National Center of
Competence in Research
“Nanoscale Science”

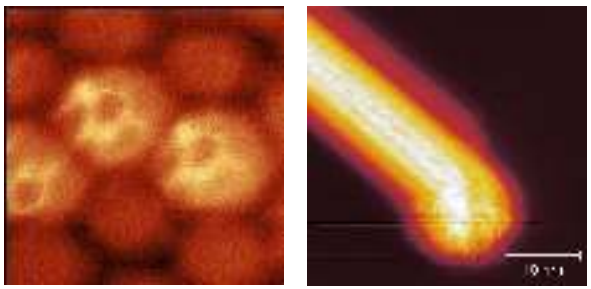
Thilo Glatzel, thilo.glatzel@unibas.ch

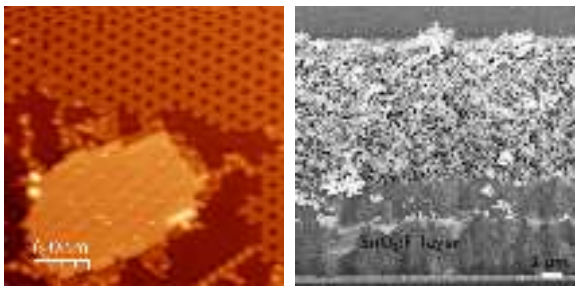
Molecular and carbon-based electronic systems

Single molecule deposition and properties on surfaces

Bottom Up

Top Down





Fundamental Knowledge
&
Functional Devices

UNI BASEL

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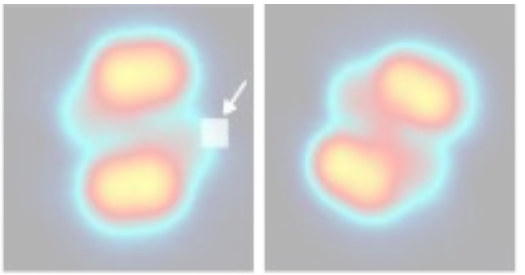
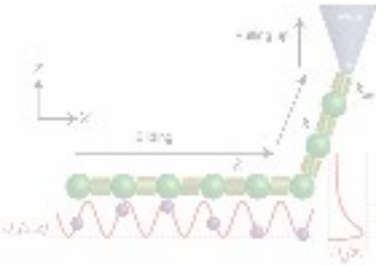
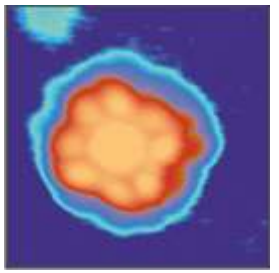
Overview

- **Introduction into SPM techniques**
  - interaction forces
  - detection mechanism & setup
- **Properties of single C_{60} molecules**
  - orientation of single molecules
  - mechanical properties
- **Manipulation of porphyrin molecules**
  - structural analysis
  - 3D force spectroscopy
  - controlled molecular manipulation
- **Formation of a molecular wire**
  - on surface reaction
  - determination of pulling forces
- **Electronic Information at submolecular scale**
  - Donor and Acceptor molecules
  - Optoelectronic excitation of CuPc

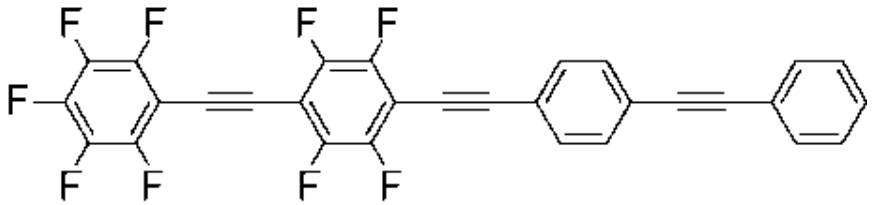


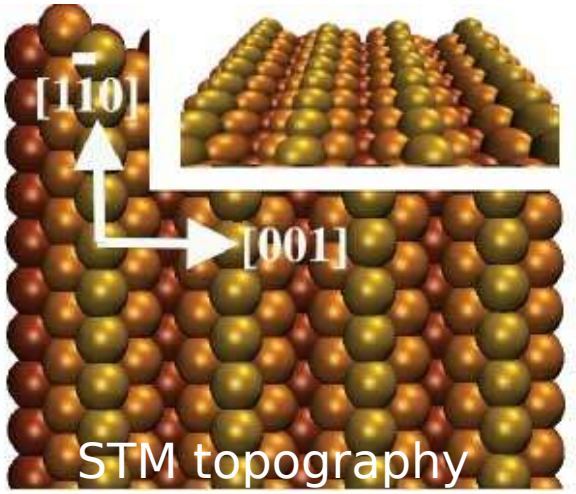




Donor and acceptor molecules

4-(4-(2,3,4,5,6-pentafluorophenylethynyl)-2,3,4,5-tetrafluorophehylethnyl)phenylethynylbenzene (FFPB)

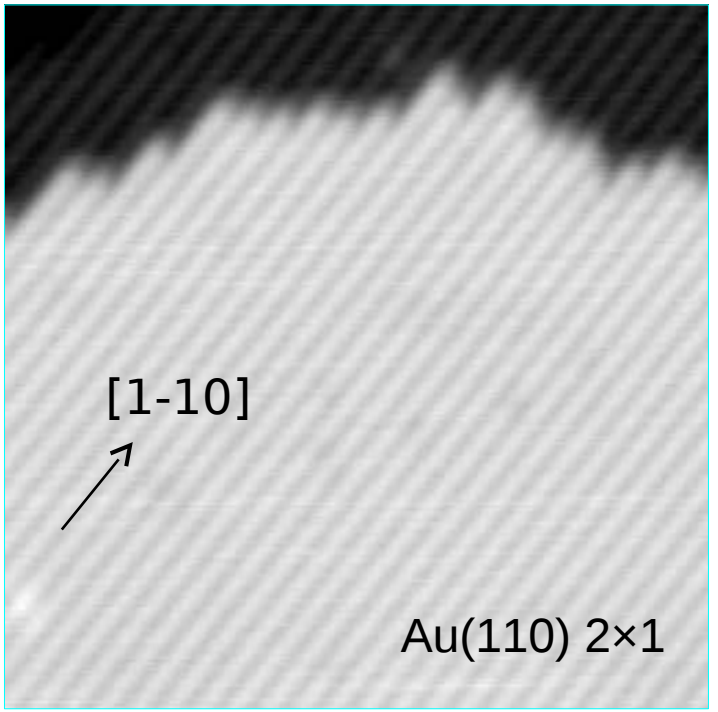




Fluorine: Strong electron affinity > acceptor
Non-Substituted carbon ring > donor

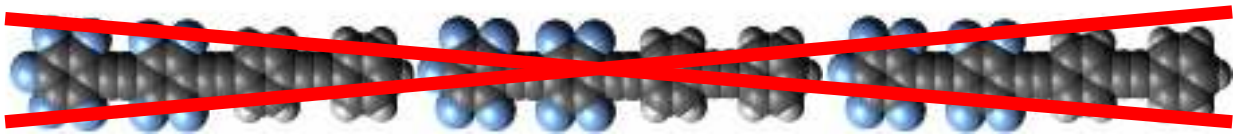
AADD molecule

Dipole: 4.27 Debye (i.e. 2.3 times larger than water)

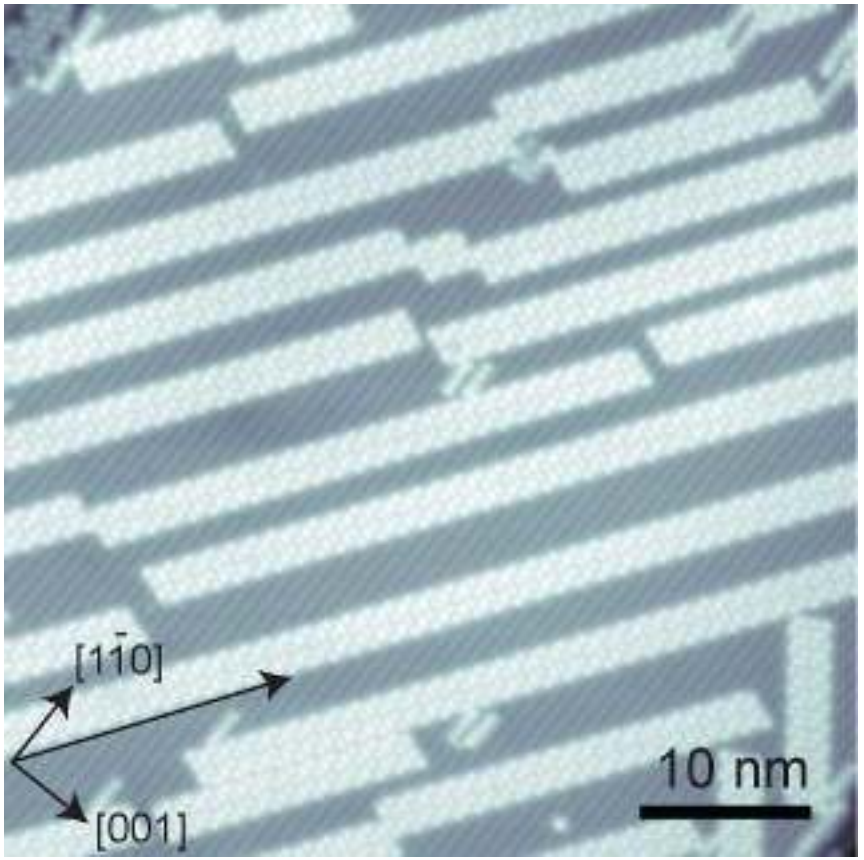


D. Matsuo et al., Chem. Lett. 39, 1300 (2010).

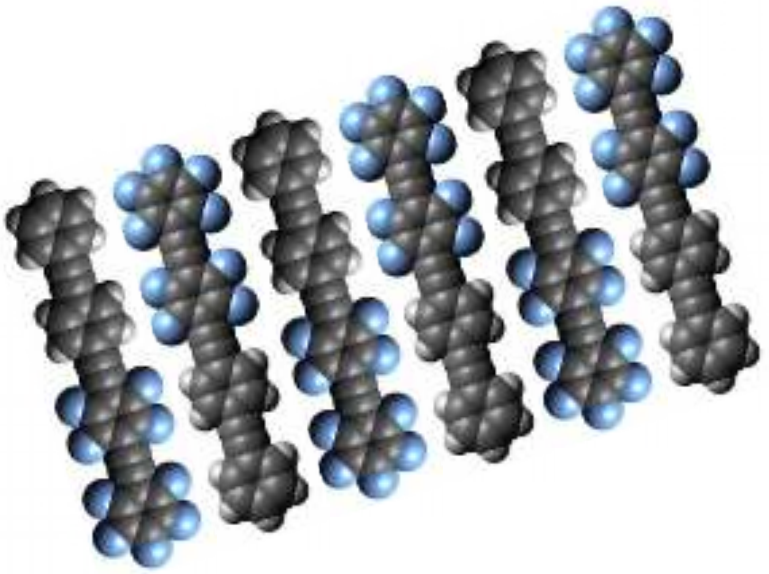
STM image – self assemble structure



Deposited on cold substrate (~120 K)
Measurement at 4.8 K

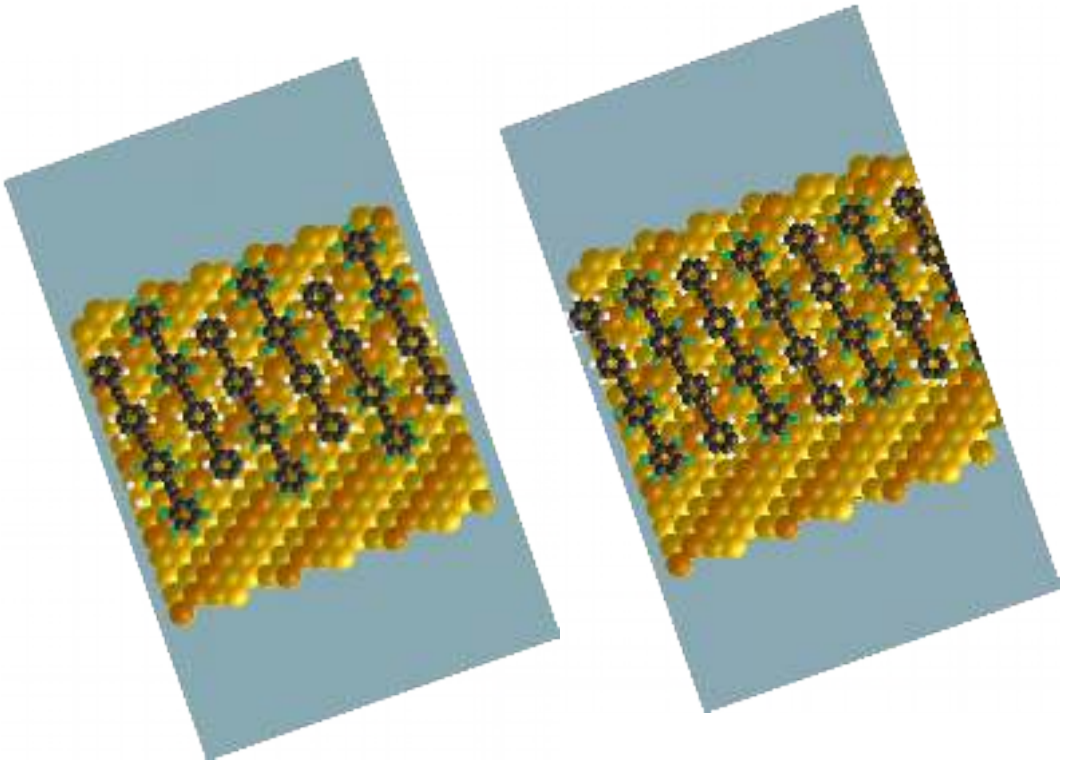


10 pA, -2.0 V



Attempt to get a real conformation
via DFT

DFT result show no difference

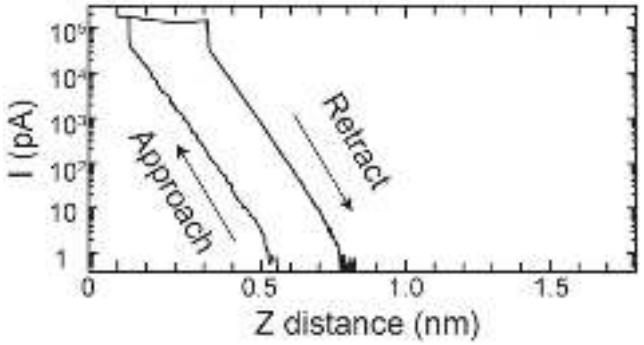


1.6 V

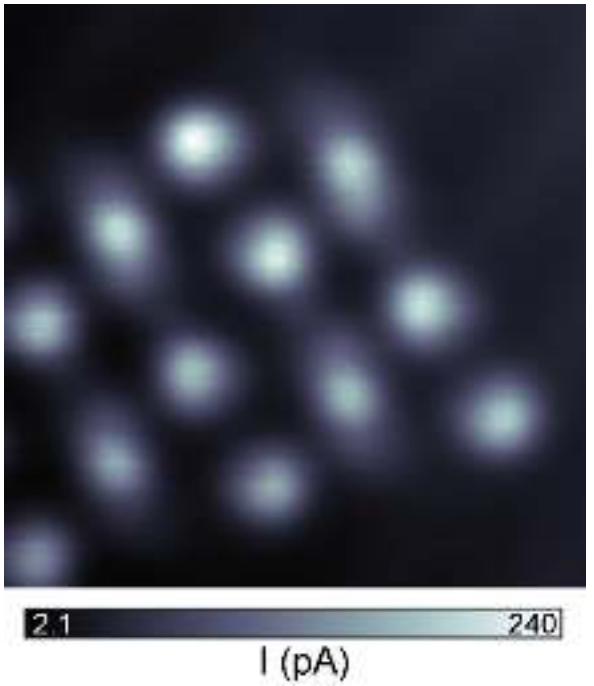
-1.6 V

Au tip
Towards seeing the chemical structure

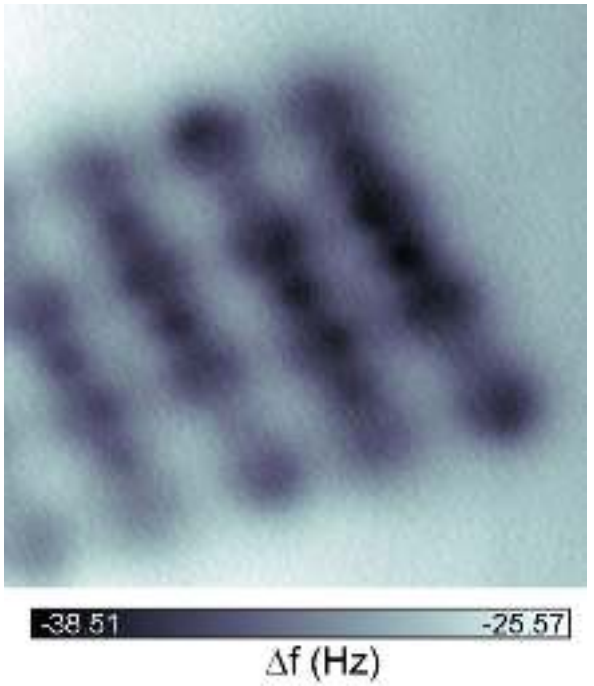
Constant height mode



Current map



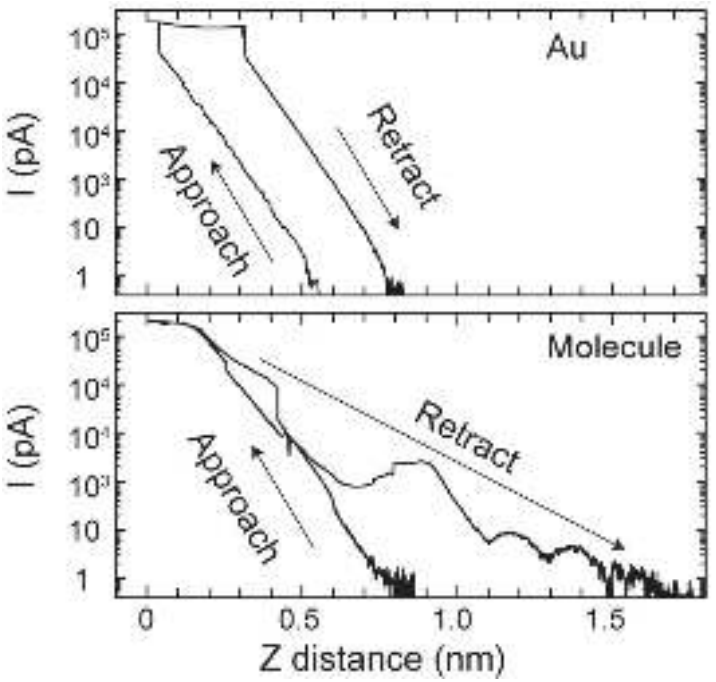
Frequency shift map



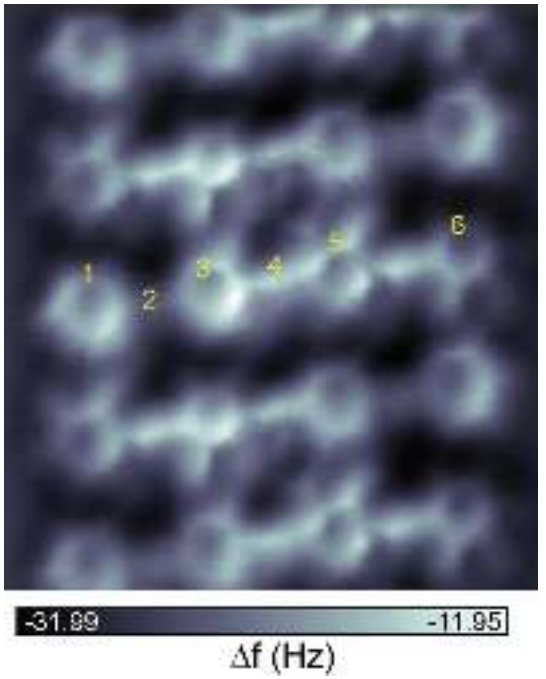
V_{bias} = 1 mV
A= 30 pm

Molecule tip

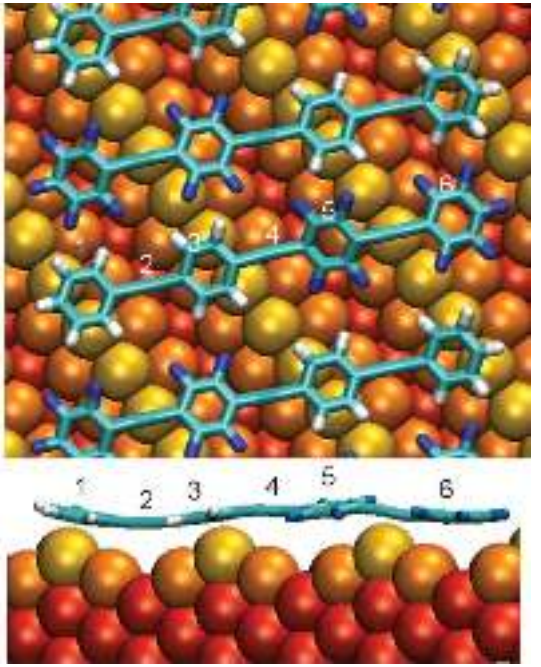
Seeing real structure in self-assembly



NC-AFM image



DFT calculation



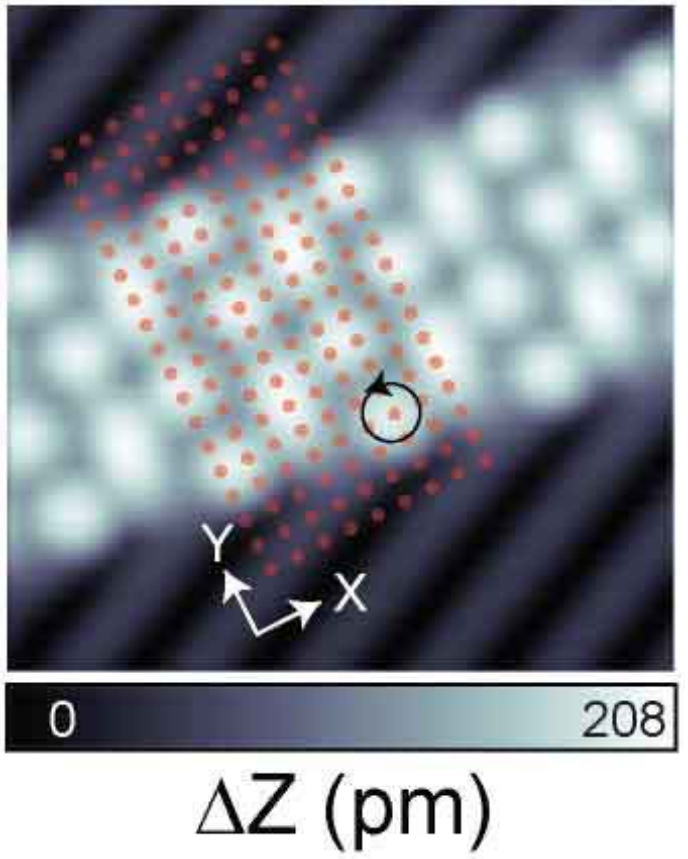
-Excellent agreement-

Quasi-static bias spectroscopy

Charge distribution

Procedure

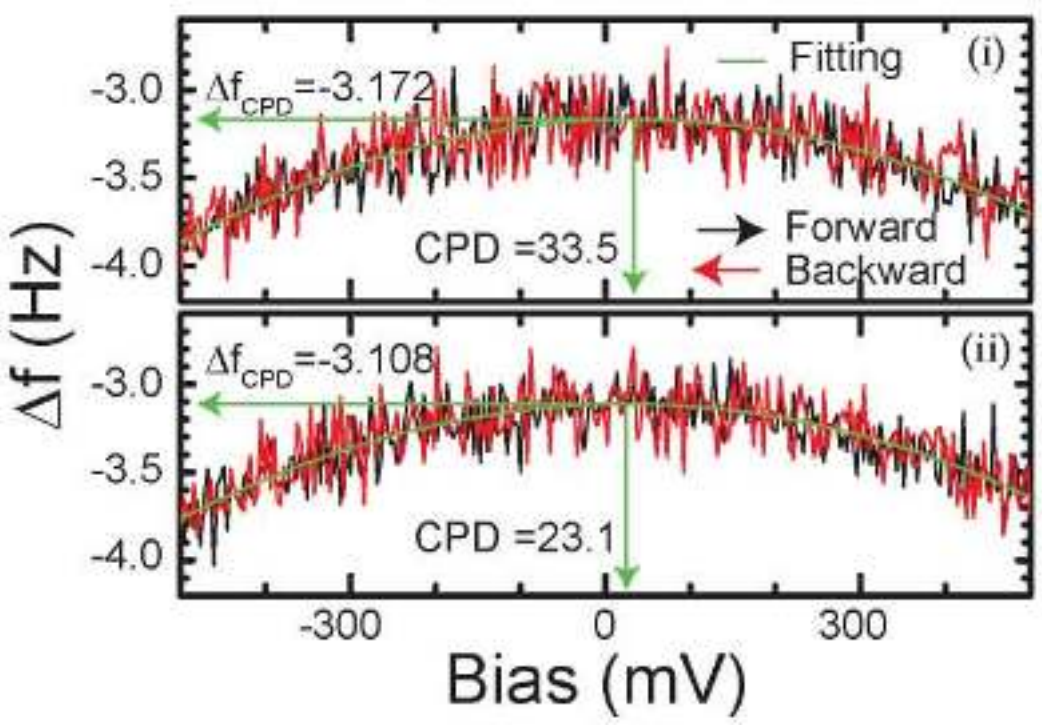
- Track to the marker site
- Turn off Z feedback
- Move to the measurement point
- Set tip closer to the sample by 50 pm
- Bias dependent measurement
- Move back to the marker site
- Turn on the Z feedback (-500 mV, 50 pA)

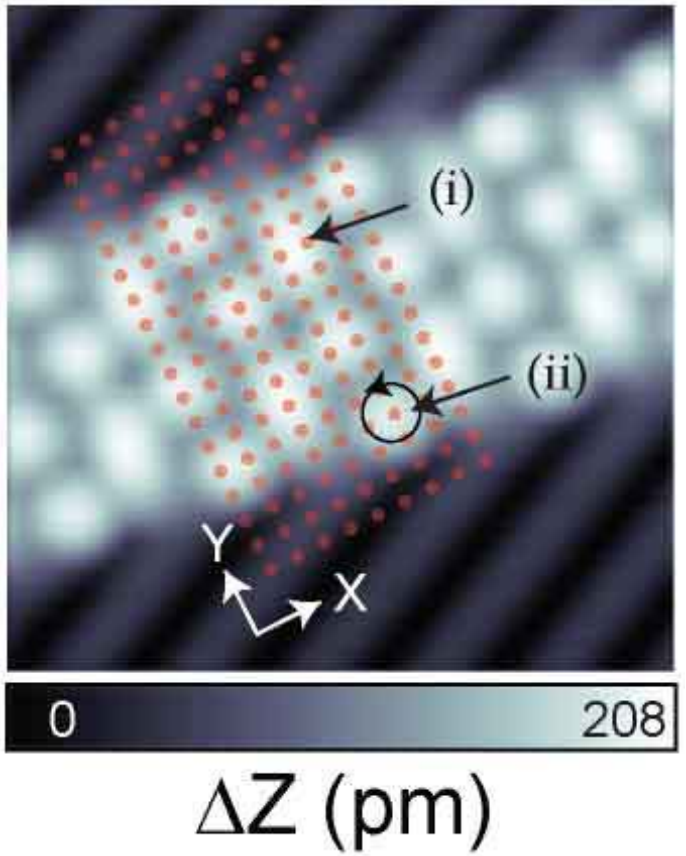


Drift-corrected dynamic force spectroscopy
S. Kawai et al., Phys. Rev. B 83, 035421 (2011).

Local contact potential difference

28× 59 grid points (1652 points)





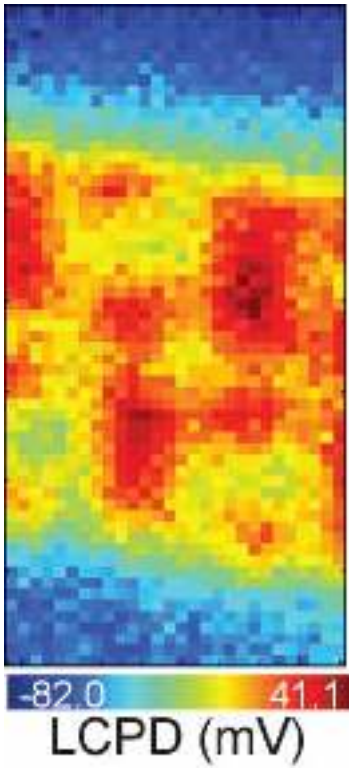
Bias sweep : ±500 mV

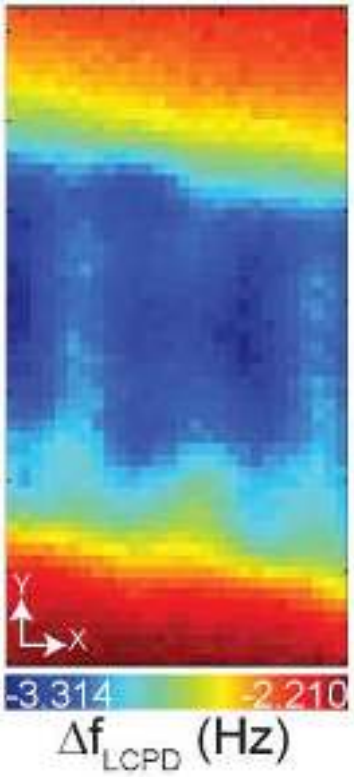
Points : 256

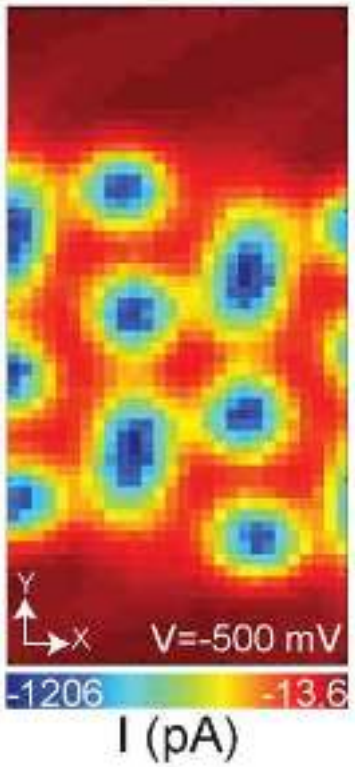
ΔLPCD = 10.4 mV

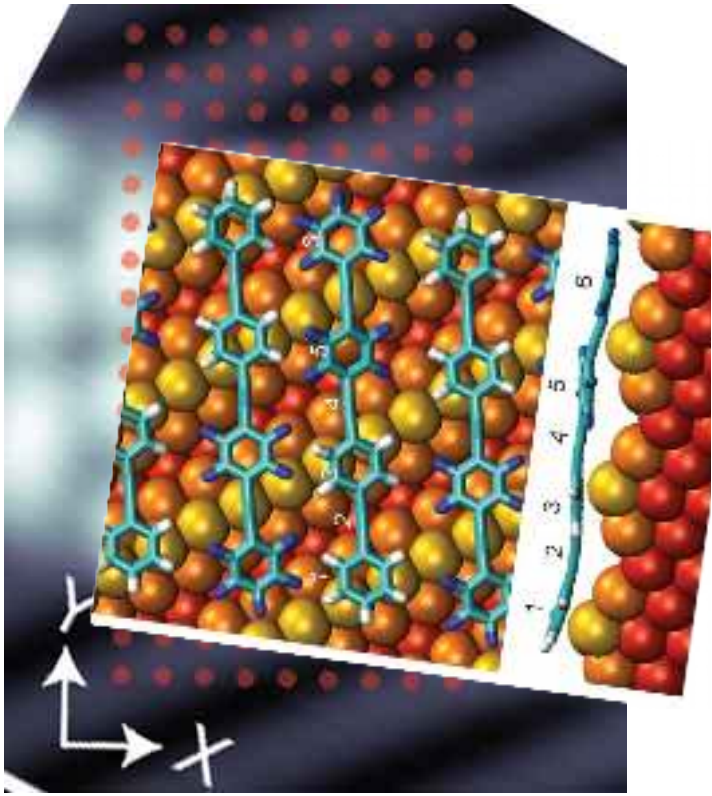
2D map extracted via Δf(x,y,V)

STM topography







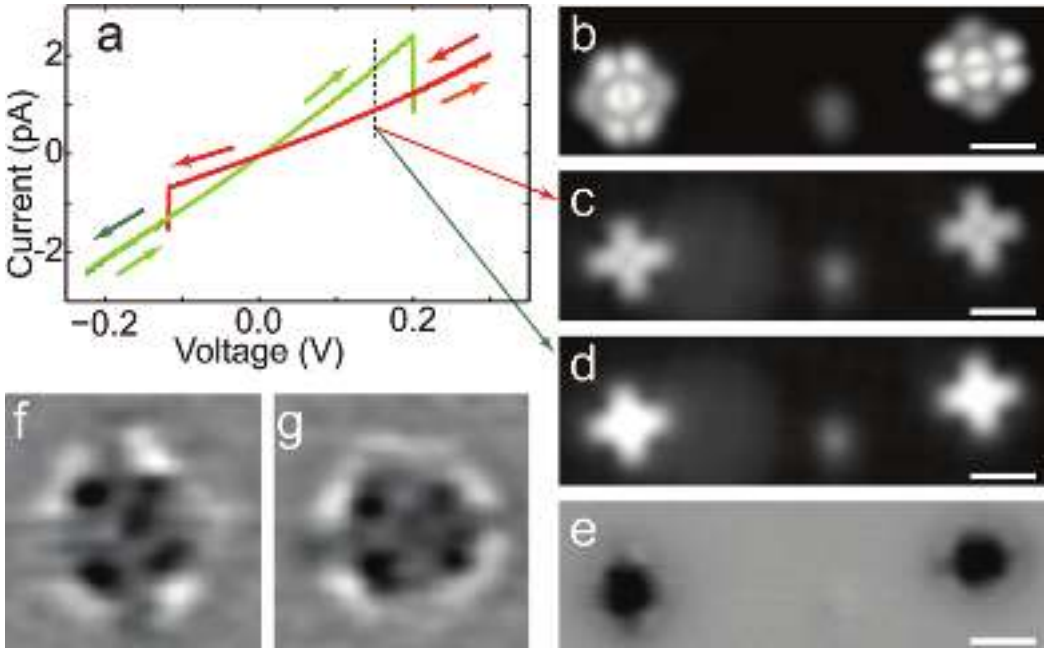


28× 59 grid points (1652 points),

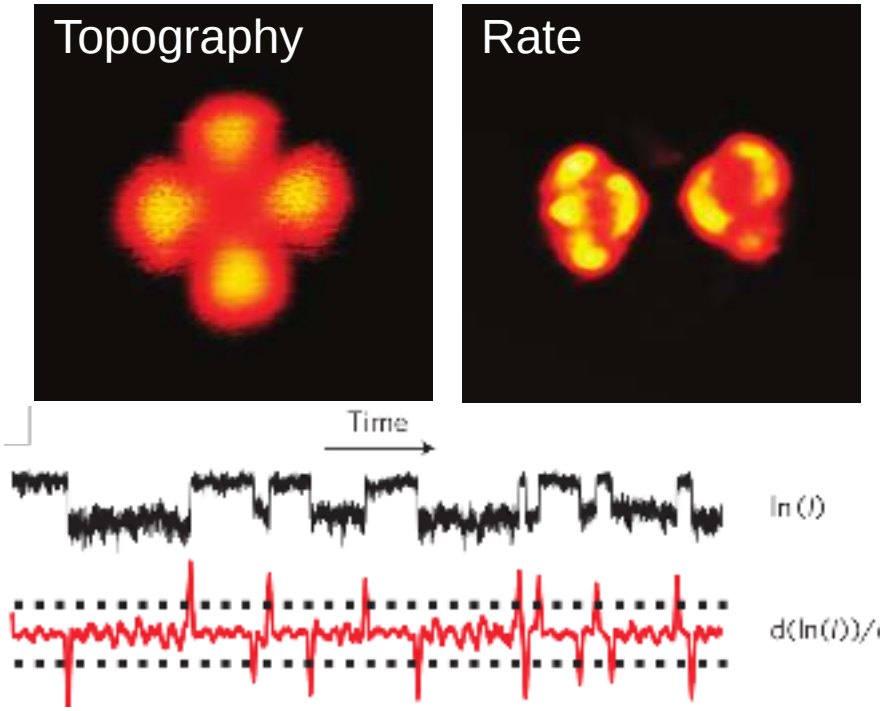
16hours33mintues, restricted by the refilling cycle of liquid He

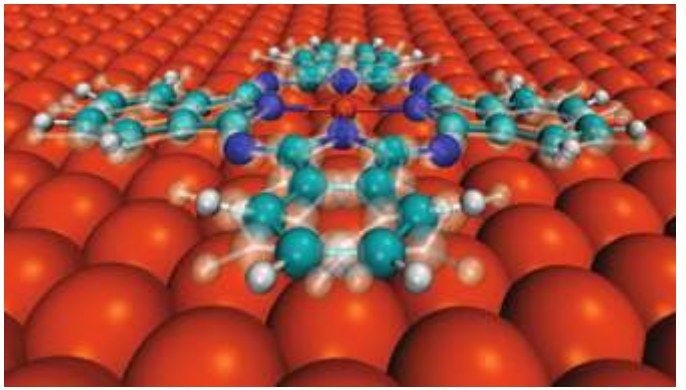
C-H and C-F induce a net dipole moment of 4.27D (H_2O ~ 2D) along the molecular axis

CuPc molecules on Cu surfaces
related publications



I. Swart et al., Nanoletters 11, 1580, (2011).

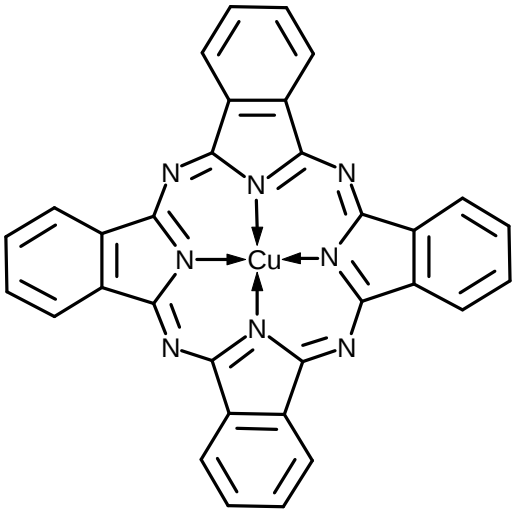


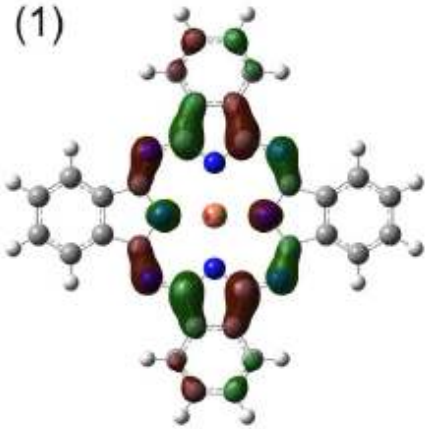


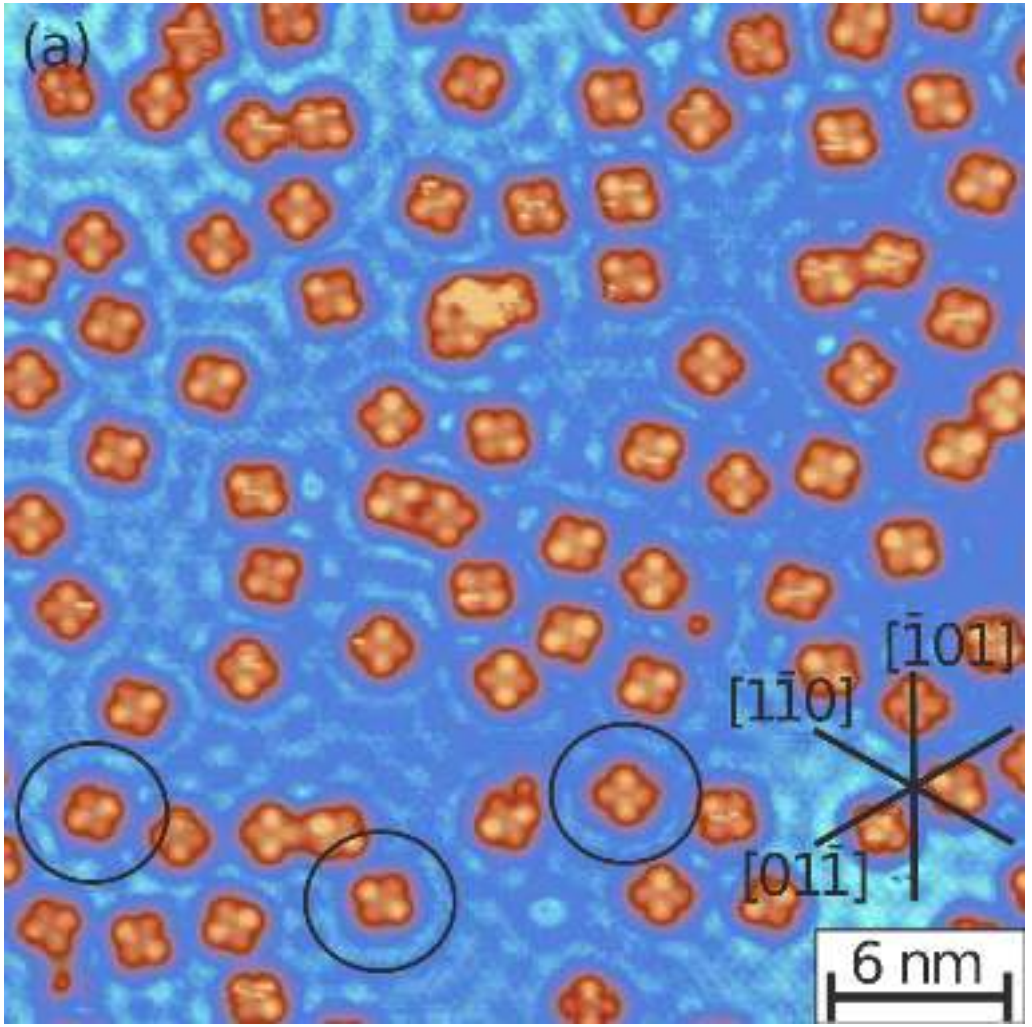
H. Karacuban et al., Surf. Sci. 603, L39, (2009).
J. Schaffert et al., Nature Mat. 12, 223, (2013).
J. Schaffert et al.,PRB 88, 075410, (2013).

CuPc deposition on Cu(111)

Cu-phthalocyanine (CuPc)

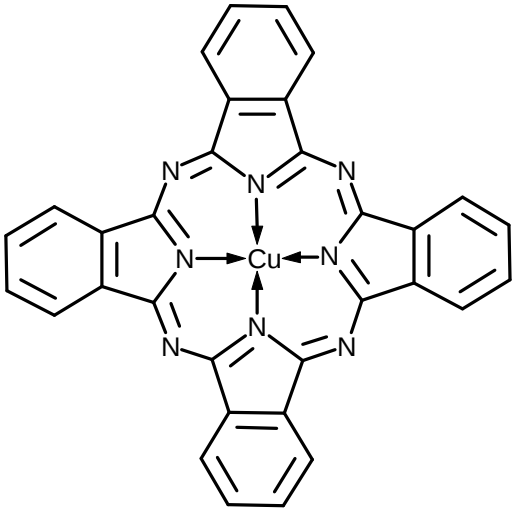


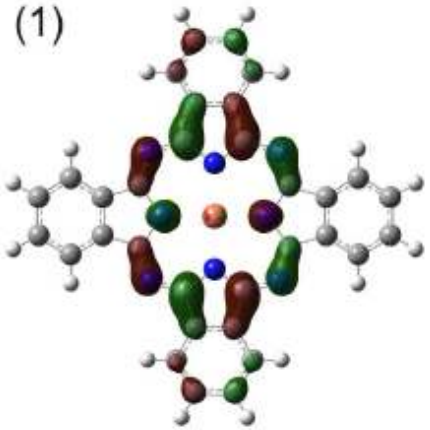




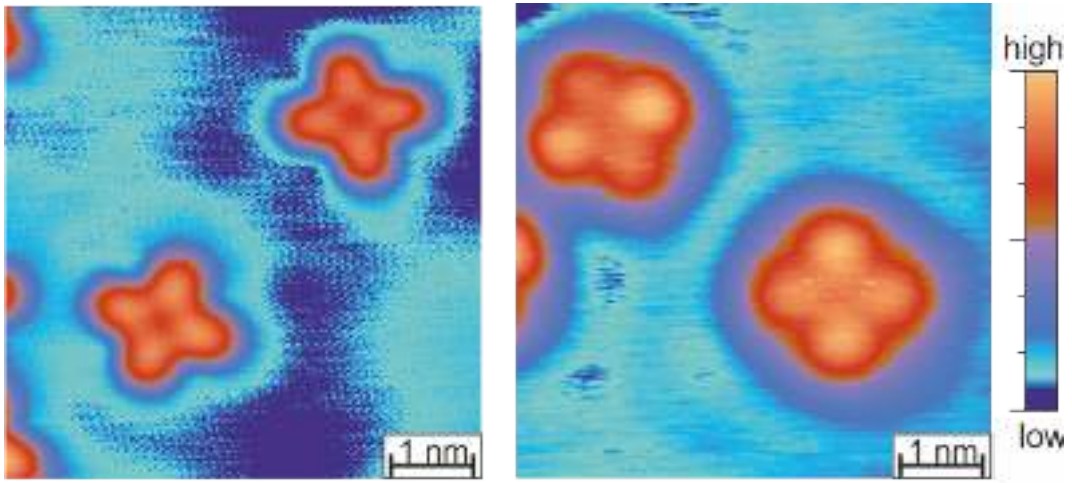
U=-200mV, I=30pA

CuPc deposition on Cu(111)





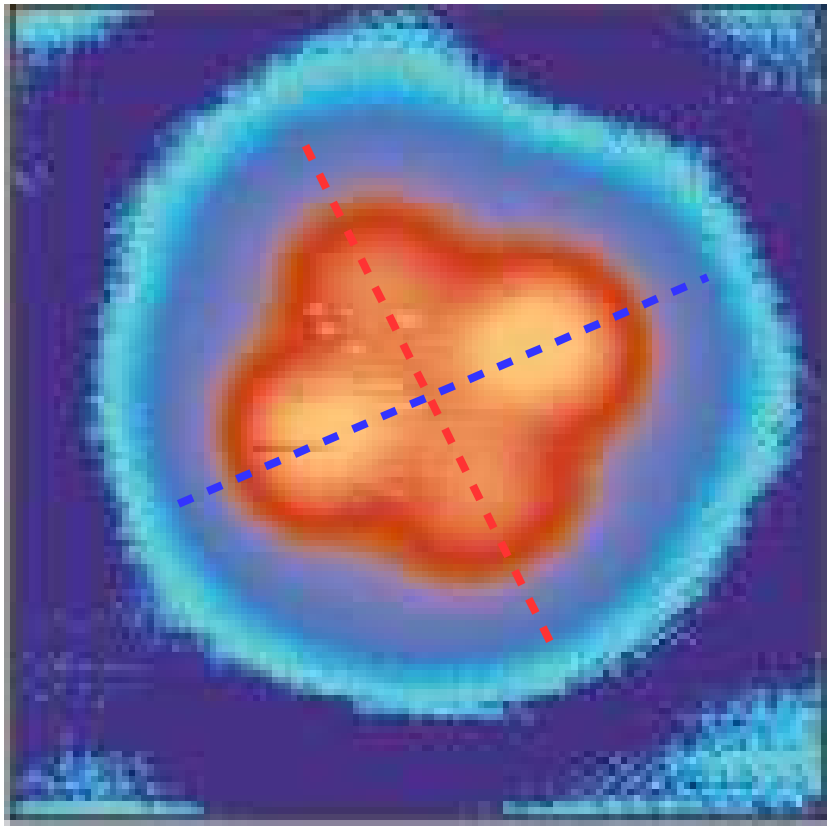
on Ag(111) on Cu(111)



structurally similar, higher interaction on Cu(111)

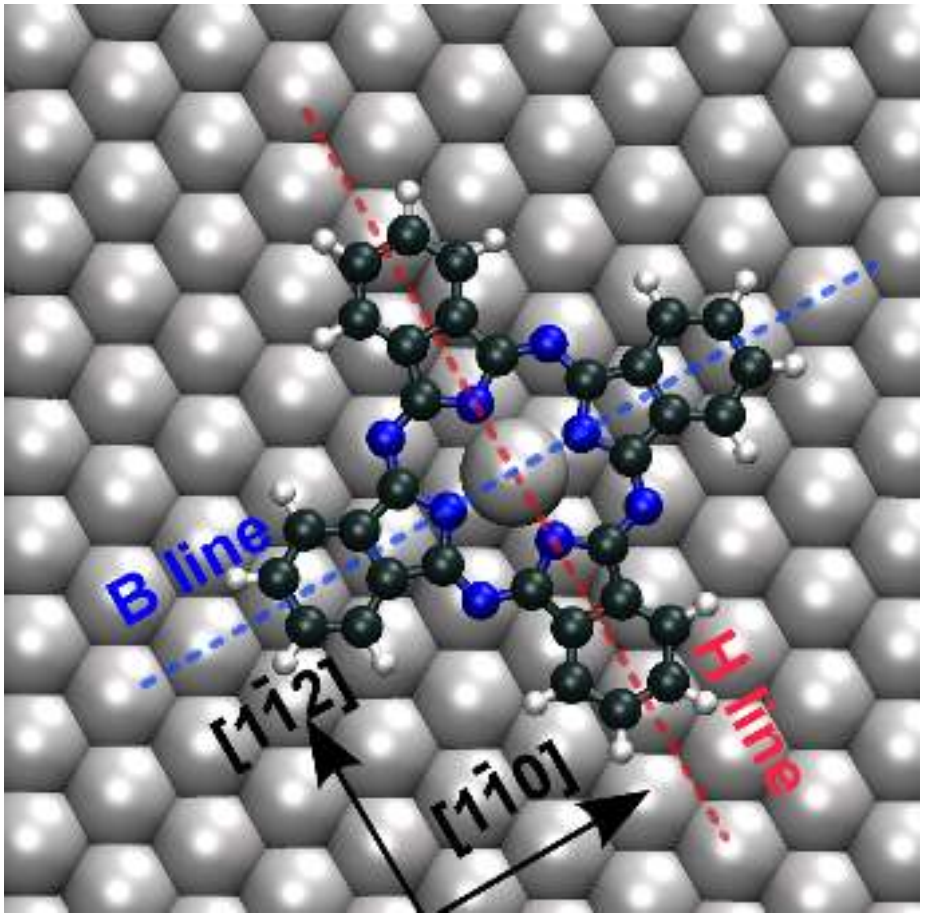
- physisorption (vdW interactions)
- chemisorption (chem. bonds)
- adsorption geometry defined by mechanical & electronic properties

CuPc on Cu(111)
Local Adsorption Geometry



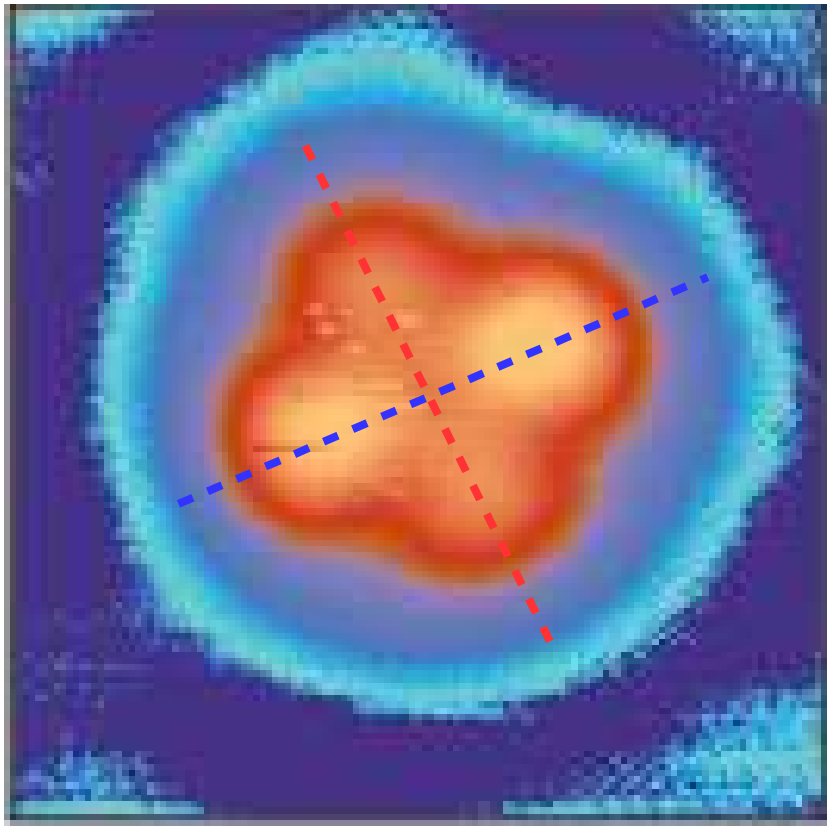
U=-200mV, I_t=30pA

DFT with VdW correction and in PBE form

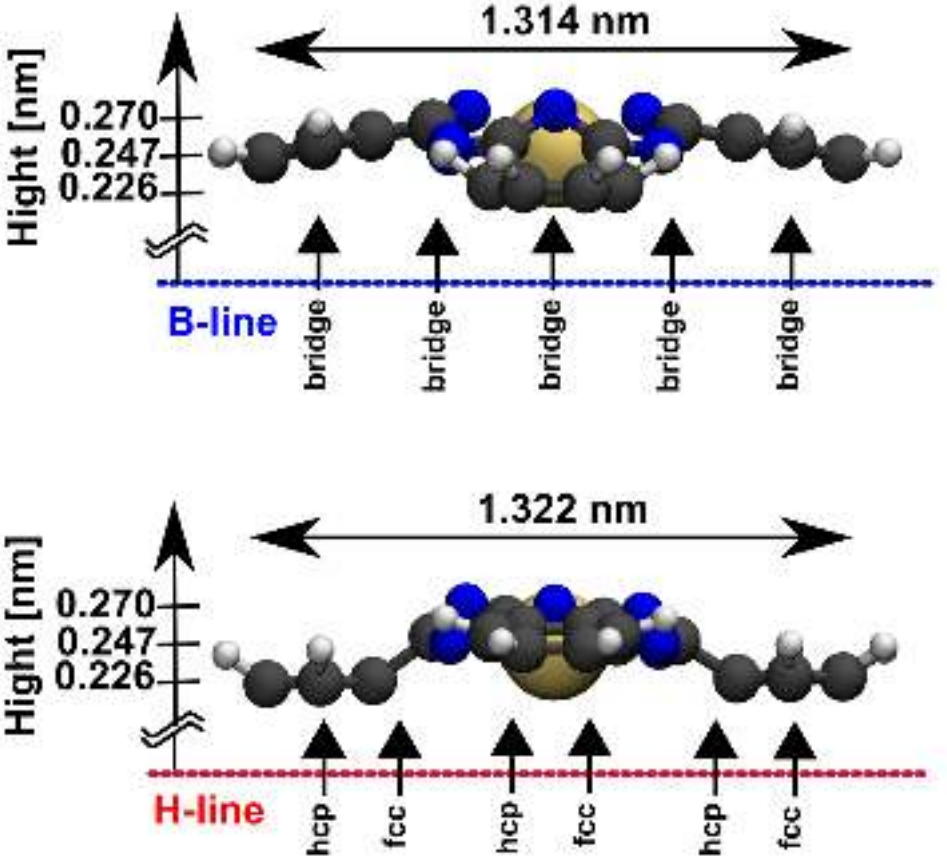


- strong interaction
- 6.58 eV/molecule
- symmetry reduction

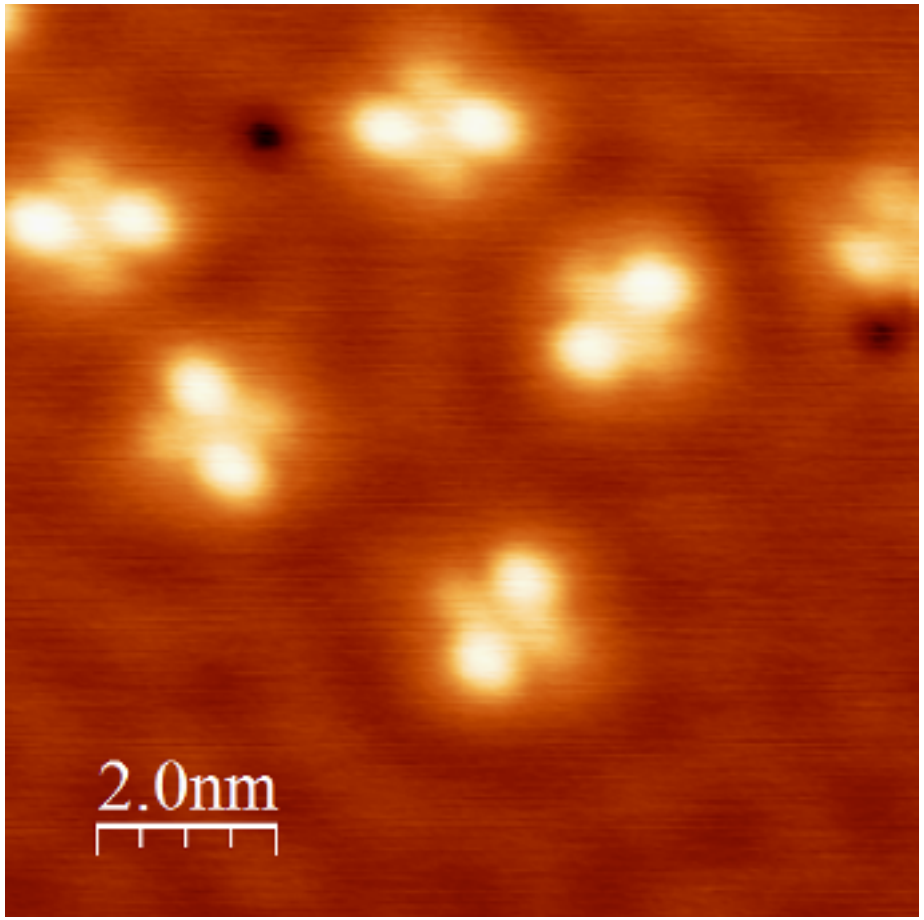
CuPc on Cu(111)
Local Adsorption Geometry



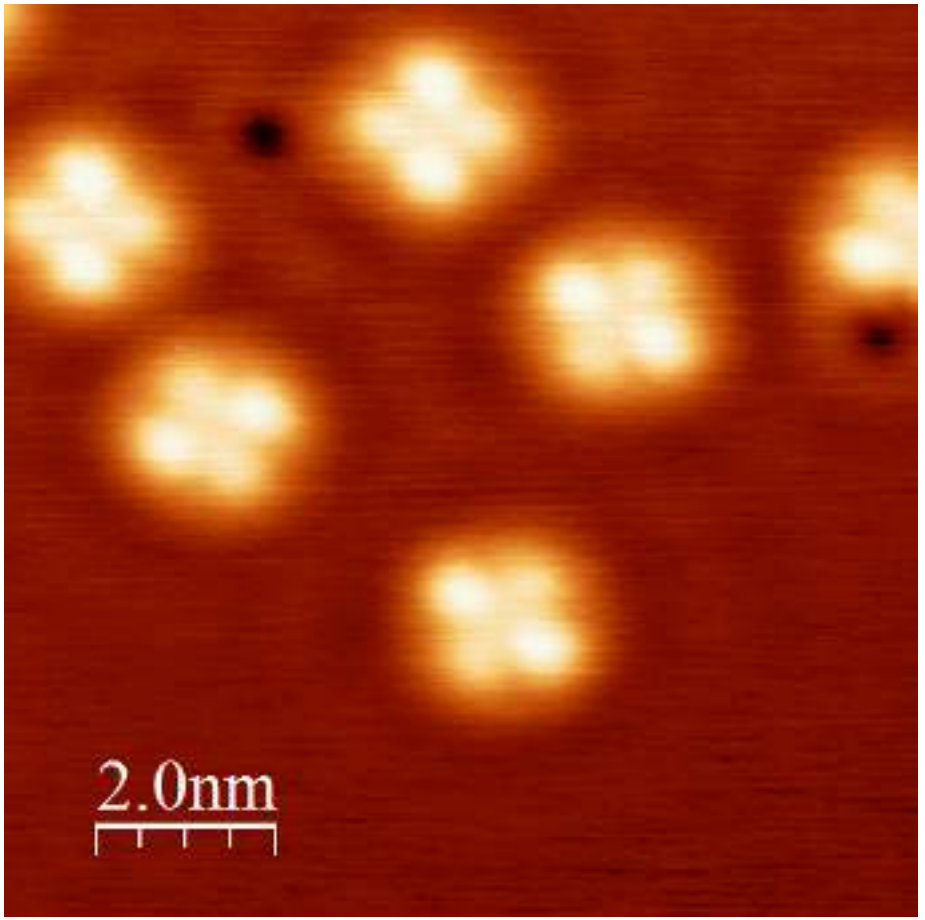
U=-200mV, I_t=30pA



CuPc switching

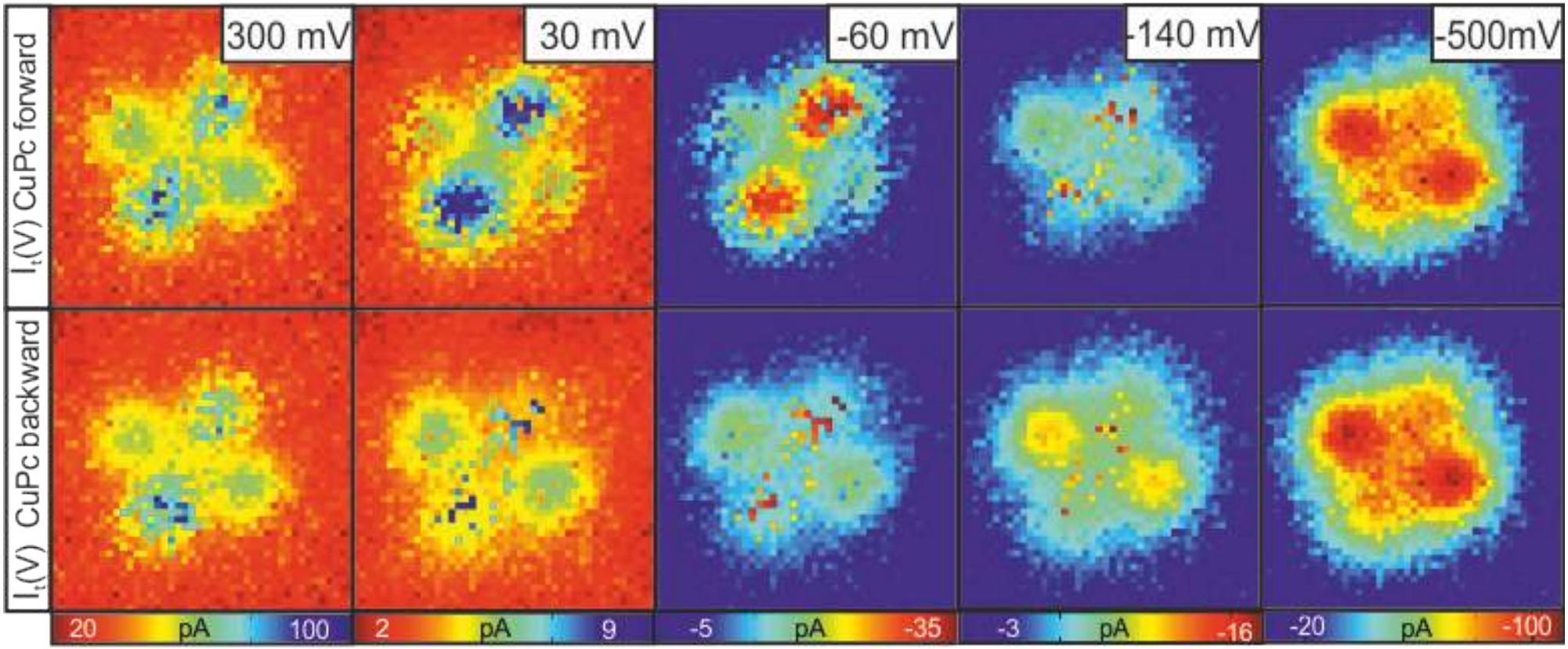


U=30 mV



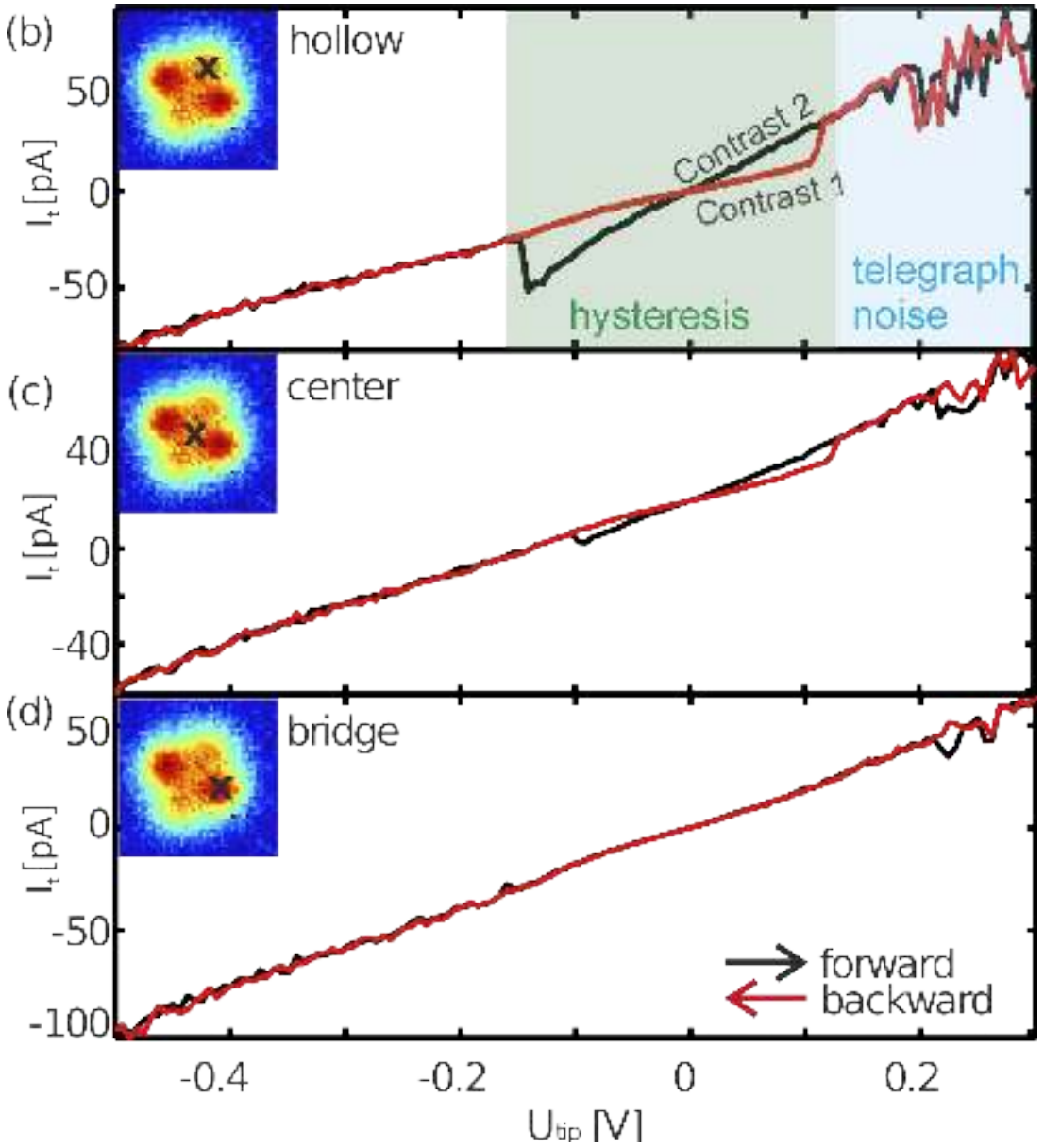
U=-30 mV

3D bias spectroscopy
current maps

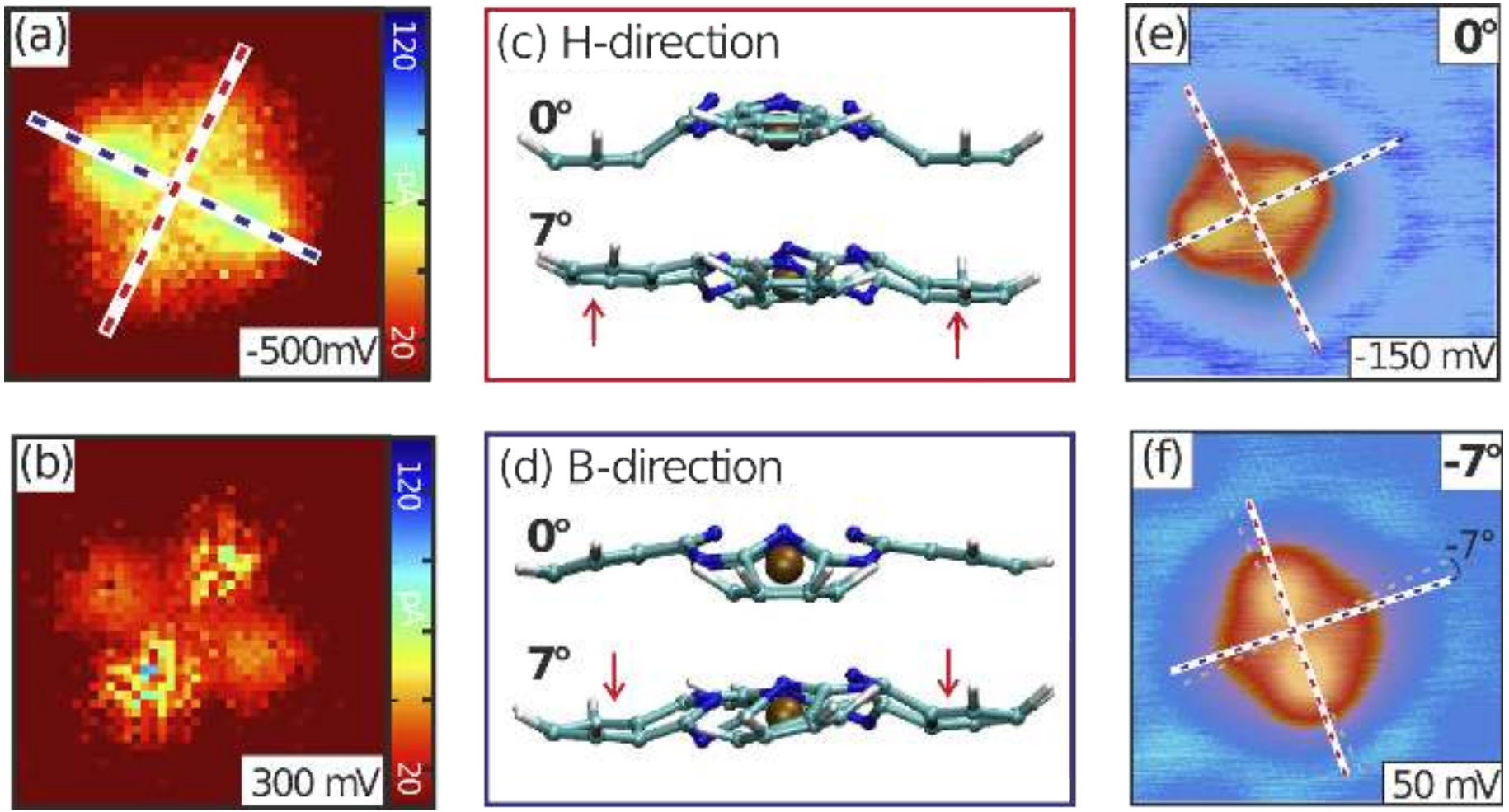


- contrast transition in simultaneously recorded $I_t(x,y,U)$
- different for forward and backward directions

3D bias spectroscopy
current curves



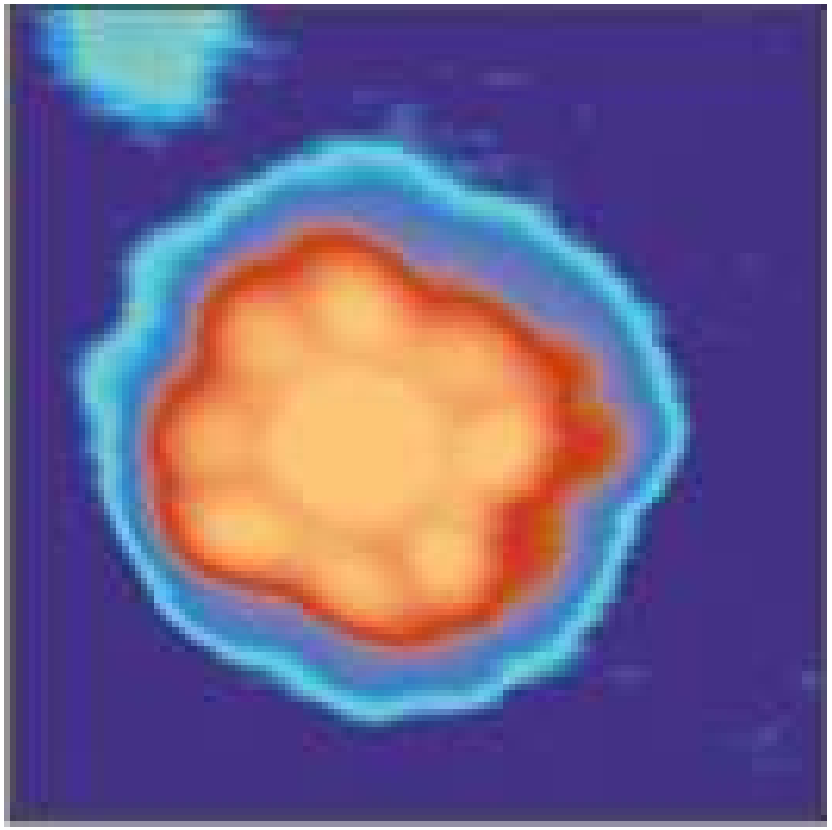
Switching Adsorption Configuration



- telegraph noise corresponds to frustrated rotations
- bistable regime: controllable switching of adsorption configuration
- can be induced upon scanning with different bias voltages

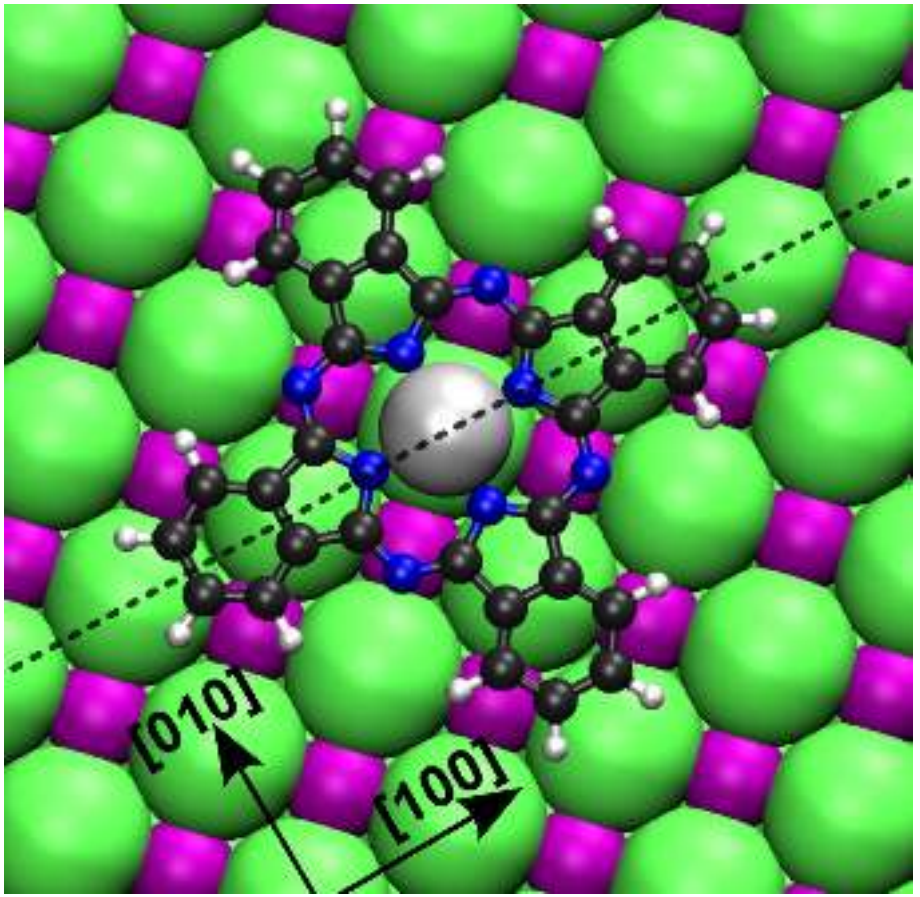
Substrate Molecule Interactions

CuPc on NaCl(2ML) / Cu(111)



U=-1.7V, I_t=4pA

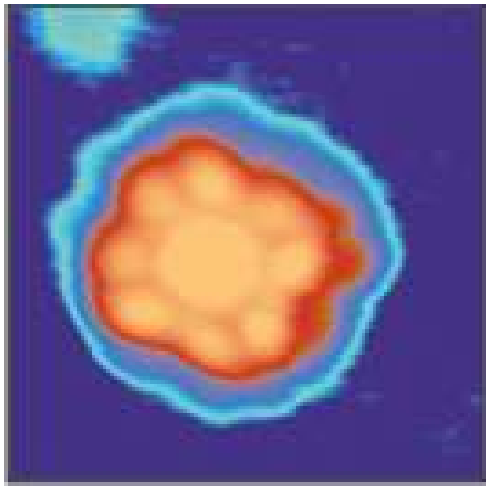
DFT with VdW correction and in PBE form



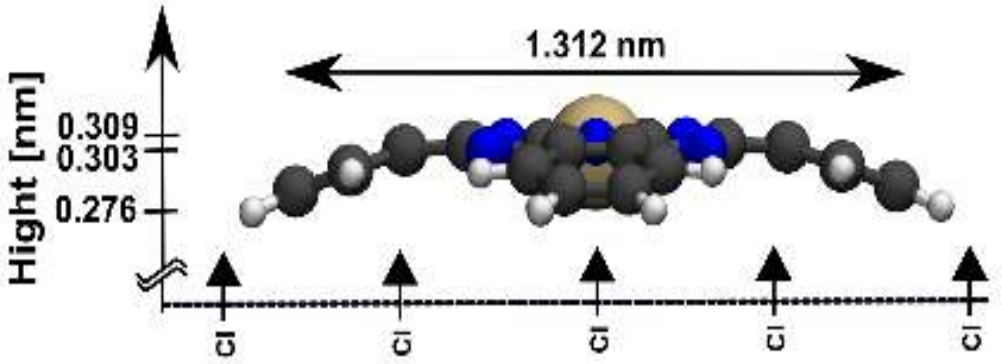
- weak interaction
- 2 eV/molecule
- symmetry preservation

Substrate Molecule Interactions

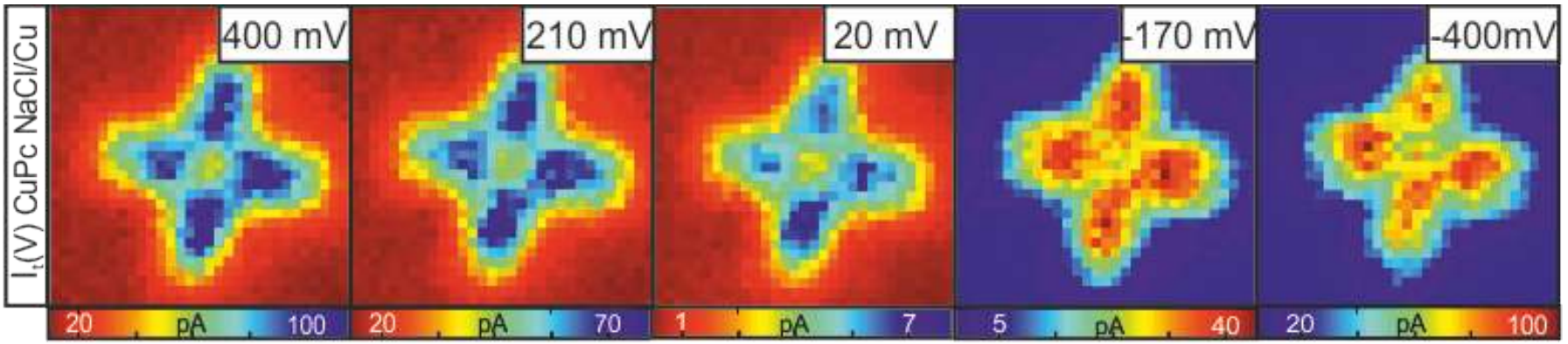
CuPc on NaCl(2ML) / Cu(111)



U=-1.7V, I_t=4pA

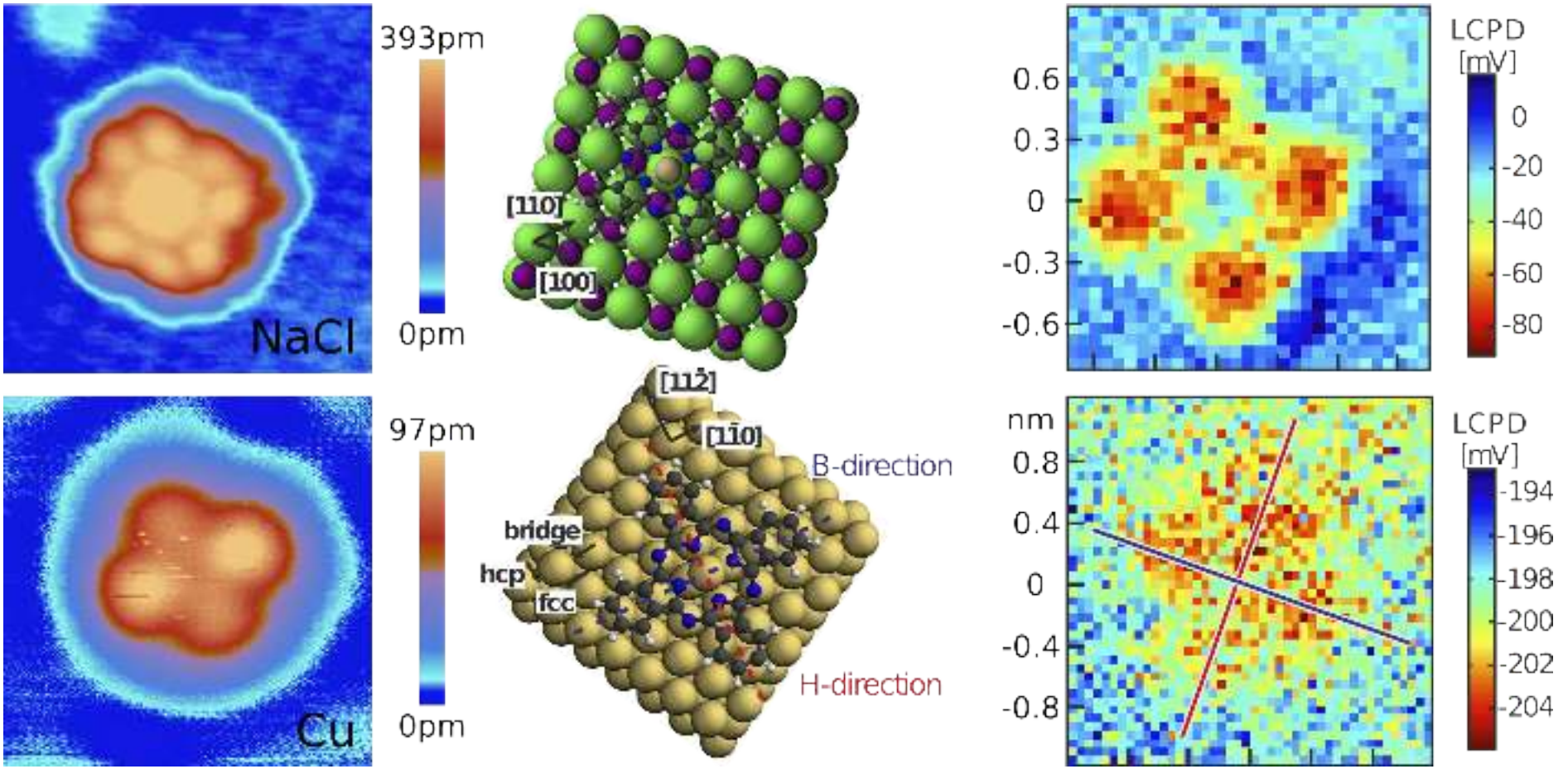


- weak interaction
- 2 eV/molecule
- symmetry preservation
- **No charging observed**



CuPC on Cu(111) and NaCl

Local Contact Potential Difference



LCPD of CuPc

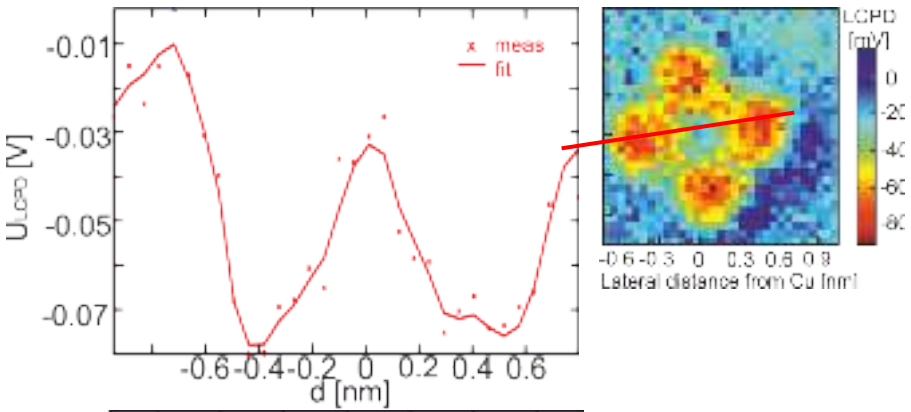
Comparison with DFT calculations

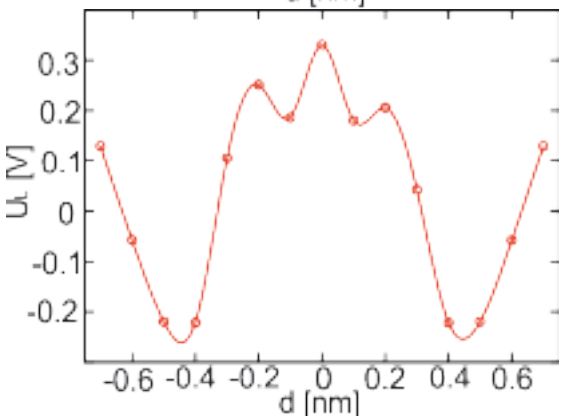
CuPc on NaCl(2ML) / Cu(111)

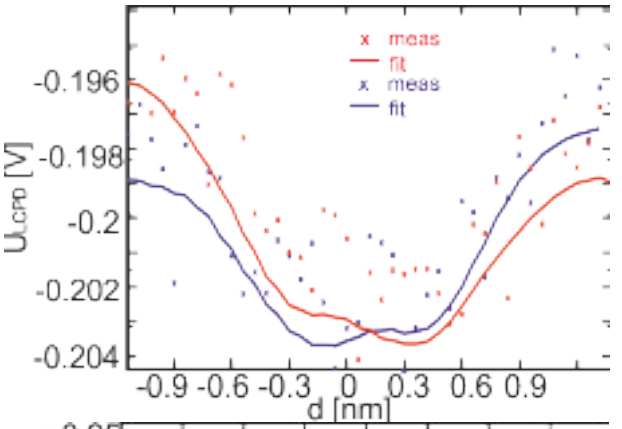
CuPc on Cu(111)

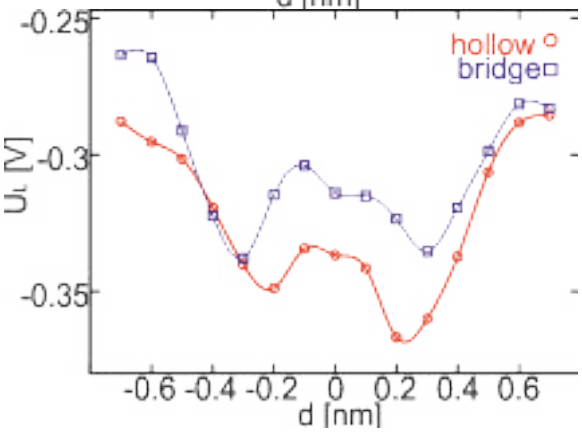
experiment

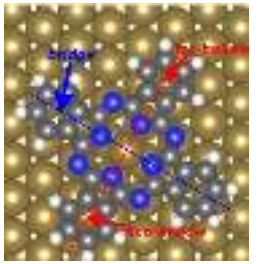
DFT







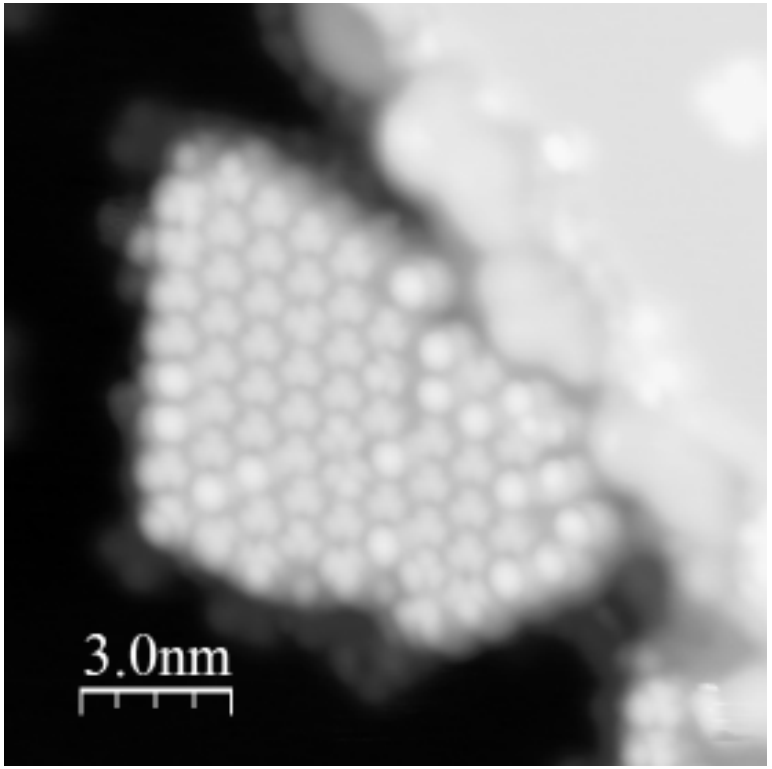




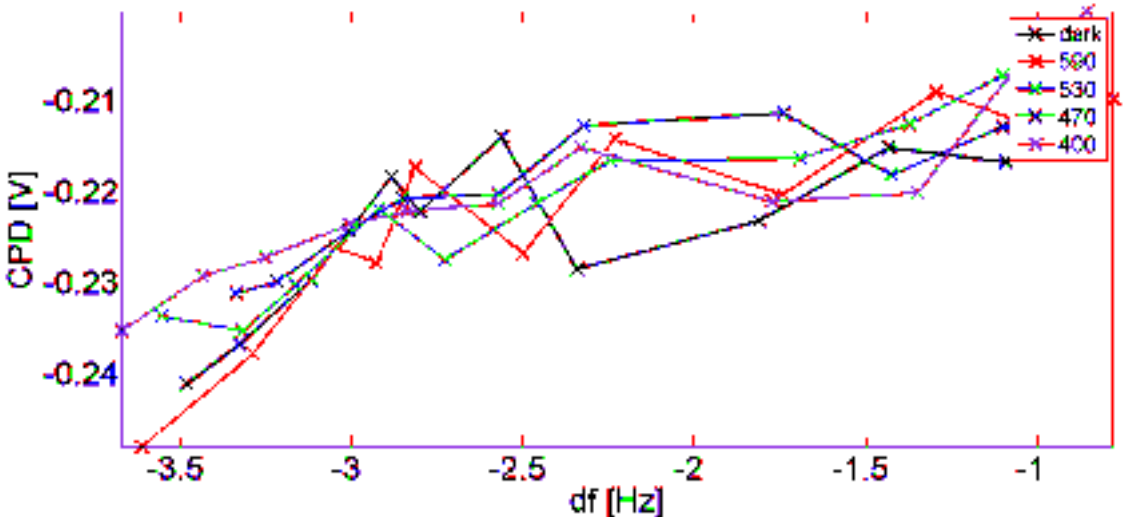
A. Sadeghi et al., Phys. Rev. B., 86, 075407 (2012)
A. Sadeghi, phd-thesis, University of Basel (2013)

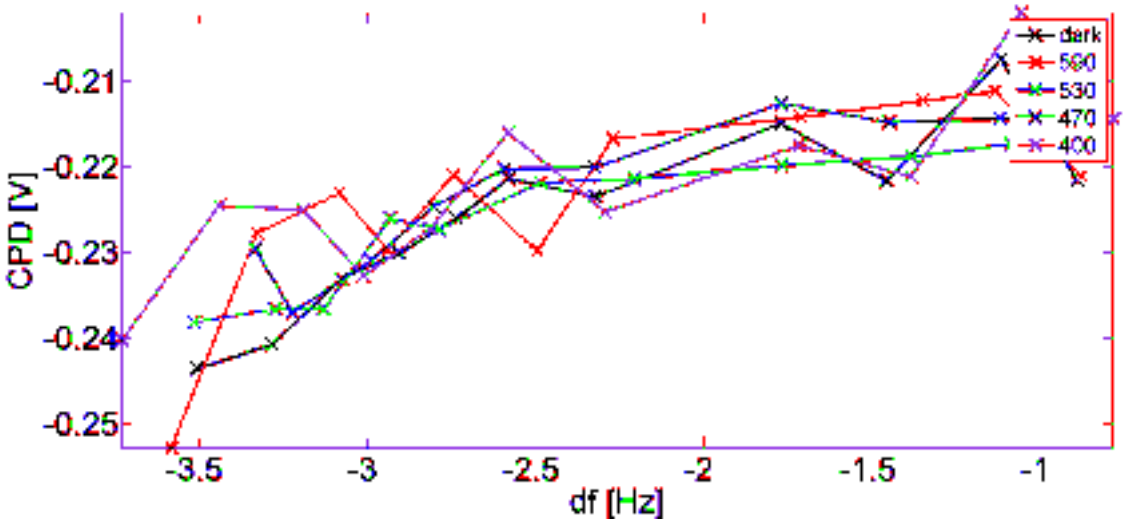
1D bias spectroscopy

CuPC-tip on C_{60} on Cu(111): under illumination



U=-1V, I=30pA

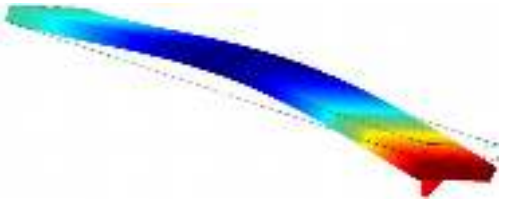




- strong electronic coupling?
- large separation?

Overview 2

- **Kelvin Probe Force Microscopy**
  - Measurement principle
  - Experimental setup



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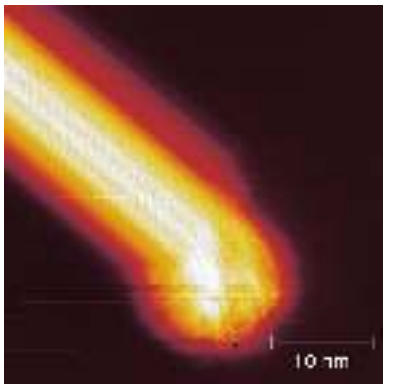
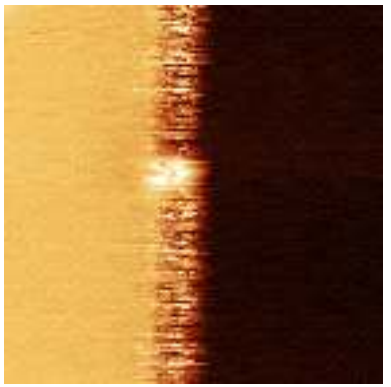
  - Multiwire assemblies on NaCl and KBr
  - Contacting and cutting molecular wires



- **Truxenes**
  - Self assemblies on KBr crystals
  - Molecular structures on patterned surfaces
  - Reconstructing surfaces
  - Single molecule at room temperature



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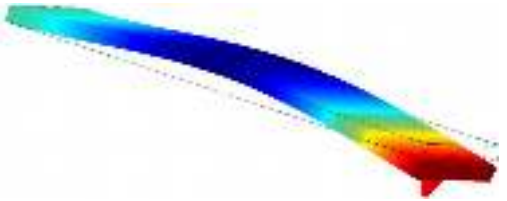

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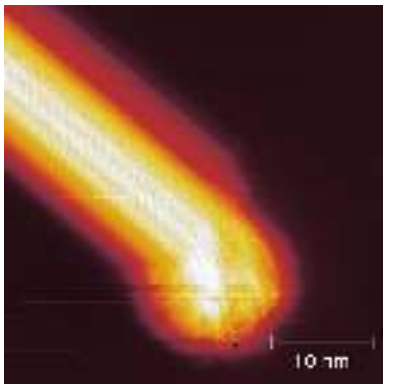

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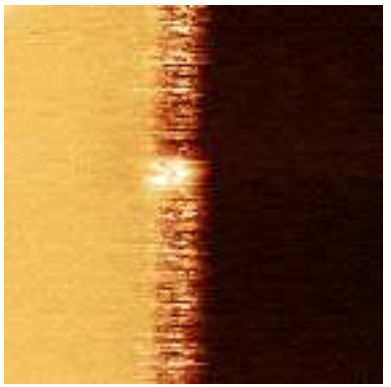


noncontact Atomic Force Microscopy

nc-AFM / KPFM principle

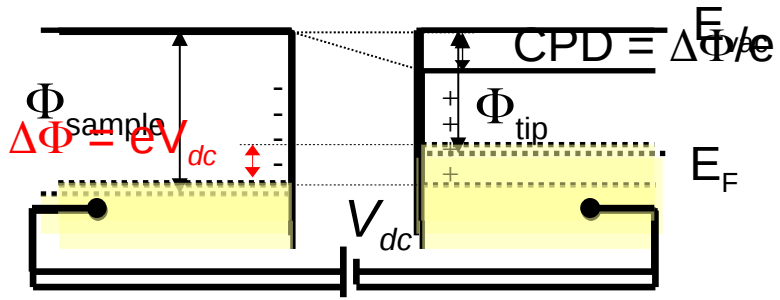
$$F_{tot} = F_{chem} + F_{mag} + F_{el} + F_{vdW}$$

bonding between tip and sample atoms (only for d < 5 Å)

only for magnetically sensitive tips

$$F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V^2$$

$$F_{vdW} = -\frac{HR}{6d^2}$$



contact potential (CPD) compensation

Kelvin Probe Force Microscopy

Principle - biomodal detection (AM-KPFM)

Potential between tip and sample:

$$V(t) = (V_{dc} - \Delta\Phi/e) + V_{ac}\sin\omega t$$

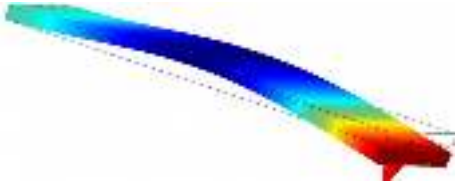
Electrostatic force:

$$F_{es} = -\frac{1}{2}\frac{\partial C}{\partial z}V^2(t) = F_{dc} + F_{\omega} + F_{2\omega}$$

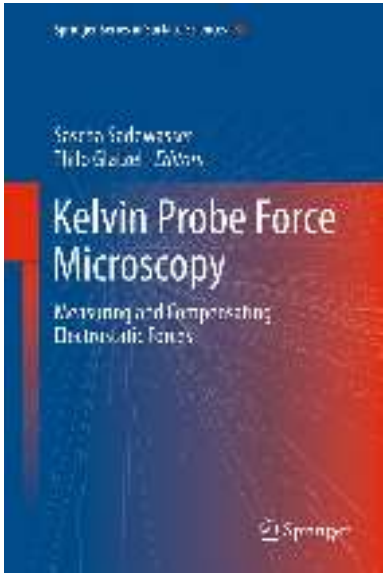
$$F_{\omega} = -\frac{\partial C}{\partial z}(V_{dc} - \Delta\Phi/e) \times V_{ac}\sin(\omega t)$$

→ CPD of the tip – sample system,
absolute determination of the work function

Second eigenmode :



$f_1 = 6.3f_0 \sim 945$ kHz
$k_1 \sim 36k_0 \sim 1100$ N/m
$Q_1 \sim 10000$ ($\Delta f_{HWHM} = 60$ Hz)
Actuated electrostatically

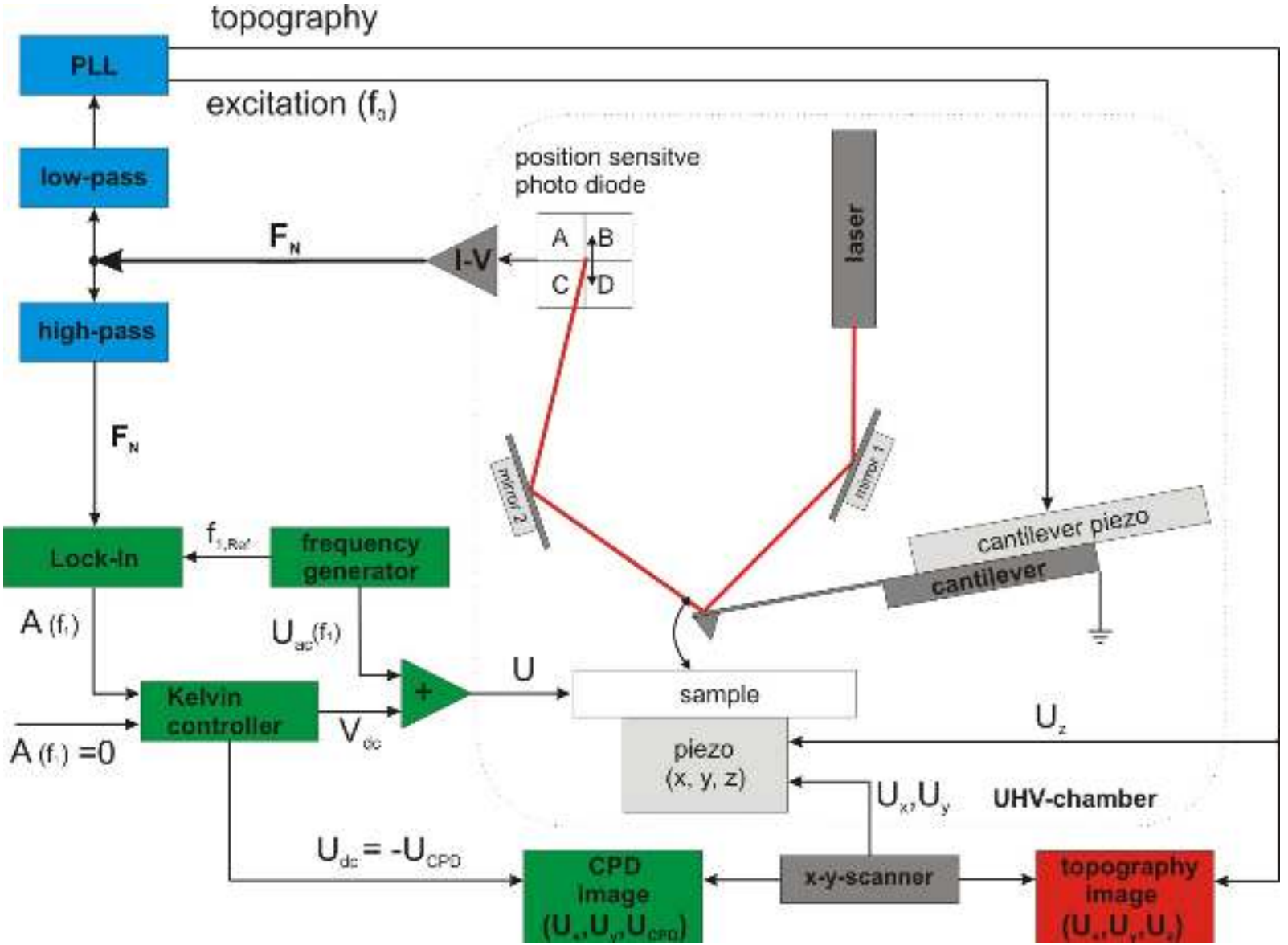


Springer 2011, Sadewasser & Glatzel

AM-KPFM:

Ch. Sommerhalter & Th. Glatzel et al.,
APL 75, 286, (1999),
ASS 157, 263, (2000),
ASS 210, 84–89, (2003).

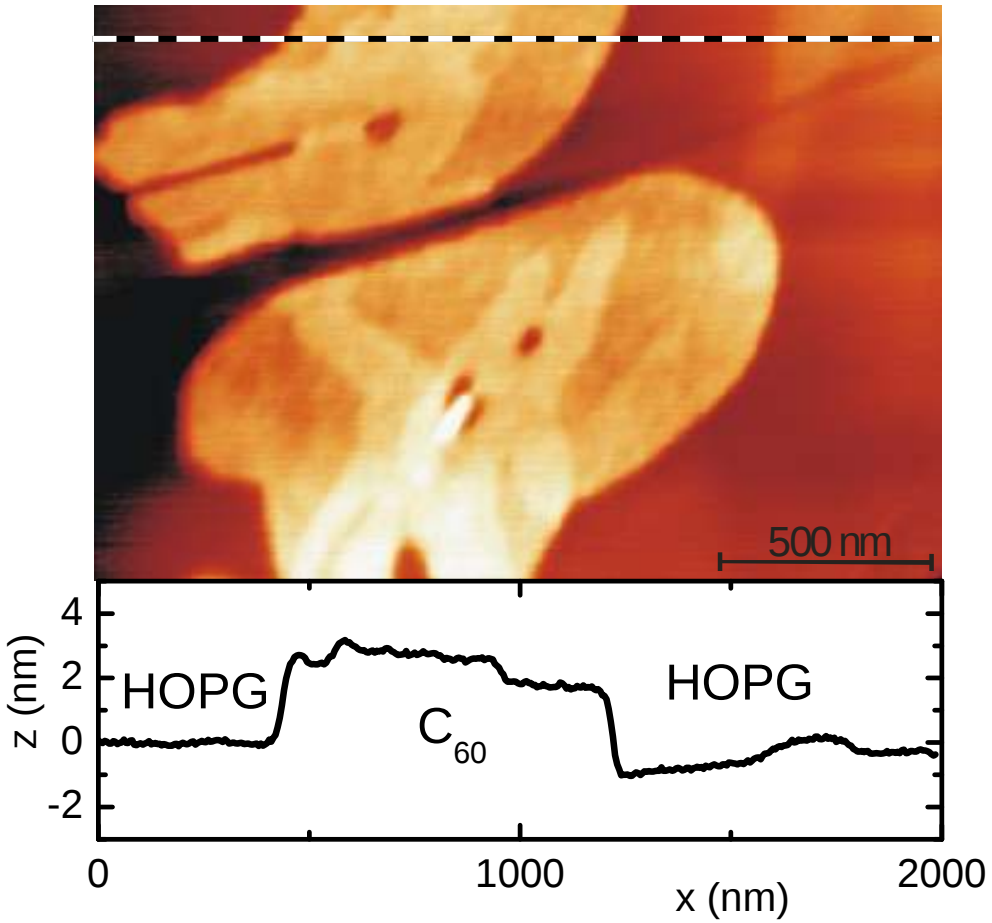
Experimental Setup
nc-AFM and KPFM



Experimental Results: nc-AFM

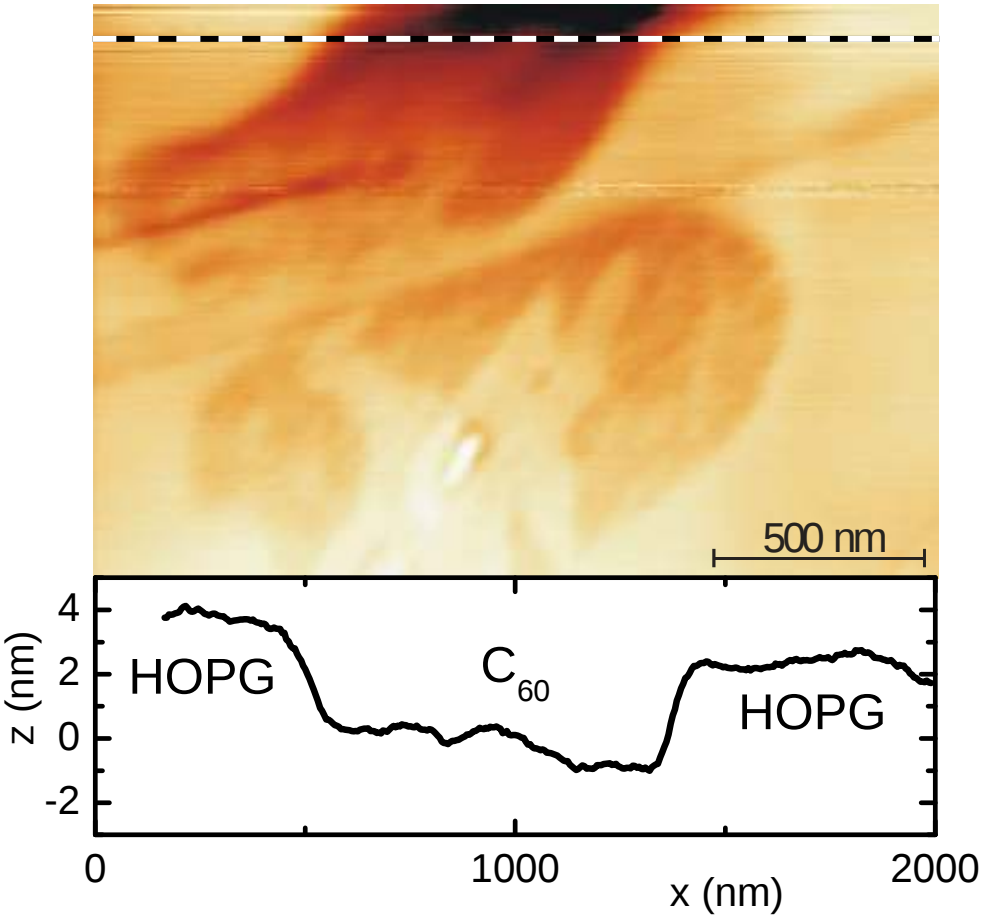
inhomogeneous sample: HOPG + ½ monolayer C_{60}

topography



V_{bias} = 0 V

topography



V_{bias} = 1.34 V

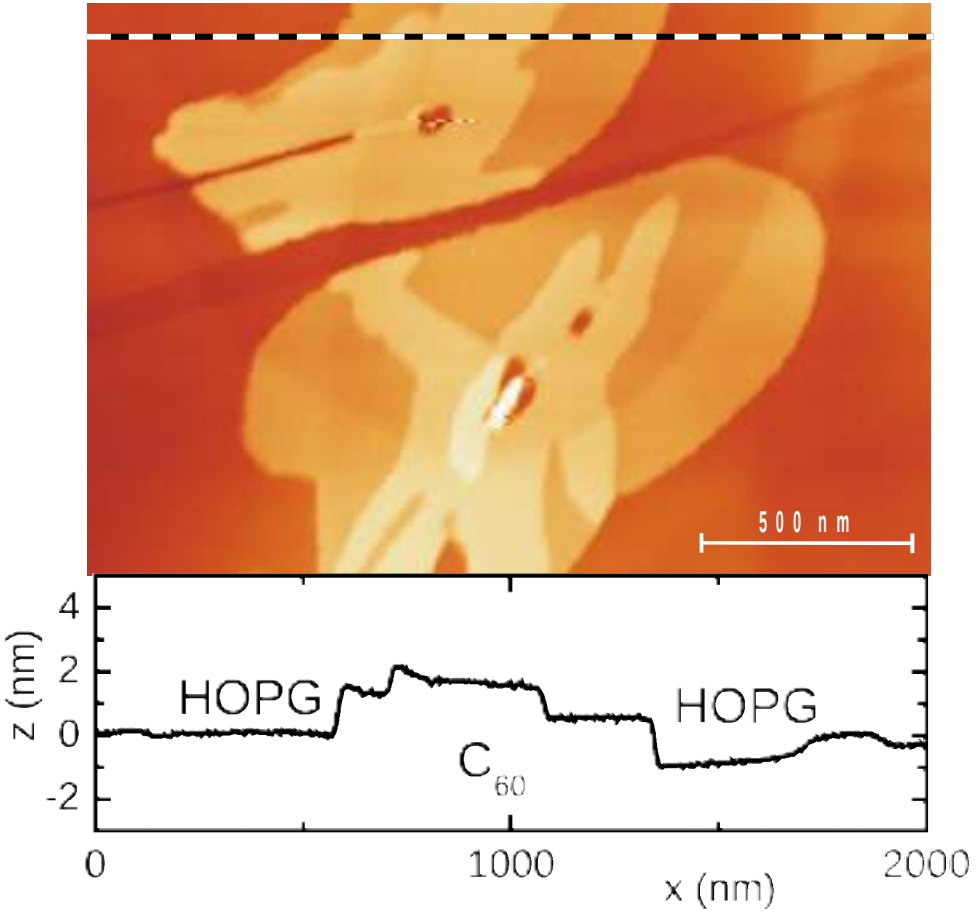
→ contrast inversion: HOPG ↔ C_{60}

S. Sadewasser et al., PRL, 2003, 91, 266101

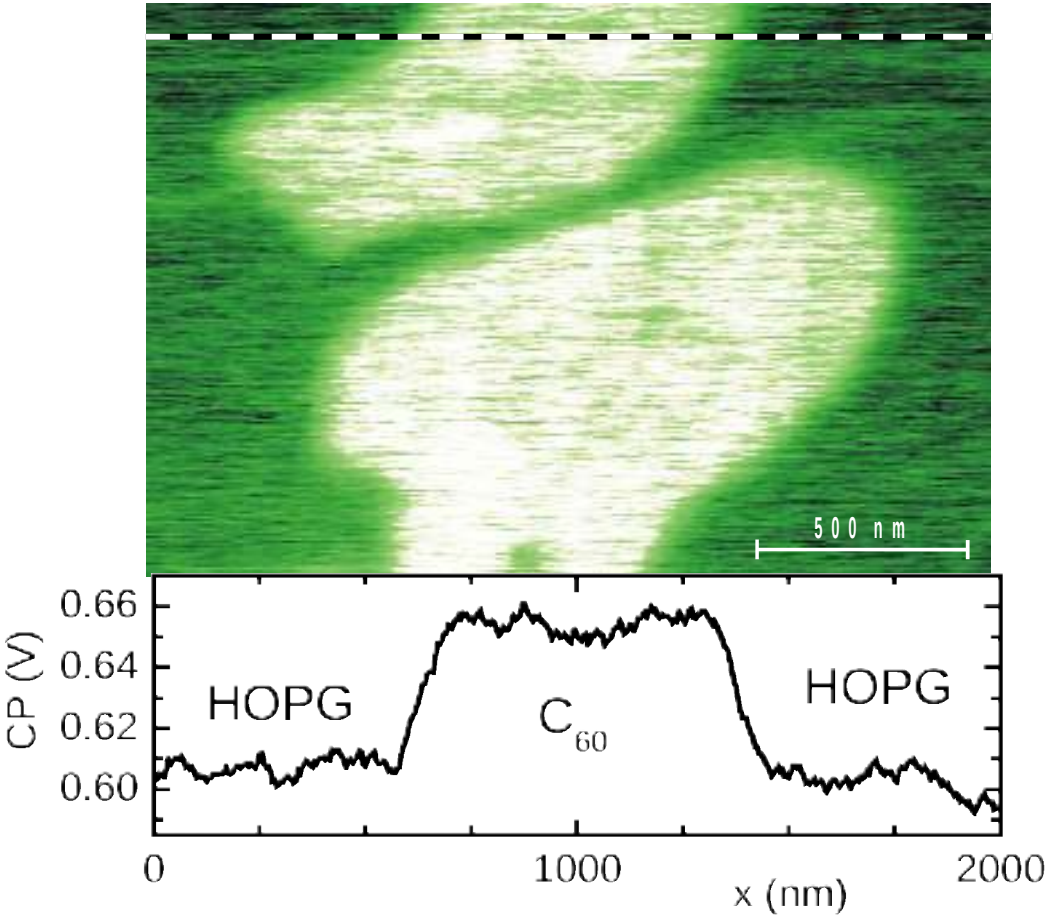
Experimental Results: KPFM

inhomogeneous sample: HOPG + ½ monolayer C_{60}

topography



contact potential



HOPG: $V_{CP} \cong 0.61$ V

C_{60}: $V_{CP} \cong 0.66$ V

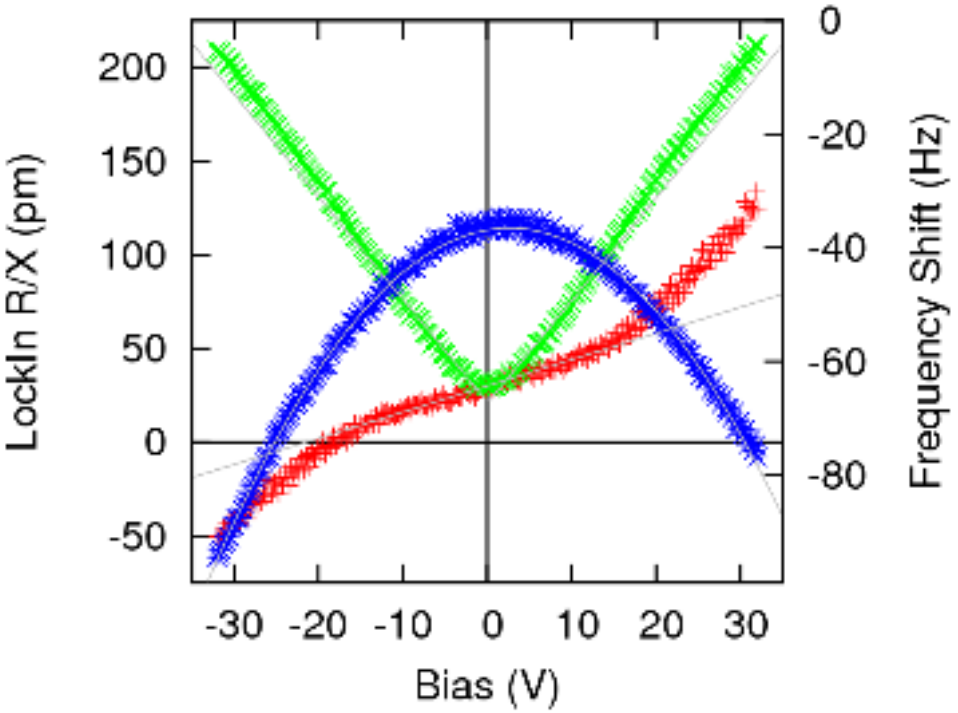
⇒ nc-AFM: residual electrostatic force for fixed V_{bias}

S. Sadewasser et al., PRL, 2003, 91, 266101

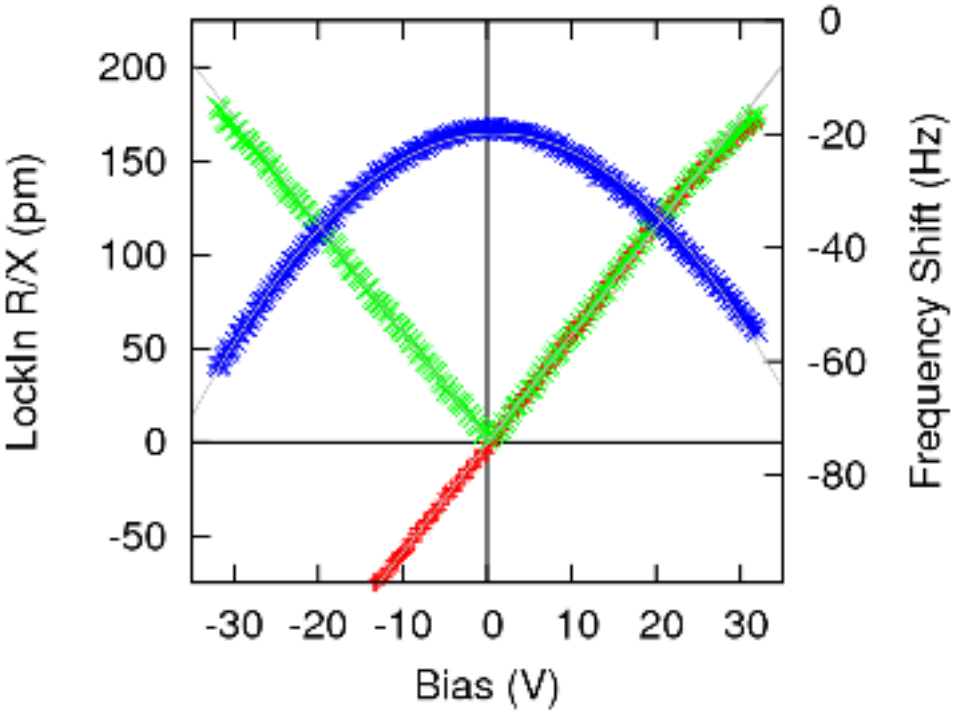
Capacitive Cross Talk

bias-spectroscopy on KBr

uncompensated



compensated & phase adjusted

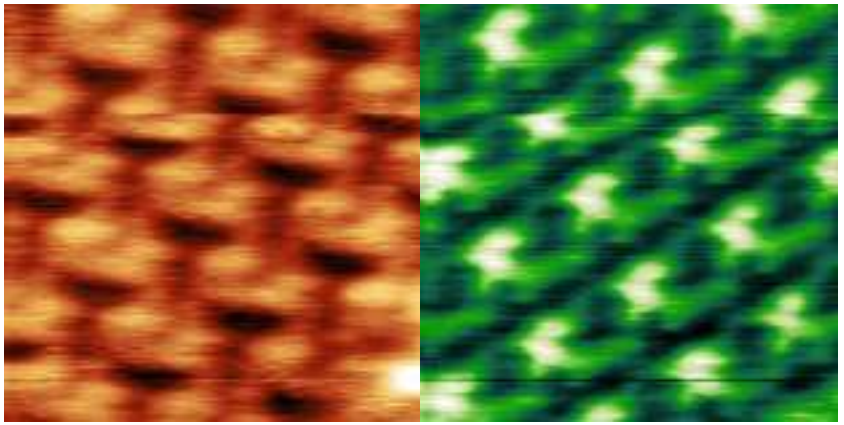


V_{AC}=1V, f_2=960.831kHz

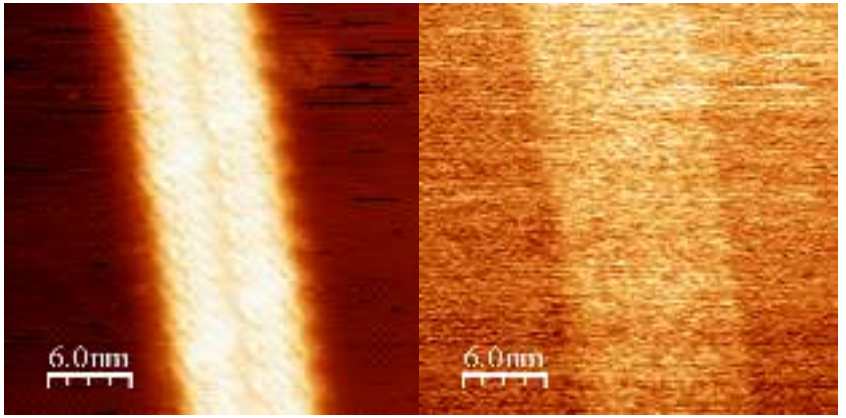
H. Diesinger et al., Ultramicroscopy 108, 773-781, (2008)

Atomic Scale Contrast in AM-KPFM

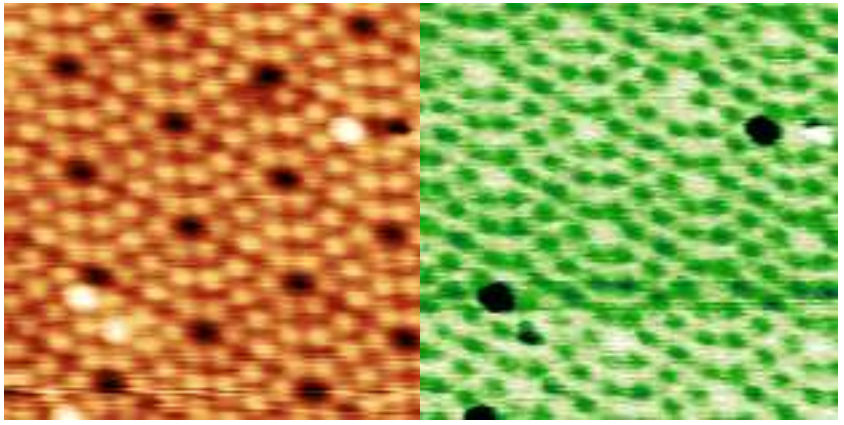
Truxenes on KBr



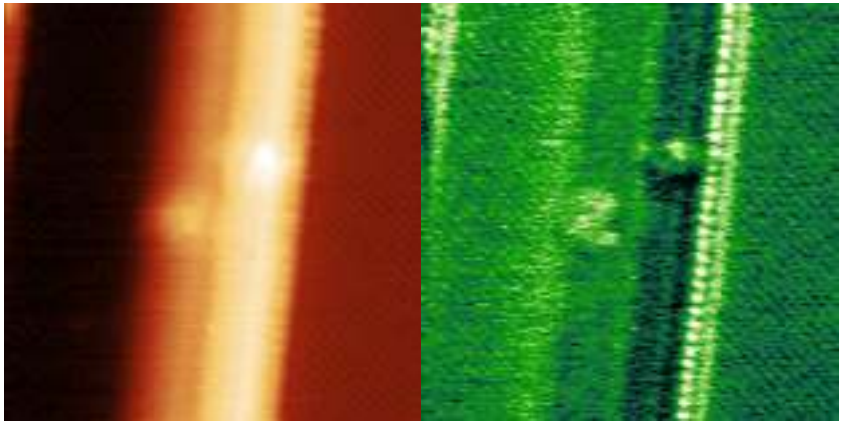
Cyano-porphyrins on 1Ml KBr



Si(111)



Au & porphyrins on Cu(111)/KBr



A. Sadeghi et al., Phys. Rev. B 86, 075407, (2012).
G. Elias et al., Beilstein J. of Nanotech. 2, 252-260, (2011).
S. Kawai et al., Nanotechnology 21, 245704, (2010).
L. Nony et al., Nanotechnology 20, 264014, (2009).
Th. Glatzel et al., Nanotechnology 20, 264016, (2009).
G. Enevoldsen et al., Phys. Rev. Lett. 100, 236104, (2008).
F Bocquet et al., Phys. Rev. B 78, 035410, (2008).

Overview 2

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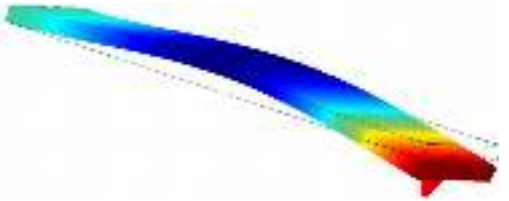
  - Experimental setup



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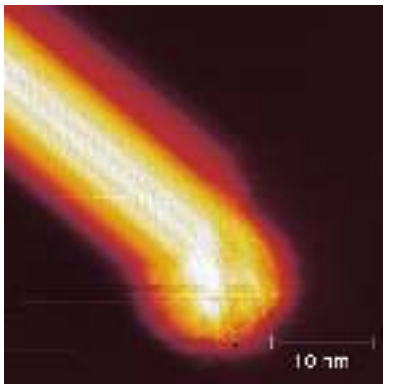

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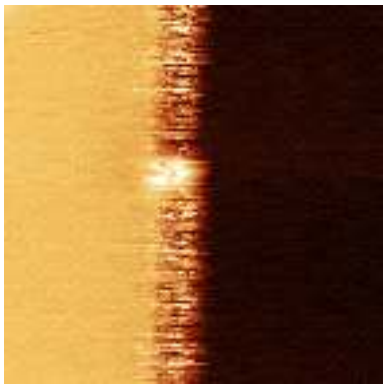
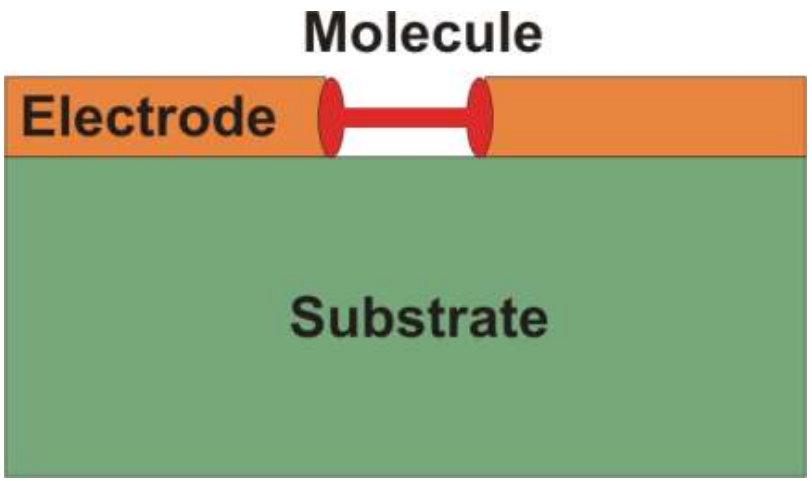
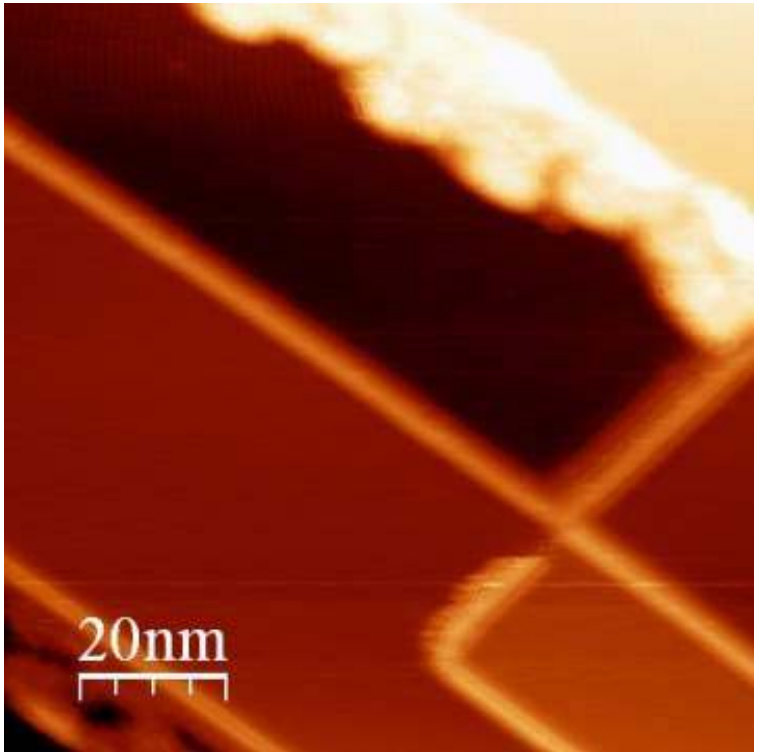


Motivation
Molecular electronics



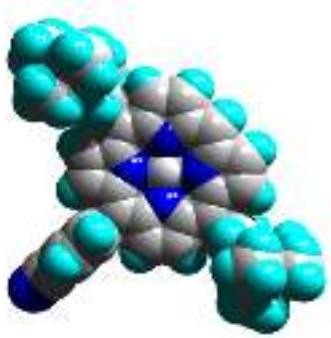


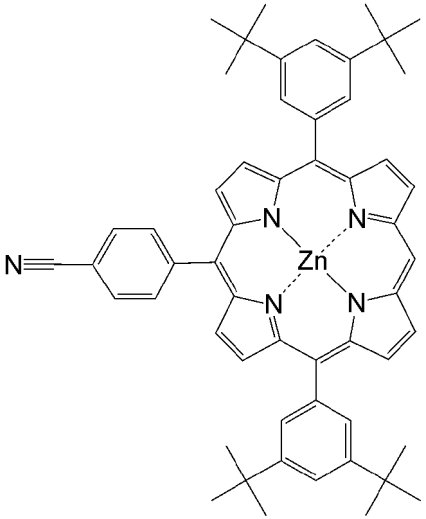
Molecules on Insulators:

- No STM possible – nc-AFM mandatory
- Low diffusion barrier but high intermolecular interaction
- Low temperatures – easier to “fix” molecules but not easy to find applications

Asymmetric Cyano-Porphyrins

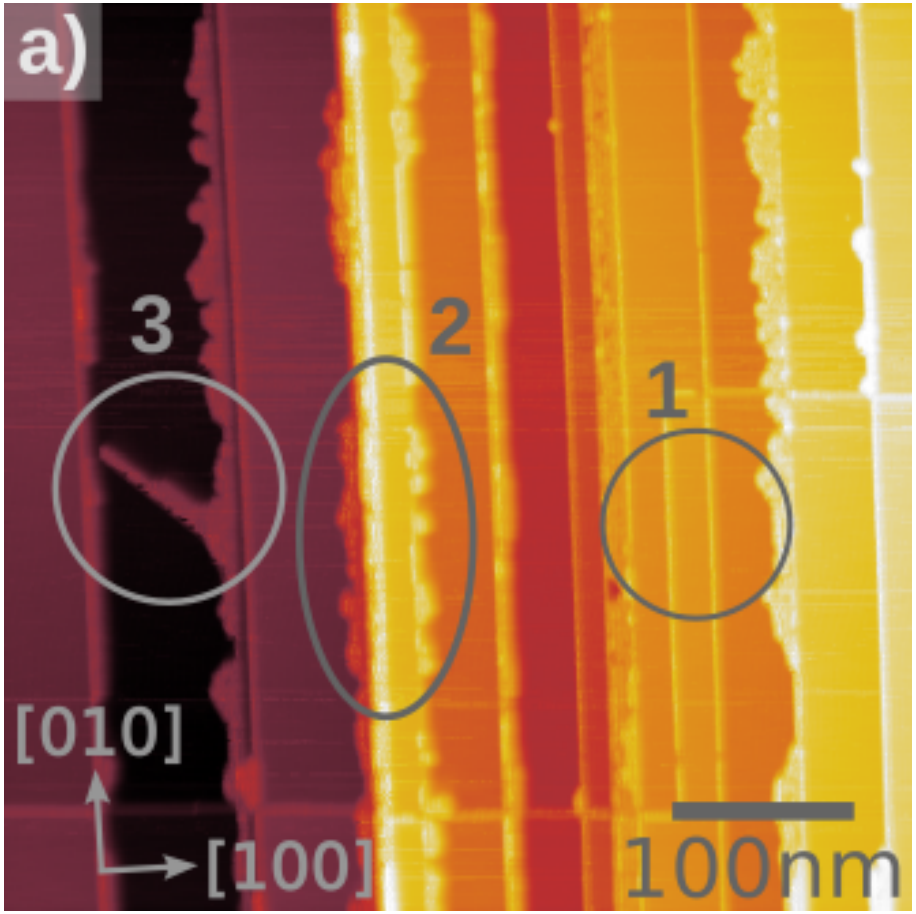
Structure and Wire Formation





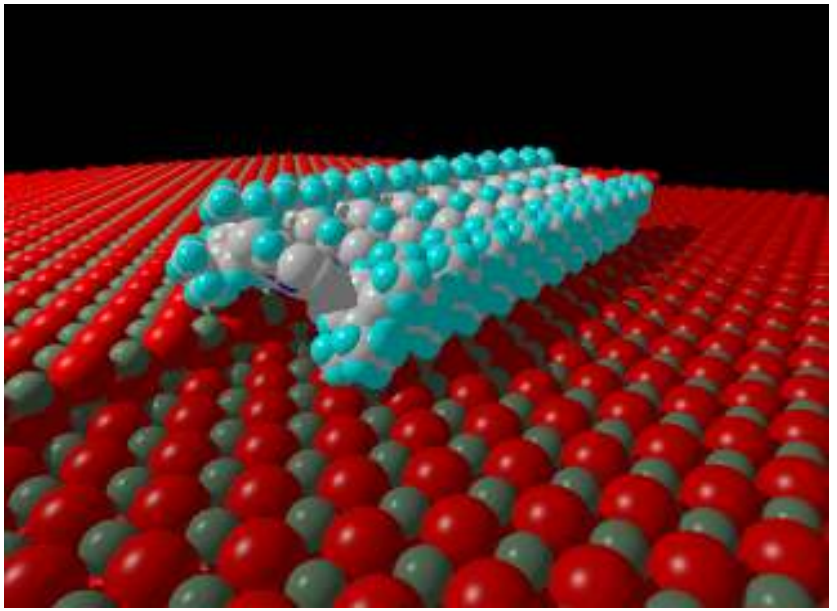
- able to π–π stack
- negative charge at the nitrogen atom induces a dipole (p ~ 4.37 D)
- two 3,5-di(tert-butyl)phenyl- groups act as spacers
- formation of mono-molecular wires
- structure growth across terraces

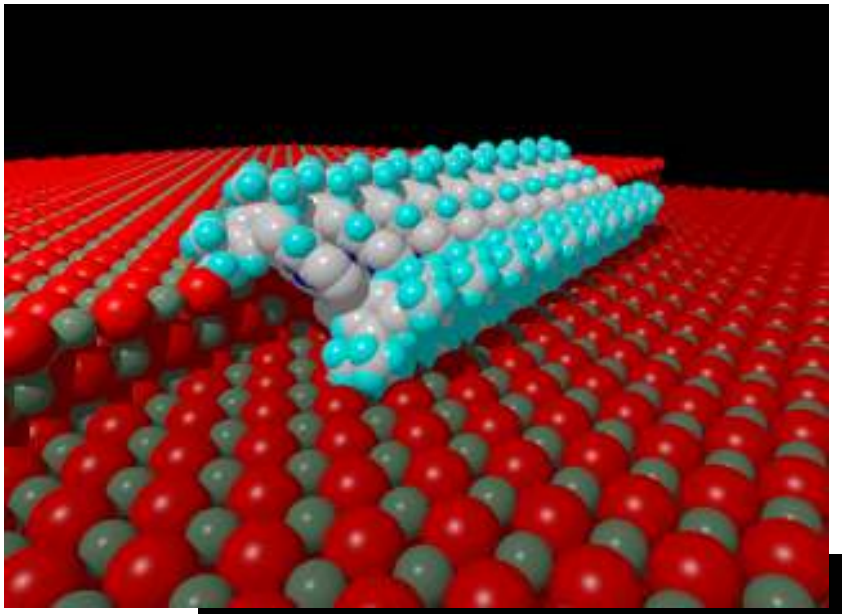
Wire Formation at step edges of KBr(001)

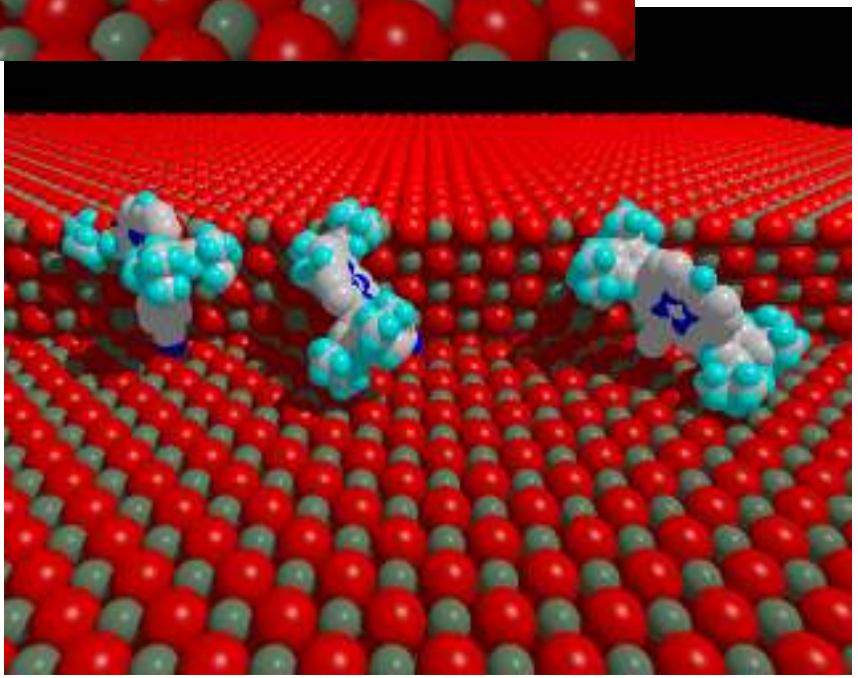


F. Cheng et al. Chem. Eur. J. 12, 6062-6070, (2006).
Th. Glatzel et al., Beilstein J. Nanotechnol. 2, 34-39, (2011).

Wire Formation
Structural model



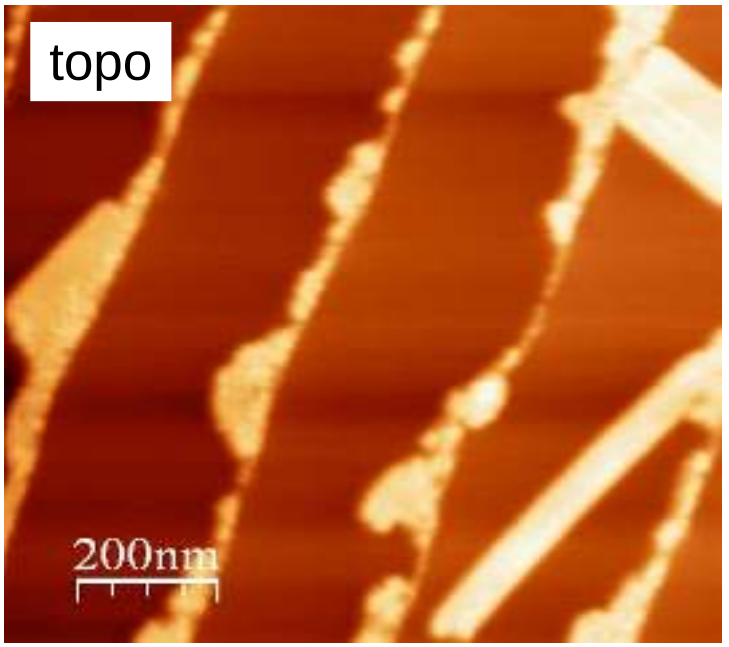




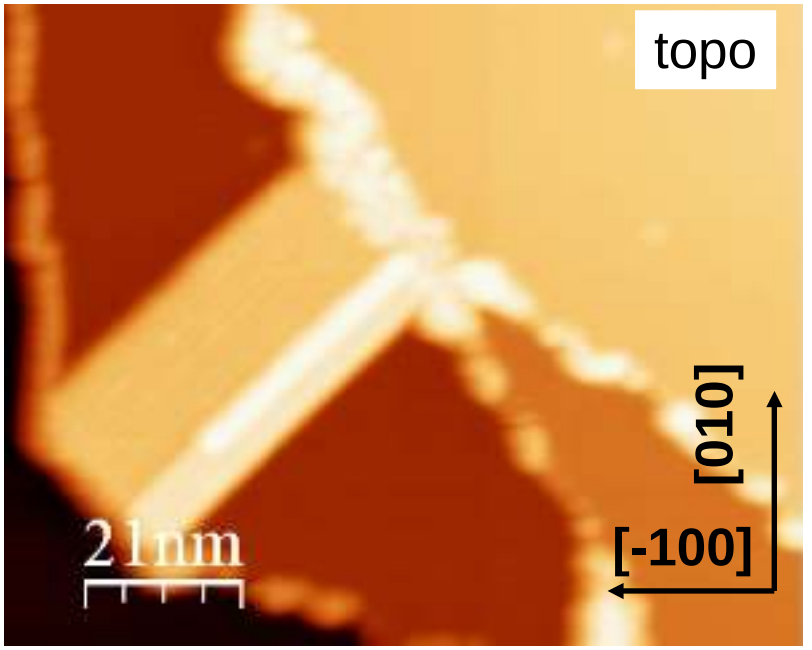
- tilt angle is determined by the side groups, the π–π stacking and the step height
- Steps higher than 3 ML prevent a π–π stacking

Th. Glatzel et al., Beilstein J. Nanotechnol. 2, 34-39, (2011).

Molecular Assemblies
Multiwires on KBr



$f_0 \approx 174054 Hz, \Delta f = -8 Hz, Q = 15k, A = 5nm$



$f_0 \approx 173886 Hz, \Delta f = -52 Hz, Q = 15k, A = 5nm$

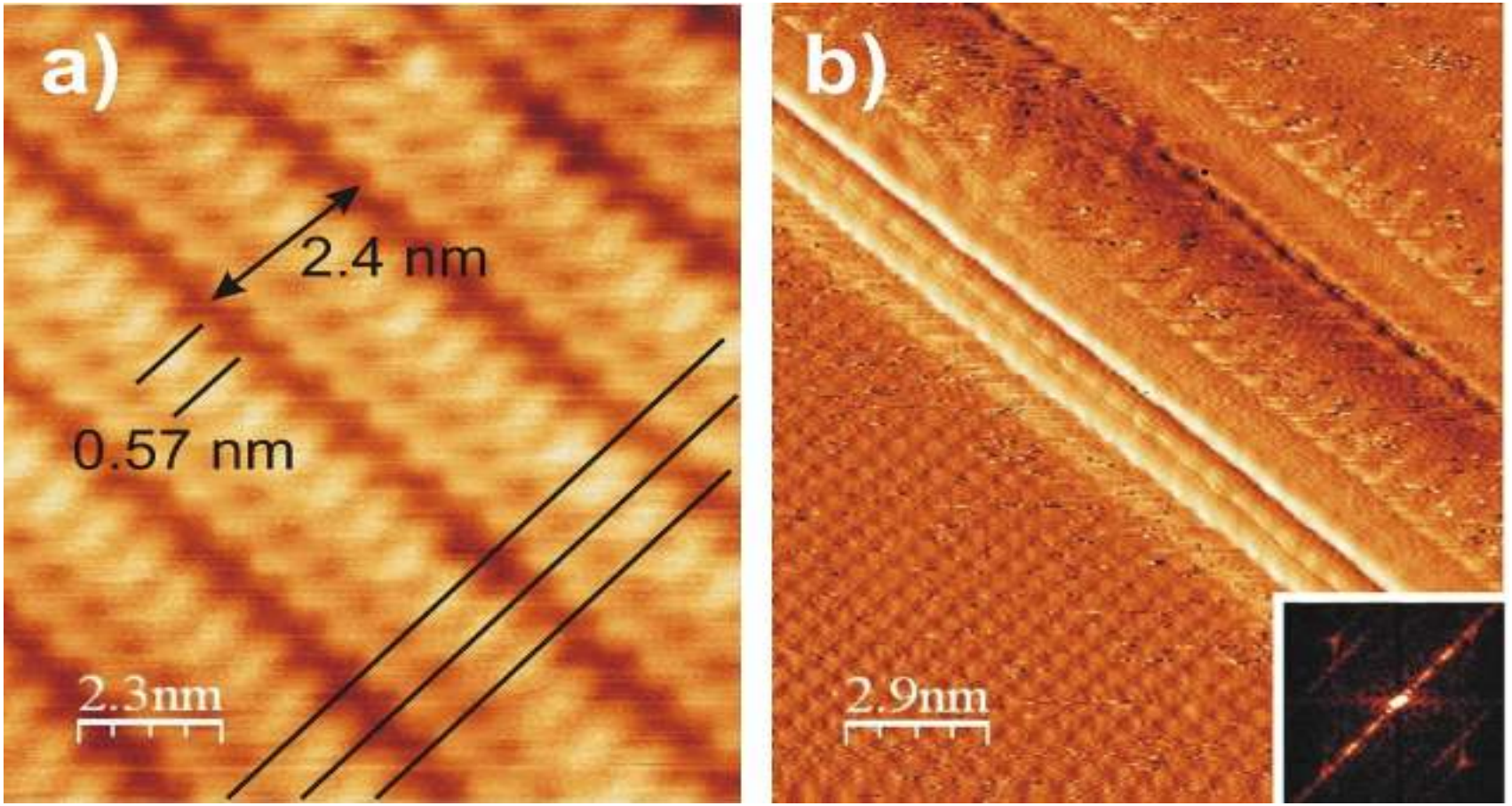
- Multiwire growth across terraces
- The <110> directions are preferred
- Different heights are visible

S. Meier, Th. Glatzel et al., Small, 2008, 4, 1115

Molecular Assemblies

High resolution imaging

Incommensurate growth in <110>

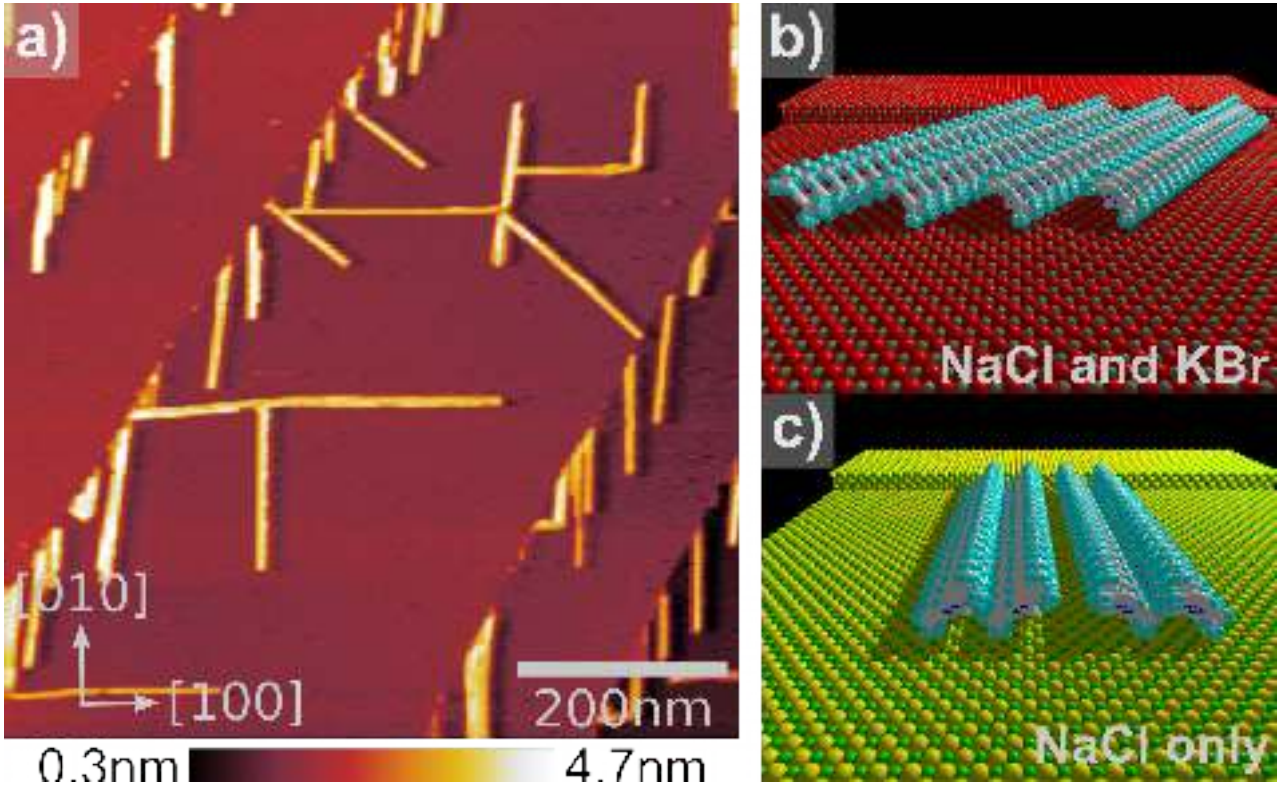


Distance between K^+ ions: <110>: 4.65 Å

<100>: 6.60 Å

S. Meier, Th. Glatzel et al., Small, 2008, 4,

Molecular Assemblies
Structural model

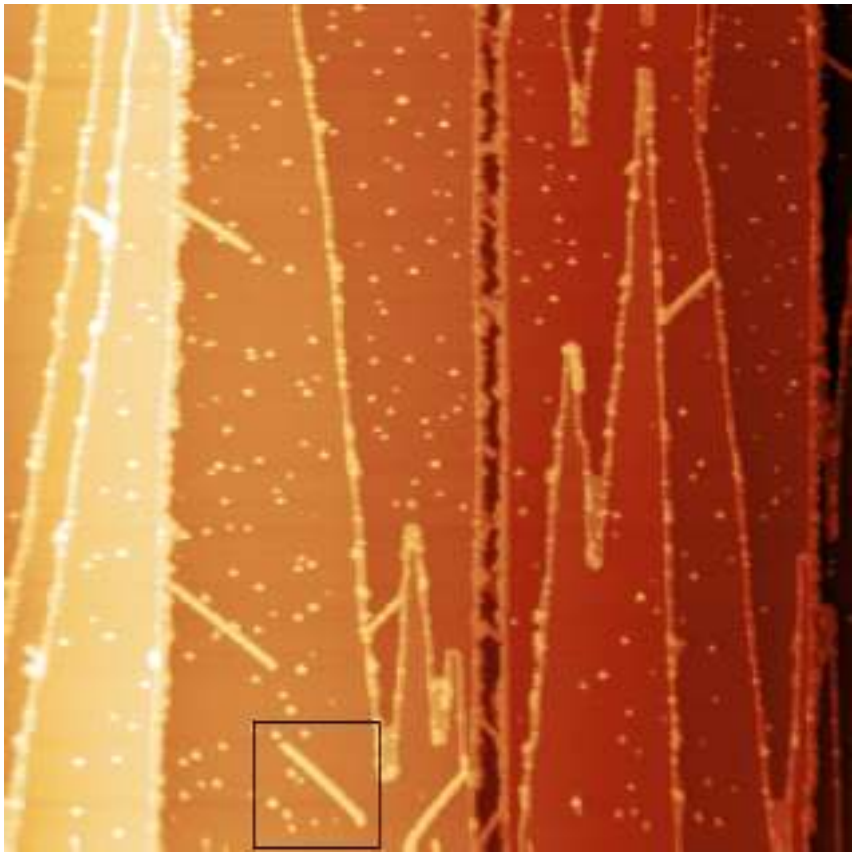


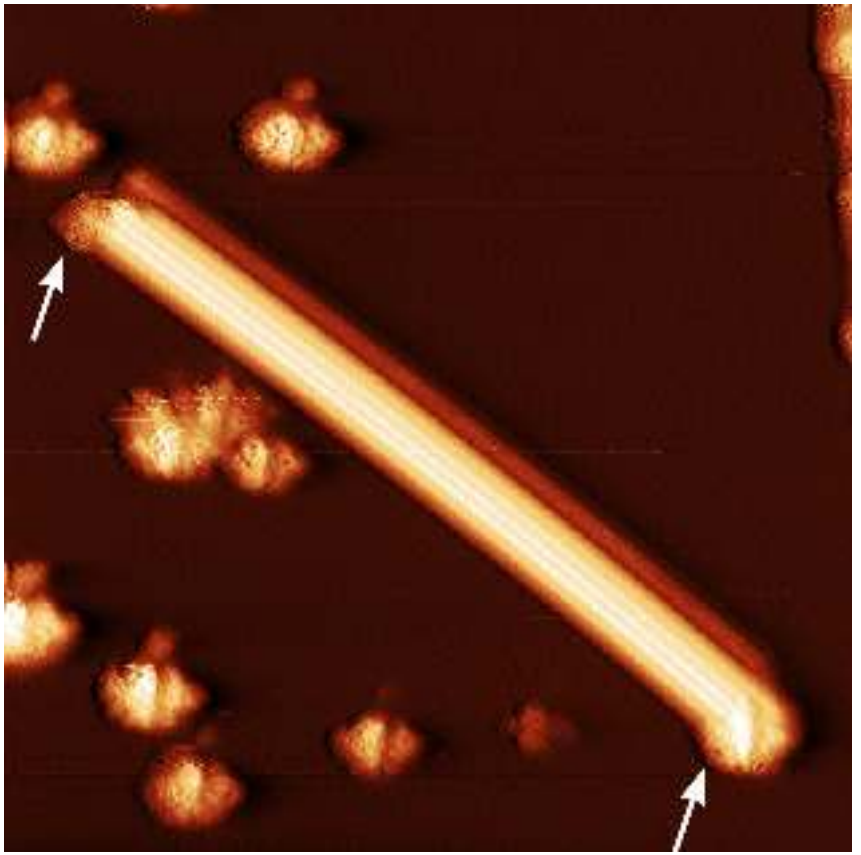
- Inter-molecular equilibrium separation ~ 5.7 Å
- Directed growth by the substrate
- Distance between Na^+ ions: <110>: 3.99 Å **<100>: 5.65 Å**
- Distance between K^+ ions: <110>: 4.67 Å <100>: 6.60 Å

Th. Glatzel et al., Beilstein J. Nanotechnol. 2, 34-39, (2011).

Contacting Molecular Assemblies

Au-Molecules-Au



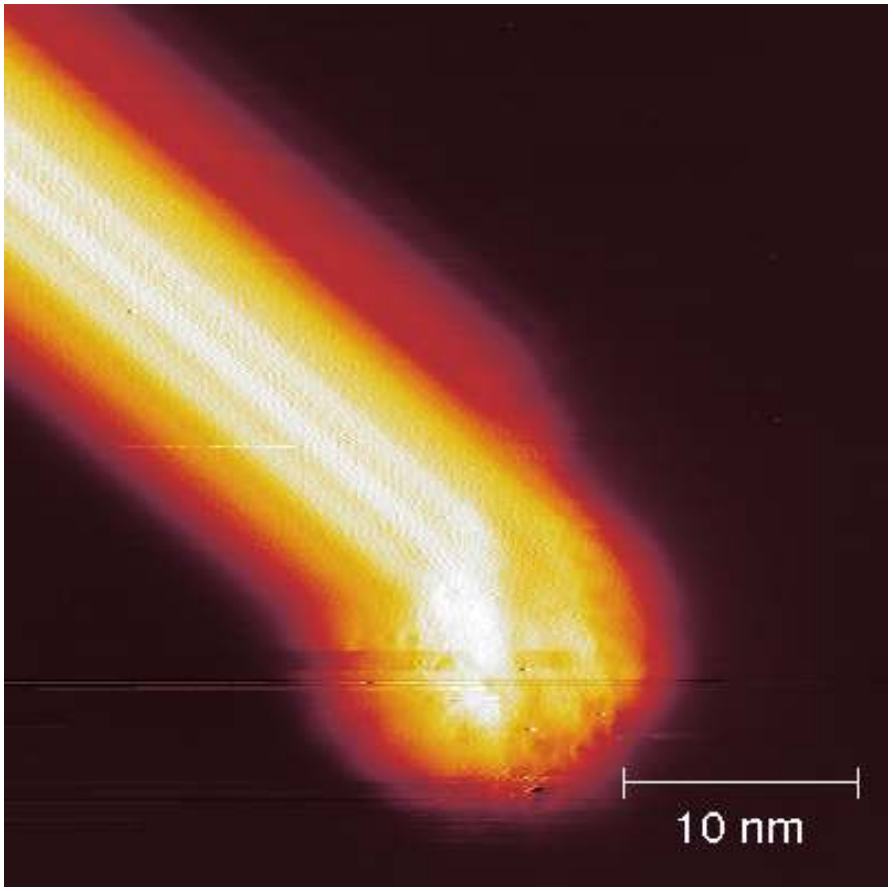


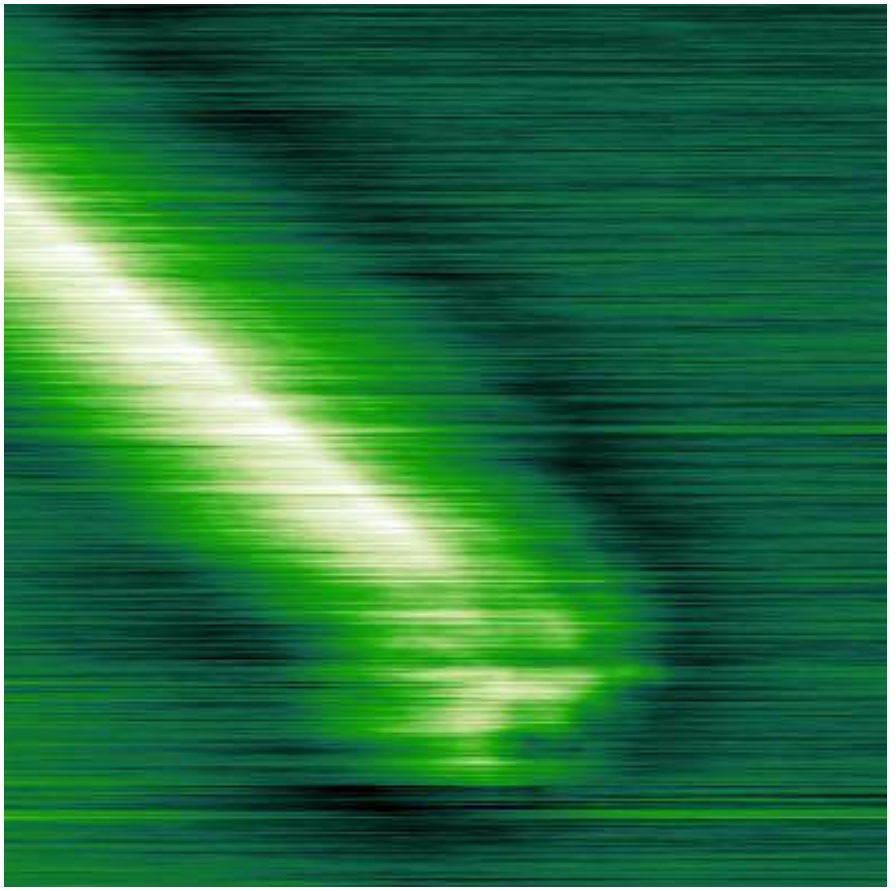
- Molecules arrange at steps and across terraces
- The growth is started/stopped at gold clusters.

Th. Glatzel et al., APL 94, 063303 (2009)

Interface of Molecules and Au

Topography and Surface Potential



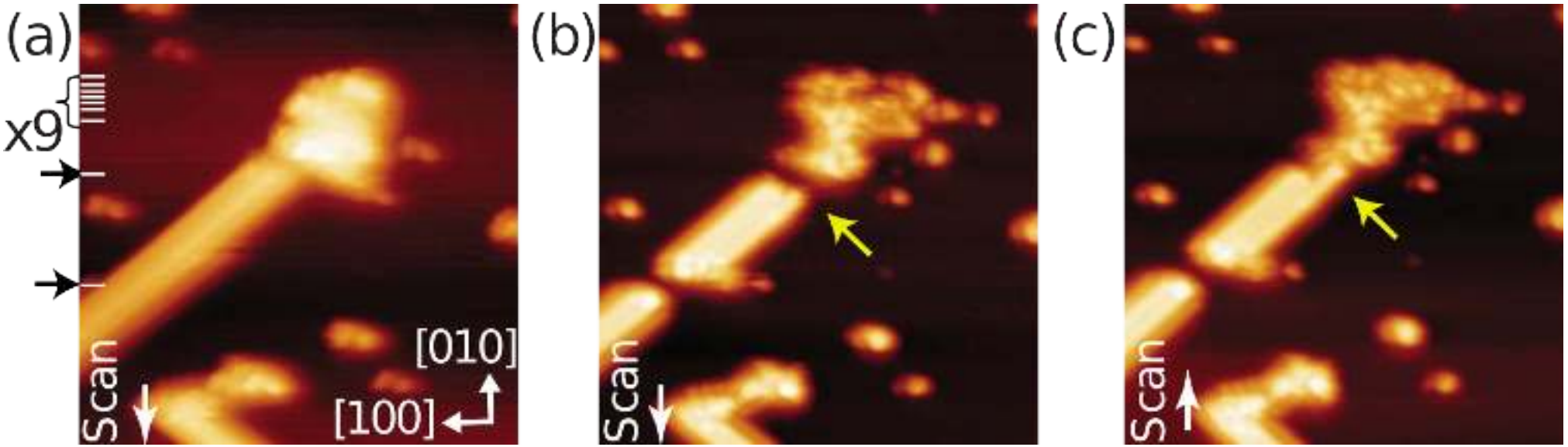


- 250 mV between the KBr surface and the Au nanoclusters
- 220 mV between Au nanocluster and the molecular wire

Th. Glatzel et al., APL 94, 063303 (2009)

Self-Healing of Molecular Wires

Topography

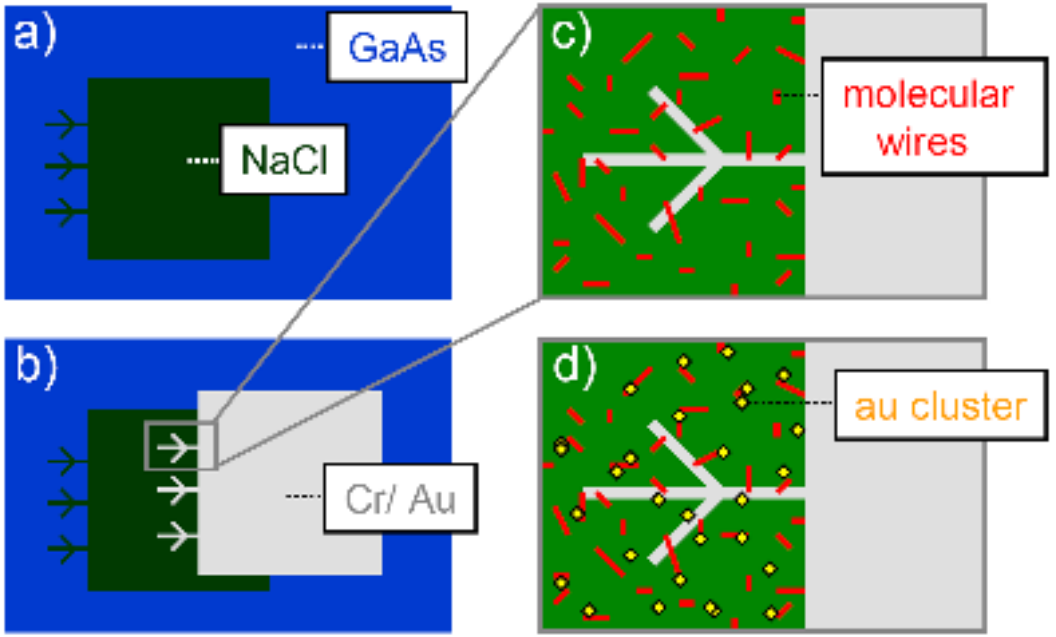


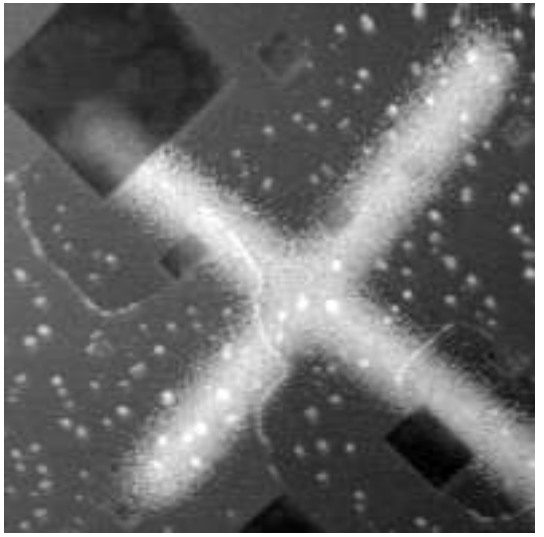
Parameter: 90x90nm^2, A = 5nm, γ = -0.5fN$\sqrt{m}$, V_{bias} = 0.43V

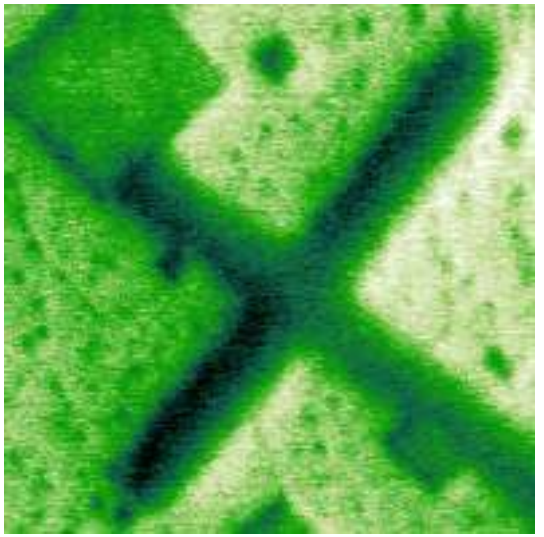
S. Kawai, Th. Glatzel et al., APL 95, 103109 (2009)

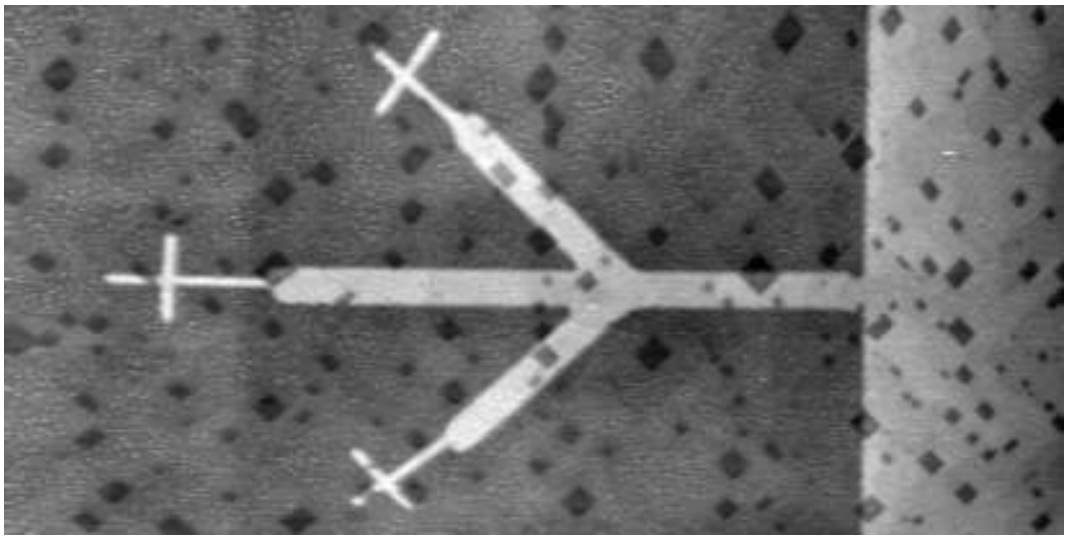
Contacting Molecular Assemblies

Nanostencil (IBM Rüschlikon)





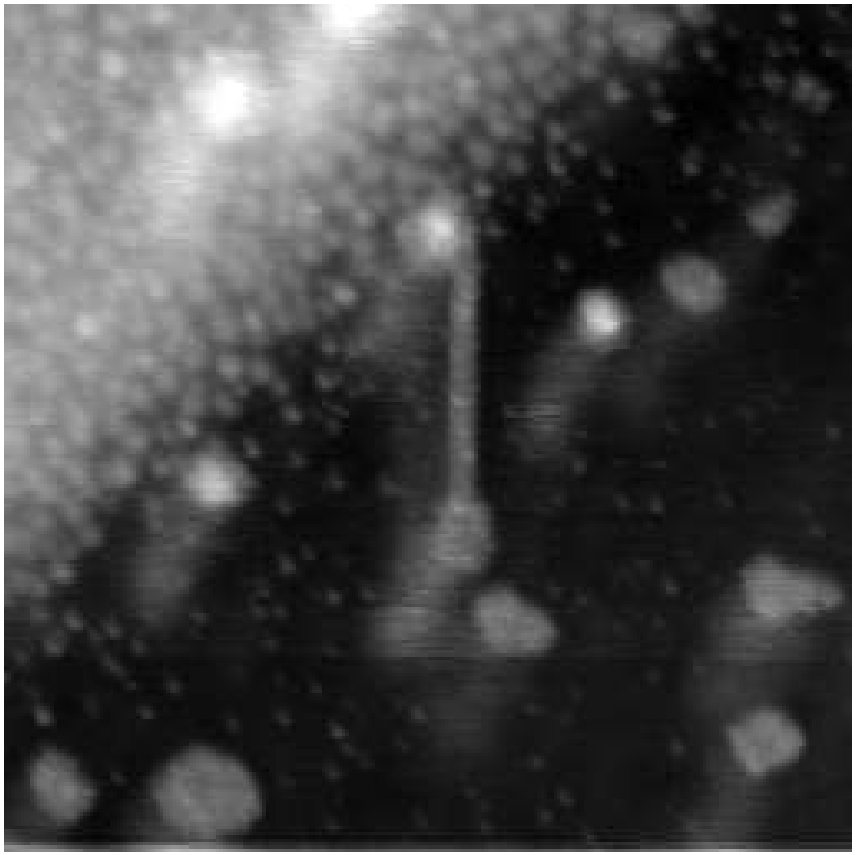




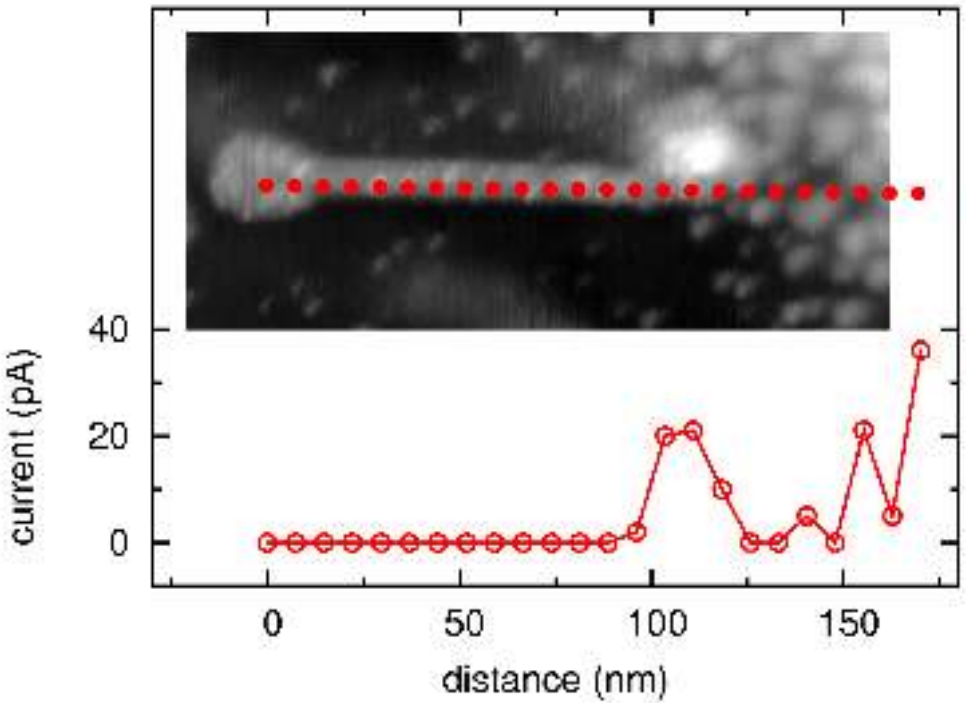
L. Gross, Th. Glatzel et al., J. Vac. Sci. Technol. B, 28, C4D34-C4D39, (2010).

Contacting Molecular Assemblies

Nanostencil (IBM Rüschlikon)



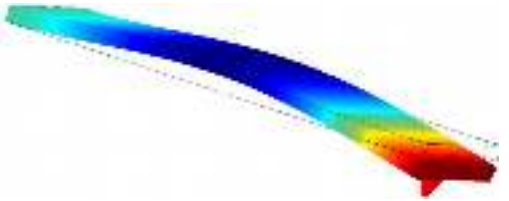
300x300nm^2



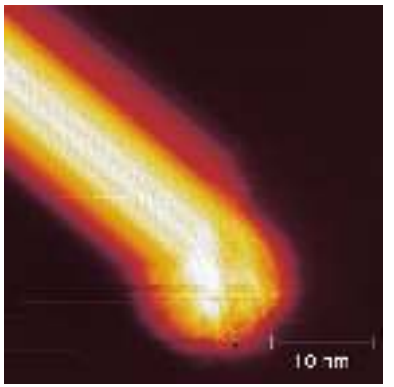
L. Gross, Th. Glatzel et al., J. Vac. Sci. Technol. B, 28, C4D34-C4D39, (2010).

Overview 2

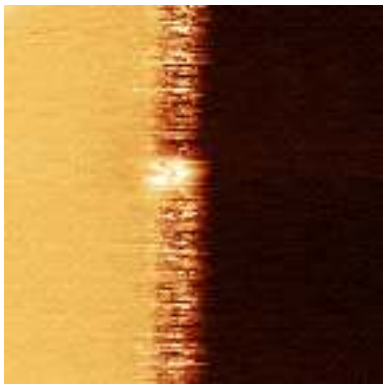
- **Kelvin Probe Force Microscopy**
  - Measurement principle
  - Experimental setup



- **Cyano-Porphyrin Wires**
  - Growth along step edges of KBr
  - Multiwire assemblies on NaCl and KBr
  - Contacting and cutting molecular wires



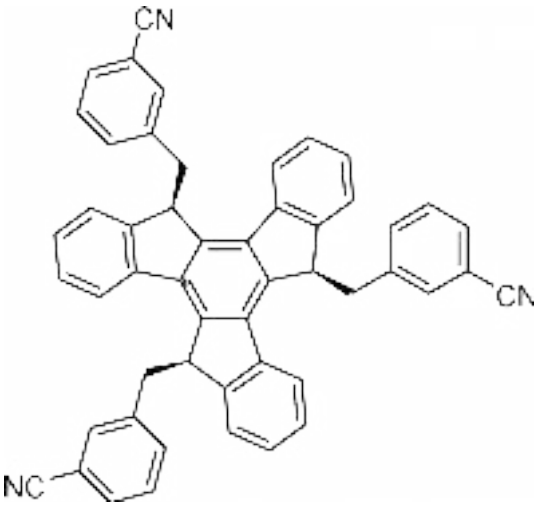
- **Truxenes**
  - Self assemblies on KBr crystals
  - Molecular structures on patterned surfaces
  - Reconstructing surfaces
  - Single molecule at room temperature

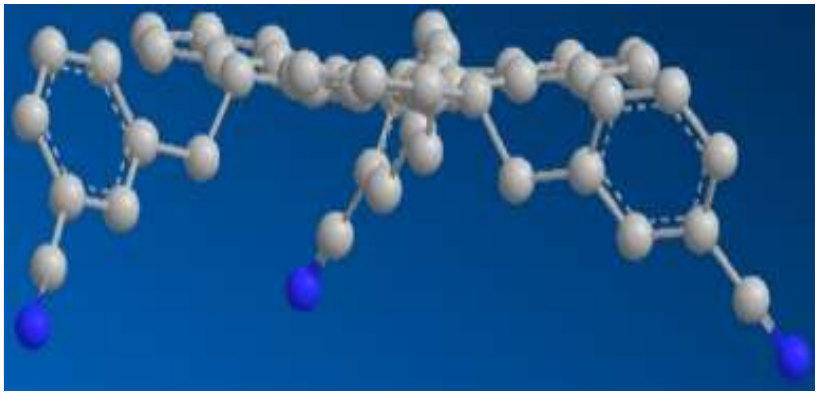


Truxenes on Patterned Surface

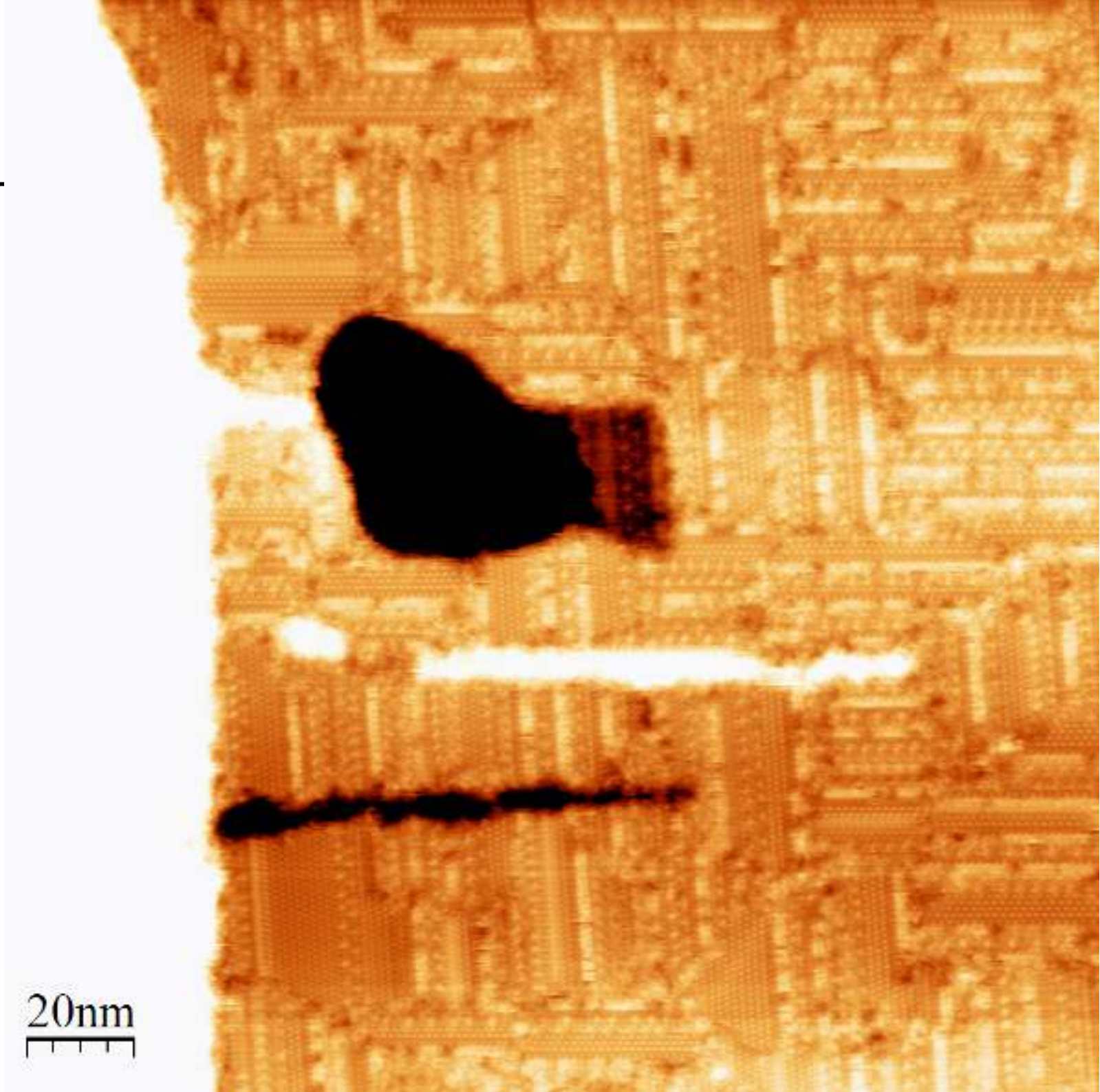
filled and unfilled pits measured at RT

- cooperation with A. Echavarren, Tarragona
- molecules has three CN groups
- better sticking to ionic surfaces expected





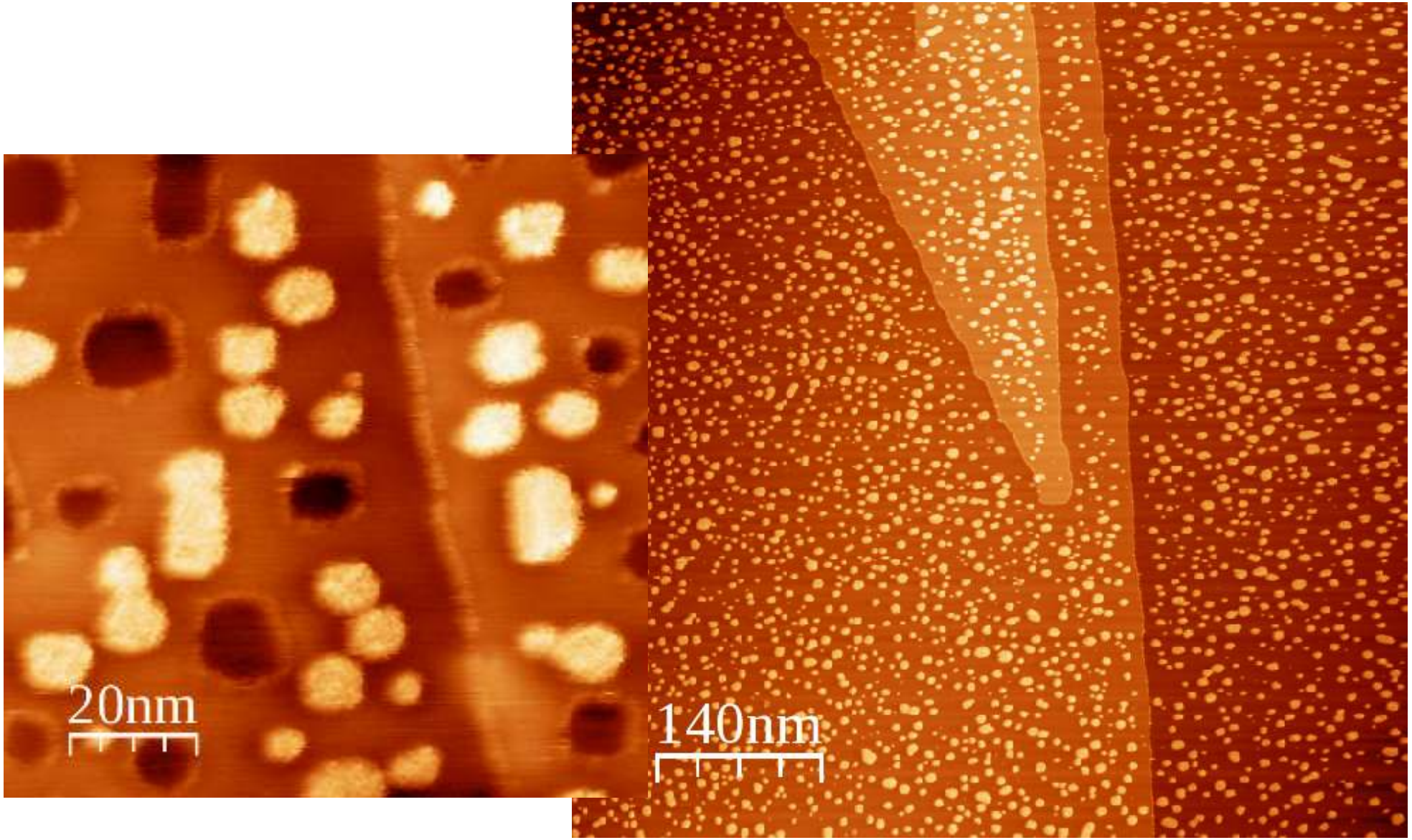
O. de Frutos et al., Chem. Eur. J. 8(13), 2879 (2002)



and the result of
post annealing at
155 C for 15 mins

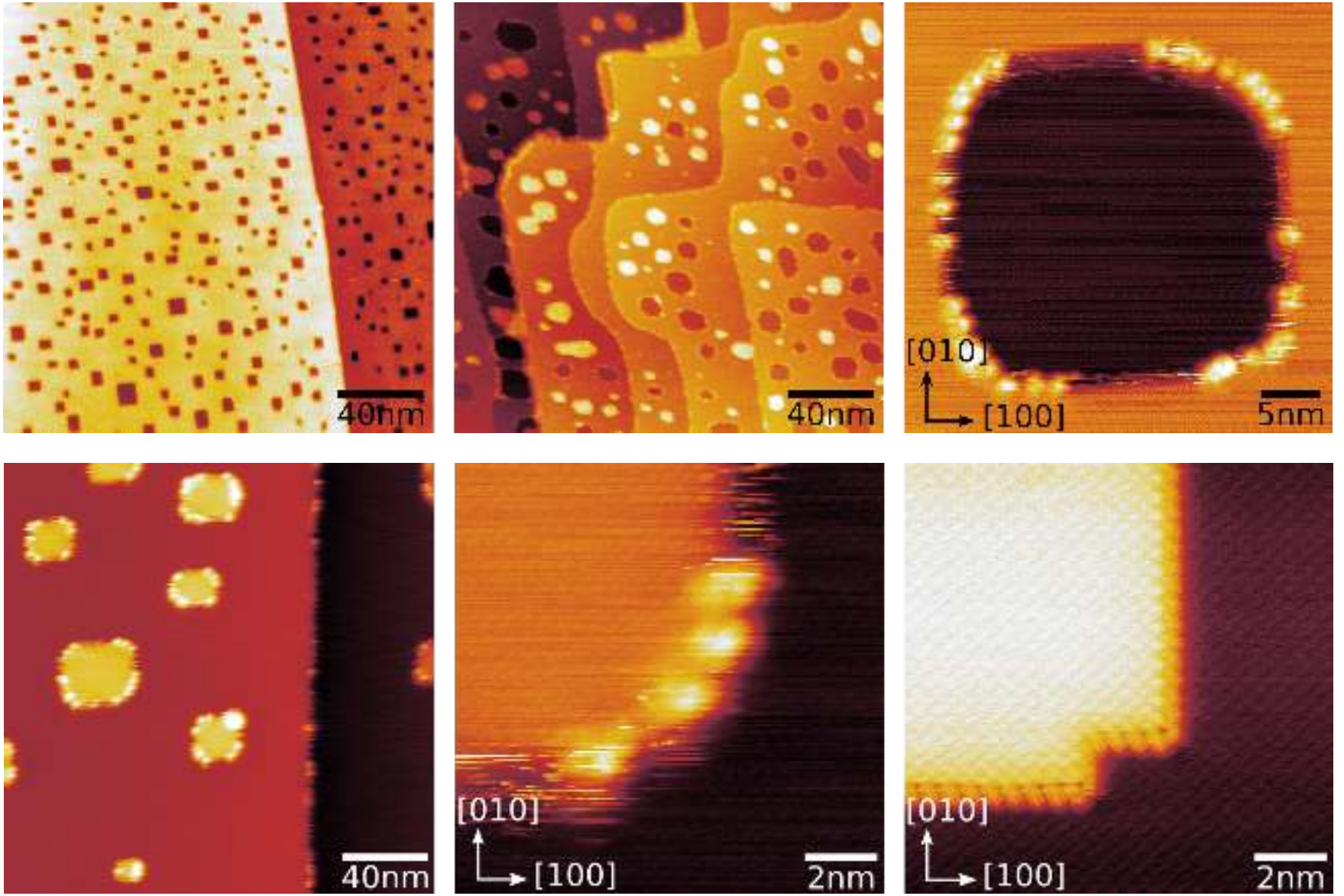
Truxenes on patterned surface

Filled and unfilled pits



Reconstruction of Ionic Surfaces

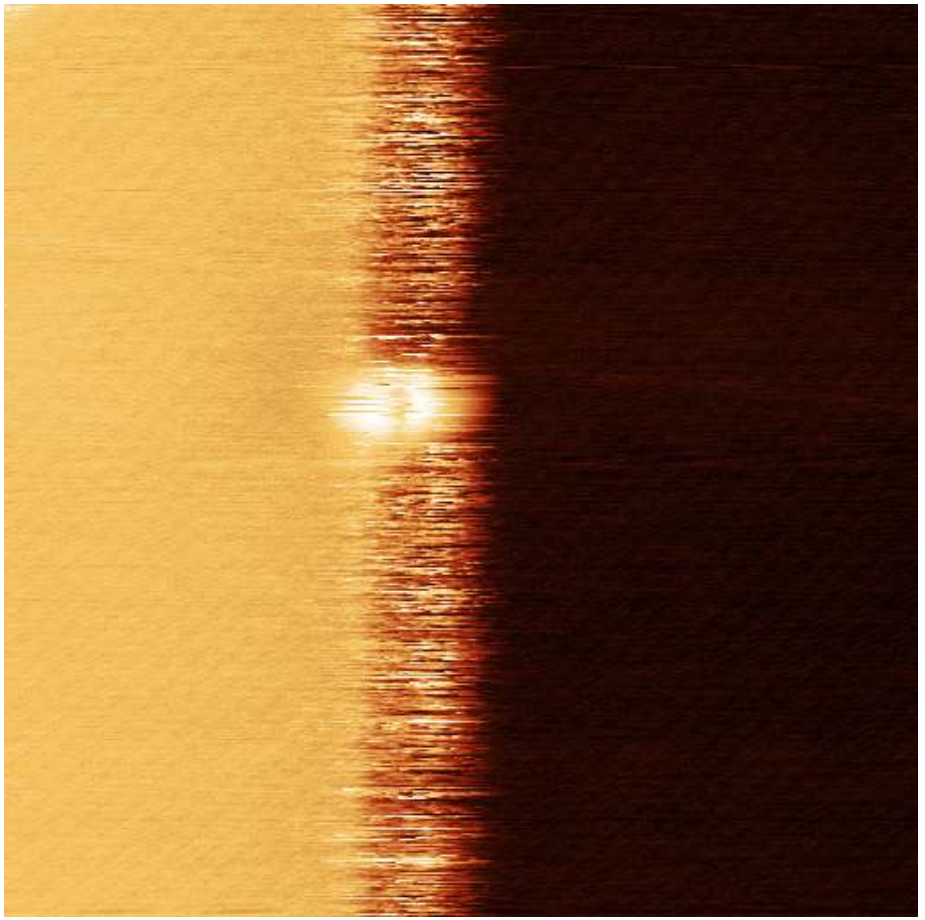
Truxene molecules

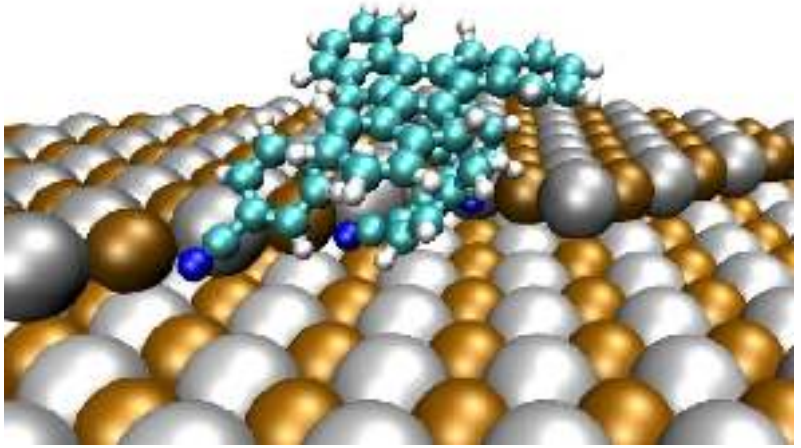


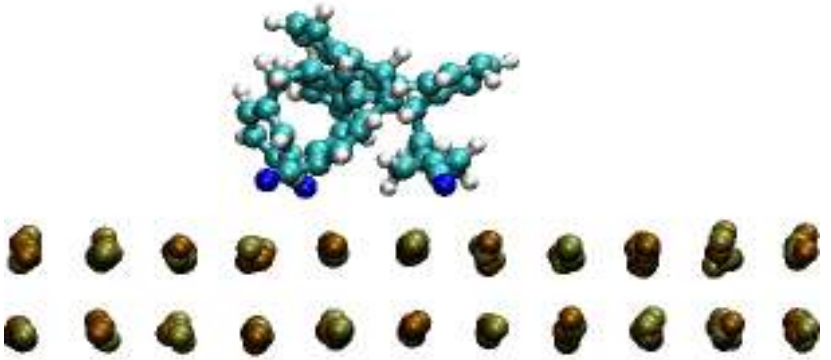
T. Trevethan, Th. Glatzel et al., Small 7, 1264, (2011)

Imaging a Single Molecule

Measurements at RT and Quantum Chemical Calculations







binding energies:

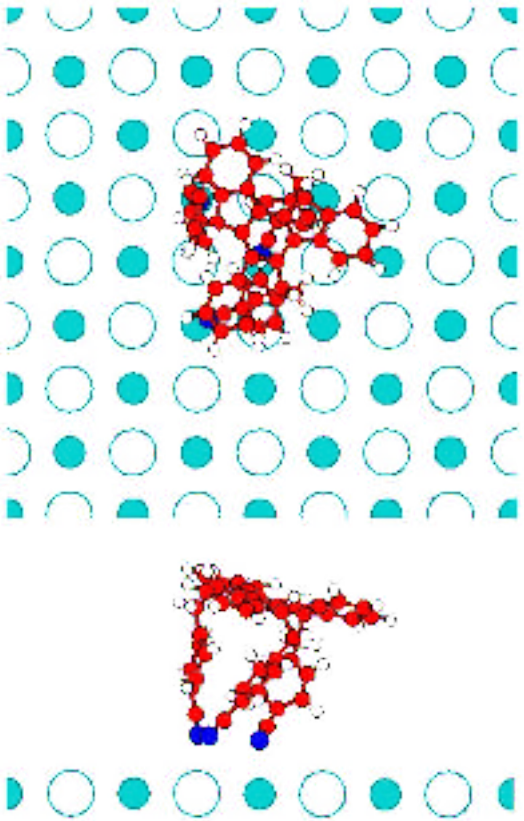
kink:	1.33 eV
step:	1.01 eV
surface:	0.42 eV

B. Such, Th. Glatzel et al. ACS Nano, 4, 3429-3439, (2010).

Calculations of adsorbed Truxenes

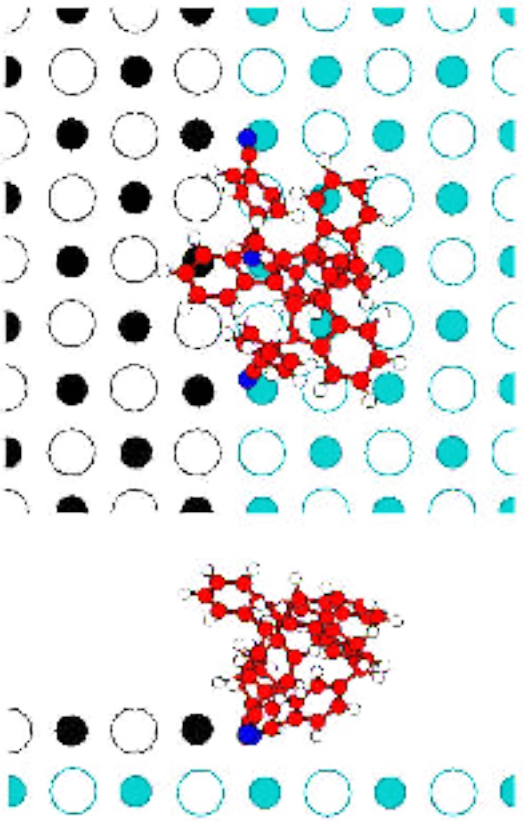
DFT calculations and MD simulations

perfect terrace



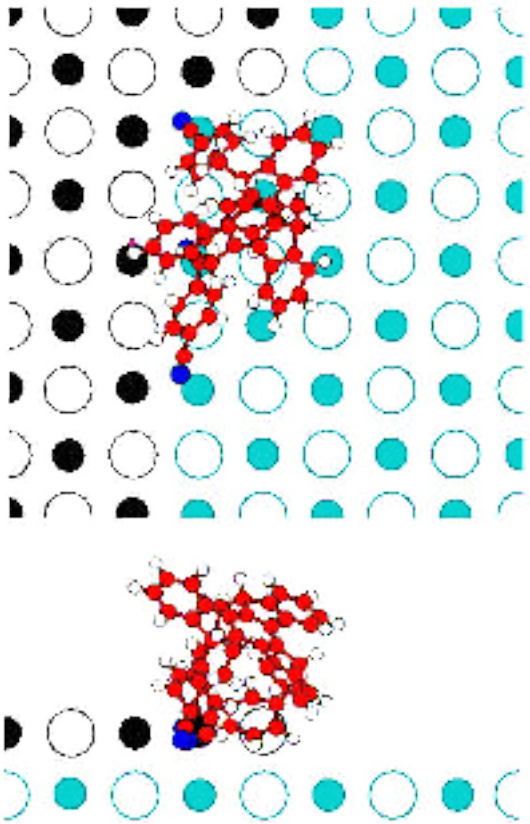
E_{bind} = 0.60eV

[100] step edge



E_{bind} = 1.01eV

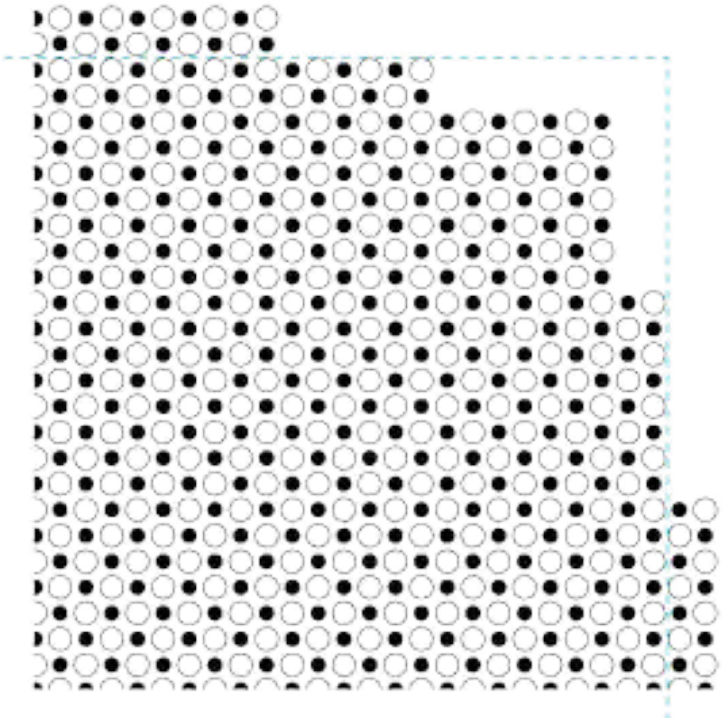
kink site

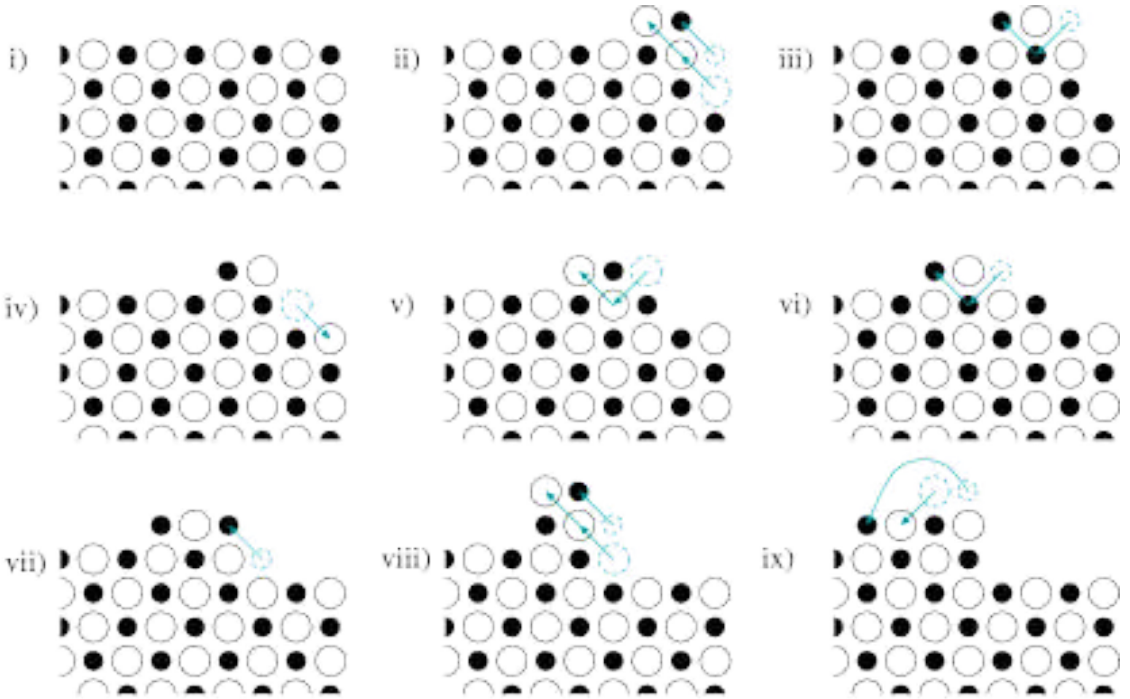


E_{bind} = 1.33eV

Potential Energy Change

Transforming the Island/Pit Structure





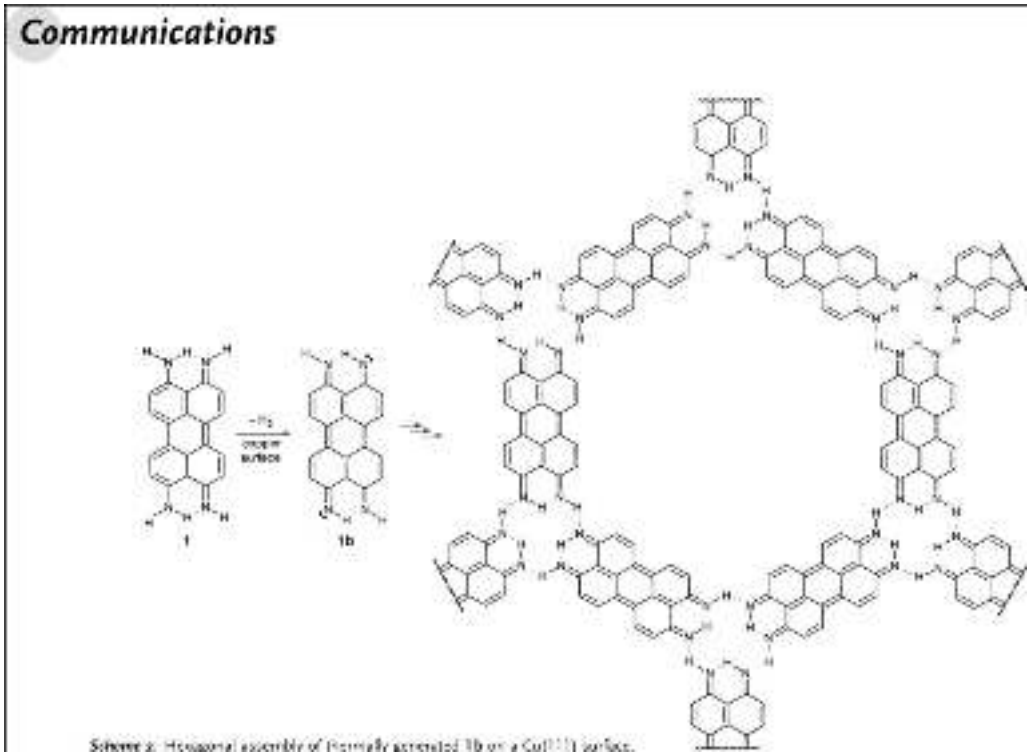
Potential energy to create a pair of kinks: - 0.44eV
Decoration by two or more truxene molecules: + 0.64eV

3D dynamic force spectroscopy at RT

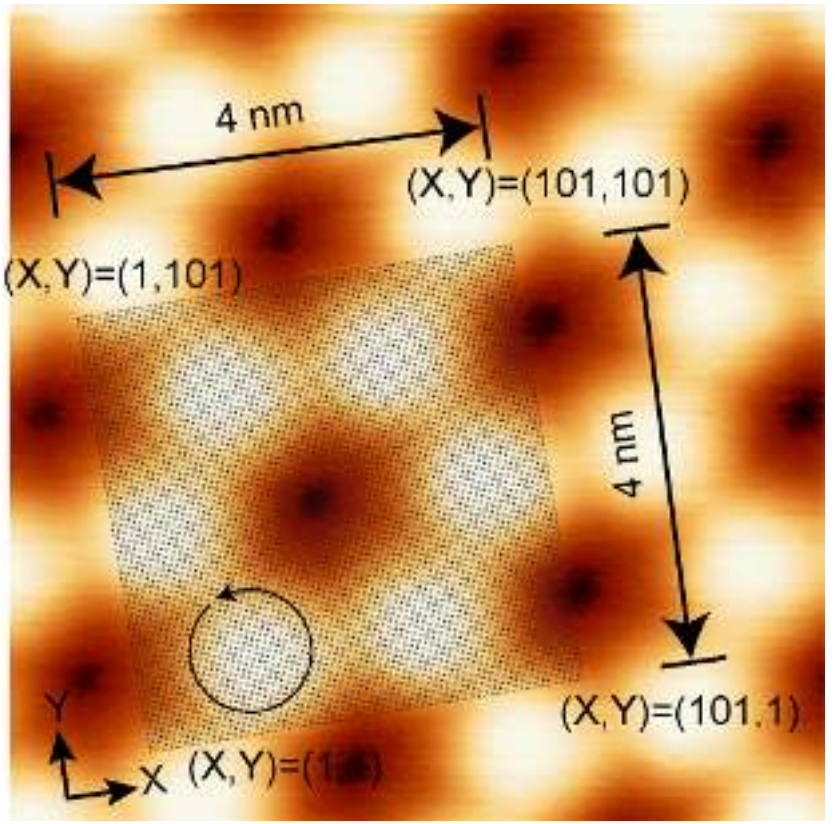
DPDI molecular network

$A_{2nd} = 400\,\text{pm}$ $A_{IR} = 50\,\text{pm}$

Cooperation with L. Gade, Th. Jung and M. Stöhr



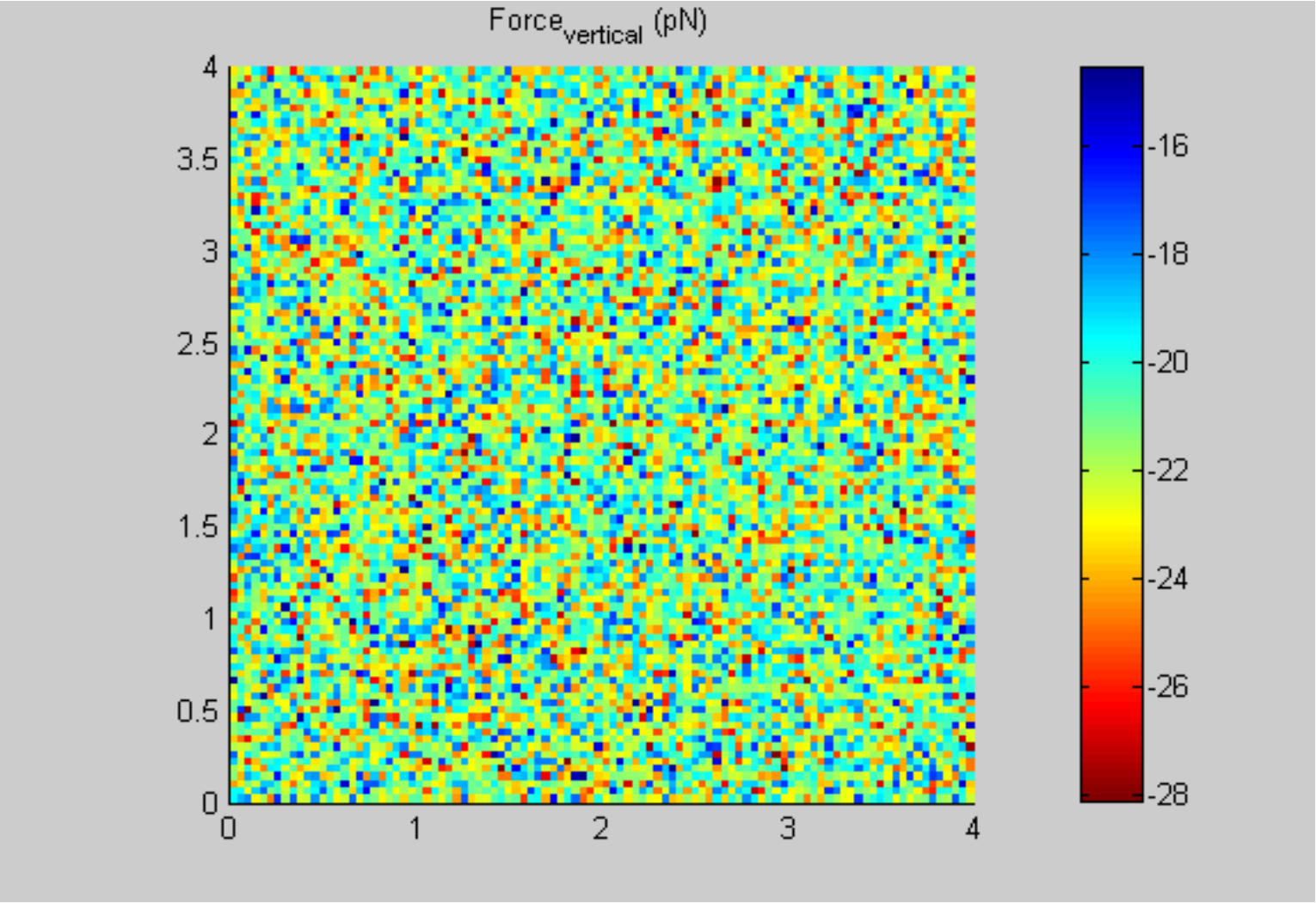
M. Stöhr; Angew. Chem. Int. Ed. 44, 7394(2005)



8 nm x 8 nm

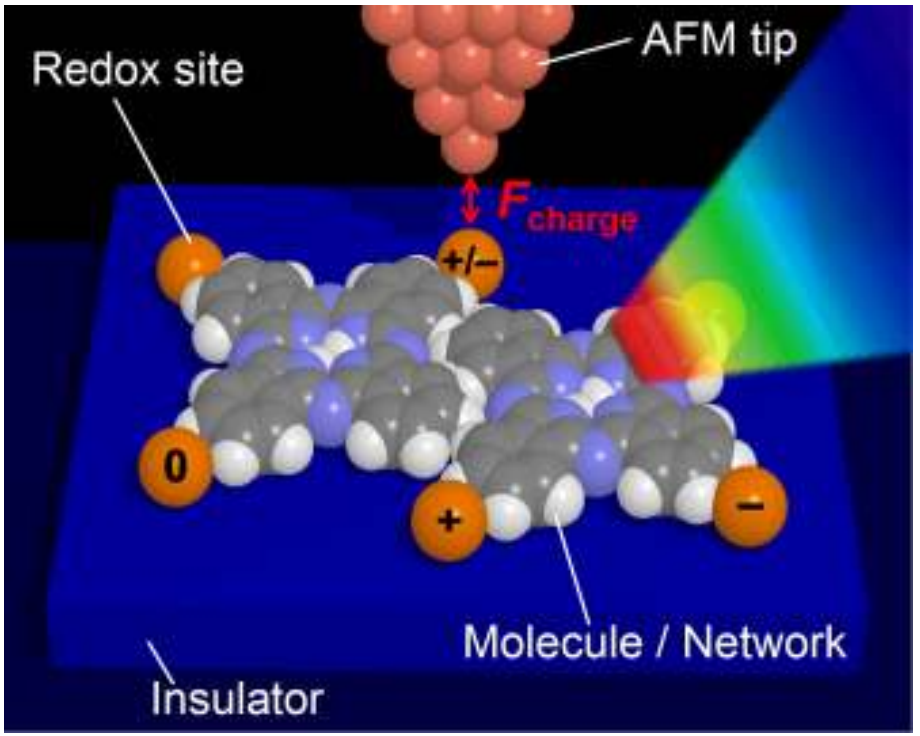
3D dynamic force spectroscopy at RT

DPDI molecular network



Conclusion

opto-electronic charge transfer processes in molecules



- locale surface potential at atomic scale - surface photovoltage
- transfer to room temperature
- stabilization and **manipulation** of molecules/atoms
- quantification of the observed signals (forces and energy)
- development of new measurement methods