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# Switching Single Azopyridine Supramolecules in Ordered Arrays on Au(111)

Yongfeng Wang,*[,†] Xin Ge,[†] Guillaume Schull,[†] Richard Berndt,[†] Hao Tang,[‡] Claudia Bornholdt,[§] Felix Koehler,[§] and Rainer Herges[§]

*Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, D-24098 Kiel, Germany, Centre d'Elaboration de Matériaux et d'Etudes Structurales, Centre National de la Recherche Scientifique, France, and Institut für Organische Chemie, Christian-Albrechts-Universität, D-24098 Kiel, Germany*

Received September 21, 2009; E-mail: yfwang@physik.uni-kiel.de

Understanding and controlling molecular switches on surfaces are of interest in both fundamental science and functional devices at the single molecule level.[1−24] External stimuli like light, temperature, electric fields, and electrons have been used to induce conformational changes of molecules on surfaces. Single molecular switches have been realized by modifying covalent bonds, e.g. by isomerization of azobenzene,[16] or ionic bonds, e.g. by inversion of tin phthalocyanine.[23] Decoupling of the reactive component of the molecule from a metal substrate by an insulating layer can be necessary as reversible switching is usually quenched on metals for the rather high barrier to overcome and the short lifetime of excitations.[12,13] In contrast to molecules, supramolecules are connected through directional, selective, and weak noncovalent interactions like hydrogen bonding. Lower energy barriers to switching may be expected for these weaker bonds. Moreover, investigations of supramolecular switches may be useful in understanding physiological activities.

Here we report on supramolecular switches of 4,4-azopyridine trimers and 4-phenylazopyridine dimers in an ordered array on Au(111). During switching, a single weak C−H...N hydrogen bond breaks and reforms. For 4,4-azopyridine, the switching mechanism occurs via electron attachment. 4-Phenylazopyridine dimer, however, can be switched by electric fields, too.

The experiments were carried out in a home-built ultrahigh vacuum scanning tunneling microscope (STM) operated at 5.8 K with a base pressure $10^{-9}$ Pa. The single-crystalline Au(111) and etched polycrystalline W tips were cleaned by repetitive cycles of $Ar^+$ sputtering and annealing. High-purity 4,4-azopyridine and 4-phenylazopyridine were dosed onto Au(111) at room temperature. After exposure, the sample was transferred into the cold STM and measured at 5.8 K. Spectra of the differential conductance (d$I$/d$V$) were measured with a standard lock-in technique.

4,4-Azopyridine forms ordered arrays of trimers, which are located at elbow sites of the Au(111) surface (Figure 1a).[25] Trimers can be reversibly switched between a linear and bent shape (Figure 1b−c). To this end, the STM tip was positioned above the encircled molecule in Figure 1b and the sample bias $V$ was increased to 1.5 V. The current $I$ was recorded until a steep drop occurred. Subsequent imaging revealed that the marked molecule rotated by ∼30° whereas the other two molecules remained unaltered. By repeating the manipulation procedure the rotated molecule can be switched back to its original position and a linear trimer is recovered. Both the linear and bent trimers are robust and can be switched many times.

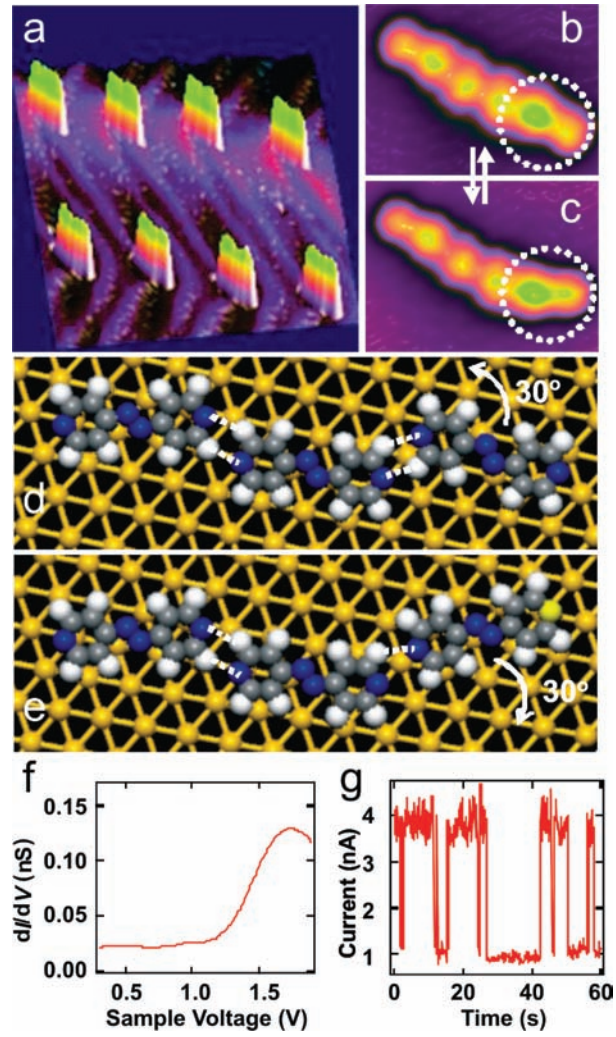


***Figure 1.*** (a) Pseudo-three-dimensional STM topograph of 4,4-azopyridine trimer array on Au(111) (−0.8 V, 0.1 nA; 32 × 32 nm$^2$). The colors correspond to a height range of 2 Å. (b, c) Reversible switching between linear and tilted trimer induced by a 1.5 V pulse onto the marked molecule (0.2 V, 0.1 nA; 3.5 × 2.6 nm$^2$). (d) Optimized supramolecular structures of linear trimer. (e) Schematic model of tilted trimer. (f) Spectrum of the marked molecule with open feedback loop and tunneling gap parameters of 2.0 V, 0.1 nA. (g) Time series of tunneling current measured on the marked molecule (b) with open feedback loop (tunneling gap parameters: 1.4 V, 4 nA).

According to our semiempirical quantum chemistry calculations using MOPAC2009, linear trimers are stabilized by weak double C−H...N hydrogen bonds between adjacent molecules (Figure 1d) (Supporting Information). The molecular rotation involved in

[†] Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität.
[‡] Centre National de la Recherche Scientifique.
[§] Institut für Organische Chemie, Christian-Albrechts-Universität.



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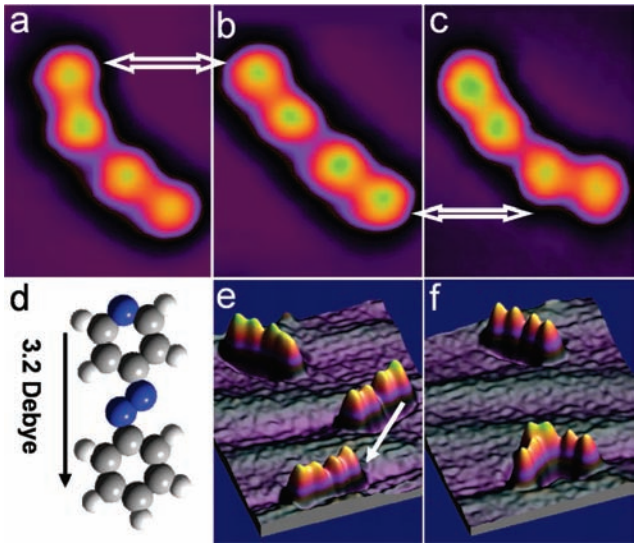


***Figure 2.*** (a−c) Reversible switching of a 4-phenylazopyridine dimer (b) by selectively rotating the upper (a, b) or lower molecule (b, c) (−0.9 V, 0.1 nA; 3.5 × 2.6 nm$^2$). (d) 4-Phenylazopyridine has a lateral dipole 3.2 D. (e) A dimer was moved to another dimer. (f) After manipulation, a trimer was observed.

switching breaks one of the C−H...N hydrogen bonds (Figure 1e). DFT calculation using VASP shows similar results (Supporting Information). The above results demonstrate reversible breaking and formation of a single C−H...N bond during switching of azopyridine supramolecules. During our measurements, we did not observe any *trans*−*cis* conformational change of isolated 4,4-azopyridine molecules.

Some insight into the switching process can be gained from spectra of the differential conductance d$I$/d$V$, which show the lowest unoccupied molecular orbital (LUMO) as a broad peak centered ∼1.6 eV above the Fermi energy. In repeated manipulation sequences, we found a threshold voltage for switching of ∼1.2 V. This corresponds well to the onset of LUMO in the d$I$/d$V$ data and suggests that the observed switching involves electron attachment. We hint that resonant transfer of a tunneling electron to the LUMO leads to a negatively charged transient state which can decay via energy transfer to molecular vibrations and finally switching. The quantum yield of the switching may be estimated from the time series of the current $I$ acquired on a switching molecule (Figure 1g). The supramolecule displays characteristic switching between two levels, which correspond to linear and bent trimers. The switching efficiency is $\sim 10^{-10}$ per electron at 1.4 V.

We performed a similar series of experiments as shown above on 4-phenylazopyridine dimers. These H-bonded dimers can be reversibly switched between linear and bent shapes at bias voltages $V \approx 1.4$ V. By selectively exciting the upper or lower molecule of a linear dimer (Figure 2b), a desired bent configuration can be obtained (Figure 2a or c). Manipulation was also successful at voltages as low as 5 mV, where electon-mediated processes are unlikely. Under these conditions, 4-phenylazopyridine dimers may still be switched by moving the tip closer to one of the constituent molecules as to increase the electric field in the tunneling gap and laterally moving the tip. Switching is also possible at intermediate voltages demonstrating that no direct mechanical contact of the tip to a molecule is required. 4,4-Azopyridine trimers, however, did not exhibit switching. Rather, one of the trimer molecules was transferred to the STM tip when attempting to induce lateral motion. We tentatively attribute this difference to the large electric dipole moment (3.2 D) of 4-phenylazopyridine.

Lateral manipulation at low bias voltage can be used to perform some supramolecular chemistry. Figure 2e and 2f show that 4-phenylazopyridine dimers can be moved toward another dimer to obtain a trimer. The fourth molecule was transferred to the tip, leading to intermediate blurring of the STM image, and was removed from the tip at a nearby surface area. The attraction among molecules in the new obtained trimer is due to a weak C−H...N hydrogen bond. The detailed mechanism of the supramolecular reaction, however, is not yet understood.

A notable feature of both 4,4-azopyridine trimers and 4-phenylazopyridine dimers is that they form ordered arrays on Au(111). The loose arrangement of the supramolecules enables local control of the switching process[26] where individual units may be selectively switched, similar to the case of the SnPc switch.[23]

In summary, 4,4-azopyridine trimers and 4-phenylazopyridine dimers have been reversibly switched in ordered arrays on Au(111). During the switching process, single weak C−H...N hydrogen bonds are broken and reformed.

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**Supporting Information Available:** Details of calculation using MOPAC2009 and calculated results by DFT using VASP. This material is available free of charge via the Internet at http://pubs.acs.org.

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