# Supercritical Carbon Dioxide Compatible Additives:

## Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography

(*Task Number: 425.031)*


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# Objectives

- **Develop chemistry platform for use of sc$CO_2$ as a solvent with traditional photoresists**
  - **Design fluorinated quaternary ammonium salts (QAS) as $CO_2$ compatible additives**
  - **Elucidate underlying mechanisms of dissolution enhancement**
  - **Apply mechanistic understanding to creation on non-fluorinated additives**

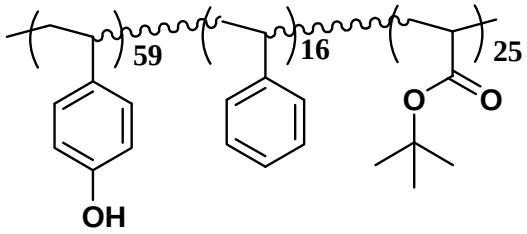
- **Extend sc$CO_2$ methods to molecular glass photoresists**

# ESH Metrics and Impact

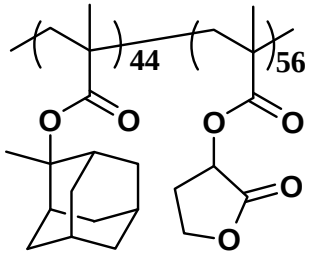
| | Usage Reduction | | | Emmision Reduction | | | |
|---|---|---|---|---|---|---|---|
| Goals/Possibilities | Energy | Water | Chemicals | PFCs | VOCs | HAPs | Other |
| Reduce organic solvents used in processing materials | No energy used to purify and treat water | Eliminate need for water usage | Up to 100% reduction of organic solvents used | N/A | Minimal use of organic solvents | Up to 100% reduction of HAPs | N/A |
| Reduce processing time / temperature | Reduce anneal process costs | N/A | N/A | N/A | N/A | N/A | N/A |
| Additive processing | N/A | N/A | Eliminate waste of costly material | N/A | Minimal use of organic solvents | N/A | N/A |

# Systems of Interest

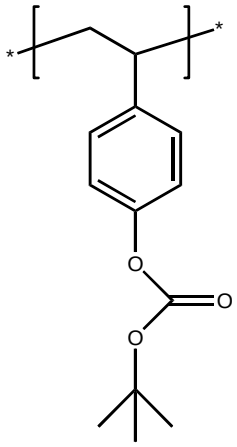
- **Model photoresists in their protected forms**




ESCAP



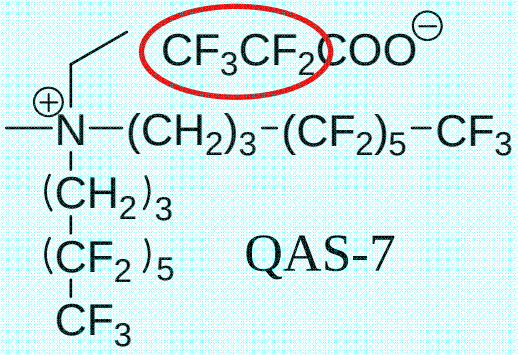

193nm-resist



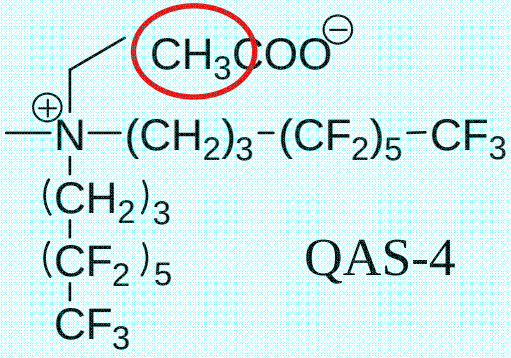

PHOST

- **QAS Additives**
  - **Previously shown to be soluble in $CO_2$**

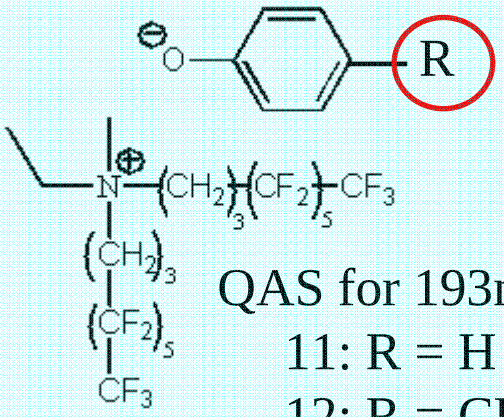
QAS for ESCAP & PHOST




QAS-7




QAS-4




QAS for 193nm-resist

11: R = H

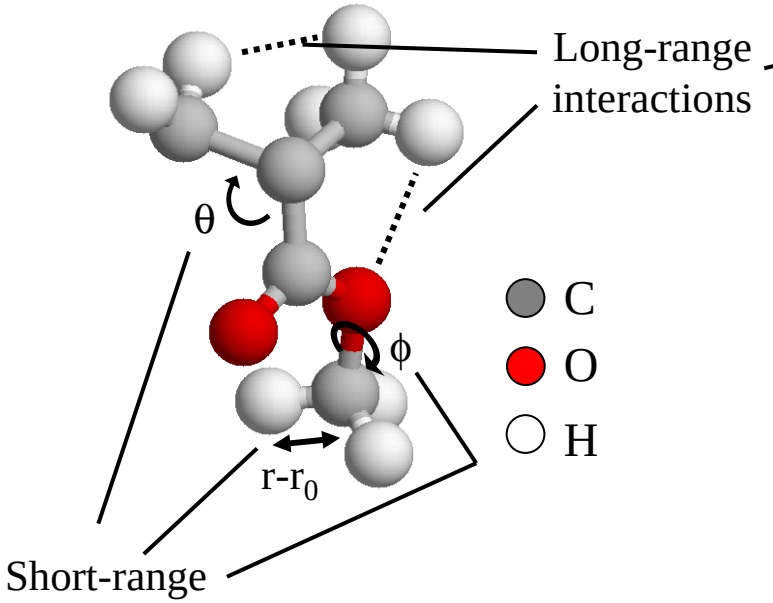
12: R = $CH_3$

13: R = $CF_3$

14: R = $NO_2$

# Model

- **Simulation allows screening of large numbers of systems and enables direct observation of molecular behavior**




-0.32 -0.32

O═C═O

0.65

charges important: scCO2 has a large quadrupole moment

OPLS Model:

$$V_{tot} = \underbrace{V_{LJ} + V_{coul}}_{\text{Intermolecular}} + \underbrace{V_{bon} + V_{ang} + V_{tors}}_{\text{Intramolecular}}$$

$$V_{LJ} = 4\cdot\varepsilon\cdot\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$V_{coul} = \frac{q_i \cdot q_j}{4\cdot\varepsilon_0\cdot\varepsilon\cdot r}$$

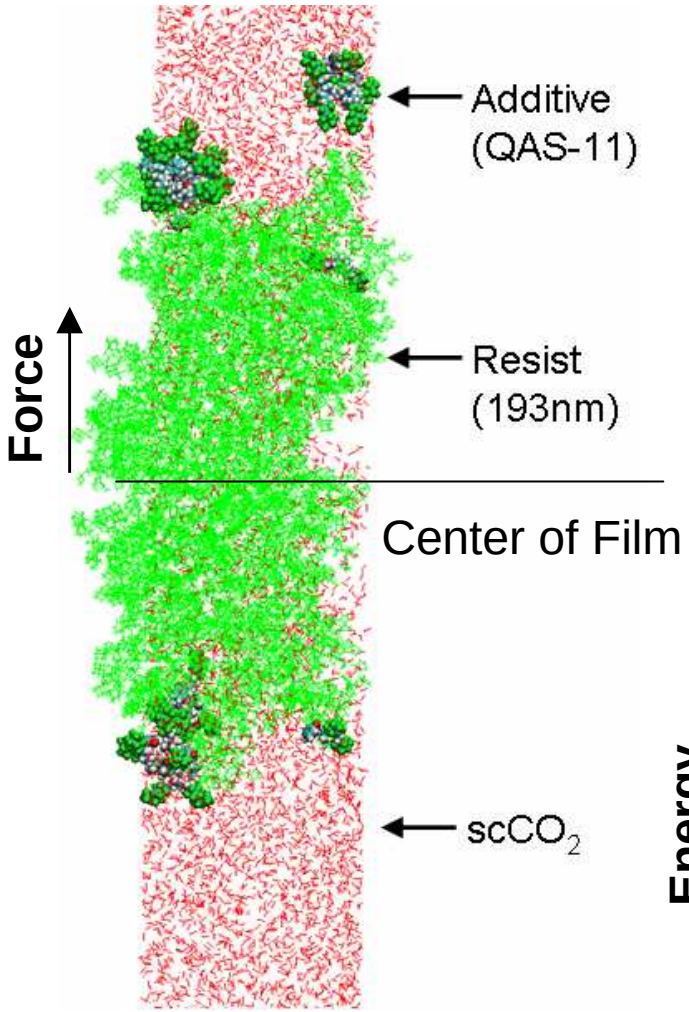
$$V_{bon} = \frac{1}{2}\cdot k_{bon}\cdot(r - r_0)^2$$

$$V_{ang} = \frac{1}{2}\cdot k_{ang}\cdot(\theta - \theta_0)^2$$

$$V_{tors} = \sum_n k_n\cdot(1 + \cos(n\cdot\phi - \phi_0))$$

- OPLS force field employed for most parameters
- We calculated charges ($q_i$) using quantum mechanics
- Process Conditions: T = 340K (~67°C)
  P = 345 bar

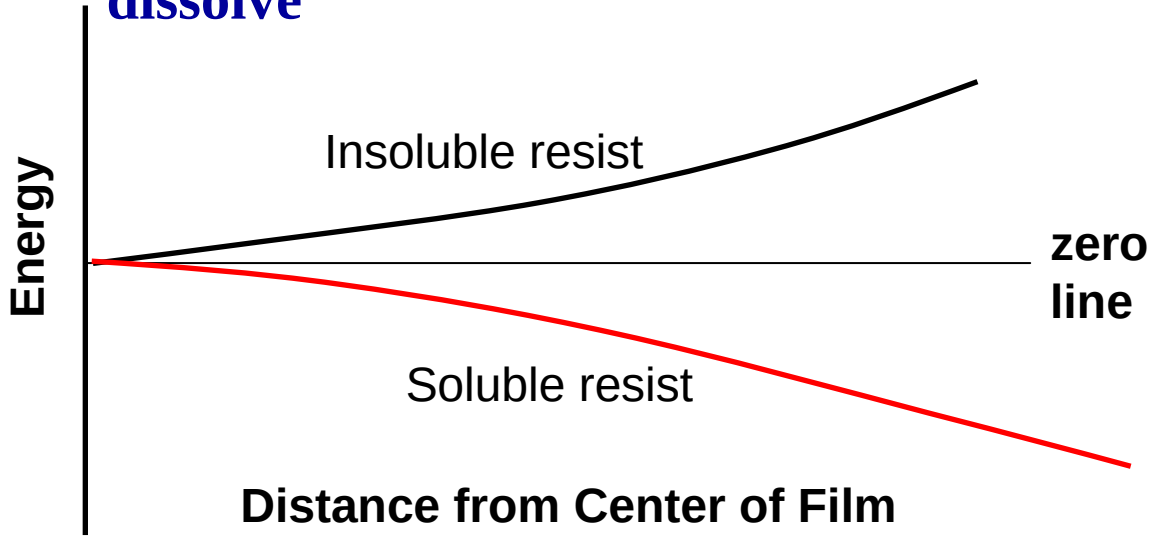
# Free Energy Calculation



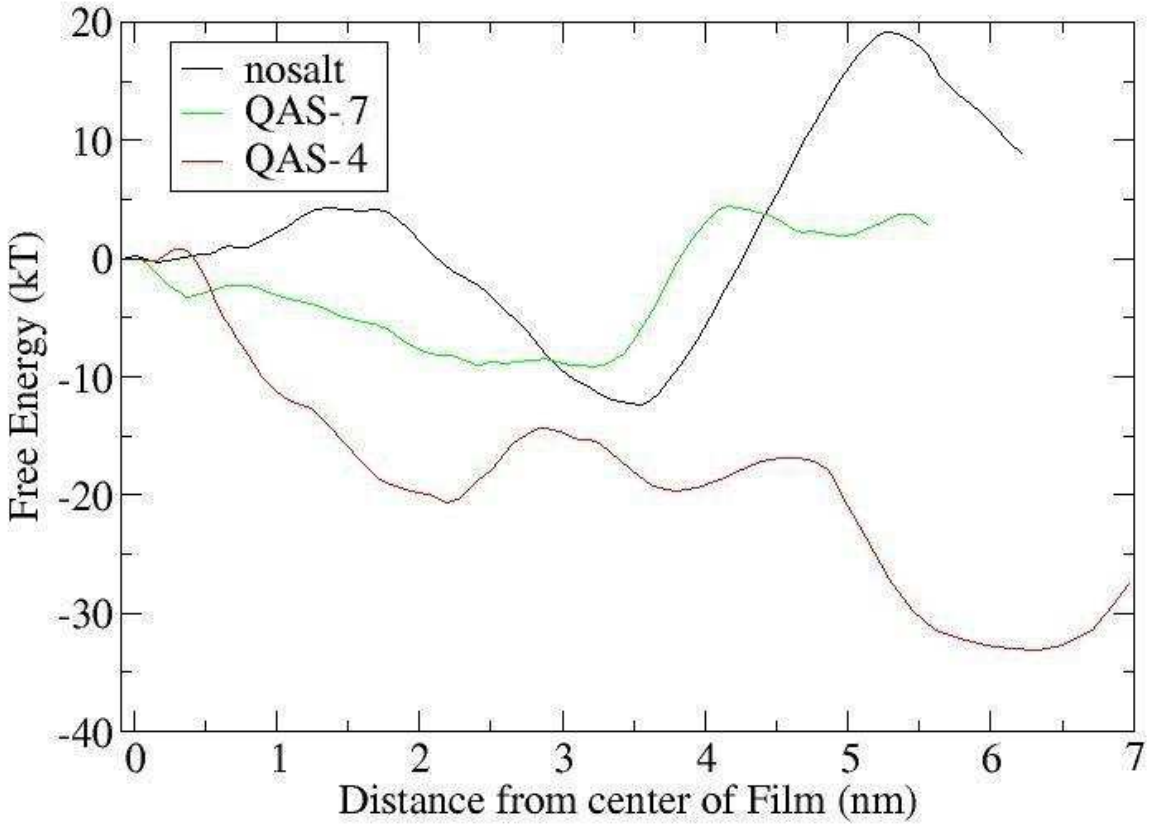

- **Thin films of resist are equilibrated in $scCO_2$ via MD simulation**
- **Integrating the force on each chain as a function of position provides free energy**

$$F(z) = \int_z^{z\infty} \langle f(z') \rangle \, dz' + F(z_o)$$

- **If the energy is lower at the surface than the center, the film is unstable and will dissolve**



# Sample Result: ESCAP Energy Curve

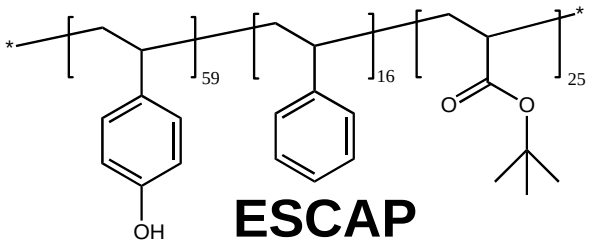


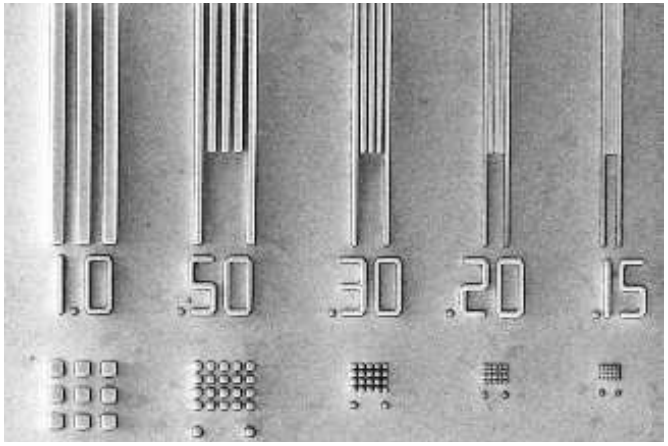

Experimental Results:

No salt – 0 nm/sec

QAS-7 – 0 nm/sec

QAS-4 – 20 nm/sec

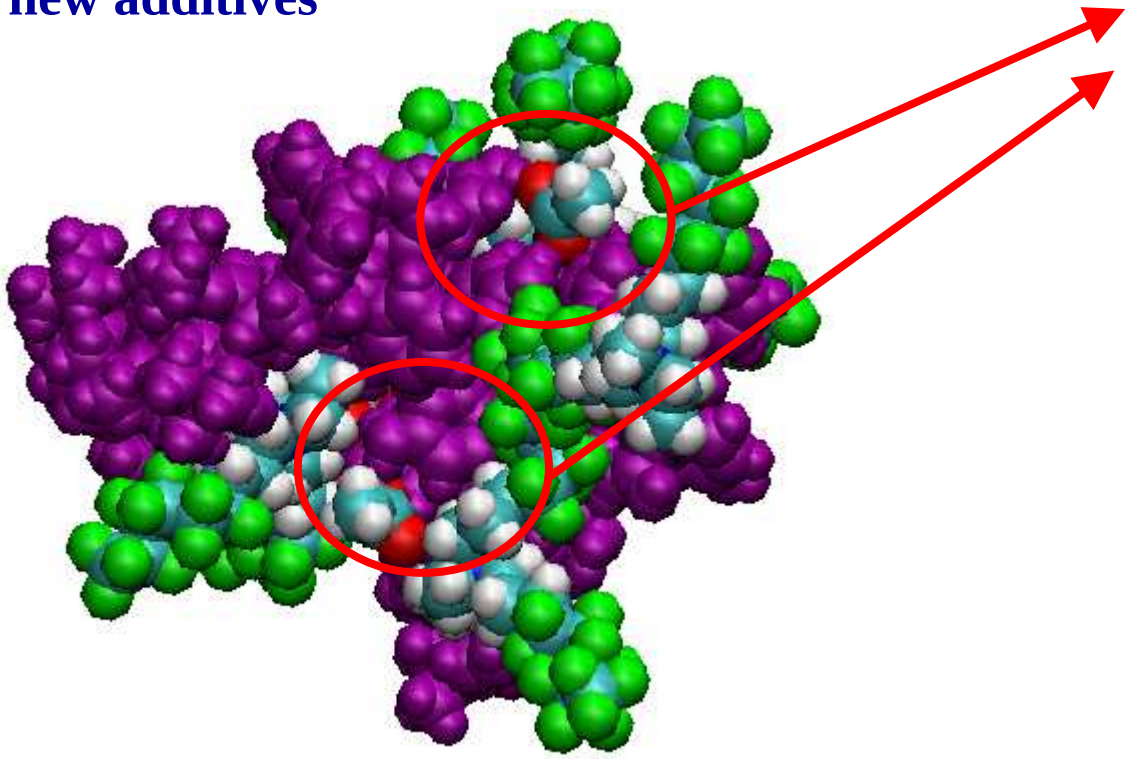


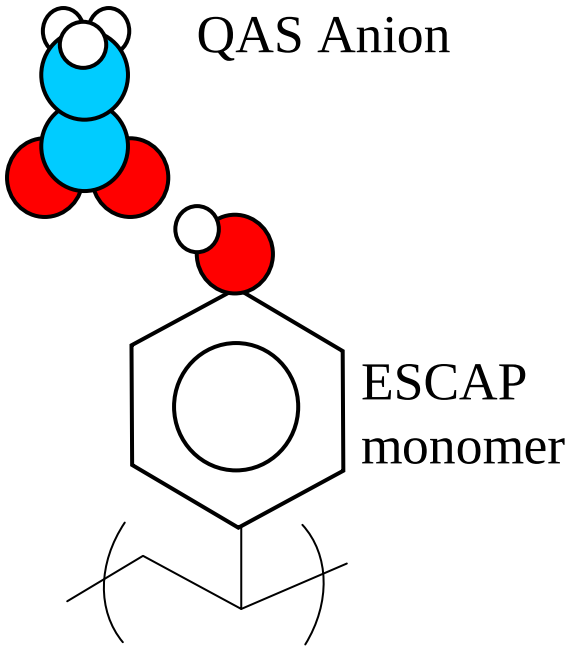




- **Only addition of QAS4 to ESCAP results in reduced energy at surface of film (right of plot), indicating eventual dissolution**
- **Viability confirmed experimentally**

# ESCAP Mechanism with QAS4

- **The –OH group of ESCAP associates with the anions; contacts last >500 ps.**
- **Reducing available polar regions increases solubility in $scCO_2$**
- **Will use understanding of mechanism to develop new additives**

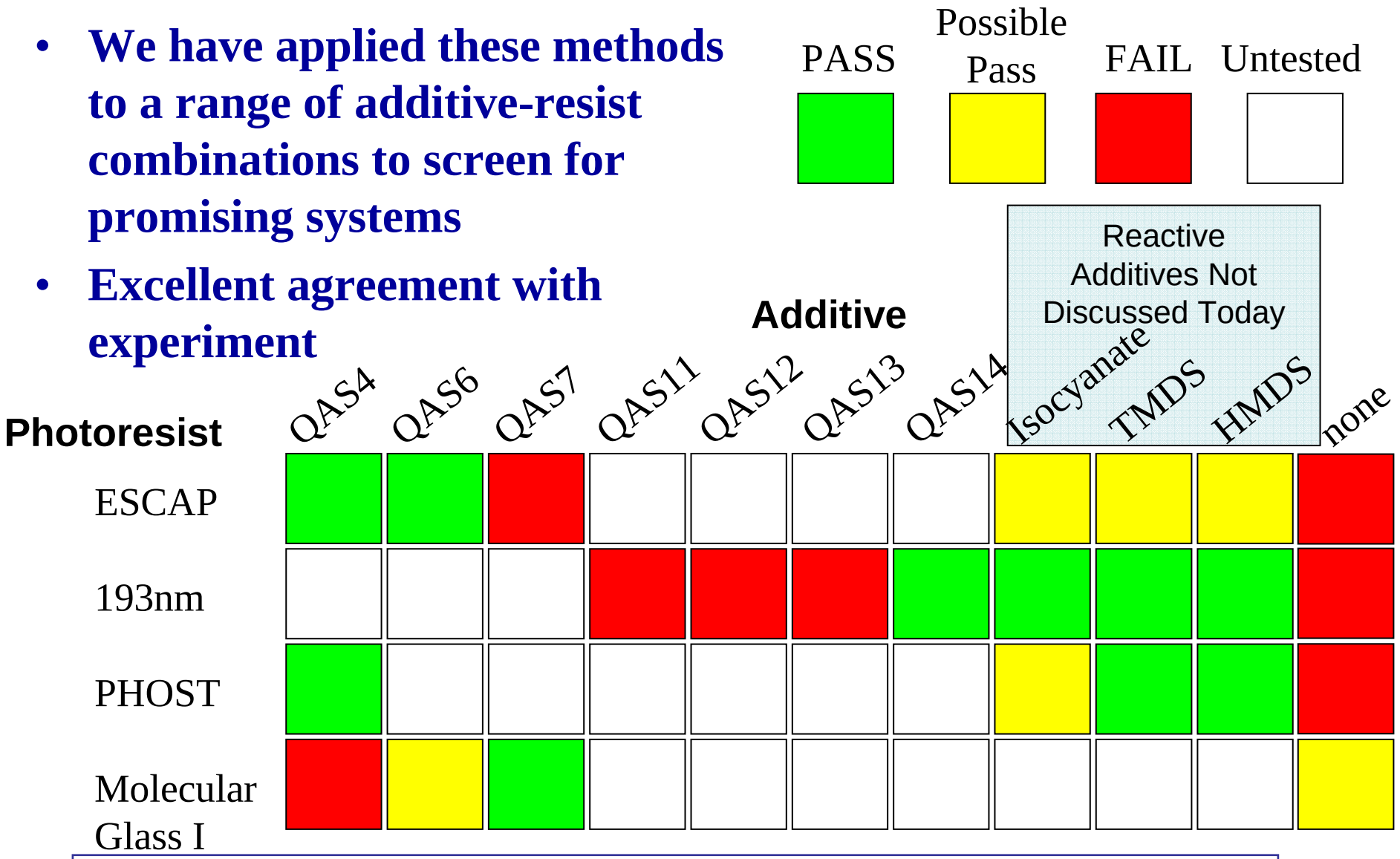





- scCO2 not shown for clarity
- **Purple** – ESCAP
- **Green** – Fluorine (QAS-4)
- **Cyan** – Carbon (QAS-4)
- **Red** – Oxygen (QAS-4)
- **White** – Hydrogen (QAS-4)

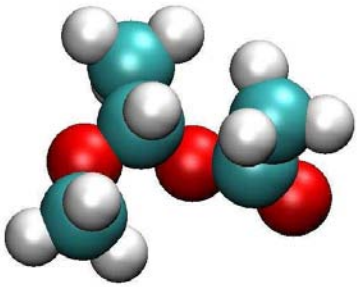
# Summary of Fluorinated Additive Results

- **We have applied these methods to a range of additive-resist combinations to screen for promising systems**
- **Excellent agreement with experiment**

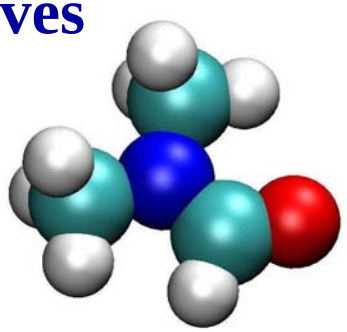


# Non-Fluorinated Systems

- **Potential Additives**

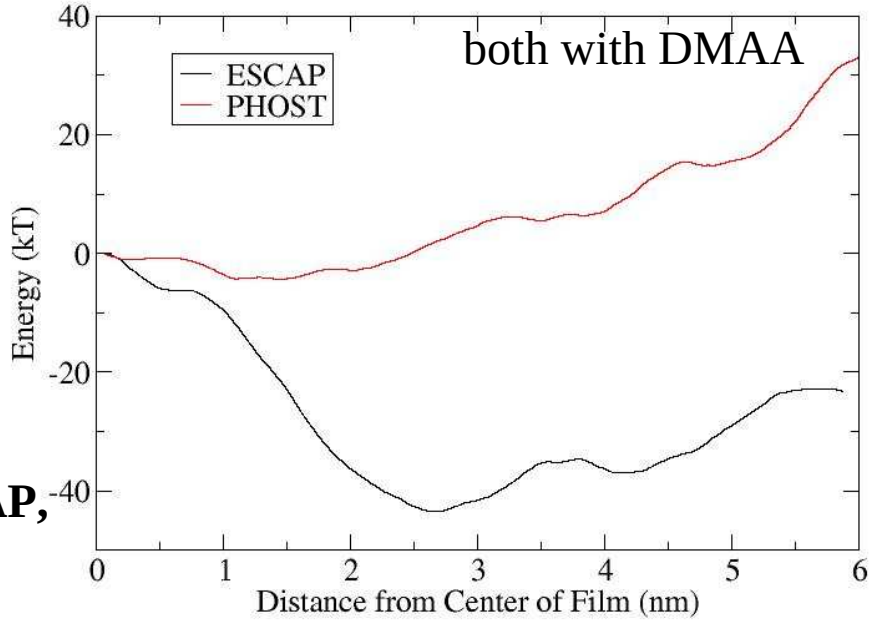


**PGMEA**

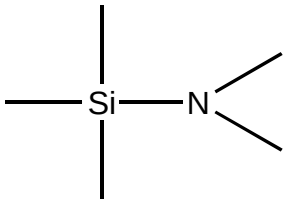


**DMAA**

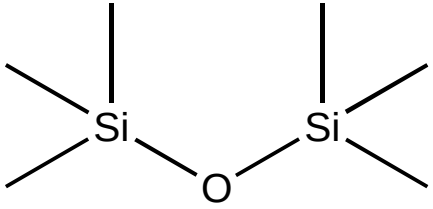
**Effective with ESCAP, but not PHOST**



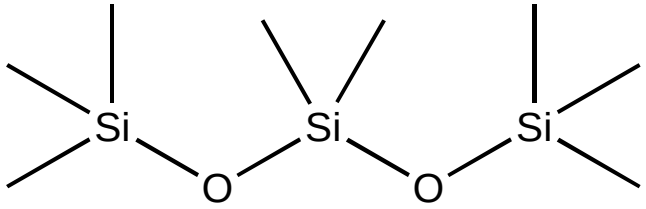

- **Alternative solvents not needing fluorinated additives**




DMTsilane



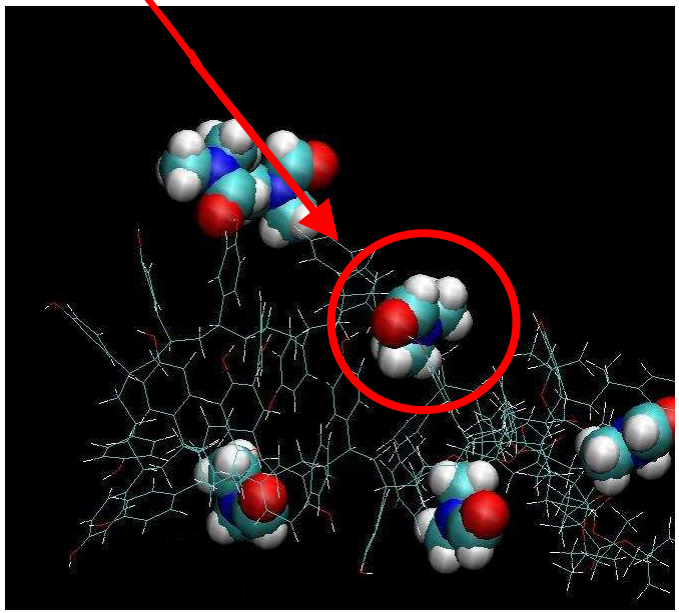

HMDsilane



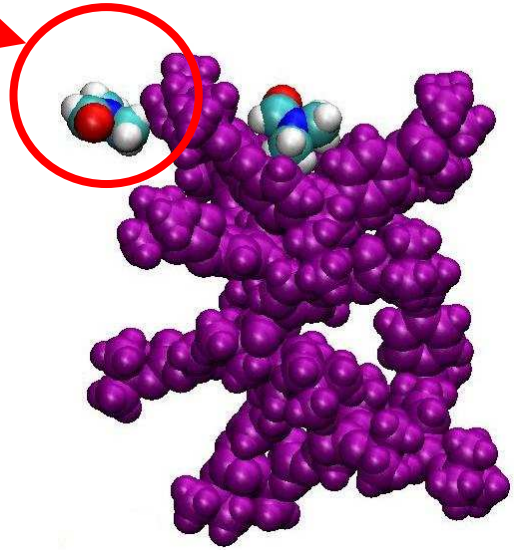

OMTsilane

# DMAA Mechanism

- **Additive was based on applying our understanding of QAS4 effectiveness on ESCAP**
- **DMAA demonstrates similar hydrogen bonding**
- **Ineffective with PHOST; obstructs terminal t-butyl group, instead exposing polar region, reducing $scCO_2$ solubility**

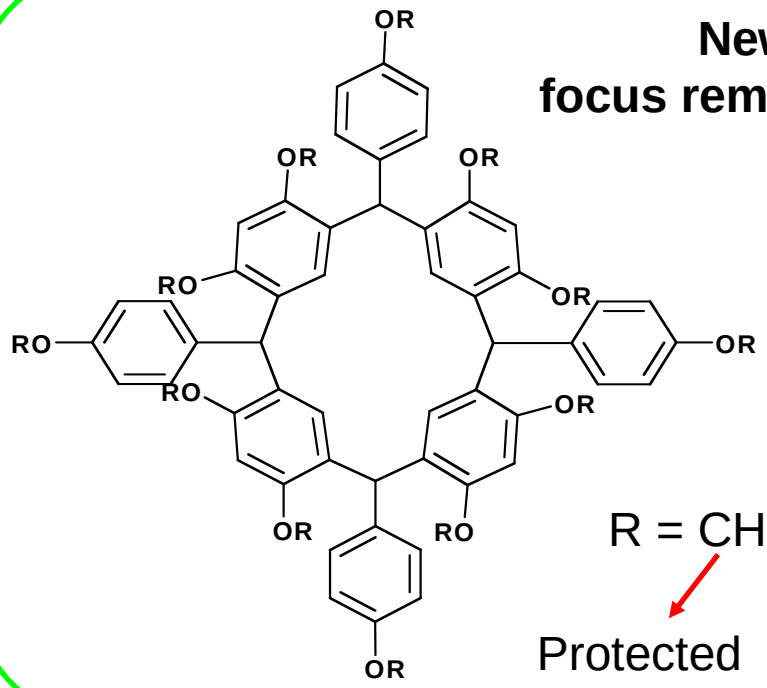


Can develop non-fluorinated additives, but they are more resist-specific



# Molecular Glass (MG) Resists

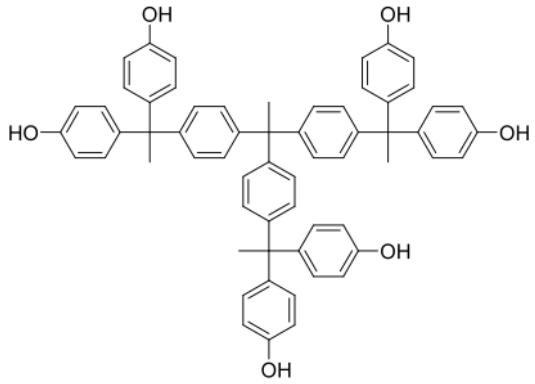
- **Molecular Glass have low LER due to small size**
- **Experimental synthesis and testing is expensive and does not guarantee results; screening via simulation saves resources**




**New MG, focus remaining slides**

$R = CH_3$ or H

Protected Unprotected

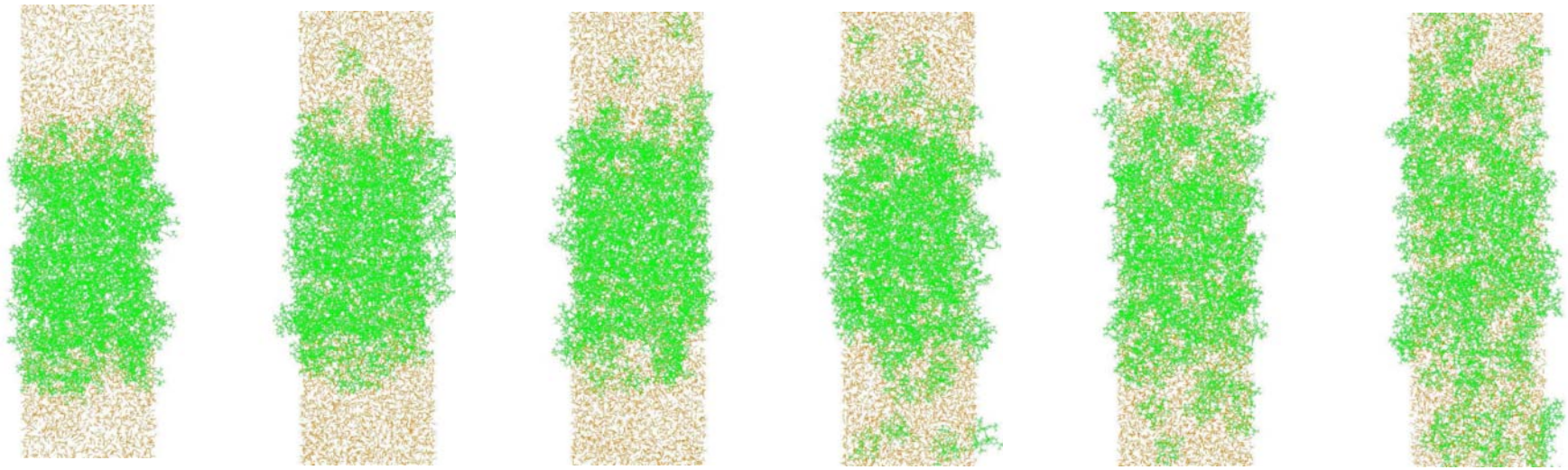



**First proposed MG in exposed form. Simulation found viable system, but synthesis yielded a liquid at process conditions**

# Molecular Glass in $scCO_2$

- **Protected MG dissolved in scCO2 without additive; unprotected form insoluble**
- **No testing with additives necessary, system shows most robust dissolution to date; no free-energy curve needed**
- **Highly promising results to be confirmed experimentally**

Time (1-2ns between images)



# Industrial Interactions and Technology Transfer

- **Regular discussions with Intel via Richard Schenker**
- **Interactions with Dario Goldfarb from IBM**
- **Interactions with Kenji Yoshimoto from Global Foundry**

# Future Plans

## Next Year Plans

- Complete characterization of bulk properties of new potential molecular glass resists and silicone-based solvents
- Verification of new materials via laboratory experiments
- Additional screening of new non-fluorinated additives for use with traditional photoresists

## Long-Term Plans

- To expand use of additives for $scCO_2$ and environmentally friendly silicone fluids for development of positive tone resists
- To create new chemistries for patterning and functionalizing small, non-polar molecules in $scCO_2$

# Publications, Presentations, and Recognitions/Awards

**Publications**

- **Tanaka M, Rastogi A, Toepperwein GN, Riggleman RA, Felix N, de Pablo JJ, Ober CK. "Fluorinated Quaternary Ammonium Salts as Dissolution Aids for Polar Polymers in Environmentally Benign Supercritical Carbon Dioxide", Chemistry of Materials (2009), 21(14), 3121-3135**
- **Rastogi A, Toepperwein GN, Tanaka M, Riggleman RA, de Pablo JJ, Ober CK. "Contact Analysis Studies of an ESCAP resist with sc$CO_2$ compatible additives", Proc. SPIE (2009)**
- **Sha J, Ober CK, "Fluorine- and Siloxane-Containing Polymers for Supercritical Carbon Dioxide Lithography", Polymer International (2009), 58(3), 302-306**

**Presentations**

- **ERC Telesminar (Oct 2008). "Environmentally Benign Development of Standard Resists in Supercritical Carbon Dioxide Using $CO_2$ Compatible Salts"**