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Reversible Photomorphism in Surface Monolayers

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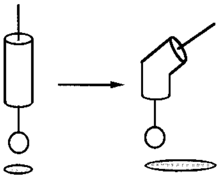
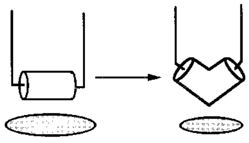
Monomolecular films of photochromic compounds receive increasing interest as novel functional molecular materials which can act as optically switchable liquid crystal devices[1] or as information storage devices,[2,3] etc. Monolayer-forming photochromic compounds can be easily prepared by incorporation of photoresponsive chromophores into single-chain amphiphilic molecules (Figure 1a). The chromophore, mostly azobenzene[4,5] or stilbene,[6,7] is normally introduced into the hydrophobic part of the amphiphile. The most prominent photochemical process of these chromophores is the *trans*−*cis* isomerization reaction. Isomerization from *trans* to *cis* in condensed monolayers was, however, reported to be strongly inhibited since the process requires a large area expansion of the chromophores[8−10] (Figure 1a). Only a few reports have succeeded to demonstrate highly efficient isomerization in a fluid monolayer[11,12] or in systems which have some free volume in the chromophore region.[13,14] We report herein a novel design of a photochromic amphiphile with an unexpected isomerization behavior in a condensed monolayer and photochemically-induced reversible phase transition and morphological change at the air−water interface.

To improve the photochemical reactivity in the condensed monolayer, we have focused on double-chain amphiphiles, the so-called "gemini-surfactants", with the basic feature of a stiff aromatic head group with directly attached charged groups.[15] In this amphiphile the chromophore should orient parallel to the surface, and the area of the chromophore is expected to be decreased with *trans*−*cis* isomerization (Figure 1b). A new type of amphiphile **1** was prepared by acylation of diaminostilbene disulfonate with hexadecanoyl chloride in water.[16] Monolayer experiments were carried out with a computer-controlled film balance (FSD-50, USI-system)[17] equipped with an epifluorescence microscope and a highly sensitive CCD camera (DXC-755, Sony). The bilayer solutions were prepared by injection of DMSO solution of **1** into water with subsequent sonication to obtain a clear solution.



a. conventional photochromic amphiphile



b. photochromic stilbene sulfonate

Figure 1. Schematic presentation of *trans*−*cis* isomerization of photochromic amphiphilic molecules.

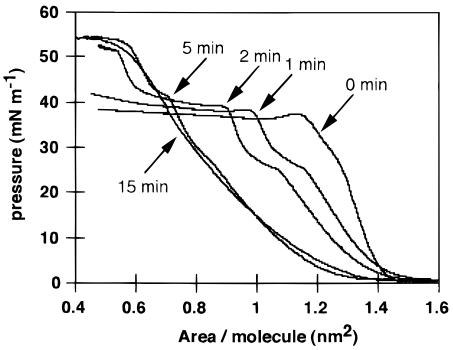
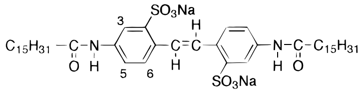


Figure 2. Effect of 366 nm photoirradiationon pressure−area isotherm of amphiphile **1** at the air−water interface. To irradiate the whole film on the water surface (15 × 45 cm^2), a multiband UV-254/366 nm lamp (UVGL-58, UVP Inc.) was fixed at 20 cm distance over the film balance. The light intensities at the air−water interface measured by a photodiode were 240 mW·cm^{-2} at 254 nm and 560 mW·cm^{-2} at 366 nm, respectively. Water subphase (purified by a Milli-Q system; >18 MΩ·cm at pH 5.5) was kept at 20 ± 0.5 °C. For the spreading solution, 5 mg of **1** was dissolved in 600 mL of DMSO and diluted to 10 mL by $CHCl_3$.



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Amphiphile **1** forms a stable monolayer after spreading from a dilute chloroform solution onto a pure water subphase. The pressure−area (π−A) isotherm shows a steep increase of the surface pressure at around 1.4 nm^2/molecule (Figure 2). This indicates that the molecules are packed closely at this area. Upon further compression the monolayer collapses at 36 mN·m^{-1}. The area per molecule of more than 1 nm^2 at the collapse point (deflection point of the curve upon compression) is very large compared to the expected area derived from the cross sections of the two alkyl chains (2 × 0.2 nm^2).[18] On the other hand, the measured area is in a good agreement with the area per molecule of the stilbene sulfonate chromophore in the side on orientation at the air−water interface. Calculations of the cross-

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[16] Bender, F.; Schulz, G. *Chem. Ber.* **1886**, *19*, 3235. 250 MHz NMR ($CDCl_3$/DMSO-d_6 1/1): 0.85 ppm (3H, t, J = 6.8 Hz, CH_3); 1.25 ppm (24H, m, CH_2); 1.59 ppm (2H, m, CO−CH_2−CH_2); 2.28 ppm (2H, t, J = 7.3 Hz, CO−CH_2); 7.5 ppm (1H, d, J = 8.8 Hz, $\overline{H}$(C6)); 7.7 ppm (1H, dd, J_{meta} = 2.4 Hz, J_{ortho} = 8.5 Hz, H(C5)); 7.96 ppm (1H, d, J = 2.4 Hz, H(C3)); 8.0 ppm (1H, s, CH═CH); 9.9 ppm (1H, s, NH). Elemental analysis ($C_{46}H_{72}N_2Na_2O_8S_2$) found (calcd): C, 60.64 (61.00); H, 8.31 (8.14); N, 3.10 (3.14); S, 7.23 (7.19).

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sectional area of **1** by using CPK molecular models reveal an area per molecule of 1.2 nm^2 for the stilbene chromophore. In this orientation both sulfonate groups are in favorable contact with water and the stilbene chromophore orients parallel to the surface even in the condensed monolayer as expected in Figure 1b.

Photochemical *trans*−*cis* isomerization of the stilbene chromophore in an aqueous bilayer solution can be confirmed by the UV−visible absorption spectrum[19] and H-NMR.[20] The absorption of *trans*-stilbene at 330 nm decreased upon 366 nm irradiation, and a new absorption peak around 255 nm, which can be assigned to *cis*-stilbene, was observed in water. During the irradiation an isosbestic point at 285 nm was preserved, which is strong evidence of a single photochemical process, the *trans*−*cis* isomerization, in the bilayer assemblies. The appearance of new peaks at 9.8 ppm (NH), 7.9 ppm (H(C3)), 7.2 ppm (HC5)), 7.0 ppm (CH═CH), and 6.7 ppm (H(C6)) in the NMR spectrum indicates the formation of the *cis* isomer of **1**. The molar ratio of *trans* and *cis* isomer at the photostationary state is calculated to be 1:9 by NMR. Irradiation of the photostationary mixture with 254 nm light led to a new photostationary equilibrium state shifted more to the *trans* isomer side (*trans*:*cis* = 9:1). In our experimental conditions, even after several irradiation cycles, no trace of photoproducts other than *cis*- and *trans*-**1** could be found both in the absorption and NMR spectra.

Upon irradiation with 366 nm at the air−water interface, the $\pi-A$ isotherm changed drastically. Figure 2 shows the irradiation time dependence of the $\pi-A$ isotherm. The *trans* monolayer was irradiated after spreading and then was compressed. A large decrease in the surface area and an increase in the collapse pressure are found in the $\pi-A$ isotherm with irradiation. It can be assumed that the stilbene moieties in the monolayer are in the photostationary equilibrium after 5 min irradiation because 15 min irradiation did not change the isotherms significantly. Judging from the results of the aqueous bilayer solution, formation of photocyclization products in these experimental conditions can be negligible after 15 min irradiation. Monolayers of **1** were transferred to quartz plates by the Langmuir−Blodgett technique at 20 mN·m^{-1} before and after irradiation, respectively. The irradiated monolayer showed a large decrease of 330 nm absorption of the *trans* isomer. Taking into account the spectral changes of absorption and NMR of the aqueous bilayer solution, the extend of isomerization at the photostationary state in the monolayer is estimated to be in the same range as in the aqueous solution. The decrease in the surface area is in good agreement with the predicted behavior of *trans*−*cis* isomerization of the stilbene chromophore in the gemini-surfactant (Figure 1).

The photoreaction can be clearly seen as a change of the surface area at constant pressure upon irradiation. After approximately 10 min, the photostationary equilibrium for the *trans*−*cis* isomerization with 366 nm light is reached. Irradiation of this monolayer with 254 nm light leads to an increase of surface area.

This finding clearly indicates that the *cis* isomer can transform to another isomer even though the transformation from *cis* to *trans* of the gemini-surfactants is supposed to be restricted due to the requirement of a large area expansion (Figure 1). Direct imaging of the surface monolayer by fluorescence microscopy[21] reveals the reason why the restricted *cis*−*trans* isomerization is allowed at the air−water interface.

Figure 3 shows fluorescence micrographs of the stilbene monolayer containing 2 mol % of octadecylrhodamine B as a fluorescence probe,[22] which is homogeneously located in fluid parts and squeezed out from crystalline parts as an impurity, respectively. Dark domains, which are representative of crystalline monolayer, were already formed directly after spreading at zero pressure when the monolayer was excited with 540 nm light. Upon compression, the domains were densely packed together at the onset of the isotherm (Figure 3a).

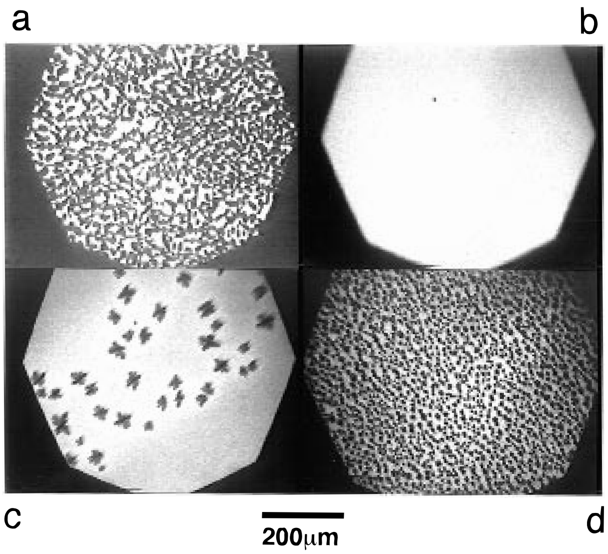

Figure 3. Fluorescence micrographs of a monolayer of **1** mixed with 2 mol % octadecylrhodamine B: before irradiation at 20 mN·m^{-1} (a); after 3 min irradiation with 366 nm light (b); after irradiation of the "melt" monolayer with 254 nm light at pressure <5 mN·m^{-1} for 2 (c) and 5 min (d).

Upon irradiation with 366 nm light for 3 min the domains seemed to "melt", and a homogeneous red fluorescence image, which is characteristic for homogeneous distribution of the probe molecules in a liquid analogous monolayer, was observed (Figure 3b). Irradiation-induced morphology change was observed at any surface pressure, from 0 mN·m^{-1} up to the collapse pressure. Upon irradiation of the melt monolayer with 254 nm light, the *cis*−*trans* isomerization proceeded and crystal domains started to reappear at pressures (Figure 3c). Taking the fluorescence imaging into consideration, it is concluded that the *cis*−*trans* isomerization is not prohibited because the *cis* isomers form a fluid monolayer where the chromophore is assumed to be mobile enough to isomerize. Regenerated *trans* isomers can diffuse to form crystalline domains in the mobile *cis* matrix.

Shape and size distribution of the regenerated crystal domains in Figure 3c is largely different from the original crystals in the as-spread monolayer (Figure 3a). The photoinduced "recrystallization process" can be controlled by changing experimental conditions, e.g. irradiation time. Size distribution of the crystalline domains in a monolayer irradiated for 2 min seemed to be more homogeneous than that of the monolayer which is irradiated for 5 min, because the short-term irradiation generates a much lower number of nuclei of the *trans* crystal than does the long-term irradiation (Figure 3c,d).

We designed in this article a new type of stilbene amphiphile that forms the first example of a photochromic monolayer showing reversible *trans*−*cis* photoisomerization in the solid analogous condensed monolayer and a photoinduced solid-to-liquid transition. We would like to call this new phenomena, "melting" and "recrystallization" of the monolayer assemblies, "photomorphism", i.e. photoinduced morphology change.[23]

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