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Reversible Photoswitching of Azobenzene-Based Monolayers Physisorbed on a Mica Surface

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The formation of compact and large-scale self-assembled monolayers (SAMs) adsorbed on a mica surface has been achieved by insertion of alkyl chains on azobenzene derivatives, leading to strong intermolecular van der Waals interactions and hydrogen bonding. The reversible photoswitching of monolayers was investigated by monitoring the variation of the thickness of the SAMs during the cis–trans isomerization of the azobenzene cores with an atomic force microscope (AFM). The absence of covalent bonds between molecules and substrate induces a molecular diffusion which leads to the complete isomerization of the molecules constituting the SAMs.

1. Introduction

The self-organization of molecules on a solid surface is one of the most convenient strategies to develop nanostructures with chemical, physical, or biological properties that can be integrated into electronic devices.^{1–5} The spontaneous formation of self-assembled monolayers (SAMs) can be obtained by using molecules designed around three basic building blocks: a headgroup interacting with the substrate, a tailgroup that defines the functionality of the outer film surface, and a spacer linking the head- and tailgroup. The self-assembly is driven mainly by lateral interactions (i.e., van der Waals, H bonds, π – π stacking, etc.) between spacer group of adjacent molecules.^{1,2} SAMs can also be used for the preparation of smart functional surfaces capable of reacting to external stimuli, such as light, electric or magnetic fields, etc.^{6,7} In this context, SAMs bearing photoactive functional units are very interesting to provide surfaces with reversible photoswitchable properties. Because of their unique photoisomerization property, azobenzene derivatives are the most promising building blocks,^{8,9} and they have been involved in many applications such as data

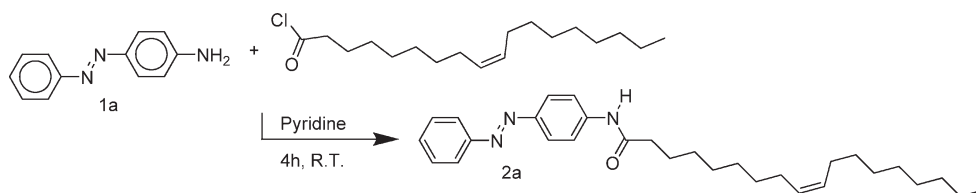
storage,^{10–13} molecular machines,^{14–19} etc. The reversible cis–trans isomerization process of azobenzene is well-known and is fully characterized even at the single molecular level.^{20–23} However, in the case of SAMs including azobenzene as the tailgroup, one of the main limitations to develop applications is the free volume required for the cis–trans isomerization due to the strong modification of the molecular structure during this process. There is a competition between the density of the SAMs coming from the lateral interaction between adjacent molecules and the free volume required for the isomerization. Therefore, in most reported cases, a small part of azobenzene was isomerized in the SAMs only. Besides, no photoisomerization has ever occurred, except when the SAMs are not very compact.^{24–27} In this paper, we report about a solution to get around this problem. The formation of compact and large-scale SAMs containing azobenzene physisorbed on a mica surface was achieved. The reversible photoswitching of SAMs has been investigated by monitoring the variation of the thickness of the SAMs during the cis–trans isomerization of the azobenzene cores with an atomic force microscope (AFM). Physisorption of molecules rather than covalent bonding gives an additional degree of freedom leading to the complete isomerization of the azobenzene tailgroups constituting the SAMs.

2. Experimental Section

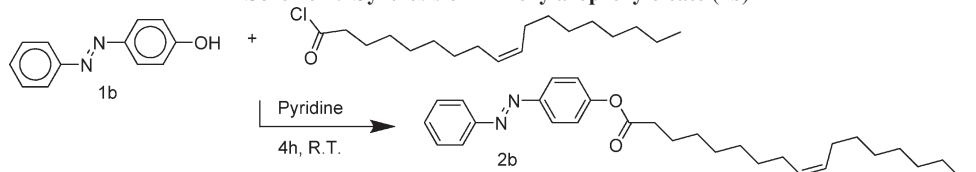
2.1. Materials. All reagents were purchased from Aldrich and used as received. The silica gel (type G) used for column chromatography was purchased from Macherey Nagel GmbH.

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Scheme 1. Synthesis of *N*-4-Phenylazophenyleamide (2a)

Scheme 2. Synthesis of 4-Phenylazophenyleate (2b)



The deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. The NMR spectra were recorded using a Bruker AC-300 MHz spectrometer. The UV-vis spectra were recorded with a Perkin-Elmer Lambda 900 apparatus. The AFM measurements were performed with Nanoscope IIIa Veeco apparatus. UV-light exposure was performed by a Spectroline E-series UV Lamp and by an OmniCure series S1000.

2.2. General Procedure. 4-Phenylazobenzene (2 g, 10 mmol), **1a**, or 4-phenylazophenol, **1b** (2 g, 10 mmol), was added to oleoyl chloride (3 g, 10 mmol) and pyridine (2 mL) at room temperature. The resulting solution was stirred for 4 h. The reaction mixture was hydrolyzed with water (100 mL) and extracted with CH_2Cl_2 (3×100 mL). The organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The orange oil obtained was purified by column chromatography (silica gel, dichloromethane, R_f close to 0.8). Compounds **2a** and **2b** were isolated by evaporation of the solvent as an orange solid in 66% yields.

2.3. *N*-4-Phenylazophenyleamide. ^1H NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$, δ): 0.89 (t, $^3J = 6.6$ Hz, 3H), 1.20–1.43 (m, 24H), 1.57 (s, 1H), 1.78 (quint, $^3J = 6.6$ Hz, 2H), 2.60 (t, $^3J = 7.7$ Hz, 2H), 5.37 (m, 4H), 7.25 (d, $^3J = 8.8$ Hz, 2H), 7.52 (m, 3H), 7.92 (d, $^3J = 7.7$ Hz, 2H), 7.96 (d, $^3J = 8.8$ Hz, 2H). ^{13}C NMR (80 MHz, CDCl_3 , 25 $^\circ\text{C}$, δ): 14.0, 22.5, 24.4, 25.4, 27.1, 29.1, 29.2, 29.3, 29.4, 29.5, 29.8, 29.9, 31.7, 37.8, 122.1, 122.7, 123.9, 129.0, 129.6, 129.9, 130.9, 150.3, 152.4, 152.6, 171.8. UV-vis (CH_2Cl_2): λ_{max} (ϵ) = 437 (463), 321 nm (16 111); HRMS (m/z) 461.

2.4. 4-Phenylazophenyleate. ^1H NMR (300 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$, δ): 0.89 (t, $^3J = 7.7$ Hz, 3H), 1.27–1.38 (m, 24H), 1.78 (quint, $^3J = 7.7$ Hz, 2H), 2.60 (t, $^3J = 7.7$ Hz, 2H), 5.37 (m, 4H), 7.35 (d, $^3J = 8.1$ Hz, 2H), 7.61 (m, 3H), 7.90 (d, $^3J = 7.7$ Hz, 2H), 7.96 (d, $^3J = 8.1$ Hz, 2H). ^{13}C NMR (80 MHz, $\text{DMSO}-d_6$, 25 $^\circ\text{C}$, δ): 14.0, 22.5, 24.7, 27.0, 27.1, 28.9, 29.0, 29.1, 29.2, 29.4, 29.6, 29.7, 31.7, 34.3, 122.1, 122.7, 124.0, 129.0, 129.6, 129.9, 130.9, 150.1, 152.5, 152.7, 171.8. UV-vis (CH_2Cl_2): λ_{max} (ϵ) = 437 (484), 321 nm (18 518); HRMS (m/z) 462.

3. Results

3.1. Synthesis. In order to develop large-scale SAMs on a mica surface, two molecules were synthesized by linking an oleyl chain (i.e., (*Z*)-9-octadecenyl) to azobenzene derivatives via standard ester or amide condensation (see Figure 1). The oleyl chain was chosen because of its long carbon chain ($\text{C}_{17}\text{H}_{33}$) which induces strong intermolecular van der Waals interactions. The amide function (**2a**) reinforces the cohesion of the SAMs by H bonding between adjacent compounds. The detailed synthesis and the spectroscopic parameters are described in the Experimental Section.

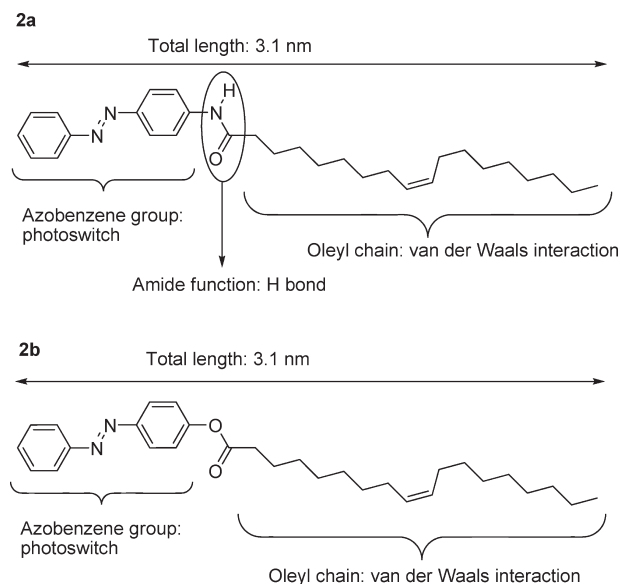


Figure 1. Molecular structures and a few parameters of *N*-4-phenylazophenyleamide (**2a**) and 4-phenylazophenyleate (**2b**).

3.2. Photoisomerization. The photoisomerization of the $\text{N}=\text{N}$ bond was investigated in a deuterated chloroform solution (CDCl_3) by UV-vis and NMR spectroscopies. The *cis*–*trans* isomerization can be qualitatively observed by UV-vis spectroscopy and quantitatively determined by NMR spectroscopy. The absorption spectra before and after UV illumination ($\lambda = 365$ nm, 90 min, 0.25 W) of compounds **2** are shown in Figure 2.

For each compound, two adsorption bands were observed at 321 and 437 nm.

After UV illumination (365 nm, 90 min, and 0.25 W), the bands centered at 321 nm are blue-shifted to 283 and 287 nm for **2a** and **2b**, respectively. The corresponding molecular extinction coefficients are divided by a factor 2.72 and 3.72 for **2a** and **2b**, respectively. The bands centered at 437 nm stay at practically the same position (435 nm), and the molecular extinction coefficients are increased from 463 and 484 to $1296 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $1282 \text{ L mol}^{-1} \text{ cm}^{-1}$ for **2a** and **2b**, respectively (Table 1).

The isomerization of the $\text{N}=\text{N}$ double bond contained in azobenzene leads to a strong modification of the molecular structure, which implies a modification of the NMR spectrum of the molecule.⁹ The NMR spectra of **2b** in $\text{DMSO}-d_6$ solution were recorded before and after UV-light illumination (365 nm, 90 min, and 2.5 W).

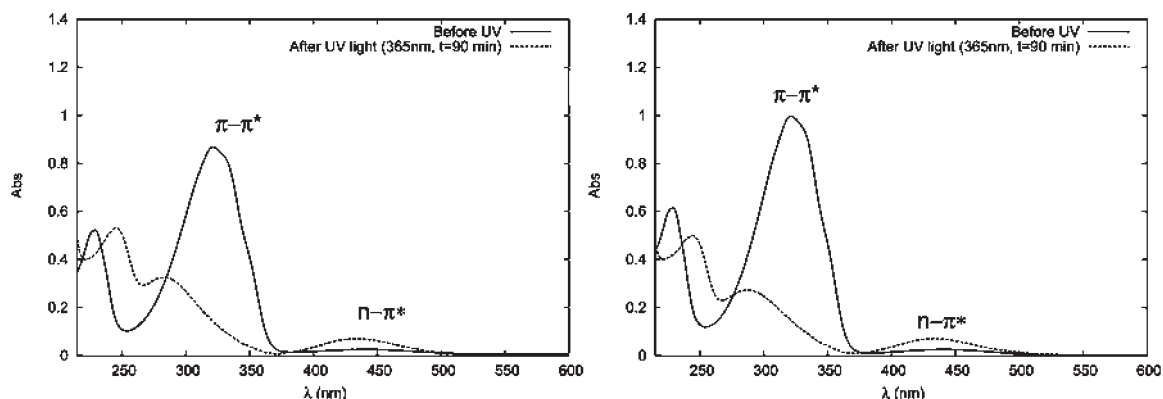


Figure 2. UV-vis spectra before and after irradiation of **2a** (left) and **2b** (right) compounds in CDCl_3 .

Table 1. Absorption Wavelengths and Molecular Extinction Coefficients of **2a** ($54 \mu\text{mol L}^{-1}$) and **2b** ($41 \mu\text{mol L}^{-1}$), in CDCl_3 , before and after UV Illumination (365 nm, 90 min, and 0.25 W)

compound	before UV		after UV	
	λ_1 (nm)/ ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	λ_2 (nm)/ ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	λ_1 (nm)/ ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	λ_2 (nm)/ ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)
2a	321/16111	437/463	283/5926	435/1296
2b	321/18518	437/484	287/4985	435/1282

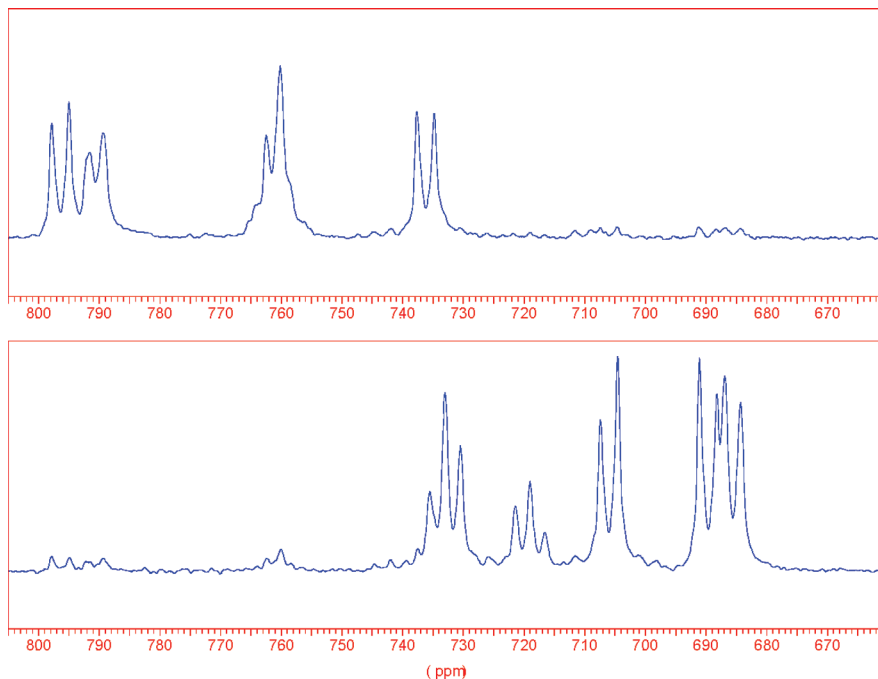


Figure 3. NMR spectra before (top) and after (bottom) UV-light irradiation (365 nm, 90 min, and 2.5 W) of **2b** in $\text{DMSO}-d_6$ solution.

As the cis-trans isomerization process does not affect the alkyl chain linked to azobenzene moiety, only the aromatic part of the NMR spectrum is described for molecule **2b** in Figure 3. The UV-light exposure leads to the appearance of signals between 6.8 and 7.4 ppm. The signals totally disappeared after heating at 70°C for 2 h. The result was the same as in the case of **2a**.

3.3. Adsorption on Mica. Molecules **2** were dissolved in dimethylformamide (DMF) to form a solution with the concentration of $4 \times 10^{-3} \text{ M}$. Substrates were freshly cleaved planes of mica ($20 \times 20 \text{ mm}^2$). Atomic force microscopy was used to acquire images in tapping mode. All images were recorded in ambient conditions. A drop of a DMF solution containing **2** was applied by spin-coating (rotation speed: 5000 rpm) to the substrates and studied by AFM after the solvent had evaporated. The

scan directions in all images were maintained uniform. Each of the images presented here was the representation of several images taken at different times to ensure reproducibility.

The large-scale image obtained on the dried **2** adsorbates on newly cleaved mica surface is shown in Figure 4. A large-scale flat layered structure is observed. The films are densely packed. A profile analysis along the line shows crenels with a height of 3.5 ± 0.2 and $3.1 \pm 0.2 \text{ nm}$ for **2a** and **2b**, respectively. The corrugation over the surface of each layer is less than 0.1 nm.

The layered structures obtained by adsorption of **2** in DMF solution on a mica surface were exposed to UV-light (365 nm, 15 s, 100 W). The shape of the adsorbate is not dramatically affected by the UV-light exposure (Figure 5), even if in the case of **2a**, a few holes are formed. However, the thickness of adsorbates

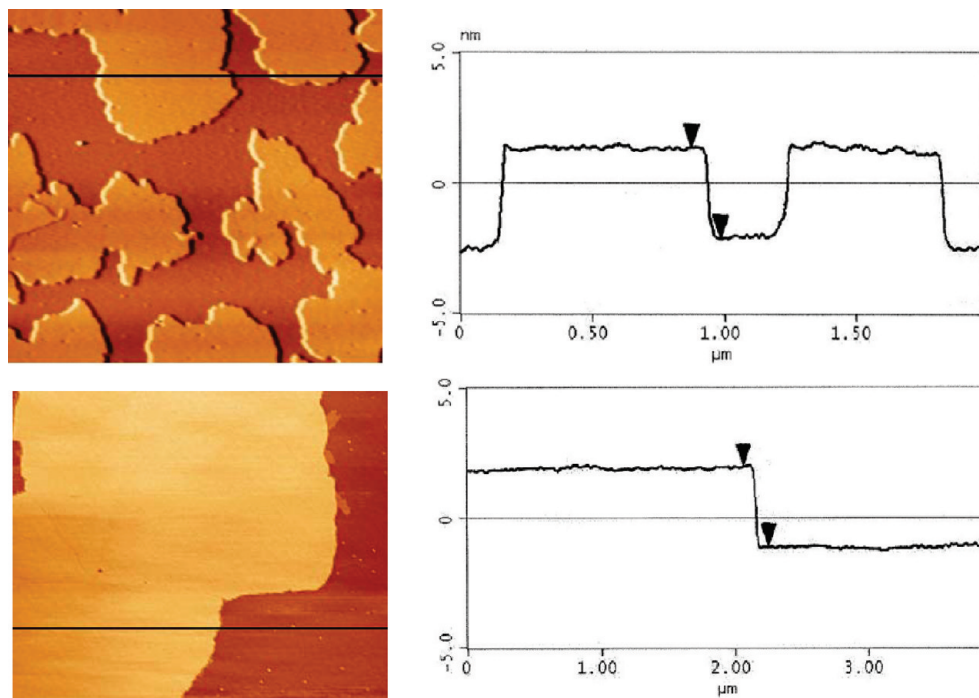


Figure 4. AFM images and z-profile of *N*-4-phenylazophenyloleamide (**2a**, top) and 4-phenylazophenyloleate (**2b**, bottom) adsorbed on a mica surface.

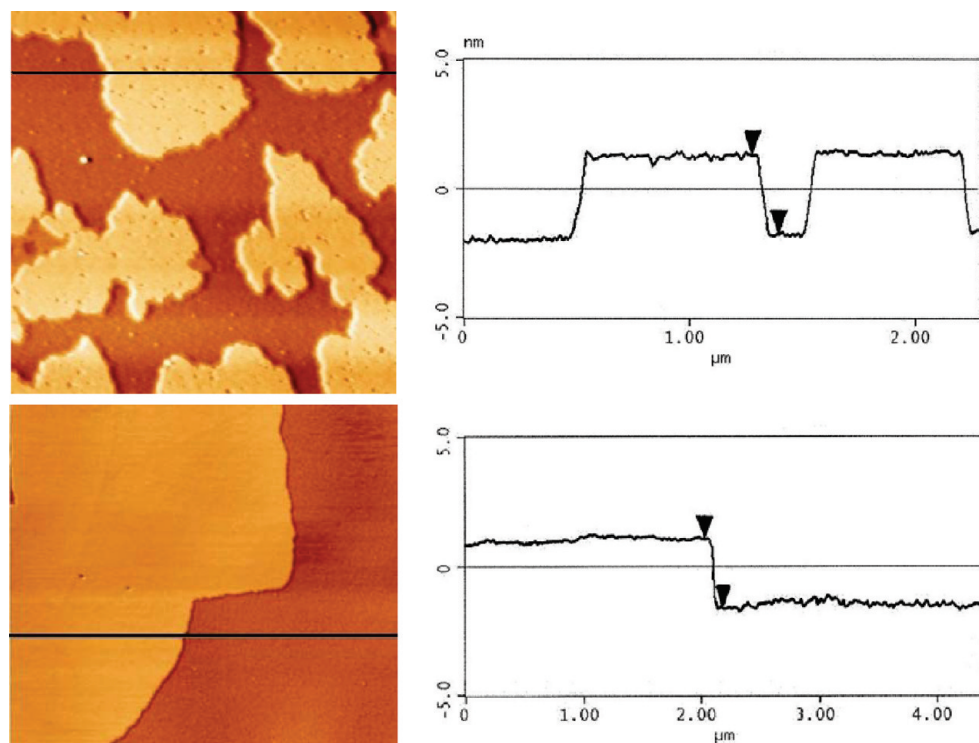


Figure 5. AFM images and z-profile of *N*-4-phenylazophenyloleamide (**2a**, top) and 4-phenylazophenyloleate (**2b**, bottom) adsorbed on a mica surface after UV-light exposure (365 nm, 15 s, 100 W).

was reduced after UV-light illumination, from 3.5 to 3.0 ± 0.2 nm and from 3.1 to 2.6 ± 0.2 nm for **2a** and **2b**, respectively.

The adsorbates obtained after UV-light exposure were stored at room temperature for 12 h. Then, AFM images were recorded (Figure 6).

Large-scale, densely packed, and well-ordered layered structures were imaged. In the case of **2a**, most of the holes, observed

after UV-light exposure, disappeared after 12 h. The thickness of the layers is 3.5 ± 0.2 and 3.1 ± 0.2 nm for **2a** and **2b**, respectively.

4. Discussion

The *cis*–*trans* isomerization of **2** was observed by UV–vis spectroscopy. Bands centered at 321 and 437 nm correspond to the π – π^* and n – π^* transition bands assigned to the azobenzene

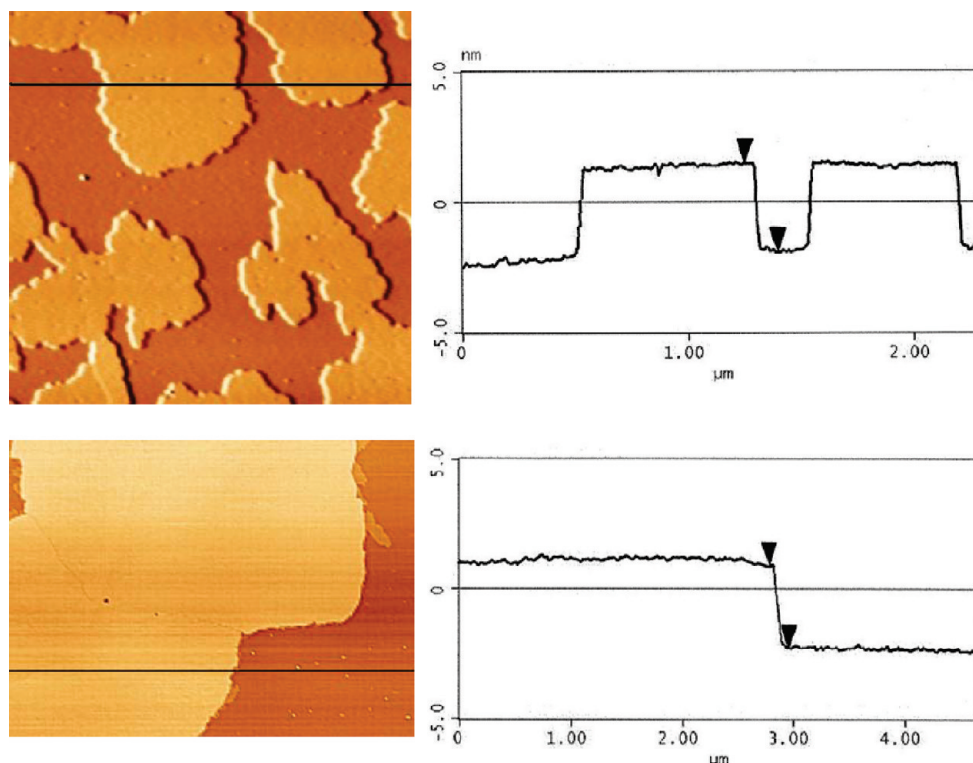


Figure 6. AFM images and z-profile of *N*-4-phenylazophenylamide (**2a**, top) and 4-phenylazophenylolate (**2b**, bottom) adsorbed on a mica surface after UV-light exposure (365 nm, 15 s, 100 W) and then 12 h at room temperature.

part, respectively. Their modifications after UV illumination are in accordance with the well-known trans-to-cis isomerization. For the $\pi-\pi^*$ transition, the blue shift of the absorption wavelength and the decreasing of the molecular extinction coefficient can be explained by structural difference between trans and cis isomers. The $n-\pi^*$ transition is due to the lone pair electrons of the nitrogen atom constituting the N=N double bond. This transition is forbidden in the trans isomer and allowed in the cis isomer. Consequently, the molecular extinction coefficient is higher in cis than in trans isomer.^{8,28}

In order to determine the conversion of trans to cis isomer, quantitatively, the NMR spectra were recorded. The signals appearing from 6.8 to 7.4 ppm are attributed to the cis isomer. The integration of these peaks gives a composition of 5% of trans isomer and 95% of cis isomer after the UV illumination. This result is in agreement with the literature data.⁹

The thickness of the adsorbates, determined by AFM experiments, is in accordance with the formation of a self-assembled monolayer constituted by molecules **2** because their length is 3.1 nm (Figure 1). The molecules cannot be grafted on a mica plane because there is no anchoring functionality. They can only be physisorbed. Therefore, molecules seem to be vertically adsorbed at a distance between 0.2 and 0.5 nm from the mica surface. The large-scale and the density of the SAMs are explained mainly by lateral interactions between adjacent molecules due to the oleyl chain. The scale or the density of SAMs is not affected by the presence (**2a**) or absence (**2b**) of H bonds.

After UV-light exposure, the thickness of all the SAMs is reduced by 0.5 nm as shown by the AFM profile measurement. This variation corresponds to the reduction in the length of molecules passing from trans to cis isomer (Figure 7).

The corrugation over the surfaces of each layer is less than 0.1 nm after UV-light, indicating that all molecules are photo-isomerized into the cis isomer. This result is remarkable because in the literature, except in the case of purely aromatic grafted SAMs on Au and Pt, the complete isomerization of a monolayer is not reported because of the competition between densely packing of SAMs and the free volume required for the isomerization process. In our case, as the SAMs are not grafted, the molecules can diffuse on the surface to allow the complete isomerization of azobenzene cores. This behavior can be directly correlated with the very different packing densities and orientation order observed for the respective SAMs after isomerization. In the case of ester-based SAMs (**2b**), no modification of the packing is observed after UV-light exposure; the thickness is only decreased. Whereas in the case of amide-based (**2a**), the thickness is decreased, too, but in addition, some holes appear. This difference can be interpreted by the presence of an H-bonding network in the case of **2a** which rigidifies the SAMs. Molecules are not as easily moved apart one from the other further as in the ester-based SAMs. Consequently, because of the strong intermolecular interactions, the isomerization process is a collective effect which splits up SAMs into small domains, separated by free volumes appearing as holes in AFM images (Figure 8).

The trans isomer being thermodynamically more stable, the isomerization from cis to trans isomers is observed after 12 h at room temperature. The thicknesses are back to its initial value. Holes have disappeared in the **2a**, indicating that the SAMs have their densely packed and well-ordered layered structure again after cis-to-trans isomerization. This phenomenon is explained by the diffusion of molecules on the mica surface only.

All these results can be explained by a model of adsorption and a scenario described in Figure 8.

The molecules can be vertically physisorbed on the mica surface pointing their aliphatic chain toward the substrate without

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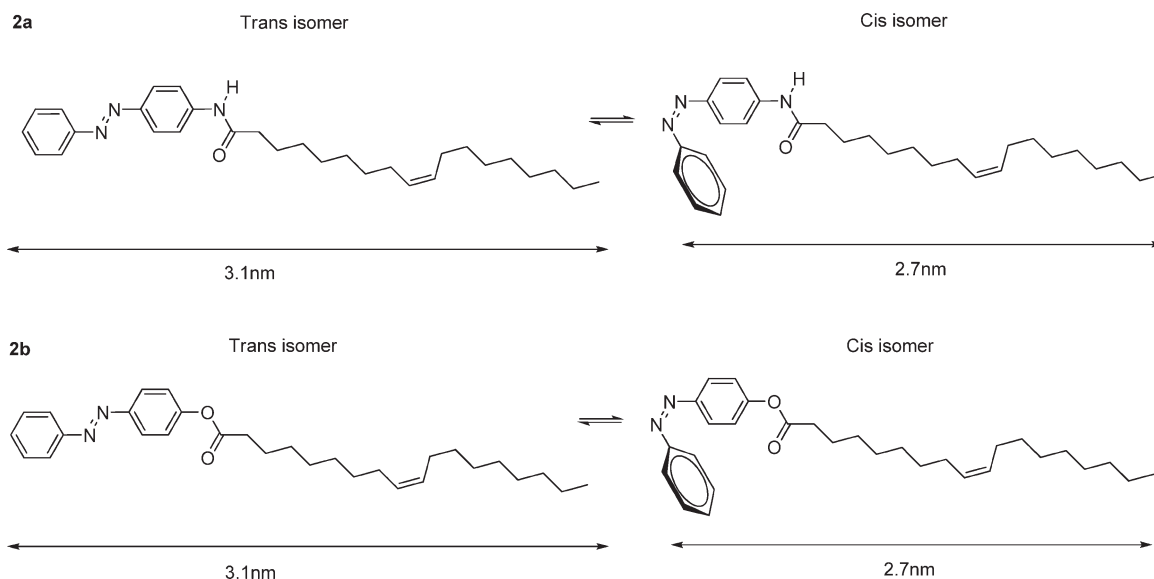


Figure 7. Length of molecules **2** in trans and cis isomers.

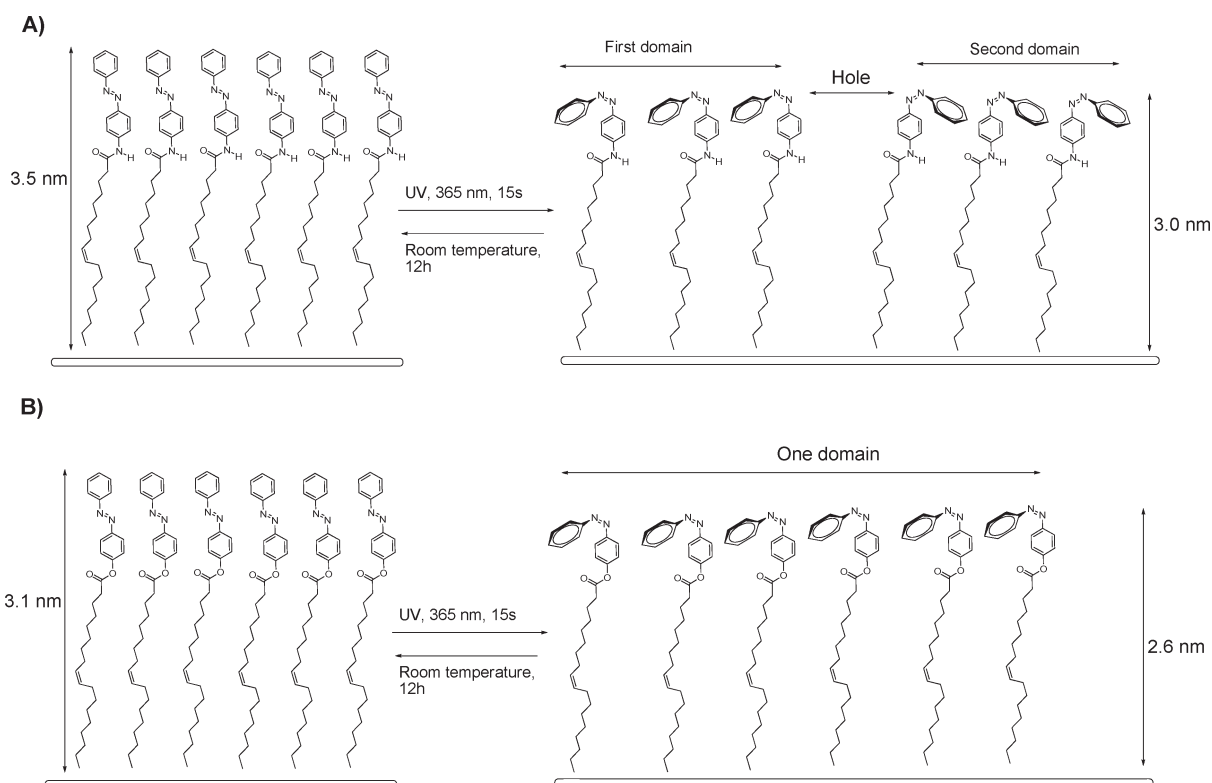


Figure 8. Summary of reversible isomerization of amide-based (A) and ester-based (B) SAMs on mica.

covalent or ionic bonds. These substrate/molecules interactions are weak, allowing the molecule diffusion on the surface.²⁹ Azobenzenes are completely cis-isomerized by UV-light. The free volume required is not a limiting factor due to the molecule diffusion induced by the absence of covalent or ionic bonds with the surface. The SAMs are reorganized, keeping their well-ordered layered structure, and the thickness has decreased in accordance with the reduction of the length of azobenzene passing from trans to cis isomer. However, if the interactions between

molecules are too strong (H bonds), photoisomerization occurs, but SAMs are split by trans–cis isomerization. Finally, the cis–trans process is achieved by storing samples at room temperature (12 h) to form SAMs in their more stable initial state.

5. Conclusion

The formation of large-scale self-assembled monolayers has been achieved on a mica surface thanks to the insertion of alkyl chain linked on an azobenzene core. Light illumination leads to a reversible photoswitching of the entire SAMs which can be monitored by AFM measurements. This phenomenon is due to weak interactions between molecules and substrate which leads to

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the physisorption of the molecules on the mica. This new approach will be useful for the development of devices for information storage.

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