COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A chiroptical molecular switch with perfect stereocontrol

Richard A. van Delden, Matthijs K. J. ter Wiel and Ben L. Feringa*

Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, The Netherlands. E-mail: feringa@chem.rug.nl; Fax: +31 50 3634296; Tel: +31 50 3634235

Received (in Cambridge, UK) 1st October 2003, Accepted 5th November 2003
First published as an Advance Article on the web 5th December 2003

A modified version of the first generation unidirectional molecular motor showed >99% stereoselectivity in photo-induced isomerizations in both directions, thus functioning as a perfect chiroptical molecular switch.

A key aspect in the bottom-up approach towards components for the nanotechnology toolbox is the pursuit of molecular systems that can perform a certain task triggered by an external input.[1] The use of light to control functions has been particularly successful. For example, sterically overcrowded alkenes have been demonstrated to function as chiroptical molecular switches[2] and unidirectional molecular rotary motors,[3] driven by light.

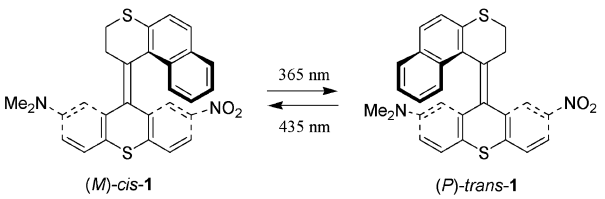
In case of molecular switches based on sterically overcrowded alkenes, a bistable system is formed by the pseudoenantiomeric *cis*- and *trans*-isomers, which due to steric hindrance adopt opposite ((*M*) and (*P*)) helical structures. Photoinduced *cis–trans* isomerization employing light of different wavelengths allows switching between two states, exemplified for **1** in Scheme 1.[4] The *cis* : *trans* ratio at the photostationary states (PSS) is governed by the ratio of molar absorption coefficients (ε) of both isomers at the wavelength employed and the ratio of the quantum yields (Φ) of interconversion of both isomers (eqn. 1). For **1**, as a result of an asymmetric donor–acceptor substituted lower half (with an electron donating dimethylamine and an electron withdrawing nitro substituent), this switching process exhibits relatively high selectivity. In *n*-hexane, irradiation with 365 nm light, due to a larger molar absorption coefficient of the *cis*-isomer at this wavelength (eqn. 1), resulted in a PSS with 40% excess of the *trans*-isomer addressing this state of the bistable (binary) system. Irradiation at 435 nm, where the molar absorption coefficient of the *trans*-isomer is largest, afforded a PSS with 80% excess *cis*-**1**. In this way both states of the binary system can be addressed by changing the irradiation wavelength. The opposite helicity of the two pseudoenantiomers offers the possibility of non-destructive read-out of the system using for example optical rotation at wavelengths outside the absorption range of the two forms, which is a distinct advantage compared to several photochromic materials examined as molecular switches.[5]

$$([cis]/[trans])_{PSS} = (\varepsilon_{trans} \times \Phi_{trans\rightarrow cis})/(\varepsilon_{cis} \times \Phi_{cis\rightarrow trans}) \quad (1)$$

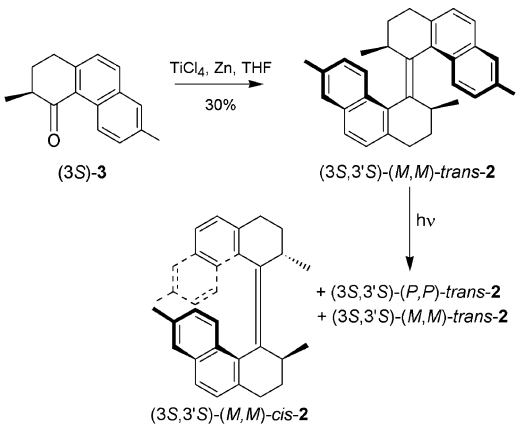
To reach these switching selectivities, both the donor and the acceptor moiety in the lower half of the molecule are absolutely essential, since the asymmetric substitution pattern causes the subtle differences in molar absorption coefficients of the isomers. Removing either one of these substituents, or replacing for example the dimethylamine for a methoxy-substituent of lower donating strength, results in a dramatic decrease in the switching selectivity. The wavelength used for irradiation is another crucial factor. In the case of **1**, irradiation at other wavelengths than those mentioned above also results in decreased selectivity. Irradiation at the isosbestic point, where the molar absorption coefficients of the *cis*- and *trans*-isomer are equal, results in a (near) 50/50 mixture of (*M*)-*cis*-**1** and (*P*)-*trans*-**1**.

Here, we report a remarkable chiroptical molecular switch **2**, lacking donor–acceptor substituents but showing >99% stereoselectivity in both directions. The chirality of the binary system can be fully controlled simply by changing the wavelength of irradiation. Compound **2** is related to the first molecular motor reported earlier.[6] The key step in the preparation of **2** is the McMurry coupling of (3*S*)-phenanthrenone **3** (Scheme 2). This reductive coupling affords the (*M*,*M*)-*trans*-**2** isomer exclusively.[7] Photoinduced *trans–cis* isomerization at rt afforded a mixture of (*M*,*M*)-*cis*-**2**, (*P*,*P*)-*trans*-**2** and (*M*,*M*)-*trans*-**2**,[8] which could be separated by preparative HPLC (Econosphere Silica; 5 μm).[9] Due to steric reasons, for both the *trans*- and *cis*-isomers of **2**, there is an energetic preference for the methyl groups at the stereogenic centers to adopt an axial orientation. Therefore the (3*S*,3′*S*)-(*M*,*M*)-*trans*-**2** and (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** forms are thermodynamically more stable. Nevertheless, (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** with diequatorial methyl substituents obtained after irradiation is also sufficiently stable at rt to study the photoisomerization processes in detail.

For molecular switch **2**, initial switching experiments were performed on both (*M*,*M*)-*trans*-**2** and (*M*,*M*)-*cis*-**2** employing polychromatic light of $\lambda \geq 280$ nm† and even under these conditions selectivities towards the diequatorial conformational isomers are extremely high for a *simple* hydrocarbon compound. For the (*M*,*M*)-*trans*-**2** to (*P*,*P*)-*cis*-**2** isomerisation at $\lambda \geq 280$ nm a PSS with a 70% excess of the (*P*,*P*)-*cis*-isomer (which is unstable at rt[9]) is reached and for the second ((*M*,*M*)-*cis*-**2** to (*P*,*P*)-*trans*-**2**) isomerisation, employing the same wavelength range a PSS with an 84% excess of the *trans*-isomer is reached, as determined by HPLC. These selectivities can never be fully accounted for by the difference in molar absorption coefficients of the two forms (*vide supra* for switch **1**). Apparently, there is an excited state preference for the isomers with diequatorial methyl groups ((*P*,*P*)-*cis*-**2** and (*P*,*P*)-*trans*-**2**) reflected in the excited state quantum yield of interconversion between the two isomers ($\Phi_{trans\rightarrow cis}$ and $\Phi_{cis\rightarrow trans}$;



Scheme 1 Donor–acceptor substituted chiroptical molecular switch **1**.



Scheme 2 Chiral overcrowded alkenes (3*S*,3′*S*)-(*M*,*M*)-*trans*-**2** and (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2**.

DOI: 10.1039/b312170d

This journal is © The Royal Society of Chemistry 2004

eqn. 1). In both isomerisation steps, coloration from a colorless to a yellow solution is visible by eye. This coloration implies a redshift of the UV/Vis absorption towards the visible. This is evident from the UV/Vis spectra of (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** and (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** (Fig. 1) and is probably due to twisting of the central olefinic bond, drastically influencing the conjugation over the central alkene.

Because of the unique absorption features, we decided to investigate the photochemical properties of sterically overcrowded alkene **2** in more detail in order to test whether the selectivity of the molecular switching could further be improved. Because of the relative stability of both the *cis* and *trans*-isomers, switching selectivities were investigated starting with (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** in *n*-hexane solution. Closer examination of the UV/Vis spectra and especially the ratio of the molar absorption coefficients of (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** and (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** (Fig. 1 inset; eqn. 1) shows that light with $\lambda \geq 280$ nm is far from ideal. As a matter of fact, in contrast to what can be expected from the observed PSS ratio, the (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** form will absorb most of the light in this spectral region. From the ratio of the molar absorption coefficients, the ideal wavelength for the forward *cis* to *trans* isomerisation was determined to be 303 nm, where the ratio of the molar absorption coefficients of the both isomers shows a minimum. Irradiation at this wavelength‡ instead of $\lambda \geq 280$ nm resulted in a near perfect photoequilibrium. A PSS consisting of >99% (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** was reached, as determined by HPLC.§

The red shift in the absorption band of (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** with respect to (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** allows specific excitation of the former diequatorial isomer. This should revert the photoequilibrium and lead to a PSS with excess (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2**. Based on the red-shifted UV/Vis band for (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2**, irradiation at the ideal wavelength of λ = 376 nm‡ resulted in a full reversal of the photoequilibrium to >99% (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** (HPLC). Alternate irradiation at λ = 303 and 376 nm resulted in switching between (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** and (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2**, respectively, with >99% selectivity. The chiroptical molecular switch can be read-out by circular dichroism which due to the opposite helical structures is dramatically different for both forms (Fig. 2). The switching cycle shown in Scheme 3 could be performed repeatedly without any sign of deterioration after four photochemical steps (Fig. 2, inset).

The subtle interplay of two chiral entities, the overall helical structure and two stereogenic centers, in **2** has led to unique stereochemical behaviour. This sterically overcrowded alkene functions as a perfect chiroptical switch where for the first time helical chirality can be controlled with complete selectivity solely by changing the wavelength of light. Crucial factors are the excited state preference for the isomer with an equatorial instead of an axial

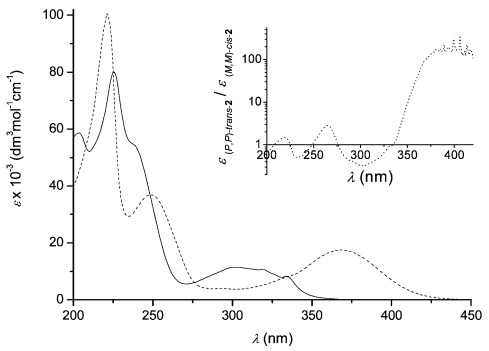


Fig. 1 UV/Vis absorption spectra of (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** (solid) and (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** (dashed). Inset: wavelength dependence of the ratio of the molar absorption coefficients of (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** and (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2**.

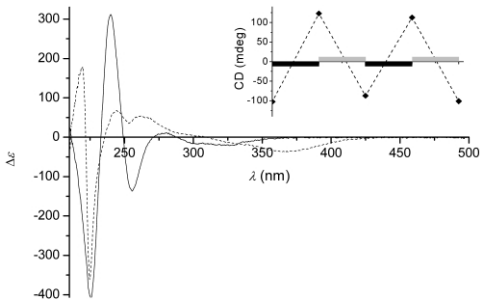
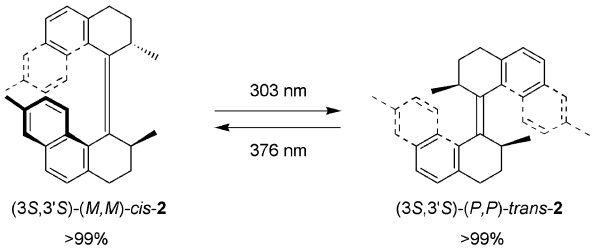


Fig. 2 Circular dichroism spectra of the PSS of the bistable switching pair (3*S*,3′*S*)-(*M*,*M*)-*cis*-**2** and (3*S*,3′*S*)-(*P*,*P*)-*trans*-**2** ($PSS_{376\ nm}$: solid line; $PSS_{303\ nm}$: dashed line). Inset: change in CD signal at 217 nm upon consecutive 303 nm (black bars) and 376 nm (grey bars) irradiation.



Scheme 3 Stereoselective chiroptical molecular switching.

orientation of the methyl substituent and the dramatic redshift in the UV/Vis absorption of the energetically less favored (*P*,*P*)-*trans* isomer compared to the (*M*,*M*)-*cis* isomer. These findings not only offer a new and useful molecular switch for the nanotechnology toolbox (in particular for switching of LC phases[10]) but also show a new concept for chiroptical molecular switches where geometrical changes rather than asymmetric substitution result in highly reversible photoswitching with complete stereocontrol.

Notes and references

† Irradiations at $\lambda \geq 280$ nm were performed with a 180 W Oriel Hg lamp adapted with a Pyrex filter.

‡ Irradiations at a specific wavelength were performed with an 150 W Oriel Xe lamp attached to an Oriel 74100 monochromator.

§ >99% selectivity means that only one form was visible in the HPLC chromatogram (Econosphere Silica; 5 μm; *n*-heptane) obtained by diode array analysis.

1 *Molecular Machines and Motors*, ed. J.-P. Sauvage and V. Amendola, *Structure and Bonding vol. 99*, Springer, Berlin, 2001.

2 B. L. Feringa, R. A. van Delden and M. K. J. ter Wiel, in *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001, ch. 5.

3 R. A. van Delden, M. K. J. ter Wiel, N. Koumura and B. L. Feringa, in *Molecular Motors*, ed. M. Schliwa, Wiley-VCH, Weinheim, 2003, ch. 23.

4 W. F. Jager, J. C. de Jong, B. de Lange, N. P. M. Huck, A. Meetsma and B. L. Feringa, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 348.

5 See for examples: *Chem. Rev.* Special Issue on *Photochromism: Memories and Switches*, ed. M. Irie, 2000, **100**, pp. 1683–1890.

6 N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152.

7 For an asymmetric synthesis of **2**, see: M. K. J. ter Wiel, N. Koumura, R. A. van Delden, A. Meetsma, N. Harada and B. L. Feringa, *Chirality*, 2000, **12**, 734.

8 The (*P*,*P*) and (*M*,*M*) forms of each geometrical isomer are diastereomeric conformations which differ in the axial or equatorial orientation of the methyl groups.

9 Full spectroscopic details on **2** will be published elsewhere: M. K. J. ter Wiel, R. A. van Delden, A. Meetsma and B. L. Feringa, manuscript in preparation.

10 R. A. van Delden, N. Koumura, N. Harada and B. L. Feringa, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4945.