Self Assembly of Ultrahydrophobic "Teflon®-Mimicking" Fluorinated (Polyhedral Oligomeric Silsesquioxanes) POSS Nano Columns

14th European Symposium on Fluorine Chemistry, Poznañ (Poland)

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Goal: Develop High Performance Polymers that REDEFINE material properties

15. SUBJECT TERMS

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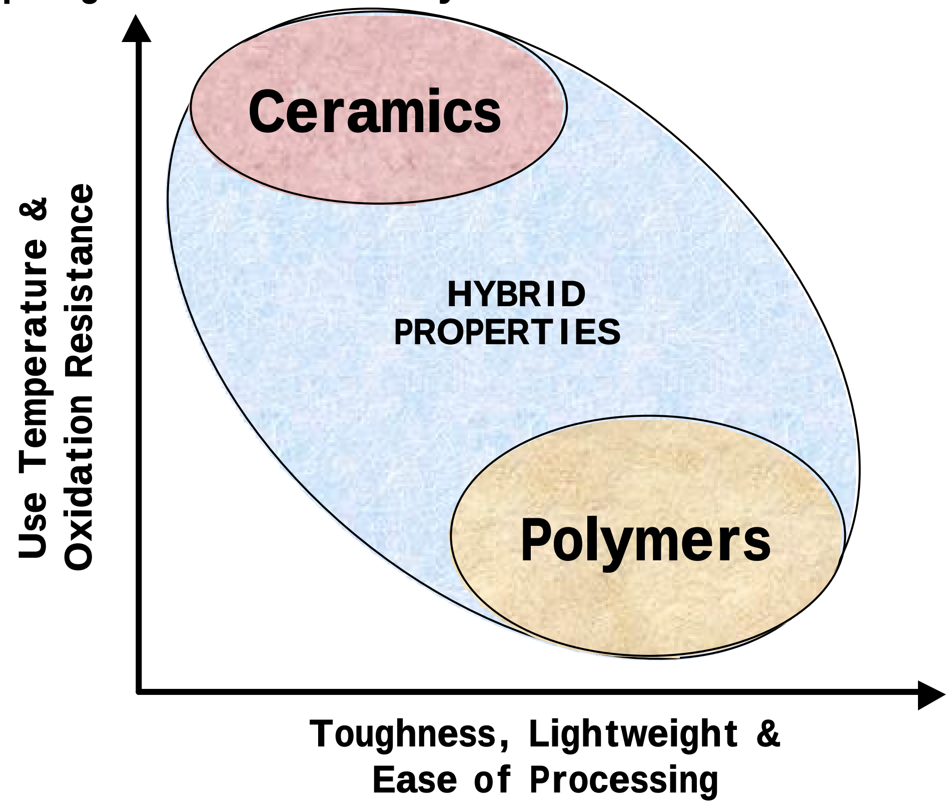
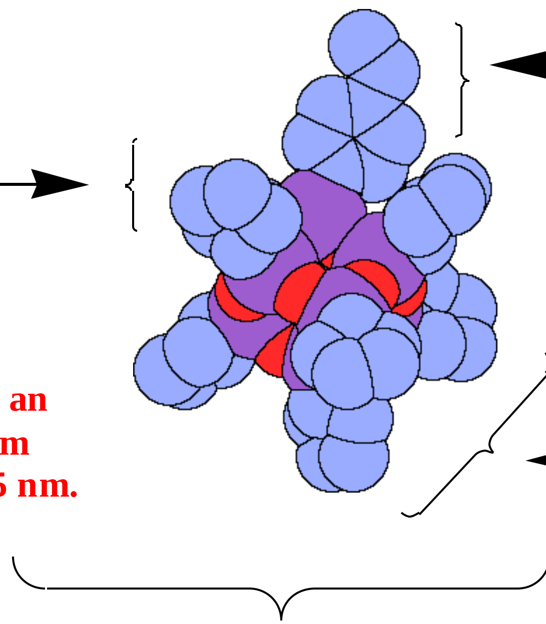
Hybrid Inorganic/Organic Polymers

Goal: Develop High Performance Polymers that REDEFINE material properties



- **Hybrid plastics bridge the differences between ceramics and polymers**

Anatomy of a POSS Nanostructure



Nonreactive organic (R) groups for solubilization and compatibilization.

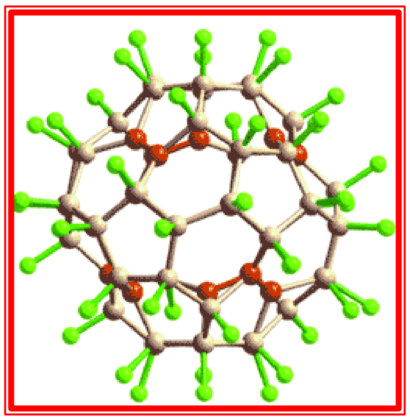
Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

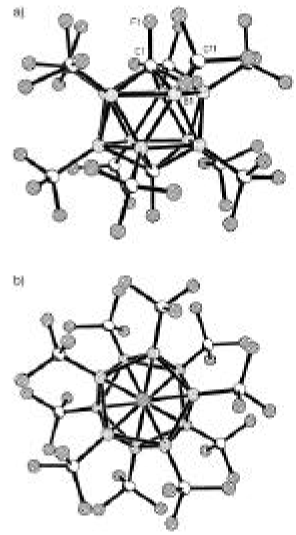
May possess one or more functional groups suitable for polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

Fluorinated Ball/Nanospheres





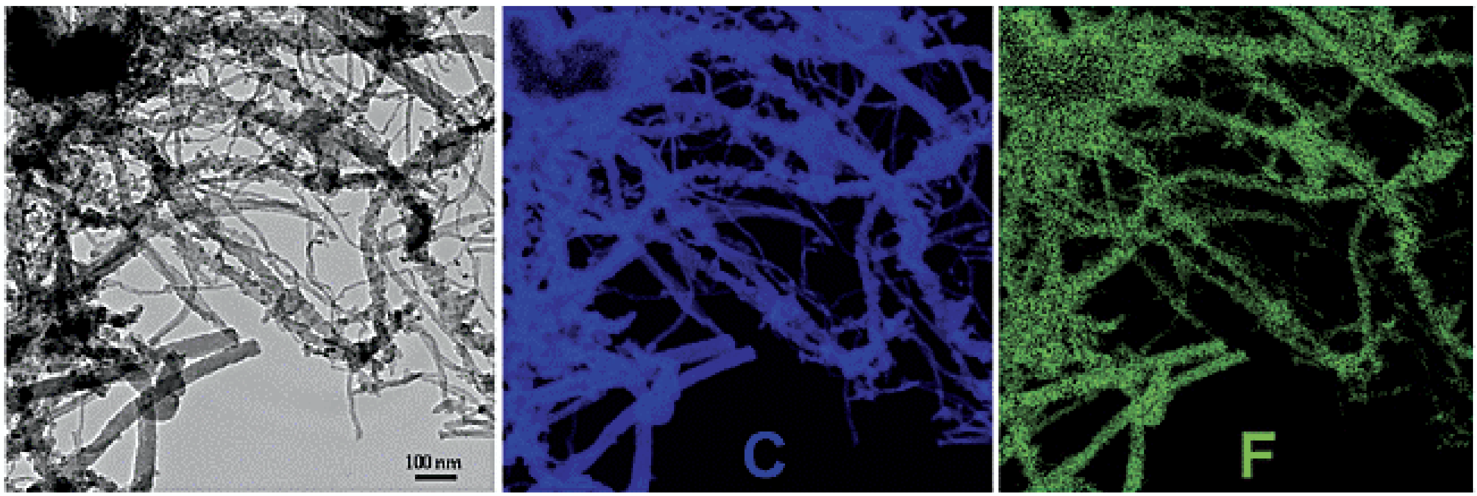
Fluorinated Fullerene ($C_{60}F_{48}$)

Perfluoro-deca-*B*-methyl-*para*-carborane

Troyanov, S. I.; Troshin, P. A.; Boltalina, O. V.; Ioffe, I. N.; Sidorov, L. N.; Kemnitz, E. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2285.

Herzog, A; Callahan, R. P.; MacDonald, C. L. B.; Lynch, V. M.; Hawthorne, M. F.; Lagow, R. J. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2121.

NanoTeflons



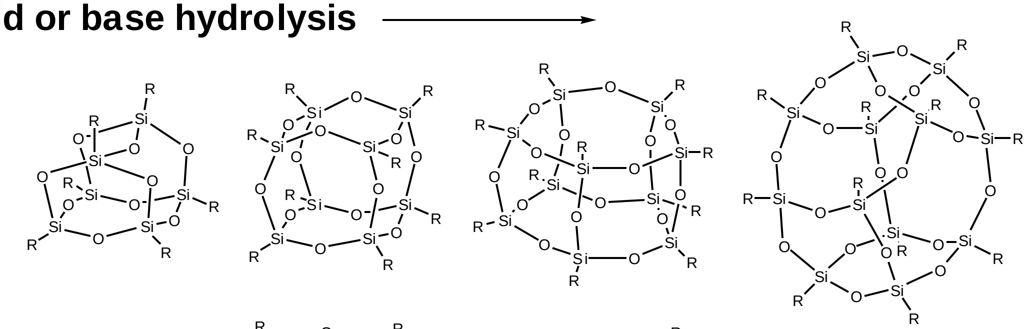
Fluorinated Carbon Nanotubes and Nanofibers

Hayashi, T.; Terrones, M.; Scheu, C.; Kim, Y. A.; Ruhle, M.; Nakajima, T.; Endo, M.
Nano Lett. **2002**, *2*, 491.

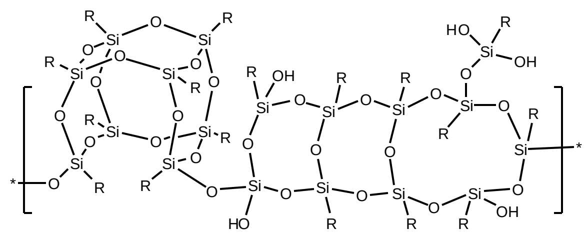
POSS Synthesis

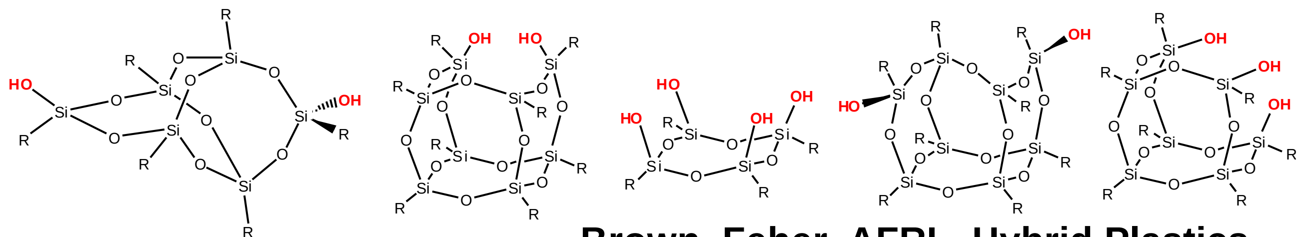
$RSiX_3$ acid or base hydrolysis →

Blendables



Resin

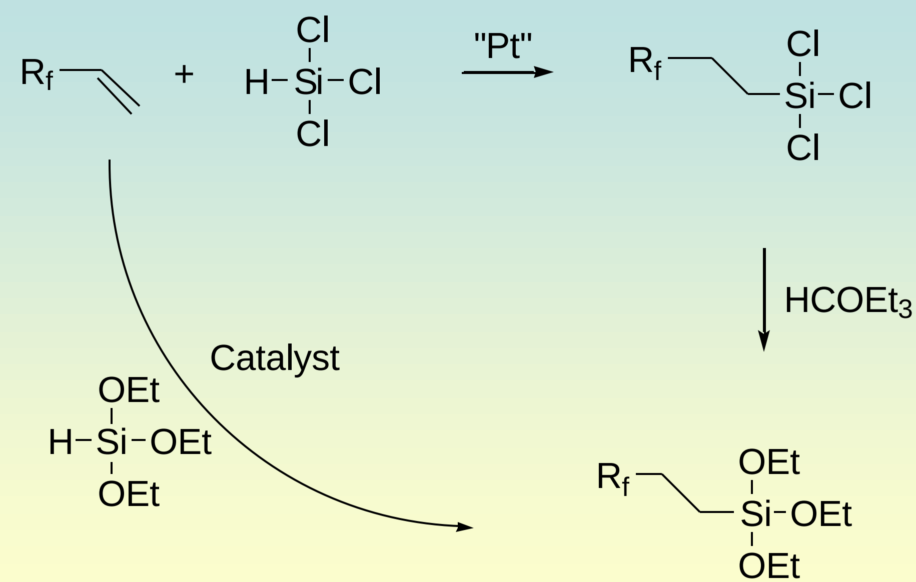




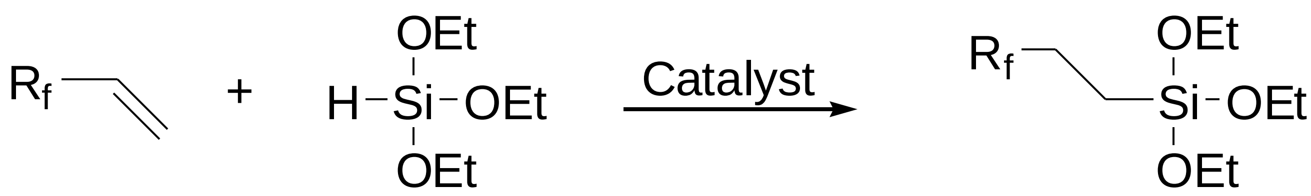
Incompletely condensed cages

Brown, Feher, AFRL, Hybrid Plastics

Synthesis using hydrosilylation



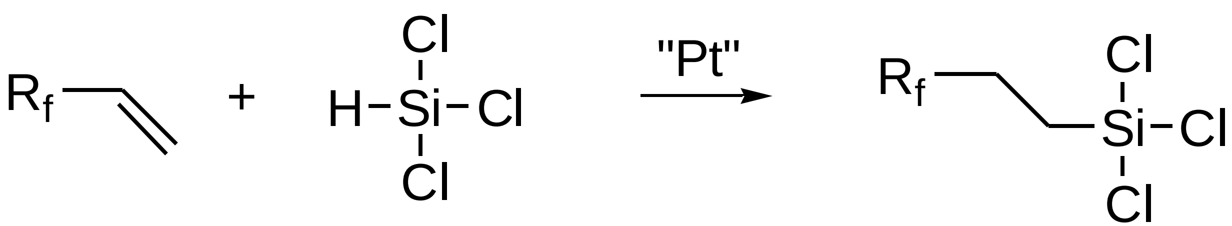
Hydrosilylation



Catalyst		Result
Karstedt (Pt)		No Reaction
H_2PtCl_6		No Reaction
$RuH_2(CO)(PPh_3)_3$		< 50% Yield
$RhCl(PPh_3)_3$		~ 50% Yield

Yield based on methylene to vinyl proton ratio in ^{1}H NMR.

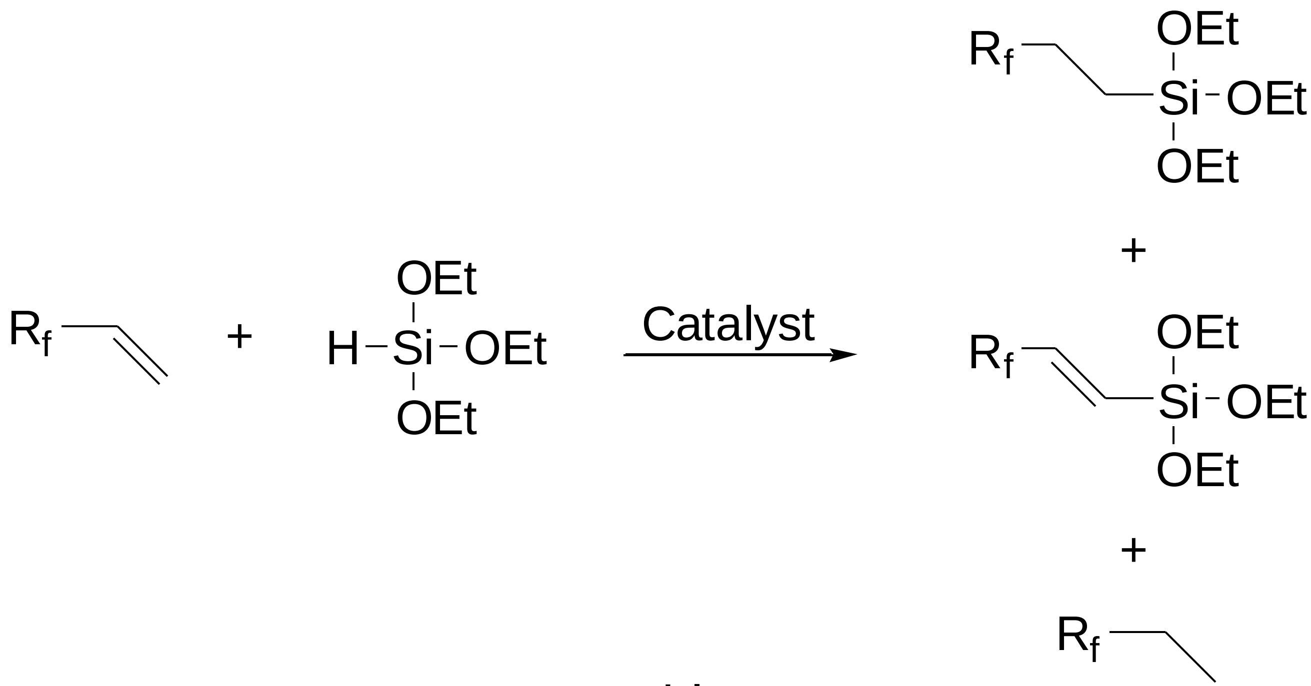
Hydrosilylation



Yield based on methylene to vinyl proton ratio in ^{1}H NMR.

H_2PtCl_6 produces quantitative yield at high temperatures with long reaction times in pressure vessel.

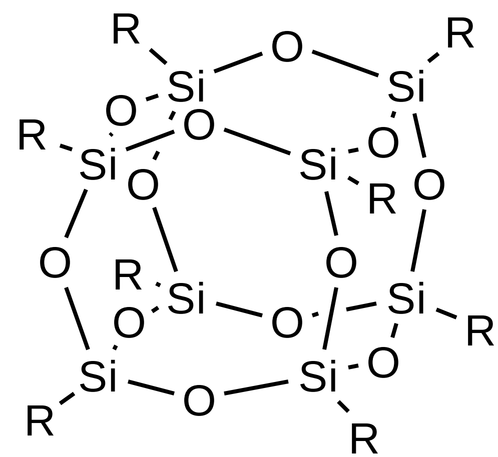
Side Reaction



Problem:
Dehydrogenative silylation product also gives vinyl peaks in ^{1}H NMR spectra

FluoroPOSS Synthesis

$$R_fSiX_3 \xrightarrow[\text{solvent}]{OH^- / H_2O}$$

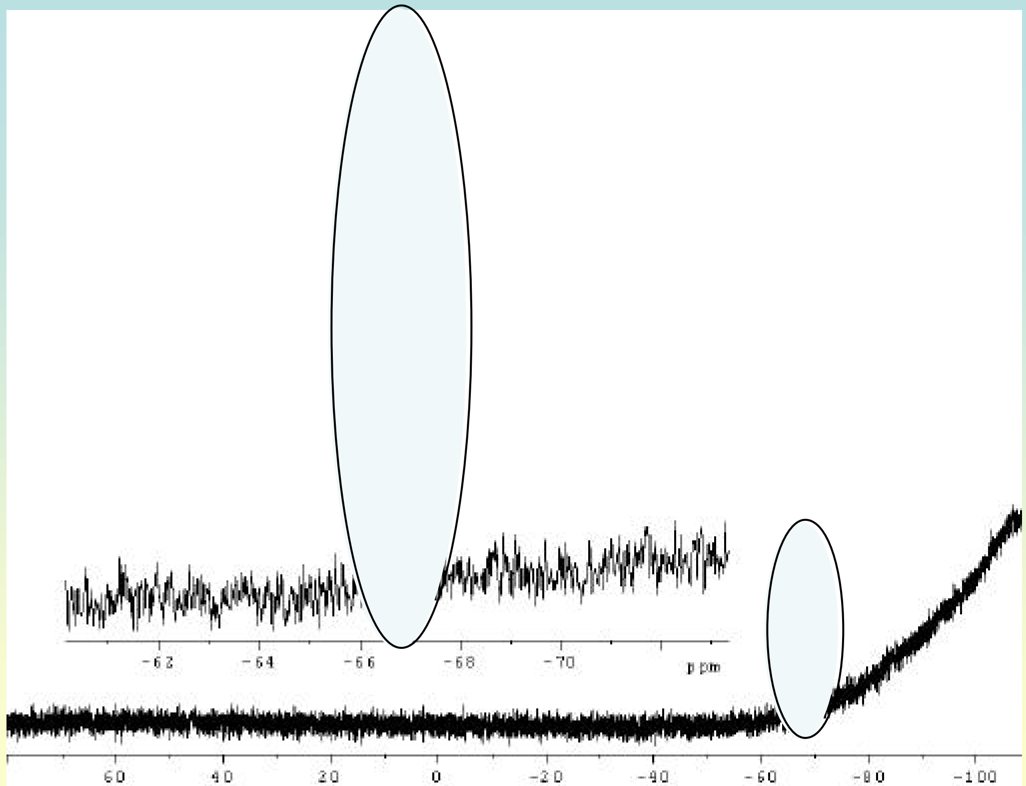


$R_{f8}T_8$

R_f = $-CH_2CH_2(CF_2)_nCF_3$
n = 3,5,7

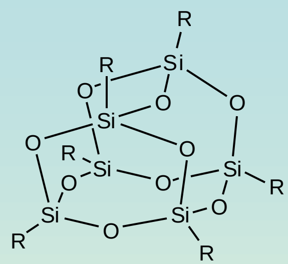
Cage mixtures can also be obtained by modifying solvent systems.

^{29}Si NMR of $Fluorodecyl_8T_8$



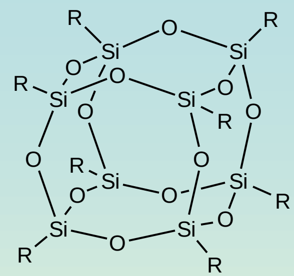
100% $Fluorodecyl_8T_8$

Isomers of Fluorodecyl$_n$T$_n$

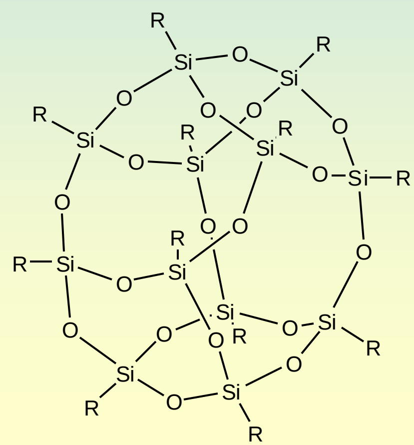


T_6 (~5%)

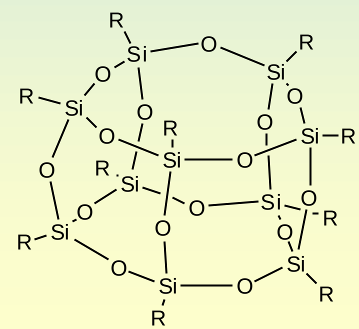
R = $-CH_2CH_2(CF_2)_7CF_3$



T_8 (~91%)
MW = 3993.54



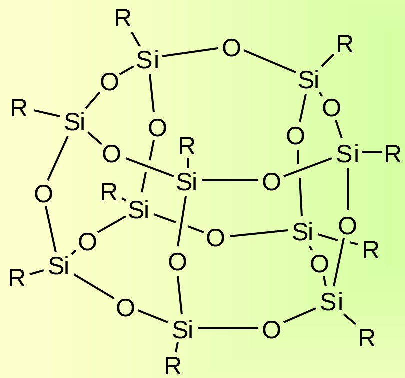
T_{12} (~3%)



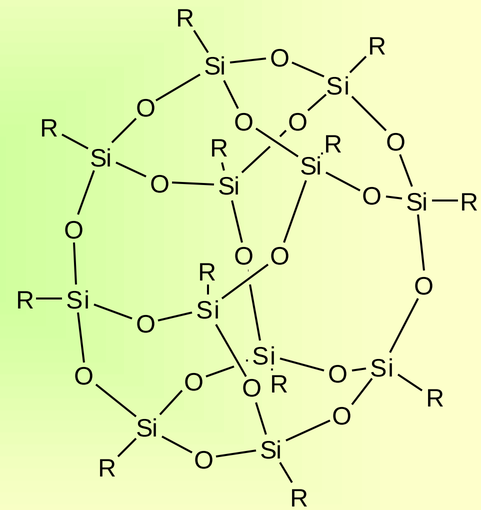
T_{10} (~1%)

3,3,3-Trifluoropropyl$_n$T$_n$

R = $-CH_2CH_2CF_3$

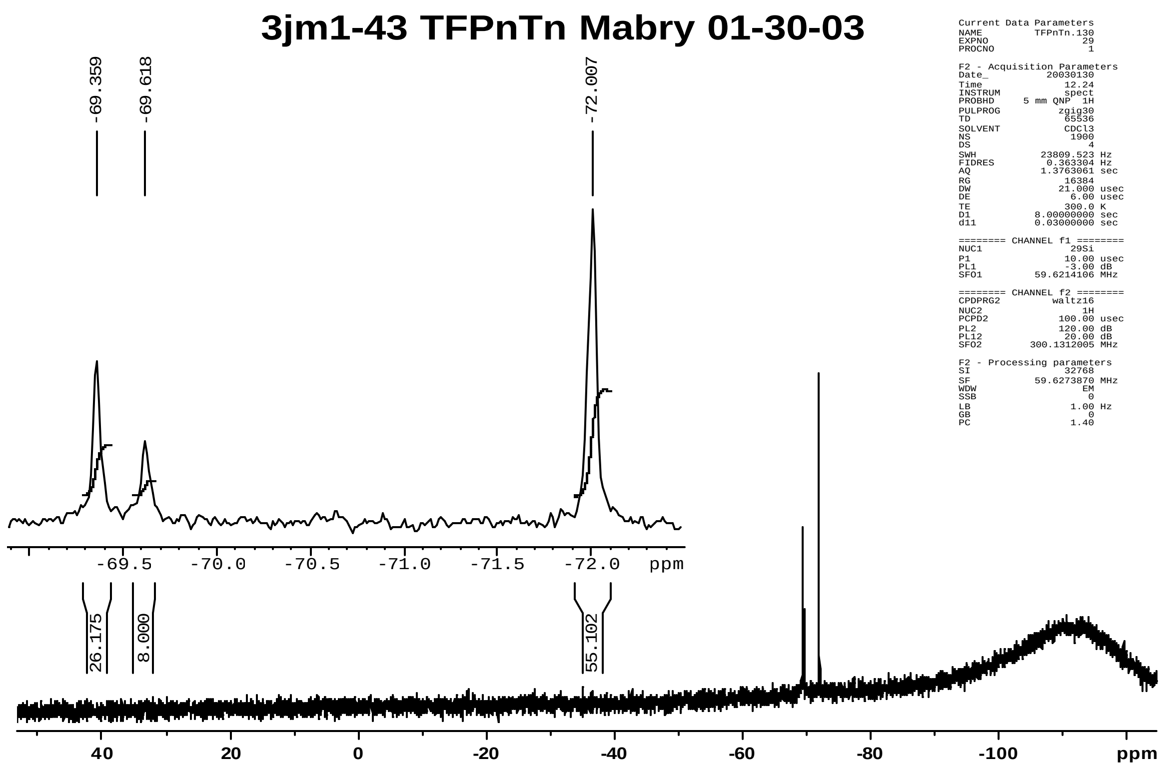


T_{10} (~11%)

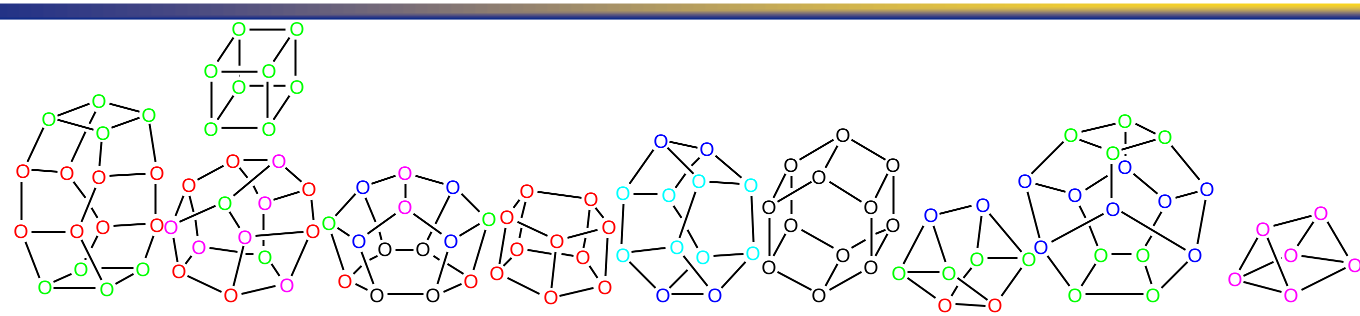


T_{12} (~89%)

3,3,3-Trifluoropropyl$_n$T$_n$

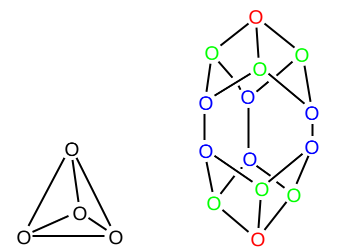


Relative energy per silicon atom (kcal/mol) for the H_nT_n series



D_{2d}-T_{16} unknown	D_{3h}-T_{14} O_h-T_8	C_{2v}-T_{14}	D_{5h}-T_{10}	D_{2d}-T_{12}	D_{6h}-T_{12} unknown	C_{2v}-T_8 unknown	D_{4d}-T_{16}	D_{3h}-T_6
-7.5	-7.3	-7.2	-7.1	-7.0	-6.9	-6.7	-6.6	-6.0

← Increasing Stability

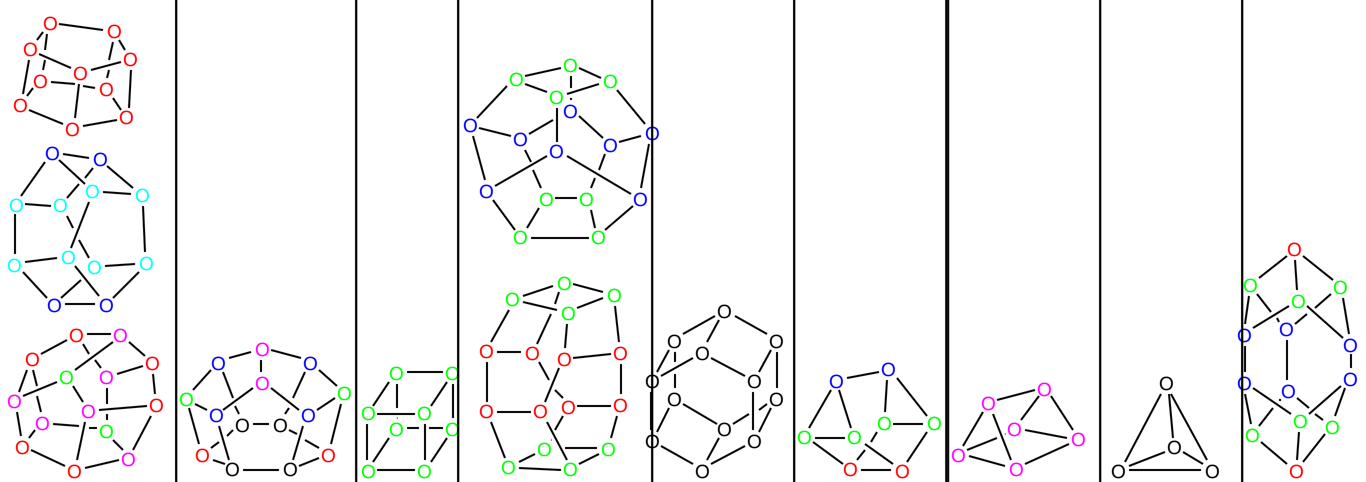


T_d-T_4
unknown
0.0

D_{3h}-T_{14}
unknown
+18.4 ???

For H_nT_n polyhedra
Pandey: J. Phys. Chem., 1998, 8704.

Relative energy per silicon atom (kcal/mol) for the Methyl$_n$T$_n$ series



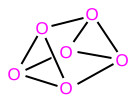
D_{5h}-T$_{10}$ D_{2d}-T$_{12}$ D_{3h}-T$_{14}$	C_{2v}-T$_{14}$	O_h-T$_8$	D_{4d}-T$_{16}$ D_{2d}-T$_{16}$ unknown	D_{6h}-T$_{12}$ unknown	C_{2v}-T$_8$ unknown	D_{3h}-T$_6$	T_d-T$_4$ unknown	D_{3h}-T$_{14}$ unknown
-8.1	-7.9	-7.8	-7.7	-7.5	-7.4	-6.7	0	+19.1

← Increasing Stability

For Me$_n$T$_n$ polyhedra Pandey: J. Phys. Chem., 2002, 1709.

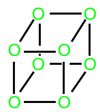
T_{18}

There are **9** possible T_{18}'s. **10 - 12** isomers are seen by GC-MS



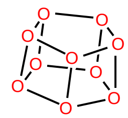
D_{3h}-T_6

6 - (3,4,4)



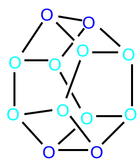
O_h-T_8

8 - (4,4,4)



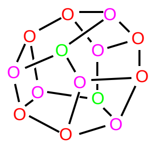
D_{5h}-T_{10}

10 - (4,4,5)



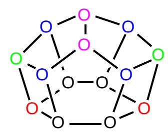
D_{2d}-T_{12}

4 - (4,4,5)
8 - (4,5,5)



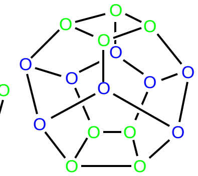
D_{3h}-T_{14}

6 - (4,5,5)
6 - (4,5,5)
2 - (5,5,5)



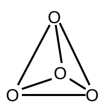
C_{2v}-T_{14}

2 - (4,4,6)
2 - (4,4,5)
4 - (4,5,6)
4 - (4,5,5)
2 - (5,5,5)



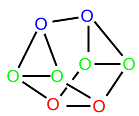
D_{4d}-T_{16}

8 - (4,5,5)
8 - (5,5,5)



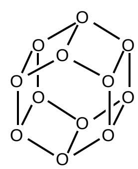
T_d-T_4
unknown

4 - (3,4,4)



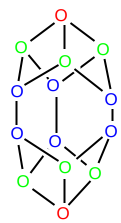
C_{2v}-T_8
unknown

2 - (3,5,5)
4 - (3,4,5)
2 - (4,4,5)



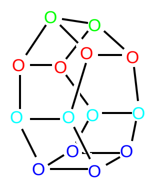
D_{6h}-T_{12}
unknown

12 - (4,4,6)



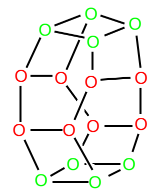
D_{3h}-T_{14}
unknown

2 - (4,4,4)
6 - (4,4,6)
6 - (4,6,6)



C_{2v}-T_{14}
unknown

4 - (4,4,6)
2 - (4,4,5)
4 - (4,5,6)
4 - (4,5,6)

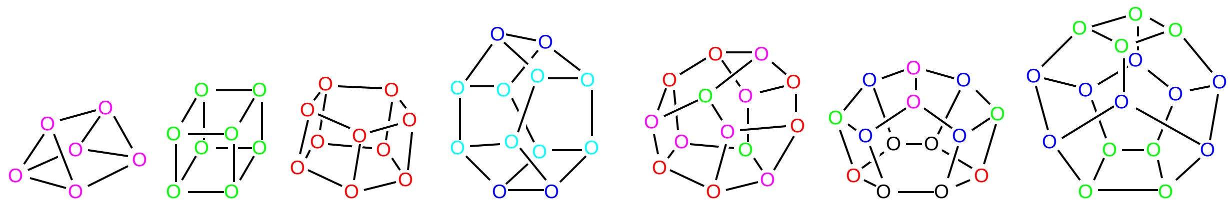


D_{2d}-T_{16}
unknown

8 - (4,4,5)
8 - (4,6,6)

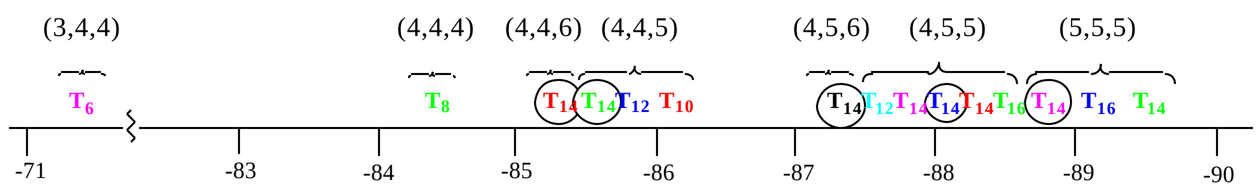
^{29}Si NMR of H_nT_n:

The assignment for the T_{16} is likely but not definitive. The T_6 is unknown.

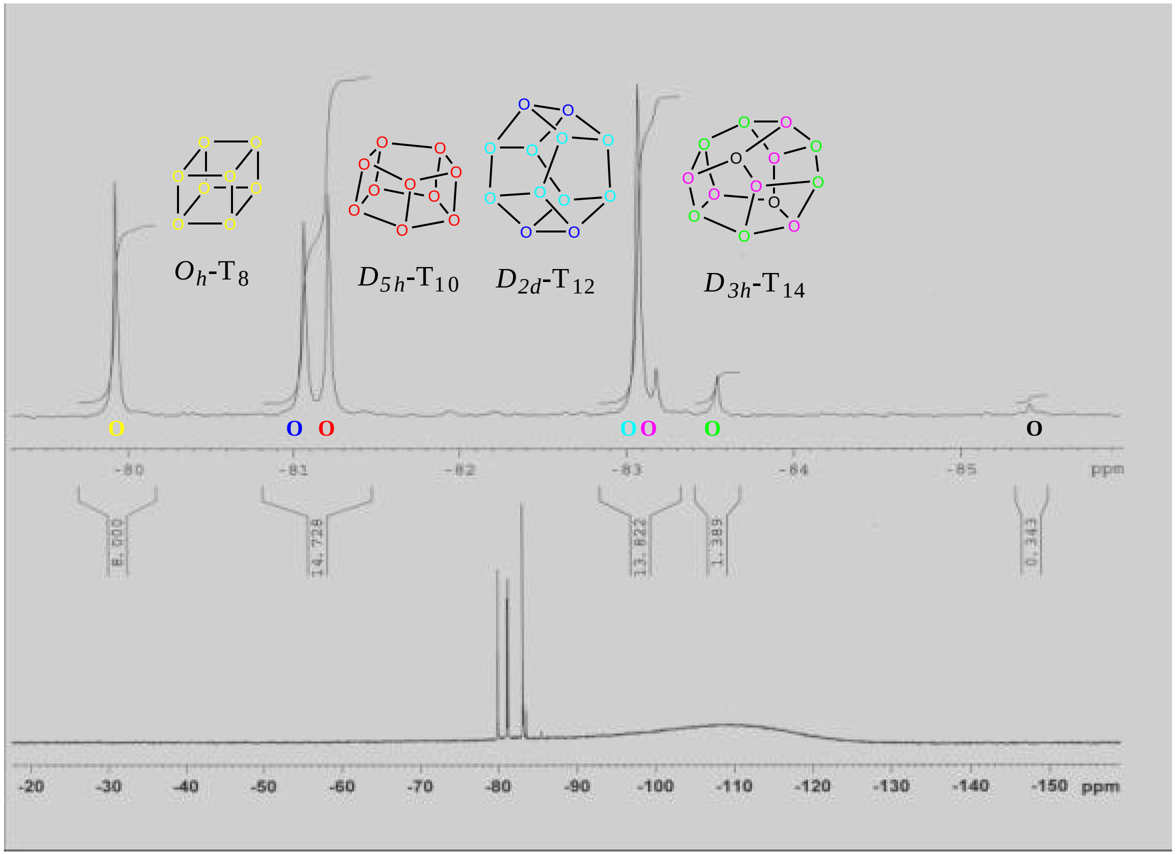


D_{3h}-T_6	O_h-T_8	D_{5h}-T_{10}	D_{2d}-T_{12}	D_{3h}-T_{14}	C_{2v}-T_{14}	D_{4d}-T_{16}
6 - (3,4,4) predict -72.5	8 - (4,4,4) -84.45	10 - (4,4,5) -86.26	4 - (4,4,5) -85.78	6 - (4,5,5) -87.89	2 - (4,4,6) -85.35	8 - (4,5,5) -88.10
			8 - (4,5,5) -87.76	6 - (4,5,5) -88.03	2 - (4,4,5) -85.76	8 - (5,5,5) -89.27
				2 - (5,5,5) -89.71	4 - (4,5,6) -87.68	
					4 - (4,5,5) -87.95	
					2 - (5,5,5) -88.72	

Agaskar: Inorg. Chim. Acta. Vol 229, 1995, p.355.



^{29}Si NMR Spectrum of Hybrids Vi_nT_n mixture

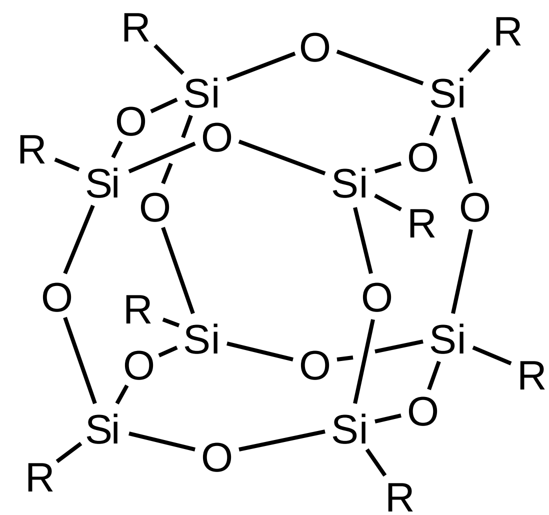


Fluorodecyl$_8$T$_8$

R = $-CH_2CH_2(CF_2)_7CF_3$

M_W = 3993.54 g/mol
ρ = 1.95 g/mL (powder)

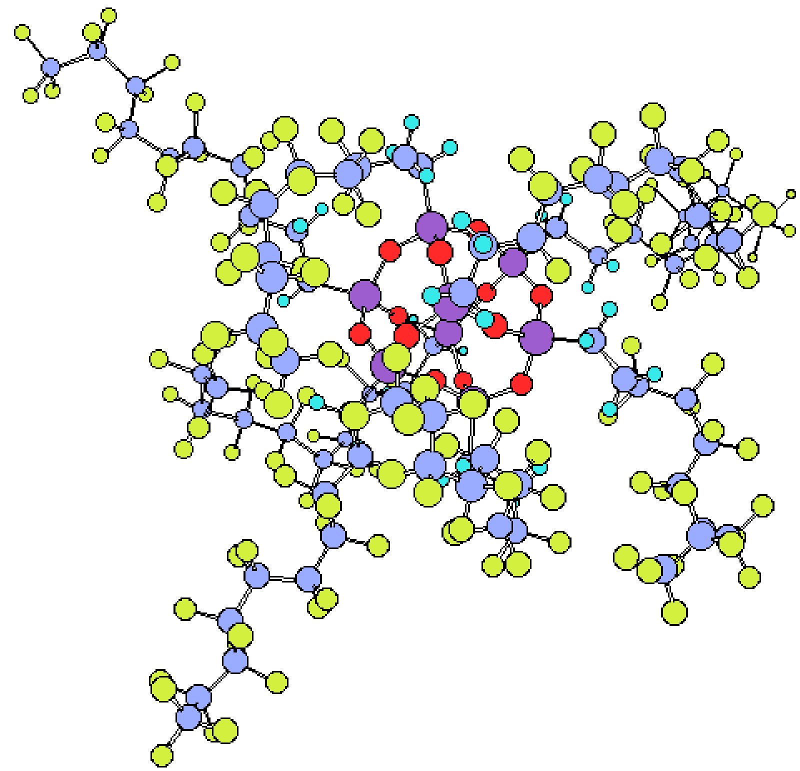
($-C_{10}H_4F_{17}$ = Fluorodecyl)



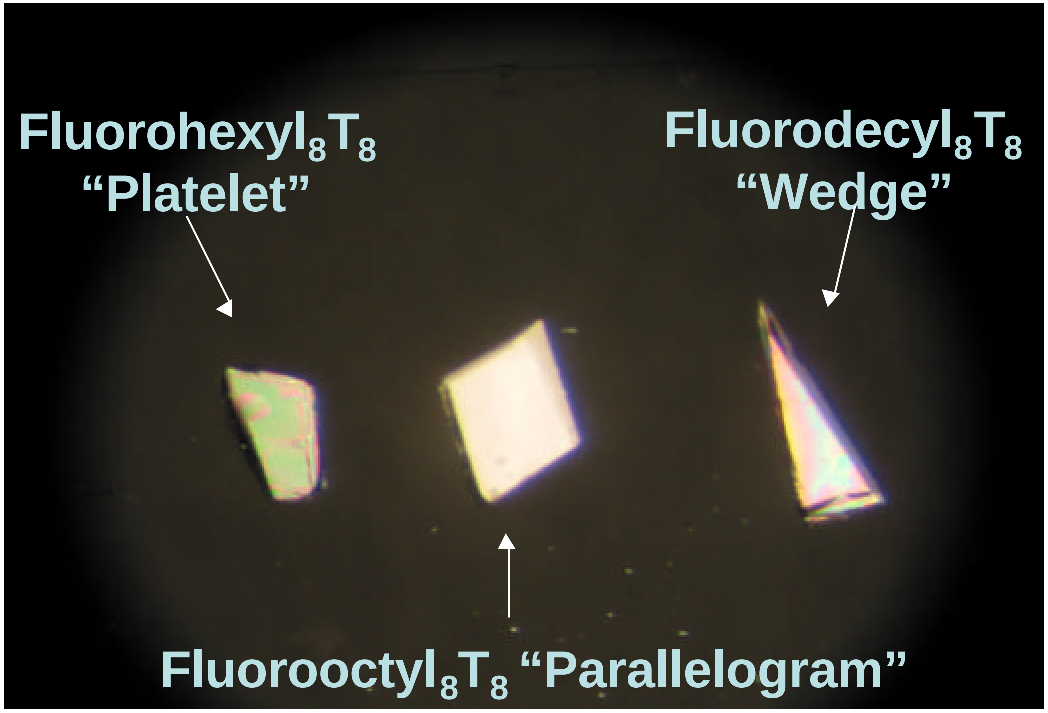
T$_8$

Cage mixtures can also be obtained by modifying solvent systems.

Gas Phase Model of Fluorodecyl$_8$T$_8$

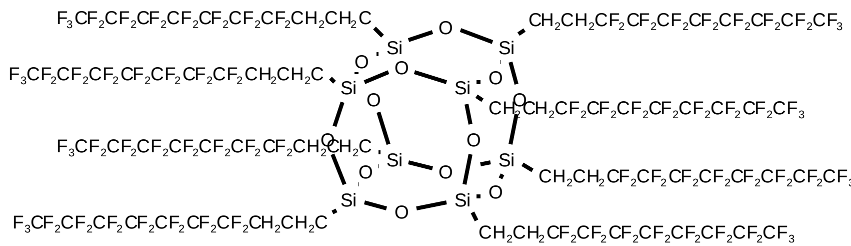


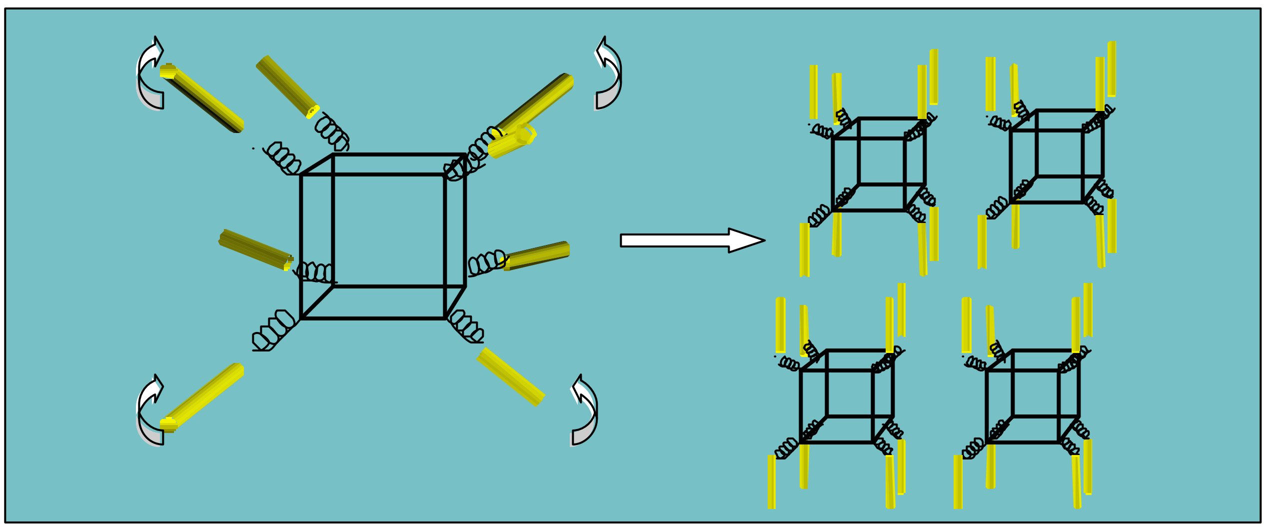
FluoroPOSS Crystals



FluoroPOSS compounds crystallize in distinctly different shapes. All structures are triclinic.

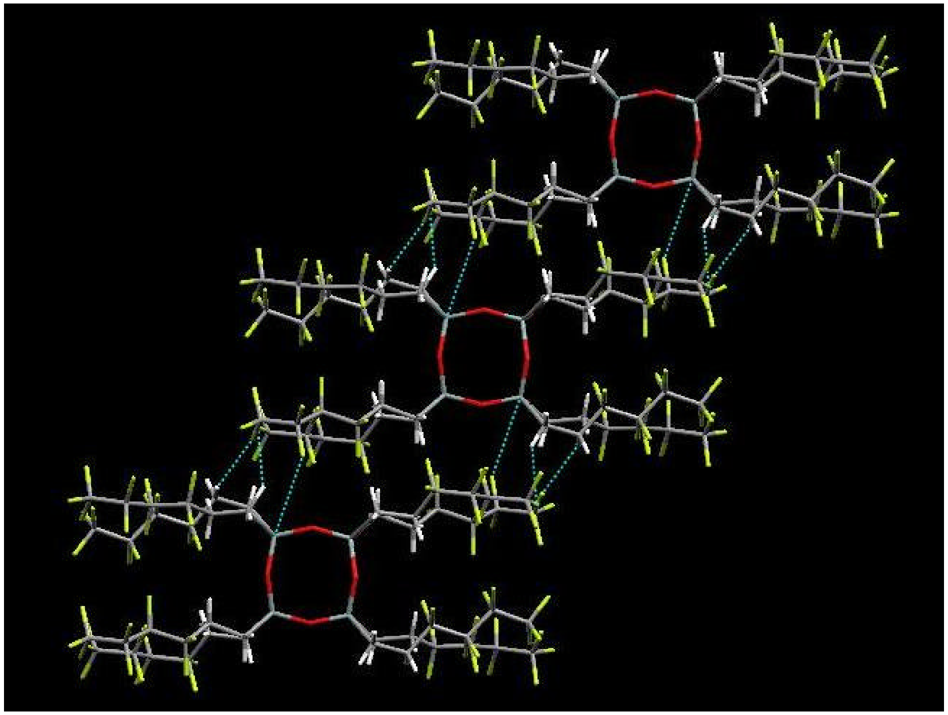
Crystal Packing





Rigid chains may be expected to extend out in all directions.

Fluorohexyl$_8$T$_8$

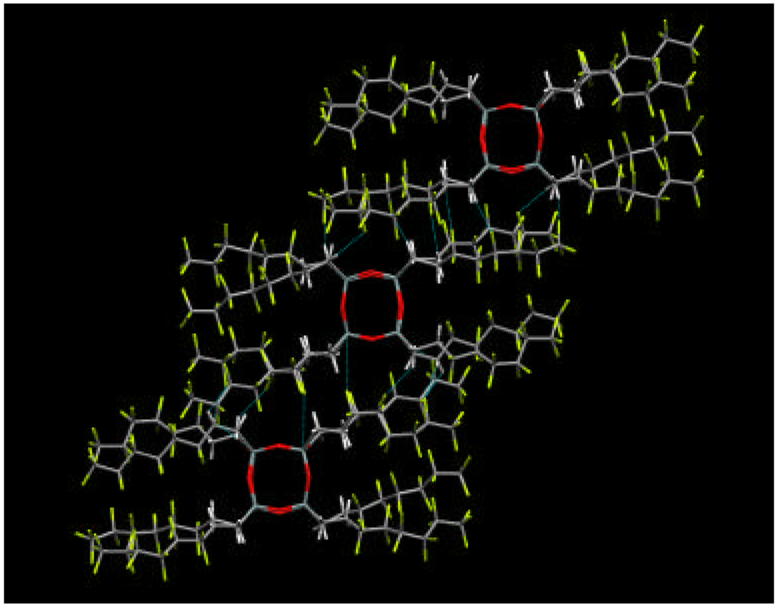


ρ **= 1.98 g/mL**

M$_w$ = 2393.33 g/mol

- Both H-F and Si-F contacts lead to the increased packing efficiency.
- Si atoms in POSS cage line up with fluorine atoms on 5th and 6th carbons in adjacent POSS fluorohexyl chains.

Fluorooctyl$_8$T$_8$

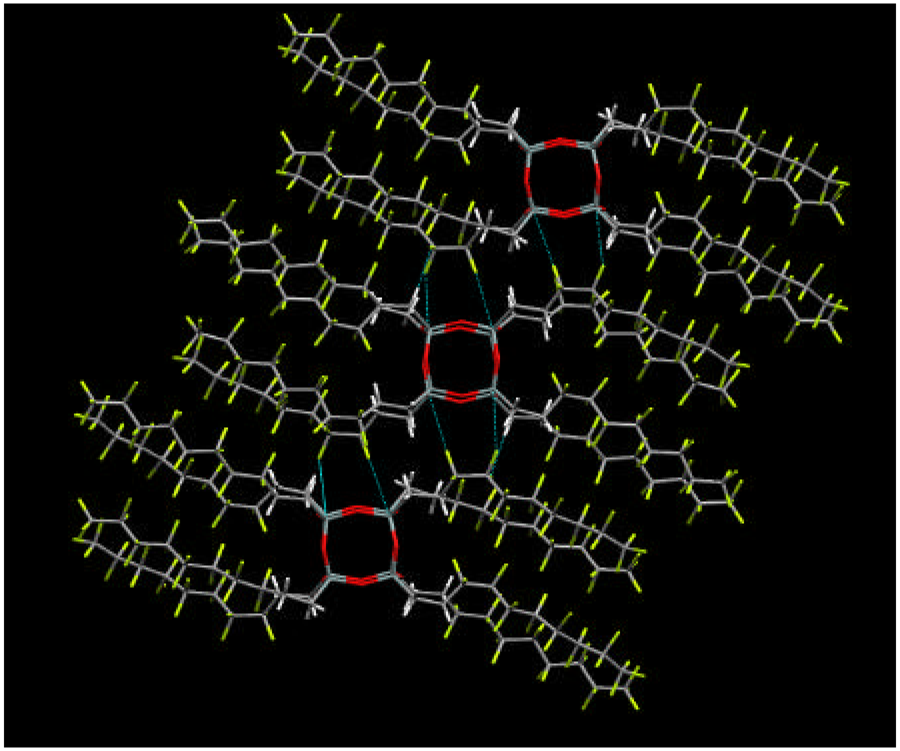


ρ = 2.05 g/mL

M_w = 3193.45 g/mol

- Longer fluorooctyl chain allows additional H-F contacts on each side of POSS cage.
- Si atoms also line up with fluorine atoms on 5th and 6th carbons in adjacent fluorooctyl chains.

Fluorodecyl$_8$T$_8$



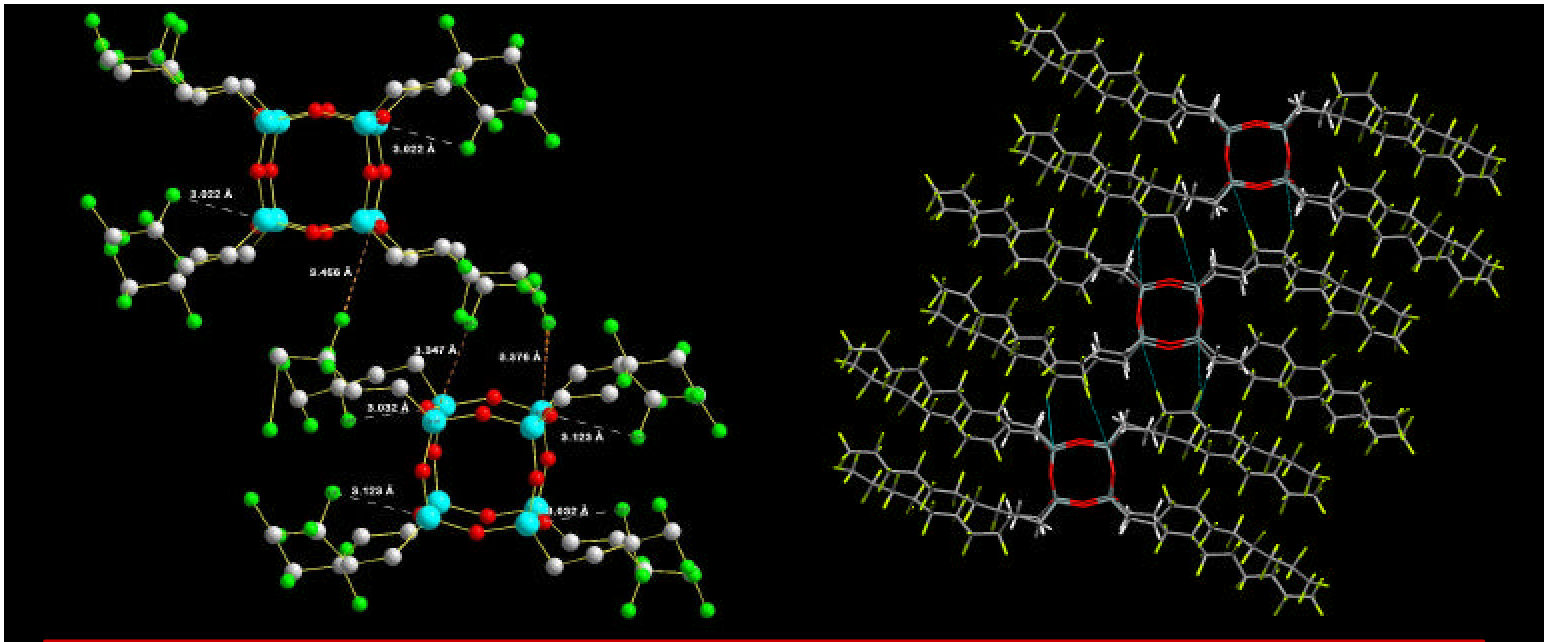
ρ **= 2.09 g/mL**

M_w = 3993.54 g/mol

- Decreased number of H-F contacts.
- Increased number of Si-F contacts.

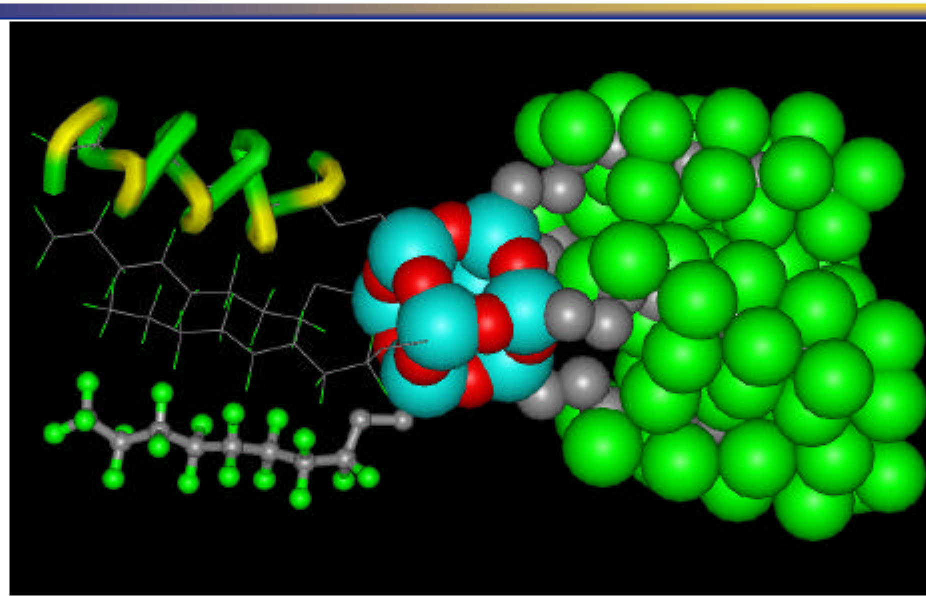
- Si atoms in POSS cage line up with fluorine atoms on 3rd and 4th carbons in adjacent POSS fluorodecyl chains.

Fluorodecyl$_8$T$_8$



- Si atoms in POSS cage line up with fluorine atoms on 3rd and 4th carbons in adjacent POSS fluorodecyl chains.
- Inter- and intra-molecular Si-F contacts maximize crystal packing.

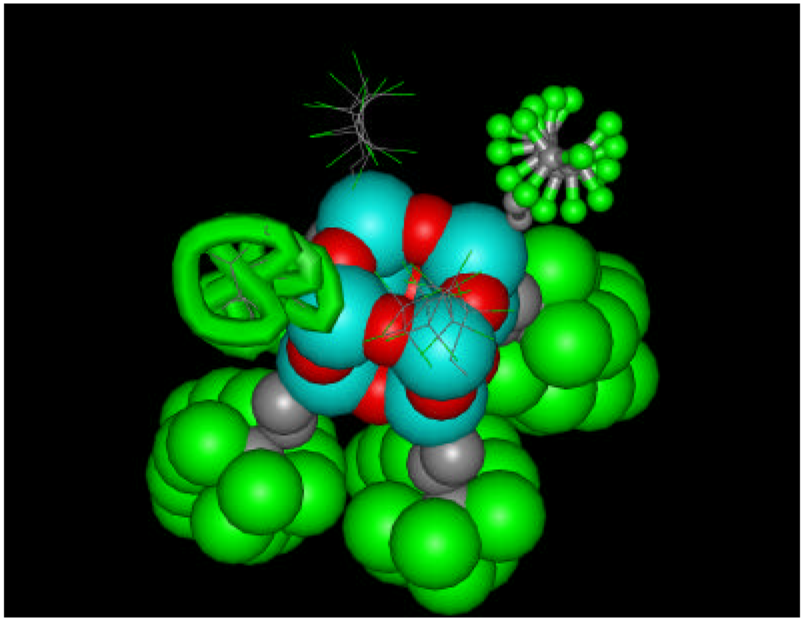
Teflon-Like Fluorodecyl$_8$T$_8$



- Free space surrounds fluorophilic core.
- Inter- and intramolecular fluorocarbon chains distances are ~5.2 Å, similar to that of Phase II PTFE at -173 °C.

Holt, D. B.; Farmer, B. L. *Polymer* **40**, *1999*, 4673.

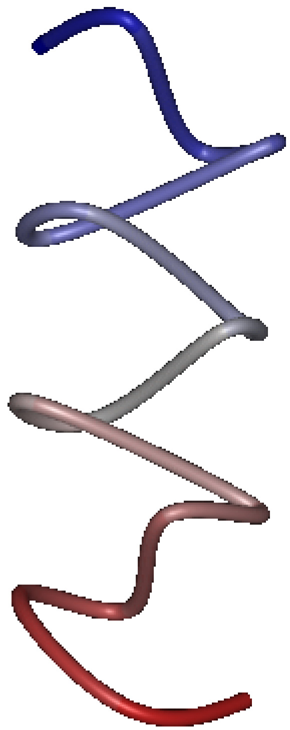
Teflon-Like Fluorodecyl$_8$T$_8$

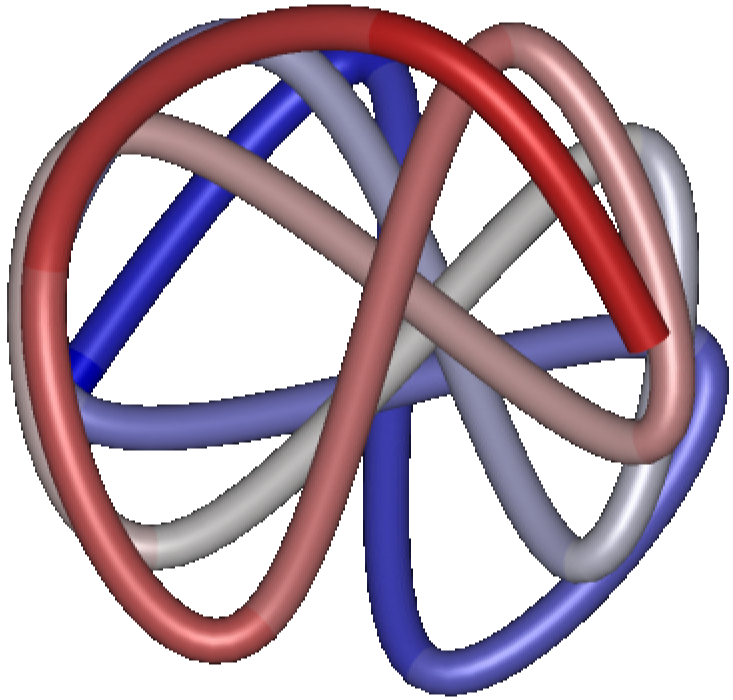


Fluoroalkyl chains have a helix of 7/3.24 (2.16), virtually identical to that of Phase II PTFE at 54/25 (2.16) or 13/6 (2.17).

Holt, D. B.; Farmer, B. L. *Polymer* **40**, *1999*, 4673.
Kerbow, D. L. In "Polymer Data Handbook"; Mark, J. E. Ed.; Oxford University Press: New York, NY, 1999, pp 842-847.

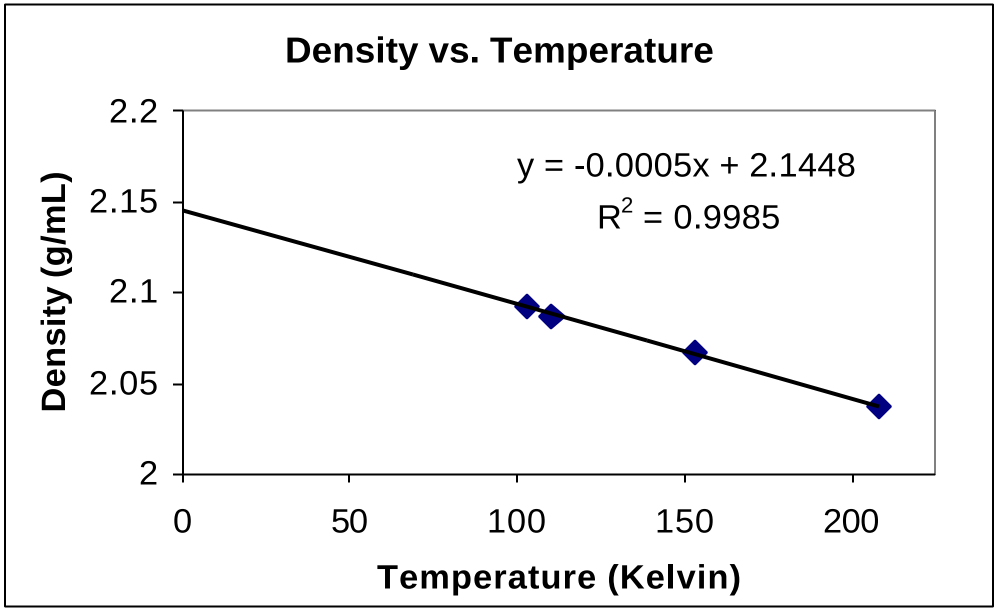
Small Molecule vs. Protein X-Ray





Trace of fluorine atoms on one fluoroalkyl group of Fluorodecyl$_8$T$_8$.

Teflon-Like Fluorodecyl$_8$T$_8$



- Fluorodecyl$_8$T$_8$ density decreases as a rate of 5×10^{-4} g/mL/K.
- Extrapolated density at absolute zero is 2.145 g/mL.
- Reversible thermal transition between -75 and -80 °C.
- Density lower than PTFE (2.3), probably due to free space in core.

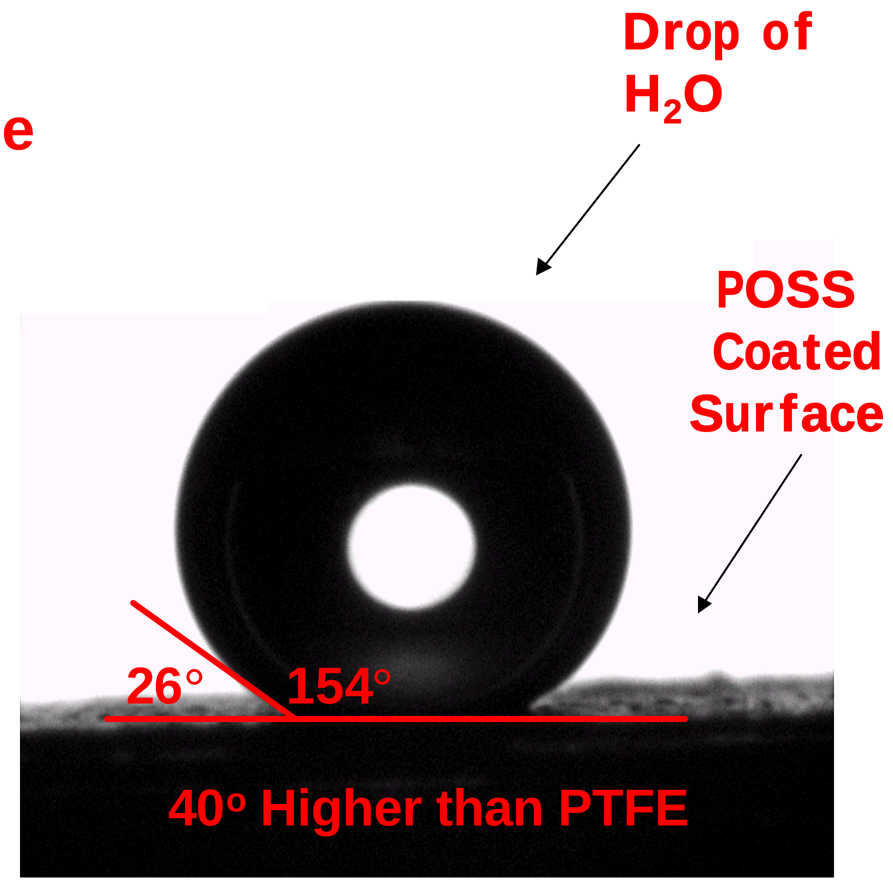
Teflon-Mimicking Summary

Property	Phase II Teflon (below 19 °C)	$Fluorodecyl_8T_8$
Intermolecular Chain Distance	~5.0 Å	~5.2 Å
Intermolecular Chain Distance	~5.0 Å	~5.2 Å
Chain Helix	54/25 (2.16) or 13/6 (2.17)	7/3.24 (2.16)
Density	2.3 g/mL	2.1 g/mL

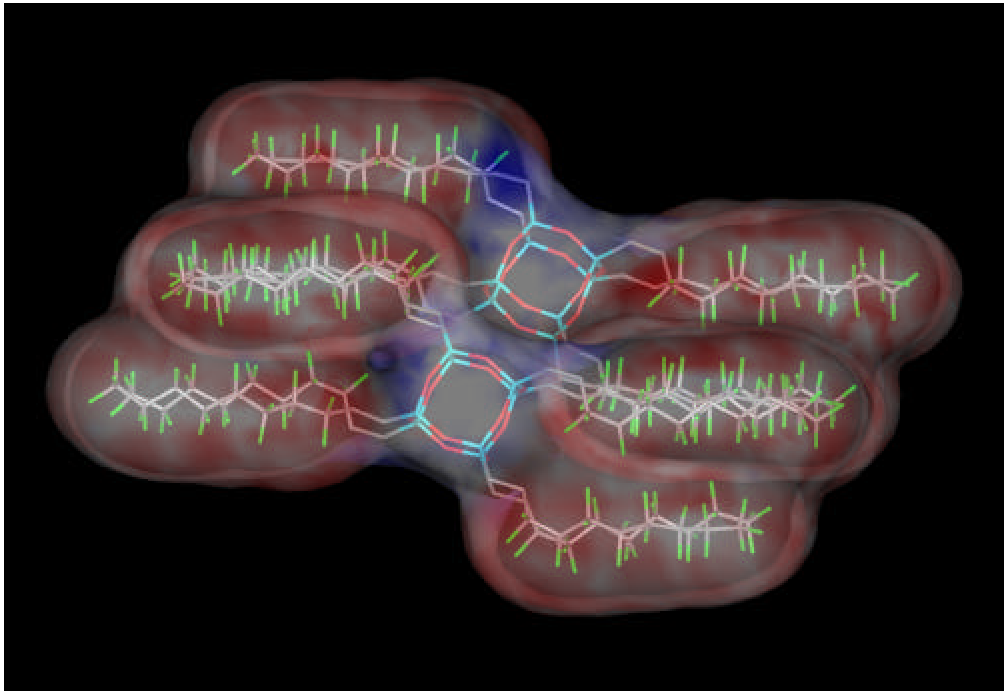
Ultrahydrophobic Nanoparticles

154° Contact Angle

- Ultrahydrophobic
- Improve the surface properties of polymers into which it is blended

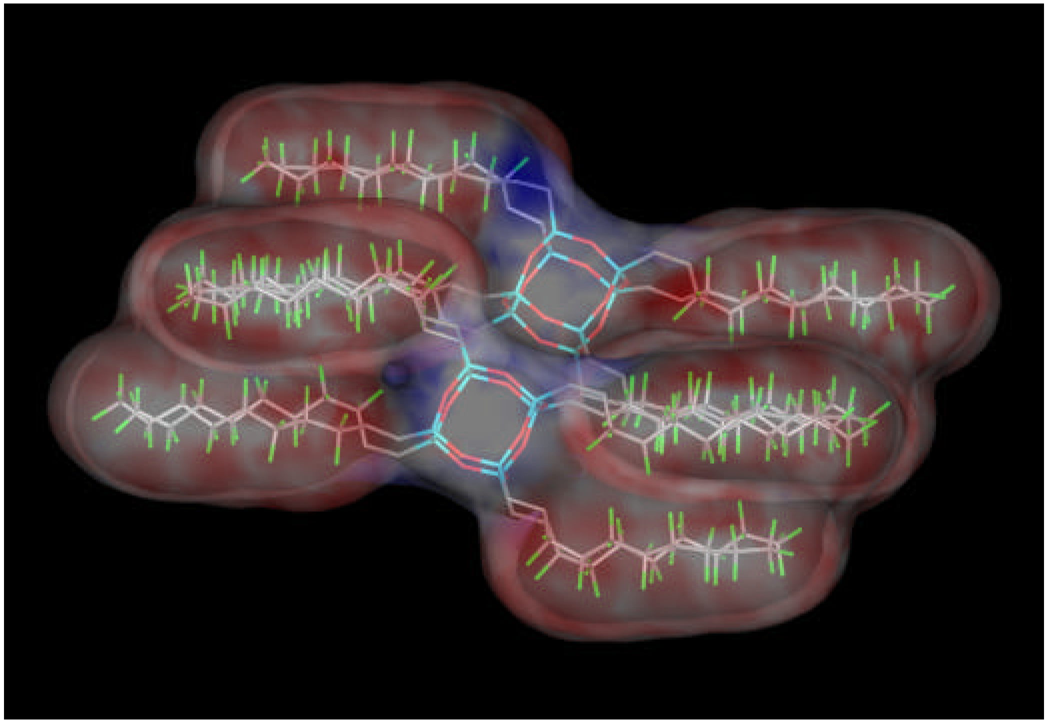


Fluorodecyl$_8$T$_8$



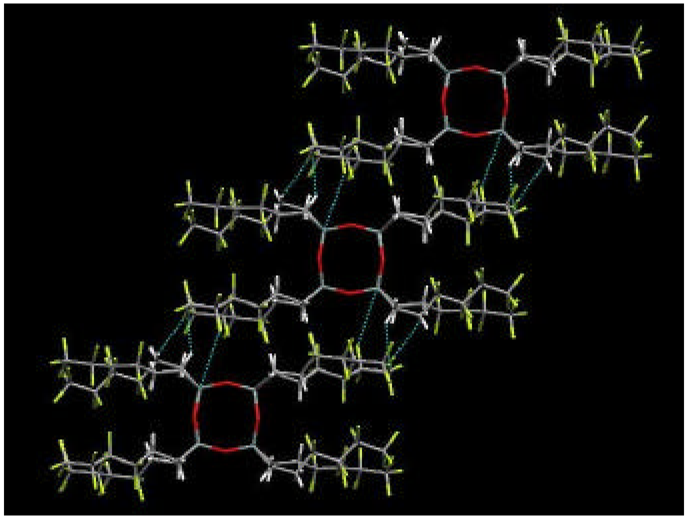
- Electrostatic potential surface of fluorodecyl POSS crystal.
- The surface appears to form a bent conformation.

Fluorodecyl$_8$T$_8$

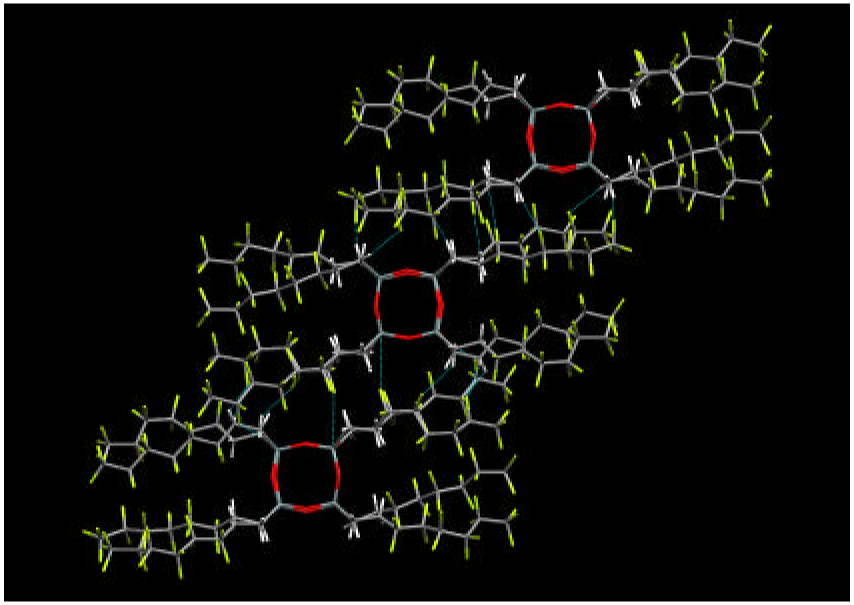


Electrostatic potential surface of fluorodecyl POSS crystal shows the negative area surrounding the fluoroalkyl chains and the positive area surrounding the core.

Fluorohexyl$_8$T$_8$ and Fluorooctyl$_8$T$_8$



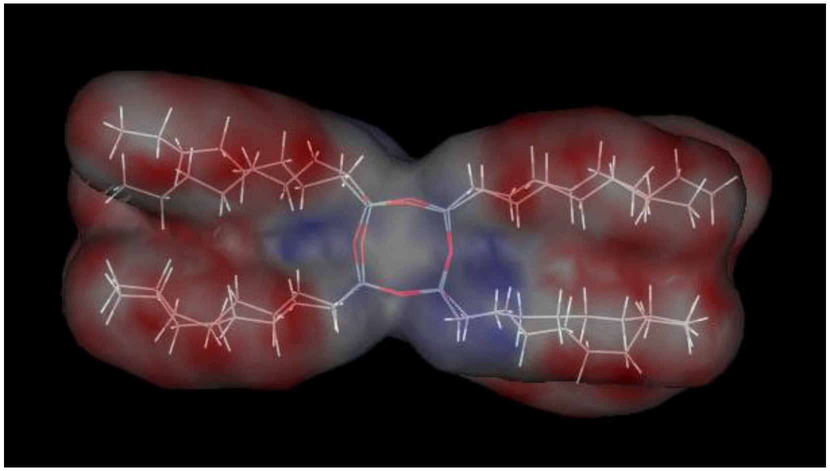
Fluorohexyl$_8$T$_8$



Fluorooctyl$_8$T$_8$

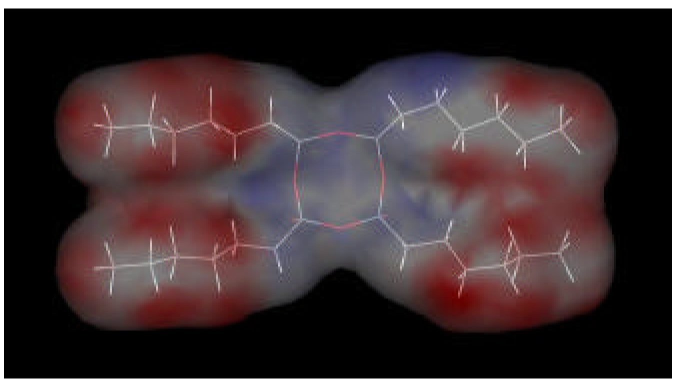
- Both H-F and Si-F contacts lead to the increased packing efficiency.
- Si atoms in POSS cage line up with fluorine atoms on 5th and 6th carbons in adjacent POSS fluorohexyl chains.

Fluorooctyl$_8$T$_8$ and Fluorohexyl$_8$T$_8$



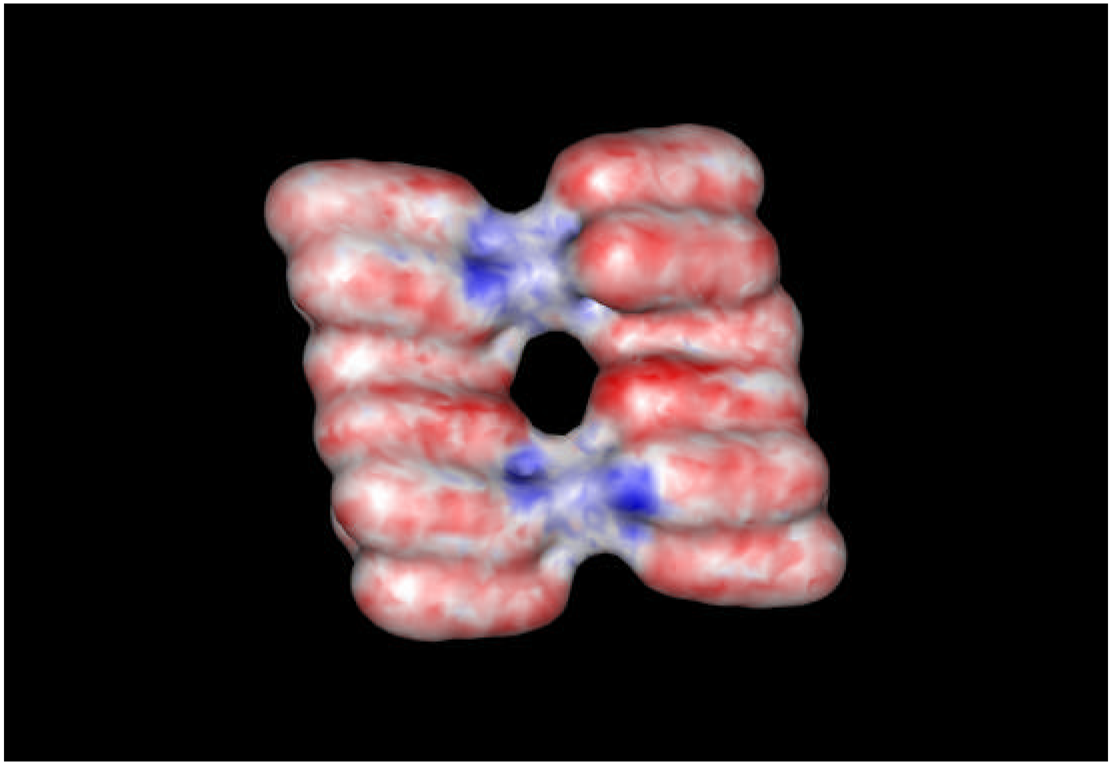
Fluorooctyl$_8$T$_8$

These compounds appear to form a flatter surface than the Fluorodecyl$_8$T$_8$.



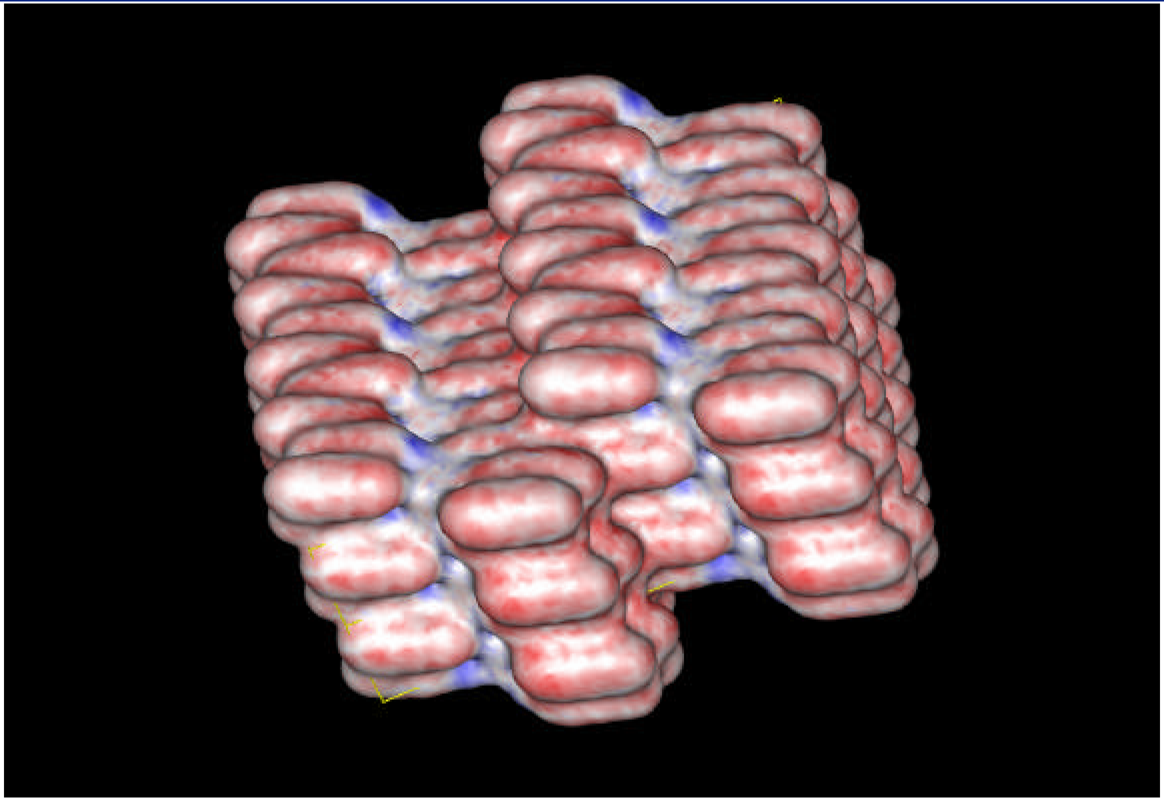
Fluorohexyl$_8$T$_8$

Electrostatic Potential



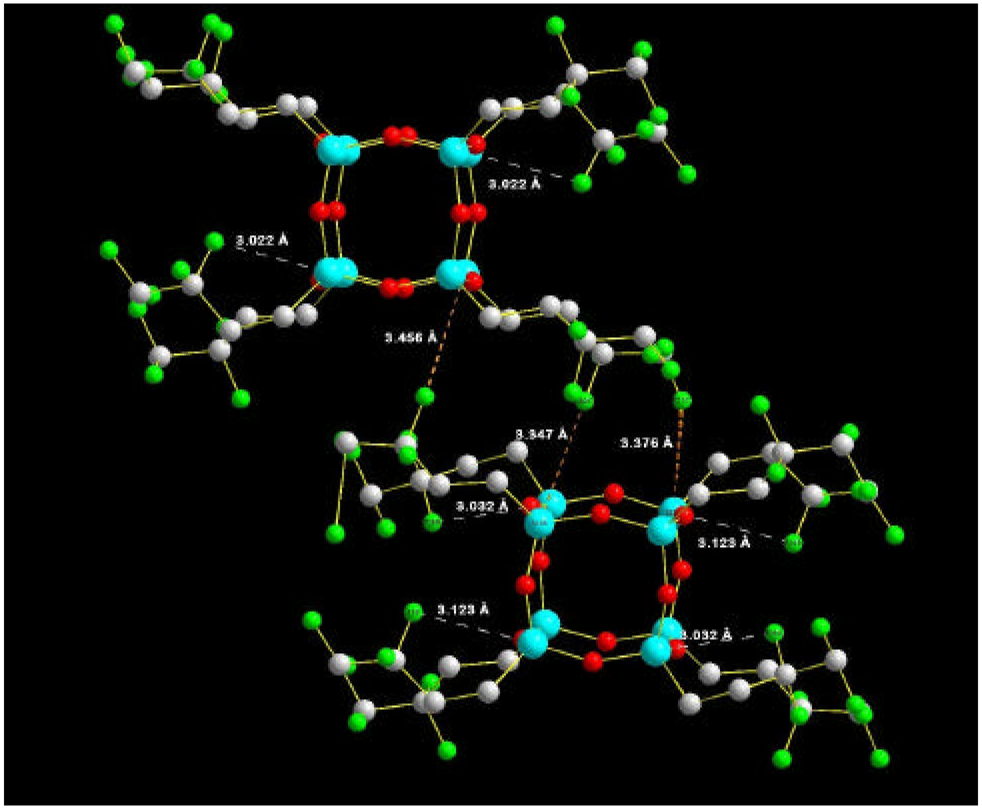
- Unique molecules within unit cell line up together, maximizing fluorine interactions.

Fluorodecyl$_8$T$_8$



Crystal packing maximizes positive-negative eletrostatic interactions.

Fluorodecyl$_8$T$_8$



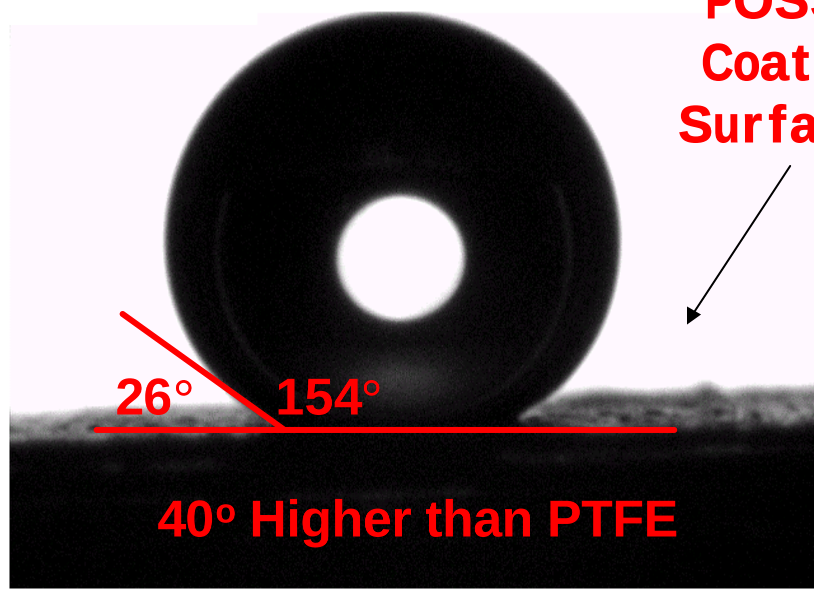
Inter- and intra-molecular Si-F contacts maximize crystal packing.

Ultrahydrophobic Nanoparticles

154° Contact Angle

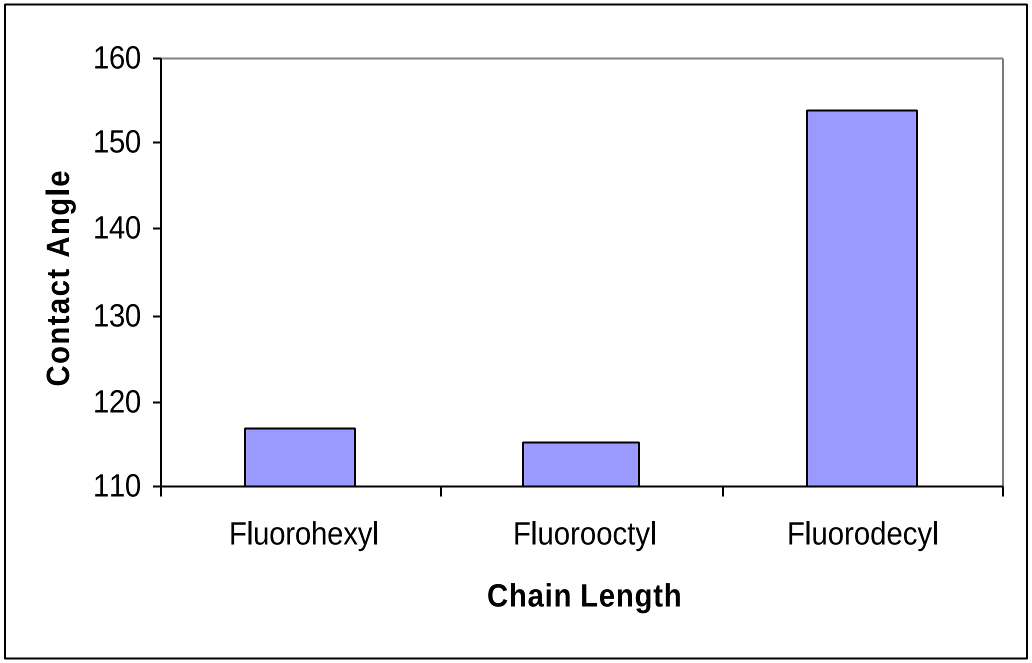
Drop of H_2O

- Ultrahydrophobic
- Improve the surface properties of polymers into which it is blended



POSS Coated Surface

FluoroPOSS Contact Angles



- Fluorohexyl and Fluorooctyl POSS have similar water contact angles.
- $Fluorodecyl_8T_8$ contact angle is much higher.

Possible Cause of Hydrophobicity

- Both surface chemistry and surface roughness contribute to hydrophobicity.
- Surface chemistry is similar for all FluoroPOSS compounds.

- Fluorohexyl and Fluorooctyl POSS have similar water contact angles.
- $Fluorodecyl_8T_8$ contact angle is much higher.

- Fluorohexyl and Fluorooctyl POSS have much flatter molecular surfaces.
- $Fluorodecyl_8T_8$ appears to have a rougher surface on a molecular scale.

Density

Compound	Density (g/mL)
• PVDF	1.75-1.78
• PCTFE	2.08-2.19
• FEP	2.12-2.17
• PTFE	2.3-2.7
• Fluoropropyl POSS	1.59
• Fluorohexyl POSS (crystal)	1.86 (1.98)
• Fluorooctyl POSS (crystal)	1.88 (2.05)
• Fluorodecyl POSS (crystal)	1.95 (2.09)

Blended POSS fluoropolymers have higher than expected densities. This may be due to POSS induced crystallite nucleation.

Conclusions

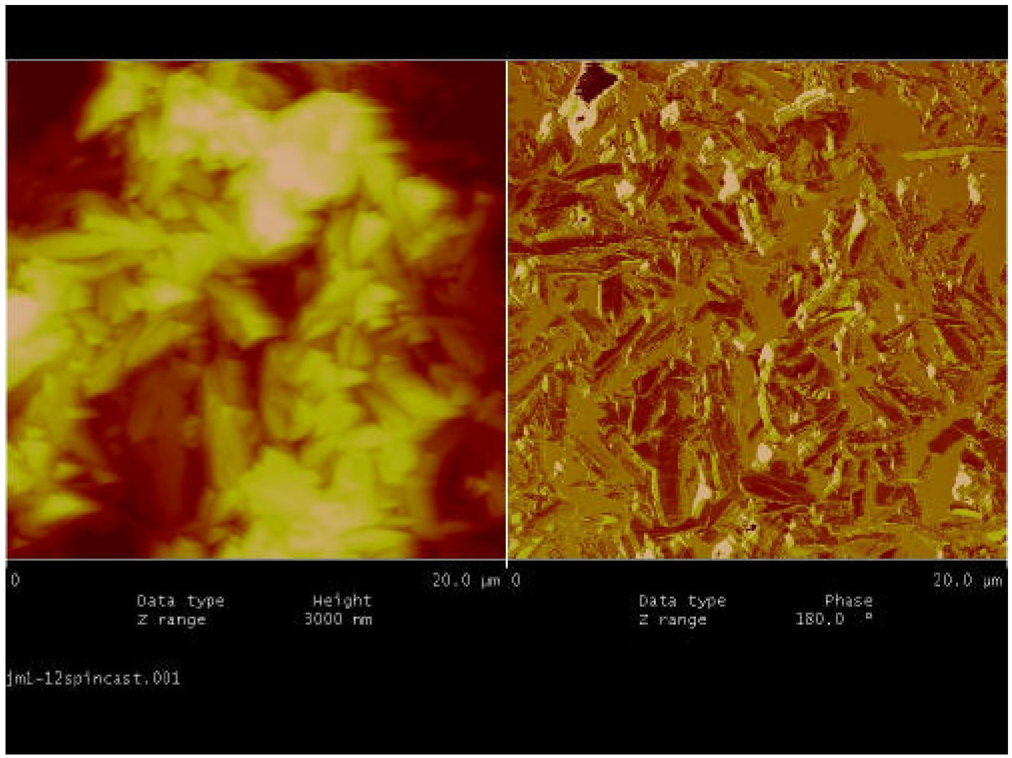
- Fluorodecyl POSS chains can be viewed as PTFE models.
- Fluorodecyl POSS surface is ultrahydrophobic.
- Hydrophobicity may be caused by surface roughness.
- FluoroPOSS increase hydrophobocity of fluoropolymers into which they are incorporated.

Summary

- Si-F and H-F contacts in crystals maximize packing density.
- Fluorodecyl POSS chains can be viewed as PTFE models.
- Bridges gap between small molecule and protein X-ray diffraction.
- Fluorodecyl POSS surface is ultrahydrophobic.
- FluoroPOSS increase hydrophobocity of fluoropolymers into which they are incorporated.
- FluoroPOSS act as a processing aid during fluoropolymer processing.

Backup Slides

AFM Image of Spin-Cast Fluorodecyl$_8$T$_8$ Surface



AFM image of spin-cast surface shows micron scale roughness.

Water Contact Angles

Polymer	No POSS	FO_8T_8	FD_8T_8
PCTFE	88°	108°	128°
FEP	97°	110°	114°
Amor. FEP	92°	100°	103°

Fluoropropyl POSS (FP_nT_n)	101°
Fluorohexyl POSS (FH_8T_8)	117°
Fluorooctyl POSS (FO_8T_8)	115°
Fluorodecyl POSS (FD_8T_8)	154°

Contact Angle and Chain Length