f	0.6233	0.3137	-0.0575	0.265	10.7(5)
C15	18f	0.6539	0.3691	0.0040	0.265	10.7(5)
H15	18f	0.6177	0.3855	0.0207	0.265	10.7(5)
H25	18f	0.6979	0.4118	-0.0251	0.265	10.7(5)
H35	18f	0.6700	0.3548	0.0642	0.265	10.7(5)
C25	18f	0.6205	0.2504	-0.0385	0.265	10.7(5)
H45	18f	0.6240	0.2440	0.0321	0.265	10.7(5)
H55	18f	0.6625	0.2495	-0.0711	0.265	10.7(5)
H65	18f	0.5725	0.2078	-0.0616	0.265	10.7(5)
O15	18f	0.5707	0.2781	-0.1859	0.265	10.7(5)
H75	18f	0.6079	0.3718	-0.1512	0.265	10.7(5)
C35	18f	0.6009	0.3236	-0.1350	0.265	10.7(5)

Table S4 Atomic co-ordinates, statistical occupancy factors and displacement parameters obtained by Rietveld refinement for **2**.

atom	Wyckoff position	*x*	*y*	*z*	sof	B_{iso} (Å^2)
Zn	12d	1/2	1/4	0	1	9.7(3)
N11	96l	0.4286	0.3347	0.0319	0.266	16.1(2)
C11	48j	0.3732	0.3732	-0.0097	0.266	16.1(2)
H11	48j	0.3625	0.3625	-0.0632	0.266	16.1(2)
C21	96l	0.4264	0.3668	0.1070	0.266	16.1(2)
Cl11	96l	0.4876	0.3362	0.1827	0.266	16.1(2)
N12	48j	0.6029	0.3037	0	0.453	16.1(2)
C12	24h	0.6183	0.3816	0	0.453	16.1(2)
H12	24h	0.5791	0.4209	0	0.453	16.1(2)
C22	48j	0.6756	0.2665	0	0.453	16.1(2)
Cl12	48j	0.6865	0.1651	0	0.453	16.1(2)

Table S5 Atomic co-ordinates, statistical occupancy factors and displacement parameters obtained by Rietveld refinement for **2-THF**.

atom	Wyckoff position	*x*	*y*	*z*	sof	B_{iso} (Å^2)
Zn	12d	1/2	1/4	0	1	7.01(13)
N11	96l	0.4277	0.3352	0.0371	0.283	12.52(12)
C11	48j	0.3731	0.3731	-0.0065	0.283	12.52(12)
H11	48j	0.3558	0.3558	-0.0555	0.283	12.52(12)
C21	96l	0.4237	0.3684	0.1116	0.283	12.52(12)
Cl11	96l	0.4829	0.3390	0.1893	0.283	12.52(12)
N12	48j	0.6029	0.3037	0	0.472	12.52(12)
C22	24h	0.6183	0.3816	0	0.472	12.52(12)
H12	24h	0.5792	0.4206	0	0.472	12.52(12)
C22	48j	0.6756	0.2665	0	0.472	12.52(12)
Cl12	48j	0.6865	0.1651	0	0.472	12.52(12)
O13	96l	-0.1611	0.2451	-0.2260	0.066	14.1(5)
C13	96l	-0.2152	0.1942	-0.1880	0.066	14.1(5)
H13	96l	-0.2097	0.1946	-0.1304	0.066	14.1(5)
H23	96l	-0.2030	0.1347	-0.2148	0.066	14.1(5)
C23	96l	-0.2990	0.2170	-0.2129	0.066	14.1(5)

H33	96l	-0.3310	0.1668	-0.2406	0.066	14.1(5)
H43	96l	-0.3310	0.2406	-0.1668	0.066	14.1(5)
C33	96l	-0.2871	0.2777	-0.2773	0.066	14.1(5)
H53	96l	-0.3021	0.3359	-0.2555	0.066	14.1(5)
H63	96l	-0.3221	0.2654	-0.3299	0.066	14.1(5)
C43	96l	-0.1994	0.2713	-0.2952	0.066	14.1(5)
H73	96l	-0.1895	0.2297	-0.3429	0.066	14.1(5)
H83	96l	-0.1763	0.3284	-0.3129	0.066	14.1(5)
O14	96l	0.5930	0.5282	0.6216	0.021	14.1(5)
C14	96l	0.5970	0.4474	0.6001	0.021	14.1(5)
H14	96l	0.5409	0.4187	0.6089	0.021	14.1(5)
H24	96l	0.6424	0.4171	0.6306	0.021	14.1(5)
C24	96l	0.6151	0.4417	0.5123	0.021	14.1(5)
H34	96l	0.5617	0.4409	0.4768	0.021	14.1(5)
H44	96l	0.6502	0.3897	0.4991	0.021	14.1(5)
C34	96l	0.6613	0.5162	0.4970	0.021	14.1(5)
H54	96l	0.7241	0.5052	0.5062	0.021	14.1(5)
H64	96l	0.6502	0.5402	0.4415	0.021	14.1(5)
C44	96l	0.6331	0.5719	0.5623	0.021	14.1(5)
H74	96l	0.6829	0.6030	0.5880	0.021	14.1(5)
H84	96l	0.5935	0.6153	0.5366	0.021	14.1(5)

Table S6 Selected *inter*-atomic distances and angles and cavity diameters obtained by Rietveld refinement for **1**, **1-DMF**, **2** and **2-THF**.

	1	**1-DMF**	**2**	**2-THF**
***d*(Zn−N) / Å**	1.96(5) – 2.00(5)	1.90(6) – 2.02 (5)	1.9308(13); 1.9442	1.956; 1.9614(11)
∢(N−Zn−N) / °	104(2) – 121(3)	100.4(16) – 124(2)	95.4(9) – 125.9(9)	94.4(6) – 126.8(6)
***d*(Zn···Zn) / Å**	5.852; 6.048	5.908; 6.057	5.920	5.958
∢(Zn−*dcim*−Zn) / °	137.2; 147.2	139.8; 147.8	144.2; 144.9	142.4; 144.2
$d(N-C)_{mean}$ **/ Å**	1.36	1.35	1.35	1.35
$d(C-C)_{mean}$ **/ Å**	1.37	1.38	1.39	1.34
$d(C-H)_{mean}$ **/ Å**	0.93	0.93	0.93	0.93
$d(Cl\cdots Cl)_{min}$[a] **/ Å**	3.80	3.67	3.75	3.68
$d(H\cdots H)_{min}$[a] **/ Å**	3.96	4.14	2.64	2.67
$d(H\cdots Cl)_{min}$[a] **/ Å**	2.89	2.82	3.13	3.12
prim. cavity diamter[b] **/ Å**	6.78	7.28	8.46	8.44
sec. cavity diameter[b] **/ Å**	4.88 (6R-A); 3.95 (6R-B)	5.61 (6R-A); 4.47 (6R-B)	5.42	5.39
window diameter[c] **/ Å**	3.72 (6R-A); 2.76 (6R-B)	3.92 (6R-A); 3.18 (6R-B)	3.92	3.97

[a]*inter*-linker distances; [b]estimated as the largest including sphere with considering van der Waals radii of Cl atoms (1.75 Å); [c]estimated as the largest circle fitting in the 6R windows with considering van der Waals radii of Cl atoms.

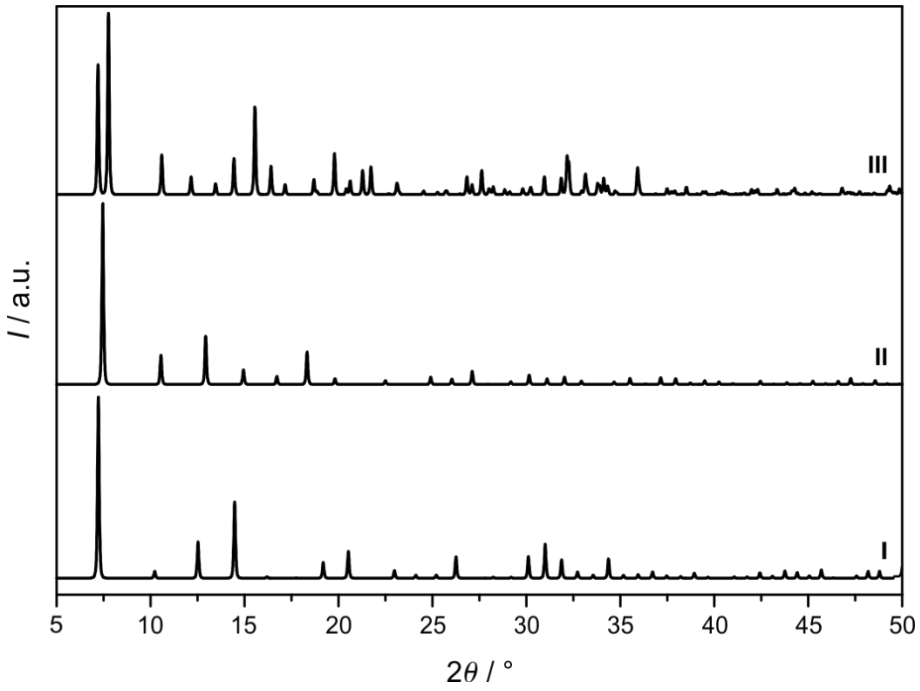

Fig. S1 PXRD patterns simulated for framework conformers **I**, **II** and **III** (CuKα1 radiation).

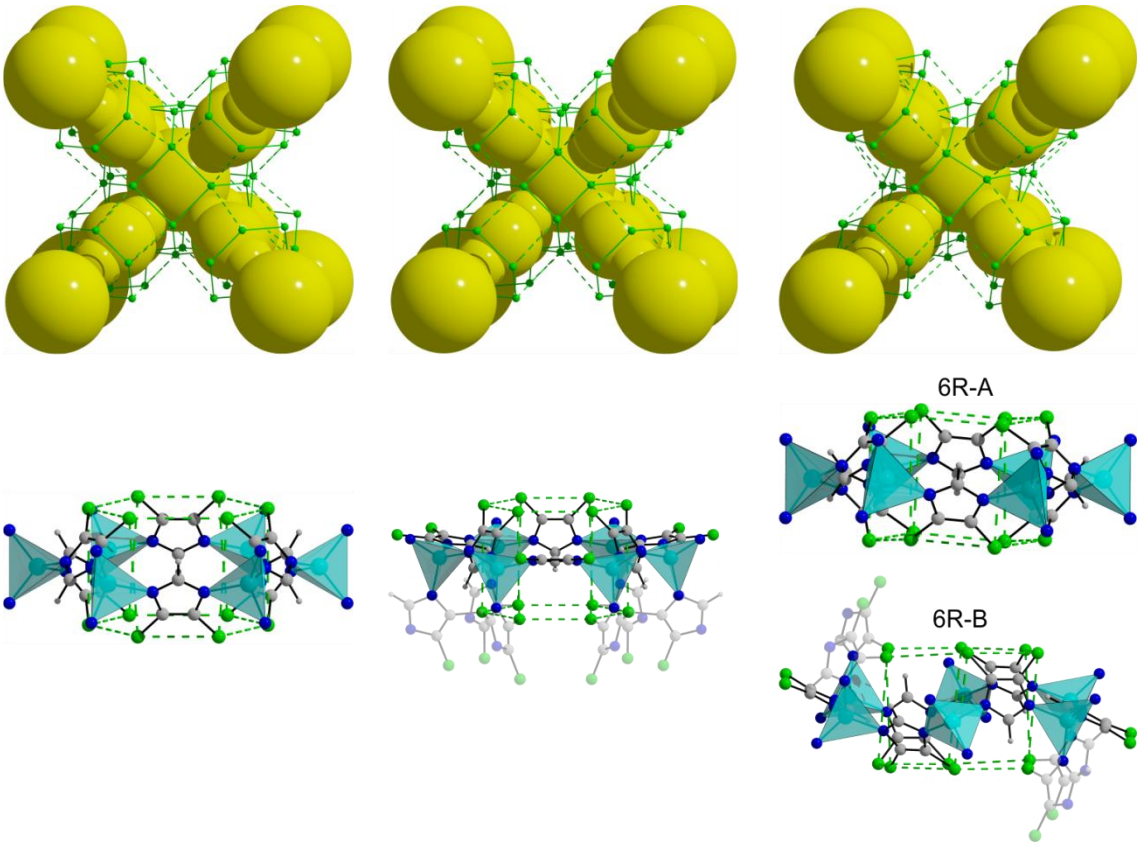

Fig. S2 The void systems in framework conformers **I**, **II** and **III** showing the primary cavities ($[4^6.6^8]$ truncated octahedra) and secondary cavities (slightly distorted $[4^6.6^2]$ hexagonal prisms). Details of the secondary cavities are shown in the lower panel. Colour code: Cyan, ZnN_4 tetrahedra; blue, N; grey, C; green, Cl; grey, H.

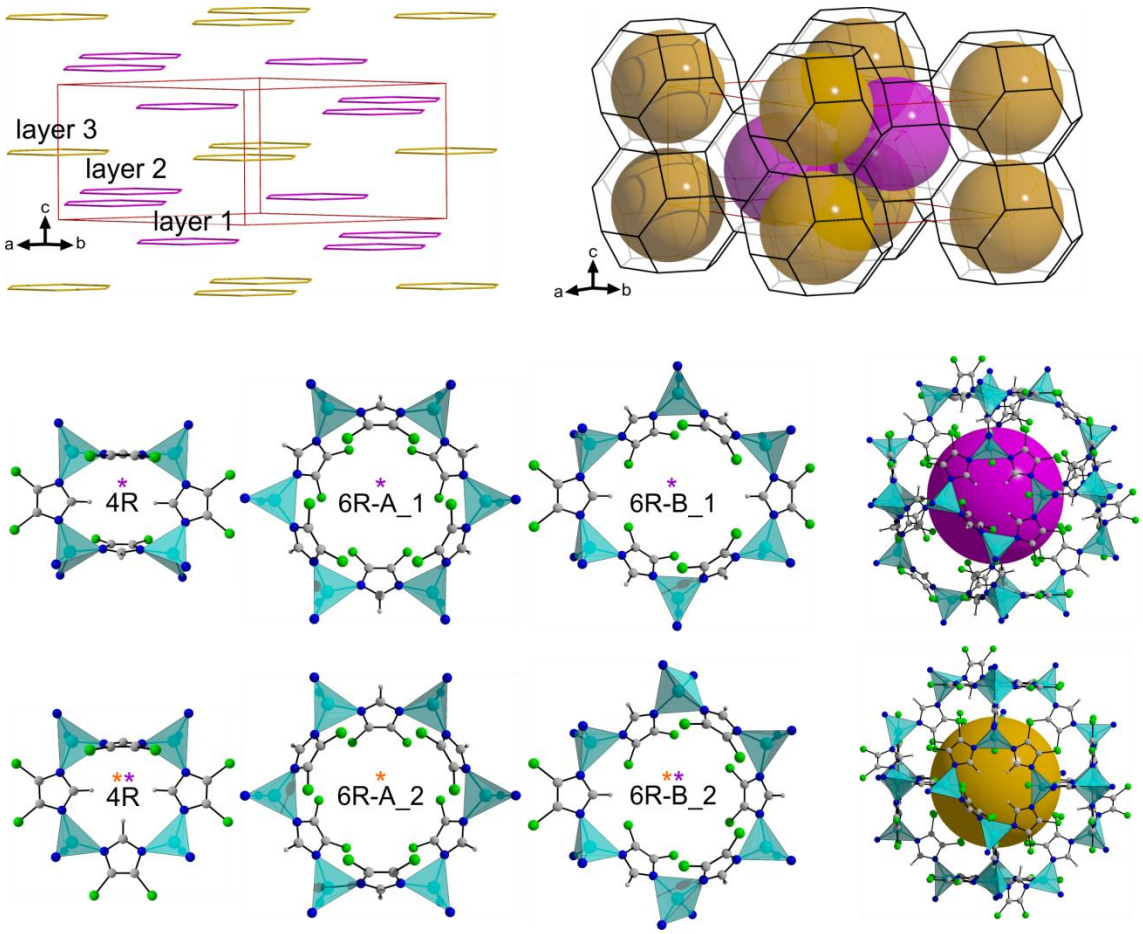

Fig. S3 Structural model of framework conformer **IV**. Upper panel: ABC stacking of 2-dimensional Periodic Building Units (non-connected planar six-rings) of the SOD topology[1] with indication of the conformations of the 6R-A rings (pink, conformation as in **III**; orange, conformation as in **I**) and SOD topology with indication of the two unique [$4^6.6^8$] cavities (pink and orange spheres). Lower panels: Unique four- and six-rings and [$4^6.6^8$] cavities. The coloured asterisks in the four- and six-rings indicate by which cavities the rings are shared. Crystal data for **IV**: Hexagonal, $P\bar{3}m1$, Z = 18, a = 25.5066 Å, c = 14.7437 Å, V = 7668.56 Å^3, ρ = 1.315 g·cm^{-3}.

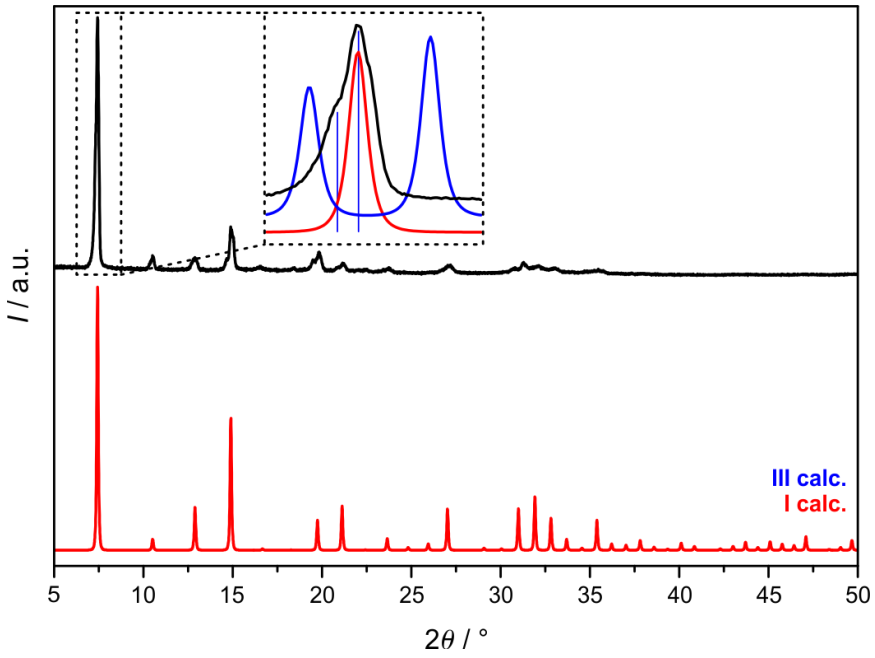

Fig. S4 Typical PXRD pattern (black profile) of a product recovered from a reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and Hdcim in 1-propanolic solution containing aqueous ammonia. For comparison a simulated pattern of **I** (red profile) is also shown. The experimental pattern reveals similarities with some patterns of intermediates of **1** and **2** (see Fig. 9). The inset shows an expansion of the region around the strongest reflection to illustrate the spitting of this reflection. For comparison simulations of that region are also shown for **I** and **III**.

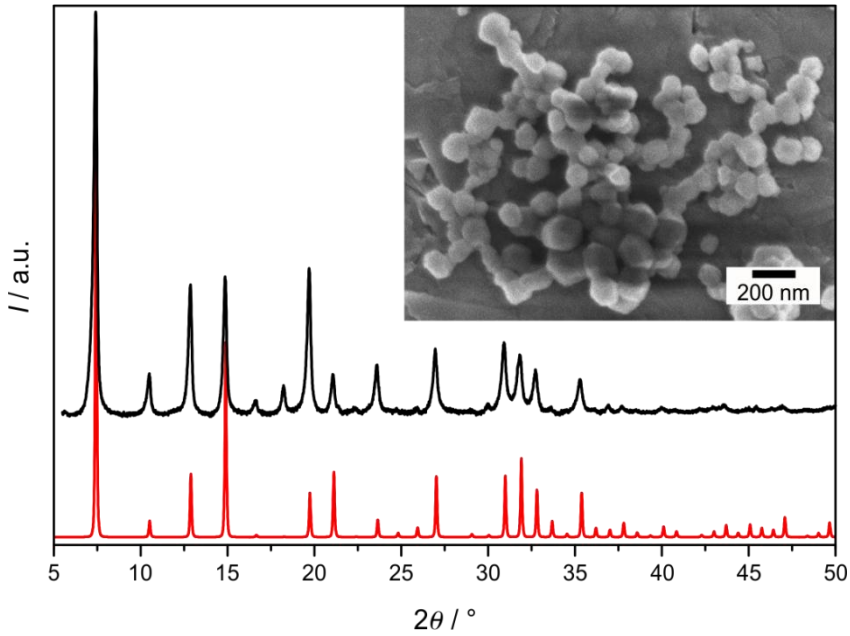

Fig. S5 Typical PXRD pattern and SEM image of as-synthesised nanocrystalline **2** obtained by reacting a mixture of $Zn(OAc)_2 \cdot 2H_2O$/Hdcim/1-mim/THF = 1:6:5:500 at 120 °C for 24 h. The nanocrystals have an averaged diameter of approximately 120 nm.

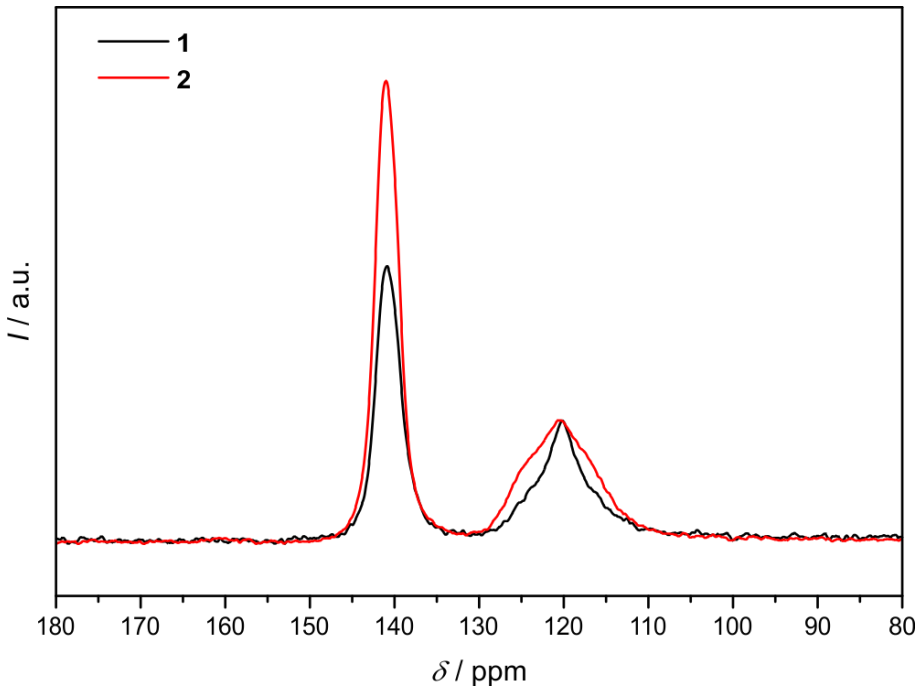

Fig. S6 $^{13}C\{^{1}H\}$ CP/MAS NMR spectra of **1** and **2**. The signals at 141 and 120 ppm are assigned to carbons carrying the hydrogen (C2) and chlorine (C4/5) atoms respectively.

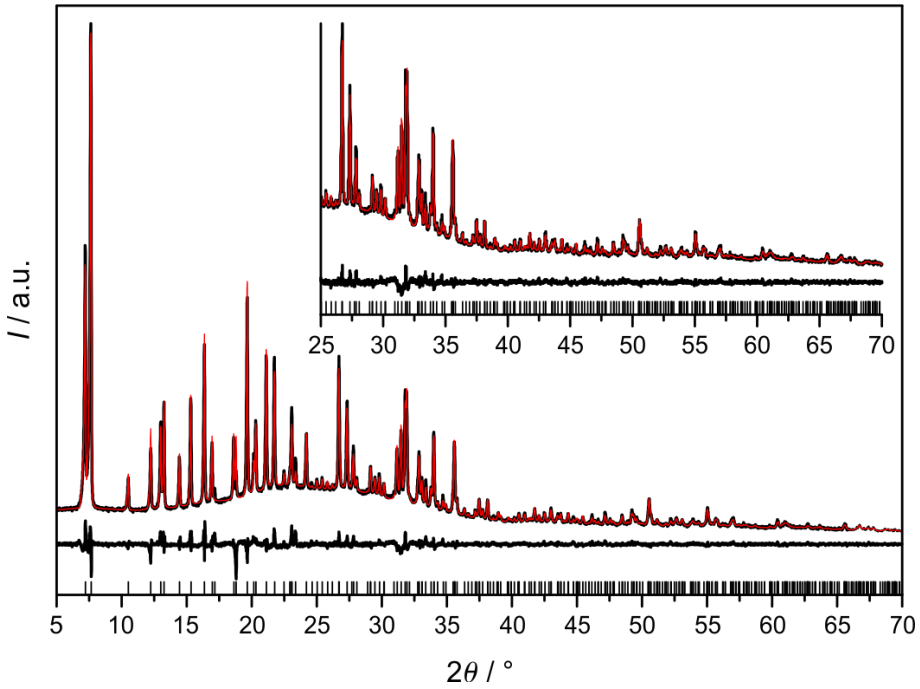

Fig. S7 Final Rietveld refinement plot for **1-DMF**. Experimental and calculated profiles are shown in black and red respectively, also shown are the difference plot and markers for allowed Bragg peaks.

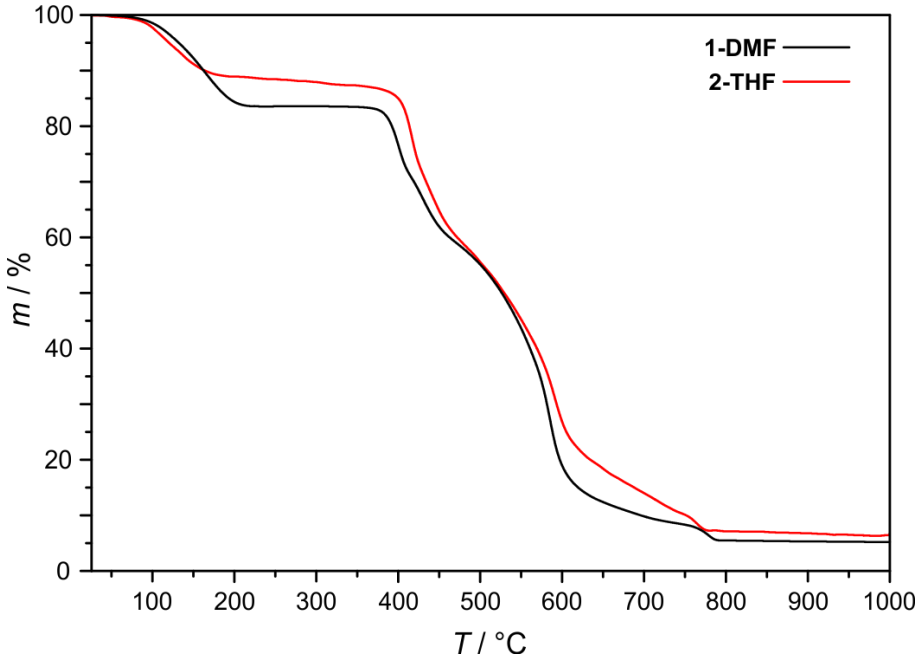

Fig. S8 TG traces of as-synthsised **1-DMF** and **2-THF** measured under a flow of air.

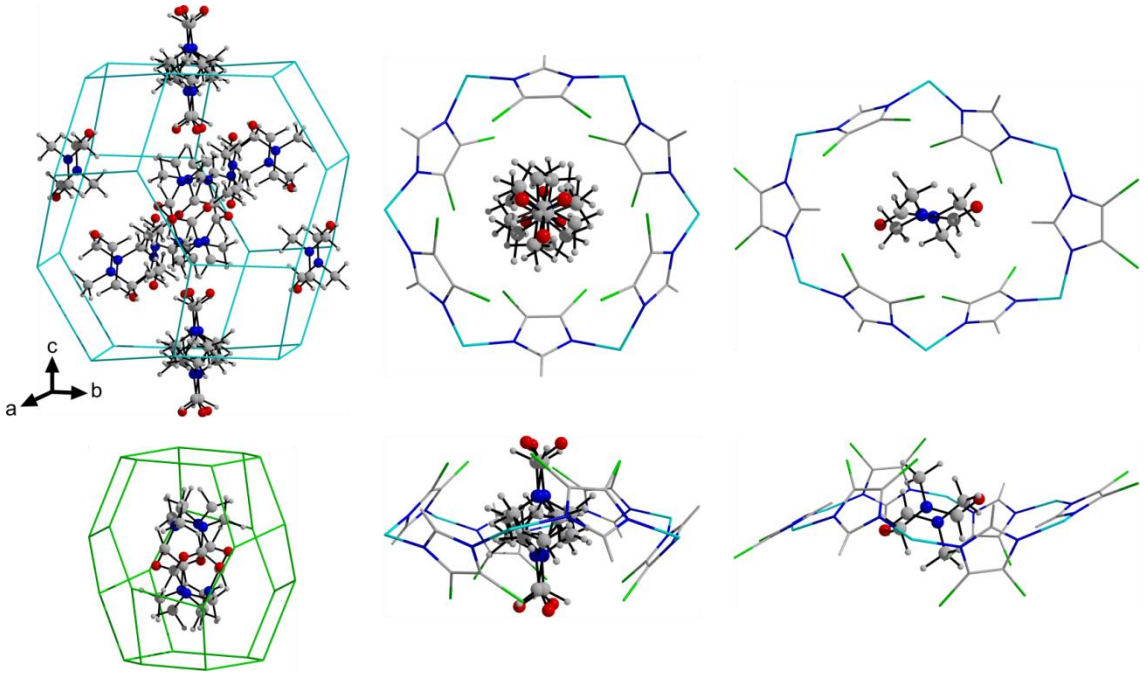

Fig. S9 In the structure of **1-DMF** the disordered DMF molecules are located in the interior of the unique [$4^6.6^8$] cavity and in the two unique six-ring windows (left, top). The statistical occupancies are 1.59 molecules per [$4^6.6^8$] cavity (left, bottom), 0.72 molecules per 6R-A ring (middle, top and bottom) and 1.00 molecules per 6R-B ring (right, top and bottom). See Fig. S2 for details of the secondary cavities (six-ring windows). Colour code: cyan, Zn; blue, N; grey, C; red, O; grey. H.

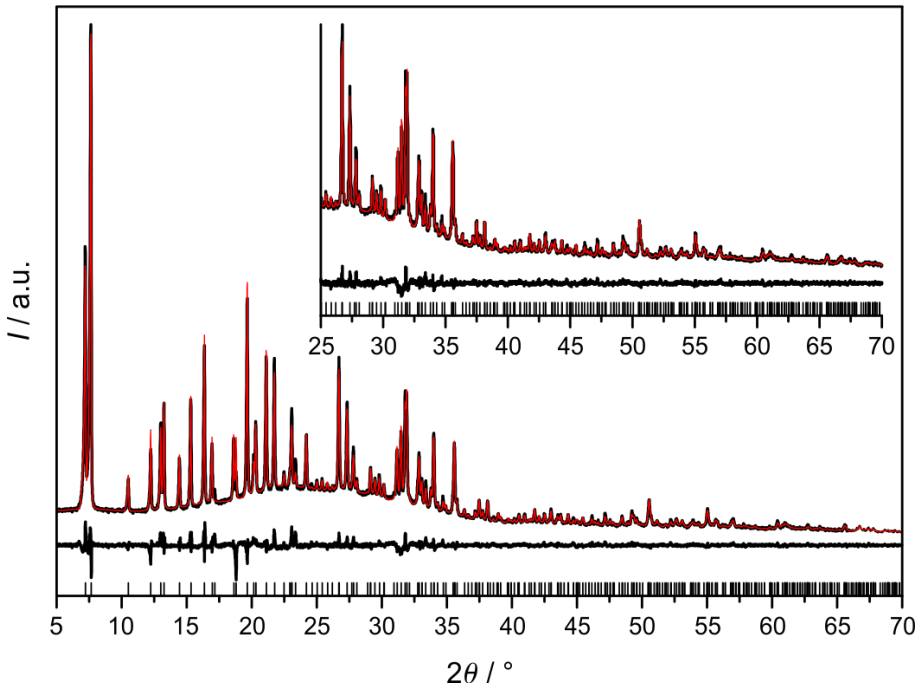

Fig. S10 Final Rietveld refinement plot for **2-THF**. Experimental and calculated profiles are shown in black and red respectively, also shown are the difference plot and markers for allowed Bragg peaks.

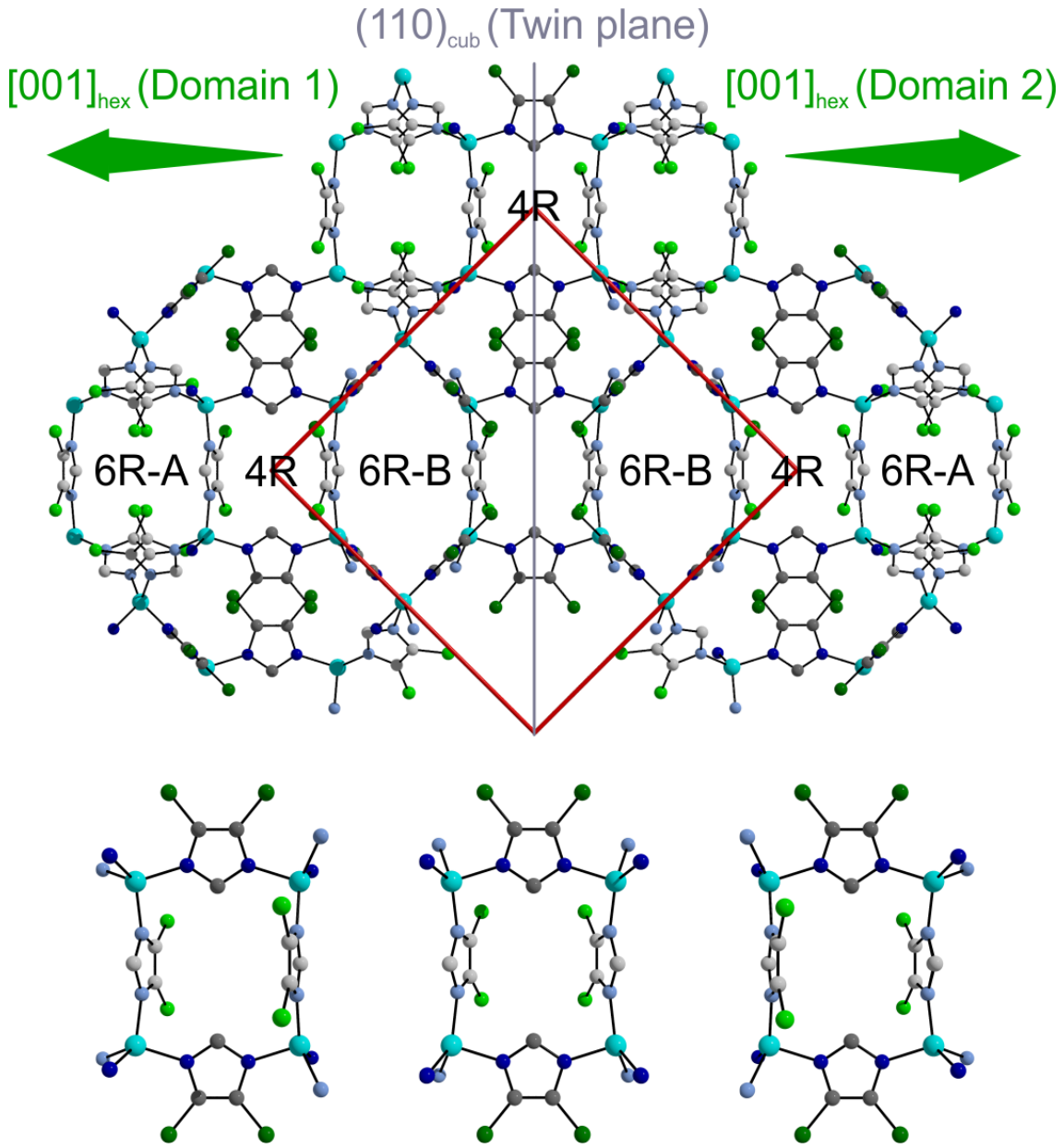

Fig. S11 Structural diagram of an ideal (110) twin boundary in a twinned crystal of **2**. The domains consist of framework conformer **III** with $R\bar{3}$ symmetry being deformed to a cubic metric. The conformations of the four-rings in the individual domains and the twin boundary are shown in the lower panel. Colour code: Cyan, Zn; blue, N; grey, C; green, Cl.

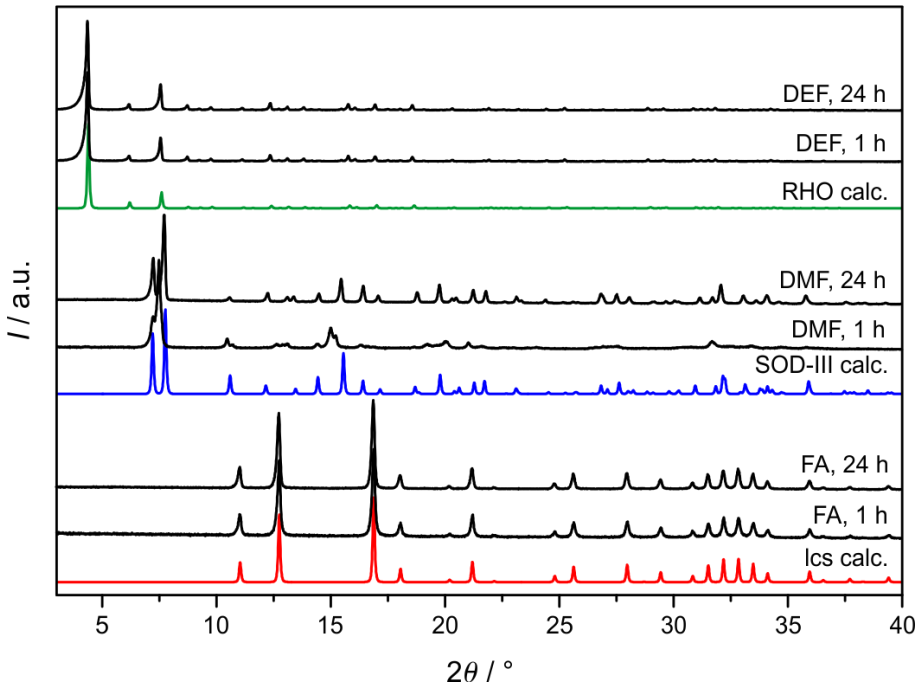

Fig. 12 Typical PXRD patterns of the products obtained in FA, DMF and DEF after 1 and 24 h (see Table 2). Also shown are simulated patterns for ZIF-72 (lcs), **III** (SOD) and ZIF-71 (RHO).

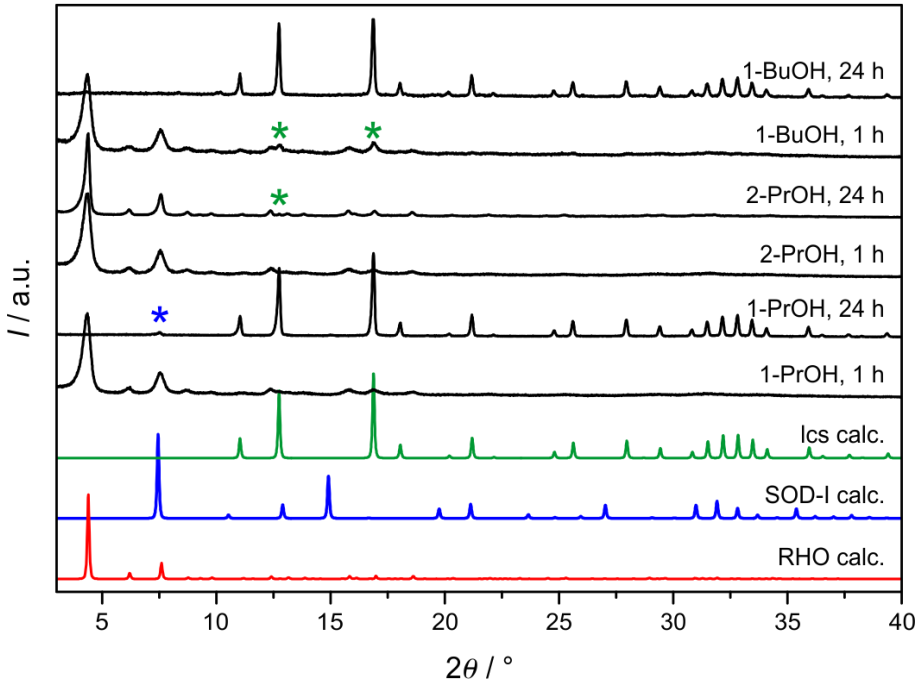

Fig. S13 Typical PXRD patterns of the products obtained in 1-PrOH, 2-PrOH and 1-BuOH after 1 h and 24 h (see Table 2). Also shown are simulated patterns for ZIF-71 (RHO), **I** (SOD) and ZIF-72 (lcs). The coloured asterisks indicate reflections assigned to minority phases.

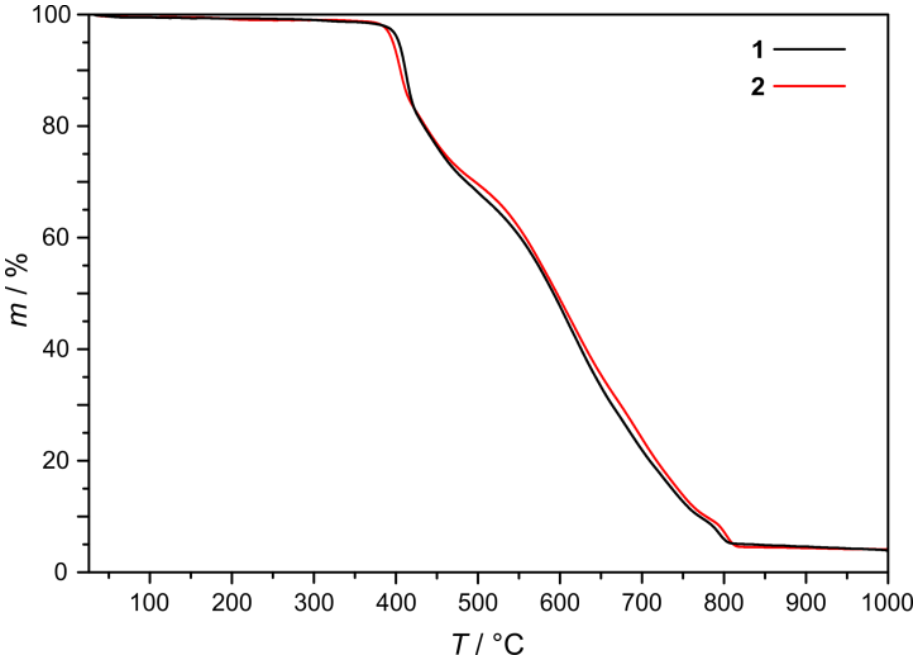

Fig. S14 TG traces of activated **1** and **2** measured in a flow of air.

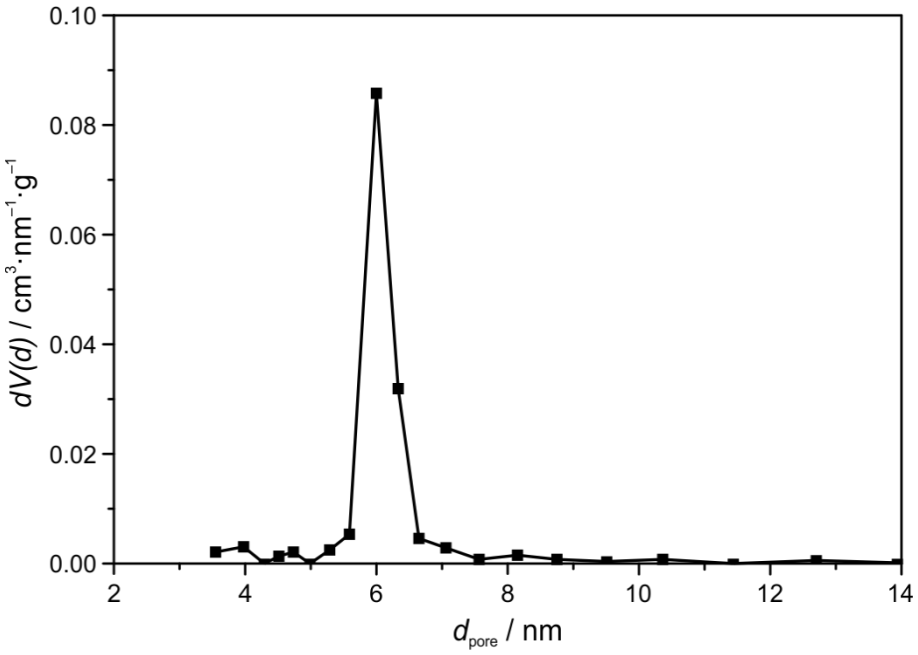

Fig. S15 Pore size distribution of **1** as estimated from the Ar desorption branch by applying the BJH method.

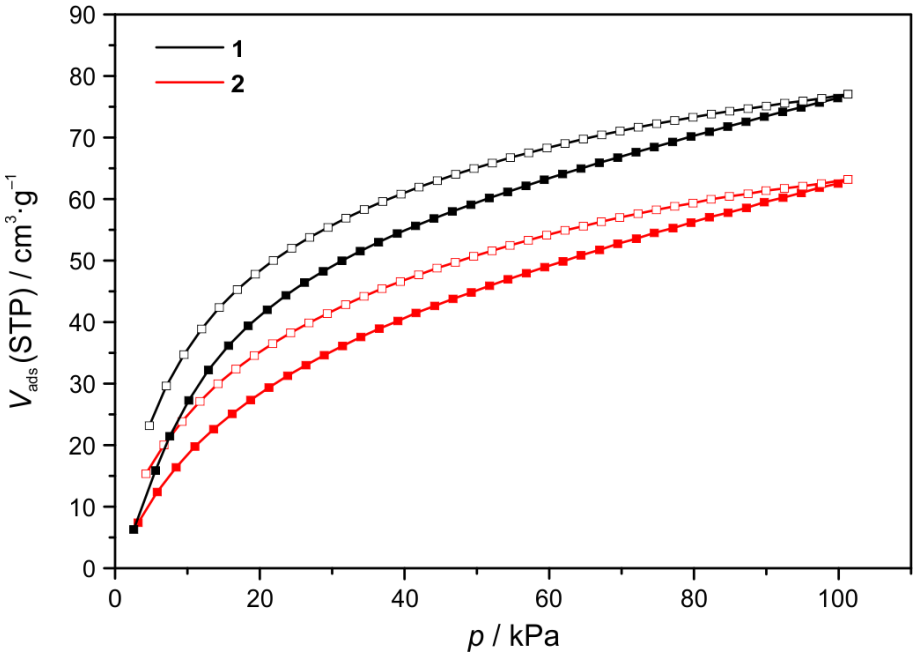

Fig. S16 CO_2 sorption isotherms for **1** and **2** measured at 0 °C. Closed and open squares correspond to the adsorption and desorption data respectively.

References

1 C. Baerlocher and L. McCusker, http://www.iza-structure.org/databases.