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Synthesis and Characterization of Thermally Irreversible Photochromic Cholesteric Liquid Crystals

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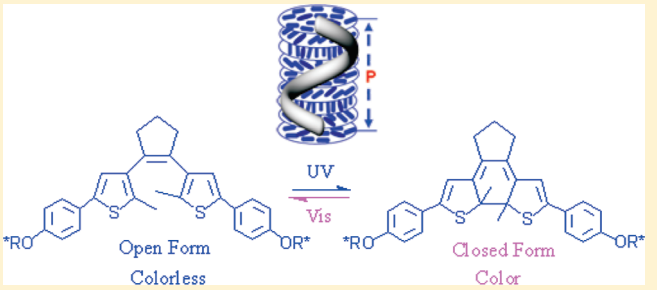
ABSTRACT: Three thermally irreversible photochromic chiral liquid crystal dithienylcyclopentenes were found not only to be able to self-organize into a phototunable helical superstructure, i.e., cholesteric phase, but also to be able to induce a photoresponsive helical superstructure in an achiral liquid crystal host. The cholesteric phase in the three chiral compounds went into a glassy phase without crystallization upon cooling. All the materials exhibited reversible photochromism with thermal stability in both solution and thin film, and their fluorescence was shifted to longer wavelength upon UV irradiation while the shifted fluorescence was recovered upon visible light irradiation. The enhanced fluorescence emission with the addition of fluoride anions was observed, and its reverse process happened with the addition of an equivalent proton.



INTRODUCTION

Photochromic molecules, that change color upon light irradiation, have attracted great attention due to their potential applications as light-driven molecular switches and devices.[1] Among all the photochromic molecules that have been reported to date, dithienylcyclopentenes hold particular promise because of their unique fatigue resistance, thermal irreversibility, and electrical conductivity.[2] Colorless open-ring dithienylcyclopentene can be transformed into the colored closed-ring form upon UV irradiation, whereas its reverse process occurs photochemically with visible light. Since the physical and chemical properties of the two forms are different, the optically reversible switching has been the basis for creating new functional materials with applications in photonics, information storage, fluorescent photoswitches, sensors, etc.[3]

It is also known that cholesteric liquid crystal (LC) can self-organize into a unique helical superstructure that reflects 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. If the material is photoresponsive, its helical structure can be optically tunable. This provides opportunities as well as challenges that are opening the door to applications such as chiral nematic photo displays that require no electronic drive and circuit.[4] Currently nonmesogenic chiral dithienylcyclopentenes have been employed as dopants in achiral LC media to form the helical superstructure,[5] and some achiral photochromic LC diarylethenes have been reported.[6] However, only minor attention has been paid to the developments of chiral LC dithienylcyclopentenes.[7] Here, we report the synthesis of three photochromic chiral LCs **7a**−**c** by covalently linking one photochromic dithienylcyclopentene moiety and two well-known mesogenic cholesteryl groups via flexible spacers of varying length (Scheme 1). To the best of our knowledge, these are the first nonfluorinated chiral LC dithienylcyclopentenes to be synthesized. The interest behind the design of the new photochromic chiral LCs with a mesogenic cholesteryl group mainly results from its rigid, long shape, chiral structure, and distinct optical property. The rigid, long shape of the cholesteryl group can induce anisotropic intermolecular interaction via van der Waals forces which can stabilize parallel molecular stacking, whereas its chiral structure can induce chirality in molecular order, i.e., helical superstructure. Meanwhile, introducing an alkylene linker helps to obtain a stable mesophase.[8]

RESULTS AND DISCUSSION

Compounds **7a**−**c** were thermally and chemically stable, and exhibited the expected reversible photochromic behavior. For example, a solution of **7a** in $CHCl_3$ is colorless where there is no absorption in the visible region, corresponding to the open-ring **7a**. Irradiation of this solution with UV light at 310 nm results in a clean photoisomerization to the closed-ring form, as evidenced by a decrease in the absorbance at 280 nm with a slight red shift to 300 nm and the appearance of new broad absorption bands at the visible region (Figure 1). The isosbestic point at 328 nm appears to indicate the change in structural isomers. Upon UV irradiation, the original colorless solution of **7a** changed from purple to green (Figure 2). The open-ring **7a** is colorless, whereas its

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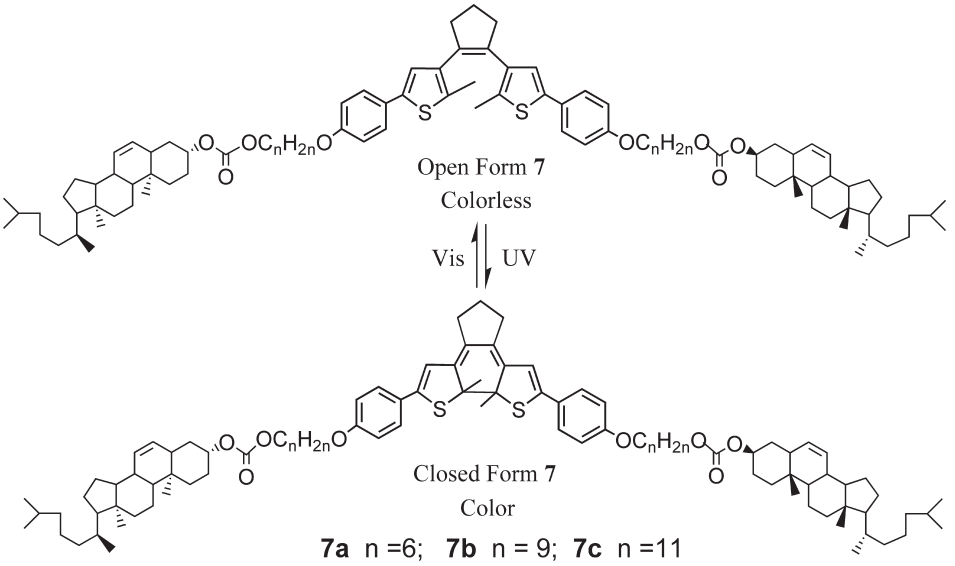
Scheme 1. Light-Driven Open-Ring and Closed-Ring Isomerization of the Photochromic LCs 7a−c



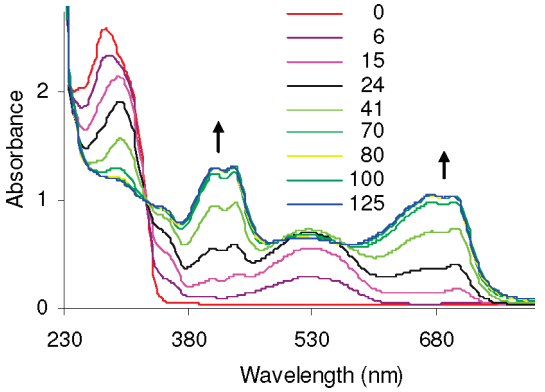


Figure 1. UV−vis spectra of **7a** (50 μM) in $CHCl_3$ at room temperature upon UV irradiation at 310 nm with different times (seconds).

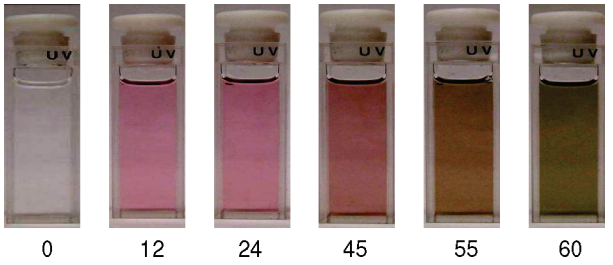


Figure 2. Photographic images of **7a** (50 μM) in $CHCl_3$ upon UV irradiation at 310 nm with different times (second). Note: the reverse process of color change occurred upon visible light at 670 nm.

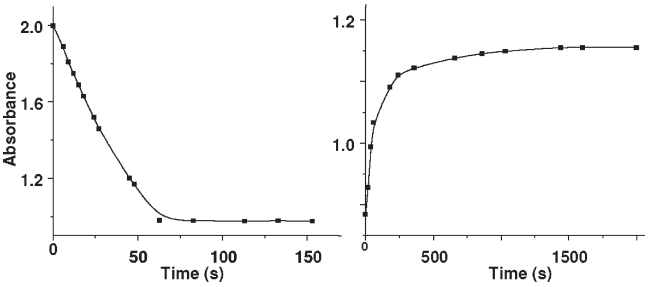


Figure 3. Absorbance at 280 nm of **7a** (50 μM) in $CHCl_3$ at room temperature upon UV irradiation at 310 nm (left, 30 mW/cm^2)) and visible light at 670 nm (right, 11 mW/cm^2) with different times.

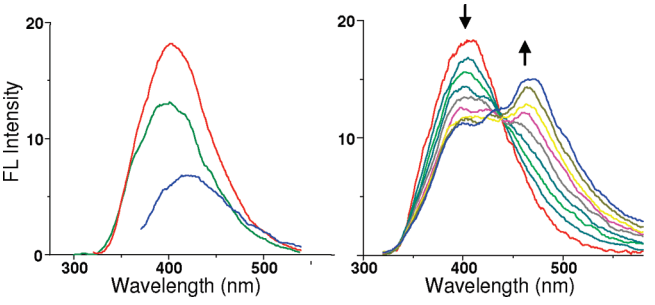


Figure 4. Fluorescence emission spectra of **7a** (50 μM) in $CHCl_3$ by different excitation wavelengths (left) at 280 nm (blue), 300 nm (red), and 350 nm (green) and by the excitation wavelength at 300 nm and under irradiation at 310 nm with every 3 s interval from red line to blue line.

closed-ring isomer is colored, which is attributed to the closed-ring form having a larger π-conjugation than its open-ring form. The photostationary state of the open-ring **7a** to its closed-ring isomer was reached within approximately 80 s under UV irradiation at 310 nm, whereas its reverse process to the open-ring form upon visible light irradiation at 670 nm takes approximately 600 s (Figure 3). The cycle was repeated many times without fatigue.

The solution of **7a** in $CHCl_3$ was excited with different wavelengths at 280, 300, and 350 nm, respectively. As seen from Figure 4, left, there was strong fluorescence emission if excited at 300 nm. Interestingly, the emission peak of the open isomer

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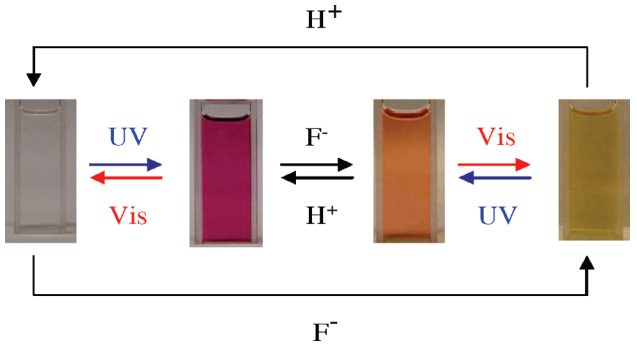


Figure 5. Photographic images of the reversible photoswitchable effect on the open and closed form of **7a** in THF under light irradiation, fluoride anions, and protons. Open-ring form solution: colorless.

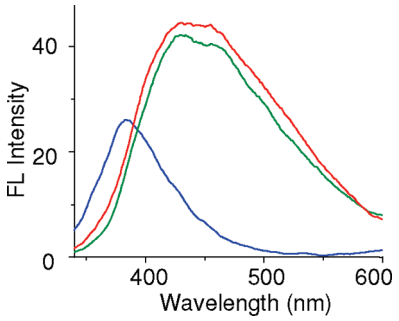


Figure 6. Fluorescence emission spectra of **7a** (50 μM) in THF excited at 310 nm. Open form, blue; open form with F^- anion, green; closed form with F^- anion, red.

Table 1. Phase Transition Temperatures (°C)[a] and Associated Enthalpies (J/g) of 7a−c

compd	heating	cooling
7a	G 66.1 (0.4) N* 123.0 (1.4) I	I 111.6 (1.8) N* 65 G
7b	G 53.8 (0.3) N* 106.8 (1.2) I	I 104.4 (1.2) N* 52 G
7c	G 67b N* 100.6 (1.4) I	I 97.9 (1.7) N* 63 G

[a] Peak temperatures in the DSC thermograms obtained during the second heating and cooling cycles at a rate of 20 °C/min; I = isotropic liquid; N* = cholesteric phase; G = glassy phase.

observed at 405 nm (excited at 300 nm) was shifted upon UV light irradiation at 310 nm and accompanied with the appearance of a new band at 468 nm (Figure 4, right).

The interaction of **7a** with F^- anions was investigated in THF solution through titration experiment. The colorless solution of **7a** in THF corresponding to the open-ring form was turned into yellow with the addition of an equivalent F^- anion (TBAF) and changed into red orange color upon UV irradiation at 310 nm, indicating the closed form with F^- (Figure 5). The broad fluorescence emission peak of open-ring **7a**, with F^- anions, increased in intensity and exhibited a red shift, whereas the reverse process happened with the addition of an equivalent proton. With UV irradiation at 310 nm, the intensity of the emission peak increased (Figure 6). This enhanced fluorescence with addition of F^- anions might result from a charge/energy transfer with F^- anions in both open- and closed-ring forms.[9]

The phase behavior of open-ring **7a−c** was investigated using differential scanning calorimetry (DSC) and crossed polarizing

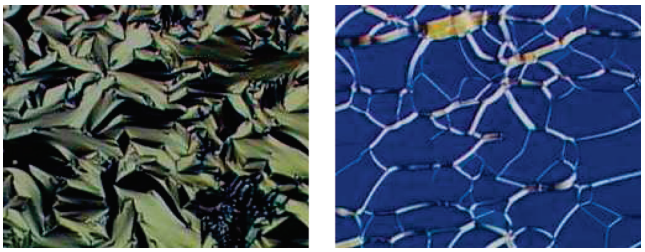


Figure 7. Crossed polarized optical texture micrograph of **7a** showing the focal conic (left) and oily (right) textures at 121 °C. Note: the oily streak texture was obtained on applying mechanical stress to the focal conic texture.

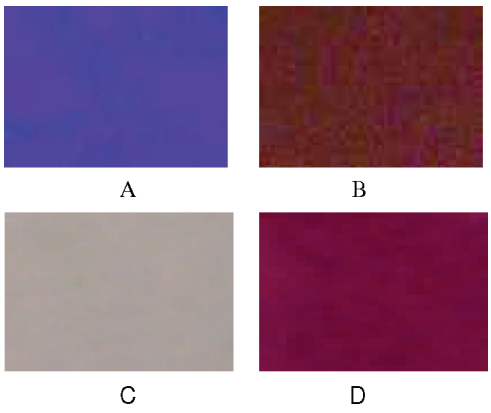


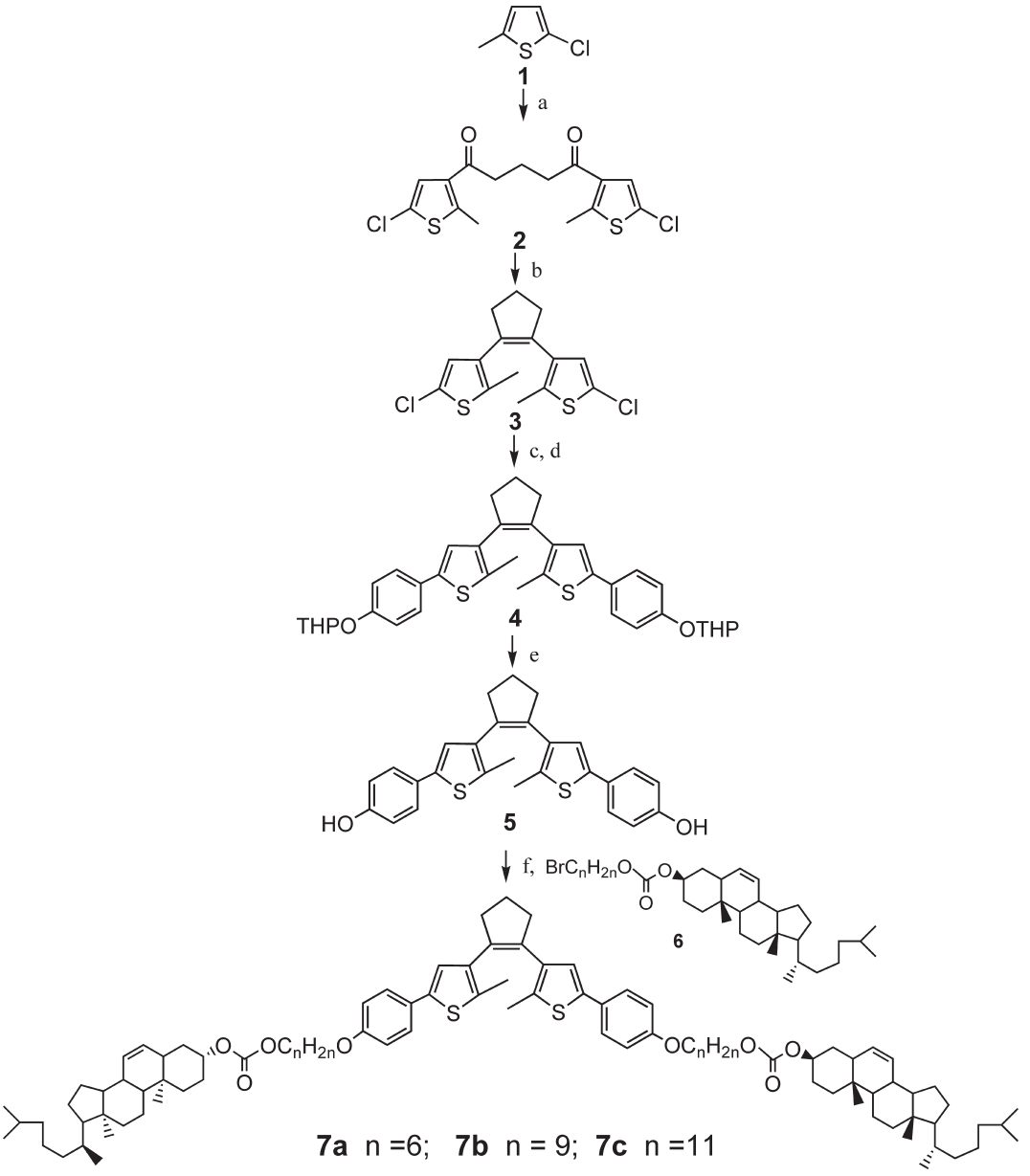
Figure 8. Crossed polarized optical texture micrograph of **7a** in a 5 μm thick planar cell after supercooling to room temperature: (A) before UV irradiation; (B) after UV irradiation at 310 nm for 5 min. Note: parts C and D are the images corresponding to A and B without polarizer.

microscope (POM) equipped with a temperature controller. The results show that all the photochromic compounds **7a**, **7b**, and **7c** have chiral nematic phases with a broad temperature range (Table 1), as evidenced by the typical oily streak texture (Figure 7, right).[10] Interestingly, the target compound **7a** exhibited the pseudofocal conic texture of chiral nematic phases. However, on applying slight mechanical shearing, it transformed to typical oily streak texture at 121 °C (Figure 7). It is worth noting here that the materials **7a−c** went into photochromic glassy LCs upon fast cooling from a chiral nematic phase without traces of crystallization on DSC, which is important for preparing self-organized solid thin film without grain boundaries with potential application in optoelectronics.[11] Figure 8A and B shows the reversible photochromic glassy thin film at room temperature with crossed polarizing microscope. Without the polarizer, the thin film of open-ring **7a** was observed to be colorless, as shown in Figure 8C, and was changed into a violet red colored thin film upon UV irradiation at 310 nm (Figure 8D). The pink colored thin film was returned to colorless upon visible light irradiation at 670 nm. Both colorless and colored thin films are thermally stable.

As expected, doping them in an achiral nematic LC host can induce a helical superstructure. For example, 10 wt % **7a** as a mesogenic dopant in a conventional achiral nematic 4-pentyl-4′-biphenylcarbonitrile (5CB) exhibited a cholesteric polygonal fingerprint texture, as shown in Figure 9, left. The liquid crystal to isotropic transition temperature for the doped 5CB is 42 °C. With UV irradiation at 310 nm (30 mW/cm^2) for 30 s, the

Figure 9. Crossed polarized optical texture micrograph of 10 wt % of **7a** in a nematic LC host 5CB at 40 °C before UV irradiation (left), after UV irradiation at 310 nm for 30 s (middle), and followed by visible light at 670 nm for 60 s (right).

Scheme 2. Synthesis of the Target Chiral Liquid Crystals 7[a]



[a] a: Glutaryl dichloride, $AlCl_3$, CS_2; b: $TiCl_3(THF)_3$, Zn, THF; c: *n*-BuLi, $B(OBu)_3$, THF; d: $Pd(PPh_3)_4$, Na_2CO_3, THF, 2-(4-iodo-phenoxy) tetrahydropyran; e: pyridinium *p*-toluenesulphonate (PPTS), CH_3OH; f: **6**, K_2CO_3, anhydrous acetone.

sample went into the isotropic phase (Figure 9 middle), whereas upon visible irradiation at 670 nm a reverse process was observed, as evidenced by the formation of the chiral nematic domain from the isotropic phase appearing as droplet nucleation followed by

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coalescence (Figure 9, right).[12] Its reverse process upon visible light irradiation was reached within 30 min.

CONCLUSION

Three photochromic cholesteric liquid crystals containing one dithienylcyclopentene moiety and two well-known mesogenic cholesteryl groups via flexible carbonyldioxyalkoxy spacers of different length, the first of their kind, were synthesized, which were found to be able to self-organize into a phototunable helical superstructure. DSC and POM studies revealed that the chiral nematic phase upon cooling went into a glassy phase without crystallization. Their reversible photochromism with thermal stability was observed in both solution and thin film, and their fluorescence emission wavelength was shifted upon UV irradiation, whereas the behavior in the shifted fluorescence was recovered upon visible light irradiation. The enhanced fluorescence was observed with the addition of fluoride anions. The reverse process happened with the addition of an equivalent proton. Furthermore, these photochromic materials as mesogenic dopants in a nematic host have a superior solubility and can induce mesophase chirality.

EXPERIMENTAL SECTION

Materials and Methods. All chemicals and solvents were used without further purification. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. Chemical shifts are in δ units (ppm) with the residual solvent peak as an internal standard. The coupling constant (J) is reported in hertz (Hz). NMR splitting signals are designated as s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60−200 mesh). Analytical TLC was performed on commercially coated 60 mesh F254 glass plates. Spots were rendered visible by exposing the plate to UV light. Elemental analysis was performed from Robertson Microlit Laboratories, Inc. The optical textures and transition temperatures were observed by optical microscopy using a Leitz polarizing microscope linked with a Linkam TMS temperature controller. Calorimetric measurements were performed in a Perkin-Elmer differential scanning calorimeter (DSC) using indium and zinc as standards for calibration. UV−visible spectra were recorded from a Perkin-Elmer Lambda spectrophotometer from 200 to 800 nm. Fluorescence measurements were performed from a Varian Cary Eclipse fluorescence spectrophotometer controlled with a slit excitation of 5 nm and scan ranges from 300 to 600 nm. The light irradiation studies were carried out by a high-pressure 100 W xenon lamp (Asahi spectra co Ltd., Japan) with a mirror module of UV and a visible range of 300−400 and 400−700 nm with respective cutoff filters.

Synthesis. The photochromic compounds **7a**−**c** were synthesized starting from 2-methylthiophene, as shown in Scheme 2.[13] Their structures were identified by ^{1}H NMR, ^{13}C NMR, and elemental anaylsis.

*1,5-Bis(5-chloro-2-methylthiene-3-yl)pentane-1,5-dione (**2**).* To a mixture of 2-chloro-5-methylthiophene (**1**) (10.60 g, 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, the 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 and dried over Na_2SO_4, 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 **2** (5.30 g, 50%). ^{1}H NMR ($CDCl_3$): 1.83−1.90 (m, 2H), 2.47 (s, 6H), 2.67 (t, J = 5.2 Hz, 3H), 7.00 (s, 2H). ^{13}C NMR ($CDCl_3$): 14.9, 17.0, 39.4, 124.1, 125.6, 133.7, 146.5, 193.6.

*1,2-Bis(2-methylthien-3-yl)cyclopentene (**3**).* A mixture of **2** (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 a 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 **1c** (0.65 g, 40%). mp 75−77 °C. ^{1}H NMR ($CDCl_3$): 1.85 (s, 6H), 1.98−2.1 (m, 2H), 2.68 (t, J = 7.3 Hz, 4H), 6.50 (s, 2H). ^{13}C NMR ($CDCl_3$): 14.1, 22.9, 38.3, 125.1, 126.6, 133.2, 134.4, 134.7.

*1,2-Bis(5′-hydroxyphenyl-2′-methylthien-3′-yl)cyclopentene (**5**).* A solution of *n*-BuLi (2.5 M, 6.5 mL) in hexane solution was added dropwise to a stirred solution of **3** (1.0 g, 3 mmol) in anhydrous THF (20 mL) at −78 °C under a nitrogen atmosphere. Then, the solution was stirred at ambient temperature for 30 min. $B(OBu)_3$ (3 mL, 10 mmol) was added dropwise to the reaction mixture in one portion, stirred for 1 h at ambient temperature, and used for further reaction without any workup. A mixture of 2-(4-iodo-phenoxy)tetrahydropyran (1.6 g, 5.3 mmol) and $Pd(PPh_3)_4$ (0.3 mg, 0.2 mmol) in THF (10 mL) was added to the above reaction mixture, and the resulting solution was stirred for 15 min at ambient temperature. Then, aqueous Na_2CO_3 (15 mL) and six drops of ethylene glycol were added. The reaction mixture was refluxed for 2 h and cooled to ambient temperature and extracted with ether (50 mL), washed with water (50 mL), dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to give a crude product **4**. The crude product (3.67 g) and PPTS (10 wt %, 175 mg) were dissolved in methanol (30 mL) and methylene chloride (5 mL). The reaction mixture was stirred overnight at ambient temperature. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to obtain **5** as a yellow viscous liquid (2.0 g). ^{1}H NMR ($CDCl_3$): 1.80−2.05 (m, 8H), 2.82 (t, 4H, J = 7.3 Hz), 6.85 (s, 2H), 6.95 (d, 4H, J = 7.4 Hz), 7.30 (d, 4H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 14.4, 23.0, 38.5, 115.7, 123.0, 126.8, 127.6, 133.4, 134.6, 136.6, 138.4, 154.9.

*Bromoalkyl Cholesteryl Ester (**6**).* To a mixture of bromoalcohol (3.2 mmol) and pyridine (0.3 mL, 3.2 mmol) in benzene (20 mL) was added a solution of cholesterol chloroformate (1.35 g, 3.0 mmol) in benzene. The reaction mixture was refluxed for 1 h. The resulting precipitated salt was removed by filtration, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography to give a white solid which was recrystallized in toluene and petroleum ether to afford ester **6**.

Data for **6a** (n = 6): Yield 65%. ^{1}H NMR ($CDCl_3$): 0.67 (s, 3H) 0.84−2.07 (m, 38H), 2.28 (m, 2H), 3.40 (t, 2H, J = 6.8 Hz), 4.11 (t, 2H, J = 6.5 Hz), 4.55 (m, 1H), 5.40 (s, 1H). ^{13}C NMR($CDCl_3$): 11.8, 18.7, 19.2, 21.0, 22.5, 22.83, 23.8, 24.2, 25.7, 27.7, 28.0, 28.1, 28.7, 29.2, 29.4, 31.8, 32.8, 34.0, 35.7, 36.1, 36.5, 36.8, 38.0, 39.5, 39.7, 42.3, 49.9, 56.1, 56.6, 67.8, 122.8, 139.3, 154.6.

Data for **6b** (n = 9): Yield 75%. ^{1}H NMR ($CDCl_3$): 0.67 (s, 3H), 0.84−2.04 (m, 38H), 2.38 (m, 2H), 3.40 (t, 2H, J = 7.0 Hz), 4.11 (t, 2H, J = 6.6 Hz), 4.46 (m, 1H), 5.40 (s, 1H). ^{13}C NMR ($CDCl_3$): 11.3, 18.2, 18.7, 20.5, 22.0, 22.3, 23.4, 23.7, 25.2, 27.2, 27.5, 27.6, 27.7, 28.1, 28.6, 28.7, 31.3, 32.3, 33.4, 35.2, 35.6, 36.0, 36.3, 37.5, 39.0, 39.2, 41.8, 49.5, 55.6, 56.1, 67.3, 122.3, 138.9, 154.1.

Data for **6c** (n = 11): Yield 81%. ^{1}H NMR ($CDCl_3$): 0.67 (s, 3H), 0.84−2.04 (m, 38H), 2.41 (m, 2H), 3.41 (t, 2H, J = 6.8 Hz), 4.10 (t, 2H, J = 6.8 Hz), 4.40 (m, 1H), 5.40 (s, 1H). ^{13}C NMR ($CDCl_3$): 11.8 18.7 19.2, 21.0, 22.5, 22.8, 23.8, 24.2, 25.7, 27.7, 28.0, 28.1, 28.6, 28.7, 29.2, 29.4, 31.8, 32.8, 34.0, 35.7, 36.1, 36.5, 36.8, 38.0, 39.5, 39.7, 42.3, 49.9, 56.1, 56.6, 67.8, 122.8, 139.3, 154.6.

Target Compounds ***7a*****−****c**. A mixture of **5** (0.11 g, 0.25 mmol) and potassium carbonate (0.10 g, 0.65 mmol) in anhydrous acetone (20 mL) was stirred for 10 min and was refluxed slowly. The solution of bromoalkyl cholesteryl ester **6** (0.55 mmol) in acetone was added dropwise to the above reaction mixture. The reaction was monitored by TLC. After completion, it was extracted with dichloromethane (40 mL), washed with water (50 mL), dried over sodium sulfate, and filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography with 10% ethyl acetate in hexane to obtain the white powders which were recrystallized twice with methylene chloride−ethanol to afford the target compound **7**.

Data for **7a** (n = 6): ^{1}H NMR ($CDCl_3$): 0.55−1.93 (m, 72H), 2.29 (d, 4H, J = 7.9 Hz), 2.83 (t, 4H, J = 7.0 Hz), 3.95 (t, 4H, J = 6.19 Hz), 4.13 (t, 4H, J = 6.6 Hz), 4.37 (m, 2H), 5.4 (s, 2H), 6.82 (t, 6H, J = 8.4 Hz), 7.38 (d, 4H, J = 8.6 Hz). ^{13}C NMR ($CDCl_3$): 11.8, 14.36, 18.72, 19.27, 21.0, 22.5, 22.8, 23.8, 24.2, 25.5, 25.7, 27.7, 28.0, 28.2, 28.6, 29.1, 31.8, 35.7, 36.1, 36.5, 36.8, 38.0, 38.4, 39.5, 39.7, 42.3, 49.9, 56.1, 56.6, 67.6, 67.8, 114.7, 122.8, 126.5, 127.3, 133.3, 134.4, 136.4, 139.3, 139.4, 154.6, 158.2. Anal. Calcd for $C_{96}H_{140}O_8S_2$: C, 77.30; H, 9.22; S, 4.12. Found: C, 77.58; H, 9.49; S, 4.31.

Data for **7b** (n = 9): ^{1}H NMR ($CDCl_3$): 0.68−2.10 (m, 99H), 2.41 (d, 4H, J = 6.0 Hz), 2.83 (t, 4H, J = 8.0 Hz), 3.95 (d, 4H, J = 6.0 Hz), 4.12 (t, 4H, J = 6.4 Hz)), 4.47 (m, 2H), 5.40 (s, 2H), 6.88 (t, 6H, J = 7.4 Hz), 7.42 (d, 4H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 11.8, 14.36, 18.71, 19.27, 21.0, 22.5, 22.8, 23.8, 24.2, 25.7, 26.0, 27.7, 28.0, 28.2, 28.6, 29.1, 29.2, 29.3, 31.8, 35.7, 36.1, 36.5, 36.8, 38.0, 38.4, 39.5, 39.7, 42.3, 49.9, 56.1, 56.6, 67.8, 68.0, 114.7, 122.8, 126.4, 127.2, 133.3, 134.4, 136.4, 139.3, 139.5, 154.6, 158.3. Anal. Calcd for $C_{102}H_{152}O_8S_2$: C, 77.79; H, 9.68; S, 4.02. Found: C, 78.01; H, 9.76; S, 4.08.

Data for **7c** (n = 11): ^{1}H NMR ($CDCl_3$): 0.66−2.02 (m, 123H), 2.41 (d, 4H, J = 6.0 Hz), 2.82 (t, 4H, J = 8.0 Hz), 3.97 (d, 4H, J = 6.0 Hz), 4.12 (t, 4H, J = 6.4 Hz), 4.46 (m, 2H), 5.39 (s, 2H), 6.87 (t, 6H, J = 7.4 Hz), 7.42 (d, 4H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): 11.8, 14.36, 18.71, 19.2, 21.0, 22.56, 22.82, 24.28, 25.7, 26.0, 27.7, 28.0, 28.2, 28.6, 29.2, 29.3, 29.4, 31.84, 35.7, 36.1, 36.5, 36.8, 38.0, 38.4, 39.5, 39.7, 42.3, 49.9, 56.1, 67.8, 68.0, 114.7, 122.8, 126.4, 122.2, 133.2, 134.4, 136.4, 139.3, 139.5, 154.6, 158.3. Anal. Calcd for $C_{106}H_{160}O_8S_2$: C, 78.12; H, 9.81; S, 3.90. Found: C, 78.27; H, 9.91; S, 3.94.

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REFERENCES

(1) (a) *Photochromism: Molecules and Systems*; Dürr, H, Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, The Netherlands, 1990. (b) *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, Germany, 2001. (c) Lemieux, V.; Gauthier, S.; Branda, N. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6820–6824. (d) Dulic, D.; Kudernac, T.; Puzys, A.; Feringa, B. L.; Van Wees, B. J. *Adv. Mater.* **2007**, *19*, 2898–2902. (e) Jin, L.; Li, Y.; Ma, J.; Li, Q. *Org. Lett.* **2010**, *12*, 3552–3555.

(2) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716. (b) Irie, M.; Kobatake, S.; Horichi, M. *Science* **2001**, *291*, 1769–1772. (c) Shibata, K.; Muto, K.; Kobatake, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 209–214. (d) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85–97. (e) Higashiguchi, K.; Matsuda, K.; Tanifuji, N.; Irie, M. *J. Am. Chem. Soc.* **2005**, *127*, 8922–8923. (f) Tian, H.; Wang, S. *Chem. Commun.* **2007**, 781–792.

(3) (a) Leimieux, V.; Spantulescu, M. D.; Baldridge, K. K.; Branda, N. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5034–5037. (b) Zhu, Y.; Yi, T.; Xiao, S.; Li, F.; Li, C.; Gao, X.; Wu, J.; Yu, M.; Huang, C. *J. Am. Chem. Soc.* **2008**, *130*, 15750–15751. (c) Jiang, G.; Wang, S.; Yuan, W.; Jiang, L.; Song, Y.; Tian, H.; Zhu, D. *Chem. Mater.* **2006**, *18*, 2335–2337. (d) Hayasaka, H.; Tamura, K.; Akagi, K. *Macromolecules* **2008**, *41*, 2341–2346.

(4) (a) Li, Q.; Green, L.; Venkataraman, N.; Shiyanovskaya, I.; Asad, Khan.; Urbas, A.; Doane, J .W. *J. Am. Chem. Soc.* **2007**, *129*, 12908–12909. (b) Ma, J.; Li, Y.; White, T.; Urbas, A.; Li, Q. *Chem. Commun.* **2010**, *46*, 3463–3465. (c) Mathews, M.; Zola, R. S.; Hurley, S.; Yang, D. K.; White, T. J.; Bunning, T. J.; Li, Q. *J. Am. Chem. Soc.* **2010**, *132*, 18361–18366. (d) Mathews, M.; Zola, R. S.; Yang, D. K.; Li., Q. *J. Mater. Chem.* **2011**, *21*, 2098–2103.

(5) (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**, *6*, 654–655.

(6) (a) Chen, S. H.; Chen, H. M. P.; Geng, Y.; Jacobs, S. D.; Marshall, K. L.; Blanton, T. N. *Adv. Mater.* **2003**, *15*, 1061–1065. (b) Frigoli, M.; Welch, C.; Mehl, G. H. *J. Am. Chem. Soc.* **2004**, *126*, 15382–15383. (c) Frigoli, M. L.; Mehl, G. H. *Chem.—Eur. J.* **2004**, *10*, 5243–5250. (d) Frigoli, M.; Mehl, G. H. *Chem. Commun.* **2004**, 818–819. (e) Frigoli, M.; Mehl, G. H. *Chem. Commun.* **2004**, 2040–2041. (f) Subramanian, G.; Lehn, J. M. *Mol. Cryst. Liq. Cryst.* **2001**, *364*, 423–251.

(7) Kim, C.; Marshall, K. L.; Wallace, J. U.; Chen, S. H. *J. Mater. Chem.* **2008**, *18*, 5592–5598.

(8) (a) Green, L.; Li, Y.; White, T.; Urbas, A.; Bunning, T.; Li, Q. *Org. Biomol. Chem.* **2009**, *7*, 3930–3933. (b) Yelamaggad, C. V.; Shashikala, I. S.; Li, Q. *Chem. Mater.* **2007**, *19*, 6561–6568.

(9) (a) Wang, S.; Shen, W.; Feng, Y.; Tian, H. *Chem. Commun.* **2006**, 1497–1499. (b) Liu, B; Tian, H. *J. Mater. Chem.* **2005**, *15*, 2681–2686. (c) Tian, H.; Feng, Y. *J. Mater. Chem.* **2008**, *18*, 1617–1622. (d) Li, Y.; Cao, L.; Tian, H. *J. Org. Chem.* **2006**, *71*, 8279–8282.

(10) Dierking, I. *Textures of Liquid Crystals*; Wiley-VCH GmBH & KGaA: Weinheim, Germany, 2003.

(11) (a) Chen, S. H.; Shi, H.; Conger, B. M.; Mastrangelo, J. C.; Tsutsui, T. *Adv. Mater.* **1996**, *8*, 998–1001. (b) Chen, S. H.; Katsis, D.; Mastrangelo, J. C.; Schmid, A. W.; Tsutsui, T.; Blanton, T. N. *Nature* **1999**, *397*, 506–508. (c) Chen, H. P.; Katsis, D.; Mastrangelo, J. C.; Chen, S. H.; Jacobs, S. D.; Hood, P. J. *Adv. Mater.* **2000**, *12*, 1283–1286. (d) Philip, H. M.; Katsis, D.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 2534–2542.

(12) Li, Q.; Li, L.; Kim, J.; Park, H.-S.; Williams, J. *Chem. Mater.* **2005**, *17*, 6018–6021.

(13) (a) Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876. (b) Lucas, L. N.; de Jong, J. J. D.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Org. Chem.* **2003**, 155–166.