



Synthesis and Characterization of Fluoropropyl POSS



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Report Documentation Page

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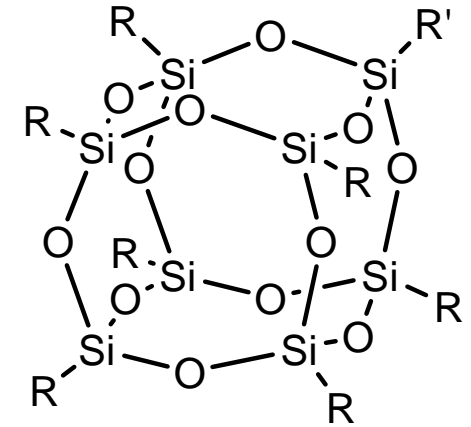
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Outline



- **POSS**
- **FluoroPOSS Synthesis**
- **Fluoropropyl POSS Synthesis**
- **Conclusion**

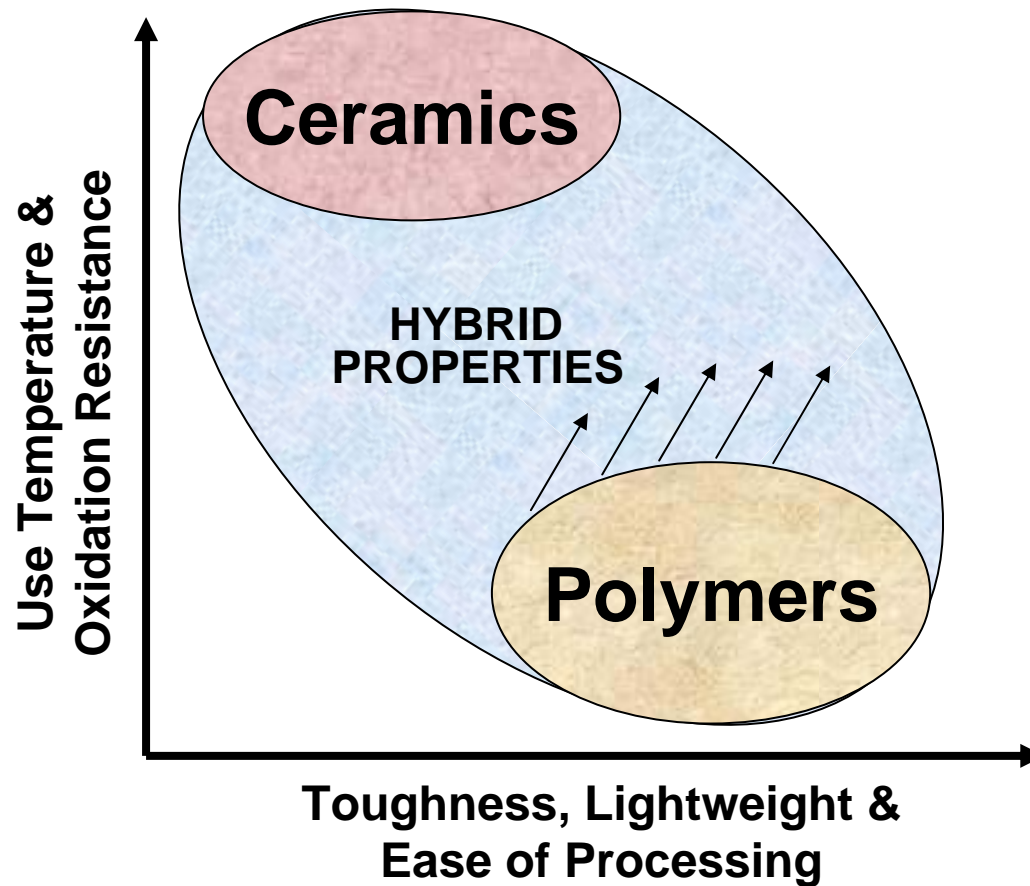




Hybrid inorganic/organic polymers



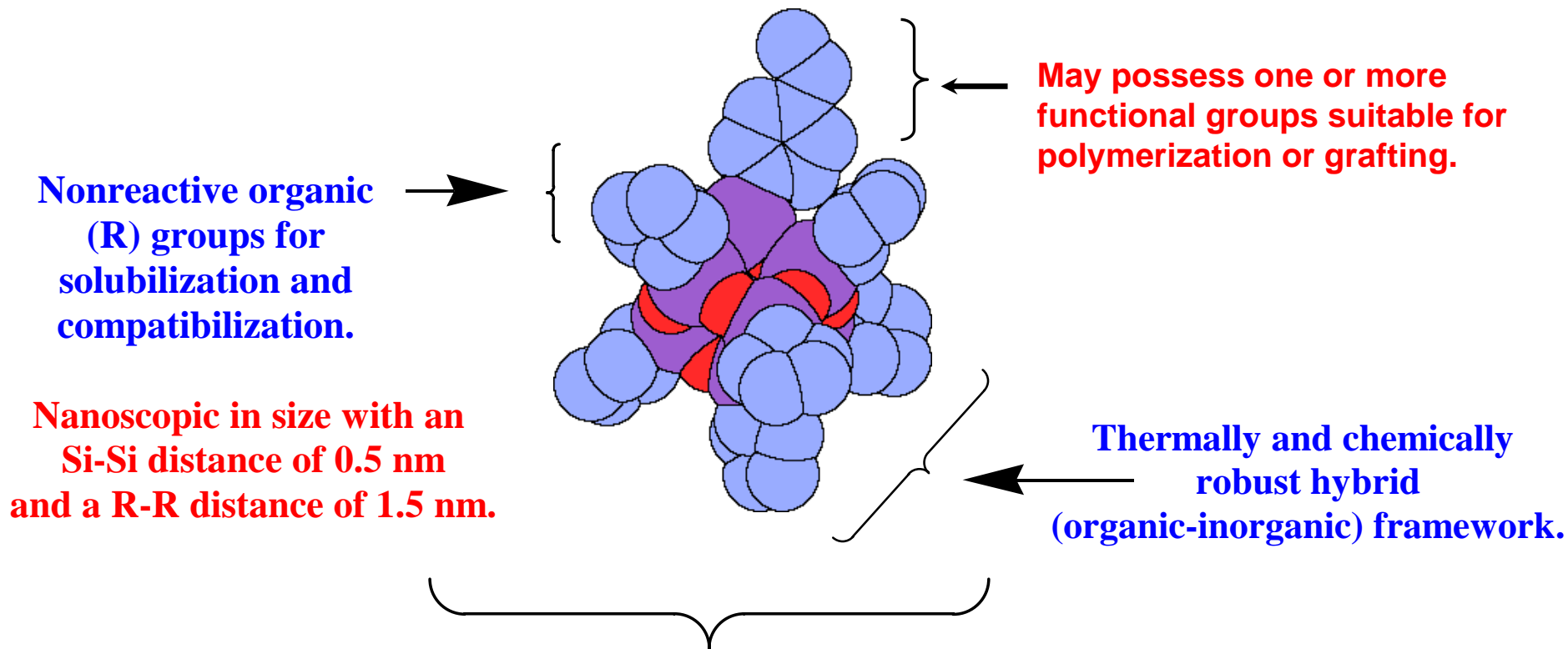
Goal: Develop High Performance Polymers that REDEFINE material properties



• Hybrid plastics bridge the differences between ceramics and polymers



Anatomy of a POSS nanostructure



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



Fluoropolymer seals



Integrated High Payoff Rocket Propulsion Technology (IHDRPT) Program

- National program focused by OSD/DDR&E/AT and coordinated with AF, NASA, Navy, Army, and industry.
- Goal-oriented technology development program for rocket propulsion.
 - Double the performance of rocket propulsion systems over current state of the art.
 - Decrease the cost of access to space for commercial and military sectors.
- Fluoropolymers are used in many seal applications in liquid rocket engines
 - Polychlorotrifluoroethylene (PCTFE)
 - Fluorinated Ethylene/Propylene (FEP)
- Fluoropolymer research is designed to:
 - Improve Isp
 - Improve Thrust to Weight ratio
 - Reduce Support Costs
 - Lengthen Mean Time Between Removal





Targeted shortfalls



Mechanical Problems

- During operation, wear ring seals preventing propellant flow from bypassing the impeller blades in the SSME turbopump warp, causing an estimated 1.5 sec loss of delivered I_{sp} .

(I_{sp} and **Thrust to Weight**)

$$1.5 \text{ sec } I_{sp} \times 3 \text{ SSMEs} \times 1000 \text{ lb payload/sec } I_{sp} \times \$8,000/\text{lb payload} =$$

\$36,000,000 per launch

- Creep (cold flow of materials under load) causes the deformation of fluoropolymer seals in LREs, limiting their functional use time. (**Mean Time Between Removal**)

Surface Property Problems

- Fuel wetting of fluoropolymer seals allows fuel to leak past seals. A costly nitrogen purge is necessary to prevent fuel contact with oxidizer. (**Reduce Support Costs and Thrust to Weight**)

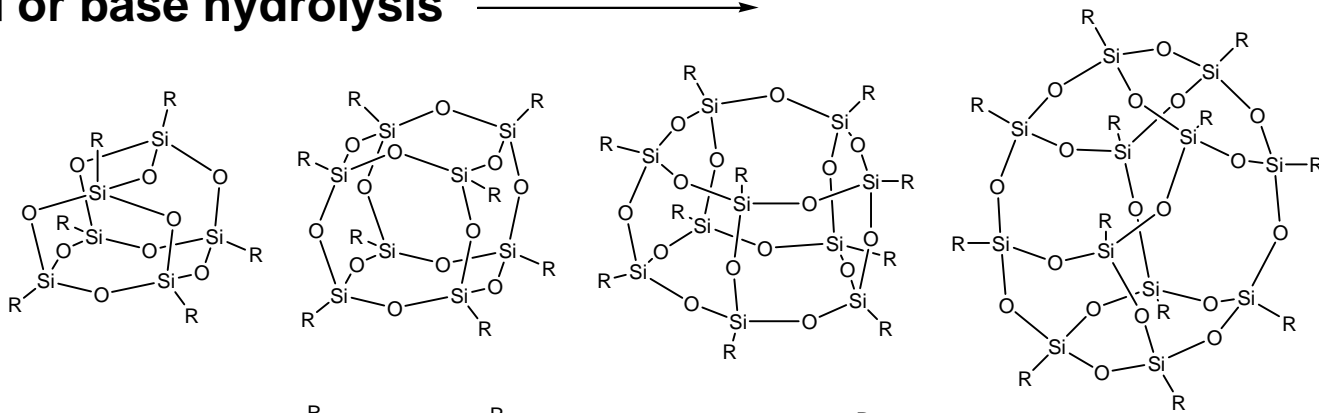


POSS synthesis

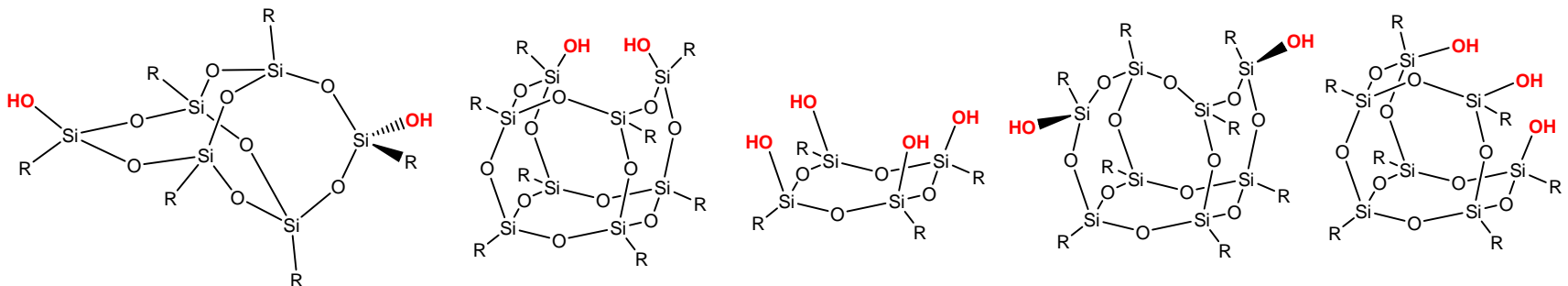
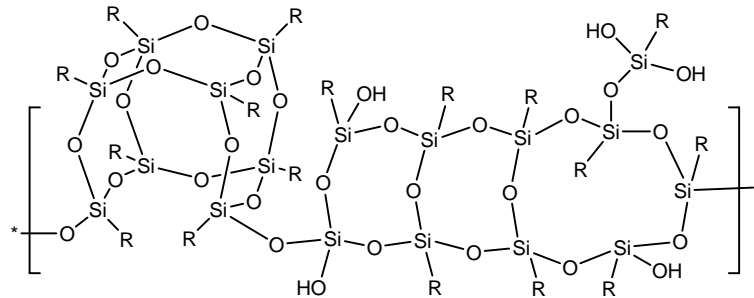


RSiX_3 acid or base hydrolysis \longrightarrow

Blendables



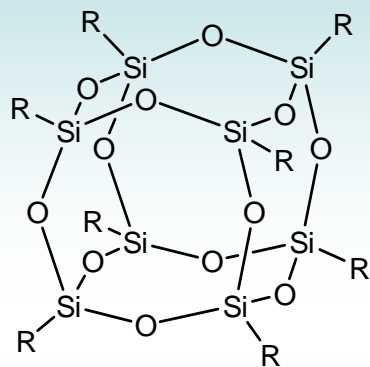
Resin



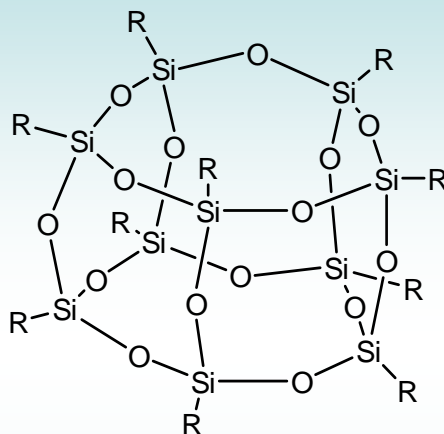
Incompletely condensed cages



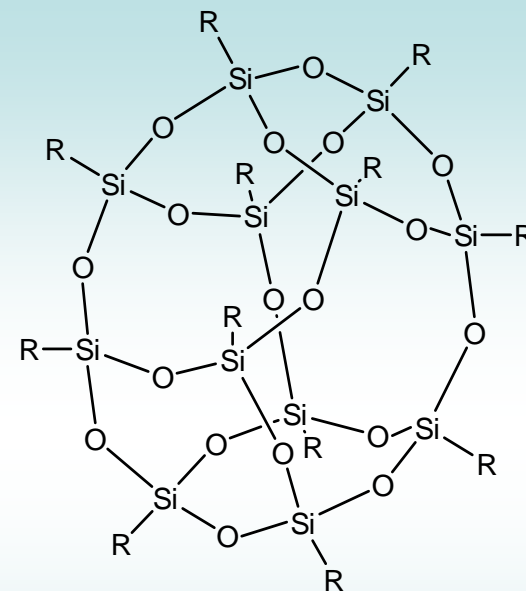
Typical isomers produced



T₈



T₁₀

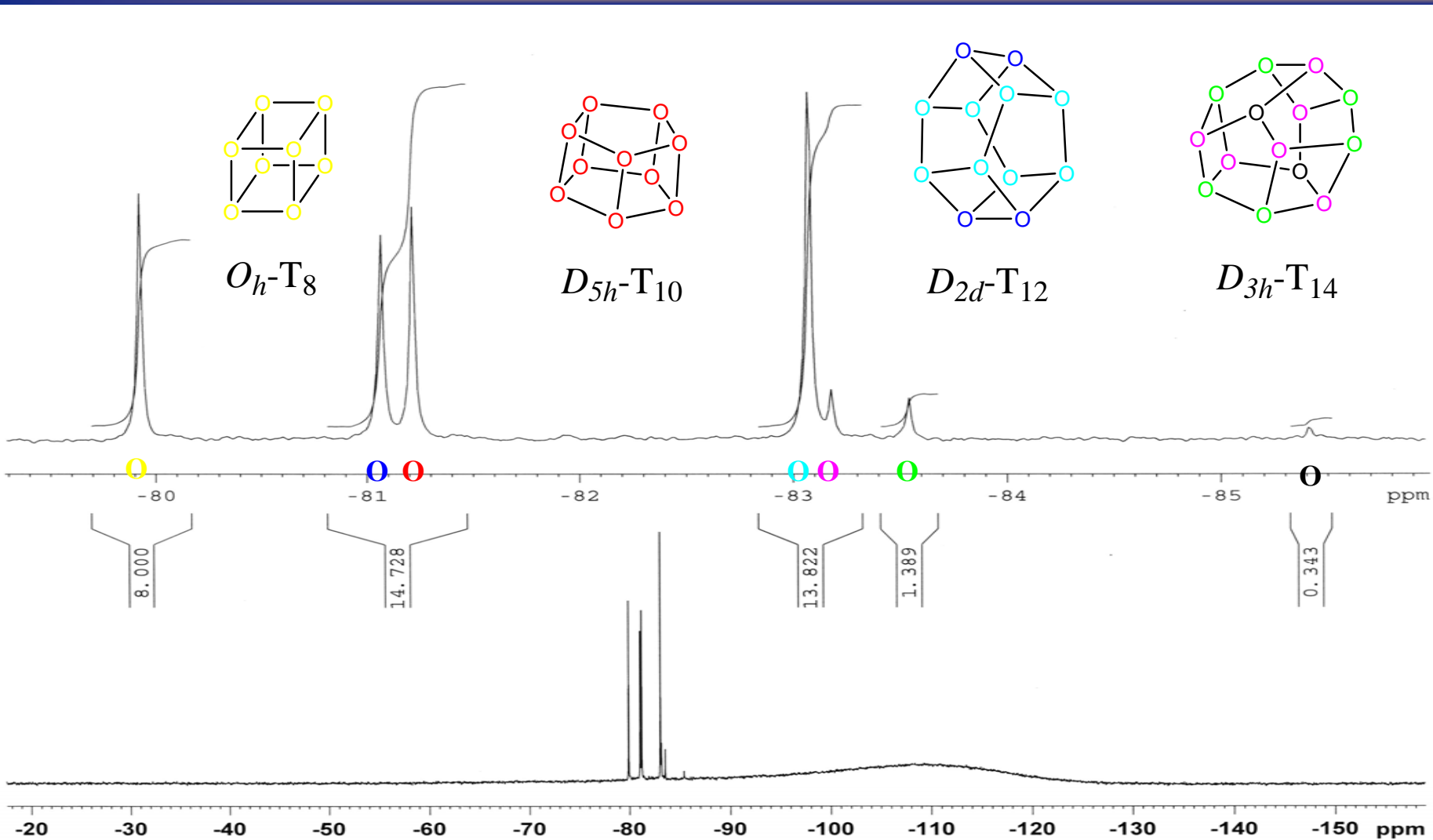


T₁₂

Most common compounds found in a cage mixture



²⁹Si NMR spectrum of cage mixture





²⁹Si NMR of Fluorohexyl cage mixture



Fluorohexyl Poss 02-08-05

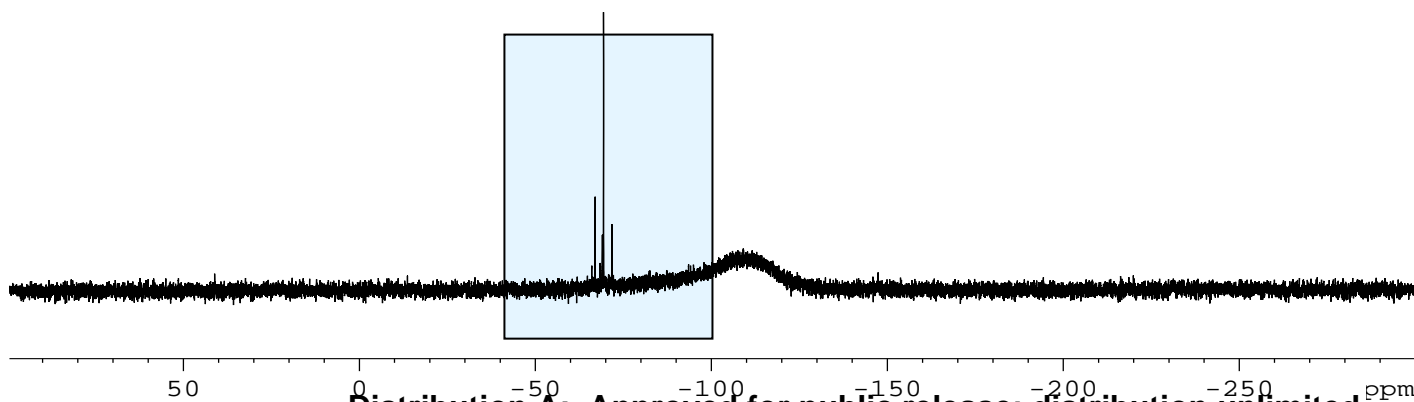
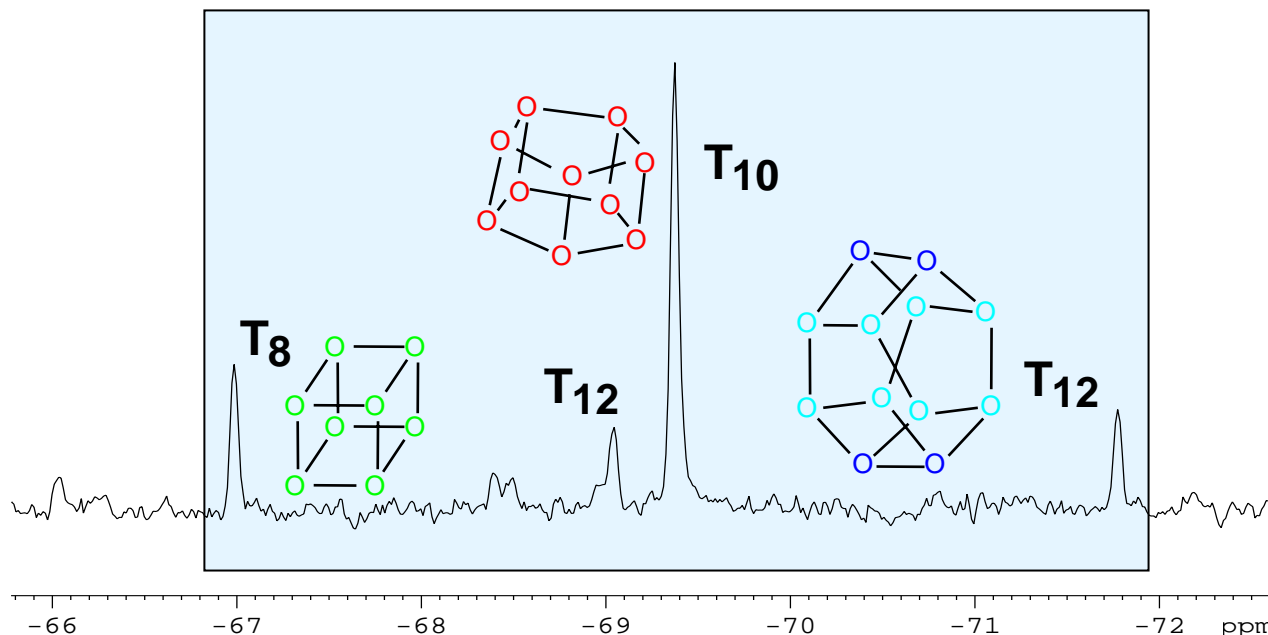
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SOLVENT Acetone
NS 385
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FIDRES 0.363304 Hz
AQ 1.3763061 sec
RG 11585.2
DW 21.000 usec
DE 6.00 usec
TE 300.0 K
D1 8.00000000 sec
d11 0.03000000 sec

==== CHANNEL f1 =====
NUC1 29Si
P1 10.00 usec
PL1 -3.00 dB
SFO1 59.6214106 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 20.00 dB
SFO2 300.1312005 MHz

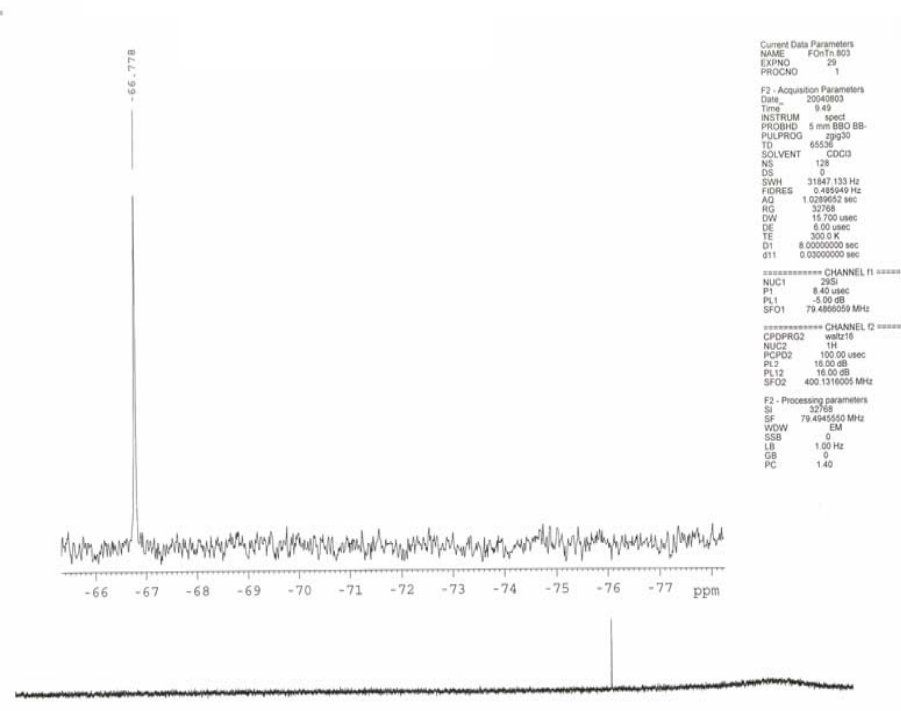
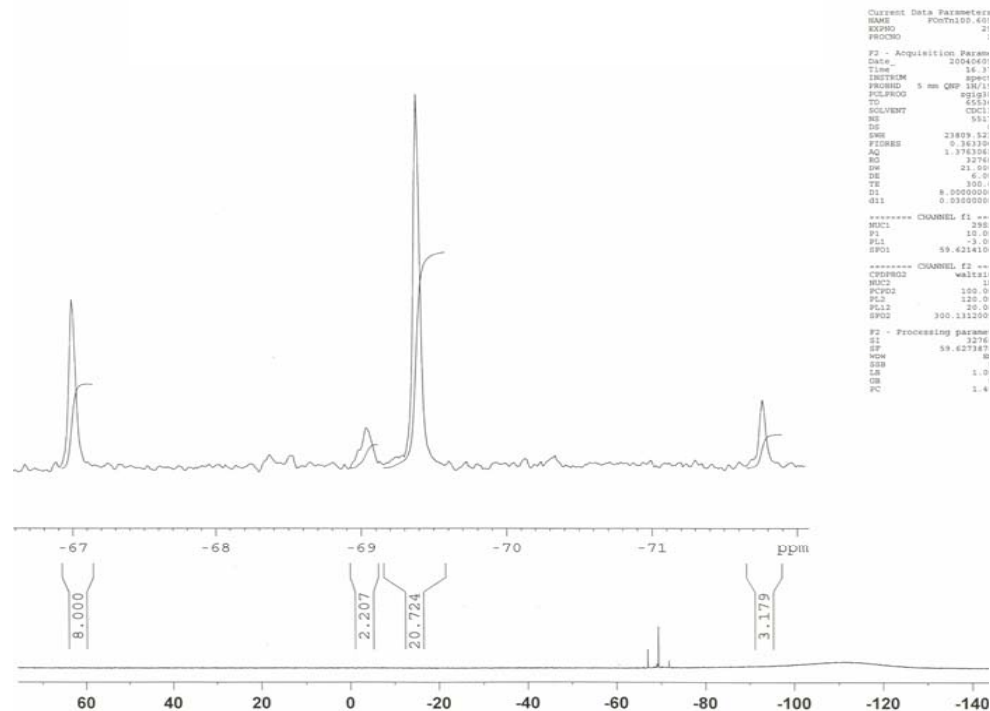
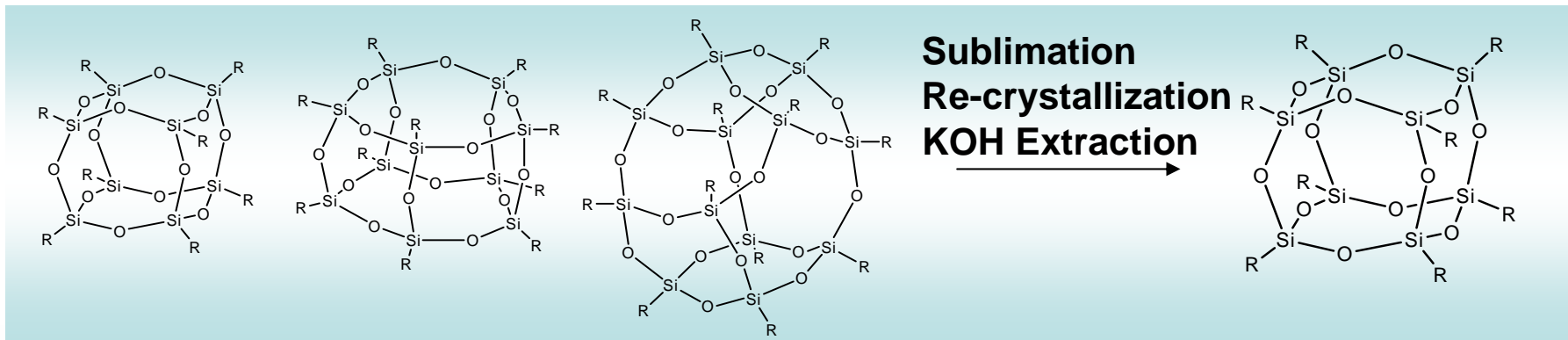
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GB 0
PC 1.40



Distribution A: Approved for public release; distribution unlimited

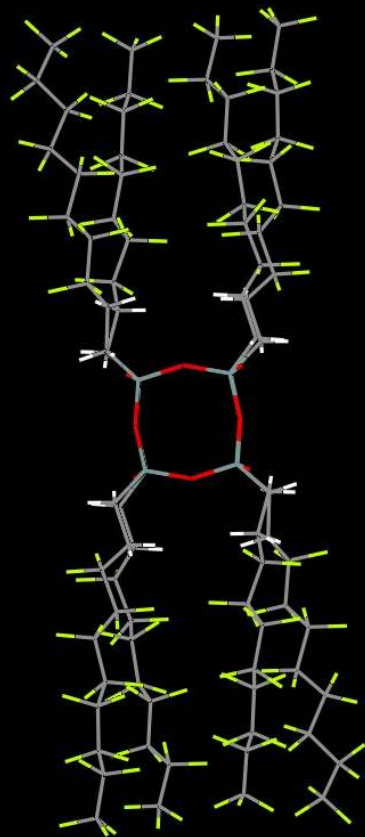


Redistribution reaction

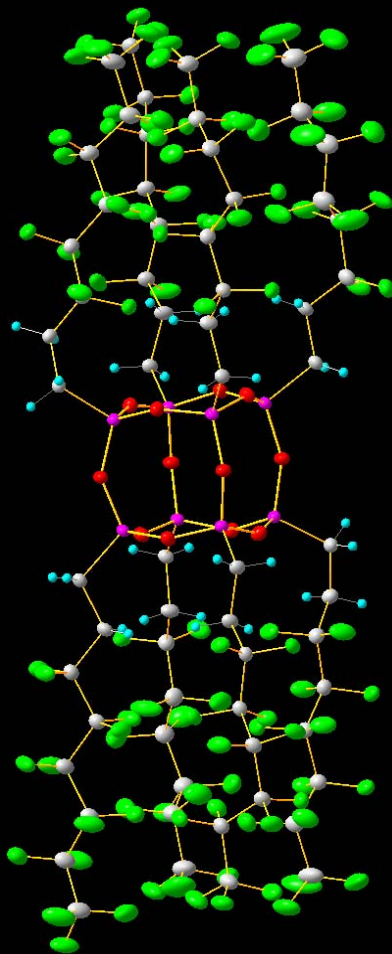




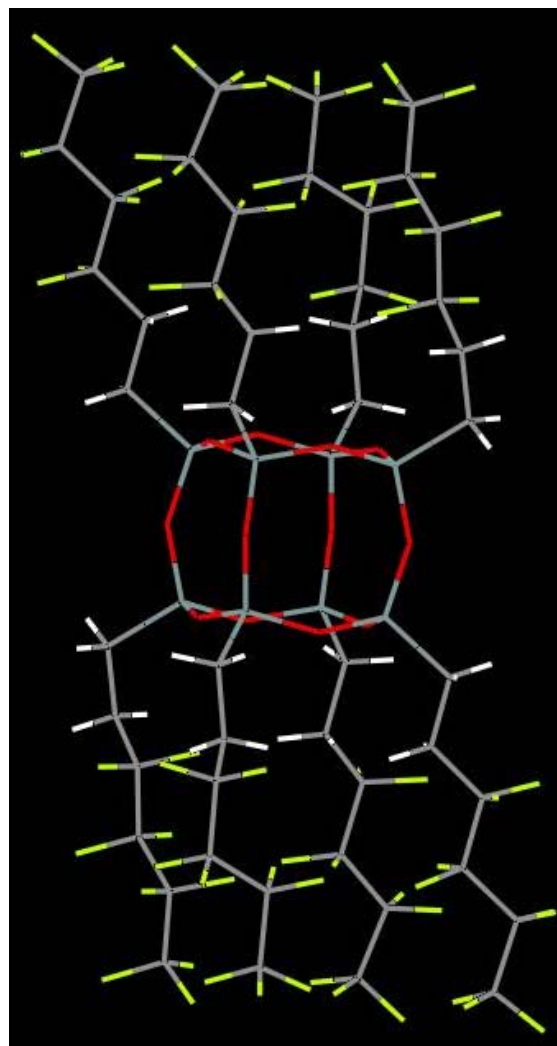
Crystal structures of FluoroPOSS₈T₈



Decyl-



Octyl-



Hexyl-

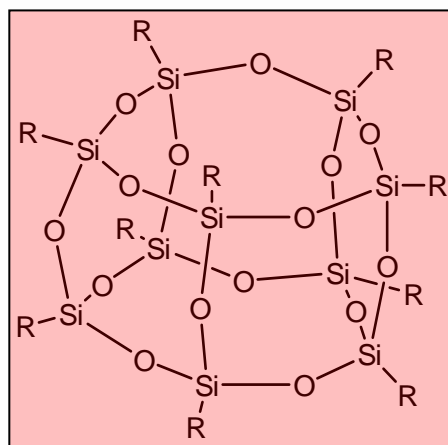
Distribution A: Approved for public release; distribution unlimited



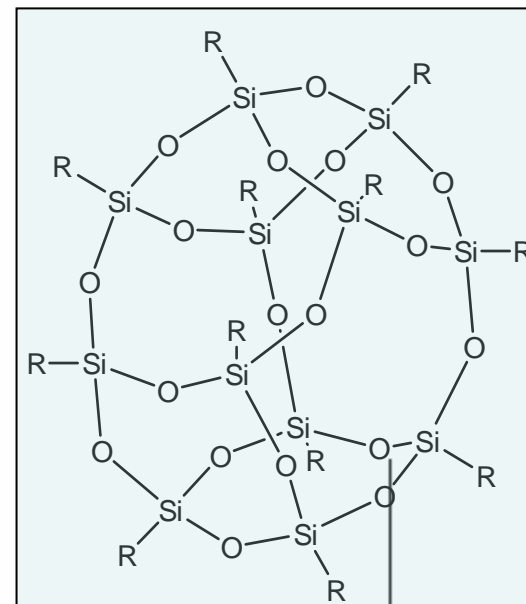
Fluoropropyl_nT_n

²⁹Si NMR

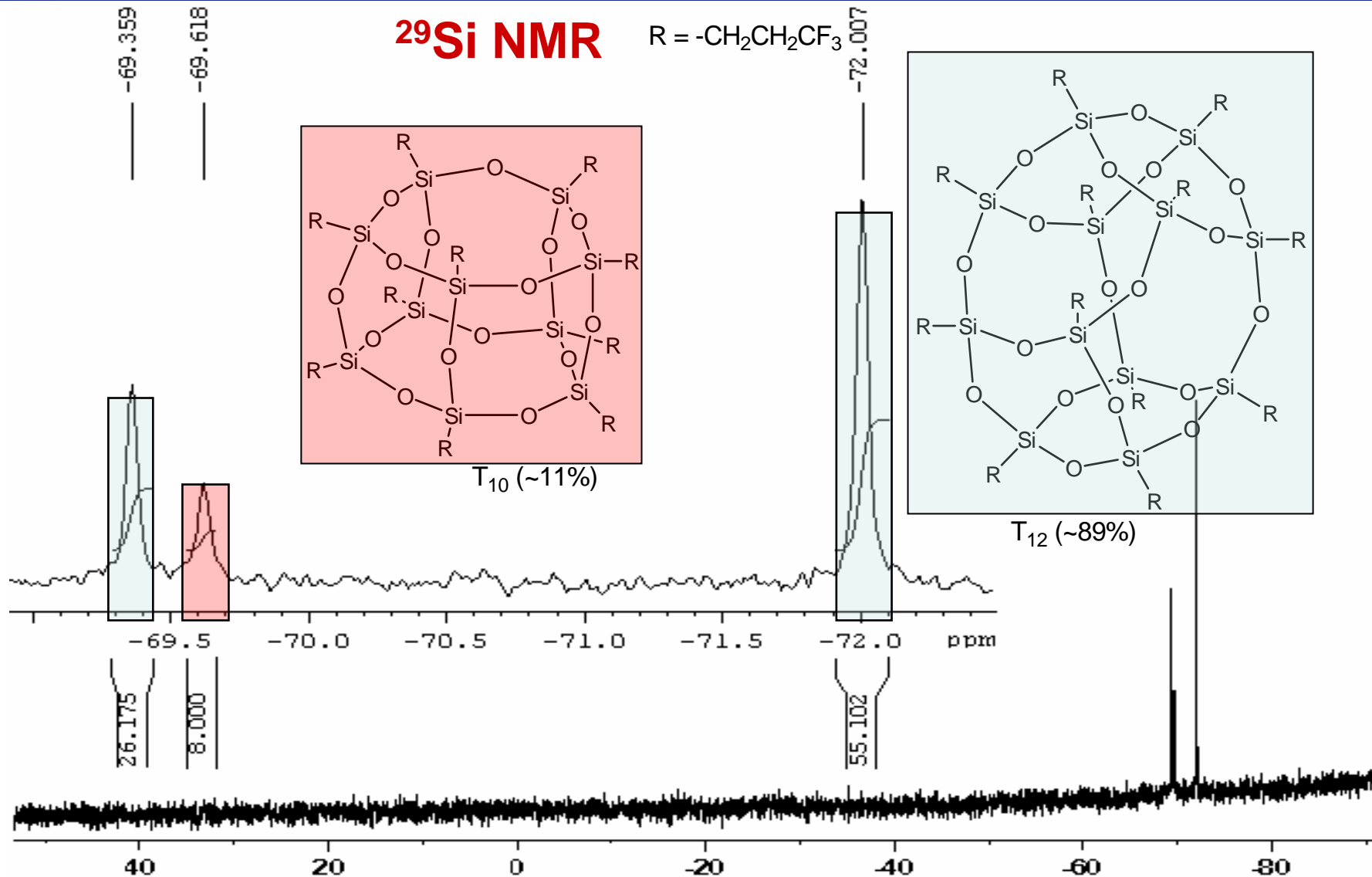
R = -CH₂CH₂CF₃



T₁₀ (~11%)

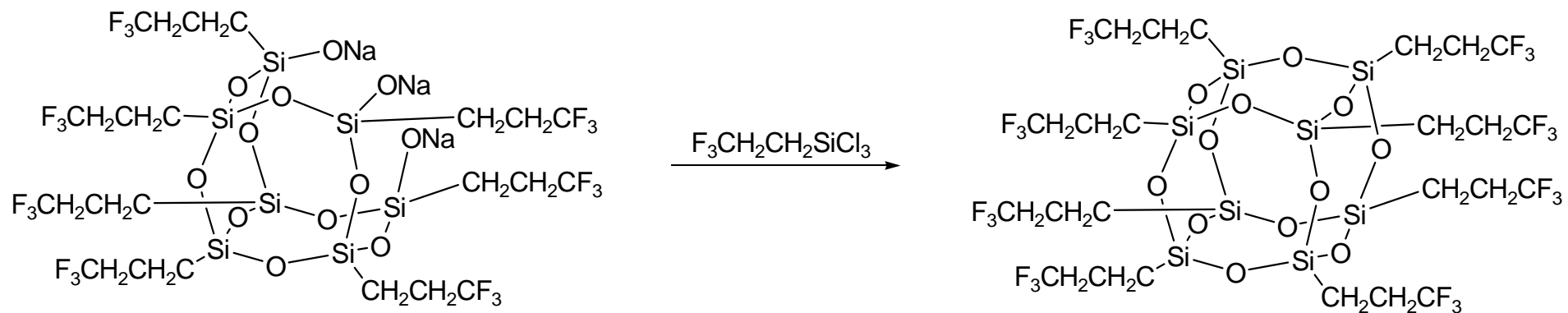
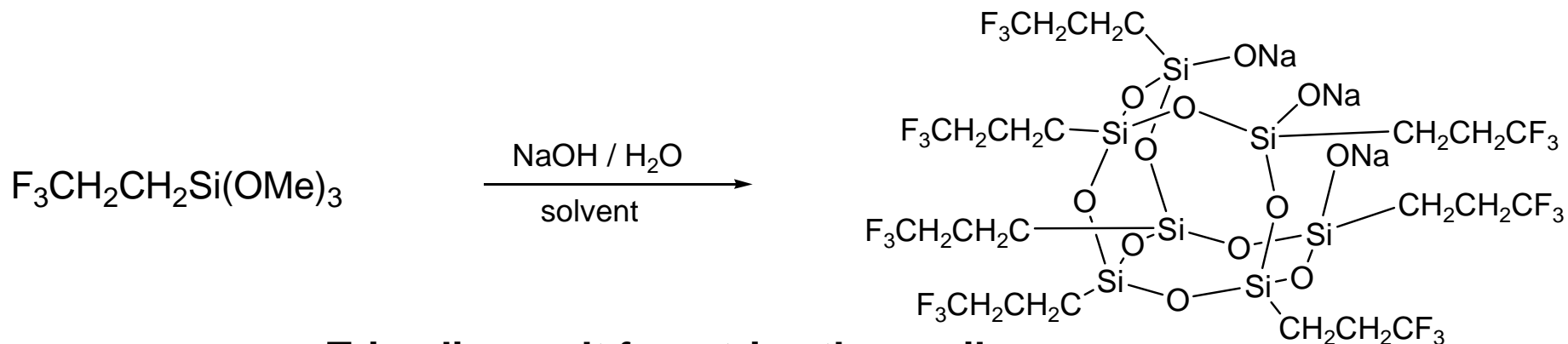


T₁₂ (~89%)





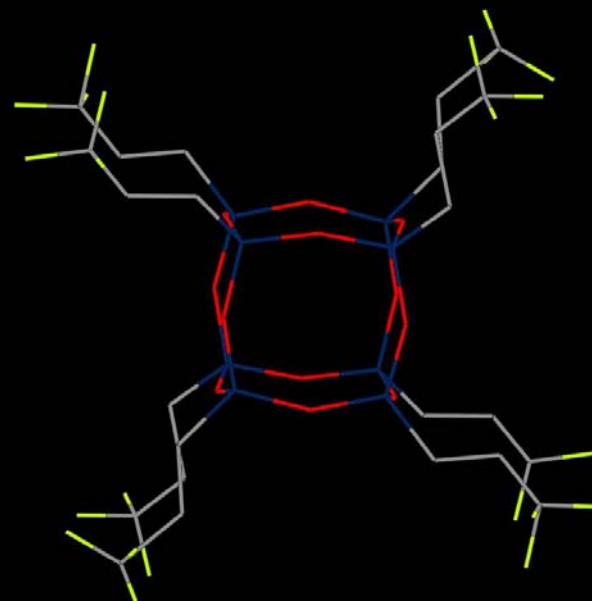
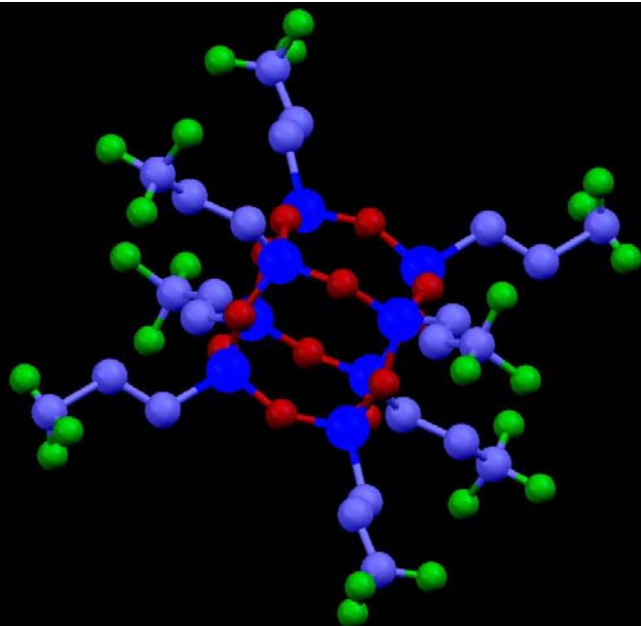
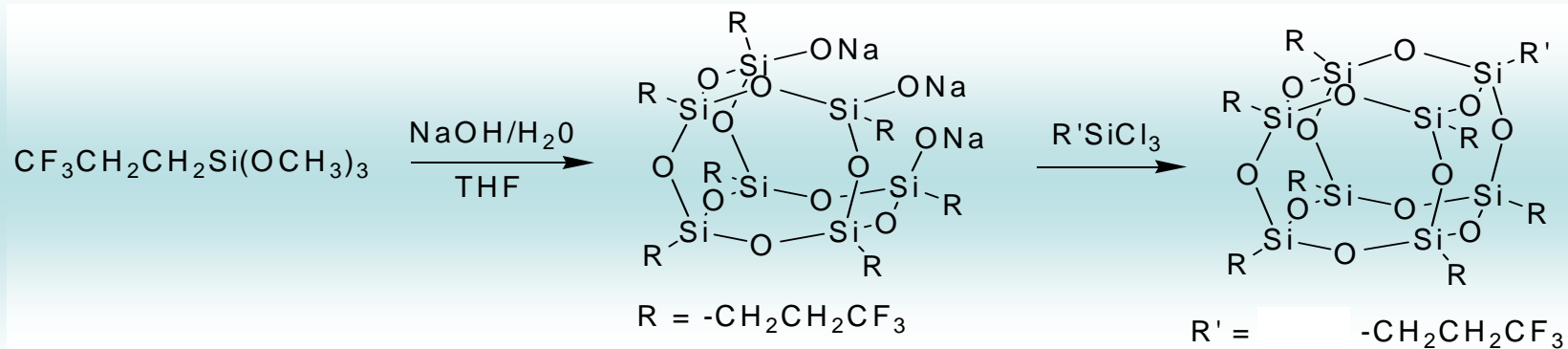
Fluoropropyl₈T₈



T₈ from trisodium salt



Trifluoropropyl T₈ POSS





29Si NMR Trifluoropropyl POSS



Corner capped Trifluoropropyl POSS

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PROCNO 1

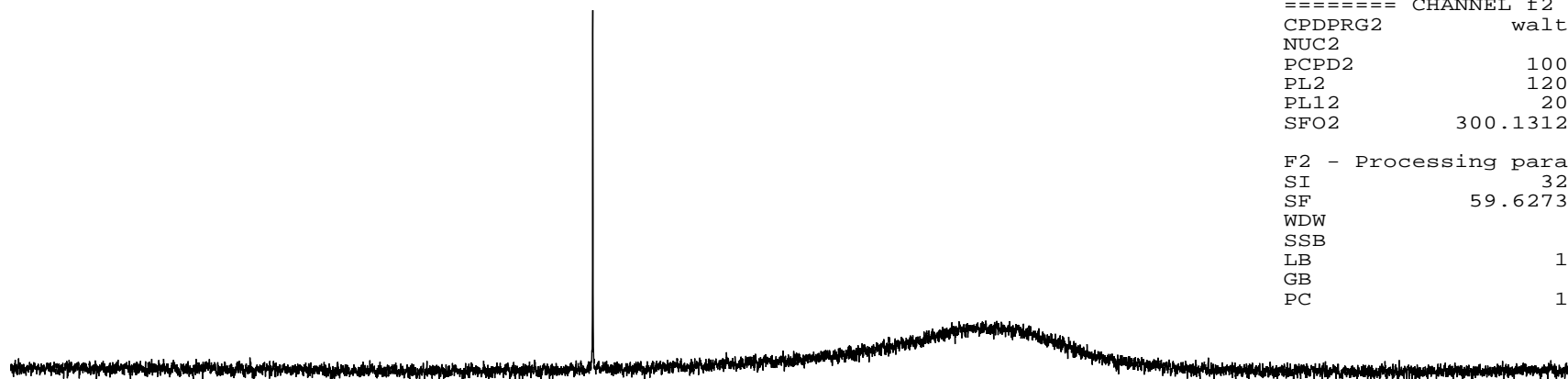
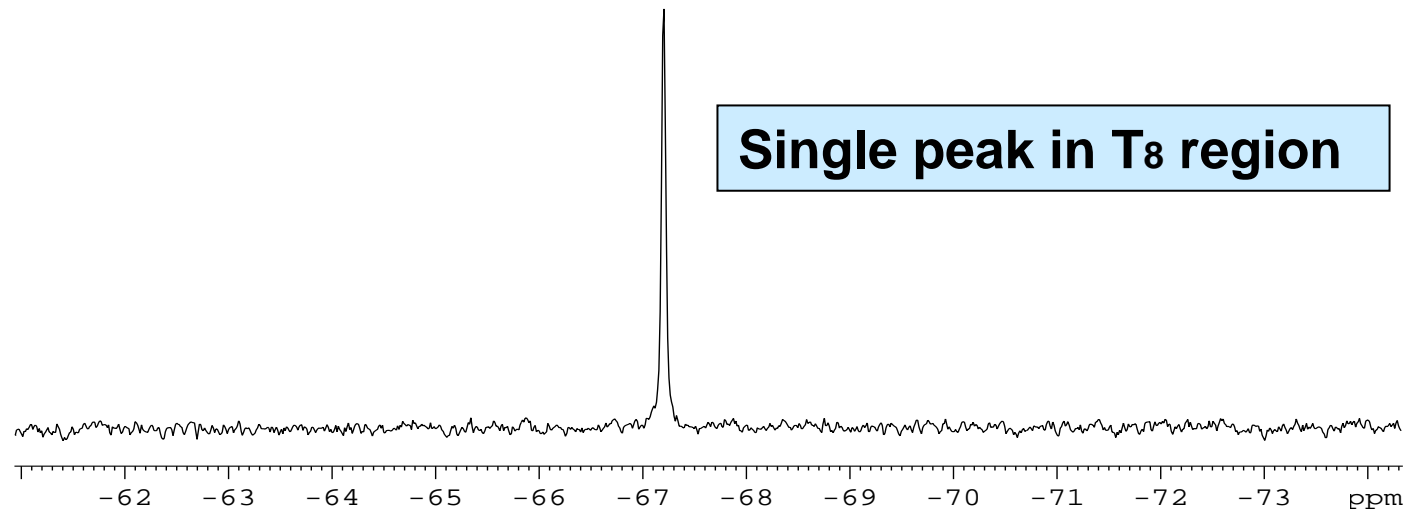
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DE 6.00 usec
TE 300.0 K
D1 8.00000000 sec
d11 0.03000000 sec

==== CHANNEL f1 =====
NUC1 29Si
P1 10.00 usec
PL1 -3.00 dB
SFO1 59.6214106 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 20.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 59.6273782 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Single peak in T₈ region



-20

Distribution A: Approved for public release; distribution unlimited

40

-160

ppm



1H NMR Trifluoropropyl POSS



Trifluoropropyl POSS

Current Data Parameters

NAME STID032
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

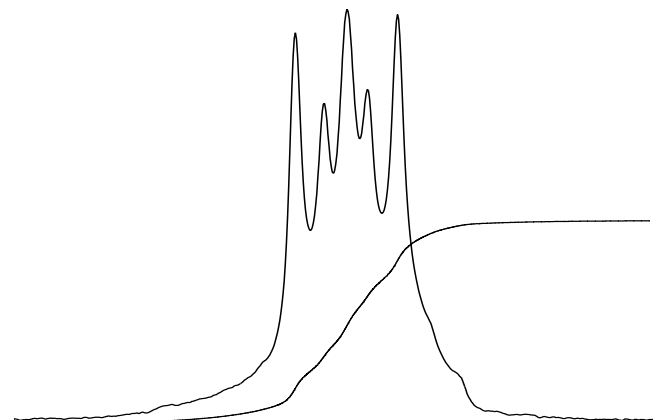
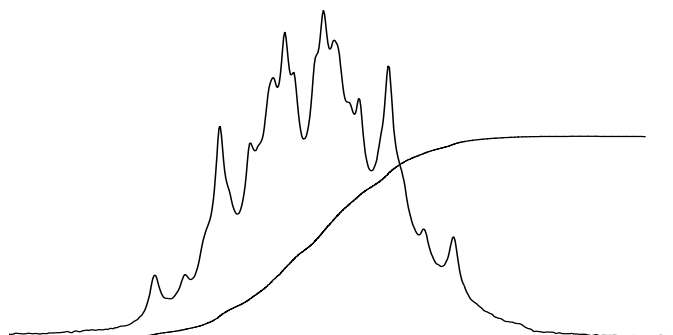
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FIDRES 0.094190 Hz
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

==== CHANNEL f1 =====

NUC1 1H
P1 9.50 usec
PL1 0.00 dB
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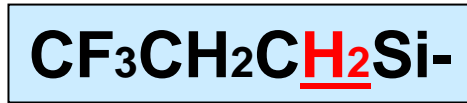


2.45 2.40 2.35 2.30 2.25 2.20 ppm

1.15 1.10 1.05 1.00 0.95 0.90 ppm

0.996

1.000



16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 ppm

Proton ratio 1:1

0.996

1.000



^{13}C NMR Trifluoropropyl POSS



Corner Capped TFP-POSS

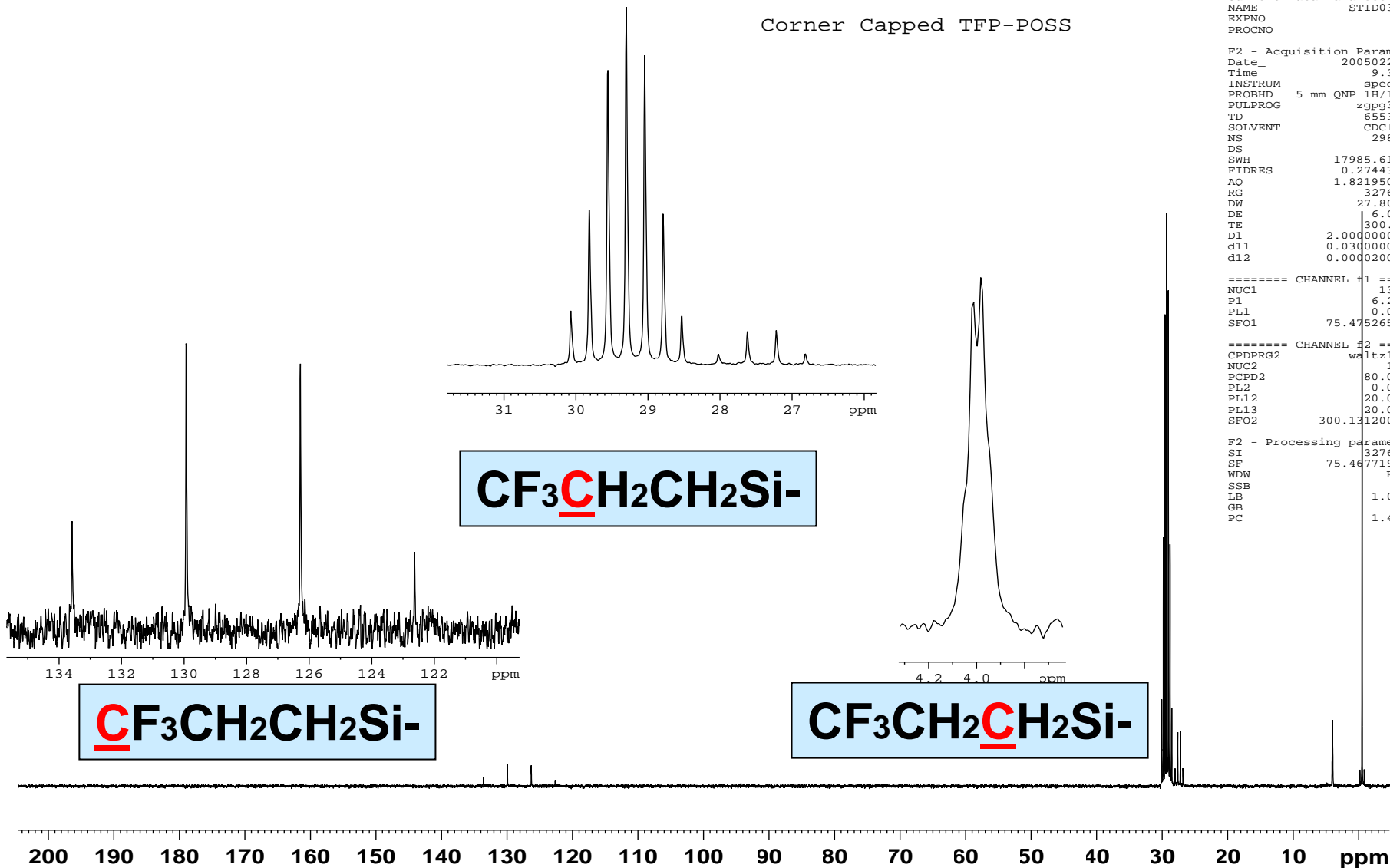
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==== CHANNEL f1 =====
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PL1 0.00 dB
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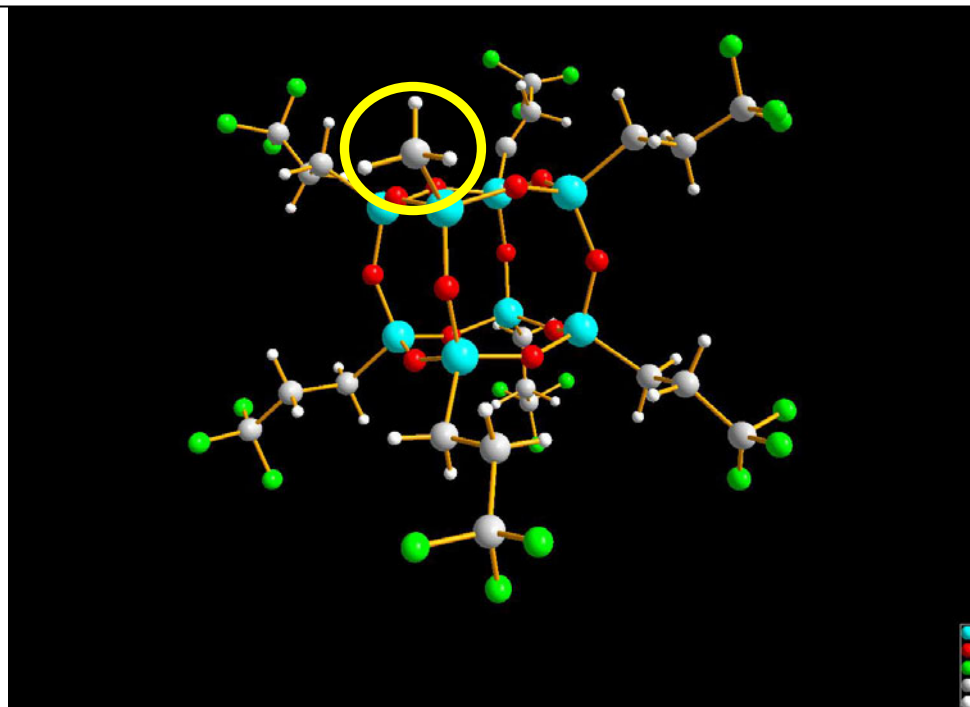
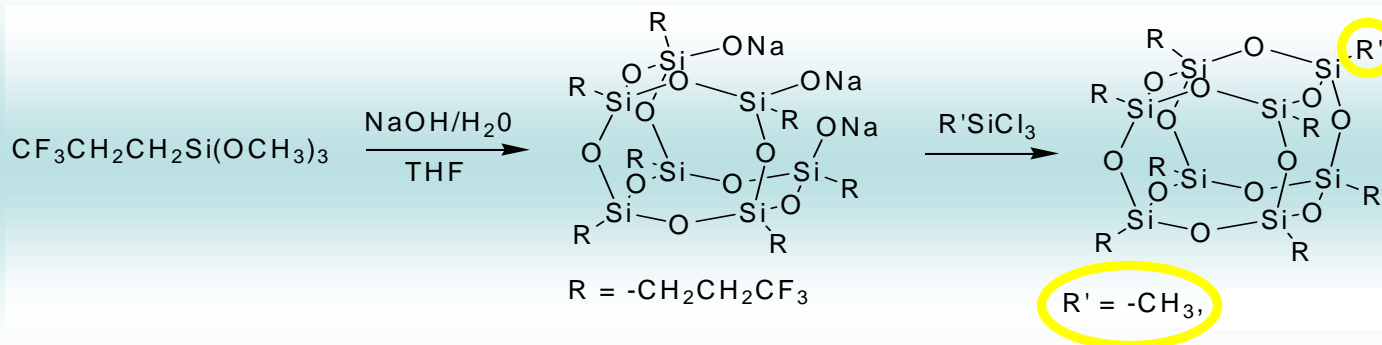
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PL12 20.00 dB
PL13 20.00 dB
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F2 - Processing parameters
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PC 1.40



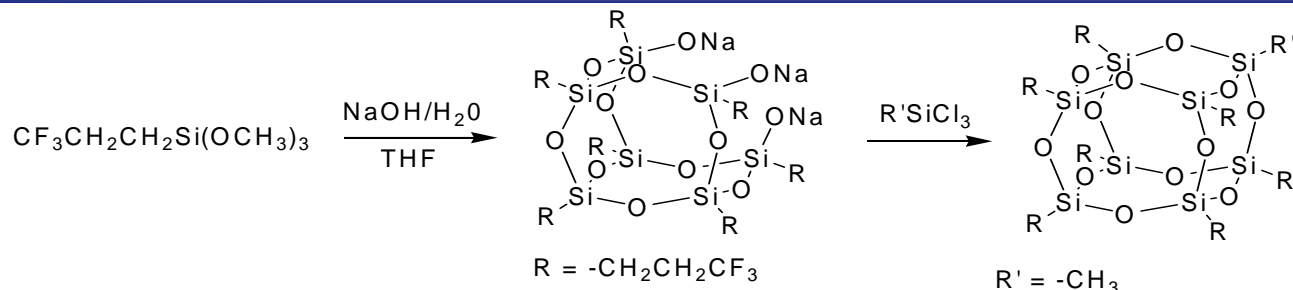


Me corner-capped Fluoropropyl T₈ POSS





Me corner-capped Fluoropropyl T₈ POSS

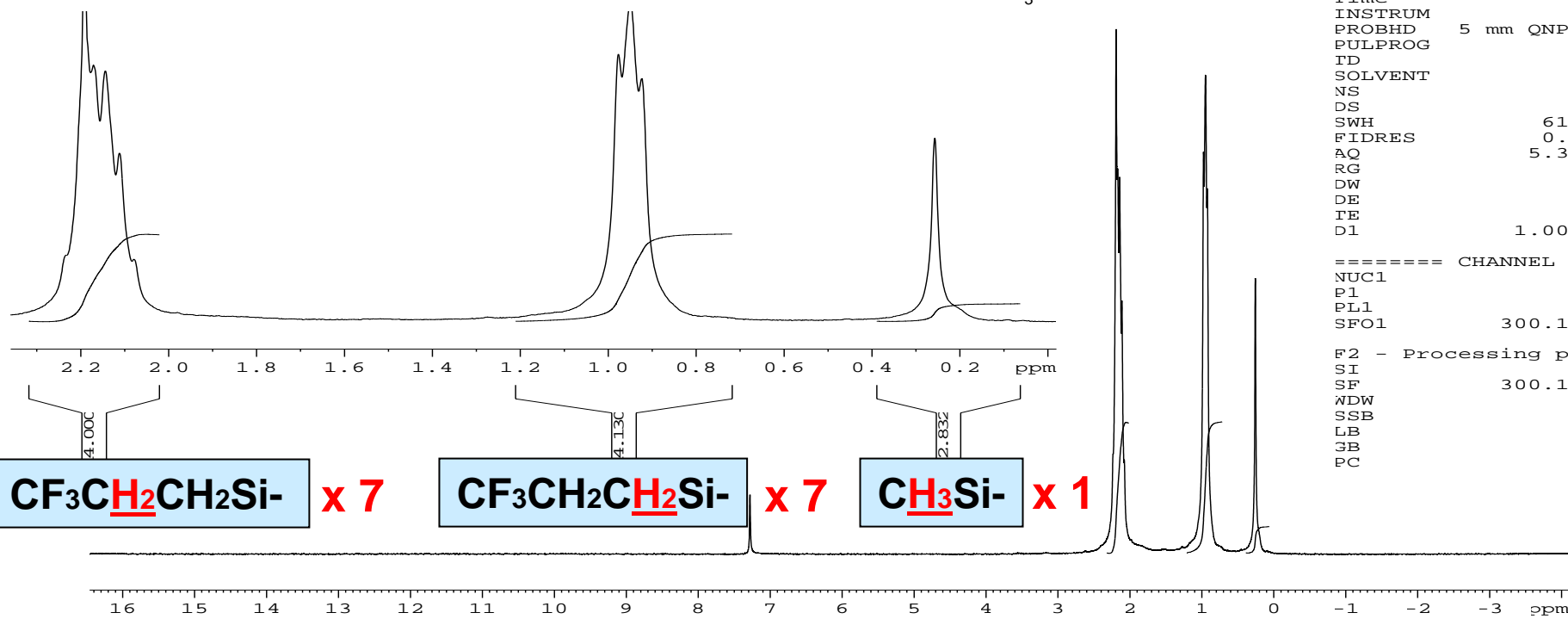


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RG 456
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SFO1 300.13185

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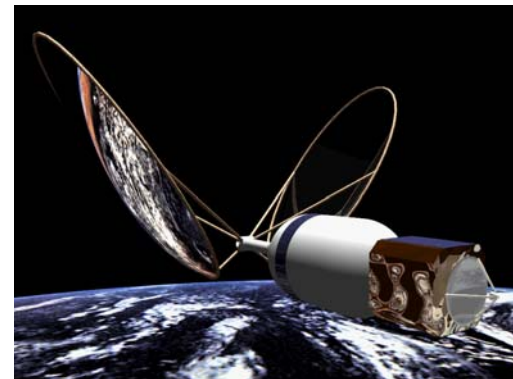
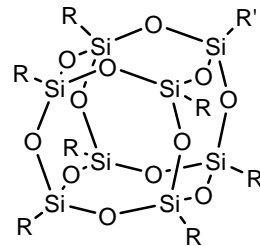
Proton ratio 14 : 14 : 3



Conclusions



- Conventional base catalyzed synthesis yields cage mixtures of fluoro-POSS
 - Redistribution method converts cage mixtures to pure T₈ POSS
- Fluoropropyl POSS does not readily convert to pure T₈ POSS as longer chained fluoro-POSS do
 - New synthetic corner-capping method produces pure T₈
- NMR and x-ray data determined that the new method was a success





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Dr. Sandra Tomczak
Mrs. Tini Vij
Dr. Darrell Marchant
Lt. Scott Iacono

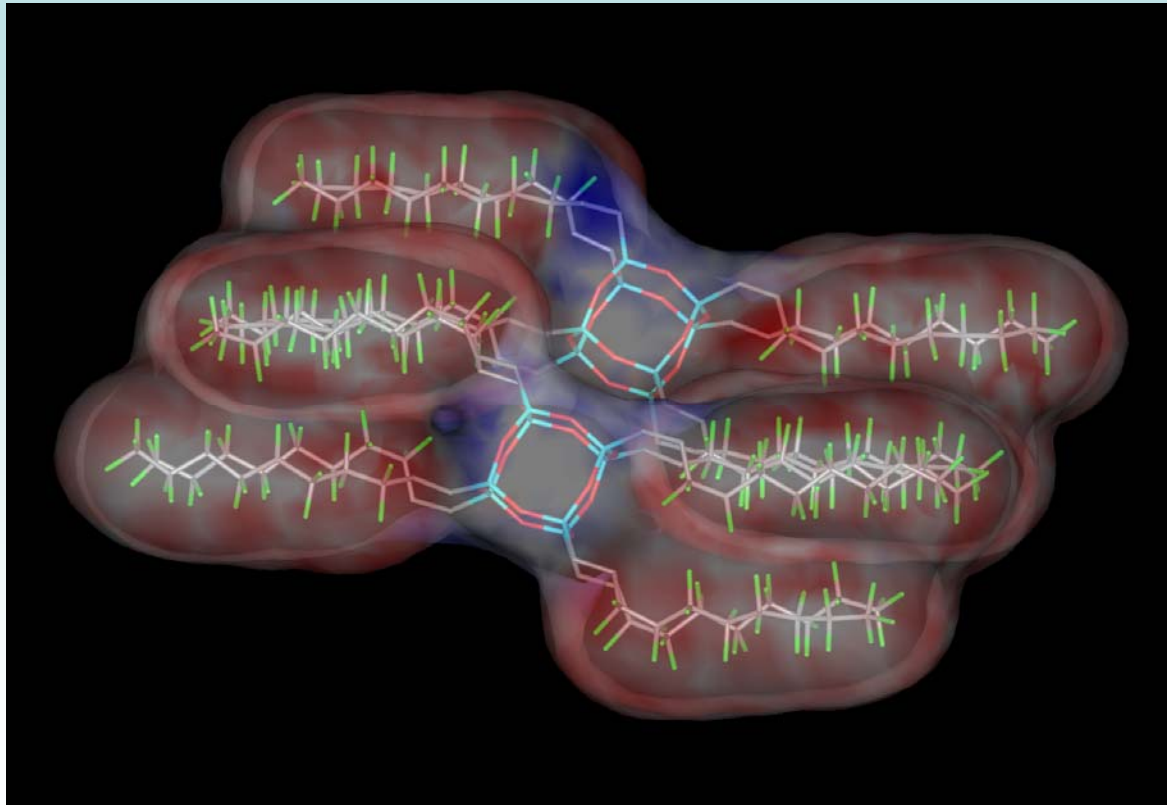


Dr. Joe Mabry
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Dr. Tim Haddad
Lt. Will Cooper
Dr. Rusty Blanski
Lt. Laura Moody
Mrs. Sarah

AFOSR, PRS



AFRL Fluoropolymer Team

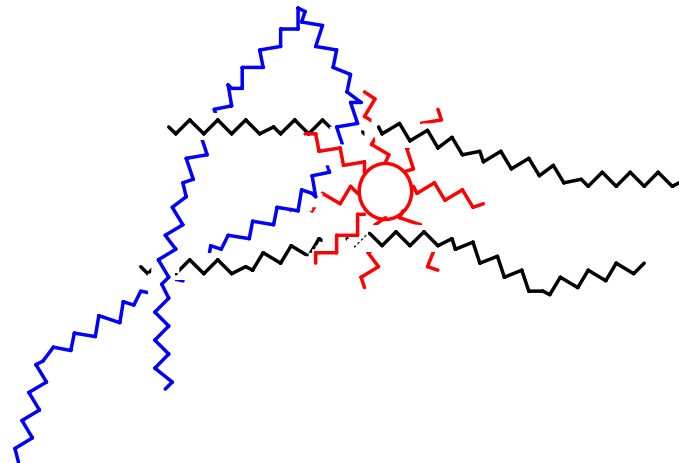
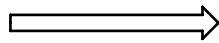
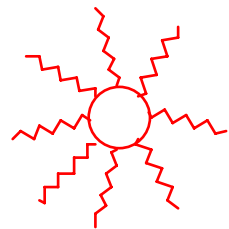
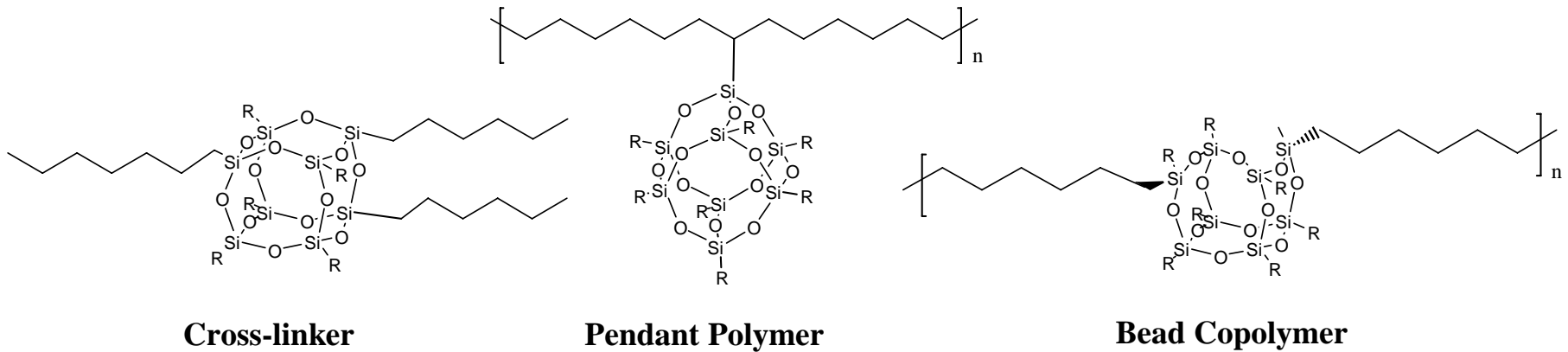


Joe Mabry
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Scott Iacono
Tim Haddad
Laura Moody
Jerry Boatz
Pat Ruth
Isha Vij

AFOSR
AFRL/PRSM
AFRL/PRSP



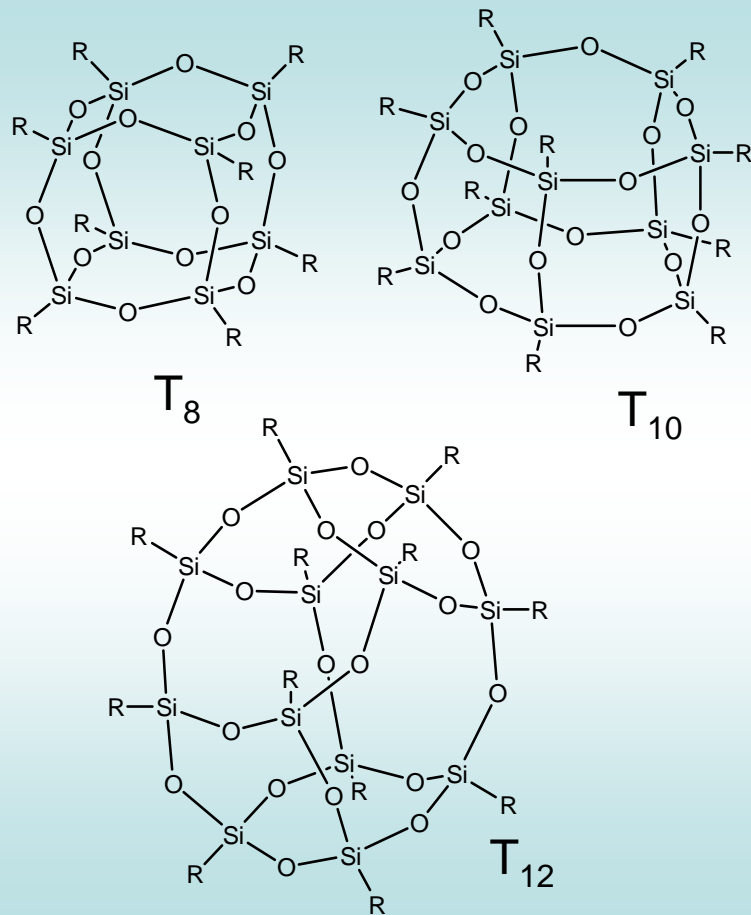
POSS polymer incorporation



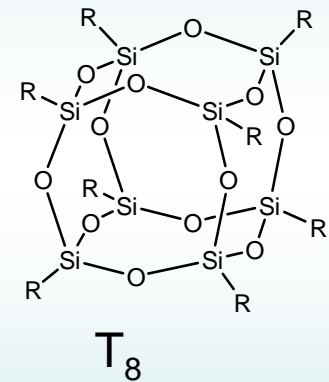
POSS Blending



Redistribution reaction



Sublimation
Re-crystallization
KOH Extraction





Abstract



- Abstract
Fluorinated polyhedral oligomeric silsesquioxanes (POSS) are under investigation for potential lubricant applications. POSS compounds are characterized by a rigid, inorganic core consisting of silicon and oxygen, offering properties similar to those of ceramics; in addition to organic functional groups protruding from the inorganic core, offering organic functionality. Synthesis of POSS generally yields cage mixtures giving varying conformations of the POSS (Si-O) core denoted by the number of silicon atoms present with T8 being the most abundant conformation. Synthesis of trifluoropropyl-POSS is an exception to this generalization which adopts a preferred T10 conformation, with a minor amount of T8 and T12 isomers. Herein, we describe an alternate synthetic route for the preparation of pure T8 trifluoropropyl-POSS not possible by conventional methods. The POSS cages are characterized by multinuclear NMR as well as low-temperature, single crystal x-ray diffraction studies.