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Diastereoselective, Synergistic Dual-Mode Optical Switch with Integrated Chirochromic Helicene and Photochromic Bis-azobenzene Moieties

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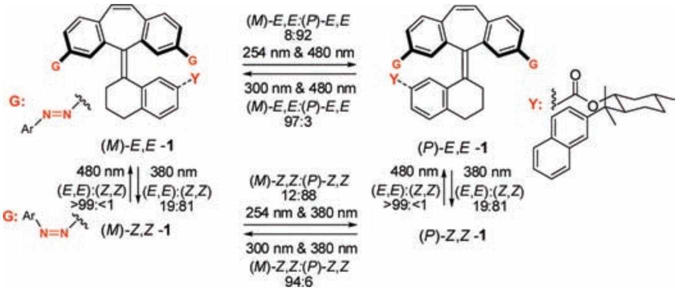
ABSTRACT



An unprecedented dual-mode optical switch by combining helicene and bis-azobenzene moieties in proximity allows for cooperative, highly diastereoselective chirochromic (92/8 to 3/97) and photochromic (>99/<1 to 19/81) switchings both in solution and in nematic LC with tunable pitches and handedness by permutation of four different metastable states.

In the past decade, information technology has progressed rapidly. Data storage and retrieval devices were developed toward miniaturization to reduce the memory units down to the molecular level. Bistable molecular switches serving as the memory units with binary logic were therefore especially targeted.[1] External mediators such as light, heat, pH change, and magnetic or electric field are potential energy sources to achieve the interconversion of the bistable molecular switches. Because light is one type of clean energy, the searches for molecular switches modulated by light are particularly attractive.[2] So far, well-known photoreversible molecular switches include sterically overcrowded olefins,[3] azobenzenes,[4] diarylethenes,[5] spiropyrans,[6] fulgides,[7] etc.

Helically shaped, overcrowded olefins (helicenes) constitute a specific type of chirochromic molecule, whose switching profile exhibits a reversible change in helical chirality. Dynamic progress of the photoinduced interconversion of a pair of (pseudo)enantiomeric helicenes can be traced by circular dichroism (CD) spectroscopy or by measuring helical pitch and handness variation in liquid crystal (LC) mesophase containing the helicene pair. Conversely, azobenzenes have been extensively explored as photochromic switches with reversible $E-Z$ photoisomerization. Integration of these two photoresponsive structural

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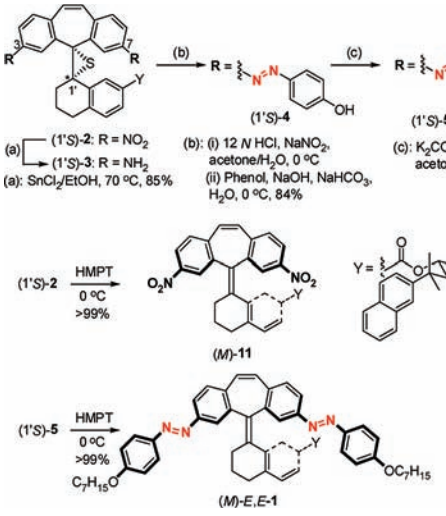
motifs in proximity may provide a unique type of memory device with dual mode permutation in a synergistic fashion. There are a few reports on azobenzenes bearing photoinert, axially chiral cores[8a−c] or photoswitchable stilbenes.[8d,e] So far, azobenzenes combined with photoresponsive chiral helicenes as dual mode, chiro- and photochromic optical switches have been relatively unexplored.[8f,g]

As an extension of our ongoing program on the uses of C_2-symmetric, dibenzosuberene (DBE)-derived helicenes as potential chirochromic LC optical switches,[3d,e] we recently sought to realize the dual-mode optical switch by appending two azobenzene units onto the C3 and C7 positions of a DBE-based helicene bearing an 8-naphthylmenthol-derived chiral ester (i.e., compound **1** in Scheme 1). Upon judicious selection of four different irradiation wavelengths, *P*−*M* isomerization of the helicene moiety or double *E*−*Z* isomerization of both the azobenzenes in **1** can be collaboratively carried out. In principle, a nematic LC phase can be induced to a cholesteric one with modulable CD, helical pitch, and handness readouts by using **1** as the chiral dopant. Therefore, four metastable cholesteric mesophases in a single nematic LC host may be identified through the dual-mode photoswitching with a dual-mode binary logic.

Scheme 1. Synthesis of (*M*)-**11** and (*M*)-*E*,*E*-**1**



The synthetic routes to a model helicene **11** and the dual-mode optical switch **1** are shown in Scheme 1.[9] A diastereomeric mixture (26:74) of 3,7-dinitroepisulfides (1′*R*)- and (1′*S*)-**2** can be prepared by a Staudinger-type, diazothioketone coupling reaction.[9] The isolated, pure (1′*S*)-**2** diastereomer was reduced by $SnCl_2{\cdot}2H_2O$ to afford (1′*S*)-**3** in 85% yield. Both the amino moieties in (1′*S*)-**3** were reacted with in situ generated HNO_2 in aqueous acetone to give the corresponding bis-diazonium salt, which was further coupled with phenol under basic conditions to furnish the corresponding bis-azobenzene (1′*S*)-**4** in 84% yield. Alkylation of both the phenolic moieties in (1′*S*)-**4** with 1-bromoheptane in the presence of K_2CO_3 and KI led to bis-azobenzene (1′*S*)-**5** in 85% yield. Reductive desulfurization of respective (1′*S*)-**2** and (1′*S*)-**5** by hexamethylphosphorous triamide (HMPT) at 0 °C gave 3,7-dinitrohelicene **11** and 3,7-bisazohelicene **1** of (*M*)-helicity (>99% yield, >99% de). Similarly, (1′*R*)-**2** can lead to 3,7-bisazo-helicene(*P*)-**1** by the same sequence of reactions.

The 3,7-dinitro-substituted helicene **11** synthesized from the episulfide (1′*S*)-**2** was confirmed to possess (*M*)-form helicity as determined by X-ray crystallographic analysis (Figure 1a). The split Cotton effects in its CD spectrum in hexanes indicate a positive exciton chirality (227 nm (+), 215 nm (−)). Similarly, (*M*)-*E*,*E*-**1** obtained from episulfide (1′*S*)-**2** also shows a positive exciton chirality of its split Cotton effects (230 nm (+), 207 nm (−)) in its CD spectrum.

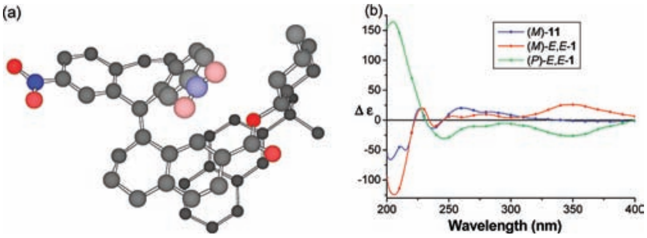


Figure 1. (a) X-ray crystal structure of (*M*)-**11** (hydrogens omitted for clarity); (b) stacked CD plots of (*M*)-**11**, (*M*)-*E*,*E*-**1** and (*P*)-*E*,*E*-**1** in hexanes.

Conversely, (*P*)-*E*,*E*-**1** synthesized from episulfide (1′*R*)-**2** shows a negative exciton chirality (249 nm (−), 204 nm (+)) based on its split Cotton effects in CD spectrum, suggesting an opposite helical chirality from (*M*)-**11** (Figure 1b).[10]

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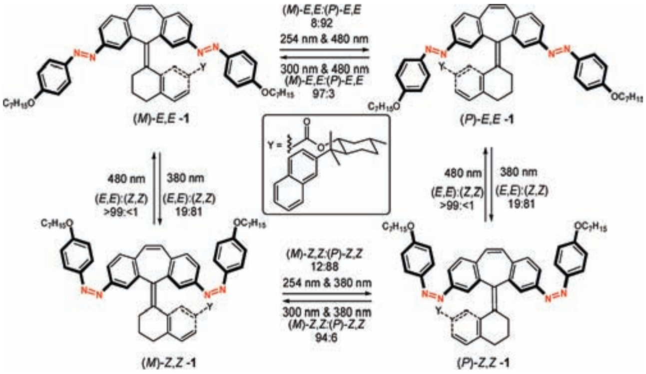
The dual-mode optical switch **1** undergoes collaborative, photochromic, and chirochromic switching reactions upon irradiation at different wavelengths (Scheme 2). Dark incubation of a solution of (*P*)-*E*,*E*-**1** in hexanes serves to prevent *E*−*Z* photoisomerization by which the absorption band at 365 nm corresponding to the two azobenzene chromophores in *E*,*E*-**1** can be maximized. Irradiation of a solution of (*P*)-*E*,*E*-**1** at 380 nm resulted in *E*→*Z* isomerization at both azobenzene moieties, as evidenced by a decrease in the $\pi-\pi^*$ transition around 365 nm and a concomitant increase in the n$-\pi^*$ transition around 490 nm (Figure 2a). In the CD spectroscopic dynamic traces, the intensity of the n$-\pi^*$ transition around 450 nm increased, and the negative Cotton effect at 254 nm was reinforced toward negative direction (Figure 2b). A photostationary state (pss) was reached after UV irradiation for about 5 min. By HPLC dynamic traces, we found that the double *E*→*Z* isomerizations in (*P*)-*E*,*E*-**1** proceed by way of (*P*)-*Z*,*E*-**1** and (*P*)-*E*,*Z*-**1**, which then completely lead to (*P*)-*Z*,*Z*-**1**.[9] Finally at the pss, only the peaks of (*P*)-*E*,*E*-**1** and (*P*)-*Z*,*Z*-**1** still remain and the ratio of (*P*)-*E*,*E*-**1**:(*P*)-*Z*,*Z*-**1** at the pss was 19:81 as determined by HPLC analysis at 253 nm (i.e., the isosbestic point in UV stacked plot in Figure 2a) detection wavelength.[9]

Scheme 2. Photoisomerization of Dual-Mode Optical Switch **1**



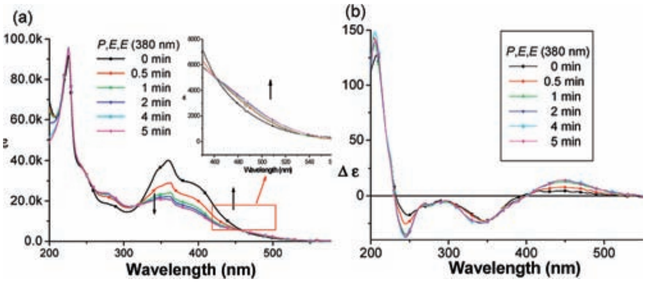


Figure 2. (a) UV−vis absorption and (b) CD stacked plots of (*P*)-*E*,*E*-**1** (10 μM) in hexanes at 25 °C under UV irradiation (380 nm at 0, 0.5, 1, 2, 4, and 5 min, respectively).

On the other hand, upon irradiation of the same (*P*)-*E*,*E*-**1** and (*P*)-*Z*,*Z*-**1** mixture (19:81) at 480 nm in 2 min resulted in complete, reversed photoisomerization back to the original (*P*)-*E*,*E*-**1** as shown by HPLC analysis.[9] Similar to (*P*)-*E*,*E*-**1**, irradiation of (*M*)-*E*,*E*-**1** in hexanes at 380 nm led to a 19:81 mixture of (*M*)-*E*,*E*-**1**:(*M*)-*Z*,*Z*-**1** at pss in 5 min as determined by HPLC analysis at 257 nm (i.e., the isosbestic point in their stacked UV plots)[9] detection wavelength. The backward photoisomerization event was also clean and complete in 2 min. In contrast, the background thermal reisomerization from *Z*,*Z*-**1** to *E*,*E*-**1** in hexanes in the dark at 25 °C takes about 24 h.[11] Notably, our system constitutes one of the most selective bis-azobenene photochromic switches. Intermediate *E*,*Z* states are often remained (7−50%) in other systems.[4b,8a,b,9] We speculate that the photoswitching processes of both the azo moieties in **1** proceed in a synergistic fashion with improved diastereoselectivity under the influence of the flanking central helicene unit.

Sequential irradiations of a solution of (*P*)-*E*,*E*-**1** in hexanes at 300 and 480 nm (0−120 and 1 min, respectively) resulted in chirochromic switch of the helicene moiety (Scheme 2). In the CD-stacked spectra, the negative Cotton effect at 249 nm and the positive Cotton effect at 204 nm were completely inverted (Figure 3a), implying a reversal of helical chirality. The pss was reached after irradiations in about 2 h. The ratio of (*P*)-*E*,*E*-**1**/(*M*)-*E*,*E*-**1** at the pss was 3:97 by HPLC analysis at 280 nm (which is an isosbestic point in their stacked UV plots) detection wavelength. Similarly, sequential irradiations of a solution of (*M*)-*E*,*E*-**1** in hexanes at 254 and 480 nm (0−90 and 1 min, respectively) led to the exciton chirality inversion of both Cotton effects at 230 and 207 nm in the CD stacked spectra (Figure 3b). The pss was reached after irradiations in about 1.5 h. The ratio of (*P*)-*E*,*E*-**1**/(*M*)-*E*,*E*-**1** at the pss was 92:8 by HPLC analysis similarly at 280 nm detection wavelength.

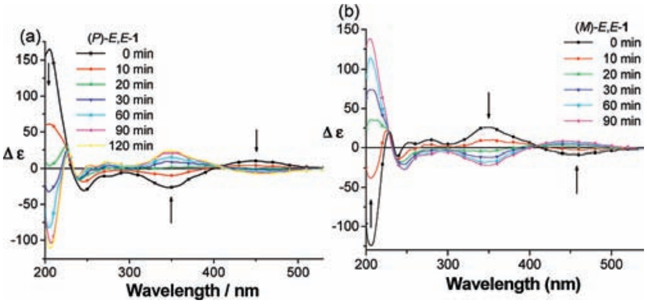


Figure 3. CD stacked plots of (a) (*P*)-*E*,*E*-**1** (10 μM) in hexanes under sequential UV and visible light irradiations at 300 and 480 nm (0−120 and 1 min, respectively) and (b) (*M*)-*E*,*E*-**1** (10 μM) in hexanes under sequential UV and visible light irradiations at 254 and 480 nm (0−90 and 1 min, respectively).

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(11) The kinetic studies of thermal reisomerization from *Z*,*Z*-**1** to *E*,*E*-**1** were described in the Supporting Information. The rate constant for the thermal reisomerization from (*P*)-*Z*,*Z*-**1** to (*P*)-*E*,*E*-**1** in the dark at 25 °C is $(5.00 \pm 0.07) \times 10^{-3}$ min^{-1}. The thermal reisomerization from (*M*)-*Z*,*Z*-**1** to (*M*)-*E*,*E*-**1** has the same rate constant.

Conversely, irradiations of a mixture of (*P*)-*E*,*E*-**1** and (*P*)-*Z*,*Z*-**1** (19:81) in hexanes at 300 and 380 nm (0−120 and 3 min, respectively) resulted in a chirochromic switch of the helicene moiety (Scheme 2). The pss was reached after irradiations in about 2 h. The ratios of (*P*)-*E*,*E*-**1**/(*M*)-*E*,*E*-**1** and (*P*)-*Z*,*Z*-**1**/(*M*)-*Z*,*Z*-**1** at the pss were 3:97 and 6:94, respectively, by HPLC analysis at 280 nm detection wavelength.[9] Similarly, sequential irradiations of a solution of (*M*)-*E*,*E*-**1** and (*M*)-*Z*,*Z*-**1** mixture (19:81) in hexanes at 254 and 380 nm (0−90 and 3 min, respectively) resulted in helicity inversion. The pss was reached after irradiations in about 1.5 h. The ratios of (*P*)-*E*,*E*-**1**/(*M*)-*E*,*E*-**1** and (*P*)-*Z*,*Z*-**1**/(*M*)-*Z*,*Z*-**1** at the pss were 92:8 and 88:12, respectively, by HPLC analysis at 280 nm detection wavelength.[9]

As expected, doping (*P*)-*E*,*E*-**1** into a nematic LC host (e.g., 0.1 wt % of **1** in LC E7 mixture[9]) leads to its phase change to a cholesteric LC phase. The helical pitch (*p*) of a cholesteric mesophase depends on optical purity γ, helical twisting power β_M, and concentration C of the chiral dopant (i.e., (*P*)-*E*,*E*-**1**) according to eq 1:

$$p^{-1} = \beta_M C \gamma \tag{1}$$

The helical sense of the induced cholesteric mesophase by (*P*)-*E*,*E*-**1** was found to be (+) by contact method.[12] The homogeneous mixture was capillary-filled into a Cano's wedge cell. Induced Cano's lines in wedge cell were observed at 25 °C under a polarized optical microscope. The helical pitch of the induced cholesteric mesophase is 21.2 μm by Cano's wedge method,[13] which corresponds to a fairly large β_M of +47.1 μm^{-1} as calculated by eq 1. The *p* value of the induced cholesteric mesophase by doping 0.1 wt % of (*M*)-*E*,*E*-**1** in E7 host is 26.0 μm, and the corresponding β_M is −38.5 μm^{-1}. The β_M value of (*P*)-*E*,*E*-**1** is larger than that of (*M*)-*E*,*E*-**1**, indicating that the fjord region of (*P*)-*E*,*E*-**1** is more sterically twisted.

To gain insights into the photoswitching efficiency of **1** directly in LC mesophases, the wedge cell containing 0.1 wt % of (*P*)-*E*,*E*-**1** in E7 was irradiated at 380 nm for 15 min, which resulted in a distinct increase in *p* value from 21.2 to 35.5 μm as evidenced by a variation in distance between two consecutive Cano's lines (panel **A** to **B**, Figure 4). Upon irradiation of the same cell at 480 nm, the *p* reverts back to the original value. Similarly, irradiation of a wedge cell containing 0.1 wt % of (*M*)-*E*,*E*-**1** in E7 at 380 nm for 15 min resulted in a distinct increase in *p* from 26.0 to 50.9 μm (panel **C** to **D**, Figure 4). Upon irradiation of the same cell at 480 nm, the pitch again reverts back to the original value. Alternate irradiation with different wavelengths results in photomodulation of the pitch in the induced cholesteric mesophase. Conversely, irradiation of a wedge cell containing 0.1 wt % of (*P*)-*E*,*E*-**1** or (*M*)-*E*,*E*-**1** in E7 at sequential 300 and 480 nm or sequential 254 and 480 nm also resulted in observed variations in the pitch and cholesteric phase handedness reversal.[9]

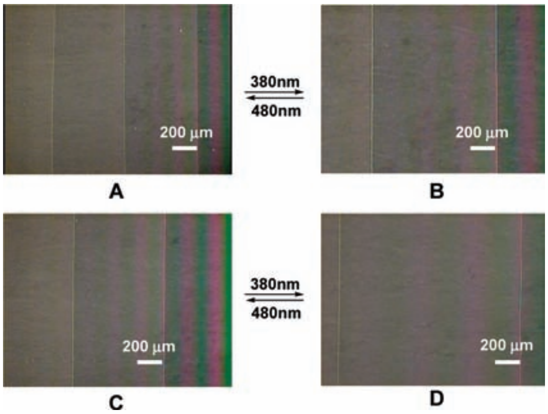

Figure 4. Polarized optical micrographs (40× magnification) of (A) 0.1 wt % (*P*)-*E*,*E*-**1** and (C) 0.1 wt % of (*M*)-*E*,*E*-**1** dissolved in E7 at 25 °C in a wedge cell (A and C, before irradiation; B and D, after irradiation at 380 nm for 15 min).

We have documented a new dual-mode optical switch possessing four different metastable states by combining helicene and azobenzene in close proximity.[14] The resultant system undergoes cooperative, reversible chirochromic and photochromic switchings with high diastereoselectivities. Our system also constitutes one of the most selective bis-azobenene photochromic switches. Nematic LC E7 dopped with **1** led to cholesteric mesophases with modulable pitches (i.e., modulable colors of refractive light) and complementary handedness.

Acknowledgment. We thank the National Science Council of Taiwan for financial support of this research.

Supporting Information Available: Syntheses of **1**−**11** with characterization data; UV−vis absorption and CD spectra, HPLC traces, and polarized optical photomicrographs of **1** before and after photoirradiation. X-ray crystallography files of (1′*S*)-**2b**, (1′*R*)-**3a**, and (*M*)-**11** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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