



# 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-H<sub>4</sub>) has been prepared and applied in the construction of water stable MOFs with low water affinity. L-H<sub>4</sub> itself crystallizes as an interpenetrated 3D hydrogen-bonded network. Reaction of L-H<sub>4</sub> with Zr<sup>IV</sup>/Hf<sup>IV</sup> 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 CO<sub>2</sub> capture, hydrocarbon separations, oil spill clean-up, and water purification.<sup>1,2</sup> This is due to their high porosity and tuneable pore shape/size and functionality.<sup>3</sup> 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.<sup>4</sup>

Research on the development of hydrophobic MOF materials has mainly focussed on particle coating and linker design strategies.<sup>5</sup> 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.<sup>6–9</sup> Efforts towards the design of MOF linkers with hydrophobic functionality have focussed on appending hydrophobic groups (*e.g.* CH<sub>3</sub>, CF<sub>3</sub>, or F) to the linker backbone. Perfluorination has proven to be particularly effective in imparting MOFs with water-repelling properties.<sup>10</sup> However, the synthetic difficulty of fluorination, reduced thermal stability of perfluorinated frameworks,<sup>11–13</sup> and

growing concerns over the negative health impact of polyfluoroalkyl substances<sup>14</sup> all stimulate research into alternative methods of linker hydrophobization.

Given our experience in the development of siloxane-based linkers for MOF construction,<sup>15–17</sup> 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,<sup>18</sup> and studies of post-synthetic incorporation of silicone units in MOF materials [either by particle coating<sup>6–8</sup> or functionalization of secondary building units (SBUs)<sup>19</sup>] 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.<sup>20</sup> We now report upon the preparation of the novel tetracarboxylic acid linker 1,3-dimethyltetrakis(*p*-carboxyphenyl)disiloxane (L-H<sub>4</sub>), its application in the preparation of isostructural Zr- and Hf-based frameworks, and studies on the hydrophobicity of these new materials.

The synthesis of L-H<sub>4</sub> 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).<sup>17</sup> 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-H<sub>4</sub> 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.<sup>21–23</sup> X-ray analysis reveals that L-H<sub>4</sub> crystallizes in the triclinic space group *P* $\bar{1}$  (no. 2). Free rotation about the Si–O bonds and the flexible Si–O–Si bond angle allows L-H<sub>4</sub> 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-H<sub>4</sub> with a bent siloxane linkage [ $\angle$  Si–O–Si = 148.2(2)°] and half a molecule of L-H<sub>4</sub> with

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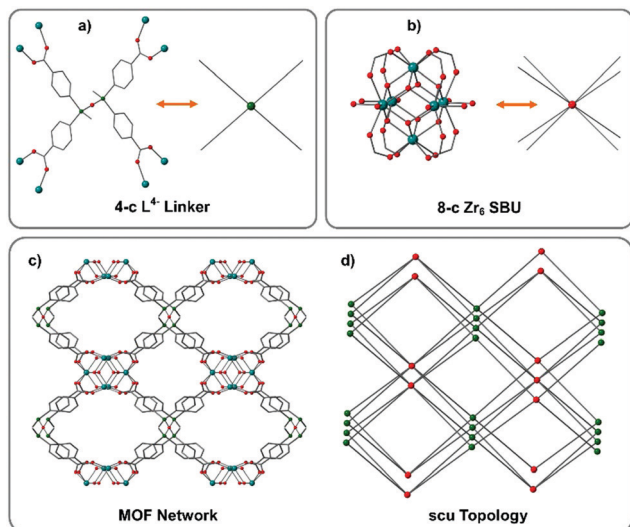
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† Electronic supplementary information (ESI) available: Full synthetic protocol and characterisation data. PXRD, TGA plots, additional topological analysis, and N<sub>2</sub> sorption isotherms for IMP-32 MOFs. CCDC 1950125–1950127. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc01186j





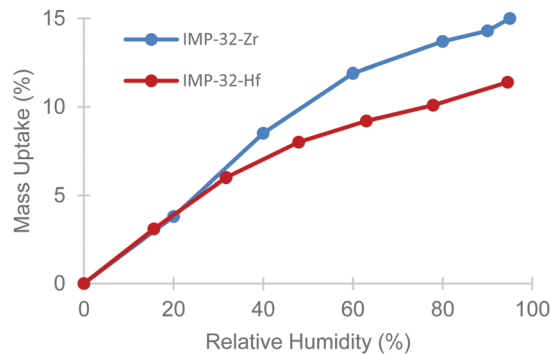


**Fig. 2** (a) Ligand environment of **L** in **IMP-32-Zr**. (b) Structure of hexanuclear  $Zr_6O_8$  SBUs in **IMP-32-Zr**. Note only the coordinating O atoms of ligated DMF molecules are shown for clarity. (c) Portion of the extended structure of **IMP-32-Zr** showing pores along the crystallographic *a* axis. Solvent molecules and hydrogen atoms omitted for clarity. Colour scheme: Zr, turquoise; O, red; C, grey; Si, green. (d) Schematic representation of the **scu** network showing the 8-connected  $Zr_6O_8$  SBU nodes (red) and the 4-connected silicon-based nodes (green).

and 63%. The two MOF samples were then subjected to a two-step activation procedure.<sup>32</sup> 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  $N_2$  sorption studies on **IMP-32-Zr** show a reversible Type-I adsorption isotherm at 77 K with a calculated BET surface area of  $1135 \text{ m}^2 \text{ g}^{-1}$  while **IMP-32-Hf** was found to possess a BET surface area of  $1001 \text{ m}^2 \text{ g}^{-1}$  (see Fig. S5 and S6, ESI,† respectively).

The robustness of Zr-MOFs is now well established,<sup>20</sup> 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.<sup>33</sup> Contrastingly, studies on coordination polymers containing tetramethyldisiloxane groups have revealed hydrophobic behaviour.<sup>34,35</sup> Hence, the incorporation of Si- $CH_3$  groups in **L-H<sub>4</sub>** 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 ( $\leq 15 \text{ wt}\%$ ) water uptake placing them among the lowest reported  $H_2O$ -adsorbing MOFs when compared to materials of similar surface areas.<sup>36,37</sup>

The aqueous stability of MOFs is crucial to their applications in gas separations in humid environments, for example in

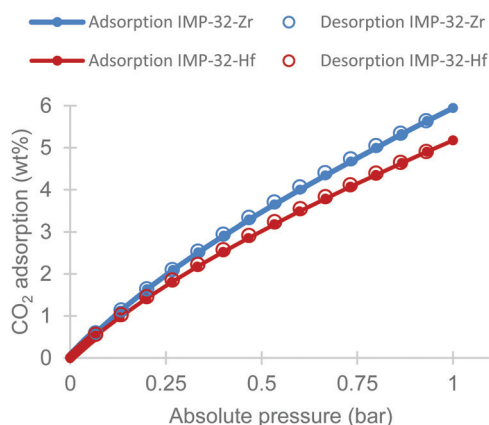


**Fig. 3** Water vapour adsorption isotherms for **IMP-32** MOFs at 23 °C.

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†). 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<sub>4</sub>** building block is readily cleaved by base to afford bis(*p*-carboxyphenyl)methylsilanol (see ESI,† for further details). Efforts to crystallize this silanol led to self-condensation re-forming **L-H<sub>4</sub>**. Studies on the coordination behaviour and application of this novel silanol are ongoing.

The  $CO_2$  uptake capacity of the **IMP-32** MOFs at 25 °C between 0–1 bar was next investigated. These studies reveal a reversible Type-I  $CO_2$  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  $CO_2$  capture performance when compared to other known low water affinity frameworks.<sup>38</sup>

In summary, the novel siloxane-based tetracarboxylic acid **L-H<sub>4</sub>** has been prepared and shown to self-assemble into a quadruply interpenetrated 3D supramolecular network. Treatment of **L-H<sub>4</sub>** with  $Zr^{IV}$  and  $Hf^{IV}$  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



**Fig. 4**  $CO_2$  sorption isotherms for **IMP-32** MOFs at 25 °C.



porosity. In addition, the **IMP-32** series represents an important addition to the rare list of MOFs with the **scu**-derived **tty** 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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