Electronic supporting information

Achiral Flexible Liquid Crystal Trimers Exhibiting Chiral Conglomerate Phases

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Characterization of trimers **I–(5,5)**, **I–(6,6)**, **I–(7,5)**, **I–(7,9)**, **I–(9,9)**, **II–(7,7)**, **III–(7,7)** and **IV–(7,7)**.

2-{4-[5-(4-(4-Octyloxyphenyl)phenyloxy)pentyloxy]phenyl}-5-{5-[4-(5-octyloxypyrimidin-2-yl)phenyloxy]pentyloxy}pyrimidine (I–(5,5)).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.40 (s, 2H, Ar-**H**), 8.41 (s, 2H, Ar-**H**), 8.26 (d, 4H, Ar-**H**, *J* = 8.0 Hz), 7.45 (d, 2H, Ar-**H**, *J* = 9.2 Hz), 7.45 (d, 2H, Ar-**H**, *J* = 8.6 Hz), 6.97 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 6.94 (d, 2H, Ar-**H**, *J* = 9.2 Hz), 6.92 (d, 2H, Ar-**H**, *J* = 9.2 Hz), 4.12 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.07 (t, 4H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.06 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.03 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 3.98 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 1.96–1.68 (m, 16H, aliphatic-**H**), 1.49–1.29 (m, 20H, aliphatic-**H**), 0.89 (t, 6H, -C**H$_3$**, *J* = 6.9 Hz). IR (KBr):ν cm^{-1}: 2925, 2868 (C-H str), 1608 (Ar-H str), 1256 (C-O str). Elemental Analysis Calcd. for C,75.5; H, 8.08; N, 6.07. Found C, 75.5; H, 7.68; N, 6.06.

2-{4-[6-(4-(4-Octyloxyphenyl)phenyloxy)hexyloxy]phenyl}-5-{6-[4-(5-octyloxypyrimidin-2-yl)phenyloxy] hexyloxy }pyrimidine (I–(6, 6)).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.40 (s, 4H, Ar-**H**), 8.27 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 7.44 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.96 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 6.93 (d, 2H, Ar-**H**, *J* = 9.2 Hz), 4.10 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.08 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.05 (t, 4H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.01 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 3.98 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 1.86–1.78 (m, 12H, aliphatic-**H**), 1.59–1.30 (m, 28H, aliphatic-**H**), 0.89 (t, 6H, -C**H$_3$**, *J* = 6.9 Hz). IR (KBr):ν cm^{-1}: 2941, 2867 (C-H str), 1608 (Ar-H str), 1249 (C-O str). Elemental Analysis Calcd. for C,75.8; H, 8.26; N, 5.89. Found C, 76.1; H, 7.93; N, 5.93.

2-{4-[9-(4-(4-Octyloxyphenyl)phenyloxy)nonyloxy]phenyl}-5-{9-[4-(5-octyloxypyrimidin-2-yl)phenyloxy]nonyloxy}pyrimidine (I–(9,9)).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.40 (s, 4H, Ar-**H**), 8.26 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.96 (d, 4H, Ar-**H**, *J* = 8.3 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 8.0 Hz), 4.07 (t, 4H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.02 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.05 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 3.99 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 3.97 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 1.85–1.69 (m, 12H, aliphatic-**H**), 1.47–1.29 (m, 40H, aliphatic-**H**), 0.89 (t, 6H, -C**H$_3$**, *J* = 6.9 Hz). IR

(KBr):ν cm^{-1}: 2933, 2851 (C-H str), 1608 (Ar-H str), 1246 (C-O str). Elemental Analysis Calcd. for C,76.6; H, 8.76; N, 5.43. Found C, 76.8; H, 8.40; N, 5.43.

2-{4-[5-(4-(4-Octyloxyphenyl)phenyloxy)pentyloxy]phenyl}-5-{7-[4-(5-octyloxypyrimidin-2-yl)phenyloxy]heptyloxy}pyrimidine (I–(7,5)).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.40 (s, 4H, Ar-**H**), 8.26 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.96 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 4.08 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.07 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.05 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.03 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 4.02 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 3.98 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 1.92–1.76 (m, 12H, aliphatic-**H**), 1.72–1.29 (m, 28H, aliphatic-**H**), 0.89 (t, 6H, -C**H$_3$**, *J* = 6.9 Hz). IR (KBr):ν cm^{-1}: 2936, 2867 (C-H str), 1608 (Ar-H str), 1252 (C-O str). Elemental Analysis Calcd. for C,75.8; H, 8.26; N, 5.89. Found C, 76.1; H, 7.93; N, 5.93.

2-{4-[9-(4-(4-Octyloxyphenyl)phenyloxy)nonyloxy]phenyl}-5-{7-[4-(5-octyloxypyrimidin-2-yl)phenyloxy]heptyloxy}pyrimidine (I–(7,9)).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.40 (s, 4H, Ar-**H**), 8.26 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 7.44 (d, 4H, Ar-**H**, *J* = 6.9 Hz), 6.96 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.08 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.07 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.03 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.01 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 3.98 (t, 4H, -OC**H$_2$**-, *J* = 6.9 Hz), 1.86–1.76 (m, 12H, aliphatic-**H**), 1.53–1.29 (m, 36H, aliphatic-**H**), 0.89 (t, 6H, -C**H$_3$**, *J* = 6.9 Hz). IR (KBr):ν cm^{-1}: 2933, 2853 (C-H str), 1608 (Ar-H str), 1246 (C-O str). Elemental Anal Calcd. for C,76.3; H, 8.60; N, 5.56. Found C, 76.6; H, 7.96; N, 5.60.

2-{4-[7-(4-(5-Octyloxypyrimidin-2-yl)phenyloxy)heptyloxy]phenyl}-5-{7-[4-(4-octyloxyphenyl)phenyloxy]heptyloxy}pyrimidine (II–(7,7)).

Potassium carbonate (1.5 mmol, 207 mg) was added to a solution of 1-(4-octyloxyphenyl)-4-(7-bromo-heptyloxy)benzene (1.5 mmol, 713 mg) and 2-(4'-hydroxyphenyl)-5-octyloxy-pyrimidine (2.0 mmol, 376 mg) in cyclohexanone (10 ml). The reaction mixture was stirred at 90 °C for 7 h. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was purified using column chromatography on silica gel with a toluene : ethyl acetate (5:1) mixture as the eluent.

The obtained white solid was recrystallized from ethanol to give 2-(4-hydroxyphenyl)-5-{7-[4-(4-octyloxyphen-1-yl)phenoxy]heptyloxy}pyrimidine. Yield 491 mg (56.2 %)

Potassium carbonate (0.3 mmol, 42 mg) was added to a solution of 2-(4-hydroxyphenyl)-5-{7-[4-(4-octyloxyphen-1-yl)phenoxy]heptyloxy}pyrimidine (0.3 mmol, 175 mg) and 5-octyloxy-2-(4-(7-bromo-heptyloxy)-phenyl)pyrimidine (0.3 mmol, 143 mg) in cyclohexanone (10 ml). The reaction mixture was stirred at 135 °C for 8 h. After filtration of the precipitate, the solvent was removed by evaporation. Then the residue was washed with hot ethanol and recrystallized fom toluene to give the desired compound **II**. Yield 249 mg (84.9 %)

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.40 (s, 4H, Ar-**H**), 8.26 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 7.44 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 6.96 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.08 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.07 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.02 (t, 4H, -OC**H$_2$**-, *J* = 6.3 Hz), 3.99 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 3.97 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 1.84–1.76 (m, 12H, aliphatic-**H**), 1.58–1.29 (m, 32H, aliphatic-**H**), 0.89 (t, 6H, -C**H$_3$**, *J* = 6.9 Hz). IR (KBr):ν cm^{-1}: 2933, 2854 (C-H str), 1608 (Ar-H str), 1247 (C-O str). Elemental Analysis Calcd. for C,76.0; H, 8.44; N, 5.72. Found C, 76.5; H, 8.19; N, 5.68.

2-{4-[7-(4-(4-octyloxyphenyl)phenyloxy)heptyloxy]phenyl}-5-{7-[2-(4-octyloxyphenyl)pyrimidin-5-yloxy]heptyloxy}pyrimidine (III–(7,7)).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.41 (s, 4H, Ar-**H**), 8.25 (d, 4H, Ar-**H**, *J* = 8.0 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.96 (d, 4H, Ar-**H**, *J* = 8.0 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.09 (t, 4H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.02 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 4.01 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 3.99 (t, 2H, -OC**H$_2$**-, *J* = 6.3 Hz), 3.98 (t, 2H, -OC**H$_2$**-, *J* = 6.9 Hz), 1.87–1.77 (m, 12H, aliphatic-**H**), 1.56–1.29 (m, 32H, aliphatic-**H**), 0.89 (t, 6H, -C**H$_3$**, *J* = 6.9 Hz). IR (KBr):ν cm^{-1}: 2938, 2854 (C-H str), 1607 (Ar-H str), 1251 (C-O str). Elemental analysis Calcd for C,76.0; H, 8.44; N, 5.72. Found C, 77.0; H, 8.06; N, 5.71.

2-{4-[7-(2-(4-Octyloxyphenyl)pyrimidin-5-yloxy)phenyloxy)heptyloxy]phenyl}-5-{7-[4-(4-octyloxyphenyl)phenyloxy]heptyloxy}pyrimidine (IV–(7,7)).

^{1}HNMR (500 MHz, $CDCl_3$, TMS): δ=8.40 (s, 4H, Ar-**H**), 8.26 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 7.45 (d, 2H, Ar-**H**, *J* = 8.6 Hz), 7.44 (d, 2H, Ar-**H**, *J* = 8.6 Hz), 6.96 (d, 2H, Ar-**H**,

J = 8.6 Hz), 6.96 (d, 2H, Ar-**H**, *J* = 8.6 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.08 (t, 4H, -OC**H**$_2$-, *J* = 6.3 Hz), 4.03 (t, 2H, -OC**H**$_2$-, *J* = 6.3 Hz), 4.00 (t, 2H, -OC**H**$_2$-, *J* = 6.3 Hz), 3.99 (t, 2H, -OC**H**$_2$-, *J* = 6.3 Hz), 3.98 (t, 2H, -OC**H**$_2$-, *J* = 6.9 Hz), 1.88–1.76 (m, 12H, aliphatic-**H**), 1.56–1.29 (m, 32H, aliphatic-**H**), 0.89 (t, 6H, -C**H**$_3$, *J* = 6.9 Hz). IR (KBr):ν cm^{-1}: 2935, 2865 (C-H str), 1608 (Ar-H str), 1248 (C-O str). Elemental analysis Calcd for C,76.0; H, 8.44; N, 5.72. Found C, 77.2; H, 7.92; N, 5.70.

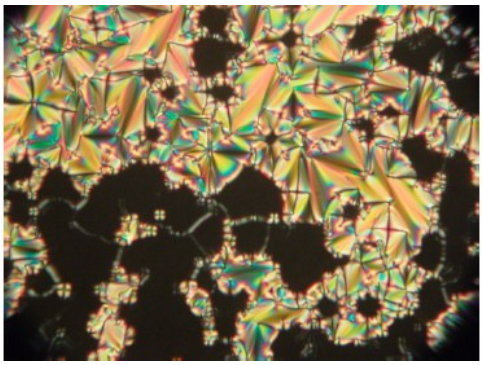
Table S1 Phase transition temperatures (°C) and $\Delta S/R$ for **I–(n,m)**.

Compound	Heating	Cooling
I–(5,5)	Cry 168.9 (20.7) Iso	Iso 163.0 (20.4) Cry
I–(6,6)	Cry 178.8 (9.5) SmC 208.1(7.1) Iso	Iso 207.2 (7.5) SmC 174.3 (-)[a] Sm[b] 171.3 (11.3) Cry
I–(7,5)	Cry 151.0 (19.1) N 157.9 (1.3) Iso	Iso 156.8 (1.3) N 150.1 (0.6) SmC 145.7 (7.3) Cry
I–(7,7)	Cry_1 144.0 (5.5) Cry_2 135.2 (8.8) N 156.9 (1.2) Iso	Iso 155.8 (1.2) N 146.4 (10.4) DC
I–(7,9)	Cry_1 130.1 (4.4) Cry_2 138.9 (8.7) N 153.6 (1.3) Iso	Iso 153.1 (1.3) N 137.8 (9.0) DC
I–(9,9)	Cry_1 120.0 (7.7) Cry_2 135.2 (12.7) N 150.4 (3.1) Iso	Iso 149.9 (2.9) N 134.1 (13.4) DC

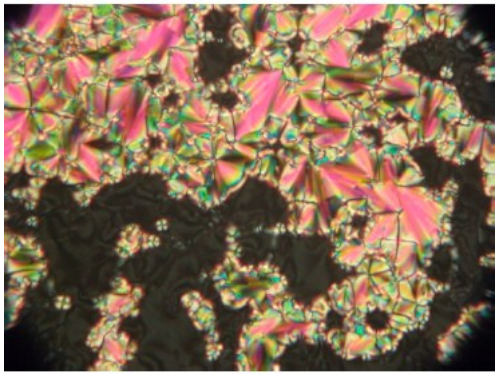
[a]Entropy change too small to be detected.

[b]Unidentified smectic phase.

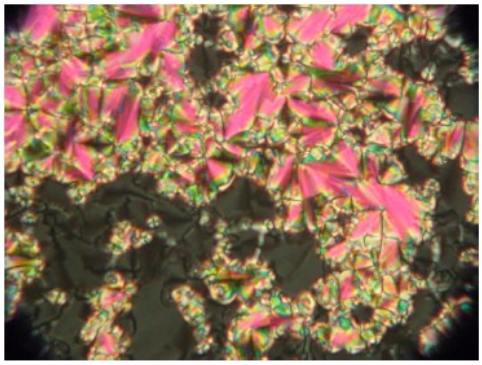
(a) SmA (160.2 °C)



(b) SmC (150.5 °C)



(c) SmX (141.6 °C)



(d) Y (133.0 °C)

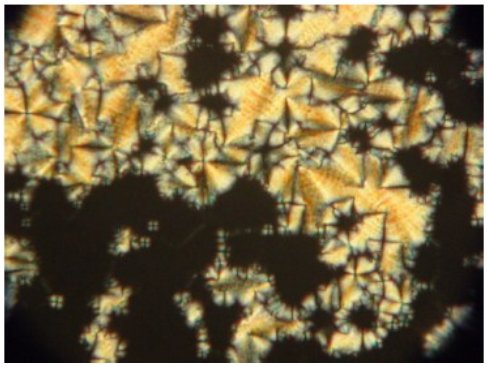


Fig. S1 Polarized optical textures of trimer **III–(7,7)** on a glass slide with a cover glass in the SmA, SmC, SmX and Y phases.

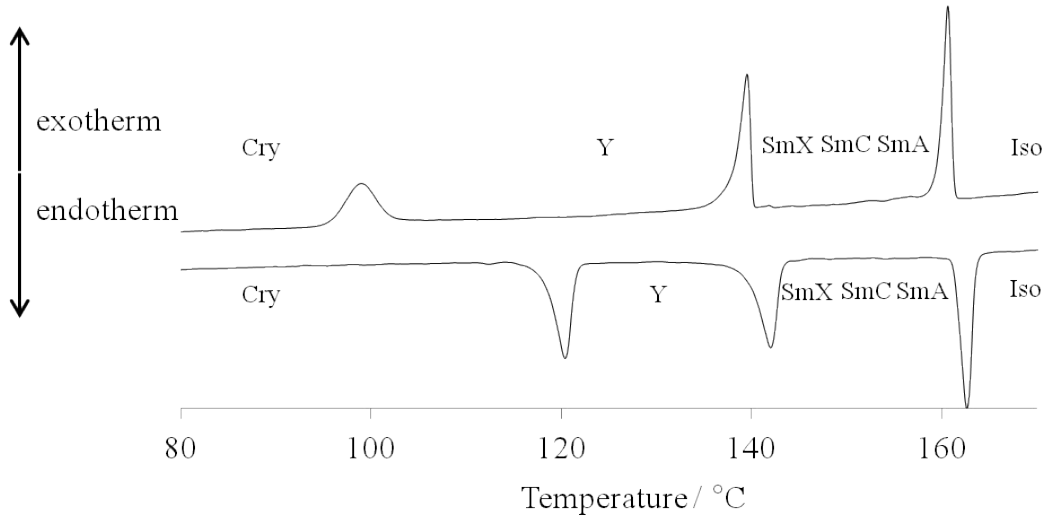


Fig. S2 DSC thermogram of trimer **III–(7,7)**. The rate of cooling and heating was 5 °C min^{-1}.