Dual-mode Photoswitching of Luminescence

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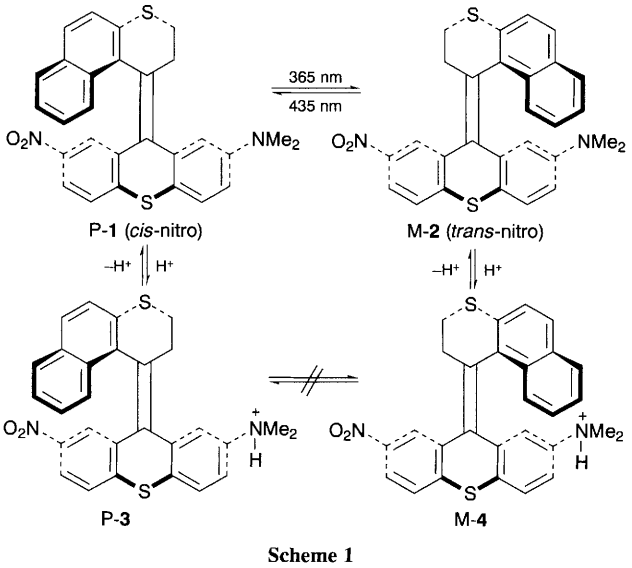
The fluorescence and chirality of photoswitchable inherently dissymmetric alkenes *cis* **1** and *trans*-2-nitro-7-dimethylamino-9-(2′,3′-dihydro-1′*H*-naphtho[2,1-*b*]thiopyran-1′-ylidene)-9*H*-thioxanthene **2** are reversibly modulated by irradiation whereas photoresponsive effects and emission are regulated by reversible protonation.

The photochromic behaviour of organic molecules has attracted considerable interest in view of the potential fabrication of reversible optical data storage and memory devices.[1,2] Of particular interest are functional units which can be modulated by more than one type of external stimulation, either chemical or physical. Chemical gated photochromism was demonstrated with diarylalkenes in which photochromism could be reversibly blocked owing to the formation of intramolecular hydrogen bonds in one of the bistable states.[3] Recently, Lehn and co-workers[4] reported a dual-mode molecular switching device in which photochromic and electrochemical properties are mutually regulated. We have been concerned with the development of chiroptical molecular switches using inherently dissymmetric alkenes.[5]

Here we report a dual-mode optical molecular switching system based on chiral helical-shaped alkenes in which chirality and fluorescence can be reversibly modulated by light; the photoresponsive effects and fluorescence can be regulated by reversible protonation whereas the different states can be read both by fluorescence spectroscopy and chiroptical techniques (Scheme 1). The chiroptical molecular switch is based on donor–acceptor substituted inherently dissymmetric alkenes *cis*- and *trans*-2-nitro-7-dimethylamino-9-(2′,3′-di-hydro-1′*H*-naphtho[2,1-*b*]thiopyran-1′-ylidene)-9*H*-thioxanthene, **1** and **2**, respectively, the synthesis and resolution of which will be reported elsewhere.[6] A highly stereoselective photochemical isomerization of P-**1** (*cis*-nitro) to M-**2** (*trans*-nitro) and *vice versa* takes place (Scheme 1). This selectivity is attributed to the interaction of the upper naphthalene moiety, located either opposite the dimethylamino arene *donor* unit or the nitro arene *acceptor* unit of the lower thioxanthene part of these molecules.

Both *cis*-**1** and *trans*-**2** are fluorescent compounds and distinct differences are seen in the UV–VIS (Fig. 1) and fluorescence spectra (Fig. 2) of these isomeric alkenes. Isosbestic points at 300, 337 and 400 nm are found in the absorption difference spectrum of enantiomerically pure P-**1** and M-**2**, as was confirmed by monitoring the UV spectra during the photoisomerization (P-**1** ⇌ M-**2**). Upon excitation of *n*-hexane solutions of P-**1** and M-**2** (5.8×10^{-6} mol dm^{-3}) at 300 nm, maximum fluorescence intensities† of 0.37 (λ_{max} 528 nm) and 0.91 (λ_{max} 531 nm) respectively, are observed. No racemization or isomerization occurs during fluorescence measurements, as confirmed by chiral HPLC and CD spectroscopy. The integrated fluorescence quantum yield [7] (400–600 nm, ethanol) of *trans*-**2** is 0.153 and of *cis*-**1** is 0.137. The fluorescence emission is ascribed to an intramolecular charge transfer transition (an $a_\pi \leftarrow l$ CT transition) of the dimethylamino donor units in **1** and **2** in accordance with the excitation and fluorescence in *N*,*N*-dimethylaniline.[8]

Irradiation of either enantiomerically pure P-**1** (*cis*-nitro) or M-**2** (*trans*-nitro)‡ at 365 nm results in a photostationary state composed of 70% M-**2** and 30% P-**1** as monitored by CD spectroscopy. Alternated irradiation using 365 and 435 nm light results in a highly diastereoselective interconversion of M-**2** (*trans*-nitro) and P-**1** (*cis*-nitro), respectively. Monitored by fluorescence spectroscopy, the two photostationary states gave emissions of 0.75 and 0.47 (relative intensities, arbitrary units;



Scheme 1

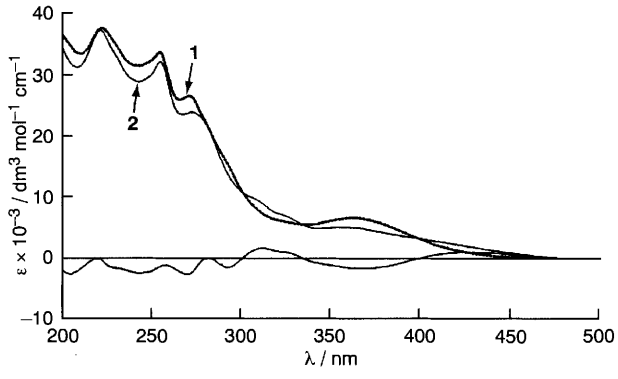


Fig. 1 Absorption spectra of **1**, **2** and the difference spectrum (*n*-hexane)

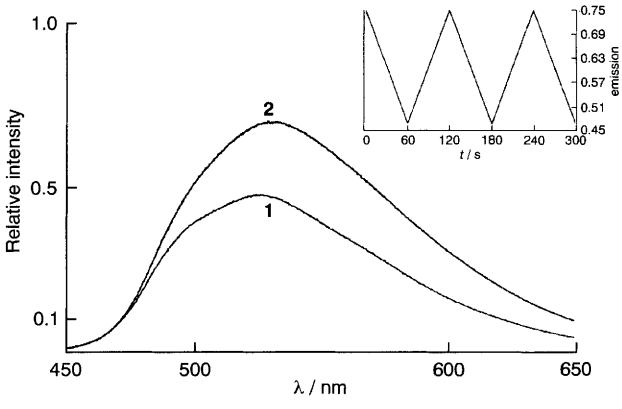
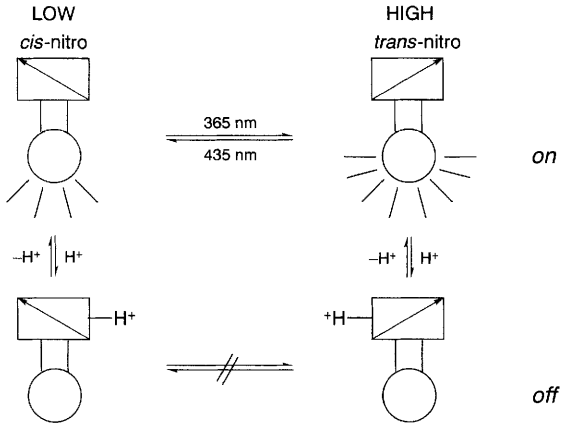


Fig. 2 Fluorescence emission spectra (*n*-hexane) of photostationary states of P-**1** and M-**2** in 90 : 10 and 30 : 70 ratios. *Insert*: Modulated emission signal during alternating irradiation at 365 and 435 nm (excitation 300 nm, irradiation time 60 s).

λ_{max} 530 nm). Fig. 2 displays the two fluorescence spectra after irradiation with 365 and 435 nm light, whereas the insert depicts the modulated fluorescence signal (excitation 300 nm) during alternating irradiation at 365 and 435 nm. The switching process can be blocked by protonation of the dimethylamino donor unit (Scheme 1). The effectiveness of the donor–acceptor system is now lost owing to a non-effective acceptor–acceptor unit in the bistable chiral alkenes. The complete protonation of the dimethylamino group using 1 equiv. of trifluoroacetic acid, was determined by ^{1}H NMR (NCH_3 at δ 3.01 in P-**1**, and at δ 3.23 in P-**3**). As a consequence the fluorescence emission is totally quenched after addition of 1 equiv. of trifluoroacetic acid. A similar pH-dependent quenching of fluorescence is seen in dimethylaniline and in *N*-arylaminonaphthalene sulfonates[8,9] and the $a_\pi \leftarrow l$ absorption band disappears on protonation of the amine. After deprotonation, using 1 equiv. of triethylamine, the fluorescence intensities of **1** and **2** (Fig. 2) are completely recovered. Furthermore, the photochemical switching between P- and M-helices (P-**1** ⇌ M-**2**) is fully restored.

The key features of the photoswitchable system 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 2. In the *on* mode, P-**1** and M-**2** have different intensity maxima in their fluorescence emission. Visualized, this means a molecule device which can be dimmed or lighted photochemically. After amine protonation in **1** or **2** the fluorescence is quenched and both the switching process and the emission are in the *off* mode (Scheme 2). Deprotonation reestablishes the molecular switching behaviour as well as the fluorescence (*on* mode).



Scheme 2 A switchable molecular device

With respect to information storage, the next sequence can be envisaged: after photochemical isomerization with 365 nm light (**1** → **2**) the information can be locked by protonation (**2** → **4**). The information can only be erased after deprotonation (**4** → **2**) followed by irradiation with 435 nm light (**2** → **1**). Also, information might be locked after writing with 435 nm light. This represents an EDRAW (erasable direct read after write) process.

We thank the 'Stichting Technische Wetenschappen' (STW) and the Dutch Foundation for Scientific Research (NWO) for their financial support. The cooperation with Dr H. P. J. M. Dekkers of the Department of Theoretical Organic Chemistry of the University of Leiden on fluorescence spectroscopy is gratefully acknowledged.

Received, 13th February 1995; Com. 5/00844A

Footnotes

† All fluorescence spectra were recorded in *n*-hexane on a SPF-500™ SIM AMINCO spectrofluorometer. Fluorescence was checked on a Spex Fluorolog DM/8, *n*-hexane, 6×10^{-6} mol dm^{-3}. Quantum yields were determined by ratioing to Rhodamine 123 (0.90) in Uvasol, ethanol 95%.

‡ The mixtures of enantiomers of *cis*-**1** and *trans*-**2** were resolved by HPLC with (+)-poly[(triphenylmethyl)methacrylate] as a chiral stationary phase. The pure enantiomers are perfectly stable under the conditions used in the experiments described here (ΔG_{rac} = 29.2 kcal mol^{-1}; 1 cal = 4.184 J).

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