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## COMMUNICATION

## Design and Synthesis of an Innovative Octacarboxy-Silsesquioxane Building Block

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**An octacarboxy-silsesquioxane was designed and synthesised through a multiple-step regioselective reaction. This novel hybrid inorganic-organic compound presents highly attractive features for application as building block, as it has a robust, rigid structure and a high number of carboxylic coordination sites organised in cubic symmetry.**

The self-assembly of well-defined building blocks into crystalline structures provides a powerful and versatile route for generating novel materials with desirable features in terms of porosity and functionality.<sup>1</sup> A renowned class of materials obtained through this approach is represented by metal-organic frameworks (MOFs), which consist of metal cation nodes connected through rigid organic linkers.<sup>2,3</sup> These crystalline materials can display two- or three-dimensional structures and reach extremely high specific surface areas. Many MOFs have been reported in recent years and their potential applications in areas ranging from gas storage and separation to chemical sensing, drug delivery and catalysis have been actively investigated.<sup>4-8</sup> In general, the structure of new MOFs stems from the features of the organic ligands employed as linkers. A widely studied class of linkers consists of molecules containing carboxyl groups as binding sites, because these groups are able to generate strong bonds with the metal centres, thus producing materials with relatively high stability. Typically, these organic linkers are planar molecules with either two or three symmetrically equivalent terminal carboxyl groups (*e.g.* terephthalic acid or 1,3,5-benzenetricarboxylic acid). Linkers with higher number of coordination sites and with a three-dimensional structure have also been developed,<sup>1</sup> but the  $sp^2$  and  $sp^3$  configuration of carbon atoms and the requirement of

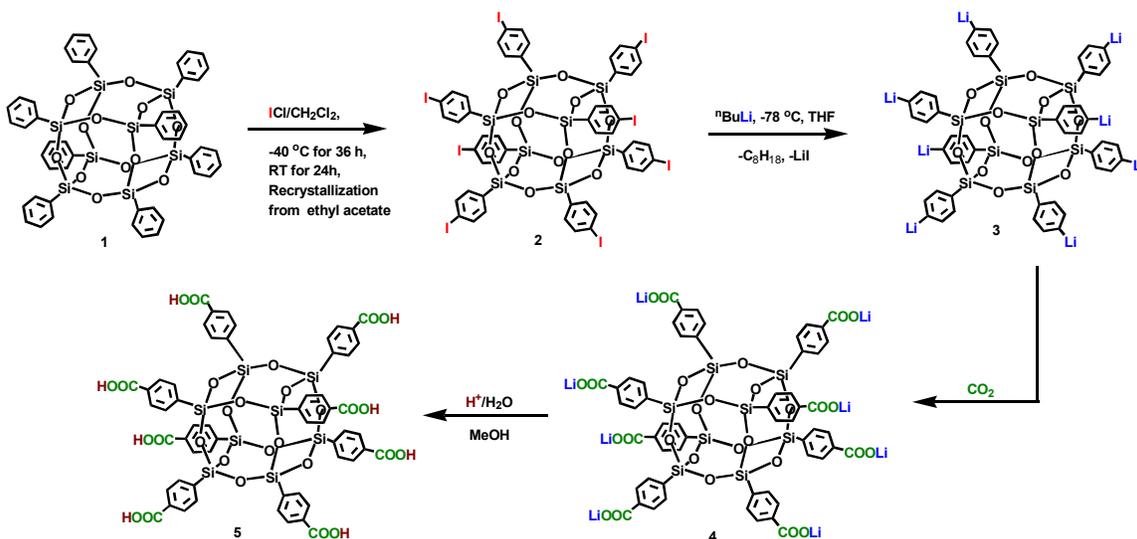
structural rigidity restricted so far the spatial organisation of organic linkers to planar or tetrahedral geometry.

Herein, we present the design and synthesis of a new hybrid inorganic-organic building block characterised by eight carboxyl groups organised around a rigid core with cubic symmetry (compound **5** in Scheme 1). This octacarboxy-silsesquioxane displays very attractive features as a building block for the fabrication of new crystalline materials as it is characterised by a rigid, well-defined structure that will maintain its directionality in the self-assembly process, and by eight symmetrically equivalent carboxyl groups that can bind to metal centers to build a periodic three-dimensional structure.

Silsesquioxanes are a family of inorganic-organic hybrid compounds finding applications ranging from catalysis to materials science,<sup>9-12</sup> whose potential as building blocks for crystalline materials is still unexplored. In our innovative design, we conceived a silsesquioxane compound in which the Si-O core grants the rigidity and the cubic symmetry of the building block and the phenyl groups provide rigid spacers that support the divergent directionality of the carboxyl groups. In order to produce a building block having the desired symmetry of the binding sites, it is essential that the carboxyl groups are all in *para*-position on the aromatic ring. For this purpose, the octa(*para*-carboxyphenyl)-silsesquioxane **5** [(HO<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-SiO<sub>1.5</sub>)<sub>8</sub>, MW = 1385.60 g/mol] was prepared via a multistep synthesis involving the regioselective modification of all the phenyl groups of the completely condensed phenyl-silsesquioxane **1** (Scheme 1). First, the commercially available compound **1** was subjected to iodination with ICl at -40 °C,<sup>13,14</sup> leading to a mixture of octaiodophenyl-silsesquioxane (**I<sub>8</sub>**, ~90%) and nonaiodinated octaphenyl-silsesquioxane (**I<sub>0</sub>**, ~10%), from which the octaiodophenyl-silsesquioxane was separated by dissolution in ethyl acetate. The iodination reaction is highly regioselective towards substitution in the *para*-position of the aromatic ring,<sup>13</sup> and octa(*para*-iodophenyl)-silsesquioxane **2** could be obtained in 30-40% yield by slow recrystallisation from the ethyl acetate solution, as indicated by <sup>29</sup>Si, <sup>13</sup>C and <sup>1</sup>H NMR analysis of the product (Fig. 1.a-c).<sup>13</sup> Elemental analysis by SEM-EDX is fully in agreement with the formation of compound **2** (Fig. S1 in the ESI). Although all the characterisation

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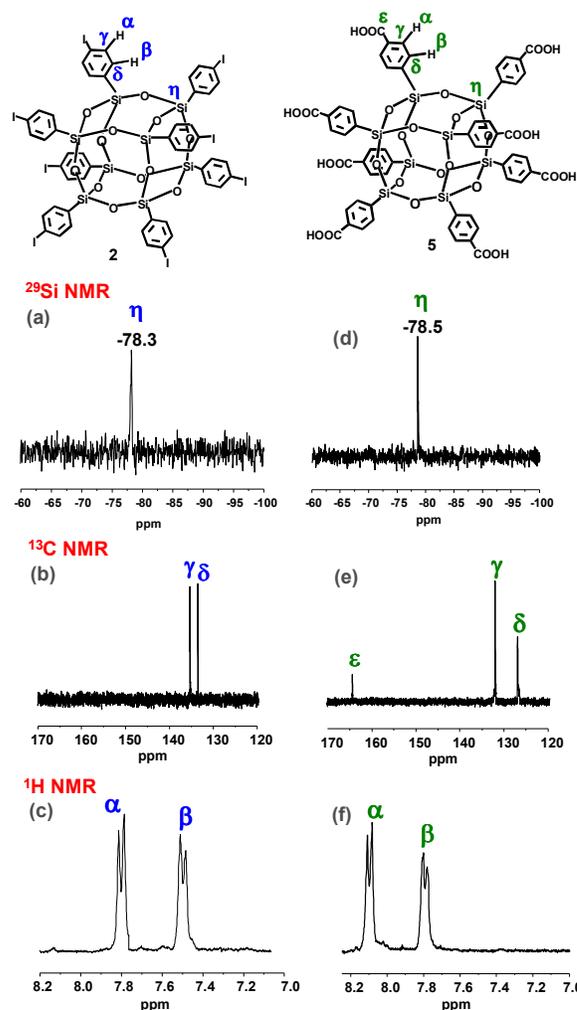
† Electronic supplementary information (ESI) available: Detailed experimental procedures, Characterisation data, Table S1 and Figures S1-S3.



**Scheme 1.** Synthesis of octa(*para*-carboxyphenyl)-silsesquioxane **5** from the completely condensed phenyl-silsesquioxane **1**, through a multi-step reaction involving sequential iodination, lithiation, carboxylation and hydrolysis.

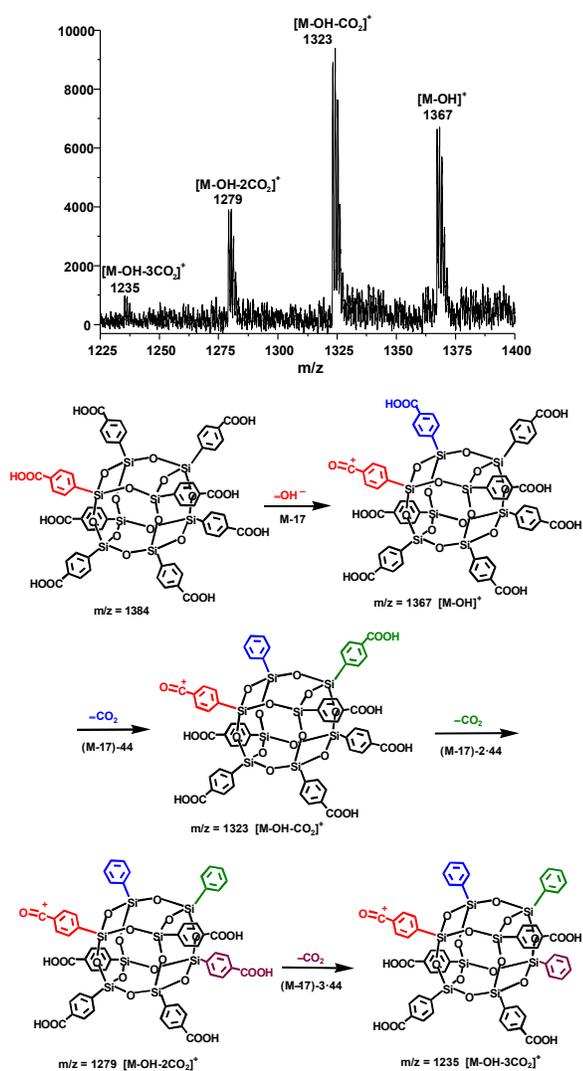
data clearly indicate the successful synthesis of the octaiodinated silsesquioxane **2**, it should be noted that the presence of small amounts of silsesquioxanes with slightly lower degree of substitution (e.g. hepta-iodinated) would not be easily detected and, therefore, cannot be completely excluded.

In the second step of the synthesis, silsesquioxane **2** was subjected to lithiation with  $n\text{BuLi}$  in THF at  $-78\text{ }^\circ\text{C}$  yielding octa(*para*-lithiophenyl)-silsesquioxane **3** as a white precipitate, which was further reacted with  $\text{CO}_2$  followed by acid hydrolysis to generate the desired final product, octa(*para*-carboxyphenyl)-silsesquioxane **5** (see SI for the detailed synthesis procedure).<sup>15</sup> The pure compound was isolated in 61% yield (relative to compound **2**) by removal of THF under reduced pressure, followed by filtration from the remaining acidic aqueous solution, washing with dichloromethane and water, redissolution in THF and precipitation by drop-wise addition of water. The identity of the octacarboxy-silsesquioxane **5** and its high purity were demonstrated by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectroscopy and by MALDI-TOF mass spectrometry. The  $^{29}\text{Si}$  NMR spectrum of compound **5** displays a single signal at  $-78.5\text{ ppm}$  (Fig. 1.d), which is characteristic of the eight equivalent silicon atoms in completely condensed cubic silsesquioxane structures.<sup>9,16</sup> The position of this signal is very similar to that of octa(*para*-iodophenyl)-silsesquioxane **2** ( $-78.3\text{ ppm}$ ), proving that the cubic Si-O cage was not altered by the synthesis process. The  $^{13}\text{C}$  NMR spectrum of silsesquioxane **5** (Fig. 1.e) presents a signal at  $164.2\text{ ppm}$  that is characteristic of the C atoms of carboxyl groups, and signals of the aromatic carbons in position 2 and 3 of the phenyl ring ( $127.0$  and  $132.1\text{ ppm}$ , respectively), which are shifted to higher field compared to the corresponding aromatic carbons in octa(*para*-iodophenyl)-silsesquioxane **2** ( $133.5$  and  $135.4\text{ ppm}$ ). The signals corresponding to C atoms in positions 1 and 4 of the phenyl ring are not observed in the  $^{13}\text{C}$  NMR spectrum because quaternary carbons have long relaxation times, which can lead to signals below the detection limit.<sup>17</sup>



**Figure 1.** NMR spectra of compounds **2** and **5**: (a, d)  $^{29}\text{Si}$  NMR; (b, e)  $^{13}\text{C}$  NMR; (c, f)  $^1\text{H}$  NMR. In all cases, the silsesquioxanes were dissolved in fully deuterated THF. A baseline correction was performed for the  $^{29}\text{Si}$  NMR spectra to remove the broad signal around  $-110\text{ ppm}$ , which originates from the borosilicate glass of the sample tube and NMR probe.

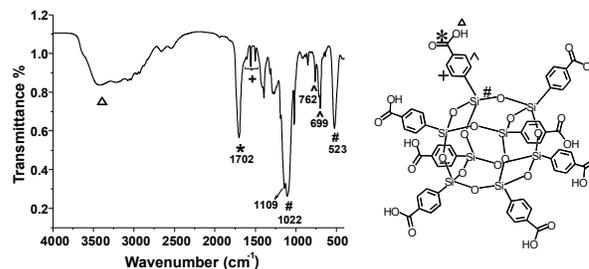
The  $^1\text{H}$  NMR spectrum of silsesquioxane **5** (Fig. 1.f) shows two doublets at 7.8 and 8.1 ppm, which are due to the H atoms on the phenyl ring. These two signals are shifted to lower field compared to the signals of the corresponding hydrogens of octa(*para*-iodophenyl)-silsesquioxane **2** (7.5 and 7.8 ppm), as an effect of the electron-withdrawing nature of the carboxyl group in *para*-position.



**Figure 2.** MALDI-TOF mass spectrum of octa(*para*-carboxyphenyl)-silsesquioxane **5** (molecular mass calculated considering only the main isotope of each element: 1384 g/mol).

The MALDI-TOF mass spectrum of octa(*para*-carboxyphenyl)-silsesquioxane **5** shows an interesting fragmentation pattern (Fig. 2). The fragment with the highest mass ( $m/z = 1367$ , 69 %) is assigned to  $[\text{M}-\text{OH}]^+$ , which corresponds to  $\alpha$ -cleavage of a hydroxyl anion in one of the eight carboxyl groups of **5**.<sup>18</sup> The following fragmentations involve the stepwise loss of three  $\text{CO}_2$  fragments from three of the remaining seven carboxyl groups of the  $[\text{M}-\text{OH}]^+$  species (Fig. 2), with the first  $\text{CO}_2$  loss giving the most intense peak in the mass spectrum ( $[\text{M}-\text{OH}-\text{CO}_2]^+$   $m/z = 1323$ , 100 %). This mass spectrum confirms that octa(*para*-iodophenyl)-silsesquioxane **2** was fully converted into octa(*para*-carboxyphenyl)-silsesquioxane **5**. The complete conversion of all iodine-substituted phenyl groups to

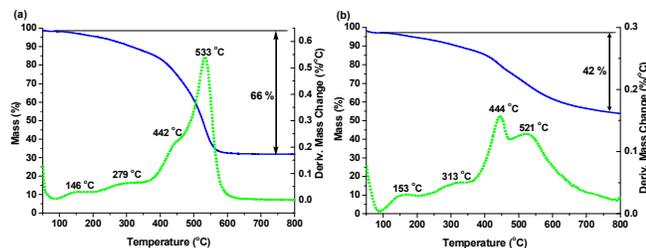
carboxyl-substituted species was confirmed by the absence of iodine in the elemental analysis of compound **5** by EDX. HPLC of this silsesquioxane presents a single peak attributed to the deprotonated compound (Fig. S2 in the ESI). Further characterisation of silsesquioxane **5** by FT-IR spectroscopy (Fig. 3) reveals a sharp peak at  $1702\text{ cm}^{-1}$  due to the stretching mode of the  $\text{C}=\text{O}$  bond in hydrogen-bonded carboxyl groups, and a wide absorption band at  $2800\text{--}3700\text{ cm}^{-1}$  due stretching of the O-H of the carboxyl groups. Additionally, the peaks at 1109, 1022, and  $523\text{ cm}^{-1}$  correspond to the characteristic Si-O-Si vibrations of the silsesquioxane framework, the signals between  $1500$  and  $1600\text{ cm}^{-1}$  are due to stretching of the  $\text{C}=\text{C}$  bonds and those at  $699$  and  $762\text{ cm}^{-1}$  to out-of-plane deformation of the phenyl groups.<sup>15,19</sup>



**Figure 3.** FT-IR spectrum of octa(*para*-carboxyphenyl)-silsesquioxane **5**.

In order to be applicable as building block in the synthesis of new materials, the silsesquioxane compound should show good solubility in a range of solvents and good stability in the acid or basic environment that might be employed in a self-assembly process. The octa(*para*-carboxyphenyl)-silsesquioxane **5** is highly soluble in methanol, ethanol, ethanol-water mixture (1:1 in vol.), THF, 1,4-dioxane, DMSO and DMF (see Table S1), and insoluble in less polar solvents as dichloromethane, aliphatic and aromatic hydrocarbons. The silsesquioxane-based building block is highly stable in acid environment, as demonstrated by the unaffected  $^{29}\text{Si}$  NMR spectrum of compound **5** after treatment with 2M HCl in THF solution at either room temperature or under reflux for 24 h, with a silsesquioxane-to-acid ratio of 1:10. Completely condensed silsesquioxane are known to undergo hydrolysis of the Si-O cage in basic environment.<sup>20</sup> However, the Si-O framework was not altered when silsesquioxane **5** was brought in contact with a basic solution of 2M triethylamine in THF at room temperature for 24 h, though the carboxyl groups reacted with the base to form the triethylammonium salt of compound **5** as a white precipitate (single signal at  $-77.9$  ppm in the  $^{29}\text{Si}$  NMR spectrum, see Fig. S3). The thermal stability of silsesquioxane **5** was investigated by TGA. When the analysis was performed in  $\text{O}_2$  flow, the compound underwent a gradual degradation with multiple mass losses. The two major mass losses, with maxima at  $442$  and  $533\text{ }^\circ\text{C}$  in the derivative curve, are assigned to the loss of the phenyl groups,<sup>19</sup> whereas the two minor mass losses at lower temperature are attributed to the partial degradation of the carboxyl groups into  $\text{CO}_2$  (Fig. 4.a). The total 66 % mass loss reached at  $600\text{ }^\circ\text{C}$  matches well with the theoretical value expected for the loss of the organic moieties of compound **5** and its oxidative transformation into silica. In  $\text{N}_2$  atmosphere, a similar multiple-step degradation process was observed (Fig. 4.b), but with a lower total mass loss (42 %). This

indicates the presence of residual carbonaceous species in the material even above 800 °C.<sup>19</sup>



**Figure 4.** Thermogravimetric analysis of octa(*para*-carboxyphenyl)-silsesquioxane **5** (blue line) and derivative curve (green dotted line). The measurements were carried out with a heating rate of 5 °C/min, either in O<sub>2</sub> (a) or in N<sub>2</sub> (b). Before the analysis, the sample was dried at 60 °C under vacuum.

In conclusion, we reported the design and synthesis of a new hybrid inorganic-organic building block characterised by a rigid structure with a high number of symmetry-related coordination sites provided by regularly-spaced carboxyl groups, and with the only degree of freedom being the rotation of the carboxyphenyl groups around the C-Si bonds. It should be noted that the potential of octa(*para*-carboxyphenyl)-silsesquioxane **5** as building block for the synthesis of three-dimensional crystalline structures is much superior compared to previously reported silsesquioxanes or spherosilicates functionalised with carboxyl groups,<sup>15,21,22</sup> none of which meets the requirements of symmetry, directionality and rigidity displayed by compound **5** due to lack of linearity and possible rotation around the bonds of the arms connected to the cubic Si-O cage. The cubic spatial organisation of the carboxylic coordination sites implies that this silsesquioxane building block can act as a node that contributes to the definition of a three-dimensional framework in a coordination-driven self-assembly process with suitable metal centers, and not as a simple spacer between metal clusters as it is the case in many MOFs. The above-mentioned features of silsesquioxane **5**, coupled with the ability of carboxyl groups to act either as monodentate or bidentate chelating sites for a metal atom or as bridge between two metal centers,<sup>1</sup> open many exciting opportunities for the synthesis of new classes of crystalline materials and supramolecular complexes. Furthermore, the carboxyl groups in compound **5** may be converted into other functional groups, such as acid halides, esters or amides, while preserving the spatial organisation of the original material. These new compounds could find relevant applications in the synthesis of dendrimers and hybrid polymers with enhanced optical, thermal or mechanical properties.<sup>23</sup>

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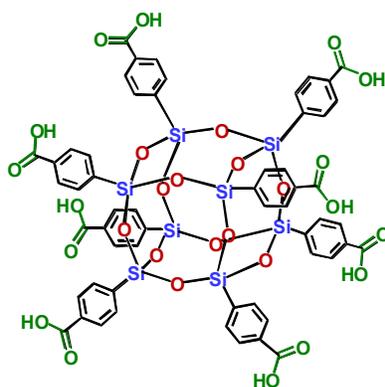
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A novel silsesquioxane compound characterised by eight carboxyl groups organised in cubic symmetry was prepared by a multi-step regioselective synthesis. This compound displays highly attractive chemical and geometrical features towards application as a building block in self-assembly processes.