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: ferina@chem.rug.nl; Fax: +31 50 3634296; Tel: +31 50 3634235

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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 switches2 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 this state of the bistable (binary) system. Irradiation at 435 nm, the largest, afforded a PSS with 80% excess of the (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 (3S)-phenanthrene 3 (Scheme 2). This reductive coupling affords the (M,M)-trans-2 isomer exclusively.7 Photoinduced cis–trans 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 cis- and trans-isomers of 2, there is an energetic preference for the methyl groups at the stereogenic centers to adopt an axial orientation. Therefore the (3S,3S)-(M,M)-trans-2 and (3S,3S)-(M,M)-cis-2 forms are thermodynamically more stable. Nevertheless, (3S,3S)-(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 λ ≈ 280 nm10 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 λ ≥ 280 nm a PSS with a 70% excess of the (P,P)-cis-isomer (which is unstable at rt)11 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 (Φcis–trans and Φtrans–cis).

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photochemical steps (Fig. 2, inset). Performed repeatedly without any sign of deterioration after four (Fig. 2). The switching cycle shown in Scheme 3 could be opposite helical structures is dramatically different for both forms. 2 Helical chirality can be controlled with complete selectivity solely functions as a perfect chiroptical switch where for the first time irradiation at the ideal wavelength of \( S = 376 \text{ nm} \). Alternate irradiation at \( S \) based on the red-shifted UV/Vis band for (3-S)-cis-2 and (3-S)-trans-2 (Fig. 1 inset; eqn. 1) shows that light with \( \lambda \approx 280 \text{ nm} \) is far from ideal. As a matter of fact, in contrast to what can be expected from the observed PSS ratio, the (3-S)-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 \( \lambda = 280 \text{ nm} \) resulted in a near perfect photoequilibrium. A PSS consisting of > 99% (3-S)-cis-2 was reached, as determined by HPLC.‡ The red shift in the absorption band of (3-S)-trans-2 with respect to (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)-(M,M)-cis-2. Based on the red-shifted UV/Vis band for (3-S)-trans-2, irradiation at the ideal wavelength of \( \lambda = 376 \text{ nm} \) resulted in a full reversal of the photoequilibrium to > 99% (3-S)-(M,M)-cis-2 (HPLC). Alternate irradiation at \( \lambda = 303 \text{ and } 376 \text{ nm} \) resulted in switching between (3-S)-trans-2 and (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 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 phases10) but also show a new concept for chiroptical molecular switches where geometrical changes rather than asymmetric substitution result in highly reversible photoswitching with complete stereocore.

Notes and references
† Irradiations at \( \lambda \approx 280 \text{ nm} \) 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-hexane) obtained by diode array analysis.
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.

Fig. 2 Circular dichroism spectra of the PSS of the bistable switching pair (3-S)\((M,M)\)-cis-2 and (3-S)-trans-2 (PSS, solid line; PSS(111) ; dashed line). Inset: change in CD signal at 217 nm upon consecutive 303 nm (black bars) and 376 nm (grey bars) irradiation.

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