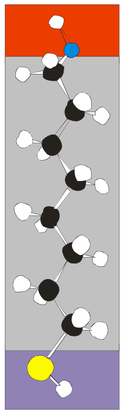
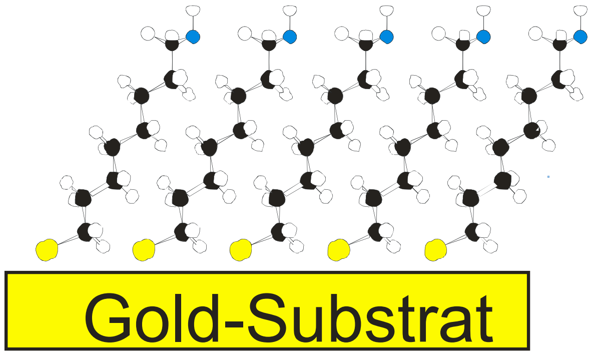
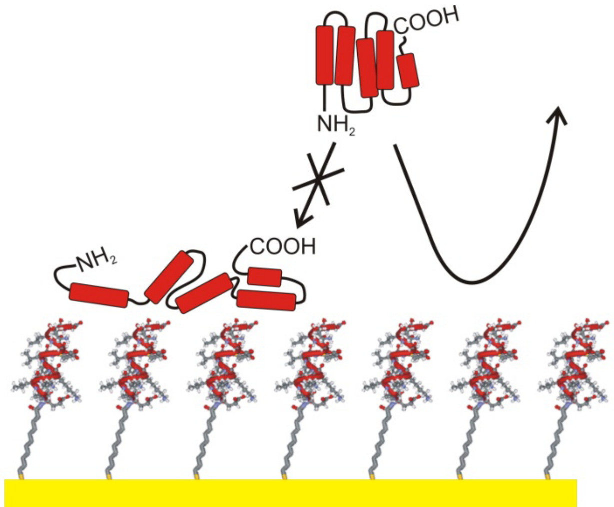
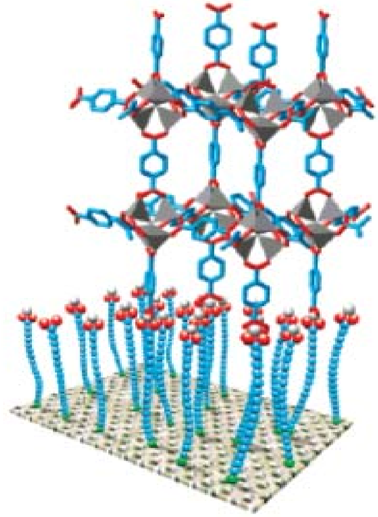
Organics at surfaces, self-assembly

Christof Wöll
Institute of Functional Interfaces (IFG)
Karlsruhe Institute of Technology, KIT





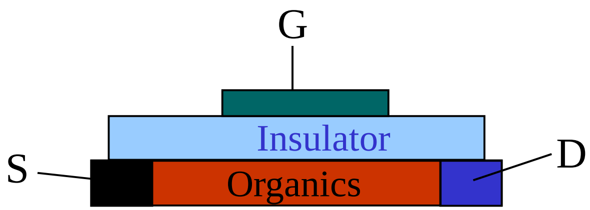




Organic Semiconductors making their way to applications

Fabrication using printing technology

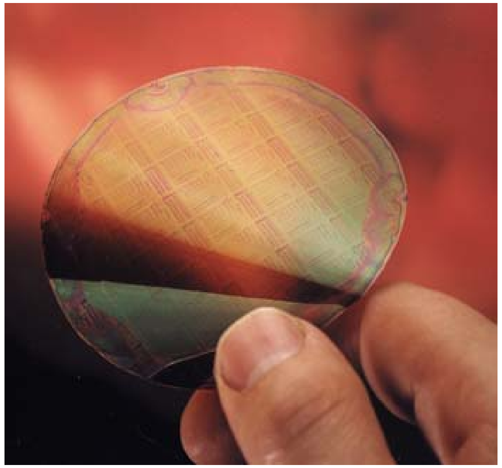
Organic Field-Effect Transistor



„cheap electronics“

„Chips on a chips bag“

Siemens (2003)



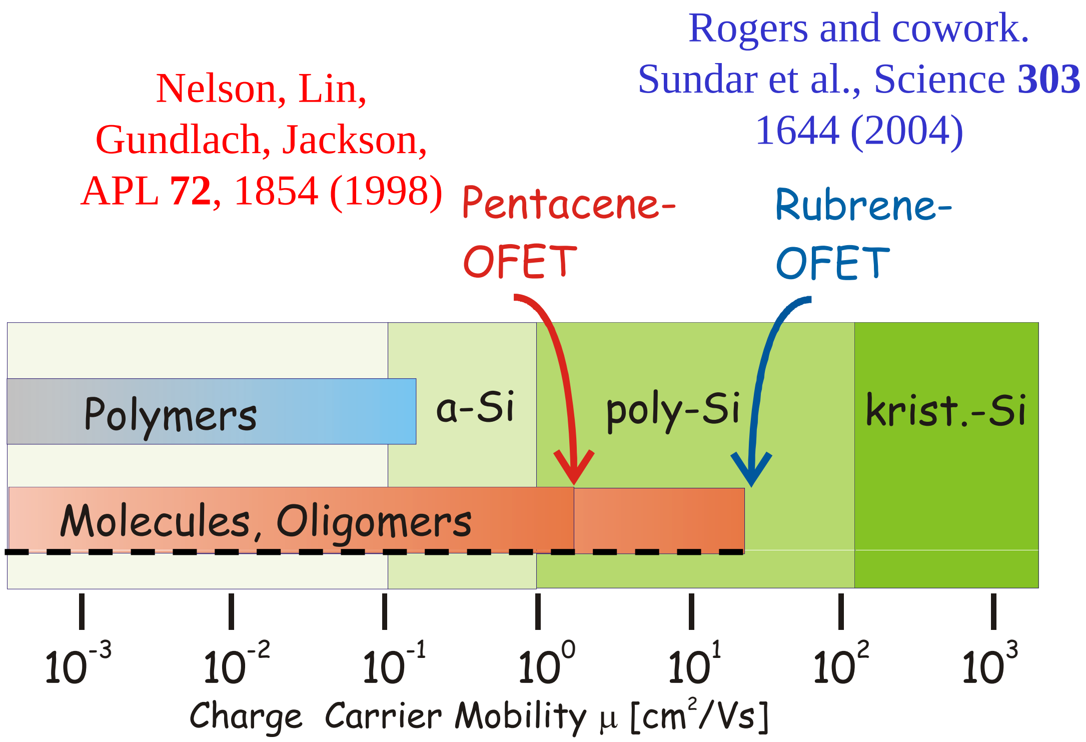
- Polymers
Oligomers with high solubility
(“amorphous” OFET‘s)

- RFID-tags

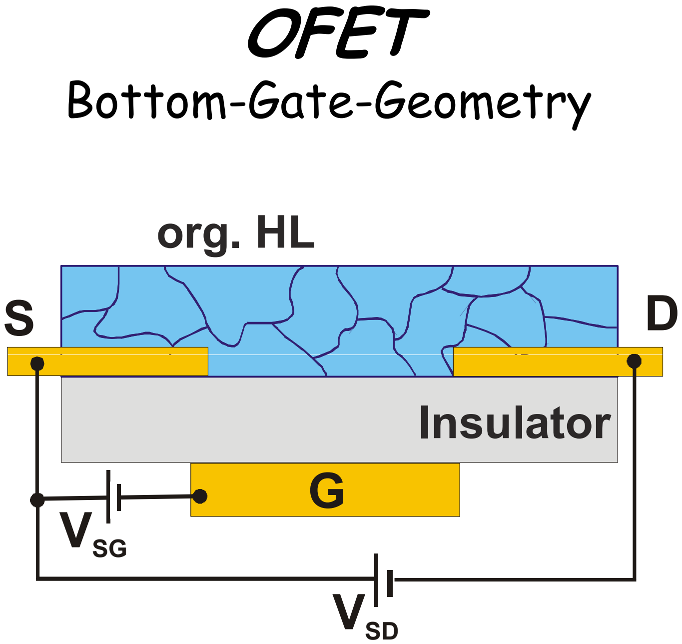
- limited charge carrier mobility causes low frequencies

www.ofet.de

Organic Semiconductors: Charge Carrier Mobilities



For "smart tag" Applications:
$\mu > 1\ cm^2/Vs$

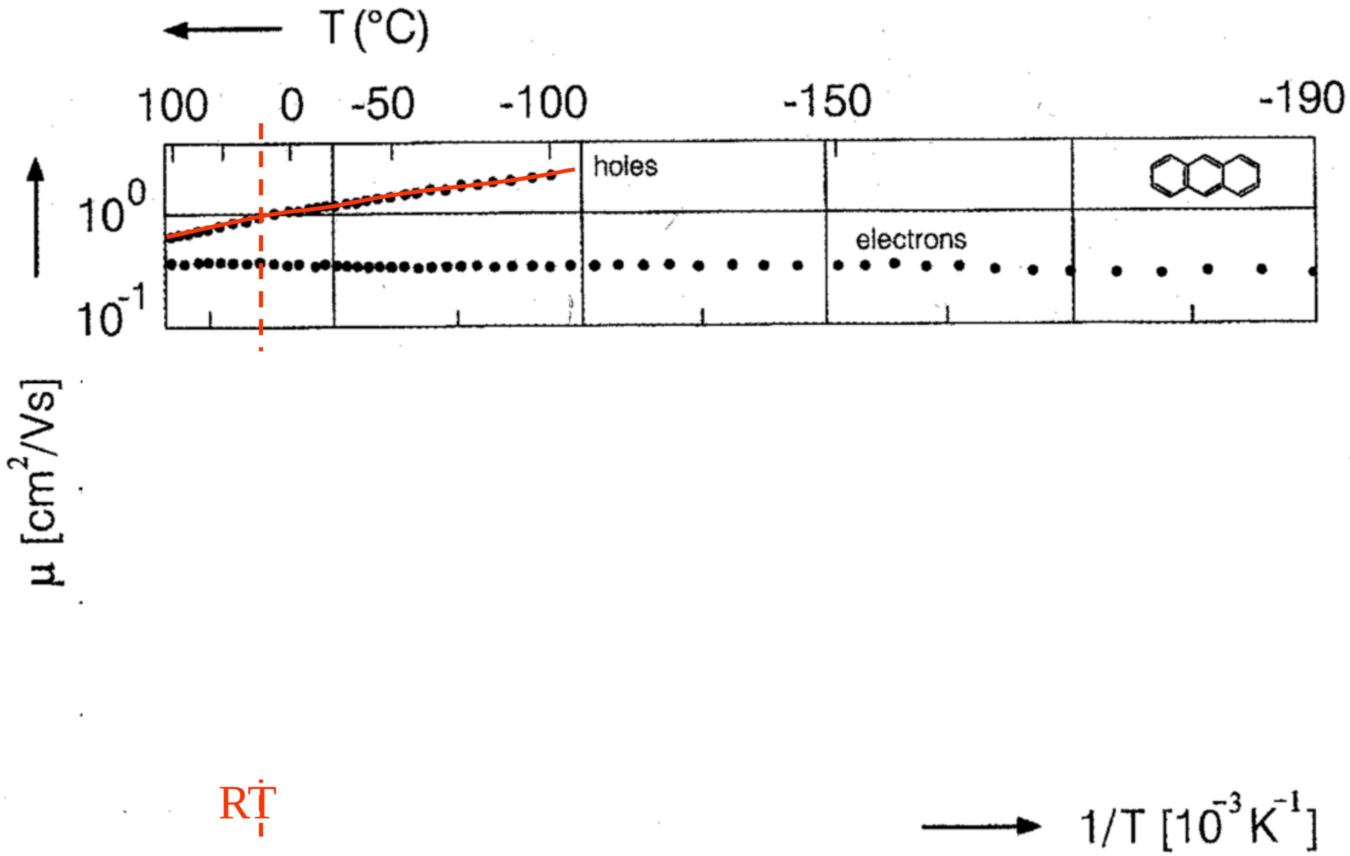


<u>Oligomers:</u>

- highly ordered, single crystals
- high purity
- main interest polycyclic aromatic hydrocarbons (Polyacenes, Benzoids)

Organic Conductors:
Conduction mechanism and influence of impurities

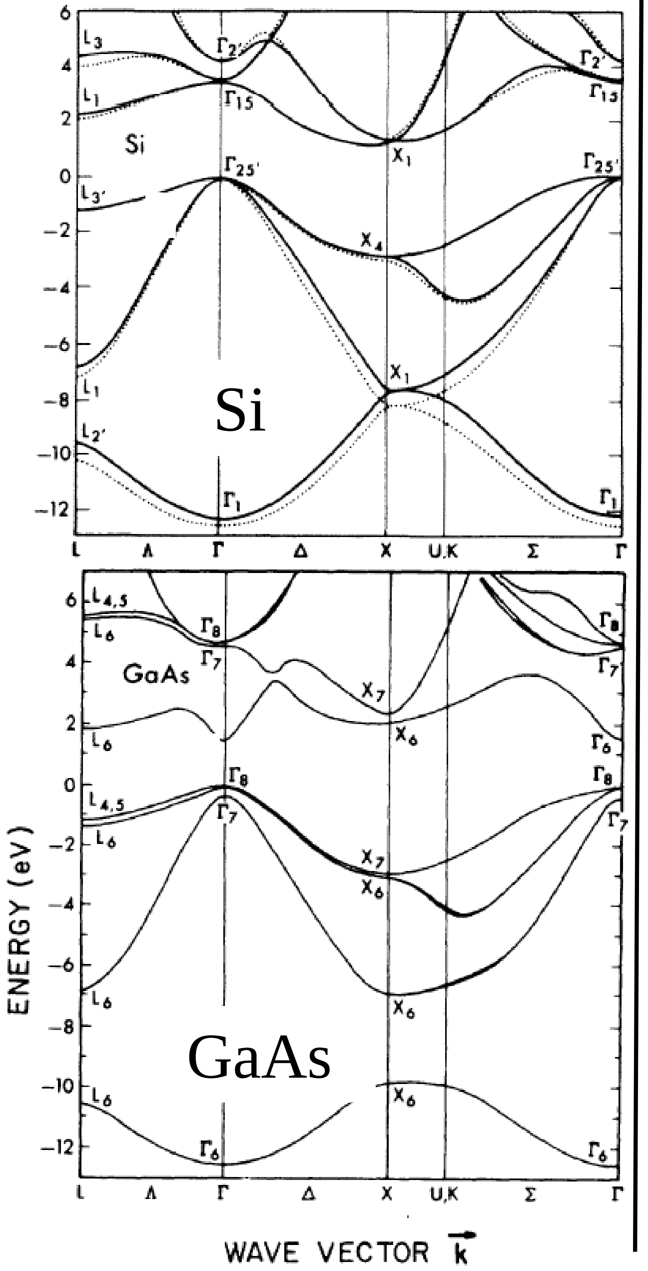
Anthracene

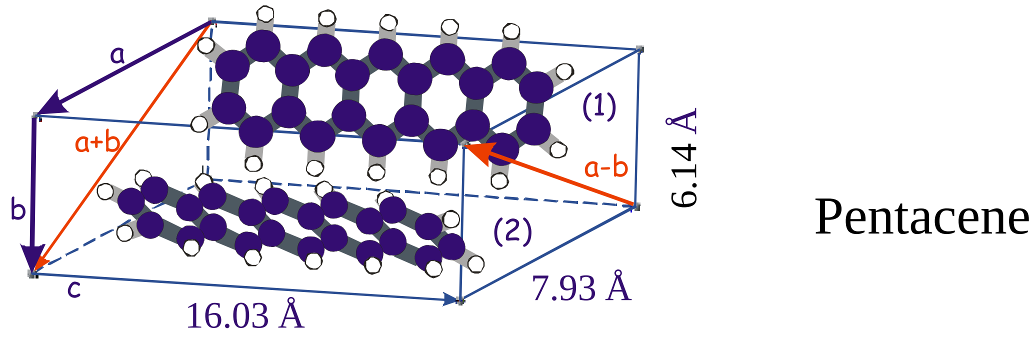


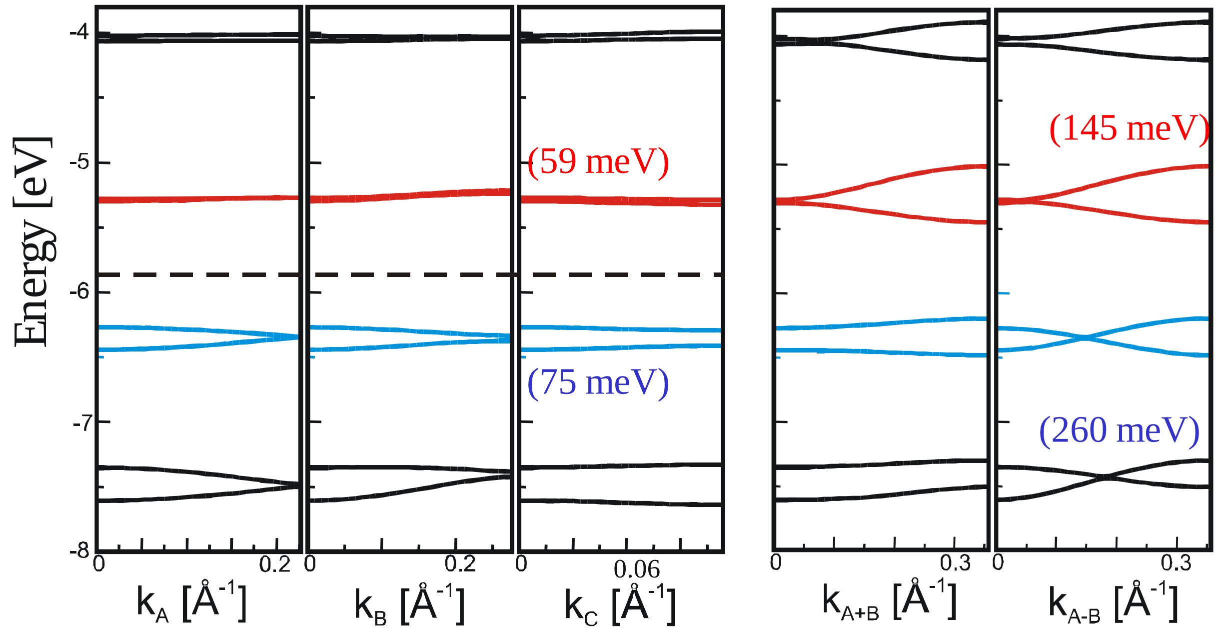
N. Karl, in:
Organic Electronic Materials
Farchioni & Grosso (Eds)
Springer,
Material Science 41 (2001)

Clear evidence for band-like transport,
at higher temperatures hopping transport

Electronic structure: Conventional vs. organic semiconductors







Precise ab-initio DFT electronic structure calculations

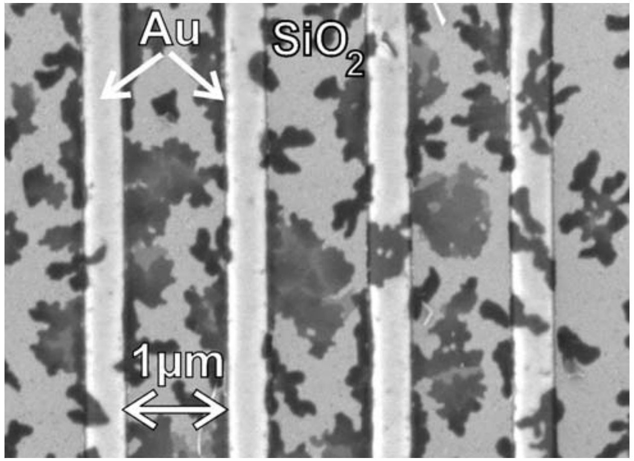
R. G. Endres, C. Y. Fong, L. H. Yang, G. Witte, and Ch. W. Comp. Mat. Sci., **29**, 362, (2004)

Nucleation & growth on bottom contact OFET-structures

co-operation with Prof. Kunze, Chair for Nano-Electronics, RUB, Bochum

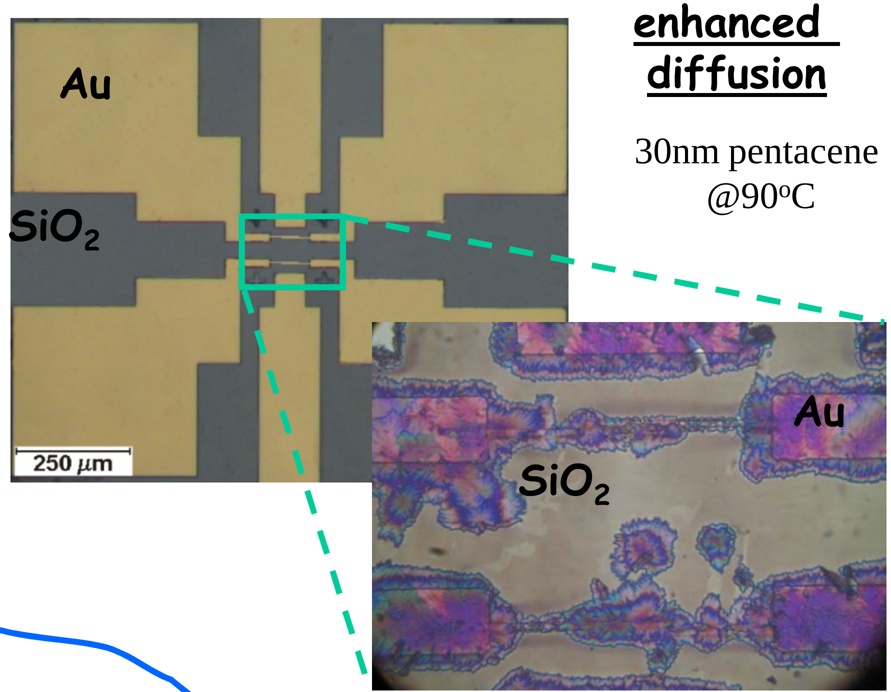
nucleation at electrodes

9nm pentacene @50^{o}C

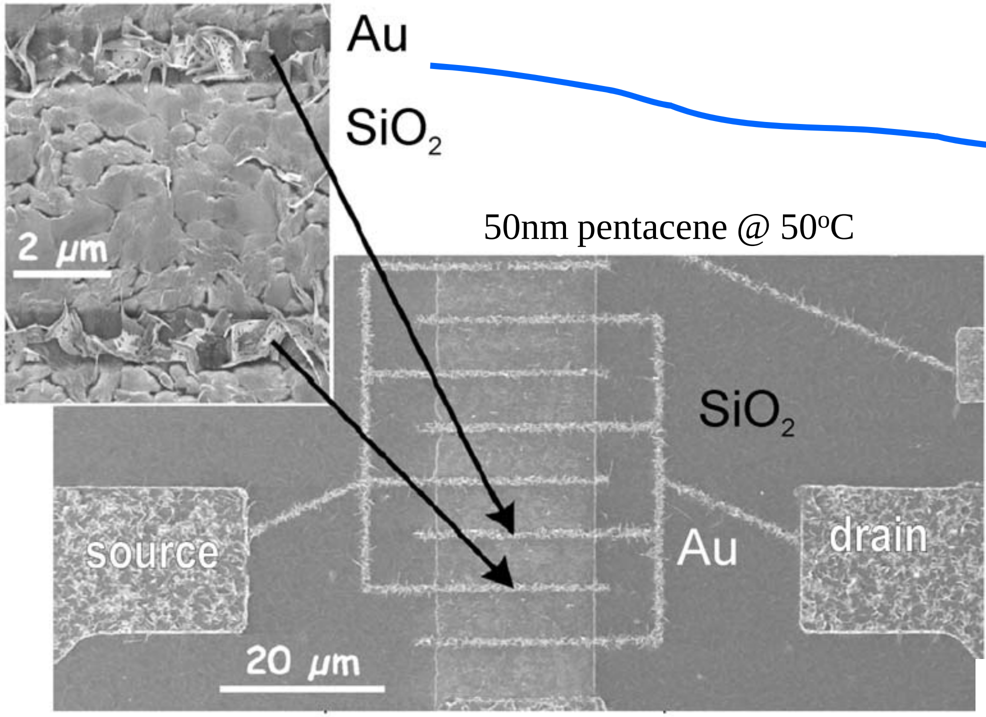


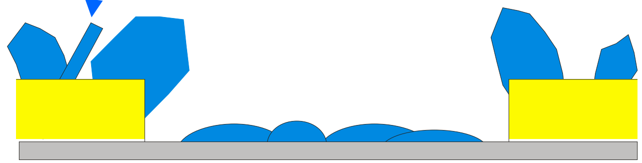
enhanced diffusion

30nm pentacene @90^{o}C



50nm pentacene @ 50^{o}C



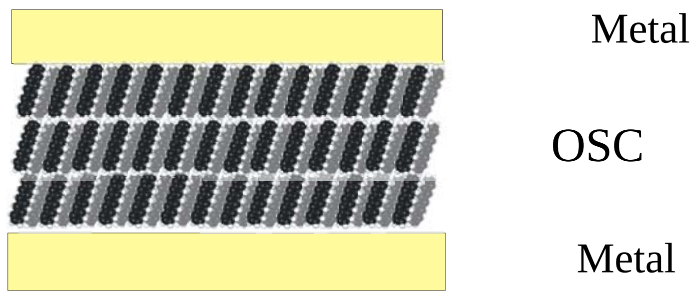


dewetting at electrodes

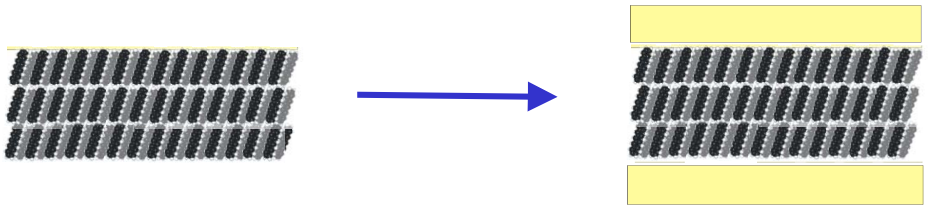
C.Bock D.V.Pham, U.Kunze, D.Käfer, G.Witte, CW
J. Appl. Phys. **100**, 114517 (2006)

It is rather difficult
to measure charge carrier mobilities
in organic semiconductors

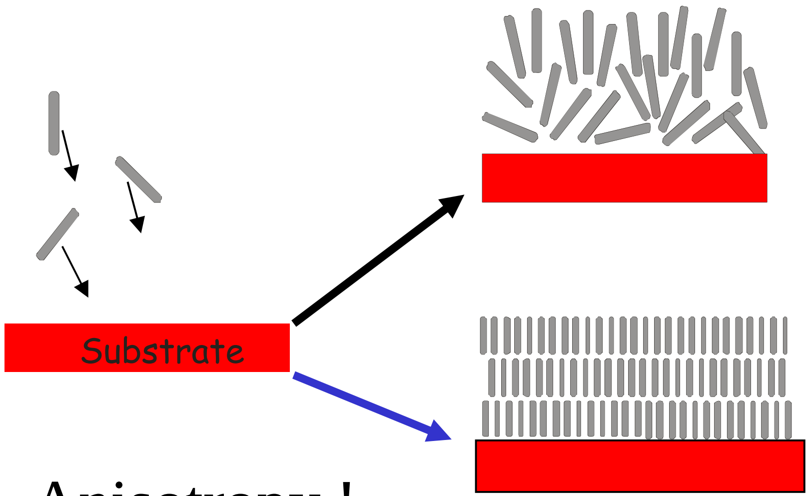
Would be good to have a model
„ideal device“



Fabrication of an „ideal" OSC-device



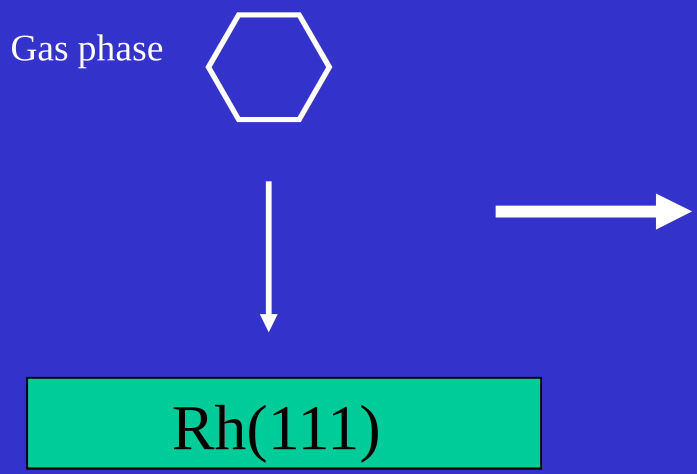
Use organic molecular beam deposition, or OMBD, in ultrahigh vacuum (UHV)



Anisotropy !

Fabrication of organic surfaces by adsorption of organic molecules on a metal substrate

Molecule (Benzene)

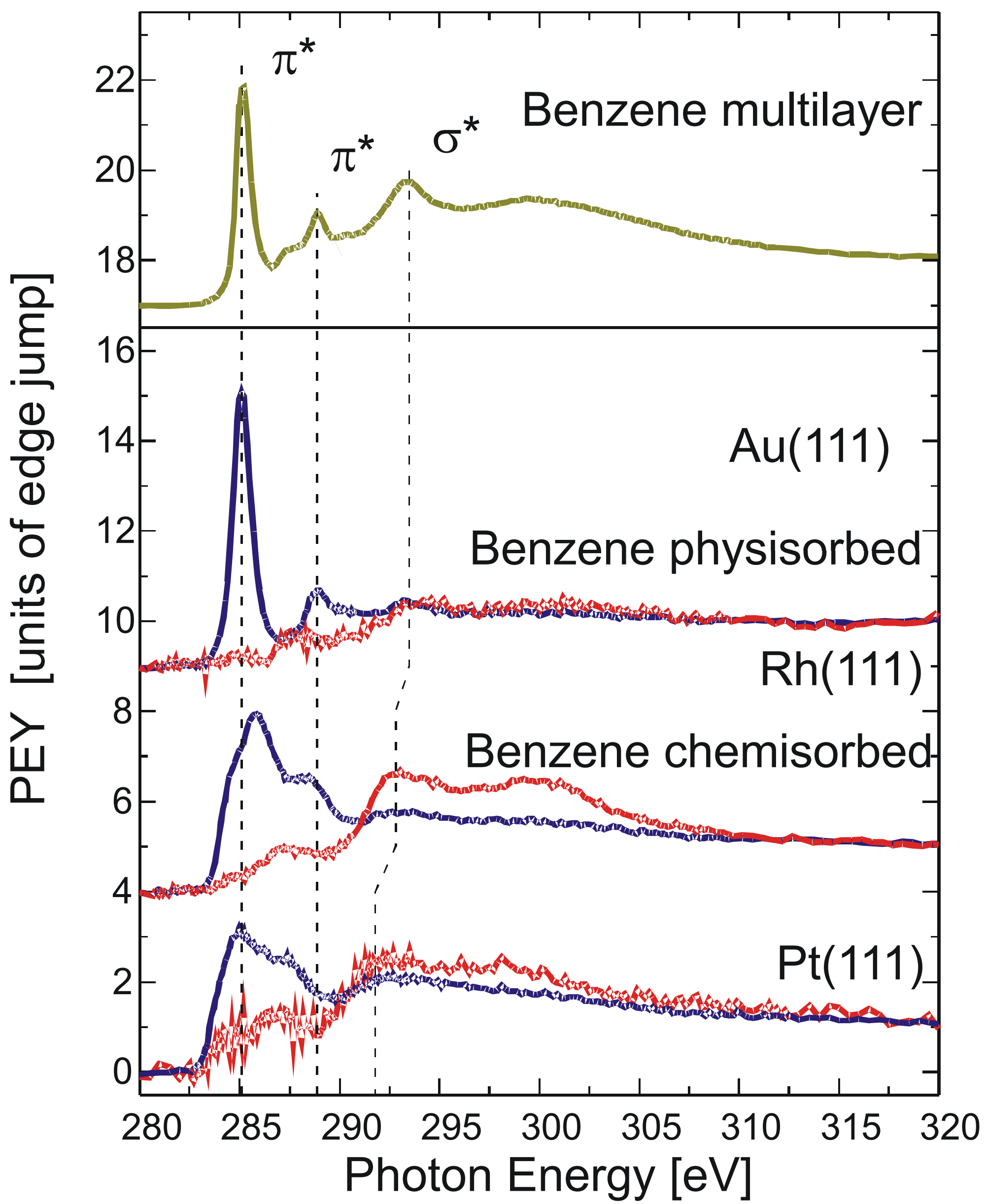


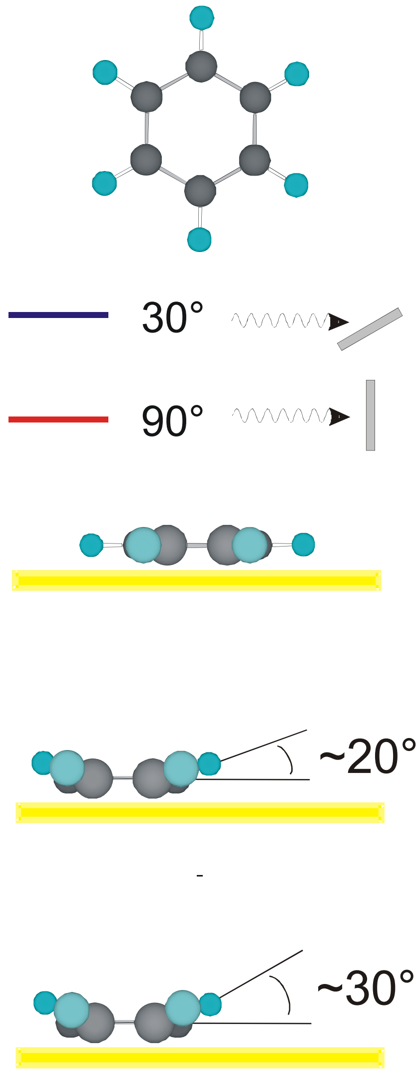
Substrate (Metal)

H.Ohtani, R.J.Wilson, S.Chiang and C.M. Mate,

Phys.Rev.Lett. **60**, 2398 (1988)

NEXAFS for benzene adsorbed on metal surfaces





Strong broadening of π*-resonance -> chemical interaction

Reduced dichroism of π*-resonance -> aplanar distortion

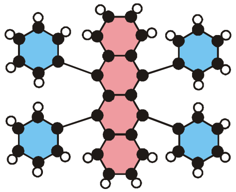
Weiss, Gebert, Wühn, Wadepohl, Wöll
JVST **A 16**, 1017-1022, (1998)

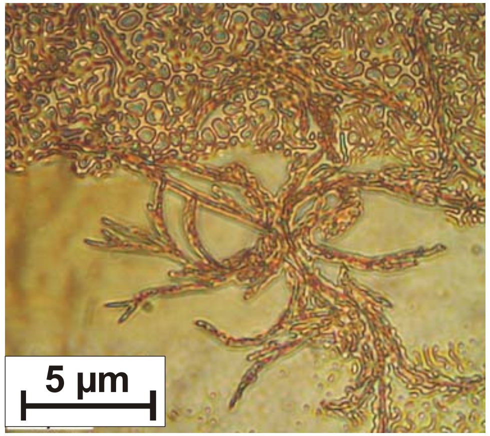
Organic molecular beam deposition of rubrene

OMBD on Au(111) & SiO_2

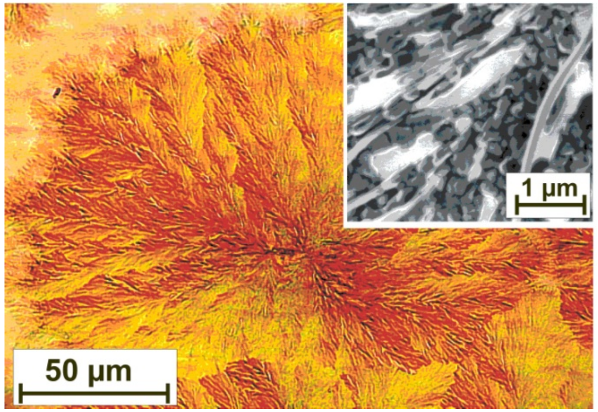
- at RT: **only amorphous films**

- at 100 °C: **dendritc growth**





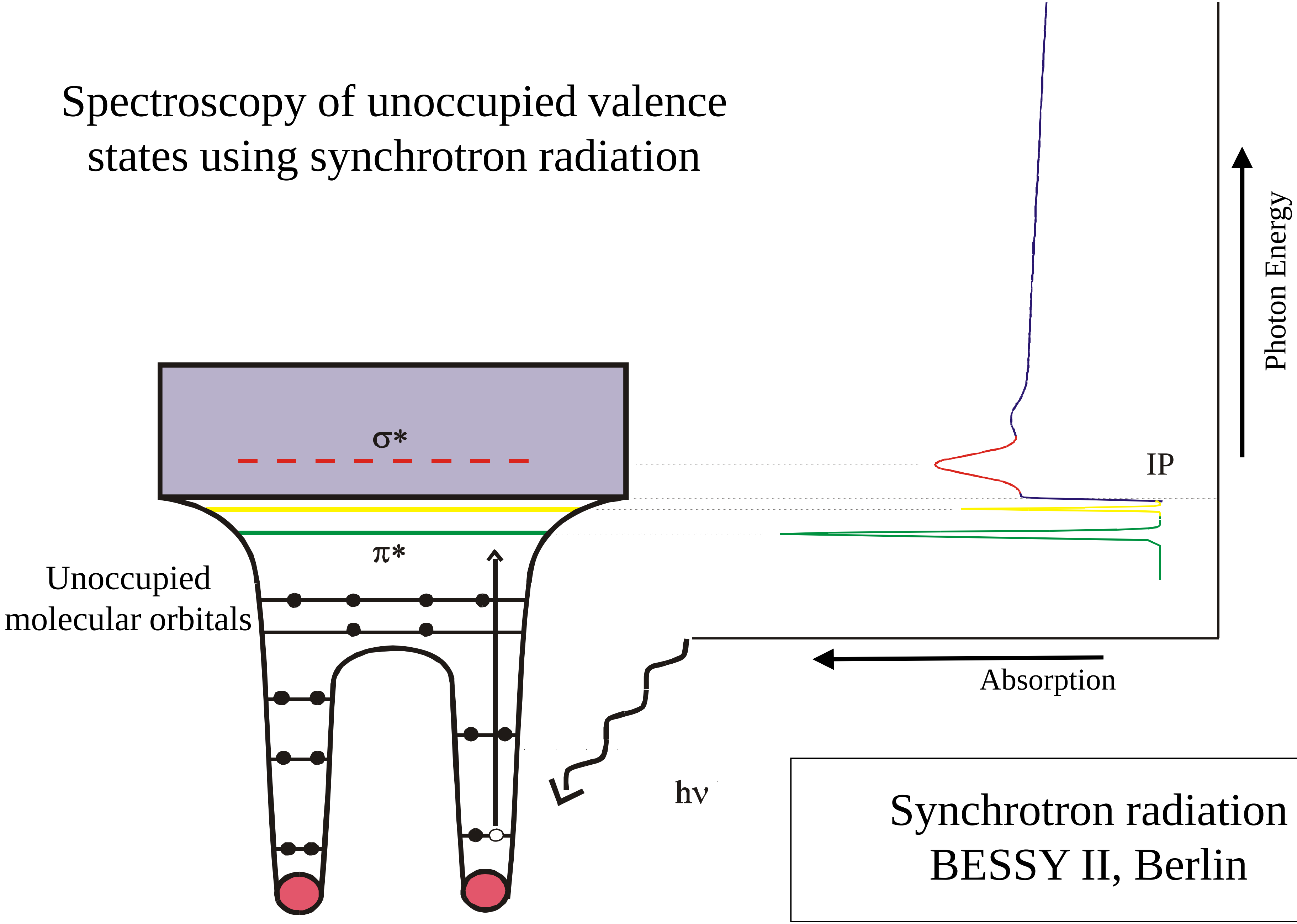
- higher substrate temperatures:
  very rough dendritic islands
  then
  dewetting & desorption
  (T_{sub}~150 °C)



What is so peculiar about rubrene ?

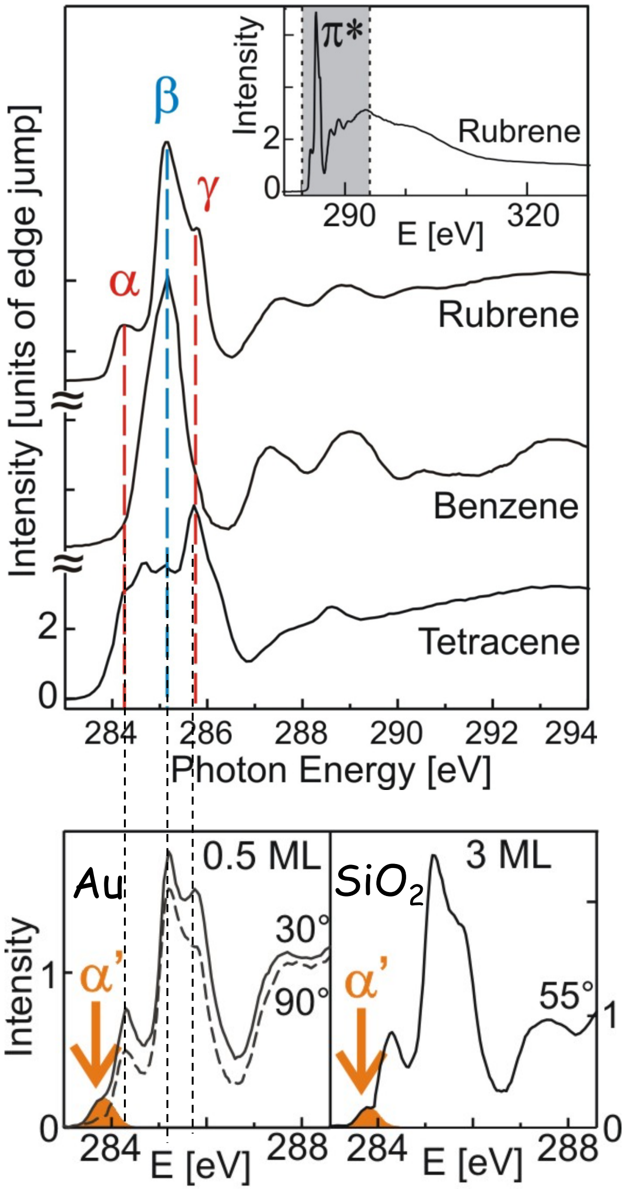
Near Edge X-ray absorption fine structure, NEXAFS

Spectroscopy of unoccupied valence states using synchrotron radiation

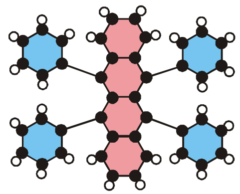


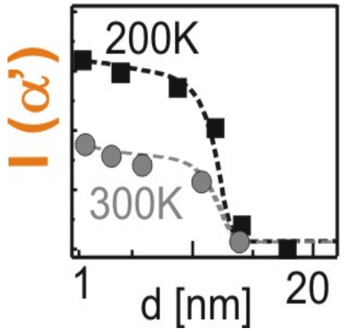
Synchrotron radiation
BESSY II, Berlin

C1s NEXAFS: OMBD of Rubrene on Au and SiO_2



Multilagen



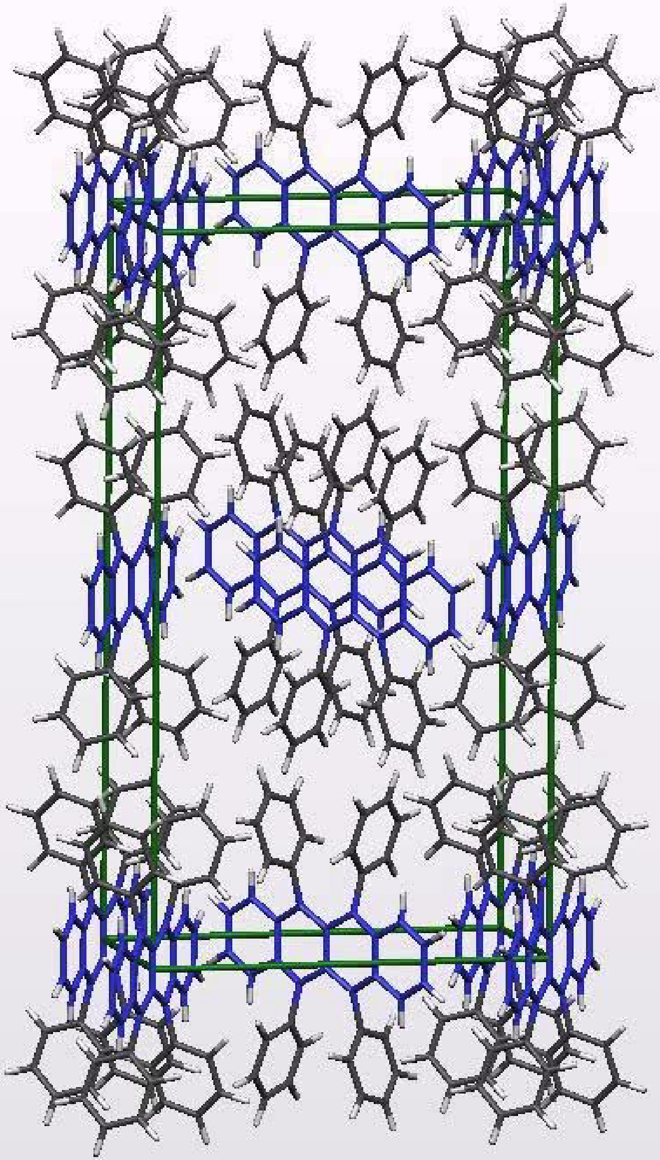


Additional π*-resonance
No contaminations

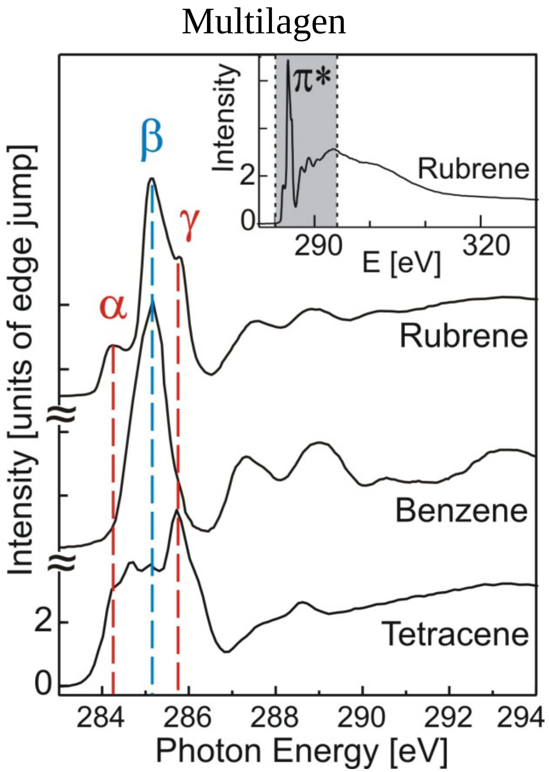
D.Käfer, L.Ruppel, G.Witte and CW, Phys. Rev. Lett. **95**, 166602 (2005)

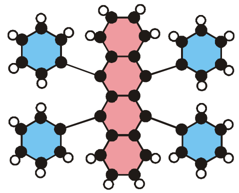
Rubrene: **the importance of molecular conformations**

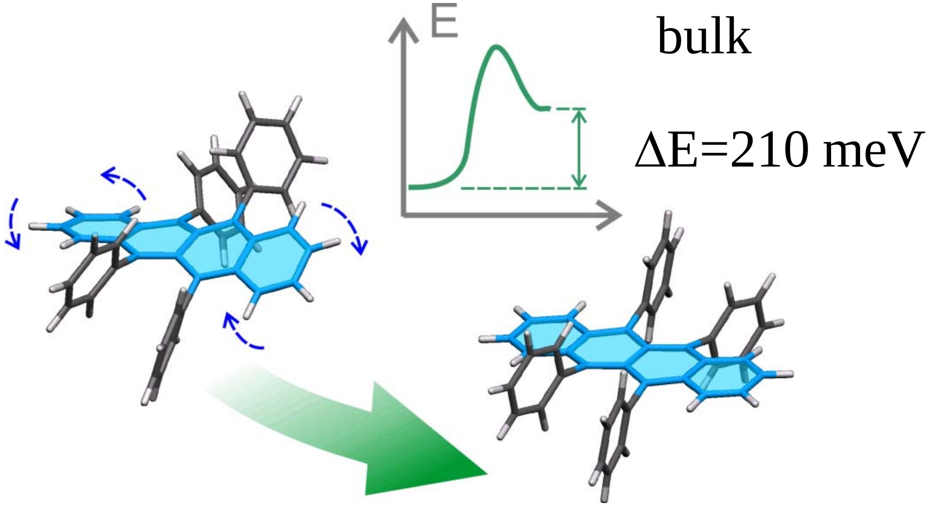
Rubrene-crystal

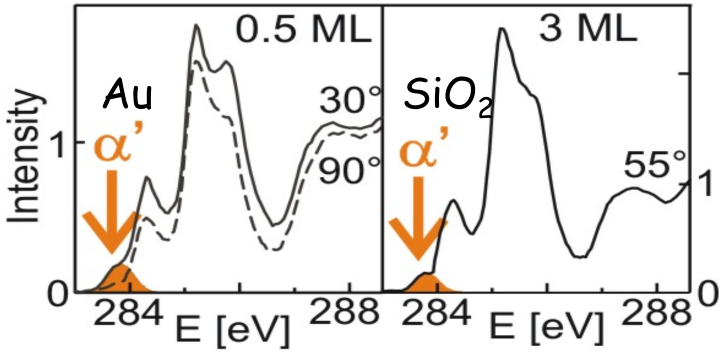


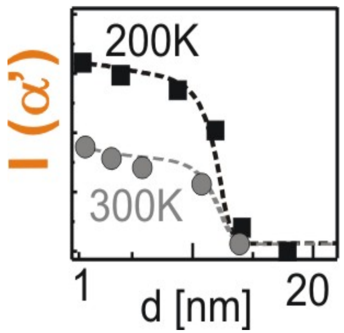
C1s NEXAFS: OMBD of Rubrene on Au and SiO_2











Twisted conformation:
additional π*-resonance

Initial growth: twisted gas-phase conformation

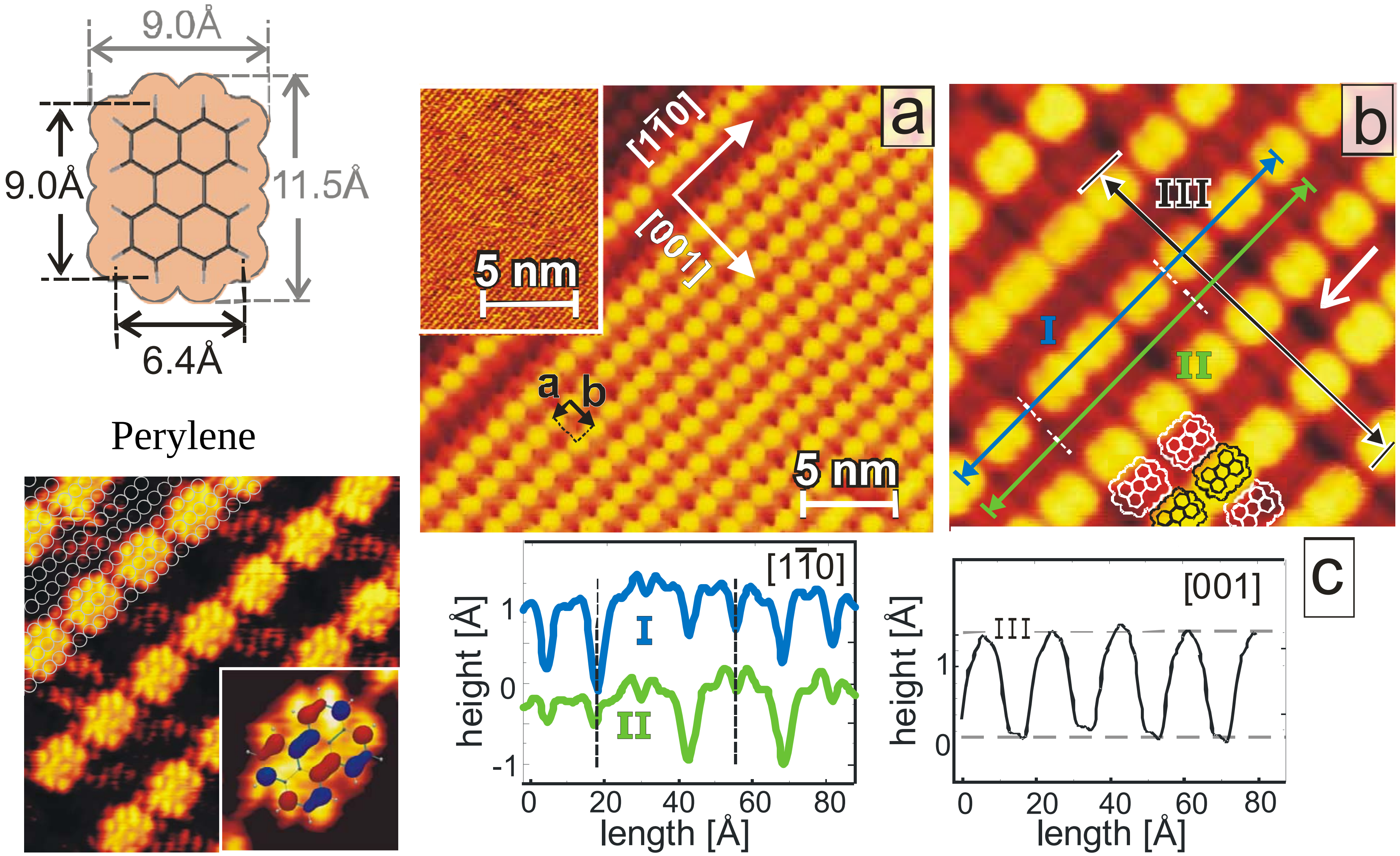
Layer thickness >12nm: Nano-crystals, no twist

D. Käfer, L. Ruppel, G. Witte and CW, Phys. Rev. Lett. **95**, 166602 (2005)

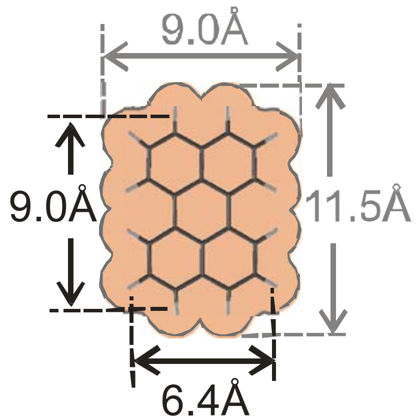
Fabrication of an „ideal" OSC-device

Rubrene is not the right molecule
for OMBD !

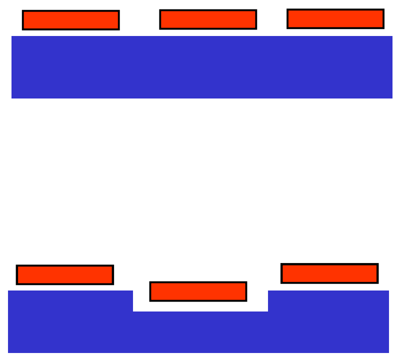
Molecules on metals: what is hard and what is soft ?
The case of perylene adsorbed on Cu(110)

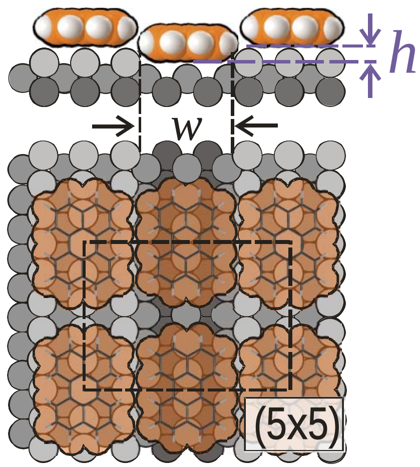


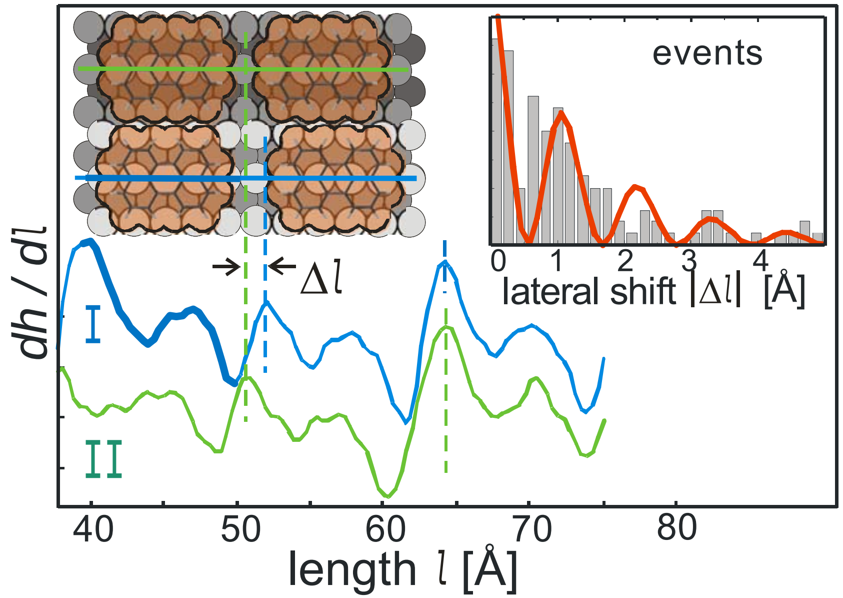
Perylene on Cu(110) - Adsorbate-induced reconstruction



Perylene

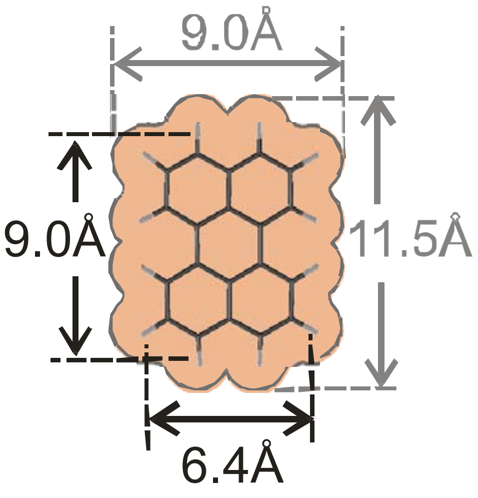






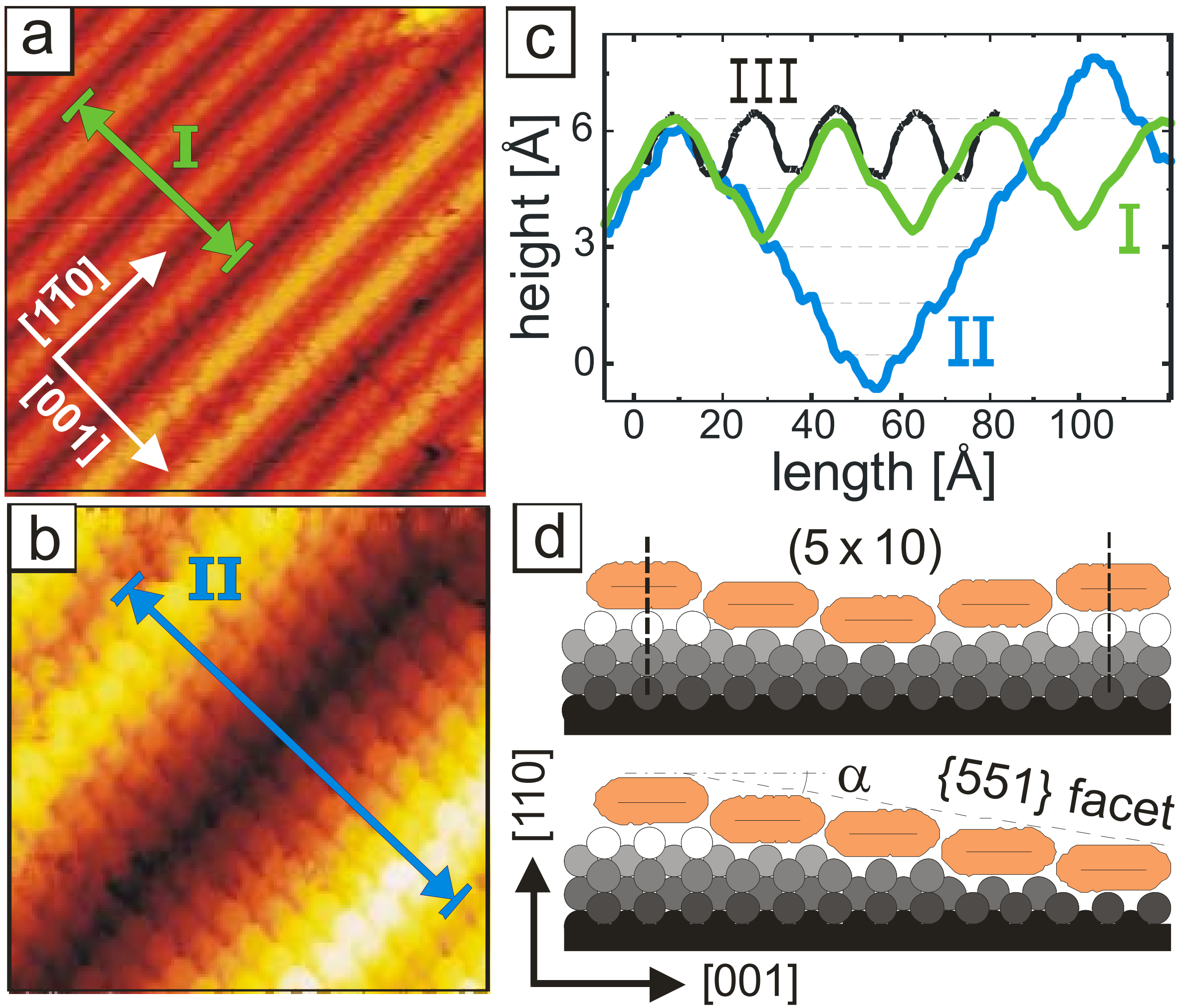
Molecules embossing a pattern into a metal

Perylene on Cu(110) - roughening at higher temperatures



Perylene

Annealing leads to faceting

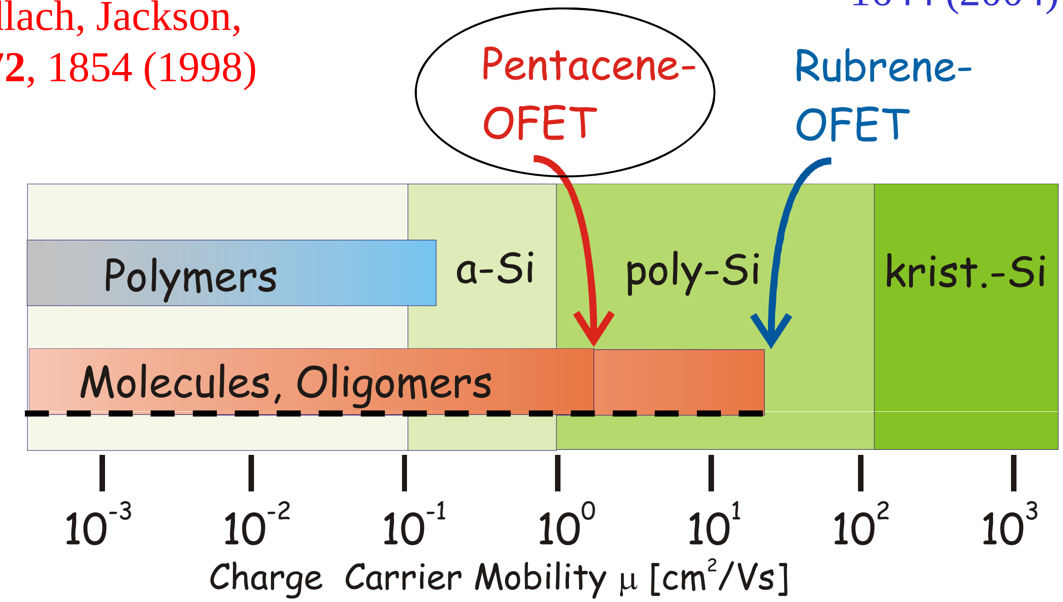


G.Witte, K.Hänel, C.Busse, A.Birkner, CW; Chem. Mater.**19**, 4228 (2007)

Organic Semiconductors: Charge Carrier Mobilities

Nelson, Lin, Gundlach, Jackson, APL **72**, 1854 (1998)

Rogers and cowork. Sundar et al., Science **303** 1644 (2004)

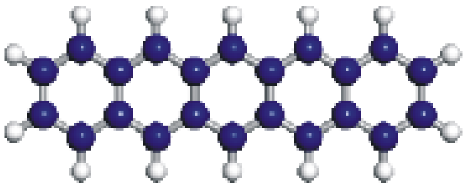


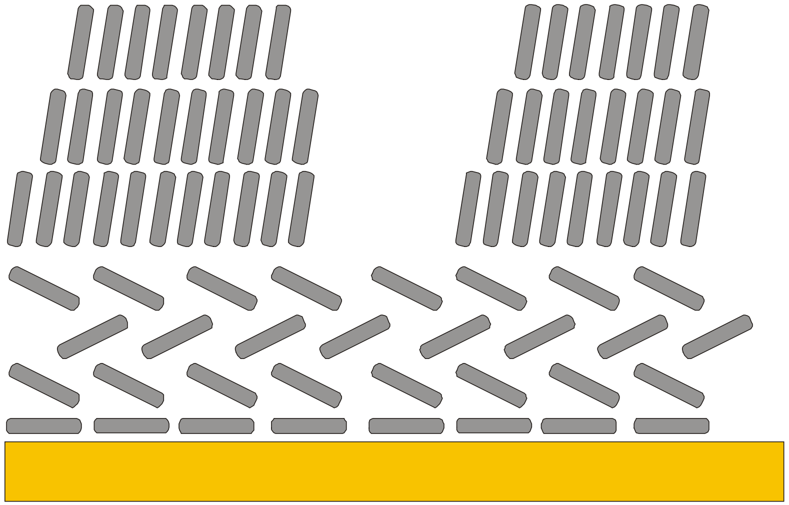
For "smart tag" Applications:

$\mu > 1\ cm^2/Vs$

Rubrene: - highly ordered, single crystals
- high purity
- not a planar aromatic molecule

Growth of pentacene on metal substrates





- no π-stacking
- Bulk structure
- dewetting

G. Beernink, T. Strunskus,G. Witte, Ch. Wöll
Appl. Phys. Lett. **85**, 398, (2004)

Orientational transitions

→ No OMBE, impossible to grow homogenous, crystalline films on a metal surface

More detailed studies: rather rule than exception in OMBD of aromatic molecules on metals

Review: Witte & Wöll ***in : Journal Materials Research,*** J. Mater. Res. **19**, 1889 (2004)

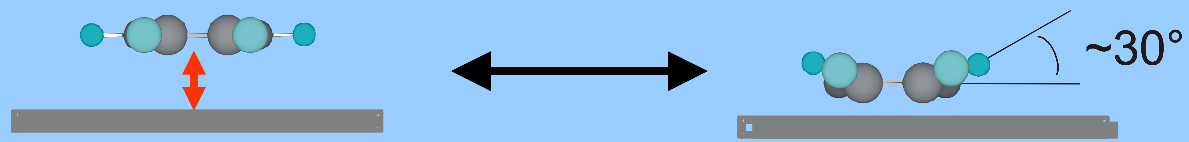
The „ideal" metal/organic interface: the problems

- Epitaxial growth only for organic molecules which exhibit „orientational precursor" in bulk
  (very few, one example is PTCDA)
- Molecular conformation of molecule may be different (rubrene)
- Variation of workfunction (adjustment of electronic level alignment) difficult

→ Need modification of metal substrate

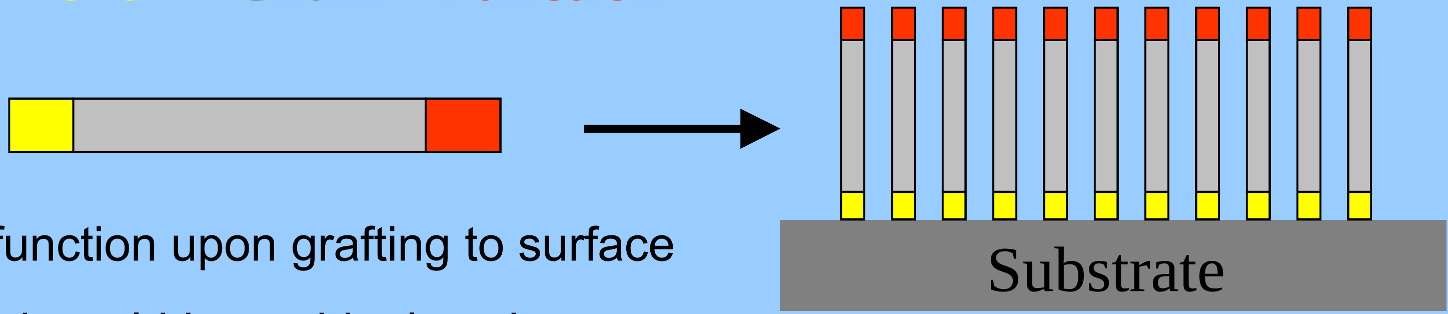
Grafting of interesting molecules to a metal substrate

- Adsorption of a simple (monofunctional) molecule not very efficient
- Either bonding is so strong that molecule is modified
- Or bonding is so weak that system is unstable at room-temperature



Example:
benzene

Better: Anchor – Chain - Function

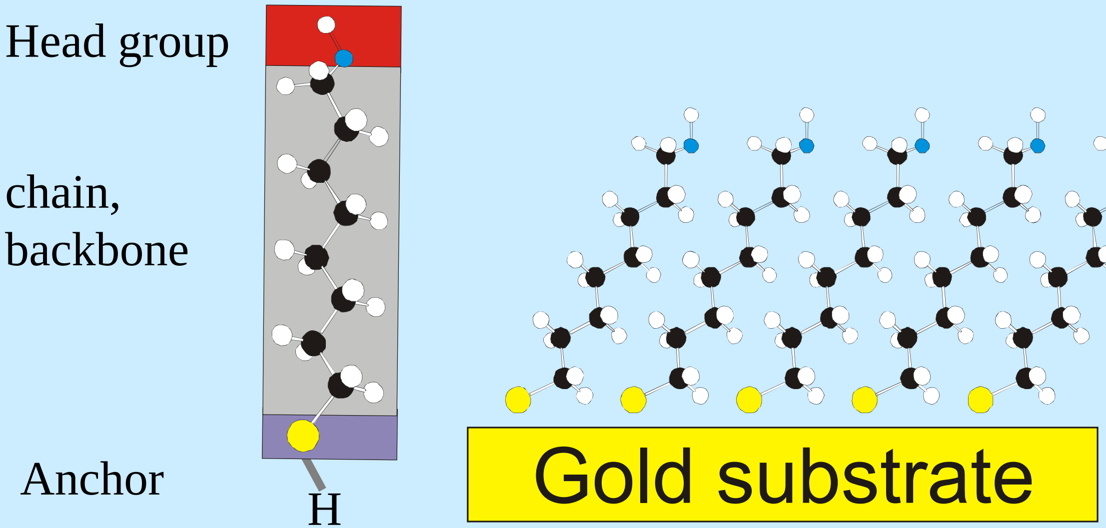


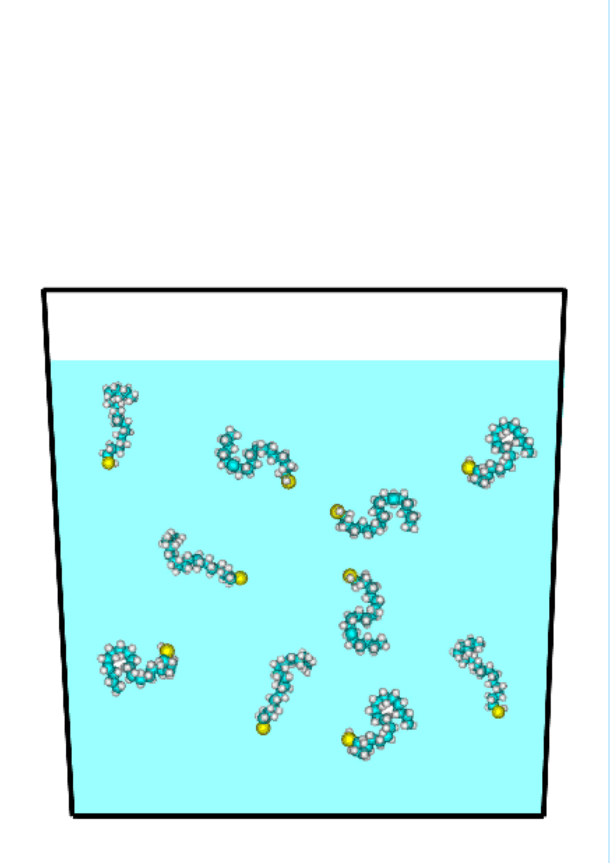
No modification of function upon grafting to surface

A covalent bond would be an ideal anchor

Most important system today: SAMs made from organothiols

Anchoring through Au-thiolate bond

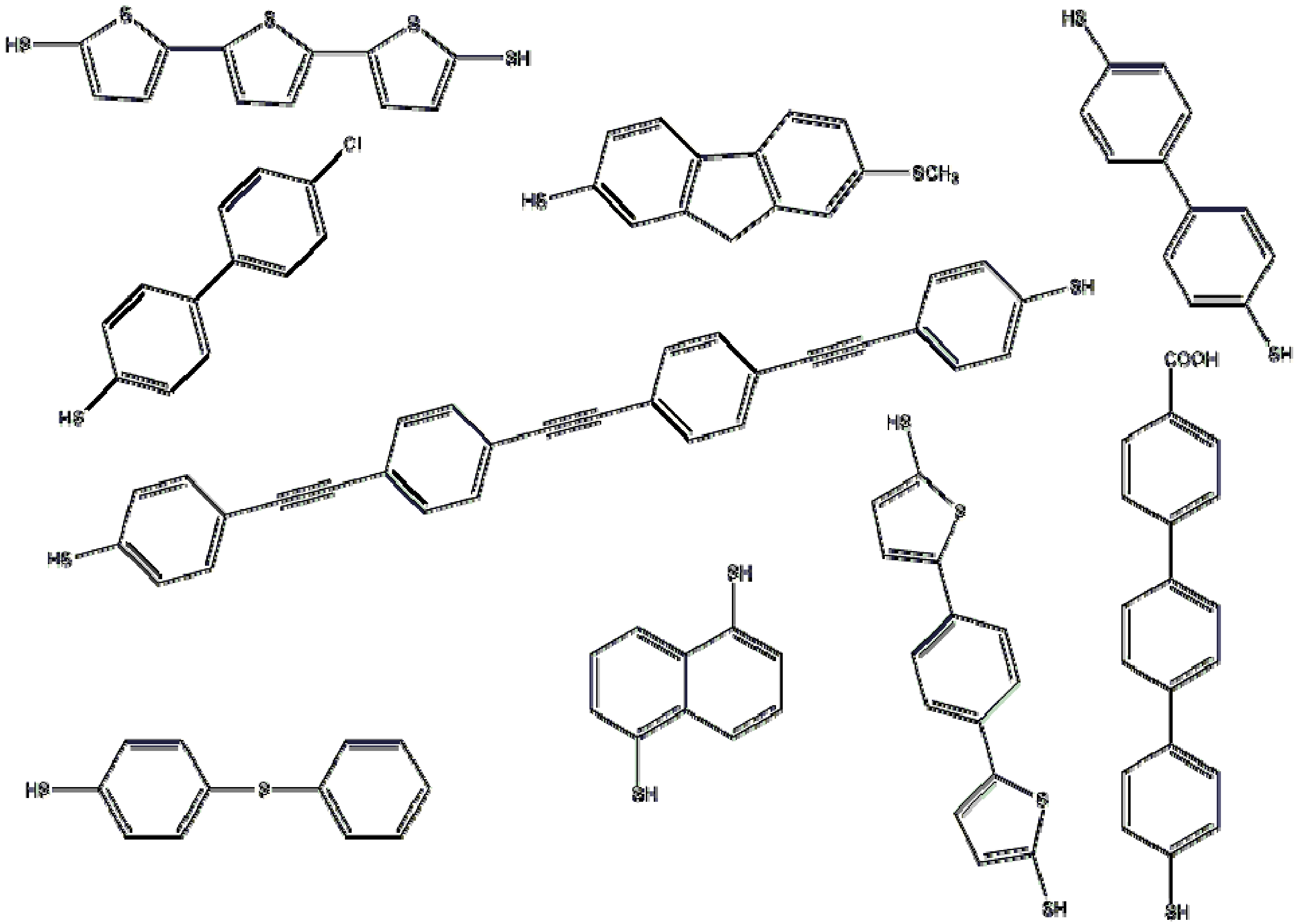




Octanethiol, alkanethiols

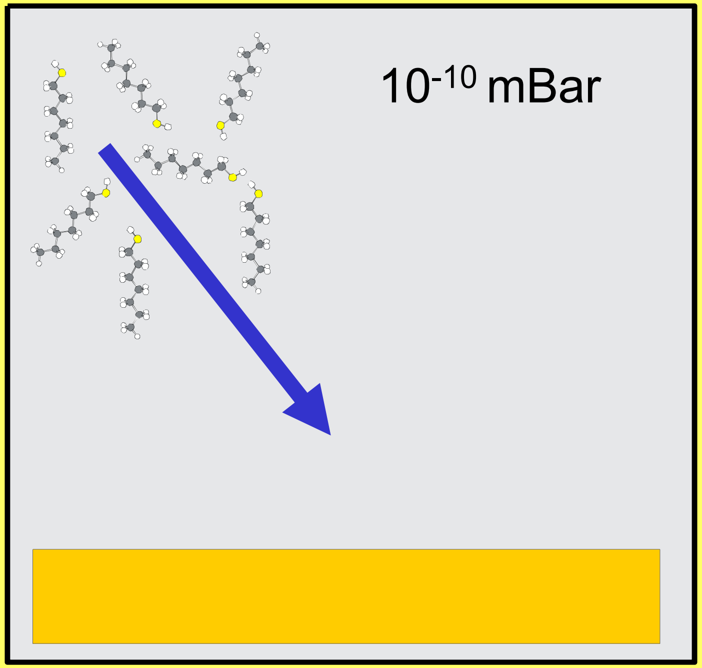
R.G. Nuzzo, D.L. Allara, J.Am.Chem.Soc. **105**, 4481, (1983)

Most organic molecules are suited for incorporation into organothiols ….

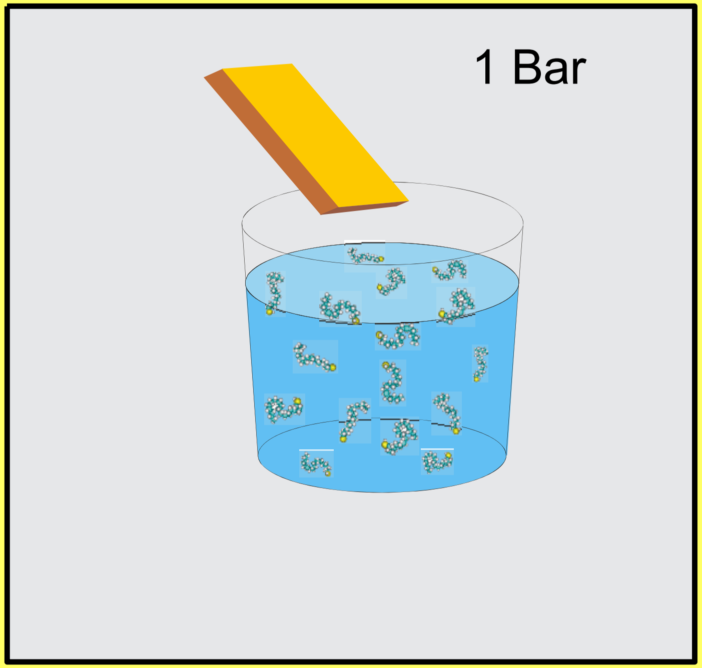


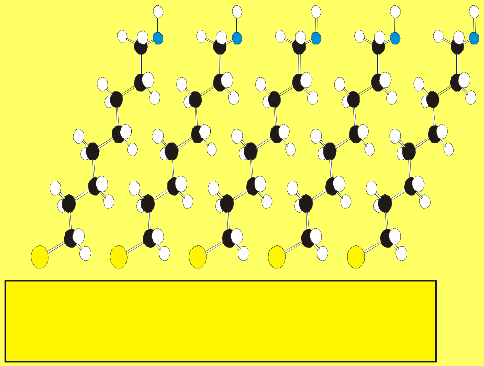
Two principal ways to fabricate SAMs …

Deposition in Ultrahigh Vacuum (UHV)



Deposition from solution (ambient conditions)

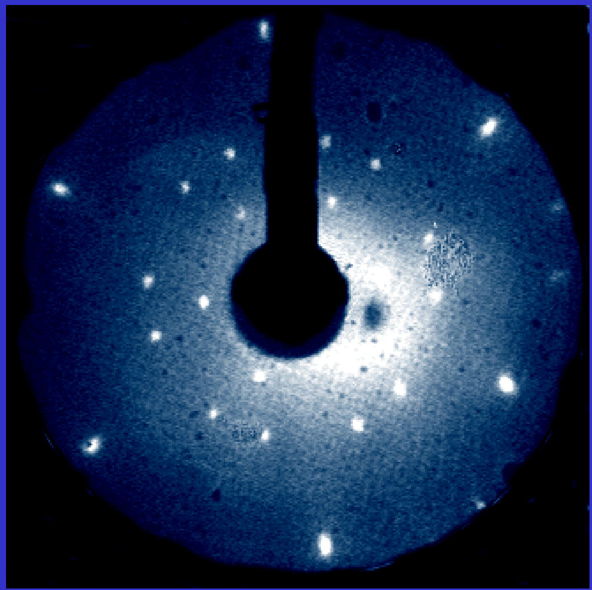




Very difficult to determine preparation method for SAM after formation!

All standard methods in Surface Science are applicable !

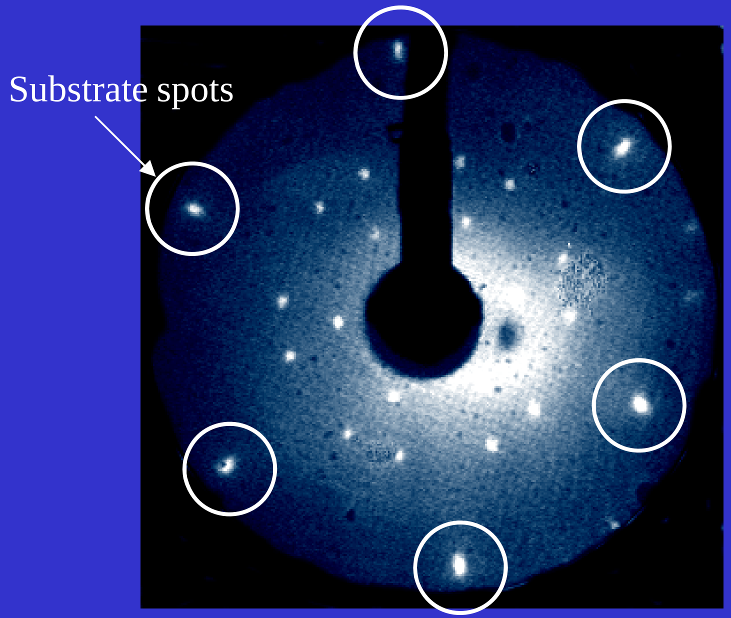
Diffraction of electrons (LEED):
Formation of highly ordered molecular adlayers



Decane thiolate

LEED
Diffraction of low energy electrons
(27 eV)

Diffraction of electrons (LEED):
Formation of highly ordered molecular adlayers

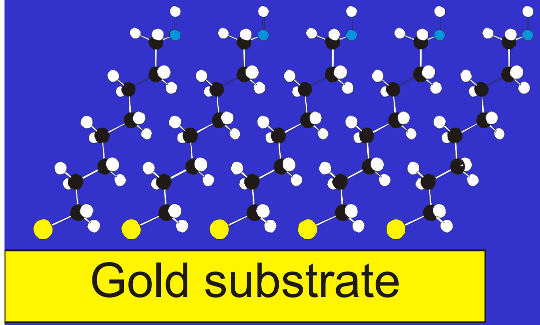


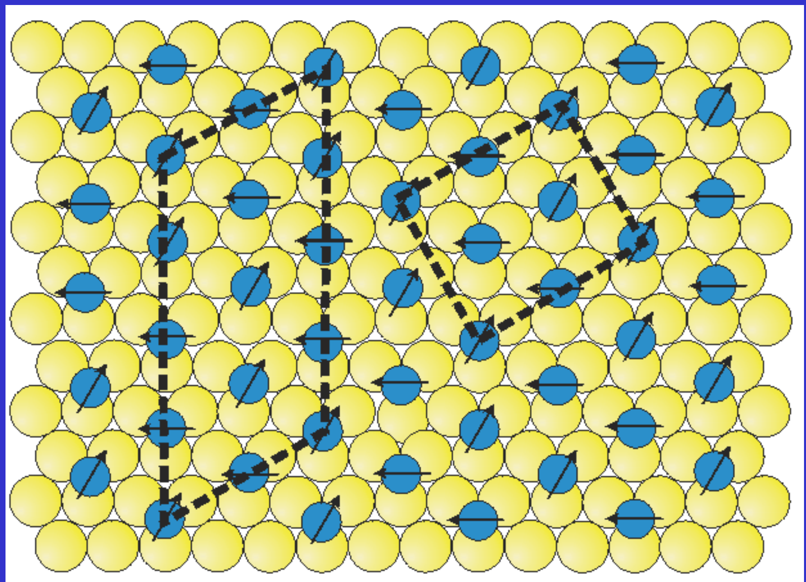
Decane thiolate

LEED
Diffraction of low energy electrons
(27 eV)

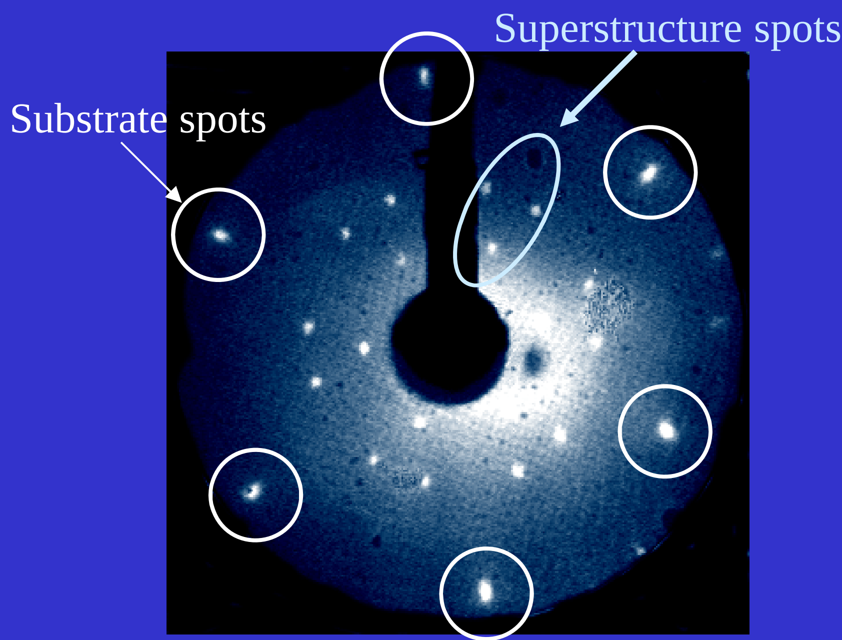
Diffraction of electrons (LEED): Formation of highly ordered molecular adlayers

Decane thiolate



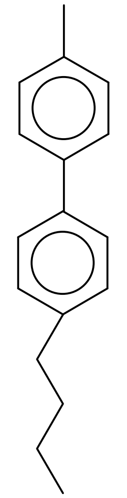


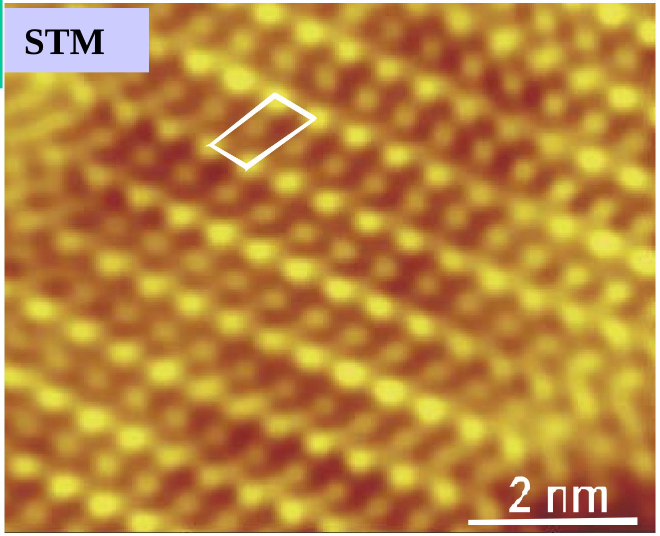
$(2\sqrt{3} * \sqrt{3})R30°$



LEED
Diffraction of low energy electrons
(27 eV)

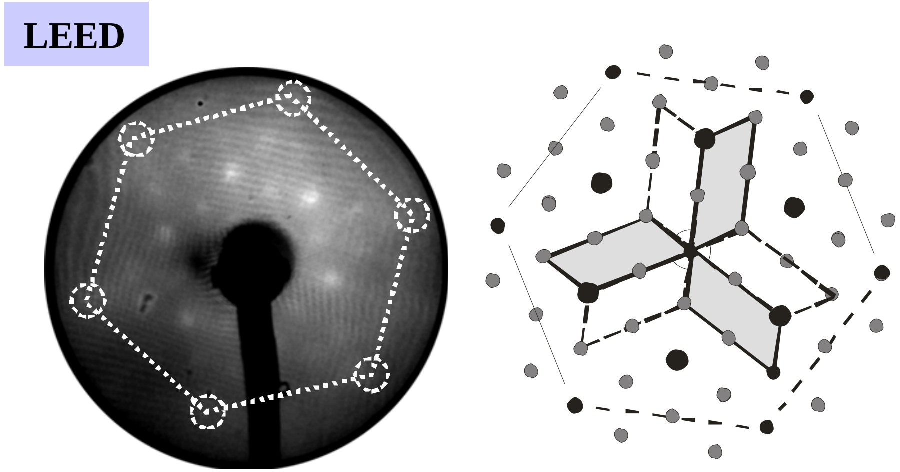
BP3





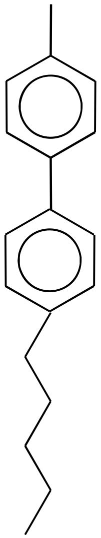
(2·√3× 3)Structure

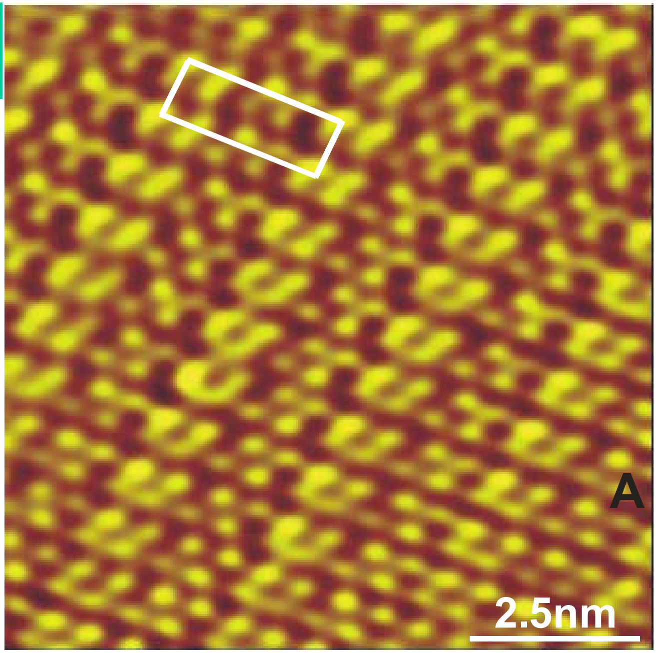
Molecular area 21.6 Å²



Left: LEED patterns recorded for a BP3 monolayer at 345 K. **Right**: Schematic diffraction pattern for the (2·√3× 3)- structure.

BP4





(5· √3×3)-Structure

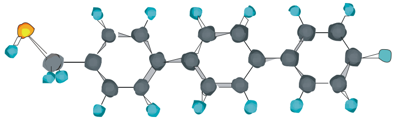
Molecular area 27.05 Å²

No ordered diffraction pattern could be observed for BP4 monolayers

Pronounced difference between odd and even number of methylene units !

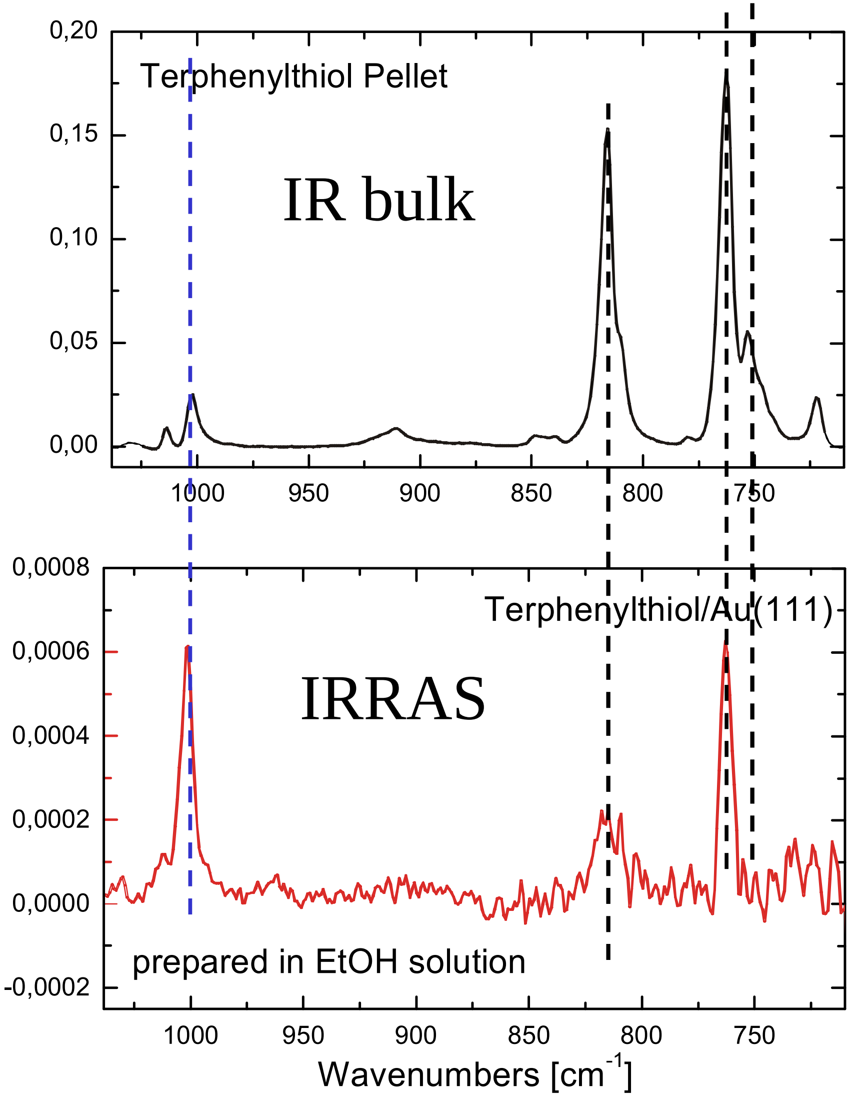
Determination of composition and molecular orientation using IR-spectroscopy

Terphenylthiol

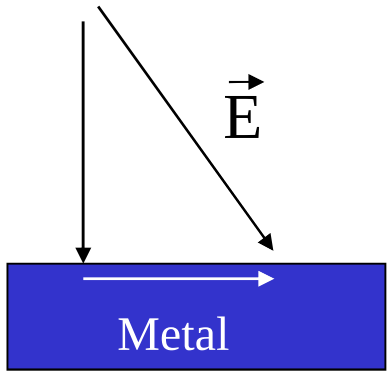


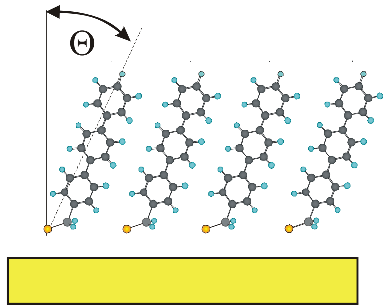
KBr pellet

Thiolat-Adlayer on Au

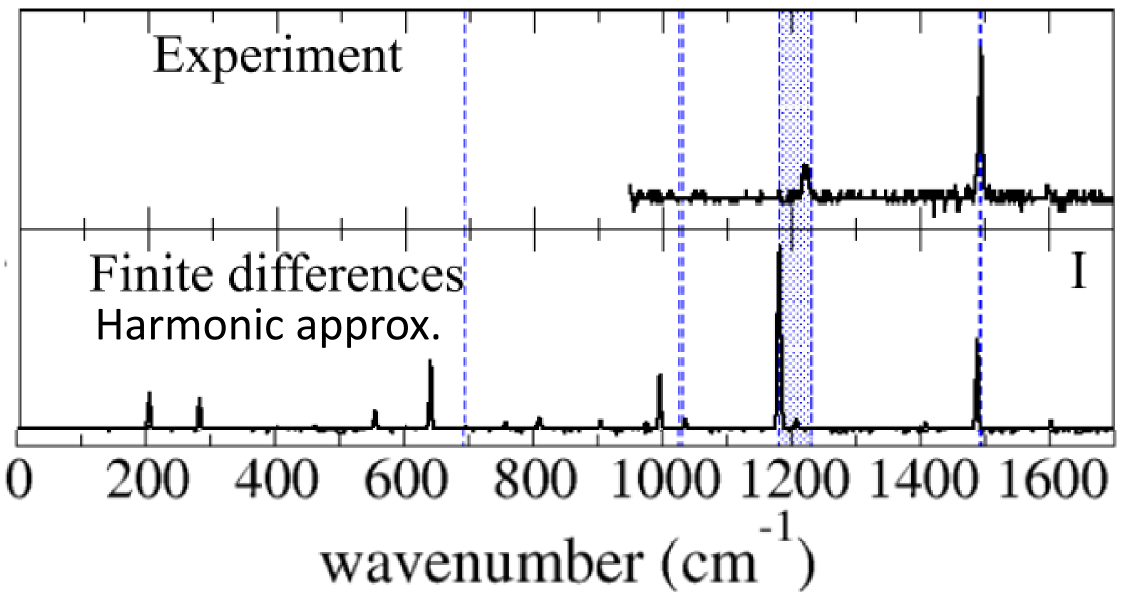


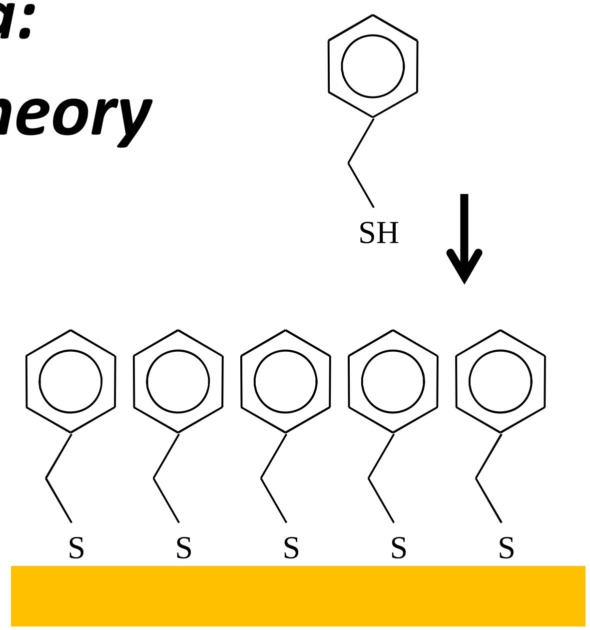
Surface selection rule





Analysis of SAM infrared data: Comparison of experiment and theory



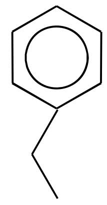


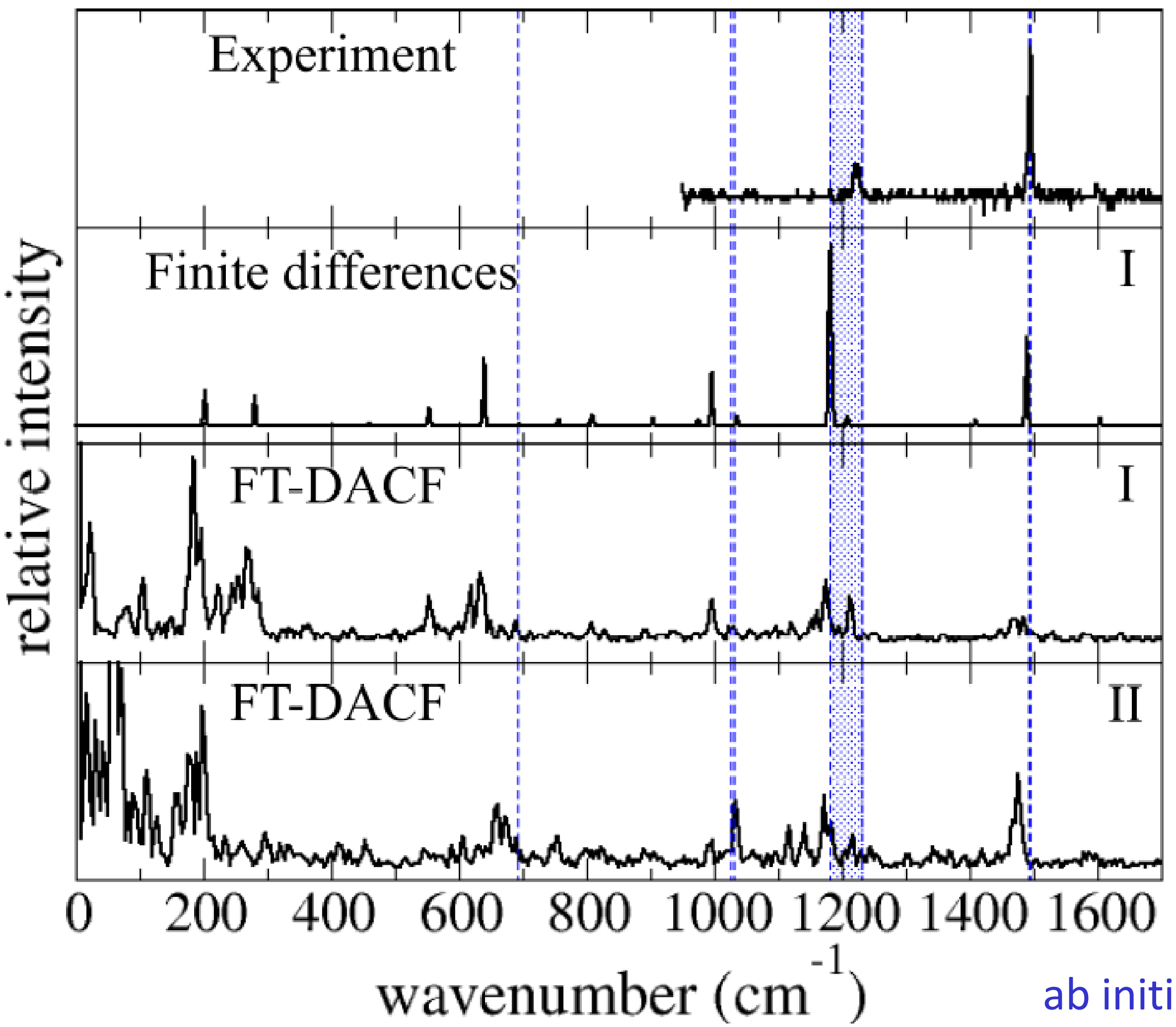
Summer School on
Modern Concepts for Creating and Analyzing
Surfaces and Nanoscale Materials
San Feliu, Spain

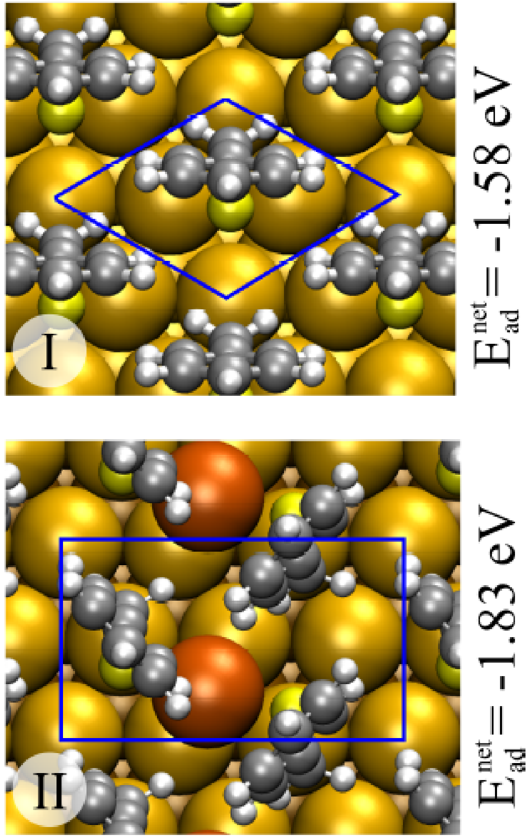
12. – 16.5.2008

Poor agreement
Between experiment
and theory

Analysis of SAM IRRAS-data: Comparison of experiment and theory



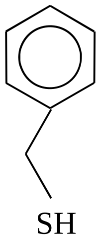


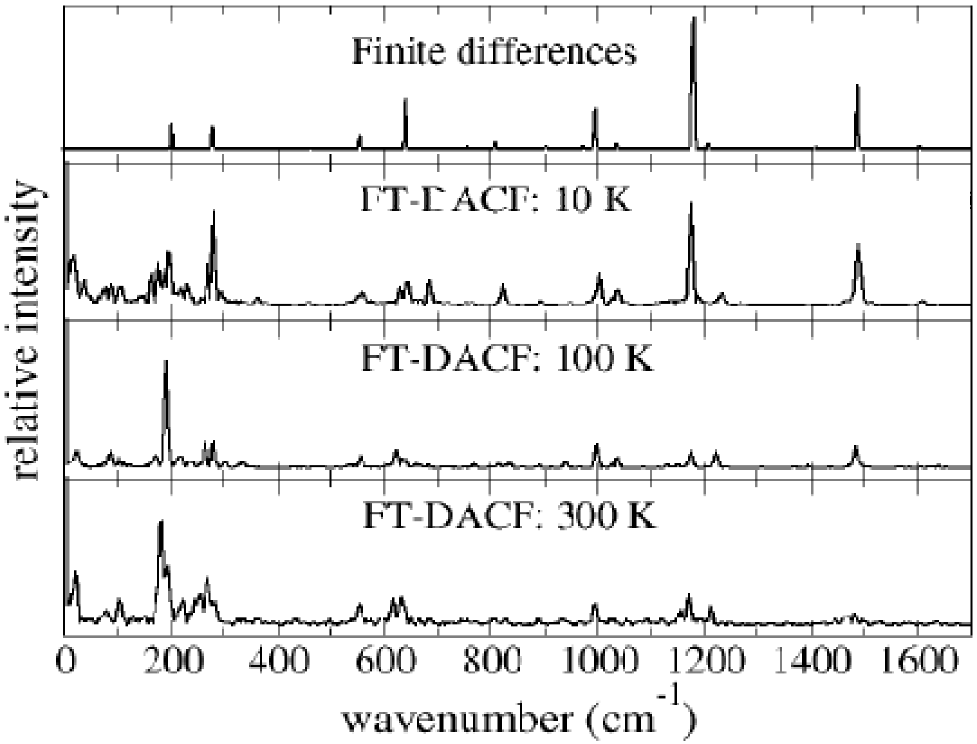


ab initio molecular dynamics simulations

Katrin Forster-Tonigold, X. Stammer, CW and A. Groß, submitted for publication

Analysis of SAM IRRAS-data: Comparison of experiment and theory





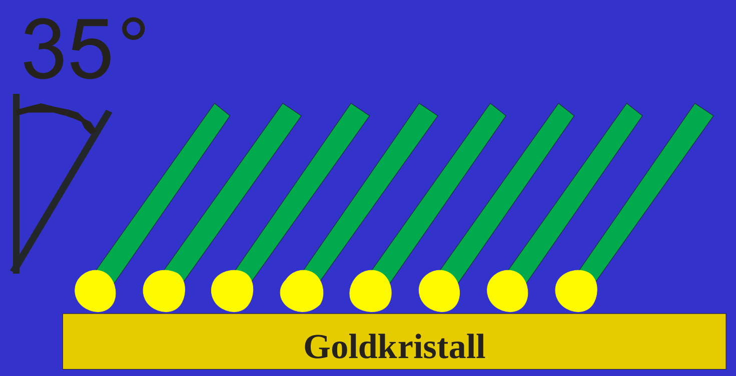
Increasing temperature

ab initio molecular dynamics simulations

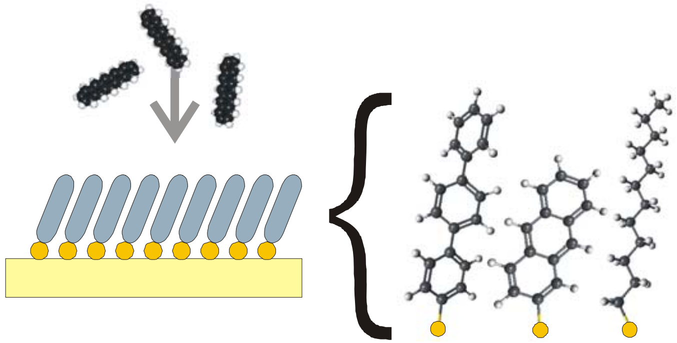
Katrin Forster-Tonigold, X. Stammer, CW and A. Groß, submitted for publication

Self-assembled monolayers fabricated by immersion of Au-substrates into solutions of organothiols

- SAMs are ultrathin organic films with extremely high structural quality (2D single crystal)
- exhibits organic surfaces mainly defined by ω-function of thiol
- Basically all traditional techniques form traditional surface science can be applied (including XPS,UPS and STM)
- Ideal model system for organic molecular beam deposition (?)



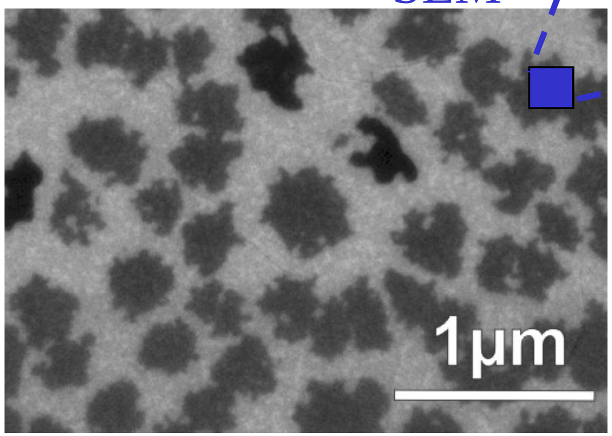
Pentacene growth on modified Au(111)-surfaces



Pentacene / **SAM**/ Au(111)

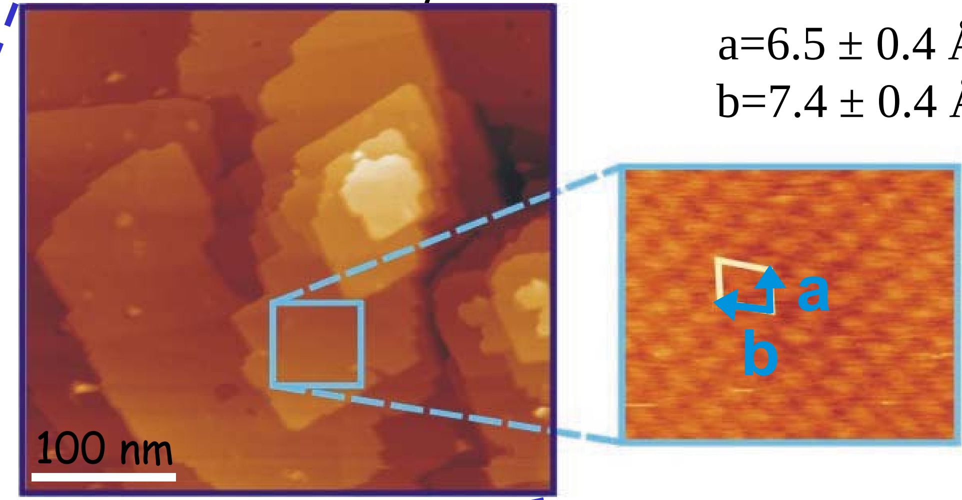
d=2nm @rt

SEM



no morphological changes
within 72 h

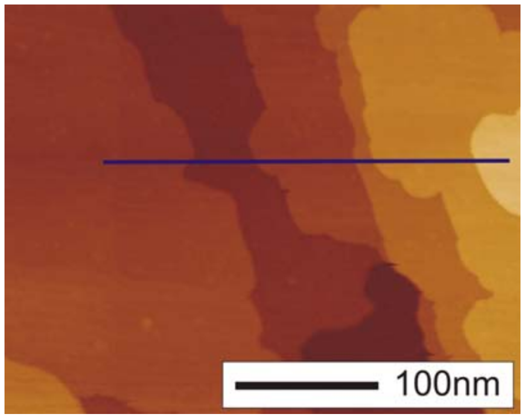
Pentacene/Phenylthiol



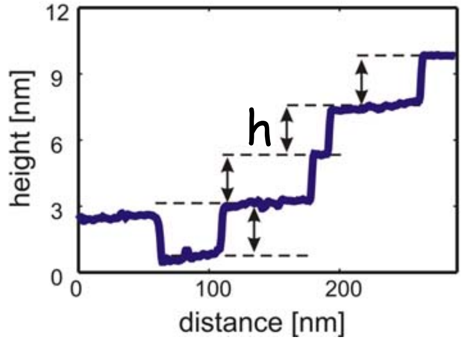
a=6.5 ± 0.4 Å
b=7.4 ± 0.4 Å

AFM data

Pentacene/Alkanethiol

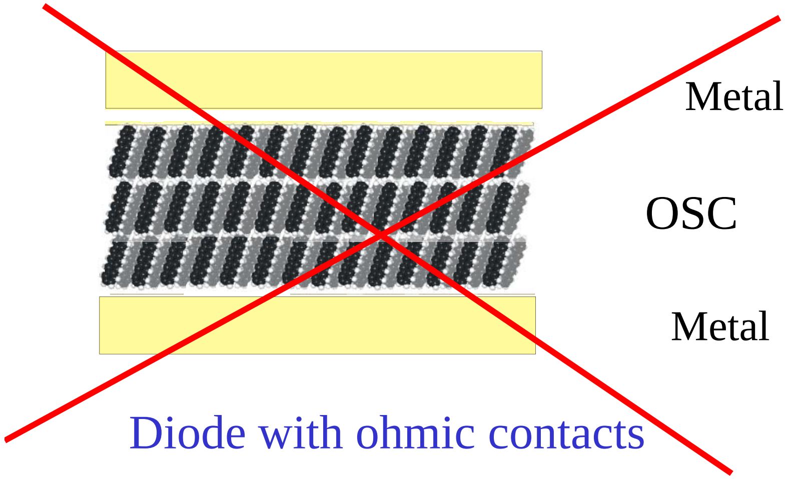


h=17 ± 3 Å

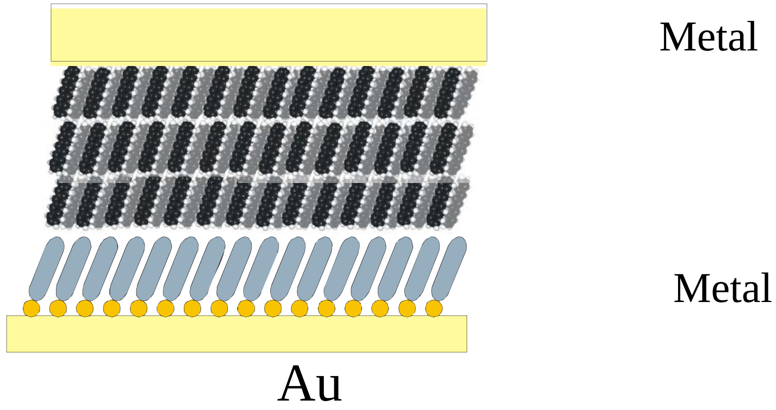


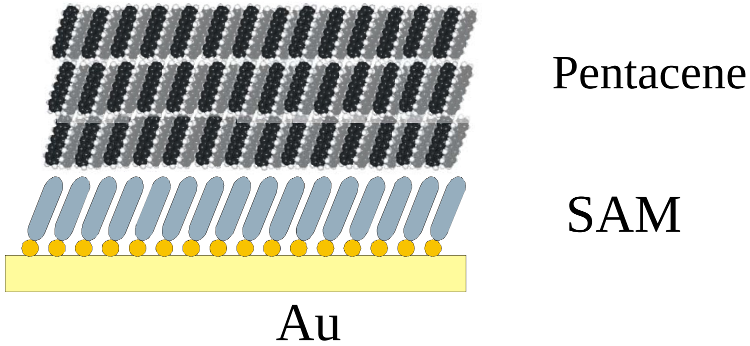
L.Ruppel, A.Birkner, G.Witte, C.Busse, T.Lindner, G.Paasch, CW, J.Appl.Phys. 102, 033708 (2007)

Fabrication of an „ideal" OSC-device

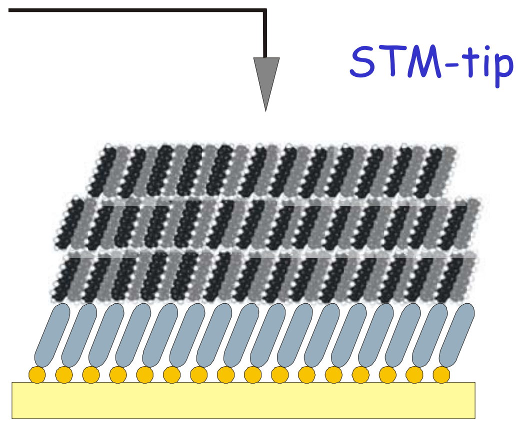


Diode with ohmic contacts



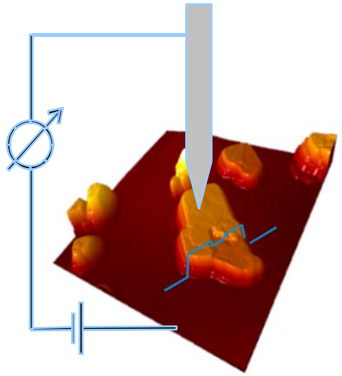


Perfect growth on modified substrate !

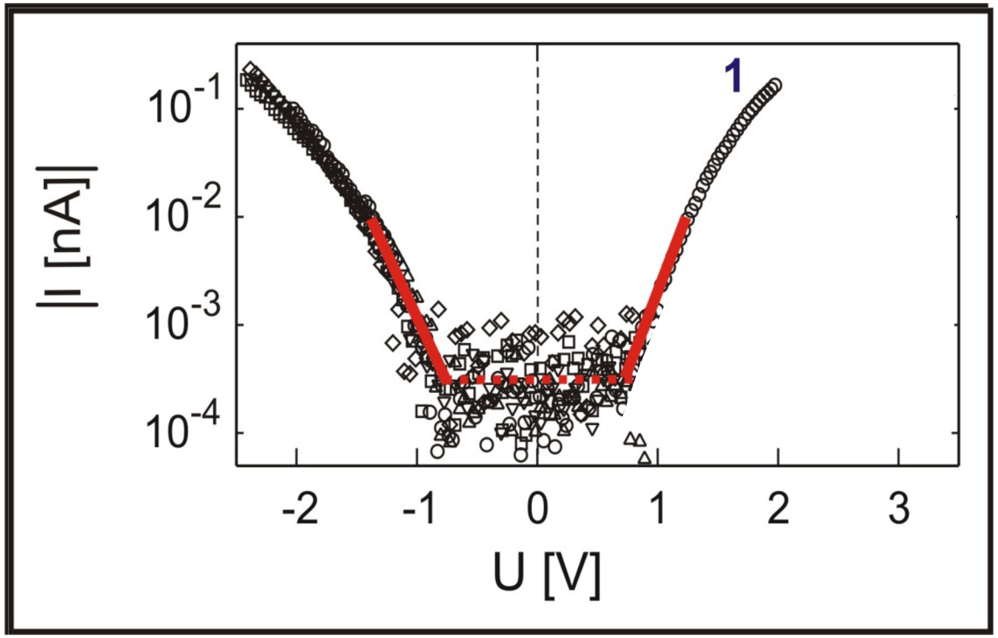


Diode with two different tunneling contacts

Current-Voltage characteristics of „diode"-setup

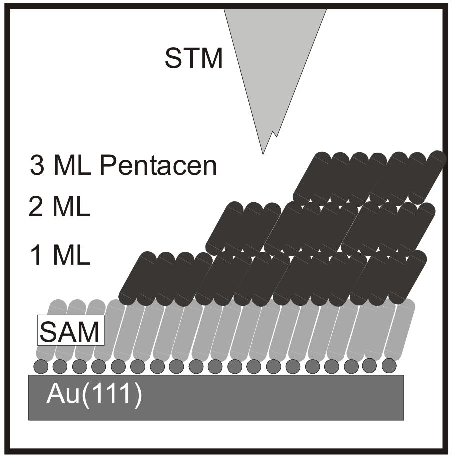


A total of ~ 50 islands have been investigated

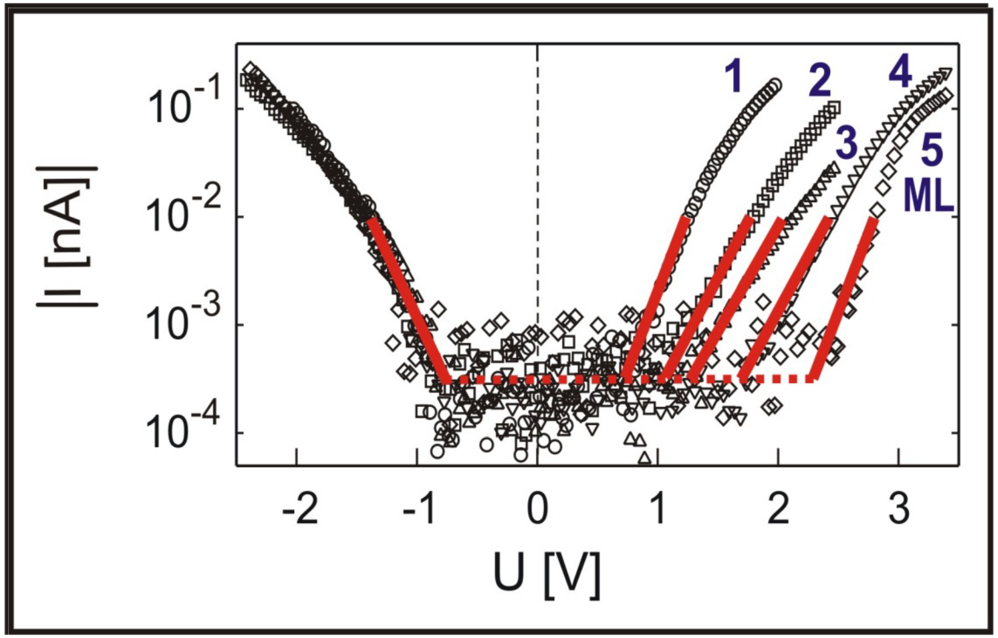


Log. plot onset values at noise level ($3 \cdot 10^{-4}$ nA)

Current-Voltage characteristics of „diode"-setup



A total of ~ 50 islands have been investigated

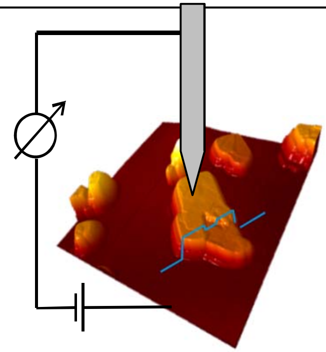


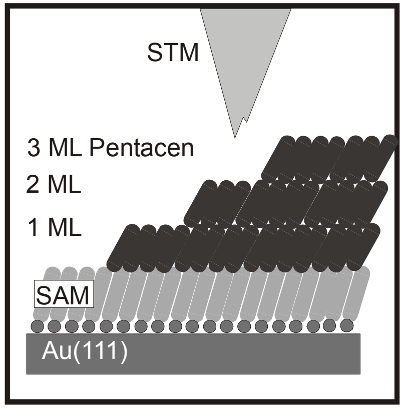
Log. plot onset values
at noise level ($3 \cdot 10^{-4}$ nA)

- asymmetric onset voltages
- thickness dependent onset voltages for positive sample bias
- onset voltage stays fixed for negative voltage

Conclusions from "model" diode

- n-conduction possible for pentacene,
  not only p-conduction
- absence of n-conduction evidence for contaminations (e-traps)
- Strong evidence for band-like transport in pentacene
  (temperature-dep.)
- Determination of mobilities should be possible,
  numerical simulations underway (difficult)





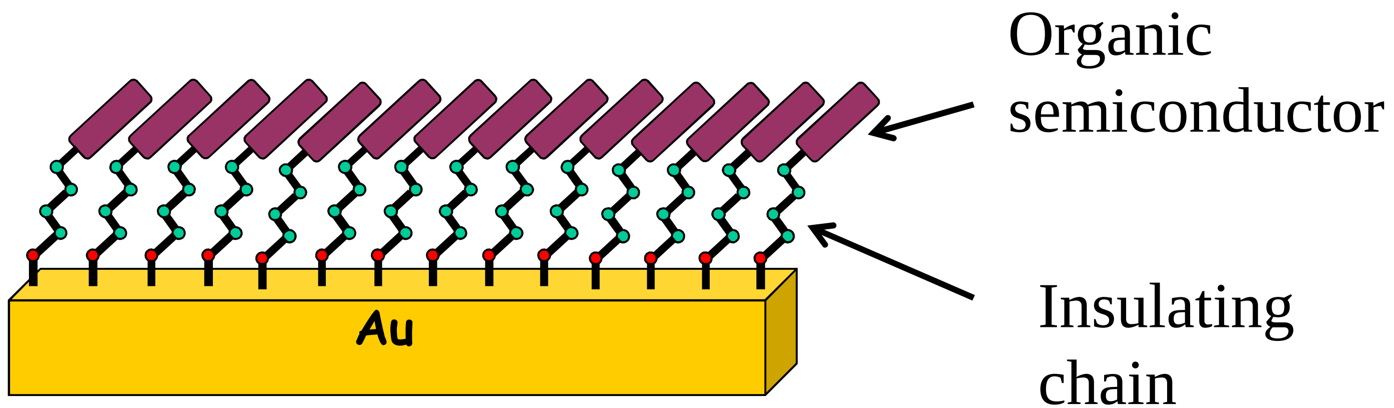
n-conduction in pentacene ? – absent in most real devices

- n-conduction for OSC in the absence of charge traps (-OH at interface)
  Chua, Zaumseil, Chang, Ou, Ho, Sirringhaus, Friend, Nature **434**, 194 (2005).

→ Crucial test: Introduce e-traps
OH-groups at organic/metal interface

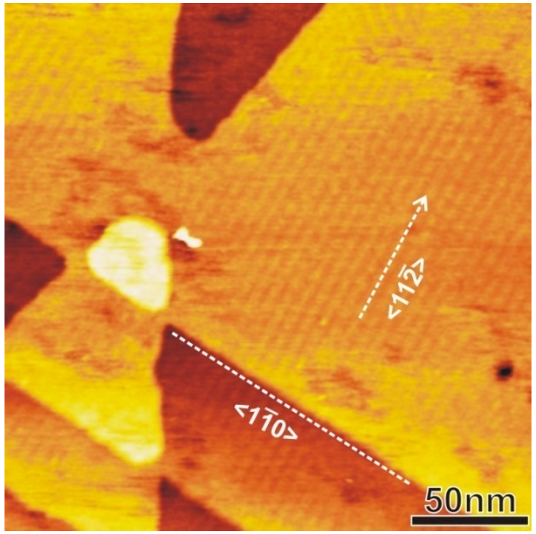
Idea:

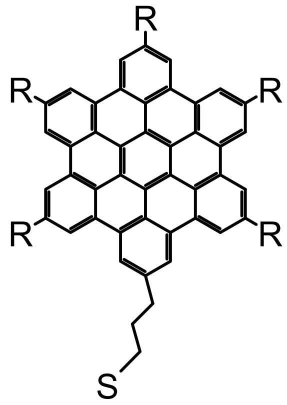
Integrate organic semiconductor and insulator to produce an OFET in a single-comonent SAM

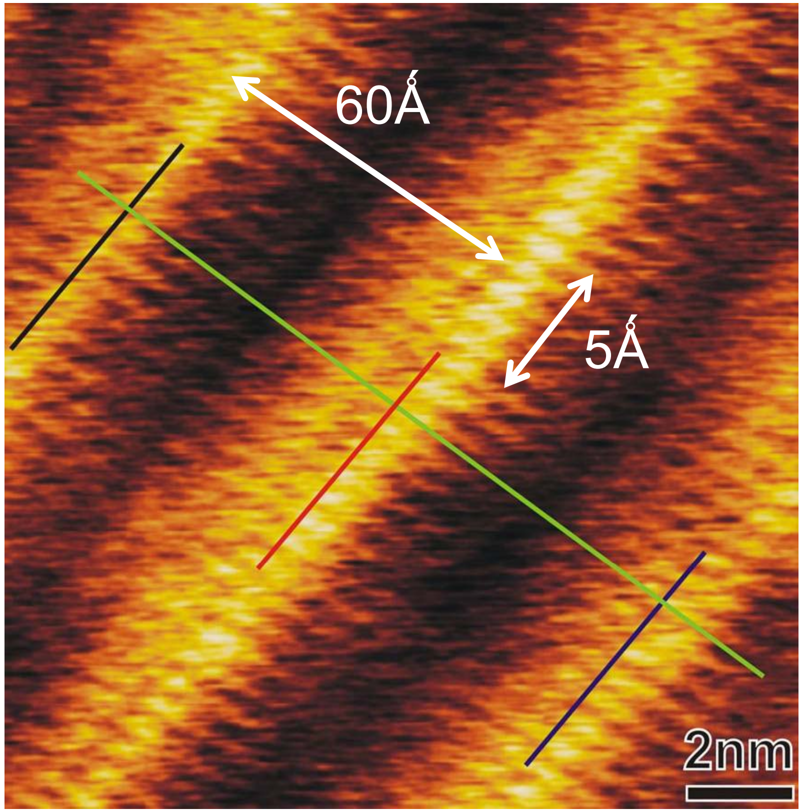


SAMs of HBC-C_3 thiol on Au(111)

Long columnar structure

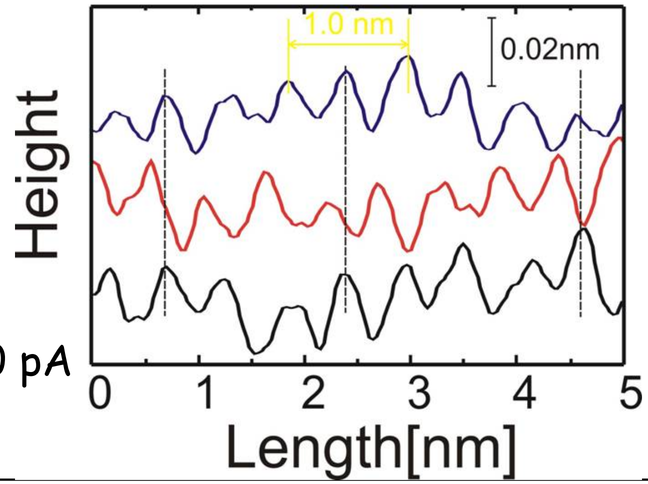


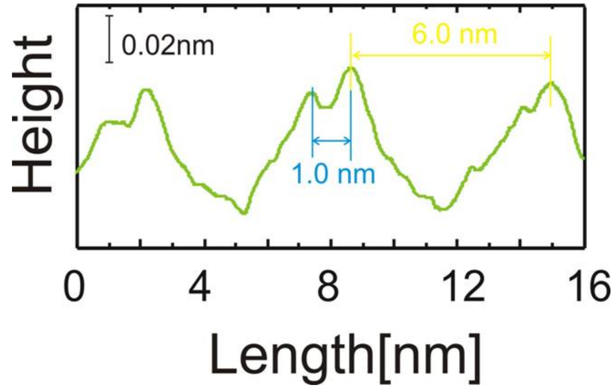




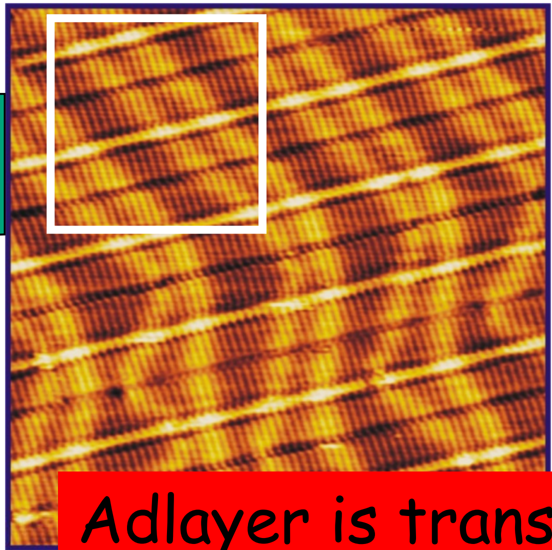
Soft tether long range ordered of parallel lamella under the guidance of π-π stacking.

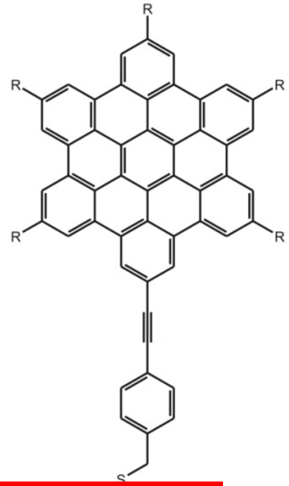
U_t=500 mV, I_t=100 pA

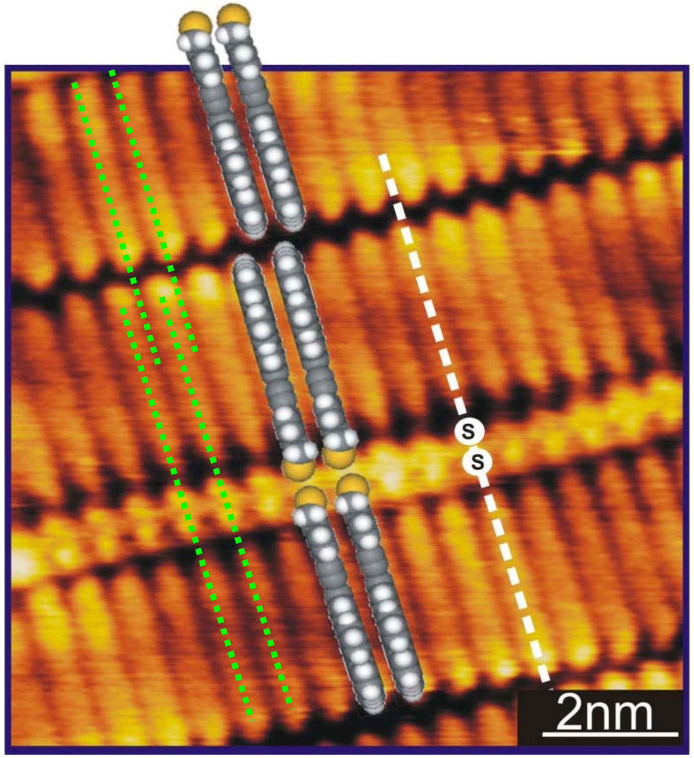




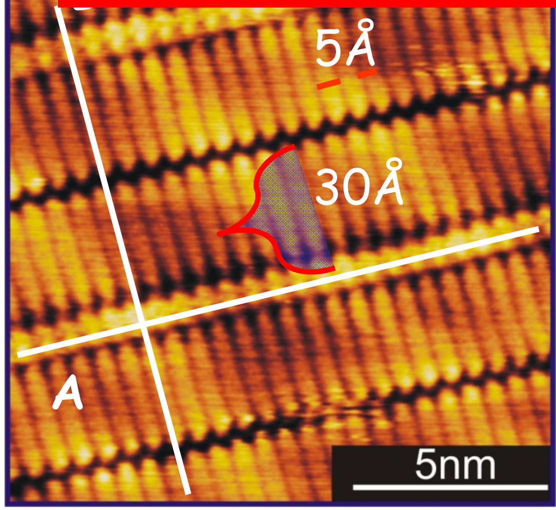
SAMs of P-HBC thiol on Au(111) (measured in UHV)

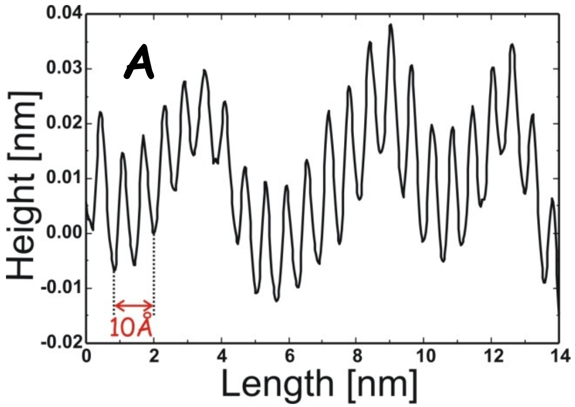


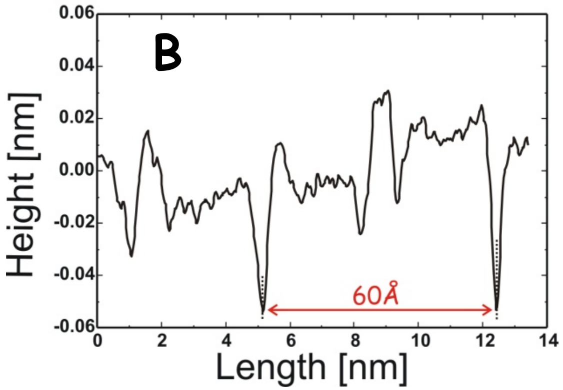




Adlayer is transparent
Disk diameter ~ 2.5-3nm



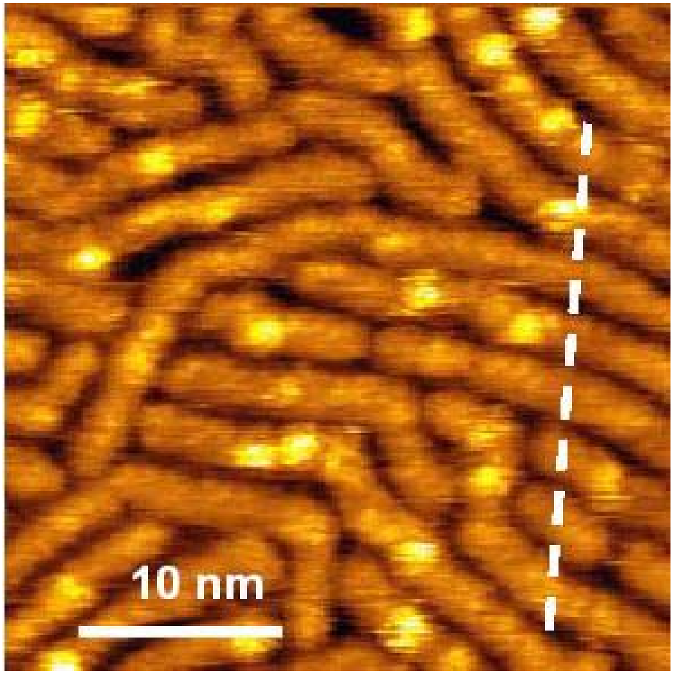




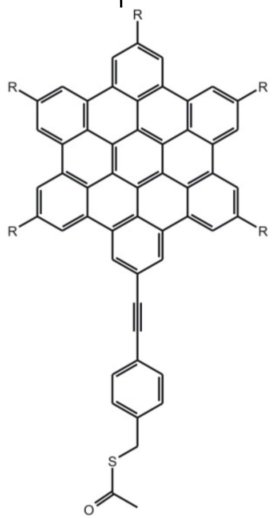
U_t=500 mV, I_t=100 pA

HBC thiol: preparation conditions matter !

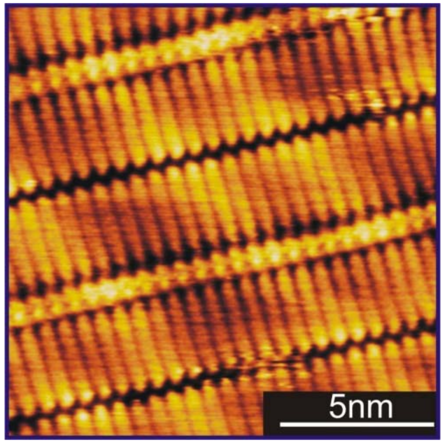
L. Piot, C. Marie, X. Dou, X. Feng,
K. Müllen, D. Fichou,
JACS 2009, **131**, 1378



Low degree of order, many defects



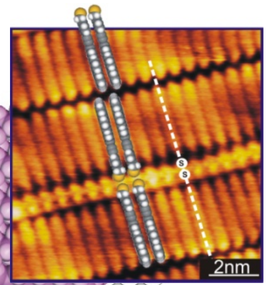
Our results
after optimization of preparation conditions

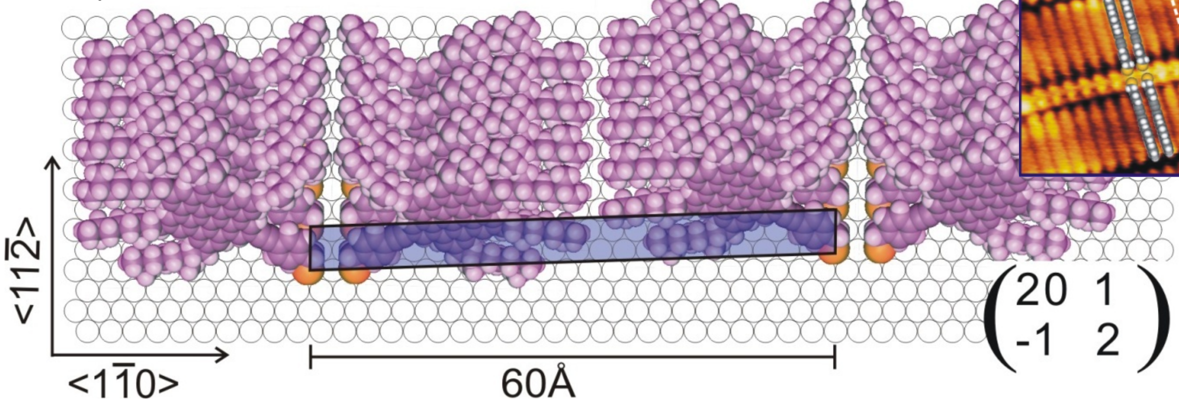


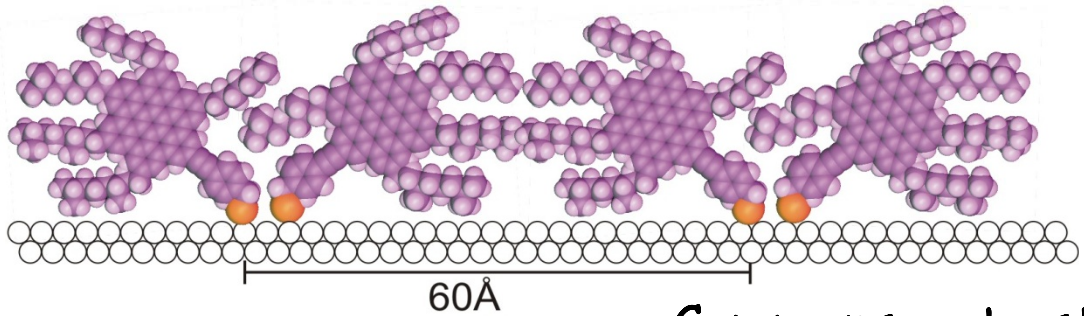
Long-range ordering,
low density of defects

Structural model of HBC modified thiol

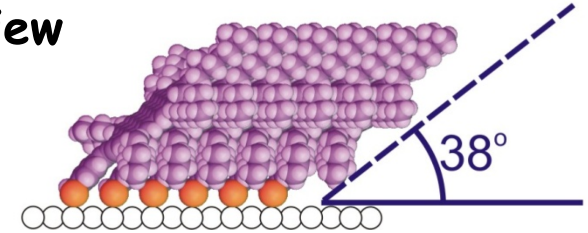
Top view





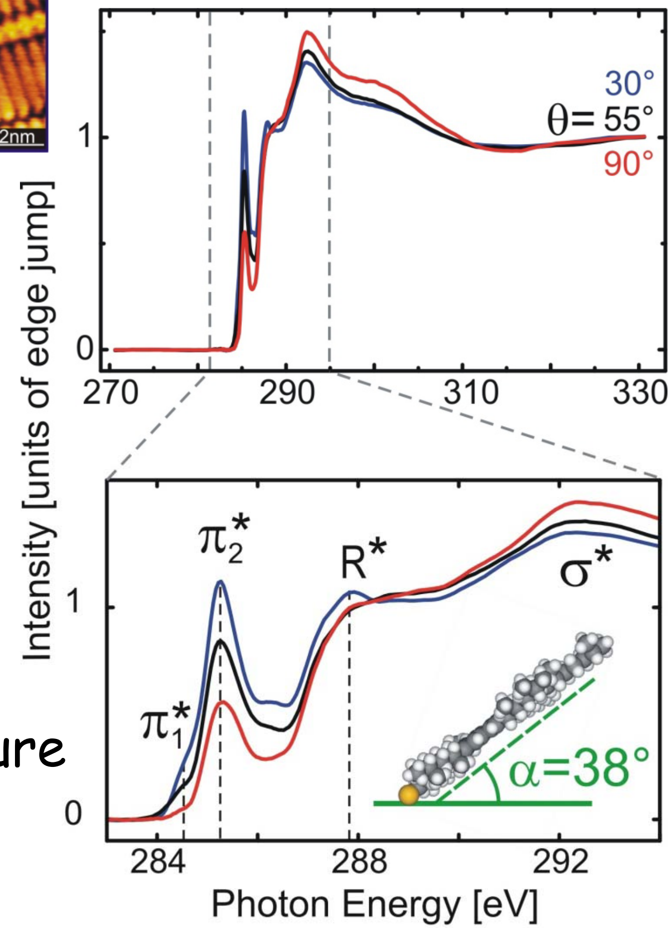


Side view



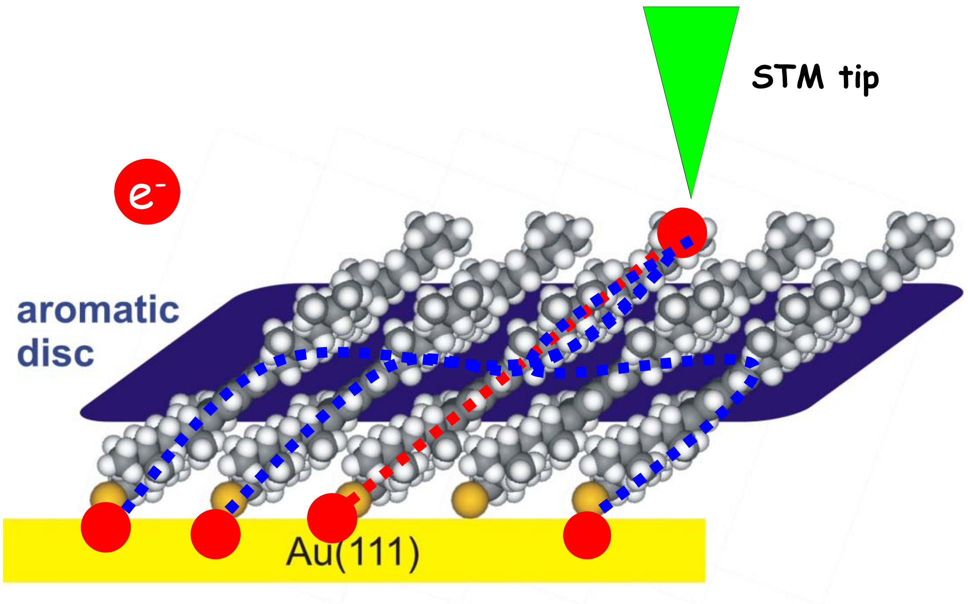
Commensurate structure
2 mol./ unit cell

NEXAFS for p-HBC-thiol

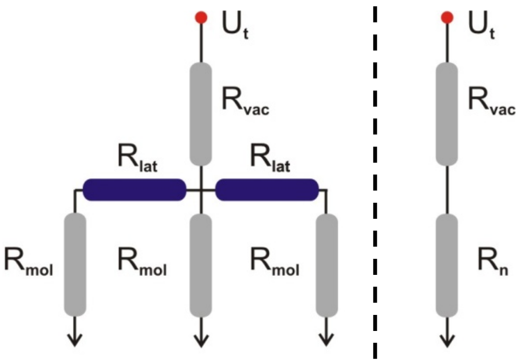


π_1^* 284.5 eV
π_2^* 285.2 eV
R* 287.8 eV
σ* 290.5 eV

Electron transport mechanism of HBC SAMs: Information from STM ?

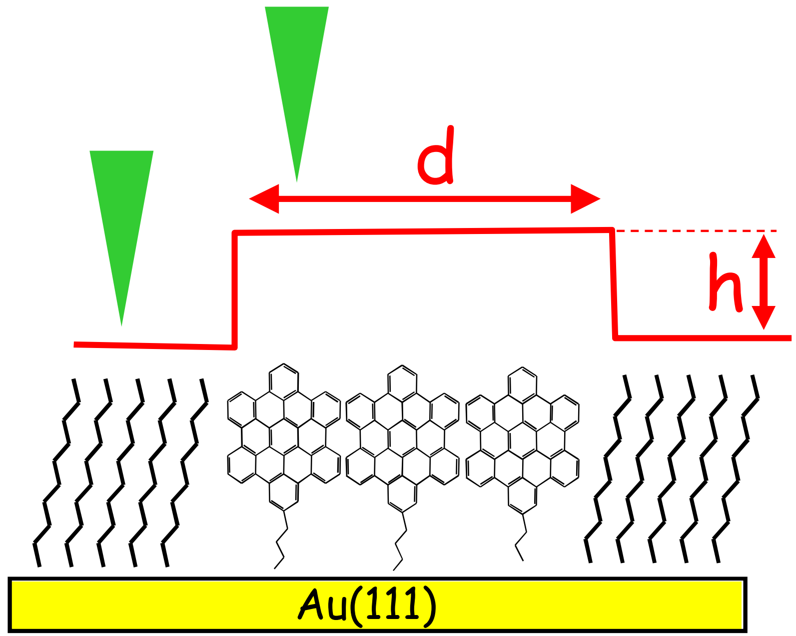


(e⁻) transport only along HBC molecule
or
(e⁻) transport also laterally



R_{mol} = Resistivity of a molecule
R_{lat} = Lateral coupling
R_{vac} = Vacuum gap

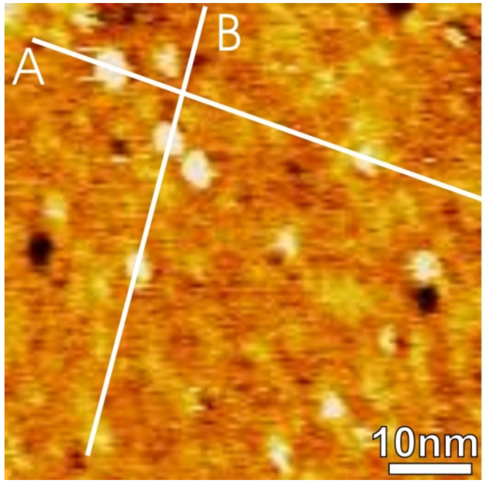
Apparent height of HBC-islands embedded in insulating matrix depends on island size

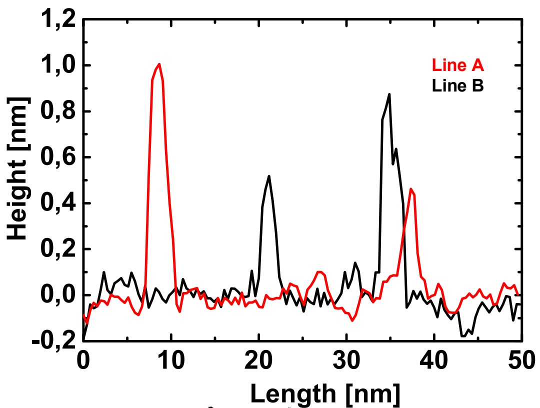


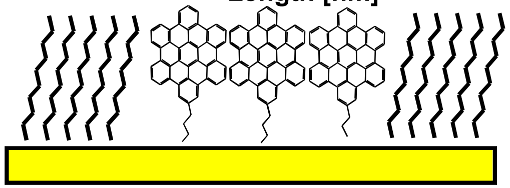
T. Ishida et al., J. Phys. Chem. B. 1999, **103**, 1686

Lateral conduction in HBC SAMs
(insertion of HBC into C10SH-SAMs)

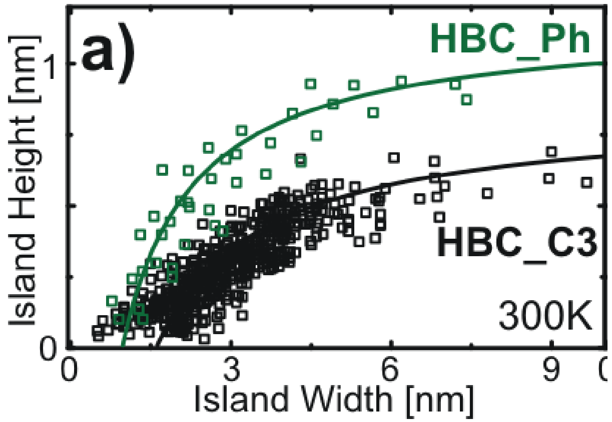
25 min insertion time

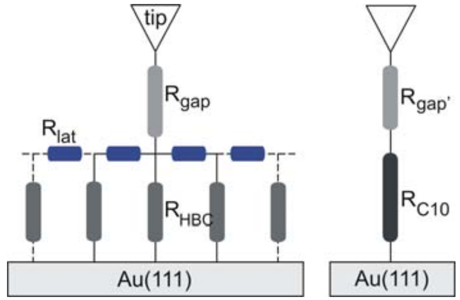






Apparent island height (Δh) vs size (d)





$$\text{width} = \frac{0.5\left(R_{tn} - R_{HBC} - C'(d_{gap} + \Delta h)e^{\alpha(d_{gap}+\Delta h)}\right)}{\frac{1}{3}R_{lat}\left(1 - \frac{R_{tn}}{R_{HBC}}\right) - R_{tn} + \left(\frac{1}{3}\frac{R_{lat}}{R_{HBC}} + 1\right)C'(d_{gap} + \Delta h)e^{\alpha(d_{gap}+\Delta h)}}$$

R_{mol} = 13.3/10.4 GΩ (300K), 11.6/9.8 GΩ (110K)

R_{lat} = 2.0/1.5 MΩ (300K), 1.7/1.0 MΩ (110K)

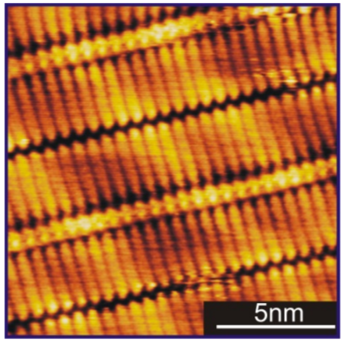
→ strong evidence for lateral transport

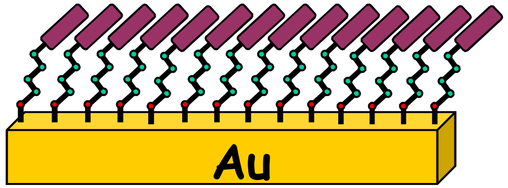
→ no strong temperature dependence (110K)

→ no hopping transport [~exp(-const/T^2)]

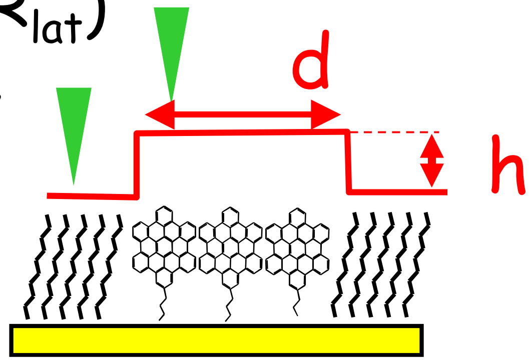
An OSC device based on SAMs ?

- HBC-thiols form SAMs
  with long range order
  Plane tilted by around 40°





- Temperature dependence suggests
  tunneling transport between HBC and Au (R_{lat})
  band-like transport parallel to the surface
  (i.e. within HBC monolayer)

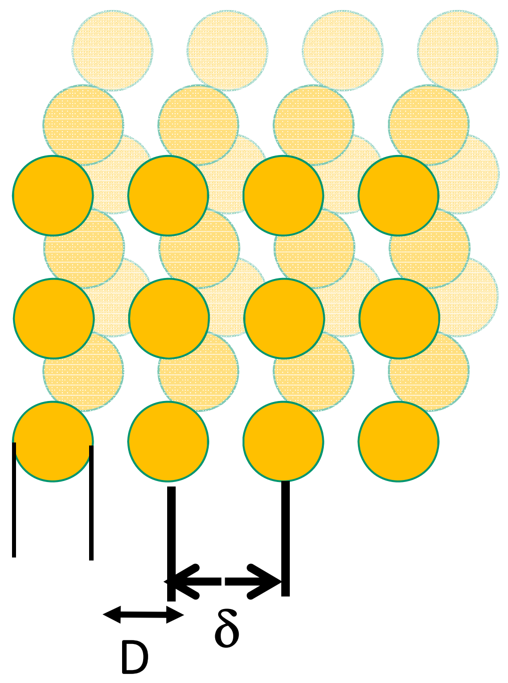


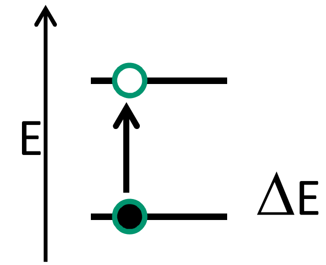
- Hopping-transport parallel to surface not consistent with exp. data
- Evidence for intrinsic e-mobilities > 5 cm^2/Vs

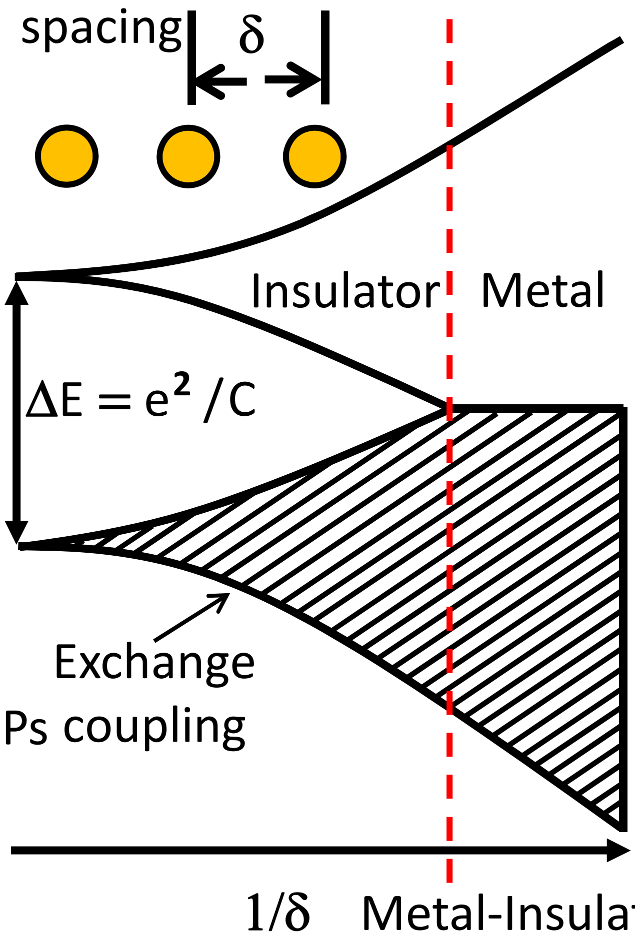
Going to three dimensions

Electronic properties of 3-d NP arrays

3d NP-arrays

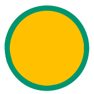




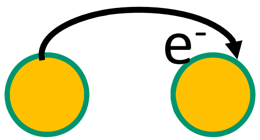


Not a metal
even for metal NPs

Metal-Insulator Transition



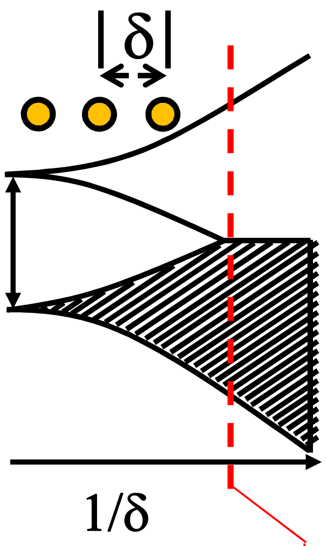
Single Particle
$\Delta E \sim E_F/N$
(3nm Au, 10^3 atoms, ~ 10 meV)

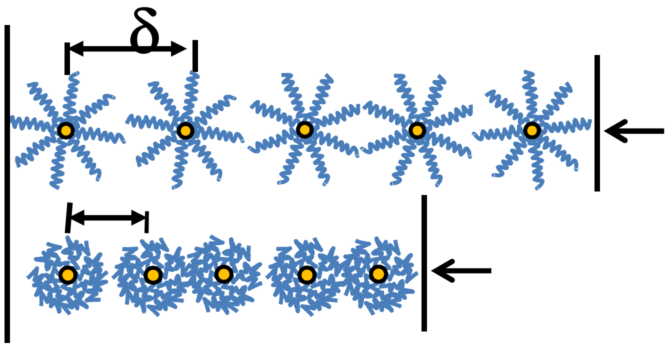


Charging a capacitor
$\Delta E = e^2/C$
(~ 0.3 eV)

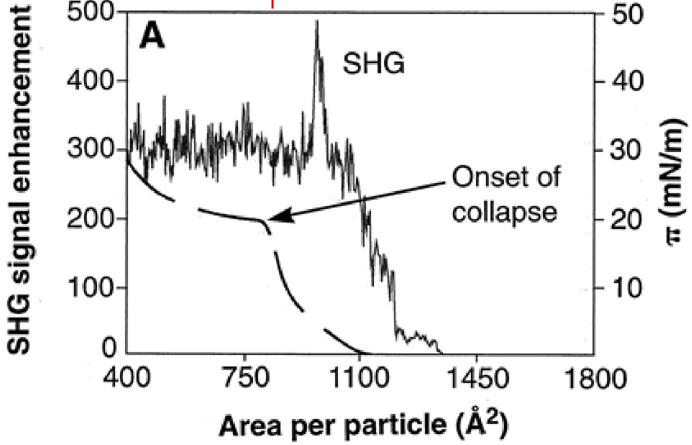
Markovich, Collier, Henrichs, Remacle, Levine, Heath, Acc Chem Res **32** (1999) 415

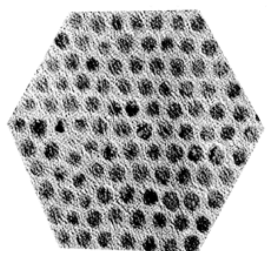
2d arrays of metal NPs : Experiment





2d - arrays

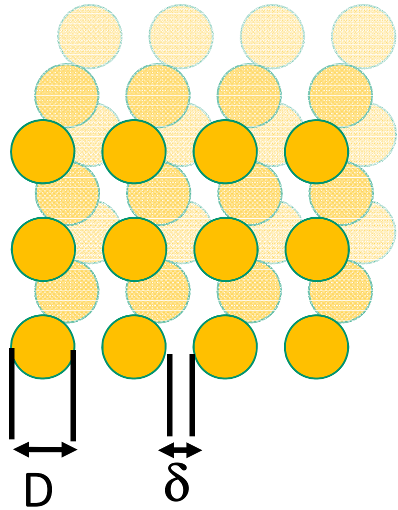




10 nm

Collier, Saykally, Schiang, Henrichs, Heath
Science 277, 1978, (1997)

3d-arrays



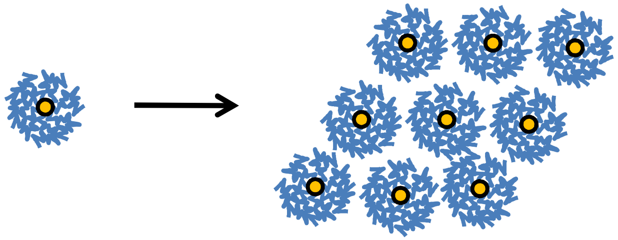
3d NP-arrays

Needed: Fabrication of 3d-array with high degree of order (XRD –peaks in all 3 dir.)

Magnetic effects,
plasmonics,
Josephson tunneling,
Superconductivity,.....

D = 1...10 nm
δ = 0.5 ... 2 nm

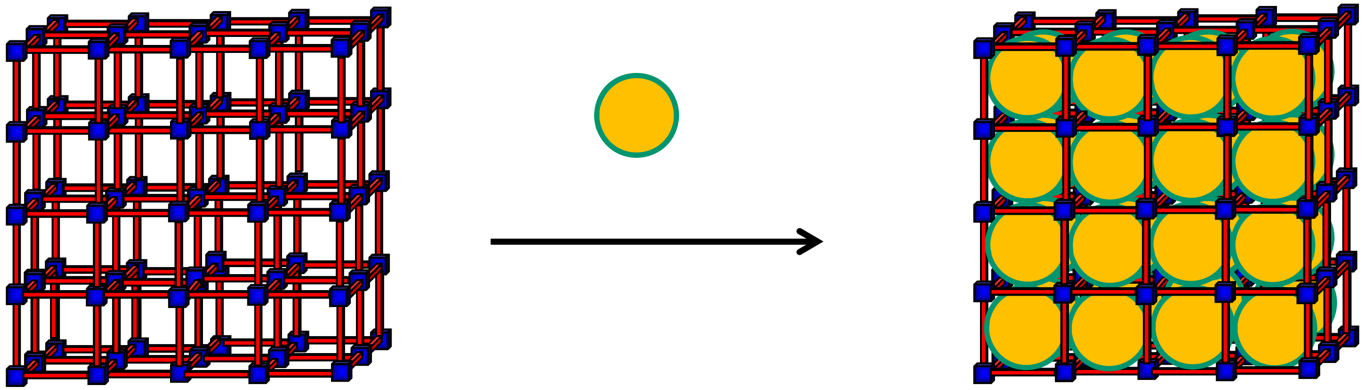
Ligand shell to avoid sintering



„...it remains a challenge to pattern superlattices with comprehensive control over internal order and overall morphologies...“

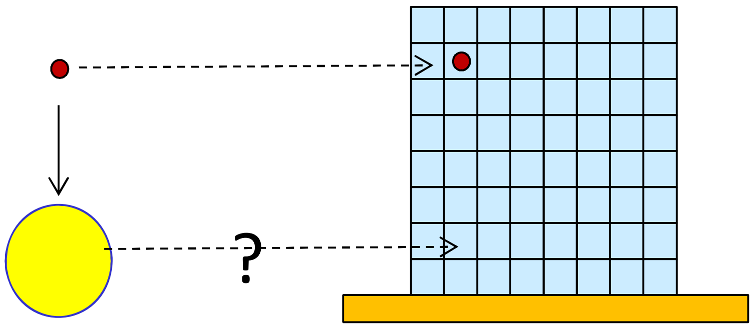
W.L. Cheng, N.Y. Park, M.T. Walter, M.R. Hartmann, D. Luo, Nature Nanotechn. 3, 683 (2008)

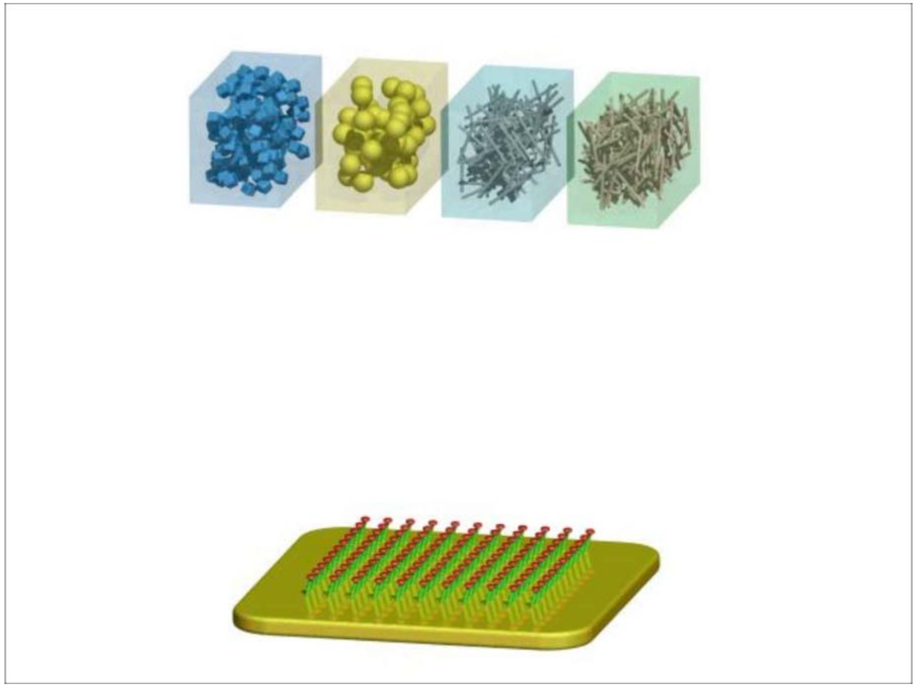
Using a 3D shelf system for assembling a 3d NP array



Problems: How can the shelf be fabricated?
How should the loading be carried out?
How can electrical contacts be provided?
What about using different types of NPs? Non-spherical?

Loading Au-clusters into SURMOFs





Christof Wöll, KIT Karlsruhe

The goal:
surface-anchored 3d arrays containing adaptable functionalities

Objects exhibiting functionality

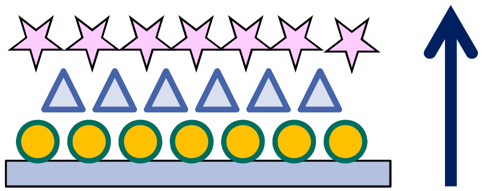
Functionality:

Static

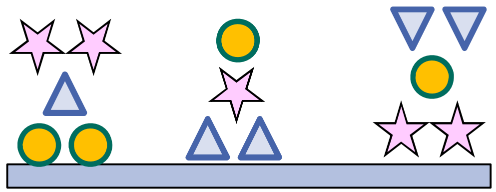
Dynamic

Switchable

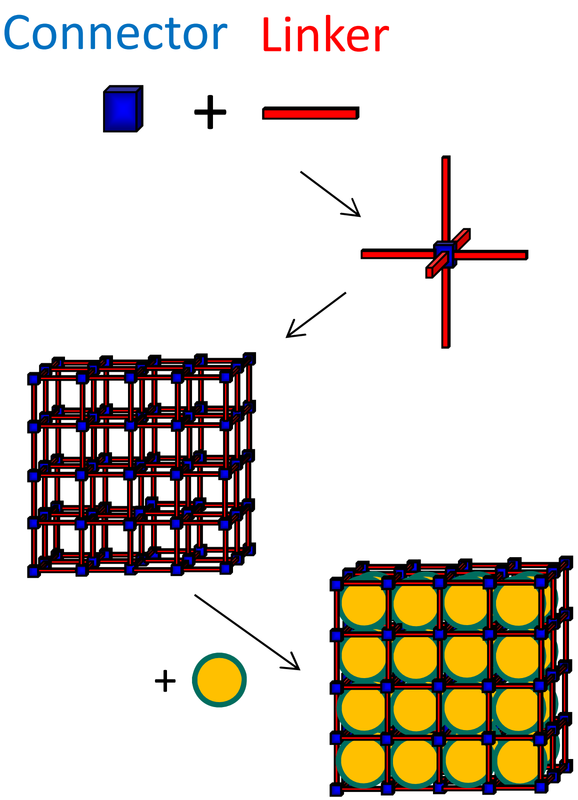
Compositional gradient



Lateral structuring



The approach:
molecular storage racks



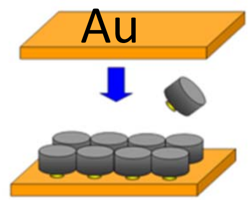
Metal-organic frameworks, MOFs

MOFs are established

But:
Conventional MOF synthesis not appropriate

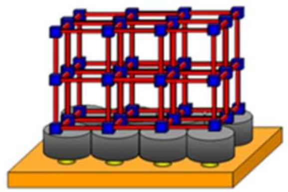
The status:
SURMOF process successfully established

Ultrahin organic layer



New process:
Liquid phase epitaxy

JACS 2007
ACIE 2009



Surface-anchored Metal-organic framework

Nat. Mat. 2009

- Oriented growth JACS 2011
- Crystalline Adv.Funct.Mat.2012
- Loading ChemComm 2012
- Electrical contacts
- Chiral information ACIE 2012
- Pores > 3 nm Nat.Sci.Rep 2012

Organics at surfaces, self-assembly

Topics

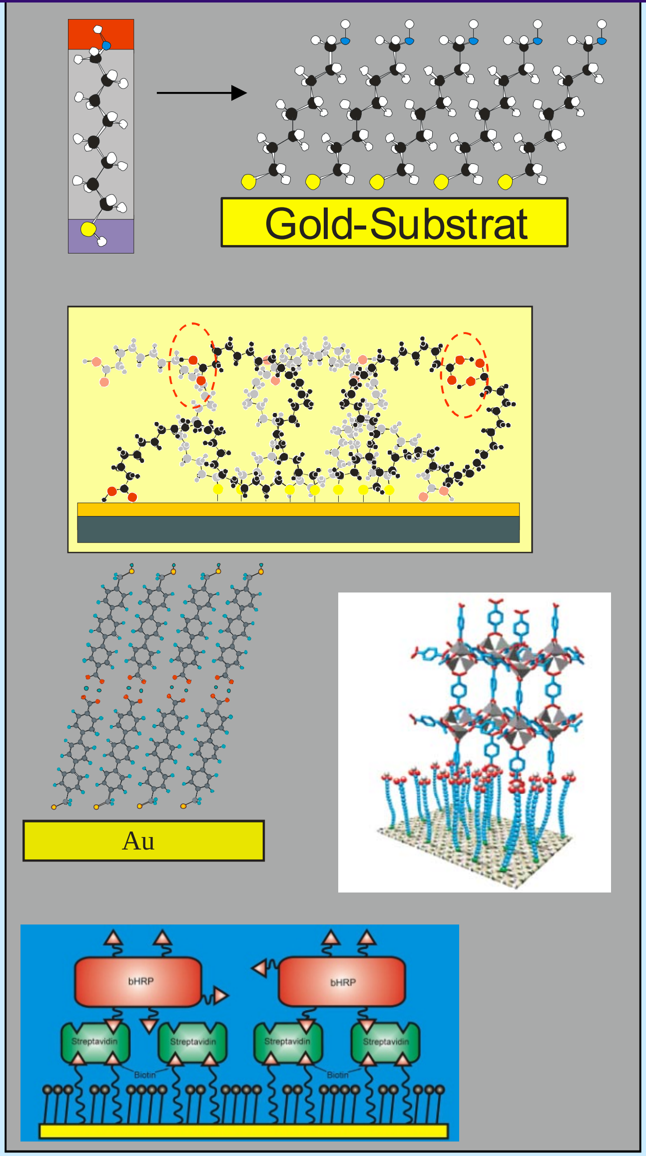
Fabrication of highly ordered molecular adlayers (SAMs) using organothiols

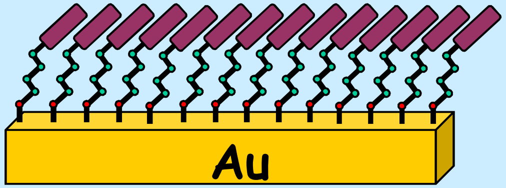
Characterization of organic surfacs

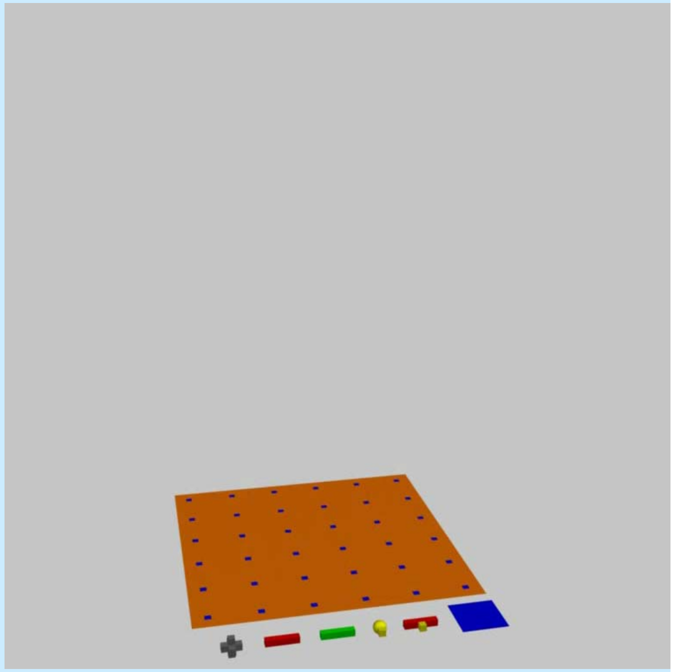
Tailoring properties of Organic Surfaces

Metal-Organic Frameworks (MOFs)

SURMOFs





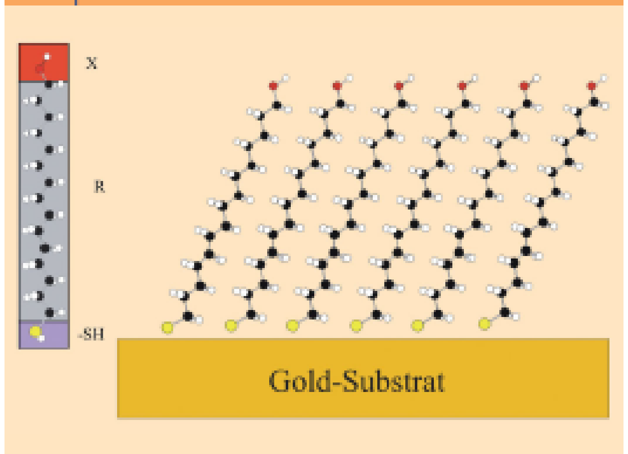


Maßgeschneiderte Organische Oberflächen

Martin Kind | Christof Wöll

Organische Oberflächen ziehen zunehmend Aufmerksamkeit auf sich. In den letzten Jahren wurden wichtige Fortschritte sowohl bei der Herstellung von Modellsystemen als auch bei der Entwicklung von neuen analytischen Techniken erzielt. In diesem Artikel sollen die Herstellung von organischen Oberflächen mit maßgeschneiderten Eigenschaften, deren strukturelle Charakterisierung sowie chemische Prozesse an diesen Oberflächen vorgestellt werden. Die faszinierenden Eigenschaften und die Vielfältigkeit der Einsatzmöglichkeiten werden anhand ausgewählter Beispiele diskutiert.

ABB. 1 | SELBSTASSEMBLIERTE MONOLAGEN



Links: Struktur eines Organothiols für die Bildung von selbstassemblierten Monolagen (SAMs) (allgemeine Struktur: HS-R-X). Die wesentlichen Bestandteile sind die aus der Sulfhydril (SH)-Einheit bestehende Ankergruppe (violett hinterlegt), eine Kopplungseinheit R (in diesem Fall eine Alkylgruppe) und eine endständige Funktion X (in diesem Fall OH). Beim Eintauchen eines Goldsubstrats in eine Lösung des Organothiols entsteht ein SAM, bei dem die Organothiole fest durch eine Schwefel-Gold-Bindung auf dem Substrat verankert sind. Die Oberfläche der SAMs wird durch die endständige Funktion definiert.

Oberflächen trennen kondensierte Materie von ihrer Umgebung. Jeder Transport von Materie muss durch diese Grenzflächen erfolgen. Handelt es sich um einen Festkörper, wird auch die Wechselwirkung mit den umgebenden Gasen oder Flüssigkeiten in erster Linie durch die Oberflächeneigenschaften dieses Festkörpers bestimmt: Haften, Gleiten, Kleben und Benetzen, alle diese Phänomene hängen von der genauen Beschaffenheit der obersten Schicht des Festkörpers ab.

Organische Oberflächen: weich und schwierig

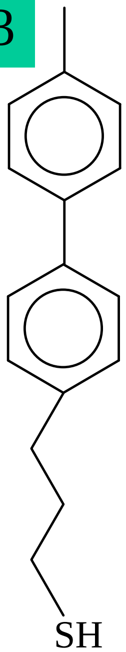
Die wirtschaftlich größte Bedeutung anorganischer Oberflächen liegt im Bereich der heterogenen Katalyse (s. Themenheft Katalyse der ChiuZ: Heft 2/2006). Aber auch organische Oberflächen spielen in vielen Bereichen des täglichen Lebens, für eine Reihe technischer Anwendungen und in zunehmendem Maße bei den Biowissenschaften eine entscheidende Rolle – Beispiele sind die Funktionsweise von Flüssigkristallbildschirmen und komplexe, sich an der Oberfläche von Zellmembranen ereignende Rezeptorvorgänge.

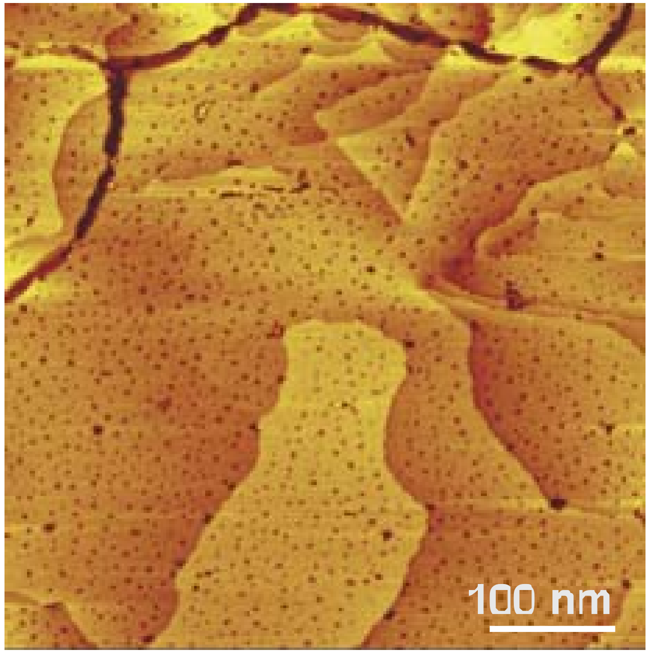
Die bedeutenden Erfolge der Oberflächenwissenschaften der letzten Jahre sind durch die Verfügbarkeit einer Vielzahl von teilweise sehr leistungsfähigen Methoden zur Untersuchung anorganischer und insbesondere metallischer Oberflächen möglich geworden; die Vergabe des Nobelpreises für Chemie an Professor Gerhard Ertl im Jahr 2007 würdigt diese Fortschritte [21]. Ein entscheidender Grund für die Entwicklungen in diesem Bereich ist die Tatsache, dass anorganische Oberflächen auch in einkristalliner also strukturell weitestgehend perfekter Form präpariert und untersucht werden können. Dadurch wird der Einsatz von Beugungsmethoden zur Bestimmung der Strukturen von Adsorbaten zumindest für Modellsysteme möglich.

Im Fall organischer Oberflächen ist die Situation weniger befriedigend. Da es sich hier um weiche und typischerweise bei niedrigen Temperaturen schmelzende oder sich zersetzende Materie handelt, ist die Herstellung hoch geordneter Oberflächen sehr problematisch. Aus diesem Grund gibt es erhebliche Schwierigkeiten bei der Herstellung von Modellsystemen, die die systematische Bestimmung der strukturellen und physikalisch-chemischen Eigenschaften von organischen Oberflächen ermöglichen.

Chem. Unserer Zeit, 2008, 42, 128 – 141

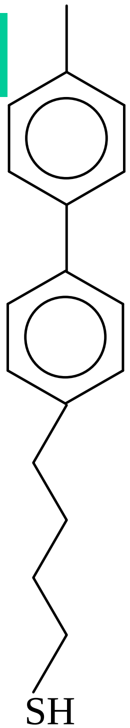
BP3

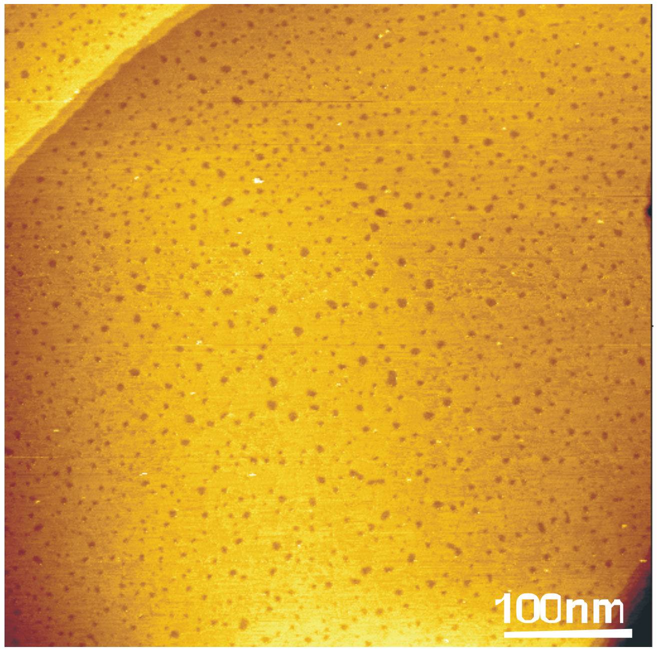




SAMs from Organothiols with oligopheny-backbone

BP4





Systematic studies by varying alkyl chain length

Circular depressions are not defects in film, corrosion of Au-substrate