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Synthesis and Characterization of Light-Driven Dithienylcyclopentene Switches with Axial Chirality

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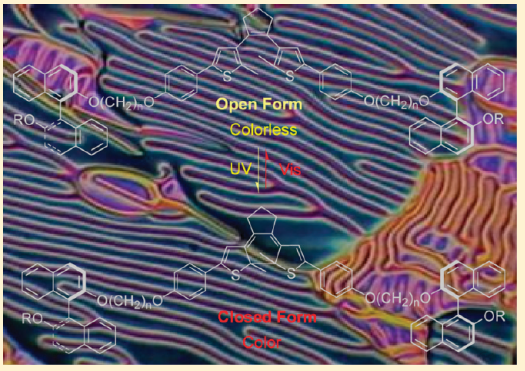
Supporting Information

ABSTRACT: Three new photochemically reversible but thermally stable dithienylcyclopentene switches with axial chirality were synthesized and characterized. All the compounds exhibited photochemically reversible isomerization with thermal stability between its open form and closed form in both organic solvent and liquid crystal host. Their photoresponsive behaviors in organic solvents were characterized by ^{1}H NMR, UV−vis, and CD spectra. These chiral molecular switches were found not only to be able to act as a chiral dopant and induce a helical superstructure in an achiral liquid crystal host but also to be able to reversibly and dynamically tune the transmittance and reflection of the resulting chiral phase upon light irradiation. The helical twisting powers, transmittance, and reflection spectra of photoswitchable cholesteric LCs were measured. Dopant **1** exhibited an unusually high helical twisting power, which is significantly larger than those of the known chiral diarylethenes reported as chiral dopants so far.



INTRODUCTION

Self-organizing chiral liquid crystal (LC) architectures with phototunable properties have proved extremely fascinating for the design and fabrication of functional devices.[1] As an example, photoresponsive cholesteric LCs can be made by doping photoresponsive chiral molecules into an achiral nematic LC host.[2] The ability of a chiral dopant to induce a twist in the director orientation of an achiral nematic LC is quantified as the helical twisting power (HTP, β) and expressed in the equation $\beta = (pc)^{-1}$, where p is the pitch length of helical superstructure and c is the chiral dopant concentration. Various kinds of photoresponsive molecules have been reported as chiral dopants for LC,[3] such as azobenzenes,[4] spirooxazines,[5] fulgides,[6] overcrowded alkenes,[7] and diarylethenes.[8] Compared with the intensively studied cholesteric LCs consisting of chiral azobenzenes, chiral diarylethenes are of a particular interest due to the advantages of thermal stability and excellent fatigue resistance. These are indispensable for applications in functional devices, such as memories and switches.[9] Upon irradiation with UV light, the diarylethenes can transform from colorless open-ring form to its colored closed-ring form. The reverse isomerization process is thermally stable and occurs only photochemically by irradiation with visible light. This thermally stable and photochemically reversible switching of diarylethenes has been the basis for the intelligent materials with promising applications in optical devices. However, to date only a few derivatives have been reported as chiral dopants capable of inducing the formations of photoswitchable cholesteric LCs.[8] The reported chiral diarylethenes exhibited low to moderate HTPs. The highest HTP was recently reported as 50 μm^{-1} in an achiral nematic host[8h] which is notably much lower than the known chiral azobenzene dopants.[4] These relatively low HTPs give rise to the requirement of higher doping concentrations, which often leads to phase separation and coloration and alters the desired physical properties of LC host. Therefore, it is of great interest to develop chiral diarylethenes with high HTPs.

Here we report the synthesis and characterization of three novel chiral dithienylethenes (*S*,*S*)-**1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**2** (Scheme 1). These compounds were found to exhibit reversible photoisomerization in both organic solvents and LC hosts upon light irradiation while showing thermal stability between photoisomers. Of significance is the unusual high HTP that (*S*,*S*)-**1a** and its enantiomer (*R*,*R*)-**1b** exhibit. To the best of our knowledge, this is the highest HTP chiral diarylethene to be synthesized.[8] The design of these new chiral dithienylethenes utilizes the combination of the photochromic dithienylcyclopentene core and two side chains containing an axially chiral binaphthyl unit which has proved to be a powerful helicity inducer in nematic LCs.[10,11] Although diarylperfluorocyclopentenes were the most commonly used diarylethenes for photoswitching applications, the diarylperhydrocyclopentene derivatives possess the advantages of low cost and ease of synthesis with comparable fatigue resistance and thermal stability.[12] Meanwhile, the introduction of flexible alkylene spacers and chains can greatly increase the solubility in organic solvents and nematic LCs.[1a]

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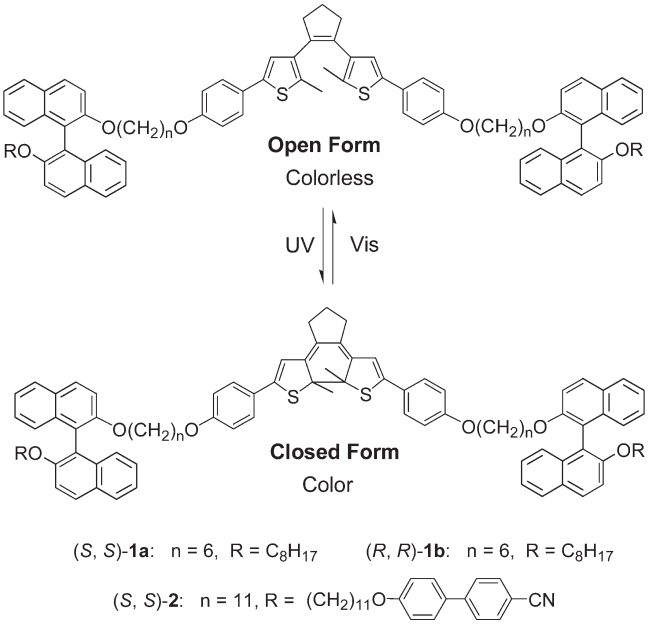
Scheme 1. Light-Driven Open-Ring and Closed-Ring Isomerization of Thermally Stable Photochromic Chiral Molecular Switches (*S*,*S*)-1a, (*R*,*R*)-1b, and (*S*,*S*)-2

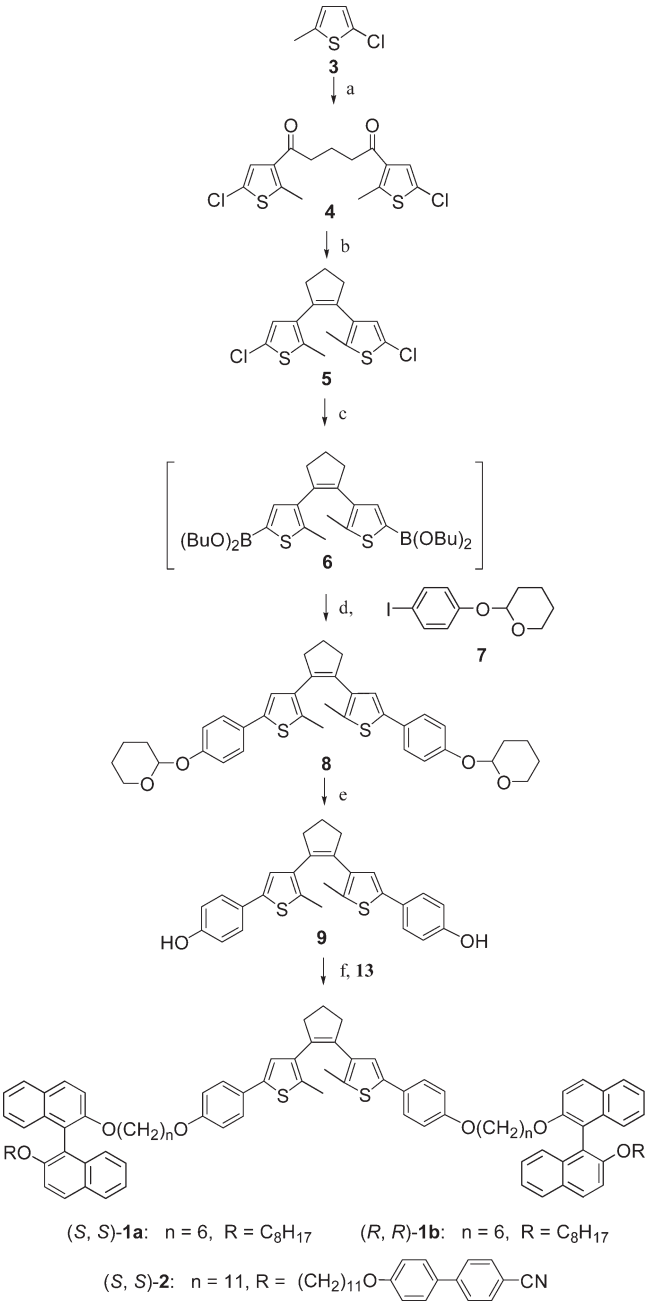


RESULTS AND DISCUSSION

(*R*,*R*)-**1b** is the enantiomer of (*S*,*S*)-**1a** and has the same properties as (*S*,*S*)-**1a** as expected. The target compound (*S*,*S*)-**2** is structurally similar to (*S*,*S*)-**1a** and has a longer spacer and is ended with a 4-cyanobiphenyl group, which resembles the structure of some nematic LC molecules. (*S*,*S*)-**1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**2** were synthesized starting from 2-chloro-5-methylthiophene **3**,[12−15] which was reacted with glutaryl dichloride to give 1,5-bis(5-chloro-2-methylthiene-3-yl)pentane-1,5-dione **4**[13] (Scheme 2). Dichloride **4** was treated with $TiCl_3(THF)_3$ and Zn to get dithienylcyclopentene **5**[13] which was converted to bis-(boronic) esters followed by the Suzuki coupling reaction with protected *p*-iodophenol **7** to obtain intermediate **8**. After removal of tetrahydropyran-protected groups, diphenol **9**[13] was reacted with bromide (*S*)-**13a**, (*R*)-**13b**, and (*S*)-**13c**, respectively, to afford the target compounds (*S*,*S*)-**1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**2**. The bromides (*S*)-**13a**, (*R*)-**13b**, and (*S*)-**13c** were prepared from (*S*) or (*R*)-1,1′-bi(2-naphthol) by Williamson ether formation or/and Mitsunobu reactions as depicted in Scheme 3. All the target compounds and intermediates were fully characterized by ^{1}H NMR, ^{13}C NMR, and HRMS or elemental analysis.

The switches (*S*,*S*)-**1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**2** are chemically and thermally stable, and their photoresponsive properties in solution were characterized by ^{1}H NMR and UV−vis spectroscopy. Distinct differences in ^{1}H NMR signals were observed between the open form and closed form both in the high-field and low-field area for (*S*,*S*)-**1a**. As shown in Figure 1, a remarkable change occurred for the protons on the thiophene moiety, which shifted from 7.02 ppm to 6.41 ppm in addition to the decrease of integration at 7.02 ppm. The protons of the benzene ring were located at 6.81 and 7.40 ppm as typical doublet peaks at the initial state, and these signals shifted slightly to low-field after photocyclization, The protons of the cyclopentene core and the methyl group moved from 2.85, 1.96, 2.08 ppm to 2.48, 1.98, 1.87 ppm, respectively. Also, very minor changes were observed for the protons on the binaphthyl moiety even if they were far away from the dithienylcyclopentene core. These changes gave clear evidence that the open isomer was transformed into the closed isomer upon UV irradiation. On the basis of the ^{1}H NMR integration areas assigned to the open isomer and the closed isomer in a dilute solution at the photostationary state of 290 nm, the photochemical conversion rate of (*S*,*S*)-**1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**2** is approximately 98%, 97%, and 92%, respectively. Figure 2 is the CD spectra of (*S*,*S*)-**1a** and (*S*,*S*)-**2**. Only slight

Scheme 2. Synthesis of (*S*,*S*)-1a, (*R*,*R*)-1b, and (*S*,*S*)-2[a]



[a] a: Glutaryl dichloride, $AlCl_3$, CS_2; b: $TiCl_3(THF)_3$, Zn, THF; c: *n*-BuLi, $B(OBu)_3$, THF; d: $Pd(PPh_3)_4$, aqueous Na_2CO_3, THF, 2-(4-iodophenoxy)tetrahydropyran **7**; e: Pyridinium *p*-toluenesulphonate (PPTS), $CH_3OH-CH_2Cl_2$; f: **13**, K_2CO_3, KI, acetone.

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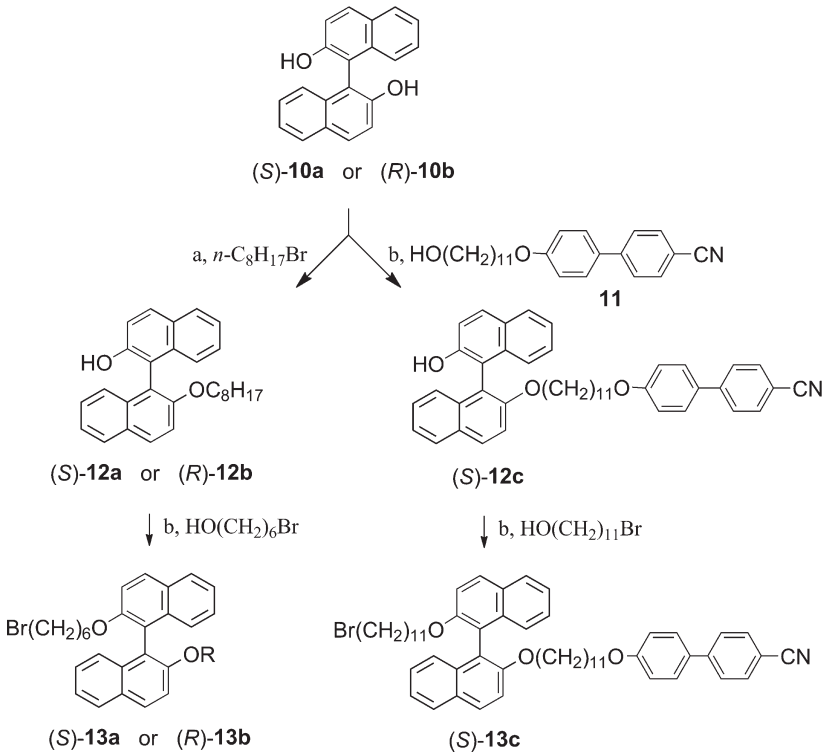
Scheme 3. Synthesis of Bromide Intermediate 13[a]



[a] a: K_2CO_3, KI, acetone; b: diisopropyl azodicarboxylate (DIAD), PPh_3, and THF.

change upon UV irradiation was observed, which can be attributed to the fact that the chiral centers are far from the dithienylcyclopentene and the photoisomerization does not cause significant morphology change.

Figure 3 is the UV−vis absorption spectra of (*S*,*S*)-**1a** and (*S*,*S*)-**2** in THF and the corresponding changes upon UV (290 nm) and visible light (520 nm) irradiations. The UV spectrum of the initial state (open form) of (*S*,*S*)-**1a** showed maximum absorption at 283 nm, and there was no absorption in the visible region. Upon irradiation at 290 nm, there was a gradual decrease seen in the absorption at 283 nm accompanied by the appearance of an absorption band in the visible region with a maximum at 525 nm, indicating the formation of the closed form.[12,16] The photostationary state ($PSS_{290\ nm}$) was reached within 60 s with UV irradiation at 290 nm. Then upon visible irradiation at 520 nm, the $PSS_{290\ nm}$ can be switched back to the initial state in about 15 min because of the photochemical transformation from closed form to open form. Absorption spectroscopic data of both open form and closed form of (*S*,*S*)-**1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**2** are summarized in Table 1. The fatigue resistance of (*S*,*S*)-**1a** and (*S*,*S*)-**2** were examined by the absorption at 525 nm, as the solutions were repeatedly irradiated with UV and visible light. Both (*S*,*S*)-**1a** and (*S*,*S*)-**2** showed excellent fatigue resistance, and no degradation was observed (Figure 4). The thermally stable, photochemically reversible switching, excellent photoconversion efficiency, and fatigue resistant properties are extremely promising for many potential applications.

As expected, doping the chiral molecules (*S*,*S*)-**1a** and (*S*,*S*)-**2** into an achiral nematic liquid crystal host can induce a chiral nematic mesophase, as evidenced by the characteristic fingerprint texture.[17] As an example, the fingerprint texture was clearly observed under crossed polarizing optical microscope when doping only 2% of (*S*,*S*)-**1a** into the achiral LC, E7, which is a eutectic mixture of cyanophenyl liquid crystals. Also the fingerprint texture was observed for the cholesteric mesophase formed by 3% of (*S*,*S*)-**2** in E7 (Figure 5). Their helical twisting powers were measured in a wedge cell by Grandjean−Cano method[18] both in E7 and 4′-pentyl-4-biphenylcarbonitrile (5CB), and the results are summarized in Table 2. Of significance is the unusually high HTP that (*S*,*S*)-**1a** and its enantiomer (*R*,*R*)-**1b** exhibit. The chiral molecular switch (*S*,*S*)-**1a** induced a left-handed helical superstructure, whereas its enantiomer (*R*,*R*)-**1b** induced a right-handed helical superstructure. The HTP of (*S*,*S*)-**2** is much lower than (*S*,*S*)-**1a**, which might result from the relatively larger molecular weight. Also the HTPs of the LC mixtures are photoswitchably controlled by the photoisomerization of dopants. Upon irradiation at 290 nm for 10 min, the HTP of (*S*,*S*)-**1a** in E7 decrease from 84 μm^{-1} to 71 μm^{-1} and can be switched back to 82 μm^{-1} upon irradiation at 520 nm (Figure 6).

It is known that cholesteric LCs can selectively reflect light according to Bragg's law. The wavelength λ of the selective reflection is defined by $\lambda = np$, where p is the pitch length of the helical structure and n is the average index of refraction of the LC material. To further examine the photoswitchable properties in LC, a mixture of 12 wt % (*S*,*S*)-**1a** in E7 was capillary-filled into a 5 μm thick glass cell with a polyimide alignment layer, and the transmittance and reflection spectra were collected. Irradiation at 290 nm for 10 min resulted in clear transmittance decrease around 520 nm (Figure 7, left) due to the photochromic behavior from colorless open form to colored closed form. Also a red shift of reflection band from 840 to 890 nm was observed (Figure 7, right), which is in agreement with the decrease of HTP.

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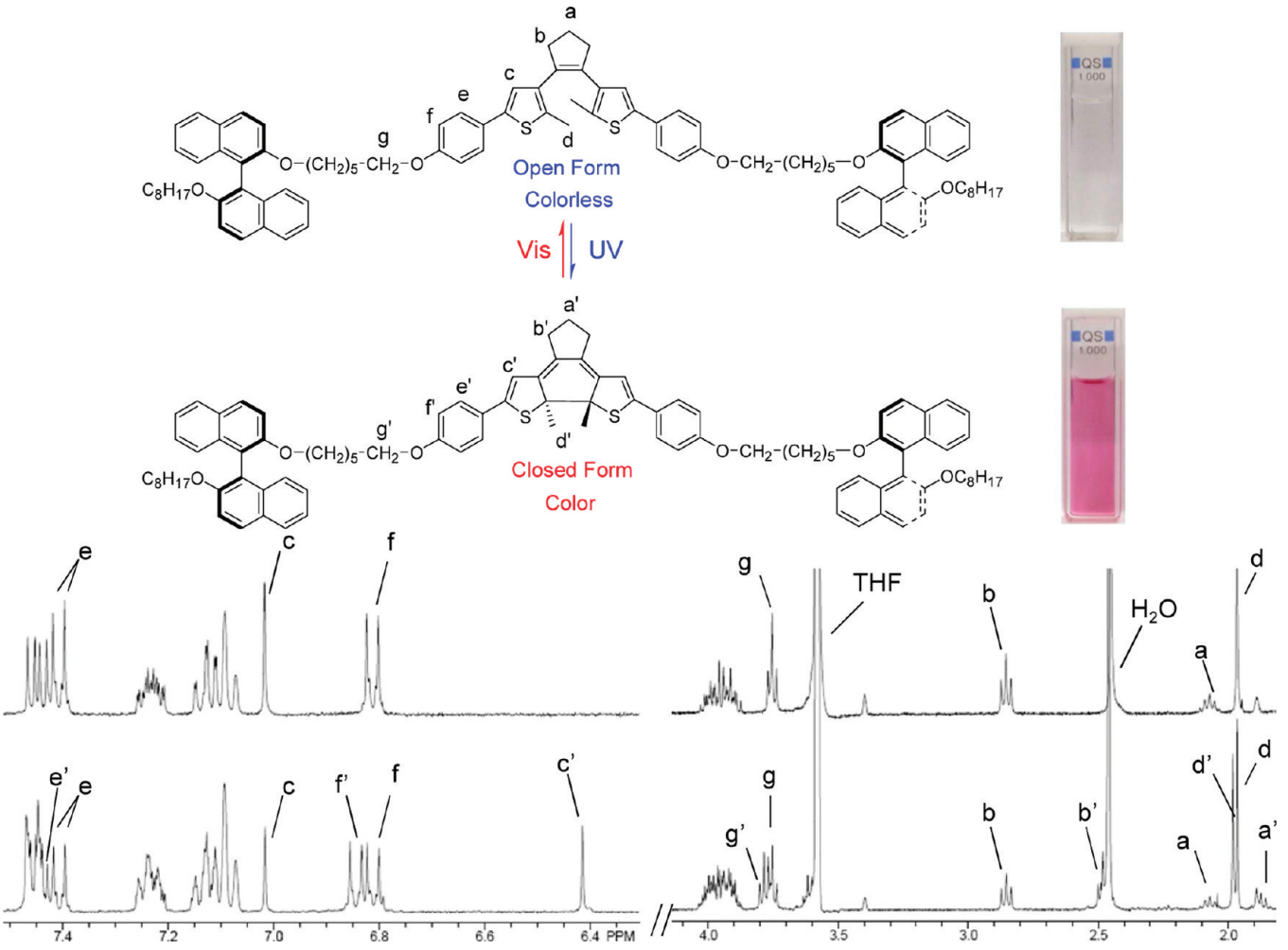

Figure 1. Photoisomerization of (*S*,*S*)-**1a** and ^{1}H NMR changes before (top) and after (bottom) UV irradiation (290 nm, 30 mW/cm^2) in THF-d_8. Note: The photochemical cyclization also generates two diastereomers of the closed-ring isomer with (*S*,*S*) and (*R*,*R*) configuration of the two new chiral centers (see Supporting Information).

CONCLUSION

Three dithienylcyclopentene derivatives (*S*,*S*)-**1a**, (*R*,*R*)-**1b**, and (*S*,*S*)-**2** containing two axially chiral binaphthyl units were designed and synthesized. Their photoswitchable properties were characterized in both organic solvents and LC hosts. Upon irradiation with UV light, their solutions in organic solvents changed from colorless to bright red, and the irradiated or photostationary state is thermally stable and can be switched back by visible light irradiation. Doping them into an achiral LC host can efficiently induce the formation of a cholesteric phase. Of note is the unusually high HTP of (*S*,*S*)-**1a** or its enantiomer (*R*,*R*)-**1b**, which is significantly larger than the HTPs previously reported for chiral diarylethenes. The chiral molecular switch (*S*,*S*)-**1a** induced a left-handed cholesteric phase whereas its enantiomer (*R*,*R*)-**1b** induced a right-handed cholesteric phase. Furthermore, the HTPs can be reversibly controlled by irradiation with UV light and visible light. The high HTP, photochemically reversible process with thermal stability, and excellent fatigue resistant properties would provide new and exciting insights into developing light-driven chiral molecular switches for practical applications.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals and solvents were purchased from commercial supplies and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on 400 or 200 MHz instrument in $CDCl_3$ or THF-d_8. Chemical shifts are in δ units (ppm) with the residual solvent peak or TMS as the internal standard. The coupling constant (J) is reported in hertz (Hz). NMR splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Column chromatography was carried out on silica gel (230−400 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F_{254} glass plates. Spots were rendered visible by exposing the plate to UV light. Melting points are uncorrected. Mass spectral data were measured with ESI or MALDI ion mode. Textures and disclination line distance changes were observed by optical microscopy using a polarizing microscope with temperature controller. The UV and visible light irradiation was carried out by a xenon light source (100 W) through a filter at 290 or 520 nm. Reflection spectra were measured with a spectrometer in the dark. The achiral nematic liquid crystals E7 and 5CB were used in the study. E7 is a eutectic mixture of LC components commercially designed for display applications and 5CB is 4′-pentyl-4-biphenylcarbonitrile.

1,5-Bis(5-chloro-2-methylthiene-3-yl)pentane-1,5-dione (4).[13] To a mixture of 2-chloro-5-methylthiophene **3** (10.60 g,

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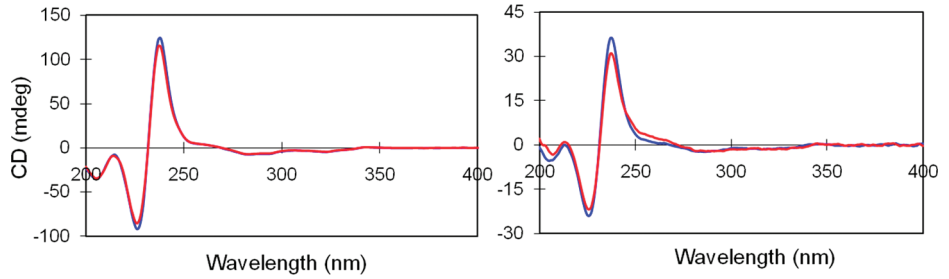

Figure 2. CD spectra changes of (*S*,*S*)-**1a** (left, 15 μM) and (*S*,*S*)-**2** (right, 5 μM) in hexane before (blue) and after (red) UV irradiation at 290 nm.

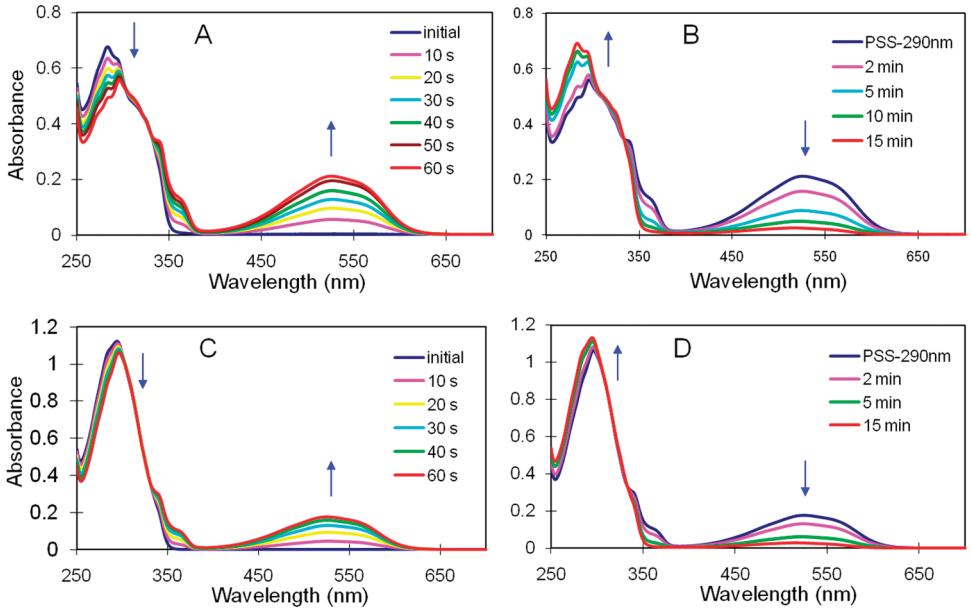

Figure 3. Photoisomerization of (*S*,*S*)-**1a** and (*S*,*S*)-**2** (10 μM in THF) monitored by UV−vis spectroscopy: open form to closed form upon UV irradiation at 290 nm of (*S*,*S*)-**1a** (A) and (*S*,*S*)-**2** (C) and reversible closed form to open form upon visible light irradiation at 520 nm for (*S*,*S*)-**1a** (B) and (*S*, *S*)-**2** (D).

Table 1. Absorption Spectroscopic Data of (*S*,*S*)-1a, (*R*,*R*)-1b, and (*S*,*S*)-2[a]

	open form		closed form	
compound/ solvent	λ_{max} (nm)	ε (10^5 cm^2 mmol^{-1})	λ_{max} (nm)	ε (10^5 cm^2 mmol^{-1})
(*S*,*S*)-**1a**/THF	283	0.67	296	0.56
			525	0.21
(*R*,*R*)-**1b**/THF	283	0.65	295	0.55
			525	0.20
(*S*,*S*)-**2**/THF	294	1.12	296	1.06
			525	0.18
(*S*,*S*)-**1a**/hexane	283	0.63	295	0.55
			525	0.19
(*S*,*S*)-**2**/hexane	291	1.13	293	1.08
			525	0.17

[a] Data were collected at room temperature before and after photoirradiation with 290 nm UV light.

80 mmol) and glutaryl dichloride (6.76 g, 40 mmol) in CS_2 (200 mL) solution was added $AlCl_3$ (11.60 g, 87 mmol) at 0 °C with vigorous stirring. The resulting mixture was stirred for 2 h at room temperature. Then ice-cold water solution was carefully added to the reaction mixture, and the water layer was extracted with diethyl ether. The combined organic phase was washed with water, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel to afford a white solid **4** (5.30 g, 50%). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.18 (s, 2H), 2.86 (t, J = 6.8 Hz, 4H), 2.65 (s, 6H), 1.99−2.12 (m, 2H). ^{13}C NMR (50 MHz): δ = 194.7, 147.6, 134.8, 126.7, 125.2, 40.5, 18.1, 16.0.

1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene (5).[13] A mixture of **4** (2.09 g, 5.8 mmol), $TiCl_3(THF)_3$ (4.29 g, 11.6 mmol), and Zn dust (0.89 g, 13.3 mmol) in dry THF (50 mL) was stirred under nitrogen atmosphere at 40 °C for 1 h. The reaction mixture was cooled to room temperature and poured through a glass filter containing silica gel that was pretreated with petroleum ether. The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford a white crystalline solid **5** (0.65 g, 40%). Mp: 75−77 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.58 (s, 2H), 2.72 (t, J = 7.4 Hz, 4H), 1.95−2.10 (m, 2H), 1.88 (s, 6H). ^{13}C NMR (50 MHz): δ = 134.7, 134.4, 133.2, 126.6, 125.1, 38.3, 22.9, 14.1.

4-(Iodophenyl)tetrahydropyran-2-yl Ether (7). To a solution of 4-iodophenol (2.20 g, 10 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (251 mg, 1 mmol) in dry CH_2Cl_2 (50 mL) was added 3,4-dihydro-2*H*-pyran (1.37 mL, 15 mmol). The resultant mixture was

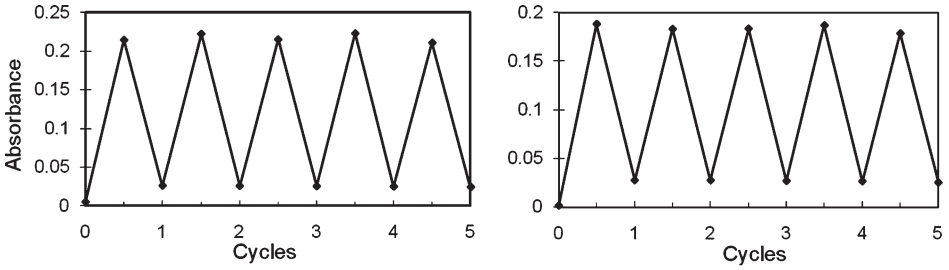

Figure 4. Cyclical absorbance of compound (*S*,*S*)-**1a** (left) and (*S*,*S*)-**2** (right) in THF (10 μM) at 525 nm as the solution was irradiated with UV light (290 nm) for 2 min and then with visible light (520 nm) for 15 min.

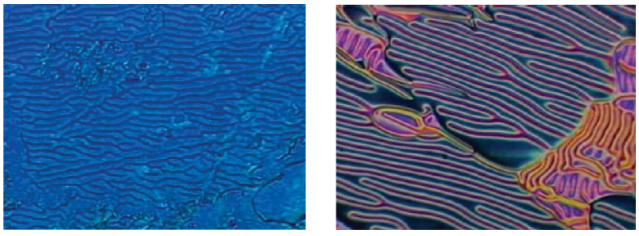

Figure 5. Crossed polarized optical textures of 2% (*S*,*S*)-**1a** in E7 (left) and 3% (*S*,*S*)-**2** in E7 (right).

stirred for 2.5 h at room temperature. The reaction mixture was diluted with diethyl ether and washed once with saturated brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography over silica gel (10% EtOAc in hexane) gave the product **7** as a white solid (2.9 g, 95%). Mp: 64−65 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.55 (dd, J = 2.0, 6.4 Hz, 2H), 6.83 (dd, J = 2.4, 6.8 Hz, 2H), 5.38 (t, J = 3.0 Hz, 1H), 3.89−3.83 (m, 1H), 3.62−3.57 (m, 1H), 2.01−1.94 (m, 1H), 1.87−1.83 (m, 2H), 1.68−1.55 (m, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 156.9, 138.2, 118.8, 96.3, 83.9, 61.9, 30.2, 25.1, 18.6. Anal. Calcd for $C_{11}H_{13}IO_2$: C, 43.44, H, 4.31; found: C, 43.34, H, 4.24. HRMS (ESI) calcd for $C_{11}H_{13}IO_2Na^+$: 326.9858, found: 326.9848.

1,2-Bis[2-methyl-5-[(*p*-((tetrahydropyran-2-yl)oxy)phenyl]-3-thienyl]cyclopentene (8). To a solution of **5** (3.28 g, 10 mmol) in anhydrous THF (100 mL) was added *n*-BuLi (1.6 M, 12.5 mL) dropwise, and the mixture was stirred at room temperature for 1 h. Then $B(OBu)_3$ (6.9 g, 8.1 mL, 30 mmol) was added and stirred at room temperature for another 1 h followed by addition of **7** (5.5 g, 18 mmol), 20% Na_2CO_3 aqueous solution (40 mL), and $Pd(PPh_3)_4$ (230 mg, 0.2 mmol). The reaction mixture was heated to reflux and stirred for 10 h. After the mixture was cooled to room temperature, the organic layer was separated and the water layer was washed with ethyl acetate (3 × 50 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography over silica gel (10% EtOAc in hexane) to give the product as brownish solid (4.2 g, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.41 (d, J = 8.8 Hz, 4H), 7.03 (d, J = 8.8 Hz, 4H), 6.93 (s, 2H), 5.43 (t, J = 3.2 Hz, 2H), 3.94−3.88 (m, 2H), 3.63−3.59 (m, 2H), 2.84 (t, J = 7.6 Hz, 4H), 2.09−2.01 (m, 4H), 1.98 (s, 6H), 1.89−1.85 (m, 4H), 1.71−1.59 (m, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 156.2, 139.5, 136.5, 134.6, 133.5, 128.3, 126.5, 123.1, 116.8, 96.3, 62.0, 38.5, 30.3, 25.2, 23.0, 18.7, 14.3. HRMS (ESI) calcd for $C_{37}H_{40}O_4S_2Na^+$: 635.2266, found: 635.2260.

1,2-Bis[2-methyl-5-(4-hydroxyphenyl)-3-thienyl]cyclopentene (9).[13] A solution of **8** (612 mg, 1 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (20 mg, 0.08 mmol) in MeOH−CH_2Cl_2 (20 mL) was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (50% EtOAc in hexane) to give the product **9** as a brownish solid (425 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.37 (d, J = 8.4 Hz, 4H), 6.90 (s, 2 H), 6.80 (d, J = 9.2 Hz, 4H), 4.77 (s, 2H), 2.83 (t, J = 7.2 Hz, 4H), 2.09 (quintet, J = 7.6 Hz, 2H), 1.98 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 154.7, 139.4, 136.5, 134.6, 133.5, 127.7, 126.8, 123.0, 115.6, 38.5, 23.0, 14.4. HRMS (ESI) calcd for $C_{27}H_{24}O_2S_2Na^+$: 467.1115, found: 467.1120.

Table 2. HTPs of Chiral Dopants (*S*,*S*)-1a, (*R*,*R*)-1b, and (*S*,*S*)-2 at Different States in the Nematic LC Host

		HTP β_M (μm^{-1})		
dopant	LC host	initial state	$PSS_{290\ nm}$	$PSS_{520\ nm}$
(*S*,*S*)-**1a**	E7	84	71	82
(*S*,*S*)-**1a**	5CB	92	77	89
(*R*,*R*)-**1b**	E7	84	71	82
(*S*,*S*)-**2**	E7	25	19	23
(*S*,*S*)-**2**	5CB	28	20	24

(*S*)-2′-Octyloxy-[1,1′]binaphthalenyl-2-ol [(*S*)-12a]. To a solution of (*S*)-1,1′-bi(2-naphthol) **10a** (1.14 g, 4 mmol), K_2CO_3 (1.66 g, 12 mmol), and KI (70 mg, 0.4 mmol) in dry acetone (40 mL) was added 1-bromooctane. The reaction mixture was then heated to reflux for 24 h. The reaction mixture was filtered through a pad of Celite to remove K_2CO_3 and then concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (10% EtOAc in hexane) to give the product (*S*)-**12a** as a colorless oil (1.57 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.00 (d, J = 9.2 Hz, 1H), 7.87 (d, J = 9.2 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 9.6 Hz, 1H), 7.38−7.25 (m, 4H), 7.22−7.17 (m, 2H), 7.04 (dd, J = 0.8, 8.4 Hz, 1H), 4.93 (s, 1H), 4.01−3.92 (m, 1H), 1.45−1.41 (m, 2H), 1.25−1.19 (m, 2H), 1.10−0.97 (m, 8H), 0.85 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 155.6, 151.2, 134.1, 133.8, 130.8, 129.6, 129.5, 129.1, 128.1, 128.0, 127.2, 126.2, 125.0, 124.9, 124.2, 123.1, 117.4, 116.3, 115.6, 115.2, 69.8, 31.6, 29.2, 29.1, 29.0, 25.5, 22.6, 14.1. HRMS (ESI) calcd for $C_{28}H_{30}O_2Na^+$: 421.2144, found: 421.2150.

(*R*)-2′-Octyloxy-[1,1′]binaphthalenyl-2-ol [(*R*)-12b]. This compound was prepared by the same procedure as that used for (*S*)-**12a** from (*R*)-1,1′-bi(2-naphthol). The spectral data are also the same as those for (*S*)-**12a**. HRMS (ESI) calcd for $C_{28}H_{30}O_2Na^+$: 421.2144, found: 421.2148.

(*S*)-2-(6-Bromohexyloxy)-2′-octyloxy-[1,1′]binaphthalenyl [(*S*)-13a]. To a magnetically stirred solution of (*S*)-**12a** (398 mg, 1 mmol) and PPh_3 (524 mg, 2 mmol) in dry THF (10 mL) at ambient temperature under N_2 atmosphere was added dropwise a mixture of 6-bromo-1-hexanol (0.27 mL, 2 mmol) and diisopropyl azodicarboxylate (404 mg, 0.4 mL, 2 mmol). The reaction mixture was then slowly heated to reflux. After being refluxed for 20 h, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel (10% EtOAc in

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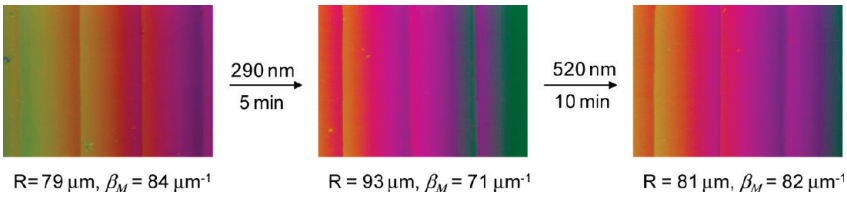

Figure 6. Change of distance (R) between Cano's lines of 2 wt % (*S*,*S*)-**1a** in E7 in the wedge cell upon irradiation at 290 nm and visibile light irradiation at 520 nm.

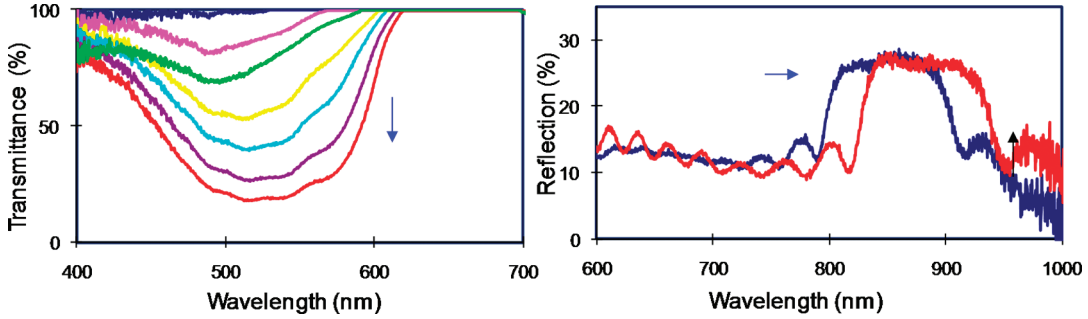

Figure 7. Transmittance (left) and reflection (right) spectra changes of 12 wt % (*S*,*S*)-**1** in LC host E7 in 5 μm thick planar cell at room temperature upon UV irradiation at 290 nm for 10 min.

hexane) to give the product (*S*)-**13a** as a colorless oil (420 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.91 (d, *J* = 9.6 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.31−7.27 (m, 2H), 7.21−7.15 (m, 4H), 3.98−3.86 (m, 4H), 3.14 (t, *J* = 7.2 Hz, 2H), 1.51−1.47 (m, 2H), 1.39−1.35 (m, 4H), 1.25−1.18 (m, 2H), 1.08−0.98 (m, 8H), 0.87−0.83 (m, 7H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 154.6, 154.4, 134.2, 134.2, 129.3, 129.2, 129.1, 129.0, 127.8, 126.0, 125.5, 123.4, 123.4, 120.8, 120.7, 115.9, 115.9, 69.8, 69.5, 33.7, 32.6, 31.7, 29.4, 29.1, 29.1, 27.5, 25.6, 24.7, 22.6, 14.1. HRMS (ESI) calcd for $C_{34}H_{41}BrO_2Na^+$: 583.2188, found: 583.2184.

(*R*)-2-(6-Bromohexyloxy)-2′-octyloxy-[1,1′]binaphthalenyl [(*R*)-13b]. This compound was prepared by the same procedure as that used for (*S*)-**13a** from (*R*)-**12b**. The spectral data are also the same as those for (*S*)-**13a**. HRMS (ESI) calcd for $C_{34}H_{41}BrO_2$ Na^+: 583.2188, found: 583.2191.

11-[(4-Cyano-4′-biphenylyl)oxy]undecanol (11). To a solution of 4′-hydroxy-4-biphenylcarbonitrile (1.95 g, 10 mmol), K_2CO_3 (4.14 g, 30 mmol), and KI (176 mg, 1 mmol) in dry acetone (50 mL) was added 11-bromo-1-undecanol (3.01 g, 12 mmol). The reaction mixture was then heated to reflux for 12 h. The reaction mixture was cooled to room temperature and filtered through a pad of Celite to remove K_2CO_3 and then concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (25% EtOAc in hexane) to give the product **11** as white solid (3.24 g, 89%). Mp: 90−91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.00 (t, *J* = 6.8 Hz, 2H), 3.64 (t, *J* = 6.8 Hz, 2H), 1.80 (quintet, *J* = 6.4 Hz, 2H), 1.59−1.55 (m, 2H), 1.49−1.45 (m, 2H), 1.36−1.25 (m, 12H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 159.8, 145.3, 132.5, 131.2, 128.3, 127.1, 119.1, 115.1, 110.0, 68.2, 63.1, 32.8, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 26.0, 25.7. Anal. Calcd for $C_{24}H_{31}NO_2$: C, 78.86, H, 8.55; found: C, 78.66, H, 8.86. HRMS (ESI) calcd for $C_{24}H_{31}NO_2Na^+$: 388.2252, found: 388.2262.

(*S*)-2′-[(11-(4-Cyano-4′-biphenylyl)oxy)undecyloxy]-[1,1′]-binaphthalenyl-2-ol [(*S*)-12c]. To a magnetically stirred solution of (*S*)-1,1′-bi(2-naphthol) **10a** (2.86 g, 10 mmol), **11** (3.65 g, 10 mmol), and PPh_3 (3.93 g, 15 mmol) in dry THF (100 mL) at ambient temperature under N_2 atmosphere was added dropwise diisopropyl azodicarboxylate (DIAD) (3.03 g, 2.95 mL, 20 mmol). The reaction mixture was then slowly heated to reflux. After being refluxed for 12 h, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel (20% EtOAc in hexane) to give the product (*S*)-**12c** as a colorless oil (5.90 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.02 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 9.6 Hz, 1H), 7.38−7.26 (m, 4H), 7.24−7.20 (m, 2H), 7.08 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.01 (d, *J* = 9.2 Hz, 2H), 5.01 (s, 1H), 4.04−3.94 (m, 4H), 1.82 (quintet, *J* = 6.4 Hz, 2H), 1.51−1.44 (m, 4H), 1.39−1.34 (m, 2H), 1.29−1.25 (m, 2H), 1.17−1.02 (m, 8H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 159.8, 155.5, 151.3, 145.3, 134.1, 133.8, 132.5, 131.2, 130.8, 129.6, 129.5, 129.1, 128.3, 128.1, 128.0, 127.2, 127.0, 126.2, 124.99, 124.95, 124.2, 123.1, 119.1, 117.4, 116.3, 115.6, 115.2, 115.1, 110.0, 69.7, 68.2, 29.5, 29.3, 29.21, 29.2, 29.0, 26.0, 25.5. HRMS (ESI) calcd for $C_{44}H_{43}NO_3Na^+$: 656.3141, found: 656.3152.

(*S*)-2-(11-Bromoundecyloxy)-2′-[11-((4-cyano-4′-biphenylyl)-oxy)undecyloxy]-[1,1′]binaphthalenyl [(*S*)-13c]. To a magnetically stirred solution of 11-bromo-1-undecanol (867 mg, 3.45 mmol), (*S*)-**12c** (1.46 g, 2.3 mmol), and PPh_3 (904 mg, 3.45 mmol) in dry THF (100 mL) at ambient temperature under N_2 atmosphere was added dropwise diisopropyl azodicarboxylate (DIAD) 697 mg, 0.68 mL, 3.45 mmol). The reaction mixture was then slowly heated to reflux. After being refluxed for 48 h, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by chromatography on silica gel (20% EtOAc in hexane) to give the product (*S*)-**13c** as a colorless oil (1.44 g, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.92 (d, *J* = 9.6 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 9.2 Hz, 2H), 7.32−7.28 (m, 2H), 7.21−7.14 (m, 4H), 7.00 (d, *J* = 8.8 Hz, 2H).4.03−3.89 (m, 6H), 3.41 (t, *J* = 7.2 Hz, 2H), 1.87−1.80 (m, 4H), 1.49−1.21 (m, 16H), 1.13−0.90 (m, 16 H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 159.7, 154.4, 145.1, 134.1, 132.4, 131.1, 129.2, 128.9, 128.2, 127.7, 126.9, 125.9, 125.4, 123.3, 120.6, 119.0, 115.7, 115.0, 109.9, 69.6, 68.1, 34.0, 32.7, 29.5, 29.3, 29.0, 28.7, 28.1, 26.0, 25.5. HRMS (ESI) calcd for $C_{55}H_{64}BrNO_3Na^+$: 888.3967, found: 888.3934.

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(*S,S*)-1,2-Bis[2-methyl-5-[*p*-(6-(1-(2-(octyloxy)naphthalen-1-yl)naphthalen-2-yloxy)hexyloxy)phenyl]-3-thienyl]cyclopentene [(*S,S*)-1a]. To a solution of **9** (700 mg, 1.58 mmol), K_2CO_3 (1.31 g, 9.48 mmol), and KI (35 mg, 0.2 mmol) in dry acetone (40 mL) was added compound (*S*)-**13a** (1.86 g, 3.31 mmol). The reaction mixture was then heated to reflux for 15 h. The reaction mixture was filtered through a pad of Celite to remove K_2CO_3 and then concentrated under reduced pressure. The residue was purified by chromatography on silica gel (5% EtOAc in hexane) to give the target product (*S,S*)-**1a** as a white solid (1.01 g, 46%). Mp 58−60 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.92 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 9.2 Hz, 2H), 7.83 (t, *J* = 9.2 Hz, 4H), 7.42−7.38 (m, 8H), 7.32−7.27 (m, 4H), 7.22−7.14 (m, 8H), 6.93 (s, 2H), 6.81 (d, *J* = 8.8 Hz, 4H), 4.00−3.87 (m, 8H), 3.73 (t, *J* = 6.4 Hz, 4H), 2.84 (t, *J* = 7.2 Hz, 4H), 2.08 (quintet, *J* = 7.2 Hz, 2H), 1.99 (s, 6H), 1.44−1.35 (m, 12H), 1.22−1.19 (m, 4H), 1.22−0.88 (m, 24H), 0.85 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 158.4, 154.6, 154.5, 139.6, 136.6, 134.6, 134.3, 133.4, 129.4, 129.3, 129.0, 127.8, 127.3, 126.5, 126.0, 125.5, 123.4, 122.9, 120.9, 120.8, 116.0, 114.8, 69.8, 69.7, 67.9, 38.5, 31.7, 29.4, 29.3, 29.1, 29.0, 25.6, 25.4, 22.6, 14.3, 14.1. HRMS (ESI) calcd for $C_{95}H_{104}O_6S_2Na^+$: 1427.7172, found: 1427.7177. Anal. Calcd for $C_{95}H_{104}O_6S_2$: C, 81.16; H, 7.46; S, 4.56. Found: C, 80.92; H, 7.55; S, 4.58.

(*R,R*)-1,2-Bis[2-methyl-5-[*p*-(6-(1-(2-(octyloxy)naphthalen-1-yl)naphthalen-2 yloxy)hexyloxy)phenyl]-3-thienyl]cyclopentene [(*R,R*)-1b]. The target compound (*R,R*)-**1b** was synthesized by the same procedure as that used for (*S,S*)-**1a**, and the spectral data are also the same as those for (*S,S*)-**1**. Mp: 57−59 °C. HRMS (ESI) calcd for $C_{95}H_{104}O_6S_2Na^+$: 1427.7172, found: 1427.7178.

(*S,S*)-1,2-Bis[2-methyl-5-[*p*-(11-(1-(2-((4-cyano-4′-biphenylyloxy)undecyloxy)naphthalen-1-yl)naphthalen-2-yloxy)-undecyloxy)phenyl]-3-thienyl]cyclopentene [(*S,S*)-2]. To a solution of **9** (380 mg, 0.85 mmol), K_2CO_3 (345 mg, 2.5 mmol), and KI (17.5 mg, 0.1 mmol) in dry acetone (10 mL) was added compound (*S*)-**13c** (1.47 g, 1.7 mmol). The reaction mixture was then heated to reflux for 15 h. The reaction mixture was filtered through a pad of Celite to remove K_2CO_3 and then concentrated under reduced pressure. The residue was purified by chromatography on silica gel (10% EtOAc in hexane) to give the product (*S,S*)-**2** as a white solid (891 mg, 52%). Mp 62−64 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.94 (d, *J* = 8.8 Hz, 4H), 7.86 (d, *J* = 8.0 Hz, 4H), 7.68 (d, *J* = 8.8 Hz, 4H), 7.63 (d, *J* = 8.4 Hz, 4H), 7.52 (d, *J* = 9.2 Hz, 4H), 7.43 (d, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 8.8 Hz, 4H), 7.31 (t, *J* = 6.8 Hz, 4H), 7.23−7.17 (m, 8H), 7.00 (d, *J* = 8.8, 4H), 6.95 (s, 2H), 6.88 (d, *J* = 8.4, 4H), 4.03−3.90 (m, 16H), 2.85 (t, *J* = 7.6 Hz, 4H), 2.09 (quintet, *J* = 7.2 Hz, 2H), 1.85 (s, 6H), 1.85−1.78 (m, 8H), 1.48−1.25 (m, 32H), 1.15−0.92 (m, 32 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 159.8, 158.3, 154.5, 145.2, 139.5, 136.5, 134.5, 134.2, 133.3, 132.5, 131.2, 129.2, 129.0, 128.3, 127.7, 127.2, 127.0, 126.5, 125.9, 125.5, 123.34, 123.31, 122.8, 120.7, 119.1, 115.8, 115.0, 114.7, 110.0, 109.9, 69.7, 68.1, 68.0, 38.5, 29.51, 29.48, 29.4, 29.3, 29.2, 29.1, 26.0, 25.6, 23.0, 14.3. MS (MALDI): *m/z* 2016 (M + H$^+$). Anal. Calcd for $C_{137}H_{150}N_2O_8S_2$: C, 81.59, H, 7.50; found: C, 81.45, H,7.46.

■ ASSOCIATED CONTENT

Supporting Information. CD spectra, measurement of pitch and helical twisting power, ^{1}H NMR changes of compound (*S,S*)-**1a** before and after UV irradiation, and copies of ^{1}H NMR and ^{13}C NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

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