Supporting Information

Novel asymmetrical single- and double-chiral liquid crystal diads with wide blue phase ranges

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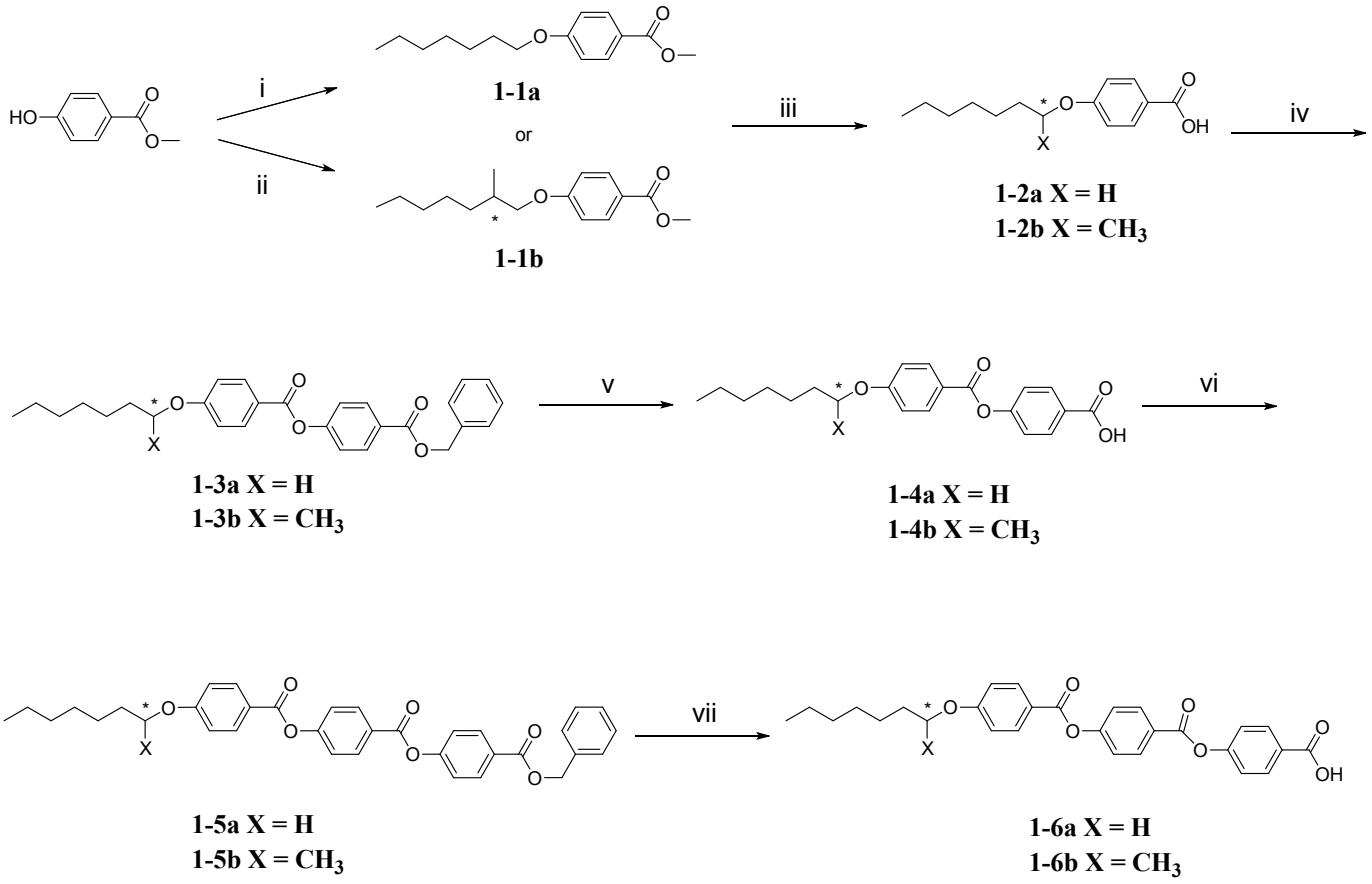
Table of Contents:

1. Preparation of materials S2
2. Scheme S1 ..... S2
3. Scheme S2 ..... S6
4. Scheme S3 ..... S8
5. Scheme S4 ..... S11
6. Figure S1 ..... S14
7. Figure S2 ..... S15
8. Figure S3 ..... S16
9. Figure S4 ..... S17
10. Figure S5 ..... S18
11. Table S1 ..... S19
12. Table S2 ..... S19
13. Table S3 ..... S19
14. Table S4 ..... S20
15. Table S5 ..... S20
16. Table S6 ..... S20

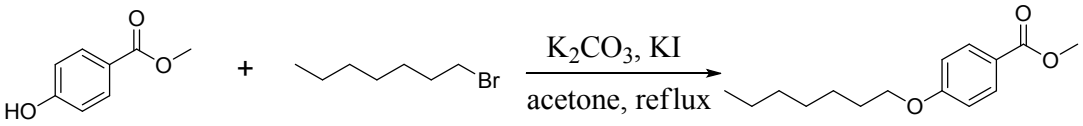
Preparation of materials.

Scheme S1



Reagents and conditions: (i) 1-bromoheptane, K_2CO_3, KI, acetone, reflux, 24 h; (ii) (S)-(+)-2-octanol, DIAD, PPh3, THF, 0 °C, 15 min, then r.t., overnight; (iii) KOH, MeOH, reflux, overnight, then HCl aqueous; (iv) benzyl 4-hydroxybenoate, DCC, DMAP, DCM, r.t., overnight; (v) H_2, 10% Pd-C, THF, r.t., 10 h; (vi) benzyl 4-hydroxybenoate, DCC, DMAP, DCM, r.t., overnight; (vii) H_2, 10% Pd-C, THF, r.t., 10 h.

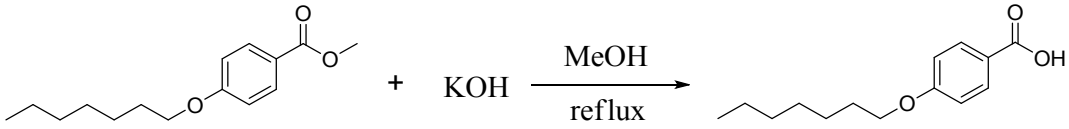
Synthesis of methyl 4-(heptyloxy)benzoate (1-1a)



A mixture of methyl 4-hydroxybenzoate (5.0 g, 32.9 mmol), 1-bromoheptane (7.07 g, 39.5 mmol), K_2CO_3 (6.82 g, 49.4 mmol) and potassium iodide (0.05 g) in dry acetone (200 mL) was stirred and refluxed under nitrogen for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was taken up in water and extracted with ethyl acetate. Then, the organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 40:1 v/v) to afford compound **1-1a** as a white solid in 93% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.95 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.98 (t, *J* = 6.3 Hz, 2H), 3.86 (s, 3H), 1.77-1.24 (m, 10H), 0.86 (t, *J* = 6.3Hz, 3H).

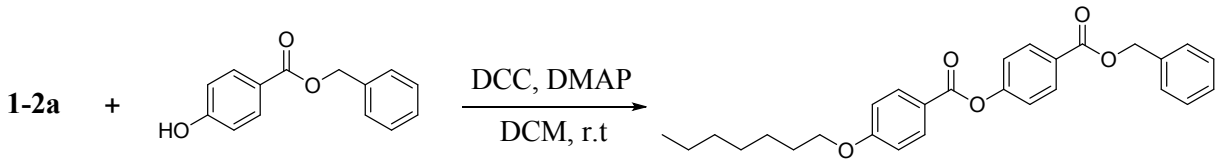
Synthesis of 4-(heptyloxy)benzoic acid (1-2a)



To a stirred solution of **1-1a** (3.68 g, 15.6 mmol) in methanol (80 mL), an aqueous solution 10 mL of potassium hydroxide (2.5 g, 44.7 mmol) was added dropwise and heated to reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure, and acidified with 6 N HCl. The precipitated product was collected by filtration and recrystallization from ethanol/H_2O (3:1 v/v) to afford compound **1-2a** as a white solid in 95% yield.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 7.85 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.01 (t, *J* = 6.3 Hz, 2H), 1.74-1.66 (m, 10H), 0.84 (t, *J* = 6.3Hz, 3H).

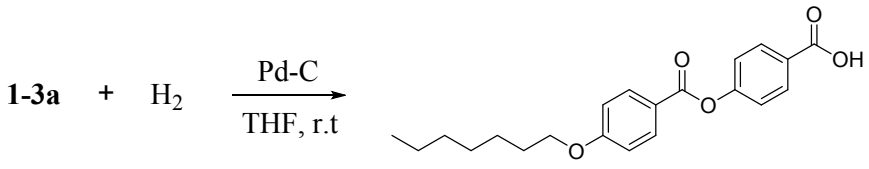
Synthesis of benzyl 4-((4-(heptyloxy)benzoyl)oxy)benzoate (1-3a)



To a stirred solution of **1-2a** (3.0 g, 12.7 mmol), benzyl 4-hydroxybenoate (2.42 g, 10.6 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.13 g, 1.06 mmol) in dry dichloromethane (100 mL), *N*,*N*-dicyclohexylcarbodiimide (DCC) (2.79 g, 13.8 mmol) were added and the reaction mixture was stirred at room temperature overnight under nitrogen. The resulting precipitate of dicyclohexylurea (DCU) was filtered off and washed with an excess of dichloromethane (20 mL). The solvent was evaporated and the crude product was purified by silica gel chromatography (*n*-hexane/dichloromethane = 1:1 v/v) to afford compound **1-3a** as a white solid in 85% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (m, 4H), 7.41 (m, 5H), 7.27 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 2H) , 5.36 (s, 2H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.70-1.61 (m, 2H), 1.41-1.25 (m, 8H), 0.86 (t, *J* = 6.3 Hz, 3H).

Synthesis of 4-(4-(heptyloxy)benzoyloxy)benzoic acid (1-4a)

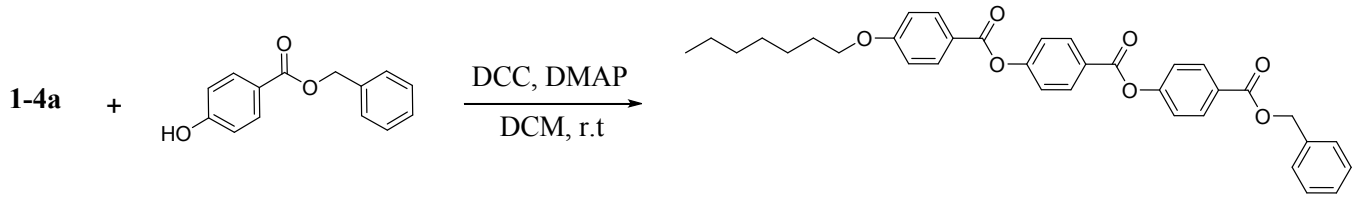


To a stirred solution of **1-3a** (2.1 g, 4.5 mmol) in tetrahydrofuran (THF) (80 mL), palladium carbon (Pd/C) (0.3 g, 10 wt%) was added. The reaction mixture was stirred at room temperature under hydrogen over 10 h. Palladium carbon (Pd/C) was

removed by filtration through Celite and washed with THF. The solvent was evaporated and the crude product was recrystallized from ethanol to give compound **1-4a** as a white solid in 95% yield.

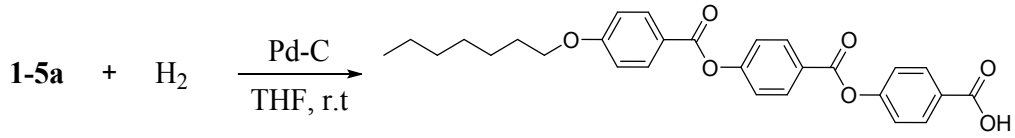
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.05 (m, 4H), 7.35 (d, *J* = 8.4 Hz 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.05 (t, *J* = 6.3 Hz, 2H), 1.70-1.61 (m, 2H), 1.41-1.25 (m, 8H), 0.86 (t, *J* = 6.3 Hz, 3H).

Synthesis of benzyl 4-(4-(4-(heptyloxy)benzoyloxy)benzoyloxy)benzoate (1-5a)



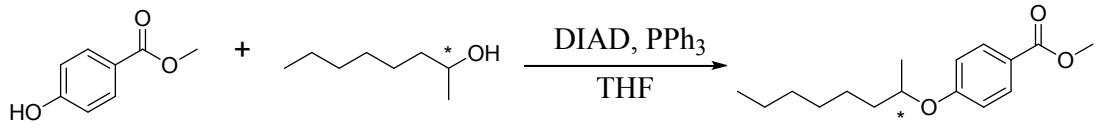
The similar manner was followed as that described above for the preparation of **1-3a**. Compound **1-5a** was obtained as a white solid in 70% yield.

Synthesis of 4-(4-(4-(heptyloxy)benzoyloxy)benzoyloxy)benzoic acid (1-6a)



The similar manner was followed as that described above for the preparation of **1-4a**. Compound **2-6a** was obtained as a white solid in 87% yield.

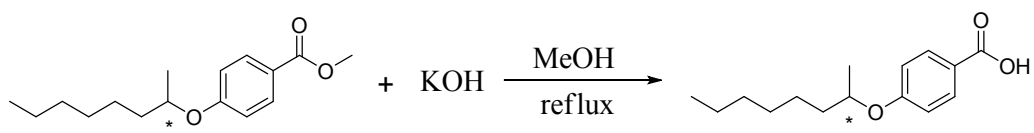
Synthesis of methyl 4-((1*R*)-1-methylheptyloxy)benzoate (1-1b)



To a solution of methyl 4-hydroxybenzoate (4.0 g, 26.2 mmol), (S)-(+)-2-octanol (3.0 g, 23.0 mmol) and triphenylphosphine (PPh_3) (10.0 g, 38.1 mmol) in dry THF (20 mL), diisopropyl azodicarboxylate (DIAD) (8.0 g, 39.5 mmol) in dry THF (10 mL) at 0°C under nitrogen were added dropwise to react for 15 min. After the mixture was warmed to room temperature and stirred overnight. The resulting mixture was quenched by water, extracted with dichloromethane, and then dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 40:1 v/v) to afford compound **1-1b** as a colorless oil in 75% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.97 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.42 (m, 1H) 3.88 (s, 3H), 1.71-1.57 (m, 2H), 1.42-1.25 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H).

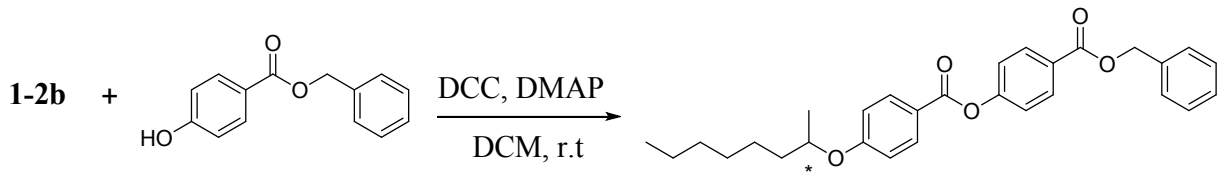
Synthesis of 4-((1*R*)-1-methylheptyloxy)benzoic acid (1-2b)



The similar manner was followed as that described above for the preparation of **1-2a**. Compound **1-2b** was obtained as a white solid in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 8.4Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.47 (t, 1H), 1.71-1.57 (m, 2H), 1.42-1.25 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H).

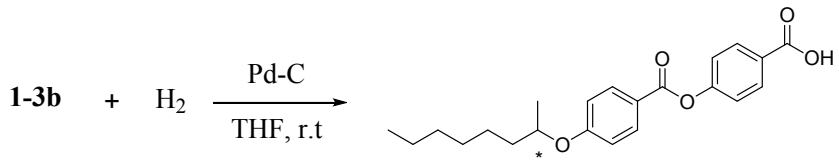
Synthesis of benzyl 4-(4-((1*R*)-1-methylheptyloxy)benzoyloxy)benzoate (1-3b)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **1-3b** was obtained as a white solid in 85% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.14 (m, 4H), 7.44-7.32 (m, 5H), 7.27-7.25 (m, 2H), 6.94 (m, 2H), 5.35 (s, 2H), 4.45 (m, 1H), 1.71-1.59 (m, 2H), 1.42-1.25 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H).

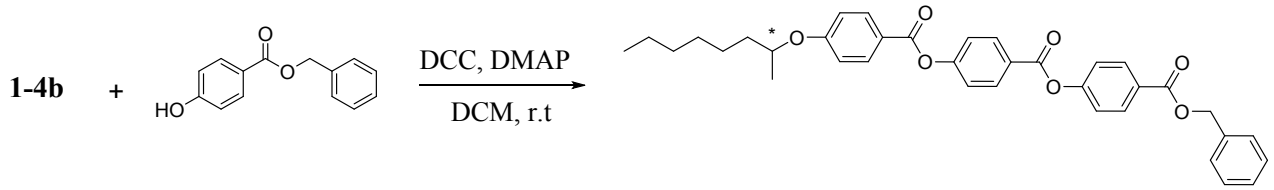
Synthesis of 4-(4-((1*R*)-1-methylheptyloxy)benzoyloxy)benzoic acid (1-4b)



The similar manner was followed as that described above for the preparation of **1-4a**. Compound **1-4b** was obtained as a white solid in 94% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.13 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.46 (m, 1H), 1.75-1.60 (m, 2H), 1.43-1.27 (m, 11H), 0.86 (t, *J* = 6.3 Hz, 3H).

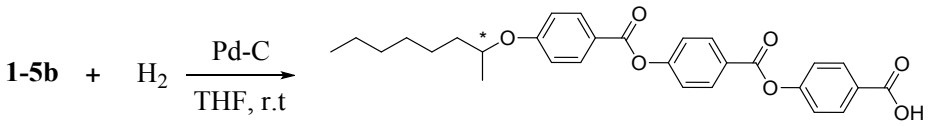
Synthesis of (S)-benzyl4-((4-((4-(octan-2-yloxy)benzoyl)oxy)benzoyl)oxy)benzoate (1-5b)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **1-5b** was obtained as a white solid in 75% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.23 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.49-7.39 (m, 9H), 6.98 (d, *J* = 8.7 Hz, 2H), 5.39 (s, 2H), 4.53-4.48 (m, 1H), 1.71-1.59 (m, 2H), 1.42-1.25 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H).

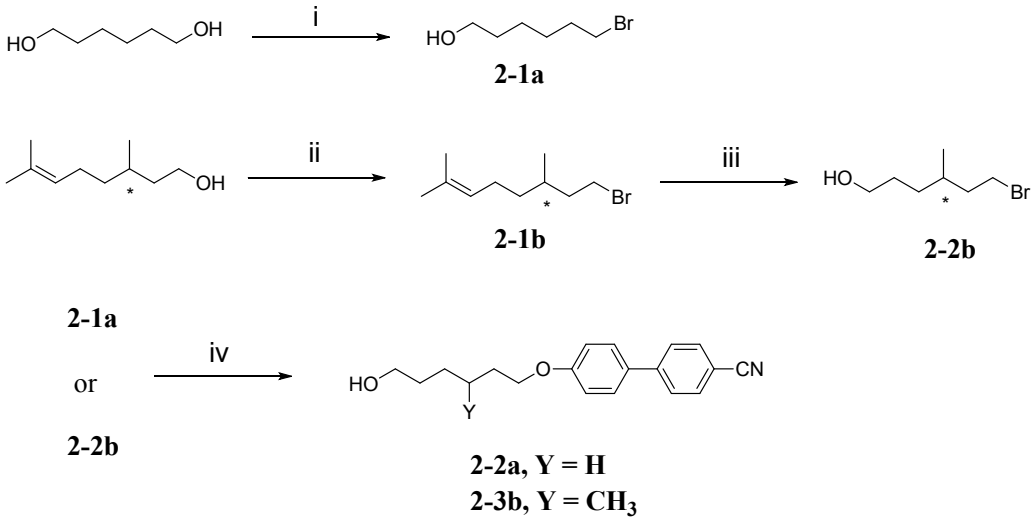
Synthesis of (S)-4-((4-((4-(octan-2-yloxy)benzoyl)oxy)benzoyl)oxy)benzoic acid (1-6b)



The similar manner was followed as that described above for the preparation of **1-4a**. Compound **1-6b** was obtained as a white solid in 89% yield.

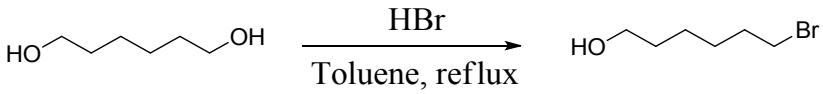
^{1}H NMR (300 MHz, DMSO-d6): δ (ppm) 8.35 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 4.71-4.65 (m, 1H), 1.73-1.61 (m, 2H), 1.33-1.27 (m, 11H), 0.90 (t, *J* = 6.3 Hz, 3H).

Scheme S2



Reagents and conditions: (i) HBr (48% in water), toluene, reflux, 18 h; (ii) CBr_4, PPh3, DCM, 0°C, then, r.t. 2 h; (iii) O_3, MeOH, -78 °C, 2h, after $NaBH_4$, MeOH, r.t., overnight, then water, H_2SO_4, (iv) 4'-hydroxy-4-biphenylcarbonitrile, K_2CO_3, KI, acetone, reflux, 24 h.

Synthesis of 6-bromo-1-hexanol (2-1a)



A mixture of 1,6-hexanediol (20.0 g, 169.2 mmol), aqueous 48% hydrogen bromide (23.0 mL, 203.1 mmol) and toluene (300 mL) was refluxed for 18 h and side product H_2O could be removed by Dean-Stark. The reaction mixture was washed with a saturated aqueous $NaHCO_3$ solution and water several times, and then the organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 5:1 v/v) to afford compound **2-1a** as a pale yellow oil in 75% yield.

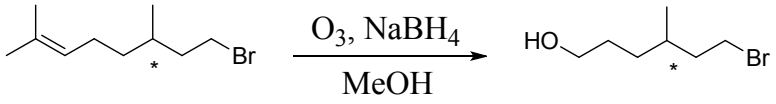
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.71 (t, *J* = 6.5 Hz, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 1.81-1.42 (m, 8H).

Synthesis of (S)-8-bromo-2,6-dimethyl-2-octene (2-1b)

To a stirred solution of (S)-3,7-dimethyloct-6-en-1-ol (5.0 g, 32.02 mmol) and carbon tetrabromide (CBr_4) (12.59 g, 38.42 mmol) in minimal dichloromethane (15 mL), a solution of triphenylphosphine (PPh_3) (10.0 g, 38.1 mmol) in DCM (10 mL) was added at 0 °C under nitrogen. After the mixture was warmed to room temperature and stirred for 2 h. The resulting mixture was poured into water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane) to afford compound **2-1b** as a colorless oil in 75% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.22 (t, *J* = 6.8 Hz, 1H), 3.41 (m, 2H), 2.02-1.51 (m, 13H), 1.12 (d, *J* = 6.2 Hz, 3H).

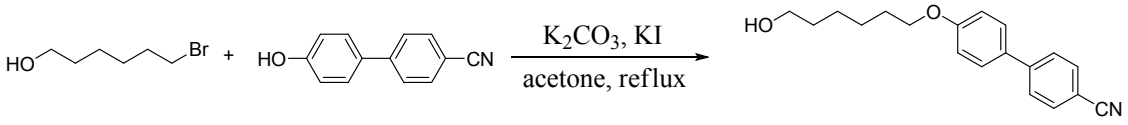
Synthesis of (S)-6-bromo-4-methylhexan-1-ol (2-2b)



A solution of **2-1b** (5.0 g, 22.93 mmol) in methanol (30 mL) at -78 °C was ozonized under a stream of ozone purge for 2 h. The solution color changed from transparent to light yellow. After termination of the ozonolysis, compound **2-1b** was monitored until disappearance by TLC. Subsequently, sodium borohydride (1.04 g, 27.52 mmol) in methanol (8 mL) were added in portions to the solution and the mixture was brought to -65 °C, and the solution color changed from light yellow to transparent. A further portion of sodium borohydride (0.52 g, 13.76 mmol) was added within 15 min, and the mixture was warmed to room temperature and stirred overnight. Water was added to the resulting mixture, and the solution was acidified with sulphuric acid and saturated with ammonium chloride and extracted with diethyl ether. The organic layer was sequentially washed with water, 10% aqueous sodium bicarbonate solution and water, and then dried with sodium sulfate. The solvent was evaporated and the crude product was purified by silica gel chromatography (*n*-hexane/ ethyl acetate = 5:1 v/v) to afford compound **2-2b** as a colorless oil in 73% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.81 (t, *J* = 6.3 Hz, 2H), 3.42 (t, *J* = 6.3 Hz, 2H), 1.81-1.21 (m, 7H), 1.13 (d, *J* = 6.2 Hz, 3H).

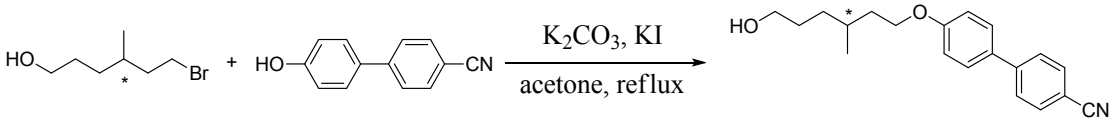
Synthesis of 6-[(4-cyano-4'-biphenylyl)oxy]hexanol (2-2a)



The similar manner was followed as that described above for the preparation of **1-1a**. Compound **2-2a** was obtained as a white solid in 91% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86 (m, 4H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 9.1 Hz, 2H), 4.15 (t, *J* = 6.3 Hz, 2H), 3.61(t, *J* = 6.4 Hz, 2H), 1.82-1.47 (m, 8H).

Synthesis of (S)-6-[(4-cyano-4'-biphenylyl)oxy]-4-methylhexanol (2-3b)

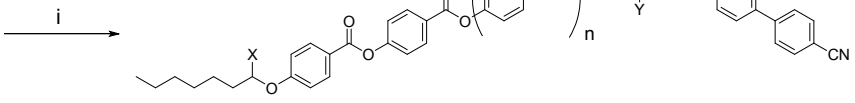


The similar manner was followed as that described above for the preparation of **1-1a**. Compound **2-3b** was obtained as a light yellow solid in 74% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.83 (t, *J* = 8.9 Hz, 4H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.9 Hz, 2H), 4.23 (t, *J* = 6.4 Hz, 2H), 4.12 (t, *J* = 6.3 Hz, 2H), 1.82-1.24 (m, 7H), 1.11 (d, *J* = 6.2 Hz, 3H).

Scheme S3

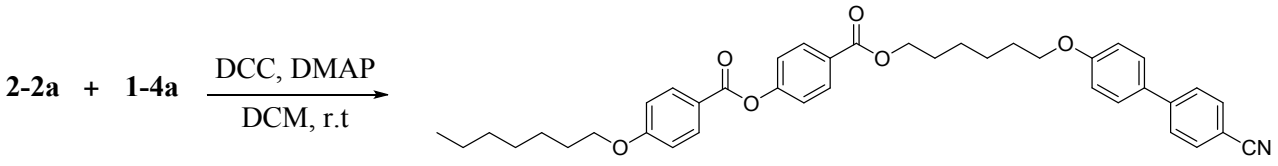
2-2a + 1-4a
or
2-3b + 1-4a
or
2-2a + 1-4b
or
2-3b + 1-4b
or
2-2a + 1-6a
or
2-3b + 1-6a
or
2-2a + 1-6b
or
2-3b + 1-6b



II-A: X = H, Y = H, n = 0
II-B: X = H, Y = CH_3, n = 0
II-C: X = CH_3, Y = H, n = 0
II-D: X = CH_3, Y = CH_3, n = 0
III-A: X = H, Y = H, n = 1
III-B: X = H, Y = CH_3, n = 1
III-C: X = CH_3, Y = H, n = 1
III-D: X = CH_3, Y = CH_3, n = 1

Reagents and conditions: (i) DCC, DMAP, DCM, r.t., overnight.

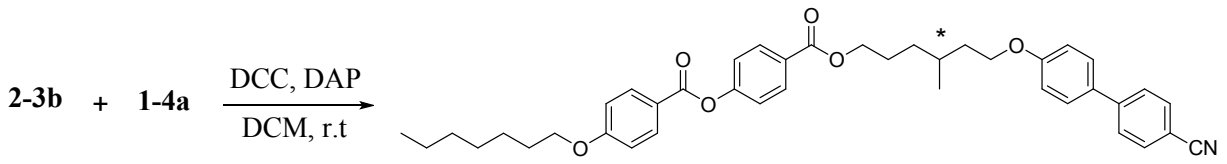
Synthesis of 6-[(4-cyano-4'-biphenylyl)oxy]hexyl 4-((4-(heptyloxy)benzoyl)oxy)benzoate (II-A)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **II-A** was obtained as a white solid in 65% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.11 (m, 4H), 7.81 (m, 4H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 9.1 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 4.41 (t, *J* = 6.4 Hz, 2H), 4.13 (m, 4H), 1.94-1.37 (m, 18H), 0.91 (t, *J* = 6.3 Hz, 3H). Anal. calcd for $C_{40}H_{43}NO_6$: C, 75.80, H, 6.84, N, 2.21; found: C, 75.45, H, 6.82, N, 2.50%.

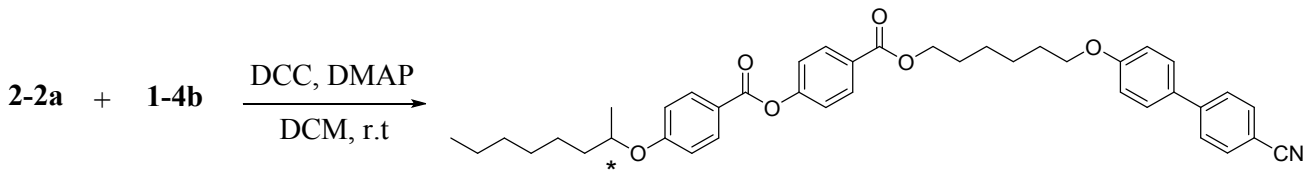
Synthesis of 6-[(4-cyano-4'-biphenylyl)oxy](3*R*)-4-methylhexyl 4-((4-(heptyloxy)benzoyl)oxy)benzoate (II-B)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **II-B** was obtained as a white solid in 67% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.21 (t, *J* = 8.8 Hz, 4H), 7.81 (s, 4H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 9.1 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 4.31 (t, *J* = 6.3 Hz, 2H), 4.12 (t, *J* = 6.4 Hz, 4H), 1.79-1.28 (m, 17H), 1.02 (d, *J* = 6.2 Hz, 3H),0.98 (t, *J* = 6.3 Hz, 3H). Anal. calcd for $C_{41}H_{45}NO_6$: C, 76.02, H, 7.00, N, 2.16; found: C, 75.98, H, 7.14, N, 2.26%.

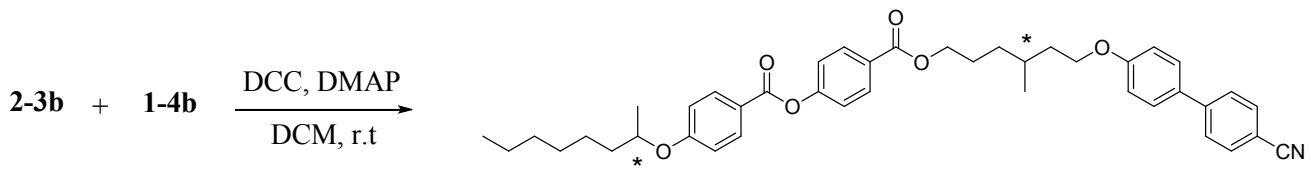
Synthesis of 6-[(4-cyano-4'-biphenylyl)oxy]hexyl 4-((4-((1*R*)-1-methylheptyloxy)benzoyl)oxy)benzoate (II-C)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **II-C** was obtained as a white solid in 67% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.21 (m, 4H), 7.72 (m, 4H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 4H), 4.5 (m, 1H), 4.42 (t, *J* = 6.4 Hz, 2H), 4.14 (t, *J* = 6.3 Hz, 4H), 1.91-1.36 (m, 21H), 0.92 (t, *J* = 6.3 Hz, 3H). Anal. calcd for $C_{41}H_{45}NO_6$: C, 76.02, H, 7.00, N, 2.16; found: C, 75.93, H, 7.17, N, 2.18.

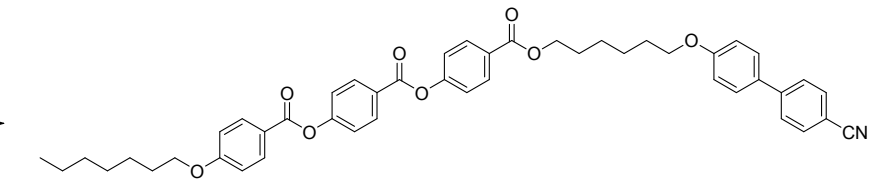
Synthesis of (S)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)-4-methylhexyl 4-((4-((R)-octan-2-yloxy)benzoyl)oxy)benzoate (II-D)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **II-D** was obtained as a white solid in 64% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.12 (d, *J* = 9.0 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 4.53-4.473 (m, 1H), 4.35 (t, *J* = 6.3 Hz, 2H), 4.10-4.04 (m, 2H), 1.79-1.28 (m, 20H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 6.3 Hz, 3H). Anal. calcd for $C_{42}H_{47}NO_6$: C, 76.22, H, 7.16, N, 2.12; found: C, 76.12, H, 7.21, N, 2.19%.

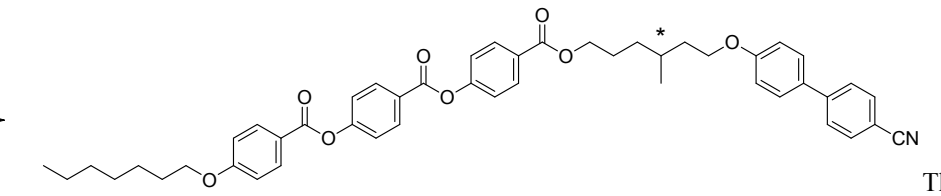
Synthesis of 6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl 4-((4-((4-(heptyloxy)benzoyl)oxy)benzoyl)oxy)benzoate (III-A)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **III-A** was obtained as a white solid in 70% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.29 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 9.0 Hz, 2H), 8.15 (d, *J* = 8.7 Hz, 2H), 7.72-7.64 (m, 4H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 4H), 4.38 (t, *J* = 6.6 Hz, 2H), 4.09 (t, *J* = 6.3 Hz, 2H), 4.04 (t, *J* = 6.3 Hz, 2H), 1.88-1.83 (m, 6H), 1.61-1.40 (m, 12H), 0.92 (t, *J* = 6.6 Hz, 3H). Anal. calcd for $C_{42}H_{47}NO_8$: C, 74.88, H, 6.28, N, 1,86; found: C, 74.80, H, 6.41, N, 1.92%.

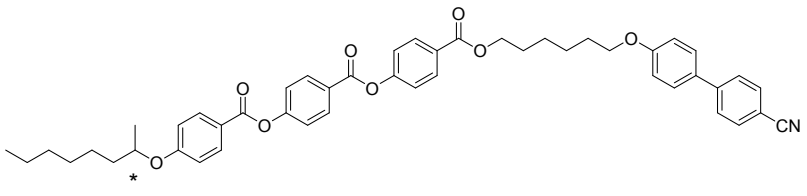
Synthesis of(S)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)-4-methylhexyl 4-((4-((4-(heptyloxy)benzoyl)oxy)benzoyl)oxy)benzoate (III-B)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **III-B** was obtained as a white solid in 62% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.28 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 8.7 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.70-7.63 (m, 4H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 9.0 Hz, 2H), 7.02-6.98 (m, 4H), 4.38 (t, *J* = 6.3 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 4H), 1.90-1.83 (m, 6H), 1.52-1.32 (m, 11H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.91 (t, *J* = 6.6 Hz, 3H). Anal. calcd for $C_{48}H_{49}NO_8$: C, 75.08, H, 6.43, N, 1,82; found: C, 75.15, H, 6.52, N, 1.89%.

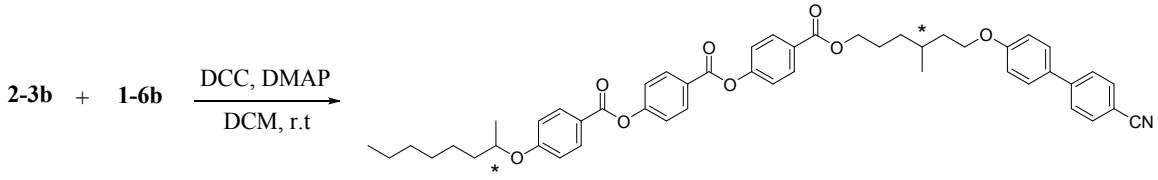
Synthesis of (R)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl 4-((4-((4-(octan-2-yloxy)benzoyl)oxy)benzoyl)oxy)benzoate (III-C)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **III-C** was obtained as a white solid in 72% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.31 (d, *J* = 8.7 Hz, 2H), 8.18 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 7.71-7.63 (m, 4H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.03-6.96 (m, 4H), 4.54-4.46 (m, 2H), 4.40 (t, *J* = 6.3 Hz, 2H), 4.08 (t, *J* = 6.3 Hz, 2H), 1.91-1.85 (m, 5H), 1.51-1.35 (m, 15H), 0.93 (t, *J* = 6.6 Hz, 3H). Anal. calcd for $C_{48}H_{49}NO_8$: C, 75.08, H, 6.43, N, 1,82; found: C, 75.13, H, 6.49, N, 1.88%.

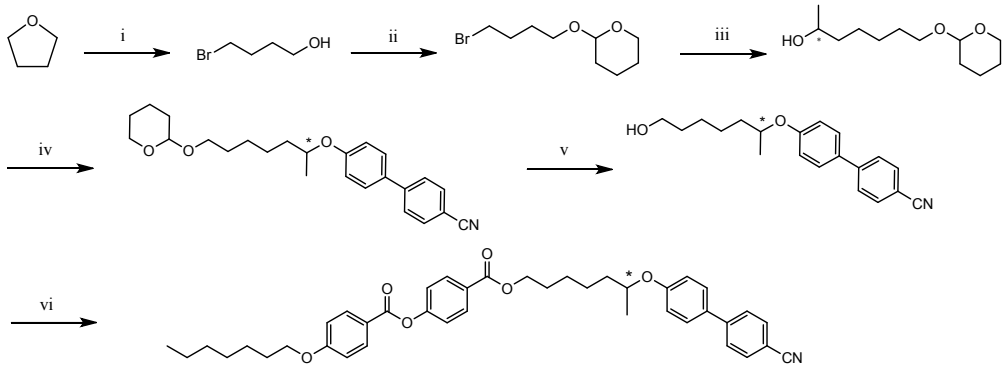
Synthesis of (S)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)-4-methylhexyl 4-((4-((4-((R)-octan-2-yloxy)benzoyl)oxy)benzoyl)oxy)benzoate (III-D)



The similar manner was followed as that described above for the preparation of **1-3a**. Compound **III-D** was obtained as a white solid in 78% yield.

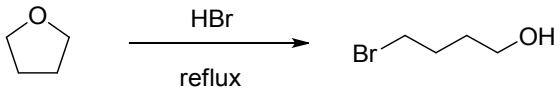
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.27 (d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* = 8.7 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.71-7.63 (m, 4H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 9.0 Hz, 2H), 7.02-6.98 (m, 4H), 4.53-4.51 (m, 1H), 4.37 (t, *J* = 6.3 Hz, 2H), 4.09 (m, 2H), 1.92-1.84 (m, 5H), 1.52-1.33 (m, 15H), 1.35 (d, *J* = 6.6 Hz, 3H), 0.91 (t, *J* = 6.6 Hz, 3H). Anal. calcd for $C_{49}H_{51}NO_8$: C, 75.27, H, 6.57, N, 1,79; found: C, 75.31, H, 6.62, N, 1.83%.

Scheme S4



Reagents and conditions: (i) HBr (48% in water), THF, reflux, 4 h; (ii) PPTS, DCM, r.t., (iii) Mg, (R)-(+)-Propylene oxide, THF, CuI, (iv) 4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile, DIAD, PPh3, THF, 0 °C, 15 min, then r.t., overnight (v) TsOH, MeOH, CH_2Cl_2, refluxed (vi) 4-((4-(heptyloxy)benzoyl)oxy)benzoic acid, DCC, DMAP, DCM, r.t., overnight.

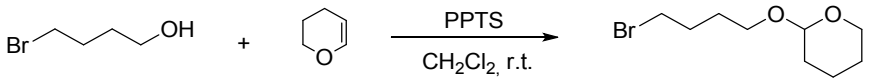
4-bromobutan-1-ol (3-1)



Tetrahydrofuran (13.5 mL, 167 mmol), aqueous 48% hydrogen bromide (9.6 g, 53.8 mmol) was dropped slowly, and the mixtur was refluxed for 4 h. The reaction mixture was washed with a saturated aqueous $NaHCO_3$ solution and water several times, and then the organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 5:1 v/v) to afford compound a pale yellow oil in 33% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 5.00 (s, 1H, -OH), 3.52 (t, *J* = 6.6 Hz, 2H, -OCH_2), 3.32 (t, *J* = 6.6 Hz, 2H, -OCH_2), 1.70-1.86 (m, 2H, -CH_2), 1.50-1.61 (m, 2H, -CH_2).

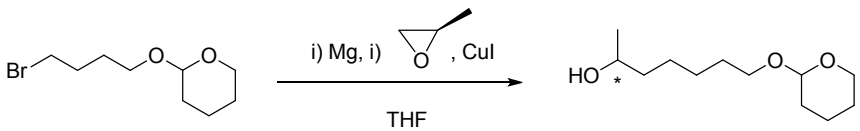
2-(4-bromobutoxy)tetrahydro-2H-pyran (3-2)



To a stirred solution of **3-1** (5 g, 33 mmol), PPTS (0.82 g, 3.3 mmol) and dry CH_2Cl_2 (100 ml), was added a solution of DHP(4.12 g, 4.9 mmol) in DCM (10 mL) at 0 °C under nitrogen. After the mixture was warmed to room temperature and stirred for 9 h. The resulting mixture was poured into water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/EtOAc = 5:1 v/v) to afford compound **3-2** as a light yellow oil in 90 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.53 (t, *J* = 3.3Hz, 1H, -OC<u>H</u>CH_2), 3.79-3.68 (m, 2H, -OCH_2), 3.47-3.33 (m, 4H, -OCH_2), 1.99-1.92 (m, 2H, -CH_2), 1.88-1.65 (m, 4H, -CH_2), 1.55-1.45 (m, 4H, -CH_2).

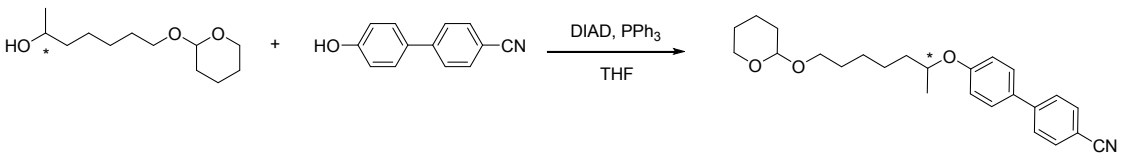
(2R)-7-((tetrahydro-2H-pyran-2-yl)oxy)heptan-2-ol (3-3)



To a stirred solution of Mg (0.308 g, 12.7 mmol) and dry THF (10 ml) was added a solution of 3-2 (2.0 g, 8.4 mmol) in dry THF (7 ml) under nitrogen. After the mixture refluxed and stirred for 5 h. A solution of (R)-(+)-Propylene oxide (0.735 g, 10.1 mmol) in dry THF (8 ml) and CuI (0.193 g, 1.01 mmol) in dry THF (7 ml) were added in the system. The resulting mixture was poured into water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/EtOAc = 5:1 v/v) to afford compound **3-3** as a yellow oil in 30 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.6 (s, 1H, -OH), 4.57 (t, *J* = 6.9Hz, 1H, -OC<u>H</u>CH_2)，3.86-3.77 (m, 2H, -OCH_2), 3.74-3.71 (m, 1H, -OC<u>H</u>CH_3), 3.51-3.37 (m, 2H, -OCH_2),1.63-1.48 (m, 14H, -CH_2) , 1.18 (d, *J*= 3Hz, 3H, -CH_3).

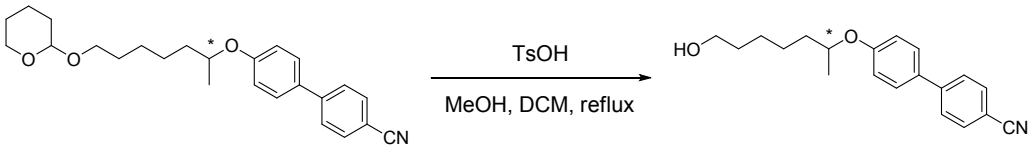
4'-(((2S)-7-((tetrahydro-2H-pyran-2-yl)oxy)heptan-2-yl)oxy)-[1,1'-biphenyl]-4-carbonitrile (3-4)



To a solution of **3-3** (2.0 g, 9.25 mmol), 4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (2.17 g, 11.1 mmol) and triphenylphosphine (PPh_3) (3.64 g, 13.9 mmol) in dry THF (100 mL) at 0 °C under nitrogen for 15 min was added dropwise with diisopropyl azodicarboxylate (DIAD) (2.81 g, 13.9 mmol) in dry THF (10 mL). After the mixture was warmed to room temperature and stirred overnight. The resulting mixture was quenched by water, extracted with dichloromethane, and then dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography to afford compound **3-4** as a white solid in 75% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.71-7.62 (m, 4H, Ar-H), 7.50 (d, *J* = 6.9Hz, 2H, Ar-H), 6.97 (d, *J* = 8.7Hz, 2H, Ar-H), 4.58-4.49 (m, 1H, -OCHCH$_2$), 4.45-4.39 (m, 1H, -OCHCH$_3$), 3.86-3.70 (m, 2H, -OCH$_2$), 3.51-3.37 (m, 2H, -OCH$_2$), 1.80-1.42 (m, 14H, -CH$_2$), 1.32 (d, *J* = 6Hz, 3H, -CHCH$_3$).

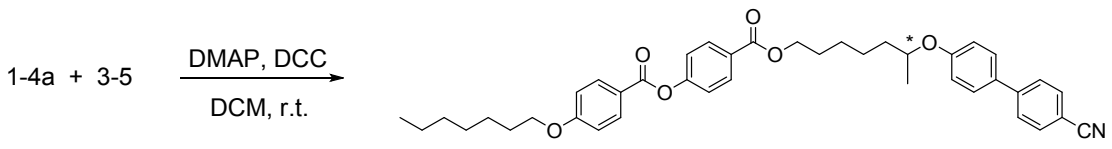
(S)-4'-((7-hydroxyheptan-2-yl)oxy)-[1,1'-biphenyl]-4-carbonitrile (3-5)



To a stirred solution of **3-4** (1.0 g, 2.54 mmol) and TsOH(0.1 g, 0.53 mmol) was dissolved in MeOH (20 ml) and CH_2Cl_2 (20 ml). The mixture was refluxed and stirred for 10 h. The resulting mixture was poured into water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated to afford compound **3-5** as a light white solid in 85 % yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.70-7.62 (m, 4H, Ar-H), 7.53 (d, *J* = 8.8Hz, 2H, Ar-H), 6.97 (d, *J*=9.1Hz, 2H, Ar-H), 4.48-4.38 (m, 1H, -OCHCH$_2$), 3.65 (t, *J* = 6.6 Hz, 2H, -OCH$_2$), 1.66-1.39 (m, 8H, -CH$_2$), 1.33 (d, *J* = 6 Hz, 3H, -CH$_3$).

(S)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)heptyl 4-((4-(heptyloxy)benzoyl)oxy)benzoate (II-76R*CB)



To a stirred solution of **1-4a** (0.51 g, 1.42 mmol), **3-5** (0.4 g, 1.29 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.21 g, 1.55 mmol) in dry dichloromethane (100 mL), *N*,*N*-dicyclohexylcarbodiimide (DCC) (4.2g, 20.36mmol) was added and the reaction mixture stirred at room temperature overnight under nitrogen. The resulting precipitate of dicyclohexylurea (DCU) was filtered off and washed with an excess of dichloromethane (20 mL). The solvent was evaporated and the crude product was purified by silica gel chromatography (*n*-hexane/dichloromethane = 1:1 v/v) to afford compound **II-76R*CB** as a white solid in 67% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.03 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.01 (d, *J* = 12 Hz, 2H, Ar-H), 7.85-7.78 (m, 4H, Ar-H), 7.65 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.35 (d, *J* = 8.7Hz, 2H, Ar-H), 7.11 (d, *J* = 9Hz, 2H, Ar-H), 7.02 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.56-4.52 (m, 1H, -OCHCH_2), 4.28 (t, *J* = 6 Hz, 2H, -OCH_2), 4.01 (t, *J* = 6.45 Hz, 2H, -OCH_2), 1.76-1.44 (m, 8H, -CH_2), 1.35-1.24 (m, 10H, -OCH_2), 0.86 (t, *J* = 6.45 Hz, 3H, -CH_3). Anal. calcd for $C_{41}H_{45}NO_6$: C, 76.02, H, 7.00, N, 2.16; found: C, 75.75, H, 6.81, N, 2.32%.

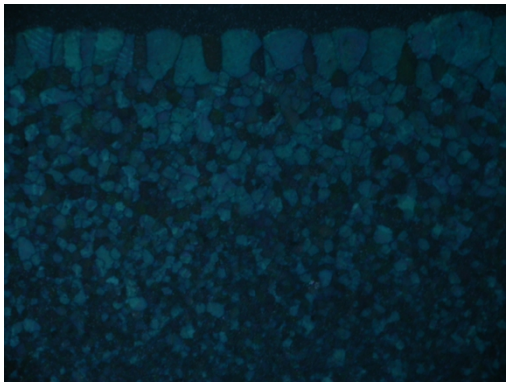


Figure S1. POM texture of **III-B** at 181.0 °C upon cooling (0.5 °Cmin^{-1}).

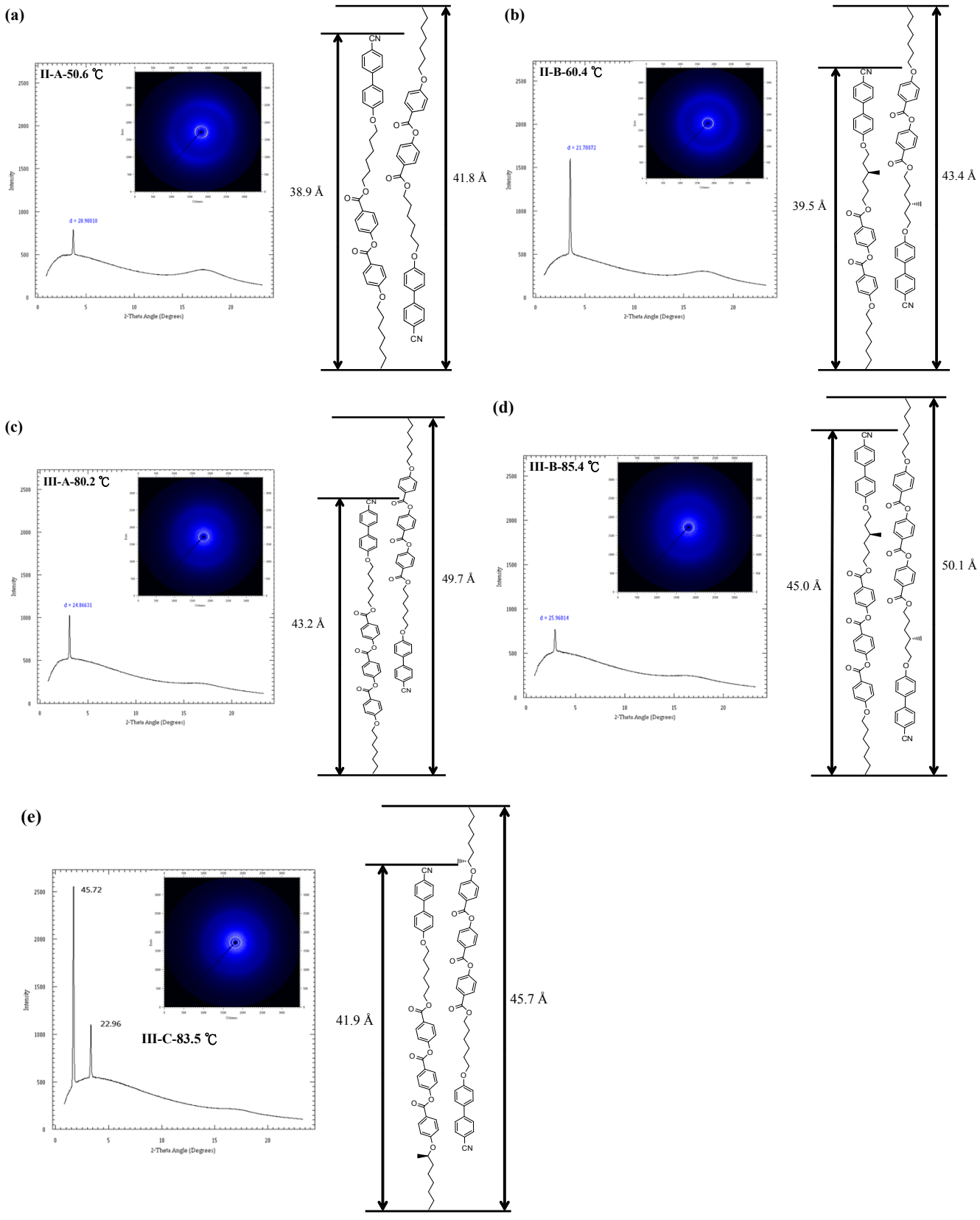


Figure S2. Powder XRD Analyses of (a) **II-A** at 50.6 °C, (b) **II-B** at 60.4 °C, (c) **III-A** at 80.2 °C, (d) **III-B** at 85.4 °C and (e) **III-C** at 83.5 °C.

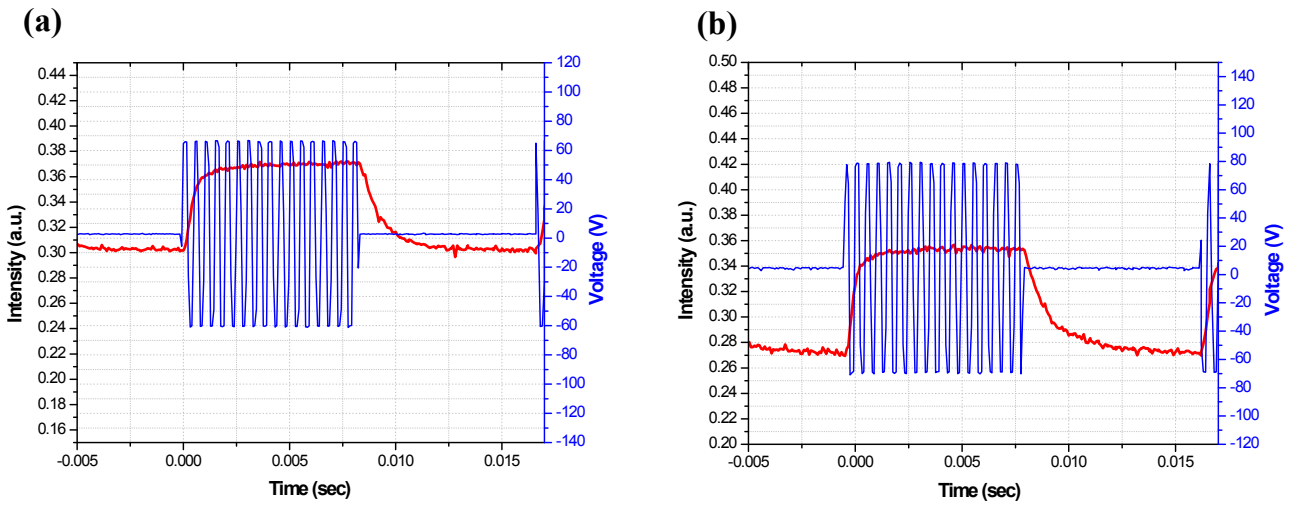


Figure S3. Diads **II-B** and **III-D** in BPs at T-$T_{I\text{-}BP}$ = -2°C. (a) Electro-optical response curves of **II-B** at 13 Vμm^{-1}. (b) Electro-optical response curves of **III-D** at 15 Vμm^{-1}.

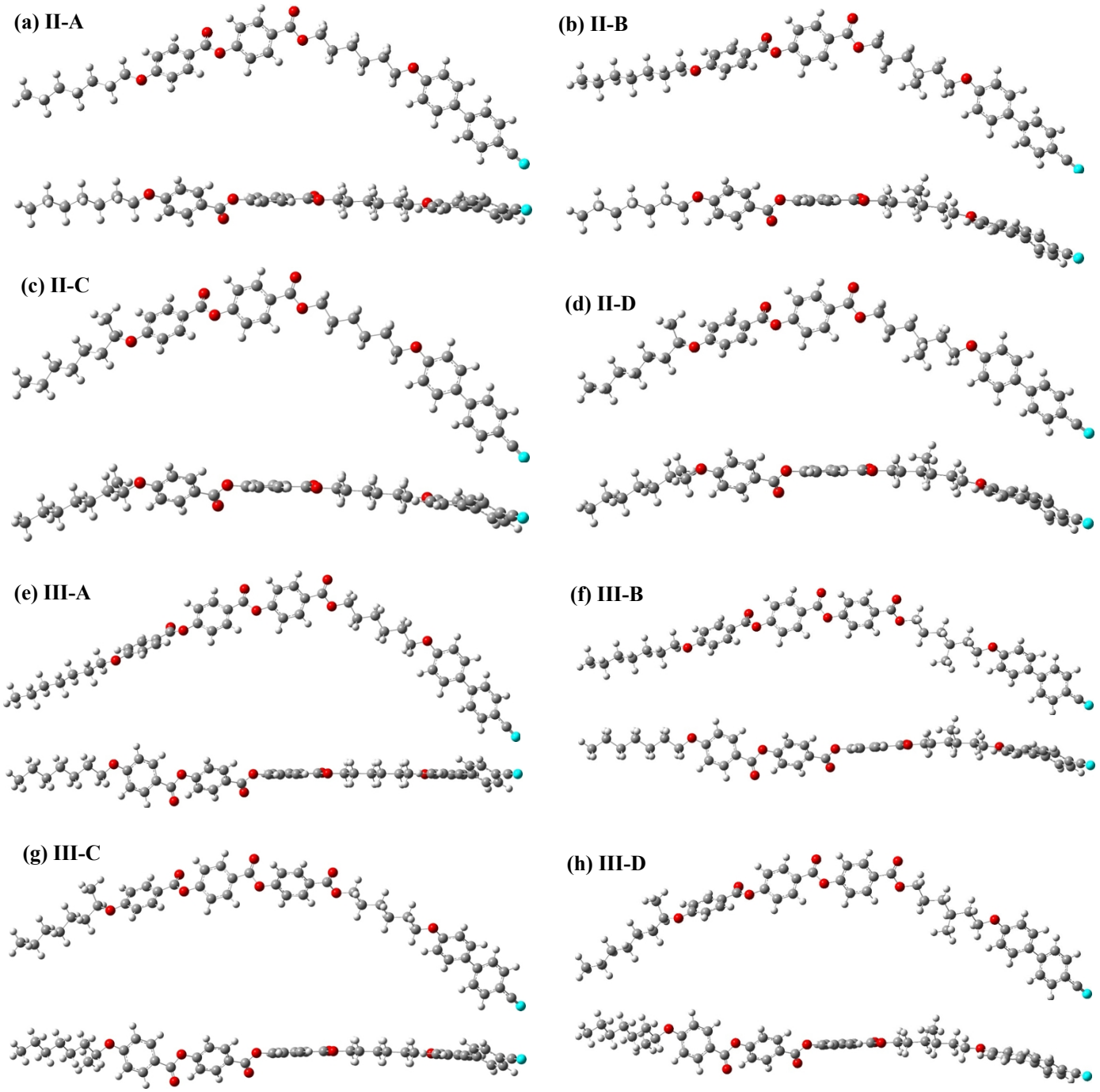


Figure S4. Molecular models of the lowest energy conformations of eight asymmetrical liquid crystal diads.

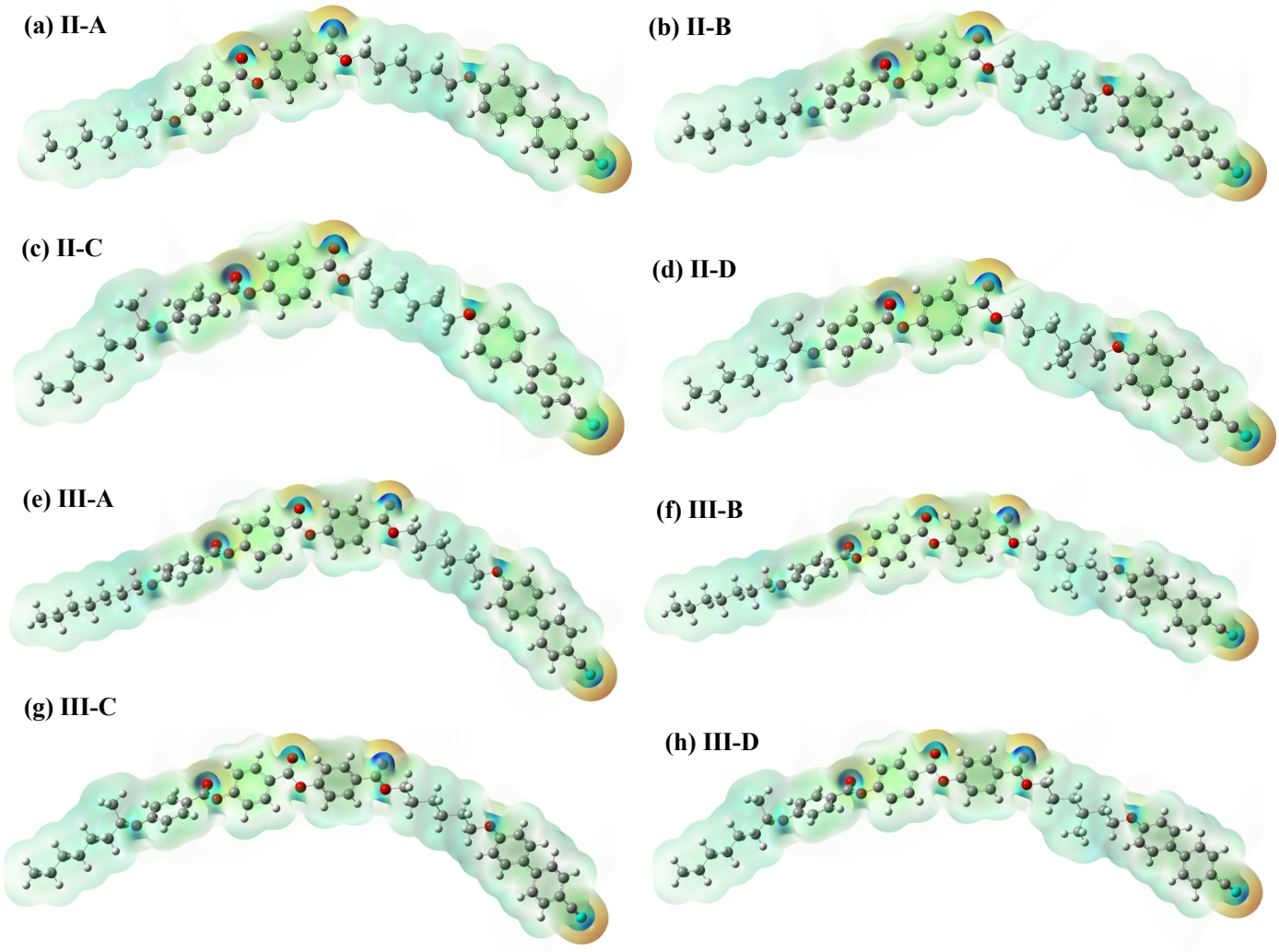


Figure S5. Molecular electrostatic potentials mapped on the electron densities of the lowest energy structures for eight asymmetrical liquid crystal diads.

Table S1 Phase transition of heating process temperatures (°C) and enthalpies (J/g) of asymmetrical liquid crystal diads.

Compound	Phase transition temperature (°C) [enthalpies (J/g)]
II-A	Cr 75.6 [1.95] SmA 89.8 [1.90] N 109.7 [0.38] Iso
II-B	Cr 65.5 [2.31] SmA 77.5 [2.03] N* 99.6 [0.62] Iso
II-C	Cr 63.3 [3.60] Iso
II-D	Cr 85.6 [15.23] Iso
II-E	Cr 33.8 [0.70] N* 42.6 [0.13] Iso
III-A	Cr 118.5 [1.49] SmA 128.8 [2.73] N 208.2 [1.23] Iso
III-B	Cr 109.8 [1.02] SmA 116.7 [2.53] N^* 193.1 [1.04] Iso
III-C	Cr 99.5 [2.01] SmA 118.3 [5.50] N^* 126.5 [11.43] Iso
III-D	Cr 75.6 [1.60] N^* 117.7 [0.52] Iso

Table S2 The powder XRD data of **II-A**, **II-B**, **III-A**, **III-B** and **III-C**

Compound	Cooling temp. (°C)	Mesophase	d-spacing (Å)	Miller index (a b c)	Molecular length L(Å)
II-A	50.6	SmA	41.8	(002)	38.9
II-B	60.4	SmA	43.4	(002)	39.5
III-A	80.2	SmA	49.7	(002)	43.2
III-B	85.4	SmA	50.1	(002)	45.0
III-C	83.5	SmA	45.7 23.0	(001) (002)	41.9

Table S3 Electric-field dependent response time values for diads **II-B** and **III-D**.

II-B	τ_{on}	τ_{off}	τ_{total}	**III-D**	τ_{on}	τ_{off}	τ_{total}
Electric field ($V\mu m^{-1}$)	(ms)	(ms)	(ms)	Electric field ($V\mu m^{-1}$)	(ms)	(ms)	(ms)
12	1.31	1.30	2.61	12	1.01	2.40	3.41
13	1.24	1.42	2.66	13	0.94	2.47	3.41
14	1.20	1.51	2.71	14	0.89	2.61	3.50
15	1.13	1.69	2.82	15	0.88	2.75	3.63
16	1.01	1.90	2.91	16	0.87	3.00	3.87

Table S4 Parameters of length, breath, biaxiality, bend angle and dihedral angle for compound **II-A**, **II-B**, **II-C** and **II-D**.

Compound	Length	Breadth	Breadth	Biaxial Parameter	Bend Angle	Dihedral Angle				
	L (Å)	W_1 (Å)	W_2 (Å)	W_1/W_2	(deg)	1, 2, 3, 4 (deg)	5, 6, 7, 8 (deg)	9, 10, 11, 12 (deg)	13, 14, 15, 16 (deg)	5, 6, 11, 12 (deg)
II-A	38.9	9.7	4.3	2.25	135.3	-0.3	44.6	1	1.5	-138.1
II-B	39.5	8.8	6.0	1.47	139.4	-0.1	46.4	1.3	0.7	-134.9
II-C	37.0	11.1	5.4	2.04	125.5	-0.6	44	1	0.2	-137.3
II-D	38.1	9.9	5.9	1.69	132	-1.3	46	0.9	0.5	-135.8

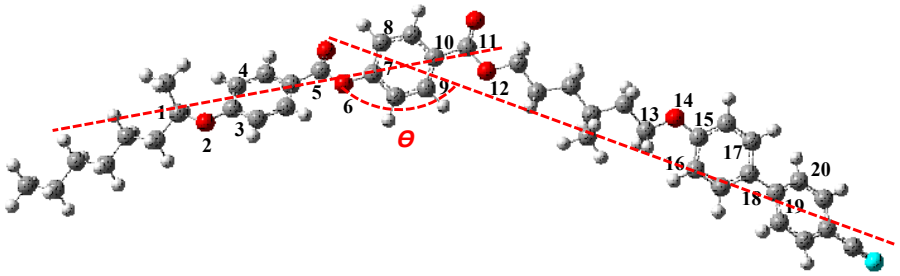


Table S5 Parameters of length, breath, biaxiality, bend angle and dihedral angle for compound **III-A**, **III-B**, **III-C** and **III-D**.

Compound	Length	Breadth	Breadth	Biaxial Parameter	Bend Angle	Dihedral Angle					
	L (Å)	W_1 (Å)	W_2 (Å)	W_1/W_2	(deg)	1, 2, 3, 4 (deg)	5, 6, 7, 8 (deg)	9, 10, 11, 12 (deg)	13, 14, 15, 16 (deg)	5, 6, 9, 10 (deg)	17, 18, 19, 20 (deg)
III-A	43.2	11	5.6	1.96	131.5	0	44.3	44.6	0.1	-136.8	-87.4
III-B	45	10.8	6.4	1.69	141.1	-0.3	42.2	44.9	0.7	-139.5	-89.6
III-C	41.9	13.2	5.8	2.28	126.5	-2.1	44.2	46.2	0.9	-136.1	-84.1
III-D	43.2	12.1	6.5	1.86	132.1	-1.5	42.5	44.6	0.9	-138.4	-88.5

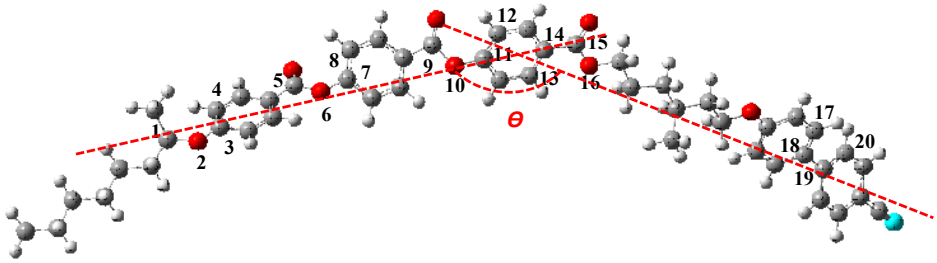


Table S6 Dipole moment of eight asymmetrical liquid crystal diads.

Compound	X	Y	Z	Total (Debye)
II-A	-10.2	0.9	-0.5	10.3
II-B	10.7	0.9	2.1	10.9
II-C	-10.2	0.7	-1.1	10.3
II-D	10.8	0.7	2.1	11.0
III-A	-11.7	1.3	-2.0	11.9
III-B	-12.6	1.7	-3.0	13.1
III-C	-12.0	1.0	-2.2	12.3
III-D	12.7	1.6	3.1	13.2