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Photoswitches

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Bidirectional Photomodulation of Surface Tension in Langmuir Films

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Abstract: Switching systems operating in a cooperative manner capable of converting light energy into mechanical motion are of great interest for optical devices, data storage, nanoscale energy converters and molecular sensing. Herein, photoswitchable monolayers were formed at the air–water interface from either a pure bis(thioxanthylidene)-based photoswitchable amphiphile or from a mixture of the photoswitchable amphiphile with a conventional lipid dipalmitoylphosphatidylcholine (DPPC). Efficient photoisomerization of the anti-folded to syn-folded geometry of the amphiphile's central core induces changes in the surface pressure in either direction, depending on the initial molecular density. Additionally, the switching behavior can be regulated in the presence of DPPC, which influences the packing of the molecules, thereby controlling the transformation upon irradiation. Bis(thioxanthylidene)-based photoswitchable monolayers provide a promising system to explore cooperativity and amplification of motion.

In nature, light-stimulated biochemical transformation is a crucial process by which optical signals are recorded and used to trigger a variety of chemical events including photosynthesis, the process of vision, ion transport, and muscle activity.^[1] Particularly interesting is the involvement of photochromic units in biological processes offering major prospects for high precision control of dynamic functions, as has been explored in recent years in optogenetics,^[2] photopharmacology,^[3] membrane transport,^[3a,4] and drug delivery.^[5] Taking inspiration from integrated complex photo-responsive systems controlling dynamic functions in nature, the design and exploration of photoswitchable molecules and materials have received major attention in the past decade.^[6] Upon irradiation, the molecules can access different isomeric states with distinct chemical and physical properties, allowing various functions of the system to be modulated with different wavelengths of light. Several applications have emerged from the ability to control the geometry of the molecules by light, such as optical memory,^[7] switchable sensors,^[2a,8] responsive surfaces,^[9] gels,^[10] liquid crystals,^[11] and delivery systems.^[1c,12] The overcrowded alkene bis(thioxanthylidene) and its derivatives are particularly attractive photochromic switches owing

to their fast photoisomerization, featuring an unique geometrical change from anti-folded to syn-folded structure (Figure 1a).^[13] The transformation is fully reversible as the syn-folded molecule thermally relaxes back to its more energetically favorable anti-folded configuration.

Figure 1. a) Molecular structure of anti-folded **1** and syn-folded **2**. b) Structural change of the switch: front view (top) and top view (bottom).

However, investigation of these photoswitchable molecules has been so far carried out mostly in solution, where the lack of control over the orientation and position of the photochromic molecules prevents exploring cooperative and amplification effects of an ensemble since the systems are naturally disordered.^[1c,14] Hence, achieving a supramolecular arrangement of such molecules is a key challenge to fabricate nano-assemblies, where the molecules can operate in a cooperative fashion via light-induced geometrical changes.^[15] While efforts have been made to operate switches in a concerted fashion, an efficient strategy is to incorporate the photoswitches into a self-assembled monolayer.^[15d,16] Among the various techniques available, the Langmuir–Blodgett (LB) method provides an elegant and fully controllable tool to achieve the assembly of responsive materials into a well-ordered monolayer at the air–water interface.^[17]

Furthermore, Langmuir films have attracted great interest owing to their potential application in modeling biological membranes to investigate drug action,^[18] permeability,^[19] and sensing.^[20] Switching a surfactant between different geometries can result in pronounced differences in surface pressure, orientation, and molecular packing.^[16d,21] Molecular transport across cell membranes employing protein channels, ion pumps, or motors proteins and their delicate interplay with the membrane organization (and pressure) are essential to natural activity. In this context, artificial membrane systems that include embedded photosensitive molecules are very attractive, although the design of such light-responsive systems remains challenging.^[21d,22] A particularly desirable feature is to control the membrane function with high temporal and spatial precision by light. Studies on photo-

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switchable artificial membrane systems include the use of azobenzene or spiropyran molecules as photochromic units.^[15b, 21c, 22a, 23]

To achieve a better understanding of the cooperative effects between neighboring amphiphilic molecules, their molecular structure, and photoswitching properties, novel photoresponsive amphiphiles have to be designed that combine excellent reversibility and stability when assembled into condensed systems. Herein we present a photoresponsive Langmuir film based on a bis(thioxanthylidene) amphiphile that shows for the first time a bidirectional photomodulation of surface pressure. To the best of our knowledge, the ability to reversibly increase and decrease pressure (and packing) in a Langmuir film at a single irradiation wavelength is unprecedented.

The amphiphile **1** contains a central bis(thioxanthylidene) unit bearing hydrophilic tetraethylene glycol and hydrophobic alkyl tails (Figure 1 a). The structure of **1** is a modified version of a bis(thioxanthylidene) that was shown to form nanotubes, by extending the hydrophilic moieties each with one ethylene glycol unit (see the Supporting information for the synthesis and characterization of **1**).^[13] By increasing the size of the hydrophilic head group, **1** was found to readily self-assemble into sheets in water as demonstrated by Cryo-TEM experiments (Supporting Information, Figure S1). Here, the Langmuir–Blodgett technique was used to obtain a stable monolayer of the amphiphile **1** at the air–water interface as well as a mixed monolayer containing both **1** and DPPC. The Langmuir film surface pressure behavior was examined systematically in response to UV irradiation and found to be dramatically influenced by the packing of the molecules. Our investigation suggests that, besides the modification of molecular structure upon irradiation, the packing mode within the Langmuir film can be used to tune the properties of the whole system.

Because of steric hindrance between the lower and upper halves (Figure 1 b), the stable isomer **1** preferentially adopts an *anti*-folded conformation with an absorption maximum at 355 nm for the $\pi \rightarrow \pi^*$ transition in the UV/Vis spectrum. When a dichloromethane solution of **1** is exposed to 365 nm light (Figure 2 a), a decrease of the band at 355 nm with a concomitant increase of the absorption at 320 nm is observed with clear isosbestic points. This corresponds to

Figure 2. a) The conversion of **1** (blue) to **2** (red) in dichloromethane upon irradiation at 365 nm and the thermal recovery (gray) monitored by UV/Vis absorption spectroscopy. Inset: the irradiation (365 nm) of **1** for 10 min at -20°C followed by thermal relaxation at 5°C for 20 min monitored by absorption at 365 nm over 6 cycles. b) Emission spectra during the irradiation process of **1** ($\lambda_{\text{exc}} = 365 \text{ nm}$) at -20°C .

the disappearance of the *anti*-folded isomer and the formation of the thermodynamically less stable *syn*-folded isomer **2** in accordance with our previous studies on bis(thioxanthylidenes), supported by DFT calculations.^[24] Furthermore, the fluorescence emission band at 480 nm disappeared completely in the process (Figure 2 b). The photoisomerization was also studied by ^1H NMR (-40°C) and provided additional evidence for the formation of *syn*-folded **2** with a photostationary state containing 80 % of the *syn*-folded isomer (Supporting Information, Figure S2). Upon increasing the temperature to 5°C , *syn*-folded **2** underwent complete thermal conversion back to the *anti*-folded **2** (Figure 2; Supporting Information, Figure S2) and a complete recovery of both the UV/Vis spectrum and ^1H NMR spectrum of **1** was observed. The irradiation/thermal recovery cycles could be repeated multiple times without noticeable signs of fatigue (inset in Figure 2 a).

A stable monolayer of *anti*-folded **1** was obtained by spreading a chloroform solution (0.07 mg mL^{-1}) onto the water–air interface. The surface pressure–area isotherm indicates a well-condensed monolayer with a collapse pressure of 45 mN m^{-1} for a molecular area of $70 \text{ \AA}^2/\text{molecule}$ (Figure 3 a). This collapse area is smaller than the estimated value of our DFT calculations, $91.1 \text{ \AA}^2$, (Figure 1 b and the Supporting Information), suggesting a highly compressed Langmuir film structure, which can be attributed to π – π

Figure 3. a) Surface pressure versus area isotherm for a monolayer of **1** at the air–water interface. b) Absorption spectra of a monolayer of **1** on quartz deposited at different compression; 23 mN m^{-1} (black) and 25 mN m^{-1} (red). c, d) Kinetics of the *anti*–*syn* photoisomerization in a monolayer of **1** as monitored by a surface pressure at the air–water interface at an initial molecular area of $92 \text{ \AA}^2/\text{molecule}$ (c) and $90 \text{ \AA}^2/\text{molecule}$ (d). The surface pressure was recorded while the monolayers of the *anti*-folded **1** were held at a constant area while being exposed to the radiation at 365 nm (30 s) and then left in the dark (120 s).

stacking of the aromatic core. As discussed earlier, the molecular properties, for example the molecular geometry, change as a consequence of the isomerization from *anti*- to *syn*-folded. We therefore set out to investigate the behavior of the monolayer upon exposure to UV light. First, the monolayer was compressed to 22.5 mN m^{-1} (corresponding to $92 \text{ Å}^2/\text{molecule}$) and the area was kept constant for the duration of the irradiation experiment. The compressed monolayer was sequentially exposed to UV irradiation (365 nm) for 30 s and kept in the dark for 2 min to allow for thermal backward isomerization. Throughout each cycle, the configuration of **1** varied between an *anti*-folded and *syn*-folded geometry, resulting first in an increase of the surface pressure by approximately 3 mN m^{-1} upon irradiation, followed by recovery of the original pressure when left standing in the dark (Figure 3c). Next, the behavior of the Langmuir film was investigated at slightly increased initial surface pressure. The monolayer was therefore compressed to 24.0 mN m^{-1} , corresponding to a molecular area of 90 Å^2 . Much to our surprise, and contrary to the behavior at lower pressures, UV irradiation (365 nm) led to a rapid decrease of the surface pressure, to 22.8 mN m^{-1} (Figure 3d). The pressure returned to the original value upon leaving the sample standing in the dark, with a slight fatigue observed over multiple cycles.^[21b] The fatigue was not observed at higher surface pressures (26 mN m^{-1} ; see the Supporting Information, Figure S3b).

To gain additional understanding of this behavior, we set out to probe the surface pressure changes upon irradiation at different initial surface pressures ranging from 16 to 29 mN m^{-1} (Figure 4; Supporting Information, Figure S3). At lower starting pressures ($16\text{--}23 \text{ mN m}^{-1}$; $100.0\text{--}91.2 \text{ Å}^2/\text{molecule}$), the surface pressure increases by $1\text{--}3 \text{ mN m}^{-1}$ upon irradiation with UV light. It was observed that the surface pressure change enhances with an increasing initial surface pressure, culminating at 22 mN m^{-1} ($\Delta 3 \text{ mN m}^{-1}$), before declining again for 23 mN m^{-1} . Interestingly, in stark contrast, upon further increase above 23 mN m^{-1} (ca. $91.2 \text{ Å}^2/\text{molecule}$), a decrease of the surface pressure ($0\text{--}1 \text{ mN m}^{-1}$) is observed upon

Figure 4. Surface pressure changes at the air–water interface in monolayer of **1** upon irradiation with UV light (365 nm) at different initial surface pressures.

irradiation with UV light. This decrease gradually levels off with increasing pressure. At initial pressures higher than 29 mN m^{-1} , the monolayer collapsed immediately upon exposure to UV light.

To the best of our knowledge, this type of dual behavior has not been observed for Langmuir films before and we propose the following model based on DFT/DFT-D3 calculations (Supporting Information). The structures of both *anti*-folded **1** and *syn*-folded **2** have been optimized by DFT/b3lyp6-31G (d,p) and the footprints of individual molecules (considered as spheres) were determined to be 91.1 and $96.5 \text{ Å}^2/\text{molecule}$, respectively. Next, the packing ability of **1** and **2** as trimers was investigated by DFT-D3 calculations, capable of describing London (long-range) dispersion interactions.^[25] As illustrated in Figure 5, the *anti*-folded **1** isomer prefers to pack as J-aggregates, with the lower half of the

Figure 5. Proposed model of the packing for supramolecular structures before and after exposure to UV irradiation based on DFT/DFT-D3 calculations at a) lower and b) higher initial pressure. The hydrophilic tetraethylene glycol and hydrophobic alkyl tails are omitted for clarity. S blue, H white, and C gray.

overcrowded alkene stacking with the upper half of the adjacent molecule (head-to-tail). On the other hand, the metastable *syn*-folded **2** assumes H-aggregate packing, with the upper half of the alkene stacking with the upper half of the adjacent (head-to-head) molecule. While the individual molecules of *syn*-folded **2** have a larger footprint than *anti*-folded **1** (see above), they are capable of more efficient packing, since, based on the DFT-D3 calculations, the three molecules of **1** and **2** occupy area of 290.3 and 262.0 Å^2 , respectively.

At low pressures ($\leq 23 \text{ mN m}^{-1}$), the molecules are presumably loosely organized in the monolayer (Figure 5a) and transition to J-aggregate packing at higher surface pressures ($\geq 24 \text{ mN m}^{-1}$, Figure 5b) to compensate for the increase of pressure. To confirm this, the Langmuir films obtained at different pressures (23 and 25 mN m^{-1}), were deposited onto quartz slides by immersing the substrate vertically (Figure 3b). Comparison of the absorption spectra of the deposited LB films indicates a bathochromic shift of the absorption band from $\lambda = 362 \text{ nm}$ to 372 nm for the monolayer at 25 mN m^{-1} compared to the one at 23 mN m^{-1} , with a concomitant sharpening of the absorption band. The red-shift and sharpening of the absorption band indicates a formation of J-aggregates.^[26,27]

In more disorganized Langmuir films at low initial pressures ($\leq 23 \text{ mN m}^{-1}$), irradiation with UV light leads to

the formation of *syn*-folded **2**, which possesses a larger footprint, imposing sterical strain within the monolayer. The strain should translate into an expansion of the monolayer; however, since the area containing the molecules is kept constant, the packing density increases, resulting in a higher surface pressure (Figure 4).^[21b,28] Contrary to that, at high initial surface pressure (≥ 24 mN m⁻¹), irradiation of *anti*-folded **1** packed in the form of J-aggregates leads to formation of *syn*-folded **2**, which is forced to assume more space-efficient H-aggregate packing due to already strained monolayer. As a consequence, a surface pressure drop is observed under these conditions (Figure 4). Based on our experimental data, we cannot exclude that some of the amphiphilic molecules are expelled from the monolayer at high pressures, thus also decreasing the surface pressure.^[29]

It has been recognized that conformational changes in biological molecules embedded in membranes are important in controlling the properties of natural membranes.^[21b,30] Therefore, the interaction between the amphiphilic photo-switch and artificial membrane components in a two component system is of particular interest for the development of responsive materials. Therefore we used **1** as a dopant in a mixture with DPPC, a lipid occurring in natural membranes. The mixture of **1** and DPPC with different ratios was first investigated by UV/Vis absorption spectroscopy in chloroform. No pronounced difference in isomerization behavior was observed upon introduction of DPPC, indicating negligible interaction between the two species in solution (Supporting Information, Figure S4). To study the influence of DPPC on the switching behavior in the Langmuir film, monolayers with two different ratios of the amphiphile **1** and DPPC (1:3 and 1:8) at the air–water interface were prepared (Supporting Information, Figure S5). The monolayers were then irradiated in the same manner as described above (Figure 6a). The mixture with low DPPC content displayed the same behavior as the monolayer consisting of pure *anti*-folded **1**, with the surface pressure changes being dependent on the initial molecular density, albeit with lower magnitude. Conversely, when the proportion of DPPC was raised to 89%, a pressure increase upon irradiation was observed for both low and high molecular density, which is in a strong contrast with the observation made for both the pure amphiphile **1** and the 1:3 mixture of **1** and DPPC (Figure 6b). These abnormal changes at high DPPC content can be explained in terms of smaller footprint of the lipid molecules. Extensive dilution of the monolayer with DPPC effectively increases the area individual molecules of **1** and **2** can occupy and thus decreases the strain within the monolayer. This allows for increase of the surface pressure upon photoisomerization even at higher initial surface pressures. At the same time, at high concentrations, DPPC can be expected to perturb efficient stacking of **1** and **2** in the form of J- and H-aggregates, thus disallowing more favorable packing of the *syn*-folded **2**. Therefore, the use of DPPC can be viewed as an effective way of modulation of shape of the curve in Figure 4, as well as the position of the inversion point. These findings demonstrate that different packing modes alter the effect of the optical switching and can, under certain circumstances, lead to inversion of the observed behavior in the Langmuir films.

Figure 6. a),b) Kinetics of the *anti*–*syn* isomerization of the mixed monolayer monitored by surface pressure at the air–water interface at low initial pressure (bottom) and high initial pressure (top). a) The ratio of the mixture is 1/DPPC = 1:3 and b) 1/DPPC = 1:8.

In conclusion, we have shown that properly designed Langmuir films of a bis(thiaxanthylidene)-based molecule exhibits remarkable bidirectional surface-response behavior upon *anti*–*syn* folded photoisomerization that depends on the interfacial organization determined by the initial molecular density. The photoisomerization results in an increase of the surface pressure at low molecular density, while at higher molecular density, a decrease of the surface pressure is observed which can be ascribed to adopting a different, more favorable, stacking of *syn*-folded **2** under these conditions. The character of the surface pressure response can be further modulated by mixing the switch with different amounts of DPPC in the monolayer. Our investigation indicates that not only the external stimuli but also the morphology and ratio of the building blocks influence the responsive properties of the Langmuir film, thus opening new avenues for reversibly changing monolayers and ultimately surface and membrane function in a controlled fashion.

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Conflict of interest

The authors declare no conflict of interest.

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