Chiroptical molecular switches

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Chiroptical Molecular Switches**

By Ben L. Feringa,* Nina P. M. Huck, and Anne Marie Schoevaars

1. Introduction

The design of molecular switches and optical devices based on bistable organic molecules is largely stimulated by the challenge of molecular memory elements and miniaturization in future technology.[1] Photochemical control of nanoscale architectures, mechanical devices, catalysts, sensors, surfaces of materials, and target directed delivery systems are some of the applications that can be envisaged. A variety of photoreversible compounds such as fulgides, diaryl alkenes, spiropyrans, and azobenzenes have been prepared and the photochromic processes involved are typically *cis-trans* isomerizations or photocyclization reactions.[2]

Although the inevitable condition of bistability is fulfilled in these systems, several requirements are essential for their application as switching devices in practice. The most prominent of these requirements are fatigue resistance, ready detectability of both forms, no thermal interconversions of the isomers in a large temperature range, and non-destructive read-out procedures. Detection is usually based on UV/VIS spectroscopy in or near the absorption bands, leading to unwanted side effects.[3] Efforts to avoid this problem[4,5] have led to the construction of light-switchable derivatives, where the photochromic event is accompanied by other changes in the molecule, such as ion complexation behavior, refractive index, or conductivity, which might be detected without interference with the photostationary state.

In the alternative approach to molecular switches, discussed here, the unique optical properties associated with the enantiomers (or pseudoenantiomers)[6] of chiral photoresponsive molecules are exploited. The photoreversible system is based on the interconversion of two chiral forms of helically shaped molecules, denoted P and M, for the right- and left-handed helical structure (Eq. 1).

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The P and M helices in the chiral optical switch represent two distinct states in a binary logic element. Non-destructive read-out in an optical recording system containing these organic materials is feasible by monitoring the change in

$$P \xrightleftharpoons[h\nu_2]{h\nu_1} M \qquad (1)$$

optical rotation at wavelengths remote from the wavelengths used for switching. The principle of an information storage system based on a chiroptical molecular switch, using stereo-isomers P and M of opposite helicity, is schematically shown in Fig. 1.
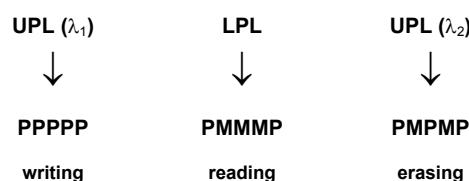
UPL (λ_1)	LPL	UPL (λ_2)
↓	↓	↓
PPPPP	PMMMP	PMPMP
writing	reading	erasing

Fig. 1. Schematic diagram of a chiral information storage device based on a chiroptical switch. Writing occurs with unpolarized light (UPL) at λ_1 (P → M), detection with linear polarized light (LPL), and erasing (M → P) with UPL at λ_2.

2. Molecular Design of Switching Units

We have developed chiroptical molecular switches using sterically-overcrowded unsymmetrical thioxanthenes **1** (Y = S). To avoid unfavorable steric interaction, the distortion of the molecular framework imparts a helical shape to these molecules. A photochemically induced stilbene-type *cis-trans* isomerization of **1** (Fig. 2) simultaneously results in reversal of the helicity, whereas the enantiomers are stable under ambient conditions.[7]
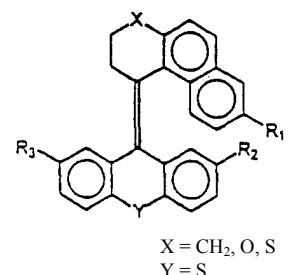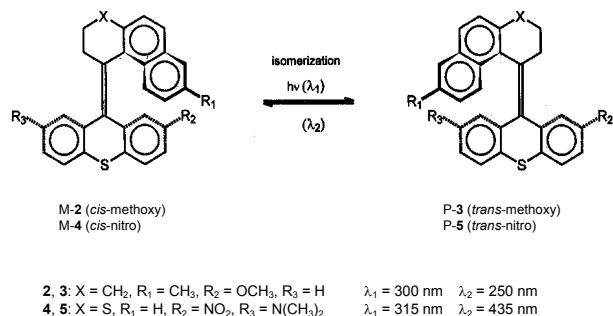
X = CH$_2$, O, S
Y = S

Fig. 2 Functional helical photoresponsive alkenes.

It was found that the racemization barriers can be tuned over a range from 50 to >126 kJ mol^{-1} by modification of the bridging unit Y in the lower half of **1**.[8] Moreover, an increased thermal and photochemical stability with respect to racemization was achieved by introduction of a bridging sulfur atom in the upper half (X = S, $\Delta G^{\neq}_{rac}$ = 122.2 kJ mol^{-1}). The switching unit can be tethered to polymers or other functional units via appropriate spacers either at the upper or lower half of **1**. The photochemical properties can also readily be tuned through substituents R$_1$-R$_3$. Giving proper molecular design, read out by optical rotation or circular dichroism remote from the switching wavelengths is possible.

3. Highly Stereoselective Optical Molecular Switching

The first chiroptical switch was realized with thioxanthene based alkenes **2** and **3** (Scheme 1).[9] Irradiation of enantiomerically pure M-**2** resulted in a photostationary state consisting of 64 % M-**2** and 36 % P-**3**. A stereospecific

M-**2** (*cis*-methoxy)   P-**3** (*trans*-methoxy)
M-**4** (*cis*-nitro)   P-**5** (*trans*-nitro)

2, **3**: X = CH$_2$, R$_1$ = CH$_3$, R$_2$ = OCH$_3$, R$_3$ = H λ_1 = 300 nm λ_2 = 250 nm
4, **5**: X = S, R$_1$ = H, R$_2$ = NO$_2$, R$_3$ = N(CH$_3$)$_2$ λ_1 = 315 nm λ_2 = 435 nm

Scheme 1. Chiroptical molecular switching process.

interconversion of pseudoenantiomers, i.e. M-*cis*-**2** to P-*trans*-**3**, was observed. A 4 % shift in the photostationary state was reached by using 250 nm wavelength light, which produces a sufficient change in chiroptical properties for detection purposes. Alternated irradiation with 300 and 250 nm light (at 3 s intervals) resulted in modulated optical rotatory dispersion (ORD) and circular dichroism (CD) signals, although 10 % racemization was seen after 20 switching cycles.

A remarkable stereoselective switching process was found when we introduced donor- and acceptor substituents in the thioxanthene lower half.[10] In M-**4**, a nitroarene acceptor moiety is facing the naphthalene chromophore in the upper half, whereas in P-**5** a dimethylaminoarene donor moiety interacts. In addition, a large bathochromic shift is found in the UV/VIS spectra of **4** and **5**, allowing the switching process to take place in the visible wavelength range.

Alternated irradiation using 365 and 435 nm light resulted in highly diastereo-selective interconversions between photostationary states, with 70:30 and 10:90

ratios of M-**4** and P-**5** respectively (Fig. 3). Thus, a 60 % difference in photostationary states and helicities is achieved, and the system was capable of 60 switching cycles without deterioration or racemization.
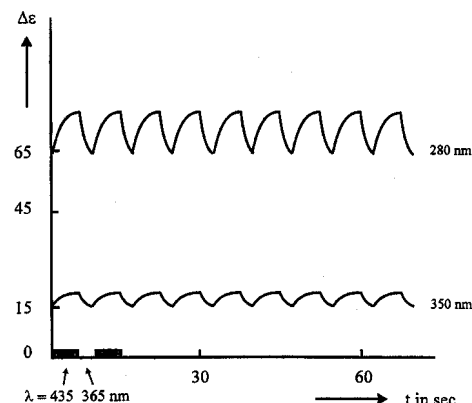
Fig. 3. Plot of $\Delta\varepsilon$ at 280 and 350 nm versus the irradiation time for the P-**4** ° M-**5** isomerization, irradiating alternately at λ = 435 and 365 nm.

The composition of the photostationary states, and as a consequence the excess of P or M chirality, is strongly dependent on wavelength and medium.[11] Photoresponsive molecules, such as **4** and **5**, in which a change in chiroptical properties is encountered, fulfil the requirements mentioned previously and have the additional characteristic that the writing, reading, and erasing cycle might occur with a single physical method.

Apart from writing (UV/vis) and reading (ORD, CD), employing this chiroptical molecular switch an EDRAW (Erasable Direct Read After Write) process might be executed using, for instance, 365 nm light for reading and erasing, i.e. M-**4** → P-**5** isomerization.

4. Gated Response

It is of particular interest to exploit these chiral switches to control various functions in multicomponent systems.[1,12] For instance, a highly desirable property of photochromic compounds is gated response. Gated photochemical reactivity implies that no molecular exchange occurs upon irradiation unless another external stimulus, either physical or chemical, is applied to the system.[13] Chemical gated photochromism was recently demonstrated with diarylethylenes, in which the photochromic and electrochemical properties were mutually regulated.[5]

Our approach focused on reversible protonation of the dimethylamine donor functionality in the donor-acceptor switch P-**4**/M-**5** (Scheme 2).[14] The switching process can be blocked by protonation of the donor unit as a non-effective acceptor-acceptor (nitro- and ammonium-substituent) unit is present in P-**6**/M-**7**. We also found that P-**4** (*cis*) and M-**5** (*trans*) are fluorescent compounds, and that
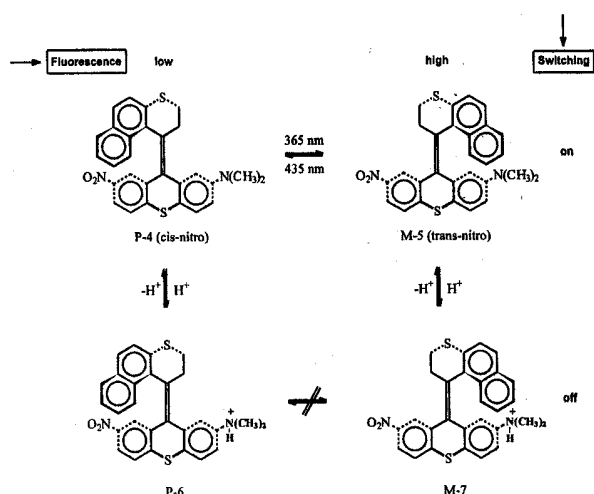
Scheme 2. Dual mode photoswitching of luminescence.

distinct differences ($\Delta\Phi$ 0.016) are seen in fluorescence intensities of the isomeric alkenes. Fluorescence emission is totally quenched after addition of one equivalent of, for instance, trifluoroacetic acid.

The key features of the photoswitchable system described here are proton-dependent photomodulation of both fluorescence and chirality, and the ability to interconvert between three distinctive states, namely *dimmed, on,* and *off,* as schematically shown in Scheme 2. In the *on* mode, P-**4** and M-**5** have different intensities in their fluorescence emission. Visualized, this means a molecular device which can be dimmed or made brighter photochemically. After amine protonation in **4** or **5** 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. De-protonation re-establishes the molecular switching behavior, in addition to the fluorescence (*on* mode).

Incorporation of crown-ethers into the chiral switches[15] offers the possibility of ion-binding dependent photomodulation, whereas the switching unit can also be applied in the photocontrol of a mechanical device, as we have demonstrated recently.

5. Chiroptical Switching between Liquid Crystalline Phases

These molecular photoswitches can be readily incorporated into polymers or in supramolecular assemblies. Apart from effective switching at the molecular level, this approach allows expression of the photochemical induced changes of molecular chirality in terms of modifications of the chirality, as well as other properties, of the macromolecular materials or supramolecular assemblies. For instance, we designed a host-guest system consisting of P-**4** and a nematic liquid crystalline (LC) material 4´-(phenyloxy)-4-biphenylcarbonitrile **8**, focusing on the development of new LC devices.[16]

LC display technology is currently based on electronic modulation of the active organic materials. The modulation of mesophases and physical properties of LC materials by photochemical reactions, i.e. photoswitching of LC phases, is a major challenge to the information technology industry. Some important advantages include speed of data processing and the possibility to develop all optical devices. It is well-known that small amounts of optically active guests added to a nematic host can induce a cholesteric phase, but reversible interconversion of a twisted and non-twisted phase by photochemical modification of the dopant has not been realized prior to our findings. Addition of 1 wt-% of enantiomerically pure P-**4** to the nematic phase obtained from **8** converts it to a cholesteric phase. With M-**5**, a similarly induced cholesteric phase is observed with the opposite screw sense.

Realizing that the twisted nematic phase is very sensitive to chemical modifications in the chiral guest molecule, we irradiated a thin film of **8**, doped with P-**4**, at 435 nm for 15 s, which results in a stable cholesteric phase (cholesteric I, Scheme 3). This indicates that the photostationary state P-*trans*-**4** ° M-*cis*-**5** (Scheme 1) is also readily attained in the LC phase. After irradiation of the film at 365 nm, a distinct decrease in the pitch of the cholesteric phase is observed, leading to the formation of the cholesteric phase II. Subsequent irradiation at 435 nm reverts the pitch to its original value.
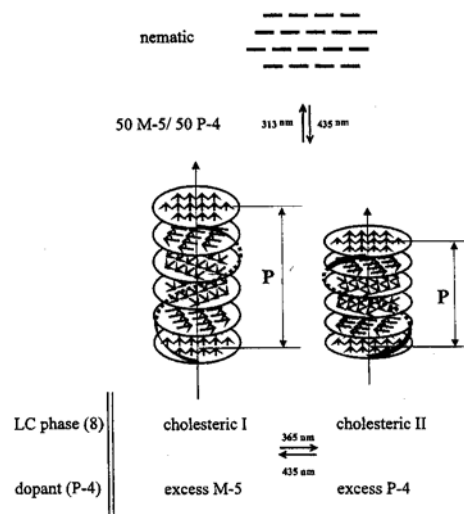
Scheme 3. Photochemical switching processes of LC phase **8** and chiral dopants.

Alternated irradiation with 435 and 365 nm light (5 min irradiation time) results in photo modulation (between 12.29 and 5.31 µm) of the pitch in the induced cholesteric phase. This modulation was perfectly stable during eight switching cycles. In addition, we could show by determination of the cholesteric screw sense by the Grandjean-Cano method that the pseudoenantiomers P-**4** and M-**5** lead to cholesteric phases of opposite handedness. Another important finding was that after exposure of a thin film of P-**4**, M-**5**, and **8**

using 313 nm light, a conversion of the cholesteric to the nematic phase is achieved, whereas the original cholesteric texture is restored with 435 nm light. Apparently, a (nearly) 50:50 ratio of opposite helices of the chiral photoresponsive guest molecule is formed at 313 nm in the LC phase, resulting in a compensated nematic phase. The complete switching cycle is illustrated in Scheme 3.

Photoswitching of the helical shaped dopant in a thin film of LC material is highly effective in the reversible conversion of cholesteric to nematic phases, as well as alternation of the macroscopic helical pitch and screw sense in the cholesteric phases. The macroscopic assembly in this three-position switch can effectively be controlled by the modulation of the ratio of helices of the dopant; these ratios depend on the wavelengths used for irradiation of the film. These results pave the way to photocontrol by introducing chiroptical switching in other films and supramolecular assemblies.

6. Conclusions

Molecular chirality is an intrinsic feature of living organisms; precise control of chirality at the molecular and macroscopic level and in supramolecular assemblies is essential to the functioning of biosystems. We achieved the control of chirality by optical molecular switches. The unique optical properties and molecular architectures associated with the enantiomers (or diastereomers) of chiral photoresponsive molecules offer intriguing prospects
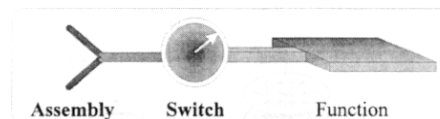

Fig. 4. Multicomponent molecular switch.

in the design of new materials, as has been illustrated by the examples presented here. Having established the possibility of modulation of the inherent chiral properties with light in these chiroptical switches and the control of the expression

of chirality in function and assembly, these molecules can serve as switching units in a wide range of other applications.

In particular, the development of multicomponent systems composed of assembly, switching, and functional units can be envisaged (Fig. 4). Subsequent formation of ordered multicomponent materials will gain great impetus from recent advances in supramolecular chemistry.

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