Supplementary Information for

Particle size effects in the kinetic trapping of a structurally-locked form of a flexible metal-organic framework

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Structure determinations of solvent-exchanged forms of [Cu(bcppm)(H_2O)]

Full spheres of diffraction data were measured at *ca*. 150 K using CCD area-detector instrumentation on single crystals mounted on nylon loops in Paratone-N. All data were measured using monochromatic Mo-$K\alpha$ radiation, λ = 0.71073 Å. N_{tot} reflections were merged to N unique (R_{int} quoted) after multiscan absorption correction (proprietary software) and used in the full matrix least squares refinements on F^2, N_o with $F > 4\sigma(F)$ being considered 'observed'. In general, anisotropic displacement parameter forms were refined for the non-hydrogen atoms; hydrogen atoms were treated with a riding model [weights: $(\sigma^2(F_o)^2 + (aP)^2 + (bP))^{-1}$; $P = (F_o^2 + 2F_c^2)/3$]. Neutral atom complex scattering factors were used; computation used the *SHELXL97* program.[1] Pertinent results are given below, in the captions to Figures S1 and S2, and in Tables S1 and S2. CIF data (excluding structure factor amplitudes) have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 1451302 [Cu(**bcppm**)(H_2O)]·acetone and 1451303 [Cu(**bcppm**)(H_2O)]·water**.** [Cu(**bcppm**)(H_2O)]·S (CCDC # 930403), [Cu(**bcppm**)(H_2O)]·ethanol (CCDC # 930405) and [Cu(**bcppm**)(H_2O)]-heated (CCDC # 930404) have been reported previously.[2]

Variata. In the crystal structure of [Cu(**bcppm**)(H_2O)]·$x$$H_2O$ 3½ well-ordered H_2O solvate molecules were located in the voids of the structure, however the relevant hydrogen atoms could not be located in the difference map.

Table S1. X-ray experimental data for solvent-exchanged forms of [Cu(**bcppm**)H_2O].

Compound	**[Cu(bcppm)H_2O]·acetone**	**[Cu(bcppm)H_2O]·water**
Empirical formula	$C_{30}H_{34}CuN_4O_8$	$C_{21}H_{30}CuN_4O_{12}$
Formula weight	642.15	594.032
Crystal system	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*
a (Å)	10.2536(2)	9.4000(2)
b (Å)	19.8774(4)	19.5102(3)
c (Å)	14.8763(7)	14.7022(2)
Volume ($Å^3$)	3032.01(17)	2696.32(8)
Z	4	4
Density (calc.) (Mg/m^3)	1.407	1.429
Absorption coefficient (mm^{-1})	0.776	0.875
F(000)	1340	1180
Crystal size (mm^3)	0.19×0.15×10.12	0.18×0.29×0.46
θ range for data collection (°)	2.62 to 29.07	2.57 to 29.13
Reflections collected	14195	15996
Observed reflections [R(int)]	3623 [0.0420]	3341 [0.0314]
Goodness-of-fit on F_2	1.052	1.110
R_1 [I>2σ(I)]	0.0454	0.0354
wR_2 (all data)	0.1320	0.0996
Largest diff. peak and hole ($e.Å^{-3}$)	0.758 and -0.444	0.532 & -0.330

Structure descriptions of solvent-exchanged forms of [Cu(bcppm)(H_2O)]

The crystal structure of [Cu(**bcppm**)(H_2O)]·S has been previously reported,[2] but as it is the parent structure to the solvent-exchanged forms presented in this paper, it will be briefly described here. [Cu(**bcppm**)(H_2O)]·S crystallises in the orthorhombic space group *Pmna*, with half a molecule of the ligand **bcppm**, half a copper(II) atom, and half a water solvate molecule in the asymmetric unit. The copper(II) centre has a square pyramidal geometry and is coordinated by one chelating di-pyrazolylmethane unit, two monodentate carboxylate donors from two seperate molecules of **bcppm**, and a single water ligand. This gives rise to a charged balanced 2D MOF with a puckered 4-connected net (Figure S1) composed of chelating dipyrazolyl moieties that bridge to adjacent copper atoms *via* the monodentate carboxylate donors. An important feature of this family of materials is the eclipse of the 2-D layers which stack along the *a*-axis in an anti-parallel fashion. This gives rise to regular diamond shaped channels with dimensions of ~15×19 Å (depending on the solvate) propagating along the *a*-axis. While the structure has solvent accessible channels along the *a*-axis (Figure S1a), the *b* and *c*-axes [Cu(**bcppm**)(H_2O)]·S are essentially close-packed (Figure S1b and c).

A well-ordered water ligand is situated directly between the 2D layers, with a Cu-O bond length of 2.302 Å while the O-Cu distance to the above layer is 2.873 Å. The former length is well within the normal range for a Cu-O bond,[3] however, the latter is too distant for the geometry of the Cu(II) centre to be considered octahedral. The hydrogen atoms of this water ligand were successfully located in the difference map, and clearly to point towards the carbonyl oxygen atoms from an adjacent layer (Figure S1c). The O-H···O distance is 2.03 Å which is within the range of a moderate hydrogen bond.[4] Therefore, the eclipse of the 2D layers and formation of the 1D channels is driven by the puckering of the 2D nets and the strong interlayer hydrogen bonding between the hydrogen atoms of the water ligands in one layer and the carbonyl oxygen atoms from an adjacent layer. This water ligand is retained in all forms including the activated material.

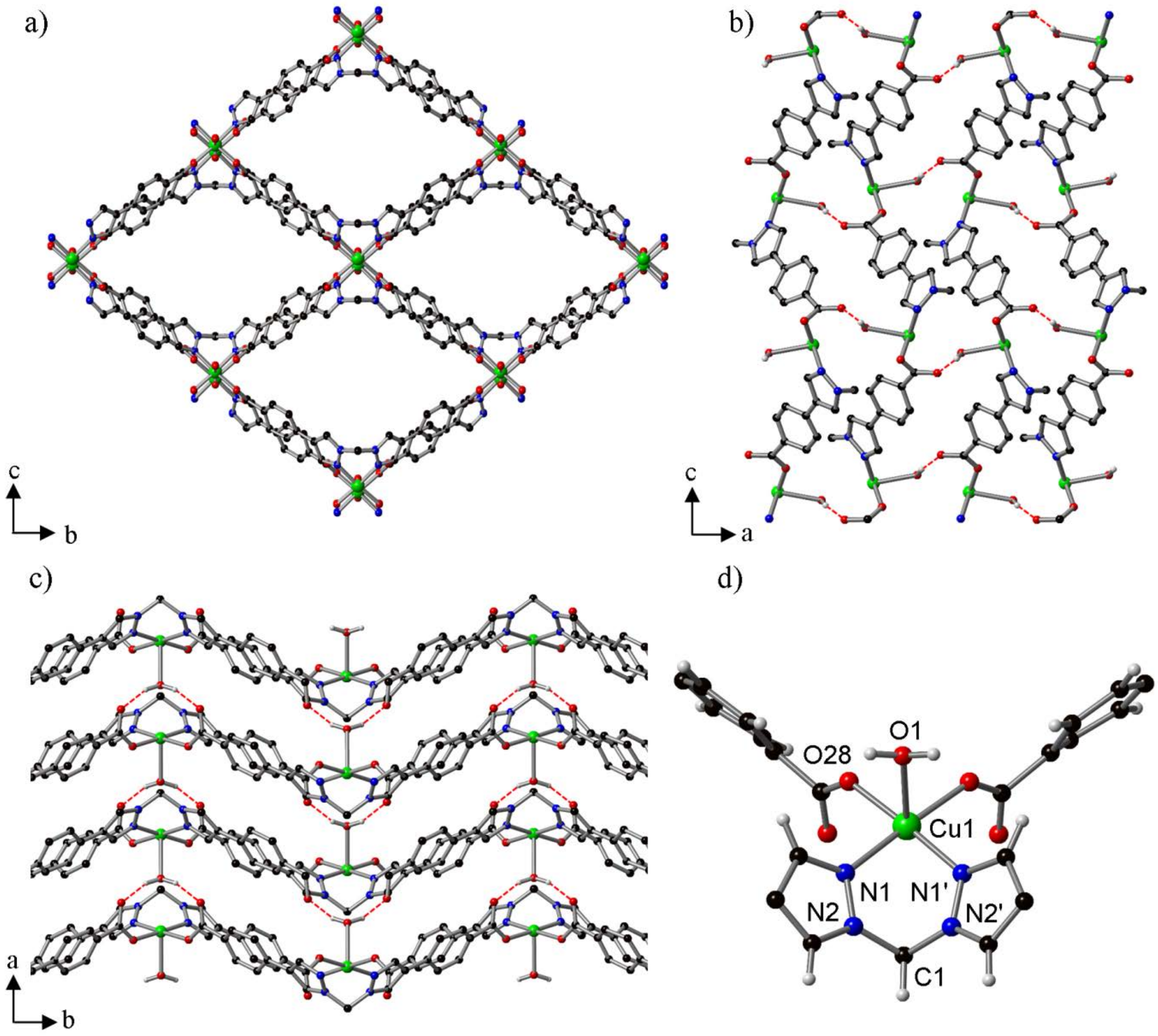


Figure S1. a) A view of the 1D channels of [Cu(**bcppm**)(H_2O)]·S along the *a* axis, b) a view along the *b* axis and c) a view along the *c* axis. Hydrogen atoms of **bcppm** are removed for clarity. (d) A view of the square pyramidal copper(II) centre of [Cu(**bcppm**)(H_2O)]·S. Hydrogen bonds are shown by the red dotted lines. Selected bond lengths [Å] and angles [°]: Cu1-N1 2.014, Cu1-O28 1.952, Cu1-O1 2.302, N2-C1-N2′ 107.50, N1-Cu1-N1′ 87.50.

The interlayer hydrogen bonding and the flexible chelating unit directly employed around the singular metal node led to an expectation of flexibility for the MOF structure. Solvent-exchanged forms of [Cu(**bcppm**)(H_2O)]·S were prepared by soaking batches of single crystals in acetone, water or ethanol before subjecting these to single crystal X-ray structure determinations. The structures are essentially isostructural, differing only in the nature of the included solvent (which was in some cases well defined but in others subject to disorder), and particularly the extent of trellis-like breathing and layer-layer contraction. The crystallographic parameters of solvent-exchanged forms of [Cu(**bcppm**)H_2O] are given below in Table S2. [Cu(**bcppm**)(H_2O)]·acetone is essentially unchanged relative to the as-synthesised version with unit cell parameters given in Table S2 that reflect a small expansion of the *b* axis and a contraction of the *c* axis (see Figure S1a to understand these structural changes). There is a small expansion of the layer-layer separation too (increase in the *a* axis, see Figure S1c). [Cu(**bcppm**)(H_2O)]·water and [Cu(**bcppm**)(H_2O)]·ethanol are structurally similar with a shorter layer-layer separation than the as-synthesised form (*a* axis contraction) but a more significant trellis-like structural change (expansion of the *b* axis and a notable contraction of the *c* axis).

Table S2. Crystallographic parameters of solvent-exchanged forms of [Cu(**bcppm**)(H_2O)].

Form	**a (Å)**	**b (Å)**	**c (Å)**	**Volume (Å^3)**
[Cu(**bcppm**)(H_2O)]·S	9.9995	19.2590	15.4339	2955.13
[Cu(**bcppm**)(H_2O)]·acetone	10.2536	19.8774	14.8763	3032.01
Δ	*0.2541*	*0.6184*	*-0.5576*	*76.88*
[Cu(**bcppm**)(H_2O)]·water	9.4000	19.5102	14.7022	2696.32
Δ	*-0.5995*	*0.2512*	*-0.7317*	*-258.81*
[Cu(**bcppm**)(H_2O)]·ethanol	9.6611	20.3319	13.6276	2676.85
Δ	*-0.3384*	*1.0729*	*-1.8063*	*-278.28*
[Cu(**bcppm**)(H_2O)]-heated	8.8000	20.7340	13.1100	2392.04
Δ	*-1.1995*	*1.4750*	*-2.3239*	*-563.09*

[Cu(**bcppm**)(H_2O)]-heated, as previously reported,[2] undergoes the most significant change (Figure S2a vs. S2b) with a continuation of the structural modifications seen for the ethanol and water-exchanged samples but a dramatically shortened *a* axis cell length as a consequence of the water ligand now bridging between symmetry related copper(II) centres in adjacent layers (Cu1a-O1 = 2.265 Å, O1-Cu1 = 2.397 Å). This occurs with a change in the coordination environment of the copper(II) centre from five coordinate to a Jahn-Teller distorted octahedral six coordinate (Figure S2c and S2d). The 3D structure that forms due to the coordination changes is also reinforced by noticeably shorter hydrogen bonding between the bridging water ligand and a carboxylate in the adjacent layer. The hydrogen bonds in [Cu(**bcppm**)(H_2O)]-heated are shortened by 0.3 Å relative to [Cu(**bcppm**)(H_2O)]·S giving a O-H···O distance of 1.73 Å.

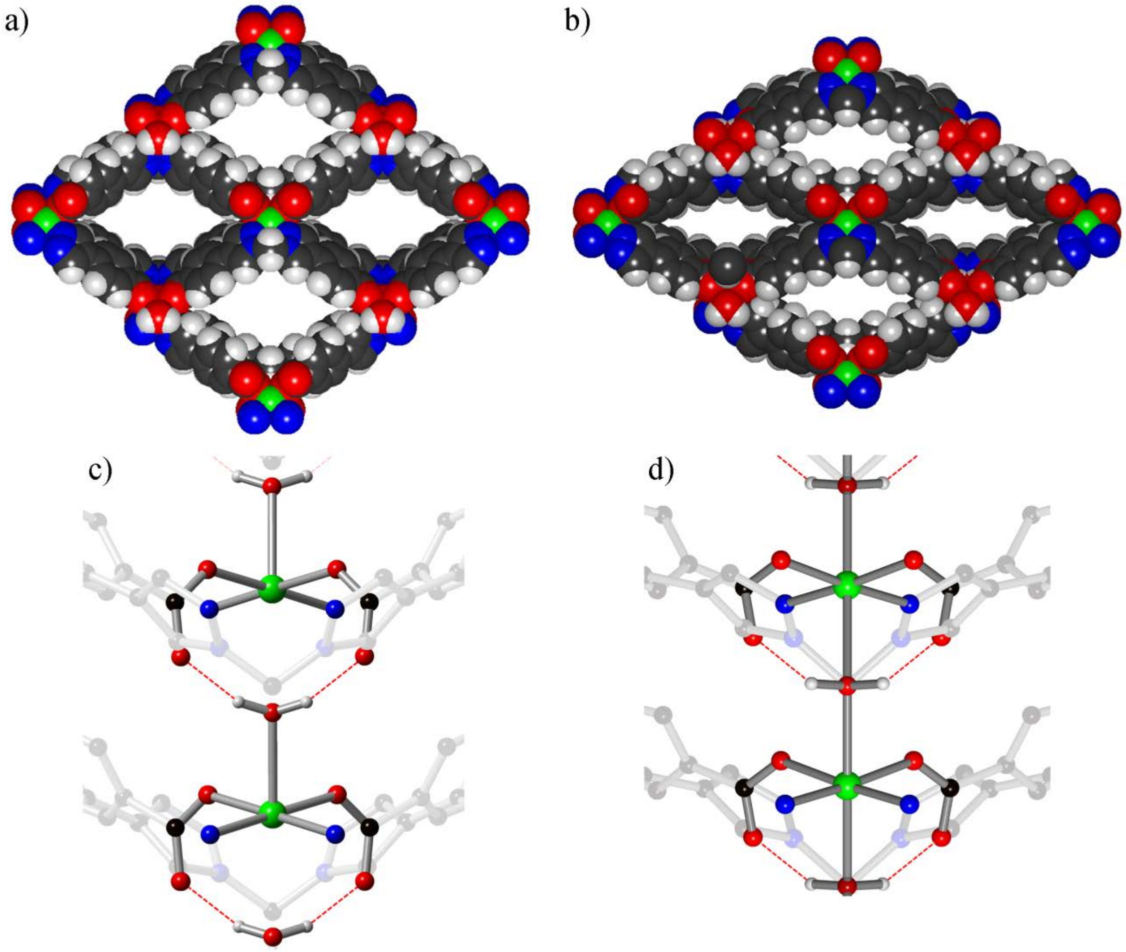


Figure S2. Space filling representations of a) [Cu(**bcppm**)(H_2O)]·S and b) [Cu(**bcppm**)(H_2O)]-heated viewed along the *a*-axis. The coordination environment of the copper(II) centre of c) [Cu(**bcppm**)(H_2O)]·S and d) [Cu(**bcppm**)(H_2O)]-heated. Red dotted lines denote hydrogen bonds.

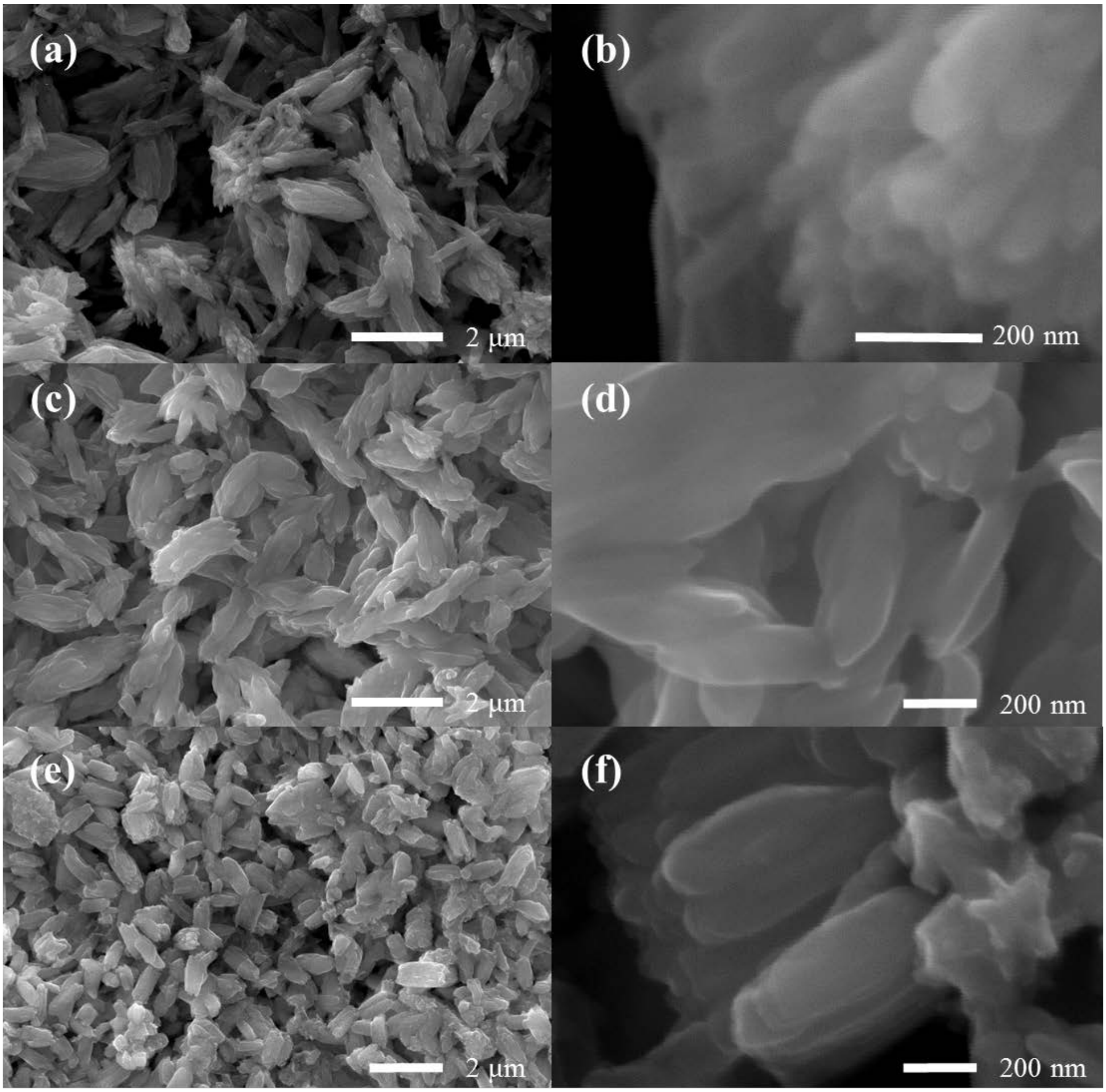


Figure S3. Additional SEM images of [Cu(**bcppm**)H_2O]·S synthesised at room temperature (a) & (b) with 0.1 M NaOH at 0.5 hrs, (c) & (d) 16 hrs, and (e) & (f) with Na_2**bcppm** at 16 hrs.

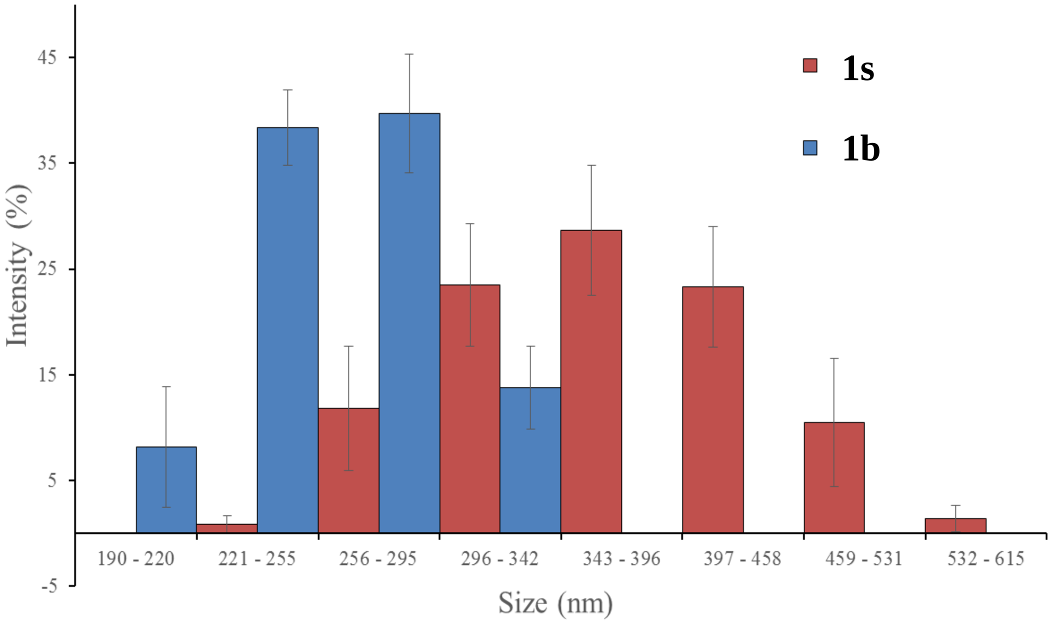


Figure S4. Average intensity from DLS experiments on samples of [Cu(**bcppm**)H_2O]·S synthesised at room temperature from 0.1 M NaOH (**1b**) and Na_2**bcppm** (**1s**) conditions.

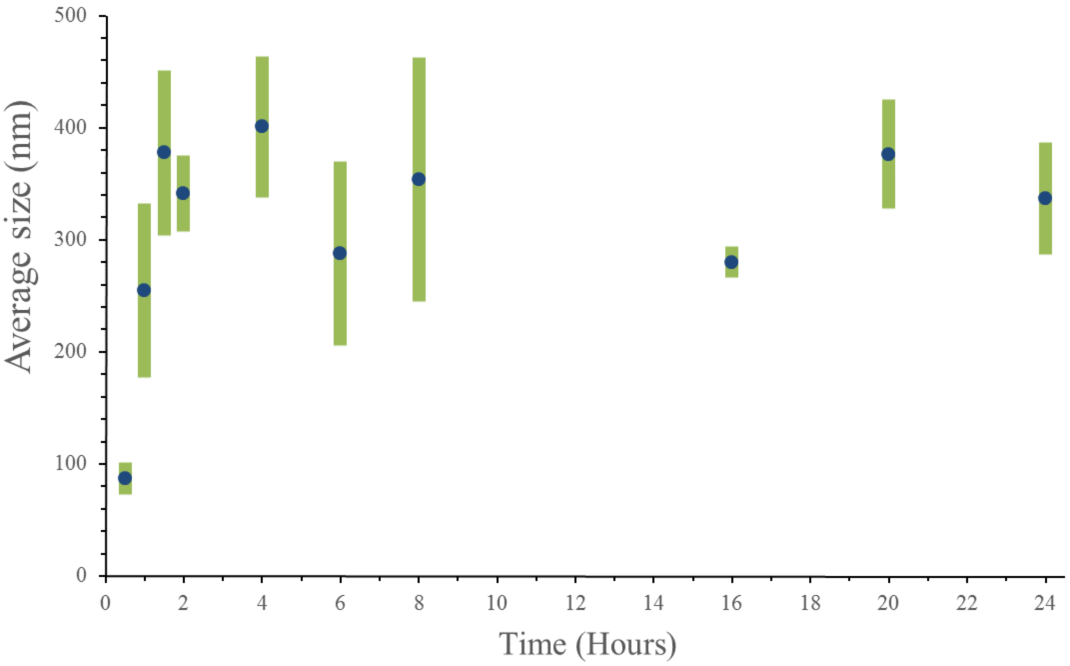


Figure S5. Average particle sizes determined from DLS experiments, demonstrating the growth of **1b**·S over 24 hours.

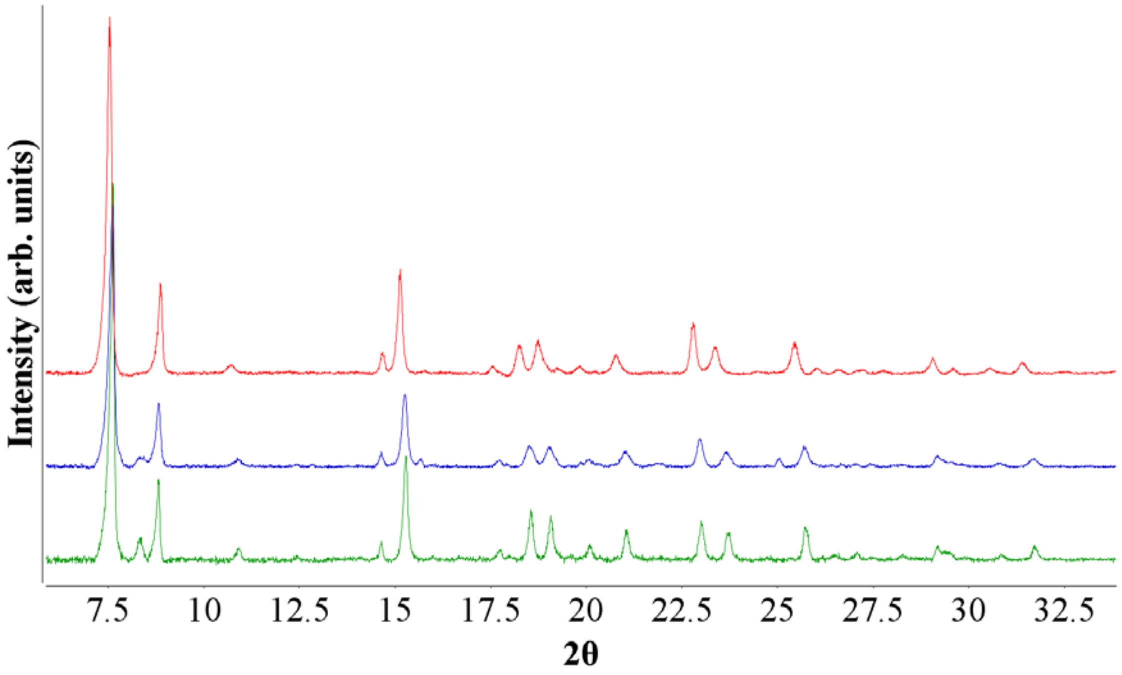


Figure S6. PXRD patterns of [Cu(**bcppm**)H_2O]·S solvothermally synthesised (green) (**1**·S), synthesised at room temperature with 0.1 M NaOH, 16 hrs, (blue) (**1b**·S) and with Na_2**bcppm** at room temperature, 16 hrs, (red) (**1s**·S). In the PXRD patterns presented the peaks at *ca.* 2θ = 7.5° and 2θ = 8.5° correspond to 011 and 020 planes respectively which reflect the breathing of the MOF. In the samples of **1**·S (green) and **1b**·S (blue) the peak at *ca.* 2θ = 8.0° corresponds to a small amount of the dried sample which forms as the material is packed into the capillaries.

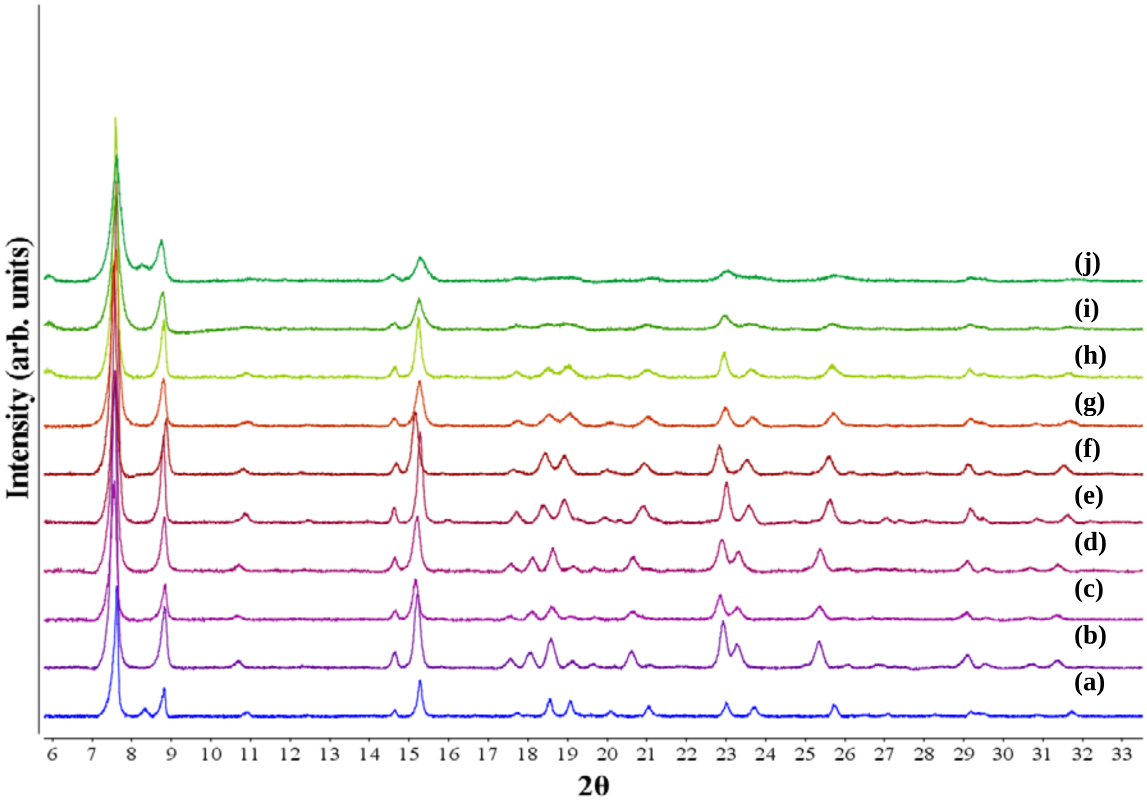


Figure S7. PXRD patterns of **1b**·S with varied reactant concentration and ligand-to-base (NaOH) ratio at 0.5 hrs, (a) normal solvothermal conditions **1**·S, (b) 36 mM ligand, 2:1, (c) 18 mM ligand, 2:1, (d) 12 mM ligand, 2:1, (e) 36 mM ligand, 1:1, (f) 18 mM ligand, 1:1, (g) 12 mM ligand, 1:1, (h) 36 mM ligand, 1:2, (i) 18 mM ligand, 1:2, (j) 12 mM ligand, 1:2. In the PXRD plots the peaks at *ca.* 2θ = 7.5° and 2θ = 8.5° correspond to 011 and 020 planes respectively which reflect the breathing of the MOF. In certain samples the peak at *ca.* 2θ = 8.0° corresponds to a small amount of the dried sample which forms as the material is packed into the capillaries.

General room temperature synthesis of [Cu(bcppm)H_2O]•S (S=solvate) with NaOH, 0.5 hrs (1b·S).

In a 20 ml screw cap vial, $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$ (36.0 mg, 0.16 mmol) and H_2**bcppm** (41.5 mg, 0.11 mmol) were dissolved in a mixture of DMF (2 ml) and ethanol (0.5 ml). Sodium hydroxide 0.1 M (0.5 ml) was injected into the stirring copper solution. The resultant solution was stirred for 0.5 h at room temperature. The product was washed with DMF (×2) and methanol (×5) resulting in a light blue microcrystalline material (8.0 mg, 16%).

Table S3. Varied reactant concentration and ligand-to-base ratio following the general experimental specified for the 0.5 hr room temperature reaction with 0.1 M NaOH.

$Cu(NO_3)_2\cdot2.5H_2O$		H_2bcppm			DMF	EtOH	NaOH		Yield	Reaction time (min)
(mg, mmol)		(mM, mg, mmol)			(ml)	(ml)	(ml, $molL^{-1}$)		(mg)	
36.0	0.16	36	41.5	0.11	2	0.5	0.5	0.1	6	30
36.0	0.16	18	41.5	0.11	4	1	1	0.05	6	30
36.0	0.16	12	41.5	0.11	6	1.5	1.5	0.033	6	30
36.0	0.16	36	41.5	0.11	2	0.5	0.5	0.2	7	30
36.0	0.16	18	41.5	0.11	4	1	1	0.1	7	30
36.0	0.16	12	41.5	0.11	6	1.5	1.5	0.066	7	30
36.0	0.16	36	41.5	0.11	2	0.5	0.5	0.4	8	30
36.0	0.16	18	41.5	0.11	4	1	1	0.2	9	30
36.0	0.16	12	41.5	0.11	6	1.5	1.5	0.133	9	30

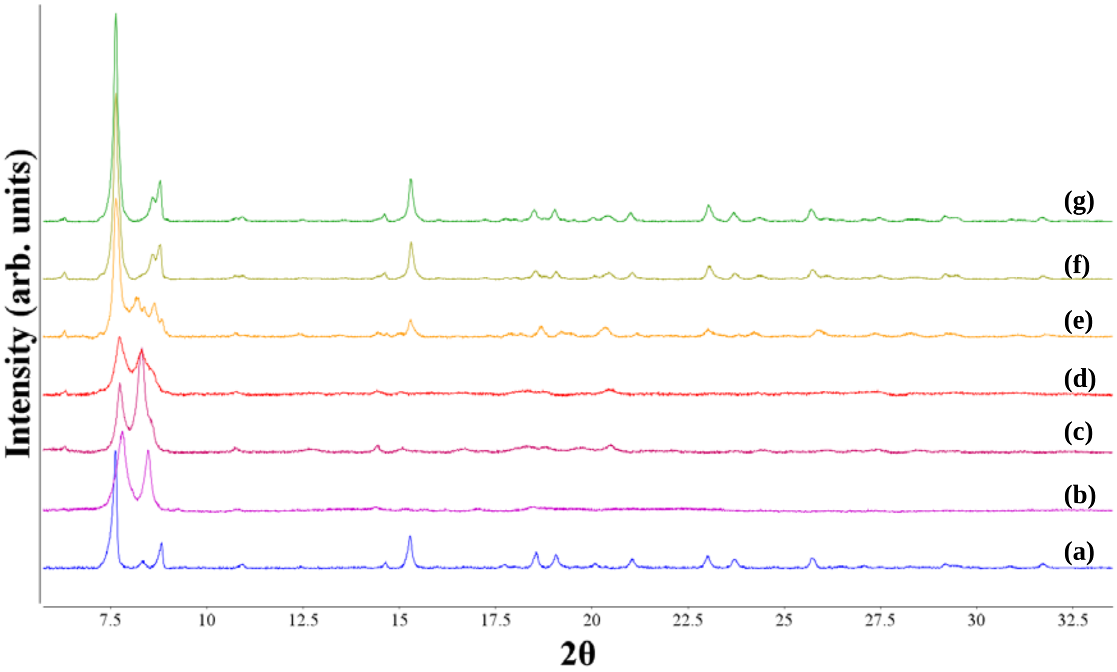
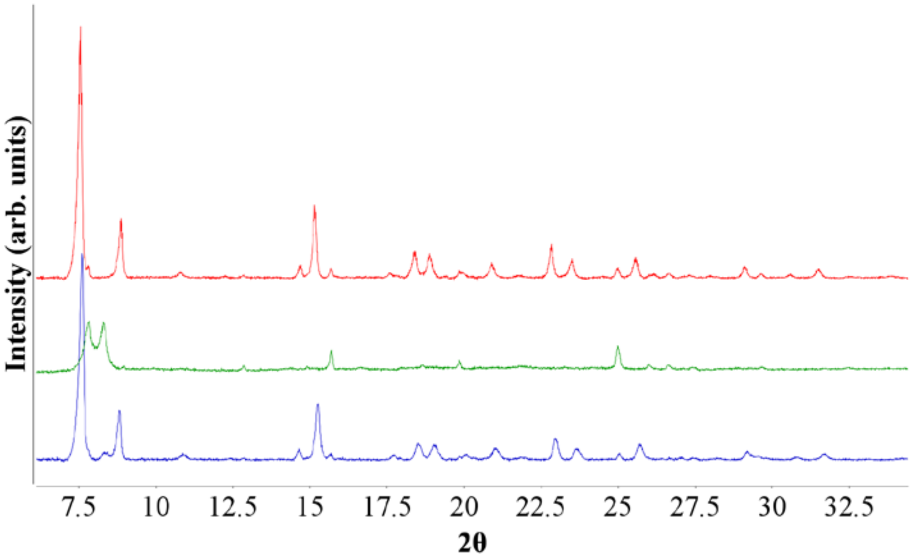


Figure S8. PXRD patterns of **1** (a) as-synthesised (methanol washed), (b) activated from acetone, resolvated in methanol for (c) 1 day, (d) 2 days, (e) 5 days, (f) 7 days and (g) 9 days. In the PXRD patterns the peaks at *ca.* 2θ = 7.5° and 2θ = 8.5° correspond to 011 and 020 planes respectively which reflect the breathing of the MOF. In the sample of **1**·S (blue) the peak at *ca.* 2θ = 8.0° corresponds to a small amount of the dried sample which forms as the material is packed into the capillaries.

(a)



(b)

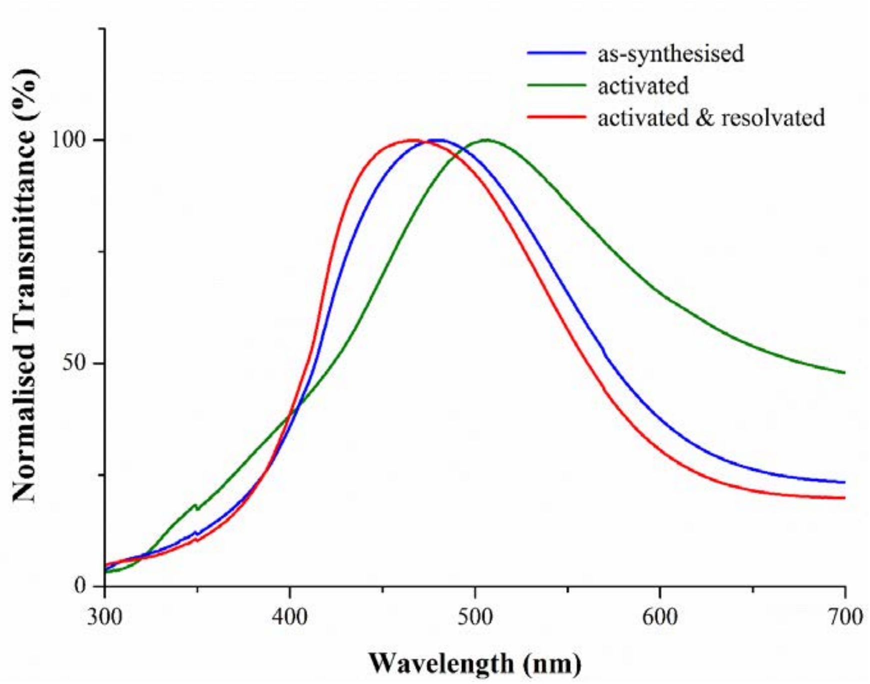


Figure S9. (a) PXRD and (b) solid state UV/vis transmittance spectra of **1b**·S as-synthesised (blue), activated (green) and activated and resolvated in methanol overnight (red). In the PXRD plots the peaks at *ca.* 2θ = 7.5° and 2θ = 8.5° correspond to 011 and 020 planes respectively which reflect the breathing of the MOF. In the sample of **1b**·S (blue) the peak at *ca.* 2θ = 8.0° corresponds to a small amount of the dried sample which forms as the material is packed into the capillaries.

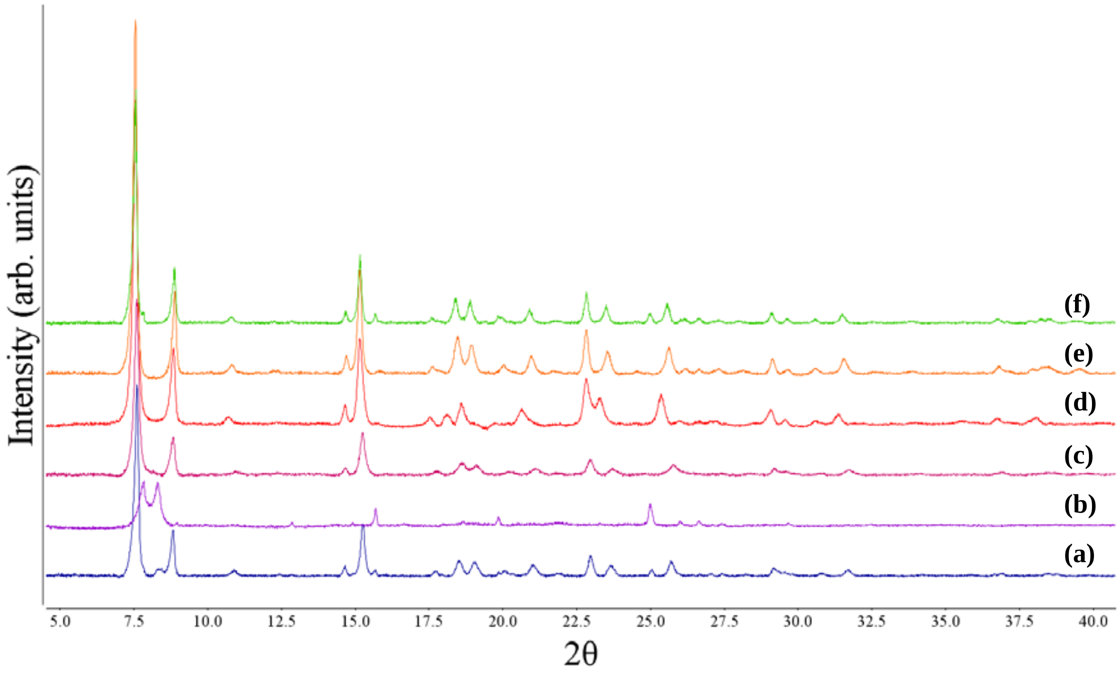


Figure S10. PXRD of (a) **1b**·S (at 16 h), (b) activated, activated and resolvated in methanol for (c) 1.5 h, (d) 3 h, (e) 4.5 h and (f) 16 h. In the PXRD plots the peaks at *ca.* 2θ = 7.5° and 2θ = 8.5° correspond to 011 and 020 planes respectively which reflect the breathing of the MOF. In the sample of **1b**·S (blue) the peak at *ca.* 2θ = 8.0° corresponds to a small amount of the dried sample which forms as the material is packed into the capillaries.

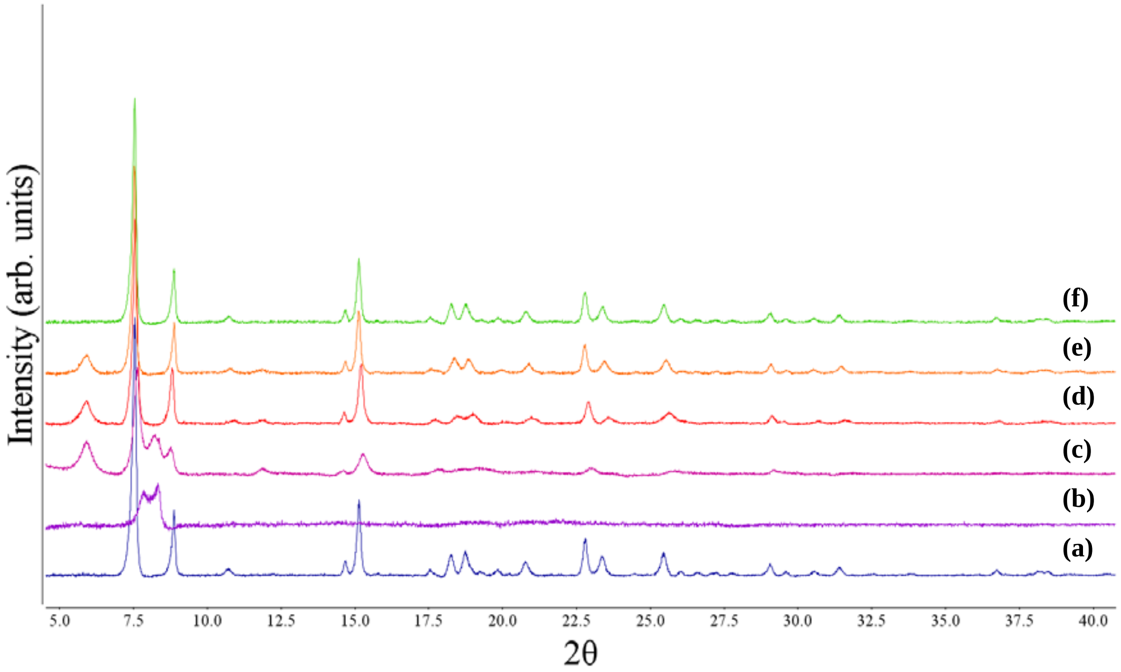


Figure S11. PXRD of (a) **1s**·S (at 16 h), (b) activated, activated and resolvated in methanol for (c) 1.5 h, (d) 3 h, (e) 4.5 h and (f) 16 h. In the PXRD plots the peaks at *ca.* 2θ = 7.5° and 2θ = 8.5° correspond to 011 and 020 planes respectively which reflect the breathing of the MOF.

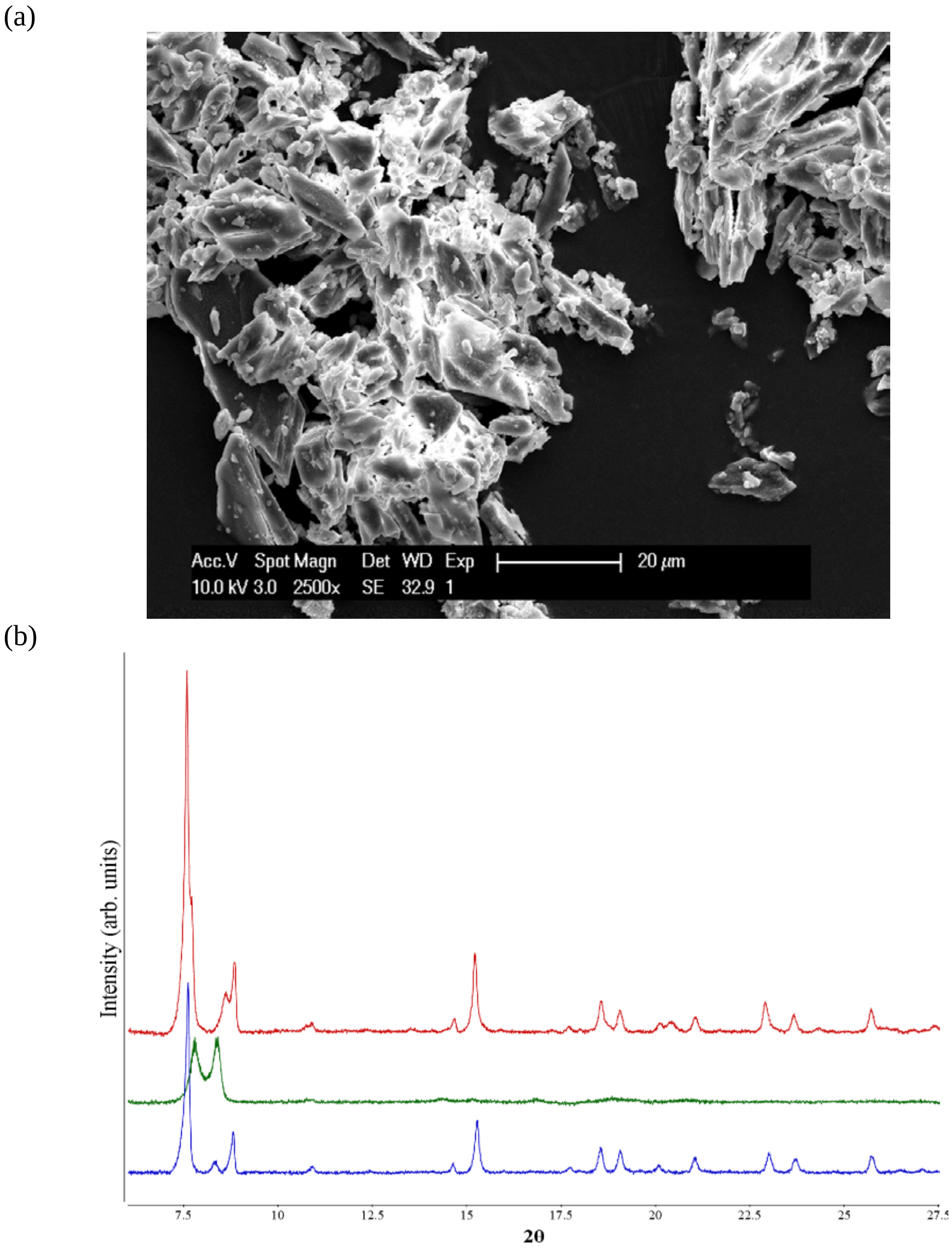


Figure S12. (a) SEM image and (b) PXRD patterns of **1**·S solvothermally synthesised and manually crushed (blue), activated (green) and, activated and resolvated overnight (red). In the PXRD plots the peaks at *ca.* 2θ = 7.5° and 2θ = 8.5° correspond to 011 and 020 planes respectively which reflect the breathing of the MOF. In the sample of **1b**·S (blue) the peak at *ca.* 2θ = 8.0° corresponds to a small amount of the dried sample which forms as the material is packed into the capillaries.

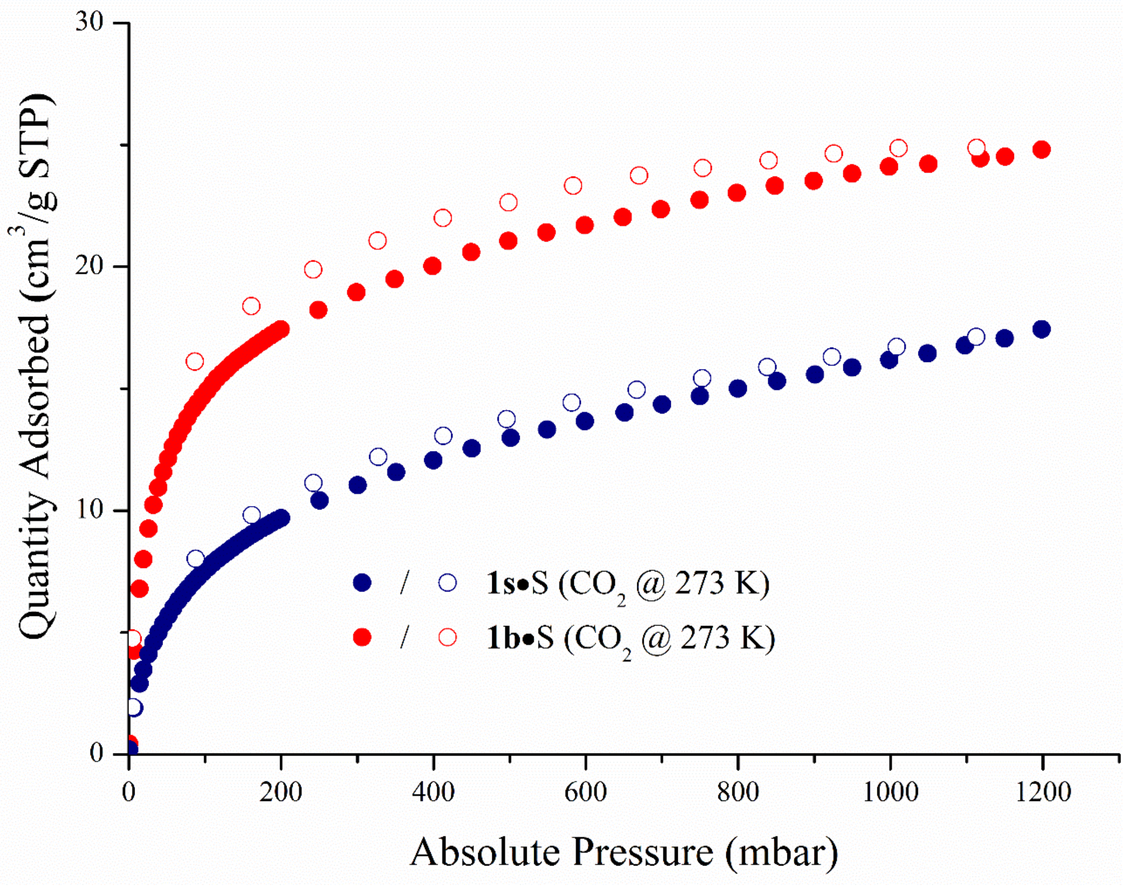


Figure S13. 273 K CO_2 isotherms of **1b**·S (blue) and **1s**·S (red). Adsorption = filled circles; desorption = open circles.

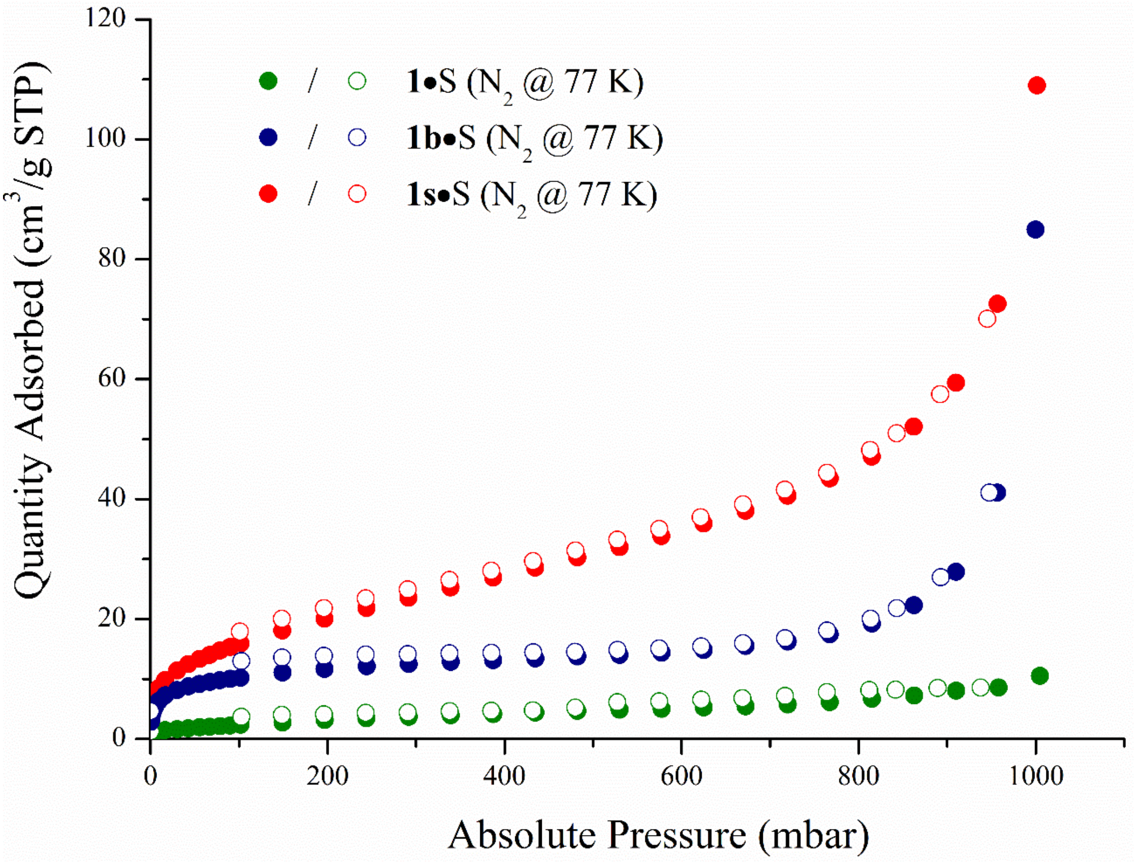


Figure S14. 77 K N_2 isotherms of **1**·S (green), **1b**·S (blue) and **1s**·S (red). Adsorption = filled circles; desorption = open circles.

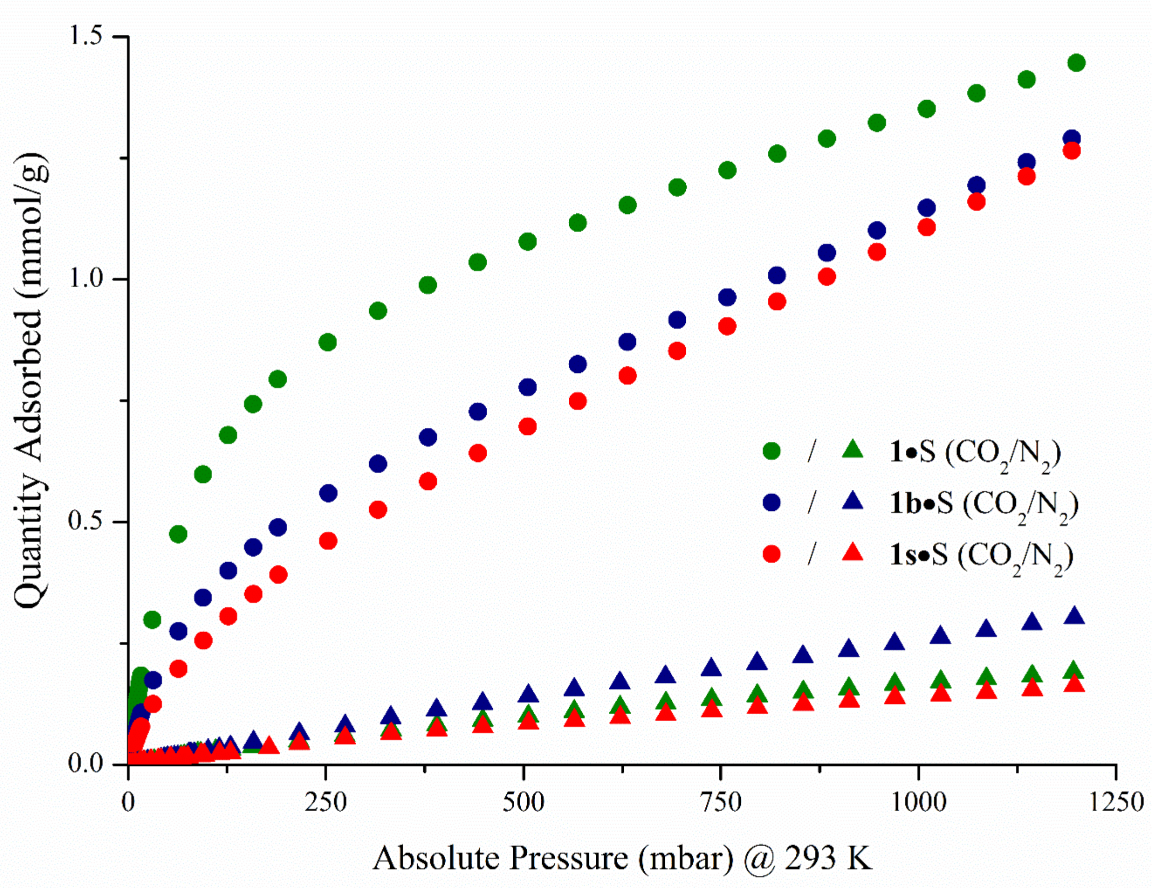


Figure S15. 293 K CO_2 and N_2 isotherms of **1**·S (green), **1b**·S (blue) and **1s**·S (red). Adsorption = filled circles; desorption = open circles.

Table S4. IAST selectivity data for **1**·S, **1b**·S and **1s**·S.

Sample	Crystal size (nm)	Selectivity (CO_2/N_2)[a]
1·S	50000	100
1b·S	402	40
1s·S	280	65

[a] 15/85 wt% mixture at 293 K and 1 atm

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