Supporting Information

Lyotropic Chiral Nematic Liquid Crystalline Aliphatic Conjugated Polymers Based on *Di*-Substituted Polyacetylene Derivatives that Exhibit High Dissymmetry Factors in Circularly Polarized Luminescence

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1. Syntheses of the Precursor Compounds

4-(1-Octynyl)-phenol (1)

4-(1-Octynyl)-phenol (**1**) was synthesized as follows. Into a 300 mL three-necked flask were added 0.16 g (0.23 mmol) of $PdCl_2(TPP)_2$, 93 mg of CuI (0.49 mmol), 1-octyne (3.00 g, 27 mmol) and 4-iodophenol (5.00 g, 23 mmol), and 120 mL THF under argon. After all the reagents were dissolved, 80 mL of 0.5 M aqueous NH_3 was added dropwise into the solution. The solution was stirred at room temperature overnight under argon atmosphere. Thin layer chromatography (TLC) indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 2 : 1). The collected liquid was evaporated and dried under vacuum and dried in vacuo to give 3.24 g (16 mmol) of **1** as a viscous deep red liquid. Yield = 70%.

Anal. Chemical Formula: $(C_{14}H_{18}O)_n$ $(202.14)_n$: Calcd. C 83.12, H 8.97, O 7.91; Found C 81.18, H 8.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, 3H, J = 6.8 Hz, $-CH_3$), 1.21–1.67 (m, 8H, $-(CH_2)_4-$), 2.39 (t, 2H, J = 7.2 Hz, –C≡C–$CH_2(CH_2)_4CH_3$), 4.75 (s, 1H, HO–Ar–C≡C–$(CH_2)_5CH_3$), 6.75 (d, 2H, J = 8.8 Hz, Ar–H *ortho* to HO–), 7.30 (d, 2H, J =8.4 Hz, Ar–H *meta* to HO–). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.0, 19.4, 22.5, 28.5, 28.8, 31.3, 88.8, 105.5, 115.1, 132.9, 159.6. HRMS (DART) calcd for $C_{14}H_{18}O$ $[M + H^+]$: 203.1430. Found: 203.1431.

4-(Phenylethynyl)phenol (2)

4-(Phenylethynyl)phenol (**2**) was synthesized as follows. The reagents 4-iodophenol (4.7 g, 21 mmol), phenyl acetylene (2.8 g, 28 mmol), $PdCl_2(TPP)_2$ (297 mg, 0.42 mmol), CuI (162 mg, 0.85 mmol), 25 mL Et_3N, and 10 mL THF were added under argon atmosphere into a 200 mL three necked flask. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The

solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 1 : 1). The product was recrystallized from *n*-hexane and dried in vacuo to give 2.7 g (13.4 mmol) of **2** as a yellowish crystal. Yield = 66%.

Anal. Chemical Formula: $(C_{14}H_{10}O)_n$ $(194.23)_n$: Calcd. C, 86.57; H, 5.19; O, 8.24; Found C 86.81, H 5.37. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.90 (s, 1H, –C≡C–Ar–*OH*), 6.81 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to –OH), 7.33 (m, 3H, Ar–H *meta* and *para* to –C≡C–C_6H_4OH), 7.43 (d, 2H, *J* = 8.8 Hz, Ar–H *meta* to –OH), 7.50 (d, 2H, *J* = 8.8 Hz, Ar–H *ortho* to –C≡C–C_6H_4OH). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 89.8, 115.3, 115.5, 127.8, 128.1, 131.3, 133.1. HRMS (DART) calcd for $C_{14}H_{10}O$ $[M + H^+]$: 195.0804. Found: 195.0806.

1-Iodo-4-(nonan-2-yloxy)benzene (3)

1-Iodo-4-(nonan-2-yloxy)benzene (**3**) was synthesized as follows. Into a 300 mL three-necked flask were added TPP (10.38 g, 40 mmol) and 4-iodophenol (9.50 g, 43 mmol) under argon gas and dissolved in THF (60 mL). In the addition funnel, a mixture of DEAD (20.00 g, 40 wt% in toluene, 40 mmol), 2-nonanol (5.20 g, 36 mmol), and 50 mL THF were prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with $CHCl_3$ (3×). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using $CHCl_3$ as eluent. The collected liquid was evaporated and dried under vacuum to give compound **3** (9.56 g, 27.6 mmol) as a light amber colored oil. Yield = 77%.

Anal. Chemical Formula: $(C_{15}H_{23}IO)_n$ $(346.25)_n$: Calcd. C, 52.03; H, 6.70; I, 36.65; O, 4.62; Found C, 52.17; H, 6.82. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, *J* = 6.8 Hz, –*CH_3*), 1.15–1.50 (m, 13H, Ar–O–CH*(CH_3)*CH_2*$(CH_2)_5$*CH_3, 1.51–1.75 (m, 2H, Ar–O–CH(CH_3)*CH_2*$(CH_2)_5CH_3$), 4.22–4.36 (m, 1H, Ar–O–*CH*$(CH_3)CH_2(CH_2)_5CH_3$), 6.65 (d, 2H, *J* = 8.8 Hz, Ar–H *meta* to –I), 7.53 (d, 2H, *J* = 8.6 Hz,

Ar–H *ortho* to –I). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.7, 36.3, 74.1, 82.1, 118.1, 138.0, 157.9. HRMS (APCI) calcd for $C_{15}H_{23}IO$ [M^+]: 346.0788. Found: 346.0783.

(*R*)-1-Iodo-4-(nonan-2-yloxy)benzene (4)

(*R*)-1-Iodo-4-(nonan-2-yloxy)benzene (**4**) was synthesized as follows. Into a 300 mL three-necked flask were added TPP (10.00 g, 38 mmol) and 4-iodophenol (9.14 g, 42 mmol) under argon gas and dissolved in THF (80 mL). In the addition funnel, a mixture of DEAD (19.26 g, 40 wt% in toluene, 38 mmol), (*S*)-(+)-2-nonanol (5.00 g, 34 mmol), and 50 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with $CHCl_3$ (3×). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using $CHCl_3$ as eluent. The collected liquid was evaporated and dried under vacuum to give compound **4** (8.12 g, 23.6 mmol) as a light amber colored oil. Yield = 68%.

Anal. Chemical Formula: $(C_{15}H_{23}IO)_n$ $(346.25)_n$: Calcd. C, 52.03; H, 6.70; I, 36.65; O, 4.62; Found C, 52.25; H, 6.76. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, 3H, *J* = 7.2 Hz, –*CH*$_3$), 1.23–1.50 (m, 13H, Ar–O–CH*(CH*$_3$*)*CH_2*(CH*$_2$*)*$_5$$CH_3$, 1.51–1.71 (m, 2H, Ar–O–CH(CH_3)*CH_2*(CH_2)$_5$$CH_3$), 4.27–4.32 (m, 1H, Ar–O–*CH*(CH_3)CH_2(CH_2)$_5$$CH_3$), 6.54 (d, 2H, *J* = 7.2 Hz, Ar–H *meta* to –I), 7.53 (d, 2H, *J* = 6.8 Hz, Ar–H *ortho* to –I). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.3, 74.1, 82.1, 118.1, 138.1, 158.0. HRMS (APCI) calcd for $C_{15}H_{23}IO$ [M^+]: 346.0788. Found: 346.0783. $[\alpha]^{25}_D$ –3.54° (*c* 1.0, $CHCl_3$).

(*S*)-1-Iodo-4-(nonan-2-yloxy)benzene (5)

(*S*)-1-Iodo-4-(nonan-2-yloxy)benzene **(5)** was synthesized as follows. TPP (10.00 g, 38.2 mmol), 4-iodophenol (9.14 g, 42 mmol) were added under argon gas into a 300 mL three necked flask,

dissolved in THF (70 mL) and then stirred. In the addition funnel, a mixture of DEAD (19.28 g, 40 wt% in toluene, 38.2 mmol), (*R*)-(−)-2-nonanol (5.00 g, 34 mmol), and 50 mL THF was prepared. After dissolving the reagents under constant stirring, the flask was placed in an ice bath and the THF solution in the addition funnel was added dropwise to the solution in the flask. The solution was left overnight at room temperature. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was washed with water and extracted with $CHCl_3$ (3×). The residue was dried over anhydrous Na_2SO_4 and the crude product was then purified by open column chromatography using $CHCl_3$ as eluent. The collected liquid was evaporated and dried under vacuum to give compound **5** (9.34 g, 27.0 mmol) as a light amber colored oil. Yield = 78%.

Anal. Chemical Formula: $(C_{15}H_{23}IO)_n$ $(346.25)_n$: Calcd. C, 52.03; H, 6.70; I, 36.65; O, 4.62; Found C, 52.59; H, 6.85. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, 3H, *J* = 7.2 Hz, –*CH*$_3$), 1.21–1.56 (m, 13H, Ar–O–CH*(CH*$_3$*)*CH_2*(CH*$_2$*)*$_5$$CH_3$, 1.64–1.72 (m, 2H, Ar–O–CH(CH_3)*CH*$_2$(CH_2)$_5$$CH_3$), 4.24–4.31 (m, 1H, Ar–O–*CH*(CH_3)CH_2(CH_2)$_5$$CH_3$), 6.64 (d, 2H, *J* = 6.4 Hz, Ar–H *meta* to –I), 7.50 (d, 2H, *J* = 6.4 Hz, Ar–H *ortho* to –I). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.3, 74.1, 82.1, 118.1, 138.0, 157.9. HRMS (APCI) calcd for $C_{15}H_{23}IO$ [M^+]: 346.0788. Found: 346.0782. $[\alpha]^{25}_D$ +3.66° (*c* 1.0, $CHCl_3$).

Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (6)

Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (**6**) was synthesized as follows. Into a 200 mL three-necked flask were added compound **3** (9.4 g, 27.1 mmol), trimethylsilylacetylene (4.00 g, 40.7 mmol), $PdCl_2(TPP)_2$ (0.38 g, 0.54 mmol), CuI (0.21 g 1.10 mmol), 30 mL Et_3N, and 120 mL THF under argon. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography using $CHCl_3$ as eluent. The

product was evaporated and dried under vacuum to give compound **6** (7.76 g, 24.5 mmol) as a light amber colored oil. Yield = 90%.

Anal. Chemical Formula: $(C_{20}H_{32}OSi)_n$ $(316.55)_n$: Calcd. C, 75.88; H, 10.19; O, 5.05; Si, 8.87. Found C, 75.80; H, 10.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (t, 9H, Ar–C≡C–Si*(CH$_3$)$_3$*), 0.64 (t, 3H, J = 7.3 Hz, Ar–O–CH(CH_3)(CH_2)$_6$*CH$_3$*), 0.91–1.31 (m, 13H, Ar–O–CH*(CH$_3$)*CH_2*(CH$_2$)$_5$*CH_3), 1.33–1.59 (m, 2H, Ar–O–CH(CH_3)*CH_2*(CH_2)$_5$$CH_3$), 4.09–4.14 (m, 1H, Ar–O–*CH*(CH_3)CH_2(CH_2)$_5$$CH_3$), 6.55 (d, 2H, J = 8.8 Hz, Ar–H *meta* to –C≡C–Si(CH_3)$_3$), 7.14 (d, 2H, J = 8.6 Hz, Ar–H *ortho* to –C≡C–Si(CH_3)$_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.0, 22.0, 24.8, 28.6, 28.9, 31.2, 35.7, 73.3, 91.5, 114.8, 132.7, 157.7. HRMS (APCI) calcd for $C_{20}H_{32}OSi$ [M + H$^+$]: 317.2295. Found: 317.2285.

(*R*)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (7)

(*R*)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (**7**) was synthesized as follows. Into a 200 mL three-necked flask were added compound **4** (3.42 g, 9.87 mmol), trimethylsilylacetylene (1.45 g, 14.81 mmol), $PdCl_2(TPP)_2$ (139 mg, 0.20 mmol), CuI (75 mg, 0.39 mmol), 20 mL Et_3N, and 70 mL THF under argon. After continuous stirring, solution was heated to 65 °C and left overnight. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography using $CHCl_3$ as eluent. The product was evaporated and dried under vacuum to give compound **7** (2.75 g, 8.69 mmol) as a light amber colored oil. Yield = 88%.

Anal. Chemical Formula: $(C_{20}H_{32}OSi)_n$ $(316.55)_n$: Calcd. C, 75.88; H, 10.19; O, 5.05; Si, 8.87. Found C, 75.67; H, 9.92. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (t, 9H, Ar–C≡C–Si*(CH$_3$)$_3$*), 0.64 (t, 3H, J = 7.3 Hz, Ar–O–CH(CH_3)(CH_2)$_6$*CH$_3$*), 1.04–1.31 (m, 13H, Ar–O–CH*(CH$_3$)*CH_2*(CH$_2$)$_5$*CH_3), 1.31–1.55 (m, 2H, Ar–O–CH(CH_3)*CH_2*(CH_2)$_5$$CH_3$), 4.09–4.14 (m, 1H, Ar–O–*CH*(CH_3)CH_2(CH_2)$_5$$CH_3$), 6.54 (d, 2H, J = 6.8 Hz, Ar–H *meta* to –C≡C–Si(CH_3)$_3$), 7.14 (d, 2H, J = 6.8 Hz, Ar–H *ortho* to –C≡C–Si(CH_3)$_3$).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.3, 73.9, 92.1, 115.4, 133.3, 158.0. HRMS (APCI) calcd for $C_{20}H_{32}OSi$ [M + H^+]: 317.2295. Found: 317.2285. $[\alpha]^{25}_D$ –0.62° (*c* 1.0, $CHCl_3$).

(*S*)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (8)

(*S*)-Trimethyl((4-(nonan-2-yloxy)phenyl)ethynyl)silane (**8**) was synthesized as follows. The reagents compound **5** (2.2 g, 6.35 mmol), trimethylsilylacetylene (0.94 g, 9.53 mmol), $PdCl_2(TPP)_2$ (89 mg, 0.13 mmol), CuI (48 mg, 0.26 mmol), 10 mL Et_3N, and 50 mL THF were added under argon atmosphere into a 300 mL three-mouthed flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography using $CHCl_3$ as eluent. The product was evaporated and dried under vacuum to give compound **8** (1.83 g, 5.78 mmol) as a light amber colored oil. Yield = 91%.

Anal. Chemical Formula: $(C_{20}H_{32}OSi)_n$ $(316.55)_n$: Calcd. C, 75.88; H, 10.19; O, 5.05; Si, 8.87; Found C, 75.89; H, 10.43. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (t, 9H, Ar–C≡C–Si*(CH$_3$)$_3$*), 0.62 (t, 3H, *J* = 7.2 Hz, Ar–O–CH(CH$_3$)(CH$_2$)$_6$*CH$_3$*), 1.00–1.28 (m, 13H, Ar–O–CH*(CH$_3$)*CH$_2$*(CH$_2$)$_5$*CH$_3$), 1.30–1.55 (m, 2H, Ar–O–CH(CH$_3$)*CH$_2$*(CH$_2$)$_5$CH$_3$), 4.10–4.14 (m, 1H, Ar–O–*CH*(CH$_3$)CH$_2$(CH$_2$)$_5$CH$_3$), 6.53 (d, 2H, *J* = 7.0 Hz, Ar–H *meta* to –C≡C–Si(CH$_3$)$_3$), 7.20 (d, 2H, *J* = 6.8 Hz, Ar–H *ortho* to –C≡C–Si(CH$_3$)$_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.0, 19.5, 22.5, 25.4, 29.1, 29.4, 31.7, 36.2, 73.8, 92.0, 115.3, 133.2, 158.2. HRMS (APCI) calcd for $C_{20}H_{32}OSi$ [M + H^+]: 317.2295. Found: 317.2284. $[\alpha]^{25}_D$ +0.67° (*c* 1.0, $CHCl_3$).

1-Ethynyl-4-(nonan-2-yloxy)benzene (9)

1-Ethynyl-4-(nonan-2-yloxy)benzene (**9**) was synthesized as follows. Into a 100 mL round-bottom flask were added compound **6** (7.39 g, 23.4 mmol), K_2CO_3 (1.61 g, 11.7 mmol), 10 mL MeOH, and 10

mL THF. After continuous stirring, solution was left overnight at room temperature. The solution was then filtered, evaporated and the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography using $CHCl_3$ as eluent. The product was evaporated and dried under vacuum to give compound **9** (5.44 g, 22.3 mmol) as an amber colored oil. Yield = 92%.

Anal. Chemical Formula: $(C_{17}H_{24}O)_n$ $(244.37)_n$: Calcd. C, 83.55; H, 9.90; O, 6.55. Found C, 83.42; H, 10.02. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 6.8 Hz, $-CH_3$), 1.19–1.47 (m, 13H, Ar–O–CH$(CH_3)$$CH_2$$(CH_2)_5$$CH_3$), 1.50–1.78 (m, 2H, Ar–O–CH$(CH_3)$$CH_2$$(CH_2)_5$$CH_3$), 2.98 (s, 1H, –O–Ar–C≡*CH*), 4.33–4.38 (m, 1H, Ar–O–*CH*$(CH_3)$$CH_2$$(CH_2)_5$$CH_3$), 6.81 (d, 2H, J = 6.8 Hz, Ar–H *meta* to –C≡C–Si$(CH_3)_3$), 7.40 (d, 2H, J = 7.0 Hz, Ar–H *ortho* to –C≡C–Si$(CH_3)_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ =14.1, 19.6, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 75.5, 83.7, 113.6, 115.5, 133.4, 158.5. HRMS (APCI) calcd for $C_{17}H_{24}O$ $[M + H^+]$: 245.1900. Found: 245.1894.

(*R*)-1-Ethynyl-4-(nonan-2-yloxy)benzene (10)

(*R*)-1-Ethynyl-4-(nonan-2-yloxy)benzene (**10**) was synthesized as follows. Into a 100 mL round-bottom flask were added compound **7** (2.65 g, 8.36 mmol), K_2CO_3 (2.31 g, 16.72 mmol), 50 mL MeOH, and 50 mL THF. After continuous stirring, solution was left overnight at room temperature. The solution was then filtered, evaporated and the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography using $CHCl_3$ as eluent. The product was evaporated and dried under vacuum to give compound **10** (1.88 g, 7.69 mmol) as an amber colored oil. Yield = 92%.

Anal. Chemical Formula: $(C_{17}H_{24}O)_n$ $(244.37)_n$: Calcd. C, 83.55; H, 9.90; O, 6.55. Found C, 83.28; H, 9.97. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, 3H, J = 7.0 Hz, $-CH_3$), 1.25–1.39 (m, 13H, Ar–O–CH$(CH_3)$$CH_2$$(CH_2)_5$$CH_3$), 1.51–1.69 (m, 2H, Ar–O–CH$(CH_3)$$CH_2$$(CH_2)_5$$CH_3$), 2.96 (s, 1H,

–O–Ar–C≡*CH*), 4.31–4.36 (m, 1H, Ar–O–*CH*(CH_3)CH_2(CH_2)$_5CH_3$), 6.78 (d, 2H, *J* = 6.8 Hz, Ar–H *meta* to –C≡C–Si(CH_3)$_3$), 7.38 (d, 2H, *J* = 7.0 Hz, Ar–H *ortho* to –C≡C–Si(CH_3)$_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.7, 22.6, 25.5, 29.1, 29.5, 31.8, 36.3, 76.6, 81.0, 113.5, 115.5, 133.4, 157.0. HRMS (APCI) calcd for $C_{17}H_{24}O$ [M + H^+]: 245.1900. Found: 245.1892. [α]$^{25}_D$ –6.24° (*c* 1.0, $CHCl_3$).

(*S*)-1-Ethynyl-4-(nonan-2-yloxy)benzene (11)

(*S*)-1-Ethynyl-4-(nonan-2-yloxy)benzene (**11**) was synthesized as follows. Compound **8** (1.80 g, 5.69 mmol), K_2CO_3 (0.39 g, 2.84 mmol), 50 mL MeOH, and 50 mL THF were added to a 100 mL round-bottom flask. The solution was stirred overnight at room temperature under argon atmosphere. The solution was then filtered, evaporated and the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography using $CHCl_3$ as eluent. The product was evaporated and dried under vacuum to give compound **11** (1.21 g, 4.94 mmol) as an amber colored oil. Yield = 87%.

Anal. Chemical Formula: ($C_{17}H_{24}O$)$_n$ (244.37)$_n$: Calcd. C, 83.55; H, 9.90; O, 6.55. Found C, 83.31; H, 10.11. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, 3H, *J* = 6.8 Hz, –*CH*$_3$), 1.21–1.40 (m, 13H, Ar–O–CH*(CH*$_3$*)*CH_2*(CH*$_2$*)*$_5$$CH_3$), 1.46–1.49 (m, 2H, Ar–O–CH(CH_3)*CH*$_2$(CH_2)$_5CH_3$), 2.91 (s, 1H, –O–Ar–C≡*CH*), 4.26–4.31 (m, 1H, Ar–O–*CH*(CH_3)CH_2(CH_2)$_5CH_3$), 6.74 (d, 2H, *J* = 8.0 Hz, Ar–H *meta* to –C≡C–Si(CH_3)$_3$), 7.33 (d, 2H, *J* = 6.8 Hz, Ar–H *ortho* to –C≡C–Si(CH_3)$_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.6, 22.6, 25.4, 29.2, 29.5, 31.8, 36.4, 75.4, 83.7, 113.5, 115.5, 133.4, 158.5. HRMS (APCI) calcd for $C_{17}H_{24}O$ [M + H^+]: 245.1900. Found: 245.1892. [α]$^{25}_D$ +6.39° (*c* 1.0, $CHCl_3$).

4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (12)

4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (**12**) was synthesized as follows. The reagents compound **9** (4.00 g, 16.4 mmol), 4-iodophenol (3.28 g, 14.9 mmol), $PdCl_2(TPP)_2$ (0.21 g, 0.30 mmol), CuI (0.11 g, 0.60 mmol), 30 mL Et_3N, and 70 mL THF were added under argon atmosphere into a 100

mL three-mouthed flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 3 : 1). The product was evaporated and dried under vacuum to give compound **12** (3.66 g, 10.89 mmol) as a reddish solid. Yield = 73%.

Anal. Chemical Formula: $(C_{23}H_{28}O_2)_n$ $(336.47)_n$: Calcd. C, 82.10; H, 8.39; O, 9.51. Found C, 81.22; H, 8.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 7.1 Hz, $-CH_3$), 1.22–1.35 (m, 13H, Ar–O–CH$(CH_3)$$CH_2(CH_2)_5CH_3$), 1.51–1.78 (m, 2H, Ar–O–CH$(CH_3)$$CH_2(CH_2)_5CH_3$), 4.31–4.42 (m, 1H, Ar–O–$CH(CH_3)CH_2(CH_2)_5CH_3$), 4.84 (s, 1H, *HO*–Ar–C≡C–Ar), 6.79 (d, 2H, J = 6.6 Hz, Ar–H *ortho* to –O–$CH(CH_3)(CH_2)_6CH_3$), 6.81 (d, 2H, J = 7.1 Hz, Ar–H *ortho* to HO–), 7.39 (d, 2H, J = 5.8 Hz, Ar–H *meta* to HO–), 7.42 (d, 2H, J = 6.1 Hz, Ar–H *meta* to –O–$CH(CH_3)(CH_2)_6CH_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.0, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 87.5, 88.5, 115.3, 115.6, 132.7, 132.9, 155.2. HRMS (DART) calcd for $C_{23}H_{28}O_2$ $[M + H^+]$: 337.2162. Found: 337.2160.

(*R*)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (13)

(*R*)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (**13**) was synthesized as follows. The reagents compound **10** (1.77 g, 7.3 mmol), 4-iodophenol (1.45 g, 6.6 mmol), $PdCl_2(TPP)_2$ (93 mg, 0.13 mmol), CuI (50 mg, 0.26 mmol), 10 mL Et_3N, and 10 mL THF were added under argon atmosphere into a Schlenk flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 3 : 1). The product was evaporated and dried under vacuum to give compound **13** (1.39 g, 4.13 mmol) as a reddish solid. Yield = 63%.

Anal. Chemical Formula: $(C_{23}H_{28}O_2)_n$ $(336.47)_n$: Calcd. C, 82.10; H, 8.39; O, 9.51. Found C, 81.03; H, 8.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 7.6 Hz, $-CH_3$), 1.23–1.33 (m, 13H, Ar–O–CH$(CH_3)$$CH_2(CH_2)_5CH_3$), 1.50–1.77 (m, 2H, Ar–O–CH$(CH_3)$$CH_2(CH_2)_5CH_3$), 4.32–4.40 (m, 1H, Ar–O–$CH(CH_3)CH_2(CH_2)_5CH_3$), 4.93 (s, 1H, *HO*–Ar–C≡C–Ar), 6.79 (d, 2H, J = 8.8 Hz, Ar–H *ortho* to –O–$CH(CH_3)(CH_2)_6CH_3$), 6.83 (d, 2H, J = 8.1 Hz, Ar–H *ortho* to HO–), 7.39 (d, 2H, J = 6.1 Hz, Ar–H *meta* to HO–), 7.41 (d, 2H, J = 8.3 Hz, Ar–H *meta* to –O–$CH(CH_3)(CH_2)_6CH_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.0, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 83.5, 84.1, 115.3, 115.6, 132.7, 132.9, 156.6. HRMS (DART) calcd for $C_{23}H_{28}O_2$ [M + H^+]: 337.2162. Found: 337.2149. $[\alpha]^{25}_D$ +3.26° (*c* 1.0, $CHCl_3$).

(*S*)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (14)

(*S*)-4-((4-(nonan-2-yloxy)phenyl)ethynyl)phenol (**14**) was synthesized as follows. The reagents compound **11** (0.90 g, 3.7 mmol), 4-iodophenol (0.74 g, 3.3 mmol), $PdCl_2(TPP)_2$ (47 mg, 0.07 mmol), CuI (26 mg, 0.13 mmol), 10 mL Et_3N, and 10 mL THF were added under argon atmosphere into a Schlenk flask and stirred. The solution was stirred at 65 °C overnight under argon atmosphere. TLC indicated completion of the reaction. After evaporation of the solvent, the residue was thoroughly washed with water and extracted with $CHCl_3$ (3×). The organic layer was dried over anhydrous Na_2SO_4. The solution was evaporated and purified by open column chromatography (silica gel, hexane/ethyl acetate = 3 : 1). The product was evaporated and dried under vacuum to give compound **14** (1.39 g, 2.94 mmol) as a reddish solid. Yield = 88%.

Anal. Chemical Formula: $(C_{23}H_{28}O_2)_n$ $(336.47)_n$: Calcd. C, 82.10; H, 8.39; O, 9.51. Found C, 81.06; H, 9.71. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 3H, J = 6.8 Hz, $-CH_3$), 1.20–1.46 (m, 13H, Ar–O–CH$(CH_3)$$CH_2(CH_2)_5CH_3$), 1.50–1.80 (m, 2H, Ar–O–CH$(CH_3)$$CH_2(CH_2)_5CH_3$), 4.32–4.40 (m, 1H, Ar–O–$CH(CH_3)CH_2(CH_2)_5CH_3$), 4.85 (s, 1H, *HO*–Ar–C≡C–Ar), 6.79 (d, 2H, J = 8.8 Hz, Ar–H *ortho* to –O–$CH(CH_3)(CH_2)_6CH_3$), 6.83 (d, 2H, J = 8.8 Hz, Ar–H *ortho* to HO–), 7.39 (d, 2H, J = 6.4

Hz, Ar–H *meta* to HO–), 7.41 (d, 2H, J = 6.0 Hz, Ar–H *meta* to –O–CH(CH_3)(CH_2)$_6$$CH_3$). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 19.7, 22.6, 25.5, 29.2, 29.5, 31.8, 36.4, 73.9, 87.5, 88.0, 115.3, 115.6, 132.7, 132.9, 155.2. HRMS (DART) calcd for $C_{23}H_{28}O_2$ [M + H^+]: 337.2162. Found: 337.2152. $[\alpha]^{25}_D$ –3.21° (*c* 1.0, $CHCl_3$).

2. Liquid Crystallinity of PA1 Polymers

PA1, having a PAPA structure, exhibited thermotropic LC behavior having a Smectic A (S_A) LC phase. Polarizing optical microscopy (POM) analysis revealed that **PA1** has a nematic LC (N-LC) phase with a sandy LC texture (Figure S1a) and no isotropic phase. The temperature ranges of the N-LC phase were 95–300 and 65–300 °C in heating and cooling processes, respectively, and thermal decomposition occurred at temperatures over 300 °C.

The LC phase of **PA1** was also investigated using X-ray diffraction (XRD). The XRD patterns of **PA1** have two sharp diffraction peaks at 5.5 and 17.9° in 2θ (Figure S1b), corresponding to distances of 16.0 and 5.0 Å, respectively. The former represents the smectic interlayer distance while the latter corresponds to the distance between phenyl nonyloxy groups. The 16.0 Å smectic interlayer distance is comparable to the 14.5 Å calculated side chain length (L_1) of the side chain having the 4-nonyloxy phenyl moiety. Whereas the side chain with the hexyl moiety has a calculated side chain length (L_2) of 6.9 Å. The lengths of the **PA1** side chains were calculated using molecular mechanics calculations.

3. Supporting Information Schemes, Figures, and Tables

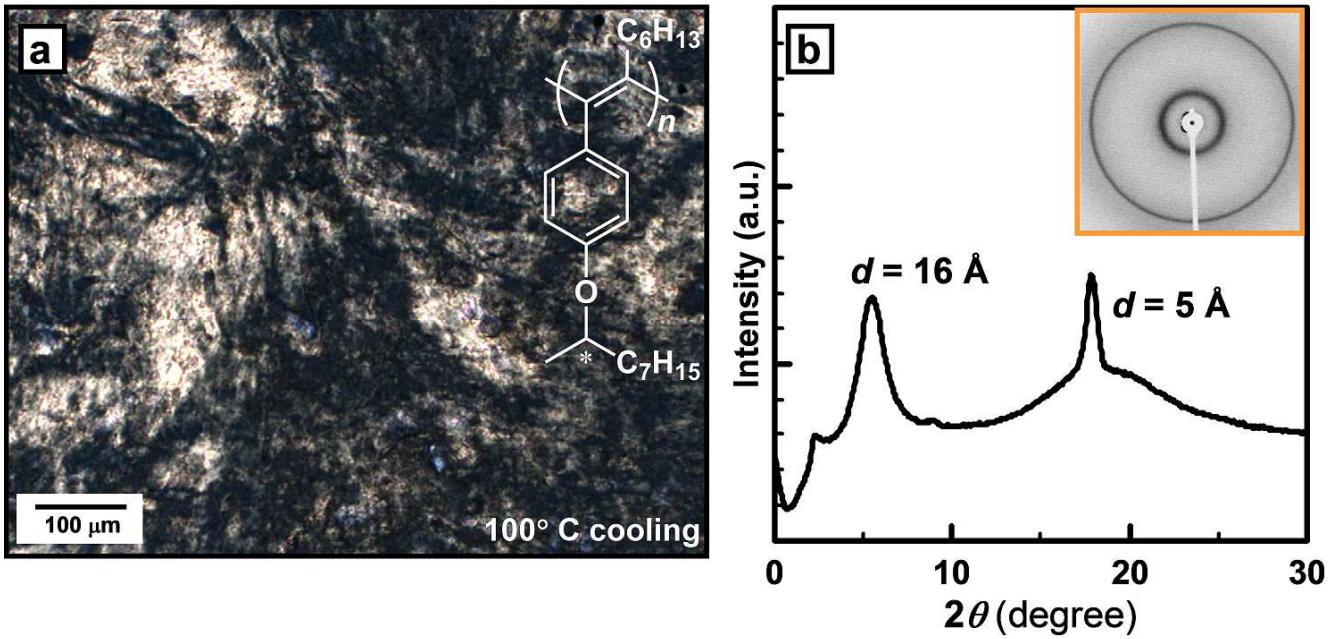

Figure S1. (a) POM image of **(*R*)-PA1** at 100 °C in cooling process. (b) XRD patterns showing the Smectic A (S_A) LC phase of **(*R*)-PA1** (5.5° and 17.9° in 2θ), inset shows the Laue pattern of the polymer.

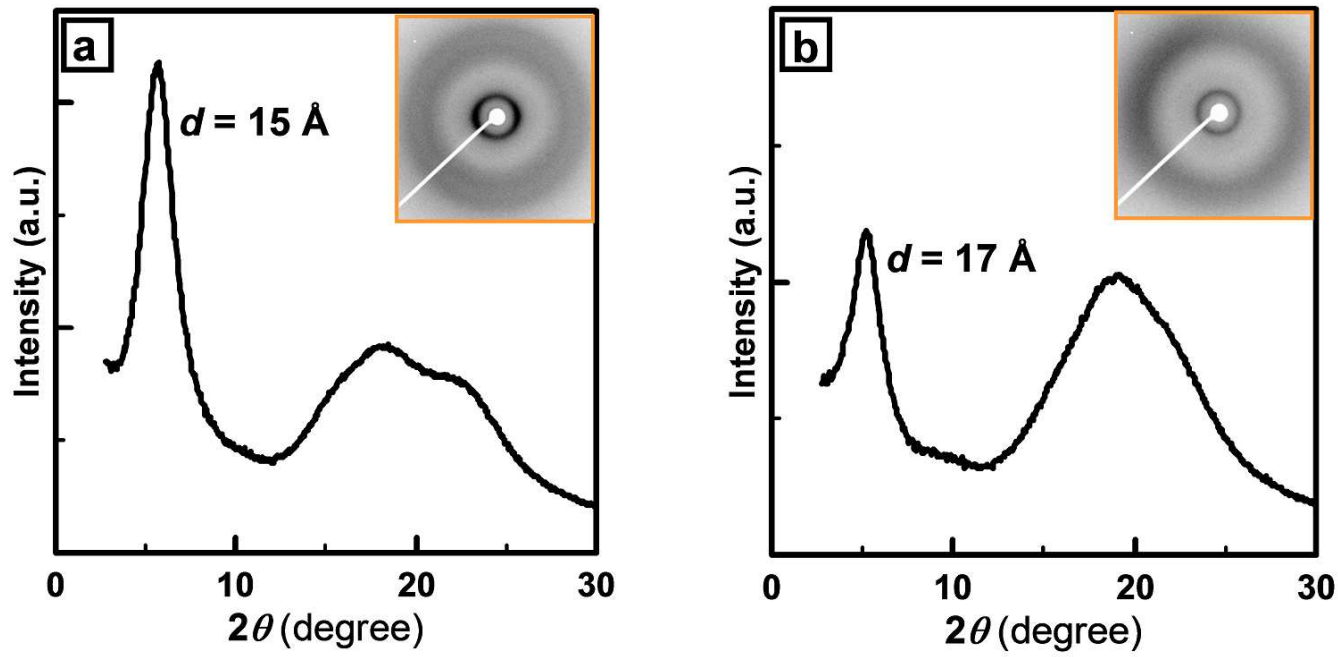

Figure S2. The XRD patterns of (a) **(*rac*)-PA2** N-LC film, and (b) **(*S*)-D1/(*rac*)-PA2** N*-LC film show reflections describing the polymer interchain distance within the N-LC (5.7° in 2θ) and N*-LC (5.2° in 2θ) domains, respectively. Inset shows the Laue pattern of the polymers.

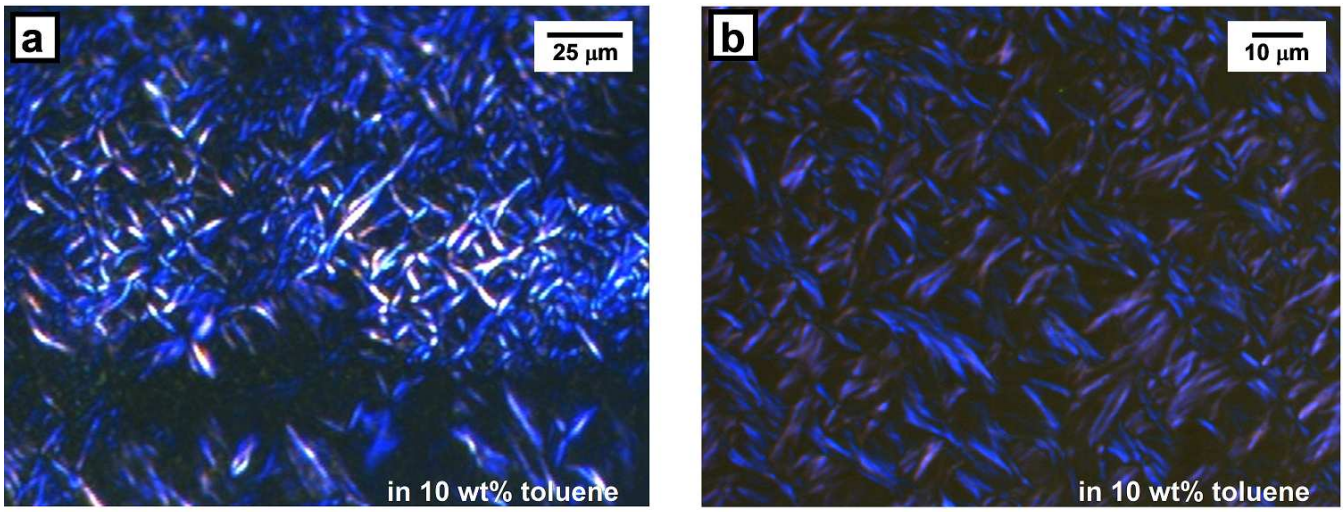

Figure S3. POM image of (a) **(*S*)-PA3**, and (b) **(*S*)-D1** doped **(*rac*)-PA3** (10 wt%) in 10 wt% lyotropic LC solution in toluene showing a fan like texture of a short pitch N*-LC phase.

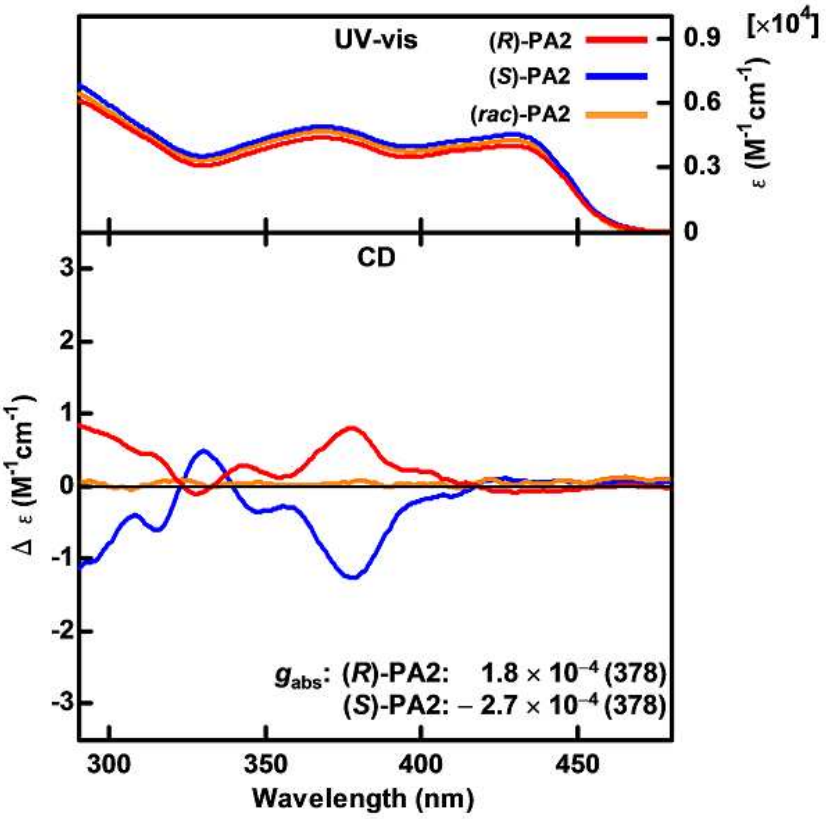

Figure S4. UV-vis (upper) and CD spectra (lower) of **PA2** in toluene solution ($c = 1.2 \times 10^{-4}$ M).

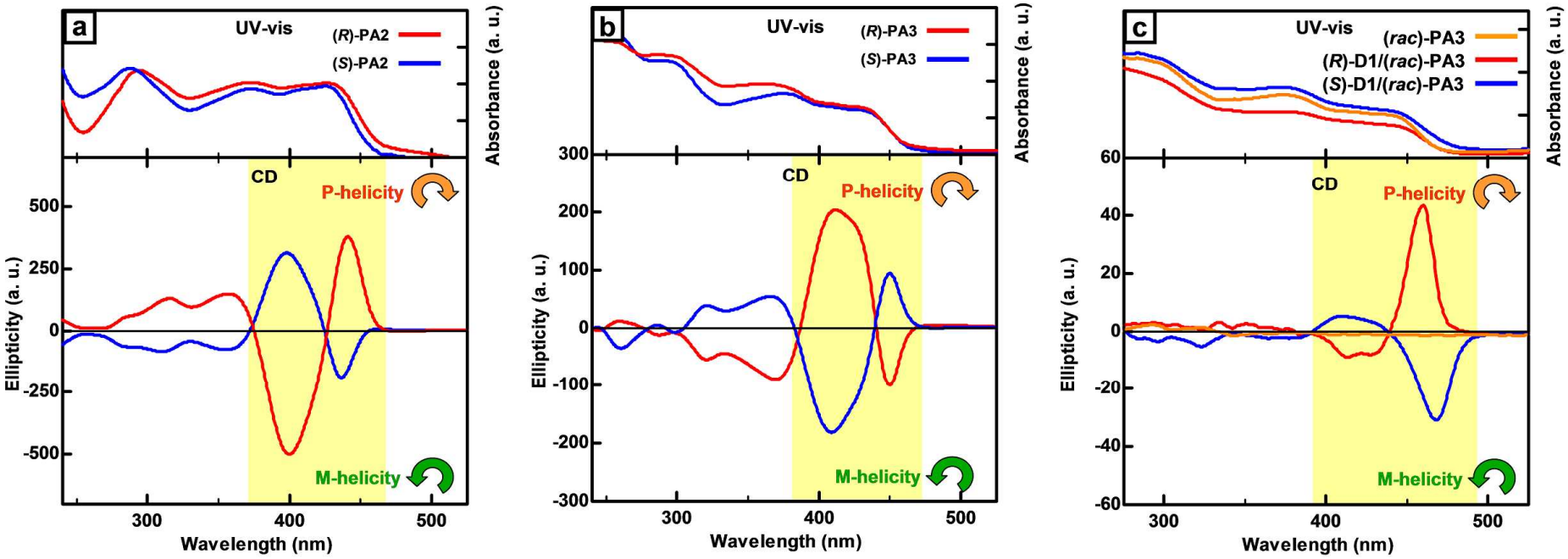

Figure S5. UV-vis (upper) and CD spectra (lower) of (a) **(*R*)-/(*S*)-PA2** cast film, (b) **(*R*)-/(*S*)-PA3** cast film, and (c) **(*R*)-/(*S*)-D1** doped **(*rac*)-PA3** (10 wt%) N*-LC film.

Table S1. Absorption dissymmetry factors (g_{abs}) of the *di*-substituted LCPAs in cast film and N*-LC film.

	g_{abs}(wavelength/ nm)[a]
(*R*)-PA2	3.7×10^{-2} (445)[b]
(*S*)-PA2	-2.4×10^{-2} (440)[b]
(*R*)-PA3	-4.6×10^{-3} (450)[b]
(*S*)-PA3	7.6×10^{-3} (451)[b]
(*R*)-D1/(*rac*)-PA3	8.0×10^{-4} (461)[c]
(*S*)-D1/(*rac*)-PA3	-2.1×10^{-3} (471)[c]

[a]Wavelength at which g_{abs} was evaluated
[b]In cast film, [c]in N*LC film

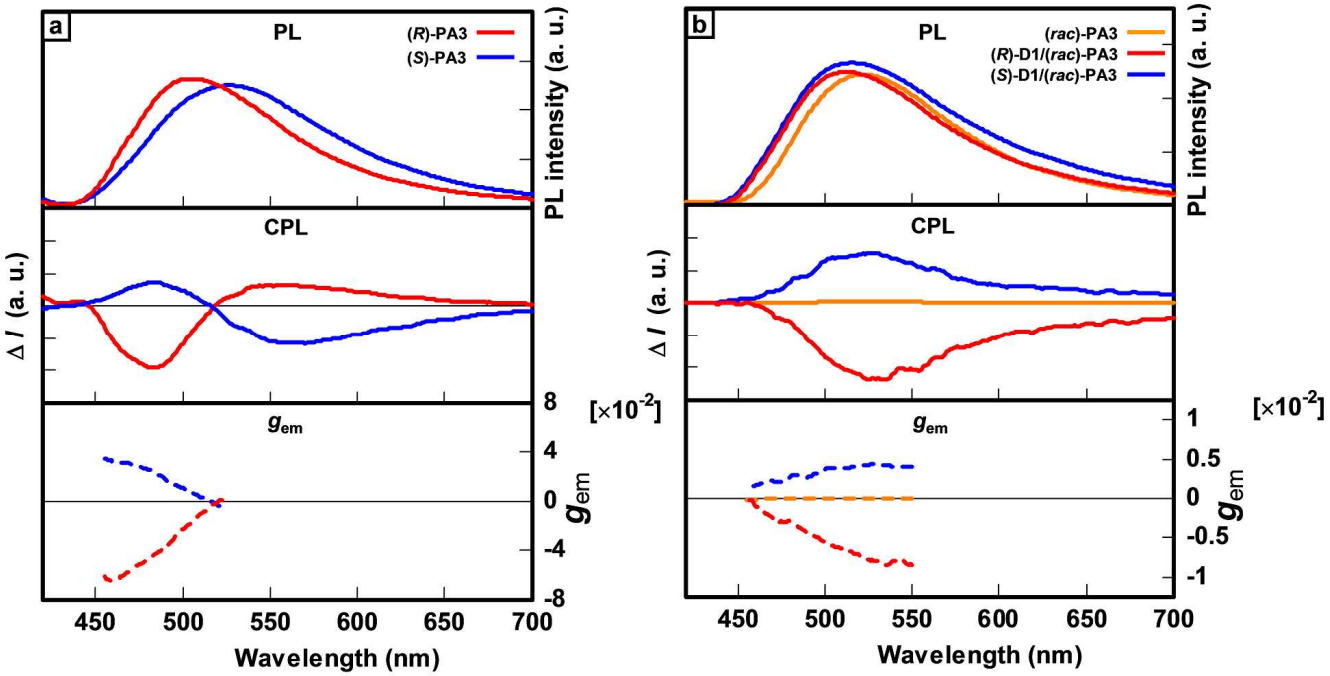

Figure S6. PL (upper), CPL spectra (middle), and g_{em} (lower) spectra of (a) **(*R*)-/(*S*)-PA3** N*-LC film, and (b) **(*R*)-/(*S*)-D1** doped **(*rac*)-PA3** (10 wt%) N*-LC film. The measurements were performed with excitation using unpolarized light at 367 nm.

Table S2. Emission dissymmetry factors (g_{em}) of the *di*-substituted LCPAs in N*-LC films.

	g_{em}(wavelength/ nm)[a]
(*R*)-PA3	-6.4×10^{-2} (458)
(*S*)-PA3	3.5×10^{-2} (456)
(*R*)-D1/(*rac*)-PA3	-8.4×10^{-3} (535)
(*S*)-D1/(*rac*)-PA3	4.2×10^{-3} (535)

[a]Wavelength at which g_{em} was evaluated