

SURFACE SCIENCE

Switching made simpler

It is possible to make a molecule act as a switch by using a scanning tunnelling microscope to change the position of just two hydrogen atoms.

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Modern electronic devices contain hundreds of millions of field-effect transistors, which perform a basic function of switching between two states, commonly known as '0' and '1'. The idea of replacing the semiconductor circuits that are presently used as switches with single molecules is a major driving force in the field of molecular electronics. To date, various molecular switches have been proposed, demonstrated and studied¹, including two-terminal devices in which the conductance can be reversibly switched between two distinctive values by changing the structure or electronic state of the molecule with an applied voltage^{2–6}. There are also three-terminal devices in which, for example, an electrochemical gate switches a molecule reversibly between its oxidized and reduced states by removing or adding an electron^{7,8}.

Writing in *Science*, Peter Liljeroth, Jascha Repp and Gerhard Meyer of the IBM Zurich Research Laboratory and the University of Regensburg⁹ describe a novel approach to single-molecule switching that does not involve changes in the structure or redox state of the molecule. This new approach relies on a process called hydrogen tautomerization in molecules of naphthalocyanine (Fig. 1). In simple terms, hydrogen tautomerization is a reaction in which both the electronic structure of the molecule and the positions of one or more hydrogen atoms change, but the overall molecular formula stays the same.

Naphthalocyanine molecules are flat and have two hydrogen atoms located in their central cavity. Depending on the position of these two atoms, the lowest unoccupied molecular orbital of the molecule can have one of two orientations. Using a low-temperature scanning tunnelling microscope (STM), Liljeroth and co-workers showed that the orientation of the

naphthalocyanine — and hence the conductance — can be switched by increasing the bias voltage between the tip and the sample until the tunnelling electrons induce tautomerization.

This orientation switching is equivalent to rotating the molecule by 90°, but it is achieved by simply changing the position of the two hydrogen atoms rather than rotating the molecule itself (Fig. 1). The switching causes a substantial change in the tunnelling current, which was measured by placing the STM tip over the molecule. Because it is reversible and does not involve changes in the molecular frame or charge, this new approach to molecular switching could prove useful in devices such as logic gates.

An important factor in the success of the experiment is the use of an ultrathin insulating film (NaCl or RbI) to adsorb the molecules. This film weakens the electronic coupling between the molecule and the underlying copper substrate. When the molecules were directly adsorbed on a copper substrate, no tautomerization or switching could be observed.

Another interesting phenomenon observed by Liljeroth and co-workers is that the switching of one molecule in a molecular assembly can be controlled by the state of a neighbouring molecule. Using STM as a manipulation tool, they bring several molecules close together and then switch one molecule by injecting current through its neighbours. The neighbouring molecules are weakly coupled, which implies that electrons can tunnel between them, but there is no significant hybridization of the different molecular orbitals.

This type of switching depends on the separation of the molecules. If the separation is large (that is, more than 16 Å), a molecule will not switch its nearest neighbours. This dependence may be used to control the switching behaviour of a molecular assembly, which, with appropriate separations, could be operated in a fashion analogous to quantum-dot cellular automata¹⁰. A related phenomenon was recently

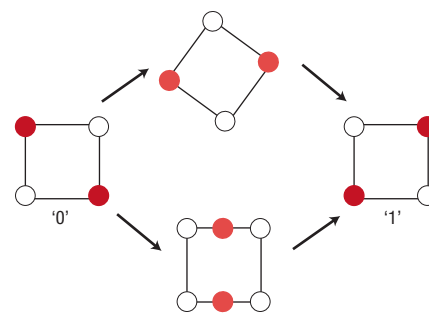


Figure 1 A molecular switch. The '0' and '1' states of a naphthalocyanine molecule have very different conductances. It would be possible to switch from '0' to '1' by rotating the molecule (top path), but it is easier to exploit a tautomerization reaction that involves just two hydrogen atoms (red circles) changing position (bottom path).

observed in arrays of porphyrin molecules on gold electrodes by Yufan He and Eric Borguet of Temple University in Philadelphia¹¹. He and Borguet showed with an electrochemical STM that the oxidation of a molecule (removal of an electron) can trigger the oxidation of a neighbouring molecule owing to charge transfer between nearest neighbours.

Although the low-temperature STM is unlikely to feature in a working molecular device, the work by Liljeroth, Repp and Meyer clearly demonstrates that it is possible to switch a molecule between two different conductance states without having to rotate the whole molecule, which could potentially be used in non-volatile memories and logic gates with extremely high densities.

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