APPLICATION OF NANOGRAFTING TO DIFFERENTIAL MEASUREMENTS OF ORGANIC SURFACE PROPERTIES

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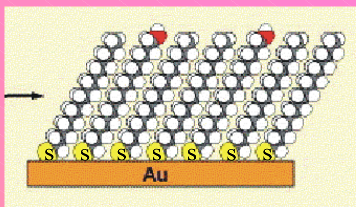
MOTIVATION

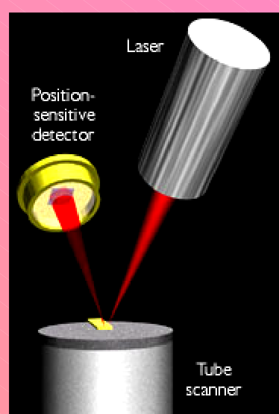
We are interested in understanding the various properties of organic thin films at the molecular level, especially in characterizing and modifying self-assembled monolayers with the power of atomic force microscopy. Such films have possible applications in electronic devices or sensors.



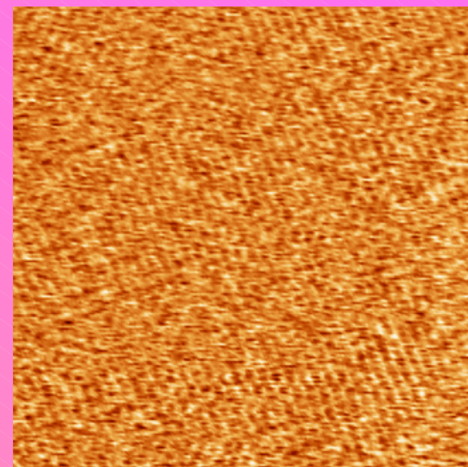
Scheme of thiol SAMs

Self-assembled monolayer of thiols are ordered molecular assemblies formed by alkanethiol molecules chemisorb on gold surfaces through the thiol headgroup.

Atomic force microscopy is able to offer local surface information at atomic resolution by sensing the force between a small sharp tip and a surface, which corresponded to the bending of the compliant cantilever the tip attached to, and is translated into the laser signal change of a position sensitive photodiode. A scanner controlled by the feedback loop will move the surface to keep the force or height constant while scanning in X-Y direction. Various new operation modes have been developed since its inception, which differ in tip operation modes, interaction forces involved and feedback maintained.

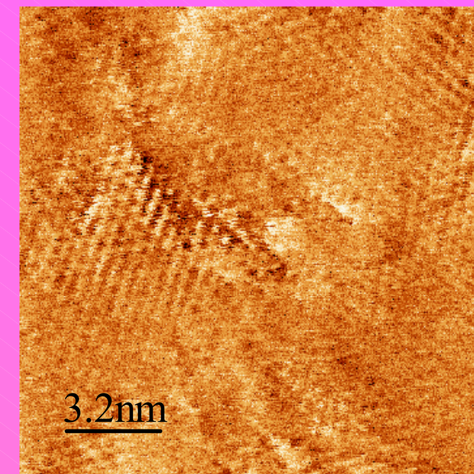


Principle of AFM



Atomic resolution image of gold(111) (100 Å ×100 Å) in friction mode

Molecular resolution image of C_{18} (100 Å ×100 Å) in friction mode



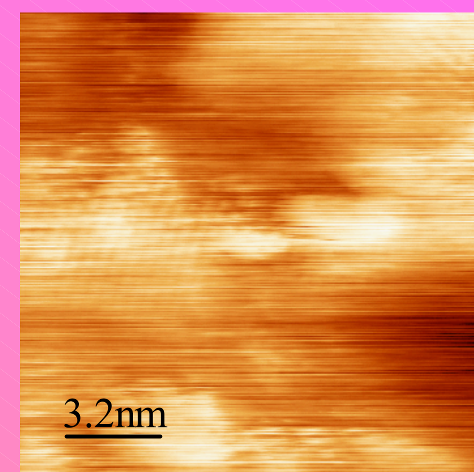
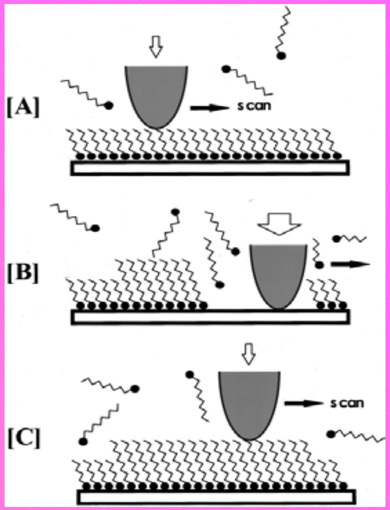


Image of CH_3-$(CH_2)_{17}$-SH layers in deflection and height modes(32 Å ×32 Å)

PRINCIPLE OF NANOGRAFTING



Our research focuses on patterning and characterizing self-assembled monolayers of thiols at nanometer scale by the nanografting technique.

Advantage:

- surface can be imaged and patterned with different molecules by the same tip under exactly the same situation. It is thus possible to compare molecular properties in a differential way, minimizing tip-induced and other environmental effects.
- By using lateral force microscopy and the conducting-tip AFM, electron transfer and friction properties of the molecules can be correlated with topography information.

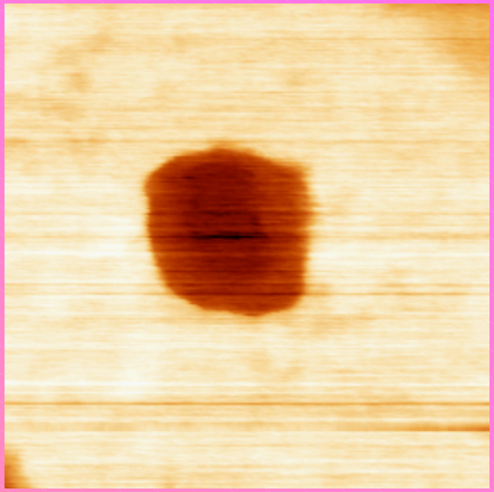
Nanografting was introduced by G.Y. Liu at Wayne State University, which procedure combines the fabrication and characterization of a nanopattern using AFM.

(A) Matrix SAM is imaged at a low imaging force in a 2-butanol solution of another thiol.

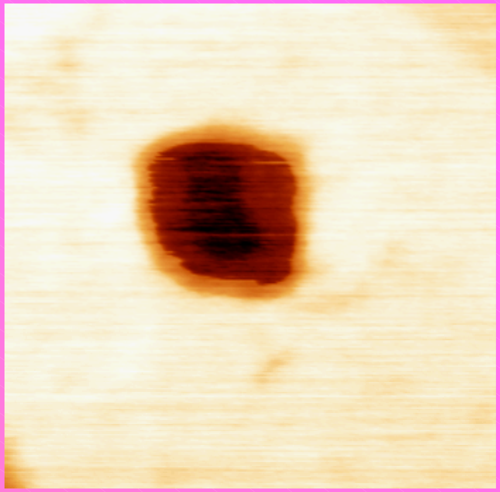
(B) At a force greater than the displacement threshold, the AFM tip displaces the adsorbates at the desired areas,the thiol molecules in the contacting solution self-assemble onto the exposed gold sites.

(C) The nanopattern is imaged at a reduced imaging force.

NANOGRAFTING APPLICATION

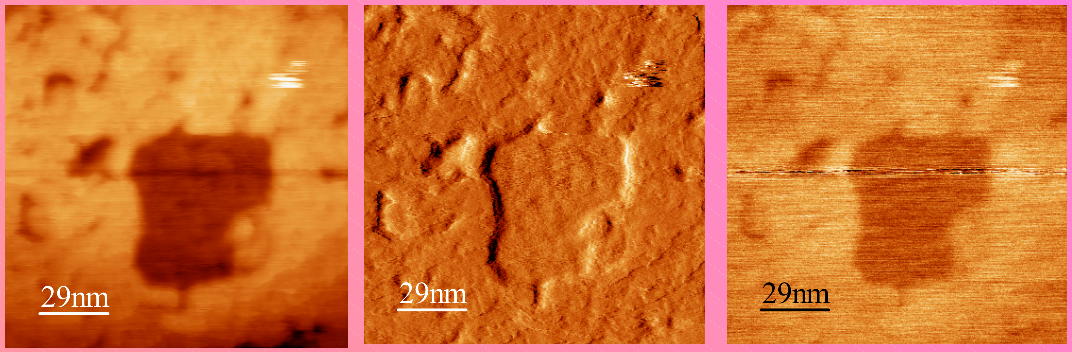


Low force
C_6-OH in C_{18} at 0.9nN
1200Å×1200Å

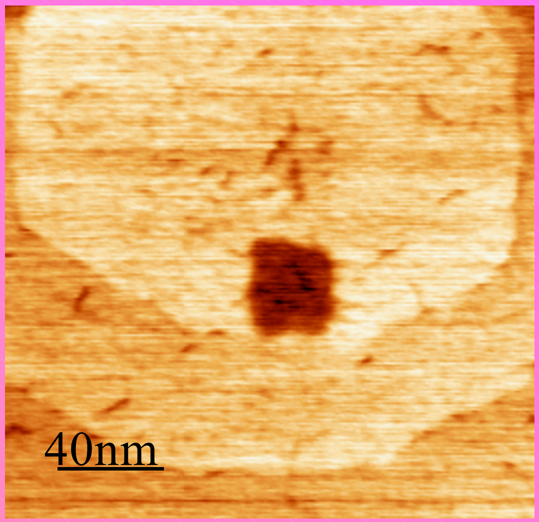


High force
C_6-OH in C_{18} at 3.6nN
1200Å×1200Å

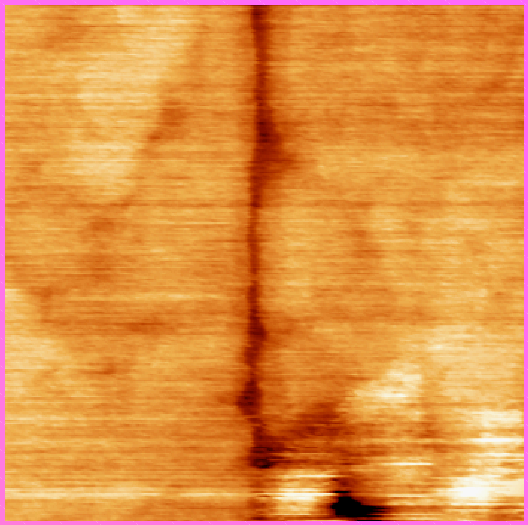
While imaging at high force, unexpected halos show up for C_6-OH and C_{11}-OH grafted in C_{18}, while they do not show up with CH_3-terminated thiols The SAM in the pit near the outer wall seems to resist compression better than that in the center of the pit.(Work of Adriana Gil.)



Images of nanoshaving C_{18} layer in
simultaneously height, deflection and friction mode(1450Å×1450Å)



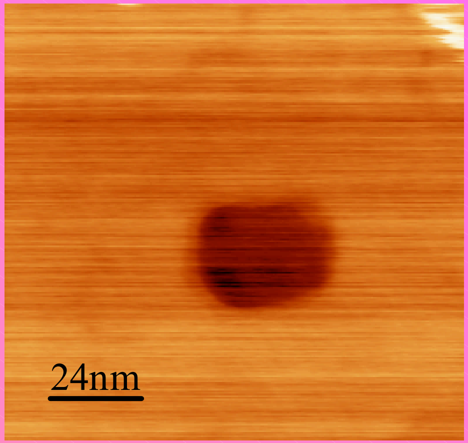
CH_3-$(CH_2)_9$-SH nanografted into a CH_3-$(CH_2)_{17}$-SH SAM (400Å×400 Å)



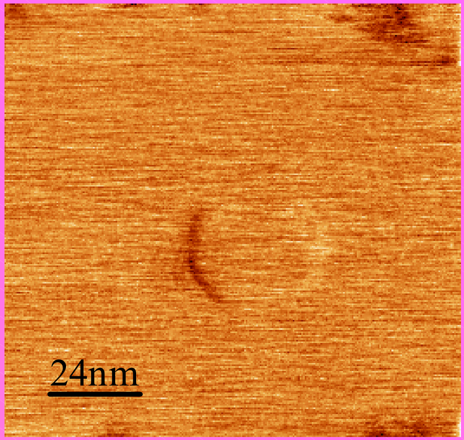
A 70 Å "line" of CH_3-$(CH_2)_9$-SH nanografted into a CH_3-$(CH_2)_{17}$-SH SAM(800 Å ×800 Å)

Measured height difference: 8.6 Å
Calculated height difference based on 1-D model: 8.67 Å

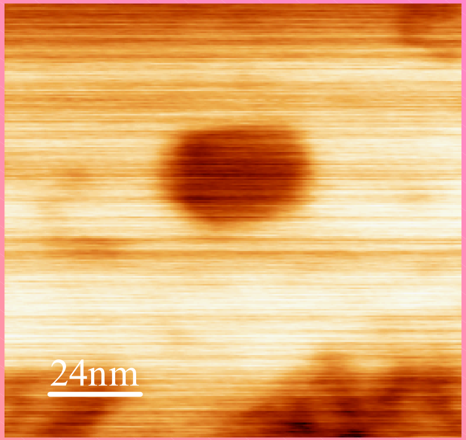
Measurement of the height difference between CH_3-$(CH_2)_{17}$-SH and CH_3-$(CH_2)_9$-SH



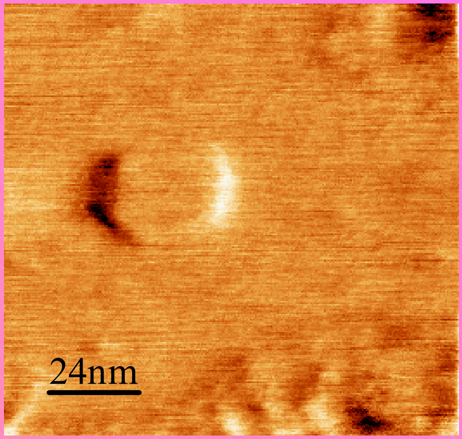
Low force height image of
0.177mMPEG molecules grafted into
C18 layer(1200Å×1200 Å)



Low force friction image of
0.177mMPEG molecules grafted into C18
layer(1200Å×1200 Å)(retrace direction)

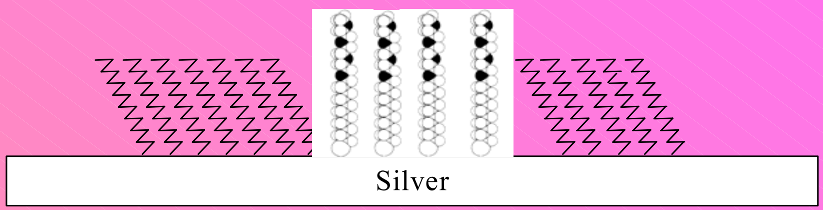


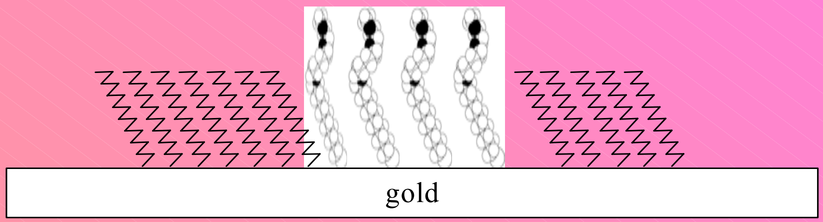
High force height image of
0.177mMPEG molecules grafted into
C18 layer(1200Å×1200 Å)



High force friction image of
0.177mMPEG molecules grafted into C18
layer(1200Å×1200 Å)(retrace direction)

While the height differences between C18 and PEG molecules remain unchanged under different imaging force, there are significant changes in friction differences.



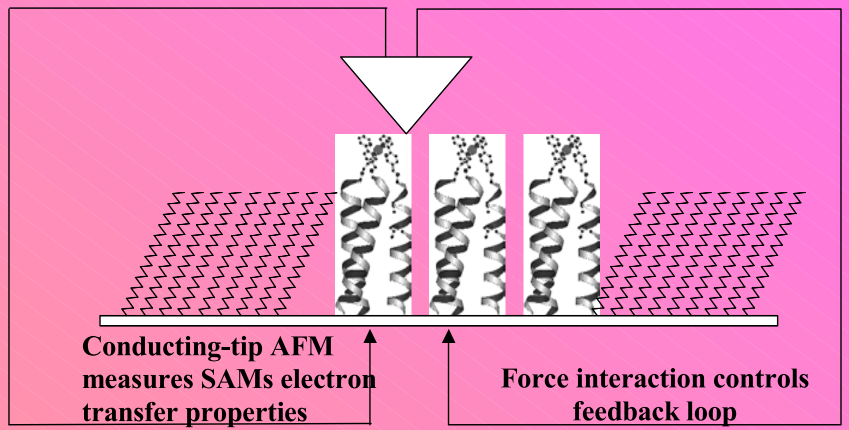


- Oligo(ethylene glycol)-Terminated Self-Assembled Monolayers are believed to have different molecular conformations on gold and silver substrates; as a consequence, their resistances to protein adsorption are different. Nanografting PEG into C_{18} layers should offer us a very good reference point. *
- SAMs frictions are also believed to be related with SAMs density. Hence, PEG SAMs should have two different friction.vs.load relationship on gold and silver substrate.**

* Feldman K, Hahner G, Spencer ND, Harder P and Grunze M J.Am.Chem.Soc. **121**, 10134(1999)

** Barrena E, Ocal C and Salmeron M J.Chem.Phys. **113** .6(2000).

FUTURE RESEARCH PLAN



- Nanografting de novo protein [Ru(P_{20})^3], whose electron transfer properties had been well studied in solution, into the SAMs of thiols. The protein is developed in the laboratory of Professor George McLendon, Chemistry Department, Princeton University.

- Combining Conducting tip-AFM and nanografting, the surface can be imaged and patterned with different molecules by the same tip, while the electron transfer properties of the surface can be measured and correlated with other properties like height information.