Achiral Flexible Liquid Crystal Trimers Exhibiting Chiral Conglomerate Phases

Haruna Sasaki,a Yoichi Takanishi,b Jun Yamamotob and Atushi Yoshizawa*a

aDepartment of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, 036-8561, Japan
E-mail: ayoshiza@hirosaki-u.ac.jp
bDepartment of Physics, Graduate School of Science, Kyoto University, Oiwake-cho, Kitashirakawa, Sakyo-ku, Kyoto, 606-8562, Japan

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

3. 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.

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

Electronic supporting information
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-Octyloxyphenyl)phenyloxy]pentyloxy}phenyl]-5-{5-[4-(5-octyloxy)pyrimidin-2-yl]phenyloxy}pyrimidine (I–(5,5)).

\(^1\)HNMR (500 MHz, CDCl\(_3\), TMS): \(\delta=8.40\) (s, 2H, Ar-\(\text{H}\)), 8.41 (s, 2H, Ar-\(\text{H}\)), 8.26 (d, 4H, Ar-\(\text{H}\), \(J = 8.0\) Hz), 7.45 (d, 2H, Ar-\(\text{H}\), \(J = 9.2\) Hz), 7.45 (d, 2H, Ar-\(\text{H}\), \(J = 8.6\) Hz), 6.97 (d, 4H, Ar-\(\text{H}\), \(J = 9.2\) Hz), 6.94 (d, 2H, Ar-\(\text{H}\), \(J = 9.2\) Hz), 6.92 (d, 2H, Ar-\(\text{H}\), \(J = 9.2\) Hz), 4.12 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 4.07 (t, 4H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 4.06 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 1.96–1.68 (m, 16H, aliphatic-\(\text{H}\)), 1.49–1.30 (m, 20H, aliphatic-\(\text{H}\)), 0.89 (t, 6H, -CH\(_3\), \(J = 6.9\) Hz). IR (KBr): \(\nu \text{ cm}^{-1}\): 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-octyloxy)pyrimidin-2-yl]hexyloxy}pyrimidine (I–(6,6)).

\(^1\)HNMR (500 MHz, CDCl\(_3\), TMS): \(\delta=8.40\) (s, 4H, Ar-\(\text{H}\)), 8.27 (d, 4H, Ar-\(\text{H}\), \(J = 8.6\) Hz), 7.44 (d, 4H, Ar-\(\text{H}\), \(J = 8.6\) Hz), 6.96 (d, 4H, Ar-\(\text{H}\), \(J = 9.2\) Hz), 6.93 (d, 2H, Ar-\(\text{H}\), \(J = 9.2\) Hz), 4.10 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 4.08 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 4.05 (t, 4H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 4.01 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.9\) Hz), 3.98 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.9\) Hz), 1.86–1.78 (m, 12H, aliphatic-\(\text{H}\)), 1.59–1.30 (m, 28H, aliphatic-\(\text{H}\)), 0.89 (t, 6H, -CH\(_3\), \(J = 6.9\) Hz). IR (KBr): \(\nu \text{ cm}^{-1}\): 2941, 2867 (C-H str), 1608 (Ar-H str), 1256 (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-octyloxy)pyrimidin-2-yl]nonyloxy]pyrimidine (I–(9,9)).

\(^1\)HNMR (500 MHz, CDCl\(_3\), TMS): \(\delta=8.40\) (s, 4H, Ar-\(\text{H}\)), 8.26 (d, 4H, Ar-\(\text{H}\), \(J = 8.6\) Hz), 6.96 (d, 4H, Ar-\(\text{H}\), \(J = 8.3\) Hz), 6.93 (d, 4H, Ar-\(\text{H}\), \(J = 8.0\) Hz), 4.07 (t, 4H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 4.02 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 4.05 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.3\) Hz), 3.99 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.9\) Hz), 3.97 (t, 2H, -OC\(_2\)H\(_2\)-, \(J = 6.9\) Hz), 1.85–1.69 (m, 12H, aliphatic-\(\text{H}\)), 1.47–1.29 (m, 40H, aliphatic-\(\text{H}\)), 0.89 (t, 6H, -CH\(_3\), \(J = 6.9\) Hz). IR
2-{4-[5-(4-Octyloxypyrimidin-2-yl)phenyloxy]pentyl]oxy[phenyl]-5-[7-[4-(5-Octyloxyphenyl)phenyloxy]heptyloxy]pyrimidine (I–(7,5)).

1HNMR (500 MHz, CDCl₃, 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, -OCH₂-, J = 6.3 Hz), 4.07 (t, 2H, -OCH₂-, J = 6.3 Hz), 4.05 (t, 2H, -OCH₂-, J = 6.3 Hz), 3.98 (t, 2H, -OCH₂-, J = 6.9 Hz), 1.92–1.76 (m, 12H, aliphatic-H), 1.72–1.29 (m, 28H, aliphatic-H), 0.89 (t, 6H, -CH₃, J = 6.9 Hz). IR (KBr):ν cm⁻¹: 2936, 2867 (C-H str), 1608 (Ar-H str), 1252 (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-[9-(4-Octyloxypyrimidin-2-yl)phenyloxy]nonyl]oxy[phenyl]-5-[7-[4-(5-Octyloxyphenyl)phenyloxy]heptyloxy]pyrimidine (I–(7,9)).

1HNMR (500 MHz, CDCl₃, 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, -OCH₂-, J = 6.3 Hz), 4.07 (t, 2H, -OCH₂-, J = 6.3 Hz), 4.03 (t, 2H, -OCH₂-, J = 6.3 Hz), 4.01 (t, 2H, -OCH₂-, J = 6.9 Hz), 3.98 (t, 4H, -OCH₂-, J = 6.9 Hz), 1.86–1.76 (m, 12H, aliphatic-H), 1.53–1.29 (m, 36H, aliphatic-H), 0.89 (t, 6H, -CH₃, 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-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 from toluene to give the desired compound II. Yield 249 mg (84.9 %)

\[^1\text{HNMR} \text{ (500 MHz, CDCl}_3\text{, TMS): } \delta=8.40 \text{ (s, 4H, Ar-H), 8.26 (d, 4H, Ar-H, } J = 8.6 \text{ Hz), 7.45 (d, 4H, Ar-H, } J = 8.6 \text{ Hz), 7.44 (d, 4H, Ar-H, } J = 9.2 \text{ Hz), 6.96 (d, 4H, Ar-H, } J = 8.6 \text{ Hz), 6.93 (d, 4H, Ar-H, } J = 8.6 \text{ Hz), 4.08 (t, 2H, -OCH}_2\text{-, } J = 6.3 \text{ Hz), 4.07 (t, 2H, -OCH}_2\text{-, } J = 6.3 \text{ Hz), 3.97 (t, 2H, -OCH}_2\text{-, } J = 6.3 \text{ Hz), 1.84–1.76 (m, 12H, aliphatic-H), 1.58–1.29 (m, 32H, aliphatic-H), 0.89 (t, 6H, -C}_3\text{H}_3\text{-, } J = 6.9 \text{ Hz). IR (KBr): } \nu \text{ cm}^{-1}: 2933, 2854 \text{ (C-H str), 1607 (Ar-H str), 1247 (O-CO str). Elemental Analysis Calcd. for } \text{C,76.0; H, 8.44; N, 5.72. Found C, 76.5; H, 8.19; N, 5.68.}\]

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

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

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

\[^1\text{HNMR} \text{ (500 MHz, CDCl}_3\text{, TMS): } \delta=8.40 \text{ (s, 4H, Ar-H), 8.26 (d, 4H, Ar-H, } J = 8.6 \text{ Hz), 7.45 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 7.44 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 6.96 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 7.45 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 7.44 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 6.96 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 7.45 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 7.44 (d, 2H, Ar-H, } J = 8.6 \text{ Hz), 6.96 (d, 2H, Ar-H, } J = 8.6 \text{ Hz). IR (KBr): } \nu \text{ cm}^{-1}: 2938, 2854 \text{ (C-H str), 1607 (Ar-H str), 1251 (C-O str). Elemental analysis Calcd for C,76.0; H, 8.44; N, 5.72. Found C, 77.0; H, 8.06; N, 5.71.}\]
$J = 8.6 \, \text{Hz}$, 6.96 (d, 2H, Ar-H, $J = 8.6 \, \text{Hz}$), 6.93 (d, 4H, Ar-H, $J = 8.6 \, \text{Hz}$), 4.08 (t, 4H, -OCH$_2^-$, $J = 6.3 \, \text{Hz}$), 4.03 (t, 2H, -OCH$_2^-$, $J = 6.3 \, \text{Hz}$), 4.00 (t, 2H, -OCH$_2^-$, $J = 6.3 \, \text{Hz}$), 3.99 (t, 2H, -OCH$_2^-$, $J = 6.3 \, \text{Hz}$), 3.98 (t, 2H, -OCH$_2^-$, $J = 6.9 \, \text{Hz}$), 1.88–1.76 (m, 12H, aliphatic-H), 1.56–1.29 (m, 32H, aliphatic-H), 0.89 (t, 6H, -CH$_3$, $J = 6.9 \, \text{Hz}$). IR (KBr): $\nu$ 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).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>I–(5,5)</td>
<td>Cry 168.9 (20.7) Iso</td>
<td>Iso 163.0 (20.4) Cry</td>
</tr>
<tr>
<td>I–(6,6)</td>
<td>Cry 178.8 (9.5) SmC 208.1 (7.1) Iso</td>
<td>Iso 207.2 (7.5) SmC 174.3 (7.1) Sm$^b$ 171.3 (11.3) Cry</td>
</tr>
<tr>
<td>I–(7,5)</td>
<td>Cry 151.0 (19.1) N 157.9 (1.3) Iso</td>
<td>Iso 156.8 (1.3) N 150.1 (0.6) SmC 145.7 (7.3) Cry</td>
</tr>
<tr>
<td>I–(7,7)</td>
<td>Cry 1 144.0 (5.5) Cry 1 135.2 (8.8) N 156.9 (1.2) Iso</td>
<td>Iso 155.8 (1.2) N 146.4 (10.4) DC</td>
</tr>
<tr>
<td>I–(7,9)</td>
<td>Cry 1 130.1 (4.4) Cry 2 138.9 (8.7) N 153.6 (1.3) Iso</td>
<td>Iso 153.1 (1.3) N 137.8 (9.0) DC</td>
</tr>
<tr>
<td>I–(9,9)</td>
<td>Cry 1 120.0 (7.7) Cry 2 135.2 (12.7) N 150.4 (3.1) Iso</td>
<td>Iso 149.9 (2.9) N 134.1 (13.4) DC</td>
</tr>
</tbody>
</table>

$^a$Entropy change too small to be detected.

$^b$Unidentified smectic phase.
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.