Reversible Photomechanical Switching of Individual Engineered Molecules at a Metallic Surface [1]

Duncan Nall, Eric Meier, Ben Osherson

[1] Comstock, Matthew J., et al. "Reversible photomechanical switching of individual engineered molecules at a metallic surface." Physical review letters 99.3 (2007): 038301.

Research is Motivated by Future Light Controlled Nanomachines

Using light to move something some nanometers can help us control nanomachines or create 'non contact' operations.

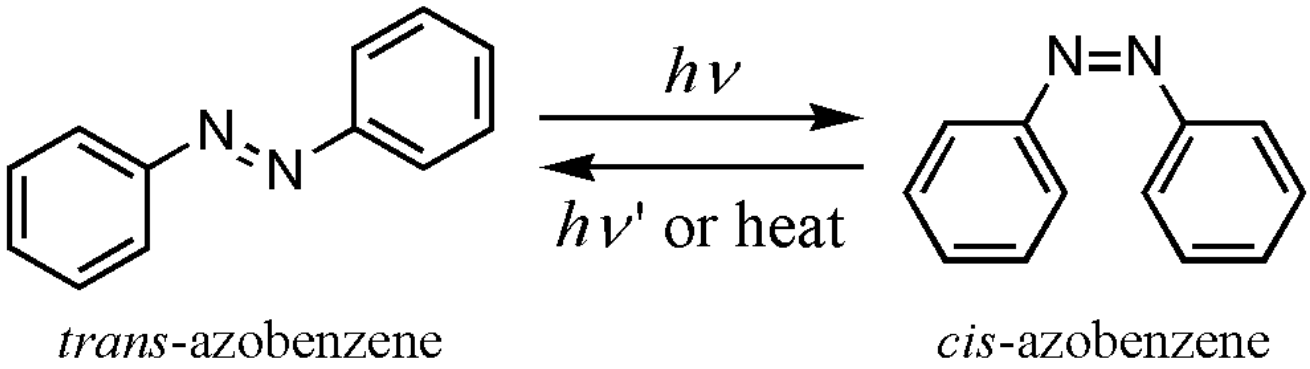
Current work in progress[1]

- Light causing expansion and contraction in a polymer
- Light controlled ion channels

[1] Comstock, Matthew J., et al. "Reversible photomechanical switching of individual engineered molecules at a metallic surface." Physical review letters 99.3 (2007): 038301.

Azobenzene as a Piston

Azobenzene can change its shape by **photoisomerization**.



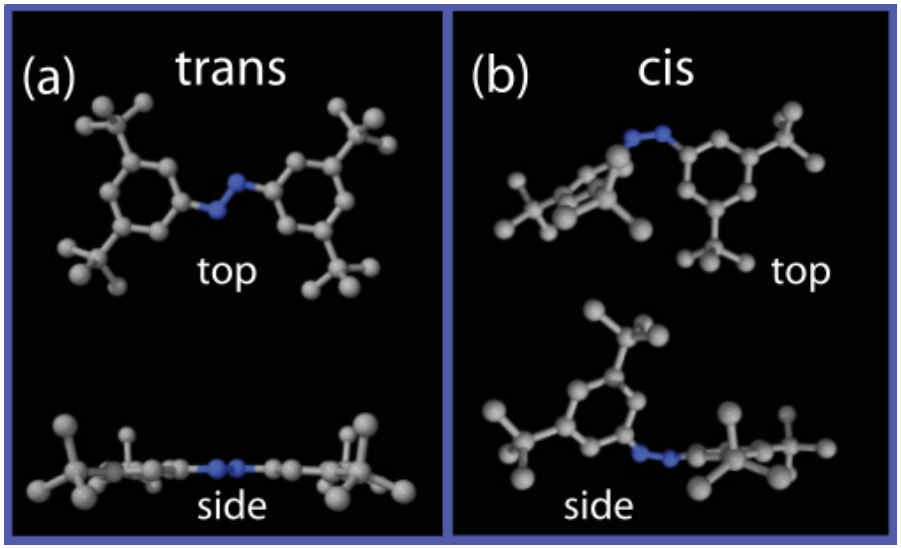
Azobenzene Structure [2]

How dependent is this photoisomerization on the environment? This experiment tests this state change in a new setup.

[2] Public domain, found on wikimedia

Setup and Key Features

Tert-butyl 'stilts' anchor azobenzene molecules to a gold surface, in a cold vacuum chamber. A STM can determine which state azobenzene molecules are in before and after light is applied.

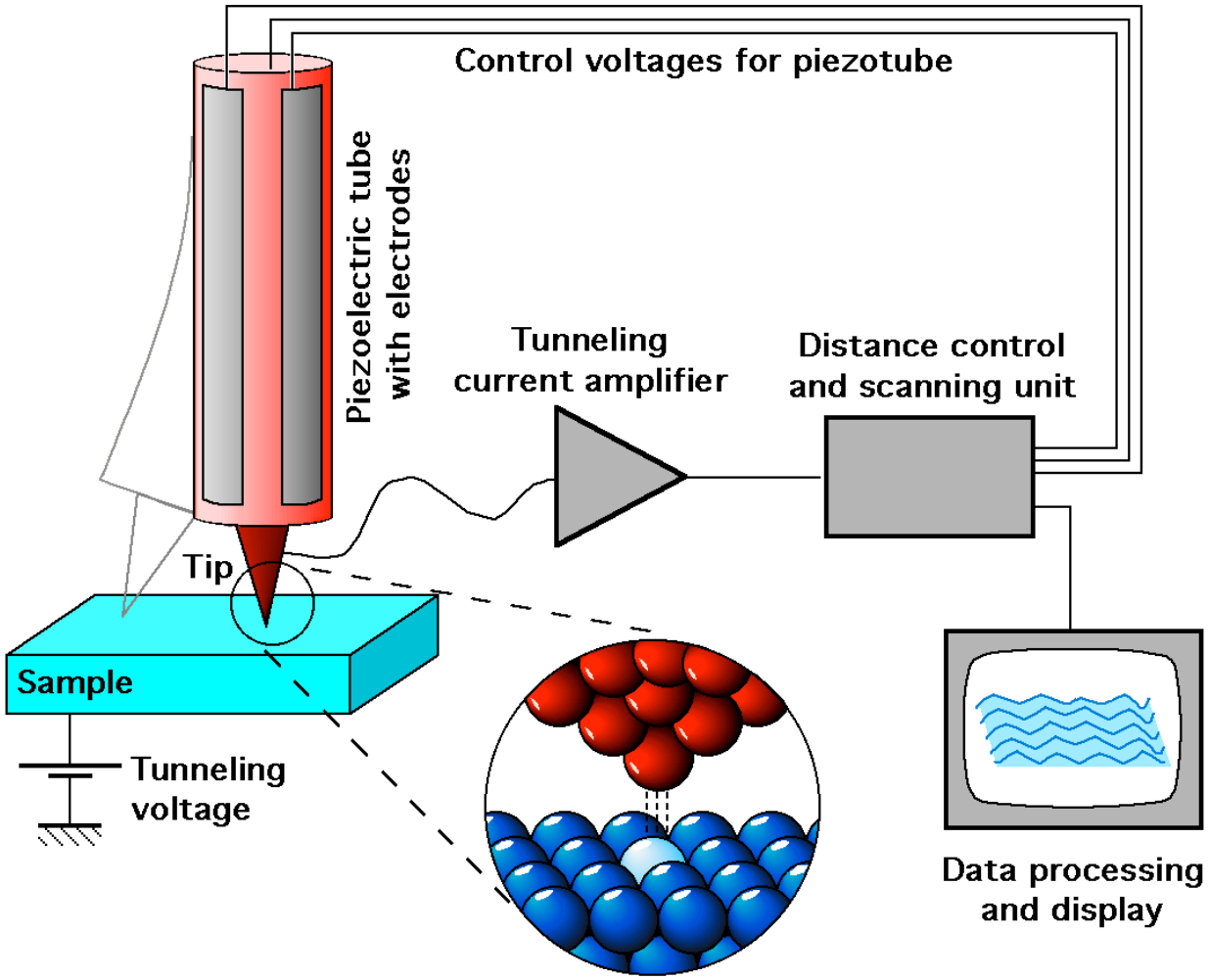


Azobenzene with Four Stilts on Gold [1]

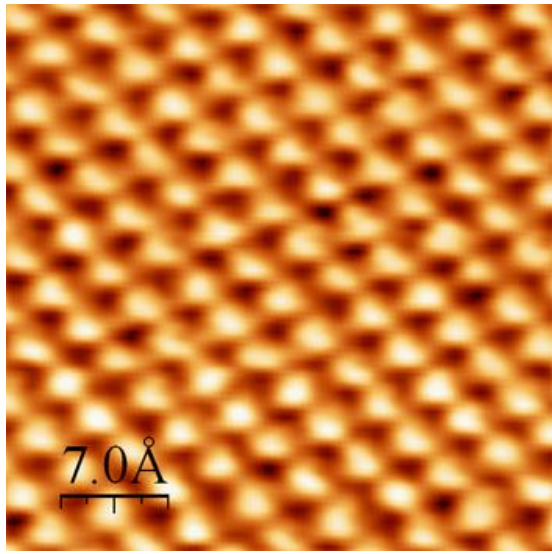
Number of tert-butyl legs can be changed, which changes the azobenzene-gold separations.

[1] Comstock, Matthew J., et al. "Reversible photomechanical switching of individual engineered molecules at a metallic surface." Physical review letters 99.3 (2007): 038301. [ALTERED]

Scanning Tunneling Microscopy

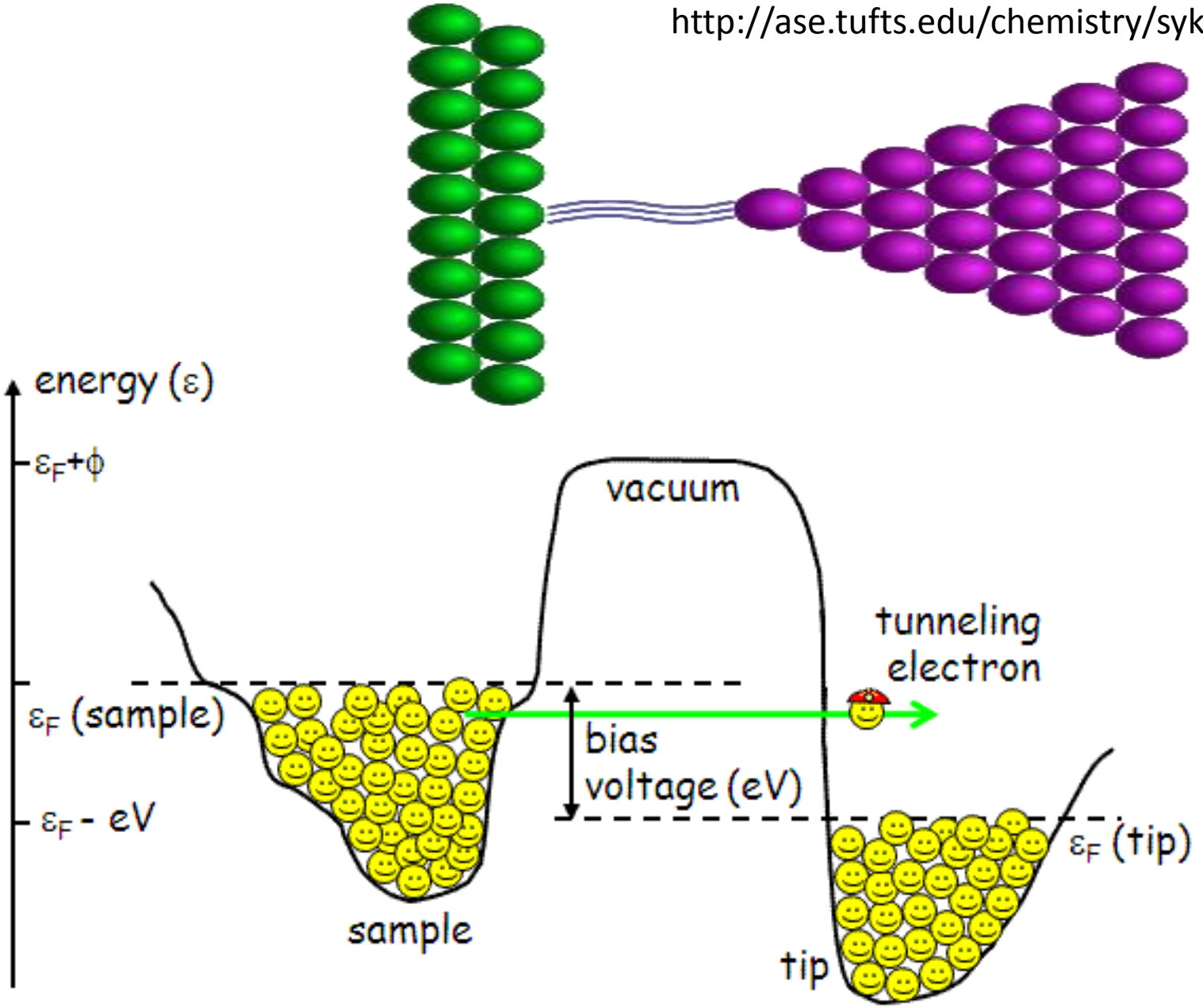


http://en.wikipedia.org/wiki/Scanning_tunneling_microscope



www.nanotec.es

http://ase.tufts.edu/chemistry/sykes/



http://hoffman.physics.harvard.edu/research/STMintro.php

Methodology

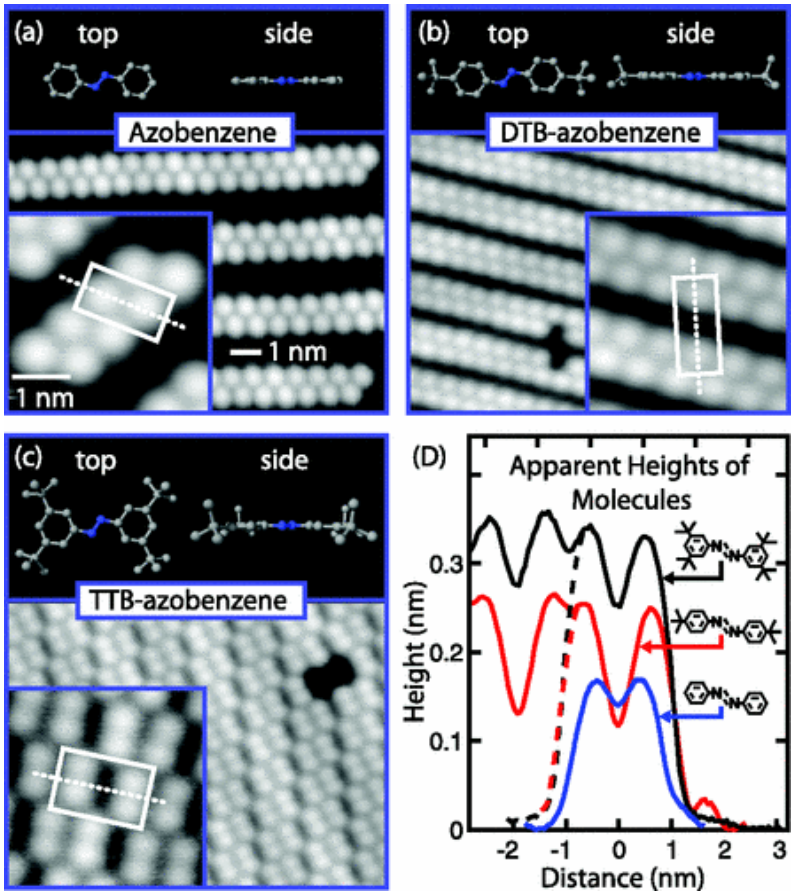
- Adsorbed Azobenzene and derivatives onto a gold surface.
- Shined UV light onto molecules to cause isomerization (trans to cis)
- Used STM to observe isomerization.
- http://www2.lbl.gov/Science-Articles/Archive/sabl/2007/Oct/assets/img/Crommie_reversible.avi

Experimental Conditions

- Ultra high vacuum STM
- Azobenzene and derivatives were annealed onto Au surface at 30 K
- UV exposure (375 nm UV laser with 90 mW/cm^2) for 3 hours to cause isomerization.
- STM image was acquired using constant current mode (50 pA).

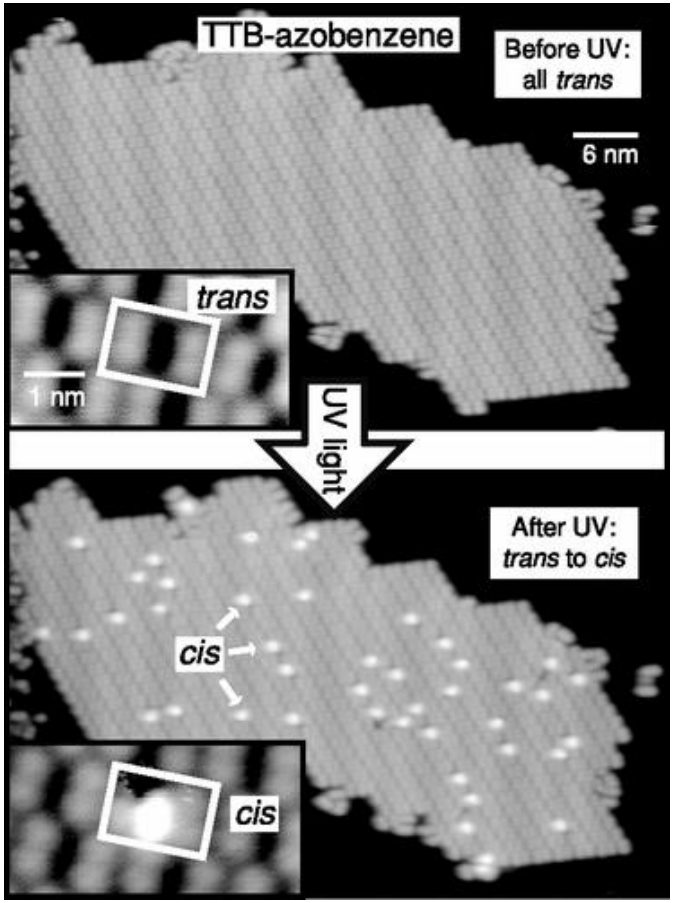
Azobenzene can be lifted with TB "legs".

- Adding tert-butyl legs to azobenzene results in effective lifting from a surface by progressively decoupling the molecule to the Au surface.
- Photoisomerization was observed only in TTB-azobenzene.



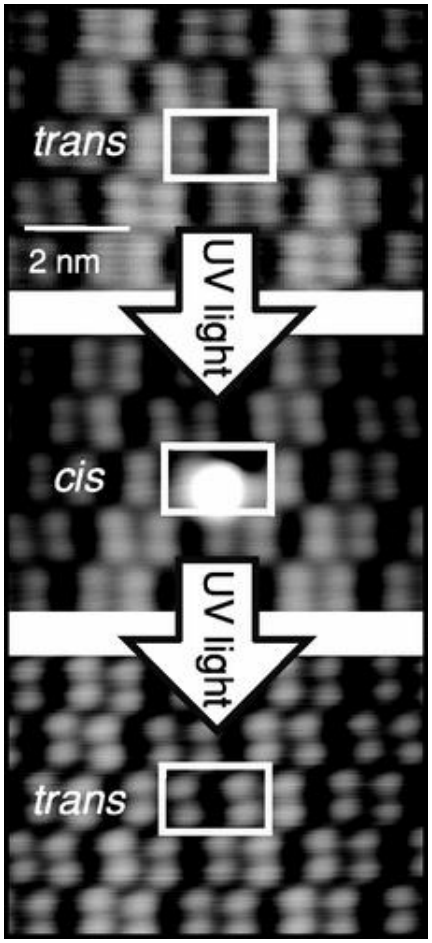
Photoswitching is 4% successful in TTB-azobenzene.

- On Au(111), photoisomerization of TTB-azobenzene was successful on 4% of the sample using a one hour, 90 mW/cm^2 UV exposure.



UV photoswitching is reversible.

- Reversible switching of a single TTB-azobenzene molecule was shown after two successive exposures to UV light at 90 mW/cm^2.

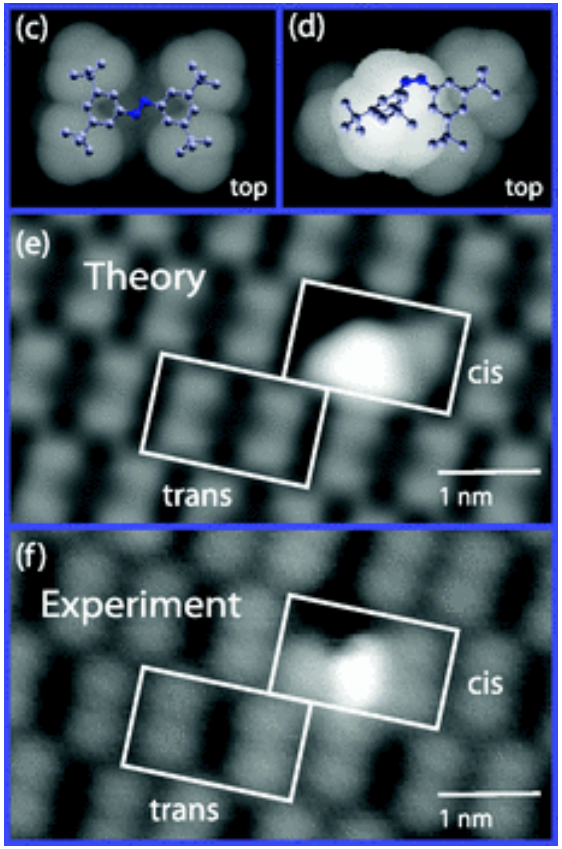


Surface-molecule coupling reduces photoswitching effectiveness.

- Interaction with the surface could make the excited electron lifetime shorter than the time it takes to switch molecular configurations.
- Hybridization of azobenzene with the surface may alter the molecular spectrum of azobenzene, resulting in reduced coupling to the UV light.

Theory matches with experiment.

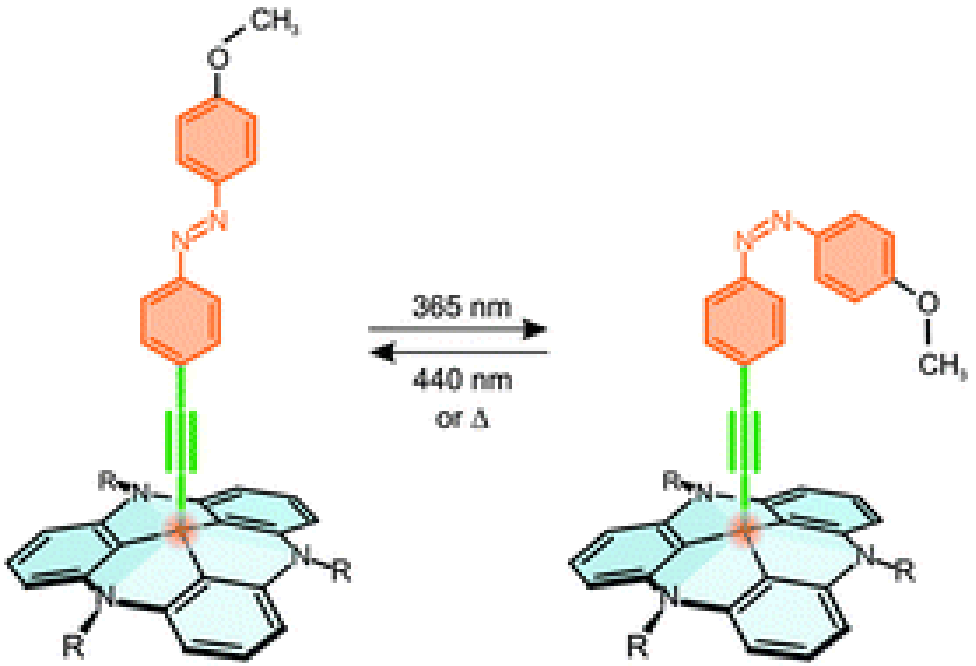
- Ab initio Density functional theory predict molecule conformations
- Siesta code to calculate Local Density of States
- Simulated scanning tunneling microscopy of the trans and cis isomers match quite well with the experimental findings.



Critical analysis of conclusions.

- … It did not really work very well. Effective switching of only 4% of these molecules after a full hour of UV exposure is not nearly efficient enough for any sort of wide scale usage.
- They propose future work to determine the cause of the drastic reduction in the photoswitching rate on a surface as compared to solution. But they offer no ideas on how to improve photoswitching given these possible causes.
- The process for reversible photoswitching is not well defined in the paper.

This paper was recently cited by:



Azobenzene with methoxy group
On TATA platform on Au surface.

Jacob et. Al, PCCP, 2014

This Experiment is a Combination of two Previous Experiments

Azobenzene in solution manipulated with light

Single-Molecule Optomechanical Cycle

T. Hugel *et al.*, Science **296**, 1103 (2002)

Azobenzene on gold manipulated with STM

Manipulation of azobenzene molecules on Au(111) using scanning tunneling microscopy

M. J. Comstock *et al.*, Phys. Rev. B **72**, 153414 (2005)

‘Steric Hindrance’ Named as Unlikely Reason for Low Success Rate

The placement of the TTB-azobenzene near the gold atoms could prevent many of the state transitions (called **steric hindrance**). However, the authors claim that this is not a major cause of the low success rate.

This claim is mostly supported by the results of a previous paper[3], but we suspect that the reference paper’s experiment is too different for this conclusion to be drawn.

[3] M. J. Comstock *et al.*, Phys. Rev. B **72**, 153414 (2005)

Questions?