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Dynamic Photoswitching of Helical Inversion in Liquid Crystals Containing Photoresponsive Axially Chiral Dopants

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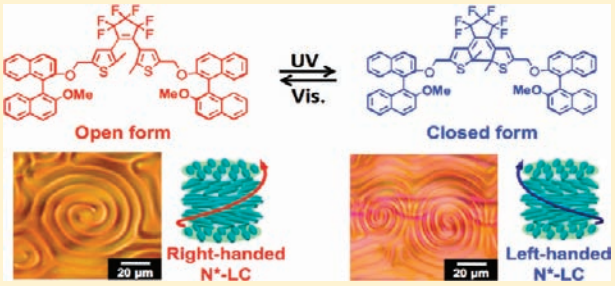
Supporting Information

ABSTRACT: Chirality switching is intriguing for the dynamic control of the electronic and optical properties in nanoscale materials. The ability to photochemically switch the chirality in liquid crystals (LCs) is especially attractive given their potential applications in electro-optic displays, optical data storage, and the asymmetric synthesis of organic molecules and polymers. Here, we present a dynamic photoswitching of the helical inversion in chiral nematic LCs (N*-LCs) that contain photoresponsive axially chiral dopants. Novel photoresponsive chiral dithienylethene derivatives bearing two axially chiral binaphthyl moieties are synthesized. The dihedral angle of the binaphthyl rings changes via the photoisomerization between the open and closed forms of the dithienylethene moiety. The N*-LCs induced by the dithienylethene derivatives that are used as chiral dopants exhibit reversible photoswitching behaviors, including a helical inversion in the N*-LC and a phase transition between the N*-LC and the nematic LC. The present compounds are the first chiral dopants that induce a helical inversion in N*-LC via the photoisomerization between open and closed forms of the dithienylethene moiety.



1. INTRODUCTION

Dynamic photoswitching of the chiral structure and the chiroptical properties in a chiral nematic LC (N*-LC) by means of external light is useful not only for the development of molecular devices and optical data storage systems[1−5] but also for the construction of an asymmetric reaction field that enables the synthesis of helical polymers.[6−9] The chiral dopants employed here are either chiral-center-containing compounds or axially chiral compounds. Axially chiral binaphthyl derivatives are feasible for controlling the helical sense and strength of the N*-LC, especially when their molecular structures have been chemically modified, such as by the introduction of long alkyl groups or mesogenic substituents onto the naphthyl rings.[10]

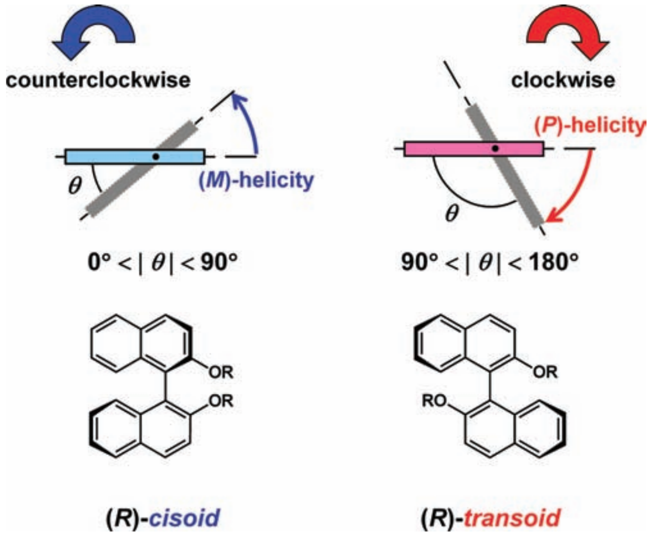


Figure 1. Structures of *cisoid* and *transoid* conformations of the binaphthyl derivatives with (*R*)-configuration.

The binaphthyl derivative is known to have a restricted freedom of internal rotation along the carbon−carbon bond between the 1 and 1′ positions of the binaphthyl rings. The helicity of the binaphthyl derivative therefore depends on the dihedral angle (θ) between the two naphthyl rings. For example, the *R*-binaphthyl derivative of the *cisoid* conformation ($0° < \theta < 90°$) and that of *transoid* conformation ($90° < \theta < 180°$) have (*M*)- and (*P*)-helicity, respectively, as described in Figure 1.[11] The binaphthyl derivatives of (*M*)- and (*P*)-helicity induce N*-LCs with left-handed (counterclockwise) and right-handed (clockwise) screw senses (helical senses), respectively, despite having the same (*R*) configuration, when they are added as chiral dopants into N-LCs.[10] For example, a nonbridged structure of the binaphthyl derivative exhibits a *transoid* conformation, and a bridged structure exhibits a *cisoid* conformation, in which the two oxygen atoms at the 2,2′-positions of the binaphthyl rings are linked with an alkyl spacer. The former conformer results in a N*-LC with a right-handed screw sense, and the latter conformer produces a

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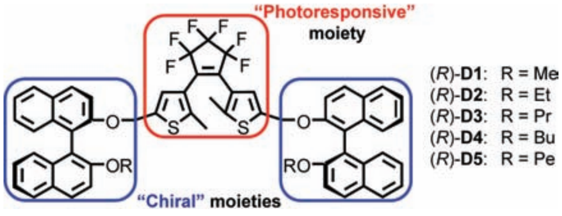
N*-LC with a left-handed screw sense.[6e,10d] Another example is that the mono- and disubstituted crown-ether-type binaphthyl derivatives with the same (*R*)-configurations give opposite screw senses to each other in N-LCs, although both of them exhibit bridged structures.[6b] These experimental facts suggest that the chirality of the binaphthyl derivative depends on the local structure around the 2,2′-positions of the binaphthyl rings, such as a bridged structure, as well as on the twisting direction and degree of the dihedral angle defined by the binaphthyl rings. The N*-LCs that contain axially chiral binaphthyl derivatives have been attracting current interest because they are useful for asymmetric reaction solvents that can provide helical conjugated polymers using achiral monomers.[6,7] If the twisting direction and/or the degree of dihedral angle in the binaphthyl derivative can be changed by photochemical perturbation, the helical twisting direction and strength of the N*-LC are also controlled. This may lead to an advanced stage of asymmetric polymerization that enables us to dynamically control helical sense and strength of the polymers and even reaction products.[6d]

It is well-known that azobenzene, flugide, and spiropyran are photochromic molecules showing reversible changes in molecular structure and absorption spectra upon photo- and thermal induction.[8] The chiral compound including azobenzene has been used as a switching chiral dopant due to its photochemical trans−cis isomerization.[3,4] However, the N*-LC containing the chiral azobenzene derivative is not feasible for the asymmetric solvent. This is because the azo group is less fatigue resistant for the photoisomerization and thermally unstable and furthermore chemically unstable to active transition metal catalysts, despite having photoresponsible function and ease of synthesis.

Therefore, it is desired for the N*-LC to have not only an external force-responsive function with fatigue resistance but also chemical and thermal stability, when the N*-LC is used as the photochemically controlled asymmetric reaction field.[6h,i] The dithienylethene derivative is one of the most promising photoresponsive compounds because of its outstanding fatigue resistance, thermal stability, and ability to undergo conformational changes between the open and closed forms via photoisomerization.[1c,12]

Here, we synthesize the novel axially chiral binaphthyl derivative bearing the dithienylethene moiety at the binaphthyl ring and use them as chiral dopants to induce N*-LCs. The N*-LCs exhibit the reversible photoswitching behavior in helical inversion and strength and phase transition. We demonstrate that the helical sense and the helical pitch of the N*-LCs are well controlled and even tuned by changing the length of the alkyl group substituted at the 2-position of the binaphthyl ring. The photoresponsive axially chiral binaphthyl derivatives, (*R*)-**D1**−(*R*)-**D5** and (*S*)-**D1**, are described in Scheme 1.

Scheme 1. Structures of Chiral Binaphthyl Derivatives Bearing Photoresponsive Dithienylethene Moieties

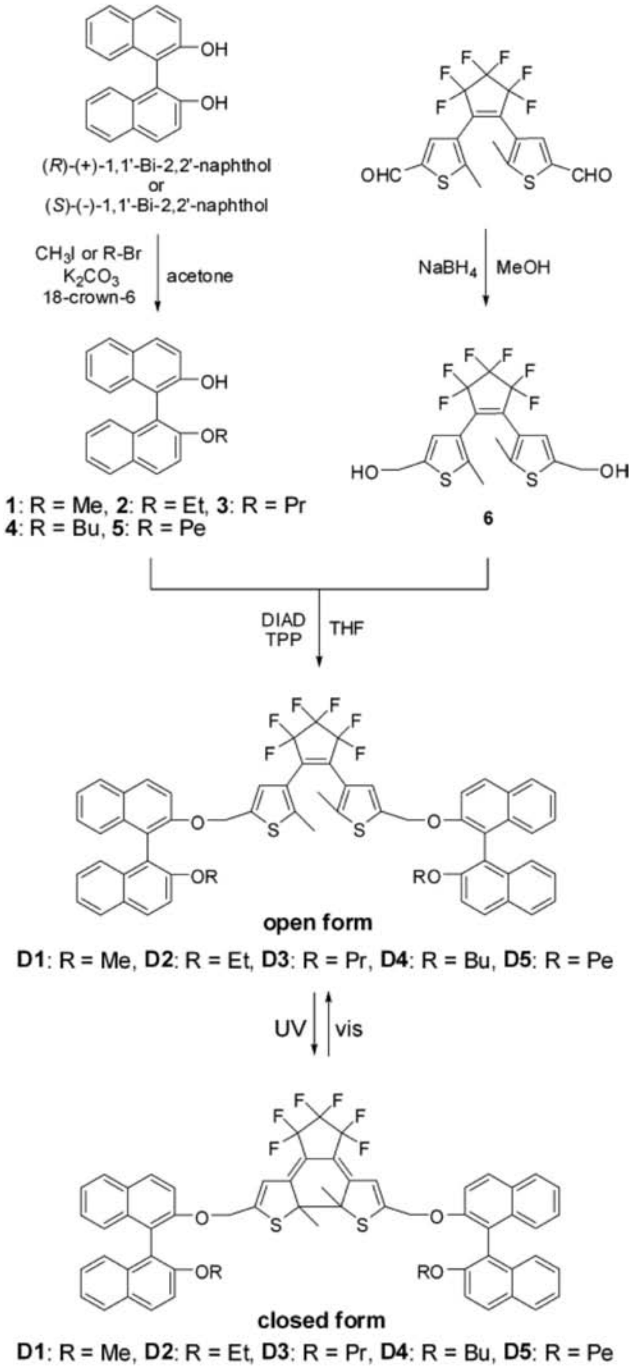


They are composed of the photoresponsive dithienylethene moiety (red frame) in the central unit and the axially chiral binaphthyl moieties (blue frames) linked with the alkyl groups in the terminal units. We focus on the control of the dihedral angle between two naphthyl rings through the conformational changes of the dithienylethene moiety. Using the present photoresponsive chiral binaphthyl derivatives as a chiral dopant to be added into the N-LC, we achieve dynamic photoswitching in the helical sense of the induced N*-LC.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. The synthetic routes are shown in Scheme 2. Binaphthyl derivatives, (*R*)-**1**−(*R*)-**5** and

Scheme 2. Synthetic Routes and Photoisomerization of the Photoresponsive Chiral Derivatives



(*S*)-**1**, were synthesized through alkaline-mediated coupling between chiroptical (*R*)-(+)- or (*S*)-(−)-1,1′-bi-2-naphthol and alkyl halides in acetone. The dithienylethene derivative **6**, which had been synthesized from 5-methylthiophene-2-carboxyaldehyde with five steps,[13,14] was coupled with (*R*)-**1**−(*R*)-**5** and (*S*)-**1** via Mitsunobu reaction in THF,[15] giving the photoresponsive chiral binaphthyl derivatives, (*R*)-D**1**−(*R*)-D**5** or (*S*)-D**1**, respectively.

The photoisomerization of the dithienylethene moiety upon irradiation with UV and visible (vis) light was examined by ^{1}H NMR measurements in $CDCl_3$. The signal observed at approximately 5.00 ppm was assigned to the methylene proton that neighbors the dithienylethene moiety with the open form. Irradiation with UV light (λ = 254 nm, 16 W) induced the photoisomerization and resulted in a new signal at approximately 4.70 ppm that corresponded to the dithienylethene moiety with the closed form. The integrated intensity of the proton signal indicated that 30% of the open form dithienylethene moiety was converted to the closed form in the photostationary state (PSS) of (*R*)-**D1**. The degree of conversion to the PSS (closed form) is determined by the following formula:[16] {[closed form]/([open form] + [closed form])} × 100. This formula was used to determine that 30% was converted to the closed form, and that the remaining 70% maintained its open form, even after irradiation with UV light. (See Figures S1−S3 in the Supporting Information.) After the subsequent irradiation of the sample with vis light (λ > 400 nm, 100 W), the proton signal of the open form reappeared. Similar degrees of conversion in PSS were observed in (*R*)-**D2**−(*R*)-**D5** and (*S*)-**D1**. Because the closed form is not completely formed even after irradiation with UV light, the expression "PSS" will be used hereafter instead of "closed form".

2.2. Absorption and Circular Dichroism. (*R*)-**D1** (open form) dissolved in isotropic *n*-heptane (1.5×10^{-5} M) showed absorption bands that corresponded to the polarized naphthyl moiety transition moments of the ^1B_b long-axis at approximately 200−250 nm, the ^1L_a short-axis at approximately 250−300 nm, and the ^1L_b long-axis at approximately 300−350 nm. After being irradiated with UV light for 15 s, the shoulder band at approximately 255 nm that is attributed to the open form of the dithienylethene moiety decreased in intensity. At the same time, the bands at approximately 340 and 515 nm that are attributed to the closed form of the dithienylethene moiety gradually increased in intensity, as shown in Figure 2a. Subsequent irradiation of vis light for 60 s after the irradiation with UV light caused an increase in the intensity for the band at approximately 255 nm and a decrease in the bands at approximately 340 and 515 nm. This means that the dithienylethene moiety returned to its original state.

The photoresponsive chiral compounds, (*R*)-**D1**−(*R*)-**D5** and (*S*)-**D1**, showed circular dichroism (CD) signals in the region of the absorption spectra. Note that the closed form of the dithienylethene derivative is known to have the same amount of (*R,R*) and (*S,S*) enantiomers of the thiophene rings.[17] (See Scheme S1 in the Supporting Information.) In fact, no Cotton effect was observed in the visible region centered around 550 nm corresponding to the absorption band of the closed form, indicating no occurrence of the diastereoselective photocyclization in the present systems. As typically shown in Figure 2b, (*R*)-**D1**−(*R*)-**D5** with (*R*)-binaphthyl derivatives exhibited CD signals, which displayed large positive and negative Cotton effects for the ^1B_b (200−250 nm) transitions and positive Cotton effects for the ^1L_a (250−300 nm) and ^1L_b (300−350 nm) transitions that correspond to the binaphthyl moieties.[11,18] (See also Figures S4−S6 in the Supporting Information.)

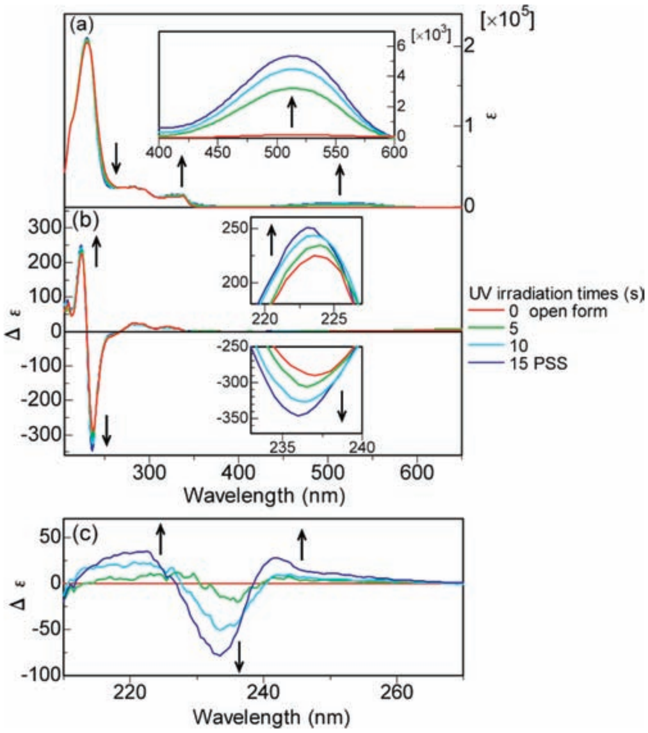


Figure 2. (a) Changes in UV−vis absorption and (b) CD spectra of (*R*)-**D1** in *n*-heptane (1.5×10^{-5} M) upon irradiation with UV light (λ = 254 nm, 16 W) for 0, 5, 10, and 15 s at 30 °C. Inset shows the expanded spectra. (c) Difference spectra given by subtraction of the CD spectrum of (*R*)-**D1** (open form) from those of (*R*)-**D1** (PSS) upon irradiation with UV light for 0, 5, 10, and 15 s.

Interestingly, when the dithienylethene moiety of (*R*)-**D1** was photoisomerized from the open form to the closed form upon irradiation with UV light for 15 s, the peaks at 223 and 237 nm that are attributed to the ^1B_b transitions of the binaphthyl moieties gradually increased. In addition, the peaks decreased in intensity after irradiation with visible light for 60 s. Figure 2c shows the different CD spectra for (*R*)-**D1** (open form) and (*R*)-**D1** (PSS), which clearly indicate an increase in $\Delta\varepsilon$ of the transition of the binaphthyl rings. Here, $\Delta\varepsilon$ is defined as $\varepsilon_L - \varepsilon_R$, where ε_L and ε_R are the molar excitation coefficients of left and right circularly polarized lights, respectively. The change in $\Delta\varepsilon$ between (*R*)-**D1** (open form) and (*R*)-**D1** (PSS), $|\Delta\varepsilon_{\text{open form}} - \Delta\varepsilon_{\text{PSS}}|$, at 233 nm was 80. Rosini et al. have reported that the $\Delta\varepsilon$ of the ^1B_b couplet at 230 nm is correlated with the dihedral angle of the binaphthyl moieties.[11f] On the basis of this correlation, the dihedral angles of (*R*)-**D1** (open form) and (*R*)-**D1** (PSS) were approximately 100° and 90°, respectively. That is, the binaphthyl moieties of (*R*)-**D1** (open form) and (*R*)-**D1** (PSS) have a *transoid* conformation [(*P*)-helicity] and an orthogonal conformation, respectively, in *n*-heptane. This result suggests that the conformational change of the dithienylethene moiety via photoisomerization in the local space around the 2-position of the binaphthyl moieties causes a change in the dihedral angle between the two naphthyl rings. The change in the dihedral angle of the binaphthyl rings upon the photoisomerization of the dithienylethene moiety would allow us to control the helical sense and/or the helical pitch of the N*-LCs induced by addition of the present binaphthyl derivatives by using alternate irradiations with UV and vis light.

The change in the dihedral angle of the binaphthyl rings upon the photoisomerization of the dithienylethene moiety is supported by the CD spectra of (*R*)-**D1** in *n*-hexane. The CD signals due to Cotton effects for the ^1B_b and ^1L_a transitions that corresponded to the binaphthyl moieties of (*R*)-**D1** increased in intensity upon the irradiation with UV light (Figure 2b and c), and they decreased in intensity upon the irradiation with vis light (Figure 3). Similar reversible changes in absorption and CD intensity due to the photoisomerization were observed in (*R*)-**D2**–**D5** (see Figures S5 and S6 in the Supporting Information). Note that (*S*)-**D1** exhibited a mirror image of the CD spectrum of (*R*)-**D1**, giving Cotton effects with opposite signs to those of (*R*)-**D1**, but showed the same change in CD intensity upon irradiations with UV and vis light as in the case of (*R*)-**D1**, as shown in Figure 3.

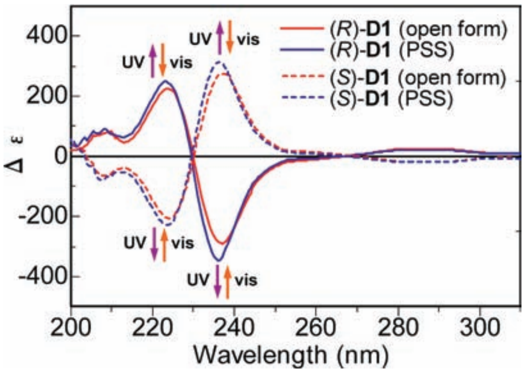
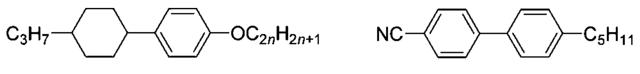


Figure 3. Changes of CD spectra of (*R*)-**D1** and (*S*)-**D1** in *n*-heptane (1.5×10^{-5} M) upon alternating irradiations of UV (λ = 254 nm, 16 W) and vis (λ > 400 nm, 100 W) lights.

2.3. Photoswitching in N*-LCs. N*-LCs were prepared by adding a small amount (1.0 mol %) of photoresponsive axially chiral compound [(*R*)-**D1**–(*R*)-**D5** and (*S*)-**D1**] as a chiral dopant into two kinds of nematic LCs consisting of phenylcyclohexyl or cyanobiphenyl mesogen, respectively, as shown in Scheme 3. The former is an equimolar mixture of N-LCs, 4-(*trans*-4-*n*-propylcyclohexyl)ethoxybenzene [PCH302] and 4-(*trans*-4-*n*-propylcyclohexyl)butoxybenzene [PCH304], abbreviated as PCH, which is chemically stable toward not only extremely reactive Ziegler–Natta catalyst such as Ti(O-*n*-Bu)$_4$–AlEt$_3$ but also other kinds of transition metal (Ni, Pd, Pt) compounds and exhibits a N-LC phase in the region from 20 to 35 °C. The latter, 4-cyano-4′-pentylbiphenyl, abbreviated as 5CB, shows a N-LC phase in the region from 24 to 35 °C, but it is reactive to catalytic species such as AlEt$_3$. These results imply that the N*-LC consisting of PCH is more favorable for the construction of dynamically controllable asymmetric reaction field because of its chemical stability.[6a,b]

Scheme 3. Structures of Nematic Liquid Crystals



PCH
[mixture of PCH302 (*n* = 1) and PCH304 (*n* = 2)]

5CB

The N*-LC induced by adding (*R*)-**D1** as a chiral dopant to PCH or 5CB showed a finger-printed texture in the polarized optical microscope (POM). Similar finger-printed textures were also observed in the N*-LCs induced by (*R*)-**D2**–(*R*)-**D5** and (*S*)-**D1**. The temperature ranges of the N* phase for PCH and 5CB were 7–31 °C and 13–30 °C, respectively, in the heating process and 0–30 °C and −5–29 °C, respectively, in the cooling process. The N*-LC that was induced by the addition of (*R*)-**D1** (open form) into the PCH-type LC showed the spiral and fingerprinted texture in POM as shown in Figure 4a. After the sample was irradiated with UV light for 30 s at 30 °C, the texture notably changed; first, the fingerprinted texture gradually changed into the Schlieren texture that is characteristic of a nematic phase. Next, the fingerprinted texture with an opposite screw sense reappeared. However, the irradiation of the N*-LC that included (*R*)-**D1** (PSS) with vis light (λ > 400 nm, 100 W) for 2 min at 30 °C gave rise to the reverse in POM.

2.4. Screw Sense of N*-LC. The screw sense of the N*-LC was next examined through the contact test based on the miscibility between two LC compounds.[19] The cholesteryl oleyl carbonate (COC), known to be left-handed, was used as the LC standard. This method is based on the observation of the mixing area between the N*-LC and the LC standard using POM. When the screw sense of the N*-LC is the same as that of the COC, the mixing area will be continuous. Otherwise, it will be discontinuous. In the contact method, the mixture of N*-LC that included (*R*)-**D1** (open form) in PCHs and the LC standard of cholesteryl oleyl carbonate (COC) with a left-handed screw sense gave a discontinuous boundary, as shown in Figure 5. This discontinuous boundary indicates that the screw sense of the N*-LC that included (*R*)-**D1** (open form) is opposite of that of the COC, that is, the right-handed one. After irradiation with UV light, the mixing area gave a continuous boundary, which indicates that the screw sense of the N*-LC that included (*R*)-**D1** (PSS) is the same as that of the COC; that is, it is left-handed. Subsequently, the irradiation with vis light for 2 min at 30 °C inverted the original screw sense from left- to right-handed. These results indicate that the N*-LCs induced by (*R*)-**D1** (open form) and (*R*)-**D1** (PSS), which possess the same (*R*)-configuration, exhibited a drastic helical inversion under alternating irradiations with UV and vis light, as was also schematically described in Figure 4a. Similarly, the N*-LC induced by (*S*)-**D1** in PCH also exhibited the photoinduced helical inversion under alternating irradiations with UV and vis light. Therefore, it is demonstrated that accompanying the photoisomerization, the N*-LCs that include (*R*)-**D1** and (*S*)-**D1** show a reversible helical inversion in the screw sense.

Although the mechanism of the reversible helical inversion in the N*-LC remains unclear, one of the plausible explanations is as follows. As schematically described in Figure S7 in the Supporting Information, the open and closed forms (PSS) of the dithienylethene moiety reversibly change to each other upon alternating irradiations of UV and vis light. In accompany with the photochemical isomerization, the binaphthyl moieties with (*R*)-configuration interchange between (*R*)-*transoid* and (*R*)-*cisoid* conformations. The stereospecific intermolecular interactions between the binaphthyl moieties of the chiral dopant and the surrounding nematic LC molecules should play a role of trigger to determine the screw sense of nematic LCs.

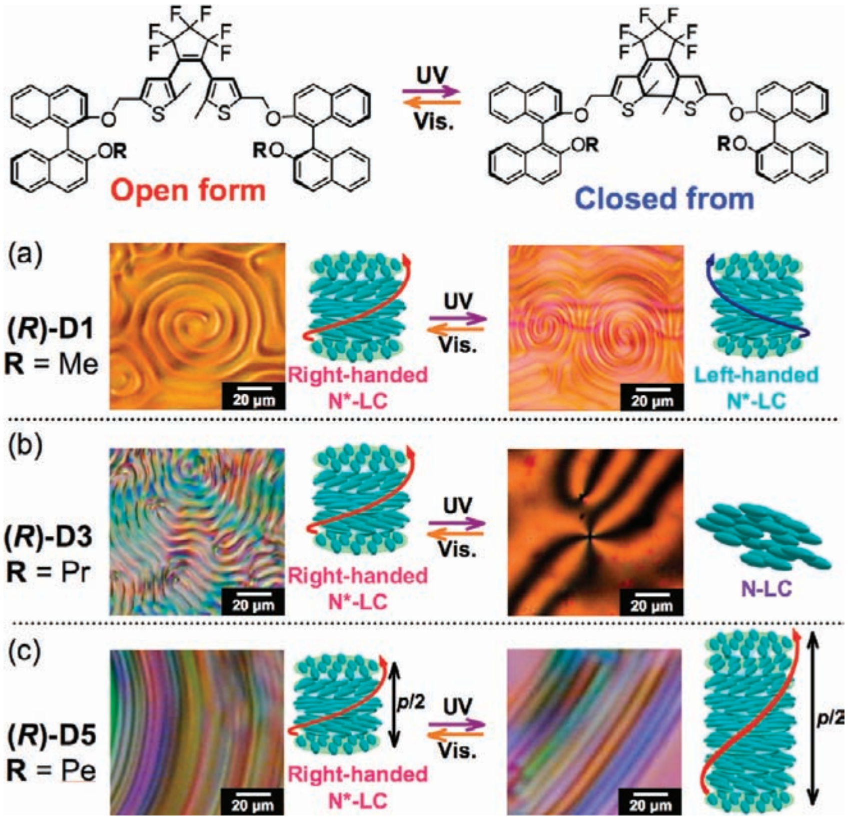


Figure 4. Polarized optical micrographs (POMs) of photoresponsive N*-LCs including (a) (*R*)-**D1**, (b) (*R*)-**D3**, and (c) (*R*)-**D5** (1.0 mol %) between the open form (left) and PSS (right) by irradiation of UV (λ = 254 nm, 16 W, handy lamp) and vis (λ > 400 nm, 100 W) light at 30 °C. Along the corresponding POMs are described schematic illustrations of (a) reversible helical inversion between N*-LCs with opposite screw senses, (b) reversible phase transition between N*-LC and N-LC, and (c) reversible change in helical pitch within N*-LC upon alternating irradiations of UV (left) and vis (right) light.

The chiral dopant consisting of dithienylethene with open form bearing (*R*)-*transoid* binaphthyl moieties induces righted-handed N*-LC; the chiral dopant consisting of dithienylethene with closed form bearing (*R*)-*cisoid* binaphthyl moieties induces left-handed N*-LC.

Meanwhile, when both N*-LCs that are induced by (*R*)-**D2** (open form) and (*R*)-**D3** (open form) and that exhibit right-handed screw senses in PCHs were irradiated with UV light for 30 s, photoinduced phase transitions from the finger-printed texture (N*-LC) to the Schlieren texture (N-LC) were observed, as shown in Figure 4b. These transitions occurred because the helical twisting powers (β_M) of (*R*)-**D2** (PSS) and (*R*)-**D3** (PSS) in PCH are insufficient (β_M = 0 to ±1.0 μm^{-1}) to induce a stable N*-LC phase. After irradiation of these mixtures with vis light for 2 min at 30 °C, the finger-printed textures with a right-handed screw sense reappeared. The reversible phase transitions between N*-LC and N-LC induced by (*R*)-**D2** and (*R*)-**D3** in PCHs occurred after irradiation with UV and vis light.

In the case of the N*-LCs induced by (*R*)-**D4** and (*R*)-**D5** in PCH, the helical pitch length of the finger-printed textures increased after irradiation with UV light, as shown in Figure 4c. Similar behaviors were observed in the N*-LCs induced by (*R*)-**D1**−(*R*)-**D3** and (*S*)-**D1** in 5CB. These results imply that the dihedral angle between the two naphthyl rings slightly changed in conjunction with the photoisomerization of the dithienylethene moiety.

2.5. Changes in Helical Twisting Powers. The helical pitch and the helical twisting power (β_M) of N*-LC were determined using the Grandjean−Cano method and the droplet method in glycerol,[20] respectively. The β_M is defined as $\beta_M = 1/(pcr)$, where p is the helical pitch and c is the molar concentration of the chiral dopant, and r is the enantiomeric purity of the chiral dopant. Here, r is assumed to be 1.[21] Positive and negative signs represent a right-handed (clockwise) and a left-handed (counterclockwise) screw sense, respectively. Table 1 summarizes the helical screw senses and helical twisting powers (β_M) of the photoresponsive chiral compounds, (*R*)-**D1**−(*R*)-**D5** and (*S*)-**D1** in PCH and 5CB. The β_M increased with an increase of the length of the alkoxy groups in the binaphthyl moiety [(*R*)-**D1**−(*R*)-**D5**], but the increase in β_M decreased the change ($\Delta\beta_M$) in β_M between the open form and PSS of the dithienylethene moiety. The β_M's of (*R*)-**D1** (open form) and (*R*)-**D1** (PSS), which have opposite screw senses to each other in PCHs, were +6.6 and −8.3 μm^{-1}, respectively. The $\Delta\beta_M$ of (*R*)-**D1** after the photoisomerization of the dithienylethene moiety in PCH was 14.9 μm^{-1}. The β_M's of (*R*)-**D2** and (*R*)-**D3** that had undergone photoinduced phase transitions between N*-LC and N-LC in PCH were 11.7 and 12.7 μm^{-1}, respectively. The $\Delta\beta_M$'s of (*R*)-**D4** and (*R*)-**D5** in PCH slightly changed by 1.9−2.4 μm^{-1} after irradiation with UV and vis light. On the other hand, the N*-LCs prepared by using 5CB as an N-LC host showed no helical inversion but only a slight change or no change in helical pitch. The $\Delta\beta_M$'s of (*R*)-**D1** and (*S*)-**D1** in 5CB changed by 5.6−5.9 μm^{-1}, and those of (*R*)-**D2** and (*R*)-**D3** in 5CB slightly changed by 0.6−1.6 μm^{-1} after irradiation with UV and vis light. There is no change in $\Delta\beta_M$ of (*R*)-**D4** and (*R*)-**D5** in 5CB.

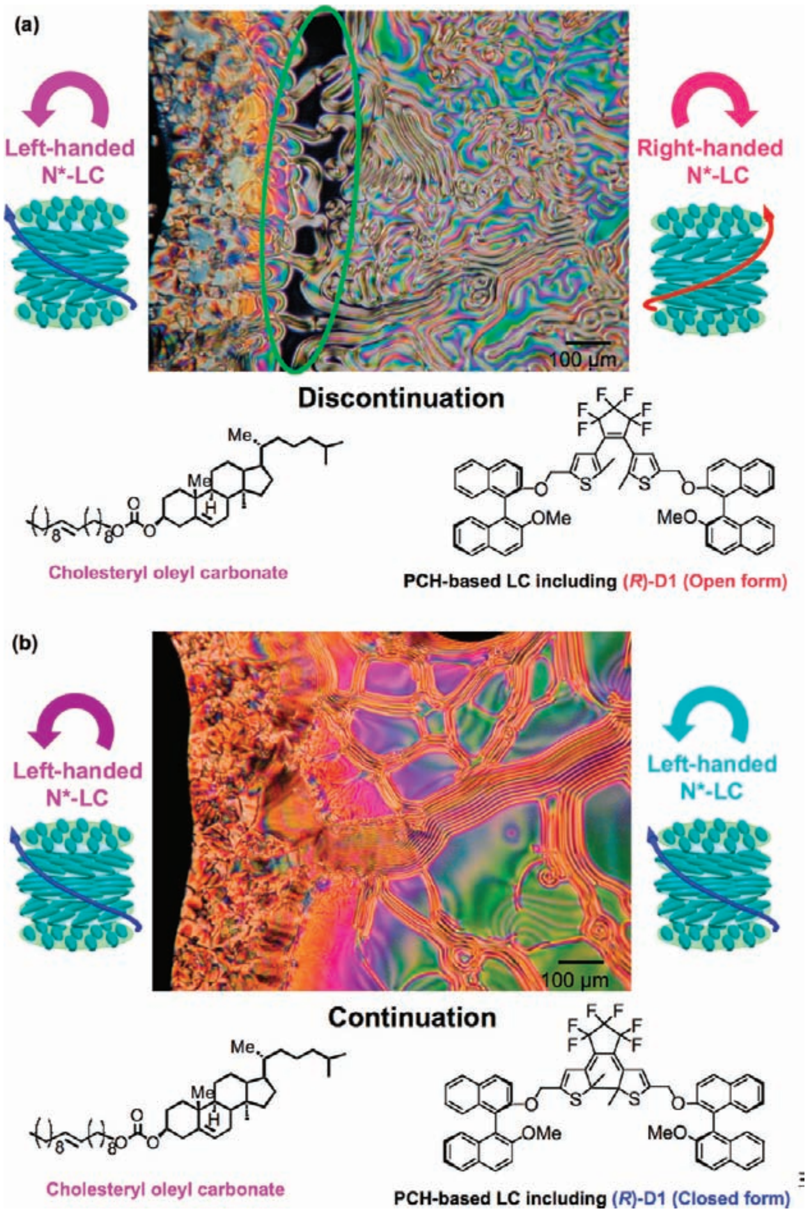


Figure 5. Contact tests between the N*-LC including (a) (*R*)-**D1** (open form) or (b) (*R*)-**D1** (PSS of closed form) and the LC standard, cholesteryl oleyl carbonate with a left-handed screw sense at 30 °C. The N*-LCs are composed of PCH302, PCH304, and (*R*)-**D1** with ratios of 100:100:2.

It is clear from the above results that the helical sense and the helical twisting power of N*-LC sensitively depend on the N-LC host. Actually, there is a notable difference in the behavior of the helical sense and/or the helical twisting power between PCH- and 5CB-based N*-LCs upon the photoisomerization of the chiral dopant. It might be argued that PCH LC molecules tend to align parallel to the naphthyl ring of the chiral dopant, and hence they are sensitively affected by the change of the dihedral angle of the binaphthyl rings (see Figure S7). Meanwhile, it can be assumed that the 5CB LC molecules tend to align parallel to the binaphthyl axis of the chiral dopant, probably due to $\pi-\pi$ interactions between the biphenyl moiety of 5CB molecule and the phenyl—phenyl fragment of the binaphthyl ring of the chiral dopant. Hence, the 5CB LC molecules are not so drastically affected by the change of the dihedral angle of the binaphthyl ring as the case of PCH LC molecules. The above-mentioned arguments, however, are based on only the initial intermolecular interaction between the chiral binaphthyl derivative and the LC molecule. The overall feature including the subsequently occurring arrangement of the rest of LC molecules followed by the construction of the closest packing structure of the N*-LC needs to be clarified by further investigations.

Figure 6 shows the changes in the helical twisting powers of (*R*)-**D1**, (*R*)-**D3**, and (*R*)-**D5** after alternating irradiations with UV and vis light. The reversible helical inversion and the change in helical pitch of N*-LC via the photoisomerization of the dithienylethene moiety upon irradiation with UV and vis light repeated for more than 10 cycles. It is worth mentioning that not only the cycle repeated, but the amplitude of the change remained consistent. The research to achieve the asymmetric polymerizations of helical conjugated polymers in the present N*-LCs is now underway and will be reported somewhere in the near future.

Table 1. Changes of the Helical Screw Senses and the Helical Twisting Powers (β_M) of the Photoresponsive PCH- and CB-Based N*-LCs with the Open Form and PSS, with Positive and Negative Signs Representing Right-Handed (Clockwise) and Left-Handed (Counterclockwise) Screw Senses,[a] Respectively

	helical twisting powers, β_M (μm^{-1}),[b] in PCHs[c]			helical twisting powers, β_M (μm^{-1}),[b] in 5CB[d]		
chiral dopant	open form	PSS	$\lvert\Delta\beta_M$ (μm^{-1})$\rvert$[e]	open form	PSS	$\lvert\Delta\beta_M$ (μm^{-1})$\rvert$[e]
(*R*)-**D1**	+6.6	−8.3	14.9	−2.2	−8.1	5.9
(*S*)-**D1**	−6.9	+7.6	14.5	+2.1	+7.7	5.6
(*R*)-**D2**	+11.7	±1.0	11.7	+6.4	+4.0	1.6
(*R*)-**D3**	+12.7	±1.0	12.7	+9.4	+8.3	0.9
(*R*)-**D4**	+15.5	+13.6	1.9	+12.3	+12.3	0
(*R*)-**D5**	+24.3	+21.9	2.4	+20.0	+20.0	0

[a]Determined with the miscibility test, in which cholesteryl oleyl carbonate (COC) is used as the N*-LC standard. [b]Measured with the Grandjean–Cano method at 30 °C. [c]Composed of PCH302, PCH304, and chiral dopant with the mole ratio of 100:100:2. [d]Composed of 5CB and chiral dopant with the mol ratio of 100:1. [e]Difference in helical twisting power (β_M) between the open form and PSS of dithienylethene moiety.

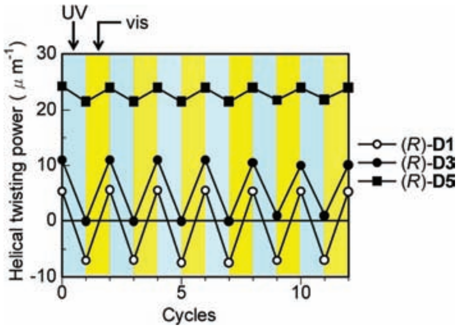


Figure 6. Reversible changes in helical twisting power (β_M) evaluated with the droplet method using glycerol for (*R*)-**D1**, (*R*)-**D3**, and (*R*)-**D5** in PCHs upon alternating irradiations of UV (blue area) and vis (yellow area) lights.

3. CONCLUSION

The photoresponsive chiral dithienylethene derivatives [(*R*)-**D1**–(*R*)-**D5** and (*S*)-**D1**] bearing two axially chiral binaphthyl moieties were synthesized and used as chiral dopants to induce the N*-LCs. The photoisomerization of the dithienylethene moieties after alternate irradiations with UV and vis light caused a reversible change in the dihedral angles of the binaphthyl rings. The photoresponsive binaphthyl derivatives were added as chiral dopants into N-LCs composed of phenylcyclohexyl or cyanobiphenyl mesogen, which induced N*-LCs. Accompanying the photoisomerization, the N*-LCs that included (*R*)-**D1** and (*S*)-**D1** showed a reversible helical inversion in the screw sense. The N*-LCs that included (*R*)-**D2** and (*R*)-**D3** showed a reversible photoswitching in the phase transitions between N*-LC and N-LC. The N*-LCs that included (*R*)-**D4** and (*R*)-**D5** showed a notable change in the helical pitch during the photoisomerization.

(*R*)-**D1** and (*S*)-**D1** are the first chiral dopants to induce a helical inversion in a N*-LC via the photoisomerization between open and closed forms of the dithienylethene moiety. The helical sense and the helical pitch of the N*-LCs that included the photoresponsive binaphthyl derivatives are well controlled and even tuned by changing the length of the alkyl group substituted at the 2-position of the binaphthyl ring. The present photoresponsive LCs, especially the N*-LCs that included (*R*)-**D1**–(*R*)-**D3** and (*S*)-**D1**, should be applicable for advanced optical memory devices with multiple read–write functions and also for helical sense-controllable asymmetric reaction fields.

4. EXPERIMENTAL SECTION

(*R*)-D1. To a mixture of dithienylethene derivative **6** (140 mg, 0.47 mmol), triphenylphosphine (TPP) (135 mg, 0.51 mmol), and (*R*)-**1** (100 mg, 0.23 mmol) in THF (10 mL), was slowly added a solution of diisopropyl azodicarboxylate (DIAD) (260 mg, 40 wt % in toluene, 0.51 mmol) in THF (20 mL) via a pressure equalized dropping funnel. The reaction mixture was stirred at 0 °C overnight under Ar. The resulting precipitate was extracted with $CHCl_3$, thoroughly washed with saturated NaCl solution, and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was purified via column chromatography (silica gel; CH_2Cl_2) to give 122 mg (53%) of compound (*R*)-**D1** as colorless powder. ^1H NMR (270 MHz, $CDCl_3$, 20 °C, TMS): δ = 1.44 (s, 6H, thienyl–CH_3), 3.70 (s, 6H, –OCH_3), 4.98 (s, 4H, –OCH_2–), 6.59 (s, 2H, thienyl–H), 7.05 (d, 1H, *J* = 7.74, Ar–H, 8′), 7.15 (ddd, 1H, *J* = 1.40, 7.54 and 7.74, Ar–H, 7′), 7.16 (d, 1H, *J* = 8.40, Ar–H, 8), 7.22–7.30 (m, 3H, Ar–H, 6, 6′, and 7), 7.37 (d, 1H, *J* = 8.90, Ar–H, 3), 7.41 (d, 1H, *J* = 9.06, Ar–H, 3′), 7.83 (d, 1H, *J* = 7.58, Ar–H, 5′), 7.86 (d, 1H, *J* = 9.22, Ar–H, 5), 7.90 (d, 1H, *J* = 9.06, Ar–H, 4′), 7.96 (d, 1H, *J* = 8.90, Ar–H, 4). FAB-MS: *m*/*z*: calcd for $C_{59}H_{42}O_4F_6S_2$, 992.24; found, 992.24 [M^+]. Anal. Calcd for $C_{24}H_{16}O_3F_6S_2$: C, 71.36; H, 4.26. Found: C, 71.65; H, 4.36.

(*R*)-D2. The procedure for the synthesis of (*R*)-**D1** was followed to prepare (*R*)-**D2** from (*R*)-**2** as a colorless powder in a 25% yield. ^1H NMR (270 MHz, $CDCl_3$, 20 °C, TMS): δ = 1.01 (t, 6H, *J* = 6.90, –OCH_2CH_3), 1.45 (s, 6H, thienyl–CH_3), 4.03 (q, 4H, *J* = 6.90, –OCH_2CH_3), 4.97 (s, 4H, –OCH_2–), 6.57 (s, 2H, thienyl–H), 7.08 (d, 1H, *J* = 6.76, Ar–H, 8′), 7.13 (d, 1H, *J* = 6.76, Ar–H, 7′), 7.15–7.35 (m, 4H, Ar–H, 7, 6, 6′, and 8), 7.37 (d, 1H, *J* = 11.1, Ar–H, 3), 7.41 (d, 1H, *J* = 11.1, Ar–H, 3′), 7.83 (d, 1H, *J* = 9.15, Ar–H, 5′), 7.86 (d, 1H, *J* = 9.15, Ar–H, 5), 7.89 (d, 1H, *J* = 11.1, Ar–H, 4′), 7.93 (d, 1H, *J* = 11.1, Ar–H, 4). FAB-MS *m*/*z*: calcd for $C_{61}H_{46}O_4F_6S_2$, 1020.27; found, 1020.27 [M^+]. Anal. Calcd for $C_{61}H_{46}O_4F_6S_2$: C, 71.75; H, 4.54. Found: C, 71.33; H, 5.24.

(*R*)-D3. The procedure for the synthesis of (*R*)-**D1** was followed to prepare (*R*)-**D3** from (*R*)-**3** as a colorless powder in a 24% yield. ^1H NMR (400 MHz, $CDCl_3$, 20 °C, TMS): δ = 0.52 (t, 6H, *J* = 7.24, –CH_2CH_3), 1.25 (m, 4H, –$CH_2CH_2CH_3$), 1.44 (s, 6H, thienyl–CH_3), 3.90–3.95 (m, 4H, –$OCH_2C_3H_7$), 5.00 (m, 4H, –OCH_2–), 6.64 (m, 2H, thienyl–H), 6.94 (d, 1H, *J* = 6.76, Ar–H, 8′), 7.13 (d, 1H, *J* = 6.76, Ar–H, 7′), 7.15–7.35 (m, 4H, Ar–H, 7, 6, 6′, and 8), 7.37 (d, 1H, *J* = 11.1, Ar–H, 3), 7.41 (d, 1H, *J* = 11.0, Ar–H, 3′), 7.83 (d, 1H, *J* = 9.15, Ar–H, 5′), 7.86 (d, 1H, *J* = 9.15, Ar–H, 5), 7.89 (d, 1H, *J* = 11.0, Ar–H, 4′), 7.93 (d, 1H, *J* = 11.1, Ar–H, 4). FAB-MS *m*/*z*: calcd for $C_{63}H_{50}O_4F_6S_2$, 1048.31; found, 1048.30 [M^+].

(*R*)-D4. The procedure for the synthesis of (*R*)-**D1** was followed to prepare (*R*)-**D4** from (*R*)-**4** as a colorless powder in a 59% yield. ^1H NMR (270 MHz, $CDCl_3$, 20 °C, TMS): δ = 0.59 (t, 6H, *J* = 7.24, –CH_2CH_3), 0.98 (m, 4H, –$CH_2CH_2CH_3$), 1.36 (m, 4H, –$CH_2C_2H_5$), 1.45 (s, 6H, thienyl–CH_3), 3.91–3.97 (m, 4H, –$OCH_2C_3H_7$), 4.97 (s, 4H, –OCH_2–), 6.57 (s, 2H, thienyl–H), 7.08 (d, 1H, *J* = 6.76, Ar–H, 8′), 7.13 (d, 1H, *J* = 6.76, Ar–H, 7′), 7.15–7.35 (m, 4H, Ar–H, 7, 6, 6′, and 8), 7.37 (d, 1H, *J* = 11.1, Ar–H, 3), 7.41 (d, 1H, *J* = 11.0, Ar–H, 3′), 7.83 (d, 1H, *J* = 9.15, Ar–H, 5′), 7.86 (d, 1H, *J* = 9.15, Ar–H, 5), 7.89 (d, 1H, *J* = 11.0, Ar–H, 4′), 7.93 (d, 1H, *J* = 11.1, Ar–H, 4). FAB-MS *m*/*z*: calcd for $C_{65}H_{55}O_4F_6S_2$, 1077.34; found, 1077.35 [M + H]. Anal. Calcd for $C_{65}H_{54}O_4F_6S_2$: C, 72.47; H, 5.05. Found: C, 72.38; H, 5.48.

(*R*)-D5. The procedure for the synthesis of (*R*)-**D1** was followed to prepare (*R*)-**D5** from (*R*)-**5** as a colorless powder in a 52% yield. ^1H NMR (270 MHz, $CDCl_3$, 20 °C, TMS): δ = 0.61 (t, 6H, *J* = 7.32, –CH_2CH_3), 0.85–0.98 (m, 8H, –$CH_2C_2H_4CH_3$), 1.38 (q, 4H,

J = 7.32, $-CH_2C_3H_7$), 1.44 (s, 6H, thienyl$-CH_3$), 3.84−4.00 (m, 4H, $-OCH_2C_4H_9$), 4.97 (s, 4H, $-OCH_2-$), 6.57 (s, 2H, thienyl−H), 7.08 (d, 1H, J = 6.76, Ar−H, 8′), 7.13 (d, 1H, J = 6.76, Ar−H, 7′), 7.15−7.35 (m, 4H, Ar−H, 7, 6, 6′, and 8), 7.37 (d, 1H, J = 9.76, Ar−H, 3), 7.41 (d, 1H, J = 8.54, Ar−H, 3′), 7.83 (d, 1H, J = 8.54, Ar−H, 5′), 7.86 (d, 1H, J = 8.53, Ar−H, 5), 7.89 (d, 1H, J = 8.54, Ar−H, 4′), 7.93 (d, 1H, J = 9.76, Ar−H, 4). FAB-MS m/z: calcd for $C_{67}H_{58}O_4F_6S_2$, 1104.37; found, 1104.37 [M^+]. Anal. Calcd for $C_{67}H_{58}O_4F_6S_2$: C, 72.81; H, 5.29. Found: C, 71.88; H, 5.40.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details for synthetic procedures of (*R*)-**D1**−(*R*)-**D5**. ^{1}H and ^{13}C NMR, UV−vis, and CD spectra of (*R*)-**D1**, (*R*)-**D3**, and (*R*)-**D5**. Schematic illustrations of reversible helical inversion. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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