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Hydrophobic Compounds

Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS)**

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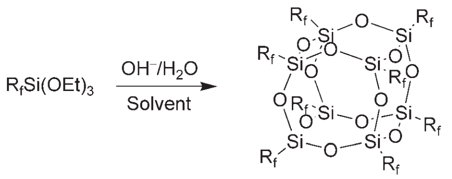
Water-repellent materials, possessing a high degree of hydrophobicity are currently under a spotlight. Preparative approaches are often inspired by naturally evolved biological systems.[1] Specifically, a leaf of the lotus plant exhibits an inherent self-cleaning mechanism resulting from micron-sized waxy nodes protruding from its surface such that water is naturally repelled, removing any foreign debris.[2,3] This cleansing mechanism, commonly referred to as the "lotus effect", has been artificially reproduced in order to prepare materials with pronounced hydrophobicity. Utilized techniques include surface patterning,[4] molecular self-assembly,[5] deposition,[6] and etching.[7] However, these examples often require aggressive chemical surface treatments, high temperature post-surface modification, or elaborate patterning. For such reasons, there exists a demand to engineer hydrophobic materials that are easy to prepare on a large scale.

Fluorinated compounds are an obvious choice for hydrophobic applications due to their low surface energy. Polyhedral molecules may also improve hydrophobic character by increasing the roughness of the material surface. There have been many reported attempts to synthesize and characterize partially or fully fluorinated polyhedra. These reports include the fluorination or fluoroalkylation of C_{60}.[8] Unfortunately, $C_{60}F_{48}$ cannot be used as a hydrophobic material, as it is metastable and is hydrolyzed in aqueous solutions.[9] The perfluorocarborane species, perfluoro-deca-β-methyl-*para*-carborane, characterized by single crystal X-ray studies, shows remarkable hydrolytic and oxidative stability.[10] Fluorinated carbon nanotubes and nanofibers have also been produced.[11] These fluorinated polyhedral compounds may be useful in hydrophobic applications, but are generally hazardous to prepare, require air and moisture sensitive manipulations, and have limited economies of scale. For these reasons, alternative fluorinated polyhedra are highly desired.

Polyhedral oligomeric silsesquioxanes (POSS) are thermally robust cages consisting of a silicon–oxygen core framework possessing alkyl functionality on the periphery. They are used for the development of high performance materials in medical, aerospace, and commercial applications.[12] POSS molecules can be functionally tuned, are easily synthesized with inherent functionality, are discreetly nano-sized, and are often commercially available. Furthermore, POSS compounds may possess a high degree of compatibility in blended polymers and can easily be covalently linked into a polymer backbone.[13] The incorporation of POSS into polymers produces nanocomposites with improved properties, such as, but not limited to, glass transition temperature, mechanical strength, thermal and chemical resistance, and ease of processing.

Attempts to produce fluorinated POSS compounds have met with little success. The hydrolysis of (3,3,3-trifluoropropyl)trichlorosilanes resulted in a mixture of products.[14] After purification, the octamer, $(3,3,3\text{-trifluoropropyl})_8Si_8O_{12}$ (**FP**) POSS was isolated in 10–32% yield. More recently, **FP** was produced by a "corner-capping" methodology that requires multiple steps, as well as the use of the moisture sensitive trisodium salt, $Na_3(3,3,3\text{-trifluoropropyl})_7Si_7O_{12}$.[15] To date, attempts to produce long-chain fluoroalkyl POSS compounds have proved unsuccessful.

Herein, we demonstrate the facile preparation of a novel class of octameric fluorinated POSS compounds (F-POSS) by the facile, single-step, base-catalyzed condensation of trialkoxysilanes in alcoholic media to produce nearly quantitative yields of octameric F-POSS compounds (Scheme 1).



FH R_f = $CH_2CH_2CF_2CF_2CF_2CF_3$
FO $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$
FD $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$

Scheme 1. Synthesis of F-POSS compounds **FH**, **FO**, and **FD**.

$(1H,1H,2H,2H\text{-NonaFluorohexyl})_8Si_8O_{12}$ (**FH**), $(1H,1H,2H,2H\text{-tridecafluorooctyl})_8Si_8O_{12}$ (**FO**), and $(1H,1H,2H,2H\text{-heptadecafluorodecyl})_8Si_8O_{12}$ (**FD**) POSS have been produced by this operationally simple, one-pot synthesis. For hydrophobicity comparative studies, **FP** (where $R_f = CH_2CH_2CF_3$) was produced using an alternate methodology.[15]

These F-POSS compounds are soluble in fluorinated solvents and their melting points lie between 122 and 140 °C. Unlike most non-fluorinated POSS compounds, thermogravimetric analysis (TGA) indicates F-POSS volatilize rather than decompose, as no residue remains after heating under either nitrogen or dry air. **FD** is the most stable compound,

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subliming at over 300 °C. F-POSS are also very dense, high molecular weight materials. For example, **FD** has a molecular weight of 3993.54 $\mathrm{g\,mol^{-1}}$ and a density of 2.067 $\mathrm{g\,cm^{-3}}$.

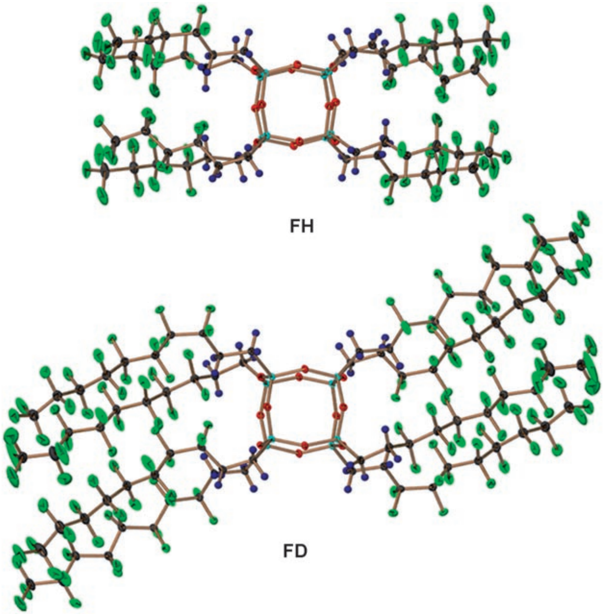

Figure 1. ORTEP representation of **FH** and **FD** POSS at 103 K, with thermal ellipsoids set at 50% probability. Green F, black C, dark blue H, red O, light blue Si.

The ability to crystallize F-POSS compounds from fluorinated solvents, using solvent evaporation/vapor diffusion techniques, enabled the growth of single crystals for high resolution (0.75 Å) X-ray diffraction studies (Figure 1). Both **FH** and **FD** are triclinic ($P1$) showing the presence of one and two crystallographically independent "half" molecules in the asymmetric unit, respectively. In both cases, there is an inversion center in the middle of the POSS core, which results in four pairs of fluoroalkyl chains with similar conformations. The molecular structure of F-POSS contains rigid, rod-like fluoroalkyl chains, which are attached to the silicon atoms of the POSS cage by flexible methylene groups. The relative arrangement of these components and resulting molecular interactions determine their thermal properties and may also contribute to surface properties, including hydrophobicity. The crystal structures of **FH** and **FD** showed a near-parallel arrangement of the fluoroalkyl chains. These result from the formation of strong intramolecular interactions between electropositive silicon and electron-rich fluorine atoms. These intramolecular contacts of approximately 3.0 Å are significantly shorter than the sum of van der Waals radii for silicon and fluorine at 2.10 and 1.47 Å, respectively.[16] The packing of **FD** results in the POSS cores resting at an angle, with respect to the linear fluoroalkyl groups (mean least square angle ca. 104°). This results in a rougher packing surface than **FH**, as seen in the electrostatic potential surfaces (Figure 2). This may also contribute to differences in hydrophobicity.

The hydrophobicity of spin-cast F-POSS surfaces was tested using water drop shape analysis and measured for the corresponding water contact angle (Figure 3). The relationship of contact angle and surface energy is governed by Young's equation, which relates the interfacial tension of the surface to the liquid and gas phases of water.[17] A trend was observed where the F-POSS static water contact angles increased with longer fluorocarbon chain length. Similar observations have been made in many fluorinated systems, including polymers,[18] copolymers,[19] and monolayers,[20] as well as corresponding to total fluorine content.[21] **FD** was surprisingly found to have a static water contact angle over 150°. In fact, **FO** and **FD** are so hydrophobic that, even with a density over 2 $\mathrm{g\,cm^{-3}}$, crystals (ca. 15 mm × 15 mm × 3 mm) of these F-POSS compounds float on the surface of water!

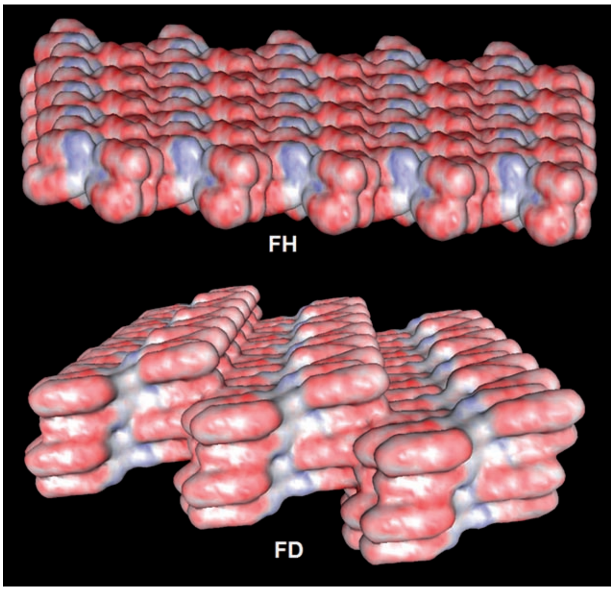

Figure 2. Electrostatic potential surfaces of **FH** and **FD** POSS.

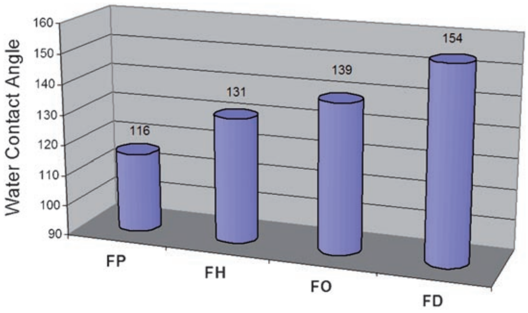

Figure 3. Graph showing water contact angles of **FP**, **FH**, **FO**, and **FD**. Hydrophobicity increases with fluoroalkyl chain length.

It is well known that hydrophobicity is a function of both surface tension and surface roughness, as demonstrated by Cassie and Baxter[22] and Wenzel.[23] Figure 4a is a height image taken with an atomic force microscope (AFM) of a spin-cast **FD** surface. This surface has a root-mean-squared (rms) roughness of approximately 4 μm. Surfaces of all F-POSS compounds were prepared in the same manner, with

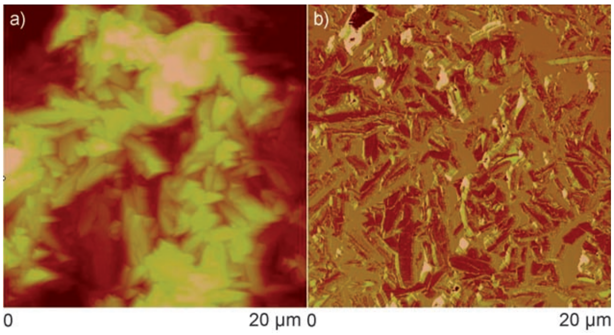

Figure 4. AFM analysis of the height (a) and phase image (b) of a spin-cast film surface of **FD**. Micron-sized crystallites can be observed in the height image. The rms roughness values for all spin-cast films were between 3 and 4 μm.

similar 3–4 μm rms surface roughness. Figure 4b is the phase image of the same surface.

In conclusion, new octameric fluorinated polyhedral oligomeric silsesquioxanes (F-POSS) have been produced by a facile "one-pot" synthetic method. The polyhedral compounds can be prepared in nearly quantitative yields and hundred gram quantities, eliminating the need for complex processes and patterning techniques to produce hydrophobic fluorinated surfaces. The compounds were shown to be thermally and hydrolytically stable and are less-hazardous to prepare than many other fluorinated compounds. These compounds are also soluble and have low melting temperatures, indicating that they may be solvent/melt-processed into polymers for desired property enhancements. The incorporation of F-POSS into polymers may produce nanocomposites with improved surface properties, including hydrophobicity. To our knowledge, **FD** is the most hydrophobic crystalline solid material known.

Experimental Section

All reagents were purchased from commercial sources and purified according to established procedures.[24]

Synthesis of **FH**: To a solution of 1*H*,1*H*,2*H*-nonafluorohexyltriethoxysilane (4.1 g) in ethanol (10 mL) was added KOH (2 mg) dissolved in deionized water (270 mg) at room temperature. After continuous stirring for 24 h, a white precipitate was filtered and washed repeatedly with ethanol. The solid was collected and redissolved in Asahiklin AK-225G (1,3-dichloro-1,1,2,2,3-pentafluoropropane), and residual KOH was extracted by washing repeatedly with deionized water. The organic layer was dried with $MgSO_4$, filtered, concentrated, and dried under vacuum to afford (1*H*,1*H*,2*H*,2*H*-nonafluorohexyl)$_8$$Si_8O_{12}$ (**FH**) as a white solid in nearly quantitative yield. **FO** and **FD** were prepared in a similar manner using 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyltriethyoxysilane and 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyltriethoxysilane, respectively.

Attempts to obtain **FP** using the same process resulted in a mixture of eight-, ten-, and twelve-membered polyhedra. Therefore, **FP** was prepared by the recently reported "corner-capping" of (3,3,3-trifluoropropyl)$_7$$Si_7O_{12}$ trisodium salt with 3,3,3-trifluoropropyltrichlorosilane.[15]

Detailed X-ray crystallography data,[25] surface preparation data, and analytical characterization data of F-POSS compounds are included in the Supporting Information.

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Keywords: fluorinated polyhedra · hydrophobicity · lotus effect · silsesquioxanes · surface roughness

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[25] Crystal data for **FH** and **FD** was collected at $T = 103.0(2)$ K using Bruker 3-circle, SMART APEX CCD with χ-axis fixed at 54.74°, running on SMART V 5.625 program (Bruker AXS: Madison, 2001). Graphite monochromated $Mo_{K\alpha}$ ($\lambda = 0.71073$ 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**). Both the structures were solved by direct methods (SHELXTL 5.10, 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 **FH**, $M_r = 2393.46$, triclinic, space group $P\bar{1}$, $a = 11.806(5)$, $b = 12.393(5)$, $c = 15.729(6)$ Å, $\alpha = 75.073(6)$, $\beta = 76.024(6)$, $\gamma = 66.151(5)°$, $V = 2009.0(14)$ Å^3, $F(000) = 1176$, $\rho_{calcd}(Z{=}1) = 1.987$ g cm^{-3}, $\mu = 0.356$ mm^{-1}, approximate crystal dimensions $0.37 \times 0.24 \times 0.20$ mm^3, θ range = 1.36 to 25.35°, 19582 measured data of which 7288 ($R_{int} = 0.0194$) unique with 718 refined parameters, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0368$, $wR2 = 0.0981$, $R1 = 0.0389$, $wR2 = 0.1002$ (all data), GOF on $F^2 = 1.038$. For **FD**, $M_r = 3993.78$, triclinic, space group $P\bar{1}$, $a = 10.352(1)$, $b = 21.984(2)$, $c = 28.653(3)$ Å, $\alpha = 102.082(1)$, $\beta = 95.702(1)$, $\gamma = 90.907(1)°$, $V = 6340.2(1)$ Å^3, $F(000) = 3888$, $\rho_{calcd}(Z{=}2) = 2.092$ g cm^{-3}, $\mu = 0.341$ mm^{-1}, approximate crystal dimensions $0.43 \times 0.30 \times 0.15$ mm^3, θ range = 1.31 to 25.37°, 49607 measured data of which 23049 ($R_{int} = 0.0203$) unique with 2125 refined parameters, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0564$, $wR2 = 0.1599$, $R1 = 0.0676$, $wR2 = 0.1728$ (all data), GOF on $F^2 = 1.005$. CCDC 608207 (**FH**) and 608209 (**FD**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.