The World's Smallest Piston

Light Reversibly Changes the Shape of Single Molecules

In a breakthrough that conjures up visions of nanosized machines, a team of Berkeley Lab scientists led by Mike Crommie has shown that single, four-legged molecules can be made to move up and down like tiny pistons, powered only by a beam of light.

Scientists have long studied how certain molecules, such as azobenzene, can undergo a shape change ("*cis* to *trans* isomerization") when exposed to light of defined wavelength. Until now, most of these analyses have focused on billions of molecules at once, using a technique called ensemble averaging. More recently however, scientists have used scanning tunneling microscopy (STM) to watch single molecules change shape, but only after prodding the molecule with the atom-sized tip of the instrument. In order to usefully apply the molecular shape change to do work on the nanoscale, a different method of "actuating" the molecules needs to be found.

The Berkeley team took a new approach to this problem by depositing azobenzene on a gold surface to see if the light-induced isomerization could be observed in single molecules. Studies showed that the change did not occur reliably. Berkeley Lab chemists in the groups of Jean Frechet and Dirk Trauner then attached "tetra-tertiary-butyl-azobenzene" group "legs" to the azobenzene to raise it above the surface and reduce the gold-azobenzene coupling.

Thousands of these four legged structures were placed on a sheet of gold. When exposed to ultraviolet light at 375 nm wavelength, some of the molecules did change shape. A second beam of light reversed this motion, causing the molecules to return to their original shape. The observed shape change for individual molecules was in excellent agreement with predictions from first principles calculations performed by Berkeley Lab physicist Steven Louie's group.

This work is still in its early stages. One challenge for the future is to get individual molecules to reversibly change shape on command. At present, it is a statistical process in which some molecules isomerize and some do not. Nevertheless, these structures hold promise for a number of applications in which reversible motion at the nanoscale is required. Several of these molecules could be pieced together to make microscopic machines capable of crawling across a surface, for example. They could also be used to make a so-called smart surface that changes properties when exposed to particular optical stimulus. Additionally they might find use as molecule-scale electrical switches that turn on and off in response to light.

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Matthew J. Comstock, Niv Levy, Armen Kirakosian, Jongweon Cho, Frank Lauterwasser, Jessica H. Harvey, David A. Strubbe, Jean M. Fréchet, Dirk Trauner, Steven G. Louie, and Michael F. Crommie "Reversible photomechanical switching of individual engineered molecules at a metallic surface," *Phys. Rev. Lett* 99**,** 038301, (2007).

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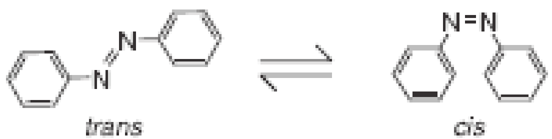
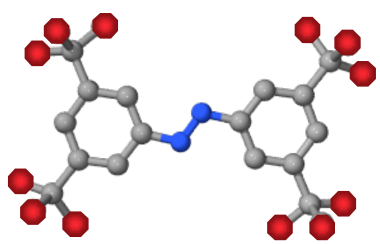
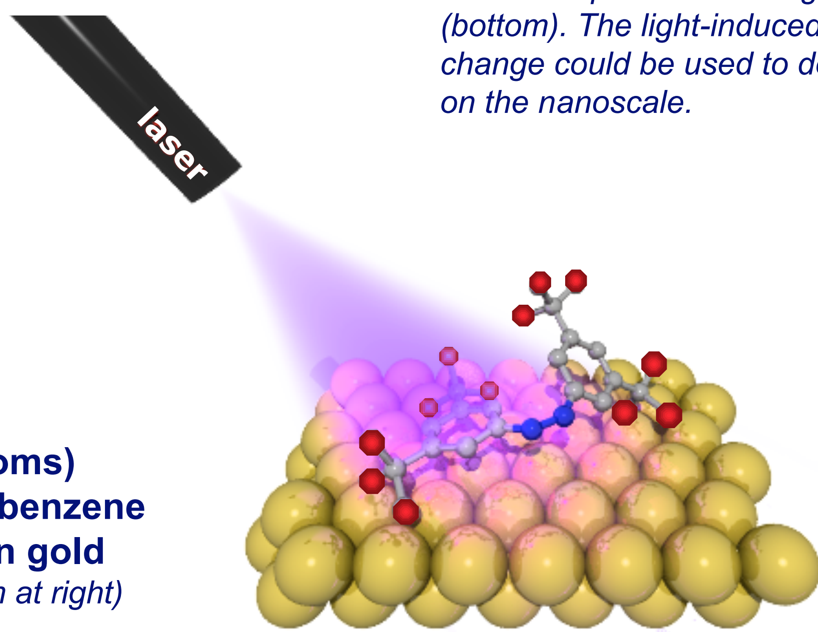
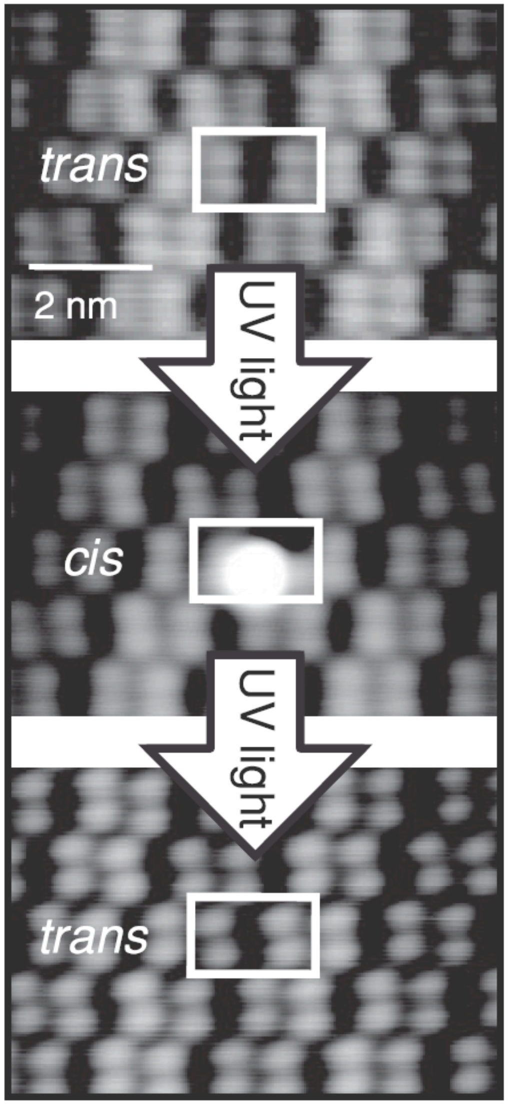


When exposed *to light, azobenzene molecules undergo a reversible shape change (cis to trans isomerization). Single molecules of a modified azobenzene compound (below) were placed on a metal surface and a laser was used to initiate the shape change.*

STM images of reversible photoinduced switching of a single modified azobenzene molecule *are shown on the right. The molecule which switches is in the white boxes. It starts out trans (top), is switched to cis after exposure to 375 nm UV light (middle panel), and is then switched back to trans after another exposure to the light (bottom). The light-induced shape change could be used to do work on the nanoscale.*







“4 legged” (red atoms) tetra-tertiary-butyl-azobenzene optically switches on gold

(trans form above, cis form at right)