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A chiroptical binaphthopyran switch: amplified CD response in a polystyrene film†

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Enantiopure 10,10′-bi(naphtho[2,3-*b*]pyran) (**5a**) has been prepared from (*R*)-BINOL by using the attachment of 1,1-diphenylallyl alcohol to positions 3 and 3′ of the binaphthalene *via* Heck coupling as a key step. The irradiation of **5a** in solution with UV light at 313 nm caused photochemical opening of only one of the pyran rings, accompanied by minor changes in the CD spectrum. Thermal ring closure occurred spontaneously with an activation barrier of 74 kJ mol^{-1}. When **5a** was immobilised in a polystyrene film, an improved switching performance, both in terms of fatigue resistance (> 10 cycles) and CD signal amplitude (> 100 mdeg, > 6 : 1 signal ratio of open/closed forms), was observed.

Introduction

The number of investigations of the spectroscopic properties of organic photochromic materials has increased considerably in recent years as a result of potential commercial applications in several important areas, such as optical data storage,[1] optical switching,[2] image processing[3] and solar energy storage.[4] Although numerous photochromic molecular systems have been explored, they belong to a small number of families:[1,5,6] benzo- and naphthopyrans (chromenes), crowded alkenes, diarylethenes, fulgides, spiropyrans and spiroxazines. Among them, naphthopyrans have especially found applications in materials that undergo variable optical absorption.[7]

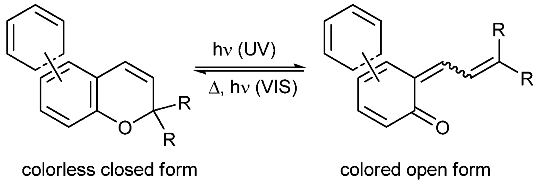
Naphthopyrans possess the ability to become coloured when irradiated with UV light.[5] This photochromic behaviour is based on a photoinduced reversible opening of the pyran ring that converts the colourless form (the ‘closed form’) into a set of isomers with the pyran ring opened (the ‘open form’). The open form reverts to the naphthopyran by a thermally-induced ring closure reaction when the light source is removed (Scheme 1). Also, due to their synthetic availability, the photochemistry of 3*H*-naphtho[2,1-*b*]pyrans and 2*H*-naphtho[1,2-*b*]pyrans has been more explored than that of 2*H*-naphtho[2,3-*b*]pyrans.[8] All of these derivatives show relatively good fatigue resistance in the solid phase, particularly when the R groups do not include a hydrogen atom bound to the α-carbon (predominantly aryl groups).

The independent detection of the state of photochromic molecular materials is required for their potential application as memory media.[1] The use of electronic absorption characteristics for this purpose often results in undesired effects, such as switching of molecules back to the former form and therefore erasing of the information. The actual challenge is to solve the problem of reading the molecule state. A frequently applied approach lies in the ‘saving’ of the written information by means of an additional signal (*e.g.* electrical) that chemically changes the molecule to a form that is stable upon optical reading.

Another possibility of how to design independent detection is to use photochromic molecules, where a structural change induced by the photochemical reaction is accompanied by modification of characteristics of the molecule other than electronic absorption. This allows reading of the state of the molecule without switching it back to the former state (for instance, a change of ion complexation, refraction index, electrochemical behaviour, polymer conformation or chiroptical characteristics). Seeing that CD signals originate from the difference in absorption of right- and left-handed circularly-polarized light, chiroptical switches could bring the possibility of ‘non-destructive readout’ only when the photoswitchable unit triggers changes to another chiral chromophore with an independent absorption.

Changes to the CD signals or other chiroptical characteristics of molecular systems containing a chiral 1,1′-binaphthalene moiety and attached photochromic unit(s)[9–13] (Fig. 1) can be associated with:

—a change of the binaphthalene dihedral angle (a CD couplet at approximately 230 nm qualitatively reflects the dihedral angle, *e.g.* **1**[9]).



Scheme 1 The reversible switching of naphthopyrans.

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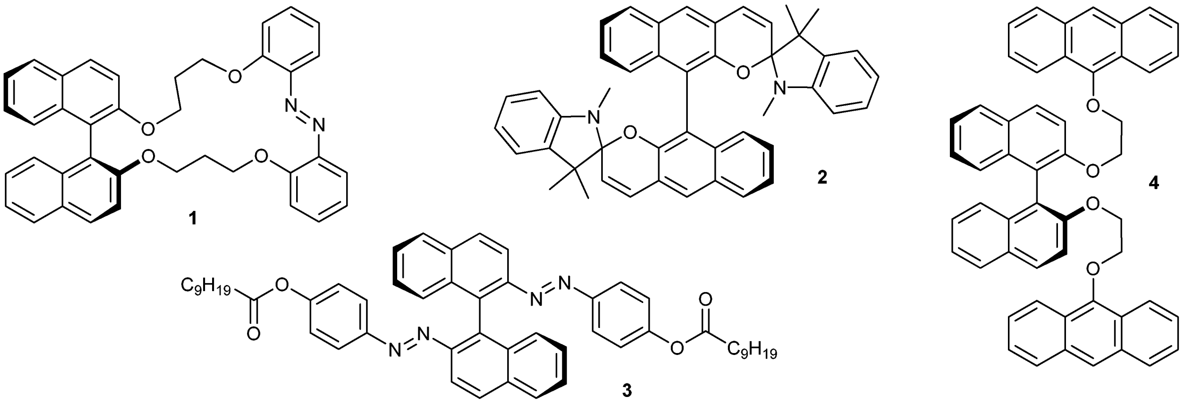


Fig. 1 Examples of binaphthalene based chiroptical switches.

—a change of conjugation to the binaphthalene and therefore a significant change to the chromophore (causing a shift of the CD band maximum, *e.g.* **2**[10]).

—a combination of both: a minor change to the binaphthalene dihedral angle as well as a slight change to the chromophore attached to binaphthalene (resulting in change of intensity of the corresponding CD bands, such as the (*E*/*Z*)-isomerisation of **3**[11]).

—a change in the supramolecular interactions between attached groups (a change of the ICD signal of chromophores in a chiral environment, *e.g.* **4**[12]).

In this work, we opted to explore possible modulation of the CD signal resulting from a significant chromophore change upon switching. For this purpose, we have designed, prepared and investigated the photochemical behaviour of a binaphthalene derivative with co-condensed pyran rings, **5** (consisting of two 2*H*-naphtho[2,3-*b*]pyran units).

Results and discussion

Synthesis

Various synthetic routes for the preparation of diarylnaphthopyrans have been described.[14] The most general and effective method involves the acid-catalysed reaction of propargyl alcohols with naphthols in the presence of a dehydrating agent (such as $CH(OMe)_3$,[14] molecular sieves[15] or activated silica[16]). However, none of them resulted in the formation of even traces of the desired product starting from BINOL (**6**). We also attempted to synthesise compound **5a** by a stepwise protocol: (i) we prepared the bispropargyl ether of BINOL in the presence of copper(I) iodide, potassium iodide and potassium carbonate in 29% yield (18 h at 90 °C), and (ii) we then tried to close the pyran ring in the presence of *N*,*N*-diethylaniline, in analogy with a previously described procedure.[17] Even this attempt failed.

Therefore, we decided to introduce allyl alcohol **7** to positions 3 and 3′ of BINOL prior to cyclisation of the pyran ring (Scheme 2). The 3,3′-diiodo precursor required for this approach, **8**, was prepared from (*R*)-BINOL (**6**) in three steps using previously described conditions: protection of the hydroxy groups as methyl ethers,[18] bis-*ortho*-lithiation and iodination,[19] and deprotection.[20] Allyl alcohol **7** was effectively (82% yield) introduced by Heck coupling using palladium acetate and potassium carbonate in acetonitrile. The obtained open-chain intermediate, **9**, was then successfully (63% yield) cyclised using activated silica in boiling toluene. Thus, the desired product, **5a**, was prepared from (*R*)-BINOL (**9**) in five steps in a 31% overall yield.

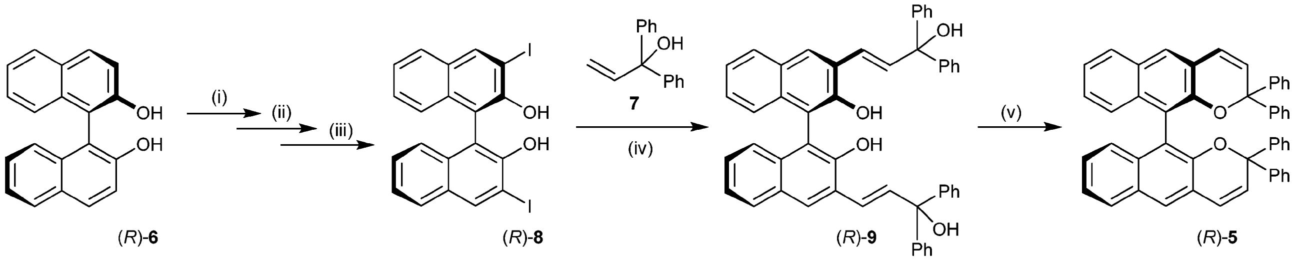
Photochromism in solution

The electronic absorption spectrum of **5a** in deuterated benzene shows two intense high energy absorption bands at 298 and 308 nm, and two minor low energy absorption bands at 354 and 370 nm (Fig. 2). The photochromic behaviour of **5** was evaluated by the continuous irradiation of (*R*)-**5a** in C_6D_6 under argon with monochromatic light at 313 nm filtered from a 125 W high pressure mercury arc. After initial irradiation, a partial increase of the high energy band absorptions was observed. However, subsequent bleaching of these bands and the appearance of a new broad band at 336 nm (the formation of methylidene quinone chromophore) was detected upon prolonged irradiation as a result of electrocyclic pyran ring-opening (Fig. 2). Colour of the sample turned yellowish.

Photochemical pyran ring-opening was found to be relatively slow, as judged by HPLC monitoring of the irradiated mixture (50% conversion of (*R*)-**5a** was reached after 79 min at 26.5 °C). Due to the required long reaction time and the partial decomposition of the reaction mixture (as observed by HPLC), it became difficult to reach the photostationary state, but this was estimated to contain 30% of ‘closed’ form (*R*)-**5a**.

Pure ‘open’ form (*R*)-**5b** was isolated by flash chromatography from a mixture irradiated for 155 min, keeping the solution ice cold during the separation. The number and character of the signals in ^1H and ^{13}C NMR spectra of **5b**, corresponding to C_1 symmetry, revealed that ring-opening of only one pyran ring took place (Scheme 3). The open chain propenylidene arm of **5b** has a prevailing *s-trans* conformation according to the spin–spin coupling constant between its inner protons (9.8 Hz). Due to overlap of the signals in the ^1H NMR spectrum, the (*E*/*Z*)-configuration of the exocyclic double bond could not be determined from NOE experiments.

The ring-closure activation barrier of 74.5 ± 5.8 kJ mol^{-1} was calculated from the bleaching rate constants determined at various temperatures (Fig. 3) using the irradiated mixtures of



Scheme 2 Synthesis of (*R*)-**5**. Reagents and conditions: (i) CH_3I (9 equiv.), K_2CO_3 (3 equiv.), acetone, reflux, 36 h, 98% yield; (ii) (1) *n*-BuLi (3.8 equiv.), TMEDA (3.2 equiv.), diethyl ether, r.t., 4 h, (2) I_2, (3.8 equiv.), −78 °C to r.t., 5 h, 63% yield; (iii) BBr_3 (5 equiv.), CH_2Cl_2, 0 °C, 4 h, 97% yield; (iv) **7** (5.2 equiv.), $Pd(OAc)_2$ (8 mol%), K_2CO_3 (1 equiv.), CH_3CN, 100 °C, 4 h, 82% yield; (v) silica, toluene, reflux, 24 h, 63% yield.

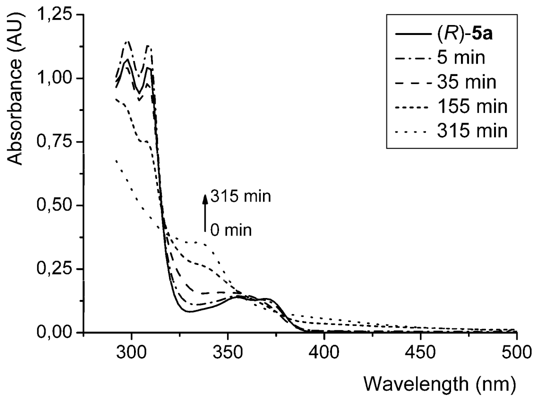
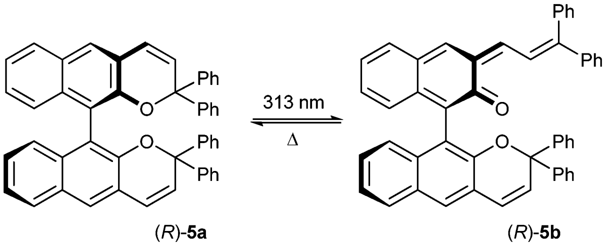


Fig. 2 The absorption spectra of (*R*)-**5** in benzene (3.5×10^{-5} M) after irradiation with UV light (313 nm) for the given time. Concentration of **5** in C_6D_6 during irradiation: 1.52×10^{-2} M.



Scheme 3 Reversible switching of binaphthopyran (*R*)-**5**.

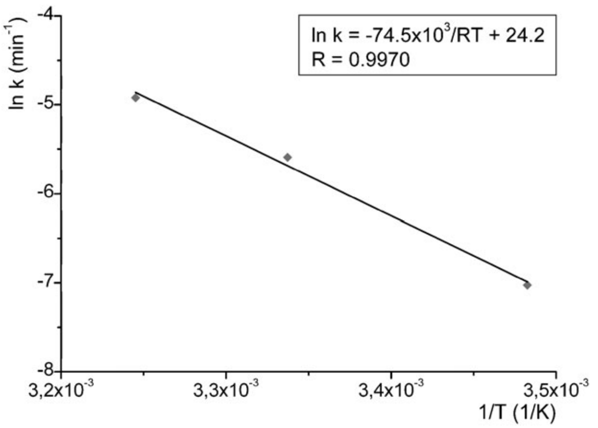


Fig. 3 Determination of the ring-closure activation barrier from the dependence of ln *k* (**5b** ring-closure rate constants) against 1/*T*.

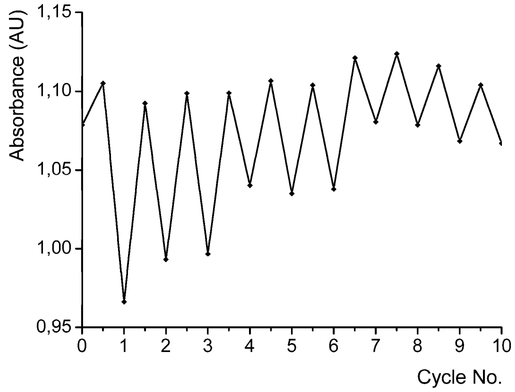


Fig. 4 Switching of the absorption intensity of (*R*)-**5** (sample irradiated/heated in C_6D_6 at $c = 1.52 \times 10^{-2}$ M, diluted by benzene to $c = 3.5 \times 10^{-5}$ M for the measurement of absorbance) at 298 nm. The increase of the intensity after irradiation with UV light (313 nm) for 5 min and the decrease after heating (84 °C) for 5 min.

(*R*)-**5a** and (*R*)-**5b**. The time dependent composition of the mixtures was analysed by HPLC.

With the aim of designing conditions for the reversible switching of (*R*)-**5** in d_6-benzene, the solution was irradiated with UV light at 313 nm for only 5 min (6.2% conversion of **5a**) to avoid potential decomposition. Then, the solution was heated under reflux for 5 min. Each time, a small sample was taken and diluted with benzene to record electronic absorption spectra. As shown in Fig. 4, a certain level of switching was observed, but serious fatigue occurred within a few cycles.

The changes in the CD spectrum of (*R*)-**5** in deuterated benzene upon irradiation and subsequent heating were examined (Fig. 5) under the conditions described above. The overlaid CD spectra do not contain clear isosbestic points (except for one at 386 nm).

This indicates a more complex character to the transformation, including the formation of by-products or more stereoisomers in a variable ratio. Moreover, the intensity changes of the major bands do not exhibit a reversible character, but their intensity gradually increases (the bisignate CD couplet shifted to a higher wavelength compared to simple binaphthalene derivatives,[21] here with a negative branch at 278 nm and a positive branch at 307 nm) or diminishes (negative band at 392 nm).

Photochromism in polymer films

For their potential application in memory devices, molecular switches are expected to be used at solid surfaces. Therefore,

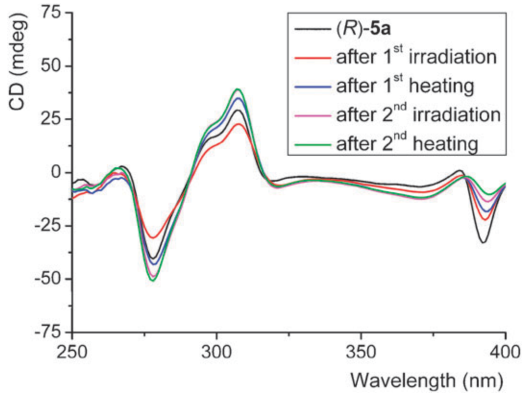


Fig. 5 The CD spectra of (*R*)- **5** in C_6D_6 (c = 1.52×10^{-2} M) before irradiation (black), after the 1st irradiation with UV light (313 nm) for 5 min (red), after the 1st heating (84 °C) for 5 min (blue), after the 2nd irradiation with UV light (313 nm) for 5 min (orange) and after the 2nd heating (84 °C) for 5 min (green).

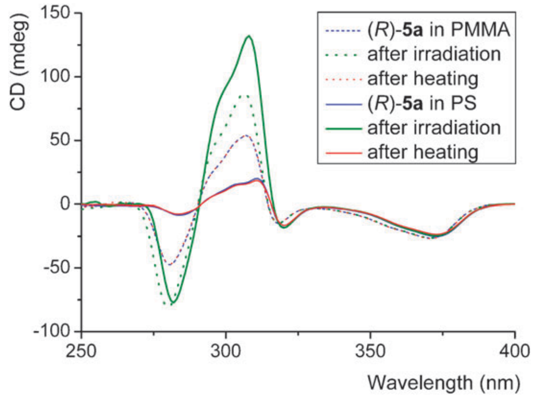


Fig. 7 The CD spectra of (*R*)-**5** in a 50 μm PS film (solid lines) and a PMMA film (dashed lines), c = 0.02 mol kg^{-1}: before irradiation (blue), after irradiation with UV light (313 nm) for 1 h (green) and after heating (70 °C) for 8 min (red).

we have prepared thin films of (*R*)-**5a** in poly(methyl methacrylate) (PMMA) and polystyrene (PS). After some experimentation, we succeeded in finding suitable conditions for irradiation and heating that kept the switching fully reversible (Fig. 6). An improved durability of switch (*R*)-**5a** after physical imprisonment in the polymer matrix could be caused by reduced side stereoconversions and interactions with oxygen and/or the recombination of activated species.

The changes in the absorbance spectrum of (*R*)-**5a** in PMMA and PS films upon switching did not exceed 9% of the intensity at the band's maximum (ESI, Fig. S22†). Interestingly, the CD spectrum of (*R*)-**5** in polymer films under the same conditions (Fig. 7) differed significantly in the intensity of the bisignate CD couplet (negative branch at 282 nm, positive branch at 308 nm). The higher amplitude CD signal in the PS film most probably results from π–π stacking interactions between switched (*R*)-**5** and the aromatic environment in the PS matrix. This interaction could lead to amplification of the chiroptical response[22] due to reversibly-enhanced helicity in the film. As a result, over a six-fold increase in the CD signal intensity of the (*R*)-**5**/PS film at 308 nm could be maintained during multiple reversible switchings (Fig. 8). The detected amplitude of the CD signal intensity (108 ± 8 mdeg at 308 nm) is one of the largest observed for binaphthalene-based chiroptical switches so far seen.[9–13]

Conclusions

In this paper, we reported the synthesis and characterisation of chiroptical molecular switch **5**, consisting of two 2*H*-naphtho[2,3-*b*]pyran units. Previously reported synthetic methods described for the preparation of naphthopyrans from naphthols did not yield the desired binaphthopyran, **5a**, from BINOL. The synthesis of **5a**, therefore, required the building up of the pyran rings through a Heck coupling of diiodo precursor **8** with allyl alcohol **7**, followed by a silica-assisted cyclisation.

The irradiation of **5a** with UV light at 313 nm caused a slow photochemical opening ($t_{1/2}$ = 79 min) of only one of the pyran rings. Reverse ring-closure occurred spontaneously with an activation barrier of 74 kJ mol^{-1}. However, the progressive stereoisomerisation and/or fading of switch **5** resulted in an

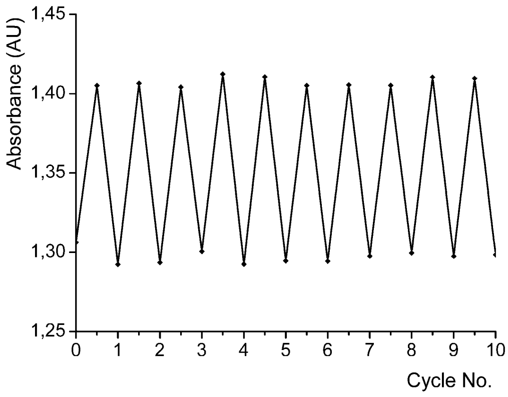


Fig. 6 Switching of the absorption intensity of (*R*)-**5** in a 50 μm PMMA film (0.02 mol kg^{-1}) at 296 nm. The increase of the intensity after irradiation with UV light (313 nm) for 1 h and the decrease after heating (70 °C) for 8 min.

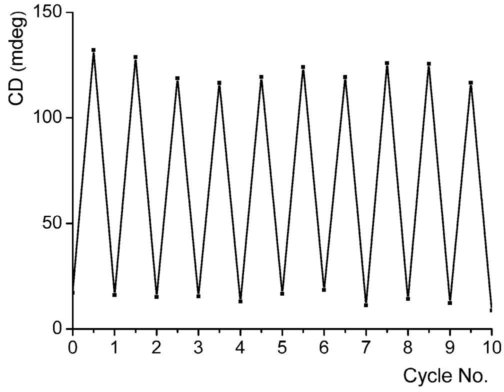


Fig. 8 Switching of the CD signal intensity of (*R*)-**5** in a 50 μm PS film (0.02 mol kg^{-1}) at 308 nm. The increase of the intensity after irradiation with UV light (313 nm) for 1 h and the decrease after heating (70 °C) for 8 min.

almost unidirectional increase/decrease of CD signal intensities upon switching in solution.

The imprisonment of **5** in a polymer film significantly improved its fatigue resistance, allowing multiple reversible switchings to be maintained. In addition, the interaction of **5** with a polystyrene film amplified its chiroptical response, as detected by increased CD signal amplitudes up to 108 mdeg during the switching (over 6 : 1 signal ratio of **5b**/**5a**).

Experimental

General

Flash column chromatography was performed on Merck silica gel (60H). Merck silica gel F254 plates were used for thin layer chromatography, and visualisation was effected using UV light (254 nm). Melting points were measured on a Electrothermal-IA9200 instrument and the values are uncorrected. Specific optical rotations were measured on a Perkin-Elmer 241 polarimeter and are given in deg cm^2 g^{-1} dm^{-1}. IR data (in cm^{-1}) were recorded on a SPECORD M 80 spectrophotometer. UV-vis spectra in solution were measured on a Hewlett Packard diode array 8245 spectrophotometer. Thin films were measured on a Shimadzu spectrometer UV 1650PC. CD spectra were measured on a Jasco J810 instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 instrument at 298 K. Chemical shifts are reported in ppm downfield of the internal standard Me$_4$Si (0.00 ppm), and the solvent was also used as a reference. The working frequency was 300 MHz for ^{1}H and 75.5 MHz for ^{13}C NMR. Coupling constants (*J*) are given in Hz. GC-MS spectra (70 eV, 150 μA, EI) were recorded on a Voyager GC-MS Finnigan instrument. Elemental analyses were determined using an Erba Science 1106 instrument. HPLC analyses were undertaken on a Chiralcel Daicel OD-H column (eluent: n-hexane–isopropyl alcohol 90/10, temperature: 21 °C, flow: 0.75 mL min^{-1}, pressure: 27.5 bar, UV detector: λ = 275 nm) and Waters Symmetry® C$_{18}$ 5 μm 3.9 × 150 mm column (eluent: methanol–water 95/5, temperature: 21 °C, flow: 0.25 mL min^{-1}, pressure: 27 bar, UV detector: λ = 254 nm) using a UV-vis detector LCD 5000.

All chemicals were used as purchased if not stated otherwise. All reactions were carried out under an argon atmosphere using Schlenk techniques. Dichloromethane and acetonitrile were dried over calcium hydride and chloroform over calcium chloride. Toluene, diethyl ether and *d*$_6$-benzene were dried over sodium/benzophenone and distilled over argon. The following compounds were prepared according to published procedures: CuCl(OH)TMEDA,[23] (8*S*,9*R*)-(−)-*N*-benzylcinchonidinium chloride,[24] (*R*)-**6**,[25] (*R*)-2,2′-dimethoxy-1,1′-binaphthalene,[18] (*R*)-3,3′-diiodo-2,2′-dimethoxy-1,1′-binaphthalene,[19] **7**[26] and (*R*)-**8**.[20] All other chemicals were of analytical grade and were used without further purification.

Preparations

(*R*)-3,3′-Bis(3-hydroxy-3,3-diphenylprop-1-en-1-yl)-1,1′-binaphthalene-2,2′-diol (9). To a solution of (*R*)-**8** (200 mg, 0.37 mmol) in acetonitrile (1 mL) were added Cs$_2$CO$_3$ (121 mg, 0.37 mmol), Pd(OAc)$_2$ (7 mg, 0.03 mmol) and **7** (391 mg, 1.9 mmol). The reaction mixture was stirred under argon at 100 °C for 4 h, diluted with dichloromethane and finally washed with brine. The organic layer was dried over Na$_2$SO$_4$, concentrated under vacuum and the residue purified by chromatography on silica gel using hexanes/ethyl acetate (5 : 1) as the eluent to give product (*R*)-**9** (R_F = 0.19, 213 mg, 82%) as a yellow solid.

Found: C, 85.20; H, 5.47. C$_{50}$H$_{38}$O$_4$ requires C, 85.44; H, 5.45%. ν_{max}(KBr)/cm^{-1} 3507 (OH), 3057 and 3025 (H$_{arom}$), 1716 (C=C$_{alkene}$), 1621 and 1598 (C=C$_{arom}$), 1211 (OH$_{arom}$), 1147 (OH$_{tert}$); δ_H(300 MHz; DMSO-*d*$_6$; Me$_4$Si) 6.16 (2H, s, 2 × O*H*$_{tert}$), 6.74 (2H, d, *J* = 8.2 Hz, C(8)*H*, C(8′)*H*), 7.07–7.49 (28H, m), 7.89 (2H, d, *J* = 8.0 Hz, C(5)*H*, C(5′)*H*), 8.23 (2H, s, C(4)*H*, C(4′)*H*), 8.30 (2H, s, 2 × O*H*$_{arom}$); δ_C(75 MHz; DMSO-*d*$_6$; Me$_4$Si) 78.6, 114.7, 123.4, 124.0, 124.3, 126.4, 126.5, 127.1, 127.3, 127.6, 128.3, 128.5, 129.1, 134.0, 138.0, 148.1, 152.3; HRMS (ESI$^+$) *m*/*z* 667.2637 [M + H$^+$ − 2H$_2$O]. C$_{50}$H$_{35}$O$_2$$^+$ requires 667.2637); $[\alpha]_D^{18}$ = +38.8 (*c* = 1 in CHCl$_3$); mp 129–131 °C.

(*R*)-2,2,2′,2′-Tetraphenyl-10,10′-bi(2*H*-naphtho[2,3-*b*]pyran) (5a). A mixture of (*R*)-**9** (100 mg, 0.14 mmol) in dry toluene (1 mL) and silica gel (300 mg, freshly activated at 120 °C) was heated under reflux for 24 h and monitored by thin layer chromatography. The hot mixture was filtered off and the silica washed with hot toluene (2 × 0.5 mL). The filtrate was concentrated under vacuum and the residue purified by chromatography on silica gel using hexanes/ethyl acetate (16 : 1) as the eluent to give product (*R*)-**5a** (R_F = 0.34, 60 mg, 63%) as a white solid.

Found: C, 90.29; H, 5.18. C$_{50}$H$_{34}$O$_2$ requires C, 90.06; H, 5.14%. ν_{max}(KBr)/cm^{-1} 3057 and 3032 (H$_{arom}$), 1624 (C=C$_{arom}$), 1250 (C–O); δ_H (300 MHz; DMSO-*d*$_6$; Me$_4$Si) 6.77–7.40 (30H, m), 7.84 (2H, s, C(5)*H*, C(5′)*H*), 7.90 (2H, d, *J* = 8.1 Hz, C(6)*H*, C(6′)*H*); δ_C(75 MHz; DMSO-*d*$_6$; Me$_4$Si) 81.7, 116.9, 121.8, 123.2, 123.8, 125.0, 125.6, 125.7, 125.9, 126.2, 126.9, 127.0, 127.6, 127.9, 128.1, 128.9, 132.1, 133.4, 144.7, 144.9, 148.4; $[\alpha]_D^{18}$ = +8.2 (*c* = 1 in CHCl$_3$); λ_{max} (benzene)/nm (ε/dm^3 mol^{-1} cm^{-1}) 298 (30 460), 308 (29 873), 354 (3626), 370 (3445); mp 123–126 °C.

(*R*)-1-(2,2-Diphenyl-2*H*-naphtho[2,3-*b*]pyran-10-yl)-3-(3,3-diphenylprop-2-enylidene)naphthalen-2(3*H*)-one (5b). (*R*)-**5a** (223 mg, 0.335 mmol) was dissolved in UV grade benzene (220 mL, *c* = 1.52 × 10^{-3} M), placed into the reactor under an argon atmosphere and irradiated at 313 nm for 155 min (HPLC: $t_{(R)}$–**5a** = 22.47 min, 52.5%; $t_{(R)}$–**5b** = 23.95 min, 47.5%). The solvent was evaporated under reduced pressure and (*R*)-**5b** separated from the residue by flash chromatography on silica gel using hexanes/ethyl acetate (20 : 1) as the eluent (R_F = 0.26). The mixture and product were kept ice cold during the separation. This gave product (*R*)-**5b** (87 mg, 39%) as a yellowish coloured solid.

δ_H(300 MHz; CDCl$_3$; Me$_4$Si) 6.42 (1H, d, *J* = 9.8 Hz, =CH–C*H*=CPh$_2$), 6.90–7.41 (25H, m), 7.50–7.54 (4H, m), 7.67 (1H, s, C(5′)*H*), 7.79 (2H, d, *J* = 8.1 Hz), 8.04 (1H, s, C(4)*H*); δ_C(75 MHz; CDCl$_3$; Me$_4$Si) 81.5, 91.9, 111.8, 114.3, 114.3, 120.7, 121.6, 122.4, 122.8, 123.5, 123.9, 124.1, 125.1, 125.1, 125.3, 125.7, 125.9, 126.1, 126.3, 126.4, 126.4, 126.7, 126.7, 126.8, 126.8, 127.1, 127.1, 127.4, 127.5, 127.5, 127.6, 127.8, 128.7, 131.6, 132.3, 132.8, 135.3, 143.3, 143.3, 148.2, 148.3, 208.0.

Switching in solution

A sample of (*R*)-**5a** (14.2 mg, 2.2×10^{-5} mol) in d_6-benzene (1.4 mL, 1.52×10^{-2} M) was placed into the NMR tube under argon and irradiated at 313 nm for 5 min. Reversible switching process was performed by heating of the sample at 84 °C in water bath for appropriate time. For UV-vis measurements, calculated volume of the sample was diluted with benzene to $c = 3.5 \times 10^{-5}$ M. CD spectra of the whole samples were recorded.

Kinetic measurements

A sample of (*R*)-**5a** (7.1 mg, 1.1×10^{-5} mol) in d_6-benzene (0.7 mL, 1.52×10^{-2} M) was placed into an NMR tube under argon and irradiated at 313 nm for 40 min. Small amounts of the sample were taken after regular time periods for HPLC analysis to determine the composition of the irradiated mixture. The ratios of **5a** and **5b**, calculated from peak areas at 254 nm, were corrected by molar ratio found from the ^{1}H NMR spectrum. The data corresponded to apparent first-order kinetics with a rate constant $k = (8.77 \pm 0.25) \times 10^{-3}$ min^{-1} and a reaction half time $t_{1/2} = 79.0 \pm 2.3$ min at 26.5 °C.

Three samples of (*R*)-**5a** (7.1 mg, 1.1×10^{-5} mol) in d_6-benzene (0.7 mL, 1.52×10^{-2} M) were placed in tubes under argon and irradiated at 313 nm for 45 min at 26.5 °C. Each sample was, after irradiation, tempered for 15 min to a different temperature (14, 26.5 and 35 °C). From each sample was taken a small amount after regular time periods (1, 0.5 and 0.25 h, respectively) for HPLC analysis to determine the composition of the mixture. The found rate constants were: $(0.89 \pm 0.11) \times 10^{-3}$ min^{-1} (14.0 °C), $(3.73 \pm 0.41) \times 10^{-3}$ min^{-1} (26.5 °C) and $(7.30 \pm 0.66) \times 10^{-3}$ min^{-1} (35.0 °C). The activation barrier for the ring-closure of (*R*)-**5b** was calculated from the dependence of the natural logarithm of the rate constant on reciprocal temperature as 74.5 ± 5.8 kJ mol^{-1}.

Switching in polymer film

Films of poly(methyl methacrylate) (PMMA; Diacon, ICI, England) and polystyrene (PS; Chemische Werke Huels, F. R. G.) were prepared by casting a 1 mL chloroform solution of the polymer (5 g/100 mL) containing the respective amount of (*R*)-**5a** onto a glass plate (28 × 35 mm). The solvent was evaporated slowly in the dark. The final concentration of (*R*)-**5a** in the films was 0.02 mol kg^{-1}. The thickness of the films was 50 μm.

The photoisomerisation of (*R*)-**5** was examined in thin polymer films in a merry-go-round set up equipped with a 125 W medium pressure mercury arc lamp and a chromate liquid filter[27] transmitting monochromatic light $\lambda = 313$ nm. Thermoisomerisation was performed in an oven at 70 °C for an appropriate time. Electronic absorption and CD spectra of the films nestled at the standard cell wall were recorded in the ordinary transmittance mode.

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