Stable metal–organic frameworks with low water affinity built from methyl-siloxane linkers†

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A tetracarboxylic acid with a methyl-substituted siloxane core (L-H₄) has been prepared and applied in the construction of water stable MOFs with low water affinity. L-H₄ itself crystallizes as an interpenetrated 3D hydrogen-bonded network. Reaction of L-H₄ with Zr⁴⁺/Hf⁴⁺ gave IMP-32-Zr/Hf – both 3D MOFs of scu topology.

Metal–organic frameworks (MOFs) have been identified as having high potential for environmental clean-up applications including CO₂ capture, hydrocarbon separations, oil spill clean-up, and water purification.¹,² This is due to their high porosity and tuneable pore shape/size and functionality.³ However, such clean-up operations require the deployment of MOFs in wet or humid conditions and consequently the hydrothermal stability and water affinity of these materials is often a limiting factor for their commercial use.⁴

Research on the development of hydrophobic MOF materials has mainly focussed on particle coating and linker design strategies.⁵ The former involves coating the pristine MOF particles with hydrophobic polymers (such as polydimethylsiloxane) but this requires post-synthetic processing and usually comes at the expense of reduced pore volumes.⁶–⁹ Efforts towards the design of MOF linkers with hydrophobic functionality have focussed on appending hydrophobic groups (e.g. CH₃, CF₃, or F) to the linker backbone. Perfluorination has proven to be particularly effective in imparting MOFs with water-repelling properties.¹⁰ However, the synthetic difficulty of fluorination, reduced thermal stability of perfluorinated frameworks,¹¹–¹³ and growing concerns over the negative health impact of polyfluoroalkyl substances¹⁴ all stimulate research into alternative methods of linker hydrophobization.

Given our experience in the development of siloxane-based linkers for MOF construction,¹⁵–¹⁷ we set out to develop a novel silicone-derived linker for the direct construction of low water affinity MOFs. Silicones are well known for their hydrophobic properties,¹⁸ and studies of post-synthetic incorporation of silicone units in MOF materials [either by particle coating⁶–⁸ or functionalization of secondary building units (SBUs)]¹⁹ suggests that such an approach may successfully lead to low water affinity materials. Siloxane-based linkers compatible with the zirconium oxide family of SBUs were specifically targeted due to the well-established thermal, chemical, and water stabilities of these units.²⁰ We now report upon the preparation of the novel tetracarboxylic acid linker 1,3-dimethyltetrakis(p-carboxyphenyl)disiloxane (L-H₄), its application in the preparation of isotoxic structural Zr- and Hf-based frameworks, and studies on the hydrophobicity of these new materials.

The synthesis of L-H₄ is outlined in Scheme 1, and is an adaptation of our previously reported protocol for disiloxane-based linker synthesis (see ESI,† for full experimental details).¹⁷ Methylbis(p-bromophenyl)silane was prepared from commercially available dichloromethylsilane.

We firstly studied the H-bonded superstructure of the linker itself with crystals of L-H₄ suitable for X-ray analysis grown via slow evaporation from a mixture of AcOH and MeOH. Extended supramolecular structures built from polycarboxylic acids have recently gained considerable attention since several such materials exhibit permanent porosity and have shown potential for gas separations.¹⁷–²³ X-ray analysis reveals that L-H₄ crystallizes in the triclinic space group P1 (no. 2). Free rotation about the Si–O bonds and the flexible Si–O–Si bond angle allows L-H₄ to adjust the orientation of its carboxylic acid groups in order to optimise dimeric hydrogen bonding with neighbouring molecules to form an extended structure. The asymmetric unit contains one complete molecule of L-H₄ with a bent siloxane linkage [≤Si–O–Si = 148.2(2)°] and half a molecule of L-H₄ with...
the central siloxane oxygen sitting on an inversion centre thus giving rise to a linear Si–O–Si linkage \([ \angle \text{Si–O–Si} = 180.00(7) \degree ]\).

Both crystallographically independent molecules are 4-connected supramolecular tectons although with differing geometries. The methyl groups of the linear siloxane molecule are in the antiperiplanar conformation and consequently the coordinating branches in the molecule are disposed with roughly square planar geometry. The methyl groups in the bent siloxane are in the gauche conformation with a torsion angle \((\text{C–Si} \cdots \text{Si–C})\) of 35.3(2)˚ resulting in the four p-carboxyphenyl arms extending in a highly distorted tetrahedral arrangement. These linear and bent L-H₄ molecules are linked via dimeric hydrogen-bonding interactions to afford a 3D hydrogen-bonded organic framework (HOF) of mog topology (see Fig. 1).

The hydrogen bonding O–O distances all lie in the range 2.58–2.64 Å, typical of the strong hydrogen bonds observed in such carboxylic acid-based HOF systems. Efficient packing in the structure is achieved by mutual interpenetration of three additional mog nets and consequently the overall four-fold interpenetrated framework is non-porous with a solvent accessible void of only 2.1% as calculated by the SOLV routine in PLATON.²⁴

We then turned our attention to the treatment of L-H₄ with Zr⁶⁰ and Hf⁶⁰ precursors for the generation of new MOF materials. Growing high quality crystals of Zr-MOFs suitable for single crystal X-ray diffraction (scXRD) studies can be particularly challenging, with Zr-MOFs typically being obtained as polycrystalline solids.²⁵ It was therefore necessary to employ formic acid as a modulator in order to prepare suitably large single crystals. Thus, treatment of L-H₄ with ZrOCl₂⋅8H₂O or HfCl₄ in a 2:1 mixture of DMF and formic acid at 100 °C for 48 h both afforded colourless needles. These crystals were found by scXRD analysis to comprise isostructural MOFs of the general formula \([\text{M}_2\text{O}_4\{\text{L}\}(_4\text{DMF})_4]_x\text{DMF}\) [IMP-32-Zr (M = Zr, x = 3) or IMP-32-Hf (M = Hf, x = 2)] and phase purity of the bulk samples was verified by powder X-ray diffraction (Fig. S4, ESI†).²⁷

In both frameworks, L-H₄ has become fully deprotonated under the solvothermal conditions employed with each of its acid groups binding to a separate metal node. The siloxane linkage is linear with the central siloxane oxygen sitting on a centre of symmetry. The Si–CH₃ groups are in the antiperiplanar conformation and consequently the coordinating branches of L are disposed in a manner such that the acid groups are at the corners of a rectangle and thus L can be simplified to a square planar 4-c node. The metallic nodes in IMP-32-Zr comprise the known 8-connected Zr₆O₈ cluster as seen in a number of reported MOFs.²⁰ The zirconium atoms sit at the corners of an octahedron where the axial edges are occupied by bridging dimonodentate carboxylate groups from eight different L molecules. The coordination sphere of each zirconium atom which sits in the equatorial plane is completed by the additional coordination of two DMF molecules. These 8-connected Zr SBUs are crosslinked by L to form a 3D MOF with 4,8-connected scu topology, infrequently encountered in Zr-MOFs (see Fig. 2).²⁸,²⁹ Another topological description of IMP-32 recognizes the 3-connected branch points centred on the terminal silicon vertices of L. This instead gives rise to the extremely rare scu-derived 3,8-connected tty topology.³⁰,³¹

The IMP-32-Zr framework has solvent-filled channels in all directions with the largest window size being approximately \(10 \times 9 \text{ Å}^2\) (centroid to centroid distances) along the crystallographic a axis. TGA analysis under N₂ of IMP-32 MOFs both showed solvent loss occurring between 30–270 °C. The framework appears to remain stable until a temperature of approximately 500 °C when the onset of decomposition occurs suggesting high thermal stability (see Fig. S5, ESI†). After theoretical removal of both the coordinated and non-coordinated solvent, the PLATON²⁴ estimated solvent-accessible void volume for IMP-32-Zr was found to be 9074.1 Å³ or 63% of the unit cell volume. The comparable values found for IMP-32-Hf are 9023.2 Å³.
and 63%. The two MOF samples were then subjected to a two-step activation procedure.\textsuperscript{32} The as-synthesized material was first soaked in DCM to exchange the DMF molecules included in the pore space. This solvent-exchanged material was subsequently soaked in the lower surface tension solvent n-hexane prior to evacuation at room temperature. PXRD measurements on the activated IMP-32 sample showed retention of crystallinity and N\textsubscript{2} sorption studies on IMP-32-Zr show a reversible Type-I adsorption isotherm at 77 K with a calculated BET surface area of 1135 m\textsuperscript{2} g\textsuperscript{-1} while IMP-32-Hf was found to possess a BET surface area of 1001 m\textsuperscript{2} g\textsuperscript{-1} (see Fig. S5 and S6, ESI,\textsuperscript{†} respectively).

The robustness of Zr-MOFs is now well established,\textsuperscript{30} but there have been comparatively few investigations on water adsorption in these systems with preliminary studies suggesting that many Zr-MOFs take up significant amounts of water and so are prone to becoming saturated.\textsuperscript{31} Contrastingly, studies on coordination polymers containing tetramethyldisiloxane groups have revealed hydrophobic behaviour.\textsuperscript{34,35} Hence, the incorporation of Si–CH\textsubscript{3} groups in L-H\textsubscript{4} was designed to impart an inherent hydrophobicity in IMP-32 MOFs without the need for hydrophobic coating agents. Dynamic vapour sorption (DVS) studies on IMP-32 MOFs confirmed their low affinity towards water with both MOFs showing limited (<4 wt\%), see Fig. 3) water uptake at relative humidity levels below 20% (relevant for separation of industrial gas streams). Even at 95% relative humidity, the IMP-32 MOFs show relatively low (<15 wt\%) water uptake placing them among the lowest reported H\textsubscript{2}O-adsorbing MOFs when compared to materials of similar surface areas.\textsuperscript{36,37}

The aqueous stability of MOFs is crucial to their applications in gas separations in humid environments, for example in post-combustion carbon capture and storage systems. The aqueous stability of IMP-32-Zr was thus further examined by immersing samples of the MOF in water or 1 M HCl for 24 hours. In both cases no change in crystallinity was observed as evidenced by PXRD (see Fig. S8, ESI\textsuperscript{†}). However, IMP-32-Zr was shown to degrade in the presence of 1 M NaOH forming an amorphous solid. This is explained by the fact that the L-H\textsubscript{4} building block is readily cleaved by base to afford bis(p-carboxyphenyl)methylsilanol (see ESI,\textsuperscript{†} for further details). Efforts to crystallize this silanol led to self-condensation reforming L-H\textsubscript{4}. Studies on the coordination behaviour and application of this novel silanol are ongoing.

The CO\textsubscript{2} uptake capacity of the IMP-32 MOFs at 25 °C between 0–1 bar was next investigated. These studies reveal a reversible Type-I CO\textsubscript{2} adsorption isotherm (see Fig. 4) with an uptake of 5.9 wt\% in IMP-32-Zr and 5.2 wt\% in IMP-32-Hf. Thus IMP-32 MOFs show promising CO\textsubscript{2} capture performance when compared to other known low water affinity frameworks.\textsuperscript{38}

In summary, the novel siloxane-based tetracarboxylic acid L-H\textsubscript{4} has been prepared and shown to self-assemble into a quadruply interpenetrated 3D supramolecular network. Treatment of L-H\textsubscript{4} with Zr\textsuperscript{IV} and Hf\textsuperscript{IV} precursors gave IMP-32-Zr/Hf which are the first Zr/Hf-MOFs incorporating siloxane-based linkers. These linkers are demonstrated to impart the resultant MOFs with very low water affinity without compromising their
porosity. In addition, the IMP-32 series represents an important addition to the rare list of MOFs with the ssu-derived ttt topology highlighting the versatility of organosilicon compounds in topology-guided synthesis of 3D MOF structures. Encouraged by the low water affinity of IMP-32 MOFs we are interested in further investigating the effectiveness of siloxane-based MOFs in the capture of a wide range of pollutants from ambient air and aqueous solution.

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Conflicts of interest
There are no conflicts to declare.

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