Dithienylcyclopentene optical switches
Jong, Jacob Jan Dirk de

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Chapter 4

Light-Driven Dynamic Pattern Formation

In this chapter, we show that incorporation of an addressable functionality into a supramolecular building block 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 as a fully reversible solution to gel phase transition, 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 leads to light-induced mass transfer, which is exploited in dynamic pattern formation. These results demonstrate clearly the feasibility of dynamic self-assembly in simple artificial systems, and open new opportunities for smart materials and nanodevices.

4.1 Introduction

Dynamic self-assembly processes are essential for the organization and a variety of other phenomena in the cell, including transport, motion, mitosis and the formation of the cytoskeleton.\(^1\) Mimicking such processes in artificial systems offers fascinating opportunities for the construction of smart materials.\(^2\) However, a major challenge in the design of non-biological systems is the temporal and spatial control of fully reversible self-assembly processes.\(^3\) Photochromic switches 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.\(^4\) Perhydrodithienyl cyclopentene switches\(^5\) are excellent candidates, since they have good photochromic properties and, when suitably functionalized, have the ability to undergo self-assembly\(^6\) as described in Chapter 3.

The aim of this research is to use perhydro dithienylethene switch 1 (Figure 4.1), described in Chapter 3, in the control over the supramolecular aggregation processes by light and electrochemical potential\(^7\) (e.g., the transition between solution and gel state). First the aggregation behavior of 1\(o\) will be discussed, after which a phase diagram can be constructed using Circular Dichroism (CD) spectroscopy for gels containing 1\(o\) and 1\(c\). Not only can the sample as a whole be addressed; it is also possible to control aggregation locally and temporally in an inhomogeneous optical field. This leads to partial gelation of the sample surrounded by solution, which is accompanied by a light-induced mass transfer. This in turn can be exploited in a fully reversible, dynamic pattern formation system.

4.2 Reversible Sol-Gel Transition

![Figure 4.1](image)

*Figure 4.1* Diarylethene switch with amide moieties for hydrogen bonding. The open form 1\(o\) can be converted to closed form 1\(c\) by UV light; a process which can be reversed by irradiation with visible light.
It is vital to understand why gelation occurs for perhydro dithienylethene switch 1, before attempting to control gelation by light. A reversible light-induced interconversion between an open form 1o and a closed form 1c (Figure 4.1) occurs with a photostationary state (PSS) of 40%. Pronounced self-assembly of 1o and 1c in non-polar solvents, e.g. aliphatic and aromatic hydrocarbons, takes place due to hydrogen bonding between the amide groups (Chapter 3.5), and results in the formation of gels above a critical gelation concentration. Transmission Electron Microscopy (TEM) of 5.4 mM gels in toluene revealed that gelation of the solvent is due to the formation of entangled fibrous networks by aggregation of 1o or 1c. 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, indicating that the fibers are well ordered with respect to the molecular packing. Regular fibers are also formed by 1c, but their diameters appear much larger than for fibers containing 1o. The different morphologies of 1o and 1c already indicate that the intermolecular interactions leading to fiber formation are different.

![Figure 4.2 Phase diagram measured by CD for 1o and 1c in toluene. The solid lines for the melting temperature (T_m) are obtained by heating a sample slowly until CD absorption is no longer observed, while cooling the sample leads to the gelation temperature (T_g, dashed line) when the signal reappears. The difference in T_m and T_g is a characteristic feature of low molecular weight gelators.](image-url)
This difference in morphology of fibers between 1o and 1c 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 4.2) were obtained for 1o and 1c by circular dichroism (CD) spectroscopy\textsuperscript{11} at concentrations between 1 and 10 mM.\textsuperscript{12} Gels containing 1c are more thermally robust, presumably due to the increased rigidity of the monomer leading to improved (stronger) packing.\textsuperscript{13} Above the melting temperature (T\textsubscript{m}) of gel 1c both 1o and 1c are in solution, and the expected photochemical conversion between 1o and 1c occurs as described in Chapter 3. Below the T\textsubscript{g} of the gel of 1o, switching in the gel takes place,\textsuperscript{6} which will be discussed in Chapters 5 and 6. In the region between the T\textsubscript{g}(1o) and the T\textsubscript{g}(1c) (\textit{vide infra}) it is possible to induce a sol to gel phase transition (and vice versa) by photochemical conversion between 1o and 1c. Indeed, the irradiation to PSS (\lambda = 313 nm) of a 1.5 mM solution of 1o in toluene at r.t. results in a transition to a gel of 1c, whereas subsequent irradiation of this gel with visible light (\lambda > 420 nm) causes its dissolution to give a solution of 1o. Thus we can control the solution to gel transition by light.

4.3 Spacial Control over Gelation

These observations prompted us to investigate whether it would be possible to generate spatially confined gel objects embedded in a solution.\textsuperscript{14} The formation of such objects, by irradiation through any sort of optical mask, requires that self-assembly followed by immobilization in the gel state takes place faster than diffusion of molecules of 1c to non-illuminated regions (Figure 4.3). No artificial molecular systems are yet known that can be assembled reversibly, on command, into spatially confined macroscopic objects, although control over the sol-gel transition was shown (Chapter 1). Unfortunately, no masks (at a reasonable price) could be bought that suited our purpose, so several attempts were made to produce some masks ourselves. Cutting pieces of paper will only give linewidths down to 1 mm, which, as it turned out, was not nearly enough to challenge our system. Most transparencies (or dia-slides) for printing are not penetrated by UV light or suffer from imperfect printing.

The holographic grating technique\textsuperscript{15} was explored for pattern formation (see the experimental section for details). The setup is shown in Figure 4.4. A Hurricane titanium sapphire laser generates 120 fs, 800 \mu J pulses at 800 nm wavelength. A fraction of the laser output at this wavelength is directed to a non-collinearly pumped optical parametric amplifier (NOPA), which allows for tunable wavelengths in the spectral range of 480-750 nm, but for our experiments it is set to generate 660 nm pulses. The output of the NOPA is focused on a SHG crystal which generates light pulses of double frequency (half
wavelength) 330 nm. After that the beam is split, giving two identical light bundles with similar phase. These two light beams can be combined (crossed) to give an interference pattern at the position of the sample. If the beams have opposite phase the waves cancel out, but, if they have the same phase, then the beams amplify each other (constructive and destructive interference). Therefore some regions in the sample receive high intensity of UV light (1o transforms to 1c) and some are dark (no switching takes place). This acts like an optical mask that creates an inhomogeneous optical field. It is thus possible to irradiate part of the sample, and the possibility for spatial gelation can now be investigated.

\[
\text{- Rate of switching} \quad \begin{array}{c}
\text{1o} \\
\text{1c}
\end{array} \quad \begin{array}{c}
\text{1o} \\
\text{1c}
\end{array} \\
\text{- Rate of gelation}
\]

\[
\text{- Rate of diffusion}
\]

**Figure 4.3** Schematic representation of the different competing processes. The switching and gelation rates need to be much faster than the rate of diffusion in order to minimize diffusion out of the irradiated areas.

A 1 mm cell containing a solution of 1o (1.5 mM) in toluene at r.t. was irradiated with crossed UV beams (\(\lambda = 330\) nm) which resulted in the formation of transparent red-colored gel patterns, which resisted gravitational flow in the areas with high UV irradiation intensity. The non-irradiated surroundings remained in the liquid state, due to the interference pattern creating locally low intensity of UV light. Clearly, UV irradiation of a solution of 1o with a non-uniform optical field results in localized photochemical conversion to 1c, which self-assembles to form a gel before diffusion of 1c to the non-irradiated areas can take place. The grating patterns obtained by this process had line spacings in the range of 75 to 5 \(\mu\)m, below which point the contrast of the pattern formed becomes blurred due to diffusion of 1c out of the irradiated area. Application of more intense irradiation accelerates the pattern formation and allows for smaller structures, albeit with reduced contrast. Typical macroscopic dimensions of the gel structures
formed in the solution were 10 µm x 5 mm x 1 mm as determined by optical microscopy. The large aspect ratio of these objects clearly demonstrates the excellent mechanical stability of the self-assembled gels in a liquid environment, and persistence of concentration gradients. The patterns were erased by irradiation with visible light (λ = 500-600 nm), and this whole cycle of pattern formation and erasing could be repeated several times. It should be noted that this photo-induced self-assembly generates dia-positive gel patterns, as opposed to dia-negative patterns which have been obtained by the irreversible photochemical decomposition of dye aggregates.16,17,18

![Figure 4.4](image)

**Figure 4.4** Setup for the holographic grating technique. See experimental for a full description.

### 4.4 Mass Gradient Formed

A graphical representation of the competing processes that occur during photo-induced pattern formation is given in Figure 4.5. Initially, only 1o is present, and upon irradiation with UV light the concentration of 1c increases in the irradiated areas at the expense of 1o. Preferential aggregation of 1c creates a relatively open fiber-like gel network. Non-aggregated molecules of 1o are capable of diffusing through the network into the irradiated areas, whereas the outward diffusion of 1c into the dark (non-irradiated) areas is greatly reduced because of its immobilization into the network structure. This implies that the monomers in the system can be captured in the irradiated area, creating not only spatially confined gel objects, but also generating concentration gradients of 1o and 1c. Indeed, uniform irradiation of the sample that already contained a preformed pattern from solution (i.e., diffusion of 1o was possible) did not result in a homogeneously colored sample. It was observed that the existing lines appear much brighter than the previously non-irradiated areas, in agreement with our model. As a control experiment, we repeated
this sequence with a sample that contained 1o in the gel state, and here (non dynamic) pattern formation followed by uniform irradiation results in a homogeneously colored sample.

Figure 4.5 Mass transfer during photo-induced gel formation in inhomogeneous optical fields. Kinetic scheme for the processes that influence the diffusion mechanism in the grating. White areas indicate positions in the sample of low UV irradiation intensity, the grey areas represent areas of high irradiation intensity. The thickness of the arrow indicates the dominance of the process.

These observations could also be quantified from the different intensity distributions for the red, green, and blue channels on a 3-color CCD camera coupled to an optical microscope (Figure 4.6). Each picture contains millions of individual pixels, which are expressed in 3 x 256 intensities as shown on the Y-axis. These colors are a function of blue (▲), green (●) or red (■) as observed by the CCD camera and the maximum value in the distribution is plotted. Samples of different concentrations of 1o were homogeneously irradiated to 1c, and subsequent, analyzed for their intensity distribution. Upon going to high concentrations, the purple color of 1c increases in intensity (e.g. absorption), which is observed as lower intensities for all three channels. This can be used to evaluate the concentration of 1c at any point in the sample. See experimental section for more details.

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 4.7). Control experiments by SEM at lower concentration showed that the amorphous material is composed of monomer, but there is not enough to form fibers.
Figure 4.6 Average intensity for the red (■), green (●), and blue (▲) channel as observed by CCD camera of an optical microscope for a gel of 1 in PSS at different concentrations.

Figure 4.7 SEM at the transition area between solution (left, where amorphous material is deposited) and gel (right, where the fiberous network can be observed. Bar = 1µm.

These observations were confirmed further by real-time dynamics measurements, which trace the optical density (OD) of the sample at λ = 650 nm where 1c absorbs while irradiating the system with UV light within the absorption band of 1o.20 In the diffusion-free case, which is obtained by uniform irradiation of the whole sample (Figure 4.8, dashed line), the OD goes to a maximum value determined by the equilibrium ratio between 1o and 1c, and then slowly decreases, presumably due to degradation of the switch. The solid line shows the OD time trace of a sample that is only locally irradiated using a narrow laser beam (ca. 1 mm diameter). The OD at the irradiated spot, e.g. the local concentration of 1c, reaches higher values than obtained by homogeneous
Light-Directed Dynamic Pattern Formation

Irradiation. This can be explained by diffusion from $1o$ from the non-irradiated areas into the irradiated area, where it is subsequently converted to $1c$. Increasing local concentration by a factor of 20 has been observed upon irradiation of small areas of a sample, showing that a considerable fraction of the switch molecules can be fixed at the irradiated spot. The magnitude of the concentration increases further depending on the ratio between the rates of diffusion of $1o$ and $1c$, which is itself dependent on the concentration and temperature of the sample as well as on the irradiation density. So, not only is it possible to have spatial control over gelation, it is also possible to introduce, based on diffusion, a mass gradient in the sample, which depletes the non-irradiated areas of $1o$.

![Figure 4.8](image)

**Figure 4.8** The optical density at $\lambda = 650$ nm at 1.5 mM as a function of the absorbed energy in UV ($\lambda = 330$ nm). The solid (→) curve shows the evolution of the optical density (OD) for irradiation with a single UV beam with a Gaussian beam profile (FWHM ~ 3 mm) and power 30 $\mu$W. The dashed (- - -) curve shows the evolution of a uniformly irradiated gel sample, for which no diffusion effects are present.

**4.5 Dynamic Reversible Patterning**

The reversibility of the aggregation and ring closure together with high stability of the photochromic system creates 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 $1c$ (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 described previously, but now with simultaneous homogeneous visible irradiation,
resulted in clear patterns (Figure 4.9a), showing that the simultaneous writing and erasing does not create difficulties during pattern formation. Apparently, the rate for ring-closure, and subsequent aggregation, is much higher then for ring-opening, which results in diffusion. After a steady state has been obtained, the sample was rotated ($\alpha = 63^\circ$) with respect to the optical field, as is shown in Figure 4.9. The horizontal grating pattern created initially (Figure 4.9a) is overlapped (Figure 4.9b), and subsequently replaced (Figure 4.9c) by the new grating pattern built up at a different angle. This demonstrates that patterns can be created dynamically, i.e. can be changed or replaced after formation. It should be noted that patterns formed starting from a gel are stable for weeks and starting from solution 1-2 days due to diffusion of 1c. This diffusion can be inhibited either by freezing the sample or by removal of the solvent, creating permanent, stable patterns.

![Figure 4.9](image_url)

**Figure 4.9** Dynamic spatially controlled self assembly in time (10-20 $\mu m$ linespacing). Micrographs of a 1.5 mM solution of 1o in toluene in a 1 mm cell, after simultaneous irradiation of the sample with a diffraction grating at $\lambda = 330$ nm (290 $\mu W$), and a homogeneous beam at $\lambda = 500-600$ nm (1 mW). Magnification 20x. (a) Taken after writing a horizontal grating pattern, 10 min. (b) after recording a second grating pattern following rotation ($\alpha = 63^\circ$) of the sample, 10 min. (c) as b, but irradiation for 90 min.

### 4.6 Conclusions

The dynamic and reversible pattern formation as reported here offers attractive prospects for future applications in the nanosciences. By manipulating the delicate balance between solution and aggregation properties of materials at the molecular level, stable, addressable, inhomogeneous micro patterns can be formed by dynamic self-assembly of molecular components. It is interesting to consider these excellent reversible properties of the photochromic self-assembly process in the context of complex responsive biological phenomena such as cytoskeleton formation. At all levels, Nature depends heavily on the creation of inhomogeneous environments in which cells function and communicate, and the ability to respond to external stimuli at the molecular level resulting in a change of
macroscopic properties is essential for common cell functions such as transport, motion and replication. The development of artificial systems with such properties, as described here, provides a major advance in the fields of smart materials, nanomachines, microfluidics, and molecular transport.

4.7 Experimental

For experimental details on dithienyl cyclopentene switches see Chapter 2. For experimental details on gelation see Chapter 3. Construction of phase diagrams by temperature dependant CD measurements is discussed in Chapter 5.

Holographic grating technique
The holographic grating technique records the diffraction efficiency of the holographic grating during its creation, and the progression of the ring closure reaction can be investigated. The schematics of the experimental setup is shown in Figure 3. UV light of tunable wavelength was generated by using a 1 kHz Ti:sapphire laser system (Hurricane, Spectra Physics) and an optical parametric amplifier (NOPA). The laser system produces 120-fs, 800-µJ pulses at 1 kHz, centered at 800 nm. About 250 µJ of that energy is used to pump a NOPA (Topas White, Light Conversion LTD), which generates 30 fs pulses tunable in the spectral region 500-750 nm. The sample was irradiated by the second harmonics of the NOPA output, which was generated in a 0.2 mm thick BBO crystal (SHG). Experiments were performed with writing pulse energies varying from 180 nJ to 0.7 nJ and centered at 330 nm. Polarization of the light was kept horizontal. The UV light passes a diffractive optics element (DO), which is a phase grating specially designed to diffract into the +1 and –1 orders about 30% of the input energy. Since only transmission optics is used after the DO element, no phase distortions are introduced between the two interacting beams. In addition the use of diffractive optics ensures optimum spatial overlap of the two writing pulses in the sample. The imaging system based on two lenses with focal strength f1 and f2 allows control of the incidence angle. The probe wavelength of 650 nm that measures the optical density, is at the edge of the absorption spectrum, in order to minimize the influence of the probe beam to the real time dynamics by means of initiating the ring-opening reaction.

Experiments for pattern formation
Toluene was used as the solvent with 1.5mM of 1o when starting measurements from solution (just above the Tm of gels containing 1o at r.t.) or > 1.8 mM when starting from the gel state. A CCD camera connected to a optical microscope was used to determine the concentration in the patterns. Trendlines were made by adding a known amount of 1o and toluene in a 1 mm quartz cuvet and subsequent irradiation with λ = 313 nm to PSS to
determine pixel content distribution of the sample. There are 3 x 256 colors for the camera, each represented by a different intensity number and expressed in blue, red, and green channel. Upon increasing the concentration, the color (absorption) becomes more intense, which is reflected by a change in the intensitie distribution averaged over all pixels. See Figure 4.10 for a general example.

Figure 4.10 For a gel containing $1\circ$, a picture obtained by the 3 color CCD camera (top left) can be expressed in 3 x 256 colors displayed in blue, red, and green (bottom left). The maximum in this graph for the colors is plotted in Figure 4.6. Upon irradiation with $\lambda = 313$ nm to the PSS the sample changes color (top right) due to the formation of $1c$, which is reflected as a change in the intensity distribution (bottom right).

References


8 Throughout the text, $1c$ refers to the photostationary state of the closed form, consisting of 40% of $1c$ with still 60% of $1o$ present as determined by $1H$ NMR spectroscopy. Initial experiments with only $1c$ showed no gelation, indicating that both $1o$ and $1c$ are essential.


12 See Chapter 5.3 for representative figures and discussion on temperature dependent CD measurements.

13 To support this further, attempts were made to determine values for enthalpy and entropy by dropping ball measurements, temperature dependent $1H$ NMR and CD spectroscopy for both $1o$ and $1c$. Unfortunately this resulted in very similar numbers for $1o$ and $1c$ with large error margin, making it impossible to draw any conclusions as to which is the dominant factor in this process.

14 M. Popinciuc is kindly acknowledged for his help on trying to produce masks for our system.


19 H. Nijland is kindly acknowledged for the SEM measurements.