Reversible Photomechanical Switching of Individual Engineered Molecules at a Metallic Surface

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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

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

Azobenzene as a Piston

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

\[
\text{trans-azobenzene} \quad \xrightarrow{hv} \quad \text{cis-azobenzene}
\]

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

[2] Public domain, found on wikimedia
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

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

Scanning Tunneling Microscopy

Control voltages for piezotube

Piezoelectric tube with electrodes

Tunneling current amplifier

Distance control and scanning unit

Tip

Sample

Tunneling voltage

Data processing and display


7.0 Å

www.nanotec.es
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.

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/cm²) 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/cm² 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/cm².
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

Azobenzene on gold manipulated with STM
Manipulation of azobenzene molecules on Au(111) using scanning tunneling microscopy
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.

Questions?