

# Deterministic Synthesis and Optical Properties of Glassy Chiral-Nematic Liquid Crystals

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A new series of morphologically stable, glassy chiral-nematic liquid crystals were synthesized following three distinct deterministic approaches. A glass transition temperature from 67 to 82 °C and a clearing temperature from 175 to 225 °C were accomplished. A helical pitch length from 188 to 210 nm emerged with enantiomeric 1-phenylethylamine as the precursors, giving rise to selective reflection in the UV region. With (+)-estrone as the chiral moiety, a selective reflection in the near-infrared was observed. The concepts of high-performance circular polarizers and optical notch filters and reflectors were illustrated with a mixture of enantiomeric glassy chiral nematics. Selective reflection wavelength can be readily tuned by varying chemical composition in terms of the ratio of enantiomers or that of chiral-nematic to nematic components.

## I. Introduction

Liquid crystals are fluids characterized by various forms of long-range molecular order. They have found extensive uses in switchable electrooptical devices, such as liquid-crystal displays and spatial light modulators. For many photonic applications, it is desirable to have materials capable of freezing liquid-crystalline order into solid state without crystallization, representing a unique class of advanced materials referred to as *glassy liquid crystals* (GLCs). Existing GLCs can be categorized into the following: laterally or terminally branched, one-string compounds with a glass transition temperature,  $T_g$ , mostly around room temperature;<sup>1,2</sup> twin molecules with an above-ambient  $T_g$  but generally lacking morphological stability;<sup>3–6</sup> cyclosiloxanes functionalized with mesogenic and chiral pendants;<sup>7–9</sup> carbosilane dendrimers exhibiting a low  $T_g$ ;<sup>10–12</sup> macrocarbocycles with mesogenic segments as part of the ring structure.<sup>13</sup> In a recent series of papers, we have implemented a new

molecular design concept in which nematic and chiral groups are chemically bonded to a volume-excluding core to prevent crystallization upon cooling.<sup>14–24</sup> As a result, the long-range order characteristic of liquid-crystal fluids is preserved in the glassy state with superior stability against thermally activated recrystallization. In addition, we have reported glassy nematics with the highest phase transition temperatures and the broadest mesomorphic fluid temperature range ever achieved.<sup>25</sup>

Of all of the GLCs, chiral nematics are of particular interest because of the potential for use as large-area nonabsorbing polarizers,<sup>26</sup> optical notch filters and reflectors,<sup>27</sup> and polarized fluorescent films.<sup>24</sup> This class

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of materials has been synthesized by a statistical approach,<sup>21,26</sup> which requires intensive workup procedures to arrive at pure components, and by a deterministic approach via 2,4-dioxo-3-oxabicyclo[3.3.1]nonane-7-carboxylic acid chloride as an unstable intermediate prepared under demanding conditions.<sup>19,27</sup> The objectives of this study include (i) exploration of novel approaches to the deterministic synthesis of glassy chiral nematics with an elevated  $T_g$  and clearing temperature,  $T_c$ ; (ii) development of enantiomeric chiral nematics with a short pitch length corresponding to selective reflection in the ultraviolet or blue region; and (iii) demonstration of a versatile device concept for selective reflection and circular polarization across the visible region to the infrared region using mixtures comprising completely miscible enantiomeric chiral nematics at varying ratios.

## II. Experimental Section

**Reagents and Chemicals.** All chemicals, reagents, and solvents were used as received from Sigma-Aldrich Chemical Co. or VWR Scientific with the exception that tetrahydrofuran (99%) was dried by distillation over sodium in the presence of benzophenone. Silica gel 60 (EM Science; 230–400 mesh) was used for liquid chromatography.

**Material Synthesis.** GLCs depicted as I–VI in Figure 1 were synthesized following the reaction in Scheme 1. The purities of all of the intermediates were monitored by thin-layer chromatography (TLC) and <sup>1</sup>H NMR spectroscopy. The procedures for the synthesis and purification of 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester and 3-(2-hydroxypropoxy)estra-1,3,5(10)-trien-17-one are provided in the Supporting Information. The synthesis and purification procedures, together with analytical and <sup>1</sup>H NMR spectral data, of all other intermediates and final products are described in what follows.

*cis,cis-1,3,5-Cyclohexanetricarboxylic Acid, Dimethyl Ester (1).* To a solution of *cis,cis-1,3,5-cyclohexanetricarboxylic acid trimethyl ester* (10.0 g, 38.7 mmol) in acetone (90 mL) was added a 0.1 M aqueous solution of K<sub>2</sub>HPO<sub>4</sub> (700 mL) and pig liver esterase (E.C. 3.1.1.1; 10 000 units).<sup>28</sup> The reaction was conducted at 28 °C over a period of 5 h, while a 0.1 N NaOH solution was added as needed to maintain a constant pH 8. The reaction mixture was then acidified to pH 2 with a 10% HCl solution for extraction with methylene chloride (200 mL × 3). Combined organic extracts were washed with H<sub>2</sub>O (300 mL × 2) and brine (200 mL × 1) and then dried over anhydrous MgSO<sub>4</sub>. The crude product resulting from evaporation of the solvent was purified by recrystallization from hexanes to yield **1** (9.12 g, 96%). <sup>1</sup>H NMR spectral data (400 MHz, CDCl<sub>3</sub>): δ 1.48–1.80 (m, 3H, H<sub>ax</sub> from –CH<sub>2</sub>–, cyclohexane), 2.20–2.55 (m, 6H, H<sub>eq</sub> from –CH<sub>2</sub>– and H<sub>ax</sub> from –CH–, cyclohexane), 3.71 (s, 6H, CH<sub>3</sub>OOC–).

*cis,cis-1,3,5-Cyclohexanetricarboxylic Acid, 1-tert-Butyl Ester 3,5-Dimethyl Ester (2).* A solution of **1** (5.50 g, 22.53 mmol) and 1,1-carbonyldiimidazole (3.72 g, 22.53 mmol) in anhydrous *N,N*-dimethylformamide (33 mL) was stirred at 50 °C for 1 h before adding anhydrous *tert*-butyl alcohol (3.34 g, 45.06 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 3.43 g, 22.53 mmol). Reaction was carried out at 60 °C under argon for 48 h. Upon addition of H<sub>2</sub>O (120 mL), the reaction mixture was acidified to pH 4 with a 2.5% HCl solution for extraction with ether (200 mL × 3). Combined ethereal extracts were washed with H<sub>2</sub>O and brine and then dried over anhydrous MgSO<sub>4</sub>. The crude product resulting from evaporation of the solvent was purified by recrystallization from hexanes to yield **2** (6.55 g, 96%). <sup>1</sup>H NMR spectral data (400 MHz, CDCl<sub>3</sub>): δ 1.45 (s,

9H, (CH<sub>3</sub>)<sub>3</sub>C–), 1.46–1.80 (m, 3H, H<sub>ax</sub> from –CH<sub>2</sub>–, cyclohexane), 2.18–2.60 (m, 6H, H<sub>eq</sub> from –CH<sub>2</sub>– and H<sub>ax</sub> from –CH–, cyclohexane), 3.71 (s, 6H, CH<sub>3</sub>OOC–).

*cis,cis-1,3,5-Cyclohexanetricarboxylic Acid, 1-tert-Butyl Ester (3).* To a solution of **2** (6.00 g, 19.98 mmol) in acetone (60 mL) was added a 0.05 N NaOH solution (80 mL). The solution was maintained at pH 11 in the course of the reaction by adding a 1 N NaOH solution as needed. The reaction was allowed to continue until both methyl esters were hydrolyzed as detected by TLC. The pH was then adjusted to 3–4 with a 5% HCl solution for extraction with ether (100 mL × 3). Combined ethereal extracts were washed with H<sub>2</sub>O and brine and then dried over anhydrous MgSO<sub>4</sub>. Evaporation of the solvent resulted in **3** as a solid (5.15 g, 95%). <sup>1</sup>H NMR spectral data (400 MHz, CDCl<sub>3</sub>): δ 1.45 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C–), 1.46–1.80 (m, 3H, H<sub>ax</sub> from –CH<sub>2</sub>–, cyclohexane), 2.18–2.60 (m, 6H, H<sub>eq</sub> from –CH<sub>2</sub>– and H<sub>ax</sub> from –CH–, cyclohexane).

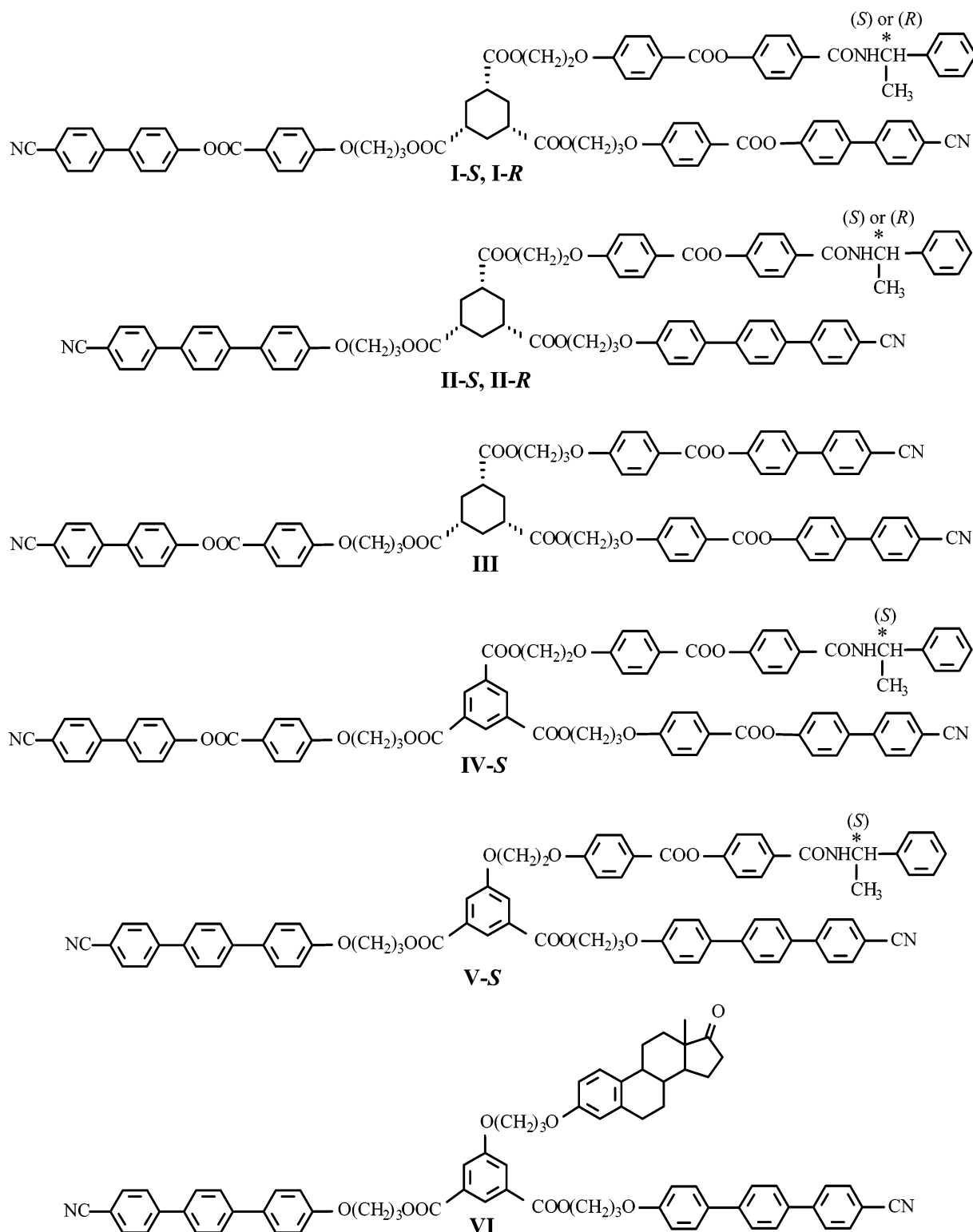
*cis,cis-1,3,5-Cyclohexanetricarboxylic Acid, 1,3-Bis[3-[4-[(4'-cyanobiphenyl-4-yloxy)carbonyl]phenoxy]propyl] Ester (4).* To a solution of **3** (0.30 g, 1.10 mmol), 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester (0.82 g, 2.20 mmol), and triphenylphosphine (0.63 g, 2.42 mmol) in anhydrous tetrahydrofuran (12 mL) was added dropwise diethyl azodicarboxylate (0.46 g, 2.64 mmol). The reaction was carried out at room temperature under argon overnight. The solvent was then evaporated off under reduced pressure, and the solid residue was dissolved in methylene chloride for purification by flash column chromatography with a solvent gradient from 0 to 4% acetone in methylene chloride. The hydrolysis of *tert*-butyl ester was accomplished in 20 mL of methylene chloride with 20 mL of trifluoroacetic acid. Upon addition of methylene chloride (30 mL), the reaction mixture was washed sequentially with H<sub>2</sub>O and brine before drying over anhydrous MgSO<sub>4</sub>. The crude product resulting from evaporation of the solvent was purified by flash column chromatography with a solvent gradient from 1 to 6% acetone in methylene chloride. Precipitation from a methylene chloride solution into cold methanol yielded **4** (0.70 g, 69%). <sup>1</sup>H NMR spectral data (400 MHz, CDCl<sub>3</sub>): δ 1.48–1.76 (m, 3H, H<sub>ax</sub> from –CH<sub>2</sub>–, cyclohexane), 2.18 (quintet, 4H, –CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>–), 2.30–2.50 (m, 6H, H<sub>eq</sub> from –CH<sub>2</sub>– and H<sub>ax</sub> from –CH–, cyclohexane), 4.15 (t, 4H, –CH<sub>2</sub>OAr), 4.32 (t, 4H, COOCH<sub>2</sub>–), 7.00–8.25 (m, 24H, aromatics).

*cis,cis-1,3,5-Cyclohexanetricarboxylic Acid, 1,3-Bis[3-[4-[(4'-cyanobiphenyl-4-yloxy)carbonyl]phenoxy]propyl] Ester 5-[4'-[[4'-[(S)-(–)-1'''-(Phenylethyl)]benzamide]-1'-oxy]benzoate-1'-oxy]ethyl Ester (I-S).* To a solution of **4** (0.25 g, 0.27 mmol), (S)-(–)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide (0.11 g, 0.28 mmol) synthesized previously,<sup>26</sup> and triphenylphosphine (0.077 g, 0.30 mmol) in anhydrous tetrahydrofuran (4 mL) was slowly added diethyl azodicarboxylate (0.056 g, 0.32 mmol). The reaction was carried out under argon at room temperature overnight. Solvent was evaporated off under reduced pressure, and the solid residue was dissolved in methylene chloride for purification by flash column chromatography with a solvent gradient from 0 to 4% acetone in methylene chloride. The product was collected by precipitation from a methylene chloride solution into methanol to yield **I-S** (0.28 g, 79%). Anal. Calcd for C<sub>79</sub>H<sub>67</sub>N<sub>3</sub>O<sub>16</sub>: C, 72.19; H, 5.14; N, 3.2. Found: C, 71.95; H, 5.09; N, 3.13. <sup>1</sup>H NMR spectral data (400 MHz, CDCl<sub>3</sub>): δ 1.48–1.76 (m, 6H, H<sub>ax</sub> from –CH<sub>2</sub>–, cyclohexane and –CH<sub>3</sub> from chiral pendant), 2.08–2.28 (m, 4H, –CH<sub>2</sub>– pendants), 2.28–2.50 (m, 6H, H<sub>eq</sub> from –CH<sub>2</sub>– and H<sub>ax</sub> from –CH–, cyclohexane), 4.00–4.55 (m, 12H, –CH<sub>2</sub>– from pendants), 5.38 (m, 1H, –CH from chiral pendant), 6.34 (d, 1H, –NH), 6.85–8.20 (m, 37H, aromatics).

*cis,cis-1,3,5-Cyclohexanetricarboxylic Acid, 1,3-Bis[3-[4-[(4'-cyanobiphenyl-4-yloxy)carbonyl]phenoxy]propyl] Ester 5-[4'-[[4'-[(R)-(+)-1'''-(Phenylethyl)]benzamide]-1'-oxy]benzoate-1'-oxy]ethyl Ester (I-R).* The procedure for the synthesis of **I-S** was followed for **I-R** (0.25 g, 71%) by using (R)-(+)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide (0.11 g, 0.28 mmol). Anal. Calcd for C<sub>79</sub>H<sub>67</sub>N<sub>3</sub>O<sub>16</sub>: C, 72.19; H, 5.14; N, 3.2. Found: C, 71.71; H, 4.93; N, 3.18. <sup>1</sup>H NMR spectral data (400 MHz, CDCl<sub>3</sub>): δ 1.48–1.76 (m, 6H, H<sub>ax</sub> from –CH<sub>2</sub>–,

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**Figure 1.** Molecular structures of the GLCs synthesized for the present study.

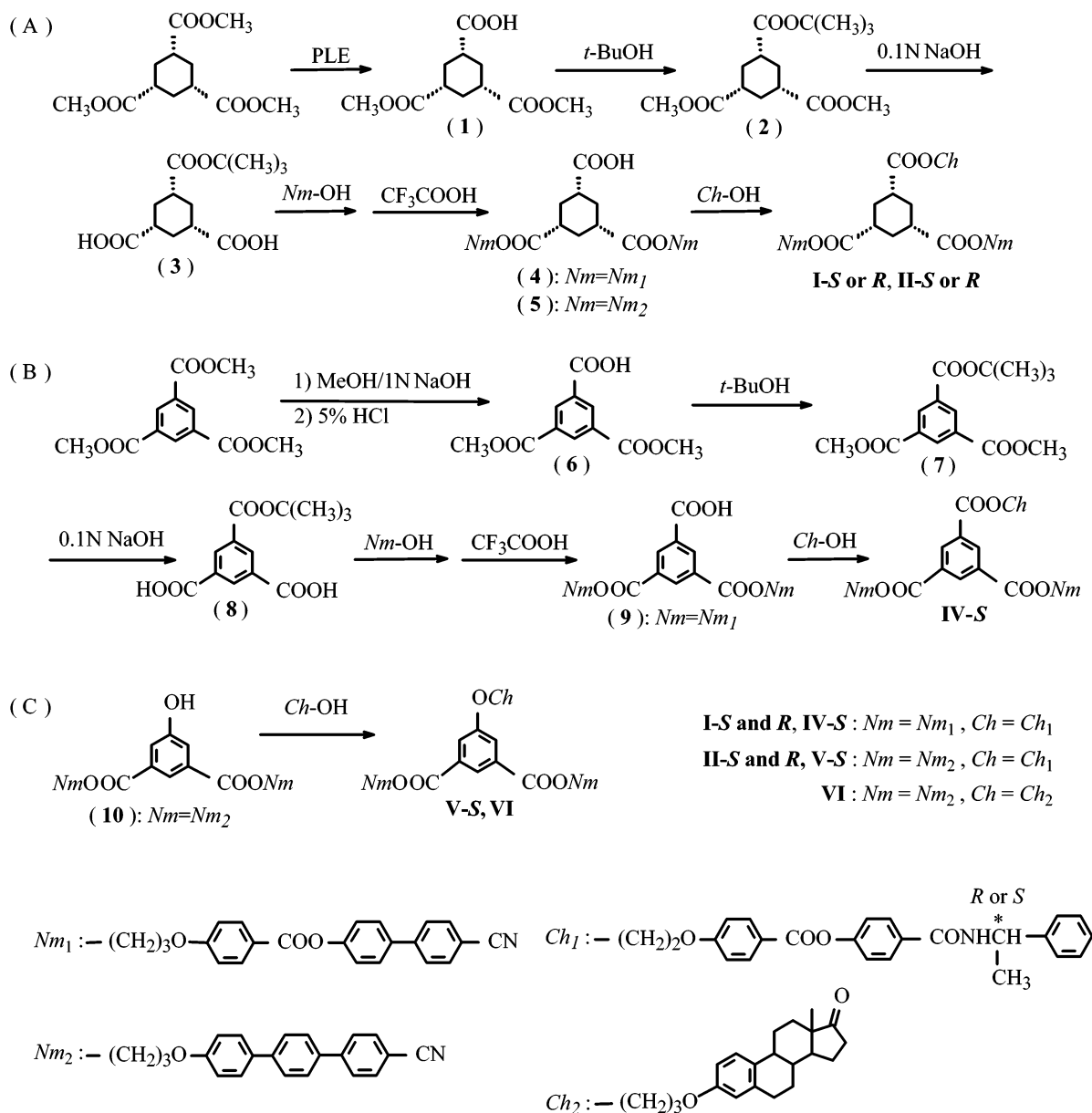
cyclohexane and  $-\text{CH}_3$  from chiral pendant), 2.08–2.28 (m, 4H,  $-\text{CH}_2-$  pendants), 2.28–2.50 (m, 6H,  $\text{H}_{\text{eq}}$  from  $-\text{CH}_2-$  and  $\text{H}_{\text{ax}}$  from  $-\text{CH}-$ , cyclohexane), 4.00–4.55 (m, 12H,  $-\text{CH}_2-$  from pendants), 5.38 (m, 1H,  $-\text{CH}$  from chiral pendant), 6.34 (d, 1H,  $-\text{NH}$ ), 6.85–8.20 (m, 37H, aromatics).

*cis,cis*-1,3,5-Cyclohexanetricarboxylic Acid, 1,3-Bis[3-(4'-cyano[1,1',4',1'']terphenyl-4-yloxy)propyl] Ester (5). The procedure for the synthesis of 4 was followed for 5 (0.70 g, 75%) by using 3-(4'-cyano-*p*-terphenyloxy)-1-propanol<sup>21</sup> (0.73 g, 2.20 mmol) instead of 4-(3-hydroxypropoxy)benzoic acid 4'-cyano-biphenyl-4-yl ester. <sup>1</sup>H NMR spectral data (400 MHz,  $\text{CDCl}_3$ ):

$\delta$  1.48–1.76 (m, 3H,  $\text{H}_{\text{ax}}$  from  $-\text{CH}_2-$ , cyclohexane), 2.16 (quintet, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 2.20–2.50 (m, 6H,  $\text{H}_{\text{eq}}$  from  $-\text{CH}_2-$  and  $\text{H}_{\text{ax}}$  from  $-\text{CH}-$ , cyclohexane), 4.09 (t, 4H,  $-\text{CH}_2-\text{OAr}$ ), 4.33 (t, 4H,  $-\text{COOCH}_2-$ ), 7.00 (d, 4H, aromatics), 7.57 (d, 4H, aromatics), 7.60–7.80 (m, 16H, aromatics).

*cis,cis*-1,3,5-Cyclohexanetricarboxylic Acid, 1,3-Bis[3-(4'-cyano[1,1',4',1'']terphenyl-4-yloxy)propyl] Ester 5-{4'-[[4'-[(S)-(-)-1'''-(Phenylethyl)]benzamide]-1''-oxy]benzoate-1'-oxy}ethyl Ester (II-S). The procedure for the synthesis of I-S was followed for II-S (0.23 g, 78%) by using 5 (0.2 g, 2.3 mmol) instead of 4. Anal. Calcd for  $\text{C}_{77}\text{H}_{67}\text{N}_3\text{O}_{12}$ : C, 75.41; H, 5.51;

## Scheme 1. Deterministic Synthesis of Chiral-Nematic GLCs



N, 3.43. Found: C, 75.27; H, 5.34; N, 3.27.  $^1\text{H}$  NMR spectral data (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.48–1.70 (m, 6H,  $\text{H}_{\text{ax}}$  from  $-\text{CH}_2-$  cyclohexane and  $-\text{CH}_3$  from chiral pendant), 2.08–2.28 (m, 4H,  $-\text{CH}_2-$  pendants), 2.28–2.50 (m, 6H,  $\text{H}_{\text{eq}}$  from  $-\text{CH}_2-$  and  $\text{H}_{\text{ax}}$  from  $-\text{CH}-$ , cyclohexane), 4.09–4.55 (m, 12H,  $-\text{CH}_2-$  from pendants), 5.36 (m, 1H,  $-\text{CH}$  from chiral pendant), 6.32 (d, 1H,  $-\text{NH}$ ), 6.80–8.20 (m, 37H, aromatics).

*cis,cis*-1,3,5-Cyclohexanetricarboxylic Acid, 1,3-Bis[3-(4'-cyano[1,1',1'']terphenyl-4-yloxy)propyl] Ester 5-{4'-[(R)-(+)-1''-(Phenylethyl)benzamide]-1''-oxy]benzoate-1'-oxy}ethyl Ester (**II-R**). The procedure for the synthesis of **II-S** was followed for **II-R** (0.22 g, 75%) by using (R)-(+)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide. Anal. Calcd for  $\text{C}_{77}\text{H}_{67}\text{N}_3\text{O}_{12}$ : C, 75.41; H, 5.51; N, 3.43. Found: C, 75.23; H, 5.42; N, 3.36.  $^1\text{H}$  NMR spectral data (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.48–1.70 (m, 6H,  $\text{H}_{\text{ax}}$  from  $-\text{CH}_2-$  cyclohexane and  $-\text{CH}_3$  from chiral pendant), 2.08–2.28 (m, 4H,  $-\text{CH}_2-$  pendants), 2.28–2.50 (m, 6H,  $\text{H}_{\text{eq}}$  from  $-\text{CH}_2-$  and  $\text{H}_{\text{ax}}$  from  $-\text{CH}-$ , cyclohexane), 4.05–4.55 (m, 12H,  $-\text{CH}_2-$  from pendants), 5.36 (m, 1H,  $-\text{CH}$  from chiral pendant), 6.32 (d, 1H,  $-\text{NH}$ ), 6.80–8.20 (m, 37H, aromatics).

*cis,cis*-1,3,5-Cyclohexanetricarboxylic Acid, 1,3,5-Tris[3-[4-(4'-cyanobiphenyl-4-yloxy)carbonyl]phenoxy]propyl] Ester (**III**). The target compound was synthesized via esterification of

*cis,cis*-cyclohexane-1,3,5-tricarboxylic acid with 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester following a previously published procedure.<sup>21</sup> Anal. Calcd for  $\text{C}_{78}\text{H}_{63}\text{N}_3\text{O}_{15}$ : C, 73.06; H, 4.95; N, 3.28. Found: C, 72.75; H, 4.67; N, 3.08.  $^1\text{H}$  NMR spectral data (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.48–1.76 (m, 3H,  $\text{H}_{\text{ax}}$  from  $-\text{CH}_2-$ , cyclohexane), 2.08–2.28 (m, 6H,  $-\text{CH}_2-$  pendants), 2.28–2.50 (m, 6H,  $\text{H}_{\text{eq}}$  from  $-\text{CH}_2-$  and  $\text{H}_{\text{ax}}$  from  $-\text{CH}-$ , cyclohexane), 4.00–4.55 (m, 12H,  $-\text{CH}_2-$  from pendants), 6.85–8.20 (m, 36H, aromatics).

1,3,5-Benzenetricarboxylic Acid, 1-*tert*-Butyl ester 3,5-Dimethyl Ester (**7**). 1,3,5-Benzenetricarboxylic acid, dimethyl ester (**6**) was prepared via monohydrolysis of trimethyl 1,3,5-benzenetricarboxylate following a literature procedure in 65% yield.<sup>29</sup> A solution of **6** (3.00 g, 12.59 mmol) and 1,1-carboxyldiimidazole (2.08 g, 12.59 mmol) in anhydrous *N,N*-dimethylformamide (18 mL) was stirred at 50 °C for 1 h before adding anhydrous *tert*-butyl alcohol (1.87 g, 25.19 mmol) and DBU (1.92 g, 12.59 mmol). Reaction was allowed to continue at 60 °C under argon for 48 h. Upon addition of  $\text{H}_2\text{O}$  (120 mL), the reaction mixture was acidified to pH 4 with a 2.5% HCl solution for extraction with methylene chloride. Combined

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methylene chloride extracts were washed with H<sub>2</sub>O and brine and then dried over anhydrous MgSO<sub>4</sub>. The crude product resulting from evaporation of the solvent was purified by flash chromatography on silica gel with a solvent gradient from 0 to 2% acetone in methylene chloride to yield **7** (3.25 g, 88%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.65 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C-), 4.0 (s, 6H, CH<sub>3</sub>COO-), 8.78–8.90 (m, 3H, Ar).

**1,3,5-Benzenetricarboxylic Acid, 1-*tert*-Butyl Ester (8).** To a solution of **7** (1.00 g, 3.40 mmol) in tetrahydrofuran (30 mL) was added a 0.1 N solution of NaOH (30 mL). The solution was maintained at pH 11.5 in the course of the reaction by adding a 1 N NaOH solution as needed. The reaction was carried out until both methyl esters were hydrolyzed as detected by TLC. The pH was then adjusted to 7 by adding a 5% HCl solution, and the volume was reduced by 50% via evaporation under reduced pressure. A precipitate formed upon addition of water (20 mL) and acidification by a 10% HCl solution. The solid was collected by filtration and further washed with water to yield **8** (0.80 g, 88%). <sup>1</sup>H NMR (400 MHz, DMSO): δ 1.59 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C-), 8.5–8.7 (m, 3H, Ar).

**1,3,5-Benzenetricarboxylic Acid, 1,3-Bis[3-[4-[(4'-cyanobiphenyl-4-yloxy)carbonyl]phenoxy]propyl] Ester (9).** To a solution of **8** (0.30 g, 1.10 mmol), 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester (0.82 g, 2.20 mmol), and triphenylphosphine (0.63 g, 2.42 mmol) in anhydrous tetrahydrofuran (12 mL) was added dropwise diethyl azodicarboxylate (0.46 g, 2.64 mmol). The reaction was carried out under argon at room temperature overnight. The solvent was then evaporated off under reduced pressure, and the solid residue was dissolved in methylene chloride for purification by flash column chromatography with a solvent gradient from 0 to 4% acetone in methylene chloride. The hydrolysis of *tert*-butyl ester was accomplished in 20 mL of methylene chloride with 20 mL of trifluoroacetic acid. Upon addition of methylene chloride (15 mL), the reaction mixture was washed sequentially with H<sub>2</sub>O and brine before drying over anhydrous MgSO<sub>4</sub>. The crude product resulting from evaporation of the solvent was purified by flash column chromatography with a solvent gradient from 1 to 6% acetone in methylene chloride. Precipitation from a methylene chloride solution into cold methanol resulted in solid product **9** (0.7 g, 68%). <sup>1</sup>H NMR (400 MHz, DMSO): δ 2.27 (m, 4H, -CH<sub>2</sub>-), 4.28 (t, 4H, -CH<sub>2</sub>OAr), 4.54 (t, 4H, COOCH<sub>2</sub>-), 7.00–8.80 (m, 27H, aromatics).

**1,3,5-Benzenetricarboxylic Acid, 1,3-bis[3-[4-[(4'-cyanobiphenyl-4-yloxy)carbonyl]phenoxy]propyl] Ester 5-{4'-[(S)-(-)-1''-(phenylethyl)]benzamide-1'-oxy]benzoate-1'-oxy}ethyl Ester (IV-S).** To a solution of **9** (0.25 g, 0.27 mmol), (S)-(-)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide (0.11 g, 0.28 mmol), and triphenylphosphine (0.077 g, 0.30 mmol) in anhydrous tetrahydrofuran (4 mL) was slowly added diethyl azodicarboxylate (0.056 g, 0.32 mmol). The reaction was carried out under argon at room temperature overnight. The solvent was evaporated off under reduced pressure, and the solid residue was dissolved in methylene chloride for purification by flash column chromatography with a solvent gradient from 0 to 4% acetone in methylene chloride. The solid product was collected by precipitation from a methylene chloride solution into methanol to yield **IV-S** (0.24 g, 67%). Anal. Calcd for C<sub>79</sub>H<sub>61</sub>N<sub>3</sub>O<sub>16</sub>: C, 72.52; H, 4.70; N, 3.21. Found: C, 72.05; H, 4.44; N, 3.18. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.63 (d, 3H, -CH<sub>3</sub> from chiral pendant), 2.37 (q, 4H, -CH<sub>2</sub>- pendants), 4.25 (t, 4H, -OCH<sub>2</sub>- from nematic pendants), 4.58 (t, 2H, -OCH<sub>2</sub>- from chiral pendants), 4.64 (t, 4H, -COOCH<sub>2</sub>- from nematic pendants), 4.81 (t, 2H, -COOCH<sub>2</sub>- from chiral pendants), 5.36 (m, 1H, -CH from chiral pendant), 6.34 (d, 1H, -NH), 6.85–9.00 (m, 40H, aromatics).

**1-{(S)-(-)-2'-[4'-[4''-(1''''-Phenylethyl)carbamoyl]phenoxy-carbonyl]phenoxy}ethoxy}-3,5-benzenedicarboxylic Acid, Bis[3-(4'-cyano-*p*-terphenyloxy)-1-propyl] Ester (V-S).** To a solution of 1-hydroxy-3,5-benzenedicarboxylic acid, bis[3-(4'-cyano-*p*-terphenyloxy)-1-propyl ester], (**10**; 0.500 g, 0.620 mmol), synthesized from 5-hydrophthalic acid following the procedures described elsewhere,<sup>25</sup> (S)-(-)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide (0.27 g, 0.667 mmol), and tri-

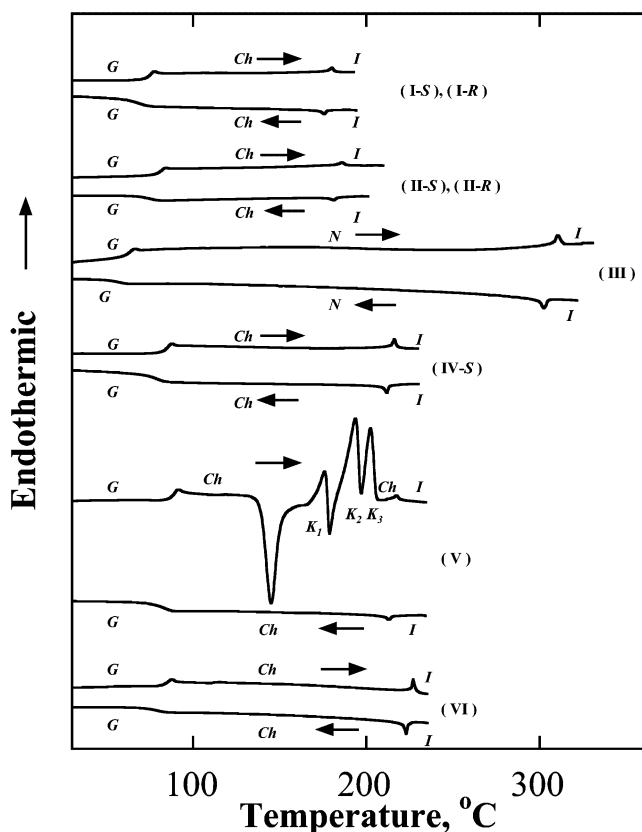
phenylphosphine (230 mg, 0.878 mmol) in 30 mL of anhydrous *N,N*-dimethylformamide and 30 mL of anhydrous tetrahydrofuran was added dropwise diethyl azodicarboxylate (0.14 mL, 0.879 mmol). After stirring at room temperature overnight, the reaction mixture was poured into 200 mL of methanol to afford a white precipitate, which was collected by filtration and then dissolved in 200 mL of methylene chloride. The resultant solution was washed with a 10% NaHCO<sub>3</sub> solution (200 mL × 2) and water (200 mL × 2) consecutively before drying over anhydrous MgSO<sub>4</sub>. Further purification was performed by silica gel column chromatography with methylene chloride/acetone (50:1) as the eluent to yield **V-S** (0.21 g, 28%). Anal. Calcd for C<sub>76</sub>H<sub>61</sub>N<sub>3</sub>O<sub>11</sub>: C, 76.56; H, 5.16; N, 3.53. Found: C, 76.09; H, 5.02; N, 3.64. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.64 (d, 3H, CHCH<sub>3</sub>), 2.31 (q, 4H, -CH<sub>2</sub>-), 4.20 (t, 4H, CH<sub>2</sub>CH<sub>2</sub>O), 4.44 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>O from chiral pendant), 4.61 (t, 4H, COOCH<sub>2</sub>CH<sub>2</sub>), 5.36 (m, 1H, -CH from chiral pendant), 6.32 (d, 1H, -NH), 6.35–8.36 (m, 40H, aromatic H).

**1-{3'-[Estra-1'',3'',5''(10'')-trien-17'-one-3-yl-oxy]-1'-propoxy}-3,5-benzenedicarboxylic Acid, Bis[3-(4'-cyano-*p*-terphenyloxy)-1-propyl] Ester (VI).** To a solution of 3-(2-hydroxypropoxy)-estra-1,3,5(10)-trien-17-one (0.22 g, 0.671 mmol), **10** (0.50 g, 0.620 mmol), and triphenylphosphine (0.23 g, 0.878 mmol) in 30 mL of anhydrous *N,N*-dimethylformamide and 30 mL of anhydrous tetrahydrofuran was slowly added diethyl azodicarboxylate (0.14 mL, 0.879 mmol). Upon stirring at room temperature overnight, the reaction mixture was poured into 200 mL of methanol to afford a white precipitate, which was collected by filtration and then dissolved in 200 mL of methylene chloride. The resultant solution was washed with a 10% NaHCO<sub>3</sub> solution and water consecutively before drying over anhydrous MgSO<sub>4</sub>. Further purification was performed by silica gel column chromatography with methylene chloride/acetone (100:1) as the eluent to yield **VI** (0.35 g, 50%). Anal. Calcd for C<sub>73</sub>H<sub>66</sub>N<sub>2</sub>O<sub>9</sub>: C, 78.61; H, 5.97; N, 2.51. Found: C, 78.18; H, 5.92; N, 2.48. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.91–2.90 (m, 27H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and H's on estrone), 4.26 (t, 2H, estrone-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 4.34 (m, 6H, estrone-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 4.59 (t, 4H, COOCH<sub>2</sub>CH), 6.67–8.30 (m, 30H, aromatic H).

#### Molecular Structures and Thermotropic Properties.

Molecular structures were elucidated with <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> (Avance-400, 400 MHz; Varian 200, 200 MHz) and elemental analysis (Quantitative Technologies, Inc.). Thermal transition temperatures were determined by differential scanning calorimetry (DSC; Perkin-Elmer DSC-7) with a continuous N<sub>2</sub> purge at 20 mL/min. Samples were preheated to beyond *T*<sub>c</sub> followed by heating at -20 °C/min down to -30 °C and then heating at 20 °C/min to beyond *T*<sub>c</sub>, furnishing the reported first cooling and second heating scans. Liquid-crystalline mesomorphism was characterized with hot-stage polarizing optical microscopy (DMLM, Leica, FP90 central processor and FP82 hot stage, Mettler, Toledo).

**Preparation and Characterization of Glassy Chiral-Nematic Films.** Optically flat fused silica substrates (25.4 mm diameter × 3 mm thickness, Esco Products; *n* = 1.458 at 589.6 nm) were coated with a nylon (for *T*<sub>c</sub> < 200 °C) or polyimide alignment (for *T*<sub>c</sub> > 200 °C) layer and uniaxially rubbed. Glassy chiral-nematic films, 4-μm thick as defined by glass fiber spacers (Bangs Laboratories), were prepared between two surface-treated substrates buffed in the same direction. Upon melting of a powdered sample, the fluid film was thermally annealed at 20 °C below *T*<sub>c</sub> for 30 min, except noted otherwise, before spontaneous cooling to room temperature by turning off the hot stage. Transmittance at normal incidence and reflectance at 6° off normal were measured with unpolarized incident light using a UV-vis-NIR spectrophotometer (Lambda-900, Perkin-Elmer). 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 (HNPB, Polaroid) and zero-order quarter waveplates (AO1521/4-355, Tower Optical Corp.) was employed to produce left- or right-handed (LH and RH) circularly polarized light. Transmittance of circularly



**Figure 2.** DSC heating and cooling scans at  $\pm 20$  °C/min of samples preheated to beyond  $T_c$ . Symbols: G, glassy; Ch, cholesteric; N, nematic; K, crystalline; I, isotropic.

polarized light was characterized by UV-vis-NIR spectrophotometry. A notch filter was comprised of two single-handed optical elements with opposite handedness, between which an index-matching fluid ( $n = 1.460$  at 589.6 nm) was filled. The buffering directions of alignment layers on the two single-handed elements were oriented perpendicular to each other.<sup>27</sup> The two reference cells referred to above for the characterization of single-handed elements were stacked together, with an index-matching fluid ( $n = 1.460$  at 589.6 nm) between the two, to serve as the reference for the characterization of a notch filter by UV-vis-NIR spectrophotometry. Cross sections of glassy chiral-nematic films were sputtered with approximately 100 Å of gold for imaging with scanning electron microscopy (LEO982 FESEM) to determine the helical pitch length.

### III. Results and Discussion

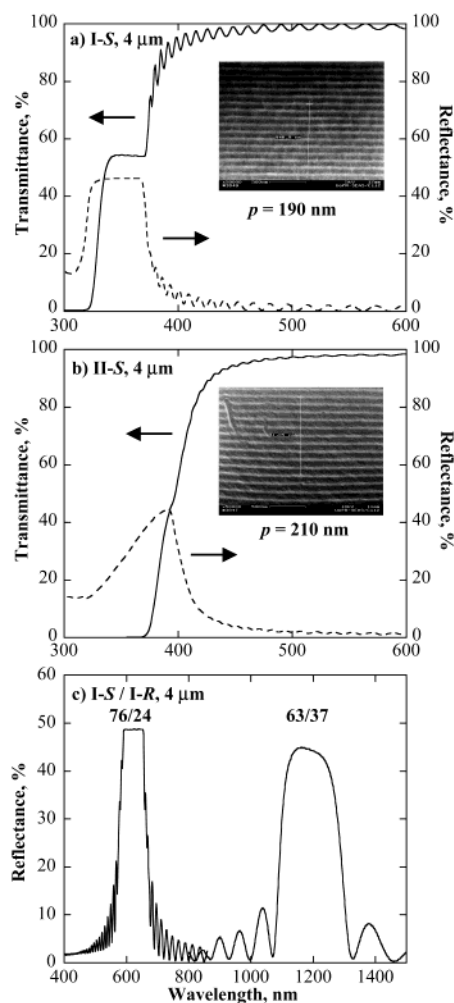
Chiral-nematic GLCs, as depicted in Figure 1, were synthesized following three distinct deterministic approaches (see Scheme 1). Based on a cyclohexane core and (*S*)- and (*R*)-1-phenylethylamine, **I-S** and **-R** and **II-S** and **-R** were synthesized starting with monohydrolysis of 1,3,5-cyclohexanetricarboxylic acid trimethyl ester by pig liver esterase.<sup>28</sup> DSC thermograms were gathered for samples that had been preheated beyond  $T_c$  followed by cooling to  $-30$  °C at a rate of  $-20$  °C/min and then heating at  $+20$  °C/min above  $T_c$ . Compiled in Figure 2 are the first cooling and second heating scans, where the liquid-crystalline order prevails below  $T_g$ . The heating and cooling scans exhibit no crystallization, indicating the morphological stability of these GLCs. From the heating scans shown in Figure 2,  $T_g$  and  $T_c$  are located at 73 and 175 °C for **I-S** and **-R** and at 82 and 186 °C for **II-S** and **-R**, respectively. The differences in transition temperatures between **I-S** and

**-R** or **II-S** and **-R** are within an experimental uncertainty of  $\pm 1$  °C. In both cases, the cholesteric fluid temperature range is over 100 °C, offering a major melt processing advantage over most of the previously reported material systems.<sup>19,26,27</sup> The broad mesomorphic fluid temperature range can be attributed to the high- $T_c$  nematic precursors to **I** and **II**: 286 °C for 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester and 310 °C with 3-(4'-cyano-*p*-terphenyloxy)-1-propanol. To assess the capability of the 4-cyano-4'-biphenylbenzoate group for the formation of a glassy nematic, **III** was also synthesized following a previously published procedure.<sup>21</sup> The DSC heating scan reveals a  $T_g$  and  $T_c$  at 67 and 310 °C, respectively, yielding an unusually broad nematic fluid temperature range. Furthermore, its morphological stability is demonstrated by the absence of crystallization in both the heating and cooling scans. In contrast, its counterpart with three [1,1',4',1'']-terphenyl-4-carbonitrile groups, namely, **XVII** and Figure 4 in a previous report,<sup>25a</sup> was found to exhibit smectic C and nematic mesomorphism in addition to a tendency to crystallize.

The supramolecular structure of a chiral-nematic liquid-crystal film is well documented.<sup>30</sup> Consisting of a helical stack of quasi-nematic layers in the Grandjean (or homogeneous) orientation, it is characterized by handedness and helical pitch length,  $p$ . Handedness describes the direction in which twisting of the nematic director occurs from one layer to the next, and  $p$  is defined as the distance over which the director rotates by 360°. The property of selective reflection can be described in terms of  $\lambda_R = p(n_e + n_o)/2$ , in which  $n_e$  and  $n_o$  are the extraordinary and ordinary refractive indices of the quasi-nematic layer, respectively. Let us consider incident unpolarized white light propagating through a LH film. Unpolarized light consists of equal amounts of LH and RH circularly polarized components. The LH circularly polarized component in the neighborhood of  $\lambda_R$  is selectively reflected, while the RH component is completely transmitted. A sufficiently thick, single-handed cholesteric film is capable of reflecting 50% of incident unpolarized light within the selective reflection band. Outside the selective reflection band, incident light is transmitted regardless of its polarization state. It follows that a stack of RH and LH chiral-nematic films tuned at the same  $\lambda_R$  will reflect 100% of incident unpolarized light within the selective reflection band without attenuating the rest of the spectrum.

To demonstrate the principle described above, samples of **I-S** and **II-S** were melt-processed into 4- $\mu$ m-thick, monodomain glassy chiral-nematic films between a pair of fused silica substrates for characterization with UV-vis-NIR spectrophotometry. The film of **I-S** exhibits a selective reflection band in the UV region, as shown in Figure 3a. The selective reflection band of the **II-S** film is obscured to a great extent (see Figure 3b) by the UV-vis absorption edge of the [1,1',4',1'']terphenyl-4-carbonitrile group. The glassy films of **I-S** and **II-S** were isolated from the substrates, and the cross sections were characterized by scanning electron microscopy. Based on the images presented as the insets in Figure 4a,b, the helical pitch length,  $p$ , was evaluated at 190 and

(30) Dreher, R.; Meier, G. *Phys. Rev. A* **1973**, *8*, 1616.



**Figure 3.** Transmission and reflection spectra of unpolared light through a 4- $\mu\text{m}$ -thick glassy chiral-nematic film of (a) **I-S** and (b) **II-S** with the scanning electron microscopic images included as insets for the determination of the helical pitch length. (c) Reflection spectra of 4- $\mu\text{m}$ -thick films comprising **I-S/I-R** at mass ratios of 76/24 and 63/37.

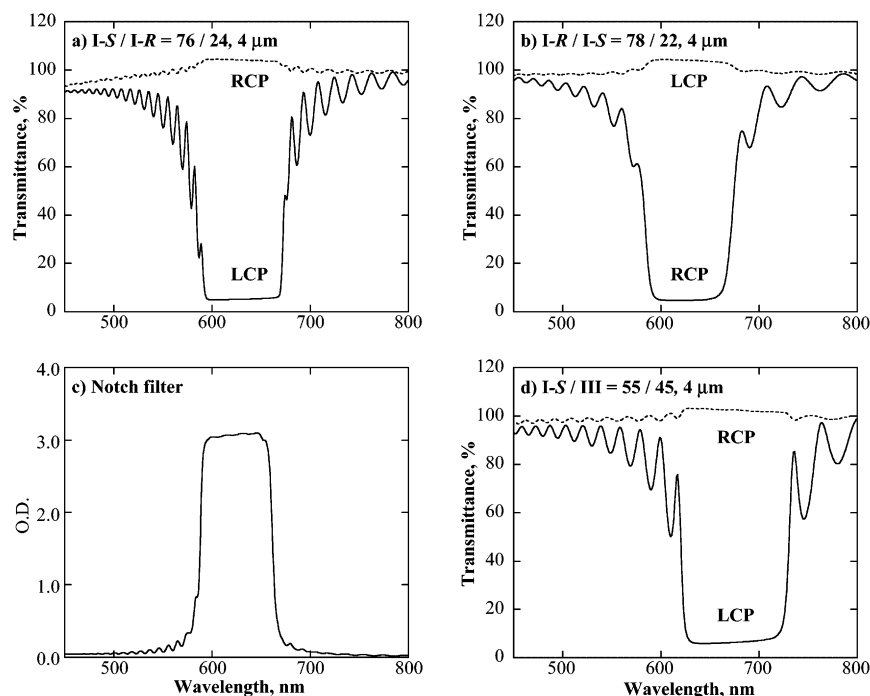
210 nm for **I-S** and **II-S**, respectively. The reported  $p$  values are accompanied by an experimental uncertainty of  $\pm 5$  nm. Individual films comprising pure **I-S** and **I-R** are essentially circular polarizers of opposite handedness, and a stack of the two films is expected to constitute an optical notch filter, all in the UV region. Mixtures of **I-S** and **I-R** at varying ratios can be readily prepared for use as circular polarizers, and hence optical notch filters and reflectors, across the visible to the infrared region, as illustrated in Figure 3c for mass ratios of 76/24 and 63/37.

As shown in Figure 4a, a 4- $\mu\text{m}$ -thick film of **I-S/I-R** at a mass ratio of 76/24 ( $T_g = 73^\circ\text{C}$ ;  $T_c = 176^\circ\text{C}$ ) is LH because it selectively reflects the LH circularly polarized component of incident unpolarized light while transmitting the RH component. The fact that there is a 5% leakage of LH circularly polarized light through a LH film and that the transmittance of RH circularly polarized light reaches 105% can be attributed to two factors: (i) handedness is preserved upon reflection from a chiral-nematic film and (ii) handedness is reversed upon reflection from a glass-air interface.<sup>27</sup> The observed 100% difference in transmittance between the two opposite circularly polarized components indicates

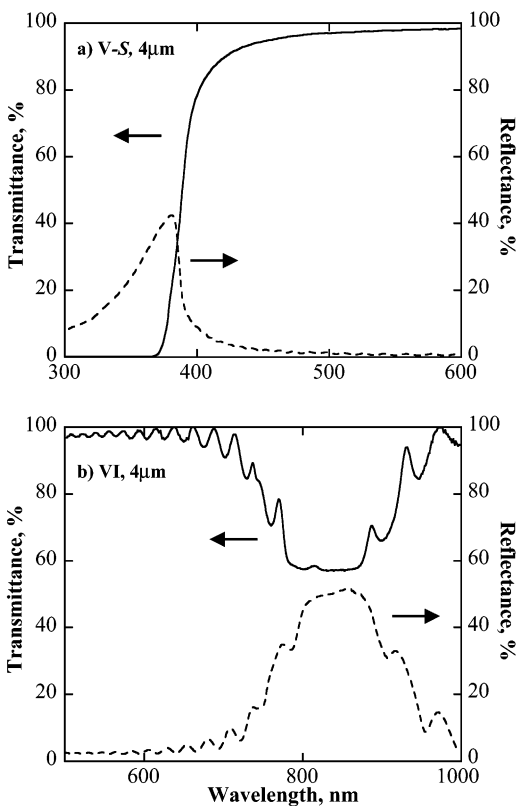
that this film is a high-performance circular polarizer. By analogy, a 4- $\mu\text{m}$ -thick chiral-nematic film comprising **I-R/I-S** at a mass ratio of 78/22 ( $T_g = 72^\circ\text{C}$ ;  $T_c = 176^\circ\text{C}$ ) is RH, as shown in Figure 4b. Note that the minor disparity in the chemical composition, 76/24 vs 78/22, needed to match up the two selective reflection bands might be because of the difference in the enantiomeric purity of the chiral precursors, (*S*)- and (*R*)-1-phenylethylamine. These two films have their selective reflection bands centered at  $\lambda_R = 625$  nm, and a stack of the two results in an optical notch filter with an extinction of 3.06 optical density units (see Figure 4c). The observed extinction is about 0.6 optical density units less than that in our previous report<sup>27</sup> in part because of the thinner films used here, 4 vs 8  $\mu\text{m}$ . As an alternative approach to wavelength tunability, a 4- $\mu\text{m}$ -thick film consisting of **I-S/III** at a mass ratio of 55/45 ( $T_g = 65^\circ\text{C}$ ;  $T_c = 239^\circ\text{C}$ ) showed a selective reflection band centered at 672 nm with a LH supramolecular structure (see Figure 4d). Note that the handedness of the **I-S/I-R** system is determined by that of the major component, while the handedness of the **I-S/III** system is determined by that of **I-S**.

Two additional approaches to the deterministic synthesis of chiral nematics were pursued. Monohydrolysis of 1,3,5-benzenetricarboxylic acid trimethyl ester was accomplished following a literature procedure<sup>29</sup> as the first step toward the synthesis of **IV-S**; see Scheme 1B. According to the DSC thermograms, **IV-S** is a morphologically stable glassy chiral nematic with a  $T_g$  at  $86^\circ\text{C}$  and a  $T_c$  at  $216^\circ\text{C}$  (based on the heating scan). A comparison of **IV-S** with **I-S** suggests that the benzene core tends to elevate phase transition temperatures over the cyclohexane core. A 4- $\mu\text{m}$ -thick monodomain film of **IV-S** yielded a selective reflection band in the UV region and a  $p = 188$  nm. With (*S*)-1-phenylethylamine as the chiral building block, a LH helical structure emerged, as in the case of **I-S** and **II-S**. Apparently, with the same nematic and chiral pendants, the helical pitch length is rather insensitive to the structure of the central core. The third approach to the deterministic synthesis of chiral nematics was conducted using 5-hydroxyisophthalic acid as the central core, which has also been incorporated in high-temperature glassy nematics.<sup>25</sup> As an illustration of the methodology, **V-S** was synthesized according to Scheme 1C for a comparison with **II-S** in terms of thermotropic and optical properties. The DSC heating scan shown in Figure 2 indicates that the benzene core or the ether linkage to the chiral pendant in **V-S** is responsible for the inferior morphological stability in view of its tendency to crystallize. Nevertheless,  $T_g$  and  $T_c$  are readily identifiable at 89 and  $217^\circ\text{C}$ , respectively. Because no crystallization was observed on cooling, the preparation of a glassy chiral-nematic film is feasible through melt processing. The absorption and reflection spectra presented for **V-S** in Figure 5a are similar to those of **II-S** shown in Figure 3b. An attempt to improve the morphological stability was successfully made using (+)-estrone as the chiral building block for **VI**. The DSC heating scan shown in Figure 2 reveals  $T_g$  and  $T_c$  at 82 and  $225^\circ\text{C}$ , respectively. As shown in Figure 5b, a glassy chiral-nematic film of **VI** has a LH helical structure with a selective reflection band centered at 830 nm. Left at room temperature for





**Figure 4.** Transmission spectra of circularly polarized light through (a) a 4- $\mu\text{m}$ -thick glassy chiral-nematic film comprising **I-S**/**I-R** at a mass ratio of 76/24 and (b) a 4- $\mu\text{m}$ -thick RH glassy chiral-nematic film comprising **I-R**/**I-S** at a mass ratio of 78/22. (c) Transmission spectrum of unpolarized light through a notch filter consisting of a stack of the single-handed films shown in parts a and b. (d) Transmission spectrum of circularly polarized light through a 4- $\mu\text{m}$ -thick glassy chiral-nematic film comprising **I-S**/**III** at a mass ratio of 55/45; this film was annealed at 140 °C for 3 h before spontaneous cooling to room temperature.



**Figure 5.** Transmission and reflection spectra of unpolarized light through a 4- $\mu\text{m}$ -thick glassy chiral-nematic film of (a) **V-S** and (b) **VI**.

up to 2 years, all of the glassy chiral-nematic films prepared for this study showed no evidence of crystallization, a demonstration of morphological stability on a long-term basis.

#### IV. Conclusions

Three distinct approaches were explored for the deterministic synthesis of chiral-nematic GLCs: mono-hydrolysis of the trimethyl ester of 1,3,5-cyclohexanetricarboxylic acid and that of 1,3,5-benzenetricarboxylic acid as well as using 5-hydroxisophthalic acid as the central core. Each chiral-nematic molecule consists of two nematic groups and one chiral group chemically bonded to a benzene or cyclohexane core. Specifically, 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester and 3-(4'-cyano-*p*-terphenyloxy)-1-propanol were used as nematogenic precursors and (*S*)- and (*R*)-1-(phenylethyl)-4-[[4-(2-hydroxyethoxy)benzoyl]oxy]benzamide and (+)-estrone as chiral precursors. A high-temperature glassy nematic was also prepared with three 4-cyano-4'-biphenylbenzoate groups to cyclohexane. The resultant GLCs were characterized by DSC, hot-stage polarizing microscopy, transmission and reflection spectrophotometry, and scanning electron microscopy. Key findings are recapitulated as follows:

(1) The glassy chiral nematics showed a  $T_g$  from 67 to 82 °C and a cholesteric fluid temperature range over 100 °C due in part to the high clearing temperatures of the nematic precursors. A glassy nematic showed a  $T_g$  at 67 °C and a  $T_c$  at 310 °C, an unusually broad nematic fluid temperature range.

(2) The chiral pendant containing (*R*)- and (*S*)-1-phenylethylamine resulted in a helical pitch length from 188 to 210 nm, yielding a selective reflection band in the UV region. In contrast, (+)-estrone as the chiral pendant led to a selective reflection in the NIR region.

(3) Selective reflection wavelength can be tuned across the visible region to the infrared region by mixing a pair of enantiomeric chiral nematics at varying ratios for the fabrication of high-performance circular polarizers and



optical notch filters and reflectors. Alternatively, tunability can be accomplished by mixing a chiral nematic with a nematic at varying ratios.

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**Supporting Information Available:** Synthesis, purification, and characterization of 4-(3-hydroxypropoxy)benzoic acid 4'-cyanobiphenyl-4-yl ester and 3-(2-hydroxypropoxy)estra-1,3,5(10)-trien-17-one. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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