Chapter 1

Diarylethene photochromic switches for reversible control of functions

In this chapter, efforts to apply diarylethene photochromic switches in the reversible control of different functions and properties of molecules and molecular systems are discussed. The chapter starts with a short introduction and characterization of molecular switches and a discussion on the diarylethene family of molecular switches in particular. Then the individual sections deal with the specific properties that can be altered by photochemical switching of diarylenes, including fluorescence, chiroptical phenomena, magnetic interactions, complexation, and supramolecular interactions. The chapter closes with a brief outline of the rest of this thesis.
1.1 Photochromism

Photochromism \(^1\) can be defined as a “reversible change, induced by light irradiation, between two states of a molecule having different absorption spectra”\(^{1a}\) (Scheme 1.1). Although the term “photochromism” indicates a change of colour as the most obvious effect detectable without any scientific tools, this difference in optical properties is always accompanied by an alteration in other physical and chemical properties. In this way the geometrical structure, oxidation/reduction potential, refractive index and dielectric constant can be manipulated. All these changes are the result of chemical transformations, which for the majority of the photochromic systems, are reversible unimolecular reactions.

\[
\begin{align*}
A & \xrightleftharpoons[\Delta \text{ or } h_v_2]{h_v_1} B
\end{align*}
\]

Scheme 1.1 Photochromism as a reversible transformation between two forms.

There are two main types of photochromic systems classified according to the thermal stability of the photochemically generated isomer. When the isomer obtained after irradiation is unstable, the back reaction occurs thermally and such chromophore is of the T-type (thermally reversible type). Most of the known photochromic compounds belong to this group. The other class of chromophores, indicated as the P-type (photochemically reversible type), contains structural units that can be converted to the original state photochemically but not thermally.

Two of the most extensively studied families of the T-type photochromic switches are azobenzenes (Scheme 1.2a) and spiropyrans (Scheme 1.2b). Azobenzenes undergo a reversible photochemical trans-cis isomerization. This distinct geometry change is at the root of most of their applications \(^2\). The cis form of azobenzenes being energetically unfavourable is unstable and returns back to the trans form also by a thermal isomerization pathway. The light-induced change in spiropyrans \(^3\) is a result of the electrocyclic ring opening of the pyran ring. Due to the subsequent rearomatization of the phenyl ring, a charge is generated at the indoline nitrogen and phenolic oxygen atoms. Indeed the extensive change in the polarity due to this zwitterionic merocyanine form generated by the UV irradiation is the most prominent feature of this family of switches.

Although for some applications the thermal instability of the switch forms might not be a drawback, thermochromism is often seen as a disadvantage. Therefore, the thermally stable P-type switches are considered the most promising candidates for practical applications. Two groups of P-type photochromic switches are known, the furylfulgides \(^4\) (Scheme 1.2c) and diarylethenes \(^5\) (Scheme 1.2d). The photochromic reaction of both of these classes of compounds is based on the electrocyclic reaction initiated by UV light irradiation. The closed-ring isomer is stable and the reversible ring-opening process is possible only by irradiation with visible light. Due to their synthetic availability and possibility of introducing many different substituents, diarylethenes are the most promising candidates for future applications.
Diarylethene photochromic switches for reversible control of functions

Scheme 1.2 Examples of photochromic compounds of the T-type a) azobenzenes, b) spiropyans and the P-type c) furylfulgides and d) diarylethenes.

Photochromic compounds can find various applications in photonic devices, such as erasable optical memory and photophysical switch components. Although at present mainly inorganic materials are used in photochromic lenses and optical memories, new organic materials with improved performance and fatigue resistance are starting to replace them. The very successful and widely used recordable and rewritable CD and DVD disks use organic dyes as the writing medium.

1.2 Diarylethenes

The best known diarylethene, stilbene or 1,2-diphenylethene 1.1 (Scheme 1.3), undergoes two photochemical processes i.e. cis – trans isomerization and photocyclization. Although in the presence of air or other oxidants the product of the second process, the dihydrophenanthrene 1.2, converts irreversibly to the phenanthrene 1.3, in the absence of oxygen compound 1.2 photochemically or thermally returns to the initial stilbene.
Scheme 1.3 The cis-trans isomerization, photocyclization and subsequent oxidation of stilbene.

To avoid the unwanted oxidation, substituents, typically methyl groups, at the 2- and 6- positions of the phenyl rings are introduced thus making the system stable even under oxidizing conditions. To address the problem of the thermal back reaction diarylethenes with various aryl groups were investigated in order to prepare a P-type chromophore. The most successful switches proved to be the ones based on the five-membered heterocycles especially the dithienylethenes\textsuperscript{5,12} (Scheme 1.4). Both the open- and closed-ring isomers are thermally stable and photochemical ring-opening/ring-closing cycles can be repeated many times without loss of photochromic performance. To prohibit the competitive photochemical cis – trans isomerization, the central ethene bond is usually constrained in the cyclic system.

Scheme 1.4 The basic switching unit of most common dithienylethenes.

The open form 1.4o is usually colourless while the closed form 1.4c, obtained after irradiation with UV light, is coloured. The difference in colour is caused by the difference in the geometry and electronic properties of the molecule. In the open form 1.4o, the two thiophene moieties can freely rotate and their electron systems are separated in a cross-conjugated manner. The nearly planar structure of the closed form 1.4c, and the conjugation that extends through the whole molecule, are the reasons for the shift of absorbance to longer wavelengths. Further shift of absorbance can be achieved by substitution of the thiophene rings. Substituents that allow extension of the conjugated system or create a donor-acceptor pattern are present in the switches with absorbance of the closed form at wavelengths over 800 nm\textsuperscript{13}.

Most of the early studies focused on the development of the photochromic switches as a basis for optical data storage devices. Such systems need to fulfill several criteria such as the thermal stability of both forms which is inevitable for effective memory, fatigue resistance that guarantees many read/write cycles, high quantum yield, fast response and non-destructive readout.

Thermal stability depends mostly on the nature of the aryl groups. While dithienylethenes are in general stable in both the open and the closed state (no change observed after several hours at 80°C), replacement of the thiophene for pyrrole\textsuperscript{14} or phenyl\textsuperscript{15}...
Diarylethene photochromic switches for reversible control of functions

rings destabilizes the closed form which in some cases returns back to the open form within minutes at room temperature. A similar destabilizing effect was observed for some dithienylethenes bearing strong electron-withdrawing groups. Fatigue resistance is a more complex phenomenon and depends on the structure of the switch and its ability to give photochemical side reactions, as well as on the environment of the switch molecules. The best results so far were obtained by incorporating the switch into a polystyrene film in the presence of singlet oxygen quenchers. Under these conditions, the switching cycle can be repeated $7 \times 10^4$ times.

The quantum yield of the cyclization reaction is for most diarylethenes in the range of $0.1 - 0.5$, while the quantum yields for the cycloreversion vary considerably from 0.1 to $10^{-5}$. The main factor influencing the quantum yield is the substitution pattern. The substituents, which extend the conjugated system, also lower the cycloreversion quantum yield. For the ring-closing reaction there is another important factor, which limits the maximal quantum yield to about 0.5. Due to its higher flexibility, the open form exists in two conformations, the parallel and the anti-parallel conformational isomers (Scheme 1.5). The photochemical ring-closing reaction is an electrocyclization involving $6\pi$ electrons, which, according to the Woodward-Hoffmann rules, can proceed only in a conrotary manner. This process is possible only if the switch is in the anti-parallel conformation, leaving the parallel conformation unreactive. For most diarylethenes there is no preference for one of the conformations, which results in a 1 : 1 mixture of the conformers in the solution. Thus, only one half of the molecules in the anti-parallel conformation is available for the ring-closing reaction and the maximal quantum yield is 0.5. For the majority of diarylethenes the parallel and antiparallel conformations are at equilibrium, with low energy barrier for their mutual interconversion. Due to their fast equilibration, the ring-closing photoreaction can result in quantitative conversion of the switch to the closed form, despite the fact that the open form is a 1 : 1 mixture of the parallel and antiparallel conformers. The amount of the anti-parallel conformation can be increased under certain circumstances, such as through confinement in the cavity of cyclodextrine. It is also possible to increase the amount of the parallel conformation up to the point where the ring-closing reaction is no longer observed. This is called gated switching and occurs when the substituents on the thiophene rings interact with each other, or with other molecules or ions (see parts 1.7 and 1.9).

![Scheme 1.5](image-url) Two possible conformations of diarylethene and their photoreactivity.

The perfection of the non-destructive readout, i.e. the ability to detect the state of the switch without disturbing it, appears to be quite challenging. The most straightforward approach, detection by optical techniques requires additional irradiation, which usually
results in the change of the switch state and a loss of information. The most successful approach appeared to be coupling the switching event to some other property than depends on the state of the switch and can be effectively detected without the danger of inducing the reverse switching process. Adding another function to the switching unit provides a way of controlling a diversity of properties and forms the basis for approaches to some advanced switching systems such as gated switches, switches with more than two states, switches dependent on supramolecular interactions or supramolecular interactions dependent on state of the switch. All those added functions make molecular switches an invaluable tool for nanotechnology and construction of molecular devices.

The remaining of this chapter will be devoted to the exploration of the potential of switches with added functionality. The chapter is divided into several parts, each dealing with a specific function that can be modulated using the diarylethene photochromic switches.

### 1.3 Switching of fluorescence

Fluorescence is the most widely studied phenomenon in combination with photochromic switching\(^{21,22}\). Due to the high sensitivity of detection, fluorescence has been proposed as a suitable non-destructive readout method with a minimal damage to stored information. The first reported diarylethene with modulation of fluorescence accompanying the photochemical reaction, was compound \(1.5^{21a,21b}\) (Scheme 1.6 and Figure 1.1). The open form \(1.5o\) shows strong emission at 589 nm when excited in the 400 – 500 nm region; while for the closed form \(1.5c\), the intensity of the emission drops to about 3% when compared to \(1.5o\). Moreover, the absorption band of \(1.5o\) with a maximum at 459 nm, which is used for the excitation, does not interfere with the ring-closing and ring-opening processes.

![Scheme 1.6 Fluorescence modulation with the diarylethene.](image_url)
A large number of diarylethenes with different fluorescent properties in the open and closed state have been reported since then. These studies are also testimony of the frequent occurrence of fluorescence in this type of molecules. Many structurally rather simple dithienylethene photochromic switches show intrinsic fluorescent behaviour (Scheme 1.7)\textsuperscript{21o,21u,21w}.

**Figure 1.1** Photomodulation of fluorescence a) UV-vis spectra of the open form 1.5o and the closed form 1.5c of the switch b) fluorescence spectra of the open form 1.5o and the closed form 1.5c of the switch (adopted from ref.21a).

The easiest way to rationally design a switch that exhibits modulation of fluorescence, is appending a fluorophore to the switching unit. Scheme 1.8 shows two examples of this approach. Both are based on the dithienylperfluorocyclopentene switching moiety with triphenylimidazole as fluorophore in 1.9\textsuperscript{21H} and 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in 1.10\textsuperscript{21V}. These fluorophores were selected due to their high fluorescence quantum yield, which enhances the sensitivity of the readout. This approach is based on a common mechanism of fluorescence quenching. In the open form, the fluorophore behaviour is only weakly or not at all influenced by the switch since the light it absorbs is usually of lower energy than that of the switching moiety. However, after ring closure the HOMO-LUMO gap of the switch becomes narrower, as reflected also by the appearance of absorption in the visible region, and energy transfer from the fluorophore to the switch can occur. Thus, the closed-ring switch moiety effectively quenches the fluorescence of the fluorophore.

**Scheme 1.7** Diarylethene switches which show photomodulation of fluorescence.
Scheme 1.8 Examples of switches with appended fluorophore.

Nevertheless, there is one problem that has to be overcome when designing this type of fluorescent switches. Energy transfer can also take place in the opposite direction and switching of the open form to the closed form may not proceed if there is fast energy transfer from the excited state of the switching moiety to the fluorophore. This indeed is the case when switches with attached porphyrine based fluorophores are used (Scheme 1.9). When attached directly or through a short linker, as in the compound 1.11\textsuperscript{23a}, energy transfer is much faster than cyclization and no photochromism can be observed. This problem can be solved by tuning the length of a linker demonstrated for compounds 1.12 and 1.13\textsuperscript{23a} or by choosing a different mode for the fluorophore attachment, as shown in compound 1.14\textsuperscript{23b,23c}.

Scheme 1.9 Porphyrines as a fluorophores attached to dithienylethenes.
Less frequently reported are switches that show fluorescence enhancement upon ring-closure (Figure 1.2). However, these compounds have one major potential advantage. If the fluorescent intensity decreases upon ring-closure as in the case of 1.5 – 1.14, the photostationary state must contain a high portion of the closed form in order to achieve sufficient fluorescence change, because the remaining open form still shows fluorescence. Thus if the ratio of the open and closed form in the photostationary state is 1:1, the switching causes only 50% drop in fluorescence. On the other hand, if the fluorescent intensity increases after ring-closure, ideally the open-ring isomer has no fluorescence, much higher modulation of fluorescence can be achieved independent of the photostationary state.

Figure 1.2 An example of a switch with enhanced fluorescence in the closed form a) switching process b) fluorescence spectra of the open and closed form upon excitation at 240 nm (adapted from ref. 21c) c) excitation wavelength dependent fluorescence modulation.

The concept that is closest to a single-molecule based memory was demonstrated using fluorescence confocal microscopy to observe and induce switching of fluorescence in photochromic compound 1.16 (Figure 1.3) at the single molecule level. The sample was prepared by spin-coating diluted toluene solution of 1.16 (2x10^{-11} M) on a polymer film (amorphous polyolefin, brand name Zeonex) to obtain low surface coverage necessary to distinguish single molecules. As most of the fluorescent diarylethenes, it shows fluorescence in the open state while the closed state is almost nonfluorescent with a 99.9% efficient energy transfer from the fluorophore to the closed diarylethene moiety. However,
in the case of a single molecule, the switching is digital, i.e. the detected signal has only two values corresponding to the open or closed form and does not depend on the photostationary state as the signal of the ensemble of the molecules. The molecules of the open form of the switch can be observed as bright fluorescent spots upon excitation with 488 nm light. Irradiation of the sample with 325 nm UV light resulted in the ring-closing reaction and the disappearance of the bright spots. However, after irradiation with visible light, the ring-opened molecules could be observed again. The fact that a single molecule can act as an information carrier is the highlight but also a drawback of this system, since the information stored depends on the stability and state of one molecule and thus could be easily lost.

**Figure 1.3** Single molecule switching; a) photoreactions of a diarylethene switch used for single-molecule fluorescence switching b) fluorescence images of single-molecule fluorescence switching. (adapted from ref 24a)

### 1.4 Switching chirality

Measuring changes in optical rotation presents a promising method for the nondestructive readout of information stored by photochromic compounds. Detection can often be performed outside the photoactive spectral region. To take advantage of this method, the molecular switch has to fulfill one important criterion. Its chiroptical properties must change as a result of the photoreaction. The diarylenes are very promising candidates, because the ring-closing reaction produces two new stereogenic centers that result in two stereoisomers (Scheme 1.10). In the absence of any chiral influence, those isomers are created in a one-to-one ratio.
Diarylethene photochromic switches for reversible control of functions

Scheme 1.10 The formation of the two isomers upon switching.

In the first reports focused on achieving stereoselectivity in the photoreaction, chiral moieties were attached to a photochromic compound (Scheme 1.11). For both compounds, 1.17 with the menthyl group as a chiral auxiliary26a and 1.18 with two 1-phenylethylamine moieties26b, the highest stereoselectivity was obtained only under very strict conditions. A diastereomeric excess (d.e.) of 86.6% was achieved after the irradiation of the toluene solution of compound 1.17 at -40°C, while no stereoselectivity was observed in n-hexane solution26a. The best d.e. of 36% was only obtained irradiating the solution of 1.18 in n-hexane/THF/methanol (4/1/0.1) mixture at -40°C26b. In both cases the stereoselectivity was strongly dependent on the polarity of the solvent and the temperature. Although the exact d.e. values were determined using chiral HPLC26a or 1H NMR in the presence of chiral chemical shift reagent26b, the change of the chiroptical properties of the molecules can be conveniently detected by CD spectroscopy26a.

Scheme 1.11 Switches with attached chiral auxiliary.

As expected, very high stereoselectivity was obtained upon switching of diarylethenes with appended chiral groups in the crystalline state27,28. The tight packing in the chiral arrangement induced in the crystals is responsible for almost complete control of the stereoselectivity. Recently, even a stereoselective switching of an achiral switch was achieved, based on the fact that it crystallized creating a mixture of enantiomorphic crystals in which the open form of diarylethene was locked in either P- or M-helical conformation29. Irradiation of the individual crystals thus resulted in creation of single enantiomers of the closed form, while upon irradiation of the mixture of crystals or a solution of diarylethene, a racemic mixture of the ring-closed product was obtained. However the use of the single
crystals in practical applications is difficult and the photoconversion is generally very low, occurring only in the top layer of the crystal.

An interesting concept was developed by the group of Branda\(^3\), based on the chiral oxazoline 1.19, which creates with copper(I) single stereoisomers of helical bis Cu(I) complex (Scheme 1.12). Both dithienylcyclopentene moieties in such complex are forced to adopt chiral conformations and after ring closure only single diastereoisomer is obtained. This is an excellent example of the translation of the molecular chirality into a supramolecular chirality of the complex which in turn dictates the selectivity during reaction at the molecular level.

![Scheme 1.12](image)

Scheme 1.12 The chiral complex of an oxazoline substituted diarylethene 1.19 with Cu\(^+\) and its stereoselective photochromic switching reaction.

Compounds with large optical rotatory power are helicenes\(^3\). The use of these compounds might enhance the sensitivity of the readout method. Switching of a compound with two helical arms 1.20 (Scheme 1.13a) was found to be stereoselective\(^3\). Only two out of four possible isomers of the helical ring closed compound 1.20c (two diastereoisomers based on the chirality of carbons taking part in the cyclization reaction (Scheme 1.10) combined with a two helical arrangements of the thianaphthalene moieties) were isolated. This observation indicates that the overall helicity is dictated by the chirality of the two reacting carbons and no racemization is taking place after ring closing. Based on this observation, a new switch 1.21o was synthesized, containing β-pinene moiety as a chiral...
structural moiety (Scheme 1.13b)\textsuperscript{32b}. Only one isomer of the helicene 1.21c with $M$ helicity and large optical rotation ($[\alpha]_{422} = 5725^\circ$) was obtained after irradiation with UV light. The ring closing reaction for switch 1.21o is completely stereoselective, and although the photostationary state contains only 40% of the ring-closed isomer 1.21c, the large optical rotation compensates for this drawback.

Scheme 1.13 Photoswitchable helicenes a) helicene without chiral moiety b) helicene containing $\beta$-pinene as a chiral structural moiety.

When studying the stereoselectivity of the ring closing reaction, it was found that for some switches bearing a chiral auxiliary, the closed form showed a CD effect in the visible region, even when the ring-closing reaction was not stereoselective and both diastereoisomers were created in nearly equal amounts\textsuperscript{33}. This can be explained by the presence of an induced CD effect. The chiral auxiliary, which has no absorption in the visible region, induces a CD effect in the diarylethene chromophore absorbing in the visible region. The absorption band in the visible region thus becomes CD active. In some cases the induced CD is even stronger than the CD signal due to the chiral diarylethene backbone\textsuperscript{34} as can be seen in Figure 1.4. Both diastereoisomers with RR and SS configuration at the central cyclohexadiene ring, respectively, show a positive CD signal in the visible region, although their CD signals in the UV region are opposite in sign.
Chapter 1

Figure 1.4 Switching of the diarylethene 1.22 with chiral substituents and CD spectra of isomers 1.22c-SS (- - -) 1.22c-RR (-----) and their 1:1 mixture (——).

1.5 Switching magnetic interactions

Molecular magnetism is based on the spin of unpaired electrons\textsuperscript{35,36}. If there is no interaction between the spins of the individual unpaired electrons, all of them behave independently creating a paramagnetic material. If the interaction exists, the electron spins align either parallel (ferromagnetic exchange interaction) or antiparallel (antiferromagnetic exchange interaction). Although typical magnetic materials are based on transition metals, organic radicals also contain unpaired electron and can exhibit interesting magnetic properties\textsuperscript{35}.

The magnetic interactions in molecules containing more than one unpaired electron depend on the distance and connection between them. Generally, modification of the connecting bridge is expected to influence their interaction. Diarylenes with the ability to modulate the electronic communication through the molecule are ideal candidates for the development of photoresponsive magnetic systems\textsuperscript{37}. Thus, in the open form of the switch the interaction between spins is weak. The strong antiferromagnetic interaction will occur only after ring closure, which results in the conjugated system extending electronic communication through the whole molecule.

The first system synthesized to explore this property was based on bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene, which is known to have excellent switching properties, high fatigue resistance and is thermally stable in both forms. To this switching moiety, two nitronyl nitroxide substituents, each bearing an unpaired electron, were attached. The resulting compound 1.23\textsuperscript{37a-d} shows typical photochemical behaviour and can be reversibly switched between the open 1.23o and the closed 1.23c form by irradiation with UV and visible light, respectively (Scheme 1.14). The light absorbance of
radicals therefore does not compromise the photochromism of the switch, although it affects the quantum yields of the photoprocesses as well as the photostationary state. While the quantum yield is decreased for both the ring-closing as well as the ring-opening photochemical reaction, the decrease for the ring-opening reaction is more pronounced, resulting in a photostationary state with a higher amount of the closed form \(^{37n}\).

**Scheme 1.14** The spin coupling photochromic system.

As expected, while the open form \(1.23o\) shows only weak antiferromagnetic coupling with exchange interaction \(2J/k_B=-2.2\) K, the closed form \(1.23c\) shows, due to the conjugated pathway connecting the two spin systems, a much stronger antiferromagnetic coupling with exchange interaction \(2J/k_B=-11.6\) K. However, the ESR spectra of both forms are almost identical containing 9 lines each, which means that the exchange interaction is much stronger than the hyperfine coupling constant for both isomers. The isolated nitronyl nitroxide radical has an ESR spectrum containing 5 lines, while the biradical composed of two coupled nitronyl nitroxides has an ESR spectrum containing 9 lines. In order to distinguish between the open and closed form by ESR spectroscopy, new systems with weaker exchange interaction were synthesized, designed to better isolate the radicals in the open form. The distance between nitronyl nitroxide moieties was increased by introduction of phenyl bridges (Scheme 1.15) \(^{37ef}\).

**Scheme 1.15** Diarylethene switches with weaker interaction between unpaired electrons.

For both diarylenes, \(1.24\) and \(1.25\), the photochemical ring closing and opening reactions are accompanied with the change in the magnetic properties. While the ESR spectrum of the open form of \(1.24\) are complex and shows 15 lines, which means that the exchange interaction between the two radicals is comparable to the hyperfine coupling constant, the ESR spectrum of the closed form of \(1.24\) shows 9 lines resulting from the
stronger exchange interaction. The open form of 1.25 has only 5 lines in the ESR spectra, suggesting that a quite long spacer is necessary to completely isolate the two radicals. The ESR spectrum of 1.25, after irradiation with UV light, shows 9 distorted lines which means that in the closed form of the switch the exchange interaction is just a little higher than the hyperfine coupling constant. For this compound the modulation of the coupling between the spins of the two radicals was exceptionally high; the exchange interaction for the closed form being about 30 times higher than for the open form.

It has been shown that the spacer between the diarylethene core and the nitronyl nitroxide can be based also on thiophenes. The more efficient π-conjugation along the thiophene spacer compared to the phenyl spacer resulted in even higher modulation of the coupling with a more than 150 fold increase in the exchange interaction upon the ring closure. 

To demonstrate cooperation between two photochromic moieties, the diarylethene dimer 1.26 was used as a three-state switching unit. The three possible states are with both switches in the open form 1.26oo, one switch in the closed and one in the open form 1.26co and both switches in the closed form 1.26cc (Scheme 1.16). The nitronyl nitroxide radicals are connected by fully conjugated pathway only in the last case. Indeed, while the ESR spectra of 1.26oo and 1.26co show only 5 lines indicating independent radicals, the ESR spectra of 1.26cc consist of 9 lines due to the coupling between the spins of the two nitronyl nitroxide radical functionalized switches.

\begin{center}
\includegraphics[width=\textwidth]{diagram.png}
\end{center}

**Scheme 1.16** Switching the magnetic interaction in a diarylethene dimer.

Recently, a system with reversed switching of the magnetic interaction was reported. In the compound 1.27o the spins of the two nitronyl nitrooxides are coupled while the diarylethene switching moiety is in the open form. The ESR spectra show 9 lines due to the strong exchange interaction. Upon irradiation with the UV light, closing of the switch breaks up the conjugated pathway between the radicals resulting in a 5 line ESR spectra for the 1.27c.
Diarylethene photochromic switches for reversible control of functions

![Scheme 1.17 Diarylethene with magnetic coupling in the open form.](image)

The magnetic properties of inorganic layered compounds with intercalated diarylethenes were also affected by the state of the switch. Two such organic-inorganic hybrid materials were prepared. One based on the cationic diarylethene intercalated in layered copper pervoskite\(^{38}\) and the other based on anionic diarylethene intercalated in cobalt layered double hydroxides\(^{39}\). In both systems some magnetic properties changed upon photochemical reaction of the diarylethene, however the changes are difficult to rationalize and no general conclusions that might lead to designed switchable magnetic materials can be drawn.

### 1.6 Switching a crystal surface

The ability of numerous diarylethene photochromic switches to undergo a reversible photochemical reaction in the crystalline state is quite unique\(^{40}\). Although photochromic crystals based on various photochromic compounds have been reported, they usually suffer from thermostability\(^{41}\). The ability of a diarylethene to form the closed-ring isomer depends on its conformation within the crystal lattice. For the antiparallel conformation of the diarylethene, only minor structural changes are required to switch from the open to the closed form\(^{42}\), thus making the photoreaction possible also in the confined environment of the crystal. The parallel conformation, unreactive in a solution, is also inert in a crystal.

The switching in a crystal can result, besides in the typical colour change, also in a change of the crystal surface morphology\(^{43}\). Upon irradiation with UV light, a crystal of 1.28o (Figure 1.5) changed colour to blue and changes on the surface of the crystal could be observed by AFM. On the (100) surface steps with a height of 1 nm appeared after irradiation, while on the (010) surface creation of valleys as deep as 10 – 50 nm were observed (Figure 1.5b-d). Both surface features disappeared almost completely after subsequent irradiation with visible light, proving this phenomenon to be reversible. These surface changes are directly related to the changes in the shape and volume of the switching molecule. The distance between the two reactive carbon atoms in 1.28 becomes shorter after a single bond is created between them upon ring-closure. Due to this shortening, also the distance between the phenyl substituents, and the length of the whole molecule decreases. Although the changes are subtle, in the order of hundredths of nanometers, they occur in every layer in the crystal and accumulate resulting in the described changes of the crystal surface morphology.
Figure 1.5 Crystal surface morphology change induced by a photochromic reaction; a) photochemical reactions of diarylethene in the crystal; b) – d) AFM images of (010) crystal surface b) before irradiation c) after irradiation with 366 nm UV light d) after subsequent irradiation with >500 nm visible light (adapted from ref. 43).

Another example of a compound capable to change crystal surface morphology is the trimethylsilyl substituted dithienylethene 1.29 (Figure 1.6)44. In this case the change of the crystal surface is more pronounced and also the mechanism responsible for this change is different. The crystal of 1.29o upon irradiation with 254 nm UV light changed colour to blue, due to formation of the closed form 1.29c, and no morphological change was observed. However, 5 min later, small fibrils started to appear on the surface of the crystal. After storing the crystal in the dark for 24 h, the fibrils reached the size of several micrometers and covered the whole surface (Figure 1.6c). Subsequent irradiation with visible light followed by storage for 24 h in the dark resulted in the disappearance of the fibrils (Figure 1.6d).

It is known that surfaces with micrometer scale roughness show superhydrophobic properties 45. A photoswitchable superhydrophobic surface was constructed using photoinduced fibril growth44. The microcrystalline film of 1.29o shows a water contact angle of 120° (Figure 1.6b). Irradiation of the film with UV light resulted in generation of the closed form of the switch 1.29c. The surface was then kept for 24 h in the dark in order to develop the fibrils, and the contact angle measurement was repeated. The new value of the water droplet contact angle was 163° (Figure 1.6c), which means that the surface became superhydrophobic (i.e. contact angle exceeds 150°). After irradiation of this superhydrophobic surface with visible light, followed by storage for 24 h in the dark, the original value of 120° for the contact angle was obtained (Figure 1.6d).
Diarylethene photochromic switches for reversible control of functions

![Diagram of Diarylethene Switches]

**Figure 1.6** Crystal surface changes induced by a photochromic reaction; a) photochromic reactivity of the diarylethene in the crystal; b) – d) SEM images of the crystal surface and changes of hydrophobicity of the surface determined by the contact angle measurements. b) before irradiation c) 24 h after irradiation with 254 nm UV light d) 24 h after subsequent irradiation with >500 nm visible light (adapted from ref. 44).

The dramatic changes in morphology of the crystals of 1.29 cannot be explained on the basis of accumulation of small changes at the molecular level. Indeed, it was observed that the process of fibril growth was prohibited when the crystals were stored below 0°C after irradiation. Upon irradiation of the crystals with UV light, the closed form 1.29c started to accumulate, causing the melting point of the crystals to decrease. The minimal melting point of 30°C was reached for the 24:76 ratio of the open to the closed form. This observation together with the fact that the fibrils contained only the closed form 1.29c, even when the crystal contains less than 50% of the closed form, suggest that the mechanism of fibril growth includes a phase change, i.e. the melting and recrystallization of 1.29c in the form of fibrils.

### 1.7 Switching complexation

Binding of metal ions by organic molecules is widely applied concept in supramolecular chemistry, especially in the context of ion sensing. Molecules that can bind and release metal ions reversibly as a response to light can be used as metal ion sensors or metal transport systems.46

Adding the complexating ability to a photochromic switch introduces two features. Binding metal to the switch alters the electron density and possibly the conformation of the switch, thus changing its spectral properties and photochemical reactivity. Changing the state of the switch by irradiation, on the other hand, can lead to a different electron
distribution and a different shape, resulting in a different coordination strength or different selectivity for various metal ions.

In the first reports, diarylethenes with complexating properties were based on crown ethers as the metal binding sites. Four articles from two groups appeared within one year describing the complexation and switching behaviour of similar compounds, depicted in Scheme 1.18. Their function was based mainly on the conformational change of the diarylethene backbone after binding the metal ion.

Scheme 1.18 Various diarylethene switches with appended crown ether moieties as metal ion binding sites.

Due to free rotation around the bond that connects the thiophene with the central cyclopentane ring, diarylethenes can exist in two conformations. As noted before, the antiparallel conformation, in which the substituents on the thiophenes are far apart, can undergo photochemical ring closure. The parallel conformation that brings substituents close to each other is photochemically inactive. When a bulky metal ion is complexated by the switch, both crown ether substituents participate in binding, thus being an example of the biscrown effect (Scheme 1.19). This is possible only if the switch adopts the unreactive parallel conformation. This was shown for the compound 1.31. The $^1$H NMR spectrum of uncomplexed compound shows two sets of signals for the parallel and antiparallel form in the ratio of $1:1$. After addition of $\text{Rb}^+$, the ratio changed to $6:1$. As expected the complexation also affected the quantum yield for the photochemical ring closure that dropped from 0.21 for the free switch to 0.02 when $\text{K}^+$ or $\text{Rb}^+$ was added. Addition of 18-crown-6 ether to the solution of the complex of the biscrown switch 1.31 with $\text{K}^+$ resulted, due to stronger complexation of $\text{K}^+$ by the crown ether, in shift of the equilibrium between parallel and antiparallel forms causing the quantum yield to increase to 0.17.
Diarylethene photochromic switches for reversible control of functions

Scheme 1.19 The structure of biscrown diarylethene and the effect of metal-ion binding on switching behaviour.

There is also an effect of switching on the complexation. From the Scheme 1.19 it is clear that after ring closure it is not possible to bind the metal ion by both crown ether substituents anymore, and as a result the binding strength should decrease. This was shown using the two phase extraction of Rb picrate. The amount of Rb+ extracted by the closed form was approximately five times lower that the amount extracted by the open form.

The properties of the other switches in Scheme 1.18 are similar, the main difference being the ion selectivity. While compound 1.30 with the 12-crown-4 ether moiety shows the highest selectivity for Na+ and Rb+, switch 1.31 with the 15-crown-5 moiety is selective for K+ and Rb+, and 1.32 with 18-crown-6 substituents is selective for K+, Rb+ and Cs+. However, for 1.32 the difference in the binding strength between open and closed forms can be observed only for Cs+ ions, suggesting that K+ and Rb+ are complexated by the single crown ether substituent and their binding is not dependent on the conformation of the switch.

A distinct feature of diarylethene switches is the change of the conjugation between the substituents present at the thiophene rings, upon switching. In the closed form, the substituents are effectively electronically coupled while in the open form no such interaction occurs. This was explored in the diarylethenes that use the change in the electron density of the complexating site as a response to the switching. Two such systems were reported (Scheme 1.20), both bearing the complexating moiety as a substituent on one of the thiophenes and electron withdrawing moiety on the other.

Scheme 1.20 Diarylethenes in which the electron desity of the complexating site alters as a response to switching.
In compound 1.36, the phenylaza-15-crown-5 acts as an ionophore and the formyl group as an electron withdrawing moiety\textsuperscript{48a}. The binding of cations by the open form of the switch is comparable to binding by the phenylaza-15-crown-5 substituted with an electron donating substituent. Upon ring closure, the formyl group exerts its electron withdrawing effect on the thiophenes, and as a consequence on the nitrogen of the azacrown moiety causing the stability constants for the complexes with metal ions to decrease. The explanation that the change is due to reduced charge density on the nitrogen, is supported by the observation that, while the decrease of the stability constants for the monocharged metal ions (Na\textsuperscript{+} and Ag\textsuperscript{+}) is within one order of magnitude, the stability constants for the Ca\textsuperscript{2+} bearing two positive charges drops almost four orders of magnitude.

A different ionophore, pyridine, was used as a metal binding site in 1.37 in order to coordinate a ruthenium porphyrin. The electron deficient-substituent in this case is the pyridinium cation. Modulation of the Lewis basicity of the pyridine nitrogen and subsequently of the stability of the complex was monitored by \textsuperscript{1}H NMR\textsuperscript{48b}. Although the change of the ratio of complex to free switch changed only slightly, from 52 : 48 for the open form of the switch to 42 : 58 for the closed form, apparently also in this case the closed form is a less effective ligand.

There are numerous other reports describing metal complexes containing diarylethene photochromic switches as ligands\textsuperscript{49}. In these cases the coordination of ligand functionalized diarylenes was used as a tool to create organometallic species and not to study the complexation event itself.

### 1.8 Switching liquid crystals

Doping liquid crystals with photochromic compounds is an effective way to amplify the effect of the switching and several diarylenes were synthesised and studied as dopants in liquid crystalline films\textsuperscript{33,50}. The most common approach was to use the diarylethene containing a chiral moiety and observe the change in the helical twisting power of the switch upon ring-closing and ring-opening processes. The first report describes the change of the cholesteric phase, created by doping the nematic liquid crystal with the chiral dithienylethene, to the nematic phase upon ring-closing reaction of the switch, induced by the irradiation with UV light\textsuperscript{33}. The opposite effect, i.e. change of the nematic phase to the cholesteric phase upon ring-closing of the diarylethene dopant was observed as well\textsuperscript{50c}.

Another approach involves the design and synthesis of diarylenes that display liquid-crystalline behaviour themselves. Several systems in which the mesogenic unit is attached to the photochromic diarylethene core were reported recently\textsuperscript{51}. The usual approach to this type of liquid crystalline switches is modular. The mesogenic unit and the diarylethene moiety are connected through a rather long linker that ensures that the switching properties are not affected by the mesogen and, on the other hand, the interaction between the mesogenic units is not restricted by the diarylethene moiety (Scheme 1.21).
Diarylene photochromic switches for reversible control of functions

Scheme 1.21 Diarylene with attached mesogenic units.

Compounds 1.38 – 1.40 differ only in the position of the mesogenic substituents at the benzothiophene unit. Except for 1.40, which shows liquid crystalline behaviour only on cooling and melts to an isotropic liquid, open forms of both 1.38 and 1.39 melt to give the tilted lamellar smectic C phase, which upon further heating changes to the nematic phase. In the photostationary state, achieved after UV irradiation (313 nm), the compounds show different behaviour. All the transition temperatures are decreased or unchanged. Moreover, in the case of 1.38 the smectic C phase changes to an unidentified smectic phase, while for the 1.39 no nematic phase can be observed.

Switch 1.41 (Scheme 1.22) is a system with mesogenic units attached to the carbon atoms on the benzothiophene rings, which are reaction centres during the photochemical process. The open form of this switch melts at 140.1°C and upon cooling exhibits a nematic phase at 96.1°C. In the photostationary state, that contains 62% of the closed form, all the phases are less stable. Melting occurs at 122.2°C and the nematic phase can be observed at 62.1°C.

Scheme 1.22 Various attachments of the mesogenic units.
All the switches with liquid crystalline behaviour 1.38 – 1.41 contain cyanobiphenyl as a mesogenic unit. It was shown\textsuperscript{51c} that this mesogen participates in the photochromic process through a fluorescence resonance energy transfer. To avoid this effect switch 1.42 (Scheme 1.22), containing a different mesogenic unit, was synthesized\textsuperscript{51f}. The disiloxane group found in the spacer was introduced for synthetic convenience. The effect of switching on the liquid crystalline behaviour of this compound is very small. While the open form melts at 2.6°C to give the nematic phase, which clears to an isotropic liquid at 54.3°C; at the photostationary state the melting occurs at 7.4°C and the nematic phase disappears at 51.3°C. However, the photostationary state contains only 24% of the closed form, which might explain the small difference in behaviour.

\begin{align*}
1.43 & \quad \text{Scheme 1.23 Compounds that behave as a photoresponsive, glassy liquid crystals.}
\end{align*}

Another approach was focused on the preparation of photoresponsive glassy liquid crystals that form a monodomain thin film. Three compounds 1.43 – 1.45 (Scheme 1.23) with a different number and type of mesogenic units were synthesized and studied\textsuperscript{51b}. Switch 1.43 is a stable amorphous glass that melts into an isotropic liquid while 1.44 shows a very complex behaviour, creating glassy and crystalline state along with nematic and smectic mesophase, depending on the temperature and direction of the temperature change. The most suitable compound for the desired application is 1.45, which shows only one nematic mesophase between 102°C and 219°C. The thin glassy nematic film of 1.45 was prepared by shearing the nematic mesophase at 210°C to induce alignment followed by slow cooling to room temperature. This 14 μm thick film shows absorption dichroism, the refractive indices for the ordinary and extraordinary beam (780 nm) are $n_o=1.5534$ and $n_e=1.6562$. Irradiation with 366 nm UV light changed the properties of the film. Although only 12% of the molecules switched to the closed form, the refractive indices changed to $n_o=1.5563$ and $n_e=1.7155$. After irradiation with 577 nm visible light the refractive indices regained the original values.

The first examples of compounds that avoid this modular approach and combine the diarylethene switching moiety with the mesogen in a rigid molecular framework are 1.46 and 1.47 (Scheme 1.24)\textsuperscript{51d}. They have increased volume density of the switchable group in the condensed phase and are potentially more efficient. Both compounds exhibit a monotropic nematic phase on cooling: 1.46 between 99.8°C and 84.2°C and 1.47 between 91.6°C and 29.8°C. Upon irradiation with UV light, high conversion to the closed form can be achieved i.e. 99% for 1.46 and 63% for 1.47, accompanied with the change in the transition temperatures. For 1.46 the melting as well as the clearing temperature decreases to 95.5°C and 74.1°C, respectively, suggesting the destabilization of the system upon ring closure. On the contrary for 1.47 the melting temperature increases slightly to 92.6°C and clearing temperature decreases to 25.8°C.
Diarylethene photochromic switches for reversible control of functions

Scheme 1.24 Switches with mesogens coupled directly to the diarylethene core.

The control of the properties of liquid-crystalline phases by light using diarylethene photochromic switches is very promising approach to new materials with potential use in optical components. Several systems presented here, show modulation of transition temperatures or even appearance and disappearance of specific liquid crystalline phase upon irradiation. However, the changes in liquid crystalline phases are, for most of the systems, only minor and the topic requires a lot of further research.

1.9 Switching other supramolecular interactions

The first example of the introduction of a hydrogen bonding motif into diarylethene switches was based on the switches 1.48 - 1.50 (Scheme 1.25), which show gated switching. The principle of gating is analogous to switches with crown-ether moieties described in section 1.6. In nonpolar solvents the unreactive parallel conformation is preferred due to hydrogen bonds created between the carboxylic acid residues. As a result, switch 1.48 undergoes a photochromic ring closing reaction in ethanol but is totally photochemically inactive in cyclohexane. Adding small amount of ethanol or other hydrogen-bond breaking compounds to the cyclohexane solution restores the photochemical reactivity of the switch. The temperature also helps in breaking the hydrogen bonding. When the switching was studied at higher temperatures in decalin, the quantum yield rose dramatically between 100°C and 150°C. 1H NMR spectroscopic analysis also confirmed the presence of only the parallel conformation of the switch in cyclohexane solution, while both conformations, parallel and antiparallel, were present in ethanol solution. Similar effects were observed also for 1.49 although the shorter spacers between quite rigid diarylethene moiety and carboxyl groups resulted in the weaker hydrogen bonding. Switch 1.49 thus showed a photochromic reaction also in cyclohexane but the quantum yield was considerably reduced compared to that in ethanol solution. Compound 1.50 with carboxyl groups attached directly to benzothiophene moiety did not show any effect of hydrogen bonding on its photochemical behaviour.
Chapter 1

Scheme 1.25 Diarylethene exhibiting gated switching.

The photoresponsive saccharide receptor 1.51 (Scheme 1.26) is based on the same principle of blocking the switch in the unreactive parallel conformation. The open form of the diarylethene switch can adopt a parallel conformation, in which both boronic acid units can cooperatively bind the saccharide molecule and create a relatively stable complex as evidenced by the lack of photochemical reactivity. The complex can be easily detected by CD spectroscopy and CD titration was used to determine the stability constant, which is 171 M\(^{-1}\) for the complex with D-glucose. From the complexation study at the photostationary state that contains 60\% of the closed form of 1.51, it was concluded that the decrease of the CD signal to 40\% indicated reduced binding affinity of the closed form.

Scheme 1.26 Diarylethene as a switchable receptor for saccharides.

Identification of the binding event by microcalorimetry was used in the study of the host-guest interaction between the switchable cyclodextrin dimer 1.52 (Scheme 1.27) as a host and tetrakis-sulfonatophenyl porphyrin as a guest. This system enables the release of the encapsulated guest molecule as a result of irradiation. The open form of the diarylethene bearing two cyclodextrin moieties is more flexible and thus can better adopt to binding of the porphyrine guest, with the stability constant being 3.3x10\(^6\) M\(^{-1}\). Unlike the previously described switch 1.51, binding the guest molecule by diarylethene 1.52 does not prohibit the photochromic reaction of the diarylethene core. Upon irradiation of the complex with 313 nm UV light, 70\% of the diarylethene converts to the closed form which, due to higher rigidity, shows weaker binding of the guest porphyrin with a stability constant 9.7x10\(^4\) M\(^{-1}\). Since the stability constant for the complex of the porphyrin with the closed form of the diarylethene host is approximately 35 times lower than that for the open form of the diarylethene host, the result of the photochromic reaction is the release of the guest.
molecule. Upon irradiation with visible light, the diarylethene is converted back to its open form causing an uptake of the porphyrine guest molecule.

\[ \text{Scheme 1.27} \] The photoswitchable cyclodextrine dimer and its guest molecule.

### 1.10 Switching self-assembly

One of the most fruitful concepts in the bottom-up approach in building molecular scale devices is self-assembly. The spontaneous organization of molecules into more complex systems has obvious advantage in creating structures with dimensions ranging from nanometers to micrometers without additional effort\(^ {55} \). The self-assembled systems are dynamic and thus sensitive to external stimuli such as temperature and chemical composition of their environment. Through intended introduction of stimuli sensitive moieties the properties of the system can be changed on demand, resulting in so called smart material. A particularly attractive stimulus in this respect is light\(^ {56} \).

Combining the diarylethene moiety with ureidopyrimidinone substituents, results in a photosensitive supramolecular polymer 1.53 (Scheme 1.28)\(^ {57} \). If two ureidopyrimidinone moieties, that tend to self-aggregate due to formation of four hydrogen bonds, are connected through a linker, long polymeric fibres can be created. The self-assembling process is strongly dependent on the nature of the linker. When the solution of the open form of 1.53 in chloroform was irradiated with UV light the accumulating closed form started to precipitate. This suggests higher aggregation of the monomers in the closed form compared to open form. The precipitation was further studied by dynamic light scattering. The solution of the open form (1.22 x 10\(^ {-4} \) M in chloroform:ethanol = 97:3) showed no particles larger than 10 nm (limit of the DLS instrument). After irradiation with UV light, particles started to appear with the size gradually increasing up to 650 nm. The process of the aggregate formation took about 3h at 25°C, after that time no change in the particle size was observed. Upon irradiation of this suspension with visible light the closed form switched back to the open form and the size of the particles decreased to 400 nm. This metastable state of the aggregated open form can be driven back to the thermodynamically stable solution of the open form by heating it to 60°C for 30 min. The NMR spectra of the open form does not show concentration dependent proton shifts in the range 1.10\(^ {2} \) to 1.10\(^ {3} \) M suggesting the aggregation takes place also in the open form. Based on the observation that only the antiparallel conformation of the switch is observed by NMR spectroscopy, the authors hypothesize that the parallel isomer, present in the amount below the NMR
detecting limit, acts as a stopper for the polymer chain formation, shortening the polymer fibers and thus making the assemblies of the open form better soluble.

Scheme 1.28 Photochromic supramolecular polymer, based on diarylethene and ureidopyrimidinone.

More complex behaviour can be observed when studying the self-assembly of the quite simple system 1.54 (Scheme 1.29). The amide functionalities attached to the dithienylethene core are weaker but more flexible hydrogen bonding units than the ureidopyrimidinones in 1.53. Under specific conditions these molecules tend to self-assemble to create a photoswitchable gel. An important feature is the presence of stereogenic centres directly attached to the amide nitrogen. The gel (Gel (α) open in Scheme 1.30) which forms upon heating a solution of the open form 1.54o (Solution open in Scheme 1.30) in an apolar organic solvents, shows a strong circular dichroism band which disappears upon melting the gel. The explanation for this observation is the supramolecular chirality of the aggregates caused by the stereoselective aggregation of the individual molecules. The created gel fibers are helical and the switch molecules embedded in the fibers are stacked in a chiral fashion. Irradiation of the open form 1.54o by the UV light results in the closed form 1.54c. Although in solution the diastereomeric ratio (R,R)-1.54c/(S,S)-1.54c is 1:1 irradiation in the gel phase is highly diastereoselective with a 98 : 2 ratio of diastereoisomers (R,R)-1.54c and (S,S)-1.54c. The supramolecular chirality of the gel fibers is thus transcribed to the molecular chirality of the switch molecules.

Scheme 1.29 Photochromic gelator.

The switching process alters not only the structure of the individual molecules of the switch but also of the whole self-assembly. The gel obtained by irradiation of 1.54o in
Diarylethene photochromic switches for reversible control of functions

the gel phase (Gel (α) closed in Scheme 1.30) becomes metastable and upon heating to solution of the closed form 1.54c (Solution closed in Scheme 1.30) and subsequent cooling a thermodynamically stable gel with inverted CD (Gel (β) closed in Scheme 1.30) is obtained. The change in the CD spectrum indicates different packing of the molecules in the helical fibers. The ring opening process performed through irradiation of this stable gel of the closed form with visible light results in a gel of the open form 1.54o (Gel (β) open in Scheme 1.30) which again is metastable and has to undergo heating-cooling cycle to give the original stable gel of 1.52o (Gel (α) closed in Scheme 1.30).

Scheme 1.30 Aggregation and switching process of the switch 1.52; α and β are different aggregated states; Δ - heating; * - cooling.

This photocontrolled gelating system was further used to reversibly create patterns in the micrometer range when irradiated through an appropriate mask59. In this case the important feature is the difference in the melting temperatures of the gels of the open and closed form. The gel of the closed form has a higher melting temperature than the gel of the open form, which allows creating gel patterns by irradiation with UV light in the temperature window between these two temperatures.

![Scheme 1.30](image)

Figure 1.7 Amplification of supramolecular chirality and its transcription into molecular chirality (adopted from ref.60).

Another interesting application of this interplay between molecular and supramolecular chirality is chiral amplification (Figure 1.7)60. In the open form, the diarylethenes exist in two conformations with different helicities (Scheme 1.29), which interconvert rapidly. Upon ring-closure, each conformation results in different stereoisomer i.e. (R,R)-1.54c is produced from (P)-1.54o and (S,S)-1.54c is produced from (M)-1.54o. When the switches in the open form already contain stereogenic centers, they can form a chiral aggregate, which prefers only one conformation, as described in previous paragraphs. Ring-closing reaction of the switches in the chiral aggregate, thus produce one stereoisomer in excess
(Figure 1.7a). If the switches in the open form do not contain stereogenic centers, no selection in the aggregated state occurs, resulting, upon the photochemical ring-closure, in the racemic mixture of the stereoisomers (Figure 1.7c). Mixing appropriate non-chiral dithienylethenes with chiral amide substituted diarylethenes \(1.54\), results in a formation of an aggregate that exhibits the supramolecular chirality, despite the fact that only fraction of the molecules in the aggregate contain stereogenic centers (Figure 1.7b). This chirality is upon ring closure transcribed not only to stereoselective formation of \(1.54c\) but also to the non-chiral diarylethene for which the cyclization becomes stereoselective.

### 1.11 Switching polymerizability

Most of the organic electronic devices are based on the conductive polymers. Easy processibility, together with the possibility of tuning properties through selection of the substitution pattern, makes these polymers superior to metal-based conductors in applications such as solar cells\(^6^1\), actuators\(^6^2\) or field effect transistors\(^6^3\). Introduction of a photochromic moiety into conductive polymers would extend the field of their applicability.

**Scheme 1.31** Photochromism and electropolymerization of a terthiophene containing diarylethene photochromic switch.

Diarylethene \(1.55\), designed to be polymerizable, contains terthiophene units connected to the central ethylene bond\(^6^4\) (Scheme 1.31). This switch shows typical photochromic behaviour, when the irradiation of the open form \(1.55o\) with UV light results in the ring-closed isomer \(1.55c\), which upon irradiation with visible light reverts back to the open form \(1.55o\). Electrooxidation of the open form \(1.55o\) at a potential of 1.3 V results in formation of a polymer film. The polymerization process is based on dimerization of the oxidized form of terthiophenes, which forms perfluorocyclopentene bridged sexithiophene polymer (Scheme 1.31). The closed form of the switch \(1.55c\) under the same conditions
Diarylethene photochromic switches for reversible control of functions

does not polymerize as a consequence of different distribution of charge in the molecule. The polymerization, dependent on the state of the switch, allows the deposition of the conducting polymer film to be controlled by light, which can be beneficial for applications requiring precise spatial control of the deposition.

1.12 Aim and outline of this thesis

The aim of this thesis is to explore the potential of molecular switches in reversible modulation of various functions and properties at the molecular level. The first part of the thesis describes several new diarylethene molecular switches; while the second part deals with modifications of the switching function of a membrane bound protein channel.

In Chapter 2, the synthesis and properties of new dithienylethene switches with a central phenanthrene moiety are described. Due to the sterically demanding phenanthrene, individual atropisomers of these switches could be isolated allowing the photochromic and thermochromic properties of each isomer to be studied separately.

Chapter 3 focuses on coupling switching behaviour with a chemical reaction. For this purpose, a dithienylfuran was designed which is photochemically inert but becomes photochromic after cycloaddition reaction of the furan moiety with a dienophile. Since the cycloaddition reaction is reversible, it provides additional control of the photochromism of the switch.

Chapter 4 deals with diarylethenes containing pyridine moieties instead of typical thiophenes. The pyridines can act as ligands interacting with protons and metal ions resulting in alteration of the photochemical properties of the switch. On the other hand, the state of the switch (i.e. open vs. closed state) influences the ability of the pyridine to bind protons and metal ions.

Chapter 5 describes a step towards functionalized surfaces. The diarylethene photochromic moiety was anchored to a gold surface using a tripod, which should ensure rigid positioning of the switch with respect to the surface. The switching behaviour was studied in solution as well as after binding the switch to gold nanoparticles and a semitransparent layer of gold on mica.

Chapters 6, 7 and 8 deals with the Mechanosensitive channel of Large conductance (MscL), a membrane protein channel that responds to increased tension in a membrane by opening to create a pore 3 nm in diameter. The channel has two basic states, the open and the closed state, and thus can be seen as a biomolecular switch. Chapter 6 briefly summarizes the structure, properties and function of this channel and serves as an introduction. The next two chapters describe the modifications of this protein channel that allow triggering of its opening and closing by stimuli other than membrane tension, changing it into a controllable nanovalve. In chapter 7 the channel protein is modified to become responsive to a change of pH of its environment and to open when the pH drops below a certain level. In chapter 8, a photosensitive channel protein is constructed through modification with the photoprotected actuator, which is further developed into a reversible light-controlled system allowing the opening and closing of the channel using a spiropyran photochromic switch.
### References


Diarylethene photochromic switches for reversible control of functions

Chapter 1

Diarylethene photochromic switches for reversible control of functions


Chapter 1


62 Smela, E. *MRS Bull.* **2008**, *33*, 197–204.
