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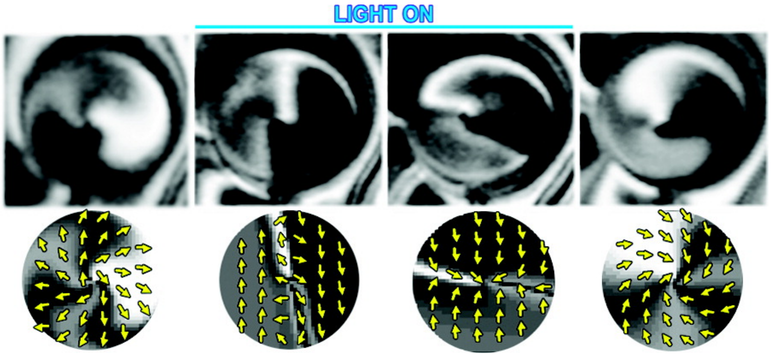

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Photoswitchable Orientational Patterns of Confined Domains in Monolayers

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Soft materials prepared from supramolecular or self-assembling strategies provide researchers with a diversity of potential technological benefits.[1] Leaving aside obvious implications for the design of sensors and devices,[2,3] model cooperative molecular systems may provide the means to unveil how noncovalent interactions in complex chemical systems can lead to the emergence of adaptive[4] and collective[5] responses to external stimuli. However, to understand the mechanism with which information is transferred through multiple-length scales, aiming to obtain functional responses and predictable outputs, a theoretical description is desired. This is often an elusive task.

We report an experimental phenomenon of collective light-induced reorientational processes at the air/water interface. More specifically, we demonstrate how a cycle of weak on/off linearly polarized illumination can totally reverse the radially symmetric pattern of orientations of stretched amphiphilic molecules assembled in condensed smectic-C-like droplets in a Langmuir monolayer (Figure 1). The photoresponsive thin film consists of a photostationary *cis*/*trans* mixture of an azobenzene-based amphiphile, which organizes itself into birefringent, circular, nearly pure *trans* droplets of diameters up to 250 μm, embedded in a matrix of untextured isotropic *cis* phase.[7] Two distinct and highly symmetric textures arise from the distribution of the projected in-plane vector field $\vec{a}$ and can be observed by polarized reflection microscopy at Brewster angle (BAM). At 35 °C and low surface pressure ($\pi < 3$ mNm^{-1}), the characteristic texture is a *splay-out* state with molecules stretching their tails outward, relative to the droplet boundary. At higher lateral pressures ($\pi > 10$ mNm^{-1}) the stretching of the molecular tails is inward, resulting in a *splay-in* configuration.[8] We show how the unidirectional transition between these two self-organized mesoscopic textures is photoinduced through a complex dynamics. The whole transition pathway described in the experiments, including transient patterns, is quantitatively explained with the aid of a theoretical model.

A typical photoswitch experiment of a *splay-out* domain (Figure 2a), with the E-field horizontally polarized for simplicity, proceeds as follows. Within seconds of illumination, molecular alignment parallel to E starts at the center of the droplet and extends progressively outward (Figure 2b). After some collectively organized transient states (Figure 2c−e), lasting about 10 s for the range of power densities in our experiments, the whole droplet is organized in two north/south semicircles of nearly perpendicular orientation to the polarization direction but, strikingly, with molecular tails pointing inward (Figure 2f). The complete reversal of the initial texture to the radially symmetric *splay-in* configuration is trivially attained after turning off the illumination (Figure 2g). This state is known to slowly relax back to the *splay-out* texture[9] (Figure 2h).

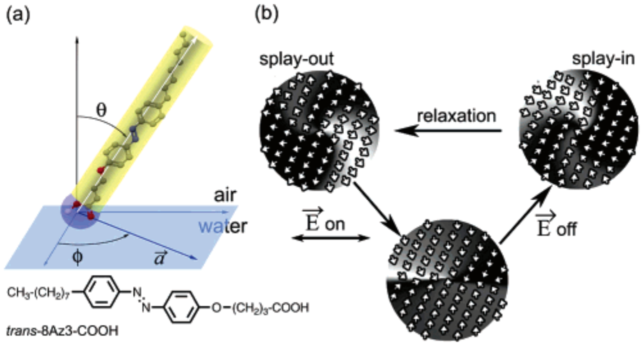

Figure 1. (a) Molecular structure of the azobenzene-based amphiphile and definition of the angular variables for molecules arranged at the air−water interface.[6] The projection on the monolayer plane defines the director field $\vec{a}$. (b) Scheme of the unidirectional photoswitch between the stable *splay-out* and unstable *splay-in* textures. The original configuration is recovered after relaxation. Interconversion between the two configurations may also be achieved through changes in the lateral pressure. Textures correspond to simulated BAM images for the given azimuth distributions.

The just reported observations can be interpreted within a theoretical framework built from the interplay of two distinct dynamics. A simple relaxational (thermodynamic) principle is invoked first in relation to a free energy functional, adapted to the labile nature of the softly condensed domains and incorporating long-range elastic forces. Coupled to this we consider two molecular direction-dependent reactions leading to a (kinetic) formalism with an anisotropic rate law, since polarized illumination is most effective for those molecules parallel to the E-field.[2] First, light absorption leads to a short-lived excited electronic state of the chromophore with rotational mobility enhancement[10] that eventually would result in a collective photomigration process of the molecular long axis out of the incident light (photoreorientation).[11−13] Second we invoke a slower alternative reaction of the chromophores which has to be capable of intervening in the collective alignment. All the experimental results point to a light-induced anisotropic extension of the H-aggregation[14] of the chromophore, thus reducing the molecular mobility, owing both to electronic and elastic reasons.

These arguments, in their most simple form, are translated into a model with two spatio/temporal-dependent state variables. The condensed SmC state of the droplets is described by means of a free-energy written in terms of the local distribution of molecular orientations ($\phi\,(x,y;t)$ for the azimuth variable) and the composition variable $c(x,y;t)$, denoting the molecular fraction of nonaggregated *trans* isomers. Taking for simplicity the origin of azimuths as the polarization direction and assuming simple first-order kinetic laws

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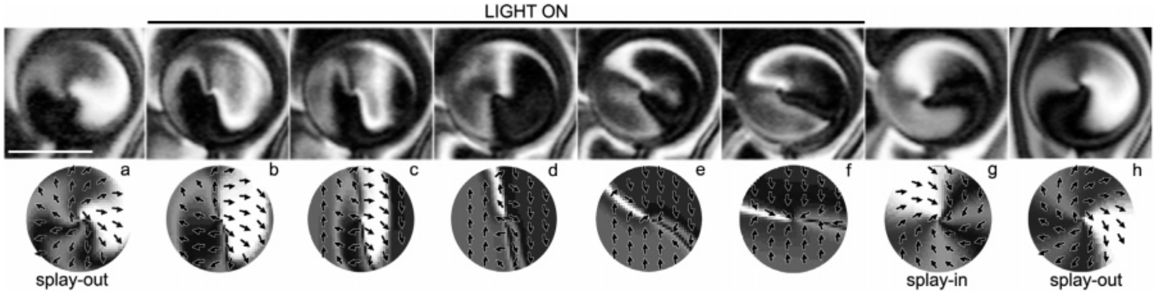

Figure 2. Photoswitch experiment of a *splay-out* droplet into the *splay-in* texture. The E-field is horizontally polarized. The bar on panel (a) is 100 μm long. Irradiation is switched off on panel f after 13s. The texture becomes a *splay-in* 8 s afterward (panel g) and fully relaxes to the original *splay-out* texture after 170 s (panel h). Lateral pressure is 0.5 mN/m. Drawings on the lower row correspond to the results of the numerical experiment. The parameters are $K_b = 0.8$, $\beta = 4$, $\lambda = 200$, $k_1 = 50$, $k_2 = 500$, in the unit system $K_s = R$ (droplet radius) $= \gamma = 1$. When the light is switched off $k_1 = 0$.

for the rate-limiting aggregation, we write for a single isolated droplet

$$\frac{\partial c}{\partial t} = -(k_1 \cos^2 \phi + k_2)c + k_2$$

$$F = \int_{\text{bulk}} \left[\frac{K_s}{2}(\vec{\nabla}\cdot\vec{a})^2 + \frac{K_b}{2}|\vec{\nabla} \times \vec{a}|^2 + \lambda(1 - c)(\vec{\nabla}\cdot\vec{a}) \right] \mathrm{d}x\mathrm{d}y - \int_{\text{bound}} \beta(\vec{a}\cdot\vec{n}_b)\mathrm{d}l$$

In the pair of equations above k_1 and k_2 stand respectively for the forward (anisotropic and proportional to the light intensity) and backward (thermal) aggregation rate constants, whereas K_s and K_b denote respectively the splay and bend elastic constants,[15] the λ-term couples the linear splay term with the composition variable, and the last integral incorporates the anisotropic part of the line tension ($\vec{n}_b$ is the normal outward unit vector). The formal scheme is closed by assuming a relaxational dynamics of the azimuth variable in search of a minimum of the free energy thermodynamic potential. First, the photoinduced kinetics prompts reorientation of central molecules to be parallel to the E-field, decreasing the λ-coupled term with $\vec{\nabla}\cdot\vec{a}$ still globally positive (Figure 2b). Progressively, vertical bands of molecules normal to the E-field propagate inward from the east/west boundaries, rendering $\vec{\nabla}\cdot\vec{a}$ almost null while the kinetics relaxes to the all-*trans* nonaggregated state (Figure 2c,d). What is left (Figure 2e,f) is a rotation of the dividing π-wall leading to a negative contribution of $\vec{\nabla}\cdot\vec{a}$ to the free energy.

In summary, we have shown how a cycle of weak on/off illumination applied to a photoresponsive Langmuir monolayer can change the pattern of molecular orientations of labile condensed droplets. The *splay-out* configuration of the droplet reveals, when forced, a balance of competing interactions within the material (light-induced reorientation out of the incident light vs light-induced H-aggregation) to eventually reach a stationary state which is further relaxed to a reversed configuration. This experiment illustrates how different processes acting synergetically may be the key if versatile reorganizations of the material are to result when adapting to changes in its environment. The smectic characteristics of the investigated material turns out to be a crucial feature and leads us to claim that what is reported here should apply similarly to thin films of other photosensitive SmC mesogens.

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Supporting Information Available: Time sequences for the experimental and numerical data in Figure 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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