

# **Spectroscopic Investigations of Azobenzene Based Self-assembled Monolayers on Gold, SiO<sub>2</sub>, and Water**

## **Dissertation**

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Signed Prof. Natascha Oppelt Dean

## Declaration

I hereby declare that the work presented in this thesis is original and my own without any help except the guidance of my supervisor Prof. Dr. Gernot Friedrichs. All the references are cited properly.

This is my first dissertation and the work has neither been used as a whole nor in parts in any other dissertation, and it has neither been published nor submitted for publication.

The dissertation complies to the Rules of Good Scientific Practice as proposed by the German Research Foundation (DFG).

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(Place)      (Date)      (Saira Riaz)



# Abstract

This study was concerned with the investigation of photo-induced molecular switching processes of azobenzene based self-assembled monolayers (SAMs) on surfaces.

The rational design of such surfaces, which often hold the potential for practical application, require a thorough understanding of the factors that control surface assembly into highly ordered architectures as well as photoswitching efficiency. The latter is often limited by steric hindrance, i.e., the lack of free volume in the molecular monolayer. This work further aimed at a demonstration of the capability of Sum Frequency Generation spectroscopy (SFG) to investigate diverse functionalized surfaces including reflective gold and transparent quartz substrates as well as monolayers at water-air interfaces.

SFG analysis of Azobenzene (AB) like 4-(11-Mercapto-undecanoxy)-4'-methylazobenzene (MeAB-OC11S), 4-(10-Mercapto-decanoxy)-4'-methylazobenzene (MeAB-OC10S) on 100 nm Au (111), (E)-12c-[4-(4-Methyl/CN phenyldiazenyl)phenyl]ethynyl-4,8,12-tri-octyl-4,8,12-triazatriangulene, (Me/CN-Azo-8-TATA) on quartz and Azobenzenecholesterol/ Dipalmitoylphosphatidylcholine (AzoChol/ DPPC) on water was used to confirm the formation of self-assembled monolayers (SAMs) on the substrate, to depict the morphology of these SAMs and to check their photoisomerizing ability. Characteristic spectra confirmed the adsorption of molecules on the surfaces with vibrational signatures of different CH units. In particular, resonances of  $\text{CH}_2$  ( $d^+$ ,  $d^-$ ,  $d_{\text{FR}}^+$ ) and  $\text{CH}_3$  ( $r^+$ ,  $r^-$ ,  $r_{\text{FR}}^+$ ) and  $\text{CH}_{\text{aromatic}}$  have been identified in SFG spectra of pure and mixed monolayers. The observed amplitude ratios of the  $d^+/r^+$  and  $r^+/r^-$  bonds confirm the presence of gauche defects in the mixed monolayer, where fitting of the spectra indicate the loss of structural order of the monolayers on dilution with coligand alkylthiol molecules.

Pure and mixed monolayers of AB thiols/ thiol on gold were used to investigate the photoisomerization efficiency as a function of the degree of surface dilution. The SFG signals of

CH<sub>3</sub> or CN SFG marker group at the phenyl group of azobenzene was used as direct measure of *trans* / *cis* isomerization of azobenzene functionalized SAMs. Moreover, different thiols with various chain lengths were used as co-ligands to get insight into steric hindrance effects. In case of gold, the non-resonant SFG background proved a challenging factor for spectrum acquisition and limited the reproducibility of these experiments. Nevertheless, it could be successfully shown that most of the investigated mixed monolayers exhibit photoswitching ability. An exception was a monolayer of MeAB-OC11S using hexadecanethiol as a co-ligand. Obviously, the long alkyl chain of the co-ligand induced strong steric hindrance and efficiently inhibited photoswitching. This result could also be confirmed by additional experiments by means of UV-Vis transmission spectroscopy. Moreover, thermal back-isomerization from the *cis* to *trans*-state with time constants in the order of 5 min to 50 min have been observed.

In addition to the systematic studies on gold, explorative SFG measurements have been performed with many different molecular systems including TATA functionalized quartz surfaces. Intense SFG signatures have been observed showing high degree of surface functionalization and molecular order. However, photoisomerization of TATA based SAMs was sensitive to aging of the sample and laser damage.

Finally, both the changes of surface pressure as well as SFG characteristics have been analyzed for Azobenzene-Cholesterol/ Dipalmitoylphosphatidylcholine (AB-Chol/DPPC) monolayers on water. Switching these layers to the *cis*-state of AB-Chol caused an increase in surface pressure going along with better aligned alkyl chains of DPPC, hence consistent with a higher spatial demand of the *cis*-state.