# Light driven reactions of single physisorbed azobenzenes Supplementary information

Maciej Bazarnik<sup>\*</sup> and Ryszard Czajka Institute of Physics, Poznan University of Technology, Nieszawska 13A, 60-965 Poznan, Poland

Jörg Henzl and Karina Morgenstern Division of Atomic and Molecular Structures (ATMOS), Leibniz University of Hannover, Appelstr. 2, D-30167 Hannover, Germany (Dated: May 25, 2011)

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#### THEORETICAL METHODS

The configuration of the gas phase molecule is obtained by density functional theory (DFT) geometry optimization using the generalized gradient approximation (GGA) functional as implemented in the Amsterdam Density Functional (ADF) software [1]. Obtained structures are adapted for adsorption on the surface as explained below. For this purpose we use the semi-empirical Parameterized Model number 3 (PM3) method. The electrostatic potential maps are built upon Zerner's Intermediate Neglect of Differential Overlap (ZINDO) ground state calculations as implemented in ArgusLab software [2].

#### **IDENTIFICATION OF ISOMERS**

The 4-anilino-4'-nitroazobenzene molecule is calculated using DFT (Supplementary Fig. 1). The *trans* form is elongated and almost two-dimensional, while the cis form is twisted with ring number 3 bent out of the plane defined by the azo group. At first sight, the two structures calculated in the gas phase fit only poorly to the STM images (Supplementary Fig. 1a,b). The electrostatic potential (ESP) of the molecule mapped onto the surface of electron density (for a ground state) show three charge maxima in the ESP map located on the amino, azo, and nitro groups (see Supplementary Fig. 1c and Fig. 1d), which should dominate the STM images [3]. The distance in the calculated model between the nitrogen atoms in amino and nitro group is 1.16 nm. The structure fits quite nicely to the 2-dot-form. The ESP map calculated for the *cis* form does not fit to the STM image of the 3-dot-form. However, the -C-N-C- bonds in the anilino group are all single bonds and as such easily rotatable. A local energy minimum in the geometry optimalization for a structure is caluclated using the PM3 method for the first ring flipped around the C-N bond axis (marked in Supplementary Fig. 1a) by about 180°. The obtained structure varies mostly in the -C-N-C- angle by about 4.5°. Distances between azo and amino groups slightly changed by less than 7.5 pm and the overall energy as cal-



FIG. 1: *Cis* and *trans* configuration of the molecule in gas phase obtained by DFT geometry optimization using the GGA functional. In (a) and (b) black colored circles represent C, blue colored ones N, red colored ones O, and gray colored ones H atoms. Aromatic rings are numbered for easier identification in the text. The marked C-N bond is used in the adaptation procedure described in the text. In (c) and (d) ESP maps calculated present the areas of high negative densities.

culated by ZINDO method increased by 59.29 kcal/mol (approximately 0.47 eV). As a result, we obtain the structure shown in Fig. 1a of the main text. The ESP map for this structure shows a reasonable agreement between the STM image and this model of *cis* isomer.

### INELASTIC ELECTRON TUNNELING MANIPULATION

In IET manipulation the tip is placed above a molecule at increased current and voltage, while recording the tunneling current to detect induced changes to the molecule. The electrons tunneling inelastically through the molecule can trigger a reaction, which is verified in a subsequent STM image. The time of the manipulation is chosen such that single events can be observed and varies with energies from 0.1 s up to 120 s.

## ILUMINATION OF THE SAMPLE

The illumination of the sample was carried out *insitu* in the STM using a 100W mercury lamp. Mercury lamps have a very rich spectra in the range of 250 to 600 nm, thus, fully covering the range of absorption (connected with the *cis-trans* isomerization) of 4-anilino-4'-nitroazobenzene. The lamp is mounted out-side the UHV system, and its light is directed through a sapphire window and an opening in the cryoshield onto the sample at an angle of close to  $85^{\circ}$  to the surface normal. Before exposure to light, an STM image is taken of a spot with a characteristic feature, e.g. step edges. Then, the STM tip is retracted as far as possible from the sample and the incoming light (around 450 nm horizontally and 250 nm vertically) in order to minimize the shado-wing effect of the tip. The same spot is imaged after irradiation as

recognized by the characteristic feature.

## LOCAL HIGH VOLTAGE-HIGH CURRENT TREATMENT

Local high voltage-high current treatment starts with establishing a tunneling contact is in such a way that the scanner is almost totally elongated (90% of the maximal length). Next the tip is completely retracted and the STM preamplifier is replaced by a resistor. A voltage of 150V is applied between the tip and the sample. Then, the tip is manually approached to the sample while the current is constantly controlled. At the point, at which a current of 1 mA is measured, the tip is held for 10 seconds and than retracted within 3 s to 6 s in dependence of the shape of the tip. After the STM preamplifier has been reconnected, the position of the tip is shifted a few microns away from the contact point and the result of the treatment is measured. A few low voltage pulses on clean spots of the sample are usually necessary to completely recover the tip after the procedure.

- \* Electronic address: Maciej.Bazarnik@put.poznan.pl
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