

## PHOTO-INDUCED INTERCONVERSION OF CONJUGATED AZOBENZENES ON METAL SURFACES

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Self-assembly of thiol functionalized organic architectures on a metal electrode represents a convenient strategy for incorporating molecules into micro- and nano-electronic circuits. Photoactive molecules, as azobenzene, are attractive systems to design and assemble photoswitchable molecular devices [1]. The photo-isomerization of conjugated azobenzenes organized in self-assembled monolayers (SAMs) on metal surfaces is reported to be hampered because of the tight packing between nearest neighbor molecules in the SAM.

Previously, the endeavour has been addressed to the formation of SAMs from alkanethiol functionalized azobenzenes chemisorbed on gold [2]. However, alkanethiol derivatives are not ideally suitable as electroactive units for nanoelectronics because of the poor conductivity of the alkane chain. Here we describe the first case of fully conjugated azobenzene derivatives (AZO, Fig. 1A) exhibiting reversible *trans-cis* photoisomerization when organized in single-component SAMs on Au(111).

Scanning Tunneling Microscopy (STM) and Near Edge X-ray Absorption Fine Structure (NEXAFS) studies have been carried out in order to characterize the molecular self-assembly across a wide range of length scales. They revealed that the AZO chains pack nearly perpendicular to the substrate, if compared to conventional alkanethiol SAMs on Au(111). The tilt angle of the molecular backbone with respect to the normal to the substrate is  $\sim 20^\circ$ , allowing the maximization of the intermolecular interactions.

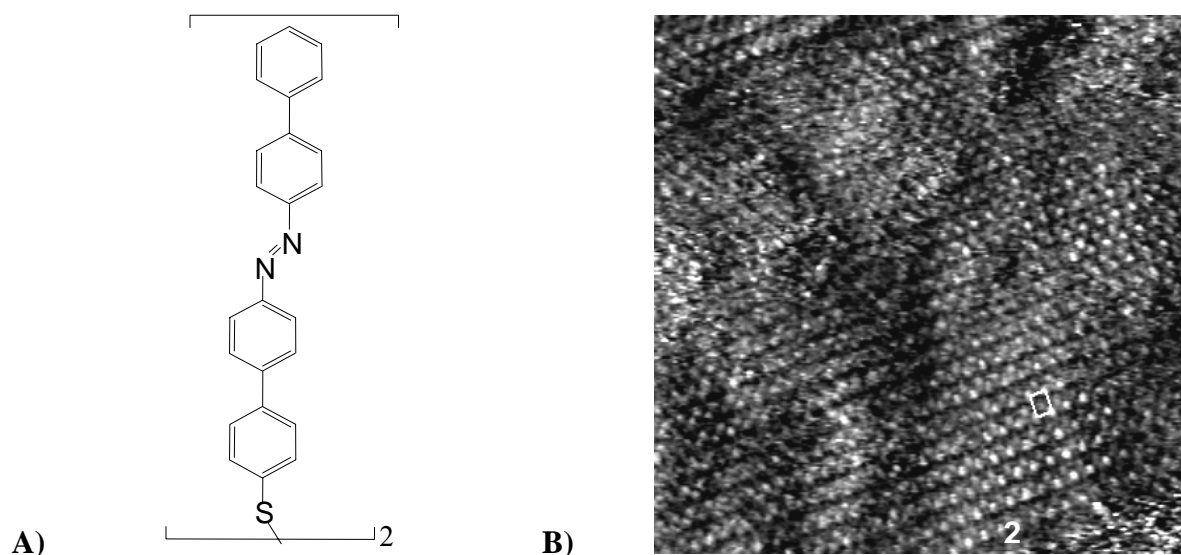
High-resolution STM current images showed that the AZO molecules assemble into a rectangular unit cell containing two molecules as shown in Fig. 1B; this behavior is similar to the case of simpler arenethiols SAMs [2]. We also found that molecules bind the substrate as dimer. The binding of the dimers is evidenced by the typical herringbone structure appearing in the SAM's domains (Fig. 1B).

Previous AFM and STM studies revealed two different patterning for the arenethiols and alkane-thiolated azobenzenes chemisorbed on Au(111); this observation has been explained in view of the existence of two different lattices: the pseudo-hexagonal and the herringbone [3]. Sub-molecularly resolved STM images recorded at different scan angles allowed us to rule out the existence of two different molecular lattices for our conjugated azobenzene thiolated derivatives. Upon change of the scan angle we observed that the herringbone structure becomes a pseudo-hexagonal patterning and vice versa, maintaining the identical unit cell size and geometry. Thus we conclude that the two lattices are equivalent. We attribute this scan angle dependence of the image contrast to the contribution of the frontier's orbitals of the conjugated molecules to the electron tunneling. Consequently the molecular packing within the dimer, consisting of two

aromatic chains assembled according to a herring-bone motif, is very likely to play a role. Such herringbone structure is thermodynamically favored since the face-to-face packing of two  $\pi$ -systems is characterized by a repulsive interaction, whereas when the  $\pi$ -systems glide one over the other or rotate away from each other the interaction becomes attractive [4].

STM measurements of the AZO SAM under UV light irradiation have been also performed. We found that both in SAM formed from solutions kept under irradiation during chemisorption and in samples incubated in the dark and post-irradiated when dried, the self-assembled monolayers mostly exhibit domains containing molecules in their *trans* conformation.

The photo-induced interconversion was also monitored by UV-Vis spectroscopy in transmission mode using transparent metal surfaces and the conductivity was measured using the drop mercury junction method [5]. The I-V characteristics of the junction, before and after irradiation through the transparent substrate, revealed changes in the electrical conduction of one order of magnitude. The current can be switched “on” and “off” several times by irradiating at different wavelengths. This proves that the conductivity of the junction can be modulated by a light driven molecular switch.



**Fig. 1:** A) Molecular structure of an azobenzene derivative (AZO1). B) Constant-current STM image of AZO1 SAM on Au(111) showing a rectangular unit cell containing two molecules. Unit cell parameters:  $a = (0.65 \pm 0.3)$  nm;  $b = (0.89 \pm 0.5)$  nm;  $\alpha = (84 \pm 3)^\circ$ . Similar unit cell was reported for arenethiols SAMs on Au(111) [2].

### References:

- [1] N. Tamai, H. Miyasaka, Chem. Rev., 100, (2000), 1875
- [2] S.D. Evans, R.S. Johnson, H. Ringsdorf L.M. Williams, H. Wolf, Langmuir, 14, (1998), 6436
- [3] H. Wolf, H. Ringsdorf and collaborators J. Phys. Chem., 99, (1995), 7102
- [4] C. A. Hunter, K. R. Lawson, J. Perkins, C. J. Urch, J. Chem. Soc. Perkin Transactions 2, (2001), 651
- [5] E. Tran, M.A. Rampi, G.M. Whitesides, Angew. Chem. Int. Ed., 43, (2004), 3835  
M. A. Rampi, G. M. Whiteside, Chem. Phys., 281, (2002), 373