

Photochromic glassy liquid crystals comprising mesogenic pendants to dithienylethene cores†

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Photochromic glassy liquid crystals were synthesized using dithienylethenes as the volume-excluding cores to which liquid crystalline mesogens were chemically bonded through alkyl spacers. Nematic, smectic, and cholesteric glassy liquid crystals were demonstrated with glass transition temperatures above 90 °C and clearing points up to 220 °C without traces of crystallization on cooling or crystalline melting on heating. A monodomain cholesteric glassy liquid crystalline film containing an enantiomeric 2-methylpropylene chiral spacer was characterized as a left-handed helical stack, exhibiting a selective reflection band centered at 686 nm, an orientational order parameter of 0.65 for the quasi-nematic layers, and a combination of reflective coloration with photoswitchable absorptive coloration.

Introduction

Organic photochromes exist in two isomeric forms that can be interconverted by photochemical means for potential applications in optical memory and photonic switching.^{1–8} To be useful in practice, a demanding set of material requirements must be met, including absence of thermal isomerization, independently addressable absorption spectra, short response time, high quantum yields, and excellent fatigue resistance. Of all the photochromic compounds that have been explored to date, dithienylethenes appear to be the most promising.⁸ Crystalline,^{9–11} liquid crystalline,^{12–14} and amorphous^{15,16} material systems have been reported. To achieve nondestructive and rewritable optical memory, numerous concepts have been demonstrated on the basis of refractive index,¹⁶ fluorescence,^{17–26} chiroptical activity,^{27–29} infrared absorption,^{30–33} and photoconductivity.³⁴ To reduce these concepts to practice, materials should most preferably be processed into a large-area solid film without grain boundaries to avoid light scattering. To this end, amorphous dithienylethenes spin-cast on a glass substrate have been reported with refractive index change serving as nondestructive and rewritable memory.¹⁶

Glassy liquid crystals (GLCs) comprise liquid crystalline mesogens chemically bonded to volume-excluding cores, such as benzene, cyclohexane, bicyclooctene, cubane, and adamantane, to prevent crystallization in the cooling process intended for glass transition.^{35–41} Because of their ability to form large-area monodomain thin films with various modes of molecular order frozen in the solid state, glassy liquid crystals are particularly useful for optoelectronics. The adoption of a photochromic volume-excluding core adds new functionalities to glassy liquid crystals. In a recent paper, we have reported the first

photochromic glassy liquid crystal consisting of a dithienylethene core with nematogenic pendants.⁴² In the resultant glassy-nematic film, the electronic transition moment of the photochromic core was shown to be uniaxially aligned, enabling anisotropic refractive indices to be used for nondestructive readout. The present study was motivated to generalize the concept of a photochromic glassy-nematic liquid crystal to both the smectic and cholesteric types through molecular design, material synthesis, and characterization of thermotropic and optical properties.

Experimental

Material synthesis

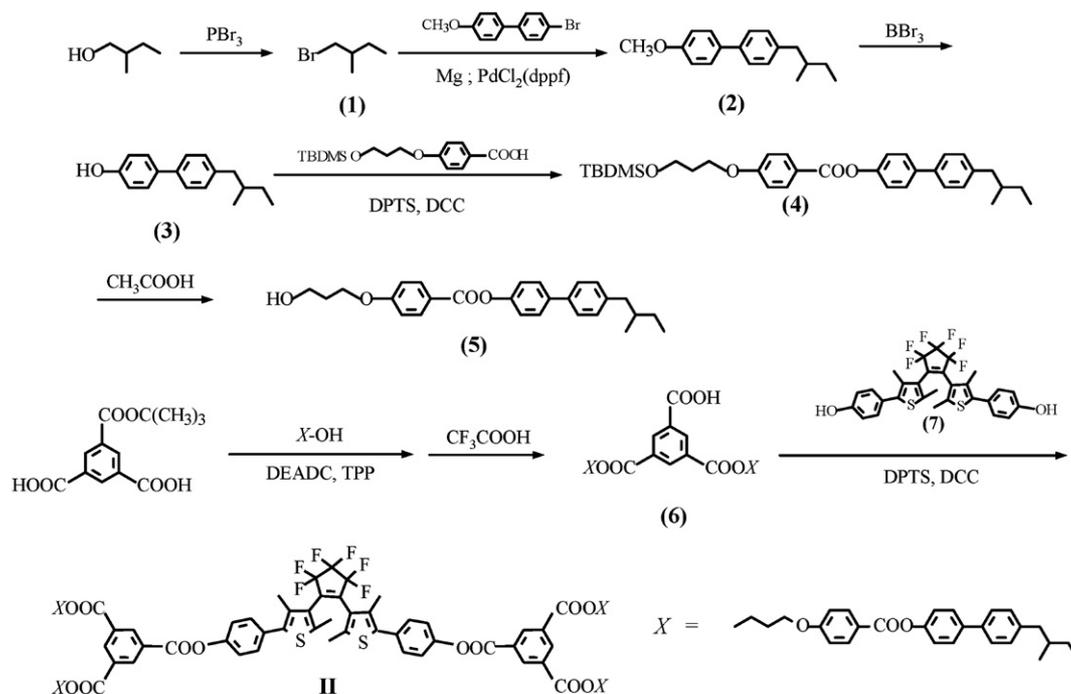
All chemicals, reagents, and solvents were used as received from commercial sources without further purification except tetrahydrofuran (THF) which was distilled over sodium and benzophenone. The following intermediates were synthesized according to the published procedures: 1,3,5-benzenetricarboxylic acid, 1-*tert*-butyl ester,⁴¹ 4-[3-[(*tert*-butyldimethyl-silyloxy)propoxy]benzoic acid,³⁹ 1,2-bis[2,4-dimethyl-5-(4-hydroxy)phenylthiophene-3-yl]perfluorocyclopentene, *viz.* **7** in Scheme 1,^{43,44} 1,2-bis(6-iodo-2-methyl-1-benzothiophene-3-yl)perfluoro-cyclopentene, *viz.* **8** in Scheme 2,⁴⁵ 3,5-dimethoxy-phenylboronic acid,⁴⁶ 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester,⁴¹ and (*S*)-4-(3-hydroxy-2-methylpropoxy)benzoic acid 4'-cyano-biphenyl-4-yl ester.⁴⁰ The procedures for the synthesis of intermediates **1–6** along with their analytical data are presented in ESI.† Compound **I** has been reported previously,⁴² and the procedures for the synthesis and purification accompanied by analytical data for **II–V** in addition to intermediates **9** and **10** are presented in what follows.

1,2-Bis[6-(3,5-dimethoxy)phenyl-2-methyl-1-benzothiophene-3-yl]perfluorocyclopentene, 9. To a mixture of **8** (1.1 g, 1.5 mmol), 3,5-dimethoxyphenylboronic acid (0.61 g, 3.4 mmol), tetrakis (triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.18 g, 0.15 mmol), and potassium carbonate (1.1 g, 7.6 mmol) was added degassed

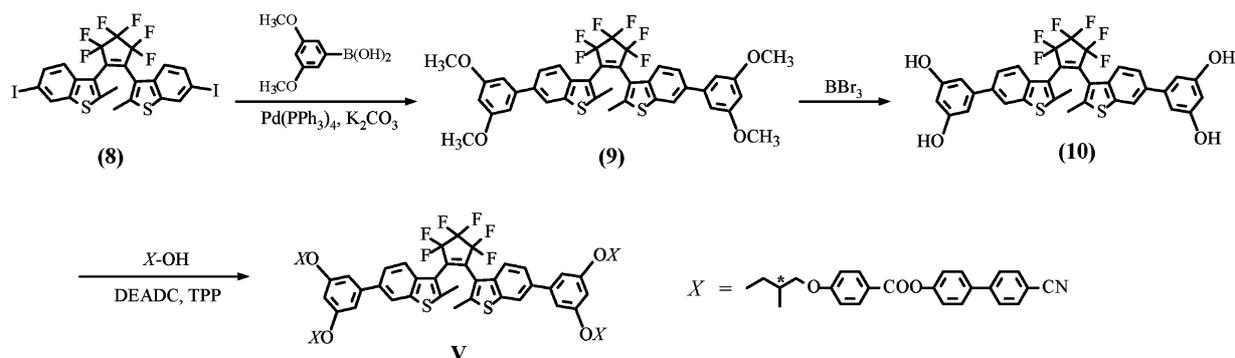
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† Electronic supplementary information (ESI) available: Synthesis and analytical data for intermediates **1–6**. See DOI: 10.1039/b810955a



Scheme 1 Synthesis of compound **II**. DPTS, 4-(dimethylamino)pyridine/*p*-toluenesulfonic acid; DCC, *N,N*-dicyclohexylcarbodiimide; DEADC, diethyl azodicarboxylate; and TPP, triphenylphosphine.



Scheme 2 Synthesis of compound **V** without altering stereochemistry at the asymmetric carbon center inherited from (*S*)-3-bromo-2-methylpropanol.

anhydrous *N,N*-dimethylformamide (15 mL). After stirring under argon at 90 °C overnight, the reaction mixture was extracted with methylene chloride. The extract was treated with brine and dried over anhydrous magnesium sulfate. After evaporation of solvent under reduced pressure, the crude product was purified by gradient column chromatography on silica gel with 0 to 3% ethyl acetate in hexanes as the eluent to afford **9** (0.49 g, 43%). ¹H NMR spectral data (400 MHz, CDCl₃): δ (ppm) parallel conformer: 2.54 (s, 6H, -CH₃), 3.84 (s, 12H, -OCH₃), 6.46 (s, 2H, aromatics), 6.69 (s, 4H, aromatics), 7.43 (d, 2H, aromatics), 7.62 (d, 2H, aromatics), 7.82 (s, 2H, aromatics); antiparallel conformer: 2.28 (s, 6H, -CH₃), 3.90 (s, 12H, -OCH₃), 6.51 (s, 2H, aromatics), 6.78 (s, 4H, aromatics), 7.65 (d, 2H, aromatics), 7.73 (d, 2H, aromatics), 7.91 (s, 2H, aromatics); parallel:antiparallel = 34:66.

1,2-Bis[6-(3,5-dihydroxy)phenyl-2-methyl-1-benzothiophene-3-yl]perfluorocyclopentene, 10. Into a solution of **9** (0.49 g, 0.66

mmol) in anhydrous methylene chloride (10 mL), a 1 M solution of boron tribromide in anhydrous methylene chloride (5.3 mL, 5.3 mmol) was added dropwise at -78 °C. The reaction mixture was warmed to room temperature and stirred under argon overnight before dilution with additional methylene chloride for washing with water. The organic portion was further washed with brine before drying over anhydrous magnesium sulfate. After evaporating off the solvent under reduced pressure, the crude product was purified by gradient column chromatography on silica gel using 0 to 3% methanol in methylene chloride as the eluent to yield **10** (0.40 g, 89%). ¹H NMR spectral data (400 MHz, DMSO-*d*₆): δ (ppm) parallel conformer: 2.54 (s, 6H, -CH₃), 6.21 (s, 2H, aromatics), 6.44 (s, 4H, aromatics), 7.45 (d, 2H, aromatics), 7.66 (d, 2H, aromatics), 8.03 (s, 2H, aromatics), 9.34 (s, 4H, -OH); antiparallel conformer: 2.33 (s, 6H, -CH₃), 6.25 (s, 2H, aromatics), 6.53 (s, 4H, aromatics), 7.65 (d, 2H, aromatics), 7.68 (d, 2H, aromatics), 8.10 (s, 2H, aromatics), 9.38 (s, 4H, -OH); parallel:antiparallel = 43:57.

1,2-Bis[2,4-dimethyl-5-[4-[3,5-bis[3-[4-[(4-(2-methylbutyl)biphenyl-4-yl)oxycarbonyl]-phenoxy]propoxycarbonyl]phencarboxyl]phenyl]thiophene-3-yl]perfluorocyclopentene, II. Intermediates **6** (0.70 g, 0.69 mmol) and **7** (0.19 g, 0.33 mmol) plus DPTS (0.010 g, 0.033 mmol) were dissolved in anhydrous methylene chloride (15 mL) into which DCC (0.15 g, 0.73 mmol) was quickly added. The reaction mixture was stirred under argon at room temperature overnight. Upon filtering off white solids, the filtrate was diluted with additional methylene chloride. The organic solution was washed with 1 M aqueous hydrochloric acid, water and brine sequentially before drying over anhydrous magnesium sulfate. The crude product was collected by evaporating off methylene chloride under reduced pressure and then purified by gradient column chromatography on silica gel using 0 to 1% acetone in methylene chloride. Precipitation from a methylene chloride solution into methanol yielded **II** (0.43 g, 51%). Anal. calcd: C, 72.53%; H, 5.58%. Found: C, 72.68%; H, 5.54%. ¹H NMR spectral data (400 MHz, CDCl₃): δ (ppm) 0.86 (d, 12H, -CH(CH₃)-), 0.93 (t, 12H, CH₃CH₂-), 1.18–1.46 (m, 8H, CH₃CH₂CH(CH₃)-), 1.69 (quartet, 4H, -CH(CH₃)-), 2.13 (s, 3H, -CH₃, antiparallel), 2.15 (s, 3H, -CH₃, parallel), 2.37–2.72 (m, 22H, -CH₃, -CH₂Ar, -COOCH₂CH₂-), 4.26 (t, 8H, -CH₂OAr-), 4.66 (t, 8H, -COOCH₂CH₂-), 7.00 (m, 8H, aromatics), 7.23–7.30 (m, 20H, aromatics), 7.46–7.52 (m, 12H, aromatics), 7.62 (m, 8H, aromatics), 8.16 (m, 8H, aromatics), 8.96 (s, 2H, aromatics), 9.04 (s, 4H, aromatics); parallel:antiparallel = 1:1.

1,2-Bis[2,4-dimethyl-5-[4-[3,5-bis[3-[4-[(R)-(2-methylbutyl)biphenyl-4-yl]oxycarbonyl]-phenoxy]propoxy-carbonyl]phencarboxyl]phenyl]thiophene-3-yl]perfluorocyclopentene, III. The procedures reported for **II** were followed for the synthesis and purification of **III** (0.68 g, 56%). Anal. calcd: C, 72.53%; H, 5.58%. Found: C, 72.40%; H, 5.66%. ¹H NMR spectral data (400 MHz, CDCl₃): δ (ppm) 0.88 (d, 12H, -CH(CH₃)-), 0.95 (t, 12H, CH₃CH₂-), 1.20–1.46 (m, 8H, CH₃CH₂CH(CH₃)-), 1.70 (quartet, 4H, -CH(CH₃)-), 2.13 (s, 3H, -CH₃, antiparallel), 2.16 (s, 3H, -CH₃, parallel), 2.36–2.72 (m, 22H, -CH₃, -CH₂Ar, -COOCH₂CH₂-), 4.27 (quartet, 8H, -CH₂OAr-), 4.67 (quartet, 8H, -COOCH₂CH₂-), 7.01 (m, 8H, aromatics), 7.23–7.30 (m, 20H, aromatics), 7.46–7.52 (m, 12H, aromatics), 7.62 (m, 8H, aromatics), 8.16 (m, 8H, aromatics), 8.96 (s, 2H, aromatics), 9.04 (s, 4H, aromatics); parallel:antiparallel = 1:1.

1,2-Bis[2,4-dimethyl-5-[4-[3,5-bis[(R)-3-[4-[(4'-cyanobiphenyl-4-yl)oxycarbonyl]phenoxy]-2-methylpropoxycarbonyl]phencarboxyl]phenyl]thiophene-3-yl]perfluorocyclopentene, IV. The procedures reported for **II** were followed for the synthesis and purification of **IV** (0.33 g, 79%). Anal. calcd: C, 70.32%; H, 4.37%; N, 2.29%. Found: C, 70.00%; H, 4.02%; N, 2.23%. ¹H NMR spectral data (400 MHz, CDCl₃): δ (ppm) 1.21 (m, 12H, -CH₃), 2.09 (s, 3H, -CH₃, antiparallel), 2.13 (s, 3H, -CH₃, parallel), 2.32 (s, 3H, -CH₃, parallel), 2.36 (s, 3H, -CH₃, antiparallel), 2.56 (m, 4H, -CH₂CH(CH₃)CH₂-), 4.08 (t, 8H, -CH₂OAr-), 4.50 (m, 8H, -COOCH₂CH₂-), 7.00 (m, 8H, aromatics), 7.25–7.30 (m, 10H, aromatics), 7.44 (d, 4H, aromatics), 7.59–7.72 (m, 24H, aromatics), 8.12 (m, 8H, aromatics), 8.91 (s, 2H, aromatics), 9.00 (s, 4H, aromatics); parallel:antiparallel = 1:1.

1,2-Bis[6-[3,5-bis[(R)-3-[4-[(4'-cyanobiphenyl-4-yl)oxycarbonyl]phenoxy]-2-methyl-propoxy]phenyl]-2-methyl-1-benzothiophene-3-yl]perfluorocyclopentene, V. DEADC (0.33 g, 1.9 mmol) was added dropwise at -78 °C to a solution of (*S*)-4-(3-hydroxy-2-methylpropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester (0.70 g, 1.8 mmol), **8** (0.29 g, 0.43 mmol), and TPP (0.50 g, 1.9 mmol) in anhydrous THF (15 mL). The reaction mixture was warmed to room temperature and stirred under argon overnight. The solvent was then removed under reduced pressure, and the solid residue was purified by gradient column chromatography on silica gel with 0 to 1% acetone in methylene chloride. Precipitation from a methylene chloride solution into methanol yielded **V** (0.15 g, 53%). Anal. calcd: C, 72.77%; H, 4.57%; N, 2.59%. Found: C, 72.59%; H, 4.26%; N, 2.56%. ¹H NMR spectral data (400 MHz, CDCl₃): δ (ppm) parallel conformer: 1.18 (d, 12H, -CH₃), 2.51 (m, 10H, -CH₂CH(CH₃)CH₂-, -CH₃), 4.10 (m, 16H, -CH₂OAr, -COOCH₂-), 6.47 (s, 2H, aromatics), 6.70 (s, 4H, aromatics), 6.96 (d, 8H, aromatics), 7.30 (d, 8H, aromatics), 7.42 (d, 2H, aromatics), 7.60 (d, 10H, aromatics), 7.67 (d, 8H, aromatics), 7.71 (d, 8H, aromatics), 7.79 (s, 2H, aromatics), 8.12 (d, 8H, aromatics); antiparallel conformer: 1.22 (d, 12H, -CH₃), 2.22 (s, 6H, -CH₃), 2.51 (m, 4H, -CH₂CH(CH₃)CH₂-), 4.10 (m, 16H, -CH₂OAr, -COOCH₂-), 6.52 (s, 2H, aromatics), 6.78 (s, 4H, aromatics), 7.00 (d, 8H, aromatics), 7.30 (d, 8H, aromatics), 7.60 (d, 8H, aromatics), 7.67 (d, 10H, aromatics), 7.71 (d, 10H, aromatics), 7.87 (s, 2H, aromatics), 8.16 (d, 8H, aromatics); parallel:antiparallel = 3:7.

Molecular structures and thermotropic properties

Molecular structures were elucidated with ¹H NMR spectroscopy in CDCl₃ or DMSO-*d*₆ (Avance-400, 400 MHz) and elemental analysis (Quantitative Technologies, Inc.). Thermal transition temperatures were determined by differential scanning calorimetry (DSC; Perkin-Elmer DSC-7) with a continuous N₂ purge at 20 mL/min. Samples were preheated to the isotropic state followed by cooling at -20 °C/min to -30 °C, furnishing the reported second heating and cooling scans. Liquid crystalline mesomorphism was characterized by hot stage polarizing optical microscopy (DMLM, Leica, FP90 central processor and FP82 hot stage, Mettler, Toledo).

Preparation and characterization of cholesteric glassy liquid crystalline films

Optically flat fused-silica substrates (25.4 mm diameter × 3 mm thickness, Esco Products; *n* = 1.459 at 589.0 nm) were spin-coated with a polyimide (PI) alignment layer (Nissan SUN-EVER) and uniaxially rubbed. Glassy chiral-nematic films of **V** were prepared between two surface-treated substrates with the film thickness defined by glass fiber spacers as 5 μm (EM Industries, Inc.). A sample of **V** was placed between two alignment-coated fused silica substrates for heating to 230 °C followed by cooling to 207 °C, at which point shearing was applied to induce alignment. The sample was then annealed for 1 h before quenching in liquid nitrogen to bypass the cholesteric-to-smectic phase transition. Transmittance at normal incidence and reflection at 6° off normal were measured with unpolarized incident light using a UV-vis-NIR spectrophotometer (Lambda-900, Perkin Elmer equipped with a beam depolarizer). Fresnel

reflections from the air–glass interfaces were accounted for with a reference cell containing an index-matching fluid ($n = 1.500$ at 589.6 nm) between two surface-treated fused silica substrates. A combination of a linear polarizer (HNP'B, Polaroid) and zero-order quarter waveplate (NQM-100-738, Meadowlark Optics) was employed to produce left- or right-handed circularly polarized light. Variable angle spectroscopic ellipsometry (V-VASE, J. A. Woollam Corp.) was performed to determine the pitch length and refractive index of a glassy-cholesteric film of **V**, as reported previously for monodisperse chiral oligofluorenes.^{48,49} The closed form of **V** was obtained by the irradiation of 365 ± 10 nm light (UV-400, Spectroline) coupled with a glass filter (UG 11 and NG12, Schott) to photostationary state. Ellipsometry was employed to characterize the orientational order parameter governing the quasi-nematic layers in the helical stack of **V** in closed form. To induce ring opening, a visible light source (UVP B-100AP, UVP LLC) coupled with a bandpass filter (577FS10-50, Andover Corporation) was used for irradiation at 577 ± 5 nm. The photon flux at 365nm was determined by a spectrophotometer equipped with an optic fiber (USB4000, Ocean Optics Inc.) and a UVX-36 radiometer (UVP, LLC). The photon flux at 577 nm was quantified by comparing its intensity with that at 365 nm, both measured with the spectrophotometer. The quantum yields of both the ring-closing and ring-opening reactions were characterized using ¹H-NMR and UV-vis absorption spectroscopic techniques for molar extinction coefficient of the closed form and the extents of photoreactions, respectively.

Results and discussion

Chart 1 presents the molecular structures of compounds **I–V** accompanied by their thermal transition temperatures as

determined by differential scanning calorimetry. Compound **I** is as reported previously,⁴² and **II** was synthesized according to Scheme 1, in which intermediate **7** was prepared with literature procedures.^{43,44} Compound **III** was synthesized following the same procedures as for **II** using (*S*)-2-methyl-1-butanol to construct the tail group. The procedures for synthesizing the hybrid chiral-nematic precursor to **IV** have been reported elsewhere.⁴⁷ Compound **V** was synthesized according to Scheme 2, where intermediate **8** was prepared following literature procedures.⁴⁵

Molecular structures of glassy liquid crystals with dithienylethene cores under investigation; phase transition temperatures expressed in °C. Symbols: *G*, glassy; *S_A*, smectic A; *S_A**, chiral smectic A; *S_C**, chiral smectic C; *S_X*, unidentified smectic; *Ch*, cholesteric; *I*, isotropic.

The heating and cooling scans at ± 20 °C/min of **I–V** preheated to 250 °C with subsequent cooling to -30 °C were gathered with differential scanning calorimetry, and the results are compiled in Fig. 1 with mesophases identified by polarizing optical microscopy. The core-pendant approach to glassy liquid crystals^{35–41} has generated photoresponsive glassy liquid crystals without traces of crystallization or crystalline melting upon heating or cooling. As independent chemical entities, cores and pendants are crystalline solids or liquid crystals that tend to crystallize, but the chemical hybrids tend to form morphologically stable glassy liquid crystals. This property is essential to the preparation of self-organized solid films without grain boundaries for potential application to optoelectronics.

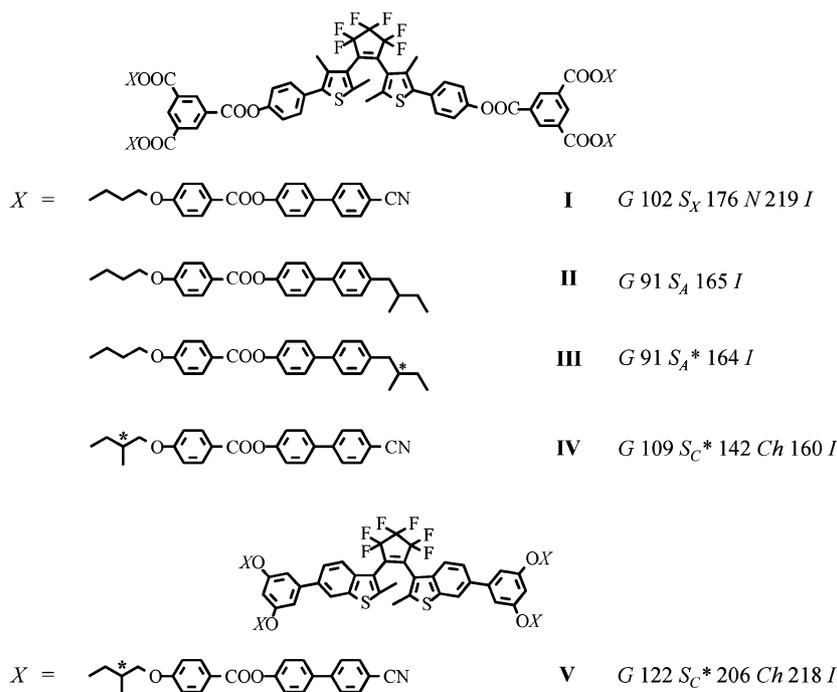


Chart 1 Molecular structures of glassy liquid crystals with dithienylethene cores under investigation; phase transition temperatures expressed in °C. Symbols: *G*, glassy; *S_A*, smectic A; *S_A**, chiral smectic A; *S_C**, chiral smectic C; *S_X*, unidentified smectic; *Ch*, cholesteric; *I*, isotropic.

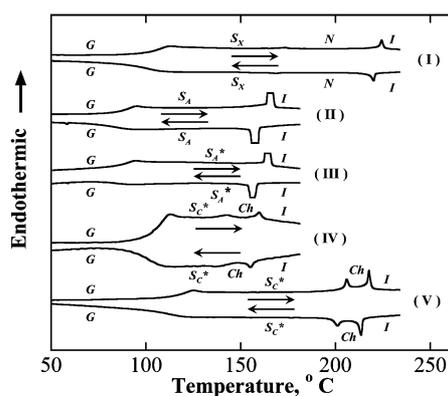


Fig. 1 Differential scanning calorimetric heating and cooling scans of I–V at 20 °C/min of samples preheated above their clearing points followed by cooling to –30 °C. Symbols: *G*, glassy; *S_A*, smectic A; *S_A**, chiral smectic A; *S_C**, chiral smectic C; *S_X*, unidentified smectic; *Ch*, cholesteric; *I*, isotropic.

With a cyano group at the end of all the nematic pendants, compound **I** exists as an unidentifiable smectic (*S_X*) fluid, as shown in Fig. 2a, from the glass transition temperature (T_g) of 102 °C to the *S_X*-to-*N* transition at 176 °C. Upon further heating, a nematic fluid identified by marbled textures in Fig. 2b exhibits a clearing point (T_c) at 219 °C. Substitution of the terminal cyano groups with racemic and enantiomeric 2-methylbutyl groups exhibit the focal conic fan textures, as shown in Fig. 2c and d, respectively, which are characteristic of smectic A (*S_A*) and chiral smectic A (*S_A**).⁵⁰ The assignment of *S_A* and *S_A** to **II** and **III**, respectively, is dictated by the stereochemical nature of the tail group. The *S_A** mesophase can be further substantiated by the electroclinic effect.⁵¹ Replacing propylene with enantiomeric 2-methylpropylene spacers produced **IV** with a T_g at 109 °C and a T_c at 160 °C, between which there is a *S_C**-to-*Ch* transition at 142 °C, where *S_C** and *Ch* represent chiral smectic C and cholesteric mesomorphism, respectively. As shown in Fig. 2f, the *Ch* phase is identified by oily streaks. For this particular compound, it was difficult to identify *S_C** in its naturally occurring state under polarizing optical microscopy because of the high melt viscosity. Therefore, the sample was sheared at 140 °C to induce alignment. In the thick area, the images shown in Fig. 2e resemble broken focal conic fan textures, but are too small to be definitive. In the thin area where helical rotation is suppressed by surface forces, shear-induced alignment with point defects was observed, as shown in Fig. 2g and h with the device shearing direction oriented along and at 45° with respect to the polarizer (or analyzer), respectively. Note the birefringence color change upon rotation, indicating unidirectional alignment. The white dots in the micrographs are the point defects, commonly observed in *S_C** samples in the bookshelf geometry which is used in surface stabilized ferroelectric liquid crystal displays. Attempts to process **IV** into chiral smectic C and cholesteric glassy liquid crystalline films by thermal annealing at appropriate temperature regimes failed to produce glassy liquid crystalline films without disclinations for optical characterization.

Fusing thiophene rings with benzene rings to form a dibenzothienylethene core in **IV** yielded another glassy liquid crystal, **V**, characterized by higher phase transition temperatures

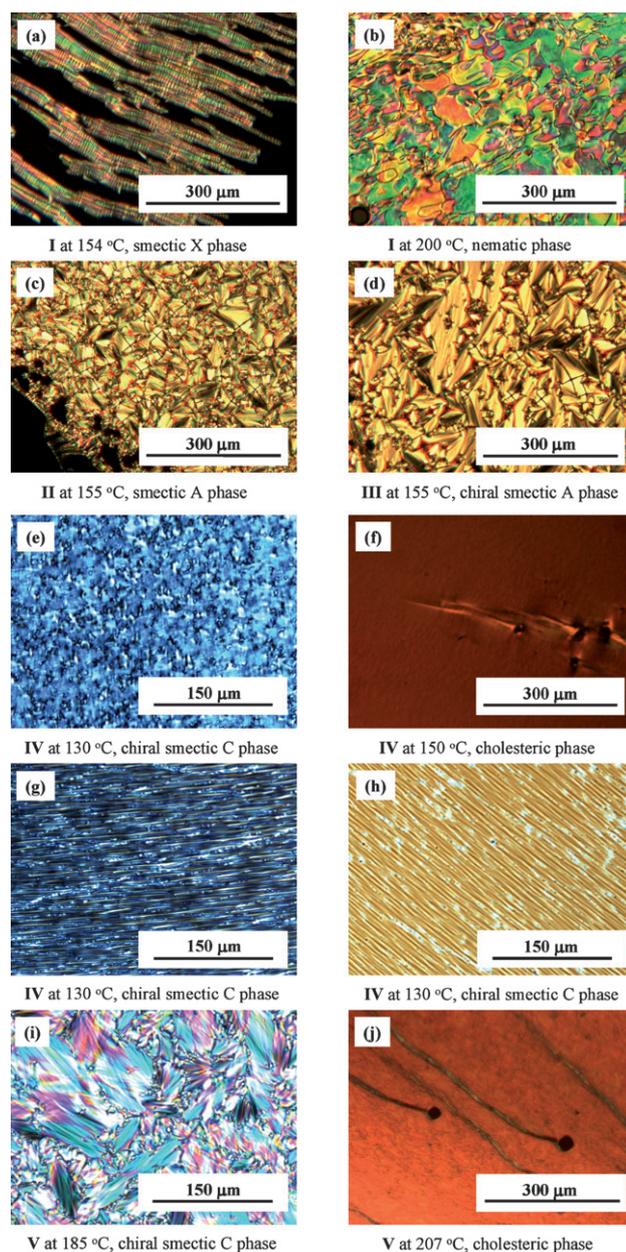


Fig. 2 Polarizing optical micrographs of I–V between crossed polarizers for mesophase identification.

presumably because of the improved linearity of the photochromic core. Specifically, a T_g at 122 °C and a T_c at 218 °C were observed with an intervening *S_C**-to-*Ch* phase transition at 206 °C, as ascertained by broken focal conic fans and oily streaks shown in Fig. 2i and j, respectively. The higher temperature range over which cholesteric mesomorphism prevails in **V** than in **IV** enabled a disclination-free cholesteric GLC film to be prepared by taking advantage of the lower cholesteric fluid viscosity during thermal annealing. The optical properties of the resultant 5 μm-thick cholesteric GLC film of **V** were characterized. Fig. 3a shows both reflectance and transmittance of unpolarized incident light close to the theoretical limit of 50%. As indicated in Fig. 3b, the cholesteric GLC film with (*S*)-3-bromo-2-methylpropanol as the chiral building block selectively reflects left-handed circularly

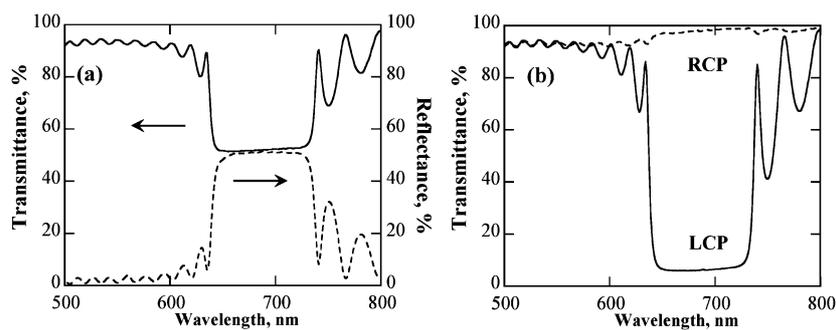


Fig. 3 (a) Transmission and reflection spectra with unpolarized incident light and (b) circularly polarized transmission spectra of a 5 μm -thick cholesteric GLC film of **V** between rubbed polyimide films.

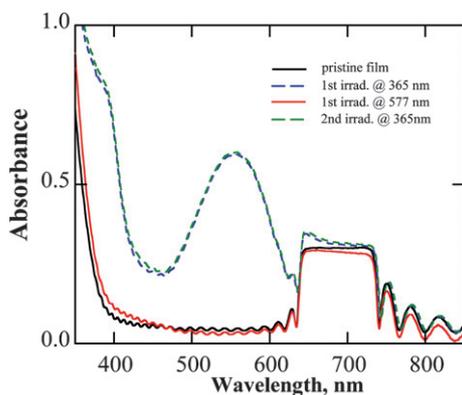


Fig. 4 Demonstration of photochromism at room temperature using a 5 μm -thick cholesteric glassy liquid crystal film of **V** in the presence of a selective reflection band centered at 686 nm.

polarized incident light while transmitting the right-handed counterpart without attenuation.

Therefore, the cholesteric GLC film of **V** consists of a left-handed helical stack of quasi-nematic layers. By analogy, a right-handed helical stack is expected of (*R*)-3-bromo-2-methylpropanol as the chiral building block in **V**. Furthermore, the mixtures of the two cholesteric GLC materials with opposite handedness at varying ratios will produce films with selective reflection wavelengths ranging from 686 nm to infinity where these two enantiomeric cholesteric GLCs are at a 1:1 ratio.

Except for the selective reflection band centered at 686 nm, the cholesteric GLC film of a pristine sample of **V** carrying an open dithienylethene core is transparent down to 400 nm, as shown in Fig. 4. The dithienylethene core undergoes ring closure upon irradiation with 20 J/cm^2 at room temperature using a UV source at 365 nm with a 20 nm bandwidth, generating an absorption peak at 555 nm with a minor perturbation on the selective reflection band. Exposure to a visible light source at 577 nm with a 10 nm bandwidth resulted in ring opening to restore the non-absorbing status. The quantum yields of the ring-closing and ring-opening photoreactions were evaluated as 0.63 and 0.02, respectively, using the ^1H NMR and UV-vis absorption spectroscopic techniques. As demonstrated in Fig. 4, the ring-closing and -opening cycle can be induced reversibly in the solid state. In a nutshell, the open form provides selective coloration alone, and the closed form furnishes a combination of reflective and

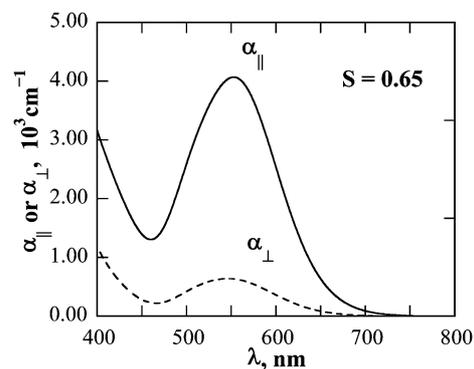


Fig. 5 Absorption dichroism extracted from ellipsometric analysis of a 5 μm -thick cholesteric glassy liquid crystal film of **V** after irradiation at 365 nm to its photostationary state.

absorptive colorations. Furthermore, the absorptive coloration can be switched on and off by photochemical means.

The film containing the closed dithienylethene ring after UV irradiation was further characterized by variable angle spectroscopic ellipsometry.^{48,49} This analysis resulted in a helical pitch length of 439 nm and an average refractive index of 1.564 at wavelengths longer than 600 nm into the near infrared region, the product of which is consistent with the selective reflection wavelength of 686 nm independently observed in Fig. 3. Absorption dichroism of quasi-nematic layers comprising the cholesteric GLC film of **V** also emerged as part of the ellipsometric analysis, as plotted in Fig. 5 in which α_{\parallel} and α_{\perp} represent absorption coefficients parallel and perpendicular to the quasi-nematic director, respectively. The absorption dichroic ratio, $R = \alpha_{\parallel}/\alpha_{\perp}$, is then used to calculate the orientational order parameter, $S = (R - 1)/(R + 2) = 0.65$, a value indicative of reasonably good order within the helical stack.

Conclusion

Glassy liquid crystals are comprised of liquid crystalline mesogens chemically bonded to volume-excluding cores. They are intended to undergo a glass transition through cooling without encountering crystallization, thereby permitting various modes of long-range molecular order characteristic of liquid crystalline fluids to be frozen in the solid state. Instead of inert volume-excluding cores—such as benzene, cyclohexane, bicyclooctene, cubane, and adamantane—dithienylethanes were successfully

incorporated to introduce photochromism into nematic, smectic, and cholesteric glassy liquid crystals. These glassy liquid crystals have glass transition temperatures above 90 °C and clearing points up to 220 °C without traces of crystallization on cooling or crystalline melting on heating. A monodomain cholesteric glassy liquid crystalline film was prepared by thermal processing for the characterization of its optical properties. With enantiomeric 2-methylpropylene as the chiral spacer between the benzene core and the 4'-cyanobiphenyl-4-yl benzoate nematogen, a left-handed quasi-nematic stack was identified with a selective reflection band centered at 686 nm. In addition, ellipsometric analysis resulted in a helical pitch length of 439 nm and an average refractive index of 1.564 beyond 600 nm into the near infrared region, the product of which is consistent with the value measured by UV-vis spectrophotometry. As part of the ellipsometric analysis, an orientational order parameter of 0.65 was also obtained for the quasi-nematic layers comprising the cholesteric stack. The feasibility of selective coloration coupled with photoswitchable absorptive coloration was demonstrated using the photochromic cholesteric glassy liquid crystalline film.

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