

Electronic Supplementary Information

Organosilicon Linkers in Metal Organic Frameworks: the Tetrahedral Tetrakis(4-tetrazolylphenyl)silane Ligand

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Experimental Procedures

General Methods

All reactions involving *n*BuLi were carried out in oven-dried glassware and were performed under an atmosphere of nitrogen. Diethyl ether and THF were dried by distillation over sodium metal prior to use. All other chemicals and solvents used in the syntheses were commercial reagent grade and were used without further purification. Tetrakis(4-cyanophenyl)silane was prepared according to literature procedures.¹ NMR spectra were recorded on a Bruker AV-400 spectrometer and Infrared spectra on a Perkin Elmer spectrum 100 series spectrometer with a universal ATR sampling accessory. Microanalytical data were obtained from the Science Technical Support Unit, London Metropolitan University. *Metal tetrazolates are potentially explosive, particularly when dry, and should be handled with appropriate care and respect.*

Synthesis of tetrakis(4-2H-tetrazol-5-yl-phenyl)silane, H₄ttps

A mixture of tetrakis(4-cyanophenyl)silane (1.00 g, 2.29 mmol), sodium azide (1.72 g, 26.4 mmol) and triethylamine hydrochloride (3.63 g, 26.4 mmol) in 25 mL toluene and 10 mL methanol was heated at reflux for 4 days. After this period the mixture was cooled to room temperature and an aqueous solution of NaOH (25 mL, 1 M) was added. The solution was then stirred for 30 mins. The resultant aqueous layer was treated with dilute HCl (1 M) until no further precipitate formed. The precipitate was collected by filtration and dissolved in a solution of NaOH (1 M). The resulting solution was treated with portions of dilute HCl (1 M) until the approximate pH of the solution reached 4. The ensuing precipitate was filtered, washed three times with distilled water and dried under vacuum at 50 °C for 2 days to give

1.03g (73 %) of $H_4ttps \cdot 4H_2O$. M.p. > 300 °C. 1H NMR (D_6 -DMSO): 11.8 (br, 4H, NH), 8.17 (d, $J = 8.0$ Hz, 8 H, Ar-H), 7.80 (d, $J = 8.0$ Hz, 8 H, Ar-H) ppm. IR (ATR): $\nu(cm^{-1}) = 3405$ (br), 1653, 1569, 1407, 1282, 1107, 1068, 929, 835, 741, 701. Anal. Calcd. (%) for $C_{28}H_{20}N_{16}Si \cdot 4H_2O$: C, 55.15; H, 3.64; N, 36.75. Found: C, 55.11; H, 3.68 ; N 36.20

Comparison of cost of precursors for syntheses of H_4ttps and H_4ttpm

The prices quoted below are the best UK prices (excluding VAT) from either Alfa Aesar (tetraphenylmethane) or Sigma-Aldrich (all other chemicals) at the time of writing (August 2013). They may not represent the cheapest available commercial prices from all suppliers. Synthetic strategies towards tetraphenylmethane have also been reported (see M. Grimm, B. Kieste and H. Kurreck, *Angew. Chem., Int. Ed. Engl.* **1986**, *24*, 1097), which could reduce the cost of starting materials for H_4ttpm but add a number of additional steps to the reaction.

H_4ttps	Silicon tetrachloride	10026-04-7	£18.40 for 100g
	4-Bromobenzonitrile	623-00-7	£60.90 for 50g
	Sodium azide	26628-22-8	£21.30 for 100g
H_4ttpm	Tetraphenylmethane	630-76-2	£499.00 for 25g
	Bromine	7726-95-6	£15.70 for 100mL
	Potassium cyanide	151-50-8	£11.50 for 25g
	Sodium azide	26628-22-8	£21.30 for 100g

Synthesis of $[H(Cu_4Cl)(ttps)_2(DMF)_4] \cdot 18DMF$ (IMP-16)

H_4ttps (50 mg, 0.08 mmol) and $CuCl_2 \cdot 2H_2O$ (28 mg, 0.16 mmol) were dissolved in a mixture of 4.5 mL DMF, 1.5 ml MeOH and 0.2 mL of dilute HCl (1 M) to give a clear solution. This

solution was subsequently heated in a sealed screw-top glass vial at 80 °C for 3 days. The mixture was allowed to cool to room temperature and the resultant pale purple crystals filtered and washed with anhydrous DMF. Yield = 100 mg (78%). IR (ATR): $\nu(\text{cm}^{-1}) = 3036$ (br), 1612, 1450, 1407, 1099, 1006, 832, 745. Anal. Calcd. (%) for $\text{C}_{68}\text{H}_{61}\text{ClCu}_4\text{N}_{36}\text{O}_4\text{Si}_2 \cdot (\text{C}_3\text{H}_7\text{NO})_6(\text{CH}_3\text{OH})_{14}$; C, 44.83; H, 5.98; N, 21.96, Found; C, 44.11; H, 5.88; N, 21.51. Note that washing and drying procedures for elemental analysis and single crystal X-ray diffraction differed so that there are minor differences in solvation.

Gas absorption measurements

Supercritical CO₂ activation was performed using a Polaron Critical Point Dryer. In a typical experiment, 100 mg of synthesized **IMP-16** were soaked in anhydrous ethanol over a period of 3 days (refreshing the solution every day) in order to remove all residual DMF from the pores. The resultant material was then filtered on a glass frit and transferred to the Critical Point Dryer. After loading the sample the dryer was flushed with CO₂ for 1 minute before closing the venting valve and cooling the chamber to 7 °C. The chamber was then filled to approximately 60% capacity, and the MOF was left to soak for 10 hours with purging of the liquid CO₂ and refilling the chamber every 2 hours. The chamber was subsequently heated to 45 °C for 2 hours and the supercritical fluid was slowly vented. After supercritical drying, samples were outgassed at 50 °C under 0.005 mbar vacuum for 10 hours. mGas adsorption isotherms for pressures in the range 0–1 bar were measured using a Beckman Coulter SA3100 instrument. N₂ isotherms at 77 K were measured in liquid nitrogen baths using Ultra high purity nitrogen (ALPHAGAZ™ 1 NITROGEN, 99.999%).

X-Ray Crystallography Supporting Information

The presumed “extra” hydrogen atom in the structure of $[\text{H}(\text{Cu}_4\text{Cl})(\text{ttps})_2(\text{DMF})_4] \cdot 18\text{DMF}$ (**IMP-16**) could not be located in the crystal structure (unsurprising given the high symmetry and the significant disorder in the coordinated and included solvent, see below), and so the atom list for the asymmetric unit is low by 0.125(H).

The chlorine atom at the centre of each Cu_4 node sits on an *mmm* position, the two unique copper centres occupy sites with *mm* symmetry, and the silicon atom is on a -4 position. The contents of the asymmetric unit are shown in Fig. S1 and Fig. S2.

Both the coordinated and the included solvent molecules were found to be highly disordered. The two coordinated solvent molecules, based on O(20) and O(30), are both disordered across sites with *mm* symmetry, and in each case only the donor oxygen atom could be located with any reliability; from an inspection of the electron density maps, combined with a knowledge of the solvents used, the most likely identity of both the coordinated and included molecules was deemed to be dimethylformamide, $\text{Me}_2\text{N}-\text{C}(\text{H})=\text{O}$, $\text{C}_3\text{H}_7\text{NO}$ (40 electrons). The best approach to handling this very diffuse electron density was found to be the SQUEEZE routine of PLATON.² This suggested a total of 1679 electrons per unit cell, equivalent to approximately 105 electrons per asymmetric unit. Because SQUEEZE does not remove electron density that is within bonding distance of defined atoms, that for the carbonyl carbon atom of each coordinated solvent molecule would not be removed, meaning that only $\text{C}_2\text{H}_7\text{N}$ for each coordinated solvent molecule would contribute to the total electron density removed by SQUEEZE. Due to the symmetry, this would amount to 0.5($\text{C}_2\text{H}_7\text{N}$) per asymmetric unit, accounting for 13 electrons, leaving 92 electrons for the included solvent. 2.25 Dimethylformamide molecules corresponds to 90 electrons, so this was used as the solvent present; this amounts to 18 dimethylformamide molecules per Cu_4 unit. Subsequent

to SQUEEZE, the carbonyl carbon of the O(30)-based coordinated solvent molecule was located and added to the atom list.

As a result of the missing NH hydrogen atom, the only partial located coordinated solvent molecules, and the absent included solvent molecules, the atom list for the asymmetric unit is low by $0.125(\text{H}) + 0.25(\text{C}_3\text{H}_7\text{N}) + 0.25(\text{C}_2\text{H}_7\text{N}) + 2.25(\text{C}_3\text{H}_7\text{NO}) = \text{C}_8\text{H}_{19.375}\text{N}_{2.75}\text{O}_{2.25}$ (and that for the unit cell low by $\text{C}_{128}\text{H}_{310}\text{N}_{44}\text{O}_{36}$) compared to what is actually presumed to be present.

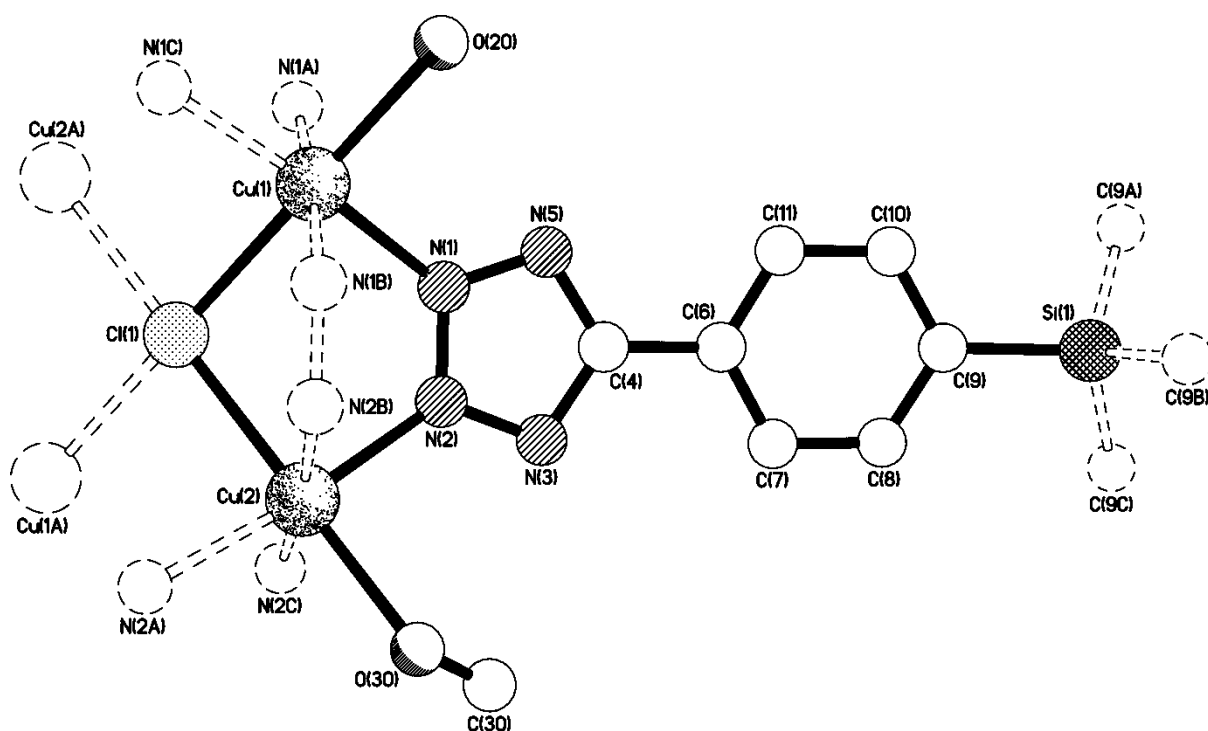


Figure S1. The crystal structure of IMP-16 showing the contents of the asymmetric unit.

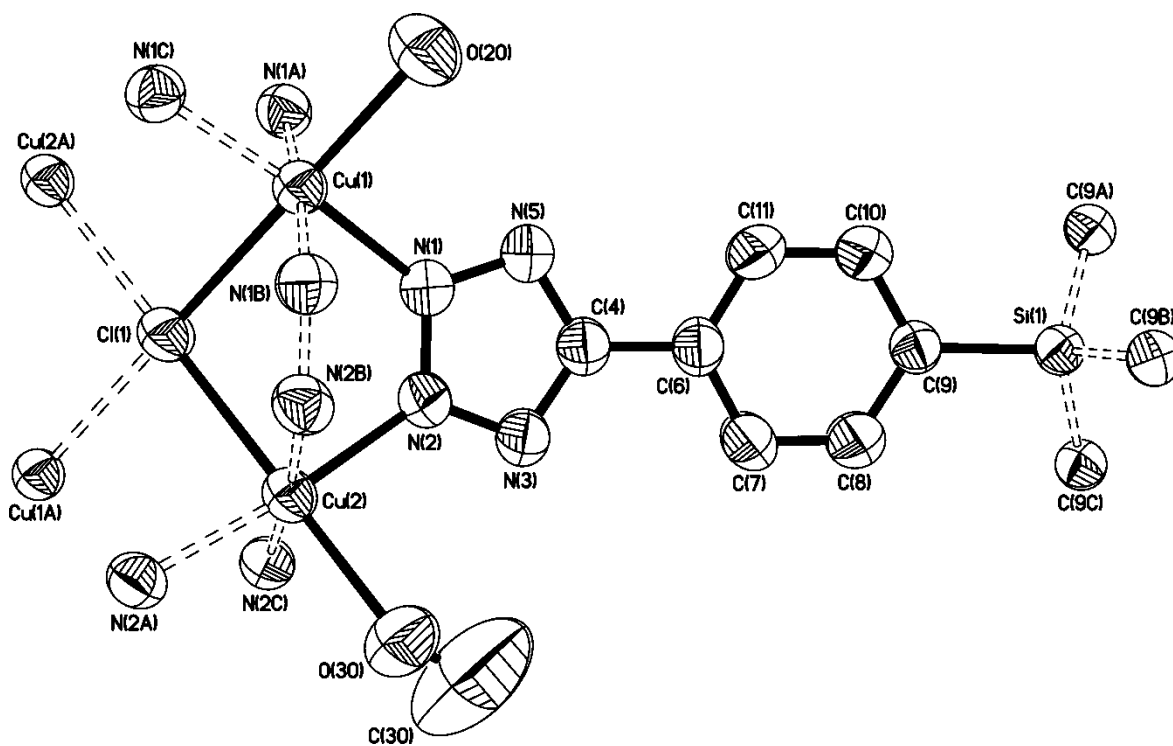


Figure S2. The crystal structure of **IMP-16** showing the contents of the asymmetric unit (50% probability ellipsoids).

Powder X-ray Diffraction Studies

Phase purity was confirmed using a Philips PW1700 series automated powder X-ray diffractometer with Cu-K α radiation and a graphite secondary crystal monochromator.

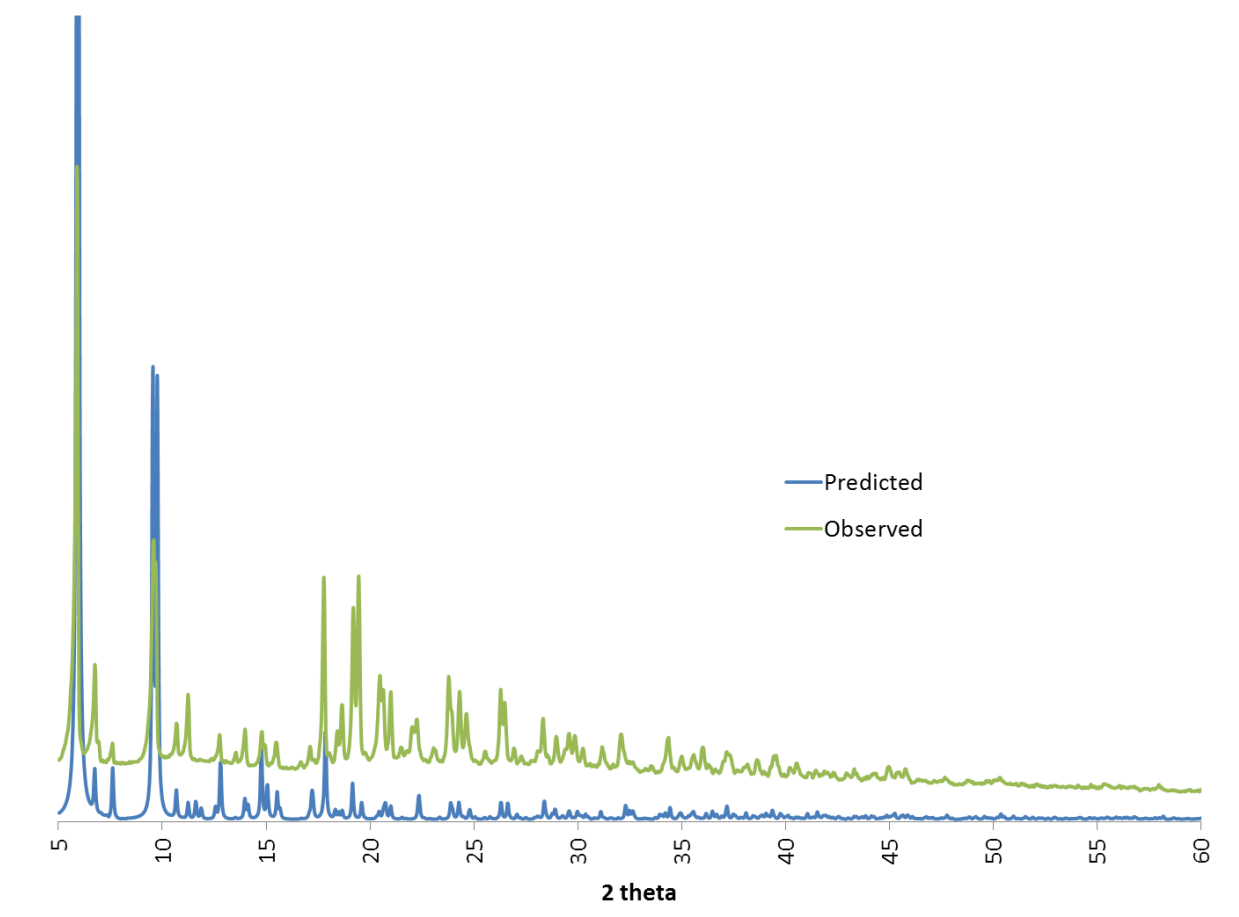


Figure S3. Powder X-ray diffraction (PXRD) patterns for **IMP-16** both calculated from the single-crystal data (Predicted) and measured experimentally on a fresh bulk sample of **IMP-16** (Observed).

Thermogravimetric Analysis of IMP16-Cu

Thermal Gravimetric Analysis (TGA) was carried out using a Perkin Elmer Pyris 1 machine, under a constant stream of dry nitrogen gas (flow rate 20 mL min⁻¹) over the temperature range of 30 to 650 °C and at a heating rate of 5 °C min⁻¹.

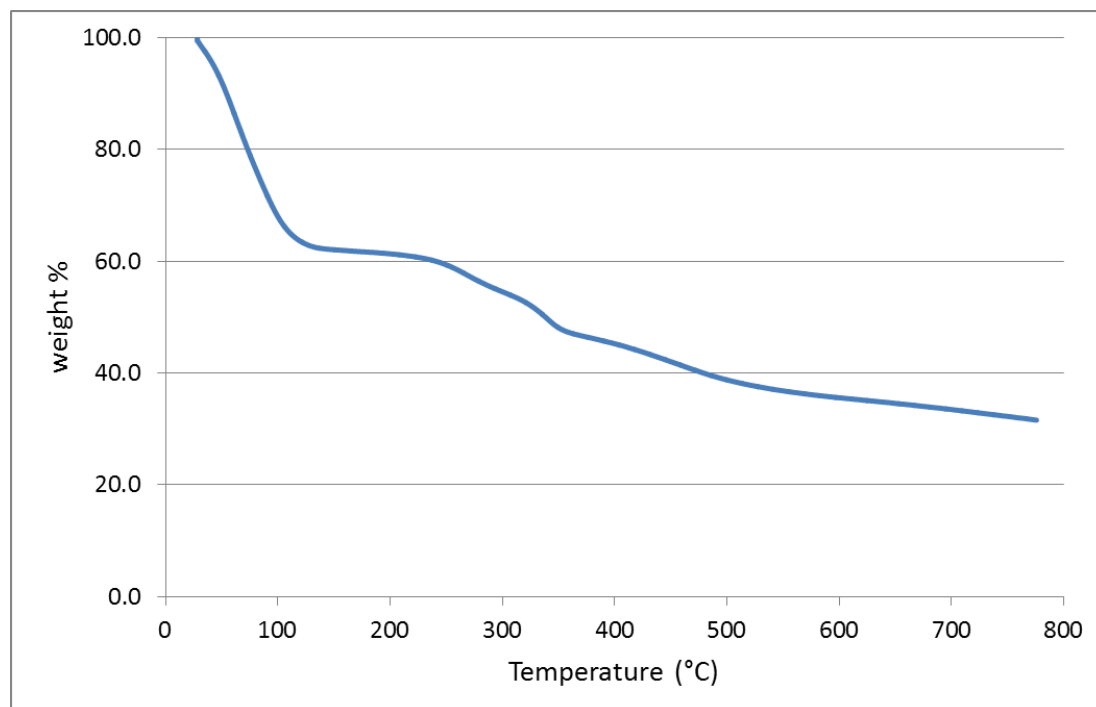


Figure S4 TGA trace for IMP-16Cu

References

1. F. Q. Liu and T. D. Tilley, *Inorg. Chem.*, 1997, **36**, 5090-5096.
2. A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13.