

## Photoswitchable Dissipative Two-Dimensional Colloidal Crystals

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**Abstract:** Control over particle interactions and organization at fluid interfaces is of great importance both for fundamental studies and practical applications. Rendering these systems stimulus-responsive is thus a desired challenge both for investigating dynamic phenomena and realizing reconfigurable materials. Here, we describe the first reversible photocontrol of two-dimensional colloidal crystallization at the air/water interface, where millimeter-sized assemblies of microparticles can be actuated through the dynamic adsorption/desorption behavior of a photosensitive surfactant added to the suspension. This allows us to dynamically switch the particle organization between a highly crystalline (under light) and a disordered (in the dark) phase with a fast response time (crystallization in  $\approx 10$  s, disassembly in  $\approx 1$  min). These results evidence a new kind of dissipative system where the crystalline state can be maintained only upon energy supply.

**P**recise regulation of the interactions governing the assembly of colloidal particles at fluid interfaces is the subject of vivid interest in the scientific community, either for the design of novel materials<sup>[1–3]</sup> or for studies of more fundamental phenomena.<sup>[4,5]</sup> Specifically, while reconfigurable structures are sought for the development of innovative devices,<sup>[6]</sup> dissipative systems are also studied to understand how matter organizes itself.<sup>[7]</sup> Devising a system that can dynamically respond in a dissipative fashion to an external stimulation is thus a desired and demanding task<sup>[8]</sup> giving rise to reconfigurable, emergent functions.<sup>[9–12]</sup> Examples of dissipative particle organizations at liquid interfaces have been reported, but only using chemical<sup>[13,14]</sup> or magnetic control.<sup>[15–17]</sup> Alternatively, light appears as a valuable stimulus for the study of dynamic assembly.<sup>[7]</sup> However, light stimulation has never been used to dynamically trigger the formation of extended two-dimensional (2D) ordered colloidal structures at fluid interfaces. Optical regulation of particle organization has been reported in the bulk (that is, in suspension) or on solid substrates. For instance, aggregation was triggered both with photoresponsive<sup>[18]</sup> and non-photo-

responsive particles.<sup>[19–21]</sup> Light was also shown to control the crystallization of colloids, either with active particles,<sup>[22,23]</sup> photoresponsive particles,<sup>[10]</sup> light-sensitive substrates,<sup>[24,25]</sup> or non-responsive colloids.<sup>[26,27]</sup> To our knowledge, the only demonstration of photocontrol of colloidal crystallization at a fluid interface was achieved using optical trapping at the interface of an oil-in-water drop and led to ordered, yet very small, assemblies.<sup>[28]</sup> Here, we describe the first system where extended 2D colloidal crystallization is induced on-demand using light as an input. The system is composed of inherently passive anionic microparticles mixed with small amounts of a cationic photosensitive surfactant. The light-induced dynamic adsorption/desorption behavior<sup>[29]</sup> of the surfactant at the air/water interface allows us to tune the particle–particle interaction with light. As a result, mm-sized colloidal assemblies are photoreversibly switched between a disordered and a highly crystalline state. We analyze both structural and dynamic features of the colloidal assemblies in response to different irradiation profiles, and perform cycles of crystallization/disassembly to assess the reversibility of the process. Strikingly, our experiments demonstrate the dissipative, out-of-equilibrium nature of the ordered colloidal assemblies, since the crystals are only formed when continuous energy supply is provided by light irradiation, whereas energy removal leads to a rapid disassembly of the colloidal structure.

We recently showed that micromolar amounts of conventional cationic surfactants (for example, dodecyltrimethylammonium bromide, DTAB) induced the adsorption of anionic particles by decreasing the adsorption barrier at the air/water interface.<sup>[30]</sup> At such low surfactant concentrations ( $\approx$  CMC/1000–CMC/100, where CMC is the critical micelle concentration), the particles adsorbed with a low contact angle ( $\approx 30^\circ$ ) and remained highly charged, forming disordered assemblies or polycrystalline patches in a particle- and surfactant-concentration-dependent manner. Here, to explore the possibility to dynamically switch particle assemblies at the air/water interface at constant composition, we used anionic polystyrene particles (diameter 5.1  $\mu\text{m}$ ) at a fixed concentration (0.01  $\text{mg mL}^{-1}$ ) and 10  $\mu\text{m}$  of the AzoTAB photosensitive surfactant<sup>[31–33]</sup> (Figure 1 A). AzoTAB is a cationic surfactant with an azobenzene moiety in its hydrophobic tail, which can isomerize from *trans* to *cis* upon suitable light irradiation (Figure 1 B). Note that 10  $\mu\text{m}$  of AzoTAB is about three orders of magnitude lower than its CMC (12.6  $\mu\text{M}$  and 14.6  $\mu\text{M}$  for the *trans* and *cis* isomers, respectively<sup>[34]</sup>), resulting in a surface tension comparable to that of pure water, regardless of irradiation conditions (Supporting Information, Figure S1). The particles were brought to the air/water interface of a suspension in a cylindrical cell by flipping it up and down using our previously described protocol<sup>[30]</sup> (Figure 1 C, top panel). We found that, similarly to the case of non-photosensitive

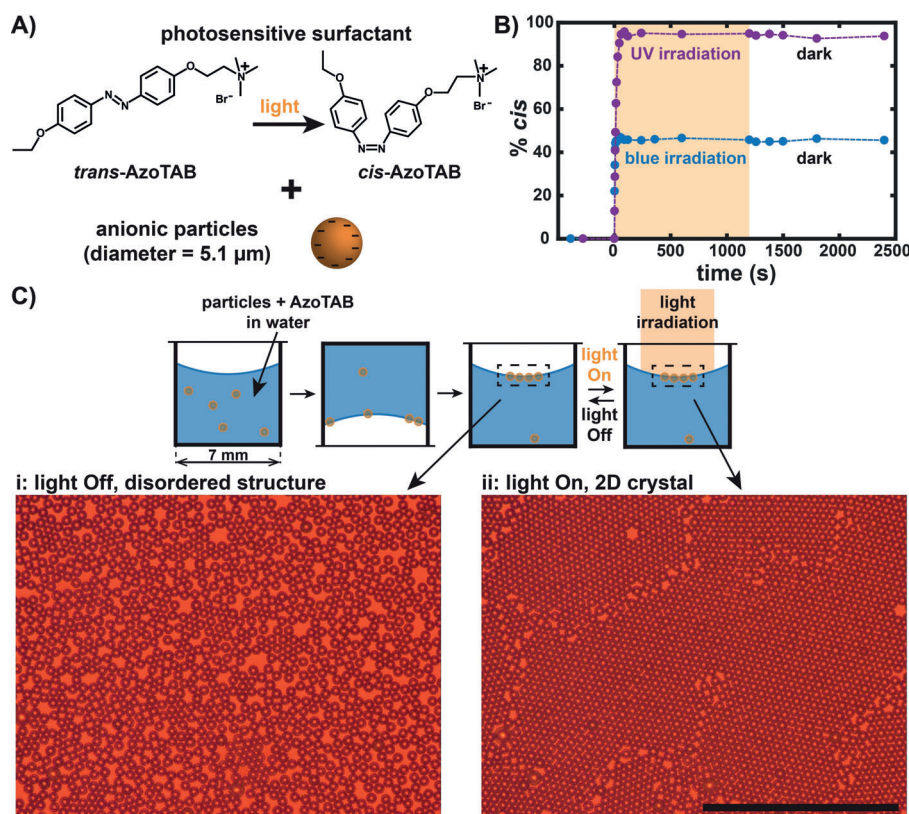
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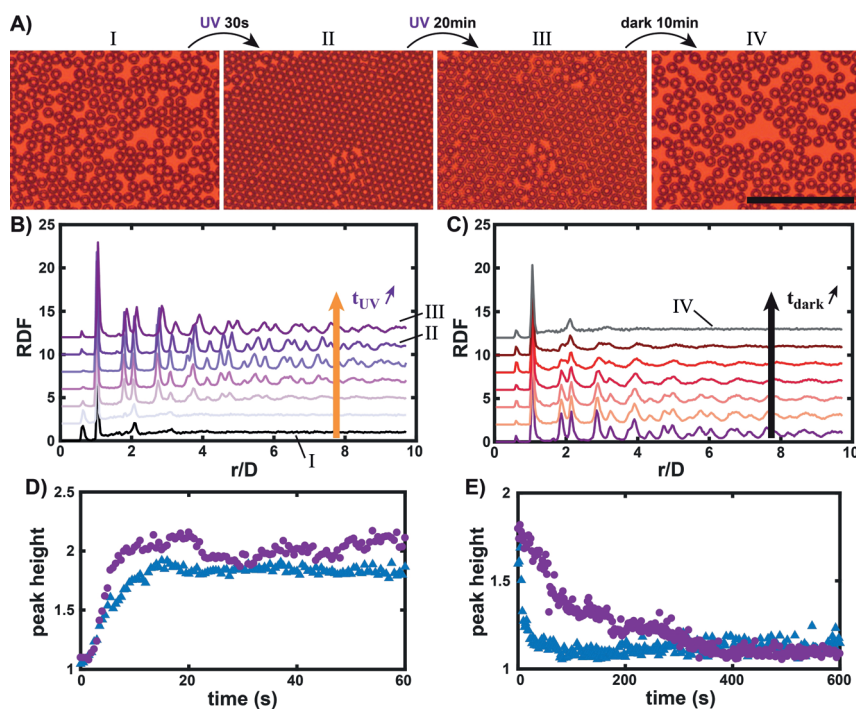
**Figure 1.** Light-induced two-dimensional colloidal crystallization at the air/water interface. A) Components of the system: the cationic photosensitive surfactant AzoTAB (10 μm), which, upon suitable light irradiation, converts from the *trans* (less polar) to the *cis* (more polar) isomer; and anionic polystyrene microparticles (5.1 μm diameter, 0.01 mg mL<sup>-1</sup>). B) Percentage of the *cis*-AzoTAB isomer in solution before, during, and after either UV (violet points) or blue (blue points) light irradiation. C) Top: set-up for particle adsorption at the air/water interface and light irradiation. A mixture of particles and AzoTAB in water is turned upside down for two hours to let particles sediment toward the interface. The sample cell is then flipped back and left overnight for adsorbed particles to accumulate at the center of the interface. Bottom: transmission microscopy images before (left) and after (right) UV irradiation for 30 s. UV and blue light irradiation was performed at 365 nm (8.1 W m<sup>-2</sup>) and 440 nm (63 W m<sup>-2</sup>), respectively. Scale bar: 100 μm.

surfactants, almost all particles adsorbed at the air/water interface and accumulated at the center of the cylindrical well containing the sample due to the slightly concave shape of the meniscus. In the absence of light irradiation, the particles formed a disordered structure containing voids (Figure 1 C-i). Irradiation of the sample with UV light (365 nm, 8.1 W m<sup>-2</sup>) promoted fast *trans*-to-*cis* isomerization of the AzoTAB molecules. By combining absorption and NMR spectroscopies, we measured the isomeric composition in the bulk, both in the dark and under UV irradiation. We found that the system was initially composed of 100% *trans* molecules and reached, after about one minute of irradiation, a photostationary state composed of 5% *trans* and 95% *cis* (Figures 1 B, S2, and S3). Strikingly, irradiation of the whole particle patch resulted in a fast and dramatic change in the organization of the particles: in a few seconds, the whole amorphous patch evolved into a mm-sized 2D crystal that remained crystalline upon irradiation (Figure 1 C-ii and Movie S1). The transition occurred through the formation of small crystallites, which, by local packing, induced a global confinement toward the patch center, followed by rearrangements and formation of large

monocrystalline domains. To our knowledge, this is the first time that such a dynamic photoresponse of a large colloidal assembly at the air/water interface is reported. A control experiment was performed with the non-photosensitive cationic surfactant DTAB having a CMC (13.4 mM<sup>[20]</sup>) close to that of AzoTAB. In that case, the structure of the adsorbed particles did not change upon extensive irradiation with UV light (Figure S4), showing that AzoTAB photoisomerization was instrumental in controlling the colloidal organization.

We then characterized the kinetics of the UV-induced disorder-to-order transition by computing the radial distribution function (RDF) from images of the colloidal patch as a function of the UV irradiation time (Figure 2). Several peaks appeared in the RDF during the first seconds of irradiation and, after about 10 s, the structure reached a stable state composed of well-defined peaks up to  $r/D=7$  (where  $r$  and  $D$  are the center-to-center interparticle distance and the particle diameter, respectively) showing long-range hexagonal packing (Figure 2 B). Interestingly, although this structure was maintained upon prolonged UV exposure (20 min, Figure 2 A-II, III), switching off the irradiation resulted in a transition back to the disordered state. The crystalline structure pro-

gressively lost its order, reaching a state similar to the initial one, that is, composed of particles in close proximity but without any long-range organization (Figure 2 A-IV). This transition took about 5 min (Figure 2 C), as evidenced by the vanishing of most of the peaks in the RDFs. These results demonstrate not only the photoreversible nature of the particle organization in our system, but also emphasize the surprising behavior that, after light removal, particles switch from a highly ordered to a disordered state in an isothermal manner. To gain a better insight into the underlying mechanisms of these dynamic processes, the response dynamics of the particle organization are compared to the isomerization characteristics of AzoTAB. UV-induced enrichment in *cis*-AzoTAB was very fast, with the bulk composition rapidly increasing from 0% to 50% within 10 s (Figure S5). After 60 s, this value reached 95% and stayed approximately constant upon extended irradiation (Figure 1 B). The transition time from disordered to crystalline particle assembly at the air/water interface thus followed similar kinetics. In contrast, when the light was switched off, the transition from the ordered to the disordered phase was achieved in a few



**Figure 2.** Temporal evolution of the structural properties of the colloidal assembly upon application and subsequent removal of a light stimulus. A) Transmission image of the center of a colloidal assembly before irradiation (I), after continuous UV irradiation for 30 s (II) and 20 min (III), and 10 min after switching off the UV stimulus (IV). Scale bar: 50  $\mu\text{m}$ . B) Radial distribution functions (RDFs) before (black curve) and after exposure to UV irradiation for 2, 4, 6, 10, 30, and 1200 s as a function of the ratio between the distance from a reference particle,  $r$ , and the particle diameter,  $D$ . The curves are vertically shifted for clarity. C) RDFs after switching off the UV stimulus, at 0, 30, 60, 120, 180, 300, and 600 s under dark conditions. D) Height of the twelfth peak in the RDF curves as a function of irradiation time for samples irradiated with UV (violet circles) or blue light (blue triangles). E) Height of the twelfth peak in the RDF curves as a function of time under dark after switching off the light stimulus for samples exposed to 20 min of UV (violet circles) or blue irradiation (blue triangles). UV and blue irradiation were applied at 365 nm ( $8.1 \text{ W}\cdot\text{m}^{-2}$ ) and 440 nm ( $63 \text{ W}\cdot\text{m}^{-2}$ ), respectively.

minutes, while the AzoTAB *cis/trans* composition was not affected in this time scale (Figure 1 B). We thus conclude that the colloidal structure was not controlled by the relative composition of *cis/trans* AzoTAB isomers in the bulk, instead we propose that it was mediated by the adsorption/desorption dynamics of AzoTAB. Upon UV-induced *trans*-to-*cis* isomerization, AzoTAB became more polar<sup>[35,36]</sup> and desorbed from the air/water interface in an analogous way to what was reported for similar photosensitive surfactants.<sup>[29]</sup> This light-induced desorption of surfactants could induce a Marangoni stress toward the irradiated area,<sup>[31,33,37–39]</sup> increasing particle confinement and promoting their crystallization. When irradiation smaller than the particle patch was used, some particle motion towards the irradiated area was observed and crystallization occurred on a larger area than the spot size (Figure S6), confirming that Marangoni-induced confinement could contribute to particle crystallization. However, our regular experiments were systematically performed with an irradiation area ( $\approx 4 \text{ mm}$ ) larger than the particle assembly ( $\approx 1 \text{ mm}$ ). Additionally, the small amount of AzoTAB in the system resulted in an undetectable surface-tension change (Figure S1). Aside from Marangoni stress, additional contri-

buted mechanisms have thus to be considered. We propose that, upon AzoTAB desorption from the air/water interface, the screening between like-charged particles by the cationic surfactants decreased while particles remained adsorbed because of the too high energy of detachment.<sup>[40]</sup> Similarly, the desorption of AzoTAB from the particle surface<sup>[32]</sup> could contribute to this increase of electrostatic repulsion. Overall, the increased electrostatic repulsion between particles added to their confinement caused by eventual Marangoni stress and the collective deformation of the interface<sup>[41]</sup> resulted in the formation of a highly crystalline structure under UV irradiation. As soon as the irradiation was removed, *trans*-AzoTAB molecules coming from the bulk could adsorb to repopulate the interface. The transition to the disordered state proceeded through particle diffusion initiated at the location of the few defects (vacancies and grain boundaries) in the crystalline structure (Movie S2), which prevented the system to be kinetically trapped in a metastable state. This resulted in a rapid evolution of the particle assembly back to the disordered state, which was the equilibrium state of our system. Therefore, the ordered structure was maintained only under continuous UV irradiation (Figure 2 A) in order to keep AzoTAB desorbing from the interface. Consequently, the 2D crystals reported here were not a minimum in the free

energy landscape of the system. On the contrary, they constituted an example of an out-of-equilibrium self-assembled structure where the structural complexity was obtained by reaching a dissipative state through the continuous consumption of energy necessary to maintain surfactant depletion from the air/water interface and from the particle surface.

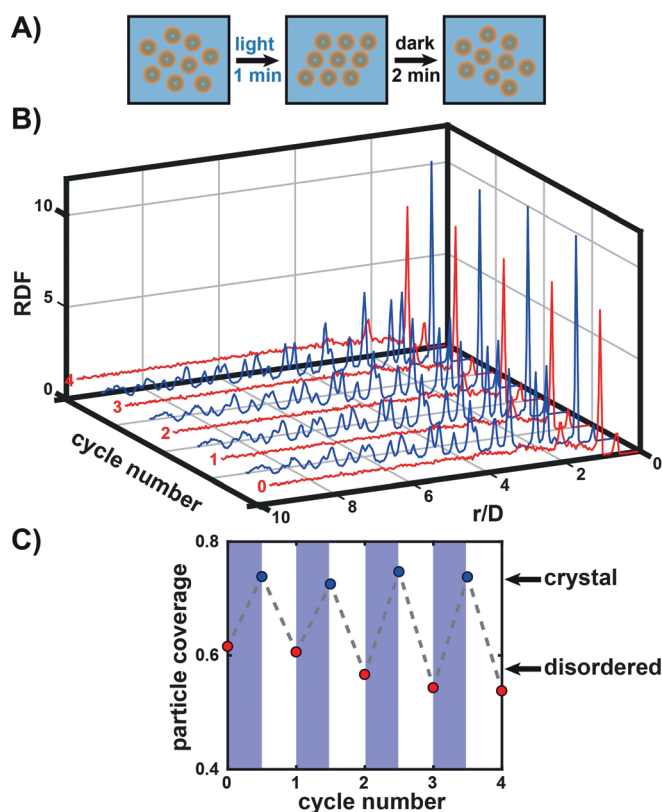
To gain more information about these dissipative colloidal crystals, we investigated whether they could be obtained with a less efficient bulk photoconversion process. To this end, we irradiated the sample with blue light (440 nm,  $63 \text{ W}\cdot\text{m}^{-2}$ ), leading to a photostationary state reached within one minute and composed of 55 % *trans* and 45 % *cis* (Figures 1 B, S2, S5, and S7). Although this photostationary state was significantly different from the one obtained after UV irradiation, the response of the colloidal assembly at the air/water interface was strikingly similar. Blue irradiation induced a fast disorder-to-order transition and the formation of extended, highly crystalline colloidal assemblies (Figure S8 and Movie S3). Crystals were maintained upon blue irradiation and switched back to the disordered phase as soon as light was switched off (Figure S8). The structural properties of the light-induced



colloidal assemblies were very similar for UV and blue irradiation, but a few differences could be noticed in the transition kinetics. Figure 2D,E shows the height of the twelfth peak in the RDFs curves ( $r/D \approx 5.8$ , long-range crystalline order signature) as a function of the irradiation time. Light-induced crystallization was achieved in around 10 s for both irradiation wavelengths (Figure 2D), but relaxation in the dark was faster after blue irradiation ( $\approx 30$  s) than after UV irradiation ( $\approx 350$  s, Figure 2E). These results first confirmed that our system was not controlled by the bulk composition of AzoTAB under light irradiation, since two different photostationary states led to very similar structures. We thus propose that it was the continuous light-induced desorption of AzoTAB that maintained the system out of equilibrium and allowed its crystallization. Interestingly, the system was shown to be history-dependent, that is, with two different kinetics under dark conditions as a function of the previously applied light wavelength. This can be explained by the different composition of the bulk, which was richer in *trans*-AzoTAB after blue irradiation (Figure 2B), leading to a faster kinetics of re-adsorption.

To assess the reversibility of the system, we applied successive light-on/off cycles on the colloidal assembly (Figure 3A), choosing blue light as the stimulus because of the faster response of the system after light removal. One minute of irradiation efficiently crystallized the whole particle assembly (Figure 3B, blue curves), whereas 2 min in the dark were enough for the system to switch back to the disordered state (Figure 3B, red curves). Several cycles of crystallization/disassembly were successfully achieved (Figure 3B and Movie S4). We also analyzed the fraction of surface occupied by particles in the center of the assembly and found that it was oscillating in phase with the light cycle, with an increase/decrease of the 2D packing density upon irradiation/dark conditions that correlated with the crystallization/disassembly process (Figure 3C). Cycles between amorphous and crystalline structures were obtained using UV light as well (Figure S9 and Movie S2), but the order-to-disorder transition after UV irradiation was slightly slower and required 5 minutes. This shows that the order can be tuned on demand with the possibility of cycling the system and adjusting its response time.

In conclusion, we have designed a photoresponsive dissipative self-assembling system composed of anionic microparticles and a cationic photosensitive surfactant in which the structural properties of the colloidal assemblies adsorbed at the air/water interface can be controlled through stimulation by light. We exploited the adsorption/desorption dynamics of the surfactant isomers at/from the water surface to control the particle–particle potential in a fast and reversible fashion. As a consequence, cycles between disordered and highly crystalline colloidal structures were achieved with a single wavelength switch, without being hindered by the very slow thermal relaxation of the excited surfactant isomers. This system represents a proof of principle of novel light-responsive 2D colloidal systems where specific properties arising from the collective organization of particles at a fluid interface can be efficiently switched on demand by means of light



**Figure 3.** Photoreversible crystallization/disassembly upon light-on/off cycles. A) Sketch of a disorder–order–disorder transition sequence driven by a cycle of blue light switched on and off. B) RDFs of the same sample subjected to cycles of blue light turned on (blue curves) and off (red curves). Each cycle consisted of irradiation with light (440 nm,  $63 \text{ W m}^{-2}$ ) for 1 min and dark conditions for 2 min. C) Fraction of the total area covered by particles in the center of the colloidal assembly in a box of  $218 \times 165 \mu\text{m}^2$  upon cycles of blue light turned on (blue background) and off (white background).

stimulation. By evidencing the emergence of a highly organized self-assembled structure that exists only through continuous energy consumption, it expands the realm of currently known dissipative systems, opening routes to man-made devices closer to biological systems and capable of properties such as adaptiveness, reconfigurability, and degradability.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** dissipative systems · interfaces · photocontrol · self-assembly · two-dimensional crystals

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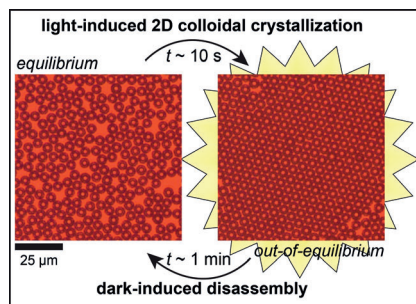
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## Communications

## Self-Assembly

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Photoswitchable Dissipative Two-  
Dimensional Colloidal Crystals



**Get organized:** The first system where the two-dimensional organization of particles at the air/water interface is controlled by light stimulation is reported. By mixing anionic microparticles and a cationic photosensitive surfactant, fast and dynamic switch between a disordered phase (in the dark) and the crystalline state is obtained on demand by light irradiation. The reverse transition takes place after switching off the light.