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Photoswitching Vertically Oriented Azobenzene Self-Assembled Monolayers at the Solid–Liquid Interface

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The design of two-dimensional molecular self-assemblies[1] offers a powerful way to fine tune the properties of surfaces. Tailoring functional monolayers is therefore highly attractive for a range of potential nanotechnological applications, for example, in molecular electronics and photonics, bio-interface engineering, catalysis, or sensoring.[2] In this context, the design of responsive switchable monolayers,[3] that is, monolayers able to undergo significant changes in their physical or chemical properties as a result of external stimuli, is of particular interest for the fabrication of smart surfaces and interfaces.[4]

Among various triggers such as molecular guests, pH, temperature or electric field, light is likely the most advantageous stimulus as it is non-invasive and combines a very high spatial and temporal resolution in addition to good compatibility with condensed phases.[5] Photoresponsive monolayers have been successfully constructed employing diarylethene derivatives chemisorbed on gold surfaces.[6,10] Diarylethene photochromes allow for convenient electronic modulation of surfaces as ring-opened and ring-closed forms have dramatically different HOMO–LUMO levels.[5c,7] However, large structural changes interesting for switching various properties of the surface such as polarity, affinity to chemical guests, or mechanics, are rather difficult to be achieved using diarylethenes.[8] For this purpose, azobenzene-containing molecules are most attractive since the azobenzene moiety is known to undergo reversible isomerization from a linear and mostly planar *trans* form to a kinked 3D *cis* form upon UV and visible light irradiation, respectively.[5,9] These photoinduced large structural changes make azobenzene an appealing candidate for the construction of photoresponsive monolayers.[10]

Due to the large geometrical difference between the structures of the *trans* and *cis* isomers, a necessary prerequisite for the occurrence of photoisomerization in azobenzene-containing monolayers is to provide sufficient free volume to the system. Decoupling the photochromic unit electronically from the conducting surface by avoiding a direct contact is also crucial to preserve the photoelectronic activity.[11] Photoswitching of azobenzene self-assembled monolayers was therefore achieved in planar physisorbed systems on surfaces by employing bulky side groups, or "legs", able to lift the functional entity above the surface[12] and in vertical chemisorbed systems on gold surfaces by using a thiolated rigid molecular rod incorporating azobiphenyl moieties.[13] The latter approach involving upright oriented azobenzenes is able to translate the extent of the isomerization at the single molecule level into *meso*-/macroscopic changes in the structure of the surface, that is, thickness and exposure of terminal groups, but its wide applicability on different substrate types has to be proven.

The use of tripodal[14] or platform-based[15] building blocks is an additional appealing approach providing sufficient space to the photochromic units and decoupling them from a conducting substrate.[16] This strategy allows immobilizing photoactive moieties in an upright fashion when chemisorbed or physisorbed on the surface, and at the same time to tune the distance between adjacent photochromes. In the more widely used self-assembled chemisorbed monolayer approach, the molecules are usually densely packed and creating space by diluting the switches by means of co-adsorption is usually not successful due to phase segregation. It is important to note that tripod and platform approaches are thus far limited to patterning of gold surfaces only.

Graphite as a stack of graphene sheets can be seen as an interesting substrate for preliminary studies on the modification of graphene, a unique 2D system that has attracted a tremendous interest in the past years.[17] Hitherto, isomerization of azobenzene containing monolayers on highly-orient-

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ed pyrolitic graphite (HOPG) has been investigated on building blocks physisorbed co-planar to the basal plane of the substrate,[18] leading to structural changes primarily in the plane of the graphite. As a result, while the *trans*-isomer based monolayer could be visualized by STM with a sub-molecular resolution, the monolayer composed entirely of *cis* isomers could never be observed at the solid–liquid interface, as a result of molecular desorption due to the inability to pack efficiently.[18a,d] Only one exception was reported thus far.[18c] New strategies to obtain *cis*- and *trans*-based physisorbed monolayers on HOPG and graphene therefore constitute an important scientific challenge.

Here, we describe a platform-based approach to decorate the HOPG surface with upright oriented photoswitchable azobenzene units with a sub-nm precision. The monolayer formed by custom-tailored azobenzene-containing building blocks in the *trans* form can be interconverted to the corresponding *cis* form monolayer leading to substantial and reversible structural reorganization, as revealed by scanning tunneling microscopy (STM) studies.

The target structure **1** (Figure 1 a) was designed to combine i) a terfluorene rigid scaffold exposing COOH groups in the α- and ω-positions to promote in-plane intermolecular recognition through H-bonding forming 1D supramolecular nanostructures,[19] ii) two dodecyl chains in the bridge position of the first and third fluorene moieties to favor physisorption on HOPG and define the spacing between adjacent molecules, iii) an asymmetric functionalization of the bridge position of the central fluorene with one group having a higher affinity for the HOPG, that is, a dodecyl chain, and a functional group, namely an azobenzene function, which is therefore forced to adopt an edge-on packing at surfaces (Figure 1 b). Such modular approach allows to tune the orientation and spacing between adjacent azobenzenes. A bulky *tert*-butyl group -$C(CH_3)_3$ attached to the azobenzene terminus further decreases the affinity of the azobenzene for HOPG, prohibiting its face-on packing and therefore promoting its edge-on packing.

Target compound **1** was assembled by Suzuki cross-coupling reaction between the central fluorene equipped with the azobenzene and a dodecyl chain, and lateral fluorenes equipped with dodecyl chains and COOH groups (see the Supporting Information). The central building block was prepared by a procedure involving a series of nucleophilic substitutions at the 9,9′-positions of 3,7-dibromofluorene by bromododecane and 1-bromo-4-nitrobenzene. The azobenzene moiety was formed by subsequent reduction of the nitrobenzene into the corresponding aniline derivative followed by oxidative coupling with 4-*tert*-butylnitrosobenzene. The simplicity of functionalizing the 9,9′-positions of fluorenes by nucleophilic substitution allows the introduction of numerous different functional units into the terfluorene pedestal, rendering this synthetic approach highly versatile and applicable to various other related problems.

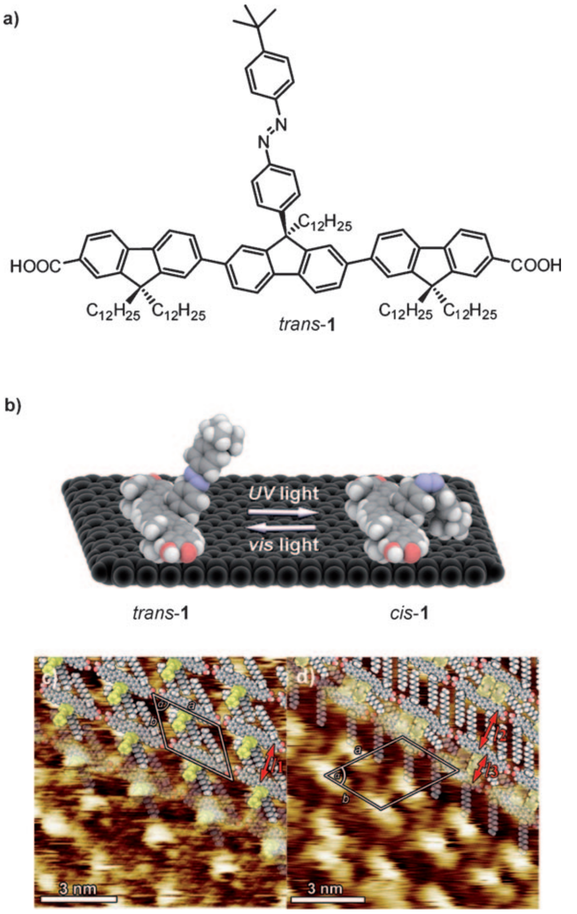

Figure 1. a) Chemical formula of *trans*-**1**. b) 3D Corey–Pauling–Koltun (CPK) models of *trans*-**1** and *cis*-**1** adsorbed on HOPG ($C_{12}H_{25}$ chains are replaced by CH_3 groups for clarity; one minimum structure is shown in which the terfluorene adopts an *anti*,*anti* conformation). STM height image of **1** at the HOPG-1-phenyloctane interface in its *trans* isomer (c) and *cis* isomer (d) obtained upon UV irradiation (354 nm) of the *trans* monolayer for ca. 1 h. Tunneling parameters: average tunneling current $I_t = 5$pA and tip bias voltage $V_t = 2$ V.

Target molecule **1** does not exhibit the typical photochromic behavior of regular azobenzene derivatives in solution since only about 34 % of the *trans* form is isomerized into the *cis* form upon irradiation at the maximum of the $\pi \rightarrow \pi^*$ transition (360 nm) in phenyloctane (solvent used for the STM investigations).[20] The partial quenching of the *trans* → *cis* isomerization results most likely from energy and electron transfers between the azobenzene unit and the terfluorene platform, a highly fluorescent chromophore. Note that also the terfluorene fluorescence is quenched in **1**.[21] Nevertheless, complete quenching of the *trans* → *cis* isomerization was likely avoided by connecting the azobenzene to the terfluorene *via* a non-conjugated sp^3-hybridized carbon linker.[22]

We initially investigated the self-assembled structures obtained by applying a drop (4 μL) of a 1 mM solution of *trans*-**1** in 1-phenyloctane. Figure 1 c shows an STM height image of the physisorbed monolayer. It reveals a monocrystalline domain contained in a hundreds of square nanometers large polycrystalline domain (Figure 2 a), which is stable over several minutes. Within the 2D crystal it is possible to identify self-assembled 1D H-bonded supramolecular polymers, as a

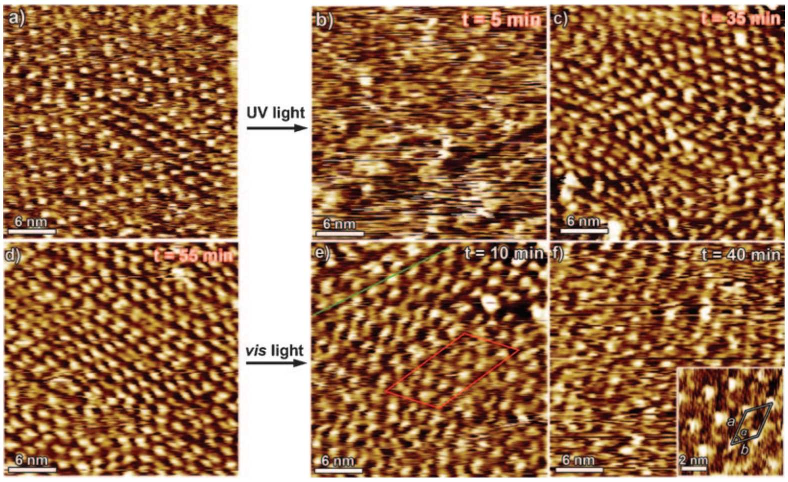

Figure 2. Structural reorganization of a monolayer of *trans*-**1** (a) to a monolayer of *cis*-**1** (d) upon UV irradiation (354 nm), and back process leading to the recovery of a monolayer of *trans*-**1** (f) upon visible irradiation (white light bulb). a)–d) Large scale STM height images of **1** at the solid–liquid interface after different irradiation time with UV light starting from a monolayer of *trans*-**1** (a); e), f) large scale STM height images of **1** at the solid–liquid interface recorded after 10 min (e) and 40 min (f) of visible irradiation (white light bulb) strating from a monolayer of *cis*-**1** (d). e) The red lines encircle a *trans*-**1** domain, the green lines encircle a *cis*-**1** domain. f) The inset highlights the unit cell of the *trans*-**1** monolayer, which is identical to the unit cell shown in Figure 1c. Tunneling parameters: $I_t = 5$ pA and $V_t = 2$ V.

result of the formation of hydrogen bonds between the carboxylic acid groups attached to the terfluorene pedestal. The crystalline structure is further stabilized by interdigitation of the alkyl chains between adjacent polymer rows. Only three out of the five dodecyl chains attached to building block **1** are physisorbed on the HOPG surface, owing to the tetrahedral geometry of sp^3-hybridized C9 atoms of the fluorenes; as a result the other two dodecyl chains point toward the supernatant solution.[17a] Interestingly, periodic brighter spots are observed within the monolayer. Considering their spacing and taking molecular modeling into account, it is possible to assign them to the upright oriented azobenzene moieties of the molecules (marked in yellow in Figure 1c) emerging as pillars from the flat 2D structure. In view of the adsorption energy of two different functional units of the central fluorene moiety (sp^3 C9 atom), that is, azobenzene unit and *n*-dodecyl alkyl chain, and the presence of heteroatoms in the azobenzene moiety together with the bulky *tert*-butyl end-group, it is most likely that the affinity for HOPG is higher for long alkyl substituent. Note that the adsorption energy of one methylene group on graphite is around 2.6 kcal mol^{-1} (11 kJ mol^{-1}, ~0.1 eV).[23] The size of the observed bright features (0.81 nm^2) is about 80% larger than the van der Waals cross-section of the azobenzene moiety of molecule **1** packed edge-on on the basal plane of HOPG (0.45 nm^2). However, such a discrepancy can be explained in view of the moiety's dynamic nature, that is, possible rotation about the fluorene–azobenzene connection C–C single bond, and the scanning speed of the STM tip. Indeed rotation about C–C single bonds can be as fast as 10^{-12} s,[24] whereas the speed of STM imaging is on the 10^{-4} s time scale. The observed crystalline domains exhibit a unit cell: $a = (2.9 \pm 0.2)$, $b = (2.2 \pm 0.2)$ nm, $\alpha = (50 \pm 2)°$ leading to an area $A = (4.88 \pm 0.47)$ nm^2, where each unit cell contains one molecule **1** (Figure 1c).

It is noteworthy that molecules **1** were found to form an ordered physisorbed monolayer at the HOPG–solution interface only upon using 1-phenyloctane as solvent. Study of this system in different solvents such as 1,2,4-trichlorobenzene (TCB), tetradecane, heptanoic acid and nonanoic acid did not produce any ordered 2D structures. It is likely that the use of polar solvents, capable to interfere with the H-bonding between the carboxylic acid groups attached to the terfluorene pedestal, disturb the formation of well ordered monolayers at the solid–liquid interface. Also the choice of the concentration of the investigated solutions turned out to be critical. Crystalline domains (Figure 2a) were observed only upon the use of 1 mM solutions of **1**. STM investigation of diluted solutions of **1** in 1-phenyloctane, that is, 100 and 10 μM, did not produce any meaningful results.

The STM image of the interface after in situ irradiation of the monolayer of **1** with UV light (354 nm) is displayed in Figure 1 and 2d. The domains, which feature a different structure if compared to that in Figure 1c, exhibit linear supramolecular architectures that can be ascribed to H-bonded supramolecular polymers of *cis*-**1**, as revealed by the following observations. First, the spacing between two adjacent 1D arrays is in this case is not always identical, as found in physisorbed monolayers of *trans*-**1** ($l_1 = 1.6$ nm). Two different spacing values between alternating polymer rows can be extracted from the STM image, that is, l_2 (1.7 nm) and l_3 (1.2 nm) as marked in red arrows in Figure 1d. In the *cis* domains, the H-bonded 1D architectures are laterally spaced according to a "dimeric" motif, where two building blocks of adjacent rows are held in close proximity. This more compact packing mode features a different tilt of the aliphatic side chains as well as azobenzene units likely interacting through van der Waals forces. Although we cannot provide an unambiguous and detailed insight into the conformation adopted by the azobenzene units, the bright features in the STM image are clearly different compared to *trans*-**1** domains. When a bright protrusion emerged at the center of *trans*-**1** molecules, in *cis*-**1** the bright features extend over the entire platform, most likely indicative of a decrease of the molecular height. Domains observed by STM exhibit a unit cell, which is very different from the one observed before irradiation: $a = (3.6 \pm 0.2)$ nm, $b = (2.9 \pm 0.2)$ nm, $\alpha = (57 \pm 2)°$ leading to an area $A = (8.75 \pm 0.63)$ nm^2, where each unit cell contains two molecules **1** (Figure 1d).

Importantly, such a dimeric motif was visualized only upon illumination of the monolayer with UV light. Finally, such observations, together with the non-photoresponsive character of the bare platform bearing no azobenzene (see molecule **1′** in the Supporting Information, Figure S4), strongly support our notion that the monolayer observed after UV light irradiation is based on *cis*-**1** molecules.

Importantly, the reversible structural reorganization of the monolayer of **1** from *trans* to *cis* motif could be monitored in real-time over several tens of minutes, taking advantage of the slow nature of the process. Figure 2 shows selected snapshots of these measurements where the *trans* domains are gradually converted into *cis* domains over a time scale of 55 min (Figure 2a-d), presumably driven by the more stable packing of the *cis* form, accumulating over time. The total coverage of the surface by the *cis* assembly is completed within 55 min of irradiation (Figure 2d). The fuzzy parts on the STM images correspond to areas where the considerably high mobility of the molecules, triggered by the irradiation process, hinders high resolution STM imaging.

The formation of *cis*-**1** monolayers, from a solution in which 66 % of molecules **1** remain in their *trans* configuration upon UV illumination, as established by UV/Vis spectroscopy, is interesting. This observation provides indirect evidence for the enhanced stability of the supramolecular architectures composed of *cis*-**1** as compared to ones formed from *trans*-**1**. This increased stability should be reflected by a significantly higher packing density of *cis*-**1** molecules when compared to *trans*-**1**, that is, a smaller area occupied by a single molecule physisorbed on the HOPG surface. Indeed, the areas occupied by single molecule in the *trans* and *cis* form amount to (4.88 ± 0.47) and (4.35 ± 0.34) nm^2, respectively. Such a difference indicates that the switching process has occurred by desorption of *trans*-**1** and subsequent re-adsorption of *cis*-**1** molecules present in the supernatant solution (as established by solution studies, after one hour irradiation at 357 nm the supernatant solution contains 34 % of *cis*-**1** molecules, see Supporting Information).

Upon irradiation of the *cis*-**1** monolayer with visible light (white light bulb) the *trans* monolayer 2D motif is reformed again (Figure 2e,f). A short illumination (Figure 2e) leads to monolayers exposing the two coexisting isomers, that is, *trans* (marked in red) and *cis* (marked in green). Further irradiation resulted in desorption of the molecules, which after some time (ca. 40 min) re-adsorb in the *trans*-type of assembly (Figure 2f), proving the reversible nature of the process.

In summary, the self-assembly of a properly designed 3D building block (**1**) exposing a vertically oriented azobenzene when physisorbed on HOPG in its *trans* form has been investigated by STM. The switching of the monolayer consisting of upright oriented *trans*-azobenzenes to the corresponding monolayer based on *cis*-azobenzenes has been triggered by light, leading to a significant structural change of the self-assembly in the third dimension (decrease of height) as well as in the plane of the substrate (different 2D packing). The present results provide the first examples of sub-moleculary resolved vertically oriented switchable photo-chromophores in physisorbed monolayers as well as vertically physisorbed azobenzenes monitored in the two switching states at the solid–liquid interface. We are currently investigating the possibility to pin this type of building blocks on carbon-based surfaces via a two-step process involving first the physisorption of the molecules with controllable spacing on the surface followed by their chemisorption via reaction with the underlying HOPG or graphene. Suitable reactive groups can be attached to the C9 positions of the fluorene units using well-established nucleophilic substitution strategies or connected to the ends of the alkyl chains. By offering the possibility to control switching of azobenzenes when placed at tunable distance of one another, our scaffold could in principle allow us to explore fundamental photochemical properties of non-interacting azobenzenes at surfaces and to develop azobenzene-based unirotational switch assemblies by performing the isomerization inside a chiral medium, or using polarized light.[25]

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