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**Silicones & Silicone-
Modified Materials**

**ACS Fall National
Meeting - Boston**

FLUORINATED SILSESQUOXANES: STRUCTURE, SOLUBILITY, AND WETTING



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Raymond Campos, Sean Ramirez, Brian Moore,
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Applied Materials Group



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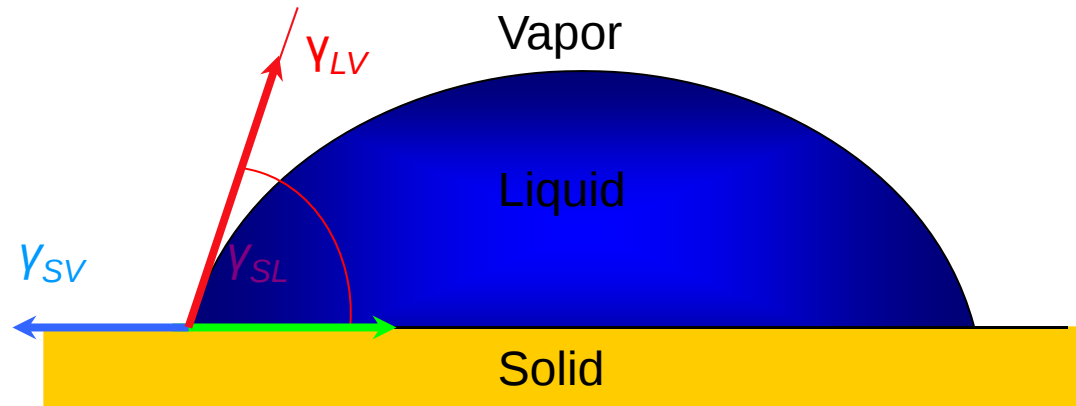
AFRL/RQR

AFOSR

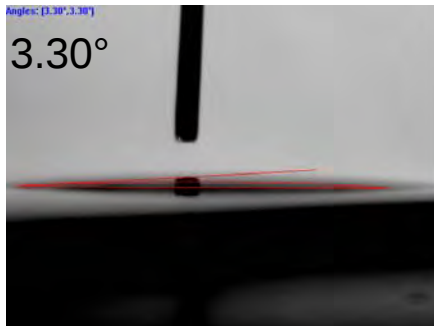




Non-wetting surfaces



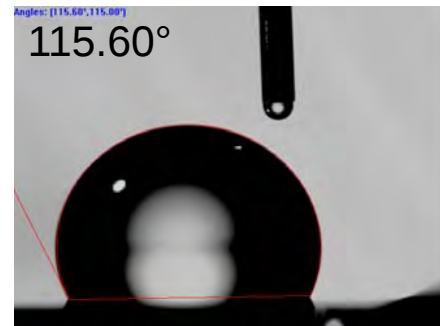
Contact angles with water:



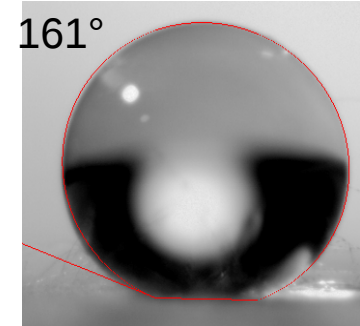
Superhydrophilic
 $\theta \sim 0^\circ$



Hydrophilic
 $0^\circ < \theta < 90^\circ$



Hydrophobic
 $\theta > 90^\circ$

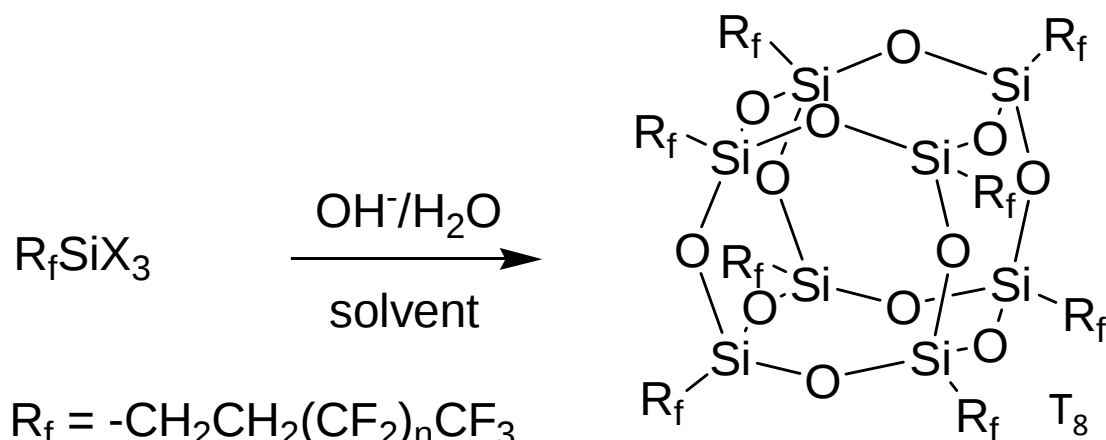


Superhydrophobic
 $\theta^* > 150^\circ$

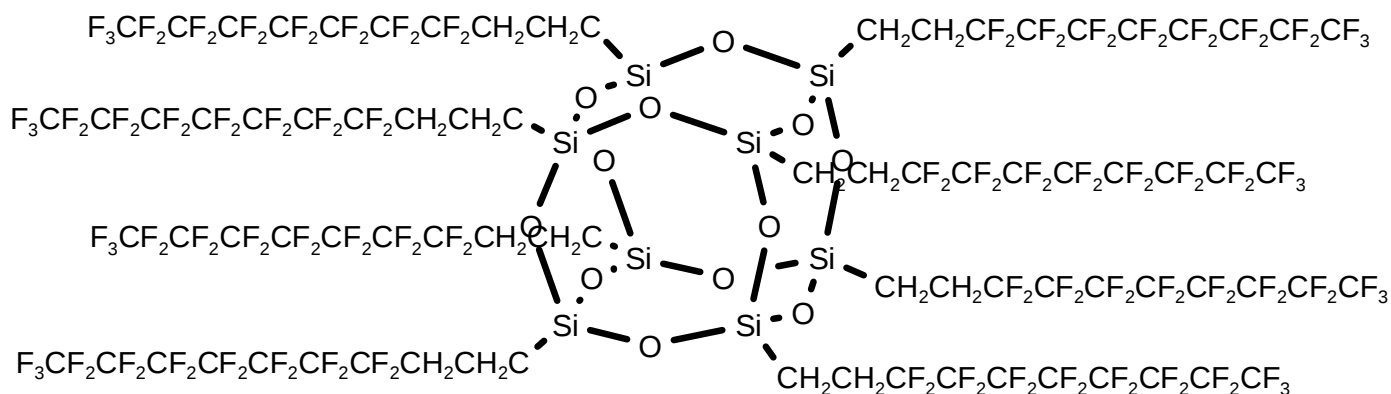
Similarly, superoleophobic surfaces display contact angle $\theta^* > 150^\circ$ with oils or alkanes



Fluorinated POSS Synthesis



- Crystalline solids
- Soluble in fluorinated solvents

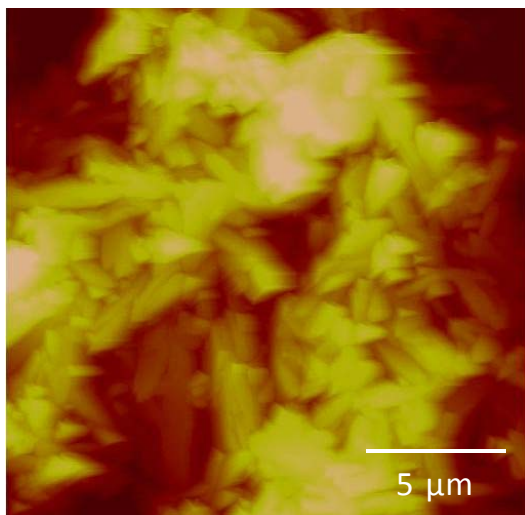


Angew Chem, 2008

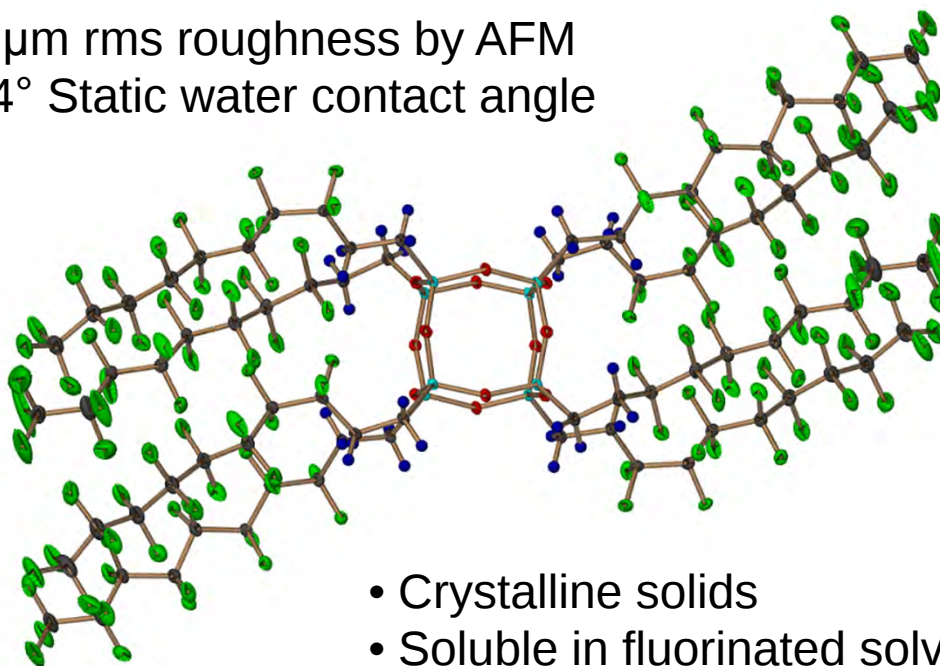
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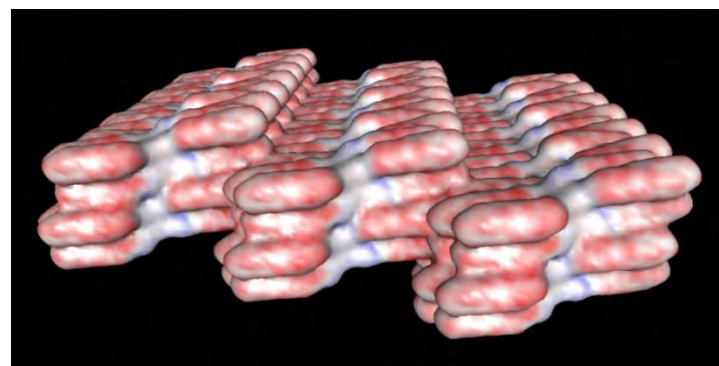
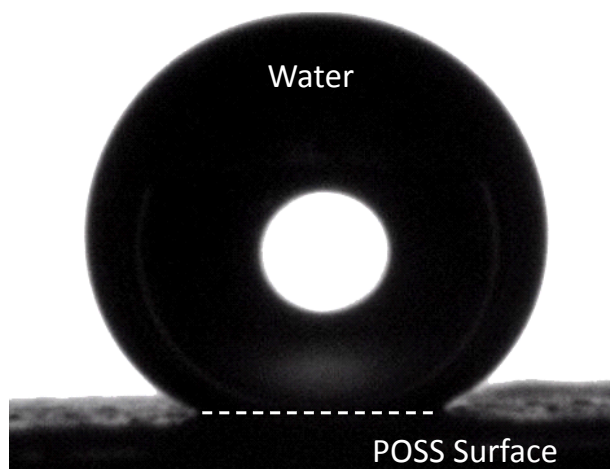
Hydrophobic Materials



- Spin-cast surface of FD POSS
- $\sim 4 \mu\text{m}$ rms roughness by AFM
- 154° Static water contact angle



- Crystalline solids
- Soluble in fluorinated solvents

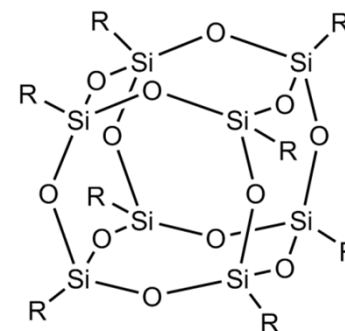
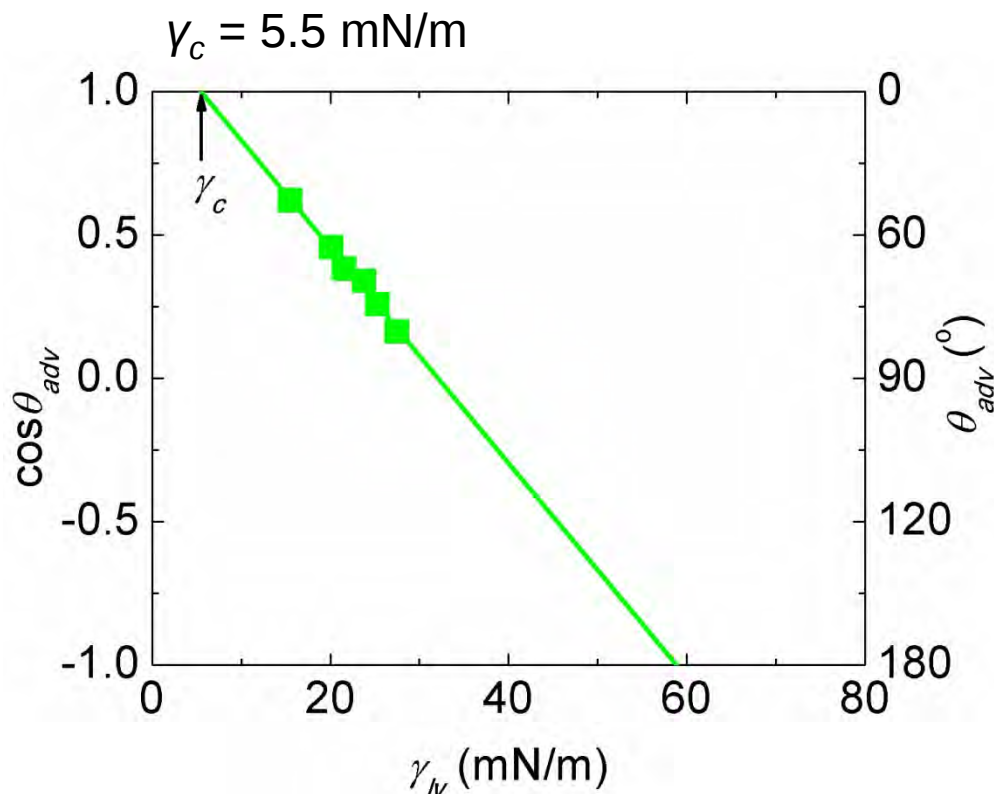


Angew Chem, 2008

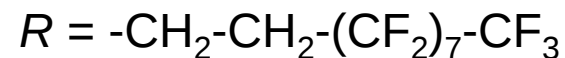
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Zisman Analysis



Fluorodecyl:



GG analysis results in
surface energy calculation
of: $\gamma_c = 8 \text{ mN/m}$

PTFE $\sim 18 \text{ mN/m}$

PDMS $\sim 24 \text{ mN/m}$

Contacting liquids:

hexadecane ($\gamma_{lv} = 27.5 \text{ mN/m}$), dodecane (25.3),

decane (23.8), octane (21.6), heptane (20.1) and pentane (15.5)

ACS AMI, 2010

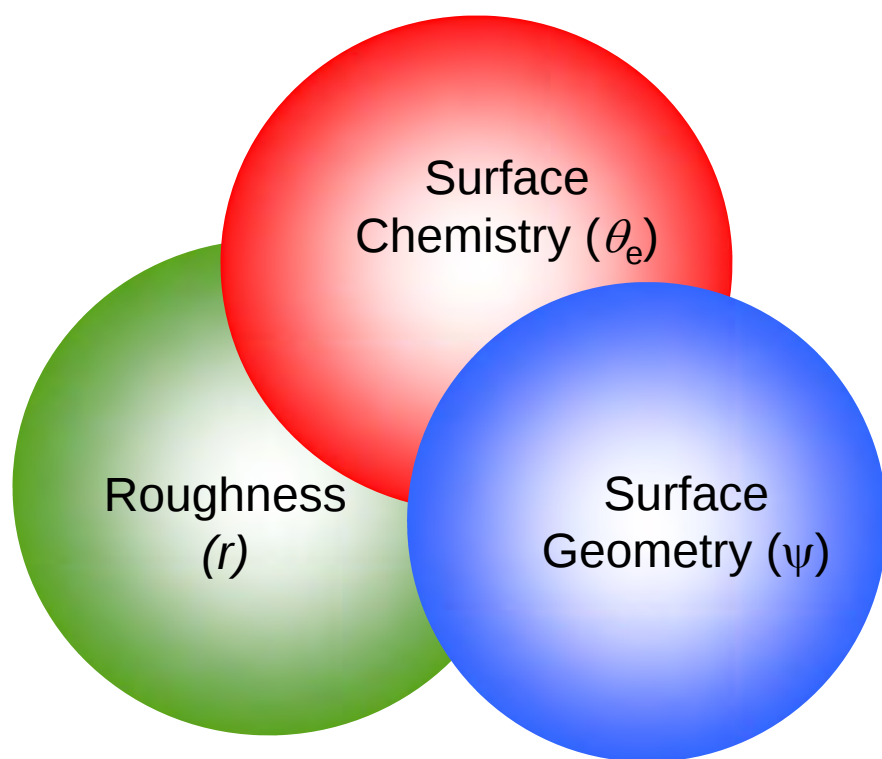
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Designing Omniphobic Surfaces



- **Constructing super-repellent surfaces**
 - Three key ingredients



PMMA + 44 wt% POSS
electrospun coating (beads on a string) morphology

Science, 2007

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Omniphobic Fabrics Repel “Everything” (even “Wetting” Fluids)



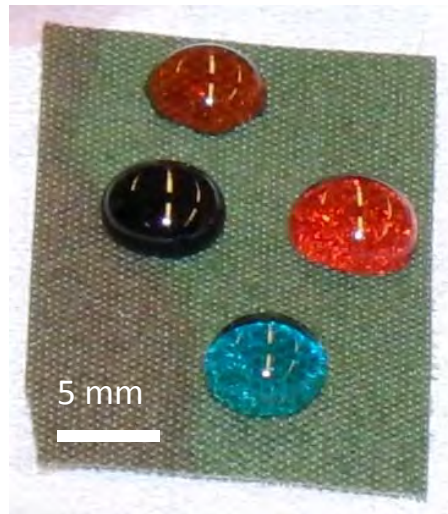
Nylon shell fabric bonded to a
Gore–Tex membrane

Dodecane

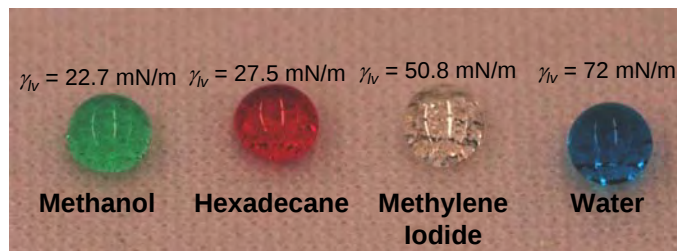
Ethylene
glycol

Rapeseed
oil

Water



Anticon 100 polyester fabric



JACS, 2013



Adv Mater, Langmuir, 2008

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Separation of Oil-Water and Emulsions



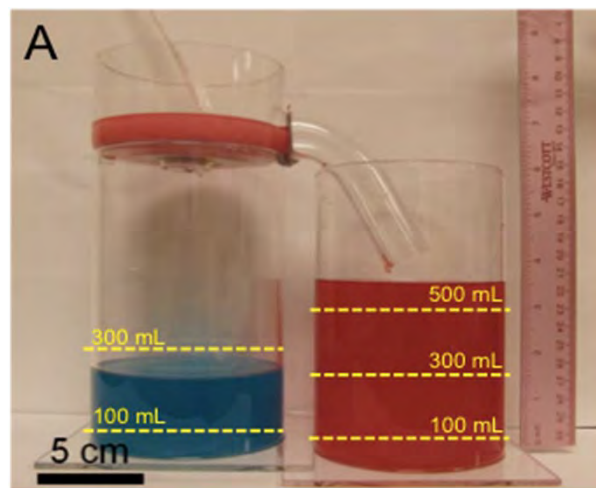
- Developed simple membranes and apparatus for gravity-driven, continuous separation of oil-water emulsions.

Superhydrophobic/
Superoleophilic



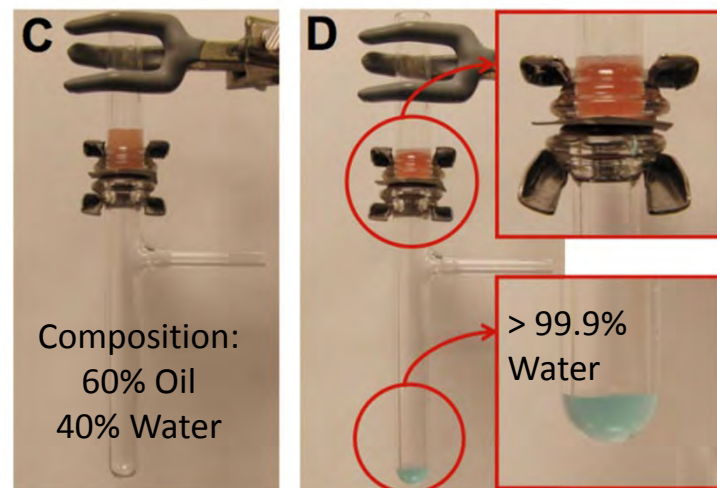
Science, 2007

Gravity Driven - Continuous Flow



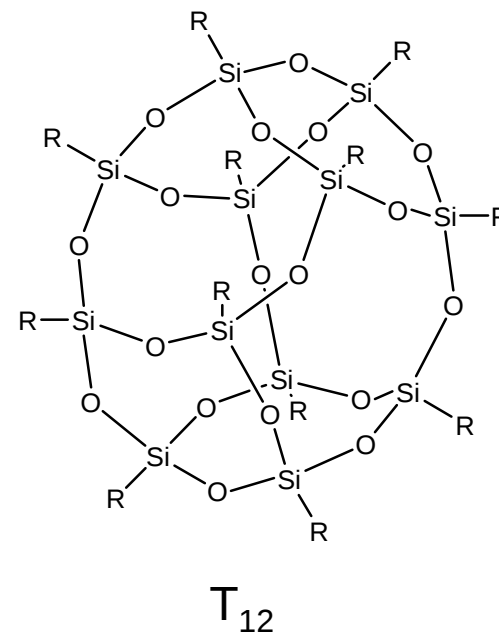
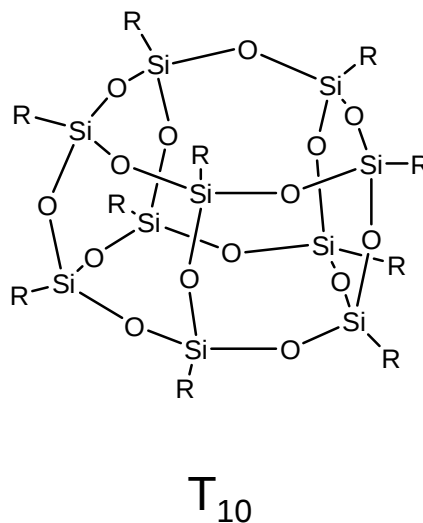
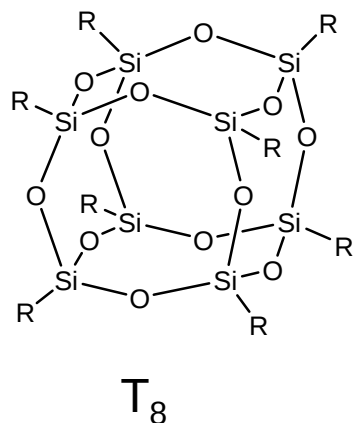
Nature Comms, 2012

Emulsion Separation





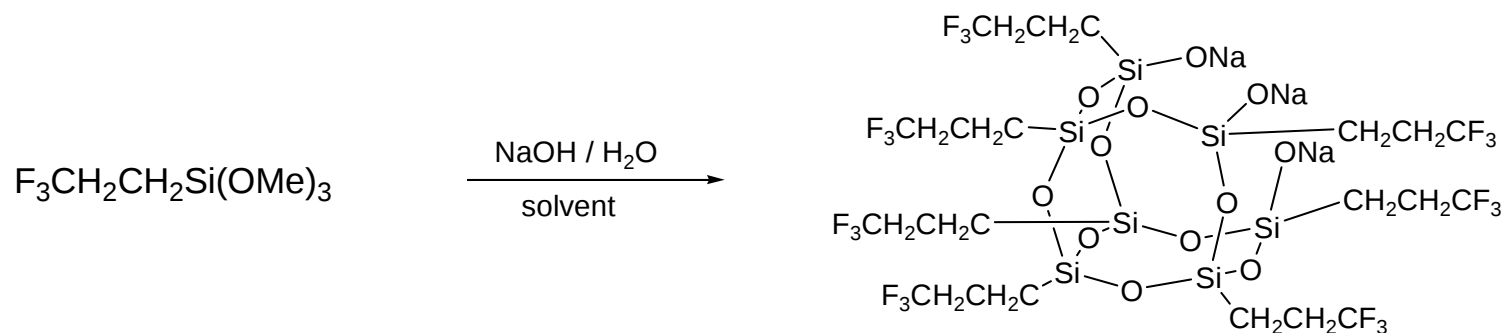
Not all F-POSS are the same!



Most common compounds found in a cage mixture

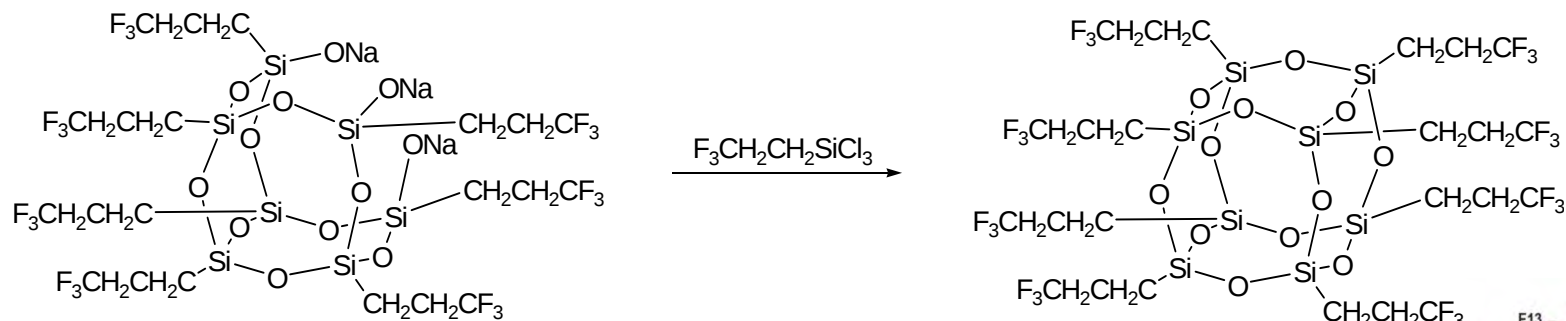


Fluoropropyl₈T₈



Trisodium salt from trimethoxy silane

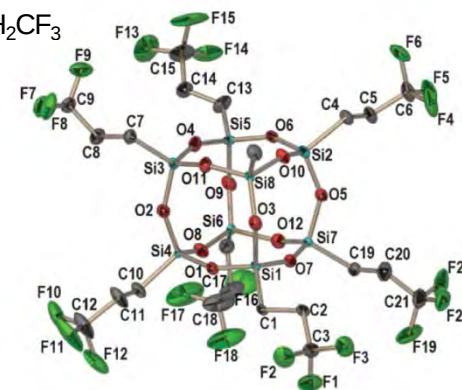
Fukuda, *Macromolecules*, 2005



T₈ from trisodium salt

Chem Comm, 2007

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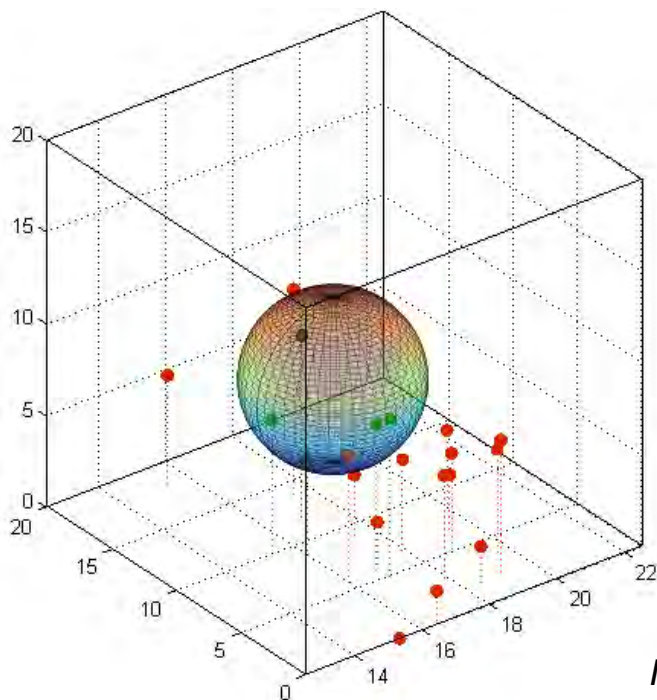
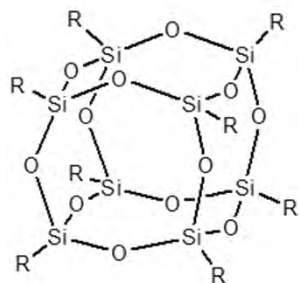




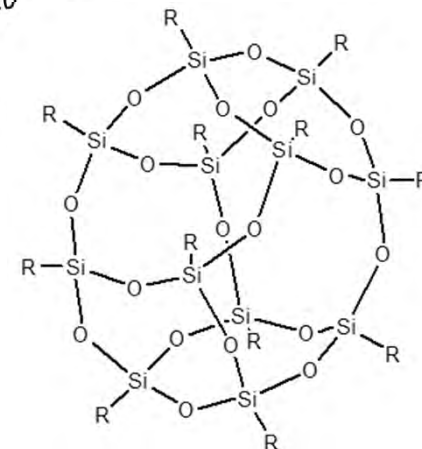
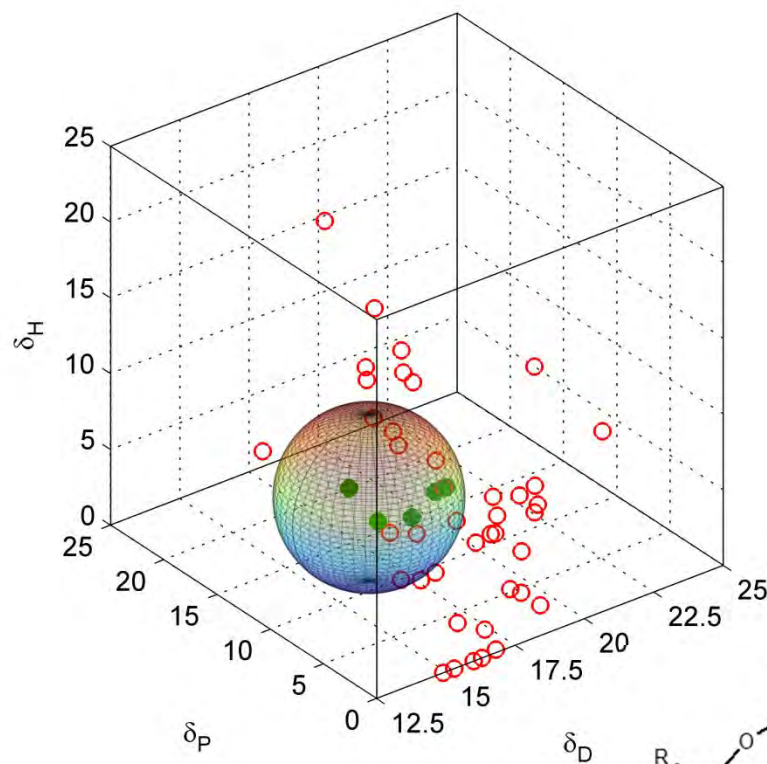
HSP Data for TFP Compounds



Octa-trifluoropropyl-POSS



Dodeca-trifluoropropyl-POSS

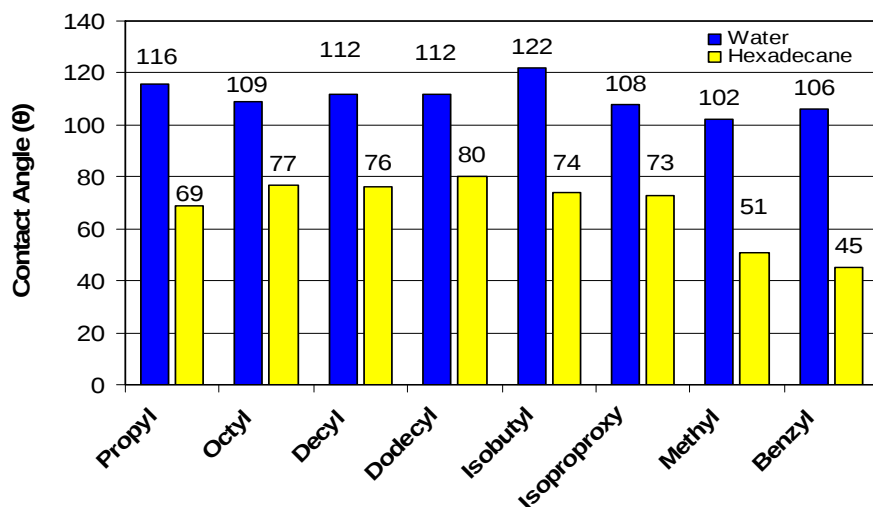
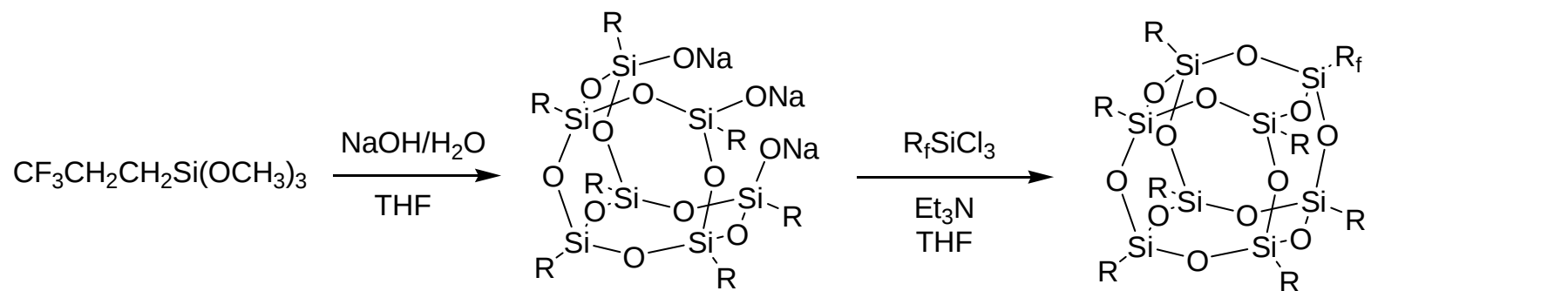


Ind Eng Chem Res, 2012

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Corner-Capped F-POSS



- Diverse architectures – linear, branched, ether
- Corner cap yields moderate to good (73–83 %)
- Soluble in common organic solvents

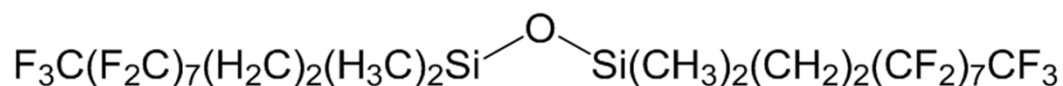
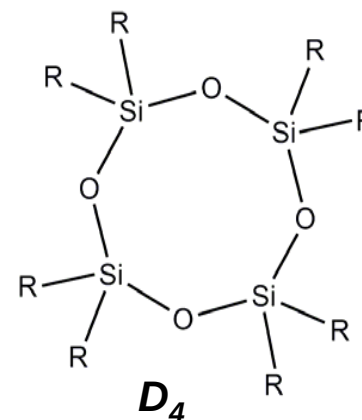
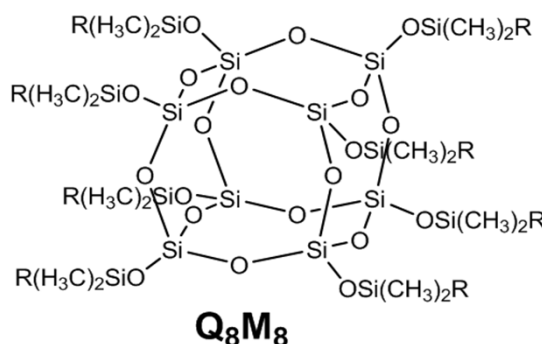
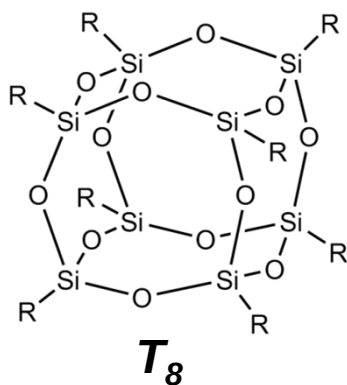
Chem Comm, 2007



Solid Surface Energy Estimation



Structure of candidate molecules



Linear disiloxane resin (M_2)

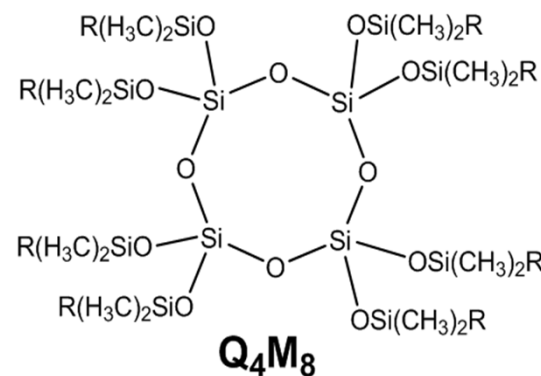
Fluorodecyl: $R_f = -CH_2CH_2(CF_2)_7CF_3$

Fluorooctyl: $R_f = -CH_2CH_2(CF_2)_5CF_3$

Fluorohexyl: $R_f = -CH_2CH_2(CF_2)_3CF_3$

Fluoropropyl: $R_f = -CH_2CH_2CF_3$

ACS AMI, 2010

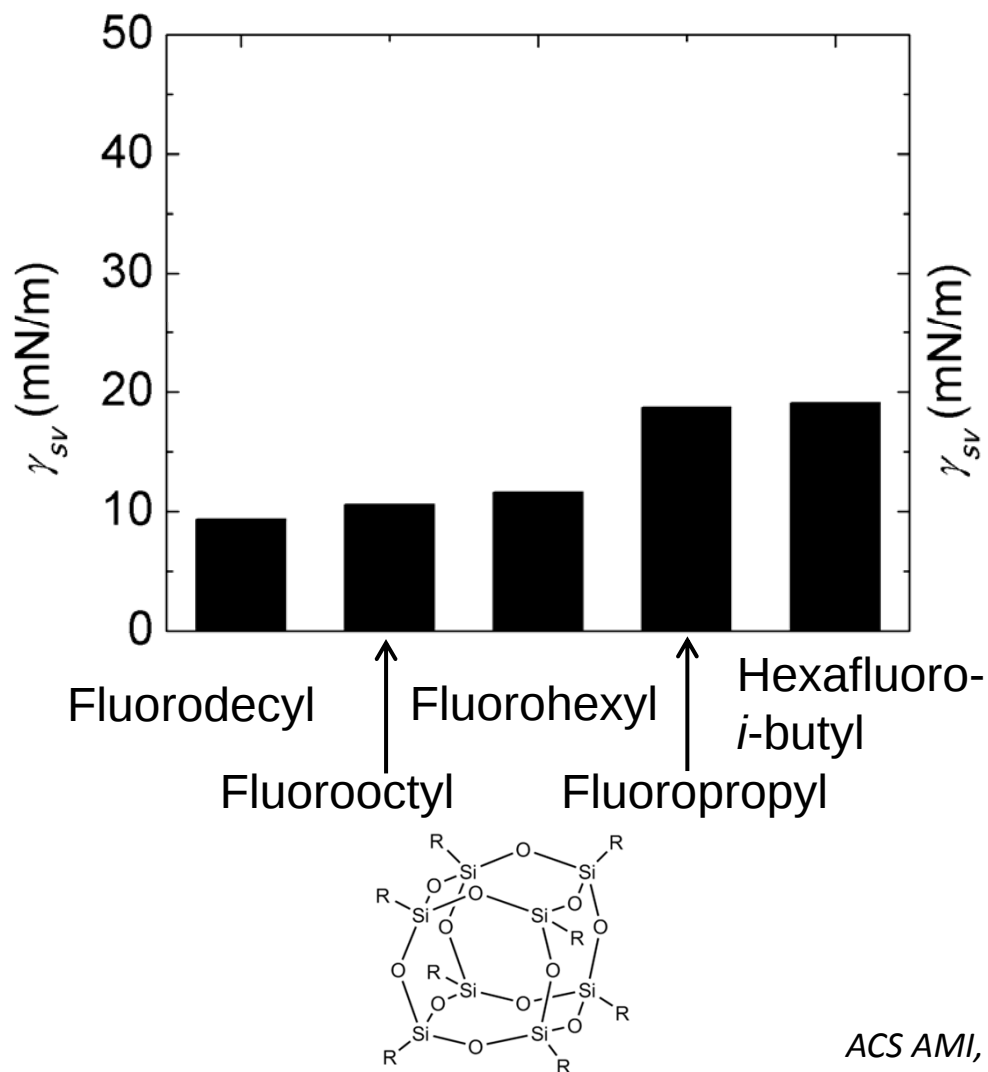




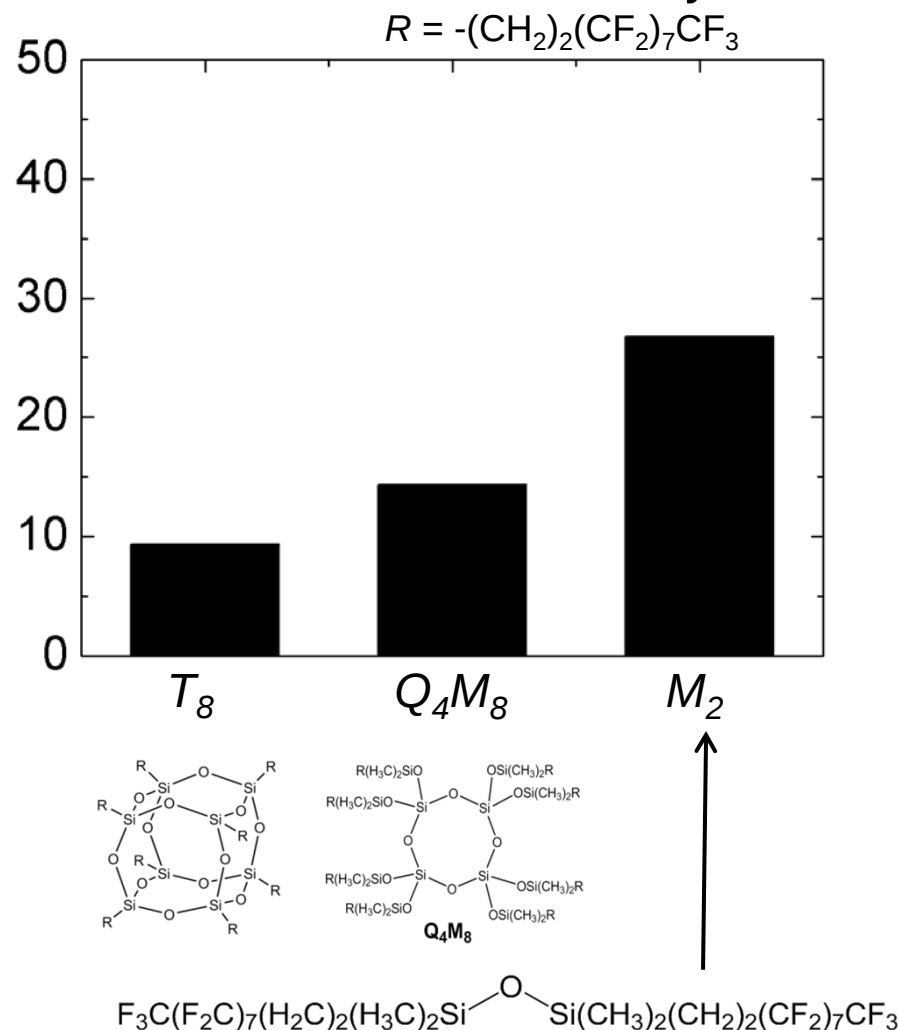
Solid Surface Energy (γ_{sv}) via Girifalco-Good Method



Molecules with a T_8 cage



Molecules with a fluorodecyl chain



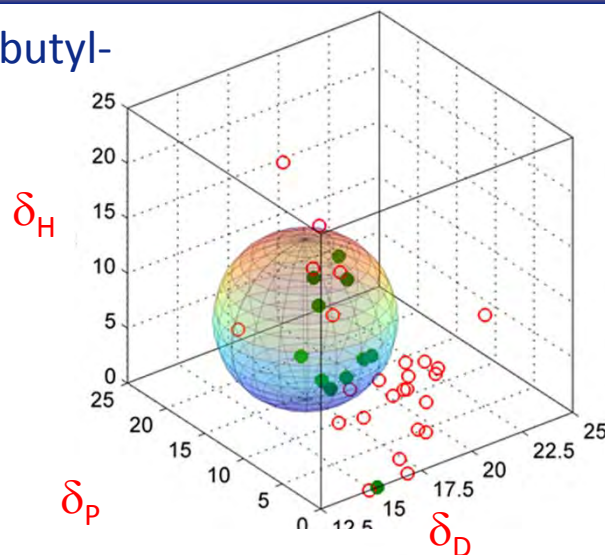
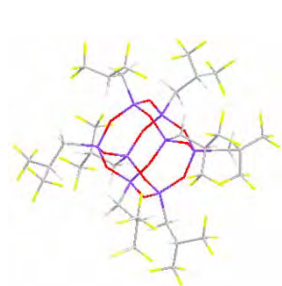
ACS AMI, 2010
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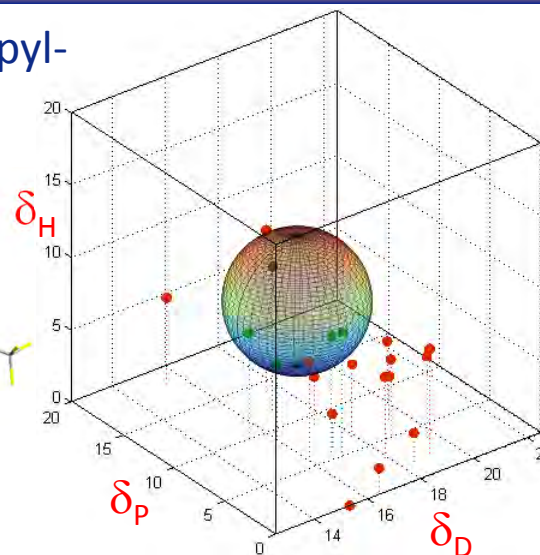
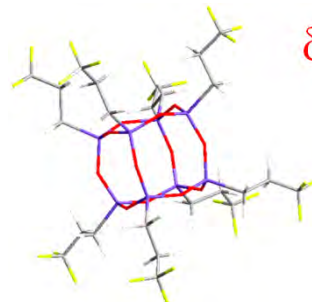
HSP Data for Fluoroalkyl Compounds



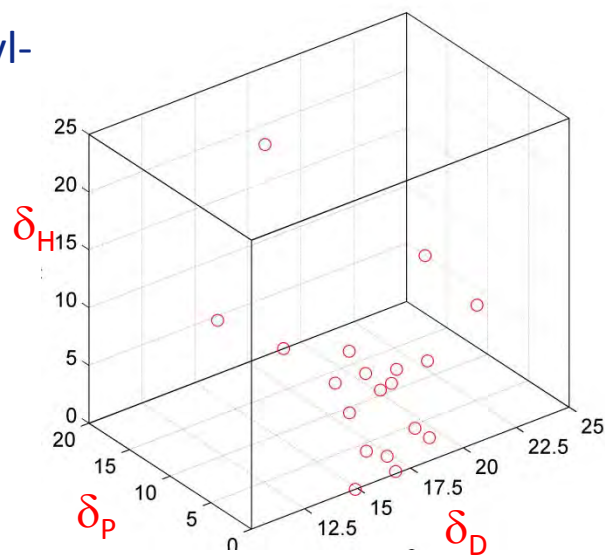
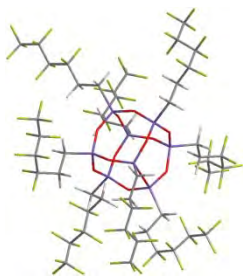
Octa-hexafluoroisobutyl-POSS



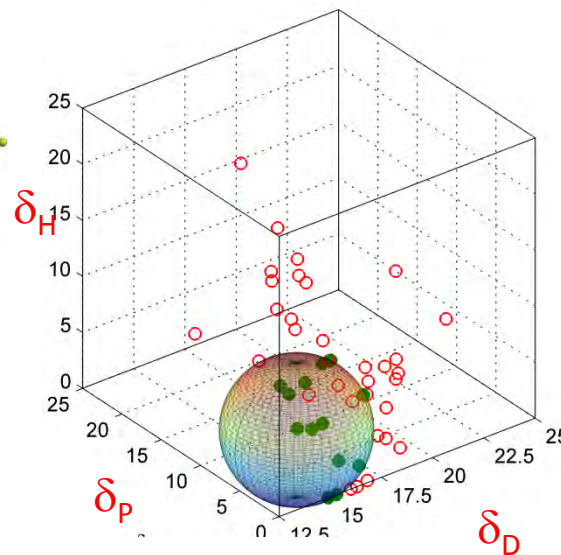
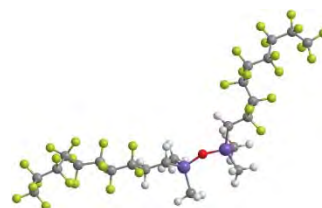
Octa-trifluoropropyl-POSS



Octa-fluorohexyl-POSS

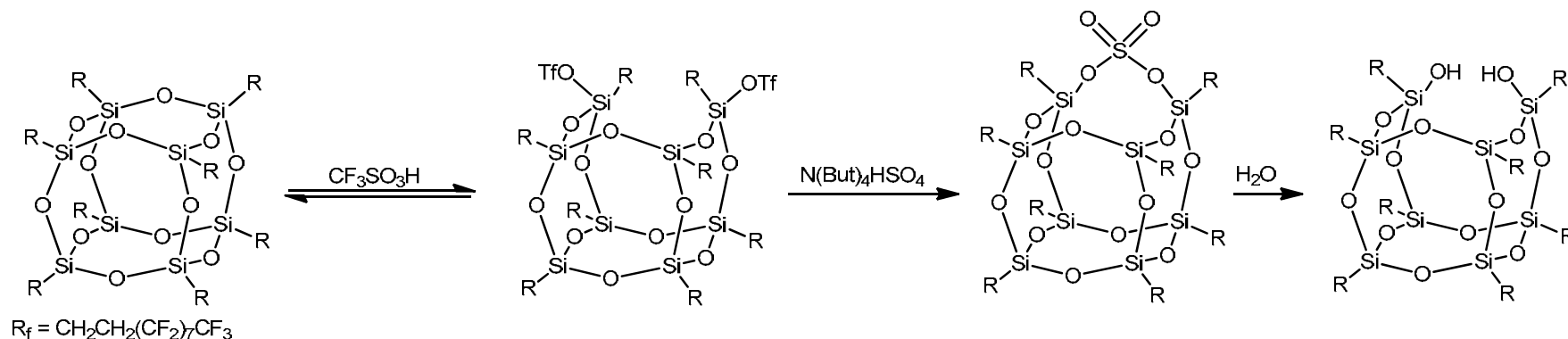


Fluorodecyl-M2

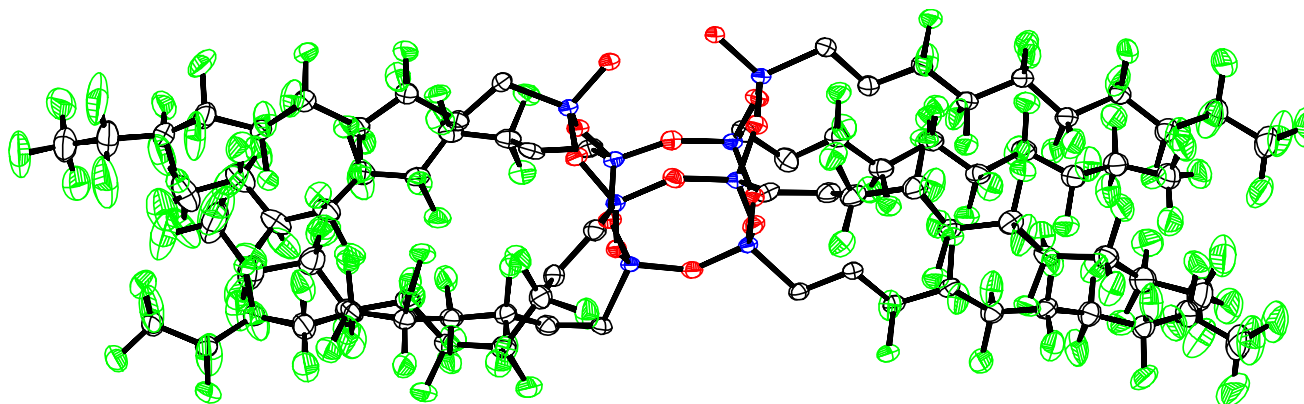




Incompletely Condensed Silsesquioxane



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



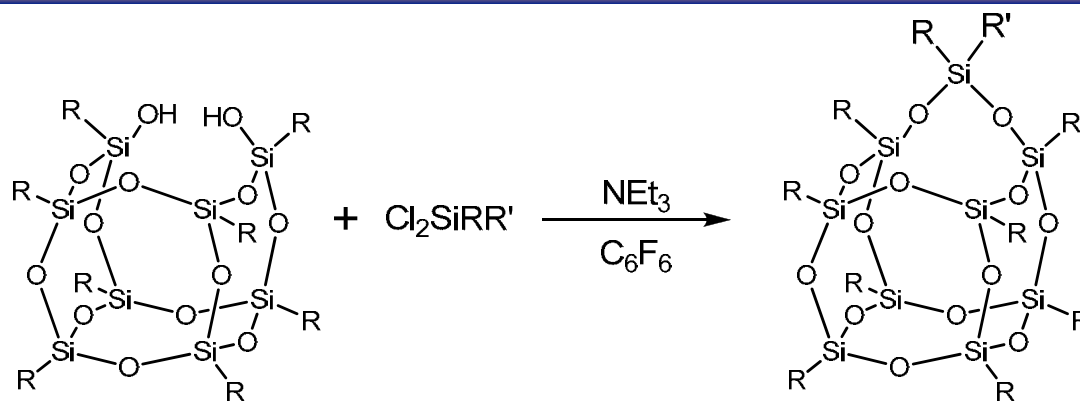
JACS, 2011

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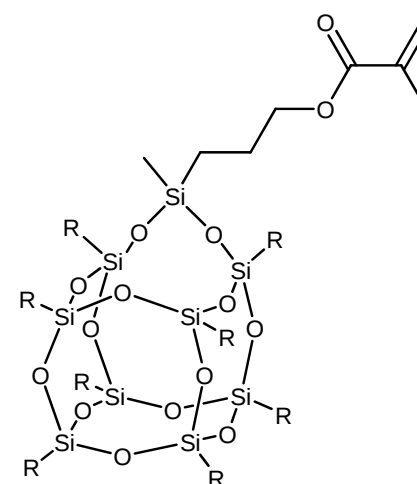
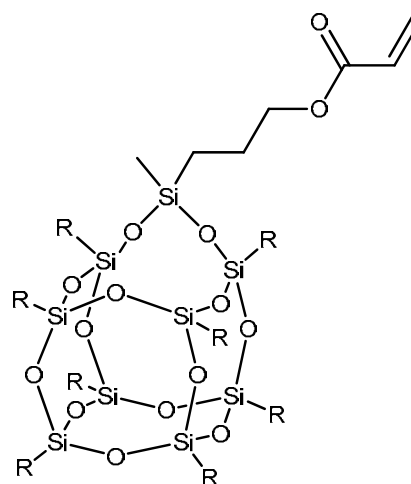
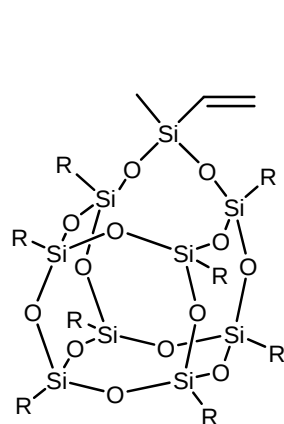
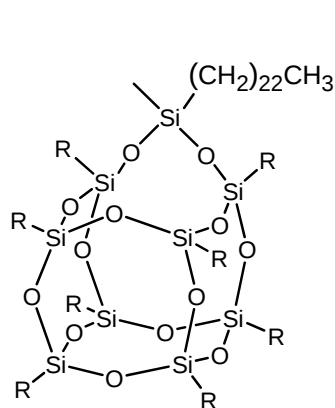


Synthesis of Disilanol FluoroPOSS

Disilanol FluoroPOSS has a molecular weight of 4009 g/mol.



- Can be reacted with functional dichlorosilane to add any desired functionality
- Platform for molecules with superhydrophobic or oleophobic properties
- A variety of fluoroPOSS compounds have been synthesized



JACS, 2011

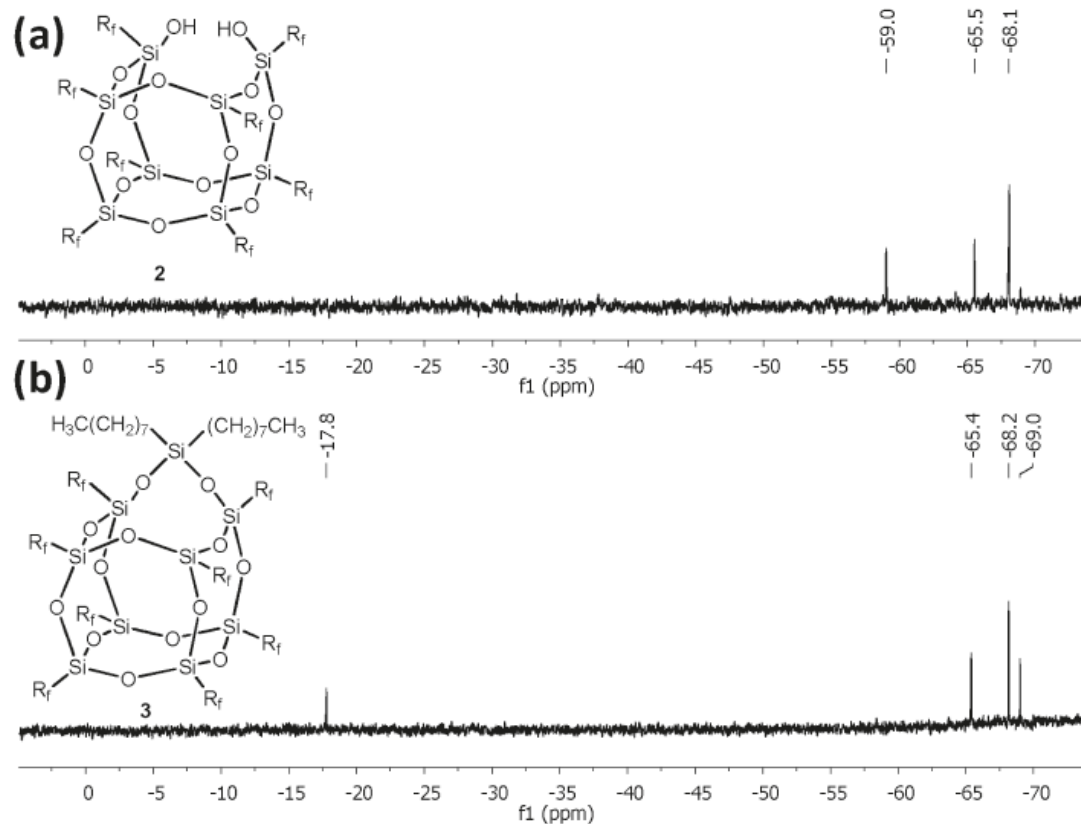
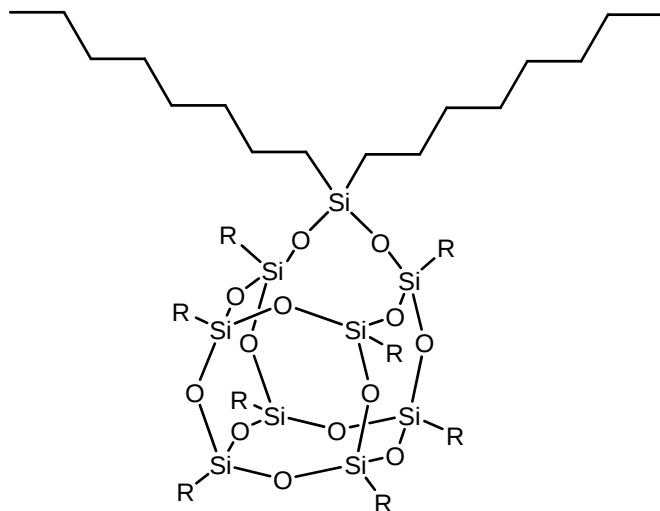
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Organic-Substituted FluoroPOSS



Dioctyl silyl FluoroPOSS



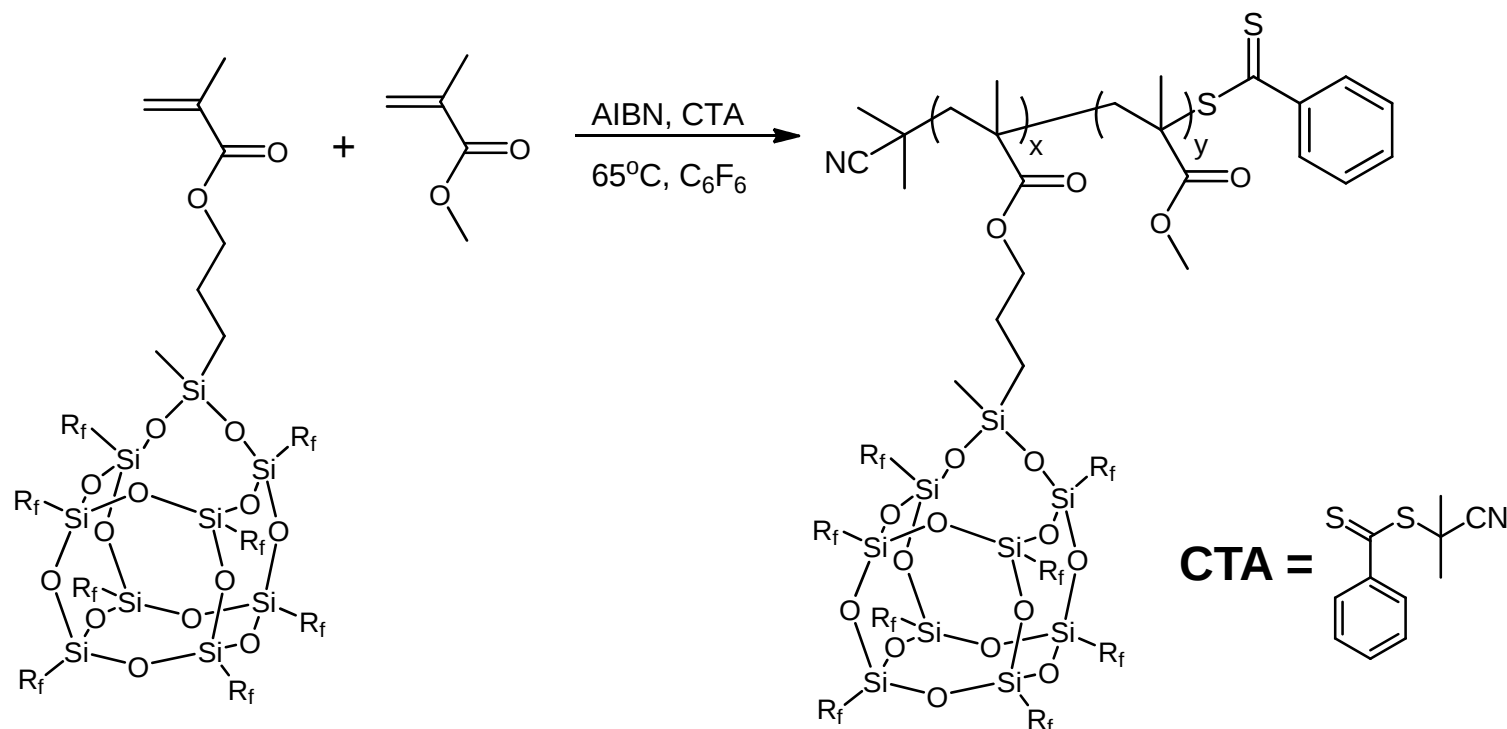
- Soluble in diethyl ether
- Can be directly blended in polymers
- Potential non-ionic surfactants

JACS, 2011

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F-POSS Copolymers



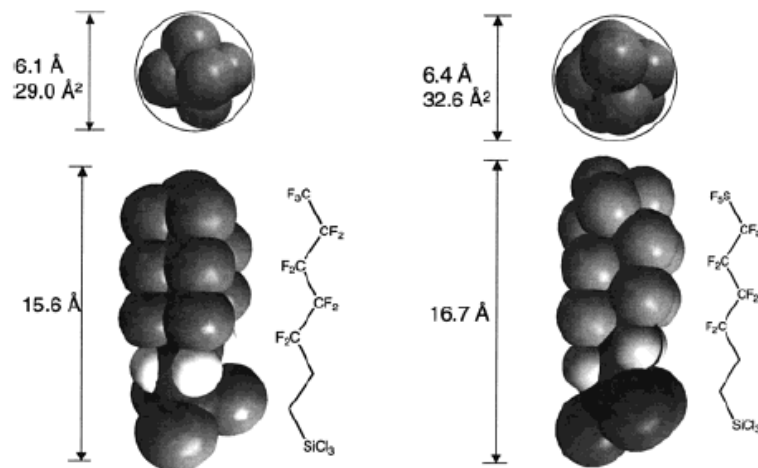
F-POSS wt% (mol%)	M_w (g mol ⁻¹)	PDI	Conv.%	T_g (°C)	Water		Hexadecane	
					(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
0	58 100	1.08	73	127	77.8 ± 1.3°	57.8 ± 2.5°	Wetted	Wetted
1 (0.02)	58 700	1.05	72	129	109.2 ± 2.4°	61.5 ± 1.9°	67.8 ± 1.4°	Wetted
5 (0.12)	23 000	1.01	30	124	117.8 ± 1.6°	95.7 ± 2.9°	76.7 ± 1.1°	68.8 ± 1.9°
10 (0.25)	26 900	1.01	29	124	118.2 ± 1.4°	101.1 ± 2.5°	77.2 ± 0.4°	69.5 ± 2.1°
25 (0.79)	37 700	1.03	41	125	120.8 ± 1.8°	97.0 ± 2.4°	82.9 ± 0.4°	74.6 ± 2.0°
F-POSS-MA	n/a	n/a	n/a	n/a	117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°

Polym Chem, 2013

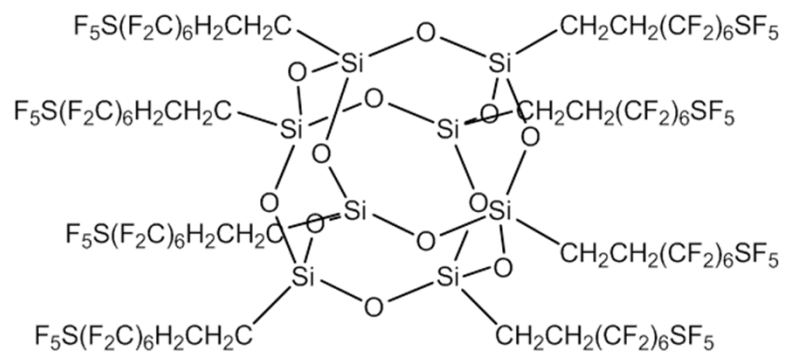
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SF₅-Terminated F-POSS



Gard, *Chem Mater*, 2000

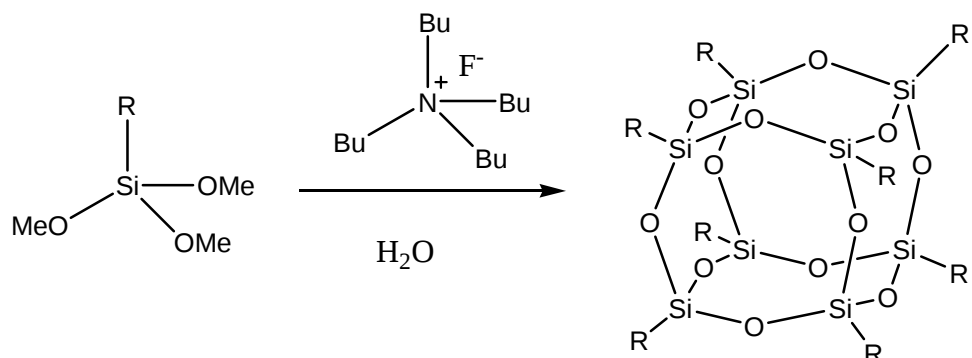


Chemical Formula: C₆₄H₃₂F₁₃₆O₁₂S₈Si₈

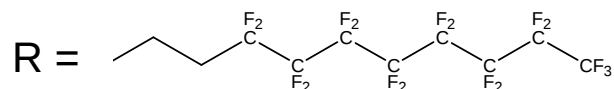
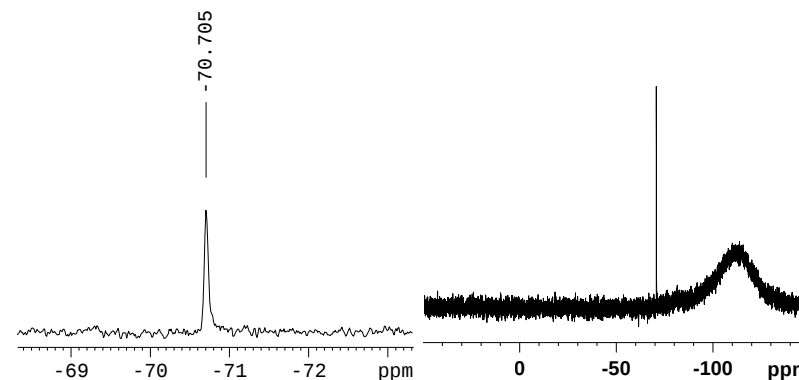
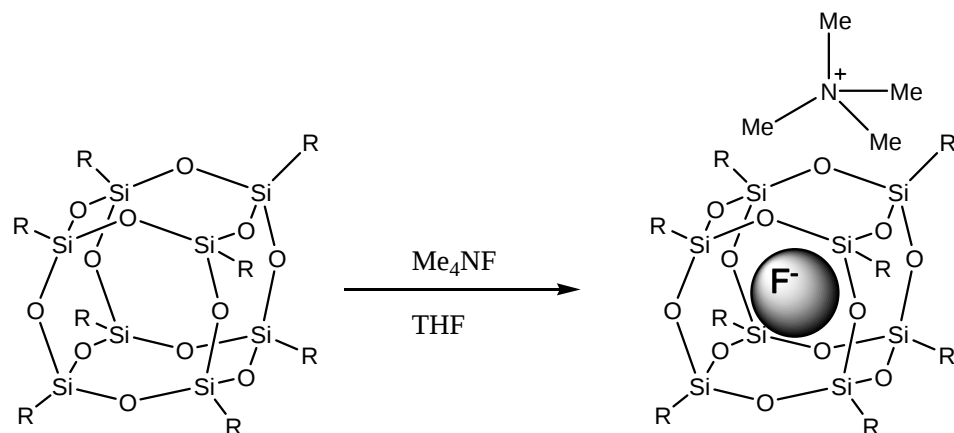
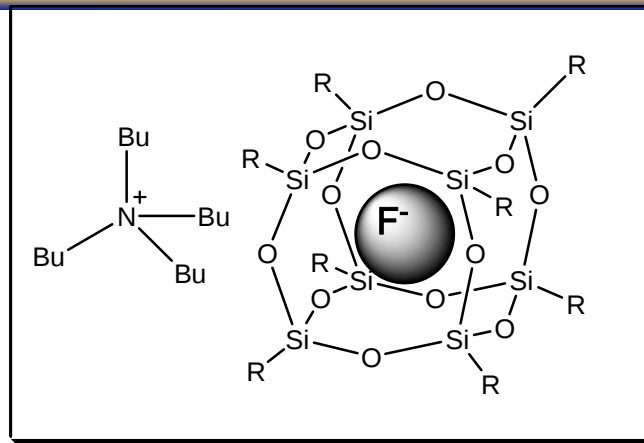
Exact Mass: 4055.56



F⁻@F-POSS



Bassindale, *Angew Chem*, 2003



Now soluble in common organic solvents!

Chem Mater, 2008

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Summary



- Solubility and wetting characteristics vary widely
- Not all types of fluorinated functionality give the same results
- Even minor changes in structure may produce drastically different results
- Solubility behavior is difficult to predict based on structure
- Prediction of water and hydrocarbon wetting behavior is also extremely difficult



Applied Materials Group



The Applied Materials Group at Edwards Air Force Base

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Silicones and Silicone-Modified Materials VII

An International Symposium at the American Chemical Society National Meeting Boston, Massachusetts, August 16-20, 2015

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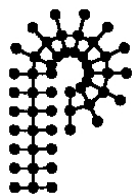
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Silicon-Containing Polymers and Composites



December 2016
Omni Hotel, San Diego, CA



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QUESTIONS?



U.S. AIR FORCE



Comparison of Surface Energy Parameters for POSS Compounds



Table 3. Computed Values of the Dispersion (γ_{sv}^d), Acidic (γ_{sv}^+), and Basic (γ_{sv}^-) Components of Solid-Surface Energy (mN/m) for Various Fluoroalkylated Silicon-Containing Moieties

	alkanes (Zisman analysis)	all liquids ^b (eq 1 with $\phi_{sl} = 1$)	diiodomethane, dimethyl sulfoxide and water (eq 5)				
	γ_c	γ_{sv}	γ_{sv}	dispersion (γ_{sv}^d)	polar (γ_{sv}^p)	acidic (γ_{sv}^+)	basic (γ_{sv}^-)
fluorodecyl T ₈	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorooctyl T ₈	7.4	10.6	10.9	10.6	0.3	0.2	0.1
fluorohexyl T ₈	8.5	11.6	47.4	11.4	36.0	20.8	15.6
fluoropropyl T ₈	19.7	18.7	38.4	19.1	19.3	11.8	7.9
hexafluoro-i-butyl T ₈	17.7	19.1	26.9	26.8	0.1	0.002	0.8
fluorodecyl T ₈	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorodecyl Q ₄	14.5	14.3	14.9	14.5	0.8	0.0	0.2
fluorodecyl M ₂	19.6	26.8	39.7	30.9	8.8	2.0	9.7

Predicted values based on Hansen Solubility Parameters (for “liquid” surfaces)

		γ_{lv} (dyn / cm)	γ_{lv}^d (dyn / cm)
Fluorodecyl T8	(est. HSP)	34.6	24.8
Fluorohexyl T8	(est. HSP)	37.7	26.2
Fluoropropyl T8		43.7	28.6
Hexafluoro-i-butyl T8		43.5	21.4
Fluorodecyl M2		30.3	20.5

- For perfluoroheptane, the predicted value of γ_{lv} of 21 dyn/cm is close to expectations
- Agreement for the dispersive component is better, but $\gamma_{lv}^d < \gamma_{lv}$ without rearrangement