Siloxane-Based Linkers in the Construction of Porous 3D MOFs

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The silicon-oxygen bond is prevalent in well-known porous materials including zeolites, organosilicas, and POSS hybrids, however, MOFs incorporating Si-O functionality are rare. This is despite the advantageous properties of this group including low toxicity, low chemical reactivity and thermal stability. In this work, three highly-connected organosilicon polycarboxylic acids (Figure 1) have been prepared and applied in the construction of MOFs. **L1**-H_6 itself crystallizes as an unusual interpenetrated 3D hydrogen-bonded framework. Reaction of **L1**-H_6 with Zn(II) gave a MOF with **fsy** topology (**IMP-18)**, the first reported[1] example of a 3D-connected MOF incorporating Si-O-Si functionality (Figure 1). Cleavage of **L1**-H_6 gives a silanol-based triacid **L2**-H_3 which is shown to give a coordination polymer (**IMP-19**) with Zn(II), consisting of 2D layers which assemble by hydrogen-bonding to afford a 3D supramolecular structure with **flu** topology. The tetracarboxylic acid **L3**-H_4 crystallizes through hydrogen-bonding to give a quadruply interpentrated structure comprising 4 identical **mog** nets. Reaction of **L3**-H_4 with Zr(IV) afforded **IMP-22**, a 3D MOF built from 8-connected Zr-based nodes cross-linked by **L3** to afford the first example of a porous MOF with the **scu**-derived **tty** topology. The structures and properties of these MOFs will be presented.

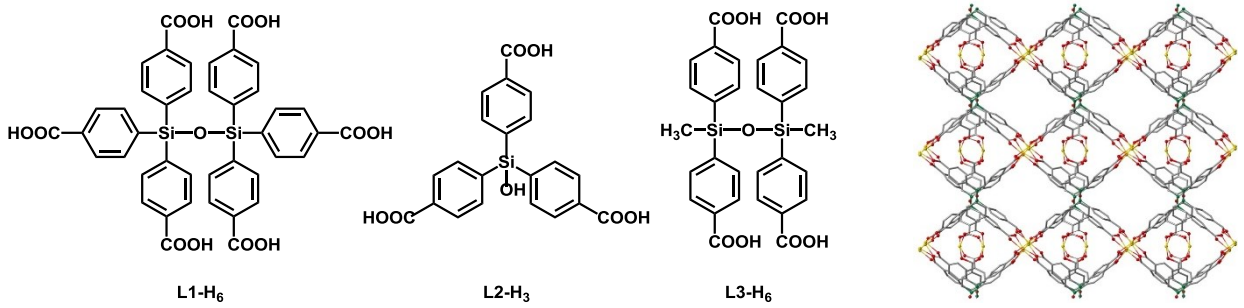

Figure 1. (Left) Carboxylic acid linkers used in the preparation of MOFs. (Right) Portion of the extended structure of **IMP-18** viewed along 010 direction.

[1] L. C. Delmas, P. N. Horton, A. J. P. White, S. J. Coles, P. D. Lickiss and R. P. Davies, Chem. Commun., 2017, 53, 12524-12527.