



	Experiment title: NIXSW study of the vertical adsorption geometry of azobenzene-derived molecular switches at defined noble metal surfaces	Experiment number: SI-1728
Beamline:	Date of experiment: from: 20/07/2008 to: 30/07/2008	Date of report: 15/02/2010
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Report: The aim of the experiment SI-1728 was to obtain a detailed understanding of the adsorption geometry and electronic structure of azobenzene-based molecular switches at defined noble metal surfaces using normal incidence X-ray standing wave (NIXSW) and density-functional theory (DFT). Particularly, experiments on adsorption of azobenzene and 3,3',5,5' tetra-tert-butyl-azobenzene (TBA) on Ag(111) surface were planned for the SI-1728 experiment.

For **azobenzene**, the analysis of NIXSW data revealed the height of $-N=N-$ bridge over the Ag(111) surface of 3.07 Å [1]. Assuming a symmetric adsorption configuration, as it was suggested by theory [2], and adopting a specially developed approach, we were able to extract the tilt angle of the azobenzene phenyl rings. The obtained value of $-1 \pm 1.5^\circ$ reveals essentially a flat geometry of the molecule [1]. These results are in a perfect agreement with the theoretically calculated ones, if the van der Waals (vdW) interactions are accounted using a semiempirical dispersion correction to the semilocal DFT [1,2]. However, if the vdW interactions are ignored and only a standard Perdew–Burke–Ernzerhof approximation (DFT-PBE) is applied, the adsorption height of the molecule comes out significantly greater (3.64 Å) [1,2]. Thus the NIXSW data are used for benchmarking the theoretical calculation schemes. The combined results of experimental and theoretical study of azobenzene/Ag(111) interface were published in Physical Review Letters [1].

For **TBA** molecule, the presence of bulky butyl groups grafted to the phenyl group results in insignificant but obvious increase of adsorption height. At the same time the coherent fraction of C1s core level appears to be very small due to many spectroscopically equivalent carbon atoms vertically distributed above the surface. Thus, adding these butyl groups to the parent azobenzene molecule induces a slight decoupling from the surface. This idea will be used further for obtaining a control over the switching behavior of

azobenzene-derivatives at metal surfaces, e.g. TBA on Au(111). Preparation of a separate publication on TBA/Ag(111) data is currently in progress.

1. G. Mercurio et al, PRL **104**, 036102 (2010).
2. E. McNellis et al. PRB **80**, 035414 (2009); E.R. McNellis PRB **80**, 205414 (2009).