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### Organic Materials for Reversible Optical Data Storage

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## 1 Introduction

The last decades of the twentieth century can be characterized as a period in which the use of computers for information storage has impinged on all parts of society. The continuously increasing amount of data to be stored and manipulated has generated the need for high speed computers and large storage capacities. One of the most important challenges in this field is the development of materials and techniques to place as much data as possible on the least amount of material. The ultimate goal would be to achieve information storage at the molecular or even at the atomic level,<sup>1</sup> whereas processing of data should occur at close to the speed of light by the use of all optical switching devices.

Digital optical data storage is a promising method, where recording of information is carried out by the use of light.<sup>2</sup> The best known example of optical recording used in a practical device is the compact disk, designed for the distribution of pre-recorded information. In recent years developments in optical recording technology have led to the commercial availability of write-once optical disks. In these systems it is possible for the user to place his own selected data on a disk, which can be read almost indefinitely. A typical field of application for these memory devices is the archiving of data. The driving forces behind these developments have been the considerable advantages of optical recording compared with other storage techniques like magnetic recording; together with the production of relatively cheap and mass-produced lasers. Important advantages are, for example: (i) the read-out of data is performed by a laser focused on the storage layer, providing a non-contact technique insensitive to dust particles and fine scratches and, (ii) the possibility of achieving high storage capacities.

Although read-only and write-once optical disks are available, there is a need for truly reversible optical recording media with the opportunity to read, write, erase and rewrite again. An even better technique is the so called direct-overwrite procedure, without the time consuming erasing step. The development of these technologies has become of prime importance in industry in recent years, probably due to the enormous commercial success of the compact disk. The most widely investigated materials at

present, for these purposes, are based on alloys of rare earth elements and transition metals as the recording substrate thereby combining the magnetic and optical recording techniques.<sup>3</sup> Although some problems still remain to be solved, it is expected that these magneto-optical recording media will replace the currently dominant mass-memories based on magnet technology in the nearby future.<sup>4</sup>

Future developments will aim at further increasing the rates of data storage and storage densities, for example by applying frequency doubled lasers, all optical writing/reading systems, and other materials. The role of organic materials in this field has become increasingly important with main emphasis on dyes and polymers as photoactive components.<sup>2</sup> The potential of organic molecular devices in the field of nanotechnology can hardly be exaggerated. This development is further stimulated by the notion that a large increase in information storage, theoretically to the molecular level, might be obtained.

## ***2 Organic Materials***

During recent years the design and synthesis of organic compounds for applications as materials has been a field of enormous growth.<sup>5</sup> Organic molecules are now widely accepted as useful synthetic building blocks in non-linear optics,<sup>6</sup> liquid crystals in modern displays,<sup>7</sup> organic (super) conductors<sup>8</sup> and ferromagnets,<sup>8b,9</sup> optical sensors<sup>10</sup> and supramolecular structures, which are ordered molecular assemblies based on molecular recognition and self-organization,<sup>11</sup> although inorganic solids still provide most of the materials for optical, electrical, magnetic and mechanical applications.<sup>12</sup> Limitations in the scope, synthetic variations and predictability of the desired properties of inorganic solids, for example, has led to a large increase in research activities towards the development of future organic materials.<sup>13</sup>

Some typical features of organic materials are: the ease of fabrication, the possibility to shape organic compounds into the desired structures by molecular engineering, the introduction and fine tuning of a large variety of physical properties by small changes in the molecular structure and the construction and characterization of simple isolated systems, which can provide solutions for fundamental problems. Disadvantages associated with stability and reliability of organic materials might be solved by structural changes. Various techniques to overcome the inferior material properties of organic crystals have been developed.<sup>11,15-17</sup>

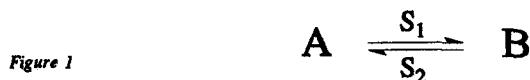
Besides crystal engineering,<sup>14</sup> the necessary ordering of organic molecules into larger macroscopic structures can be obtained by Langmuir-Blodgett techniques,<sup>15</sup> the aggregation of surfactant molecules into micelles and vesicles,<sup>16</sup> doping in polymer

matrices, or by self-assembly through molecular recognition processes.<sup>11,17</sup> The flexibility in the synthetic pathways allows the introduction of functional groups for attachment or incorporation into polymers thereby often drastically improving the material properties. The typical properties of polymers like ease of processibility, mechanical strength, long-term stability etc. combined with the above mentioned advantages of organic molecules will be the basis for a whole new range of molecular devices.<sup>18</sup>

### 3 Molecular Switches

The demand for high storage densities, high switching rates, all optical switching devices and miniaturization in future technology and the rapidly growing knowledge about the construction of structurally ordered organic materials have largely stimulated the search for organic molecules suited for applications in switching devices. The synthesis of molecular switches and molecular storage elements can give answers to fundamental questions on the level of molecular and nanoscale dimensions, and leads to further developments of model concepts with respect to possible modes of operation of molecular memories.

The basic requirement for a switch is bistability, i.e. the occurrence of two different forms of a molecule, which can be interconverted by means of an external source. Any material or device that has two stable states which can be reversibly switched from one state to another and which states at any instant can be identified, can in principle be used as a memory element in a digital computer using binary logic. This is illustrated schematically in Figure 1. A and B represent the two different forms of a bistable system, whereby  $S_1$  and  $S_2$  refer to different stimuli to effect the reversible switching behaviour.



The bistability might be based on various properties of molecules like electron transfer, isomerizations, differences in complexation behaviour and photocyclizations, whereas light, heat, pressure, magnetic or electric fields, chemical reactions etc. can be used to achieve the change in the bistable state.<sup>19</sup>

Photoreversible compounds, where the reversible switching process is based on photochemically induced interconversions, play an important role in this extended field. Photochromism, which is defined as the reversible change, induced by light irradiation, between two states of a molecule having different absorption spectra, can be the basis for a molecular switch.<sup>20</sup>

Although the inevitable condition of bistability is fulfilled by photochromic behaviour, the molecules must cope with many other necessary demands to be suitable for a practical device. Apart from economical, environmental and technical restrictions,<sup>21,22</sup> the most important requirements for the use of photochromic compounds as molecular switches are:

- photochemical switching between the two forms should be possible.
- no thermal interconversion of the isomers should occur in a large temperature range (e.g. -20 – 80 °C), allowing storage of information almost infinitely.
- the isomers should be fatigue resistant, with the possibility to perform the write/erase cycle many times, and no thermal or photochemical degradation to any side products should occur.
- both forms should be readily detectable.
- a non-destructive read-out procedure should be available; this read-out method should not interfere with or erase the written data.
- high quantum yields should be achieved, allowing an efficient switching process and avoiding the necessity of long irradiation times.
- fast response times should be reached, leading to fast switching cycles.
- retention of all the properties is necessary when the switchable compound becomes part of a macromolecular structure.

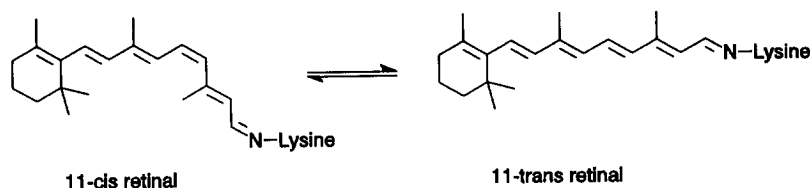
In general, the development of a molecular switching or optical data storage device will first of all involve the design and synthesis of molecules which possess the aforementioned properties, followed by incorporating these compounds into supra-molecular assemblies, in order to obtain ordered molecular systems.<sup>23</sup>

From the many photochromic compounds proposed as being applicable for an optical data storage system or a molecular device,<sup>24</sup> only a few come close to meeting all these requirements. Typical examples of reversible photochromic processes are *cis-trans* isomerizations or photocyclization reactions. Although the initially developed molecules, in which the bistability is based on these processes, were far from being appropriate for a practical device due to severe shortcomings, recent improvements have brought much closer the practical realization of a molecular switching device based on organic molecules, as will be illustrated in the following paragraphs. The basic principles of several types of photochromic compounds, including the feasibility of these molecules to act as molecular switches, will be discussed. These examples will also demonstrate how molecular engineering can improve the properties drastically and will emphasize the strength of Langmuir-Blodgett techniques and/or polymeric matrices to obtain stable materials.

## 4 Cis-Trans Isomerizations

### 4.1 Introduction

Cis-trans isomerization of olefinic compounds, involving a  $180^\circ$  rotation around a carbon-carbon double bond, forms the basic process of vision. The absorption of photons results in the conversion of 11-cis retinal ( $\lambda_{\max} = 498$  nm), bound as a Schiff base via the amino acid lysine to the protein opsin together forming rhodopsin, to 11-trans retinal ( $\lambda_{\max} = 380$  nm, Scheme 1).<sup>25,26</sup>



Scheme 1

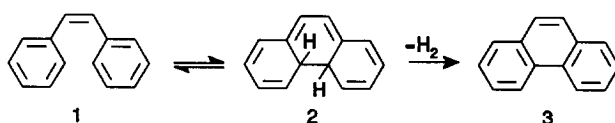
The structural disturbance induced by the cis-trans isomerization of the retinal moiety of rhodopsin leads to a conformational change of the whole protein molecule and, via a cascade of reactions, this eventually creates a nerve pulse responsible for the visual process. In this process, a light pulse is converted to a physical change in another part of the system, a principle which has been "copied from nature" in a number of photochromic systems to be discussed in the following sections. The photochemical and thermal stability, the high quantum yield ( $\Phi = 0.67$ ) and the high reversibility ( $> 10^6$  cycles) of this naturally optimized switch, has encouraged the research for possible applications of retinal derivatives in reversible optical data storage.

Bacteriorhodopsin, a pigment closely related to rhodopsin, with retinal as the photoresponsive element in the all-trans form, is being developed into a switching device.<sup>27</sup> This protein is available in large amounts, stable under rather extreme conditions (pH, salt concentrations, etc.) and still exhibits excellent photochemical activity when dissolved in polymer films. The protonated all-trans Schiff base of retinal (the B-form,  $\lambda_{\max} = 570$  nm) can be converted to the deprotonated cis isomer (the M-form,  $\lambda_{\max} = 412$  nm) by irradiation at 568 nm ( $\Phi = 0.64$ ) with a switching time in the  $\mu$ -second range. The B and M states in principle represent the codings (0 and 1) for digital information. Read-out of the written data was proposed to be executed by a laser diode at 750 nm. The practical use of this system, however, is limited by the short life-time (10 ms) of the M-state of the naturally occurring bacteriorhodopsin. Recently the life-time was increased to 200 s by the use of mutated bacteriorhodopsin, and by using holographic

techniques it was possible to store patterns of digital information.<sup>27</sup> Further developments of bacteriorhodopsin as key element in optical devices strongly depend on the availability of variants with two thermally stable states.

#### 4.2 Stilbenes<sup>28</sup>

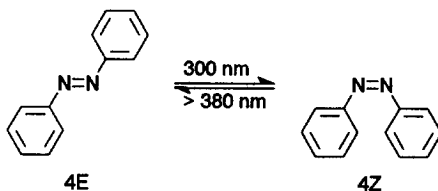
The cis-trans isomerization of stilbenes has been extensively investigated and documented.<sup>29</sup> The application of stilbene derivatives for reversible optical switching processes has however been limited due to unwanted side reactions. Cis stilbene **1** can undergo a photochemical ring closure to a dihydrophenanthrene **2**, which can easily be oxidized by oxygen to phenanthrene **3** (Scheme 2).<sup>30</sup> Photochemical dimerization to a substituted cyclobutane can also readily occur. Recently some more promising results were obtained by the use of thioindigo stilbene analogues.<sup>31</sup>



Scheme 2

#### 4.3 Azobenzenes

Azobenzenes exist in two isomeric forms, the E (trans) and Z (cis) form (Scheme 3), which can be recognized by their difference in UV-absorption spectra.<sup>32</sup> In 1937, Hartley was the first to establish the influence of light on the configuration of the N=N double bond.<sup>33</sup> The photoisomerization of azobenzenes leads to a photostationary state, where the cis/trans ratio is dependent on the wavelength used. For the non-substituted azobenzene irradiation at 313 nm gives approximately 80% of the Z isomer, whereas at 365 nm only 40% Z isomer is formed.<sup>34</sup> In principle, azobenzenes could function as molecular switches by applying light of different wavelengths to obtain varying amounts of cis and trans isomers, where the excess of one of the two isomers can be detected by the change in UV absorption spectra.



Scheme 3

Two major problems prohibiting the use of azobenzenes as molecular switches are: (i) thermal reisomerization of the Z isomer to the more stable E isomer, with lifetimes of the Z state varying from minutes to several days at room temperature,<sup>20</sup> and (ii) the detection method to assess the isomer ratio is based on UV measurements at the absorption bands of the isomers, which can influence the photostationary state by causing isomerization processes, i.e. a destructive read-out procedure. Because the introduction of other substitution patterns has not lead to a significant increase in the thermal stability,<sup>20,35</sup> research has been focused on applying polymeric liquid crystals combined with Langmuir-Blodgett techniques to reduce the reisomerization activity (Section 4.3.1). Approaches towards non-destructive read-out methods are based on the idea that a configurational change in one part of the molecule induced by the cis/trans isomerization of the azo-bond can lead to changes in structure (reversible host-guest chemistry, Section 4.3.2), transmittance (reversible gel formation, Section 4.3.3), conductivity (Section 4.3.4) or helicity (optical rotation, Section 4.3.5) in other parts of the molecules or matrices, which can be detected without interference with the cis/trans ratio. A very promising method, involving a selective reduction of the cis isomer, is outlined in Section 4.3.6.

#### 4.3.1 Polymeric liquid crystals

Polymers are excellent supporting materials for the practical use of photochromic compounds by introducing stability and easy processibility. Another important advantage of polymeric materials is the feature that below the glass transition temperature ( $T_g$ ), the segmental motion of the polymer chain is frozen in and this phenomenon can in principle increase the life-time of the stored information. The structural variations induced by the cis/trans isomerization of the azobenzene units can be stabilized in this glassy state. Liquid crystalline polymers offer the additional advantage that the macroscopic orientation can be influenced by external forces, such as an applied electric or magnetic field and therefore control of the strongly anisotropic properties can be achieved, leading to differences in, for example, absorption or refractive index. Different mesophases can be used for the construction of an optical data storage system<sup>36</sup> as has been shown by Tazuke<sup>37</sup> and Wendorff<sup>38</sup> (*vide infra*). Tazuke and co-workers explored polymeric acrylates with mesogenic p-methoxy-phenyl benzoates **5** doped with 4-butyl-4'-methoxyazobenzene (**6**) as the photoswitchable molecule orientated by an applied magnetic field (Figure 2). The observed mesophase was dependent on the configuration of the photochromic azo-dye. The trans  $\rightarrow$  cis isomerization of the doped azobenzene (5 mol%), upon photoirradiation at 366 nm, brings about the phase transition of the host polymeric liquid crystal from the nematic to the isotropic phase. The initial state could be recovered by irradiation with visible light (525 nm).



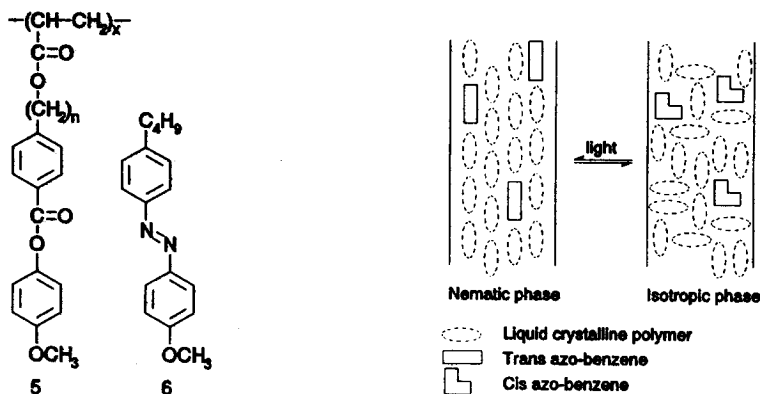
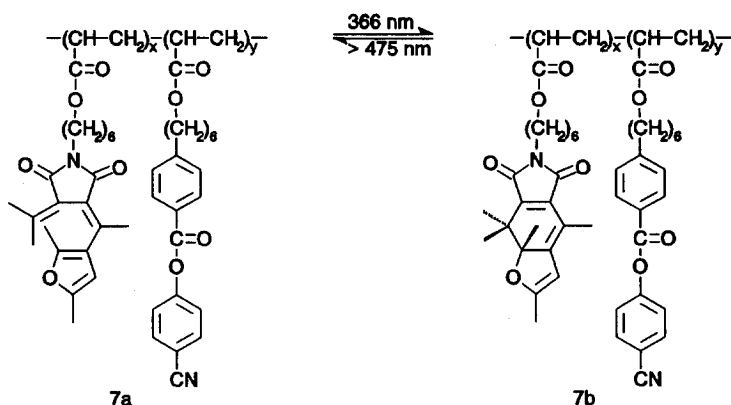


Figure 2

This phase behaviour is schematically drawn in Figure 2. The conversion to the "bent" cis isomer leads to a disturbance of the alignment of the polymer, which can no longer form the nematic phase and therefore a transition to the random isotropic phase is observed. The read-out procedure is based on the complete loss of birefringence of the system upon formation of the isotropic phase, which can be monitored by the use of linearly polarized light from a He-Ne laser at 633 nm transmitted through a pair of crossed polarizers. By this method the nematic phase is seen as a light spot and the isotropic phase as a dark spot. These molecules show no absorbance at the wavelength of the monitor light (633 nm) and consequently the read-out is completely non-destructive. The rapid thermal cis-trans conversion (i.e. at 58 °C the trans form was recovered in 50% after 15 min) could be suppressed by cooling the polymer below  $T_g$ . For example, after local irradiation at 366 nm of a polymer film (5,  $n = 3$ ,  $M_w = 4000$ ), the film was rapidly cooled to -20 °C, kept below the  $T_g$  (20 °C) and the isotropic phase remained unchanged even after 5 weeks. The same processes were revealed in polymers with covalently attached azobenzene units.<sup>37a,b</sup> Wendorff and co-workers used the bistability of azobenzenes in combination with the variation of the refractive index in liquid crystals, which is strongly dependent on the orientation of the mesogenic groups. By using holographic techniques the storage and projection of images was demonstrated.<sup>38,39</sup>

These examples illustrate the conversion of photosignals in a physical change of the whole system, a similar principle as used for the visual process described in Section 4.1. A major drawback of these systems is the low mobility of the polymer in the glassy state preventing a fast reorientation of the mesogens in response to a cis-trans isomerization. Reorientation can only occur in the liquid crystalline phase leading to a fast thermal disappearance of the written information.<sup>40</sup>

In further studies attempts have been made to solve this problem by the use of liquid crystalline polymers with spiropyrans or fulgides as side groups (*vide infra*). Spiropyrans still proved to be thermally unstable and showed in addition thermochromism<sup>41</sup> of the spiropyran group, which can interfere with the induced photochromism. A very promising result was reported by Ringsdorf and co-workers, who described liquid crystalline polymers **7a** with thermally irreversible photochromic properties by using fulgide side groups, which did not show any thermochromic behaviour.<sup>42</sup> When an UV-irradiated film ( $\lambda = 366$  nm, to effect the ring closure of the fulgide in **7a** to the 7,7a-dihydrobenzofuran in **7b**) was kept in the dark, no change in absorption was observed even after 300 h at 22 °C (Scheme 4).



Scheme 4

The reverse decolouration was effected by irradiation with visible light ( $\lambda > 475$  nm). The necessary change in the mesophase can now directly occur in the liquid crystalline phase of the polymer, without the unfavourable cooling below the  $T_g$ . Preliminary results revealed the possibility of optical storage of images in a film of this photochromic polymer.

### 4.3.2 Reversible host-guest chemistry

Host-guest chemistry has mainly been concerned with the synthesis of host compounds which showed a pronounced selectivity for certain types of guests.<sup>17,43,44</sup> The opportunity to control this complexation behaviour reversibly by changing the conformation of the host molecule would open up the possibility to use for instance crown ethers as chemical switches (schematically shown in Figure 3).

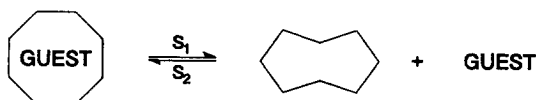
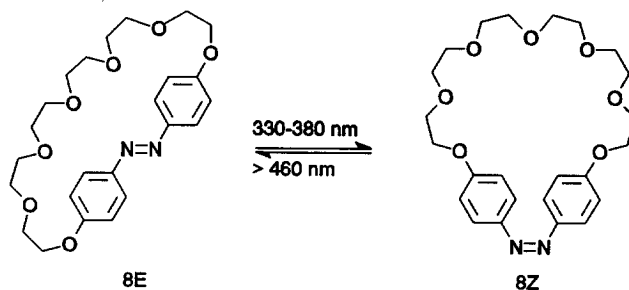


Figure 3

In 1979, Shinkai described the possibility to control the conformation of crown ethers by the isomerization of N=N double bonds,<sup>45</sup> leading to a photoswitchable host-guest system modifying the complexation behaviour of the azacrown ether **8** (Scheme 5).<sup>46</sup>



Scheme 5

By irradiation of the pure E isomer at 330-380 nm a photostationary state was formed with 70-80 % excess of the Z-isomer as determined by UV spectroscopy. The E-isomer could be recovered quantitatively by irradiation ( $\lambda > 460$  nm) or by thermal reisomerization. The E-isomer showed no extraction capability for alkali metal cations, which can be explained by the stretched arrangement of the polyethylene glycol units. After isomerization to the Z-form, which afforded a larger cavity (the distance between the para positions decreased from 0.90 to 0.55 nm<sup>47</sup>) the crown ether perfectly binds Na<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup>. As a consequence of the rather stable complexes formed the thermal reisomerization was totally suppressed by the addition of the cations. These compounds were called "all or nothing switches", since the E-isomer **8E** has no complexation ability, whereas the Z-isomer **8Z** showed excellent complexation.<sup>48</sup> The bistability in this system is based on whether complexation occurs or not.

Although the principles of a photoswitchable host-guest system were demonstrated, the detection method is based on differences in UV absorption, which can interfere with the written information, by effecting the *cis*/*trans* ratio. Related studies described the effect of azo units incorporated in azacryptands,<sup>45</sup> azaphanes<sup>49</sup> and azacyclodextrins.<sup>50</sup>

#### 4.3.3 Reversible gel formation

Steroids functionalized with an anthracenyl group are known to effect gelation of organic fluids.<sup>51</sup> Shinkai and co-workers have described an approach to realize reversible gel formation by using a cholesterol molecule functionalized with a photoswitchable azobenzene moiety.<sup>52</sup> 4-Methoxyazobenzene was coupled via an ester linkage to a cholesterol derivative to form molecule **9** (Figure 4), which proved to be an excellent gelator; as little as 0.5 mg of *trans* **9** could gelatinize 1.0 ml of butanol at 15 °C ( $T_{\text{gel}}$ ).

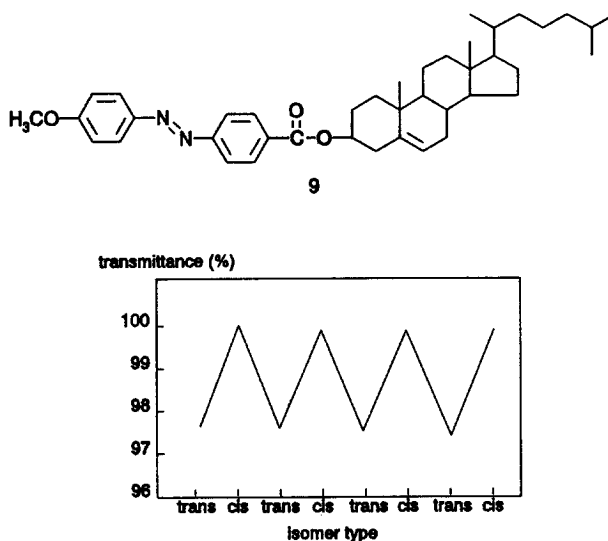


Figure 4

This gel formation could be influenced by a configurational change in the gelator structure via *cis*-*trans* photoisomerization of the azobenzene part. Photoirradiation by a Hg lamp ( $330 < \lambda < 380$  nm) afforded a photostationary state with 38% of the *cis* isomer, with a  $T_{\text{gel}}$  of 2 °C. The gelation temperature for this *cis* enriched mixture was significantly lower as for the pure *trans* isomer and at higher temperatures a clear solution

was observed. The thermal reversion to the trans isomer was reported to be very slow in the dark, although no quantitative data were given. However, cis **9** was rapidly isomerized to trans **9** by irradiation at  $\lambda > 460$  nm. Alternate photoirradiation at 10 °C by UV and Vis light showed the feasibility of a molecular switch. As shown in Figure 4, trans **9** provided the gel with 97.8% transmittance, whereas the cis/trans mixture (38/62) showed 100% transmittance. The bistability of this system is based on whether gel formation occurs or not and is detected by the change in transmittance. Although basically the possibility of a switching process has been demonstrated, the realization of a practical device is limited so far due to the use of a solvent.

#### 4.3.4 Changes in conductivity

The principle of an organic switching device by the photochemically induced change in conductivity of a Langmuir-Blodgett film consisting of a charge transfer complex functionalized with an azobenzene group was reported by Tachibana.<sup>53</sup>

The molecule **10** can be described schematically to be composed of a "switching unit" (the azobenzene), a "transmission unit" (the alkyl chain) and a "working unit" (the charge transfer complex between tetracyanoquinone (TCNQ) and the pyridinium cation) as depicted in Figure 5.

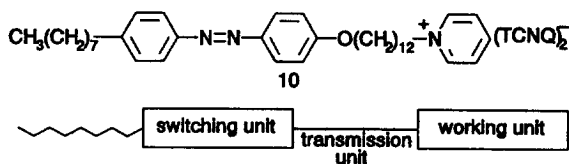


Figure 5

Upon photoirradiation of the pure trans isomer at 356 nm the conversion to the cis isomer was estimated to be 25%, with a half-life for the thermal cis to trans isomerization of 3 h at room temperature. By irradiation at 436 nm the trans azobenzene could be regenerated. The measured conductivity of the Langmuir-Blodgett film was enlarged by approximately 30% for the 25:75 cis/trans mixture compared to the pure trans isomer. A (preliminary) explanation for this behaviour was that the trans to cis isomerization, which causes a conformational change in the azobenzene area, enhanced the ordering of the TCNQ column and hence the conductivity of the Langmuir Blodgett film. By alternate irradiation with UV/Vis light, a modulated conductivity signal was obtained and the feasibility of a molecular switch demonstrated as shown in Figure 6. After ten cycles a decrease of 1% in absorbance was found, probably due to some unwanted side reactions.

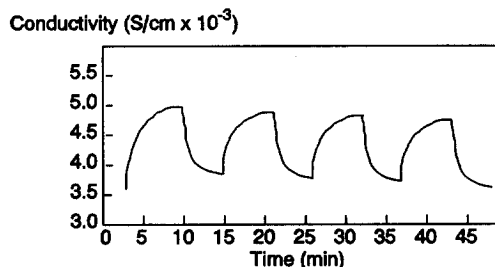


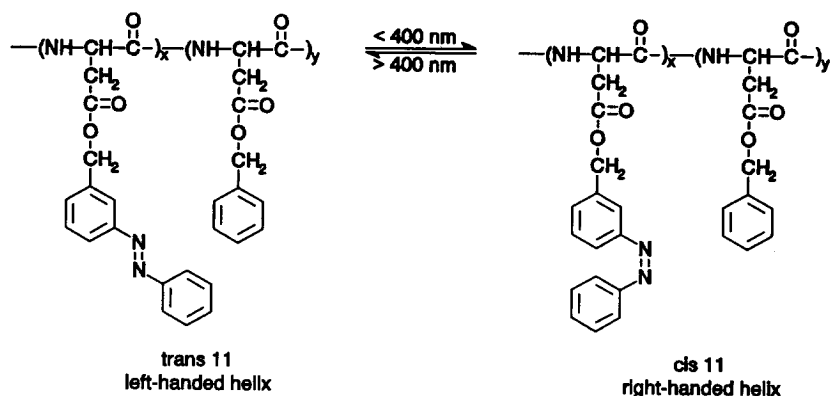
Figure 6

These results indicate that conductivity of a system can be controlled by an external light pulse. The detection of the two bistable forms is based on conductivity and therefore cannot influence the *cis*/*trans* ratio leading to non-destructive read-out. A major drawback still remains the rather fast thermal *cis* to *trans* isomerization.

#### 4.3.5 Reversible helicity of polypeptides

The occurrence of helix formation in the secondary structure of polypeptides is a well known phenomenon.<sup>54</sup> The incorporation of photoresponsive azobenzene moieties in these polymers might effect light-induced conformational changes of the helicity. After the pioneering results found by Goodman on (phenylazo)phenylalanine polymers,<sup>55</sup> Ueno and co-workers reported a change in the chiroptical properties of polyaspartates by the *cis*-*trans* isomerization of azobenzene units in the side chains.<sup>56</sup>

A copolymer consisting of  $\beta$ -benzyl L-aspartate and  $\beta$ -(*m*-benzylazo)benzyl L-aspartate **11** ( $x = 0.49$ ) formed a left-handed helix in the all-*trans* configuration (with a small amount of right-handed helix as determined by CD measurements, ratio 86:14, Scheme 6). Upon irradiation of **11** at  $\lambda < 400$  nm, inducing the *trans*  $\rightarrow$  *cis* isomerization, the content of the right-handed helix changed from 14 to 100%, dependent on solvent effects. Even much lower fractions of azo units accomplished this helicity reversal; only 9.7% of azo groups were necessary to change the percentage of the right handed helices from 9% to 74%. For the thermal decay in the dark, a half-life of 24 h at 40 °C was found. The reverse isomerization process to the *trans* compound was effected by photoirradiation at  $\lambda > 400$  nm, with the concomitant change in helicity. This helicity reversal can be followed by monitoring the large change in optical rotation, offering a method for non-destructive read-out in optical recording by using a read-out light wavelength far distant from the write-in wavelength.<sup>57</sup> It should be emphasized that optical rotation can be measured at many different wavelengths without interference with the absorption spectra of the two conformers.



Scheme 6

Further exploration of this method should emphasize: (i) the investigation of this concept in polymer matrices; so far these studies have only been carried out in solution (for an approach based on the photochromism of spiropyrans doped in films of chiral polymers, see Section 5.5.2) and (ii) the improvement of the rather low thermal stability of the cis form, leading to a rapid disappearance of the written information. Similar results were found by Ciardelli and co-workers in poly(L-glutamate) functionalized with azobenzene chromophores.<sup>58</sup> They also reported conformational changes in chiral copolymers consisting of methacrylate functionalized azobenzenes and (-) menthyl methacrylate units, although much smaller effects were found.<sup>59</sup>

#### 4.3.6 Selective reduction method

The most important disadvantage prohibiting further development of azobenzenes into practical switching devices is the unwanted thermal reversion of the cis isomer, as outlined in the previous sections. An elegant and promising method to circumvent this problem was reported by Liu and co-workers by using a selective reduction procedure for the cis isomer to a hydrazobenzene.<sup>60</sup> The proposed storage system is based on the combination of two types of reversible processes, namely photochemical cis-trans isomerization and electrochemical oxidation and reduction.<sup>61</sup>

By using both processes it was possible to store information photoelectrochemically. The principle of this storage system is based on two observations: (i) the cis azobenzene derivative can be reduced to a hydrazobenzene at more anodic potential than the trans form, and (ii) the hydrazobenzene derivative is exclusively oxidized to the trans form.

This concept was demonstrated by irradiation of a Langmuir-Blodgett film of the azobenzene derivative **12** in aqueous solution by a He-Cd laser (325 nm) to induce a local trans-cis isomerization, followed by switching the potential of the entire film to a voltage where only the cis azobenzene is reduced to the hydrazo derivative (Figure 7). Electrochemical writing was also proposed to be possible by irradiating the entire film and then controlling the reduction area of cis-state.<sup>62</sup> Detection of the stored information is possible by the difference in UV absorption.

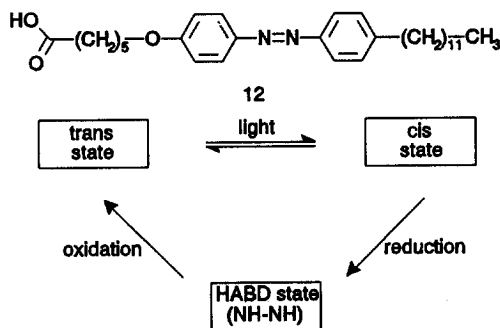


Figure 7

Two important advantages underline the importance of this approach: (i) the large difference between the absorption spectra of two forms owing to the conversion of the azo chromophore to the hydrazo functionality, allowing both bistable states to be read separately, and (ii) the possibility of non-destructive read-out of the stored information, because both photochemical isomerization *and* electrochemical reduction are needed for the renewed formation of the hydrazobenzene state.

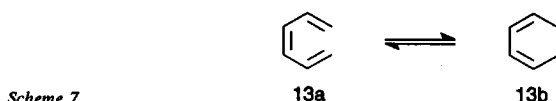
The written information can be erased by oxidizing the entire film, by application of another voltage to the original trans form. These reversible isomerization  $\rightarrow$  reduction  $\rightarrow$  oxidation cycles could be repeated several hundred times, without discernible change.



## 5 Photocyclizations

### 5.1 Photochromic Valence Tautomerism

Photochromic valence tautomerism is defined as a reversible change in colour due to a shift in the position of bonds in a molecule. The basic principle of such a process can be illustrated by the isomerization of 1,3,5-hexatriene (13a) into 1,3-cyclohexadiene (13b) and vice versa (Scheme 7), whereby the photochemical and thermal ring opening and closure are governed by the Woodward-Hofmann rules.<sup>63</sup>



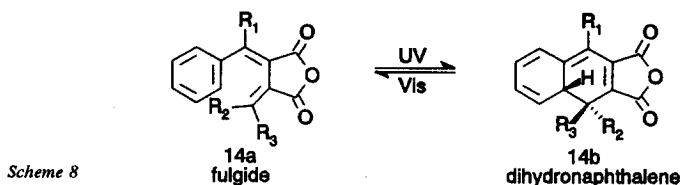
Scheme 7

The limited number of switching cycles, due to the occurrence of side reactions, has to some extent been overcome by structural improvements, as will be outlined in the following sections. Examples of this type of photochromic compound, which have been developed into candidates for optical data storage, include fulgides (Section 5.2), diarylalkenes (Section 5.3) and azulenes (Section 5.4, a 10-electron cyclization). In Section 5.5, the possible applications of spiropyrans are discussed, where the reversibility is based on heterolytic bond cleavage *and* a cycloreversion process.

### 5.2 Fulgides

After the discovery of the photochromic behaviour of fulgides by Stobbe,<sup>64</sup> the exploration of these molecules as potential candidates for erasable and rewritable organic photomemory systems was largely due to Heller.<sup>65</sup> Fulgides are derivatives of dimethylene-succinic anhydrides, substituted with an aromatic ring.

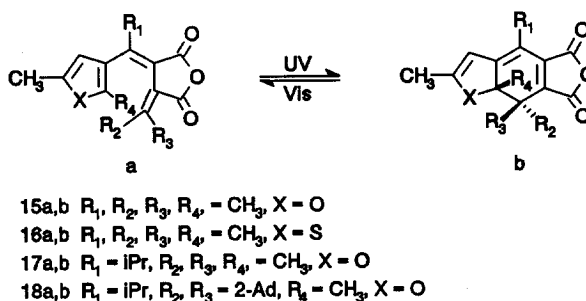
The bistability is based on a reversible photochemical conrotatory electrocyclization,<sup>63</sup> similar to the 1,3,5 hexatriene cyclization. Upon irradiation with UV light, the mostly colourless fulgide 14a is transformed into a coloured dihydronaphthalene structure 14b. The reverse reaction can be induced by irradiation with visible light (Scheme 8).



Scheme 8

The difficulties encountered with applying fulgides for memory devices are mostly related to the observation of unwanted side reactions: (i) the photochemical isomerization of the *Z*-isomer to the *E*-isomer ( $R_1$  and the phenyl group in **14a** interchanged), (ii) the observation of sigmatropic proton shifts leading to undesirable side products (the hydrogen drawn in the dihydronaphthalene structure **14b** can shift to other positions), and (iii) the disrotatory ring opening due to the competing fast thermal reverse reaction of **14b**, which occurred within a few minutes at room temperature.

Structural improvements suppressed the sigmatropic shifts by the replacement of hydrogen atoms by alkyl groups<sup>66</sup> and the thermal reverse reaction could be slowed to a large extent by the introduction of heterocyclic aromatic rings like furyl and thienyl groups<sup>67</sup> as shown in **15** and **16** in Scheme 9 (in Section 5.3.2, the effect of heterocyclic rings on the thermal stability will be explained).



Scheme 9

The introduction of a methyl substituent  $R_4$  into the 2-position of the 3-thienyl group of the fulgide **16a** not only eliminated the irreversible photochemical and thermal hydrogen-shifts but also prevented the thermal disrotatory ring opening, because of the severe steric interactions which would arise between the  $R_4$  and the  $R_3$  methyl groups in the *cis* position in **16b**. The photochemical symmetry allowed conrotatory ring opening back to the *E*-fulgide is unaffected. The dihydrobenzo[*b*]furan **16b** was thermally stable up to 160 °C, but was converted back into the *E*-fulgide quantitatively upon exposure with white light (Scheme 9).<sup>68</sup>

Kurita and co-workers replaced the methyl group  $R_1$  by an isopropyl group in the furyl functionalized fulgides and as a consequence **17** did not show any *E/Z* isomerization and had an efficient quantum yield for the photochromic process ( $\Phi = 0.62$ ,  $\lambda = 366$  nm).<sup>69</sup> The rather low value of  $\Phi$  for the photochemical reverse reaction ( $\Phi = 0.04$ ,  $\lambda = 492$  nm), could be improved by using an adamantylidene substituted fulgide **18** ( $\Phi = 0.28$ ,  $\lambda = 492$  nm).<sup>70</sup> These experiments were also carried out in polymer films, with the highest quantum yields obtained for the fulgide **17** dissolved in polystyrene ( $\Phi = 0.12$

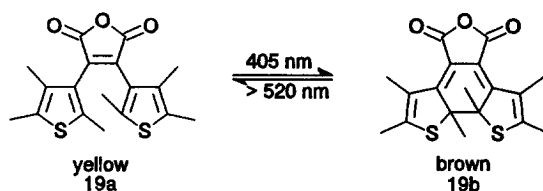
and 0.10, respectively for the colouration and decolouration interconversions).<sup>71</sup> In further studies other heterocyclic rings, like 4-pyrazolyl, 3-indolyl and 4-oxazolyl groups were introduced,<sup>72</sup> which showed low photochemical fatigue (< 0.03% each cycle, for the oxazolyl), compared with the furyl based fulgides (50% degradation after 100 cycles in toluene). The thermal back reaction to the fulgide in the case of the oxazolyl derivative dissolved in a PMMA film proved to be very slow (only 5% after 10 days at 80 °C).<sup>72b</sup>

The read-out procedure for the different states of the fulgide is based on detection of the change in absorption bands of the two isomers, which could lead to interference with the written data as has already been stated in the previous sections. Recently, a first approach towards a non-destructive detection method was reported by Kurita and co-workers which combines the advantages of the above properties of fulgides with a Brønsted acid-base equilibrium (see Section 4.3.1 for a non-destructive read-out method based on the detection of different mesophases in polymeric liquid crystals with fulgide side-chains).<sup>73</sup>

### 5.3 Diarylalkenes

In addition to cis-trans isomerization, stilbene derivatives can undergo a reversible cyclization reaction upon ultraviolet irradiation as has been shown in Section 4.2 (Scheme 2). The formation of the unwanted phenanthrene derivative **3** can be excluded by the substitution of methyl groups for the two hydrogens sensitive to oxidative elimination. The limited value of this photochromic process to optical data storage is the low thermal stability of the photogenerated dihydro-form **2**, which reverts quickly (3 min, 30 °C) to the open ring form.

Irie and co-workers reported the preparation of thermally stable diarylalkenes by using furan or thiophene groups instead of the phenyl rings.<sup>74</sup> The possible cis-trans isomerization of the central double bond, an unwanted side reaction observed for the fulgides in Section 5.2, was prevented in the cyclic acid anhydride derivative **19a** (Scheme 10).



Scheme 10

Upon UV irradiation at 405 nm in benzene, the yellow open form **19a** was converted to the brown closed dihydro form **19b** and could be regenerated by exposure to visible light ( $\lambda > 520$  nm) with quantum yields ranging from 0.07 - 0.12. The photogenerated ring closed form was stable for more than 12 h at 80 °C, did not show any thermochromic behaviour and no detectable fatigue was observed even after 100 colouration and decolouration cycles. The remarkable increase in thermal stability of the ring closed heterocyclic compound compared with the phenyl derivative can be ascribed to the difference in aromatic stabilization energy which is lost in the cyclization process. In the case of 1,2-diphenylethene, the energy barrier for the cycloreversion reaction becomes very small due to an increase in ground-state energy of the ring closed form, caused by the destruction of the aromatic conjugation (the aromatic stabilization energy was calculated to be 27.7 kcal.mol<sup>-1</sup>). For 1,2-di(3-furyl)ethene, the ground state energy for the ring closed form is lowered, because of the minor loss in aromatic stabilization energy (9.1 kcal.mol<sup>-1</sup>), leading to a larger reaction barrier for the decolouration process.<sup>75</sup>

The thermal stability of the closed form could be further increased by replacing the two inner methyl groups in these molecules by trifluoromethyl substituents (no ring opening was observed even after 80h at 100 °C!).<sup>76</sup> This influence was explained by the larger stabilization effect of the trifluoromethyl groups on the attached *sp*<sup>3</sup>-carbon (in the ring closed form) compared with the *sp*<sup>2</sup>-carbon (in the ring open form), as has been reported for other pericyclic reactions.<sup>77</sup>

Further investigations are focused on shifting the absorption bands for both isomers to longer wavelengths by the introduction of different functionalities<sup>78,79</sup> with the aim to use conventional laser sources such as the Ar ion laser ( $\lambda = 488, 514$  nm), He-Ne laser ( $\lambda = 633$  nm) or the cheap diode laser ( $\lambda = 780$  nm) for the switching process. The introduction of an indole ring, as in **20**, shifted the absorption as far as 800 nm, but unfortunately low thermal stability of the closed form was observed (Figure 8).<sup>80</sup>

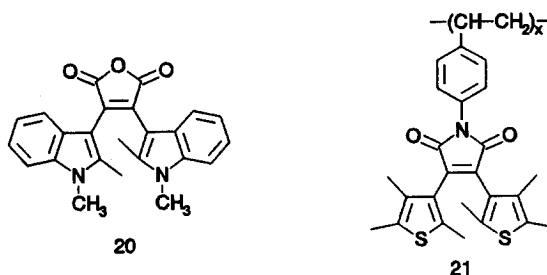


Figure 8

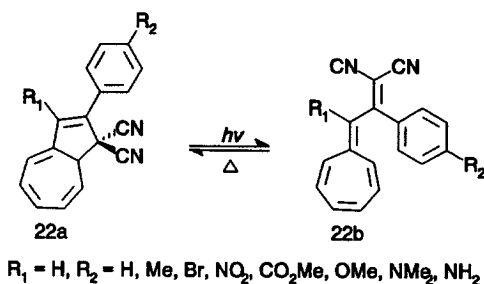
The absorption intensity decreases to 50% of the initial intensity in 3 h at 80 °C, in agreement with the aromatization stabilization energy calculated for the related 1,2-di(pyrrolyl)ethene (13.8 kcal.mol<sup>-1</sup>, half-life 32 min at 20 °C).

Recently, Irie and co-workers demonstrated that, via the introduction of carboxylic acid groups into the diarylalkenes, the photochromism of these molecules could be blocked due to the formation of intramolecular hydrogen bonds in one of the bistable states and control by using various solvent mixtures was possible (i.e. chemical gated photochromism).<sup>81</sup>

Although very promising results are obtained with these stilbene analogs, the detection method is still based on differences in absorption spectra of the two bistable states and therefore potentially destructive. The incorporation of a bis-thienyl alkene into a polystyrene backbone has been achieved (Figure 8), which might eventually lead to a non-destructive read-out method based, for example, on changes in liquid crystalline behaviour, as found for polymers with azobenzene molecules (Section 4.3.1), but until now no switching results with polymer **21** have been reported.<sup>82</sup>

#### 5.4 Azulenes

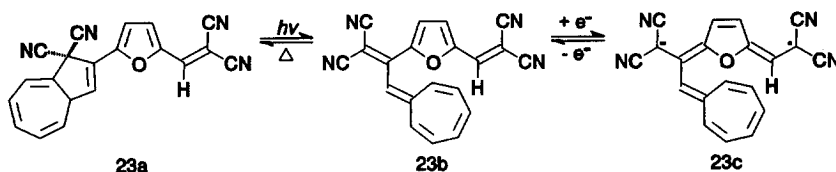
Photochromism based on a 10-electron cycloreversion of a dihydroazulene **22a** (DHA) into a vinylheptafulvene **22b** (VHF) by irradiation at 366 nm ( $\Phi = 0.55$ ) has been described by Daub and co-workers.<sup>83</sup> This rearrangement could be rendered visible by a change of colour from yellow to red as a result of the shift of the long wavelength absorption band at 350-360 nm for **22a** to 460-490 nm for **22b** (Scheme 11). The VHF structure reverts thermally to the DHA chromophore with half-lives ranging from a few seconds to 1-2 days strongly depending upon the substitution patterns and the temperature.<sup>84</sup> Similar behaviour was observed in a polymer matrix of polymethylmethacrylate.<sup>85</sup>



Scheme 11

This ring opening reaction is accompanied by a large change in the electronic structure of the  $\pi$  system. In the VHF structure **22b**, conjugation can occur between the  $R_2$  substituent and the strongly electron-withdrawing cyanovinyl unit, known as an excellent acceptor in donor/acceptor type organic molecules for applications in non-linear optics.<sup>6,86</sup> The thermal ring closure to the DHA **22a** prevents this interaction, resulting in a large change in the absorption spectra. By introducing a dimethylamino  $R_2$  group, the NLO properties might be activated by light induced molecular switching between the non-conjugated DHA and the conjugated VHF.<sup>85</sup>

By functionalizing a dihydroazulene with a dicyanovinylfuryl moiety as in **23a**, the conversion of light-pulse sequences into time-dependent current signals was demonstrated, allowing for a non-destructive read-out of the two bistable states (Scheme 12).<sup>87</sup>



Scheme 12

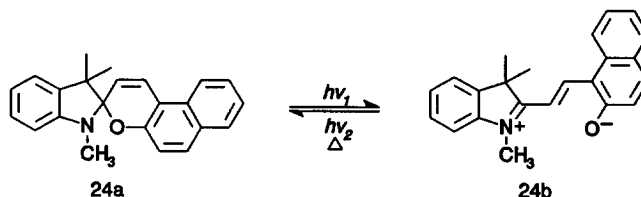
Cyclic voltammetry studies revealed the inertness of the DHA structure **23a** at a potential of  $-1050$  mV, but the VHF state **23b** is reduced to a radical anion **23c**, leading to a change in the measured current. By subjecting the dihydroazulene to a photomodulated amperometry technique whereby light pulse irradiation under constant potential is applied, a modulated current signal was found ( $\pm 100$   $\mu$ A fluctuations) and a switching characteristic comparable with Figure 6 was obtained (the current values on the y-axis). Due to the very fast thermal back reaction at room temperature of the DHA molecule **23a** used here, this switching process was executed at  $-50$   $^{\circ}$ C.

The conversion of photosignals into electric current has been extended and in some cases improved by the introduction of other active groups for the electron transfer process such as nitro- and amino-substituted aryl groups,<sup>88</sup> ferrocenes<sup>89</sup> and anthraquinone moieties.<sup>90</sup> Major improvements of the thermal stability of the VHF state are still required.

### 5.5 Spiropyrans

In 1956 Hirshberg was the first to recognize the potential of photochromism observed in spiropyrans, as it was proposed that the cycle of colouration and bleaching can form the basis for a photochemical memory device.<sup>91,92</sup> These findings initiated vigorous research on the possible use of these molecules as photoresponsive materials in, for example, reversible light filters in sunglasses and reversible optical recording media.<sup>93</sup>

The photochromic behaviour of spiropyrans is based on the reversibility between the colourless "closed" spiropyran form **24a** and the coloured "open" merocyanine dye **24b** via heterolytic cleavage of the spiro oxygen-carbon bond (Scheme 13). By ultraviolet irradiation of the spiro form, the merocyanine is formed which reverts either by irradiation with visible light or thermally to the closed form.<sup>94</sup> The initial results of Hirshberg were based on the spiroindoline structure **24a** shown in Scheme 13, which could be reversibly switched between the two states for at least 15 times, although only at very low temperatures ( $-100\text{ }^{\circ}\text{C}$ ).



Scheme 13

Important disadvantages of this type of molecule in reversible switching processes are: low thermal stability of the coloured form (ranging from a few seconds to several hours at room temperature), photochemical side reactions (degradation) and the occurrence of thermochromic behaviour<sup>41</sup> which might interfere with the photochromic process. Besides temperature, concentration and solvent effects,<sup>94,95</sup> the thermal back reaction is strongly dependent on the molecular structure and the surrounding matrix.

By modifying the basic structure through introduction of a nitro substituent (see Scheme 14), the zwitterionic merocyanine **25b** was stabilized by the electron-withdrawing group and life-times in solution ranging from minutes to several hours were reported.<sup>94</sup> Much research effort in this area is based on the use of **25** or derivatives thereof (see Sections 5.5.1 and 5.5.2). Recent attempts have focused on achieving a bathochromic shift of the long wavelength absorption maximum of the coloured form within the range of the diode laser wavelength (780 nm), to be able to use a readily available cheap laser for the switching and read-out process.<sup>96,97</sup> By replacing the oxygen by a sulfur atom,

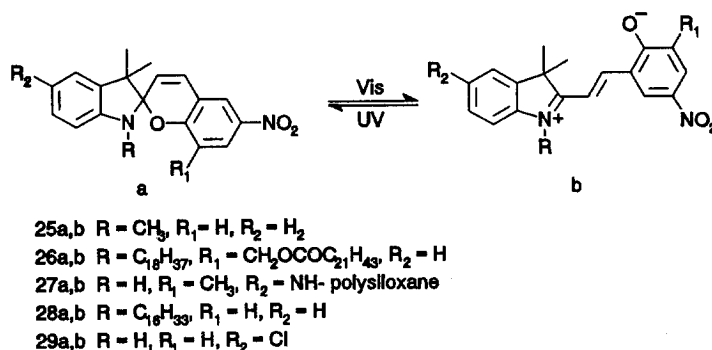
the absorption spectra of the resulting merocyanines extend to wavelengths as long as 900 nm. However, these structural changes have led so far to a thermally very unstable merocyanine with a half-life of 36 s in acetone<sup>97</sup> and low fatigue resistance (after 30 switching cycles the absorption intensity of the coloured form decreased to 50% of the initial value).<sup>96</sup>

The dependence of the reverse thermal process on the mobility of the surrounding medium can be ascribed to the large change in molecular shape between the two isomers and research has been focused on increasing the thermal stability of the merocyanine form by using different matrices (Section 5.5.1). Furthermore, a non-destructive read-out method has been developed based on a change of optical rotation of a chiral polymer induced by the photochromism of a spiropyran molecule (Section 5.5.2).

### 5.5.1 "Matrix effects" on the photochromism of spiropyrans

The conversion of the spiropyran into the zwitterionic merocyanine dye is accompanied by a separation of charges and therefore a large change in dipole moment is observed. Dipolar structures are able to aggregate and, apart from the restricted mobility, the increase in thermal stability of the "open" dye molecule in matrices is ascribed to the formation of two different types of aggregates: H-aggregates, which exhibit an absorption that is blue-shifted relative to that of a non-aggregated dye, and J-aggregates, which show a red-shifted absorption.<sup>98</sup> The J- and H-aggregates have, respectively, parallel and antiparallel arrangements of the molecular dipoles in stacks and are strongly dependent on structure, concentration and solvent.<sup>99</sup>

The formation of J-type aggregates was reported by Ando and co-workers using Langmuir-Blodgett techniques to obtain a monolayer of nitro-spiroindoline benzo-pyran derivative **26a** functionalized with two long alkyl chains (Scheme 14).<sup>100</sup>



Scheme 14



After UV irradiation at 35 °C, this monolayer exhibit a sharp and intense absorption at 618 nm, compared with 580 nm of the monomeric form, which could be ascribed to the formation of J-aggregates. The half-life in the dark of this J-aggregated merocyanine dye was  $10^4$  times longer than observed for conventional spiropyrans.<sup>101</sup>

Krongauz and co-workers have observed the formation of H-type aggregates in liquid crystalline polyacrylates<sup>102</sup> and polysiloxanes<sup>103</sup> containing a spiropyran unit in the side chain, leading to the formation of the three primary colours. Upon UV irradiation at -20 °C, the polymer film of the *yellow* polysiloxane derivative **27a** ( $\lambda_{\text{max}} = 370$  nm) turned *blue*, which colour can be ascribed to isolated merocyanine dyes ( $\lambda_{\text{max}} = 580$  nm). After heating above -10 °C and thereby increasing the mobility of the polymer chain, the colour of the film turns *red* ( $\lambda_{\text{max}} = 550$  nm), a hypsochromic shift due to the physical aggregation of the merocyanine dyes (Figure 9). This red film is thermally stable below the glass transition temperature ( $T_g = 10$  °C) and the fading of the colour takes several days at room temperature. However, on irradiation with visible light, the red colour rapidly changes to yellow, indicating the formation of the closed spiropyran.

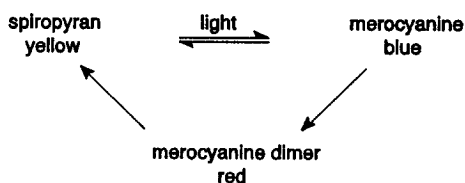


Figure 9

Although these two examples illustrate the possibility of obtaining a large increase in thermal stability due to aggregation phenomena, the detection method is still based on (destructive) absorption differences between the two forms.

Improvement of the thermal decay rate for the merocyanine structure was also achieved by applying bilayer membranes,<sup>104</sup> lyotropic liquid crystalline phases,<sup>105</sup> micelles,<sup>106</sup> monolayers<sup>107</sup> and bilayer-clay matrices.<sup>108</sup> In the last case, by using a bilayer clay consisting of montmorillonite, didodecyldimethylammonium chloride and the spiropyran **26a** (Scheme 14), the decolouration of the J-aggregated form was calculated to be  $1.1 \times 10^7$  (!) times slower than for the monomeric form.

Interesting approaches towards non-destructive read-out methods could be based on observed potential/current changes across a polyvinyl chloride membrane,<sup>109</sup> a bilayer lipid membrane containing glyceryl-1-monoolein<sup>110</sup> or a stearic acid membrane<sup>111</sup> containing spiropyran **28a**, which are ascribed to charge density changes in the membrane originating from the open zwitterionic merocyanine form. These membranes offer the opportunity to transduce a light signal into an electric output.

Parthenopoulos and Rentzepis have outlined the principles of a three dimensional optical storage memory based on two photon excitation of spiropyran **29a** embedded in a polymer matrix<sup>112</sup> leading to an increase in storage density of a factor  $10^4$  compared with a two dimensional memory. The practical use is still limited due to the thermal instability (a life-time of several minutes at room temperature for the open form was reported) and fatigue.<sup>113</sup>

### 5.5.2 Change in Optical Rotation Power

Ichimura and co-workers were able to induce a reversible change of optical rotation in the cholesteric liquid crystalline polymer poly(benzyl L-glutamate) (**30**, PBLG) by the photochromism of 1-4 mol% of spiropyran **25a** (see Scheme 14) dissolved in the polymer.<sup>57,114</sup> Upon alternate exposure with UV and visible light of a polymer film containing 4 mol% of **25a**, the optical rotation fluctuated as depicted in Figure 10. The amplitude decreased gradually as the repetition number increased due to photochemical degradation of the photochromic compound.

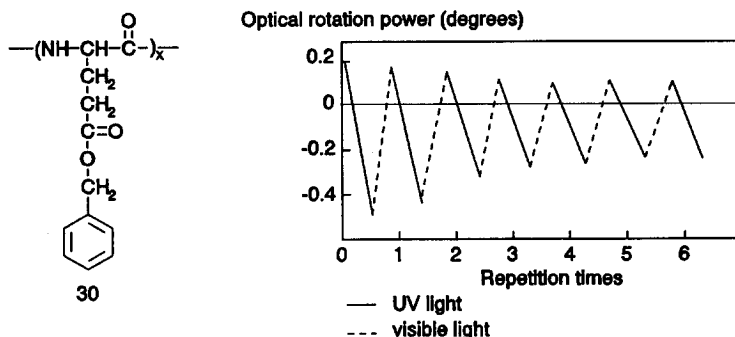


Figure 10

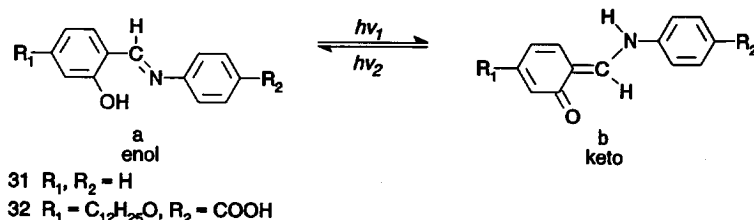
The indolinospiran **25a** possesses one stereogenic center at the spiro position, which disappears upon formation of the merocyanine. The possibility that the change in optical rotation could be ascribed to the formation of the optically active spiro compound, induced by the chiral reaction medium, was excluded on the basis of the large optical rotation differences measured. For example, the observation of  $\alpha_D = 1^\circ$  for a film of thickness  $1\mu\text{m}$  requires an  $[\alpha_D] = 100,000^\circ$ , which is extremely large compared with optical rotations of "ordinary" chiral compounds. The reversible change in the chiroptical properties was ascribed to the differences in interactions of the spiropyran **25a** and the

coloured chromophore **25b** with the chiral polymer structure, which resulted in modification of the circular dichroism transitions of the polymer by the merocyanine molecule.

As already indicated in Section 4.3.4, detection of both isomers can be performed by measuring the change in optical rotation, without interference with the written information. Disadvantages so far are the rather fast photochemical degradation and the low thermal stability of the merocyanine form (life-time 20-50 min, depending on concentration).

### 6 Photochromic Keto-Enol Tautomerism.

Photochromic keto-enol tautomerism refers to a photochemically induced proton shift between the keto and enol isomers of a molecule,<sup>115</sup> as can readily occur in *N*-salicylideneaniline (**31a**, Scheme 15), where it is accompanied by a rotation of the phenolic ring to form the trans-keto form **31b**. The stable ground state configuration is described by the cis-enol configuration **31a** with an intramolecular hydrogen bond between the oxygen and the nitrogen.<sup>116</sup> Upon irradiation with UV light, in the solid state, the colourless cis-enol is converted to the red trans-keto form, which might be reversibly bleached either photochemically, using visible light, or thermally.



Scheme 15

These compounds have been proposed as possible candidates for optical switching devices,<sup>117</sup> due to several important advantages: 1) excellent fatigue resistance, with only a very small amount of photochemical destruction;<sup>118</sup> 2)  $10^4$ - $10^5$  cycles, which can be compared with magnetic technology,<sup>24b</sup> and 3) the proton transfer reaction occurs in the picosecond time scale ( $< 10^{-12}$ ).<sup>119</sup>

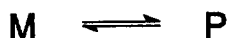
The major problem to be solved is the low thermal stability (fading of the red colour in 3 h at 25 °C) of the trans-keto form; a reasonable stability was only observed in the

solid state, not suitable for the generation of materials. Furthermore, isomerization to the *cis*-keto form can occur, which leads to a fast thermal back reaction.

An approach to increasing the thermal stability of the keto form "outside" the crystalline state, was described by Saito and co-workers, who formed Langmuir-Blodgett multilayers from a salicylideneaniline **32** functionalized with a long alkyl chain and a hydrophilic carboxylic acid.<sup>120</sup> The rate constant for the thermal back reaction was of the same order of magnitude as in the crystalline state ( $k = 10^{-3} \text{ s}^{-1}$  at room temperature), indicating that a highly ordered and densely packed structure of **32** in the multilayer caused the suppression of the thermal reverse reaction.

### 7 Chiroptical Molecular Switches

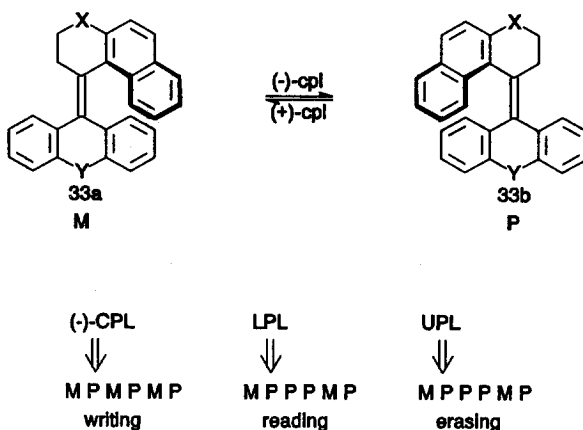
In an alternative approach to molecular switches use is made of the unique optical properties associated with the enantiomers of chiral photoresponsive molecules. Chirality offers intriguing prospects in the design of new optical organic materials.<sup>121</sup> We devised photoreversible systems based on interconversion of enantiomers (or pseudoenantiomers) of inherently dissymmetric molecules (Scheme 16).<sup>122,123</sup> The two chiral forms of the -helically shaped- molecules are denoted P and M, for the right and left handed helical structure, respectively.



Scheme 16

Bistability is the result of M or P helicity whereas non-destructive read-out is possible via monitoring the change in optical rotation using linearly polarized light (LPL) at wavelengths remote from the switching wavelength. In contrast: *achiral* photoresponsive azobenzenes or merocyanine dyes have been used to induce changes in chiroptical properties in polypeptides and cholesteric liquid crystalline polymers (*vide supra*).

The principle of a chiroptical molecular switch using circularly polarized light (CPL) for writing is shown in Scheme 17. Reading can be achieved with LPL and erasing with unpolarized light (UPL, photochemical racemization). The inherently dissymmetric (sterically overcrowded) alkenes **33** combine a helical structure with bistability, as a stilbene type photoisomerization can occur. Irradiation of racemic **33** with (-)-CPL or (+)-CPL is supposed to shift the equilibrium to an excess of P or M enantiomer, respectively (*deracemization*), depending on the anisotropy factor  $g$ .<sup>124</sup>



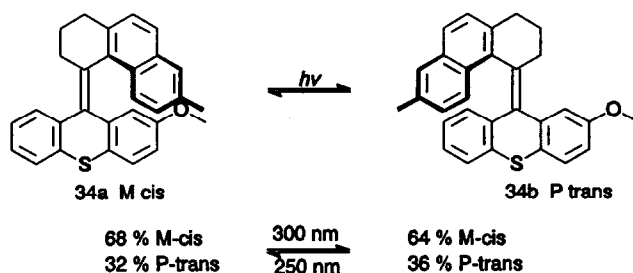
Scheme 17

Resolution of several chiral alkenes **33** ( $X, Y = -, O, S$ ) was achieved and thermal racemization barriers strongly dependent on  $X$  and  $Y$  were observed ( $X = \text{CH}_2, O, S, Y = - > 30 \text{ kcal.mol}^{-1}$ ;  $X = O, Y = S, 21.7$ ;  $X = \text{CH}_2, Y = S, 26.3$ ;  $X = S, Y = S, 28.9$ ).<sup>125</sup>

Irradiation at  $\lambda = 300 \text{ nm}$  of **P-33b** ( $X = O, Y = -$ ), which is stable to thermal racemization at ambient temperatures, resulted in a rapid photoisomerization ( $\Phi = 0.25$ ) without significant degradation. Although the  $g$ -factor ( $3.9 \cdot 10^{-3}$  for **33**,  $X = O, Y = -$ ) indicated that the optical enrichment should be approximately 0.2 % upon irradiation with CPL, photoreversibility between **M** and **P 33** upon alternating irradiation with (-)-CPL and (+)-CPL has not been unequivocally established so far.

A chiroptical switch has, however, been realized based on the principle of photoreversibility between pseudoenantiomers<sup>126</sup> of the inherently dissymmetric alkene **34** (Scheme 18).

For these alkenes, unsymmetrically substituted in the lower part, photochemical cis-trans isomerization was found to be stereospecific and is accompanied by reversal of helicity. The thermal racemization of **M-cis** into **P-cis**, in the temperature range 50-90 °C, showed first order kinetics with  $\Delta G^\ddagger = 26.4 \text{ kcal.mol}^{-1}$ , whereas no thermal **M-cis-34a**  $\rightleftharpoons$  **P-trans 34b** isomerizations were observed between 0-60 °C. Optically pure **M-cis** (or **P-trans**) showed two distinguishable photostationary states after irradiation with 250 and 300 nm UV light, respectively (see Scheme 18).



Scheme 18

The photostationary state can be shifted using different wavelengths. Detection of the various photostationary states, i.e. different M-cis/P-trans ratios was achieved by ORD or CD measurements. The feasibility of the chiroptical switch based on **34** is shown in Figure 11. Alternated irradiation at 250 and 300 nm resulted in a modulated CD signal at 232 or 262 nm in the example shown. The switching process could be repeated at least 10 times without notable racemization or changes in UV or CD spectra.<sup>127</sup> It is expected that the photoisomerization process will strictly depend upon the matrix employed, i.e. **34** physically or covalently attached to polymers.

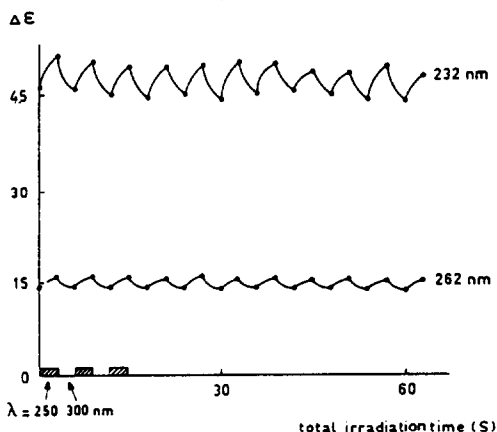
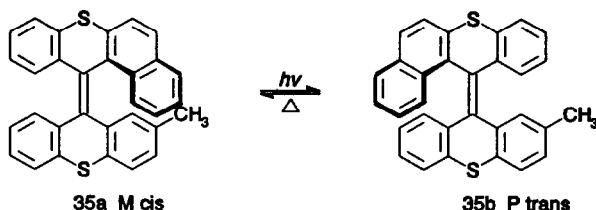


Figure 11 Plot of  $\Delta\epsilon$  vs irradiation time at  $\lambda = 232$  nm (upper curve) and  $\lambda = 262$  nm (lower curve) for **34a**  $\rightleftharpoons$  **34b** irradiated alternately at  $\lambda = 250$  nm and  $\lambda = 300$  nm; switching time 3 s.

Important problems that remain to be solved are improved thermal stability, increased fatigue resistance and structural modifications to achieve switching with visible light.

Two major improvements were recently realized using enantiomerically pure 12-(2'-methyl-9'H-thioxanthene-9'-ylidene)-12H-benzo[a]thioxanthene (**35**), which showed a stereospecific photochemical *and* thermal isomerization of the M-cis into the P-trans isomer (and vice versa) with a large thermal isomerization barrier ( $\Delta G^\ddagger = 28.6 \text{ kcal.mol}^{-1}$ ).<sup>128</sup> Besides high thermal stability, it should be noted that no permanent damage will be inflicted in switches based on **35**, in case thermal isomerization should occur, since heat *and* light induce the same process.



Scheme 19

## 8 Molecular Electronics

### 8.1 Introduction

The photochromism described in the preceding sections involved changes of chemical bonds such as cis-trans isomerization or heterolytic bond cleavage. These processes can be a limiting factor to achieve fast-response times and the isomerization reactions can be accompanied by unwanted side reactions. A very high speed memory could be based on the photoinduced transfer of a single electron, without the occurrence of other, more complex, rearrangements.

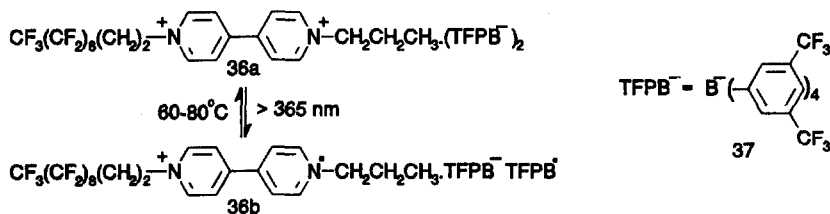
Investigations towards the development of molecular switches based on electron transfer are also stimulated by related research efforts, which concentrate on reducing the dimensions of the currently used macroscopic electronic devices, such as transistors and rectifiers.<sup>129</sup> The term "molecular electronics" has been introduced and these studies intend to achieve signal processing on the molecular scale and the construction of devices which approach the size of individual molecules.<sup>130,131</sup> Because of the various problems associated with addressing single molecules,<sup>23,132</sup> it seems more appropriate

to use organized molecular aggregates as electronic components for this type of nanotechnology, i.e. the development of *supramolecular* electronic devices.<sup>11</sup> In order to function as real electronic circuitry such a molecular entity should be connected in some way to other elements of the molecular electronic device. Therefore, the development of a (supra)molecular device will involve the design and synthesis of molecules which possess the required properties, followed by incorporation of these compounds into well-defined supramolecular architectures, and finally connection of these basic units to other components. The availability of working supramolecular electro-optical devices might eventually lead to the construction of a "molecular computer", in which the various parts consist of units with the size reduced to the (supra)molecular scale. Although the principles of molecular switches (see Sections 1-7 of this article), rectifiers,<sup>133</sup> transistors<sup>134</sup> and even molecular wires<sup>11</sup> have been demonstrated, the actual realization of a molecular computer can still be considered as a dream of the future.<sup>135,136</sup>

In the following sections the electron transfer in viologens and donor- $\sigma$ -acceptor molecules will be discussed as well as their potential to function as molecular switches. In Section 9, a fascinating example of a "molecular shuttle", obtained by self-assembling of organic compounds, is described.

## 8.2 Viologens

Photochromism based on a single electron transfer, via the excited state of an ion-pair charge transfer complex between the 4,4'-bipyridinium ion **36a** and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB<sup>-</sup>) (**37**) in the solid state and in solution, has been described by Nagamura and co-workers.<sup>137,138</sup> Irradiation of this salt at the CT absorption band ( $\lambda > 365$  nm) generated new absorptions in the visible region with main peaks at 396 and 605 nm, observed by a colour change from pale yellow to blue. These peaks are characteristic of a 4,4'-bipyridinium radical cation **36b** (Scheme 20) and this radical formation was confirmed by the observation of a broad singlet e.s.r spectrum.



Scheme 20



The generation and reverse reaction of these radical cations could be repeated for more than ten cycles by irradiation at room temperature and then heating at 60–80 °C to induce the reverse thermal process. This reverse reaction was described as very rapid, but no quantitative data were given. These viologens also showed electrochromism, which is the property to change colour reversibly in response to an applied external electric field.<sup>139</sup>

Important drawbacks of this system are: (i) sensitivity towards oxygen, which destroys the radical formed, and (ii) the limited life-time of the radical cation. The life-time could be drastically improved by the use of monolayers obtained by Langmuir-Blodgett techniques<sup>140</sup> (recovery of the starting charge transfer complex after 4 h) or with a 4,4'-pyridinium salt incorporated in the polymer main chain,<sup>141</sup> with a decay time of about 72 h at 20 °C. At elevated temperatures the life-time of the radical cation was strongly reduced and the authors proposed a high speed and high density data storage system, where information can be written ( $\lambda > 365$  nm), read by a diode laser and erased thermally.<sup>141</sup> The irradiation experiments in polymer films had to be conducted in vacuo to avoid the previously mentioned destructive effect of traces of oxygen. No data have been reported so far on the rate of colouration so far which would provide an exact value for the high speed electron transfer, that might be expected.

### 8.3 Donor- $\sigma$ -Acceptor Molecules

In their theoretical studies, Aviram and Ratner have proposed that compounds consisting of a donor and acceptor group connected via a non-conjugated bridging moiety might function as a molecular diode.<sup>129,130</sup> The basic requirement for a diode is that movement of electrons in one direction should be much faster than in the opposite direction, which would allow the processing of electronic signals. A molecular diode should be obtained by rapid charge separation, upon photoexcitation of the molecule by a laser pulse, via electron transfer from the donor to the acceptor group (Figure 12). The recombination of the charges is prevented due to the non-conjugated bridging group and can only occur via tunneling processes.<sup>130</sup>

Verhoeven and co-workers have demonstrated rapid photoinduced intramolecular electron transfer in molecules with a 1,4-dimethoxy-naphthalene group as the photoexcitable electron donor and a dicyanoethylene group as the electron acceptor, interconnected by a rigid bridge (**38**, Figure 12).<sup>142</sup> The charge separation between the donor and acceptor, interconnected via 12  $\sigma$ -bonds (corresponding to a distance of 15 Å), occurred in  $1.4 \cdot 10^{-9}$  s.

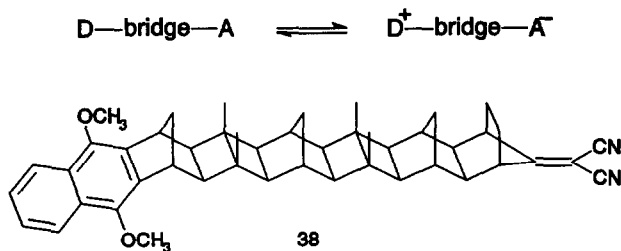


Figure 12

This remarkably fast long-range intramolecular process was ascribed to through-bond electron transfer, although  $\sigma$ -bonds are normally considered as insulating. The recombination of the two charges proved to be a much slower process and a life-time of  $0.7 \cdot 10^{-6}$  s was measured for the charge-separated species.<sup>143,144</sup> The detection of the two states can be performed by non-destructive methods, because the presence of two opposite charges within a single molecule changes the conductivity of the medium containing the compound. Further developments of this system in order to function as a molecular switch or a molecular diode will depend on the possibility to increase the life-time of the charged dipolar molecule.

A significant increase of the stability of the dipolar state might be obtained by a conformational change, which can accompany the intramolecular electron transfer, as has been observed for compounds with a less-rigid bridge.<sup>145,146</sup> An example of this type of molecule is shown in Figure 13.

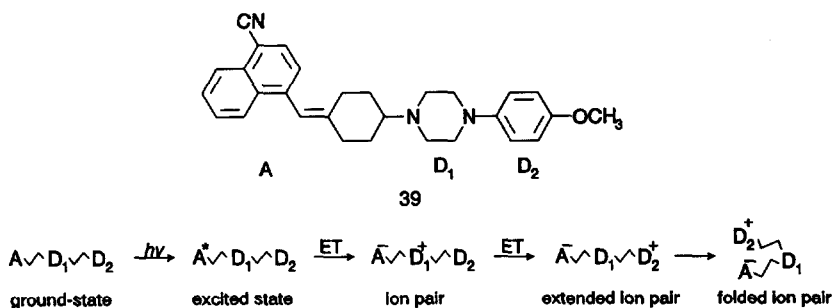


Figure 13

Compound **39** contains a cyanonaphthyl moiety as the electron acceptor (A) and two arrayed donor units, namely a piperazine (**D**<sub>1</sub>) and a methoxyphenyl (**D**<sub>2</sub>) group and is sufficiently rigid to exist in an extended conformation in the neutral ground state. Upon photoexcitation charge separation occurs to give an ion pair, followed by further conversion to an extended ion pair (see Figure 13). The electrostatic interaction between these opposite charges pulls the ends together and leads to a folding of the molecule in a period of  $10^{-9}$  s. This conformational change, which was predicted from geometry-optimized semi-empirical calculations, was confirmed by NMR studies, time-resolved fluorescence and conductivity measurements.<sup>145</sup>

The prerequisites for the occurrence of this "harpooning" process are: (i) the use of a nonpolar solvent (n-hexane), where the solvent stabilization of the species in the charge-transfer state is only small, (ii) a strong D-A couple which provides a driving force large enough to enable long-range charge separation even in nonpolar solvents, and (iii) the presence of a molecular framework which is rigid enough to establish a well-defined stretched ground-state conformation, but sufficiently flexible to allow folding under the electrostatic force.

Important factors which will influence the life-time of the folded charged state are the favourable electrostatic interaction between the two ends of the molecule and the "elasticity" of the bridging group, which can be the driving force for the renewed formation of the extended ion pair, but unfortunately no data for the reverse process have so far been reported. Although the principle of a molecular switch between the neutral and a charged folded species has been demonstrated, further elaboration is necessary to establish the potential of this system to operate as a molecular electronic device.<sup>147</sup>

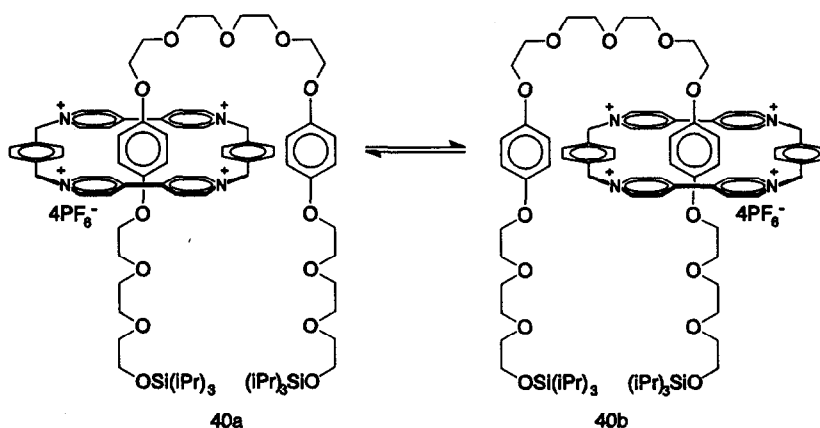
## 9 "Molecular Meccano"

Self-assembly and self-organization of organic molecules has been recognized as an important chemical approach to incorporate molecular-size fragments into macroscopic arrays in a highly controlled and precise manner.<sup>11,148</sup> The future perspectives to apply supramolecular chemistry, the chemistry of the non-covalent intermolecular bond,<sup>17</sup> for the handling of signals on the nanoscale has been thoroughly discussed by Lehn.<sup>11</sup>

In order to obtain organic materials suited for the storage and transfer of information, Stoddart and associates have developed a synthetic methodology based on the idea of assembling carefully designed small molecular components in a template-directed manner, for which the term "Molecular Meccano" was invented.<sup>149</sup> The molecular subunits are not held together by classical covalent bonds but rather by twining and interlocking, i.e. the mechanical interactions responsible for the existence of catenanes, rotaxanes and

knots.<sup>150,151</sup> These interlocked molecular structures were prepared in low yield and considered merely as academic curiosities<sup>150</sup> until Stoddart and co-workers described the syntheses of catenanes and a rotaxane which were able to function as "molecular trains" and a "molecular shuttle", respectively.<sup>152,153</sup> The principle of such a "molecular machine" will be illustrated by the switching mechanism observed in the molecular shuttle.<sup>153</sup>

The [2]-rotaxane **40**, which can operate as a molecular shuttle, is shown in Scheme 21 and consists of a molecular assembly in which a tetracationic bis-pyridinium cyclophane moves back and forth like a shuttle (**40a**  $\rightleftharpoons$  **40b**) between two "stations" (the hydroquinol units) which are situated symmetrically in a polyether "thread" terminated at the ends by large tris(isopropyl)silyloxy groups that act as "stoppers". The positively charged cyclophane ring will be attracted equally by the two identical electron-rich hydroquinol groups and therefore "jump" back and forth between the two stations. Temperature dependent <sup>1</sup>H NMR spectra indicated that this process occurred 500 times every second.<sup>154</sup>



Scheme 21

This rotaxane was obtained in the relatively high yield of 32%, which was ascribed to the favourable electrostatic attraction between the positively-charged tetracationic pyridinium moiety and the polyether oxygen atoms and charge transfer interactions between the  $\pi$ -electron accepting tetrapyridinium rings and the  $\pi$ -electron donating hydroquinol rings (i.e.  $\pi/\pi$ -stacking) during the formation of this compound.<sup>155</sup>

Although this shuttling behaviour can form the basis for a molecular switch, an important problem to be solved is how to move the tetrapyrindinium unit *selectively* from one hydroquinol unit to the other, i.e. how to control this molecular switch. Stoddart suggested the insertion of non-identical stations along the polyether thread in order to be able to address these stations selectively by chemical, electrochemical or photochemical means. A possibility might be the use of an electric current, whereby one modified station will attract the ring more strongly than the other at a certain value of the electric current. By switching the applied current off, the cyclophane ring will be able to move to the other station. Therefore by switching the current on and off, the tetracationic unit should be driven to and from the stations in a controlled manner.

So far, this rotaxane forms a intriguing example of a dynamic (supra)molecular system, but future developments have to be awaited to discover if it is actually possible to control the movement of the cyclophane ring, which might eventually lead to the technology for building "molecular machines".<sup>149</sup>

## 10 Conclusions and prospects

Multidisciplinary approaches, based on recent advances in photonics and new organic photoactive materials will beyond doubt play a key role in future (nano)-technology developments. The photochromic behaviour of many different organic molecules has been proposed in reversible optical memory devices but numerous other applications are envisaged.<sup>20,156</sup> It is therefore not surprising that the development of new photochromic processes is an active research area.<sup>157,158</sup>

Apart from the large number of necessary properties for a photochromic compound to be suitable for a practical data storage system, as has been extensively discussed in the preceding sections, the most important requirement is probably the availability of a non-destructive read-out method. The writing procedure (the interconversion between the two bistable states) occurs by photoirradiation at different wavelengths, leading to changes in the isomer ratio at the photostationary state. The read-out method is usually based on detection of this ratio by UV/Vis techniques in or near the absorption bands of the isomers, which can influence the photostationary state or cause unwanted side reactions, i.e. a destructive detection procedure. Solutions to this problem have led to the construction of light-switchable derivatives, where the photochromic event is accompanied by other changes in the molecules, which can be detected without interference with the written data. Different approaches to achieve this purpose have been described in this review, including, for example changes in liquid crystalline mesophases, gel-state, complexation behaviour, conductivity/current, helicity and aggregation behaviour.

Difficulties encountered with the photoresponsive molecules reported until now are: low thermal stability of one of the two isomers (azobenzenes, azulenes), the use of difficultly controllable aggregates (spiropyrans), oxygen sensitivity (viologens), destructive read-out methods (diarylalkenes, fulgides) and unwanted side reactions (keto-enol tautomerizations).<sup>159</sup> Non-destructive read-out methods based on current/conductivity measurements can lead to practical problems due to the simultaneous use of different techniques for the writing and detection procedure. The application of liquid crystalline polymers or chiral polypeptides to achieve a detectable change in orientation or conformation are highly promising, but might prevent the use of other matrices with possible improvement of important material properties. In various related applications, electro-optical devices based on organic dyes have high potential.<sup>6</sup>

Photoresponsive molecules, in which a change in chiroptical properties is encountered, can fulfil the requirements mentioned previously and have as additional characteristics that the writing, reading and erasing cycle might occur by using a single physical method. Given proper molecular design, read-out by optical rotation remote from the switching wavelengths is possible.

In further developments towards the practical realization of molecular switching devices, fatigue resistance and thermal irreversibility can always be a limiting factor for a particular organic material. Although impressive progress has been made, for instance with diarylethylenes,<sup>74-81</sup> several other systems need substantial improvement on these points.

A highly desirable property of photochromic compounds is gated response. Gated photochemical reactivity means that no molecular change occurs upon irradiation at any wavelength but when another external stimulation, either chemical or physical, is applied a photochemical reaction occurs.<sup>160</sup> Recently, the first examples of chemical-gated photochromic molecules were reported, in which photoresponsive effects can be blocked by reversible acid-base reactions<sup>73</sup> and reversible hydrogen bond formation,<sup>81</sup> respectively.

The formation of ordered (macro-)molecular and multicomponent systems gains enormous impetus from the recent advances in supramolecular chemistry. About the role of photoresponsive organic molecular- or supramolecular-systems as components in molecular robotics, molecular machinery or multiaddressable devices with a variety of tunable functions can only be speculated upon, but it offers a great stimulus for the organic molecule designer.

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