

# Chiroptical Molecular Switches

Ben L. Feringa,\* Richard A. van Delden, Nagatoshi Koumura, and Edzard M. Geertsema

Laboratory of Organic Chemistry, Stratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

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## I. Introduction

The design of molecular switches and trigger elements offers a formidable challenge on the road toward miniaturization in future technology<sup>1–3</sup> and the development of materials for information storage and retrieval at the molecular level.<sup>4</sup> Stimulated by the success of digital optical data systems, in which recording of information is carried out by light, and realizing the demand for high storage densities, high switching rates, and all optical devices, the search for molecular memory elements for data processing by light has gained great impetus in the past decade.<sup>5</sup> The use of organic materials offers the advantage of easy fabrication, the possibility to shape organic compounds into the desired structures by molecular engineering, the fine-tuning of a large variety of physical properties by small changes in the structure, and the characterization of single isolated structures

to allow the study of fundamental problems.<sup>6</sup> Disadvantages associated with *stability and order* can often be solved by structural modification. It is also relevant to be noted that advances in the construction of nanosize structures<sup>7</sup> or patterned surfaces<sup>8</sup> with well-defined organization of several organic components, based on the principles of self-assembly processes,<sup>9</sup> proceed at a considerable pace.

Although the development of molecular switching systems for reversible data storage remains an important objective, the emphasis partly shifts toward supramolecular chemistry, nanotechnology, and optobioelectronics in order to achieve control of structure and function.<sup>3,4</sup>

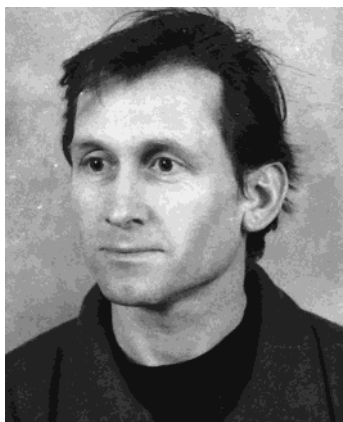
Photochemical control of nanoscale architectures,<sup>10</sup> mechanical devices,<sup>11</sup> catalysts,<sup>12</sup> transport systems,<sup>13</sup> sensors,<sup>14</sup> surface properties of materials,<sup>15</sup> and target-directed delivery systems<sup>16</sup> are only a few applications that can be envisaged.

The basic requirement for a molecular switch is bistability, i.e., the occurrence of two different forms of a molecule, which can be interconverted by means of an external stimulus. The bistability can be based on a variety of properties of molecules such as electron transfer, isomerizations, and differences in complexation behavior, whereas light, heat, pressure, magnetic or electric fields, pH change, or chemical reactions can be used to achieve the interconversion of the bistable states.<sup>4,5,17</sup>

Photoreversible compounds (Figure 1), where the reversible switching process is based on photochemically induced interconversions, are particularly attractive. Photochromism, which is defined as reversible change induced by light irradiation, between two states of a molecule having different absorption spectra is commonly associated with such systems.<sup>18</sup>

A and B represent the two different forms of a bistable system, whereby  $\lambda_1$  and  $\lambda_2$  refer to the different wavelengths used to effect the reversible switching behavior. A variety of photoreversible compounds including fulgides, azobenzenes, sterically overcrowded stilbenes, spiropyrans, diarylethenes, salicylideneimines, viologens, and azulenes have been studied, and the photochromic processes involved are typically (cis–trans) isomerization, photocyclization, photoinduced electron transfer, and keto–enol tautomerism.<sup>4,18</sup>

Despite the fact that the inevitable condition of photochemical bistability is fulfilled in these systems, a number of requirements are essential for applications as molecular switching or trigger elements. The



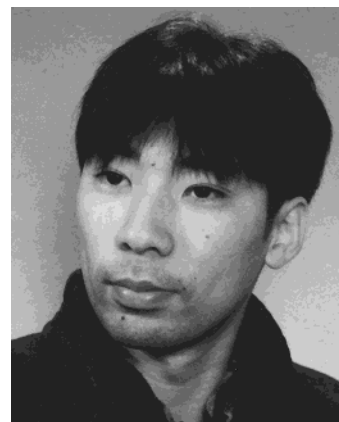
Ben L. Feringa received his Ph.D. degree from the University of Groningen in 1978 with Professor Hans Wynberg. He has been a research scientist with Royal Dutch Shell at the research center in Amsterdam and at the Shell Biosciences Laboratories in Sittingbourne, U.K., from 1978 to 1984. He then joined the Department of Chemistry at the University of Groningen as a lecturer. In 1988 he was appointed Professor at the same university. He was a Visiting Professor at the University of Leuven, a JSPS fellow, and 1997 recipient of the Pino gold medal of the Italian Chemical Society. His research is mainly focused on stereochemistry, and his research interests include organic synthesis, asymmetric catalysis and catalytic oxidation, molecular switches and motors, self-assembly, and new organic materials.



Richard A. van Delden was born in 1974. He started his studies in the group of Professor B. L. Feringa at the University of Groningen in 1994 on the excited-state properties of chiroptical molecular switches based on sterically overcrowded alkenes. In 1996 he spent six months in the group of Professor M. M. Green, Brooklyn Polytechnic University, performing research on the chiral properties of binaphthalene solubilized in aqueous polymer solutions. On the basis of these projects he received his B.A. degree in Organic Chemistry with honors in 1997. In the same year he started his Ph.D. study under the guidance of Professor B. L. Feringa on chirality aspects of different helical-shaped molecules both in solution as well as in organized media, with the chiroptical molecular switches as a basis.

most important are the following: (1) fatigue resistance (numerous write/erase cycles should be possible without concomitant thermal or photochemical degradation); (2) thermal stability (thermal interconversion of the isomers should not take place in a large temperature range (e.g.,  $-20$  to  $80$  °C)); (3) detectability (both forms should be readily detectable); (4) nondestructive read out (the detection method should not interfere with or erase the stored information).

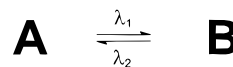
Fast response times, high quantum yields of interconversion, retention of the photochemical properties when the photochromic compound is incorporated in, e.g., a polymeric matrix, organized on a surface,



Nagatoshi Koumura was born in Nagoya, Japan, in 1971. He graduated from Tohoku University, Faculty of Sciences, in 1994 and received his Ph.D. degree from Tohoku University in 1999 under the direction of Professor Nobuyuki Harada. Currently, he is working as a postdoctoral fellow in the group of Professor Ben L. Feringa. He is involved in the synthesis and investigation of physical properties of molecular machines based on overcrowded alkenes, and his research interests include structural and physical organic chemistry. His major achievement was the establishment of a light-driven monodirectional molecular rotor based on biphenanthrylidene molecules.



Edzard M. Geertsema was born in Groningen, The Netherlands, on December 22, 1970. He received his B.A. degree in Chemistry from the University of Groningen in 1996. Part of his undergraduate research was performed at Ehime University, Matsuyama, Japan, where he joined the group of Professor F. Toda and focussed on solid-state Diels–Alder reactions with inclusion complexes. Currently, he is pursuing his Ph.D. degree in Organic Chemistry at the University of Groningen under the direction of Professor B. L. Feringa. His research includes the asymmetric synthesis of overcrowded alkenes and investigation of the properties of functionalized bithioxanthylidenes.



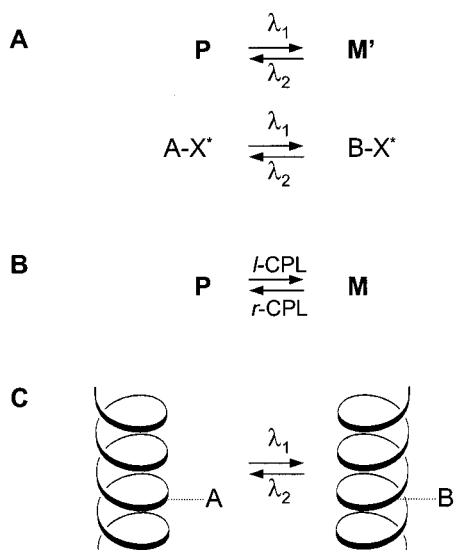
**Figure 1.** Schematic representation of a molecular switch.

or becomes part of a multicomponent assembly, as well as the various technical requirements to construct optical devices are additional factors that can play a decisive role.<sup>5,19</sup>

UV–Vis spectroscopy is the most common detection technique for these photochromic materials, sampling in the absorption bands. However, this often leads to undesired side effects.<sup>20</sup> Efforts to avoid such problems<sup>21</sup> resulted in the construction of light-switchable molecules in which the photochromic event is accompanied by changes in other properties, for instance, complexation of ions,<sup>22</sup> refractive

index,<sup>23</sup> electrochemical behavior,<sup>15,24</sup> or conformational changes in polymers.<sup>25</sup> Also, the modulation of the organization of large ensembles of molecules (and simultaneously the physical properties) in gels,<sup>26</sup> liquid crystals,<sup>27</sup> and Langmuir–Blodgett-films<sup>15,28</sup> represents a means to avoid destructive read out.

In the alternative approaches to molecular switches, which are the subject of this review, the unique properties associated with stereoisomers of chiral photoresponsive molecules and chiral supramolecular systems are exploited. Single handedness in its key components is an intrinsic feature of living organisms.<sup>29</sup> Precise control of chirality at the molecular and macroscopic level and in supramolecular assemblies is indispensable for the structure and properties of many natural materials and essential to the functioning of biosystems.<sup>30</sup> The use of light to control chirality in a reversible manner might therefore offer intriguing prospects and a powerful principle for the design of molecular switches and new photochromic materials. The left- (*S* or **M**) and right-handed (*R* or **P**) forms of a chiral compound represent two distinct states in a molecular binary logic element. As shown in Figure 2, a photorevers-



**Figure 2.**

ible system can be based on the interconversion of two chiral forms of helically shaped molecules, denoted **P** and **M**.<sup>31</sup>

A major advantage of *chiral optical switches*, compared to the photochromic systems summarized above, is that nondestructive read out of an optical recording system containing these organic materials is feasible by monitoring the optical rotation at wavelengths remote from the wavelengths used for switching. In contrast, read out using absorption or emission spectroscopy, monitoring near the switching wavelengths, often results in partial reversal of the photochromic process used to store the information. Chiroptical techniques offer the attractive feature that the change in chirality of the photochromic system can be detected. Although the use of circular dichroism (CD) read out still might be destructive, optical rotatory dispersion (ORD) measurements can be performed readily outside the absorption region.

Furthermore, when the chiral photochromic compounds are employed to control other (chiral) properties, such as, for instance, the organization of a liquid-crystalline phase (section V), nondestructive read out is easily accomplished.

Figure 2 schematically shows various chiral switching systems based on photochromic molecules: (A) Diastereomeric photobistable molecules. In this case the photochromic compound consists of two diastereomeric forms, i.e., **P** and **M'** helices, which can undergo photoisomerization by irradiation at two different wavelengths  $\lambda_1$  and  $\lambda_2$ . A closely related system (**A**–**X\***) involves an achiral photochromic unit (**A**), but the presence of a chiral auxiliary (**X\***) controls the change in chirality during the photochromic event. (B) Enantiomeric photobistable molecules. Two enantiomers are interconverted at a single wavelength by changing the handedness of the light. Unless *chiral light* is used, irradiation of enantiomerically pure **P** or **M** will always lead to a racemic mixture due to identical absorption of both enantiomers, irrespective of the wavelengths. By employing *l*- or *r*-circularly polarized light (*l*- or *r*-CPL), enantioselective switching in either direction might be accomplished. (C) Achiral photobistable molecules in a chiral assembly. The photoisomerization process induces changes in the chirality of the surrounding matrix, for instance, in the helical structure of a chiral polymer (as illustrated) or the chiral phase of a liquid-crystalline material. The photochemical event is recorded in this case via a chiral response of the structure, organization, or (chiroptical) properties of the larger ensemble.

In this review the various basic principles and molecular structures that have been explored to assemble chiral optical molecular switches will be discussed. Several approaches toward the photostimulation of functions using these chiroptical molecular switches are presented. Furthermore, applications of chiral photochromic compounds in the control of supramolecular organization and materials properties will be illustrated.

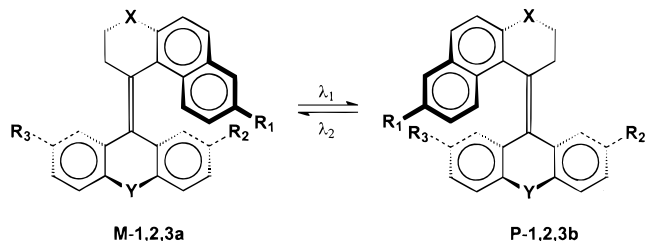
## II. Chiral Photochromic Molecules

### II.1. Overcrowded Alkenes

#### II.1.1. Pseudoenantiomers

Pseudoenantiomeric chiroptical switches are based on so-called sterically overcrowded alkenes (Scheme 1).<sup>32–34</sup> The molecules consist of an unsymmetrical upper part (tetrahydrophenanthrene or 2,3-dihydronaphtho(thio)pyran) connected via a double bond to a symmetric lower part (xanthene, thioxanthene, fluorene). To avoid unfavorable steric interactions around the central olefinic bond, the molecules are forced to adopt a helical shape. The chirality in these inherently dissymmetric alkenes, denoted **M** and **P** for left- (**1,2,3a**) and right-handed helices (**1,2,3b**), respectively,<sup>31</sup> therefore originates from distortion of the molecular framework. The tetrahydrophenanthrene-type upper part is bulky enough to inhibit fast racemization by movement of the aromatic moieties of the upper and lower halves through the mean plane of the molecules, but there is sufficient confor-

**Scheme 1. Chiroptical Molecular Switch Based on Pseudoenantiomers of Overcrowded Alkenes **M-1**, **2**, **3a** and **P-1**, **2**, **3b**<sup>a</sup>**



<sup>a</sup> **1**: R<sub>1</sub> = H, R<sub>2</sub> = OMe, R<sub>3</sub> = NO<sub>2</sub>, X = S, Y = S. **2**: R<sub>1</sub> = Me, R<sub>2</sub> = OMe, R<sub>3</sub> = H, X = CH<sub>2</sub>, Y = S. **3**: R<sub>1</sub> = NMe<sub>2</sub>, R<sub>2</sub> = NO<sub>2</sub>, R<sub>3</sub> = H, X = S, Y = S.

mational flexibility in the upper and lower halves to prevent excessive distortion of the central olefinic bond,<sup>35</sup> which could lead to rapid racemization. These overcrowded alkenes show structural resemblance to helicenes<sup>36</sup> and feature both a *cis*- and a *trans*-stilbene chromophore in the same molecule. A photochemically induced stilbene-type *cis*–*trans* isomerization<sup>37</sup> simultaneously results in reversal of the helicity.

The crucial step in the synthesis of overcrowded alkenes is formation of the central, sterically demanding, double bond. The diazo–thio ketone coupling method<sup>38</sup> was successful in connecting the upper and lower halves since steric constraints are gradually introduced via a sequence involving 1,3-dipolar cycloaddition to five-membered thiadiazoline, nitrogen elimination to three-membered episulfide, and finally sulfur extrusion to afford the alkene.<sup>39</sup>

It was found that the racemization barriers could be tuned over a range from 12 to >30 kcal mol<sup>-1</sup> by modification of the bridging unit X and Y in the upper and lower half of the inherently dissymmetric alkenes.<sup>40</sup> For instance, the influence of the (hetero) atom X on the magnitude of the racemization barrier of thioxanthenes (Y = S) (Scheme 1) is very pronounced. Going from oxygen to sulfur, the Gibbs energy of activation increases from 24.9 to 28.9 kcal mol<sup>-1</sup> (Table 1) with a simultaneous change of the

**Table 1. Racemization Barriers of **1**, **2**, and **3** Type Structures for Different Bridging Moieties X,Y (R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = H)**

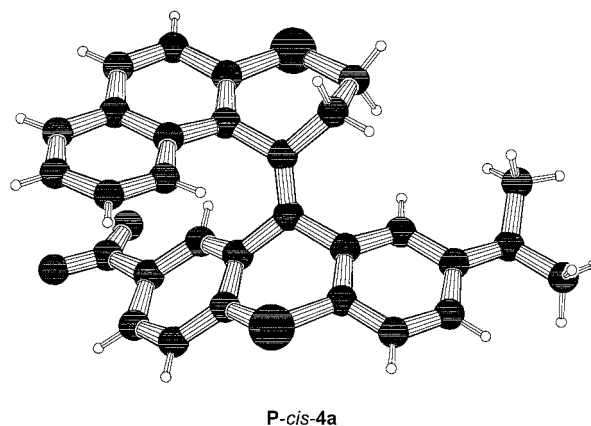
X	Y	racemization barrier (kcal mol <sup>-1</sup> )	C <sub>2</sub> –C <sub>11</sub> distance (Å)
O	O	24.9 ± 0.3	2.34
CH <sub>2</sub>	O	27.4 ± 0.2	2.48
S	O	28.0 ± 0.2	2.75
S	S	28.9 ± 0.1	2.75
S	CHCH	29.0 ± 0.3	3.10

interatomic distance C<sub>2</sub>–C<sub>11</sub> from 2.34 to 2.75 Å. The effect of enlarging this interatomic distance will be that the naphthalene unit of the upper half is pushed toward the thioxanthene moiety, and as a consequence, the steric hindrance at the so-called *fjord region* and the barrier for racemization are enhanced.<sup>40,41</sup>

Apparently there is a delicate balance between ground-state distortion, due to twisting and folding, and helix inversion.<sup>34,42</sup> The ability to tune the

barriers for thermal and photochemical racemization and isomerization processes is essential in the construction of a stable chiroptical switch based on **1**.

The molecular structure of *cis*-2-nitro-7-(dimethylamino)-9-(2',3'-dihydro-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene **4** (Figure 3) is illustra-



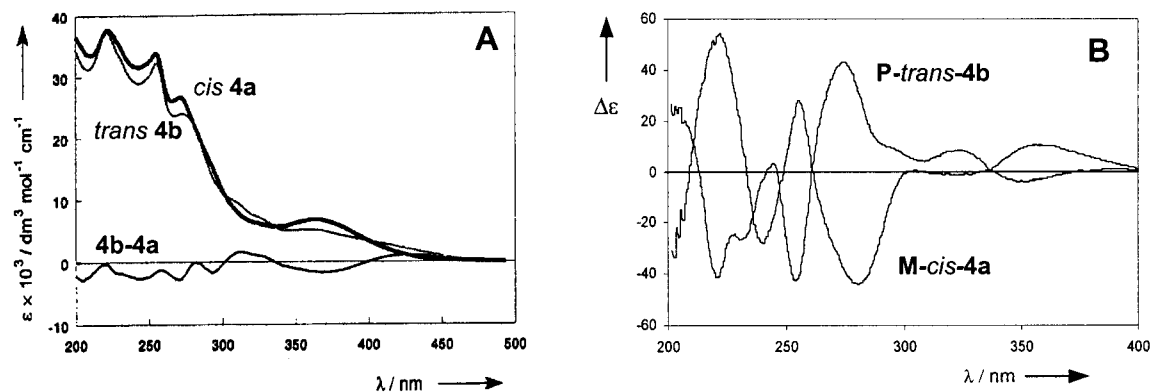
**Figure 3.** Pluto diagram of the crystal structure of **P-cis-4a**.

tive of the anti-folded helical shape of this type of chiral switch, in which the top and bottom halves are tilted up and down, respectively, relative to the plane of the central alkene. The arrangement shows only slight deviation from planarity at the central double bond (the dihedral angle is 5.4°) and a normal bond length (1.353 Å), although the extent of twisting and folding can vary considerably.<sup>35,40,43</sup>

The first chiroptical switching process was realized with thioxanthene-based alkenes **M-cis-2a** and **P-trans-2b** (R<sub>1</sub> = Me, R<sub>2</sub> = OMe, R<sub>3</sub> = H, X = CH<sub>2</sub>, Y = S) (Scheme 1).<sup>43</sup> Irradiation of enantiomerically pure **M-cis-2a** at 300 nm resulted in a photostationary state consisting of 64% **M-cis-2a** and 36% **P-trans-2b** as a consequence of a stereospecific interconversion of **M-cis** to **P-trans** isomers. A shift of 4% in the photostationary state was reached by using 250 nm wavelength light, which produced a sufficient change in the chiroptical properties for easy detection. Alternated irradiation (3 s intervals) at 250 and 300 nm resulted in a photomodulation of ORD and CD signals, but after 20 switching cycles, 10% racemization was observed.

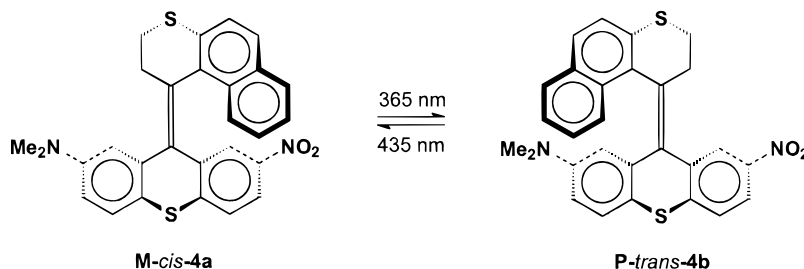
To improve the stability toward racemization, to tune the wavelengths for photoisomerization, and to increase the stereoselectivity of the photochromic process, a benzo[*a*]thioxanthylidene moiety was introduced.<sup>44</sup>

A remarkable enhanced stability ( $\Delta G_{\text{rac}} = 29.2$  kcal mol<sup>-1</sup>) and a highly stereoselective switching process was found with **4** containing donor and acceptor substituents in the thioxanthene lower half (Scheme 2).<sup>45</sup> In **M-cis**-isomer **4a**, the naphthalene chromophore is facing a nitro–arene acceptor moiety, whereas in **P-trans-4b**, a dimethylamino–arene donor moiety is close to the naphthalene chromophore. Besides causing relatively large differences in absorption spectra between **M-cis-4a** and **P-trans-4b**, which determine the large differences in isomeric composition in the photostationary states upon ir-

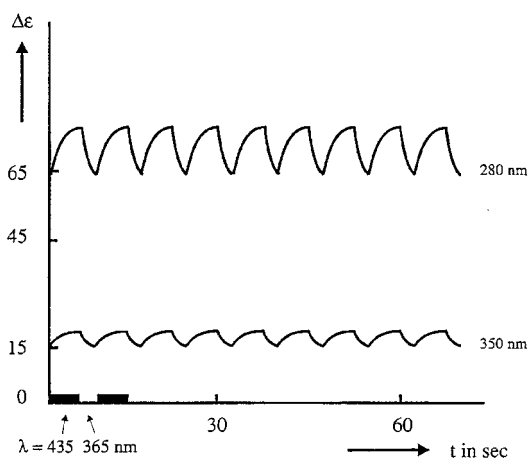


**Figure 4.** UV (A) and CD (B) spectra of **M-cis-4a** and **P-trans-4b**.

**Scheme 2. Stereoselective Photoisomerization of Donor–Acceptor-Substituted Molecular Switch 4**



radiation at the appropriate wavelengths, the substituent effects also resulted in a large bathochromic shift in the UV–Vis spectra of **4a** and **4b**, allowing the switching process to take place near the visible region of the spectrum (Figure 4). Alternated irradiation of enantiomerically pure **4** using 365 and 435 nm light resulted in diastereoselective interconversions between photostationary states composed of **M-cis-4a** and **P-trans-4b** with 30:70 and 90:10 ratios, respectively (CD detection, Figure 5).



**Figure 5.** Plot of  $\Delta\epsilon$  at 280 and 350 nm versus the irradiation time for the **M-cis-4a**  $\rightleftharpoons$  **P-trans-4b** isomerization, irradiation alternately at  $\lambda = 435$  and 365 nm.

In this case, a 60% difference in photostationary states and reversal of helicity was achieved and it was possible to perform 80 switching cycles without deterioration or racemization. The composition of the photostationary states, and as a consequence the excess of **M** or **P** helices, is strongly dependent on wavelength, medium, and substituents.<sup>45</sup> For instance, a pseudoracemate<sup>46</sup> of **4** (50:50 ratio of **M-cis-**

**4a** and **P-trans-4b**) was found at 313 nm, whereas no stable photostationary states were reached upon irradiation of **2** in polar solvents such as ethanol and chloroform. The introduction of a weaker donor moiety, as in **M-cis-1a** ( $R_1 = \text{H}$ ,  $R_2 = \text{OMe}$ ,  $R_3 = \text{NO}_2$ ,  $X = \text{S}$ ,  $Y = \text{S}$ ), resulted in low stereoselectivity.<sup>47</sup> In contrast, by enhancing the difference in donor–acceptor interactions via introduction of the dimethyl-amino donor group in the upper part, as in structure **3** ( $R_1 = \text{Me}_2\text{N}$ ,  $R_2 = \text{NO}_2$ ,  $R_3 = \text{H}$ ,  $X = \text{S}$ ,  $Y = \text{S}$ ), a 99:1 ratio of **M-cis-3a** and **P-trans-3b** was found upon irradiation at 435 nm. Although an extremely high stereoselectivity in this switching process is seen, this photochromic system suffers from poor reversibility compared to **4**.<sup>48</sup>

The photoresponsive systems based on chiral overcrowded alkenes, in which a change in the chiroptical properties is encountered, fulfill several of the requirements given earlier, and the high quantum yield ( $\Phi = 0.24\text{--}0.72$ ) for the photochromic process in either direction is an important feature. The reversibility during a large number of cycles remains to be established. Another critical issue for application in any information storage system is the response time.<sup>4</sup> On the basis of available photochemical data, it appears that high-speed switching is precluded, in particular when the chiroptical switches are incorporated in polymer matrices.<sup>47</sup> Recently it was, however, shown by using ultrafast laser spectroscopy that the cis–trans isomerization in overcrowded alkenes takes place in microseconds and the isomerization mechanism probably involves a strongly polar twisted phantom state.<sup>49</sup> An important characteristic of these chiroptical switches is the possibility to execute the writing, reading, and erasing cycle with a single physical method. Apart from writing (UV–Vis) and reading (nondestructive by ORD remote from the switching wavelengths), these chiral pho-

tochromic materials might be employed for an EDRAW (erasable direct read after write).<sup>3,50</sup>

### 11.1.2. Enantiomers

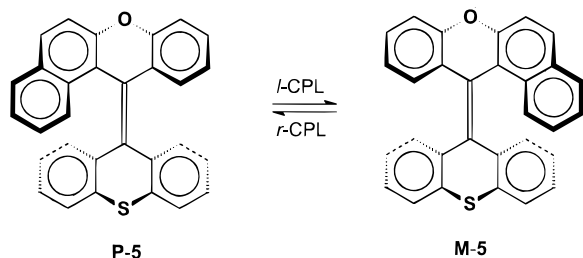
Following the pioneering studies by Kuhn,<sup>51</sup> a number of enantio-differentiating photochemical reactions using CPL have been reported.<sup>52</sup> It is therefore evident that the dynamic control of molecular chirality by means of circularly polarized light must be feasible provided the enantiomers of the compound are thermally stable but simultaneously show bistability upon irradiation. The enantiomeric excess that can be expected in the photostationary state is given by eq 1.

$$ee_{\text{pss}} = g/2 = \Delta\epsilon/2\epsilon \quad (1)$$

The selectivity of the molecular switch based upon CPL irradiation is governed by the anisotropy factor  $g$ , and for inherently dissymmetric alkenes,  $g$  seldom exceeds 1% and therefore  $ee$ 's below 0.5% are to be expected.<sup>53</sup>

Of the large number of sterically overcrowded alkenes that were synthesized,<sup>54</sup> compound **5** satisfied the requirements for a successful CPL switch (Scheme 3). Decisive factors are (a) irradiation with

#### Scheme 3. Photochemical Interconversion of P-5 and M-5 upon Irradiation with *l*- or *r*-CPL Light

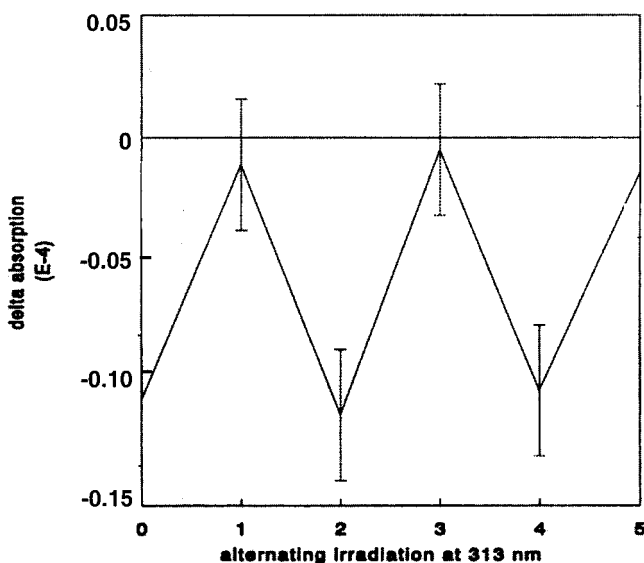


CPL light should cause the interconversion of enantiomers without any photodestruction; (b) the compound exhibits a high  $g$  factor; (c) the enantiomers should be thermally stable ( $\Delta G_{\text{rac}} > 21 \text{ kcal mol}^{-1}$ ); (d) the quantum efficiency for photoracemization should be high (since the rate of photoresolution is exponentially related to this quantity).<sup>55</sup>

The enantiomers of **5** were stable at ambient temperatures ( $\Delta G_{\text{rac}} = 25.9 \text{ kcal mol}^{-1}$ ) and fatigue resistant. They show a stereospecific photochemical isomerization process that reverses the helicity of the molecules and large circular dichroism (CD) absorptions, and optical rotations ( $[\alpha]_{436}^{20} = 900^\circ$ ), which are essential for detection of small  $ee$ 's, were found (Scheme 3). A rapid photoracemization of **P-5** was observed upon irradiation at 300 nm with unpolarized light ( $\Phi_{\text{rac}} = 0.40$ ; *n*-hexane), and the experimental  $g$  value ( $g = -6.4 \times 10^{-3}$  at 314 nm) indicates that an  $ee$  of 0.3% could be expected under ideal conditions.<sup>56</sup>

There are three switching steps involved in a CPL-based switch: (i) after irradiation of a racemate (**M,P**) with chiral light, one of the enantiomers (**P** or **M**) will be present in excess; (ii) irradiation at a single wavelength with alternating *r*- or *l*-CPL will result in modulation between right- and left-handed helices; (iii) the racemate will be obtained again after irradiation

with linearly polarized light (LPL). Deracemization and switching of **P,M-5** was indeed accomplished by irradiation at 313 nm with CPL.<sup>57</sup> Figure 6

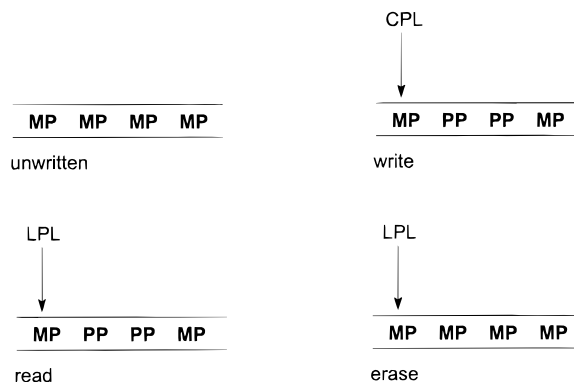


**Figure 6.** Difference in CD absorption at 313 and 400 nm ( $\Delta\epsilon_{313} - \Delta\epsilon_{400}$ ) for a solution of **5** ( $9 \times 10^{-5} \text{ mol L}^{-1}$ ) in *n*-hexane upon alternating irradiation with *l*- and *r*-CPL ( $\Delta\epsilon_{400}$  is used as an internal reference value to enhance accuracy). Irradiation was carried out with a 200-W high-pressure mercury lamp equipped with a water filter, a 10-nm bandwidth mercury line filter (313 or 400 nm), a polarization filter, and a  $\lambda/4$  plate (340 nm). The desired wavelength was selected by an interference filter. LPL was generated with a polarization filter, and CPL was generated from this LPL with a 340-nm  $\lambda/4$  plate. Irradiations of degassed alkene solutions were performed in 2-cm quartz CD cells.

illustrates the modulation of the CD absorption upon successive irradiations with *l*- and *r*-CPL. The switching occurred between photostationary states with  $ee$ 's of 0.07% and  $-0.07\%$  for **P** and **M** helices, respectively. Using LPL at the same wavelength, racemic **5** was obtained. The low  $g$  factor and the rather long irradiation times (approximately 30 min to reach the photostationary state) with the photobistable system based on **5** are key problems that need improvement.

The principle of a potential data storage system based on **5** is depicted in Scheme 4. Irradiation of a

#### Scheme 4. Proposed Optical Data Storage System Based on Optical Switching of Enantiomers<sup>a</sup>



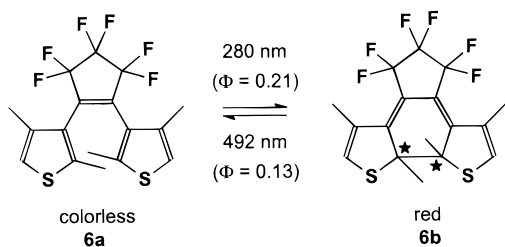
<sup>a</sup> Writing is done with circularly polarized light and reading and erasing with linearly polarized light.

racemate (**M,P**) using *r*- or *l*-CPL generates **P**-enriched or **M**-enriched regions, respectively. Detection is achieved using LPL by measuring optical rotatory dispersion (ORD) in reflection or transmission outside the absorption band. Written information can be erased by LPL (or unpolarized light) at the original wavelength generating (**M,P**) again. In principle, this system constitutes a three-position switch of racemic, **P**-enriched and **M**-enriched **5** with the distinct advantage that all the processes can be performed at a single wavelength merely by changing the chirality of the light.

## 11.2. Diarylethenes

Photochromic diarylethenes, which undergo a reversible photocyclization, are among the most promising photoswitches known today.<sup>4,58</sup> A reversible pericyclic reaction can take place in these compounds as irradiation with UV light of the colorless (nonconjugated) open form leads to the closed (colored) form, which can undergo ring-opening again with visible light. The introduction of 2-substituted heteroarene moieties eliminates the low thermal stability of the dihydro form, which is the main origin of the limited applicability of the reversible photocyclization of stilbene derivatives (Scheme 5).<sup>59</sup>

**Scheme 5. Photochemical Switching of Diarylethene 6<sup>a</sup>**



<sup>a</sup> Asterisk (\*) denotes stereogenic center.

Bridging the central alkene bond, to prevent unwanted *cis*–*trans* isomerization, is another key structural improvement. The introduction of a perfluorocyclopentene moiety led to the development of the perfluorocyclopentenebisthien-3-yl system **6** which is not sensitive to hydrolysis and shows excellent thermal and chemical stability as well as high fatigue resistance.<sup>60</sup> A drawback is the tedious synthesis based on perfluorocyclopentene, and recently reported cyclopentene analogues that are readily accessible via intramolecular McMurry coupling provide a useful alternative.<sup>61</sup> The groups of Irie and

Lehn have developed a series of diarylethenes, which covers the whole visible spectrum, by tuning the conjugation length and introduction of donor and acceptor substituents.<sup>58,62</sup>

The conrotatory ring closure<sup>63</sup> by irradiation of a symmetric dithienylethene **6a** generates the *C*<sub>2</sub>-symmetric closed forms (*S,S*)- and (*R,R*)-**6b**. The resolution by chiral HPLC of a number of these chiral closed forms was reported.<sup>64</sup> Upon ring-opening, the stereochemical information is however lost.

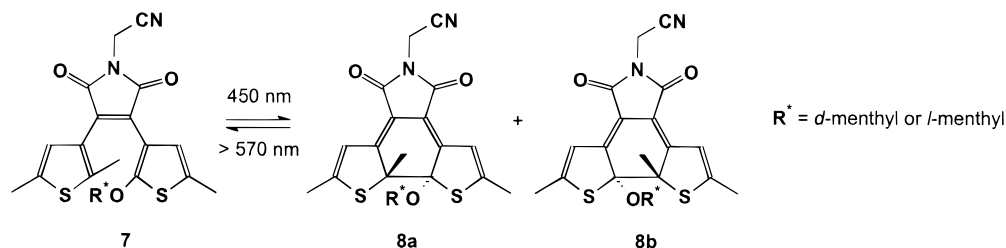
By introduction of an *l*- or *d*-menthyl moiety at the 2-position of the benzo[*b*]thiophene ring in a diaryl-maleimide-based switch **7**, a diastereoselective photocyclization could be accomplished (Scheme 6).<sup>64</sup> Irradiation at 450 nm in toluene at 40 °C resulted in the formation of **8** with a diastereomeric excess (de) of 86.6%.

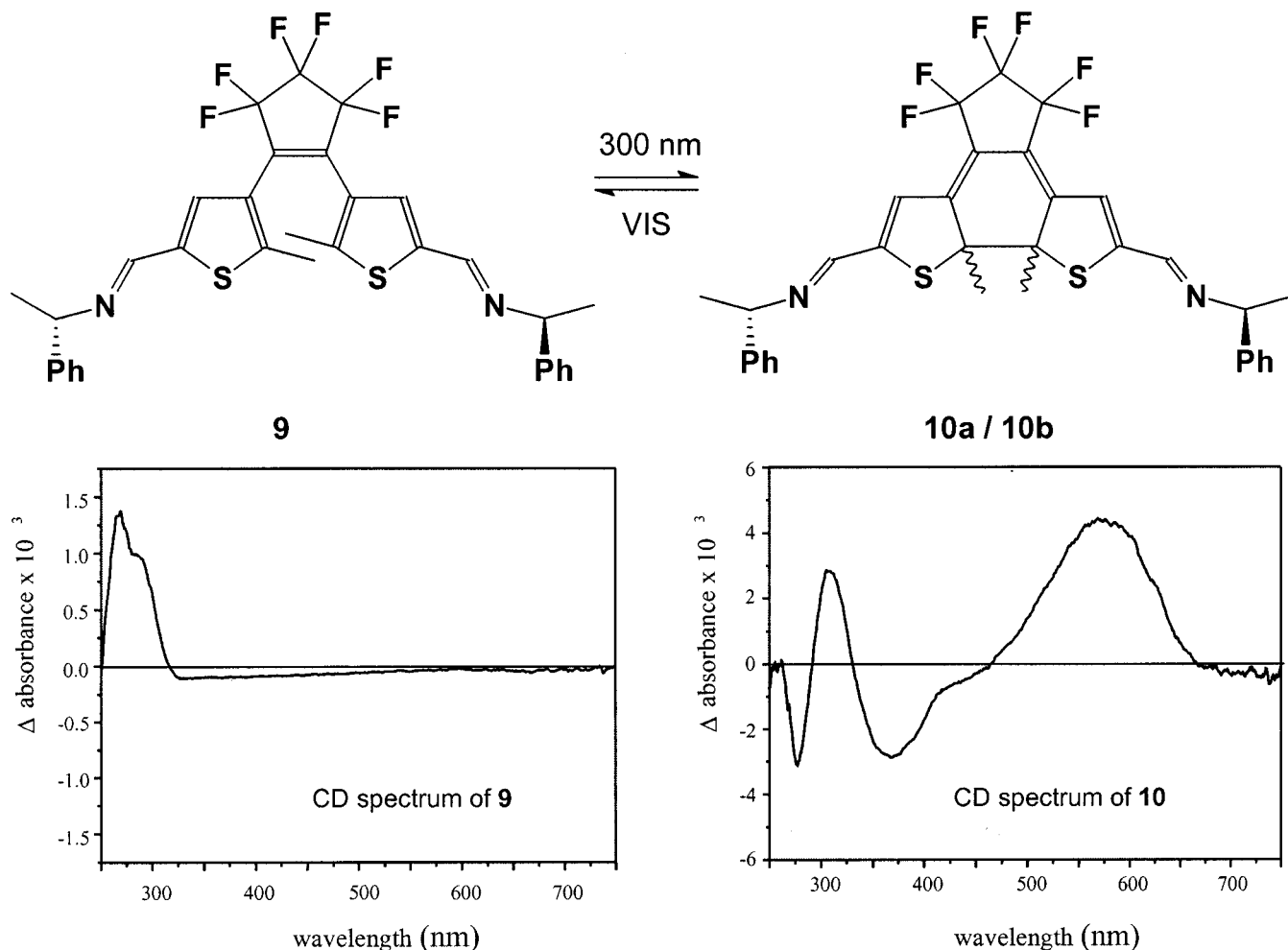
The solvent polarity was found to play an important role, as asymmetric cyclization was observed in THF and toluene but not in an apolar solvent like hexane. Upon photoexcitation, **6a** (Scheme 5) can adopt two conformations, planar and twisted, and photocyclization only proceeds through the planar conformation.<sup>64</sup> In the case of diarylethene **7**, containing a menthol chiral auxiliary, there are two diastereomeric planar conformations leading to the two diastereomers of cyclic product **8**. The strong solvent dependency of the asymmetric induction was attributed to lowering of the excited-state energy of the unreactive twisted form in more polar solvents providing a relaxation pathway for the less favorable planar diastereomer. As a consequence, the stereoselectivity in the photocyclization process is enhanced. The photochromic system might be used as a nondestructive read-out system but faces the problems of irradiation times and high sensitivity to temperature and medium effects.

In other cases it was found that even if the diastereoselectivity is almost zero in the photocyclization, the open and closed form show very distinct CD spectra.<sup>65</sup>

For instance, the bisimine-modified diarylethene **9**, containing (*S*)- $\alpha$ -phenylethylamine chiral auxiliary groups, did not show any CD effects beyond 325 nm in the open form but exhibits a distinct CD band at 575 nm after ring closure (Figure 7). It should be noted that the diastereomeric excess of **10** is only approximately 10%. The chiral perturbation of the closed conjugated form can be used for the “visible expression of chirality” of a chiral auxiliary group not absorbing in the visible range.<sup>65</sup>

**Scheme 6. Diastereoselective Photocyclization of Chiral Diarylethene Derivative 7**

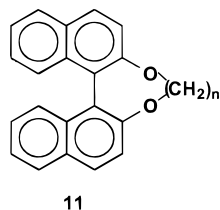




**Figure 7.** Chiroptical switch based on diarylethylene–bis-imine and CD spectra of the open form **9** and closed form **10**.

### II.3. Binaphthyl Derivatives

In an approach toward chiral photochromic triggers for liquid-crystalline materials, the photoracemization of a series of bridged binaphthyl derivatives **11** was investigated using time-resolved laser spectroscopy (Figure 8).<sup>66</sup> As is the case with 1,1'-binaphthyl



**Figure 8.** Cyclic acetals of 1,1'-binaphthol **11**.

itself,<sup>67</sup> photoracemization occurs in the triplet state by atropisomerism. The triplet lifetimes for the various bridged binaphthyls **11** are not deviating significantly, arguing against a bond-cleavage pathway as an alternative photoracemization mechanism.<sup>68</sup>

Smaller values for the dihedral angles around the bond connecting the two naphthalene parts in **11** will enhance the ground-state energies. The racemization of the binaphthyls through the triplet state will also depend on the same parameters that govern the

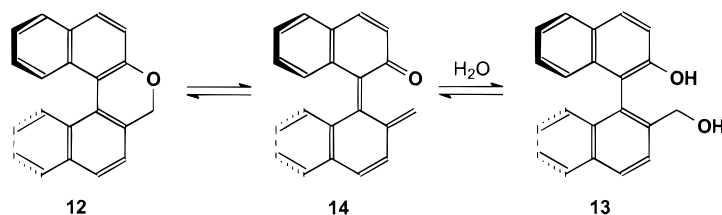
strain energy and as a consequence the activation barrier for the naphthalene rings to adopt a planar geometry in the transition state. The activation barrier for atropisomerism and the efficiency of intersystem crossing determine, therefore, to a large extent the photoracemization process. The photoresolution of these compounds and the induction of twisted nematic LC phases (vide infra) by irradiation with CPL was not successful due to either a low  $g$  factor or inefficient photoracemization.

Another approach was based on the photochromic behavior of 1,1'-binaphthylpyran (Scheme 7).<sup>69</sup> Irradiation of **12** ( $\lambda > 350$  nm; CH<sub>3</sub>CN/H<sub>2</sub>O) resulted in the formation of diol **13**, and irradiation at 254 nm reversed this process leading to pyran **12**.

Both pyran **12** and diol **13** were resolved, and a racemization barrier of 26 kcal mol<sup>-1</sup> was determined for **12**. Irradiation of optically active **12** leads to optically active **13** and concomitant photoracemization. A low efficiency of the photoracemization ( $\Phi_{\text{rac}} = 0.0025$ ) was found for **12**, making it less suitable as a CPL switch. In the reverse photochromic process, irradiation of optically active **13** leads to optically active **12** and no racemization of **13** is seen.

Nanosecond laser flash photolysis revealed the formation of 1,1'-binaphthyl quinone methide **14** acting as a key intermediate in both the photoracemization and the photochromic processes.

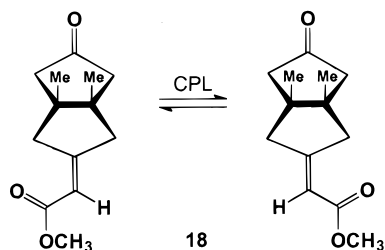


**Scheme 7. Chiral Photochromic 1,1'-Binaphthylpyran 12**

The major reaction of **14** was found to be the electrocyclization to **12**, and both photochromic and photoracemization reactions proceed through the ground state of **14**. This appears to be the first observation of photoracemization of a binaphthyl derivative that does not proceed through a triplet state. As the thermal racemization of **14** ( $k = 5 \times 10^{-2} \text{ s}^{-1}$ ) as well as the addition of  $\text{H}_2\text{O}$  are much slower than electrocyclization to **12** and rather low  $g$  factors ( $g_{\lambda > 360 \text{ nm}} = +0.002$ ) were observed, the potential for application as a LC trigger in a suitable spectral region is rather limited.

**II.4. Axially Chiral Aryl–Methylene Cycloalkanes**

A series of optically active aryl–methylene cycloalkanes was designed by Schuster and co-workers as chiroptical triggers (Figure 9).<sup>70</sup> Most of these compounds exhibit axial chirality, and due to the presence of a styrene-type chromophore, irradiation will lead to isomerization of the olefinic bond which results in racemization (Scheme 8).

**Scheme 8. Photoresolution of Axially Chiral Phototrigger **18** by CPL Irradiation**

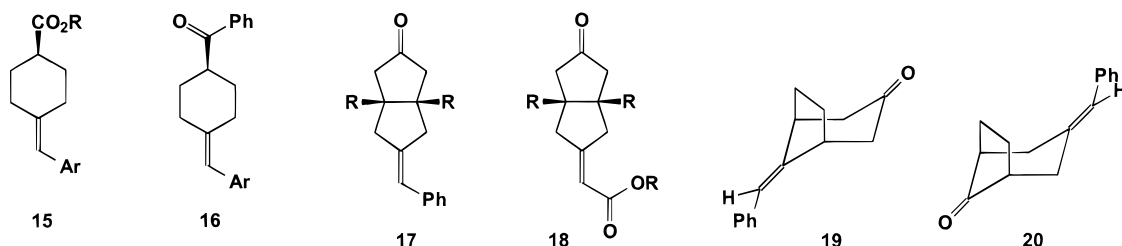
As the goal was the control of chirality by CPL irradiation, the photochemical reaction should exclusively lead to racemization with high quantum efficiency and the  $g$  factor should be sufficiently large to yield an ee in the photostationary state that can be readily detected. Optically active esters **15** and ketones **16** were obtained through Horner–Emmons olefination of the corresponding 4-ketocycloalkane-esters, employing the Hanesian asymmetric olefination<sup>71</sup> or a classical resolution as the key steps. Irradiation of methylester **15** ( $\text{R} = \text{Me}$ ) at 254 nm

leads to a fast and selective racemization process. In contrast, for the arylesters and ketones, photoisomerization and photodecomposition were found to be competing processes. Ester **15** ( $\text{R} = \text{Me}$ ) however has a very low anisotropy factor ( $g_{251} = 7.5 \times 10^{-5}$ ). Much higher values for  $g$  can be expected from inherently chiral chromophores and by exploiting the exciton coupling between the two chromophores present in arylester and ketones. The magnitude of  $g$  could indeed be increased by a few orders of magnitude. Both a suitable  $g$  factor and selective photoisomerization are however required for a successful CPL switch (see section II.1.2).

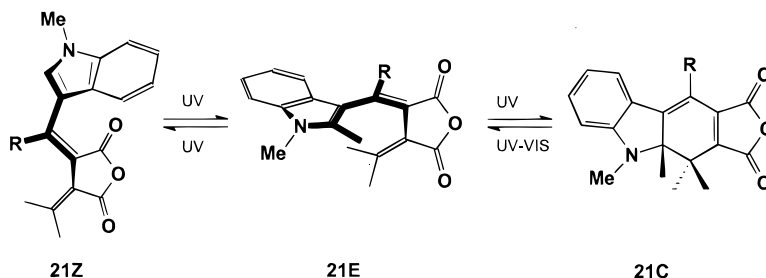
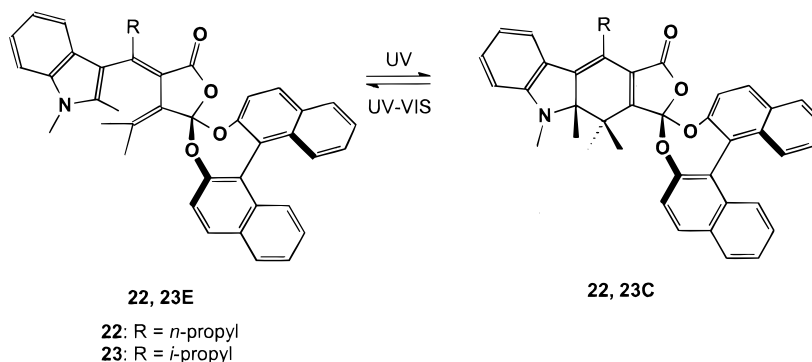
A considerable improvement was achieved by separating the light-absorbing and photoisomerization units in axially chiral bicyclo[3,3,0]- (**17**, **18**) and [3,2,1]-octan-3-one (**19**) systems (Figure 9). The ketone  $n-\pi^*$  transition is forbidden, resulting in a small extinction coefficient ( $\epsilon$ ) and often a large  $g$  value. Furthermore, the incorporation of a ketone chromophore in a rigid skeleton prevents a decrease of  $\Delta\epsilon$  due to averaging effects by conformers with opposite CD,<sup>72</sup> and in addition, very large  $\Delta\epsilon$  values have been observed with inherent dissymmetric (twisted) ketones.<sup>73</sup>

Irradiation of ketone **18** at  $\lambda > 305 \text{ nm}$  resulted in a selective and highly efficient photoracemization process. Typical features are fatigue resistance after 12.5 h of irradiation and a high quantum yield of 0.45 ( $\max \Phi_{\text{rac}} = 0.50$ ). Similar results were obtained for other bicyclo[3.3.0]octan-3-ones. For the bicyclo[3.2.1]-octan-3-one **19**, selective photoracemization at 313 nm with approximately 30% efficiency was found, whereas the isomeric ketone **20** shows photodecomposition, probably following a Norrish type I cleavage, which makes it unsuitable as an optical switching element.

The favorable photochemical and chiroptical properties, in particular the relatively high  $g$  factor of  $10.5 \times 10^{-3}$  at 305 nm, for compound **18** allowed Schuster to demonstrate the partial photoresolution by irradiation with circularly polarized light (Scheme 8).<sup>74</sup> The enantiomeric excess ( $[\gamma]_{\text{PSS}}$ ) in the photostationary state upon irradiation of racemic **18** depends on  $\Delta\epsilon$  and  $\epsilon$  (eq 1).



**Figure 9.** Alkylidenecycloalkane phototrigger.

**Scheme 9. *E,Z*-Isomerization and Photocyclization Processes for Indolyfulgide **21****

**Scheme 10. Diastereoselective Photochromism of Binaphthol-Based Indolyfulgides **22** and **23****


After 400 min of irradiation, a PSS was reached and on the basis of the CD spectrum a  $[\gamma]_{\text{PSS}}$  of 0.4%, in accordance with the value calculated on the basis of  $g_i$ , was observed. Furthermore, a nearly mirror-image CD spectrum was found when the handedness of the CPL was changed.

For ketone **19**, a high anisotropy factor  $g_{313} = 0.0502$  was found. Photoresolution by CPL irradiation at 313 nm as monitored again by CD spectroscopy, albeit a slow process (47 h irradiation) resulted in an exceptionally high enantiomeric excess of 1.6%.<sup>75</sup> The favorable  $g$  factor for these systems could be exploited in a CPL data storage system as shown in Scheme 4, but again, the response time needs considerable improvement.

These photoresolution processes involve rotation around the olefinic bond of the styrene moiety, which occurs rapidly from the triplet state. In the bichromophoric systems discussed here, absorption of light induced an  $n-\pi^*$  transition of the ketone resulting in a short-living (1–2 ns) excited singlet state. Intersystem crossing to the ketone triplet state is followed by intramolecular through-bond triplet–triplet energy transfer<sup>37,76</sup> to the lower lying styrene or  $\alpha,\beta$ -unsaturated ester chromophore<sup>77</sup> resulting in the isomerization process.

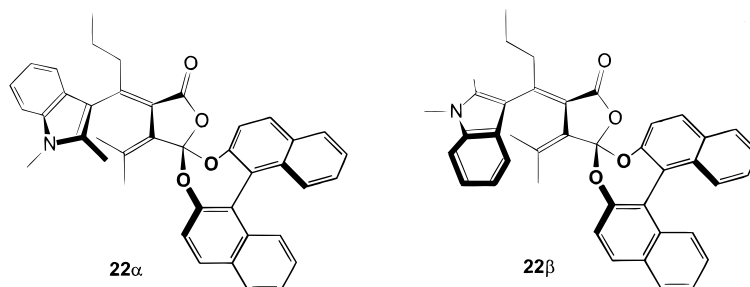
## 11.5. Fulgides

Following the discovery of the photochromic behavior of fulgides by Stobbe<sup>78</sup> at the beginning of the century, there has been considerable interest in these molecules as potential candidates for erasable and rewritable organic optical memory systems.<sup>79</sup> The bistability is based on the reversible photochemical conrotatory electrocyclozation of the 1,3,5-hexatriene moiety (Scheme 9). The introduction of alkyl substituents suppressed undesired sigmatropic hydrogen shifts,<sup>80</sup> and the thermal reverse reaction could be

circumvented by using a variety of heterocyclic derivatives such as furyl- and indolyfulgides.<sup>81</sup> A typical example is the indolyfulgide **21**.<sup>82</sup> The photochromic reaction involves the open-colorless and conformationally mobile *E*-form (often in equilibrium with the *Z*-form) and the closed-colored and rigid *C*-form.

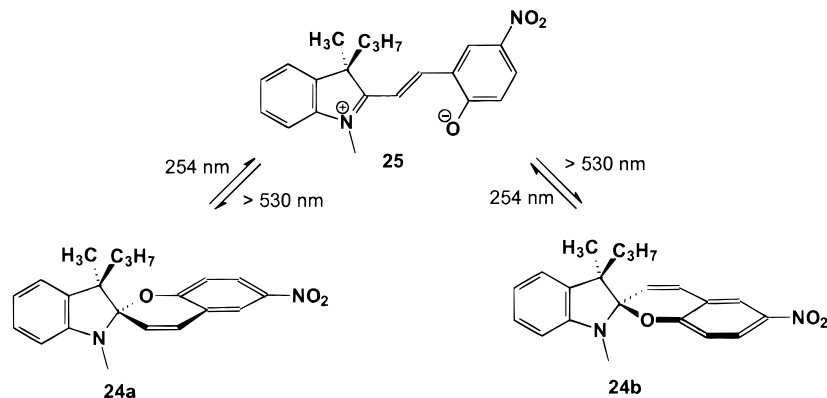
All three isomers are chiral as a result of a stereogenic center in the closed *C*-form and a helical conformation in the open (*E* and *Z*) structures. Enantiotopomerization was demonstrated, by dynamic NMR studies, for the *E*-form of a furylfulgide.<sup>83</sup> Introduction of an isopropyl group (R = *i*-Pr) in the fulgides reduced the *E*–*Z* isomerization drastically,<sup>84</sup> and as a consequence, the *E*-isomer of *i*-Pr-substituted indolyfulgide **21** could be resolved by chiral HPLC. An activation energy for thermal racemization of 25.6 kcal mol<sup>-1</sup> was obtained for the *E*-isomer. Irradiation at 405 nm in toluene resulted in a photostationary state with a high excess of the colored form (*E*:*C* = 19:81) without formation of the *Z*-isomer. Irradiation with visible light at  $\lambda > 580$  nm led to the ring-opened form **21E**, exclusively. The switching between the photostationary states was readily followed by CD. A major drawback is the gradual photoracemization at 405 nm.

In a different approach, binaphthol was introduced as a chiral auxiliary (Scheme 10).<sup>85</sup> In this case diastereoselective photochromism was observed between the open (**P**)-**22E** form and the closed (9*a*,*S*)-**22C** forms. In this case, the stereochemical features of the chiral photochromic system are more complicated. The open form occurs as two major conformers designated  $\alpha$  and  $\beta$ , e.g., (**P**)-**22E $\alpha$**  and (**P**)-**22E $\beta$** , in a 57/43 ratio in a rapid equilibrium at room temperature (Figure 10). Only (**P**)-**22E $\alpha$**  adopts the right geometry for rapid photocyclization, and therefore, photochemical ring closure is accompanied by (**P**)-



**Figure 10.** Structure of two conformers **22E $\alpha$**  and **22E $\beta$** ; **P** indicates the helical configuration of the open form; thermal isomerization involves rotation of the indole moiety interconverting **22 $\alpha$**  and **22 $\beta$**  (and vice versa).

### Scheme 11. Diastereoselective Photochromism of Spiropyran **24**



**22E $\beta$**  to (**P**)-**22E $\alpha$**  interconversion. Irradiation at 366 nm generates a PSS with **22C/22E** = 86/14 and a diastereomeric ratio of 95/5 for the closed form. Subsequent irradiation at 495 nm regenerates the open form {(**P**)-**22E $\alpha$** /**(P)**-**22E $\beta$**  = 57/43;  $\Phi_{\text{decoloration}} = 0.18$ }.

The stereoisomerization processes were found to depend strongly on the substituent pattern; for instance, *i*-Pr-derivative **23** (R = *i*-Pr) shows slow isomerization (125 days at 6 °C) between the diastereoisomers of the open *E*-form as well as photodecomposition.

Although further improvements are required, the easy and nondestructive detection by the change in optical rotation and the reasonable fatigue resistance (70% of the signal after 300 cycles) are attractive features of this diastereoselective photochromic system.

## II.6. Spiropyrans

Hirshberg proposed that the photochromism of spiropyrans could form the basis for a photochemical memory device.<sup>86</sup> These photoresponsive materials have found application as light filters in, e.g., sun glasses and as optical recording media, and numerous studies have been devoted to this class of photochromic compounds.<sup>87</sup> The photochromic (and thermochromic) behavior is due to the interconversion of the closed spiropyran form and the open merocyanine dye. UV irradiation leads to the open form, which reverts to the closed form either thermally or by irradiation with visible light. The spiro carbon atom is a stereogenic center in the spiropyran, but as a consequence of the achiral nature of the merocyanine form, the photochromic process will always lead to

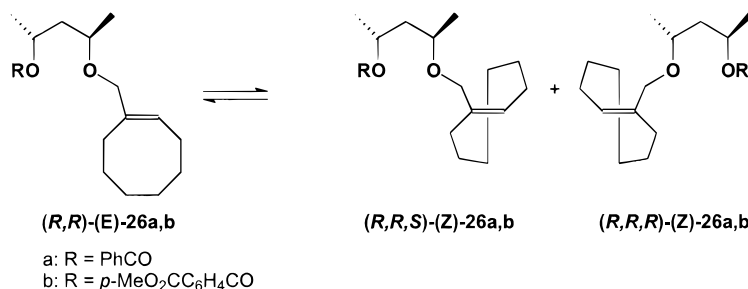
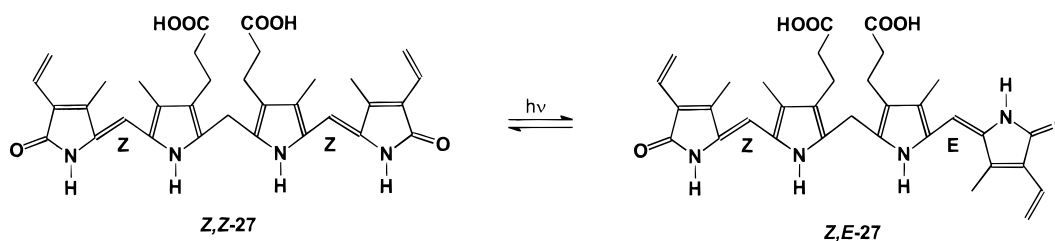
racemization. When a chiral substituent remote from the spiro center was present, diastereoisomers of spiropyran could be isolated but rapid epimerization of the spiropyran moiety occurred.<sup>88</sup> By the introduction of a stereogenic center at position 3 vicinal to the spiro carbon in **24**, photochemical switching of optical activity could be accomplished (Scheme 11).<sup>89</sup>

A diastereomeric ratio of 1.6/1.0 was found, and a change in CD absorption at 250 nm was monitored upon irradiation with UV (254 nm) and with visible (>530 nm) light. An intriguing temperature-dependent CD was observed, which was attributed to an inversion of the diastereomeric composition at low temperatures. Also, a photochromic transition-metal complex, based on  $\eta^6$ -spirobenzopyran tricarbonyl chromium, has been reported; a diastereoselective ring-closure is observed which is attributed to an intramolecular metal–oxygen interaction.<sup>90</sup>

## II.7. Tethered Cyclooctene

On the basis of a number of studies on the sensitized enantio-differentiating *E*–*Z* photoisomerization of cyclooctene, it became evident that the geometry of singlet exciplexes that are involved determine to a large extent the stereochemical course of the process.<sup>91</sup> In an approach to control the exciplex geometry, the cyclooctene moiety in **26** was connected covalently to arylcarboxylate sensitizers via a (2*R*,4*R*)-2,4-pentanediol chiral tether (Scheme 12).<sup>92</sup>

Upon irradiation of the benzoate derivative **26a**, a PSS was reached with a *Z/E* ratio of 8/10 and a diastereomeric excess of 19%. A forward *E* to *Z* isomerization showed a relatively high diastereoselectivity, but the reverse reaction, the *Z* to *E* isomerization, did not show any diastereodifferentiation.

**Scheme 12. Diastereoselective Photoisomerization of Cyclooctene **26** by Intramolecular Sensitization****Scheme 13. Structure of Bilirubin-III $\alpha$  **27** and  $Z \rightleftharpoons E$  Photoisomerization**

The latter finding was attributed to very fast intramolecular quenching accelerated by the high strain of the *Z*-isomer.

The highest diastereoselective photoisomerization was observed with terephthalate derivative **26b** (de = 44%) which compares favorably to the intermolecular chiral photosensitizations using chiral benzoates with which stereoselectivity never exceeded 7%.<sup>91,92</sup>

**II.8. Bilirubin-III $\alpha$  Photoisomerization**

The principle of the chiroptical switch based on the symmetrical substituted bilirubin-III $\alpha$  **27** involves the interconversion of the two diastereoisomers of this bichromophoric molecule in a complex with the human serum albumin (HSA).<sup>93</sup> The orientation of the two chromophores in the protein complex leads to strong exciton coupling in the CD.<sup>94</sup> Irradiation switching between the diastereoisomers results in large changes in the chiroptical properties. The natural yellow pigment bilirubin-IX $\alpha$ , which is not optically active, forms a 1:1 complex with HSA resulting in intense bisignate CD absorptions. *Z*–*E* photoisomerization in this complex resulted in a significant change in the CD spectra, but due to competing photocyclization of bilirubin-IX $\alpha$ , it is less suitable for the development of a chiroptical switch.<sup>95</sup> On the contrary, bilirubin-III $\alpha$  did not show photocyclization, and selective interconversion of the *Z,Z*-isomer to the *Z,E*-isomer in the bilirubin-III $\alpha$ /HSA complex was observed (Scheme 13).

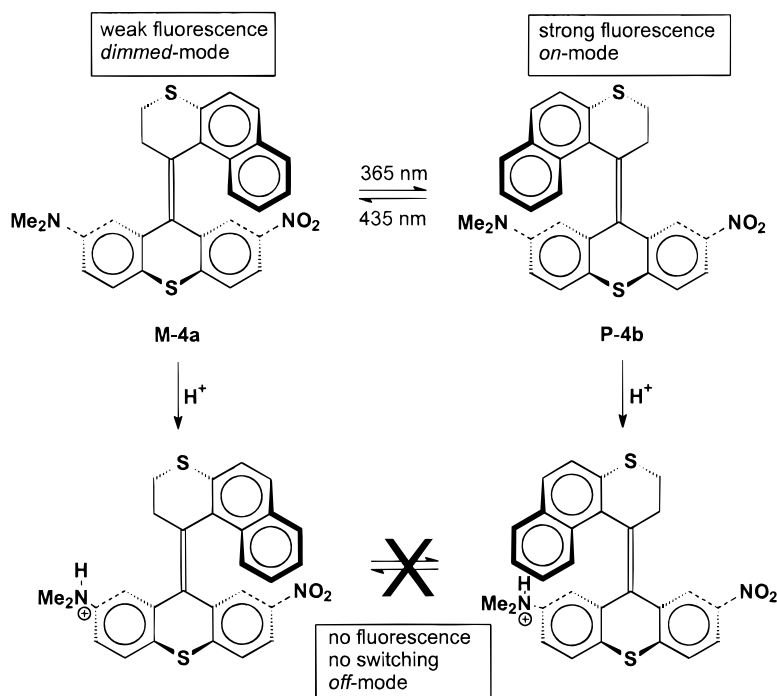
Switching between photostationary states containing 32% (*Z,E*)-bilirubin-III $\alpha$ /HSA and 20% (*Z,E*)-bilirubin-III $\alpha$ /HSA was accomplished using blue ( $\lambda = 430$  nm) and green ( $\lambda = 544$  nm) light. The changes in CD are readily detected, and after 10 switching cycles, only a small decrease (1.5%) in the CD signal was observed.<sup>93</sup> The strong exciton coupling and the effective modulation might be exploited in chiral-protein free-tetrapyrrole-based chiroptical switches.

**III. Multifunctional Chiral Switches****III.1. Photoswitching of Luminescence**

A change in the fluorescence emission from the different forms involved in the photochromic system has been observed in a number of multifunctional switches.<sup>96</sup> Modulation of fluorescence is a particularly attractive feature as fluorescence offers an additional read-out method and is highly sensitive to probe medium and excited-state effects. An on/off switching of the emission was found in the binaphthol-based indolylfulgide chiral photochromic system (Scheme 9).<sup>97</sup> The open form *E* did not exhibit fluorescence when excited at  $\lambda > 300$  nm. In contrast, the closed form *C* (absorption maximum = 471 nm) showed a weak but distinct fluorescence ( $\lambda_{\text{max}} = 610$  nm;  $\Phi = 0.01$ ) when excited with 470 nm light in toluene.

Dual-mode photoswitching of luminescence was observed in the case of chiral overcrowded alkenes.<sup>98</sup> A highly desirable property of multifunctional photochromic systems is gated response.<sup>99</sup> Gated photochemical reactivity implies that no molecular change occurs upon irradiation unless another external stimulus, either physical or chemical, is applied to the system.<sup>24c,24e,62a,96,100</sup> A major advantage is the possibility to lock (or protect) stored information in the photobistable material. A number of chemical gated photochromic systems in which, for instance, ion binding or photochromic and electrochemical properties are mutually regulated have been reported.<sup>101</sup> In the case of the donor–acceptor-substituted overcrowded alkenes, it was observed that reversible protonation of the dimethylamine donor moiety could be used to regulate the photochemical event (Scheme 14). The switching process of both the *cis* and *trans* forms was blocked by the addition of, e.g., trifluoroacetic acid. The donor–acceptor-substituted lower half in **M-cis-4a** and **P-trans-4b**, essential for stereoselective photoisomerization, was converted in an ineffective acceptor–acceptor

## Scheme 14. Dual-Mode Photoswitching of Fluorescence



(nitro and ammonium) substituted unit.

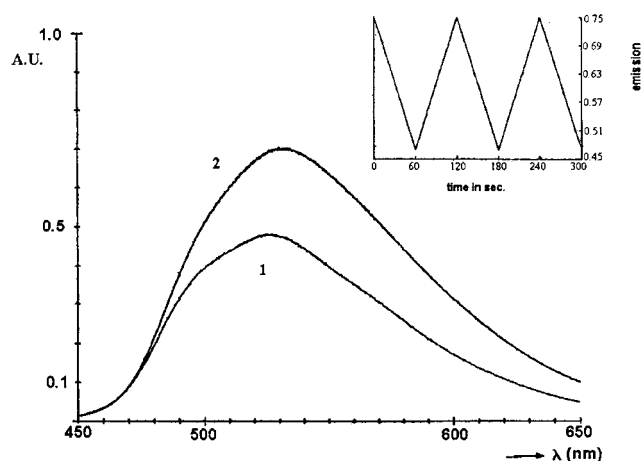
Upon excitation of **P-trans-4b** and **M-cis-4a** at 300 nm, fluorescence was observed at  $\lambda_{\text{max}} = 531$  and 528 nm, respectively. The integrated fluorescence quantum yield (400–600 nm; ethanol) of **P-trans-4b** is 0.153 and of **M-cis-4a** is 0.137. The fluorescence emission is attributed to an intramolecular charge transfer of the dimethylamine donor unit and is in accordance with the fluorescence in *N,N*-dimethylaniline.<sup>102</sup> Photomodulation of emission was achieved (Figure 11). Protonation of these photochromic com-

lation of chirality and fluorescence can be accomplished as well as switching between three distinctive states: *on*, *dimmed*, and *off* (Scheme 14). For this system, two states with different intensities of fluorescence, the *on* and *dimmed* state, are observed. After protonation, fluorescence is quenched and both switching and emission are in the *off* mode, which constitutes a locking step. Deprotonation reestablishes the photoswitching and fluorescent properties (*on* mode). Using time-resolved fluorescence spectroscopy and measuring circularly polarized luminescence, it was recently found that the chirality of the fluorescent excited states strongly depends on the polarity of the solvent.<sup>104</sup>

Another interesting recent example concerns a 2,11-diaza[3,3](9,10)anthracene paracyclophane substituted with two chiral camphanic acid moieties; in this case the photointerconversion in one direction is accompanied by circularly polarized chemiluminescence.<sup>105</sup>

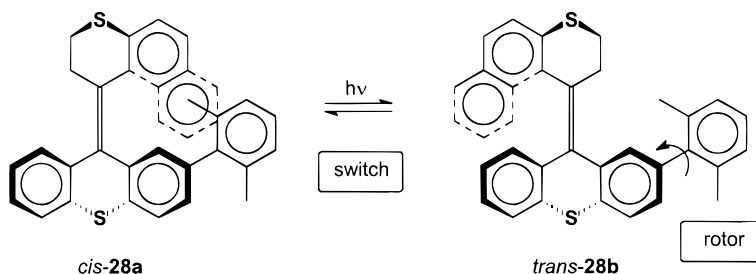
## III.2. Control of Motion

Control of mechanical effects, in particular translational or rotational motion by light,<sup>11,106</sup> offers a considerable challenge in the design of multifunctional photoswitchable systems. An approach toward a switchable molecular rotor involves control of the rotation around a single bond in a photoswitchable molecule modified with a biaryl-type rotor (Scheme 15). The thioxanthene-based helical-shaped overcrowded alkene that can adopt a *cis* and *trans* geometry was functionalized with a xylyl group as a potential rotor. Photoisomerization between the *cis-28a* and *trans-28b* helices could cause a distinct difference in the steric hindrance for the biaryl rotation as the xylyl moiety faces the large naphthalene unit in the case of the *cis* conformation. Dynamic



**Figure 11.** Fluorescence emission spectra (*n*-hexane) of photostationary states of *cis-4a* and *trans-4b* in 90:10 and 30:70 ratios (A.U. = arbitrary units, relative intensities). Inset: modulated emission signal during alternating irradiation at 365 and 435 nm (excitation 300 nm, irradiation time 60s).

pounds also resulted in complete quenching of the emission, whereas after deprotonation, using triethylamine, fluorescence intensities of **M-cis-4a** and **P-trans-4b** were fully recovered.<sup>103</sup> With this gated photochromic system, proton-dependent photomod-

**Scheme 15. Switchable Molecular Rotor**

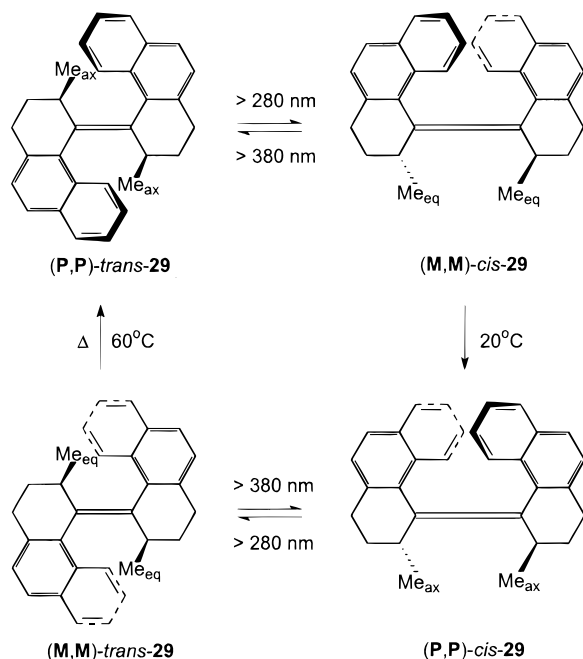
NMR studies revealed barriers for the biaryl rotation of  $\Delta G^\ddagger = 19.0$  and  $19.7$  kcal mol<sup>-1</sup> for the *cis* and *trans* isomers, respectively. In contrast with expectation, the barrier for *trans* was higher than that for *cis*, a feature which was supported by semiempirical calculations. The observed isomerizations were attributed to distinct differences in the chiral conformations and steric effects associated with folding in the molecules. Related unusual dynamic behavior in other helical-shaped alkenes was recently observed.<sup>107</sup>

The above example suffers from a small difference in energy barriers and inefficient photoswitching. Recently we demonstrated that the intrinsic handedness associated with chiroptical molecular switches can be used to accomplish monodirectional rotatory motion controlled by light.<sup>108</sup> When (3*R*,3'*R*)-(P,P)-*trans*-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene **29**, which is stable due to the favorable axial arrangement of the two methyl substituents, was irradiated with appropriate UV light, the diaxial *cis* form of similar helicity (P,P-*cis*-**29**) was formed (Scheme 16). Low-temperature irradiation

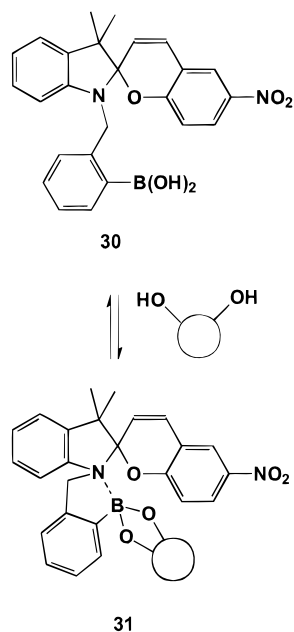
of the two methyl substituents. Continued irradiation using light of the same wavelength resulted in a second isomerization, leading to the unstable diequatorial (M,M)-*trans* compound that was readily converted back to the diaxial (P,P)-*trans* starting compound upon heating to 60 °C. The total process involves a full monodirectional 360° rotation of one-half of the molecule relative to the other half. This rotation is driven by the two photochemical and two thermal isomerization steps, and the absolute configurations of the two stereogenic centers completely govern the directionality. These findings prove the principle of a light-driven molecular rotor.

**III.3. Molecular Recognition**

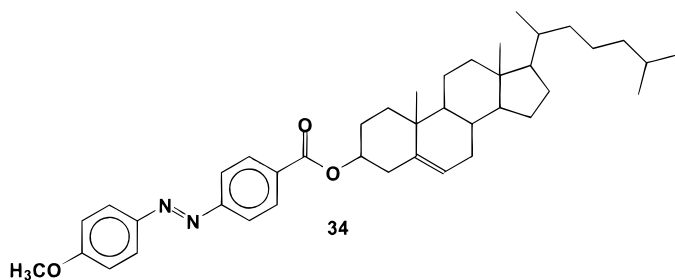
Following the pioneering work of Shinkai<sup>109</sup> on photoresponsive host-guest systems, in particular the use of photoactive crown ethers to control complexation, a number of studies have focused in recent years on controlling molecular recognition by means of external stimuli such as light.<sup>110</sup> Results obtained so far have confirmed the notion that the control of such complex functions is still difficult to achieve and the efficiency falls behind that of biological control elements.<sup>111</sup> On the other hand, photoactive systems, which mimic specific features of biosystems, are usually much easier to study. Photoactive receptor systems were, for instance, developed to control sugar binding in a reversible manner. A saccharide receptor, containing a diarylethene photoswitchable group, was able to change the binding event of glucose. The diarylethene was functionalized with two boronic acids,<sup>112</sup> and it was found that the carbohydrate preferentially forms esters with the boronic acid moieties in the parallel conformer of the ring-opened form in which the boronic acids face each other. The complexation was 40% blocked after irradiation with UV light, but irradiation with visible light to the ring-opened form fully restored the complexation ability.<sup>113</sup> Employing nitro-spiroprans bearing a boronic acid group, diols and sugars were detected by color change (Scheme 17). In this photochromic compound **30**, an intramolecular interaction of the boronic ester with the tertiary amine can take place. The closed form **31** interconverts upon irradiation to the merocyanine form with simultaneous disappearance of the tertiary amine group. In particular, *cis*-diols show a high affinity to form boronic esters and the diol and sugar binding process can be controlled photochemically by switching from the closed to the open form. Detection can take place visually by the observation of a change of color.<sup>114</sup>

**Scheme 16. Light-Driven Monodirectional Molecular Rotor**

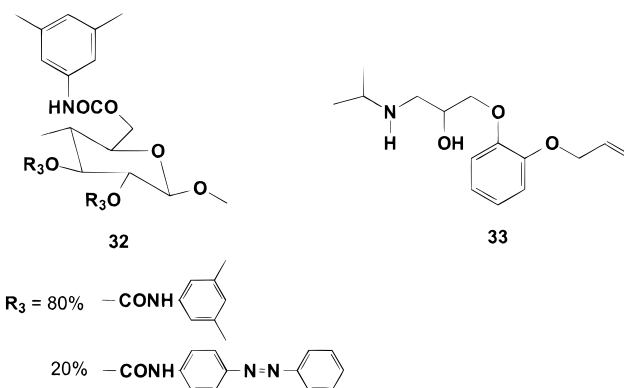
tion experiments proved that this irreversible process involved a (M,M)-*cis* intermediate that was only stable below -40 °C due to the equatorial arrange-

**Scheme 17. Boronic Acid Modified Spiropyran 30 for Reversible Sugar Binding**


In a different approach, complexation of spiropyran in cyclodextrins (CDs) was used to control the photochemical reaction.<sup>16</sup> A sulfonic acid functionalized spiropyran formed a 1:1 inclusion complex with CDs. However, only the closed form of the spiropyran was bound to  $\beta$ -CD, and as a result, no photochemical reaction was observed. Comparison of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD showed that only the pyran moiety of the sulfonic acid modified spiropyran was included in the cavity of  $\beta$ - and  $\gamma$ -CD whereas the small cavity of  $\alpha$ -CD prevents complexation. Furthermore, the stability of the inclusion complex of  $\beta$ -CD with spiropyran was higher than the stability of the complex with  $\gamma$ -CD, which was attributed to the larger number of water molecules excluded from the  $\beta$ -CD cavity. Similar observations were made for a nitro-spiropyran-modified  $\beta$ -CD. Complexation of the closed nitro-spiropyran in  $\gamma$ -CD and simultaneous addition of small guests, such as cyclohexanol, depressed the photoisomerization. Larger guests, for instance, *l*-borneol, enhanced the isomerization process because the spiropyran is displaced from the cavity by a guest molecule.<sup>115</sup> When a nitro-spiropyran was attached to a  $\beta$ -CD via an indoline moiety instead of the benzopyran moiety, solvent-polarity-dependent photochromism was observed.<sup>116</sup>

**Scheme 18. Reversible Photochemical Control of Gel Formation, Modulated Transmittance of an *n*-Butanol Gel<sup>a</sup>**


<sup>a</sup> Inset adapted from ref 119.

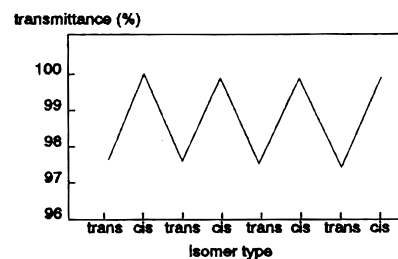


**Figure 12.** Azobenzene-functionalized cellulose derivative **32** for photocontrol of chiral recognition in a membrane consisting of **33**.

To achieve photocontrol of chiral recognition in a membrane, cellulose and amylose derivatives bearing a [4-(phenylazo)phenyl]carbamate residue attached to the glucose units were prepared.<sup>117,118</sup> The chiral recognition during enantioselective adsorption from a racemic mixture is effected by the cis-trans ratio of the azobenzene units. The trans isomer of the modified polysaccharides (**32**) showed higher enantioselectivity than the cis isomer when incorporated in a membrane of compound **33**. Switching between the two states in the membrane resulted in a change in the enantiomeric excess of the adsorbed material from 43% (trans) to 38% (cis) for the system depicted in Figure 12. The difference in chiral recognition was attributed to a difference in ordering of the polymer and a change in solubility. Notwithstanding the demonstration of a promising principle, major improvements on selectivity, rate, and efficiency of the photoisomerization are necessary.

### III.4. Reversible Gel Formation

Shinkai reported reversible gel formation by using cholesterol functionalized with a photoreversible azobenzene moiety.<sup>119</sup> 4-Methoxyazobenzene was attached via an ester linkage to cholesterol (Scheme 18), and the resulting compound **34** proved to be an excellent gelator. For instance, only 0.5 mg of *trans*-**34** forms a gel with 1.0 mL of *n*-butanol at 15 °C ( $T_g$ ). Gel formation was effected by photoisomerization as irradiation ( $330 < \lambda < 380$  nm) afforded a photostationary state with 38% cis isomer and a  $T_g$  of 2 °C. The thermal reisomerization to the trans form was



slow in the dark, but rapid *cis*–*trans* isomerization took place upon irradiation at  $\lambda > 460$  nm. Alternated irradiation at 10 °C provided a gel with 97.8% transmittance for *trans*-**34**, whereas the *cis*–*trans* mixture (38/62) showed 100% transmittance. In addition, the *trans*-azobenzene-modified gelators show a CD effect because they form helical aggregates. In contrast, the *cis* isomers did not show a CD effect and hence the sol–gel phase transition can be controlled by light with nondestructive read out by CD.<sup>26b,120</sup>

#### IV. Photochromic Polymers

The development of photochromic macromolecular materials for optical data storage<sup>121</sup> and the construction of biomaterials in which the structure and functions can be regulated by light has seen rapid progress in recent years.<sup>4c,14c,122</sup> A number of reviews cover various aspects of photochromic polymers and photoswitchable biomaterials.<sup>4c,14c,123</sup> Only chiral photochromic polymers will be discussed as far as key stereochemical features are involved. For other (material) aspects of photoresponsive optically active polymers, the reader is referred to reviews. Polymers are excellent supporting materials for practical applications of photochromic compounds because they cause relative stability and easy processability. The occurrence of a glass transition temperature ( $T_g$ ) might offer another important advantage. Below  $T_g$  the segmental motion of the polymer chain is frozen, and this effect might be used to enhance the lifetime of the stored information. For instance, in the case of the structural variation induced by the *trans*–*cis* isomerization of azobenzenes, the stability of the *cis* form can be stabilized in the glassy state.<sup>23b,124</sup> Several photoresponsive stereochemical effects have been observed: (i) the chiral matrix imposes particular geometrical constraints to an achiral photochromic unit; (ii) the change in structure of the two achiral isomeric forms induces a change in the conformation or organization of a chiral macromolecular matrix; or (iii) the chirality of the polymer is modulated due to the presence of a chiral photo-switch. Reversible stereochemical changes are inherent to many photoswitches in biological systems.<sup>125</sup> Illustrative of this is rhodopsin, the photoresponsive unit responsible for the process of vision. The photochromic retinal molecule is covalently bound to the membrane protein opsin, and upon exposure to light the **11-*cis*** isomer is converted into the **11-*trans*** isomer in a very fast process. The photochemical isomerization triggers a number of events including a change in the conformation of the protein and membrane permeability, ultimately leading to a neural signal.

##### IV.1. Chiral Matrix Effects

Matrix effects on the photochromism of spiropyran have been extensively studied, mainly in order to enhance the stability of the open form. The conversion of the (chiral) spiropyran to the zwitterionic merocyanine dye (Scheme 11) is accompanied by a large change in dipole moment. Dipolar structures

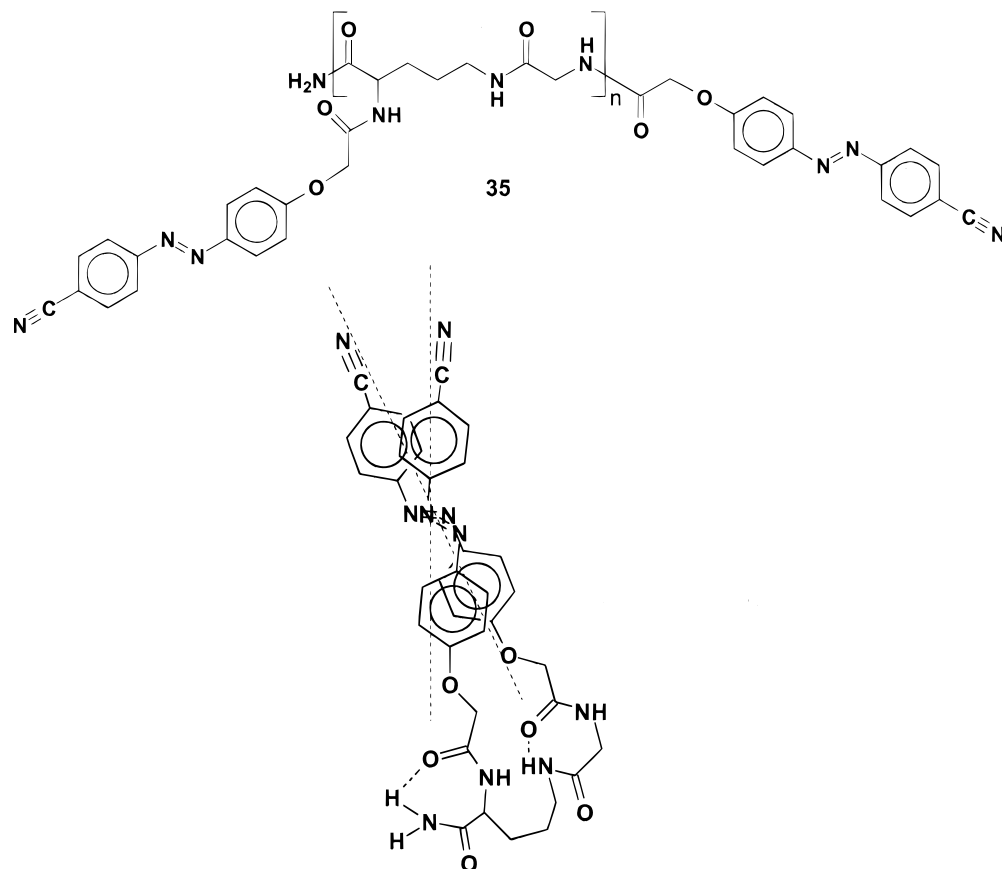
are able to aggregate, and besides restricted mobility, the enhanced thermal stability of the open form in several matrices is attributed to the formation of H-aggregates or J-aggregates.<sup>126</sup> The H- and J-aggregates have, respectively, antiparallel and parallel arrangements of the molecular dipoles in stacks.<sup>127</sup> Langmuir–Blodgett monolayers,<sup>128</sup> liquid-crystalline polyacrylates and polysiloxanes,<sup>129</sup> bilayer membranes,<sup>130</sup> micelles,<sup>131</sup> bilayer–clay matrices,<sup>132</sup> and poly(vinyl chloride) membranes<sup>133</sup> have been used as matrices. The reverse reaction decoloration was found to be up to  $10^7$  times slower in J-aggregates, and storage density could be enhanced by a factor of  $10^4$ . With chiral spiropyran now available, it is challenging to address the stereochemical changes that might be exerted by the matrix in these photobistable systems.

In an approach toward new materials for erasable holographic data storage, the structural properties of peptide-like oligomers were used to impose orientational order on azobenzene chromophores attached to it (**35**; Figure 13). Optical storage in photorefractive polymers<sup>134</sup> based on azobenzenes involves photoisomerization in which the chromophore undergoes a number of random reorientations through reversible *trans*–*cis* isomerization cycles. When the transition moment of the stable *trans*-azobenzene is oriented perpendicular to the polarization direction of the incident linearly polarized light, a stationary orientation is obtained. A local modulation of the refractivity is observed due to this anisotropic alignment of the chromophores. Oligomers were constructed of L-ornithine oligomerized through the  $\delta$ -amino groups, and a cyanoazobenzene was attached to the  $\alpha$ -amino group via carbonyl linkers or through glycine at the N-terminus. The peptide backbone might impose a helical stacking of the chromophores, and the number of stationary orientations is expected to be reduced (and as a consequence the anisotropy enhanced). Holographic gratings with this photochromic material were obtained with a first-order diffraction efficiency of 76% in 300 s, which is near the maximum that can be expected. High thermal stability and long lifetimes were found for these holograms. A remarkable stereochemical effect, which might point to an essential role of the molecular chirality for proper stacking, was observed when the glycine linker was replaced by L- or D-alanine. A significant decrease of writing time was observed in the first case, whereas, in contrast, the D-alanine-modified system showed inefficient diffraction.

##### IV.2. Polymer-Modified Chiral Switches

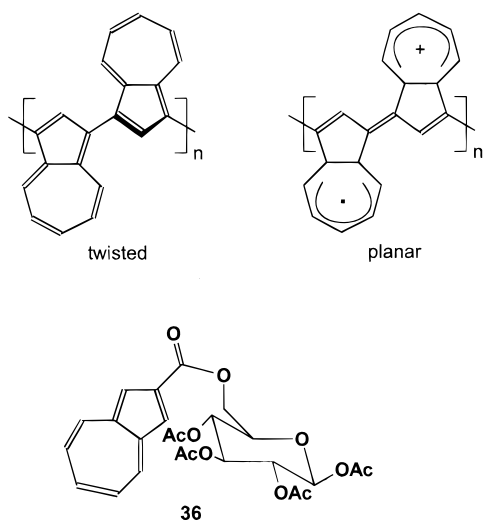
Very few polymer systems have been described in which the switching unit itself is chiral. A number of molecular switches,<sup>135</sup> including multicomponent switches,<sup>24c,100</sup> have been developed using azulene-type compounds.<sup>136</sup> The bistability is based on a photochemical  $10\pi$ -electron cycloreversion of dihydroazulenes or the electron-transfer properties of azulenes. A chiroptical switch was constructed with a chiral polyazulene.<sup>136,137</sup> A distinct feature of polyazulenes is the possibility of a nonplanar configuration of the neutral form whereas upon oxidation the





**Figure 13.** Helically stacked azobenzene-substituted peptide oligomers **35**.

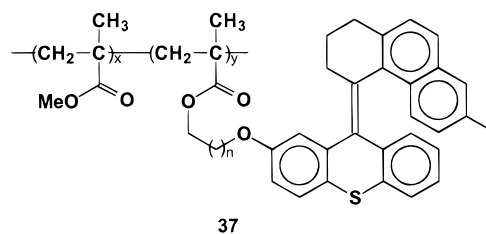
**Scheme 19. Chiroptical Redox Switch Based on Polybiazulene**



conducting biazulenoid subunit presumably adopts a more planar geometry (Scheme 19). The oxidative polymerization of 6-*O*-(2-azulenecarbonyl)- $\beta$ -D-glucopyranose-1,2,3,4-tetraacetate **36** on a transparent ITO electrode resulted in a conducting polymeric film with a negative CD couplet at 367 and 404 nm. The negative CD couplet was attributed to a twisted biazulene subunit with *R* configuration. Electrochemical oxidation resulted in the disappearance of the CD absorption, whereas reduction to the neutral form reestablished the CD band. This chiroptical switching can be explained by the involvement of

a neutral twisted state and a planarized conducting state.

A chiroptical molecular switch **37** based on polymer-bound overcrowded alkenes has been constructed (Figure 14).<sup>138</sup> Side-chain-functionalized optically ac-



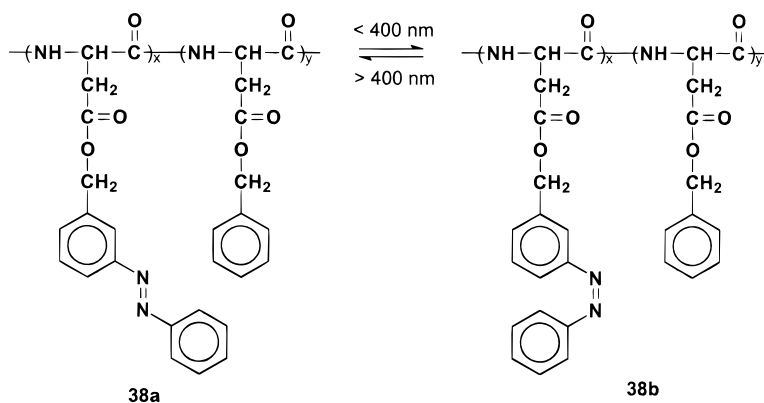
**Figure 14.** Methacrylate copolymer modified with chiroptical switch **37**.

tive copolymers were prepared from methyl methacrylate and methacrylates connected via spacers to a thioxanthene-based photochromic unit. Polymers with 2–6 carbon spacers and loadings of photoactive units up to 4.7% showed excellent film-forming properties and a distinct change in CD spectra upon irradiation. However, the irradiation times required to reach the photostationary states are much longer than in the case of chiral doped polymer films<sup>48</sup> and furthermore these films suffer, thus far from low diastereoselectivity during photomodulation.

### IV.3. Chiral Photochromic Polymers

A large number of photochromic polypeptides have been studied as the  $\alpha$ -helix and  $\beta$ -structures of these polymers offer attractive possibilities to accomplish

## Scheme 20. Cis–Trans Isomerization of Azobenzene Covalently Bound to Polyaspartate 38



reversible photoinduced structural changes in the material. The photochromic effect can result in, e.g., helix reversals, random coil- $\alpha$ -helix transitions, modulation of redox processes, change in aggregation and disaggregation, or amplification of the changes triggered by light. In the pioneering studies by Goodman, polypeptides based on *L-p*-phenylazophenylalanine were used.<sup>139</sup> Photoisomerization of the azobenzene side chain, however, did not affect the main chain conformation. A change in chiroptical properties was observed with polyaspartates, due to helix reversal that occurs as a result of the cis–trans isomerization of azobenzene units in the side chains (Scheme 20).<sup>140</sup> A copolymer consisting of  $\beta$ -benzyl-*L*-aspartate and  $\beta$ -(*m*-benzylazo)benzyl-*L*-aspartate **38a** in the all-trans form showed a strong preference to adopt a left-handed helix (ratio 86:14). Trans–cis photoisomerization leads exclusively to right-handed helices, and the presence of only 9.7% azo groups was sufficient to provide a 70% preference for right-handed helices. Photoirradiation at  $\lambda > 400$  nm effected the reverse photochromic process with concomitant reversal of helicity. The helicity reversal can be followed by monitoring a large change in optical rotation, offering a method for nondestructive read out, and the process depends on temperature and type of polyaspartate.<sup>141</sup>

A major problem associated with azobenzene-based photoswitches is the rather low thermal stability of the cis form. When the photochromic behavior of poly(*L*-glutamic acid)<sup>142</sup> modified with azobenzene side chains was studied, a slow thermal decay of the cis isomer was observed (approximately 200 h is required to restore the trans form). However, sulfonated azobenzenes such as azobenzenesulfonyl modified poly(*L*-lysine) are highly stable in the cis form, and thermal decay is not seen at room temperature for several weeks.<sup>143</sup> Photoisomerization in organic solvents did not change the CD spectrum in the peptide region, but a reversible change in the CD absorption or optical rotation associated with the azo chromophore was observed. This means that photoisomerization does not effect the peptide main chain in this polymer, but the chirality of the main chain is reflected in a modulation of the chiroptical properties of the azobenzene chromophore. Related switching effects were observed with poly(phenylazophenylalanines).<sup>144</sup> In contrast the photoisomerization in water in the pH range 5–7 resulted in a reversible

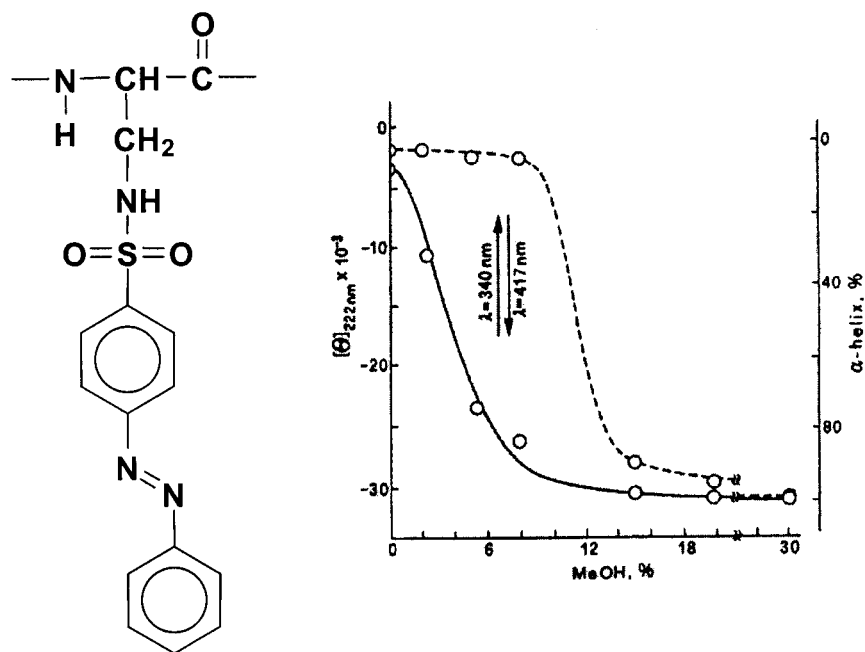
unfolding of the peptide. The effect is attributed to a higher degree of dissociation of neighboring carboxylic acid groups following trans–cis isomerization of the azo moieties. Related helix–coil transitions have been reported for poly(*L*-glutamic acid) modified with azobenzene sulfonate side chains.<sup>145,146</sup>

In the presence of the surfactant dodecylammonium chloride at its critical micellar concentration, irradiation of azo-modified poly(*L*-glutamic acid) at 350 nm induced a trans–cis isomerization and simultaneously a coil–helix transition as detected by CD.<sup>147</sup> This remarkable change in folding was explained by a change in hydrophobic interaction. The rodlike apolar trans form dissolves in the hydrophobic core of the micelle, whereas with the skewed polar cis form, decreased hydrophobic interactions result in expulsion of the chromophores out of the micelles and a change in the peptide conformation to adopt the  $\alpha$ -helix takes place.

Related photochromic effects and conformational changes of polypeptides containing azobenzene units have been observed with poly(*L*-lysine),<sup>148</sup> poly(*L*-ornithine),<sup>149</sup> poly(*L*- $\alpha$ , $\gamma$ -diamino-butanoic acid),<sup>150</sup> and poly(*L*- $\alpha$ , $\beta$ -diamino-propanoic acid).<sup>151</sup> Furthermore, several poly(*L*-lysine)s<sup>152</sup> and poly(*L*-glutamic acid)s<sup>153</sup> containing spiropyran photochromic units in the side chains have been investigated.

Photoinduced variations in the helical structure were also observed with poly(*N-p*-phenylazobenzenesulfonyl-*L*-lysine) (**39**) in hexafluoro-2-propanol (HFP), depending upon the amount of methanol present in the system (Figure 15).<sup>143</sup> In pure HFP, both the trans and cis forms are random coils, whereas in HFP/MeOH, both forms adopt a helix structure. Alternated irradiation at 340 and 417 nm was found to effect the folding and unfolding of the polypeptide chains, but the response of the conformational change depended on the amount of MeOH present and was different for the two forms. In a selected solvent range, the protonation/deprotonation of the sulfonamide functionality apparently depends on the trans–cis photoisomerization and was denoted as a key factor in the control of the polypeptide folding. The combined effect of solvent and light on the chiroptical properties of this polymer comprises chiral gated photoresponsive systems.

Polypeptides modified with photochromic units have, furthermore, been used to effect reversible changes in organization of monolayers and thin films

**39**

**Figure 15.** Methanol dependency of CD absorption for poly(*N*-*p*-phenyl-azobenzylsulfonyl-L-lysine) **39** upon irradiation at 417 and 340 nm (adapted from ref 143b).

(photomechanical effects),<sup>154</sup> aggregation behavior, and solubility,<sup>155</sup> to control orientation and optical properties in Langmuir–Blodgett-films,<sup>156</sup> to construct photoresponsive amphiphilic systems,<sup>157</sup> and for photoregulation of membrane permeability.<sup>158</sup> Photocontrol of the conformation of a cyclic peptide, using an azobenzene moiety as a photoresponsive unit in the cyclic compound, has also been accomplished.<sup>159</sup>

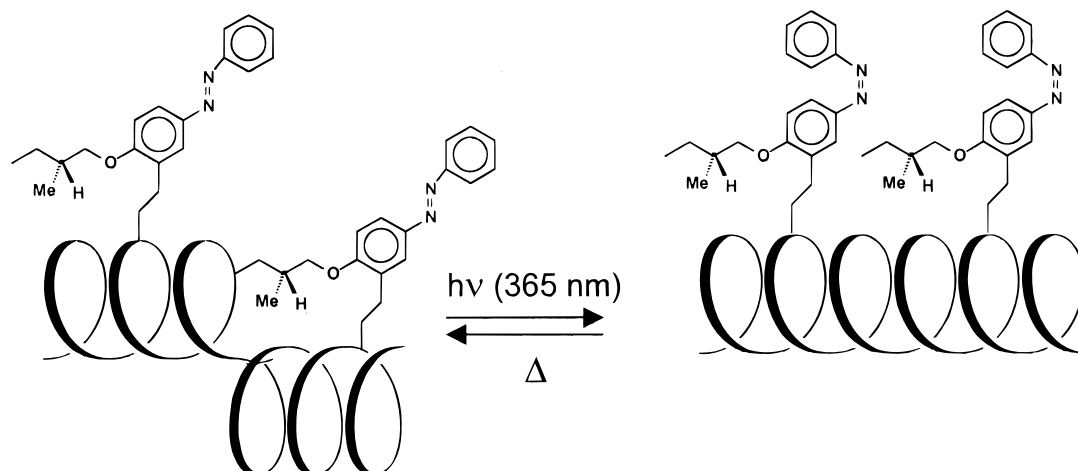
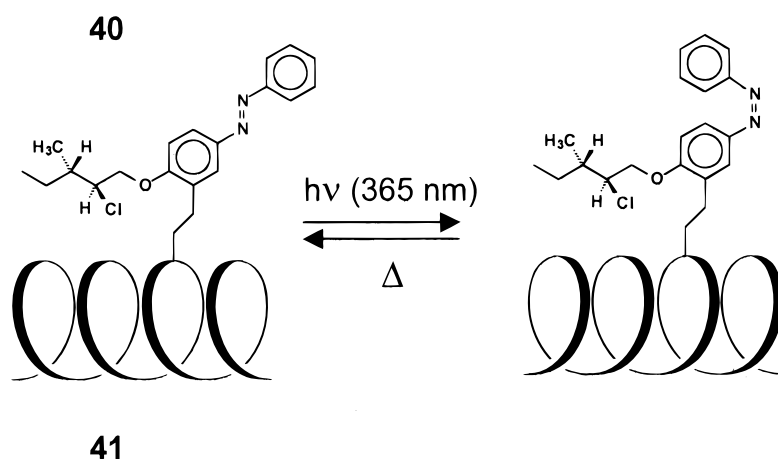
Photoresponsive polymethacrylates functionalized with azobenzene chromophores containing optically active substituents that are intrinsically dissymmetric were prepared, and this feature results in a permanent dipole in these materials. As a result, they exhibit second-order nonlinear responses.<sup>160</sup>

Photochemical modulation of the helical structure has also been demonstrated with chiral polyisocyanates. A dynamic helical conformation is present in polyisocyanates, and in the case of achiral monomers, the polymer consists of a racemic mixture of **P** and **M** helical chains (or helical segments in a long polymer chain).<sup>161</sup> In the presence of chiral side groups, the polymer chains become diastereomeric and the incorporation of a small number of chiral side chains in copolymers results in a strong preference for one helical twist sense. The high cooperativity which is leading to a strong amplification of chirality is called the “sergeants and soldiers” effect.<sup>162</sup> Copolymers were prepared with chiral azobenzene side groups containing one (**40**) or two stereogenic centers (**41**), respectively (Scheme 21). Upon photoisomerization, the polyisocyanate exhibited a change in ORD and CD spectra reflecting a shift in the population of the helical segments but the preferred helical sense was the same in both states (Scheme 21A).<sup>163</sup>

With copolymer containing two stereocenters in the photochromic side chain, a much more pronounced stereochemical change occurs and an inversion in the helical twist sense upon photochemical trans–cis photoisomerization was found (Scheme 21B).<sup>164</sup>

A number of copolymers of chiral azobenzene-substituted isocyanates were prepared to assess the interaction between chiral side chain and helical main chain. A delicate balance of effects including the distance and nature of stereocenters, solvent, and concentration of azo chromophores is apparent.<sup>165</sup> By incorporating the stereocenter in a short two-carbon spacer, a much higher helical preference and molar ellipticity in the CD was induced at lower chiral chromophore concentrations compared to systems with more remote stereocenters. The cis isomer showed enhanced helical twist sense, and an additional advantage is the improved thermal stability of the cis form (half-life 40 h; RT).<sup>166</sup> In a recent study of the correlation between the isomerization of the photoswitchable chiral group and the helicity of the main chain, it was found that the relation between the ratio of trans and cis isomers and the helical preference can be linear or nonlinear.<sup>167</sup> A linear relation was found for low concentrations or lower chiral inductive effects of the side groups. The helical conformation is controlled by the stronger inducing isomer or the group present at higher concentration in accordance with the majority rule of Green.<sup>168</sup>

The photocontrol and amplification of chirality through these dynamic helical polymeric systems offers intriguing possibilities for new multifunctional photoswitchable materials in view of the important role of helical organization in biopolymers and the attractive materials properties of these photochromic polymers.

**Scheme 21. Chiral Photoswitchable Polyisocyanates<sup>a</sup>****A****B**

<sup>a</sup> (A) Schematic representation of the shift in equilibrium between **P** and **M** helices upon irradiation. (B) Illustration of **P** to **M** helix transition in polyisocyanates upon photoisomerization of the azobenzene unit. (Adapted from refs 163 and 164.)

**V. Chiroptical Molecular Switching of Liquid-Crystalline Phases**

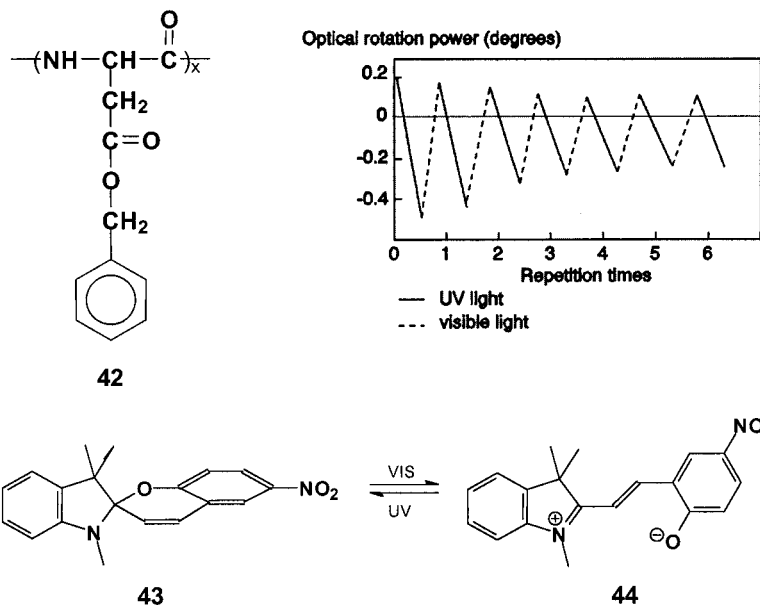
Liquid-crystalline (polymeric) materials offer the advantage that the macroscopic orientation can be influenced by external forces, such as an applied electric or magnetic field. Therefore, control of strongly anisotropic properties can be achieved, resulting in differences in, for example, absorption, reflection, or refractive index.<sup>169</sup> LC display technology is currently based on electronic modulation of the liquid-crystalline phase containing the organic components. The modulation of mesophases and physical properties of LC materials by light, i.e., photoswitching of LC phases, offers a major challenge of significance for the information technology industry. Advantages include the possibility to develop all optical devices and enhance the speed of data processing.

**V.1. Polymer Liquid Crystals**

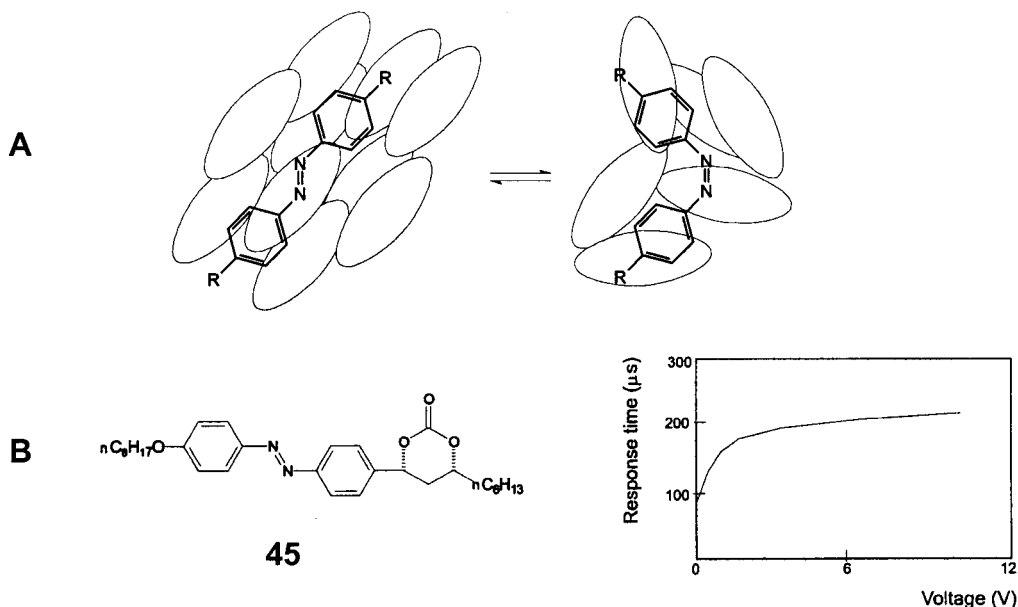
The different mesophases, obtained by doping polymer liquid crystals with photochromic guest molecules or by covalently attaching photochromic side chain units, can be used for the construction of

optical data storage systems,<sup>170</sup> as demonstrated by Tazuke<sup>124,171</sup> and Wendorff.<sup>172</sup> Major improvements were achieved by Ringsdorf<sup>173</sup> using copolymers of acrylates with LC side groups and thermally irreversible photochromic fulgide side groups. A variety of new photochromic polymer liquid crystals have been reported in recent years.<sup>174</sup>

A reversible change in optical rotation in the cholesteric liquid-crystalline polymer poly(benzyl)-L-glutamate **42** by the photochromism of 1–4% of spiropyran **43** dissolved in the polymer was shown by Ichimura.<sup>141,175</sup> Alternated exposure of the doped polymer film to UV and visible light resulted in a fluctuation of the optical rotation (Scheme 22), although a gradual decrease due to photochemical degradation was observed. Indolinespiran **43** contains a stereogenic center at the spiro position, while merocyanine **44** is achiral. The observation of  $\alpha_D = 1^\circ$  for a film of thickness 1  $\mu\text{m}$  requires  $[\alpha]_D = 100\,000^\circ$ , which is considered an extremely large optical rotation for a small chiral compound. This excludes the formation of an optically active spiro compound, induced by the chiral medium as the origin of the change in optical rotation. The change in chiroptical properties is most probably due to the

**Scheme 22. Change in Optical Rotation of Poly(benzyl)-L-glutamate 42 Induced by Photochromism of Dopant Spiropyran 43<sup>a</sup>**


<sup>a</sup> Inset adapted from ref 175.

**Scheme 23<sup>a</sup>**


<sup>a</sup> (A) *trans*-Azobenzene stabilizes the LC phase, whereas *cis*-azobenzene disrupts the LC phase. (B) Ferroelectric azobenzene **45** based LC (left side) with switching response time of 90 μs (right side). (Scheme adapted from ref 179a.)

difference in interaction of the neutral spiropyran form and the zwitterion merocyanine form with the chiral polymer matrix.

In a different approach, photochromic azobenzenes attached to a chiral polysiloxane backbone, which exhibit ferroelectric properties, were used.<sup>176</sup> The *trans*–*cis* photoisomerization of the azobenzene unit induces changes in the ferroelectric polymer liquid crystal by disrupting the LC phase, which was measured as a drop in the spontaneous polarization. However, the thermal isomerization process is much faster in the LC phase than in solution (100 min instead of 7 h). The influence of the ferroelectric matrix on the isomerization process was found to be strong and might also negatively affect the thermal stability.

## V.2. Doped Liquid Crystals

The addition of a photoactive dopant to a liquid crystal can induce large changes in the LC phase, for instance, in the case of an azobenzene, as a result of the large configurational change upon photoisomerization. The *trans* form is rodlike and therefore stabilizes the liquid-crystalline phase. The *cis* form is bent and generally destabilizes the LC phase (Scheme 23A).<sup>177</sup>

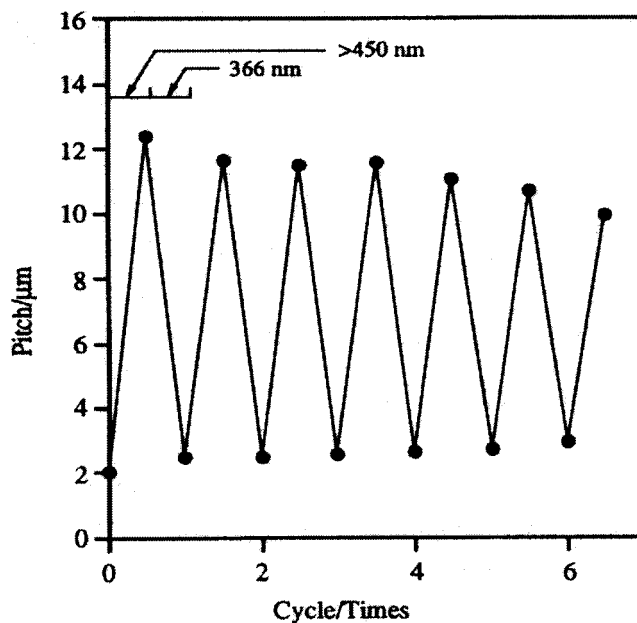
Optically active azobenzene **45**, bearing a chiral syn-cyclic carbonate and long alkyl chains, was employed as a dopant in ferroelectric liquid crystals (Scheme 23B).<sup>178,179</sup> Ferroelectric liquid crystals exhibit a chiral smectic phase and respond to an electric field on a time scale of seconds as a result of

spontaneous polarization. The chiral cyclic carbonate unit induces large spontaneous polarization. Trans-cis photoisomerization ( $\lambda = 355$  nm) effectively caused the change of the chiral smectic C phase (SmC\*) into a smectic A phase (SmA), whereas thermal cis-trans isomerization restored the SmC\* phase. The photoisomerization in the ferroelectric LC phase showed a fast response time of 90  $\mu$ s, which is a highly desirable property.

It is long known that small amounts of optically active guests added to nematic liquid-crystalline host compounds can induce cholesteric (twisted nematic) phases.<sup>180</sup> The nature of the resulting cholesteric phase strongly depends on the helical twisting power (HTP) of the chiral dopant.<sup>181</sup> Changes in the structure or stereochemistry of the chiral dopant might be reflected in a significant change in the organization of the LC phase. Several approaches have recently been followed to accomplish reversible switching of liquid-crystalline materials between twisted and nontwisted phases by photochemical modification of the chiral dopant molecule. Irreversible light-induced changes include the conversion of a cholesteric to a nematic phase by photodestruction of a chiral guest<sup>182</sup> or by photoracemization of the guest.<sup>66,70</sup> Using the optically active 1,1'-binaphthyl derivative **11** (section II.3) as dopant in the  $K_{15}$  nematic phase, a cholesteric phase was introduced. Photoracemization of **11** at 334 nm causes the conversion to the compensated nematic LC phase. The reversal of the process, e.g., photoresolution, using CPL irradiation was however not successful. Related diastereomeric phototriggers for LC phases were based on acetals and ketals of 1,1'-binaphthol. In these so-called chirochromic triggers,<sup>183</sup> one chiral part (the acetal) is fixed whereas the other part can be switched by light. Some of these acetals were found to undergo photoepimerization, although quantum yields are low and they appear to be unsuitable to control LC phases.

Janicki and Schuster<sup>184</sup> achieved reversible light-induced changes in the optical properties of cholesteric liquid crystals. For this purpose, an achiral indole fulgide (section II.5) ( $E \rightarrow C$ ,  $\Phi = 0.040$ ,  $\lambda_{\max} = 584$  nm;  $C \rightarrow E$ ,  $\Phi = 0.051$ ,  $\lambda_{\max} = 385$  nm) was doped together with a chiral binaphthyl ether in a nematic liquid crystal. The small amount of the photostable chiral binaphthyl ether (1.35 wt %) induces a cholesteric LC phase with a pitch of 26.1  $\mu$ m. Relatively large amounts of indole fulgide (5 wt %) were required to observe the effects of the photoisomerization of the fulgide in the LC phase. Alternated irradiation resulted in a pitch change of the induced cholesteric liquid crystal of 30% due to ring opening and ring closure of the fulgide. It was also established that nondestructive read out with polarization microscopy was possible.

Mixtures of nematic 4-cyano-4'-pentylbiphenyl- and bisnaphthol-based chiral fulgide derivatives **22** (Figure 16) were also shown to form stable cholesteric LC phases.<sup>185</sup> As the helical twisting power ( $\beta_m$ ) of the closed form of **22C** ( $\beta_m = -42.7 \mu\text{m}^{-1}$ ) is considerably larger than that of the open form **22E** ( $\beta_m = -6.9 \mu\text{m}^{-1}$ ), a large change in the pitch of the cholesteric

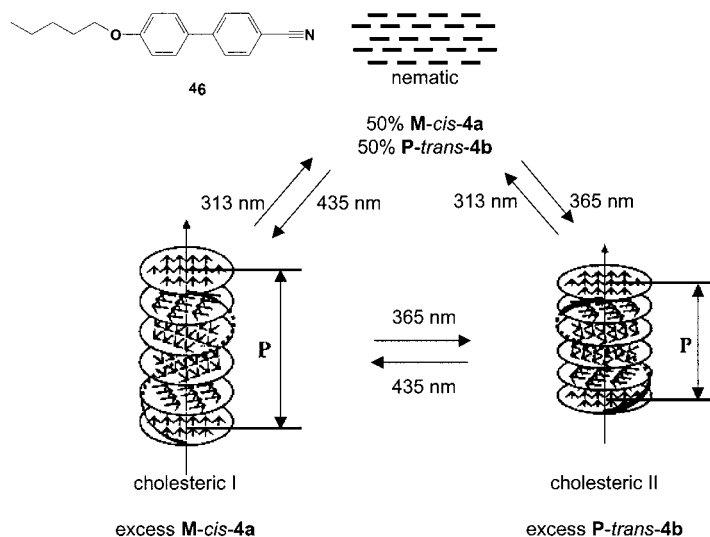
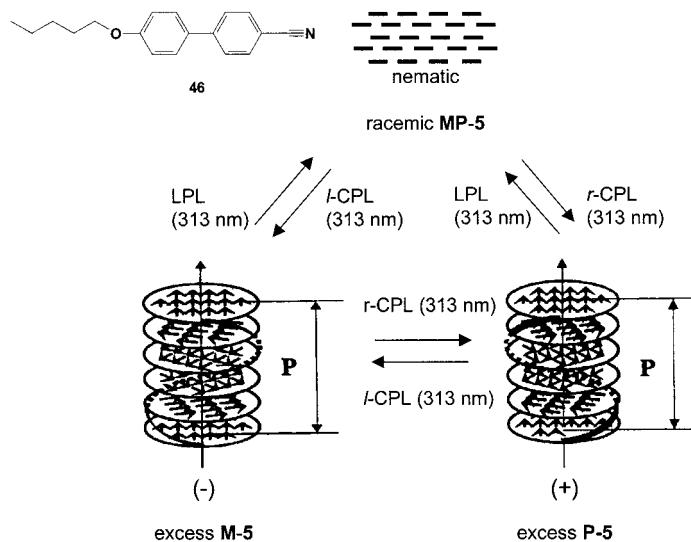


**Figure 16.** Reversible change of pitch of the cholesteric phase of 4-cyano-4'-pentylbiphenyl induced by **22** by photoirradiation. Concentration:  $1.22 \times 10^{-2}$  mol dm<sup>-3</sup>. Starting with **22C** at 30°C. Irradiation time > 450 nm, 5 min; 366 nm, 60 min. (Reprinted with permission from ref 185. Copyright 1997 Chemical Society of Japan.)

phase could be reached upon photochemical switching of the fulgide. The difference in pitch decreased, however, gradually after several cycles due to diminished fatigue resistance. Also, photomodulation of the spontaneous polarization of a ferroelectric liquid crystal by a transverse dipole modulation of a chiral indigo dopant has been reported.<sup>186</sup>

In contrast to the method employing a chiral dopant in combination with a photochromic material to modulate the pitch of an induced cholesteric LC phase,<sup>184</sup> an optically active photoresponsive guest molecule might be applied. Using this approach, the reversible photochemical modulation of the helical pitch as well as the screw sense of a cholesteric (twisted nematic) LC phase was accomplished.<sup>187</sup> Furthermore, the reversible transition between a cholesteric and nematic phase upon irradiation was seen. The host system consisted of 4'-(pentyloxy)-4-biphenylcarbonitrile **46** which upon addition of 1 wt % of the guest enantiomerically pure *P-trans-4b* (Scheme 2) was converted into the cholesteric phase. Irradiation of a thin film of this material at 365 nm resulted in a distinct decrease in the pitch of the cholesteric phase, whereas subsequent irradiation at 435 nm reverted the pitch to its original value (Scheme 24). Alternated irradiation with 435 and 365 nm light (5 min irradiation time) resulted in photomodulation (between 12.29 and 5.31  $\mu$ m) of the pitch in the cholesteric phase. This modulation was stable during 8 switching cycles. Measurements of the cholesteric screw senses (using the Grandjean-Cano method)<sup>188</sup> indicated that the pseudoenantiomers *P-trans-4b* and *M-cis-4a* led to cholesteric phases of opposite handedness.

Furthermore, it was observed that with 313 nm light a conversion of the cholesteric to the nematic phase occurred whereas the original cholesteric phase

**Scheme 24. Photochemical Switching Processes of LC-Phase 46 and Chiral Dopants *M-cis-4a* and *P-trans-4b***

**Scheme 25. Switching between Three Different Liquid-Crystalline States after Irradiation at One Wavelength<sup>a</sup>**


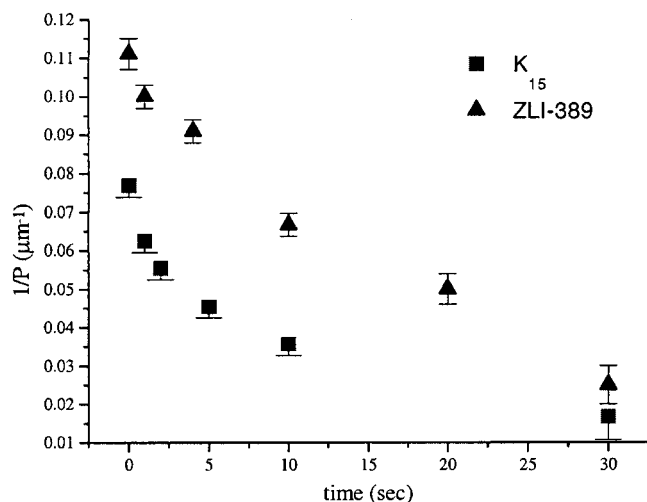
<sup>a</sup> Nematic liquid crystal 46 and dopant 5 were used.

was restored after irradiation at 435 nm. Apparently a near 50:50 ratio of opposite helices of the photosensitive guest molecule (pseudoracemate) is formed at 313 nm, which results in a compensated nematic phase. The mesoscopic assembly in this three-position switch (Scheme 24) can effectively be controlled by the modulation of the ratio of the helices of the dopant; these ratios depend on the wavelengths used for irradiation of the LC film. These findings also indicate that the photostationary state *P-trans-4b*, *M-cis-4a* is attained in the LC phase. Recently it was established, using a large number of LC phases doped with chiroptical switches based on overcrowded alkenes, that nearly the same stereoselectivities as well as stabilities for the chiroptical switches are obtained in the LC phases as those in solution. The switching times were, however, increased in the LC phase compared to solution.<sup>189</sup>

A different design of a LC-compatible chiral optical switch was based on bis-imine-modified diarylethene (Figure 7).<sup>190</sup> Using *K*<sub>15</sub> and ZLI-389 as LC materials

with 2–4% of **9** as chiral dopant, stable cholesteric phases were obtained and switching from the open to the closed form and back (30–50 s) resulted in the disappearance and reappearance of the cholesteric phase. Moreover, the pitch could be changed gradually with irradiation time as illustrated in Figure 17, and as a consequence, the basic features of a multi-mode LC switch have been demonstrated. Further improvements on switching rates, the wavelengths used for the control of the cholesteric and nematic phases, and the pitch values might be achieved by structural modifications of the photochromic unit and the chiral auxiliary.

As it was demonstrated that the chirality of the photobistable compounds could be modulated by irradiation with left or right circular polarized light,<sup>57,74</sup> a next step would be the application of these compounds as chiral control elements for the LC phase. Photoresolution by CPL of a racemic photobistable dopant in a nematic LC phase could induce a cholesteric LC phase.<sup>32,69</sup> Furthermore, the sensitivity



**Figure 17.** Change of the reciprocal of the pitch value with irradiation time: 2.0 wt % of **9** in ZLI-389 at 52°C and in  $K_{15}$  at 32°C (irradiation with 300 nm light).

of the cholesteric LC material to the structure of the dopant<sup>180</sup> might be exploited in switching of the chirality of the cholesteric LC phase upon irradiation with CPL. In a series of papers, Schuster and co-workers<sup>52c,66</sup> reported approaches toward the development of CPL phototriggers for liquid-crystal-based optical switches. As optically active (arylmethylene) cycloalkane derivatives can induce a cholesteric phase,<sup>191</sup> a large number of optically active (arylmethylene) cyclohexanes **15** and **16** were examined in their propensity to form cholesteric phases when added to nematic  $K_{15}$  and ZLI-467.<sup>70</sup> In all cases, cholesteric phases were observed with  $\beta_m$  values ranging from 1.6 to 29.1  $\mu\text{m}^{-1}$ . Upon irradiation of ZLI-467 doped with 2.3% of (*R*)-**15** ( $R = \text{CH}_3$ ) at  $\lambda > 230$  nm, rapid photoracemization and simultaneous conversion to the nematic phase was observed. However, photoresolution of racemic **15** and the reverse of this process, e.g., nematic to cholesteric phase transition, was not achieved. In this series of photochromic dopants, high  $\beta_m$  values were often associated with low  $g$  factors or the molecules show the reverse behavior. The macroscopic helical pitch  $p$  of a cholesteric liquid crystal is determined by the concentration of the chiral photochromic dopant, the helical twisting power  $\beta_m$ , and the enantiomer excess  $[\text{ee}]_{\text{pps}}$  in the photostationary state of the CPL photoresolution. The pitch is inversely related to  $[\text{ee}]_{\text{pps}}$  according to  $p = 1/C \cdot \beta_m \cdot [\text{ee}]_{\text{pps}}$ .<sup>192</sup> As  $[\text{ee}]_{\text{pps}}$  is related to the anisotropy factor  $g_i$  ( $[\text{ee}]_{\text{pps}} = g_i/2$ ), both  $\beta_m$  and  $g_i$  should be significantly large to be able to detect a cholesteric phase. With axially chiral bicyclo[3,3,0]octan-3-one (**18**), photoracemization induced an increase of the cholesteric pitch, ultimately leading to a (racemic) nematic phase.<sup>74</sup> Despite the high  $g$  factor, photoresolution of **18** (Scheme 8) doped in *trans*-*n*-heptyl-4-(*p*-cyano)phenylhexane did not lead to a cholesteric texture as a consequence of a low  $\beta_m$  (5.5  $\mu\text{m}^{-1}$ ).

It should be noted that structural compatibility (closest packing model<sup>193</sup>) between LC material and dopants is also an important factor.<sup>180</sup> Benzylidene cyclohexane photoswitchable units were also incorporated in mesogenic compounds such as axially

chiral 1-benzylidene-4-[4'-((*p*-alkylphenyl)ethynylphenyl)cyclohexanes. The anisotropy factor  $g_i$  and therefore the ee upon photoresolution appeared to be too small to induce a cholesteric phase.<sup>194</sup>

The principle of a CPL-based LC switch was demonstrated in our laboratory with racemic overcrowded alkene (**P,M-5**, Scheme 3) doped in 4'-(pentyloxy)-4-biphenylcarbonitrile **46**.<sup>57</sup> Irradiation of a 50  $\mu\text{m}$  film of **46** doped with **P,M-5** (20 wt %) at 313 nm for 90 min with *l*-CPL resulted in a small excess (ee = 0.07%) of **M-5** and a cholesteric phase. Irradiation with *r*-CPL also resulted in a cholesteric phase but with a reversed screw sense. Subsequent irradiation with linear polarized light (LPL) at 313 nm reconvered the system to a nematic phase. The switching cycles are shown in Scheme 25.

Switching between LPL and CPL results in a nematic versus cholesteric phase modulation. Switching between *l*-CPL and *r*-CPL modulates the chirality of the cholesteric phase. The photochemical switching processes are entirely controlled by the changes in the chirality of the light at a single wavelength. It should be noted that the amount of dopant is relatively high, a very small ee is observed, and as a consequence a pitch of the LC phase is found which is too large for direct measurement. These features might be improved by structural modification enhancing  $g_i$  as well as the compatibility with the LC material. The CPL-based liquid-crystalline switch represents an amplification mechanism as the chirality of the CPL light is transferred via photoresolution of the dopant and amplified in the chiral (cholesteric) organization of the LC material.<sup>195</sup>

## VI. Summary and Outlook

Recent progress in the development of chiral optical molecular switches has been discussed. In summarizing the various chiral photochromic molecules that were constructed, two key features emerge from the approaches to incorporate the element of chirality in photochemical bistable molecules. First, there is the distinct advantage of using chiroptical properties of the molecules for nondestructive read out in molecular information storage and handling systems. For instance, monitoring the change in optical rotation remote from the wavelengths of switching ensures nondestructive read out. Second, the change in chirality associated with the structure of the photo-bistable molecule can be employed as a control or trigger element, tunable by light.

Successful chiroptical switches include the photochemical interconversion of diastereoisomers, photoepimerization, helix reversals, and spirocyclizations. Using circularly polarized light, photoresolution and interconversion of enantiomers of axially chiral- and helical-shaped bistable molecules has been accomplished. Incorporation of photoactive units in multifunctional switches allowed the control of, e.g., luminescence, motion, recognition, and assembly processes. Photochromic polymers represent a major effort in this field. Approaches include the control of the matrix by light in photorefractive information storage systems, the synthesis of polymer-based phototrigger elements, and the control of the confor-



mation of the polymer (i.e.,  $\alpha$ -helix,  $\beta$ -structure of peptides). Considerable progress has been made in the control of the organization of liquid-crystalline materials by light using chiroptical molecular switches; these materials are of significance for future display technology. It is evident from the various systems developed so far that the field of chiroptical molecular switches is still in a premature state. The main focus has been on photobistable compounds exploiting the change in chiroptical properties as an alternative read-out mechanism compared to the large number of, e.g., photochromic compounds known today. Some systems, including azobenzenes, overcrowded helical alkenes, and diarylethylenes, have shown large changes in chirality and good fatigue resistance in a number of photochemical cycles. Others have merely been used, so far, to demonstrate the principle of a light-induced change in chirality. Specific advantages and shortcomings of the individual chiral photochromic systems have been discussed. The critical issues associated, in general, with the development of photochromic organic compounds for data storage and handling and other photoactive materials pertain to the chiroptical switches discussed. In particular, this holds for the quantum yields, number of cycles, reversibility, fatigue resistance, switching rates, and integration with other functions. However, considerable recent progress is seen in the use of photochromic organic compounds in rewritable optical data storage materials, holographic materials, and photochromic lenses. For future applications in nanoscale digital data storage systems, organization at the molecular level will also be an important challenge that needs to be addressed. In light of potential future application, the use of chiroptical switches as trigger elements in the control of LC phases (section V) or polymer properties (section IV) seem to hold most promise at present.

The development of "smart" materials in which the structure and properties can be modulated externally by light gets an extra dimension if one realizes that simultaneously the chirality of the system can be changed. Control of molecular and supramolecular chirality is often a decisive factor in, e.g., recognition, assembly, transport, and catalysis. Besides the attractive features for molecular-based and light-driven memory elements as outlined here, the change in chirality associated with the photoisomerization process offers attractive perspectives for the tuning of other functions. Control of the direction of motion in molecular-level machines, organization and properties of polymers and supramolecular systems, photoswitching of biomaterials and enzymes, asymmetric catalysis tunable by light, light-driven LC devices, delivery and transport systems controlled by external light triggering, and modification of surfaces and interfaces by chiral switching elements represent only a few of the challenges and scientific targets ahead.

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