

Electronic Supplementary Information

An Organosilicon Hexacarboxylic Acid and its use in the Construction of a Novel Metal Organic Framework Isorecticular to MOF-5

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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. 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. Powder diffraction studies were carried out on a Philips PW1700 series automated powder X-ray diffractometer with Cu-K α radiation and a graphite secondary crystal monochromator.

Synthesis of 1,4-phenylenebis(tris(4-bromophenyl)silane)

A solution of *n*-BuLi (2.5 M, 14 ml, 35 mmol) in 20 ml Et₂O was slowly added to a solution of 1,4-dibromobenzene (8.3 g, 35 mmol) in 30 mL Et₂O at -78 °C. The resultant reaction mixture was allowed to stir for 1 hour at -78 °C before warming to 0 °C. 1,4-Bis(trisethoxysilyl)benzene (2 ml, 5.04 mmol) was then added dropwise and the reaction mixture stirred for a further 12 hours. The reaction was then quenched by addition of 10 ml H₂O and the organic layer was separated, washed with brine, dried over MgSO₄ and the volatiles removed *in vacuo*. Recrystallisation of the resultant solid from EtOAc gave pure 1,4-phenylenebis(tris(4-bromophenyl)silane). Yield = 1.75g (1.64 mmol, 32.5 %). M.p. = 129-133 °C. Anal. Calcd. for C₄₂H₂₈Br₆Si: C,

47.22; H, 2.64. Found: C, 47.36; H, 2.63 %. ^1H NMR (CDCl_3): δ = 7.55 (d, 12 H, $\text{SiC}_6\text{H}_4\text{Br}$), 7.53 (s, 4 H, $\text{SiC}_6\text{H}_4\text{Si}$), 7.38 (d, 12 H, $\text{SiC}_6\text{H}_4\text{Br}$). ^{13}C NMR (CDCl_3): δ = 137.7, 135.7, 135.6, 131.6), 131.4, 125.4. IR (ATR): $\nu(\text{cm}^{-1})$ = 1569, 1478, 1376, 1129, 1065, 1008, 805, 729. M/S (EI+); m/z = 1068 (M^+), 990 (M^+-Br), 911 (M^+-2Br), 833 (M^+-3Br), 755 (M^+-4Br).

Synthesis of 1,4-phenylenebis(tris(4-carboxyphenyl)silane) (L-H₆)

A solution of 1,4-phenylenebis(tris(4-bromophenyl)silane) (1.5 g, 1.4 mmol) in 30 ml THF was added drop-wise to a solution of *n*-BuLi (2.5 M, 3.4 ml, 8.4 mmol) at -78 °C and stirred at this temperature for 60 minutes. CO_2 was then bubbled through the cooled solution for 2 h, before warming to room temperature and stirring for an additional 12 h. The crude product was then precipitated by addition of 2 mL 1 M HCl and filtered. Dissolution in 1 M NaOH followed by precipitation with 2.5 M HCl and washing with H_2O and CHCl_3 gave the pure product L-H₆ in 97% yield (1.17 g). M.p. > 300°C. Anal. Calcd. for $\text{C}_{44}\text{H}_{34}\text{O}_{12}\text{Si}$: C, 67.11; H, 3.99. Found: C, 66.87; H, 3.85. ^1H NMR ($(\text{CD}_3)_2\text{CO}$): δ = 8.01 (d, 12 H, J = 7.9 Hz, $\text{SiC}_6\text{H}_4\text{CO}_2\text{H}$), 7.63 (d, 12 H, J = 7.9 Hz, $\text{SiC}_6\text{H}_4\text{CO}_2\text{H}$), 7.62 (s, 4 H, $\text{SiC}_6\text{H}_4\text{Si}$). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$): δ = 167.6, 138.2, 136.6, 136.1, 132.8, 129.3. IR (ATR): $\nu(\text{cm}^{-1})$ = 3026, 2659, 2530, 1687, 1600, 1555, 1498, 1390, 1279, 1184, 1129, 1089, 1019, 848, 758, 698 cm^{-1} . M/S (ESI-): m/z = 857 (M^-).

Synthesis of [Zn₄O(L)] (IMP-15)

A mixture of Zn(NO₃)₂·6H₂O (50 mg, 0.18 mmol) and L-H₆ (50 mg, 0.06 mmol) in 2 ml of DMA and 2 ml of H₂O was heated to 100 °C in a screw-top vial for 1 day. The mixture was allowed to cool to room temperature and the resultant colourless block crystals filtered and washed with DMA and water. Yield = 59.8 mg (49 % based on L-H₆). Anal. Calcd. for C₄₈H₃₄O₁₃Si₂Zn₄·(C₄H₉NO)_{2.6}(H₂O)_{5.7} %; C, 48.32; H, 4.36; N, 2.51, Found; C, 48.31; H, 4.35; N, 2.52. Note that washing and drying procedures for elemental analysis and single crystal X-ray diffraction differed so that there are minor differences in solvation.

X-Ray Crystallography Supporting Information

Despite a ca. 93 hour data collection to a resolution of only 0.84 Å using Cu-K α radiation, the data set for IMP-15 was somewhat weak with a mean I/σ of only ca. 5.6. Additionally, the resulting structure was found to be highly disordered; in fact, only the silicon Si(1) and the central oxygen O(20) are ordered (Fig. S1). The central oxygen sits on a -3 position, Zn(1) on a 3 position, and Zn(2) in a general position. However, the operation of the -3 symmetry, creates a Zn₈O cube out of the two zinc positions, and this only makes chemical sense if viewed as two 50% occupancy C₁-related interpenetrating Zn₄O tetrahedra (Fig. S3).

Three orientations of ca. 41, 35 and 24% occupancy were identified for the C(1) to O(9) benzoic acid unit. Their geometries were optimised (including treating the aryl rings as idealised hexagons with a side length of 1.39 Å), and the thermal parameters of adjacent atoms were restrained to be similar. The central aryl unit of the 1,4-phenylenebis(tris(4-carboxyphenyl)silane) ligand was found to be disordered across a -3 position. Two unique complete orientations were identified of ca. 9 and 7% occupancy were identified for the C(11) to C(16) aryl ring. The two rings were treated as idealised hexagons with a side length of 1.39 Å, and the thermal parameters of adjacent atoms were restrained to be similar. Only the Zn(1), Zn(2), Si(1) and O(20) atoms were refined anisotropically, the remainder were refined isotropically.

The included solvent was found to be highly disordered, and the best approach to handling this electron density was found to be the SQUEEZE routine of PLATON.¹ This suggested a total of 2180 electrons per unit cell, equivalent to 545 electrons per

LZn₄O unit. The crystal was grown from dimethylacetamide [Me₂NC(=O)Me, C₄H₉NO, 48 electrons]. 11.4 dimethylacetamide molecules equates to 547.2 electrons, and this was rounded down to 11 molecules per LOZn₄ unit (which equates to six asymmetric units) for simplicity. The atom list for six asymmetric units is thus low by C₄₄H₉₉N₁₁O₁₁ (and that for the unit cell by C₁₇₆H₃₉₆N₄₄O₄₄) compared to what is actually presumed to be present.

Despite all these issues, the fundamental nature of the network present is clear.

- 1 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.

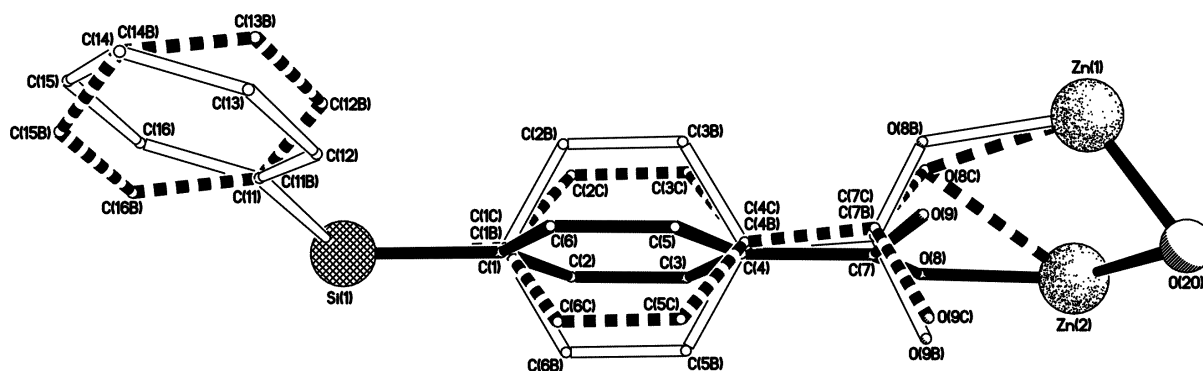


Figure S1 The molecular structure of the asymmetric unit in the structure of IMP-15 showing the disorder of the benzoate [major orientation, dark bonds, *ca.* 41% occupancy; intermediate orientation, open bonds, *ca.* 35% occupancy; minor orientation, dark dashed bonds, *ca.* 24% occupancy] and aryl [major orientation, open bonds, *ca.* 9% occupancy; minor orientation, dark dashed bonds, *ca.* 7% occupancy] groups.

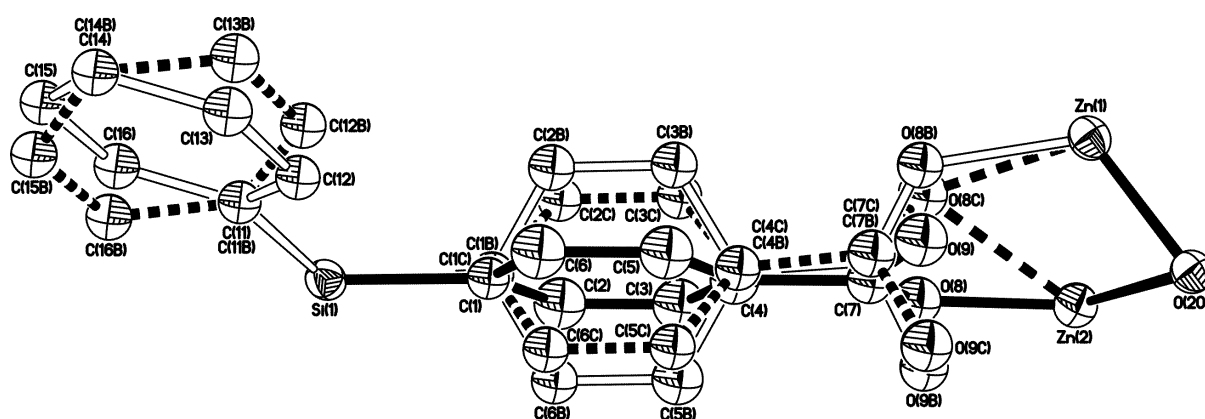


Figure S2 The molecular structure of the asymmetric unit in the structure of IMP-15
(10% probability ellipsoids).

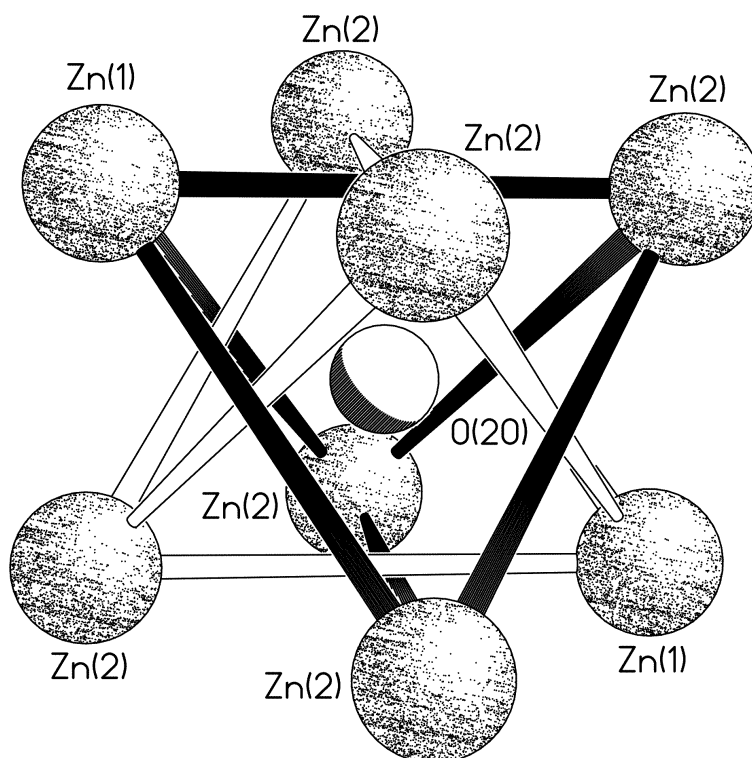


Figure S3 The central Zn_4O unit in the molecular structure of IMP-15 showing the disorder at the central oxygen atom consisting of two 50% occupancy C_1 -related interpenetrating Zn_4O tetrahedra.

Thermogravimetric Analysis of IMP-15

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 600 °C and at a heating rate of 5 °C min⁻¹.

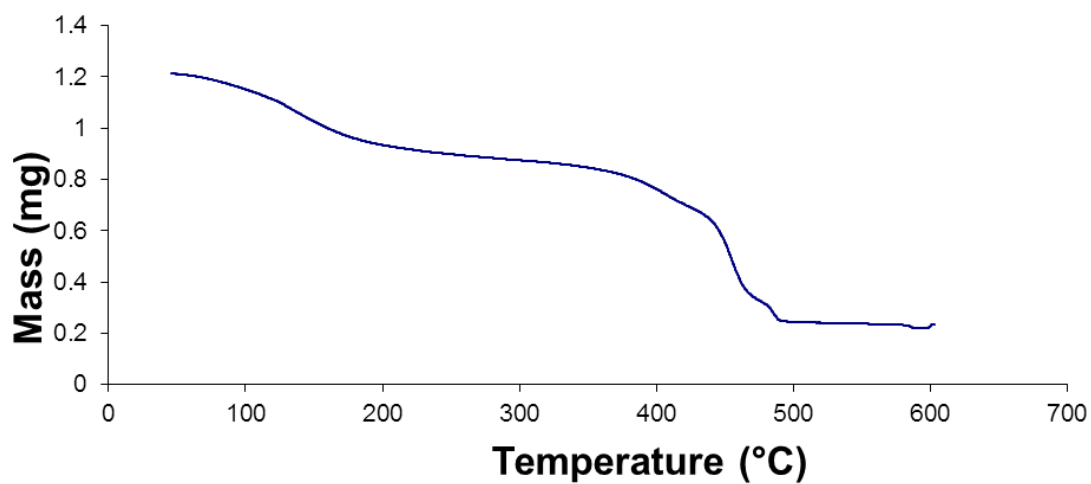


Figure S4 TGA trace for IMP-15