

From Self-Assembled Monolayers to Polymer Brushes

Rainer Jordan

Chair of Macromolecular Chemistry
Faculty of Chemistry and Food Chemistry
School of Science



Ultrathin, Thin, and Thick(er) Films on Solid Substrates

Monolayers

Multilayers

PSMs

Brushes

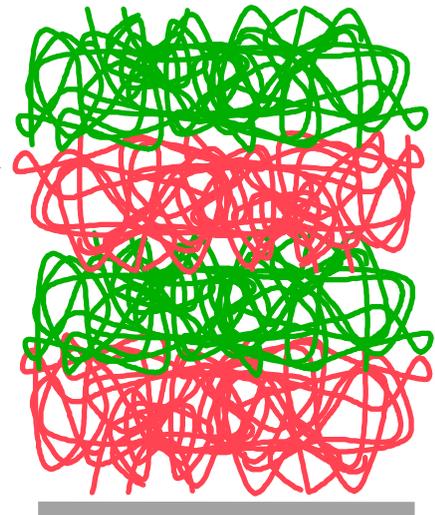
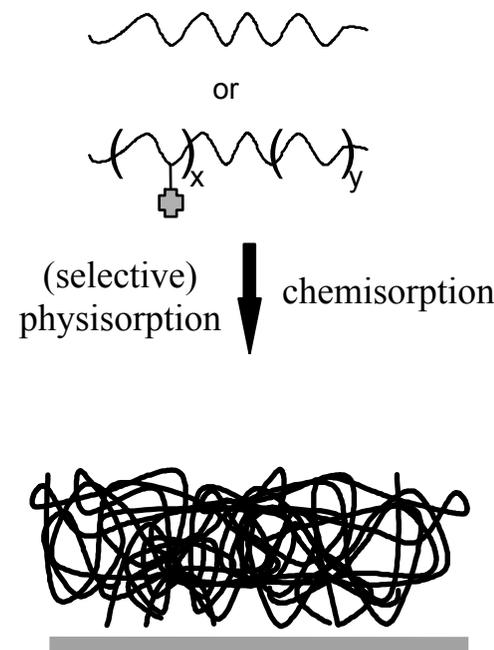
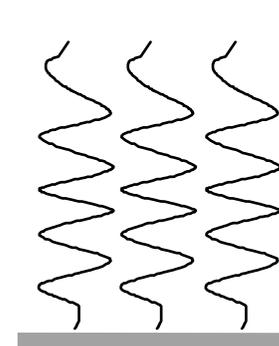
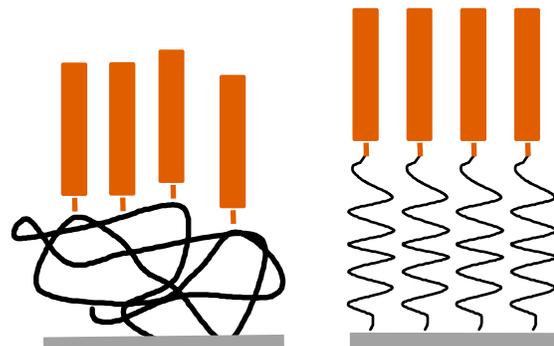
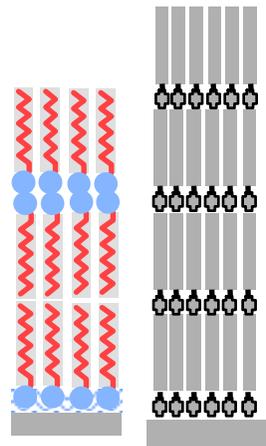
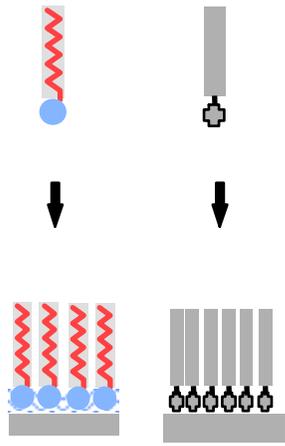
Polymer Layers

Self-assembly / LB-Deposition

Grafting-from / Grafting onto

Grafting onto

Casting



Å

Å - nm

Some nm

More nm-μm

nm - μm

μm

nanoscopic

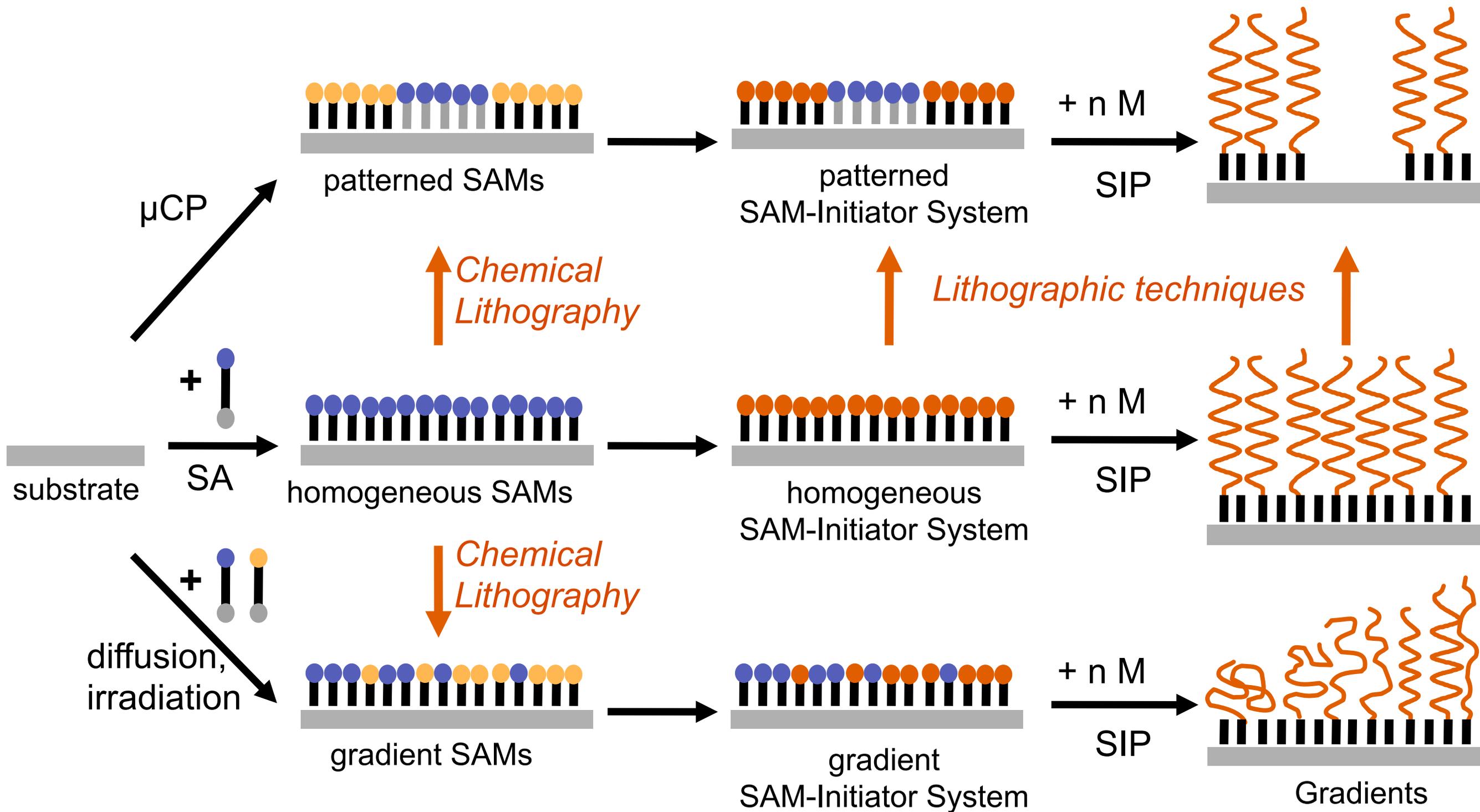
microscopic

PROBLEM:

ORDER

MOBILITY

Overview: From Self-assembled Monolayers to Polymer Brushes



PART I

Self-assembled Monolayers

SAMs

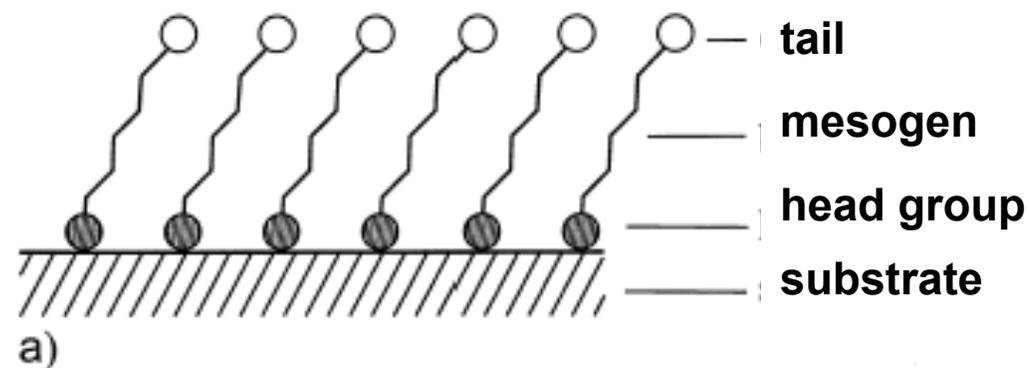
Definition: Self-assembled monolayers (SAMs)...

...are ordered, chemically and thermally stable two-dimensional aggregates that are formed **spontaneously** by the adsorption of surface active molecules onto a solid. The surface active molecule should feature:

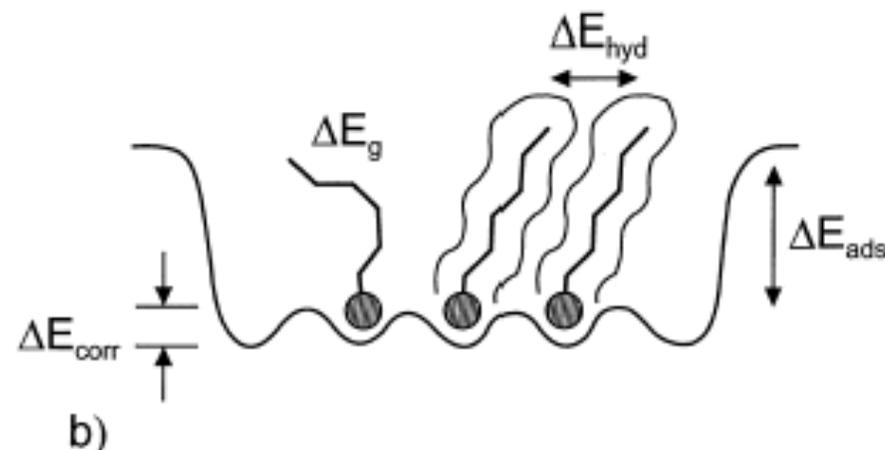
1. **a head group**, suitable for strong interactions or even chemical bonding with the surface,
2. **a mesogenic moiety** responsible for the 2D packing and favorable lateral interactions with the next neighbors and
3. **a tail or end group** determining the properties of the newly formed solid surface.

The SA of a film is a concerted interplay of various forces.

The overall stability of a SAM is determined by all inter- and intramolecular forces in the film.



(a) Cartoon of a SAM. Shaded circle indicates adsorbed or chemisorbed head group and open circle end group, which can be chosen from variety of chemical functionalities.



(b) Schematic of different energies. ΔE_{ads} stands for **adsorption energy**, ΔE_{corr} **corrugation (rippling)** of substrate potential experienced by molecule, ΔE_{hyd} **van der Waals interaction** of (hydrocarbon) tails, and ΔE_{g} energy of gauche defect (or, generally, deviation from fully stretched backbone).

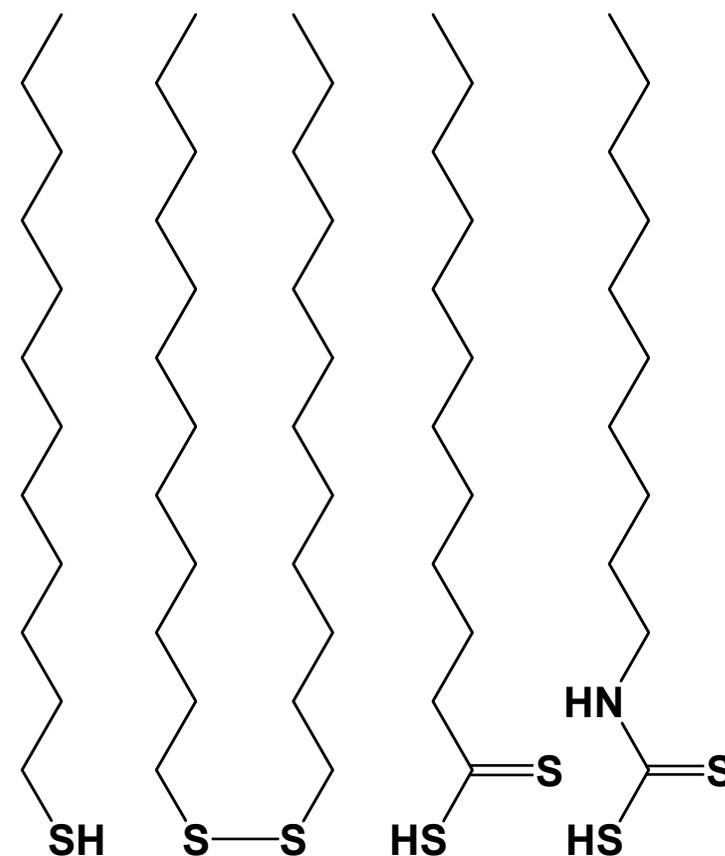
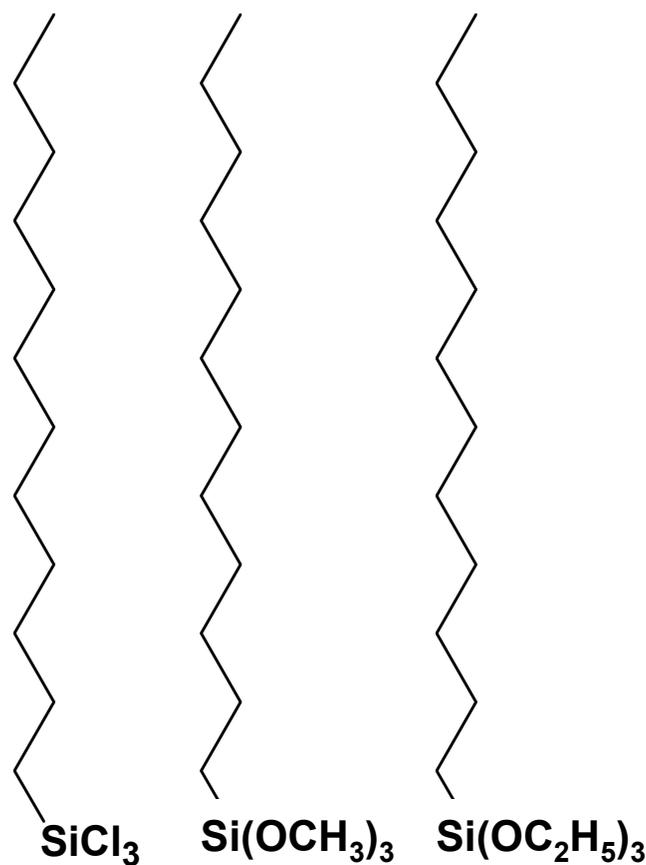
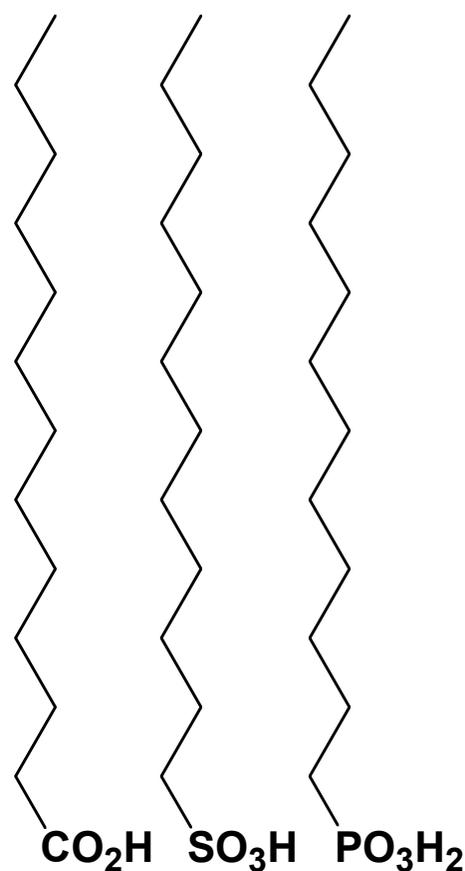
Substrate	Ligand, Precursor	Binding
Au	RSH, ArSH (thiols)	RS-Au
Au	RSSR' (disulfides)	RS-Au
Au	RSR' (sulfides)	RS-Au
Au	RSO₂H	RSO₂-Au
Au	R₃P	R₃P- Au
Ag	RSH, ArSH	RS-Ag
Cu	RSH, ArSH	RS-Cu
Pd	RSH, ArSH	RS-Pd
Pt	RNC	RNC-Pt
GaAs	RSH	RS-GaAs
InP	RSH	RS-InP
SiO₂ , oxides	RSiCl₃ , RSi(OR')₃	siloxane
Si/Si-H	(RCOO)₂ (neat)	R-Si
Si/Si-H	RCH=CH₂	RCH₂CH₂Si
Si/Si-Cl	RLi, RMgX	R-Si
metal oxides	RCOOH	RCOO⁻--- MO
metal oxides	RCONHOH	RCONHOH--- MO
ZrO₂	RPO₃H₂	RPO₃²⁻ -- - Zr^{IV}
In₂O₃/SnO₂ (ITO)	RPO₃H₂	RPO₃²⁻ --- Mⁿ⁺

G. Whitesides, Y. Xia,
Angew. Chem. 1998

R. Jordan, *From self-assembled
monolayers to polymer brushes*
Wiley-VCH 2003

Various types of SAMs – End Group // Substrate

- Acids (RCOOH, RSO₃H, RPO₃H₂) on oxide surfaces (AgO, Al₂O₃, Fe₂O₃)
- Trichlorosilanes (RSiCl₃), Trialkoxysilanes (RSi(OAlkyl)₃) on OH surfaces (SiO₂ (Si-OH), Al₂O₃, OH-substituted polymers)
- Sulfur compounds on metallic surfaces (Au, Ag, Cu, Pt, Pd) and on GaAs.



AgO, Al₂O₃, Fe₂O₃,...

Al₂O₃, TiO₂, SiO₂,...

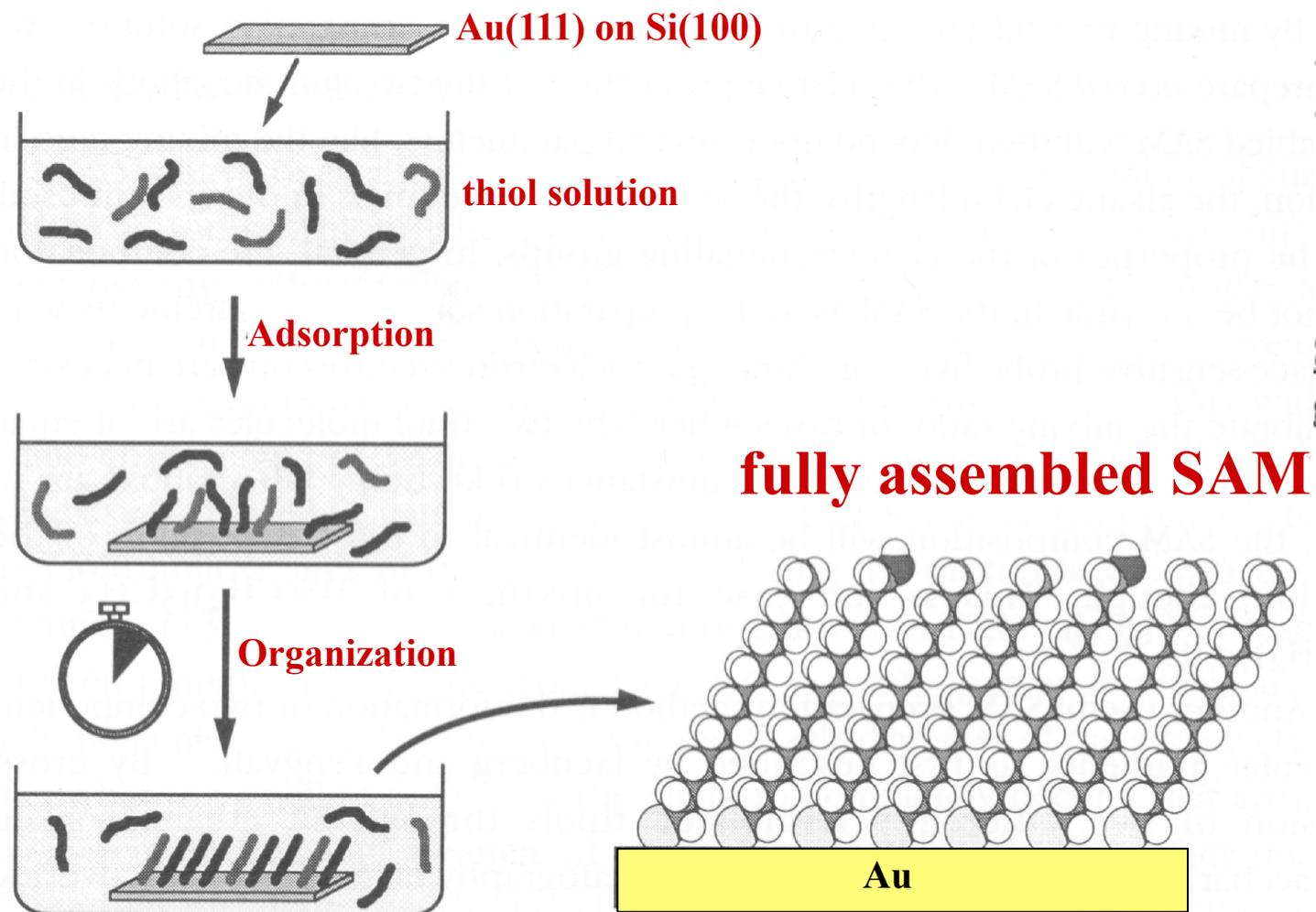
Au, Ag, Cu, Pt, Pd,...

oxides

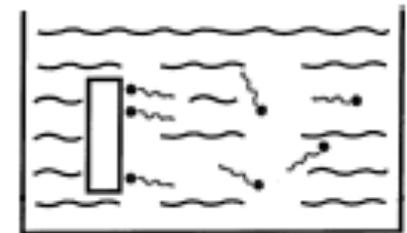
coin metals

SAMs of Thiols – Experimental

In the preparation of SAMs, the substrate is immersed into a dilute (10 mM to 1 mM) solution of the desired thiol. For thiols on gold, initial adsorption is fast (seconds); then an organization phase follows which should be allowed to continue for **> 15 h** for best results.



Self-Assembled Monolayers
grown from solution



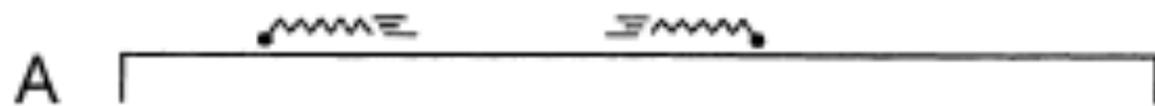
Self-Assembled Monolayers
grown from vapor



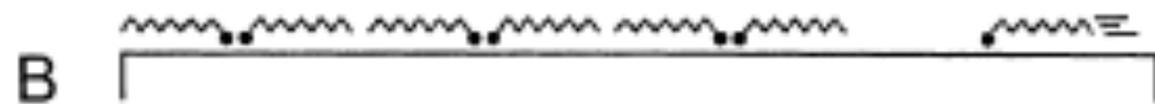
Alkanethiols – Film Formation

Evolution of structures of decanethiol on Au(111) during growth. (not all are stable equilibrium structures).

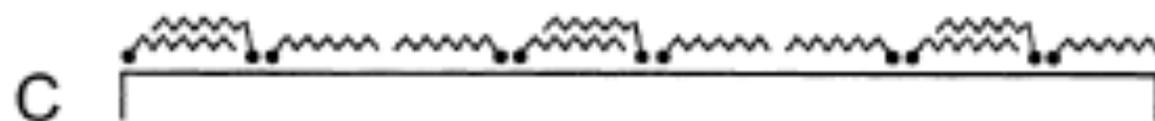
Preparation method: Adsorption from the gas phase in UHV conditions



(A) "Lattice gas" at very low coverage.



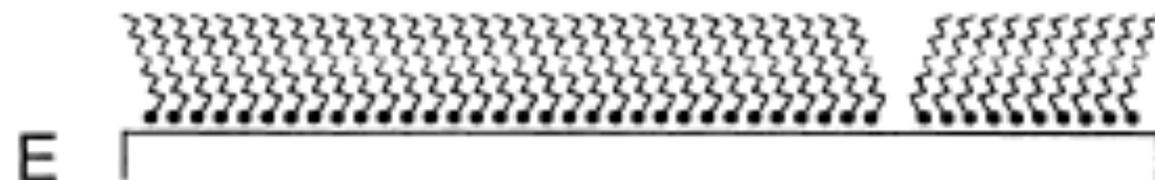
(B) Striped phase (for which two slightly different structures were reported).



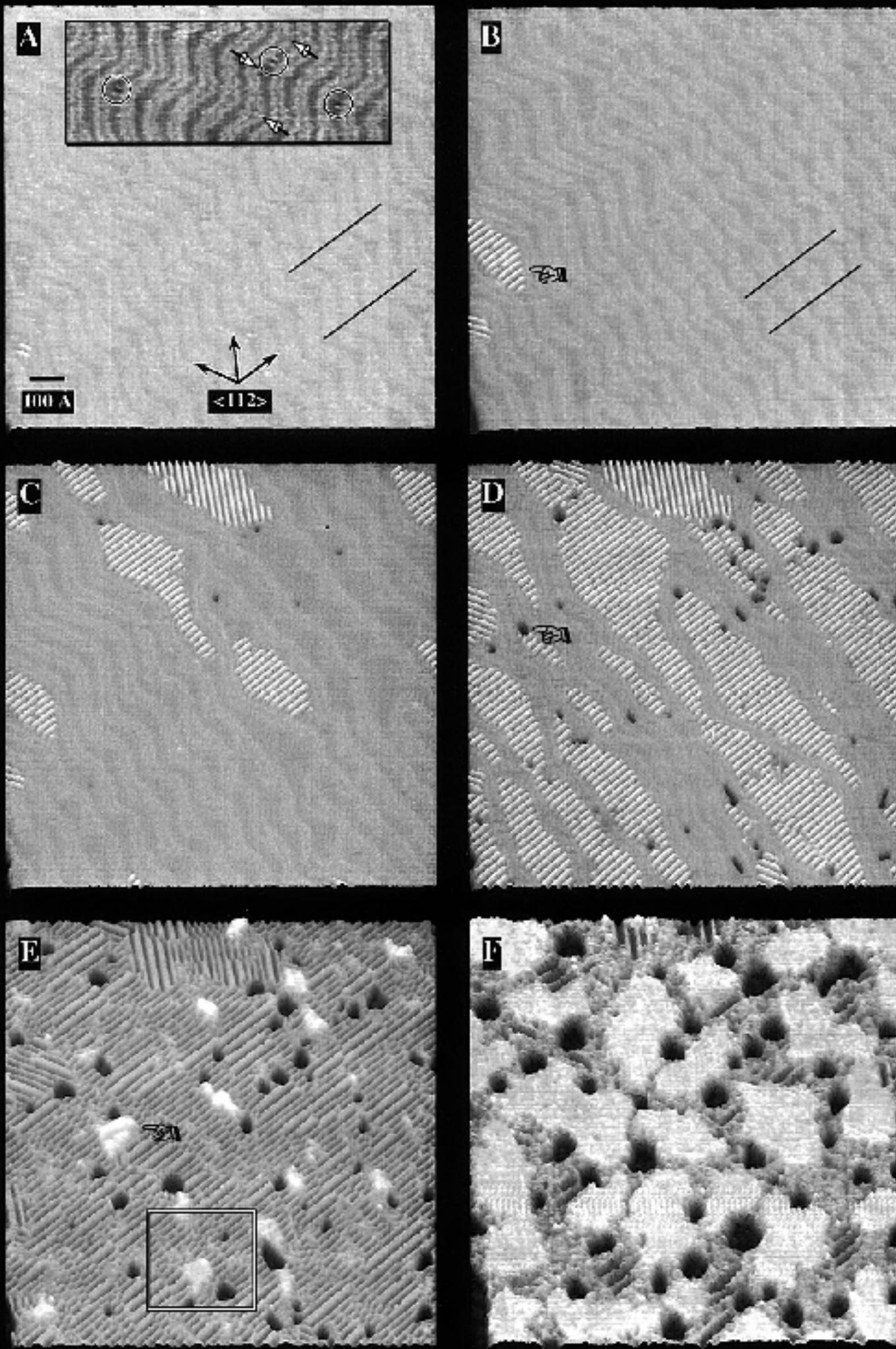
(C) Intermediate structure



(D) Intermediate structure



(E) Standing-up Phase, which superlattice of hexagonal ($\sqrt{3} \times \sqrt{3}$)R30° base or rectangular ($2\sqrt{3} \times 3$) unit cell.



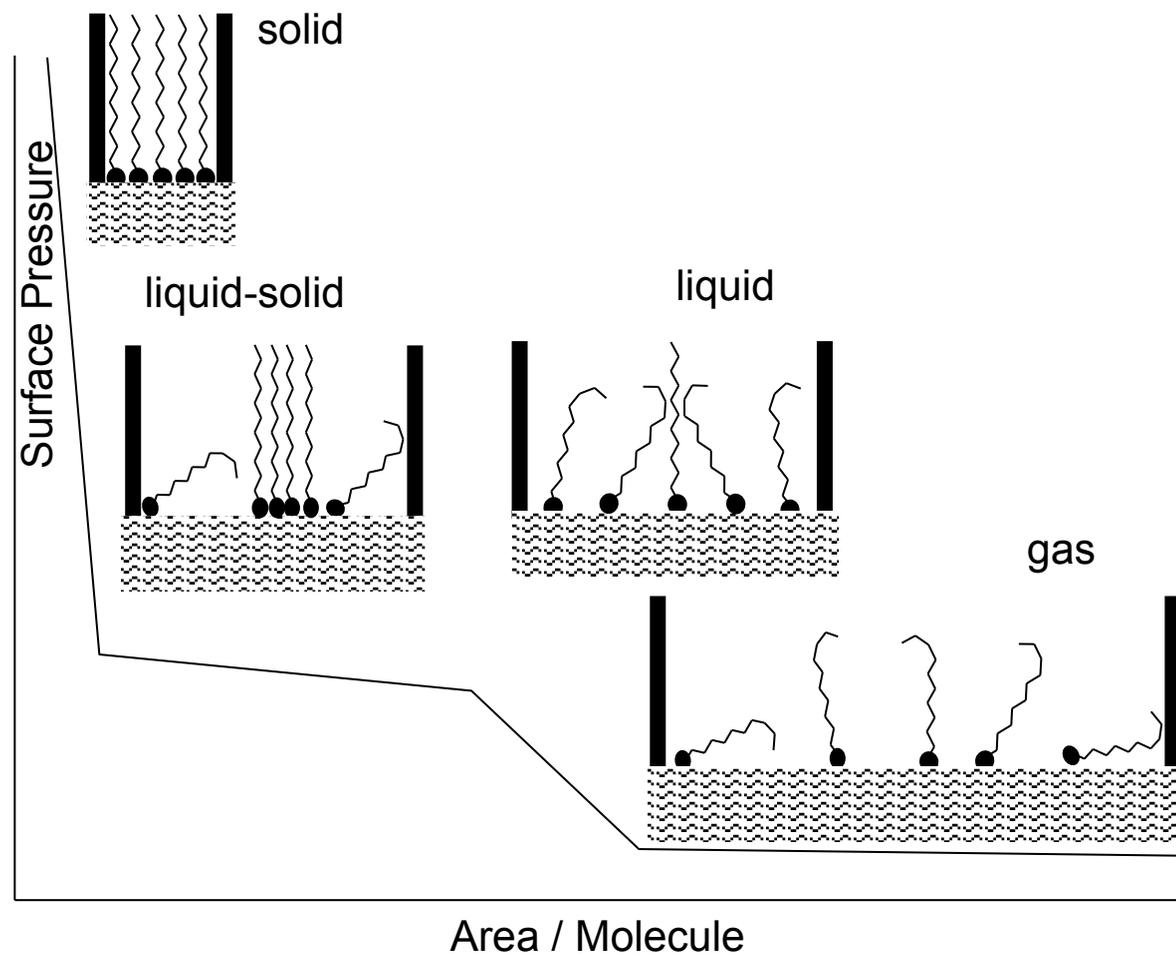
Constant-current STM scans for increasing exposures of mercaptohexanol vapor on Au(111).

- (A) clean "herringbone" reconstructed **Au(111) surface**; the inset shows three stable islands nucleated between herringbone double rows after first stage of exposition.
- (B) **Striped phase** island (pointing finger).
- (C) Continued striped phase growth displacing herringbone elbows.
- (D) Continued striped phase growth with Au vacancy islands (pointing finger) becoming visible.
- (E) Nucleation of **standing-up phase** within striped phase.
- (F) Growth of standing-up phase at expense of striped phase until saturation.

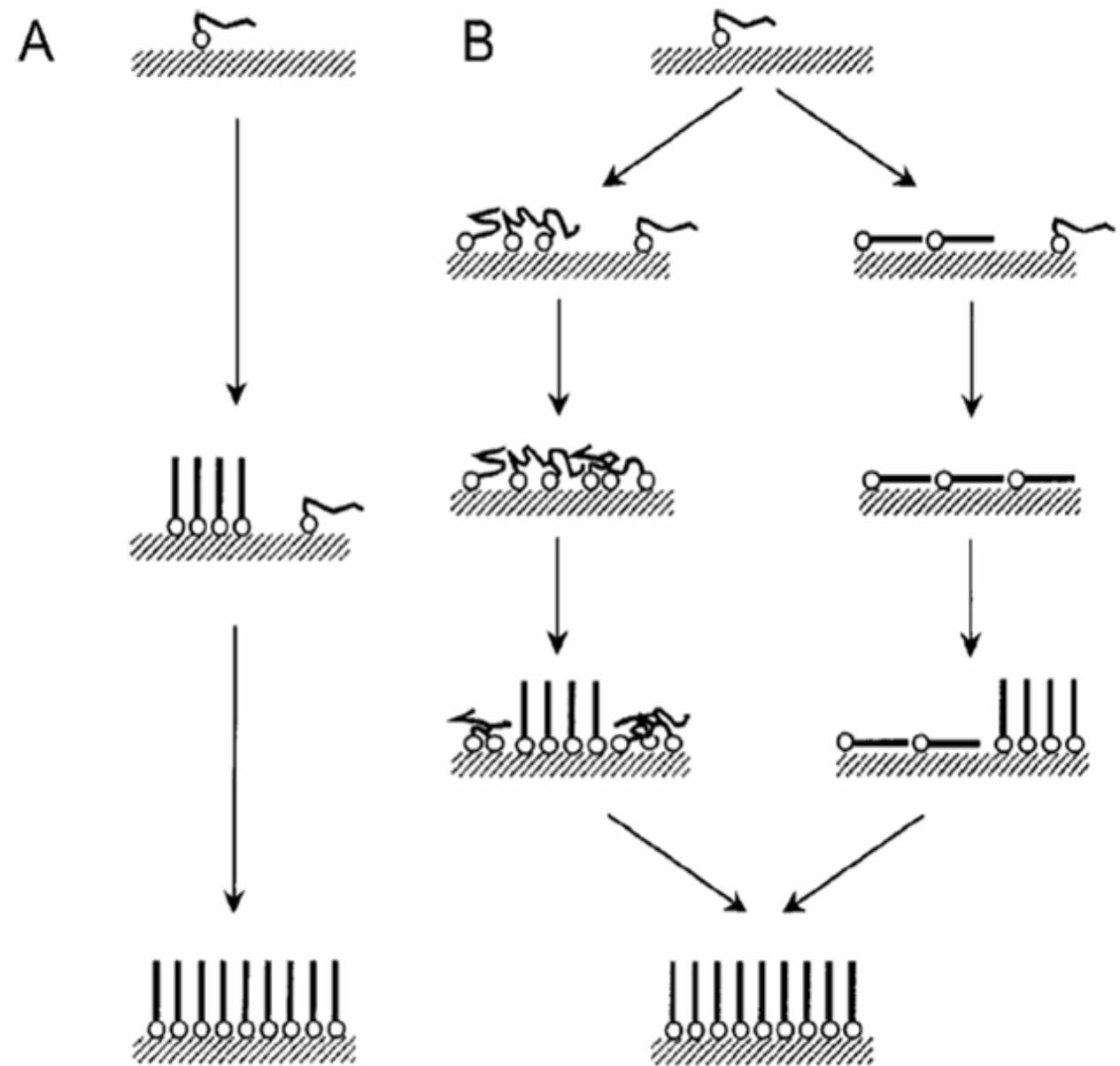
From G.E. Poirier, *Langmuir* 1999.

LB-FILMS vs. SAMs

Langmuir-Blodgett Monolayers



Self-assembled Monolayers



Alkanethiols – Film Formation Self-Assembly

The SFG signal is a measure for the amount of surface bonded groups in a non-centrosymmetric environment:

Different time scales (including long-time effects) in solution-growth of docosanethiol (SH-(CH₂)₂₁-CH₃) on Au, derived from vibrational mode intensity (detected by SFG) as function of immersion time.

1. First step is the chemisorption of sulfur head group, i.e., signal similar to that of the previous Langmuir isotherm. (*strong increase of v_{as}*)

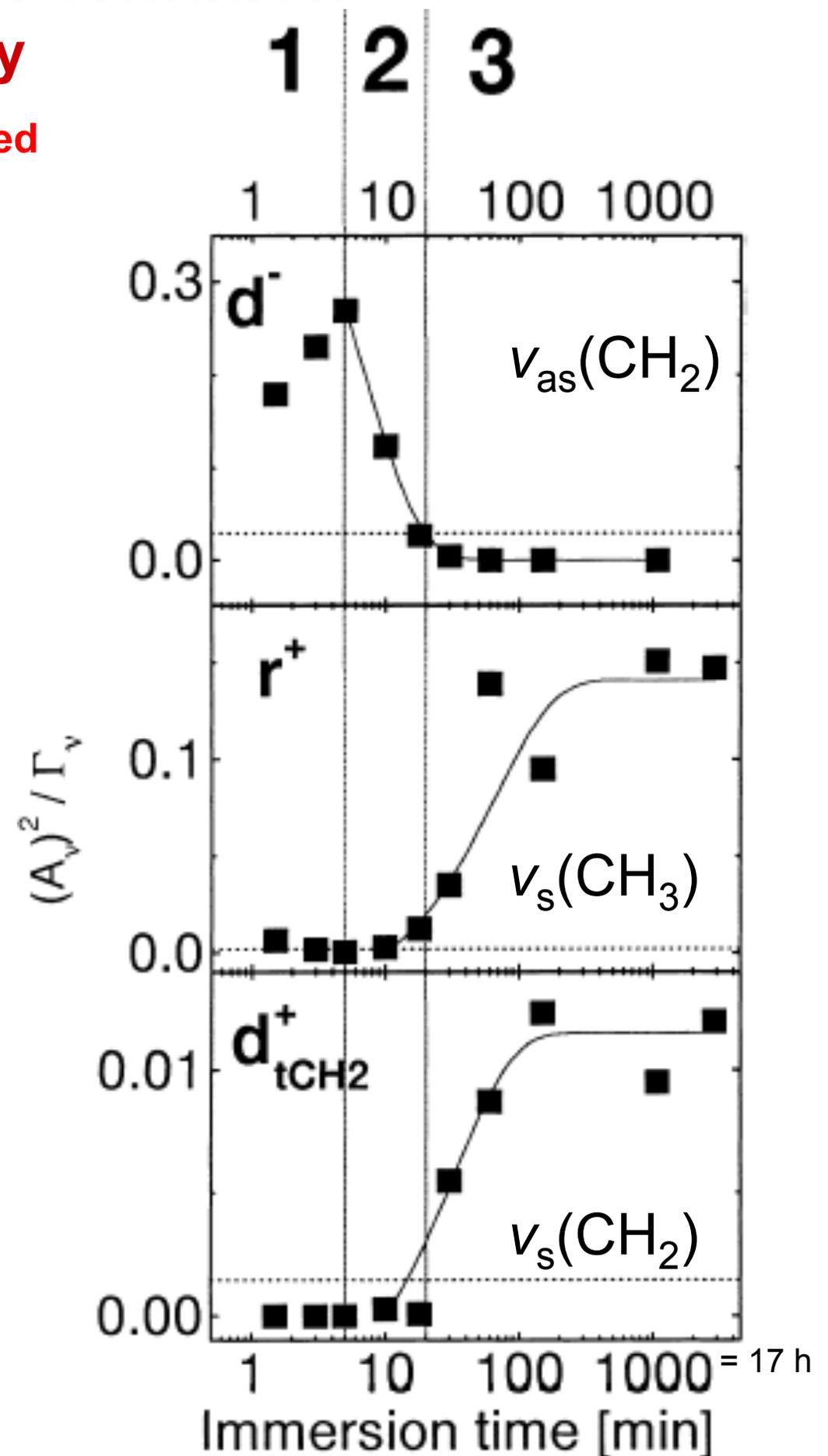
- FAST

2. Second phase corresponds to a straightening of chains, represented by *decrease of the d^- mode (antisymmetric CH₂ becomes invisible)*. CH₂ group adjacent to end group already exhibits slower ordering (represented by $d_{tCH_2}^+$ mode; symmetric).

- 3- 4 TIMES SLOWER

3. End of chain shows slowest ordering, as evidenced by evolution of $d_{tCH_2}^+$ mode of end groups (increase of *symmetric; CH₃ and CH₂*).

- 35 – 70 TIMES SLOWER

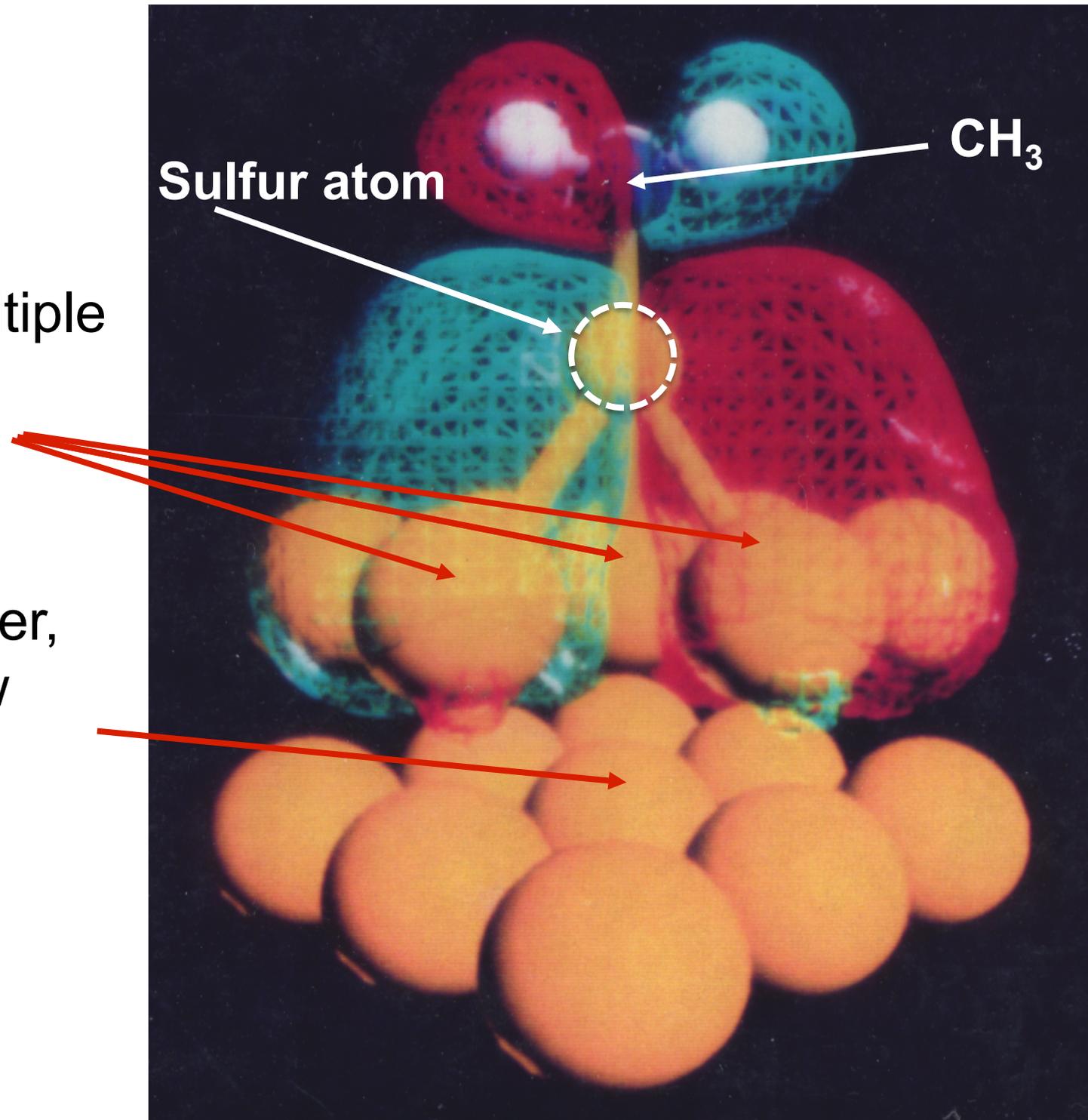


SAMs from Thiols – Chemistry

A side-view of the p-bonding orbital between the SCH_3 adsorbate and the $\text{Au}(111)$ surface in the hollow site position.

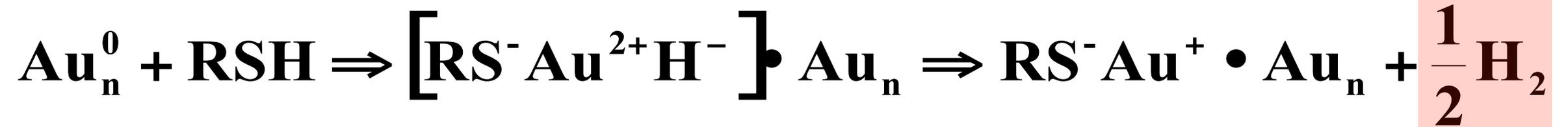
The bonding is NOT with a single gold atom, but with multiple gold atoms at the surface.

A gold atom in the second layer, directly underneath the hollow site, participates in the bonding.



SAMs from Thiols – Chemistry

Chemisorption of thiols on Au(111) give Au⁺ thiolate (RS⁻) species probably by:



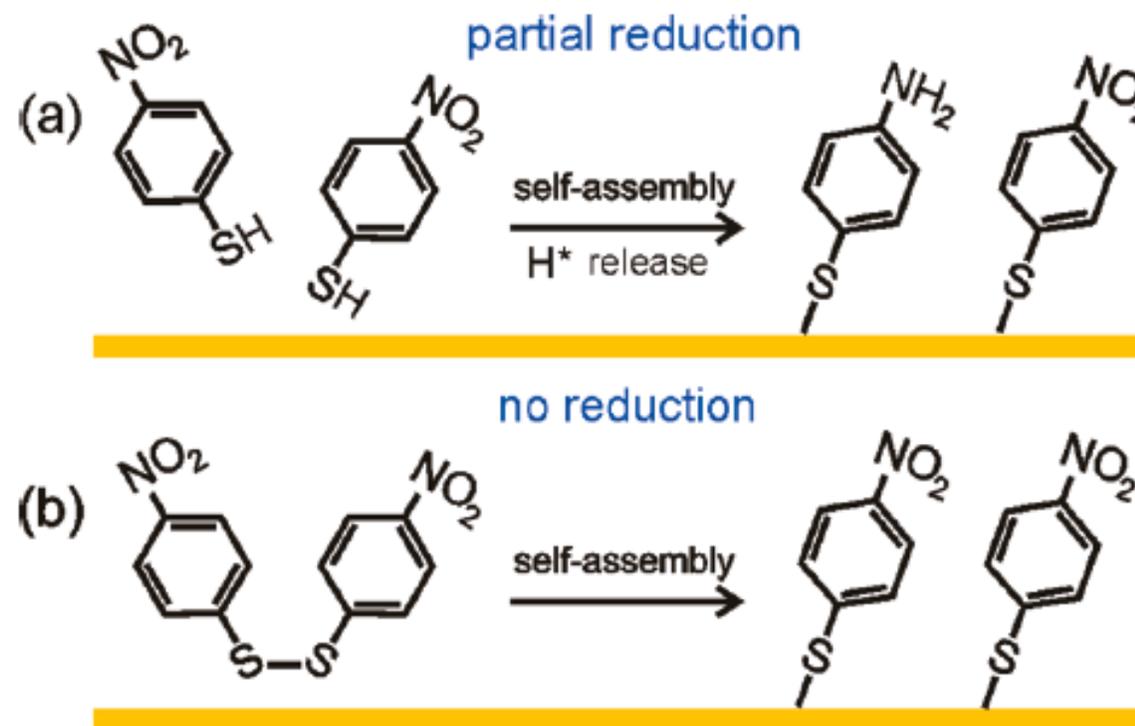
- The adsorbing species is the thiolate.
- The heat of adsorption is ~28 kcal/mol.
- The homolytic surface-S bond strength is ~44 kcal/mol.
- The proton leaves as H₂ – however even in 3D SAMs on nanoparticles with high surface area/mass *no* H₂ could be detected until ...

SAMs from Thiols – Chemistry

H₂ found!

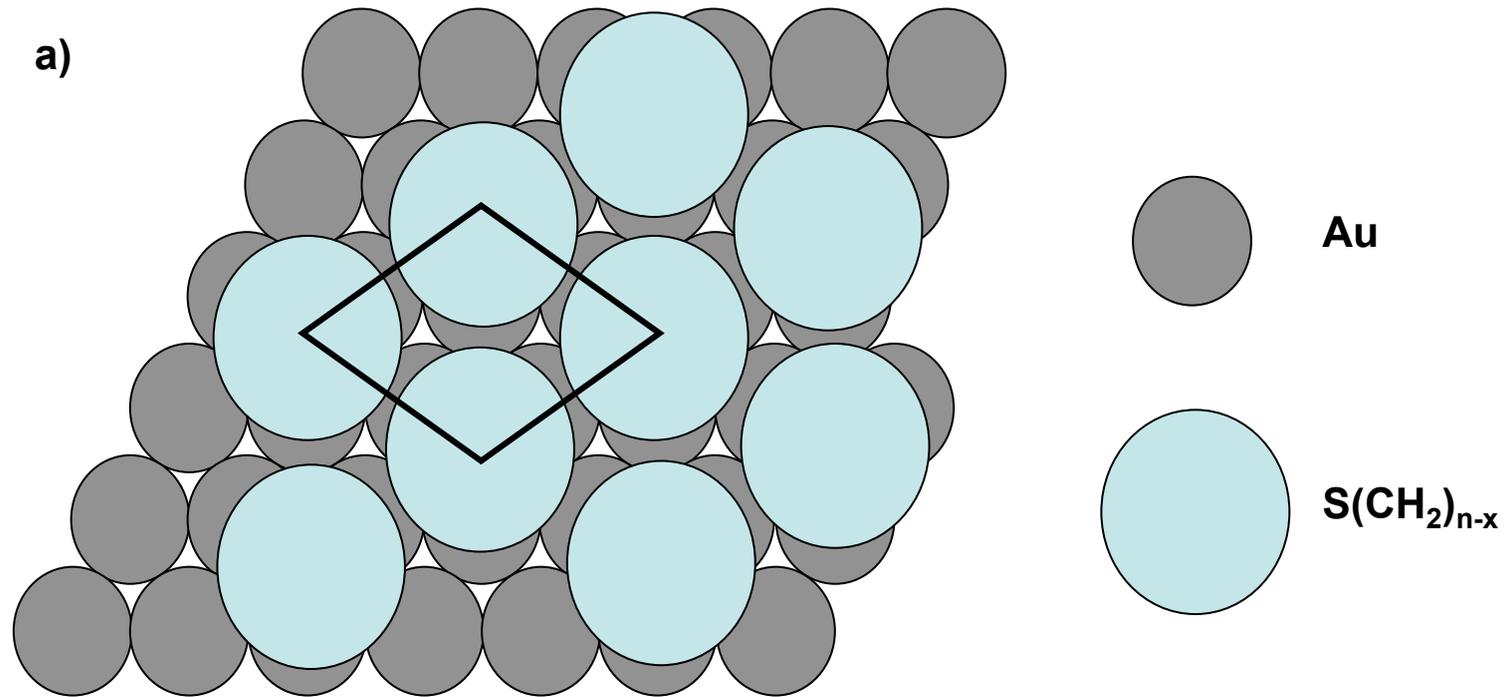
L. Kankate, A. Turchanin, A. Götzhäuser,

On the release of hydrogen from the S-H groups in the formation of self-assembled monolayers of thiols.
Langmuir **2009**, 25, 10435-10438.

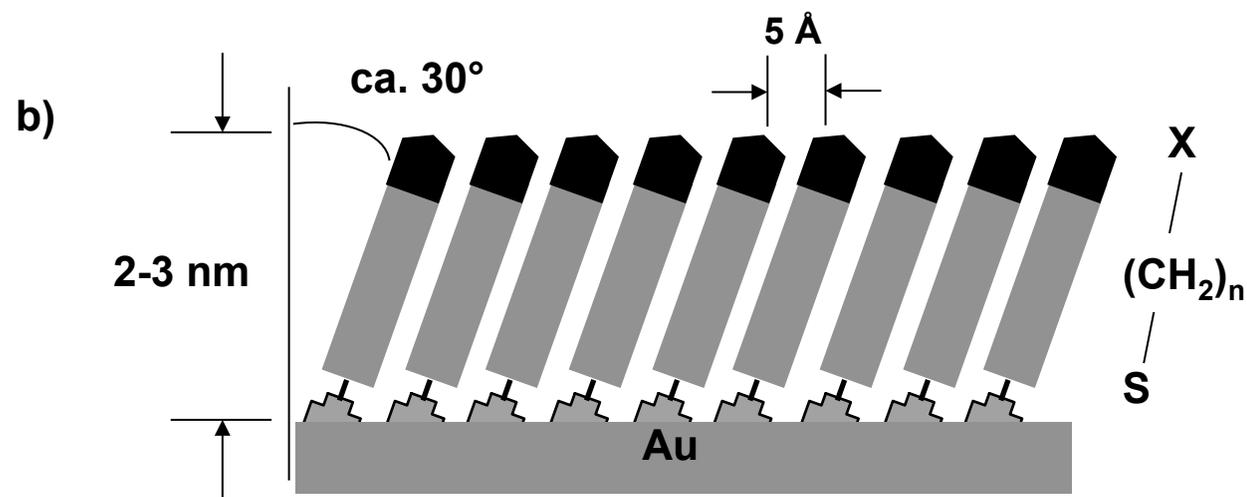


As determined by XPS, SA of thiols lead to a partial reduction of a nitro group to amine, while adsorption of the analogue disulfide compound did not show signs of reduction. **The reduction of the nitro headgroups is accounted to the released H^{*}.**

Alkanethiols – Stand-up Phase

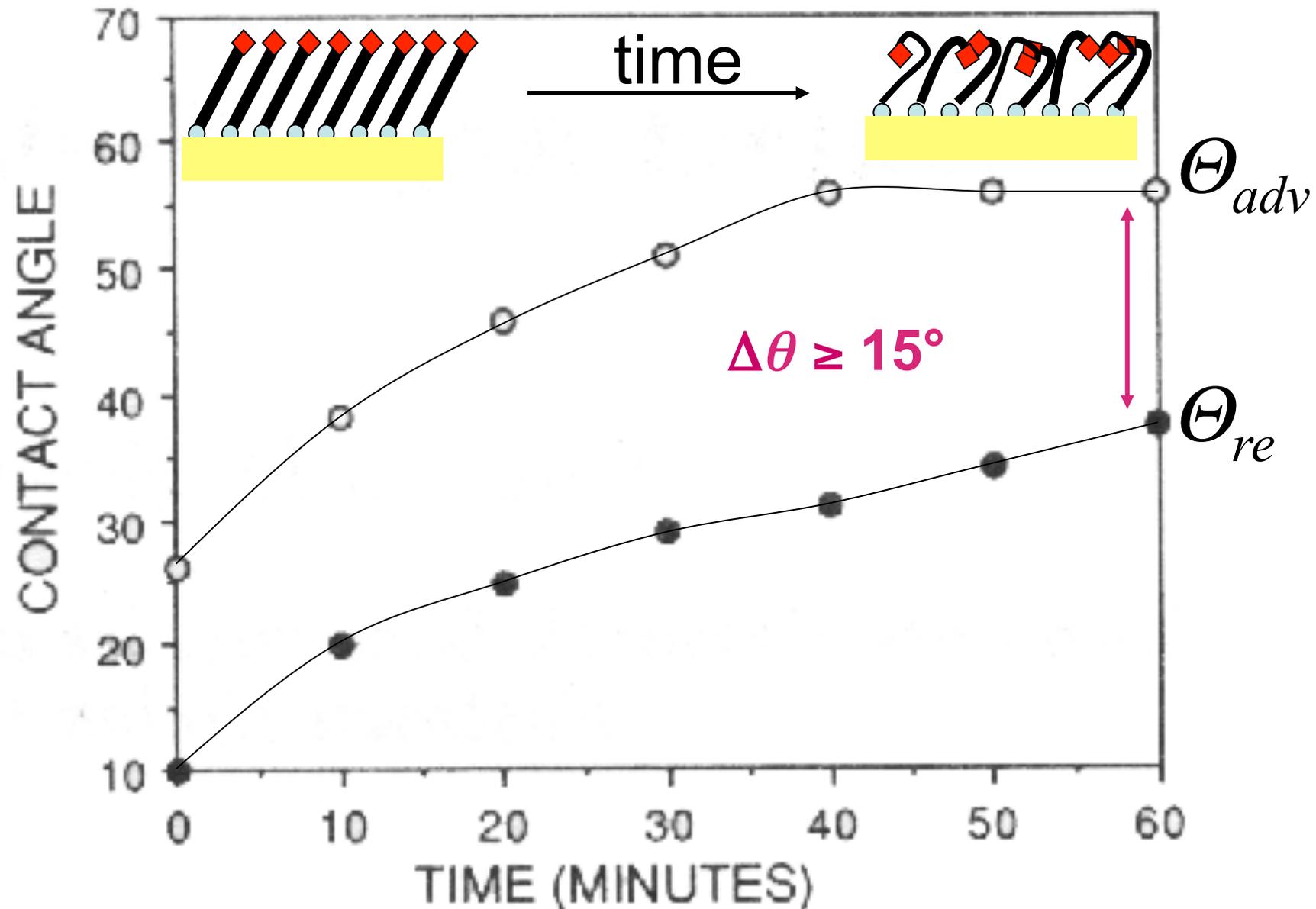


A schematic model of the $(\sqrt{3}\times\sqrt{3})R30^\circ$ overlayer structure formed by alkanethiolate SAMs on Au(111). This structure places the thiols in S...S distance of 4.99 \AA , which results in their tilt to reestablish the vdW interchain interactions. The angle can be deduced using FTIR spectroscopy.



Alkane Mesogen: Surface Reconstruction

Advancing and receding water contact angles on SAMs of HUT [HO(CH₂)₁₁SH] SAMs on Au(111)



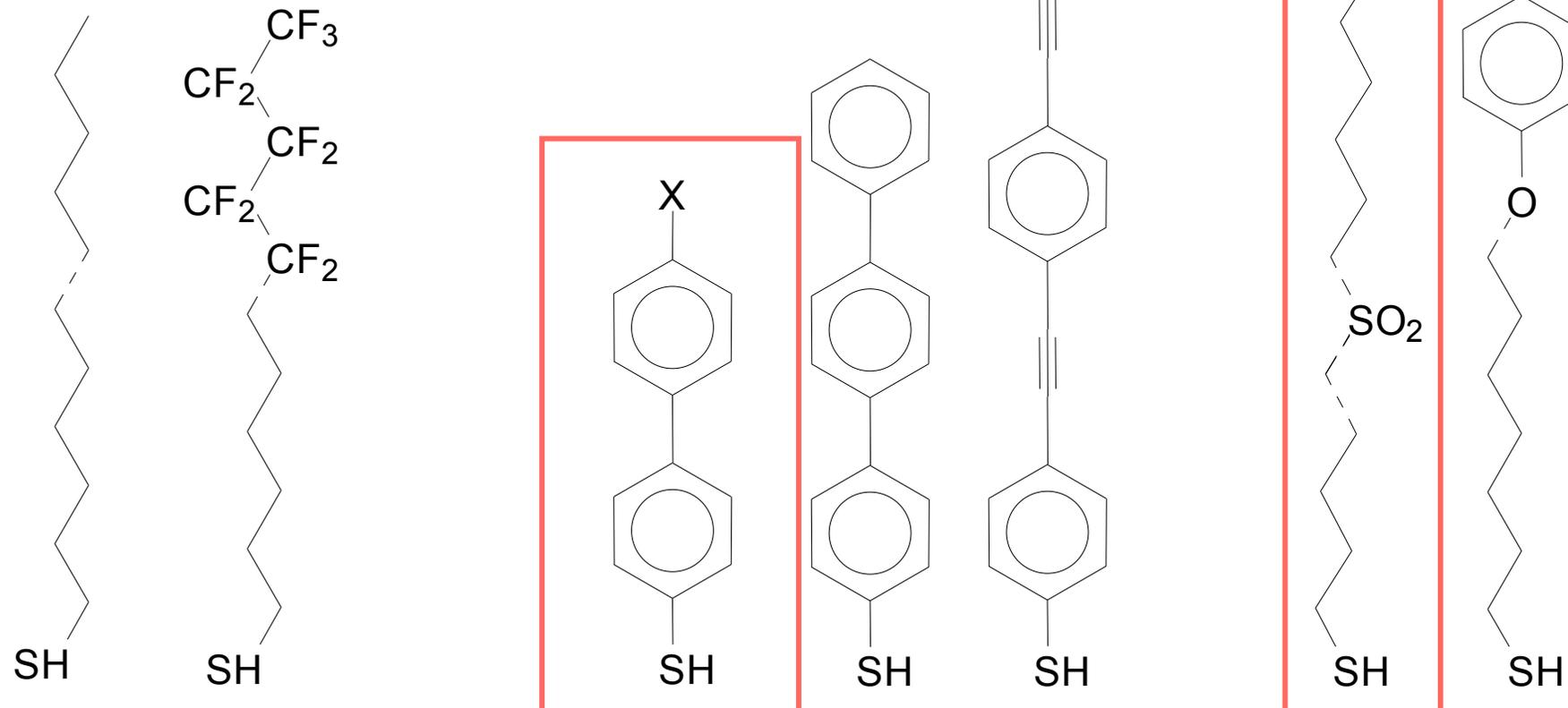
Highly polar surfaces of SAMs of n-alkylthiols undergo surface reconstruction when exposed to air to minimize the surface free energy

Various types of SAMs – Different Mesogens

In e.g. alkane thiols or silanes the ordering ('crystallization') lateral stability is provided by vdW – interactions between the methylene groups. Further stability can be introduced by e.g. dipole-dipole – interactions or $\pi\pi$ -interactions of aromatic mesogenes:

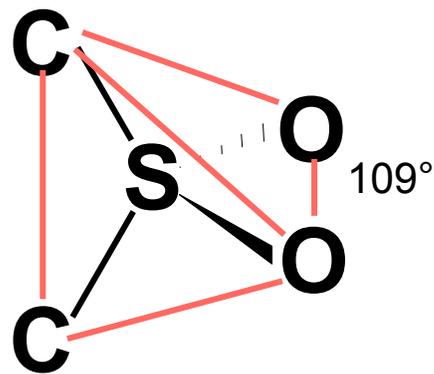
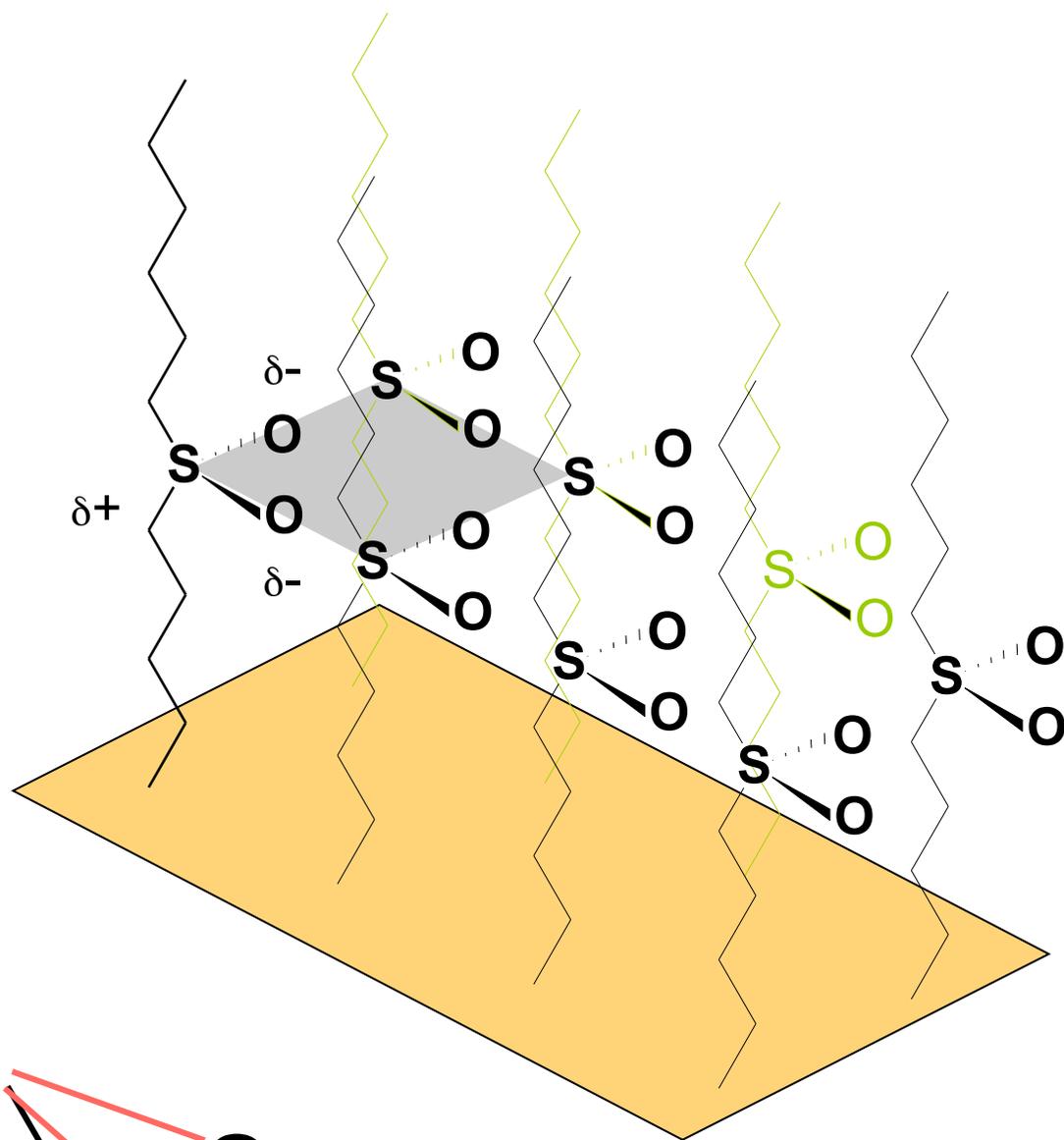
$(\text{CH}_2)_n$: with $n > 10$ stable SAMs are formed

$(\text{O})_n$: with $n \geq 2$ stable SAMs are formed



a.s.f....

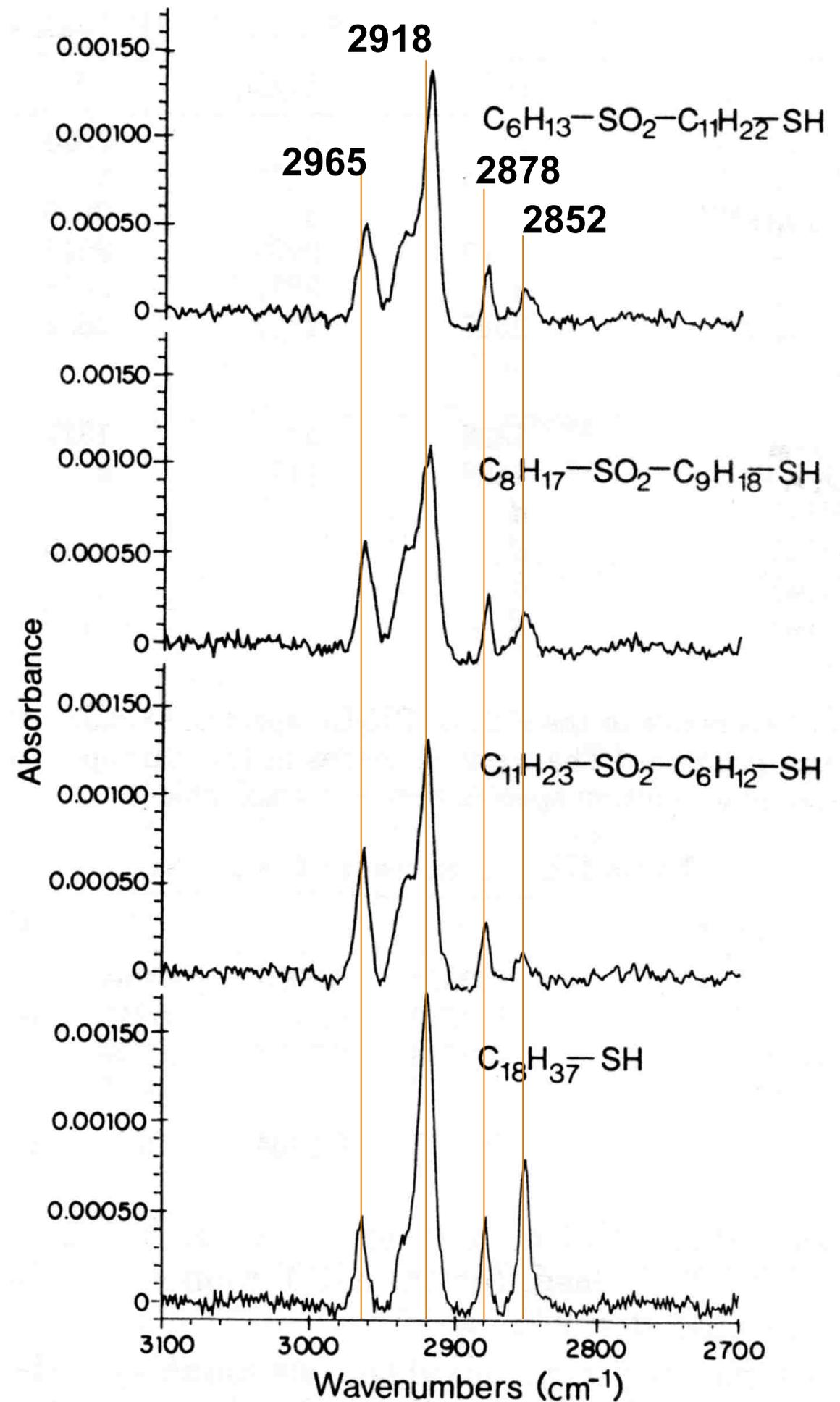
Various types of SAMs – Different Mesogens



in-plane dipole moment of the sulfone group: 1.6 D

S – O: 1.79 Å

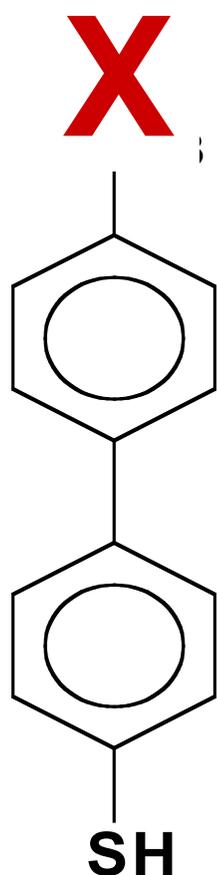
C – H: 1.1 Å → Introduction of free-volume ?



Self-Assembled Monolayers of RIGID Biphenyl Thiols

Why BIPHENYL?

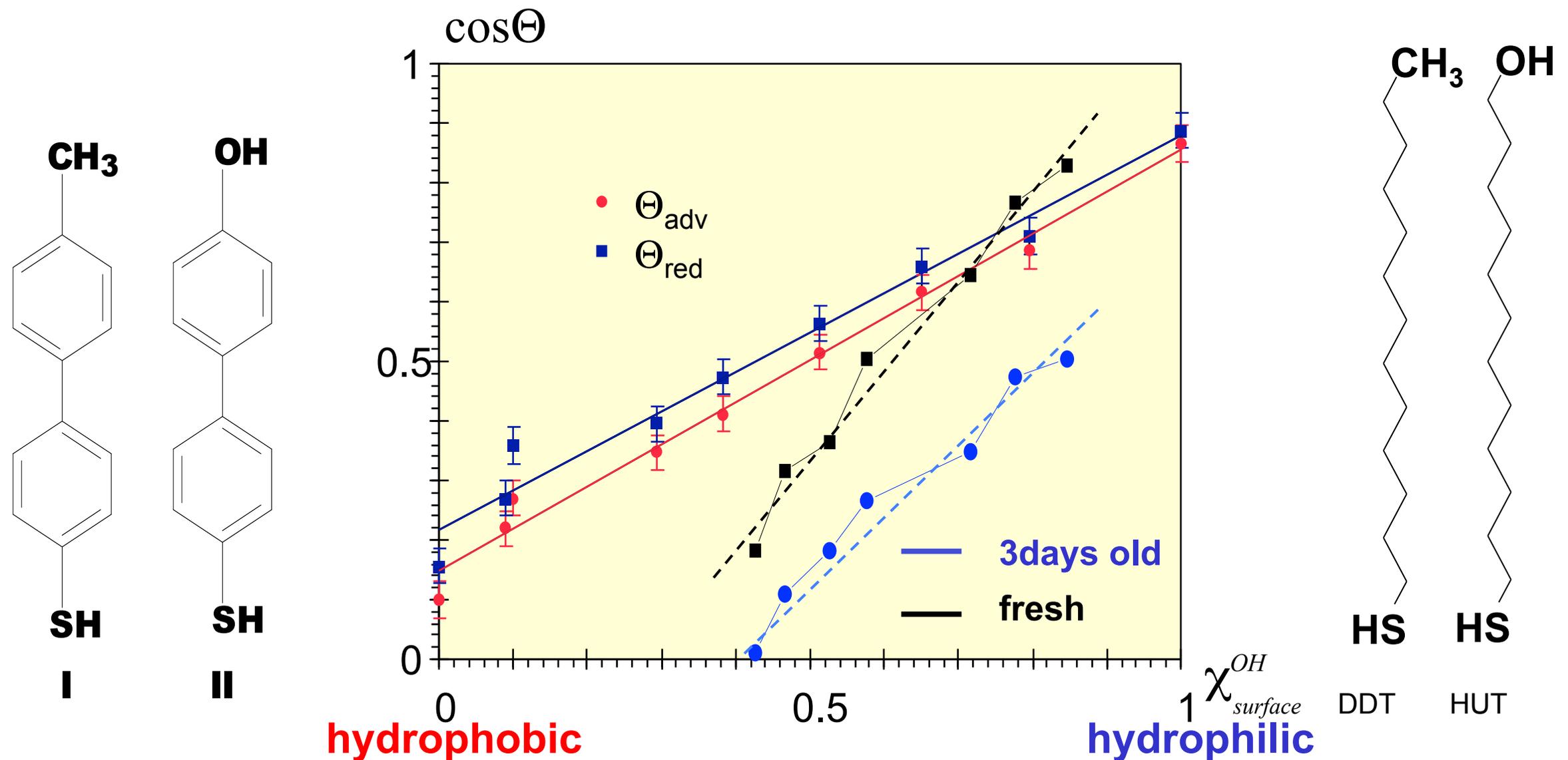
- Rigid system
 - biphenyl is an effective mesogenic moiety for SA
 - conjugated system
 - different reactivity of thiol group
 - different molecular dipole moment
- } **DIFFERENT SA BEHAVIOR**



X = 23 different functionalities:

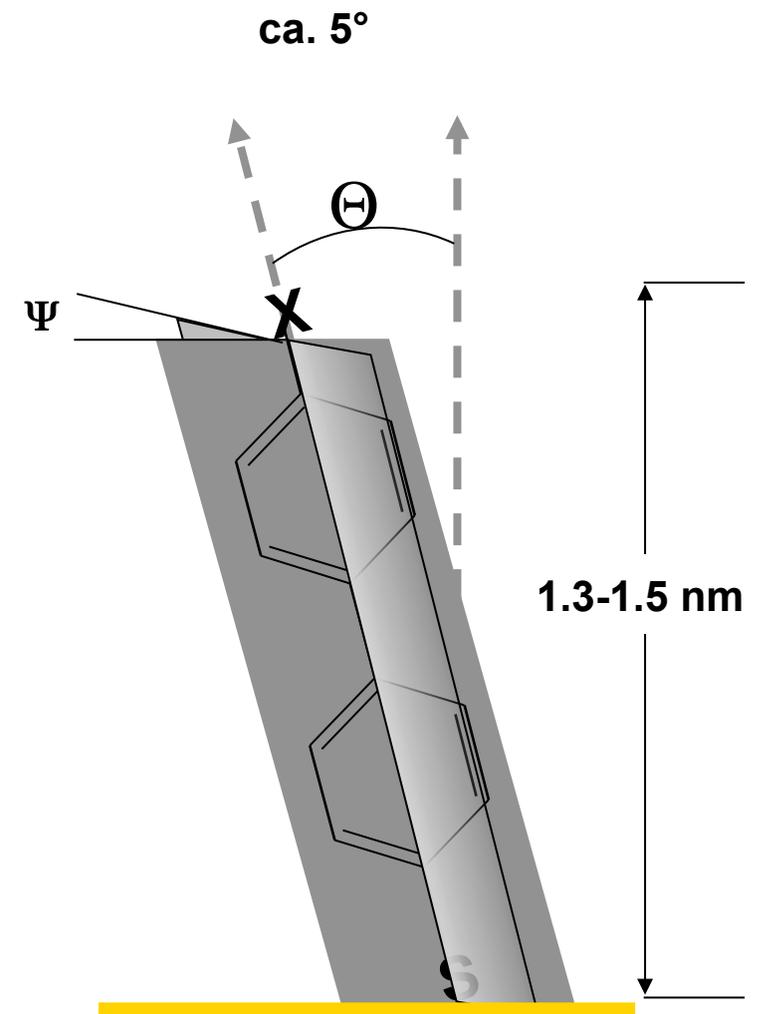
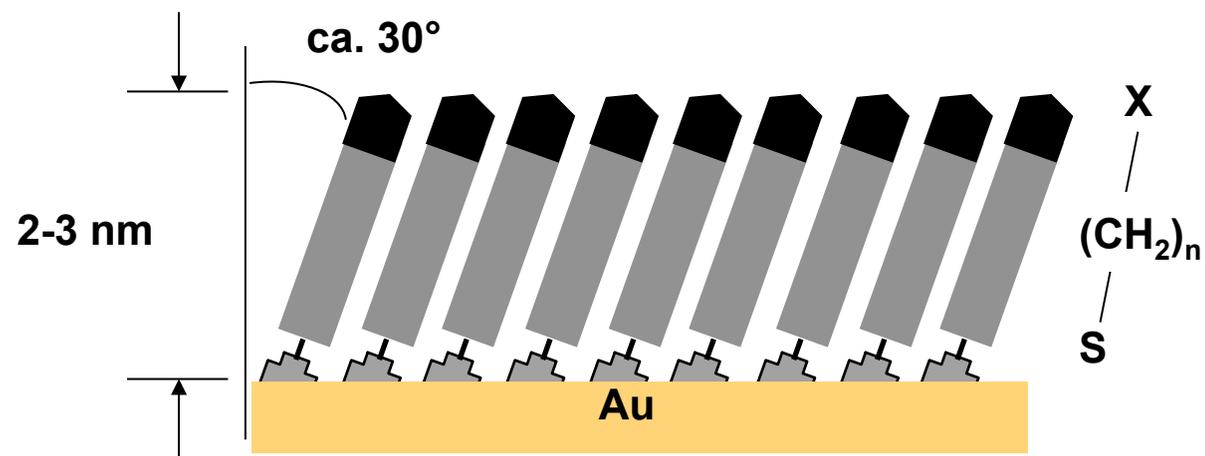
e.g. -H, -CH₃, -CF₃, -OH, -SH, -SCH₃, -F, -Cl, -Br, -I,
-NO₂, -NH₂, -COCH₃, -COOR, -CN...

Self-Assembled Monolayers Alkanethiols vs. Biphenylthiols



- Small hysteresis – uniform layer no surface reorientation
- Linear relationship – ideal mixture at the surface
- Stable θ for weeks – **no surface reconstruction**
- Higher absolute values – polarizable system

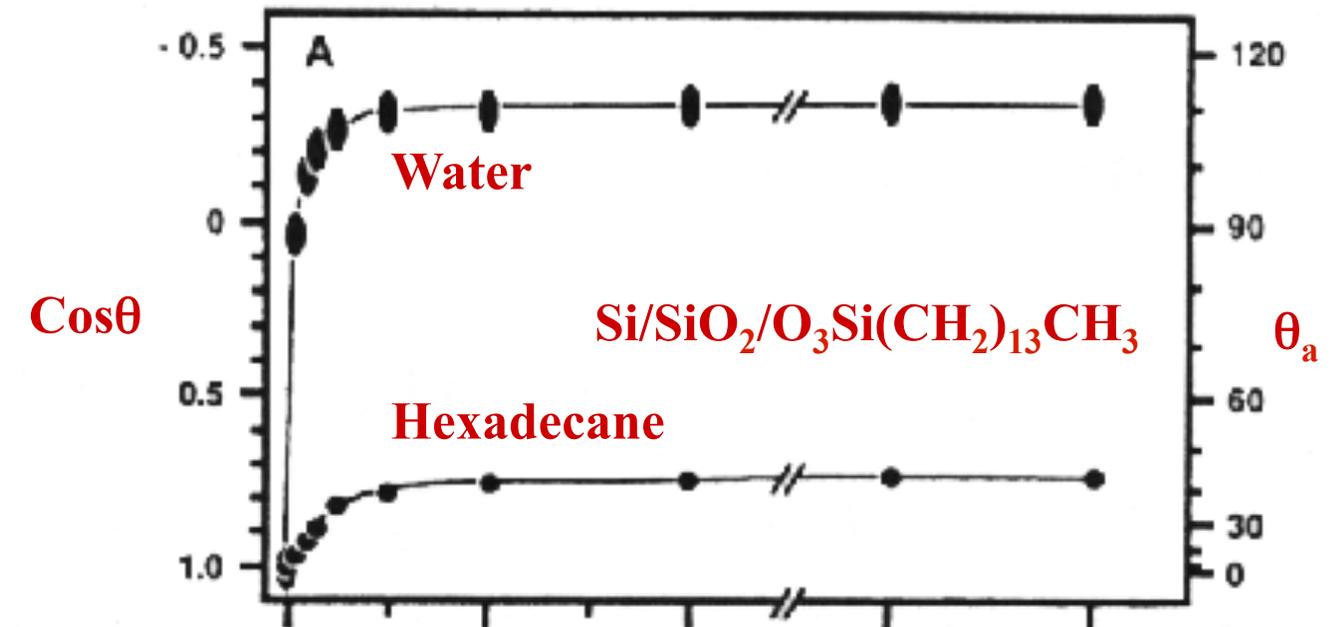
Self-Assembled Monolayers Alkanethiols vs. Biphenylthiols



Various types of SAMs – Alkylsilanes

SAM formation of tetradecyltrichlorosilane (TTS, $C_{14}H_{29}SiCl_3$) on silicon at 20°C and 30% relative humidity.

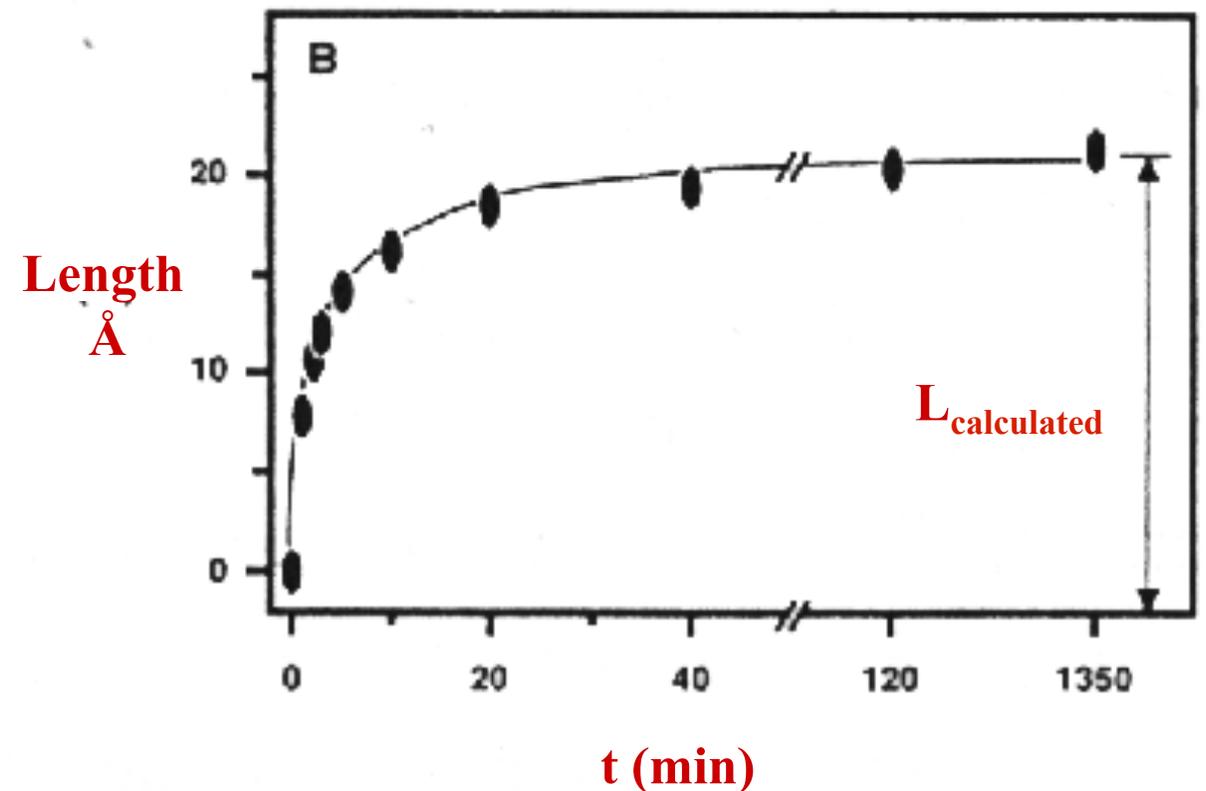
Contact angle:



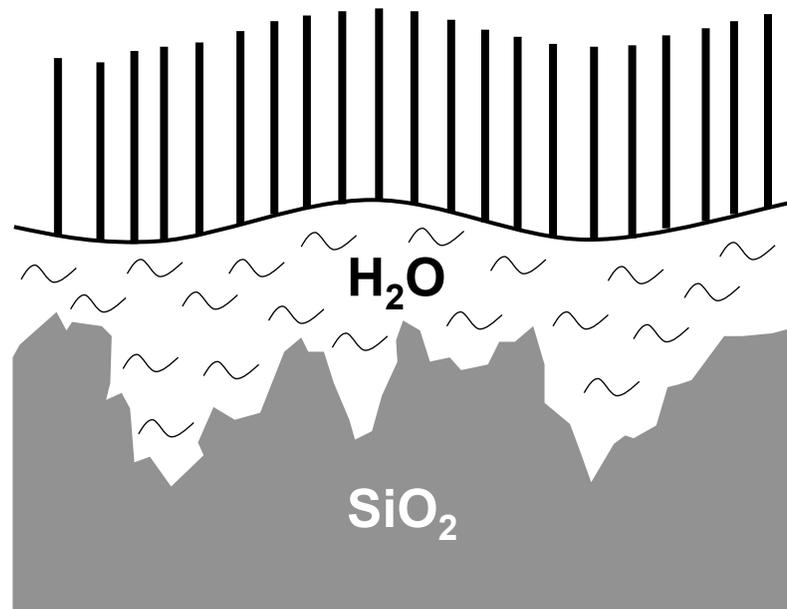
SAM thickness:

The calculated thickness is 21.1 Å based on an all-*trans* configuration.

Alkyl chains are perpendicular to the surface.

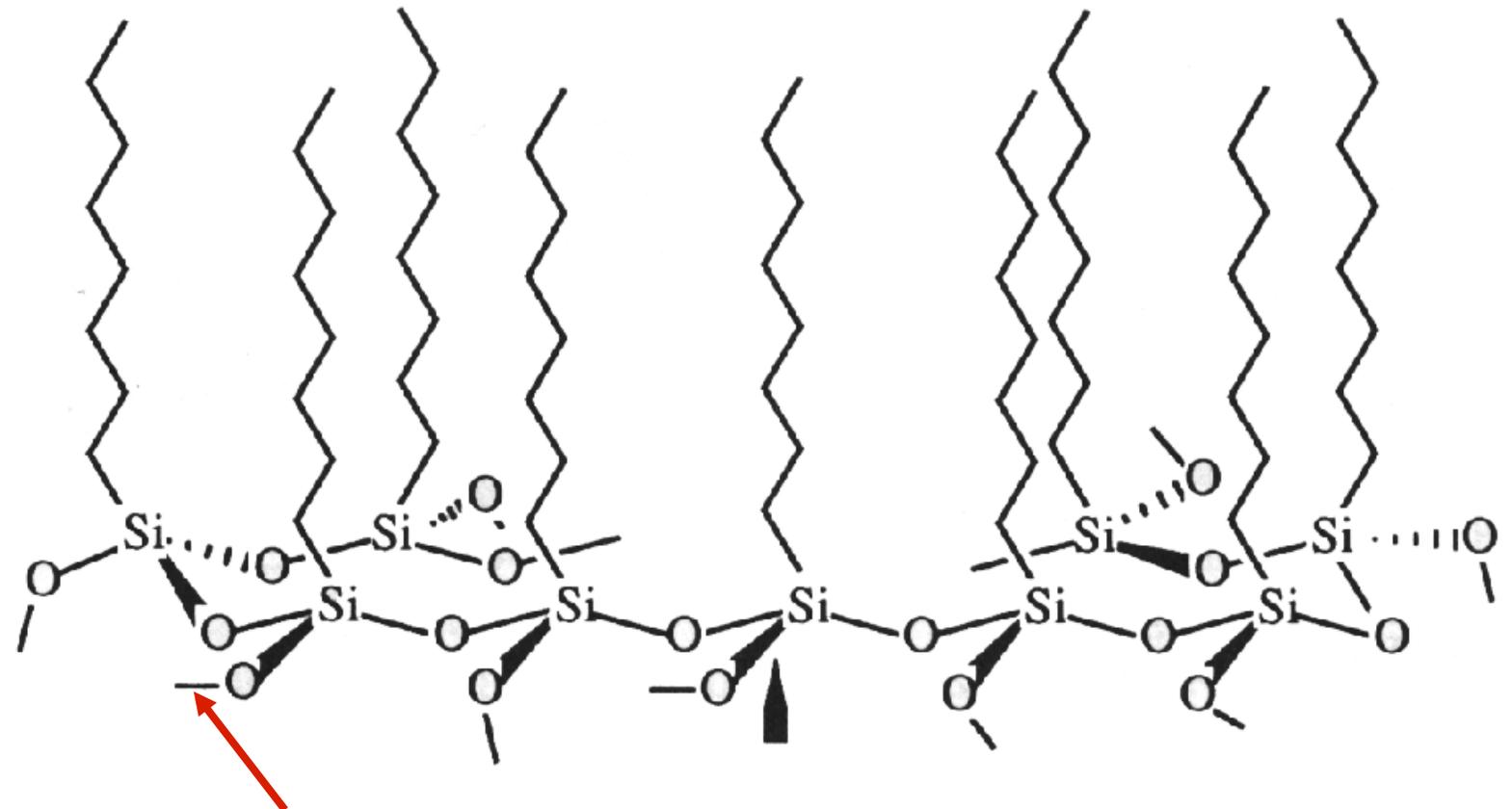


A schematic description of the polysiloxane formed *in situ* at the monolayer substrate interface.



Proposed Model by Silberzan et al. :
P. Silberzan, L. Leger, D. Ausserre, J. J. Benattar,
Langmuir **1991**, 7, 1647-1651.

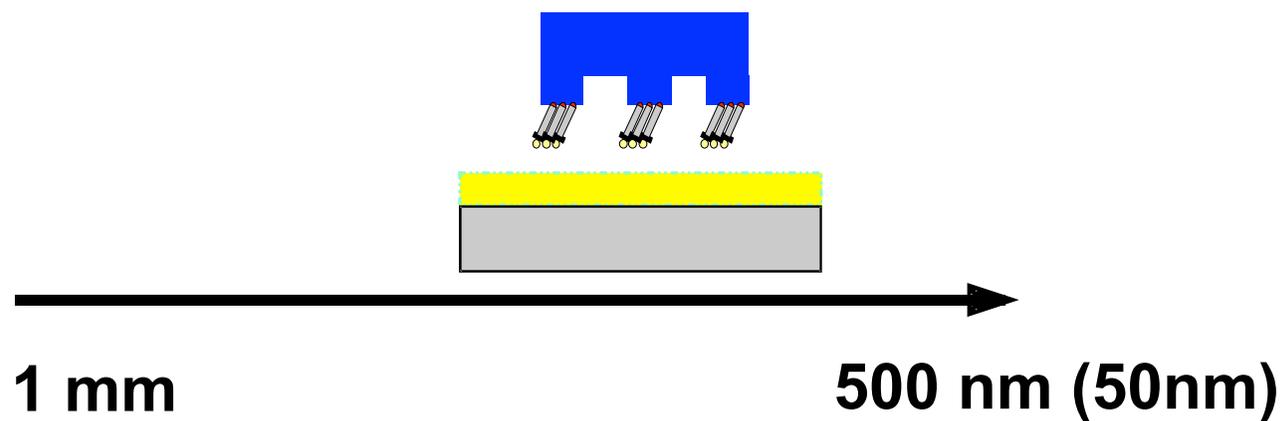
„The fact that the roughness is lower for silanated wafers is compatible with a vision in which the layer is not linked to the surface by all the individual molecules but, rather, forms a "net" where molecules are linked to each other; this net would be bonded to the surface by only a few bonds.“



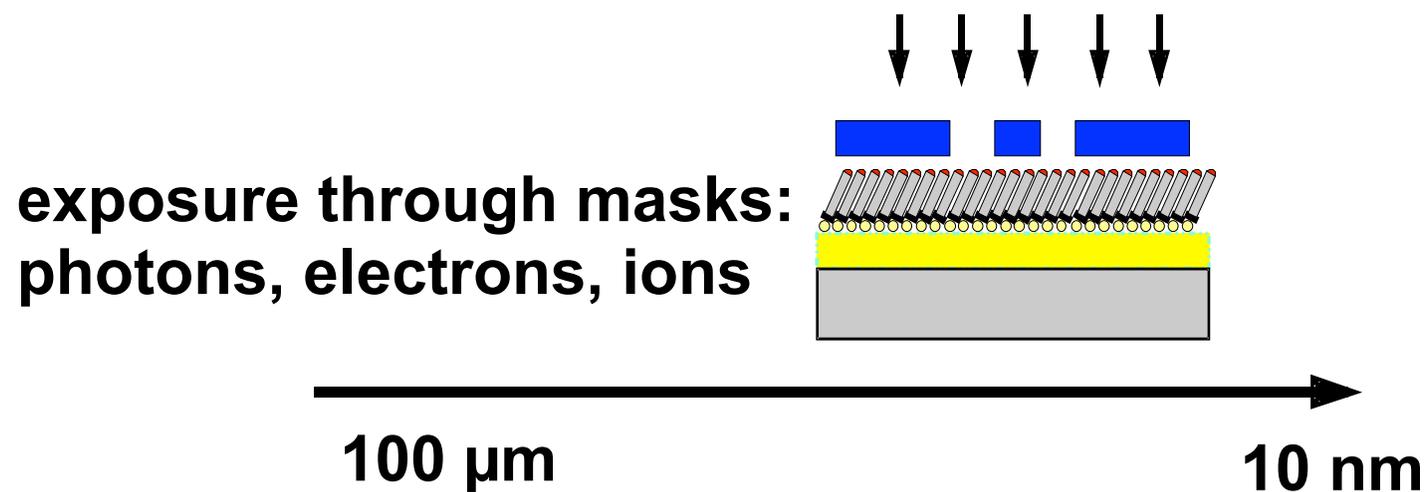
The equatorial Si-O bonds that can be connected either to another polysiloxane chain or to the surface

Lateral Patterning of SAMs

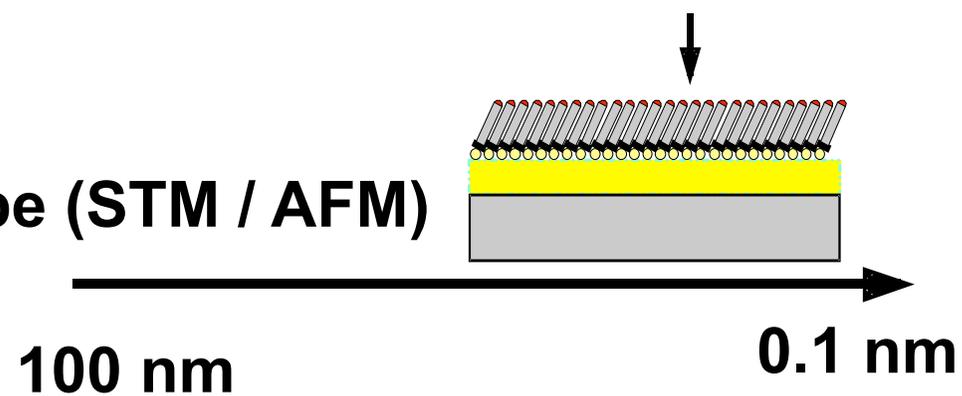
material deposition
"printing"



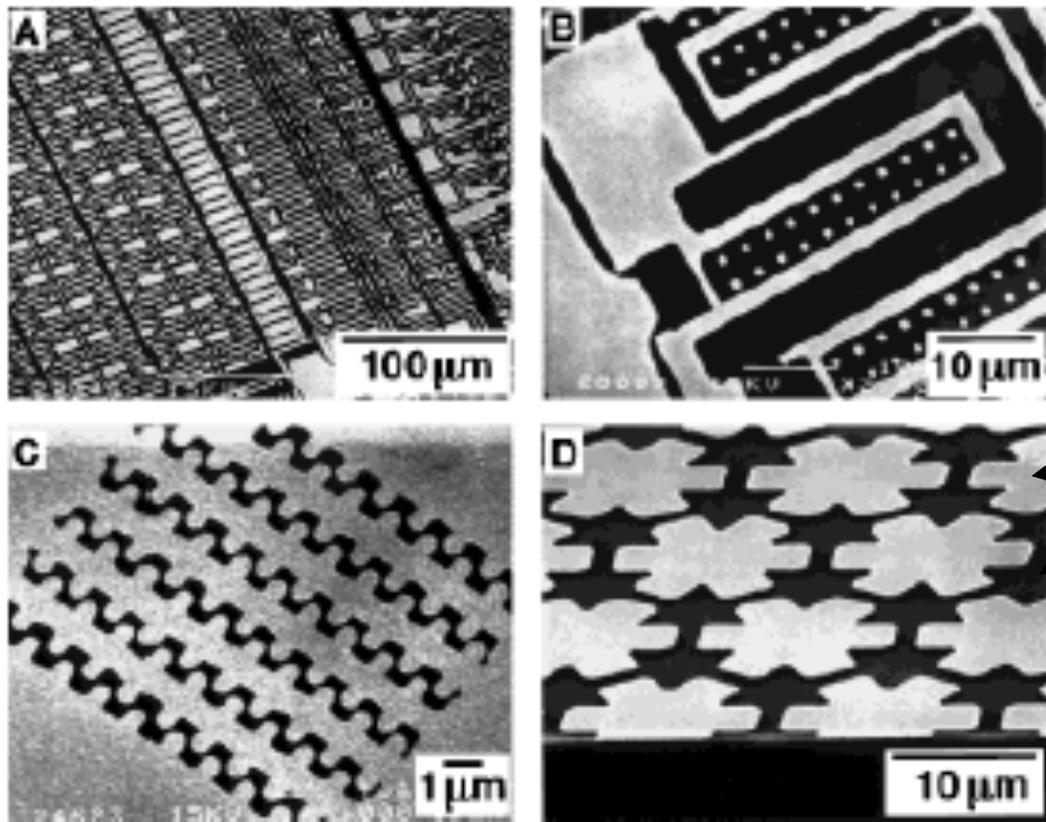
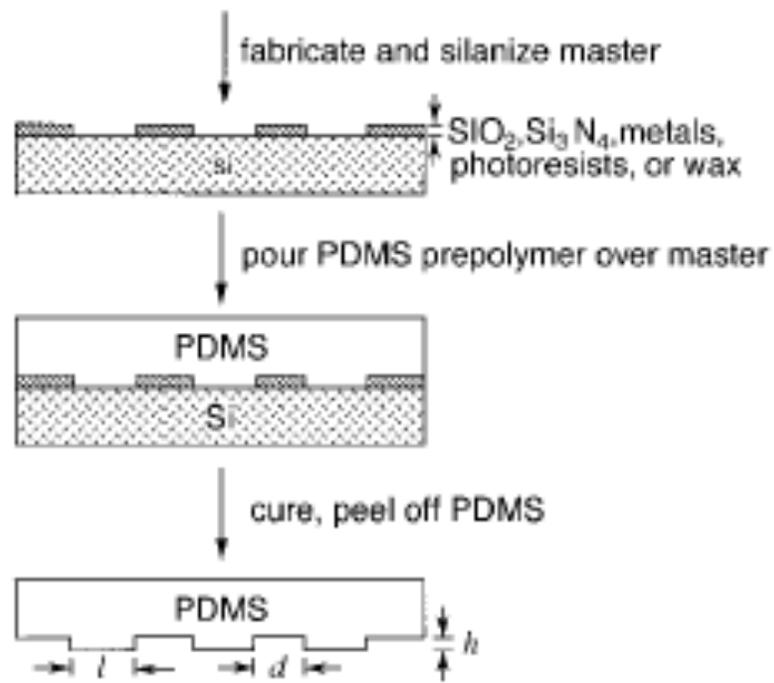
material modification
"lithography"



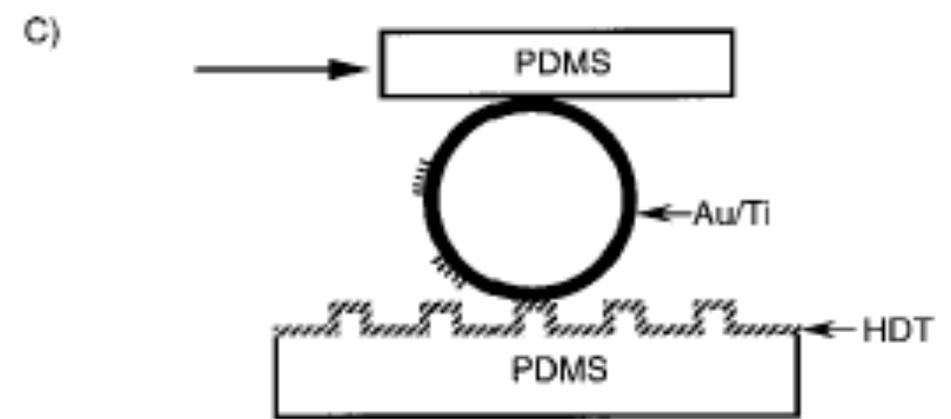
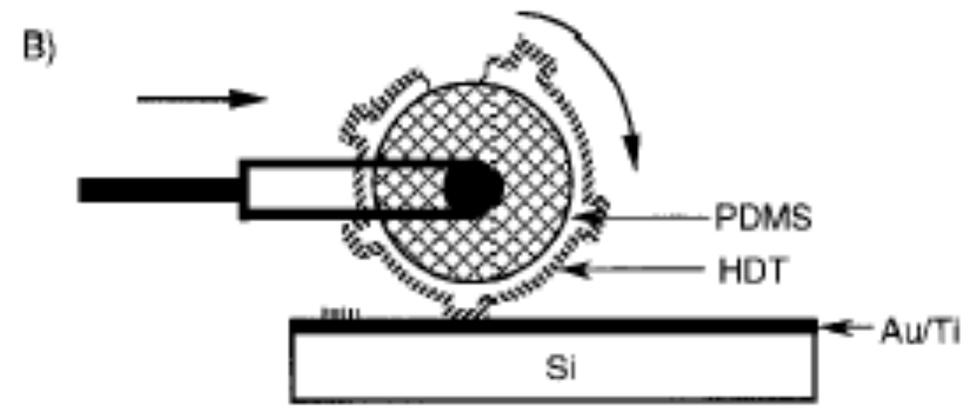
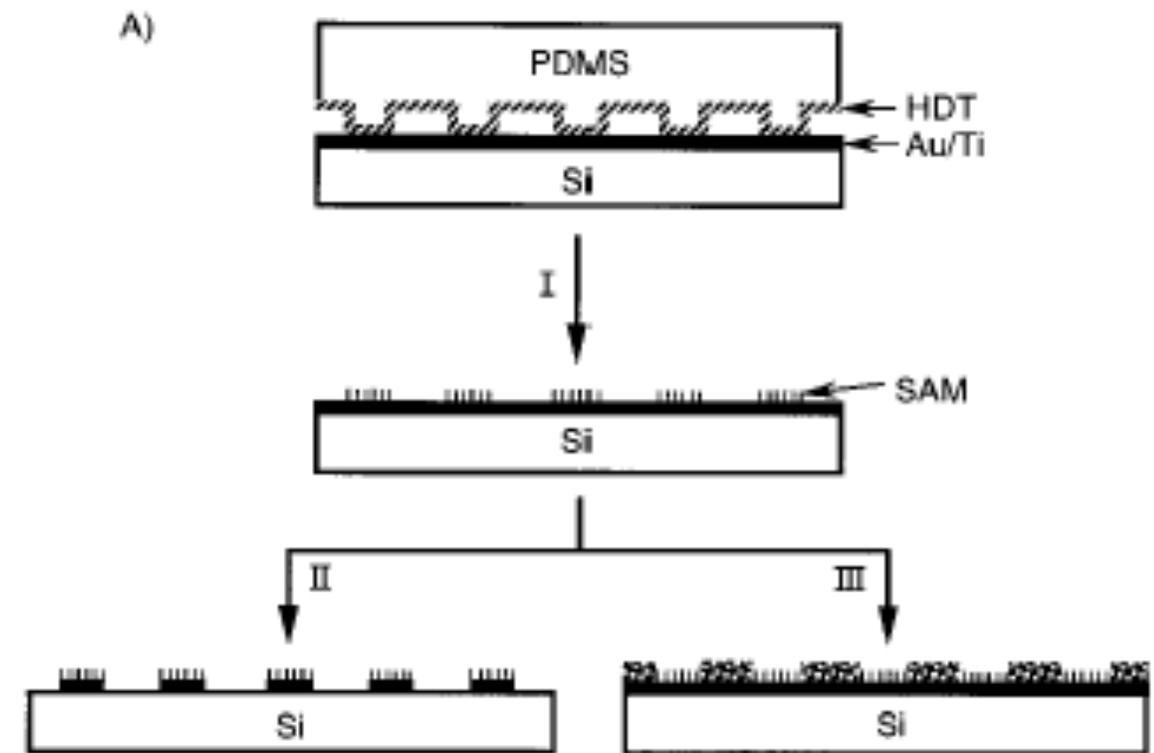
direct writing: e-beam
proximal probe (STM / AFM)



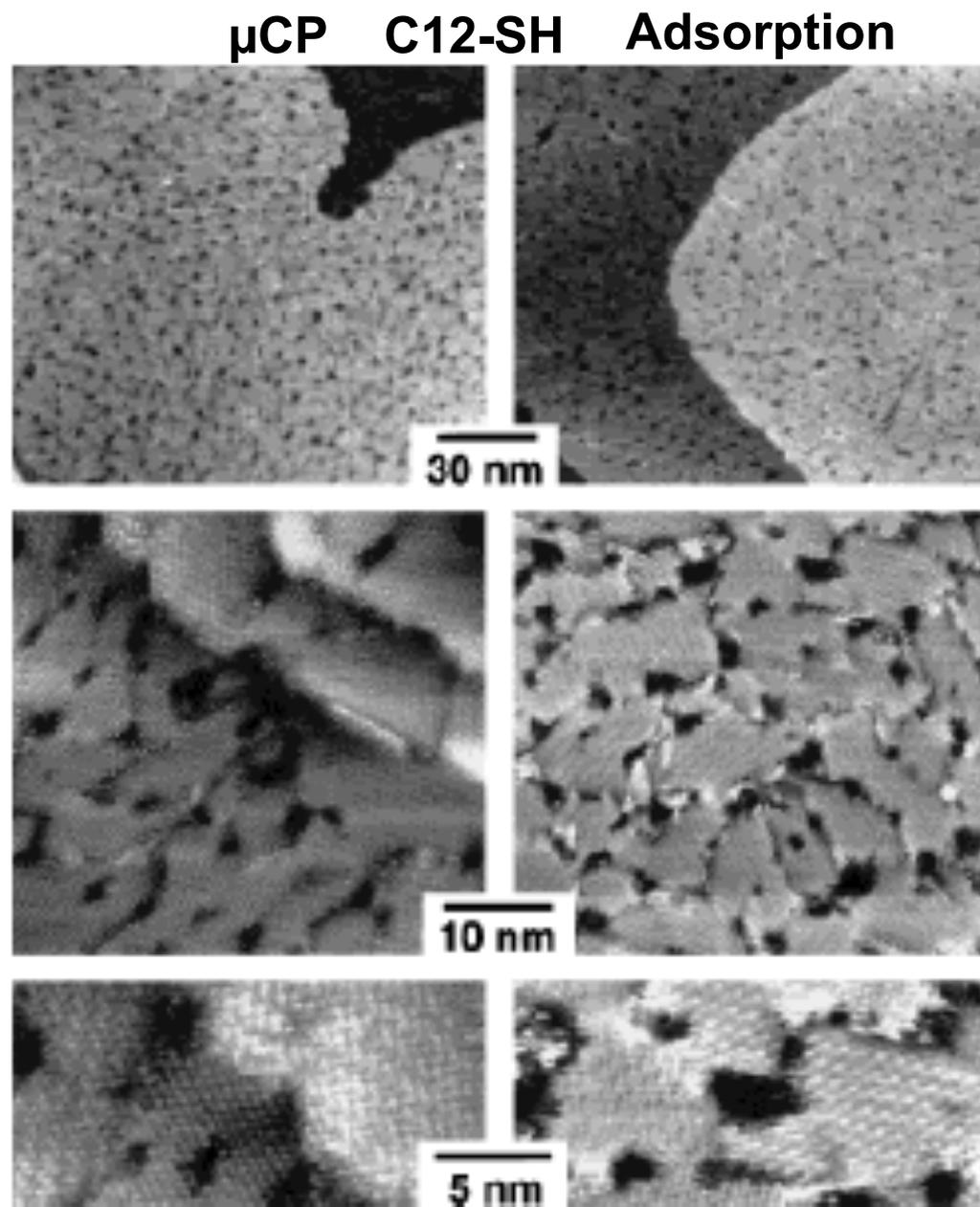
Mixed SAMs – Patterned SAMs : μ CP



Ag
Si/SiO₂



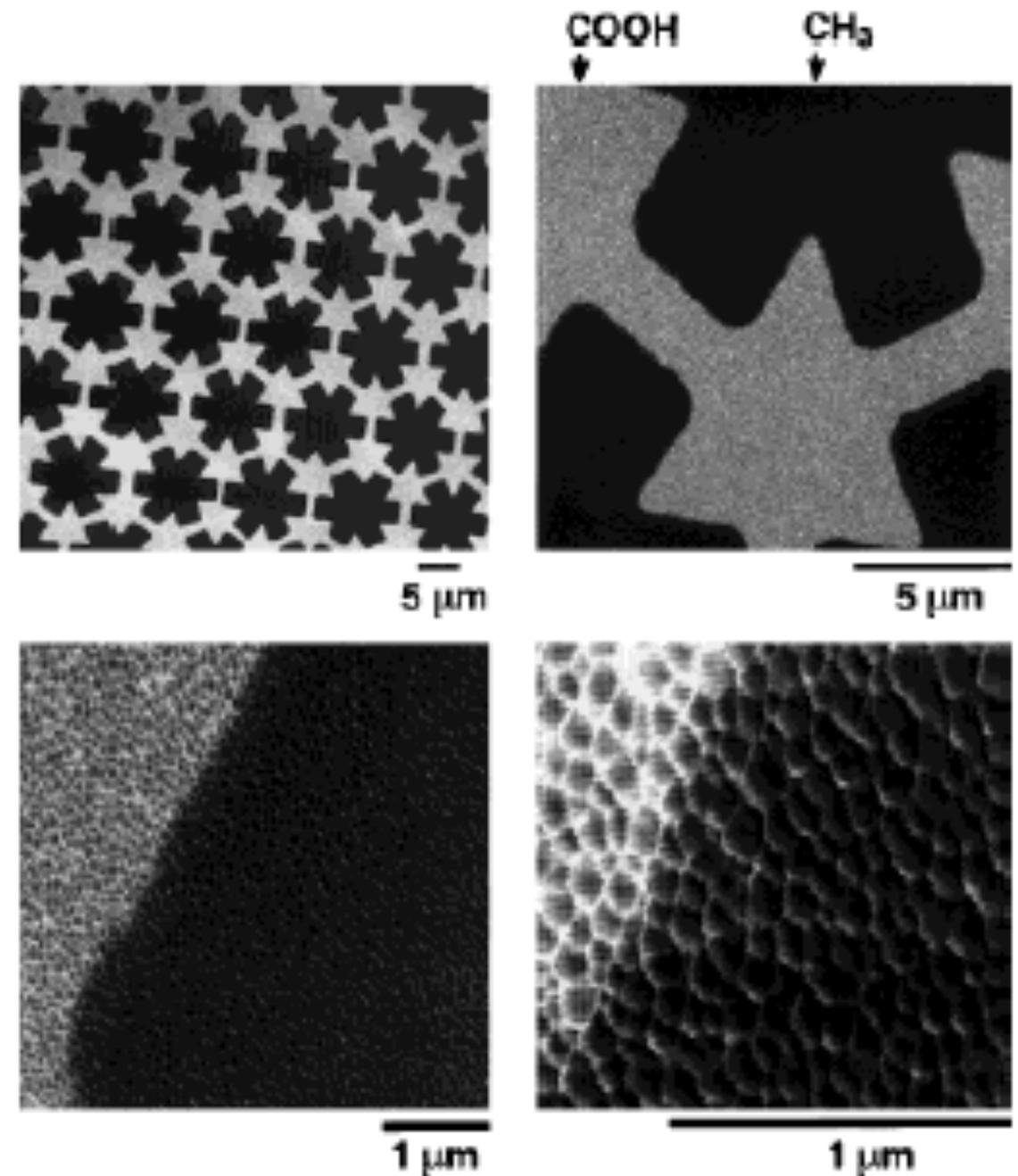
SEM images of test patterns on layers of silver (A, B, C: 50 nm thick; D: 200 nm thick) that were fabricated by μ CP with HDT followed by chemical etching in an aqueous solution of ferricyanide (Whitesides et al. 1998).



Comparison of STM images of SAMs of dodecanethiol (DDT) on Au(111) formed by μ CP and by adsorption from solution.

μ CP: a solution of DDT in ethanol as the "ink" ; $t = 10$ s

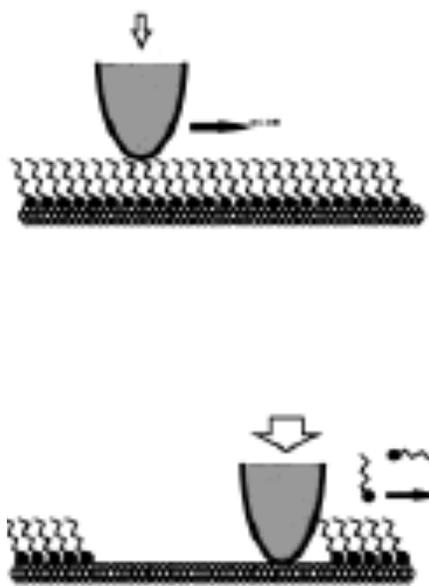
Adsorption: equilibrated with a solution of DDT in ethanol for about 18 h.



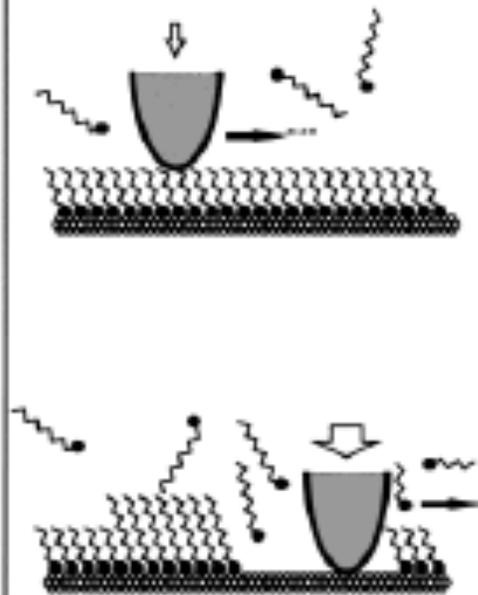
LFM. The surface was printed in HDT; the remaining regions were then derivatized with $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ by immersing the patterned sample in a solution containing the second thiol. Relatively high frictional forces between the probe and the surface were detected in regions covered with a COOH-terminated SAM (light), and relatively low frictional forces were measured over regions covered with a CH_3 -terminated SAM (dark).

Patterned SAMs : Scanning Probe Lithography

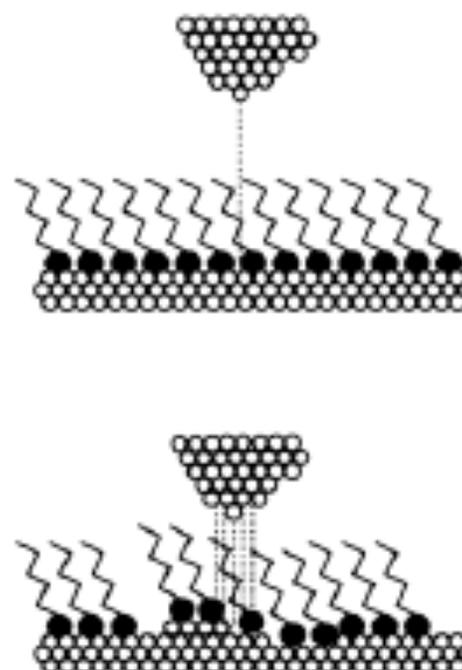
Nanoshaving



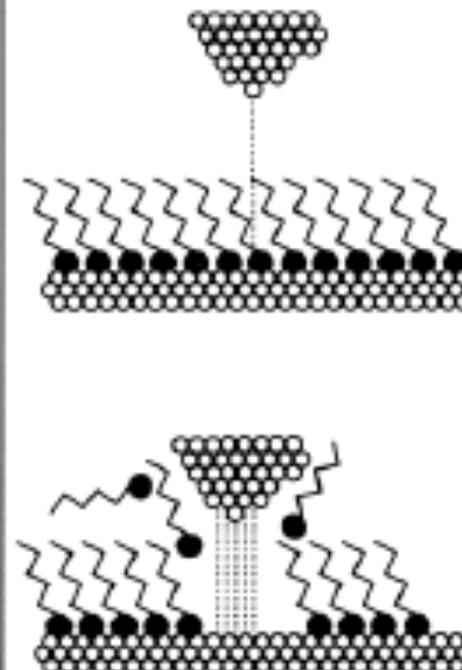
Nanografting



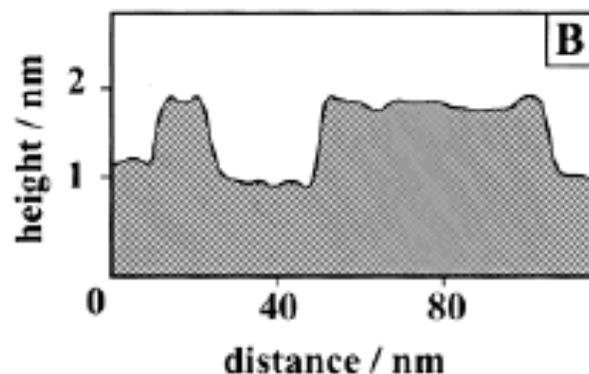
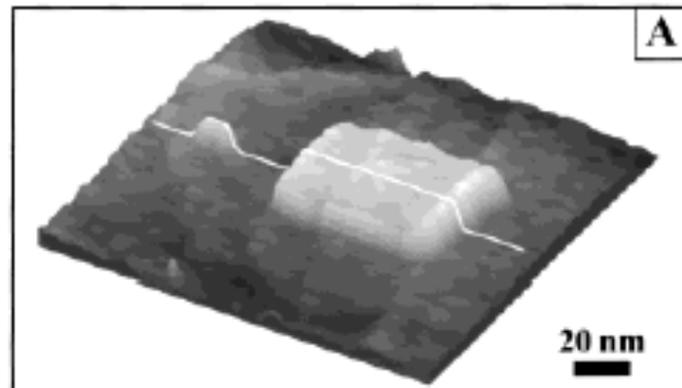
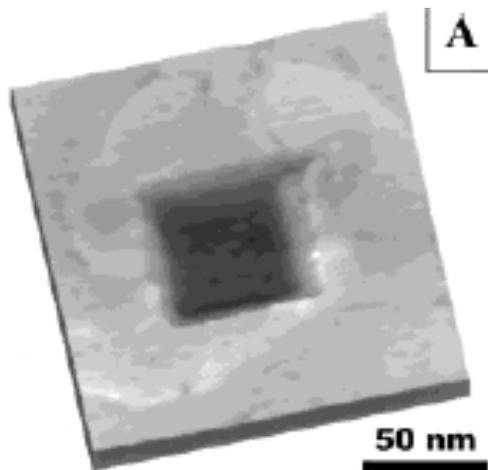
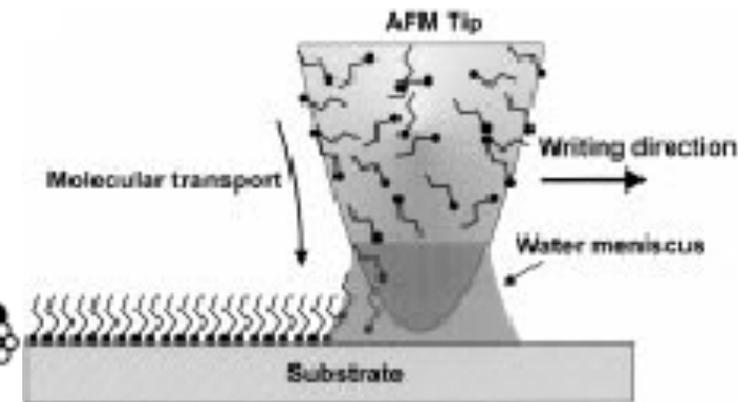
Electron-induced diffusion



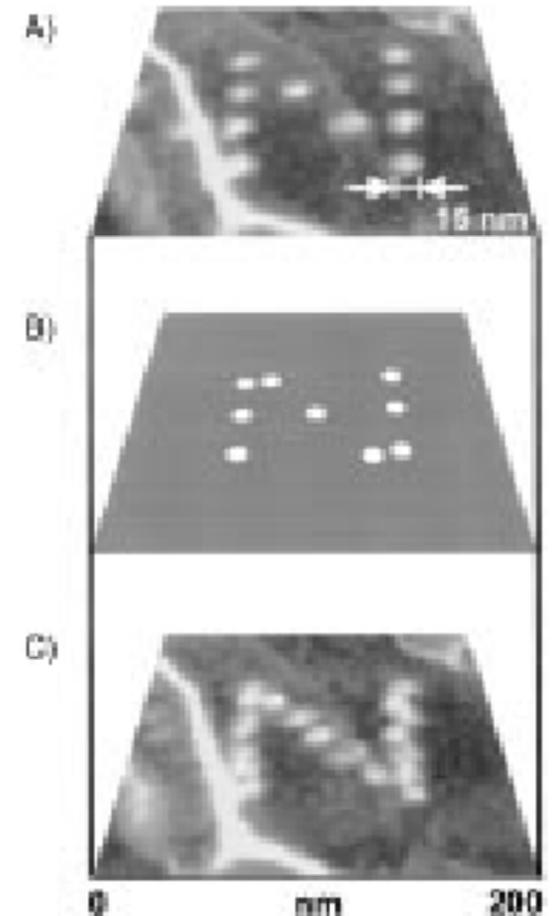
Electron-induced evaporation



Dip-pen



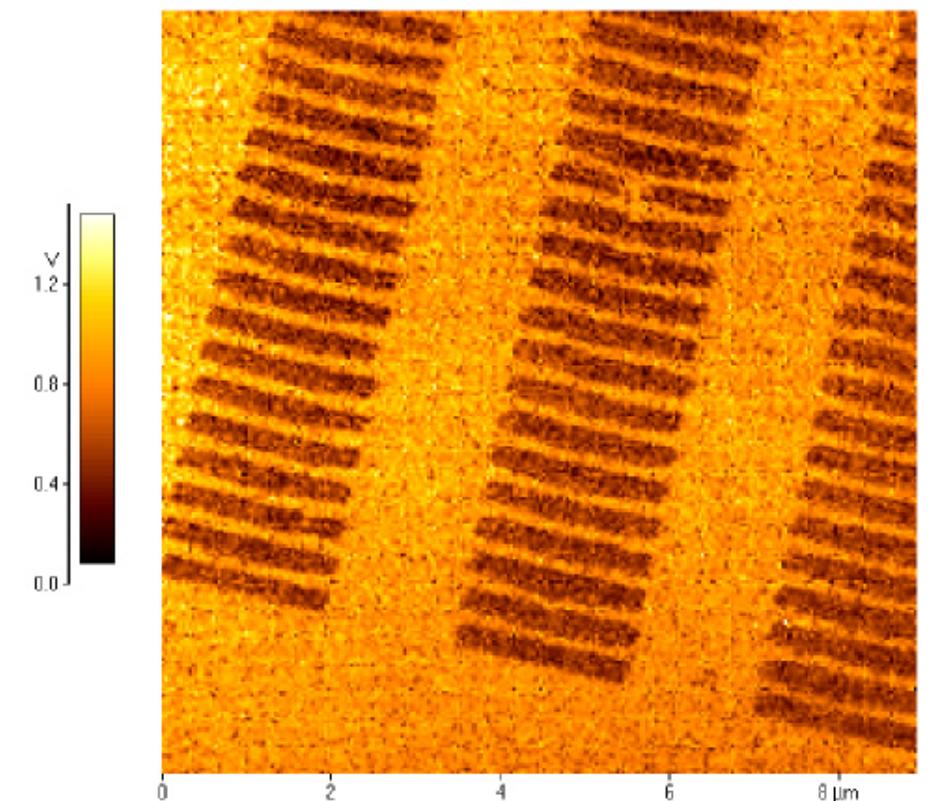
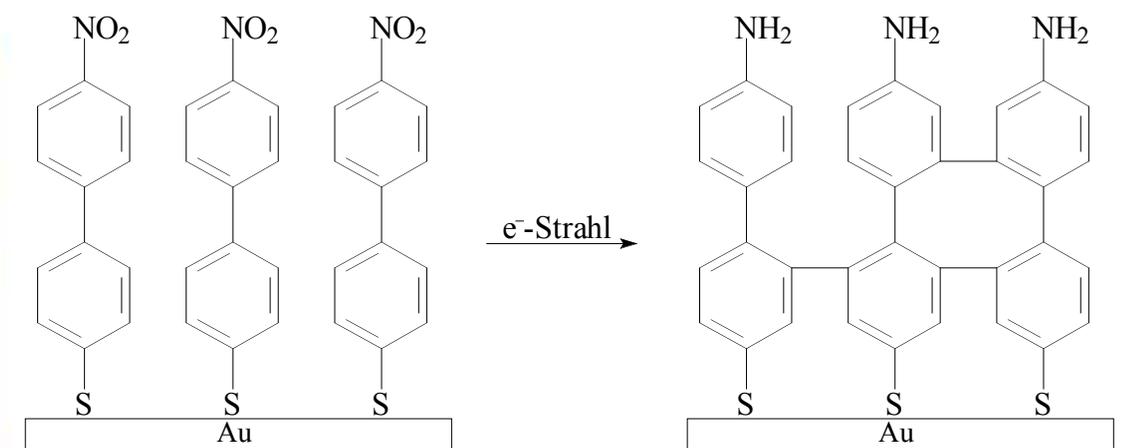
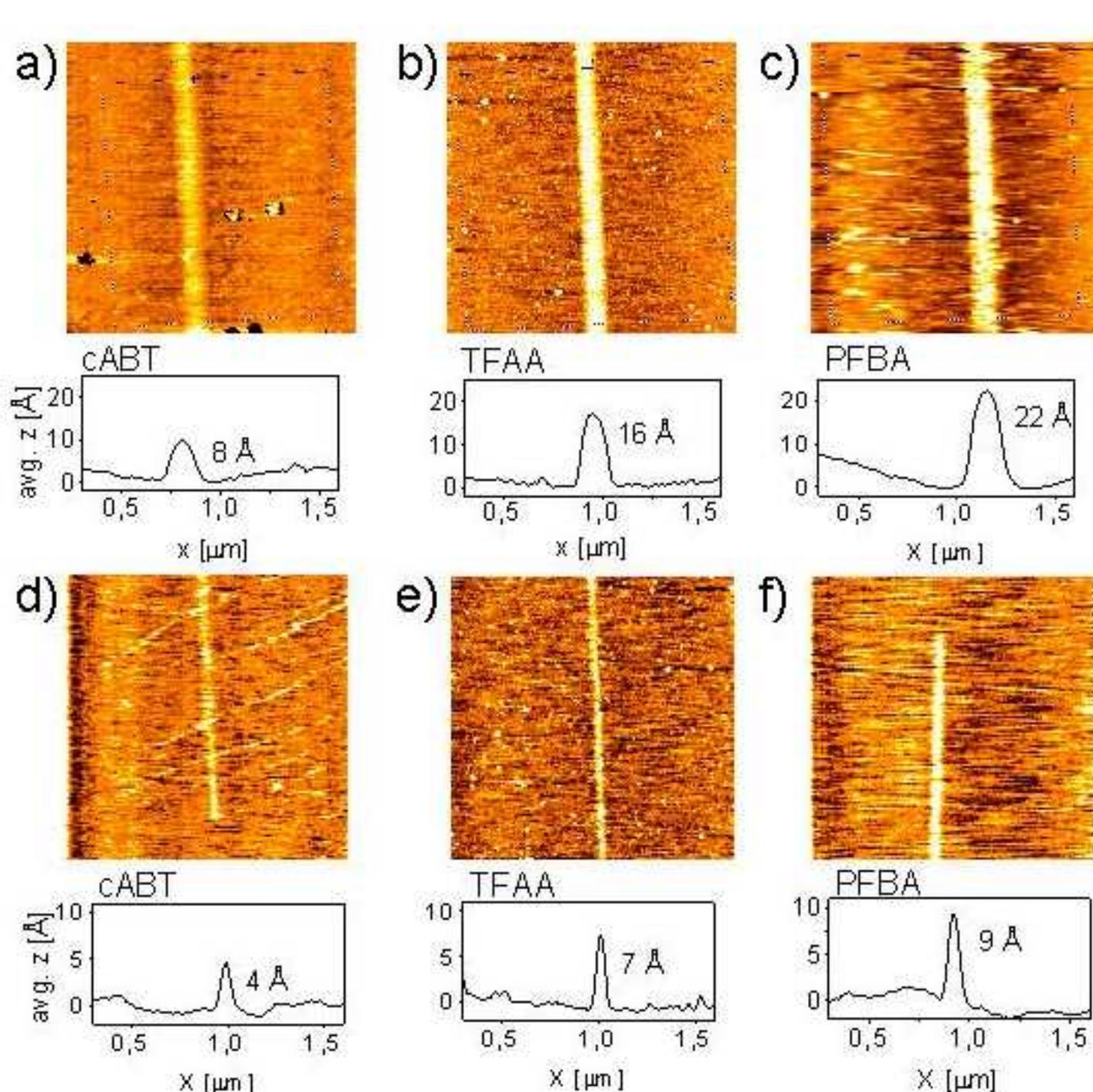
$C_{18}S$ nanoislands (3×5 and $50 \times 50 \text{ nm}^2$) in the matrix of a $C_{10}S$ monolayer using nanografting. (B), the $C_{18}S$ islands are 8.8 \AA higher than the surrounding $C_{10}S$ monolayer



Consecutive position of $C_{16}S$ dots (15 nm) on Au(111) LFM-image.

160 nm^2 topographic images of $C_{18}S/Au(111)$ with thiols shaved away from a 50 nm^2 square

Mixed SAMs – Patterned SAMs : Chemical Lithography



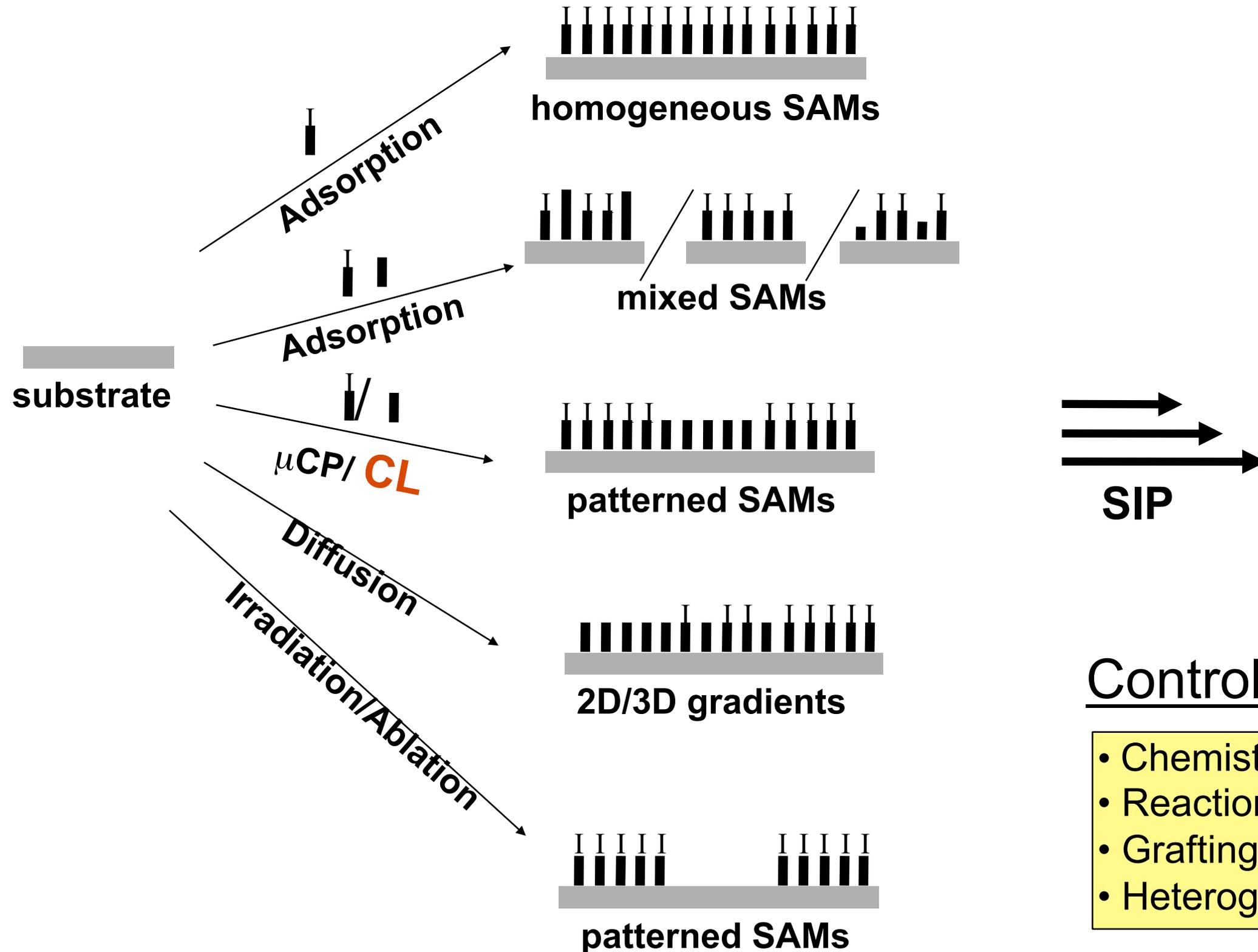
Lateral force AFM image of a NBT SAM/Au after e^- -beam exposure (10000 $\mu\text{C}/\text{cm}^2$ at 300 eV) through a 150 nm stencil mask.

AFM Images and averaged height profiles of lines that were written with a focused electron beam into a nitrobiphenylthiol monolayer. a-c) **100 nm** lines after electron exposure (a) and immobilization of TFAA (b) and PFBA (c). d-f) **20 nm** lines after electron exposure (d) and immobilization of TFAA (e) and PFBA (f).

M. Grunze et al. *Surf. Sci.* 2000

M. Grunze et al. *Adv. Mat.* 2001

SAMs: Tailored Surfaces as Initiator Systems for Surface-Initiated Polymerization (SIP)



Control of:

- Chemistry
- Reaction sites
- Grafting density
- Heterogeneity

Thank you!

to be continued with...

PART II

Polymer Brushes