Anchoring and LT-STM/STS characterization of single organic molecules at semiconducting and insulating surfaces

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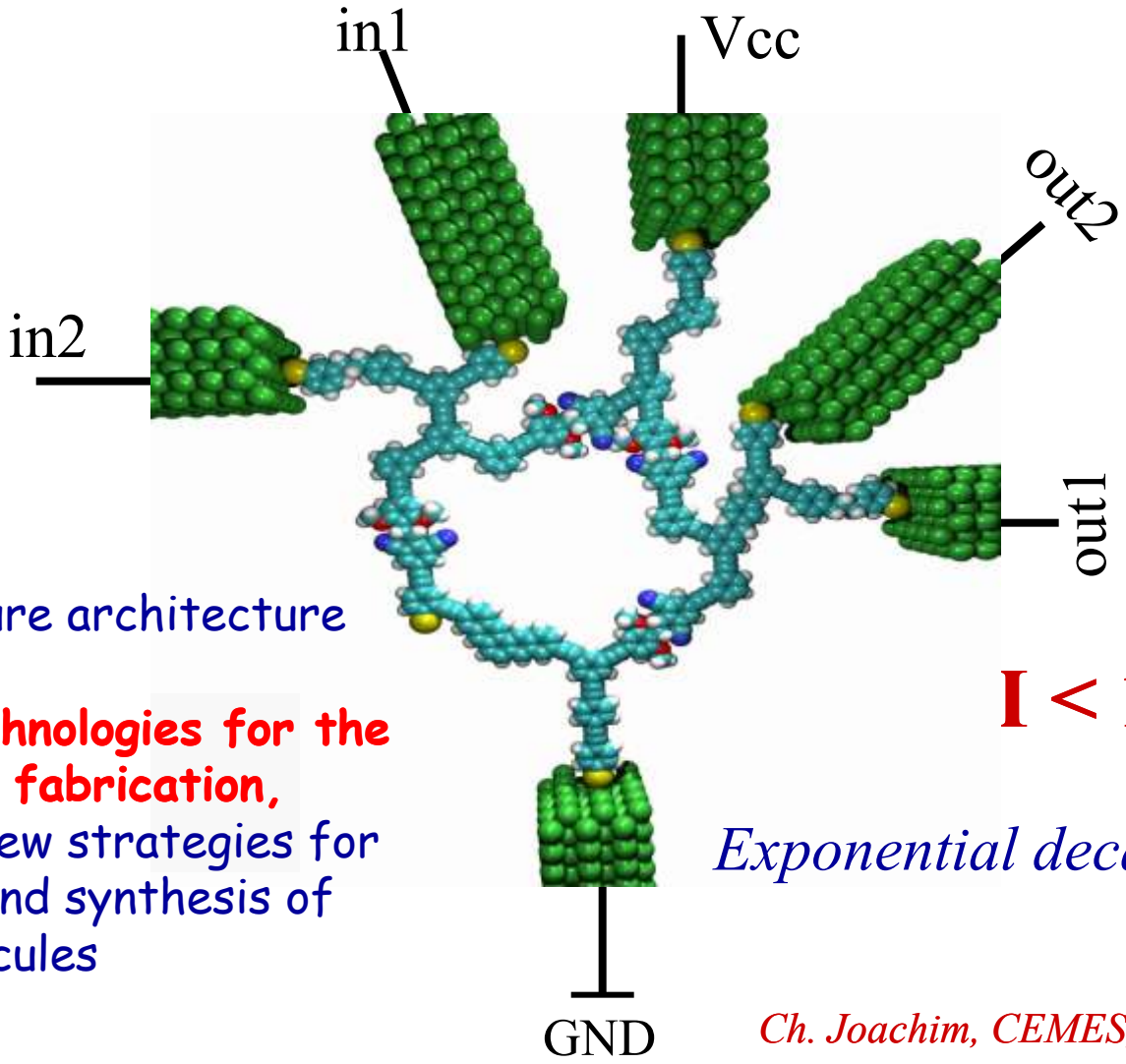
Research for applications in single molecule electronics



(1) molecular structure architecture development,

(2) atomic-scale technologies for the molecular circuit fabrication,

(3) development of new strategies for chemical design and synthesis of the desired molecules

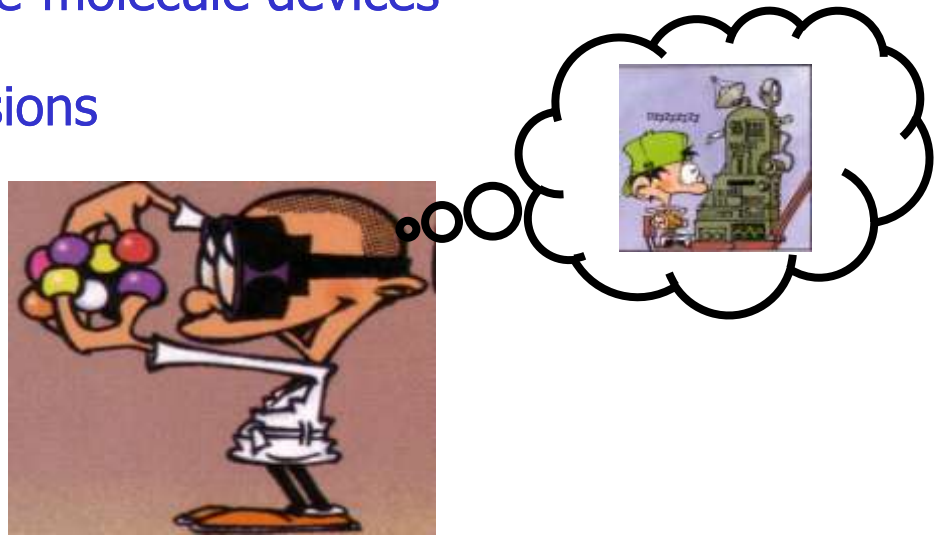
I < 1 fA

Exponential decay?

Ch. Joachim, CEMES, Toulouse

Outline:

1) Motivation and experimental details
2) AIII-BV semiconductor (001) reconstructed surfaces as suitable templates
3) PTCDA, CuPc, VL molecule deposition and assembling on AIII-BV (001) surfaces
4) Assembling of PTCDA and VL molecules on ultrathin KBr layers grown on InSb (001)
5) Chiral helicene molecules as prospective linkers for single-molecule devices
7) Conclusions



Acknowledgement:

Large fraction of this work has been supported by the EC Integrated Project „Computing Inside Single Molecule Using Atomic Scale Technologies, Pico-Inside"

Laboratory „nano-device" for measurements of the electron transport in single molecules

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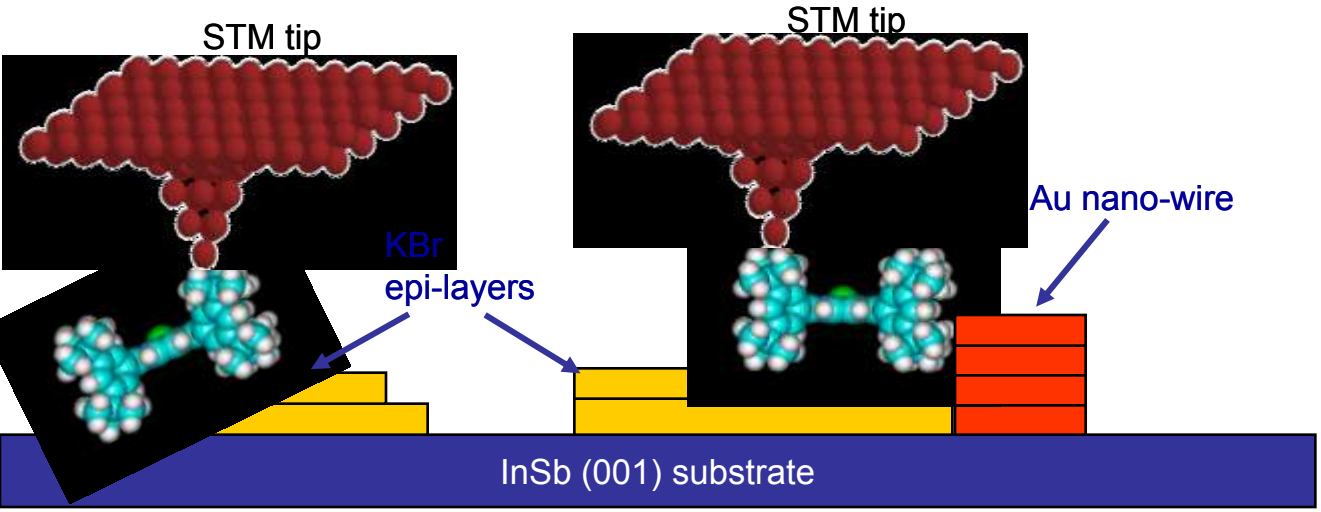

Tasks:

- adsorption/self-assembling of the molecules
- atomically resolved diagnostics (imaging, spectroscopy)
- molecule manipulation with atomic precision
- substrate preparation/ reconstruction/MBE

The molecule is assambled either across a nano-island step edge (insulator/semiconductor), or upon an insulator layer attached to a conductive nanowire. STM tip acts as a probe electrode; a role of the second electrode is taken by the conductive substrate.

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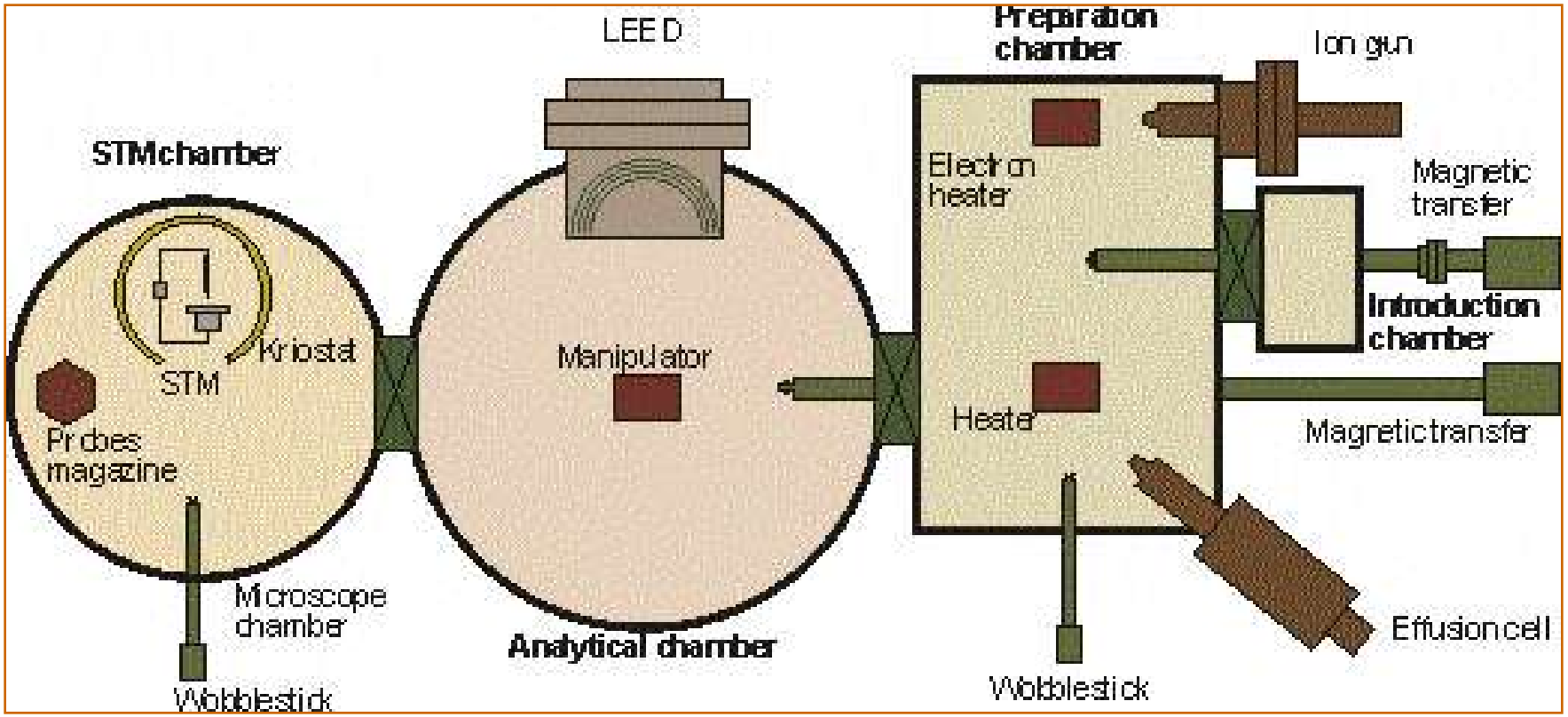
Experimental Setup



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EXPERIMENTAL DETAILS

- UHV multichamber systems including MBE, AES, LEED, QMS, STM, NC-AFM, all interconnected in UHV
- Base vacuum: 5 x 10^{-11} mbar
- Substrates: sputter-cleaned (Ar^+), annealed up to 900 K, As_2 exposed (if necessary for some GaAs reconstructions)
- Effusion cells: PTCDA, CuPc, VL, [11] Helicene

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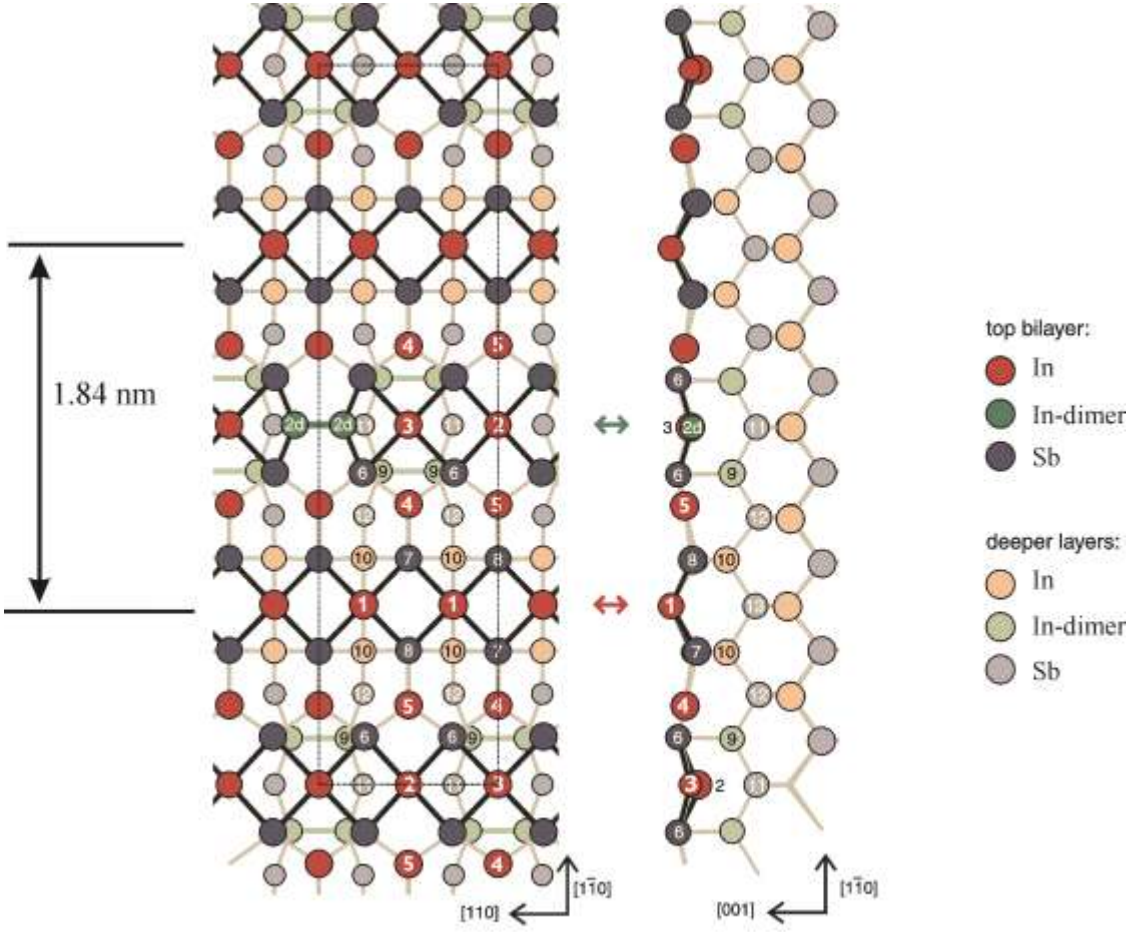
Kumpf's model of InSb (001) c(8x2) STRUCTURE



C. Kumpf et al. Phys. Rev. Lett. 86, 3586 (2001)

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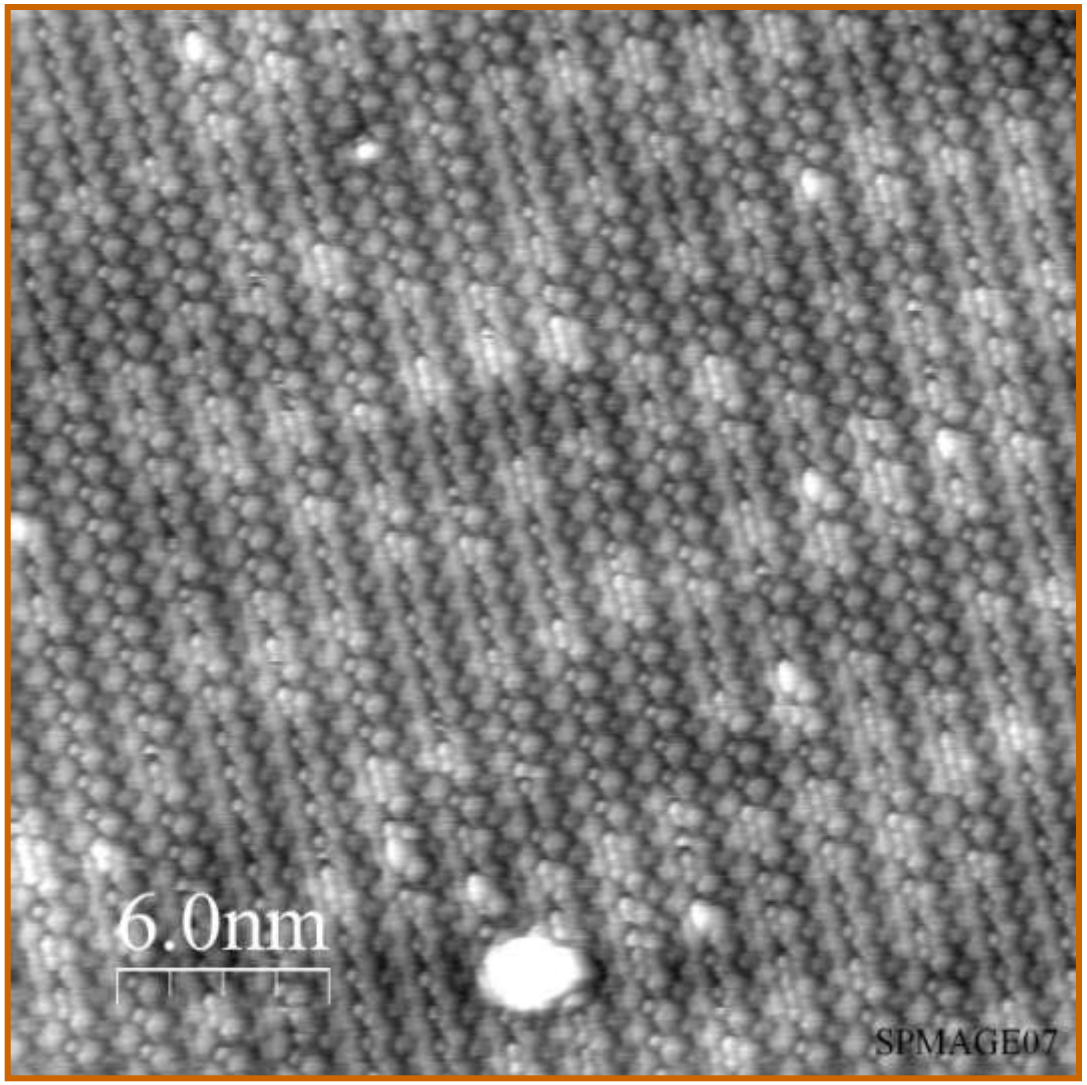
LT STM on InSb(001) c(8x2)



Atomically resolved image

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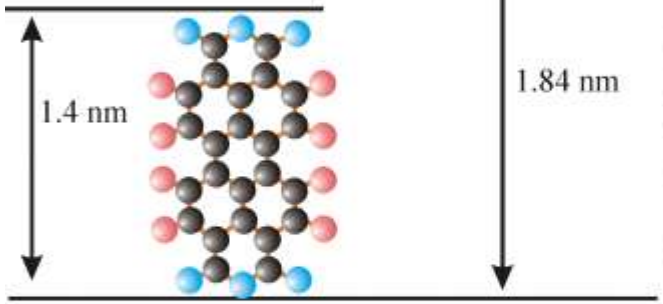
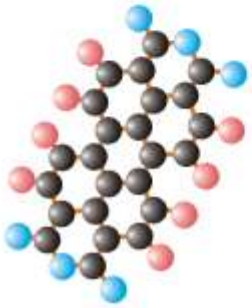
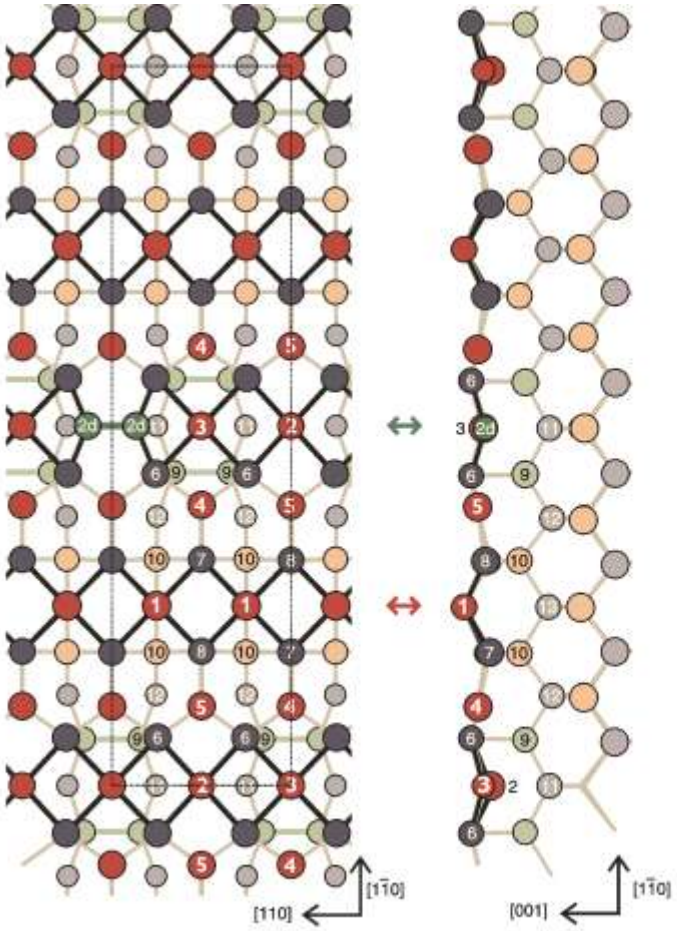
PTCDA AND InSb STRUCTURE

3,4,9,10 perylene-tetracarboxylic-dianhydride (PTCDA)





InSb (001) c(8x2)



C. Kumpf et al. Phys. Rev. Lett. 86, 3586 (2001)

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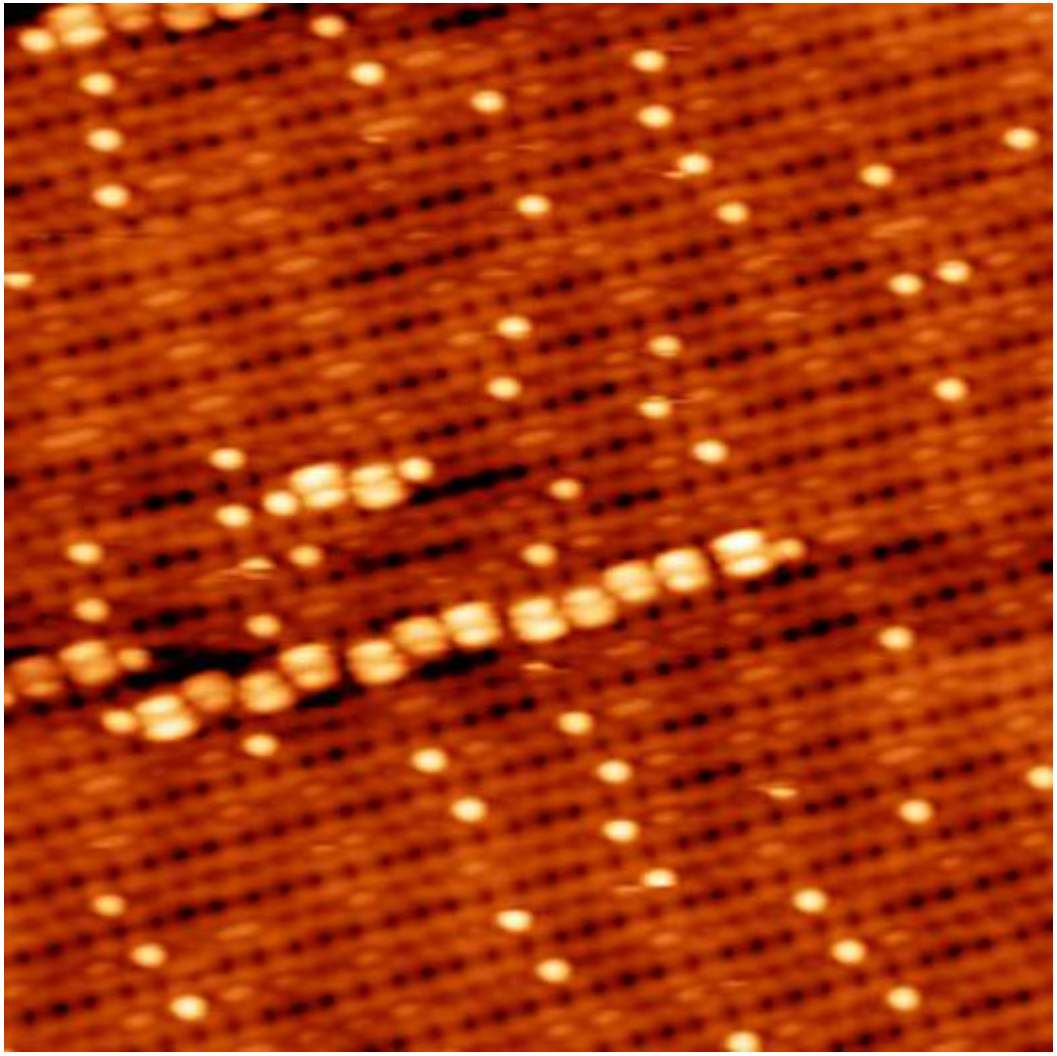
PTCDA molecule on InSb



- sample bias -1.0V
- molecules are seen as double bright protrusion
- pinning of the molecular chains by charge density waves

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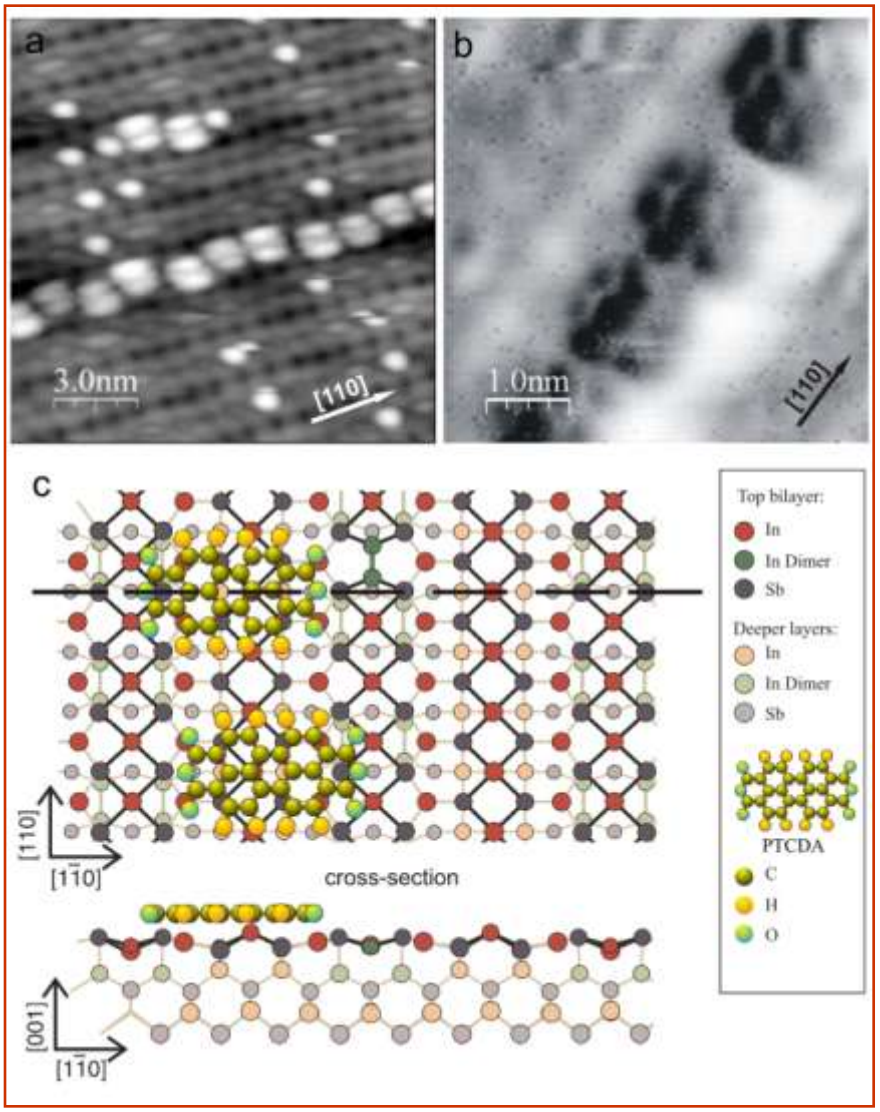
PTCDA molecule on InSb



PTCDA molecules assembled on reconstructed InSb (001) surface. a) Topography map of occupied states taken at 77 K and the sample bias of -1.0 V; b) Tunneling current map taken at 77 K and the sample bias of -0.75 V; c) "ζ-model" of the c(8x2) InSb (001) surface with a schematic model illustrating possible adsorption sites of PTCDA molecules.

G. Goryl, et al., Nanotechnology, 2008

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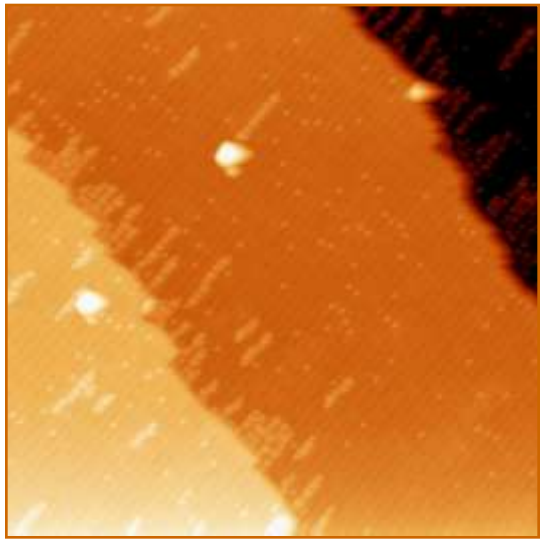
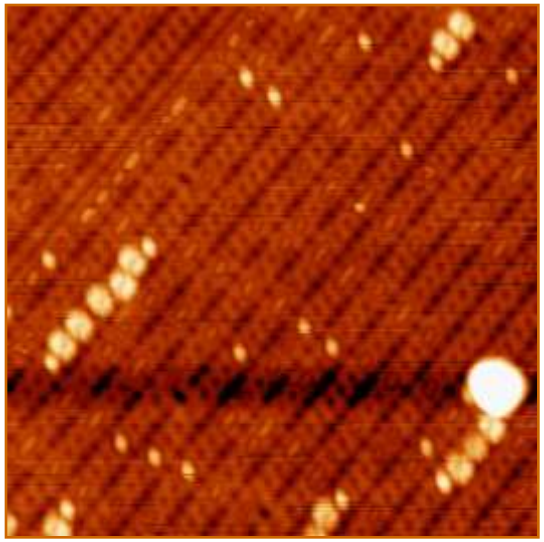
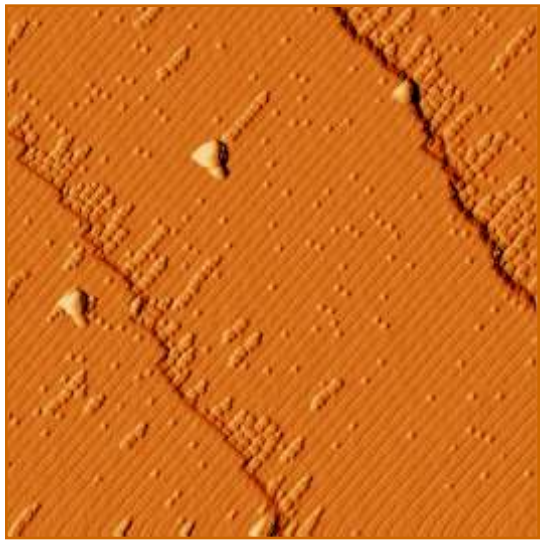
STM: PTCDA/InSb at T=77K, occupied states; U=1V, I=0,04nA

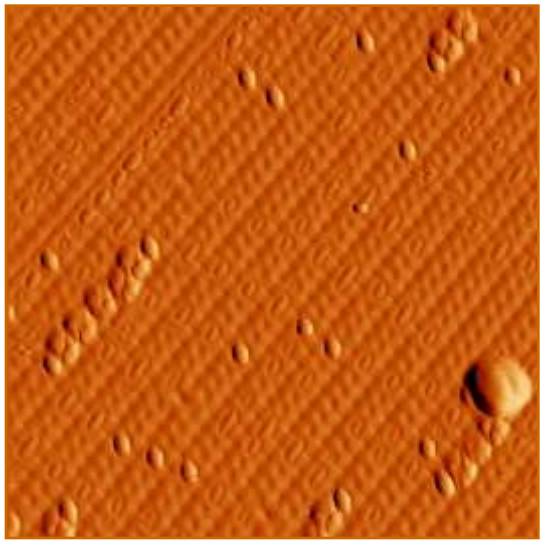


topography





current



100 nm x 100 nm

30 nm x 30 nm

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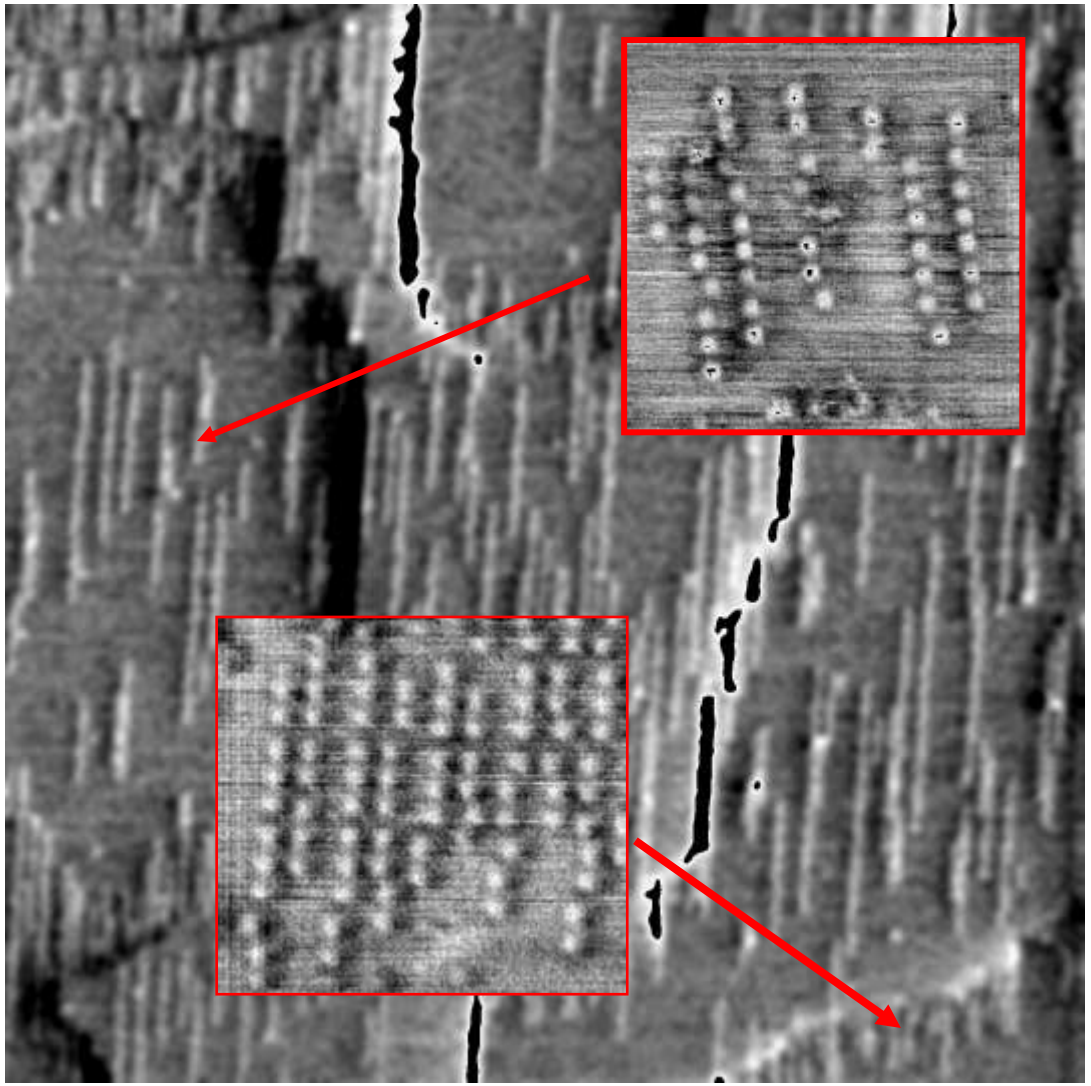
DFM of 0.07 ML PTCDA/InSb (001) C(8X2)

300 nm x 300 nm

T= 450 K,
0.15 ML/min

(1 ML ~ 8.5 x 10 ^{13})



J. J. Kolodziej, M. Goryl, J. Konior, F. Krok, M. Szymonski, Nanotechnology, 18 (2007) 135302.

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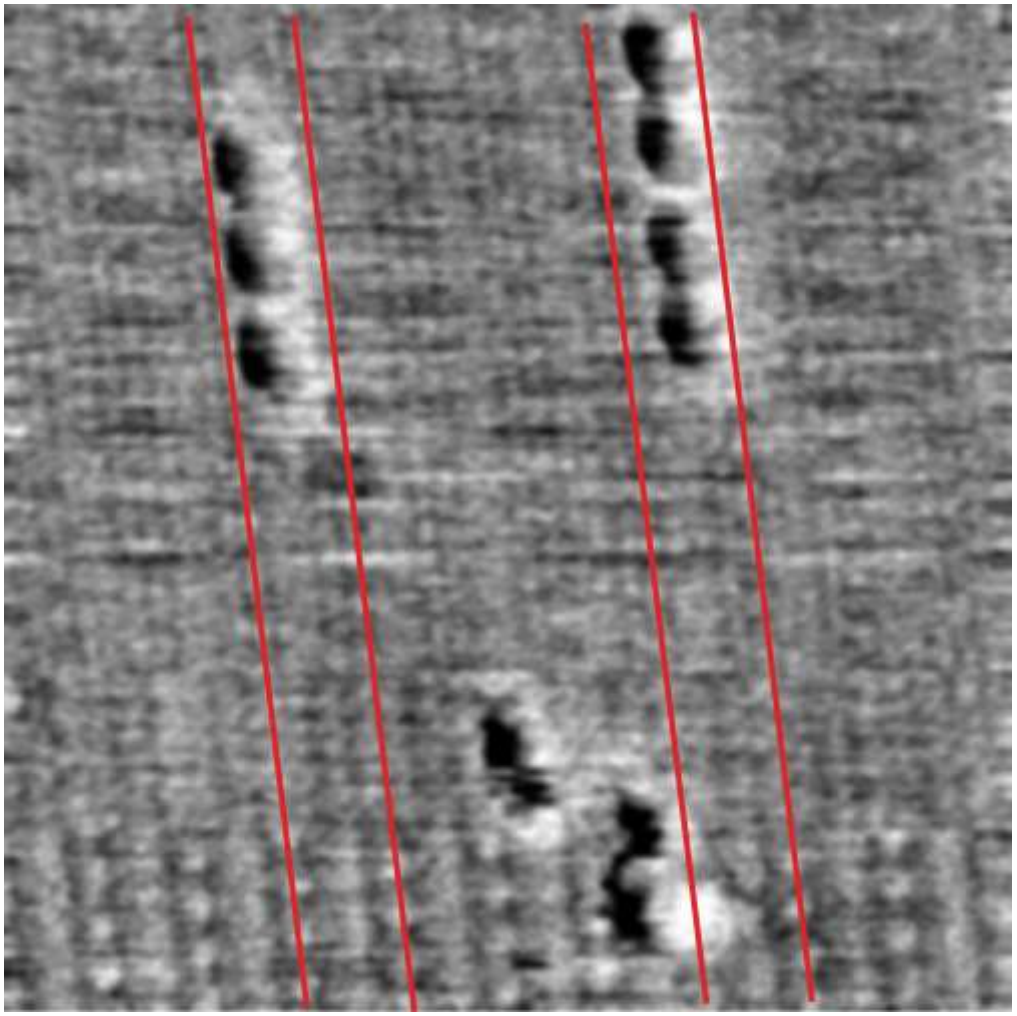
PTCDA /InSb (001) c(8X2)

20 nm x 20 nm



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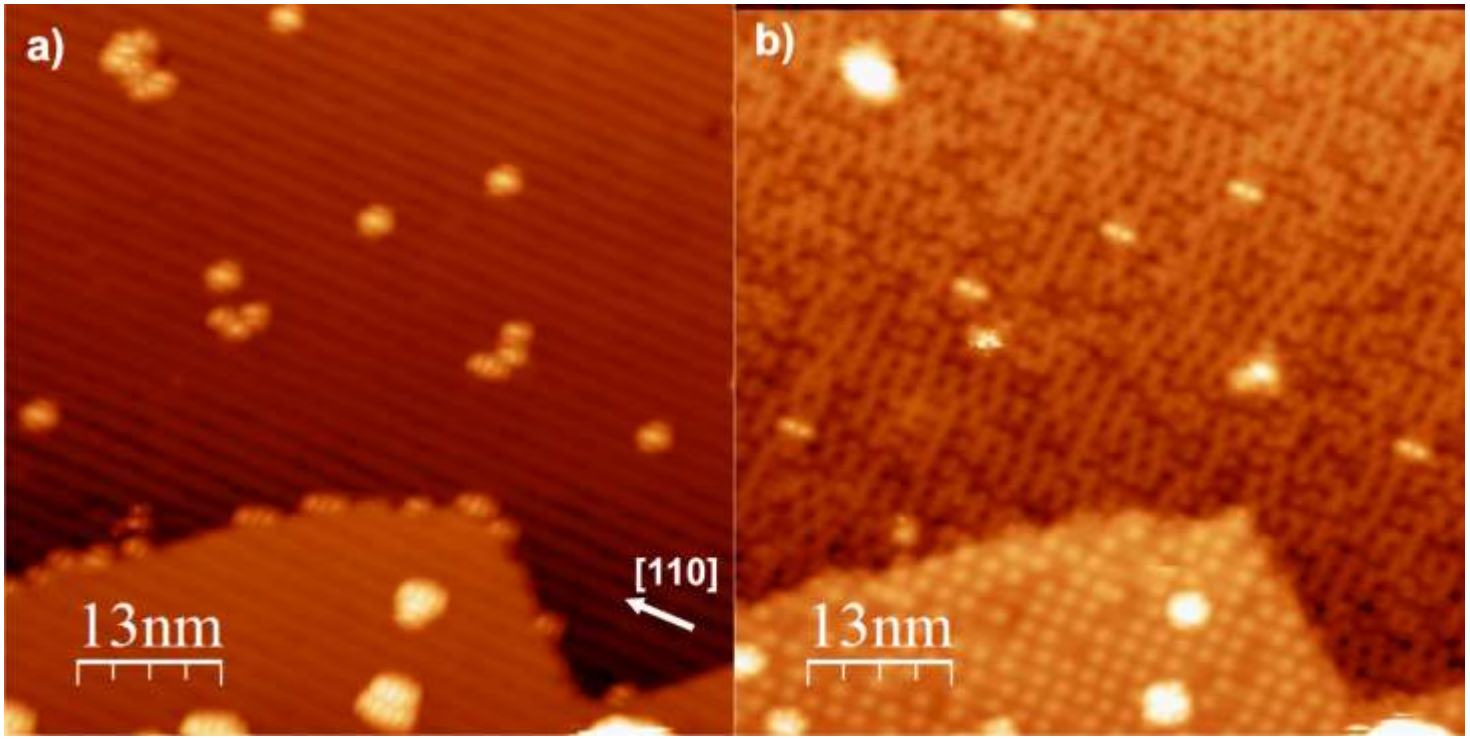
PTCDA /KBr/InSb (001) c(8X2)



A pair of 63x63 nm2 STM images showing the same area taken with a) U=-2,3V, I=6pA; b) U=2,3V, I=6pA. The region in the upper part of the images is covered by a monolayer of KBr, while in the lower part an edge and a small fragment of a second-layer island is visible. Protrusions in filled state image a) are PTCDA molecules.

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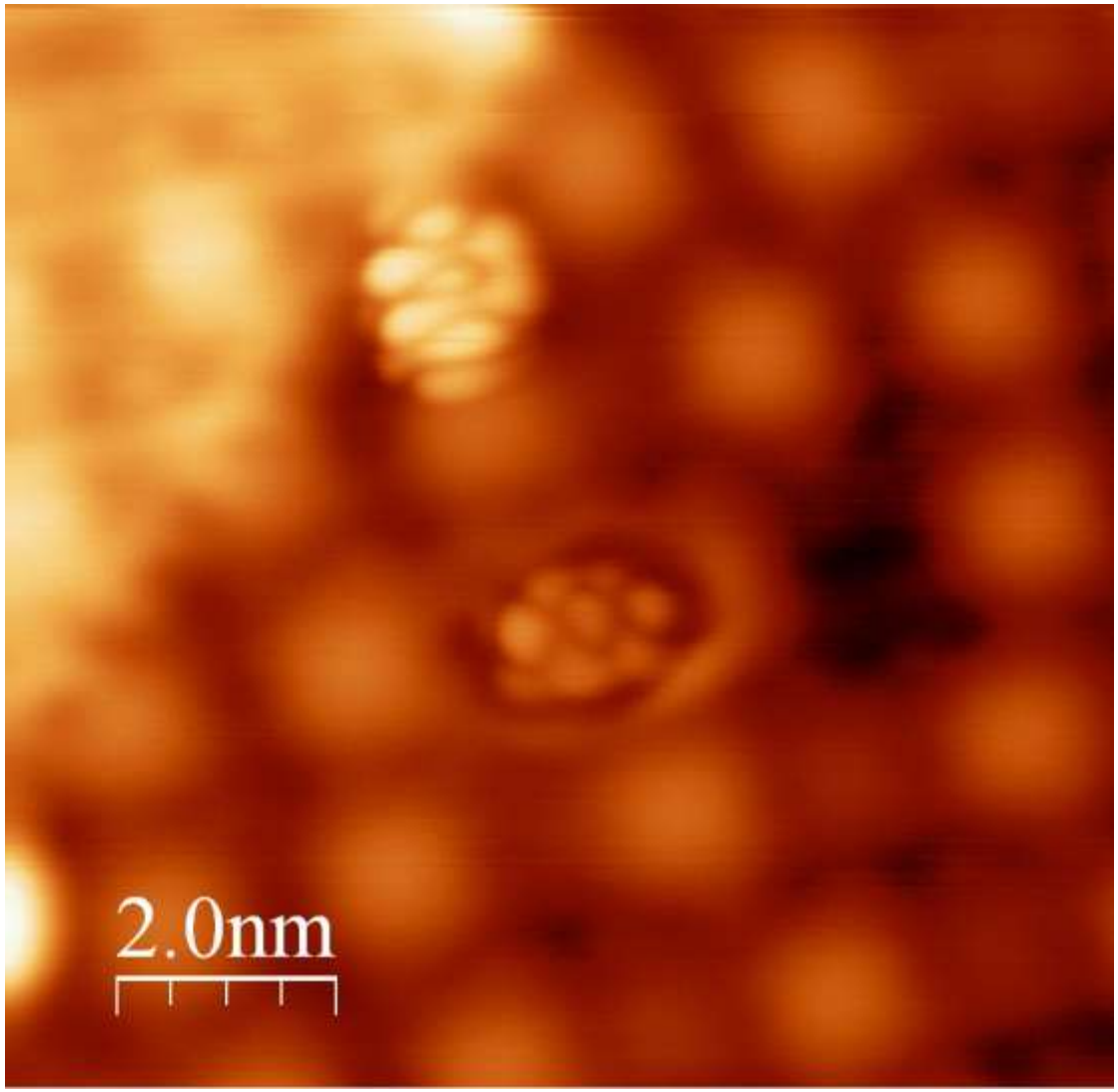
PTCDA /KBr/InSb (001) c(8X2)



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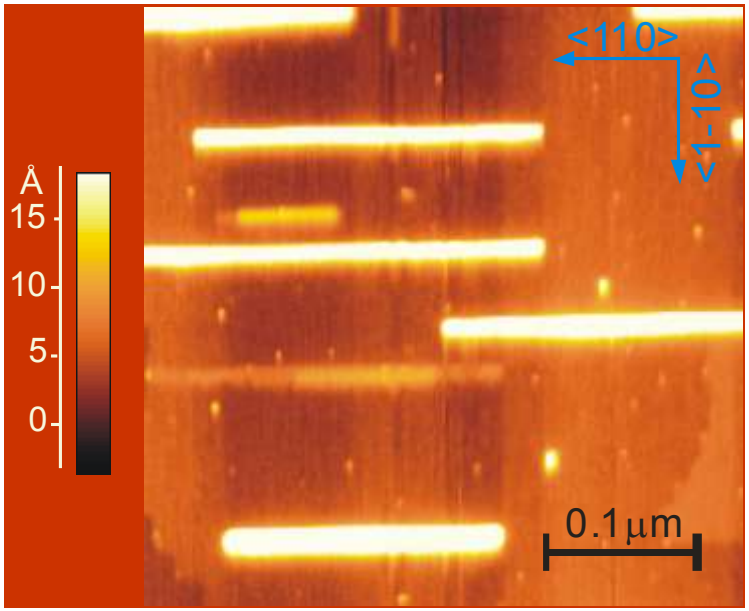
Nanowires assembled in Au/InSb(001) system at 600K

DFM



Local CPD mapping allows for following conclusions: -low height wires (1-2 layers) have the same chemical nature as the substrate, higher wires have CPD clearly different from the substrate corresponding to large Au islands.

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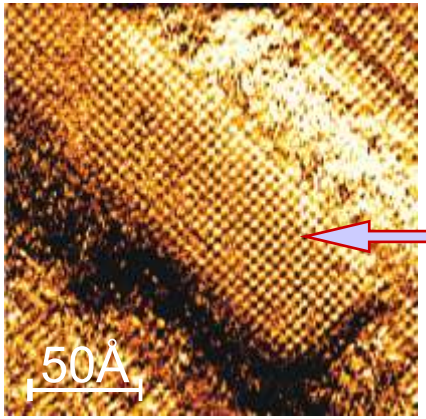
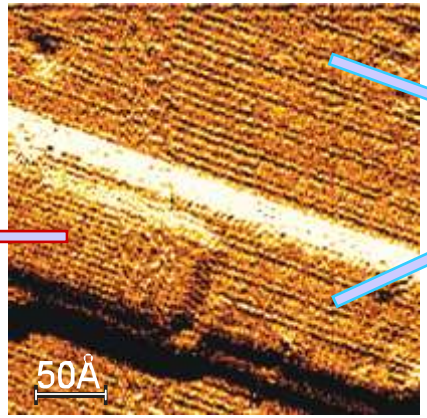
High resolution structural (DFM) and chemical (KPFM) analysis of the nanowire

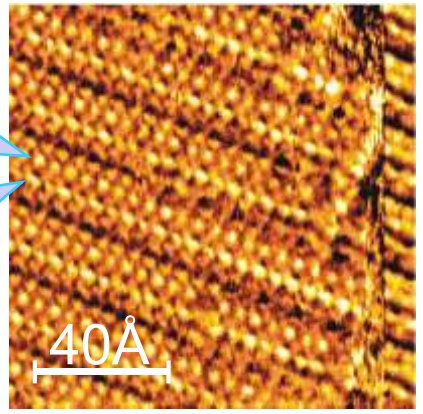
DFM- Δf map

DFM- Δf map

DFM- Δf map







Low wires have InSb structure!!!
High wires have Au structure!!!

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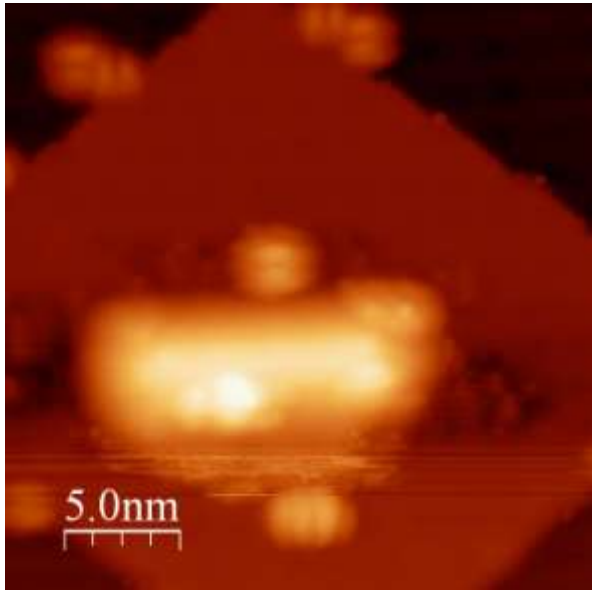
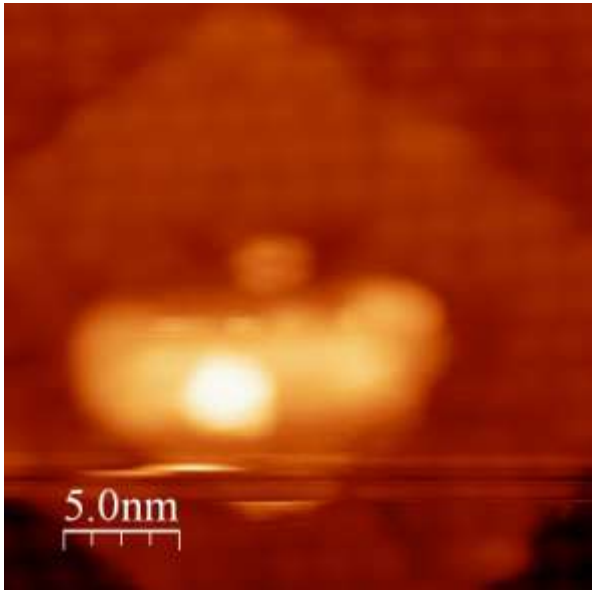
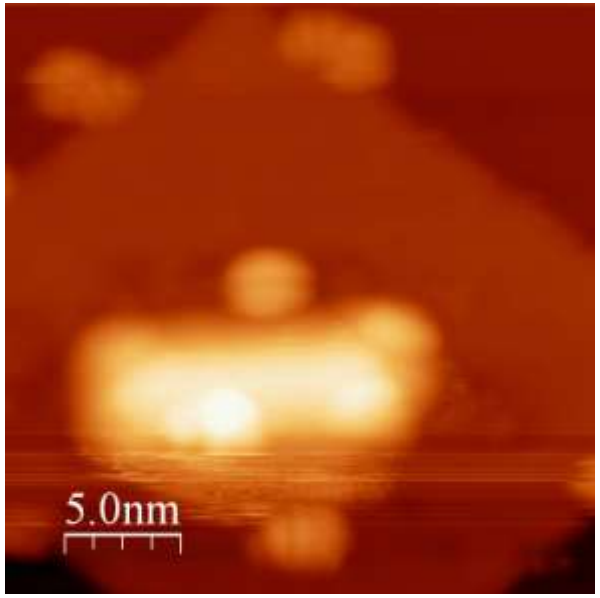
PTCDA /KBr/InSb (001) c(8X2) + Au nanowire







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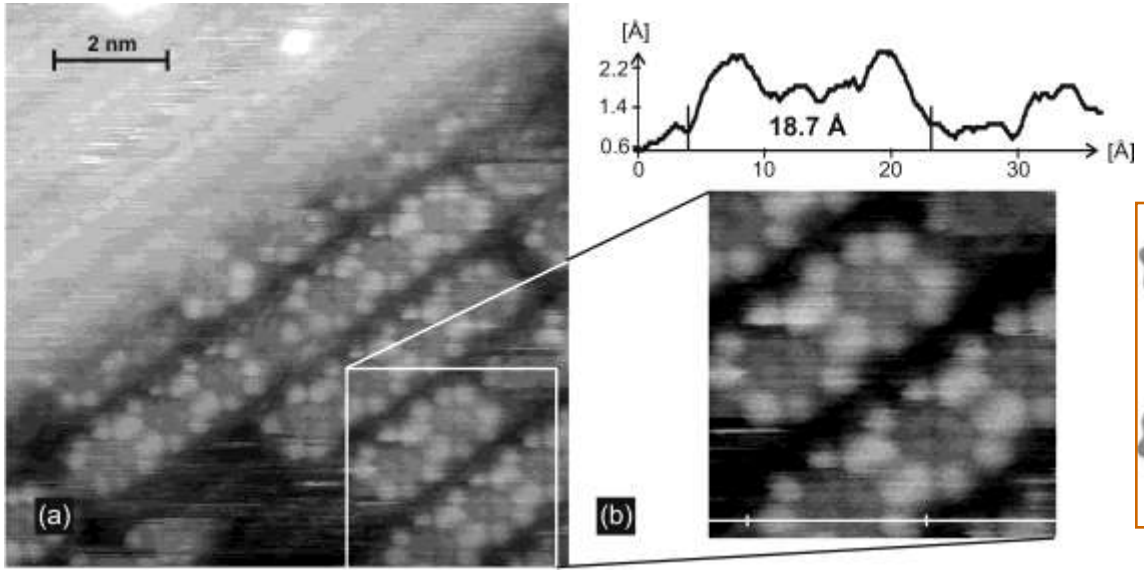
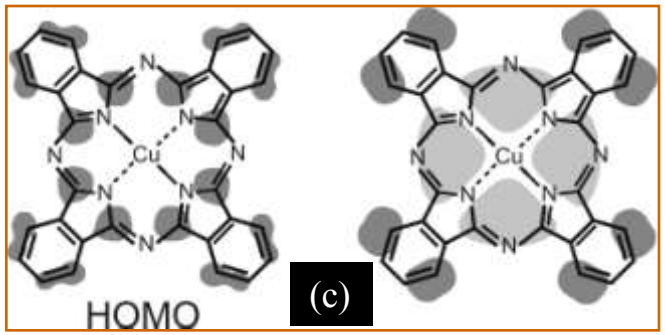
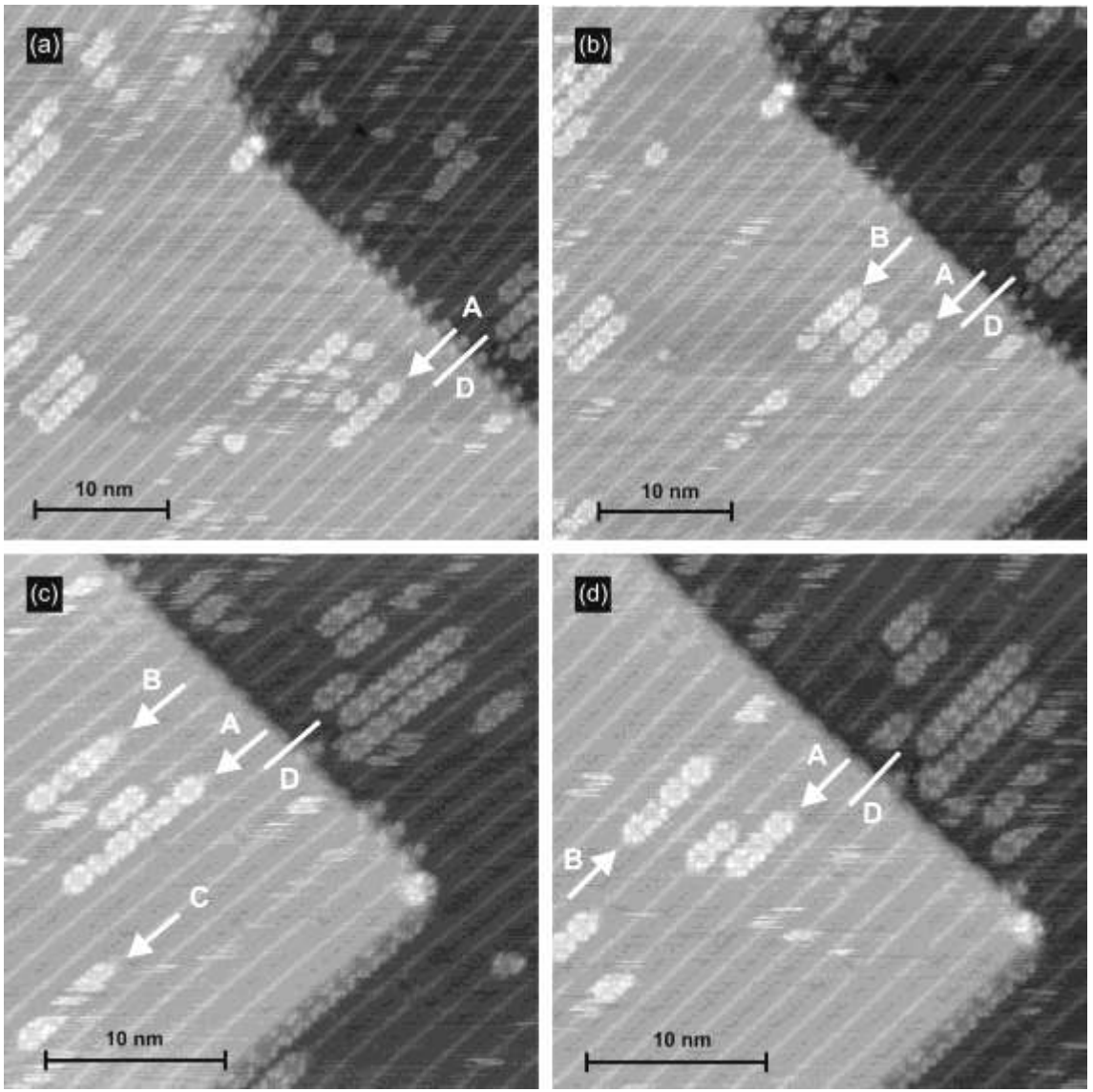
STM image of the InSb surface with 0.3 ML CuPc deposited at 573 K





(a). STM image size: 15 nm ´ 15 nm, sample bias: -1 V, tunneling current: 0.6 nA. (b) Cross section along the long axis of the CuPc molecule (white solid line) indicating an additional fourfold structure in the STM contrast. (c) Schematic comparison of the experimental STM contrast recorded at negative sample bias (-1 V) with the DFT calculations of Lee for HOMO

Sequence of STM images of InSb surface with 0.07 ML CuPc deposited at 573 K



Demonstration of the tip-induced modification and the detail of decorated step edges. (a) 40 nm x 40 nm, -1 V, 0.3 nA. (b) 40 nm x 40 nm, -1 V, 0.15 nA. (c) and (d) 30 nm x 30 nm, -1 V, 0.15 nA.

Helicene molecules as prospective linkers in single-molecule computing device

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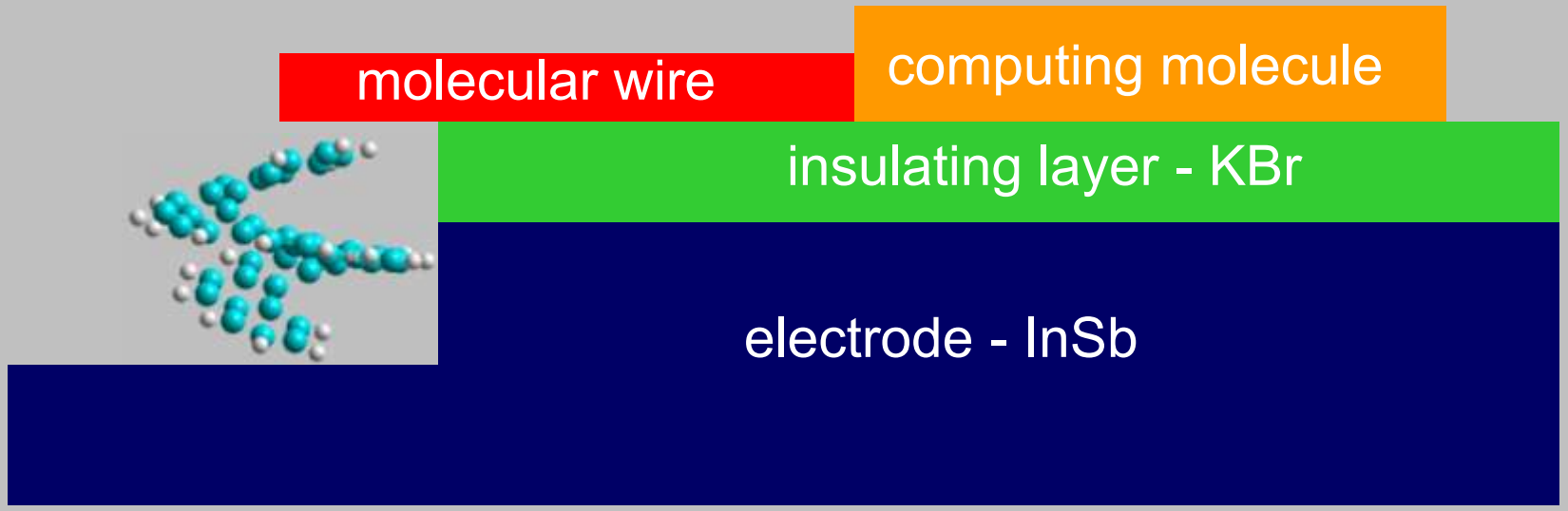

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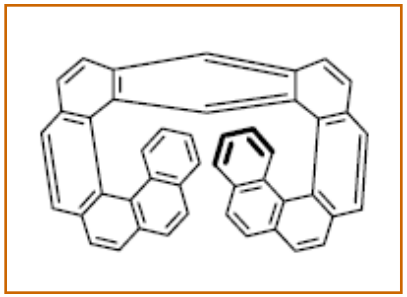
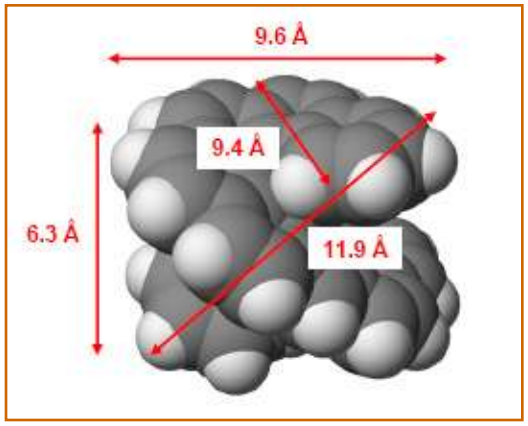
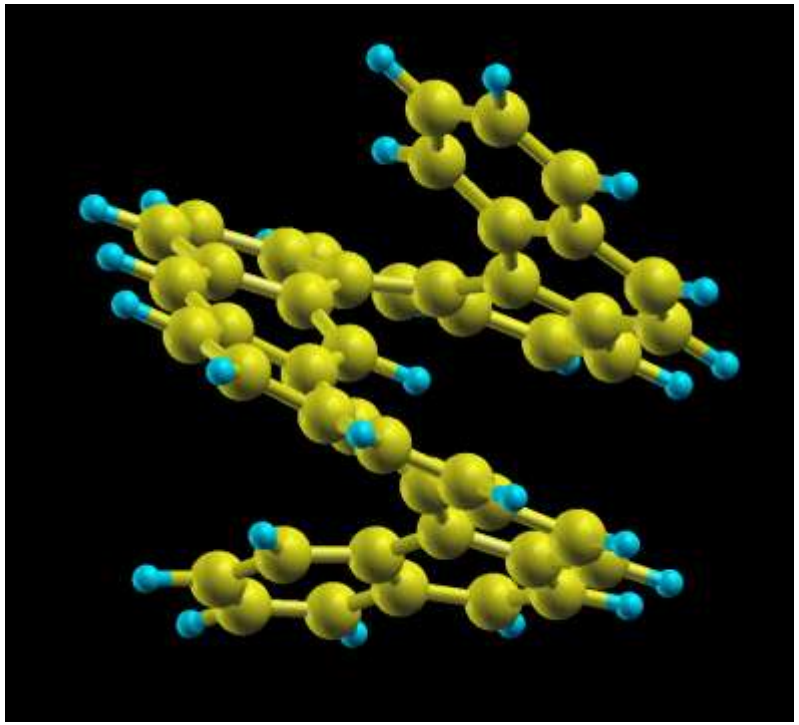
[11]Helicene molecules

- Molecules were deposited using a standard effusion cell
- Coverage: 0.02ML
- Evaporation rate: 0.33ML/min
- Pressure range during evaporation process: 10^{-10}mbar







Courtesy of Irena Stara and Ivo Stary,
Institute of Organice Chemistry and Biochemistry ASCR, Prague

DFT (6-31G**) => E_{LUMO}-E_{HOMO}=3.3eV

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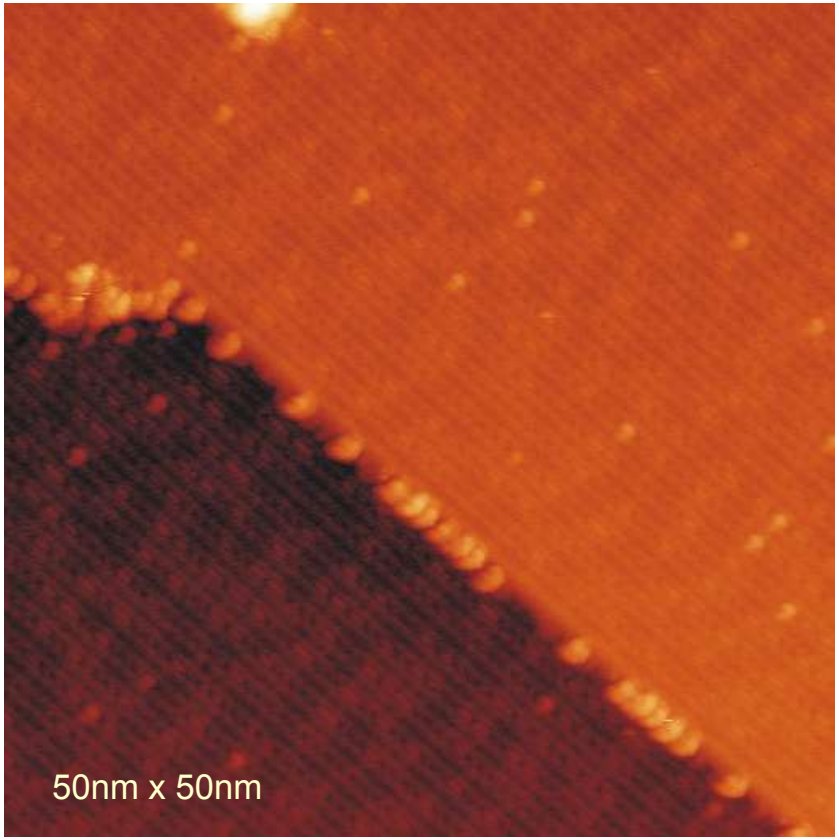
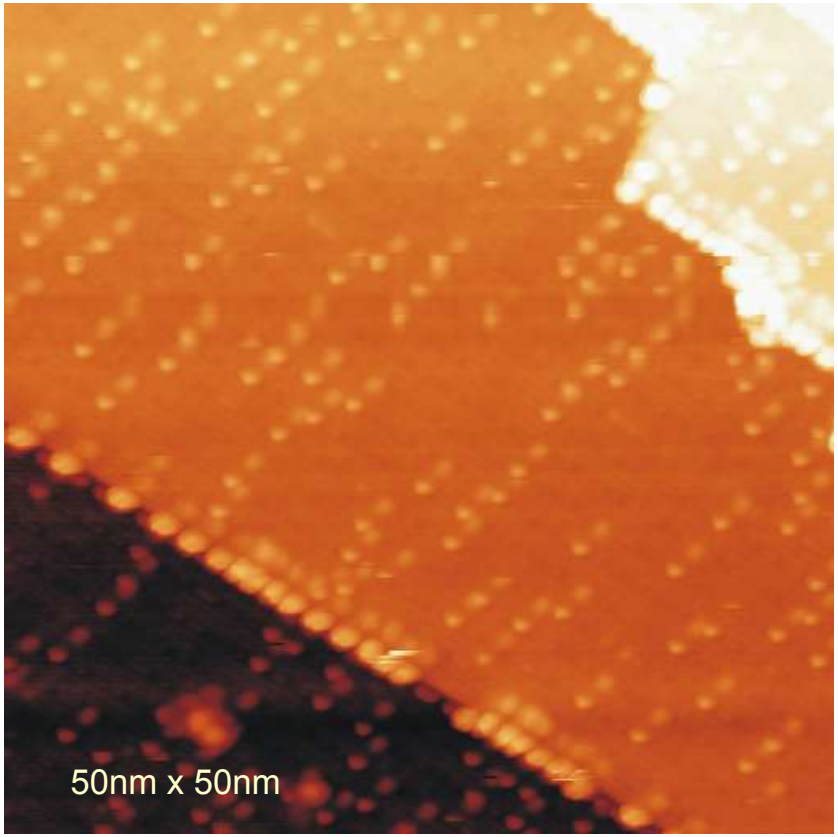
Extremely low coverage

Racemic mixture



Left-handed enantiomer



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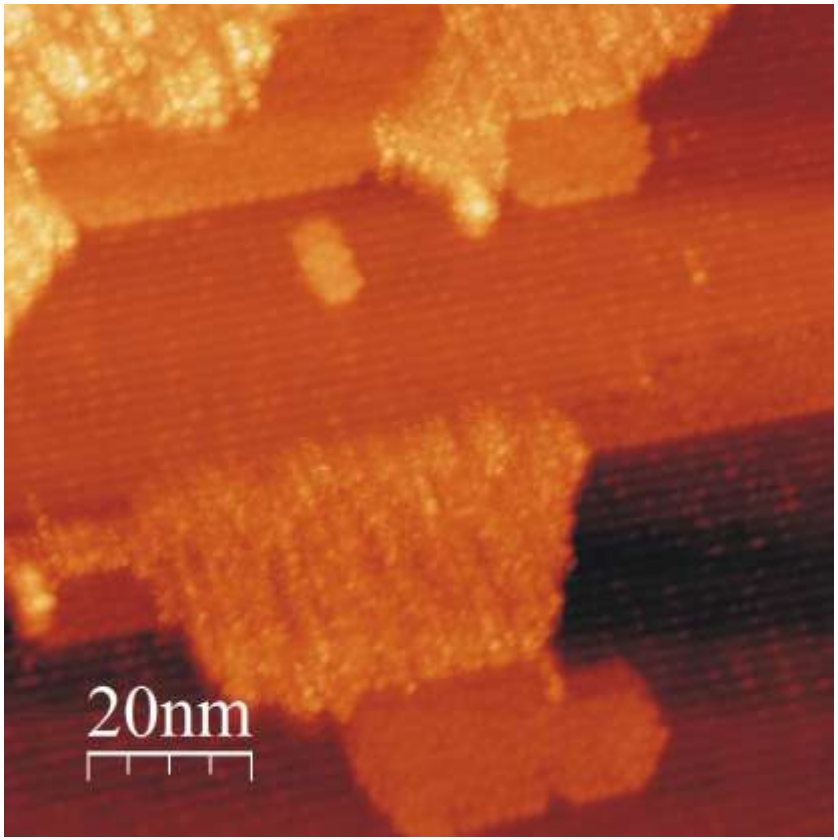
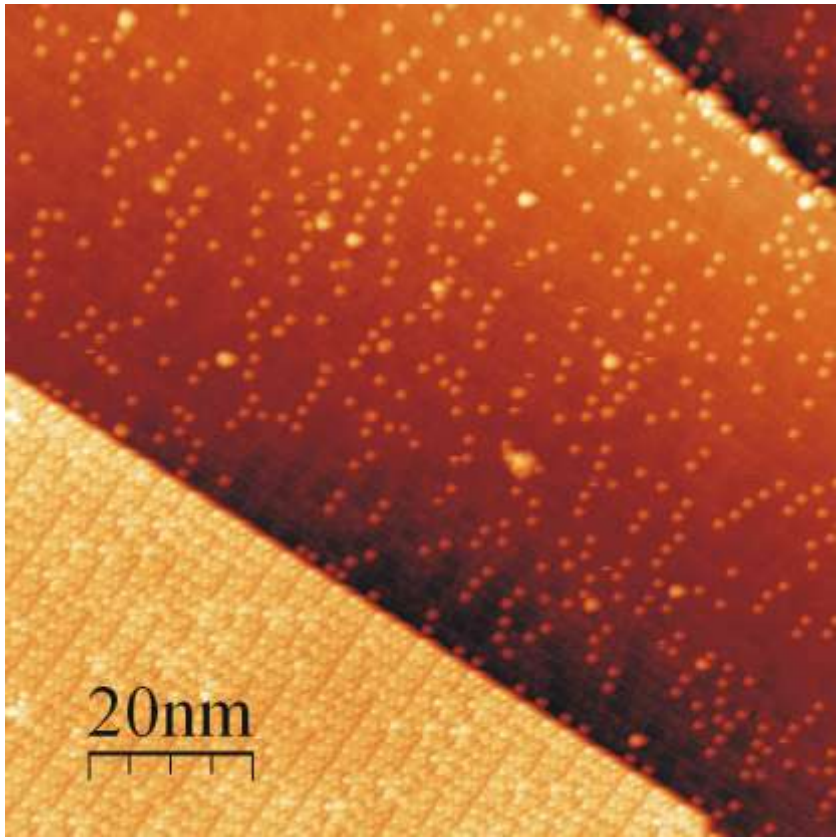
Higher coverage

Racemic mixture



Left-handed enantiomer



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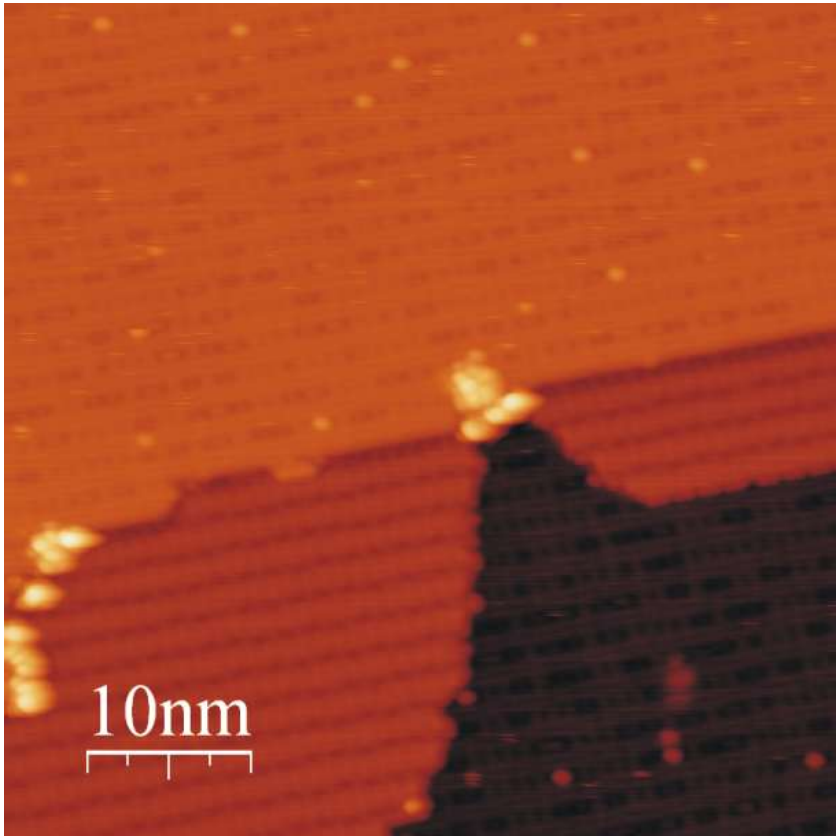
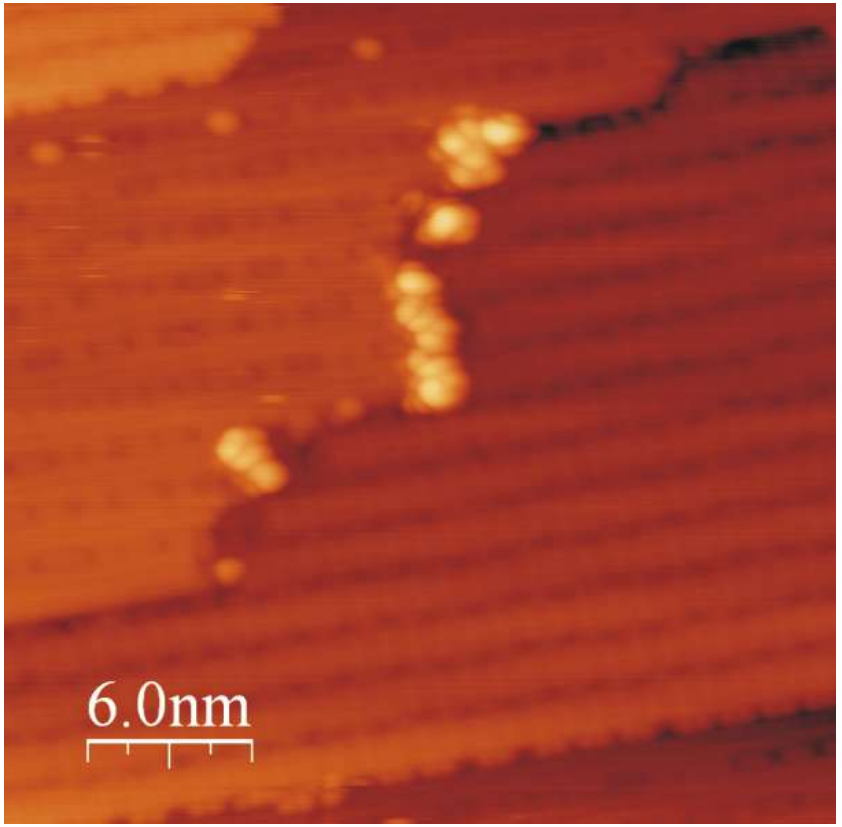
[11]Helicenes on KBr/InSb





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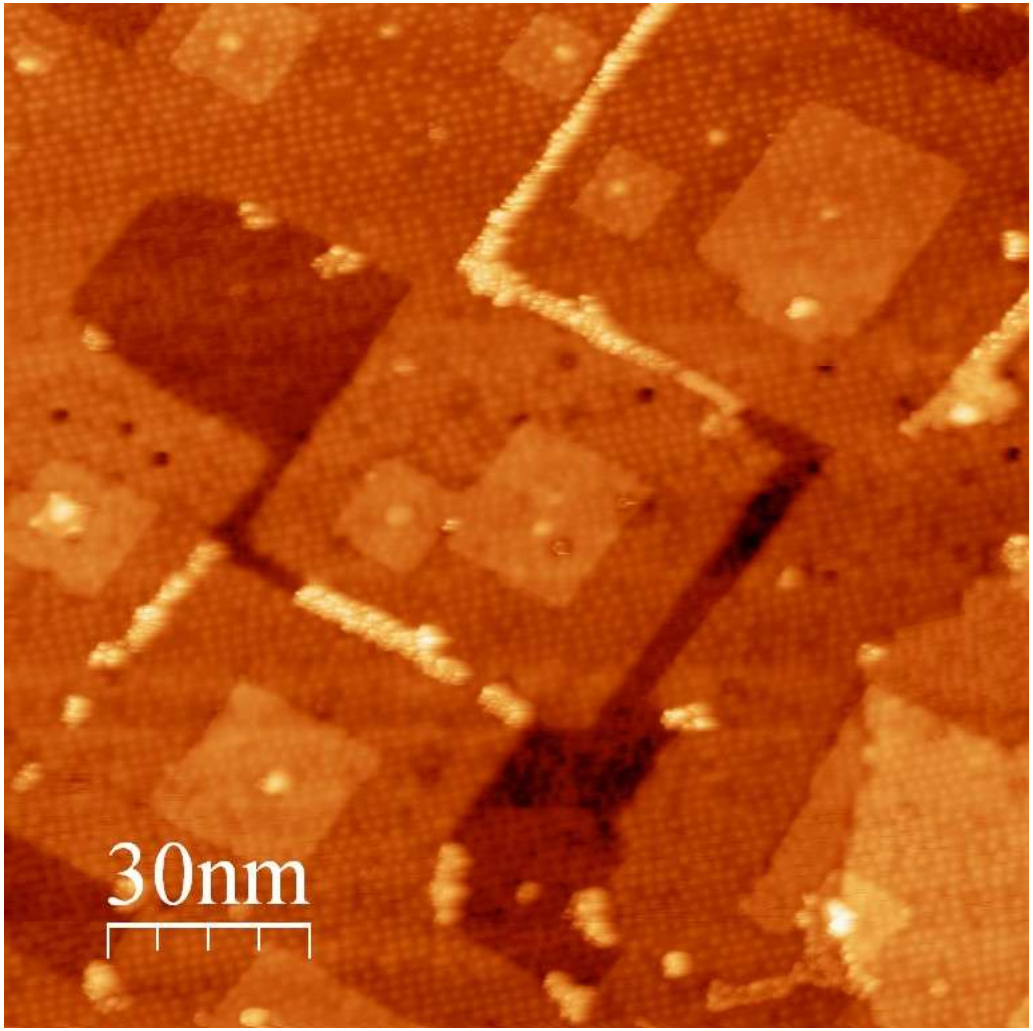
[11]Helicenes on KBr/InSb



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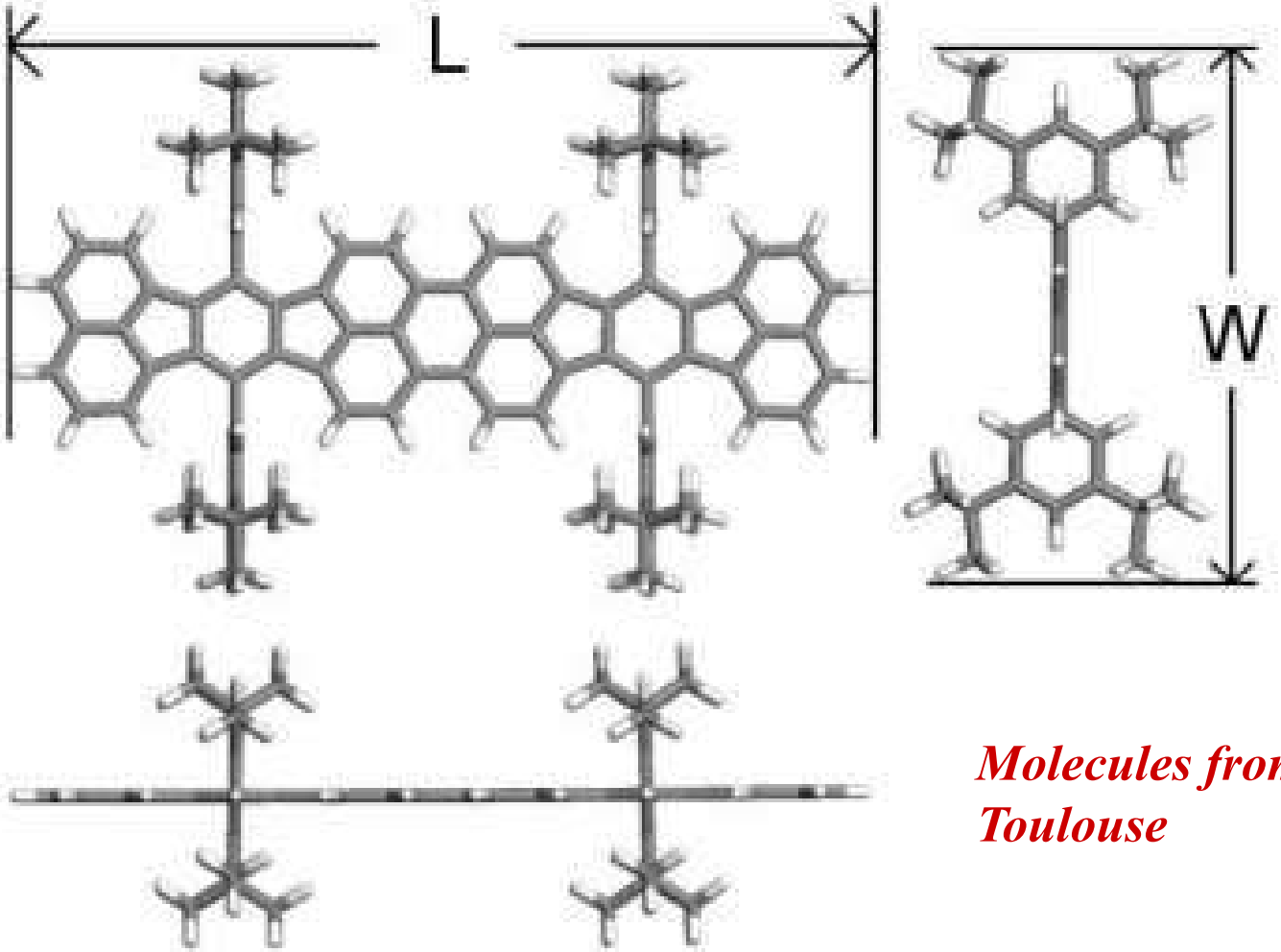
Violet Landers



Molecules from CEMES, Toulouse

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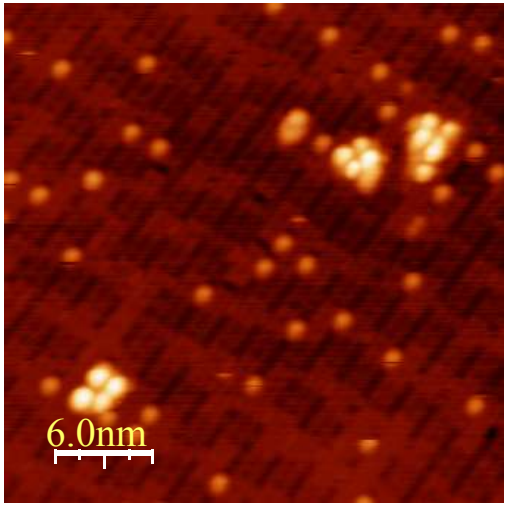
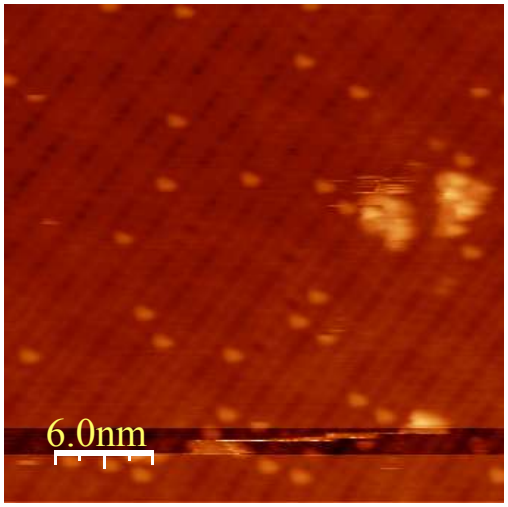
Violet Landers – STM manipulation

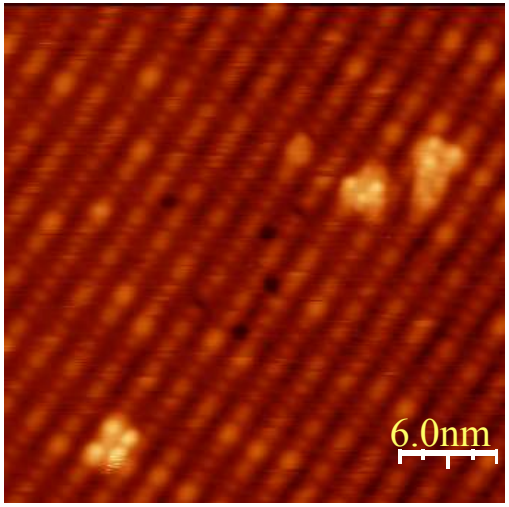
Before -2.5V



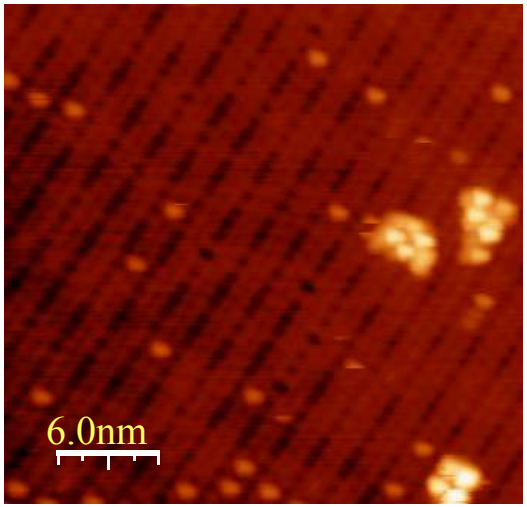
During -1V



Before +2.5V



After-1V



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SUMMARY

- **PTCDA/InSb (001) c(8x2): efficient diffusion of PTCDA molecule along [110] at 300 –500 K, formation of long molecular chains along [110], good candidate for manipulation of single molecules, forms wetting layer at 1 ML coverage**
- **PTCDA on GaAs (001) c(8x2)/(4x6) mostly “sticks where it hits”**
- **[11]helicenes have long diffusion length on InSb(001) c(8x2), they are trapped by terrace edges; high resolution [11]helicene images are similar to simulated shapes of HOMO and LUMO for the free molecule**
- **At higher coverage [11]helicenes on InSb(001) form islands: ordered when formed from one-type enantiomers, not-ordered when islands are racemic**
- **[11]helicenes could serve as linkers between the electrode and the computing molecule**
- **Violet Landers and CuPc have been imaged and manipulated with STM tip**

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