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

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S *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 superoleophobic 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 (^{1}H, ^{13}C, ^{19}F, and ^{29}Si), 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 superoleophobic 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(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)-POSS (F-POSS) possesses a periphery of long-chain fluorinated alkyl groups and has been determined to possess the lowest surface energy value (γ_{sv} = 9.3 mN/m) of any crystalline solid.[2] Superhydrophobic and superoleophobic 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 nonreactive 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)$_7$$Si_7O_9$-$(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 co-workers.[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 acidic[8] 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 toward an incompletely condensed long-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/superoleophobic coatings and other low surface energy materials.

A multistep synthetic procedure (Scheme 1) 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 $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(OTf)_2$ (**1a**). Due to an equilibrium between the open and closed-cage silsesquioxane frameworks, the ^{29}Si NMR spectra are complex. There is,

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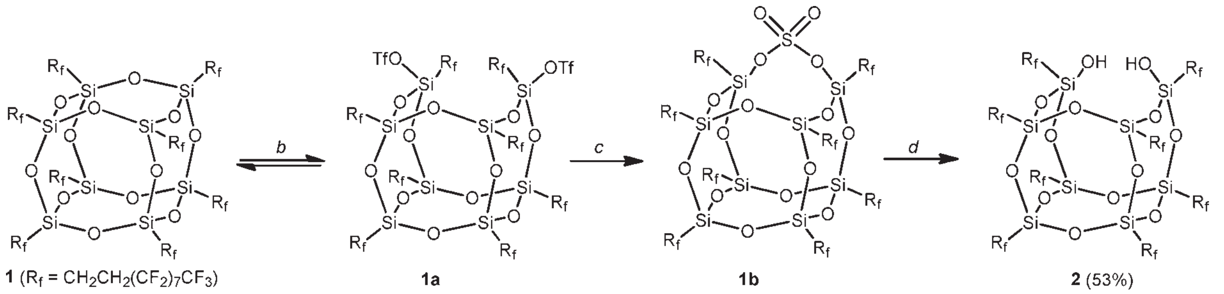
Scheme 1. Synthesis of Incompletely Condensed Fluoroalkyl Silsesquioxane[a]



[a] Conditions: All reactions were performed in C_6F_6 at 25 °C. [b]CF_3SO_3H, 75 min; [c]$NBut_4HSO_4$, 30 min; [d]$(CF_3)_2CH_2OH/H_2O$ (10:1), 12 h.

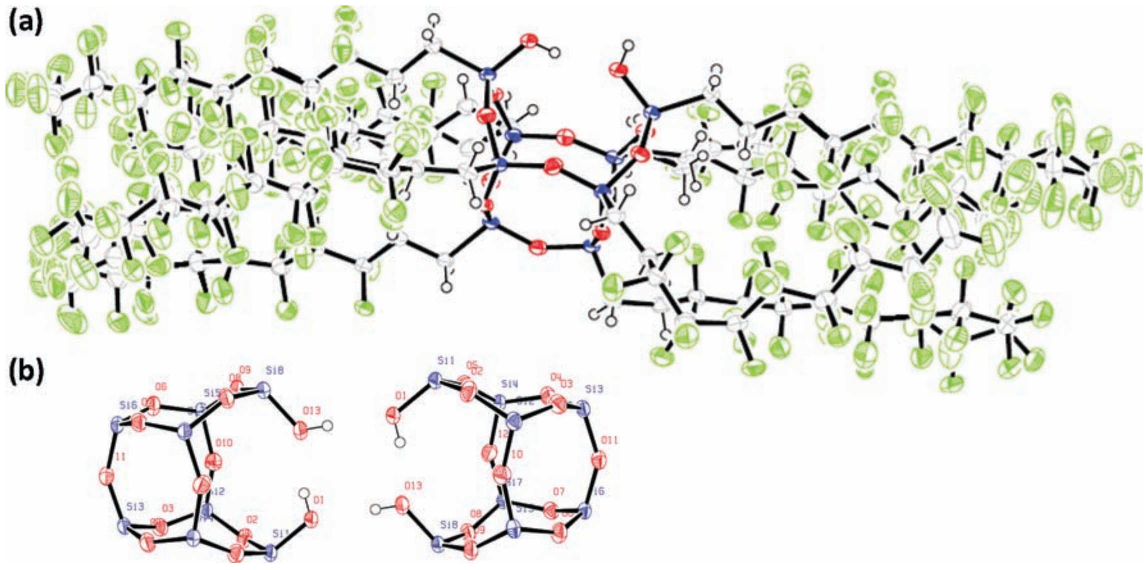


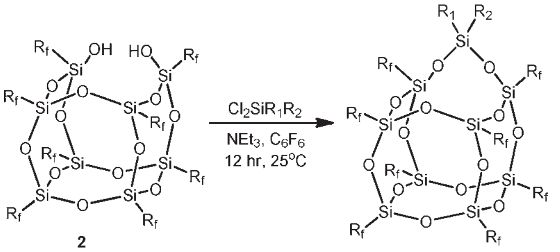
Figure 1. (a) ORTEP representation of **2** in crystal form at 100 K. The fluorinated chains contain substantial disorder. (b) F-POSS dimer displaying hydrogen-bonding interactions between inter- and intramolecular silanols (fluorinated chains omitted for clarity). Thermal ellipsoids shown at 50%. Green, F; gray, C; red, O; blue, Si; white, H.

however, clear evidence of the formation of **1a** as observed by ^{29}Si 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 **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 $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{13}(SO_2)$ (**1b**) over a 30 min period using an excess of $NBut_4HSO_4$ 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 ^{29}Si resonances at −64.5, −65.7, and −67.3 ppm (2:2:4). Similar to **1a**, **1b** reverts readily to **1** during any workup 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.[8] The reaction mixture is subsequently added to a polar fluorinated solvent/water (10:1) mixture to convert **1b** to $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(OH)_2$ (**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 C_6F_6 and ethyl acetate mixtures. Compound **1** precipitates from this solution; the soluble compound **2** is later precipitated from a $CHCl_3$ solution. The principal side product in each of these reactions was **1**, which was subsequently recycled. Combustion analysis and multinuclear NMR (^1H, ^{13}C, ^{19}F, and ^{29}Si) were used to confirm the structure of **2** (see Figure 2a). The ^{29}Si 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 **2** was obtained from C_6F_6 and determined to be monoclinic $P2_1/c$.

This structure contains rigid, helical-like fluoroalkyl chains, similar to **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 ^{29}Si NMR spectra. The crystal packing of **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 Å^3) for **2** compared to **1** (6340 Å^3).[3a] Hydrogen bonding between silanols on incompletely condensed silsesquioxanes has previously been observed for alkyl based POSS triols and diol.[4d,12] A dimeric contact is established from the intermolecular silanols at a distance of 2.798 Å. These intermolecular silanols are slightly closer than the intramolecular silanols, O(1)···O(13) at a distance of 2.810 Å and are still reactive to chlorosilanes.

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



2

	R_1	R_2	Yield
3	$-(CH_2)_7CH_3$	$-(CH_2)_7CH_3$	49%
4	$-C_6H_5$	$-C_6H_5$	61%
5	$-CH_3$	$-CH=CH_2$	59%
6	$-CH_3$	$-CH_2CH_2CH_2OC(O)CH=CH_2$	67%
7	$-CH_3$	$-CH_2CH_2CH_2OC(O)C(CH_3)=CH_2$	64%

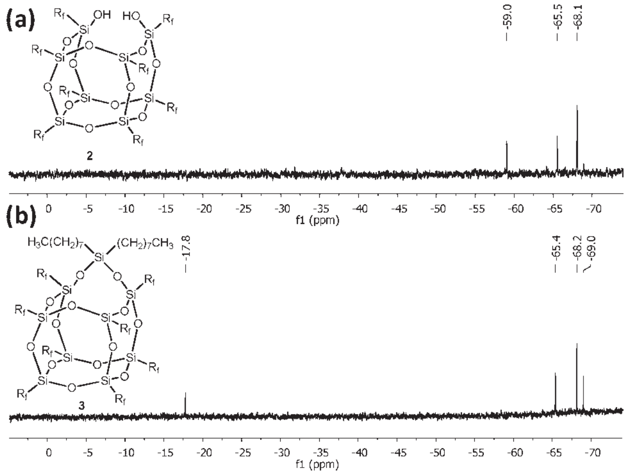


Figure 2. ^{29}Si NMR of (a) **2** and (b) **3**.

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 NEt_3 produced compound **3** (ca. 46% yield) with the loss of HCl. The primary side product isolated during the reaction was the initial starting material, **1**. Multinuclear NMR (^{1}H, ^{13}C, ^{19}F, and ^{29}Si), FT-IR, and combustion analysis were used to confirm the structure of **3**. The ^{29}Si resonances were −17.8, −65.4, −68.2, and −69.0 ppm, with a ratio of 1:2:4:2 (Figure 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 solvent 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 included 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 and low hydrocarbon content of the phenyl and vinyl groups on the POSS cage to overcome the fluorine character of the fluoroalkyl chains.

Table 1. Dynamic Contact Angle Measurements

	water		hexadecane	
functional group on F-POSS[a]	θ_{adv}, deg	θ_{rec}, deg	θ_{adv}, deg	θ_{rec}, deg
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
$Si-((CH_2)_7CH_3)_2$ (**3**)	117.9 ± 0.5	95.5 ± 0.4	69.1 ± 1.2	23.1 ± 1.2
$Si-(C_6H_5)_2$ (**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
$Si-((CH_3)((CH_2)_3OC(O)CCH{=}CH_2)$ (**6**)	118.2 ± 1.0	90.6 ± 1.0	76.8 ± 0.3	64.8 ± 1.0
$Si-(CH_3)((CH_2)_3OC(O)C(CH_3){=}CH_2)$ (**7**)	117.1 ± 0.6	93.8 ± 1.5	78.1 ± 0.4	63.0 ± 1.2

[a] F-POSS compounds were spin-cast from solutions of Asahiklin-225 (10 mg/mL) at a rate of 900 rpm for 30 s onto 1-in. silicon wafers following literature procedure.[2] Compound **2** was cast from C_6F_6 solution at a rate of 1400 rpm. Sample surface roughness was measured at <5 nm rms roughness for all samples via atomic force microscopy and optical profilometry.

The influence of functionality on non-wetting behavior was determined by examining static 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 **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, θ_{rec}-θ_{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 **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 ~7°. 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.

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 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 superoleophobic material properties.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed experimental procedures, analytical data, crystallography data, and ^{29}Si NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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