Sfb 658 – A1

Freie Universität Berlin

02.05.2013

Molecules on metal surfaces investigated with scanning tunneling microscopy

A look into the project A1

Johannes Enslin

Outline

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1. Switches on surfaces
2. Basics of STM
3. Ring-opening and closing switches
   - Thermal induced switching
   - Photoinduced switching
   - Indentifying the isomers
4. Electron transport in molecular switches
   - Conductivity
   - Lifting up a molecule
   - Lifting of switches
5. Summary

Switches on surfaces

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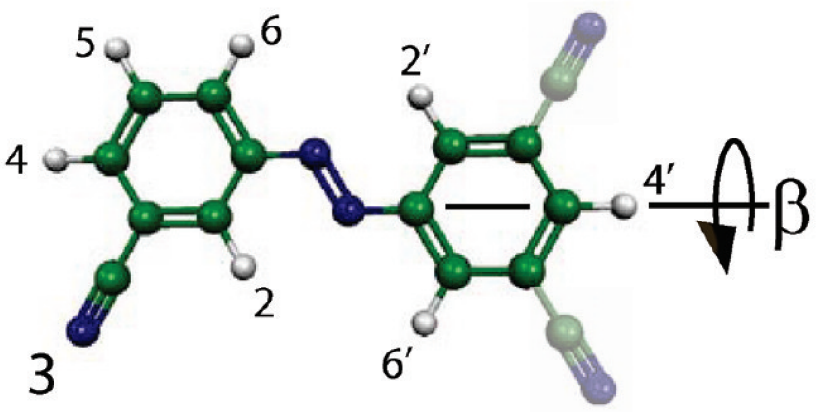
- Two meta-stable states
- Reversible switching
- External stimulus
- Surface affects switching ability
- Conformation can change
- Application of electrical contacts

DMC



N. Henningsen *et al*., J. Phys. Chem. Lett. **2**, 55 (2011).

- On Au tans-isomer stable
- On Cu cis-isomer stable (covalent bond of Azobridge to substrate)

  ⟹ No reversible switching

[Solution: DMC + Co on Au-surface]

Basics of STM

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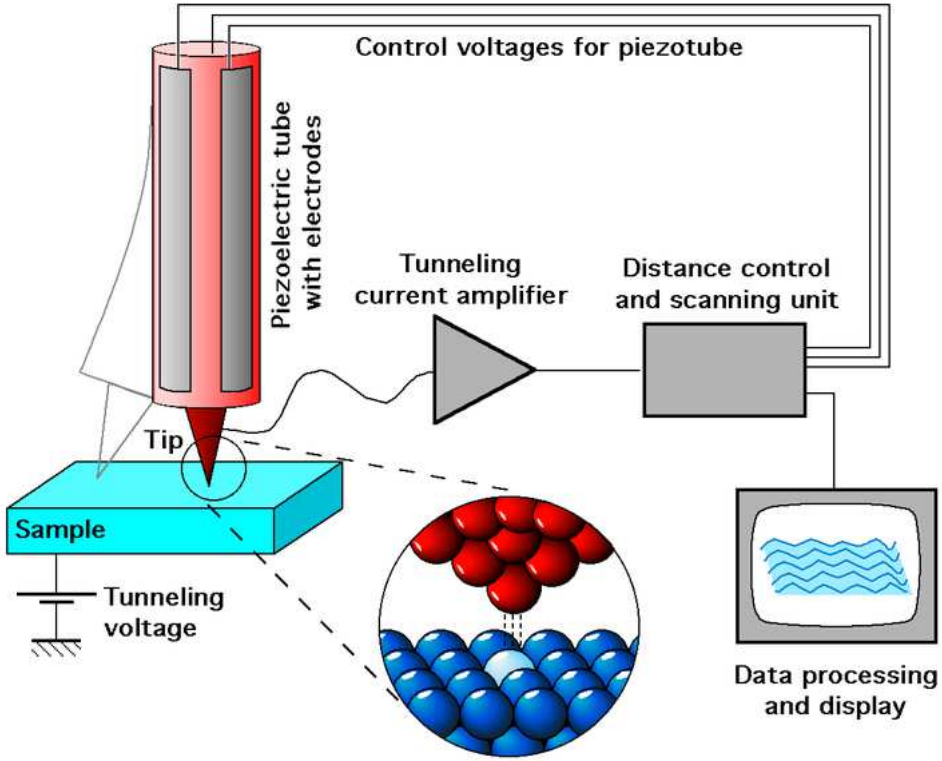
Scanning tunneling microscope



http://www.iap.tuwien.ac.at/www/surface/STM_Gallery/index

- Based on tunneling effect
- Distance tip-sample 5-10Å
- Voltage difference applied
- Ultra high vacuum
- Low temperatures (4K)

Basics of STM

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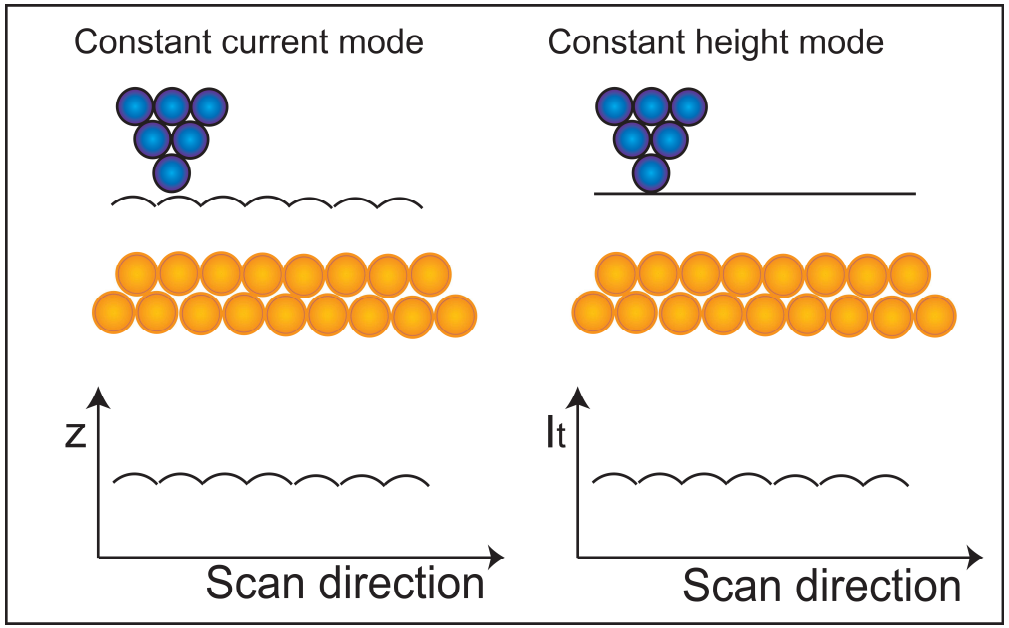
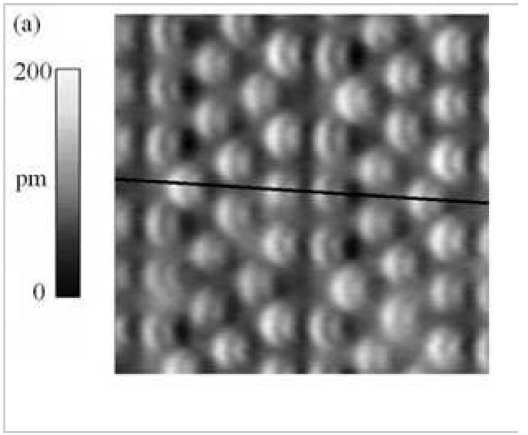
Topographic images



Fernández Torrente, Isabel: Local spectroscopy of bi-molecular self-assemblies (2008)

STM image of Si



Introduction to Scanning Tunneling Microscopy: Second Edition, C. Julian Chen, Oxford 2007

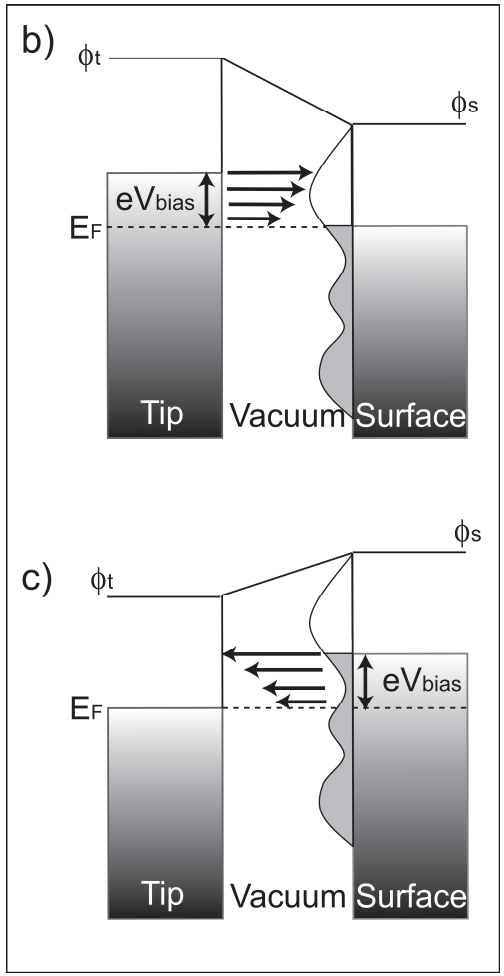
Constant current mode:

- Distance tip-surface adjusted
- Constant tunneling current

Constant height mode:

- Bias voltage constant
- Tip-sample distance constant
- Tunneling current observed

Basics of STM



Fernández Torrente, Isabel: Local spectroscopy of bi-molecular self-assemblies (2008)

- Positive sample bias
- Tunneling from tip to sample
- Occupied tip states
  ⟶ empty surface states
- Range of E_F to E_F+eV_{bias}

- Negative sample bias
- Tunneling from sample to tip

Basics of STM

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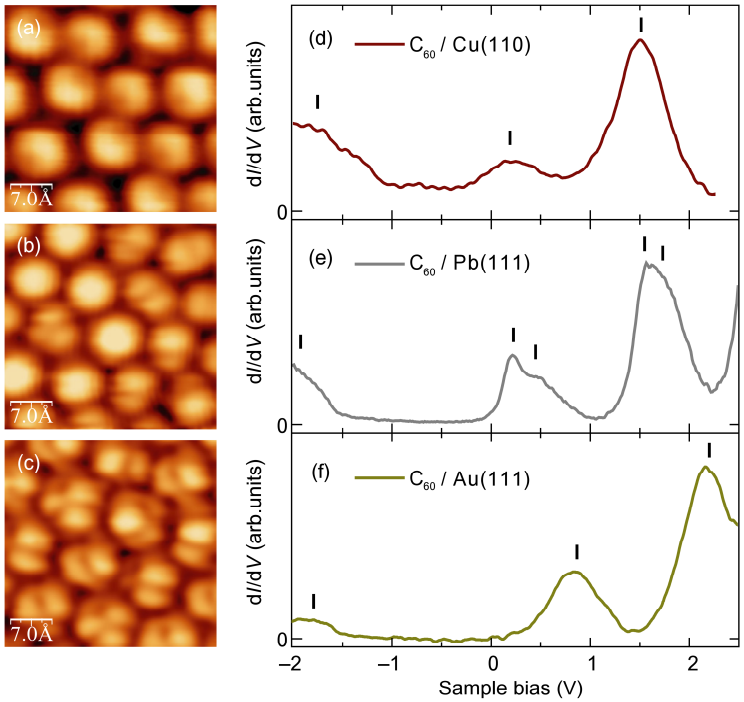
Scanning tunneling spectroscopy

STM and STS measurements of C_{60} on metal surfaces

Cu

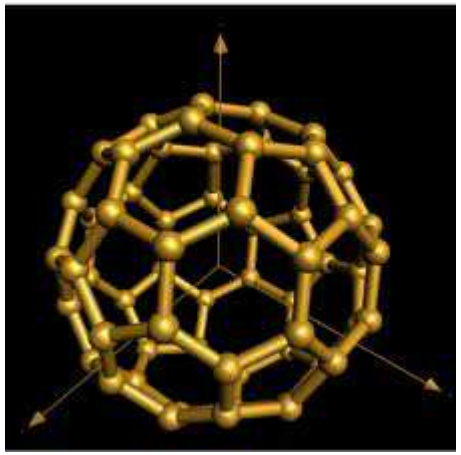
Pb

Au



G. Schulze *et al.*, NJP **10**, 065005 (2008).

- Local information
- Electronic, vibronic, magnetic properties
- Identification of molecules/isomers
- Characteristic fingerprints
- Identification of LUMO (+1)



www.hopf.chem.brandeis.edu

Outline

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1. Switches on surfaces
2. Basics of STM
3. Ring-opening and closing switches
   - Thermal induced switching
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Ring-opening and closing switches

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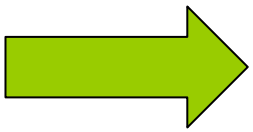
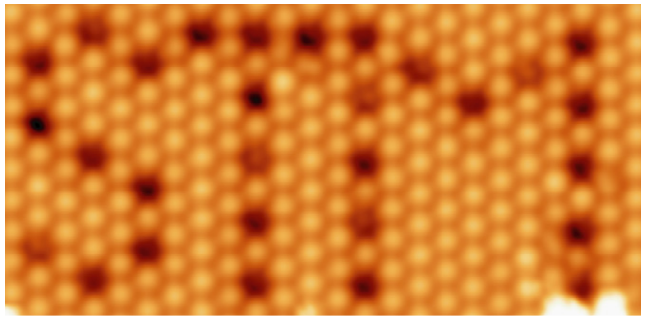
How to identify open or closed isomers on surfaces:

Observe:

- Change of electronic configuration
- Change of geometry (unit cell)
- Change of location of orbitals
- Change of conductivity





- High resolution
- STM as tool
- Combination of STM and AFM

G. Schulze *et al.*, NJP **10**, 065005 (2008).

Ring-opening and closing switches

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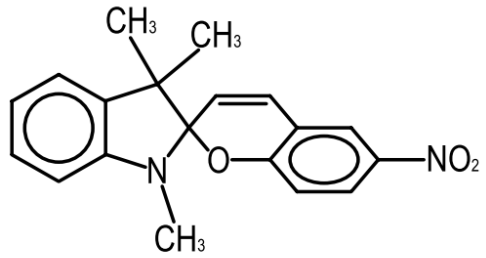
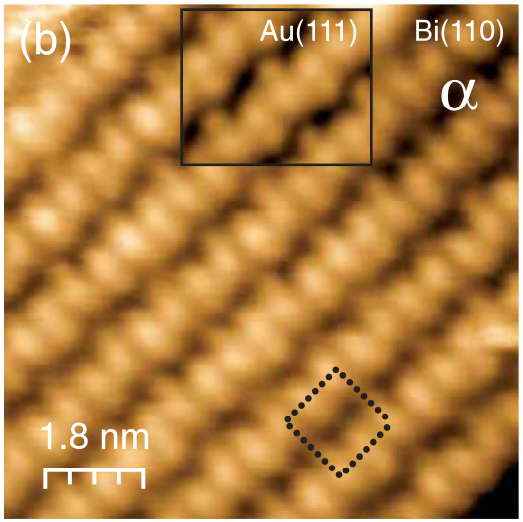
Ring-opening and closing of Spiropyran monolayers on a Bi surface

Spiropyran (SP)



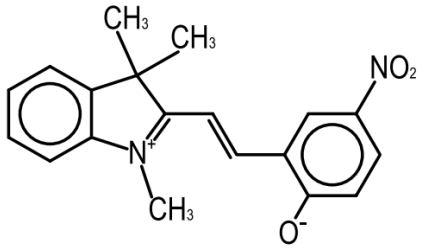


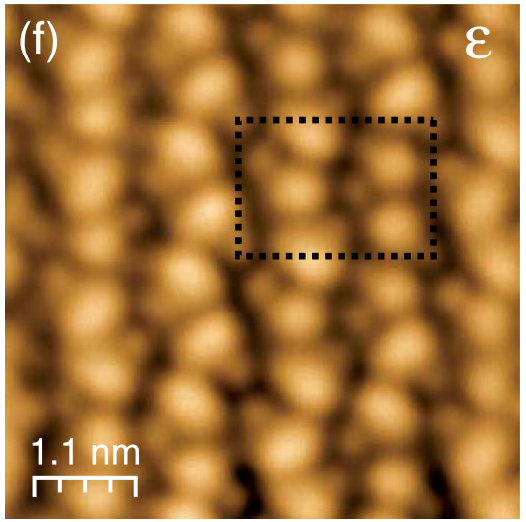
Exposure with blue laser light

Or thermal energy

Images here: Thermal energy

Merocyanine (MC)





Pictures: G. Schulze *et al.*, Phys. Rev. Lett. **109**, 026102 (2012).

Ring-opening and closing switches

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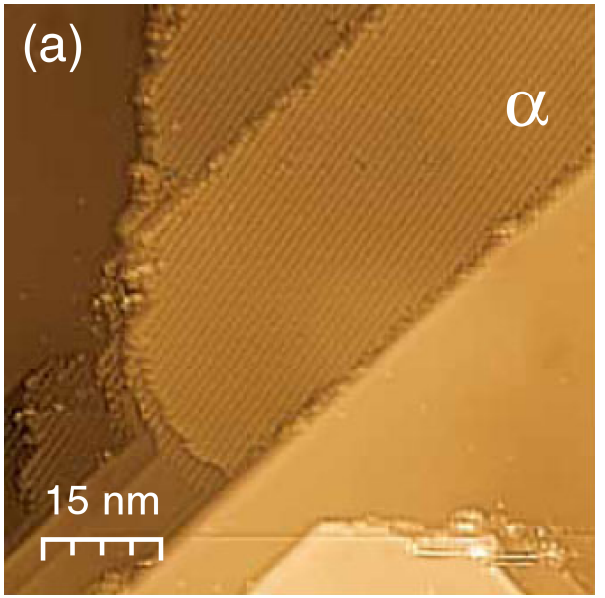
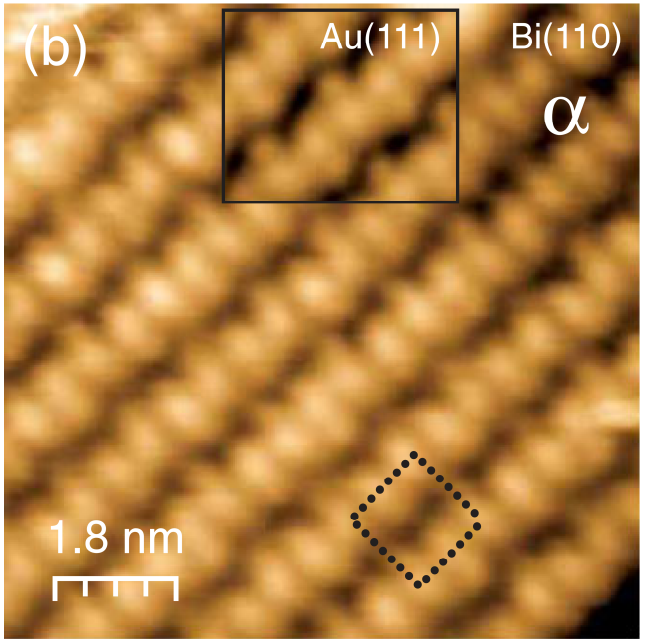
Temperature induced switching:

- Self-assembled islands
- Similar to SP on Au(111)
- Temperatures below 270K



Self-assambled SP- islands



Pictures: G. Schulze *et al*., Phys. Rev. Lett. **109**, 026102 (2012).

Ring-opening and closing switches

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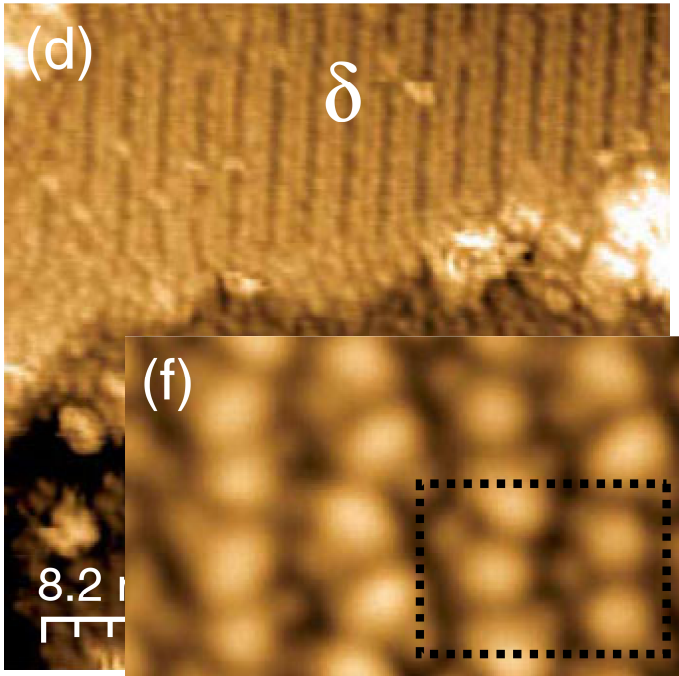
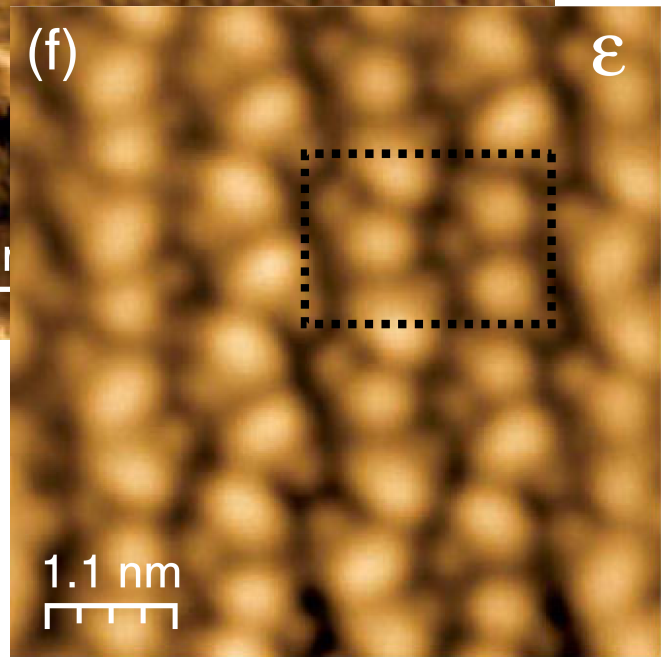
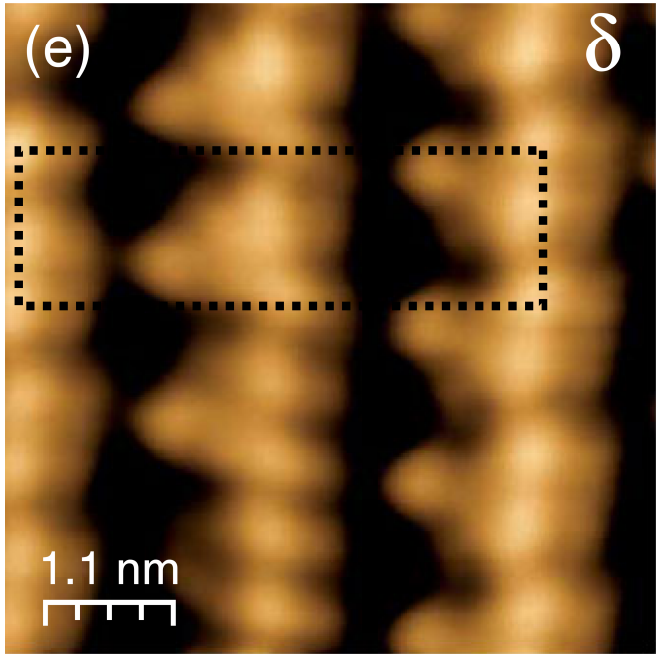
Temperature induced switching:





- At 330K: Two new phases ε and δ
- At 350K: δ-phase survives

→ All SP are switched to MC (thermal energy)



Pictures: G. Schulze *et al.*, Phys. Rev. Lett. **109**, 026102 (2012).

Ring-opening and closing switches

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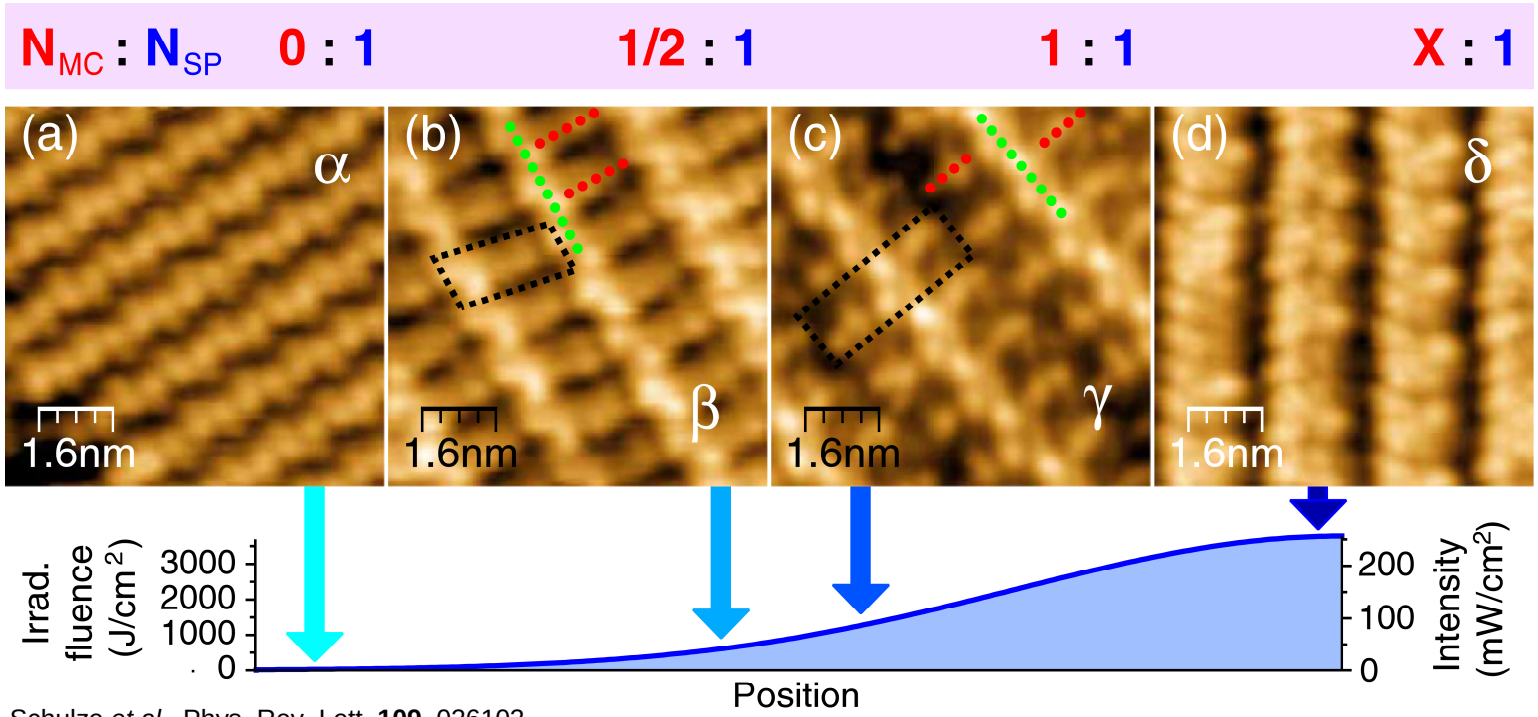
Inducing the Ring-opening with light:

Exposure with blue laser spot, power distribution: Gaussian

→ Distribution of different laser intensities

→ Dependence of the photon fluence on isomerization



Pictures: G. Schulze *et al.*, Phys. Rev. Lett. **109**, 026102 (2012).

Ring-opening and closing switches

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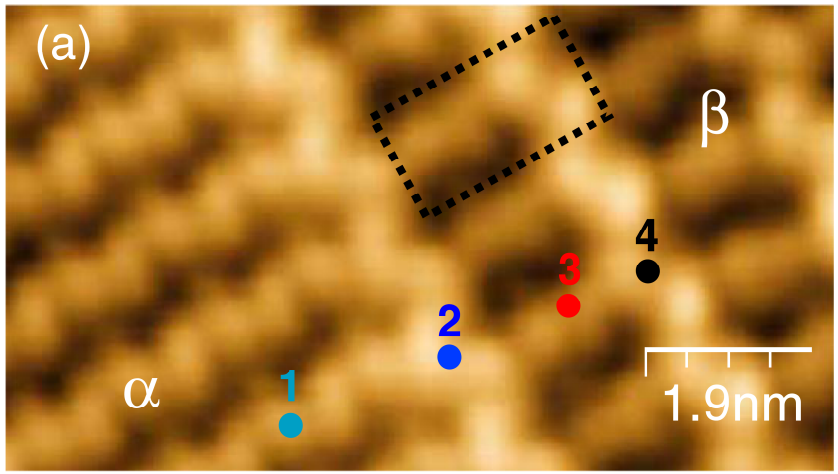
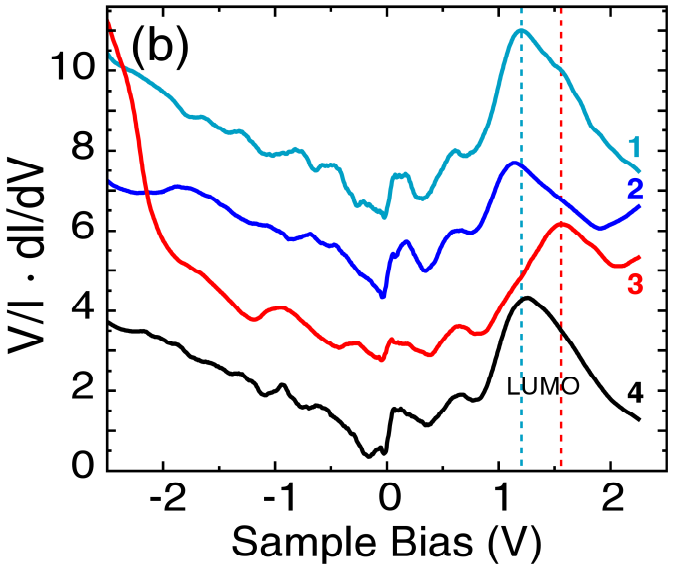
Identifying the isomers

- STS measurements at the spots marked below
- Border region of α- and β-phase
- Differences in LUMO and under -2V
- Brighter spots identified as SP
- Spot 3: MC



STM measurement



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Electron transport in molecular switches

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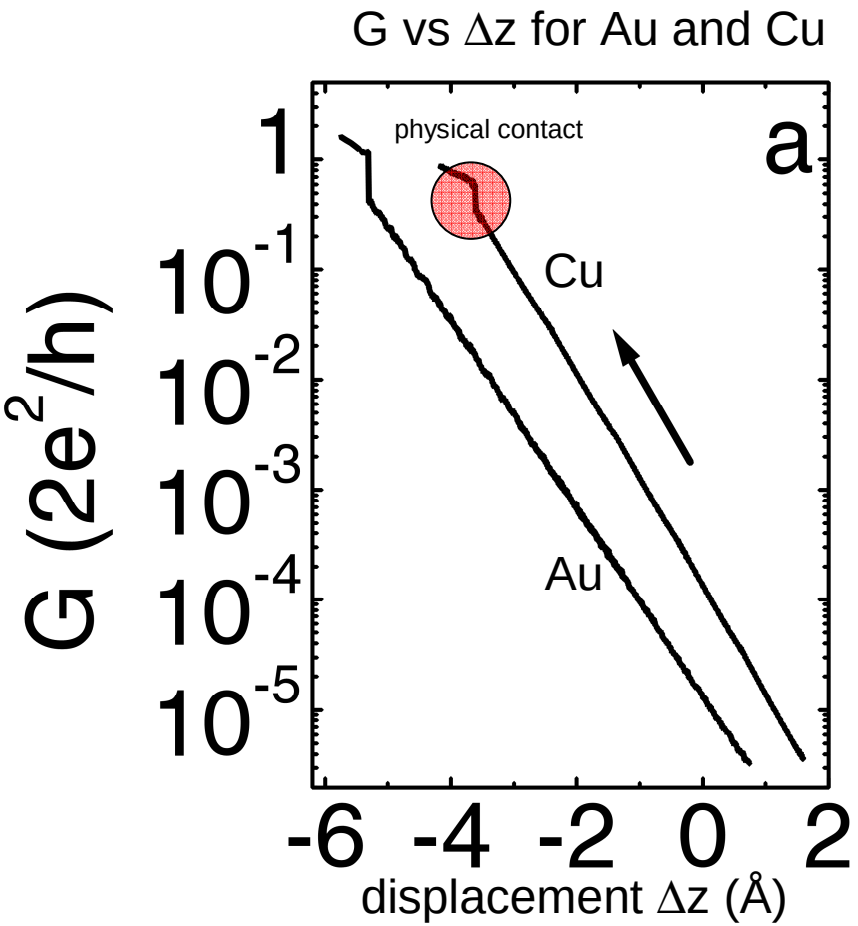
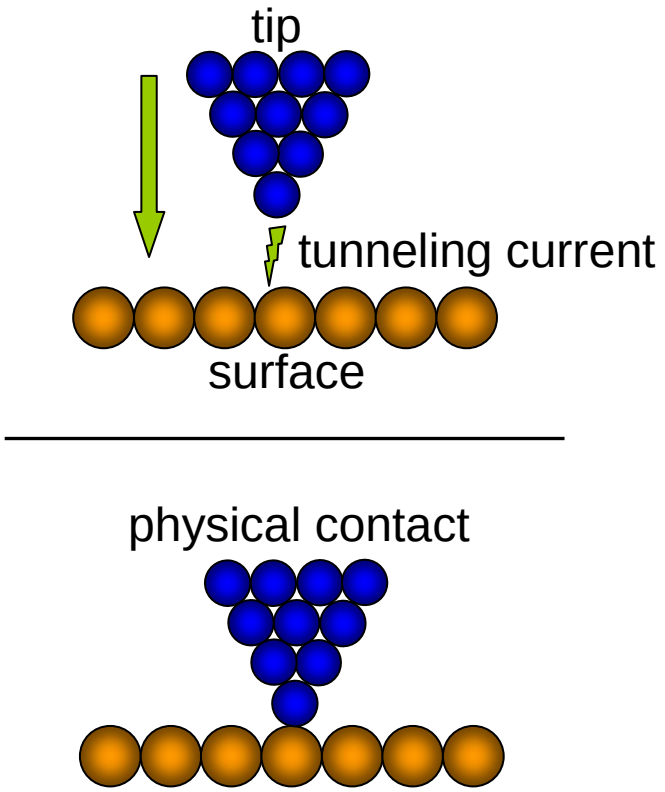
Conductivity measurements





L. Limot *et al.*, Phys. Rev. Lett. **94**,126102 (2005).

Electron transport in molecular switches

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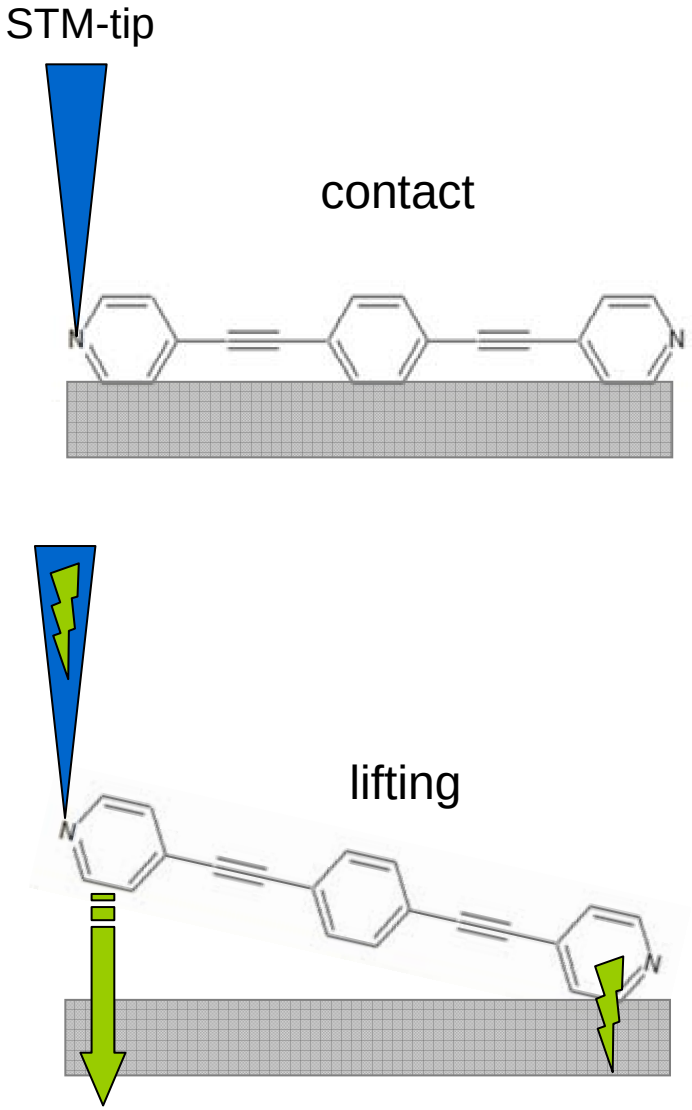
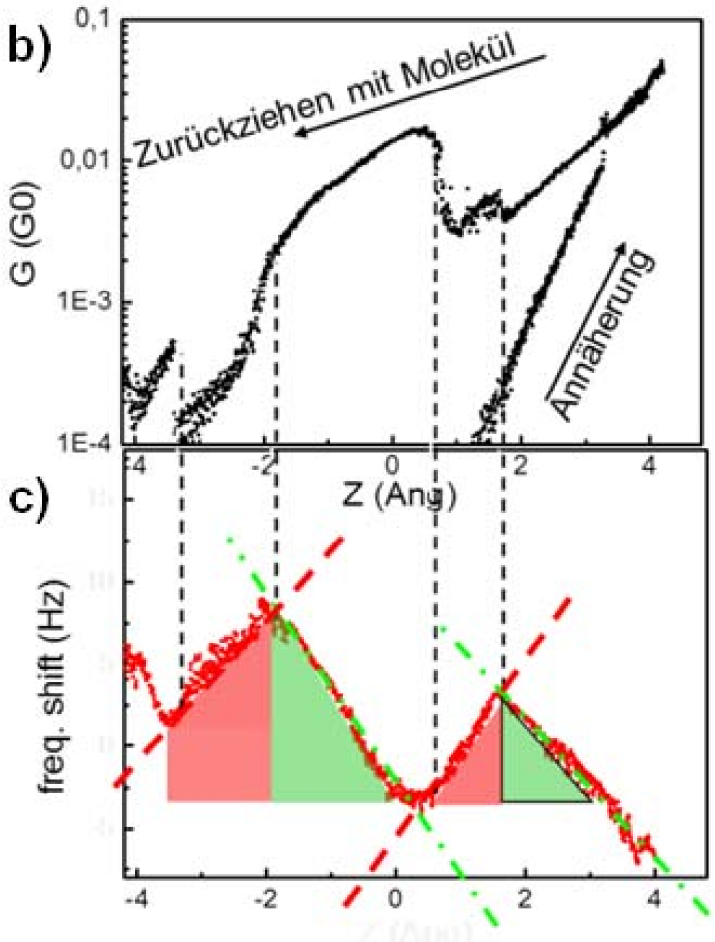


Lifting of a molecule

- Physical contact between tip and molecule
- Lifting up the molecule
- Binding energy molecule-surface < tip-molecule
- Vertical conductivity (STM)
- Rigidity of the molecule (AFM)

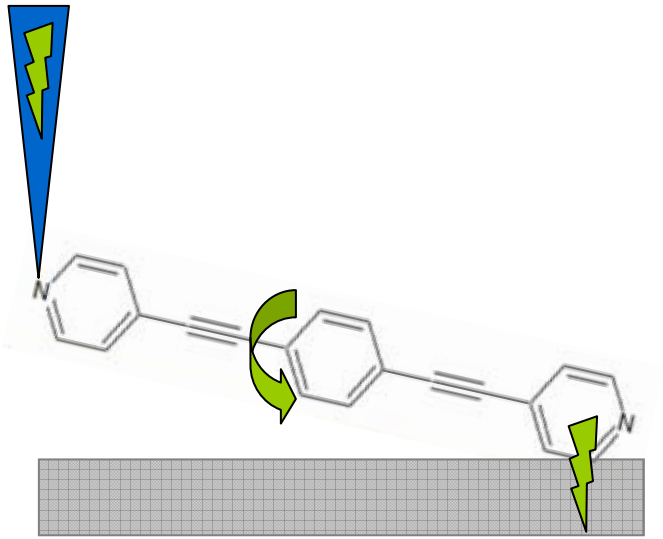
Pictures: Finazierungsantrag Sfb 658 A1

Electron transport in molecular switches



- Bringing the tip close to the molecule
- Physical contact
- Lifting the molecule
- Peaks in conductivity

  → Change of geometry



Pictures: Finazierungsantrag Sfb 658 A1

Electron transport in molecular switches

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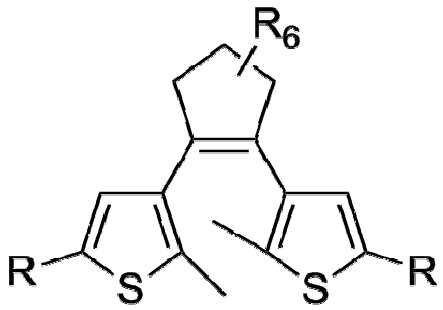
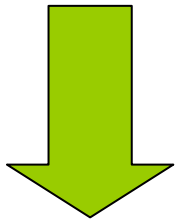
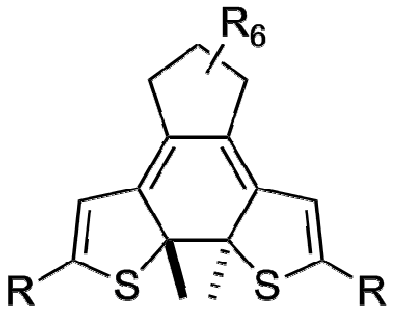
Dithienylethene (prototype molecular switch):

- Closed Isomer: conjugate π–electron system breaks up with ring opening
- Open and closed form different conductivity
- Open and closed form same length



open form
(generally colorless)





closed form
(generally colored)

Achievements:

Characterization of adsorption properties and charge transport

Electron induced switching

Pictures: http://en.wikipedia.org/wiki/File:Dithienylethene.png

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Examination of switching processes between different

- Conformations
- Oxidation stages
- Spin states

Especially

- Ring-opening and closing
- Conductivity through a molecule (+switching it)
- Identification of spin states
- Manipulation of spin states
- Optimization of the switching efficiency