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Kemisk Forening and the Nano-Science Center, University of Copenhagen announce a joint seminar on June 3rd at 15:15, HCØ Aud. 2:

Nano Meccano

An Integrated Systems-Oriented Approach to Molecular Electronics

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The development of molecular electronic devices for memory and logic applications in computing presents one of the most exciting contemporary challenges in nanoscience and nanotechnology. One basis for such a device is a two-terminal molecular switch tunnel junction that can be electrically switched between high- and low-conductance states. Towards this end, the concepts of molecular recognition and self-assembly have been pursued actively for synthesizing two families of redox-controllable mechanically interlocked molecules—bistable catenanes and bistable rotaxanes—as potential candidates for solid-state molecular switch tunnel junctions. In the case of a two-terminal molecular switch tunnel junction, the objective is to design a molecule that, at a specific voltage, switches from a stable structure (isomer) to another, metastable isomer with a different conductivity: the molecule needs to remain in the metastable state until either another voltage pulse is applied or thermal fluctuations cause a return to the ground state. The two states of the molecule correspond to the ON and OFF states of the switch and the finite stability of the metastable state leads to a hysteretic current/voltage response that forms the basis of the switch. However, such switching behavior can also arise from the intrinsic device capacitance, from charge storage in defect sites at the molecule/electrode interface, or from electrochemical modification of the electrode materials. Such artifacts can be ruled out by careful control experiments, but some other, non-molecular mechanism may nevertheless contribute to the switching response. Thus the challenge is not just to rule out artifacts, but also to verify that the effect is molecular in origin by establishing a correlation to solution-phase observations.

Molecular switch tunnel junction devices that contain a monolayer of bistable mechanically interlocked molecules—both [2]catenanes and [2]rotaxanes that are bistable—have been sandwiched between silicon (or carbon nanotubes) and metallic electrodes. These devices can be voltage-switched between a stable Off and a metastable On state. We attribute these observations to an electrochemically driven translation of a viologen-containing ring from a tetrathiafulvalene recognition site to a dioxynaphthalene one to form the metastable state. The free energy barrier for relaxation back to the ground state provides an opportunity to correlate the devices with molecular properties in solution.

To establish this correlation, we have performed variable temperature electrochemical measurements to quantify the metastable-to-ground state relaxation of these molecular switches not only in solution, but also in self-assembled monolayers and in polymer matrices, as well as in the molecular switch tunnel junctions. The free energy barriers to relaxation of the switches in these four different environments are, respectively, 16, 18, 18, and 21 kcal mol^{-1} at room temperature. Thus, although the corresponding relaxation rates slow down by a factor of 10000 as the molecules are increasingly confined, the mechanism remains the same. IT IS UNIVERSAL.

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