Supplementary Material (ESI) for PCCP

An electron induced switching process within supramolecular-assemblies of an azobenzene derivate on Au(111)

- Supporting Information -

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A. dI/dV-spectra of *cis**-isomer

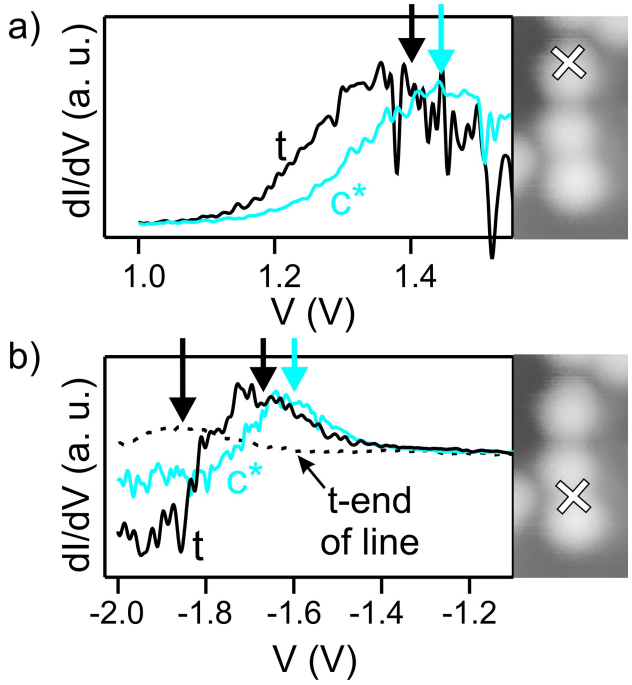

FIG. 1. dI/dV spectra. Black: Molecule in *trans*-configuration (marked with t). Cyan: Molecule in *cis**-configuration (marked with c*). Both molecules are within a meandering line. Arrows mark positions of molecular peaks as determined by Gaussian fits. Insets: STM image of molecule (I=310 pA, V= 125 mV, (2.6 x 1.3) nm^2). Cross indicates position of tip during spectra acquisition. a) Lock-In parameters: ν= 626 Hz, V_{mod}= 10 mV. b) Dashed black line: Molecule in *trans*-configuration at the end of a meandering line. Lock-In parameters: ν= 956 Hz, V_{mod}= 10 mV.

Figure 1 shows dI/dV-data in the positive (negative) bias regime taken on both configurations bonded within a meandering line. The spectra are measured on the single (double) protrusion C (A and B) (see Figure 2 in article) where the LUMO (HOMO) has its major weight (see Figure 3 of article). The tip position during the data acquisition is indicated by a cross in the insets of Figure 1.a and b and is the same for both configurations. For the *trans*-configuration the LUMO lies at (1.40 ± 0.02) V (see article), while for the *cis**-configuration this state is slightly shifted to 1.44 V (see Figure 1.a). A slightly larger shift is also observed for the HOMO (see Figure 1.b). The HOMO of the *trans*-isomer is located at -1.67 V, while this orbital is found at -1.60 V for the *cis**-isomer.

The shift for both orbitals is with 0.07 V (HOMO) and 0.04 V (LUMO) quite small

reflecting the small changes in the geometric structure of the surface-modified isomers. For comparison, the LUMO of TBA on Au(111) shifts by 0.3 V as deduced by two-photon photoemission.[Hagen *et. al.*, J. Chem. Phys. **129**, 164102 (2008)] There the geometry is more altered than in our case because the *cis*-configuration is three-dimensional. This change in dimensionality leads to a smaller contact area with the surface. Both affect the energetic position of the orbital. The importance of bonding is exemplified for the LUMO of the *trans*-configuration at the end of a meandering line (Figure 1.b). There the orbital is shifted to -1.85 V, *i.e.* by -0.18 V.

B. Movie of electron induced manipulation

The movie consists of a serie of manipulation as described in the article. Between each image of the movie both star structures are manipulated on different molecules.