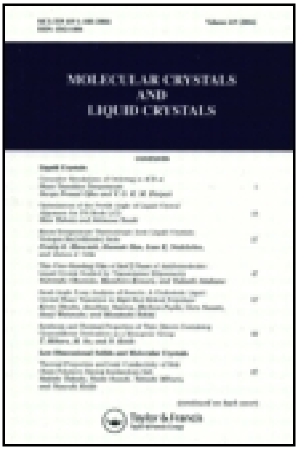

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Optically Induced Switching of Azobenzene Containing Self Assembling Monolayers Investigated by Kelvin Probe and Scanning Force Microscopy

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Optically Induced Switching of Azobenzene Containing Self Assembling Monolayers Investigated by Kelvin Probe and Scanning Force Microscopy

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The light induced switching of self-assembled monolayers containing azobenzenes is observed in situ by the Kelvin probe method. The switching process is optimized by preparing monolayers from mixed solutions of azobenzene thiols and n- alkylene thiols. In a film the efficiency of the E/Z-isomerization depends on both the spacer length between azobenzene group and gold surface as well as the free volume in the film, tuned by the n-alkylene thiol fraction in the mixture. An optimum was found in a mixed self-assembling film containing 33% 4-fluoromethyl-4'-(10-carboxy-decyloxy) azobenzene in a dodecane thiol matrix. The structure of the films were characterized by FTIR and AFM.

Keywords: Kelvin technique; surface potential; AFM; SAM; azobenzene; isomerization

1. INTRODUCTION

The optical E/Z isomerization of azobenzenes [1,2,3,4] is one of the most intensely researched molecular switches. The redistribution of the electrons during the isomerization changes the optical, dielectrical, and chemical properties of the azobenzene-containing materials. The geometrical changes created by this

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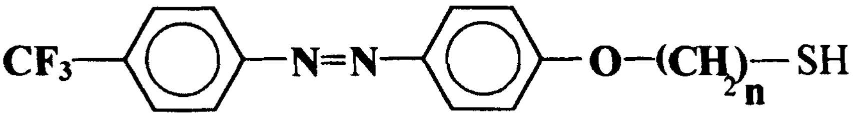
isomerization can lead to a global restructuring of thin films based on azobenzene compounds. Because of these properties the azobenzene-containing compounds possess a great potential for application in optoelectronics, electronics, and in sensors.

The self assembling of azobenzenethiols on a gold surface [5,6,7], forced by chemical adsorption, creates stable and well ordered optically active monolayers (SAM). Due to the strong chemical bond between sulfur and gold, they are more stable against destruction by irradiation than layers produced by other techniques, e.g. Langmuir-Blodgett[8] and spin coating. The examination of the switching properties of azobenzene-containing SAM discloses the effectiveness of the E/Z isomerization for densely packed structures on the one hand and the effect of the nearby gold surface on the excitation of the $\pi\pi^*$-system by light on the other hand. This interaction is often described by the Foerster radius [9,10].

New azobenzene-containing thiol compounds with carbohydrogen spacers of different length (6, 10, and 12 carbon atoms: fig. 1) between the two functional groups were synthesized to vary the distance between the azobenzene group and the gold surface. The free volume of the films, necessary for the isomerization, was modified by preparing SAM from solutions with different ratios of azobenzene thiol and dodecane thiol. The structure and the switching properties of the films were experimentally characterized by Kelvin methods [11,12], AFM, and FTIR. Molecular modeling was used to draw a realistic picture of the film.



AZO –C n

n = 6, 10, 12

FIGURE 1 Fluorinated azobenzene thiol with different spacers for preparing optically switchable SAM's

The redistribution of the electrons in the azobenzene group while adsorbing light at a wavelength of λ_1 = 360 nm (E state) and λ_2= 450 nm (Z state) leads to a change in the molecular dipole moment. In noncentrosymmetric films (SAM), this should result in a change of the macroscopic surface potential. This change is measured in situ using the Kelvin probe method (fig. 4). We assess the effectiveness of the switching in the real film by comparing the measured Kelvin signal (ΔU_{exp}) with the expected change of the dipole moment (ΔU_{max}) in the SAM during isomerization using the calculated values of a single molecule in a realistic model of the film.

FTIR spectroscopy is used to confirm the chemical structure of the used compounds. The IR transmission spectra of the solution, used to form the SAM, and spectra, obtained from reflection at the covered gold surface, are compared to give information about the orientation of the molecules in the film. The surface of the SAM is examined by STM/AFM before and after irradiation to demonstrate possible changes of the film structure during isomerization.

2. METHODS

Materials

Due to the molecular symmetry the single azobenzene moiety has no dipolemoment in Z state [13]. Only an unsymmetrical substitution at the ends of the azobenzene moiety leads to a permanent molecular dipolemoment. We synthesized an azobenzene unit with a fluorinated endgroup in a three-step process. 4-Trifluoromethyl aniline (purchased from Aldrich) was coupled with phenol to give 4-trifluoromethyl-4'-hydroxy azobenzene in the first step. Alkylation with α,ω-dibromoalkylenes to the respective bromides follows. Both steps are very similar to the procedure described earlier [14]. The resulting compounds were converted into the corresponding thiols using the method of Brace [15]. The synthesized thiol compounds, see fig. 1, were purified by recrystallisation from ethanol and analyzed by elementary analysis, IR-, and ^{1}H-NMR-spectroscopy.

The IR transmission spectra of the synthesized compounds show characteristic absorption bands which confirm the chemical structure of the investigated bulk material. Bands at 2925 cm^{-1}, 2856 cm^{-1}, 1473 cm^{-1}, 1465 cm^{-1}, and 720 cm^{-1} belong to the long aliphatic chain. The bands at 1603 cm^{-1}, 1581 cm^{-1}, 1420 cm^{-1}, and 854 cm^{-1} belong to the para substituted phenylene rings. The CF_3-groups show intensive absorption bands at 1326 cm^{-1} and between 1100 and 1170 cm^{-1}. The ether bridges absorb at 1256 and 1066 cm^{-1}.

Molecular Modeling

Molecular modeling was performed to verify the validity of the assumed model in detail. We used the CERIUS^2 modeling platform. The data for the (111) gold surface were taken from literature. A unitcell was created with the two upper atomic layers of a (111) gold surface placed on the bottom. The molecules are grafted to this surface using its thiol ends. The AZO-C10 molecules were generated according their chemical structure using a Dreiding force field. The height of the unitcell was chosen so that the free end of the molecules could not interact with the gold atoms in the above unitcell. It is at 10 nm. There are 7×7 gold atoms per layer in the unitcell, defining the lateral dimensions of the array. The nine molecules are grafted at places chosen randomly so that they occupy an average 0.48 nm^2 each, a value reported by Ringsdorf et al. [16] and in agreement with our own AFM measurements. Several configurations were produced. The state of the molecule, either cis or trans, was taken also for random with an even probability for both states. Figure 2 shows a typical example. Here three azo groups are in the cis state.

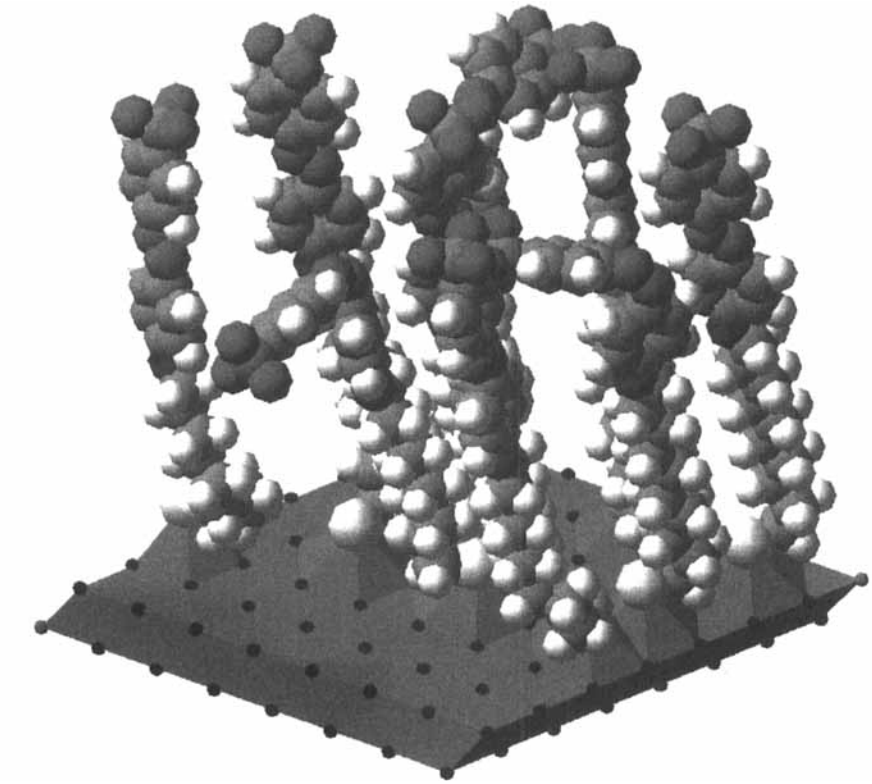


FIGURE 2 Model of the SAM of AZO-C10 on Au(111) (See Color Plate IV at the back of this issue)

The charges for the molecule were taken from a MOPAC calculation with AM1 for the aromatic part. The molecular dipole moments were determined to

3.9 D in the Z state and 4.8 D in the E state. The polarity of the sulfur-gold bond was taken into account by charging the sulfur atoms individually and smearing the according gold charge over the first gold layer. The second gold layer was charged to keep the unitcell neutral.

A molecular dynamics calculation was performed at equivalent 300 K to equilibrate the system. The result approves the picture of the upright standing molecule on the gold surface. There is enough free space so that single molecules can perform the E/Z isomerization. The change of dipole moment perpendicular to the surface results to $\Delta m_{\perp}= 1.3$ D per switching molecule. This change should be visible by the Kelvin probe method.

Self assembling

A 150 nm thick gold (111) film was evaporated on freshly cleaved mica in high vacuum (BALZERS-PLS) with a deposition rate of 0.25 nm/s. Before deposition the mica was degassed by keeping it for several hours at 350°C. This temperature was maintained during the whole evaporation. Finally, the coated substrate was cooled slowly to room temperature in a nitrogen atmosphere. The gold films were characterized by STM. The detected terraced gold areas show the typical monoatomic steps and the characteristic hexagonal patterns of an Au(111) orientation.

The freshly prepared substrates were dipped into 10^{-3} molar ethanol solutions of azobenzene and left there for 24 h. After removing the substrates from the solution they were rinsed with pure ethanol to remove not grafted molecules and then dried in floating nitrogen. The resulting surface quality was examined by STM/SFM, (see fig.3).

IR Spectroscopy / STM, SFM

Infrared spectra of the SAM's were recorded with the FTIR spectrometer Magna 550 (Nicolet Instruments) at a resolution of 4 cm^{-1}. The SAM of AZO-C6, AZO-C10, and AZO-C12 were measured in a reflection-adsorption mode (RAS) at an angle of incidence of 80 deg. and p-polarized radiation. One thousand single spectra were accumulated to get a sufficient signal-to-noise ratio. In addition, a transmission spectrum of AZO-C6 prepared as a KBr-pellet was recorded with non-polarized radiation, to compare the results of RAS with a spectrum of the bulk material.

The AFM and STM measurements were performed with a SA1/BD2 microscope (Park Scientific) in air and at room temperature. The SFM operated in con-

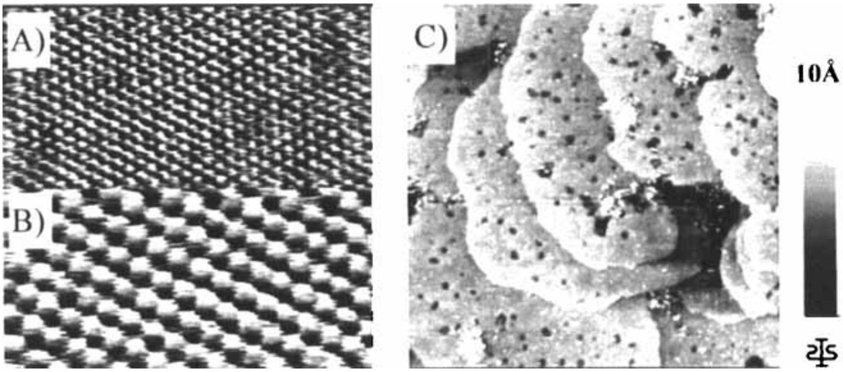


FIGURE 3 SPM image of Au(111) and AzoC 10 – SAM on Au(111) A) Au(111) substrate, (10nm × 5nm); B) Molecular resolved AzoC10 on Au(111), (10nm × 5nm); C) Macroscopic image (500nm × 500nm) with etch holes in the Au surface

tact mode. Pictures with atomic resolution were recorded in constant height mode. The other images were measured in constant force mode. The probe was a sharp standard Si_3N_2 cantilever with a length $l = 200$ μm and a spring constant $k = 0.032$ N/m (Park Scientific). The effective force $F \approx 10$ nN was small enough to prevent a destruction of the investigated films. The STM operated in constant current mode with $U_T = 1.2$ V and $I_T = 20$ pA. Pt-Ir tunneling tips were used.

Surface Potential Measurement

The registration of the optical transmission or reflection spectra is used as a common method of observing the E/Z isomerization of azobenzenes in solution and in thin films, e.g. LB-films or spin coating films. It uses the characteristic light absorption for the E and Z state. In the present work a more surface-sensitive method is used to suit our ultra thin (1.5 nm) SAM. The change of the molecular dipole moment, caused by optically switching between the two states of the azobenzene group, is observed directly from the SAM by measuring the surface potential. The Kelvin probe technique (using a "ΔΦ Besoke" GmbH device[17]) allows it without any mechanical contact with the SAM on the metal surface (fig. 4). An active measuring area of ca. 2 mm^2 is sufficient to give a signal with a resolution of about 1 mV. The switching between the stationary states E and Z of the azobenzene was induced by irradiation with alternating colored light of $\lambda_1 = 450$ nm and $\lambda_2 = 350$ nm from a HQL lamp. The light intensities were 20 mW/cm^2 and 15 mW/cm^2 respectively.

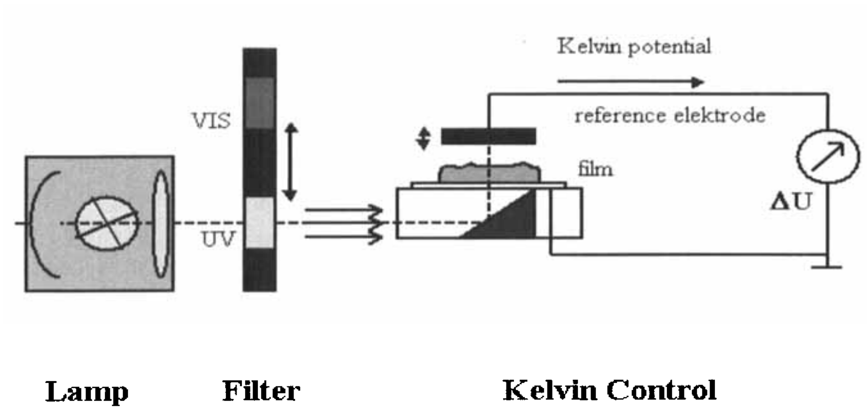


FIGURE 4 Measuring the surface potential by the Kelvin probe technique while illuminating a film with uv – or vis light

3. RESULTS AND DISCUSSION

Beside the chemical structure, the FTIR investigations reveal a picture of the molecular orientation of the grafted azobenzene by comparing the transmission spectrum of the bulk material with the reflection spectra of the SAM. The in-plane ring vibrations and the ether vibrations appear in both kinds of spectra. The stretching vibrations of the long alkyl chain at 2925 cm^{-1} and 2856 cm^{-1} together with the out-of-plane CH- vibration of the phenyl rings at 854 cm^{-1} are absent in the reflection spectra (RAS).

The p-polarized radiation of the RAS-experiment (angle of incidence: 80 deg.) interact only with such transition moments which possess a component normal to the surface. All vibrations with transition moments in the plane of the surface remain undetected. Under the plausible assumption that the chemical structure of the molecules, except of the thiolgroup, remains unchanged during film formation, the spectra indicate a conformation where the molecules are normally oriented to the surface of the substrate. Only in this case, the transition moments of the CH_2-stretching vibrations at 2925 cm^{-1} and 2856 cm^{-1} and of the out-of-plane ring vibration at 854 cm^{-1} are parallel to the surface. Therefor they do not interact with p-polarized radiation.

The AFM micrographs of a SAM, built of only azobenzene-containing thioles, reproduce the characteristic structure (see fig. 3). They show a molecular resolution with a high order. Its shape is best described by a rhomboid lattice with the parameter a = 0.61 nm, b = 0.78 nm, and ca. 90deg. In agreement with the findings of Sawondy [18] and Nishida [19, 20] these parameters do not change with different lengths of the alkylic spacer between the thiol and the azobenzene. The characteristic structure is retained even after several optical switches.

A SAM, containing azobenzene, reacts with a change in the surface potential on the irradiation with light that switches the azobenzene units between the Z and E state. Fig. 5 shows typical plots of the surface potential against time, which are characterized by the height ΔU_{exp} of the step, generated by the incoming light, and a time constant τ. The time dependence of the step height and the relaxation time is estimated for different lengths of the aliphatic spacer (6, 10, and 12 carbon atoms in the backbone) and for different fractions of dodecane thiol in the solution from which the SAM was formed. The surface potential remains unchanged for irradiated SAM's made from dodecan thiol only. This allows the conclusion, that there is no light induced generation of charges in this films that could influence the surface potential. Therefore changes of surface potential can be attributed to the presence of azobenzene and the changes of its molecular dipolemoment connected with the optical E/Z isomerization.

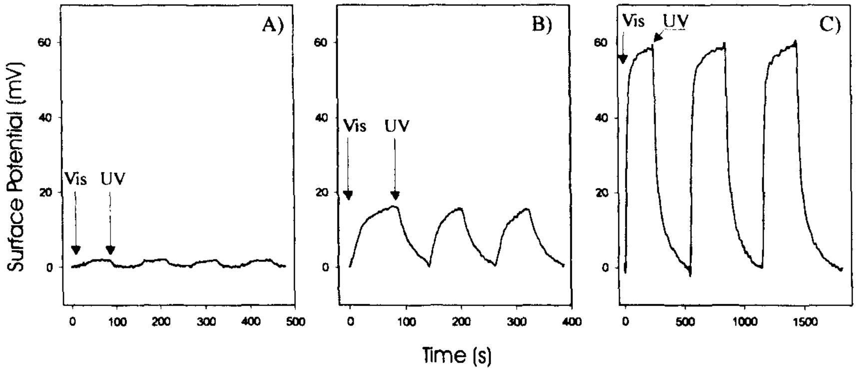


FIGURE 5 Surface potential plots of different SAM's illuminated by alternating uv- and vis light against time, measured by Kelvin method A) AZO C6 SAM n=6; B) AZO C10 SAM n=10; C) Mixed SAM of 33% AzoC10 and 67 % dodecane thiol

The amplitude ΔU_{exp} is growing up with an increasing azobenzene fraction in the solution (fig.6). It reaches a maximum at 33% azobenzene thiol. There are two explanations for the non linear behavior of the curve. The adsorption isotherms for the azobenzene and alkyl thiol can differ. This means that the ratio between the two substances is different in the solution and in the SAM. It was not possible to measure the mixing ratio of the film by means of either force or tunneling scanning microscopy because it was impossible to find a clear difference

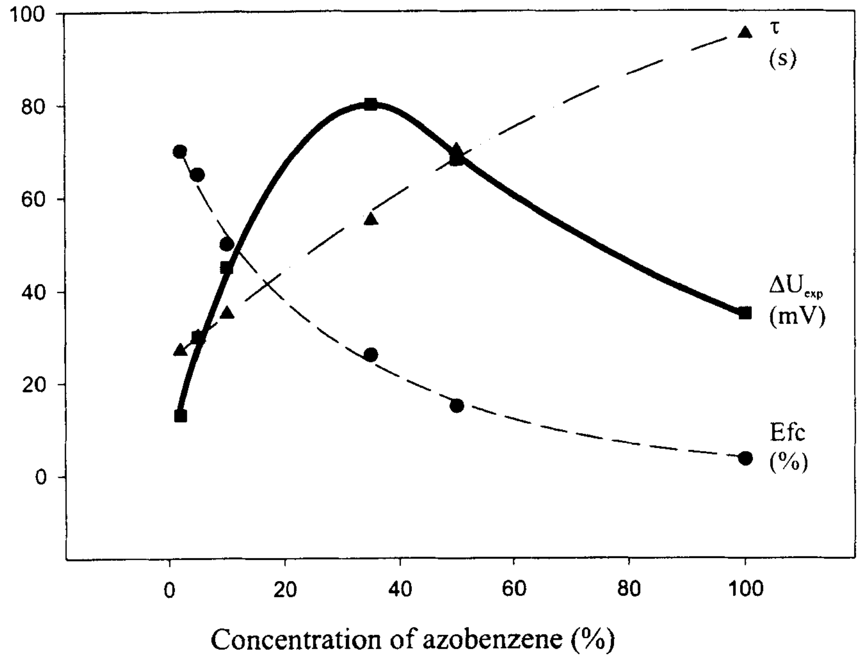


FIGURE 6 Amlitude (ΔU), time constant (τ) and efficiency (*Efc*) of optically induced switching of mixed SAM's in relation to the concentration of azobenzene

in the heights of the molecules above the surface to identify azobenzene thiol or dodecan thiol. A second reason for the nonlinearity could be an aggregation[21] of equal molecules in the SAM. Since the azobenzene has a footprint approximately two times greater in the E than in the Z state, the molecules are hindered from switching in a densely packed azobenzene domain. Easily switchable are only those molecules at domain boundaries or near point defects inside a domain. This argument is confirmed by the observed absence of any photoinduced destruction of the film.

Following an usual approach in percolation theory, the sum of circumferences P_d of the azobenzene domains in the SAM can be given by:

$$P_d = k(k_{azo})^n,$$

where k is a constant and $n < 1$. k_{azo} is the fraction of azobenzene-containing molecules in the mixed SAM. This relation is only valid until the domains start to coalescent. Then the circumference and also the number of swichable azobenzene molecules is decreased with further increasing the concentration k_{azo}. The measured ΔU_{exp} should show a significant maximum between low and high concentration of azobenzene in mixed SAM's. This is exactly what was observed in our experiments.

In a further approximation, the domains can be taken as of circular shape. A simple geometrical consideration shows in this case, that ca. 78% of the surface is covered by azobenzenes. An AZO-C10 molecule occupies a two times greater area than a dodecan molecule. The isomerization of one molecule is taken to happen independently from the isomerization of its neighbors. This simplest model places the maximum of switching at $k_{azo} \approx 36\%$! This value is in good agreement with the measured maximum of ΔU_{exp} at ca. 33% azobenzene in the initial solution.

The experimentally observed dependence of the switching timeconstant τ on the concentration of azobenzene (see fig. 6) shows an interdependence of switching neighbors as well as an influence of the free volume on to the switching kinetics.

Based on the found structural features of the SAM and using the calculated molecular dipole moments in both E and Z configuration, a change of the normal component of the dipole moment during the isomerization $\Delta m_{\perp}$ can be calculated. This allows to get an upper limit for ΔU in the case were all azobenzene units perform isomerization:

$$\Delta U = \varepsilon^{-1} \cdot \Delta m_{\perp} \cdot \sigma(k_{azo}/100).$$

Here ε is the relative dielectric constant and σ is the surface density of azobenzene molecules in a pure AZO-C10 SAM. Together with the measured ΔU_{exp} the fraction of molecules taking part in the isomerization can be defined as an efficiency E_{fc} of switching:

$$E_{fc} = \Delta U_{exp} / \Delta U_{max}.$$

The dependence of E_{fc} on k_{azo} is shown in fig. 6. With increasing k_{azo} the number of molecules at the circumference of a domain and at point defects inside a domain decreases relative to the molecules in the domains. Hence E_{fc} is decreasing too.

In a pure azobenzene film only molecules at point defects will perform isomerization. The number of point defects in the SAM is closely related to the quality of the gold surface. As a result, the measured ΔU of pure azo SAM on differently prepared Au surfaces (Au(111), sputtered Au, ...) varies [22]. Smaller crystallites and a higher roughness lead to greater ΔU_{exp}. The estimated E_{fc} is therefor a value of the quality of the SAM.

4. SUMMARY

Switchable monolayers of azobenzene thiols were prepared by self assembling technique on gold surfaces.

The switching process (E-Z photoisomerization) can be monitored in situ by the Kelvin probe technique if the switching is accompanied by an effective change of dipoles in the film.

The efficiency of the E/Z- isomerization in a film depends firstly on molecular properties (dipole, spacer), secondly on the supramolecular structure of the film (free volume, packing), and thirdly on the quality of the substrate (quenching, roughness).

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