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14. ABSTRACT Polyhedral oligomeric silsesquioxane (POSS) compounds comprised of a functionalized silicon-oxygen core framework have received much interest as robust nanoscale building blocks for the development of high performance materials. Notable applications include surface modified supports, ¹ semiconducting materials, ² atomic oxygen resistant coatings, ³ and high use temperature composites. ⁴ A plethora of POSS compounds with the general formula (RSiO _{1.5}) ₈ can be prepared possessing a rigid, cubic core diameter of 0.3–1.0 nm through either an acid- or base-catalyzed condensation with functionalized organosilane monomers (e.g., RSiCl ₃ or RSi(OMe) ₃). ⁵ Derivatized nanosized POSS silicas can be incorporated into polymers assembling architectures such as, but not limited to blended composites, ⁶ branched polymers, ⁷ as well as incompletely condensed cages. ⁸ Such hybrid organic-inorganic systems show an improvement of polymer properties such as glass transition, mechanical toughness, chemical resistance, ease of processing, fire resistance, and atomic oxygen permeability.					
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Hydrophobic and Oleophobic Fluoroalkyl Functionalized Silsesquioxane Nanostructures

(Preprint)

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Polyhedral oligomeric silsesquioxane (POSS) compounds comprised of a functionalized silicon-oxygen core framework have received much interest as robust nanoscale building blocks for the development of high performance materials. Notable applications include surface modified supports,¹ semiconducting materials,² atomic oxygen resistant coatings,³ and high use temperature composites.⁴ A plethora of POSS compounds with the general formula (RSiO_{1.5})₈ can be prepared possessing a rigid, cubic core diameter of 0.3–1.0 nm through either an acid- or base-catalyzed condensation with functionalized organosilane monomers (e.g., RSiCl₃ or RSi(OMe)₃).⁵ Derivatized nanosized POSS silicas can be incorporated into polymers assembling architectures such as, but not limited to blended composites,⁶ branched polymers,⁷ as well as incompletely condensed cages.⁸ Such hybrid organic-inorganic systems show an improvement of polymer properties such as glass transition, mechanical toughness, chemical resistance, ease of processing, fire resistance, and atomic oxygen permeability.

Attempts to fabricate low-energy surfaces, by mimicking plants and insects in nature, to produce ultrahydrophobic materials continues to gain interest.⁹ Of particular interest, many plant species including the lotus leaf exhibit a peculiar self-cleaning mechanism as result of micron-sized nodes decorated on the leaf surface.¹⁰ Coined the “lotus leaf effect”, the intrinsic non-wetting mechanism induces water beading and is naturally repelled from the surface removing any foreign debris.¹¹ In addition, insect species such as water strider possess oriented spindled microsetae that induce a non-wetting effect allowing this class of spider to walk on the surface of water.¹² There are many reported approaches that successfully produce artificial biologically replicated non-wetting surfaces including self-assembly¹³ and chemical deposition¹⁴ of low surface energy molecules, fabrication of micron-sized ordered arrays by lithography,¹⁵ and etching a surface to generate nano- and micron-sized roughness.¹⁶ However, these approaches produce materials that require harsh chemical and/or thermal treatments, use of expensive starting materials, require arduous lithography methods, produce inhomogeneous layered surfaces, generate poorly adhered non-covalent coatings, and almost all such techniques lack the ability to achieve a viable material for scale-up.

Herein, we present a new class of functionalized POSS compounds that possess a nanometer-sized fluorinated shell of fluoroalkyl appendages around the core POSS scaffold. The products were prepared from commercially available materials, eliminating the need for elaborate air/moisture sensitive manipulations, and they are amenable to a hundred-gram scale. By utilizing the ability to functionalize POSS templates, the formulation of such fluorine-derived siloxanes demonstrated a high degree of oleophobicity in addition to hydrophobicity. We introduce these thermally robust POSS materials as low surface energy compatibilizers for solvent, melt, or mechanical blending into polymer systems. Using these fluoroalkyl POSS compounds as modifiers could potentially yield water and oil repellant nanocomposites with enhanced physicochemical properties.

Corner capped POSS compounds **2–7** were prepared by the condensation of the hepta(3,3,3-trifluoropropyl)tricycloheptasiloxane trisodium silanolate **1** with fluoroalkyltrichlorosilanes in the presence of triethylamine (Scheme 1). Corner capping with commercially available functionalized

fluoroalkylchlorosilanes affords diverse architectures producing variable linear chain extensions (2–5), a branched structure (6), and a branched ether (7). The preparation of 2 has been reported elsewhere by base-catalyzed condensation of (3,3,3-trifluoropropyl)trichlorosilane, albeit in poor yields, requiring extensive reaction time for conversion leading to a mixture of octahedral (T_8) and decahedral (T_{10}) structures.¹⁷ In comparison, this corner capping methodology offers improved yields (73–83%) of functionalized compounds 2–7 with the exclusive formation of desired T_8 cages. In addition to full characterization employing multinuclear NMR (^1H , ^{13}C , ^{19}F , and ^{29}Si), an X-ray structure of 2 was resolved as shown in Figure 1. Furthermore, an interesting physical property-structural relationship was observed for compounds 2–5. Melting points were depressed from 2 (234–237 °C) as linear fluoroalkyl chain length increased for compounds 3–5 (88–107 °C). Since attempts to grow crystals of 3–5 were difficult due to poor intermolecular Si-F bonding, it does support the observation for the lowering of melting points. The decrease in melting points is valued for suitability in low temperature melt processing of fluoroalkyl POSS for the preparation of nanocomposites.

Contact angle measurements were performed on spin casted surfaces of POSS compounds 2–7 using water drop shape analysis (Table 1). The application of water and hexadecane on these surfaces showed non-wetting behavior and are considered hydrophobic and oleophobic, respectively. Water drops did not adhere to the film surface, showing a minimal degree of hysteresis, and rolled off as the film was tilted beyond 90°. The prepared films possess micron-scaled surface roughness that contributes to the non-wetting behavior known as the Cassie state.^{16e} As an example, Figure 2 shows the surface a spin cast film of 4 that measures an average surface roughness of 20 nm. As the morphology is similar with all spin cast films of 2–5, it was shown that the nature of hydro- and oleophobicity is also attributed to the extent of fluorine content around the POSS core shell. A contact angle comparison by corner capping 1 with an aliphatic group 8 ($\text{R} = \text{CH}_3$) and an aromatic group 9 ($\text{R} = \text{CH}_2\text{CH}_2\text{Ph}$) lowered the water contact angle by 10%, but significantly decreased the oil repellency by 36% on average. Hyperbranching as shown for 6 was observed to produce the highest degree of water and oil repellency.

Furthermore, hydrophobicity was lowered for **7** due to surface hydrogen bonding of a measured water drop with the ether functionality inducing wetting; however, oil repellency was unaffected.

We have demonstrated a new class of fluorinated POSS materials possessing both a high degree of water and oil repellency. By controlling the degree of fluorine as well as spatial substitution, we were able to tune the materials to exhibit desired wetting and processing properties. We anticipate these materials will be used as drop-in modifiers for composite blends to enhance mechanical and physiochemical properties.

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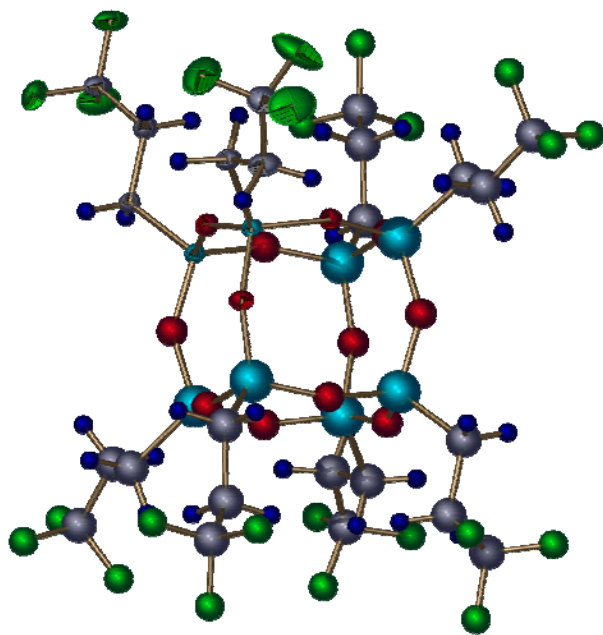


Figure 1. X-Ray structure of **2**.

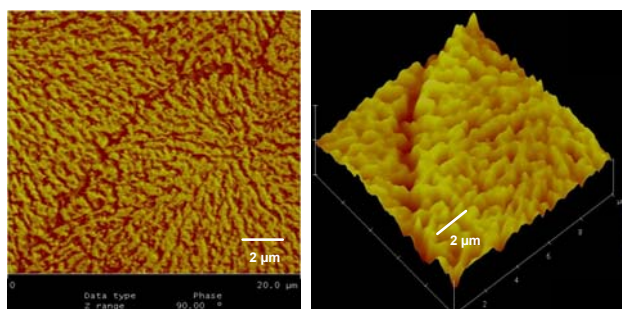


Figure 2. AFM of **4** taken of a spin cast film with notable surface roughness (right inset).

Scheme 1. Preparation of Fluoroalkyl₈T₈ POSS Corner Capped Materials via Condensation with Trisodium Silanolate **1.**

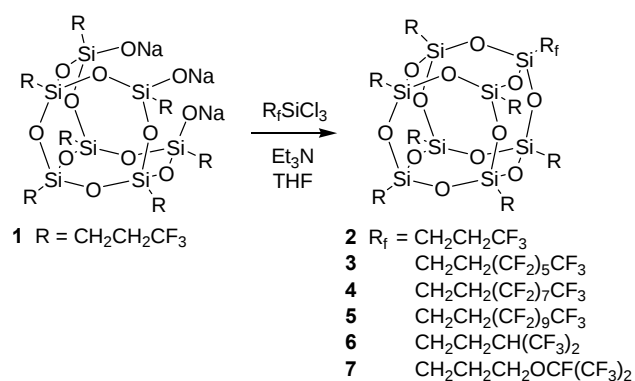
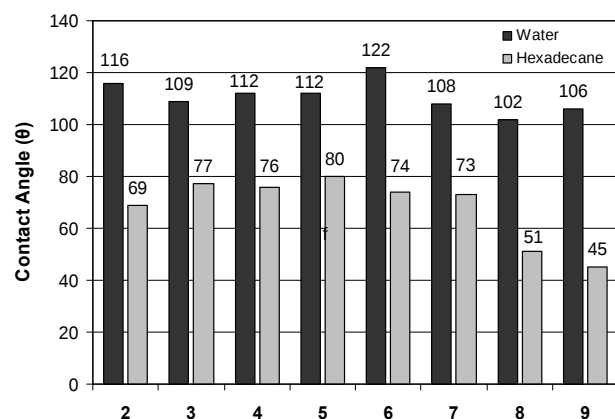


Table 1. Water and Hexadecane Contact Angles of Fluoroalkyl₈T₈ POSS.

Supporting Information Available: Characterization of all new compounds and X-ray structural information on **2** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Supporting Information

Materials. (3-Heptafluoroisopropoxy)propyltrichlorosilane, (3,3,3-trifluoropropyl)trichlorosilane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane, and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane were purchased from Gelest and used without further purification. Hexafluoroisobutene and propylheptafluoroisobutylethertrichlorosilane, 1H,1H,2H,2H-perfluorododecyltrichlorosilane was obtained from SynQuest. Fluorochemicals. Hepta(3,3,3-trifluoropropyl)tricycloheptasiloxane trisodium silanolate **1** was prepared using a procedure published elsewhere.¹ All other materials were purchased from Aldrich and purified by standard methods.²

General Experimental Methods. All reactions were carried out under an atmosphere of nitrogen unless otherwise indicated. Flasks were oven or flamed-dried and allowed to cool in dry box or desiccator prior to use. ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR data was obtained on a Bruker AXS SMART APEX and chemical shifts were reported in part per million (δ ppm). ¹H NMR was reported downfield from tetramethylsilane (δ 0.0) and are, in all cases, referenced to the residual proton resonance peaks: δ 7.24 for chloroform-*d* and δ 2.09 for acetone-*d*₆. The ¹³C NMR chemical shifts were reported in ppm relative to the center peak of the multiplet for deuterated solvents: δ 77.0 (t) for chloroform-*d* and 30.6

for acetone- d_6 . ^{19}F NMR was referenced to CFCl_3 and recorded with proton decoupling. ^{29}Si NMR was referenced to tetramethylsilane (δ 0.0) and was recorded with inverse-gated proton decoupling with a 12 second pulse delay in order to minimize (negative) nuclear Overhauser effects. Coupling constants for all spectra are reported in Hertz (Hz). Melting points (mp) were measured using a Mel-Temp melting point apparatus and are uncorrected.

Contact Angle Measurements. Powder films were prepared by dissolving the fluoroalkyl POSS in the minimal amount of hexafluorobenzene followed by mechanical agitation. The films were spin cast at 2500 RPM onto borosilicate glass plates producing a well-adhered coating. Contact angle analysis was performed on a FDS Dataphysics Contact Analyzer System. The contact angles were determined via the software suite or via graphical fitting of the contact tangents in the captured image. Both approaches gave the same nominal value within ± 2 degrees. Static contact angle values reported were an average of three values measured on various areas of the coated surface.

X-Ray Structure of 2. Crystallographic data for **2** was been submitted to the Cambridge Crystallographic Data Center with publication number CCDC 629369. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

Octa(3,3,3-trifluoropropyl)- T_8 -Silsesquioxane (2). Compound **2** was synthesized using a modified preparation reported initially by Fukada.¹ This variation was observed to produce a higher yield of **2** compared to the aforementioned reported procedure. To a stirred solution of hepta(3,3,3-trifluoropropyl)tricycloheptasiloxane trisodium silanolate **1** (4 g, 3.5 mmol) in THF (70 mL, 0.05 M) is added 3,3,3-trifluoropropyltrichlorosilane (0.871 mL, 5.25 mmol) at room temperature. Triethylamine (0.488 mL, 3.5 mmol) is then immediately added drop wise to the mixture. The mixture was stirred at room temperature for 3 h. After filtering the white precipitated salts, the filtrate was concentrated under reduced pressure. The crude product was then suspended in methanol, collected by vacuum filtration, washed repeatedly with methanol, and dried under reduced pressure to obtain the title compound as a free flowing white powder (3.71 g, 76%). Mp 234–237 °C (from THF); ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 300

MHz): δ 2.35–2.28 (m, 16H), 1.04–0.99 (m, 16H); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$, 75 MHz): δ 128.1 (q, $J = 274$ Hz), 27.4 (q, $J = 30.2$ Hz), 4.0, –0.5 (t, $J = 25.5$ Hz); ^{29}Si NMR ($(\text{CD}_3)_2\text{CO}$, 59.6 MHz): δ –67.3; ^{19}F NMR ($(\text{CD}_3)_2\text{CO}$, 376 MHz): δ –69.8 (24F); Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{F}_{24}\text{O}_{12}\text{Si}_8$: C, 24.16; H, 2.70; F, 38.21. Found: C, 21.16; H, 2.70; F, 38.21.

Tridecafluoro-1,1,2,2-tetrahydrooctylhepta(3,3,3-trifluoropropyl)- T_8 -Silsesquioxane (3).

Tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (1.54 mL, 5.25 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)- T_8 -silsesquioxane **2** to obtain the title compound as a white solid (4.12 g, 82%). Mp 104–106 °C (from THF); ^1H NMR ($(\text{CD}_3)_2\text{CO}$ with 10 vol% THF, 300 MHz): δ 1.06–1.02 (m, 14H), 2.38–2.29 (m, 14H); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$ with 10 vol% THF, 75 MHz): δ 128.0 (q, $J = 275$ Hz), 125.0–115.0 (m, unresolved complex peak splitting), 27.9 (q, $J = 30.1$ Hz), 26.3 (t, overlap with THF peak), 4.5, 2.5; ^{29}Si NMR ($(\text{CD}_3)_2\text{CO}$ with 10 vol% THF, 59.6 MHz): δ –67.2, –67.4; ^{19}F NMR ($(\text{CD}_3)_2\text{CO}$, 283 MHz): δ –69.2–(–69.3) (m, 21F), –81.6 (t, $J = 9.9$ Hz, 3F), –116.2 (t, $J = 13.2$ Hz, 2F), –121.7 (2F), –123.4 (2F), –123.9 (2F), –126.7 (2F); Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{F}_{24}\text{O}_{12}\text{Si}_8$: C, 24.13; H, 2.23; F, 44.76. Found: C, 24.25; H, 2.12; F, 44.97.

Heptadecafluoro-1,1,2,2-tetrahydrodecylhepta(3,3,3-trifluoropropyl)- T_8 -Silsesquioxane (4).

Heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (1.80 mL, 5.25 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)- T_8 -silsesquioxane **2** to obtain the title compound as a white solid (4.30 g, 80%). Mp 88–90 °C (from THF); ^1H NMR ($(\text{CD}_3)_2\text{CO}$, 300 MHz): δ 2.39–2.30 (m, 14H), 1.61–1.00 (m, 14H); ^{13}C NMR ($(\text{CD}_3)_2\text{CO}$ with 50 vol% hexafluorobenzene, 100 MHz): δ 127.5 (q, $J = 205.4$ Hz), 122.0–107.0 (m, unresolved complex peak splitting), 27.4 (q, $J = 30.0$ Hz), 24.5 (t, $J = 21.0$ Hz), 3.5, 1.3; ^{29}Si NMR ($(\text{CD}_3)_2\text{CO}$, 59.6 MHz): δ –67.2, –67.3; ^{19}F NMR ($(\text{CD}_3)_2\text{CO}$, 376 MHz): δ –69.8 (21F), –82.2 (3F), –116.9 (2F), –122.8–(–124.5) (10F), –127.3 (2F); Anal. Calcd for $\text{C}_{31}\text{H}_{32}\text{F}_{38}\text{O}_{12}\text{Si}_8$: C, 24.13; H, 2.09; F, 46.78. Found: C, 24.35; H, 1.83; F, 50.49.

1H,1H,2H,2H-Perfluorododecylhepta(3,3,3-trifluoropropyl)-T₈-Silsesquioxane (5). 1H,1H,2H,2H-Perfluorododecyl trichlorosilane (1.80 g, 5.25 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)-T₈-silsesquioxane **2** to obtain the title compound as a white solid (2.10 g, 73%). Mp 105–107 °C (from THF); ¹H NMR ((CD₃)₂CO, 300 MHz): δ 2.36–2.30 (m, 14H), 1.60–1.01 (m, 14H); ¹³C NMR ((CD₃)₂CO, 75 MHz): δ 128.1 (q, *J* = 272.3 Hz), 120.0–105.0 (m, unresolved complex peak splitting), 27.4 (q, *J* = 30.2 Hz), 24.6 (t, *J* = 23.2 Hz), 4.0, 1.8; ²⁹Si NMR ((CD₃)₂CO, 59.6 MHz): δ –67.2, –67.3; ¹⁹F NMR ((CD₃)₂CO, 376 MHz): δ –69.9 (21F), –82.2 (3F), –116.9 (2F), –122.9 (10F), –123.8 (2F), –124.5 (2F), –127.3 (2F); Anal. Calcd for C₃₃H₃₂F₄₂O₁₂Si₈: C, 24.12; H, 1.96; F, 48.56. Found: C, 24.38; H, 1.71; F, 51.84.

Hexafluoroisobutylhepta(3,3,3-trifluoropropyl)-T₈-Silsesquioxane (6). Compound **6** was prepared in two steps. First, hexafluoroisobutene (30 mL, 0.25 mol), trichlorosilane (31 mL, 0.30 mol), and H₂PtCl₆ (1.2 mL, 0.025 mol, 2 M in isopropanol) were charged in a sealed tube. The vessel was purged with nitrogen, sealed, and placed in a preheated oil bath at 80 °C for 24 h. The crude mixture was fractionally distilled (65 °C, 200 mmHg) to obtain the hexafluoroisobutyltrichlorosilane as a colorless liquid (54 g, 67%). ¹H NMR ((CD₃)₂CO, 300 MHz): δ 3.313–3.22 (m, 6H), 1.90 (d, *J* = 6.6 Hz, 2H); ¹³C NMR ((CD₃)₂CO, 75 MHz): δ 123.5 (q, *J* = 278.5 Hz), 44.6 (p, *J* = 30.1 Hz), 18.8; ²⁹Si NMR ((CD₃)₂CO, 59.6 MHz): δ 8.1; ¹⁹F NMR ((CD₃)₂CO, 376 MHz): δ –68.7 (6F).

In the final step, hexafluoroisobutyltrichlorosilane (1.57 g, 5.25 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)-T₈-silsesquioxane **2** to obtain the title compound as a white solid (3.21 g, 73%). Mp 234–236 °C (from THF); ¹H NMR ((CD₃)₂CO, 300 MHz): δ 3.8–3.6 (m, 1H), 1.07–1.03 (m, 14H), 1.4 (d, *J* = 7.1 Hz, 2H), 2.40–2.27 (m, 14H); ¹³C NMR ((CD₃)₂CO, 75 MHz): δ 128.1 (q, *J* = 273.5 Hz), 43.6 (p, *J* = 28.4 Hz), 27.3 (qd, *J* = 30.4, 6.0 Hz), 6.1, 3.9; ²⁹Si NMR ((CD₃)₂CO, 59.6 MHz): δ –67.3, –70.6; ¹⁹F NMR ((CD₃)₂CO, 376 MHz): δ –69.60 (6F), –69.82 (9F), –69.84 (3F), –69.93 (9F); Anal. Calcd for C₂₅H₃₁F₂₇O₁₂Si₈: C, 23.81; H, 2.48; F, 40.67. Found: C, 23.87; H, 2.40; F, 40.89.

(3-Heptafluoroisopropoxy)propylhepta(3,3,3-trifluoropropyl)-T₈-Silsesquioxane (7). (3-

Heptafluoroisopropoxy)propyltrichlorosilane (1.28 mL, 5.25 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)-T₈-silsesquioxane **2** to obtain the title as a white solid (3.43 g, 75%). Mp 70–71 °C (from THF); ¹H NMR ((CD₃)₂CO, 300 MHz): δ 4.12–4.10 (m, 2H), 2.35–2.24 (m, 14H), 1.90–1.88 (m, 2H), 1.04–0.97 (m, 14H), 0.91–0.87 (m, 2H); ¹³C NMR ((CD₃)₂CO, 75 MHz): δ 128.7 (q, *J* = 274 Hz), 120.0 (dd, *J* = 37.5 Hz), 70.4, 23.7 (q, *J* = 30.0 Hz), 7.7, 4.6; ²⁹Si NMR ((CD₃)₂CO, 59.6 MHz): δ –66.1, –67.3, –67.5; ¹⁹F NMR ((CD₃)₂CO, 376 MHz): δ –69.9 (21F), –80.3 (6F), –121.2 (1F); Anal. Calcd for C₂₇H₃₄F₂₈O₁₃Si₈: C, 24.51; H, 2.59; F, 40.20. Found: C, 24.61; H, 2.56; F, 40.42.

Phenylethylhepta(3,3,3-trifluoropropyl)-T₈-Silsesquioxane (8). Phenylethyltrichlorosilane (255 μL, 1.32 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)-T₈-silsesquioxane **2** to obtain the title compound as a white solid (570 mg, 54%). Mp 109–111 °C (from THF); ¹H NMR ((CD₃)₂CO, 300 MHz): δ 7.19–7.28 (m, 5H), 2.82 (t, *J* = 8.1 Hz, 2H), 2.39–2.21 (m, 14H), 1.16 (t, *J* = 8.4 Hz, 2H), 1.06–0.90 (m, 14H); ¹³C NMR ((CD₃)₂CO, 75 MHz): δ 143.9, 128.7, 128.2, 128.1 (q, *J* = 274 Hz), 126.2, 27.3 (dq, *J* = 30.0, 4.0 Hz), 15.5, 4.0; ²⁹Si NMR ((CD₃)₂CO, 59.6 MHz): δ –66.4, –67.4, –67.7; Anal. Calcd for C₂₉H₃₇F₂₁O₁₂Si₈: C, 29.00; H, 3.10; F, 33.21. Found: C, 29.85; H, 3.14; F, 32.95.

Methylhepta(3,3,3-trifluoropropyl)-T₈-Silsesquioxane (9). Methyltrichlorosilane (118 μL, 1.00 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)-T₈-silsesquioxane **2** to obtain the title compound as a white solid (425 mg, 72%). Mp 168–170 °C (from THF); ¹H NMR ((CD₃)₂CO/CDCl₃ (50:50, v:v), 300 MHz): δ 1.84–1.75 (m, 14H), 0.58–0.51 (m, 14H), –0.16 (s, 3H). ¹³C NMR ((CD₃)₂CO/CDCl₃ (50:50, v:v), 75 MHz): δ 127.7 (q, *J* = 274.2 Hz), 27.7 (qd, *J* = 30.5, 4.0 Hz), –5.0, 4.2–4.1 (m); ²⁹Si NMR ((CD₃)₂CO/CDCl₃ (50:50, v:v), 59.6 MHz): δ –64.8, –67.5, –68.0.

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