

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 19-03-2012		2. REPORT TYPE Briefing Charts		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Silicon-Containing Polymers and Composites				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Joseph M. Mabry				5d. PROJECT NUMBER	
				5f. WORK UNIT NUMBER 23030521	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSM 9 Antares Road Edwards AFB CA 93524-7401				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-VG-2012-081	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for public release; distribution unlimited. PA# 12226.					
13. SUPPLEMENTARY NOTES For presentation at the 243 rd ACS National Meeting, San Diego, CA, 25-29 March 2012 and publication in Polymer Preprints, March 25, 2012.					
14. ABSTRACT Many hydrophobic surfaces exist in nature, but there is no naturally occurring oleophobic surface. There is plenty of academic and commercial interest in the development of oleophobic surfaces. The focus is on commercially available textiles. This presentation shows that fluoroPOSS are superhydrophobic. FluoroPOSS polymer composite surfaces can be superhydrophobic and superoleophobic. Superhydrophilic and superoleophobic surfaces have been developed. Such surfaces are ideal for the separation of both free-oil and oil-water emulsions. These membranes, for the first time, allow continuous-flow oil-water emulsion separation. Functionality will allow the covalent attachment of these low energy materials to substrates of choice.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Joseph M. Mabry
Unclassified	Unclassified	Unclassified	SAR	39	19b. TELEPHONE NUMBER (include area code) N/A



Silicon-Containing Polymers and Composites

Silicones and Silicone-Modified Materials
ACS National Meeting
28 March 2012



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Motivation



- Many hydrophobic surfaces exist in nature but there is no naturally occurring oleophobic surface
- Plenty of academic and commercial interest in the development of oleophobic surfaces
- Focus on commercially available textiles



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www.gfn.com/sowhatsyourpoint/wp-content



www.defense-technologynews.blogspot.com

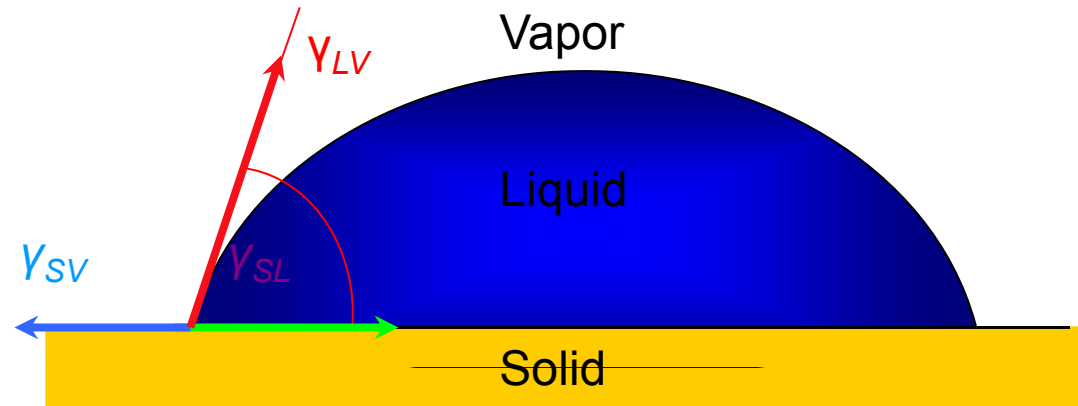


www.tressugar.com

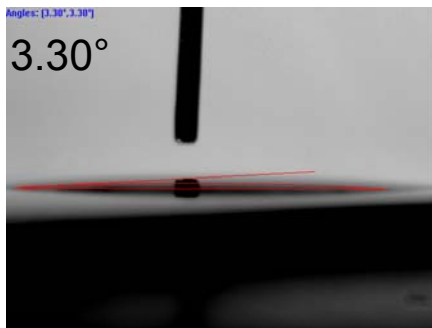
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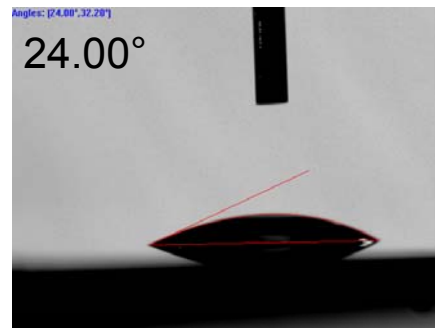
Non-wetting surfaces



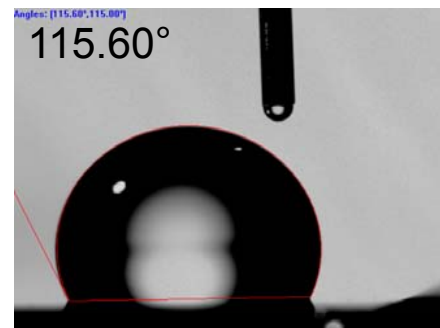
Contact angles with water:



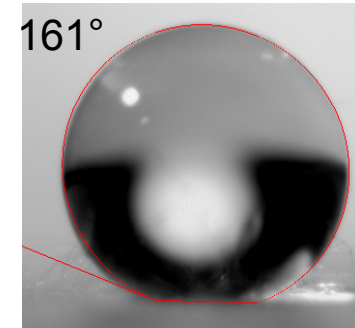
Superhydrophilic
 $\theta \sim 0^\circ$



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



Hydrophobic
 $\theta > 90^\circ$



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

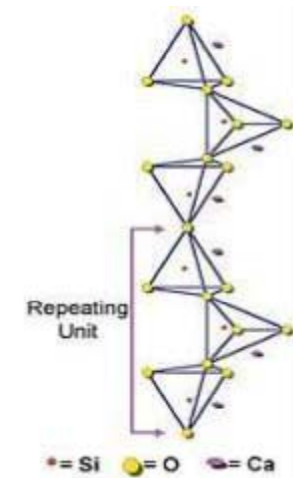
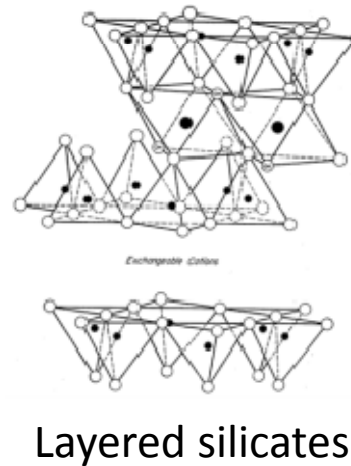
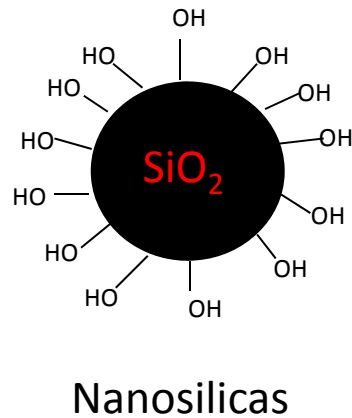
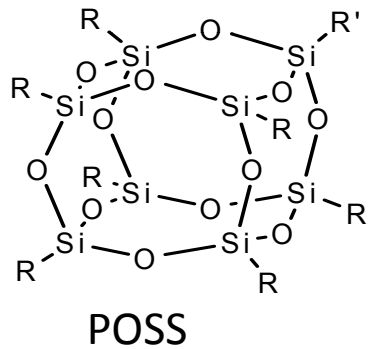
Similarly, superoleophobic surfaces display contact angle $\theta^* > 150^\circ$ with oils or alkanes



Nanocomposite Materials

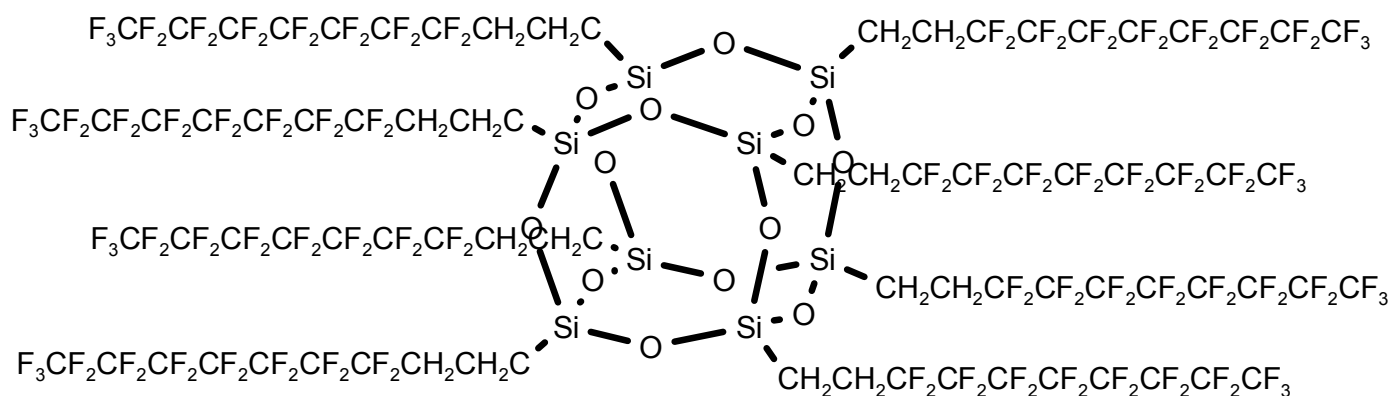
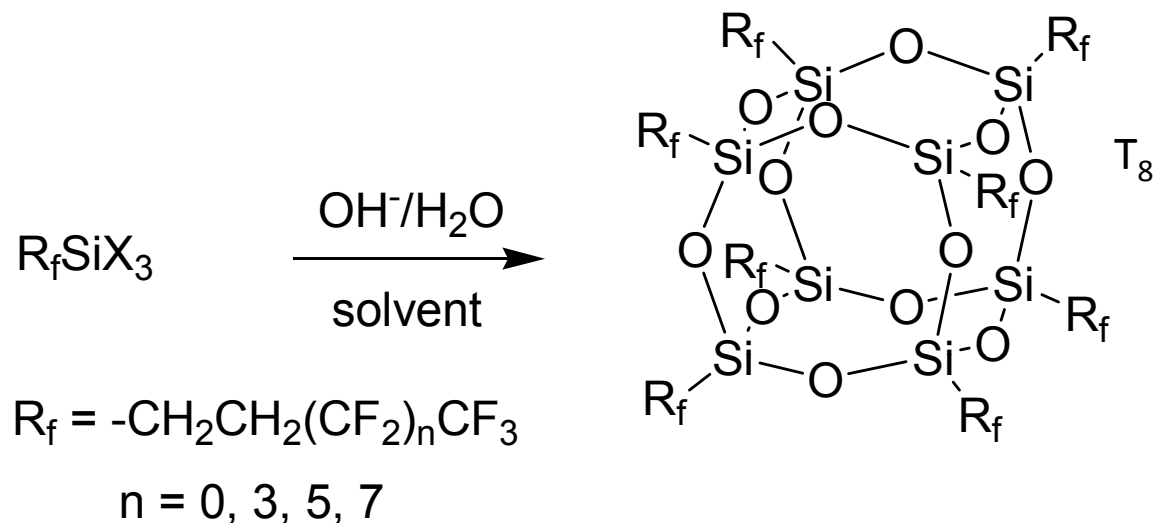


Silicon-containing compounds





Fluorinated POSS Synthesis

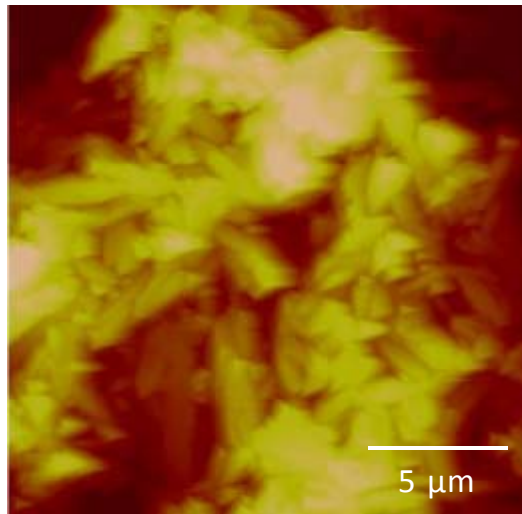


Angew Chem (2008)

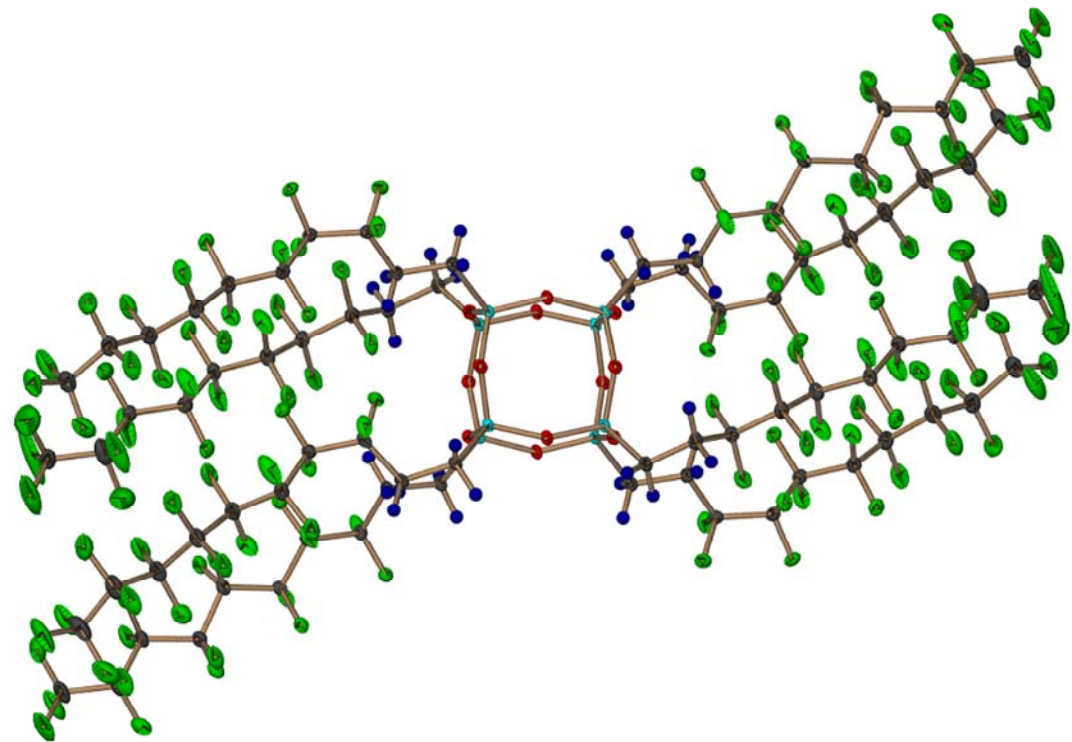
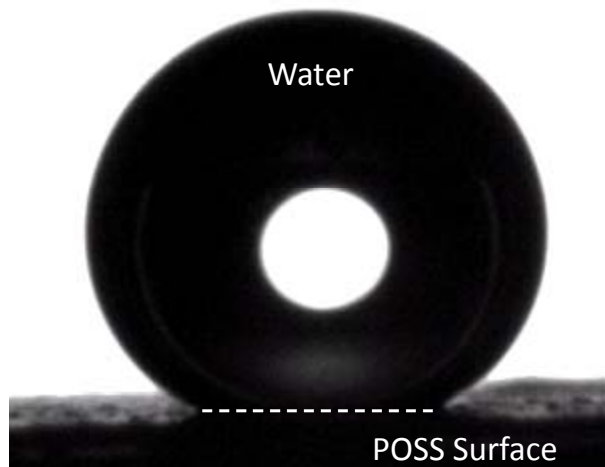
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Hydrophobic Materials



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



Angew Chem (2008)

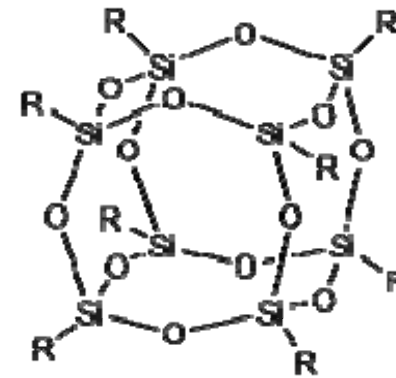
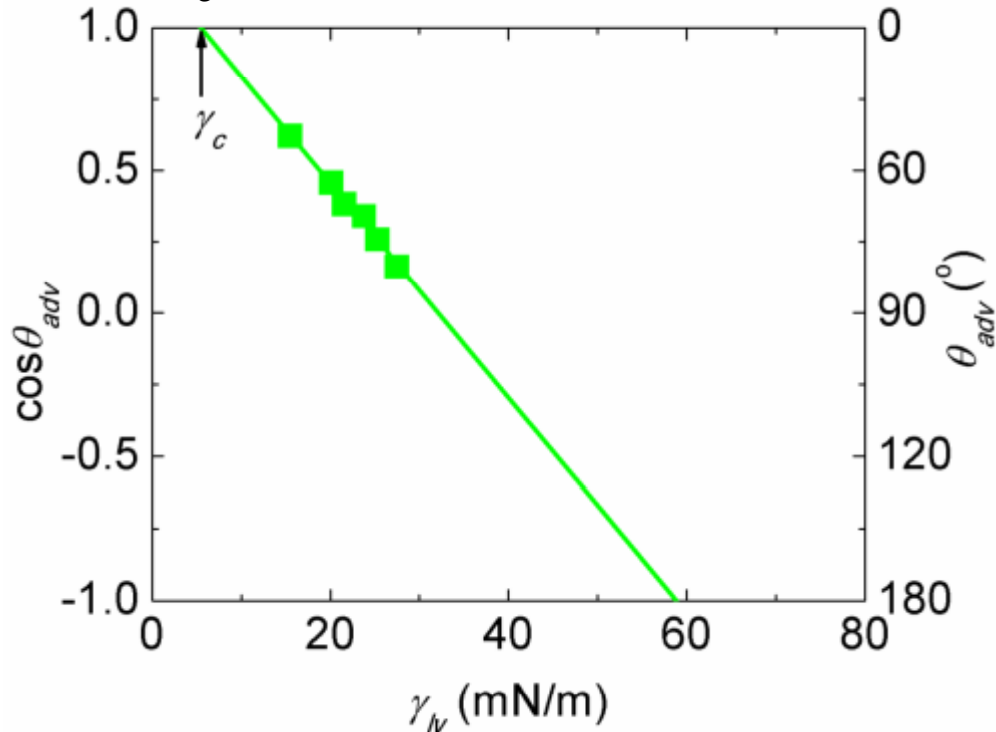
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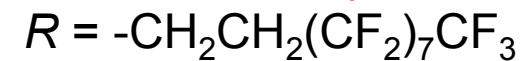
Low Surface Energy Materials



$\gamma_c = 5.5$ mN/m by Zisman analysis



Fluorodecyl:



Similarly, GG analysis results in surface energy calculation of: $\gamma_c = 8$ mN/m

Contacting liquids:

hexadecane ($\gamma_{lv} = 27.5$ mN/m), dodecane (25.3), decane (23.8), octane (21.6), heptane (20.1), and pentane (15.5)

ACS AMI (2010)

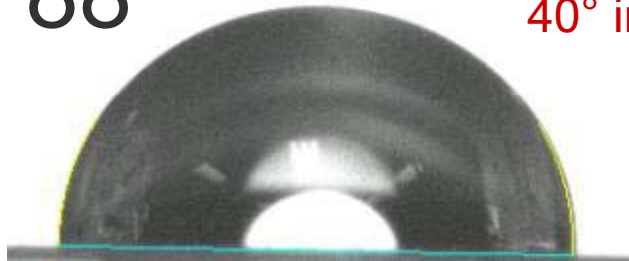
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Water/Oil Repellant Nanocomposites



88°

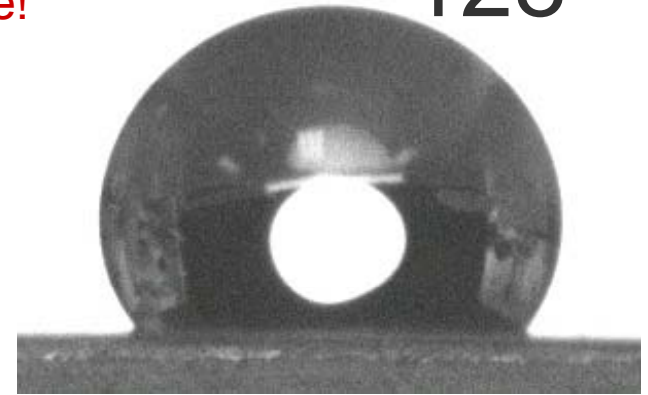


Polychlorotrifluoroethylene (PCTFE)

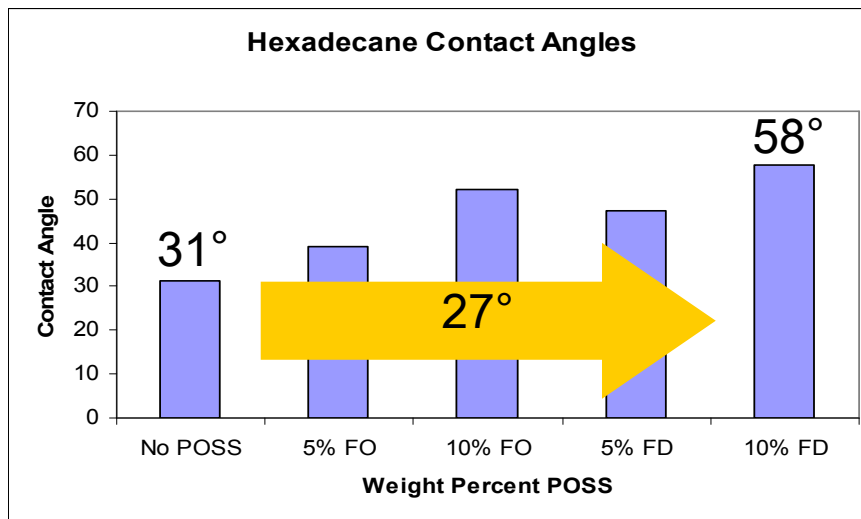
40° increase in water contact angle!

10% POSS

128°



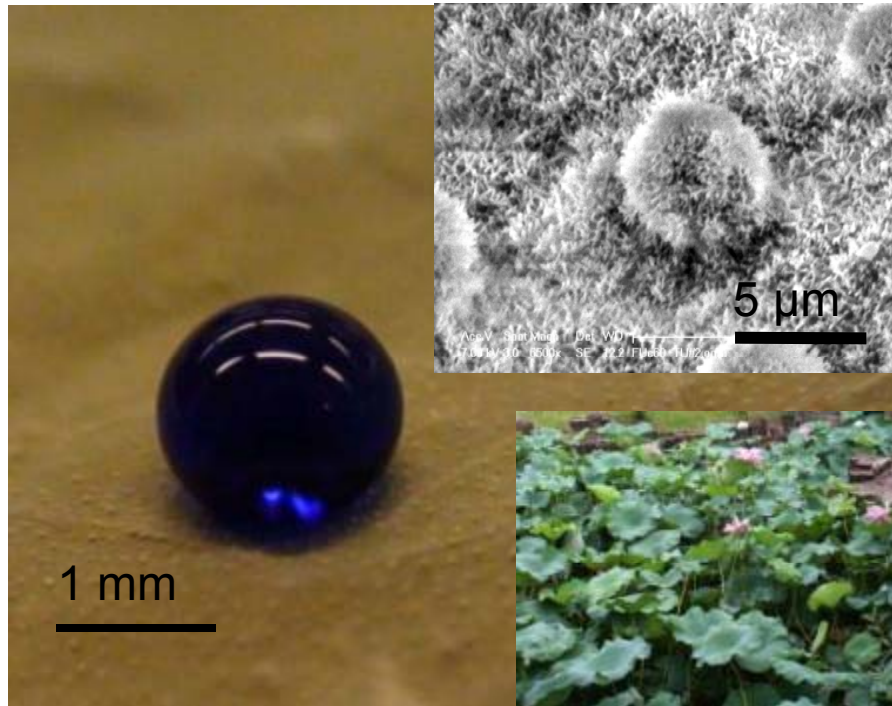
PCTFE with 10% Fluorodecyl₈T₈



Increase in hexadecane contact angle less than desired



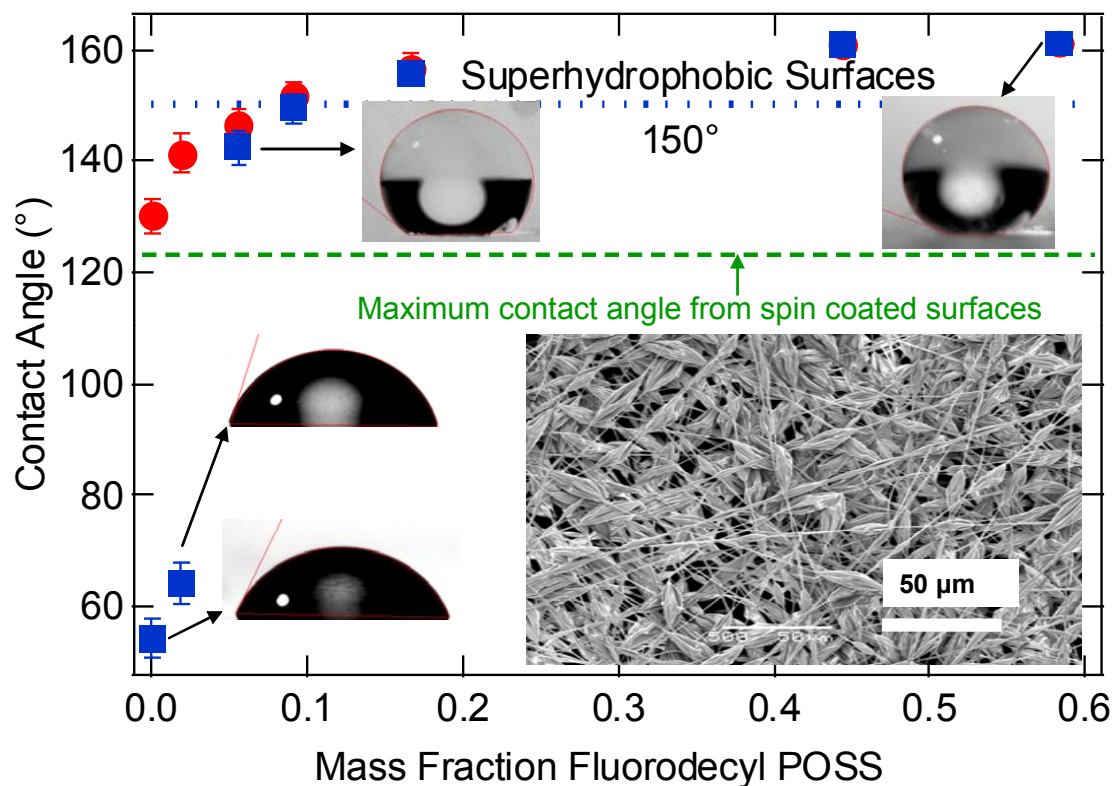
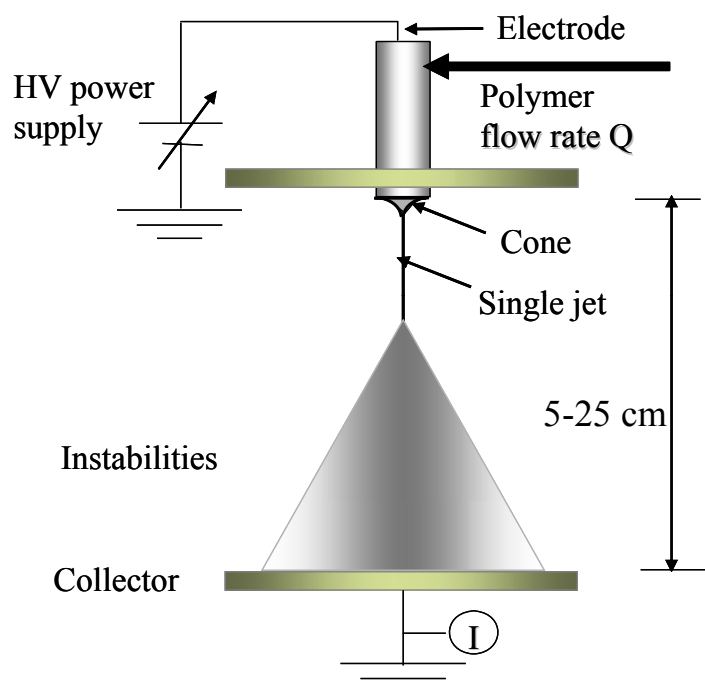
The Lotus Leaf



Water, $\gamma_{LV} = 72.1 \text{ mN/m}$

Hexadecane, $\gamma_{LV} = 27.5 \text{ mN/m}$

On most surfaces, $\theta_{oil} < \theta_{water}$. This is because the surface tension (γ_{LV}) of water is significantly higher than that for oils.

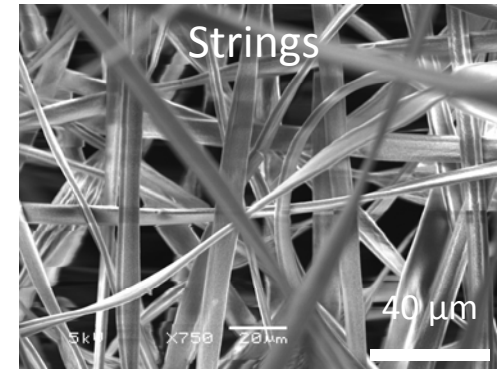
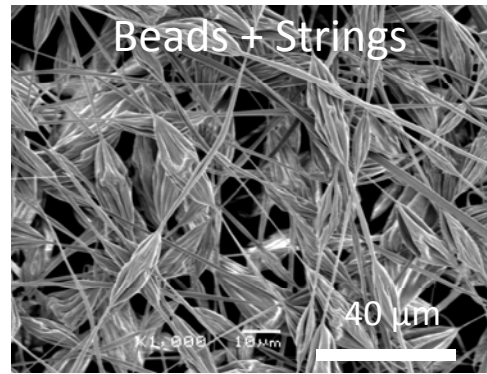
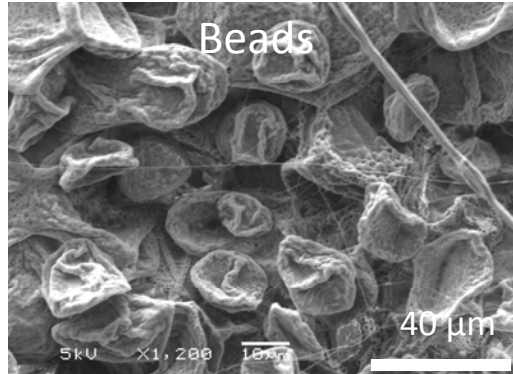


- ‘Beads on a string’ morphology, with high roughness and porosity
- A single step process - surface turns superhydrophobic for all POSS concentrations > 10 wt%

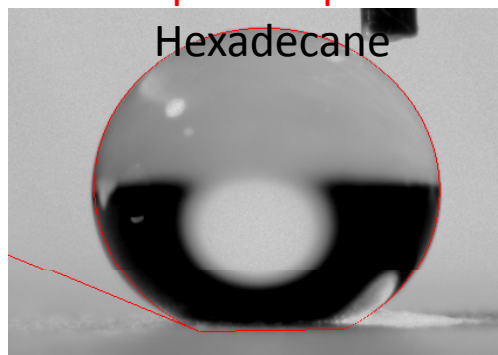
Science (2007)

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Each surface is composed of PMMA+POSS – 44 wt% blend; contact angle for hexadecane on corresponding spincoated surfaces = $q_{adv} = q_{rec} = 79^\circ$.



Superoleophobic!

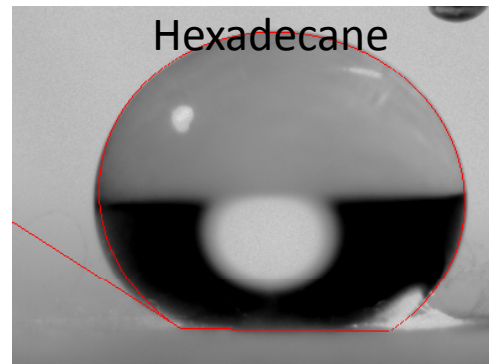


$$q_{adv}^* = 156^\circ$$

$$q_{rec}^* = 150^\circ$$

Water contact angles

$$q_{adv}^* = q_{rec}^* = 165^\circ$$



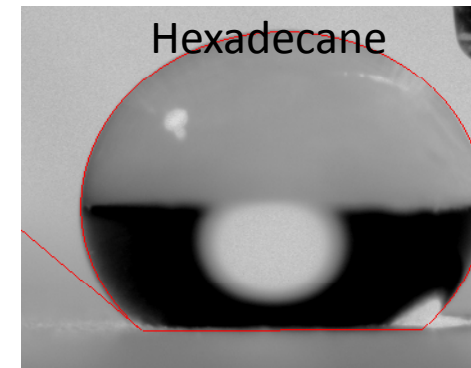
$$q_{adv}^* = 153^\circ$$

$$q_{rec}^* = 141^\circ$$

$$q_{adv}^* = q_{rec}^* = 163^\circ$$

Science (2007), PNAS (2008).

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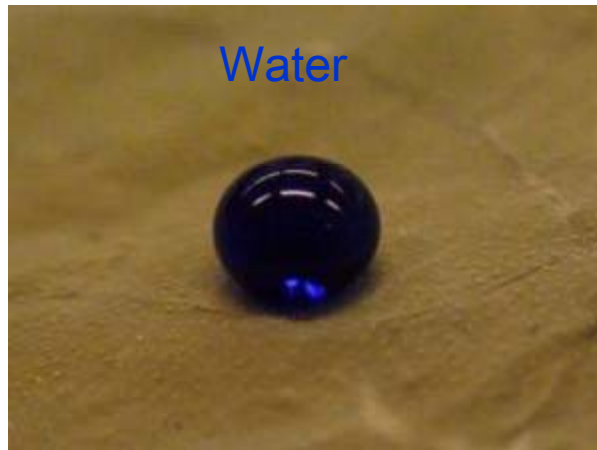
$$q_{adv}^* = 147^\circ$$

$$q_{rec}^* = 120^\circ$$

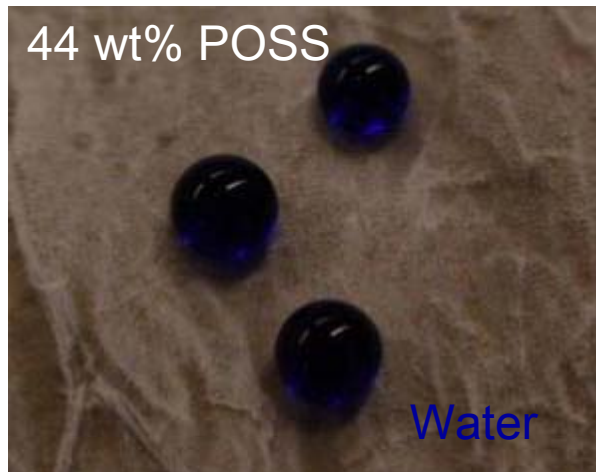
$$q_{adv}^* = q_{rec}^* = 162^\circ$$



Comparison with Lotus Leaf



Coat with electrospun fibers



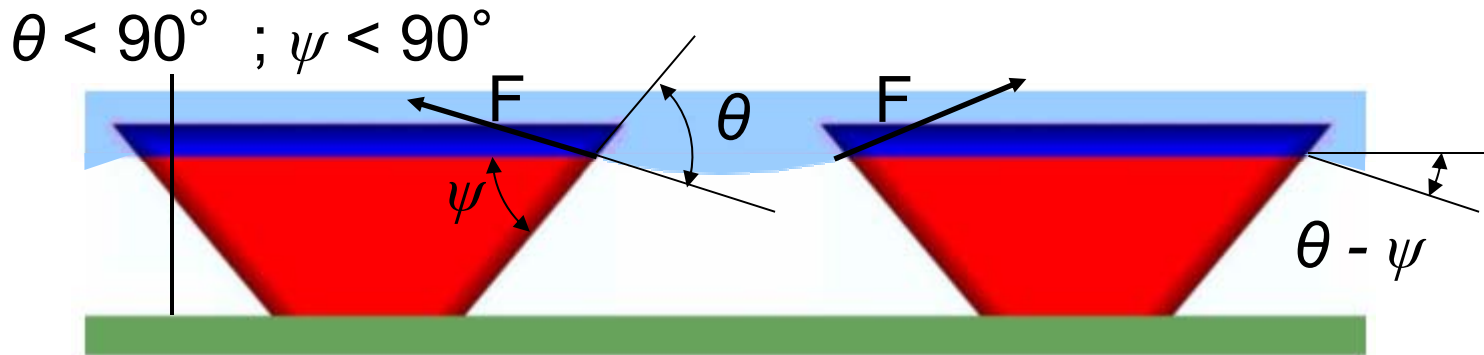
Coat with electrospun fibers



Science (2007), *PNAS* (2008).
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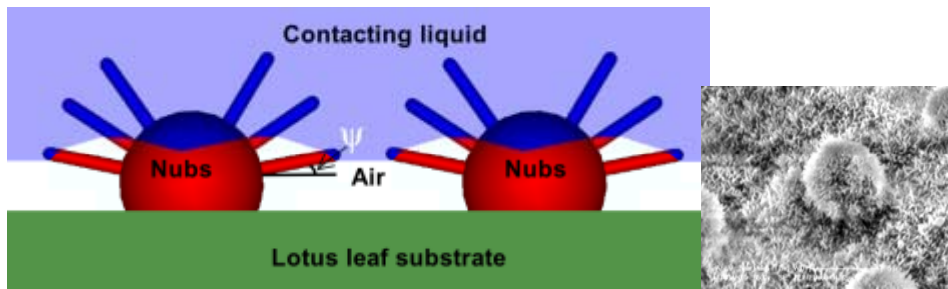


Critical role of re-entrant texture ($\psi < 90^\circ$)

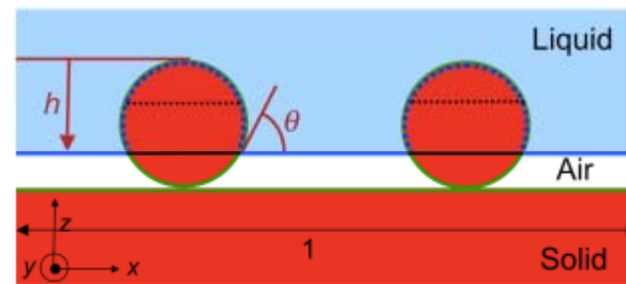


It is possible to support a composite interface even if $\theta < 90^\circ$

Re-entrant curvature : $180^\circ > \theta > 0^\circ$



Lotus Leaf

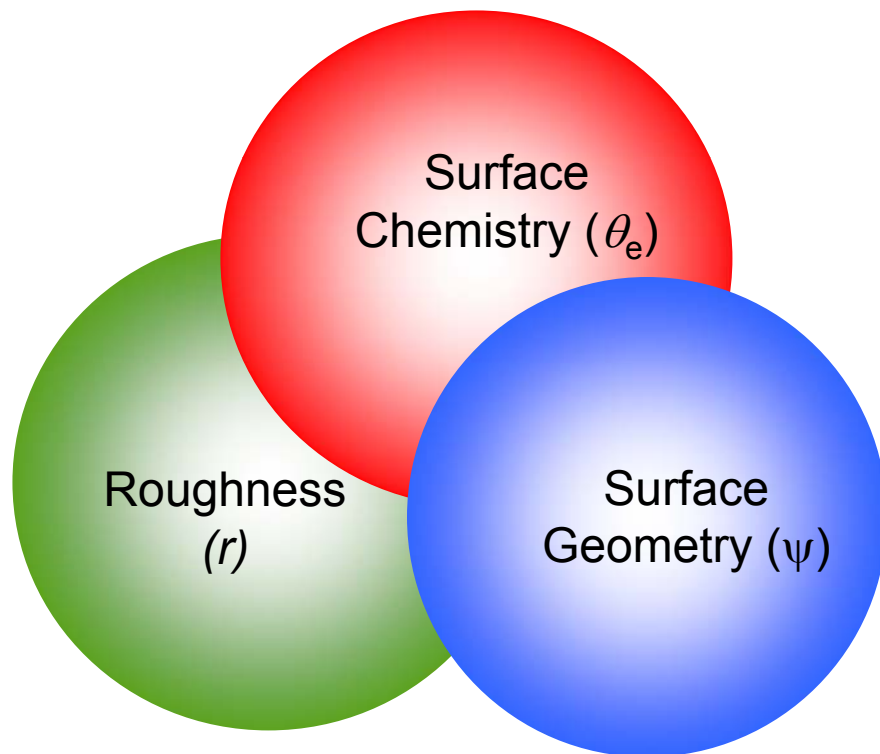


Cylinders / Fibers

Herminghaus, *Euro. Phys. Lett.* (2000), *Science* (2007); PNAS (2008)

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

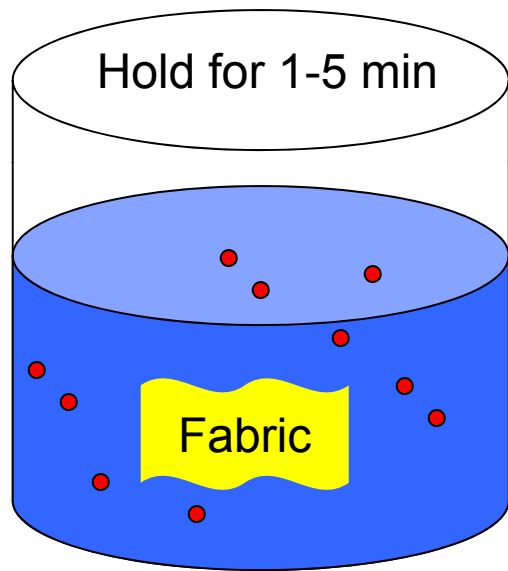


PMMA + 44 wt% POSS
electrospun coating (beads on a string) morphology

Science (2007)

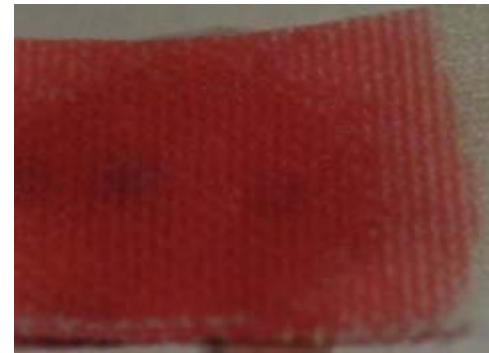
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Hexadecane ($\gamma_V = 27.5 \text{ mN/m}$) on an as-received commercial polyester fabric



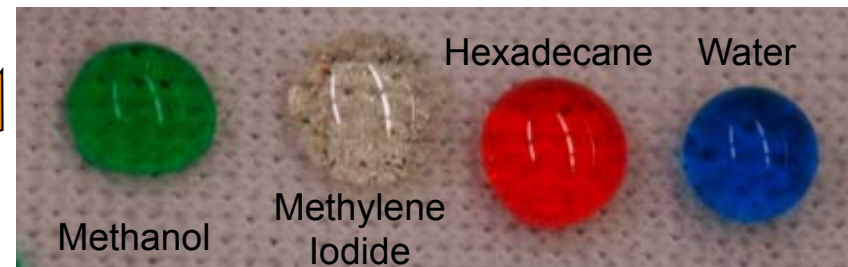
Solution of fluorodecyl POSS in Asahiklin (30 mg/ml)

Dip



Before

Dry (heat in oven at 60° C for 20 minutes)



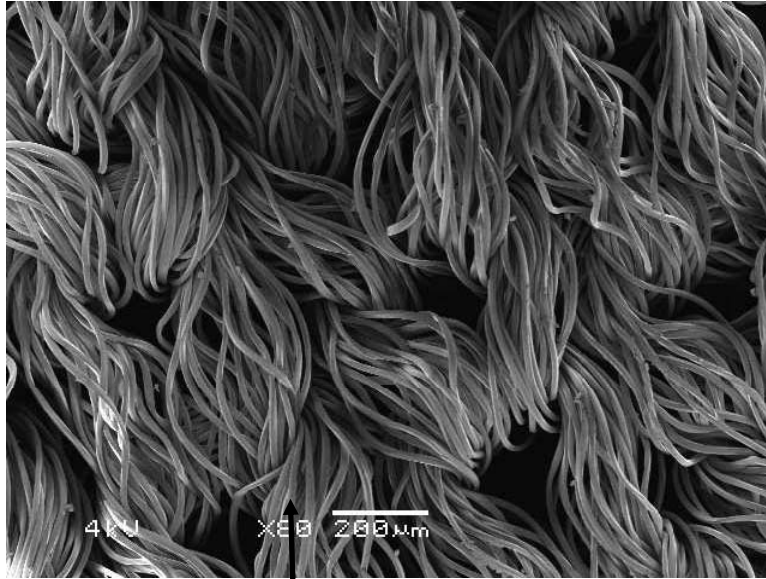
After dip-coating with a solution of fluorodecyl POSS

Adv Mater (2008)

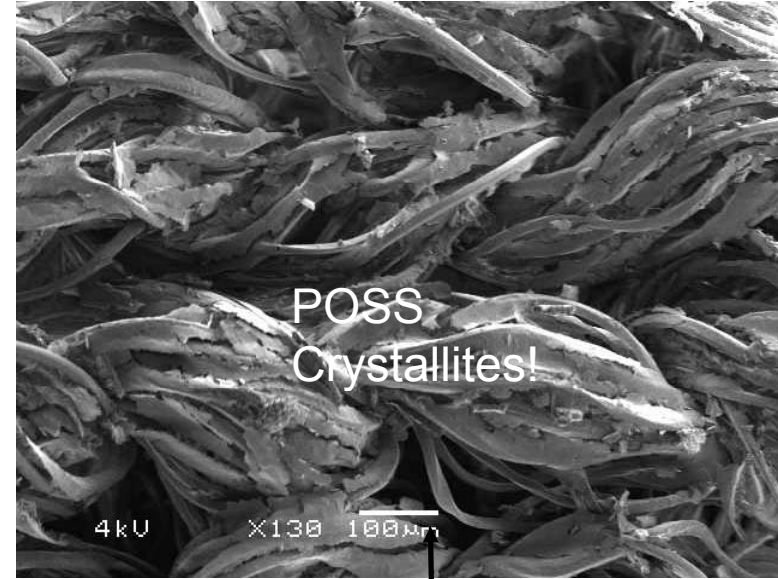
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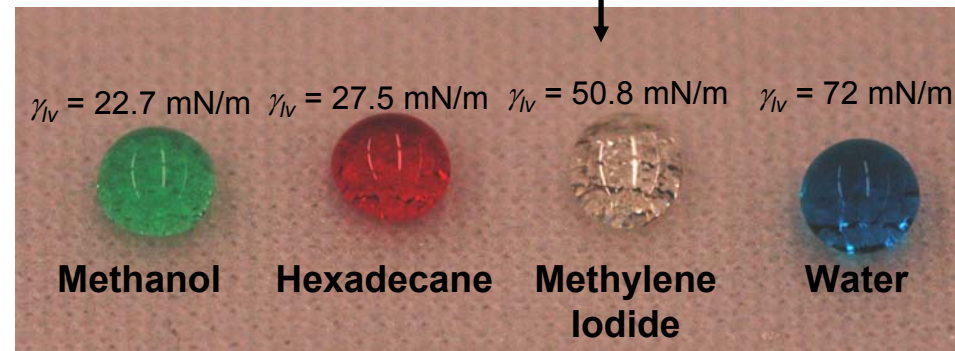
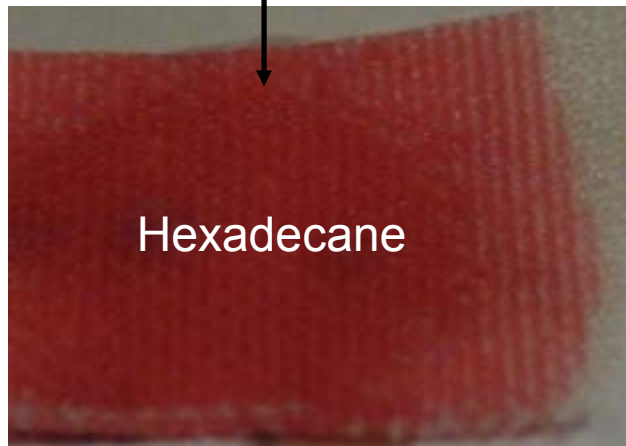
Dip-Coated Polyester Fabric



Before coating

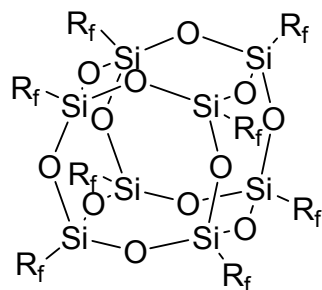


After coating with fluorodecyl POSS in Asahiklin (30 mg/ml)



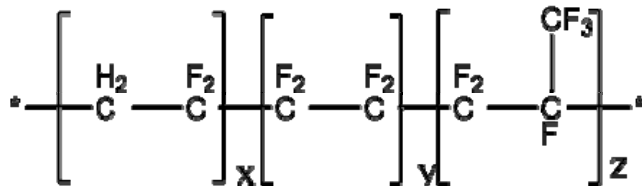


Dip-coating process for conformal coating of textured surfaces



$R_f = -CH_2-CH_2-(CF_2)_7-CF_3$
Fluorodecyl POSS

$\gamma_{sv} \approx 8 \text{ mN/m}$



Tecnoflon® (BR9151)

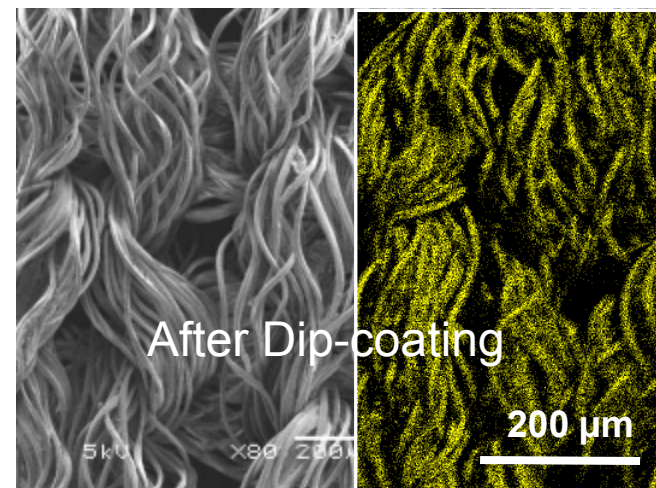
Fluoro-elastomer from
Solvay-Solexis

$\gamma_{sv} \approx 18 \text{ mN/m}$

Anticon 100 polyester fabric



EDAXS spectrum for fluorine



50:50 mixture, total solids = 10 mg/ml

Dip in Asahiklin solution for 5 minutes

Air dry to remove solvent

Heat treat at 60 °C for 30 minutes

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Superhydrophobic/Superoleophilic

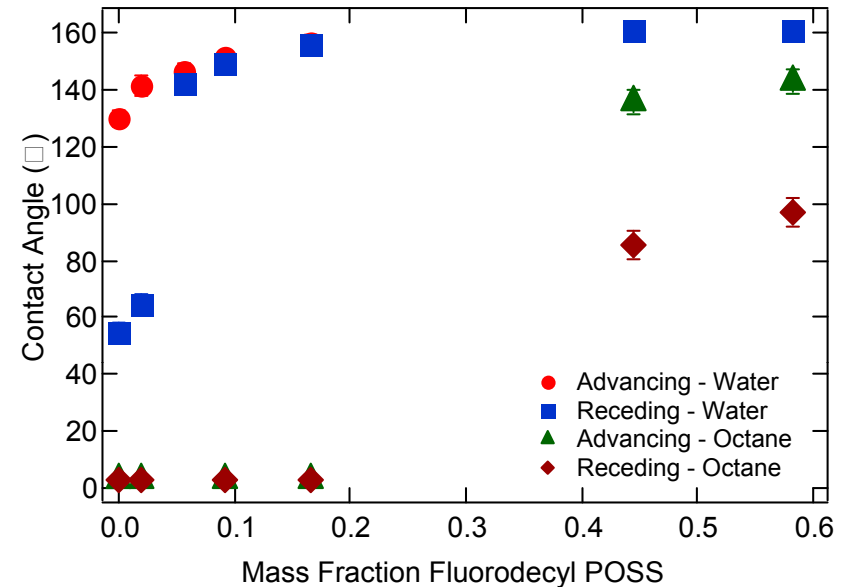


Designing Superoleophobic Surfaces

Anish Tuteja,¹ Woojae Choi,² Minglin Ma,³ Joseph M. Mabry,² Sarah A. Mazzella,³ Gregory C. Rutledge,¹ Gareth H. McKinley,^{2*} Robert E. Cohen^{1*}



Superhydrophobic
Superoleophilic

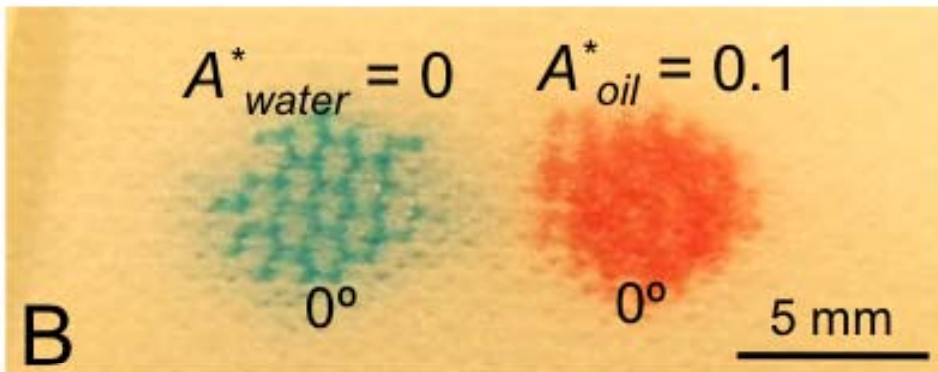
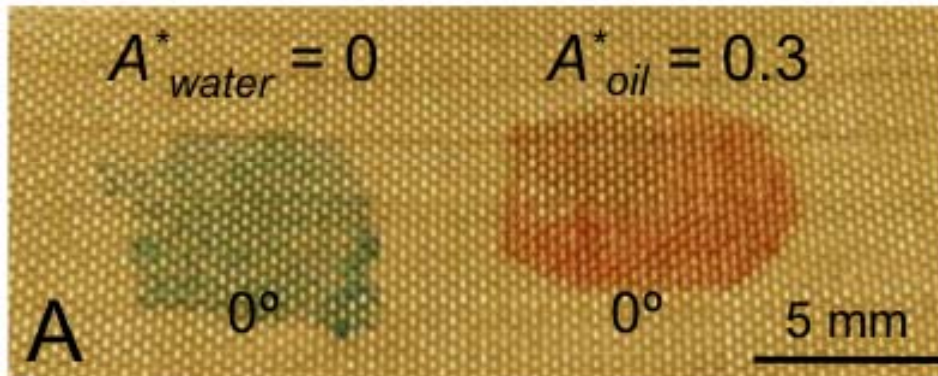


At low POSS concentrations many surfaces are *both* superhydrophobic and superoleophilic ($\theta^*_{alkane} \approx 0^\circ$). Thus, these porous surfaces form ideal membranes for separating mixtures / dispersions of alkanes (oils) and water

But...water is more dense than hydrocarbons!

Science (2007)

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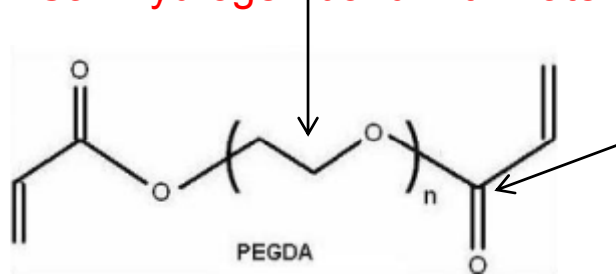
A and **B**. Neat x-PEGDA dip-coated stainless steel mesh 100 and polyester fabric **C**. An apparatus with a mesh 100 coated with neat x-PEGDA Both water and rapeseed oil permeate through.

Manuscript in preparation

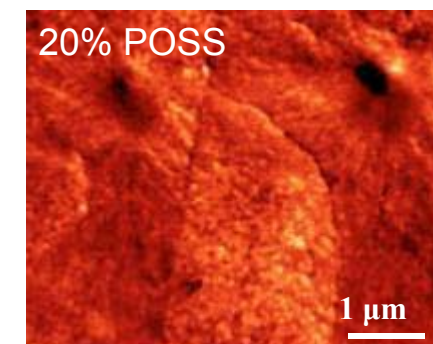
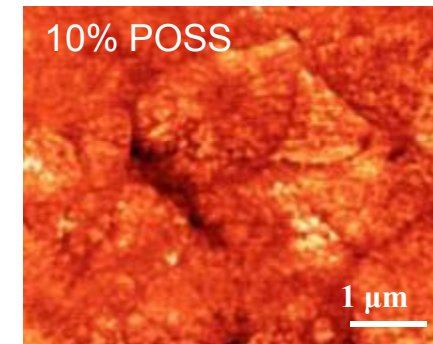
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PEGDA + Fluorodecyl POSS

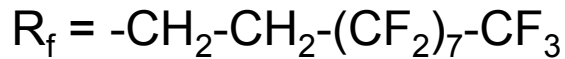
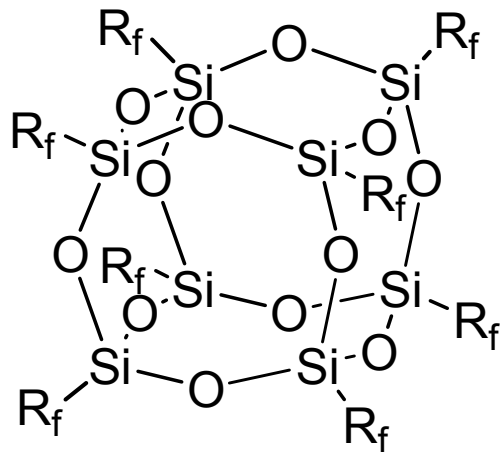
Can hydrogen bond with water



AFM Phase images of spin-coated PEGDA + POSS films



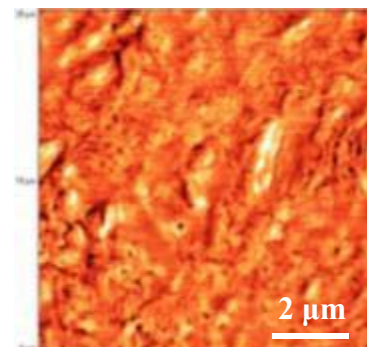
Fluorodecyl POSS molecules preferentially segregate to the air interface and crystallize.



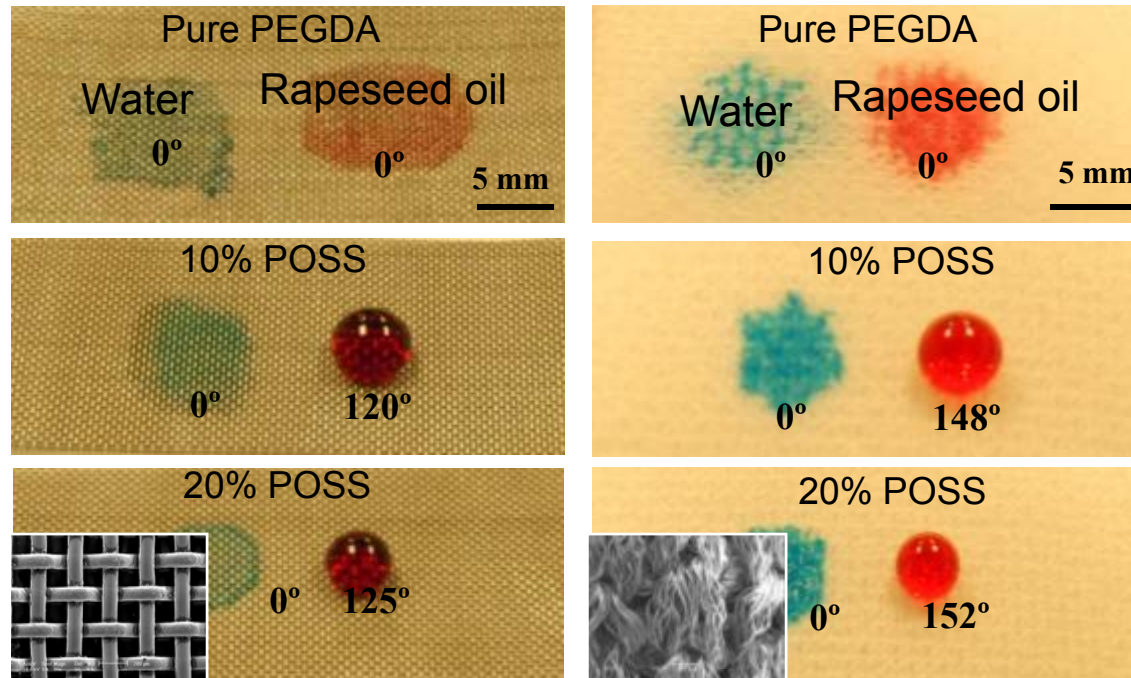
Fluorodecyl POSS

$\gamma_{sv} \approx 8 \text{ mN/m}$

20% POSS
Under water



Surfaces with inherent re-entrant curvature **dip-coated** with PEGDA + POSS blends



Stainless Steel Wire Mesh

Commercial Polyester Fabric

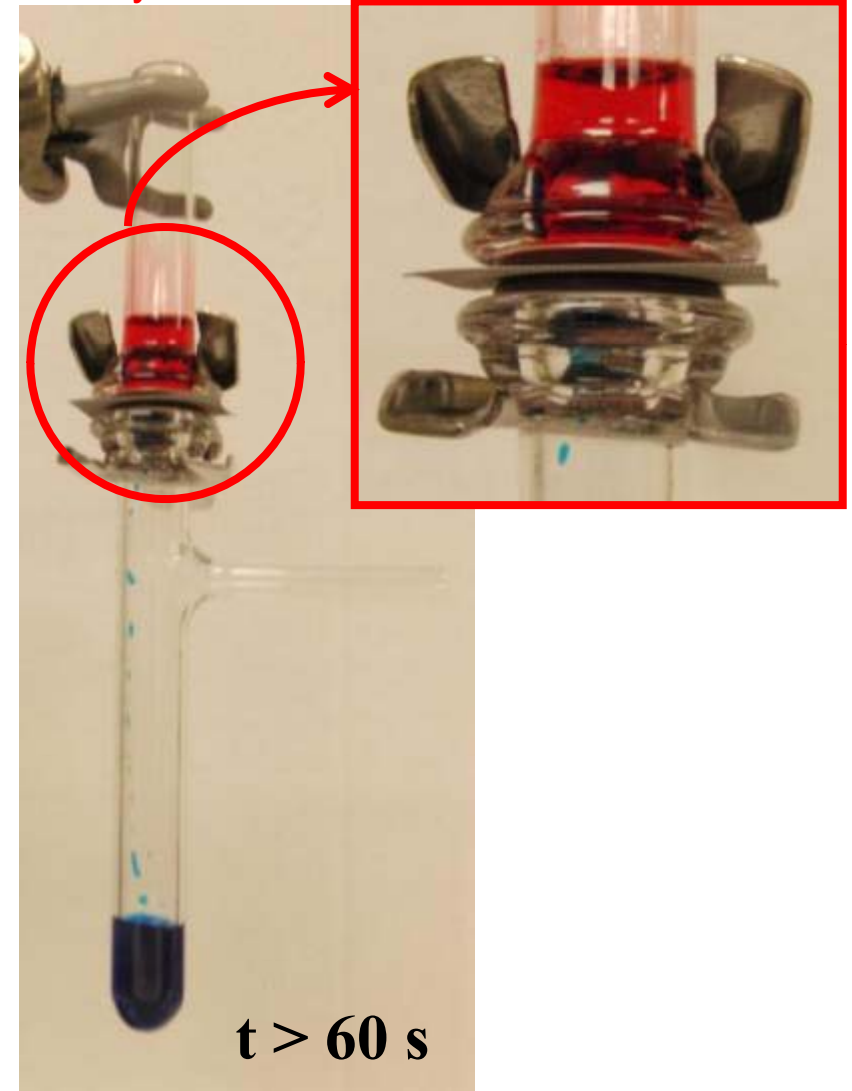
PEGDA surface reconfiguration leads to superhydrophilic behavior.

Manuscript in preparation

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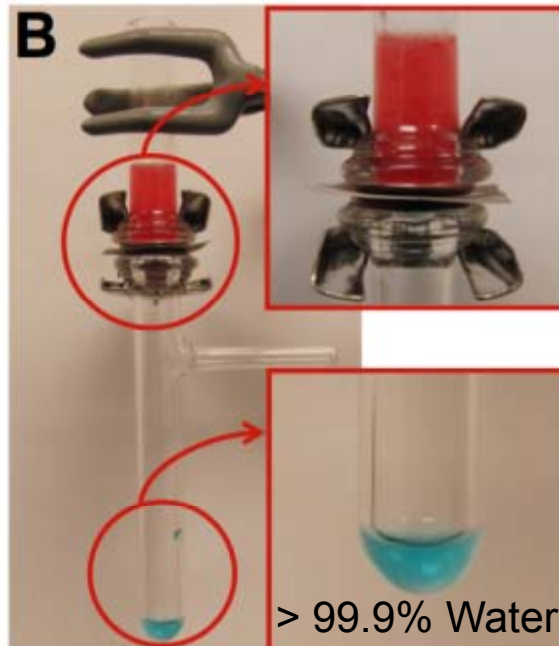
Free Oil – Water separation

Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.

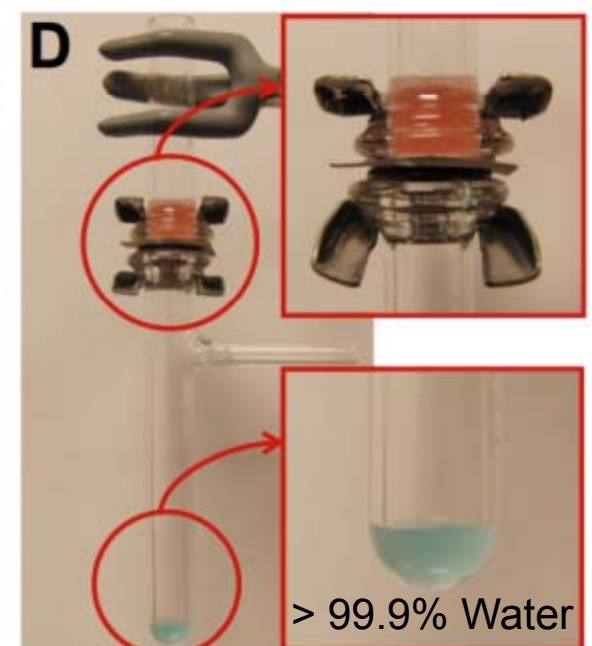
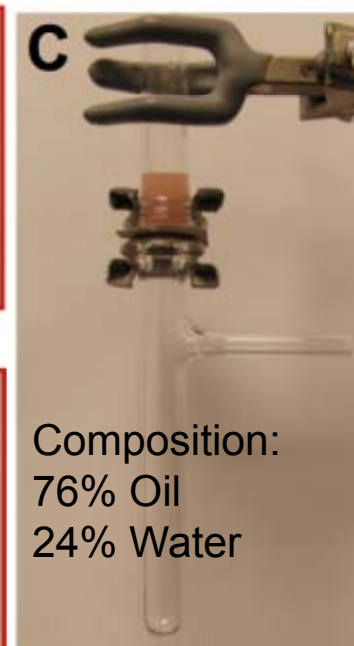


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Water-in-Oil Emulsion



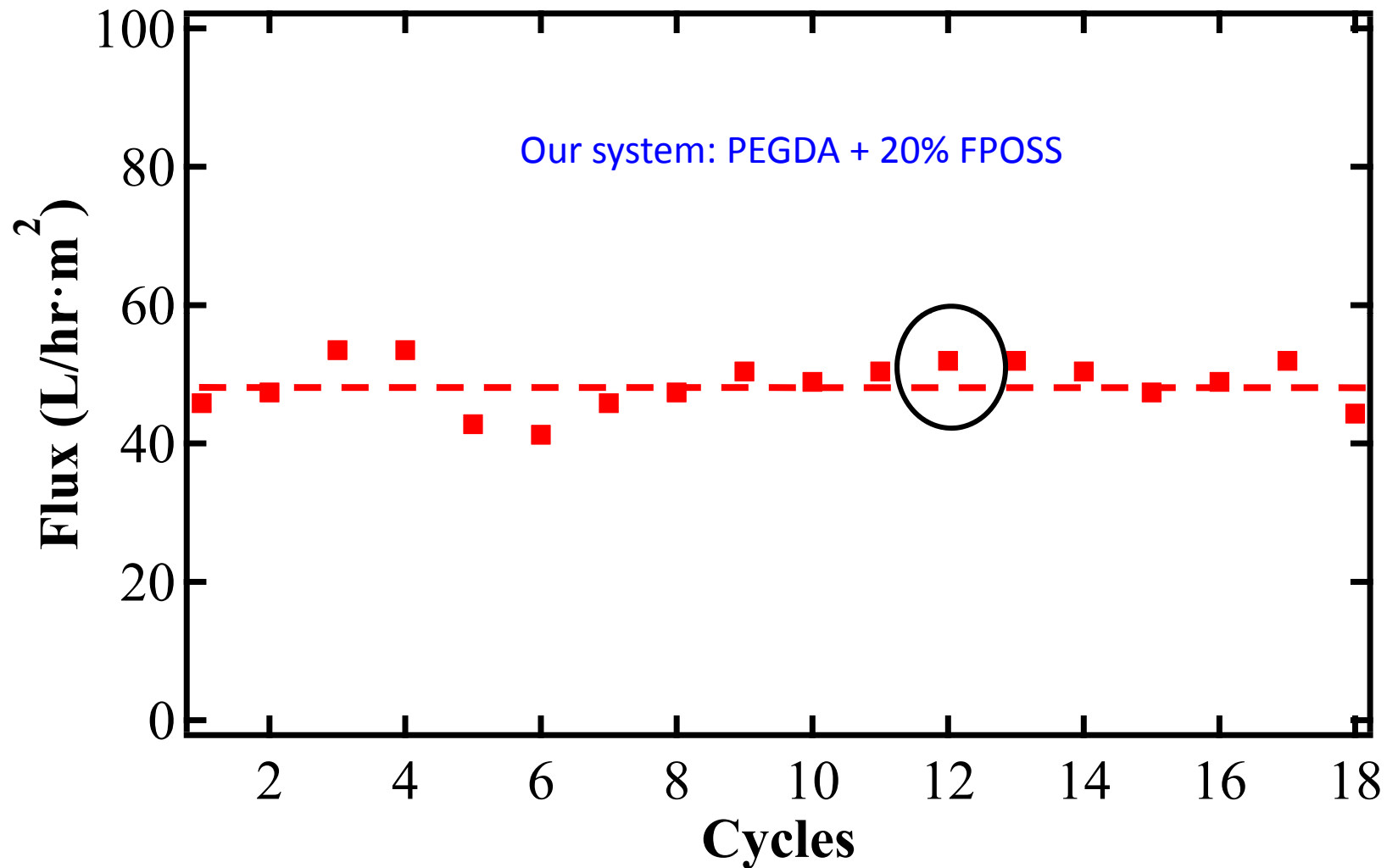
Oil-in-Water Emulsion

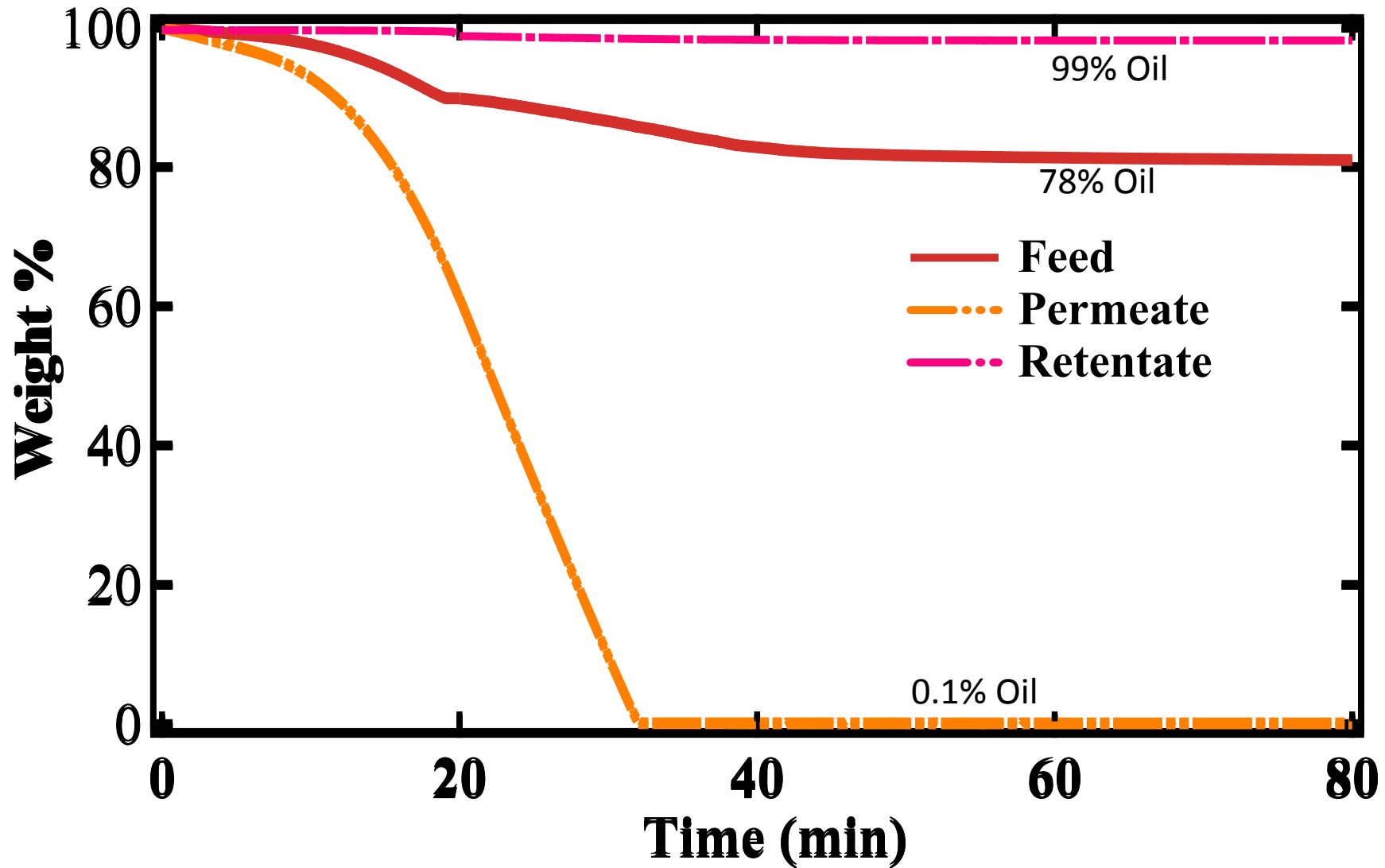


A simple, scalable, gravity-based system for the separation of both oil-in-water and water-in-oil emulsions. This is one of the first gravity-based systems to achieve such high emulsion separation efficiencies.

Manuscript in preparation

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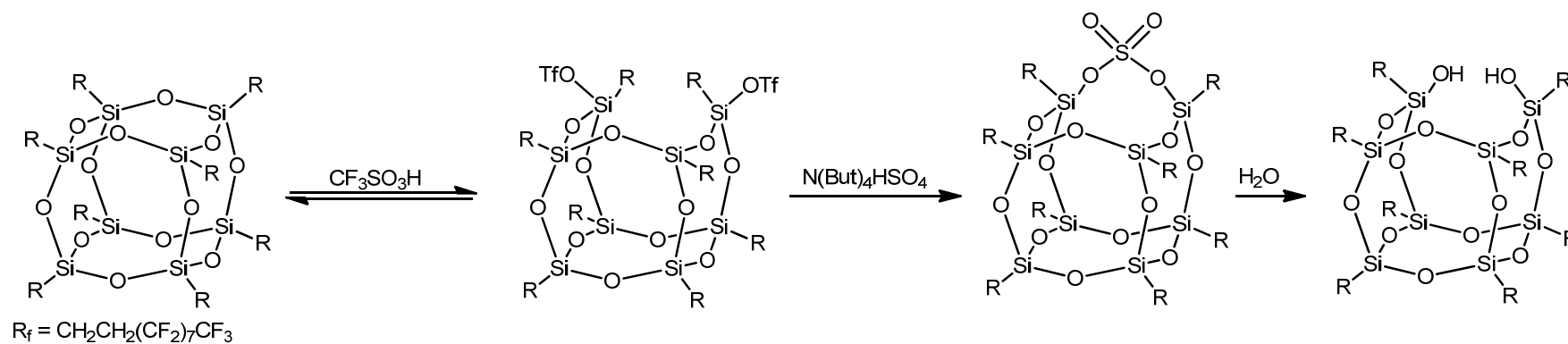


Manuscript in preparation

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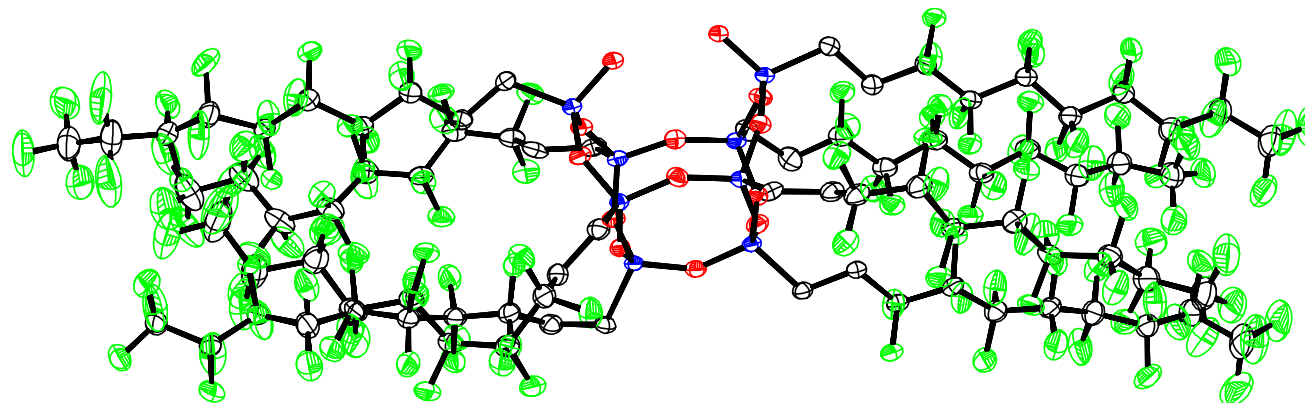
Incompletely Condensed Silsesquioxane



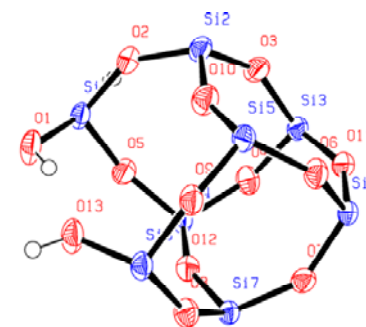
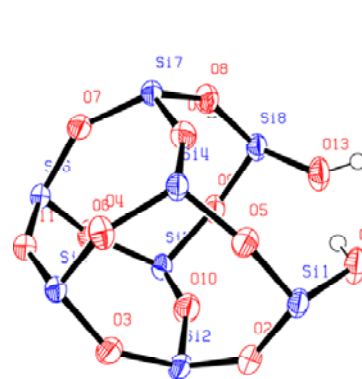
- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.*



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

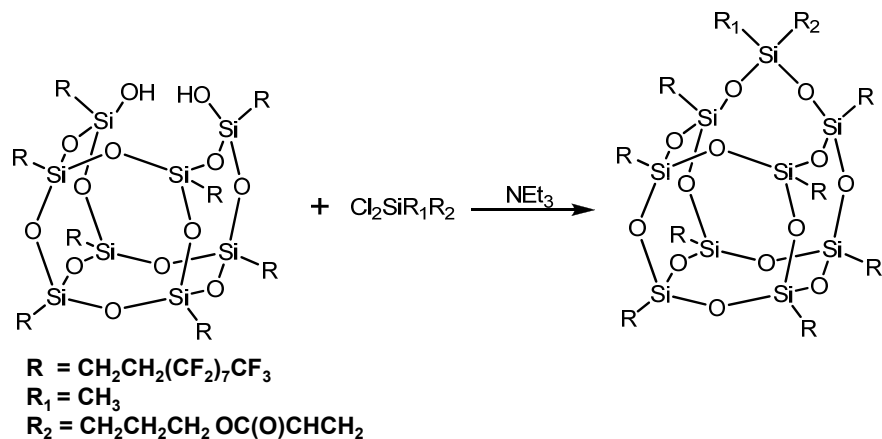


Ramirez, S. M.; Diaz, Y. J.; Campos, R.; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.*, **2011**, 133, 20084.

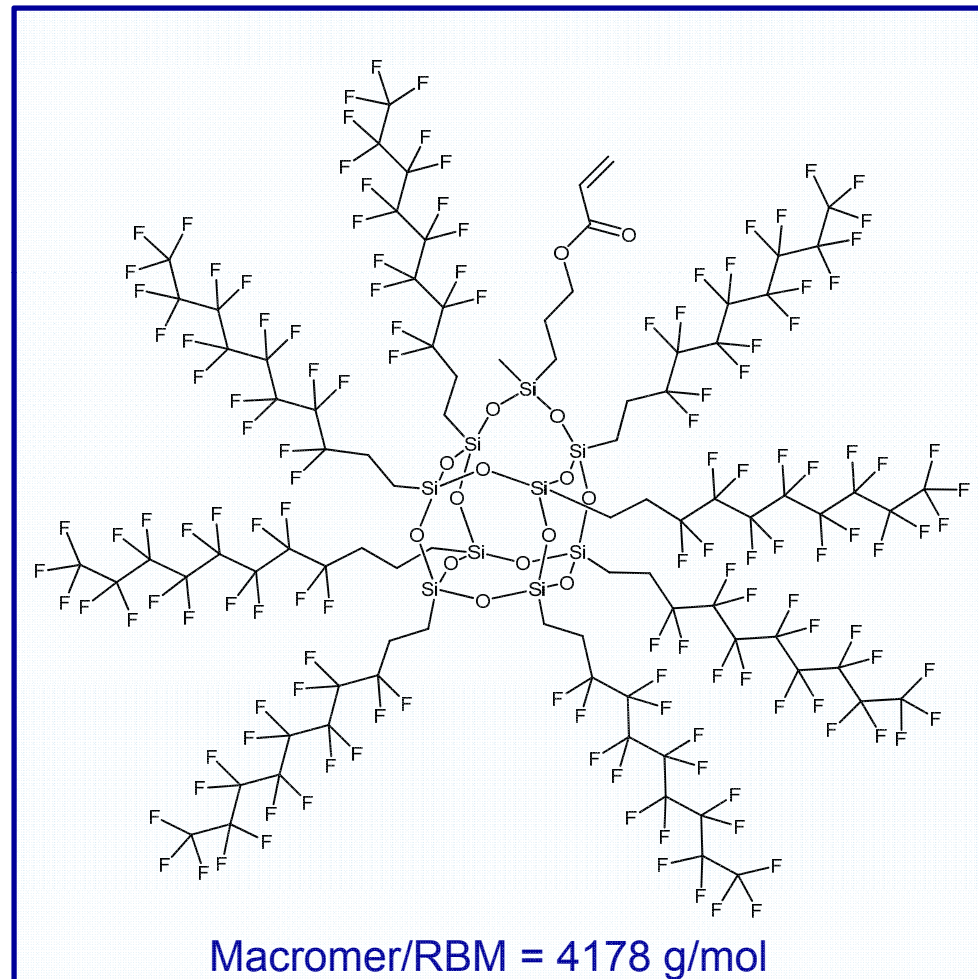
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Edge Capping Reactions

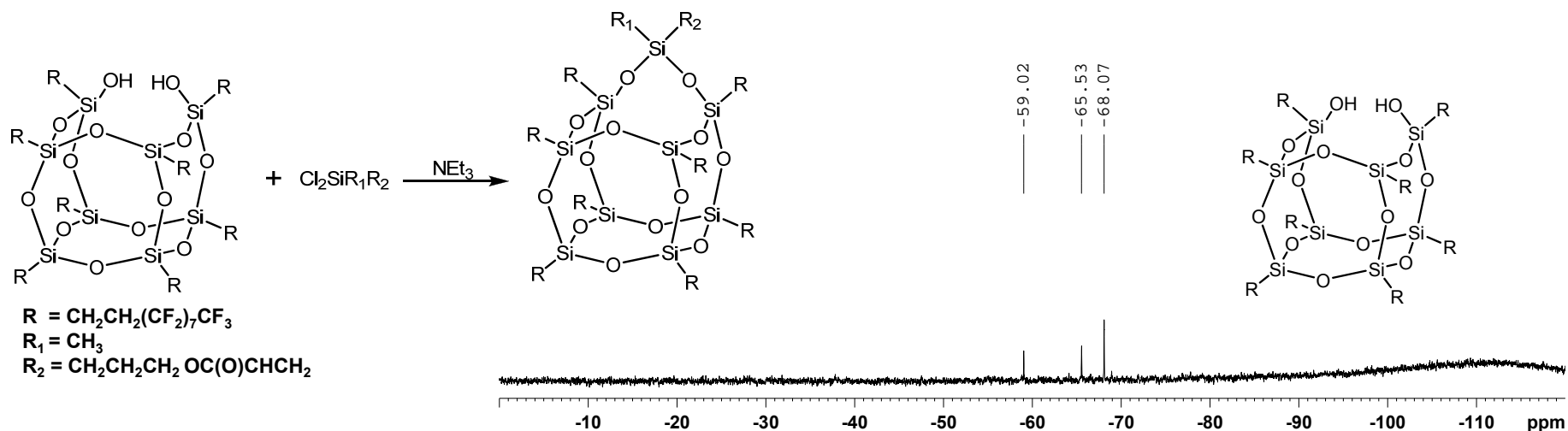


- Edge capping reactions typically have 40-70% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes

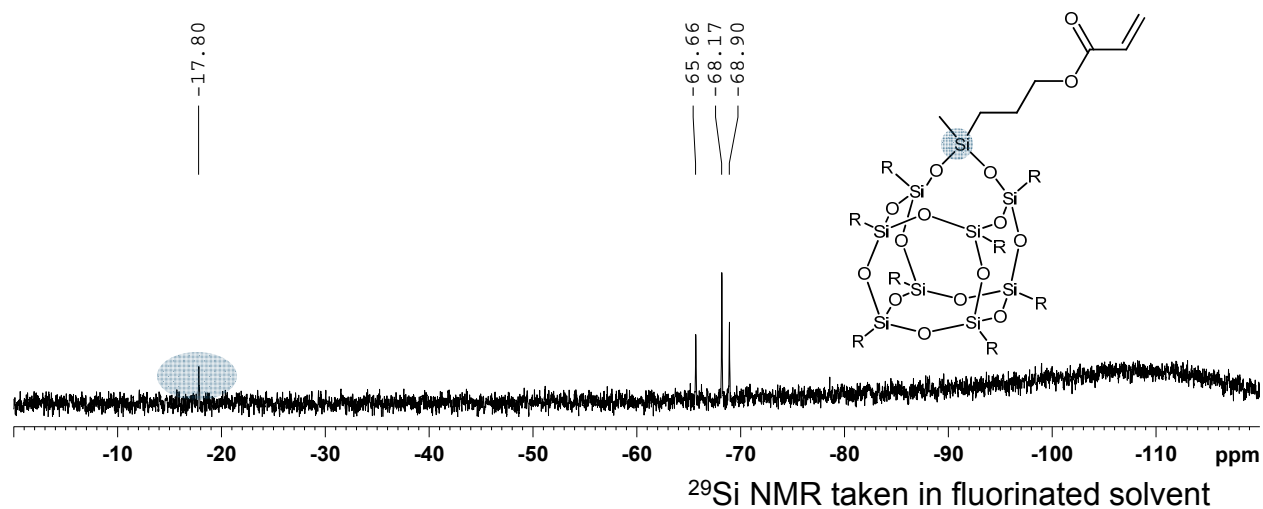




Edge Capping Reactions

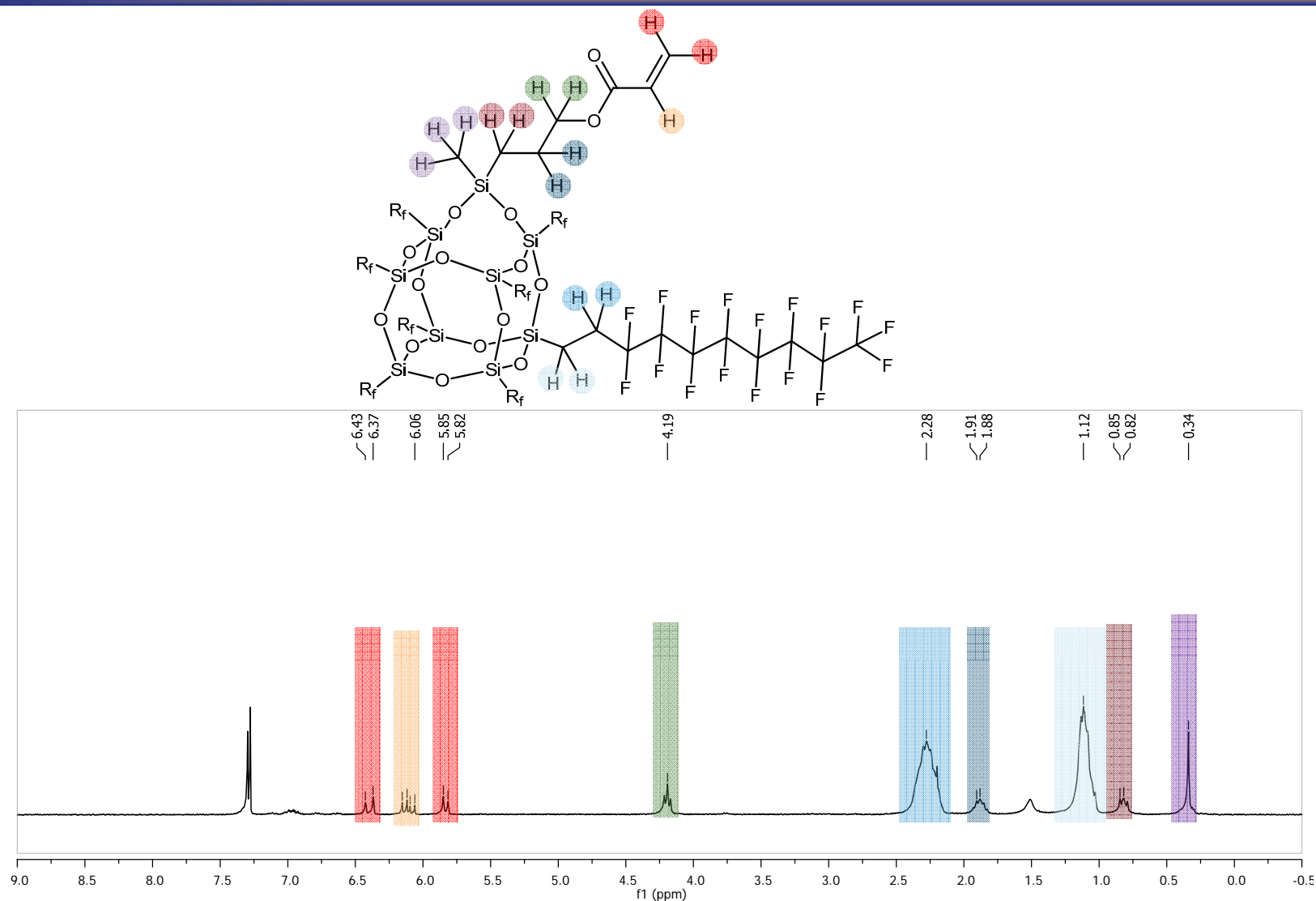


- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**





^1H NMR Characterization of Compounds

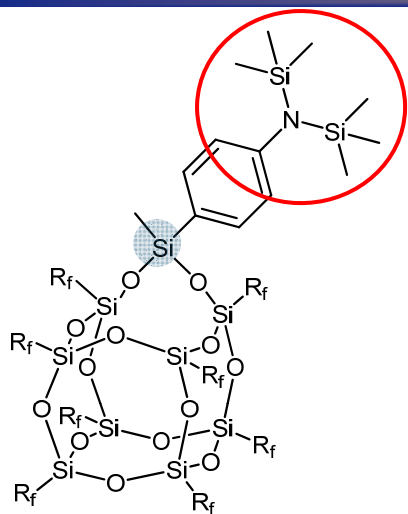


^{19}F NMR taken in diethyl ether. ^1H NMR taken in $\text{C}_6\text{F}_6/\text{CDCl}_3$ mixture.

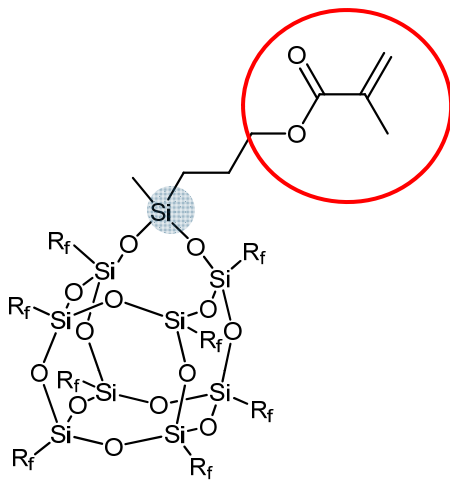
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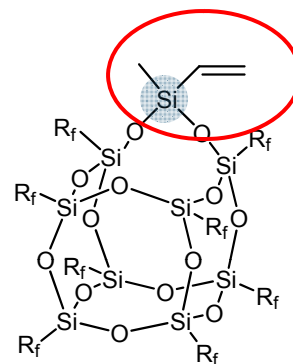
F-POSS Structures Synthesized



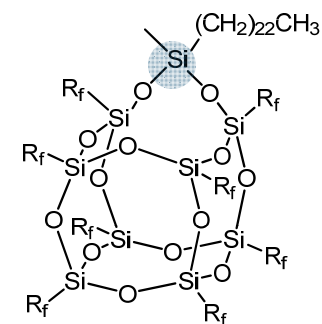
-29.5 ppm



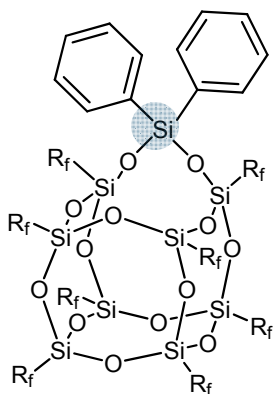
-17.8 ppm



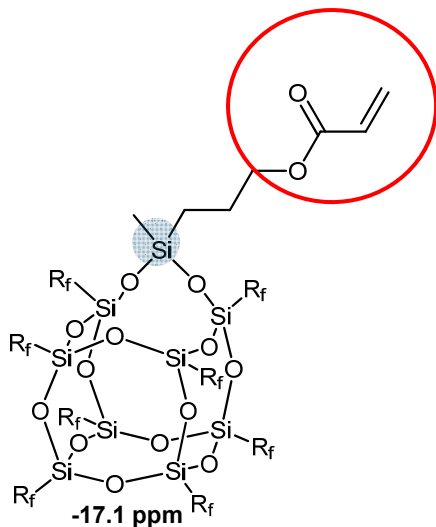
-32.1 ppm



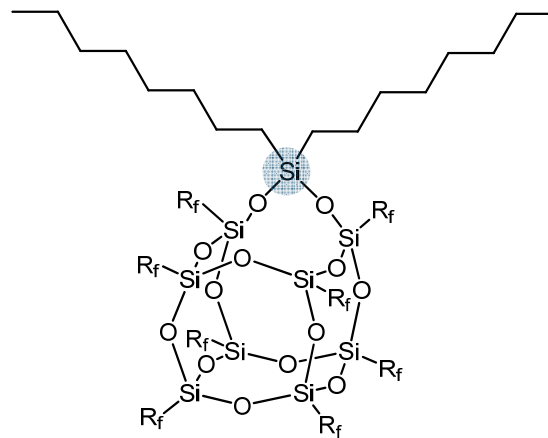
-17.8 ppm



-45.5 ppm



-17.1 ppm



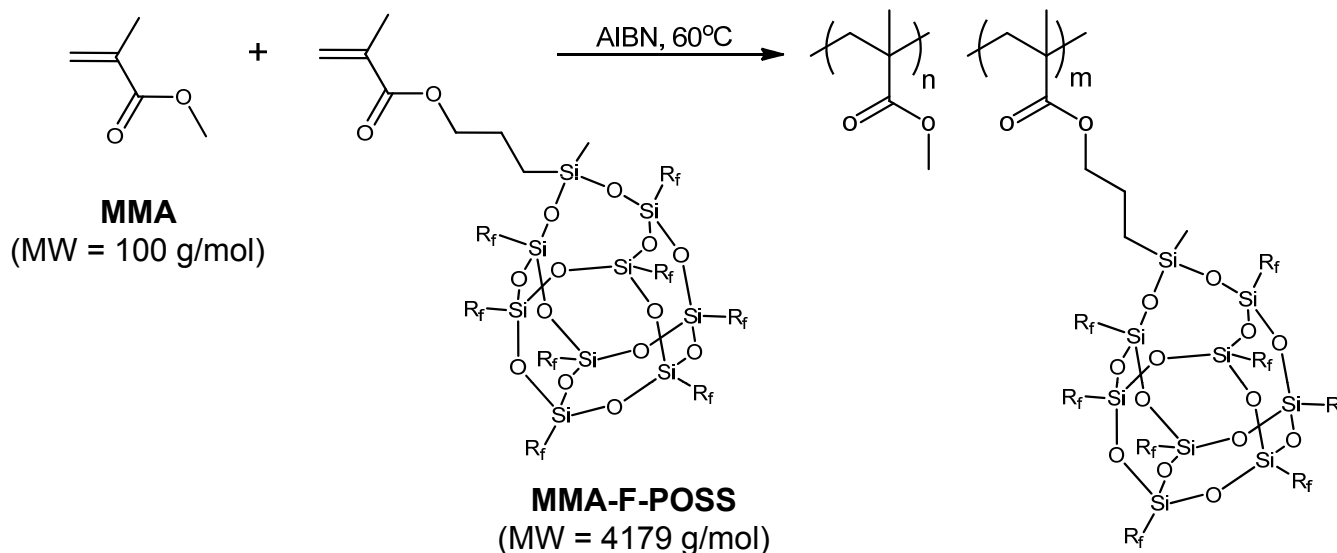
-17.9 ppm

R = CH₂CH₂(CF₂)₇CF₃

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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.



Summary



- **FluoroPOSS are superhydrophobic**
- **FluoroPOSS polymer composite surfaces can be superhydrophobic and superoleophobic**
- **Superhydrophilic and superoleophobic surfaces have been developed**
- **Such surfaces are ideal for the separation of both free-oil and oil-water emulsions**
- **These membranes, for the first time, allow continuous-flow oil-water emulsion separation**
- **Functionality will allow the covalent attachment of these low energy materials to substrates of choice**



Acknowledgements



Prof. Gareth McKinley & Bob Cohen
Superoleophobic Surfaces



Professor Anish Tuteja
Oil/Water Separation Membranes



Polymer Working Group
Fluorinated POSS

Financial Support



Air Force Office of Scientific Research



Air Force Research Laboratory, Propulsion Directorate



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Mr. Brian Moore
Dr. Joe Mabry
Mr. Kevin Lamison
Dr. Josiah Reams

Financial Support:

Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate



PWG Presentations



Who	What	When
Joe Mabry	Si Polymers & Composites	8:30
Andy Guenthner	Silicon Cyanate Esters	9:20
Sean Ramirez	F-POSS Disilanol	10:30
Anish Tuteja	Oil/water separation	10:55
Greg Yandek	Architecture effects on POSS	1:30



PWG Posters



Who

Andy Guenthner

Tim Haddad

Brian Moore

Dana Pinson

Patrick Ruth

Kevin Lamison

Vandana Vij

Yvonne Diaz

What

Solubility Parameters

POSS Dianilines

Architecture effects on solubility properties

Si-containing imide oligomers

Silica-Reinforced Fluoropolymers

Separation Membrane Breakthrough Pressure

Fluorinated silane modified perfluorooctynes

Incompletely-Condensed Fluorinated POSS

QUESTIONS?



U.S. AIR FORCE