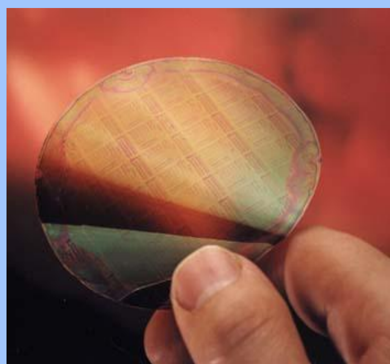
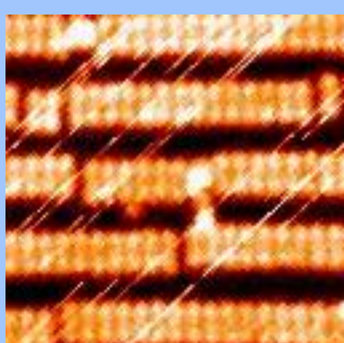
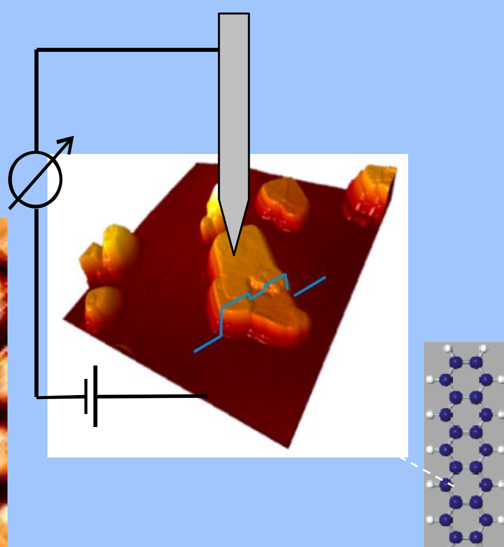
When soft meets hard matter: from molecular monolayers to organic electronics





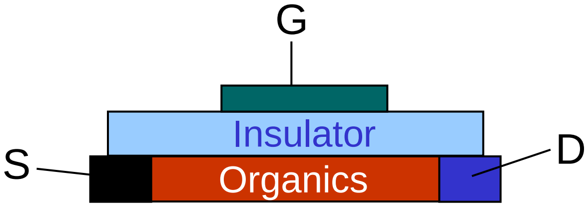


Institute of Functional Interfaces (IFG)
Karlsruhe Institute of Technology, KIT
North Campus

Organic Semiconductors making their way to applications

Fabrication using printing technology

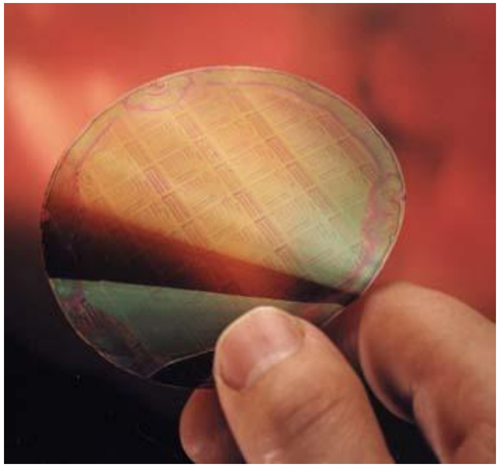
Organic Field-Effect Transistor



„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

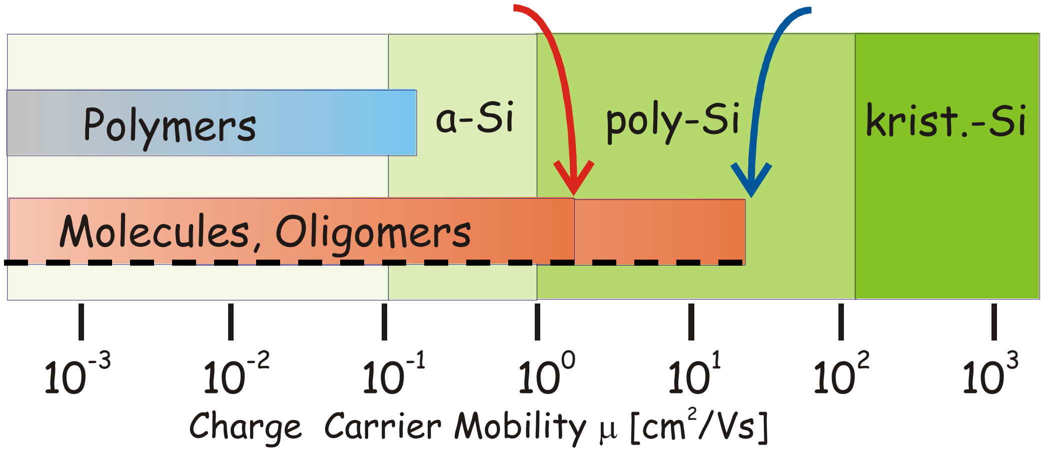
Organic Semiconductors: Charge Carrier Mobilities

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

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

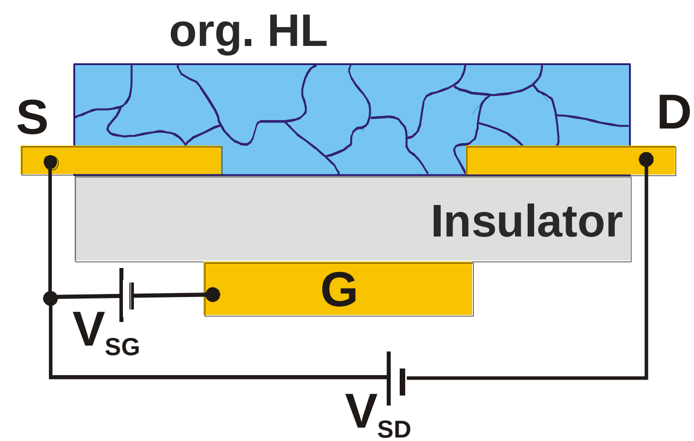
Pentacene-OFET

Rubrene-OFET



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

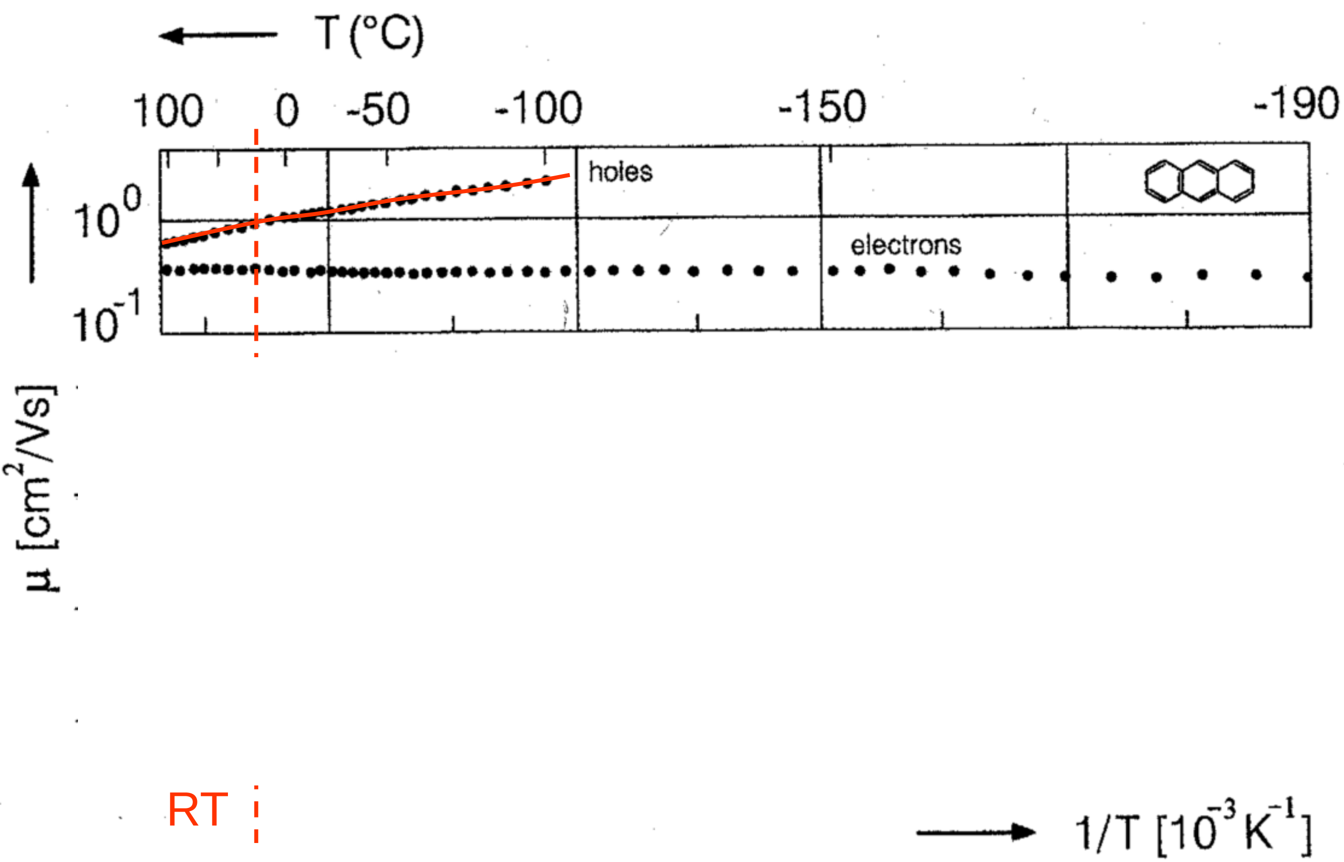
OFET
Bottom-Gate-Geometry



<u>Oligomers</u>: - highly ordered, single crystals
- high purity
- main interest polycyclic aromatic hydrocarbons (Polyacenes, Benzoide)

Organic Conductors:
Conduction mechanism and influence of impurities

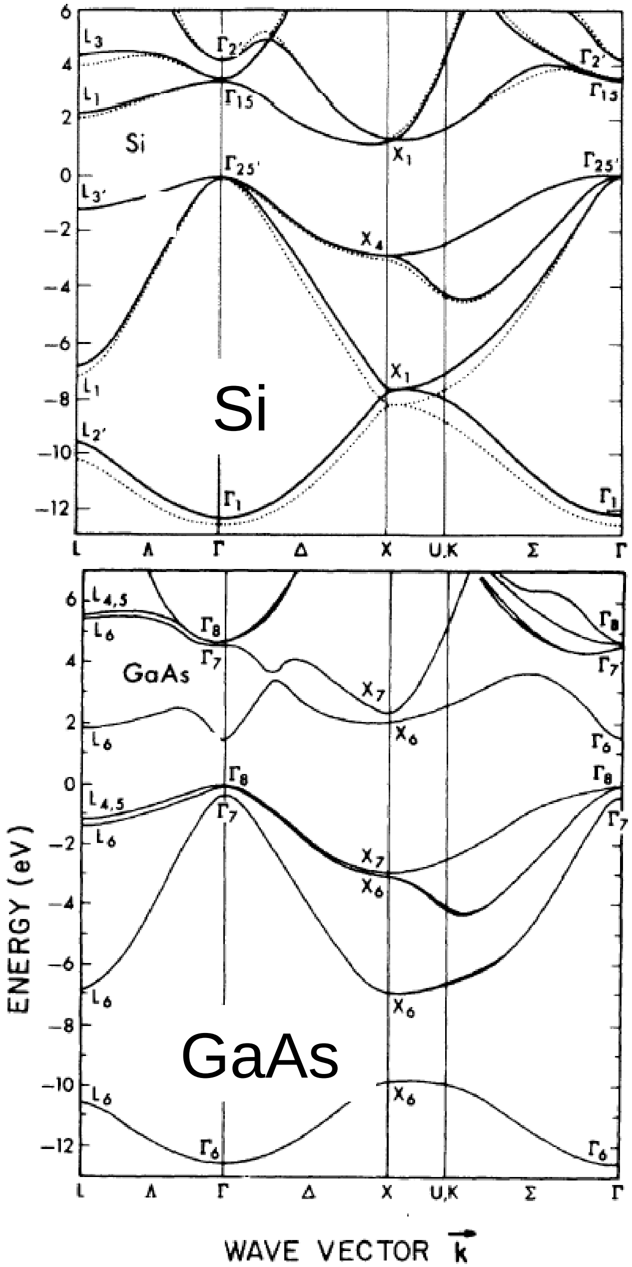
Anthracene

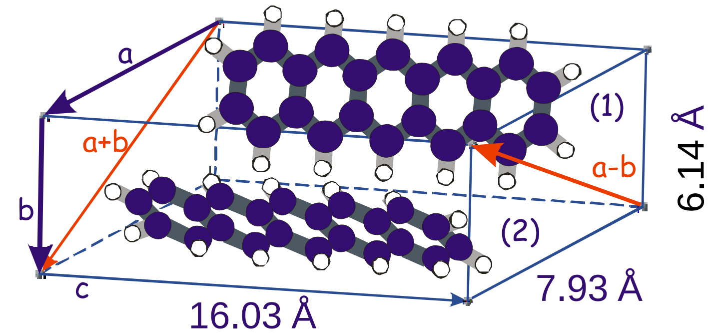


N. Karl, in:
Organic Electronic Materials
Farchioni & Grosso (Eds)
Springer,
Material Science 41 (2001)

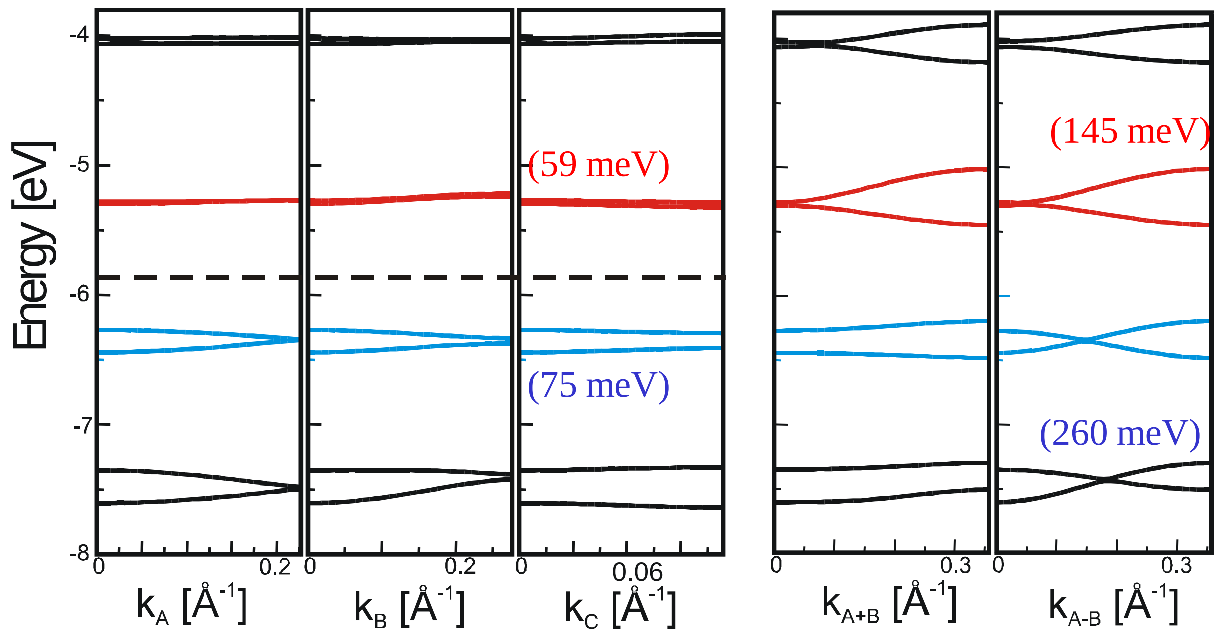
Clear evidence for band-like transport,
at higher temperatures hopping transport

Electronic structure: Conventional vs. organic semiconductors





Pentacene

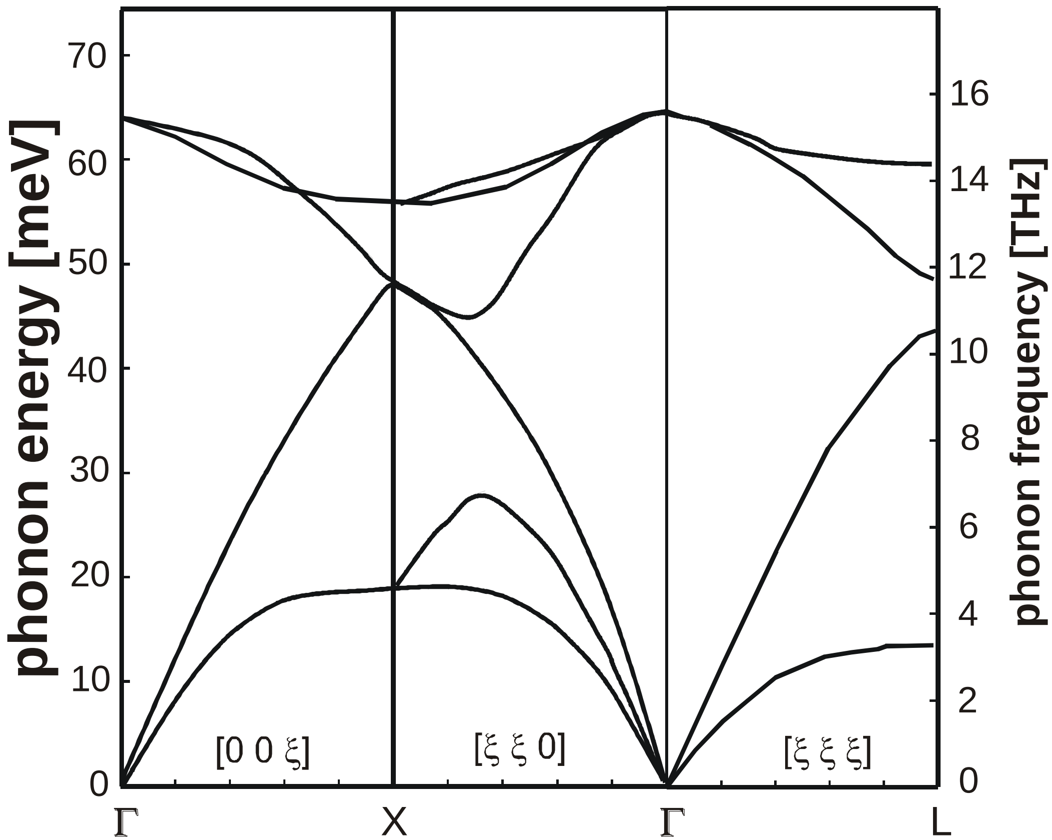


Precise ab-initio DFT electronic structure calculations

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

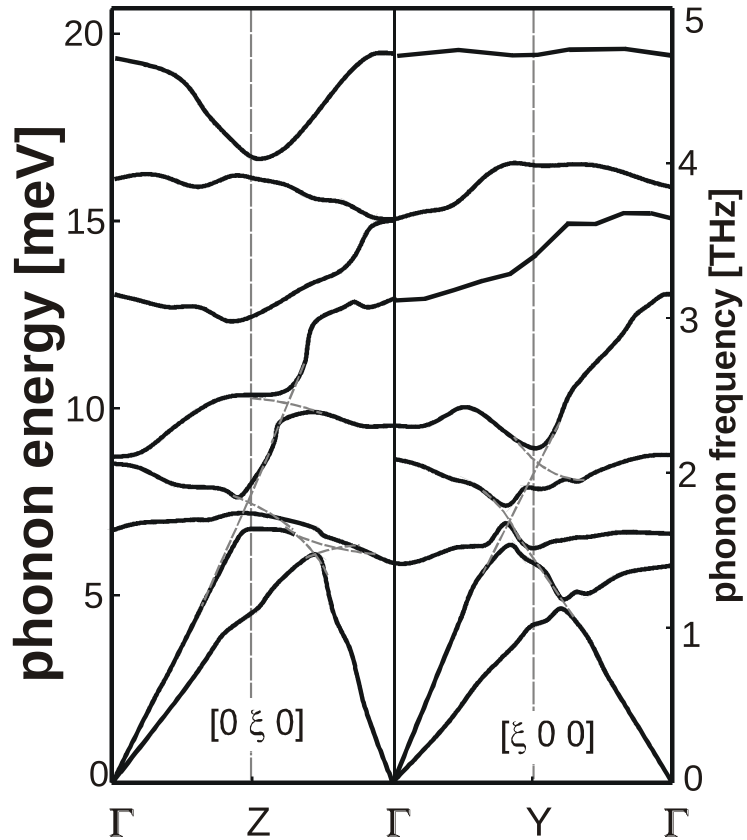
Hard vs. soft: Phonon frequencies

Silicon



$T_m = 1687$ K

Anthracene



$T_m = 489$ K

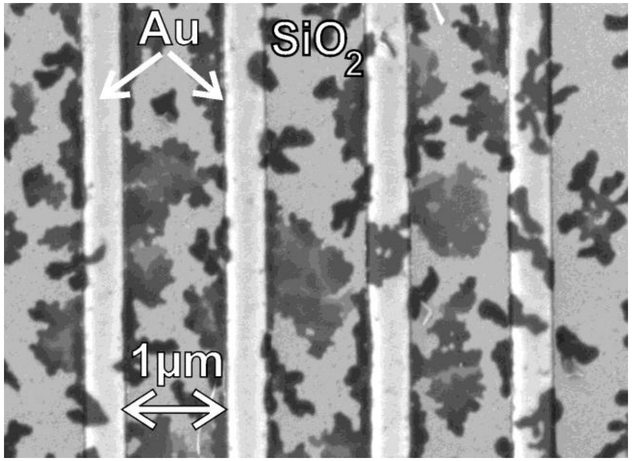
Electron-phonon coupling? Stress, strain ? Anisotropy?

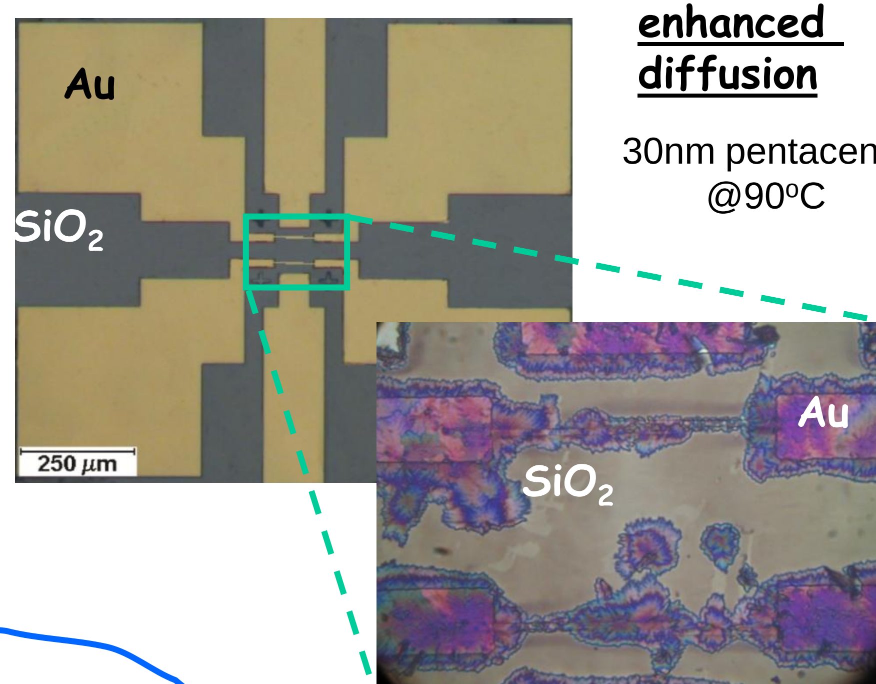
Nucleation & growth on bottom contact OFET-structures

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

nucleation at electrodes

9nm pentacene @50ºC

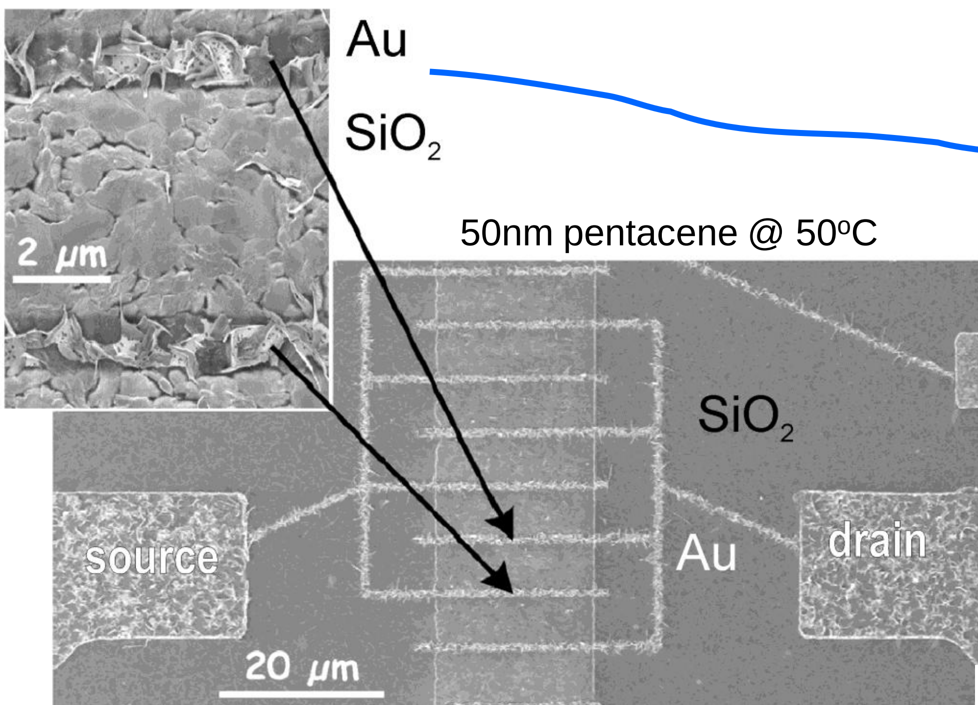


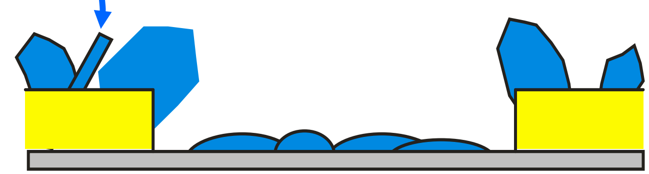


enhanced diffusion

30nm pentacene @90ºC

50nm pentacene @ 50ºC



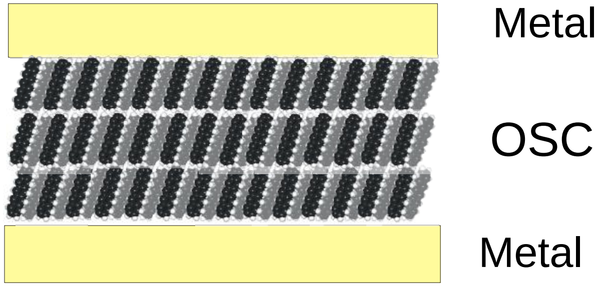


dewetting at electrodes

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

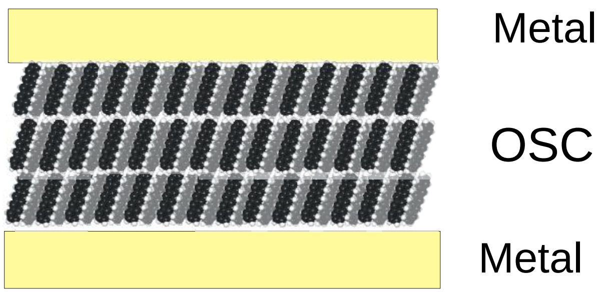
It is rather difficult
to measure charge carrier mobilities
in organic semiconductors

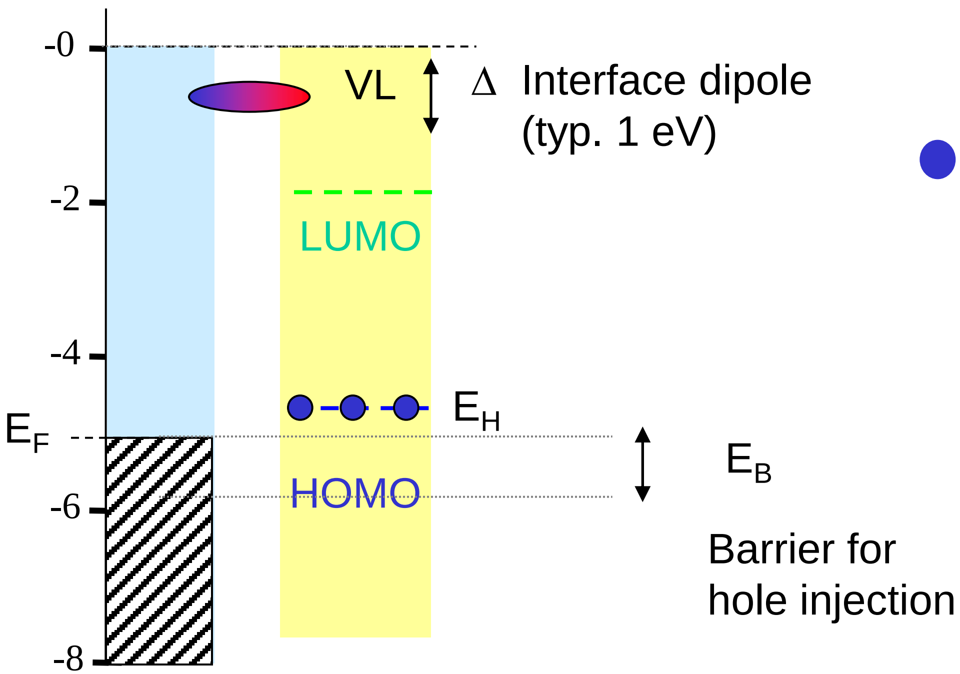
Would be good to have a model „ideal device“



Fabrication of an „ideal“ OSC-device

Diode with ohmic contacts





Interface dipole even for noble gases ?

Experimental observation:

- S. Narioka, H. Ishii, D. Yoshimura, M. Sei, Y. Ouchi, K. Seki, S. Hasegawa, T. Miyazaki, Y. Harima, K. Yamashita, Appl. Phys. Lett. **67** 1899 (1995)
- I.G. Hill, A. Rajagopal, A. Kahn Appl. Phys. Lett. **73**, 662, (1998)

Review: H. Ishii, K. Sugiyama, E. Ito, K. Seki Adv. Mater. **11**, 605 (1999)

- Theoretical explanation: (ab-initio, WF-based, MP2)

Not DFT !

P.S. Bagus, V. Staemmler, C.W. Phys. Rev. Lett. **88**, 28301 (2002)

G. Witte, S. Lukas, P.S. Bagus, C. W. Appl. Phys. Lett., **87**, 263502 (2005)

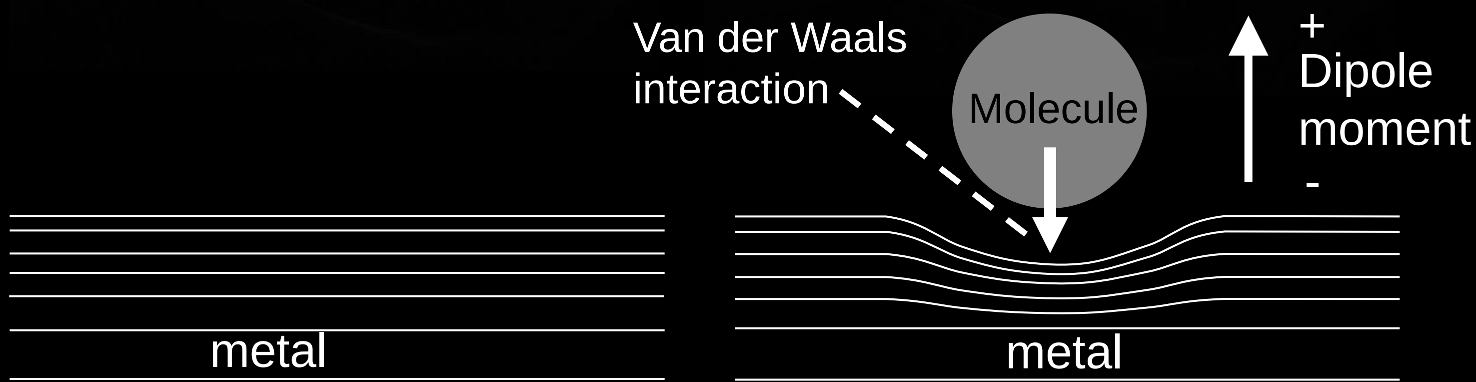
P.S. Bagus, K. Hermann, C.W. J. Chem. Phys. **123**, 184109 (2005)

Work function changes at surfaces: The cushion effect

or

When hard meets soft matter

Charge density contours

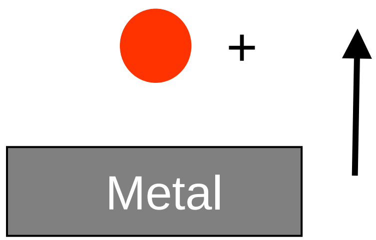
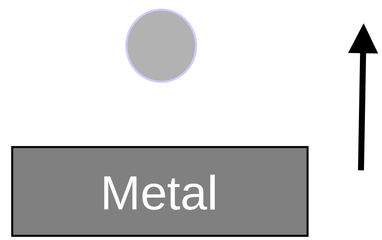
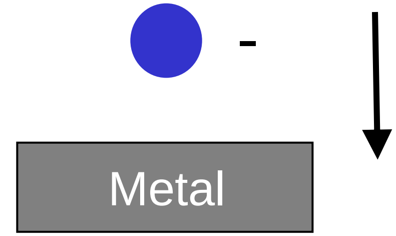


Ab-initio calculations for Xe/Cu(111): $\Delta\Phi = -1.0$ eV (work function is reduced!)

Two mechanisms : Pauli Exclusion and Surface Response To Xe

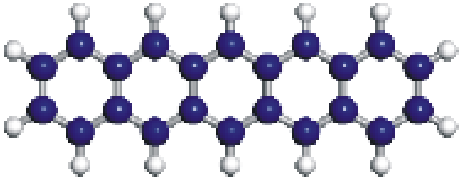
P.S.Bagus, V.Staemmler, CW, Phys.Rev.Lett.88, 28301 (2002); G.Witte, S.Lukas, P.S Bagus, CW, Appl.Phys.Lett 87, 263502 (2005)

Adjusting the work-function of a metal

	Electropositive (e.g. Cs, Na,…)  	Uncharged (e.g. Xe, alkanes, …)  	Electronegative (e.g. I, Cl,…) 
Prediction	Workfunction decrease	No workfunction change	Workfunction increase
Thorough analysis (Experiment, ab-initio theory)	Substantial decrease (Pauli repulsion + electrostatic)	Substantial decrease (Pauli repulsion)	Small workfunction decrease for I (cov. dependant !) Pauli repulsion, electrostatics, polarization

P.S.Bagus, D.Käfer, G.Witte, CW, Phys.Rev.Lett. ***100***, 126101 (2008)

Growth of pentacene on metal substrates



Pentacene

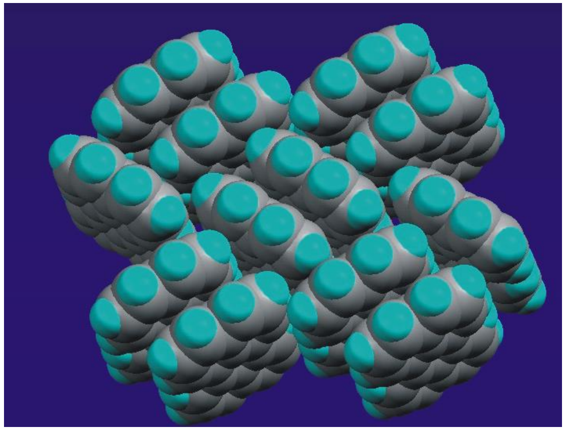
- no π-stacking
- Bulk structure
- dewetting

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

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

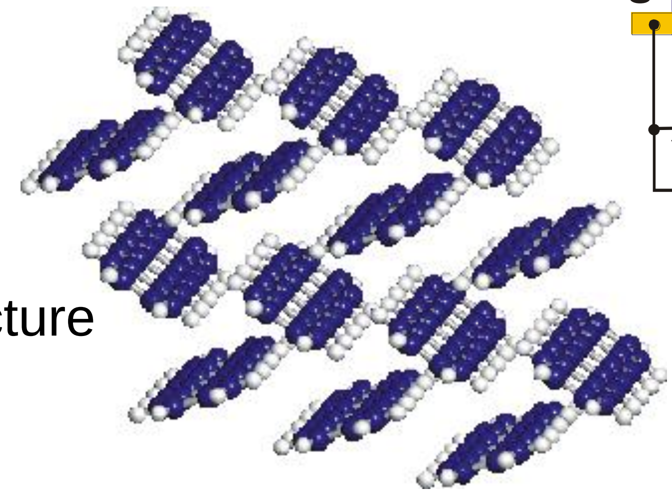
Principles of OMBD: Bulk properties

- The importance of orientational precursors

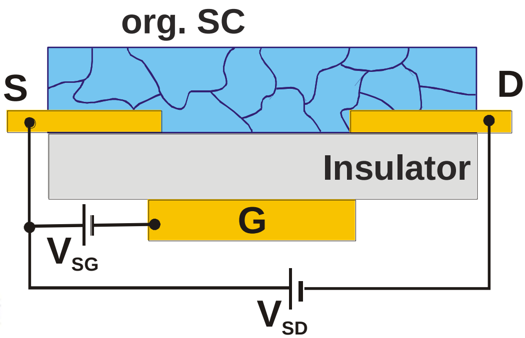


Perylene

Bulk structure



Pentacene



OFET

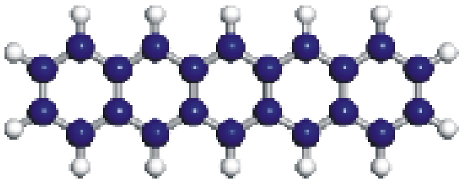
No orientational precursor for planar growth

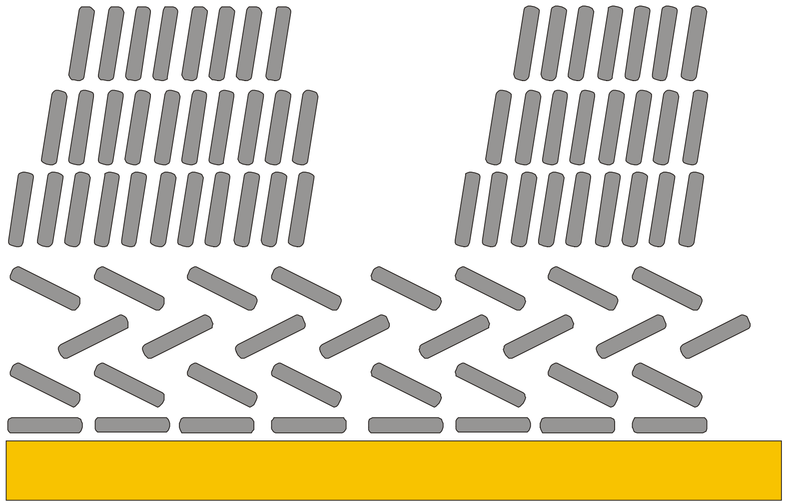
-> Problems in coating of metals (bottom-contact problematic)

herring-bone motif, molecular axis normal to planes

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

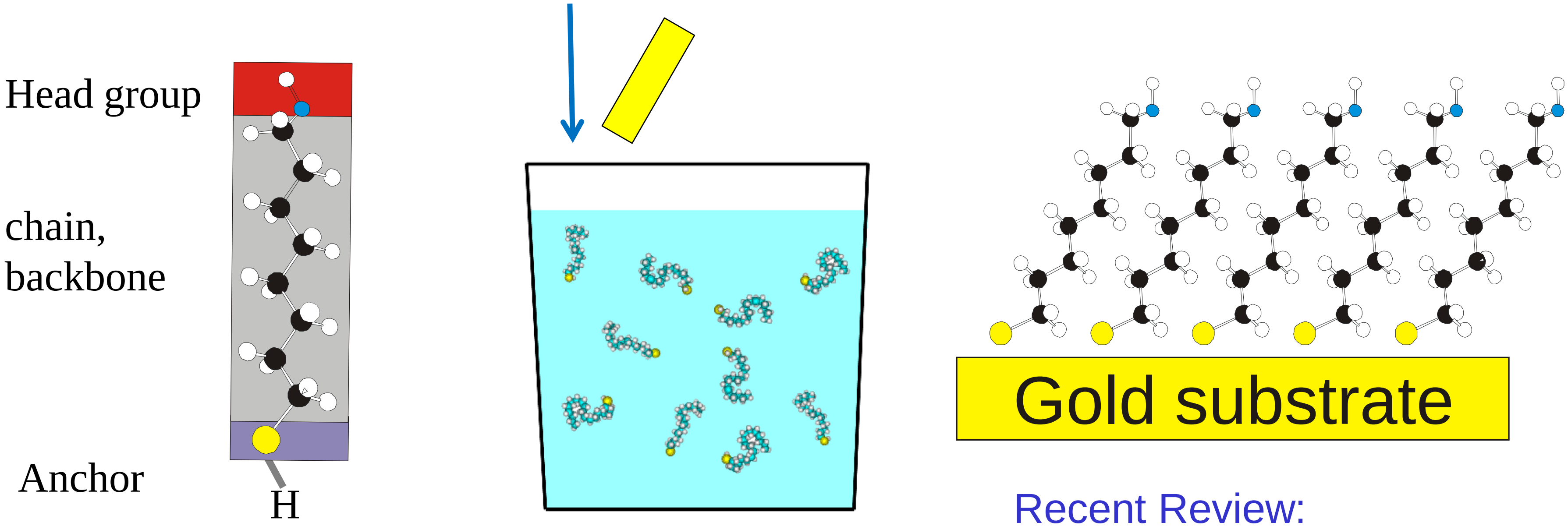
Growth of pentacene on metal substrates





- Surface modification needed

SAMs as model-systems for molecule-based interfaces



Octanethiol, alkanethiols

Recent Review:
M. Kind and Ch. Wöll
Prog. Surf. Sci. **84**, 230 (2009)

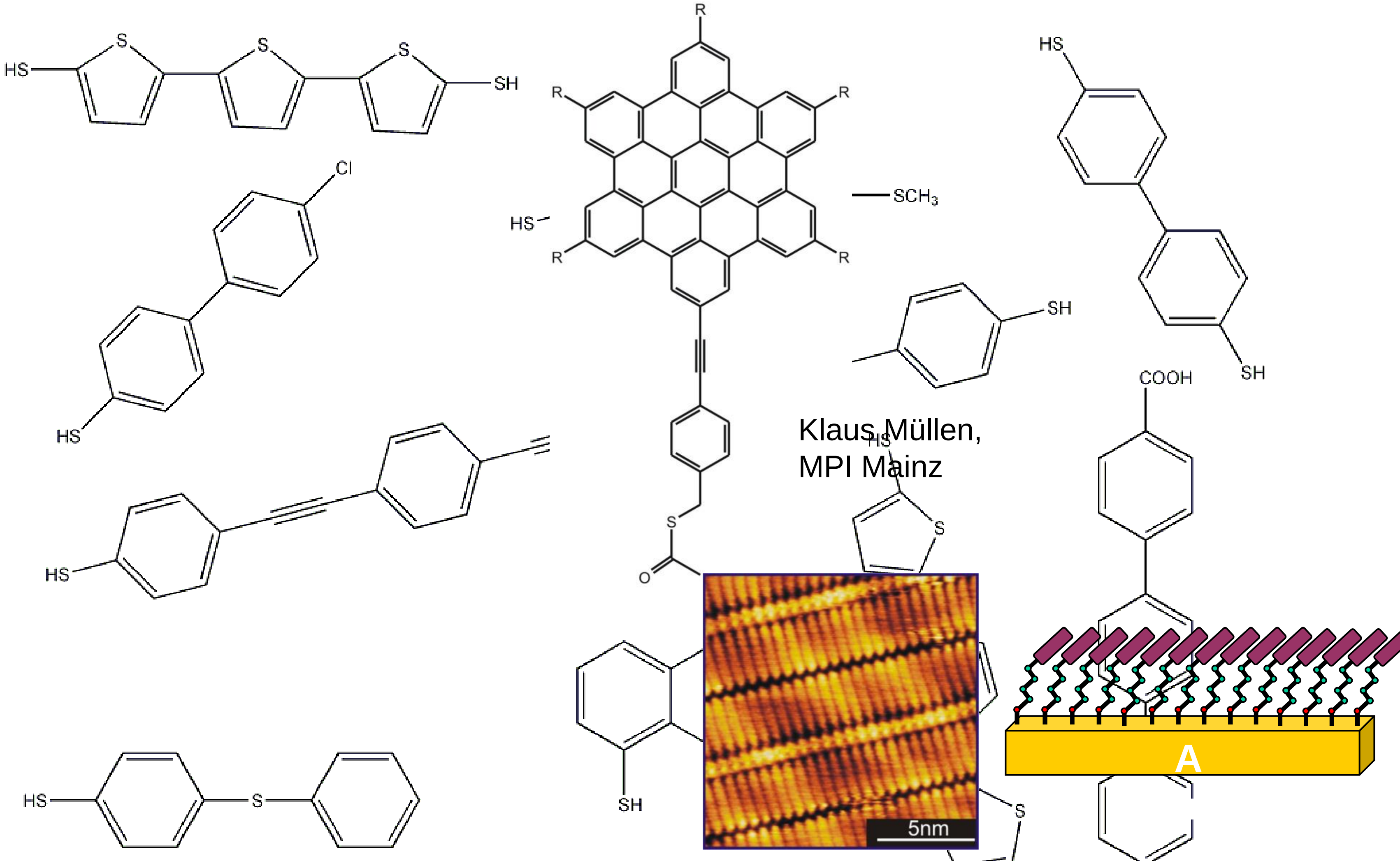
High structural perfection, limited only by substrate quality

Precise control of interface dipole possible

G.Heimel, L.Romaner, E.Zojer, J.Bredas
Nano Letters **7**, 932, (2007)

Potential not yet fully exploited – insulator vs. OSC

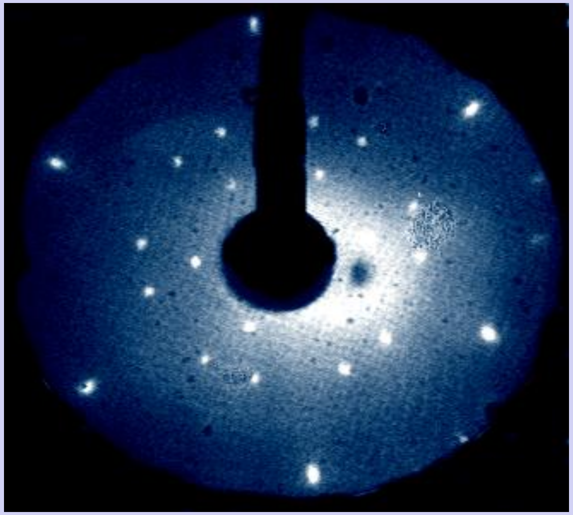
Most organic molecules are suited for attaching a thiol anchor ….



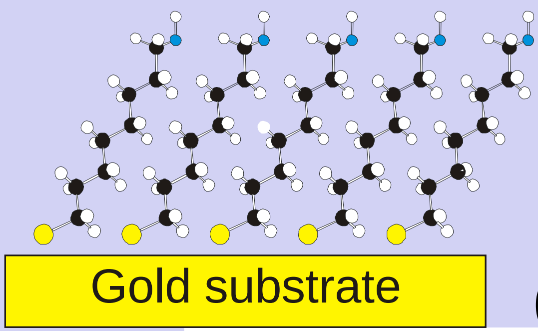
Käfer, Bashir, Witte, Müllen, CW
Adv. Mat. **22**,384 (2010)

SAMs exhibit organic surfaces with a structural quality defined by the Au(111) substrate !

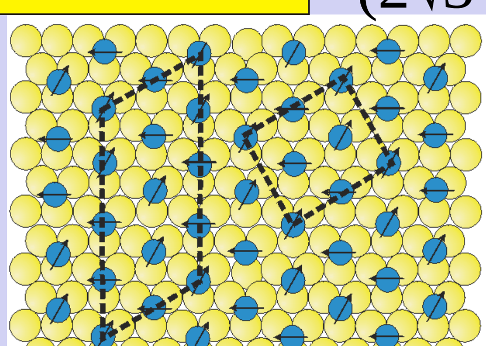
SAMs: Highly ordered molecular adlayers

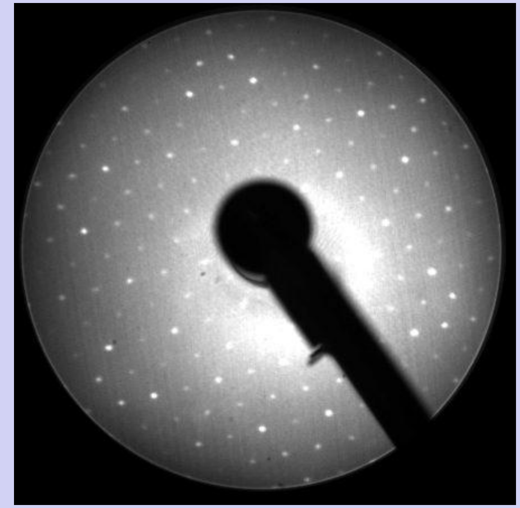


Decane thiolate (27 eV)

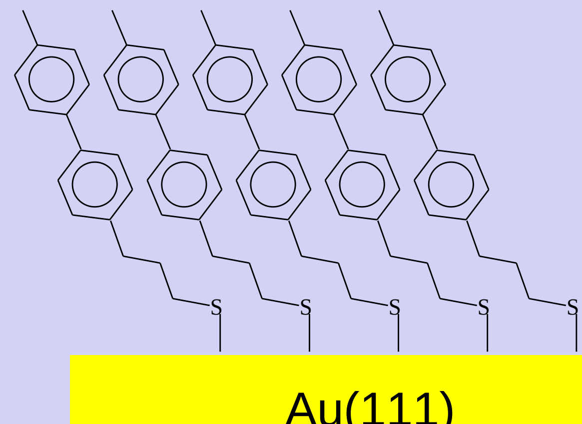


$(2\sqrt{3}*\sqrt{3})R30°$





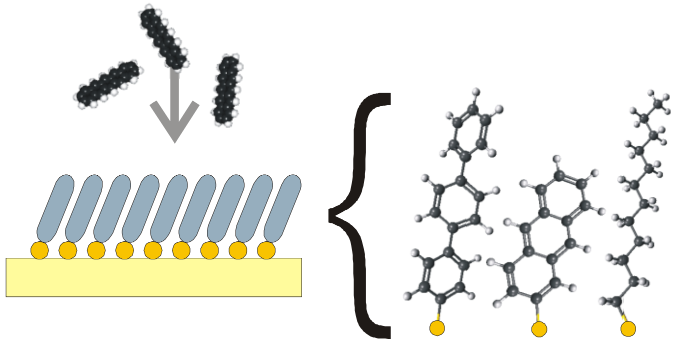
Biphenyl-butane-thiolate (64 eV)



$(2\sqrt{3}*6)R30°$

G. Pirug et al., FZ Jülich, FRG

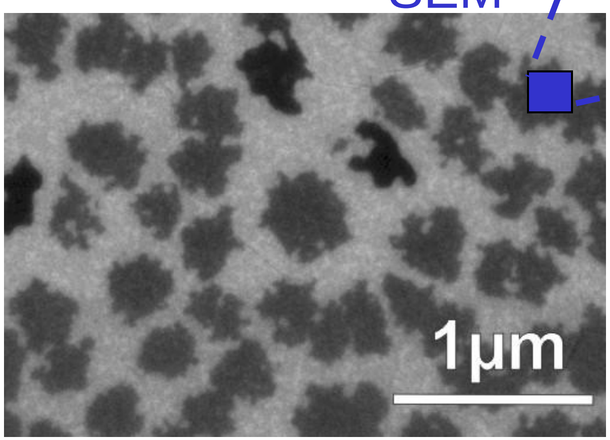
Pentacene growth on modified Au(111)-surfaces



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

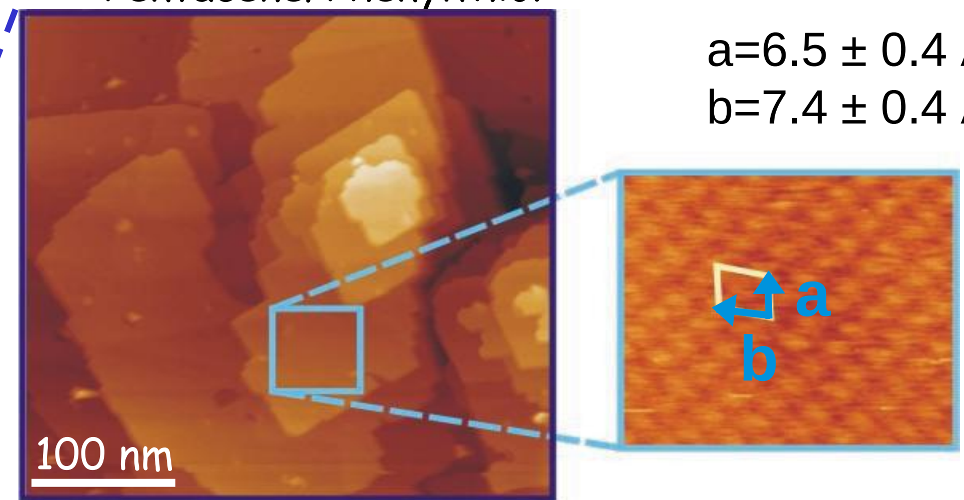
d=2nm @rt

SEM



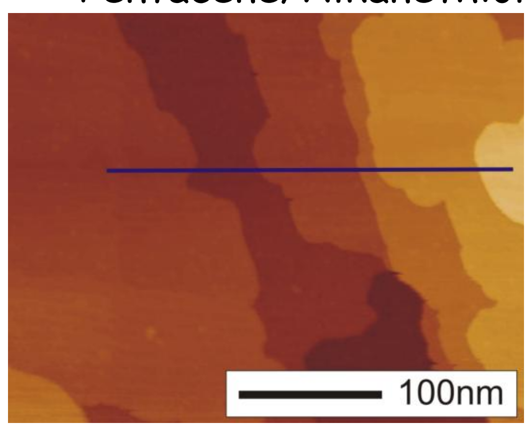
no morphological changes within 72 h

Pentacene/Phenylthiol

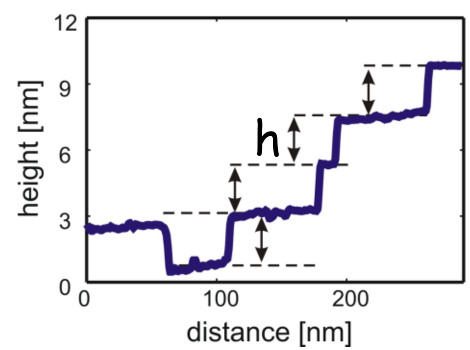


a=6.5 ± 0.4 Å
b=7.4 ± 0.4 Å

Pentacene/Alkanethiol

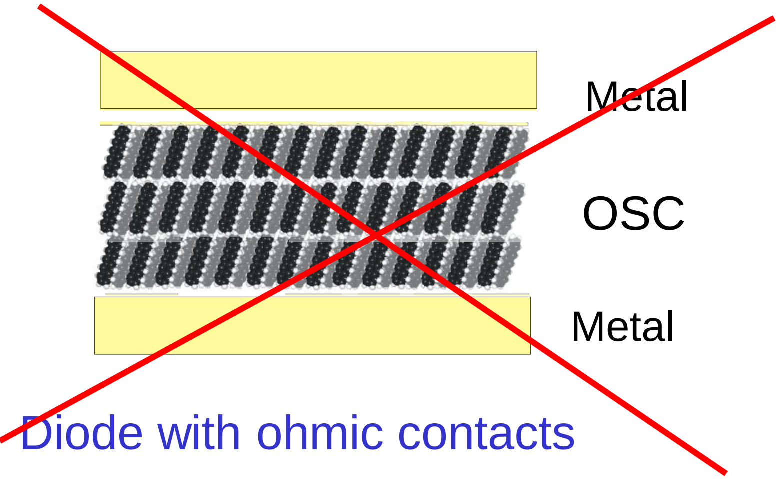


h=17 ± 3 Å

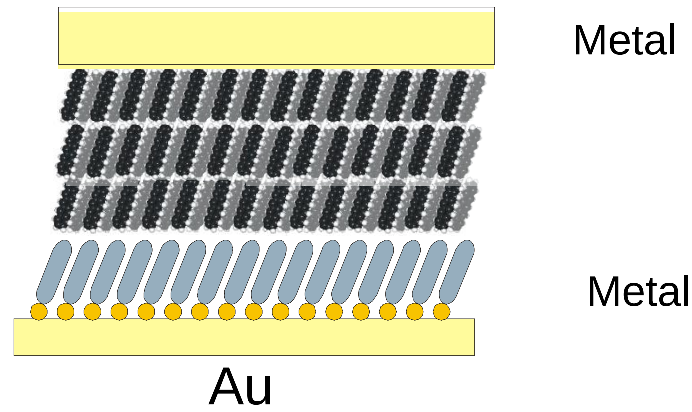


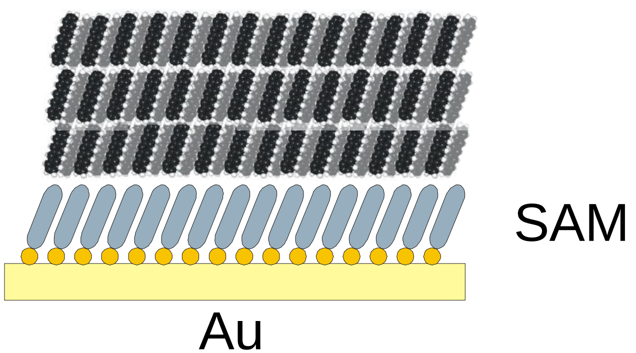
L.Ruppel, A.Birkner, G.Witte, C.Busse, T.Lindner, G.Paasch, CW, J.Appl.Phys. 102, 033708 (2007)

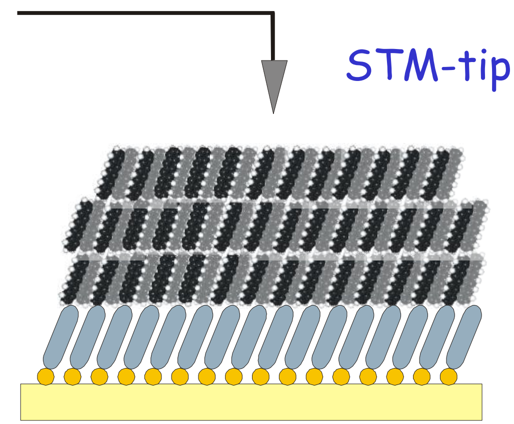
Fabrication of an „ideal" OSC-device



Diode with ohmic contacts

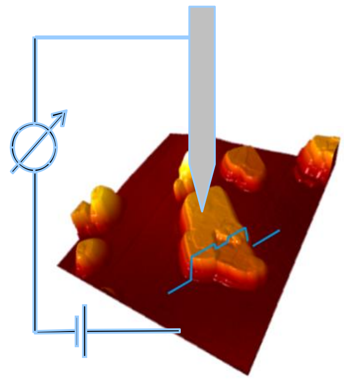






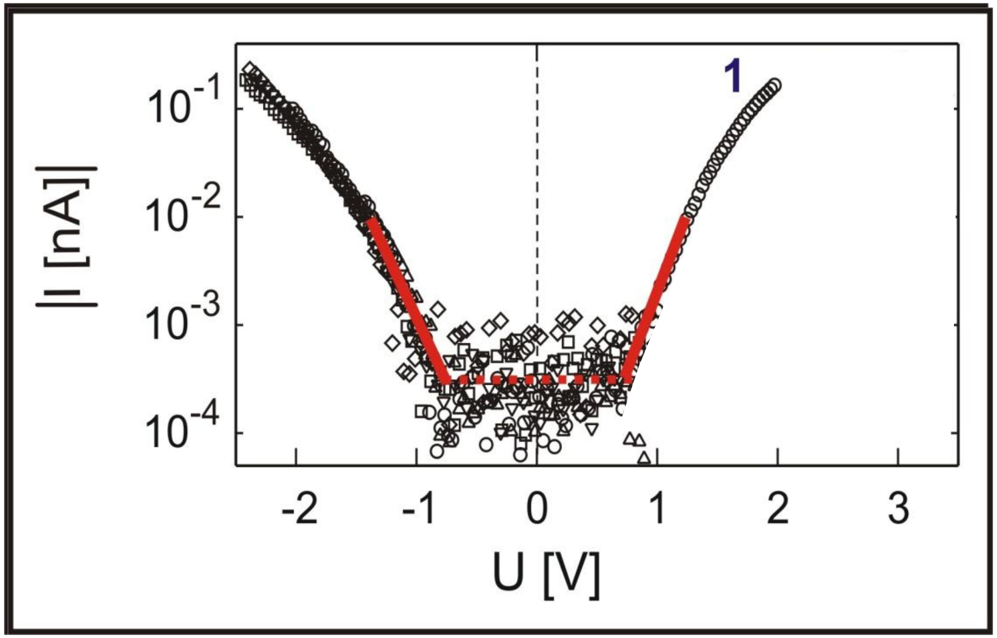
Diode with two different tunneling contacts

Current-Voltage characteristics of „diode"-setup

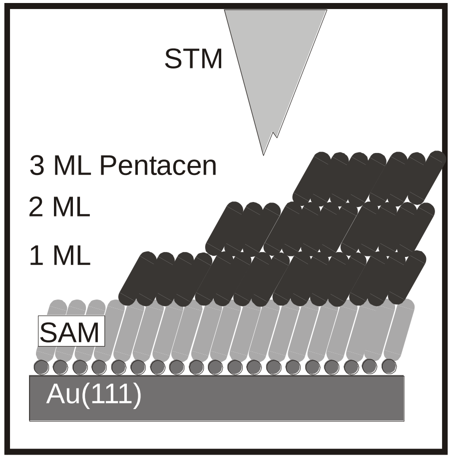


Log. plot onset values
at noise level (3·10^{-4} nA)

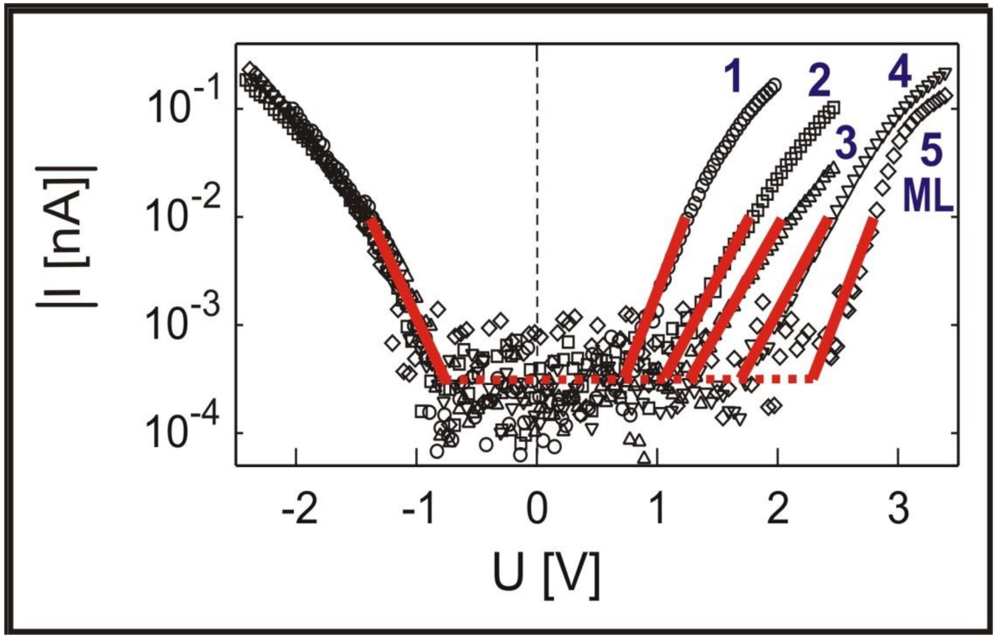
A total of ~ 50 islands have been investigated



Current-Voltage characteristics of „diode"-setup



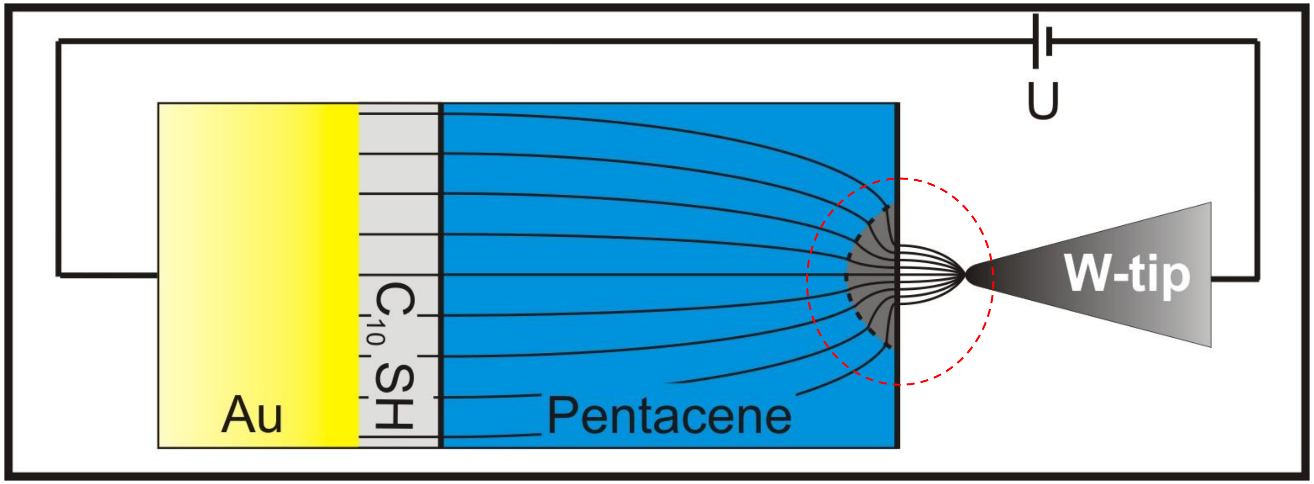
A total of ~ 50 islands have been investigated



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

Our hypothesis: Space charge effects



100 pA, 1nm^2

->10^4 A /cm^2

High charge density below tip leads to formation of space charge limited (SCL) region

Child‘s law for SCL-transport:

$$j = \frac{9}{8} \mu \varepsilon_r \varepsilon_0 \frac{U^2}{d^3}$$

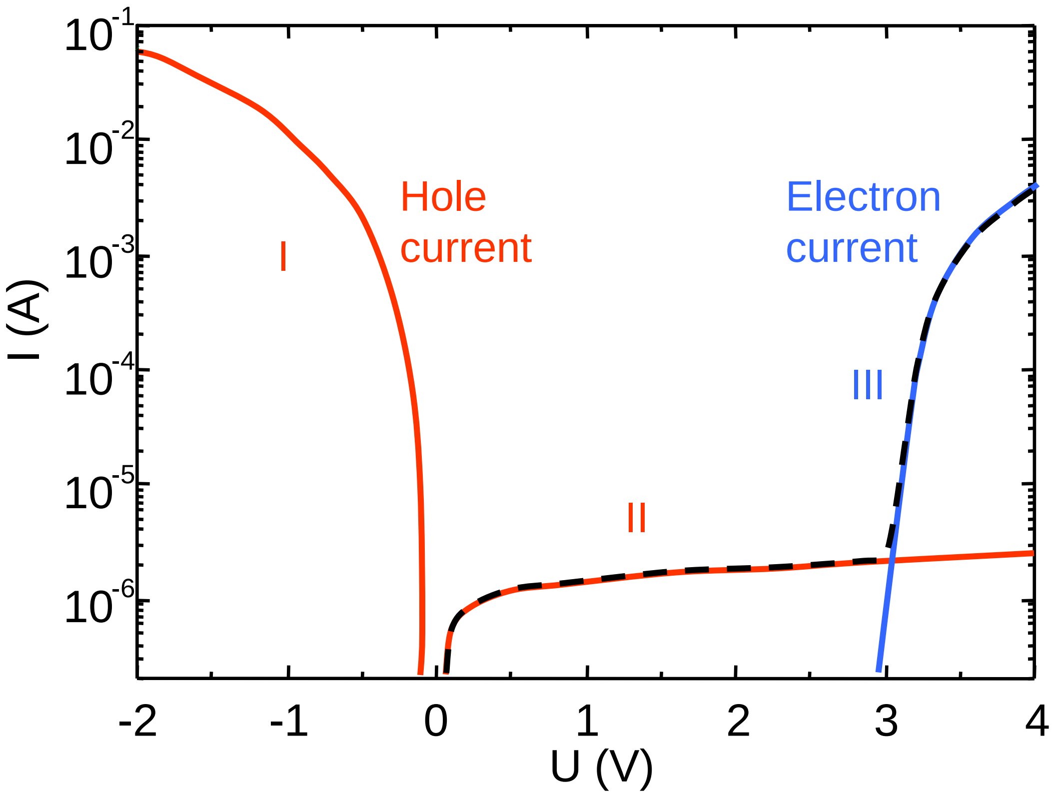
Smaller electric field for thicker layers

explains dependence on film thickness d

Confirmed by experiments at low temperature (70K)

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

Analysis of numeric simulation



- I: holes injected below tip

  (e⁻ tunnel from VB to tip, always enough electrons)

- II: holes injected at substrate, low h density, few e⁻ tunnel form tip to VB

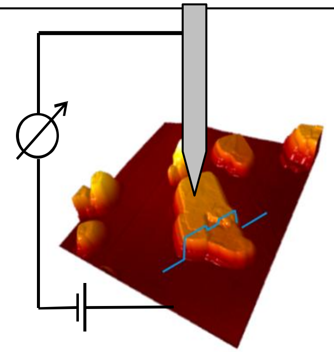
- III: voltage drop between tip and VB becomes so large that CB opens

Only p-conduction -> true diode behavior (rectification)

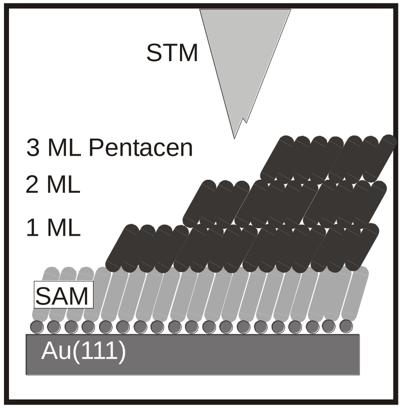
Onset at pos. bias implies n-conduction, transport through CB (rarely observed for PC)

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

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)

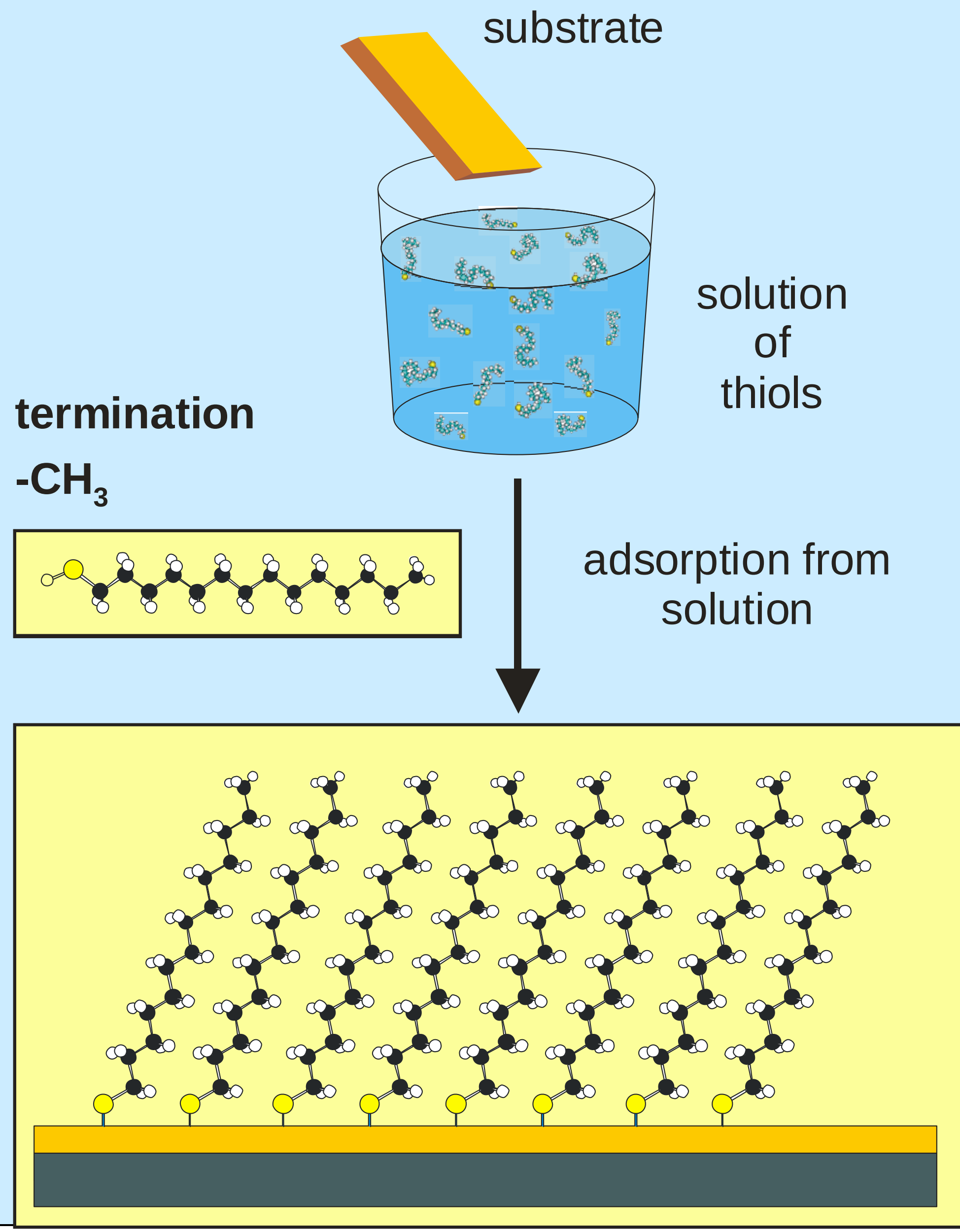


n-conduction in pentacene ? – absent in most real devices

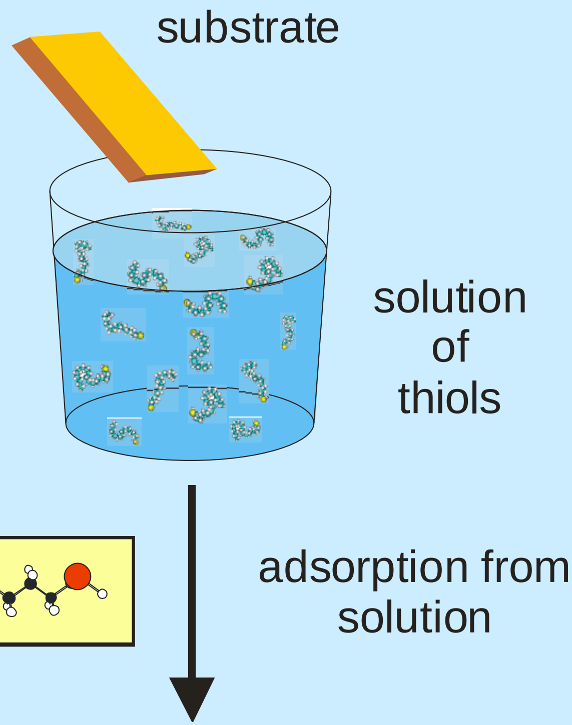
- n-conduction for OSC in the absence of charge traps (-OH at interface)
Chua, Zaumseil, Chang, Ou, Ho, Sirringhaus, Friend, Nature **434**, 194 (2005).

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

Modification of SAM-surface

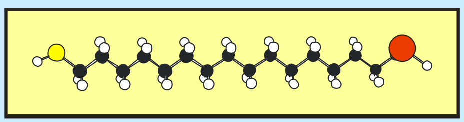


Modification of SAM-surface

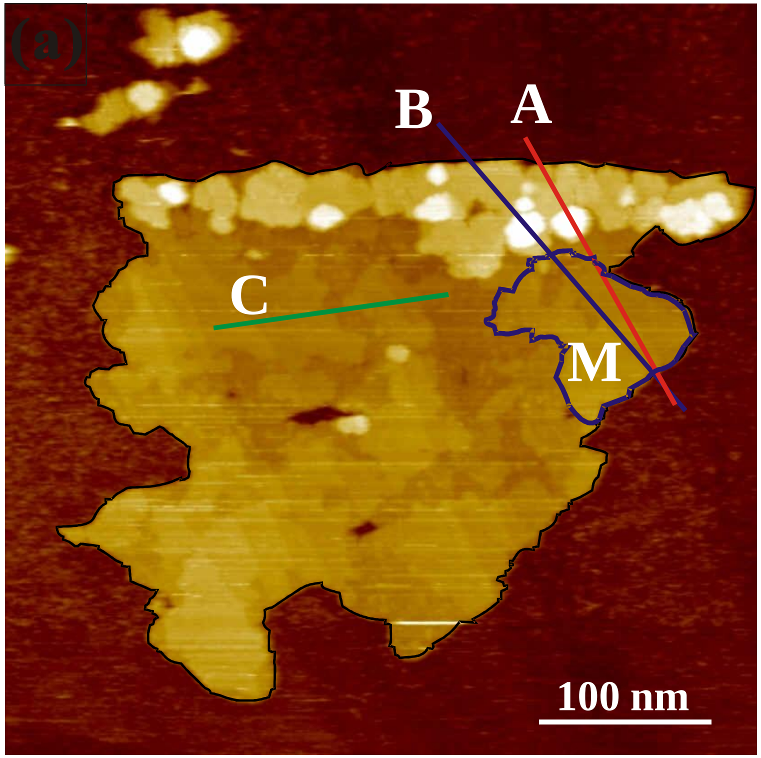


termination

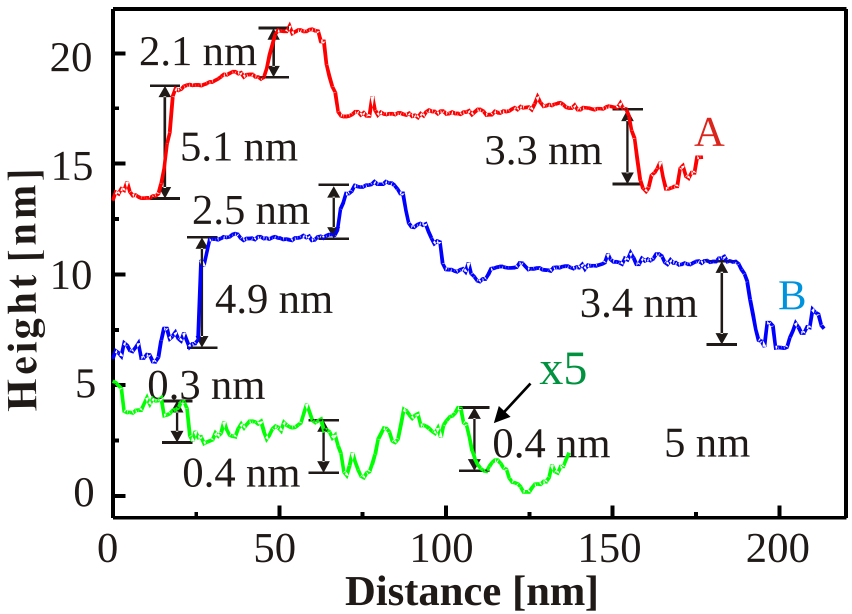
-OH



Well-defined pentacene-layers grown on OH-terminated SAM



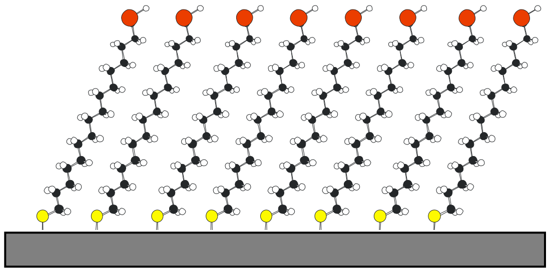
-2.5 V 0.05 nA



Stable STM imaging at negative bias

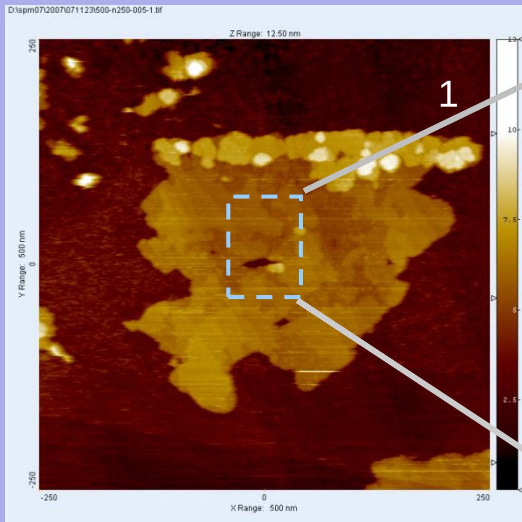
1 nm pentacene film on a OH-terminated SAM

M: double layer of pentacene, rest single layer

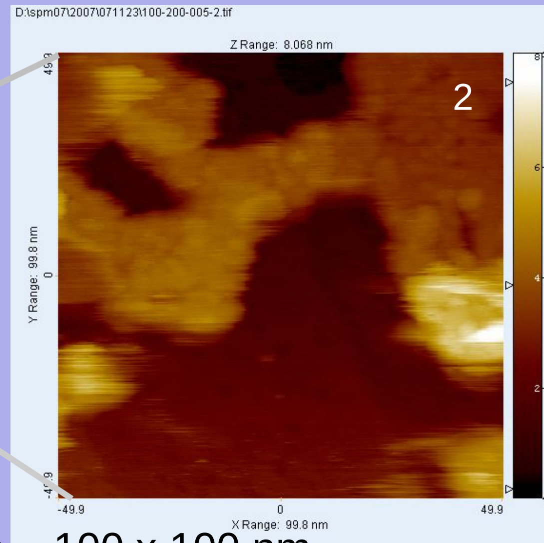


Similar growth mode as on CH_3-terminated SAM

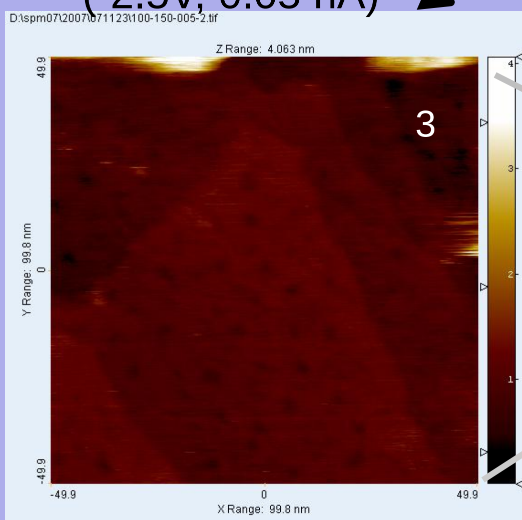
Pentacene deposited on OH-terminated SAM



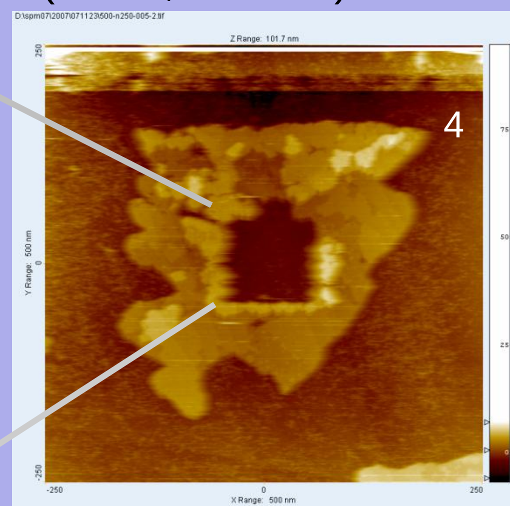
500 x 500 nm
(-2.5V, 0.05 nA)



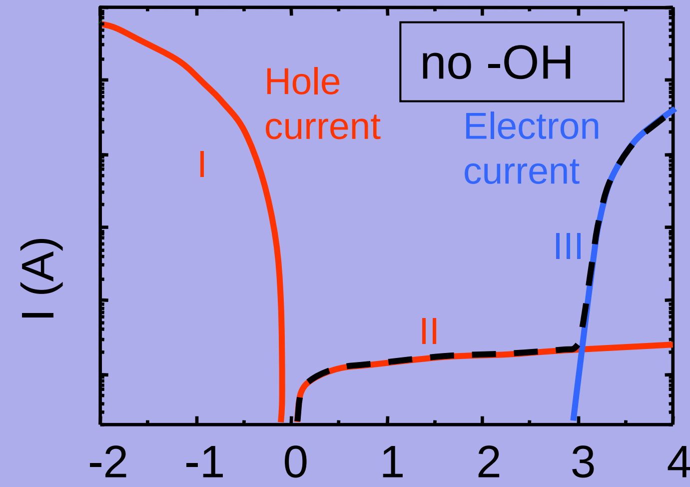
100 x 100 nm
(+2.0V, 0.05 nA)

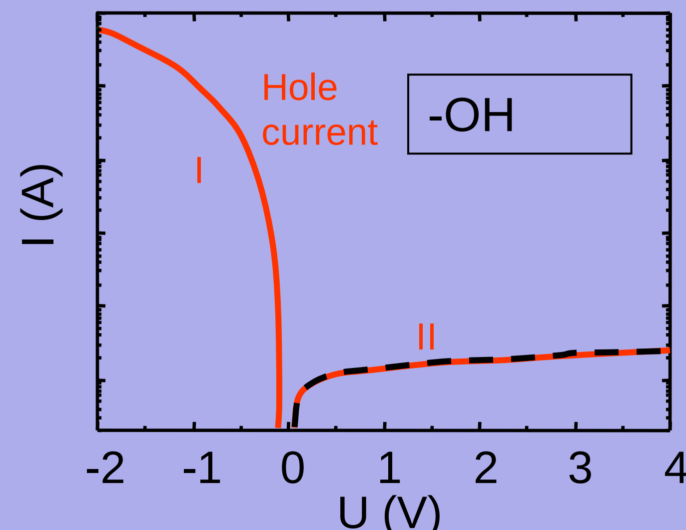


100 x 100 nm
(+1.5V, 0.05 nA)



500 x 500 nm
(-2.5V, 0.05 nA)

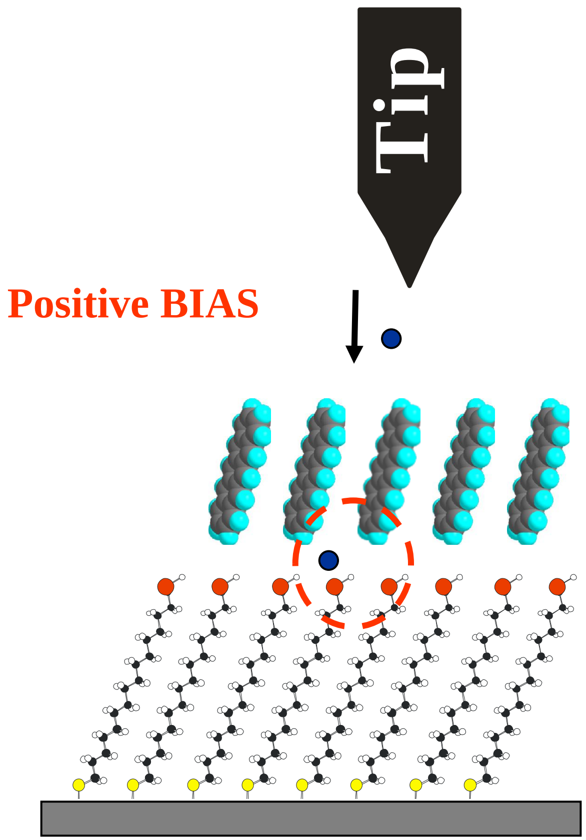


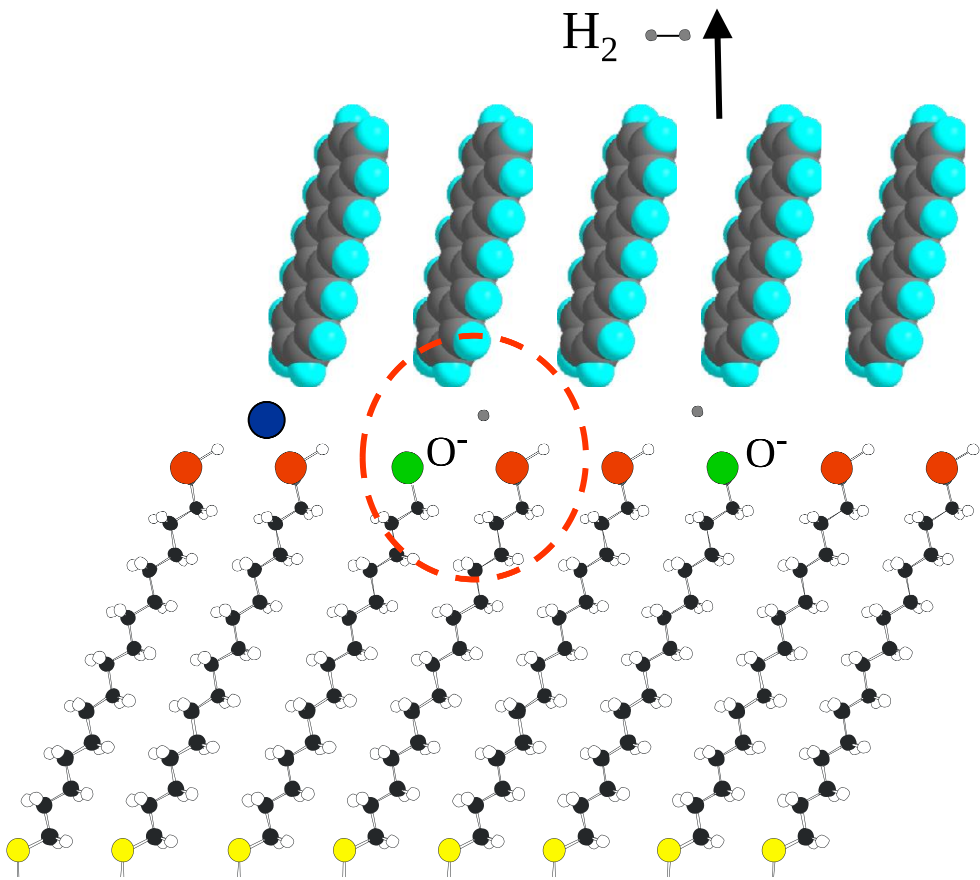


- n-transport absent
- imaging at positive bias
- damages PC-islands
- Full support of interpretation

Z.-H- Wang, D. Käfer, A. Bashir, J. Götzen, A. Birkner, G.Witte, CW PCCP, in print (2010), DOI: 10.1039/b924230a

Trapping of electrons at OH groups



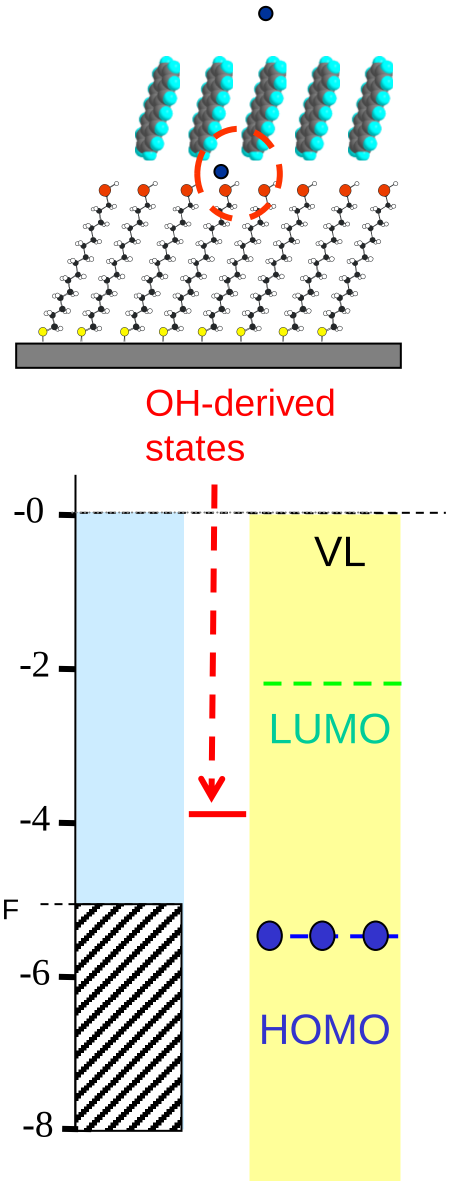


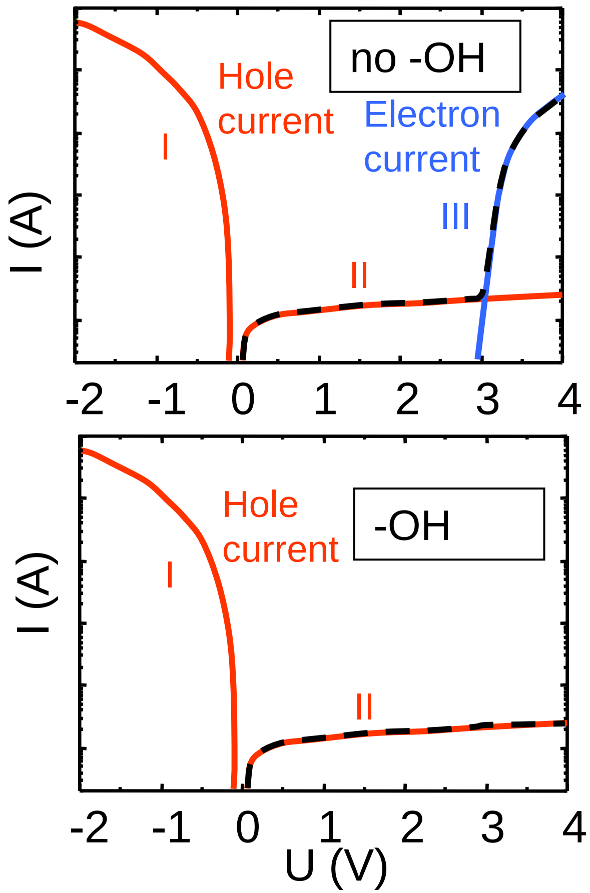
Corresponding studies for alcohols in solvents:

$$e^-_{solv} + ROH \rightleftarrows \{e^-:ROH\}_{solv} \rightarrow RO^- + H^\bullet,$$ H* then reacts with solvent

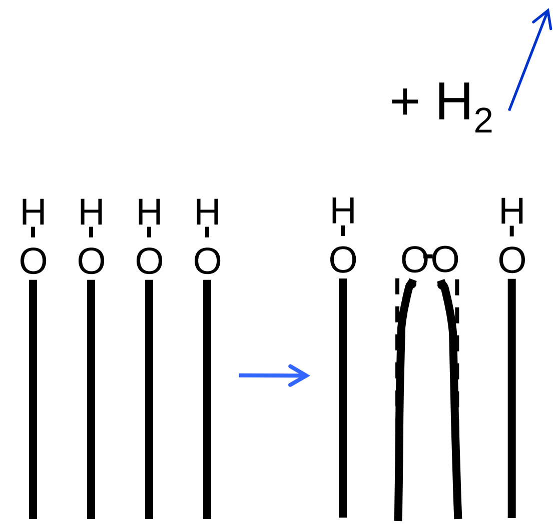
I.Shkrob and M.Sauer, J.Phys.Chem.A **109**, 5754 (2005)

OH-traps at organic-organic interface



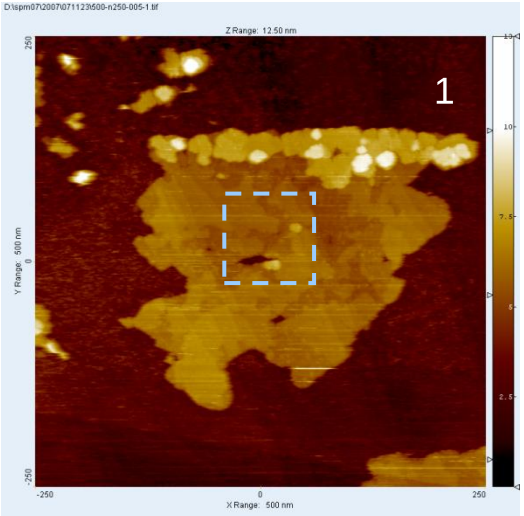


What happens after e^- being trapped at OH-groups ?

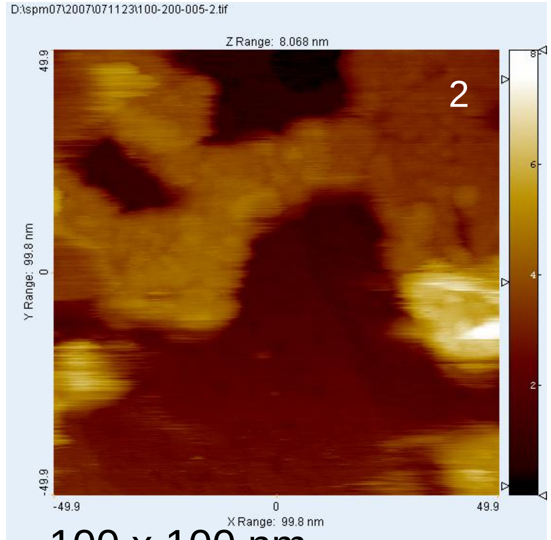


H-abstraction should lead to structural rearrangement of SAM
Irreversible changes ?

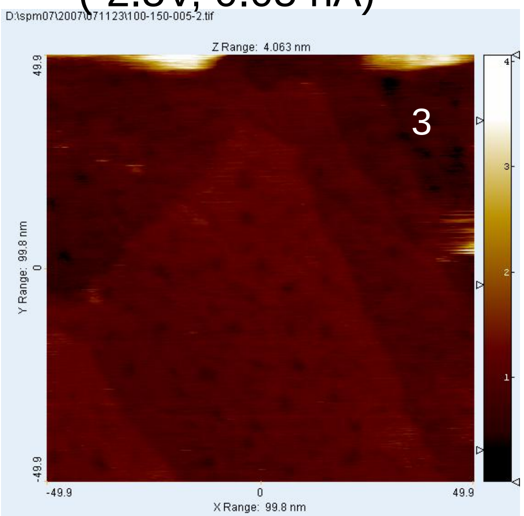
Structural changes resulting from loading of OH-traps with e^-



500 x 500 nm
(-2.5V, 0.05 nA)

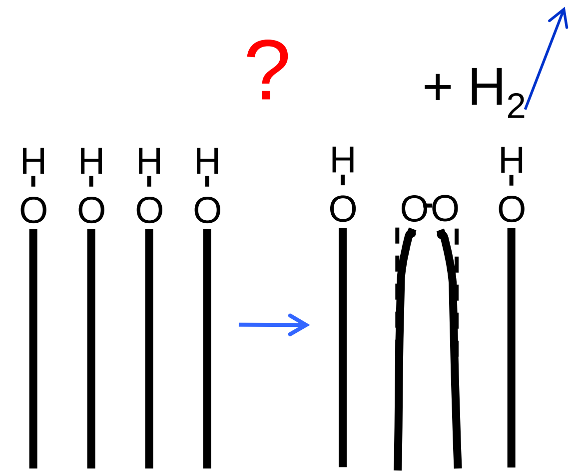


100 x 100 nm
(+2.0V, 0.05 nA)



100 x 100 nm
(+1.5V, 0.05 nA)

Indistinguishable from STM micrographs recorded before deposition



Irrevsible structural changes ?

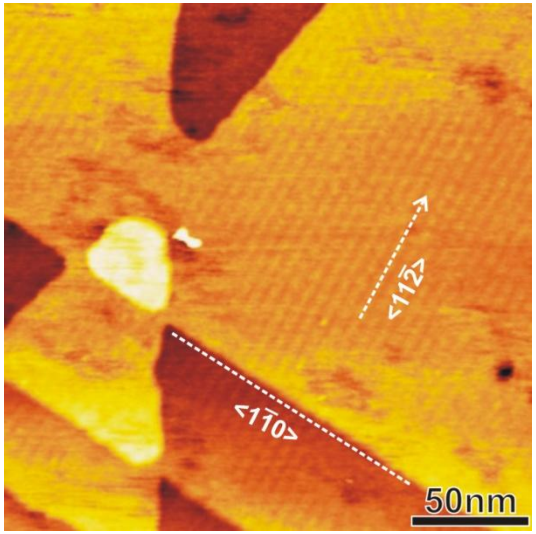
- No changes seen when imaging SAM surface after removal of pentacene

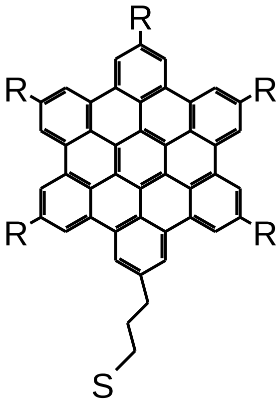
→ Strong evidence for reversible filling of OH trap states

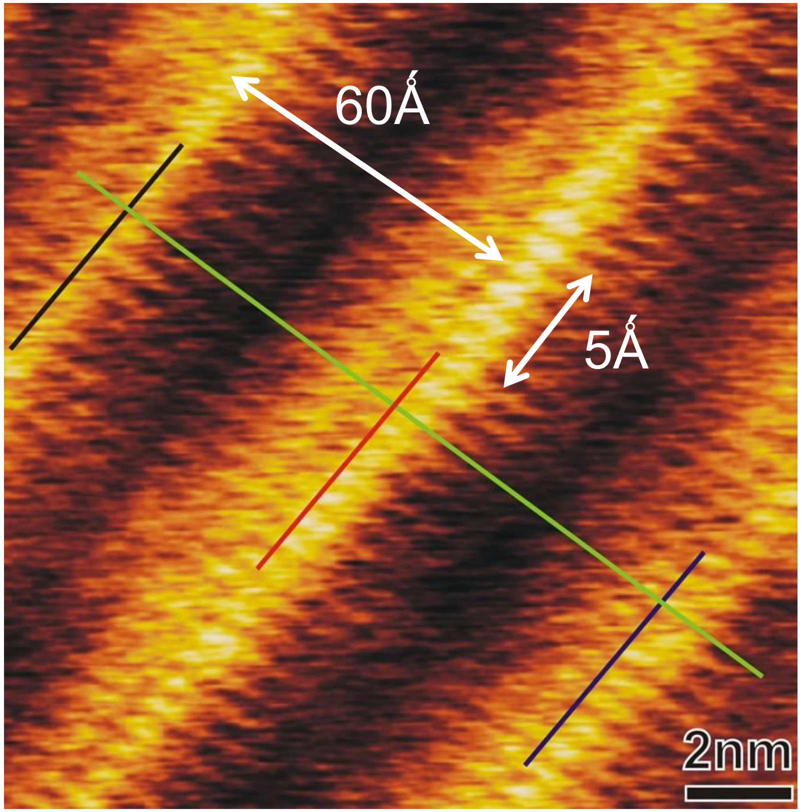
Z.-H- Wang, D. Käfer, A. Bashir, J. Götzen, A. Birkner, G.Witte, CW PCCP, **12**, 4317 (2010)

SAMs of HBC-C_3 thiol on Au(111)

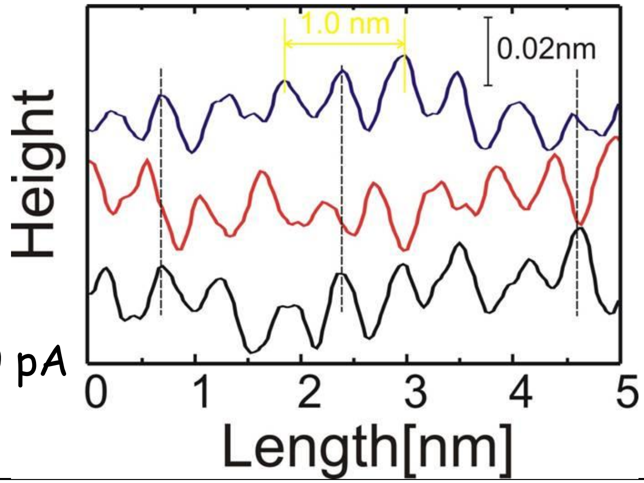
Long columnar structure

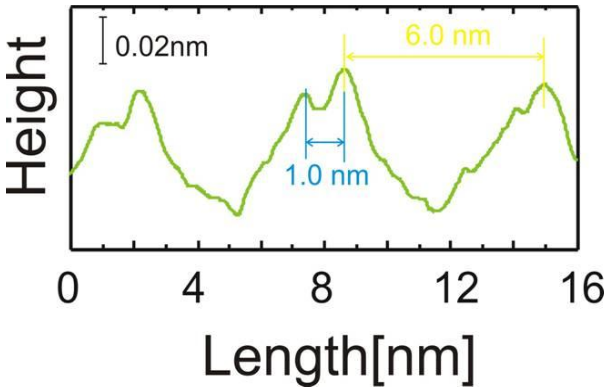






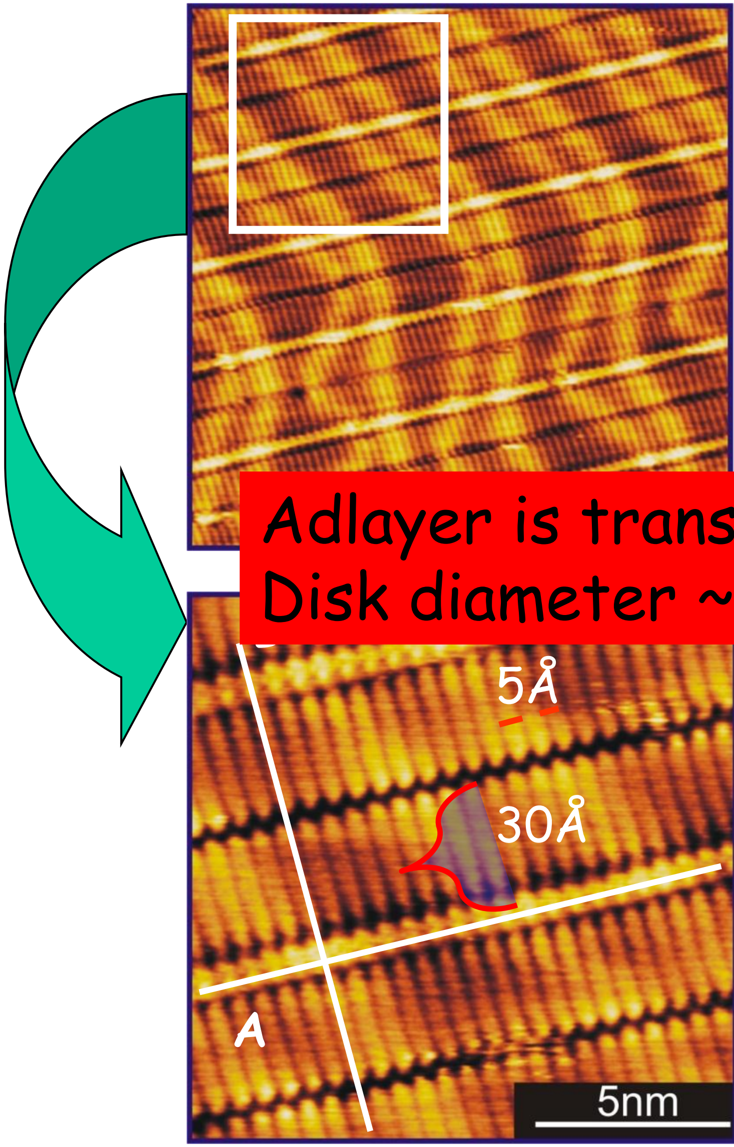
Soft tether long range ordered of parallel lamella under the guidance of π-π stacking.

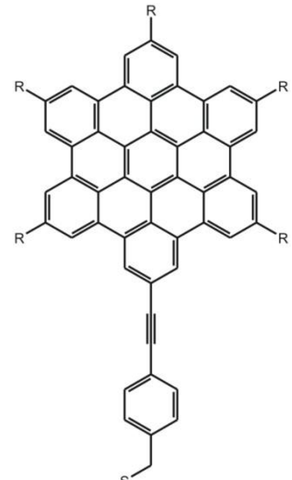




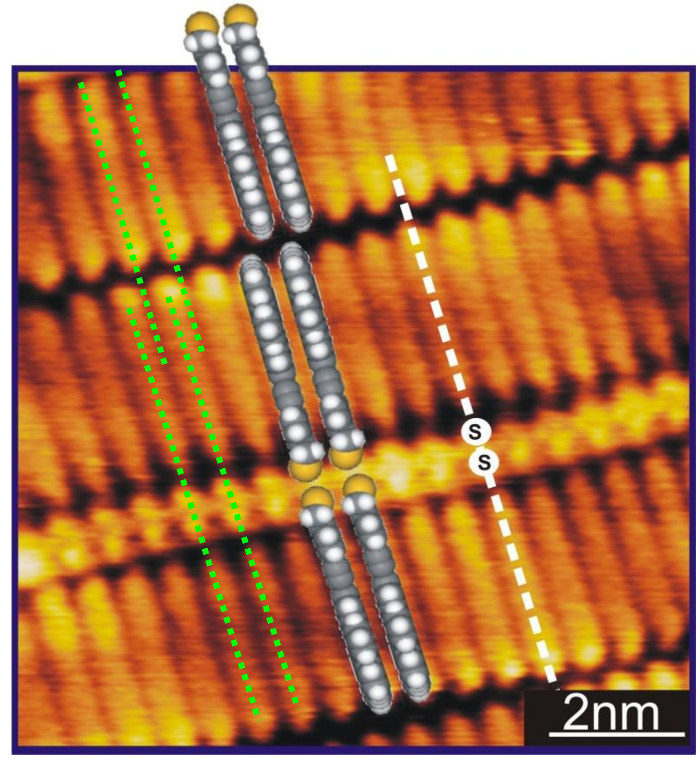
U_t=500 mV, I_t=100 pA

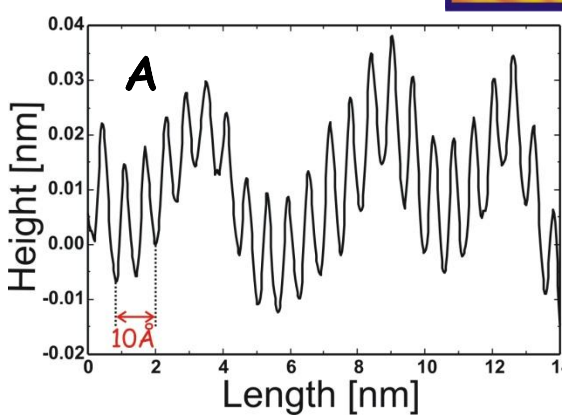
SAMs of P-HBC thiol on Au(111) (measured in UHV)

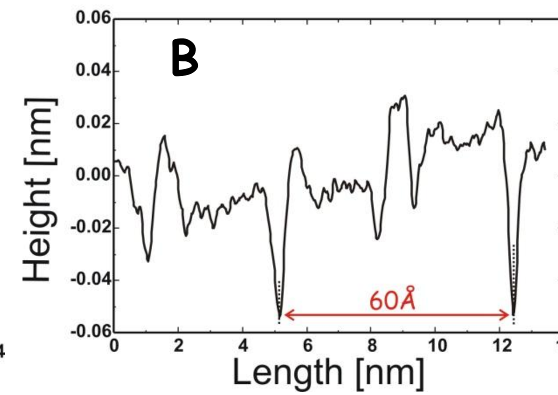




Adlayer is transparent
Disk diameter ~ 2.5-3nm



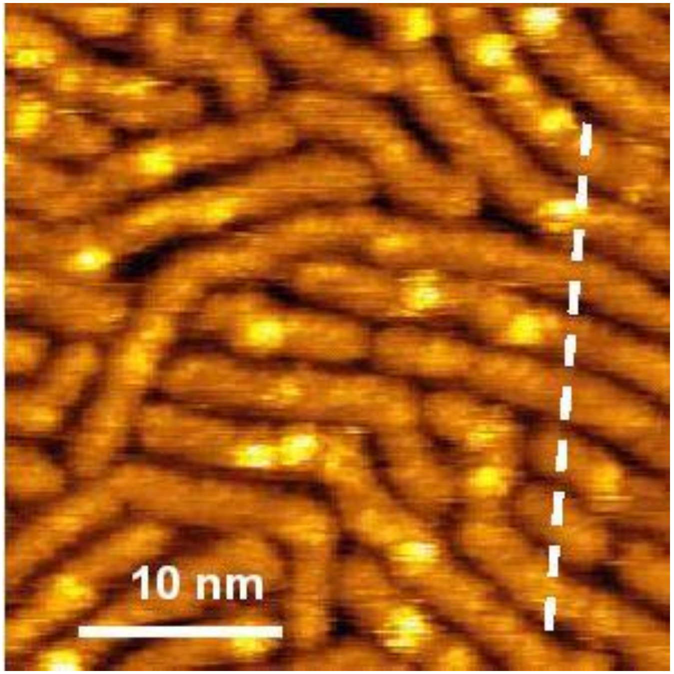




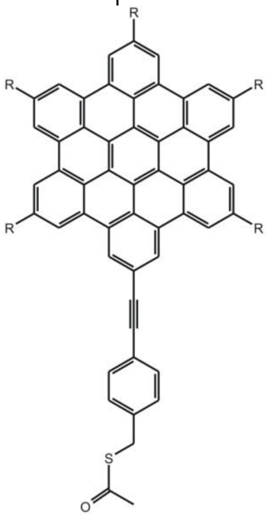
U_t=500 mV, I_t=100 pA

HBC thiol: preparation conditions matter !

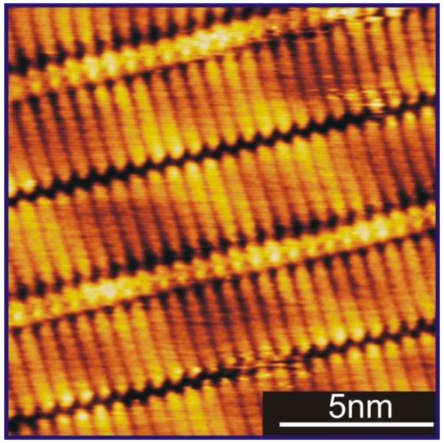
L. Piot, C. Marie, X. Dou, X. Feng,
K. Müllen, D. Fichou,
JACS 2009, **131**, 1378



Low degree of order, many defects



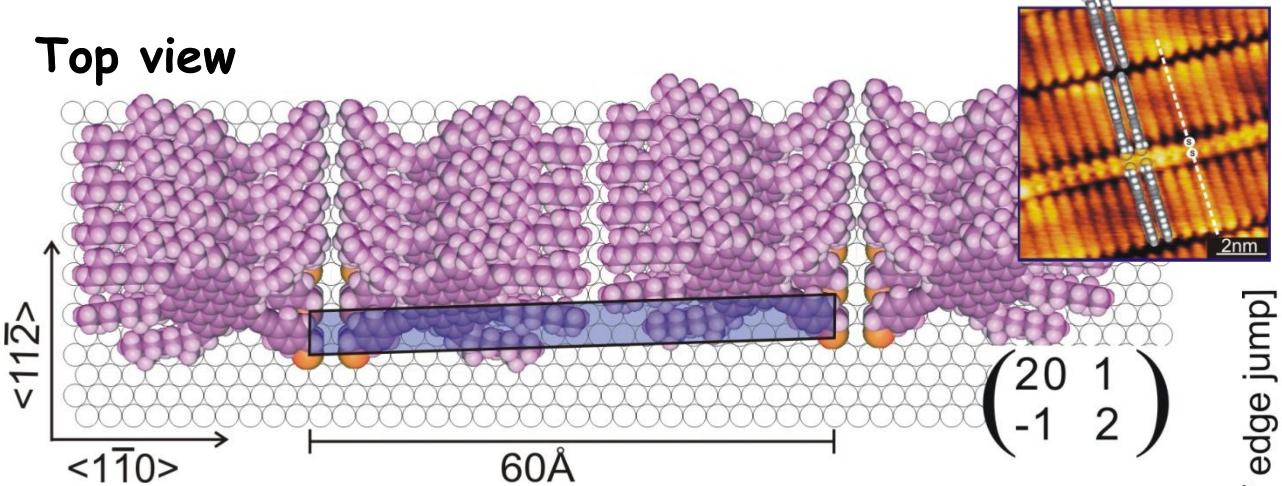
Our results
after optimization of preparation conditions



Long-range ordering,
low density of defects

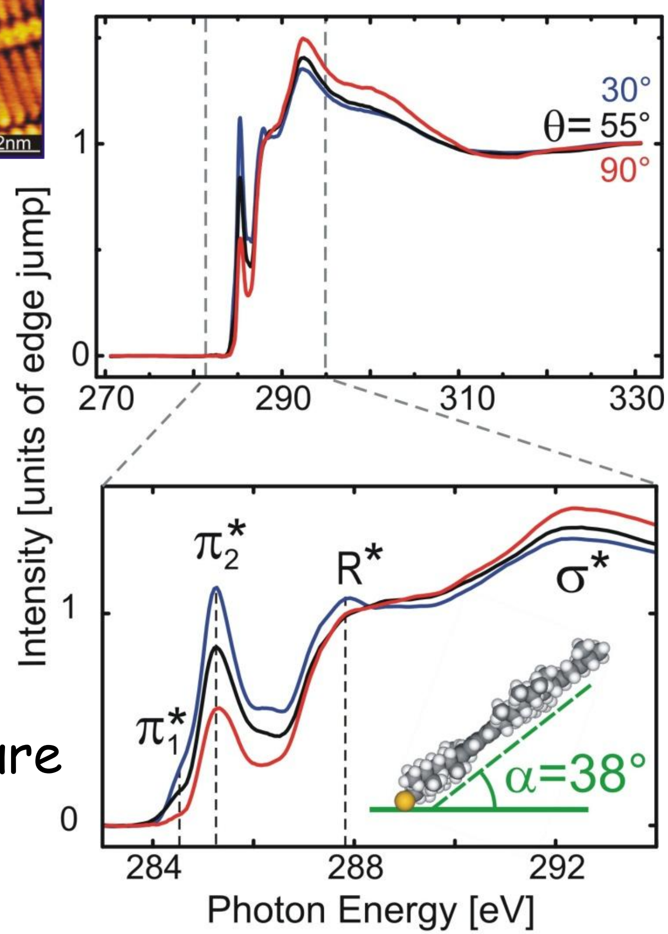
Structural model of HBC modified thiol

Top view

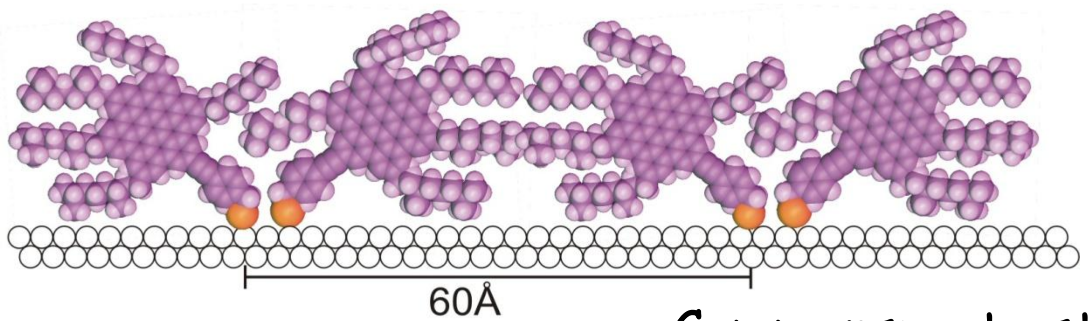


$$\begin{pmatrix} 20 & 1 \\ -1 & 2 \end{pmatrix}$$

NEXAFS for p-HBC-thiol

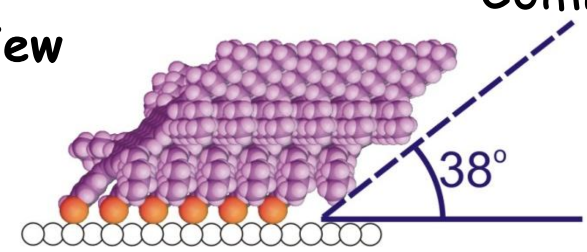


π_1^*	284.5 eV	R*	287.8 eV
π_2^*	285.2 eV	σ*	290.5 eV

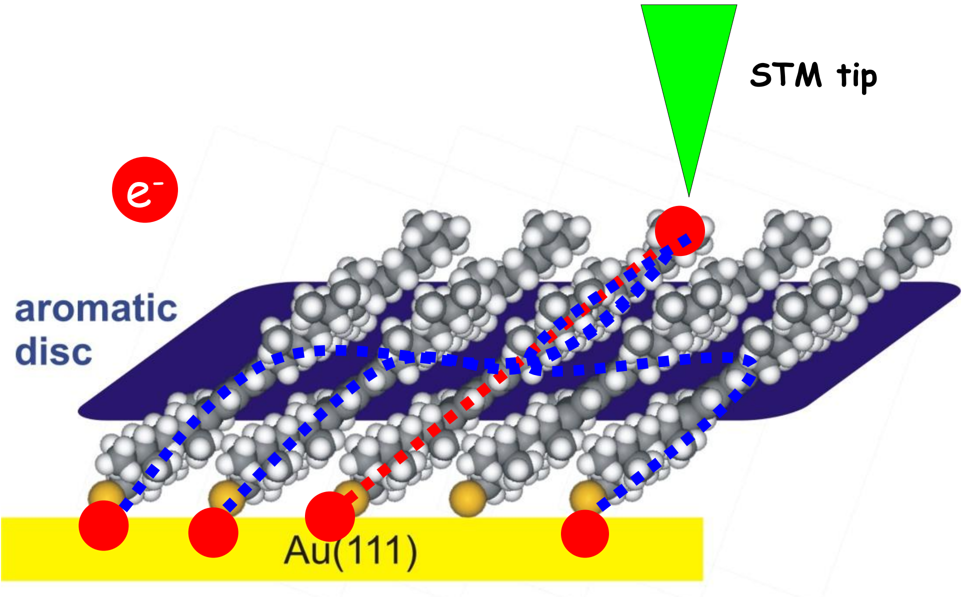


Commensurate structure
2 mol./ unit cell

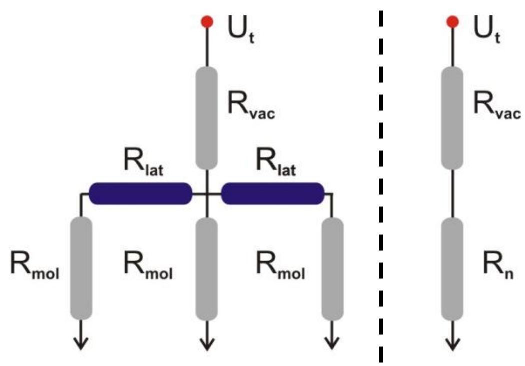
Side view



Electron transport mechanism of HBC SAMs: Information from STM ?

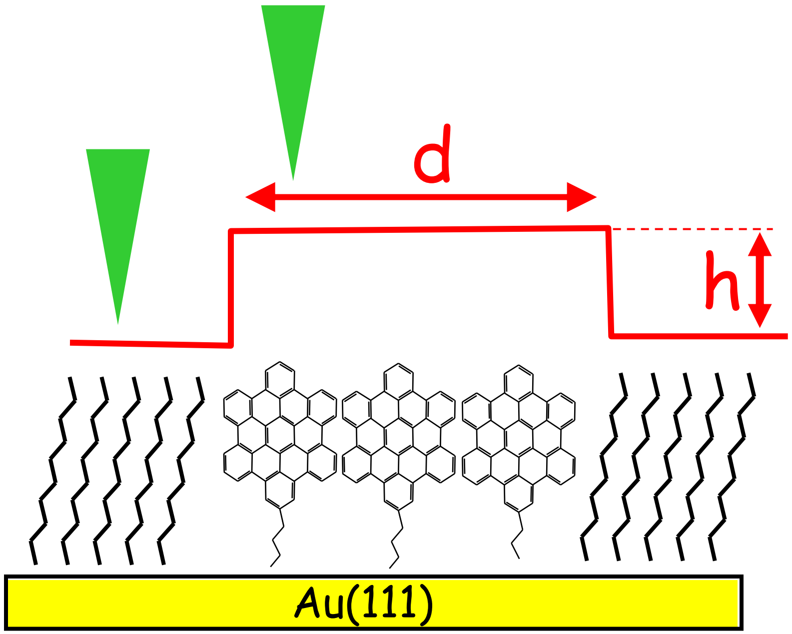


(e⁻) transport only along HBC molecule
or
(e⁻) transport also laterally



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

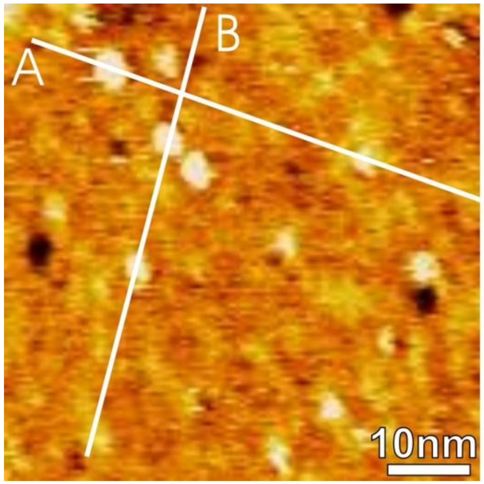
Apparent height of HBC-islands embedded in insulating matrix depends on island size

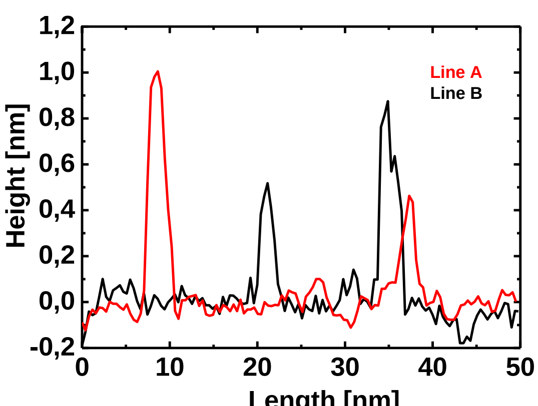


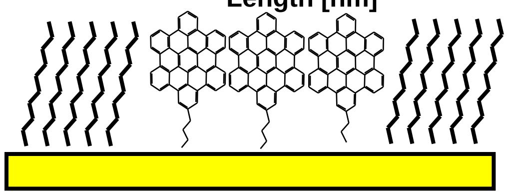
T. Ishida et al., J. Phys. Chem. B. 1999, **103**, 1686

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

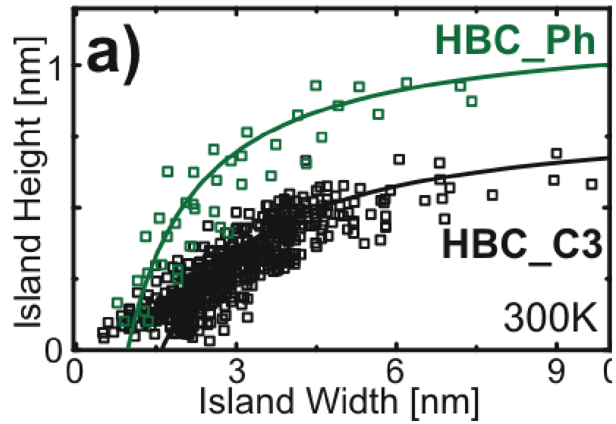
25 min insertion time

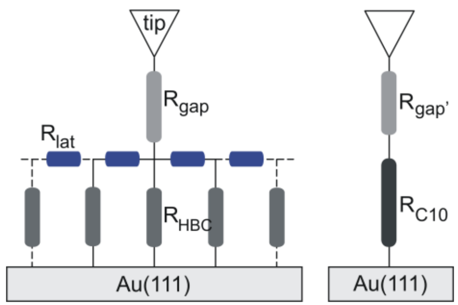






Apparent island height (Δh) vs size (d)





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

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)

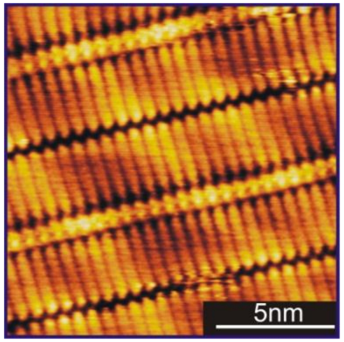
→ strong evidence for lateral transport

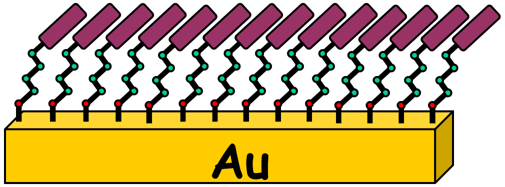
→ no strong temperature dependence (110K)

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

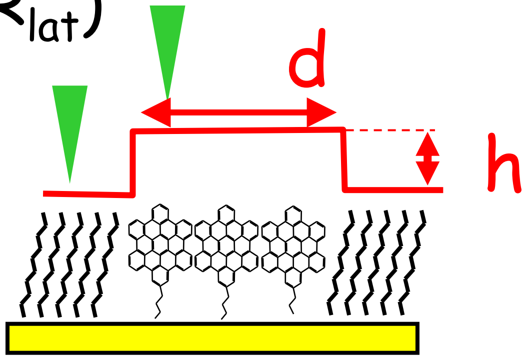
An OSC device based on SAMs ?

- 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

Topics:

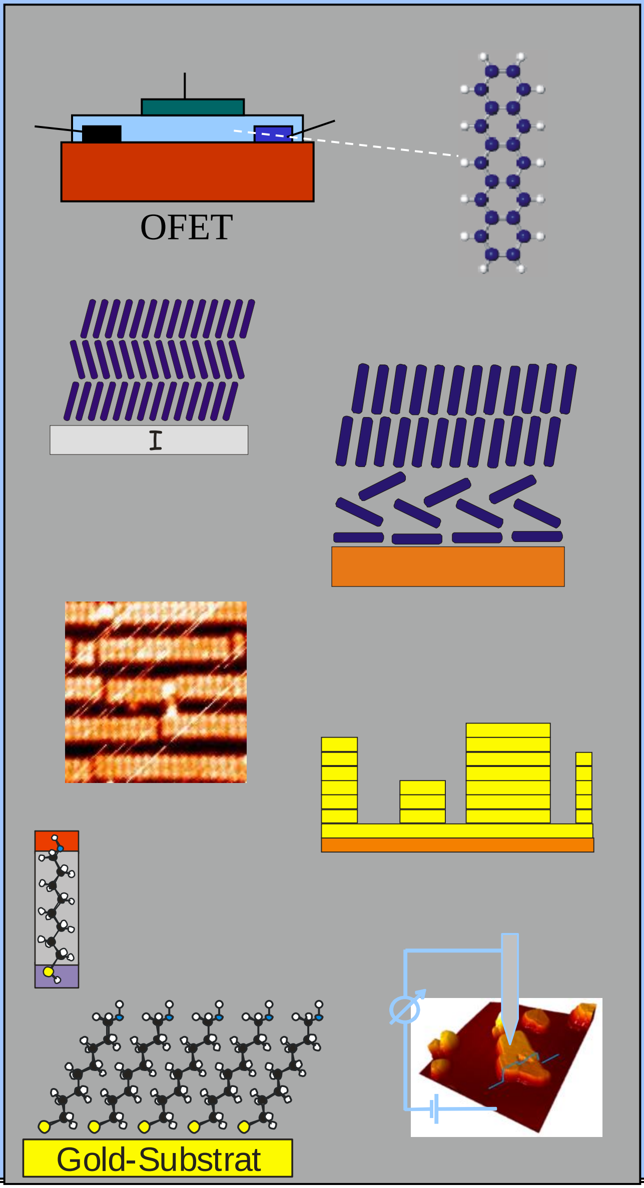
Organic electronics, OFETs
Work function
Electronic level alignment

Flat aromatic molecules grown on metal substrates

Using SAMs for substrate modification

Importance of model devices

SAM-based method to measure mobilities in OSCs



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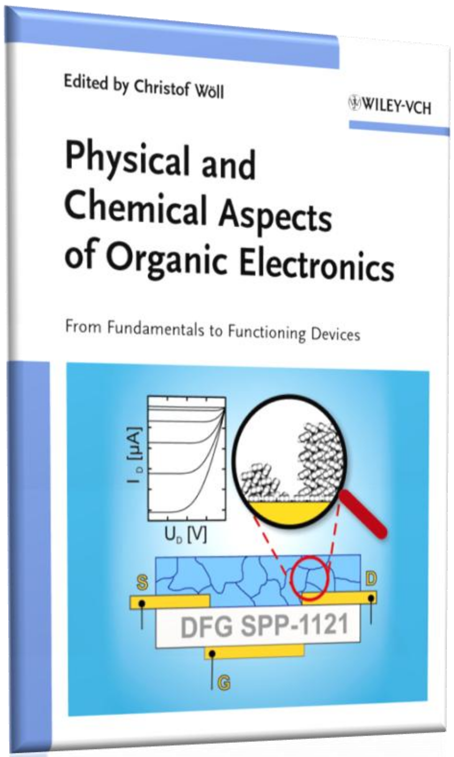
Physical and Chemical Aspects of Organic Electronics

From Fundamentals to Functioning Devices



Summarizes the state-of-the-art of a topic that has been the focus of intense recent research…

- **Covers the topic from the synthesis of appropriate materials to the testing of real devices.**
- **Special emphasis has been made on the difference between inorganic semiconductors such as Si, Ge and GaAs and organic semiconductors (OSC).**
- **Brings together experts from a variety of different fields who describe their approaches to organic electronics.**

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