Angewandte Chemie

Molecular Devices

Light-Driven Dynamic Pattern Formation[**]

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Dynamic self-assembly processes are essential for organization and various phenomena in nature,[1] and mimicking of such processes in artificial systems offers fascinating opportunities for the construction of smart materials.[2] However, a major challenge in the design of nonbiological systems is the temporal and spatial control of fully reversible self-assembly processes.[3] Here, we report the incorporation of an address-

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[**] We would like to thank the MSC$^+$ for financial support, H. Nijland for the SEM measurements, and M. Popinciuc for useful discussions and help.

Angew. Chem. 2005, 117, 2425–2428

DOI: 10.1002/ange.200462500

able functionality into a supramolecular building block which allows control over the spatial and temporal self-organization of the molecular material. Light-induced reversible switching of a molecular system between an aggregated and non-aggregated state is manifested at the macroscopic level by a fully reversible sol–gel phase transition[4] and results in spatially confined structure formation in an inhomogeneous optical field. The reversibility of aggregation and the unique photochemically induced, spatially confined self-assembly that leads to light-induced mass transfer is exploited in dynamic pattern formation. These results clearly demonstrate the feasibility of dynamic self-assembly in simple artificial systems and will open new opportunities for smart materials and nanodevices.

Photochromic switches[5] have been exploited successfully in the control of host–guest systems, chiral aggregates, polymers, and gels, and particularly promising in this field are responsive self-assembling molecules in which an addressable function is incorporated.[6] We have designed a diarylethene switch that combines excellent photochromic properties with the ability to undergo self-assembly.[7] A reversible light-induced interconversion between an open form **1** and a closed form **2** (Figure 1 a) occurs,[8] and pronounced self-assembly of **1** and **2** in nonpolar solvents (e.g. aliphatic and aromatic hydrocarbons) takes place as a result of hydrogen bonding between the amide groups to result in the formation of gels above a critical gelation concentration.[4] Transmission electron microscopy (TEM) of gels (5.4 mM) in toluene revealed that gelation of the solvent is caused by the formation of entangled fibrous networks by aggregation of **1** or **2**. Fibers formed by **1** are very thin, with diameters as small as 20–25 nm, and the regular elongated shape of the fibers must arise from a strong anisotropic process, which indicates that the fibers are well-ordered with respect to the molecular packing.

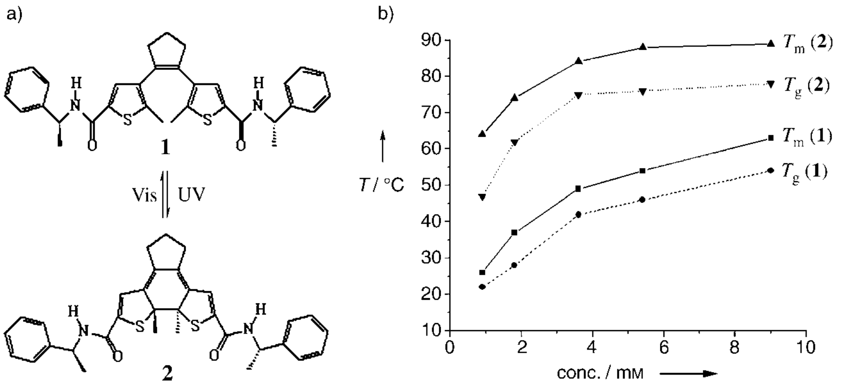

Figure 1. a) Dithienylcyclopentene switch with amide moieties for hydrogen bonding: the open form **1** can be converted into the closed form **2** by UV light, a process which can be reversed upon irradiation with visible light. b) Phase diagrams for **1** and **2** in toluene as measured by CD spectroscopy. The melting temperatures (T_m, ——) were obtained by heating the sample slowly until no CD absorption was observed, whereas the gelation temperatures (T_g) were obtained upon cooling the sample. The difference in T_m and T_g is a characteristic feature of low-molecular-weight gelators.[4] Note that T_m and T_g are independent of the rates of heating or cooling in the range 0.25–2 °C min^{-1}.

Regular fibers are also formed by **2**, but their diameters appear much larger than that for **1**. The different morphologies of **1** and **2** already indicate that the intermolecular interactions which lead to the formation of fibers are different. This difference in morphology of fibers between **1** and **2** is also reflected by the difference in the thermal stability of their gels, which is characterized by the concentration-dependent gel–sol phase-transition temperature. Phase diagrams (Figure 1 b) were measured for **1** and **2** by circular dichroism (CD) spectroscopy at concentrations between 1 and 10 mM.[9] Gels that contain **2** are much more thermally robust, presumably owing to the increased rigidity of the monomer.

Above the melting temperature (T_m) of gel **2** in solution the expected photochemical conversion between **1** and **2** occurs (Figure 1 b), and below the gelation temperature (T_g) of a gel of **1** the previously reported stereoselective gel-to-gel switching takes place.[7] In the region between T_g(**1**) and T_g(**2**), it is possible to induce a sol-to-gel phase transition (and vice versa) by photochemical conversion between **1** and **2**. Indeed, irradiation ($\lambda = 313$ nm) of a solution of **1** (1.5 mM) in toluene at room temperature results in a transition to a gel of **2**, whereas subsequent irradiation of this gel with visible light ($\lambda > 420$ nm) causes it to dissolve to give a solution of **1**. These observations prompted us to investigate whether it would be possible to generate spatially confined gel objects embedded in a solution. The formation of such objects, by irradiation through an optical mask or by holographic imaging,[10] requires that self-assembly followed by immobilization in the gel state takes place faster than diffusion of molecules of **2** to nonilluminated regions. To the best of our knowledge, no artificial molecular systems are yet known that can be reversibly assembled, on command, into spatially confined macroscopic objects.

A solution of **1** (1.5 mM) in toluene contained in a 1-mm cell was irradiated with crossed UV beams ($\lambda \approx 330$ nm)[10] at room temperature which resulted in the formation of transparent red-colored gel patterns that resist gravitational flow, whereas the nonirradiated surroundings remained in the liquid state. UV irradiation of a solution of **1** with a nonuniform optical field results in the localized photochemical conversion to **2**, which self-assembles to form a gel before diffusion of **2** to the nonirradiated areas can take place. The grating patterns obtained by this process had line spacings in the range of 75 to 5 µm, below which point the contrast of the pattern formed becomes blurred owing to diffusion of **2** out of the irradiated area. Application of more-intense irradiation accelerates the pattern formation and gives rise to smaller structures, although with reduced contrast. Typical macroscopic dimensions of the gel structures that formed in the solution were 10 µm × 5 mm × 1 mm. The large aspect ratio of these objects clearly demonstrates the excellent mechanical stability of the self-assembled gels in a liquid environment and persisting concentration gradients. The patterns could be erased by irradiation with visible light, and this whole cycle of pattern formation and erasing could be repeated several times. Note that this photoinduced self-assembly generates diapositive gel patterns, as opposed to dianegative patterns, which have been obtained by the irreversible photochemical decomposition of dye aggregates.[11–13]

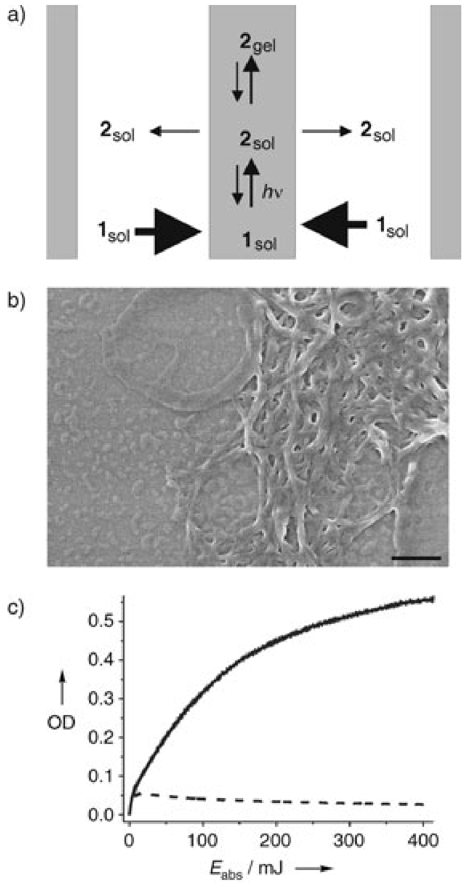

Figure 2. Mass-transfer during photoinduced gel formation in inhomogeneous optical fields. a) Kinetic scheme for the diffusion mechanism in the grating. White areas indicate positions of low UV irradiation intensity in the sample, while darker areas represent areas of high irradiation intensity. The thickness of the arrow indicates the dominance of the process. b) SEM image at the transition area between solution and gel (scale bar = 1 μm). c) Optical density (OD) at $\lambda = 650$ nm of a solution at 1.5 mM as a function of the absorbed energy in the UV region ($\lambda = 330$ nm). The solid line (——) shows the evolution of the optical density for irradiation using a single UV beam with a Gaussian beam profile (FWHM ≈ 3 mm) and 30 μW power. The dashed line (-----) shows the evolution of a uniformly irradiated sample for which no diffusion effects are present. FWHM = full-width at half maximum.

A graphical representation of the competing processes is given in Figure 2a. Initially, only **1** is present, and upon irradiation with UV light the concentration of **2** increases at the expense of **1** to create a relatively open fiberlike network. Nonaggregated molecules of **1** are capable of diffusing through the network into the irradiated areas, whereas the outward diffusion of **2** is greatly decreased because of its immobilization into the network structure. This implies that the monomers in the system can be captured in the irradiated area to create not only spatially confined gel objects but also to generate concentration gradients of **1** and **2**. Indeed, uniform irradiation of the sample with UV light below $T_g(\mathbf{2})$ after pattern formation from solution did not result in a homogeneously colored sample. It was observed that the existing lines appear much brighter than the previously nonirradiated areas, in agreement with our model.[14] As a control experiment, we repeated this sequence with a sample that contained **1** in the gel state, and here (nondynamic) pattern formation followed by uniform irradiation resulted in a homogeneously colored sample. Scanning electron microscopy (SEM) of the patterned samples revealed sharp boundaries between areas with a fibrous network and almost empty areas with minor amounts of deposited amorphous material (Figure 2b).[15] These observations were further confirmed by real-time dynamics measurements, which trace the optical density (OD) of the sample at $\lambda = 650$ nm where **2** absorbs while the system is irradiated with UV light within the absorption band of **1**.[16] In the diffusion-free case, which is obtained by uniform irradiation of the whole sample (Figure 2c, dashed line), the OD reaches a maximum value which is determined by the equilibrium ratio between **1** and **2**. The solid line shows the OD trace of a sample that is only locally irradiated by using a narrow laser beam (≈1-mm diameter). The OD at the irradiated spot (e.g. the local concentration of **2**) reaches higher values. An increase in the local concentration by a factor of 20 was observed upon irradiation of small areas of a sample and shows that a considerable fraction of the switch molecules can be fixed at the irradiated spot. The magnitude of the increase in concentration further depends on the ratio between the rates of diffusion of **1** and **2**, which itself is dependent on the concentration and temperature of the sample as well as on the irradiation density.

The reversibility and low degradation of the photochromic system suggest the possibility of dynamic self-assembly and pattern formation. This feature was exploited by irradiation of the sample with a second irradiation beam at a wavelength in the absorption region of the closed form ($\lambda = 500$–600 nm). This beam provides a pathway for exploitation of the dynamic nature of the system by disassembling patterns that are no longer being formed by the grating setup. Repeating the experiments previously described, but now with homogeneous visible irradiation, resulted in clear patterns and shows that simultaneous writing and erasing does not create difficulties during pattern formation. As shown in Figure 3, the initially created horizontal grating pattern (a) is overlapped (b), and subsequently replaced (c) by a second grating pattern built up at a different angle. This shows clearly that patterns can be created dynamically; that is, the patterns can be changed or replaced after formation. Note that patterns formed from a gel are stable for weeks, whereas those starting from solution are stable for only 1–2 days owing to diffusion of **2**. This diffusion can be inhibited either by freezing the sample or by removal of the solvent to create permanent stable patterns.

The dynamic and reversible pattern formation as reported here offers attractive prospects for future applications in nanotechnology. By manipulation of the delicate balance between solution and aggregation properties of materials at

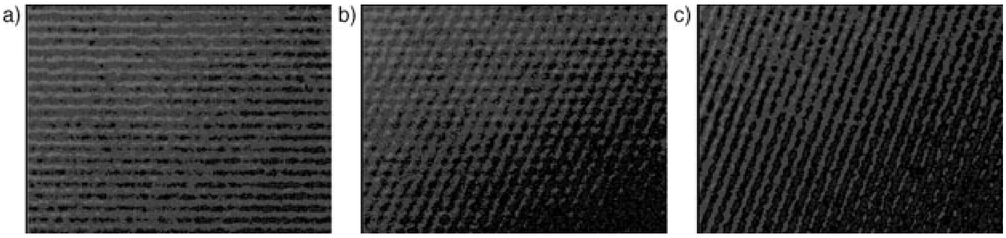

Figure 3. Dynamic spatially controlled self-assembly in time. Micrographs (20× magnification) of a solution of **1** (1.5 mM) in toluene in a 1-mm cell after simultaneous irradiation of the sample with a diffraction grating at $\lambda = 330$ nm (290 μW) and a homogeneous beam at $\lambda = 500$–600 nm (1 mW). Images taken a) after writing a horizontal grating pattern (irradiation: 10 min), b) after recording a second grating pattern following rotation of the sample (irradiation: 10 min), and c) as for (b), but after irradiation for 90 minutes.

the molecular level, stable addressable inhomogeneous micropatterns can be formed by dynamic self-assembly of molecular components in a fully reversible way. Self-assembling systems that can dynamically respond to external stimuli by a clear and appropriate response will be crucial for the development of artificial systems in the fields of smart materials, nanomachines, microfluidics, and molecular transport.

Received: November 2, 2004

Keywords: aggregation · gels · phase transitions · photochromism · self-assembly

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[8] Throughout the text, **2** refers to the photostationary state of the closed form, which consists of 40% of **2** with 60% of **1** still present. Initial experiments with only **2** showed no gelation, which indicates that the presence of both **1** and **2** is essential.

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