Development of Novel non-PFOS Based Photoacid Generators & Their Performance

Yi Yi, Ramakrishnan Ayothi, Christopher Ober*

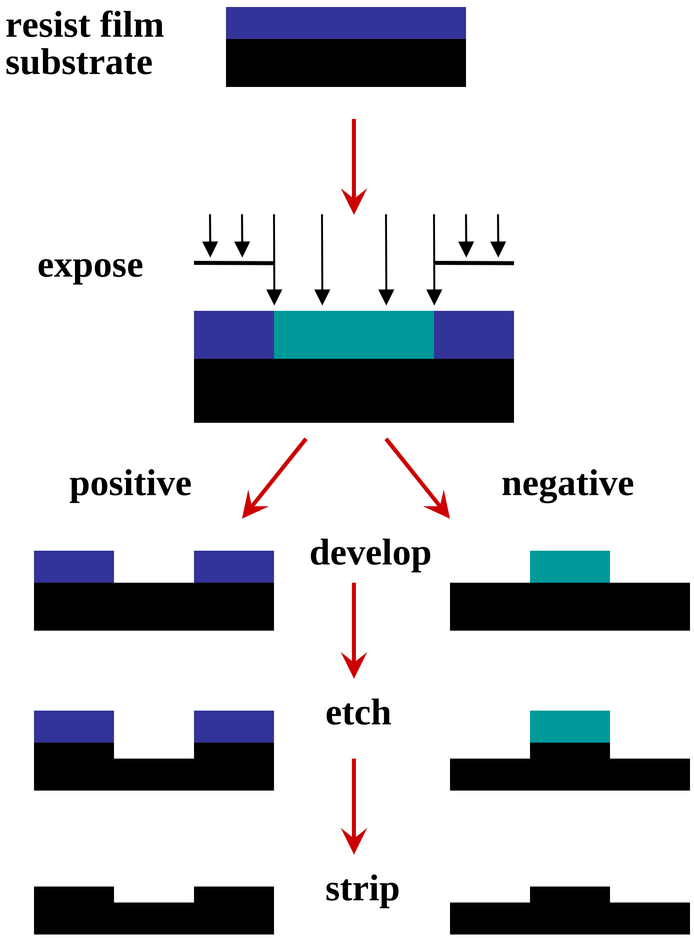
Materials Science & Engineering
Cornell University
Ithaca, NY 14850
***cober@ccmr.cornell.edu**

Outline

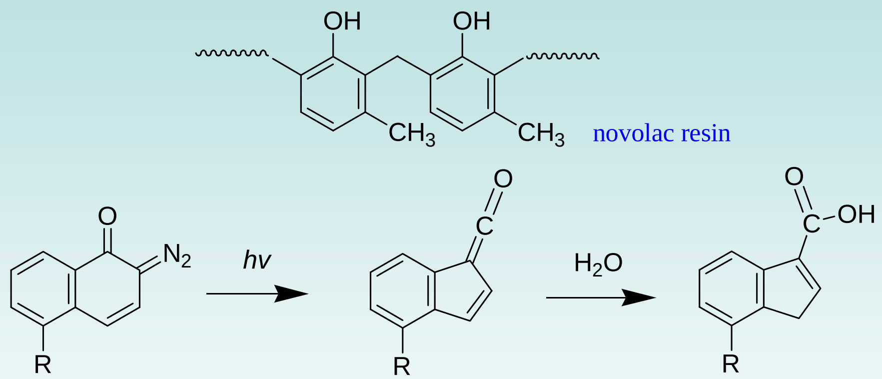
- **Background: Chemical Amplification and Photoacid Generator;**
- **Environment Issues of PFOS Chemicals;**
- **Objective: Preparation and Evaluation of non-PFOS Based PAGs;**
- **Conclusions**

Photolithography

Lithography Imaging Process

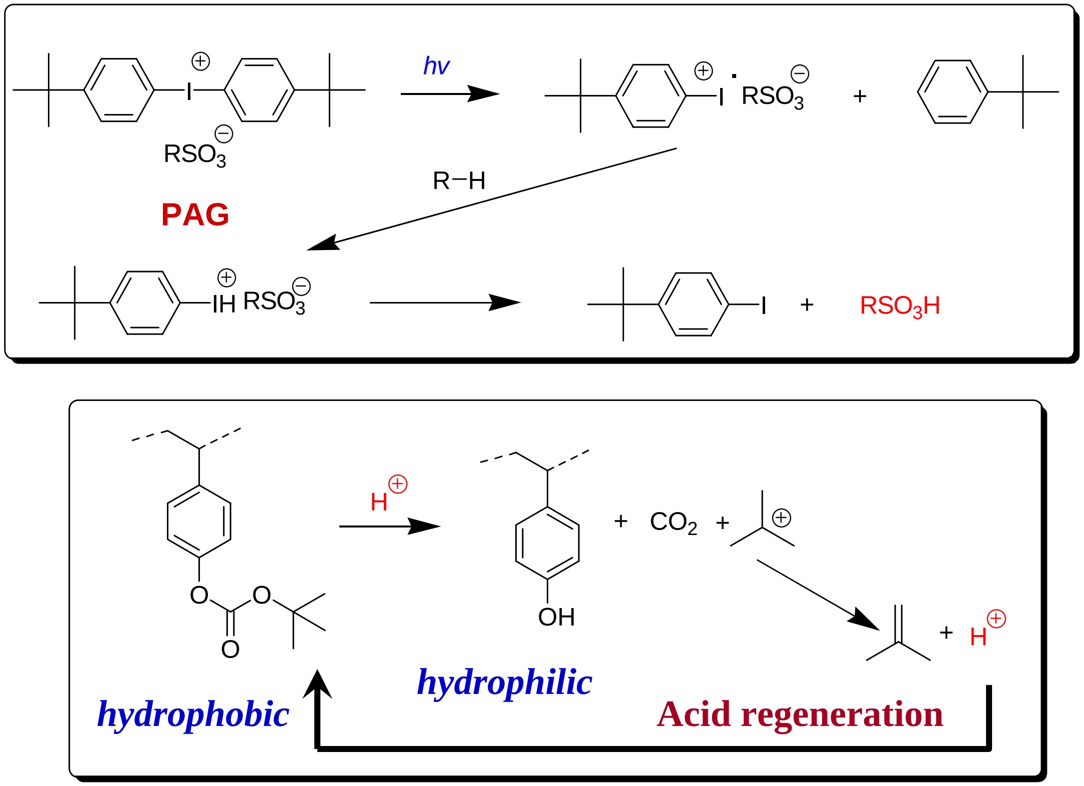


Diazonaphthoquinone/novolac positive resist for 365 nm



insufficient sensitivity & poor imaging quality at shorter wavelength.

The Concept of Chemical Amplification



high quantum yield

low Dose (1 – 5 mJ/cm^2)

PAG makes a difference!

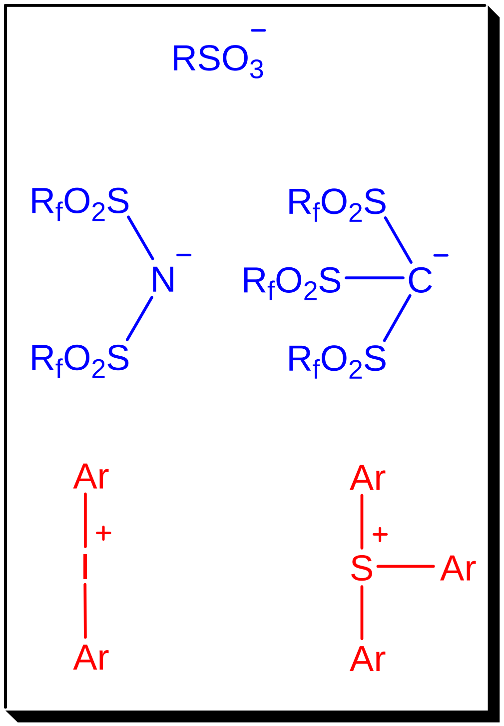
***All phtolithographic technologies including 248 nm,193 nm and next generation lithography such as EUV, e-beam, X-ray require* Chemical Amplification Photoresists.**

Itoh, H. *Adv. Polym. Sci.* 2005, *172*, 37.

Classes of Photoacid Generators (PAGs)

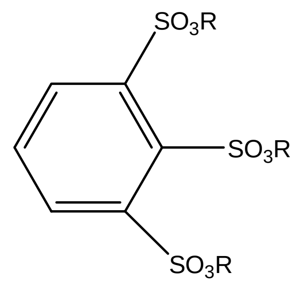
Ionic PAGs

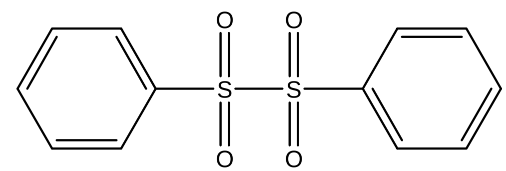
Onium salts

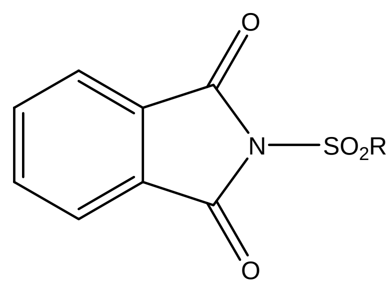


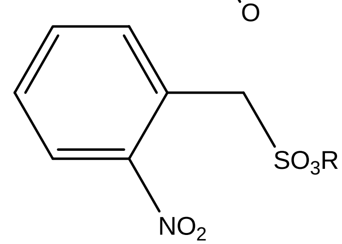
Non-ionic PAGs

Sulfonate Esters/Sulfones

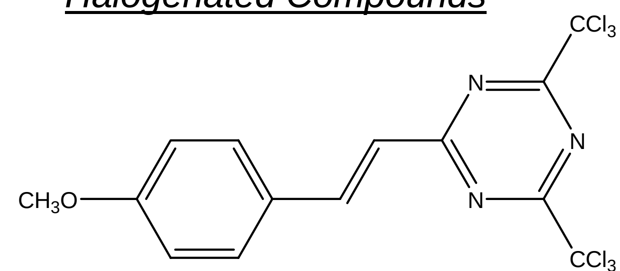






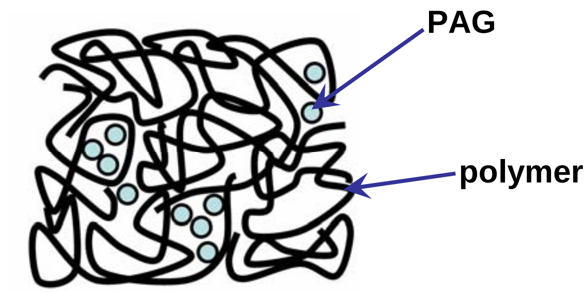


Halogenated Compounds

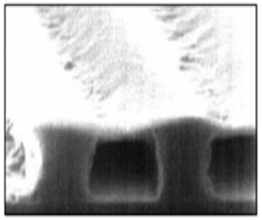


Impact of PAG Structure On Resist Performances

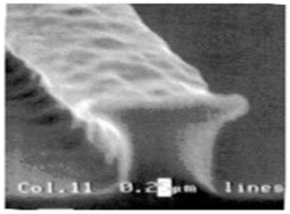
PAG Distribution



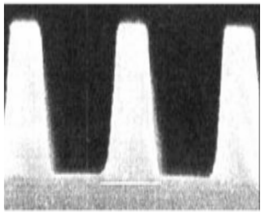
PAG clustering



T-topping

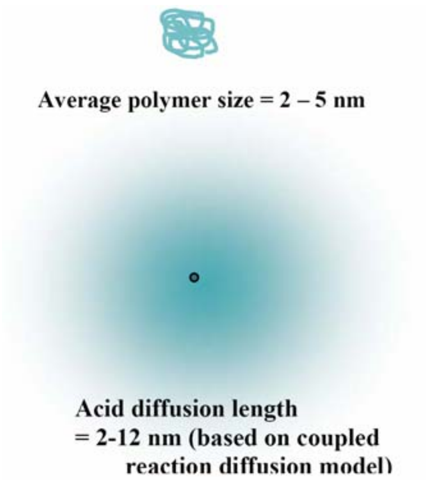


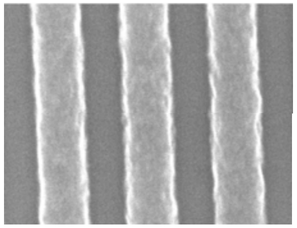
Skin



Footing

Acid Diffusion



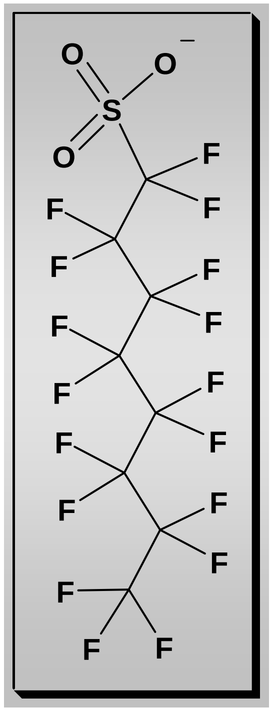


LWR

Perfluorooctane Sulfonate (PFOS) based PAGs

Why:

- **Strong photoacid (pK_a = -11) — sensitivity & photospeed**
- **non-polar tail — solubility, miscibility & thermal stability**
- **Large acid size (272 cm^3/mol) — low acid volatility/diffusion length**



<u>Why not</u>:

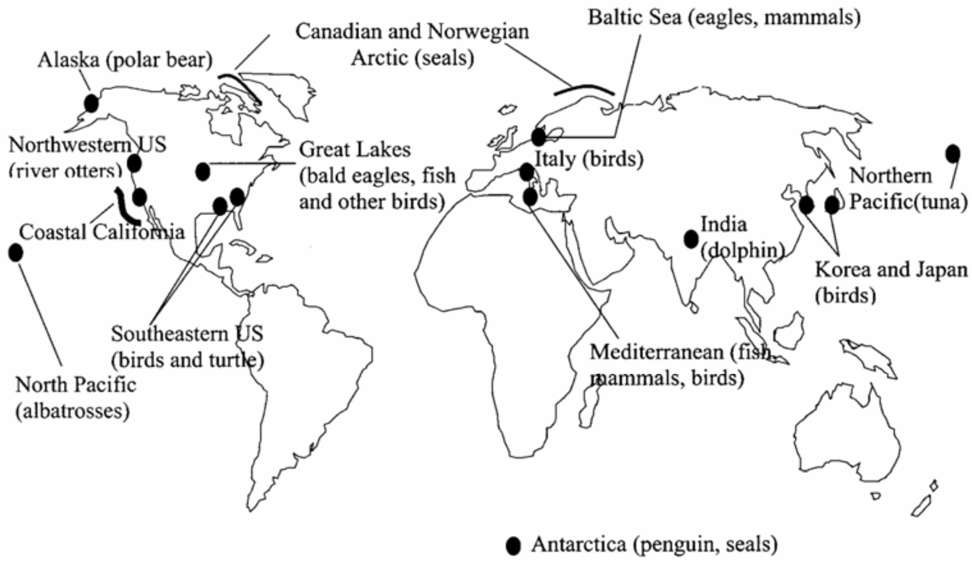
- **Self assembly — segregation**
- **Fluorine absorption — EUV transparency**
- **Persistence & Bioaccumulation— EHS concerns**

SHORTER CHAIN?

Perfluorobutane Sulfonate (C= 4) is good but its use is limited.

PFOS: a Global Pollutant

Global Distribution of PFOS in Wildlife



Environ. Sci. Technol. **2001,** ***35*****, 1339.**

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Published online: 21 March 2001; | doi:10.1038/news010322-6

FOC: it's everywhere

Tom Clarke

Another class of chemicals may soon make the environmental blacklist.

A new class of compounds may have to be added to the list of recalcitrant pollutants that accumulate in the tissues of animals around the globe.

Even the pristine poles bear traces of PFOS.

Using a highly sensitive new technique, researchers at Michigan State University have detected traces of a commercially produced polymer, perfluorooctane sulphonate (PFOS), in a surprisingly wide variety of wildlife -- from Arctic seals to Ganges river dolphins and Mississippi turtles[1].

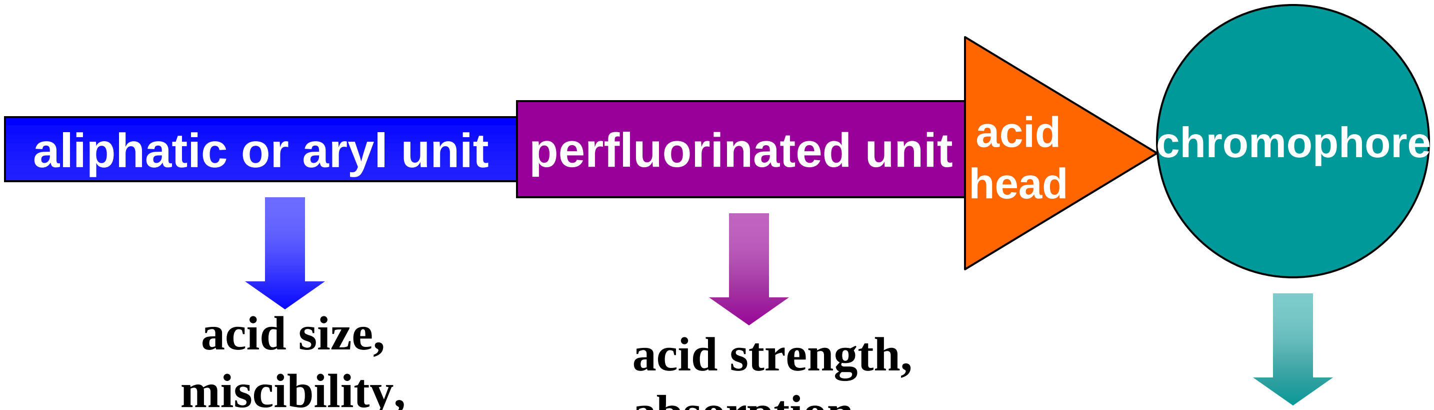
The EPA proposed a significant new use rule (SNUR) for PFOS in 2000

***PFOS* was found in 10 of 10 umbilical cord blood samples from babies born in U.S. hospitals in 2004, at concentrations ranging from 1.6 to 5.8 ng/g (wet weight, in whole blood). It was also found in 3 of 3 adult blood samples, at concentrations ranging from 3.6 to 16.2 ng/g (wet weight, in whole blood).**

from Environmental Working Group report, July 14 2005

We do need next generation PAGs which are environment friendly and have no bioaccumulation.

Modular Design of Novel non-PFOS Based PAGs

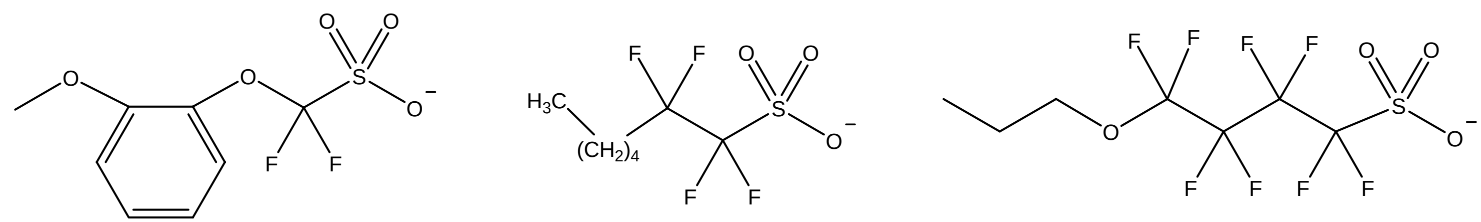


**acid size,
miscibility,
thermal stability,
absorption, outgassing.**

**acid strength,
absorption**

**photosensitivity,
absorption,
thermal stability.**

examples:



Arch Fuji 3M

***practical consideration**: yield & purification.*

Objectives

PAG design & synthesis

1. Practical methods
2. Basic characterization
3. Physical and photochemical properties

Lithography (DUV & EUV)

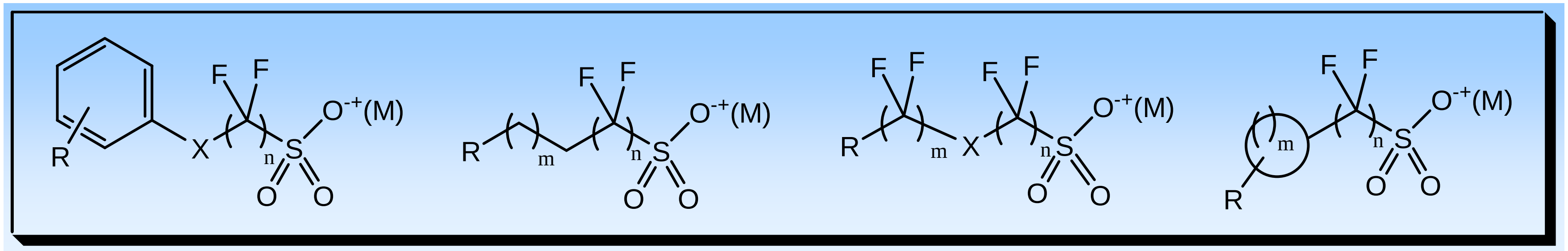
1. PAG sensitivity
2. PAG Miscibility
3. Outgassing and Leaching
4. LER to PAG structures
5. Conventional resists and molecular glass resists

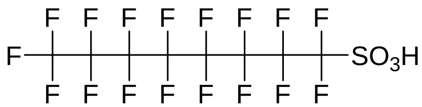
non-PFOS PAGs

ESH Profile

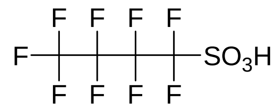
1. Bioaccumulation Potential
2. Biodegradation probability
3. Toxic effects
4. Structural and Electronic factors

General structures of Cornell PAGs





272 cm^3/mol



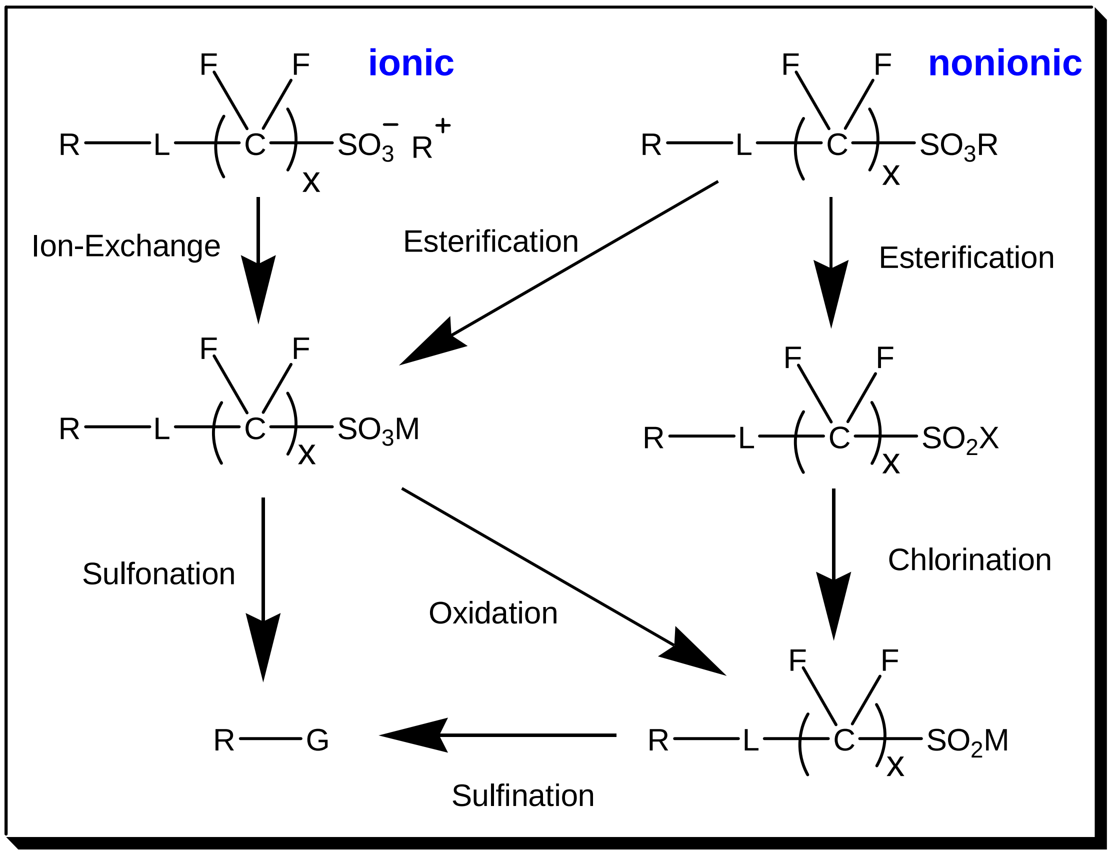
162 cm^3/mol

- **Acid size: 150 ~ 240 cm^3/mol**
- **Acid transparency: aromatic groups for EUV, alkyl groups for 193 nm**
- **Miscibility: ether, ester or nitroxide groups**
- **Outgassing: chromophores**

Ober, C. K. et al. *US Pat. Appl.* 2005/028420.

Ober, C. K. et al. *US Patent Pending.*

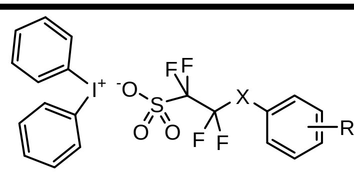
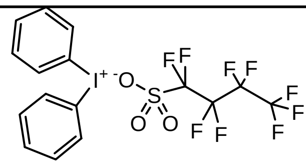
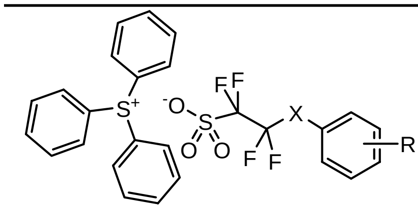
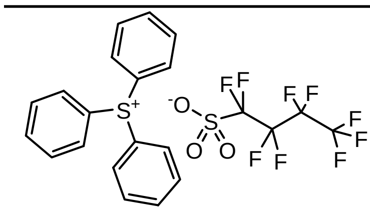
Retro Synthetic Scheme for non-PFOS PAG Synthesis



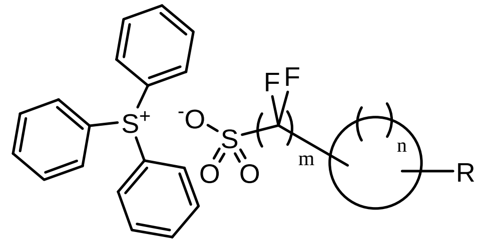
The purity of the samples is confirmed by Elemental Analysis.

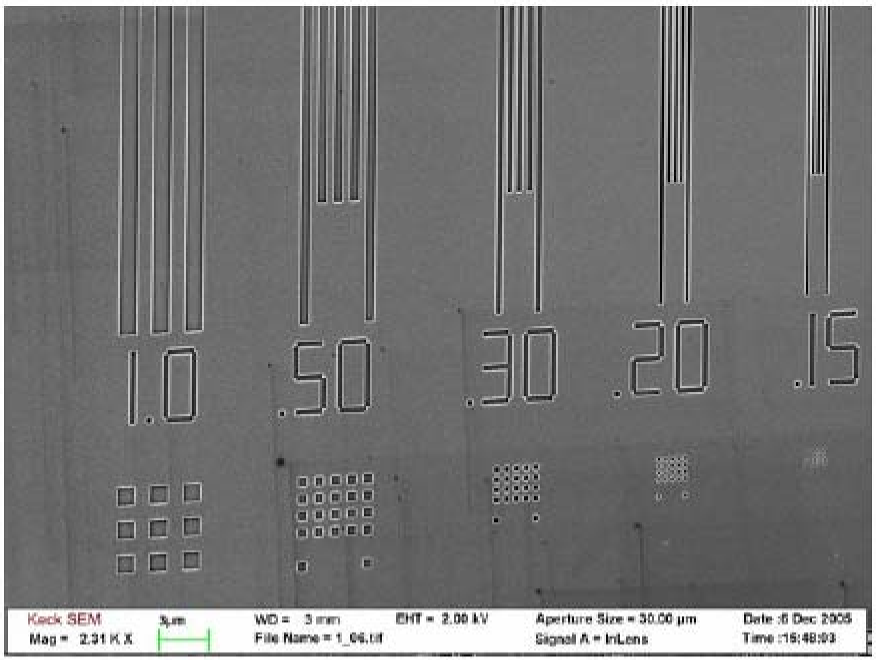
The samples are soluble in most of common and industry organic solvents.

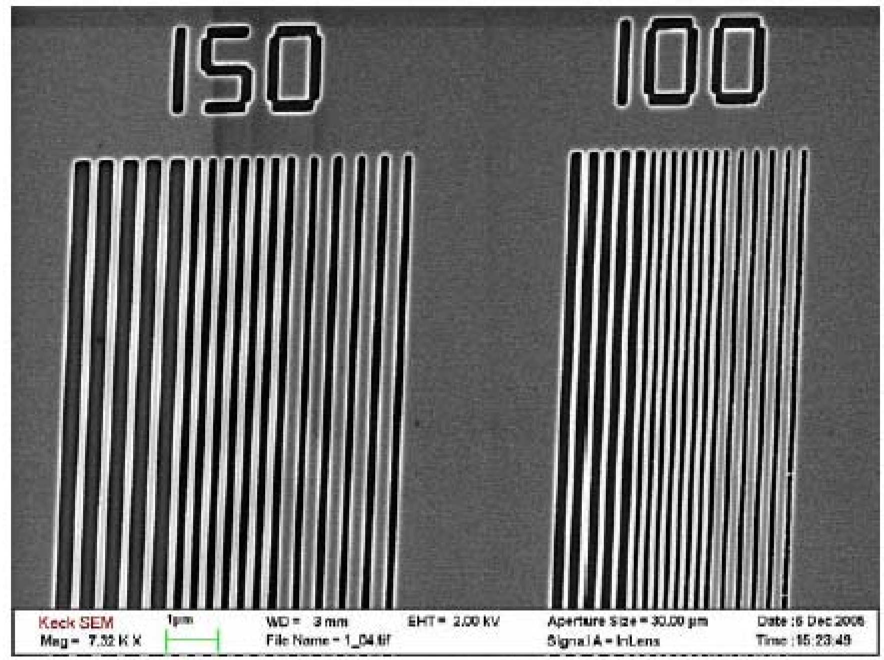
Cornell PAG Sensitivity @ 254 nm

	PAG	E_0 (mJ/cm^2)
1		**1.36**
2		**1.36**
3		**1.53**
4		**1.70**

Cornell PAG Performance @ E-beam with ESCAP

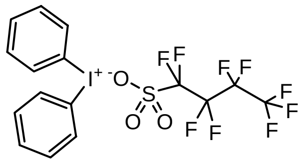






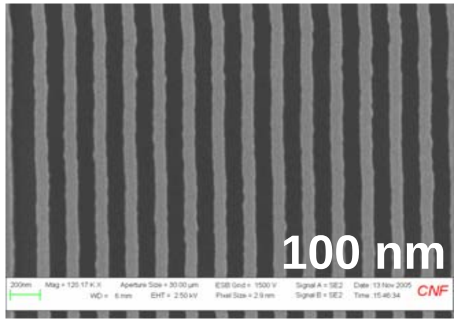
PAG Anion Effect on Resolution and LER by E-beam Lithography

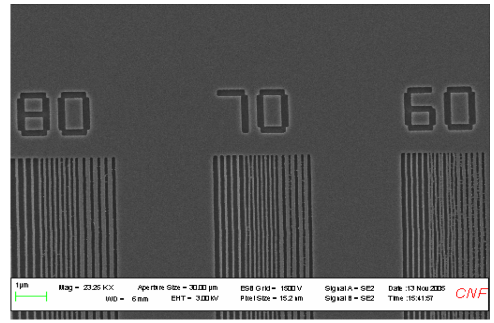
control



162 cm³/mol

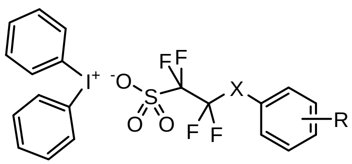
pK_a(Taft) = - 4.99





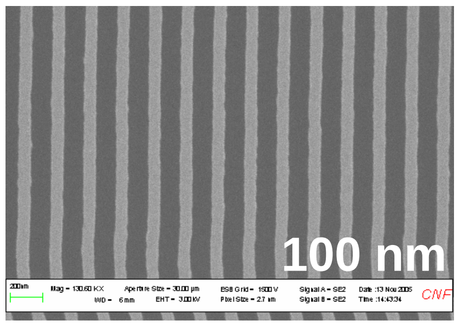
E_{size} = 16 μC/cm²

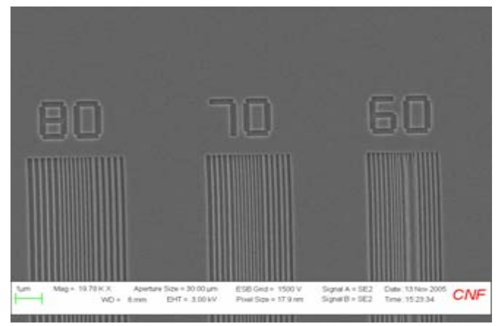
1



170 cm³/mol

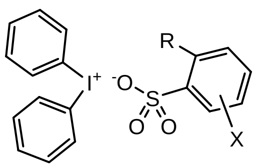
pK_a(Taft) = - 4.86





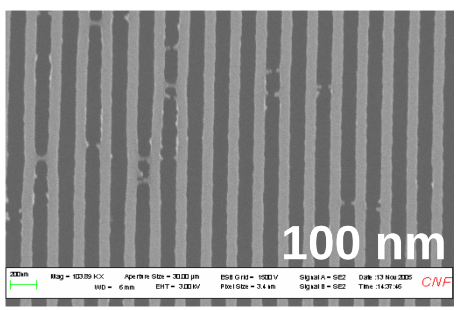
E_{size} = 24 μC/cm²

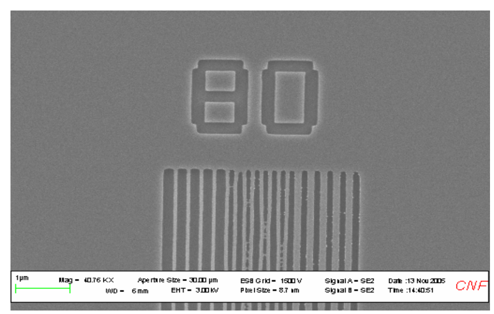
2



155 cm³/mol

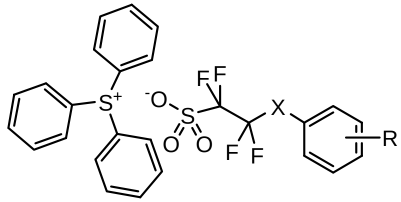
pK_a(Taft) = - 4.10

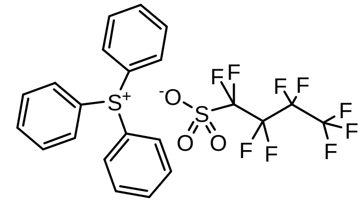




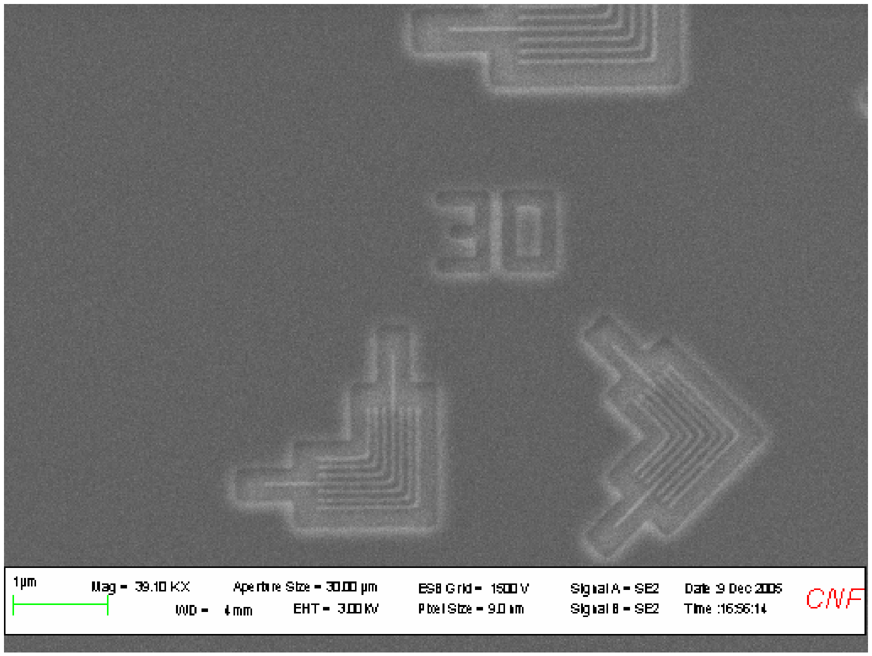
E_{size} = 32 μC/cm²

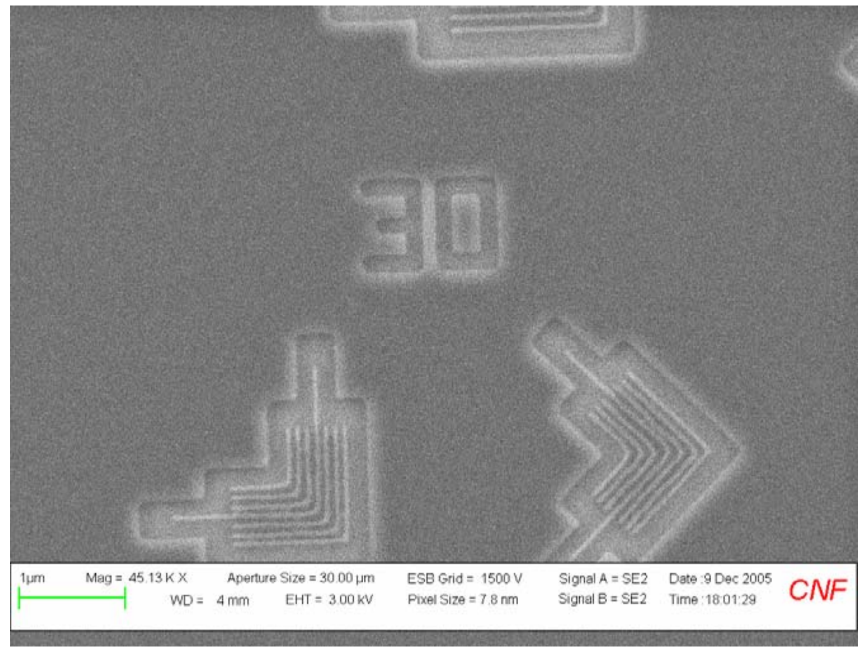
Cornell PAG Performance @ EUV with Acrylic Resist





control

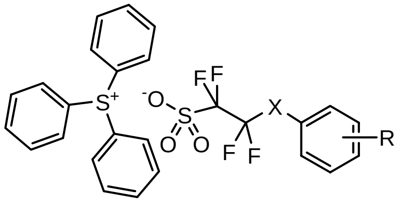


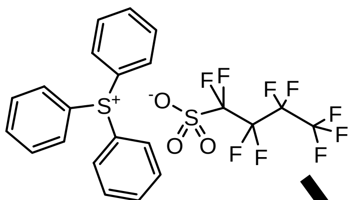


E_0 (100 nm) < 4.9 mJ/cm^2; Es = 7.5 mJ/cm^2;
LER (100 nm L/S) : 7.7 ± 0.8 nm

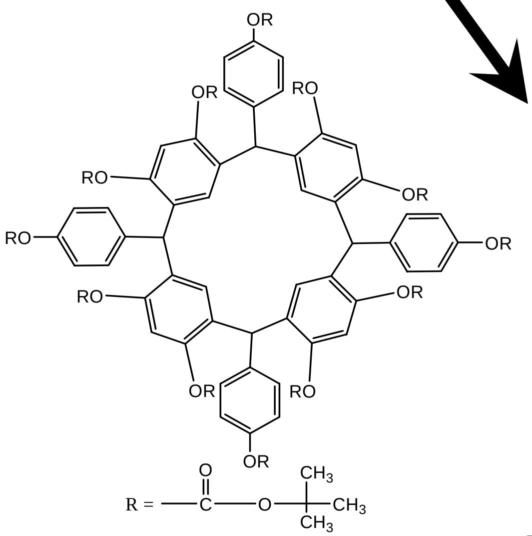
E_0 (100 nm) < 6.4 mJ/cm^2; Es = 8.6 mJ/cm^2;
LER (100 nm L/S): 8.0 ± 0.6 nm

Cornell PAG Performance @ EUV With Molecular Glass Resist

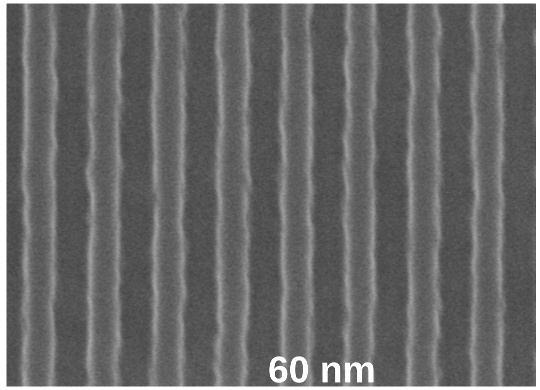


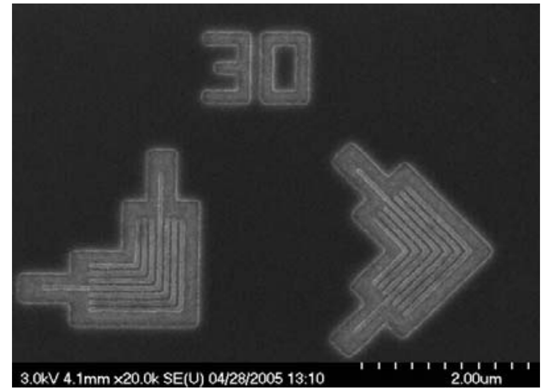


control

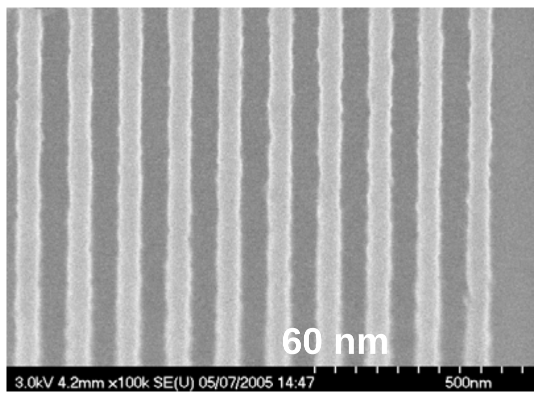


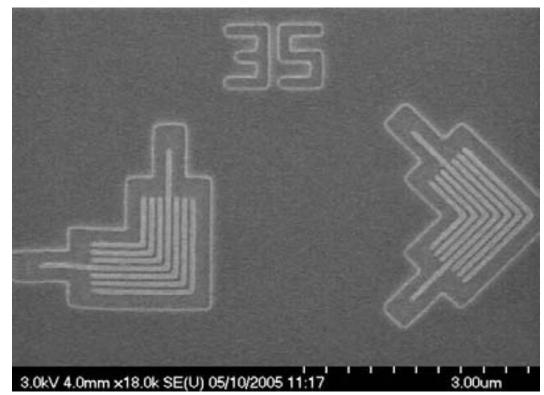
Molecular Glass Resist





E_s = 21.0 mJ/cm^2; R = 25-30 nm; LER (60 nm L/S) = 5.0 nm

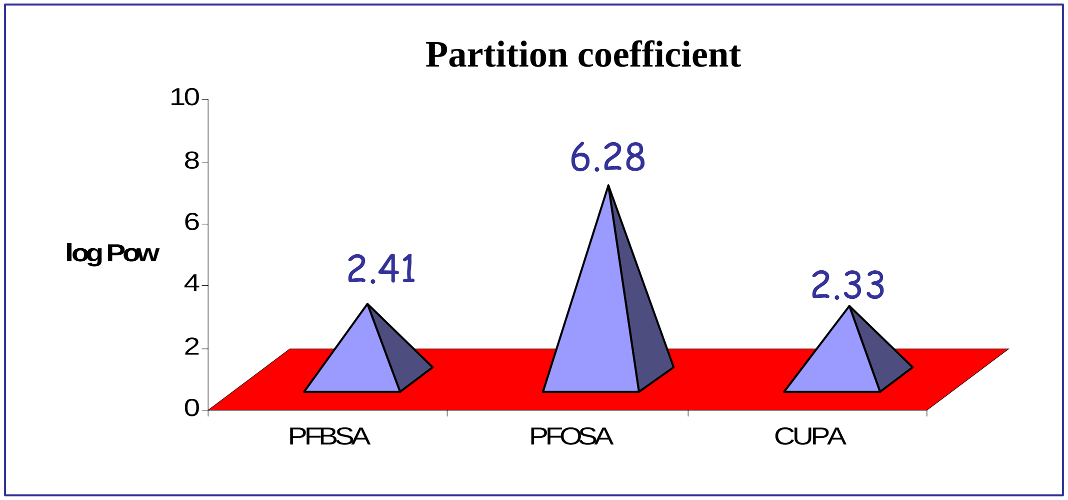


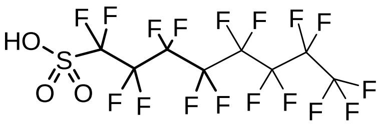


E_s = 39.0 mJ/cm^2; R = 30-35 nm; LER (60 nm L/S) = 4.3 nm

Ober C. K. et al. *J. Mater. Chem. (Advance Article, DOI: 10.1039/b514065j), 2006.*

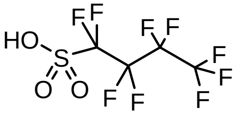
Estimation of Environmental Fate of the Photoacids





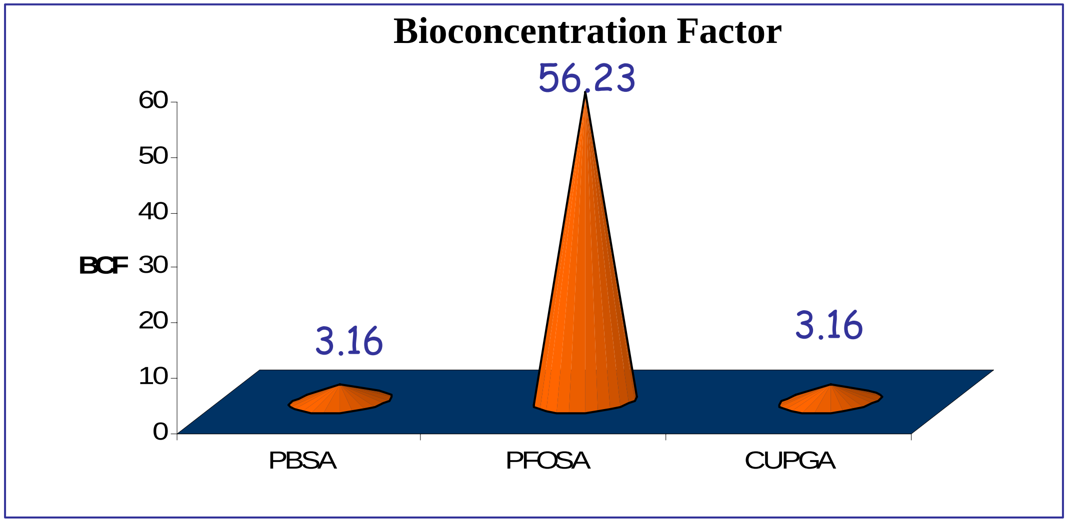
PFOSA

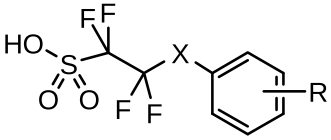
persistent
bioaccumulation



PFBSA

persistent
no bioaccumulation

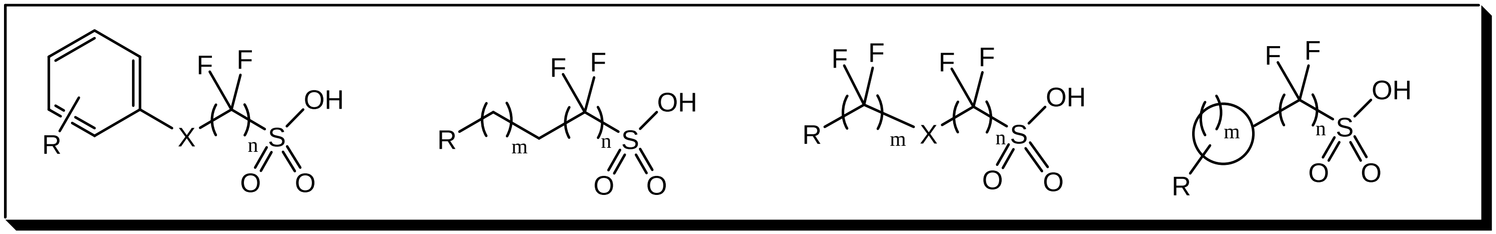




CUPGA ?

Estimated by Estimation Program Interface (EPI) Suite

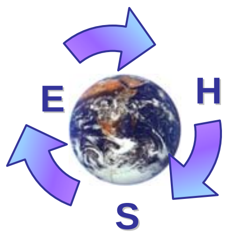
Evaluation of Environmental Fate of the Photoacids



Collaborating with *Prof. Reyes Sierra* in Univ. of Arizona

- **Develop analytical methods for compound detection;**
- **Evaluate bioaccumulation potential;**
- **Study inhibitory effects;**
- **Investigate fate in wastewater treatment systems.**

Cornell University



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TUCSON ARIZONA

Summary

- Developed A Series of non-PFOS PAGs Containing Less Fluorine by Simple Chemistry;
- The non-PFOS PAGs have high sensitivity, good resolution and good LER @ DUV, E-beam &EUV;
- The performance of non-PFOS PAGs are comparable to those of PFBS based PAGs;
- The non-PFOS PAGs have low bioaccumulation according to simulation.

Acknowledgement

Ober Research Group

<u>Intel Corporation</u>

Dr. Yueh Wang
Dr. Heidi Cao

Cornell Nanoscale Science and Technology Facility

Lawrence Berkerly National Lab