Synthesis and Control of Molecular Machines

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The main goal of this project is to develop controllable, operational nanomachines and nanomotors adhered to surfaces [1]. We are using the tools of organic chemistry to synthesize new compounds that will form the subunits of molecular-mechanical assemblies. Such a "bottom-up" approach should allow us to flexibly build-in machine functionality at the molecular level. Functional molecular systems will be fabricated using both self-assembly techniques and single-molecule manipulation. Scanned probe techniques and in situ transmission electron microscopy (TEM) will be used to characterize molecular machine operation at the Ångstrom level.

We have synthesized a number of test molecules to be used as components of nanomachines in which motion is stimulated by an external electromagnetic field. We have focused mainly on unsymmetrical porphyrin, dipolar azobenzene and functionalized nanotubes. Porphyrins are well known for their many important roles as the photo- and chemo-active sites in a variety of protein-based biomolecules. The structure of a basic tetraphenylporphyrin scaffold is shown in Figure 1. Our interest in porphyrin arises from the idea that it might act as a functionalized pinwheel or gear through rotation around the center metal ion. Tetraphenylporphyrin derivatives were chosen for this study because they provide a highly versatile scaffold for introducing molecular diversity. The mechanical functionality of azobenzene arises from its well-known cis/trans isomerization (see Figure 2). Once anchored to a surface, this isomerization should lead to reversible mechanical hinge motion. We intend to link functional ligands to the termini of azobenzene molecules to create flexible, multi-purpose molecular-mechanical hinges. Some examples of functional groups that may be mechanically manipulated via the cis-trans isomerization include fullerenes, dendrimers, and oligophenylacetylenes. Nanotubes, on the other hand, form an excellent linear nanomechanical scaffold for creating new mechanical structures that have both rotational and translational degrees of freedom.

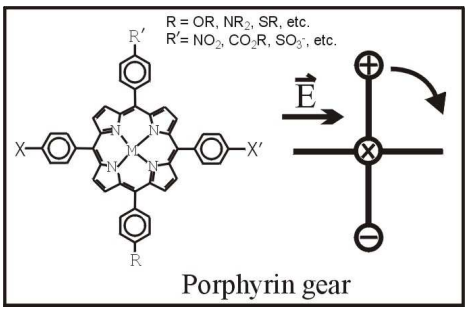

Figure 1. Tetraphenyl phorphyrin molecular gear.

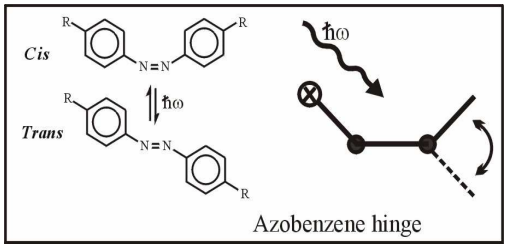

Figure 2. Azobenzene / molecular hinge.

Over the last year we have focused on characterizing, manipulating, and actuating these nanomachine molecular components. In order to observe the behavior of azobenzene on a well characterized and relatively inert surface we deposited it onto Au(111). Using a variable temperature scanning tunneling microscope (STM) we were able to image individual azobenzene molecules at 100K (see Figure 3). The molecules appear as double-lobe structures having a net length of ~10Å. This is comparable to the extension that is expected for azobenzene, implying that each lobe marks the location of a benzene ring. In this low coverage regime we find that we can manipulate the conformation of the molecule on the Au surface via voltage pulses applied to

the tip of the STM. Figure 3 shows an azobenzene molecule that has been rotated by 90° by changing the bias of the STM tip. In these images it is not clear if the molecule is in the cis or trans configuration. We feel that it is significant that we have demonstrated the ability to manipulate individual azobenzene molecules, as this opens the door to more complex molecular re-arrangements in the future. Bias-dependent imaging shows significant energy-dependent structure in the molecule, and this is currently being investigated. We have also begun optical excitation experiments to see if it is possible to optically switch the isomeric state of the azobenzene. We will also investigate the possibility of using light-harvesting dendrimers to enhance azobenzene optical response.

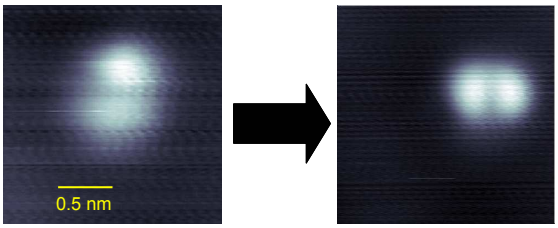

Figure 3. STM image of a single azobenzene molecule changing its conformation by 90° under the influence of the tip of an STM.

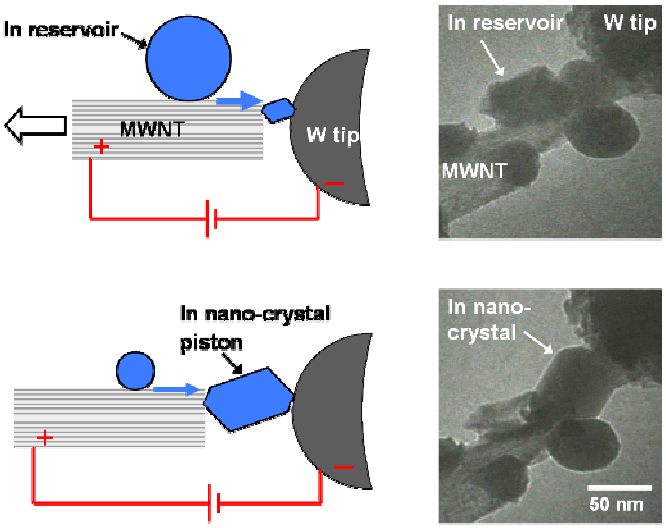

Figure 4. (left) Schematic drawing of a nanocrystal-driven electromechanical actuator. With a given polarity of the supplied current, the indium (In) nanocrystal located at the junction of a tungsten (W) tip and the nanotube (MWNT) grows, as In atoms are supplied by a nearby In reservoir. The growing In nanocrystal pushes on the nanotube, providing its linear motion relative to the tip. The entire process is fully reversible with opposite polarity of the applied voltage.
(right) TEM images of the nanoactuator system taken 40 sec. apart corresponding to the stages shown to the (left).

Using multi-wall carbon nanotubes (MWNTs) as a scaffold, we have fabricated a fully controllable, reversible nanoactuator system which uses a nanocrystal as the driving element. Figure 4 (left) shows a schematic of such a nanoactuator while high resolution images (right) taken with TEM show the functioning of the device. A tungsten tip can be seen in the upper right-hand corner, and a MWNT bundle can be seen oriented diagonal to the image. Decorating the nanotubes are tiny crystals of indium metal. We apply ±0.9 V between the tip and bundle, which drives ~12μA through the bundle. Depending upon the polarity of the supplied current, the indium nanocrystal located at the tip/nanotube junction alternately grows and shrinks as it exchanges mass with a nearby reservoir. These size changes drive the linear motion of the nanotube relative to the tip. This on-demand, reversible growth of individual nanocrystals is an entirely novel process, and the physics is still being explored. The use of a crystalline working 'fluid' for pneumatic actuation is also completely new, and may lead to applications that are thermodynamically forbidden with vapor and liquid-based engines.

References

[1] For further information about this project email Michael Crommie crommie@socrates.berkeley.edu, Alex Zettl azettl@physics.berkeley.edu, Jean Frechet frechet@cchem.berkeley.edu.