Thermal and Mechanical Actuation of Single-Molecule Rotors
(Result of the month 11/2008)

Surface-supported thioethers (RSR) are a simple, robust system with which to investigate the fundamentals of molecular rotation. Low-temperature scanning tunneling microscopy (LT-STM) was utilized to study the molecular motion of individual thioether molecules which appeared as linear shapes at low temperature, but as the surface temperature was increased, they imaged as hexagons as they begun to rotate faster than the timescale of imaging. The temperature dependence of rotation for methyl, ethyl, butyl and hexyl sulfide indicated that the barrier for rotation stems from the second CH2 group from the S atom. The torsional barrier (~1.2 kJ/mol) and pre-exponential factor were quantified from Arrhenius plots of single-molecule motion. The STM tip was used to manipulate the thioethers and reveal that when the molecules are close together, the van der Waals interaction between alkyl chains hinders their rotation.

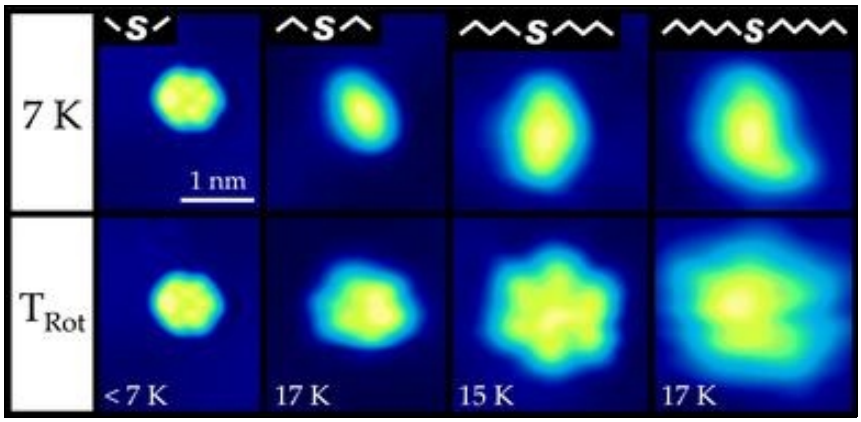

Figure 1. Constant current STM images showing a set of thioether rotors: dimethyl, diethyl, dibutyl, and dihexyl sulfide and the corresponding temperature at which rotation begins. Dimethyl sulfide rotates even at 7 K, diethyl, dibutyl and dihexyl sulfide all begin to rotate at a temperature around 16 K. V_{tip} = -0.3 V, I = 9 pA.

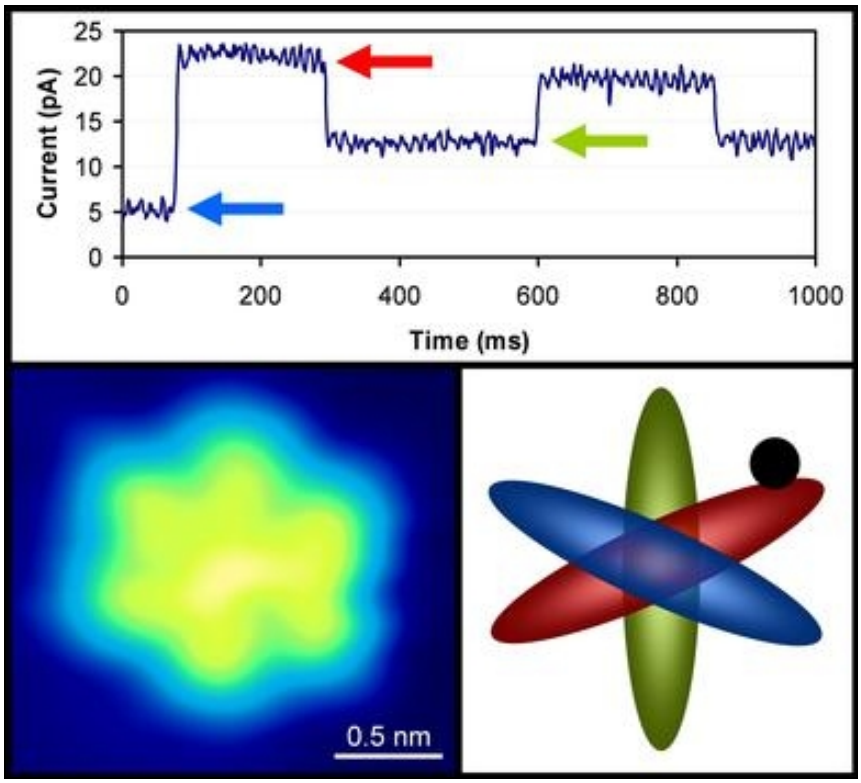

Figure 2. Plots of the tunneling current (I) vs. time (t) reveal that the molecules reside in three inequivalent molecular orientations (green, red, and blue) with respect to the STM tip position (black dot). Changes in the position of the thioether alkyl tail result in three distinct levels of tunneling current from which the rotation rate of the molecule and even the direction of rotation can be measured.

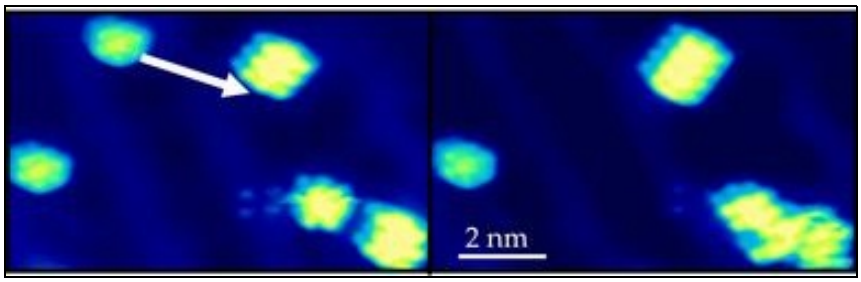

Figure 3. The proximity to surrounding molecules can be mechanically controlled to actuate the rotation of dibutyl sulfide. STM images show how the rotation of an individual molecule can be switched off by moving it toward a chain of three molecules fixed on the surface; Vtip = -0.3 V, I = 15 pA, (During Manipulation: V_{tip} = -0.05 V, I = 120 nA) Temp = 78 K.

Additional information :

Authors
Ashleigh E. Baber, Heather L. Tierney, and E. Charles H. Sykes
Department of Chemistry
Tufts University

Medford, Massachusetts
02155-5813

Name and email of corresponding author
Charles H. Sykes
charles.sykes@tufts.edu

URL of Institute web-pages
www.chem.tufts.edu/

URL of Journal(s)
www.acsnano.org/

This result has been obtained with : **OMICRON LT STM**