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DEPARTAMENTO DE QUÍMICA

Películas Moleculares Autoensambladas: Aplicaciones en Nanociencia y Nanotecnología

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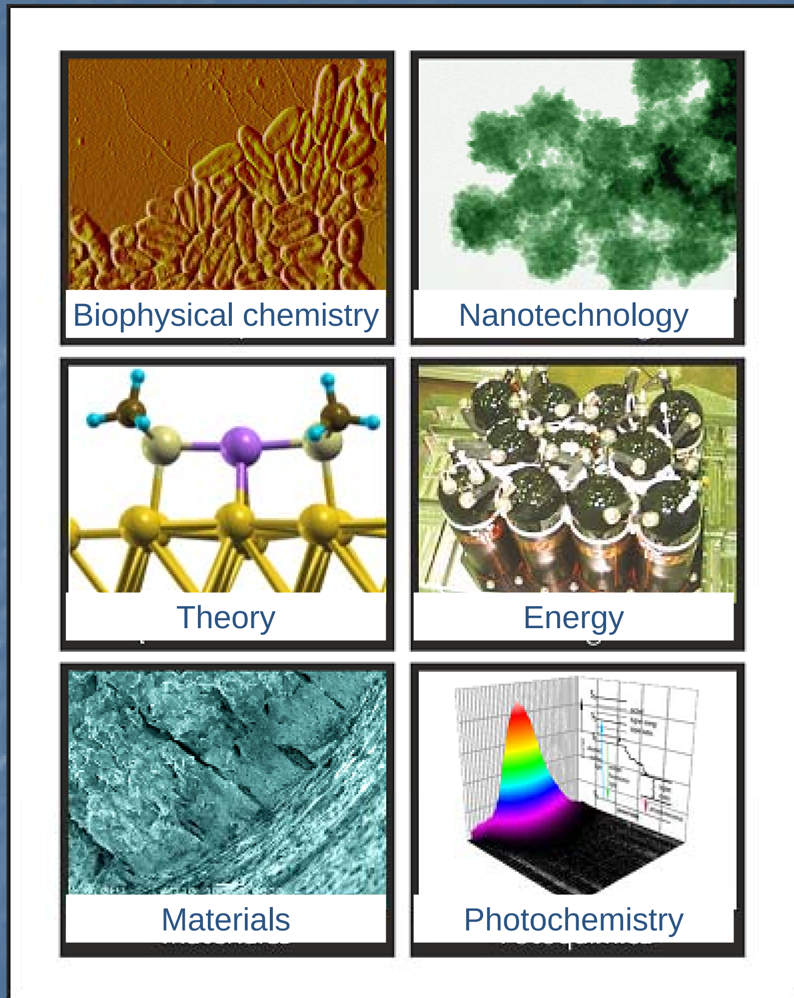
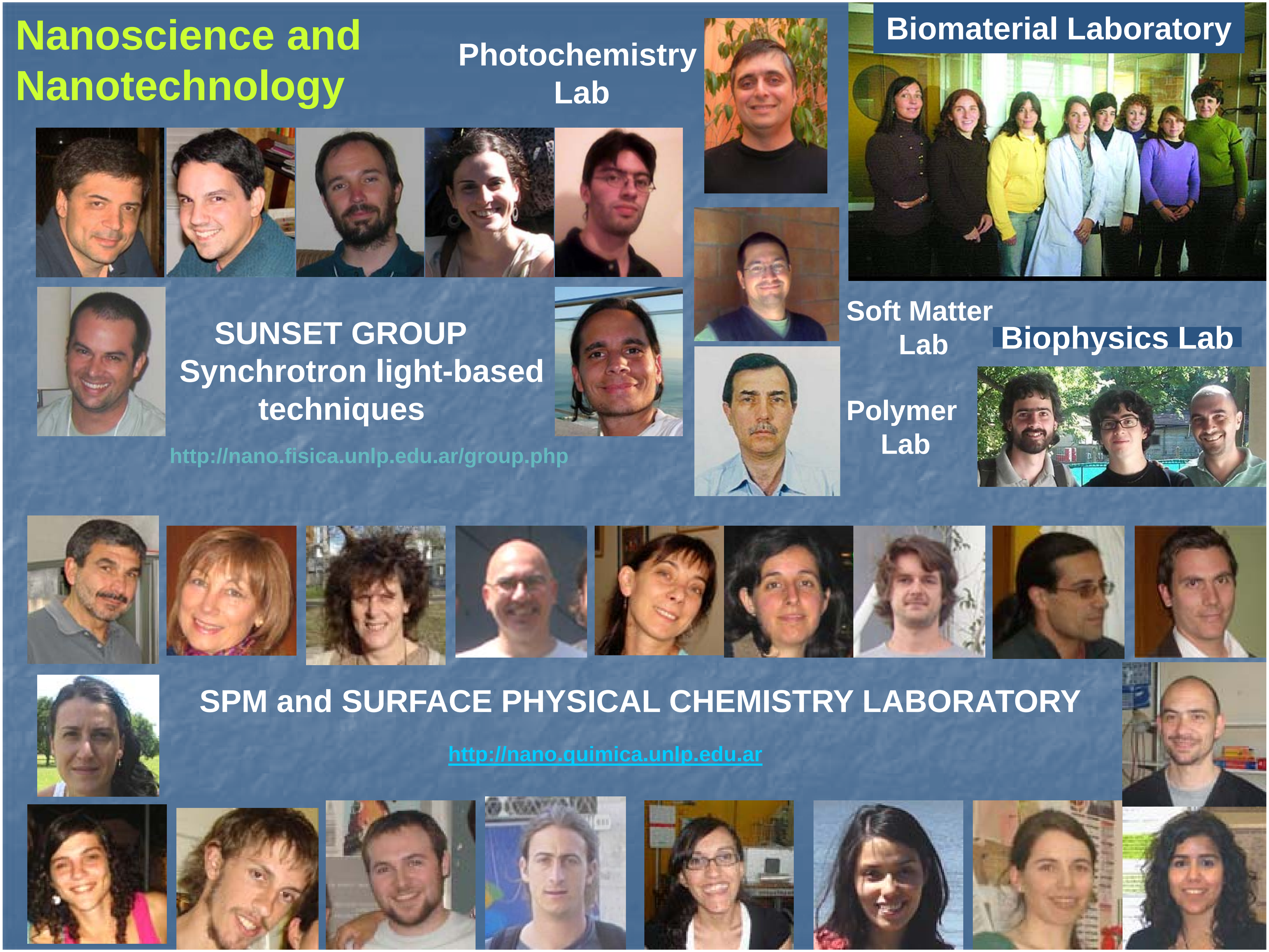


80 researchers
80 PhD students
30 technicians

$$$$$$$
CONICET
ANPCyT
UNLP
CIC



Nanoscience and Nanotechnology
Photochemistry Lab
Biomaterial Laboratory
SUNSET GROUP
Synchrotron light-based techniques
http://nano.fisica.unlp.edu.ar/group.php
Soft Matter Lab
Biophysics Lab
Polymer Lab
SPM and SURFACE PHYSICAL CHEMISTRY LABORATORY
http://nano.quimica.unlp.edu.ar

Research Projects :

$$$$$$$$$
ANPCyT
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UNLP
EU-Commission
Royal Society

Physical-Chemistry of Molecular Self-Assemblies

Molecular Self-Assembly from Gas Phase

Sensors and Biosensors

Gas Sensors and Energy Storage Materials

Nanofabrication Methods

Nanomaterials for Electrocatalysis and Electroanalysis

Nanomaterials of Biomedical Interest

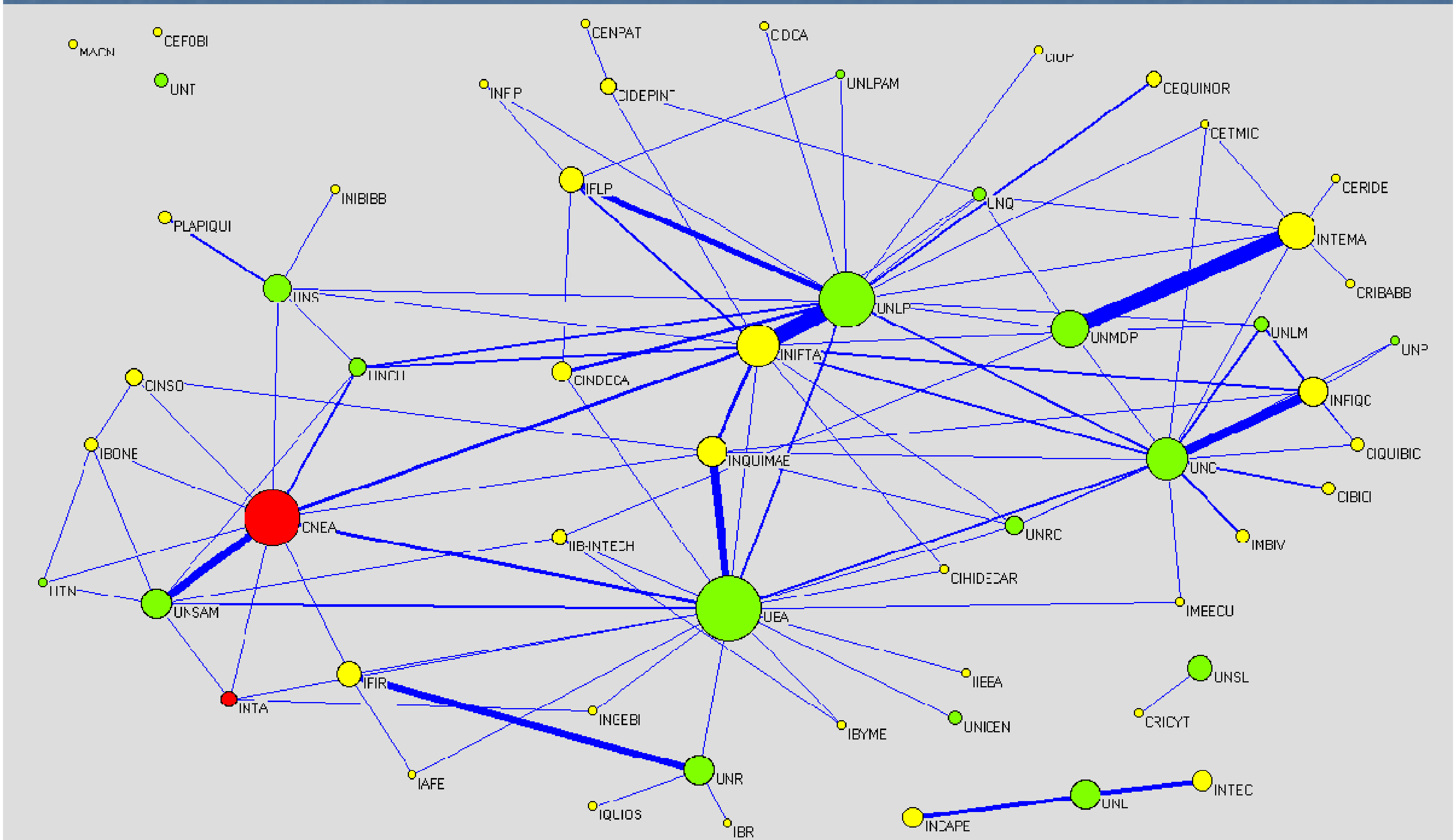
Surface Modification in the Nano/Microscale Appplied to Biomedical Technologies

Modeling Nanostructures Evolution

Modification of Nanomaterials using Organic Synthesis

Characterization of Nanomaterials with UHV and X-Ray Absorption Techniques

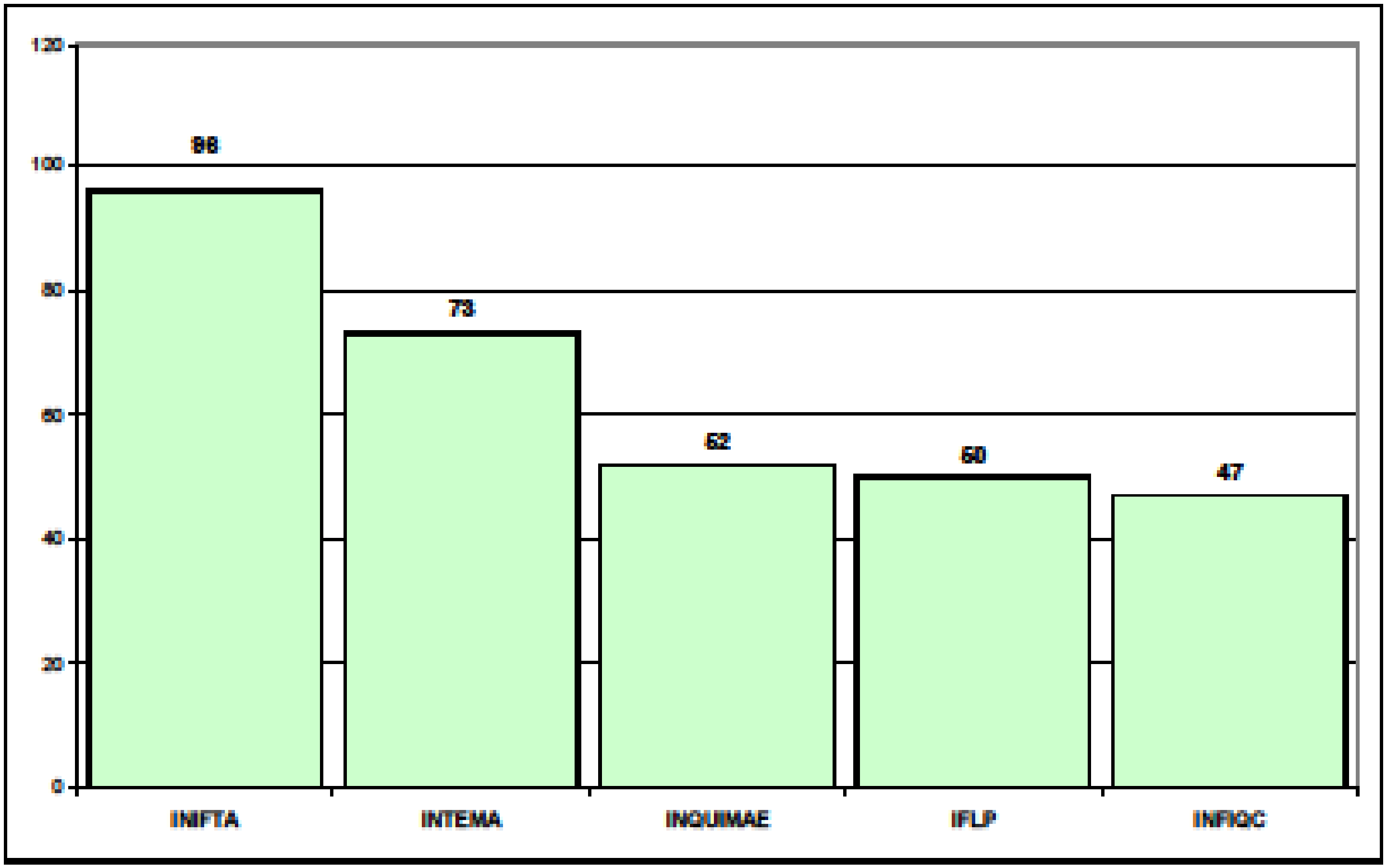
Nanoscience and Nanotechnology Map: scientific production and conectivity map (Argentina 2007)



Source: CAICYT-CONICET

INIFTA: Scientific Production in Nanoscience and Nanotechnology

Gráfico 14. Publicaciones argentinas en nanotecnología de institutos CONICET (2000-2006)

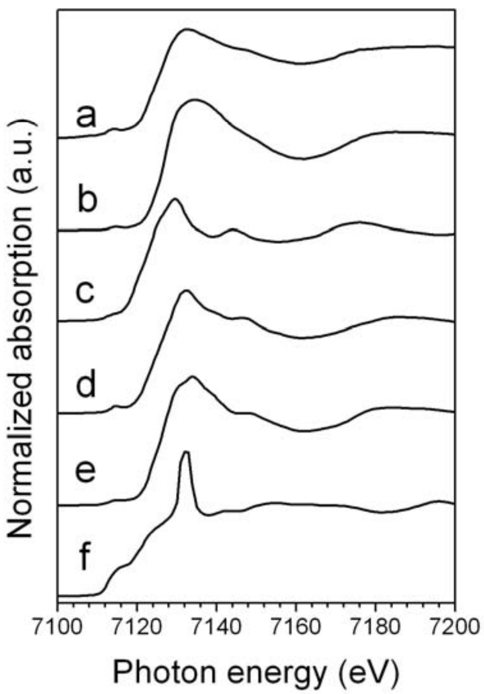


Fuente: Elaboración propia a partir de datos de SCI-WOS.

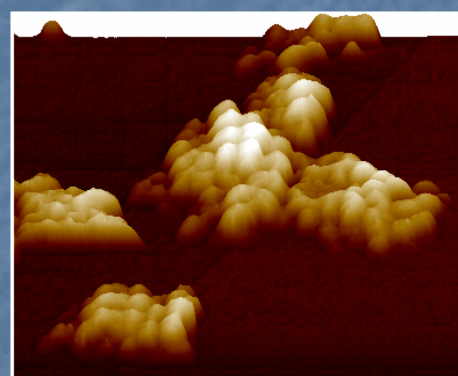
Source: CAICYT-CONICET

X-Ray Absorption Lab

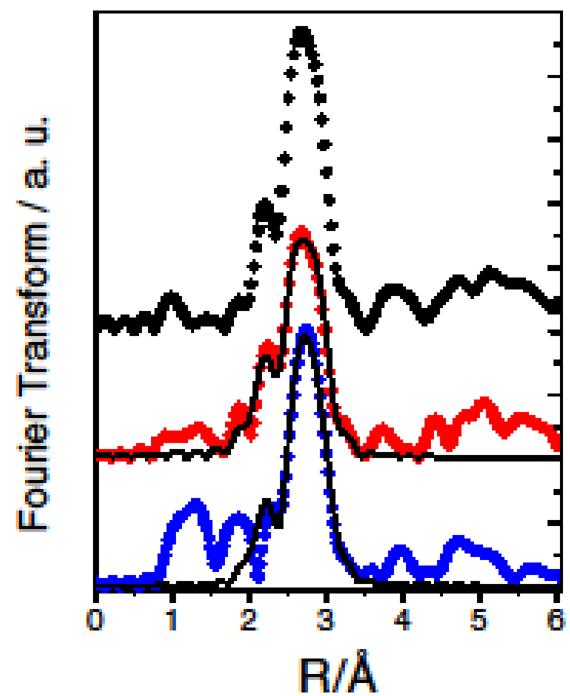
Characterization of Nanomaterials



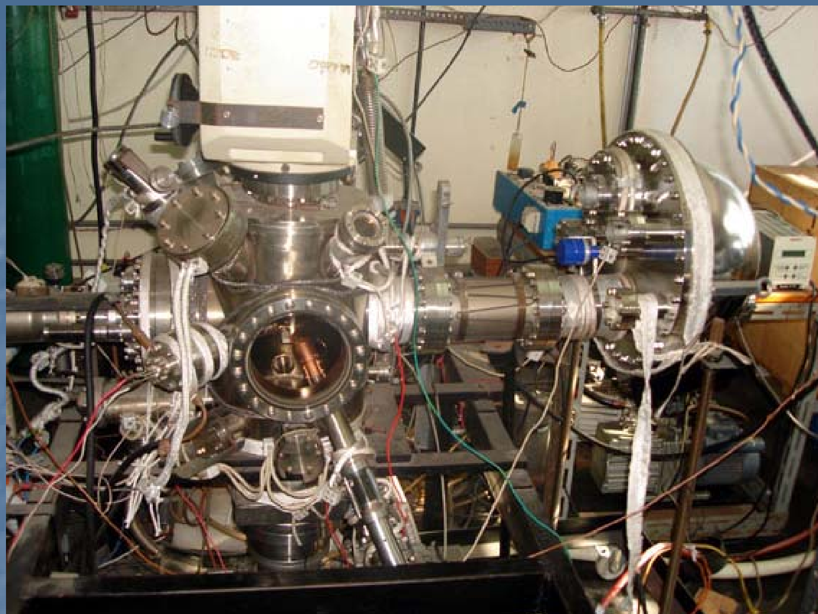
XANES



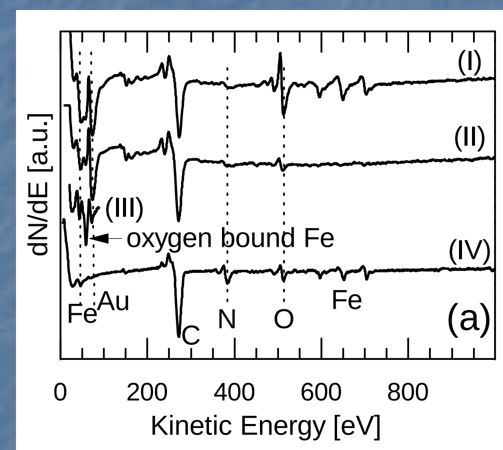
EXAFS



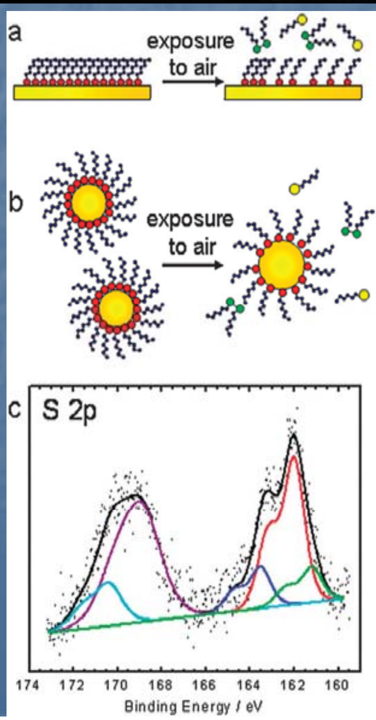
Surface Analysis Lab

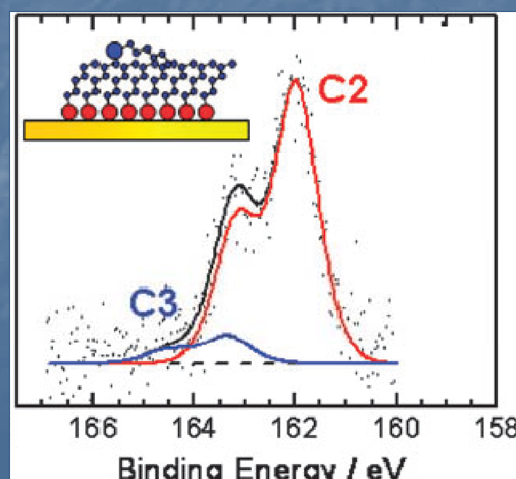


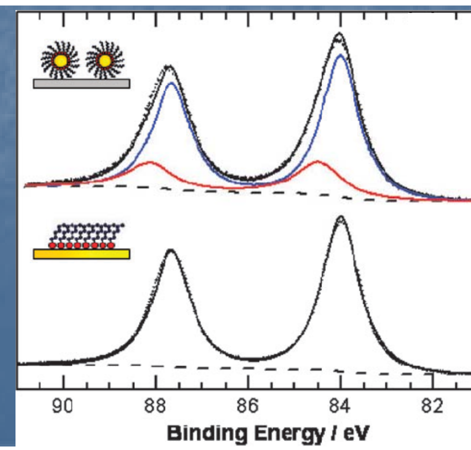
XPS
AES
TPD



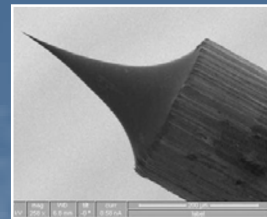
Surfaces and nanoparticles

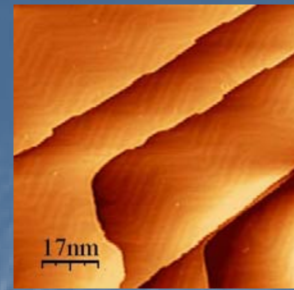


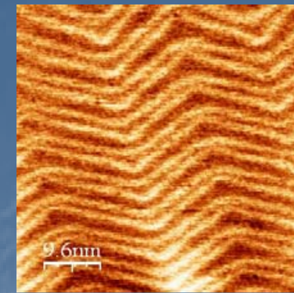




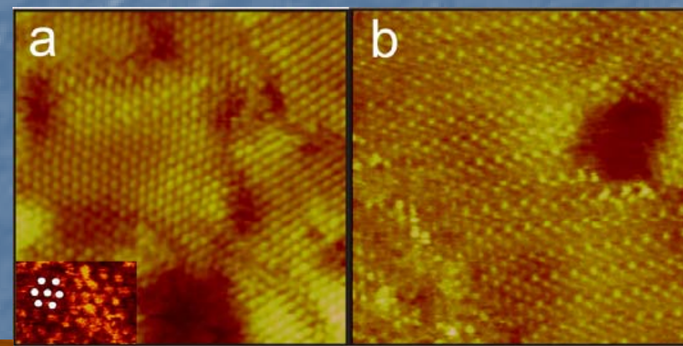
SPM Lab: STM,ECSTM, STS

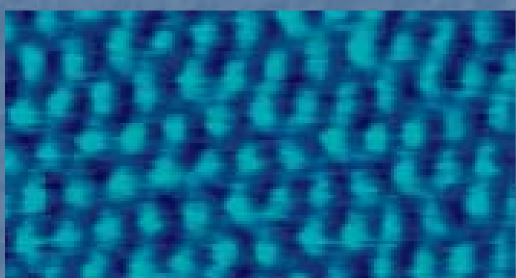


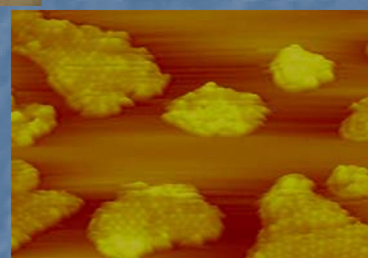




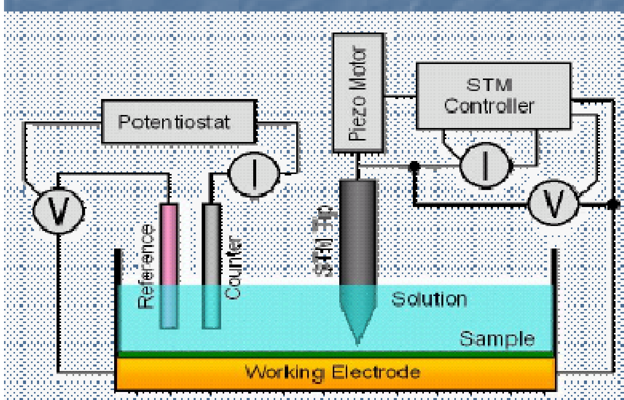
Surfaces
Atoms.
Molecules
Nanoparticles

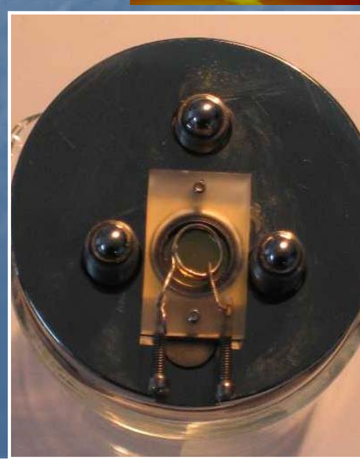


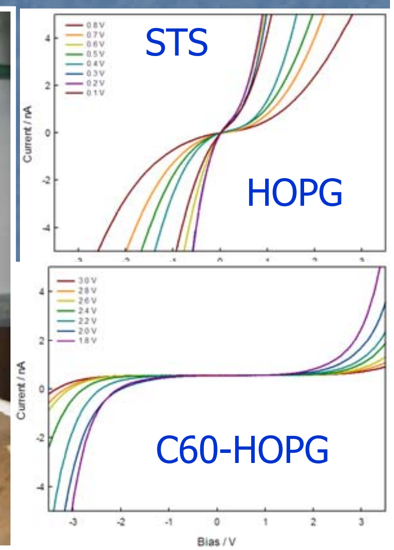




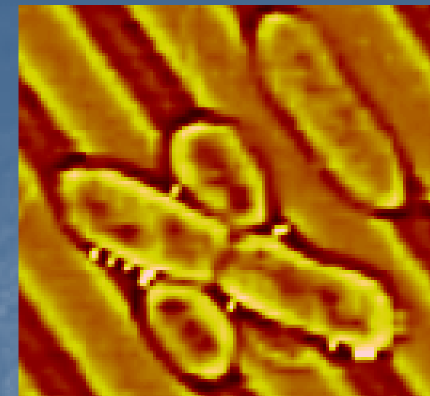
4 STM-AFM working in liquids, controlled atmospheres, and air

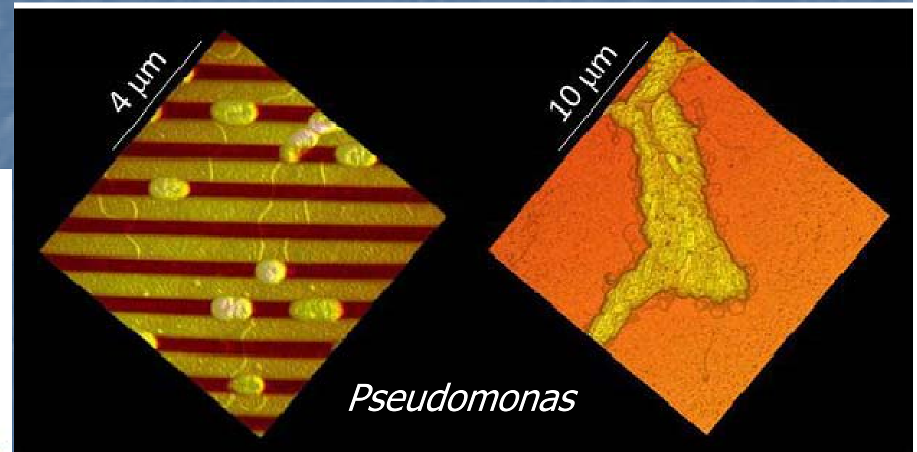


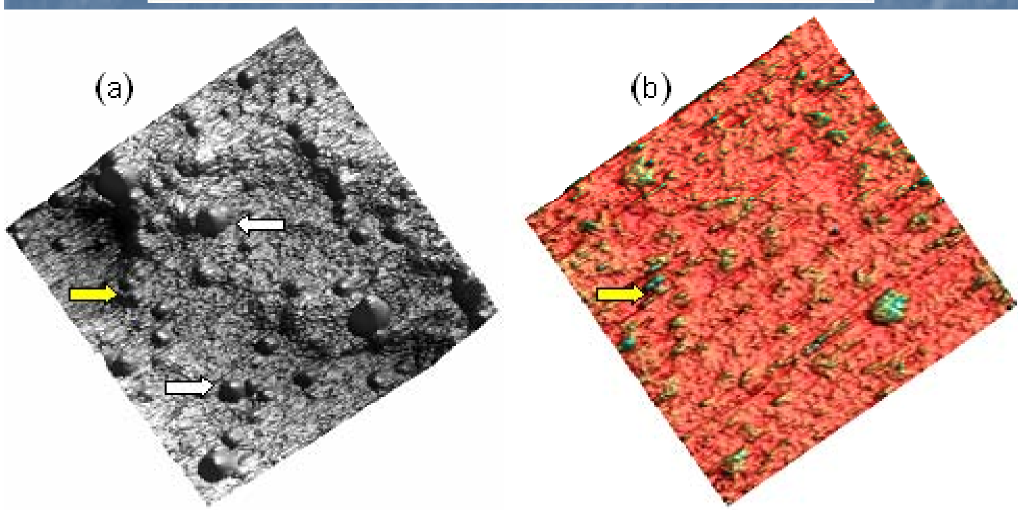


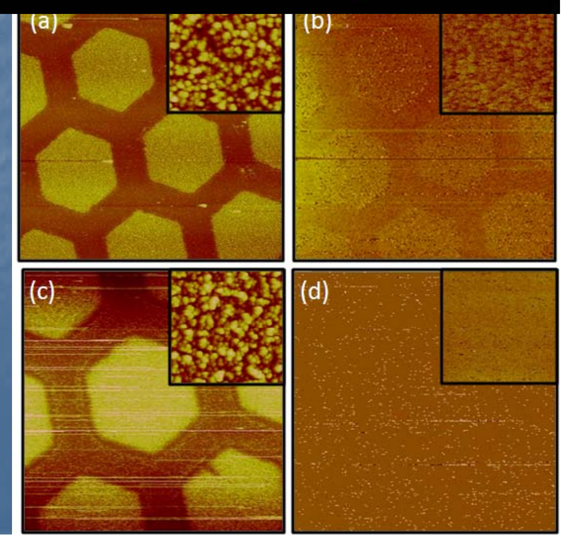


SPM Lab: AFM and ECAFM

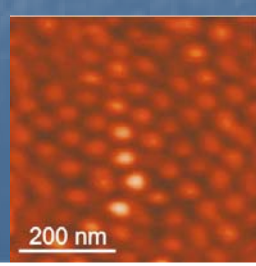


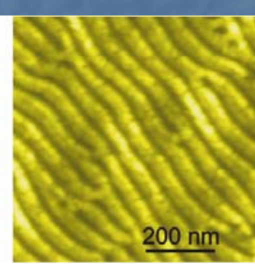


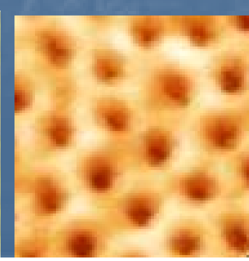




Biomaterials, cells, magnetic materials

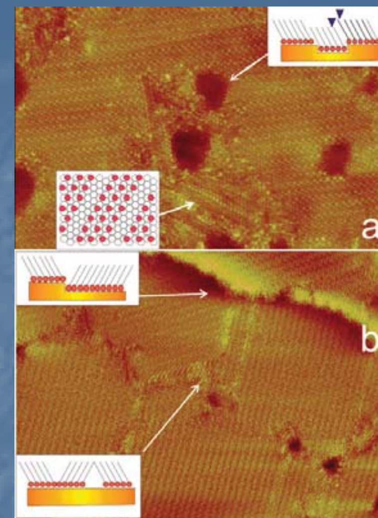


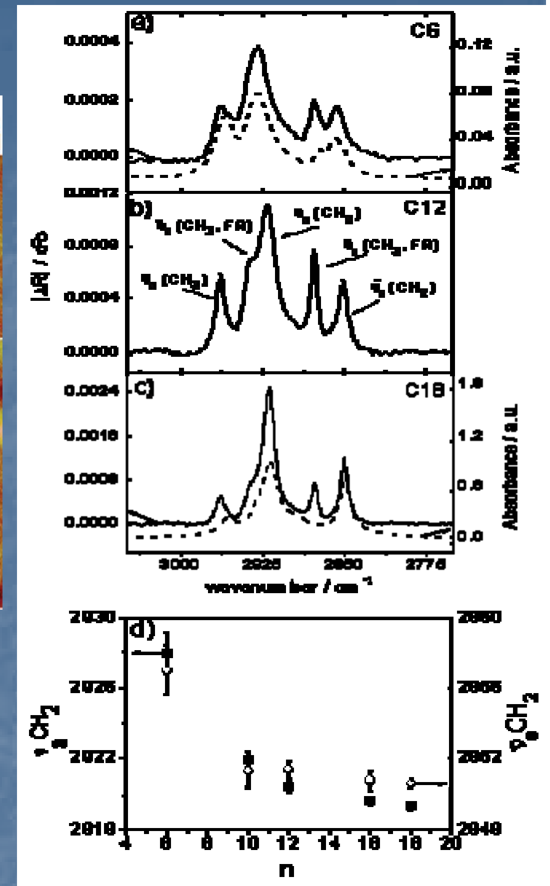




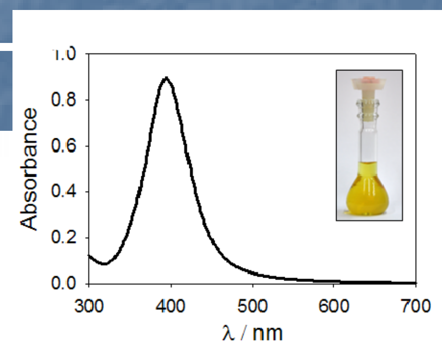
Spectroscopy Lab

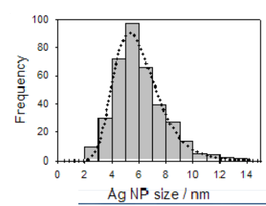
IR-ATR

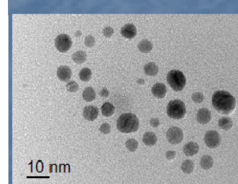


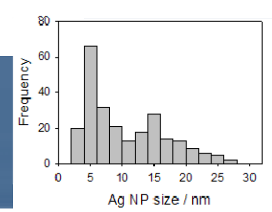


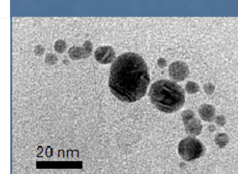
UV-Vis

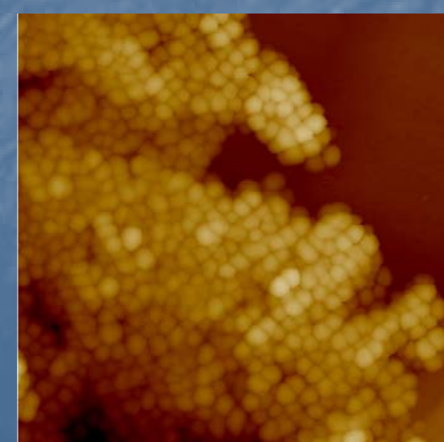






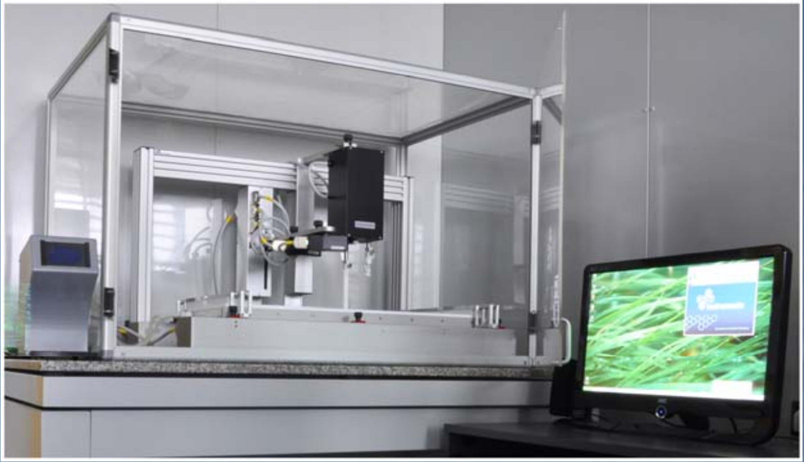






Nano/micromicrofabrication

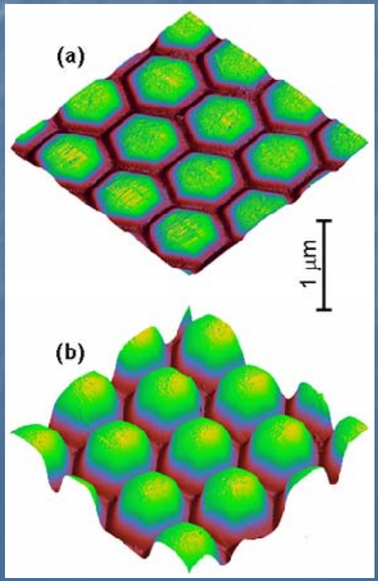
PVD



Langmuir - Blodgett

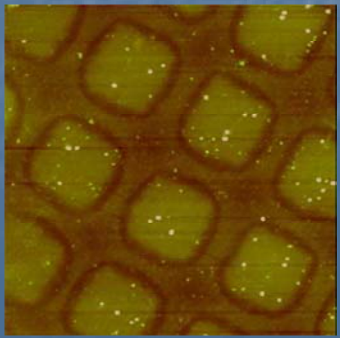
Stencil lithography

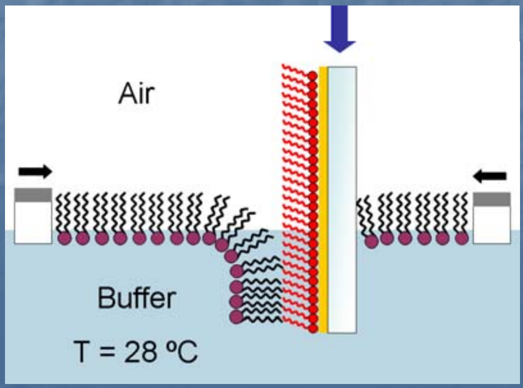
Ordered films of nanoparticles and lipids

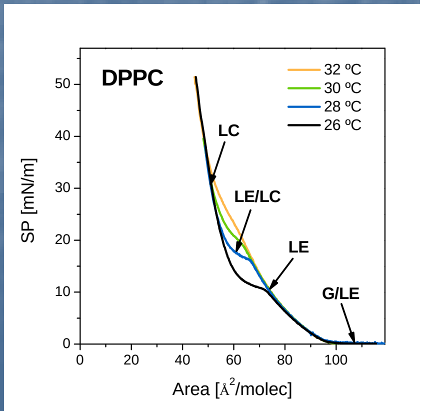


Three dimensional structures

(Metals, fullerenes)

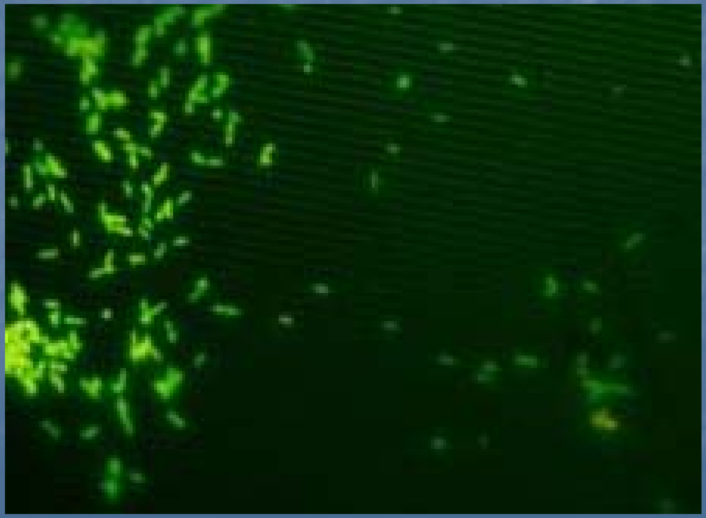


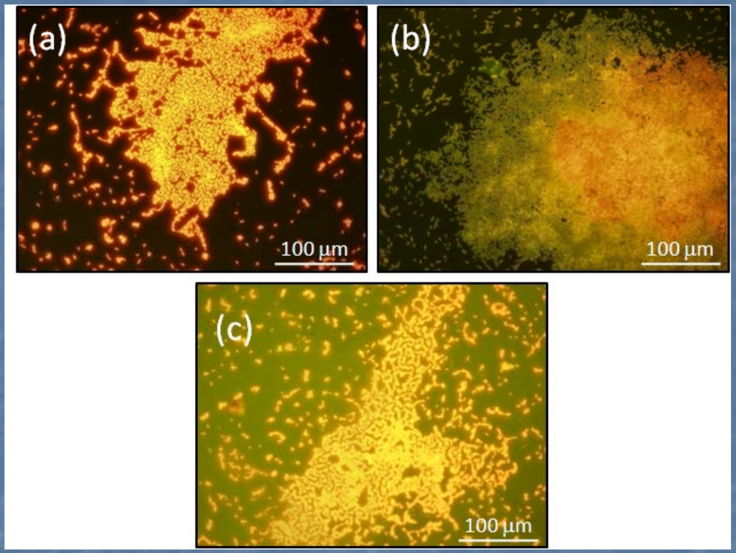


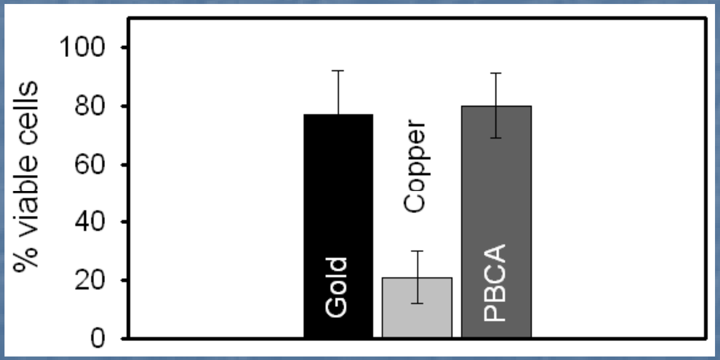


Cell and Bacterial Culture Lab

Fluorescence Microscopy







Bacteria and cell adhesion to nano/microstructured surfaces

Physical-Chemistry of Molecular Self-Assemblies

Self-assembly is a branch of nanoscience and nanotechnology in which atoms, molecules, objects, devices, and systems form structures without external prodding

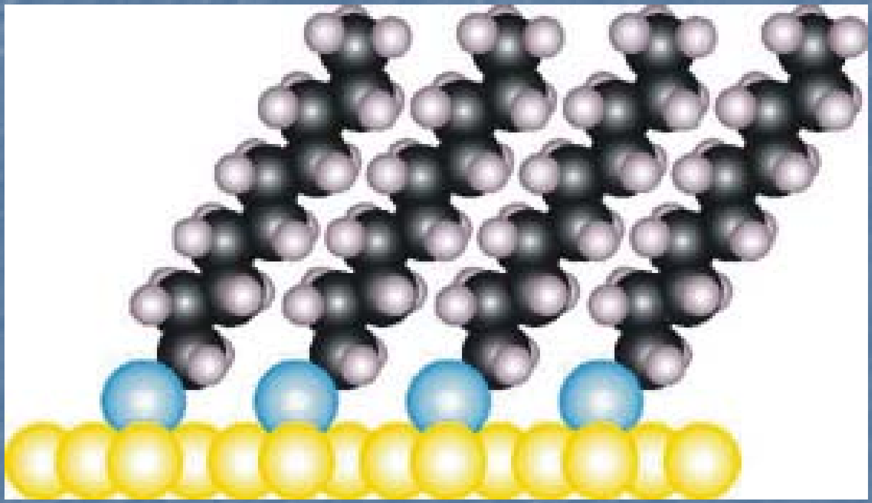
In self-assembly, the individual components contain in themselves enough information to build a template for a structure composed of multiple units.

An example is the construction of a monolayer, in which a single layer of closely-packed atoms or molecules stick to a surface in an orderly and closely-packed fashion.

TWO-DIMENSIONAL MOLECULAR FILMS: tailoring surface chemistry

Self assembled monolayers (SAMs)

Typical SAM structure



Terminal group

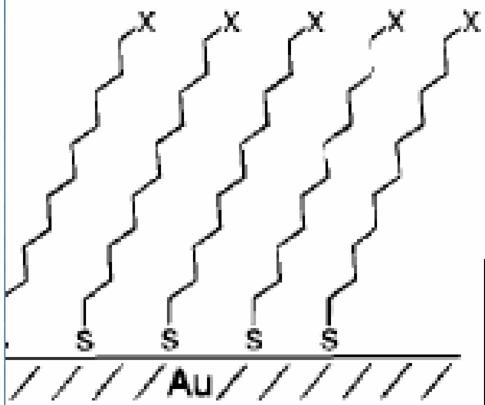
Hydrocabon chain

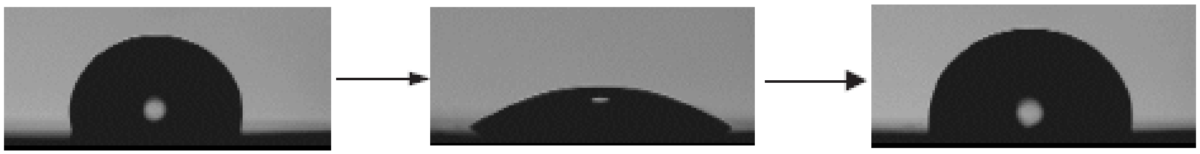
Reactive head (linker)

substrates
metals, semiconductors, oxides
molecules
silanes, phosphonates, thiols

Self-assembly: molecular-substrate, molecule-molecule, molecule-solvent interactions

Tailoring the Surface Chemistry of Materials

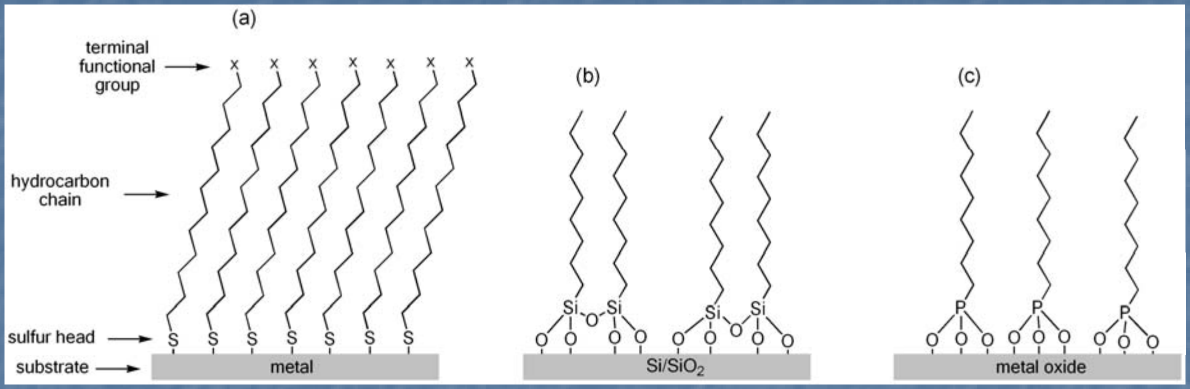




X-groups	Function	Applications
CH_3	Hydrophobic (80-110°)	Patterning
$-CF_3$	Hydrophobic (100-130°)	Patterning
-OH	Hydrophilic (<20°)	1. Patterning
-COOH	1. Hydrophilic (<10°) 2. Reactive	1. Patterning 2. Crystal nucleation&growth 3. Further reaction
$-(CH_2CH_2)_nOH$	Hydrophilic (20°<θ<50°)	Bio surface chemistry
$-NH_2$	Reactive	Further reaction
$-CH=CH_2$	Reactive	Further reaction

Molecular engineering of surfaces using self-assembled monolayers

The self-assembly of molecules into structurally organized monolayers (SAMs) uses the flexibility of organic chemistry and coordination chemistry to generate well-defined, synthetic surfaces with known molecular and macroscopic properties



All kind of surfaces

Metals (thiols,selenols)

Semiconductors (thiols, silanes)

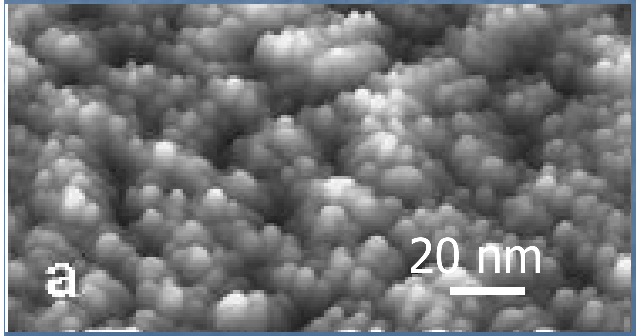
Oxides (phosphonates ,fatty acids)

All kind of topography

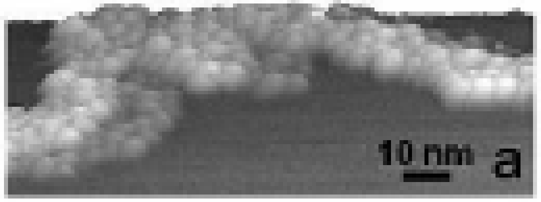
Easy preparation

Liquid phase

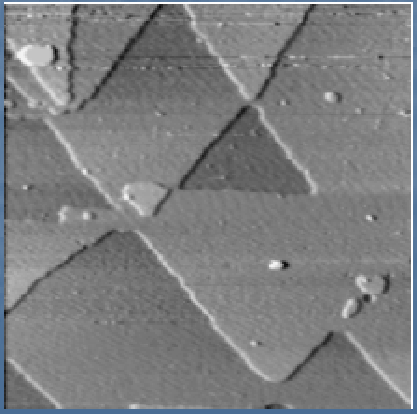
Gas phase



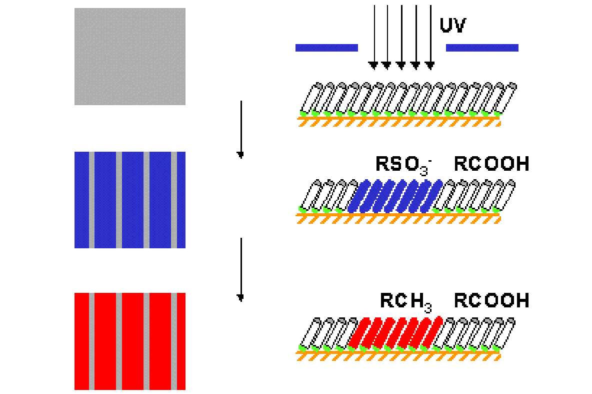
Rough surfaces

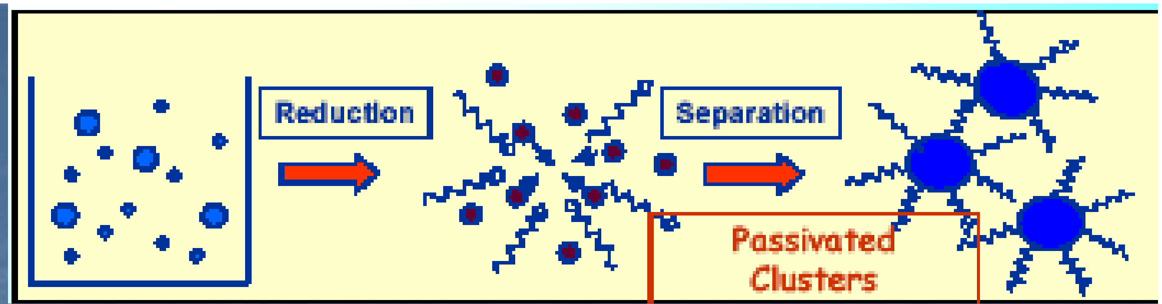


Nanoparticles



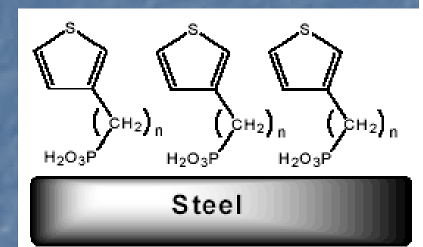
planar



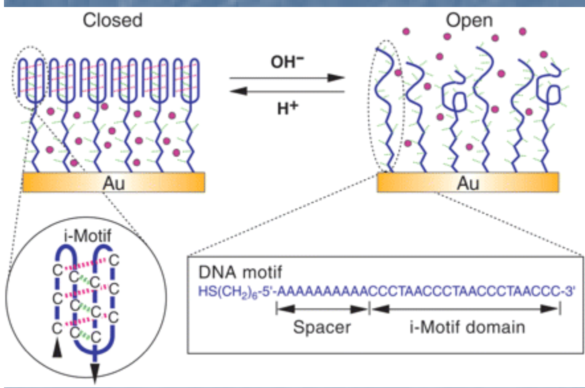


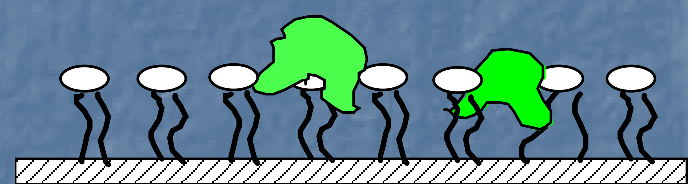
Applications:

Material protection
Molecular electronics
Biosensors
Actuators
Lithography
Biorecognation
Molecular motors
and more.........

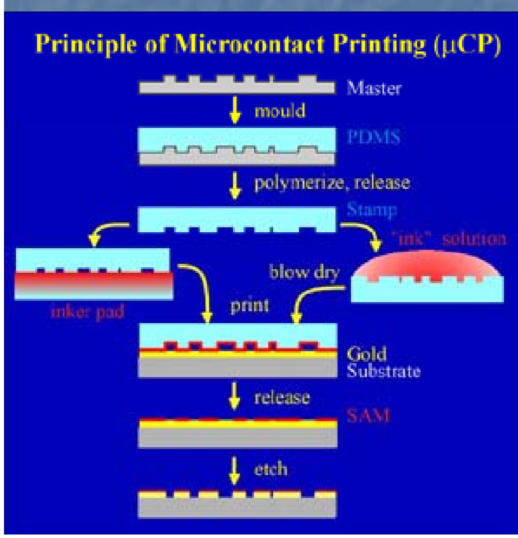


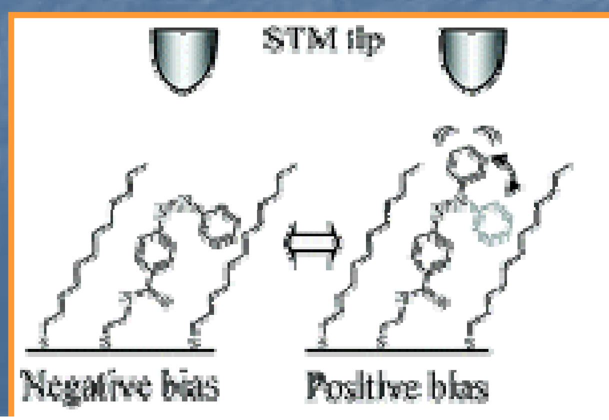
Protective coatings

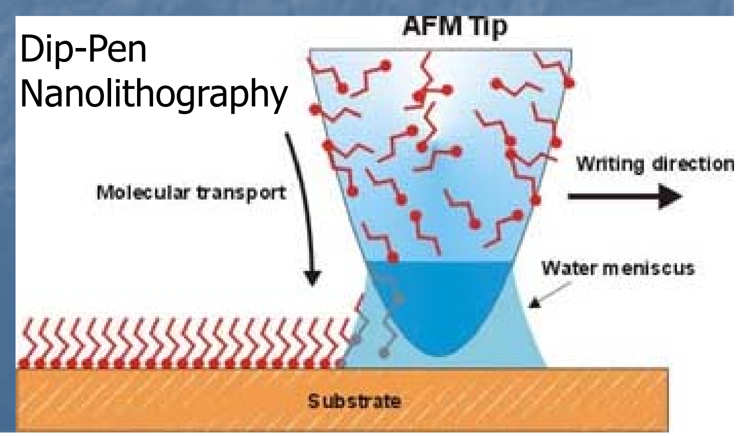




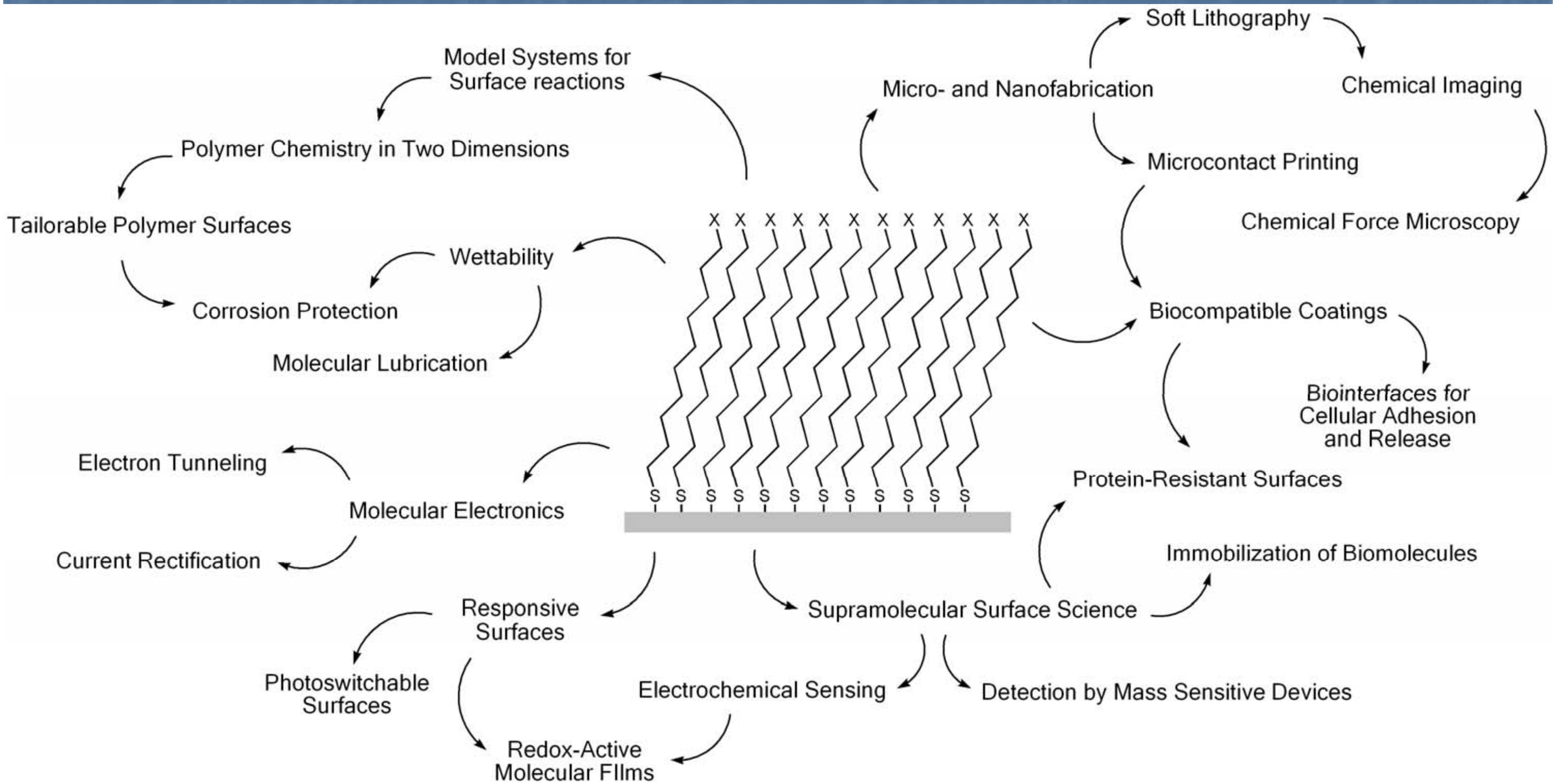
Biomimetic surfaces
Lipase on phospholipid SAM



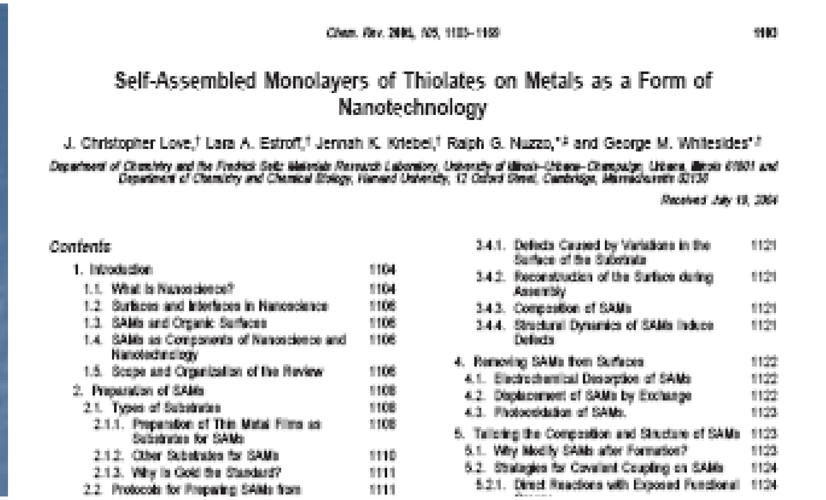




Molecular engineering of surfaces using self-assembled monolayers: applications



Thiol SAMs on metals and semiconductors: a model system



Chem. Rev. 2005, 105, 1103−1169 1103

Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology

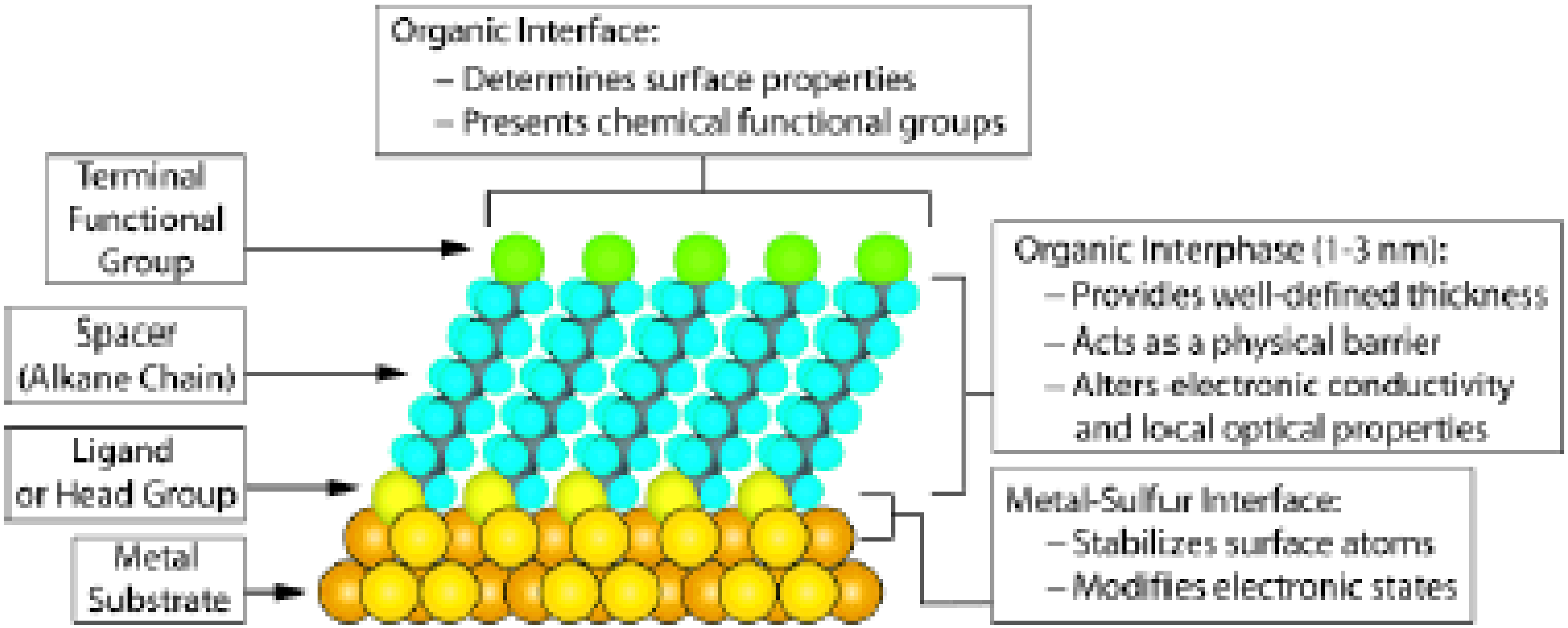
J. Christopher Love,† Lara A. Estroff,† Jennah K. Kriebel,† Ralph G. Nuzzo,*‡ and George M. Whitesides*†

Department of Chemistry and the Frederick Seitz Materials Research Laboratory, University of Illinois—Urbana—Champaign, Urbana, Illinois 61801 and Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138

Received July 19, 2004

Contents

Thiol SAMs can be formed on Au, Ag, Cu, Pd, Pt, Ni, GaAs, …….

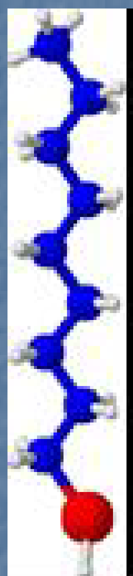


Thiol SAMs on metals : a model system

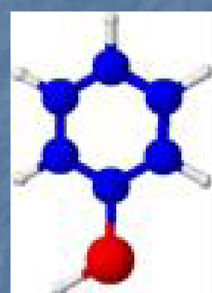
The molecules

Ordered SAMs

Suitable for STM imaging



Aliphatic thiol

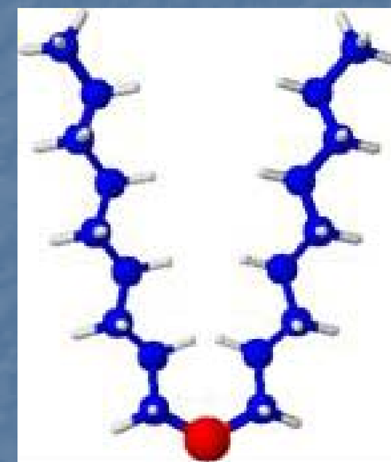


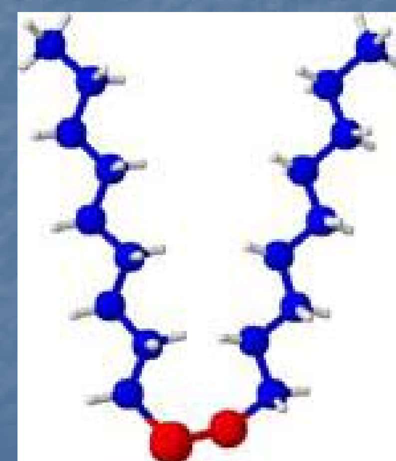
Aromatic thiol

Dithiols

Disordered SAMs

Dialkyl sulfides





Dialkyl disulfides

red: S , blue: carbon, white: H

Thiol SAMs preparation

Solution deposition

Inmersion

Electrochemistry

Gas phase deposition

Solution deposition: an easy and low cost method

Reaction (in both phases)

$$CH_3\text{-}(CH_2)_n\text{-}H_2CSH + M \longrightarrow CH_{3\text{-}}(CH_2)_n\text{-}H_2CS\text{-}M + 1/2H_2$$

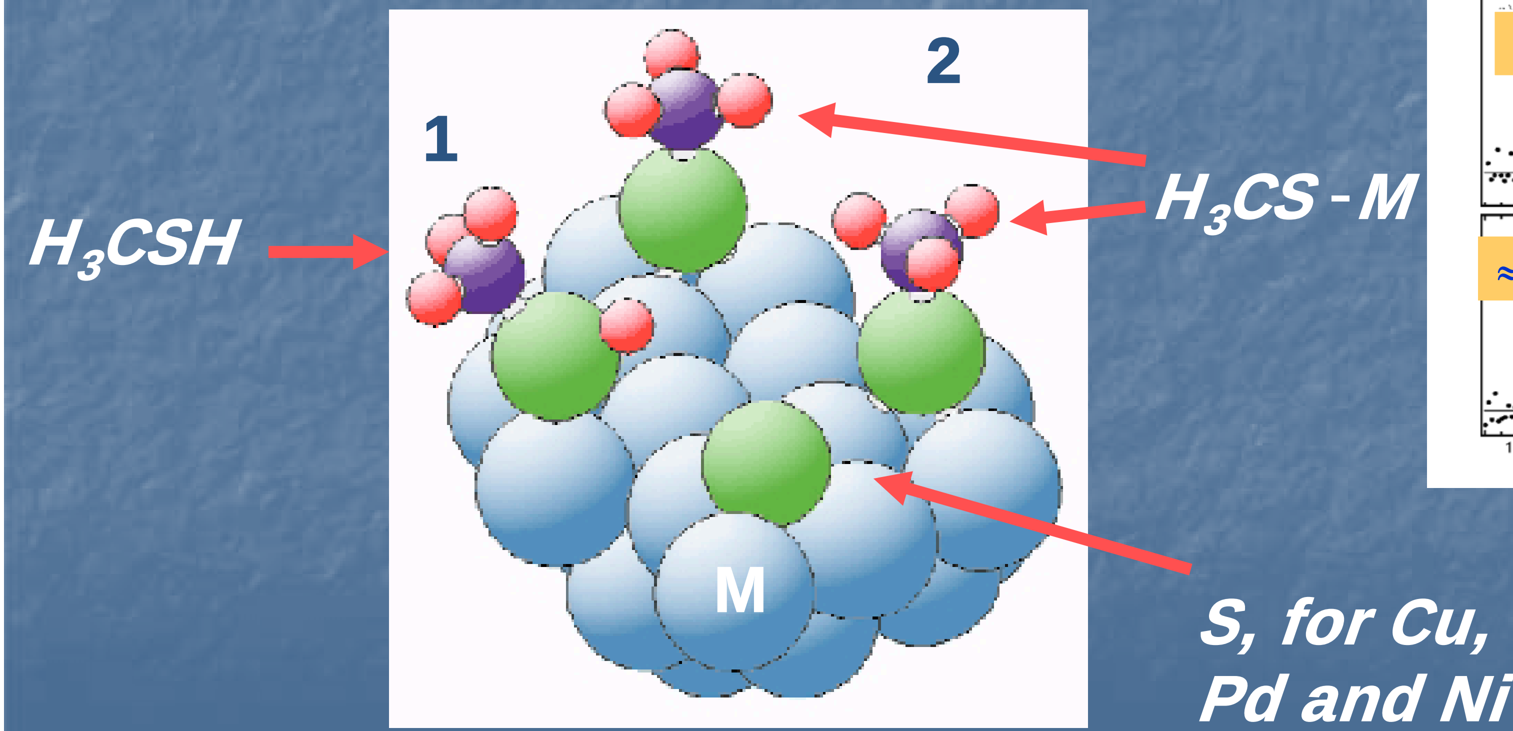
M is a clean metal or semiconductor surface

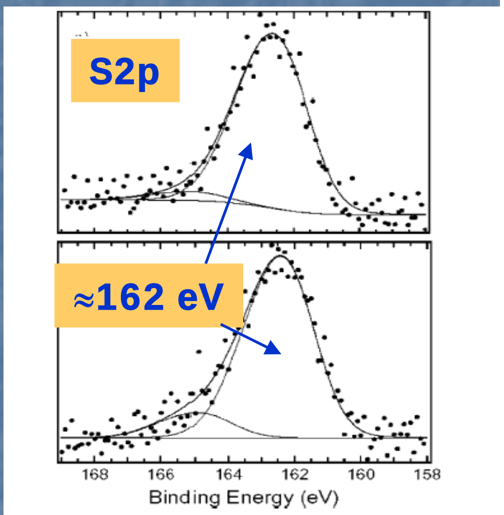
$$CH_3-(CH_2)_n-H_2CSH + M \longrightarrow CH_3-(CH_2)_n-H_2CS-M + 1/2H_2$$

on the surface $H_3CS-|-H$

(1) Physisorption — **10 Kcal / mol**

(2) Chemisorption → Thiolate bond — **40-80 Kcal / mol**





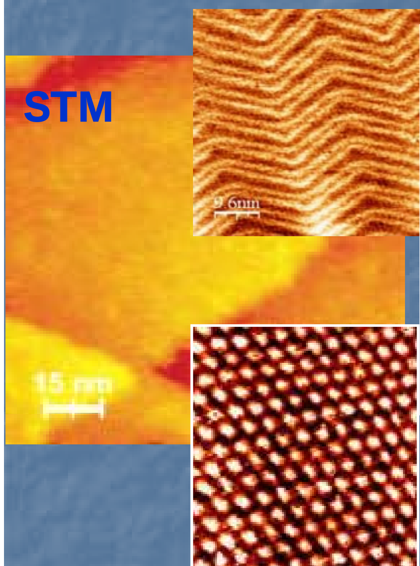
XPS

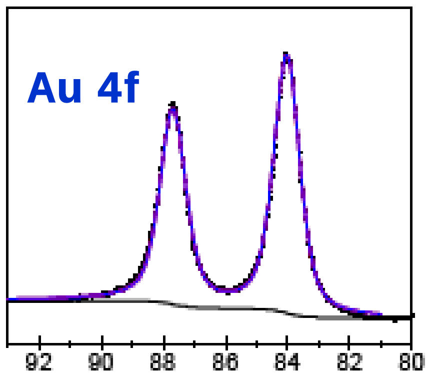
Solution deposition

Au surfaces

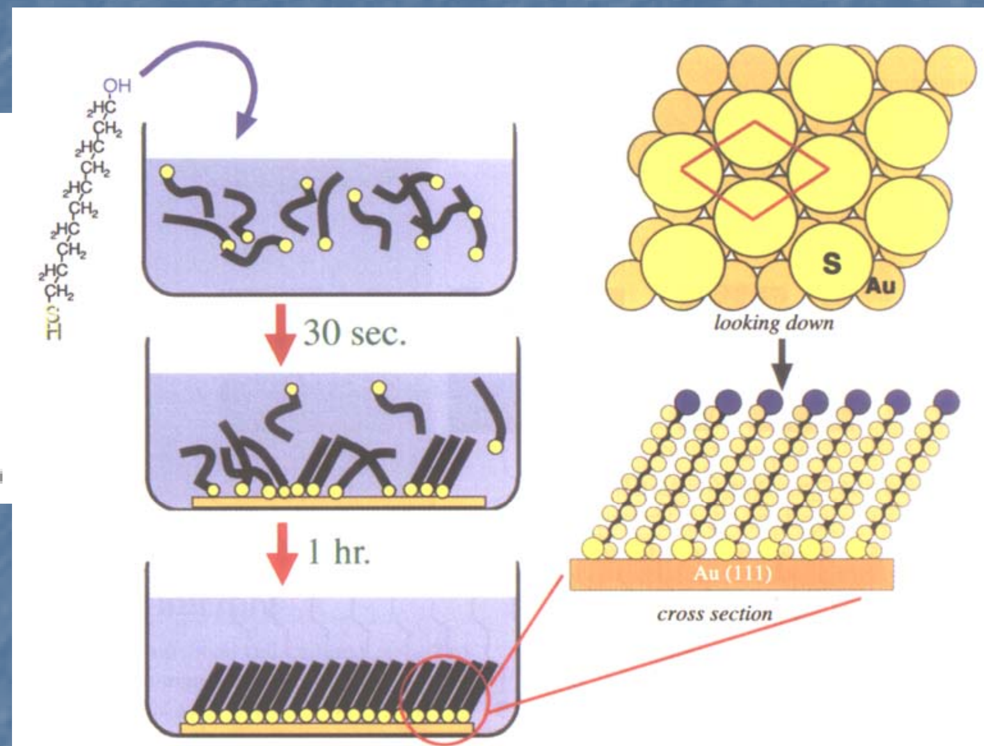
Solvent: ethanol, hexane, etc

Clean Au (111)





Substrate immersion

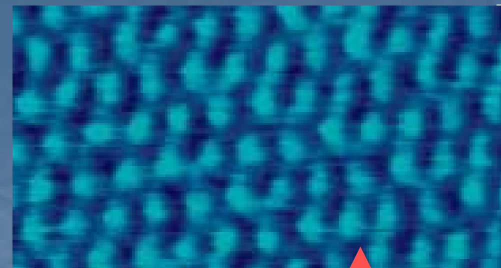


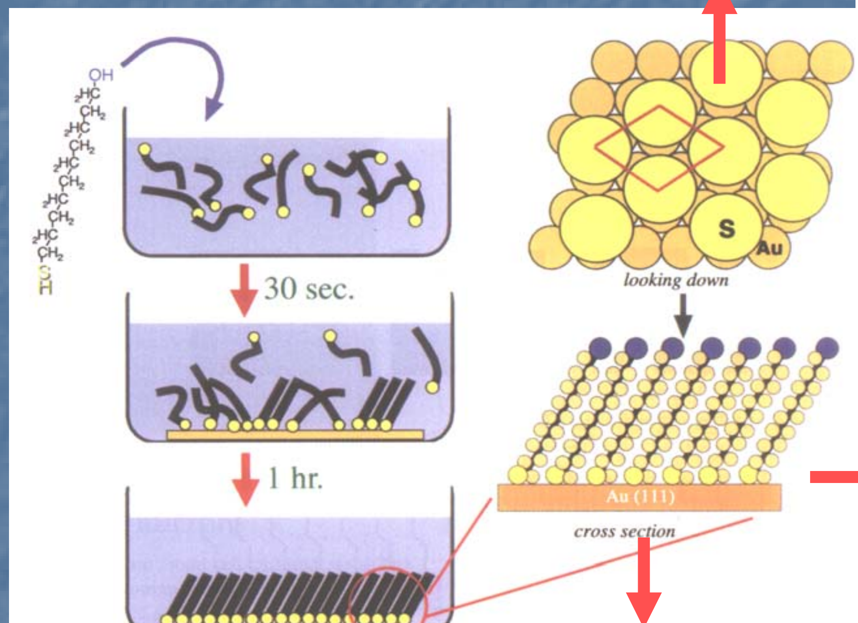
$$CH_3\text{-}(CH_2)_n\text{-}H_2CSH + Au \longrightarrow CH_3\text{-}(CH_2)_n\text{-}H_2CS\text{-}Au + 1/2H_2$$

STM:

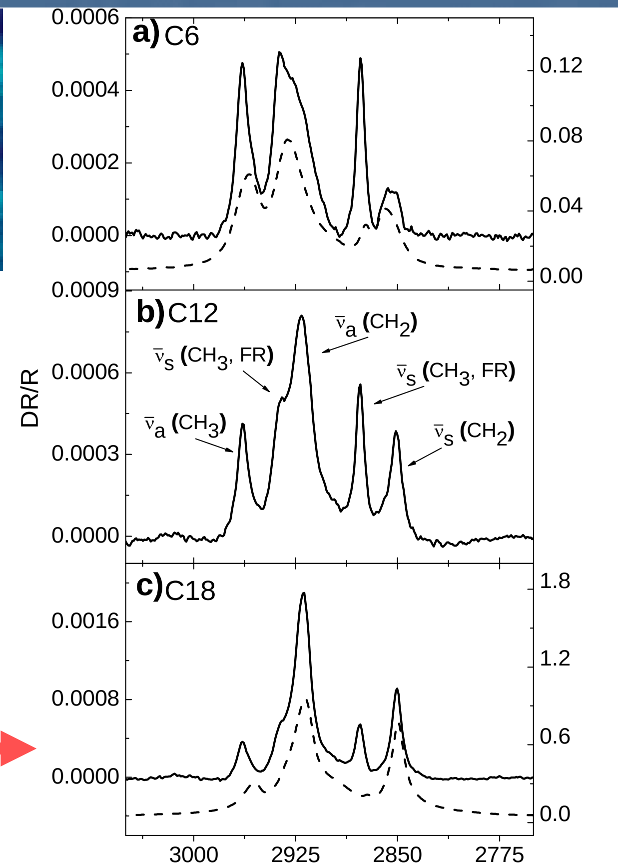
Ordered molecular Domains

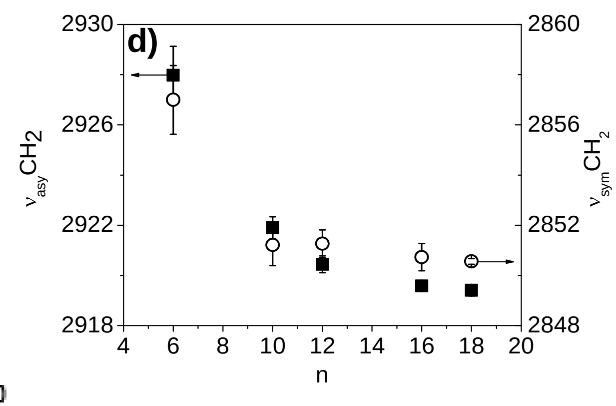
d =0.5 nm





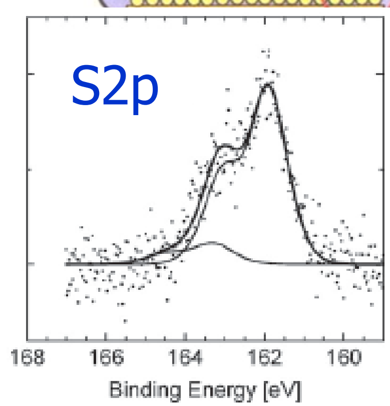
IR: ordered tilted chains

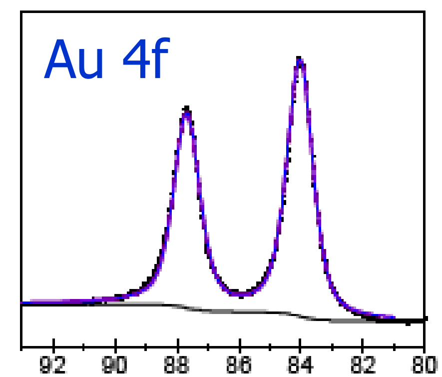




XPS:

Strong covalent Au-S bond (thiolate)





Grumelli, Méndez De Leo,Bonazzola, Zamlynny, Calvo, Salvarezza, 2010, 26 (11), 8226–8232

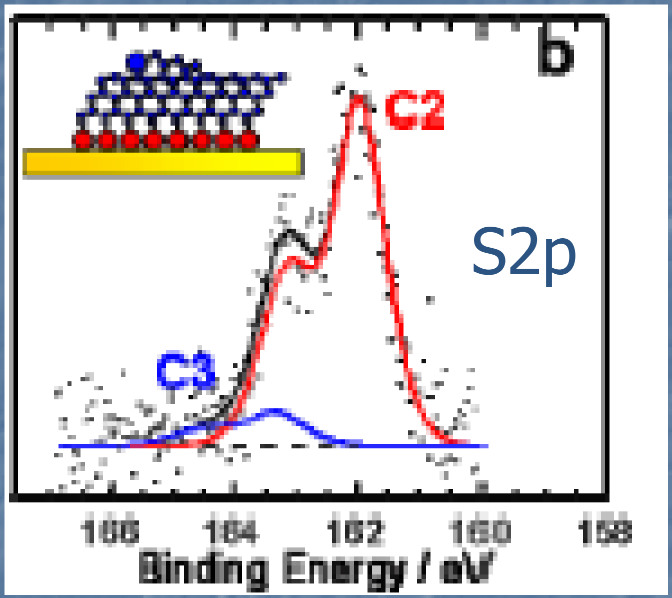
The chemistry S-Au bond

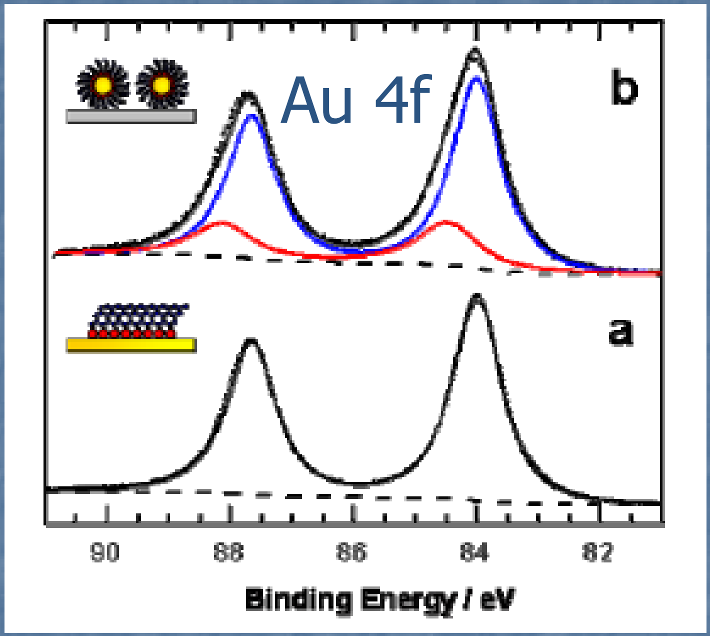
CH_3-$(CH_2)_n$-H_2CS^{-}- nAu^{+}

XPS

The S atoms in the SAMS

The Au atom





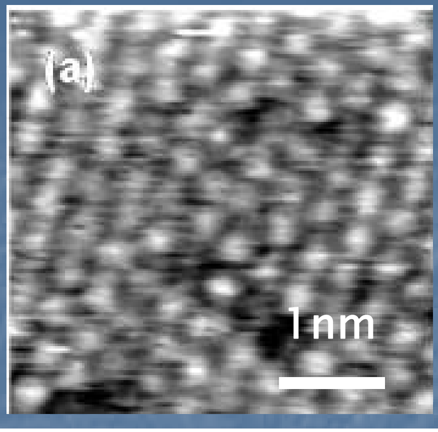
Model	E_b(eV)	Bader Charge/e		ΔW(eV)	Δd(D)
		S Atom	Au adatom		
U	-1.82	-0.2		-1.5	-0.9

Vericat, Vela, Benitez, Carro, Salvarezza *Chemical Society Reviews*, 2010, **39**, 1805-1834

Solution deposition
Ag and Cu

STM image 4x4 nm²
Propanethiol on Ag(111)

d=0.47 nm



Spontaneous native oxide reduction

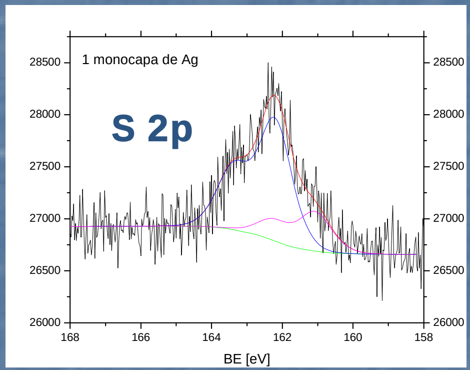
Ag

$$3\ Ag_2O + R\text{-}SH \rightarrow R\text{-}SO_2OH + 6\ Ag$$

$$Ag + R\text{-}SH \rightarrow R\text{-}S\text{-}\ Ag + ½\ H_2$$

Solvents: ethanol , hexane

Azzaroni, O.; Vela, M. E.; Andreasen, G.; Carro, P.; Salvarezza, R. C. *J. Phys. Chem. B* 2002, *106*, 12267



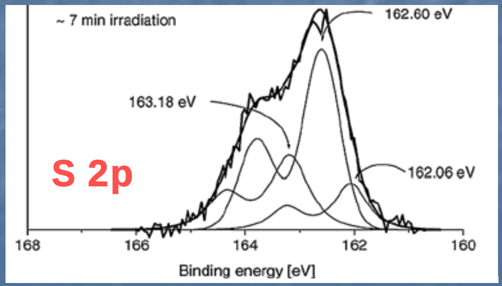
Cu

$$3\ Cu_2O + R\text{-}SH \rightarrow R\text{-}SO_2OH + 6\ Cu$$

$$Cu + R\text{-}SH \rightarrow R\text{-}S\text{-}\ Cu + ½\ H_2$$

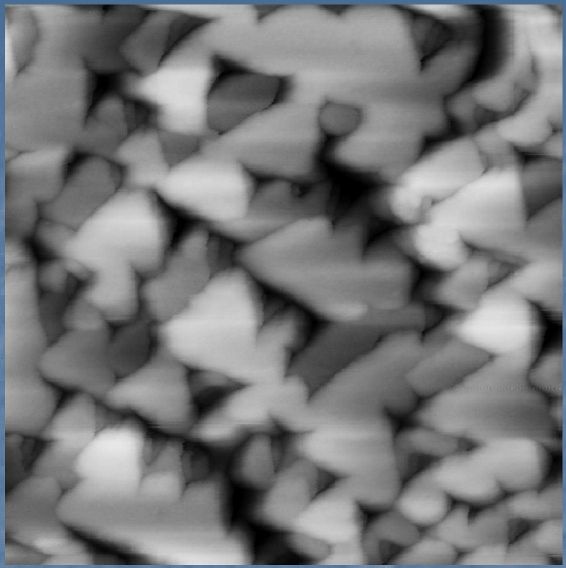
Solvents: hexane, toluene

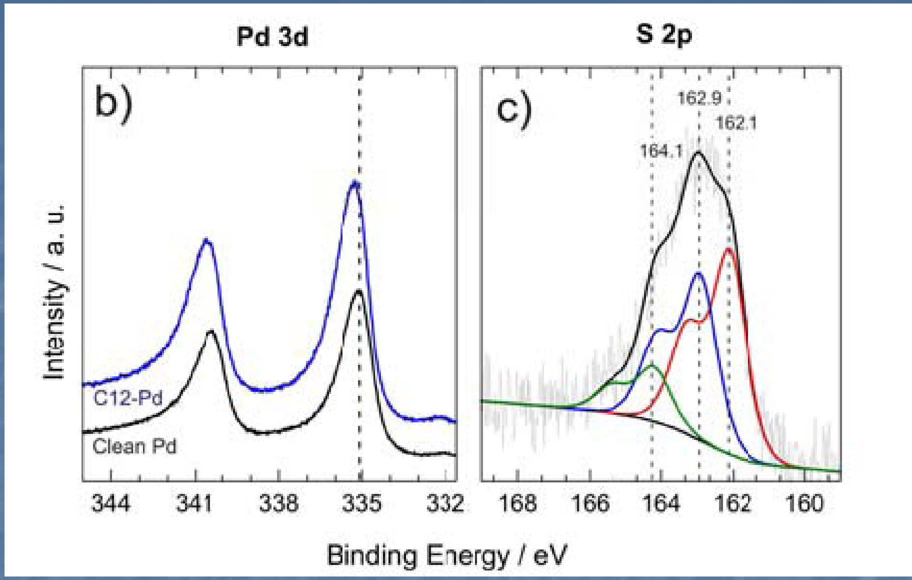
O. Azzaroni, M. E. Vela, M. Fonticelli, G. Benıtez, P. Carro, B. Blum, and R. C. Salvarezza *J. Phys. Chem. B* **2003,** *107,* 13446



XPS
Dodecanethiol on Cu(111)

Solution deposition: SAMs on Pd



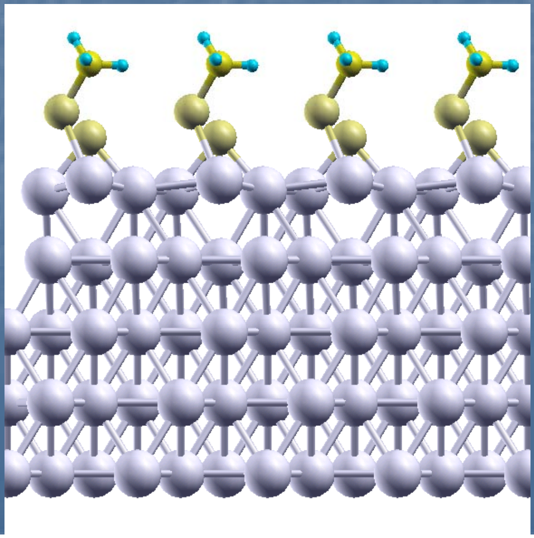


Pd substrate

162.1 eV: 48%, 162.9 eV: 39%, 164.1: 13%

θ *S* ≈ 0.8, θ *Sulfide* ≈ 0.4. θ *thiolate* ≈ 0.30

Corthey, G.; Rubert, A. A.; Benitez, G. A.; Fonticelli, M. H.; Salvarezza, R. C. *Journal Physycal Chemistry C* **2009**, *113*, 6735-6742

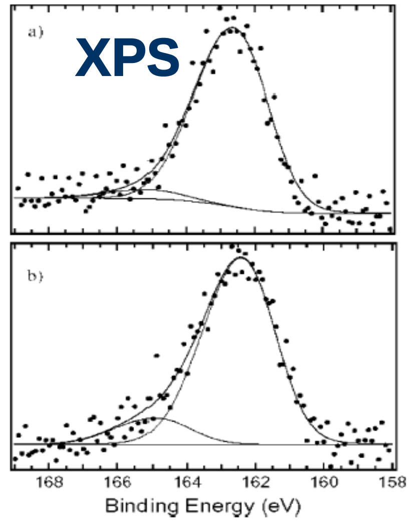


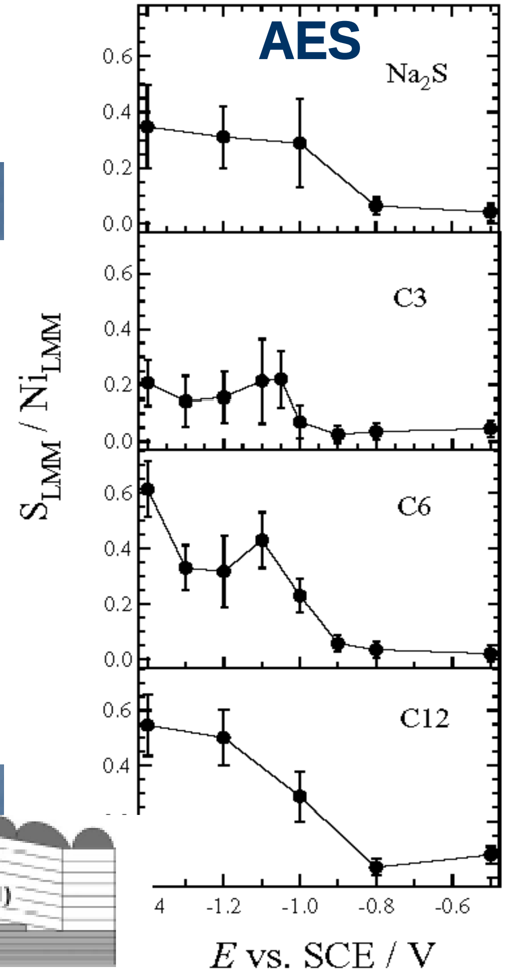
Electrochemical-induced dodecanethiolate self-assembly on Ni(111)

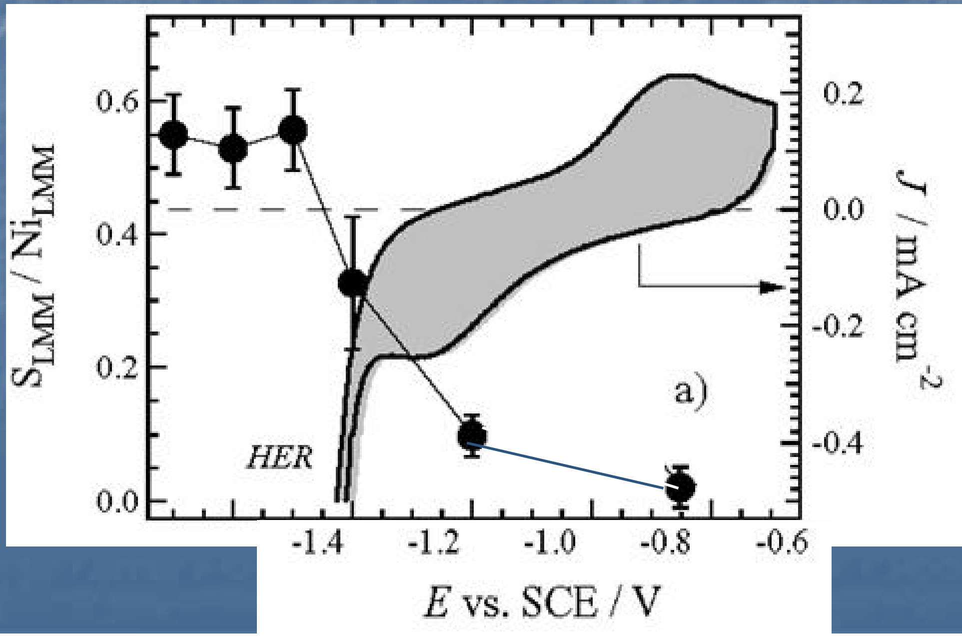
$$NiO + 2e^- + H_2O \longrightarrow Ni + 2OH^-$$

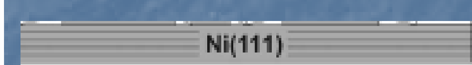
dodecanethiol–saturated aqueous 1 M NaOH

$$R\text{-}S^- + Ni \longrightarrow R\text{-}S\text{-}Ni + e^-$$





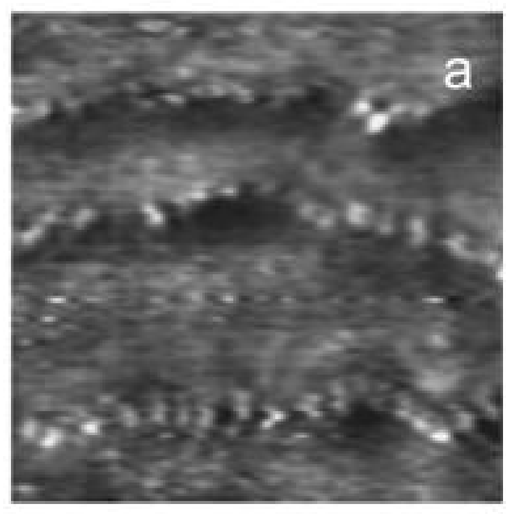




Bengió, Fonticelli, Benítez, Hernández Creus, Carro, Ascolani, Zampieri, Blum, Salvarezza

J. Phys. Chem. B **2005,** *109,* 23450-23460

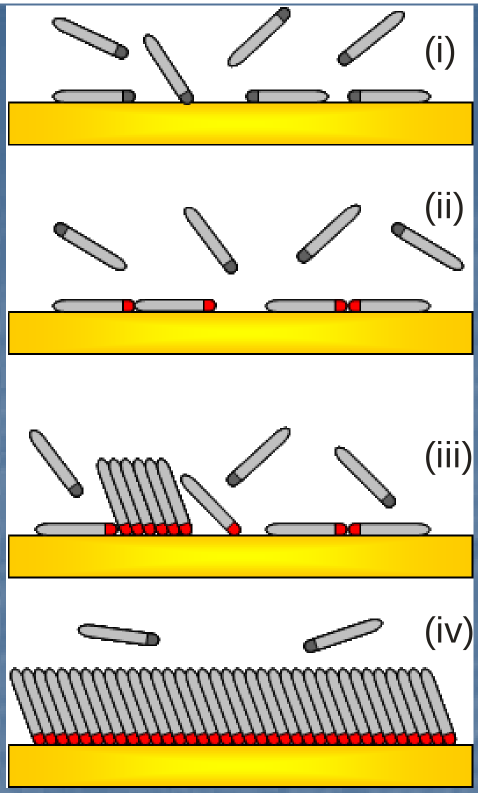
The self-assembly process

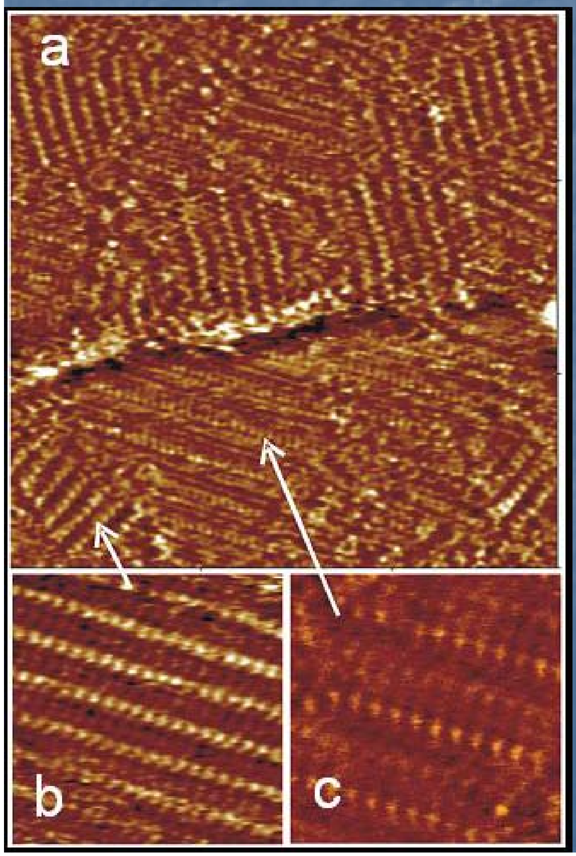


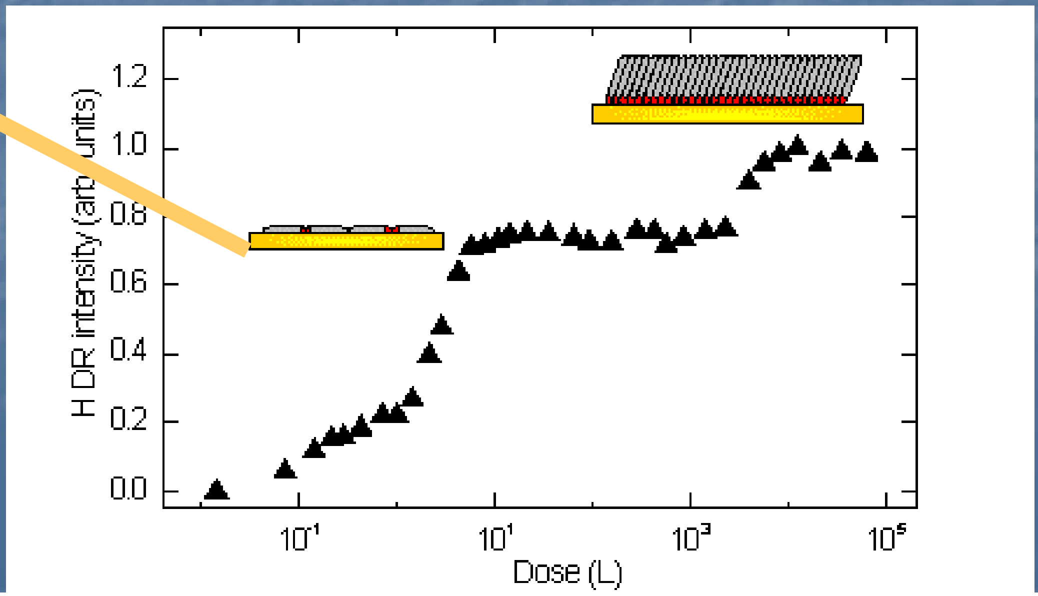
1)Physisorption
(not observed by STM)

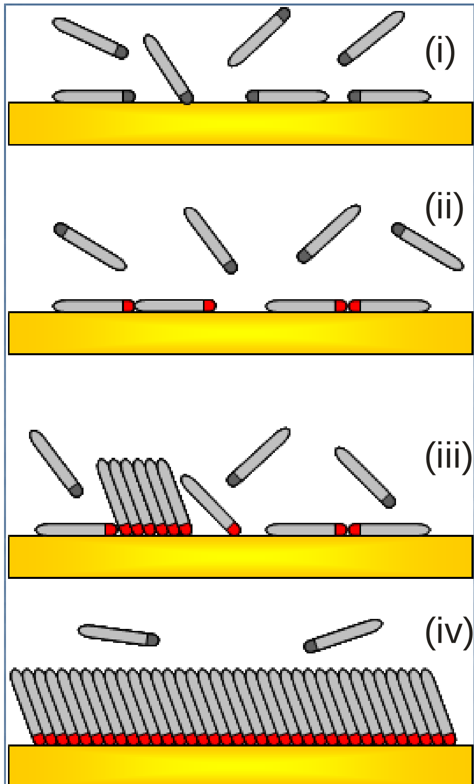
2) Adsorption at defects (bright spots at step edges)

3) Parallel configuration:
(stripe phase)





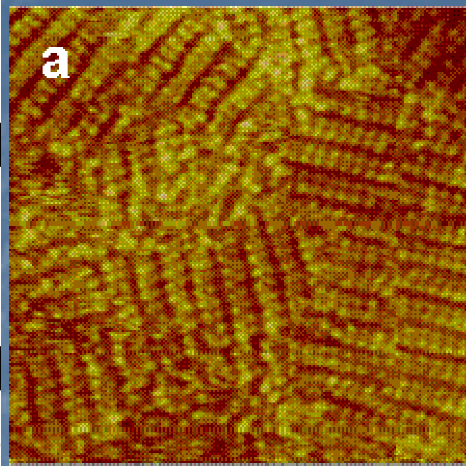


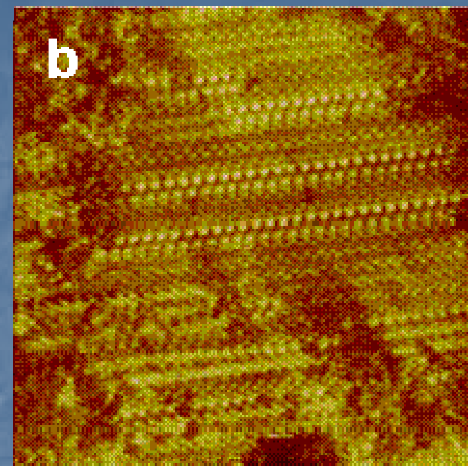


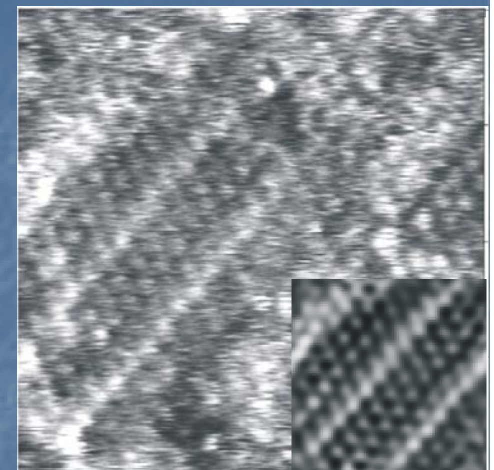
(4×√3) Tilt 50º

(2√3 x 2√3)

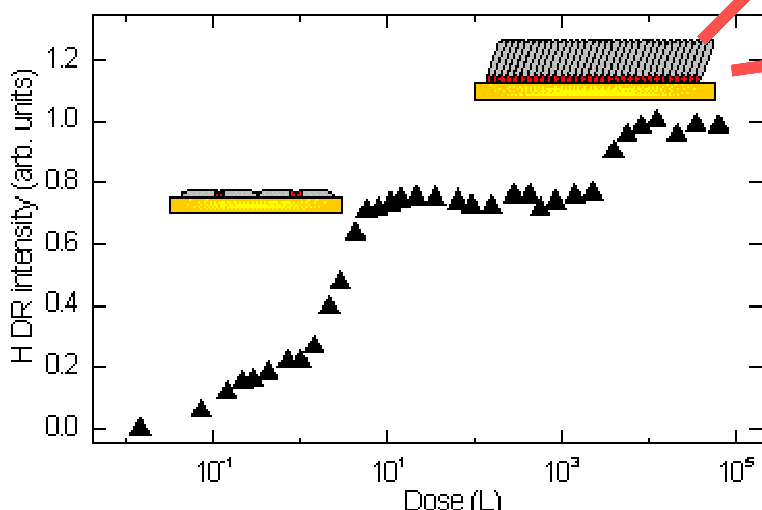
(6×√3) Tilt 30º

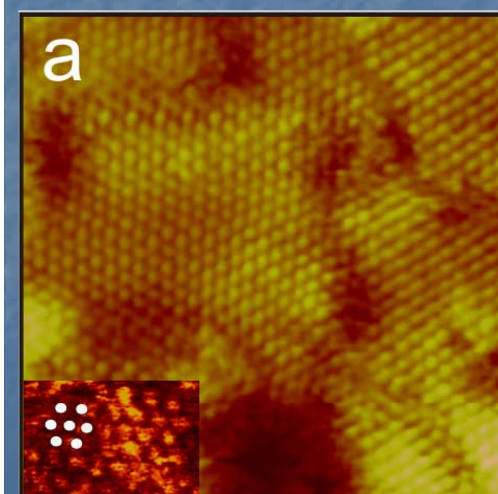


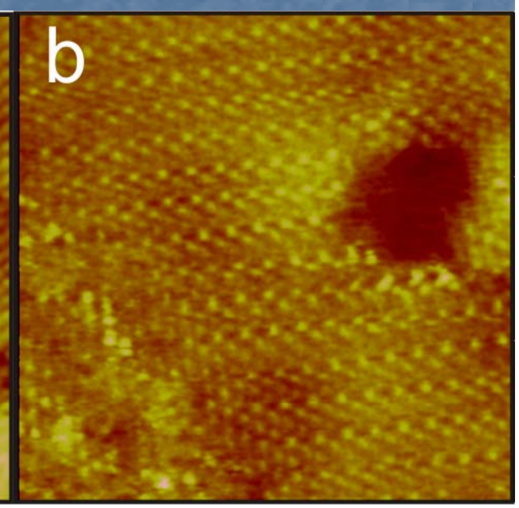




4) Standing up configuration







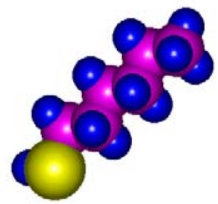
(√3 x 2√3)R30º

c(4x2)

Vericat, Vela, Benitez, Carro, Salvarezza
Chemical Society Reviews, 2010, **39**, 1805-1834

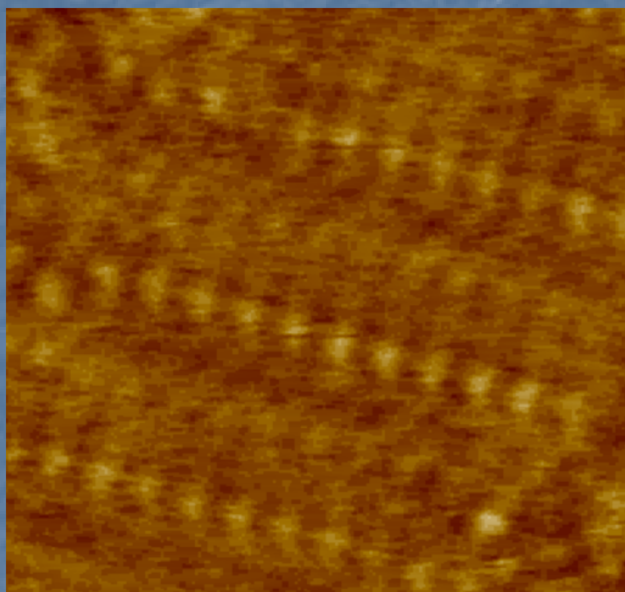
Stable Surface Structures

Stable (Low Coverage) Phases: stripped phase



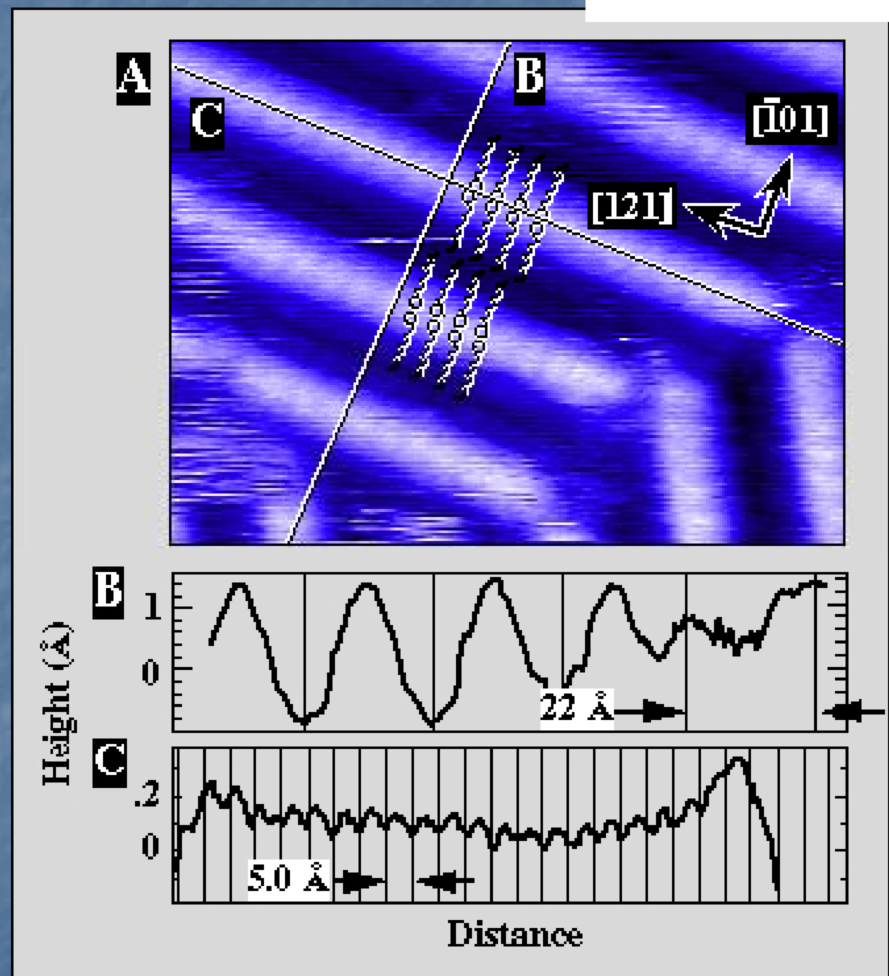
STM: Hexanethiolate on Au(111)

Lying down molecules



Solution deposition+annealing

C. Vericat, M.E. Vela ,R.C. Salvarezza
Physical Chemistry Chemical Physics, 7, 3258 (2005)

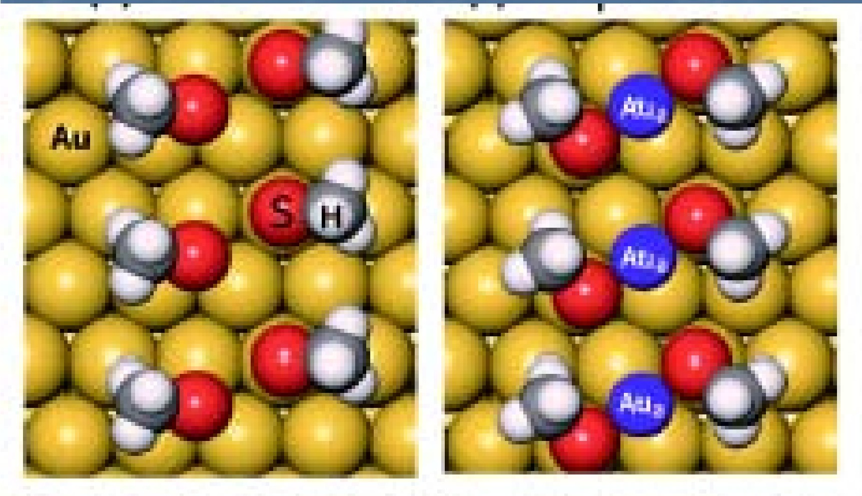


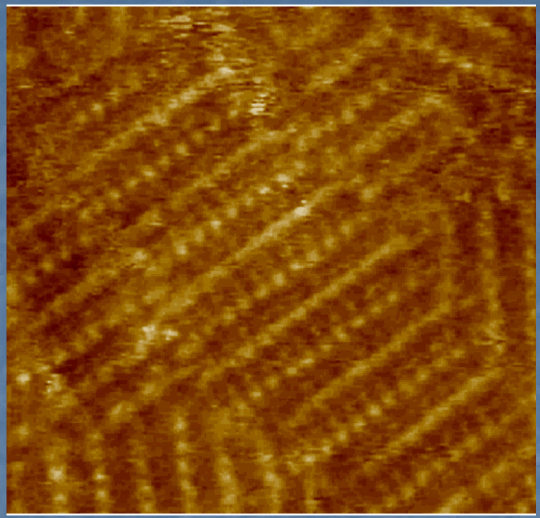
gas phase

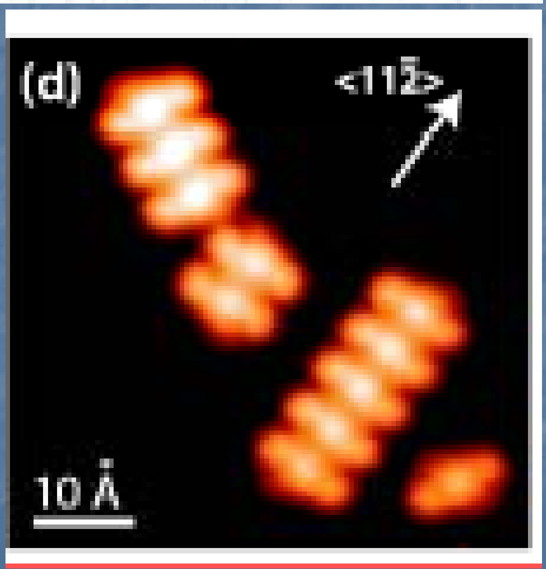
G. E. Poirier, Chem. Rev. 97 4, 1117, (1997)

R. Staub *et al.* Langmuir 14, 6693 (1998).

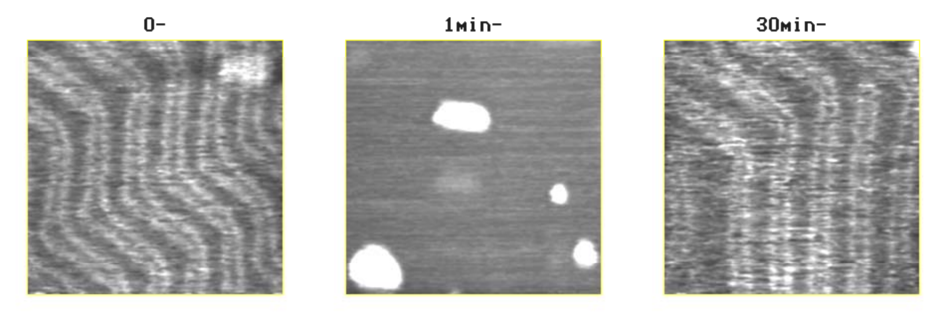
Stripped phase parallel configuration







J.T. Yates, *et al*
PRL **97**, 146103 (2006)



22x√3 ⟶ Au(1x1) ⟵ 22x√3

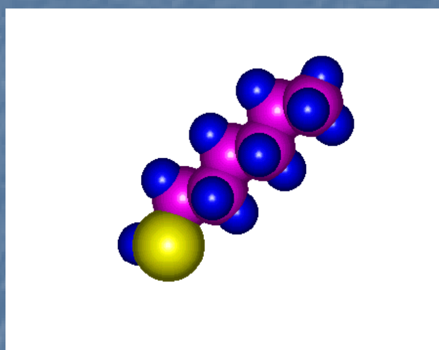
Lifting of the reconstruction

↓

adatoms

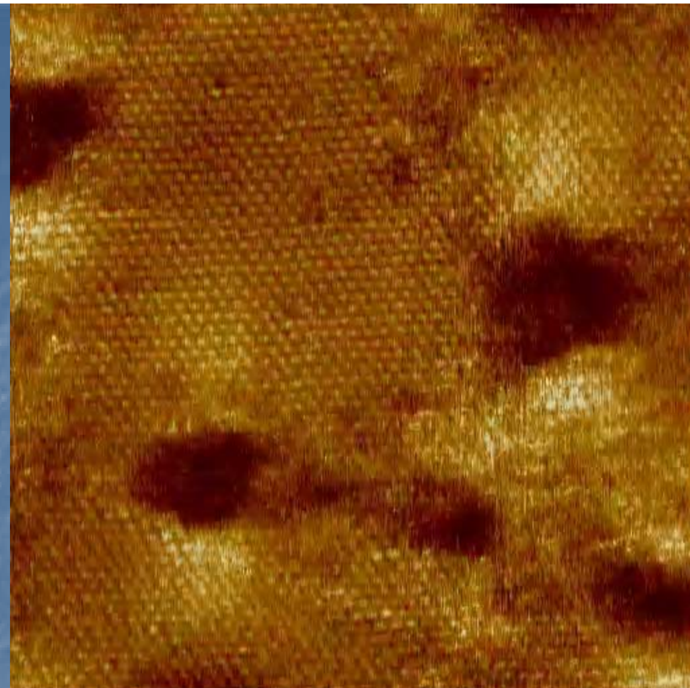
Stable (high coverage) phases

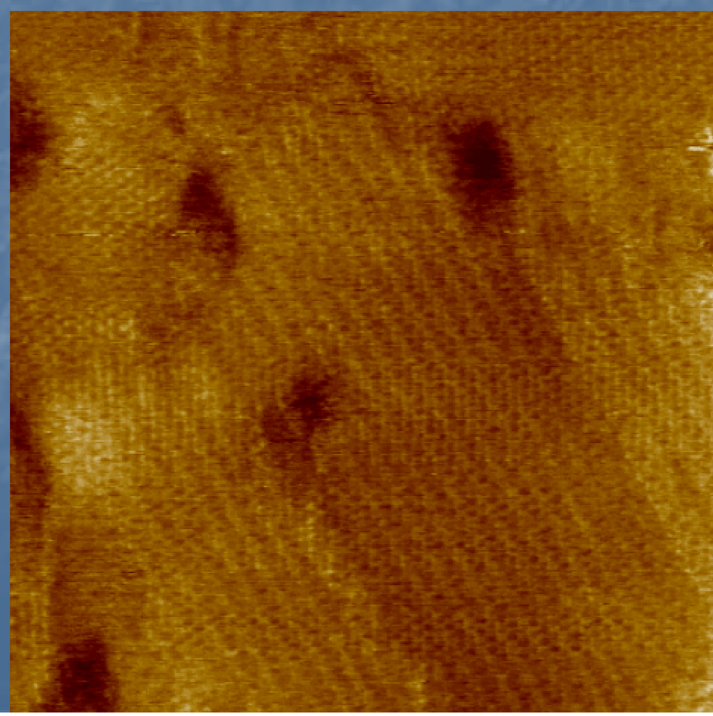
hexanethiolate on Au(111)



Standing up molecules

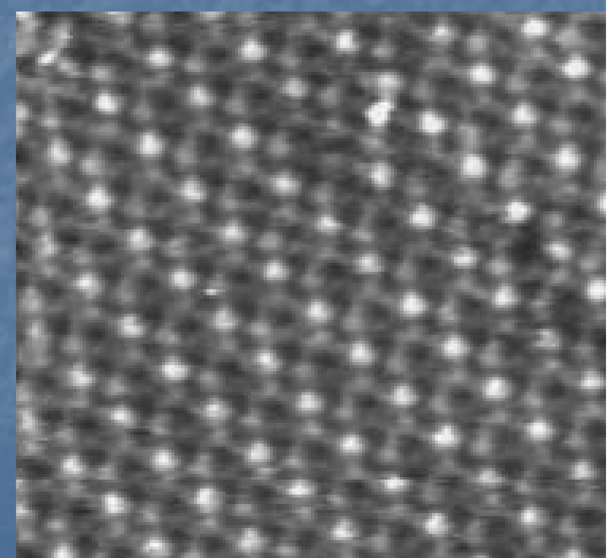
Adsorption time: 24 hs



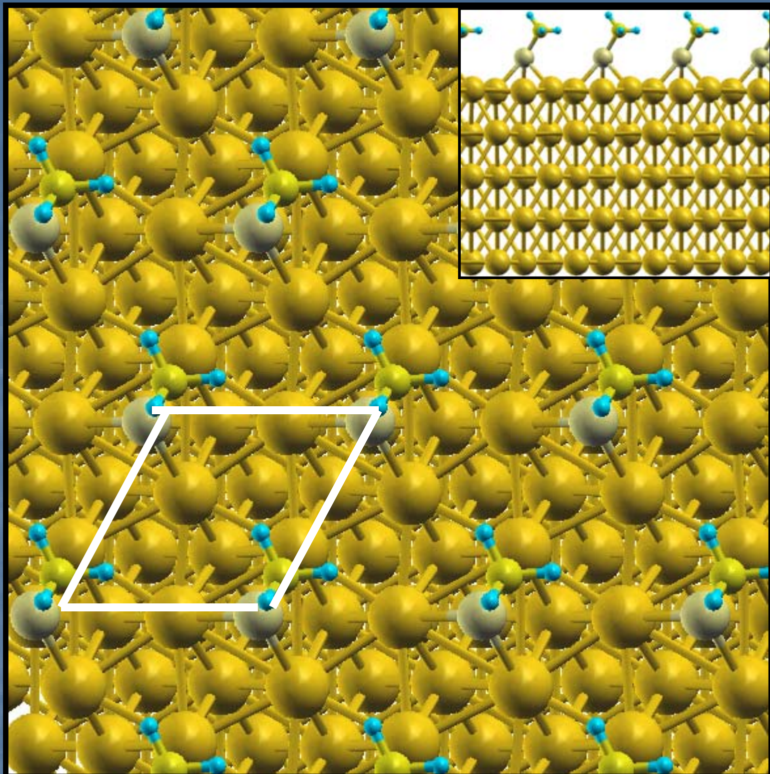


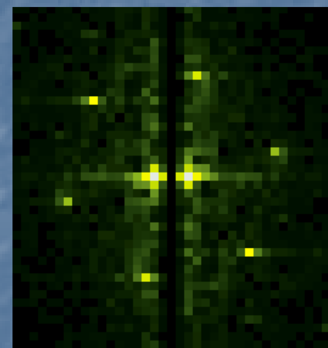
$\sqrt{3} \times \sqrt{3}$ R30°

d= 0.5 nm

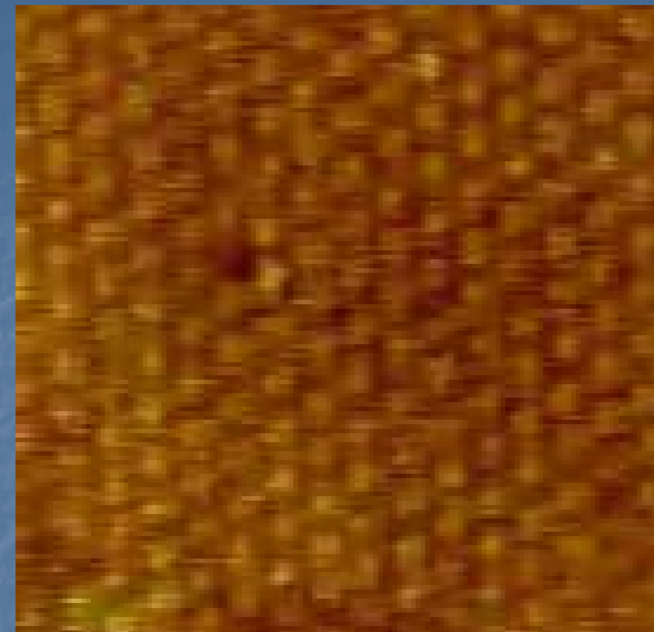


rectangular c(4x2)



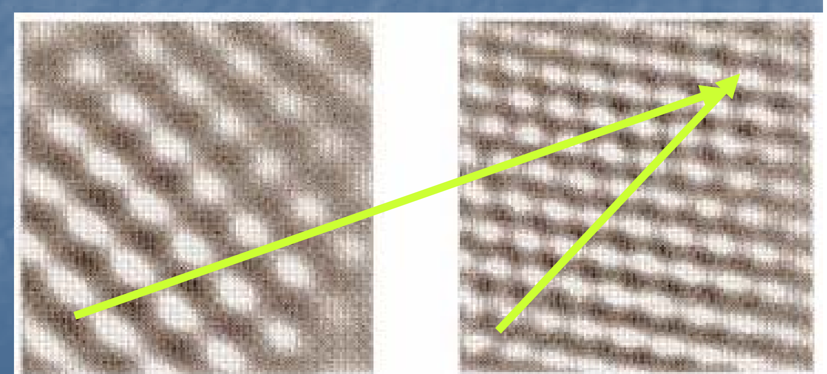


STM



AFM

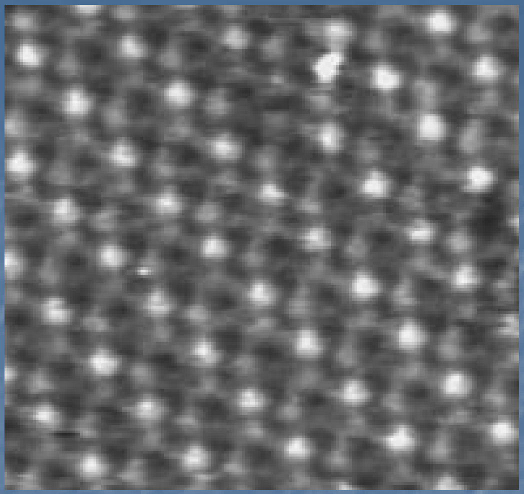
$\sqrt{3} \times \sqrt{3}$ R30°



Thiol → Au(111)

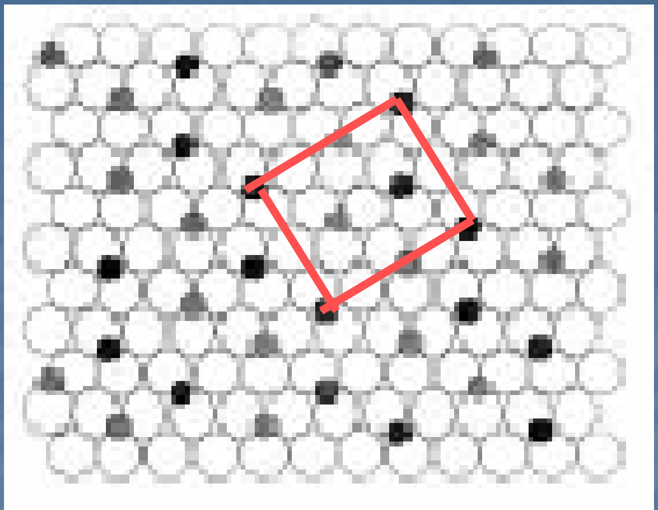
Force

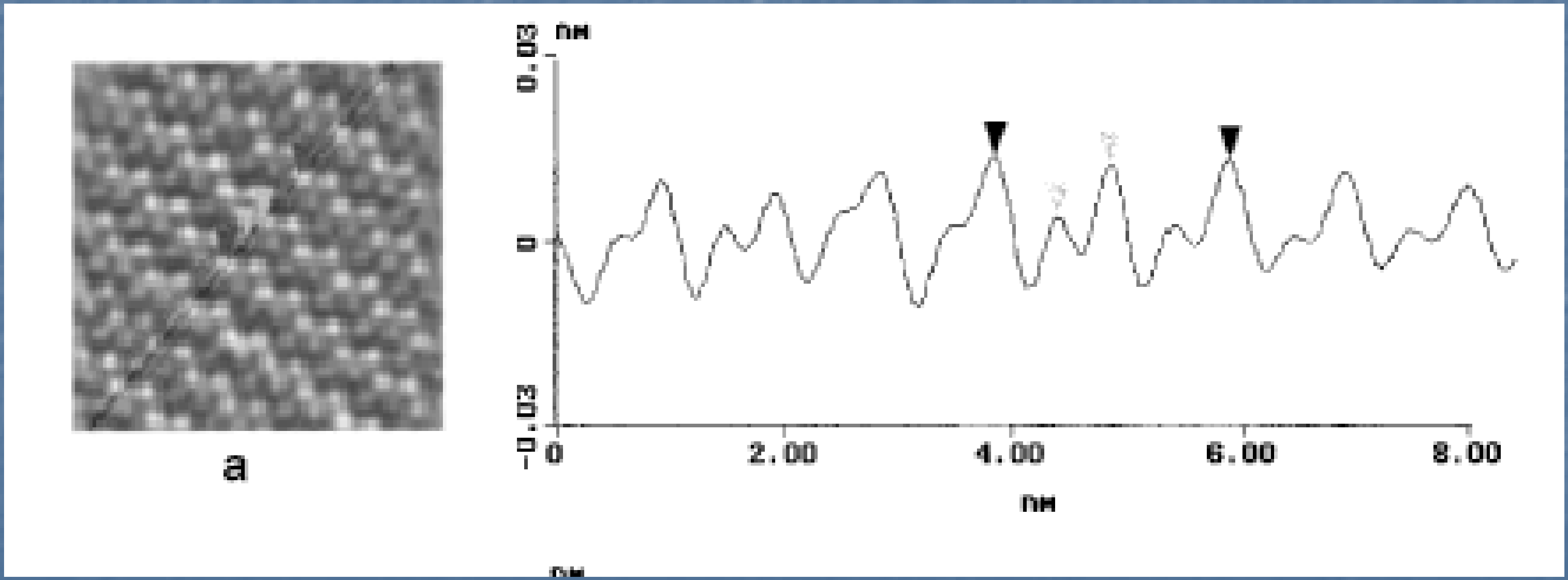
Thiol coverage: 1/3
Thiol-thiol distance: 4.97 A
Tilt angle: 30°



Rectangular

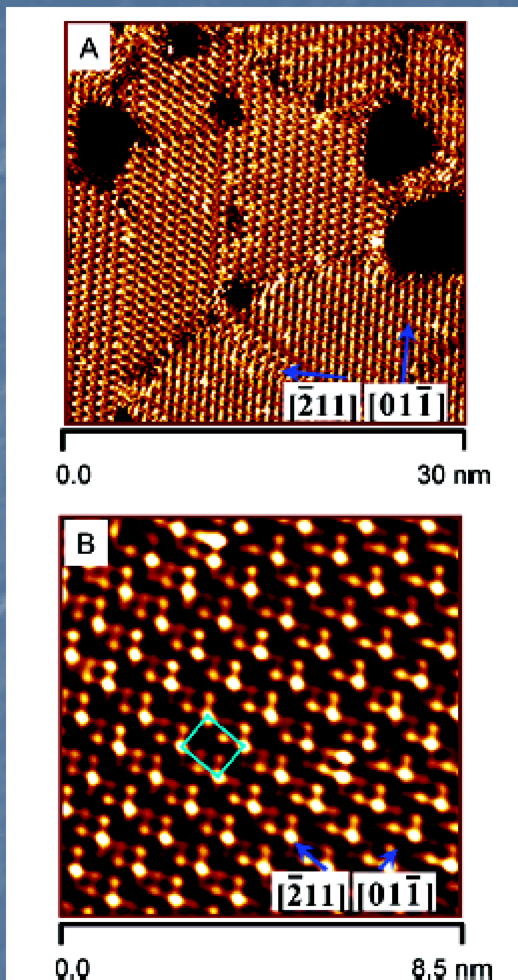
C(4x2)





F. Teran Arce, M. E. Vela, R. C. Salvarezza, A. J. Arvia
Langmuir 1998, *14,* 7203-7212

c(4x2)



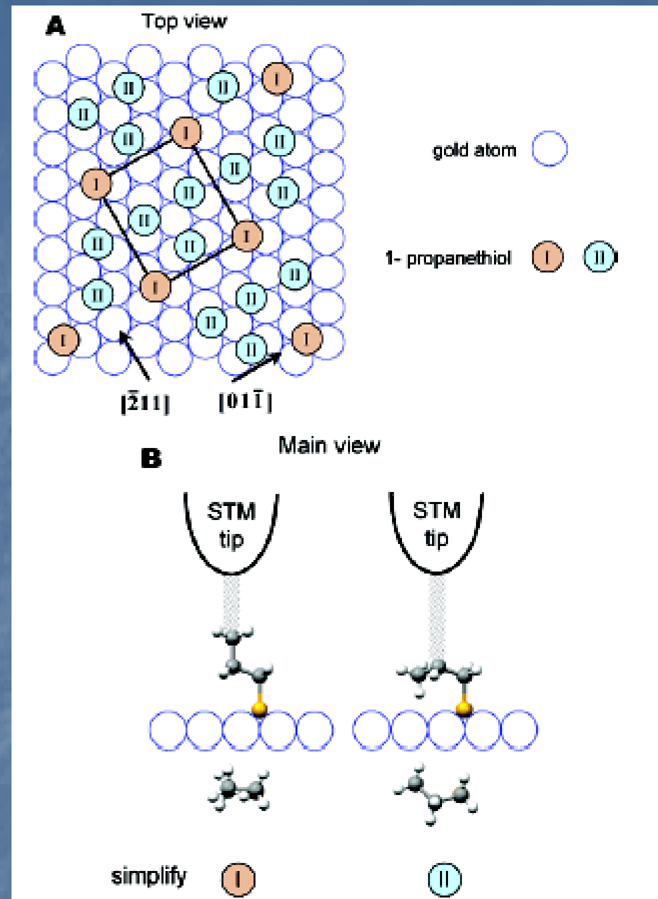


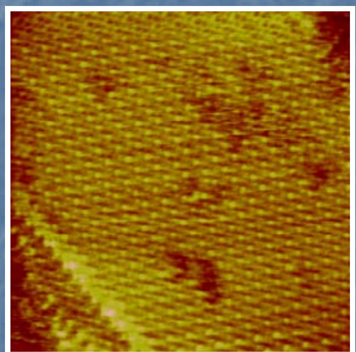
Figure 9. (A) Possible surface model for a $(2\sqrt{3} \times 3)$ R30° unit cell containing four 1-propanethiol molecules, and (B) a proposed illustration of two configurations of adsorbed 1-propanethiol and corresponding tunneling pathways.

Jingdong Zhang, Qijin Chi, and Jens Ulstrup, **Langmuir 22 6203 (2006)**

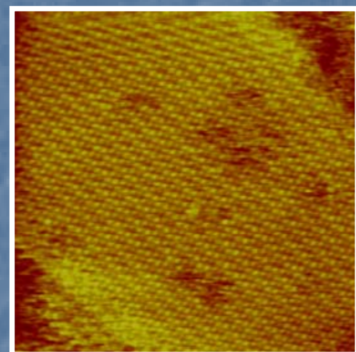
Reversible Transformations in real time (in situ STM)

$c(4\times2) \leftrightarrow \sqrt{3}\times\sqrt{3}\ R30°$

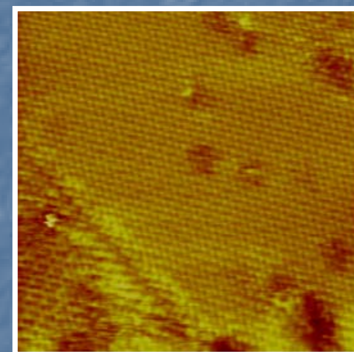
The energy difference between these structures is low



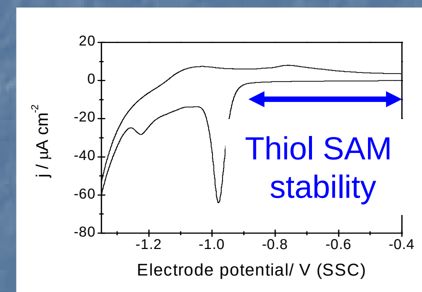
Rect. c(4x2)

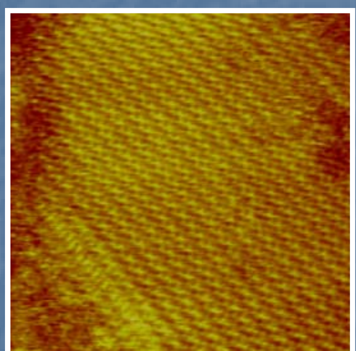


Zig- zag c(4x2)

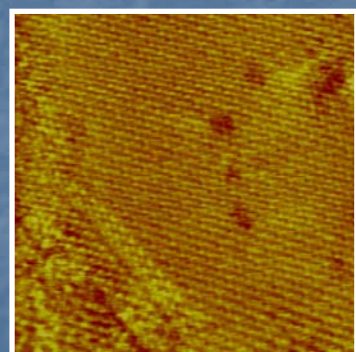


$\sqrt{3}\times\sqrt{3}$ R30°

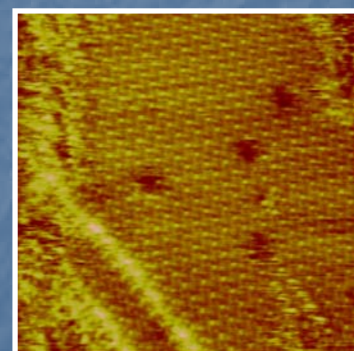




Zig- zag c(4x2)



$\sqrt{3}\times\sqrt{3}$ R30°



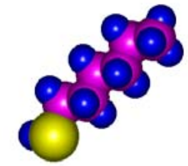
Rect. c(4x2)

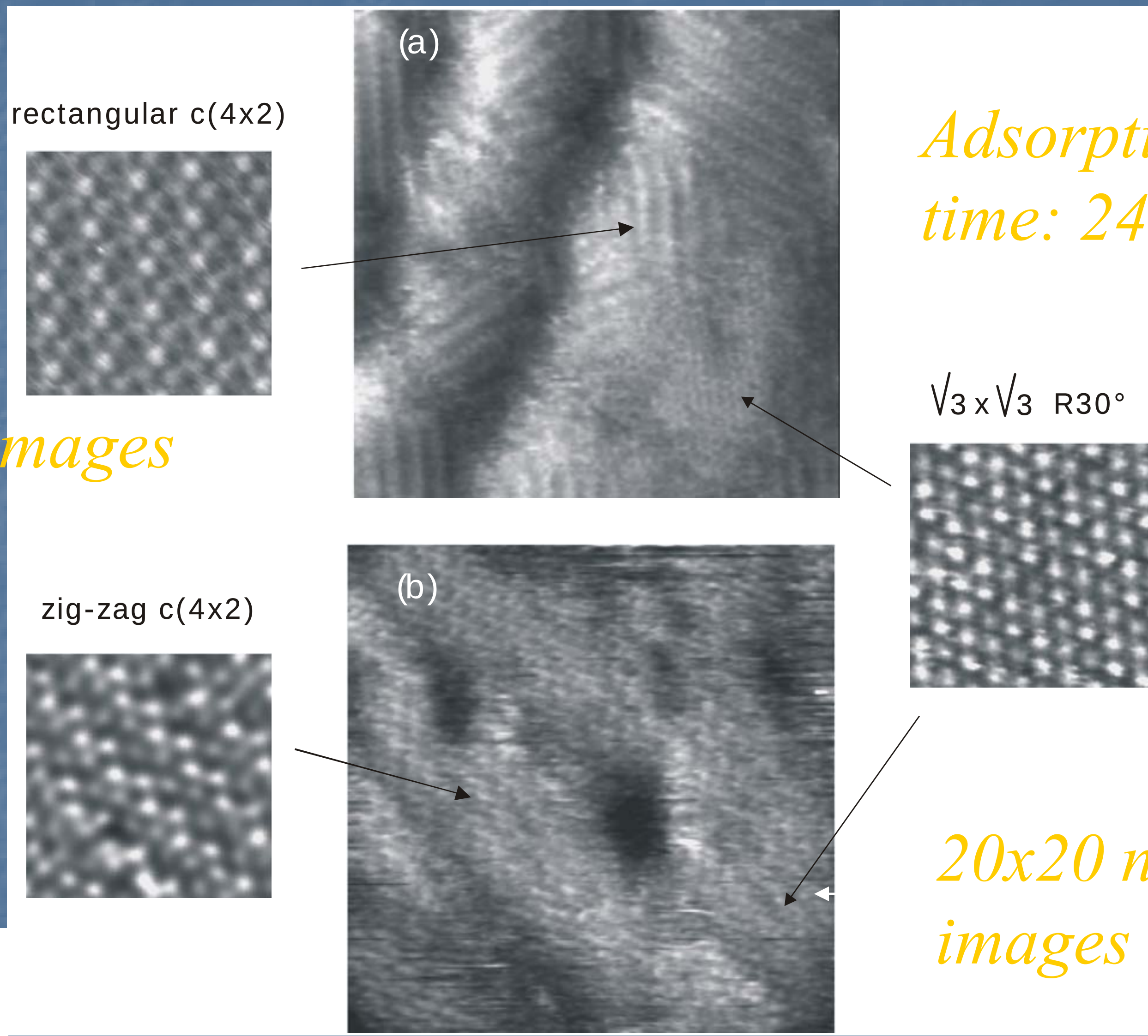
ECSTM
(20x20 nm^2
NaOH 0.1 M)

C. Vericat, G. Andreasen, M.E. Vela, H. Martin, R.C. Salvarezza, J. Chem. Phys. 115 (2001) 6672-6678

Stable phases

(a) hexanethiolate on Au(111)



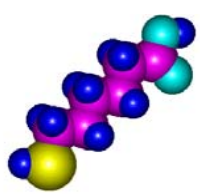


4x4 nm² images

Adsorption time: 24 hs

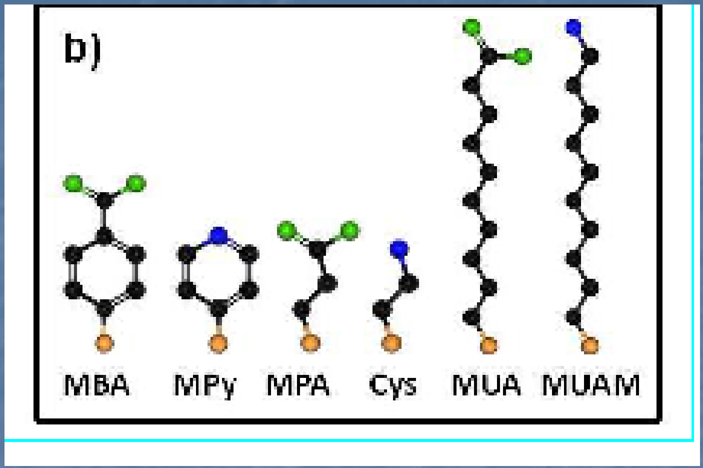
4x4 nm²

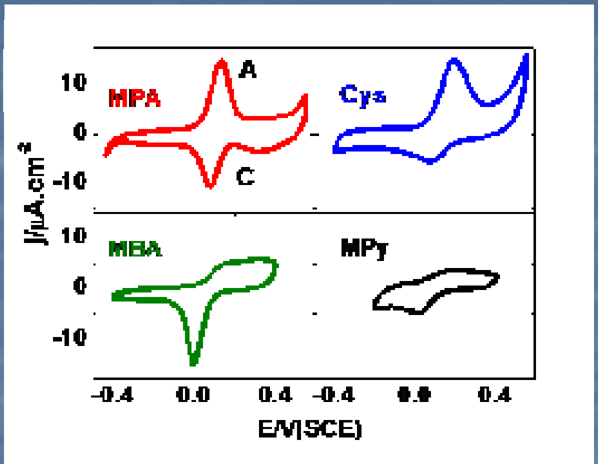
20x20 nm² STM images



(b) 11-mercaptoundecanoic acid on Au(111)

Trapping and delivery of metallic ions: Cu(II)

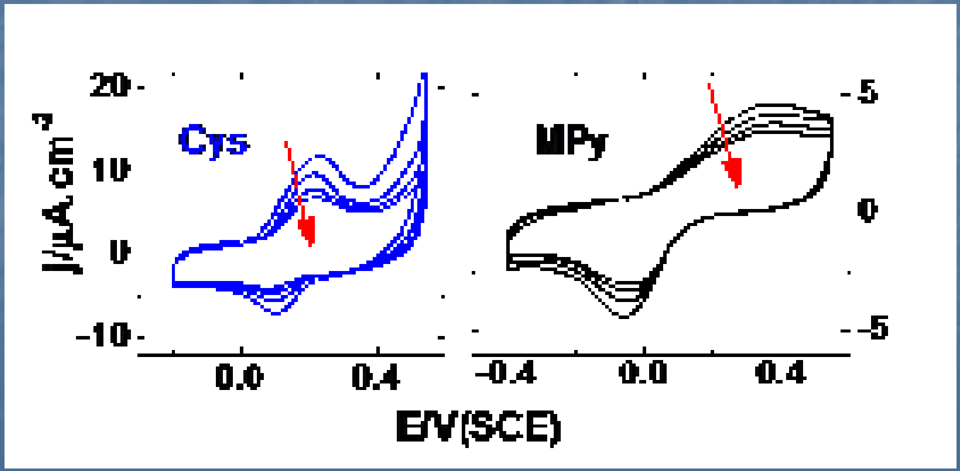




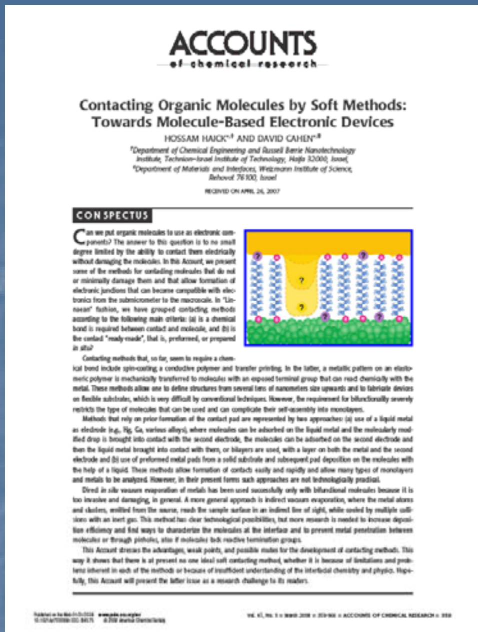
Cu(II)/Cu(I)

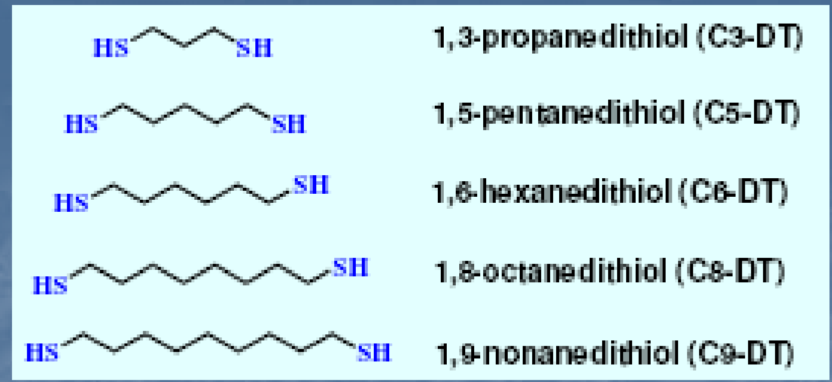
Electrochemical ions sensing, metallization

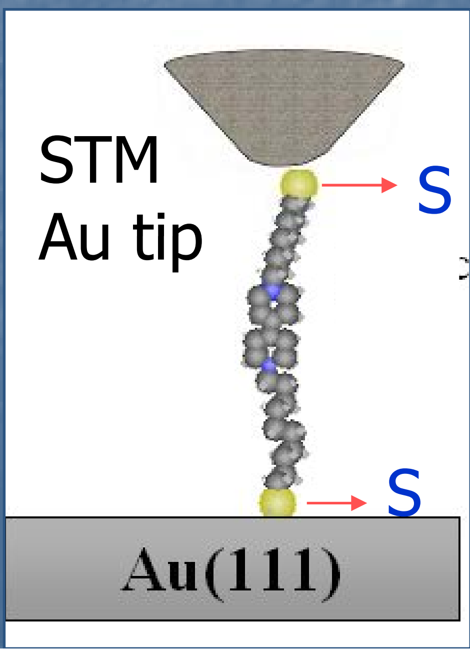
Delivery of Cu ions



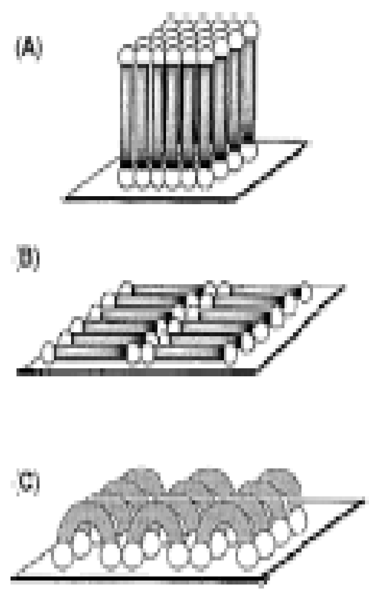
Dithiols on Au (111)







Challenges



Schematic representations of three possible orientations of α,ω-organodithiols on the metal surface corresponding to the (A) stand-up, (B) lie-down, and (C) looped monolayer assembly structures.

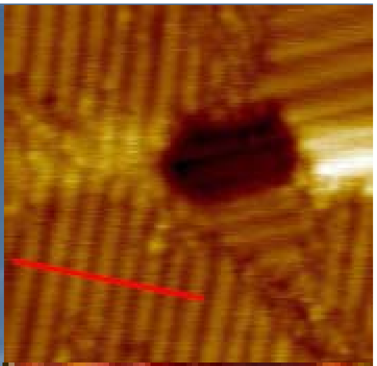
Yang et al. J. Org. Chem. 2000, 65, 871-877.

Dithiols on Au (111)

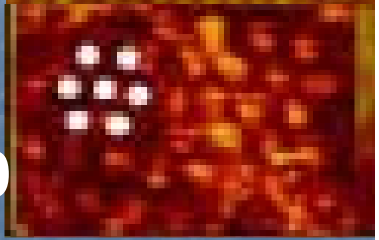
Paralell configuration

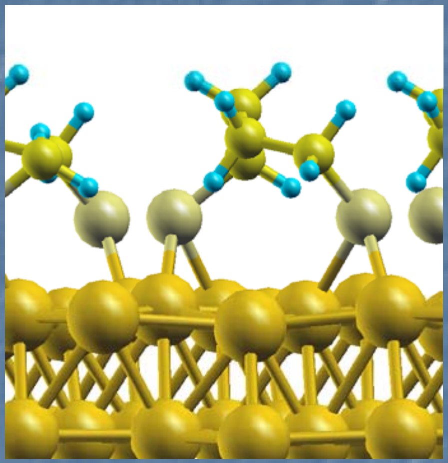
Vertical configuration

parallel

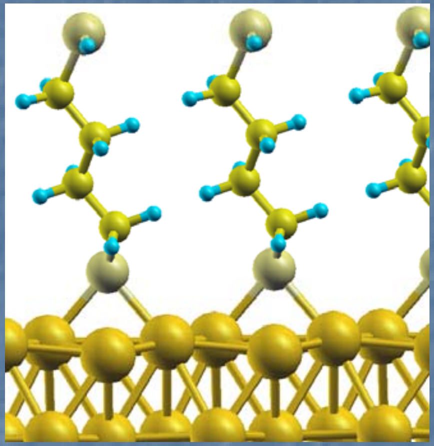


Vertical √3x√3 R30





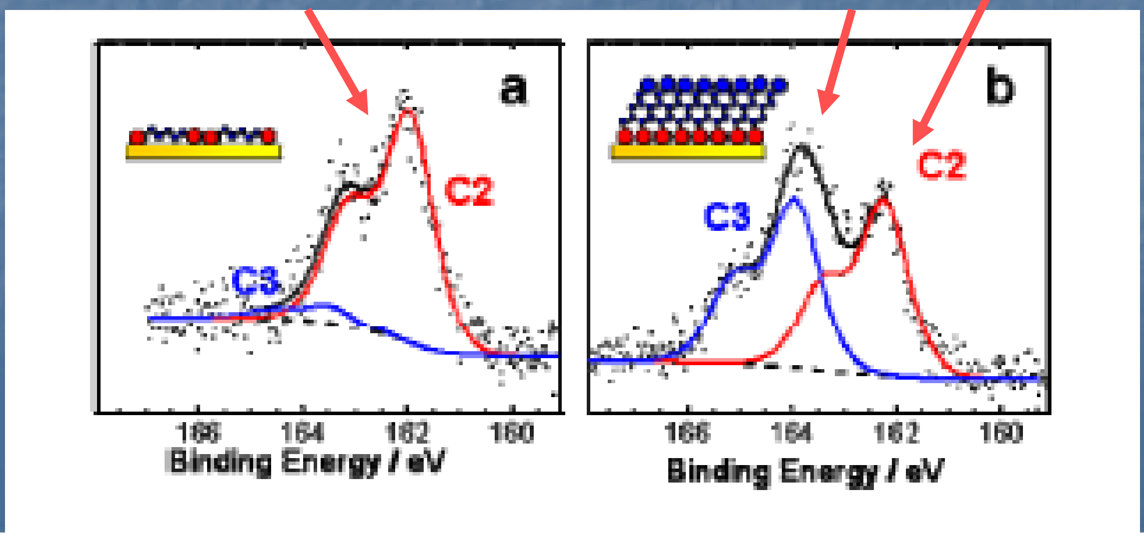
XPS S 2p

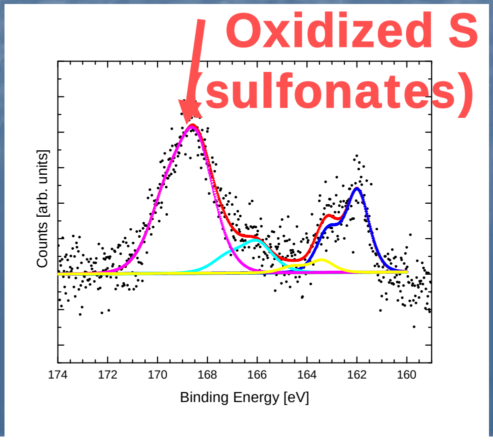


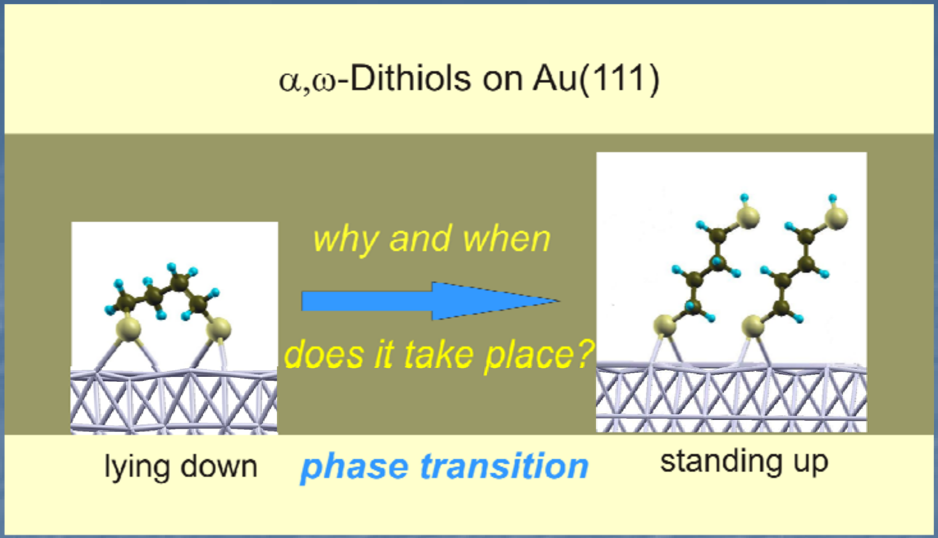
Only thiolates

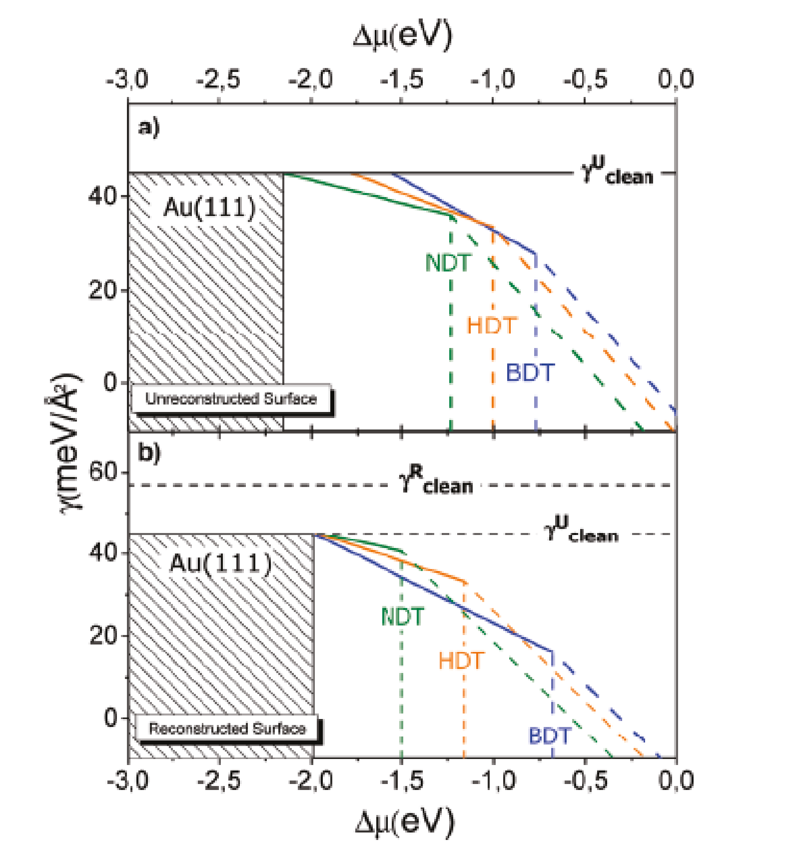
free SH+thiolate

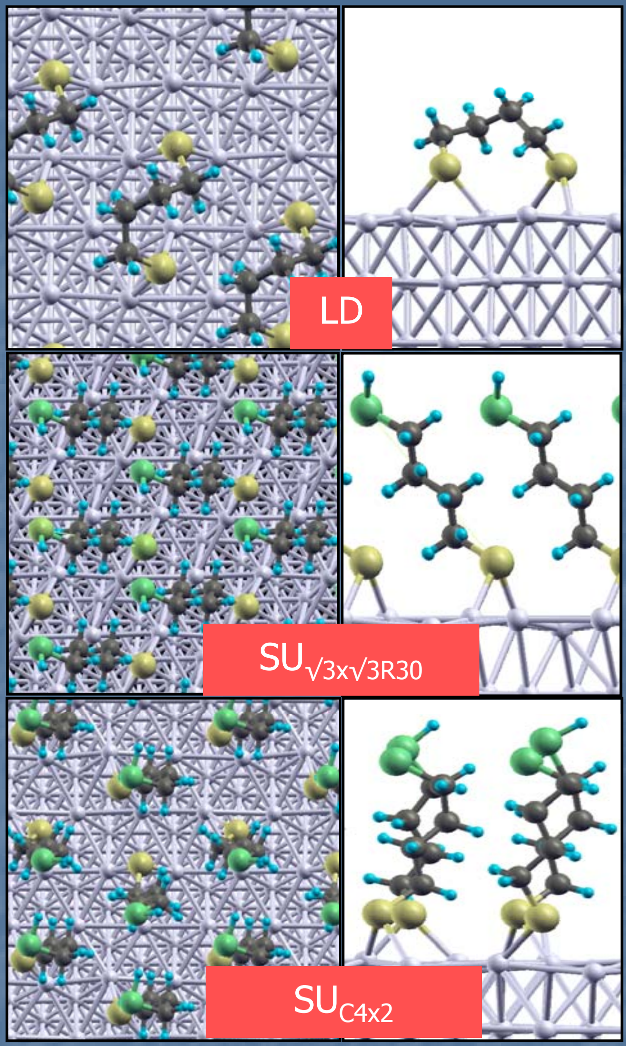
Surface Structures
More disorder
Easy Oxidation of the free SH





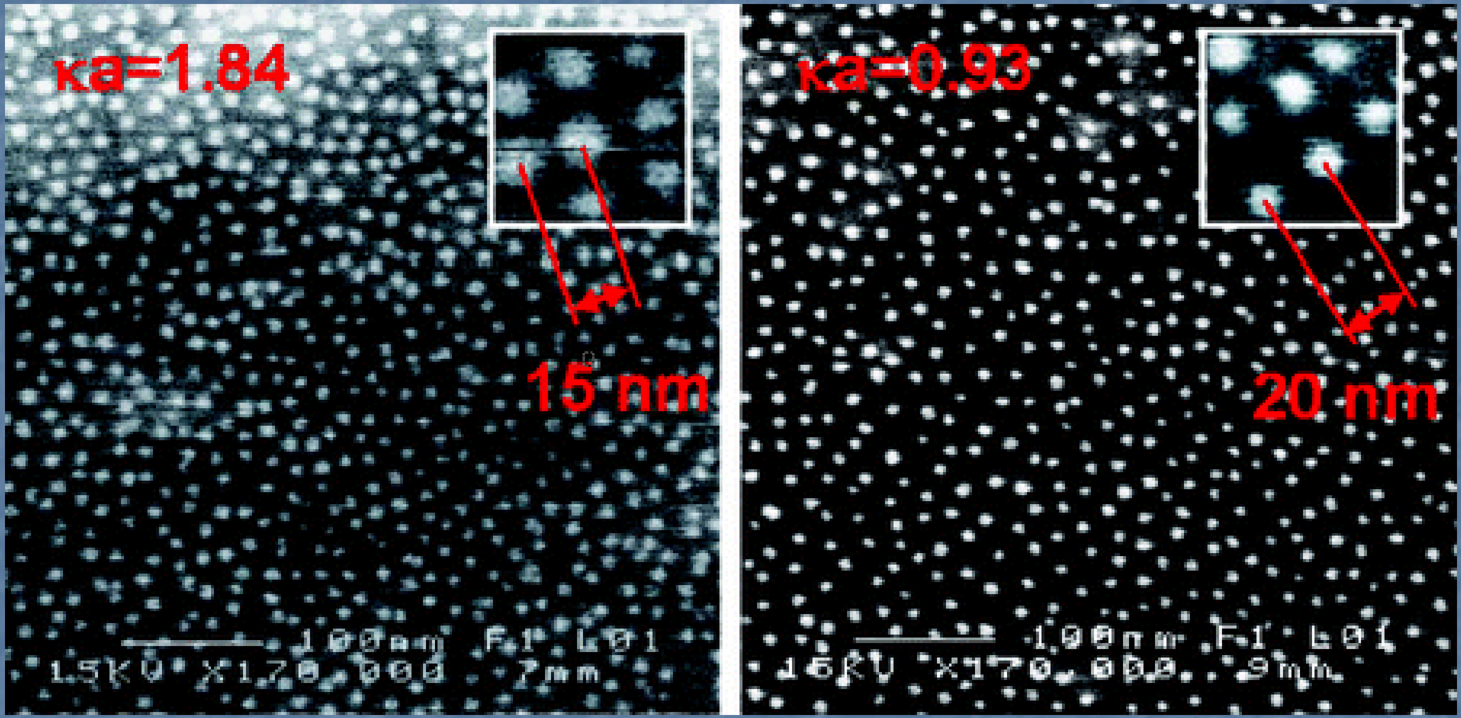






P. Carro, A. Hernandez Creus,
A. Muñoz, R. C. Salvarezza
Langmuir. 2010 15;26, 9589-95

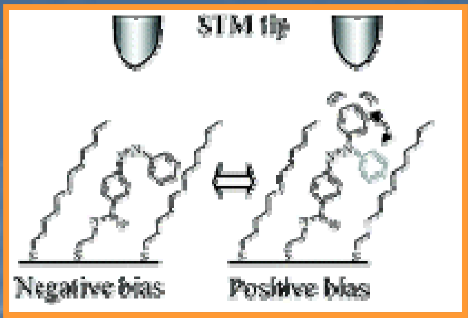
Self-Arrangement of Gold Nanoparticles on Octanedithiol Monolayer

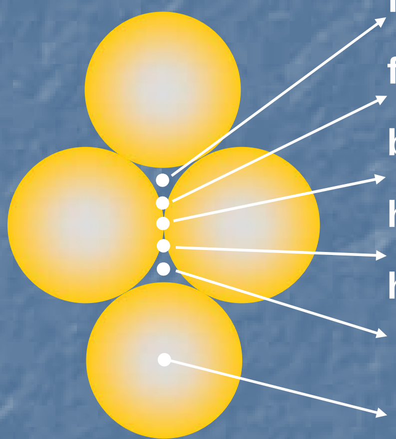


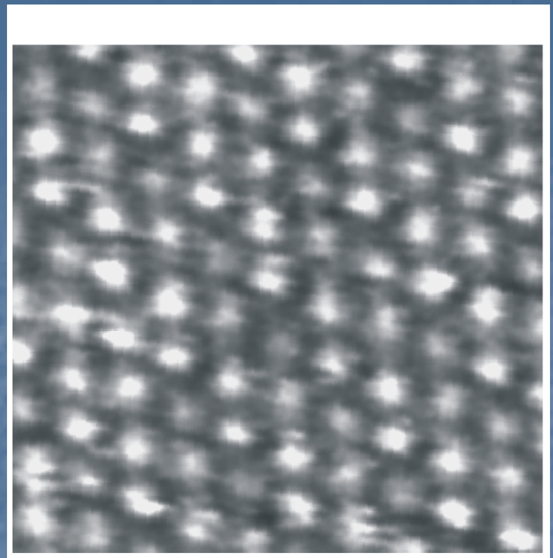
Lundgren, Bjrefors, Olofsson, Elwing

Nano Lett., 2008, 8 (11), pp 3989–3992

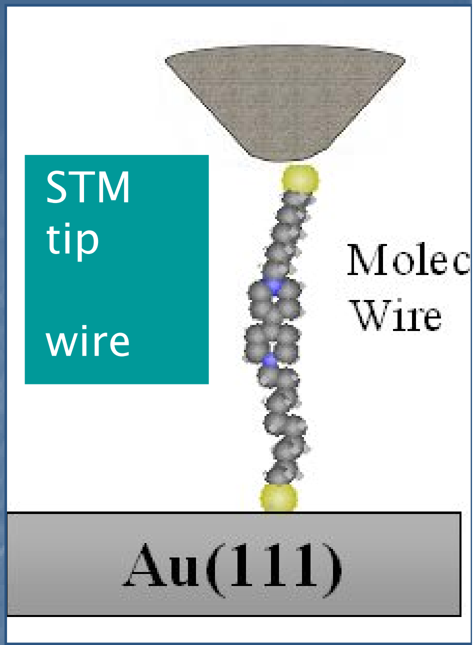
Adsorption sites



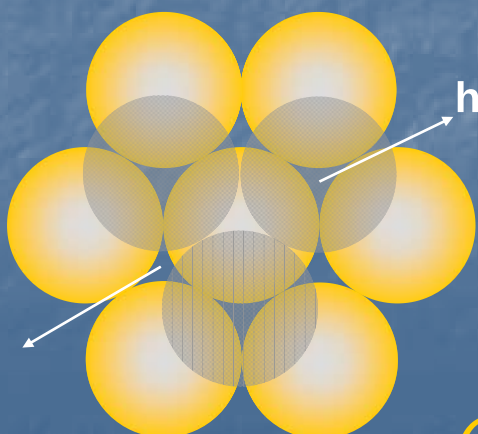




$\sqrt{3} x \sqrt{3}$ R30°



Single molecule conductance



DFT: bridge–fcc

Standing waves/ Photoelectron diffraction: top

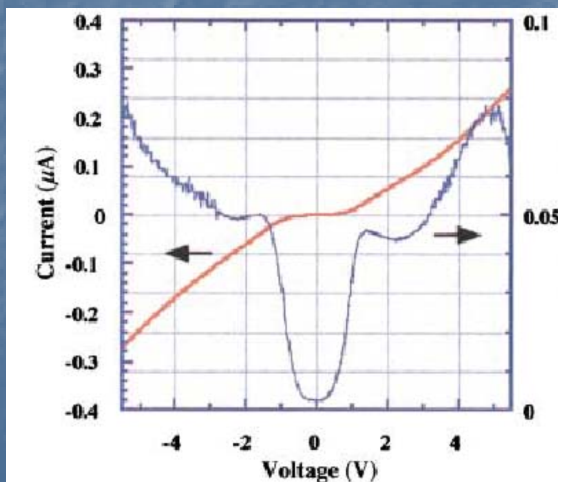
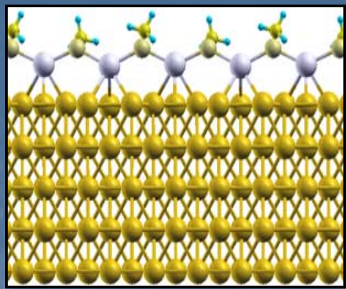


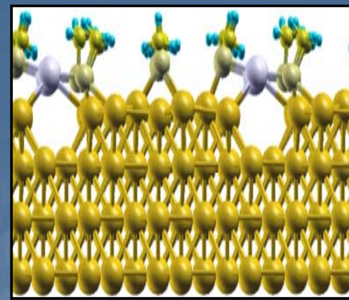
Figure 11. The I-V (red) and G-V (blue) characteristics of a single molecule.

MRS BULLETIN/FEBRUARY 2001

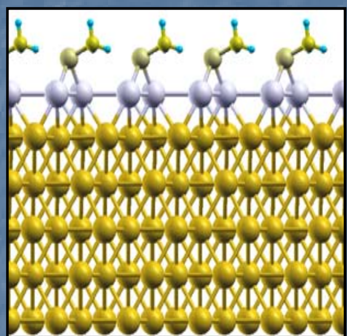
CH_3-$(CH_2)_n$-H_2CS +- nAu -

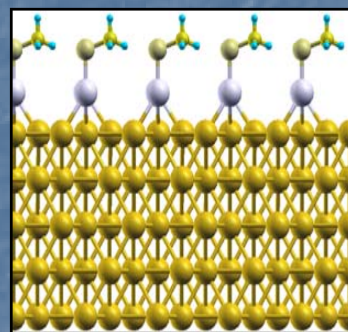


?



....is the Au(111) surface reconstructed upon thiol adsorption?

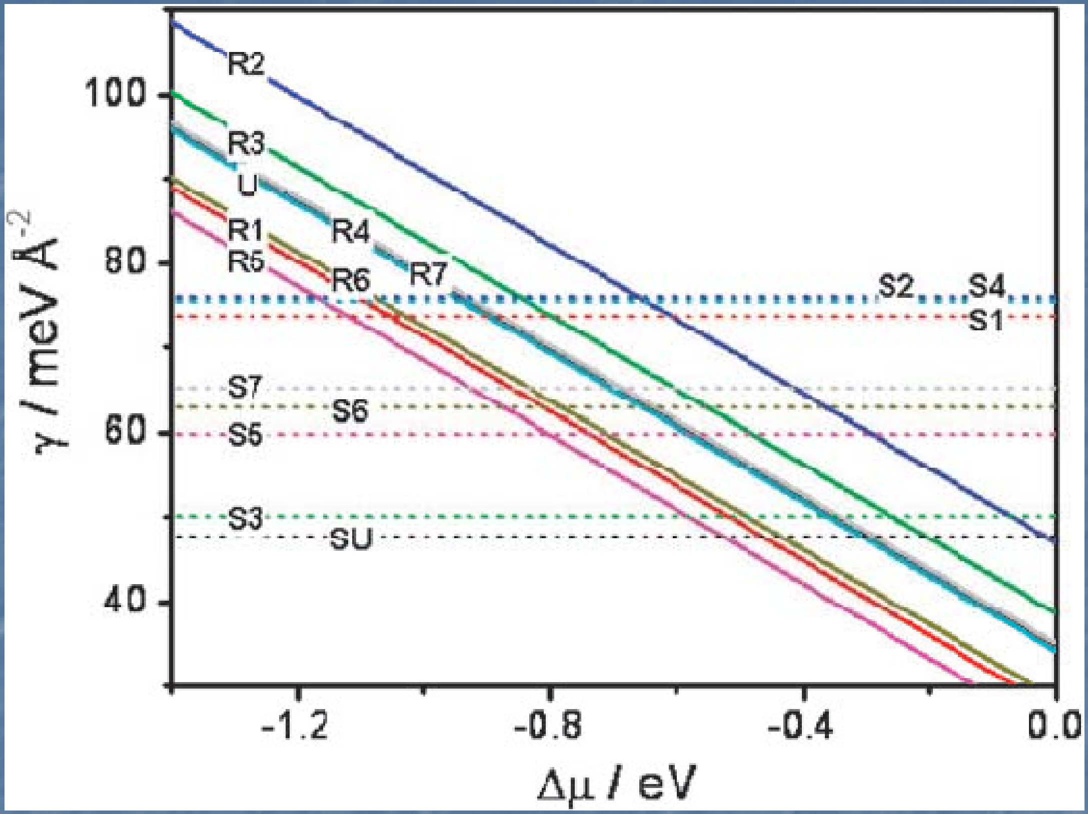


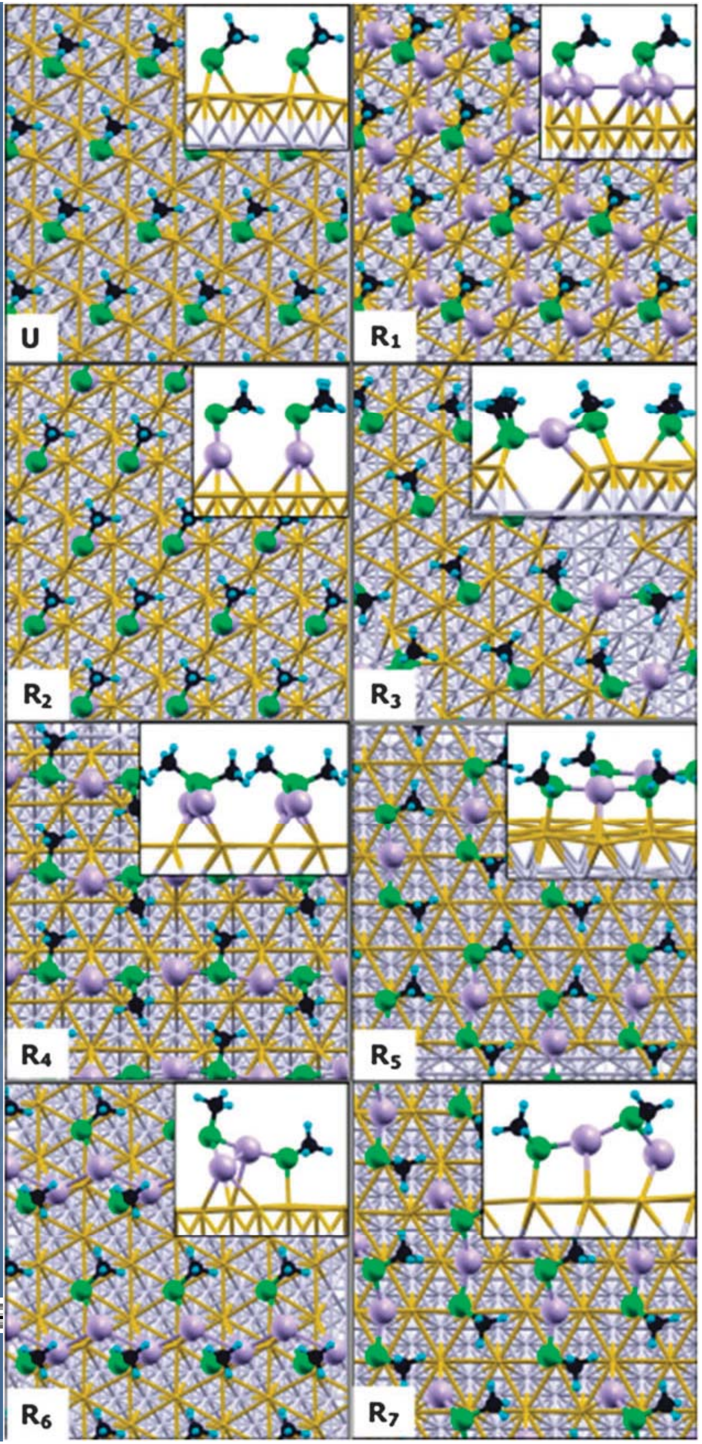


Yu, Bovet; Satterley; Bengio; Lovelock. ; Milligan; Jones; Woodruff ; Dhanak. *Phys. Rev. Lett.* **2006**, *97*, 166102.
Mazzarello, ; Cossaro; Verdini; Rousseau, Casalis; Danisman ; Floreano; Scandolo; Morgante,; Scoles. *Phys.Rev.Lett.* **2007**, *98*, 016102.
Grönbeck, H.; Häkkinen, H. *J. Phys. Chem. B* **2007,** *111,* 3325.
Molina, M. L.; Hammer, B. *Chem. Phys. Lett.* **2002**, *360*, 264. and more…….

8 models in the last years!!!
Diffraction techniques give contradictory results

The S-Au interface

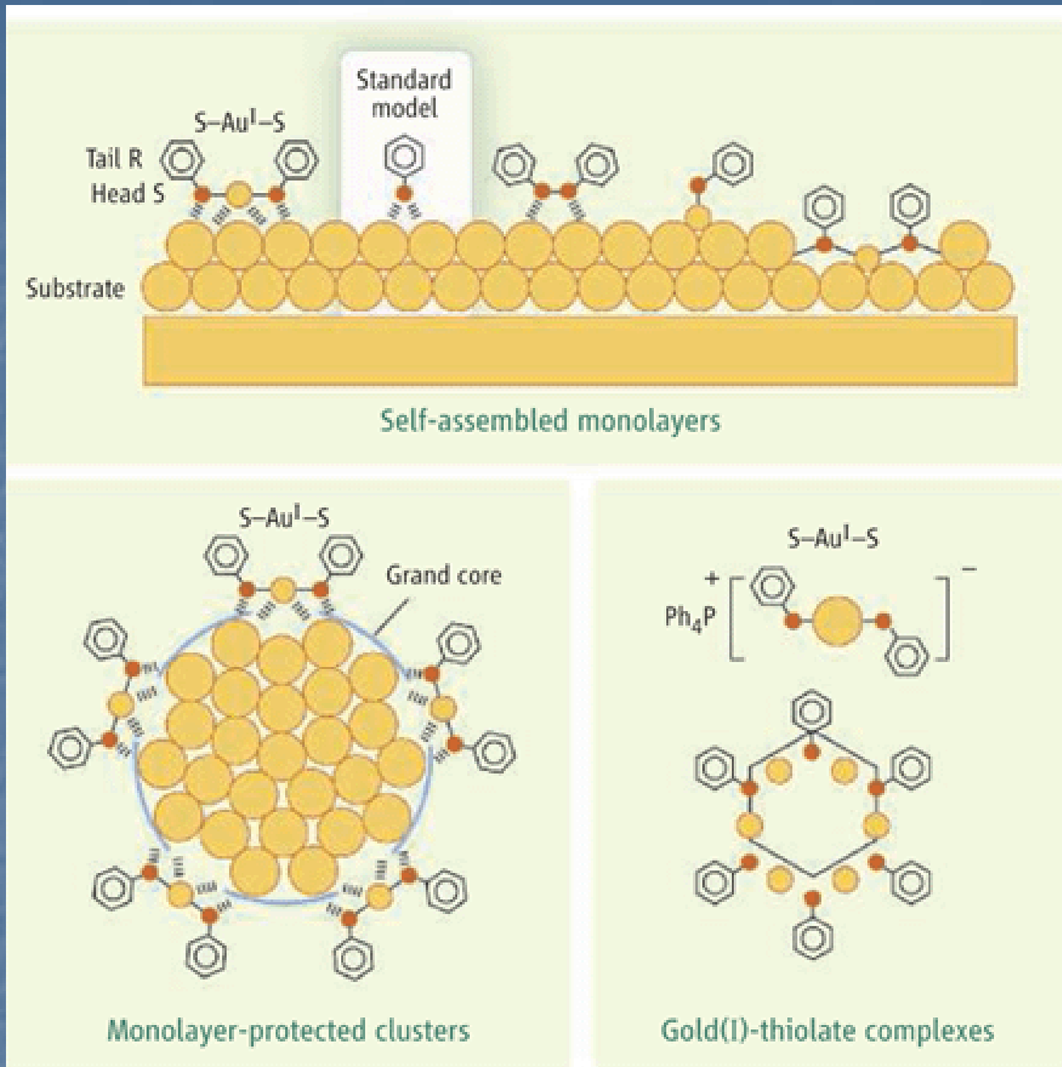


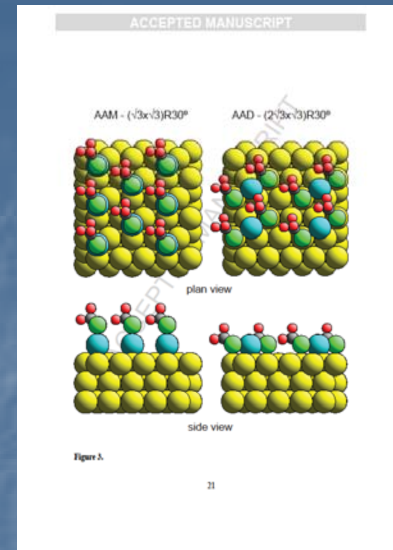


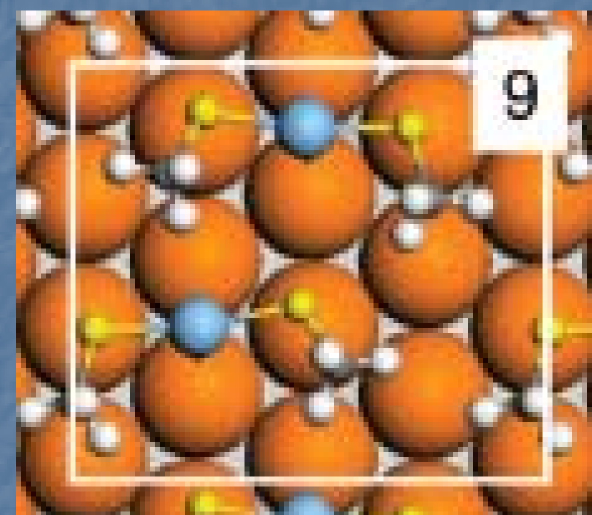
$$\Delta\mu = \mu - \frac{1}{2} g_{(CH_3S)_2}$$

Pilar Carro, Roberto Salvarezza, Daniel Torres, and Francesc Illas

THE JOURNAL OF PHYSICAL CHEMISTRY C 2008, 112 (48), 19121-19124

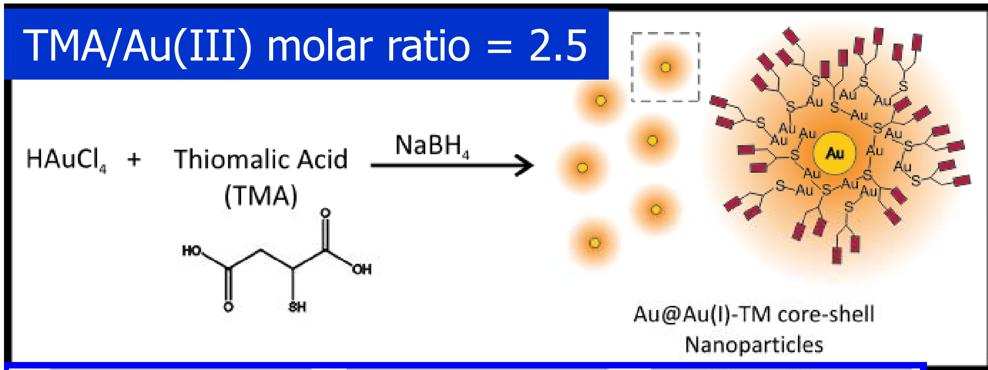


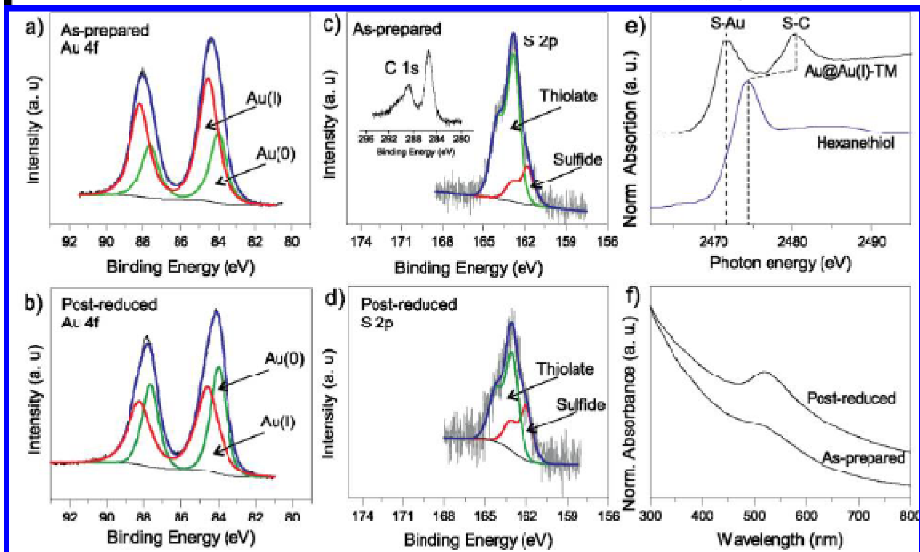


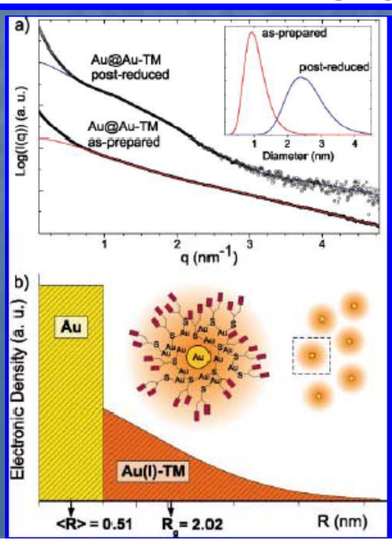


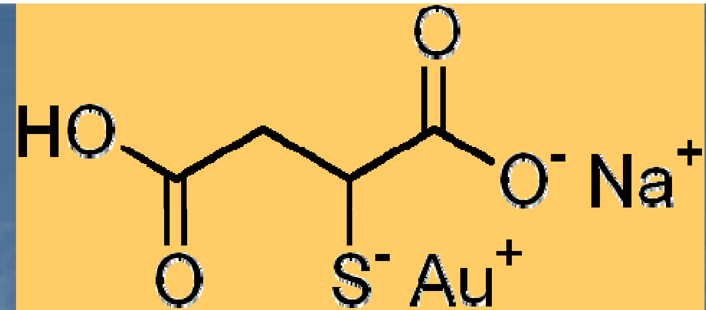
Walter, Akola, Lopez-Acevedo, Jadzinsky, Calero, Ackerson, Whetten, Grönbeck, Häkkinen
PNAS July 8, 2008 . 105 , 9157-9162

H. Gronbeck,H Hakkinen,R L. Whetten
J.Phys.Chem C 112, 15940 (2008)

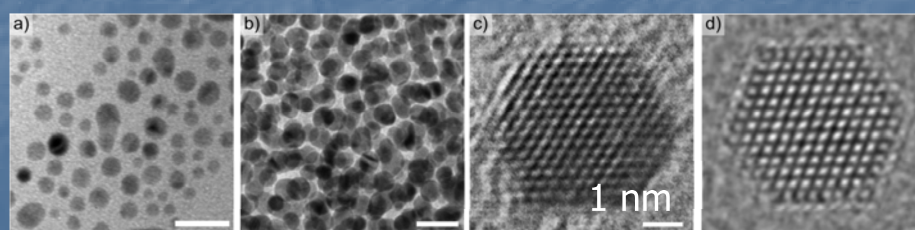








Myochrysine
Gold thiomalate

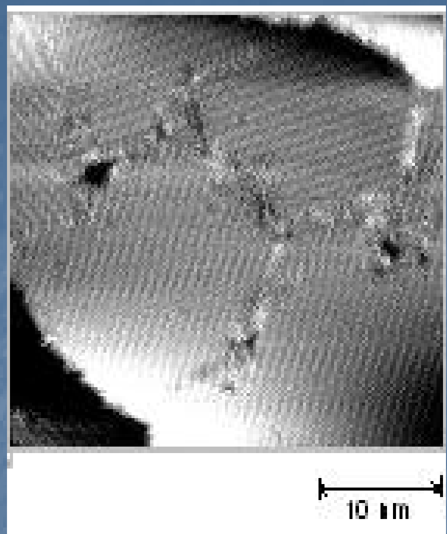


ACS NANO

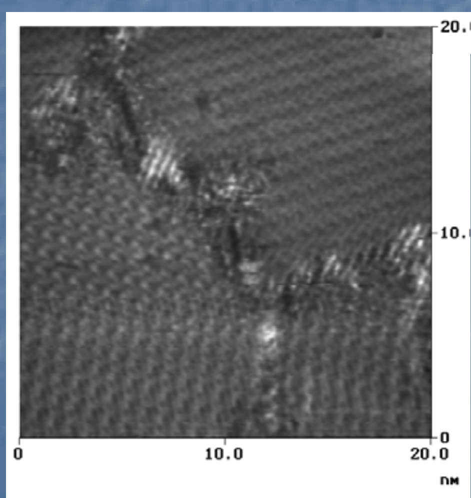
Corthey, Giovanetti, Ramallo-López, Zelaya, Rubert, Benitez, Requejo, Fonticelli, Salvarezza 4 3413-3421 (2010).

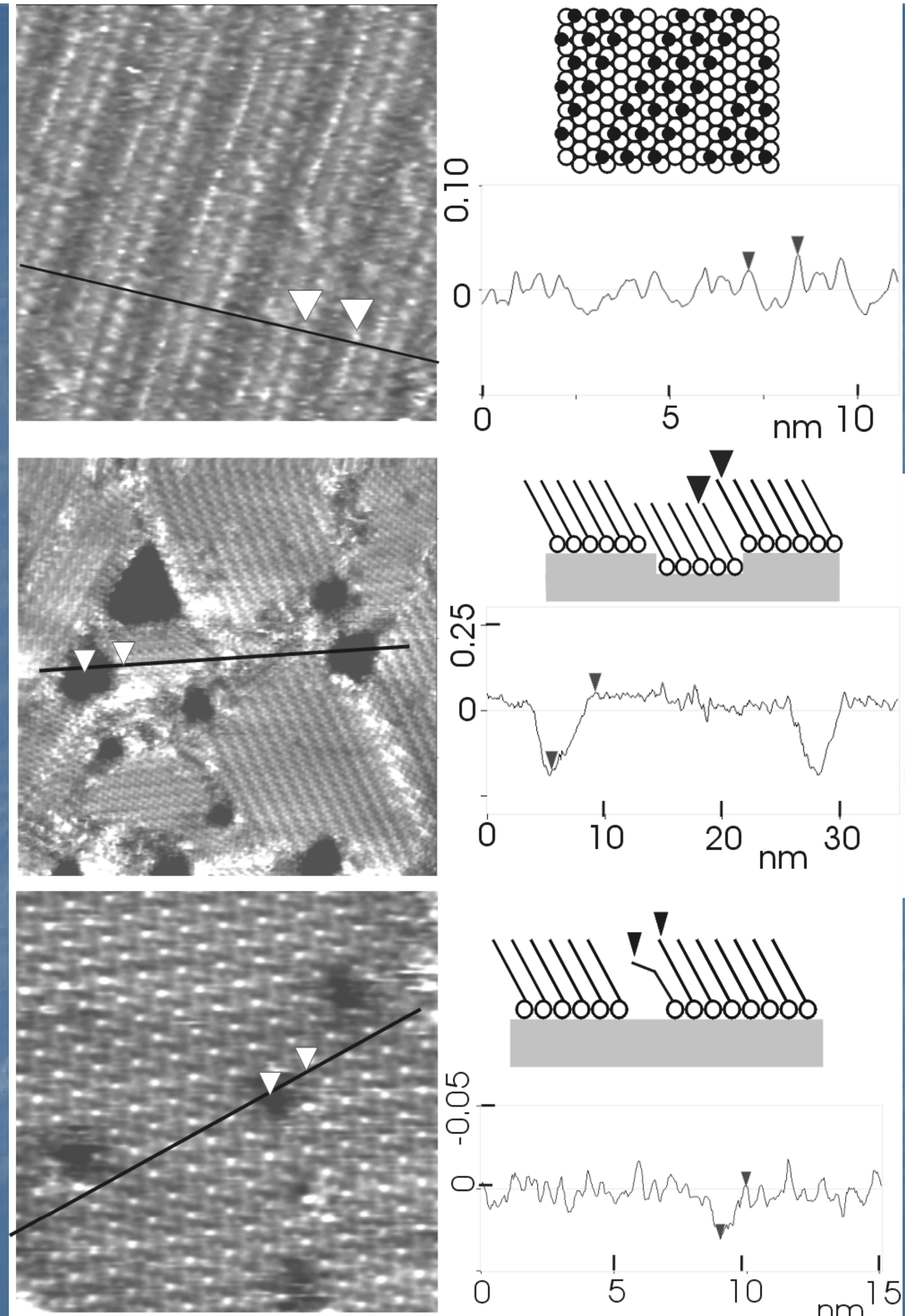
SAM quality

Structural defects



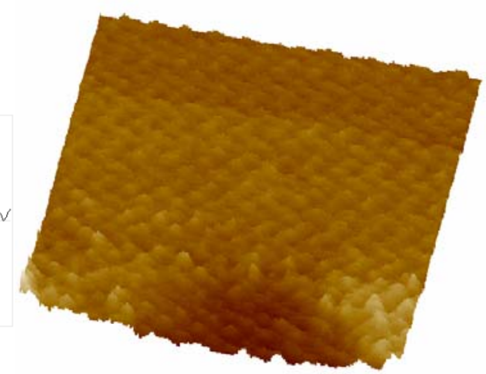
Domain boundaries





Missing rows in √3 x√3 R30

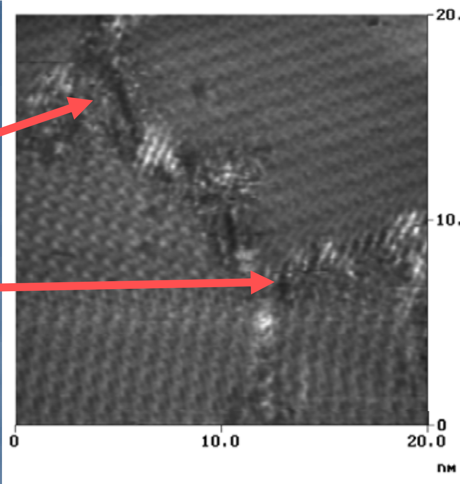
Depressions



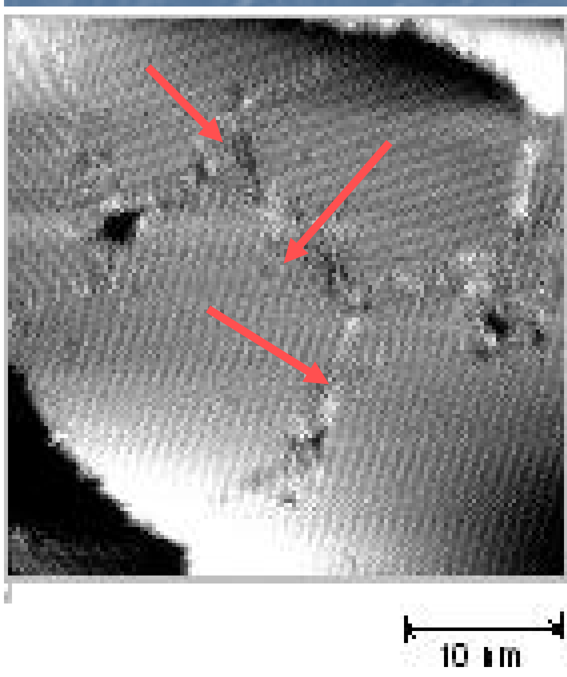
Molecular defects

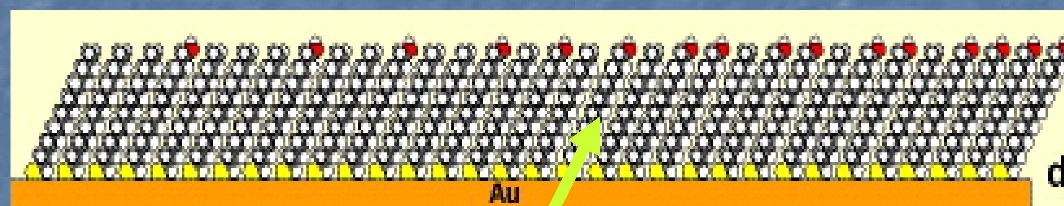
Benítez, Vericat, Tanco, Remes Lenicov, Castez, Vela, Salvarezza Langmuir **20** 5030 (2004)

Domain boundaries



Preferred paths for transport of ions, water and molecules



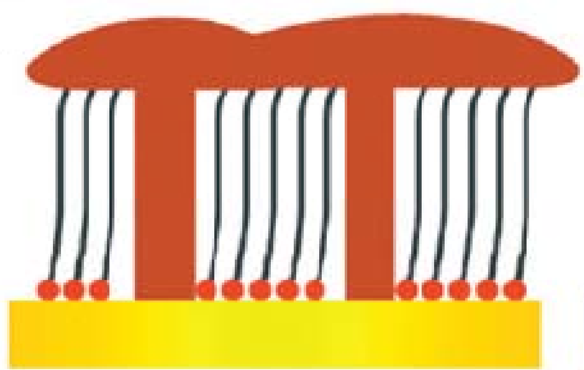


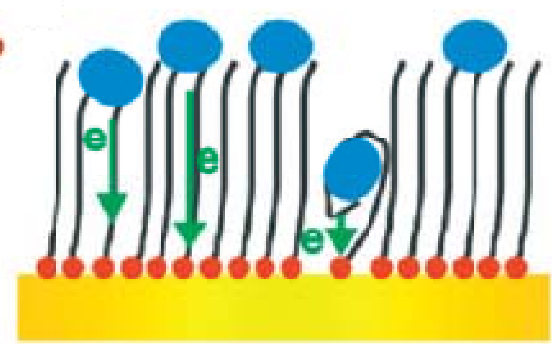
Ideal situation defect-free thiol SAM

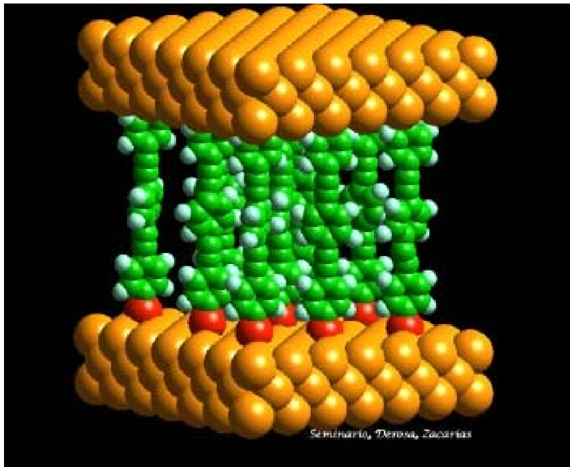
metallization

Charge transfer

Real situation

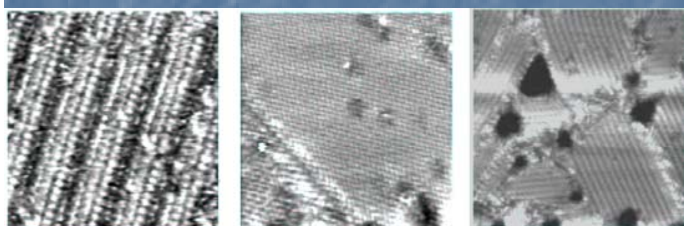






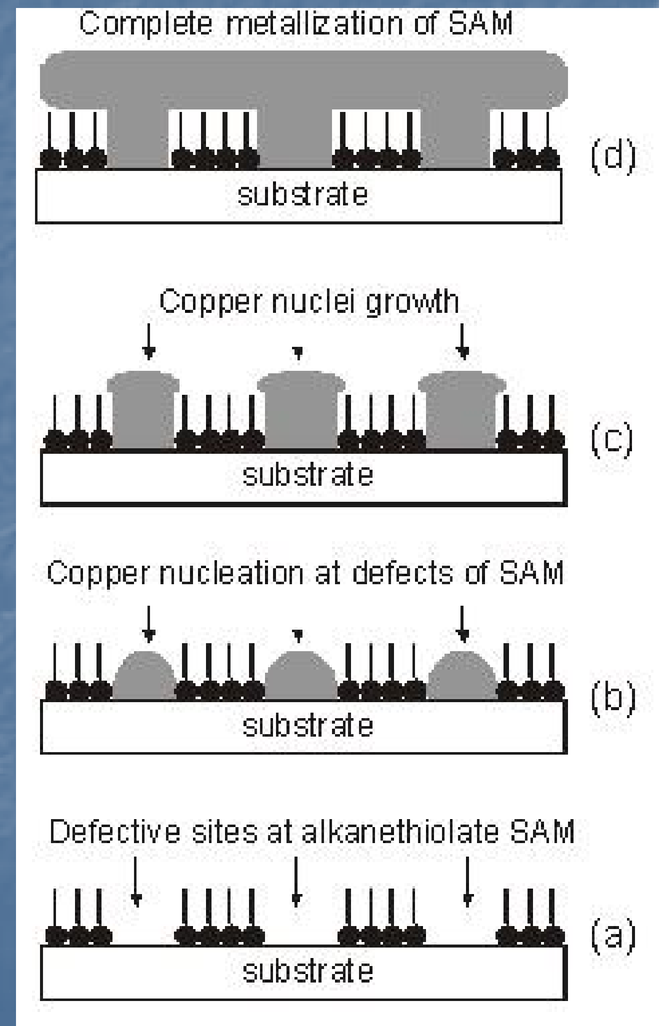
Thiol –based Electronic devices

Top-contact problem



Defects at SAMs

Metal penetration into SAMs



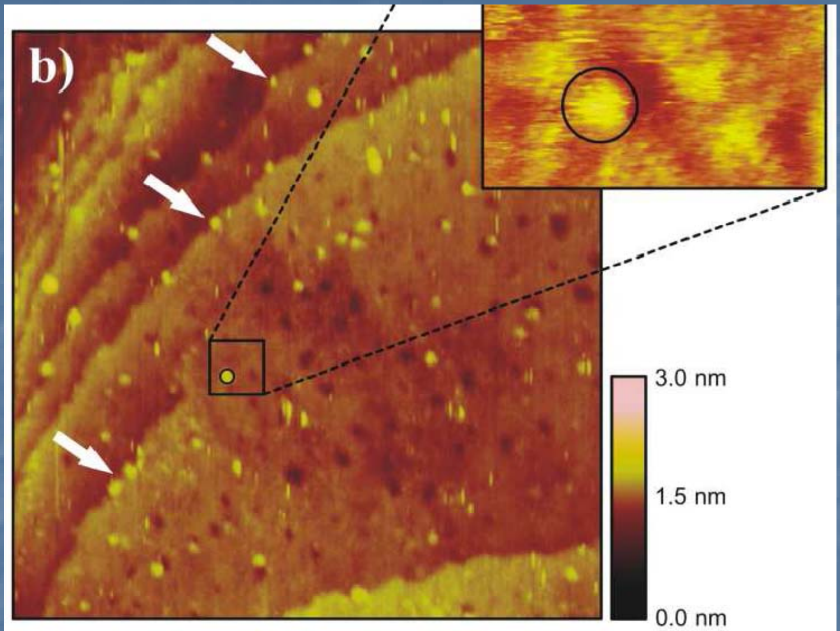
One of the biggest problems with molecule-based devices is poor yield. Often the overall device yield will be significantly less than 10 %, sometimes less than 1 %. Most of the degradation occurs at the final metallization step, which it is called the "top contact problem

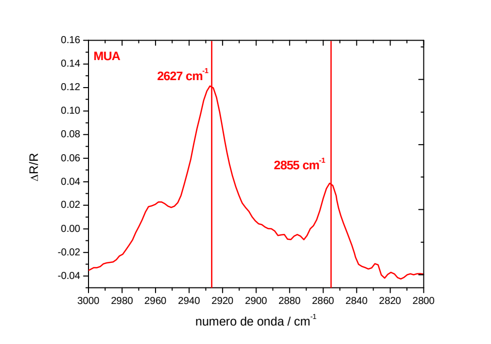
Decrease defect density (annealing)
Use functionalized thiols (-SH,-COOH, -OH, -OCH$_3$)
Induce cross-linking in phenyl thiol by electron irrediation

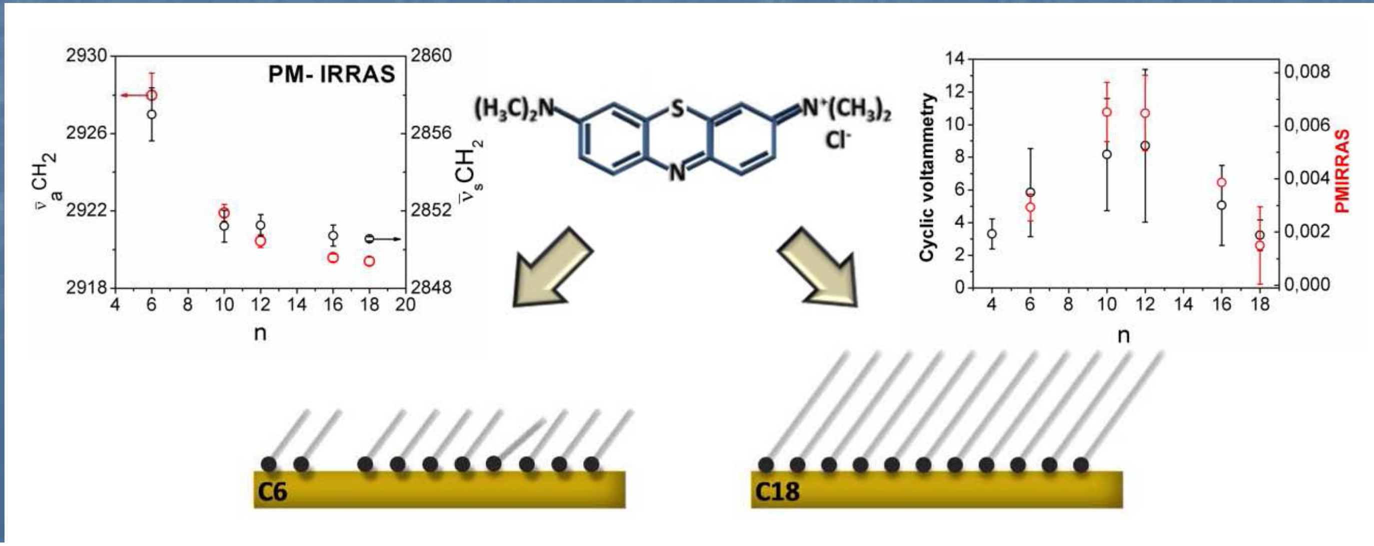
Conformational defects: chain disordering
Incorporation of Methylene Blue in SAMs

STM

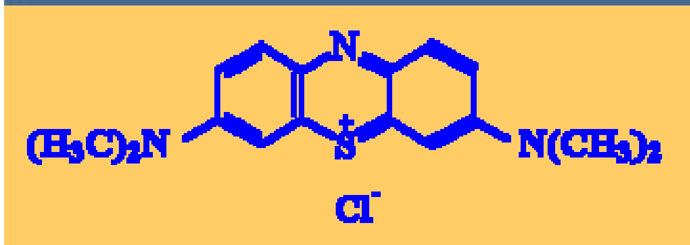
Grumelli, Méndez De Leo, Bonazzola, Zamlynny Calvo, Salvarezza Langmuir, ***2010*** *26, 8226-8232*







PMIRRAS



178 J.P. Tardivo et al.

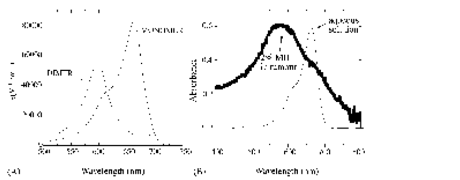
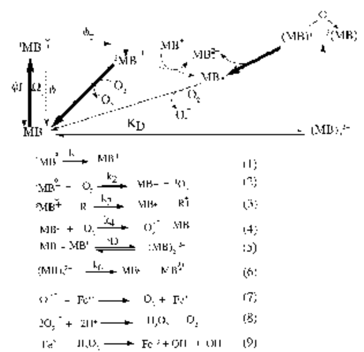
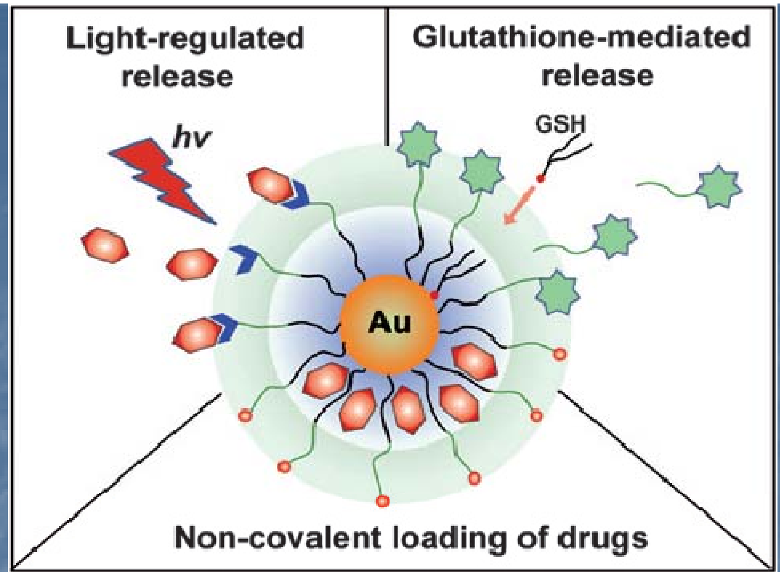
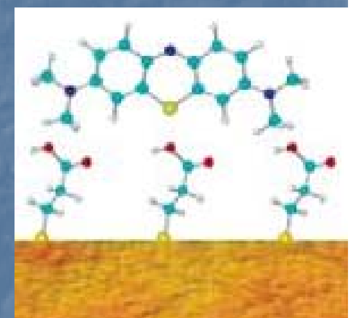


Figure 1 (A) Absorbance spectra of dimer and monomer species of MB. (B) Dark line: absorption spectrum obtained with a reflectance spectrophotometer (Ocean Optics USB2000) equipped with pulsed xenon light source, of a skin cancer in which a 2% MB aqueous solution was injected locally; thin line: absorbance spectra of a diluted MB aqueous solution ([MB] = 20 μM).



Scheme 2 Methylene blue photochemical reaction routes where MB^+, $^1MB^{+*}$, $^3MB^{+*}$ are methylene blue ground state, singlet and triplet excited states, respectively, $MB^•$ and $MB^{•2+}$ are methylene blue semi-reduced and semi-oxidized radicals, respectively, Ω_1 is light absorption, ϕ_f, ϕ_{nr}, ϕ_T, are fluorescence, nonradiative and triplet quantum yield. Reactions (1—4) represent the deactivation routes of MB^+ excited state and radical species where (1) is the $^3MB^{+*}$ spontaneous decay, (2) is the reaction of $^3MB^{+*}$ with molecular oxygen, (3) is the redox suppression of $^3MB^{+*}$ by reducing agents, (4) is the oxidation of $MB^•$ by molecular oxygen returning the ground state dye and forming superoxide, (5) is the ground state dimerization constant, (6) is the redox suppression of ($^3MB^+$- - - -MB)* after exciting ground state dimers, (7—9) are Fenton reactions. The relative position of the species presented in this scheme do not represent their actual energy level. Modified from Ref. [20].





Incorporation (delivery) of methylene blue into (from) hydrocarbon chains

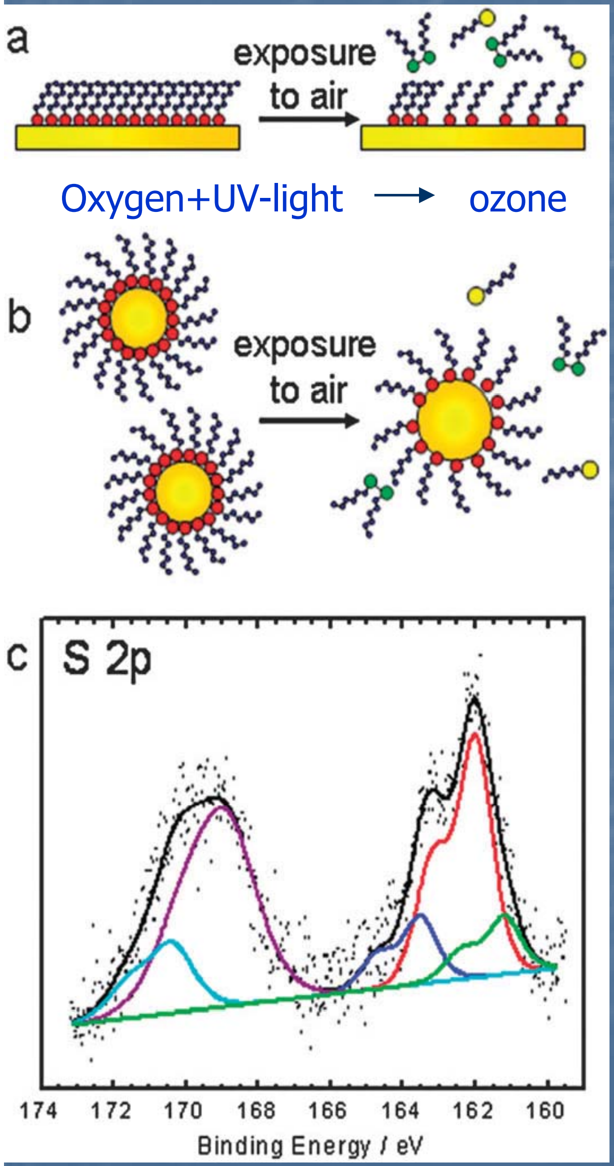
Methylene blue is a photosensitizer used to create singlet oxygen when exposed to both oxygen and light. Mb is used to kill cancer cells

Methylene blue combined with light has been used to treat resistant plaque psoriasis, AIDS-related Kaposi's sarcoma, West Nile virus, and to inactivate staphylococcus aureus, HIV-1, Duck hepatitis B, adenovirus vectors, and hepatitis C.

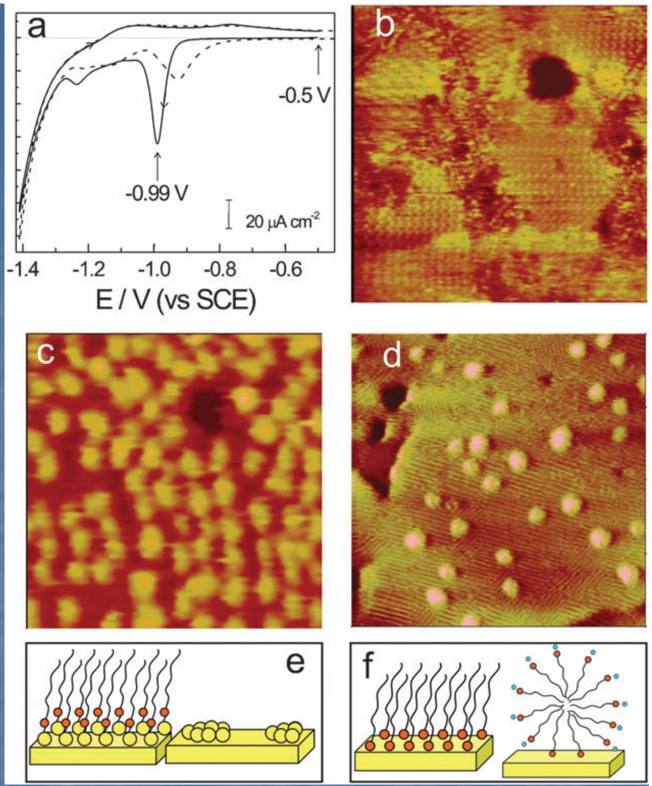
SAMs stability

SAMs stability

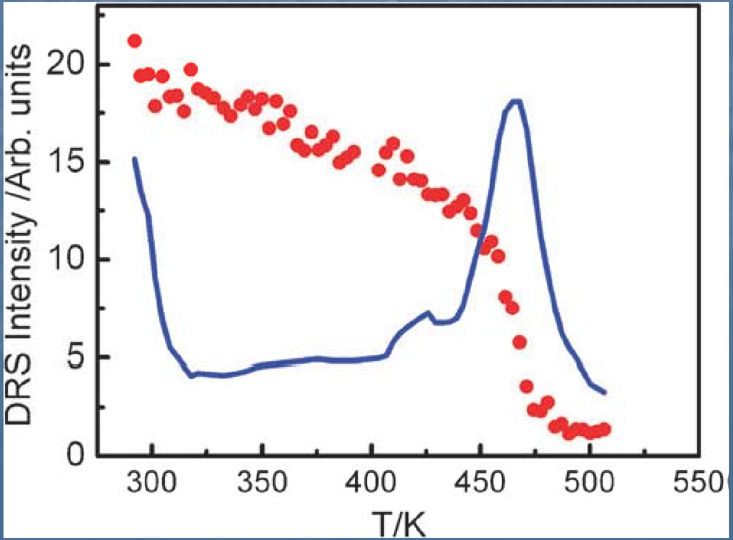
Chemical stability



Electrochemical stability

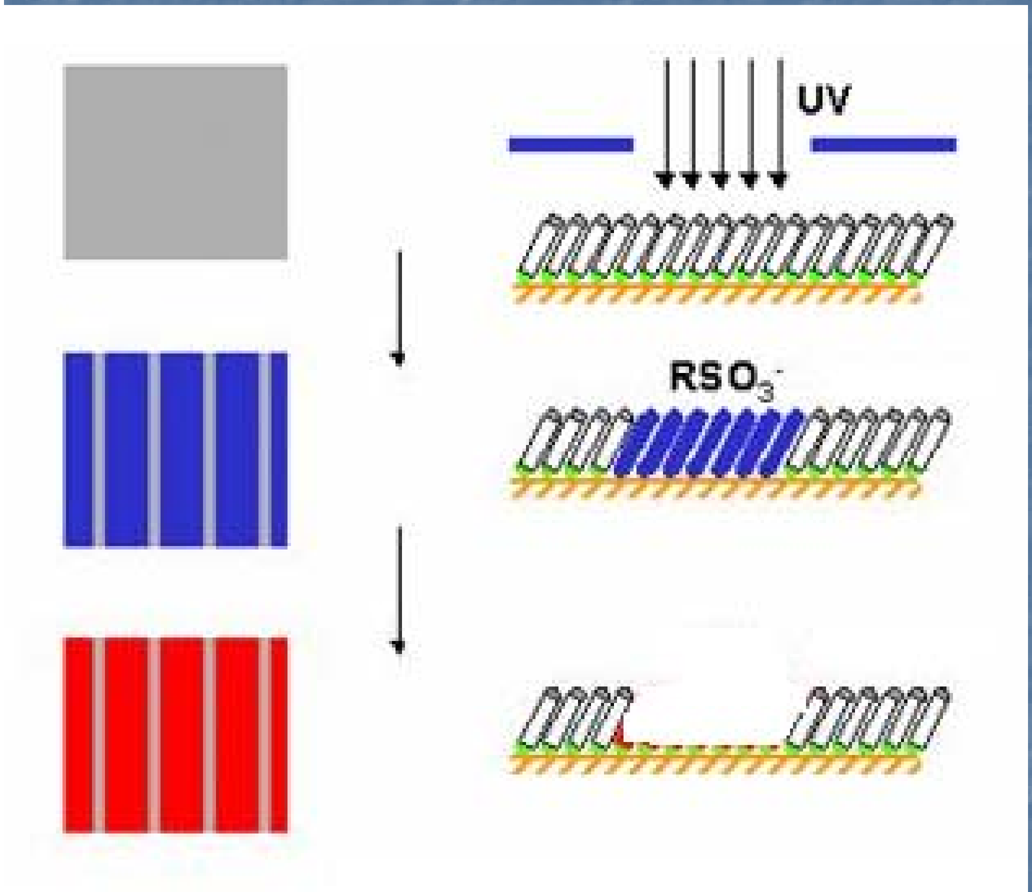


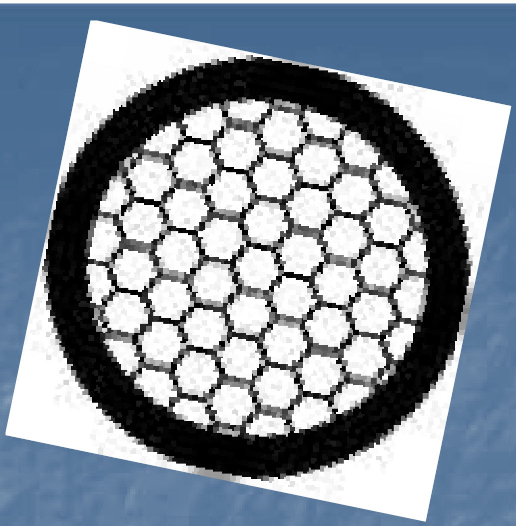
Thermal stability

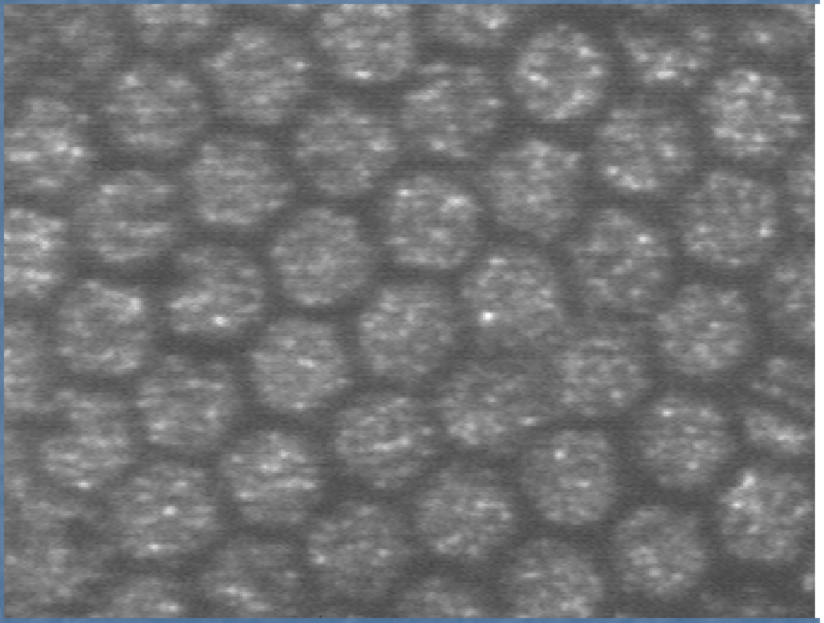


Chemical stability

Photolithography: SAMs as Resists



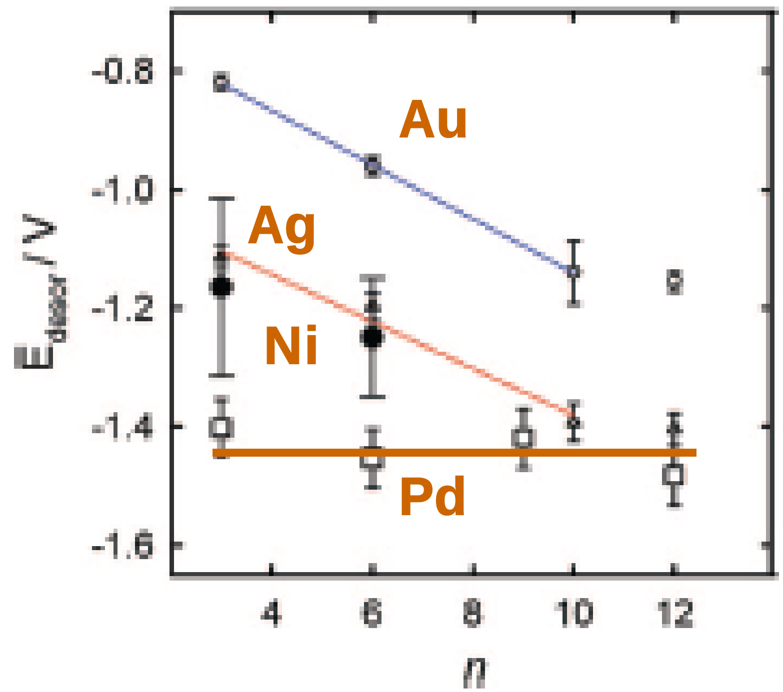


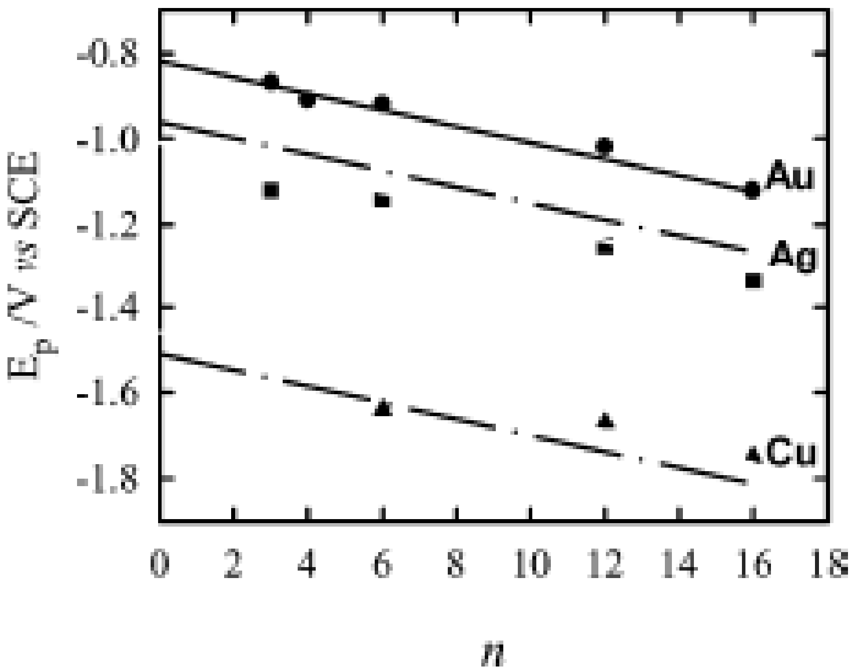


O. Azzaroni, P.L. Schilardi, R.C. Salvarezza
"Encyclopedia of Nanoscience and Nanotechnology",American Scientific Publishers, Vol. 5, 835-850 (2004).

Electrochemical Stability on Different Subtrates

E_p vs number of C atoms

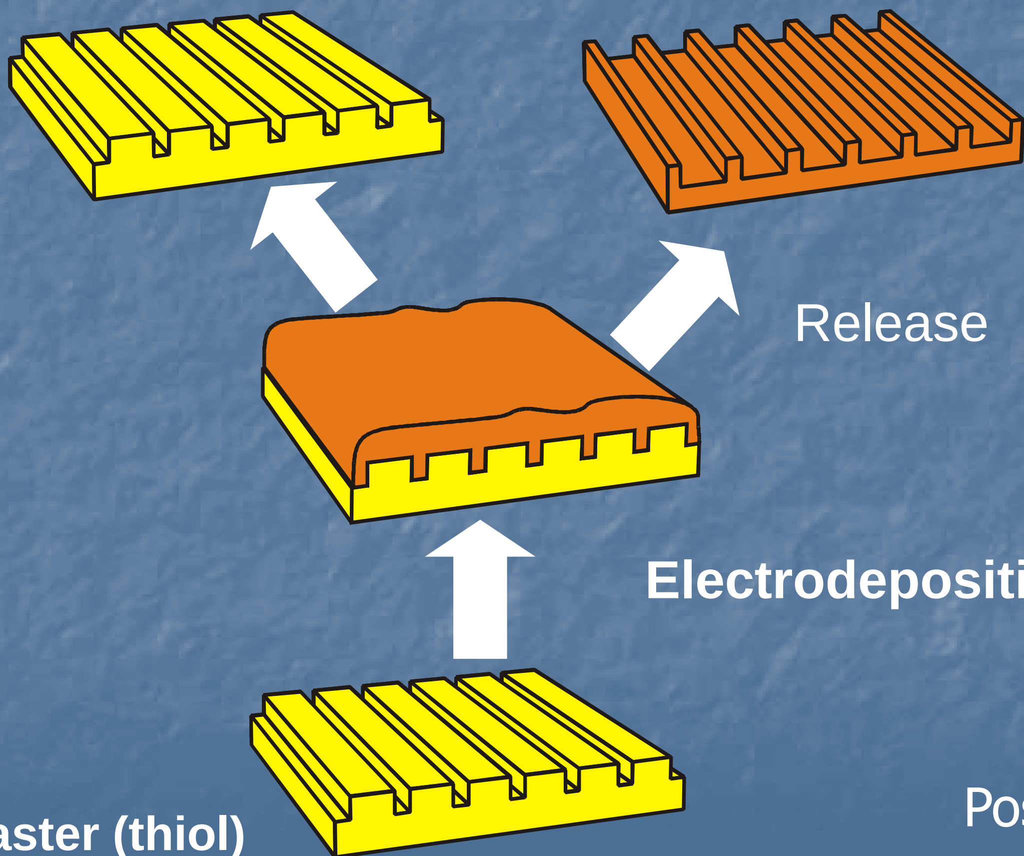




Cu > Pd > Ni = Ag > Au

Surface Modification: Electrochemical soft-lithography for molding metals and oxides

Methyl-terminated SAMs as anti-adherent layers



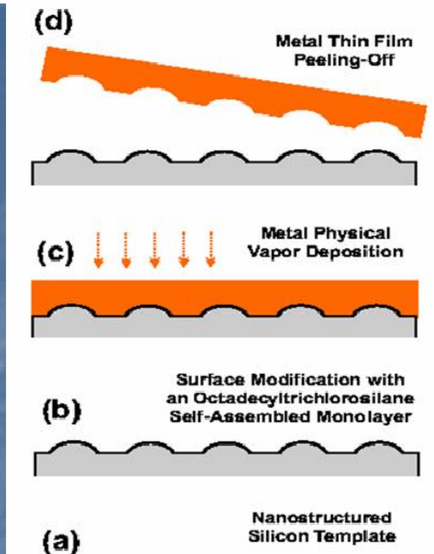
Stability against reductive desorption

Cu > Pd > Ni = Ag > Au

Cu is the best option for masters due to the high SAMs stability

Select C12 or C16 alkanethiols

Positive: defects at SAMs allow electric contact



Salvarezza et al

Nano Letters,
1, 291-294 (2001)

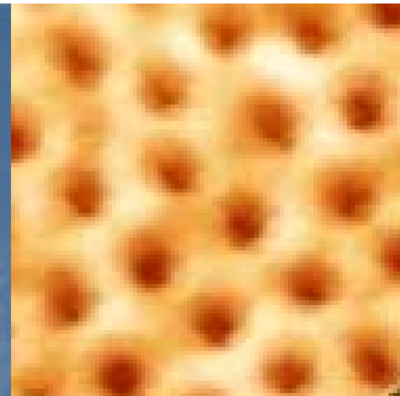
Advanced Materials
16, 405 (2004)

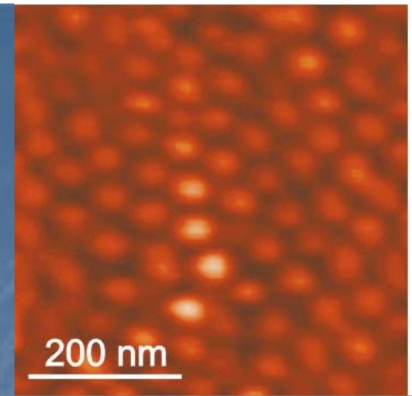
Small 1, 300 (2005)

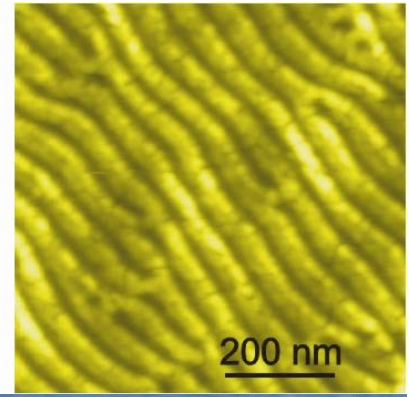
Chemistry European J.
12, 38, (2006)

ACS Nano,

2, 2531 (2008))





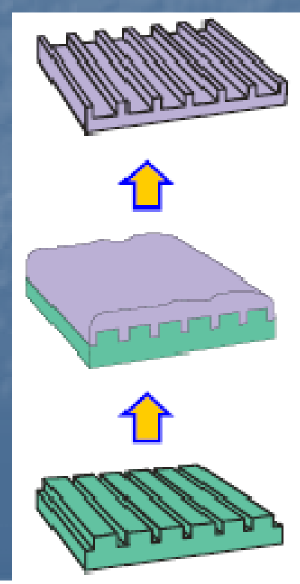


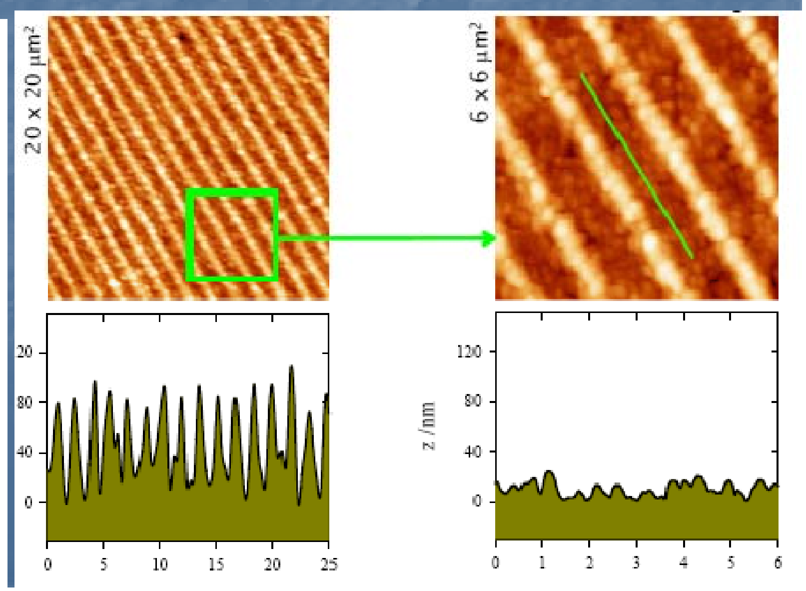
nanostructures

Molding using molecular antiadherent layers (thiols)

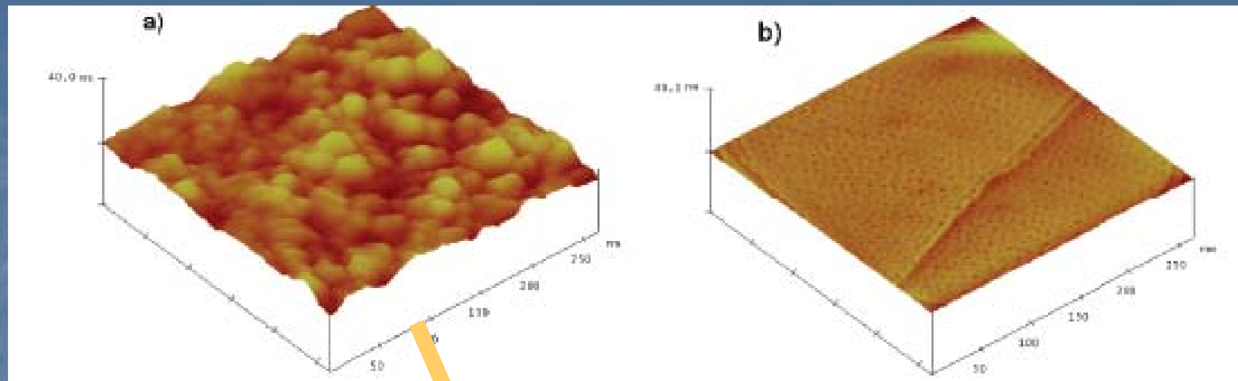
Molded materials: (metals, oxides, alloys)

microstructures

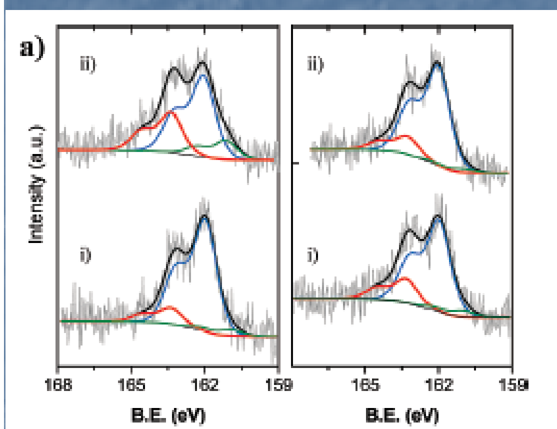




Enhanced Stability of Thiolate Self-Assembled Monolayers (SAMs) on Nanostructured Gold Substrates

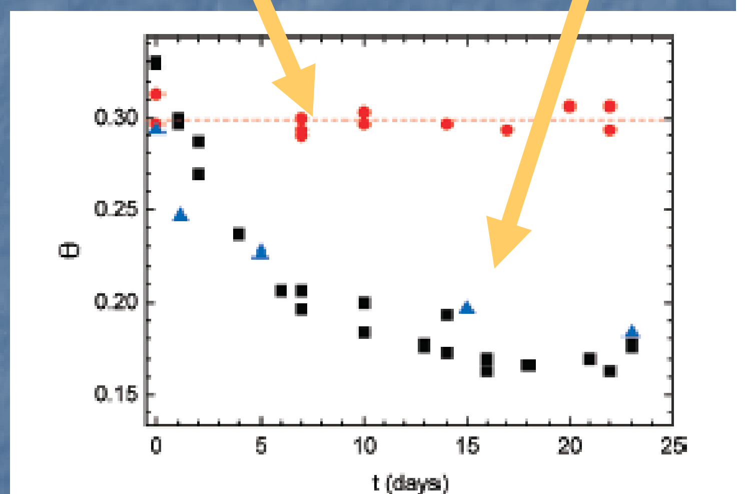


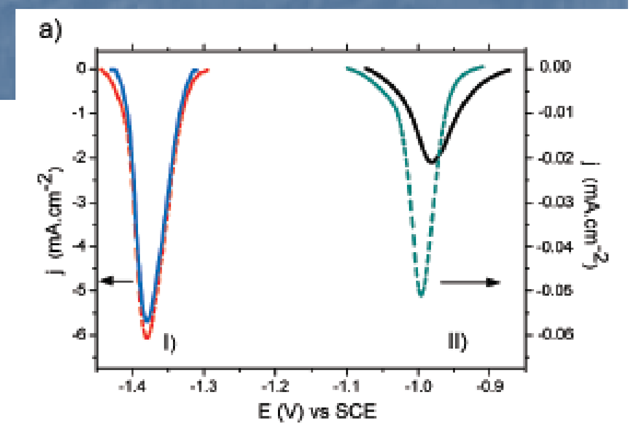
XPS-S2p



Planar rough

Chemical stability



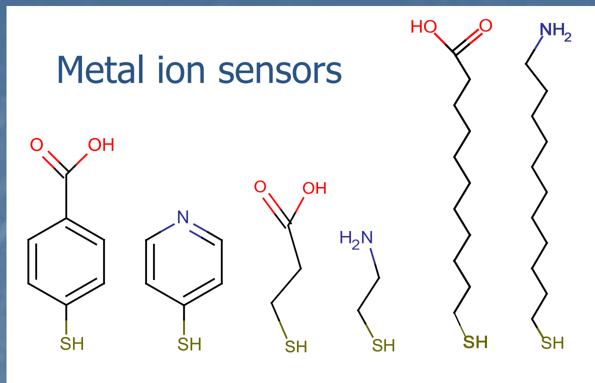


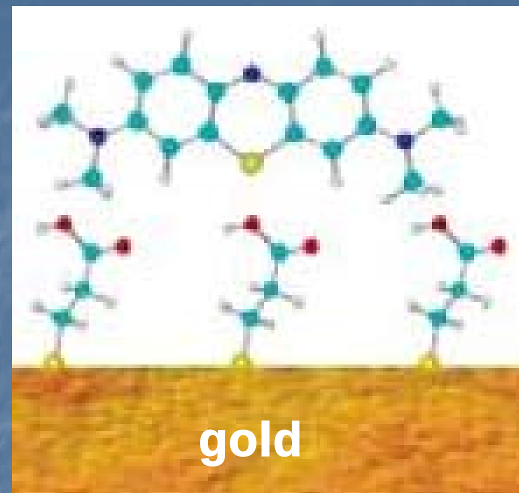
Electrochemical stability

Cortes, Rubert, Benitez, Carro, Vela, Salvarezza

Langmuir 2009, 25 (10), 5661-5666

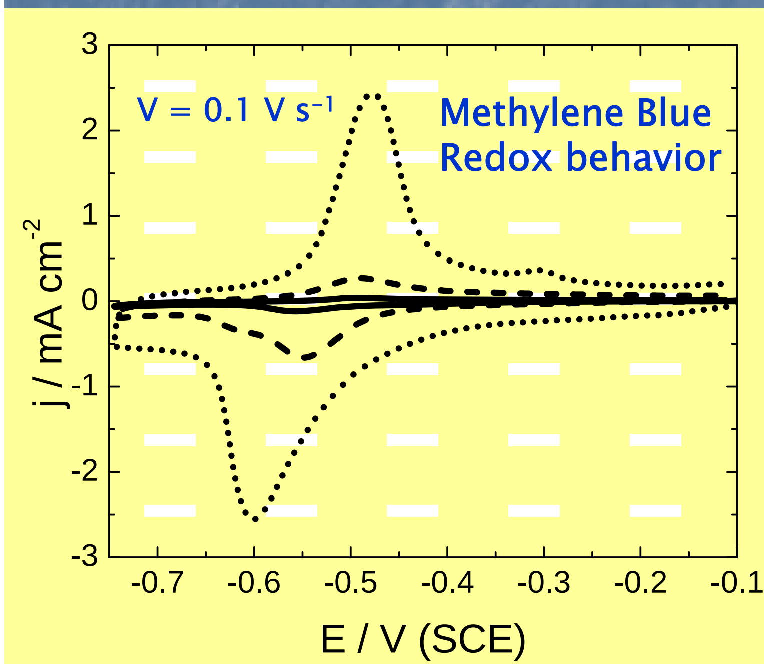
Electrochemical and optical sensors

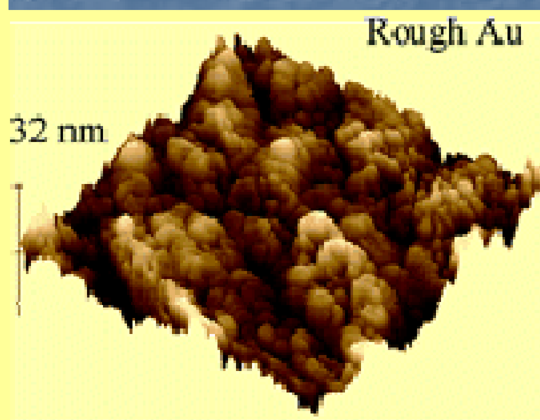


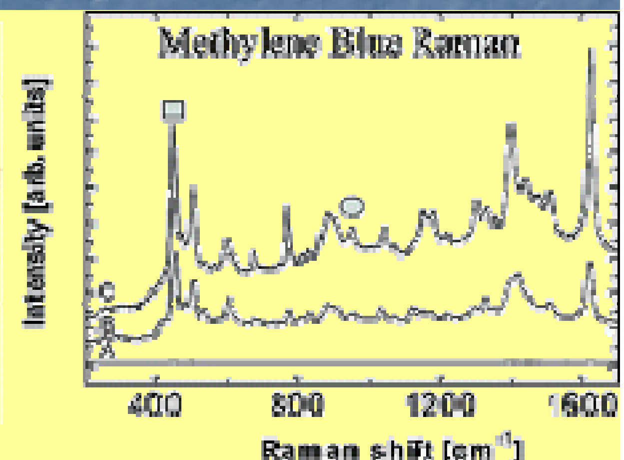


methylene blue

negatively charged thiol





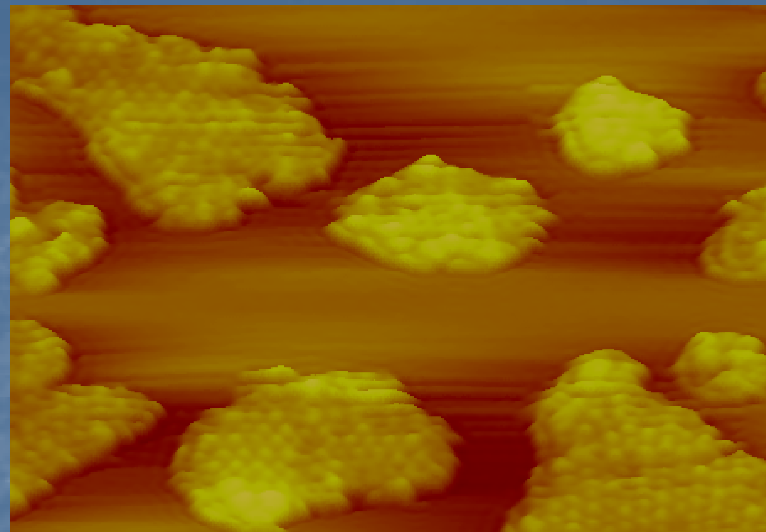


C. Vericat, G. A. Benitez, M. E. Vela, R. C. Salvarezza, N. G. Tognalli, and A. Fainstein

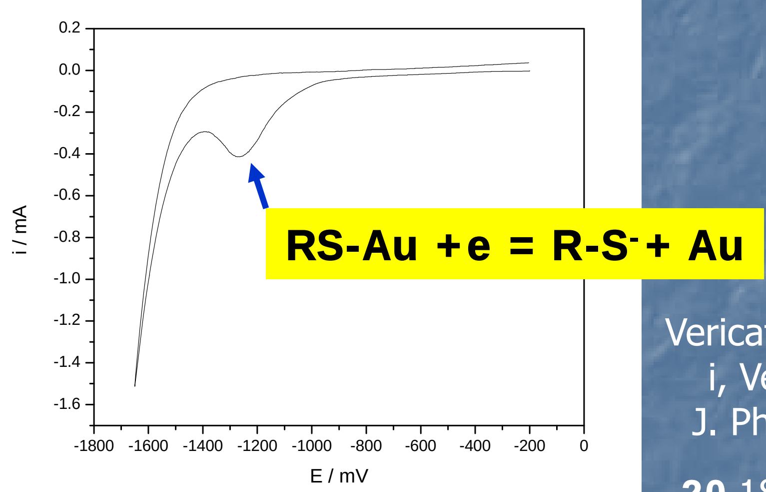
Langmuir **2007**, *23,* 1152-1159

Thiol-capped Au nanoparticles on HOPG

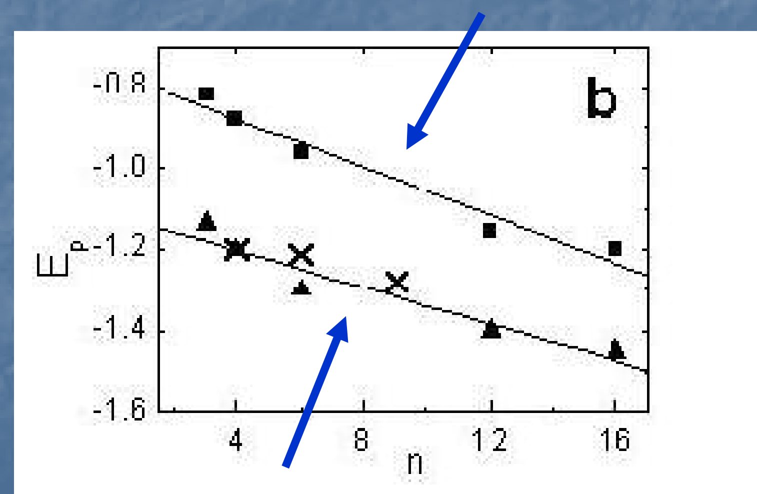
2.7 nm



STM images



planar



Vericat, Benitez, Grumelli, Vela, Salvarezza J. Phys. Cond. Matter **20** 184004 1-8 (2008).

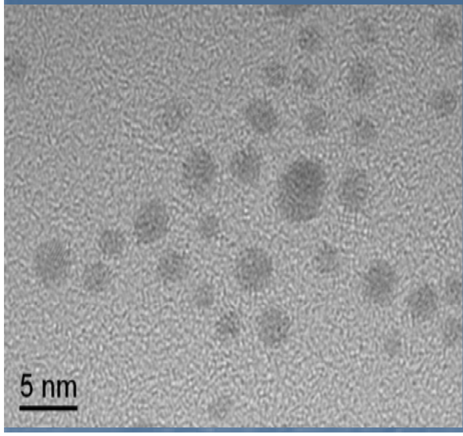
Table 1. Binding Energies (E_b) and Adatom Surface Coverage (θ_{adatom}) for the Different Surface Structures Shown in Figure 5

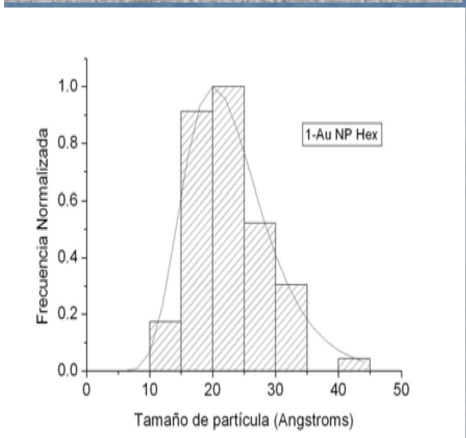
model	a	b	c	d
E_b (eV)	−1.82	−2.05	−2.14	−2.02
θ_{adatom}	0	0.667	0.333	0.333

Rough surfaces and nanoparticles

Modification and delivery of thiol-capped nanoparticles

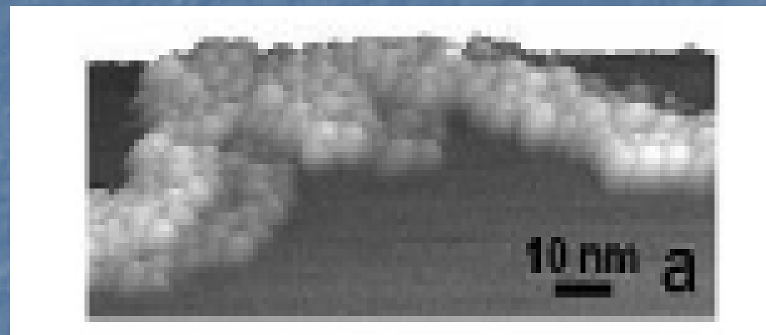
AuNP





TEM

Adsorption on graphite



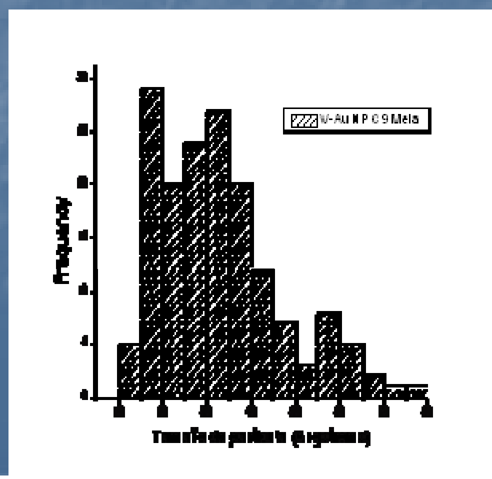
STM

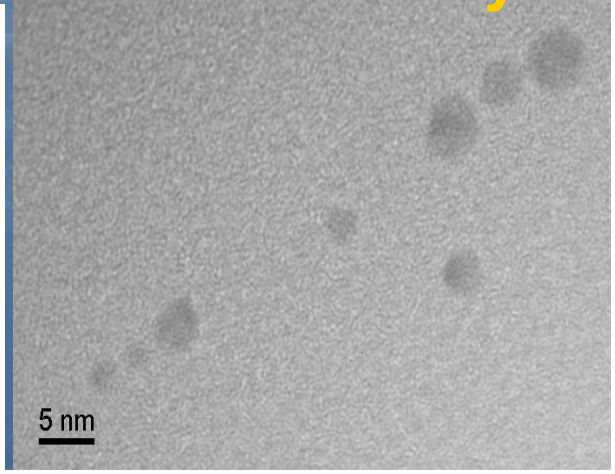
Electro-deposition of iron-melanin

Thiol desorption

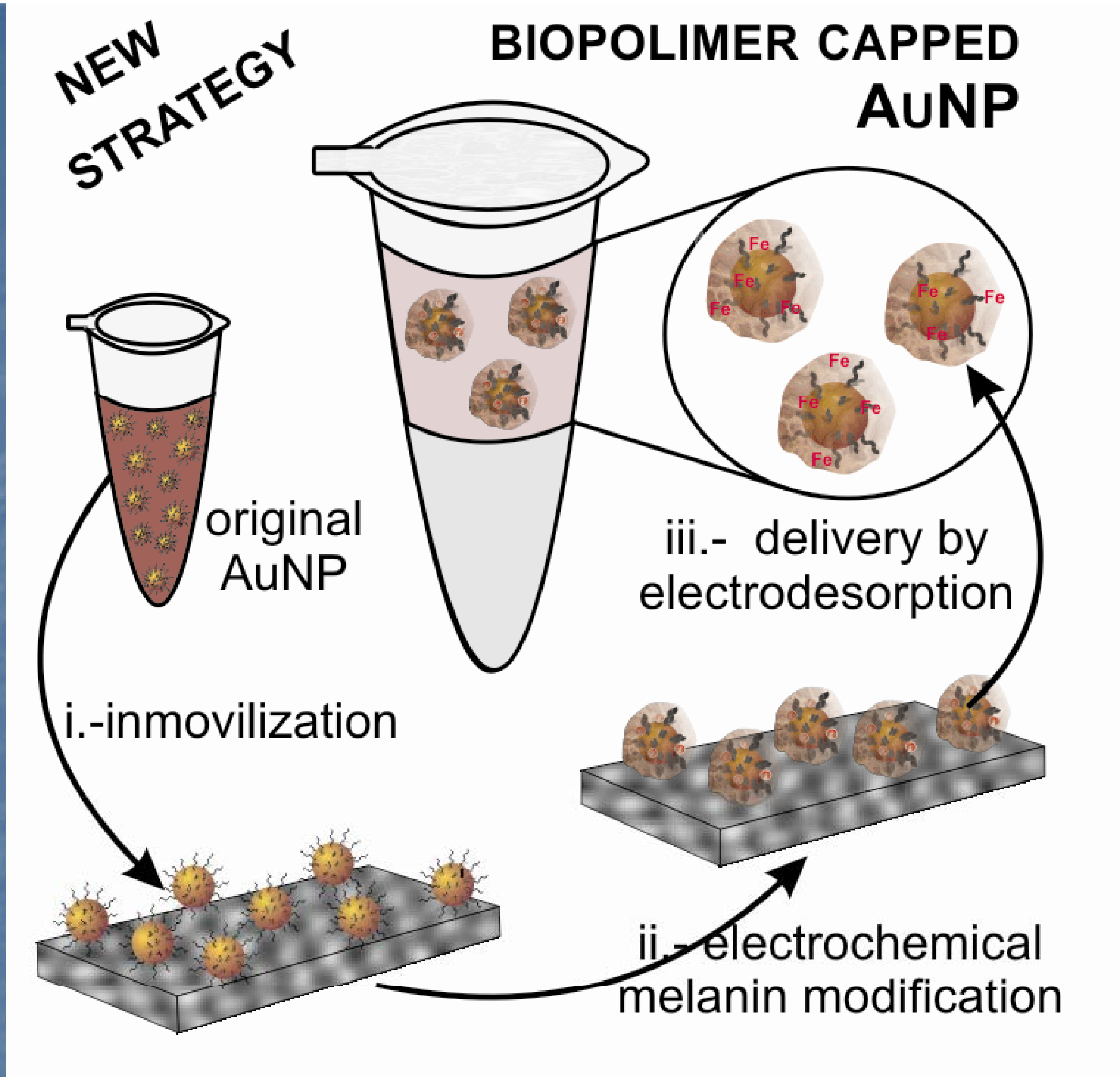
Iron-melanin covered AuNP

Delivery





Melanin biopolymer+
Iron oxide= biocompatible
and magnetic particles



Grumelli, Vericat, Benítez, Ramallo-López, Giovanetti, Requejo, Moreno, González Orive, Hernández Creus, Salvarezza.

CHEMPHYSCHEM 10, 370-373 (2009)

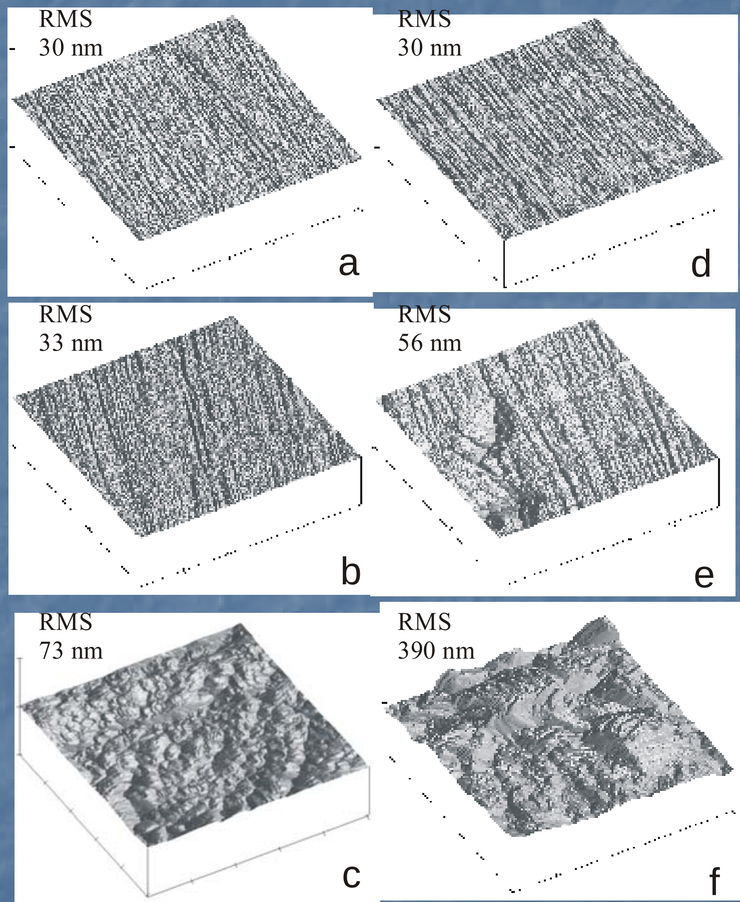
SAMS Applications

Corrosion protection

Cu polished substrate

Thiol-covered Cu

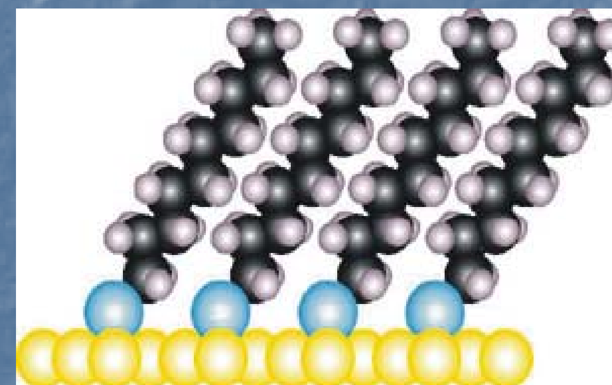
Thiol-free Cu



0.1 M NaCl
4 days immersion

1M Na Cl
4days immersion

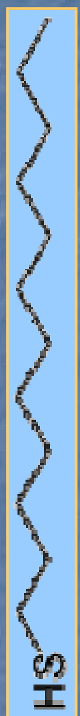
Highly hidrophobic chains



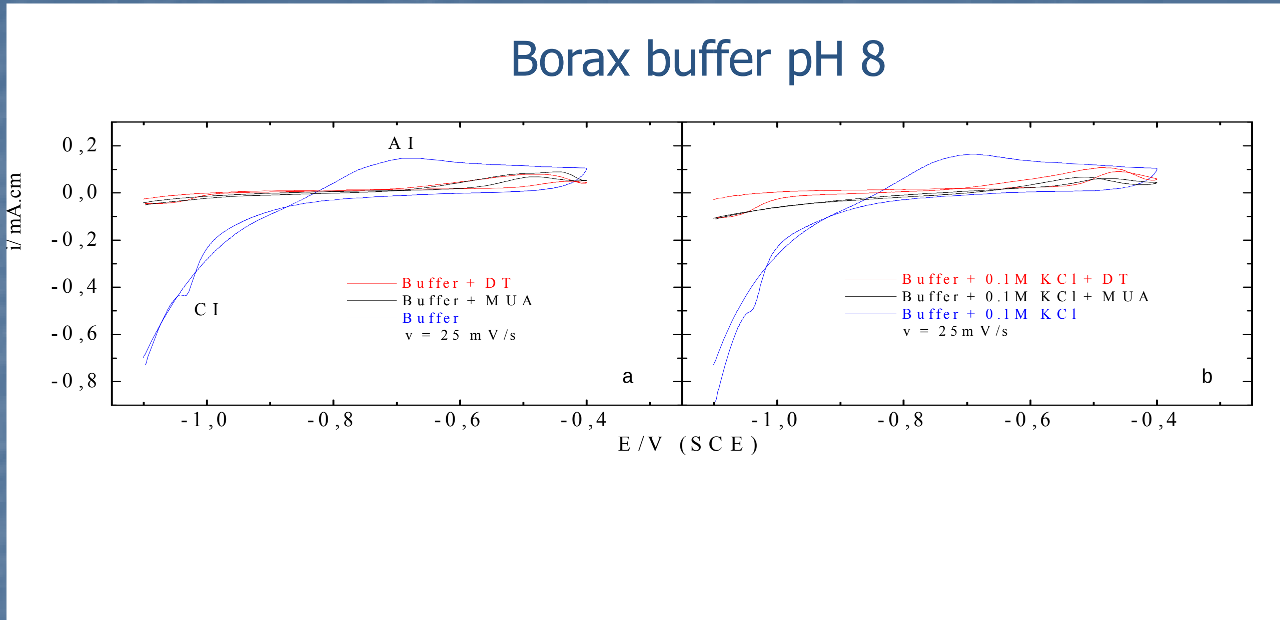
Blocking the transport of water and hydrated species to the metal surface

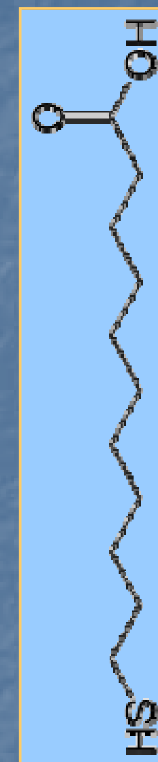
*A. Azzaroni, M. Cipollone, M.E. Vela, R.C. Salvarezza Langmuir, **17**, 2483(2001)*

Protection of dodecanethiol and mercaptoundecanoic acid SAMs to iron and carbon steel against corrosion



DT





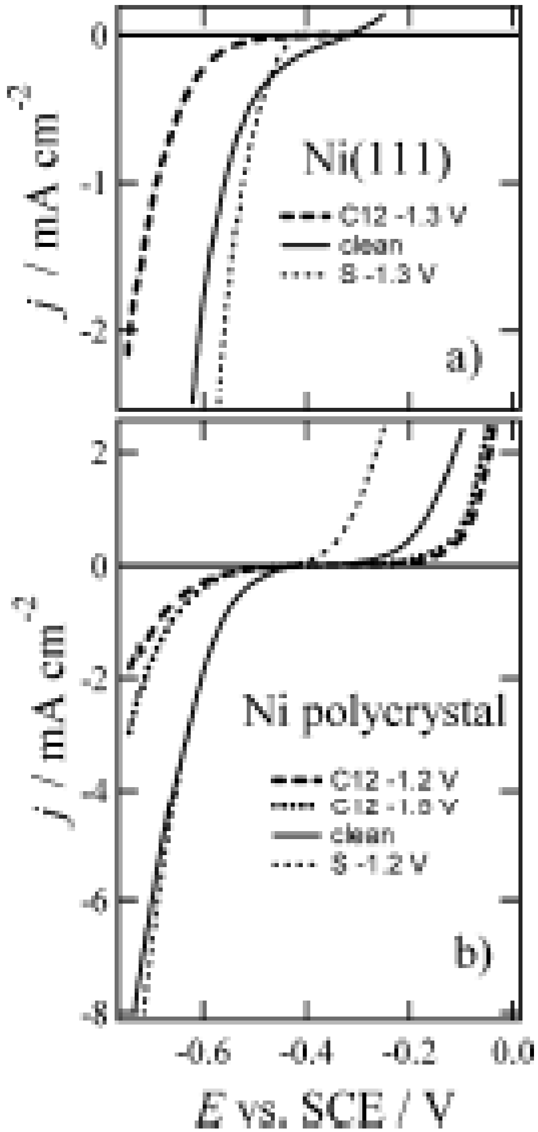
MUA

Inhibition efficiency of the hydrogen evolution reaction by DT and MUA at two cathodic potentials

Inhibition efficiency, I_E	DT	MUA	DT in Cl^-	MUA in Cl^-
E = -1.05 V	96 %	91 %	90 %	76 %
E = -1.0 V	91 %	92 %	81 %	81 %

Weber, Dick, Benítez, Vela, Salvarezza, Electrochimica Acta 54 (2009) 4817–4821

Dodecanethiol SAMs on Ni

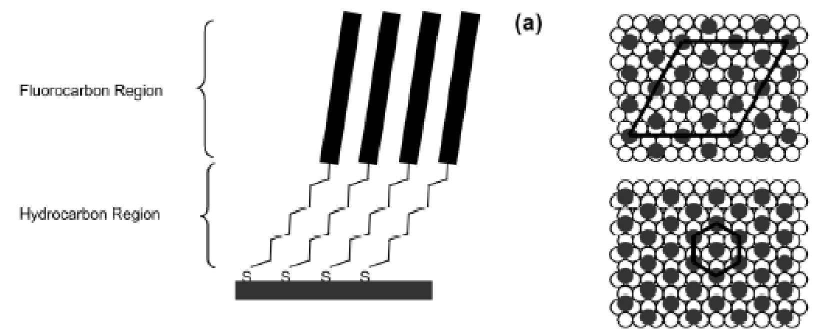


In general: only partial inhibition, risk of pitting

Bengió, Fonticelli, Benítez, Hernández Creus, Carro, Ascolani, Zampieri, Blum, Salvarezza, J. Phys. Chem. B 2005, 109, 23450-23460

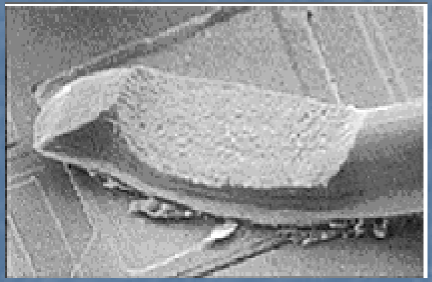
Fluorinated self-assembled monolayers

David Barriet, T. Randall Lee
Current Opinion in Colloid and Interface Science 8 (2003) 236.242



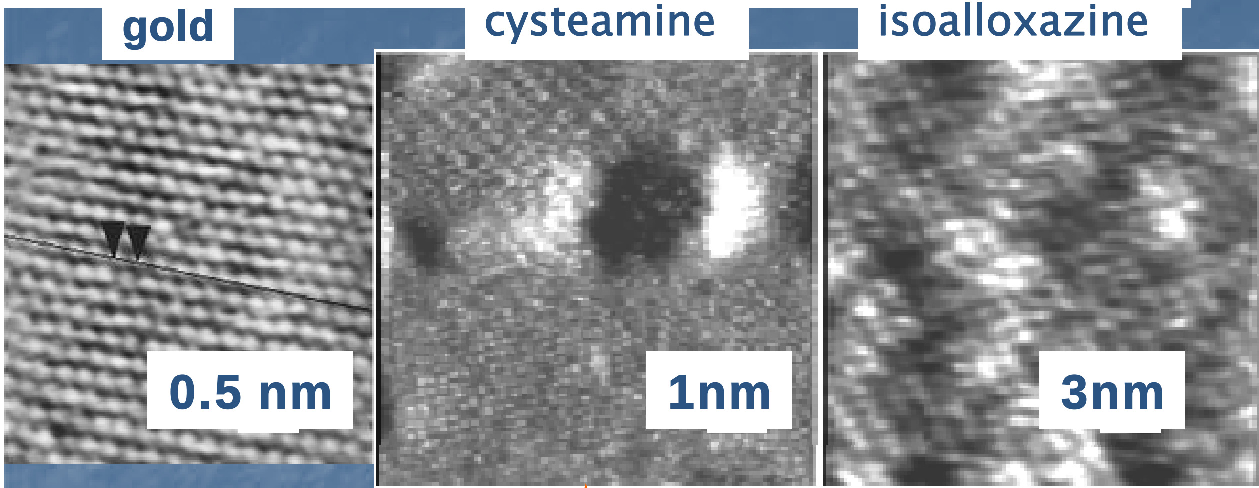
Defects at SAMs: Risk of pitting, their use is limited to atmospheric corrosion

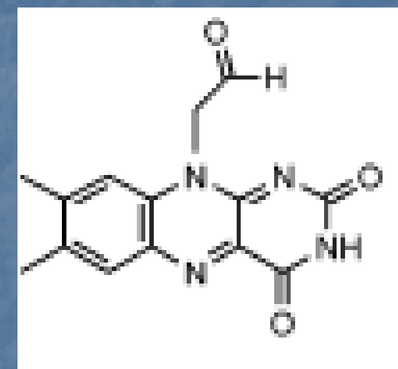
ORGANIC FILMS FOR PROTECTION OF COPPER AND BRONZE AGAINST ACID RAIN CORROSION
G. Brunoro, A. Frignani, A. Colledan, C. Chiavari
Corrosion Science, Vol. 45, pp. 2219-2231 (2003).
INHIBITION OF COPPER CORROSION BY SILANE COATINGS
F. Zucchi, V. Grassi, A. Frignani, G. Trabanelli
Corrosion Science, Vol. 46, pp. 2853-2865 (2004).

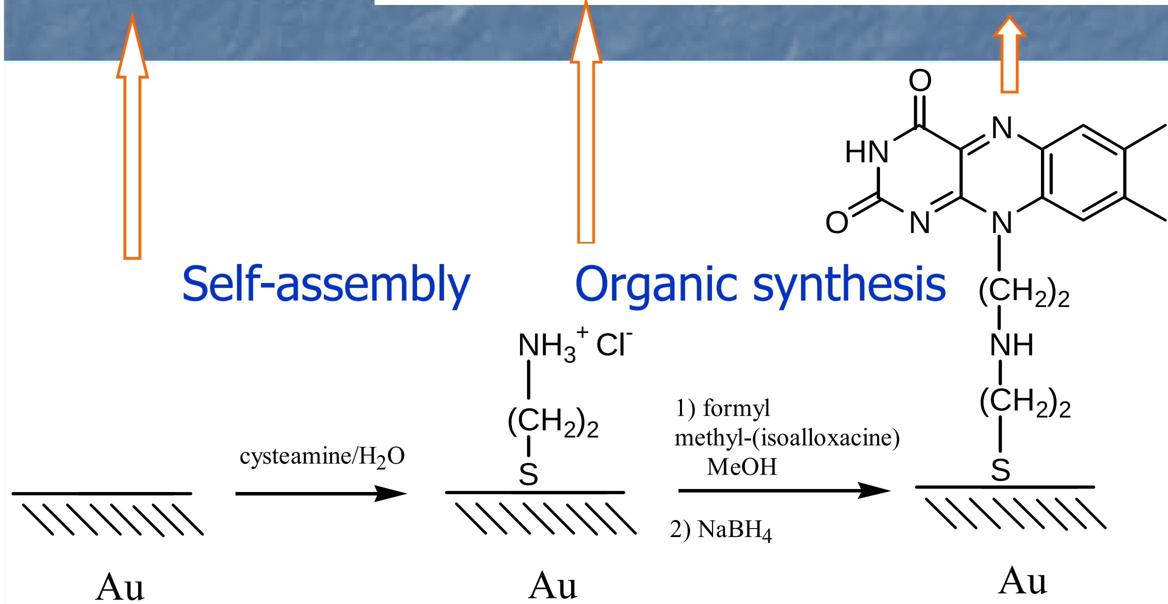


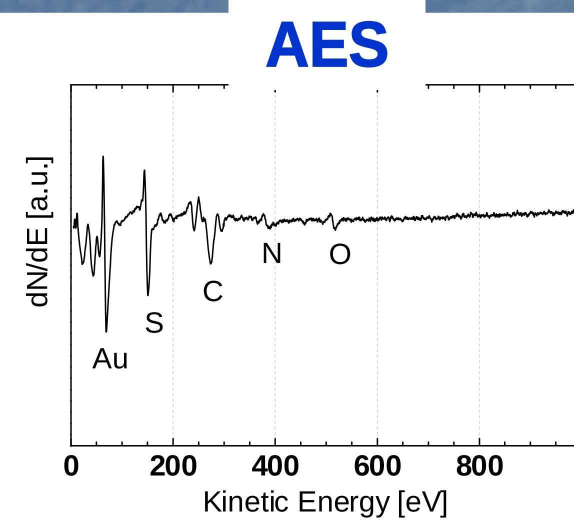
Corrosion Inhibition by Thiol-Derived SAMs for Enhanced Wire Bonding on Cu Surfaces
Caroline M. Whelan Michael Kinsella Hong Meng Ho, Karen Maex
Department of Electrical Engineering, Katholieke Universiteit Leuven, Belgium , JES January 8, 2004)

Biosensors: Covalent binding to functionalized SAMs

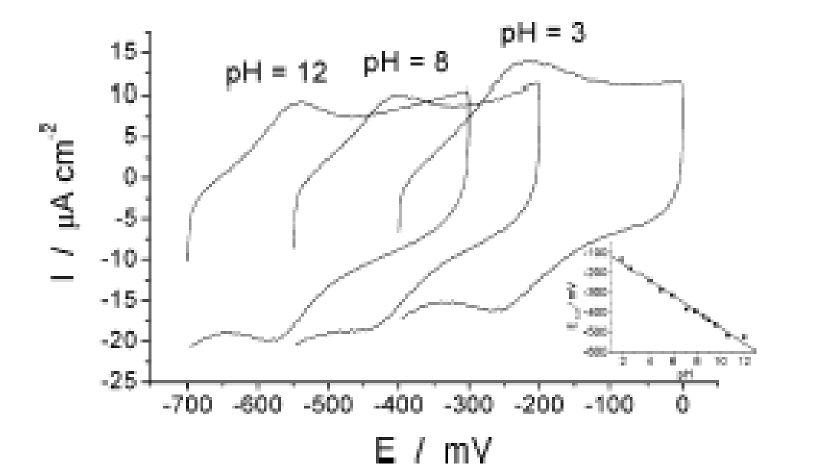






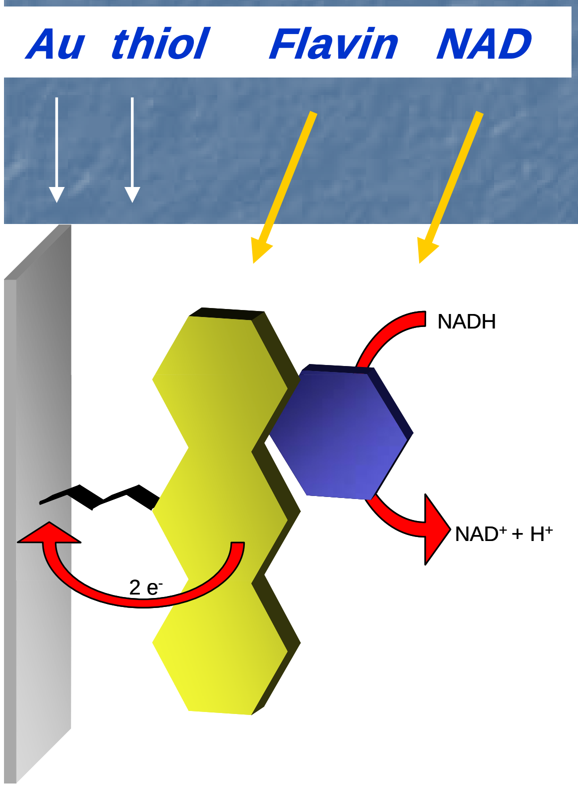


E. J. Calvo, M. Rothacher†, C. Bonnazzola ,j. Wheeldon†, R. Salvarezza , M. E. Vela, G. Benitez, Langmuir 21,7907-7911, 2005



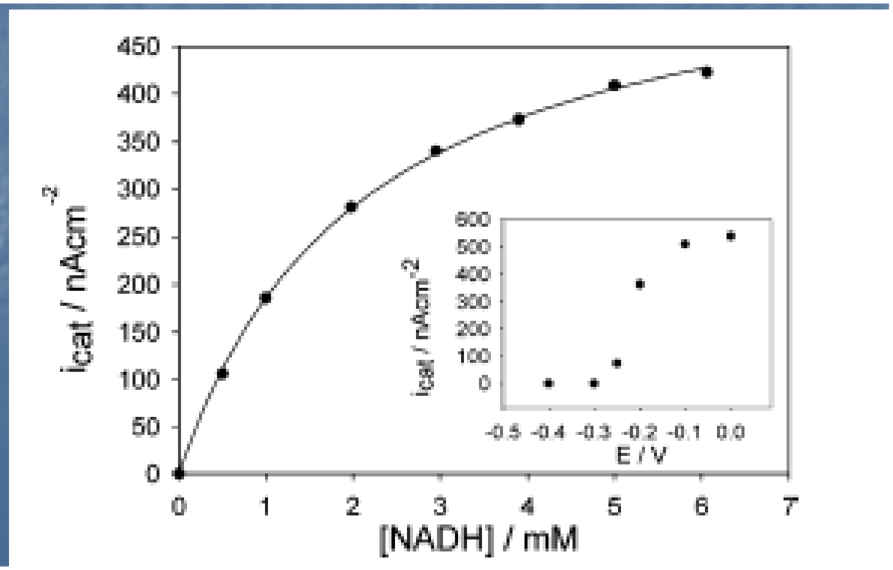
$$Fl_{ox} + 2H^+ + 2e \rightarrow FlH_2$$

Electrochemical activity of the Flavin supported on thiolate-covered gold



NADH oxidation

$$\beta\text{-NADH} + S{-}Fl_{ox} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S{-}Fl_{ox}NADH \xrightarrow{k_2} S{-}Fl_{red} + NAD^+$$



Tethered bimolecular lipid membranes—A novel model membrane platform

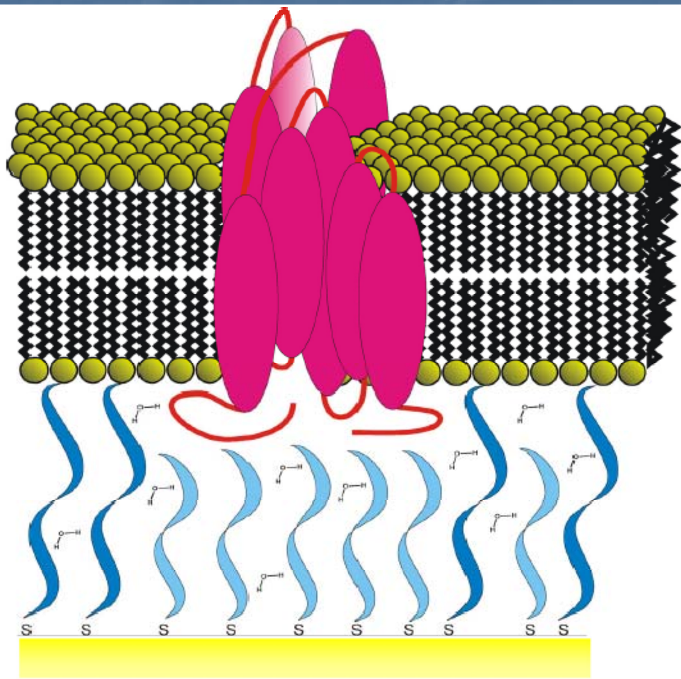
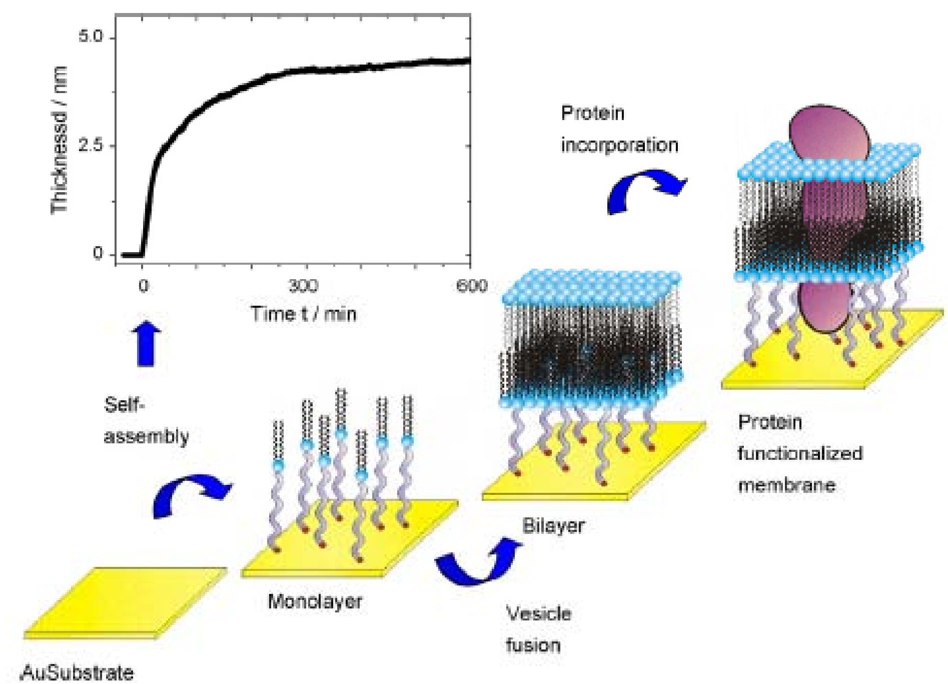


Fig. 1. The tethered bimolecular lipid membrane (tBLM) architecture.

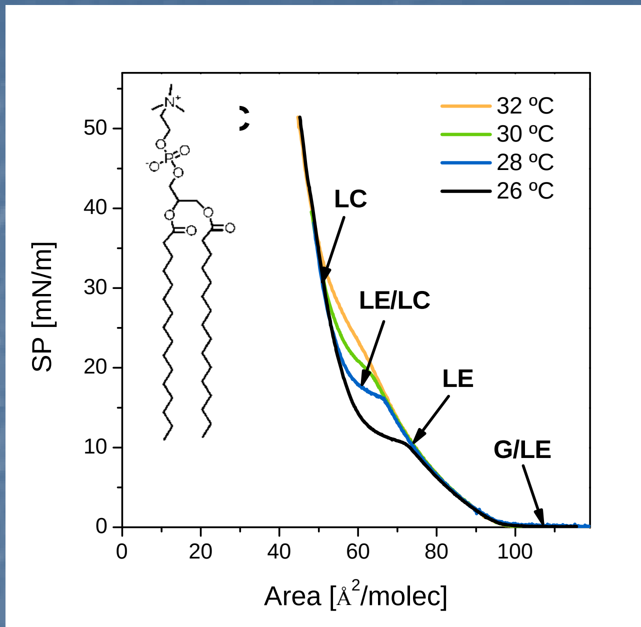
The chemical variety of the anchor group has been extended recently from thiol- or disulphide groups designed for the covalent binding of the tether lipids to Au substrates to silane-based chemistry for reaction with the silanol groups of glass substrates or the non-metallized SiO2-gate electrodes of transistors, and to phosphonate chemistry for alumina surfaces

W. Knoll et al. / Electrochimica Acta 53 (2008) 6680–6689

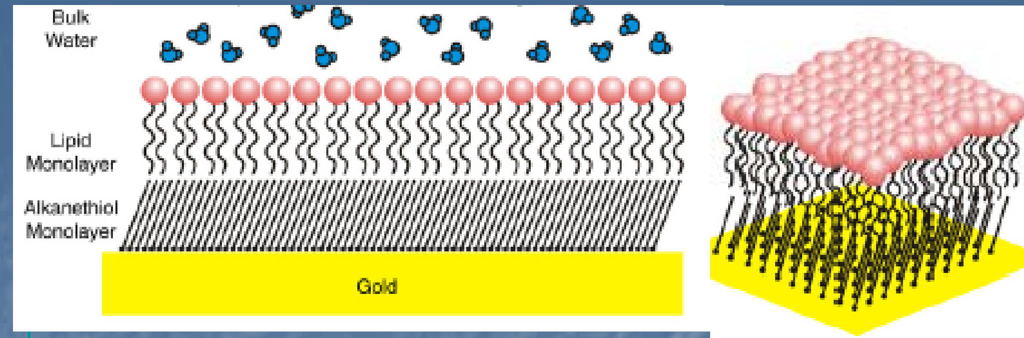


Wolfgang Knoll et al
Electrochimica Acta
53 (2008) 6680–6689

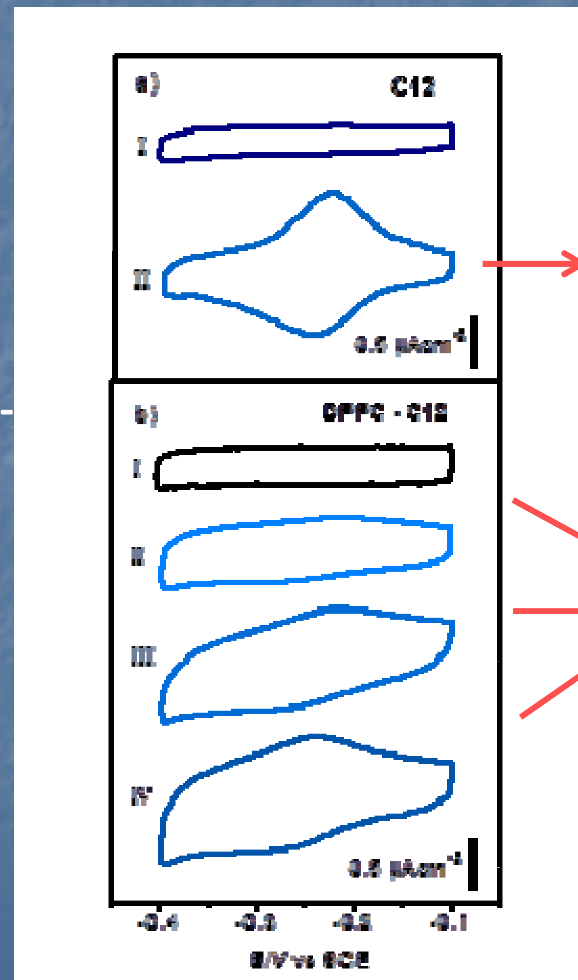
Biomimetic systems: Hibrid membranes



P sup vs molecular Area at different T



C12



MB

DPPC-C12

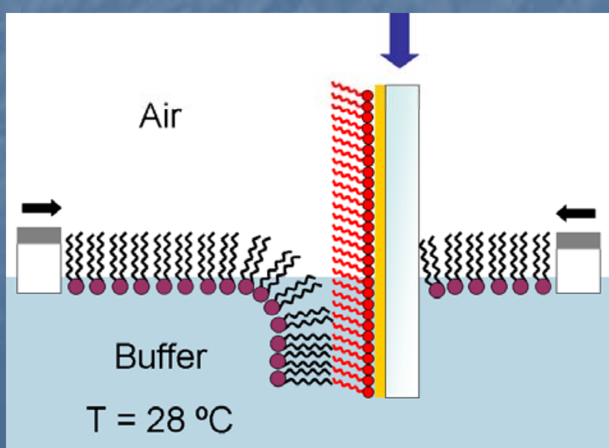
LC

LE/LC

LE

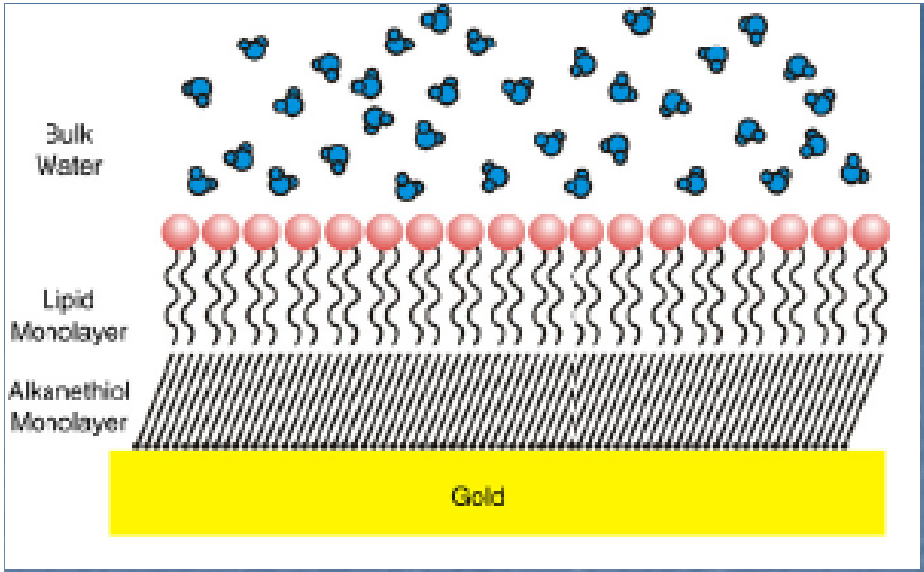
MB

B. Maggio et al CIQUIBIC



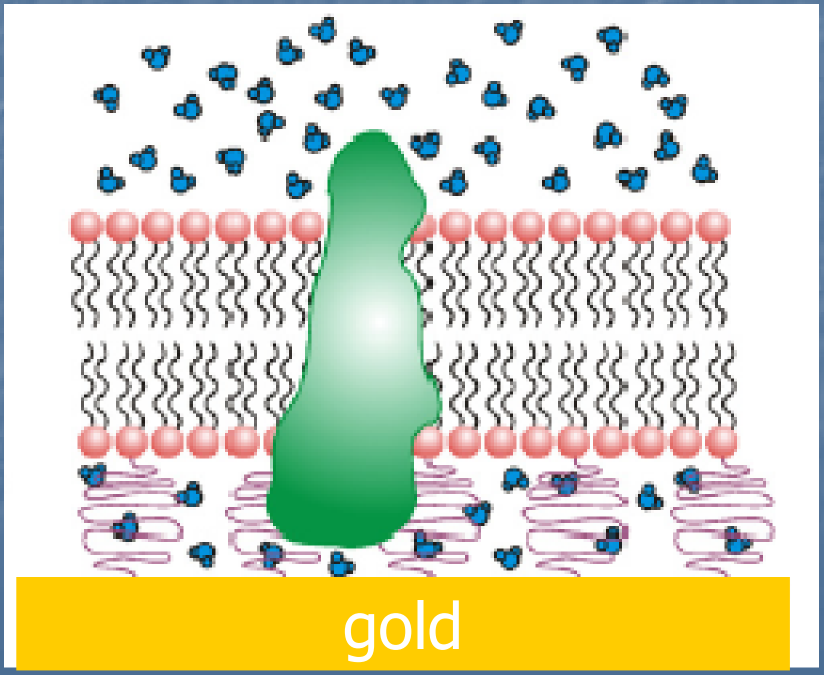
Lipid transfer to C12-Au

dipalmitoylphosphatidylcholine

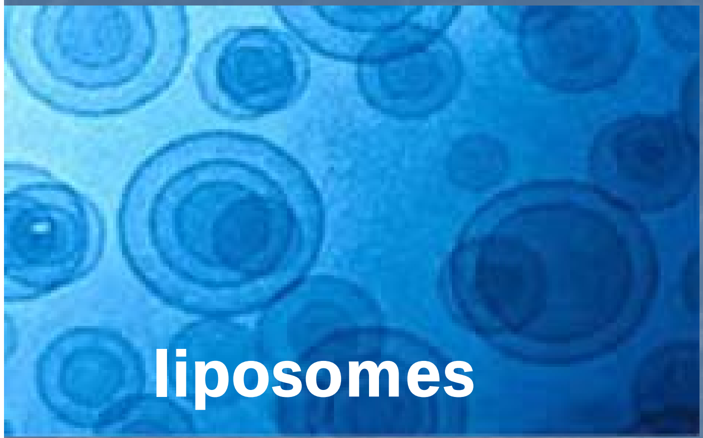


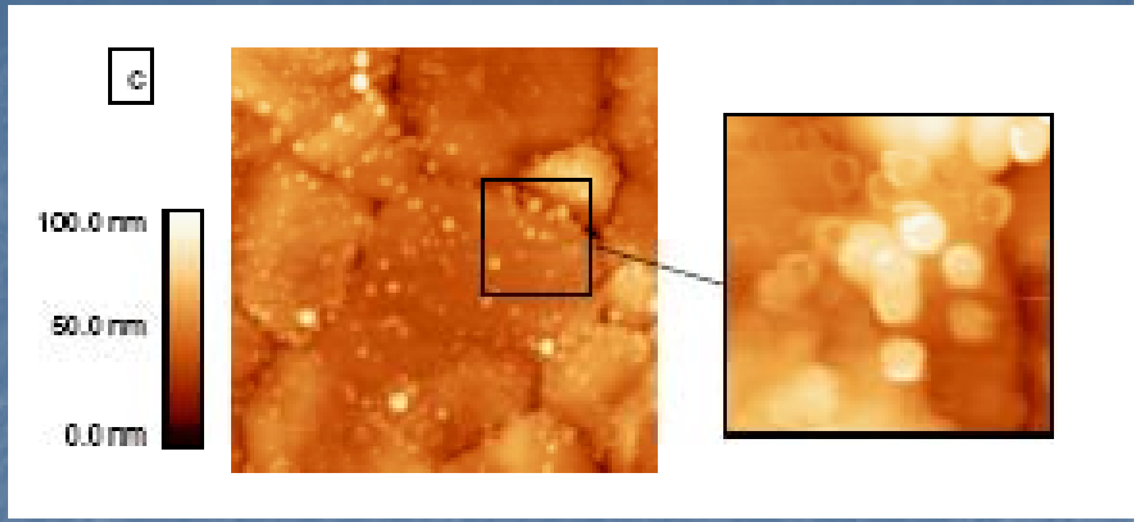
Hibrid Phospholipid Bilayers

Phospholipid Bilayers

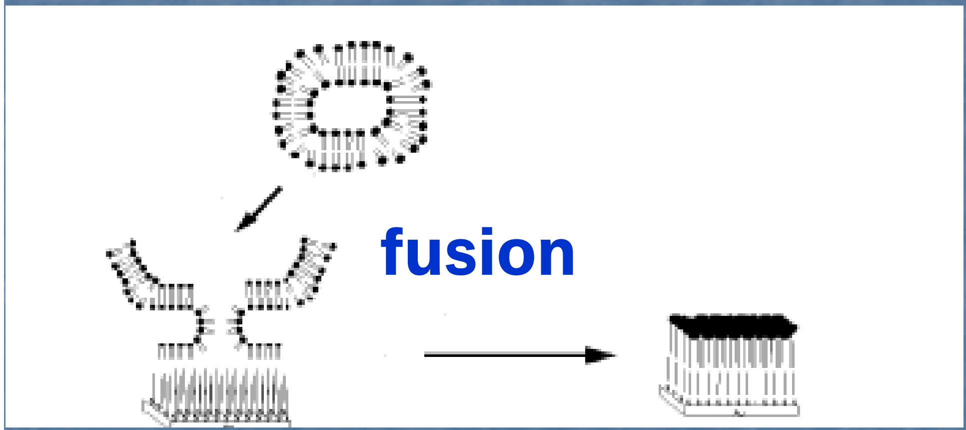


PHOSPHOLIPID BILAYERS



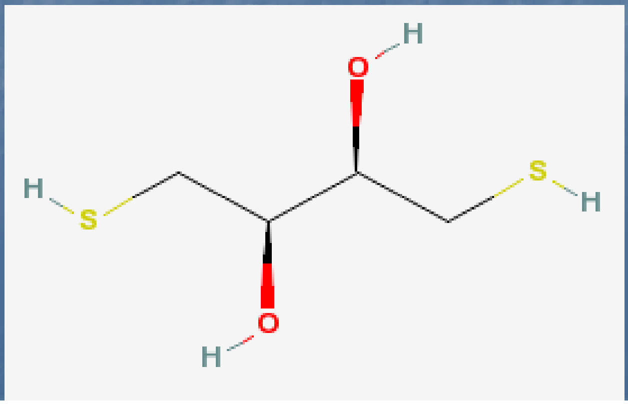


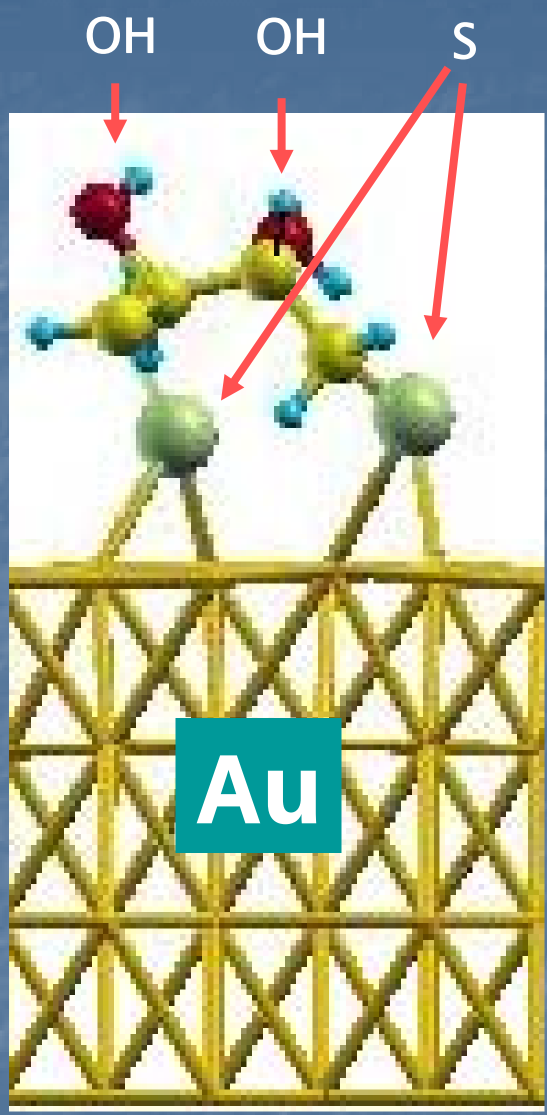
Liposomes on Au



Hydroxylated Au surfaces

Dithiothreitol



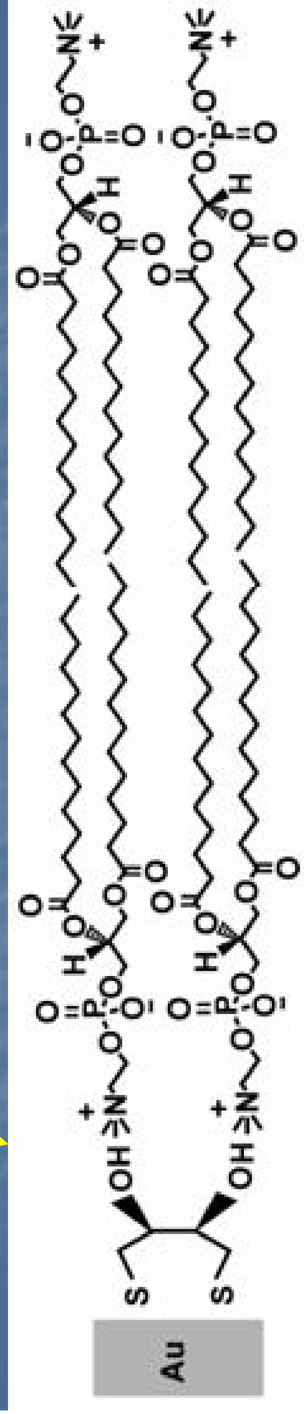


Why hydrophilic surfaces ??

because they promote liposome and vesicle fusion

system bilayer

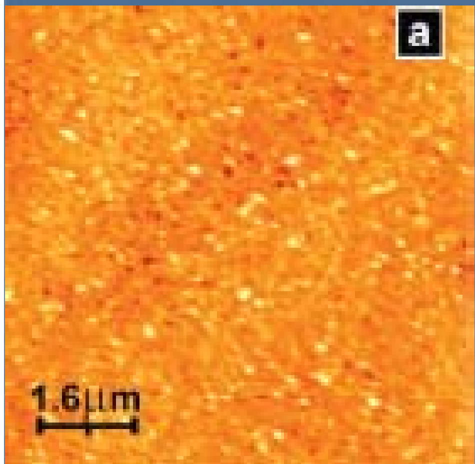
Dithiothreitol on Au

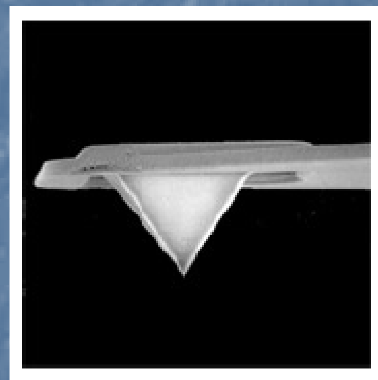


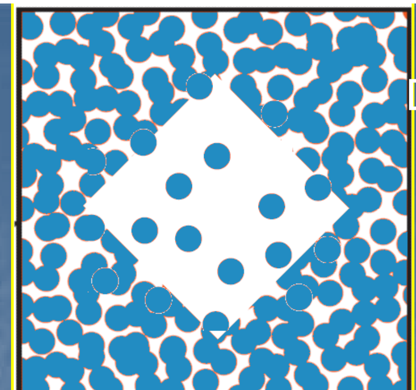
Optimizacion por DFT

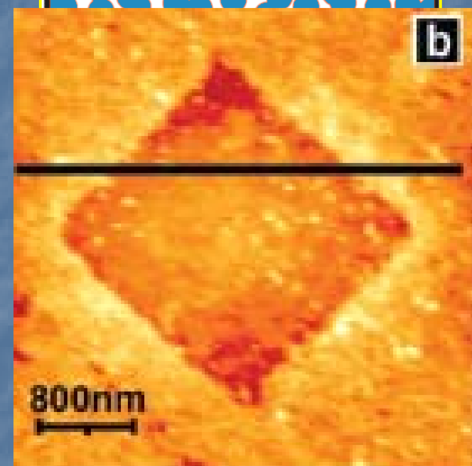
T B. Creczynski-Pasa, M A Daza Millone, M L. Munford, V R. de Lima, T O. Vieira, G. A. Benitez, A. Pasa, R C. Salvarezza, M E Vela, PCCP , in press

AFM in liquids

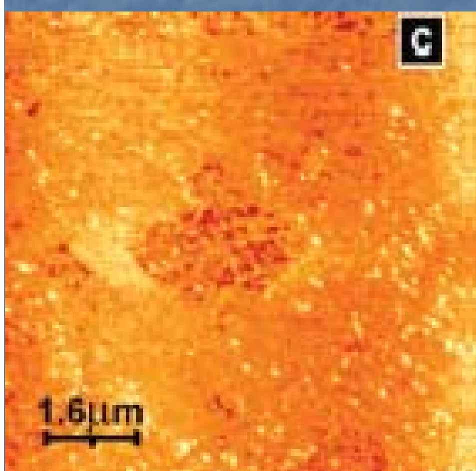


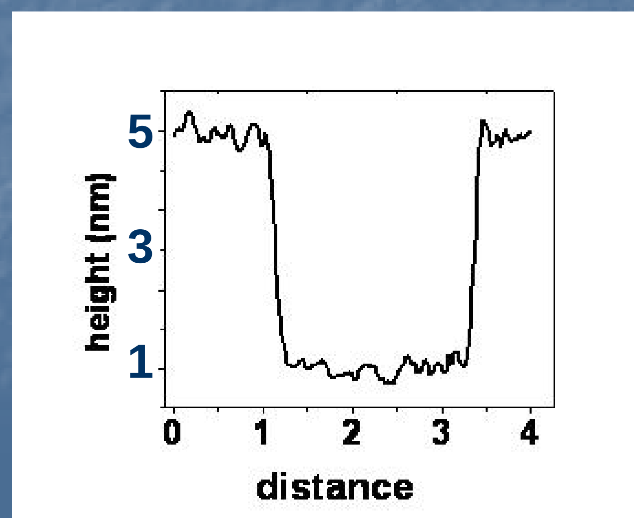




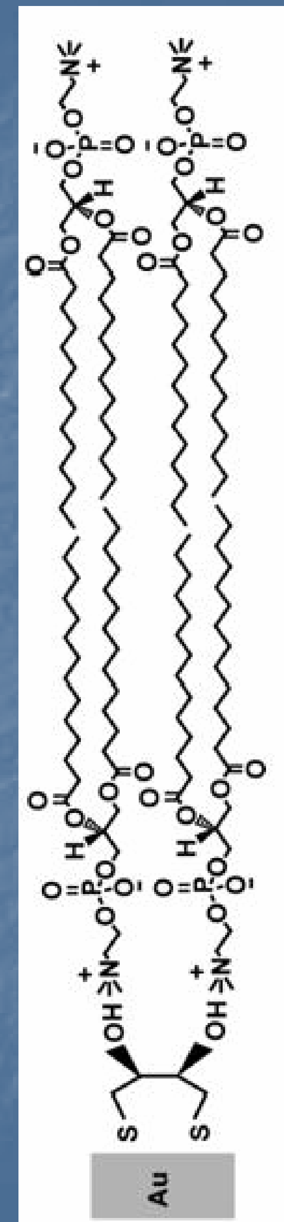


Self-healing

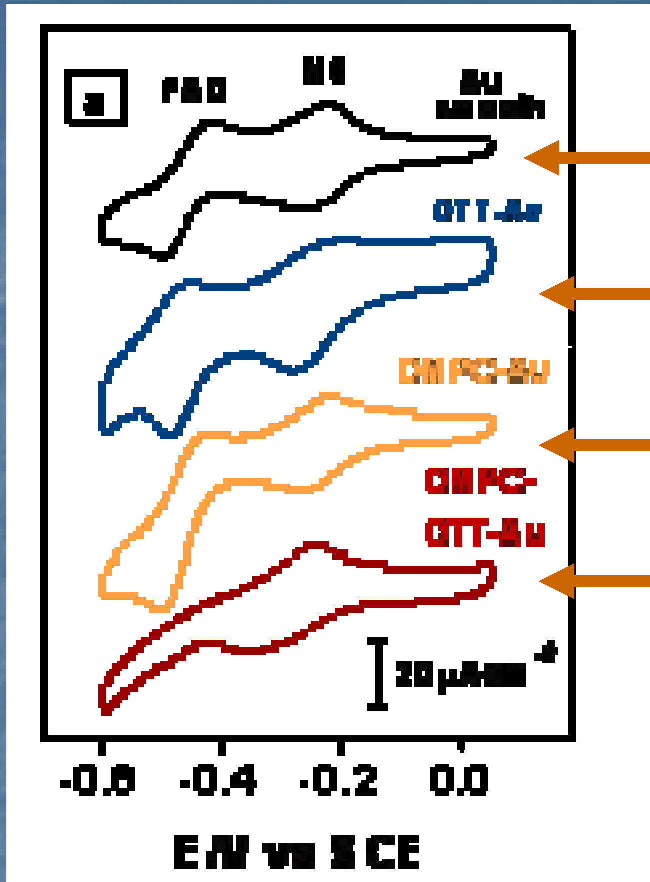




Dimyristoylphosphatidylcholine



Electrochemical sensing of molecules : FAD-MB mixtures



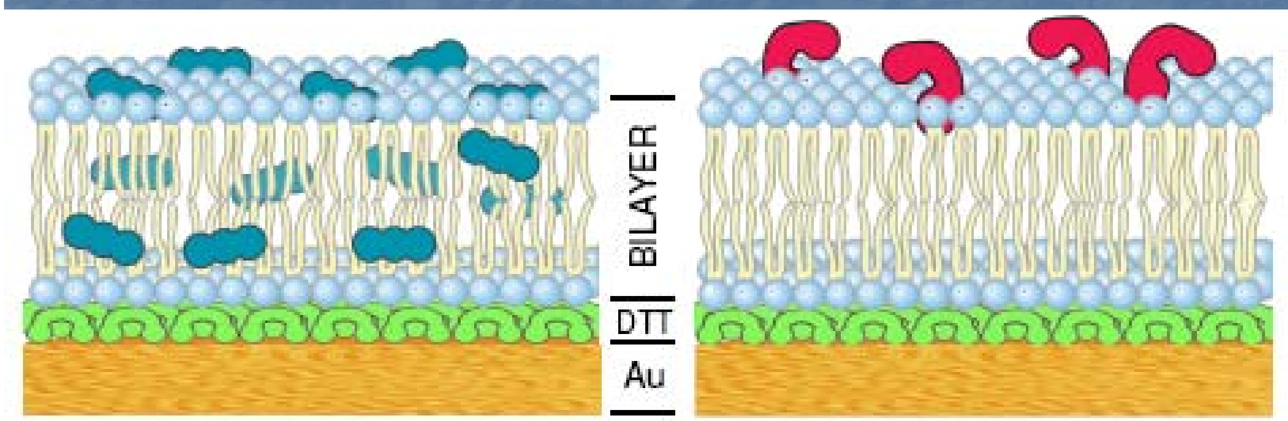
Au

Dithiothreitol (DTT) on Au

DMPC on Au

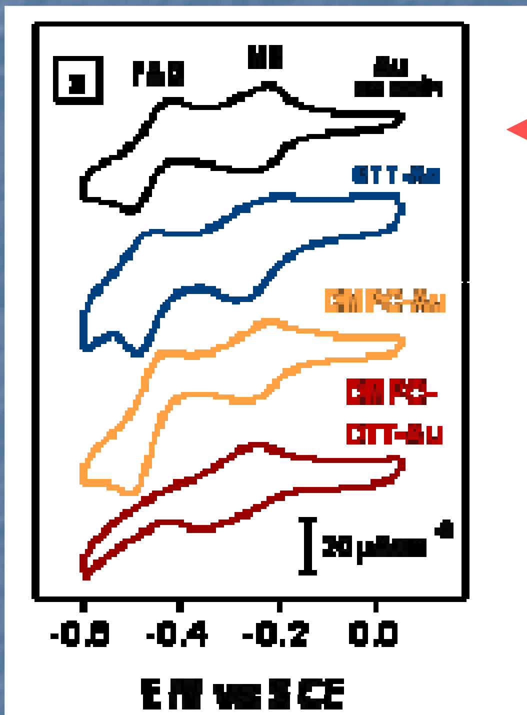
Dimyristoylphosphatidylcholine (DMPC) on DTT-Au

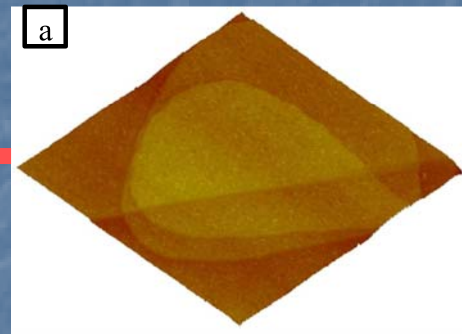
5×10^{-6} M MB + 10^{-5} M FAD in 0.1M phosphate buffer pH = 7.4

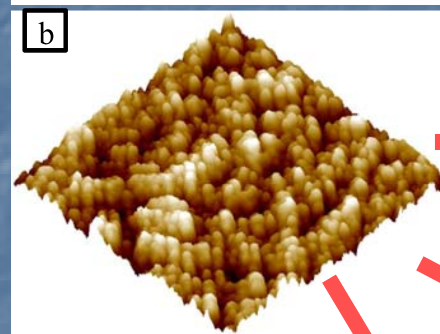


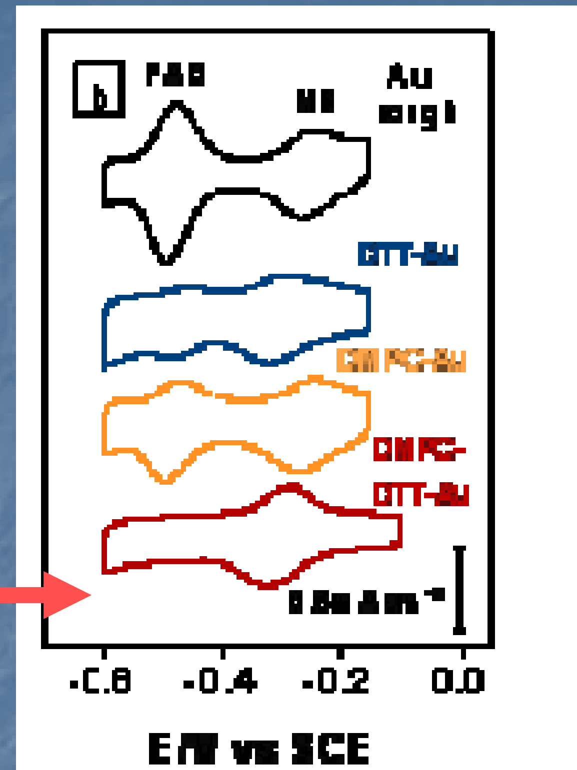
Creczynski-Pasa, Daza Millone, de Lima, Vieira, Benitez, Pasa, Salvarezza, Vela
***Phys. Chem. Chem. Phys.*, 2009, 11, 1077 - 1084**

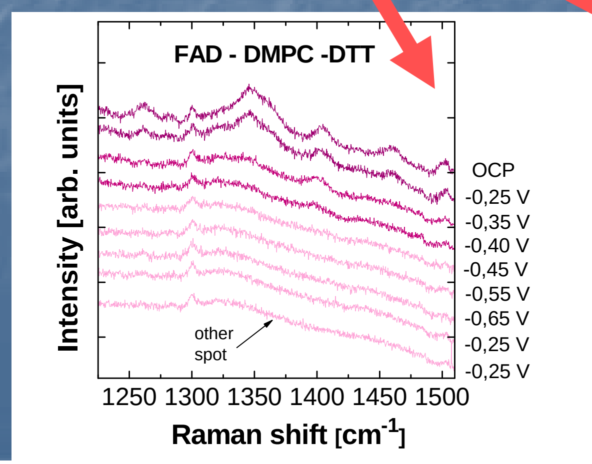
Phospholipid covered Nanostructured Au for optical and electrochemical sensing of molecules : FAD-MB mixtures

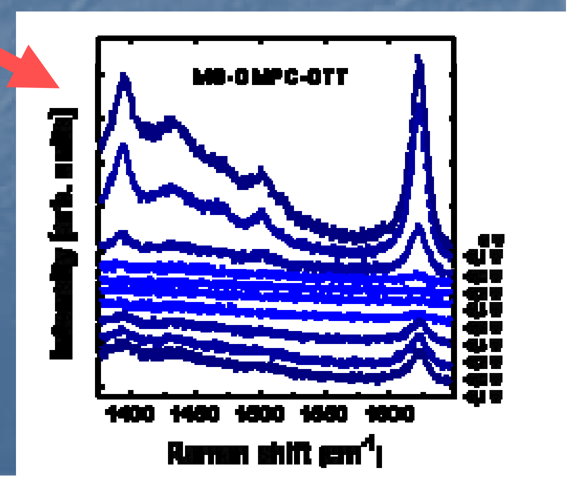








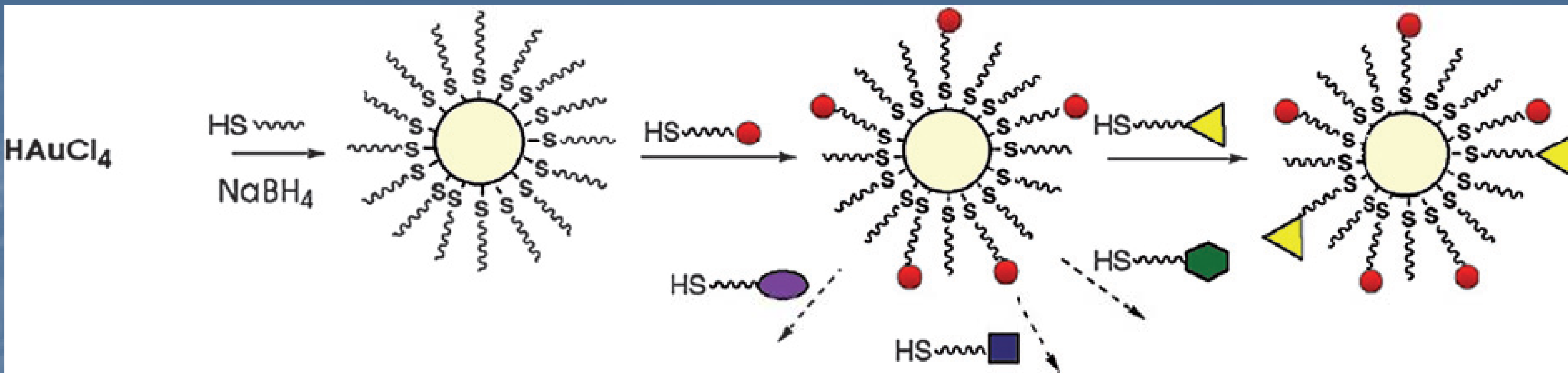


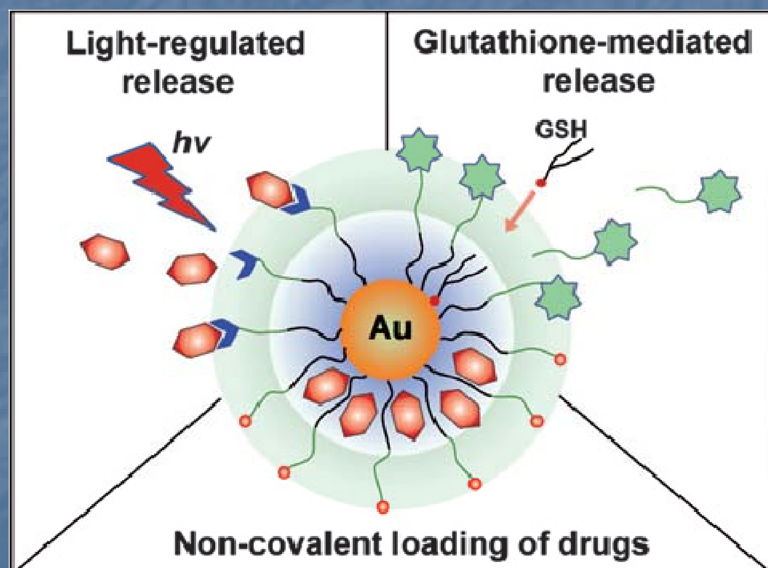


Daza Millone, Vela, Salvarezza,
Creczynski-Pasa,Tognalli, Fainstein

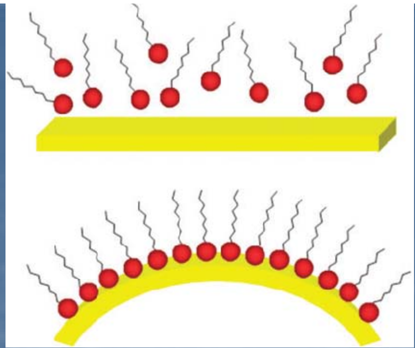
CHEMPHYSCHEM

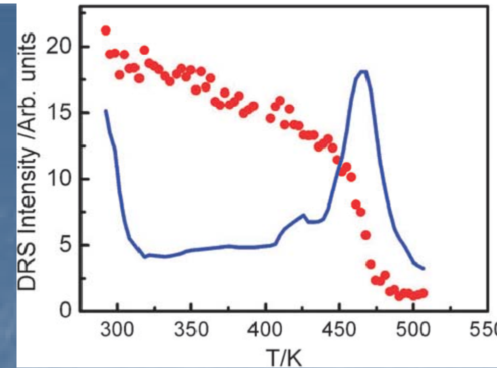
10, 1927-1933 (2009)

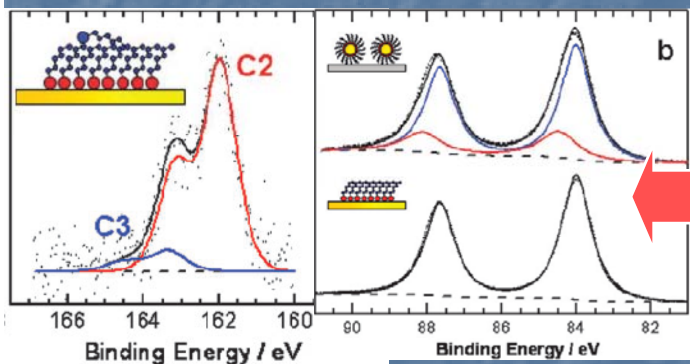

HAuCl$_4$
HS
NaBH$_4$
S
HS
HS
HS
HS
HS

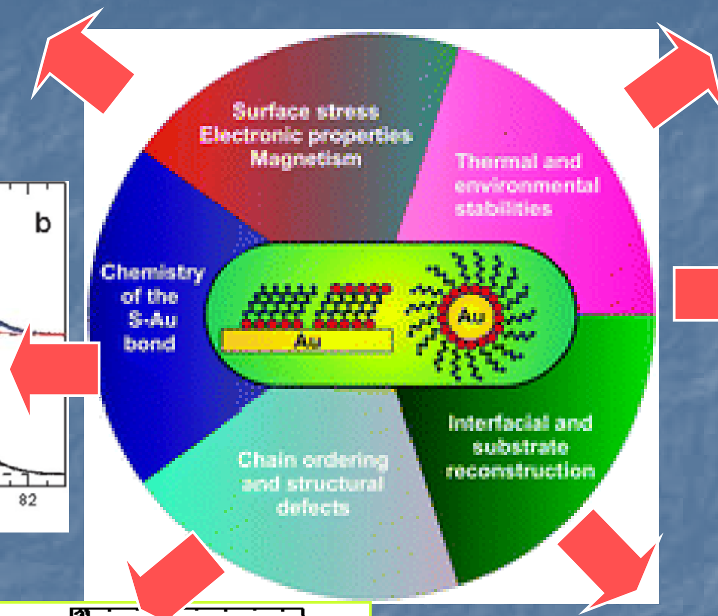

Light-regulated release
Glutathione-mediated release
hv
GSH
Au
Non-covalent loading of drugs

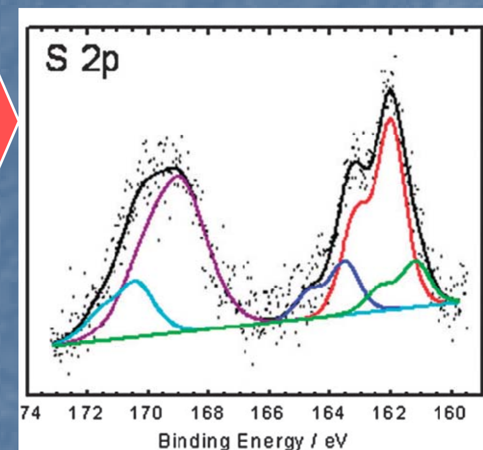
challenges

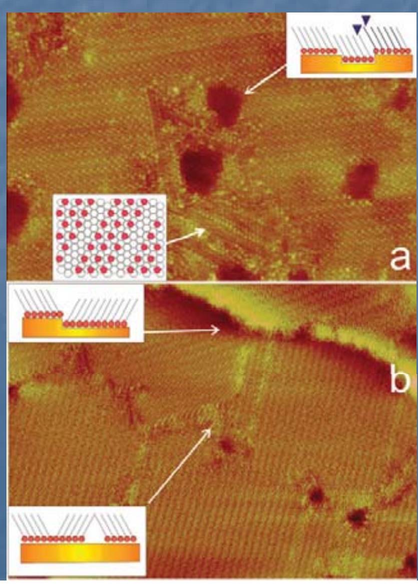


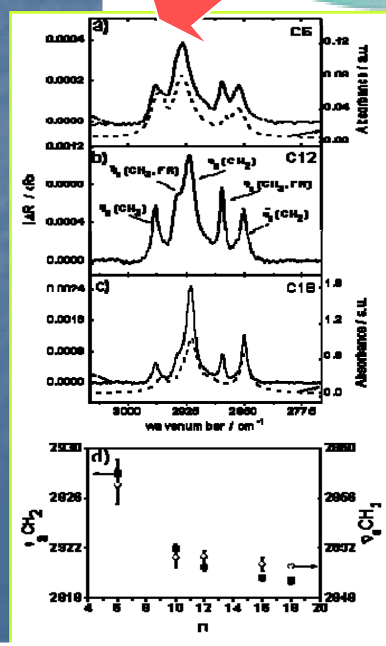


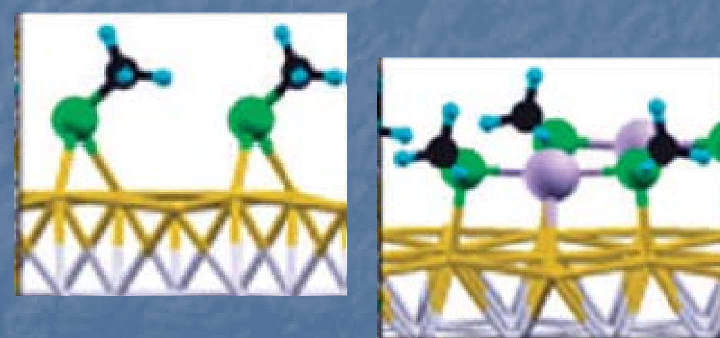






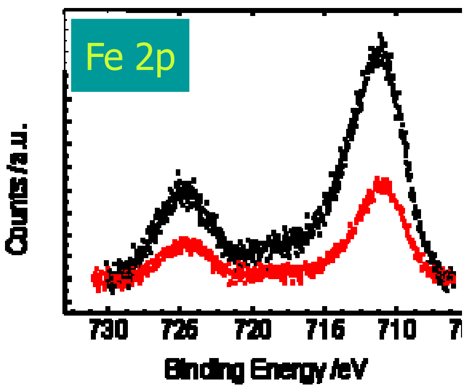


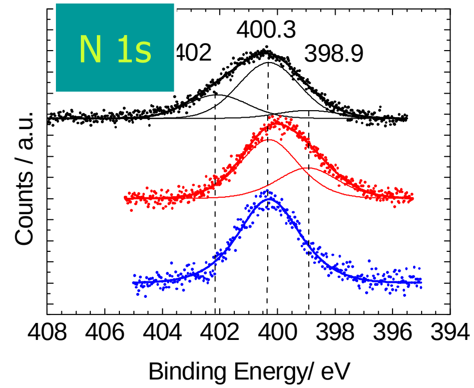


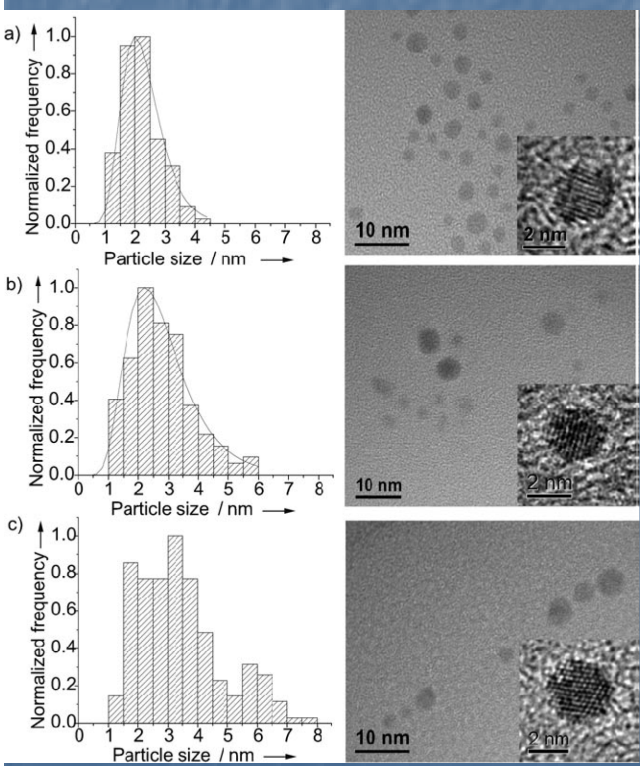


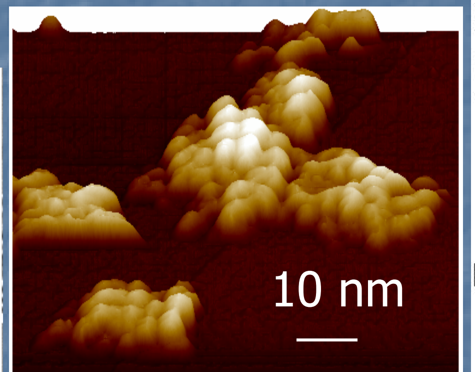
Vericat, Vela, Benitez, Carro, Salvarezza
Chemical Society Reviews, 2010, **39**, 1805-1834

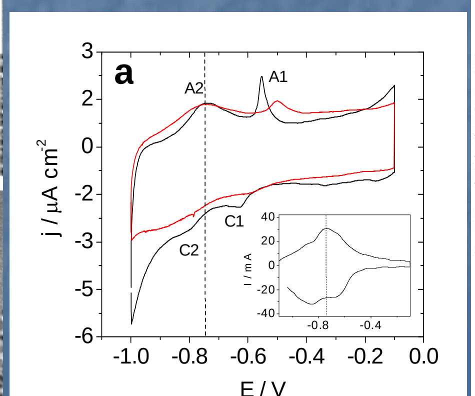
Melanin-iron modified Au Nanoparticles on HOPG

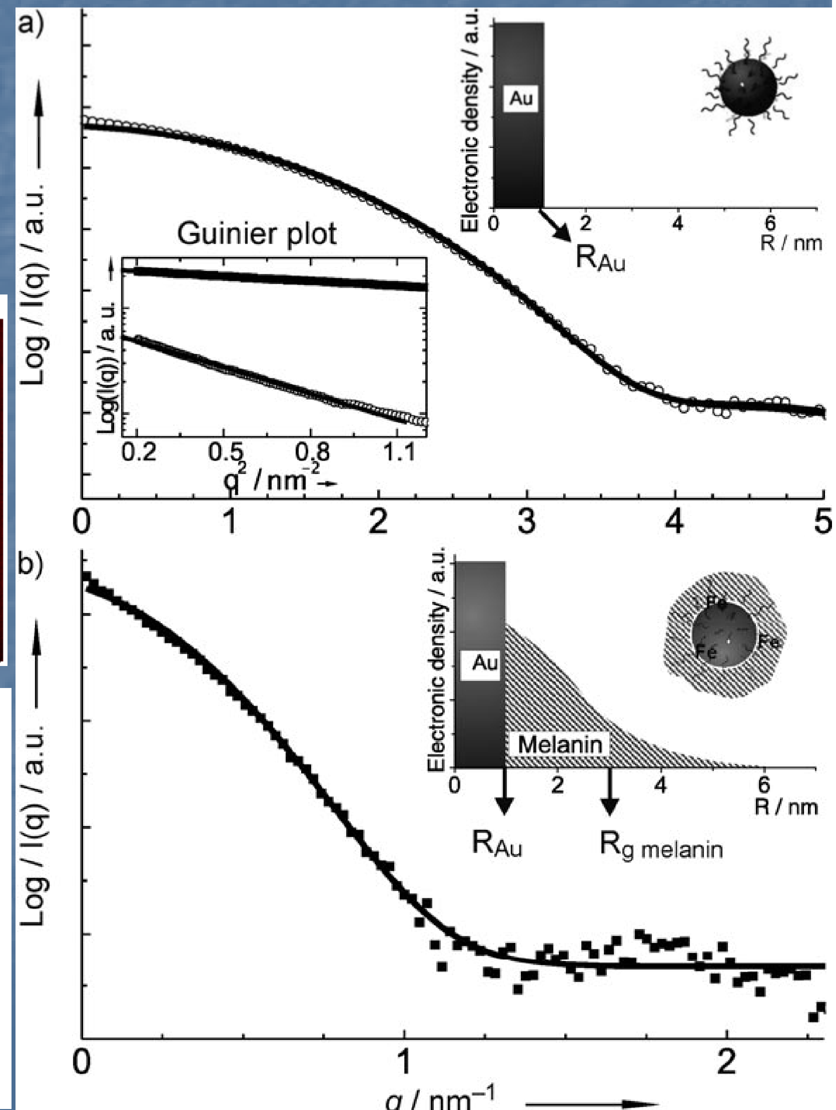




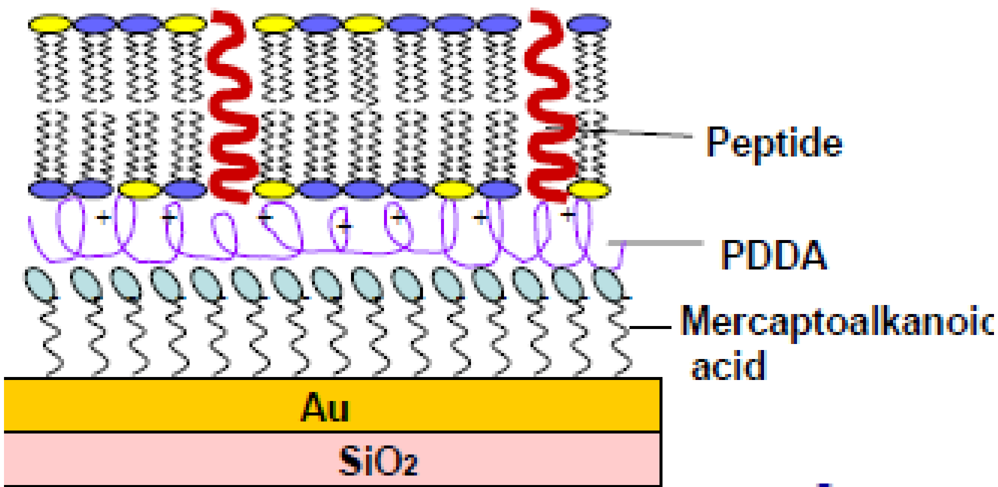


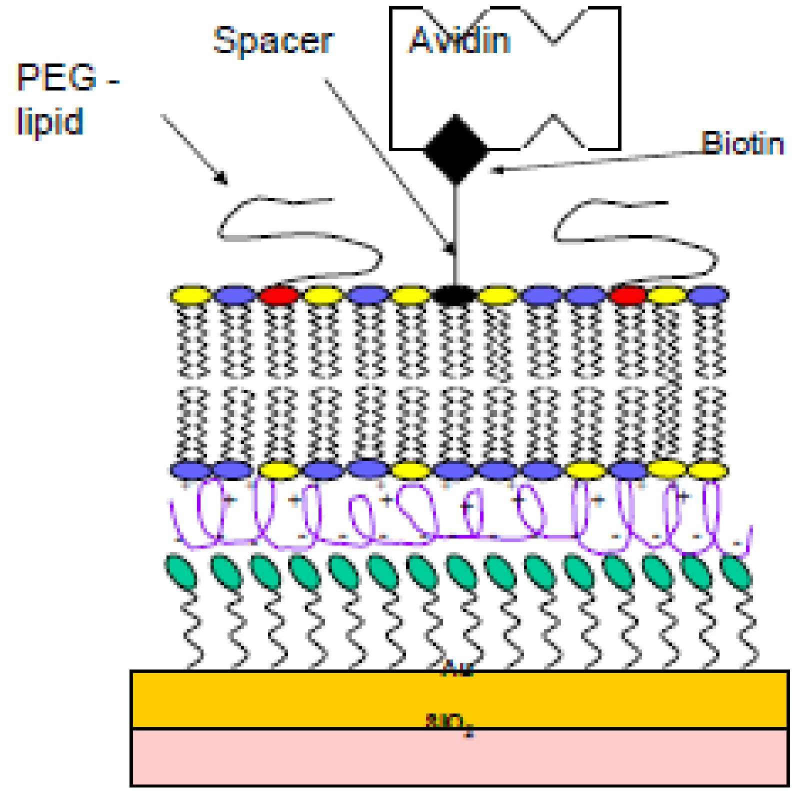






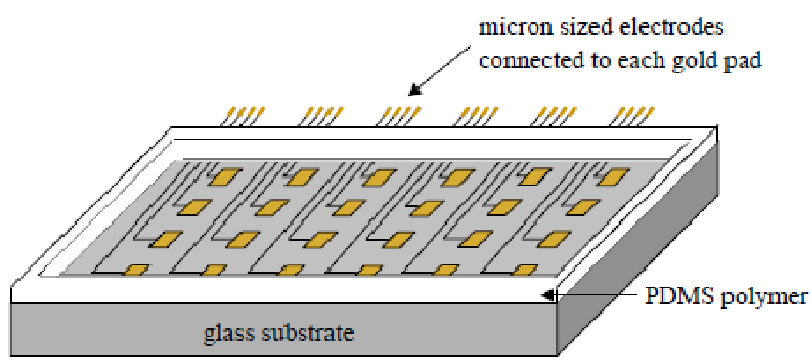
Requirements (to mimic the real cell membrane):
- Stable planar bilayer
- Fluid bilayer (lateral mobility)
- Aqueous environments on both sides of bilayers
- Preserve biological activity for molecules inserted
- Sensing or screening proteins/peptides/ligands





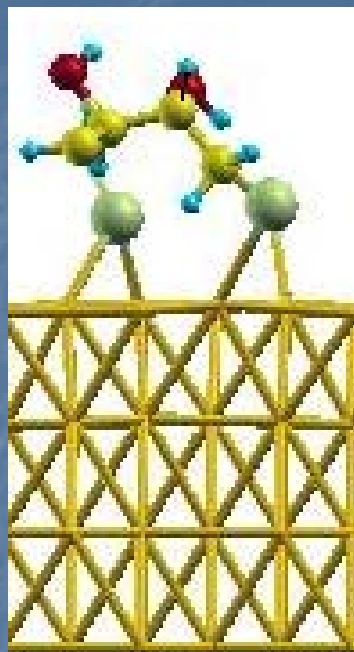
PDDA poly(diallyl dimethyl ammonium) chloride

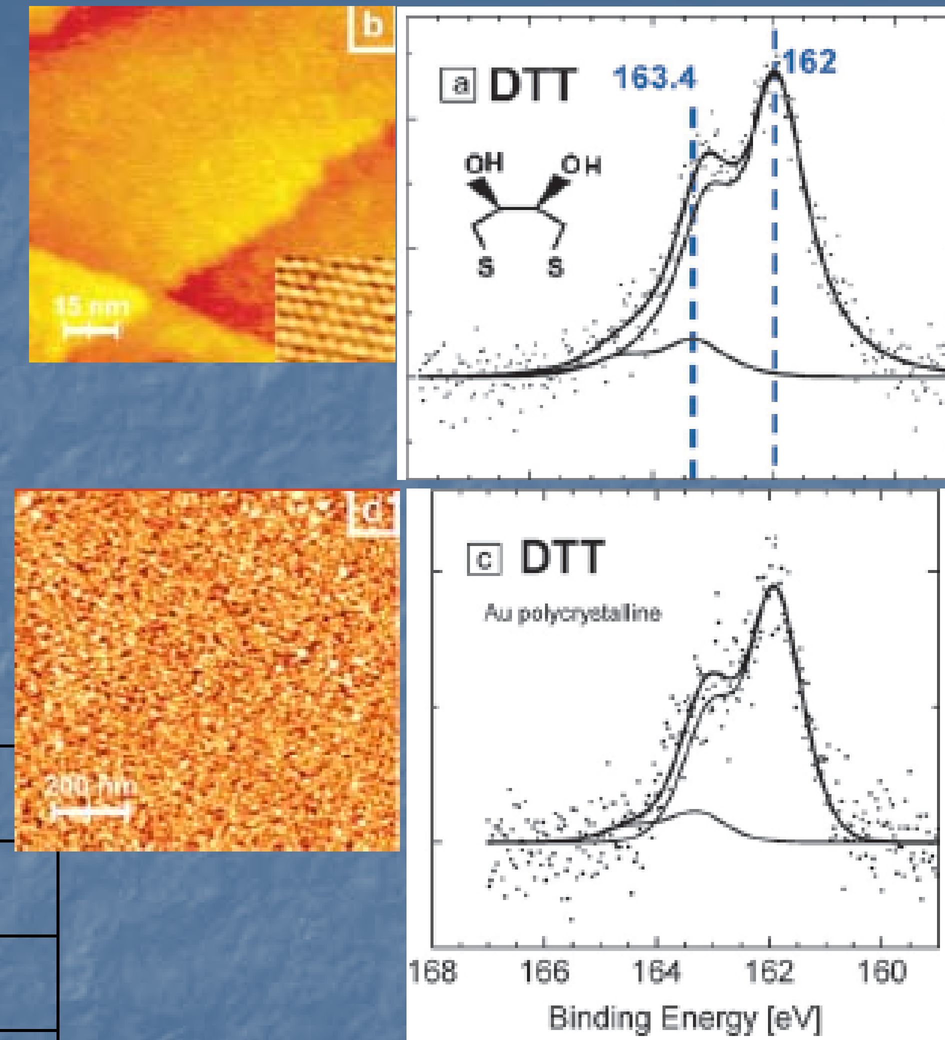
Supported lipid bilayers as micro-array biosensors



Tuning molecular configuration

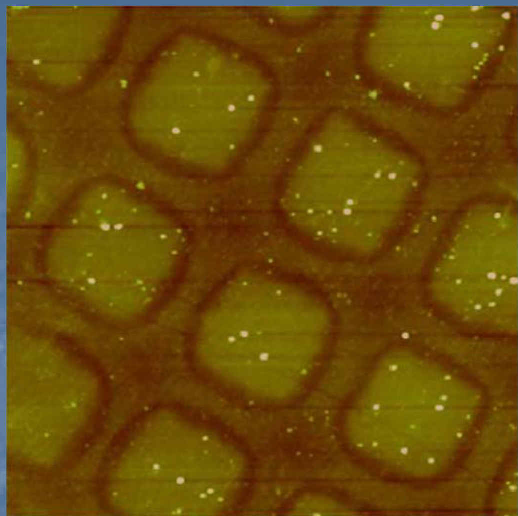
S 2p

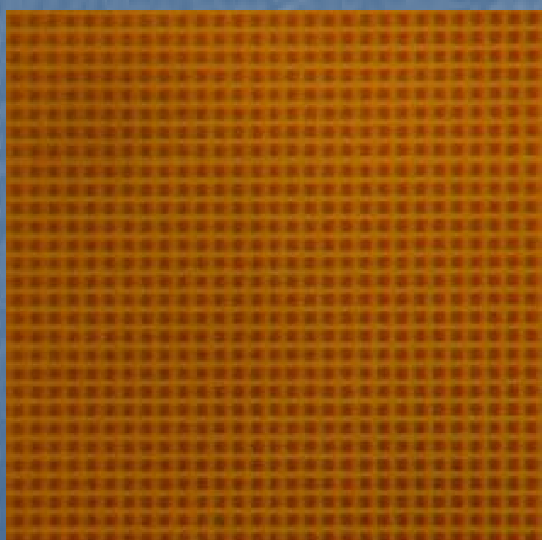


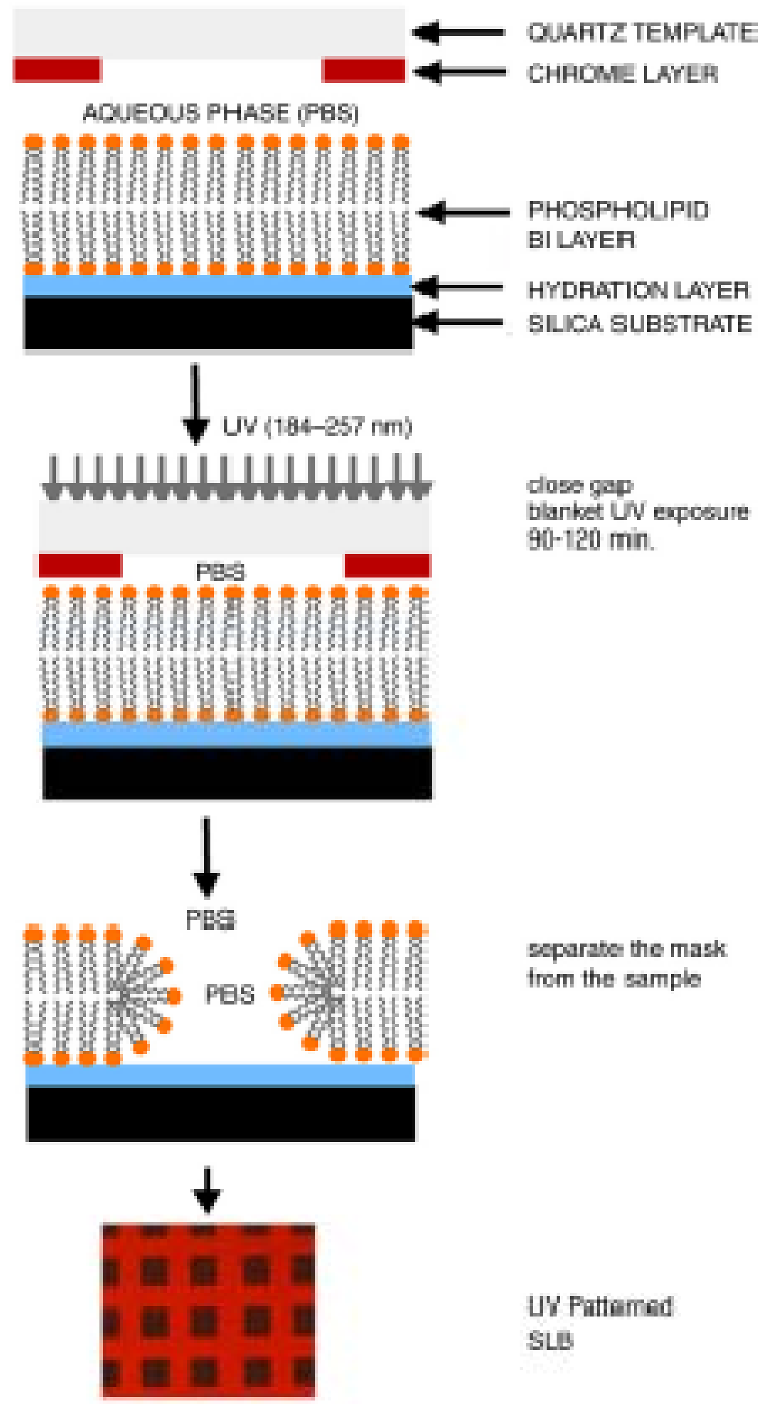


Sample	S/Au ratio
DTT 30 min, 5mM, 25ºC	0.15
DTT 30 min , 5mM,60ºC	0.12
DTT 30 min,50µM 60ºC	0.07
C3 24 hs, 50µM, 25ºC	0.07
C4 24 hs, 50µM, 25ºC	0.07

XPS

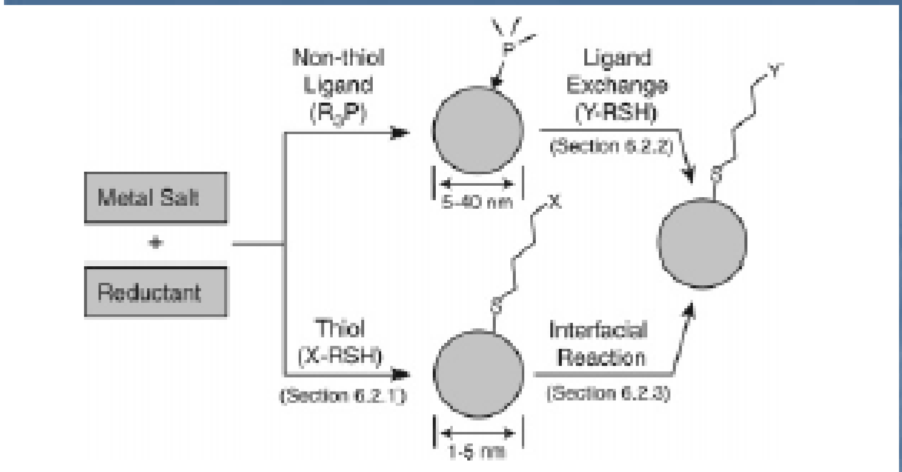





QUARTZ TEMPLATE
CHROME LAYER
AQUEOUS PHASE (PBS)
PHOSPHOLIPID
BI LAYER
HYDRATION LAYER
SILICA SUBSTRATE
UV (184–257 nm)
close gap
blanket UV exposure
90-120 min.
PBS
PBS
PBS
separate the mask
from the sample
UV Patterned
SLB

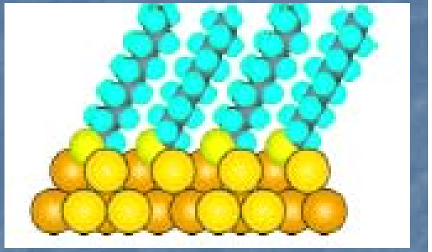
SAMs on curved surfaces: Nanoparticles

Curved surfaces accomodate more S (1/3)

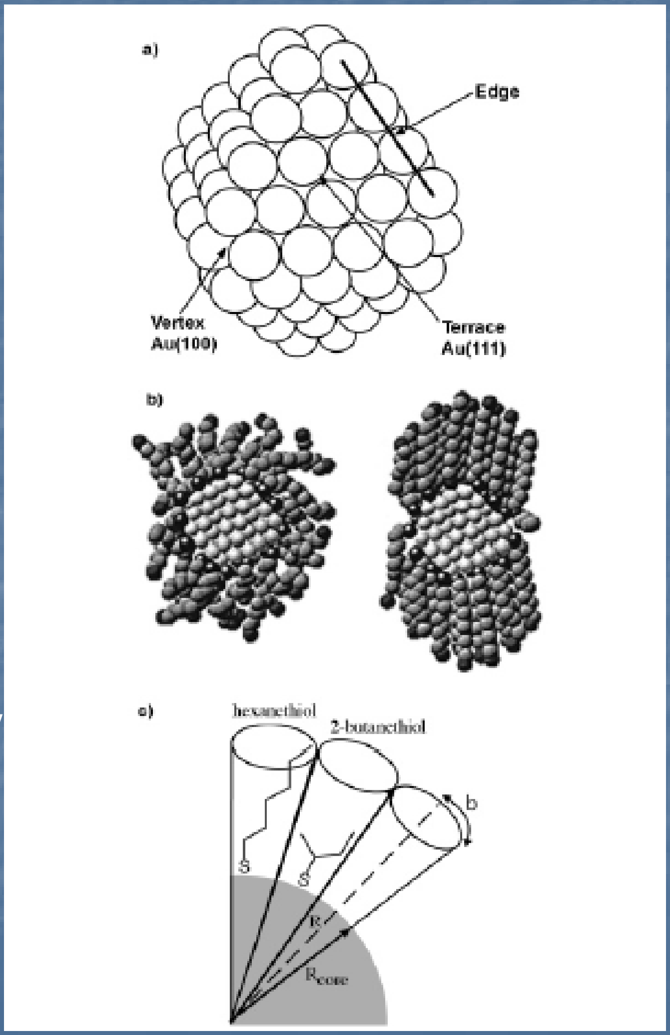


$$AuCl_4^- \text{ (toluene)} + RSH \rightarrow (-Au^ISR-)_n\text{(polymer)} \quad (2)$$

$$(-Au^ISR-)_n + BH_4^- \rightarrow Au_x(SR)_y \quad (3)$$



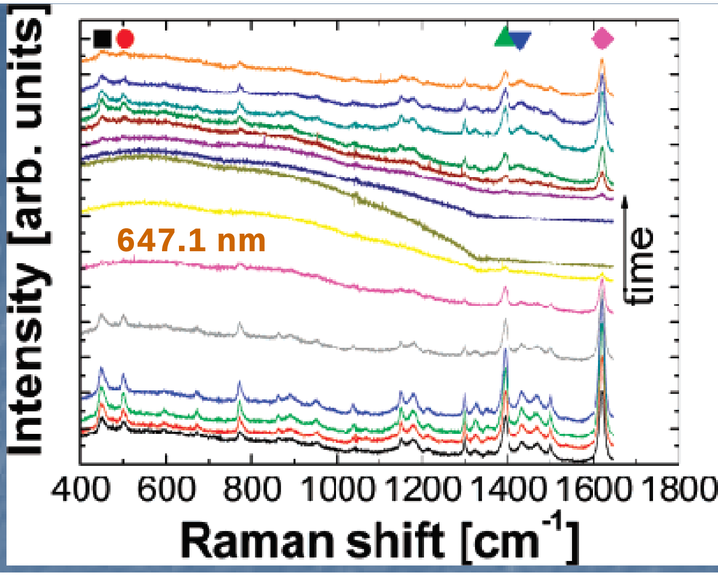
planar vs curved surfaces

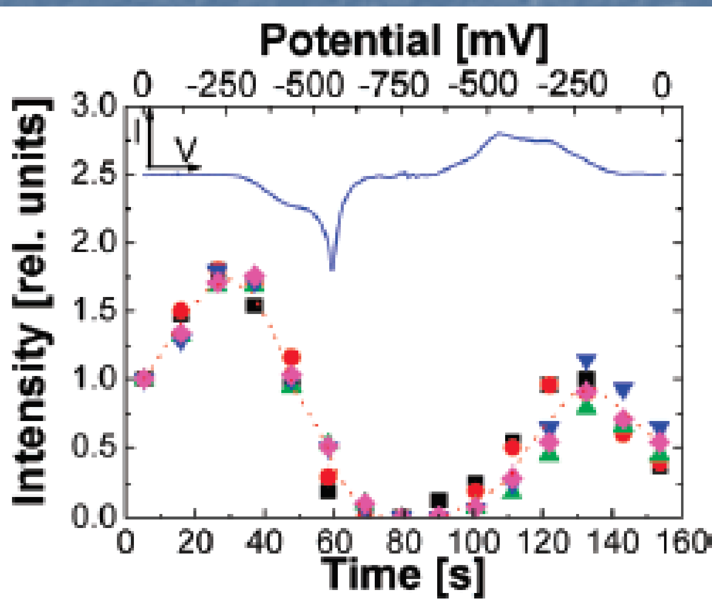


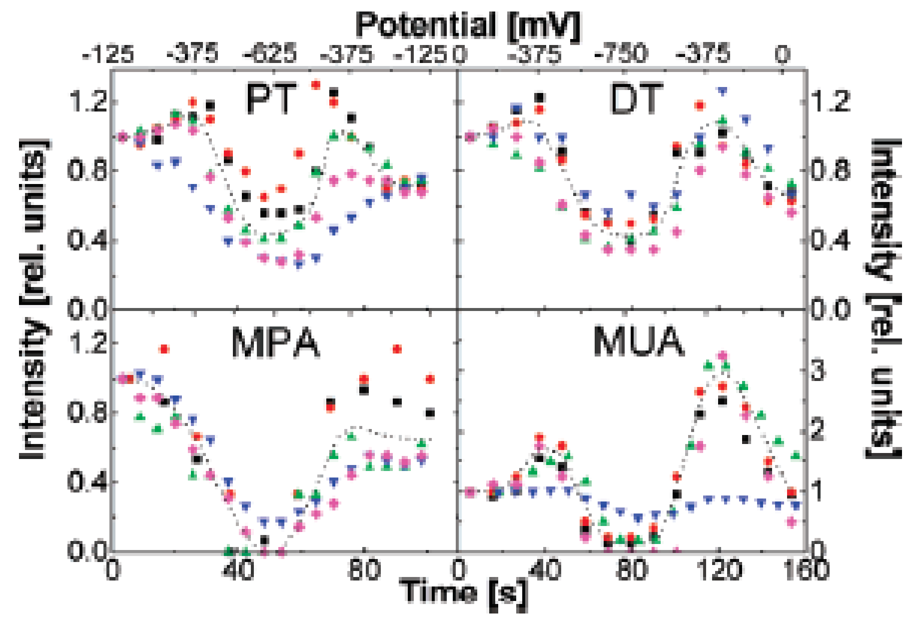
K

Love, Estroff, Kriebel, Nuzzo, Whitesides
Chemical Reviews, 2005, Vol. 105, No. 4 1121

In Situ Raman Spectroscopy of Redox Species Confined in Self-Assembled Molecular Films



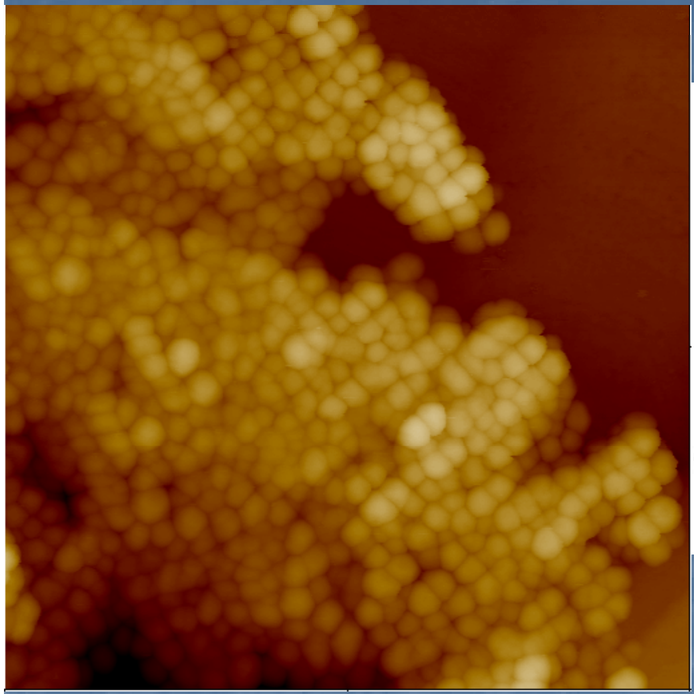


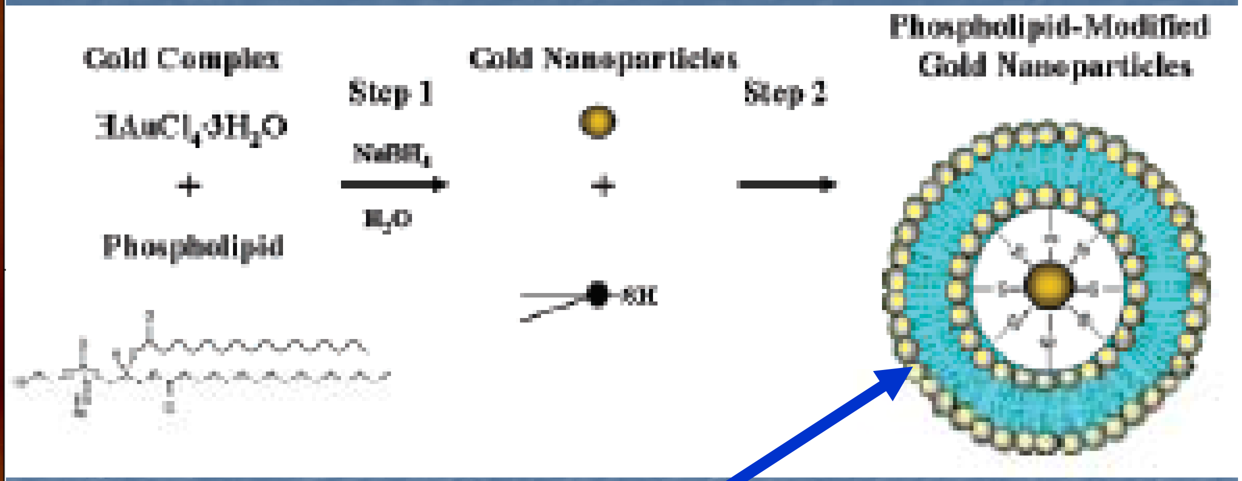


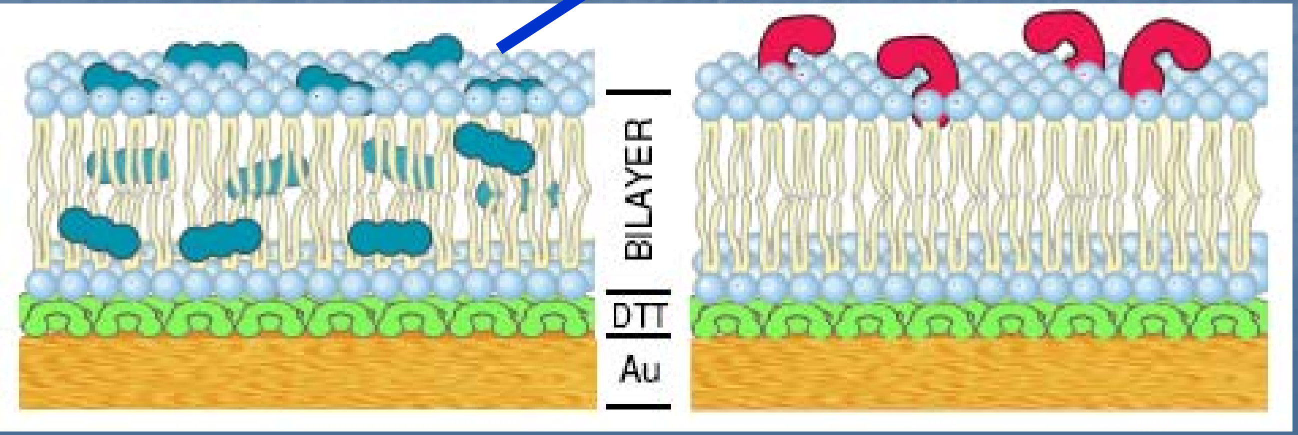
C-N-C skeleton bending (448 cm^{-1} square), C-N-C skeleton bending (500 cm^{-1} circle), C-N symmetric stretching (1395 cm^{-1}, up triangle), C-N asymmetric stretching(1433 cm^{-1} down triangle), C-C ring stretching (1620 cm^{-1})

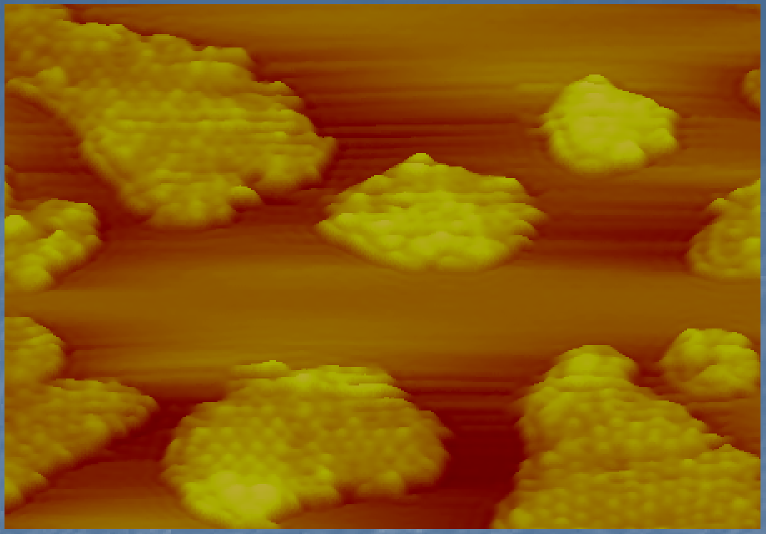
Tognalli, Fainstein, Vericat, Vela, Salvarezza

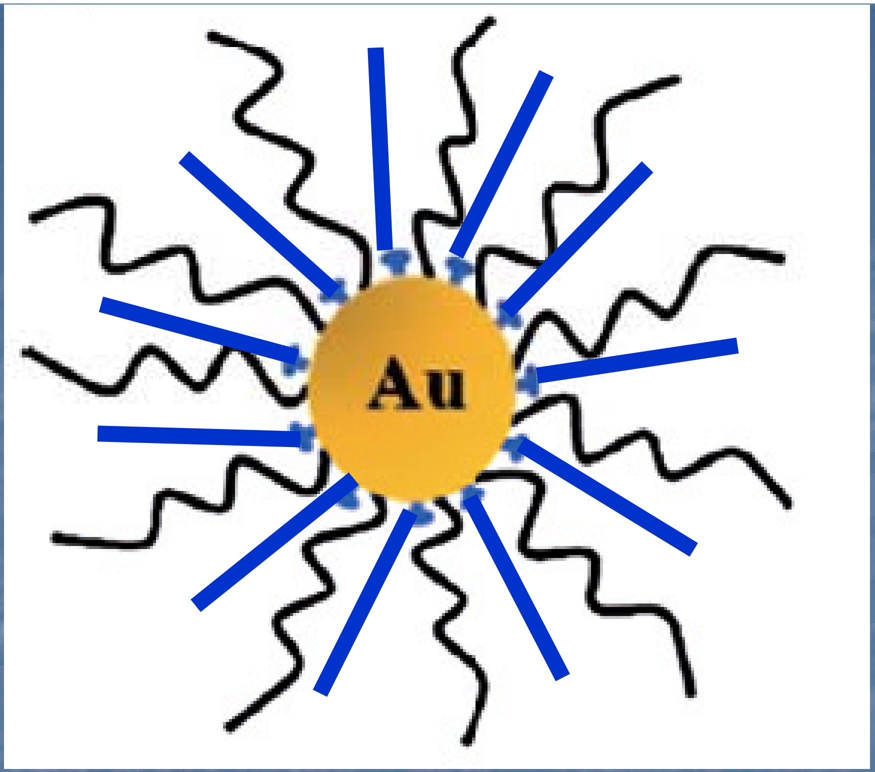
J. Phys. Chem. C **2008,** *112,* 3741-3746




Gold Complex
$HAuCl_4 \cdot 3H_2O$
+
Phospholipid
Step 1
$NaBH_4$
H_2O
Gold Nanoparticles
+
SH
Step 2
Phospholipid-Modified
Gold Nanoparticles


BILAYER
DTT
Au

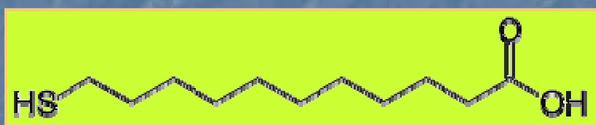


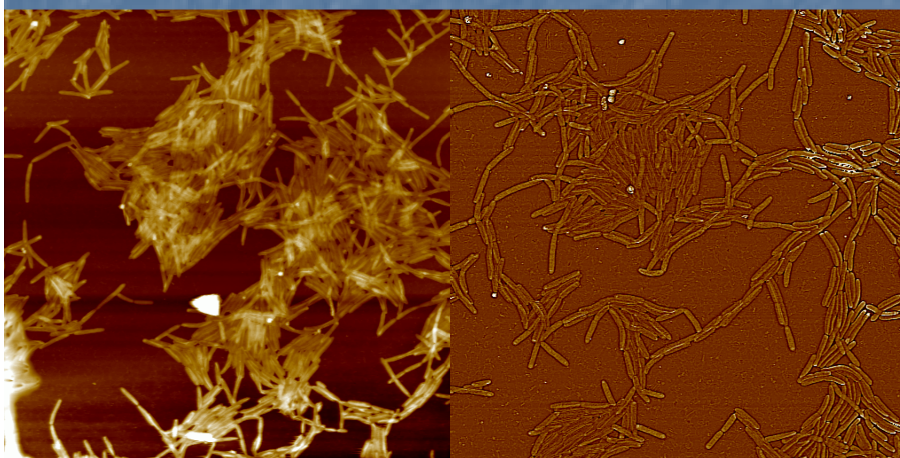

Au

Bacterial adhesion on self assembled monolayers on Au (SAMs)

Pseudomonas fluorescens, Incubation time: 18 hours
Atomic force microscopy

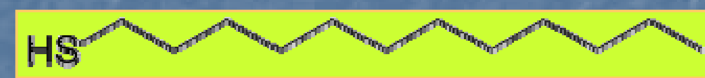
Hydrophilic surfaces

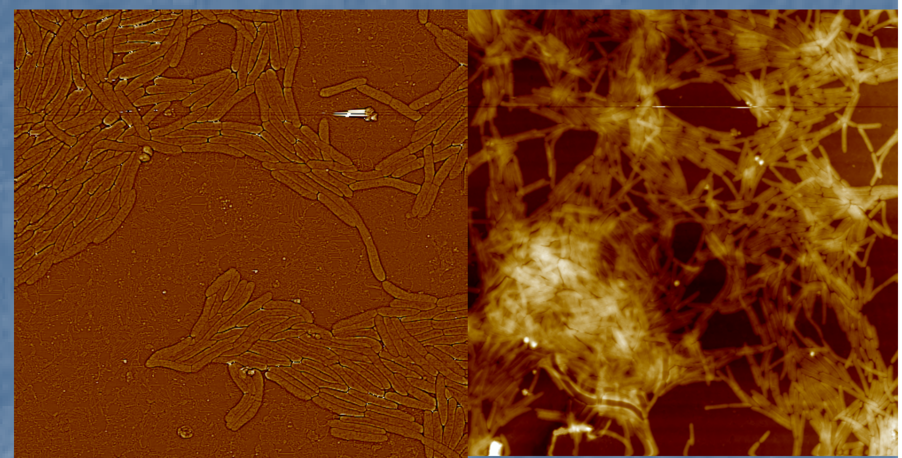




- Isolated bacteria
- Attached bacteria to the hydrophilic substrate are shorter

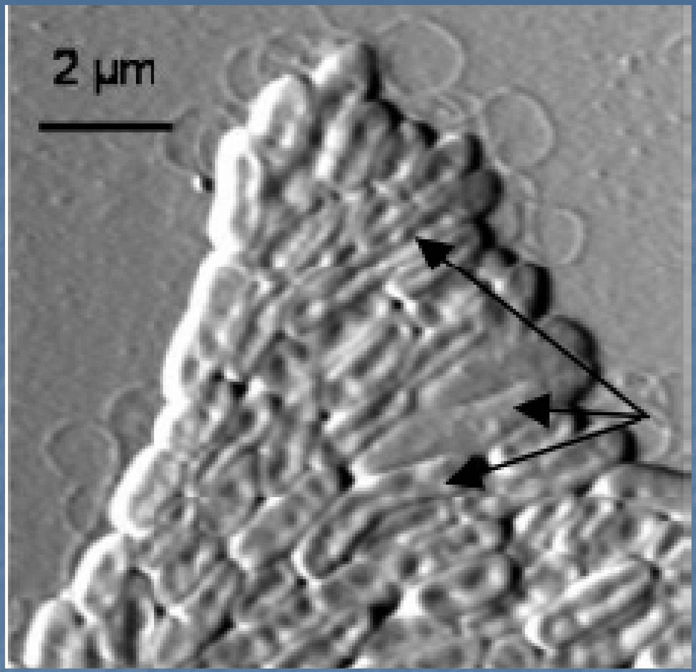
Hydrophobic substrate



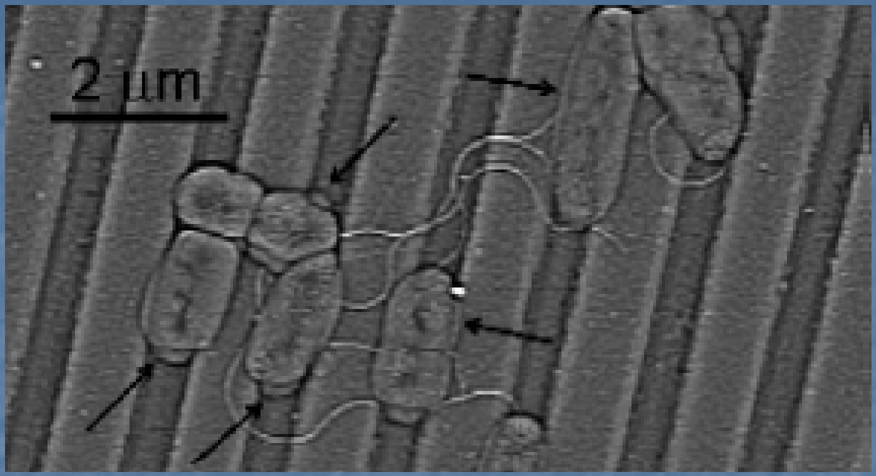


- Dense clusters of bacteria
- Attached pseudomonas are longer

Combining Surface Chemistry and Microstructure

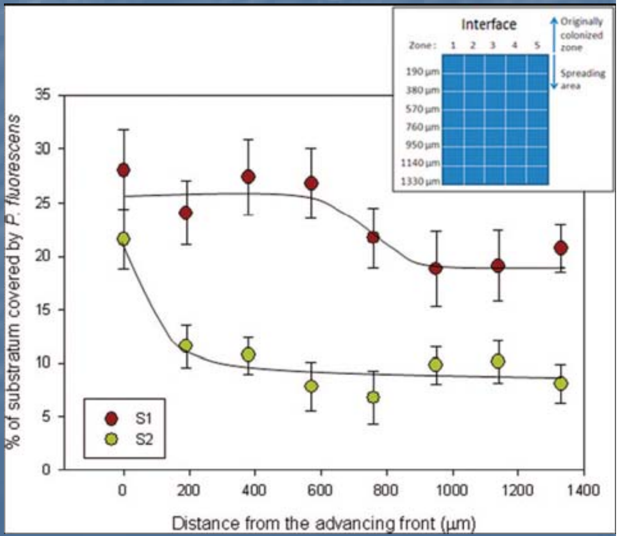


Raft



Raft inhibition

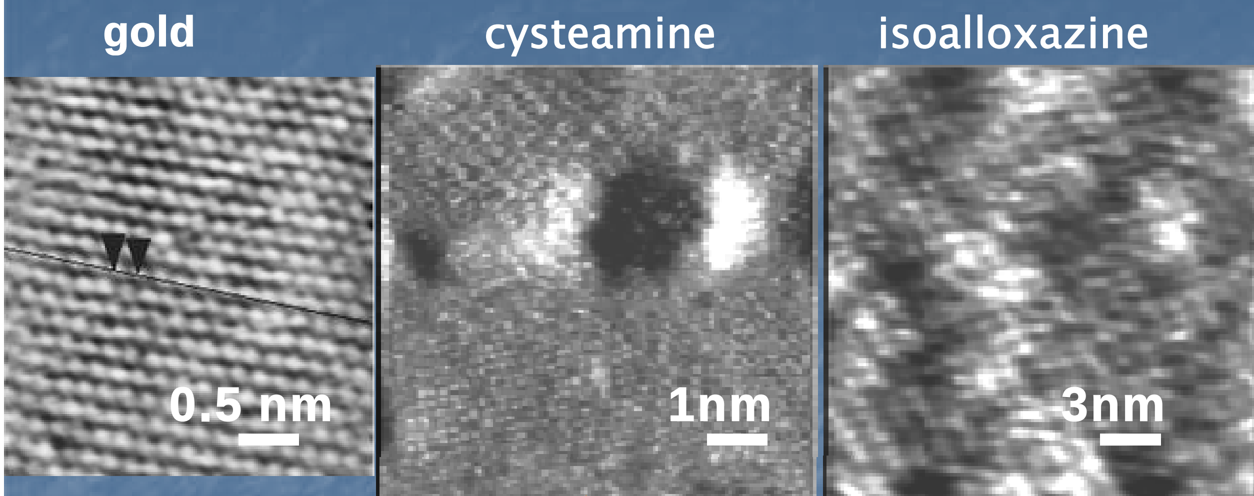
Decrease in the colonization rate



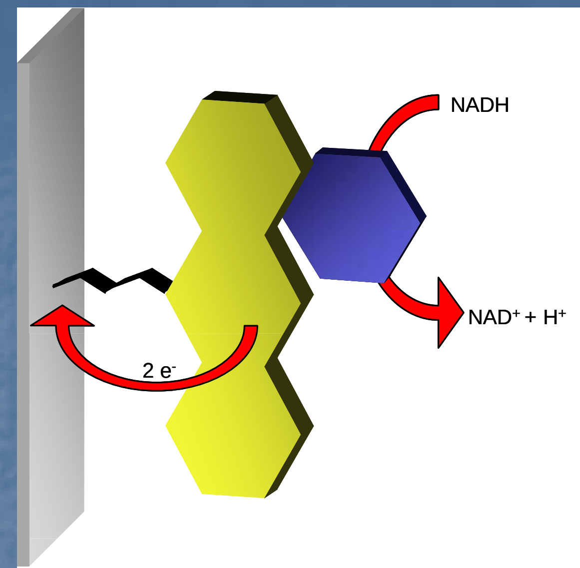
Díaz, Schilardi, dos Santos Claro, Salvarezza, Fernández Lorenzo

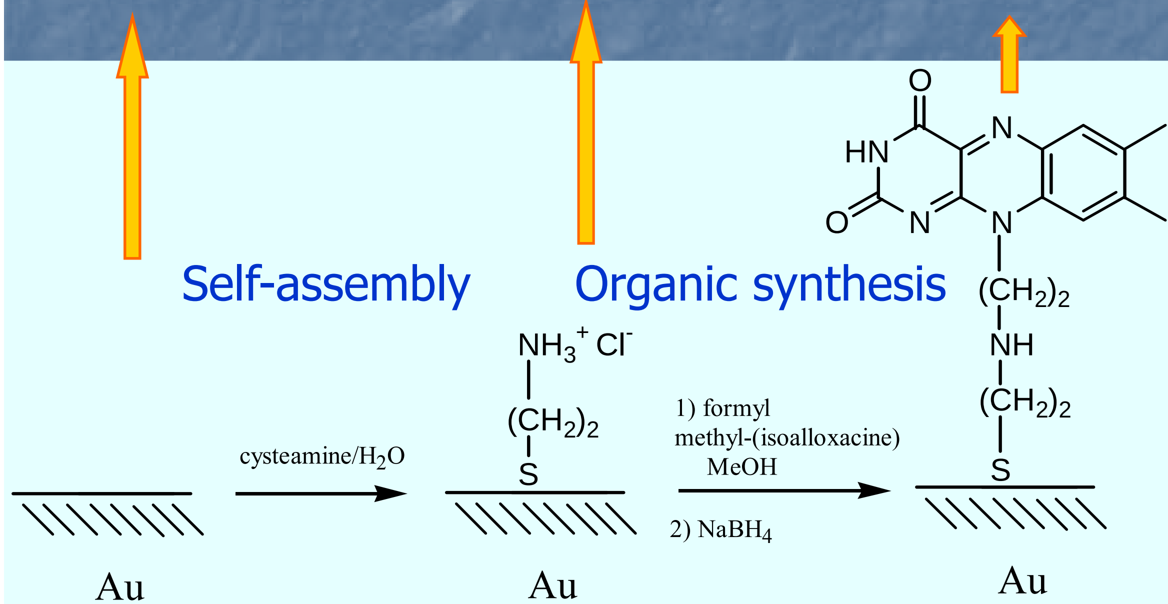
ACS APPLIED MATERIALS & INTERFACES **1, 136-143 (2009)**

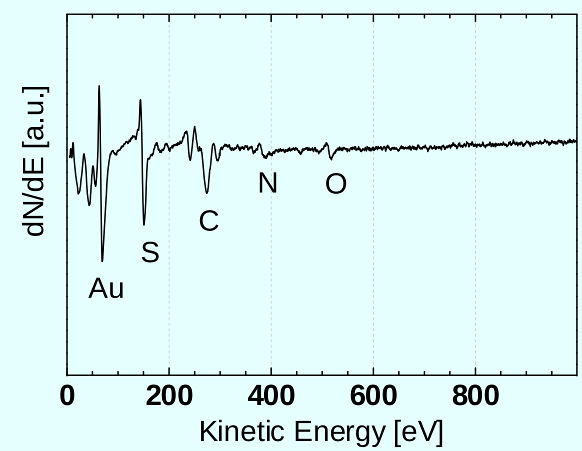
Biosensors: Covalent binding to functionalized SAMs



Au isoalloxazine

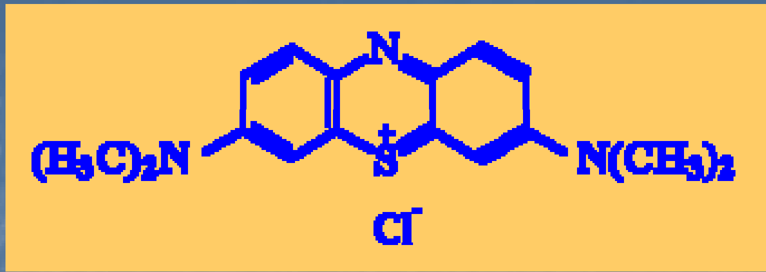


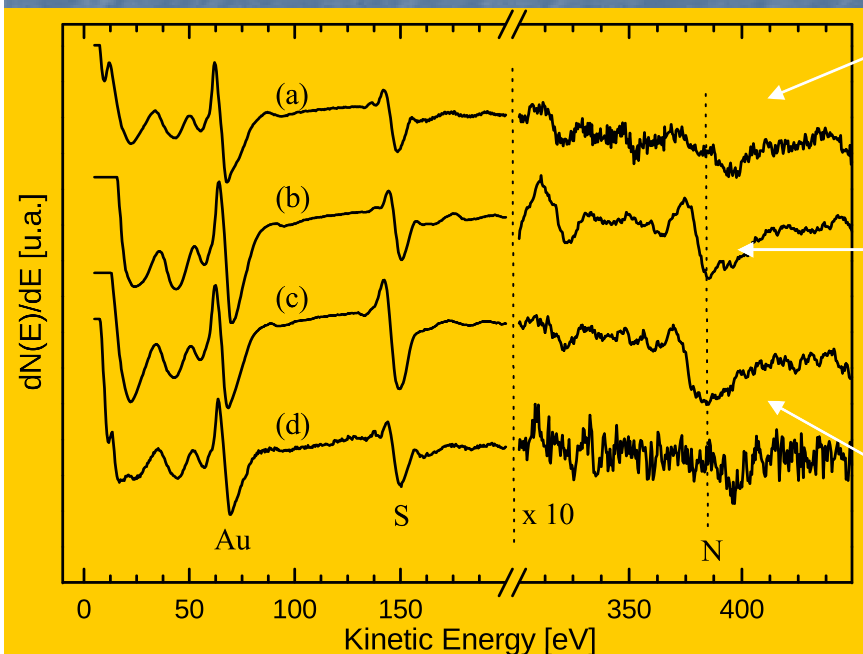




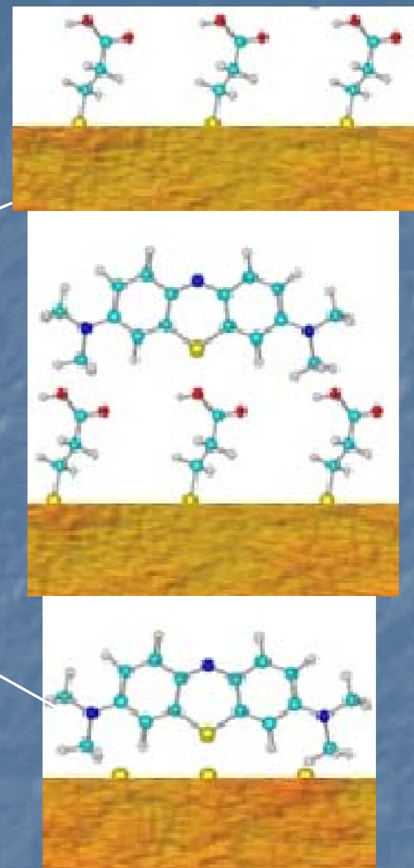
E. J. Calvo, M. Rothacher†, C. Bonnazzola ,j. Wheeldon†, R. Salvarezza , M. E. Vela, G. Benitez, *Langmuir* 21,7907-7911, 2005

Trapping molecules and ions: Methylene Blue on thiol SAMs

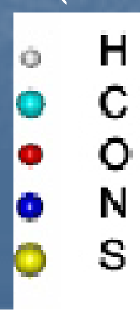




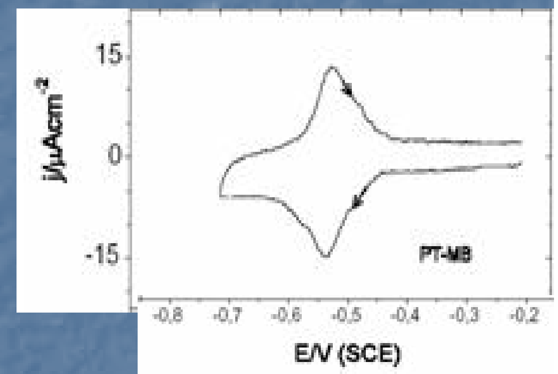
AES spectra



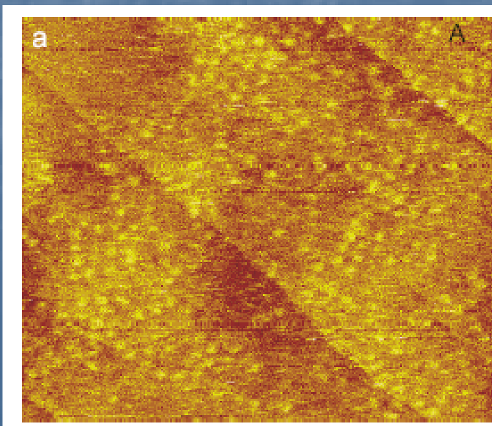
Au(111)



voltammetry of MB trapped in SAMs

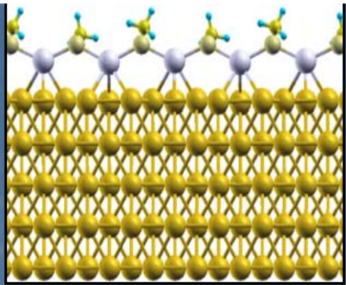


STM of trapped MB molecules

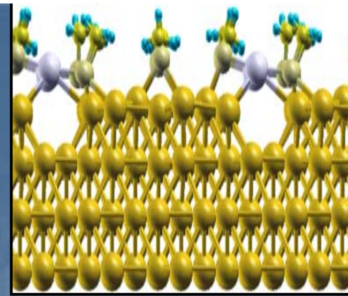


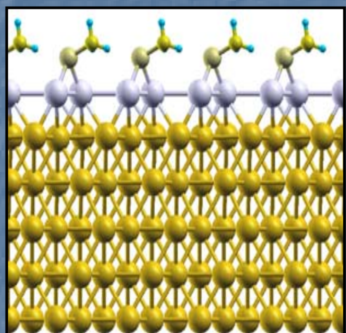
Benítez, Vericat, Tanco, Remes
Lenicov, Castez, Vela, Salvarezza
Langmuir, 20, 5030-5037 (2004).

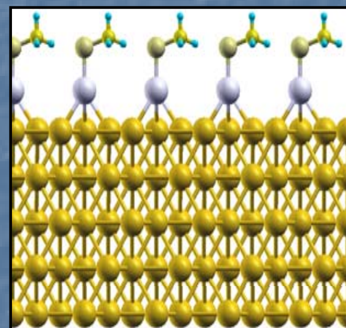
Muchas gracias!!!



?







....is the Au(111) surface reconstructed upon thiol adsorption?

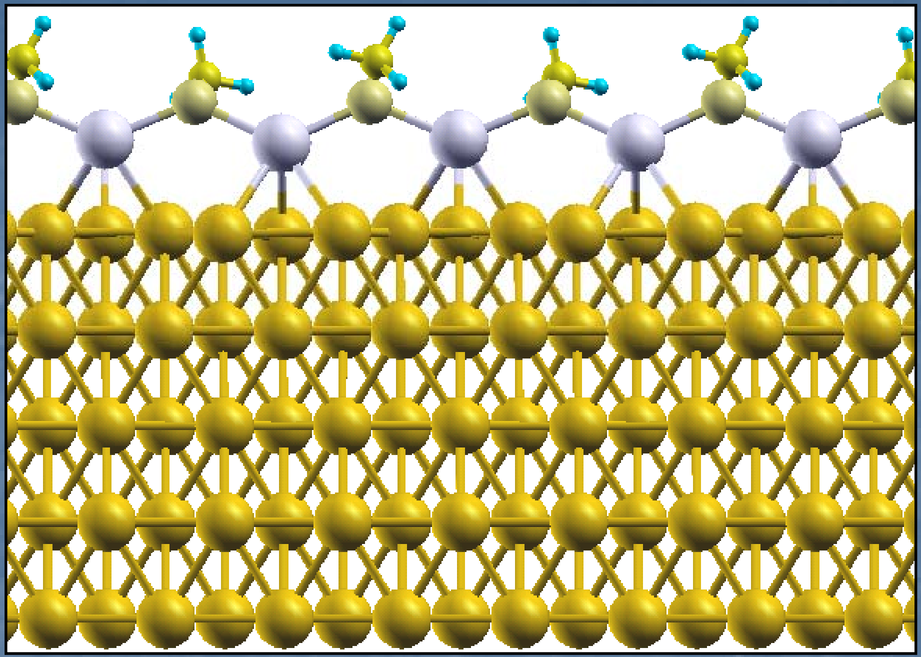
Yu, Bovet; Satterley; Bengio; Lovelock. ; Milligan; Jones; Woodruff ; Dhanak. *Phys. Rev. Lett.* **2006**, *97*, 166102.
Mazzarello, ; Cossaro; Verdini; Rousseau, Casalis; Danisman ; Floreano; Scandolo; Morgante,;
Scoles. *Phys.Rev.Lett.* **2007**, *98*, 016102.
Grönbeck, H.; Häkkinen, H. *J. Phys. Chem. B* **2007**, *111,* 3325.
Molina, M. L.; Hammer, B. *Chem. Phys. Lett.* **2002**, *360*, 264.

$$\gamma(\Delta\mu) = \frac{1}{A}\left[E^{CH_3S/Au} - N_{Au}E^{Au}_{Bulk} - N_{CH_3S}\Delta\mu\right] - \gamma_{clean}$$

Reuter, K.; Scheffler, M.
Phys. Rev. B. **2002**, *65*, 035406

$$\Delta\mu = \mu - \frac{1}{2}g_{(CH_3S)_2}$$

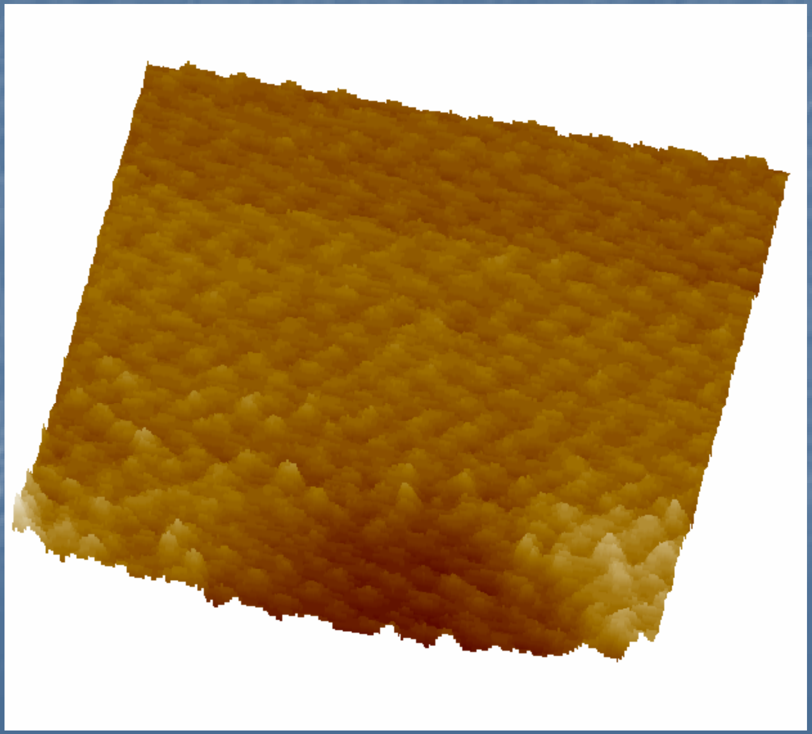
Torres, D.; Carro, P.; Salvarezza, R. C.;
Illas, F. *Phys. Rev. Lett.* **2006**, *97*, 226103



Vacancy model
0 K

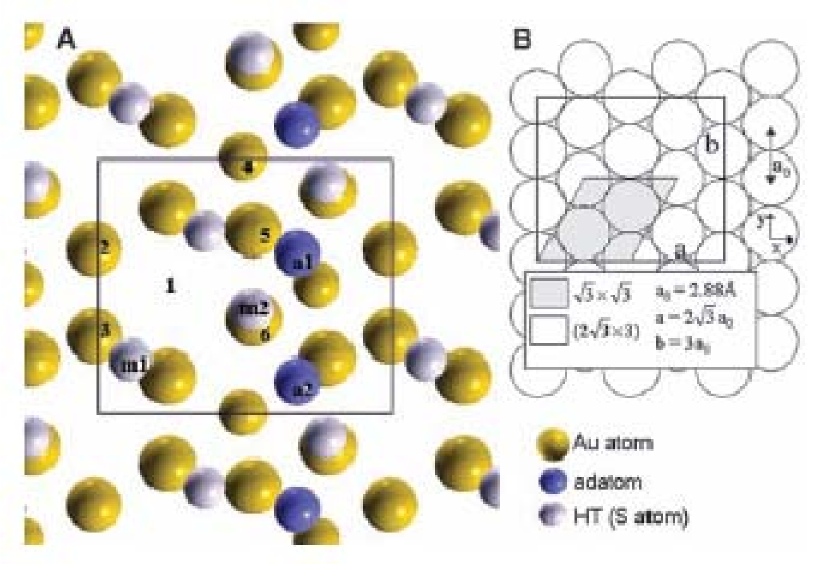
Molina, Hammer

Chem. Phys. Lett. **2002**, *360*, 264



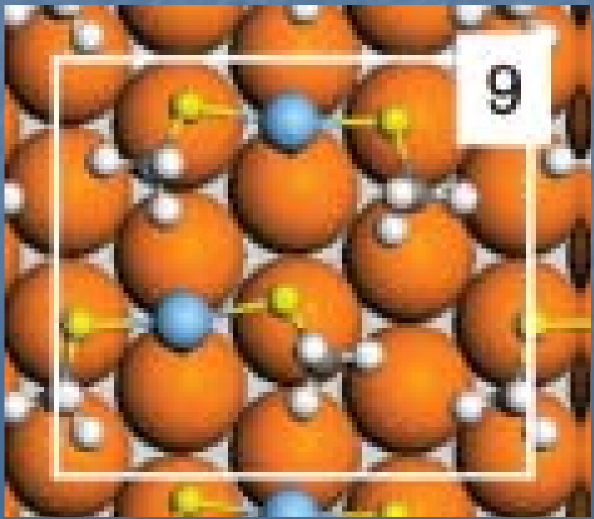
Vacancy island
298 K

X-ray Diffraction and Computation Yield the Structure of Alkanethiols on Gold(111)



Cossaro, Mazzarello, Rousseau, Casalis, Verdini, Kohlmeyer, Floreano,Scandolo,Morgante, Klein, Scoles, *Science* **321**, 943 (2008)

Gold-Thiolate Complexes Form a Unique *c*(4 × 2) Structure on Au(111)



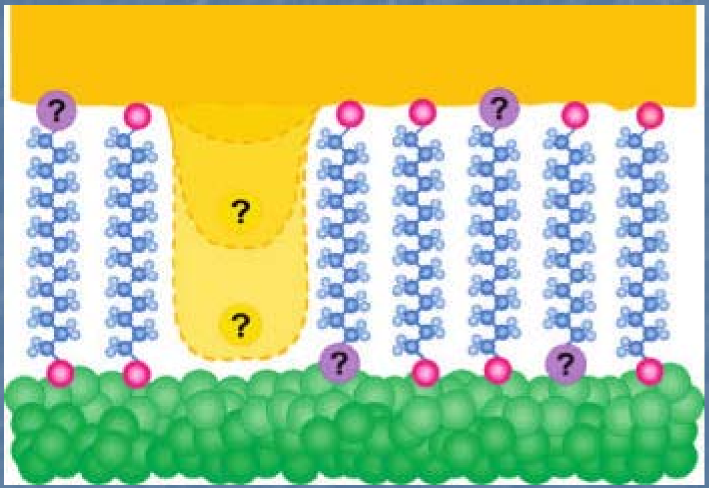
H. Gronbeck,H Hakkinen,R L. Whetten

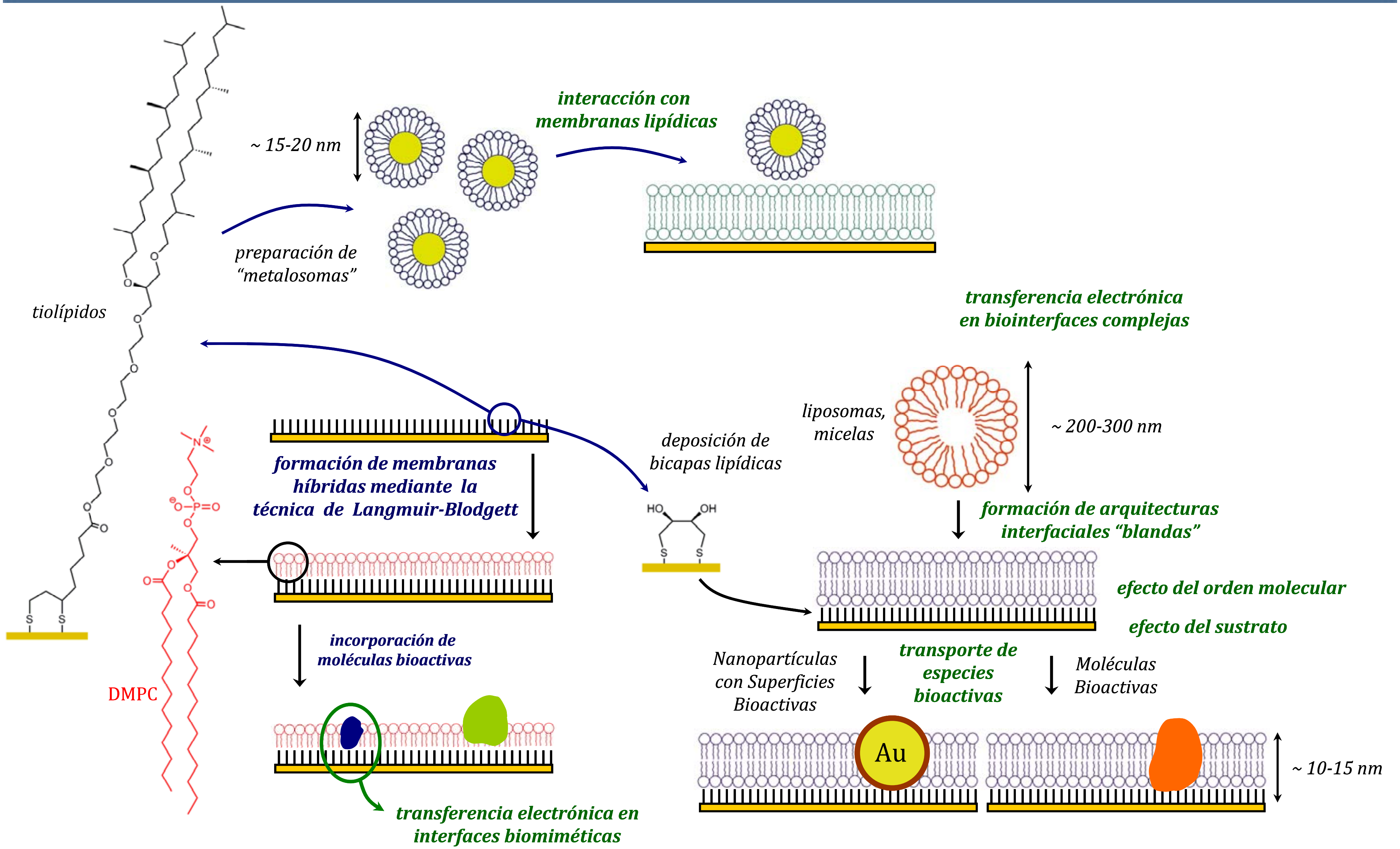
112, 15940 (2008)

SAM quality

SELF ASSEMBLY

SURFACE STRUCTURES



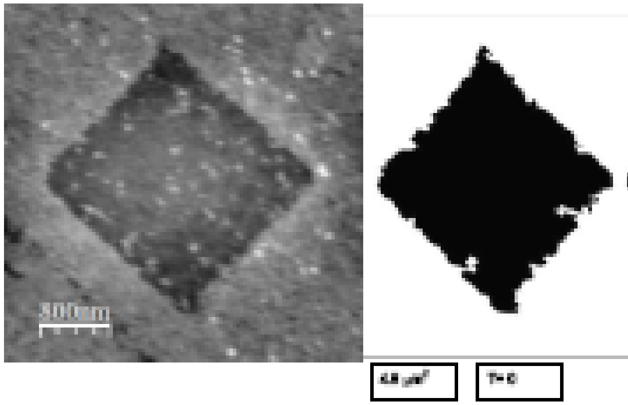


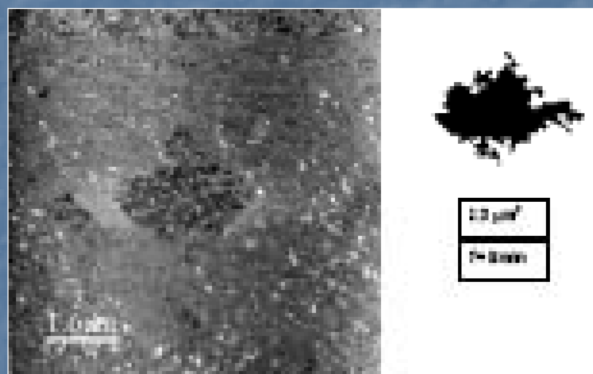
tiolípidos
DMPC
preparación de "metalosomas"
~ 15-20 nm
interacción con membranas lipídicas
transferencia electrónica en biointerfaces complejas
formación de membranas híbridas mediante la técnica de Langmuir-Blodgett
deposición de bicapas lipídicas
liposomas, micelas
~ 200-300 nm
formación de arquitecturas interfaciales "blandas"
efecto del orden molecular
efecto del sustrato
incorporación de moléculas bioactivas
Nanopartículas con Superficies Bioactivas
transporte de especies bioactivas
Moléculas Bioactivas
Au
~ 10-15 nm
transferencia electrónica en interfaces biomiméticas

Phospholipid Mobility

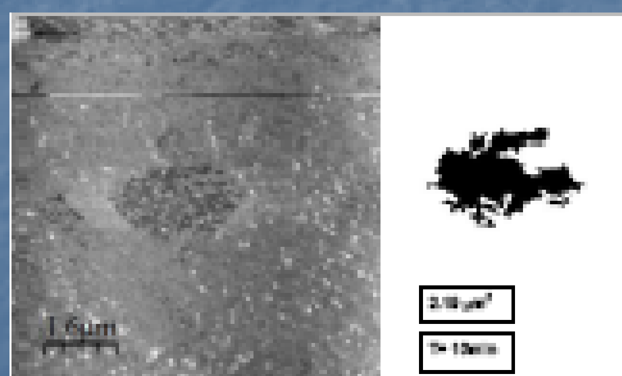
$$L^2 = 2\,Dt$$

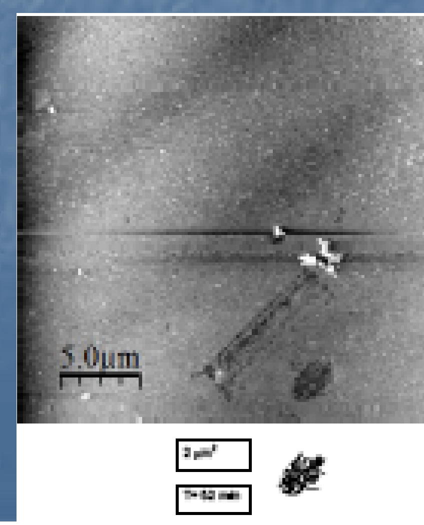
$$D \approx 10^{-11}\ cm^2\ s^{-1}$$

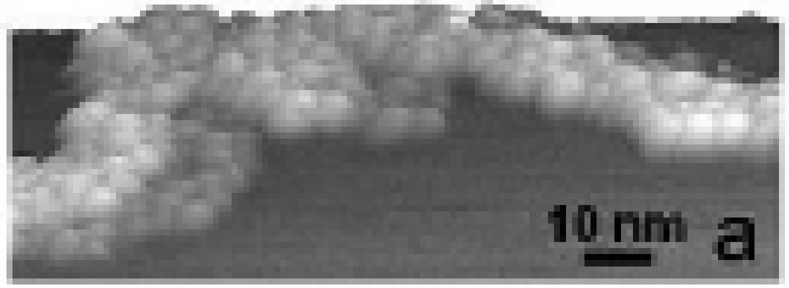




Time

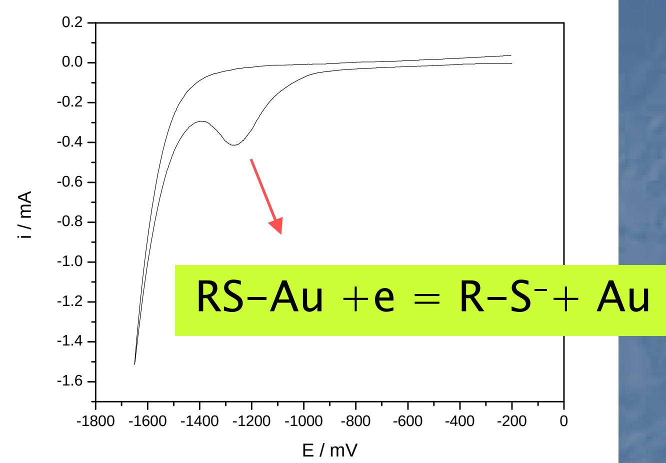




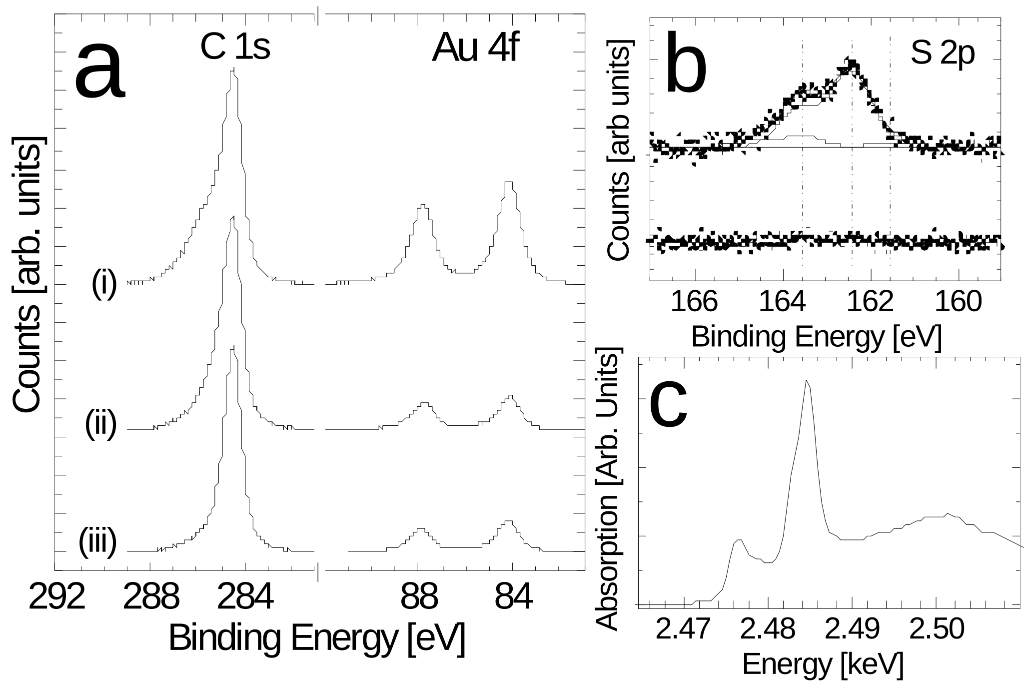


butanethiolate-capped Au nanoparticles (3 nm) on HOPG

Adsorption, Cleaning and delivering Au Nanoparticles

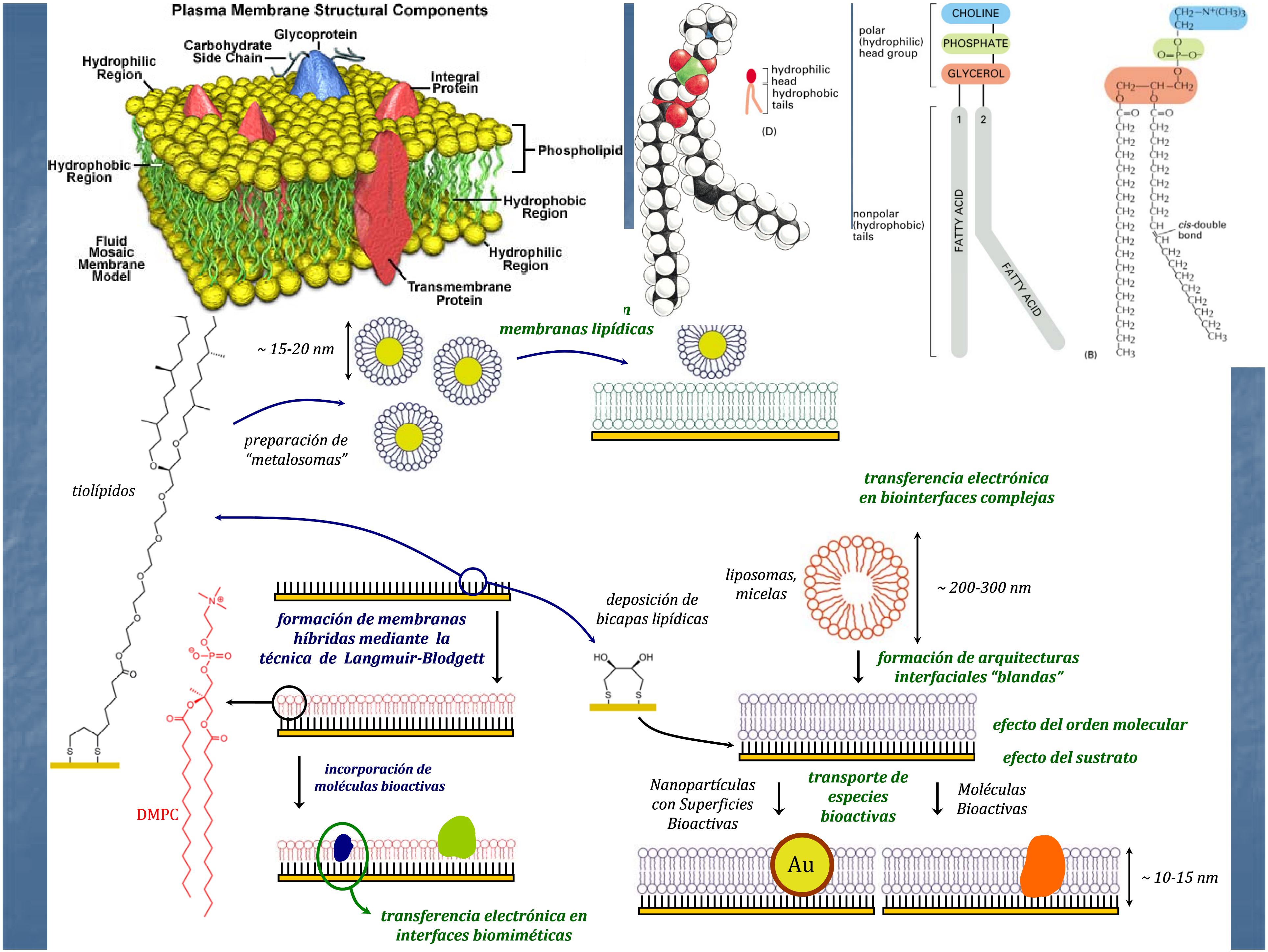


D. Grumelli, C. Vericat, G. Benitez, M.E. Vela, L.J. Giovanetti, J.M. Ramallo-Lopez, F.G. Requejo, A.F. Craievich, Y.S. Shon, R.C. Salvarezza
Journal Physical Chemistry C:, 111, 7179 (2007)



Before desorption

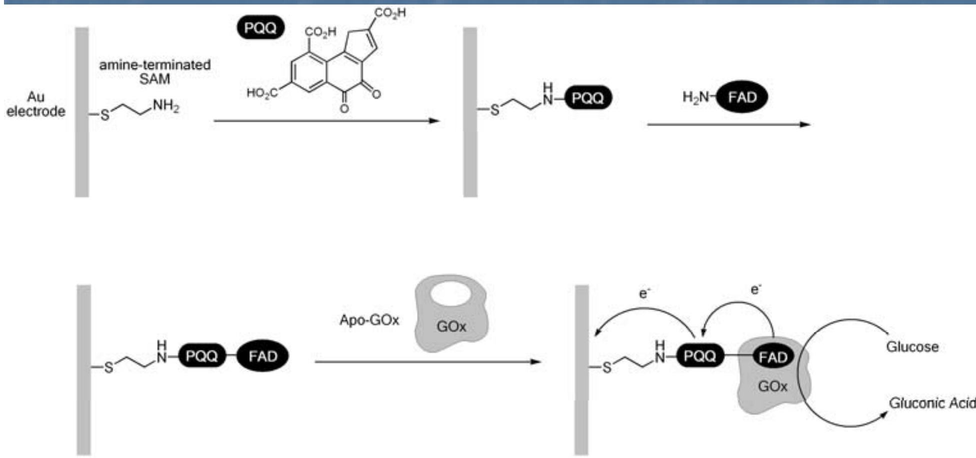
After desorption



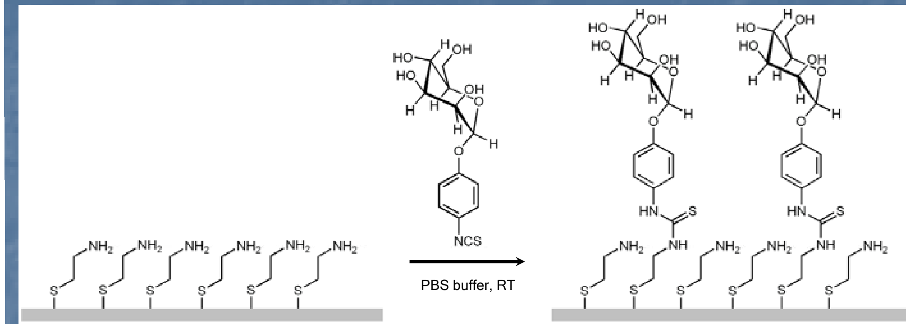
Plasma Membrane Structural Components
Glycoprotein
Carbohydrate Side Chain
Hydrophilic Region
Integral Protein
Phospholipid
Hydrophobic Region
Hydrophobic Region
Hydrophilic Region
Fluid Mosaic Membrane Model
Transmembrane Protein
hydrophilic head
hydrophobic tails
(D)
polar (hydrophilic) head group
nonpolar (hydrophobic) tails
CHOLINE
PHOSPHATE
GLYCEROL
1
2
FATTY ACID
FATTY ACID
cis-double bond
(B)
membranas lipídicas
~ 15-20 nm
preparación de "metalosomas"
tiolípidos
transferencia electrónica en biointerfaces complejas
liposomas, micelas
~ 200-300 nm
deposición de bicapas lipídicas
formación de membranas híbridas mediante la técnica de Langmuir-Blodgett
formación de arquitecturas interfaciales "blandas"
efecto del orden molecular
efecto del sustrato
DMPC
incorporación de moléculas bioactivas
Nanopartículas con Superficies Bioactivas
transporte de especies bioactivas
Moléculas Bioactivas
Au
~ 10-15 nm
transferencia electrónica en interfaces biomiméticas

Self-assembled monolayers as structural and functional elements

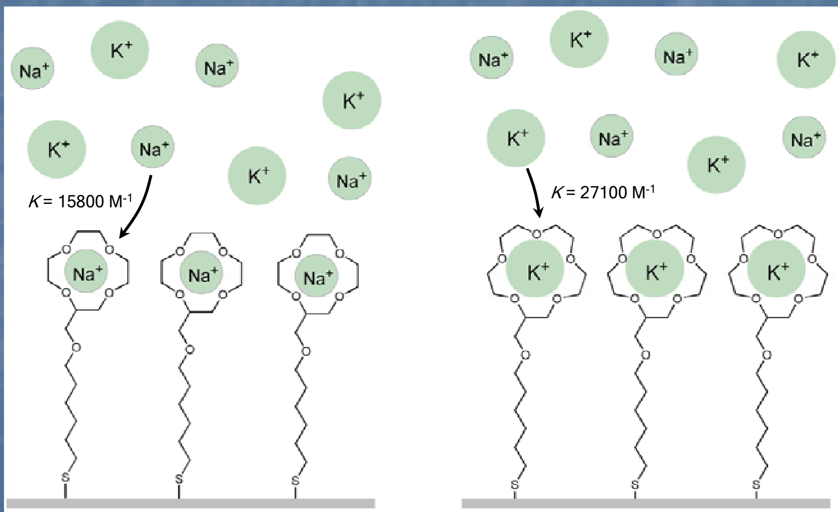
Biosensors



Biorecognition



Sensors



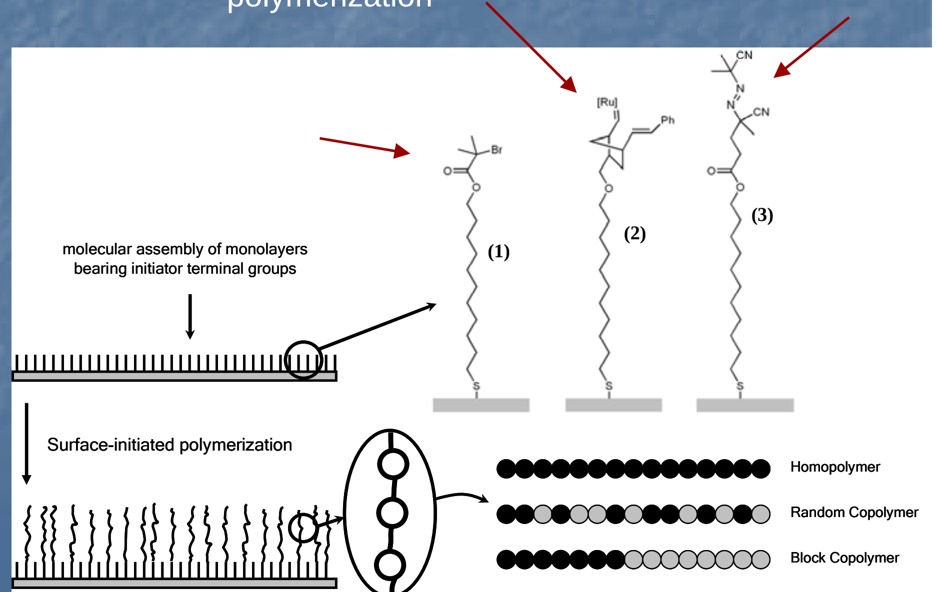
12-crown-4-capped SAM
Na+-selective monolayer

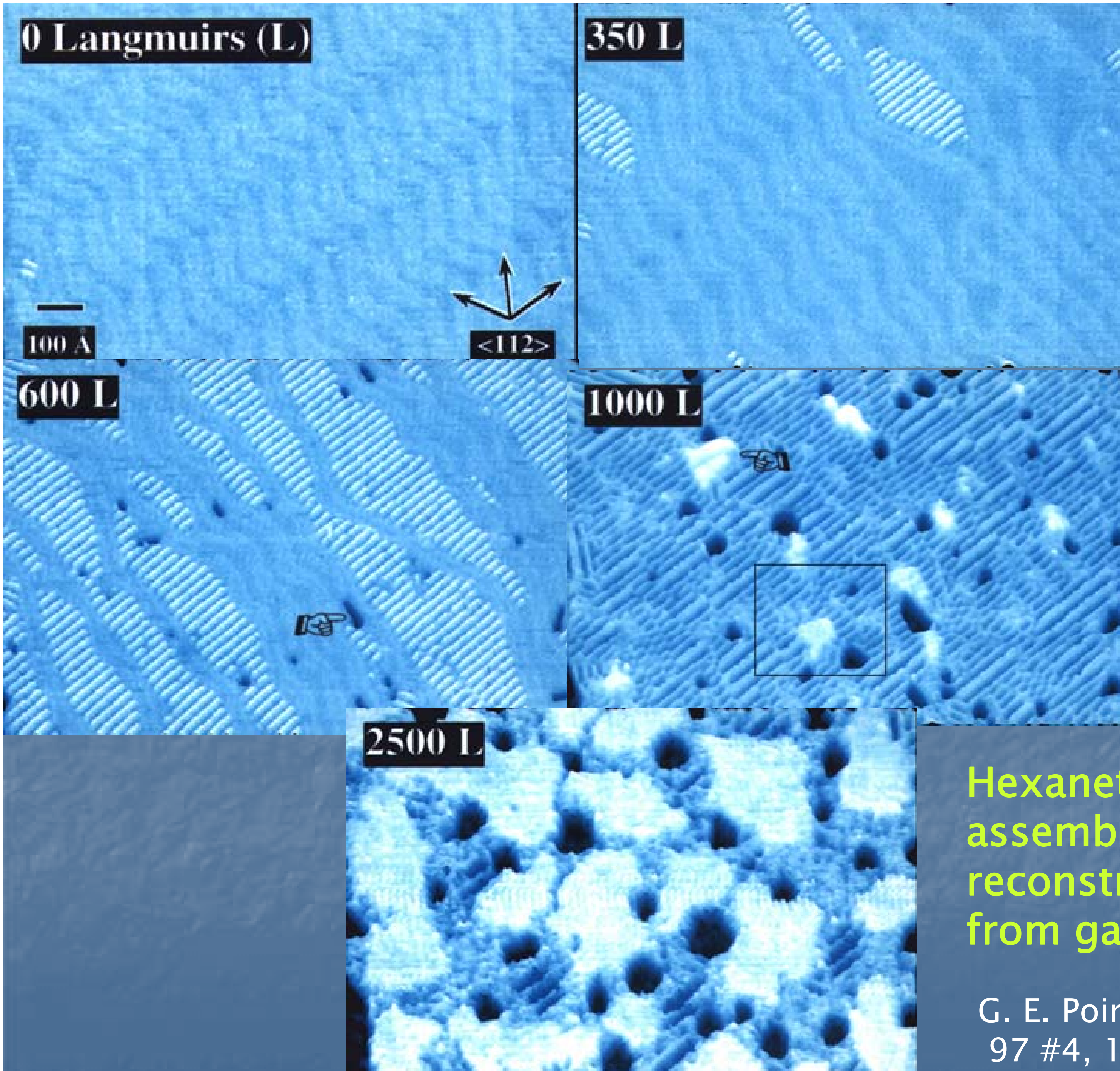
15-crown-5-capped SAM
K+-selective monolayer

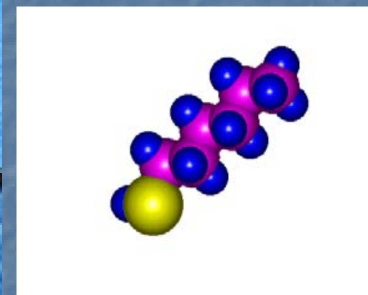
Responsive surfaces

ring-opening metathesis polymerization

thermal free radical polymerization.

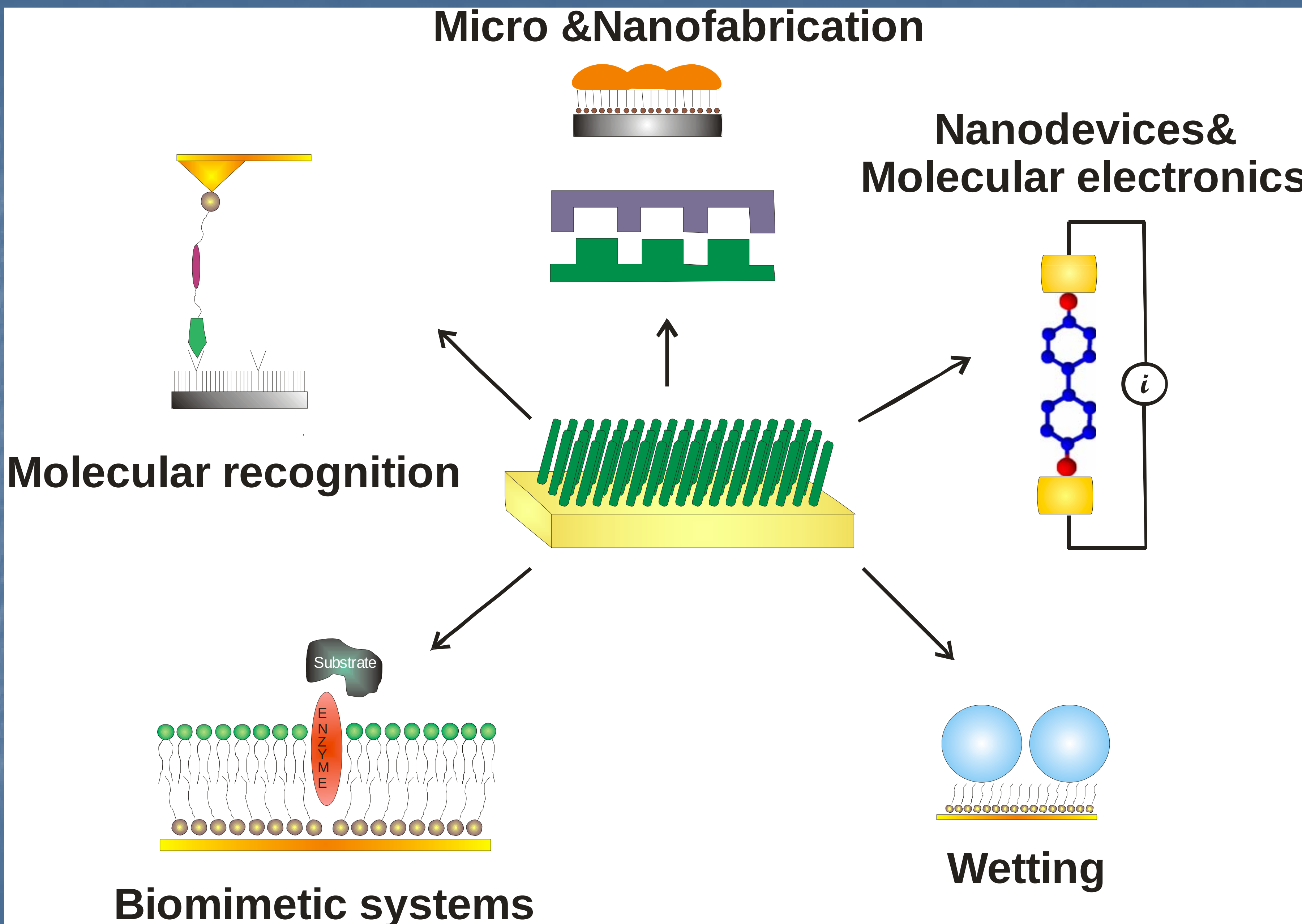






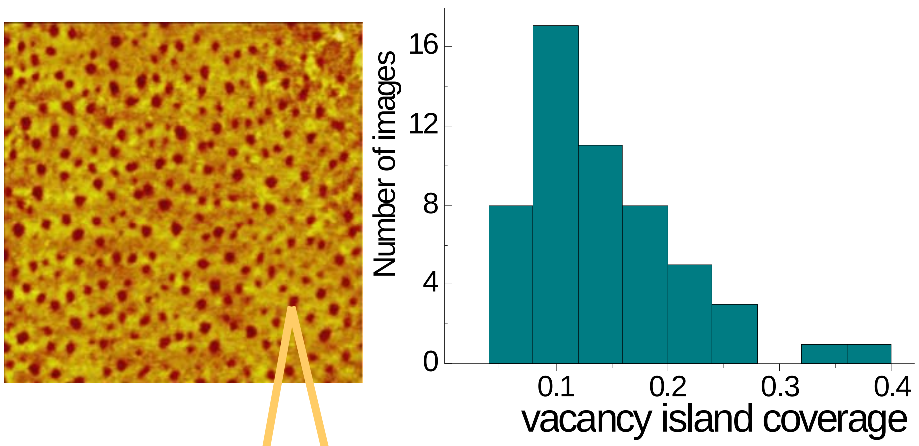
Hexanethiolate self-assembly on reconstructed Au(111) from gas phase

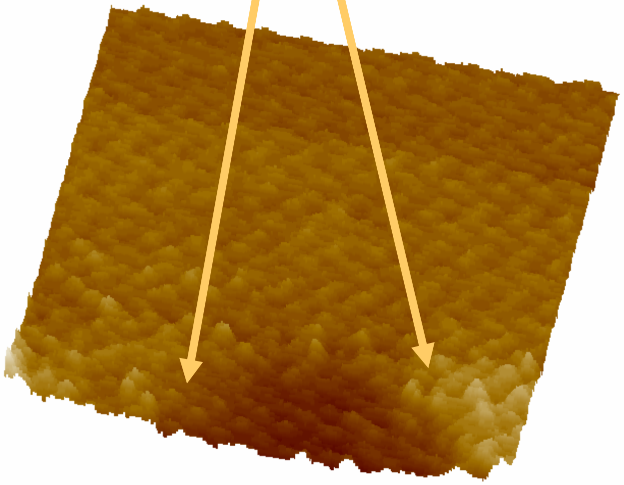
G. E. Poirier, Chem. Rev. 97 #4, 1117, (1997)



Micro &Nanofabrication
Nanodevices&
Molecular electronics
Molecular recognition
i
Substrate
ENZYME
Biomimetic systems
Wetting

Can STM help to elucidate the nature of the Au-S interface??



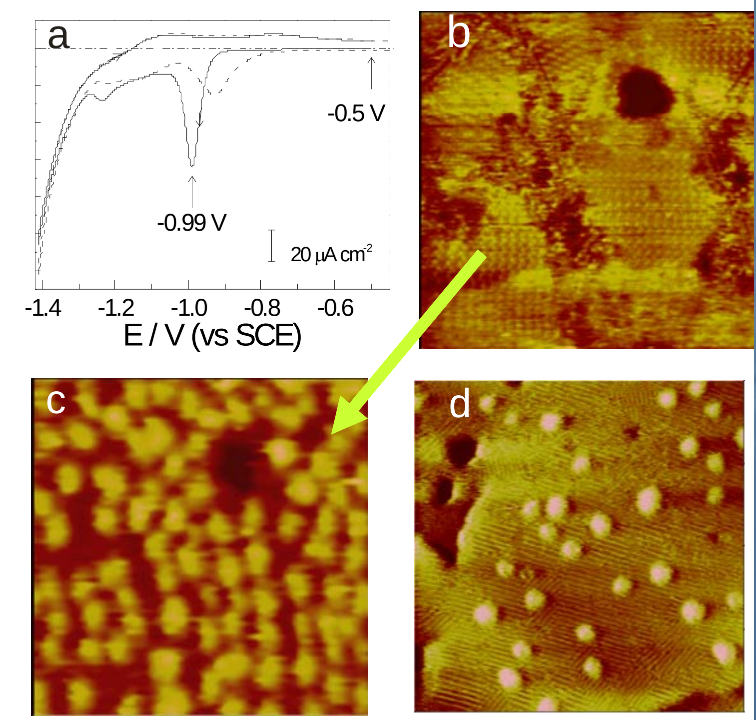


R-S-Au-S-R vs RS-Au

0.165 0.33

Island or vacancy coverage

Desorption experiments:
Au adatom islands



Source of adatoms
vacancy islands

INIFTA
CONICET
UNLP
FACULTAD DE CIENCIAS EXACTAS
DEPARTAMENTO DE QUÍMICA

SPM & Surface Physical Chemistry Group

Roberto Salvarezza
María Elena Vela
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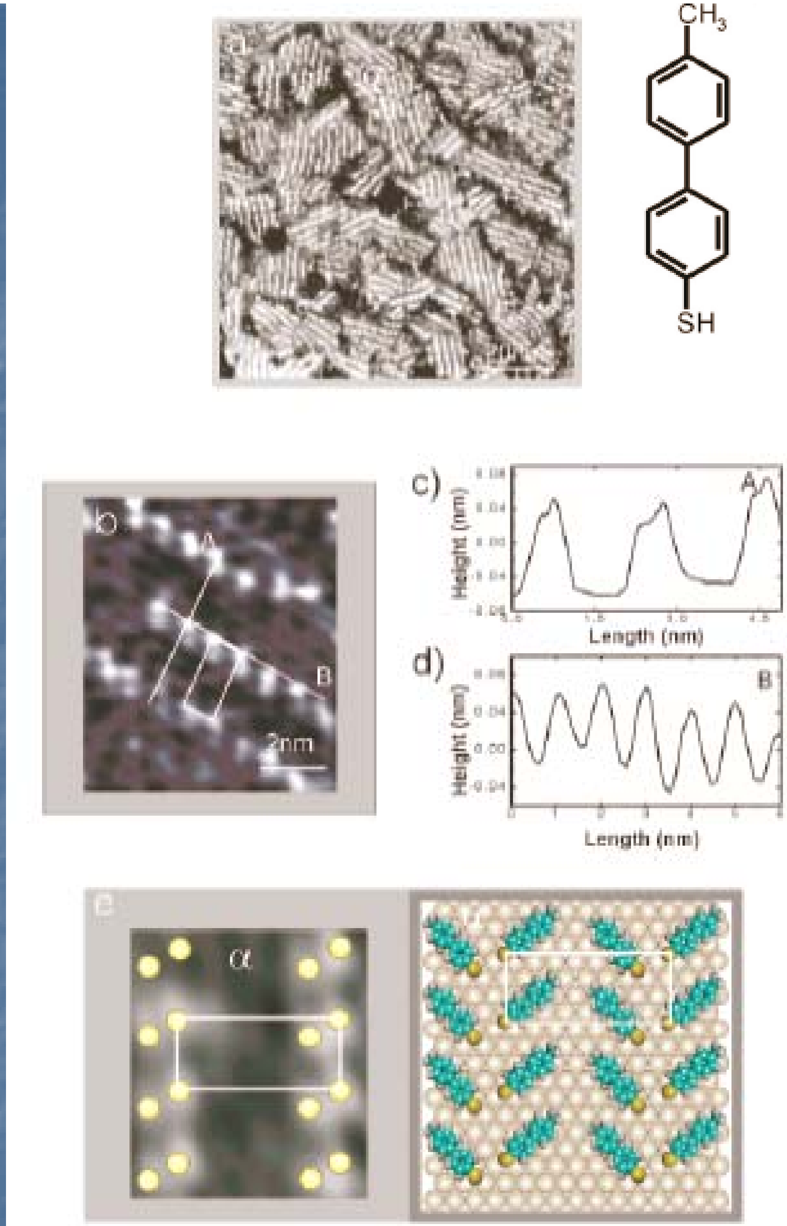
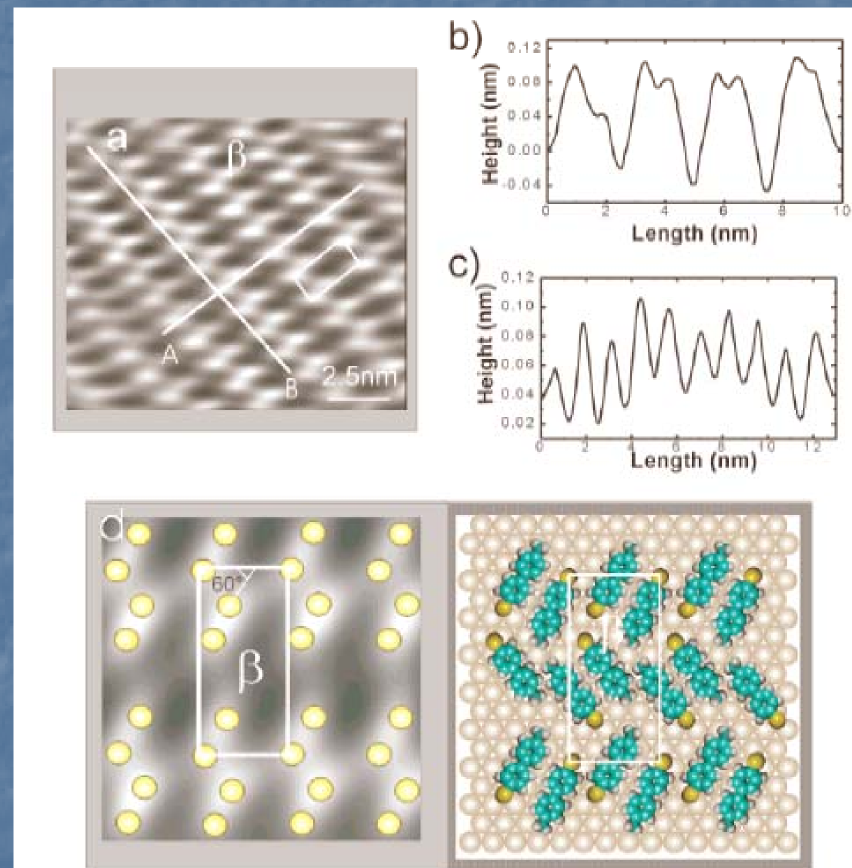
Guillermo Benítez
Mariano Fonticelli
Carolina Vericat
Doris Grumelli
Federico Castez
Francisco Ibañez
Aldo Rupert
Cecilia Dos Santos Claro
Antonieta Daza Millone
Carolina Díaz
Gaston Corthey
Emiliano Cortes
Constanza Flores
Eva Pensa
Alejandra Floridia
Julio Azcarate

http://nano.quimica.unlp.edu.ar

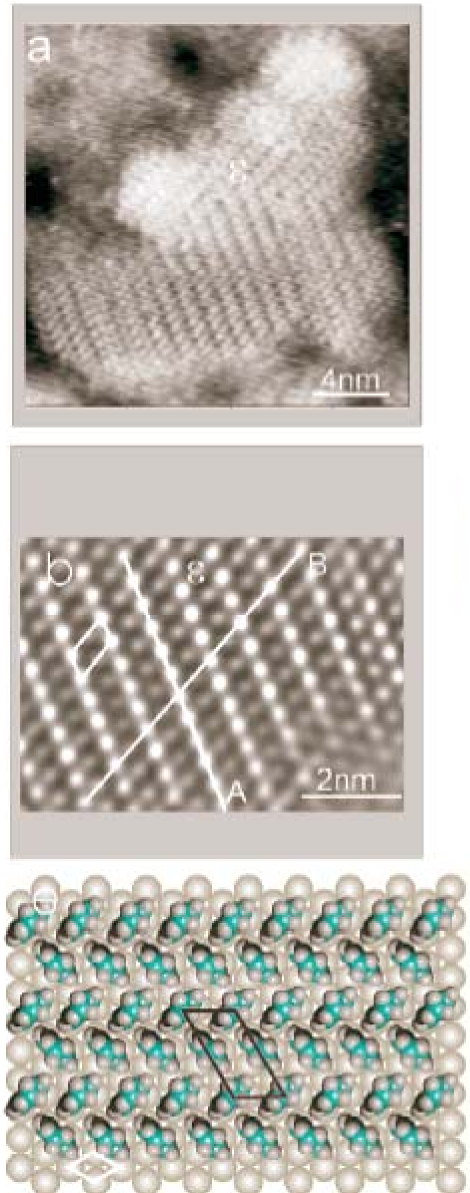
Aromatic Thiols



stripe phase
(lying down)

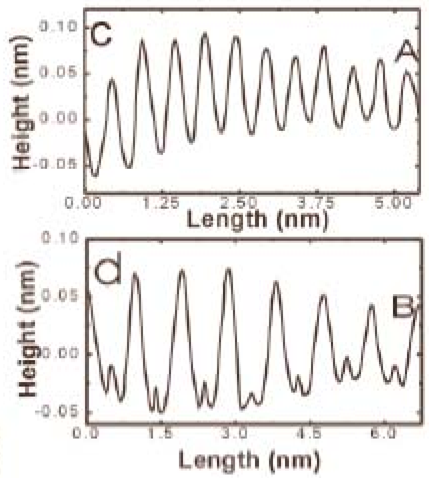


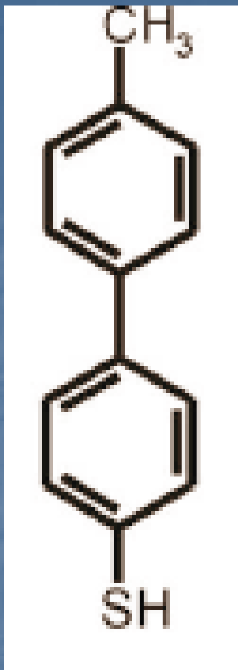
W. Azzam, C. Fuxen,.A. Birkner, H-.T. Rong,M. Buck, C. Woll
Langmuir 2003, *19,* 4958-4968

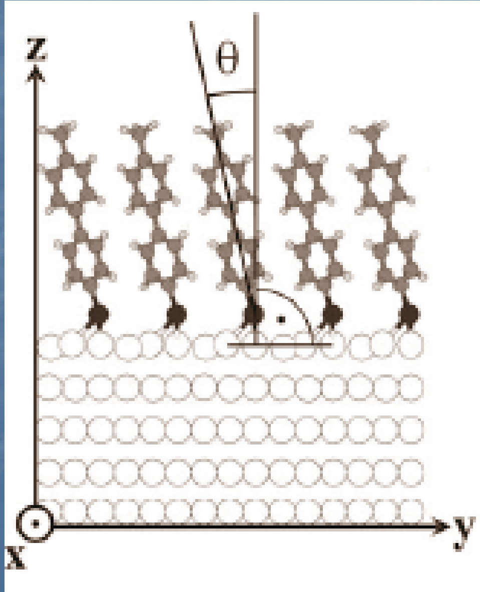


Standing up phase

2√3x√3 R30°
Tilt 30°

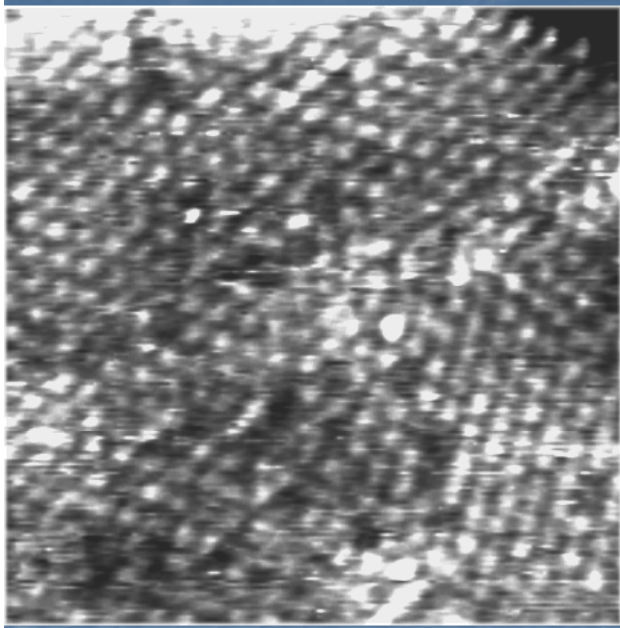




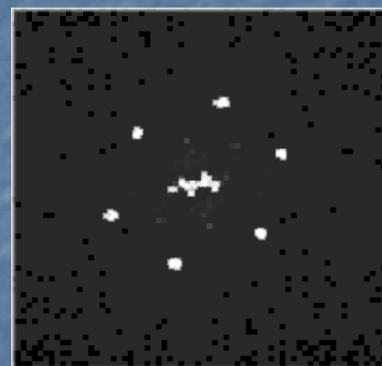


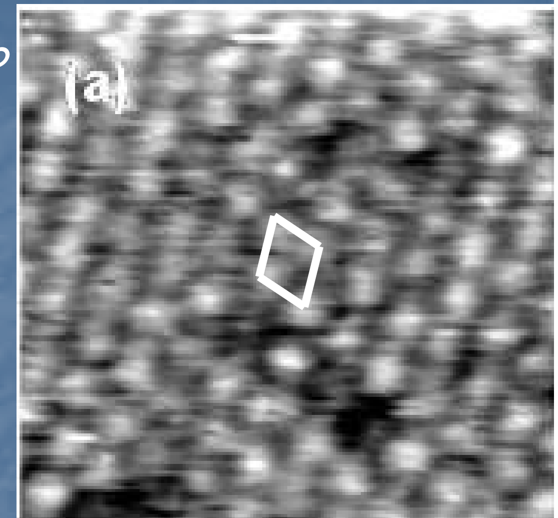
Alkanethiol SAMs on Ag(111)

Number carbon atoms > 2



distorted $\sqrt{7} \times \sqrt{7}$ R 19.1°
propanethiolate lattice





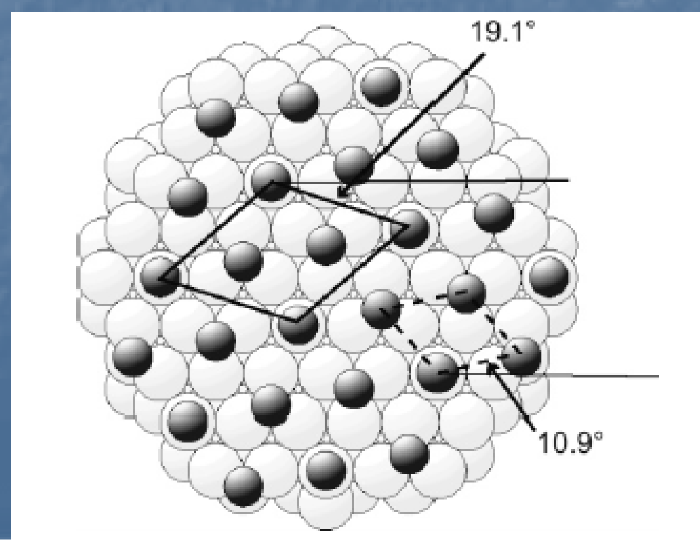
d = 0.47 nm

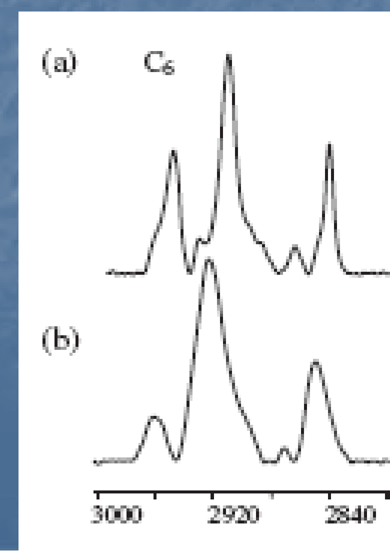
Azzaroni, O.; Vela, M. E.; Andreasen, G.; Carro, P.; Salvarezza,R. C. *J. Phys. Chem. B* 2002, *106*, 12267

methanethiol on Ag(111)

$\sqrt{7} \times \sqrt{7}$ R 19.1°

d = 0.43 nm

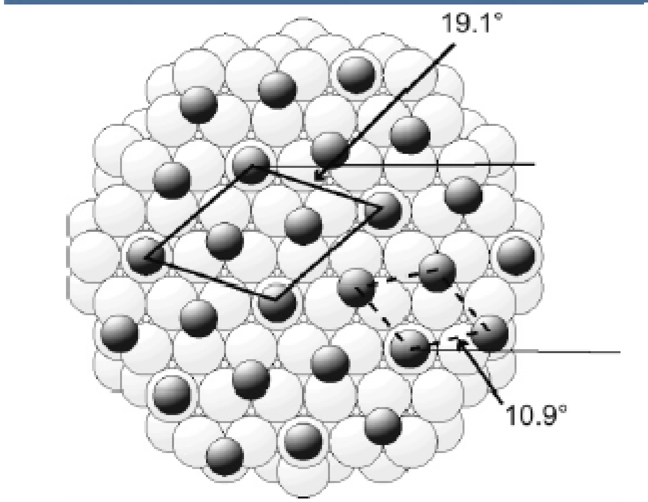


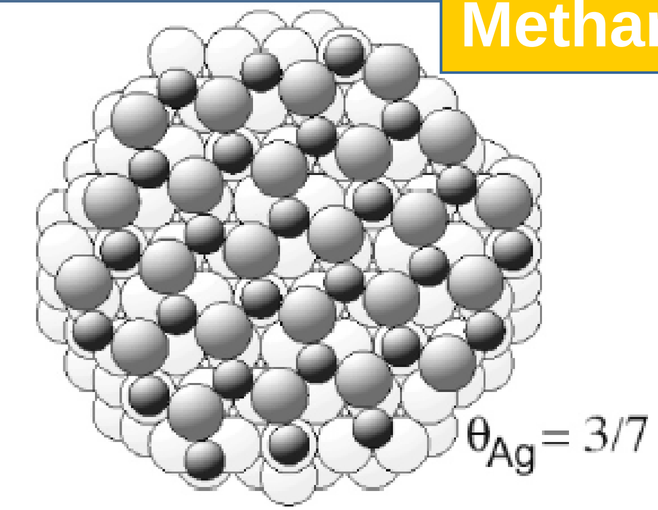


Unreconstructed

Reconstructed (model A)

Methanethiol on Ag(111)





Yu, Driver, Woodruff
***Langmuir* 2005, *21*, 7285**

J. Phys. Chem. B 110, 2164 (2006)

Parameter[a]	U	A
E_b, eV	-0.28	-0.75
d_{12}, %	-0.03	0.62
z_e(S), Å	1.883 (2.388)	0.651 (0.762)
r(S-Ag), Å	2.537 (2.434)	2.662 (2.672)
r(S-C), Å	1.834	1.836
α(S-C-H), º	108	110
α(surf-S-C), º	147 (123)	178 (179)

D. Torres, P. Carro, R.C. Salvarezza, F. Illas Physical Review Letters, 97,226103 (2006)