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13. SUPPLEMENTARY NOTES Conference paper for the American Chemical Society National Conference, San Diego, California in 25-29 March 2012.					
14. ABSTRACT Incompletely-condensed fluoroalkyl-functional Polyhedral Oligomeric SilSesquioxanes (F-POSS) have been synthesized <i>via</i> a scaleable three-step synthetic process with an overall yield of 52%. The primary byproduct of each step in the synthesis is the completely-condensed F-POSS starting material, which enables the recycling of the starting materials. The incompletely condensed structures were readily reacted with a variety of functional dichlorosilanes to introduce reactive or unreactive functionality and produce unsymmetrical F-POSS structures. Chemical structures were confirmed by elemental analysis, multinuclear NMR (¹ H, ¹³ C, ¹⁹ F, and ²⁹ Si), and FT-IR methods. Single crystal X-ray diffraction was used to elucidate the crystal structure of the precursor F-POSS disilanol. The functionalized F-POSS structures were found to possess variable solubility properties, generally superior to those of the closed-cage F-POSS starting material. Dynamic contact angle measurements of these compounds were examined using water and hexadecane as the wetting liquids. Copolymers of poly(methyl methacrylate) containing F-POSS were synthesized from methacrylate F-POSS macromers. These novel structures can be used as building blocks for the development of low surface energy materials.					
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16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 31	19a. NAME OF RESPONSIBLE PERSON Joseph Mabry
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FUNCTIONALIZED FLUORINATED POLYHEDRAL OLIGOMERIC SILSESQUOXANE (F-POSS)

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ACS Meeting 2012



Polymer Working Group



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Dr. Joseph Mabry
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Dr. Josiah Reams



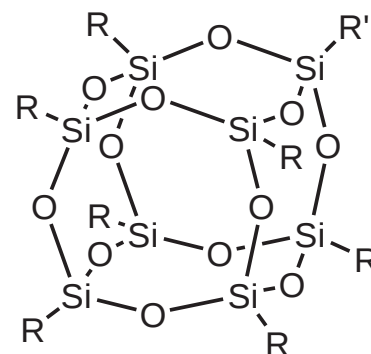
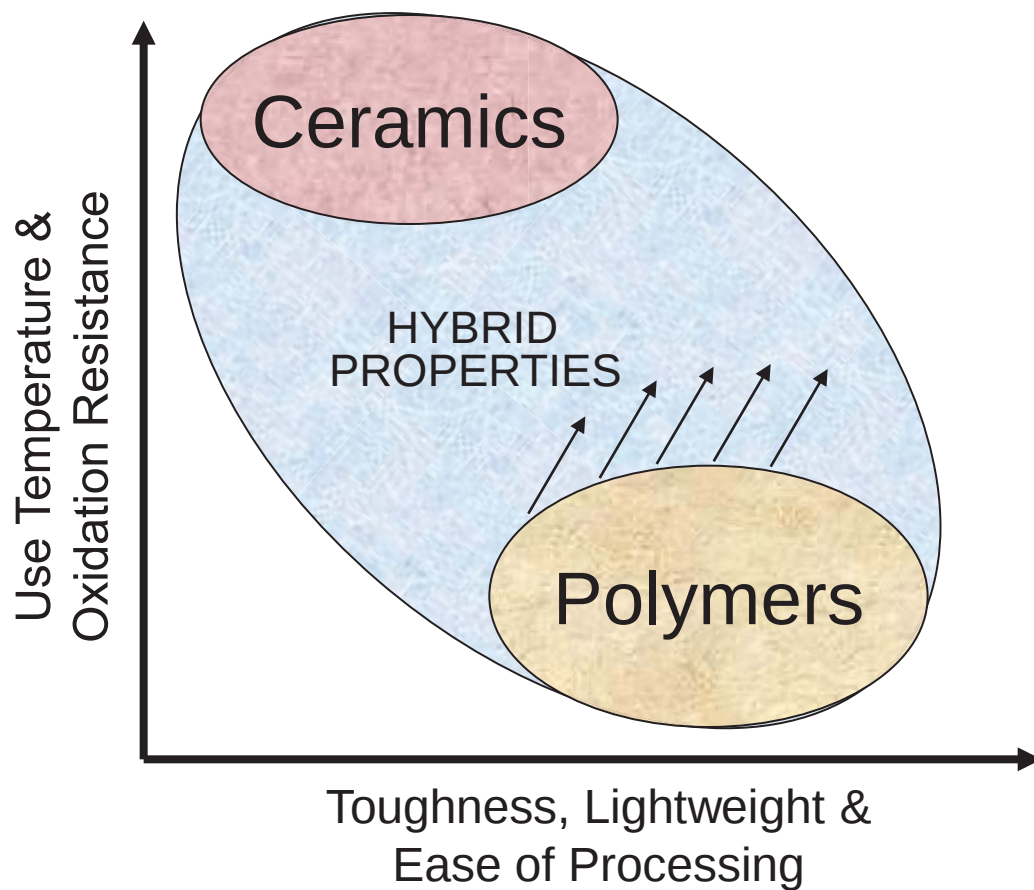
Mr. Brian Moore
Mr. Kevin Lamison
Dr. Tim Haddad
Dr. Andy Guenthner
Dana Pinson

Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate

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Hybrid Inorganic/Organic Polymers

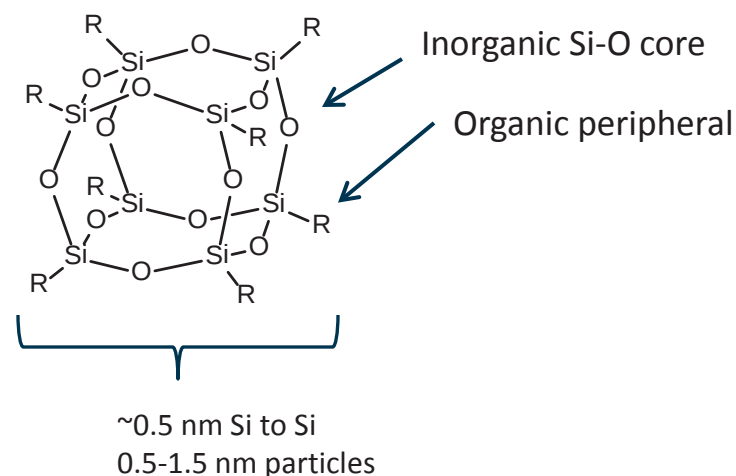




POSS (RSiO_{1.5})_n



- Organic-inorganic framework
- Well-defined, 3-D nanostructure
- Can carry functional groups
- Thermally and chemically robust
- Used in thermoset and thermoplastic polymers, temperature nanocomposites, coatings, surface modifiers, and many other applications



Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* **2010**, 110, 2081.

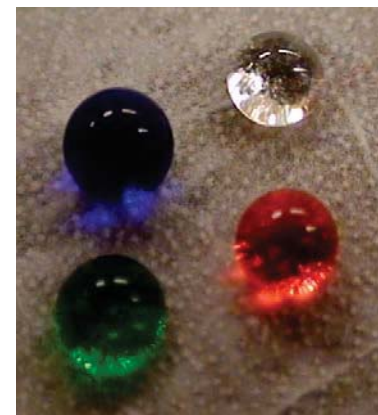
Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Current Opinion in Solid State and Materials Science* **2004**, 8, 21.

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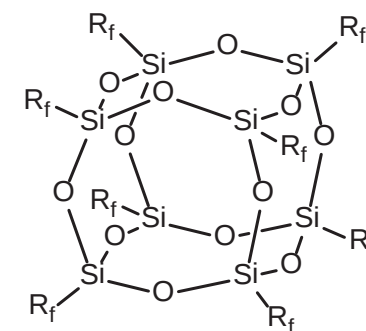


Introduction F-POSS

- Fluorinated polyhedral oligomeric silsesquioxane (F-POSS) possesses one of the lowest surface energies leading to the creation of superhydrophobic and oleophobic surfaces
- Close-caged structures are accessible and have proven versatile in polymer composites
 - Limitations
 - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
 - Open door for use a *building block* material for *low surface energy materials*
- Applications
 - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
 - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
 - Effects on polymer composite properties
 - Wetting, phase behavior, solubility, etc....



PMMA + 44 wt% POSS electrospun coating (beads on a string) morphology (water, methanol, diiodomethane, octane)



Fluorodecyl POSS
 $R_f = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$

(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; (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; (f) 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.

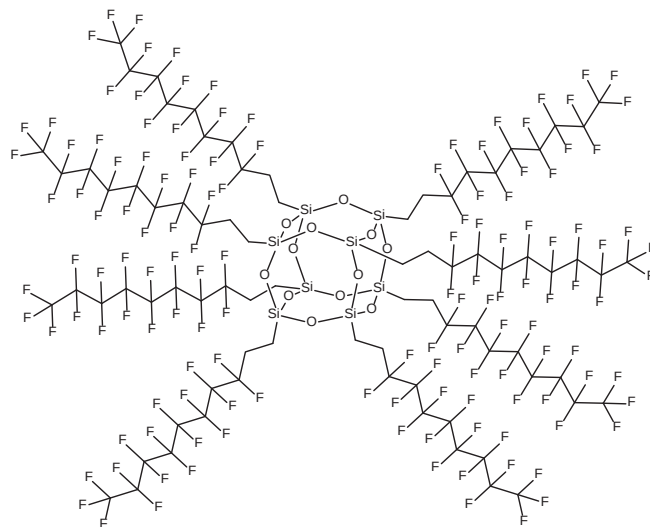


Fluorinated polyhedral oligomeric silsesquioxane (F-POSS)



F-POSS, a subclass of POSS which consists of a silicon-oxide core $[\text{SiO}_{1.5}]$ with a periphery of long-chain fluorinated alkyl groups.

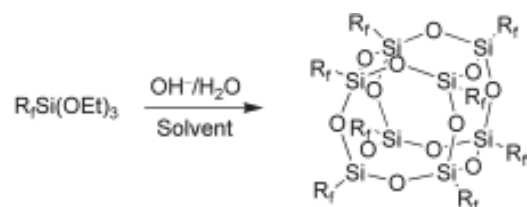
F-POSS possesses one of the lowest surface energies leading to the creation of superhydrophobic and oleophobic surfaces.



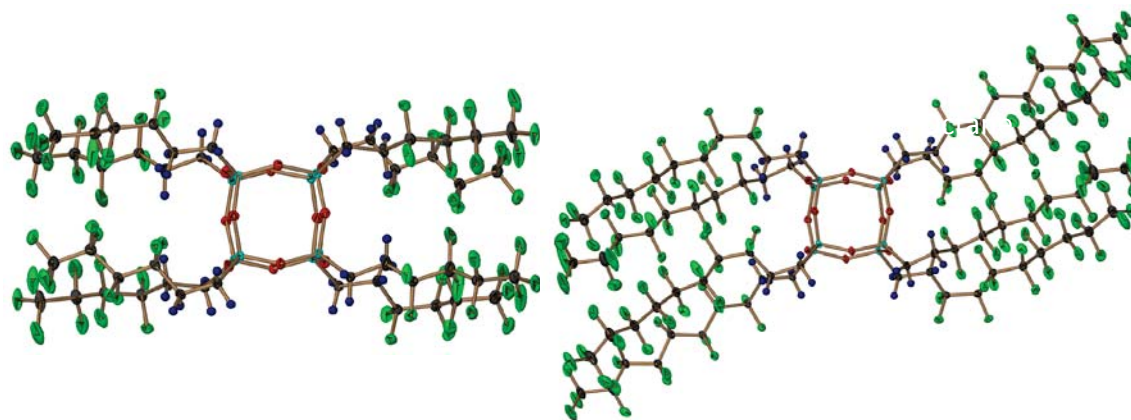
(a) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D., *Angew. Chem., Int. Ed.* **2008**, 47, 4137-4140; (b) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W., Jr., *Macromolecules* **2007**, 40, 9517-9522; (c) Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M., *Chem. Commun.* **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; (c) 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; (f) 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.



Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS)

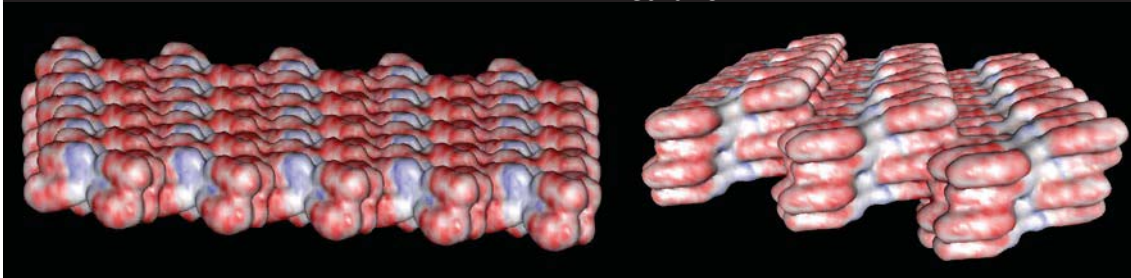


FH $R_f = \text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$
 FO $\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$
 FD $\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$



Fluorohexyl₈T₈

Fluorodecyl₈T₈
Methanol



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

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. (right)

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Functional F-POSS

- Close-caged structures are accessible and have proven versatile in polymer composites
 - Limitations
 - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
 - Open door for use a *building block* material for *low surface energy materials*
- Applications
 - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
 - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
 - Effects on polymer composite properties
 - Wetting, phase behavior, solubility, etc....



Methods to Produce Incompletely Condensed Silsesquioxanes



- Bottom-up approach
 - Acid or base mediated from RSiCl_3 or RSi(OR)_3
 - Condensation reaction
 - Balance of stoichiometry, temperature, reaction time, patience, and luck
 - Stopping POSS synthesis early, before cage fully condenses
 - More common approach
- Top-down Approach
 - Strong acid or base mediated
 - Starting from a POSS cage
 - Conversion of Si-O-Si bonds to Si-O⁽⁻⁾ C⁽⁺⁾ or Si-OH bonds
 - Opening up POSS cage

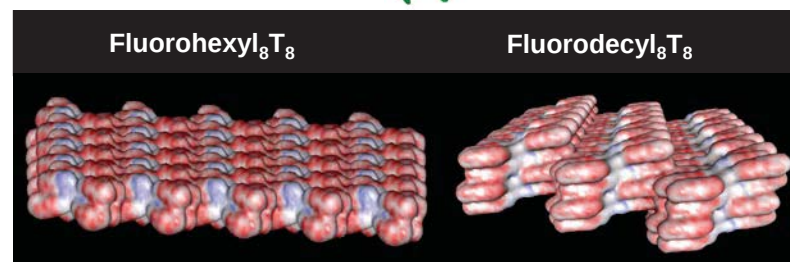
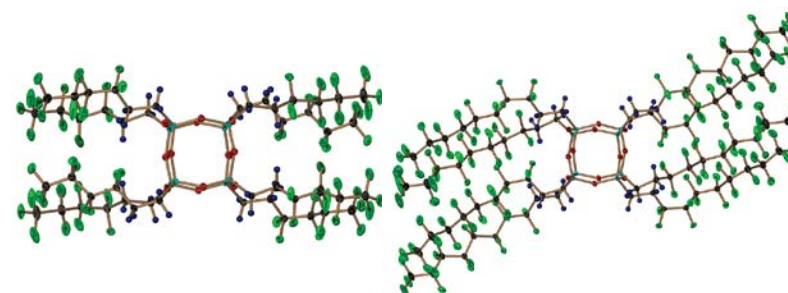
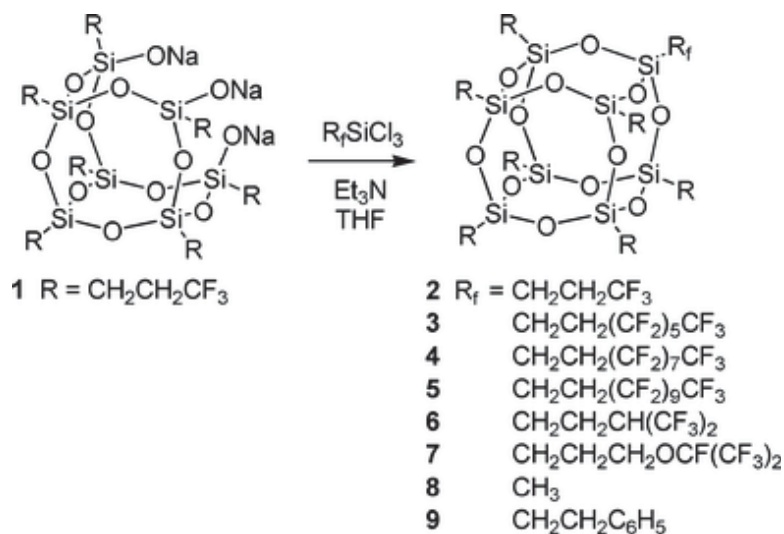
Which method can be applied to F-POSS?

Feher, F. J.; Terroba, R.; Ziller, J. W. *Chemical Communications* **1999**, 2309. Feher, F. J.; Newman D.A.; Walzer, J.M., *J. Am. Chem. Soc.*, **1989**, 111, 1741. Feher, F. J.; Soulivong, D.; Nguyen, F.; Ziller, J. W. *Angew.Chem. Inter. Ed.* **1998**, 37, 2663. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* **1998**, 1279.



Trifluoropropyl Example

- Small chain F-POSS (propyl) have been developed and studied
- Demonstrate the robustness of an incompletely condensed silsesquioxane to functionalization





Methods to Produce Incompletely Condensed Silsesquioxanes



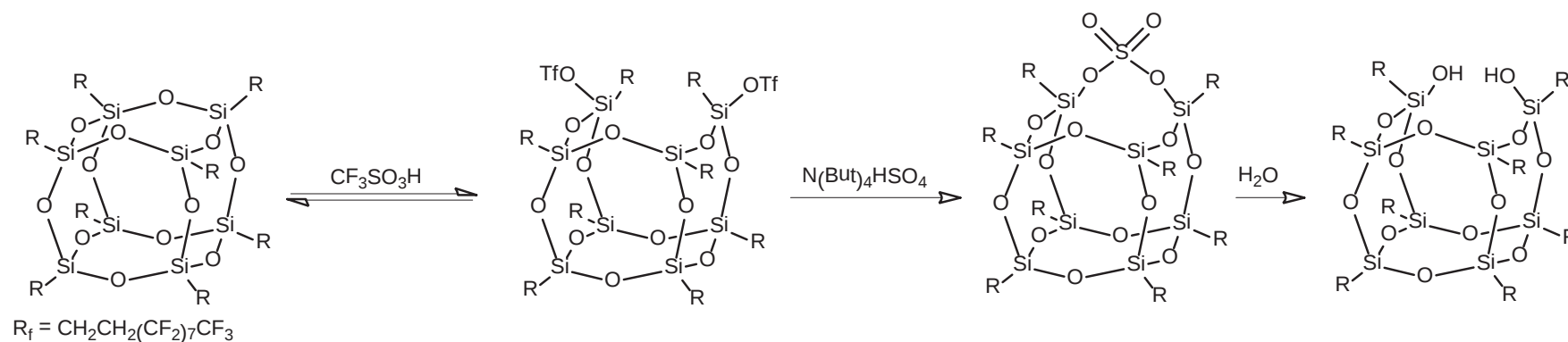
- Bottom-up approach
 - Acid or base mediated from RSiCl_3 or RSi(OR)_3
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 - Balance of stoichiometry, temperature, reaction time, patience, and luck
 - Stopping POSS synthesis early, before cages closes
 - More common approach
- Top-down Approach
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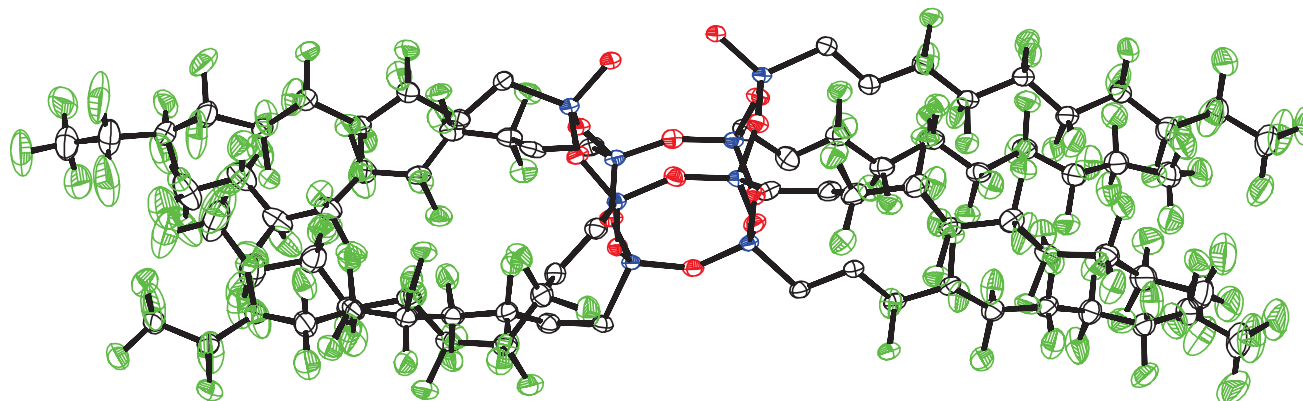
Incompletely Condensed Silsesquioxane



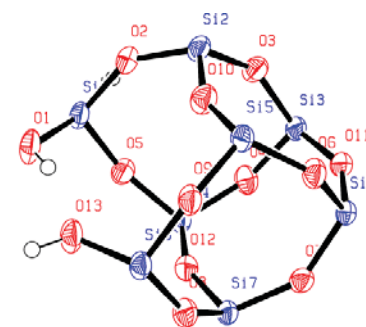
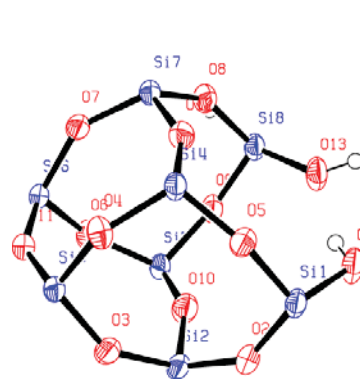
- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.*



X-Ray Crystal Structure of Disilanol



- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- M_r =, monoclinic, space group $P2(1)/c$, $a=11.84(10)$ Å, $b=57.11(6)$ Å, $c=19.06(2)$ Å, $\alpha=90.00^\circ$, $\beta=92.21(10)^\circ$, $\gamma=90.00^\circ$, $V=12878(2)$ Å³



Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, **2011**, 133, 20084.

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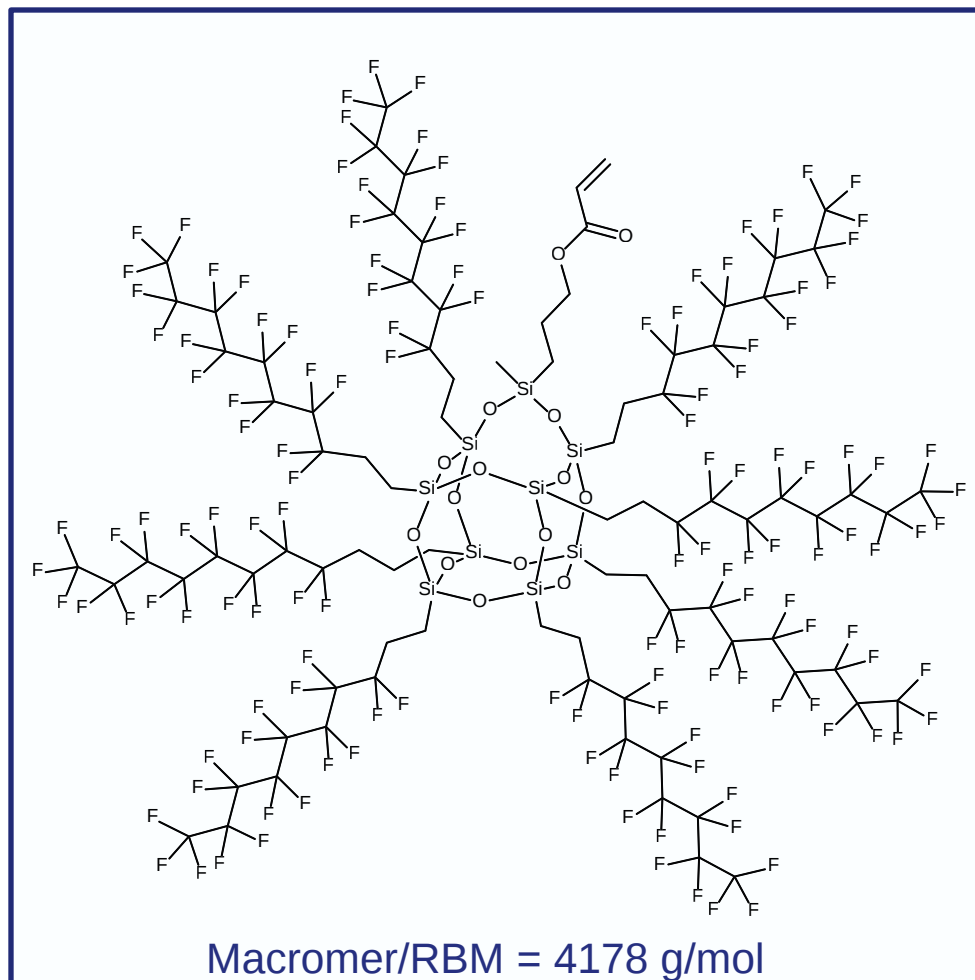


Edge Capping Reactions



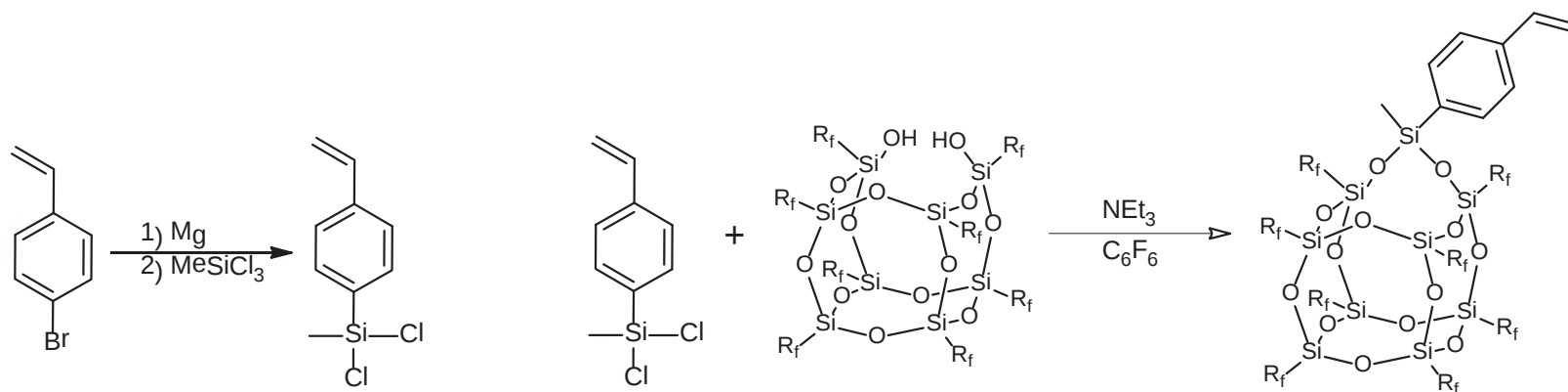
$\text{R} = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$
 $\text{R}_1 = \text{CH}_3$
 $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{OC(O)CHCH}_2$

- Edge capping reactions typically have 40-70% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes



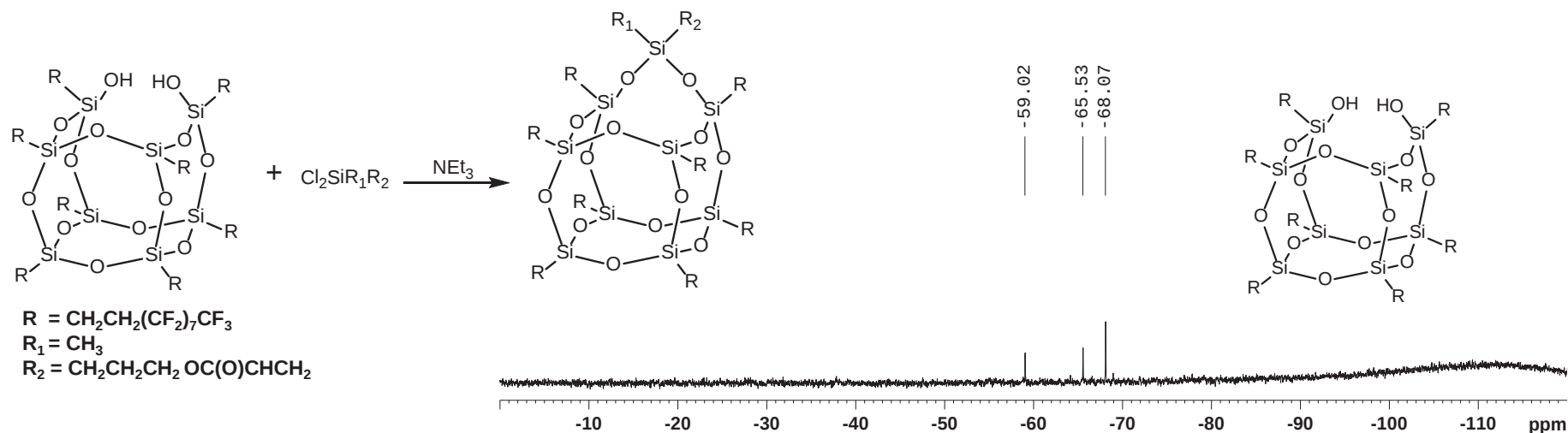


Styrene Monomer Synthesis

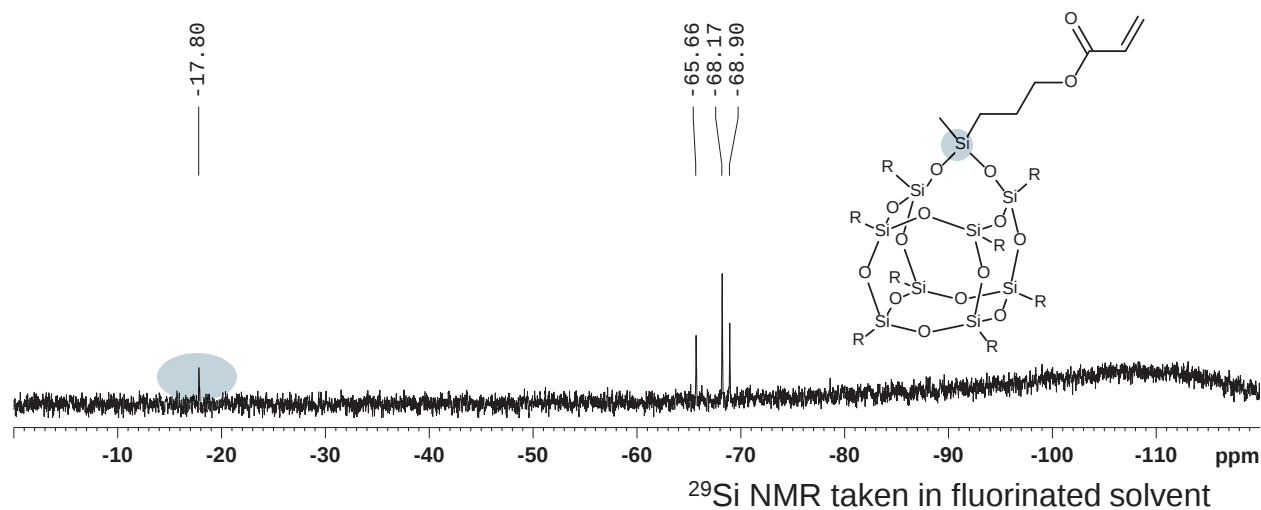




Edge Capping Reactions



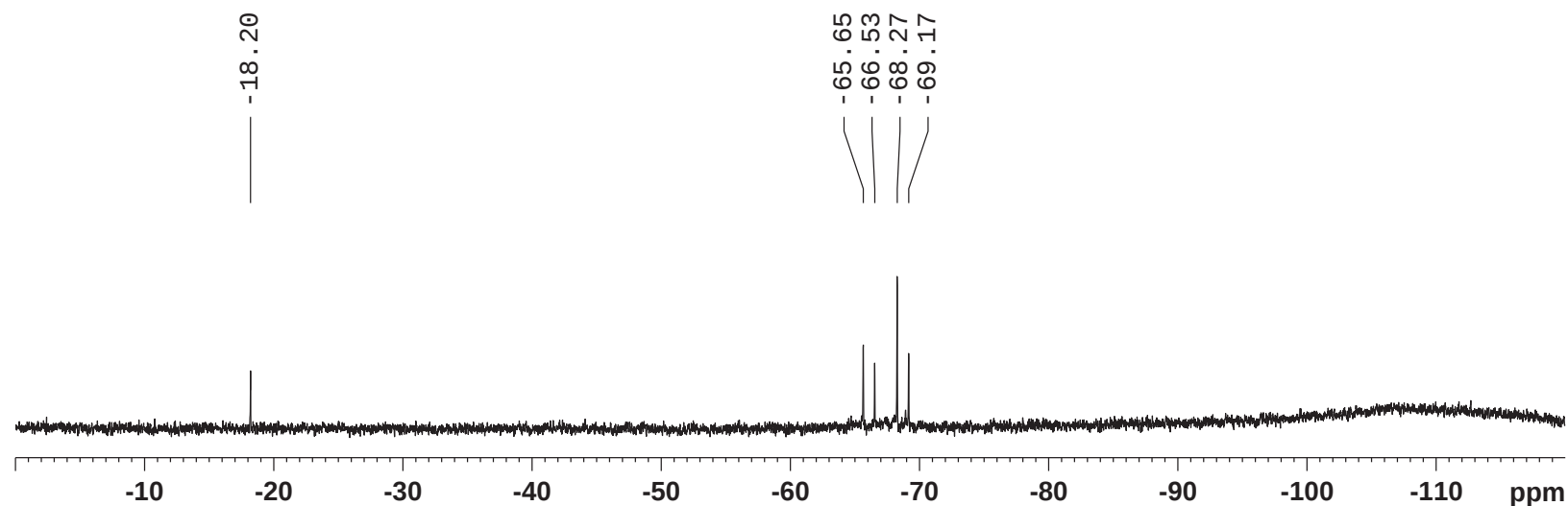
- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**





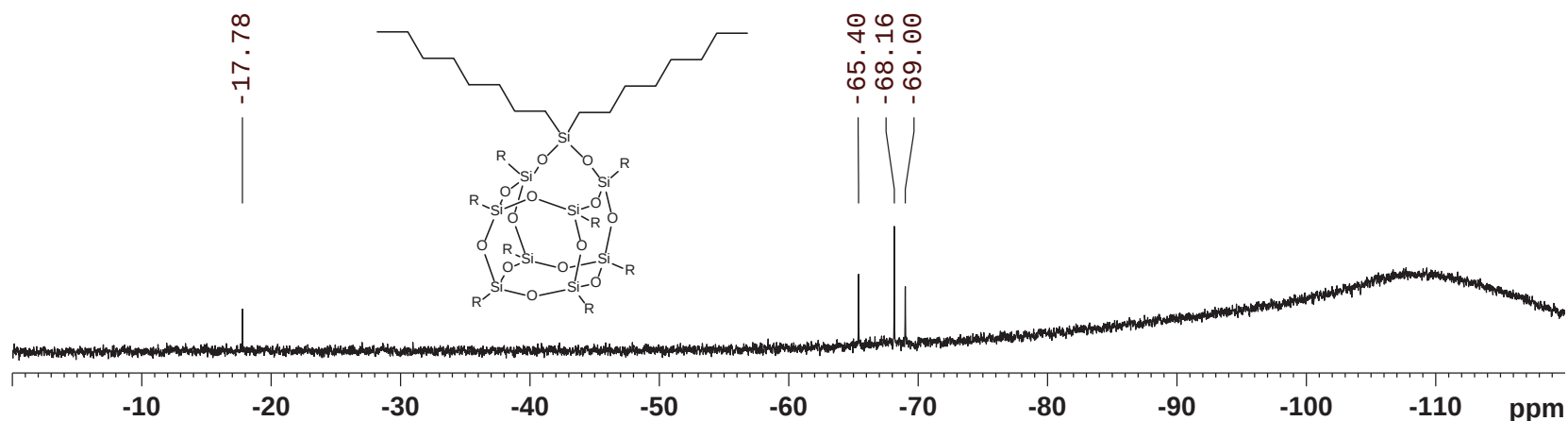
Separation of T₈ from Product

Before



²⁹Si NMR taken in fluorinated solvent

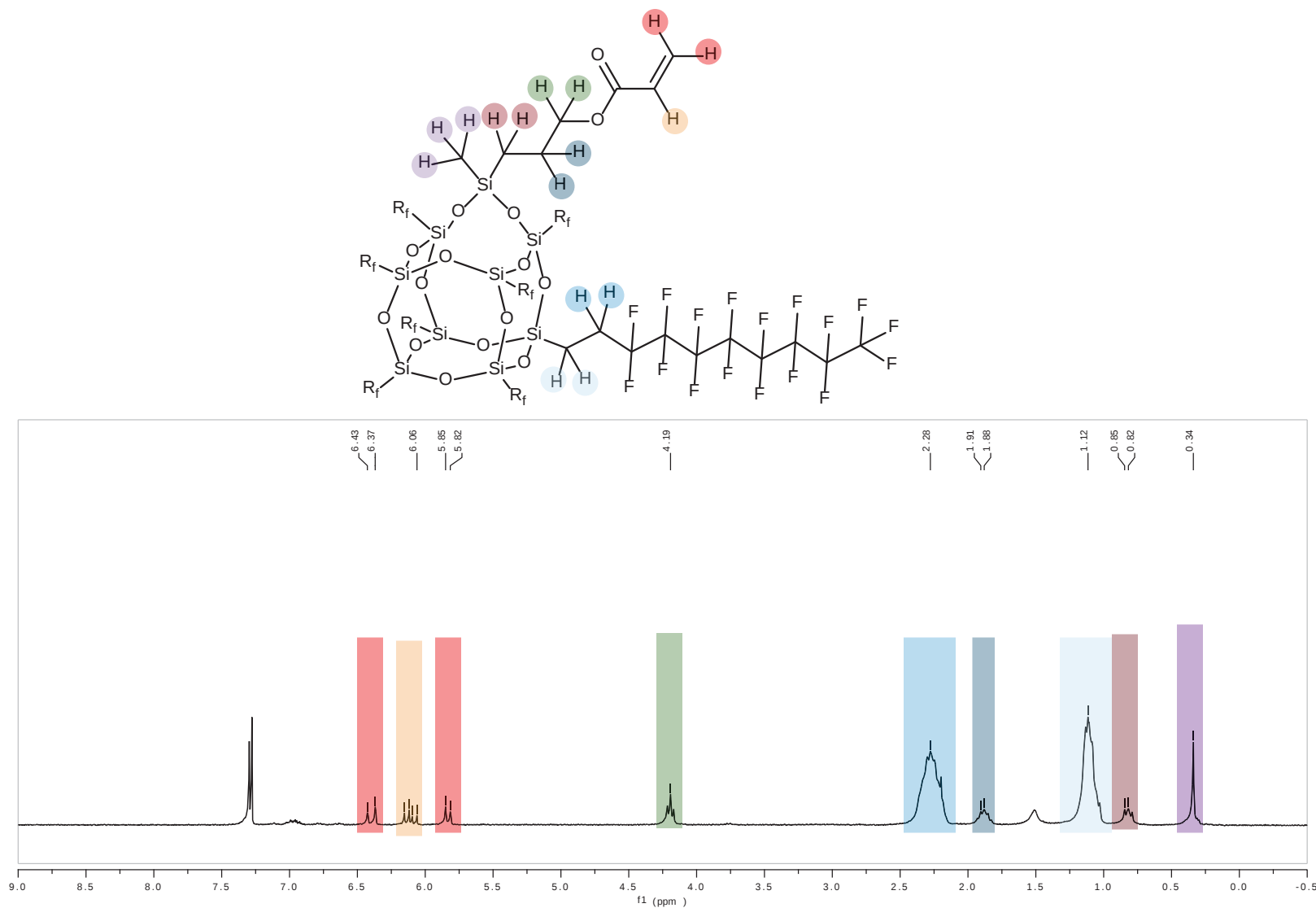
After



²⁹Si NMR taken in diethyl ether-d₁₀



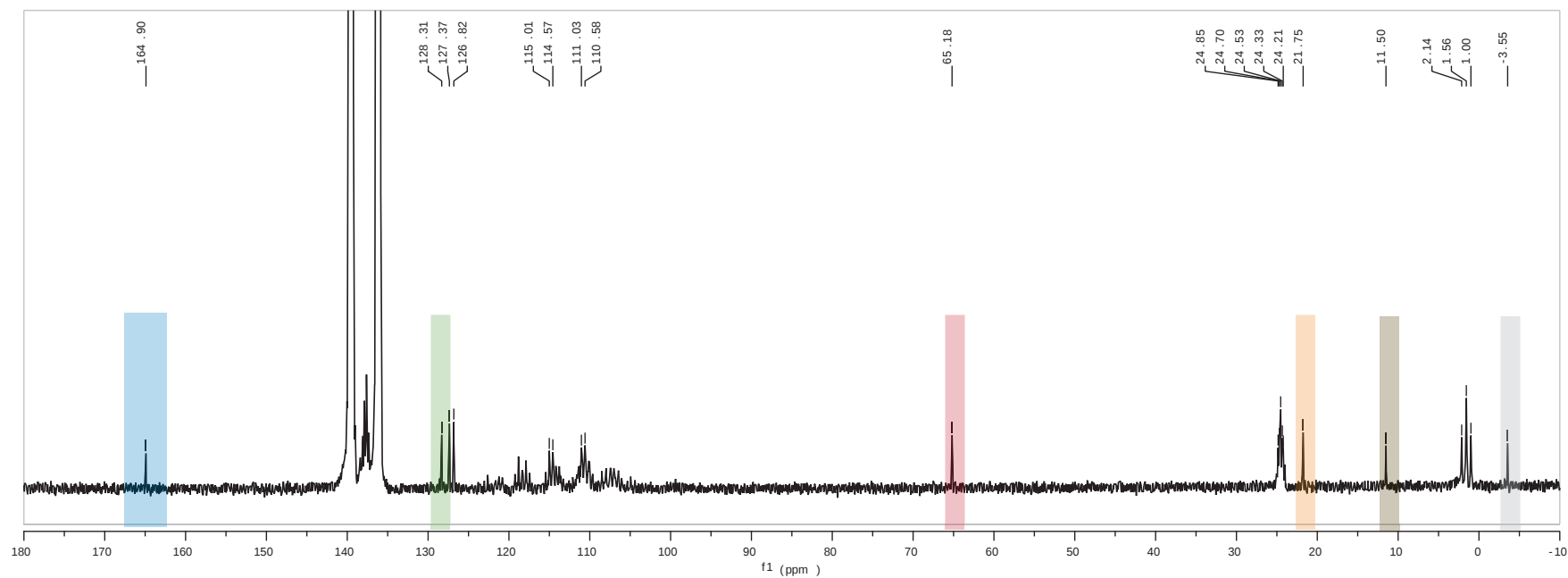
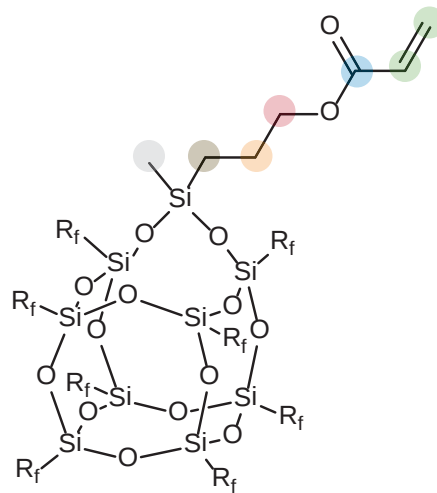
^1H NMR Characterization of Compounds



^{19}F NMR taken in diethyl ether. ^1H NMR taken in $\text{C}_6\text{F}_6/\text{CDCl}_3$ mixture.



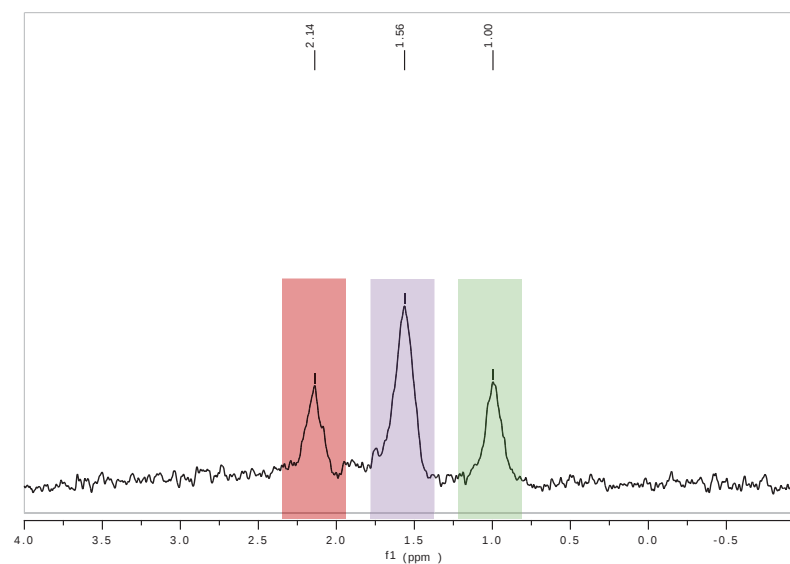
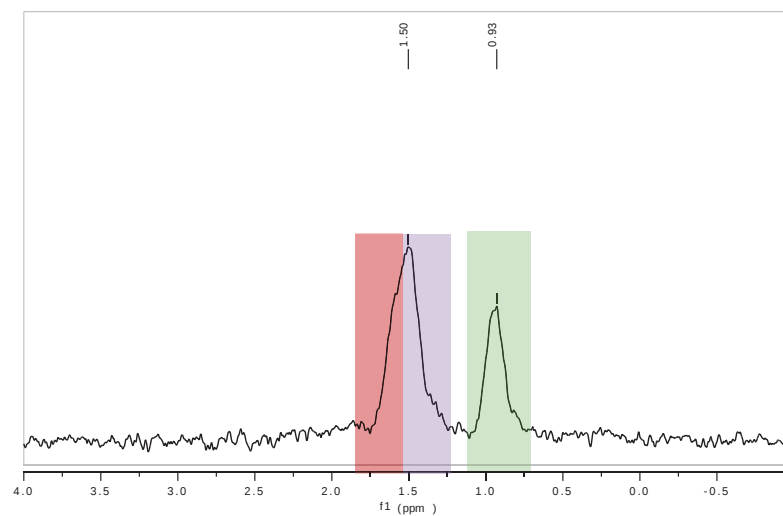
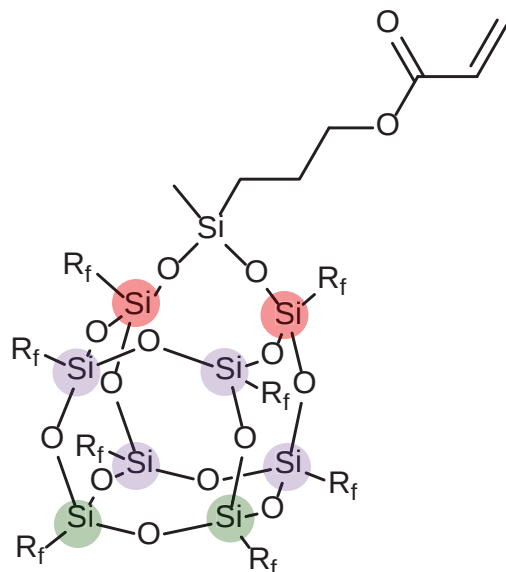
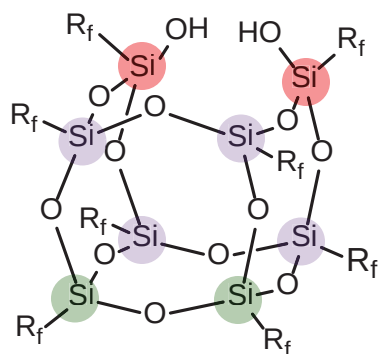
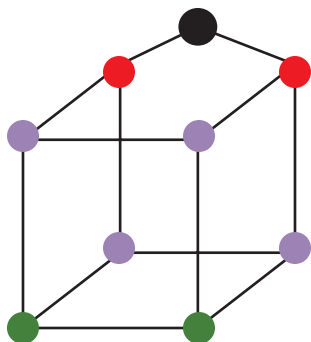
^{13}C NMR Characterization of Compounds



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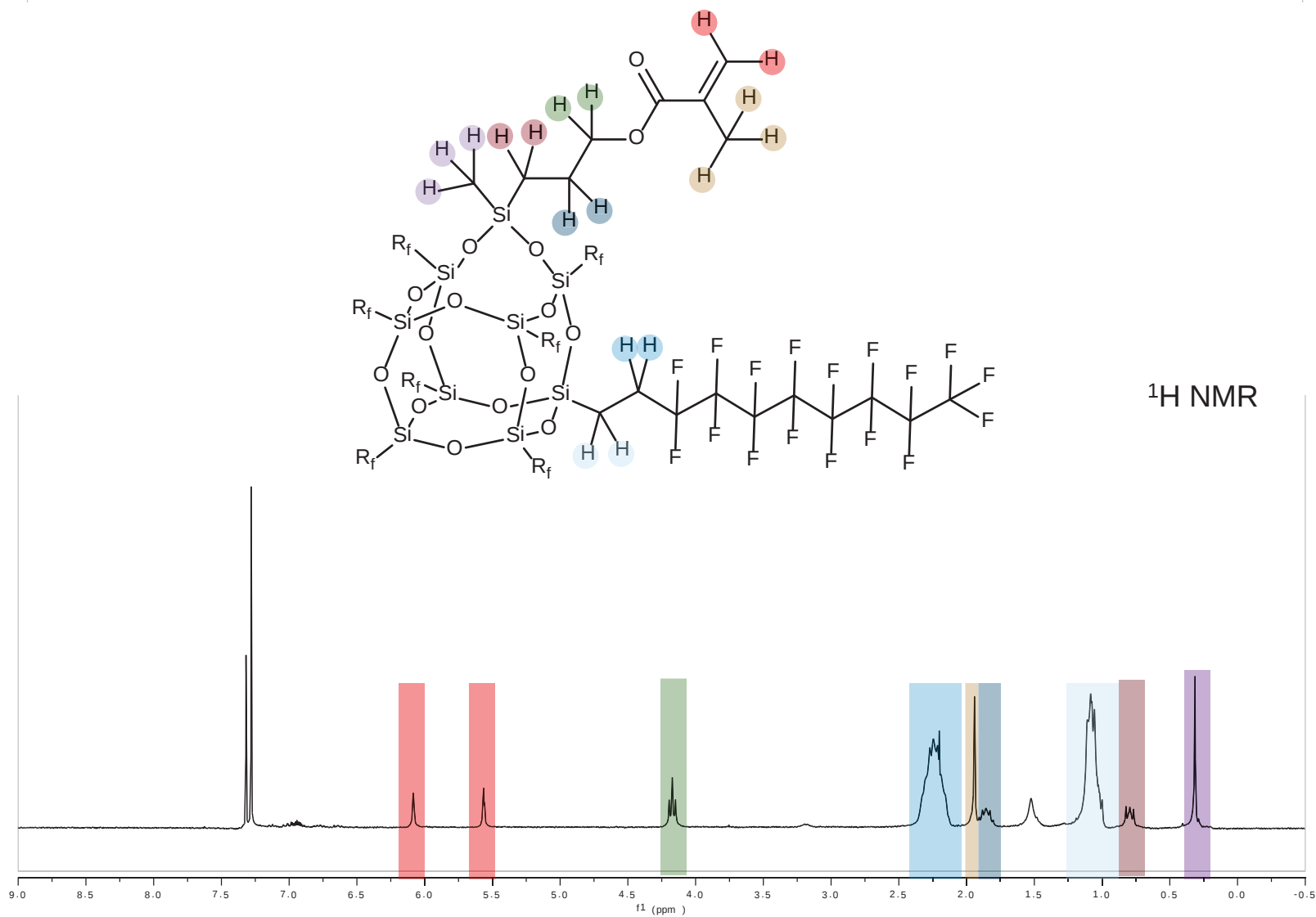
^{13}C NMR Characterization of Compounds



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^1H NMR Characterization of Compounds

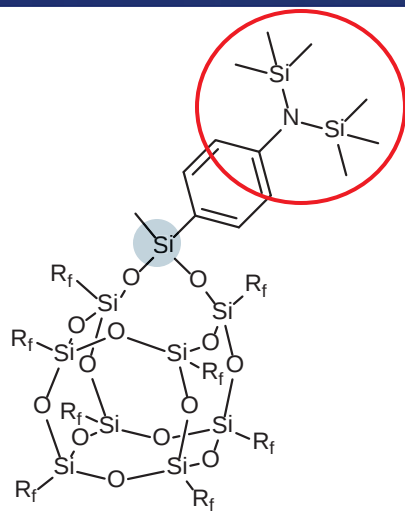


^{19}F NMR taken in diethyl ether. ^1H NMR taken in $\text{C}_6\text{F}_6/\text{CDCl}_3$ mixture.

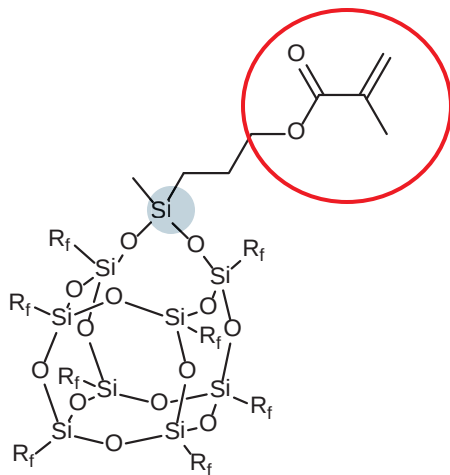
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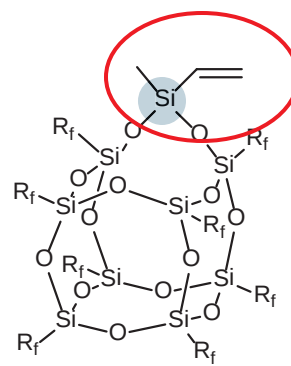
F-POSS Structures Synthesized



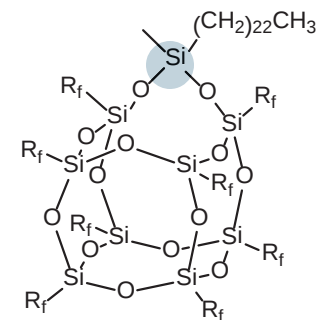
-29.5 ppm



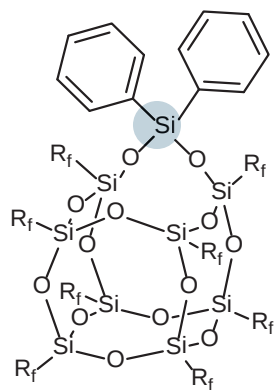
-17.8 ppm



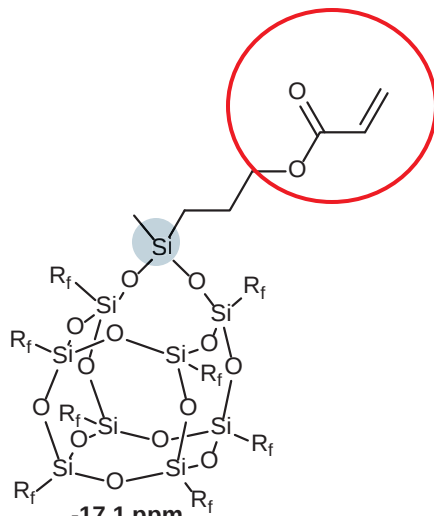
-32.1 ppm



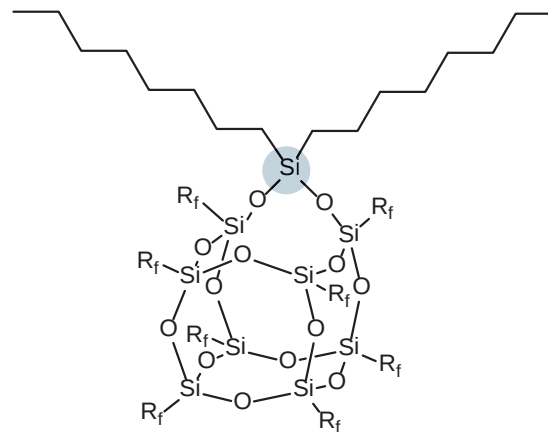
-17.8 ppm



-45.5 ppm



-17.1 ppm



-17.9 ppm

$R = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$

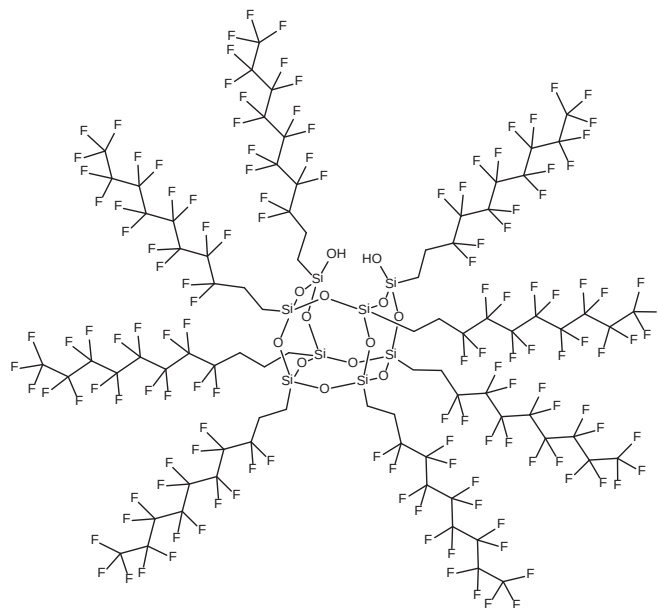
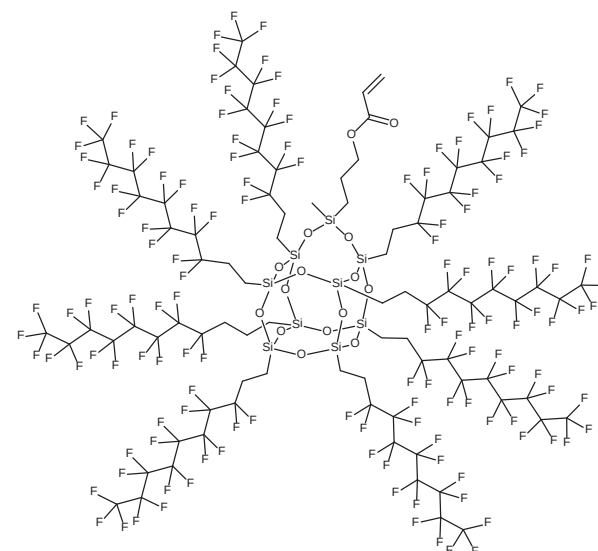
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Contact Angle Measurements



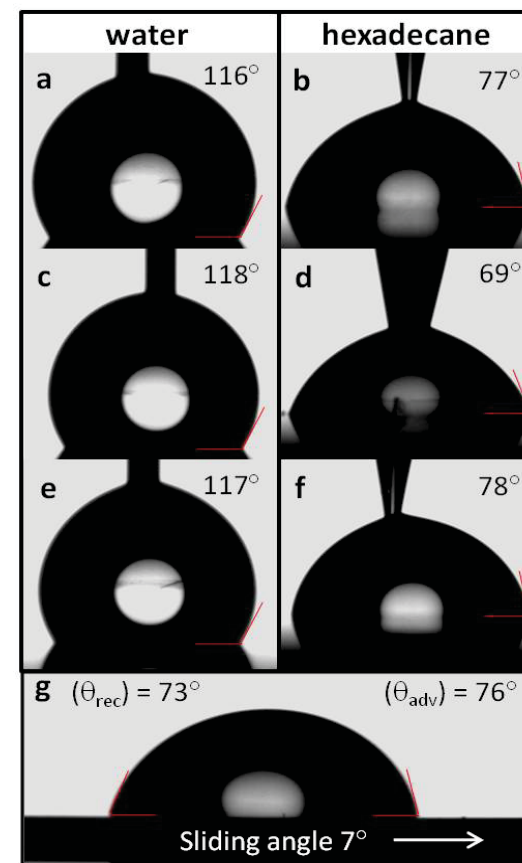
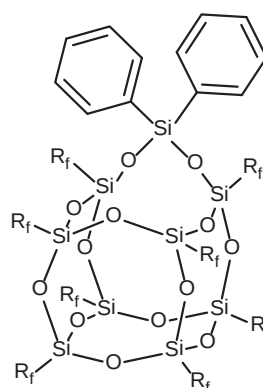
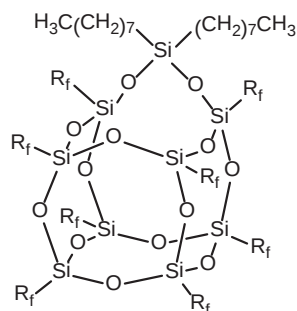
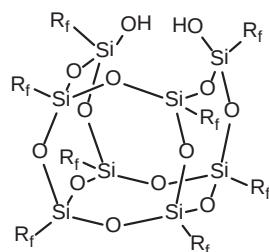
- Non-wetting surfaces can be developed by a combination of three parameters
 - Chemical functionality (high fluorine content)
 - Roughness (micro- and nanoscale)
 - Surface Geometry (re-entrant curvature)
- *What type of influence will functional groups have on F-POSS surface properties?*
- *Solvent impact?*





Contact Angle Measurements

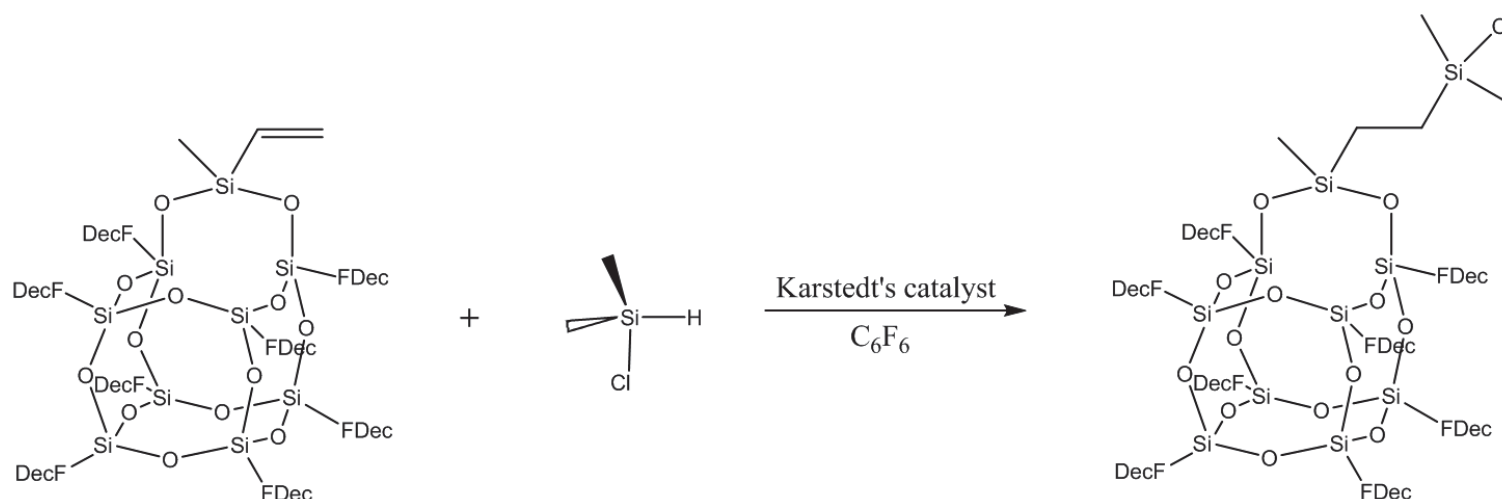
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Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10 μL) rolling off surface coated with compound **diphenyl** (g).



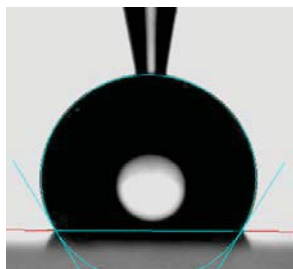
F-POSS Silane Coupling Reaction



- Chlorosilyl-functional fluoroPOSS compound synthesized from the Pt(II) catalyzed hydrosilylation of vinyl-functional fluoroPOSS and dimethylchlorosilane
- Desired compound successfully synthesized in high yield
- Characterized by 1H , ^{13}C , ^{19}F , and ^{29}Si NMR



Dynamic Contact Angle Measurements



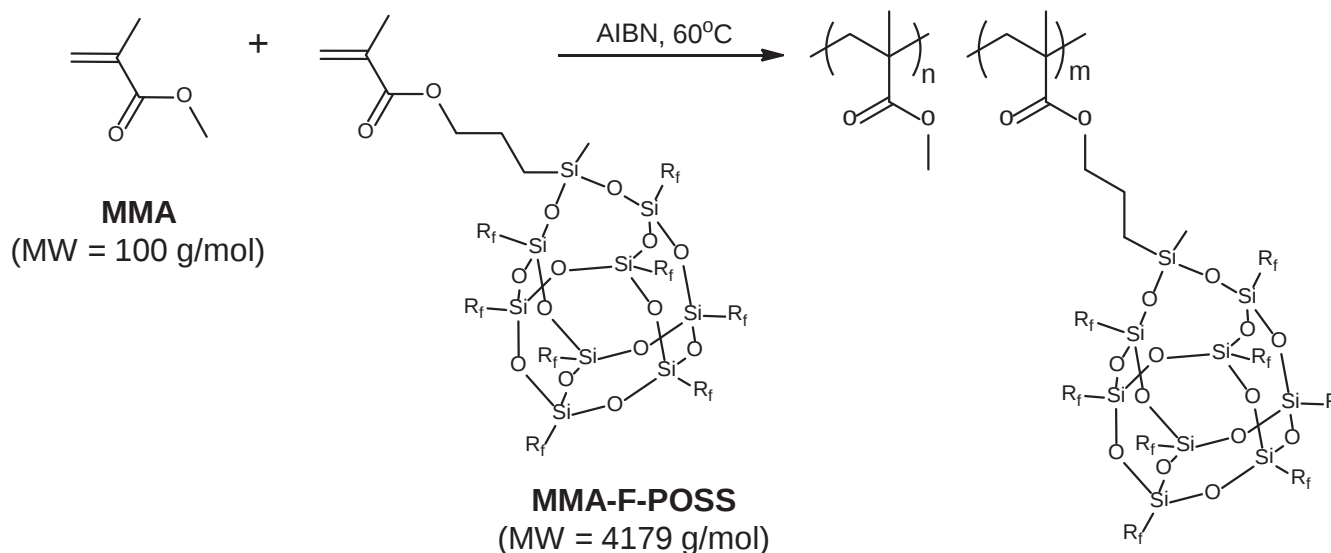
<i>Functional Group on F-POSS</i>	<i>water</i>		<i>hexadecane</i>	
	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
F-POSS*	$124 \pm 0.5^\circ$	$109.6 \pm 0.7^\circ$	$79.1 \pm 0.4^\circ$	$65.1 \pm 0.5^\circ$
Si-(OH) ₂	$116.8 \pm 0.4^\circ$	$111 \pm 0.6^\circ$	$77.4 \pm 0.4^\circ$	$74.4 \pm 0.8^\circ$
Si-(CH ₃)(CH=CH ₂)	$116.2 \pm 0.4^\circ$	$100.6 \pm 0.8^\circ$	$78.4 \pm 0.3^\circ$	$70.6 \pm 2.3^\circ$
Si((CH ₃)((CH ₂) ₃ OC(O)CCH=CH ₂)	$118.2 \pm 1.0^\circ$	$90.6 \pm 1.0^\circ$	$76.8 \pm 0.3^\circ$	$64.8 \pm 1.0^\circ$
Si-(CH ₃)((CH ₂) ₃ OC(O)C(CH ₃)=CH ₂)	$117.1 \pm 0.6^\circ$	$93.8 \pm 1.5^\circ$	$78.1 \pm 0.4^\circ$	$63.0 \pm 1.2^\circ$
Si-(CH ₃)((CH ₂) ₂₂ CH ₃)	$117.9 \pm 0.4^\circ$	$96.9 \pm 1.9^\circ$	$78.0 \pm 0.4^\circ$	$16.2 \pm 5.5^\circ$
Si-(C ₆ H ₅) ₂	$116.2 \pm 0.4^\circ$	$110.5 \pm 0.5^\circ$	$76.0 \pm 0.8^\circ$	$73.2 \pm 0.4^\circ$
Si-((CH ₂) ₇ CH ₃) ₂	$117.9 \pm 0.5^\circ$	$95.5 \pm 0.4^\circ$	$69.1 \pm 1.2^\circ$	$23.1 \pm 1.2^\circ$

Samples (10 mg/mL) were spin casted on oxygen-plasma cleaned Si wafers at 900 rpm for 30 seconds. Contact angle measurements were run in triplicate. Surface roughness < 5nm (AFM and Optical Profilometry).

*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.



Initial Copolymerizations

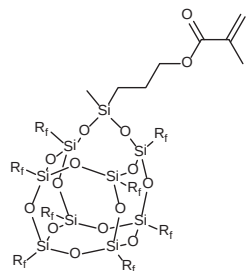


Sample #	Weight (g)		Weight (%) F-POSS	Monomer (mmol)		Mol Ratio (MMA:MMA-F- POSS)	Initiator (mol %)	Conversion (%)	Weight (%) FPOSS*
	MMA-F-POSS	MMA		MMA-F-POSS	MMA				
1	0.085	1.31	6.3	0.02	13.1	655	0.5	42	2.74
2	0.362	1.31	21.6	0.09	13.1	145	0.2	71	14.4
3	0.50	3.50	12.5	0.12	35.0	291	1		
4	1.00	3.00	25.0	0.24	30.0	125	1	62.5	
5	2.00	2.00	50.0	0.47	20.0	42	0.2	92.5	

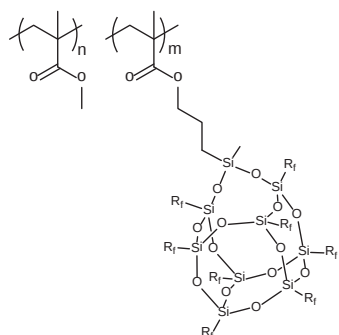
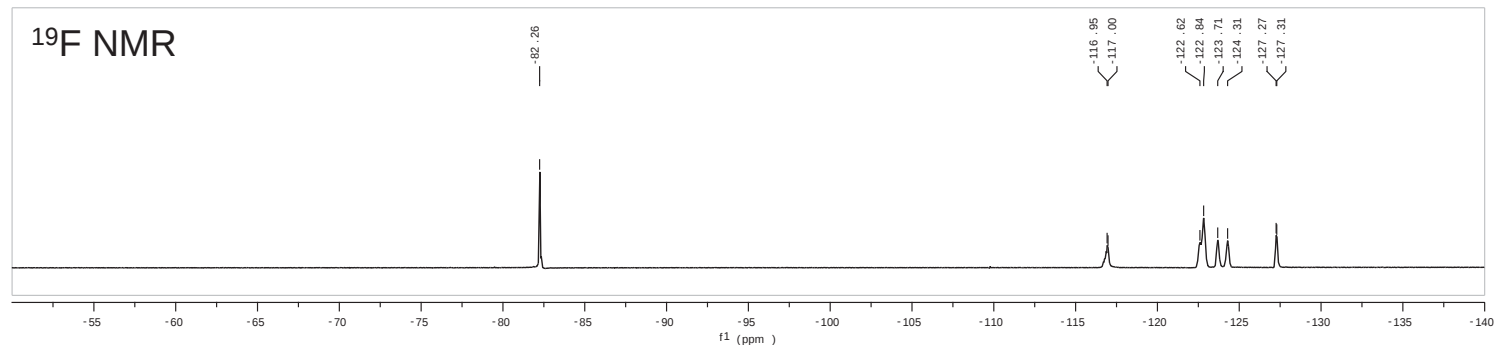
*Weight (%) of F-POSS was calculated from elemental analysis of Fluorine content in the final polymer.



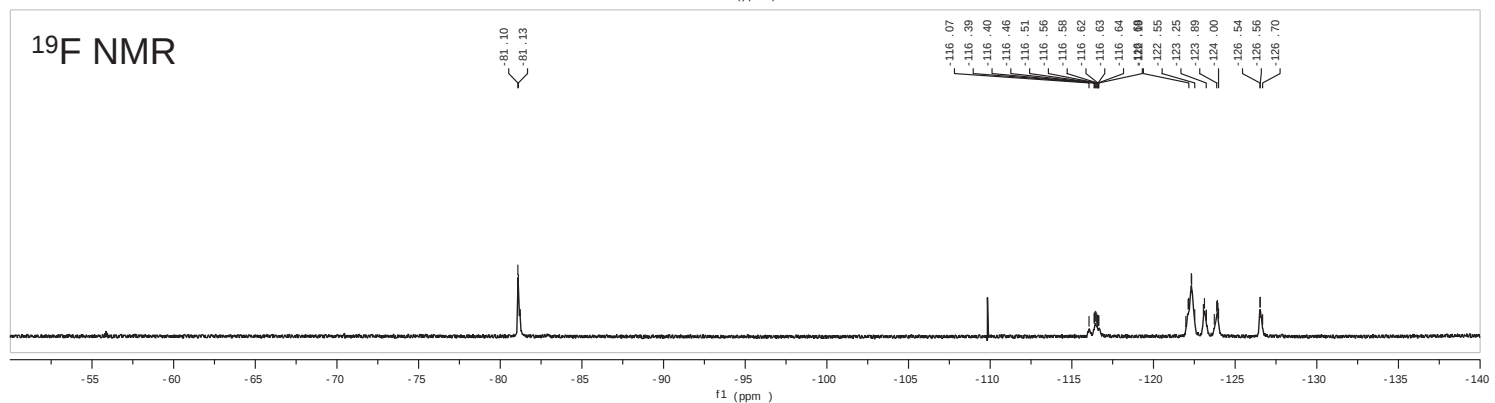
NMR Characterization of Copolymers



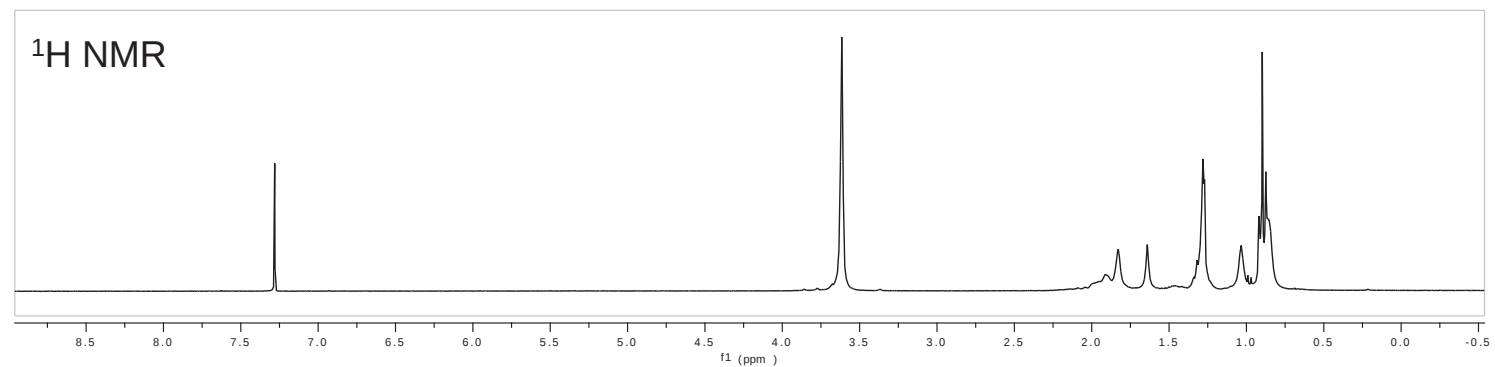
^{19}F NMR



^{19}F NMR

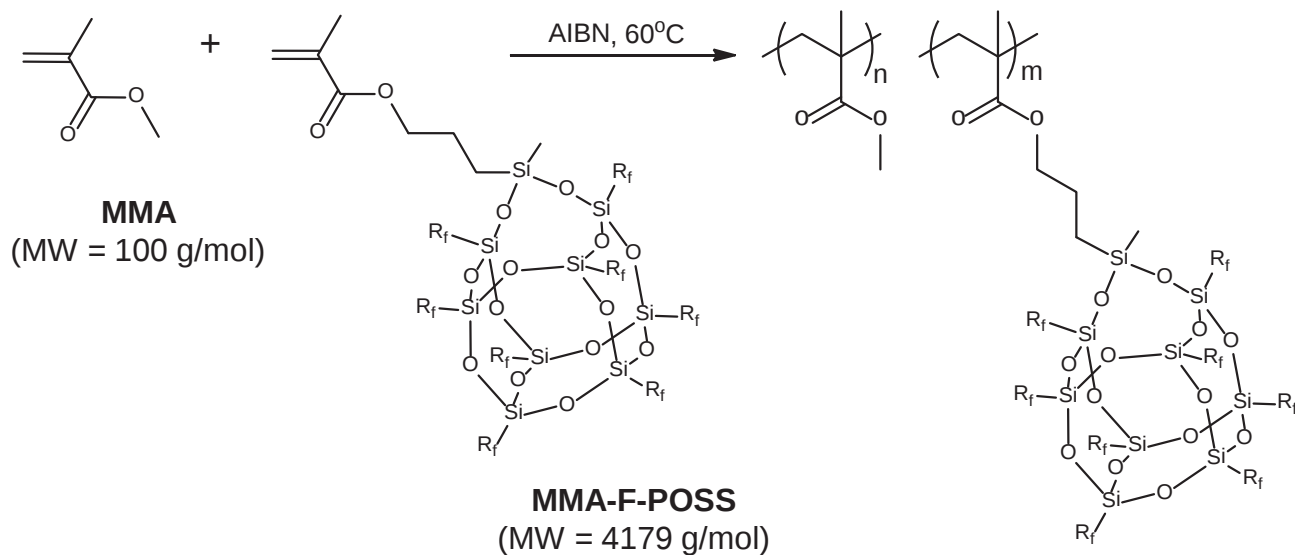


^1H NMR





Initial Copolymerizations



Sample #	Weight (%)F-POSS	Mol Ratio (MMA:MMA-F- POSS)	Conversion (%)	Weight (%) FPOSS*	T _g (°C)	Solubility
1	6.3	655	42	2.74	165	PMMA solvents
2	21.6	145	71	14.4	165	PMMA solvents (takes time)
3	12.5	291				
4	25.0	125	62.5		126	PMMA solvents with small amount of AK-225G
5	50.0	42	92.5		127	THF-AK225G mixture (suspension)



Summary



- Structures were demonstrated to be reactive towards a variety of dichlorosilanes
- Solubility of F-POSS compounds were shown to be influenced by chemical functionality
- Functionality was shown to be influential on contact angle measurements
- F-POSS compounds have a near limitless potential in producing a variety of new hydrophobic, oleophobic, or omniphobic polymer composites.
 - Reaction mechanisms, polymer composites, block copolymers, etc....