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Electronic Supplementary Information

Siloxane-Based Linkers in the Construction of Hydrogen Bonded Assemblies and Porous 3D MOFs

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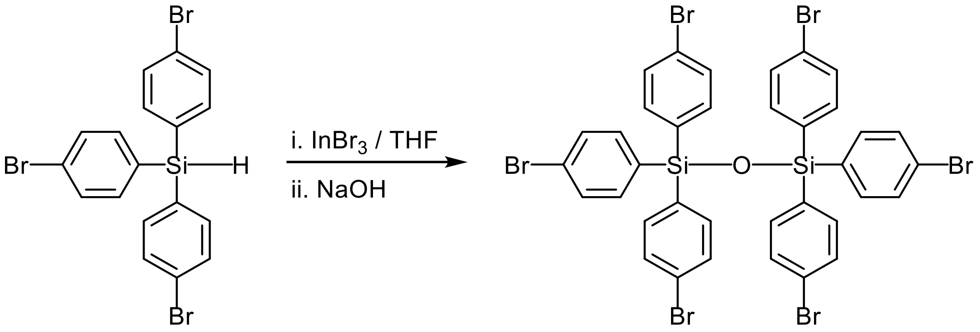
General Methods:

NMR spectra were recorded on a Bruker 400 MHz spectrometer and all chemical shifts are reported in δ (ppm) using the relevant residual solvent peaks as internal standards.[1] Mass spectra were recorded using a Waters LCT Premier (ESI) spectrometer. Powder X-ray diffraction (PXRD) studies were performed using a Panalytical MPD X-ray diffractometer with Cu-K_α radiation. Thermogravimetric analysis was carried out under a nitrogen atmosphere using a Mettler Toledo instrument under a constant stream of dry nitrogen gas (flow rate 50 mL min^{-1}) over the temperature range 30−800 °C and at a heating rate of 5 °C min^{-1}. BET surface area measurements were carried out using a Micromeritics TriStar II Plus instrument and Micromeritics MicroActive software. X-ray data was collected using a Rigaku FRE+ (**IMP-18** and **IMP-19**) or Agilent Xcalibur PX Ultra (**L1**-H_6) diffractometer. A summary of the crystallographic data is presented in Table S1.

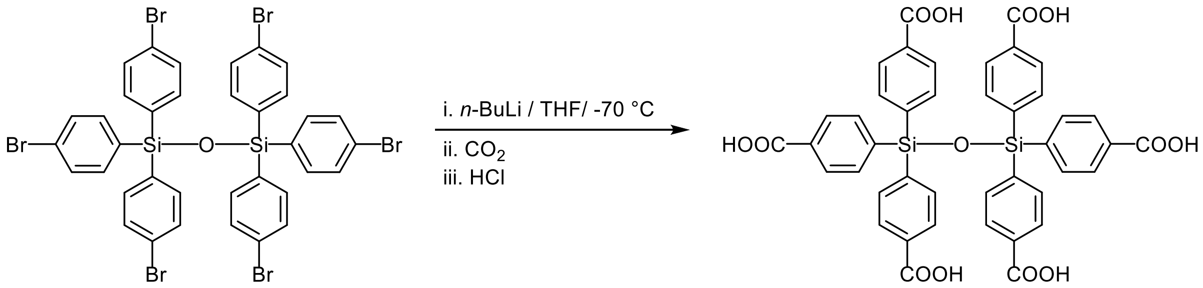
Synthesis:

Hexa(4-bromophenyl)disiloxane



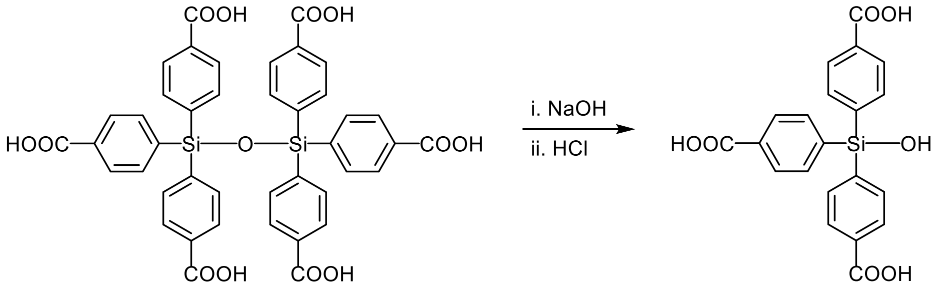
Hexa(4-bromophenyl)disiloxane was synthesized via modification of the procedure reported by Kumar Reddy *et al.*[2] Tris(4-bromophenyl)silane (2.0 g, 4 mmol) was dissolved in THF (20 mL) and indium(III) bromide (0.2 g, 0.5 mmol) was introduced to the vessel; followed by stirring of the resultant solution for 10 min. Aqueous sodium hydroxide (4M, 0.75 mL, 3 mmol) was then slowly added and the open vessel allowed to stir at room temperature for 12 hours. The reaction mixture was decanted to separate the liquid component from the white solid that had precipitated during the course of the reaction. The mixture was then reduced to approximately 5 mL using a rotary evaporator and was subsequently taken up in chloroform (20 mL). This mixture was washed with H_2O (7 mL) and the $CHCl_3$-containing layer collected. Methanol (15 mL) was slowly added to this solution until hexa(4-bromophenyl)disiloxane precipitated as a white solid which was isolated by suction filtration: 1.78 g (88 %). M.p. 294.5 - 296 °C; Anal. Calcd. for $C_{36}H_{24}Br_6OSi_2$: C, 42.89; H, 2.40; N, 0.00. Found: C, 42.93; H, 2.32; N, <0.1; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.44 (d, 12H, J = 8.32 Hz, Ar-H), 7.21 (d, 12H, J = 8.32 Hz, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 136.5, 132.7, 131.5, 125.9; ^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = -17.4; MS (ESI-): calcd for $C_{36}H_{25}O_2{}^{79}Br_3{}^{81}Br_3Si_2$ m/z = 1024.6432; found m/z = 1024.6305 $[M - H + H_2O]^-$; IR (ATR): ν (cm^{-1}) = 1572, 1478, 1376, 1117, 1092 (Si-O), 1066, 1010, 812, 735.

*Synthesis of hexa(4-carboxyphenyl)disiloxane (**L1-H$_6$**)*



Hexa(4-carboxyphenyl)disiloxane was synthesized via modification of the procedure reported by Davies *et al.*[3] A 2.5 M solution of *n*-butyllithium (4.8 mL, 12 mmol) was added to a vessel containing anhydrous THF (40 mL) under a N_2 atmosphere and cooled to -70 °C. A solution of Hexa(4-bromophenyl)disiloxane (2.0 g, 2 mmol) in THF (20 mL) was then slowly injected and a bright pink colour quickly developed which gradually faded after the addition was complete. After 1.5 h, CO_2 was gently bubbled through the mixture (for approximately 2.5 h) after which the reaction was allowed to warm to room temperature overnight with constant stirring. The reaction was quenched with 1 M HCl (20 mL) and the organic layer was separated and evaporated to afford a cream solid. This was washed with EtOAc (2 x 5 mL) and Hexa(4-carboxyphenyl)disiloxane was collected by filtration as a white solid: 1.3 g (79 %). M.p., decomposed above 245 °C; Anal. Calcd. for $C_{42}H_{30}O_{13}Si_2$: C, 63.15; H, 3.79; N, 0.00. Found: C, 58.71; H, 3.84; N, <0.1; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 13.06 (s, 6H, COOH), 7.90 (d, 12H, J = 8.20 Hz, Ar-H), 7.55 (d, 12H, J = 8.20 Hz, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) = 167.0, 138.4, 134.7, 132.9, 128.7; ^{29}Si NMR (80 MHz, DMSO-d_6) δ (ppm) = -20.1; MS (ESI-): calcd (monoisotopic) for $C_{42}H_{29}O_{13}Si_2$ m/z = 797.1147; found m/z = 797.1133 $[M - H]^-$; IR (ATR): v (cm^{-1}) = 2870 (Br, O-H), 1554, 1498, 1418, 1390, 1288, 1099 (Si-O), 1018, 850, 760, 711, 556, 492.

*Synthesis of tris(4-carboxyphenyl)silanol (**L2-H$_3$**)*



Hexa(4-carboxyphenyl)disiloxane (50 mg, 63 µmol) was dissovled in 1 M NaOH (5 mL) and stirred for 5 minutes before 2.5 M HCl (5 mL) was added resulting in precipitation of a white solid. Tris(4-carboxyphenyl)silanol was collected by suction filtration: 42 mg (82 %). M.p. >300 °C; Anal. Calcd. for $C_{21}H_{16}O_7Si$: C, 61.76; H, 3.95; N, 0.00. Found: C, 62.93; H, 3.96; N, <0.1; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 13.05 (s, 6H, COOH), 7.97 (d, 6H, J = 8.00 Hz, Ar-H), 7.69 (d, 6H, J = 8.00 Hz, Ar-H); ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm) = 167.2 (COOH), 141.0, 134.7, 132.1, 128.5; ^{29}Si NMR (80 MHz, DMSO-d_6) δ (ppm) = -19.3 ; MS (ESI-): calcd (monoisotopic) for $C_{22}H_{17}O_9Si$ m/z = 453.0642; found m/z = 453.0641 $[M – H + HCOOH]^-$; IR (ATR): v (cm^{-1}) = 3028 (O-H), 1691, 1556, 1416, 1391, 1286, 1186, 1099 (Si-O), 1019, 847, 807, 759, 705.

$[Zn_3(L1)(H_2O)_3]\cdot 7DMF$ (IMP-18)

L1-H_6 (0.050 g, 63 µmol) and $ZnNO_3\cdot 6H_2O$ (0.059 g, 188 µmol) were combined in a glass vial to which DMF (6 mL) was added and the mixture sonicated until all reagents had dissolved. The vials were sealed and slowly heated in an oven to 85 °C over 2 hours, held at 85 °C for 46 hours and cooled gradually to room temperature over 6 hours. Colourless crystals were collected by suction filtration which were washed with fresh DMF (3 × 5 mL) and air dried. Yield = 37 mg (38 %). IR (ATR): ν (cm^{-1}) = 1654, 1609, 1543, 1499, 1387, 1256, 1100, 1064, 1017, 773, 728, 707, 659.

$[Zn_2(L2)(OH)(H_2O)(DMF)]\cdot 2H_2O\cdot 3DMF$ (IMP-19)

L2-H_3 (0.10 g, 125 µmol) and $ZnNO_3\cdot 6H_2O$ (0.11 g, 375 µmol) were combined in a glass vial to which DMF (10 mL) was added and the mixture sonicated until all reagents had dissolved. Water (5 mL) was added and the vials were sealed and slowly heated in an oven to 80 °C over 3 hours, held at 80 °C for 48 hours and cooled gradually to room temperature over 36 hours. Colourless crystals were collected by suction filtration which were washed thrice with chloroform (3 × 5 mL) and air dried. Yield = 53 mg (47 %) IR (ATR): ν (cm^{-1}) = 3200 (br), 1656, 1598, 1541, 1402, 1101, 893, 771, 725, 555, 484.

L1-H_6 HOF Network

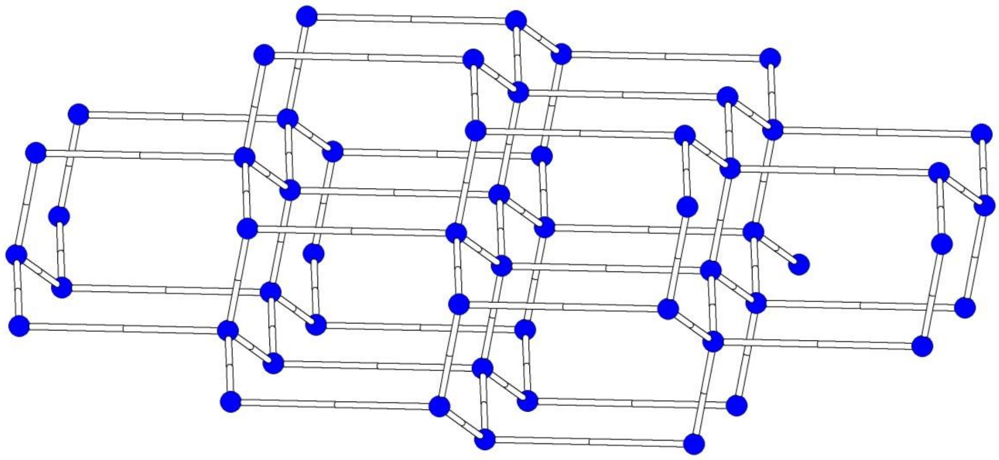


Figure S1: Topological view of HOF built from **L1**-H6 when the molecule is considered as two tetrahedral nodes conjoined forming a **dia** network. Structure has been optimised using Systre[4] such that the ideal symmetry of the crystal net has been assumed.

IMP-18 MOF Network

The **IMP-18** framework has channels which run along the 100, 001 and 010 directions with the largest windows being *ca.* 13 × 13 Å^2 along the 010 direction. These are filled with highly disordered solvent which was removed using the SQUEEZE routine of Platon (see supporting information for details). After theoretical removal of both the coordinated and non-coordinated solvent, Platon estimates the solvent-accessible void volume for **IMP-18** to be 9006.4 Å^3 or 58.5 % of the unit cell volume. Thermogravimetric analysis (TGA) of **IMP-18** (Figure S2) showed a 36 % weight loss in the temperature range 30 – 215 °C and this is thought to correspond to loss of the guest DMF and coordinated water molecules. A further 33 % loss between 390 and 520 °C is attributed to decomposition of the framework. Desolvation of the framework was attempted by heating at 80 °C under dynamic vacuum for 48 hours.

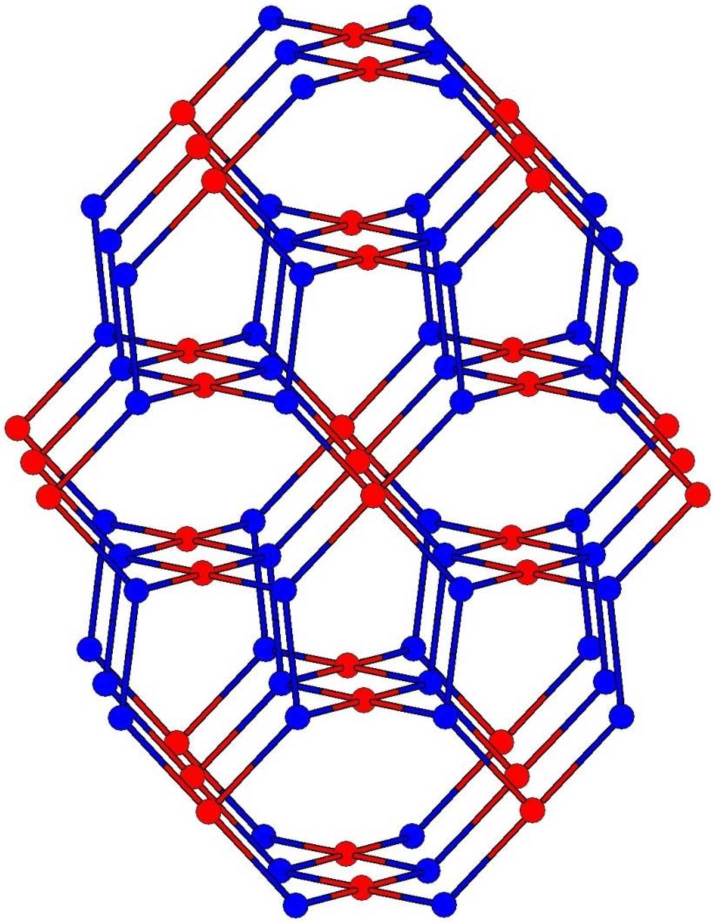


Figure S2: Topological view of **IMP-18** when **L1** is considered as two tetrahedral nodes conjoined. Structure has been optimised using Systre[4] such that the ideal symmetry of the crystal net has been assumed. This topology has not been previously reported to the best of our knowledge. The point symbol for this 4,4,4-c net is {4.6^3.8^2}4{4^2.6^2.8^2}2{6^2.8^4} with stoichiometry (4-c)(4-c)4(4-c)2.

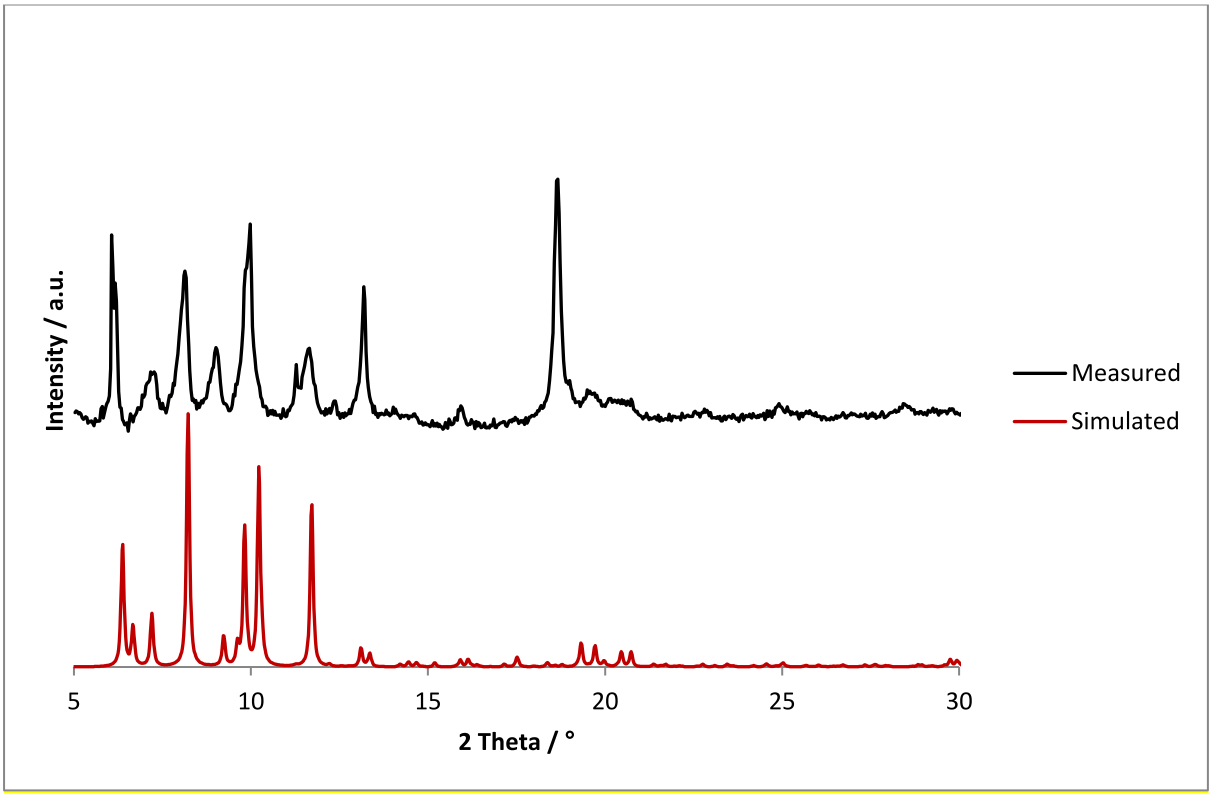


Figure S3: Overlaid PXRD diffractograms for **IMP-18**. Simulated (bottom) and as-synthesized material (top). Correlation of the two plots clearly shows the presence of **IMP-18** in the bulk product, however a small number of addition peaks can also be seen (eg at 2θ = 13.2, 18.6) which can be attributed to an impurity formed during the solvothermal synthesis protocol.

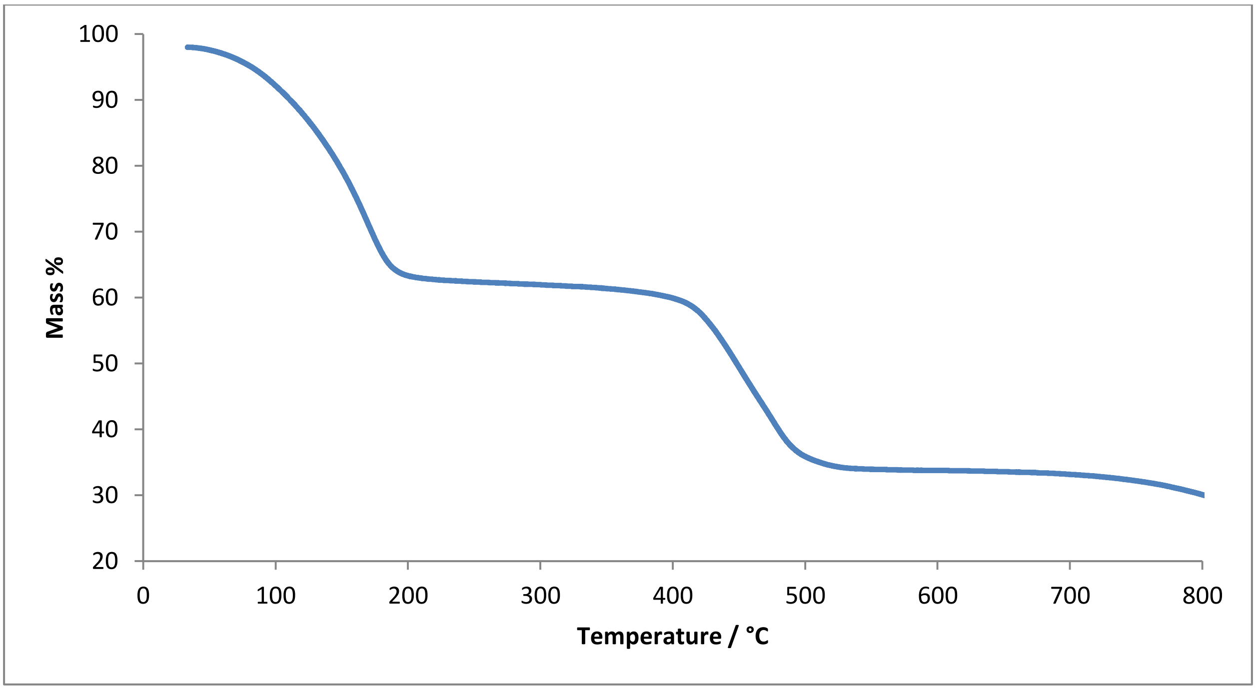


Figure S4: TGA trace for IMP-18

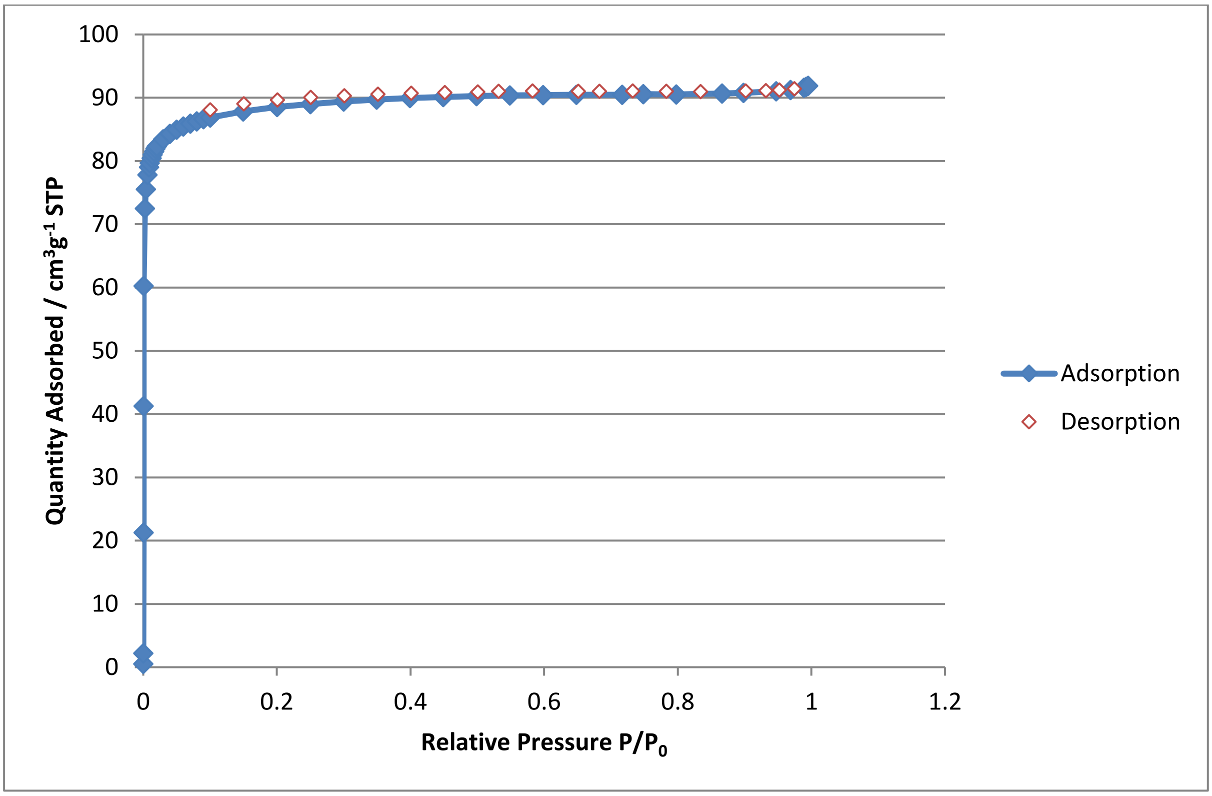


Figure S5: N_2 adsorption isotherm (77K) for dried **IMP-18**

IMP-19 MOF Network

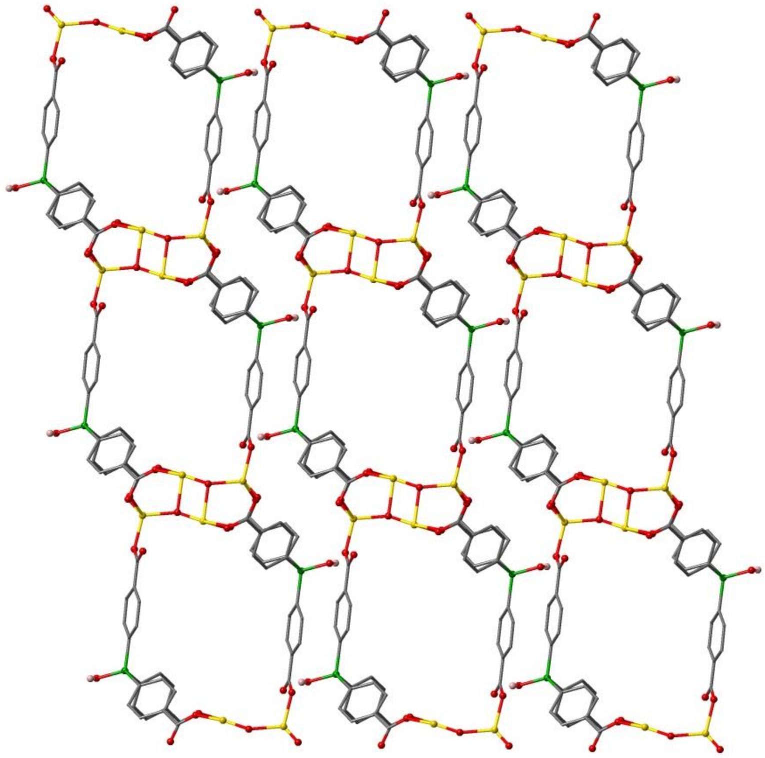


Figure S6: Three hydrogen-bonded layers in **IMP-19** viewed along the b axis (disorder, solvent molecules and non-silanol hydrogen atoms omitted for clarity. Colour scheme: Zn, gold; O, red; C, grey; Si, green; H, pink.

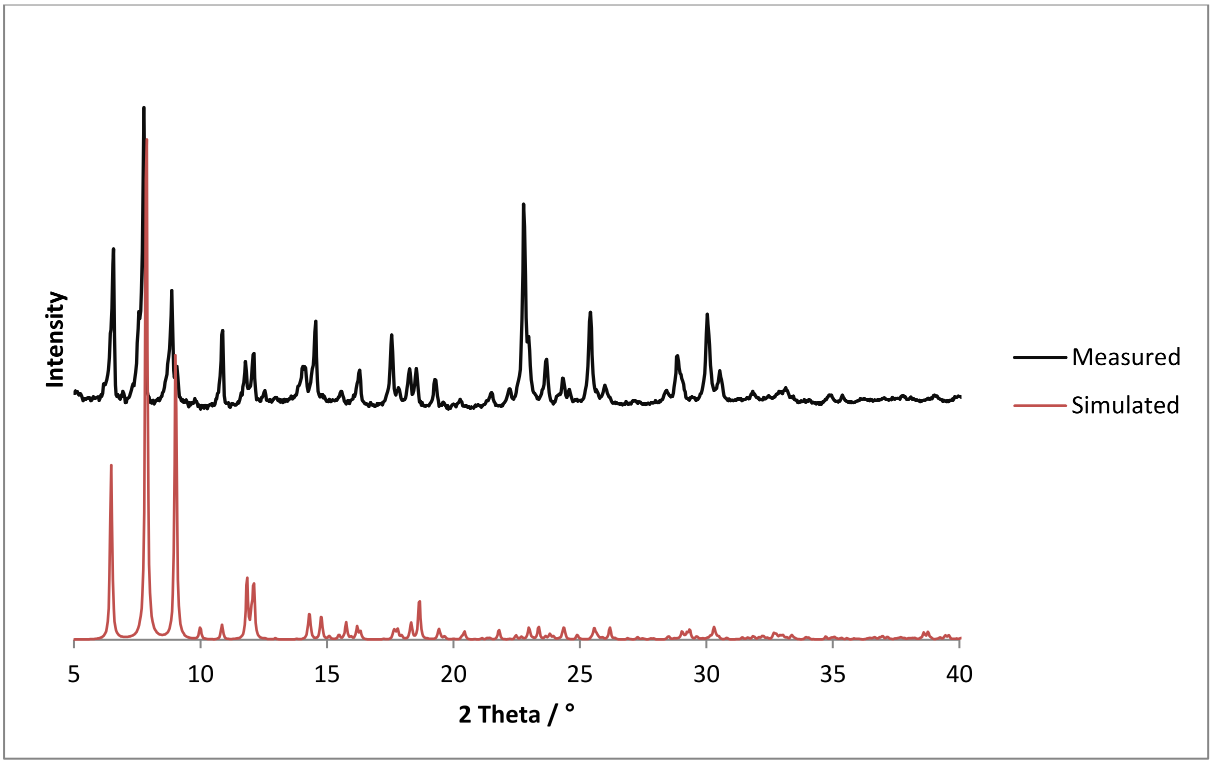


Figure S7: Overlaid PXRD diffractograms for **IMP-19**: Simulated (bottom) and as-synthesized material (top). Correlation of the two plots clearly shows the presence of **IMP-19** in the bulk product, however a small number of addition peaks can also be seen (eg at 2θ = 22.8, 25.4) which can be attributed to an impurity formed during the solvothermal synthesis protocol.

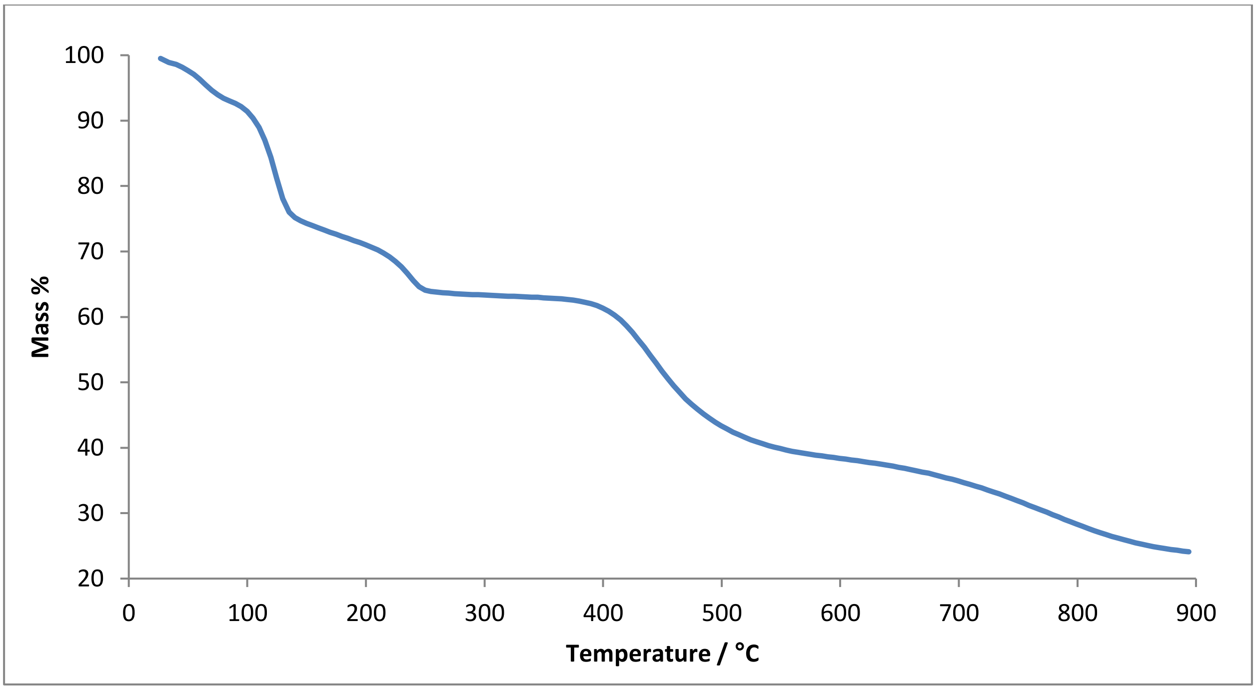


Figure S8: TGA trace for **IMP-19**

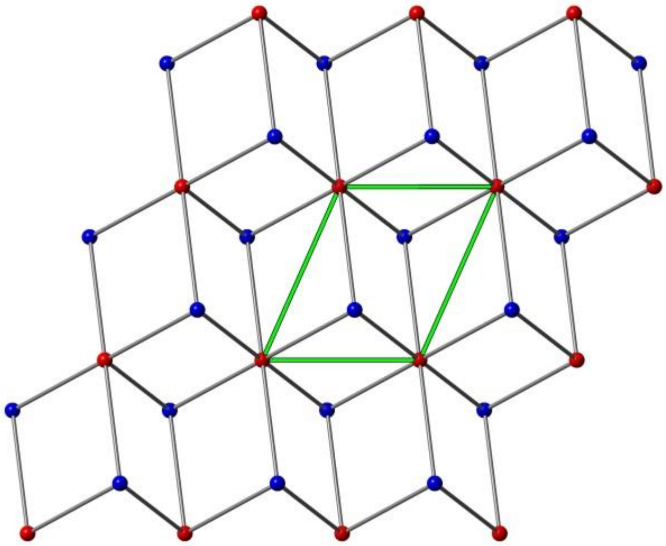


Figure S9: Schematic representation of the **kdg** topology of the 2D sheets in **IMP-19**

Table S1: Crystal Data, data collection parameters and refinement parameters for **L1**-H_6, **IMP-18** and **IMP-19.** CCDC deposition numbers are 1566035, 1566036 and 1566037 respectively.

Data	**L1**-H_6	**IMP-18**	**IMP-19**
Formula	$C_{42}H_{30}O_{13}Si_2$	$C_{42}H_{24}O_{16}Si_2Zn_3$	$C_{33}H_{48}N_4O_{15}SiZn_2$
Solvent	$2(C_2H_4O_2)$	$7(C_3H_7NO)$	$3(C_3H_7NO)$, $2(H_2O)$
Formula Weight	918.94	1036.90	1548.57
Color, habit	colourless tablets	colourless needles	colourless blades
Crystal size / mm	0.34 × 0.31 × 0.07	0.20 × 0.03 × 0.03	0.26 × 0.14 × 0.04
Temperature / K	173(2)	100(2)	100(2)
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	$Pmc2_1$	P-1
a / Å	17.0954(9)	13.2462(5)	12.2548(9)
b / Å	17.1816(4)	27.7134(10)	12.8569(9)
c / Å	17.3736(7)	24.5341(9)	14.9698(10)
α / deg	93.458(3)	90	112.029(5)
β / deg	105.795(4)	90	93.340(4)
γ / deg	104.490(3)	90	105.787(3)
V / $Å^3$	4708.8(4)	9006.4(6)	2069.7(3)
Z	4	4	2
D_c / (g cm^{-3})	1.296	0.7647	1.443
Radiation used	Cu Kα	Mo Kα	Mo Kα
μ / mm^{-1}	1.297	0.854	0.882
2θ max / deg	148	50	50
No. of unique reflections			
measured	18029	16230	9473
observed $\|F_o\| > 4\sigma(\|F_o\|)$	10623	10870	8338
No. of variables	1056	950	538
R_1(obs), ${}_wR_2$(all)	0.0808, 0.2750	0.0870, 0.2551	0.0606, 0.2552

References

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4. O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2003, **59**, 351-360.