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Switching of Chirality by Light

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Optically active photoresponsive molecules are described by which control of chirality is achieved by light. These chiroptical molecular switches are based on inherently dissymmetric overcrowded alkenes and the synthesis, resolution and dynamic stereochemical properties are discussed. Introduction of nitro-acceptor and dimethylamine-donor substituents in a naphto [2,1-b]thiopyran-1′-ylidene-9H-thioxanthene helical shaped alkene resulted in a highly diastereoselective modulation of photostationary states with 70%-M or 90%-P helicity, respectively. The chiroptical switches offer attractive prospects as control elements for (supra)molecular functions and organization. This is demonstrated in dual mode photoswitching of luminescence and photoswitching between liquid crystalline phases.

Keywords: optical switches, chirality control, overcrowded alkenes, helicity, photoresponsive materials, liquid crystals, luminescence

INTRODUCTION

Control of chirality at the molecular and supramolecular level plays a central role in such divers area's as new drug development, asymmetric synthesis and materials research. It comprises fundamental aspects of chiral recognition [1], the design of enantioselective catalysts [2] or the development of novel (supra)molecular architectures [3].

Molecular chirality offers intriguing possibilities in the design of new photoactive organic materials [4]. Stimulated by the challenge to develop all optical devices, new materials for optical data storage and molecular memory elements photochemically bistable organic molecules have attracted considerable interest in recent years [5]. A variety of photoreversible compounds such as fulgides, diaryl alkenes, spiropyrans and azobenzenes have been prepared and the photochromic [6] processes involved are typically cis-trans isomerizations or photocyclization reactions [4–7].

A number of important requirements are inevitable for photobistable organic compounds to be useful as molecular switches: i. no thermal interconversion of the isomers in a large temperature range, ii. ready detectability of both forms, iii. fatigue resistance i.e.: no thermal or photochemical degradation, iv. non-destructive readout procedures and v. retention of all properties when the photobistable compound is incorporated in a macromolecular material.

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$$M \underset{h\nu\,(\lambda_2)}{\overset{h\nu\,(\lambda_1)}{\rightleftharpoons}} P \qquad \text{Equation 1}$$
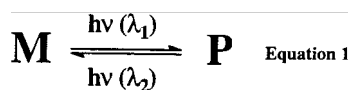
We devised photoreversible systems based on the interconversion of enantiomers or pseudo enantiomers of inherent dissymmetric molecules (eq. 1). The term pseudo enantiomers is used in this context to indicate the opposite helicity of the inherent dissymmetric molecules.
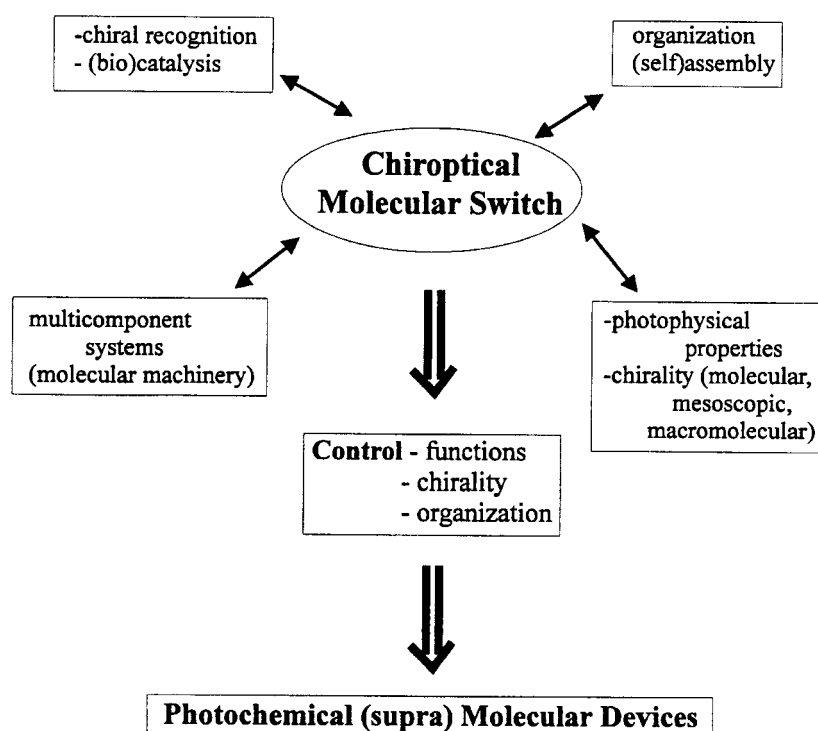
In this approach the properties of *chiral photoresponsive molecules* are exploited. Switching occurs between two chiral forms of helical shaped molecules; M indicates a left-handed helix and P a right-handed helix. The P and M helices represent two distinct states in a binary logic element. Read-out procedures in photochromic materials are generally based on UV/VIS spectroscopy often leading to undesired side effects, although changes in other properties accompanying the photochromic event have been explored for non-destructive detection [4,8].

A major advantage of the chiral optical switch, discussed here is the possibility to achieve non-destructive read-out by monitoring the change in optical rotation at wavelengths remote from the switching wavelengths.

If we are successful in the control of chirality in photoresponsive molecules the unique optical- and molecular properties of (pseudo-)enantiomers offer attractive prospects for a variety of applications. The key role for a chiroptical molecular switch is illustrated in Scheme 1.

Essential control elements, ultimately leading to supramolecular photochemical devices, are: function, chirality and organization. These aspects will be discussed as well as the synthesis of the photoreversible chiral molecules.

-chiral recognition
- (bio)catalysis

organization (self)assembly

Chiroptical Molecular Switch

multicomponent systems (molecular machinery)

-photophysical properties
-chirality (molecular, mesoscopic, macromolecular)

Control - functions
- chirality
- organization

Photochemical (supra) Molecular Devices

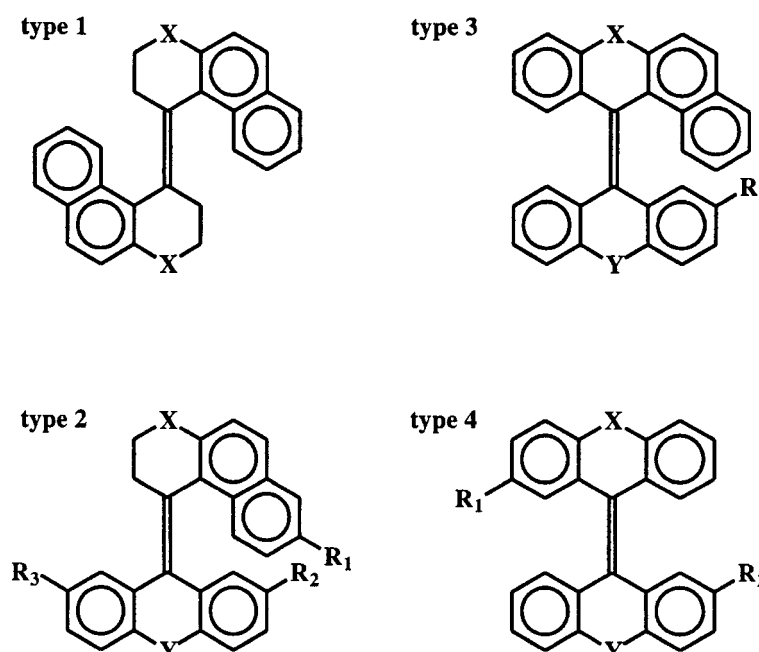SCHEME 1

INHERENT DISSYMMETRIC ALKENES

The chiroptical molecular switches are based on inherent dissymmetric sterically overcrowded alkenes and comprise 4 classes of compounds (Scheme 2).

Type 1 alkenes are biphenanthrylidenes incorporating a double helical structure [9], type 2 has a tetrahydrophenanthrene upper half with an anthracene-like lower half [10]. Type 4 alkenes are so-called symmetrically overcrowded alkenes which include the well known bisfluorenylidenes and bisxanthylidenes [11,12]. Type 3 alkenes feature structural elements of the other classes [13]. In order to avoid unfavourable steric interactions the distortion of the molecular framework imparts a helical shape to these molecules. An essential structural feature of these alkenes (except type 1) is furthermore the simultaneous presence of a *cis-* and a *trans* stilbene unit in the same molecule.

The key step in the synthesis of the overcrowded alkenes is the formation of the central double bond. The highly strained tetrahydrophenanthrene based type 1 alkenes are synthesized by a McMurry coupling of the corresponding ketones [8]. The other types of olefins consist of different upper and lower parts, therefore an "unsymmetrical" coupling method is required. The diazo-thioketone coupling is the most commonly used procedure in these cases [14].

Depending on the type of alkene a "diazo upper half" and a "thioketone lower half" can be coupled or the reverse building blocks can be used. A typical example is given in Scheme 3. The hydrazone **1** is oxidized to the corresponding diazo-compound **2** and subsequent 1,3-dipolar cycloaddition with thioketone **3** results in a thiadiazolidine as an intermediate, which readily loses nitrogen by a thermal extrusion process to form episulfide **4**. The episulfide is desulfurised by reduction with copper powder to the alkene which is obtained as a *cis-trans* mixture. When this method does not succeed, which is often the case with more hindered molecules like the episulfide precursors for type 3 olefins, LiAlH$_4$ or PPh$_3$ are used for desulfurization. The Peterson olefination [15] is another

SCHEME 2
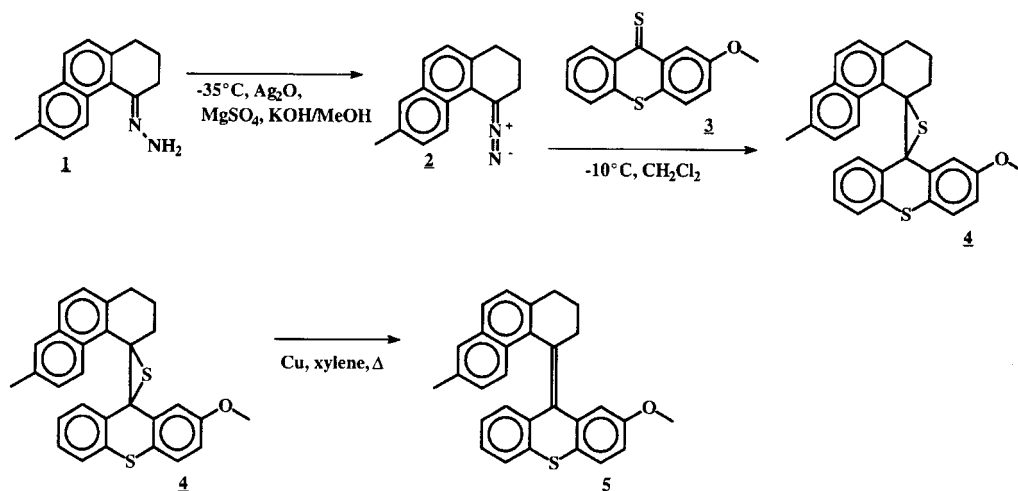
SCHEME 3

useful method to synthesize unsymmetrical alkenes. The trimethylsilyl derivative of the lower part is deprotonated with n-BuLi and coupled with the ketone of the upper part resulting in the desired olefin. However, this procedure is not appropriate for synthesis of alkenes of type 1 and 2, since it does not allow the use of ketones with α-hydrogen atoms, which can be abstracted under basic conditions. The geminal dichloride coupling, originally developed by Schönberg and Nickel,[16] proved to be suitable for molecules of type 4 consisting of the same subunits in the upper and lower part. In this synthetic procedure the ketone is first converted to the corresponding geminal dichloride and subsequently brought into reaction with copper to yield the symmetrical overcrowded alkene.

A common structural feature of type 2, 3 and 4 alkenes is a strongly folded geometry. The molecular structures based on X-ray analyses, shown in figure 1a and 1c, illustrate typical examples. Type 4 alkene 9-(2′-methyl-9′H-thioxanthene-9′-ylidene)-9H-xanthene (**6**) has an anti-folded structure. The folding is best illustrated by the angles between the mean planes through the phenyl rings in each tricyclic unit being 36° for the xanthene and 51° for the thioxanthene

part, respectively. The central double bond show a slight torsion as illustrated by the Newman projection (figure 1b), with a twist angle of 4.8°.

For the donor-acceptor substituted molecule **7** (a type 2 alkene) again an anti-folded structure is seen, in which the top and bottom halves are tilted up and down, respectively, relative to the plane of the central double bond to avoid severe non-bonded interactions and to generate a helical shape. The arrangement about the central alkene bond is nearly planar (dihedral angle 0.4–5.4°) and a normal value of 1.35 Å is found for the C_4–C_9' bond.

The racemic alkenes were resolved by chiral high performance liquid chromatography (HPLC) with (+)-poly(triphenylmethylmethacrylate) as a chiral stationary phase. This method was successful for the separation of all four types of overcrowded alkenes synthesized so far (X = CH_2, O, S; Y = O, S, –). The only restriction is that the racemization barrier (ΔG_{rac}) has to be sufficiently high to avoid (partly) racemization at room temperature (>87.9 kJ mol⁻¹).

An attractive feature in the structural design of the chiral overcrowded alkenes, discussed here, is the possibility to tune the racemization
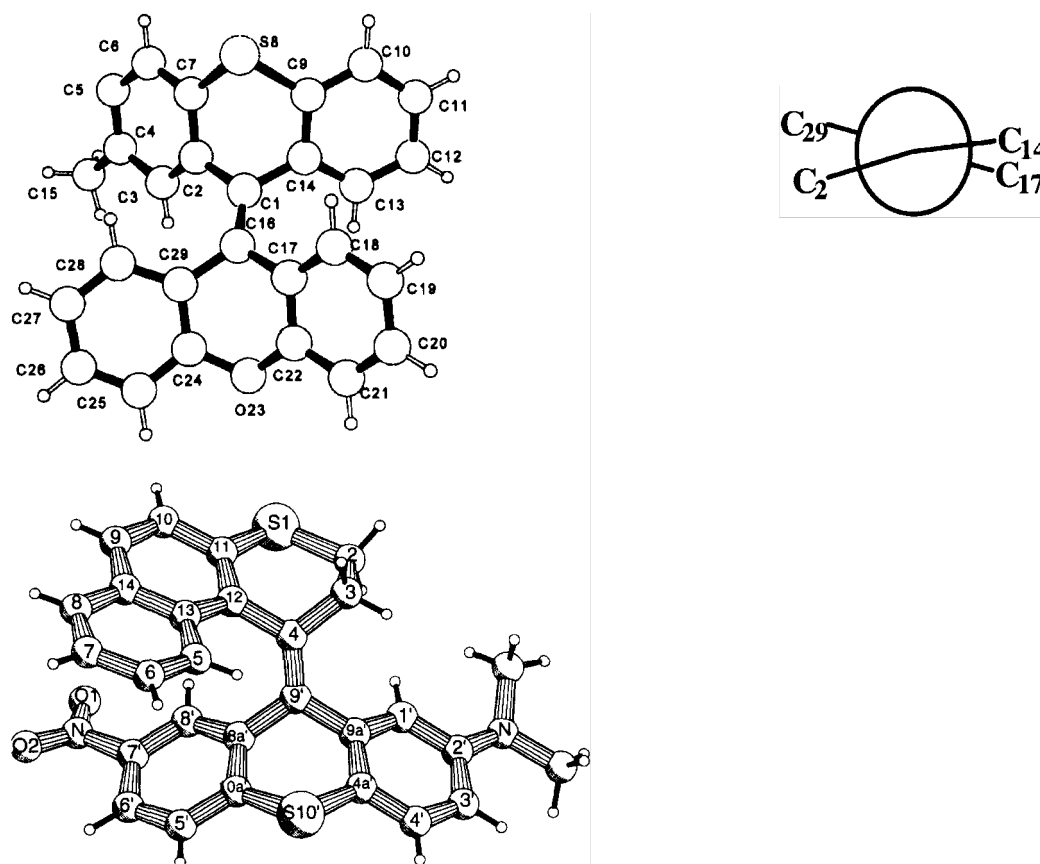
FIGURE 1A X-ray structure of *6*; (b)Newman projection of *6*; along C_1-C_{16}; (c)X-ray structure of *7*.

barriers by modification of the bridging unit in the lower half of the alkenes [12a]. For instance a surprisingly high thermal racemization barrier of 114.6 kJ mol^{-1} was found for 2-methyl-9H-thioxanthene-9-(9H-thioxanthen-9-ylidene) *8*, a value exceeding the barrier for bixanthylidenes [17] (75.3 kJ mol^{-1}) by 39.3 kJ mol^{-1}.

Systematic modification of the atom X, bridging the aryl-moieties in the lower half of alkenes *8–11* allowed a comparison of the racemization barriers and the aryl-X bond lengths. The data in Table I clearly indicate a remarkable correlation: a large increase in racemization barrier is found when the aryl-X bond is lengthened. This "remote bond length effect" can be explained by the fact that a longer aryl-X bond will force the aromatic halves of the lower part of the molecule

into the direction of the upper thioxanthene moiety. Since during racemization two peri H- peri H (H_1-H_1'; H_8-H_8') passages have to take place, the smaller aryl-aryl distance between the lower and upper halves will clearly enhance the steric barrier for this process.

Circular dichroism (CD) spectroscopy was extensively used for all alkenes for determination of the absolute configuration and to assess quantitatively the changes in helicity upon irradiation [12,18].

An extensive discussion of CD effects is beyond the scope of this article [12,18,19]. Typical UV and CD spectra of type 2 alkene i.e. M-*cis* *12* and P-*trans* *13*, are shown in figure 2. Strong UV absorption around 230 nm and medium intense absorptions at 310 and 330 nm are accompanied
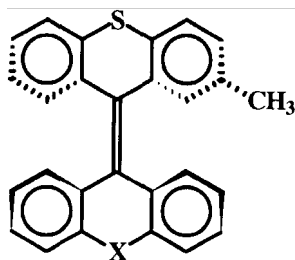
TABLE I   Racemization barriers of overcrowded ethylenes

compound	X	Aryl-X bond length Å	racemization barrier kJ mol^{-1}
8	S	1.77	114.6 ± 0.8
9	C(CH$_3$)$_2$	1.52	105.0 ± 1.3
10	NCH$_3$	1.42	89.1 ± 2.1
11	O	1.38	<83.7

by strong CD absorptions in particular in the short wavelength region ($\Delta\varepsilon$ typically 15–200). UV spectra for *cis*-**12** and *trans*-**13** are nearly identical although small but distinct differences are observed in extinction coefficients.

The CD spectra for M-*cis*-**12** and P-*trans*-**13** are mirror images in the short wavelength region, below 250 nm, while at longer wavelengths these spectra are clearly different. This remarkable feature is due to the fact that, although **12** and **13** are diastereomers the overall helicity shows a mirror image relationship (e.g. pseudo enantiomers) and determines the major CD effects.

THE SWITCHING PROCESS

Type 2 and type 3 alkenes that are substituted at the lower part, e.g. alkenes with four different substituents around the central double bond, are possible candidates to construct a *cis-trans* type of chiroptical molecular switch. Thus upon irradiation with light of an appropriate wavelength a stilbene type *cis-trans* isomerization occurs. However, larger quantum yields for photoisomerization and an enhanced thermal stability favor type 2 over type 3 alkenes.

Scheme 4 summarizes the various isomerization pathways of a tetrahydrophenanthrene based type 2 alkene.

Investigations concerning the thermal and photochemical behaviour, have revealed the occurrence of *cis-trans* isomerization (M-*cis* ⇌ P-*trans*) and conformational inversion simultaneously. The photochemically induced interconversion of P and M helices can be detected by monitoring the change in optical activity using CD or ORD spectroscopy at wavelengths remote from those used to effect *cis-trans* isomerization. This implies that "non-destructive" read-out is feasible.

The first successful *cis-trans* chiroptical switch developed in our group was a methoxy substituted alkene of type 2, 4-[9'-(2'-methoxythioxanthylidene)]-7-methyl-1,2,3,4-tetrahydrophenanthrene (**12/13**)[10]. Irradiation of M-**12** (*cis*) in n-hexane at 300 nm yielded a mixture of 64% M-**12** and 36% P-**13** whereas similar irradiation at 250 nm yielded a photostationary state with 68% M-**12** and 32% P-**13**. Successive irradiations during 30 sec at these two wavelengths resulted in modulation of the photostationary states with d.e.'s of 28% and 36%, respectively.

A remarkable improvement in the selectivity of the chiroptical switch was found by introducing strong donor- and acceptor substituents in the lower thioxanthene half (Scheme 5) [20]. The UV/VIS spectra of **14** (*cis*-nitro) and **15** (*trans*-nitro) are clearly distinctable and show a large bathochromic shift allowing the switching pro-
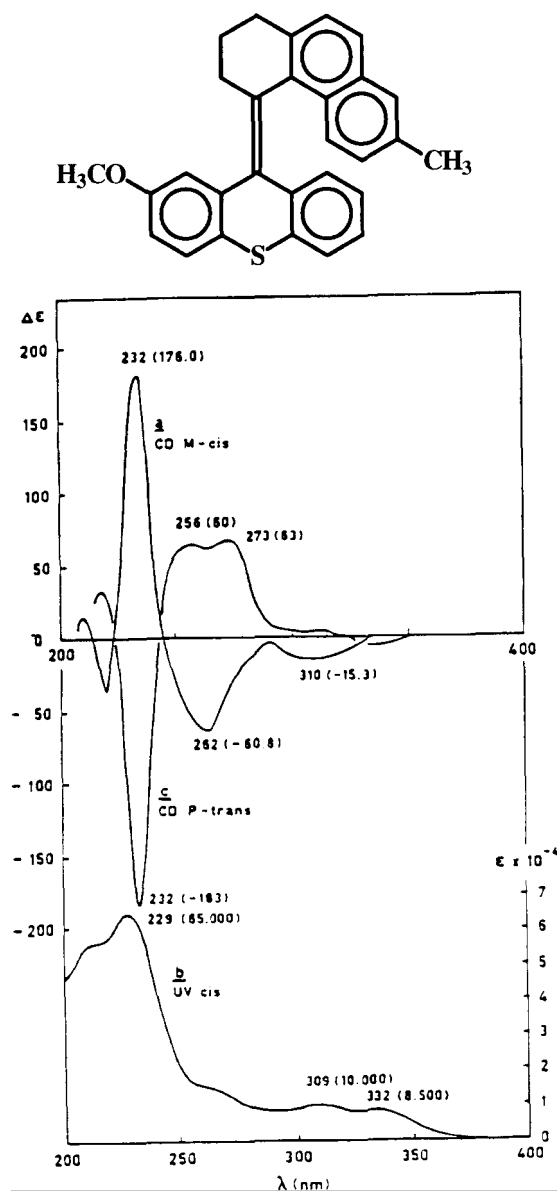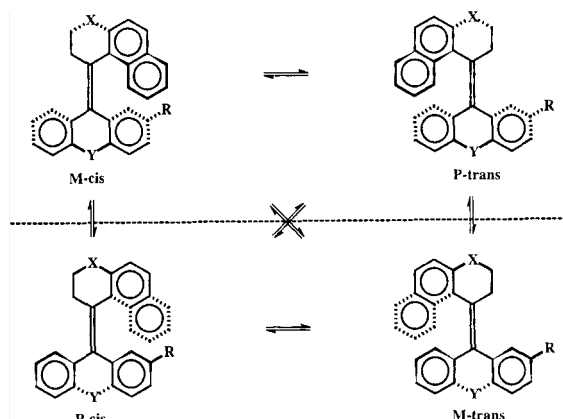
SCHEME 4   The M-cis ⇌ P-trans switch, and the enantiotopic P-cis ⇌ M-trans switch. Under working conditions none of the processes that cross the dashed line and lead to racemization are allowed.

FIGURE 2   UV spectrum of *cis*-**12** in n-hexane and the CD spectra of M-**12** (*cis*) and P-**13** (*trans*) in hexane/isopropanol 9:1.

cess to take place in the visible. Furthermore the introduction of a sulfur atom in the upper half (X = S) increases the thermal and photochemical stability towards racemization (ΔG_{rac} = 122.2 kJ·mol^{-1}). During the switching process the naphthalene moiety in the upper half has alternated
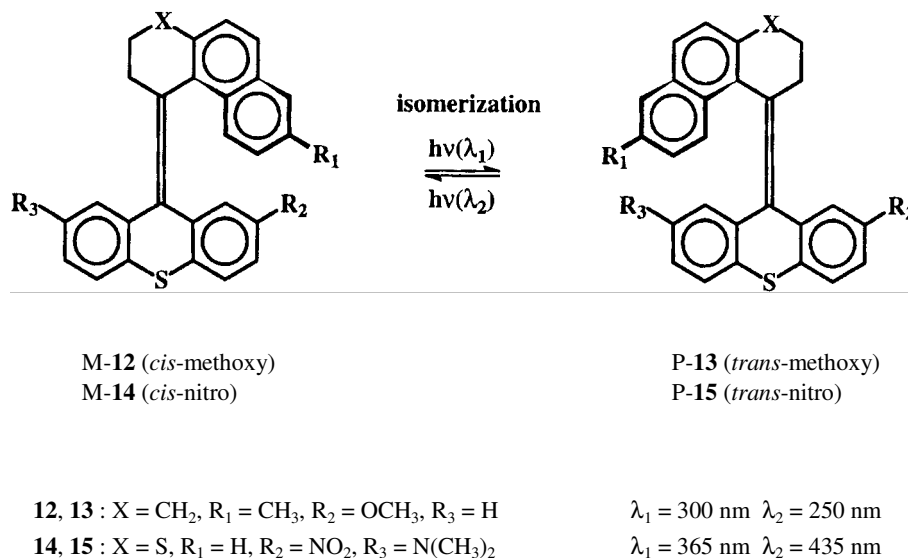
interactions with the nitroarene acceptor moiety in M-**14** and the dimethylamino donor moiety in P-**15**.

The extrema at longer wavelengths in the UV/VIS difference spectrum of **14** and **15** are at 365 and 435 nm and these represent wavelengths at which after irradiation large differences in the composition of photostationary states can be expected. A stereospecific photochemical *cis-trans* isomerization takes place readily monitored by CD, ^{1}H NMR spectroscopy and HPLC analysis (Scheme 5). Alternated irradiation at 365 nm and 435 nm resulted in a highly diastereoselective interconversion between photostationary states with ratio's of 70 : 30 and 10 : 90 of M- and P- respectively. Therefore, we were able to switch between photostationary states with 40% and 80% diastereomeric excess, respectively, with high wavelength dependent diastereoselectivities.

Racemization or deterioration of **14** and **15** was not observed during 60 switching cycles. The observations that the CD effects are large and show a mirror image relationship at many wavelengths and the fact that the switching process occurs between photostationary states in

M-**12** (*cis*-methoxy)   P-**13** (*trans*-methoxy)
M-**14** (*cis*-nitro)   P-**15** (*trans*-nitro)

12, **13** : X = CH$_2$, R$_1$ = CH$_3$, R$_2$ = OCH$_3$, R$_3$ = H λ_1 = 300 nm λ_2 = 250 nm
14, **15** : X = S, R$_1$ = H, R$_2$ = NO$_2$, R$_3$ = N(CH$_3$)$_2$ λ_1 = 365 nm λ_2 = 435 nm

SCHEME 5   Chiroptical molecular switching process.

which either of the pseudo enantiomers M-**14** or P-**15** is present in large excess makes the switch relatively insensitive towards racemization.

The donor-acceptor based switch allows photochemical control of the chirality with a notable selectivity, an increased stability and a switching process to be executed in the visible.
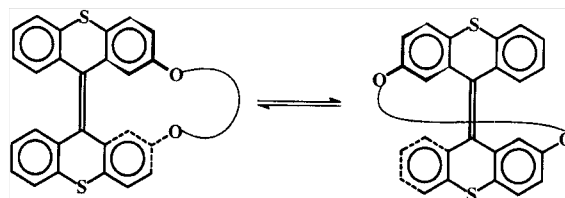
GATED RESPONSE SYSTEMS

A highly desirable property of photochromic systems is gated response, meaning that photoresponsive effects are blocked upon irradiation unless another external stimulus, either physical or chemical, is applied. Recently, Lehn and co-workers demonstrated electrochemical gated photochromism with a dual-mode molecular switching device in which photochromism could be reversibly blocked by an electrochemical reaction [8,21].

In order to achieve gated response in the chiroptical switches we chose two different approaches, one of them based on reversible protonation and the other on reversible complexation of a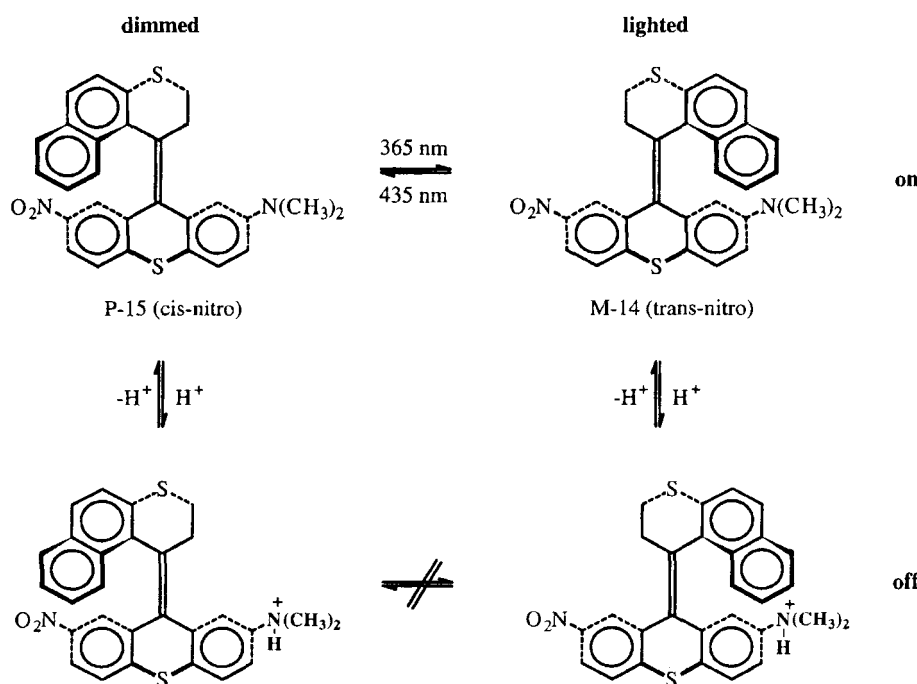lkali metal ions with a covalently bound crown ether host. An elegant example of an aza-crown ether photoswitchable host-guest system was developed by Shinkai and co-workers [22]. It can be imagined that the photoresponsive properties of the chiroptical switch can reversibly be locked by complexation at a crown ether unit attached to the switch. The synthetic accessibility of crown ether bound chiroptical switches and their ion complexation was investigated with new bisthioxanthylidene crown ethers (Scheme 6) [23].

Another approach is focussed on reversible protonation of the dimethylamino donor functionality in the donor-acceptor switch M-**14**, P-**15** (Scheme 7).

It was shown that the switching process can be blocked by protonation of the donor unit. The high effectiveness of the donor-acceptor system

SCHEME 6   Chiral switchable crown-ethers.

dimmed   **lighted**

$$\xrightarrow[435 \text{ nm}]{365 \text{ nm}}$$

P-15 (cis-nitro)   M-14 (trans-nitro)

on

$-H^+ \updownarrow H^+$ $-H^+ \updownarrow H^+$

off
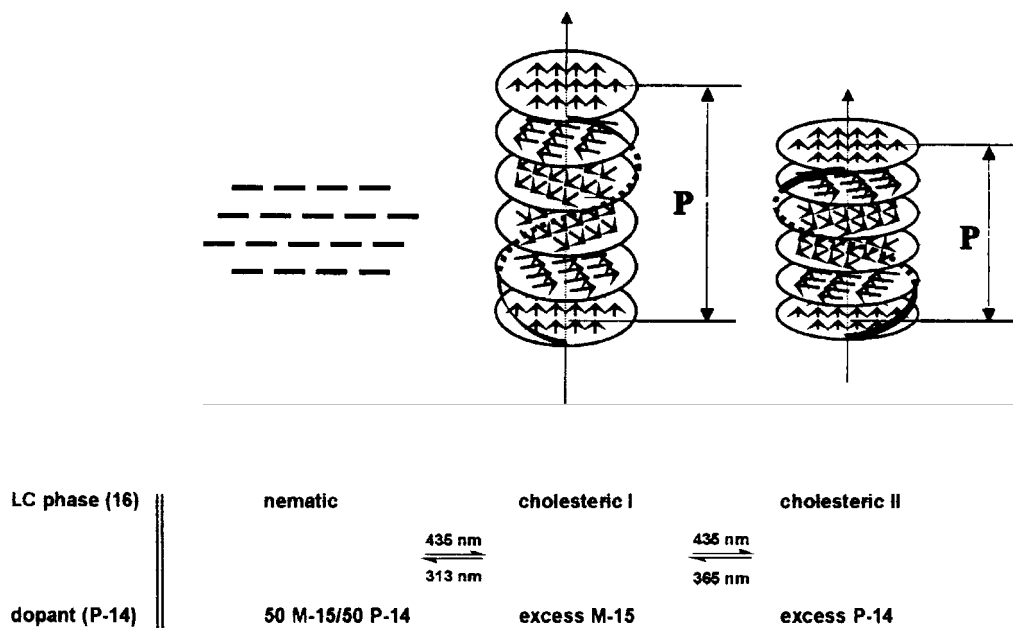
SCHEME 7   A switchable molecular device.

is now lost due to a non-effective acceptor-acceptor unit in the chiroptical switch. P-**15** and M-**14** are also fluorescent compounds and distinct differences ($\Delta\Phi = 0.016$) are seen in fluorescence intensities. Fluorescence emission is totally quenched after complete protonation. After deprotonation fluorescence intensities are completely recovered and the photochemical switching between P- and M- helices is fully restored. The key features of the "dual mode photoswitching of luminescence" [24] described here are the proton-dependent photomodulation of fluorescence and chirality and the ability to interconvert between three distinctive states, namely *dimmed*, *on* and *off*, as shown in Scheme 7. In the *on* mode, P-**15** and M-**14** show at the maxima different intensities in their fluorescence emission. Visualized, this means a molecular device which can be dimmed or lighted photochemically. After amine protonation the fluorescence is quenched and both the switching process and the emission are in the *off* mode. This

constitutes a locking device for information storage. Deprotonation reestablishes the molecular switching behaviour as well as the fluorescence (*on* mode).

LIQUID CRYSTALLINE (LC) SWITCH

For possible applications in optical data storage systems, the switching process should be executed in an organized matrix. The chiroptical molecular switch was therefore incorporated as a guest in a liquid crystalline host material.

The modulation of the mesophases and physical properties of LC materials by reversible photochemical reactions is a major challenge for information technology. We designed a host-guest system consisting of P-**15** and a nematic liquid crystalline material 4'-(pentyloxy)-4-biphenylcarbonitrile **16** for the development of new LC optical devices. It is well known that small

LC phase (16)	nematic	cholesteric I	cholesteric II
		435 nm $\rightleftharpoons$ 313 nm	435 nm $\rightleftharpoons$ 365 nm
dopant (P-14)	50 M-15/50 P-14	excess M-15	excess P-14

SCHEME 8   Photochemically switching processes of LC-phase (**16**) and chiral dopant P-**15**.

amounts of optically active guest molecules added to a nematic host induce a cholesteric phase. By doping 1 wt% of enantiomerically pure P-**15** to the nematic host **16** the nematic phase converts to a cholesteric phase. By irradiation with light of the proper wavelength the cholesteric phase can be converted to a nematic phase or, alternatively the cholesteric phase can be modulated [25]. Both the helicity and the pitch of the cholesteric phase change upon changing the chirality of the dopant P-**15** by irradiation. All these processes are fully controlled by light and fully reversible. The complete switching cycle is illustrated in Scheme 8.

These findings make it possible to modify liquid crystalline phases by means of light and also to control the optical properties of liquid crystalline phases by optical means.

CONCLUSIONS AND PROSPECTS

Chiral photoresponsive molecules were designed based on helical shaped inherent dissymmetric alkenes incorporating a stilbene type chromophore in their molecular structures. High stereoselectivity was achieved in the photochemical switching of the helicity. The change in chiroptical properties can be exploited as a mean of nondestructive read-out in a binary logic memory element incorporating these chiral photochromic materials. Additional characteristics, which are attractive for potential data storage systems, are the possibility to perform a writing, reading and erasing cycle by a single physical method and the feasibility to achieve gated response. Furthermore it was demonstrated that amplification of the photochemically induced change in helicity of the photoresponsive molecules to changes in mesoscopic organization can be achieved.

The control of helicity both at the molecular- and mesoscopic level by light holds promise for the photochemical control of chirality in a variety of supramolecular materials. Having realized chiroptical molecular switches these systems might be incorporated, as light addressable units, in multicomponent devices. Chirality is an essential element in recognition, catalysis and assembly processes in living nature and the possibility to control molecular chirality by light of-

fers a bright stage for an molecular designer to address bioprocesses.

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