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Incompletely-Condensed Fluoroalkyl Silsesquioxanes and Derivatives: Precursors for Low Surface Energy Materials

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KEYWORDS Polyhedral oligomeric silsesquioxane, silsesquioxane, fluorinated polyhedral oligomeric silsesquioxane, POSS, F-POSS, fluoroPOSS, low surface energy, POSS disilanol

Supporting Information

ABSTRACT: A novel synthetic method was developed for the controlled functionalization of Fluorinated Polyhedral Oligomeric SilSesquioxanes (F-POSS), which are useful as low surface energy materials for superhydrophobic and oleophobic materials. Utilizing triflic acid, open-cage compounds were created and then reacted with a variety of dichlorosilanes to produce functional F-POSS structures possessing alkyl, aryl, and acrylate based moieties. The crystal structure for an endo,endo disilanol F-POSS compound was determined by single crystal X-ray diffraction. The chemical structures were confirmed using multinuclear NMR spectroscopy (¹H, ¹³C, ¹⁹F, and ²⁹Si), FT-IR, and combustion analysis. Dynamic contact angle measurements of these compounds were taken with water and hexadecane. These novel structures were found to possess excellent wetting-resistant behavior, similar to that of the parent F-POSS compound. They are the first well-defined fluorinated nano-building blocks with a controlled level of reactive functionality for the development of new superhydrophobic and oleophobic materials.

Polyhedral Oligomeric SilSesquioxanes (POSS) each possess a cage-structure of silicon-oxide [SiO_{1.5}] at their core, which is surrounded by aliphatic or aromatic organic functionality.¹ Octakis(1H,1H,2H,2H-heptafluorodecyl) POSS (F-POSS) possesses a periphery of long-chain fluorinated alkyl groups, and has been determined to possess the lowest surface energy value ($\gamma_{sv} = 9.3$ mN/m) of any crystalline solid.² Superhydrophobic and oleophobic surfaces have been produced using F-POSS, either cast on a substrate or blended into a polymer matrix.²⁻³ To date, F-POSS have been used as standalone compounds, without any reactive chemical functionality. This limits solubility in common solvents, as well as the mechanical robustness and abrasion resistance of surfaces containing these materials. To overcome these limitations, the development of an incompletely-condensed F-POSS compound with silanol functionality has been desired to

enable new, robust, low surface energy hybrid materials. Incompletely-condensed silsesquioxane frameworks have emerged as excellent synthons for creating hybrid inorganic-organic materials and have been used as models for silica,⁴ catalyst support,⁵ and precursors for silsesquioxane containing polymers.⁶ Previously, all functionalizable POSS structures contained either an alkyl or aryl periphery.^{1a}

Unfortunately, there is no viable synthetic strategy to produce long-chain F-POSS compounds possessing additional reactive or non-reactive functionality. Utilizing a previously patented technique,⁷ synthesis of *long-chain* F-POSS-(ONa)₃ (>3 carbon atoms) was not possible, although a modification of this method was used to successfully produce (3,3,3-trifluoropropyl)₇Si₇O₉(ONa)₃, which can be derivatized with long-chain fluorinated trichlorosilanes to produce low surface energy materials.^{3c} Although this synthetic strategy was successful, it was limited by the short chain length of the trifluoropropyl groups on the trisilanol because shorter chains do not possess the same magnitude of liquid repellency as longer fluoroalkyl chains.²

Alternative synthetic strategies for alkyl- and aryl-based incompletely-condensed silsesquioxanes have included top-down approaches, such as POSS cage edge-opening developed by Feher and coworkers.⁸ Feher's work described the opening of completely-condensed POSS cage edges through a multistep synthetic methodology to create Si-OH bonds in varying degree *via* an acidic⁸ or basic route.⁹ While these methods have proven successful for the synthesis of incompletely-condensed compounds possessing alkyl- and aryl-functionality, the synthesis of incompletely-condensed long-chain F-POSS compounds has not been achieved. This is presumably due to the fact that the highly-symmetrical F-POSS compounds have low solubility in organic solvents, as well as the inherent difficulty introducing water hydrolysis to a superhydrophobic compound. Herein, we report the synthesis of the first incompletely-condensed F-POSS, disilanol Fluorinated Polyhedral Oligomeric SilSesquioxane (F-POSS-(OH)₂). This work represents the first viable synthetic strategy towards an incompletely-condensed long-

Scheme 1. Synthesis of Incompletely-Condensed Fluoroalkyl Silsesquioxane^a

^aConditions: All reactions were performed in C₆F₆ at 25 °C. ^bCF₃SO₃H, 75 mins. ^cNBut₄HSO₄, 30 mins, ^d(CF₃)₂CH₂OH/H₂O (10:1), 12 hrs.

chain fluoroalkyl POSS compound. These reactive open-cage structures were subsequently modified with non-fluorinated symmetric and asymmetric dichlorosilanes to produce functionalized F-POSS for applications in superhydrophobic/oleophobic coatings and other low surface energy materials.

A multi-step synthetic procedure was developed to convert the closed-cage F-POSS compound **1** to an incompletely-condensed silsesquioxane structure (**2**) following a methodology similar to that pioneered by Feher *et al.*^{8c} The first step opens a single edge of the F-POSS framework with triflic acid (TfOH) to form (CF₃(CF₂)₇CH₂CH₂)₈Si₈O₁₁(OTf)₂ (**1a**). Due to an equilibrium between the open and closed-cage silsesquioxane frameworks, the ²⁹Si NMR spectra are complex. There is, however, clear evidence of the formation of **1a** as observed by ²⁹Si NMR resonances at -62.6, -65.0, and -67.7 ppm, integrated in a 2:2:4 ratio, which are attributed to the ditriflate POSS cage (**1a**).^{8c} Unfortunately, the ditriflate intermediate is highly unstable and each attempt to isolate **1a** resulted in a complete reversion to compound **1**. This was attributed to the strong electron-withdrawing effects of the fluorinated alkyl groups. To overcome this difficulty, the ditriflate compound was subsequently converted to a bridged sulfate compound (CF₃(CF₂)₇CH₂CH₂)₈Si₈O₁₃(SO₂) (**1b**) over a 30 minute period using an excess of NBut₄HSO₄ to rapidly bridge the open edge with a sulfate group. This results in the reaction mixture separating into two liquid layers; a yellow aqueous layer and a clear, colorless fluorinated solvent layer containing both **1b** and **1**. The bridging sulfate moiety appears to stabilize the electron-withdrawing F-POSS cage framework, leading to another NMR observed intermediate with ²⁹Si resonances at -64.5, -65.7, and -67.3 ppm (2:2:4). Similar to **1a**, **1b** reverts readily to **1** during any work-up procedure, making it difficult to isolate the pure compound. Compared to Feher's work, these fluorinated intermediates are highly unstable with respect to their alkyl counterparts.^{8c, 11} The reaction mixture is subsequently added to a polar fluorinated solvent/water (10:1) mixture to convert **1b** to (CF₃(CF₂)₇CH₂CH₂)₈Si₈O₁₁(OH)₂ (**2**) in good overall yield (ca. 53%). Any attempt at this conversion without a polar fluorinated solvent does not result in the desired product because the reaction requires water to be miscible with the fluorinated solvent. The disilanol compound **2** is best purified from residual **1** through the subtle solubility differences between the open and closed structures in C₆F₆ and ethyl acetate mixtures. Compound **1** precipitates from this solution; the soluble compound **2** is later precipitated from a CHCl₃ solution. The principle side product in each of these reactions was compound **1**, which was subsequently recycled. Combustion analysis and multinuclear NMR (¹H, ¹³C, ¹⁹F, and

²⁹Si) were used to confirm the structure of **2**. The ²⁹Si NMR spectrum of **2** displayed peaks at -59.0, -65.5, -68.1 ppm, with an integration ratio of 2:2:4, due to the C_{2v} symmetry of the silsesquioxane. The peak at -59.0 ppm is attributed to the silanol groups on the POSS framework.

While the absolute stereochemistry of the intermediates shown in scheme 1 is not proven, the presence of these structures is supported by the rigorous work by Feher.^{8c} Compound **1b** must have a bridging endohedral geometry, which converts to the endohedral disilanol **2**, whose structure was confirmed by single crystal X-ray diffraction (Figure 1).¹¹ The crystal structure for compound **2** was obtained from C₆F₆ and determined to be monoclinic P2(1)/c. This structure contains rigid, helical-like fluoroalkyl chains, similar to compound **1**, which are attached to the open Si-O framework by methylene groups. From the structure, the 2:2:4 ratio of silicon atoms is clearly visible, confirming the Si integration values established by ²⁹Si NMR spectra. The crystal packing of compound **2** reveals a dimeric structure with two F-POSS cages forming intermolecular hydrogen bonds between silanol groups on adjacent cages (Figure 1). This induces an increase in the lattice volume (12884 Å³) for compound **2** compared to compound **1** (6340 Å³).^{3a} Hydrogen bonding between silanols on incompletely-condensed silsesquioxanes has previously been observed for alkyl based POSS triols and diols.^{4d, 12} A dimeric contact is established from the intermolecular silanols at a distance of 2.798 Å. These intermolecular silanols are slightly closer to than intramolecular silanols, O(1)···O(13) at a distance of 2.810 Å and are still reactive to chlorosilanes.

The incompletely-condensed silsesquioxane **2** can readily react with a variety of dichlorosilanes (Scheme 2). For example, the condensation of **2** with bis(*n*-octyl)dichlorosilane in the presence of triethylamine produced compound **3** (ca. 46% yield) with the loss of HCl. The primary side product isolated during the reaction was the initial starting material, compound **1**. Multinuclear NMR (¹H, ¹³C, ¹⁹F, and ²⁹Si), FT-IR, and combustion analysis were used to confirm the structure of **3**. The ²⁹Si resonances were -17.8, -65.4, -68.2, and -69.0, with a ratio of 1:2:4:2. The resonance at -17.8 ppm was attributed to dioctyl-functionalized Si atom. Large C-H stretches observed at 2974 and 2871 cm⁻¹ in the FT-IR spectrum also confirmed the presence of the added hydrocarbon chains. To demonstrate the utility of the edge closing reaction, additional dichlorosilanes were employed in reactions with **2** to produce compounds **4-7** (Table 1). The synthesis of each of these compounds was also confirmed using combustion analysis, FT-IR, and multinuclear NMR spectroscopy (see supporting information). The long-chain fluoroalkyl periphery on **1** results in desirable low surface energy characteristics. However, this limits the choice of sol-

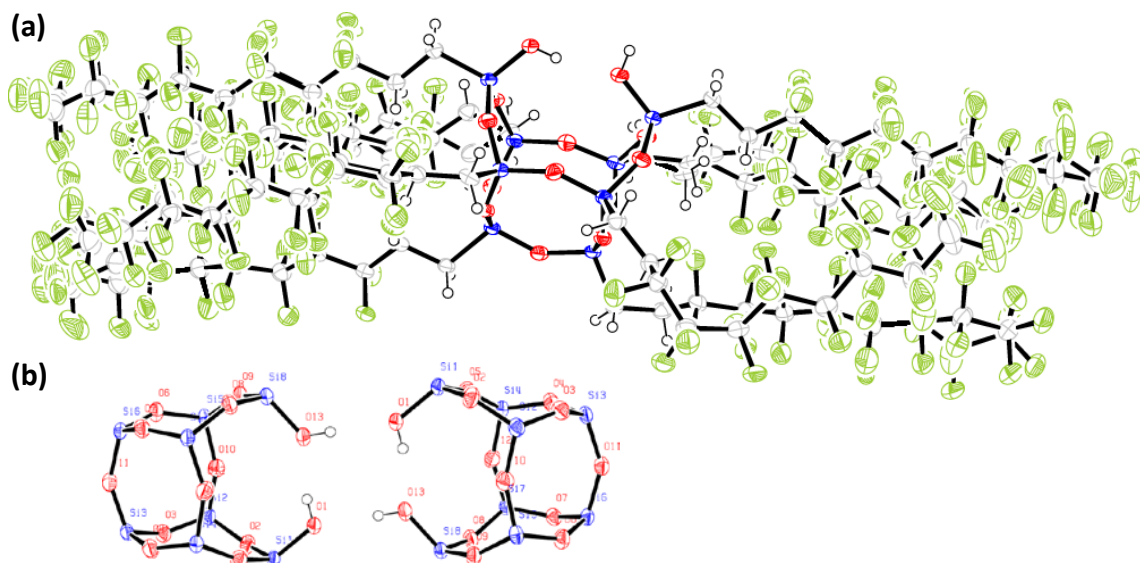


Figure 1. (a) ORTEP representation of compound **2** in crystal form at 100 K. The fluorinated chains contain substantial disorder. (b) F-POSS dimer displaying hydrogen bonding interactions between inter- and intra-molecular silanols (fluorinated chains omitted for clarity). Thermal ellipsoids at 50%. Green F, Grey C, Red O, Blue Si, White, H.

Scheme 2. Synthesis of Functionalized F-POSS Compounds. $R_f = -CH_2CH_2(CF_2)_7CF_3$.

vent to strictly fluorinated solvents.^{3a} Interestingly, once a non-fluorinated segment is added to an edge of F-POSS, the solubility properties change dramatically. For example, the long hydrocarbon chains present in compound **3** expanded F-POSS solubility to include non-fluorinated solvents such as Et_2O and $CHCl_3$. Even small organic modifications, such as the acrylate and methacrylate moieties on structures **6** and **7**, were sufficient to expand the solubility of F-POSS to non-fluorinated solvents, such as Et_2O . However, phenyl (**4**) and vinyl (**5**) groups did not improve the solubility of F-POSS in non-fluorinated solvents. Presumably, this can be attributed to the rigidity of the phenyl and vinyl groups on the POSS cage.

The influence of functionality on non-wetting behavior was determined by examining static (Figure 2) and dynamic contact angles of water and hexadecane on spin-cast films of F-POSS on Si wafers (Table 1). Smooth surfaces (<5 nm rms roughness) were prepared to minimize any influence of surface roughness and topology.² The open-cage framework of compound **2** did not display any adverse effect on the wetting behavior of the material. This was attributed to the dimeric structure formed with silanols shielded from the surface of the film. A slight increase in contact angle hysteresis, $\theta_{rec} - \theta_{adv}$, for

the modified compounds (**3**, **5-7**) was observed when wetted with water. This slight increase was not observed for compounds wetted with hexadecane except for compound **3**. The structure of **3** contains long aliphatic chains that potentially favor interaction with a long-chain organic solvent, such as hexadecane. Compounds **2** and **4** displayed the lowest hexadecane hysteresis values of all compounds and possessed sliding angles of $\sim 7^\circ$ (Figure 2e). These initial measurements demonstrate that modifications of the F-POSS structure were found to be influential on wetting properties, either increasing or decreasing contact angle hysteresis.

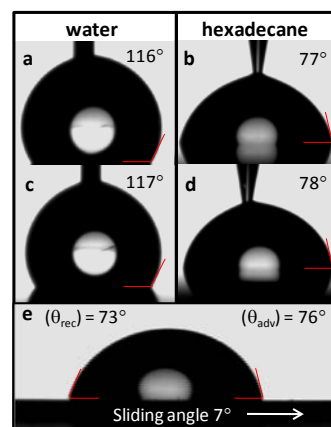


Figure 2. Static contact angles of Si wafer surfaces coated with smooth surfaces of compounds **2** (a) and (b), and **4** (c) and (d). Image of hexadecane droplet (10 μ L) rolling off surface coated with compound **4** (e).

In summary, the first successful synthesis of disilanol F-POSS compounds from fully condensed F-POSS was accomplished in a three-step reaction process. The disilanol F-POSS crystal structure indicates the silanol groups are hydrogen bonded *via* intermolecular interaction. The disilanol structure was demonstrated to be reactive toward dichlorosilanes, producing a variety of functional F-POSS structures, which were found to display similar wetting

TABLE 1. Dynamic Contact Angle Measurements

Functional Group on F-POSS ^a	Water		Hexadecane	
	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
F-POSS (1)	124 ± 0.5°	109.6 ± 0.7°	79.1 ± 0.4°	65.1 ± 0.5°
Si-(OH) ₂ (2)	116.8 ± 0.4°	111 ± 0.6°	77.4 ± 0.4°	74.4 ± 0.8°
Si-((CH ₂) ₇ CH ₃) ₂ (3)	117.9 ± 0.5°	95.5 ± 0.4°	69.1 ± 1.2°	23.1 ± 1.2°
Si-(C ₆ H ₅) ₂ (4)	116.2 ± 0.4°	110.5 ± 0.5°	76.0 ± 0.8°	73.2 ± 0.4°
Si-(CH ₃)(CH=CH ₂) (5)	116.2 ± 0.4°	100.6 ± 0.8°	78.4 ± 0.3°	70.6 ± 2.3°
Si((CH ₃)((CH ₂) ₃ OC(O)CCH=CH ₂) (6)	118.2 ± 1.0°	90.6 ± 1.0°	76.8 ± 0.3°	64.8 ± 1.0°
Si-(CH ₃)(CH ₂) ₃ OC(O)C(CH ₃)=CH ₂) (7)	117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°

^aF-POSS compounds were spin-cast from solutions of Asahiklin-225 (10 mg/mL) at a rate of 900 rpm for 30 seconds onto 1- inch silicon wafers following literature procedure.² Compound 2 was cast from C₆F₆ solution at a rate of 1400 rpm. Sample surface roughness was measured at < 5 nm rms roughness for all samples via atomic force microscopy (AFM) and optical profilometry.

properties to unmodified F-POSS. Thus, a novel tunable structure now provides unprecedented access to fluorinated building blocks for low surface energy materials. The methacrylate and acrylate monomers are currently being investigated in a variety of copolymers and are expected to deliver new robust, abrasion resistant, superhydrophobic and oleophobic material properties.

ASSOCIATED CONTENT

Supporting Information. Supporting information contains detailed experimental procedures of all compounds, analytical data, crystallography data, and ²⁹Si NMR spectra.

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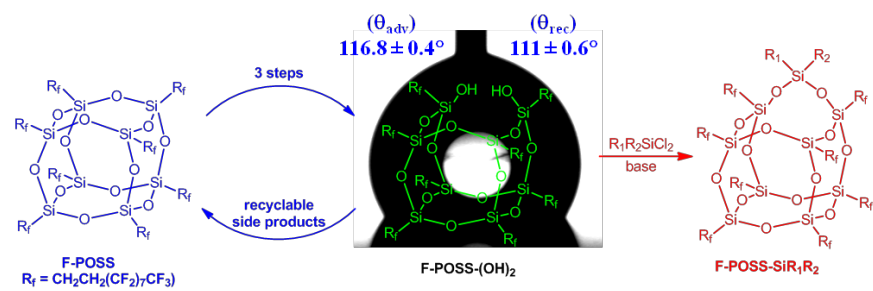
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REFERENCES

- (a) Cordes, D. B.; Lickiss, P. D.; Rataboul, F., *Chem. Rev.* **2010**, *110* (4), 2081-2173; (b) Lickiss, P. D.; Rataboul, F., *Adv. Organomet. Chem.* **2008**, *57*, 1; (c) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T., *Chem. Rev.* **1995**, *95*, 1409-1431.
- (a) Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., *ACS Appl. Mater. Interfaces* **2010**, *2*, 3544-3554.
- (a) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D., *Angew. Chem., Int. Ed.* **2008**, *47*, 4137-4140; (b) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W., Jr., *Macromolecules* **2007**, *40*, 9517-9522; (c) Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M., *Chem. Commun.* **2007**, 4992-4994; (d) Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H., *Adv. Mater.* **2009**, *21*, 2190-2195; (e) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 18200-18205, S18200/1-S18200/29; (f) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E., *Science* **2007**, *318*, 1618-1622; (g) Iacono, S. T.; Budy, S. M.; Smith, D. W., Jr.; Mabry, J. M., *J. Mater. Chem.* **2010**, *20*, 2979-2984.
- (a) Ohde, C.; Limberg, C.; Stösser, R.; Demeshko, S., *Inorganic Chemistry* **2010**, *49* (5), 2479-2485; (b) Lucenti, E.; Feher, F. J.; Ziller, J. W., *Organometallics* **2006**, *26* (1), 75-82; (c) Feher, F. J.; Soulivong, D.; Lewis, G. T., *J. Am. Chem. Soc.* **1997**, *119* (46), 11323-11324; (d) Feher, F. J.; Newman, D. A.; Walzer, J. F., *J. Am. Chem. Soc.* **1989**, *111* (5), 1741-1748; (e) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W., *J. Am. Chem. Soc.* **1992**, *114* (10), 3859-3866; (f) Dijkstra, T. W.; Duchateau, R.; van Santen, R. A.; Meetsma, A.; Yap, G. P. A., *J. Am. Chem. Soc.* **2002**, *124* (33), 9856-9864.
- (a) Duchateau, R.; van Meerendonk, W. J.; Huijser, S.; Staal, B. B. P.; van Schilt, M. A.; Gerritsen, G.; Meetsma, A.; Koning, C. E.; Kemmere, M. F.; Keurentjes, J. T. F., *Organometallics* **2007**, *26* (17), 4204-4211; (b) Wada, K.; Itayama, N.; Watanabe, N.; Bundo, M.; Kondo, T.; Mitsudo, T.-a., *Organometallics* **2004**, *23* (24), 5824-5832; (c) Duchateau, R., *Chem. Rev.* **2002**, *102* (10), 3525-3542; (d) Feher, F. J.; Tajima, T. L., *J. Am. Chem. Soc.* **1994**, *116* (5), 2145-2146; (e) Cho, H. M.; Weissman, H.; Wilson, S. R.; Moore, J. S., *J. Am. Chem. Soc.* **2006**, *128* (46), 14742-14743.
- (a) Haddad, T. S.; Lichtenhan, J. D., *Macromolecules* **1996**, *29* (22), 7302-7304; (b) Haddad, T. S.; Viers, B. D.; Phillips, S. H., *J. Inorg. Organomet. Polym. Mater.* **2001**, *11* (3), 155-164; (c) Pielichowski, K. N.; Njuguna, J.; Janowski, B.; Pielichowski, J., *Adv. Polym. Sci.* **2006**, *201*, 225-296; (d) Phillips, S. H.; Haddad, T. S.; Tomczak, S. J., *Current Opinion in Solid State and Materials Science* **2004**, *8*, 21-29; (e) Shockey, E. G.; Bolf, A. G.; Jones, P. F.; Schwab, J. J.; Chaffee, K. P.; Haddad, T. S.; Lichtenhan, J. D., *Appl. Organomet. Chem.* **1999**, *13*, 311-327; (f) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J., *Macromolecules* **1995**, *28* (24), 8435-7; (g) Koh, K.; Sugiyama, S.; Morinaga, T.; Ohno, K.; Tsujii, Y.; Fukuda, T.; Yamahiro, M.; Iijima, T.; Oikawa, H.; Watanabe, K.; Miyashita, T., *Macromolecules* **2005**, *38*, 1264-1270.
- (a) Yoshida, K.; Ito, K.; Oikawa, H.; Yamahiro, M.; Morimoto, Y.; Ohguma, K.; Wantabe, K.; Ootake, N. Producing Process for Silsesquioxane Derivative Having Functional Group and Silsesquioxane Derivative. U.S. Pat. Appl. 0068074, Apr. 4, **2004**. (b) Oikawa, H.; Watanabe, K.; Ootake, N.; Kazuhiro, Y.; Iwatani, K. Novel Silicon Compounds and Process for Preparation Thereof. U.S. Pat. Appl. 0143081 Jul. 22, **2004**.
- (a) Feher, F. J.; Soulivong, D.; Eklund, A. G., *Chem. Commun.* **1998**, 399-400; (b) Feher, F. J.; Soulivong, D.; Nguyen, F., *Chem. Commun.* **1998**, 1279-1280; (c) Feher, F. J.; Soulivong, D.; Nguyen, F.; Ziller, J. W., *Angew. Chem., Int. Ed.* **1998**, *37* (19), 2663-2667.
- (a) Feher, F. J.; Phillips, S. H.; Ziller, J. W., *Chem. Commun.* **1997**, 829-830; (b) Feher, F. J.; Terroba, R.; Ziller, J. W., *Chem. Commun.* **1999**, 2309-2310.
- Feher, F. J.; Nguyen, F.; Soulivong, D.; Ziller, J. W., *Chem. Commun.* **1999**, 1705-1706.
- CCDC 843485 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- Liu, H.; Kondo, S.; Tanaka, R.; Oku, H.; Unno, M., *J. Organomet Chem* **2008**, *693*, 1301-1308.



SUPPORTING INFORMATION

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Figure S1. F-POSS compounds produced

S1. Methods and Materials

Materials. F-POSS (**1**) was synthesized according to literature procedure.^{3a} Trifluorosulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$, Aldrich), diphenyldichlorosilane (Gelest), (3-acryloxypropyl) methyldichlorosilane (Gelest), vinylmethyldichlorosilane (Gelest), and (3-methacryloxypropylmethyldichlorosilane (Gelest) were distilled prior to use. Tetrabutyl ammonium hydrogen sulfate ($\text{NBut}_4\text{HSO}_4$, Aldrich), hexafluoroisopropanol ($((\text{CF}_3)_2\text{CHOH}$, Synquest), hexafluorobenzene (C_6F_6 , Synquest), di-*n*-octadichlorosilane (Gelest), 1,3-dichloro-1,2,2,3,3-pentafluoropropane (AK-225G, AGC Chemicals Americas), and hexadecane (Aldrich) were used without further purification, unless otherwise stated. All reactions were performed under nitrogen.

Characterization. ^1H , ^{13}C , ^{19}F , and ^{29}Si NMR spectra were obtained on Bruker 300-MHz and 400-MHz spectrometers using 5 mm o.d. tubes. An inverse gated 30° pulse with a 12 sec delay was used to acquire ^{29}Si NMR spectra. Combustion analysis was performed by Atlantic Microlab, Inc. Norcross, GA. FT-IR measurements were measured on a Perkin Elmer Spectrum BX. Surface roughness measurements were taken on a Digital Instruments Nanoscope IV (AFM) and a Veeco WykoNT930 optical profilometer.

Surface Measurements. Dynamic contact angles experiments were conducted on a dataphysics OCA20 goniometer. Experiments consisted of placing a 3 μL drop of probing liquid onto a test substrate, adding an additional 2 μL through a dispensing needle at a rate of 0.2 $\mu\text{L}/\text{sec}$, and then removing 3 μL at 0.2 $\mu\text{L}/\text{sec}$. Consecutive frames (20-100) of experiment video during the addition and removal of probing liquid, where constant advancement or recession of the contact line was observed, were used to measure the advancing and receding contact angles, respectively. Measurements were made from a “tangent lean” fit using Dataphysics droplet fitting software.

X-Ray Crystallography Data. Single crystals for compound **2** were grown from slow evaporation of **2** in hexafluorobenzene, resulting in clear platelets. Crystal data for **2** was collected at $T=100.0$ (K) using Kusing Bruker 3-circle, SMARTAPEX CCD with c-axis fixed at 54.748 , running on SMART V 5.625 program (Bruker AXS: Madison,2001). Graphite monochromated $\text{Cu}_{K\alpha}$ ($\lambda= 1.54179$ Å) radiation was

employed for data collection and corrected for Lorentz and polarization effects using SAINT V 6.22 program (Bruker AXS: Madison, 2001), and reflection scaling (SADABS program, Bruker AXS: Madison, WI, 2001). Structure was solved by direct methods (SHELXL-97, Bruker AXS: Madison, 2000) and all non-hydrogen atoms refined anisotropically using full-matrix least-squares refinement on F^2 . Hydrogen atoms were added at calculated positions. For **2**, M_r =, monoclinic, space group P2(1)/c, $a=11.833(2)$ Å, $b=57.141(11)$ Å, $c=19.069(4)$ Å, $\alpha=90.00^\circ$, $\beta=92.20(3)^\circ$, $\gamma=90.00^\circ$, $V=12884(4)$ Å³, $F(000)=7816$, $\rho_{\text{calcd}}(Z=2)=2.068$ gcm⁻³, $\mu=3.183$ mm⁻¹, approximate crystal dimensions 0.60 x 0.35 x 0.20 mm³, θ range = 0.71 to 24.74°, 122186 measured data of which 21422 ($R_{\text{int}}=0.0608$, $R\sigma=0.0379$) unique with 3715 refined parameters, 14705 restraints were applied, final R indices [$I>2\sigma(I)$]: $R_1=0.0915$, $wR_2=0.1918$, $R_1=0.0857$, $wR_2=0.1893$ (all data), GOF on $F^2=1.230$. CCDC 843485 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-Ray Refinement of 2. The asymmetric unit shows a large amount of positional and rotational disorder among most of the fluorinated carbon chains. Therefore, in order to have an effective convergence, a large number of restraints were applied to the model. The thermal behavior of the structure was restrained using SIMU and DELU commands for Si1 to F36C. The ISOR command was applied to the F atoms due to their high disorder. The distances between C-C and C-F were restrained with the SAME command, using Si1 to F17 arm as the model unit for the other fluorinated segments since this segment contained no disorder. Fluorinated carbons from C23 to F34B contained two positional disordered chains and were mediated with the SUMP command. The EADP command was applied to F95 F95a, C84 C84a, and C85 C85a due to disorder. After a stable minimum was reached, hydrogen atoms were added at calculated positions to the alpha and beta carbon atoms. Hydrogen on O1 and O13 were added using DFIX to restrain their distances (0.84 anstroms) to their respective oxygen atoms.

S2. Experimental

Synthesis of $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(OH)_2$ (2) To a stirred solution of F-POSS (41.0 g, 10.3 mmol) in C_6F_6 (100 mL) at 25 °C CF_3SO_3H (9.00 mL, 102 mmol) was added. This solution was stirred for 75 min and $NBut_4HSO_4$ (17.0 g, 50.01 mmol) was added under a N_2 blanket. The heterogeneous solution was stirred for an additional 30 min. Stirring was then discontinued and the reaction mixture separated into two layers. The clear colorless bottom layer was subsequently removed and poured into a solution of $(CF_3)_2CHOH:H_2O$ (10:1, 50 mL) and stirred for 12 h. Ethyl acetate (350 mL) then poured into the reaction mixture and subsequently filtered to remove any unreacted F-POSS. The filtrate was collected and concentrated forming a waxy solid. This was then suspended in chloroform (300 mL) and filtered. The filtrand was collected, dried under vacuum for 18 h at 50 °C to yield the desired product as a solid free-flowing white powder (21.8 g, 53%). 1H NMR (300 MHz, $C_6D_6:C_6F_6$, ppm) δ 4.20 (br, 2H), 2.44 (br m, 16H) 1.19 (br m, 16H); δ ; ^{13}C NMR (C_6F_6 , ppm) δ 123-105 (CF_2 , CF_3) 24.5 ($SiCH_2CH_2$), 1.5 ($SiCH_2CH_2$), 1.0 ($SiCH_2CH_2$). ^{19}F NMR ($CDCl_3$) δ ; -82.3 (3F), -116.9 (2F), -122.8 (6F), -123.7 (2F), -124.3 (2F), -127.3 (2F). ^{29}Si NMR (C_6F_6 , ppm) δ -59.0, -65.5, -68.1 (1:1:2). IR (25 °C, KBr, cm^{-1}): 2990, 2960, 1452, 1240, 1155, 976, 904, 814, 705, 660. Anal. Calcd. for $C_{80}H_{34}F_{136}O_{13}Si_8$ (found): C, 23.95 (23.99), H, 0.85 (0.75), F, 64.41 (64.72).

General Synthesis of F-POSS Compounds. $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(O_2Si((CH_2)_7CH_3)_2)$ (3). A solution containing di-*n*-octyldichlorosilane (0.170 g, 0.552 mmol) and compound 2 (2.01 g, 0.501 mmol) in C_6F_6 (8.00 mL) were stirred together for 20 min. To this a solution of NEt_3 (136 μ L, 0.978 mmol) in C_6F_6 (1.00 mL) was added slowly and the reaction mixture was stirred for 12 h. This solution was then filtered and poured into ethyl acetate, at which time, a white solid precipitated (1) formed. This solid was removed *via* vacuum filtration and the filtrate was concentrated and dissolved in diethyl ether and filtered. The filtrate was collected and cooled to 0 °C affording a white precipitate. The precipitate was collected and dried under vacuum to afford a white powder (3) (1.05 g, 49%). 1H NMR

(CDCl₃:C₆F₆, ppm) δ 2.26 (br m, 16H), 1.52-1.25 (br m, 26H), 1.15-1.01 (m, 14H), 0.88 (m, 6H), 0.76 (m, 4H). ²⁹Si NMR ((CD₃CD₂)₂O, ppm) δ -17.8, -65.4, -68.2, -69.0 (1:2:4:2). ¹³C NMR (C₆F₆, ppm) 123-105 (CF₂, CF₃), 33.1, 31.6, 29.2, 29.1, 24.6 (m), 22.6, 22.1, 14.8, 2.2, 1.6, 1.0. ¹⁹F NMR ((CD₃CD₂)₂O, ppm) δ -82.3 (3F), -116.9 (2F), -122.8 (6F), -123.7 (2F), -124.3 (2F), -127.3 (2F). IR (25 °C, KBr, cm⁻¹): 2974, 2871, 1149, 1213, 1153, 976, 904, 814, 706, 663. m.p. = 64.8 - 66.9 °C. Anal. Calcd. for C₉₆H₆₆F₁₃₆O₁₃Si₉ (found): C, 27.04 (27.01), H, 1.56 (1.52), F, 60.59 (60.38).

(CF₃(CF₂)₇CH₂CH₂)₈Si₈O₁₁(O₂Si((C₆H₅)₂)) (4). This compound was not soluble in diethyl ether and was purified using a similar procedure as compound 2 above, using an ethyl acetate:hexafluorobenzene solvent mixture. Yield 61%. ¹H NMR (CDCl₃:AK-225G: ppm) δ 7.69 (mm, 4H), 7.46 (mm, 6H), 2.12 (br m, 16H), 1.06 (mm, 8H), 0.99 (mm, 8H). ¹³C NMR (C₆F₆, ppm) δ 133.4, 133.0, 127.07, 126.7, 123-105 (m, CF₂, CF₃), 24.4 (m), 2.0, 1.4, 0.9. ²⁹Si NMR (C₆F₆, ppm) δ -45.0, -65.8, -68.0, -68.2 (1:2:2:4). ¹⁹F NMR (CDCl₃:C₆F₆, ppm) δ -82.3 (3F), -116.9 (2F), -122.8 (6F), -123.7 (2F), -124.3 (2F), -127.3 (2F). IR (25 °C, KBr, cm⁻¹) 2987, 2943, 1729, 1149, 1213, 1153, 976, 904, 814, 706, 663. m.p. = 120.2 - 122.8 °C. Anal. Calcd. for C₉₂H₄₂F₁₃₆O₁₃Si₉ (found): C, 26.36 (26.22), H, 1.01 (0.91), F, 61.64 (61.38).

(CF₃(CF₂)₇CH₂CH₂)₈Si₈O₁₁(O₂Si((CH₃)CH=CH₂)) (5). This compound was not soluble in diethyl ether and was purified using a similar procedure as compound 3 above, using perfluorohexanes as solvent. Yield 59%. ¹H NMR (CDCl₃:C₆F₆, ppm) δ 6.23-5.85 (m, 3H), 2.41 (br m, 16H), 1.15 (br m, 16H), 0.47 (s, 3H); ²⁹Si NMR δ -32.1, -62.2, -68.7, -68.8, -69.1 (1:2:2:2:2). ¹³C NMR (C₆F₆, ppm) δ 134.0, 132.9, 123-105 (m, CF₂, CF₃), 24.5 (m), 2.1, 1.48, 1.0, -4.0. ¹⁹F NMR (CDCl₃:C₆F₆, ppm) δ -82.3 (3F), -117.3 (2F), -123.0 (6F), -123.8 (2F), -124.4 (2F), -127.3 (2F). IR (25 °C, KBr, cm⁻¹): 2987, 2943, 1729, 1149, 1213, 1153, 976, 904, 814, 706, 663. m.p. = 83.3 - 84.8 °C. Anal. Calcd. for C₈₃H₃₈F₁₃₆O₁₃Si₉ (found): C, 24.42 (24.28), H, 0.99 (0.81), F, 63.30 (63.00).

$(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(O_2Si((CH_3)((CH_2)_3OC(O)CH=CH_2))$ (6). Yield 67%. 1H NMR ($(CD_3CD_2)_2O$, ppm) δ 6.39 (dd, $J=17.3$ Hz, $J=1.5$ Hz, 1H), 6.11 (dd, $J=10.3$ Hz, $J=10.3$, 1H), 5.83 (dd, $J=10.4$ Hz, $J=1.5$, 1H), 4.19 (t, 2H), 2.25 (br m, 16H), 1.88 (m, 2H), 1.12 (br m, 16H), 0.85 (t, 2H), 0.34 (s, 3H). ^{13}C NMR (C_6F_6 , ppm) 164.9, 128.3, 127.3, 123-105 (m, CF_2 , CF_3), 65.2, 24.5 (m), 11.5, 2.1, 1.6, 1.0, -3.5. ^{29}Si NMR ($(CD_3CD_2)_2O$, ppm) δ -18.0, -65.8, -68.3, -69.1 (1:2:4:2). ^{19}F NMR ($(CD_3CD_2)_2O$, ppm) δ -82.2 (3F), -116.8 (2F), -122.6 (6F), -123.7 (2F), -124.4 (2F), -127.3 (2F). IR (25 °C, KBr, cm^{-1}): 2990, 2947, 1734, 1149, 1213, 1153, 976, 904, 814, 706, 663. m.p. = 76.3 - 78.2°C. Anal. Calcd. for $C_{87}H_{44}F_{136}O_{15}Si_9$ (found): C, 25.08 (25.18), H, 1.06 (1.06), F, 62.02 (62.23).

$(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(O_2Si((CH_3)((CH_2)_3OC(O)C(CH_3)=CH_2))$ (7). Yield 64%. 1H NMR ($(CD_3CD_2)_2O$, ppm) δ 6.01 (m, 1H), 5.56 (m, 1H), 4.16 (t, 2H) 2.25 (br m, 16H), 1.92 (s, 3H), 1.84 (m, 2H), 1.09 (br m, 16H), 0.76 (t, 2H), 0.26 (s, 3H). ^{13}C NMR (C_6F_6 , ppm) δ 166.0, 122.7, 122.6, 123-105 (m, CF_2 , CF_3), 65.4, 24.32 (m), 21.7, 15.9, 11.6, 2.2, 1.6, 1.0, -3.6. ^{29}Si NMR ($(CD_3CD_2)_2O$, ppm) δ -18.1, -66.1, -68.6, -69.3 (1:2:4:2). ^{19}F NMR ($(CD_3CD_2)_2O$, ppm) δ -82.26 (3F), -116.9 (2F), -122.6 (6F), -123.7 (2F), -124.3 (2F), -127.3 (2F). IR (25°C, KBr, cm^{-1}): 2979, 2947, 1729, 1149, 1213, 1153, 976, 904, 814, 706, 663. m.p. = 73.2 - 75.9°C. Anal. Calcd. for $C_{88}H_{46}F_{136}O_{15}Si_9$ (found): C, 25.29 (25.01), H, 1.11 (0.95), F, 61.82 (61.53).

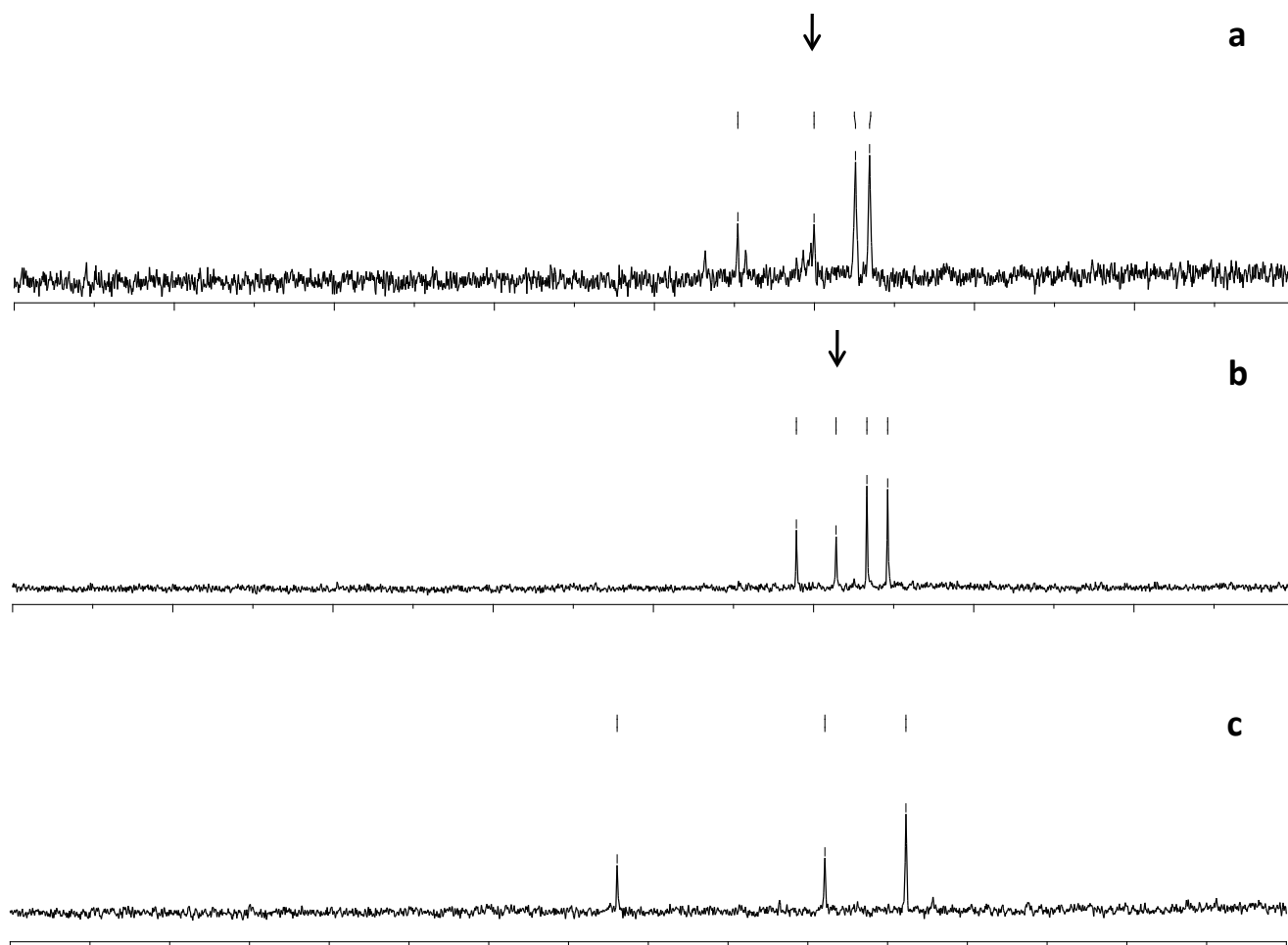


Figure S2. ^{29}Si NMR spectra: a) 60 minutes into reaction of **1** with triflic acid, b) 30 minutes after addition of $\text{NBut}_4\text{HSO}_4$ to reaction mixture, and c) compound **2** after purification. Arrow points to Si resonance from residual starting material compound **1**.

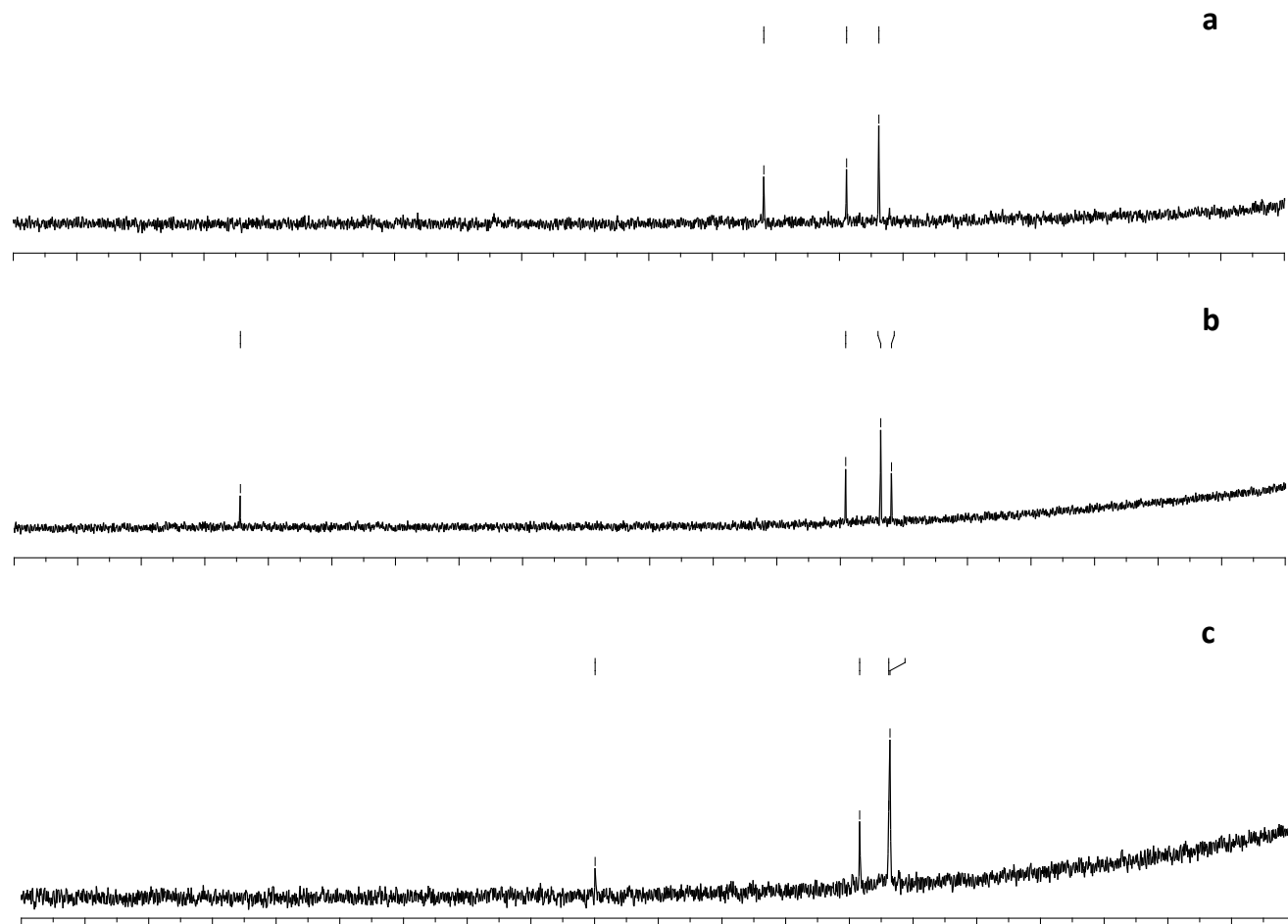


Figure S3. ^{29}Si NMR spectra of compounds a) 2, b) 3, and c) 4.

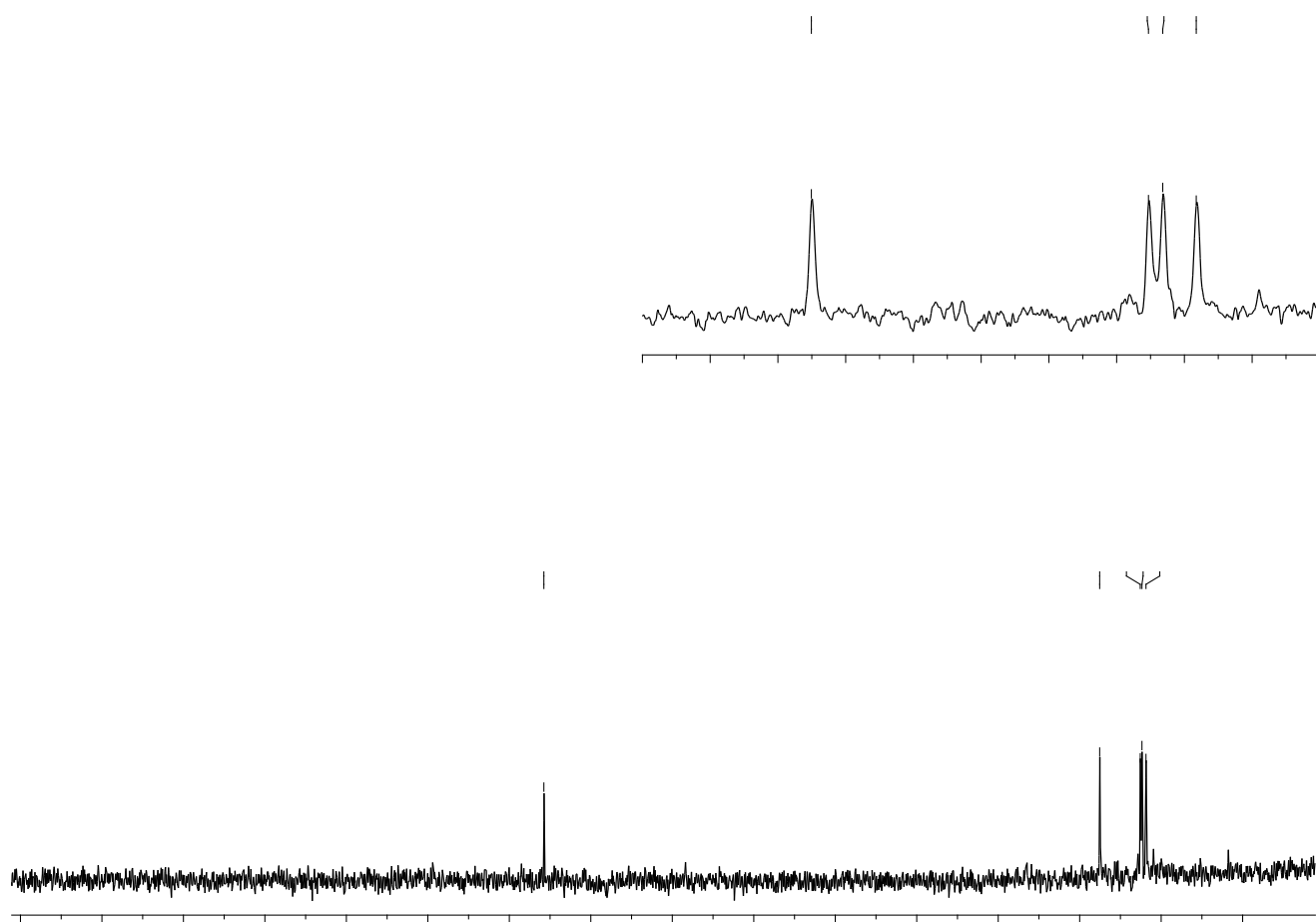


Figure S4. ^{29}Si NMR spectra of compounds 5.

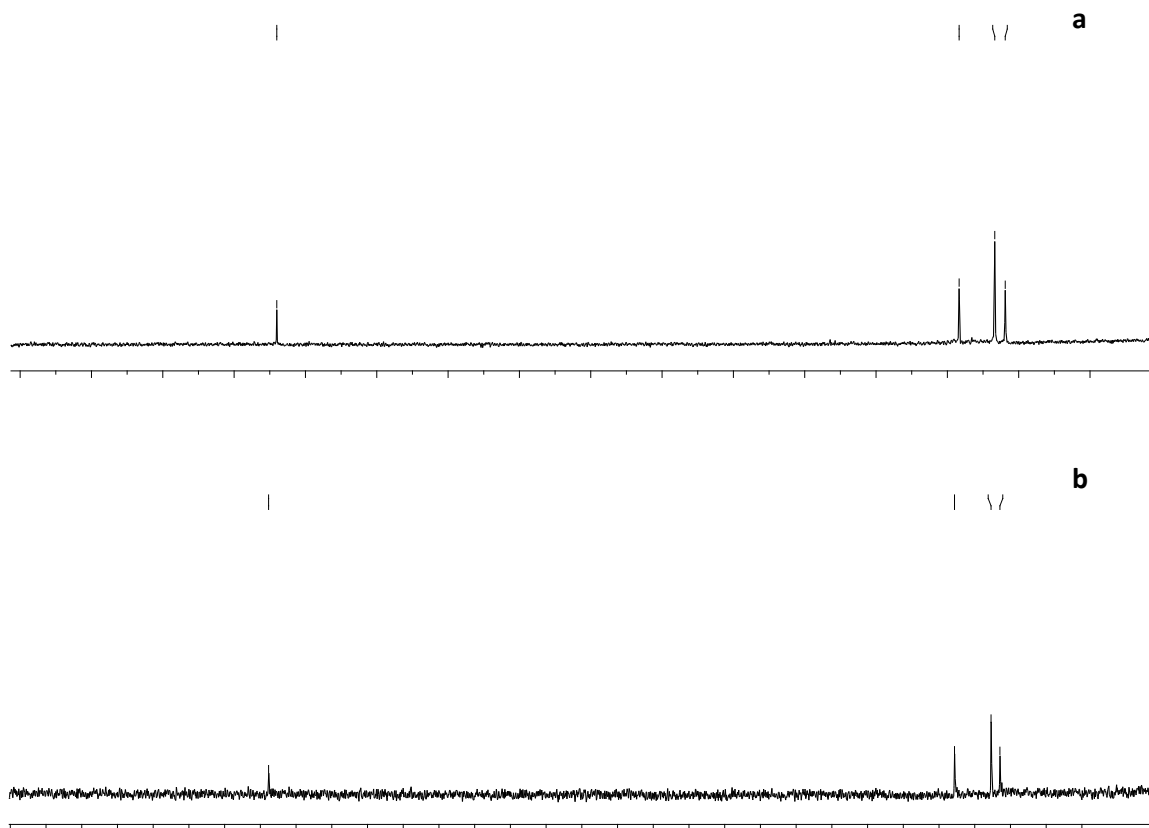


Figure S4. ^{29}Si NMR spectra of compounds a) **6** and b) **7**.

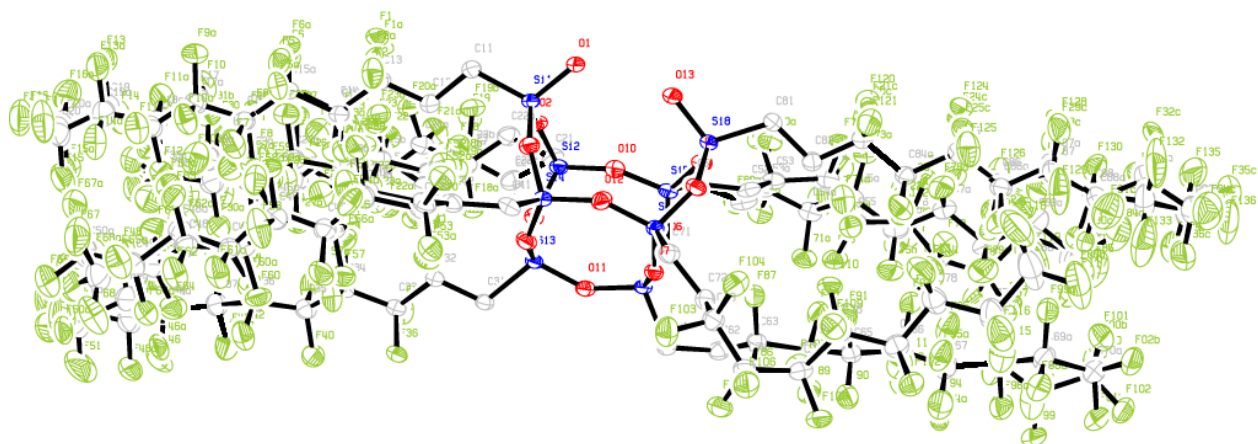


Figure S6. Labeled ORTEP of compound **2**. Thermal ellipsoids are shown at 50% probability. Green F, Grey C, Red O, Blue Si. White, H.

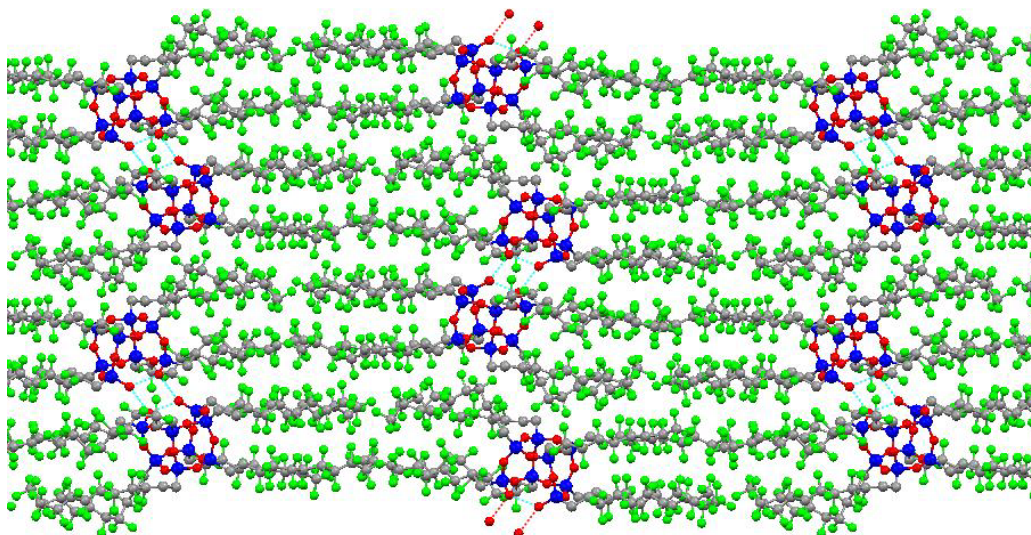


Figure S7. Crystal packing of compound 2 illustrating hydrogen bonds between silanols on silsesquioxanes. Green F, Grey C, Red O, Blue Si. White, H

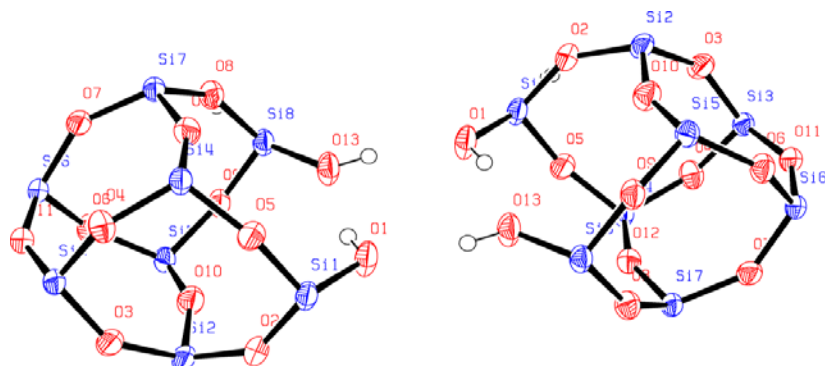


Figure S8. Zoom in view of hydrogen bonding dimer displaying hydrogen bonding interactions between inter- and intramolecular silanols. Fluorinated chains are omitted for clarity.

(1) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D. *Angew. Chem., Int. Ed.* **2008**, 47, 4137.