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Photochemically Reversible and Thermally Stable Axially Chiral Diarylethene Switches

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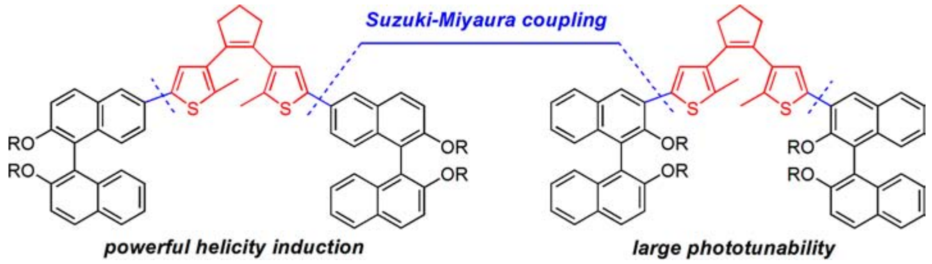
ABSTRACT



A series of dithienylcyclopentenes containing axially chiral 1,1′-binaphthyl units were successfully synthesized by a Suzuki–Miyaura protocol. All these compounds exhibited photochemically reversible isomerization with thermal stability in both organic solvent and a liquid crystal (LC) host. When doping into an achiral LC host, some of them exhibited very high helical twisting powers. Reversible reflection wavelength tuning in the visible region and LC phase switching between nematic and cholesteric upon light irradiation were demonstrated.

Photochromic molecules that can reversibly change their absorption spectra upon light irradiation have attracted a great deal of attention because of their promising applications as smart light-driven molecular switches and artificial nanomachines.[1] Among all the photochromic compounds, diarylethenes are particularly fascinating owing to their superior thermal stability and excellent fatigue resistance. Upon irradiation with UV light, they can transform from a colorless open-ring form to a colored closed-ring form. The reverse process is thermally stable and occurs only by visible light irradiation. The photochemically reversible switching of diarylethenes with good thermal stability constitutes the basis for their widespread applications, such as photomemories and switches.[2]

It is also known that a chiral molecule can introduce its chirality into an achiral nematic liquid crystal (LC) host to form a self-organized, optically tunable helical superstructure, i.e. cholesteric LC (CLC),[3] which can selectively reflect light according to Bragg's law. The reflection wavelength is defined by $\lambda = np$, where p is the pitch length of the helical structure and n is the average refractive index of the LC material. The ability of a chiral molecule to twist the nematic mesogens is expressed as helical twisting power (HTP),

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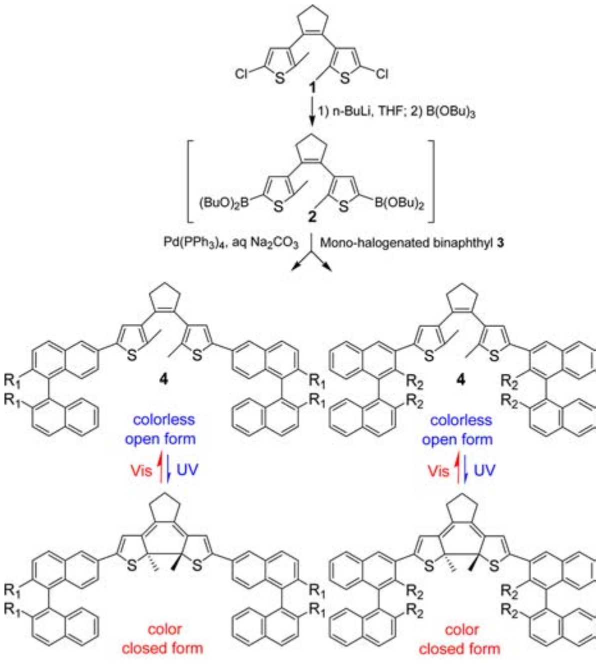
which can be quantified as $\beta = (pc)^{-1}$, where c is the chiral dopant concentration. When a chiral photochromic compound is employed as a dopant, it is possible to control the pitch length and the reflection wavelength of the helical superstructure by light, which paves the way to applications in optically addressable displays, optical data storage, and photonics.[4] However, compared with other intensively studied photoresponsive dopants such as azobenzenes,[5] less attention was paid to diarylethenes. To date only a few examples with chiral diarylethene dopants have been reported mostly because of their low HTPs or very minor tunability.[6]

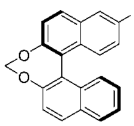
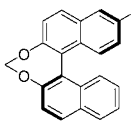
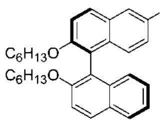
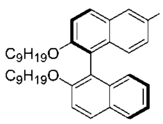
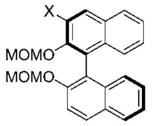
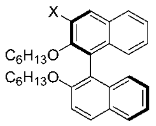
Scheme 1



(*S*,*S*)-**4a**: R$_1$= OCH$_2$-(bridged); (*R*,*R*)-**4b**: R$_1$= OCH$_2$-(bridged)
(*S*,*S*)-**4c**: R$_1$= OC$_6$H$_{13}$; (*S*,*S*)-**4d**: R$_1$= OC$_9$H$_{19}$
(*S*,*S*)-**4e**: R$_2$= OCH$_2$OCH$_3$; (*S*,*S*)-**4f**: R$_2$= OC$_6$H$_{13}$

To tailor chiral diarylethenes with satisfactory functionalities for device performance, e.g., high HTPs or remarkable tunabilities, we present here a series of novel photochemically reversible and thermally stable axially chiral dithienylcyclopentene switches (*S*,*S*)-**4a**, (*S*,*S*)-**4c**–**f**, and (*R*,*R*)-**4b**, which were successfully constructed by a Suzuki–Miyaura coupling protocol (Scheme 1).[7] The design of these molecules utilizes the combination of the photochromic dithienylcyclopentene core with two axially chiral binaphthyl units, which has proven to be powerful helicity inducers for CLCs.[8]

Table 1. Suzuki–Miyaura Reaction between Boronate Ester **2** and Binaphthyl-Derived Halides **3a**–**h**

entry	halides		product	yield
1		(*S*)-**3a**	(*S*,*S*)-**4a**	78%
2		(*R*)-**3b**	(*R*,*R*)-**4b**	75%
3		(*S*)-**3c**	(*S*,*S*)-**4c**	78%
4		(*S*)-**3d**	(*S*,*S*)-**4d**	76%
5		(*S*)-**3e** : X = Br (*S*)-**3f** : X = I	(*S*,*S*)-**4e** (*S*,*S*)-**4e**	32% 77%
6		(*S*)-**3g** : X = Br (*S*)-**3h** : X = I	(*S*,*S*)-**4f** (*S*,*S*)-**4f**	35% 68%

Monohalogenated binaphthyl derivatives (*S*)-**3a**, (*S*)-**3c**–**h**, and (*R*)-**3b** were designed and synthesized for the coupling reactions (see Supporting Information). The boronate ester **2** was generated in situ from dichloride **1**[9] and directly used for the coupling reaction with halides **3**. A standard Suzuki reaction condition was employed to examine the reactivity of the substrates, in which 5 mol % of Pd(PPh$_3$)$_4$ was used as the catalyst and aqueous Na$_2$CO$_3$ was used as the base.[9b] A good yield (78%) was obtained for the reaction of (*S*)-**3a** and **2** under this condition (Table1, entry 1). Other attempts such as screening bases or solvents did not improve the yield notably. Aryl bromide with electron-donating groups shows only low to moderate reactivities in Suzuki reactions, evidencing the good yield might result from the high nucleophilicity of perhydrocyclopentene-based boronate ester **2**. The reactions

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(6) (a) Denekamp, C.; Feringa, B. L. *Adv. Mater.* **1998**, *10*, 1080–1082. (b) Uchida, K.; Kawai, Y.; Shimizu, Y.; Vill, V.; Irie, M. *Chem. Lett.* **2000**, 654–655. (c) Yamaguchi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *Mol. Cryst. Liq. Cryst.* **2000**, *345*, 287–292. (d) Yamaguchi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *Chem. Mater.* **2000**, *12*, 869–871. (e) Yamaguchi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *Mol. Cryst. Liq. Cryst.* **2001**, *365*, 861–866. (f) Yamaguchi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *J. Mater. Chem.* **2001**, *11*, 2453–2458. (g) van Leeuwen, T.; Pijper, T. C.; Areephong, J.; Feringa, B. L.; Browne, W. R.; Katsonis, N. *J. Mater. Chem.* **2011**, *21*, 3142–3246. (h) Li, Y.; Urbas, A.; Li, Q. *J. Org. Chem.* **2011**, *76*, 7148–7156. (i) Hayasaka, H.; Miyashita, T.; Nakayama, M.; Kuwada, K.; Akagi, K. *J. Am. Chem. Soc.* **2012**, *134*, 3758–3765. (j) Li, Y.; Urbas, A.; Li, Q. *J. Am. Chem. Soc.* **2012**, *134*, 9573–9576.

(7) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.

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of (*R*)-**3b**, (*S*)-**3c**, and (*S*)-**3d** with **2** under the same reaction conditions also gave the corresponding products with good yields (Table 1, entries 2−4). When the bromides (*S*)-**3e** and (*S*)-**3g** were used as the substrates, only low yields of products (*S*,*S*)-**4d** and (*S*,*S*)-**4e** were obtained. This might be due to the strong electron-donating effect and the steric hindrance of methoxymethoxy groups at the 2,2′-position. By using more active iodide substrates (*S*)-**3f** and (*S*)-**3h**, the yields can be successfully improved to 77% and 68% respectively (Table 1, entries 5, 6).

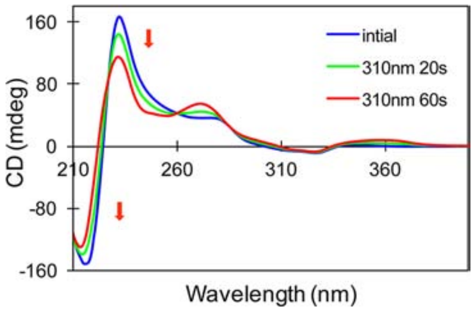

Figure 1. CD spectra of (*S*,*S*)-**4a** (20 μM in CH_3CN) upon UV irradiation. It takes about 60 s to reach the photostationary state.

The photoswitching properties of (*S*,*S*)-**4a**, (*S*,*S*)-**4c**−**f**, and (*R*,*R*)-**4b** were first investigated in organic solvents. The solution of (*S*,*S*)-**4a** in THF was colorless at the initial state. Upon UV irradiation at 310 nm, the solution color changed immediately to fresh purple, indicating the transformation of (*S*,*S*)-**4a** from its open form to closed form.[5a] The irradiated state was thermally stable and was able to switch back to its initial state by visible light irradiation at 550 nm (30 mW cm^{-2}). The absorption spectra are included in the Supporting Information (Figure S2). The excellent fatigue resistance was also confirmed by repeated irradiation of the solution with UV and visible light (Figure S4).The chiroptical properties of (*S*,*S*)-**1a** were investigated by CD spectra. As shown in Figure 1, the strongest bisignated exciton couplet between 210 and 250 nm is due to the coupling of the two ^1B_b transitions located on distinct naphthalene rings, while the couplets at around 280 and 320 nm are related to the ^1L_a and ^1L_b transitions of naphthalene.[10] Upon UV irradiation, the exciton couplet at 230 nm weakened significantly while a shoulder exciton developed at 270 nm. The distinct changes gave clear evidence that the conformation of binaphthyl moieties was affected by photoisomerization; therefore, the chiroptical properties of this compound can be modulated by light.

Table 2. HTPs of Diarylethene Dopants at Different States in Nematic LC Host[a]

		HTP (β)		
dopant	LC host[b]	initial state	PSS_{UV}	$\Delta\beta/\beta$ (%)[c]
4a	E7	+154	+160	+4%
4a	Zli-1132	+156	+173	+11%
4b	E7	−154	−160	+4%
4c	E7	−115	−99	−14%
4c	Zli-1132	−87	−65	−25%
4c	5CB	−118	−114	−3%
4d	E7	−77	−70	−9%
4d	5CB	−86	−82	−4%
4e	E7	+14	+19	+40%
4e	Zli-1132	+4	+6	+50%
4f	E7	+11	+22	+100%
4f	Zli-1132	+9	+13	+44%

[a] $\beta = 1/(pc)$, where p is the pitch of the cholesteric phase, c is the molar fraction of the dopant in LC host. [b] E7 is a eutectic mixture of LC components commercially designed for display applications, and 5CB is 4′-pentyl-4-biphenylcarbonitrile. Zli-1132 is a mixture of 4-(4-alkylcyclohexyl)benzonitrile and 4-(4-alkylcyclohexyl)-4′-cyanobiphenyl derivatives. [c] Percent change in β observed from initial state to PSS_{UV}.

Doping these compounds into nematic hosts can efficiently induce the formation of cholesteric LCs with a characteristic fingerprint texture (see Supporting Information Figure S6). Their HTPs in different nematic LC hosts were measured in wedge cells by the Grandjean−Cano method, and the results are summarized in Table 2. Using different LC hosts resulted in different intermolecular associations between the dopant and the host as evidenced by the variation in HTP values and change upon UV irradiation. Interestingly, it was found that the HTPs and the changes were dependent on the incorporation style of binaphthyl units. Compounds (*S*,*S*)-**4a,c,d** and (*R*,*R*)-**4b** in which the binaphthyl was introduced through the 6-position exhibited very high HTPs, while incorporation of binaphthyl through the 3-position gave the products (*S*,*S*)-**4e** and (*S*,*S*)-**4f** with low HTPs and a large change upon UV irradiation. For example, the HTP of (*S*,*S*)-**4a** in E7 at the initial state was 154 μm^{-1} while compound (*S*,*S*)-**4e** exhibited a very low HTP of 11 μm^{-1} with a remarkable increase to 22 μm^{-1} upon UV irradiation. It is established that the dihedral angle (θ) of two naphthalenes in binaphthyl derivatives plays a key role in their cholesteric induction abilities.[8b] Both the *transoid* conformation ($\theta > 90°$) and the *cisoid* conformation ($\theta > 90°$) of binaphthyl derivatives can efficiently induce the helicity with high HTPs, while the *quasi-orthogonal* conformations ($\theta \approx 90°$) only have very weak induction ability. For the *S* configuration, the *transoid* conformation induces a left-handed CLC and the *cisoid* conformation induces a right-handed CLC. To interpret the property−structure relationship, the handedness of the induced CLCs was examined by the contact method and the sign (−) and (+) represent left-handed and right-handed screw sense, respectively. As expected, (*S*,*S*)-**4a** induced right-handed CLCs, which can be attributed to the fact that the binaphthyl unit is fixed with a methylene tether and thus has a small dihedral angle of ∼55°.[8a] Compound (*R*,*R*)-**4b** as the enantiomer of (*S*,*S*)-**4a** has the same HTP values with the opposite handedness. The unbridged binaphthyls in compounds (*S*,*S*)-**4c** and (*S*,*S*)-**4d**

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(10) Di Bari, L.; Pescitelli, G.; Salvadori, P. *J. Am. Chem. Soc.* **1999**, *121*, 7998–8804.

are conformationally more flexible, and the left-handedness indicated that the binaphthyls might stabilize in a *transoid* conformation. Based on the very low HTPs, the θ in (*S*,*S*)-**4e** and (*S*,*S*)-**4f** were estimated to be ~90° which might be due to the rigid structures and the steric hindrance between substitution groups at 2,2′ positions and the dithienylcyclopentene core. This kind of structure was also found to be very sensitive to photoisomerization as revealed by the large variation in HTPs. These results also confirmed the subtle dependence of cholesteric induction behavior on the molecular structure of both the dopant and the nematic LC host.

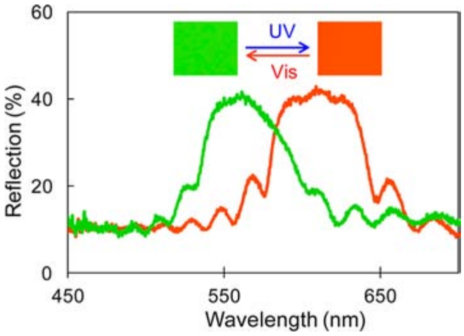

Figure 2. Reflection spectra changes of 5.0 wt % of (*S*,*S*)-**4a** in Zli-1132 in 5 μm thick planar cell. The reflection colors (inset) were taken from a polarized reflective mode microscope.

Utilization of the high HTP of (*S*,*S*)-**4a** enabled a visible light reflective cholesteric LC to be formulated by doping only 5.0 wt % of (*S*,*S*)-**4a** into the achiral nematic LC Zli-1132. This mixture was capillary-filled into a 5 μm thick planar aligned cell with antiparallel rubbing directions. As seen in Figure 2, the reflection wavelength of this cell at the initial state is ~620 nm, which was blue-shifted to 560 nm upon UV irradiation due to the increase of HTP. The photoswitching process was also confirmed by the direct observation of the reflection color changing from red to green under a reflective mode microscope (Figure 2, inset). The reverse process can be achieved by visible light irradiation at 550 nm.

Due to the significant HTP changes upon light irradiation, (*S*,*S*)-**4f** was successfully employed as an LC switch, i.e. reversibly switching the LC phase between nematic and cholesteric. When doping 4.4 wt % of (*S*,*S*)-**4f** into E7, the low HTP at the initial state is not sufficient for helicity induction and the microscopic texture with conoscopic observation confirmed the nematic state (Figure 3). Upon UV irradiation, a characteristic fingerprint texture of the cholesteric phase appeared due to the dramatic increase of HTP and formation of a helical superstructure. The cholesteric state is thermally stable and can be driven back to the nematic state upon visible light irradiation.

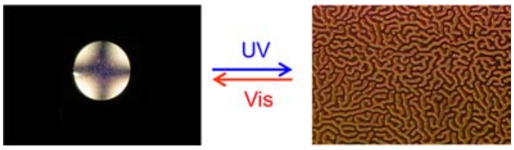

Figure 3. Crossed polarized optical texture and conoscopic observations (inset) of 4.4 wt % of (*S*,*S*)-**4f** in E7 in 5 μm thick homeotropic aligned cell before (left) and after (right) UV irradiation at 310 nm.

In conclusion, a series of novel photochemically reversible and thermally stable dithienylcyclopentene switches containing two axially chiral binaphthyl units were designed and synthesized. The Suzuki–Miyaura coupling between binaphthyl-derived halides with diboronate ester gave the products with good yields. Their photoswitching properties were characterized in both organic solvents and LC media. Furthermore, their cholesteric induction behavior was found to be dependent on the incorporation style of binaphthyl units. Attachment of binaphthyl through the 6-position generated very high HTP compounds, among which (*S*,*S*)-**4a** was successfully employed to tune the reflection color in the visible range. When the binaphthyl units were introduced through the 3-position, the products show significant changes in HTP during photoisomerization. Compound (*S*,*S*)-**4f** was found to be capable of reversibly switching the LC phase between nematic and cholesteric. The novel structures, high HTPs, and the interplay between structure and chiroptical properties would provide impetus toward developing more powerful diarylethene switches for practical applications.

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Supporting Information Available. Details of the synthesis, characterization data, copies of ^{1}H and ^{13}C NMR spectra, and measurement of HTP. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.