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Hydrogen Bond-Directed Assembly of Silsesquioxanes Cubes: Synthesis of Carboxylic Acid POSS Derivatives and the Solid State Structure of Octa[2-(p-carboxyphenyl)ethyl] Silsesquioxane†

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The octa[2-(p-carboxyphenyl)ethyl] and octa[2-(4-carboxy-1,1'-biphenyl)ethyl] silsesquioxane were synthesised under mild reaction conditions upon hydrogenolysis of the corresponding benzyl-ester derivatives. The octa[2-(p-carboxyphenyl)ethyl] silsesquioxane was shown to self assemble upon formation of carboxylic acid dimers. The presence of eight carboxylic acid functional groups allowed to obtain an ordered silsesquioxane hybrid network. The X-ray crystal structures of the octa-ester and of the octa-acid were determined. The three-dimensional conformation of the ester provided an interpenetrated compact packing of the molecular building blocks without any specific supramolecular interaction. The two-dimensional character of the acid and the directionality of the hydrogen bond pattern of a dimer of acid led to the formation of hydrogen-bonded ribbons. It showed that functionalized silsesquioxane precursors capable of hydrogen bonding are of interest to generate nanostructured materials through self-organization processes. Moreover, the use of carboxylic acid groups is interesting not only because of their ability to form carboxyl dimer strutures by hydrogen bonding but also because of their ability to form metal carboxylate derivatives that may lead to new organised hybrid metal organic silica frameworks.

Introduction

The synthesis of solids under mild reaction conditions such as the "chimie douce" approach[1,2] allowed the design of a wide variety of useful materials for applications in such different fields as energy, environment, transports, construction or health. Sol-gel chemistry was extended to organosilicon precursors 25 years ago upon sol-gel hydrolysis condensation of an organic molecule that was functionalized by two or more $Si(OR)_3$. It led to hybrid organic-inorganic silica-based materials whose composition, combining organic substructures and siloxane units, was defined at the molecular level.[3,4] Diverse materials containing organic substructures and silicate units were reported.[5,6,7] They are amorphous materials that exhibit a variety of specific properties: porosity, hydrophobic, catalytic, optical properties…[8,9,10,11,12] They were synthesized under kinetically controlled conditions, which means that the properties of the materials are dependent on the reaction conditions during the synthesis.

On the basis of molecular and supra-molecular organic chemistry, new synthetic strategies have therefore been developed to achieve the control of the structure of the material at nanoscale. The use of supra-molecular interactions to provide external templating for the structuration of the porosity of silica[13,14,1516] was extended to the generation of ordered mesoporous organosilicas.[17,18,19,20] The self-assembly properties of organic substructures during the hydrolysis-condensation reactions of organoalkoxysilanes also offered the possibility to direct the formation of the hybrid silica network. The generation of layered materials by the use of hydrophobic interactions during the hydrolysis condensation of alkyl trialkoxysilanes containing 12-18 carbon atoms in the alkyl groups was first described by Kuroda *et al* [21]. Our group developed a route to self-assembled hybrid bridged silsesquioxanes by taking advantage of intermolecular hydrogen bonding, hydrophobic or π–π interactions, which assembled the organic fragments and thus directed the hydrolysis and condensation of the alkoxysilyl groups. Organised solids were generated by the transcription of the structure of supra-molecular assemblies of informed precursors into a solid material.[22,23,24] This approach proved to be useful for example in tuning the optical and charge transport properties of organic materials through the control of the 3-D organisation of the self-assembled organic substructures.[25,26] Although some crystalline self-assembled hybrid bridged silsesquioxanes were reported[27,28,29] the medium long-range ordering was most often limited to a lamellar arrangement of the organic substructures and the silica part of the network was essentially amorphous. The synthesis of crystalline silsesquioxane hybrid network still remains a challenge.

The synthesis of crystalline material - particularly metal–organic frameworks (MOFs)[30,31,32,33,34,35] and covalent organic frameworks (COFs)[36,37] - using molecular precursors represents a very attractive route. The group of Kuroda recently reported the construction of a regular supra-

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molecular assembly of cage siloxanes. The spherosilicate building blocks assembled by hydrogen bonding owing to the presence of silanol functional groups.[38] We wanted to explore the controlled assembly of the molecular silsesquioxane building blocks as an alternative route to crystalline hybrid materials. Polyhedral oligomeric silsesquioxanes (POSSs), $(RSiO_{1.5})_n$ with various organic substituents were easily accessible and organic/inorganic hybrid nanocomposites based on POSS derivatives have attracted considerable interest.[39,40,41,42,43,44,45] The POSS substructure represented a well-defined silica substructure, which upon functionnalisation by organic group with self-assembly properties could form crystalline hybrid network. We thought that hydrogen-bonding interactions would be appropriate for directing the 3D structure arrangement of the hybrid material.[22,38] Here, we report the formation of crystalline materials from cage T8 silsesquioxanes functionalised with carboxylic acid groups. The supra-molecular assembly of an octa-acid resulted from the dimerization of the carboxylic acid groups, which acted as hydrogen donors and hydrogen acceptors. In the solid state, the linear arrangements of the silsesquioxane cubes seemed to be directed by hydrogen bonding.

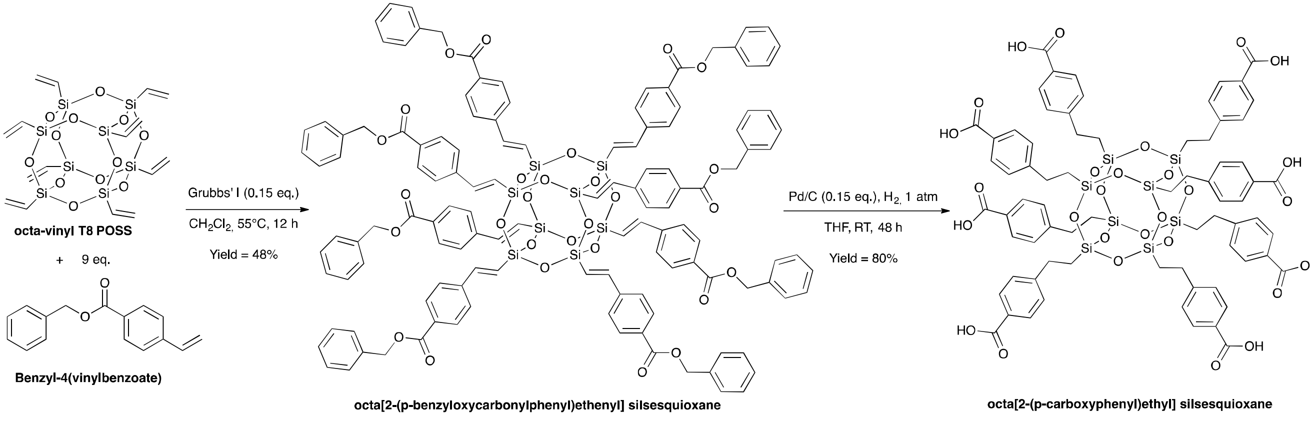
Results and discussion

Synthesis of POSS derivatives:

A readily available amino functionalised silsesquioxane such as octa(3-aminopropyl) silsesquioxane[46,47,48] would be of interest as a precursor capable of hydrogen-bonding. However, whereas the compound was easily isolated as ammonium salt, the free amine derivative was less stable owing to the basicity of the functional group. The neutralization of the salt to the free amine was difficult to accomplish without compromising the silsesquioxane cage structure. Carboxylic acid derivatives seemed more stable and functionalised sperosilicates[49] or silsesquioxanes[50,51,52],[53] have been repoted. It led to luminescent material upon complexation with terbium.[54,55] We thus decided to explore carboxylic acid derivatives that easily formed a dimer structure even in solution. A straightforward synthesis of carboxylic acid functionalised silsesquioxanes has been reported by hydrolysis of cyano derivatives with 9-molar sulphuric acid at 100°C.[52] However, the obtained compound was not soluble and solid state ^{29}Si NMR indicated major T3 substructure with c.a. 2% of T2 substructure meaning that some ring opening of the POSS cube structure occurred to give Si-OH groups. Moreover, the resulting solid was not soluble in any solvent even at high temperature. It may be indicative that some condensation of the Si-OH had occured leading to oligomeric or polymeric materials. We therefore looked for mild reaction conditions to generate pure and soluble silsesquioxane cube derivatives. Various methods have been reported to prepare functionalised silsesquioxane cubes $[RSiO_{3/2}]_8$, particularly for those that are not accessible by direct synthesis via hydrolytic condensation of $RSiX_3$.[39] The transformation reactions of simple silsesquioxane cubes require the achievement of quantitative reactions at the eight silicon atoms of the cube. Hydrosilylation reactions of the simple hydrido-silsesquioxane $[HSiO_{3/2}]_8$ have been used. However, the vinyl silsesquioxane[56,57] $[CH_2{=}CHSiO_{3/2}]_8$ was interestingly found to undergo easily cross-metathesis reactions to generate substituted derivatives of POSS[58]. The bulky vinyl silsesquioxane cube did not undergo self-metathesis and appeared to be an excellent substrate for cross-metathesis upon reaction with a variety of terminal alkenes. The reaction was stereo-selective in most cases leading to the *E*-alkenylene isomers as the major product.[59] However, we considered the hydrogenation of vinylidene metathesis products into ethylidene derivatives in order to get a single compound. Moreover, an ethylidene linker could introduce some flexibility in the formation of supra-molecular assembly of the free acid.

The octa[2-(p-carboxyphenyl)ethyl] silsesquioxane was synthesized in two steps from the readily available octa-vinyl silsesquioxane as shown in Scheme 1. We first protected the 4-vinyl benzoic acid as the benzyl ester upon reaction with benzyl alcohol in the presence of N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride and DMAP [60]. It was then reacted with octa-vinyl silsesquioxane in CH_2Cl_2 in the presence of Grubbs'I catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$.[61] The resulting octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane was isolated in 48 % yield.

Scheme 1. Synthesis of the **octa[2-(p-carboxyphenyl)ethyl] silsesquioxane**



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The ^{1}H NMR indicated doublets for the vinyl proton with a J = 19 Hz coupling consistent with an *E*-configuration of the C=C bond (H_a and H_b, Figure 1a). ^{29}Si NMR showed a sharp singlet at -78.8 ppm consistently with a T3 [$Si(OSi)_3C_{sp2}$] environment of the eight silicon atoms of the silsesquioxane cube. (See SI, Figure S4) The ester was then treated by hydrogen at atmospheric pressure in the presence of Pd/C. It allowed both the hydrogenolysis of the benzyl ester functional group and the hydrogenation of the vinylic C=C bonds to give octa[2-(p-carboxyphenyl)ethyl] silsesquioxane isolated in 80% yield. The octa-acid was obtained as a colourless solid soluble in common organic solvents such as THF. Its IR spectrum showed as expected highly broad ν_{OH} vibration around 3000 cm^{-1} and $\nu_{C=O}$ vibration at 1683 cm^{-1}. Hydrogenation of the C=C double bond was established in ^{1}H NMR by the appearance of two new resonances at 0.88 ppm (H_a) and 2.67 ppm (H_b) (Figure 1b). The sharp singlet at 12.79 ppm (H_e) was also consistent with the hydrogenolysis of the ester group to the free acid.

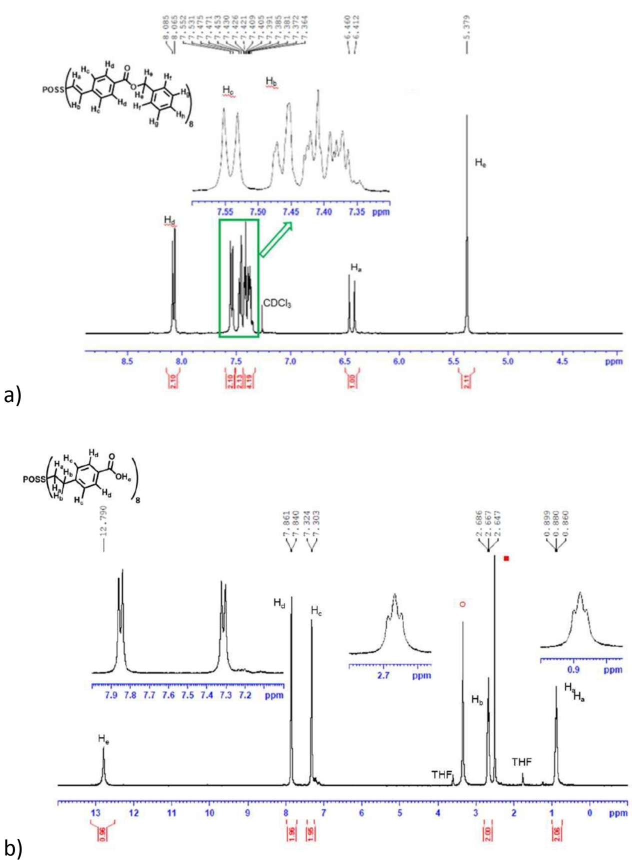

Figure 1. ^{1}H NMR spectra of a) Octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane in CDCl$_3$ and b) Octa[2-(p-carboxyphenyl)ethyl] silsesquioxane in DMSO-d6. ■DMSO, ○H_2O

The integrity of the silsesquioxane cube structure was shown by a sharp resonance at -67,3 ppm in ^{29}Si NMR in agreement with T3 [$Si(OSi)_3C_{sp3}$] environment of the eight silicon atoms (Figure 2).

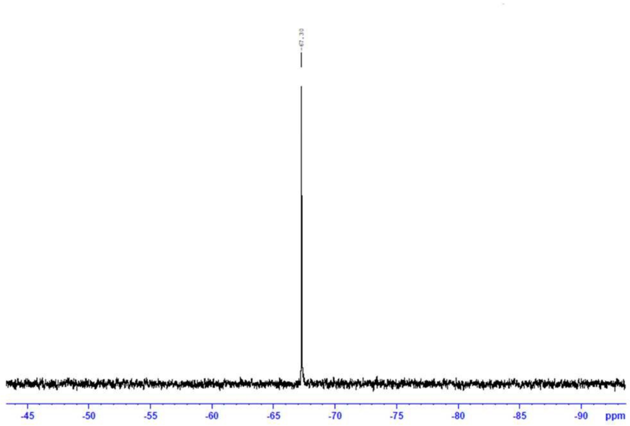

Figure 2. ^{29}Si NMR spectrum of octa[2-(p-carboxyphenyl)ethyl] silsesquioxane in DMSO-d6.

The octa-acid obtained under neutral reaction condition appeared soluble and quite stable. In the solid state it was a microcrystalline material as shown in the powder X-ray diffraction diagram (Figure 3). The IR spectrum with a broad ν_{O-H} band is consistent with the existence of inter-molecular interactions by hydrogen bonding. This is indicative of the formation of supramolecular network in the solid. Additionaly, the octa-acid was easily converted into its sodium carboxylate derivative upon treatment with an equivalent amount of sodium bicarbonate in water.

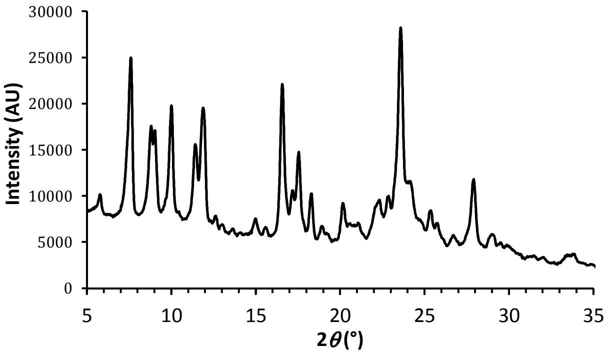

Figure 3. PXRD pattern of the **octa[2-(p-carboxyphenyl)ethyl] silsesquioxane**

We also prepared the biphenyl derivative in order to have longer organic spacers possibly leading to a different arrangement in the porous hybrid network. The octa[2-(4-carboxy-1,1'-biphenyl)ethyl] silsesquioxane was obtained in a similar way (scheme 2). The benzyl 4-vinyl-[1,1'-biphenyl]-4'-carboxylate was obtained from p-bromobenzoic acid upon esterification with benzyl alcohol followed by Suzuki coupling with p-styrylboronic acid. It was then reacted as above-mentionned with octa-vinyl silsesquioxane using Grubbs'I catalyst to give octa[2-(4-benzyloxycarbonyl-1,1'-biphenyl) ethenyl] silsesquioxane in 70% yield. Consistently, the ^{1}H NMR showed a doublet for the vinyl proton with a J = 19 Hz coupling (Ha and Hb, Figure 4a) and the ^{29}Si NMR with a sharp singlet at -78.3 ppm (See SI, Figure S12).

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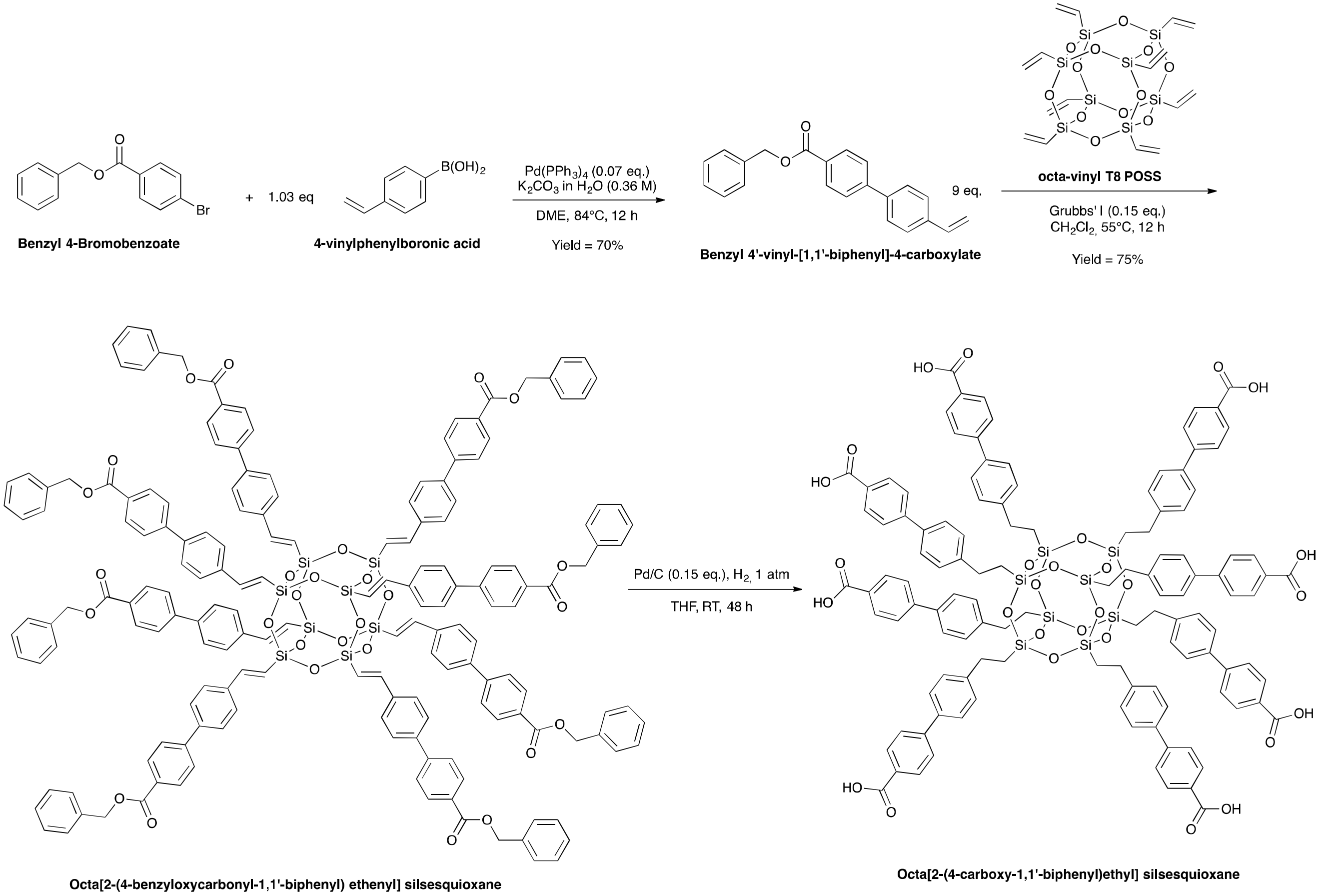
Scheme 2. Synthesis of the **octa[2-(4-carboxy-1,1'-biphenyl)ethyl] silsesquioxane.**



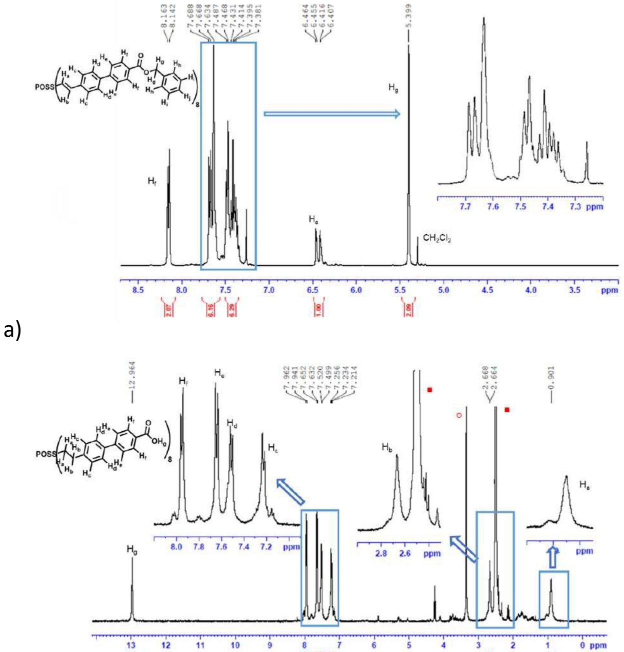


Figure 4. ^1H NMR spectrum of a) Octa[2-(4-benzyloxycarbonyl-1,1'-biphenyl) ethenyl] silsesquioxane in $CDCl_3$ and b) Octa[2-(4-carboxy-1,1'-biphenyl)ethyl] silsesquioxane in DMSO-d6. ■DMSO, ○H_2O

As for the phenylene derivative, palladium-catalysed hydrogenolysis of the biphenylene ester led to hydrogenation of the vinylic C=C bond to yield the octa[2-(4-carboxy-1,1'-biphenyl)ethyl] silsesquioxane. (Figure 4b) Again, hydrogenation of the C=C double bond was established in ^1H NMR by the appearance of two new resonances at 0.90 ppm (H_a) and 2.67 ppm (H_b). (Figure 1b) The sharp singlet at 12.79 ppm (H_g) was consistent with the hydrogenolysis of the ester group to the free acid.

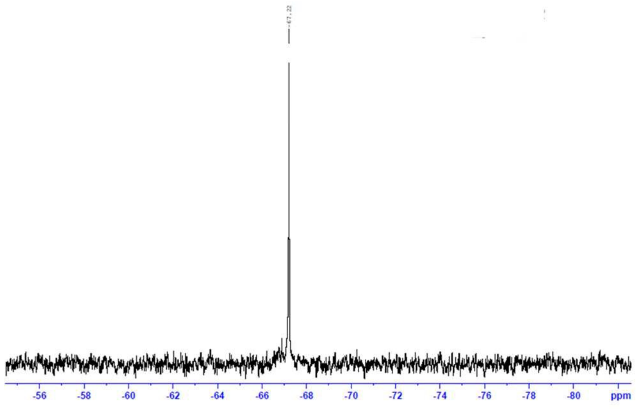


Figure 5. ^{29}Si NMR spectrum of Octa[2-(4-carboxy-1,1'-biphenyl)ethyl] silsesquioxane octa-acid in DMSO-d6.

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It showed a sharp singlet at -67.2 ppm in ^{29}Si NMR, as expected for the T3 [$Si(OSi)_3C_{sp3}$] environment of the eight silicon atoms of the silsesquioxane cube. (Figure 5)

X-Ray crystal structure of POSS derivatives and solid-state assembly through hydrogen bonding

We were interested in studying the self-assembly properties of the octa[2-(p-carboxyphenyl)ethyl] silsesquioxane. The presence of eight carboxylic acid functions could lead to a 3D network upon formation of intermolecular dimer structures by hydrogen bonding. Both the octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane and the octa acid formed crystal from THF solutions. We studied the solid-state structure of the two new POSS derivatives for comparison. The ester derivative without self-assembly properties had a rigid vinylene linker between the silsesquioxane cube and the organic; whereas in the acid derivative capable of self-association the ethylene linker was much more flexible and could adapt different conformations.

Recrystallization of both the ester and the acid derivatives furnished single crystals suitable for X-Ray diffraction. (Table 1).

Table 1. Crystallographic data

	octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane	**octa[2-(p-carboxyphenyl)ethyl] silsesquioxane**
formula	$C_{128}H_{104}O_{28}Si_8$	$C_{76}H_{80}O_{29}Si_8$, 0.6753 C_4H_8O
formula weight	2314.84	1754.22
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a (Å)	13.7763(12)	10.894(3)
b (Å)	16.0926(12)	12.114(3)
c (Å)	17.8036(10)	15.800(3)
α (°)	82.048(5)	85.936(10)
β (°)	72.999(6)	76.182(9)
γ (°)	68.508(8)	78.08(2)
volume (Å^3)	3509.9(2)	1980.6(8)
Z	1	1
Cell measurement temperature	175	100
D (g/cm^3)	1.095	1.471
R_1	0.0989	0.0586

The compounds crystallised on an inversion center in the same *P*-1 space group and their elemental unit exhibited different geometries (Figure 6).

On the one hand, the rigidity of the vinylene linker in the ester derivative and its *trans* configuration guided the organic pods into a cubic symmetry with the organic substituents radiating diagonally from the Si atoms around the inorganic core (Figure 6a). This three-dimensional molecular structure was also encountered in the octa-styryl silsesquioxane described by Marciniec *et al.*[59] On the other hand, in the case of the acid derivative, the flexibility of the ethylene linker and, more importantly, the orientation given by the hydrogen bond network resulted in a rod-like bi-dimensional conformation of the whole molecule with two groups of four podes oriented into two opposite directions (Figure 6b).

In both cases, the Si-O bond lengths fell in the range 1.60-1.63 Å, as found in other siloxanes (Table 2).[39] However, the Si-O-Si angles in the POSS core varied significantly within a single molecule (ester or acid). As already observed in the literature, the Si-O-Si angle fell in the range 138° - 165° (Table 2) and the nonbonded Si•••Si distances in the range 3.0 Å - 3.2 Å, (Table 3). These wide ranging angles are due to the propensity of many of the structures to deform and adopt conformations that minimize the spaces that would occur in the lattice if they were to point ideally toward the vertices of a cube.

Table 2. Bond lengths (Å) and bond angles (deg) in octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane and octa[2-(p-carboxyphenyl)ethyl] silsesquioxane (mean values).

	octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane	**octa[2-(p-carboxyphenyl)ethyl] silsesquioxane**
Si-O	1.614	1.625
Si-O-Si	158.8	163.5
	149.2	142.7
	138.3	141.1

Table 3. Nonbonded Si•••Si distances (Å) in a) octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane and octa[2-(p-carboxyphenyl)ethyl] silsesquioxane.

octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane	**octa[2-(p-carboxyphenyl)ethyl] silsesquioxane**
SI1-SI5 = 3.172	SI2-SI1 = 3.210
SI3-SI8 = 3.174	SI3-SI4 = 3.209
SI1-SI8 = 3.028	SI2-SI4 = 3.085
SI3-SI5 = 3.028	SI3-SI1 = 3.077
SI1-SI3 = 3.095	SI2-SI3 = 3.069
SI8-SI5 = 3.093	SI4-SI1 = 3.074

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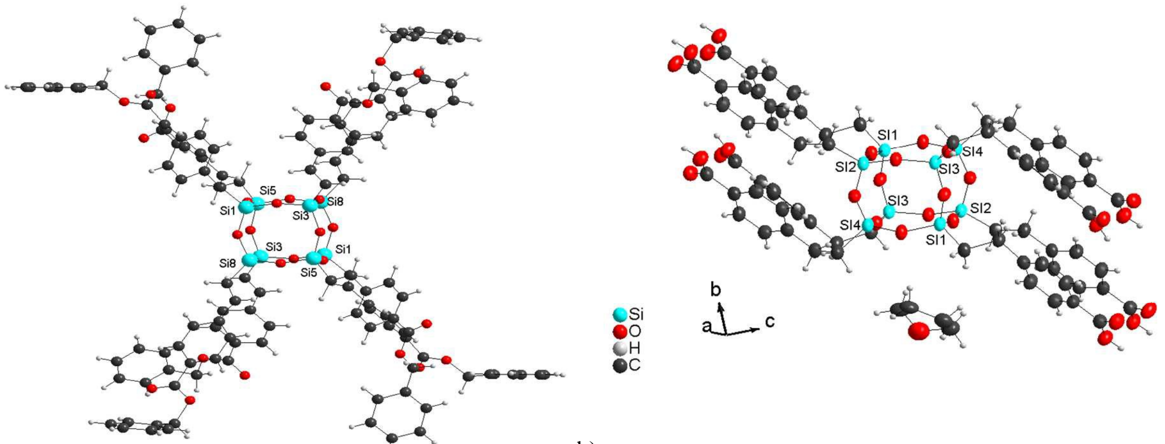

a) b)

Figure 6. Asymmetric units of the crystal structures of a) octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane and b) octa[2-(p-carboxyphenyl)ethyl] silsesquioxane

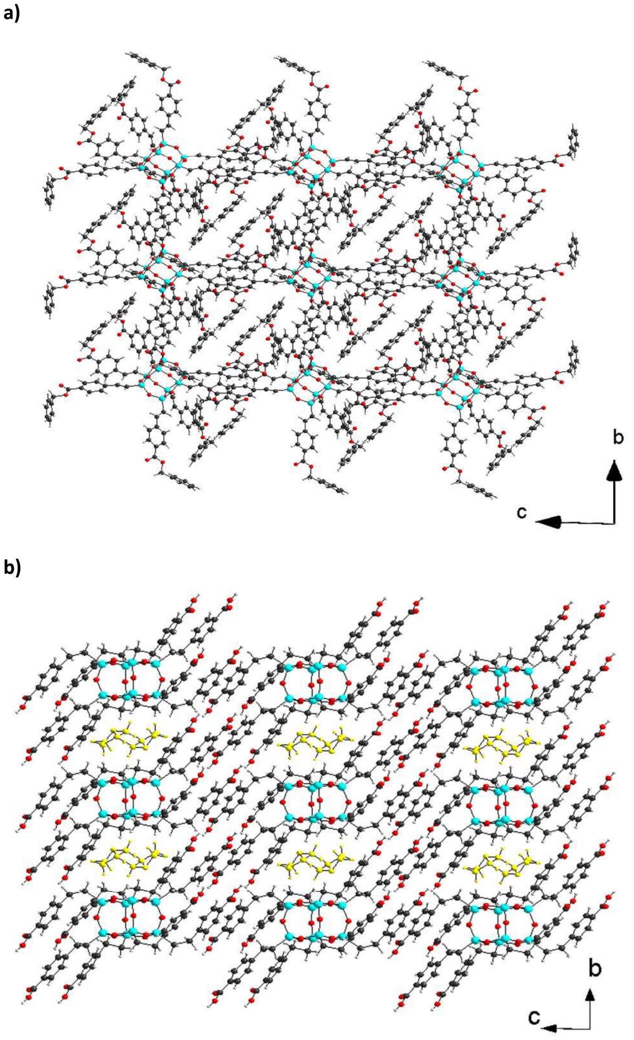

Figure 7. Crystal packing of a) octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane and b) octa[2-(p-carboxyphenyl)ethyl] silsesquioxane.

The different molecular architectures resulted in the distorsion of the molecules (Table 3). In particular, the inorganic core of the acid derivative was compressed in the direction of the formation of hydrogen-bonded ribbons along the c axis. This was attested by the increase of the Si•••Si distances along the a and b axises and a diminutions along the c axis compared to the ester. The two different molecular conformations resulted in two different types of supramolecular organization (Figure 7). The three-dimensional conformation of the ester provided an interpenetrated compact packing of the molecular building blocks without any specific supramolecular interaction. (Figure 7a) The shortest carbon-carbon distances could be observed (C32•••C35 = 3.777 Å and C33•••C36 = 3.760 Å on Figure 8a) between two phenyl rings of two different styryl functions. These were higher than the sum of the van der Waals radius of the carbon atoms (3.54 Å) and the distance expected for π−π stacking interaction.[62]

The bidimensional character of the acid and the directionality of the hydrogen bond pattern of a dimer of acid led to the formation of hydrogen-bonded ribbons. (Figure 7b, Figure 8b) Indeed, the octa-acid self-organised through $R^2_2(8)$ hydrogen bond motif according to Etter *et al.* classification[63]. The distance between the different oxygen atoms engaged as hydrogen bond donors and acceptors were in the range of hydrogen-bonded acid dimers (d(D-H…A) = d(O10•••O11) = 2.57(2); d(O12•••O9) = 2.63(2); d(O13•••O8) = 2.64(2); d(O7•••O14) = 2.65 (2)). The ribbons (red and blue on Figure 5b) are aligned and the whole structured was stabilised by the inclusion of a molecule of THF (yellow on figure 8b).

The presence of eight carboxylic acid functional groups allowed to obtain ordered silica-based hybrid materials by hydrogen bond-directed assembly of the silsesquioxanes cubes. It provided a soft-chemical approach to crystalline hybrid silica materials.

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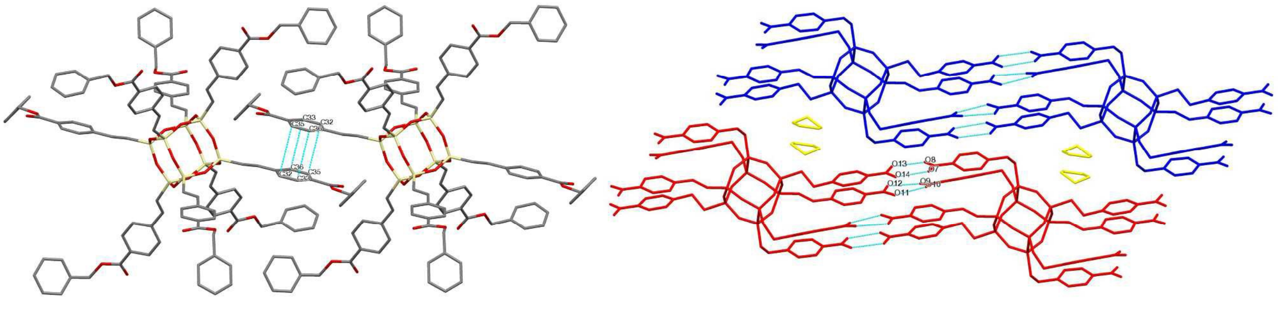

a) b)

Figure 8. Different contacts present in the structures of a) octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane and b) octa[2-(p-carboxyphenyl)ethyl] silsesquioxane (Hydrogen atoms have been omitted for clarity)

Conclusions

In conclusion, we have demonstrated the formation of a crystalline organosilica by associating molecularly designed precursors. Silsesquioxane cubes are useful building blocks of hybrid silica based nanomaterials because of the rigid silica framework and their easy functionalisation. We reported the synthesis and regular arrangement of silsesquioxane cages through hydrogen bonding. This approach should be quite general and various supramolecular assemblies could be constructed by hydrogen bonding between designed functionalized silsesquioxane cages. It should allow the formation of stable molecular crystals stabilized by hydrogen bonding networks. The use of carboxylic acid groups is interesting because of their ability to form hydrogen bonds and also because of their ability to form metal carboxylate derivatives. It may lead to hybrid metal organic silica frameworks. Moreover the structure and properties of the organic linkers can be varied to reach new organized materials.

Experimental section

General:

All chemicals and solvents were of reagent grade. N,N-dimethylformamide, (DMF), and tetrahydrofuran (THF) were dried under 4Å molecular sieves. Octa-vinyl silsesquioxane was prepared as described in the literature (ref 56). Samples were also purchased from Sigma-Aldrich. Nuclear magnetic resonance spectra (NMR) were recorded on a Bruker 400 MHz in deuterated chloroform or dimethylsulfoxyde. IR spectra were performed with a Spectrum 100 FT-IR spectrometer from Perkin Elmer.

Synthetic procedures:

Benzyl-4(vinylbenzoate)[64] **.** In a 100 mL round bottom flask under nitrogen, para-vinylbenzoic acid (7 mmol., 1 eq), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydro-chloride (EDC.HCl) (8,5 mmol. 1,2 eq) and *N,N*-diméthyl-4-aminopyridine (DMAP) (0,7 mmol. 0,1 eq) were dissolved in dichloromethane (60 mL). Benzyl alcohol (8.5 mmol., 1.2 eq) was then added dropwise. The mixture was stirred and refluxed for 3hrs. After cooling, it was washed with water (3x20 mL) and the organic layer was dried over magnesium sulfate. The solvent was then evaporated and the crude product was purified over a column of silica gel (eluent cyclohexane/ diethylether 95/5) to yield a colourless oil (yield 80 %). **^{1}H NMR** (400 MHz, CDCl$_3$) δ (ppm) 8.09 (d, 2 H, J = 8,4 Hz) ; 7.47 (m, 4H) ; 7.40 (m, 3 H) ; 6.77 (m, 1H) ; 5.88 (d, 1H, J = 17.6 Hz) ; 5, 41 (d, 1 H, J = 11.2 Hz) ; 5.40 (s, 2 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ (ppm) : 166.2 (1C) ; 142.1 (1C) ; 136.2 (1C) ; 136.1 (1C) ; 130.1 (2C) ; 129.3 (1C) ; 128.7 (2C) ; 128.3 (1C) ; 128.2 (2C) ; 126.2 (2C) 116.6 (1C) ; 66.7 (1C).

Benzyl 4-Bromobenzoate[65]**.** As shown above, benzyl alcohol (7.9 mmol., 1.4 eq) was added dropwise to a solution containing para-bromobenzoic acid (5.5 mmol., 1 eq), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC.HCl) (7.2 mmol., 1,3 eq) and *N,N*-diméthyl-4-aminopyridine (DMAP) (0.7 mmol., 0.1 eq) in dichloromethane (60 mL). After addition, it was refluxed for 12hrs, cooled to r.t. and washed with water (3x20 mL). The organic layer was dried over magnesium sulphate and the solvent was removed under vacuum. The crude product was chromatographed on a silica column (eluent cyclohexane/ diethylether 9/1) to give a colourless solid (yield 70%). **^{1}H NMR**(400 MHz, CDCl$_3$) δ (ppm) : 7.92 (d, 2H, J = 8.8 Hz) ; 7.75 (d, 2H, J = 8.8 Hz) ; 7.47 (d, 2H, J = 8.4 Hz) ; 7. 40 (m, 3H) ; 5.35 (s, 1H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ (ppm) : 164.9(1C) ; 131.9 (2C) ; 131.2 (2C) ; 128.7 (1C) ; 128.5 (2C) ; 128.2 (1C) ; 128.1 (2C) ; 127.5 (1C) ; 66.5 (1C).

Benzyl 4'-vinyl-[1,1'-biphenyl]-4-carboxylate: As shown above, a solution of 4-vinylphenylboronic acid (4.3 mmol.), benzyl 4-bromobenzoate (4.1 mmol.) in dimethoxyethane (30 mL) was placed in a 100 mL round bottom flask under nitrogen. After 20mn, an aqueous solution of potassium carbonate (3 mol. eq in 34 mL of water) was added, followed by tetrakis(triphenylphosphine)palladium(0) (0.07 mmol). The mixture was refluxed for 12hrs. The solvent was then removed under vacuum and the remaining aqueous phase was extracted with ethyl acetate. The organic layer was dried over anhydrous magnesium sulphate. After removal of the solvent, the crude product was purified over a silica column (eluent cyclohexane/dichloromethane: 6/4). The pure product was obtained as a colourless solid (yield 70%). **^{1}H NMR** (400 MHz, DMSO *d-6*)) δ (ppm) : 8.06 (d, 2H, J = 8.4 Hz) ; 7.85 (d, 2H, J = 8.4 Hz) ; 7.73 (d, 2H, J = 8.4 Hz) ; 7.60 (d, 2H, J = 8.4 Hz) ; 7.48 (d, 2H, J = 7.2 Hz) ; 7.40 (m, 3H) ; 6.79 (m, 1H), 5.92 (d, 1H, J = 17.6 Hz) ; 5.38 (s, 2H) ; 5.32 (d, 1H, J = 10.8 Hz). **^{13}C NMR** (100

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MHz, DMSO *d-6*)) δ (ppm) : 165.9 (1C) ; 144.8 (1C) ; 138.6 (1C) ; 137.7 (2C) ; 136.7 (1C) ; 136.5 (1C) ; 130.4 (2C) ; 129.0 (2C) ; 128.9 (1C) ; 128.6 (1C) ; 128.4 (2C) ; 127.7 (2C) ; 127.3 (2C) ; 115.6 (1C)

Metathesis reactions:

In a round bottom flask under nitrogen, octa-vinyl T8 POSS (0.8 mmol., 1 eq), the functionalized styrene derivative (7.2 mmol., 9 eq) and the Grubbs'I catalyst: benzylidene-bis(tricyclohexyl-phosphine), dichlororuthenium [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] (0.18 mmol., 0.15 eq) were placed in solution with 60 mL of dichloromethane. The mixture was stirred at 55 °C for 12hrs. The advancement of the reaction was followed by ^{1}H NMR.

Octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane. The crude mixture was poured into 150 mL of methanol. The white precipitate was dissolved in the minimum quantity of dichloromethane. It was chromatographed on a silica gel column (eluent cyclohexane / dichloromethane (2/8). A colourless solid was isolated and recrystallized from a mixture of dichloromethane/cyclohexane to yield octa[2-(p-carboxyphenyl) ethenyl] silsesquioxane octa-benzyl ester (yield 48 %). Mp: 115°C; **IR spetrum** (ATR) ν (cm^{-1}) : 3066, 3034, 2998, 2936, 2851, 1714, 1605, 1567, 1498, 1455, 1410, 1375, 1269, 1221, 1202, 1159, 1076, 1015, 990, 913, 836, 830, 829, 748, 695, 654; **^{1}H NMR** (400 MHz, CDCl$_3$) δ (ppm) : 8.07 (d, 2 H, J = 8 Hz) ; 7.55 (d, 2 H, J = 8.4 Hz) ; 7.40 (m, 6 H) ; 6.43 (d, 1 H, J = 19.2 Hz) ; 5.38 (s, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ (ppm) : 166.0 (1C) ; 148.4 (1C) ; 141.3 (1C) ; 136.0 (1C) ; 130.5 (1C) ; 130.2 (2C) ; 128.7 (2C) ; 128.4 (1C) ; 128.3 (2C) ; 126.9 (2C) ; 120.0 (1C) ; 66.9 (1C). **^{29}Si NMR** (79.5 MHz, CDCl$_3$) δ (ppm) : - 78.8. **MS (Maldy-Tof in positive ionisation**) m/z (M+Na) = obsd 2335.4, calc 2335,48; **Analysis :** *calc.* : % C : 66.41 % H : 4.53 ; % ; found: % C : 66.26 ; % H : 4.54.

Octa[2-(4-benzyloxycarbonyl-1,1'-biphenyl) ethenyl] silsesquioxane. As described above, the crude product was obtained as a white precipitate upon pouring the crude reaction mixture in 150 mL of methanol. It was purified by column chromatography (silica column, eluent cyclohexane / dichloromethane (2/8). The colourless solid collected, was recrystallized from a mixture of solvents (dichloromethane/cyclohexane), in a 75 % yield. Mp: 180°C ; IR **spectrum** (ATR) ν (cm^{-1}) : 3031, 2926, 2851, 1714, 1606, 1575, 1555, 1523, 1495, 1455, 1421, 1379, 1376, 1266, 1203, 1158, 1076, 989, 988, 912, 831, 830, 798, 765, 700, 695. **^{1}H NMR** (400 MHz, CDCl$_3$) δ (ppm) : 8.16 (d, 2 H, J = 8.4 Hz) ; 7.65 (m, 6 H) ; 7.40 (m, 6 H) ; 6.35 (d, 1 H, J = 19.2 Hz) ; 5.42 (s, 2H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ (ppm) : 166.3 (1C) ; 148.6 (1C) ; 144.9 (1C) ; 140.5 (1C) ; 137.2 (1C) ; 136.1 (1C) ; 130.3 (2C) ; 129.2 (1C) ; 128.7 (4C) ; 128.3 (1C) ; 128.2 (2C) ; 127.6 (2C) ; 126.9 (2C) ; 118.0 (1C) ; 66.9 (1C). **^{29}Si NMR** (79.5 MHz, CDCl$_3$) δ (ppm) : - 78.3. **Analysis :** *calc.* : % C : 72.30 % H : 4.69 ; % ; *found* : % C : 70.63 % H : 4.64.

Hydrogenation reactions:

The above POSS benzyl ester derivatives (0.18 mmol., 1 eq) were dissolved in 150 mL of THF. The catalyst 10% Pd/C (0.02 mmol., 0.10 eq) was added and the solution was stirred vigorously. The flask was then connected to a hydrogen balloon and stirred for 48h. The advancement of the reaction was followed by ^{1}H NMR. The catalyst was then removed by filtration and the solvent was removed. The crude product was obtained as highly viscous colourless oil. It was soluble in THF and recrystallized from a THF/heptane mixture.

Octa[2-(p-carboxyphenyl)ethyl] silsesquioxane. The compound was obtained as a colourless powder (yield 80%). Mp: 280°C (decomposition); **IR spectrum** (ATR) ν (cm^{-1}): 3200-2600 (broad band), 1683, 1610, 1603, 1514, 1420, 1297, 1288, 1081, 1017, 939, 837, 803, 797, 751, 695. **^{1}H NMR** (400 MHz, DMSO *d-6*) δ (ppm): 12.79 (s, 1H); 7.85 (d, 2 H, J = 8.2 Hz) ; 7.31 (d, 2 H, J = 8.2 Hz); 2.67 (m, 2 H); 0.88 (m, 2 H). **^{13}C NMR** (100 MHz, DMSO *d-6*) δ (ppm) : 167.7 (1C), 148.9 (1C), 129.8 (2C) ; 128.9 (1C), 128.5 (2C) ; 28.8 (1C) ; 12.9 (1C). **^{29}Si NMR** (79.5 MHz, DMSO *d-6*) δ (ppm) : - 67.3. **MS (Maldy-Tof in positive ionisation)** m/z (M+Na) = m/z 1631.2, calc 1631.23. ; **MS (Maldy-Tof in negative ionisation)**: (M-H) = obsd 1607.1, calc 1607.21; **Analysis:** *calc.* : % C : 53.71 ; % H : 4.51 ; *found* : % C : 53.56 ; % H : 4.57.

Sodium octa[2-(p-carboxylatephenyl)ethyl] silsesquioxane. 0.66 mmol. of sodium bicarbonate was added to a suspension of the octa-acid (0.08 mmol.) in 50 ml of water. After heating at 60°C for 12hrs, 30ml of toluene were added to the homogeneous solution. The solid that formed (yield 80%) was isolated after evaporation of the solvents. **IR spectrum** (ATR) ν (cm^{-1}): 2962,1674,1590, 1567, 1397, 1213, 1111, 997, 852, 781, 763, 702; **^{1}H NMR** (400 MHz, D$_2$O) δ (ppm): 7.81 (d, 2 H, J = 8,.4 Hz) ; 7.37 (d, 2 H, J = 8.2 Hz); 2.81 (m, 2 H); 1.03 (m, 2 H). **MS (Maldy-Tof in positive ionisation)** m/z (M+Na) = obsd 1807 calc 1807.08; M = 1785; M-Na = 1763.3; M-2Na = 1741.3; M-3Na = 1720.3; M-4Na = 1697.3; M-5Na = 1675.3; M-6Na = 1653.3; M-7Na = 1631.3

Octa[2-(4-carboxy-1,1'-biphenyl)ethyl] silsesquioxane. **IR spectrum** (ATR) ν (cm^{-1}): 3200-2600 (broad band), 1681, 1607, 1578, 1527, 1498, 1447, 1427, 1302, 1289, 1083, 1005, 822, 814, 769, 694. **^{1}H NMR** (400 MHz, DMSO *d-6*) δ (ppm) : 12.96 (s, 1H) ; 7.95 (d, 2H, J = 8.4 Hz) ; 7.64 (d, 2H, J = 8 Hz); 7.51 (d, 2H, J = 8.4 Hz) ; 7.22 (d, 2H, J = 8 Hz) ; 2.66 (m, 2H); 0.91 (m, 2H). **^{29}Si NMR** (79.50 MHz, CDCl$_3$) δ (ppm): - 67.2 **MS (Maldy-Tof in negative ionisation)** m/z (M-H) = obsd 2215.5, calc 2215.48.

Crystal preparation and X-ray diffraction:

a) Octa[2-(p-benzyloxycarbonylphenyl)ethenyl] silsesquioxane

The octa-ester was dissolved in a minimum of tetrahydrofuran in a test-tube and placed in a Schlenk tube containing another test-tube filed with hexane. Crystals were grown by slow diffusion of hexane vapours at room temperature. **X-ray structure determination.** Crystal evaluation and data collection were performed on a Rigaku Oxford-Diffraction Gemini-S diffractometer with sealed-tube Mo-*K*□ radiation using the *CrysAlis Pro* programme[66]. The same programme was used for the integration of the data using default parameters, for the empirical absorption correction using spherical harmonics employing symmetry-equivalent and redundant data, and the correction for Lorentz and polarization effects. The crystal structure was solved using the *ab-initio* iterative charge flipping method with parameters described elsewhere[67] using the

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Superflip programme[68,69] and it was refined using full-matrix least-squares procedures as implemented in *CRYSTALS*[70] on all independent reflections with I>2□(I).

Although of reasonable size, the diffracting power of this crystal was rather low. Beyond 0.9 Å there was no significant diffraction spots and it was therefore decided to cut the data at 0.9 Å for refinement. In order to regularize the geometry of some phenyl rings distance restraints were used and one phenyl ring was refined as a rigid body. The solvent molecules, probably two, were heavily disordered and the Squeeze procedure, as implemented in PLATON,[71] was used to take into account their contribution to the diffracted signal. The squeezed volume was 902 Å^3 and the number of solvent electrons 196 per unit cell.

The H atoms were all located in a difference map, but repositioned geometrically. They were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C---H in the range 0.93-0.98 Å) and U_{iso}(H) (in the range 1.2-1.5 times U_{eq} of the parent atom). Then their positions were refined with riding constraints[72]. Crystal data - formula: $C_{128}H_{104}O_{28}Si_8$, moiety: $C_{128}H_{104}O_{28}Si_8$, T = 175 K, M_r = 2314.84 gmol$^{□1}$, crystal size = 0.15x0.23x0.31 mm^3, triclinic, spacegroup P-1, a = 13.7763(12) Å, b = 16.0926(12) Å, c = 17.8036(10) Å, α = 82.048(5)º, β = 72.999(6)º, γ = 68.508(8)º, V = 3509.9(2) Å^3, Z = 1, ρ_{calcd} = 1.095 gcm$^{□3}$, μ = 0.140 mm$^{□1}$, $\Theta_{\max}$ = 27.861º, experimental resolution = 0.88 Å, 13712 reflections measured, 13712 unique, 7005 with $I>2\sigma(I)$, R_{int} = 0.041, $<\sigma(I)/I>$ = 0.0587, 697 refined parameters, $R_1(I>2\sigma(I))$ = 0.0989, $wR_2(I>2\sigma(I))$ = 0.1254, R_1(all data) = 0.1262, wR_2(all data) = 0.1518, GOF = 1.1368, $\Delta\rho$(min/max) = -0.63/1.10 eÅ$^{□3}$.

b) Octa[2-(p-carboxyphenyl)ethyl] silsesquioxane

The crystals of the octa-acid were grown by slow evaporation of a tetrahydrofuran solution. **X-ray structure determination** *Data collection*. Because of the small crystal volume and small scattering power, synchrotron radiation was required for structure determination. Microdiffraction patterns were recorded at the ID23-2 structural biology microfocus beamline (European Synchrotron Radiation Facility – ESRF, Grenoble) where the beam was focused down to approximately 8 µm in diameter.[73] Each sample was mounted on a nylon loop embedded with Paratone oil from Hampton Research (Figure 9). Several crystals were tested to select a single crystal of suitable quality for data collection. The best acid crystal was approximately 60x20x5 µm^3. Data were collected by the oscillation technique using a two-dimensional pixel detector (DECTRIS Pilatus3 2M; ~253.7x288.8 mm^2, 1475 x 1679 pixels and a pixel size of 0.172 x 0.172 µm^2). The measurements were carried out at a fixed temperature of 100 (2) K using an Oxford 700 Cryostream device. **X-ray diffraction**. *Structure Solution and Refinement***.** The frames were indexed and the reflections integrated using the XDS software suite.[74] Each reflection intensity was corrected from the action of intensity loss due to air absorption. XDS (in the CORRECT step) applied Lorentz and polarization factors as well as factors that partially compensate from damage and absorption effects to intensities and standard deviations of all reflections. These factors were determined from many symmetry-equivalent reflections usually found in the data images so that their integrated intensities become as similar as possible. Therefore, due to the small scattering volume of the crystal, absorption effects due to the crystal itself were expected to be very weak.

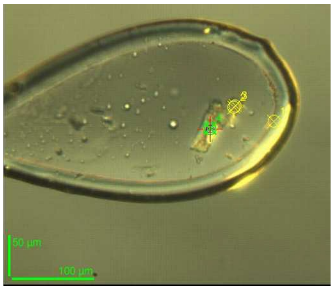

Figure 9. Crystal of **octa[2-(p-carboxyphenyl)ethyl] silsesquioxane** mounted on a nylon loop embedded with Paratone oil from Hampton Research.

The crystal structure of the non-hydrogen atoms was determined by direct methods using SHELXS97.[75] Refinement was carried out with SHELXL97. After a few least-squared cycles, anisotropic displacement parameters were employed on all Si, O and C atoms. The hydrogen atoms were placed in idealised positions with C-H = 0.95 Å during the refinement. Rings were refined without any constraints. SHELXS97 and SHELXL97 were used through the WinGX Graphical User Interface.[76] **Crystal data for octa-acid**: $C_{76}H_{80}O_{29}Si_8$, 0.6753 C_4H_8O triclinic, P-1 (no.2), a = 10.894(3) Å, b = 12.114(3) Å, c = 15.800(3) Å, α = 85.936(10)°, β = 76.182(9)°, γ = 78.08(2)°, V = 1980.6 (8) Å^3, T = 100(2) K, R_1 = 0.0586 for 4132 independent observed reflections [F > 4σ(Fo)], S = 1.026. Data collection: φ scans, 0.3° oscillation range, 1 pass of 0.04 s exposure time per image, 1200 images, λ = 0.8729 Å, 7/8 multibunch mode.

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Notes and references

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† CCDC 1508340 and CCDC 1509522 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Electronic Supplementary Information (ESI) available: [Experimental Details, ^{1}H, ^{13}C, ^{29}Si NMR spectra and Maldy spectra].

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Hydrogen Bond-Directed Assembly of Silsesquioxanes Cubes: Synthesis of Carboxylic Acid POSS Derivatives and the Solid State Structure of Octa[2-(p-carboxyphenyl)ethyl] Silsesquioxane†

Voisin Doria, Flot David, Van der Lee Arie, Dautel Olivier and Moreau Joel J. E.

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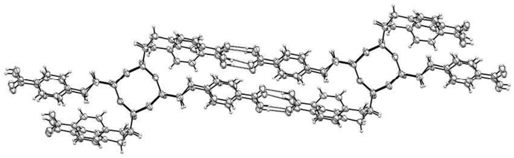

A crystalline organo-silica network was constructed through a self-organization process by assembling organic functionalised silsesquioxane cages capable of hydrogen bonding.