Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Liquid Crystallinity-Embodied Imidazolium-Based Ionic Liquids and Their Chiral Mesophases Induced by Axially Chiral *Tetra*-Substituted Binaphthyl Derivatives

Sangbum Ahn, Shohei Yamakawa, and Kazuo Akagi*

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

EMAIL ADDRESS: akagi@fps.polym.kyoto-u.ac.jp

♦**Contents**

Methods

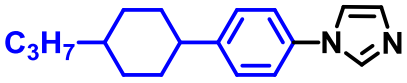
Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured in chloroform-*d* using ethereal EX400 400 MHz or JEOL AL-400 400 MHz NMR spectrometer. Chemical shifts are represented in parts per million downfield from tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed at Microanalytical Center of Kyoto University. High-resolution mass spectra (HRMS) were measured at the Technical Center of Department of Synthetic Chemistry and Biological Chemistry of Kyoto University. Microscope observation was carried out under crossed nicols using a Carl Zeiss Axio Imager M1m polarizing microscope equipped with a Carl Zeiss AxioCam MRc5 digital camera and a LinkamTH600PM and L600 heating and cooling stage with temperature control. Phase transition temperatures were determined using a TA Instrument Q-100 differential scanning calorimeter (DSC) with a constant heating/cooling rate of 2°C/min. X-Ray diffraction (XRD) measurements were performed with a SmartLab 9 kW, 45 kV–200 mA; CuKα_1 target wavelength (1.5406 nm), CBO-f (point-like beam optic), parallel-beam (PB mode), slit (5°, 0.5 mm, 1 mm), 2D detector (PILATUS 100K, 150 mm) and 5 degrees per minute, Rigaku, Japan. Specific rotations of chiral dopants were measured by Polarimeter (JASCO P-2300). The helical twisting power (HTP) of chiral dopants was measured by using Cano wedge cell. The N*-LC systems were prepared by adding nematic host LC (4-pentyl-4′-cyanobiphenyl; **5CB**) and chiral dopants (**5CB**: dopant = 100: 0.5 molar ratio). The HTP values is $\beta=(pc)^{-1}$, where β is the helical twisting power, p is helical pitch, and c is the concentration of the chiral dopant. The pitch was determined according to the equation $p = 2a \times \tan\theta$, where a represents the distance between the Grandjean lines and θ is the wedge angle of wedge cells (EHC, KCRK-03, $\tan\theta = 0.0083$). The ionic conductivity of LCILs was measured by using

Solartron 1260 analyzer with a Linkam TH600PM and L600 as temperature controller. The bulk resistance of LCILs was measured by the impedance Nyquist plots. The ionic conductivity of LCILs was calculated by using the area and the distance between the electrodes.

Materials

All experiments were performed under an argon atmosphere using Schlenk/vacuum line techniques. Tetrahydrofuran (THF), toluene, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and H_2O were distilled prior to use. 1-Bromo-4-(4-propylcyclohexyl)benzene (**PCH3Br)** was purchased from Kanto Chemical, Inc. and used directly for synthesis.

1. Synthesis of PCH3-IM



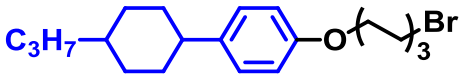
PCH3-IM

1-Bromo-4-(4-propylcyclohexyl)benzene (**PCH3Br**, 5.00 g, 17.78 mmol), Imidazole (1.82 g, 26.67 mmol), CuI (0.68 g, 3.56 mmol), Cs_2CO_3 (11.59g, 35.56 mmol), and dimethylformamide (DMF) were stirred in a three-necked flask under dry argon flow at 120 °C. After 3 days, the solvent of reaction mixture was removed under reduced pressure, and the obtained residue was extracted with chloroform, washed with water and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude

product was passed through a column chromatograph with chloroform, and purified by recrystallisation with hexane and chloroform. A white solid of **PCH3-IM** (2.96 g) was obtained (yield: 62 %). ^{1}H-NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 0.91 (m, 3H, –C*H*$_3$), 1.08 (m, 2H, –C*H*$_2$–), 1.23 (m, 2H, –C*H*$_2$–), 1.33–2.50 (m, 10H, *cyclohexane* –C*H*$_2$–),7.18–7.24 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.3 (m, 4H, phenyl–*H* and imidazole *H*), 7.81 (s, 1H, imidazole *H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.40, 20.03, 33.47, 34.34, 36.98, 39.66, 44.17, 118.37, 121.55, 128.17, 130.26, 135.26, 135.69, 147.49. Anal., calcd for $C_{18}H_{24}N_2$: C, 80.55 %; H, 9.01 %; N, 10.44 %, Found: C, 80.39 %; H, 8.85 %; N, 10.39 %. HRMS (FAB, *m/z*): Calc. 268.1939, Found: 269.2007.

2. Synthesis of mesogenic groups with flexible spacers

1-(6-Bromohexyloxy)-4-propylcyclohexyl)benzene; **Br-C$_6$-PCH3**

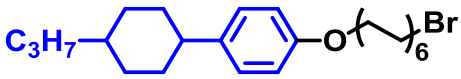


Br-C$_6$-PCH3

6-Bromo-1-hexanol (1.50 mL, 10.99 mmol) was added to the solution of 4-(4-propylcyclohexyl)phenol (2.00 g, 9.16 mmol), TPP (3.12 g, 11.91 mmol) in THF in Ar condition. The mixture was cooled to 0 °C and dropwised DEAD (2.2 mol/L in toluene, 6.25 mL, 13.74 mmol) for overnight at room temperature. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **Br-C$_6$-PCH3** 3.14 g (yield = 90 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.9 (m, 3H,

–CH_3), 1.07–1.53 (m, 12H, –CH_2–), 1.77–1.90 (m, 8H, *cyclohexane*–CH_2–), 2.40 (t, 1H, *J*= 12.0 and 12.0 Hz, phenyl–*cyclohexane*–), 3.43 (t, 2H, *J*= 6.8 and 6.8 Hz, Ar–O–CH_2–), 3.95 (t, 2H, *J*= 6.4 and 6.8 Hz, Ar–COO–CH_2–), 6.82 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.12 (d, 2H, *J*= 8.8 Hz, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.43, 20.05, 25.35, 27.95, 29.19, 32.73, 33.65, 33.79, 34.60, 37.04, 39.76, 43.75, 67.68, 114.25, 127.61, 140.06, 157.15. HRMS (FAB, *m/z*): Calc. 380.1715, Found: 380.2053. Anal. Calcd for$C_{21}H_{33}BrO$: C, 66.13 %; H, 8.72 %; Br, 20.95 %; O, 4.19 %, Found: C, 65.88 %; H, 8.71 %; Br, 21.19 %; O, 4.36 %.

1-(12-Bromododecyloxy)-4-propylcyclohexyl)benzene;**Br-C_{12}-PCH3**

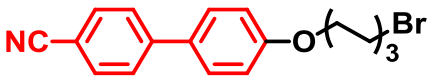


Br-C_{12}-PCH3

12-Bromo-1-dodecanol (2.91 g, 10.99 mmol) was added to the solution of 4-(4-propylcyclohexyl)phenol (2.00 g, 9.16 mmol), TPP (3.12 g, 11.91 mmol) in THF in Ar condition. The mixture was cooled to 0 °C and dropwised DEAD (6.25 mL, 2.2 mol/L in toluene, 13.74 mmol) for overnight at room temperature. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **Br-C_{12}-PCH3** 4.8 g (yield = 94 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.92 (m, 3H, –CH_3), 1.07–1.53 (m, 25H, –CH_2–), 1.72-1.88 (m, 8H, *cyclohexane*–CH_2–), 2.40 (t, 1H, *J*= 12.0 and 12.0 Hz, phenyl–*cyclohexane*–), 3.42 (t, 2H, *J*= 7.2 and 6.8 Hz, Ar–O–CH_2–), 3.93

(t, 2H, *J*= 6.4 and 6.8 Hz, Ar–COO–C*H*$_2$–), 6.83 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.11 (d, 2H, *J*= 8.4 Hz, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.42, 20.05, 26.08, 28.18, 28.77, 29.37, 29.39, 29.43, 29.51, 29.53, 29.55, 32.85, 33.65, 34.02, 34.60, 37.04, 39.76, 43.74, 67.96, 114.25, 127.57, 139.93, 157.24. HRMS (FAB, *m/z*): Calc. 464.2654, Found: 465.1353. Anal. Calcd for$C_{27}H_{45}BrO$: C, 69.66 %; H, 9.74 %; Br, 17.16 %; O, 3.44 %, Found: C, 69.58 %; H, 9.79 %; O, 3.43 %.

4′-(6-Bromohexyloxy)-1,1′-biphenyl-4-carbonitrile; **Br-C$_6$-CB**

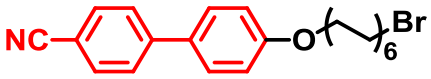


Br-C$_6$-CB

Into a 250 mL round-bottom flask was added 4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (3.00 g, 15.37 mmol), 1,6-dibromohexane (18.63 mL, 122.94 mmol), and K_2CO_3 (4.25 g, 30.74 mmol) in acetone (100 mL). The mixture was refluxed for 24 hr at 60 °C and then cooled to room temperature. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **Br-C$_6$-CB** 4.73g (yield = 86 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 1.52 (m, 4H, –C*H*$_2$–), 1.82–1.90 (m, 4H, –C*H*$_2$–), 3.42 (t, 2H, *J*=6.8 and 6.4 Hz, –C*H*$_2$–Br), 4.00 (t, 2H, *J*= 6.0 and 6.4 Hz, Ar–O–C*H*$_2$–), 6.99 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.5 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.65 (d, 2H, *J*= 8.8 Hz, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 25.27, 27.89, 29.03, 32.65, 33.76, 67.88, 110.04, 115.08, 119.08, 127.05, 128.32, 131.30, 132.54, 145.21,

159.71. HRMS (FAB, *m/z*): Calc. 357.0728, Found: 358.0793. Anal. Calcd for$C_{19}H_{20}BrNO$: C, 63.70 %; H, 5.63 %; Br, 22.30 %; N, 3.91 %; O, 4.47 %, Found: C, 63.47 %; H, 5.63 %; Br, 22.56 %; N, 3.90 %; O, 4.62 %.

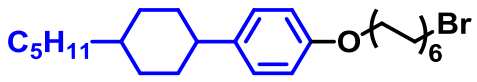
4′-(12-Bromododecyloxy)-1,1′-biphenyl-4-carbonitrile; **Br-C_{12}-CB**



Br-C_{12}-CB

Into a 250 mL round-bottom flask was added 4′-hydroxy-[1,1′-biphenyl]-4-carbonitrile (3.00 g, 15.37 mmol), 1,12-dibromododecane (40.34 g, 122.94 mmol), and K_2CO_3 (4.25 g, 30.74 mmol) in acetone (100 mL). The mixture was refluxed for 24 hr at 60 °C and then cooled to room temperature. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **Br-C_{12}-CB** 5.98g (yield = 88 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 1.29–1.57 (m, 16H, –C*H*$_2$–), 1.77–1.89 (m, 4H, –C*H*$_2$–), 3.42 (t, 2H, *J*= 6.8 and 6.8 Hz, –C*H*$_2$–Br), 4.00 (t, 2H, *J*= 6.8 and 6.4 Hz, Ar–O–C*H*$_2$–), 6.99 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.53 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.69 (d, 2H, *J*= 8.8 Hz, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 26.03, 28.18, 28.76, 29.23, 29.43, 29.51, 29.53, 32.84, 34.03, 68.18, 110.05, 115.11, 119.10, 127.07, 128.31, 131.25, 132.56, 145.29, 159.83. HRMS (FAB, *m/z*): Calc. 441.1667, Found: 442.1731 (M+H). Anal. Calcd for$C_{25}H_{32}BrNO$: C, 67.87 %; H, 7.29 %; Br, 18.06 %; N, 3.17 %; O, 3.62 %, Found: C, 67.93 %; H, 7.49 %; Br, 18.12 %; N, 3.14 %; O, 3.58 %.

1-(12-Bromododecyloxy)-4-pentylcyclohexylbenzene; **Br-C_{12}-PCH5**

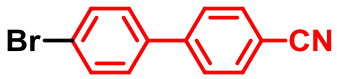


Br-C_{12}-PCH5

12-Bromo-1-dodecanol (3.88 g, 14.61 mmol) was added to the solution of 4-(4-propylcyclohexyl)phenol (3.00 g, 12.17 mmol), TPP (4.15 g, 15.83 mmol) in THF in Ar condition. The mixture was cooled to 0 °C and dropwised DEAD (8.30 mL, 2.2 mol/L in toluene, 18.26 mmol) overnight at room temperature. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **Br-C_{12}-PCH5** 4.8 g (yield = 92 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ =0.87-0.91 (t, 3H, *J*= 7.2 and 7.6 Hz, –C*H*$_3$), 1.00–1.04 (m, 2H, –C*H*$_2$–), 1.28–1.41 (m, 20H, –C*H*$_2$–), 1.72–1.87 (m, 8H,*cyclohexane*–C*H*$_2$–), 2.40 (t, 1H, *J*= 12.0 and 12.0 Hz, phenyl–*cyclohexane*–), 3.40–3.42 (t, 2H, *J*= 6.8 and 6.8 Hz, Ar–O–C*H*$_2$–), 3.90–3.93 (t, 2H, *J*= 6.4 and 6.8 Hz, Ar–COO–C*H*$_2$–), 6.80–6.83 (d, 2H, *J*= 8.8 Hz, phenyl–*H*), 7.09–7.12 (d, 2H, *J*= 8.8 Hz, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.13, 22.73, 26.08, 26.68, 28.20, 28.78, 29.40, 29.44, 29.52, 29.53, 29.56, 32.24, 32.86, 33.69, 34.04, 37.34, 37.42, 43.75, 67.96, 114.25, 127.58, 139.93, 157.24. HRMS (FAB, *m/z*): Calc. 492.2967, Found: 493.3038 (M+H). Anal. Calcd for$C_{29}H_{49}BrO$: C, 70.57 %; H, 10.01 %; Br, 16.19 %; O, 3.24 %, Found:C, 70.57 %; H, 10.23 %, O, 3.02 %.

3. Synthesis of chiral dopants

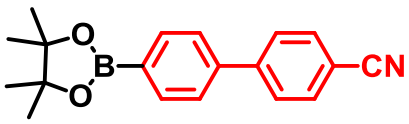
4′-Bromo-(1,1'-biphenyl)-4-carbonitrile; **1**[1]



1

4,4′-Dibromo-1,1′-biphenyl (4.50 g, 14.42 mmol) and copper(I) cyanide (1.29 g, 14.42 mmol) refluxed in DMF for 6 hrs. The organic solvent was removed by rotary evaporation. The mixture was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) and recrystallisation from ethanol afforded **1** 2.2 g (yield = 59.1 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ =7.44–7.47 (m, 2H, phenyl–*H*), 7.59–7.65 (m, 4H, phenyl–*H*), 7.72–7.74 (m, 2H, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 111.36, 118.73, 12.184, 127.54, 128.77, 129.01, 129.01, 132.29, 132.41, 132.72, 133.00, 138.06, 144.42. HRMS (FAB, *m/z*): Calc. 256.9840, Found: 256.9909. Anal. Calcd for$C_{13}H_8BrN$: C, 60.49 %; H, 3.12 %; Br, 30.96 %; N, 5.43 %, Found: C, 60.28 %; H, 3.30 %; Br, 30.73 %; N 5.40 %.

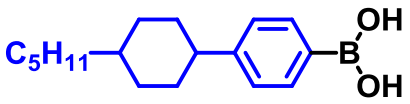
4′-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1′-biphenyl-4-carbonitrile; **2**[2]



2

4′-Bromo-(1,1′-biphenyl)-4-carbonitrile (1.00 g, 3.87 mmol), bis(pinacolato)diboron (1.08 g, 4.26 mmol), potassium acetate (1.14 g, 11.63 mmol), and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) ($Pd(dppf)Cl_2$) (85.1 mg, 0.12 mmol) were added in DMSO. The mixture was refluxed for 48 hr at 80 °C and then cooled to room temperature. The crude product was purified by silica gel column chromatography (eluents: EtOAc /*n*-hexane = 0.5) afforded **2** 0.91 g (yield = 76.7 %). ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ =1.37 (s, 12H, –C*H*$_3$), 7.59–7.61 (d, 2H, *J*= 8.0 Hz, phenyl–*H*), 7.69–7.74 (m, 4H, phenyl–*H*), 7.91–7.93 (d, 2H, *J*= 8.4 Hz, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 24.89, 25.03, 84.03, 111.16, 118.91, 126.50, 127.83, 132.60, 135.52, 141.67, 145.47. HRMS (FAB, *m/z*): Calc. 305.1587, Found: 306.1659 (M+H). Anal. Calcd for$C_{19}H_{20}BNO_2$: C, 74.78 %; H, 6.61 %; B, 3.54 %; N, 4.59 %; O, 10.48 %, Found: C, 74.86 %; H, 6.80 %; N, 4.48 %.

4-(4-Pentylcyclohexyl)phenylboronic acid; **3**

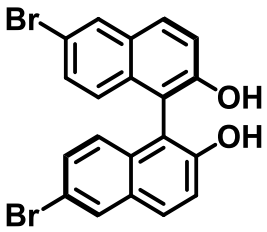


3

1-Bromo-4-(4-pentylcyclohexyl)benzene (5.00 g, 16.17 mmol), Mg (0.78 g, 32.33 mmol) were stirred in dried THF for 5 hrs. The mixture was cooling down −78 ^{o}C and dropwised solution of trimethyl borate (3.60 mL, 32.33 mmol) in THF. The reaction was stirred for 12 hr and then added HCl and ethanol. The crude product was extracted with H_2O and $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. Purification by silica gel column chromatography (eluents: $CHCl_3$→ethyl acetate) afforded **3**

2.44 g (yield = 55 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.87–0.891 (m, 3H, –C*H*$_3$), 1.04–1.09 (m, 2H, –C*H*$_2$–), 1.25–1.32 (m, 7H, –C*H*$_2$– and cyclohexane *H*–phenyl), 1.45–1.95 (m, 8H, cyclohexane–*H*), 2.49–2.55 (t, 1H, *J*= 12.0 and 12.4 Hz, cyclohexane *H*–phenyl), 7.27 (m, 1H, phenyl–*H*), 7.34–7.36 (d, 2H, *J*=8.0 Hz, phenyl–*H*), 7.65–7.67 (d, 1H, *J*=7.6 Hz, phenyl–*H*), 8.14–8.16 (d, 1H, *J*= 7.6 Hz, phenyl –*H*).

(*R*)-6,6′-Dibromo-(1,1′-binaphthalene)-2,2′-diol; **(*R*)-4**

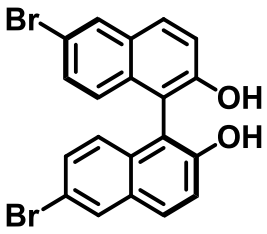


(*R*)-4

Bromine (0.79 ml, 15.37 mmol) was added slowly to a solution of (*R*)-(1,1′-binaphthalene)-2,2′-diol (2.00 g, 6.96 mmol) in CH_2Cl_2 at –78 ^{o}C. The resulting mixture was warmed to room temperature. The reaction mixture was cooled to 0 ^{o}C, and a solution of $Na_2S_2O_3$ in water was added. The residue extracted with H_2O and $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. Purification by silica gel column chromatography (eluents:$CHCl_3$) and reprecipitation (*n*-hexane)afforded **(*R*)-4** 2.9 g (yield = 94 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 6.94–6.96 (d, 2H, *J*=8.8 Hz, naphthalene–*H*), 7.35–7.39 (m, 4H, naphthalene–*H*), 7.87–7.89 (d, 2H, *J*=9.2 Hz, naphthalene–*H*), 8.04–8.04(d, 2H, *J*=2.0 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 110.63, 118.01, 118.97, 125.87, 130.45, 130.58,

131.88, 152.97. HRMS (FAB, *m/z*): Calc. 441.9204, Found: 440.9140 (M-H).

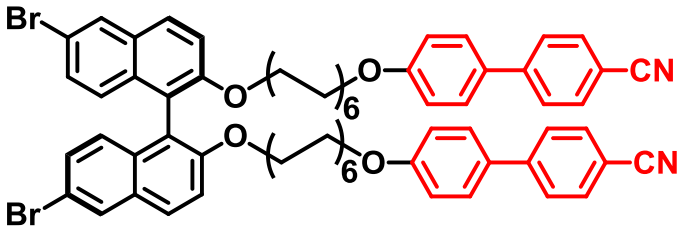
(*S*)-6,6′-Dibromo-(1,1′-binaphthalene)-2,2′-diol; **(*S*)-4**



(*S*)-4

Bromine (0.79 ml, 15.37 mmol) was added slowly to a solution of (*S*)-(1,1′-binaphthalene)-2,2′-diol (2.00 g, 6.96 mmol) in CH_2Cl_2 at −78 ^oC. The resulting mixture was warmed to room temperature. The reaction mixture was cooled to 0 ^oC, and a solution of $Na_2S_2O_3$ in water was added. The residue extracted with H_2O and $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. Purification by silica gel column chromatography (eluents:$CHCl_3$) and reprecipitation (*n*-hexane) afforded **(*S*)-4** 2.78 g (yield = 90 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 6.94–6.96 (d, 2H, *J*=8.8 Hz, naphthalene–*H*), 7.35–7.39 (m, 4H, naphthalene–*H*), 7.87–7.89 (d, 2H, *J*=9.2 Hz, naphthalene–*H*), 8.04–8.04(d, 2H, *J*=2.0 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 110.64, 118.01, 118.96, 125.87, 130.44, 130.56, 130.67, 130.86, 131.87, 152.95. HRMS (FAB, *m/z*): Calc. 441.9204, Found: 440.9139 (M–H).

(*R*)-2,2′-CB012-6,6′-Br-binaphthalene; **(*R*)-5**

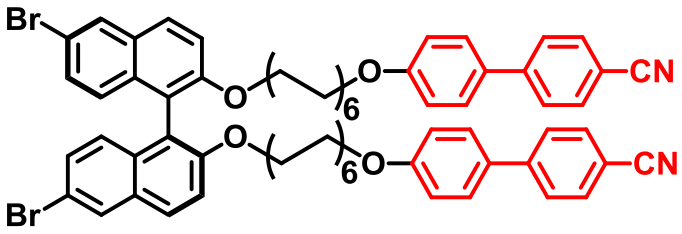


(*R*)-5

(*R*)-4 (1.00 g, 2.25 mmol), K_2CO_3 (1.24 g, 9.0 mmol), and **Br-C_{12}-CB** (2.19 g, 4.95 mmol) were added in acetone. The mixture was refluxed for 48 hr at 60 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$) afforded **(*R*)-5** 2.25g (yield = 86 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ =0.88 (m, 4H, –C*H*$_2$–), 0.99 (m, 8H, –C*H*$_2$–), 1.11(m, 4H, –C*H*$_2$–), 1.20–1.47 (m, 20H, –C*H*$_2$–), 1.79–1.82 (m, 4H, –C*H*$_2$–), 3.88–4.02 (m, 8H, –O–C*H*$_2$–), 6.96–6.99 (m, 6H, –O–phenyl–*H* and naphthalene–*H*), 7.24–7.26 (m, 2H, biphenyl–*H*), 7.38–7.41 (d, 2H, *J*= 9.2 Hz, biphenyl–*H*), 7.50–7.52 (d, 4H, *J*= 8.8 Hz, biphenyl–*H*), 7.62–7.64 (d, 4H, *J*= 8.4 Hz, biphenyl–*H*), 7.67–7.69 (d, 4H, *J*= 8.0 Hz, naphthalene–*H*), 7.81–7.83 (d, 2H, *J*= 8.8 Hz, naphthalene–*H*), 7.98–7.99 (d, 2H, *J*= 1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.89, 15.30, 18.35, 18.48, 18.64, 18.69, 18.71, 18.80, 57.37, 58.72, 98.96, 99.20, 104.22, 105.54, 106.36, 108.19, 109.20, 116.16, 117.41, 117.46, 118.54, 118.84, 119.30, 120.37, 121.64, 121.67, 134.35, 143.83, 148.88. HRMS (FAB, *m/z*): Calc. 1164.4015, Found: 1165.4082 (M+H). Anal. Calcd for$C_{70}H_{74}Br_2N_2O_4$: C, 72.03 %; H,

6.39 %; Br, 13.69 %; N, 2.40 %, O, 5.48 %, Found: C, 71.89 %; H, 6.32 %; Br, 13.76 %; N 2.43 %; O,5.51 %.

(*S*)- 2,2′-CB012-6,6′-Br-binaphthalene; **(*S*)-5**

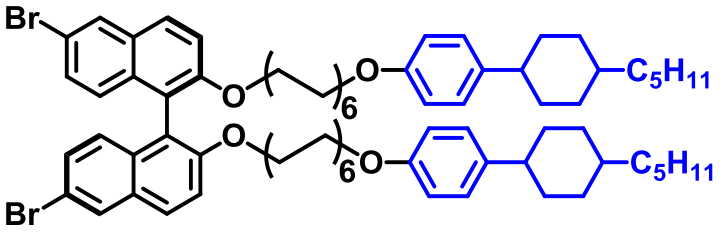


(*S*)-5

(*S*)-4(1.00 g, 2.25 mmol), K_2CO_3 (1.24 g, 9.0 mmol), and **Br-C_{12}-CB** (2.19 g, 4.95 mmol) were added in acetone. The mixture was refluxed for 48 hr at 60 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$) afforded **(*S*)-5** 2.1g (yield = 80 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.88 (m, 4H, –C*H*$_2$–), 0.99 (m, 8H, –C*H*$_2$–), 1.11 (m, 4H, –C*H*$_2$–), 1.22–1.47 (m, 20H, –C*H*$_2$–), 1.77–1.83 (m, 4H, –C*H*$_2$–), 3.87–4.02 (m, 8H, –O–C*H*$_2$–), 6.96–6.99 (m, 6H, –O–phenyl–*H* and naphthalene–*H*), 7.24–7.26 (m, 2H, biphenyl–*H*), 7.38–7.41 (d, 2H, *J*= 9.2 Hz, biphenyl–*H*), 7.50–7.52 (d, 4H, *J*= 8.8 Hz, biphenyl–*H*), 7.62–7.64 (d, 4H, *J*= 8.4 Hz, biphenyl–*H*), 7.67–7.69 (d, 4H, *J*= 8.0 Hz, naphthalene–*H*), 7.81–7.83 (d, 2H, *J*= 8.8 Hz, naphthalene–*H*), 7.98–7.99 (d, 2H, *J*= 1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm):25.66, 26.06, 29.12, 29.25, 29.29, 29.43, 29.58, 34.06, 68.18, 69.53, 97.14, 110.06,

115.09, 116.40, 117.24, 119.11, 120.05, 127.13, 128.33, 128.38, 129.02, 129.45, 130.20, 131.26, 132.57, 140.97, 145.28, 150.08, 154.75, 159.81. HRMS (FAB, *m/z*): Calc. 1164.4015, Found: 1165.4083 (M+H). Anal. Calcd for$C_{70}H_{74}Br_2N_2O_4$: C, 72.03 %; H, 6.39 %; Br, 13.69 %; N, 2.40 %, O, 5.48 %, Found: C, 71.95 %; H, 6.35 %; Br, 13.73 %; N 2.34 %, O, 5.47 %.

(*R*)-2,2′-PCH5012-6,6′-Br-binaphthalene; **(*R*)-6**

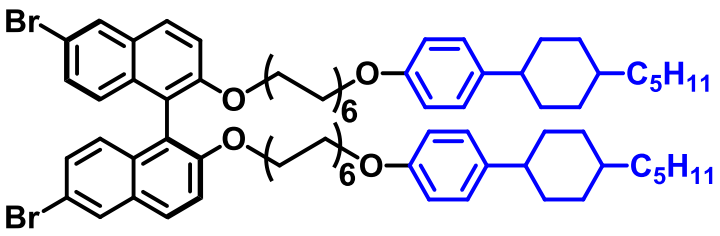


(*R*)-6

(*R*)-4 (1.00 g, 2.25 mmol), K_2CO_3 (1.87 g, 13.51 mmol), and **Br-C_{12}-PCH5** (2.44 g, 4.95 mmol) were added in acetone. The mixture was refluxed for 48 hr at 60 °C and then cooled to room temperature. The organic solvent removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$) afforded **(*R*)-6** 2.25g (yield = 79 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ =0.87-0.91 (m, 10H, –C*H*$_2$– and –C*H*$_3$), 1.04–1.11 (m, 16H, –C*H*$_2$–), 1.23–1.52 (m, 42H, –C*H*$_2$–), 1.75–1.78 (m, 4H, –C*H*$_2$–), 1.84–1.86 (m, 8H, cyclohexane–*H*), 2.37–2.43 (t, 2H, *J*= 12.0 and 12.4 Hz, cyclohexane *H*–phenyl), 3.88–3.95 (m, 8H, –O–C*H*$_2$–), 6.81–6.83 (d, 4H, *J*= 8.8 Hz, –O–phenyl–*H*), 6.96–6.98 (d, 2H, *J*= 9.2 Hz, naphthalene–*H*), 7.09–7.11 (d, 4H, *J*=

8.8 Hz, phenyl–*H*), 7.24–7.26 (m, 2H, naphthalene–*H*), 7.38–7.40 (d, 2H, *J*= 9.2 Hz naphthalene–*H*),7.80–7.82 (d, 2H, *J*=8.8 Hz, naphthalene–*H*), 7.98–7.96 (d, 2H, *J*=1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.12, 22.72, 22.98, 25.64, 26.11, 26.67, 28.93, 29.11, 29.38, 29.40, 29.44, 29.48, 29.58, 32.23, 33.67, 34.60, 37.32, 37.41, 43.73, 67.94, 69.51, 114.23, 116.39, 117.21, 120.04, 127.11, 127.57, 128.36, 129.42, 129.75, 130.18, 132.56, 139.91, 154.75, 157.23. HRMS (FAB, *m/z*): Calc. 1266.6614, Found: 1267.6694 (M+H). Anal. Calcd for$C_{78}H_{108}Br_2O_4$: C, 73.80 %; H, 8.58 %; Br, 12.59 %; O, 5.04 %, Found: C, 73.64 %; H, 8.60 %; Br, 12.36 %, O, 4.98 %.

(*S*)- 2,2′-PCH5012-6,6′-Br-binaphthalene; **(*S*)-6**

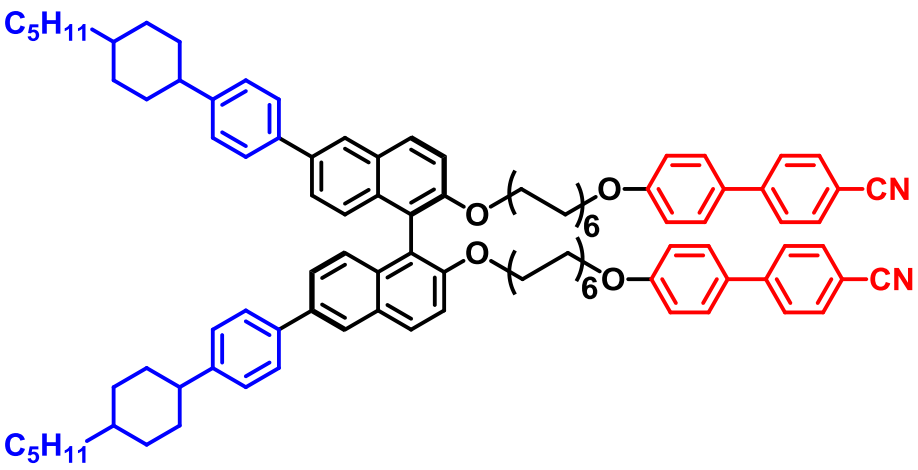


(*S*)-6

(*S*)-4 (1.00 g, 2.25 mmol), K_2CO_3 (1.87 g, 13.51 mmol), and **Br-C$_{12}$-PCH5** (2.44 g, 43.95 mmol) were added in acetone. The mixture was refluxed for 48 hr at 60 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$) afforded **(*S*)-6** 2.31g (yield = 81 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.87–0.91 (m, 10H, –C*H*$_2$– and –C*H*$_3$), 1.04–1.11 (m, 16H, –C*H*$_2$–), 1.23–1.52 (m, 42H,

–CH_2–), 1.74–1.78 (m, 4H, –CH_2–), 1.84–1.86 (m, 8H, cyclohexane–*H*), 2.36–2.43 (t, 2H, *J*= 12.0 and 12.4 Hz, cyclohexane *H*–phenyl), 3.86–3.93 (m, 8H, –O–CH_2–), 6.81–6.83 (d, 4H, *J*= 8.8 Hz, –O–phenyl–*H*), 6.96–6.98 (d, 2H, *J*= 9.2 Hz, naphthalene–*H*), 7.09–7.11 (d, 4H, *J*= 8.8 Hz, phenyl–*H*), 7.23–7.26 (m, 2H, naphthalene–*H*), 7.38–7.40 (d, 2H, *J*= 9.2 Hz naphthalene–*H*), 7.81–7.83 (d, 2H, *J*= 9.6 Hz, naphthalene–*H*), 7.98–7.96 (d, 2H, *J*= 1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm):14.51, 23.10, 26.03, 26.50, 27.50, 29.49, 29.67, 29.78, 29.83, 29.84, 29.86, 29.97, 32.60, 34.05, 34.98, 37.71, 37.78, 44.10, 68.30, 69.86, 114.52, 116.68, 117.48, 120.33, 127.37, 127.82, 128.61, 129.67, 129.99, 130.44, 132.81, 140.15, 154.97, 157.44. HRMS (FAB, *m/z*): Calc. 1266.6614, Found: 1267.6695 (M+H). Anal. Calcd for$C_{78}H_{108}Br_2O_4$: C, 73.80 %; H, 8.58 %; Br, 12.59 %; O, 5.04 %, Found: C, 73.61 %; H, 8.76 %; Br, 12.39 %, O, 4.90 %.

(*R*)-D2:

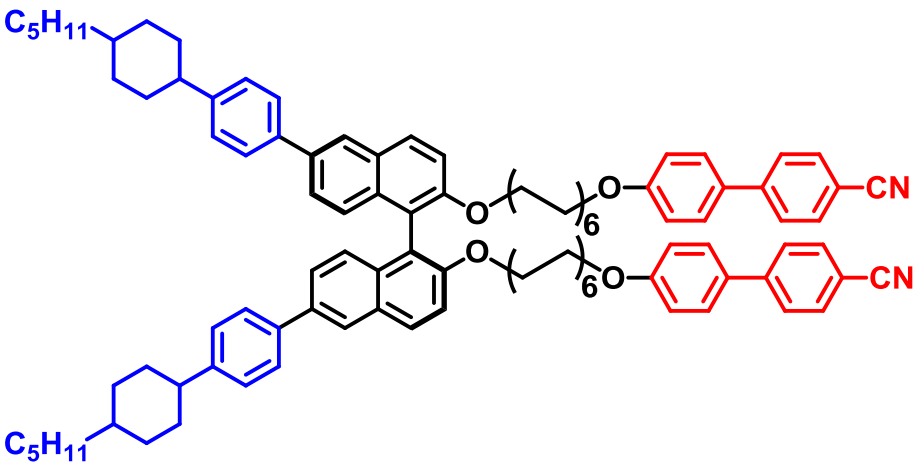


(*R*)-D2

(*R*)-5 (0.40 g, 0.34 mmol), **3** (0.24 g, 0.86 mmol), $NaHCO_3$ (0.17 g, 2.06 mmol), and account of Pd $(TPP)_4$ were added in THF and H_2O. The mixture was refluxed for 48 hr at

75 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **(*R*)-D2** 0.46g (yield = 91.6 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.88 (m, 10H, –C*H*$_2$– and –C*H*$_3$), 0.99–1.1 (m, 16H, –C*H*$_2$–), 1.16–1.32 (m, 30H, –C*H*$_2$–), 1.42–1.52 (m, 10H, –C*H*$_2$–), 1.75–1.80 (m, 4H, –C*H*$_2$–), 1.85–1.94 (m, 8H, cyclohexane–*H*), 2.47–2.53 (t, 2H, *J*= 12.0 and 12.4 Hz, cyclohexane *H*–phenyl), 3.88–4.00 (m, 8H, –O–C*H*$_2$–), 6.96–6.99 (m, 4H, –O–phenyl–*H* and naphthalene–*H*), 7.24–7.29 (m, 6H, phenyl–*H*), 7.41–7.52 (m, 8H, phenyl–*H*), 7.58–7.63 (m, 8H, phenyl–*H*), 7.66–7.68 (m, 4H, phenyl–*H*), 7.95–7.97 (d, 2H, *J*= 9.2 Hz, naphthalene–*H*), 8.03 (d, 2H, *J*= 1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.11, 22.73, 25.68, 26.05, 26.67, 29.17, 29.26, 29.40, 29.44, 29.46, 29.54, 32.24, 33.65, 34.39, 37.37, 37.42, 44.31, 68.20, 69.85, 110.09, 115.11, 116.24, 119.09, 120.65, 125.37, 125.79, 126.04, 127.03, 127.07, 127.24, 128.32, 129.33, 129.56, 131.27, 132.56, 133.34, 136.08, 138.78, 145.28, 146.73, 154.62, 154.64, 159.84. HRMS (FAB, *m/z*): Calc. 1464.9561, Found: 1465.9654 (M+H). Anal. Calcd for$C_{104}H_{124}N_2O_4$: C, 85.20 %; H, 8.53 %; N, 1.91 %, O, 4.36 %, Found: C, 85.05 %; H, 8.55 %; N, 1.66 %; O 4.40 %. Specific rotation: $[\alpha]^{25}_{589} = -26.70 \text{deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$ (1 g/L, $CHCl_3$). HTP: 584 μm^{-1} (in 5CB).

(*S*)-D2:

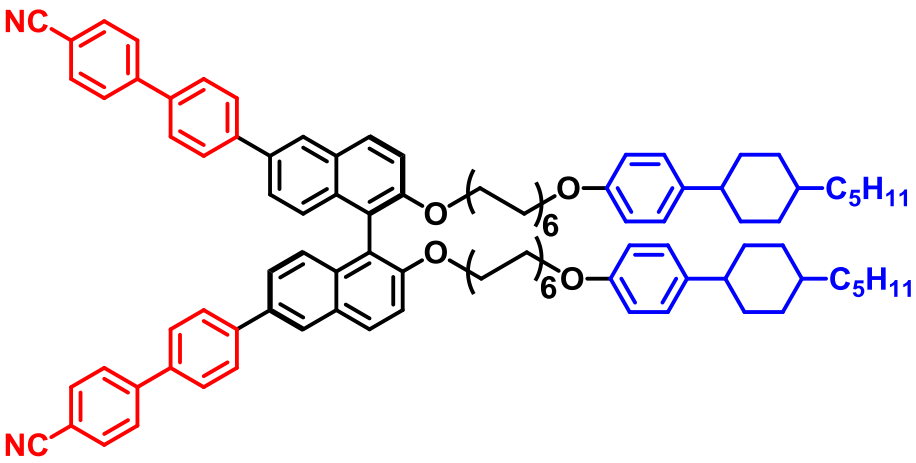


(*S*)-D2

(*S*)-5 (0.40 g, 0.34 mmol), **3** (0.24 g, 0.86 mmol), $NaHCO_3$ (0.17g, 2.06 mmol), and account of Pd $(TPP)_4$ were added in THF and H_2O. The mixture was refluxed for 48 hr at 75 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **(*S*)-D2** 0.40g (yield = 80.3 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.88 (m, 10H, –C*H*$_2$– and –C*H*$_3$), 0.99–1.1 (m, 16H, –C*H*$_2$–), 1.16–1.32 (m, 30H, –C*H*$_2$–), 1.42–1.52 (m, 10H, –C*H*$_2$–), 1.75–1.80 (m, 4H, –C*H*$_2$–), 1.85–1.94 (m, 8H, cyclohexane–*H*), 2.47–2.53 (t, 2H, *J*= 12.0 and 12.4 Hz, cyclohexane *H*–phenyl), 3.88–4.00 (m, 8H, –O–C*H*$_2$–), 6.96–6.99 (m, 4H, –O–phenyl–*H* and naphthalene–*H*), 7.24–7.29 (m, 6H, phenyl–*H*), 7.41–7.52 (m, 8H, phenyl–*H*), 7.58–7.63 (m, 8H, phenyl–*H*), 7.66–7.68 (m, 4H, phenyl–*H*), 7.95–7.97 (d, 2H, *J*= 9.2 Hz, naphthalene–*H*), 8.03 (d, 2H, *J*= 1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm):

14.11, 22.73, 25.68, 26.05, 26.67, 29.17, 29.26, 29.40, 29.44, 29.46, 29.54, 32.24, 33.65, 34.39, 37.37, 37.42, 44.31, 68.20, 69.85, 110.09, 115.11, 116.24, 119.09, 120.65, 125.37, 125.79, 126.04, 127.03, 127.07, 127.24, 128.32, 129.33, 129.56, 131.27, 132.56, 133.34, 136.08, 138.78, 145.28, 146.73, 154.62, 154.64, 159.84. HRMS (FAB, *m/z*): Calc. 1464.9561, Found: 1465.9607 (M+H). Anal. Calcd for $C_{104}H_{124}N_2O_4$: C, 85.20 %; H, 8.53 %; N, 1.91%, O, 4.36%, Found: C,83.93 %; H, 8.60 %; N, 1.8 7%, O 4.33 %. Specific rotation: $[\alpha]^{25}_{589} = +26.91 \text{deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$ (1 g/L, $CHCl_3$). HTP: 600 μm^{-1} (in 5CB).

(*R*)-D3:

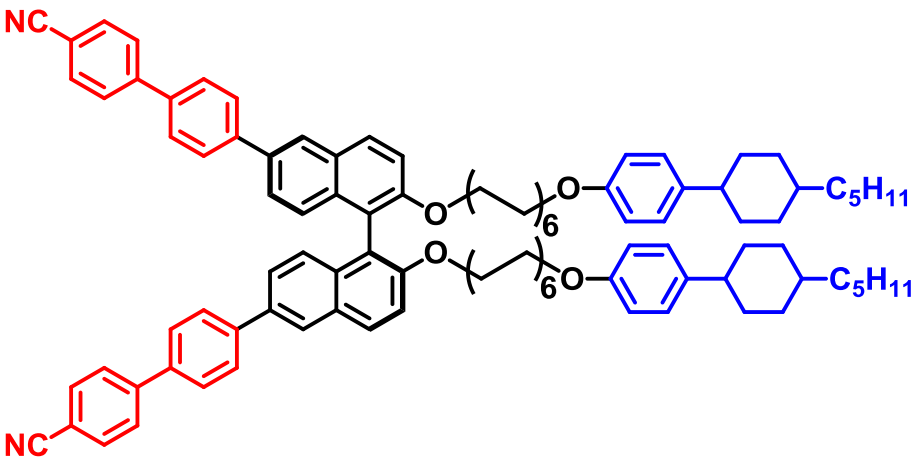


(*R*)-D3

(*R*)-6 (0.60 g, 0.47 mmol), **2** (0.36 g, 1.18mmol), $NaHCO_3$ (0.239 g, 2.84 mmol), and account of Pd $(TPP)_4$ were added in THF and H_2O. The mixture was refluxed for 48 hr at 75 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-

hexane = 1) afforded **(*R*)-D3** 0.58g (yield = 84 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.87–90 (m, 7H, –C*H*$_2$– and –C*H*$_3$), 1.00–1.44 (m, 61H, –C*H*$_2$–), 1.67–1.73 (m, 4H, –C*H*$_2$–), 1.84–1.86 (m, 8H, cyclohexane–*H*), 2.47–2.53 (t, 2H, *J*= 12.0 and 12.4 Hz, cyclohexane *H*–phenyl), 3.86–4.00 (m, 8H, –O–C*H*$_2$–), 6.79–6.81 (d, 4H, *J*= 8.8 Hz, –O–phenyl–*H*), 7.09–7.11 (d, 4H, *J*= 8.8 Hz, O–phenyl–*H*), 7.29–7.31 (d, 2H, *J*= 8.4 Hz, phenyl–*H*), 7.46–7.48 (d, 2H,*J*= 9.2 Hz, phenyl–*H*), 7.52–7.55 (dd, 2H, *J*= 2.0 and 6.8 Hz, phenyl–*H* and naphthalene–*H*), 7.66–7.72 (m, 12H, phenyl–*H* and naphthalene–*H*), 7.79–7.81 (d, 4H, *J*= 8.4 Hz, phenyl–*H*), 8.01–8.03 (d, 2H, *J*= 9.2 Hz, naphthalene–*H*), 8.13 (d, 2H, *J*=2.0 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.13, 22.73, 25.71, 26.11, 26.67, 29.17, 29.39, 29.44, 29.48, 29.57, 29.58, 32.23, 33.67, 34.60,37.33, 37.41, 43.74, 67.91, 69.70, 110.83, 114.21, 116.24, 118.97, 120.35, 125.43, 125.87, 126.24, 127.48, 127.60, 127.76, 129.41, 129.59, 132.65, 133.67, 134.92, 137.58, 139.97, 141.60, 145.17, 154.97, 157.20. HRMS (FAB, *m/z*): Calc. 1464.9561, Found: 1465.9621 (M+H). Anal. Calcd for$C_{104}H_{124}N_2O_4$: C, 85.20 %; H, 8.53 %; N, 1.91 %, O, 4.36 %, Found: C, 85.02 %; H, 8.76 %; N, 1.94 %, O, 4.40 %. Specific rotation: $[\alpha]^{25}_{589}$ = –60.17 deg · dm^{-1} · g^{-1}· cm^3 (1 g/L, $CHCl_3$). HTP: 473.0 μm^{-1} (in 5CB).

(*S*)-D3:

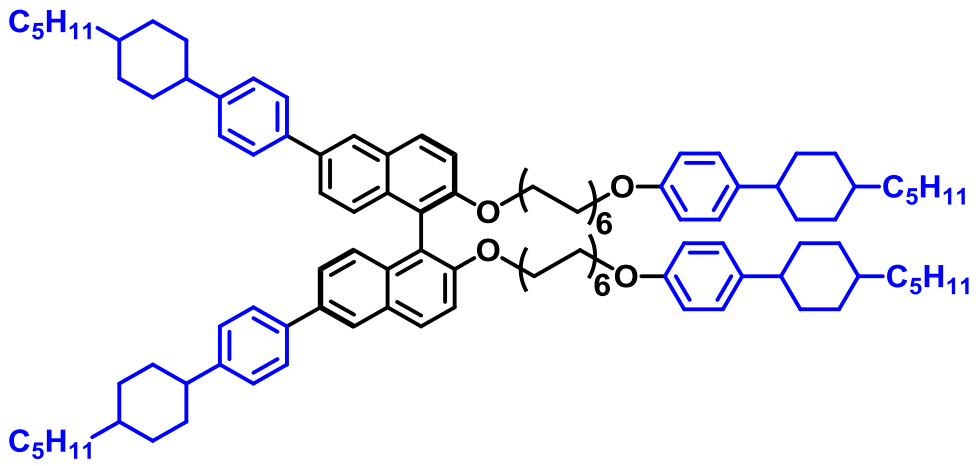


(*S*)-D3

(*S*)-6 (0.60 g, 0.47 mmol), **2** (0.36 g, 1.18 mmol), $NaHCO_3$ (0.239 g, 2.84 mmol), and account of Pd $(TPP)_4$ were added in THF and H_2O. The mixture was refluxed for 48 hr at 75 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **(*S*)-D3** 0.56g (yield = 81 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.87–0.90 (m, 7H, –C*H*$_2$– and –C*H*$_3$), 1.00–1.44 (m, 61H, –C*H*$_2$–), 1.67–1.74 (m, 4H, –C*H*$_2$–), 1.84–1.86 (m, 8H, cyclohexane–*H*), 2.36–2.42 (t, 2H, *J*= 12.0 and 12.4 Hz, cyclohexane *H*–phenyl), 3.86–4.03 (m, 8H, –O–C*H*$_2$–), 6.78–6.81 (d, 4H, *J*= 8.8 Hz, –O–phenyl–*H*), 7.09–7.11 (d, 4H, *J*= 8.8 Hz, O–phenyl–*H*), 7.29–7.31 (d, 2H, *J*= 8.4 Hz, phenyl–*H*), 7.46–7.48 (d, 2H, *J*= 9.2 Hz, phenyl–*H*), 7.52–7.54 (dd, 2H, *J*= 2.0 and 6.8 Hz, phenyl–*H* and naphthalene–*H*), 7.66–7.72 (m, 12H, phenyl–*H* and naphthalene–*H*), 7.79–7.81 (d, 4H, *J*= 8.4 Hz, phenyl–*H*), 8.01–8.03 (d, 2H, *J*= 9.2 Hz,

naphthalene–*H*), 8.12 (d, 2H, *J*= 2.0 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.18, 22.78, 25.76, 26.16, 26.72, 29.21, 29.44, 29.49, 29.53, 29.61, 32.27, 33.72, 34.65, 37.38, 37.45, 43.76, 67.92, 69.71, 110.79, 114.16, 116.18, 120.29, 125.34, 125.78, 126.16, 127.40, 127.50, 127.67, 129.33, 129.50, 132.55, 133.59, 134.83, 137.48, 139.87, 141.50, 145.05, 154.86, 157.09. HRMS (FAB, *m/z*): Calc. 1464.9561, Found: 1465.9626 (M+H). Anal. Calcd for$C_{104}H_{124}N_2O_4$: C, 85.20 %; H, 8.53 %; N, 1.91 %, O, 4.36 %, Found: C, 85.00 %; H, 8.44 %; N, 1.96 %, O, 4.46 %. Specific rotation: $[\alpha]^{25}_{589}$ = + 60.95deg · dm^{-1} · g^{-1}· cm^3 (1 g/L, $CHCl_3$). HTP: 470 μm^{-1} (in 5CB).

(*R*)-D4:

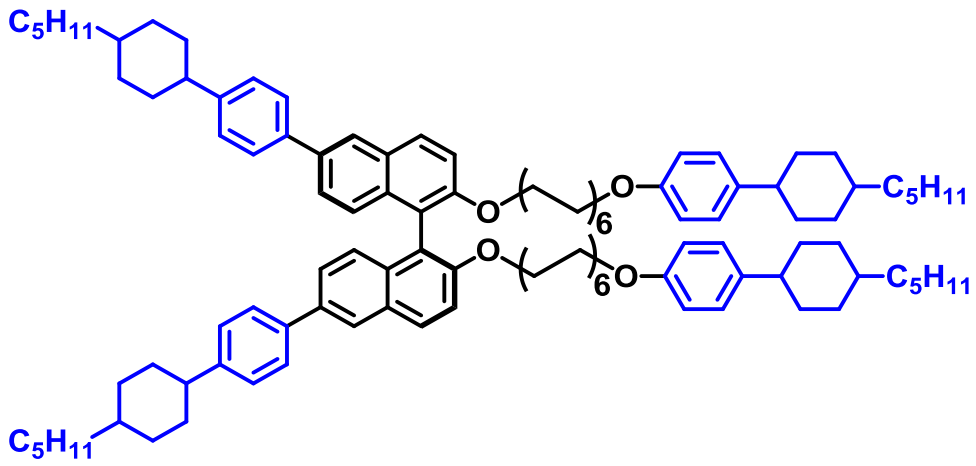


(*R*)-D4

(*R*)-6 (0.30 g, 0.237 mmol), **3** (0.162 g, 0.59 mmol), $NaHCO_3$ (0.119 g, 1.42 mmol), and account of Pd $(TPP)_4$ were added in THF and H_2O. The mixture was refluxed for 48 hr at 75 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by

rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **(*R*)-D4** 0.32g (yield = 87 %) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ =0.87–1.49 (m, 90H, –C*H*$_2$– and –C*H*$_3$), 1.72–1.86 (m, 20H, –C*H*$_2$–and cyclohexane–*H*), 2.40–2.50 (tt, 4H, *J*= 12.0 and 12.4 Hz, cyclohexane–*H*), 3.89–3.97 (m, 8H, –O–C*H*$_2$–), 6.80–6.83 (d, 4H, *J*= 8.8 Hz, phenyl–*H*), 7.09–7.11 (d, 4H, phenyl–*H*), 7.23–7.29 (m, 6H, naphthalene–*H*), 7.41–7.48 (dd, 4H, *J*= 8.8 an 9.2 Hz, phenyl–*H*), 7.59–7.61 (d, 4H, *J*= 8.0 Hz, phenyl–*H*), 7.95–7.97 (d, 2H, , *J*= 9.2 Hz, naphthalene–*H*),8.03 (d, 2H, *J*= 1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.13, 20.72, 22.73, 25.68, 26.11, 26.68, 29.18, 29.40, 29.48, 29.58, 32.24, 32.61, 33.64, 33.69, 34.37, 34.61, 37.34, 37.42, 39.24, 43.75, 44.31, 45.63, 67.96, 69.84, 109.60, 114.24, 125.39, 127.04, 127.24, 127.58, 129.31, 129.52, 133.31, 135.15, 136.03, 138.80, 139.92, 143.37, 146.69, 154.61, 157.25. HRMS (FAB, *m/z*): Calc. 1567.2160, Found: 1568.2239 (M+H). Anal. Calcd for$C_{112}H_{158}O_4$: C, 85.77 %; H, 10.15 %; O, 4.08 %, Found: C, 85.87 %; H, 10.29 %, O, 4.17 %. Specific rotation: $[\alpha]^{25}_{589} = -37.06\ \text{deg} \cdot \text{dm}^{-1} \cdot \text{g}^{-1} \cdot \text{cm}^3$ (1 g/L, $CHCl_3$). HTP: 628 μm^{-1} (in 5CB).

(*S*)-D4:



(*S*)-D4

(*S*)-6 (0.30 g, 0.24 mmol), **3** (0.16 g, 0.59 mmol), $NaHCO_3$ (0.12 g, 1.42 mmol), and account of Pd $(TPP)_4$ were added in THF and H_2O. The mixture was refluxed for 48 hr at 75 °C and then cooled to room temperature. The organic solvent was removed by rotary evaporation. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification by silica gel column chromatography (eluents: $CHCl_3$/*n*-hexane = 1) afforded **(*S*)-D4** 0.31g (yield = 84%) of white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ =0.87–1.49 (m, 90H, –C*H*$_2$– and –C*H*$_3$), 1.72–1.94 (m, 20H, –C*H*$_2$–and cyclohexane–*H*), 2.39–2.50 (tt, 4H, *J*= 12.0 and 12.4 Hz, cyclohexane–*H*), 3.89–3.97 (m, 8H, –O–C*H*$_2$–), 6.80–6.83 (d, 4H, *J*= 8.8 Hz, phenyl–*H*), 7.09–7.11 (d, 4H, phenyl–*H*), 7.23–7.29 (m, 6H, naphthalene–*H*), 7.41–7.49 (dd, 4H, *J*= 8.8 an 9.2 Hz, phenyl–*H*), 7.59–7.61 (d, 4H, *J*= 8.0 Hz, phenyl–*H*), 7.95–7.97 (d, 2H, , *J*= 9.2 Hz, naphthalene–*H*), 8.03 (d, 2H, *J*= 1.6 Hz, naphthalene–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ from TMS, ppm): 14.14, 22.73, 25.68, 26.11, 26.68, 29.19, 29.41, 29.44, 29.48, 29.58, 32.24,

33.57, 33.64, 33.69, 34.37,34.61, 37.34, 37.42, 43.75, 44.31, 67.96, 69.83, 114.21, 114.24, 125.39, 127.04, 127.24, 127.58, 129.33, 129.52, 133.31, 136.03, 138.80,139.92, 157.25. HRMS (FAB, *m/z*): Calc. 1567.2160, Found: 1568.2234 (M+H). Anal. Calcd for$C_{112}H_{158}O_4$: C, 85.77 %; H, 10.15 %; O, 4.08 %, Found: C, 85.52 %; H, 10.09 %, O, 4.01 %. Specific rotation: $[\alpha]^{25}_{589}$ = +37.75 deg · dm^{-1} · g^{-1}· cm^3 (1 g/L, $CHCl_3$). HTP: 624 μm^{-1} (in 5CB).

Table S1. Phase transition temperature and enthalpies values of LCILs

		Phase transition temperature (°C)	Enthalpies values (J/g)
LCIL-1	cooling process	**I** 82.0 **C**	**I** 87.3 **C**
	heating process	**C** 103.9 **I**	**C** 86.1 **I**
LCIL-2	cooling process	**I** 175.8 **S_mA** 115.2 **C**	**I** 12.4 **S_mA** 41.6 **C**
	heating process	**C_1** 108.9 **C_2** 127.9 **S_mX** 150.1 **S_mA** 176.3 I	**C_1** 0.4 **C_2** 8.0 **S_mX** 32.5 **S_mA** 10.6 **I**
LCIL-3	cooling process	**I** 88.7 **N** 57.4 **C**	**I** 4.0 **N** 1.7 **C**
	heating process	**C**53.4 **N** 84.1 **M** 91.4 **I**	**C** 2.3 **N** 1.0 **M** 3.6 **I**
LCIL-4	cooling process	**I** 95.7 **N** 42.2 **C**	**I** 3.7 **N** 3.3 **C**
	heating process	**C**42.8 **N** 96.5 **I**	**C** 4.6 **N** 4.6 **I**

* C : crystalline, C_1 and C_2: phase transition of crystal to crystal, S_mA: smectic A phase, S_mX: smectic X phase, N: nematic phase, M: mesophase, I: isotropic phase. Heating and cooling ratios are 2 °C/min.

4. Electrochemical windows of LCILs

We evaluated the electrochemical windows (available potential regions) of the LCILs using cyclic voltammetry (CV). The voltammograms were recorded in CH_3CN containing 0.1 M tetrabutylammonium perchlorate (TBAP). Ag/AgCl and platinum were used as reference electrode and working electrode, respectively. The oxidation and reduction potentials of **LCIL-2**, **3**, and **4** were observed. The electrochemical window is determined as a range of cathodic and anodic potential limits, and could be an index to evaluate solvents and electrolytes used for electrochemical reaction. The results are shown in Table S2 and Figure S1. The electrochemical windows of the LCILs are above a 2 V range in room temperature by CV measurement, and the LCILs are useful for anisotropic electrochemical polymerization.

Table S2. Electrochemical peak potentials of LCILs.

	E_{CL} (V)	E_{RED} (V)	E_{AL} (V)	E_{OX} (V)	*EW* (V)
LCIL-2	−1.00	−1.21	0.94	1.14	2.14
LCIL-3	−0.94	−1.18	0.90	1.16	2.08
LCIL-4	−1.00	−1.22	0.74	1.16	1.74

∗ E_{CL}: cathodic potential limit, E_{RED}: potential in reduction process,

E_{AL}: anodic potential limit, E_{OX}: potential in oxidation process,

EW: electro chemical window (available potential region)

∗The electrochemical windows were measured using a platinum working electrode and silver chloride reference electrode in 0.1 M TBAP acetonitrile solution with a scan rate of 100 mV/s.

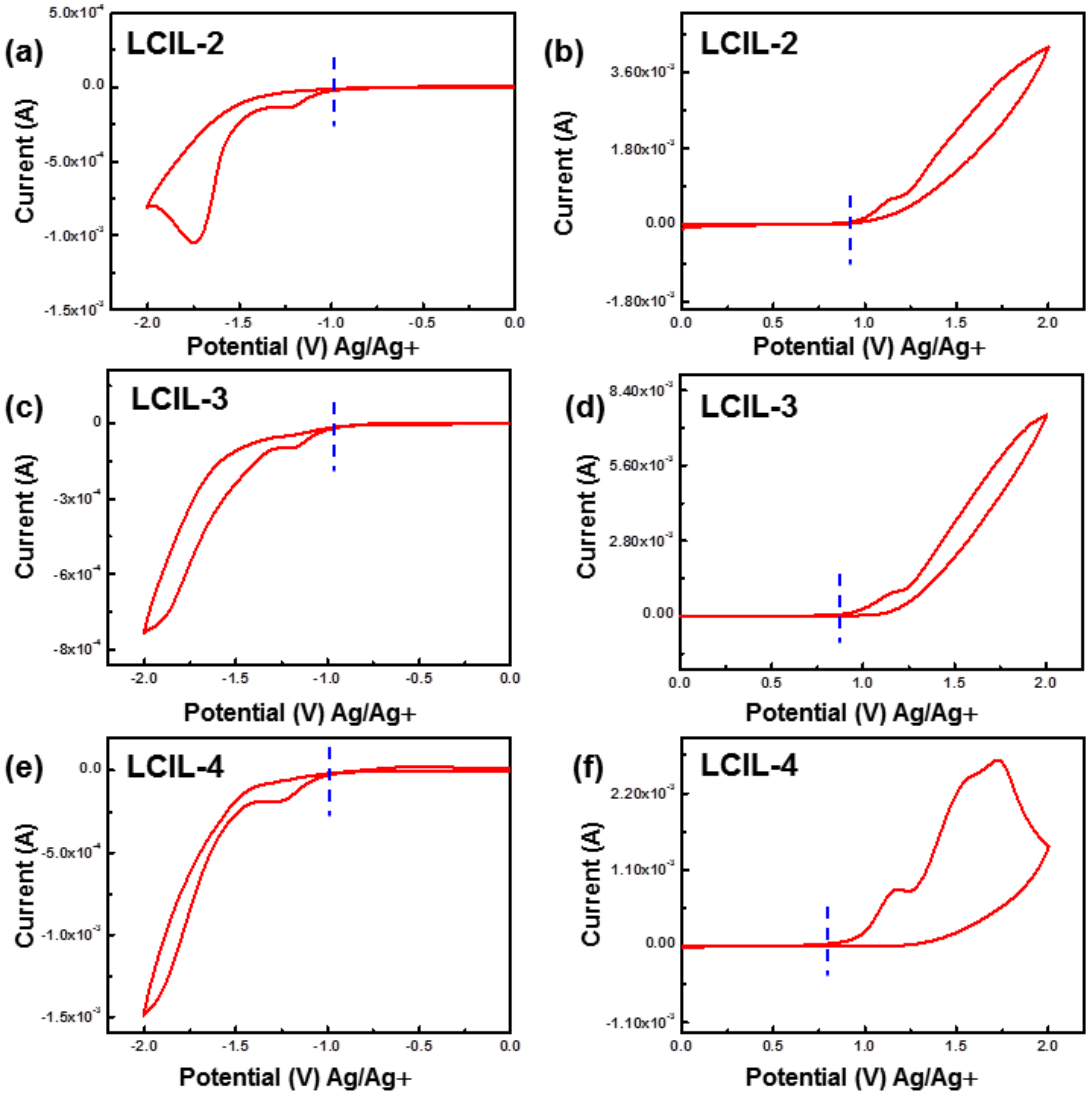
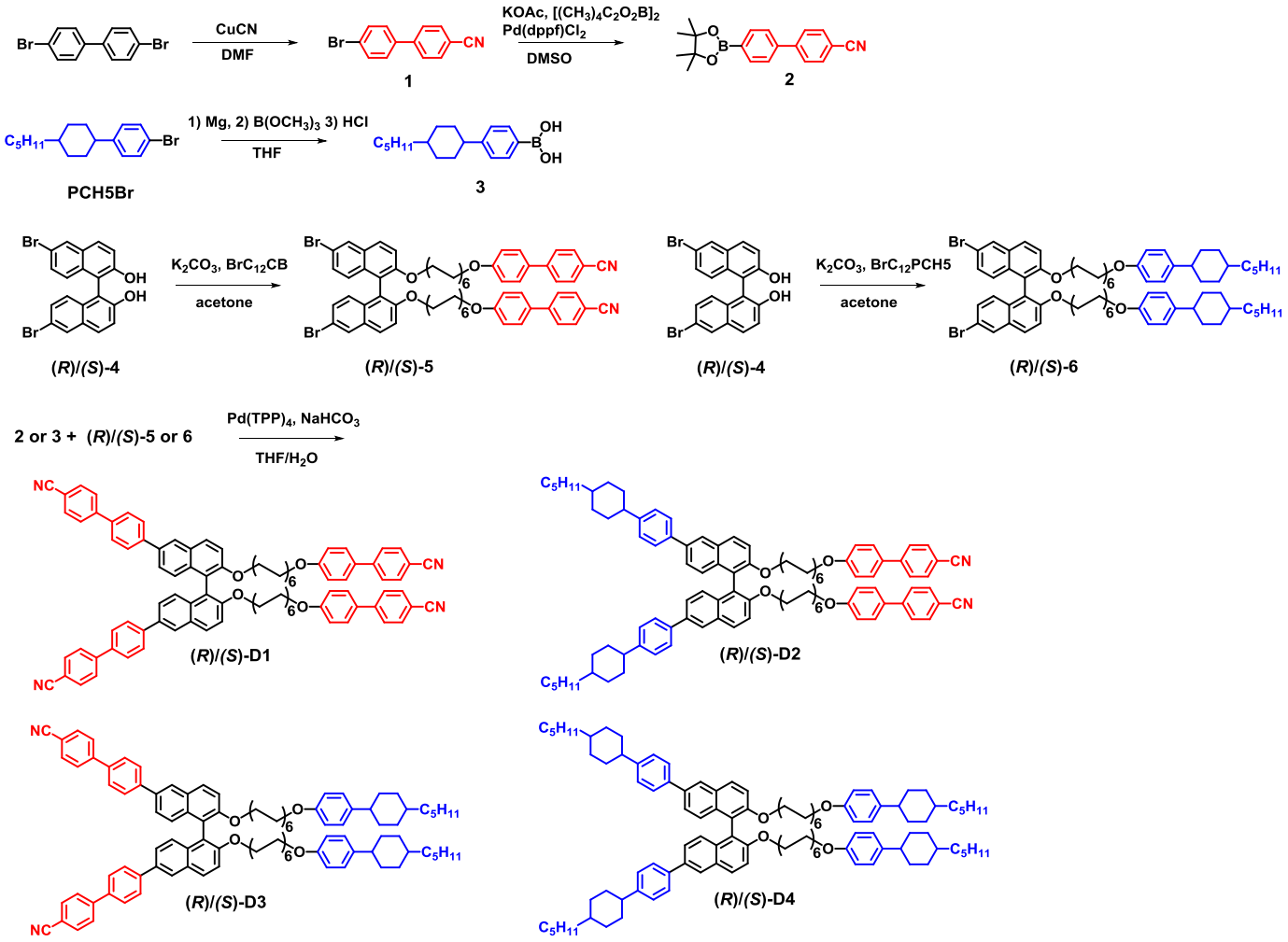


Figure S1. CV curves of LCILs, (a) and (b) **LCIL-2**, (c) and (d) **LCIL-3**, (e) and (f) **LCIL-4**.



Scheme S1. Synthetic routes of *tetra*-substituted binaphthyl derivatives.

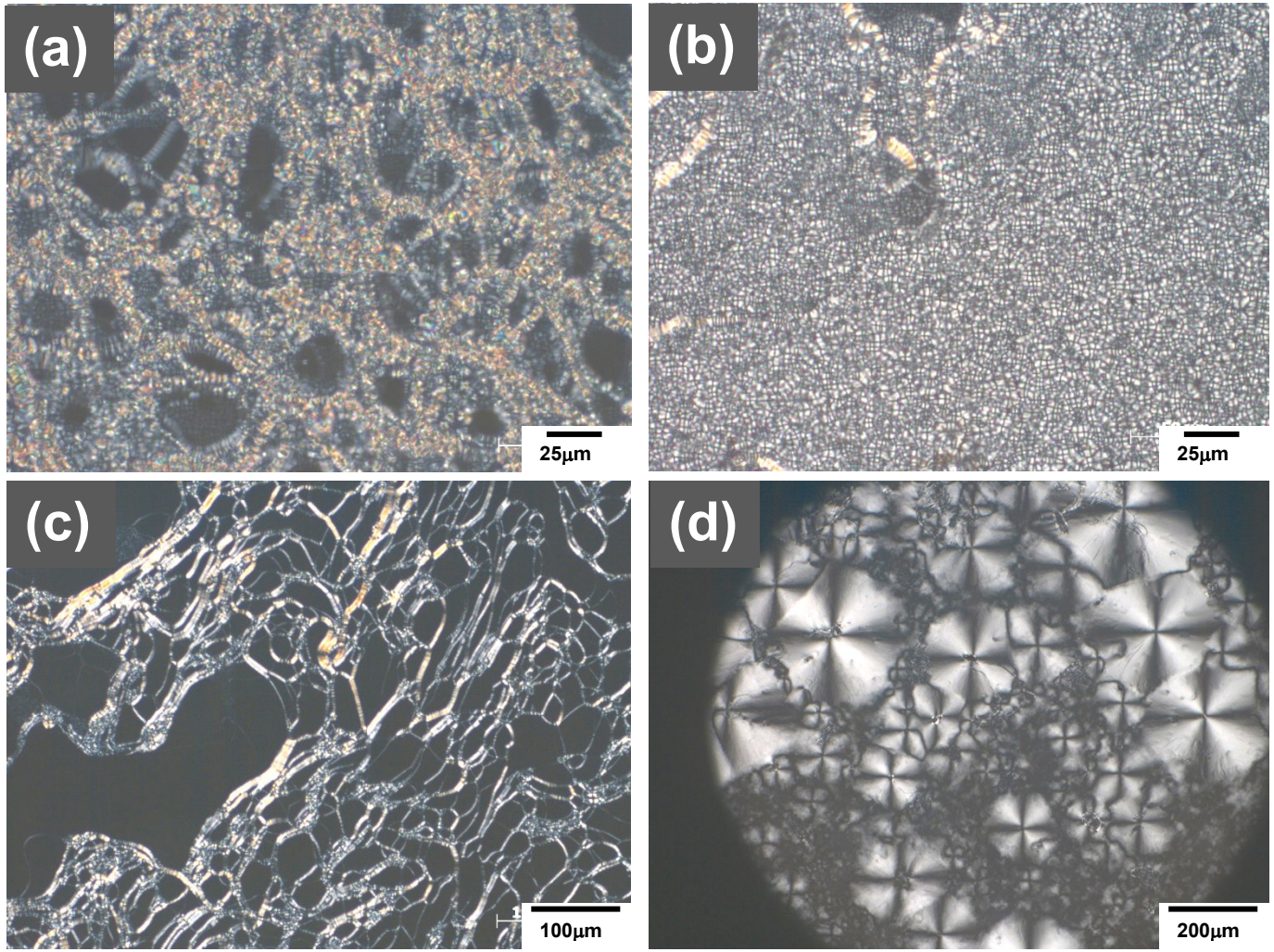


Figure S2. POM images of **LCIL-2**; (a) oily-streak texture of smectic phase at 160 °C in heating process, (b) focal conic texture of smectic phase at 150 °C in cooling process, (c) oily-streak texture of smectic phase at 140 °C in cooling process, (d) crystal phase at 100 °C in cooling process.

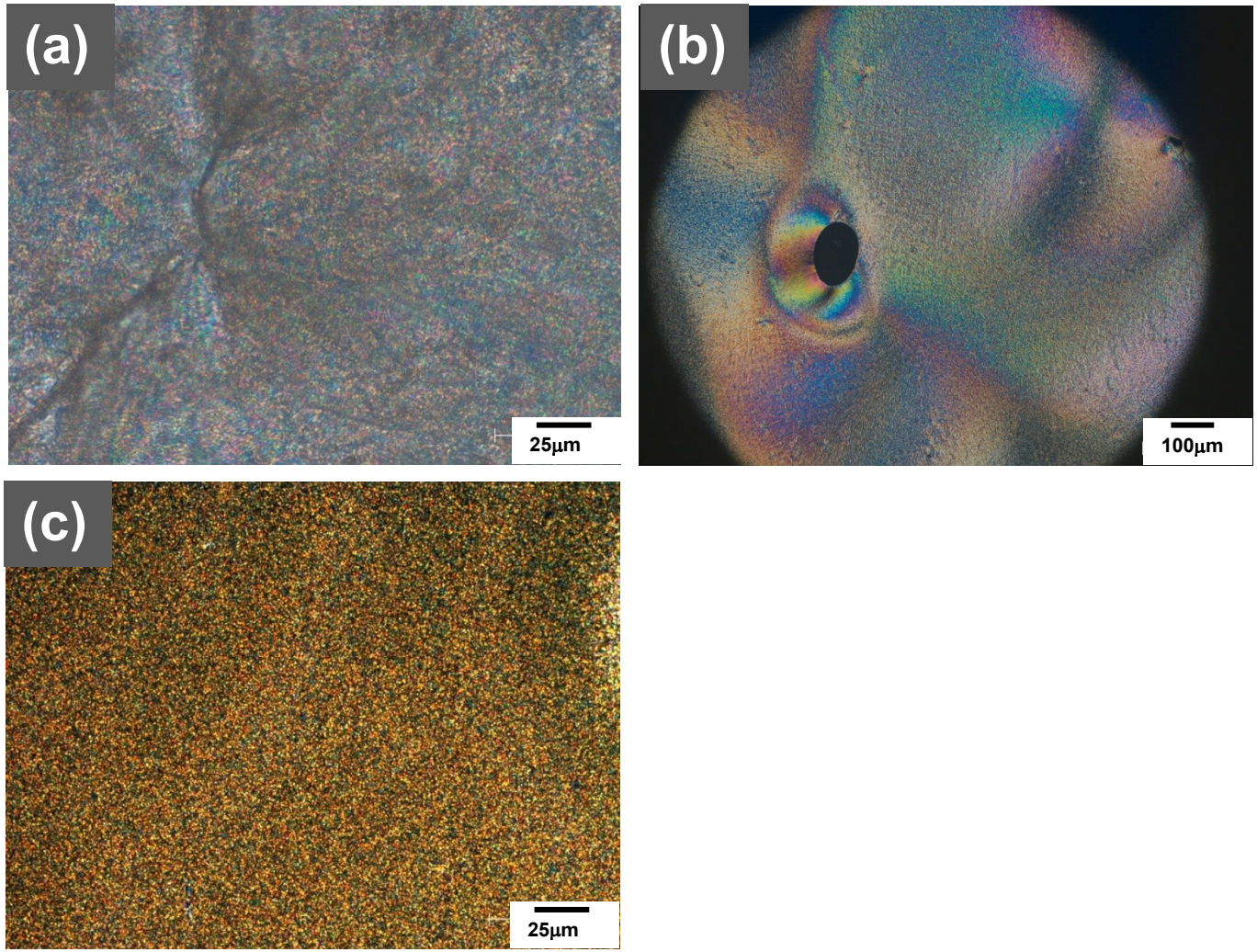


Figure S3. POM images of **LCIL-3**; (a) sand-like texture of nematic phase at 70 °C in heating process, (b) Schlieren texture of nematic phase at 90 °C in cooling process, (c) sand-like texture of nematic phase at 80 °C in cooling process.

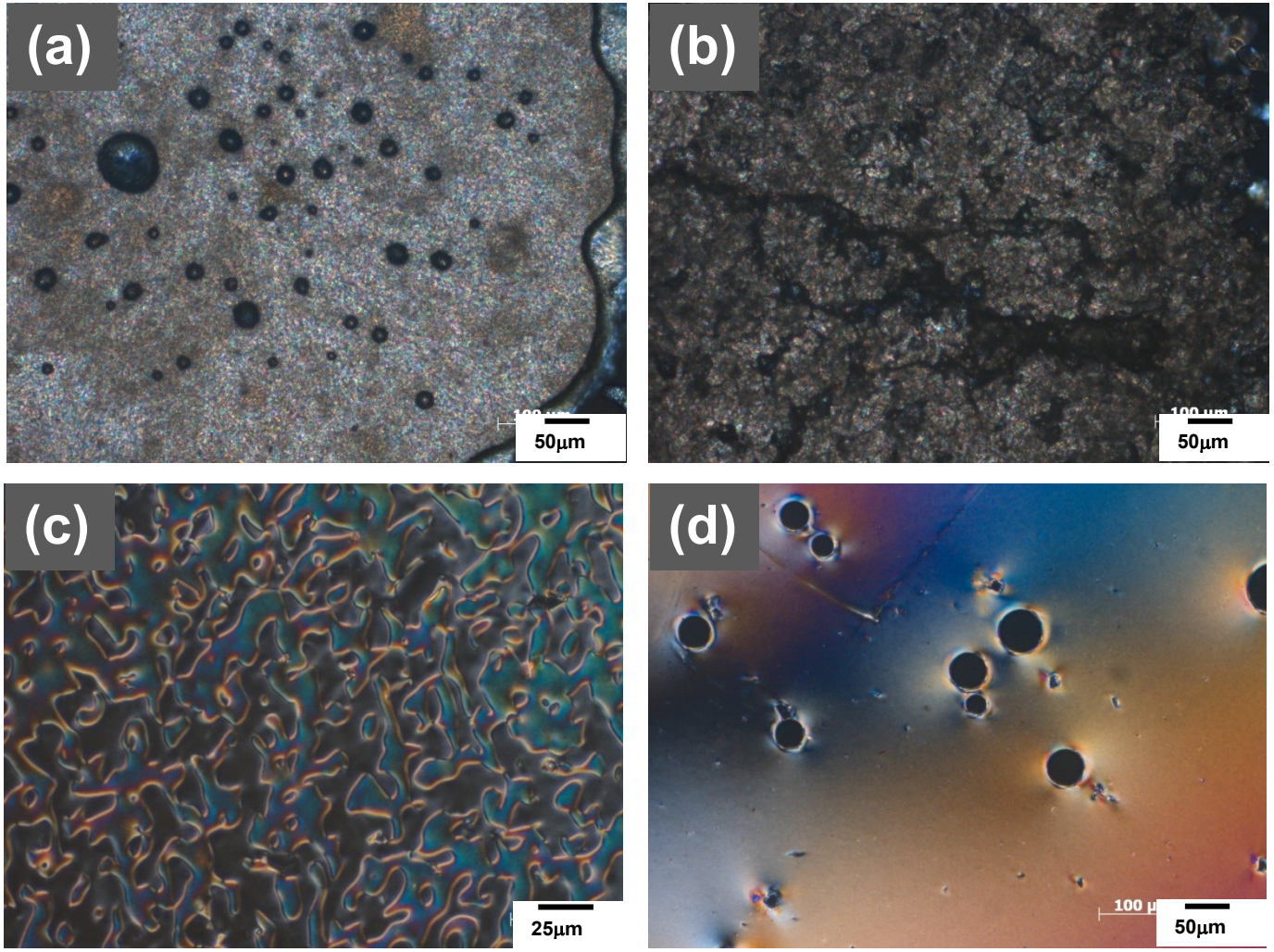


Figure S4. POM images of **LCIL-4**; (a) sand-like texture of nematic phase at 80 °C in heating process, (b) crystal phase at 110 °C in heating process, (c) marble texture of nematic phase at 90 °C in cooling process, (f) Schlieren texture of nematic phase at 75 °C in cooling process.

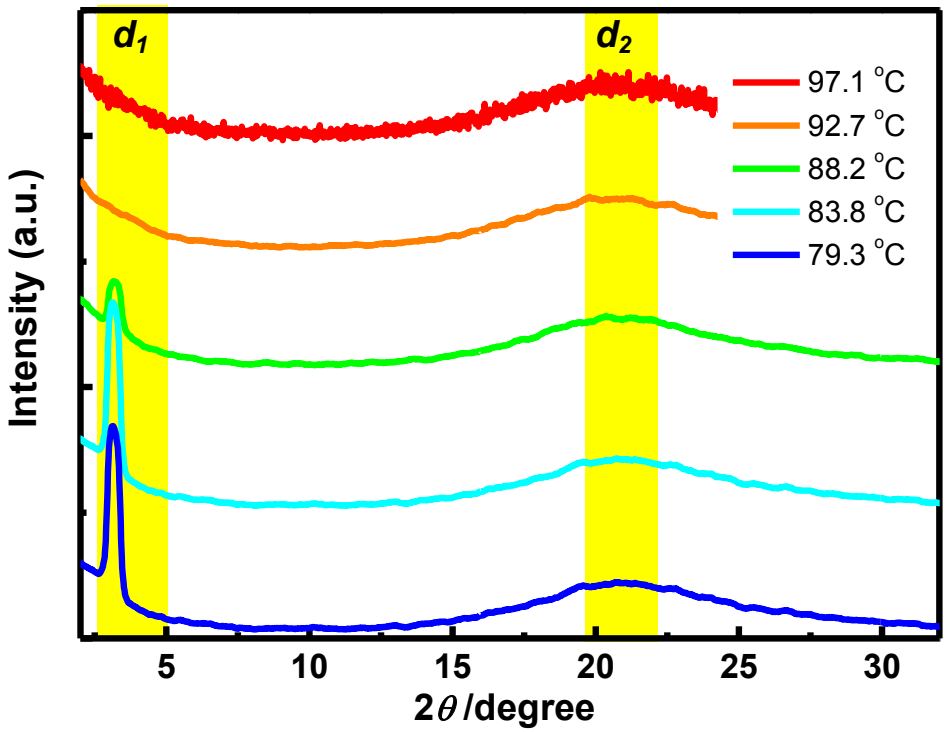


Figure S5. Temperature dependence of X-ray diffraction profiles for **LCIL-3** in isotropic and nematic phases**.**

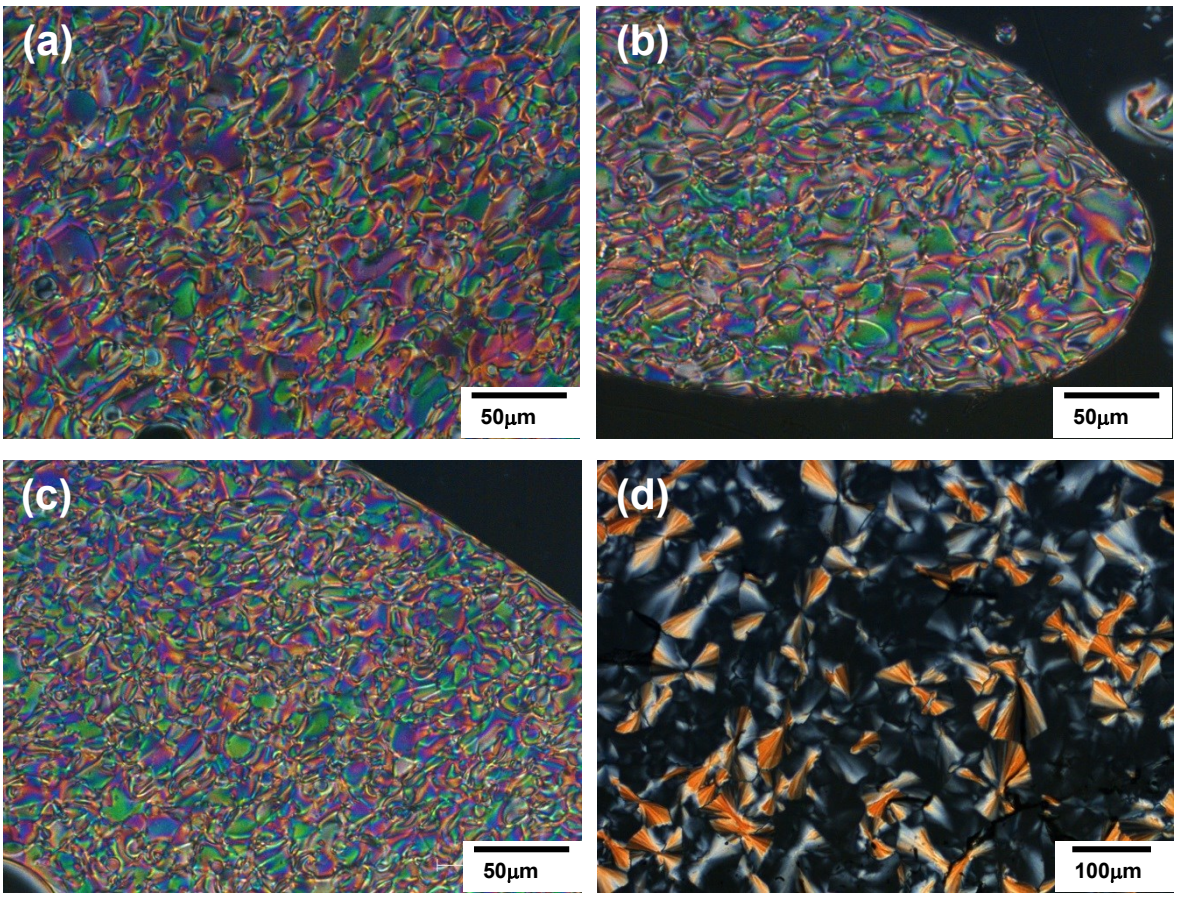


Figure S6. POM images of the mixture of **LCIL-4** and **(*R*)-D4** at 80 °C in cooling process. (a) system 1 [**LCIL-4** : **(*R*)-D-1** = 100 : 10 in mole ratio], (b) system 2 [**LCIL-4** : **(*R*)-D4** = 100 : 20 in mole ratio], (c) system 3 [**LCIL-4** : **(*R*)-D4** = 100 : 30 in mole ratio], and (d) system 4 [**LCIL-4**: **(*R*)-D4** = 100 : 40 in mole ratio].

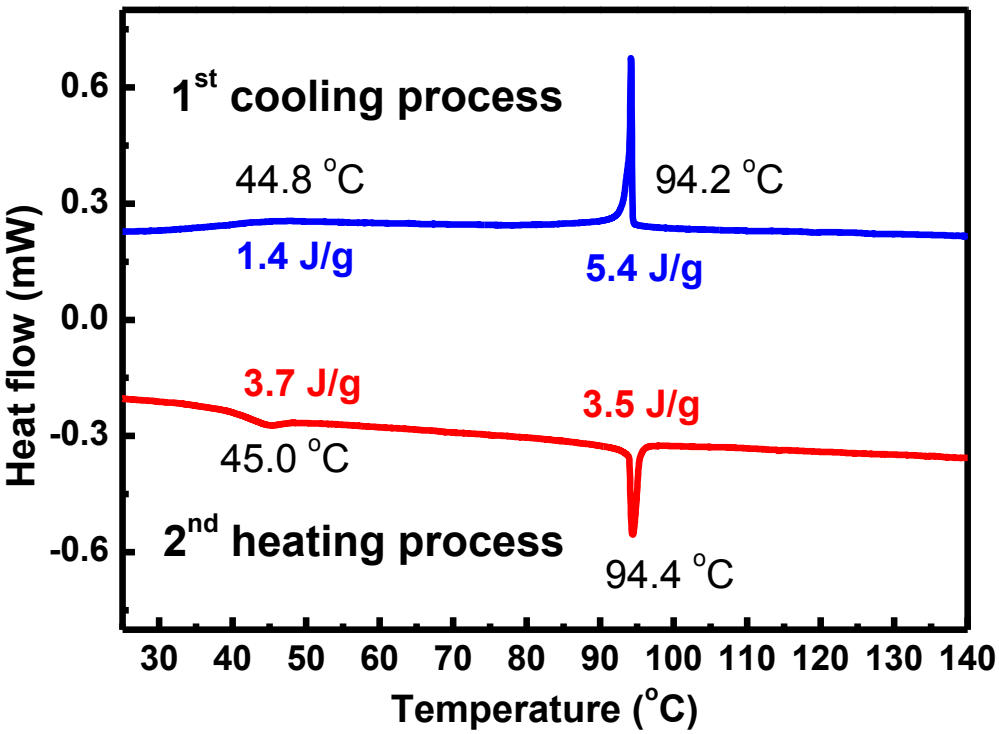


Figure S7. DSC curves of the mixture of **LCIL-4** and **(*R*)-D1** [**LCIL-4** : **(*R*)-D1** = 100 : 5 in mole ratio].

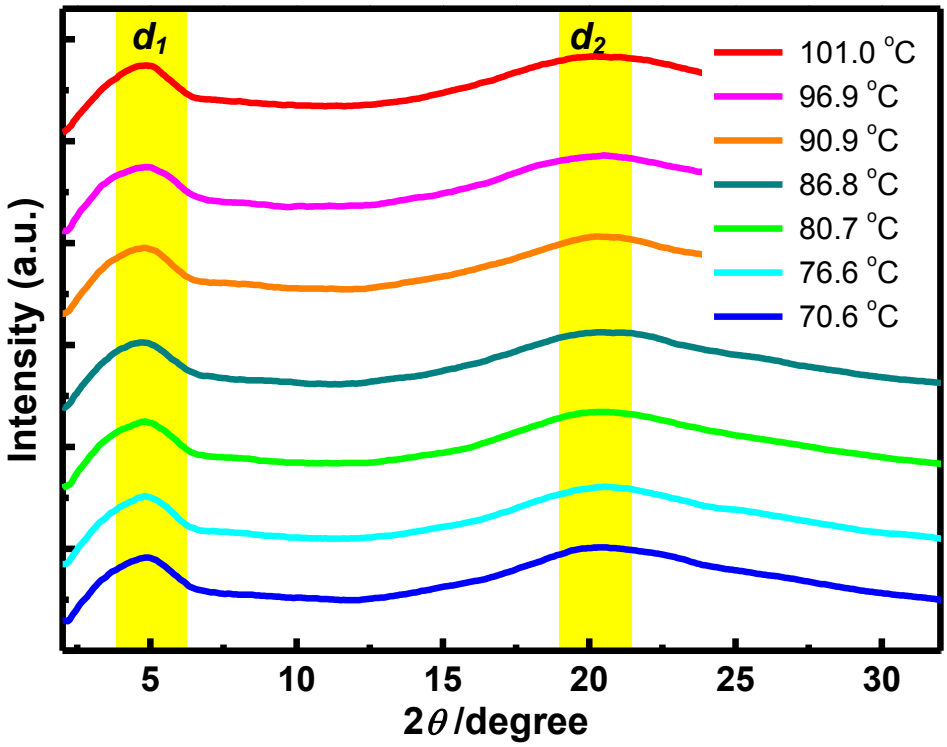


Figure S8. Temperature dependence of X-ray diffraction profiles of the mixture of **LCIL-4** and **(*R*)-D1**in N*-LC phase [**LCIL-4** : **(*R*)-D1** = 100 : 5 in mole ratio]

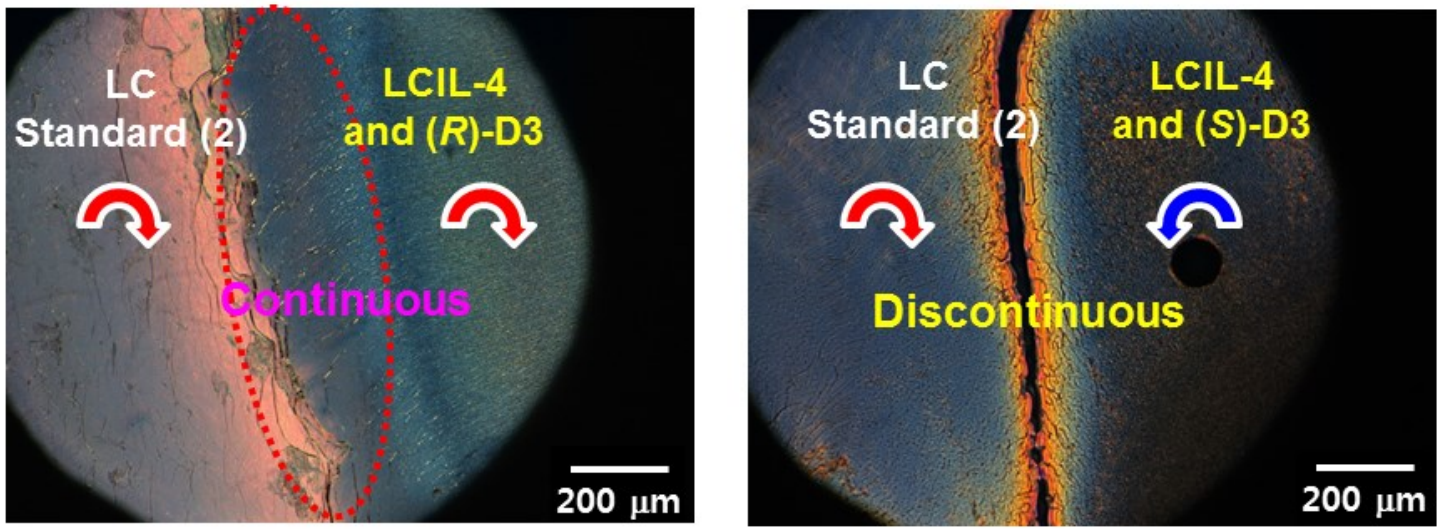


Figure S9. Contact test of LC standard (2) and the mixture of **LCIL-4** with chiral dopant at 85 °C. (a) **LCIL-4** with **(*R*)-D3**, (b) **LCIL-4** with **(*S*)-D3**. The mixing mole ratio of **LCIL-4** and the chiral dopant is 100 : 1.

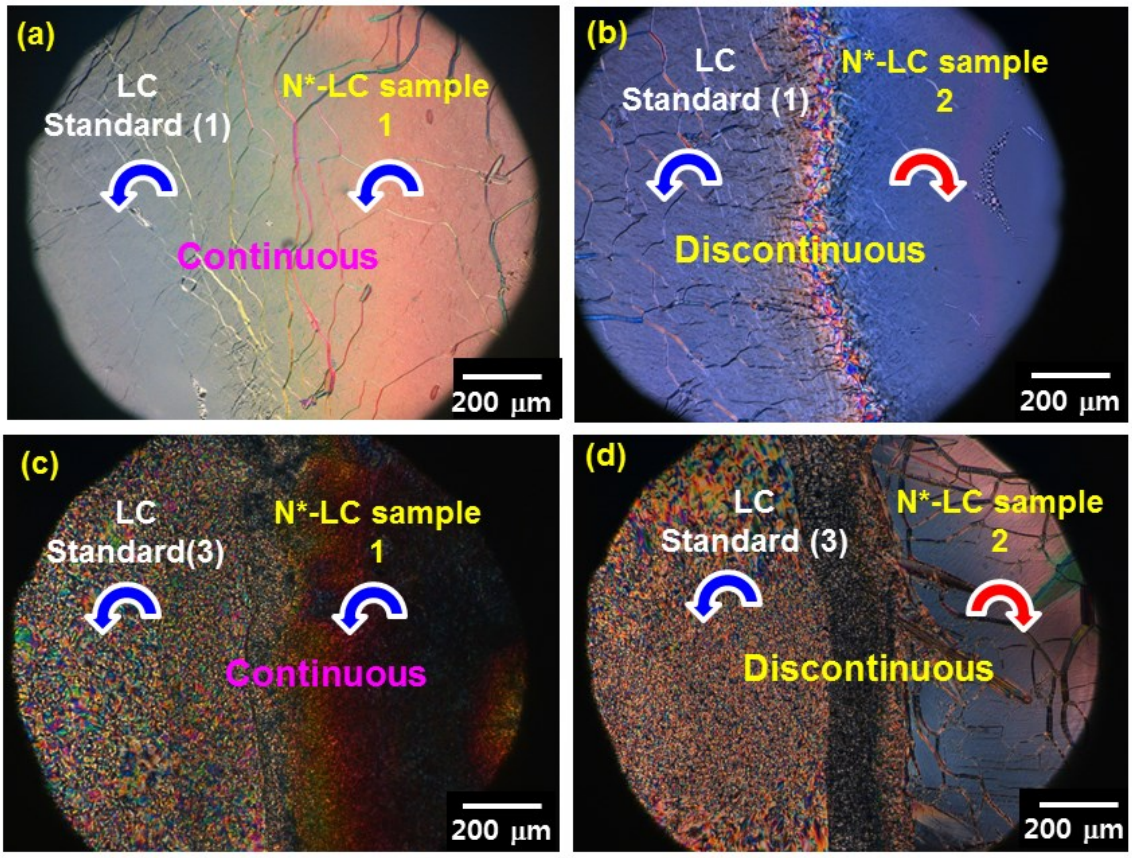


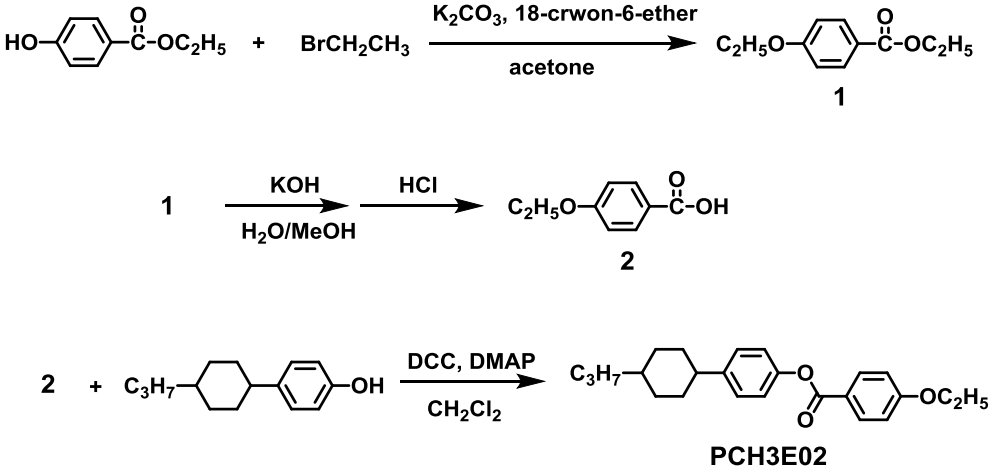
Figure S10. Contact test of LC standards and N*-LC samples [**PCH302** : **PCH304** : **PCH3E02** : **(*R*)-/(*S*)-D2** = 100 : 100 : 100: 3 in mole ratio]. (a) LC standard (1) and N*-LC sample 1 [**PCH302** : **PCH304** : **PCH3E02** : **(*S*)-D2** = 100 : 100 : 100: 3 in mole ratio] at 80 °C, (b) LC standard (1) and N*-LC sample 2 [**PCH302** : **PCH304** : **PCH3E02** : **(*R*)-D2** = 100 : 100 : 100: 3 in mole ratio] at 80 °C, (c) LC standard (3) and N*-LC sample 1 at 23 °C, (d) LC standard (3) and N*-LC sample 2 at 23 °C. LC standard (1) is cholesteryl pelargonate with left-handedness. LC standard (3) is cholesteryl oily carbonate with left-handedness.

8. Synthesis of PCH3E02

4-Ethoxybenzoic acid (2). Ethyl 4-hydroxybenzoate (10 g, 60.18 mmol), bromoethane (18 mL, 240.7 mmol), K_2CO_3 (24.95 g, 180.5 mmol) and a catalytic amount of 18-crown-6 were dissolved in acetone (100 mL). The mixture was stirred for 24 h at 60 °C. The mixture was removed using acetone in vacuo and the residue was extracted with H_2O and $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The organic solvent was removed by rotary evaporation. Purification was achieved by silica gel column chromatography (*n*-hexane/$CHCl_3$ = 1) and hydrolysis by refluxing in KOH solution and methanol at 75 °C for 3 hours. The mixture was acidified with HCl, extracted with $CHCl_3$, washed with a saturated NaCl solution, and dried over anhydrous sodium sulfate. The precipitate was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was purified with silica gel column chromatography ($CHCl_3$: Hexane = 1/1) to give 9.6 g (y = 96 %) of **2** as white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 1.37–1.41 (m, 3H, –C*H*$_3$), 4.12–4.15 (t, 2H, –OC*H*$_2$–), 6.99–7.01 (d, *J* = 9.04 Hz, 2H, phenyl–*H*), 7.97–7.99 (m, 2H, phenyl–*H*).

4-(4-Propylcyclohexyl)phenyl-4-ethoxybenzoate (PCH3E02). A solution of **2** (9 g, 54.12 mmol), *p*-(*trans*-4-propylcyclohexyl)phenol (PCH300) (14.18 g, 64.95 mmol), *N,N*′-dicyclohexylcarbodiimide (DCC) (13.4 g, 64.95 mmol) and 4-dimethylaminopyridine (DMAP) (7.93 g, 64.95 mmol) were dissolved in CH_2Cl_2, and was stirred for 12 hours at room temperature. The crude product was extracted with $CHCl_3$. The organic layer was washed with saturated NaCl solution and dried over anhydrous sodium sulfate. The precipitate was removed by filtration, and the filtrate was evaporated under reduced pressure.

The residue was purified with column chromatography (silica gel; $CHCl_3$: Hexane = 1/1) to give 19.23 g (yield = 97 %) of **PCH3E02** as white powder. ^{1}H-NMR (400MHz, $CDCl_3$, δ from TMS, ppm) δ = 0.89–0.92 (m, 3H, –C*H*$_3$), 1.00–1.09 (q, 2H, *J* = 10 and 12 Hz, –C*H*$_2$–), 1.20–1.49 (m, 10H, cyclohexane and –C*H*$_2$–), 1.85–1.92 (t, 4H, *J* = 14 Hz, –C*H*$_2$–), 2.45–2.51 (t, 1H, *J* = 12 Hz, cyclohexane), 4.08–4.13 (m, 2H, –OC*H*$_2$–), 6.94–6.96 (d, 2H, *J* = 8.8, phenyl–*H*), 7.09–7.11 (d, 2H, *J* = 8.8, phenyl–*H*), 7.22–7.24 (d, 2H, *J* = 8.4 Hz, Phenyl–*H*), 8.12–8.14 (d, 2H, *J* = 11.2 Hz, phenyl–*H*). ^{13}C-NMR ($CDCl_3$, 100 MHZ, δ fro m TMS, ppm): 14.43, 14.67, 20.05, 33.56, 34.44, 37.02, 39.73, 44.12, 63.77, 114.22, 121.39, 121.83, 127.71, 132.24, 145.25, 149.0, 163.24, 165.1. HRMS (FAB, *m/z*): Calc. 366.2195 Found: 367.2226. Anal. Calcd for $C_{24}H_{30}O_3$: C 78.65 %; H 8.25 %; O 13.10 %, Found: C 78.40 %; H 8.27 %.



Scheme S2. Synthetic routes of PCH3E02.

9. CD spectra

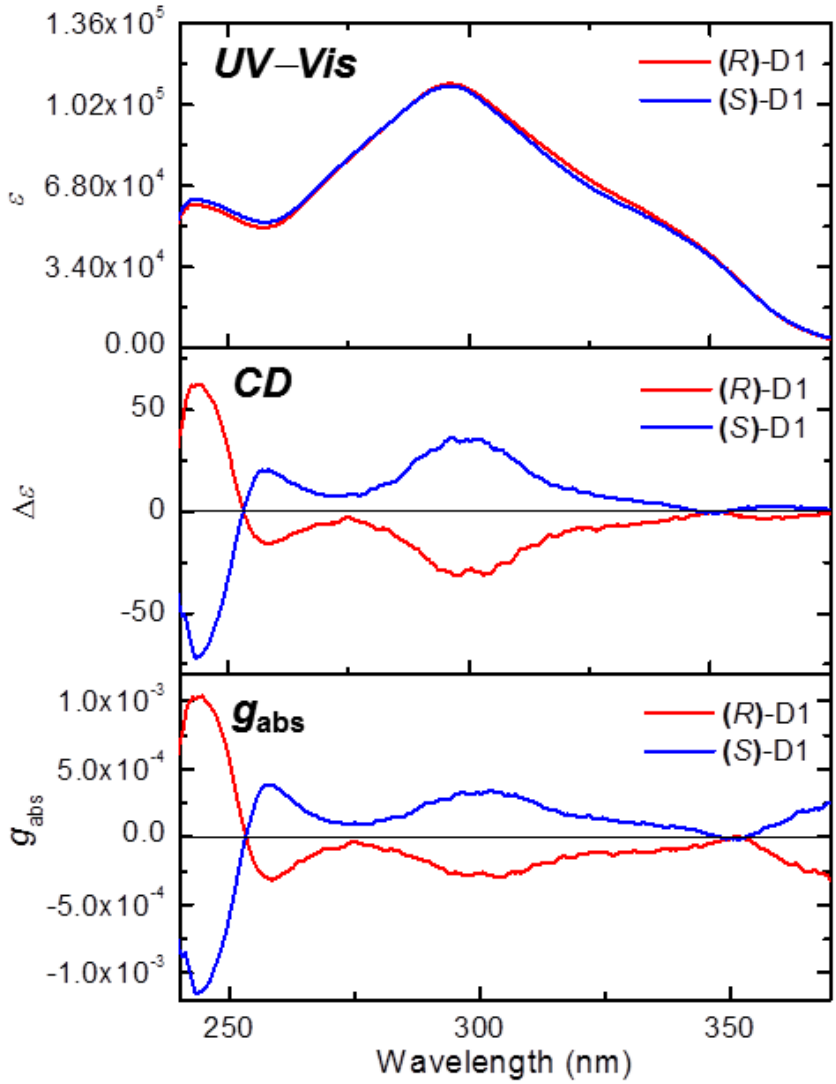


Figure S11. UV−Vis, CD, and g_{abs} spectra of **(*R*)/(*S*)-D1** in $CHCl_3$ ($c = 2.5\times10^{-5}$M).

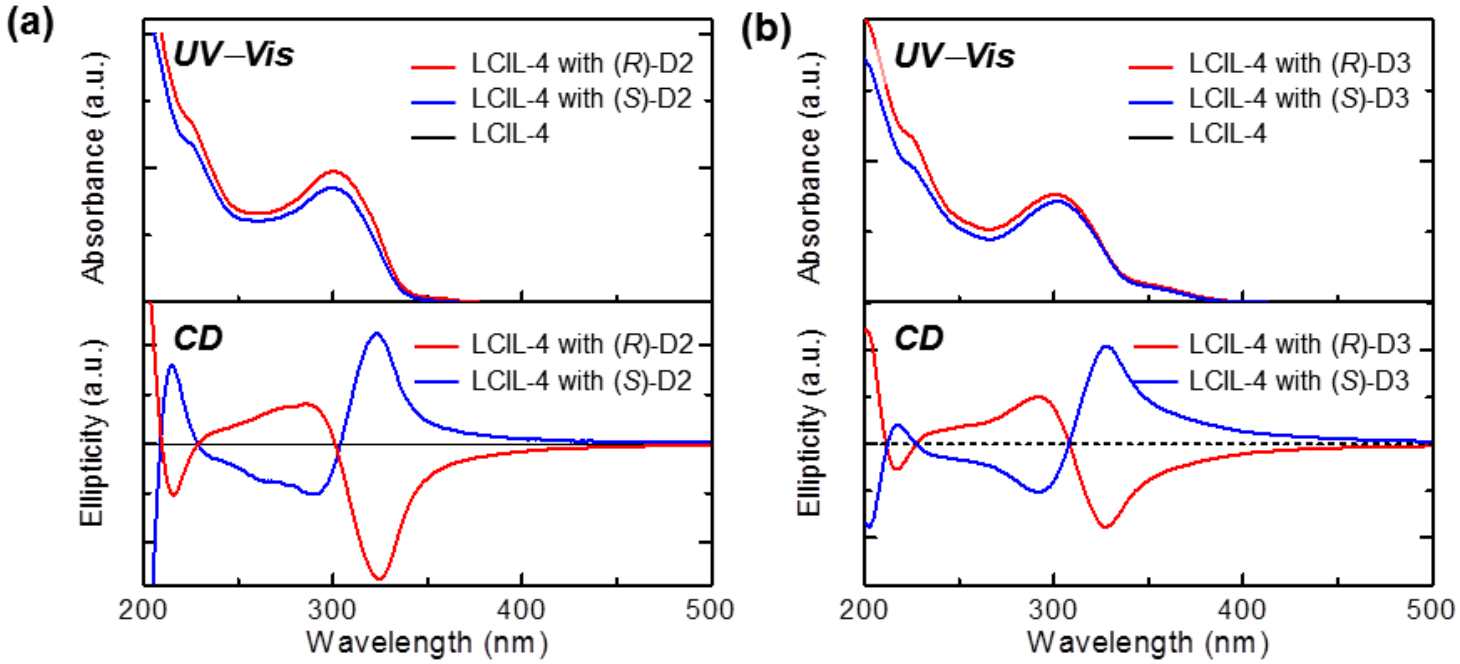


Figure S12. UV–Vis and CD spectra of the mixtures of **LCIL-4** with **(*R*)/(*S*)-D2** and **D3** in cast film. (top) UV–Vis absorption, and (bottom) CD spectra of the mixtures of **LCIL-4** and **(*R*)/(*S*)-**dopants. Red, blue, and black lines indicate the mixtures containing **(*R*)-** and **(*S*)-**dopants and **LCIL-4**, respectively.

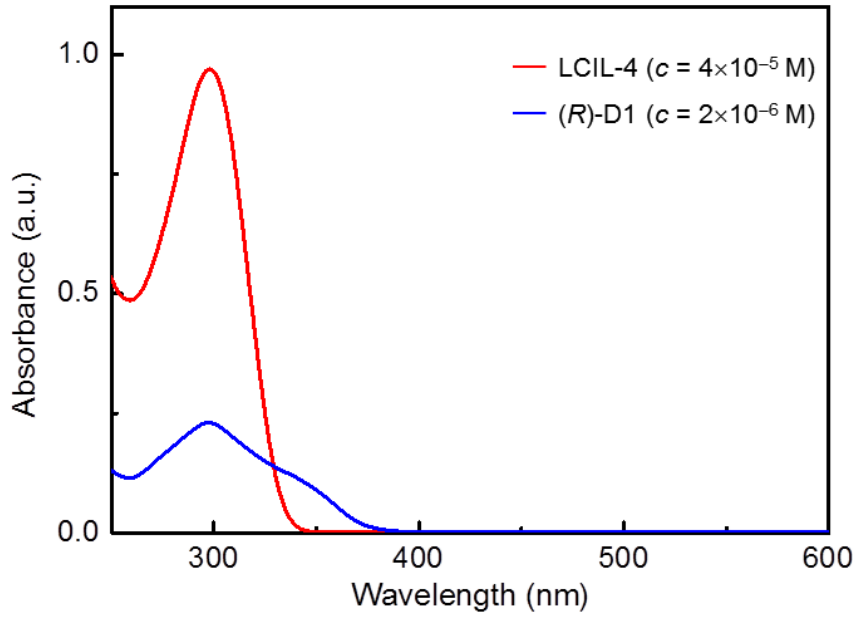


Figure S13. UV–Vis spectra of **LCIL-4** (c = 4.0×10^{-5}M) and **(*R*)-D1** (c = 2.0×10^{-6}M) in $CHCl_3$.

Reference

1. J. M. McNamara, W. B. Gleason, *J. Org. Chem*., 1976, **41**, 1071.

2. S. Yu, J. Saenz, J. K. Srirangam, *J. Org. Chem*., 2002, **67**, 1699–1702.