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Supporting Information

Tolane-Based Bent Bolaamphiphiles Forming Liquid Crystalline Hexagonal Honeycombs with Trigonal Symmetry

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1. Synthesis and analytical data

1.1 2,6-Diiodo-4-methylphenol 2[1]

A solution of *p*-cresol (1.62 g, 15.0 mmol) in 20 % ammonium hydroxide (12 mL) and methanol (6 mL) was stirred vigorously as a suspension of I_2 (7.6g, 30.0 mmol) and KI (9.96 g, 60.0 mmol) in H_2O (15 mL) was added dropwise. The solution was stirred for 2 h at RT. The mixture was extracted with ethyl acetate (3×40 mL). The combined organic phase was washed with brine dried over $NaSO_4$, and the solvent was removed *in vacuo*. The residue was purified by recrystallization (ethanol). Yield 52%; yellow crystal; m.p. 54-56°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47 (s, 2 H, Ar**H**), 5.56 (s, 1 H, O**H**), 2.20 (s, 3 H, C**H**$_3$).

1.2 General procedure for the synthesis of 2-alkoxy-1,3-diiodo-5-methylbenzenes 3/*n*

To a mixture of K_2CO_3 (0.62 g, 4.5 mmol), 2,6-diiodo-4-methylphenol (1.08 g, 3.0 mmol) in dry DMF (12 mL), the appropriate 1-bromo-*n*-alkane (3.3 mmol) was added. The mixture was heated to 95 °C and stirred for 20 h. After the reaction was complete (TLC), the mixture was cooled to RT, poured into ice water (60 mL) and acidified with 10% HCl to pH = 4-5. The mixture was extracted with ethyl acetate (3×50 mL). The combined extracts were washed with brine (3×30 mL) and dried over anhydrous Na_2SO_4, then the solvent was removed *in vacuo*. The residue was purified by column chromatography or recrystallization (petroleum ether).

2-Hexyloxy-1,3-diiodo-5-methylbenzene 3/6: Yield 86%; colorless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 (s, 2 H, Ar**H**), 3.94-3.92 (t, *J* = 6.6 Hz, 2 H, ArOC**H**$_2$), 2.22 (s, 3 H, ArC**H**$_3$), 1.92-1.86 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.56-1.51 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.38-1.36 (m, 4 H, C**H**$_2$), 0.93-0.90 (t, *J* = 6.7 Hz, 3 H, C**H**$_3$).

2-Dodecyloxy-1,3-diiodo-5-methylbenzene 3/12: Yield 84%; colorless crystal, m.p. 27-28°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 (s, 2 H, Ar**H**), 3.94-3.91 (t, *J* = 6.5 Hz, 2 H, ArOC**H**$_2$), 2.23 (s, 3 H, ArC**H**$_3$), 1.92-1.86 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.55-1.50 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.39-1.27 (m, 16 H, C**H**$_2$), 0.89-0.87 (t, *J* = 6.1 Hz, 3 H, C**H**$_3$).

1,3-Diiodo-5-methyl-2-tetradecyloxybenzene 3/14: Yield 78%; colorless crystal, m.p. 37-38°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 (s, 2 H, Ar**H**), 3.94-3.91 (t, *J* = 6.5 Hz, 2 H, ArOC**H**$_2$), 2.22 (s, 3 H, ArC**H**$_3$), 1.91-1.88 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.55-1.52 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.39-1.26 (m, 20 H, C**H**$_2$), 0.89-0.87 (t, *J* = 6.0 Hz, 3 H, C**H**$_3$).

2-Hexadecyloxy-1,3-diiodo-5-methylbenzene 3/16: Yield 76%; colorless crystal, m.p. 48-49°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56 (s, 2 H, Ar**H**), 3.94-3.91 (t, *J* = 6.3 Hz, 2 H, ArOC**H**$_2$), 2.22 (s, 3 H, ArC**H**$_3$), 1.91-1.88 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.55-1.52 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.39-1.26 (m, 24 H, C**H**$_2$), 0.89-0.87 (t, *J* = 5.9 Hz, 3 H, C**H**$_3$).

1,3-Diiodo-5-methyl-2-octadecyloxybenzene 3/18: Yield 75%; pale yellow crystal, m.p. 32-34°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 (s, 2 H, Ar**H**), 3.94-3.91 (t, J = 6.6 Hz, 2 H, ArOC**H**$_2$), 2.23 (s, 3 H, ArC**H**$_3$), 1.92-1.89 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.55-1.52 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.39-1.24 (m, 28 H, 14C**H**$_2$), 0.89-0.87 (t, J = 6.8 Hz, 3 H, C**H**$_3$).

2-Docosyloxy-1,3-diiodo-5-methylbenzene 3/22: This compound was synthesized according to literature[2] and NMR data corresponded to that reported in the literature.

1.3 General procedure for the synthesis of compounds 7/*n* by Sonogashira coupling[3]

The appropriate 2-*n*-alkoxy-1,3-diiodo-5-methylbenzene **3/*n*** (0.5 mmol) and 4-(4-ethynylphenoxymethyl)-2,2-dimethyl-1,3-dioxolane **6**[4] (0.28 g, 1.2 mmol) were dissolved in a mixture of dry THF (7 mL) and dry triethylamine (5 mL) under a nitrogen atmosphere. Then a mixture of $Pd(PPh_3)_4$ (35 mg, 0.05 mmol), CuI (23 mg, 0.12 mmol) was added, and the solution was stirred for overnight at RT. Ethyl acetate (30 mL) was added into the mixture, and washed with with water (3×10 mL) and brine (3×10 mL), the organic layer were separated and dried over anhydrous Na_2SO_4, and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography (petroleum ether : ethyl acetate : chloroform = 10 : 1 : 1).

7/6: Yield 80%; pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.46-7.44 (d, J = 8.6 Hz, 4 H, Ar**H**), 7.26 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 8.6 Hz, 4 H, Ar**H**), 4.50-4.47 (m, 2 H, OC**H**), 4.25 (t, J = 6.3 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.19-4.16 (m, 2 H, ArOC**H**$_2$CH), 4.09-4.07 (m, 2H, OC**H**$_2$), 3.98-3.92 (m, 2 H, ArOC**H**$_2$CH), 3.91-3.90 (m, 2 H, OC**H**$_2$), 2.28 (s, 3H, ArC**H**$_3$), 1.87-1.83 (m, 2H, ArOCH$_2$C**H**$_2$), 1.60-1.56 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.47 (s, 6 H, C**H**$_3$), 1.41 (s, 6 H, C**H**$_3$), 1.33-1.27 (m, 4 H, C**H**$_2$), 0.85-0.83 (t, J = 7.1 Hz, 3 H, C**H**$_3$).

7/12: Yield 78%; pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.46-7.45 (d, J = 7.0 Hz, 4 H, Ar**H**), 7.24 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 7.2 Hz, 4 H, Ar**H**), 4.51-4.47 (m, 2 H, OC**H**), 4.26-4.24 (m, 2 H, ArOC**H**$_2$CH$_2$), 4.21-4.12 (m, 2 H, ArOC**H**$_2$CH), 4.12-4.02 (m, 2 H, OC**H**$_2$), 4.02-3.95 (m, 2 H, ArOC**H**$_2$CH), 3.95-3.82 (m, 2H, OC**H**$_2$), 2.28 (s, 3H, ArC**H**$_3$), 1.87-1.83 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.60-1.56 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.47 (s, 6 H, C**H**$_3$), 1.41 (s, 6 H, C**H**$_3$), 1.30-1.22 (m, 16 H, C**H**$_2$), 0.89-0.87 (m, 3 H, C**H**$_3$).

7/14: Yield 86%; pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44-7.42 (d, J = 8.6 Hz, 4 H, Ar**H**), 7.22 (s, 2 H, Ar**H**), 6.88-6.86 (d, J = 8.6 Hz, 4 H, Ar**H**), 4.48-4.44 (m, 2 H, OC**H**), 4.24-4.22 (t, J = 6.4 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.17-4.14 (m, 2 H, ArOC**H**$_2$CH), 4.07-4.04 (m, 2 H, OC**H**$_2$), 3.96-3.93 (m, 2 H, ArOC**H**$_2$CH), 3.90-3.87 (m, 2 H, OC**H**$_2$), 2.26 (s, 3 H, ArC**H**$_3$), 1.85-1.82 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.59-1.53 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.45 (s, 6 H, C**H**$_3$), 1.39 (s, 6 H, C**H**$_3$), 1.30-1.19 (m, 20 H, C**H**$_2$), 0.87-0.84 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

7/16: Yield 83%; pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.45-7.43 (d, J = 8.6 Hz, 4 H, Ar**H**), 7.23 (s, 2H, Ar**H**), 6.89-6.87 (d, J = 8.6 Hz, 4 H, Ar**H**), 4.48-4.44 (m, 2 H, OC**H**), 4.24-4.22 (t, J = 6.4 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.16-4.14 (m, 2 H, ArOC**H**$_2$CH), 4.07-4.05 (m, 2 H,

OC**H**$_2$), 3.96-3.92 (m, 2 H, ArOC**H**$_2$CH), 3.90-3.86 (m, 2 H, OC**H**$_2$), 2.28 (s, 3 H, ArC**H**$_3$), 1.85-1.83 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.60-1.53 (m, 2H, ArOCH$_2$CH$_2$C**H**$_2$), 1.45 (s, 6 H, C**H**$_3$), 1.39 (s, 6 H, C**H**$_3$), 1.30-1.20 (m, 24 H, C**H**$_2$), 0.88-0.85 (t, J = 6.6 Hz, 3 H, C**H**$_3$).

7/18: Yield 64%; pale yellow crystal, m.p. 47-48°C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.46-7.45 (d, J = 8.4 Hz, 4 H, Ar**H**), 7.24 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 8.6 Hz, 4 H, Ar**H**), 4.50-4.47 (m, 2 H, OC**H**), 4.26-4.23 (t, J = 6.2 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.19-4.17 (m, 2 H, ArOC**H**$_2$CH), 4.09-4.06 (m, 2 H, OC**H**$_2$), 3.98-3.95 (m, 2 H, ArOC**H**$_2$CH), 3.93-3.90 (m, 2 H, OC**H**$_2$), 2.28 (s, 3 H, ArC**H**$_3$), 1.87-1.84 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.60-1.55 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.47 (s, 6 H, C**H**$_3$), 1.41 (s, 6 H, C**H**$_3$), 1.30-1.21 (m, 28 H, C**H**$_2$), 0.89-0.86 (t, J = 6.4 Hz, 3 H, C**H**$_3$).

7/22: Yield 88%; pale yellow crystal, m.p. 49-51°C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.46-7.45 (d, J = 8.3 Hz, 4 H, Ar**H**), 7.25 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 8.4 Hz, 4 H, Ar**H**), 4.50-4.48 (m, 2 H, OC**H**), 4.25-4.23 (t, J = 6.0 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.20-4.17 (m, 2 H, ArOC**H**$_2$CH), 4.07-4.06 (m, 2 H, OC**H**$_2$), 3.98-3.96 (m, 2 H, ArOC**H**$_2$CH), 3.93-3.90 (m, 2 H, OC**H**$_2$), 2.28 (s, 3 H, ArC**H**$_3$), 1.90-1.79 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.60-1.56 (m, 2H, ArOCH$_2$CH$_2$C**H**$_2$), 1.47 (s, 6 H, C**H**$_3$), 1.41 (s, 6 H, C**H**$_3$), 1.24-1.21 (m, 36 H, C**H**$_2$), 0.89-0.86 (t, J = 6.3 Hz, 3 H, C**H**$_3$).

1.5 General procedure for the deprotection of the 1,2-O-isopropylidene groups to yield the bolaamphiphilies 1/*n*[4,5]

7/*n* (0.5 mmol) was dissolved in CH$_3$OH (30 mL) and PPTS (120 mg) was added. The mixture was refluxed for 12 h, then cooled to RT, and extracted with chloroform (3×30 mL). The combined extracts were washed with aqueous saturated NaHCO$_3$ solution (3×30 mL) and H$_2$O (3×30 mL), dried over anhydrous Na$_2$SO$_4$, then the solvent was removed *in vacuo*. The residue was purified by column chromatography (petroleum ether : acetone = 3 : 2).

1/6: Yield 85%; colorless crystal. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.47-7.46 (d, J = 8.0 Hz, 4 H, Ar**H**), 7.24 (s, 2 H, Ar**H**), 6.91-6.89 (d, J = 7.9 Hz, 4 H, Ar**H**), 4.32-4.2 (m, 2 H, ArOC**H**$_2$CH$_2$), 4.2-4.12 (m, 2 H, ArOC**H**$_2$), 4.12-3.96 (m, 4 H, C**H**$_2$OH, C**H**OH), 3.92-3.82 (m, 2 H, ArOC**H**$_2$), 3.82-3.66 (m, 2 H, C**H**$_2$OH), 2.70-2.50 (m, 2 H, O**H**), 2.28 (s, 3 H, ArC**H**$_3$), 2.05-2.00 (m, 2 H, O**H**) 1.91-1.80 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.37-1.20 (m, 6 H, C**H**$_2$), 0.86-0.84 (m, 3 H, C**H**$_3$); ^{13}C NMR (CHCl$_3$, 125 MHz): δ = 159.3, 158.9, 134.0, 133.4 , 133.2, 118.1, 116.8, 115.0 , 93.4 , 85.2, 74.9, 70.8, 69.7, 64.0, 32.3-20.8, 14.4 (multi carbons in alkyl chain); Elemental analysis calcd (%) for C$_{35}$H$_{40}$O$_7$ (572.69): C 73.40, H 7.04; Found: C 73.31, H 7.06.

1/12: Yield 87%; colorless crystal. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.47-7.45 (d, J = 8.6 Hz, 4 H, Ar**H**), 7.24 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 8.6 Hz, 4 H, Ar**H**), 4.26-4.24 (t, J = 6.3 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.16-4.07 (m, 2 H, ArOC**H**$_2$), 4.06-4.05 (m, 4 H, C**H**$_2$OH, C**H**OH), 3.86-3.84 (m, 2 H, ArOC**H**$_2$), 3.77-3.74 (m, 2 H, C**H**$_2$OH), 2.77-2.65 (m, 2 H, O**H**), 2.28 (s, 3 H, ArC**H**$_3$), 2.21-2.13 (m, 2 H, O**H**) 1.89-1.83 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.59-1.53 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.32-1.21 (m, 16 H, C**H**$_2$), 0.89-0.86 (t, J = 6.7 Hz, 3 H, C**H**$_3$); ^{13}C NMR (CHCl$_3$, 125 MHz): δ = 159.2, 158.9, 134.0, 133.8, 133.2, 118.1, 116.8, 115.0, 93.4, 85.2, 74.9, 70.7, 69.7, 64.0, 32.3-20.8,

14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{41}H_{52}O_7$ (656.85): C 74.97, H 7.98; Found: C 74.90, H 8.00.

1/14: Yield 87%; pale yellow waxy solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47-7.45 (d, J = 8.7 Hz, 4 H, Ar**H**), 7.25 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 8.7 Hz, 4 H, Ar**H**), 4.26-4.24 (t, J = 6.4 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.17-4.11 (m, 2 H, ArOC**H**$_2$), 4.10-3.96 (m, 4 H, C**H**$_2$OH, C**H**OH), 3.87-3.84 (m, 2 H, ArOC**H**$_2$), 3.78-3.75 (m, 2 H, C**H**$_2$OH), 2.62-2.61 (m, 2 H, O**H**), 2.28 (s, 3 H, ArC**H**$_3$), 2.10-2.00 (m, 2 H, O**H**) 1.87-1.83 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.61-1.53 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.32-1.21 (m, 20 H, C**H**$_2$), 0.89-0.86 (t, J = 6.5 Hz, 3 H, C**H**$_3$); ^{13}C NMR ($CHCl_3$, 125 MHz): δ = 159.3, 158.9, 134.0, 133.4, 133.2, 118.1, 116.8, 115.0, 93.4, 85.2, 74.9, 70.7, 69.7, 64.0, 32.3-20.8, 14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{43}H_{56}O_7$ (684.90): C 75.41, H 8.24; Found: C 75.32, H 8.25.

1/16: Yield 77%; pale yellow waxy solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47-7.45 (d, J = 8.0 Hz, 4 H, Ar**H**), 7.24 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 8.0 Hz, 4 H, Ar**H**), 4.26-4.24 (t, J = 6.1 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.19-4.10 (m, 2 H, ArOC**H**$_2$), 4.10-4.00 (m, 4 H, C**H**$_2$OH, C**H**OH), 3.87-3.84 (m, 2 H, ArOC**H**$_2$), 3.80-3.70 (m, 2 H, C**H**$_2$OH), 2.28 (s, 3 H, ArC**H**$_3$), 1.87-1.84 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.57-1.53 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.32-1.21 (m, 24 H, C**H**$_2$), 0.89-0.86 (t, J = 6.1 Hz, 3 H, C**H**$_3$); ^{13}C NMR ($CHCl_3$, 125 MHz): δ = 159.3, 158.9, 134.2, 133.4, 133.2, 118.1, 116.8, 115.0, 93.5, 85.2, 74.9, 70.79, 69.7, 64.0, 32.3-20.8, 14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{45}H_{60}O_7$ (712.95): C 75.81, H 8.48; Found: C 75.74, H 8.50.

1/18: Yield 84%; pale yellow waxy solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.46-7.44 (d, J = 8.6 Hz, 4 H, Ar**H**), 7.23 (s, 2 H, Ar**H**), 6.88-6.86 (d, J = 8.7 Hz, 4 H, Ar**H**), 4.25-4.23 (t, J = 6.3 Hz, 2 H, ArOC**H**$_2$CH$_2$), 4.13-4.10 (m, 2 H, ArOC**H**$_2$), 4.03-4.02 (m, 4 H, C**H**$_2$OH, C**H**OH), 3.85-3.82 (m, 2 H, ArOC**H**$_2$), 3.76-3.73 (m, 2 H, C**H**$_2$OH), 3.20-3.05 (s, 2 H, O**H**), 2.73-2.60 (s, 2 H, O**H**), 2.26 (s, 3 H, ArC**H**$_3$), 1.88-1.82 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.58-1.52 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.30-1.20 (m, 28 H, C**H**$_2$), 0.88-0.86 (t, J = 6.6 Hz, 3 H, C**H**$_3$); ^{13}C NMR ($CHCl_3$, 125 MHz): δ = 159.2, 158.9, 134.0, 133.5, 133.3, 118.1, 116.7, 115.0, 93.5, 85.1, 74.9, 70.8, 69.5, 64.0, 32.4-20.8, 14.6 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{47}H_{64}O_7$ (741.01): C 76.18, H 8.71; Found: C 76.09, H 8.73.

1/22: Yield 83%; colorless solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47-7.45 (d, J = 8.0 Hz, 2 H, Ar**H**), 7.25 (s, 2 H, Ar**H**), 6.90-6.88 (d, J = 8.0 Hz, 4 H, Ar**H**), 4.26-4.23 (t, J = 6.1 Hz, 4 H, ArOC**H**$_2$CH$_2$), 4.13-4.06 (m, 6 H, ArOC**H**$_2$, C**H**$_2$OH, C**H**OH), 3.90-3.82 (m, 2 H, ArOC**H**$_2$), 3.80-3.72 (m, 2 H, C**H**$_2$OH), 2.68-2.60 (m, 2 H, O**H**), 2.28 (s, 3 H, ArC**H**$_3$), 2.19-2.17 (m, 2 H, O**H**), 1.87-1.84 (m, 2 H, ArOCH$_2$C**H**$_2$), 1.63-1.48 (m, 2 H, ArOCH$_2$CH$_2$C**H**$_2$), 1.25-1.21 (m, 36 H, C**H**$_2$), 0.88 (t, J = 6.1 Hz, 3 H, C**H**$_3$); ^{13}C NMR ($CHCl_3$, 125 MHz): δ = 159.2, 158.9, 134.0, 133.5, 133.2, 118.1, 116.8, 115.0, 93.4, 85.2, 74.9, 70.7, 69.6, 64.0, 32.3-20.8, 14.5 (multi carbons in alkyl chain); Elemental analysis calcd (%) for $C_{51}H_{72}O_7$ (797.11): C 76.85, H 9.10; Found: C 76.78, H 9.12.

2. Additional Data

2.1 XRD data

Table S1 Crystallographic data of the mesophases of compounds **1/*n***[a]

Compound	*T*/°C	Phase plane group	θ_{obs}/°	d_{obs}/nm	*hk*	d_{calc}/nm	d_{obs}-d_{calc}/nm	*a*/nm
1/14	35	$Col_{hex\text{-}3}/p3m1$	1.864	2.37	10	2.37	0.00	2.74
			3.736	1.18	20	1.19	-0.01	
			4.923	0.90	21	0.90	0.00	
			6.472	0.68	22	0.68	0.00	
			10.10	0.44	diff			
1/16	35	$Col_{hex\text{-}3}/p3m1$	1.840	2.40	10	2.40	0.00	2.77
			3.698	1.20	20	1.20	0.00	
			4.869	0.91	21	0.91	0.00	
			6.422	0.69	22	0.69	0.00	
			10.05	0.44	diff			
1/16+H_2O	25	$Col_{hex\text{-}3}/p3m1$	1.732	2.55	10	2.55	0.00	2.95
			3.419	1.29	20	1.28	0.01	
			9.940	0.45	diff			

[a] θ_{obs}: experimental scattering angle; d_{obs}: experimental and d_{calc}: calculated *d* spacing; *hk*: assigned indices for 2D phases (Col_{hex}), *a*: lattice parameters used to calculate d_{calc} with an error of the calculated parameters in the order of 0.1 nm.

Table S2 Calculations of molecular volumina (V_{mol}), volumina of the hypothetical unit cells (V_{cell}) and number of molecules in these unit cells (n_{cell}) of compounds **1/14** and **1/16**

Comp.	*a*/nm	V_{cell}	V_{mol}	f_R	$n_{cell,cryst}$	$n_{cell,liq}$	n_{cell}	n_{wall}
1/14	2.74	2.93	0.958	0.40	3.06	2.40	2.73	1.82
1/16	2.77	2.99	1.008	0.43	2.97	2.33	2.65	1.77

[a] V_{cell} = volume of the unit cell defined by $a^2 \times \sin(60°) \times 0.45$ nm; V_{mol} = molecular volume as calculated using crystal volume increments;[6] n_{cryst} = number of molecules in the unit cell, calculated according to $n_{cell} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$; n_{liqu} = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{liqu} = 0.55/0.7 \times n_{cryst}$; n_{cell} = number of molecules in the unit cell in the LC phase estimated as the average of that in the n_{cryst} and n_{liqu}; n_{wall} = number of molecules in the cross section of the cylinder walls as calculated from n_{cell} divided by the number of cylinder walls in the unit cell, i.e. for $Col_{hex\text{-}3}/p3m1$, n_{cell} is divided by 1.5; f_R = volume fraction of the lateral chain with respect to the total molecular volume.

2.2 Textures

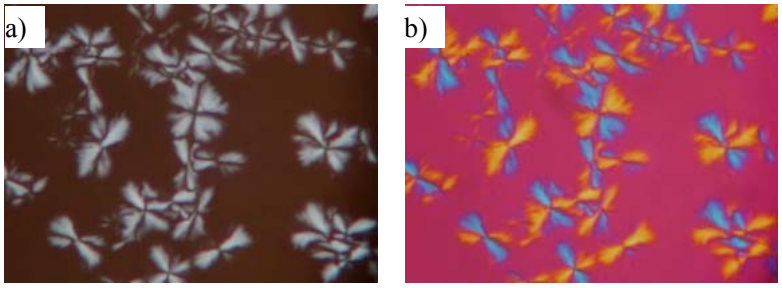

Fig. S1 (a) Crystallization of **1/12** as observed at T = 30°C between crossed polarizers (b) with additional λ-plate, indicating that the crystalline phase has positive birefringence in contrast to the LC phases of compounds **1/*n***.

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