Chapter 1

Photochromic molecules

In this chapter, the concept of photochromism is introduced. After a general introduction into photochemistry and photochromism, various popular classes of photochromic molecules are discussed. Their properties are summarized using information from computational and ultrafast spectroscopic studies reported in the literature. Finally, this chapter considers the immobilization of photochromic molecules by means of self-assembly and how this affects their photochromic behavior.
1.1 Photochemistry and photochromism

Photochemically driven processes are important as well as ubiquitous. Plants use it to convert light to energy through a process known as photosynthesis. Animals use it to detect light with their eyes and synthesize vitamin D. Ozone in the earth’s stratosphere, which absorbs a large part of the Sun’s UV light, is formed photochemically. It is safe to say that life as we know it would not be possible without photochemistry.

A typical photochemical process starts with the absorption of a photon (Figure 1.1). The energy absorbed in this way can cause the excitation of an electron from an occupied orbital, often the one highest in energy (the HOMO), to an unoccupied orbital, often the one that is the lowest in energy (the LUMO). From here on, multiple processes are possible, the majority of which are photophysical in nature rather than photochemical. For example, the system may relax from its excited state back to its ground state through the emission of a photon. This can take place in a direct fashion (fluorescence) or via a state with a different multiplicity (phosphorescence). Alternately, the excess energy may be released to the medium as heat in a process known as internal conversion.

![Figure 1.1 Simplified view of the photoexcitation of an electron from the HOMO to the LUMO.](image)

A photoexcited system can undergo a photochemical process (i.e. a photoinduced change in structure) if the above mechanisms for relaxation are not easily accessible and/or less favorable. Two types of photochemical reactions can be distinguished. The first are adiabatic reactions, in which the reaction is confined to a single potential energy surface (Figure 1.2, left). When such a reaction is complete, relaxation to the ground state surface can take place by one of the mechanisms described above. The second and more common are diabatic reactions, in which the reaction involves two potential energy surfaces (Figure 1.2, right). These reactions are often more complex in nature – intersections between the two potential energy surfaces may exist and can play an important role in the determining whether the photochemistry is productive or not.
A special type of photochemical reactivity that has interested chemists for decades is photochromism.\textsuperscript{1} Photochromism is defined as the reversible photochemically driven transformation of a system between two isomers with different UV/vis absorption spectra (Scheme 1.1). Molecules exhibiting this behavior attract much interest as they can be used as molecular switches\textsuperscript{2} in larger systems, for example in organic electronic devices\textsuperscript{3} or optical data storage.\textsuperscript{4}

\textit{Figure 1.2} Potential energy surfaces diagram of an adiabatic photoreaction (left) and a diabatic photoreaction (right). ‘R’ is reactant, ‘P’ is product.

\textit{Scheme 1.1} Reversible photochemically driven interconversion between two isomers.

In the next section, popular classes of organic photochromic molecules will be discussed.

\textbf{1.2 Popular classes of organic photochromic molecules}

\textbf{1.2.1 Spiropyrans}

Spiropyrans consist of two fused heterocyclic rings, one of which is a pyran derivative (Scheme 1.2).\textsuperscript{5,6} Irradiation with light, typically in the UV region, induces the conversion of a spiropyran into a zwitterionic merocyanine isomer, which absorbs strongly in the visible region. Irradiation with visible light induces the conversion from merocyanine isomer back to the spiropyran isomer. Depletion of the merocyanine isomer also proceeds thermally, though examples of thermally stable merocyanine isomers have been reported.\textsuperscript{7} In addition, examples of spiropyrans that are sensitive to other stimuli, such as redox potential\textsuperscript{8} and pH,\textsuperscript{9} have been described.
Based on computational chemical studies on simplified spiropyran models, it has been proposed that the photoinduced merocyanine formation takes place along a \((\pi \rightarrow \pi^*)\) excited state that is able to relax to the ground state through a conical intersection.\(^{10,11}\) However, a more recent study on a complete spiropyran model suggests that conical intersections do not play a role in this reaction.\(^{12,13}\) Instead, the initially obtained \((\pi \rightarrow \pi^*)\) excited state is able to undergo internal conversion into a \((\pi \rightarrow \sigma^*)\) excited state, after which relaxation takes place from a valley with a narrow \(S_1-S_0\) energy gap (Figure 1.3). Also, the process was determined to be virtually barrierless, which is in agreement with experimental observations.\(^{14}\)

**Figure 1.3** Formation of the merocyanine isomer is the result of a \(S_0 \rightarrow S_1\) excitation. Though multiple conical intersections between the \(S_0\) and \(S_1\) energy profiles exist (left), it has been found that the process is more likely to travel via a hydrogen-out-of-plane (HOOP) geometry that lies close to one-bond-flipping (OBF; simultaneous C–O elongation and \(\alpha\) dihedral torsion) path (right). Reprinted with permission from Liu, F.; Kurashige, Y.; Yanai, T.; Morokuma, K. J. Chem. Theory Comput. 2013, 9, 4462–4469. Copyright 2013, American Chemical Society.
1.2.2 Azobenzenes

Azobenzenes consist of two phenyls attached to a central azo moiety (Scheme 1.3). The trans isomer is typically the lowest in energy and can be converted to the cis isomer upon irradiation with UV light which, based on computational studies as well as transient Raman experiments, is believed to result in excitation to the S₁(n→π*) or S₂(π→π*) state (the latter of which relaxes rapidly to the S₁ state). Rotation of the two phenyl groups with respect to the central N=N moiety then allows the system to proceed through a conical intersection and subsequently results in the formation of the cis isomer.


The reverse reaction can be induced by photoirradiation in the visible region as well as thermally. However, depending on the substitution pattern on the two phenyls, the thermal relaxation can take place through two mechanisms: an out-of-plane rotation around the central N=N bond or an in-plane inversion on one of the nitrogen atoms (Scheme 1.4). Which of these is the predominant mechanism hereby depends on the substitution pattern on the phenyl rings. A third mechanism which involves S₀→T₁→S₀ intersystem crossing has also been suggested. This mechanism has a very low thermal barrier but whether it is the predominant mechanism depends on the strength of the S₀–T₁ spin orbit coupling of the system.
1.2.3 Diarylethenes

Diarylethenes are a class of photochromic compounds that consist of two aromatic groups connected to a central olefin, similar to azobenzenes. However, through the use of a cyclic olefin photochemical excitation cannot result in cis-trans isomerization. Instead, the compound will undergo a conrotatory six-electron electrocyclization which results in the formation of a ring-closed isomer (Scheme 1.5). Contrary to that which is typically the case for spiropyans and azobenzenes, the photochemical product is thermally stable and thus requires irradiation with visible light in order to switch it back to the open-ring isomer. For several systems reported, chromism can also be induced electrochemically. The most popular molecular design for diarylethenes is comprised of two thiophene moieties, typically substituted as in Scheme 1.5. These systems are referred to as dithienylethenes.

The photochemical switching of dithienylethenes has been the topic of various studies, both theoretical and experimental. Both the ring closing and ring opening reactions are believed to proceed through a conical intersection that connects the $S_1$ and $S_0$ potential energy surfaces (Figure 1.4). The ring opening reaction has been found to display strong temperature dependence at low temperatures, indicating that a barrier is present. This barrier has also been predicted theoretically. It has been reported that changes in the substitution pattern of the thiophene moieties reduce the height of the barrier (see also chapters 3 and 4).
1.2.5 Hemithioindigos

Hemithioindigo photochromic switches consist of a hemithioindigo moiety and a hemistilbene moiety joined at the central olefin.\textsuperscript{31} The Z-isomer is typically the lowest in energy but can be converted to the E-isomer by irradiation with UV (Scheme 1.6), which takes place with a concomitant bathochromic shift in the UV/vis absorption spectrum. The reverse E→Z isomerization can be induced by irradiation at a longer wavelength but can for some systems also takes place thermally.

\textbf{Scheme 1.6} Photochemical reactivity of a hemithioindigo.
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The body of literature describing the photoreactivity of hemithioindigos is much smaller than that describing aforementioned photochromes. As such, detailed knowledge of the photochemical processes involved is somewhat limited. Using time-resolved spectroscopy and computational chemistry, de Vivie-Riedle and co-workers found that both photoisomerization processes are devoid of thermal barriers. They were able to locate various conical intersection connecting the $S_0$ and $S_1$ potential energy surfaces, two of which are believed to lead to $E \rightarrow Z$ and $Z \rightarrow E$ isomerization whereas others function as pathways for rapid nonradiative decay. In addition, they found that the photochemical behavior stems from the weakly heterosymmetric biradicaloid character of the olefin and that this character (and thus the photochemical behavior) is highly dependent on the choice of substituents (e.g. electron donating or electron withdrawing). This is in agreement with findings regarding the switching behavior of push-pull azobenzene systems and has implications for the design of overcrowded alkene photoswitches and motors (vide infra).

1.2.6 Overcrowded alkenes

Lastly, a class of photochromic compounds that displays rotation around a sterically crowded central olefinic bond should be mentioned. The photochromism displayed by these systems is reminiscent of that of stilbene, the hydrocarbon analogue of azobenzene (Scheme 1.7). However, while for stilbene the photochemical cis–trans isomerization has to compete with photochemically induced electrocyclization, overcrowded alkenes are able of repetitive cis–trans isomerization as their sterics and/or substitution patterns effectively suppress the competing electrocyclization process.

Scheme 1.7 Photochemical reactivity of stilbene.

Bistryclic aromatic enes (BAEs), one subclass of overcrowded alkenes, consist of two aromatic tricyclic moieties connected through a central olefin (Scheme 1.8a). Steric interactions force the these systems to be nonplanar and allow them to adopt various conformations, whereby interconversion between these conformations can be achieved photochemically, thermally, and/or electrochemically (Scheme 1.8b–e).
When considering the photochemical reactivity of BAEs, considerable information can be obtained from the archetypical stilbene compound which has been studied extensively through computational and spectroscopic methods. Early CASPT2 studies suggest that the trans→cis photoisomerization of stilbene starts with a $S_0 \rightarrow S_2$ excitation,\textsuperscript{36} however, more recent computational LR-TDDFT studies,\textsuperscript{37} spin-flip TDDFT,\textsuperscript{38} and XMCQDPT2 studies\textsuperscript{39} suggest an $S_0 \rightarrow S_1$ excitation is the first step. After photoexcitation, the system has to overcome a low thermal barrier (experimentally determined to be $\approx -14$ kJ/mol)\textsuperscript{40,41} before it relaxes to the ground state through a minimum energy crossing point (MECP).\textsuperscript{39} Irradiation of the cis isomer conversely seems to result in an $S_0 \rightarrow S_1$ or $S_0 \rightarrow S_2$ excitation (which were found to be close in energy\textsuperscript{39}) after which an almost barrierless relaxation\textsuperscript{41} to the ground state via a minimum energy crossing point\textsuperscript{39} yields the trans isomer.

A second subclass of overcrowded alkenes that can be distinguished consists of systems that have a larger aromatic system, such as tetrahydrophenanthrene and dihydrotetraphene moieties.\textsuperscript{42} Compared to BAEs, the resulting increase in steric crowding reduces the number of observable conformations to four diastereomers. In addition, the increased steric crowding inhibits
conformational inversion as depicted in Scheme 1.8c, causing the system to be able to isomerize only between two pseudoenantiomeric states (Scheme 1.9). Such systems are typically referred to as chiroptical switches.42,43

**Scheme 1.9** Photochemical reactivity of a chiroptical molecular switch. By choice of substituent for \( R^1 \) and \( R^2 \), the two pseudoenantiomers will have nonidentical UV/vis absorption spectra, making it possible to selectively address one isomer.

When a chiroptical switch is modified by the introduction of a stereogenic center next to the central olefin, the resulting system will behave very differently: instead of displaying reversible two-way switching, it will be capable of making a complete rotation around the central olefin (Scheme 1.10).43 The origin of this behavior is that the stereogenic center causes the product of the photochemical \( E \rightarrow Z \) isomerization, often referred to as the ‘unstable form’, to lie significantly higher in energy. For the majority of systems, thermally induced \( E \rightarrow Z \) isomerization in the reverse direction is not possible (see also chapter 7) and, as such, these can only relax by undergoing an irreversible, thermally driven helix inversion.43 Repeating the \( E \rightarrow Z \) isomerization and subsequent helix inversion causes the system to return to its original state at which point one full rotation has been made. Systems which display this behavior are known as ‘(rotary) molecular motors’. Those consisting of two tetrahydrophenanthrene moieties are referred to as ‘first-generation’ whereas those with a single xanthene/fluorene moiety (such as the one depicted in Scheme 1.10) are referred to as ‘second-generation’.43
Computational studies into the photochemically driven $E \rightarrow Z$ isomerization of the second-generation motor depicted in Figure 1.5 have shown that photoirradiation causes the excitation of an electron to the anti-bonding $\pi$ orbital of the central olefin.\textsuperscript{44} After excitation, relaxation from the $S_1$ PES to the $S_0$ PES can then proceed through one of two minimum energy conical intersections (MECIs) that were located not far from the ground state geometries (Figure 1.5).\textsuperscript{44,45} For either isomer, the path on the $S_1$ PES from its Frank–Condon state towards a nearby conical intersection seam was almost barrierless, indicating quick relaxation to the ground state (which is partially in agreement with spectroscopic studies\textsuperscript{46}). Furthermore, it was found that the quantum yield for the stable→unstable photoisomerization was 2.3 times that of the reverse process,\textsuperscript{45} which is in agreement with the experimentally observed stable/unstable ratio at the photostationary state.\textsuperscript{47} Conical intersections were also found to play a significant role in the photochemical behavior of a first-generation system.\textsuperscript{48}
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Figure 1.5 Contour plots of the $S_0$ (left) and $S_1$ (right) PES of the molecular motor depicted above. Herein, ‘$M_{S0}$’ and ‘$P_{S0}$’ correspond to the unstable and stable isomers, respectively. ‘$M_{S1}$’ and ‘$P_{S1}$’ correspond to minima on the $S_1$ PES that are geometrically the closest to $M_{S0}$ and $P_{S0}$, respectively. ‘$C_{1}$’ and ‘$C_{2}$’ indicate positions of minimum energy crossing points between the $S_0$ and $S_1$ surface. Reprinted with permission from Kazaryan, A.; Lan, Z.; Schäfer, L. V.; Thiel, W.; Filatov, M. J. Chem. Theory Comput. 2011, 7, 2189−2199. Copyright 2011, American Chemical Society.

1.3 Photochromism in self-assembled monolayers

There is a desire to immobilize the photochromic systems on surfaces for use in several applications, such as molecular electronics. The most popular approach is through self-assembly,\textsuperscript{49,50} in which a layer of the molecules of interest is formed by their spontaneous adsorption on the surface. However, various studies on self-assembled monolayers (SAMs) of photochromic molecules have shown that immobilization can have a significant effect on the molecule’s photochemical behavior.

One commonly proposed rationale for altered photochemical behavior upon immobilization is electronic interaction between the surface and the monolayer. Feringa, van Wees, and co-workers found for a series of three dithienylethenes that, upon immobilization, one system could only be switched from the ‘closed’ to the ‘open’ isomer whereas the other two systems retained their ability to
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switch bidirectionally (Scheme 1.11). It was hypothesized that the LUMO of the ‘problematic’ system may lie close to the LUMO of the gold substrate it was immobilized on, allowing energy transfer to the substrate to take place. This rationale was subsequently confirmed in a study employing ultrafast spectroscopy that showed that, after excitation, energy transfer to the gold would take place on the picosecond timescale. These observations show that small changes in the structure of a photochrome can have a large effect on its photochemical behavior when immobilized. The topic of quenching of photochemistry by the surface is discussed further in chapter 4.

Scheme 1.11 The three photochromic systems studied by Feringa, van Wees, and co-workers (ref. 51).

In addition, there have also been reports of monolayers that show diminished photochromic performance due to steric hindrance that is the result of tight packing. This latter phenomenon has been observed for azobenzenes, which undergo a large change in shape upon cis–trans isomerization. Consequently, a sterically crowded monolayer may slow down or even fully inhibit azobenzene photochromism. It should be noted that, in some studies, delocalized excitonic coupling has been suggested to play as role as well.

1.4 Aim and outline of this thesis

The work described in this thesis explores how photochromic systems behave, can be modified, and can be adapted for use in applications that go beyond basic photochromism in solution. Important aspects that will hereby be addressed are how certain modifications to the molecular structure affect photochromic behavior and how immobilization can be achieved without altering this behavior.
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Chapter 2 provides an introduction into computational quantum chemistry which, in addition to various spectroscopic methods, will be used throughout this thesis to gain insight in molecular properties and processes. Its aim is to introduce basic concepts in quantum chemistry, explain the most popular theories for the study of individual molecules, and discuss applications that are potentially useful for a (physical) organic chemist.

In chapter 3, the photochromic behavior of an asymmetric dithienylethene is studied. This is compared with the behavior of related systems and a rationale is provided for differences observed.

Chapter 4 focusses on the immobilization of one symmetric and two asymmetric dithienylethenes on a gold substrate. One of the main aspects hereby investigated is whether or not the photochromic properties of the asymmetric dithienylethenes are retained upon immobilization.

In chapter 5, it is attempted to improve the immobilization of photochromic systems by the use of a tripodal anchoring group. Compared with the anchoring group used in chapter 4, the tripodal group is designed to provide more control over the position and orientation of the photochromic unit with respect to the surface while at the same time separating it from the surface by a larger distance. The stability of the tripodal anchor and its effect on photochromic behavior are investigated in solution as well as after self-assembly on gold.

Chapter 6 presents a dithienylethene substituted with chiral side groups which is used as a dopant in order to induce a cholesteric liquid crystalline phase in a nematic phase. It is demonstrated that the dopant shows the highest values of helical twisting power so far for dithienylethene-based dopants.

Chapter 7 is a medley of three computational studies. First, a method is investigated for studying the thermal $E$-$Z$ isomerization displayed by overcrowded alkenes and molecular motors. Secondly, the spectroscopic properties and switching behavior of a double azobenzene switch are investigated. Finally, the spectroscopic and thermochemical behavior of hemithioindigo switches is investigated.

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