

REPORT DOCUMENTATION PAGE

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Wetting properties of polysiloxane networks modified in situ with fluoroalkyl-substituted linear and POSS cage structures

Raymond Campos, Sean M. Ramirez,
and Joseph M. Mabry

August 17, 2015

ACS National Conference

Paradigms for low energy surfaces

Crystalline surfaces

- Immobilized chemical moieties with low polarizability (e.g. fluorine)
 $CF > CF_2 > CF_3 > SF_5$
- High crystallinity to prevent surface reorganization when in contact with liquids, biofouling sources, etc.

Extreme liquid repellency when combined with surface roughness and re-entrant geometry

“liquid-like” surfaces

- low energy barriers between metastable states
- Metal oxide surfaces and liquid-infused materials (e.g. SLIPS)

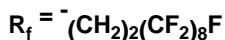
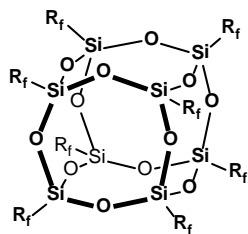
Fluorine content not required to repel low surface tension liquids?

Low CA hysteresis despite lower contact angle values

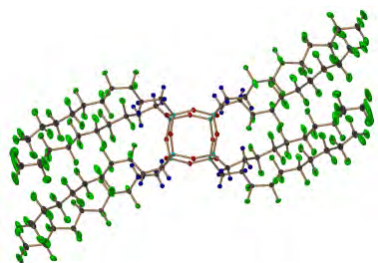
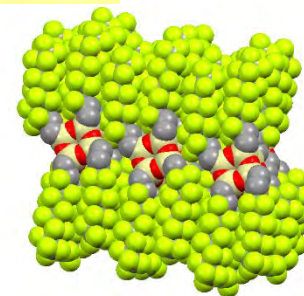
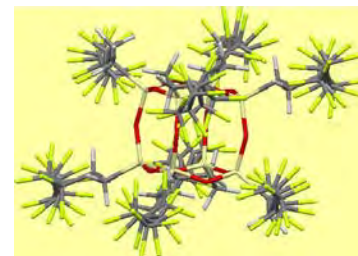
Surface modification of PDMS/siloxane networks

- Primarily oxide formation via O₂ plasma, UV/ozone, etc. and subsequent functionalization
- Functional PDMS (e.g. residual vinyl groups in network)
- Functional silsesquioxane networks

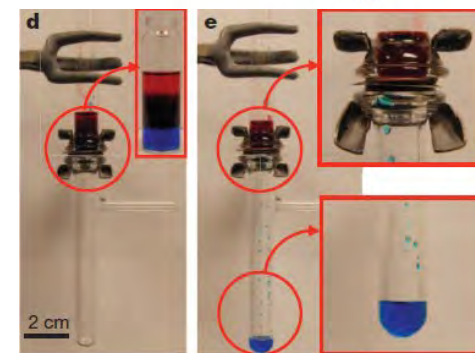
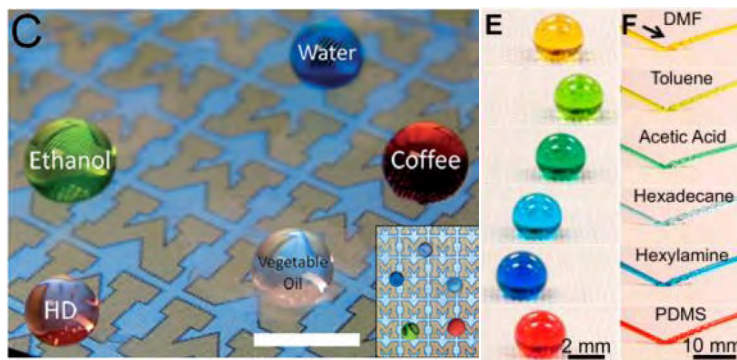
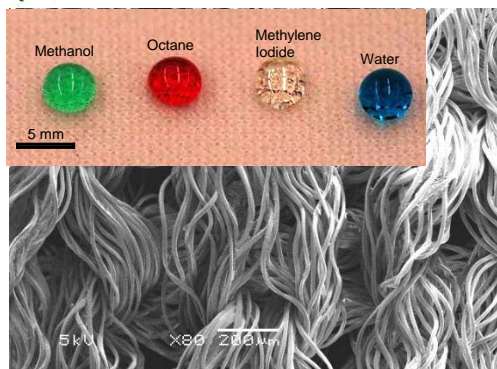
Properties of Fluorodecyl₈T₈ POSS



- ↪ Extremely low surface energy
- ↪ Surface migration in polymers
- ↪ Surface responsive behavior



Enabling....



**Superomniphobic fabrics
via dip-coating**

Choi *et al.*, *Ang. Chem.*, 2009

**Transparent
Omniphobicity**

Golovin *et al.*, *Ang. Chem.*, 2013

**Extreme
Omniphobicity**

Pan *et al.*, *JACS.*, 2012

**Oil/water emulsion
gravity separation**

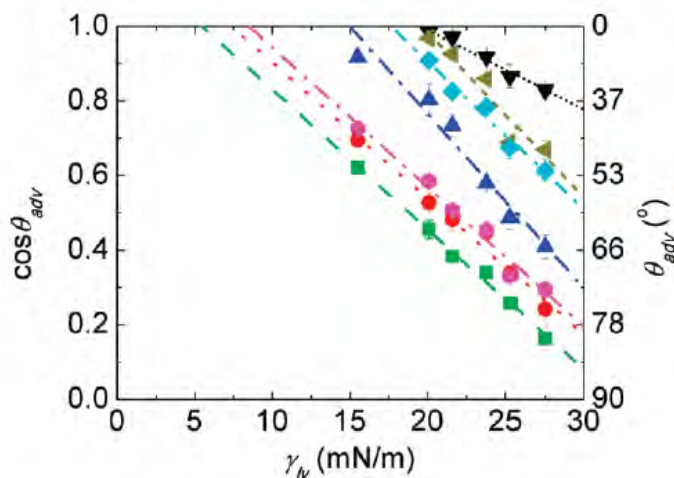
Kota *et al.*, *JACS.*, 2012

Surface Energy of Fluorodecyl₈T₈ POSS

fluorodecyl₈T₈ POSS

5.5 mN/m (Zisman analysis)*

8.8 – 10.2 mN/m (Girafalco-Good analysis)*



Zisman analysis

(only alkane probing liquids used)

| | |
|--|---|
| | Fluorodecyl T ₈ , R = -(CH ₂) ₂ -(CF ₂) ₇ -CF ₃ |
| | Fluorooctyl T ₈ , R = -(CH ₂) ₂ -(CF ₂) ₅ -CF ₃ |
| | Fluorohexyl T ₈ , R = -(CH ₂) ₂ -(CF ₂) ₃ -CF ₃ |
| | Fluoropropyl T ₈ , R = -(CH ₂) ₂ -CF ₃ |
| | Hexafluoro- <i>i</i> -butyl T ₈ , R = -CH ₂ -CH(CF ₃) ₂ |
| | Fluorodecyl Q ₄ , R = -(CH ₂) ₂ -(CF ₂) ₇ -CF ₃ |
| | Fluorodecyl M2, R = -(CH ₂) ₂ -(CF ₂) ₇ -CF ₃ |

*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Fluoroalkylated Silicon-Containing Surfaces-Estimation of Solid-Surface Energy. *ACS Applied Materials and Interfaces* 2010, 2 (12), 3544-3554.

Surface Energy of Fluorodecyl₈T₈ POSS

fluorodecyl₈T₈ POSS

5.5 mN/m (Zisman analysis)*

8.8 - 10.2 mN/m (Girafalco-Good analysis)*

Why?

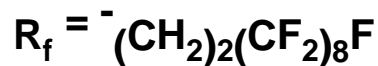
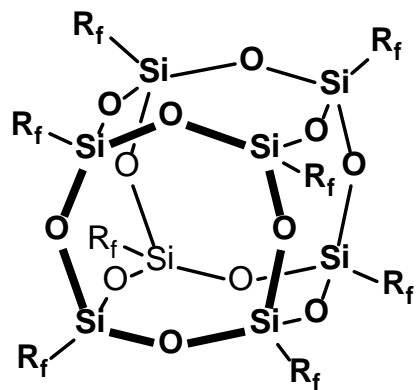
Polytetrafluoroethylene
CF₃-(CF₂)_n-CF₃

18 - 20 mN/m (Zisman analysis)

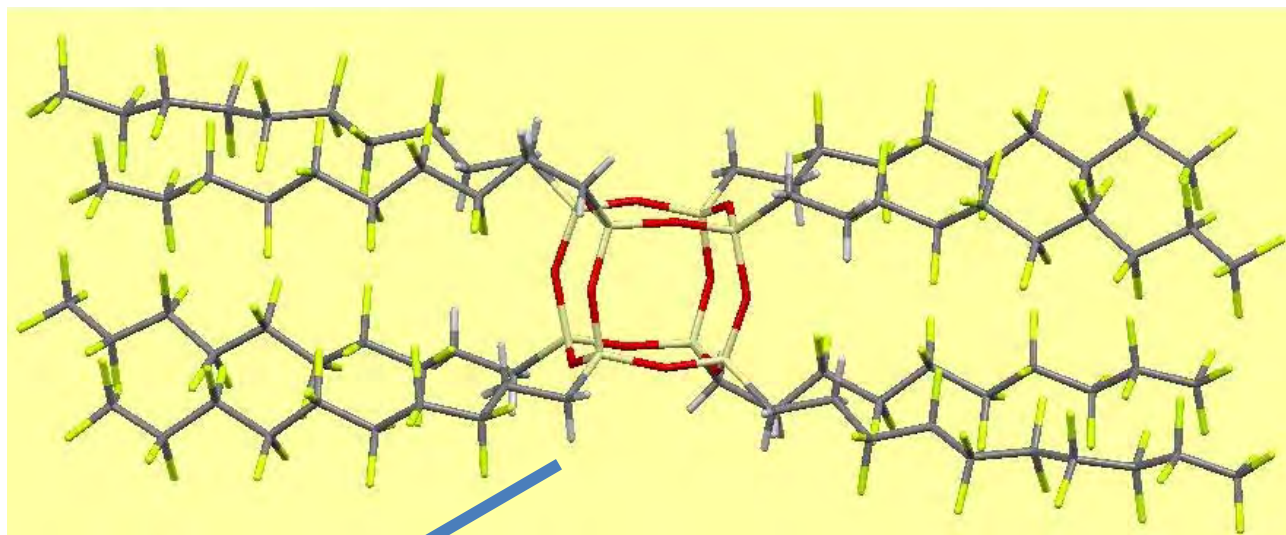
CF₃ monolayer

6.7 mN/m (Zisman analysis)

*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., Fluoroalkylated Silicon-Containing Surfaces-Estimation of Solid-Surface Energy. *ACS Applied Materials and Interfaces* 2010, 2 (12), 3544-3554.



Fluorodecyl₈T₈ POSS



Rotate ~ 90°

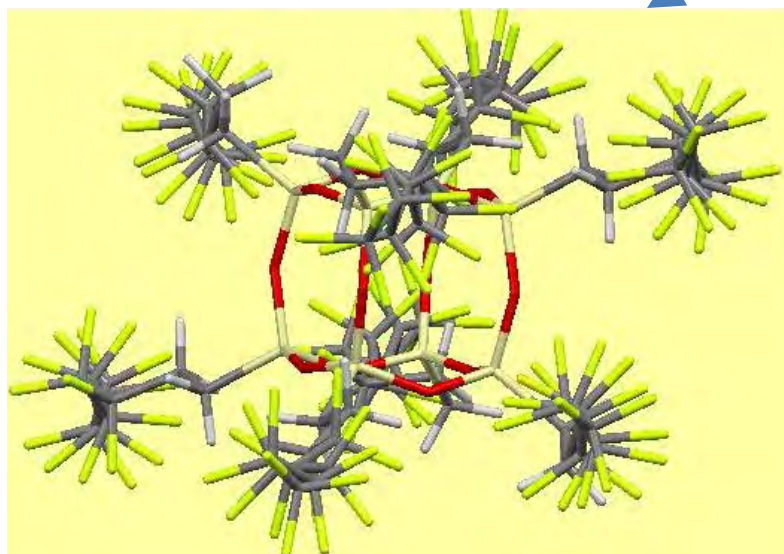
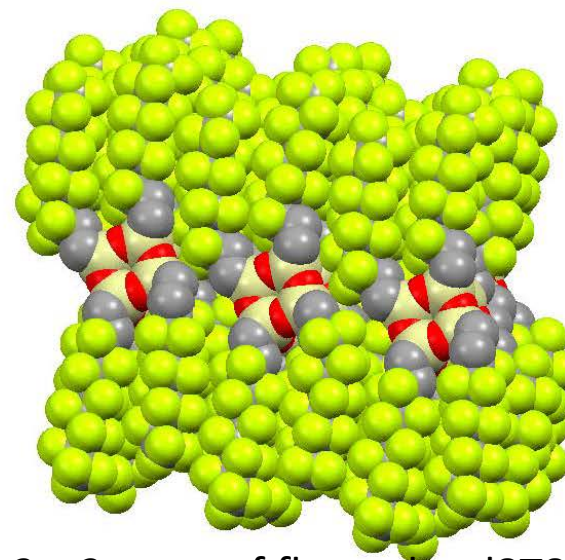
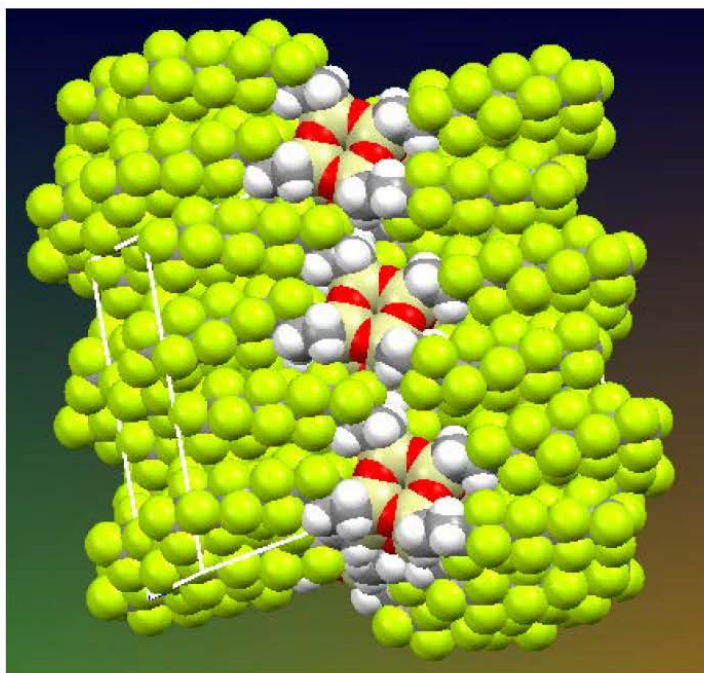
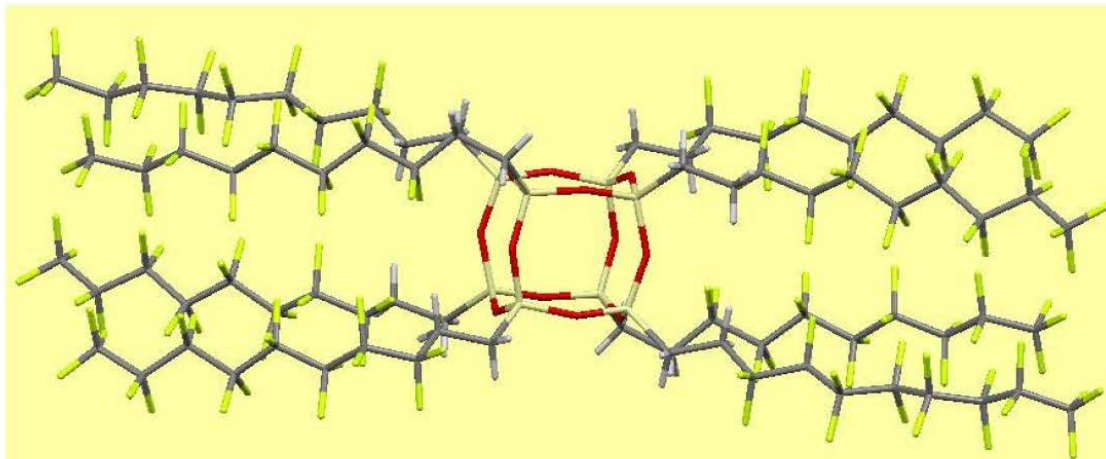
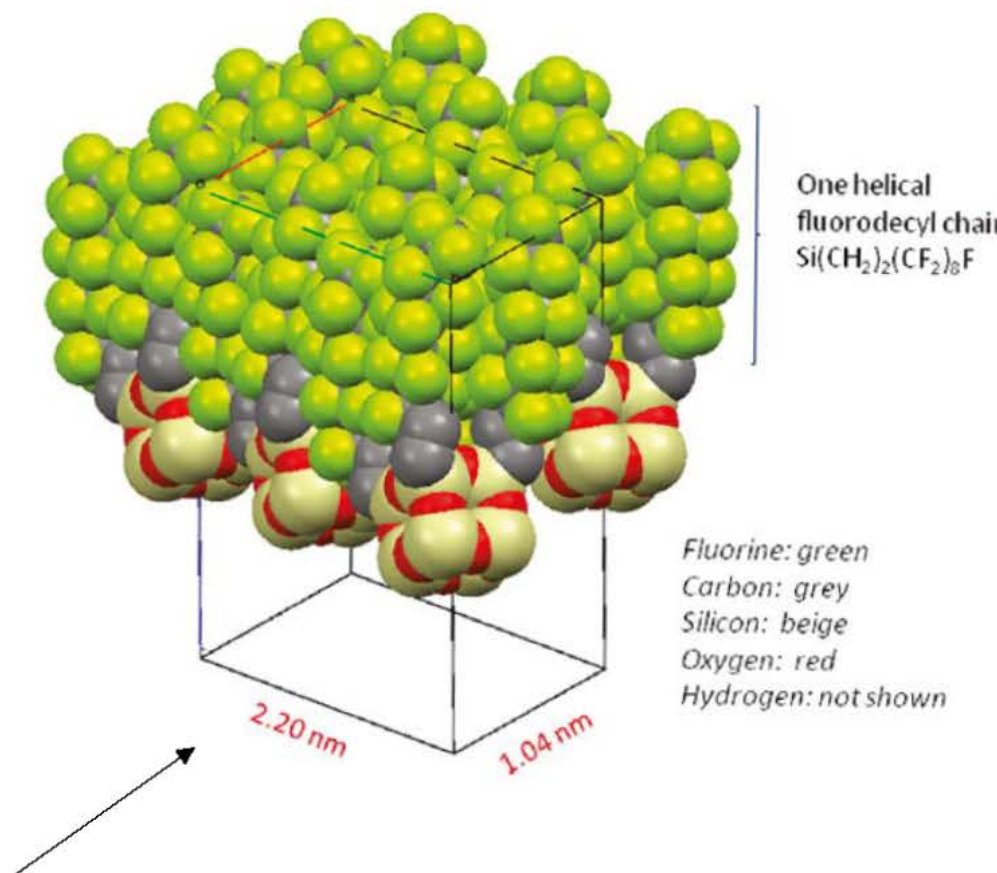
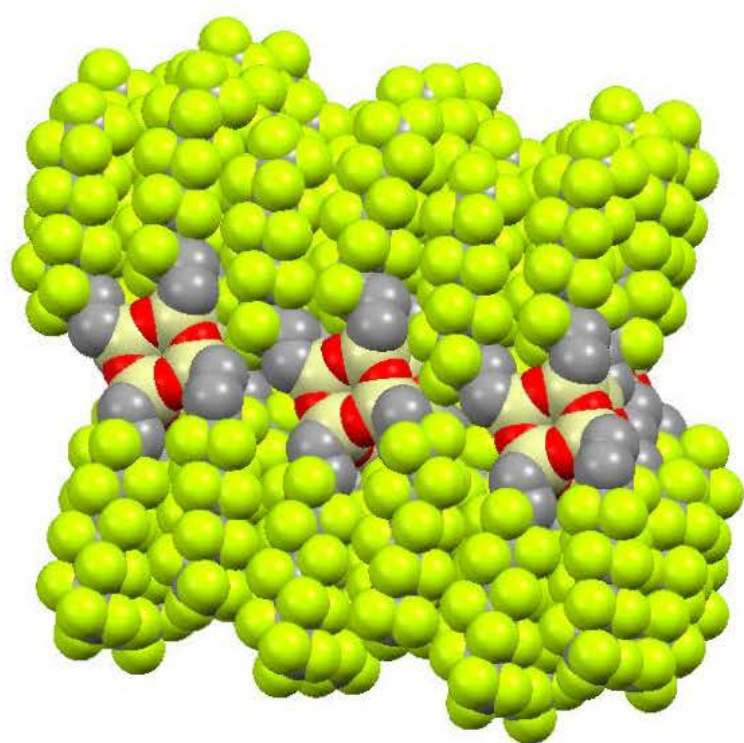


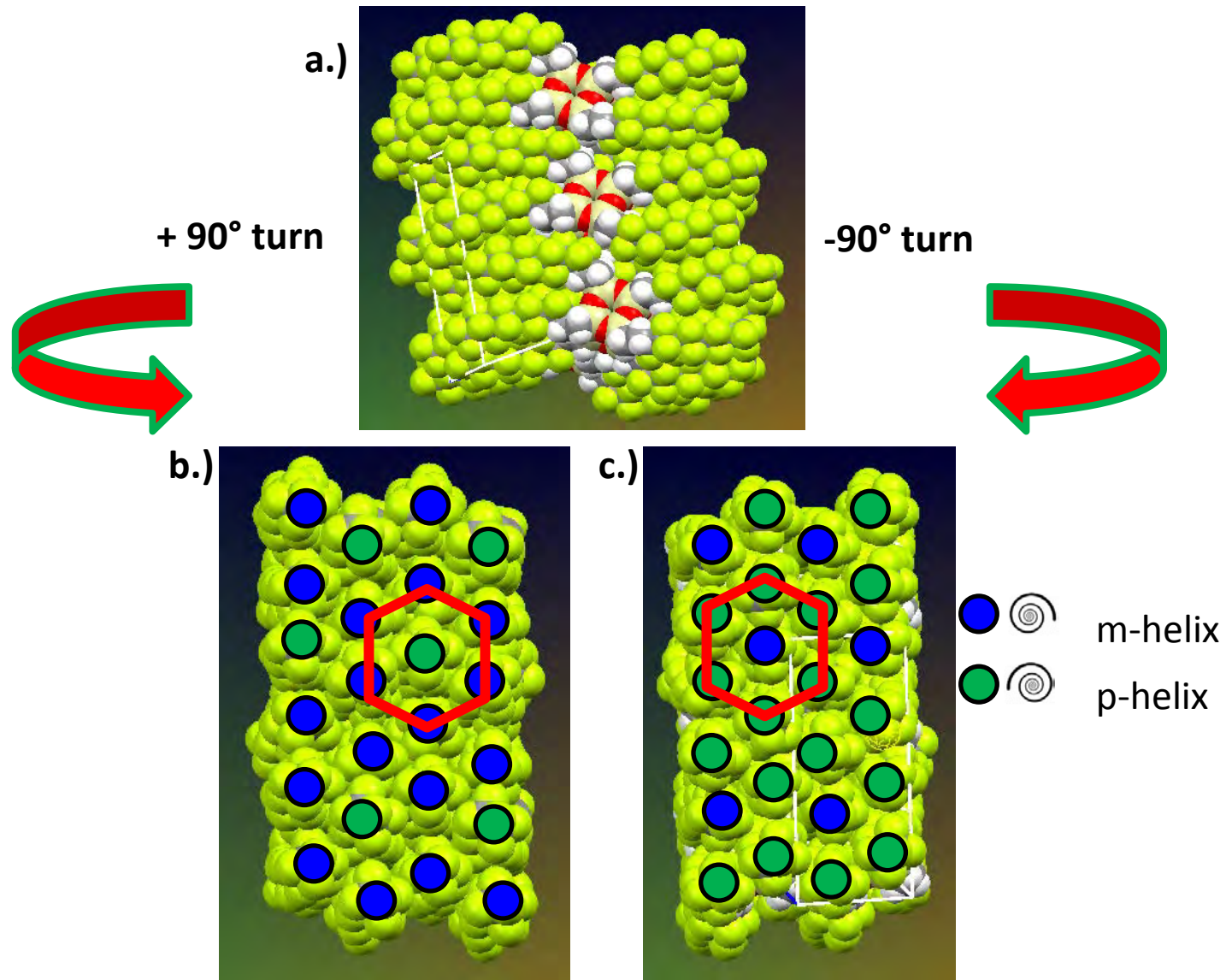
Image displaying the helical conformation of fluorodecyl substituents in the solid state packing of fluorodecyl₈T₈ POSS

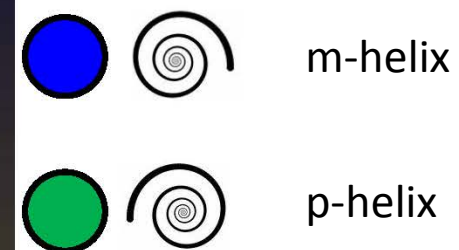
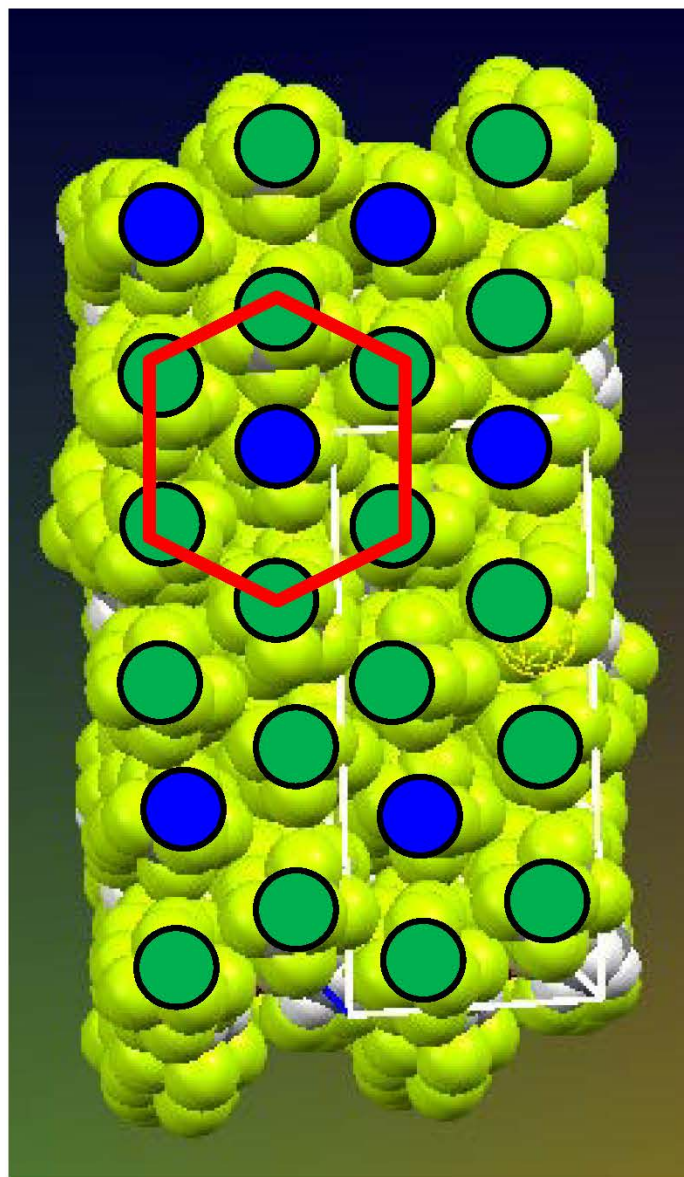
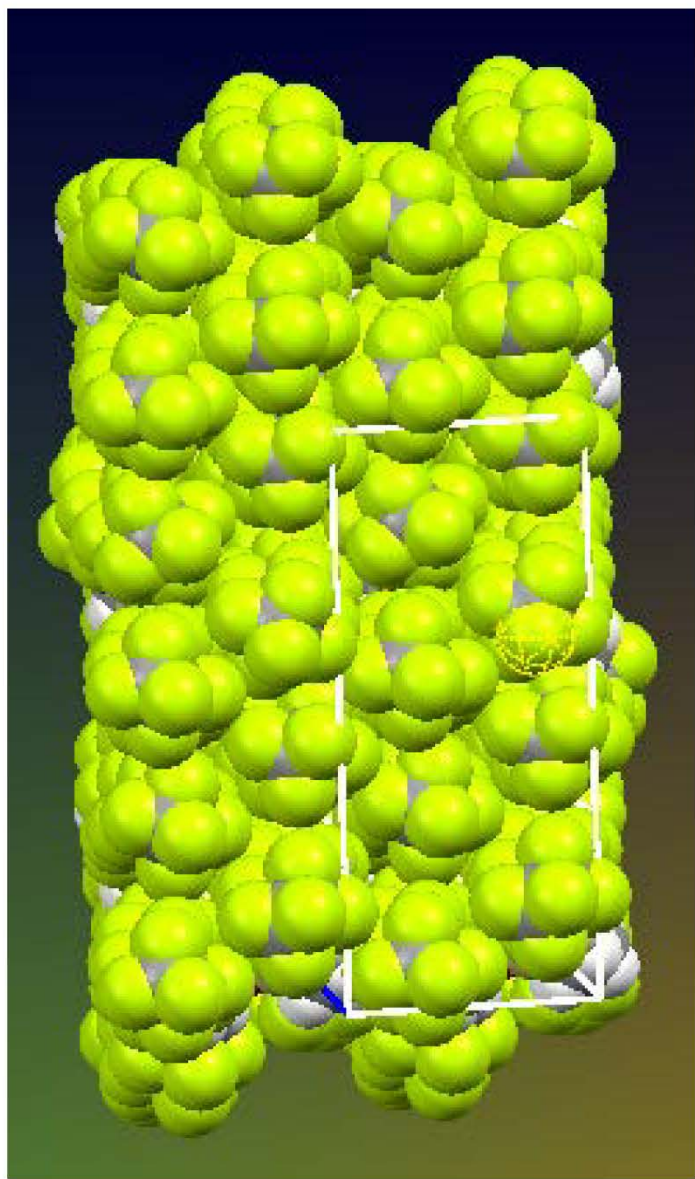


3 x 2 array of fluorodecyl8T8 POSS cages displaying a lamella-type packing

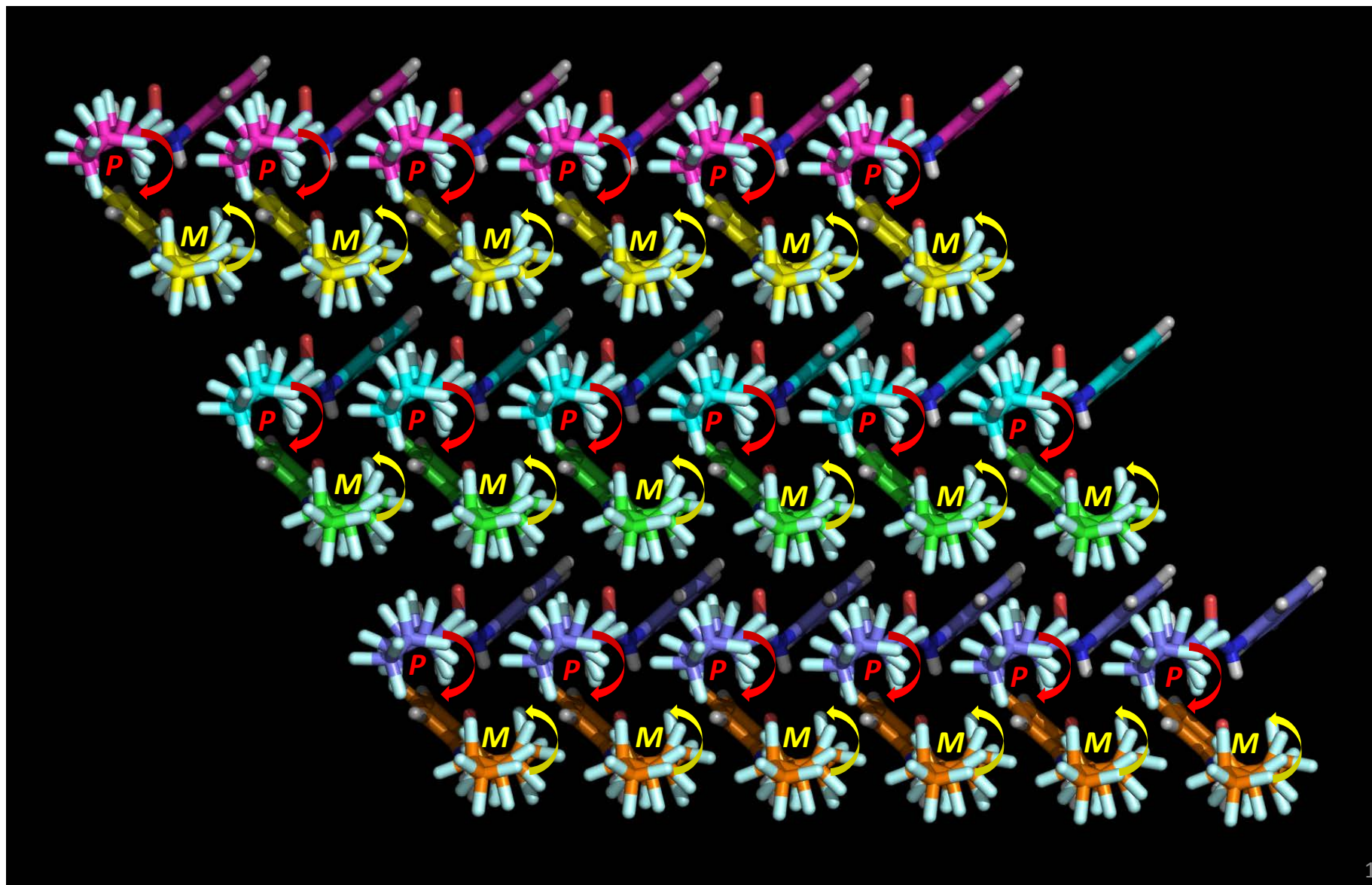


Campos, R., Haddad T. S., *et al.*, *Langmuir* **2011**, 27 (16), 10206-10215.





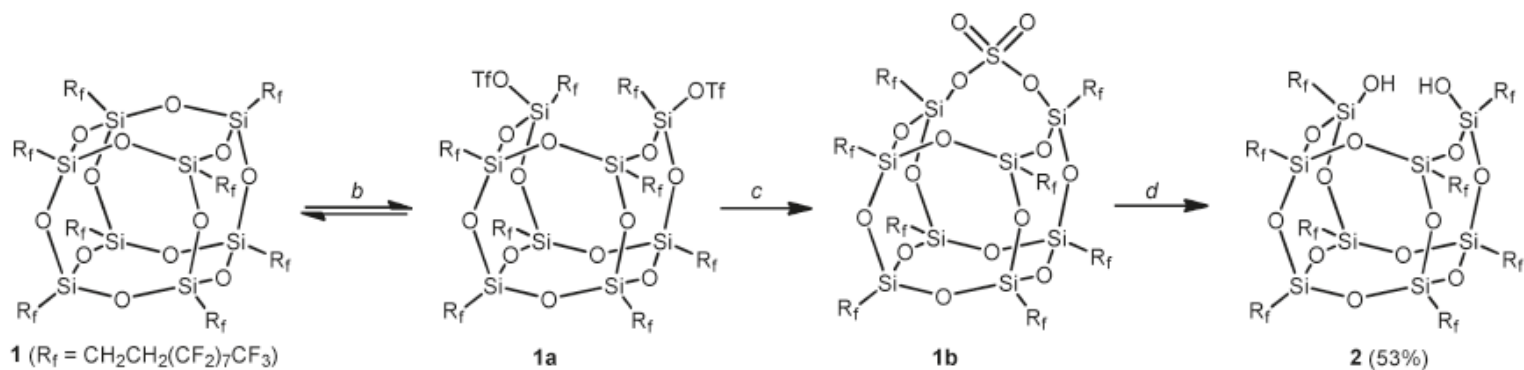
Helical crystal packing of fluoroalkyl-substituted urea



Distribution A: Approved for public release; distribution is unlimited.

Functional Fluorodecyl POSS Compounds Enabled by Incompletely Condensed Intermediate

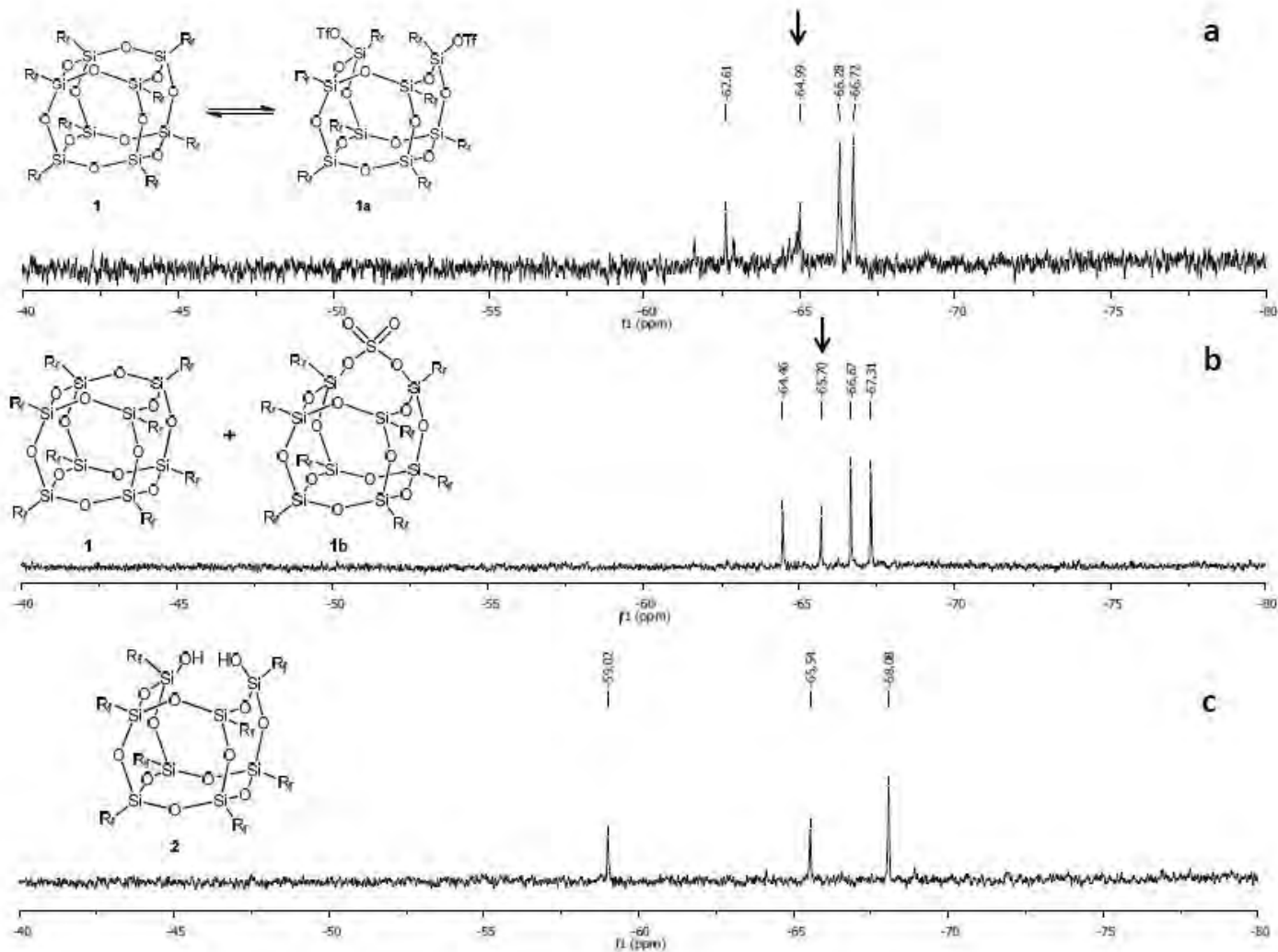
Scheme 1. Synthesis of Incompletely Condensed Fluoroalkyl Silsesquioxane^a



^a Conditions: All reactions were performed in C_6F_6 at 25 °C. ^b $\text{CF}_3\text{SO}_3\text{H}$, 75 min; ^c $\text{NBut}_4\text{HSO}_4$, 30 min; ^d $(\text{CF}_3)_2\text{CH}_2\text{OH}/\text{H}_2\text{O}$ (10:1), 12 h.

Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS*, **2011**, *133*, 20084.

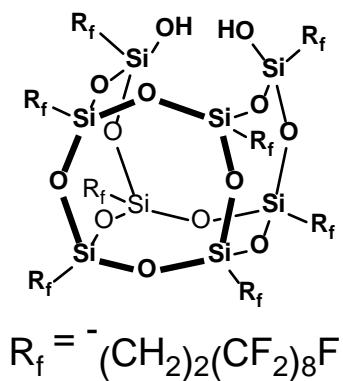
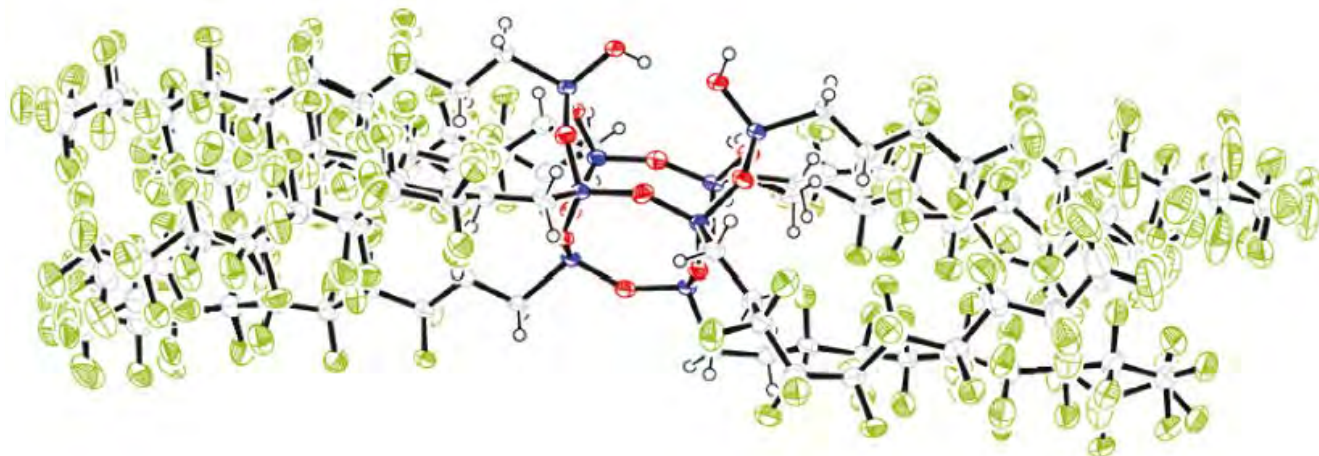
^{29}Si NMR Spectra of fluorodecyl POSS disilanol Intermediates and Product



Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS*, 2011, 133, 20084.

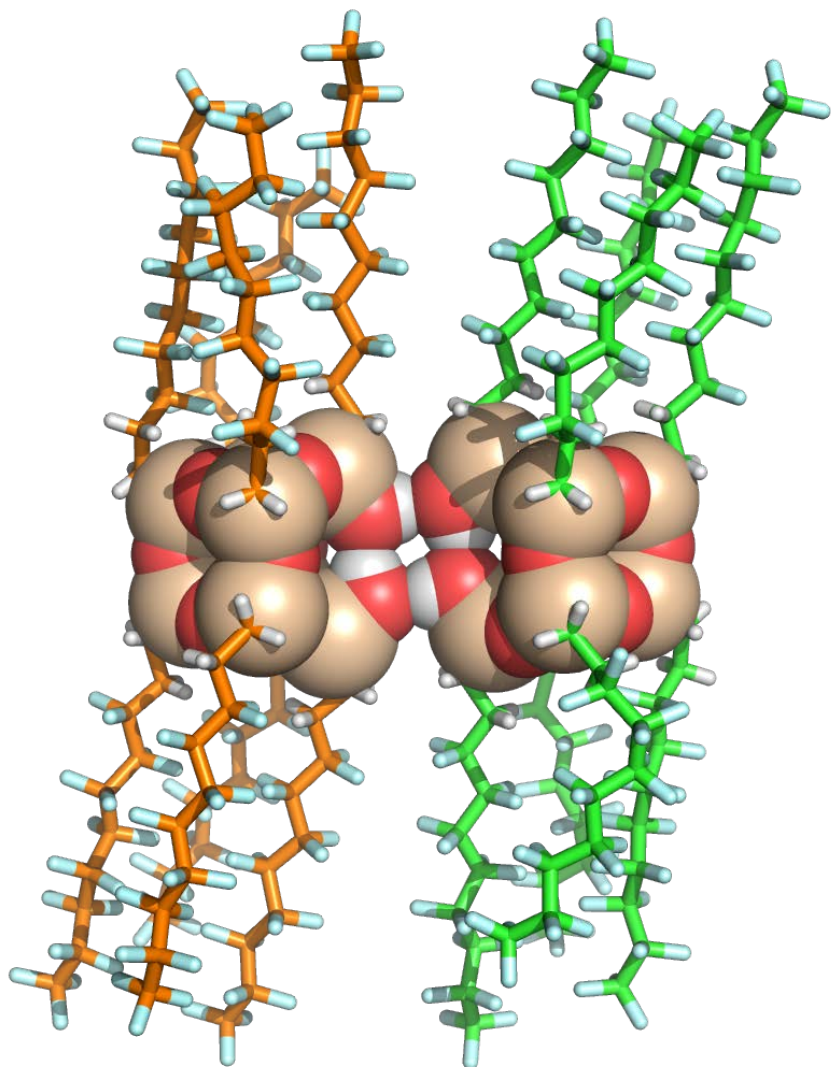
Distribution A: Approved for public release; distribution is unlimited.

ORTEP representations of Fluorodecyl POSS Disilanol crystal structure

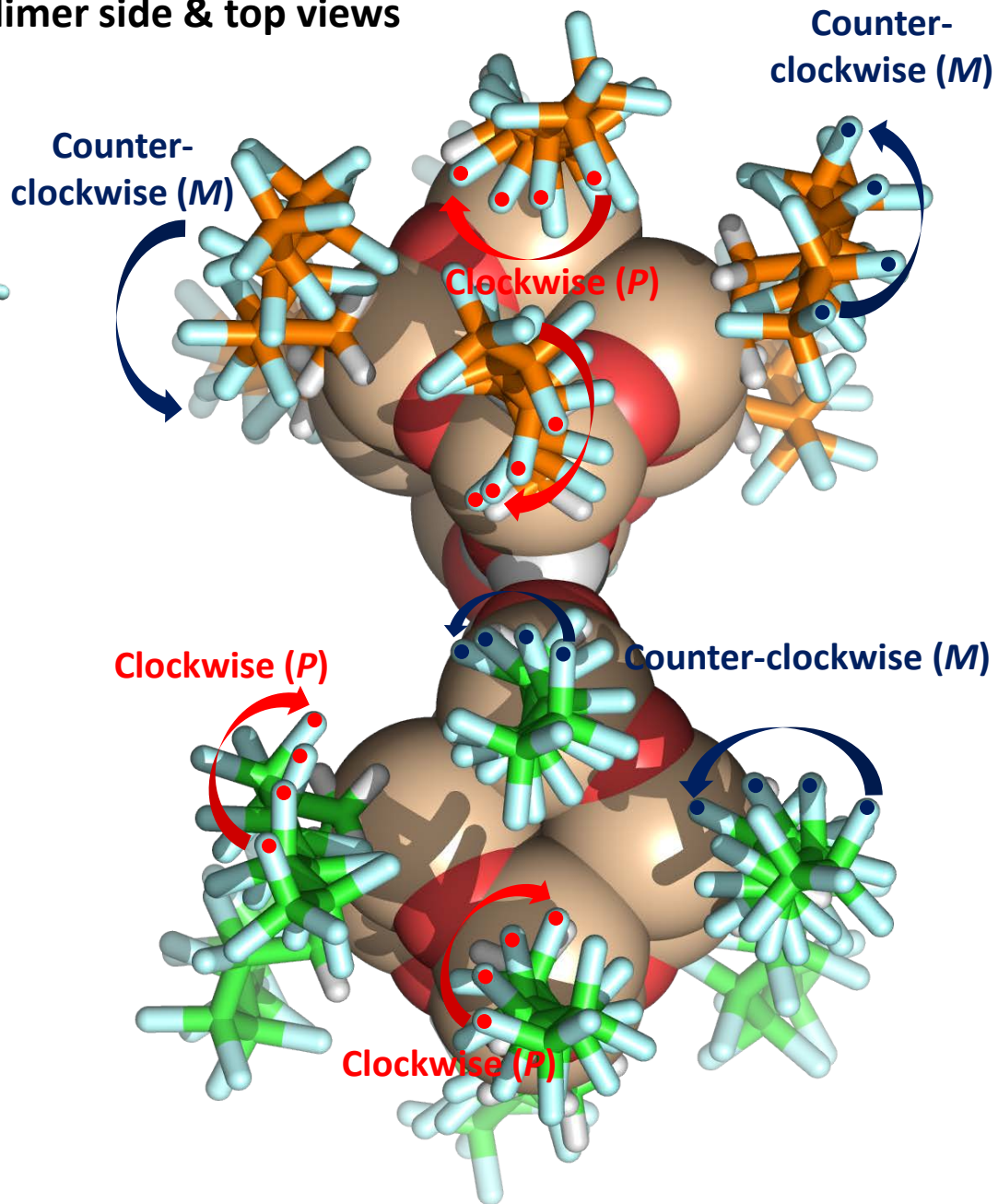


Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS*, 2011, 133, 20084.

F-POSS cage dimer side & top views

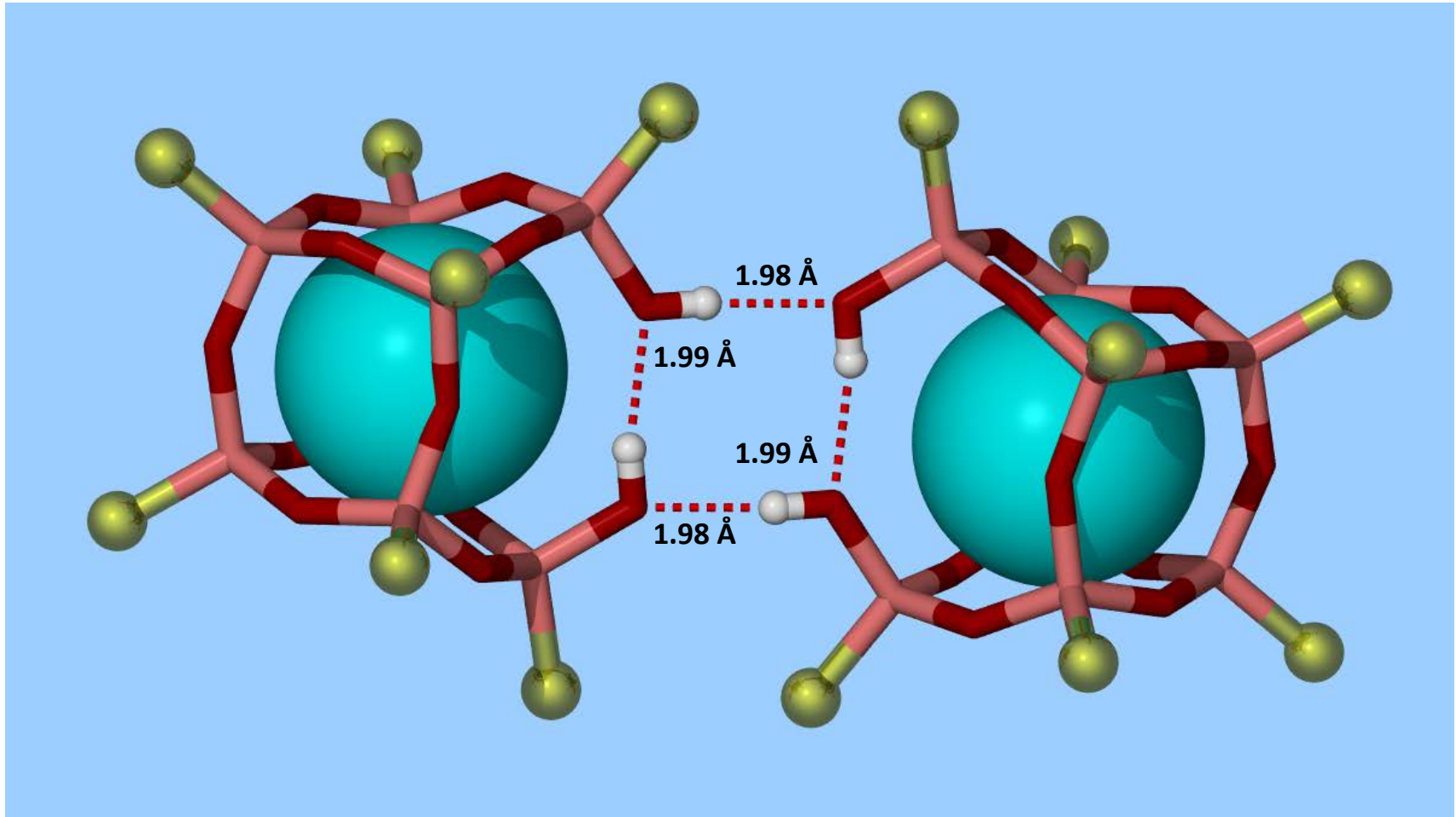


Side view

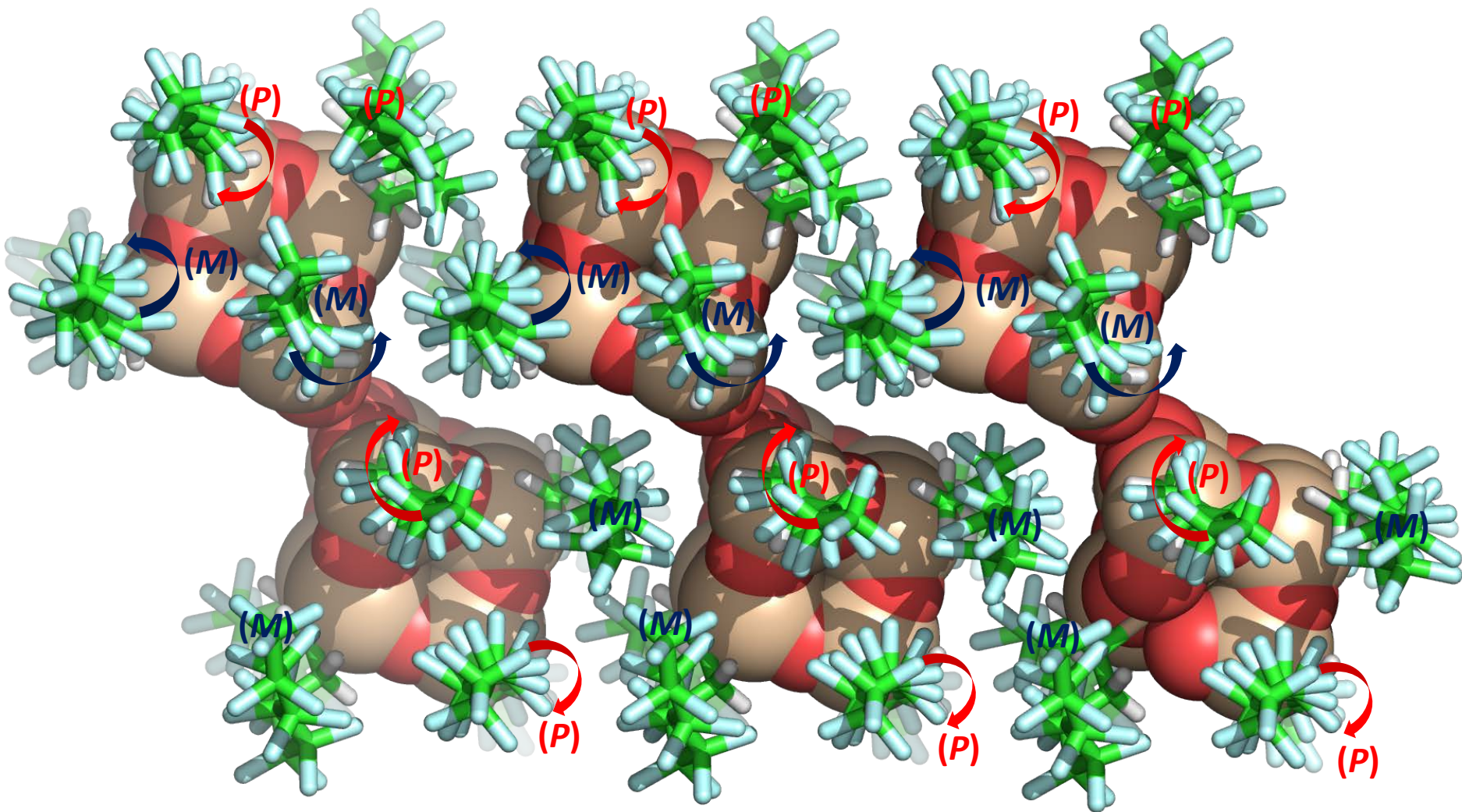


A view from the top

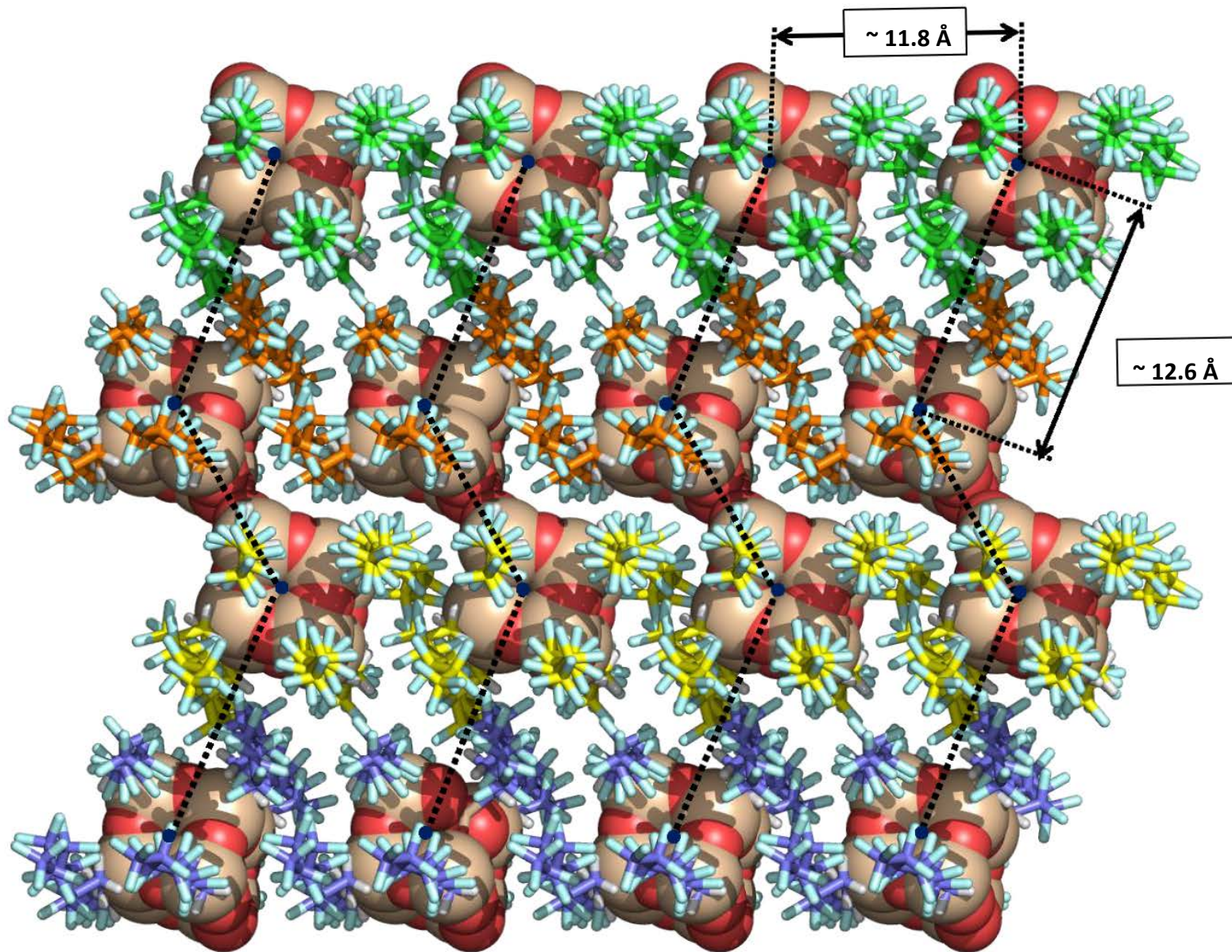
**F-POSS cage dimer (fluoroalkyl side chains shown as golden spheres):
2 intermolecular OH...O - bonds that hold dimer structure together**



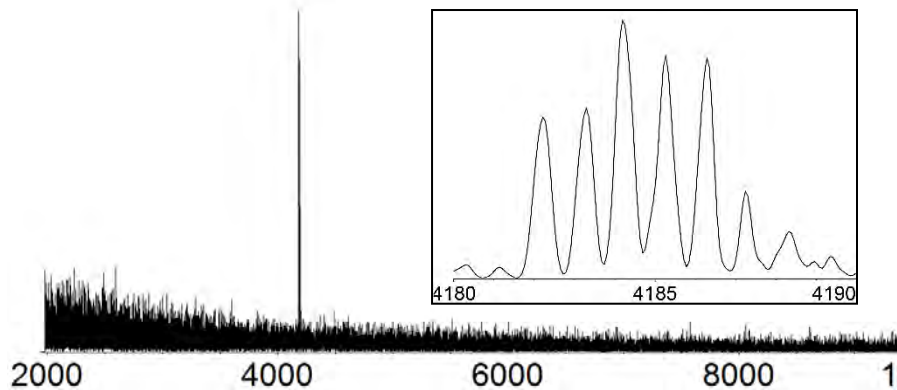
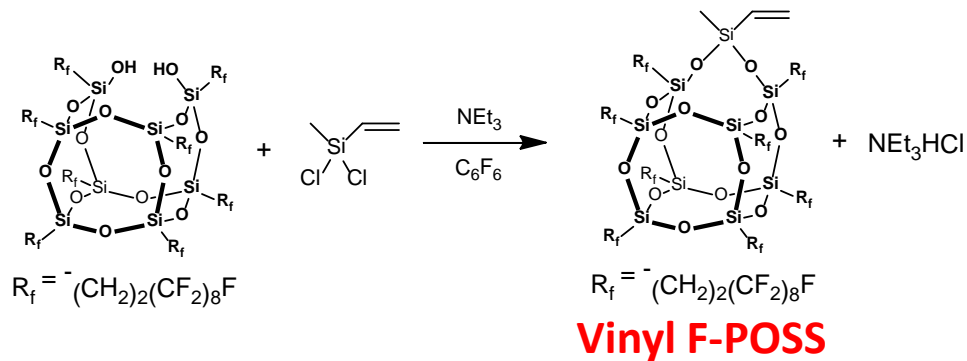
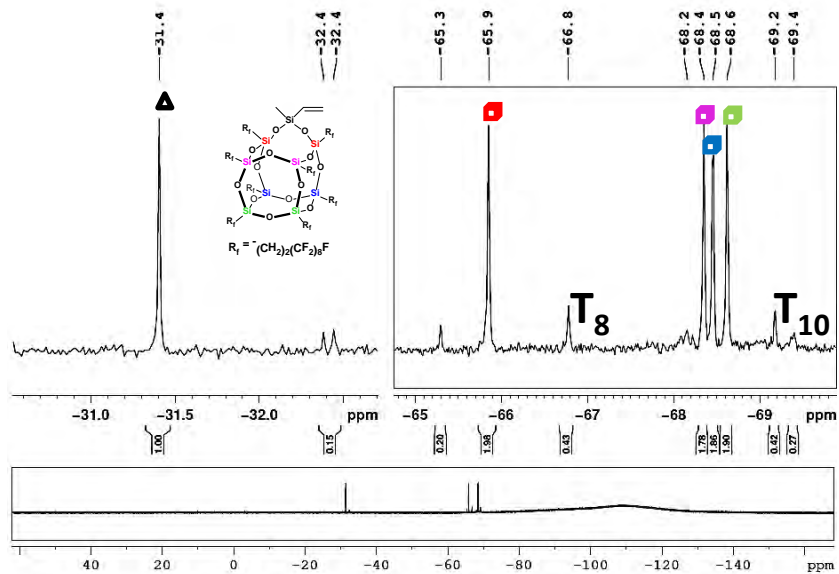
F-POSS cage array: 3 dimers (6 cages) – top view



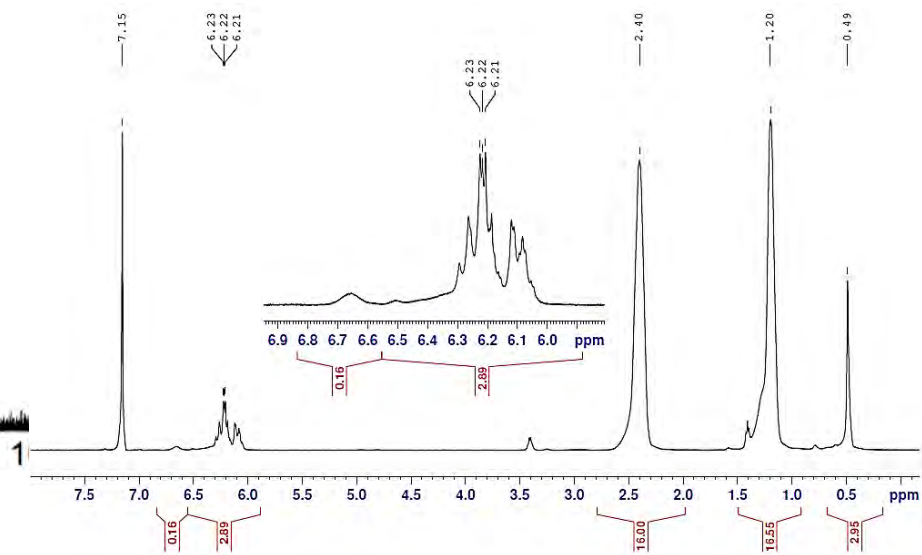
F-POSS cage “zigzag” array (16 cages) – top view



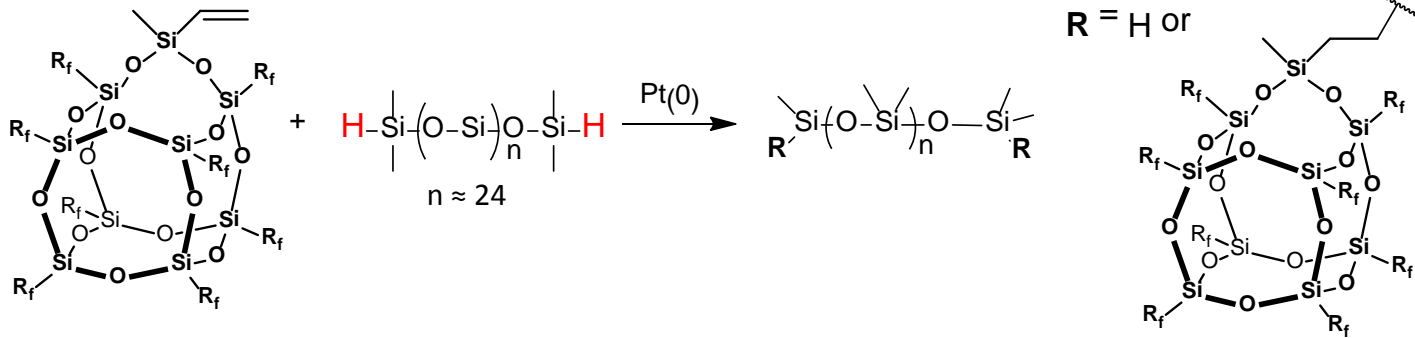
Fluorodecyl₈T₈D₁(methyl, vinyl) POSS



Theoretical $[\text{M}\cdot\text{Ag}]^+ = 4185.71$ Da



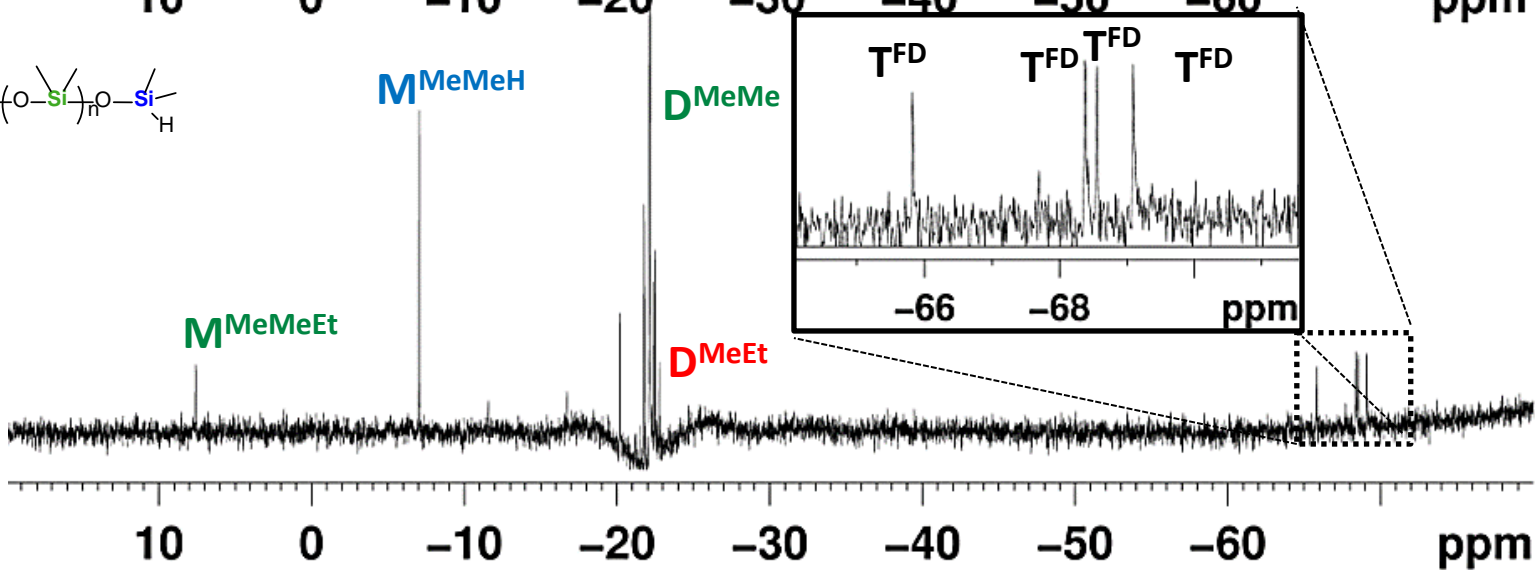
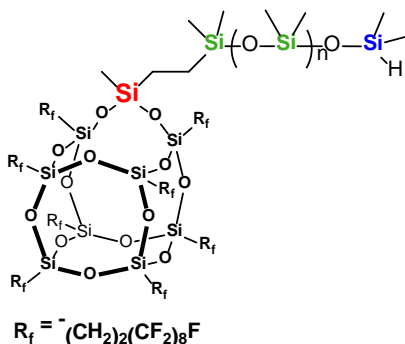
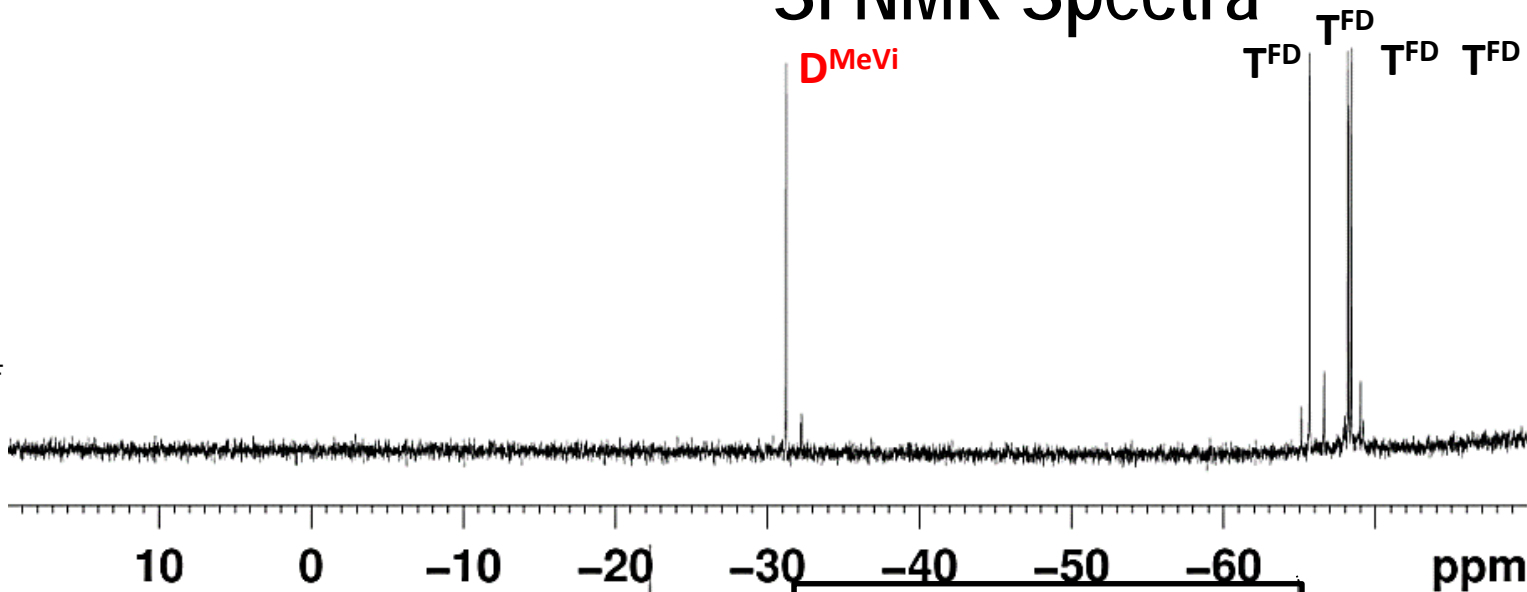
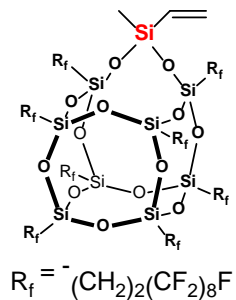
F-POSS Grafting to PDMS via Hydrosilylation



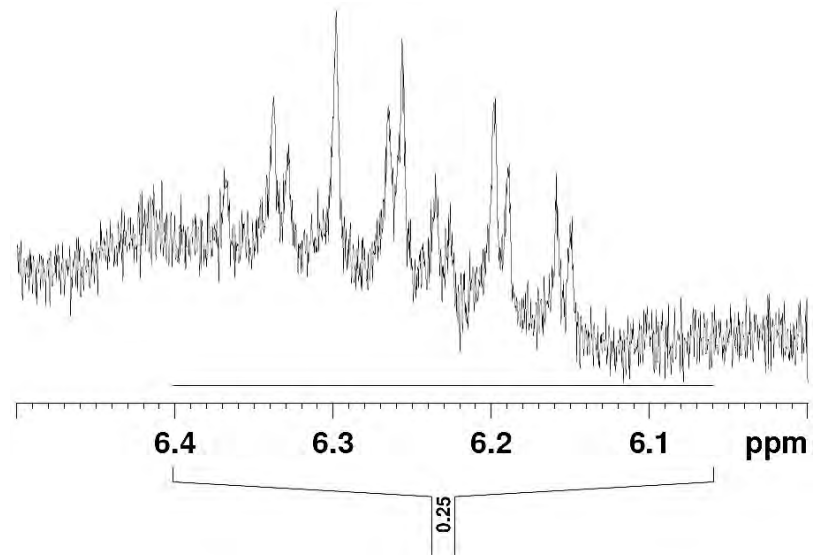
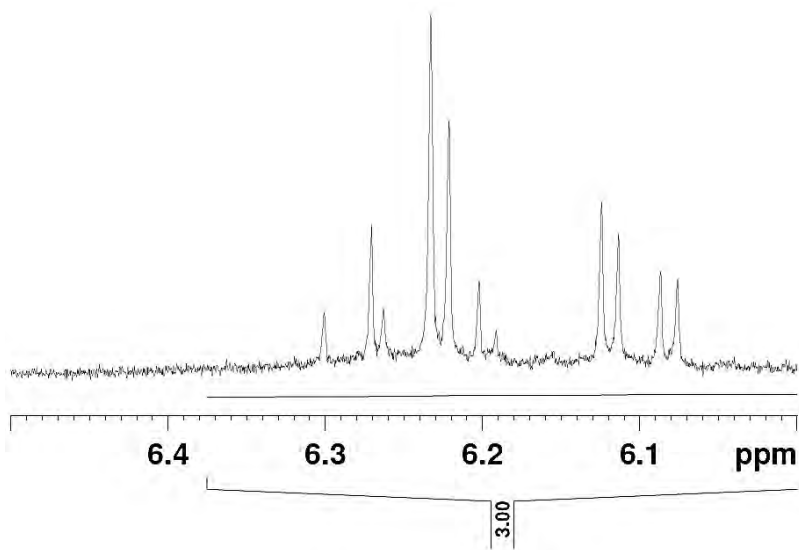
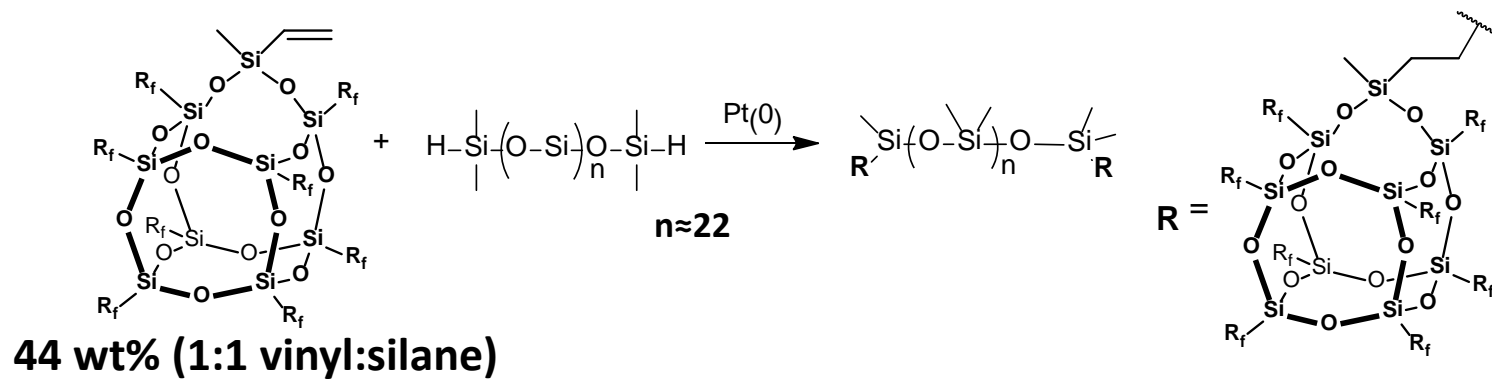
1, 5, 10, 20, 44 wt%

Vinyl: silane, 1:32, 1:8, 1:4, 1:2, 1:1

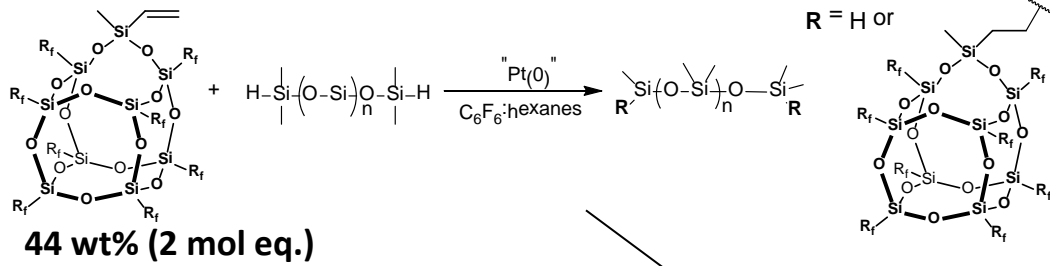
Complete Conversion at 10 wt% F-POSS: ^{29}Si NMR Spectra



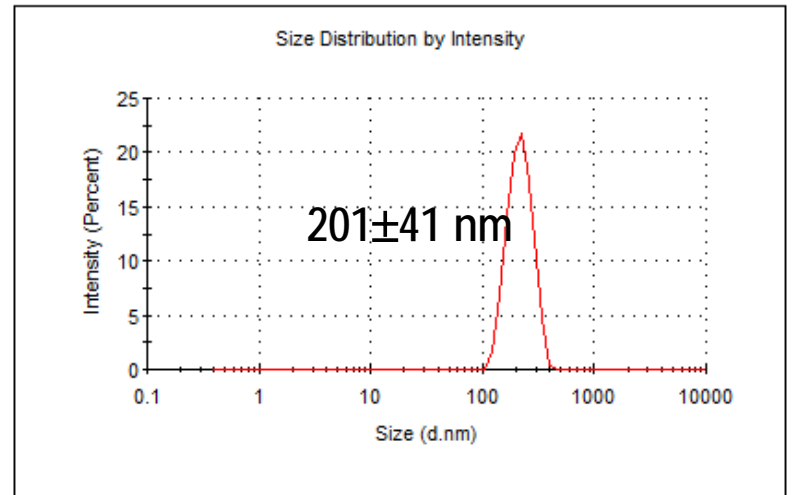
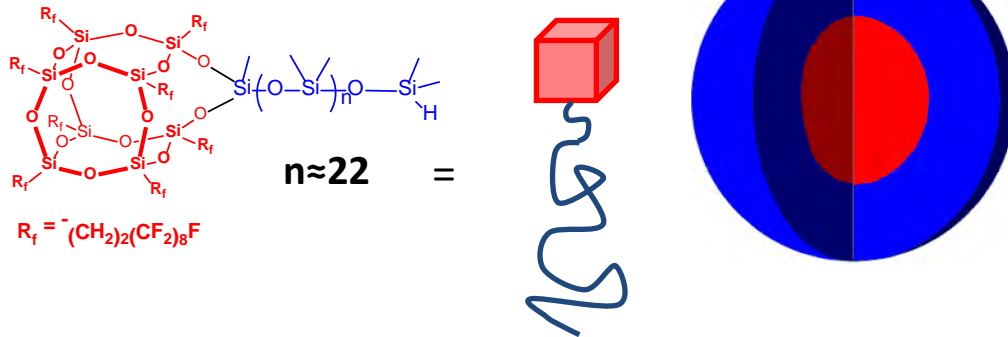
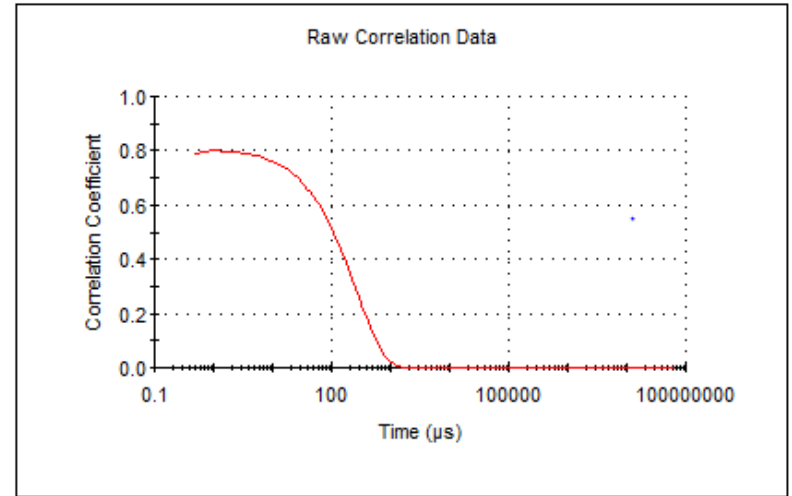
Incomplete Conversion at ≥ 20 wt% F-POSS: ^1H NMR Spectra



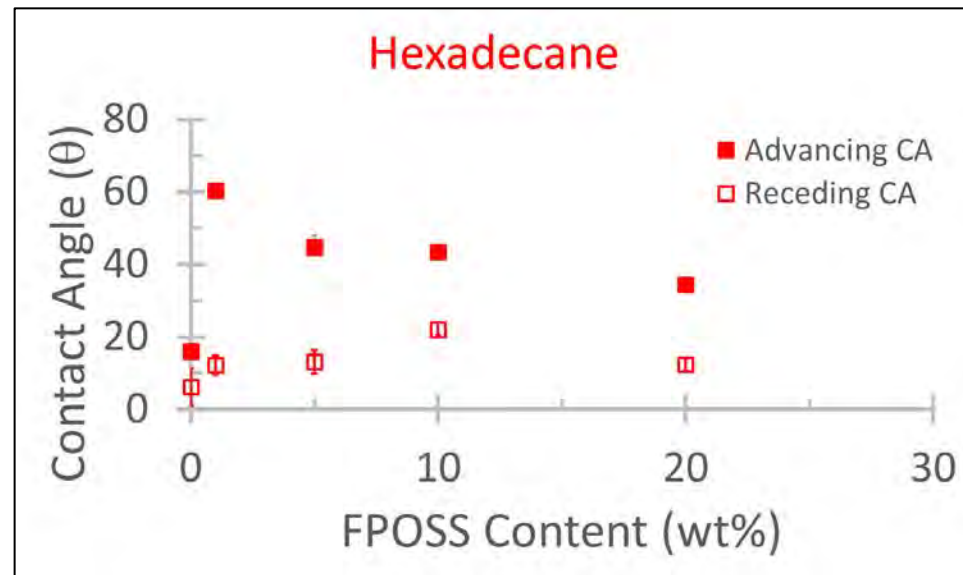
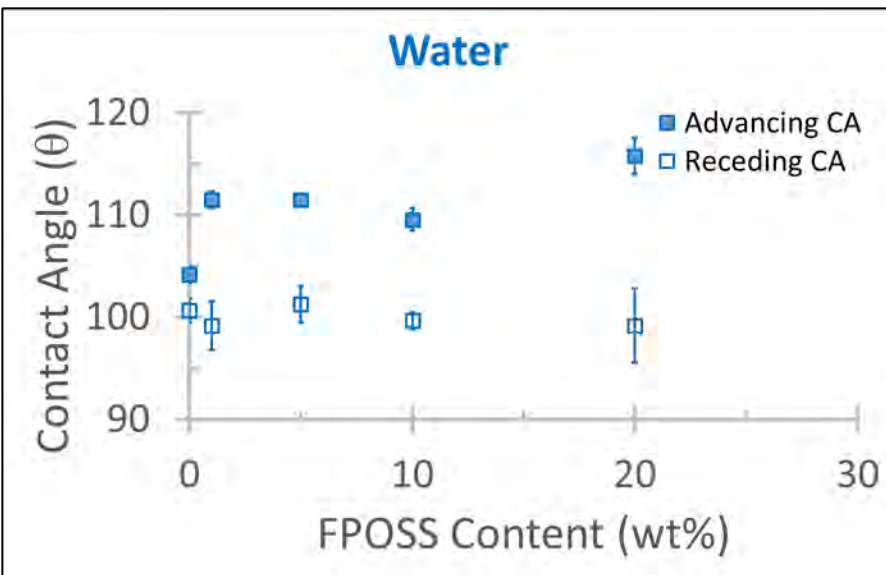
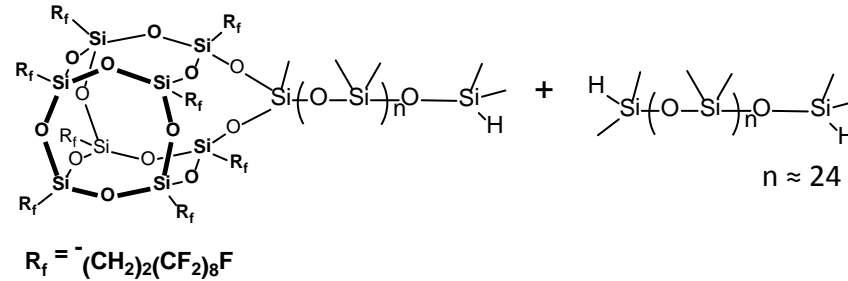
F-POSS PDMS Amphiphile Aggregation



Crude rxn. mix.
 4:1 C₆F₆:hexanes



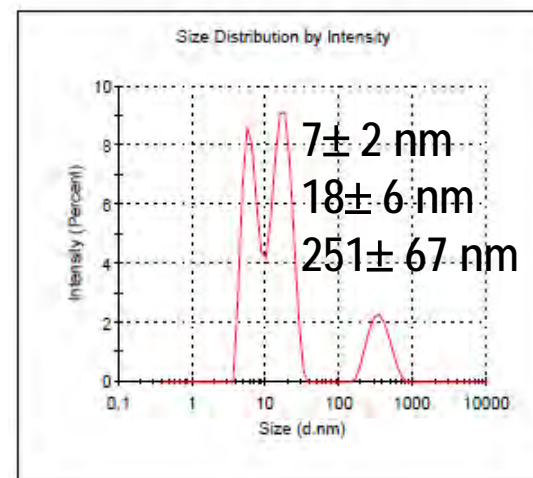
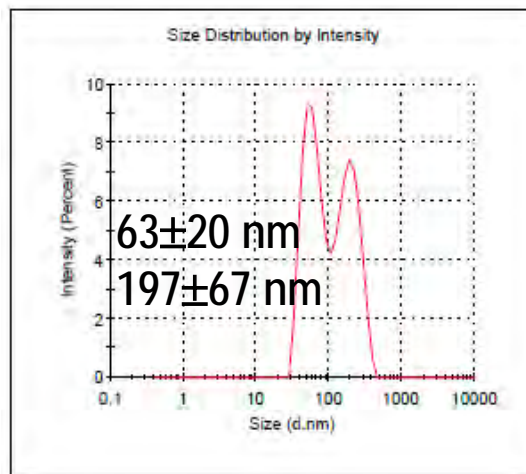
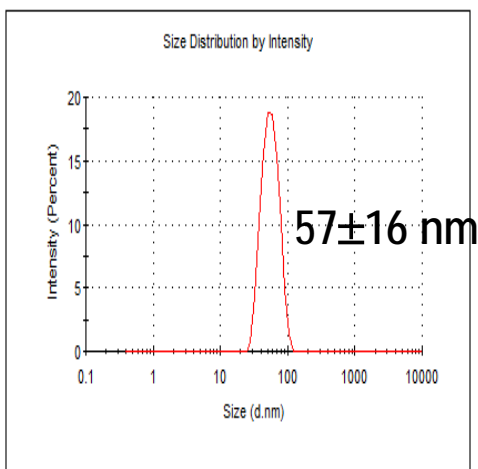
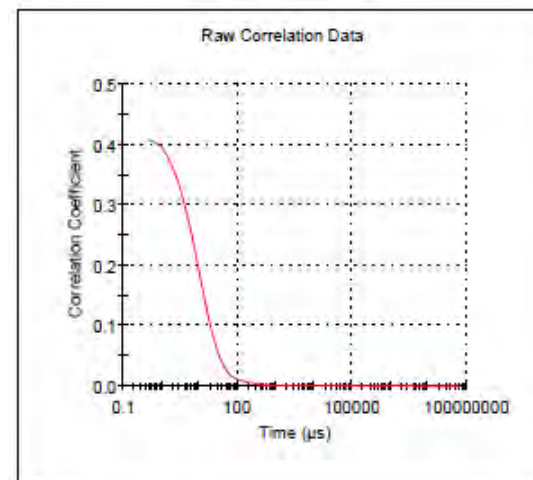
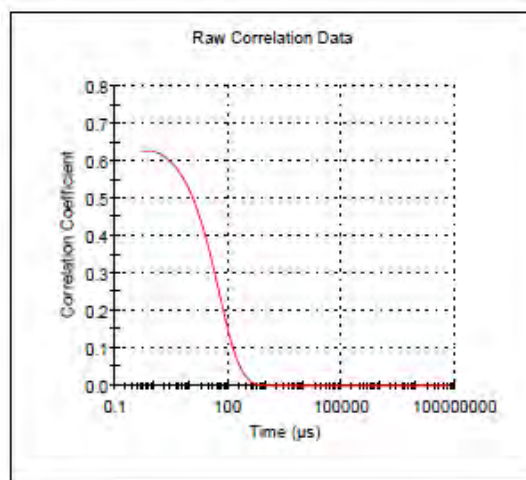
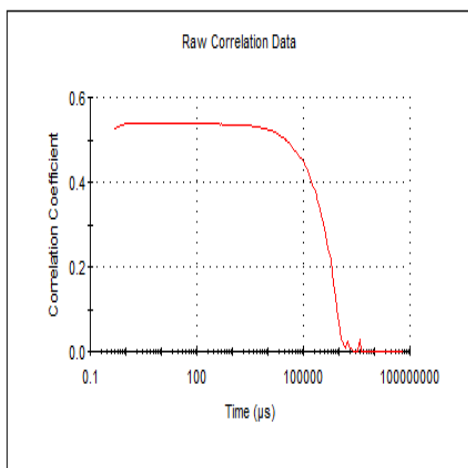
Surface Wetting of Fluorodecyl POSS -PDMS Amphiphiles



Pure fluorodecyl₈T₈ POSS: Water $\theta_{adv}/\theta_{rec} = 124^\circ/116^\circ$

Hexadecane $\theta_{adv}/\theta_{rec} = 80^\circ/61^\circ$

F-POSS PDMS Amphiphile Aggregation: Dynamic Light Scattering

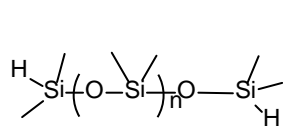


PDMS (1000 cSt)
0.001 M, 25 C

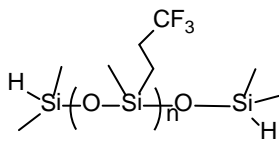
CDCI3
0.001 M, 25 C

AK225
0.001 M, 25 C

Thermal Stability of FPOSS-PDMS Micelles

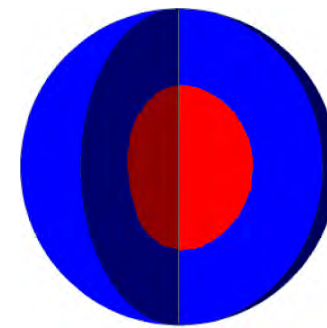
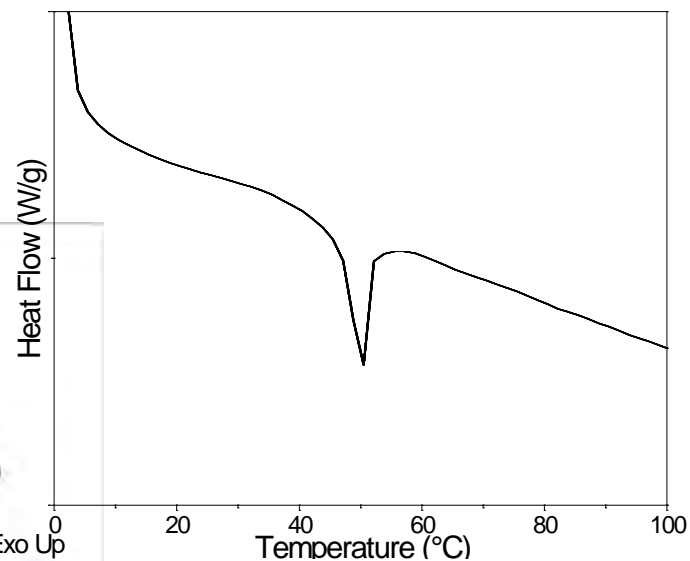
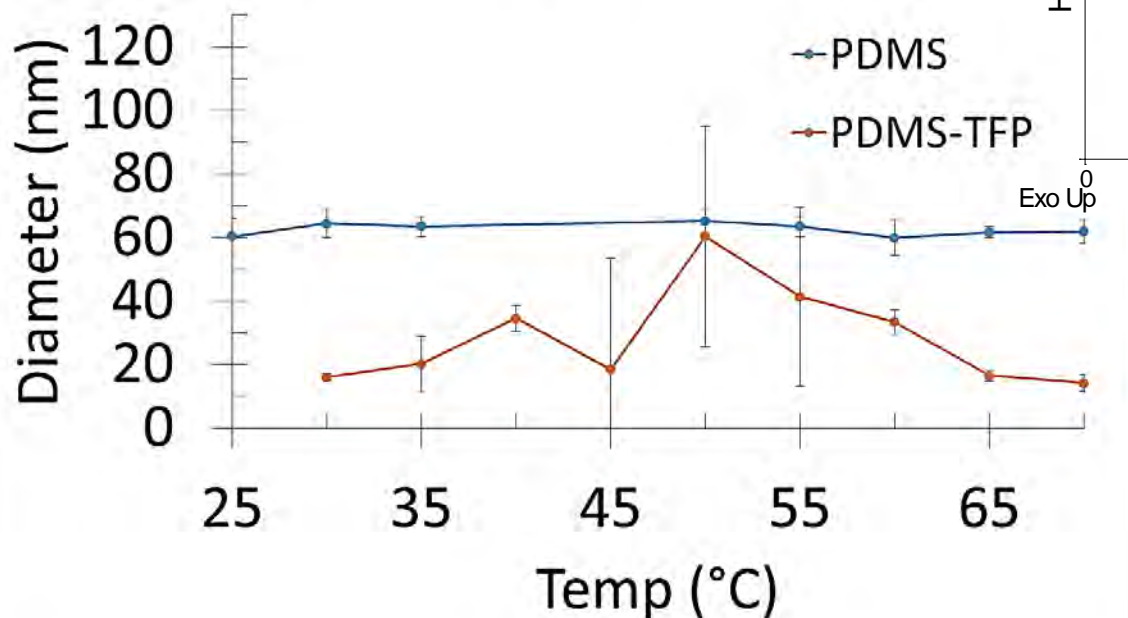


PDMS



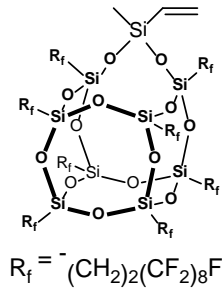
PDMS-TFP

5 wt% FPOSS-PDMS



In fluorinated matrix

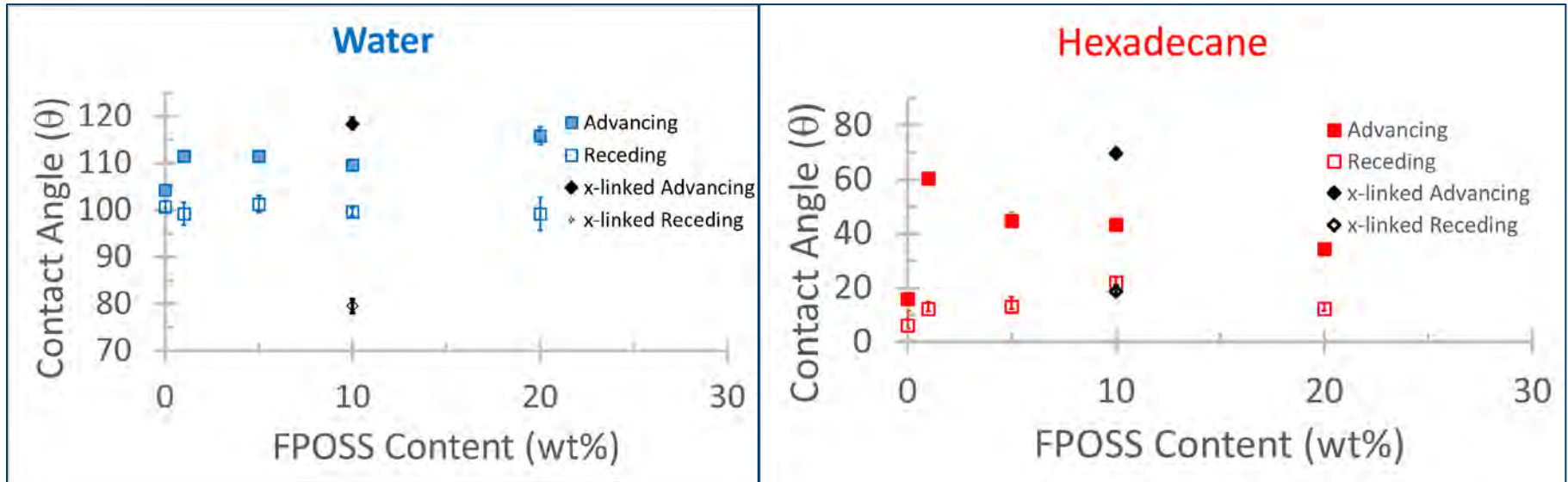
Surface Wetting of Fluorodecyl POSS-Enchained PDMS Elastomers



+ Sylgard 184
10:1 base:curative

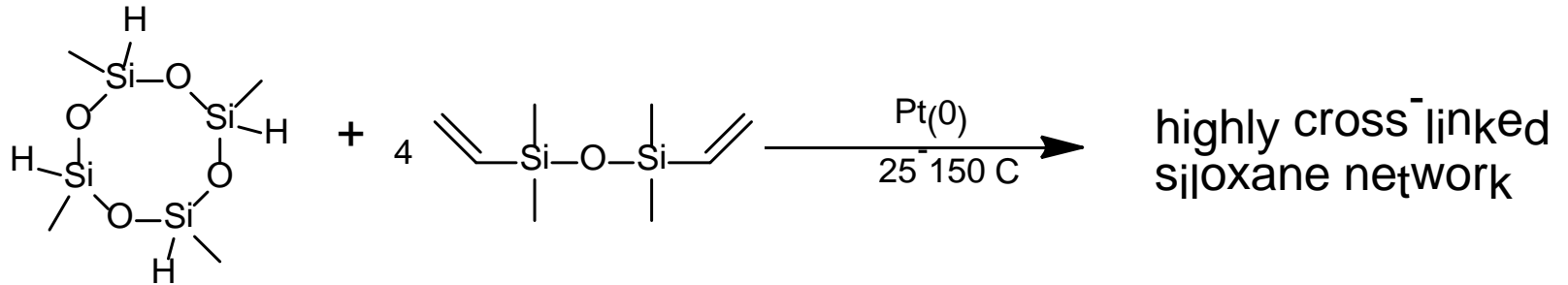
$\xrightarrow[45^\circ\text{C}/17\text{ hrs}]{70^\circ\text{C}/4\text{ hrs}}$

F-POSS enchained PDMS Elastomer
(Black diamonds in figures)



Pure fluorodecyl₈T₈ POSS: Water $\theta_{adv}/\theta_{rec} = 124^\circ/116^\circ$
Hexadecane $\theta_{adv}/\theta_{rec} = 80^\circ/61^\circ$

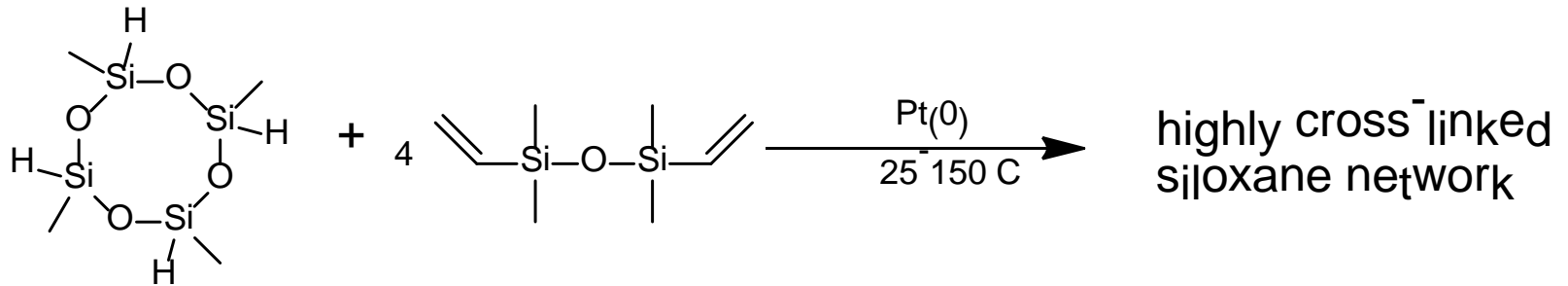
Surface modification of highly crosslinked siloxane networks



ethanol $\theta_{\text{stat}} / \theta_{\text{adv}} / \theta_{\text{rec}} = 8.9$
 22.88 ± 2.46
 0
 isopropanol completely wets and spreads

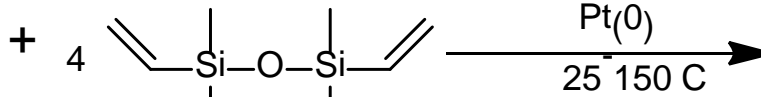
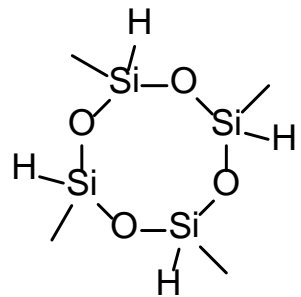
| | $\theta_{\text{adv}} / \theta_{\text{rec}} (^{\circ})$ |
|-------------------|--|
| Water | $99.5 \pm 0.6 / 93.2 \pm 0.5$ |
| Hexadecane | $33.6 \pm 0.3 / 28.9 \pm 0.3$ |
| Heptane | $<5 / 0$ |
| methanol | $29.3 \pm 0.5 / 18.3 \pm 2.4$ |

Surface modification of highly crosslinked siloxane networks



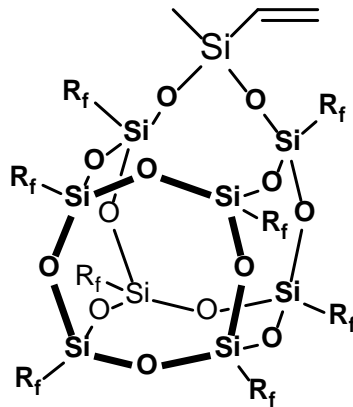
| | $\theta_{adv} / \theta_{rec}$ (°) |
|-------------------|-----------------------------------|
| Water | $99.5 \pm 0.6 / 93.2 \pm 0.5$ |
| Hexadecane | $33.6 \pm 0.3 / 28.9 \pm 0.3$ |
| Heptane | $<5 / 0$ |
| methanol | $29.3 \pm 0.5 / 18.3 \pm 2.4$ |

Surface modification of highly crosslinked siloxane networks



highly cross-linked siloxane network w/ covalently bound FPOSS surface

+ 1 Wt%



(0.63 wt% fluorine) $R_f = \text{-(CH}_2\text{)}_2\text{(CF}_2\text{)}_8\text{F}$

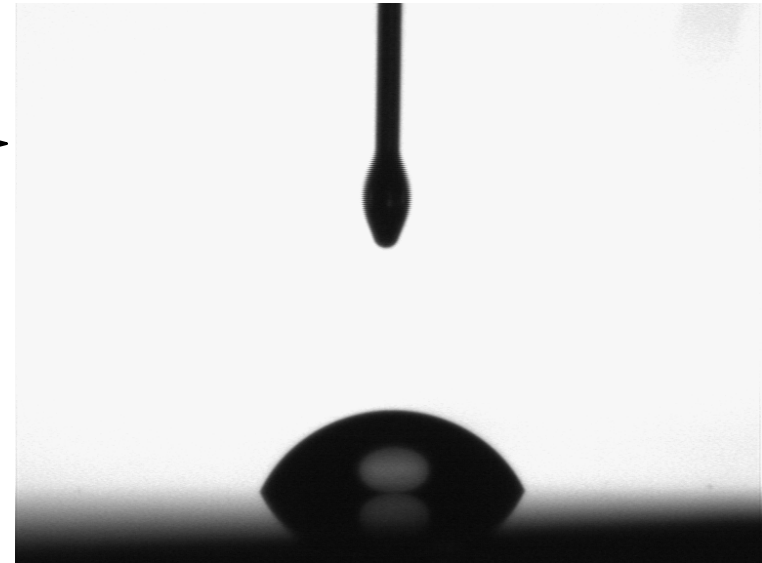
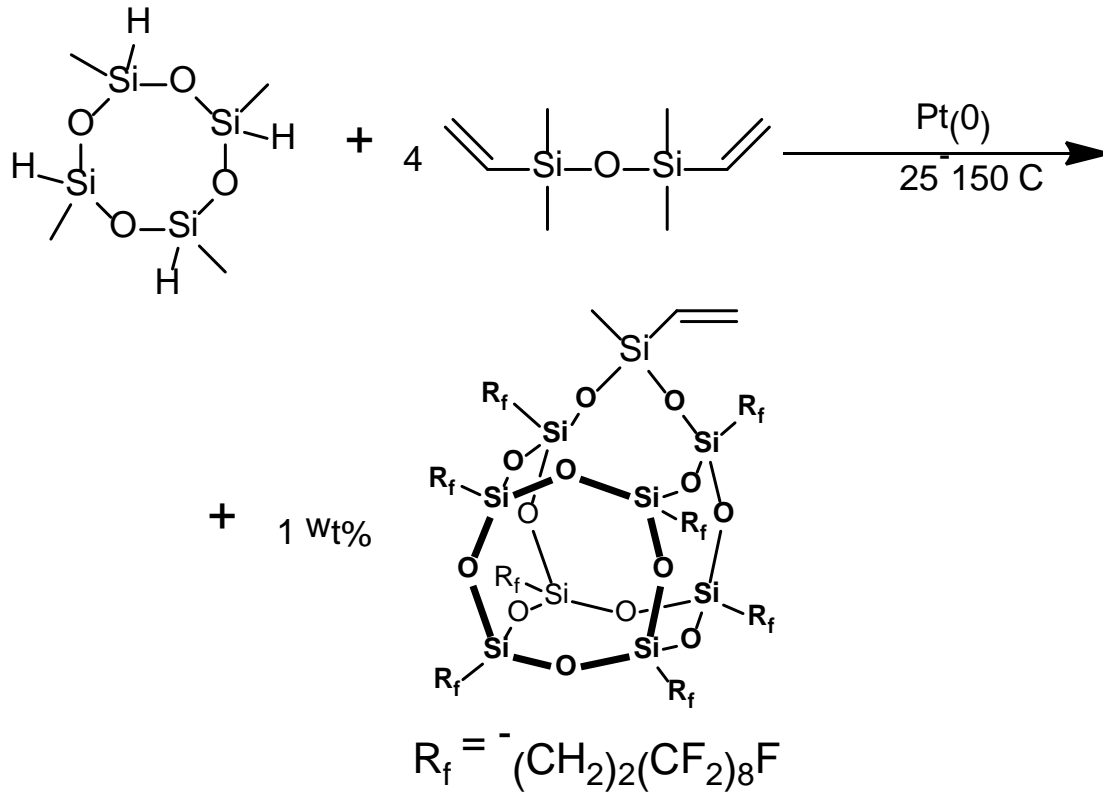
isopropanol $\Theta_{\text{stat}} / \Theta_{\text{adv}} / \Theta_{\text{rec}} = 54.35 \pm 4.41$
 70.94 ± 1.05
 40.5 ± 0.86

ethanol $\Theta_{\text{stat}} / \Theta_{\text{adv}} / \Theta_{\text{rec}} = 60.588 \pm 7.62$
 73.97 ± 1.0075
 41.4 ± 1.2725

$\Theta_{\text{adv}} / \Theta_{\text{rec}} (\text{°})$

| | |
|-------------------|-------------------------------|
| Water | $116.5 \pm 0.3 / 102 \pm 1.1$ |
| Hexadecane | $76.3 \pm 0.5 / 62 \pm 1.0$ |
| Heptane | $56.1 \pm 0.9 / 39.2 \pm 1.2$ |
| methanol | $75.2 \pm 0.9 / 49.9 \pm 1.5$ |

Surface modification of highly crosslinked siloxane networks



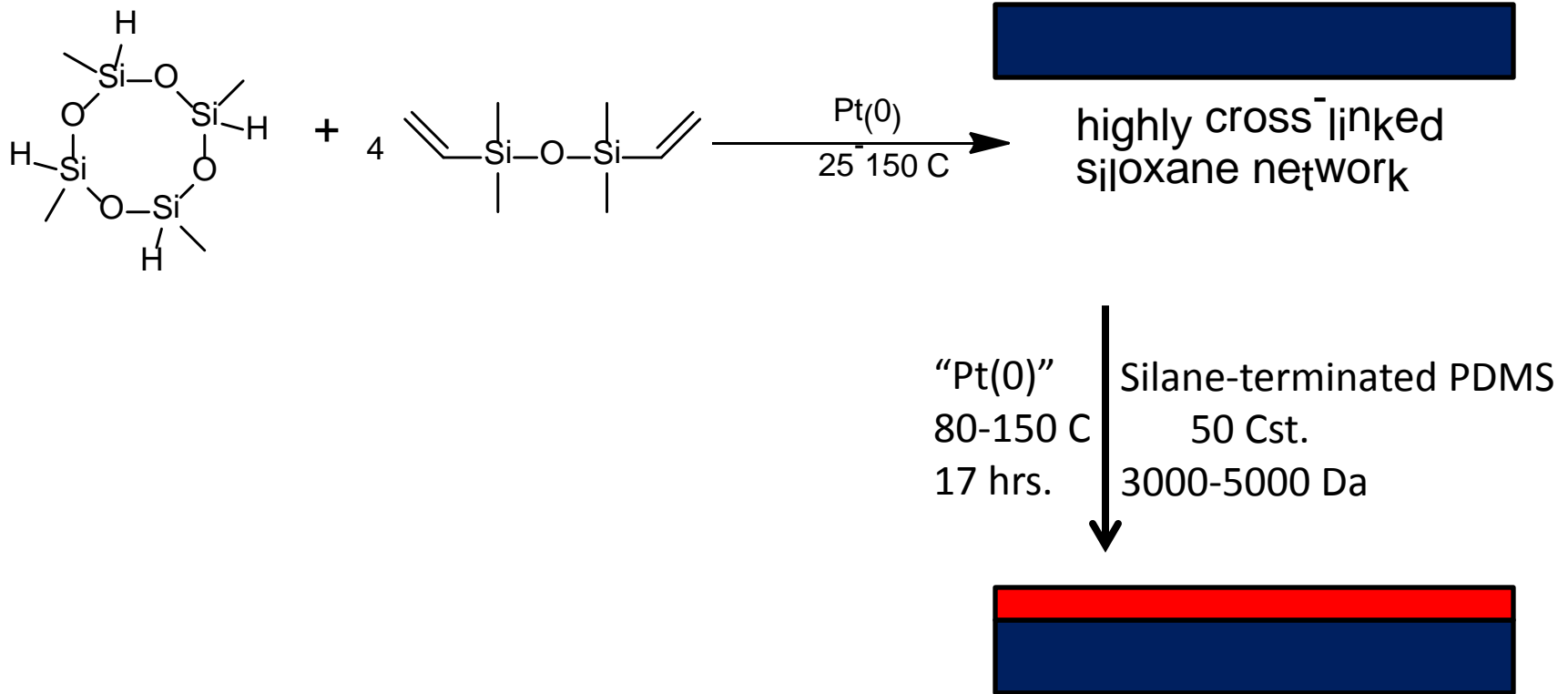
$\theta_{\text{adv}} / \theta_{\text{rec}} (^{\circ})$

| | |
|-------------------|-------------------------------|
| Water | $116.5 \pm 0.3 / 102 \pm 1.1$ |
| Hexadecane | $76.3 \pm 0.5 / 62 \pm 1.0$ |
| Heptane | $56.1 \pm 0.9 / 39.2 \pm 1.2$ |
| methanol | $75.2 \pm 0.9 / 49.9 \pm 1.5$ |

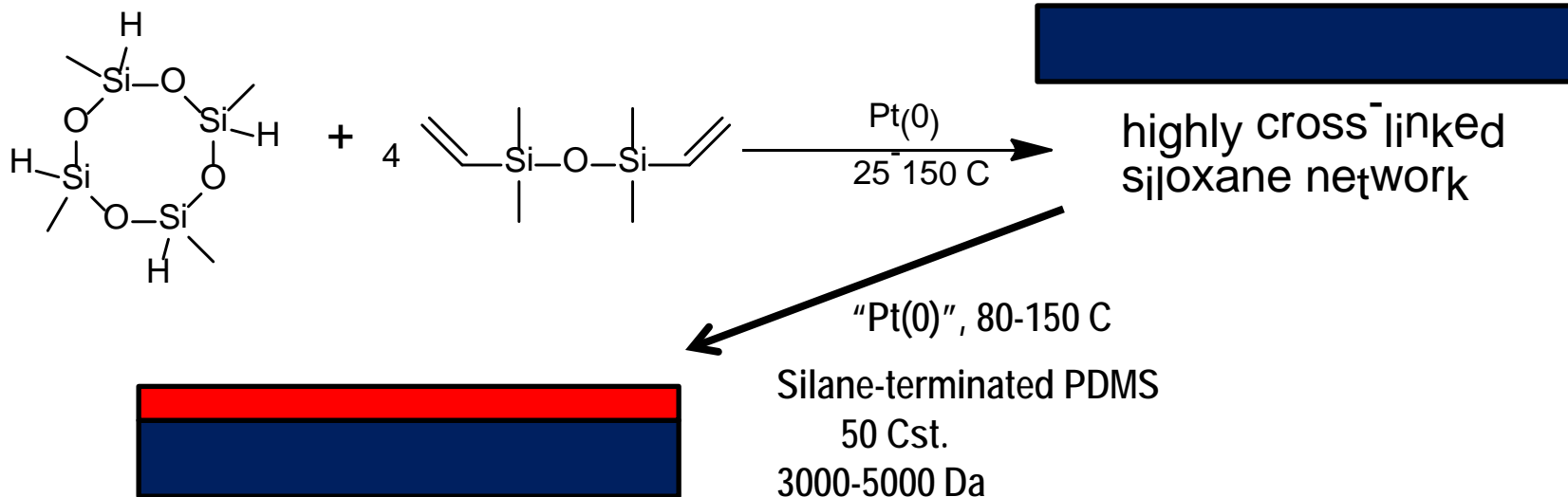
What about “liquid-like” surfaces and
post-cure surface modification?

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Post-cure surface modification of highly crosslinked siloxane networks with silane-terminated oligo(dimethylsiloxane)



Post-cure surface modification of highly crosslinked siloxane networks with silane-terminated oligo(dimethylsiloxane)



| | $\theta_{adv} / \theta_{rec}$ (°) |
|-------------------|-----------------------------------|
| Water | $110.7 \pm 0.3 / 89.4 \pm 0.5$ |
| Hexadecane | $47.8 \pm 0.4 / 17.5 \pm 0.7$ |
| Heptane | $7.3 \pm 1.9 / 0$ |
| methanol | $40.8 \pm 0.4 / 35.5 \pm 0.6$ |

| | $\theta_{adv} / \theta_{rec}$ (°) |
|-------------------|-----------------------------------|
| Water | $99.5 \pm 0.6 / 93.2 \pm 0.5$ |
| Hexadecane | $33.6 \pm 0.3 / 28.9 \pm 0.3$ |
| Heptane | $<5 / 0$ |
| methanol | $29.3 \pm 0.5 / 18.3 \pm 2.4$ |