

## Supporting Information

### Facile Synthesis of Hydrophobic Fluoroalkyl Functionalized Silsesquioxane Nanostructures

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**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, propylheptafluoroisobutylethertrichlorosilane, and 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.<sup>1</sup> All other materials were purchased from Aldrich and purified by standard methods.<sup>2</sup>

**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. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>29</sup>Si NMR data was obtained on a Bruker AXS SMART APEX and chemical shifts were reported in part per million ( $\delta$  ppm). <sup>1</sup>H NMR was reported downfield from tetramethylsilane ( $\delta$  0.0) and are, in all cases, referenced to the residual proton resonance peaks:  $\delta$  7.24 for chloroform-*d* and  $\delta$  2.09 for acetone-*d*<sub>6</sub>. The <sup>13</sup>C NMR chemical shifts were reported in ppm relative to the center peak of the multiplet for deuterated solvents:  $\delta$  77.0 (t) for chloroform-*d* and 30.6 for acetone-*d*<sub>6</sub>. <sup>19</sup>F NMR was referenced to CFCl<sub>3</sub> and recorded with proton decoupling. <sup>29</sup>Si NMR was referenced to tetramethylsilane ( $\delta$  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). Combustion analysis was obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Melting points (mp) were measured using a Mel-Temp melting point apparatus and are reported uncorrected.

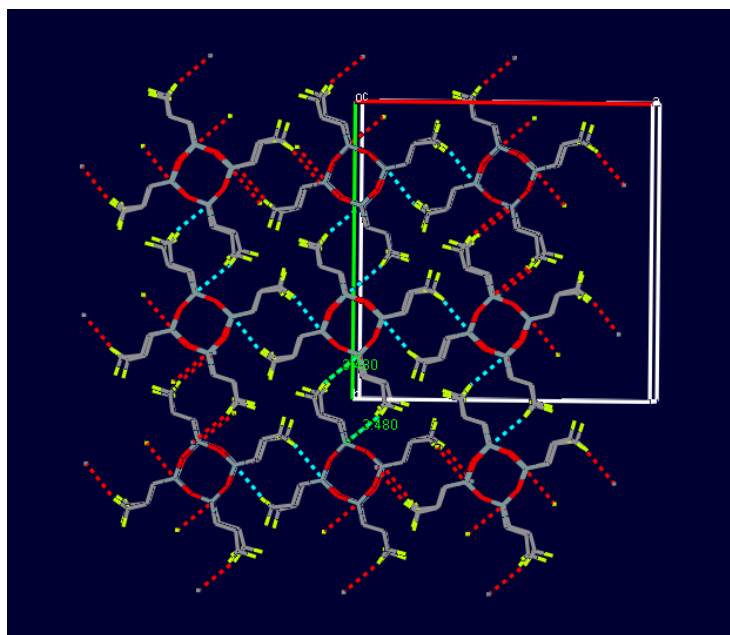
**Contact Angle Measurements.** Powder surfaces were prepared by dissolving the fluoroalkyl POSS in the minimal amount of hexafluorobenzene followed by mechanical agitation. The surfaces were spin cast at 2500 RPM onto borosilicate glass plates producing a well-adhered coating. Contact angle analysis 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  $\pm 2$  degrees. Static contact angle values reported were an average of three values measured on various areas of the coated surface.

**X-Ray Structure Database.** Crystallographic data for **2** and **8** has been submitted to the Cambridge Crystallographic Data Center with publication number CCDC 629369 and 642077, respectively. Copies can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

**X-Ray Refinement of 2.** The asymmetric unit shows an ordered (C1-C3) and a disordered (C4-C6) trifluoropropyl chains, which were refined with occupancies of 67% and 33%, respectively. During the refinement of disordered trifluoropropyl groups, the disorder originates from the alpha carbon (C4). Therefore, in order to have an effective convergence, the C-C distances as well as the C-F distances in these chains were restrained to be same using SADI while the thermal behavior was restrained using SIMU and DELU commands. After a stable minimum was reached, hydrogen atoms were added at calculated positions to the alpha and beta carbon atoms.

The importance of THF in crystal lattice stabilization is supported by the fact that alternating between the POSS layers is a layer containing the THF molecules, also running along the c-axis. The THF molecule is also disordered and the oxygen atom flops above and below the hydrocarbon plane. Consequently, there are four disordered oxygen atoms above and four atoms below the hydrocarbon moiety, which results in extensive hydrogen bonding (H...F and H...O) not only due to the neighboring POSS cage, but also to the disordered trifluoropropyl chains. The THF...POSS interactions result from O(1)...H and O(2)...H contacts at 2.662 and 2.675 Å, respectively (along the c-axis), whereas the F(6)...H contacts dominate the ab-plane with distances ~2.5 Å. Interestingly, the hydrogen atoms located on the  $\alpha$ -carbon of the fluorocarbon chain are forced into a conformation that promotes additional H...O contacts, namely H(1)...O(solvent) and H(4)...O(solvent) at 2.499 and 2.630 Å. Since these contacts are not very strong, THF is rapidly lost from the lattice upon exposing to air at ambient conditions.

The disorder in the THF molecule was much more difficult to model as this molecule shows both positional as well as rotational disorder. The positional disorder stems from the two different envelope conformations of the THF molecules with oxygen atoms lying above and below the mean plane formed by the carbon atoms. In the major component, refined with an occupancy of 83%, the oxygen atoms is located 0.3758 angstrom above the mean plane, whereas in the minor component, the oxygen atoms is located -0.4165 angstrom below this plane. This model was further rotationally disordered due to the four-fold axis passing through the THF molecule. The final model refined satisfactorily by fixing the site occupancy for each of the four disordered positions to 0.25 (with total occupancy as 1.0), and constraining all C-C and C-O distances to 1.52(01) and 1.43(01) angstrom, respectively. The thermal behavior was modeled for all the carbon and oxygen atoms using SIMU, DELU and ISOR commands. Without the use of these restraints, the structure showed unusually large thermal motion of the fluoroalkyl chains and the THF ring.



**Fig S1** Packing diagram of **2** along c-axis showing dimeric nature of intermolecular Si...F contacts.

**X-Ray Refinement of 8.** The  $\text{Si}_8\text{O}_{12}$  ring shows positional disorder with two components refined with an occupancy ratio of 36:64. The two POSS ring conformations were stabilized using the ISOR and BUMP commands in the refinement file. The only ordered trifluoropropyl chain is located on Si2, which is also the common atom for the two disordered POSS cubes. This ordered fragment was used to model the trifluoropropyl groups C13, C14, C15 (F13, F14 and F15) and its disordered component C13' > F15' using the SAME command (ratio 57:43), where the C-C and C-F distances were restrained using SADI. The  $\text{CF}_3$  group located on C21 shows rotational disorder where two orientations were refined with occupancies of 66:34, restraining all the C-F and F...F distances with SADI. The C-F distances in the trifluoropropyl group on C15 and C21 were fixed using DFIX with a distance of 1.32(01) angstrom. The trifluoropropyl groups located on Si1 and Si6 show disorder in the alpha and beta carbon positions, which share the terminal  $\text{CF}_3$  group. For C1 and C2, this disorder is refined with an occupancy of 71:29, whereas in the case of C16 and C17, the disorder is of the ratio of 80:20. In both these cases the C-C distances are restrained to be the same using SADI. In order to model the thermal motion effectively, SIMU and DELU commands were used to generate thermal restrains.

**Octa(3,3,3-trifluoropropyl)-T<sub>8</sub>-Silsesquioxane (2).** Compound **2** was synthesized using a modified preparation reported initially by Fukada.<sup>1</sup> 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);  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 300 MHz):  $\delta$  2.35–2.28 (m, 16H), 1.04–0.99 (m, 16H);  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 75 MHz):  $\delta$  128.1 (q,  $J = 274$  Hz), 27.4 (q,  $J = 30.2$  Hz), 4.0, –0.5 (t,  $J = 25.5$  Hz);  $^{29}\text{Si}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 59.6 MHz):  $\delta$  –67.3;  $^{19}\text{F}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 376 MHz):  $\delta$  –69.8 (2F); 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, 24.33; H, 2.66; F, 38.45.

**Tridecafluoro-1,1,2,2-tetrahydrooctylhepta(3,3,3-trifluoropropyl)- $\text{T}_8$ -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)- $\text{T}_8$ -silsesquioxane **2** to obtain the title compound as a white solid (4.12 g, 82%). Mp 104–106 °C (from THF);  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$  with 10 vol% THF, 300 MHz):  $\delta$  1.06–1.02 (m, 14H), 2.38–2.29 (m, 14H);  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$  with 10 vol% THF, 75 MHz):  $\delta$  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;  $^{29}\text{Si}$  NMR ( $(\text{CD}_3)_2\text{CO}$  with 10 vol% THF, 59.6 MHz):  $\delta$  –67.2, –67.4;  $^{19}\text{F}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 283 MHz):  $\delta$  –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  $\text{C}_{29}\text{H}_{32}\text{F}_{34}\text{O}_{12}\text{Si}_8$ : 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)- $\text{T}_8$ -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)- $\text{T}_8$ -silsesquioxane **2** to obtain the title compound as a white solid (4.30 g, 80%). Mp 88–90 °C (from THF);  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 300 MHz):  $\delta$  2.39–2.30 (m, 14H), 1.61–1.00 (m, 14H);  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$  with 50 vol% hexafluorobenzene, 100 MHz):  $\delta$  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;  $^{29}\text{Si}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 59.6 MHz):  $\delta$  –67.2, –67.3;  $^{19}\text{F}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 376 MHz):  $\delta$  –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)- $\text{T}_8$ -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)- $\text{T}_8$ -silsesquioxane **2** to obtain the title compound as a white solid (2.10 g, 73%). Mp 105–107 °C (from THF);  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 300 MHz):  $\delta$  2.36–2.30 (m, 14H), 1.60–1.01 (m, 14H);  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 75 MHz):  $\delta$  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;  $^{29}\text{Si}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 59.6 MHz):  $\delta$  –67.2, –67.3;  $^{19}\text{F}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 376 MHz):  $\delta$  –69.9 (21F), –82.2 (3F), –116.9 (2F), –122.9 (10F), –123.8 (2F), –124.5 (2F), –127.3 (2F); Anal. Calcd for  $\text{C}_{33}\text{H}_{32}\text{F}_{42}\text{O}_{12}\text{Si}_8$ : C, 24.12; H, 1.96; F, 48.56. Found: C, 24.38; H, 1.71; F, 51.84.

**Hexafluoroisobutylhepta(3,3,3-trifluoropropyl)- $\text{T}_8$ -Silsesquioxane (6).**

Compound **6** was prepared in two steps. First, hexafluoroisobutene (30 mL, 0.25 mol), trichlorosilane (31 mL, 0.30 mol), and  $\text{H}_2\text{PtCl}_6$  (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%).  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 300 MHz):  $\delta$  3.313–3.22 (m, 6H), 1.90 (d,  $J = 6.6$  Hz, 2H);  $^{13}\text{C}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 75 MHz):  $\delta$  123.5 (q,  $J = 278.5$  Hz), 44.6 (p,  $J = 30.1$  Hz), 18.8;  $^{29}\text{Si}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 59.6 MHz):  $\delta$  8.1;  $^{19}\text{F}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 376 MHz):  $\delta$  –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)- $\text{T}_8$ -silsesquioxane **2** to obtain

the title compound as a white solid (3.21 g, 73%). Mp 234–236 °C (from THF); <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 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); <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 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; <sup>29</sup>Si NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 59.6 MHz): δ –67.3, –70.6; <sup>19</sup>F NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 376 MHz): δ –69.60 (6F), –69.82 (9F), –69.84 (3F), –69.93 (9F); Anal. Calcd for C<sub>25</sub>H<sub>31</sub>F<sub>27</sub>O<sub>12</sub>Si<sub>8</sub>: 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)-T<sub>8</sub>-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)-T<sub>8</sub>-silsesquioxane **2** to obtain the title as a white solid (3.43 g, 75%). Mp 70–71 °C (from THF); <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 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); <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 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; <sup>29</sup>Si NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 59.6 MHz): δ –66.1, –67.3, –67.5; <sup>19</sup>F NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 376 MHz): δ –69.9 (21F), –80.3 (6F), –121.2 (1F); Anal. Calcd for C<sub>27</sub>H<sub>34</sub>F<sub>28</sub>O<sub>13</sub>Si<sub>8</sub>: C, 24.51; H, 2.59; F, 40.20. Found: C, 24.61; H, 2.56; F, 40.42.

**Methylhepta(3,3,3-trifluoropropyl)-T<sub>8</sub>-Silsesquioxane (8).** Compound **8** was synthesized using a modified preparation reported initially by Fukada.<sup>1</sup> This variation was observed to produce a higher yield of **8** compared to the aforementioned reported procedure. Methyltrichlorosilane (118 μL, 1.00 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)-T<sub>8</sub>-silsesquioxane **2** to obtain the title compound as a white solid (425 mg, 72%). Mp 168–170 °C (from THF); <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO/CDCl<sub>3</sub> (50:50, v:v), 300 MHz): δ 1.84–1.75 (m, 14H), 0.58–0.51 (m, 14H), –0.16 (s, 3H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO/CDCl<sub>3</sub> (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); <sup>29</sup>Si NMR ((CD<sub>3</sub>)<sub>2</sub>CO/CDCl<sub>3</sub> (50:50, v:v), 59.6 MHz): δ –64.8, –67.5, –68.0.

**Phenylethylhepta(3,3,3-trifluoropropyl)-T<sub>8</sub>-Silsesquioxane (9).** Phenylethyltrichlorosilane (255 μL, 1.32 mmol) was used to corner cap using the procedure outlined for the preparation of octa(3,3,3-trifluoropropyl)-T<sub>8</sub>-silsesquioxane **2** to obtain the title compound as a white solid (570 mg, 54%). Mp 109–111 °C (from THF); <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 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); <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 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; <sup>29</sup>Si NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 59.6 MHz): δ –66.4, –67.4, –67.7; Anal. Calcd for C<sub>29</sub>H<sub>37</sub>F<sub>21</sub>O<sub>12</sub>Si<sub>8</sub>: C, 29.00; H, 3.10; F, 33.21. Found: C, 29.85; H, 3.14; F, 32.95.

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