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X-ray crystal structures, packing behavior and thermal stability studies of a homologous series of *n*-alkyl-substituted polyhedral oligomeric silsesquioxanes

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Abstract

The homologous series of octa-*n*-alkylsilsesquioxanes (*n*-alkylPOSS) was prepared by hydrosilylation of octahydrido-octasilsesquioxane H₈T₈ with terminal *n*-alkenes in good yields (*n* = 2–18). The compounds were characterized by NMR spectroscopy (¹H, ¹³C, ²⁹Si), MALDI-TOF and ESI MS. Most of them have also been characterized using X-ray crystallography, including some polymorphs. The packing systems of the octa-*n*-alkylsilsesquioxanes are reported. Two types of packing have been observed, rod-like and disk-like (interdigitated). Some *n*-alkylPOSS crystals were formed in which the chains are tilted away from the axes of the cubic core. It was also observed that as alkyl-chains are flexible they can take up a variety of conformations. Melting points of the homologous series showed an odd-even alternating effect for alkyl chains longer than four CH₂ units. The TGA of *n*-alkylPOSS under nitrogen showed that the thermal stability temperatures are between 200 and 400 °C. Pyrolysis-gas chromatography/mass spectrometry has been used to elucidate the thermal degradation process of T₈(*n*-C_nH_{2n+1})₈ (*n* = 11 and 18). Thermal cracking along the whole alkyl chain was observed rather than simple loss of the complete arm.

Keywords: Silsesquioxane cage, X-ray crystal structure, nanoassembly, conformation arrangement, thermal stability and odd-even alternation.

1 Introduction

Polyhedral Oligomeric Silsesquioxanes (POSS) are of interest as building blocks for inorganic/organic hybrid materials^{1, 2}, in which the inorganic segment is expected to provide particular properties, such as thermal stability for example, cardiovascular applications³ and, nanocomposites with excellent thermal properties.^{4, 5} POSS is a cage-like molecule with the formula (RSiO_{3/2})_n, abbreviated R_nT_n, where organic substituents (R_n) are attached to a silicon-oxygen cage. The most common POSS cages are found in the octahedral silsesquioxanes, which have a cubic structure and the formula (RSiO_{3/2})₈ and these are called T₈ cages. They are also of great interest because of their nanoscale inorganic core (Si₈O₁₂: 0.5 ± 0.7 nm) and highly symmetric octafunctionality, which makes these compounds ideal for use in the construction of inorganic/organic hybrid nanomaterials. and furthermore they are considered to be interesting model compounds for nanomaterials.⁶⁻⁸ Recently, we have developed a new synthetic route to simple silsesquioxane cages using tetra-*n*-butylammonium fluoride (TBAF in

THF) in the presence of small amounts of water (5%), to catalyze the hydrolysis of organyltrialkoxysilanes^{9, 10} ($\text{RSi}(\text{OR}')_3$ (where R is a chemically stable constituent and R' is alkyl)). The yields are in the range 20–95%, which is a great improvement on other literature routes. We have also investigated the possibility of encapsulating a fluoride ion within a silsesquioxane cage. Indeed, we have developed an interesting synthetic strategy to this new class of silsesquioxane cage such that we now have examples of a fluoride ion encapsulated in cages with a range of functionalities.^{11, 12} We have reported^{11, 12} also a facile, single-step strategy for the preparation of a novel class of POSS compound containing an encapsulated fluoride anion with electron-withdrawing groups attached, using tetrabutylammonium fluoride (TBAF) with traces of water, with or without a solvent. The products were prepared from commercially available materials such as $\text{EWG}-(\text{CH}_2)_n\text{-Si}(\text{OEt})_3$ (where $n = 1\text{--}3$ and EWG is an electron-withdrawing group). The electron-withdrawing group also needs to be a poor leaving group. Interestingly, this strategy led to only the T_8 cage as the dominant product with excellent yields, even on a large scale, 81–95% (**Scheme 1**). A wide range of interesting functionalities of $\text{T}_8[\text{EWG}-(\text{CH}_2)_n]_8\text{TBAF}$ have been synthesized.

Octafunctional octasilsesquioxanes are 1.2–1.4 nanometres in diameter and, from the perspective of nanoassembly, have functional groups in each octant of Cartesian space, such that, when they pack, they either align in quasi-linear self-assembly and layer-by-layer within a lamellar fashion, or interdigitate (**Figure 1**).

Figure 1. Possible octafunctional octasilsesquioxane packing models

In this work we are interested in details of the crystalline structures of POSS and their thermal behavior in terms of having a proper understanding of the crystalline structure in POSS-based nanomaterials or POSS blending polymer.

Our main interest in the identification and characterization of pertinent structural features of a series of hydrocarbon derivatives of T_8 , n -alkylsilsesquioxanes, was initially stimulated by the observation that T_8 cages with small, short chain substituents have molecular symmetry close to octahedral (O_h), whereas those with a bigger substituent have rod-like uniaxial symmetry (eg. D_{4h}).¹⁰

The first question was whether this change happens at a particular chain length, or whether it is a gradual process. A second reason for studying these compounds is that there is an interest in the packing of hydrocarbons^{13, 14} and the alkyl-substituted T_8 cages may be considered to resemble straight-chain alkanes in their packing arrangements. Additionally, functionalized silsesquioxanes are used increasingly in blends with polymers, and understanding how they pack may help in the understanding of the properties of these polymer blends.¹⁵ We were also interested in comparing the melting temperatures of the octa-*n*-alkyl-substituted octasilsesquioxane derivatives, $T_8(C_nH_{2n+1})_8$ (where $n = 2-18$), to provide information on their thermal behavior.

2 Experimental Section

Materials. Reagents were obtained from the Aldrich Chemical Company (alkene, trichlorosilane, Karstedt's catalyst, solvents). All reagents and silanes were stored under nitrogen. The platinum catalyst was a 0.02 molar solution of H_2PtCl_6 in *i*-propyl alcohol. Karstedt's catalyst (platinum-divinyltetramethyldisiloxane complex) was a 0.03 molar solution in xylene. Solvents used for synthesis: solvent purifications followed the procedures summarised: Hexane was stored over Linde 3 Å, molecular sieves, and distilled over sodium wire before use. Toluene was dried over calcium hydride powder, left for 24 h, and then distilled over sodium wire and benzophenone and stored over Linde 4 Å molecular sieves. Dichloromethane was dried and neutralized by passing it through an Al_2O_3 column, and degassed (deoxygenised) under vacuum while frozen in liquid nitrogen. All of the liquid substrates were dried and degassed by bulb-to-bulb distillation over 4 Å Linde molecular sieves unless otherwise stated.

Synthesis of alkyl-substituted octasilsesquioxanes

Using Olsson's method¹⁶ octaethyl T_8 , octa-*n*-propyl T_8 and octa-*n*-butyl T_8 were prepared by refluxing a dilute solution of the hydrolyzate of (C_nH_{2n+1}) trichlorosilane (where $n = 1-3$) in strong methanolic hydrogen chloride (**Scheme 1**). After work-up the residue was gradually heated to 225 °C in a sublimation apparatus at 5 mmHg and kept at this temperature for 30 minutes. The yield of crystals that sublimed into the receiver was 1.10 g, 35% (**2**); 1.4 g, 37% (**3**), and 1.4 g, 34% (**4**). Compounds **2** and **3** were recrystallized from different solvents, but unfortunately we could not obtain a crystal structures of **2**. Crystals of the ethyl-substituted octasilsesquioxane **2** undergo two phase transitions within the temperature range from 300K to 100K with lowering of the symmetry from rhombohedral to triclinic. At room temperature T_8 (ethyl)₈ exhibits a plastic phase.^{17, 18}

Scheme 1. Synthesis of the octa-*n*-alkylsilsesquioxanes **2-4**

We followed Agaskar's^{19, 20} synthetic route to accomplish the synthesis of the T_8H_8 cage (**1**): a polar solution containing methanol, hydrochloric acid and iron(III) chloride ($FeCl_3$) was mixed with a solution of trichlorosilane in a toluene/hexane solvent, giving a mixture of $T_8H_8/T_{10}H_{10}$ ($H_8Si_8O_{12}/H_{10}Si_{10}O_{15}$) that can be easily separated by washing with hexane to give the pure T_8H_8 with a yield of 17.5%. The syntheses of the octa-*n*-alkylsilsesquioxanes **4–15** have been achieved without solvent by the platinum-catalyzed hydrosilylation of octahydrogensilsesquioxane^{20, 21} with different terminal alkenes (C_nH_{2n} , where $n = 5–18$) in sealed vials (**Scheme 2**).

The solution was refluxed for 3 h with stirring. The disappearance of the Si–H bond ($\nu = 2250\text{ cm}^{-1}$) was confirmed by IR spectroscopy. After work-up the residue was subject to column flash chromatography on silica gel using hexane as the eluent. Product isolation was accomplished in near-quantitative yields with very little Markovnikov addition (α -addition), possibly due to the bulk of the silsesquioxane.²²

Scheme 2. Synthesis of the octa-*n*-alkylsilsesquioxanes **5–16** via hydrosilylation

These silsesquioxanes were characterized by 1H , ^{13}C and ^{29}Si -NMR spectroscopy, mass spectrometry and elemental analysis. The ^{13}C NMR spectra provide evidence that no Markovnikov addition (α -addition) had taken place. Mass spectroscopy and ^{29}Si -NMR confirm the identity, and the lack of additional signals and resonances suggests a high degree of purity. This is in agreement with data reported in the literature.^{20, 22}

Synthesis of octahydrosilsesquioxane (**1**)

Iron(III) chloride (anhydrous) (100 g, 616 mmol) was mixed with concentrated HCl (12 M, 40 cm³) in methanol (80 cm³), hexane (700 cm³) and toluene (100 cm³). A solution of trichlorosilane (50.86 cm³) in hexane (300 cm³) was added to the biphasic mixture drop by drop using a pressure equalizing funnel over a period of six hours. The reaction mixture was stirred for a further hour. The upper hexane layer was transferred to another round-bottom flask and stirred with sodium carbonate (28 g) and calcium chloride (20 g) overnight. After filtration, the solvent was removed using a rotary evaporator. A white solid was produced. This was recrystallized from hexane to give the pure product as white needle-shaped crystals (2 g, 8.7%). Mp < 300 °C (dec). 1H NMR (300 MHz, $CDCl_3$) /ppm: $\delta = 4.24$ (s, 8H, Si-H). ^{13}C NMR (75.5 MHz, $CDCl_3$) /ppm: 130.1 (CH), 136.1 (CH₂). ^{29}Si NMR (79.3 MHz, $CDCl_3$) /ppm: $\delta = -84$. IR (Nujol): ν/cm^{-1} 2960 (C-H), 2292 (Si-H), 1102 (Si-O), 862, 723.

Synthesis of octaethyloctasilsesquioxane (2)

To 110 cm³ of methanol in round-bottom flask 250 cm³ was added, while swirling by hand, (5 cm³) ethyltrichlorosilane, then rapidly methanolic hydrogen chloride, 70 cm³, and finally, again, rapidly 5 cm³ of concentrated HCl. The solution was refluxed for 48 h and the supernatant liquid was carefully decanted and discarded. The crude product was washed once with methanol and dissolved in a small amount of diethyl ether. The solution was transferred to a sublimation apparatus and the solvent carefully removed on a water bath. The residue was gradually heated to 225 °C at 10 mmHg and kept at this temperature for 30 m. The crystals sublimed into the receiver. The residue solidified on cooling to give a transparent resin of polysiloxanes. In order to remove lower and more volatile siloxanes the sublimate was recrystallized from 40 cm³ acetone. For analysis the product was recrystallized once more from acetone and sublimed *in vacuo* (1.10 g, 35%). Mp 281.8 °C. ¹H NMR (300 MHz, CDCl₃) /ppm: δ = 0.98 (t, 24H, ³J_{H,H} = 7.86 Hz, CH₃), 0.61 (t, 16H, ³J_{H,H} = 7.68 Hz, SiCH₂). ¹³C NMR (75.5 MHz, CDCl₃) /ppm: δ = 6.49 (SiCH₂), 4.08 (CH₃). ²⁹Si NMR (79.3 MHz, CDCl₃) /ppm: δ = -65.73. IR (KBr disk): ν/cm⁻¹ 2971 (ν_{C-H}), 2956 (ν_{C-H}), 2940 (ν_{C-H}), 2893, 1510, 1248, 1227, 1109 (ν_{as(Si-O-Si)}), 1008, 757, 692, 559 (ν_{s(Si-O-Si)}), 467 (ν_{Si-O}), 391. Elemental analysis calcd. for C₁₆H₄₀O₁₂Si₈ (M.W 649.17): %C = 29.60, %H = 6.21. Found %C = 29.01, %H = 6.31. MS (MALDI-TOF): m/z (%): 649.1 [M]⁺, 1010.6, 1001.6, 962.9, 934.9, 906.8, 751.5, 668.6, 650.1, 649.1, 638.4.

Synthesis of octa-*n*-propyloctasilsesquioxane (3)

To 110 cm³ methanol in a 250 cm³ flask was added, while swirling by hand, first ethyltrichlorosilane (5 cm³) dropwise, then rapidly 70 cm³ methanolic hydrogen chloride and finally rapidly 5.0 cm³ concentrated HCl. The solution was refluxed for 48 h. The supernatant liquid was carefully decanted and discarded. The crude product was washed once with methanol and dissolved in a small amount of diethyl ether. The solution was transferred to a sublimation apparatus and the solvent carefully removed on a water bath. The residue was gradually heated to 225 °C at 10 mmHg and kept at this temperature for 30 m. The crystals sublimed into the receiver. The residue solidified on cooling to give a transparent resin of polysiloxanes. In order to remove lower and more volatile siloxanes the sublimate was recrystallized from 40 cm³ acetone. For analysis the product was recrystallized once more from acetone and sublimed *in vacuo* (1.4 g, 37%). Mp 213.0 °C. ¹H NMR (300 MHz, CDCl₃) /ppm: δ = 1.44 (sextet, 16H, ³J_{H,H} = 7.5 Hz, CH₂), 0.96 (t, 24H, ³J_{H,H} = 7.35 Hz, CH₃), 0.61 (t, 16H, ³J_{H,H} = 7.68 Hz, SiCH₂). ¹³C NMR (75.5 MHz, CDCl₃) /ppm: δ = 17.33 (SiCH₂), 16.35 (CH₃), 14.43 (CH₂). ²⁹Si NMR (79.3 MHz, CDCl₃) /ppm: δ = -66.89. IR (KBr disk): ν/cm⁻¹ 2943 (ν_{C-H}), 2950 (ν_{C-H}), 2882, 1462, 1251 (ν_{C-H}), 1232, 1115, 1012 (ν_{as(Si-O-Si)}), 756, 691, 570 (ν_(O-Si-O)), 470 (ν_{Si-O}), 543, 385. Elemental analysis calcd. for C₂₄H₅₆O₁₂Si₈ (MW 761.38) %C = 37.68, %H = 7.41. Found: %C = 37.66, %H = 7.81. MS (MALDI-TOF): m/z (%): 1075.7, 1001.6, 885.3, 847.2, 761.38 [M]⁺, 761.2, 768.2 [M+Li]⁺, 751.5 [M+Li-Me]⁺, 668.6, 638.4, 522.6, 550.6.

Synthesis of octa-*n*-butyloctasilsesquioxane (4)

To 110 cm³ methanol in a 250 cm³ flask was added, while swirling by hand, first butyltrichlorosilane (5g) dropwise, then rapidly 70 cm³ methanolic hydrogen chloride, and finally rapidly 5.0 cm³ concentrated HCl. The

solution was refluxed for 48 h. The supernatant liquid was carefully decanted and discarded. The crude product was washed with methanol and dissolved in a small amount of diethyl ether. The solution was transferred to a sublimation apparatus and the solvent carefully removed on a water bath. The residue was gradually heated to 225 °C at 10 mmHg and kept at this temperature for 30 m. The crystals sublimed into the receiver. The residue solidified on cooling to give a transparent resin of polysiloxanes. In order to remove volatile siloxanes the sublimate was recrystallized from 40 cm³ of acetone. For analysis the product was recrystallized once more from acetone and sublimed *in vacuo*. Recrystallization from hexane gave colorless crystals (1.4 g, 34%). Mp: 70–72 °C. ¹H NMR (300 MHz, CDCl₃) /ppm: δ = 1.42–1.33 (m, 32H, CH₂), 0.88 (t, ³J_{H,H} = 7.05 Hz, 24 H, CH₃), 0.62 (t, ³J_{H,H} = 8.79 Hz, 16H, SiCH₂). ¹³C NMR (75.5 MHz, CDCl₃) /ppm: δ = 25.65, 25.02, 13.79, 11.67. ²⁹Si NMR (79.3 MHz, CDCl₃) /ppm: δ = –66.62. IR (KBr disc): ν/cm^{–1} 2931, 2923, 2864, 1462, 1454 (ν_{C-H}), 1272, 1261, 1104 (ν_{as(Si-O-Si)}), 720, 552 (ν_{s(Si-O-Si)}), 550 (ν_(O-Si-O)), 470 (ν_(Si-O)). X-ray data are given in the Supporting Information.

Synthesis of octa-*n*-pentyl octasilsesquioxane (5)

Octahydrosilsesquioxane (200 mg, 0.47 mmol) and pentene (264.38 mg, 3.78 mmol, 8.05 eq) in toluene (3 cm³) were placed in a small vial, and 200 μl of a 3 % solution of Karstedt's catalyst (Pt-divinyltetramethyldisiloxane complex) in xylene added. The mixture was stirred and heated at 80 °C. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{–1}. The solvent was removed under vacuum. The product was purified by chromatography using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent. The product was recrystallized from hexane to give the product (0.8g, 90%), mp: 24–25 °C. ¹H NMR (300 MHz, CDCl₃) /ppm: δ = 1.41–1.31 (m, 48H, CH₂), 0.88 (t, ³J_{H,H} = 7.10 Hz, 24 H, CH₃), 0.62 (t, ³J_{H,H} = 8.78 Hz, 16H, SiCH₂). ¹³C NMR (75.5 MHz, CDCl₃) /ppm: δ = 35.26, 22.56, 22.32, 13.95, 11.67. ²⁹Si NMR (79.3 MHz, CDCl₃) /ppm: δ = –66.48. IR (KBr disc): ν/cm^{–1}: 2931(ν_{C-H}), 2942 (ν_{C-H}), 2850 (ν_{C-H}), 1465 (ν_{C-H}), 1384, 1276, 1253, 1111, 1090 (ν_{as(Si-O-Si)}), 561. Elemental analysis calcd. for C₄₀H₈₈O₁₂Si₈ (M.W. 985.8): %C = 48.742, %H = 9.00. Found %C = 48.31, %H = 9.43. MS (MALDI-TOF): m/z (%): 985.4 [M+H]⁺, 991.4 [M+Li]⁺, 962.9, 934.8, 906.8, 878.8, 751.4, 696.6, 668.6, 640.6. This compound has been fully characterized, and X-ray data are given in the Supporting Information.

Synthesis of octa-*n*-hexyl octasilsesquioxane (6)

Octahydrosilsesquioxane (200 mg, 0.47 mmol) and 1-hexene (0.96 mg, 3.77 mmol, 8.02 eq) were placed in a small vial, and 10 μl of a Speier's catalyst, H₂PtCl₆ in isopropanol, added. The mixture was stirred and heated at 80 °C. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{–1}. The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent. The product was recrystallized from hexane (0.48g, 94%). Mp 28–30 °C. ¹H NMR (300 MHz, CDCl₃) /ppm: δ = 1.50–1.22 (m, 64H, CH₂), 0.88 (t, 24H, ³J_{H,H} = 6.57 Hz, CH₃), 0.60 (t, 16H, ³J_{H,H} = 6.78 Hz, SiCH₂). ¹³C NMR (75.5 MHz, CDCl₃) /ppm: δ = 32.37, 31.60, 22.77, 22.58, 14.12, 12.00. ²⁹Si NMR (79.3 MHz, CDCl₃) /ppm: δ = –66.65. IR (Nujol): ν/cm^{–1} 2956 (ν_{C-H}), 2926(ν_{C-H}), 2858 (ν_{C-H}), 1466, 1407, 1378, 1282, 1230, 1192, 1109 (ν_{as(Si-O-Si)}), 689, 561 (ν_(O-Si-O)), 470 (ν_(Si-O)).

Synthesis of octa-*n*-heptyloctasilsesquioxane (7)

Octahydrosilsesquioxane (600 mg, 1.41 mmol) and 1-heptene (1.1 g, 11.34 mmol, 8.03 eq) were placed in a small vial, and 60 μ l of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent. The product was recrystallized from hexane (1.57g, 92 %). Mp 31.4 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: δ = 1.50–1.27 (m, H, CH_2), 0.88 (t, 24H, J = 6.6 Hz, CH_3), 0.60 (t, 16H, J = 7.32 Hz, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: δ = 17.33 (SiCH_2), 16.35 (CH_3), 14.43 (CH_2). ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: δ = –66.64. IR (Nujol): ν/cm^{-1} 2730 ($\nu_{\text{C-H}}$), 2679 ($\nu_{\text{C-H}}$) ($\nu_{\text{as(Si-O-Si)}}$), 1231, 1175, 1120, 1021 ($\nu_{\text{as(Si-O-Si)}}$), 965, 786, 762, 689, and 660 ($\nu_{\text{s(Si-O-Si)}}$). X-ray data are given in the Supporting Information.

Synthesis of octa-*n*-octyloctasilsesquioxane (8)

Octahydrosilsesquioxane (600 mg, 1.41 mmol) and 1-octene (1.27 g, 11.34 mmol, 8.03 eq) were placed in a small vial, and 60 μ l of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent. The product was recrystallized from hexane (1.73g, 93% yield), mp: 39–41 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: δ = 1.50–1.26 (m, 96H, CH_2), 0.88 (t, 24H, J = 6.42 Hz, CH_3), 0.60 (t, 16H, $^3J_{\text{H,H}}$ = 7.14Hz, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: δ = 32.71, 31.98, 29.14, 13, 11.98. ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: δ = –66.64. IR (Nujol): ν/cm^{-1} 2752 ($\nu_{\text{C-H}}$), 1283 ($\nu_{\text{C-H}}$), 1243, 1198, 1130, 795, 795 and 711. MS (MALDI-TOF): m/z (%): 1320.82 [M^+], 1328.8 [$\text{M}+\text{Li}^+$], 1331.8, 1323.8 (isotopes). Elemental analysis calcd. for $\text{C}_{64}\text{H}_{136}\text{O}_{12}\text{Si}_8$ (M. W. 1322.44): %C = 58.13, %H = 10.37. Found; %C = 58.00, %H = 10.49. X-ray data are given in the Supporting Information.

Synthesis of octa-*n*-nonyloctasilsesquioxane (9)

Octahydrosilsesquioxane (600 mg, 1.41 mmol) and 1-nonene (1.43 g, 11.34 mmol, 8.03 eq) were placed in a small vial, and 15 μ l of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent. The product was recrystallized from hexane (1.9g, 93%). Mp 46–47 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: δ = 1.50–1.26 (m, 32H, CH_2), 0.88 (t, 24H, $^3J_{\text{H,H}}$ = 6.42 Hz, CH_3), 0.60 (t, 16H, $^3J_{\text{H,H}}$ = 6.6 Hz, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: δ = 32.75, 32.03, 29.65, 29.49, 29.45, 22.85, 22.78, 14.14, 1201. ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: δ = –66.64. IR (Nujol): ν/cm^{-1} 2863 ($\nu_{\text{C-H}}$), 2741 ($\nu_{\text{C-H}}$), 2675, 1410 ($\nu_{\text{C-H}}$), 1311, 1285, 1264, 1251, 1225, 1203, 1182, 1112, 892, 795, 764, 720, 571 ($\nu_{\text{(O-Si-O)}}$), 481 ($\nu_{\text{(Si-O)}}$). Elemental analysis calcd. for $\text{C}_{72}\text{H}_{152}\text{O}_{12}\text{Si}_8$: %C = 60.28, %H = 10.68. Found: %C = 6.28, %H = 10.69.

Synthesis of octa-*n*-decyloctasilsesquioxane (10)

Octahydrosilsesquioxane (400 mg, 0.94 mmol) and 1-decene (1.06 g, 7.55 mmol, 8.02 eq) were placed in a small vial, and 15 μ l of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent. The product was recrystallized from hexane (1.2g, 91%). Mp: 56–58 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: δ = 1.50–1.26 (m, 40H, CH_2), 0.88 (t, 24H, $^3J_{\text{H,H}}$ = 6.42 Hz, CH_3), 0.60 (t, 16H, $^3J_{\text{H,H}}$ = 6.96 Hz, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: δ = 32.73, 31.01, 29.77, 29.77, 29.68, 29.47, 29.43, 22.84, 22.75, 14.13, 11.99. ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: δ = –66.48. IR (Nujol): ν/cm^{-1} 2741 ($\nu_{\text{C-H}}$), 2672, 1412, 1293, 1276, 1265, 1242, 1216, 1205, 1185, 1114, 889, 852, 721, 709, 683, 562 ($\nu_{\text{O-Si-O}}$), 470 ($\nu_{\text{Si-O}}$). MS (MALDI-TOF): m/z (%): 1545.07 [M^+], 1569.1 [$\text{M}+\text{Na}^+$], 1572.1, 1549.1 (isotope). Analysis initially attempted with DCTB matrix and AgNO_3 cationizing agent, and DHB matrix with NaOAc , but both these approaches failed to give sample-related ions. Next, dithranol matrix with KOAc was tried, and a very weak [$\text{M}+\text{K}^+$] signal was observed. Further analyses with NaOAc and LiCl agents yielded the expected cationized species, with signal intensity increasing as the cations became smaller. Most lower-mass species are matrix related, but some may also be derived from the sample. Elemental analysis calcd. for $\text{C}_{80}\text{H}_{168}\text{O}_{12}\text{Si}_8$ (M.W 1546.87): %C = 62.12, %H = 10.95. Found: %C = 61.60, %H = 11.04. X-ray data are given in the Supporting Information.

Synthesis of octa-*n*-undecyloctasilsesquioxane (11)

Octahydrosilsesquioxane (200 mg, 0.47 mmol) and undecene (617.47 mg, 4.00 mmol, 8.50 eq) in toluene (1 cm^3) were placed in a small vial, and 200 μ l of a 3 % solution of Karstedt's catalyst (Pt-divinyltetramethyldisiloxane complex) in xylene added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified by chromatography using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent. Recrystallization from hexane afforded colorless crystals (0.6g, 85% yield). Mp 58–59 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: δ = 1.45–1.12 (m, 144H, CH_2), 0.88 (t, 24H, $^3J_{\text{H,H}}$ = 6.78 Hz, CH_3), 0.60 (t, 16H, $^3J_{\text{H,H}}$ = 8.07 Hz, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: δ = 32.7 (CH_2), 32.0 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3), 12.00 ($\text{CH}_2\text{-Si}$). ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: δ = –66.6. IR (Nujol): ν/cm^{-1} 2921 ($\nu_{\text{C-H}}$), 2852 ($\nu_{\text{C-H}}$), 1462, 1434, 1305, 1118.3, 957, 857, 570 ($\nu_{\text{O-Si-O}}$), 480 ($\nu_{\text{Si-O}}$). MS (MALDI-TOF): m/z (%) 1657.19 [M^+], 1681.2 [$\text{M}+\text{Na}^+$], 1665.2 [$\text{M}-\text{CH}_3 + \text{Na}^+$], 1659.2. Elemental analysis calcd. for $\text{C}_{88}\text{H}_{184}\text{O}_{12}\text{Si}_8$ (M.W 1659.08): %C = 63.71, %H = 11.18. Found; %C = 64.04, %H = 11.86.

Synthesis of octa-*n*-dodecyloctasilsesquioxane (12)

Octahydrosilsesquioxane (400 mg, 0.94 mmol) and 1-dodecene (1.27g, 7.55 mmol, 8.02 eq) were placed in a small vial, and 60 μ l of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H

bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent to obtain the title compound as a white solid (1.5g, 90%). Mp $67.5\text{--}68.5\text{ }^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: $\delta = 1.45\text{--}1.25$ (m, 64H, CH_2), 0.87 (t, 24H, $^3J_{\text{H,H}} = 6.52\text{ Hz}$, CH_3), 0.59 (t, 16H, $^3J_{\text{H,H}} = 7.52\text{ Hz}$, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: $\delta = 32.73$, 31.99, 29.83, 29.76, 29.45, 22.83, 22.74, 14.13, 11.99. ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: $\delta = -66.6$. IR (Nujol): ν/cm^{-1} 2732 ($\nu_{\text{C-H}}$), 2668 ($\nu_{\text{C-H}}$), 1412, 1311, 1297, 1278, 1271, 1253, 1243, 1226, 1209, 1182, 1116, 943, 923, 892, 866, 802, 775, 761, 723, 709, 561 ($\nu_{(\text{O-Si-O})}$), 470 ($\nu_{(\text{Si-O})}$). Elemental analysis calcd. for $\text{C}_{96}\text{H}_{200}\text{O}_{12}\text{Si}_8$ (M.W 1771.29): %C = 65.69, %H = 10.57. Found: %C = 65.08, %H = 11.31. MS (MALDI-TOF): m/z (%): 1769.32 [M^+], 1777.3 [$\text{M}+\text{Li}^+$], 1780.3 (isotope).

Synthesis of octa-*n*-tridecyloctasilsesquioxane (13)

Octahydrosilsesquioxane (200 mg, 0.47 mmol) and tridecene (729.4 mg, 4.00 mmol, 8.50 eq) in toluene (1 cm^3) were placed in a small vial, and 200 μl of a 3 % solution of Karstedt's catalyst (Pt-divinyltetramethyldisiloxane complex) in xylene added. The mixture was stirred and heated at $80\text{ }^{\circ}\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent to obtain the title compound as white solid (0.8g, 90%). Mp $64.5\text{--}65.4\text{ }^{\circ}\text{C}$. Recrystallization from hexane afforded colorless crystals. ^1H NMR (300 MHz, CDCl_3) /ppm: $\delta = 1.40\text{--}1.25$ (m, 176H, CH_2), 0.88 (t, 24H, $J = 6.39\text{ Hz}$, CH_3), 0.60 (t, 16H, $J = 7.14\text{ Hz}$, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: $\delta = 32.72$ (CH_2), 31.98 (CH_2), 29.82 (CH_2), 29.75 (CH_2), 29.69 (CH_2), 29.44 (CH_2), 22.83 (CH_2), 22.73 (CH_2), 14.14 (CH_3), 11.99 ($\text{CH}_2\text{-Si}$). ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: $\delta = -66.65$. IR (Nujol): ν/cm^{-1} 2968 ($\nu_{\text{C-H}}$), 2921, 2865, 1465, 1408, 1307, 1179, 1118, 888, 839, 571 ($\nu_{(\text{O-Si-O})}$), 474 ($\nu_{(\text{Si-O})}$). MS (MALDI-TOF): m/z (%): 1882.2 [M^+], 1840.0 [$\text{M}-\text{C}_3\text{H}_7^+$], 1826.1 [$\text{M}-\text{C}_4\text{H}_9^+$], 1812.0 [$\text{M}-\text{C}_5\text{H}_{11}^+$], 1797.9 [$\text{M}-\text{C}_6\text{H}_{13}^+$], 1797.9 [$\text{M}-\text{C}_7\text{H}_{15}^+$], 1770.9 [$\text{M}-\text{C}_8\text{H}_{17}^+$], 1755.9 [$\text{M}-\text{C}_9\text{H}_{19}^+$], 1727.8 [$\text{M}-\text{C}_{11}\text{H}_{23}^+$], 1699.7 (100%) [$\text{T}_8(\text{C}_{13}\text{H}_{27})_7 + \text{H}^+$], [$\text{T}_8(\text{C}_{13}\text{H}_{27})_6 + 2\text{H}^+$].

Synthesis of octa-*n*-tetradecyloctasilsesquioxane (14)

Octahydrosilsesquioxane (400 mg, 0.94 mmol) and 1-tetradecene (1.48g, 7.55 mmol, 8.02 eq) were placed in a small vial, and 60 μl of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at $80\text{ }^{\circ}\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent. A white solid was obtained after removal of the solvent (1.75g, 93%). Mp $74\text{--}75\text{ }^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: $\delta = 1.50\text{--}1.25$ (m, 72H, CH_2), 0.87 (t, 24H, $^3J_{\text{H,H}} = 6.42\text{ Hz}$, CH_3), 0.59 (t, 16H, $^3J_{\text{H,H}} = 6.78\text{ Hz}$, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: $\delta = 32.73$, 31.99, 29.84, 29.74, 29.70, 29.45, 22.84, 22.74, 14.14, 11.99. ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: $\delta = -66.48$. IR (Nujol): ν/cm^{-1} 2935 ($\nu_{\text{C-H}}$), 2913 ($\nu_{\text{C-H}}$), 2846, 1466, 1093 ($\nu_{\text{as}(\text{Si-O-Si})}$), 722. Elemental analysis calcd. for $\text{C}_{112}\text{H}_{232}\text{O}_{12}\text{Si}_8$ (M.W 1995.72): %C = 67.40, %H = 11.72. Found: %C = 64.62, %H = 11.38. MS (MALDI-TOF): m/z (%): 1993.57 [M^+], 2001.6 [$\text{M}+\text{Li}^+$], 2004.6 (isotope).

Synthesis of octa-*n*-hexadecyloctasilsesquioxane (15)

Octahydrosilsesquioxane (400 mg, 0.94 mmol) and hexadecene (1.69 g, 7.55 mmol, 8.02 eq) were placed in a small vial, and 60 μ l of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent. The product was obtained as white solid (1.9g, 91%). Mp 77–78 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) /ppm: δ = 1.45–1.21 (m, 88H, CH_2), 0.88 (t, 24H, $^3J_{\text{H,H}}$ = 6.6 Hz, CH_3), 0.59 (t, 16H, $^3J_{\text{H,H}}$ = 7.88 Hz, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: δ = 32.71, 31.96, 29.82, 29.77, 29.70, 29.41, 22.82, 22.71, 14.13, 11.97. ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: δ = -66.6. IR (Nujol): ν/cm^{-1} 2922 ($\nu_{\text{C-H}}$), 2850 ($\nu_{\text{C-H}}$), 1465 (ν_{CH_3}), 1376, 1177, 1119, 1092 ($\nu_{\text{as(Si-O-Si)}}$), 762, 720, 680 ($\nu_{\text{s(Si-O-Si)}}$), 570 ($\nu_{(\text{O-Si-O})}$), 480 ($\nu_{(\text{Si-O})}$). Elemental analysis calcd. for $\text{C}_{128}\text{H}_{264}\text{O}_{12}\text{Si}_8$ (M.W 2220.14): %C = 69.25, %H = 11.98. Found; %C = 69.03, %H = 12.05. MS (MALDI-TOF): m/z (%): 2220.14 [M^+], 2226.8 [M+Li^+], 2232.8 (isotope).

Synthesis of octa-*n*-octadecyloctasilsesquioxane (16)

Octahydrosilsesquioxane (400 mg, 0.94 mmol) and 1-octadecene (1.90 g, 7.54 mmol, 8.02 eq) were placed in a small vial, and 10 μ l of Speier's catalyst, H_2PtCl_6 in isopropanol, added. The mixture was stirred and heated at 80 $^\circ\text{C}$. The reaction was followed by IR spectroscopy and reaction was stopped on disappearance of the Si-H bond stretch at 2256 cm^{-1} . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane as eluent to obtain the title compound as a waxy product (2.1g, 91%). ^1H NMR (300 MHz, CDCl_3) /ppm: δ = 1.50–1.22 (m, 64H, CH_2), 0.88 (t, 24H, $^3J_{\text{H,H}}$ = 6.57 Hz, CH_3), 0.60 (t, 16H, $^3J_{\text{H,H}}$ = 6.78 Hz, SiCH_2). ^{13}C NMR (75.5 MHz, CDCl_3) /ppm: δ = 32.71, 31.95, 29.83, 29.580, 29.75, 29.70, 29.43, 29.40, 22.82, 22.71, 14.13, 11.97. ^{29}Si NMR (79.3 MHz, CDCl_3) /ppm: δ = -66.6. IR (Nujol): ν/cm^{-1} 2945 ($\nu_{\text{C-H}}$), 2844 ($\nu_{\text{C-H}}$), 2845 ($\nu_{\text{C-H}}$), 1468 ($\nu_{\text{C-H}}$), 1121, 1090 ($\nu_{\text{as(Si-O-Si)}}$), 721, 560 ($\nu_{(\text{O-Si-O})}$), 470 ($\nu_{(\text{Si-O})}$). MS (MALDI-TOF): m/z (%): 2444.57 [M^+], 2444.0, 2345.8 ($\text{M}-\text{C}_7\text{H}_{15}$), 2219.8 ($\text{M}-\text{C}_{16}\text{H}_{33}$), 2190.8 ($\text{M}-\text{C}_{18}\text{H}_{37}$), 2033.5, 1937.6, 1700.3, 1684.3, 1448.1 ($\nu_{\text{C-H}}$), 1432.1. Elemental analysis calcd. For $\text{C}_{144}\text{H}_{296}\text{O}_{12}\text{Si}_8$ (M.W 2444.57): %C = 70.75, %H = 12.20. Found; %C = 70.63, %H = 12.51. MS (ESI negative ion): m/z (%) 2219.8 [$\text{M}-\text{C}_{16}\text{H}_{23}$] $^+$, 2190.8 (100%) [$\text{M}-\text{C}_{18}\text{H}_{37}$] $^+$, 2444.0 [M^+].

Characterization. All NMR spectra were obtained using either a JEOL EX 400 NMR and JEOL lambda 300 NMR spectrometer instrument and chemical shifts are reported in parts per million (δ ppm). The pulse delay for ^{29}Si NMR spectra were standardised at 20 seconds in order to minimize (negative) nuclear Overhauser effects unless stated otherwise. ^1H , ^{13}C and ^{29}Si NMR spectra were recorded at room temperature (25 $^\circ\text{C}$), using deuterated chloroform (CDCl_3). The NMR internal reference compound was Tetramethylsilane (TMS) (δ 0.0). The spectral data point position of these compounds was accurately located before acquisition. Coupling constants for all spectra are reported in Hertz (Hz). FT-IR spectra were recorded on a Nicolet – 205 FT-IR spectrometer or Perkin-Elmer 1710 Infrared Fourier Transform instrument in the range 400-4000 cm^{-1} in Nujol. Melting Points were determined on an Electrothermal Digital melting point apparatus. MALDI-TOF and ESI

experiments were performed by the National Mass Spectrometry Service Centre based at the University of Wales, Swansea, UK. Micro-analysis of the samples was performed by MEDAC Ltd. of Brunel University, UK. Analytical thin-layer chromatography was performed using silica gel 60 F254 pre-coated plates (0.25 mm thickness) with a fluorescent indicator. Flash column chromatography was performed using silica gel 60 (230-400 mesh) from EM Science. Pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS): samples were pyrolyzed using a CDS Pyroprobe 5000 connected via a 1500 valve interface to an Agilent Technologies 6890 gas chromatograph coupled to an Agilent technologies 5973 mass selective detector. The GC was fitted with a SGE BPX5 capillary column (30 m; 0.25 mm ID; 0.25 μ m film thickness). The MSD was operated in electron ionization mode at 70 eV, scanning a mass range of 50-400 amu. The samples were pyrolyzed at 610 °C at a rate of 20 °C ms⁻¹ where they were held for 15 s under a He flow with the interface at 250 °C. The GC injector was operated in split mode (20:1) at a temperature of 250 °C and with a column flow rate of 1.1 ml min⁻¹. The oven temperature was held at 30 °C for 2 min then programmed to 250 °C at 5 °C min⁻¹. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of 20 and 10 °C/min using TGA- STA 1500 rheometric scientific and Mettler Toledo DSC822 instruments, respectively.

X-ray Crystallography. Crystals of **4**, **5**, **7**, **7b**, and **8** (as well as the poor-quality crystals of **6** and **11** that did not lead to satisfactory structure refinements) were examined at 120 K with Bruker-Nonius rotating-anode X-ray sources (Mo K α radiation, λ = 0.71073 Å) and CD detectors at Southampton University. Data for the weakly-scattering crystals of **6b** and **10** were obtained with synchrotron radiation (λ = 0.6946 Å) at Daresbury SRS station 9.8 with a Bruker APEXII CCD diffractometer; the data collection temperature was 210 K because further cooling led to significant crystal degradation, probably with phase transitions. Minor disorder was resolved in the case of **5**. Details of crystallographic data and results are in the Supporting Information. Programs were standard Bruker and Nonius control and data processing software, members of the SHELX/SHELXTL family,^{23, 24} local programs, and Mercury.^{25, 26} Mercury 3.0 software (crystal structure visualization) has been used to measure and display distances, angles and torsion angles.

3 Results and discussion

3.1 Single-crystal X-ray diffraction of octa-*n*-alkylsilsesquioxanes

We have investigated by X-ray crystallography the crystal structures of the series of octa-*n*-alkylsilsesquioxanes (where *n* = 3–18) and the self-assembly structure of octa-*n*-alkylsilsesquioxane molecules. The first crystallographic analysis of polyhedral organosilsesquioxanes was carried out by Barry,²⁷ who studied the smallest alkylsilsesquioxane octamers (methyl-, ethyl-, *n*-propyl- and *n*-butylsilsesquioxanes). The efficiency of the packing is influenced mostly by the size of the attached organic groups. Barry studied the effect of the different organic substituents on the crystal cell parameters^{17, 28, 29} and found that the intra-plane packing of the POSS molecules is relatively open. More precise crystal structures of some of these compounds were achieved later.^{26–28}

Recently, we have reported the rod-like structure of $T_8[n-C_8H_{17}]_8$ ¹⁰ (**8b**), where the octyl chains do not interdigitate with neighboring molecules, and the arrangement is reminiscent of mesogenic silsesquioxane compounds. The rod-like packing system of octa-*n*-octylsilsesquioxanes allows an inter-layer distance of 8.519 Å, which is only a little longer than the shortest corresponding inter-layer distance in T_8Me_8 , 8.441 Å.³⁰

To date, no investigations have been carried out on the analogous crystal structures of other $T_8(C_nH_{2n+1})_8$ where $n > 4$. We have succeeded in crystallizing such a series of *n*-alkylsilsesquioxanes octamers from $n = 4$ to $n = 11$. We obtained suitable crystals of most of the octa-*n*-alkylsilsesquioxane series by slow evaporation of a single solvent, or co-solvent system, at room temperature. X-ray crystallography data are tabulated in **Table 1**. Single-crystal X-ray data reveal the expected structures in the triclinic space group $P\bar{1}$ and half of the centrosymmetric molecule in the asymmetric unit for most of the silsesquioxanes. Exceptions are compounds **5** and **7b** which have the tetragonal space group $P4/n$ and with one-quarter of each of four and two independent molecules in the asymmetric unit, respectively (**Figure 2**). In addition, the long *c* axis increases as a function of the length of the organic substituents for the triclinic structures with one molecule in the unit cell.

Figure 2. The four and two independent molecules, respectively, in the tetragonal crystal structures of octapentyloctasilsesquioxane **5** (A) and octaheptasilsesquioxane **7b** (B), with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity

Table 1. Crystallographic data and the solvents used for recrystallization of T₈(C_nH_{2n+1})₈

Entry	11 ^a T ₈ Undecyl ₈	10 T ₈ Decyl ₈	8 T ₈ Octyl ₈	8b T ₈ Octyl ₈	7 T ₈ Heptyl ₈	7b T ₈ Heptyl ₈	6 ^a T ₈ Hexyl ₈	6b T ₈ Hexyl ₈	5 T ₈ Pentyl ₈	4 T ₈ Butyl ₈
Chain	C11	C10	C8	C8	C7	C7	C6	C6	C5	C4
Crystals grown from	Chloroform	Hexane	Hexane	Hexane	Hexane/ MeOH	Hexane	Hexane	Hexane	Hexane	Hexane
Temperature (K)	293	210	120	120	120	120	120	210	120	120
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Tetragonal	Triclinic	Triclinic	Tetragonal	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 4/ <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 4/ <i>n</i>	<i>P</i> $\bar{1}$
Unit cell dimensions										
<i>a</i> (Å)	8.741(3)	8.554(5)	8.5348(2)	8.5186(4)	8.5414(10)	21.4407(4)	8.999(4)	8.664(4)	26.4815(5)	9.5947(9)
<i>b</i> (Å)	9.359(4)	9.232(5)	9.1768(3)	9.1418(4)	8.9275(12)	21.4407(4)	9.301(4)	9.475(4)	26.4815(5)	9.6312(8)
<i>c</i> (Å)	33.642(13)	30.970(18)	25.1451(9)	25.8700(13)	23.110(3)	15.4535(3)	18.938(5)	20.486(8)	15.6221(5)	13.6739(13)
α (deg)	85.540(10)	97.556(6)	85.506(1)	80.073(2)	84.579(6)	90	80.88(2)	78.122(4)	90	75.877(6)
β (deg)	84.988(11)	93.843(6)	84.329(2)	82.611(2)	87.068(7)	90	81.96(2)	80.489(4)	90	80.373(4)
γ (deg)	84.278(11)	97.615(6)	87.938(2)	84.185(3)	89.294(8)	90	84.65(2)	85.953(4)	90	80.569(5)
Volume (Å ³)	2721.4(18)	2394(2)	1952.96(11)	1961.52(16)	1752.0(4)	7104.0(2)	1545.6(11)	1621.9(12)	10955.3(5)	1198.09(19)
Z	1	1	1	1	1	4	1	1	8	1
Density (calculated) (g / cm ³)	1.012	1.073	1.124	1.120	1.147	1.132	1.180	1.124	1.195	1.211
CSD Refcode or deposition	-	882280	882279	HALJEK	882276	882275	-	894863	882278	882277
Reference	This work	This work	This work	10	This work	This work	This work	This work	This work	This work

^aPreliminary data were obtained for these structures, but they were of poor quality from non-single crystal samples and satisfactory structure refinement could not be achieved; limited results are included here for comparison with other polymorphs with precisely determined structures.

We have been unable to obtain crystals of $T_8(C_nH_{2n+1})_8$, where $n = 14, 16$ and 18 , that were suitable for single-crystal X-ray structure determination. Although these compounds appear to be highly crystalline, we were unable to grow large crystals.

However, powder X-ray diffraction can be used to investigate the long-range order of these materials, and provides complementary information regarding the crystal phase present and the size of crystallites.

The powder X-ray diffraction (XRD) patterns (X-ray wavelength = $1.5406 \text{ \AA}$ for CuK_{α}) of $T_8(C_{14}H_{29})_8$ (**14**) and $T_8(C_{18}H_{37})_8$ (**16**) are shown in **Figure 3**. These compounds show some similarity in their XRD patterns, and both of them exhibit three principal diffraction peaks. The X-ray diffraction pattern of $T_8(C_{14}H_{29})_8$ (**14**) exhibits Bragg peaks at $2\theta = 20.82, 22.54$, and 23.82° corresponding to $d = 4.26, 3.94$, and $3.73 \text{ \AA}$, respectively. $T_8(C_{18}H_{37})_8$ (**16**) gives Bragg peaks at $2\theta = 21.04, 22.78$, and 24.04° corresponding to $d = 4.22, 3.90$, and $3.69 \text{ \AA}$, respectively. The two structures are thus likely to be rather similar.

Figure 3. Powder XRD patterns of $T_8(C_{14}H_{29})_8$ (**14**) and $T_8(C_{18}H_{37})_8$ (**16**)

3.2 Polymorphic forms of *n*-alkyl-POSS

The phenomenon of polymorphism, in which a compound can adopt more than one crystal structure, is well known³¹ and currently the subject of both experimental³² and theoretical interest.^{33, 34} Central to the understanding of the origin and control of polymorphic form is the ability to describe and interpret the essential similarities and differences in intermolecular interactions in a series of polymorphic structures. In some cases these may be rather straightforward, as in the pairs **6** and **6b**, and **8** and **8b** (**Figure 5**), where differences in packing occur for molecules of similar conformation. Alternatively it may be the result of some gross difference in conformation of the molecule in the different structures, as in **7** and **7b** (**Figure 4**).

Table 1 gives the crystallographic data for each of the pairs of polymorphs **7** and **7b** (which were recrystallized from different solvents), and **8** and **8b**, for which pairs reliable precise structures have been determined. The three structures **7**, **8** and **8b** belong to the triclinic space group $P\bar{1}$ with a single centrosymmetric molecule in the unit cell. However, **7b** has the tetragonal space group $P4/n$ with two independent molecules each lying on a C_4 rotation axis. Inspection of the structures **7** and **7b** did not reveal any packing similarities (**Figure 4**). **8** and **8b** were crystallized from the same solvent (hexane), and they differ only in the detailed conformation of the alkyl chains of the molecules (**Figure 5**). In these cases factors such as the temperature of recrystallization, the concentration of the compound in solution, purity of the solvent, and the rate of recrystallization may influence the final crystal form. The octa-*n*-heptyloctasilsesquioxane **7** was crystallized using hexane/methanol as solvent system and its X-Ray crystal structure reveals that the molecules align in quasi-linear self-assembly and in a laminar structure (**Figure 4-7**). However, when only hexane was used for recrystallization, the X-Ray crystal structure reveals that the alkyl chains interdigitate in a three-dimensional fashion as shown in **Figure 4-7b**. The effect of solvent on the morphology of octa-*n*-heptyloctasilsesquioxane is unknown. These structures are the result of a fine balance of van der Waals interactions between the hydrocarbon chains and the cage framework.³⁵

Figure 4 X-Ray crystal structures of octa-*n*-heptyloctasilsesquioxane, **7** and **7b**, with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

Figure 5 X-Ray crystal structures of octa-*n*-heptyloctasilsesquioxane, **8** and **8b** (from reference 10), with displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

3.3 Packing behavior of structurally different *n*-alkyl-substituted polyhedral oligomeric silsesquioxanes

n-Alkyl-POSS molecules have alkyl chains that are flexible and a POSS cage that is rigid, leading to a range of potential crystal packing arrangements or polymorphs. The highest symmetry structure arrangement of a nanostructure POSS cage with eight substituents is one in which the substituents point away from the vertices of a cube and leave large spaces between them (**Figure 1b**). However, such an arrangement is inefficient in terms of packing, leaving much empty space. In fact the alkyl substituents are relatively flexible in the POSS molecules and crystallize in a range of different conformations. The two most common packing arrangements of alkyl-POSS cages are (a) one in which the substituents around a pair of opposite faces align orthogonal to these two faces to provide a rod-like geometry and organize themselves into layers, as shown in **Figure 1c**, and (b) one in which the substituents on two opposite faces of the POSS core are spaced out radially in the plane of the face to form a more disk-like structure which forms columns that can be arranged parallel to each other in a two-dimensional lattice.

The rod-like structure can be clearly seen for $T_8[n-C_7H_{15}]_8$ (**7**), $T_8[n-C_8H_{17}]_8$ (**8b**), $T_8[n-C_{10}H_{21}]_8$ (**10**) and $T_8[n-C_{11}H_{23}]_8$ (**11**), where the alkyl arms do not interdigitate with neighboring molecules, and also in $T_8[n-C_4H_9]_8$ (**4**) and $T_8[n-C_6H_{13}]_8$ (**6**, **6b**), where the alkyl arms do interdigitate to some extent with neighboring molecules, resembling to some extent **1d**. However, the disk-like structure is seen in $T_8[n-C_5H_{11}]_8$ (**5**) and $T_8[n-C_7H_{15}]_8$ (**7b**). The occurrence of these two arrangement in our alkylsilsesquioxane series are pointed reminiscent of packing of some mesogenic compounds mainly in calamitic liquid crystals (a rod-like structure composed of two or more aromatic and aliphatic rings connected in one direction) or discotic liquid crystals (the flat-shaped aromatic core that makes molecules stack in one direction is defined as the mesogen).³⁶

Further aspects of interest in the packing structures of T_8R_8 species are: the arrangement of the substituents around the POSS core; the closest cage-center to cage-center distances for each structure; closest contacts for different cages; and the distances between arms in the same molecular cage.

These properties are examined below and more details are provided of each compound's structure. The packing system will be systematically discussed in terms of the two different morphological categories: the rod-like structure and the disk-like structure.

3.3.1 The rod-like structure morphology

Many liquid crystals³⁷ are based on rod-like building blocks, held together by a combination of hydrogen bonding, π - π stacking and van der Waals interactions. The silsesquioxane cage has been functionalized with a variety of mesogens to give liquid crystalline compounds.³⁸ Whilst we have not examined in detail the liquid crystalline properties of octa-*n*-alkylsilsesquioxane, we have studied their rod-like packing systems, which reveal similarities in packing along the *b* axis. For comparison, all the packing systems of this series are viewed along the *b* axis of the unit cell in the following Figures, and the hydrogen atoms have been omitted for clarity.

Octa-*n*-butylsilsesquioxane **4** formed laminar parallel layers (**Figure 6**). The closest cage-center to cage-center distance is about 9.595 Å, which is a little longer than the shortest analogous distance in the T_8 octyl₈ structure, 9.519 Å, and in the T_8 Me₈ structure, 8.441 Å. The arms are packed with interdigitation to some extent.

Figure 6. Packing diagram of $T_8\text{butyl}_8$ (**4**) viewed along the b axis of the unit cell

The packing diagram shows that the alkyl substituents are distorted away from the lines extending to the vertices of a cube in order to minimize the free space in the crystal structure. The butyl arms from the same cage are aligned and the distance between the two arms increases slowly with the distance from the cage (the shortest distance that separate two arms in the same cage is 4.186 Å and the longest distance is 6.280 Å) (**Figure 7**).

Figure 7. Molecular structure of $T_8\text{butyl}_8$ (**4**)

Octa-*n*-hexylsilsesquioxane **6b** also forms parallel layers similar to **4**. The interlayer distance is slightly decreased to about 8.999 Å compared with **4** and **8b**. The alkyl groups are slightly interdigitated. As we have seen previously in the crystal structure of **4**, the hexyl arms are aligned and the distance between two arms increases smoothly with increasing length of the chain. The shortest distance that separates the two arms in the cage is 4.290 Å and longest distance is 5.905 Å, less than that measured for **4**.

Octa-*n*-heptylsilsesquioxane (**7**) also forms parallel layers similar to (**4**) and (**6b**) (**Figure 8**). In this case, the alkyl chains of the neighboring molecules do not interdigitate but pack and align themselves antiparallel to each other with respect to the layers, leaving a gap within the layers of 3.525 Å. The closest contact between the alkyl

chains in the layer is about 3.525 Å and the closest cage-center to cage-center distance is decreased to 8.541 Å, smaller than that in **4** and **6b**.

Figure 8. Packing diagram of $T_8\text{heptyl}_8$ (**7**) viewed along the b axis of the unit cell

In the case of octa- n -octylsilsesquioxane (**8**) the layered packing shows tilted chains with respect to the basal plane of the cage³⁹ (although in all rod-like structures the alkyl chains run approximately parallel to each other) (**Figure 9**). This packing behavior is not observed for the short alkyl-chain analogues **4**, **6b** and **7**. The tilting of the side chains and the layers allows them to close-pack into a structure with little free volume, which loosely approximates to the observed packing pattern of saturated hydrocarbons with increasing alkyl chain length.⁴⁰

The octyl chains of the neighboring molecules of octa- n -octylsilsesquioxane do not interdigitate but are aligned antiparallel to each other with respect to the layers, leaving a gap within the layers. The closest contact between the alkyl chains in the layer is about 4.063 Å, and the closest cage-center to cage-center distance of 8.535 Å is virtually the same as 8.541 Å in **7**. The shortest distance that separates the two arms in the same cage is 3.996 Å and the longest distance is 5.507 Å.

Figure 9. Packing diagram of $T_8\text{octyl}_8$ (**8**) viewed along the b axis of the unit cell

A recognizable tilt is also observed in the octa- n -decylsilsesquioxane **10**. The packing diagram of **10** shows that the closest contact of the alkyl chains between the two layers is slightly smaller (3.731 Å) than in **8**. The decyl

chains in the same POSS cages of **10** are aligned so that the shortest distance that separates the two arms in the same cage is about 4.113 Å, and the longest distance is 5.537 Å.

As we have seen, the crystals contain molecules packed with different systems, leaving some space within the layers and between the alkyl chains in the same cage. In order to correlate the free spaces in the crystal structures, the distances illustrated in **Figure 10** of the $T_8(C_nH_{2n+1})$ crystal structures have been calculated and tabulated in **Table 3**.

Figure 10. The measured distances of $T_8(C_nH_{2n+1})_8$ crystal structures. For clarity hydrogen atoms have been omitted.

Table 2 shows that the intermolecular distances between the end groups of the even- and odd-numbered *n*-alkyl chains, namely the CH₃ groups, in the crystal lattice are frequently separated by between 3.50 and 4.50 Å, apart from **6b** (C6(b)) which has a larger distance at 6.078 Å. The Si...Si distances reveal that the distances between the layers are generally in the range 7.90–9.60 Å; however, the Si...Si distance of **8** (C8(b)) is considerably longer at 12.58 Å.

Table 2. Data of distances in crystal structures of $T_8(C_nH_{2n+1})_8$									
Entry Chain	11 C11	10 C10	8 C8	8b C8(b)	7 C7	7b C7(b)	6b C6(b)	5 C5	4 C4
Closest contacts end to end [Å]	3.654	3.731	4.063	6.078	3.525	3.739	4.542	3.762	3.828
Si...Si [Å]	8.741	8.554	8.535	12.580	8.541	7.980	9.475	8.007	9.595
Shortest contacts between alkyl chains [Å]	4.243	4.113	3.803	4.012	3.945	4.651	4.120	4.604	5.094
Longest contacts between alkyl chains [Å]	5.523	5.537	5.278	5.606	5.621	9.357	5.650	13.469	6.028

3.3.2 The disk-like structure morphology

Disk-like self-organizing systems have been observed widely in liquid crystals and micelles.^{41, 42} Here, we demonstrate a disk-like morphology which has been observed, for the first time, in two of our octa-*n*-alkylsilsesquioxanes, namely, octa-*n*-pentylsilsesquioxane (**5**) and octa-*n*-heptylsilsesquioxane (**7b**), both crystallizing in the tetragonal system in contrast to the other triclinic members of the series. Both of these compounds are substituted with an odd number of carbon atoms (*n* = 5 and 7). Inspection of the disk-like structures reveals packing similarities along the *c* axis. Subsequently, for the purpose of comparison, all packing systems of this series are viewed along the *c* axis of the unit cell.

The crystallographic data reveal that octa-*n*-pentylsilsesquioxane (**5**) and octa-*n*-heptylsilsesquioxane (**7b**) both crystallize in the tetragonal crystal system with space group $P4/n$ and with four and two independent molecules, respectively, one-quarter of these constituting the asymmetric unit in each case. Octa-*n*-pentylsilsesquioxane (**5**) has a highly interdigitated crystal structure (**Figure 11**). The eight ligands point approximately to the vertices of a larger cube (O_h -like symmetry). In this conformation there is much space between the ligands, and efficient packing would not be possible without interdigitation.

The shortest chain distance between two cages, one on the top of another, is about 3.762–3.778 Å, and the shortest chain distance between vertically adjacent cages is about 3.915 Å. Interestingly, there is a puckered four-carbon chain, aligned with a similar chain from a different cage in an anti-parallel arrangement. The shortest distance between these two folded chains is about 4.384 Å.

Figure 11. Crystal structures of $T_8\text{pentyl}_8$ (**5**) (A) and $T_8\text{Heptyl}_8$ (**7b**) (B)

When the octa-*n*-heptylsilsesquioxane crystal structure (**7b**) is viewed along the *a* axis we can see (**Figure 11**) that the heptyl chains interdigitate with those of adjacent molecules in the crystal lattice. This interdigitation results in the four heptyl chains pointing away from the vertices of a cube, leaving a large space between them (**Figure 12**). The shortest chain distance between the two cages (stacked exactly one above the other) is about 3.739 Å, and the shortest chain distance between two vertically adjacent cages is about 3.840–3.903 Å, which is slightly smaller than that measured for **5**. The long-range packing reveals that the disk-like form (**Figure 12**) leads to columns of interdigitated cages.

Figure 12. Packing diagrams of $T_8pentyl_8$ (5) (A) and $T_8heptyl_8$ (7b) (B)

Interestingly, the packing diagram of $T_8heptyl_8$ (7b) shows the molecules to be arranged in a distorted columnar hexagonal array when viewed along the c axis (**Figure 12**).

The core–core separation in the columnar packing of $T_8pentyl_8$ (5) is of the order of 7.789 Å (**Figure 13A**), so that there is a considerable distance between cages. Since the aliphatic chains that surround the core interdigitate, the intercolumnar distance is 13.182 Å (**Figure 13B**). This suggests that interactions between neighboring alkyl chains within the same column are likely to be stronger than interactions between neighboring columns.

Figure 13. The core–core separation and the intercolumnar distance in the columnar packing of $T_8pentyl_8$ (5) viewed along the a axis (i) and c axis (ii) of the unit cell.

In the columnar packing of $T_8heptyl_8$ (7b) the core–core separation is not significantly different from (5), 7.795 Å (**Figure 14A**). This distance again represents a considerable gap. As the aliphatic chains that surround the core interdigitate, the intercolumnar distances depend on the lateral chain length, and for 7b this is 14.158 Å and 21.441 Å in different directions (**Figure 14B**). Therefore, as before, interactions between neighboring alkyl arms within the same column are likely to be stronger than interactions between neighboring columns.

Figure 14. The core–core separation and intercolumnar distances in the columnar packing of T_8 heptyls (**7b**) viewed along the a axis (A) and c axis (B) of the unit cell

The packing systems in **5** and **7b** are similar, resembling a 3D intermeshing gear.⁴³ These arrangements are reminiscent of crystalline molecular machines.⁴⁴

3.4 Stereochemistry of hydrocarbon-functionalized POSS cages

The crystal structures of octa- n -alkylsilsesquioxanes can adopt a different packing behavior, depending upon the chain length. We have also examined the stereochemistry of each of the eight alkyl chains of each cage. We have used Mercury 2.3 software⁴² in order to understand the conformation and packing behavior of the chains within the lattice. We have calculated the chain torsion angles of octa- n -alkylsilsesquioxanes. An analysis of all the torsional angle data of the octa- n -alkylsilsesquioxanes reveals both staggered and antiperiplanar skeletal geometry of the alkyl chains. The rod-like geometry is facilitated by two opposing pairs of alkyl chains having a *gauche* conformation for the SiCCC torsion angles (Figure 15). Interestingly, some small twists away from the antiperiplanar conformations were observed in the terminal torsion angle of some of the alkyl chains (for **10**, **8b** and **6b**).

Figure 15. *Gauche* conformation for the SiCCC torsion angles

3.5 Odd–even effect on the densities and melting properties of octa- n -alkyl silsesquioxanes

An odd–even alternating effect has been previously reported for the melting temperatures of n -alkanes by Boese *et al.*⁴⁰ The experimental X-ray densities of n -alkanes reported by Boese⁴⁰ also show a clear odd–even effect. The densities of the alkanes usually increase with the increasing number of carbon atoms.

Bolln *et al.*²² first demonstrated that the melting temperatures of the homologous series of octa-*n*-alkyl-substituted T₈ derivatives (T₈(*n*-C_nH_{2n+1})₈ where n=1–10) do not show a monotonic increase with increasing chain length. Instead the melting temperatures of the members with an even number of carbon atoms are higher than those members with odd numbers. This result is exactly what had been originally proposed by Baeyer⁴⁵ in 1877 about the melting temperatures of fatty acids.

Our interest is focused on the effect of odd- and even-numbered alkyl chains on the thermal behavior of the homologous series of octa-*n*-alkyl-substituted T₈ derivatives T₈(*n*-C_nH_{2n+1})₈ (where n=2–18) and on their densities. The melting temperatures of the octa-*n*-alkylsilsesquioxanes have been determined using an electrothermal digital melting point apparatus. The values obtained were in good agreement with those that have been reported by Bolln *et al.*²²

Table 3 below shows the melting temperatures of T₈(*n*-C_nH_{2n+1})₈ together with the densities calculated from X-ray data. Compound **3** displays a relatively high melting temperature (281–282 °C), whereas the melting temperatures of **4** (71.3 °C) and **5** (25.0 °C) are much smaller. To understand the change in the melting temperature of **4** and **5**, we need to examine the packing diagrams of **4** and **5**. **4** is packed in the rod-like form, and the butyl groups interdigitate, leaving less free space in the crystal structure, and this leads to an increase in van der Waals forces, such that it requires more energy to separate the molecules. By contrast, **5** is packed in a columnar form, and while the pentyl chains interdigitate with adjacent molecules, the packing diagram reveals more free space and thus weaker van der Waals interaction.

Table 3. The melting temperatures and densities of the T₈(*n*-C_nH_{2n+1})₈ with decreasing number of carbon atoms.

	Entry	Chain	Mp (°C)	Density (g.cm ⁻³)
T ₈ (Octadecyl) ₈	16	C18	81.3	
T ₈ (Hexadecyl) ₈	15	C16	77.5	
T ₈ (Tetradecyl) ₈	14	C14	75.2	
T ₈ (Tridecyl) ₈	13	C13	65.4	
T ₈ (Dodecyl) ₈	12	C12	68.5	
T ₈ (Undecyl) ₈	11	C11	59.2	1.012
T ₈ (Decyl) ₈	10	C10	58.4 (60.5) ^a	1.073
T ₈ (Nonyl) ₈	9	C9	47.1 (47.6) ^a	
T ₈ (Octyl) ₈	8	C8	41.2 (51.0) ^a	1.124
T ₈ (Heptyl) ₈	7	C7	31.4 (31.5) ^a	1.147
T ₈ (Hexyl) ₈	6b	C6	28.5 (36.5) ^a	1.124
T ₈ (Pentyl) ₈	5	C5	25.0 (24.0) ^a	1.195
T ₈ (Butyl) ₈	4	C4	71.3 (69.5) ^a	1.211
T ₈ (Propyl) ₈	3	C3	213.0 (212.0) ^a	
T ₈ (Ethyl) ₈	2	C2	281.9 ^b	

^b lit. 282–285°C (reported by Olsson, 1958)¹⁶

^a reported by Bolln *et al.*²²

The trends in the melting temperatures of the octa-*n*-alkylsilsesquioxanes with longer *n*-alkyl chains, from **5** to **18**, show a clear odd-even effect, in which the compounds with an odd number of carbon atoms display generally lower melting temperatures (**Figure 16**). A similar behavior is seen for the melting temperatures of several other homologous series. The trends also show that with short alkyl chains the T₈ unit predominantly determines the packing patterns and interactions of the molecules; in contrast, for longer *n*-alkyl chains the flexible alkyl chains control the packing in a in a most probably layered type of packing.²² The even-numbered *n*-alkyl chains pack more efficiently. The reasons for this are not immediately apparent.

Figure 16. Trends in the melting temperatures of T₈(*n*-C_nH_{2n+1})₈ with increasing number of carbon atoms.

Figure 17 below shows that the experimental X-ray densities of the T₈(*n*-C_nH_{2n+1})₈ series (*n*=4–11) that we obtained decreases more-or-less monotonically with extending chain length and we do not observe an odd-even effect like that of *n*-alkane densities.⁴⁰

Figure 17. Trend in the densities of the octa-*n*-alkylsilsesquioxanes with increasing number of carbon atoms.

3.6 Thermogravimetric analysis (TGA) studies

Thermogravimetric analysis (TGA) was employed to study the thermal degradation of the T₈(*n*-C_nH_{2n+1})₈ series (*n*=3–18) under a nitrogen atmosphere (**Figure 18**).

The TGA curves show no weight loss at around 100°C, which demonstrates that the compounds are anhydrous. They also show that, with increasing alkyl chain length, the onset of the weight loss is found to shift to higher temperatures (166 °C for $n = 3$, 353 °C for $n = 10$). The total weight loss of all $T_8(n-C_nH_{2n+1})_8$ derivatives at 500 °C is above 80%, and is thus larger than the organic fraction of the materials. This is probably due to partial sublimation of the compounds under the nitrogen atmosphere.^{22, 46}

Figure 18. TGA traces of 3–18 under N₂ atmosphere

3.7 Pyrolysis-GC-MS of $T_8(n-C_{11}H_{23})_8$ and $T_8(n-C_{18}H_{37})_8$

Pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS) has been used to elucidate the thermal degradation process of $T_8(n-C_nH_{2n+1})_8$ ($n = 11$ and 18) ($[C] = 1\text{mg}/1\text{ml}$). Figure 19 shows the chromatograms obtained, suggesting that for $T_8(n-C_{11}H_{23})_8$ and $T_8(n-C_{18}H_{37})_8$ thermal cracking of the alkyl chain is observed rather than simple loss of the complete arm.

(A)

(B)
Figure 19. Chromatogram of pyrolysed $T_8(n-C_{11}H_{23})_8$ (A) and $T_8(n-C_{18}H_{37})_8$ (B)

Conclusions

The members of the series of octa-*n*-alkylsilsesquioxanes were prepared by hydrosilylation of H_8T_8 with *n*-alkenes in good yields and many have also been characterized using single-crystal X-ray crystallography. The octa-*n*-alkylsilsesquioxanes either align in quasi-linear self-assembly and layer-by-layer within a lamellar fashion, or interdigitate. Some of them can adopt different polymorphic forms. Two types of packing systems have been observed, rod-like and disk-like. In addition, some alkylPOSS crystals were formed in which the chains are tilted. It was also observed that the alkyl chains are flexible and can take up a variety of conformations. A *gauche* conformation was observed for the SiCCC torsion angles, and also some small twists away from the antiperiplanar conformations in the terminal torsion angle of some even-numbered alkyl chains of *n*-alkylPOSS. The homologous series exhibits high melting points for compounds with short alkyl chains, and relatively low melting points with an odd-even effect for alkyl chains longer than four CH_2 units. An odd-even effect of densities of *n*-alkylPOSS was not observed, in contrast to *n*-alkanes. The TGA of *n*-alkylPOSS has shown that, on increasing the alkyl chain length, the weight loss onset shifts to a higher temperatures and the total weight loss of all $T_8(n-C_nH_{2n+1})_8$ derivatives at 500 °C exceeds 80%, which is larger than the organic fraction of the materials; this may be due to partial sublimation of the compounds under the nitrogen atmosphere. Thermal cracking of the alkyl chain was observed rather than simple loss of the complete arm in pyrolysis-gas chromatography/mass spectrometry for two of the compounds.

This study provides a detailed description of the crystal packing of octa-*n*-alkylsilsesquioxanes as well as their conformation, polymorphic behavior and thermal stability, which could have a use in developing materials or templating polymer structures by addition of suitable silsesquioxanes.

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Supporting Information Available: Crystallographic information for 7 structures in cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>. The structures have also been deposited at the Cambridge Crystallographic Data Centre, and the respective deposition numbers are given in Table 1; the data may be retrieved from <http://www.ccdc.cam.ac.uk/products/csd/request/> by quoting these numbers.

References and notes

1. Lickiss, P. D.; Rataboul, F. *Adv. Organomet. Chem* **2008**, 57, 1-116.
2. Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, 110, (4), 2081-2173.
3. Ghanbari, H.; Mel, A. d.; Seifalian, A. M. *Int. J. Nanomedicine.* **2011**, 6 775-786.
4. Wallace, W. E.; Guttman, C. M.; Antonucci, J. M. *J. Am. Soc. Mass. Spectrom.* **1999**, 10, (3), 224-230.
5. Tsuchida, A.; Bolln, C.; Sernetz, F. G.; Frey, H.; Mülhaupt, R. *Macromolecules* **1997**, 30, (10), 2818-2824.
6. Suresh, S.; Zhou, W.; Spraul, B.; Laine, R. M.; Ballato, J.; Smith, D. W. *J. Nanosci. Nanotechnol.* **2004**, 4, (3), 250-253.
7. Laine, R. M. *J. Mater. Chem.* **2005**, 15, (35-36), 3725-3744.
8. Kannan, R. Y.; Salacinski, H. J.; Butler, P. E.; Seifalian, A. M. *Acc. Chem. Res.* **2005**, 38, (11), 879-884.
9. Bassindale, A. R.; Liu, Z.; MacKinnon, I. A.; Taylor, P. G.; Yang, Y.; Light, M. E.; Horton, P. N.; Hursthouse, M. B. *Dalton Trans.* **2003**, (14), 2945-2949.
10. Bassindale, A. R.; Chen, H.; Liu, Z.; MacKinnon, I. A.; Parker, D. J.; Taylor, P. G.; Yang, Y.; Light, M. E.; Horton, P. N.; Hursthouse, M. B. *J. Organomet. Chem.* **2004**, 689, (21), 3287-3300.
11. Bassindale, A. R.; Pourny, M.; Taylor, P. G.; Hursthouse, M. B.; Light, M. E. *Angew. Chem. Int. Ed.* **2003**, 42, (30), 3488-3490.
12. Bassindale, A. R.; Parker, D. J.; Pourny, M.; Taylor, P. G.; Horton, P. N.; Hursthouse, M. B. *Organometallics.* **2004**, 23, (19), 4400-4405.
13. Nelson, P. N.; Ellis, H. A. *Dalton. Trans.* **2012**, 41, (9), 2632-2638.
14. Simon, S. A.; McIntosh, T. J. *BBA-Biomembranes* **1984**, 773, (1), 169-172.
15. Li, G.; Wang, L.; Ni, H.; Pittman, C. U. *J. Inorg. Organomet. Polym.* **2001**, 11, (3), 123-154.
16. Olsson, K. *Ark. Kemi* **1958**, 13, 367.
17. Larsson, K. *Ark. Kemi* **1960**, 16, 209-214.
18. Georg, H. M.; Isabel, M. S. *Appl. Organomet. Chem.* **1999**, 13, (4), 261-272.
19. Agaskar, P. A. *Inorg. Chem* **1991**, 30, 2707.
20. Bassindale, A. R.; Gentle, T. E. *J. Mater. Chem.* **1993**, 3, (12), 1319-1325.
21. Herren, D.; Bürgy, H.; Calzaferri, G. *Helv. Chim. Acta* **1991**, 74, (1), 24-26.
22. Bolln, C.; Tsuchida, A.; Frey, H.; Mülhaupt, R. *Chem. Mater.* **1997**, 9, (6), 1475-1479.
23. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112-122.
24. Sheldrick, G. M. *SADABS, Program for area detector adsorption correction, Institute for Inorganic Chemistry, University of Gottingen, Germany.* **1996**.
25. Van Der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A.* **1990**, 46, (3), 194-201.
26. Spek, A. L. *Acta Cryst* **2009**, D65, 148-155
27. Barry, A. J.; Daudt, W. H.; Domicone, J. J.; Gilkey, J. W. *J. Am. Chem. Soc.* **1955**, 77, (16), 4248-4252.
28. Larsson, K. *Ark. kemi.* **1960**, 6, 203.
29. Larsson, K. *Ark. kemi* **1960**, 16, 215.

30. Handke, B.; Jastrzębski, W.; Mozgawa, W.; Kowalewska, A. *J. Mol. Struct.* **2008**, 887, (1–3), 159-164.
31. Hiremath, R.; Basile, J. A.; Varney, S. W.; Swift, J. A. *J. Am. Chem. Soc.* **2005**, 127, (51), 18321-18327.
32. Davey, R. J.; Blagden, N.; Potts, G. D.; Docherty, R. *J. Am. Chem. Soc.* **1997**, 119, (7), 1767-1772.
33. Woodley, S. M.; Battle, P. D.; Gale, J. D.; Richard, A.; Catlow, C. *PCCP* **1999**, 1, (10), 2535-2542.
34. Price, S. L.; Wibley, K. S. *J. Phys. Chem. A* **1997**, 101, (11), 2198-2206.
35. Rademeyer, M.; Kruger, G. J.; Billing, D. G. *CrystEngComm* **2009**, 11, (9), 1926-1933.
36. Miao, J.; Zhu, L. *J. Phys. Chem. B* **2010**, 114, (5), 1879-1887.
37. Yongtao, S.; Xizeng, F.; QiLin, C.; Xiao, P. *Chem. J. Internet.* **2005**, 7, 30.
38. Saez, I. M.; Goodby, J. W. *J. Mater. Chem.* **2005**, 15, (1), 26-40.
39. Mohanambe, L.; Vasudevan, S. *J. Phys. Chem. B* **2006**, 110, (29), 14345-14354.
40. Boese, R.; Weiss, H.-C.; Bläser, D. *Angew. Chem. Int. Ed.* **1999**, 38, (7), 988-992.
41. Percec, V.; Cho, C. G.; Pugh, C.; Tomazos, D. *Macromolecules* **1992**, 25, (3), 1164-1176.
42. Cuesta, J. A.; Sear, R. P. *Eur. Phys. J. B* **1999**, 8, (2), 233-243.
43. Perret, F.; Lazar, A. N.; Shkurenko, O.; Suwinska, K.; Dupont, N.; Navaza, A.; Coleman, A. W. *CrystEngComm* **2006**, 8, (12), 890-894.
44. Khuong, T.-A. V.; Nuñez, J. E.; Godinez, C. E.; Garcia-Garibay, M. A. *Acc. Chem. Res.* **2006**, 39, (6), 413-422.
45. Baeyer, A. *Ber. Chem. Ges* **1877**, "From this compilation it can be seen that without any exception a member with an odd number of carbon atoms has a lower melting point than that with an additional carbon atom, while in both series the melting points increase with the exception of the first members. If there is a general law in this pattern it would be the easiest to study the melting points of the anilides and normal fatty acids and it would be desirable that colleagues who have the necessary material available would expand our knowledge in this direction. A law which would say that in homologous series a odd number of carbon atoms has a relatively lower melting point than those with an even number would have a considerable interest in molecular physics and ask for investigations if the crystal form, solubility etc. are correlated with the nature of the number, which is expressed by the quantity of carbon atoms", 10, 1286.
46. Mantz, R. A.; Jones, P. F.; Chaffee, K. P.; Lichtenhan, J. D.; Gilman, J. W.; Ismail, I. M. K.; Burmeister, M. J. *Chem. Mater.* **1996**, 8, (6), 1250-1259.