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The World's Smallest Piston

Scientists use light to reversibly change the shape of single molecules

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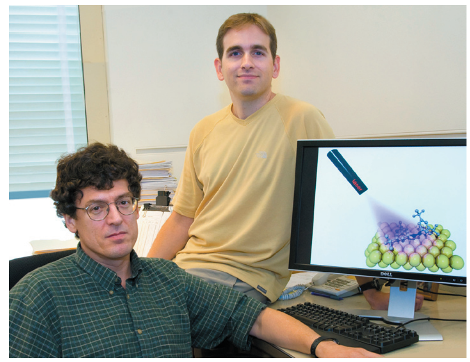
Tomorrow's nanosized machines may share something in common with the workhorses of yesteryear. A team of Berkeley Lab and UC Berkeley scientists have developed a four-legged molecule that moves up and down like a tiny piston, powered only by a beam of light.



Michael Crommie (left) and Matthew Comstock with a computer rendering of their handiwork, a molecule that churns up and down, powered only by light

(Photo Roy Kaltschmidt)

Although still very early in the investigational stages, these molecules hold promise for a number of applications in which reversible action at the nanoscale is required. Several of these molecules could be pieced together to make microscopic machines capable of crawling across a surface. They could also be used to make a so-called smart surface that changes properties when exposed to a stimulus like light. Or they could form electrical switches that turn on and off in response to light.

Led by Michael Crommie, a physicist in Berkeley Lab's Materials Sciences Division and UC Berkeley's Department of Physics, the scientists attached four "legs" to an azobenzene molecule and then placed thousands of these legged structures onto a sheet of gold. When they exposed the sheet to ultraviolet light, some of the molecules changed shape and lifted themselves above the surface. A second beam of light reversed this action, causing the molecules to plop back down onto the gold sheet.

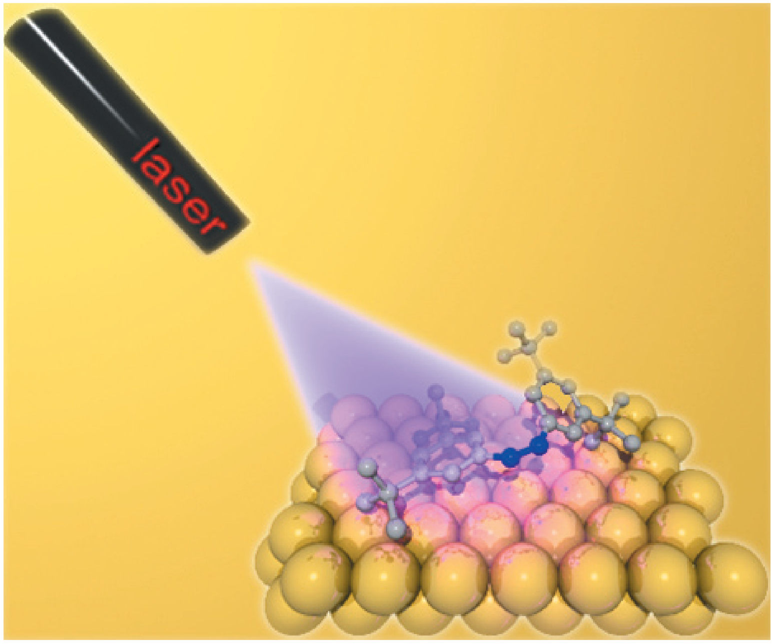
The team observed this up-and-down motion using scanning tunneling microscopy (STM), a technology capable of imaging single atoms. It allowed the scientists to watch individual molecules rise and fall like a nanoscale game of whack-a-mole.

"We are combining STM with light to understand how single molecules change shape, and we found a molecular system that reversibly changes its structure," says Crommie. "We eventually want to harness this action and develop nanosized machines capable of work."

Scientists have long studied how molecules such as azobenzene change shape in the presence of light. But most of these analyses have focused on billions of molecules at once, using a technique called ensemble averaging, which only reveals how large groups of molecules contort themselves. Scientists have also used STM to watch single molecules change shape, but only after prodding the molecule with the atom-sized tip of the STM instrument. In this work, however, the Berkeley team used a remote source, light, to reversibly change the structure of a molecule and observe this change at the single-molecule scale.

"This is new territory. We have used STM to zoom in on single molecules and observe their reversible light-induced changes," says Crommie.

The team began with an azobenzene molecule, which is known to change shape when exposed to light. However, the light-induced, shape-changing characteristic of azobenzene is damped when the molecule is attached to a surface. For reasons not entirely understood, the interaction between azobenzene and the surface suppresses the molecule's ability to rearrange itself when it absorbs a photon. And this is a potential deal-breaker if the molecule is to be used in nanosized machines and switches, because such devices will most likely be affixed to a surface.



Reversible motion at the molecular scale is just what scientists need to develop nano-scale machines and other applications.

To reduce the coupling between azobenzene and the surface, chemists from the Berkeley Lab research groups of Jean Fréchet and Dirk Trauner attached legs to the molecule, with each leg composed of a four-carbon group called tert-butyl. These legs raise the azobenzene molecule slightly above the gold surface, which to some degree disentangles it from the surface's influence.

"The legs free the molecule from being interfered with by the metallic surface," says Matthew Comstock of Berkeley Lab's Materials Sciences Division, who is also a graduate student in UC Berkeley's Department of Physics.

Next came the test. When placed on the gold surface and illuminated by ultraviolet light, azobenzene molecules with zero and two legs did not change shape—but molecules with four legs did. Later, when the four-legged molecules were hit with another beam of light, they folded back to their original shape.

It isn't yet clear how the four-legged molecule is able to disentangle itself from the gold surface and reversibly rearrange its structure, but the answer lies in the fact that quantum mechanics takes over at the atomic scale. In this world, the atoms in azobenzene and the atoms in the gold surface share common electrons, and even the same vibrations. These shared effects inhibit azobenzene molecules that lie close to the surface from changing shape. But lift the molecule slightly above the surface—in this case on legs—and the constraining influence of these overlapping particles and vibrations diminishes.

"As we lift the molecule off of the surface, fewer electrons are shared between the atoms in the molecule and surface, and there is also less sharing of vibrations among the atoms," says Crommie. "This allows the molecules to change shape when they absorb a single photon. And this shape change can be harnessed to perform work."

Crommie adds, however, that they can't get the molecules to reversibly change shape on command. Instead, it's a statistical process in which some molecules rearrange their structure and some don't. In the future, they hope to refine the process so that they have more control over the molecules' shape changes.

"We need to learn how much light to use—and what color of light to use—in order to optimize the molecules' performance," says Comstock. "Ultimately, we have a great hope that we can assemble these into much more complicated machines."

In addition to Crommie and Comstock, other Berkeley Lab and UC Berkeley scientists who contributed to this research include Jongweon Cho, Jessica Harvey, Armen Kirakosian, Frank Lauterwasser, Niv Levy, Steven Louie, and David Strubbe.

Additional information

"Reversible photomechanical switching of individual engineered molecules at a metallic surface," by 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, appears in the July 20 issue of *Physical Review Letters* and is available online to subscribers at http://link.aps.org/abstract/PRL/v99/e038301.

More about Michael Crommie's research is at http://www.physics.berkeley.edu/research/crommie/index.html.