Electronic Supplementary Information

Stable Metal-Organic Frameworks with Low Water Affinity Built from Methyl-Siloxane Linkers

Luke C. Delmas,[a] Andrew J. P. White,[a] David Pugh,[b] Arwyn Evans,[c] Mark Antonin Isbell,[c] Jerry Y. Y. Heng,[c] Paul D. Lickiss[a] and Robert P. Davies*[a]

[a] Molecular Sciences Research Hub, Department of Chemistry, Imperial College London, White City, London, UK, W12 0BZ.

[b] Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London, UK, SE1 1DB

[c] Department of Chemical Engineering, Imperial College London, South Kensington, London, UK, SW7 2AZ.

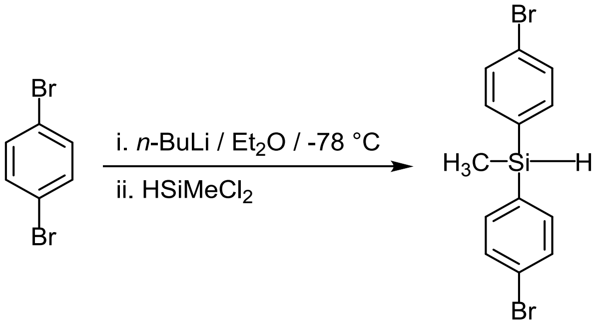
*E-mail: r.davies@imperial.ac.uk; Tel: +44 (0)207 5945754

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 Micromass Autospec Premier spectrometer (EI) or Waters LCT Premier spectrometer (ESI). 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}. Water sorption measurements were carried out using a Surface Measurement Systems DVS2000 water vapour sorption analyser. BET surface area measurements were carried out using a Micromeritics TriStar II Plus instrument and Micromeritics MicroActive software. Single crystal X-ray diffraction data was collected using an Oxford Diffraction Xcalibur 3 (**L**-H_4), a Rigaku FRE+ diffractometer equipped with HF Varimax confocal mirrors, an AFC12 goniometer and HG Saturn 724+ detector (**IMP-32**-Zr) or a Rigaku 007HF diffractometer equipped with Varimax confocal mirrors, an AFC11 goniometer and HyPix 6000 detector (**IMP-32**-Hf). A summary of the crystallographic data is presented in Table S1.

Synthesis:

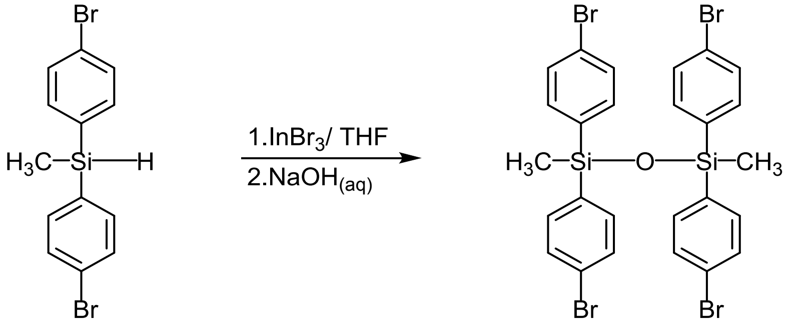
Bis(4-bromophenyl)methylsilane



Bis(4-bromophenyl)methylsilane was synthesized via an adapted protocol reported by Ishikawa and co-workers.[2] 1,4-Dibromobenzene (10.0 g, 42 mmol) was taken up in dry diethyl ether (50 mL) under an inert atmosphere in a round-bottomed flask and placed in an acetone-dry ice bath. A 2.5 M solution of *n*-butyllithium in hexanes (17 mL, 42 mmol) was slowly added and the resulting mixture allowed to stir for 2 h. The dry-ice acetone bath was exchanged with an ice bath and the mixture was warmed to 0 °C. Subsequently, the solution was transferred by cannula into a flask containing $HSiMeCl_2$ (2.20 mL, 21.2 mmol) in dry diethyl ether (5 mL) held at -78 °C. A white precipitate formed on mixing of the two solutions and, following completion of the addition, the mixture was allowed to stir overnight while slowly warming to room temperature. The reaction was quenched with water (20 mL) and the ethereal phase separated. The aqueous phase was washed with diethyl ether (30 mL) and the combined ethereal extracts were evaporated to give a translucent oil. The oil was dissolved in hexanes

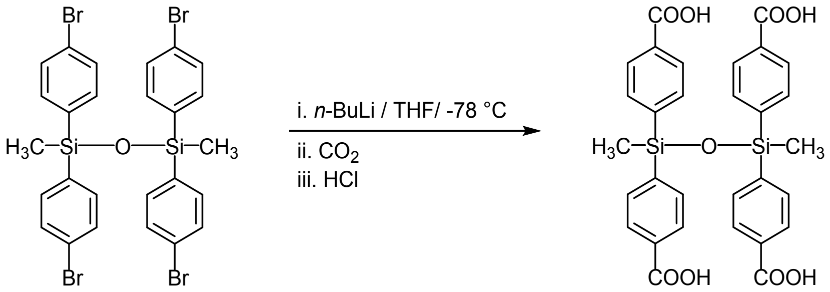
(20 mL) and the insoluble material removed via filtration. The filtrate was rapidly cooled in a dry-ice/acetone bath until a white solid deposited onto the surface of the glass. The liquid was decanted and the solid residue rinsed twice with cold hexanes (2 × 10 mL). The flask was then allowed to warm to ambient temperature and bis(4-bromophenyl)methylsilane was isolated as a colourless oil: 5.3 g (70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.51 (d, 4H, J = 8.29 Hz, Ar-H), 7.38 (d, 4H, J = 8.29 Hz, Ar-H), 4.88 (q, 1H, $^{3}J(^{1}H^{1}H)$ = 3.84 Hz, $J^{29}Si\text{-}^{1}H$ = 198 Hz, Si-H) 0.60 (d, 3H, $^{3}J(^{1}H^{1}H)$ = 3.84 Hz, $J^{13}C\text{-}^{1}H$ = 122 Hz, Si-CH_3); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 136.4, 133.7, 131.4, 124.9, -5.01; ^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = -17.2; MS (EI+): calcd. (monoisotopic) for $C_{13}H_{12}Br_2Si$ m/z = 353.9075; found m/z = 353.9083 $M^{+\cdot}$; IR (ATR): ν (cm^{-1}) = 2960 (C-H), 2130 (Si-H), 1570, 1478, 1376, 1253 (Si-CH_3), 1111, 1066, 1010, 873, 834, 800, 741, 721.

1,3-Dimethyltetrakis(4-bromophenyl)disiloxane



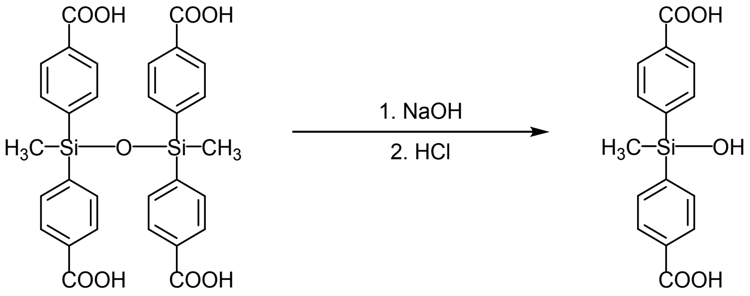
Bis(4-bromophenyl)methylsilane (2.0 g, 5.6 mmol) was dissolved in THF (10 mL) and indium(III) bromide (0.3 g, 0.8 mmol) was added in one portion allowing the resultant mixture to stir for 10 min. Aqueous NaOH (4M, 1.1 mL, 4.4 mmol) was then slowly added and the mixture allowed to stir at room temperature overnight. Hexanes (20 mL) and water (10 mL) were added to the mixture and the organic phase separated, dried ($MgSO_4$) and evaporated to afford a colourless oil. The latter was purified by column chromatography using hexanes and ethyl acetate (8:1 v/v) as the eluent to afford the title compound as a colourless viscous oil: 1.06 g (52 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.46 (d, 8H, J = 8.29 Hz, Ar-H), 7.28 (d, 8H, J = 8.29 Hz, Ar-H), 0.54 (s, 6H, $J(^{13}C^{1}H)$ = 120 Hz, $^{2}J(^{29}Si^{1}H)$ = 6.86 Hz); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 135.5, 135.4, 131.3, 125.2, -0.65; ^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = -9.0; MS (EI+): calcd. for $C_{25}H_{19}O^{79}Br_2{}^{81}Br_2Si_2$ m/z = 710.7667; found m/z = 710.7686 $[M - CH_3]^+$; IR (ATR): ν (cm^{-1}) = 2953 (C-H), 1571, 1478, 1376, 1258 (Si-CH_3), 1109, 1065 (Si-O), 1009, 828, 786, 752, 738, 723.

1,3-Dimethyltetrakis(4-carboxyphenyl)disiloxane



1,3-Dimethyltetrakis(4-carboxyphenyl)disiloxane was prepared according to modification of the procedure reported by Davies and co-workers.[3] A 2.5 M solution of n-BuLi in hexanes (2.2 mL, 5.5 mmol) was added to a flask containing dry THF (40 mL) under N_2 and held at -78 °C. A solution of 1,3-dimethyltetrakis(4-bromophenyl)disiloxane (1.0 g, 1.4 mmol) in dry THF (20 mL) was then slowly added to the vessel and the mixture allowed to stir for 2 h. Carbon dioxide was subsequently bubbled through the mixture for 3 hours after which the mixture was allowed to stir overnight, gradually warming to ambient temperature. The reaction was quenched with 1 M HCl (15 mL) and the organic layer was separated and concentrated to an oily mixture. The flask was rapidly cooled in liquid nitrogen and the crude product solidified on the walls of the flask. The colourless supernatant was discarded and THF (10 mL) was added to dissolve the crude compound. Hexanes (30 mL) were subsequently added as an antisolvent resulting in a white suspension. Evaporation of the solvents afforded the product as a white solid: 0.62 g (78 %). M.p., decomposed above 290 °C; Anal. Calcd. for $C_{30}H_{26}O_9Si_2$: C, 61.42; H, 4.47. Found: C, 61.50; H, 4.51; ^{1}H NMR (400 MHz, DMSO-D_6) δ (ppm) = 13.0 (s, 4H, COOH), 7.91 (d, 8H, *J* = 8.29 Hz, Ar-H), 7.63 (d, 8H, *J* = 8.29 Hz, Ar-H), 0.67 (s, 6H, Si-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.1, 141.8, 133.7, 132.1, 128.5, -1.21; ^{29}Si NMR (80 Hz, $CDCl_3$) δ (ppm) = -9.25; MS (ESI-): calcd. (monoisotopic) for $C_{30}H_{25}O_9Si_2$ m/z = 585.1037; found m/z = 585.1028 $[M - H]^-$; IR (ATR): ν (cm^{-1}) = 2960 (C-H), 2821 (O-H), 2661, 2546, 1686, 1413, 1390, 1287, 1260 (Si-CH_3), 1098, 1051 (Si-O-Si), 1017, 781, 753, 729, 698, 523.

Bis(4-carboxyphenyl)methylsilanol



1,3-Dimethyltetrakis(4-carboxyphenyl)disiloxane (50 mg, 85 μmol) was taken up in 1 M NaOH (5 mL) and stirred for 2 hours before 2.5 M HCl (5 mL) was added causing precipitation of a white solid. The title compound was collected by centrifugation, washing once with water (5 mL): 37 mg (72%). Decomposed above 250 °C; Anal. Calcd. for $C_{15}H_{14}O_5Si$: C, 59.59; H, 4.67; N, 0.00. Found: C, 59.70; H, 4.72; N, <0.1; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) = 12.98 (s, 2H, COOH), 7.92 (d, 4H, *J* = 8.26 Hz, Ar-H), 7.68 (d, 4H, *J* = 8.26 Hz, Ar-H), 6.85 (s, 1H, Si-OH), 0.59 (s, 3H, Si-CH_3); ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm) = 167.3, 143.8, 133.8, 131.6, 128.3, -1.26 ; ^{29}Si NMR (80 MHz, DMSO-d_6) δ (ppm) = -8.7 ; MS (ESI-): calcd. (monoisotopic) for $C_{15}H_{13}O_5Si$ m/z = 301.0532; found m/z = 301.0527 $[M – H]^-$; IR (ATR): ν (cm^{-1}) = 3643 (Si-OH), 2958 (C-H), 2853 (br, O-H), 1686, 1682, 1597, 1553, 1500, 1418, 1390, 1318, 1289, 1257, 1188, 1134, 1098 (Si-O), 1050, 1017, 933, 906, 825, 784, 751, 722, 700, 667.

$[Zr_3O_4(L)(DMF)_4]\cdot 3DMF$ *(IMP-32-Zr)*

L-H_4 (0.030 g, 51 μmol) and $ZrOCl_2\cdot 8H_2O$ (0.036 g, 112 μmol) were combined in a glass vial to which DMF (2 mL) and formic acid (1 mL) were added and the mixture sonicated until all reagents had dissolved. The vials were sealed and slowly heated in an oven to 100 °C over 3 hours, held at 100 °C for 44 hours and cooled gradually to room temperature over 3 hours. Colourless crystals were collected by suction filtration which were washed with fresh DMF (3 × 5 mL) and air dried. Yield = 48 mg (66 %). IR (ATR): ν (cm^{-1}) = 1655, 1584, 1536, 1498, 1394, 1100, 846, 772, 727.

$[Hf_3O_4(L)(DMF)_4]\cdot 2DMF$ *(IMP-32-Hf)*

L-H_4 (0.020 g, 34 μmol) and $HfCl_4$ (0.044 g, 136 μmol) were combined in a glass vial to which DMF (2 mL) and formic acid (1 mL) were added and the mixture sonicated until all reagents had dissolved. The vials were sealed and slowly heated in an oven to 100 °C over 3 hours, held at 100 °C for 44 hours and cooled gradually to room temperature over 3 hours. Colourless crystals were collected by suction filtration which were washed with fresh DMF (3 × 5 mL) and air dried. Yield = 35 mg (64 %). IR (ATR): ν (cm^{-1}) = 1651, 1580, 1536, 1416, 1256, 1103, 1055, 790, 764, 664.

L-H_4 HOF Network

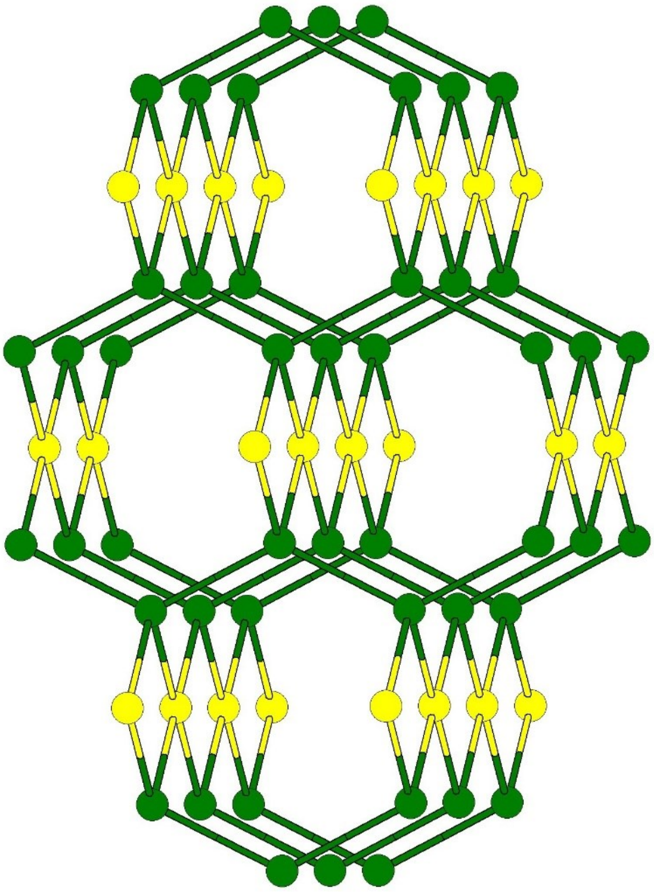


Figure S1: Topological view of a single **mog** net in the HOF built from **L**-H_4. Structure has been optimised using Systre[4] such that the ideal symmetry of the crystal net has been assumed. Square planar nodes corresponding to the linear siloxane molecules shown in yellow and tetrahedral nodes corresponding to bent siloxane molecules shown in green.

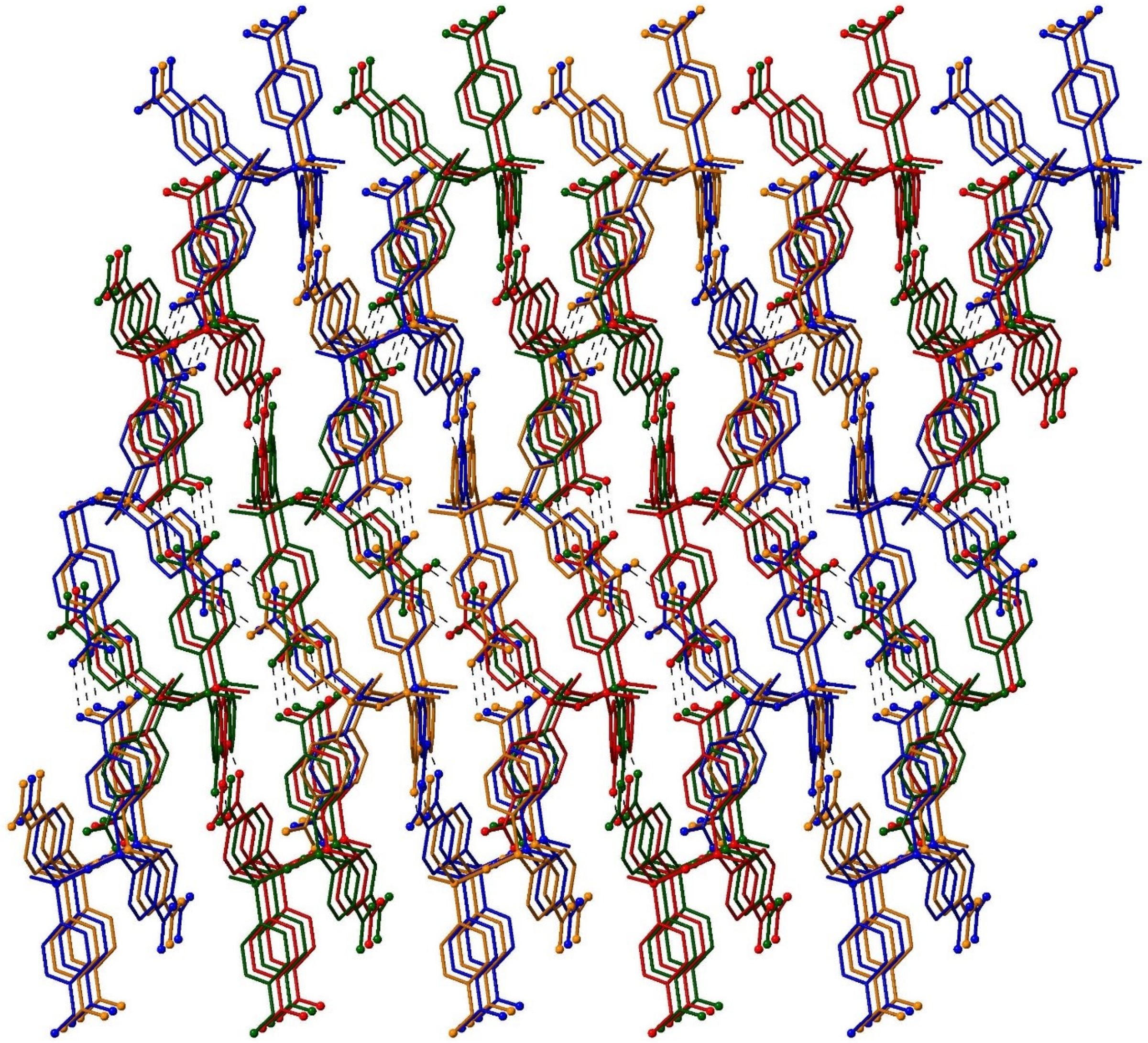


Figure S2: Portion of the extended structure of the HOF built from **L**-H_4 showing quadruple interpenetration. Discrete nets shown in blue, gold, red, and green. Hydrogen bonds shown by black dashed lines.

IMP-32 MOF Networks

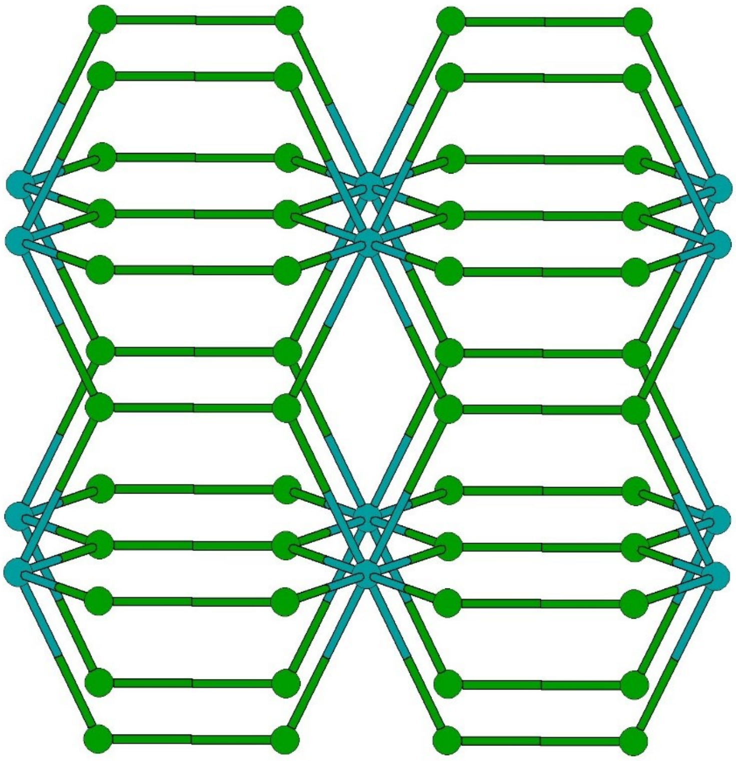


Figure S3: Topological view of the **IMP-32 tty** framework when **L** is considered as two 3-c nodes conjoined. Structure has been optimised using Systre[4] such that the ideal symmetry of the crystal net has been assumed. Ligand nodes shown in green and Zr-based nodes in turquoise.

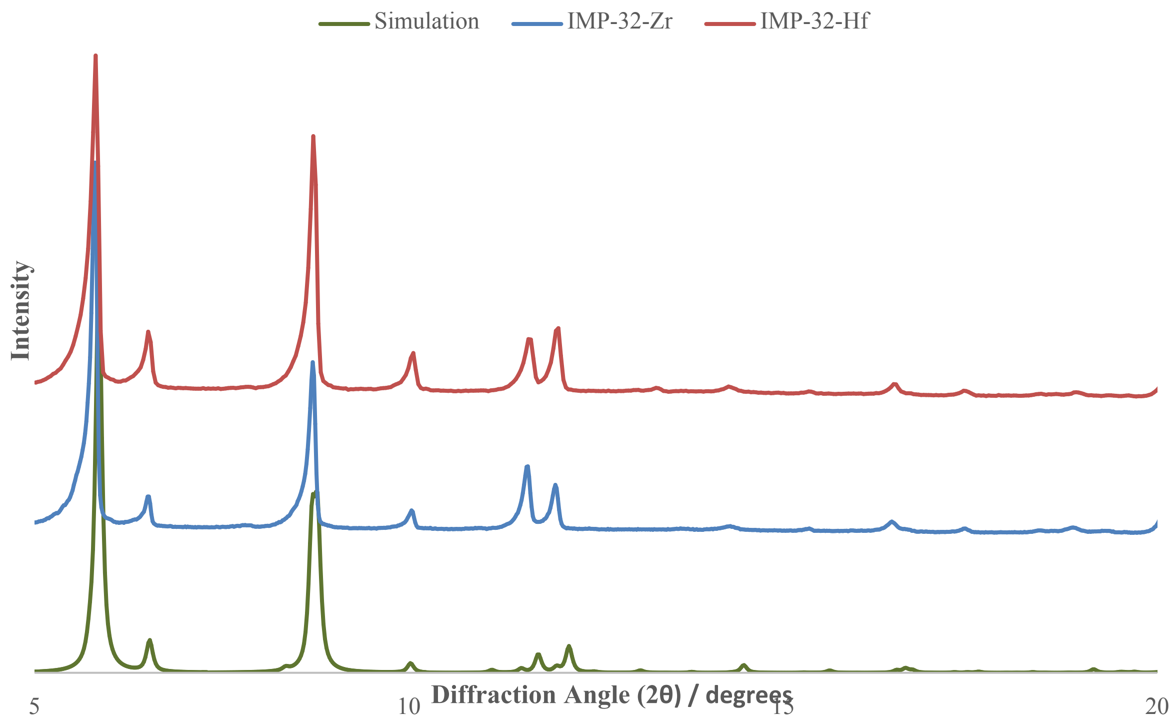


Figure S4: Overlaid PXRD diffractograms for activated samples of **IMP-32**-Zr/Hf with simulated plot from **IMP-32**-Zr single crystal data.

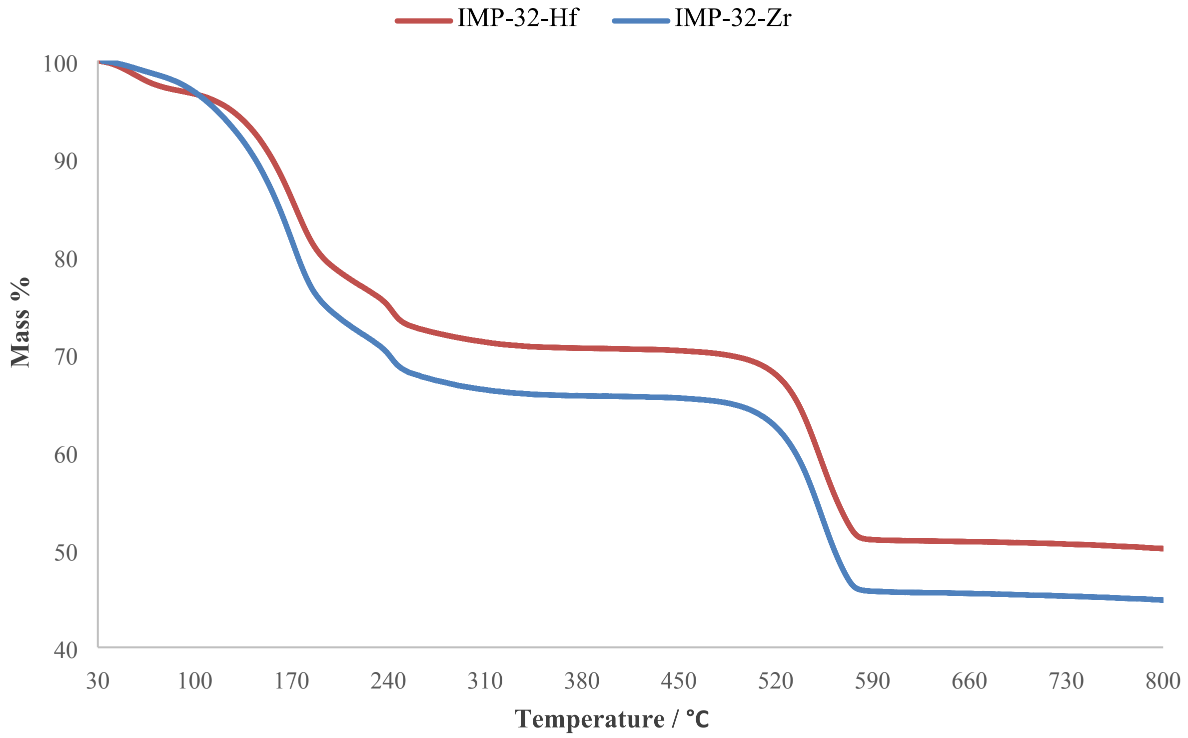


Figure S5: TGA trace for **IMP-32** MOFs

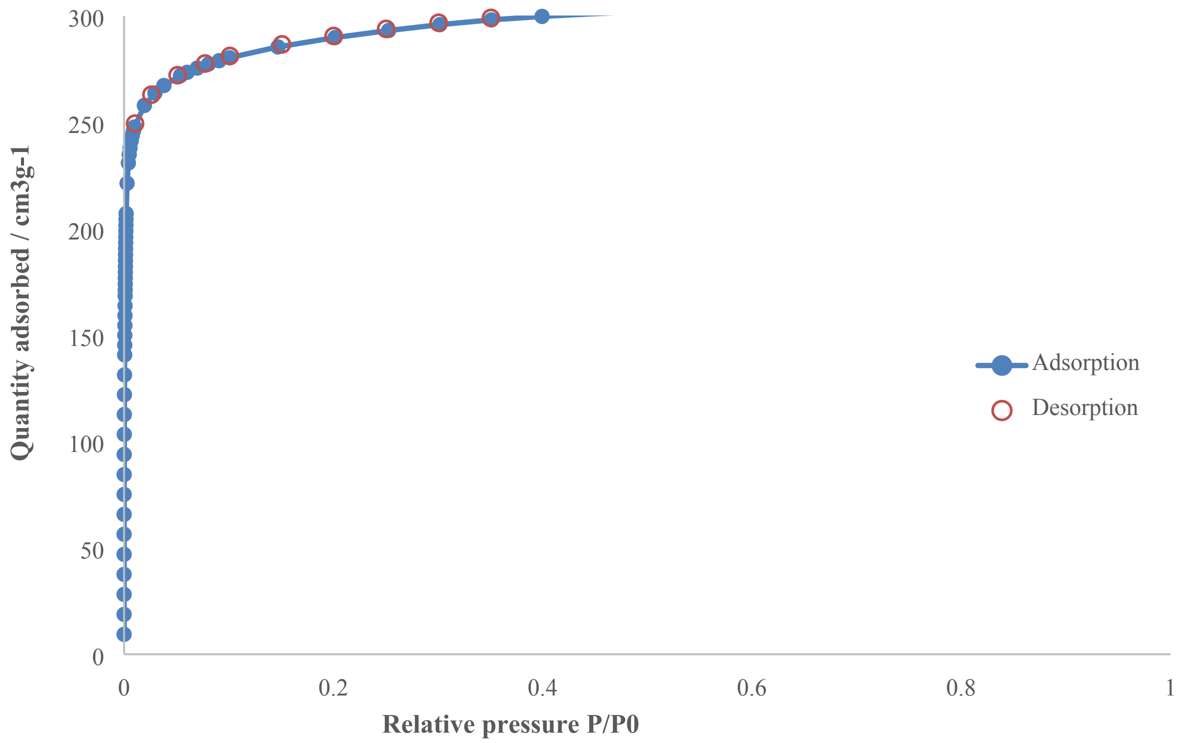


Figure S6: N_2 adsorption isotherm (77 K) for dried **IMP-32**-Zr

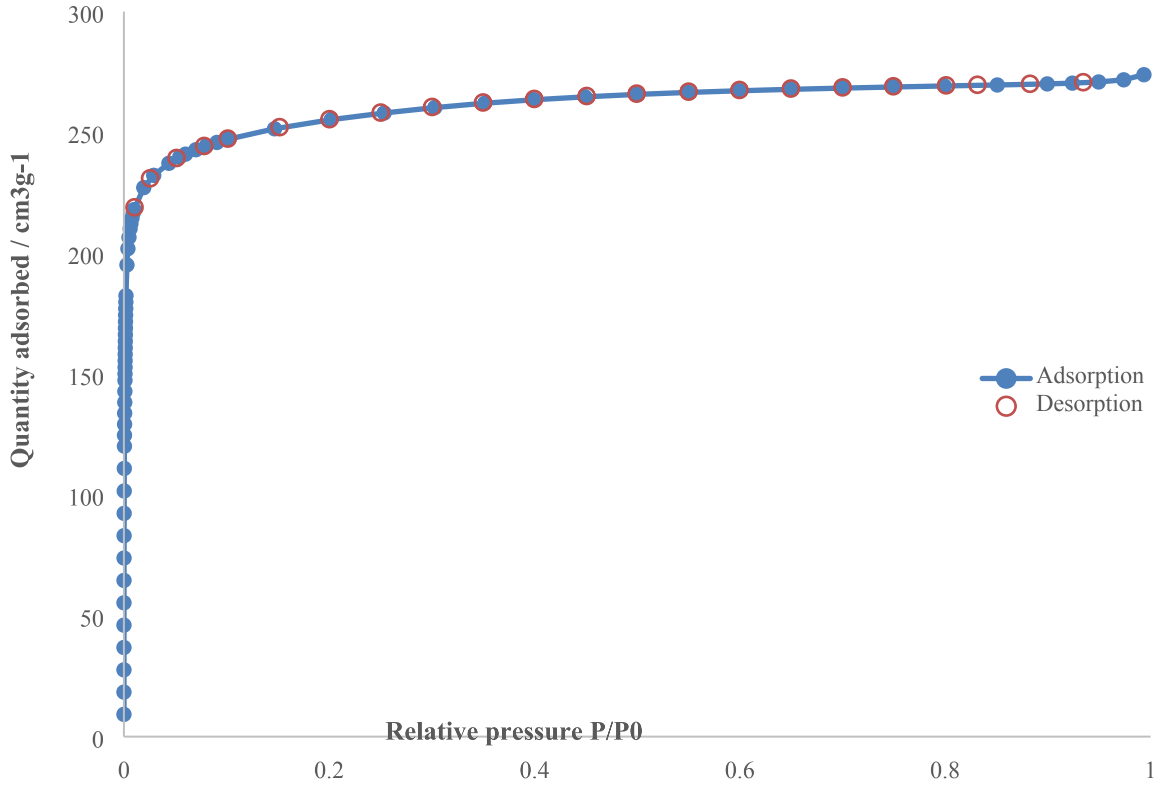


Figure S7: N_2 adsorption isotherm (77 K) for dried **IMP-32**-Hf

Dynamic Vapour Sorption (DVS) Measurements

In this investigation a DVS2000 (Surface Measurement Systems, London, UK) dynamic vapour sorption (DVS) gravimetric analyser was used to study the water vapour adsorption capacity of **IMP-32** MOFs. The DVS system allows for the direct measurement of water mass adsorbed at the surface of the sample at controlled water vapour concentrations. Samples of approximately 10 mg in mass were placed in the equilibration chamber at 23 °C. All samples were dried under air at 0% relative humidity (RH) until no change in mass was observed in the sample. The water vapor adsorption isotherms were obtained by measuring the sorption values between 0% to 95% RH at various increments. The equilibrium vapor sorption amount was established when no increase in mass was observed. The total dry and wet gas flow was measured at 200 cm^3/min in all experiments.

Stability studies of IMP-32-Zr

Samples of **IMP-32**-Zr were soaked as specified in the legend of Figure S8 below and recovered by suction filtration. The air-dried samples were then analysed by pXRD.

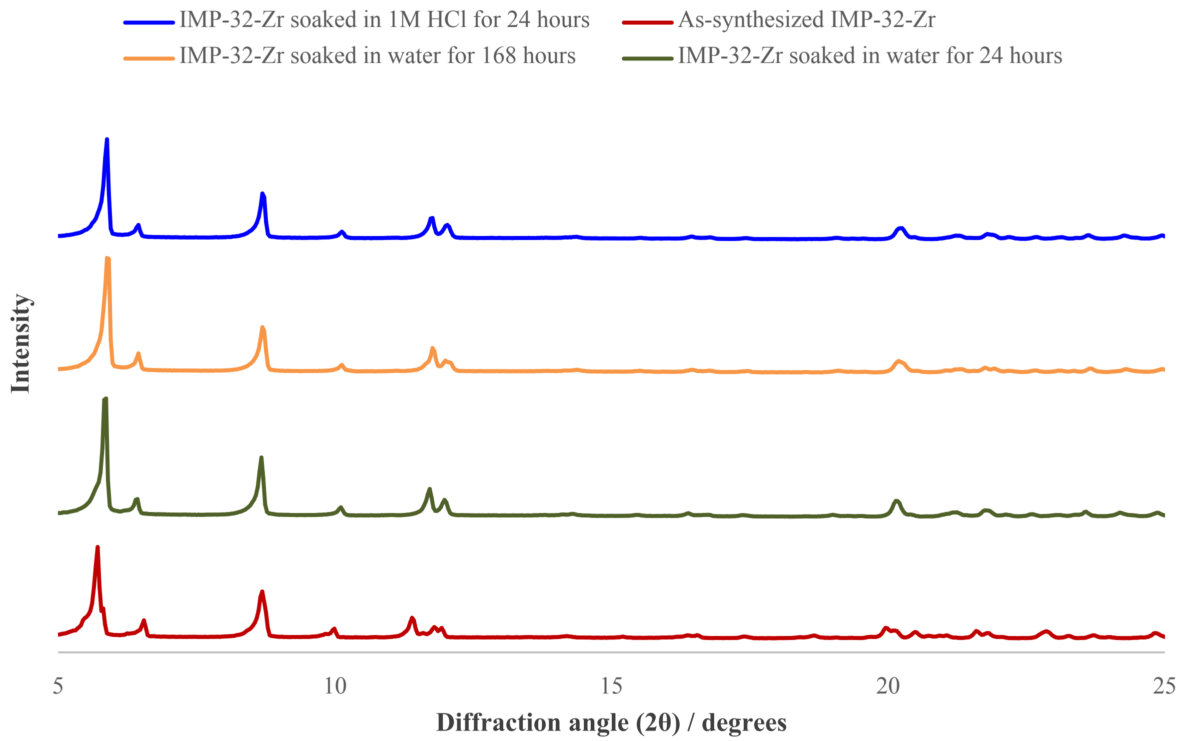


Figure S8: Overlaid PXRD diffractograms for treated samples of **IMP-32**-Zr

Crystallographic Data

Table S1: Crystal Data, data collection parameters, and refinement parameters for **L**-H_4, **IMP-32-Zr** and **IMP-32-Hf.**

Data	**L**-H_4	**IMP-32**-Zr	**IMP-32**-Hf
CCDC	1950125	1950126	1950127
Formula	$C_{30}H_{26}O_9Si_2$	$C_{21}H_{25}N_2O_{8.5}SiZr_{1.5}$	$C_{21}H_{25}N_2O_{8.5}SiHf_{1.5}$
Solvent	-	1.5(C_3H_7NO)	(C_3H_7NO)
Formula Weight	586.69	715.99	810.35
Color, habit	colourless blocks	colourless prisms	colourless plates
Crystal size / mm	0.25 × 0.10 × 0.05	0.10 × 0.03 × 0.01	0.10 × 0.03 × 0.01
Temperature / K	173(2)	103(2)	100(2)
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	*P*-1	*Ibam*	*Ibam*
a / Å	9.1221(5)	17.2986(5)	17.21910(16)
b / Å	10.3996(5)	30.7451(6)	30.6244(2)
c / Å	24.2182(12)	27.0210(6)	27.1584(3)
α / deg	83.396(4)	90	90
β / deg	80.039(4)	90	90
γ / deg	79.810(4)	90	90
V / Å^3	2218.7(2)	14371.0(6)	14321.3(2)
Z	3	16	16
D_c / (g cm^{-3})	1.317	1.324	1.503
Radiation used	Mo Kα	Mo Kα	Mo Kα
μ / mm^{-1}	0.172	0.526	8.665
2θ max / deg	50	50	50
No. of unique reflections			
measured	8749	8406	6986
observed $\|F_o\| > 4\sigma(\|F_o\|)$	4434	5153	6809
No. of variables	576	241	258
R_1(obs), $_wR_2$(all)	0.0727, 0.1972	0.0591, 0.1826	0.0496, 0.1447

References

1. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.
2. M. Ishikawa, K. Watanabe, H. Sakamoto and A. Kunai, *J. Organomet. Chem.*, 1993, **455**, 61-68.
3. R. P. Davies, R. J. Less, P. D. Lickiss, K. Robertson and A. J. P. White, *Inorg. Chem.*, 2008, **47**, 9958-9964.
4. O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2003, **59**, 351-360.