

Electronic Supporting Information

Linear symmetric liquid crystal trimers exhibiting supramolecular chiral architectures

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1. Characterization of trimers **I-n**.
2. Fig. S1 Polarized optical textures of trimer **I-9** on a glass slide without a cover glass in the DC phase at 120 °C between uncrossed polarizers.
3. Fig. S2 XRD profile of trimer **I-3** in the DC phase at 70 °C.
4. Fig. S3 SEM images of the surface structures for trimers **I-3**, **I-7** and **I-11**.
5. Fig. S4 Optical textures of a sample of trimer **I-5** between uncrossed polarizers in the DC phase at 140 °C. The sample was cooled down from the isotropic liquid at 190 °C. The sample thickness was 200 μm.
6. Fig. S5 (a) Optical textures at 124 °C and (b) SEM image of the cross section area of trimer **I-9** with a sample thickness of 200 μm. The sample was cooled form the isotropic liquid at 136 °C.
7. Fig. S6 Optical textures of an equimolecular mixtures of trimers **I-3** and **I-5**.
8. Fig. S7 SEM image of the surface structure of a mixture of **I-7** (50 mol%) and **I-11** (50 mol%).
9. Fig. S8 SEM image of the surface structure of a mixture of **I-** (50 mol%) and **I-7** (50 mol%).

1. Characterization of trimers **I-n**.

4,4'-Bis{7-[4-(5-octylpyrimidin-2-yl)phenyloxy]propyloxy}biphenyl (I-3)

¹HNMR (500 MHz, CDCl₃, TMS): δ_{H} /ppm: 8.56 (s, 4H, Ar-**H**), 8.34 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 7.00 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 6.96 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 4.25 (t, 4H, -O-CH₂-, *J* = 6.0 Hz), 4.21 (t, 4H, -O-CH₂-, *J* = 6.0 Hz), 2.59 (t, 4H, -Ar-CH₂-, *J* = 7.7 Hz), 2.31 (quint, 4H, -O-CH₂-CH₂-, *J* = 6.2 Hz), 1.63 (quint, 4H, -Ar-CH₂-CH₂-, *J* = 6.2 Hz), 1.33–1.26 (m, 20H, aliphatic-**H**), 0.87 (t, 6H, -CH₃, *J* = 6.0 Hz). IR (KBr) ν cm⁻¹: 2923, 2852 (C-H str), 1607 (Ar-H str), 1243 (C-O str). Elemental analysis (%): Calc. for C₅₄H₆₆N₄O₄: C, 77.66; H, 7.97; N, 6.71. Found C, 77.85; H, 7.95; N, 6.65.

4,4'-Bis{7-[4-(5-octylpyrimidin-2-yl)phenyloxy]pentyloxy}biphenyl (I-5)

¹HNMR (500 MHz, CDCl₃, TMS): δ_{H} /ppm: 8.56 (s, 4H, Ar-**H**), 8.34 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.98 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.94 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.07 (t, 4H, -O-CH₂-, *J* = 6.3 Hz), 4.03 (t, 4H, -O-CH₂-, *J* = 6.6 Hz), 2.59 (t, 4H, -Ar-CH₂-, *J* = 7.4 Hz), 1.94–1.87 (m, 8H, aliphatic-**H**), 1.73–1.59 (m, 8H, aliphatic-**H**), 1.33–1.26 (m, 20H, aliphatic-**H**), 0.88 (t, 6H, -CH₃, *J* = 6.9 Hz). IR (KBr) ν cm⁻¹: 2925, 2854 (C-H str), 1607 (Ar-H str), 1245 (C-O str). Elemental analysis (%): Calc. for C₅₈H₇₄N₄O₄: C, 78.16; H, 8.37; N, 6.29. Found C, 78.23; H, 8.38; N, 6.26.

4,4'-Bis{7-[4-(5-octylpyrimidin-2-yl)phenyloxy]hexyloxy}biphenyl (I-6)

¹HNMR (500 MHz, CDCl₃, TMS): δ_{H} /ppm: 8.56 (s, 4H, Ar-**H**), 8.33 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.98 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 6.94 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.05 (t, 4H, -O-CH₂-, *J* = 6.6 Hz), 4.01 (t, 4H, -O-CH₂-, *J* = 6.6 Hz), 2.59 (t, 4H, Ar-CH₂-, *J* = 7.7 Hz), 1.86–1.84 (m, 8H, aliphatic-**H**), 1.67–1.62 (m, 4H, aliphatic-**H**), 1.59–1.56 (m, 8H, aliphatic-**H**), 1.33–1.26 (m, 20H, aliphatic-**H**), 0.88 (t, 6H, -CH₃, *J* = 6.9 Hz). IR (KBr) ν cm⁻¹: 2922, 2854 (C-H str), 1607 (Ar-H str), 1243 (C-O str). Elemental analysis (%): Calc. for C₆₀H₇₈N₄O₄: C, 78.39; H, 8.55; N, 6.09. Found C, 78.41; H, 8.43; N, 6.01.

4,4'-Bis{7-[4-(5-octylpyrimidin-2-yl)phenyloxy]heptyloxy}biphenyl (I-7)

¹HNMR (500 MHz, CDCl₃, TMS): δ_{H} /ppm: 8.57 (s, 4H, Ar-**H**), 8.34 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.98 (d, 4H, Ar-**H**, *J* = 9.1 Hz), 6.94 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.04 (t, 4H, -O-CH₂-, *J* = 6.6 Hz), 3.99 (t, 4H, -O-CH₂-, *J* = 6.3 Hz), 2.59 (t, 4H, -Ar-CH₂-, *J* = 7.7 Hz), 1.86–1.79 (m, 8H, aliphatic-**H**), 1.67–1.60 (m, 4H, aliphatic-

H), 1.54–1.27 (m, 32H, aliphatic-**H**), 0.88 (t, 6H, -CH₃, *J* = 6.9 Hz). IR (KBr) ν cm⁻¹: 2926, 2852 (C-H str), 1606 (Ar-H str), 1241 (C-O str). Elemental analysis (%): Calc. for C₆₂H₈₂N₄O₄: C, 78.61; H, 8.72; N, 5.91. Found C, 78.14; H, 8.62; N, 5.74.

4,4'-Bis{7-[4-(5-octylpyrimidin-2-yl)phenyloxy]octyloxy}biphenyl (I-8)

¹HNMR (500 MHz, CDCl₃, TMS): δ_H /ppm: 8.56 (s, 4H, Ar-**H**), 8.33 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.98 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 4.03 (t, 4H, -OCH₂-, *J* = 6.6 Hz), 3.98 (t, 4H, -OCH₂-, *J* = 6.6 Hz), 2.59 (t, 4H, -Ar-CH₂-, *J* = 7.7 Hz), 1.85–1.78 (m, 8H, aliphatic-**H**, *J* = 7.0), 1.63 (quint, 4H, -Ar-CH₂-CH₂-, *J* = 7.4), 1.50–1.26 (m, 36H, aliphatic-**H**), 0.88 (t, 6H, -CH₃, *J* = 6.9 Hz). IR (KBr) ν cm⁻¹: 2921, 2852 (C-H str), 1607 (Ar-H str), 1242 (C-O str). Elemental analysis (%): Calc. for C₆₄H₈₆N₄O₄: C, 78.81; H, 8.89; N, 5.74. Found C, 78.85; H, 8.97; N, 5.67.

4,4'-Bis{7-[4-(5-octylpyrimidin-2-yl)phenyloxy]nonyloxy}biphenyl (I-9)

¹HNMR (500 MHz, CDCl₃, TMS): δ_H /ppm: 8.56 (s, 4H, Ar-**H**), 8.33 (d, 4H, Ar-**H**, *J* = 9.1 Hz), 7.44 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.97 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 6.93 (d, 4H, Ar-**H**, *J* = 8.6), 4.02 (t, 4H, -O-CH₂-, *J* = 6.6 Hz), 3.98 (t, 4H, -O-CH₂-, *J* = 6.6 Hz), 2.59 (t, 4H, -Ar-CH₂-, *J* = 7.7 Hz), 1.84–1.77 (m, 8H, aliphatic-**H**, *J* = 7.0), 1.63 (quint, 4H, -Ar-CH₂-CH₂-, *J* = 7.4 Hz), 1.48–1.26 (m, 40H, aliphatic-**H**), 0.88 (t, 6H, -CH₃, *J* = 7.2 Hz). IR (KBr) ν cm⁻¹: 2920, 2851 (C-H str), 1607 (Ar-H str), 1240 (C-O str). Elemental analysis (%): Calc. for C₆₆H₉₀N₄O₄: C, 79.00; H, 9.04; N, 5.58. Found C, 79.15; H, 8.72; N, 5.62.

4,4'-Bis{7-[4-(5-octylpyrimidin-2-yl)phenyloxy]undecyloxy}biphenyl (I-11)

¹HNMR (500 MHz, CDCl₃, TMS): δ_H /ppm: 8.56 (s, 4H, Ar-**H**), 8.33 (d, 4H, Ar-**H**, *J* = 8.6 Hz), 7.45 (d, 4H, Ar-**H**, *J* = 9.2 Hz), 6.97 (d, 4H, Ar-**H**, *J* = 9.2), 6.92 (d, 4H, Ar-**H**, *J* = 8.6), 4.02 (t, 4H, -O-CH₂, *J* = 6.6 Hz), 3.97 (t, 4H, -O-CH₂-, *J* = 6.6), 2.59 (t, 4H, Ar-CH₂-, *J* = 7.7 Hz), 1.83–1.76 (m, 8H, aliphatic-**H**), 1.63 (quint, 4H, -Ar-CH₂-CH₂-, *J* = 7.4 Hz) 1.47–1.26 (m, 48H, aliphatic-**H**), 0.88 (t, 6H, -CH₃, *J* = 6.9 Hz). IR (KBr) ν cm⁻¹: 2920, 2851 (C-H str), 1607 (Ar-H str), 1242 (C-O str). Elemental analysis (%): Calc. for C₇₀H₉₈N₄O₄: C, 79.35; H, 9.32; N, 5.29. Found C, 79.10; H, 9.33; N, 5.17.

2. Fig. S1

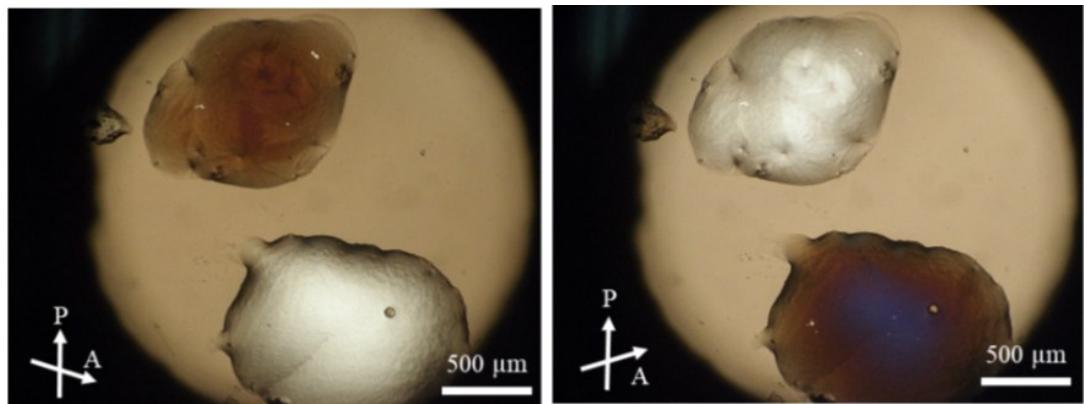


Fig. S1 Polarized optical textures of trimer **I-9** on a glass slide without a cover glass in the DC phase at °C between uncrossed polarizers.

3. Fig. S2

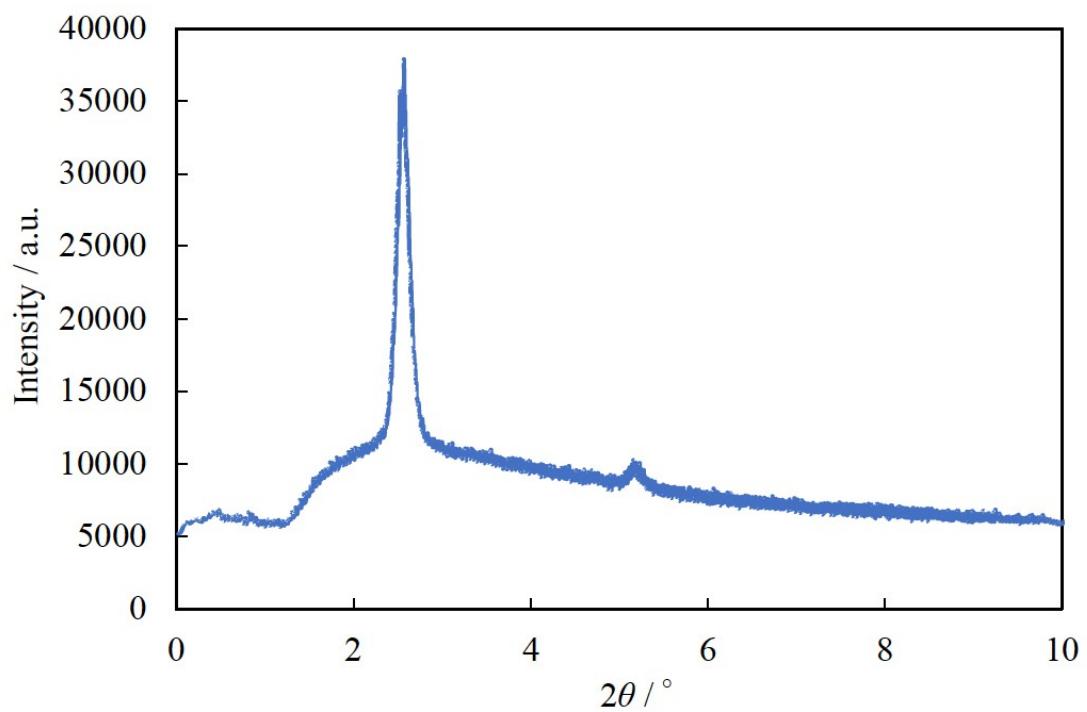
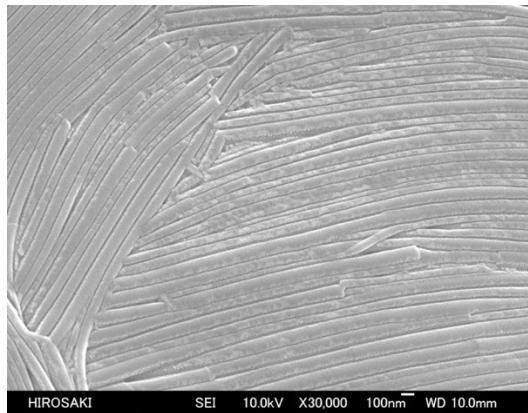


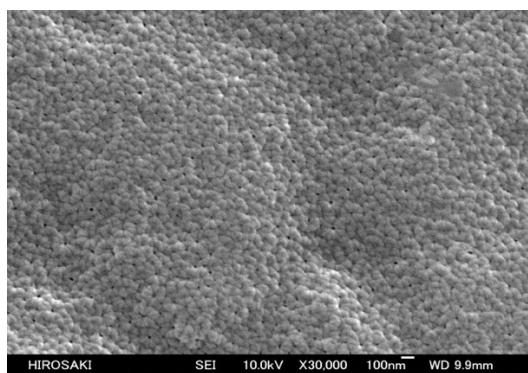
Fig. S2 XRD profile of trimer **I-3** in the DC phase at 70 °C.

4. Fig. S3

(a) **I-3**



(b) **I-7**



(c) **I-11**

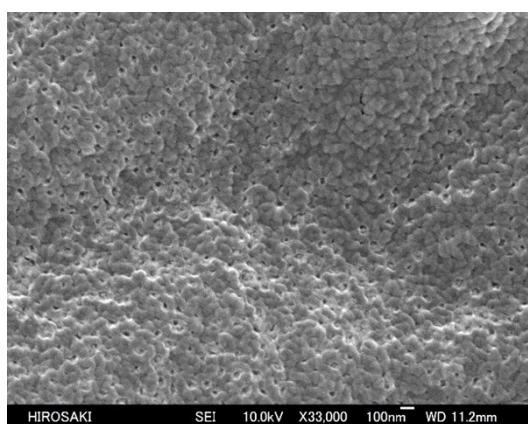


Fig. S3 SEM images of the surface structures for trimers **I-3**, **I-7** and **I-11**.

5. Fig. S4

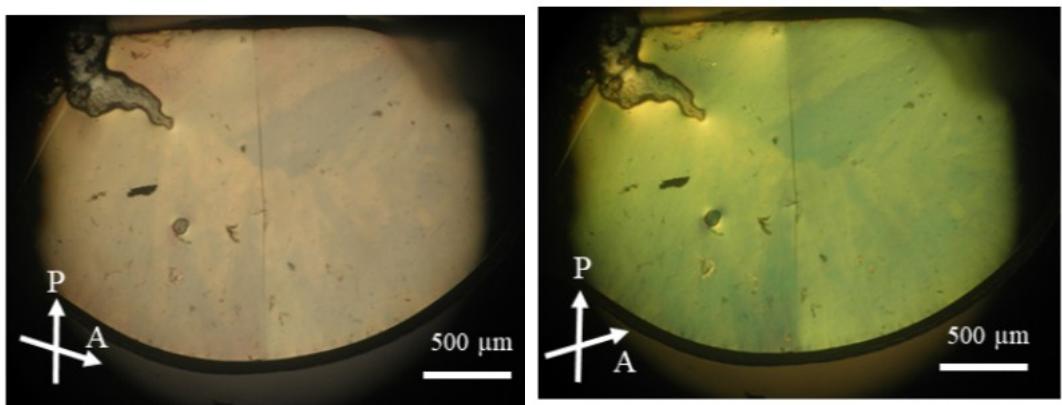


Fig. S4 Optical textures of a sample of trimer **I-5** between uncrossed polarizers in the DC phase at 140 °C. The sample was cooled down from the isotropic liquid at 190 °C. The sample thickness was 200 μm .

6. Fig. S5

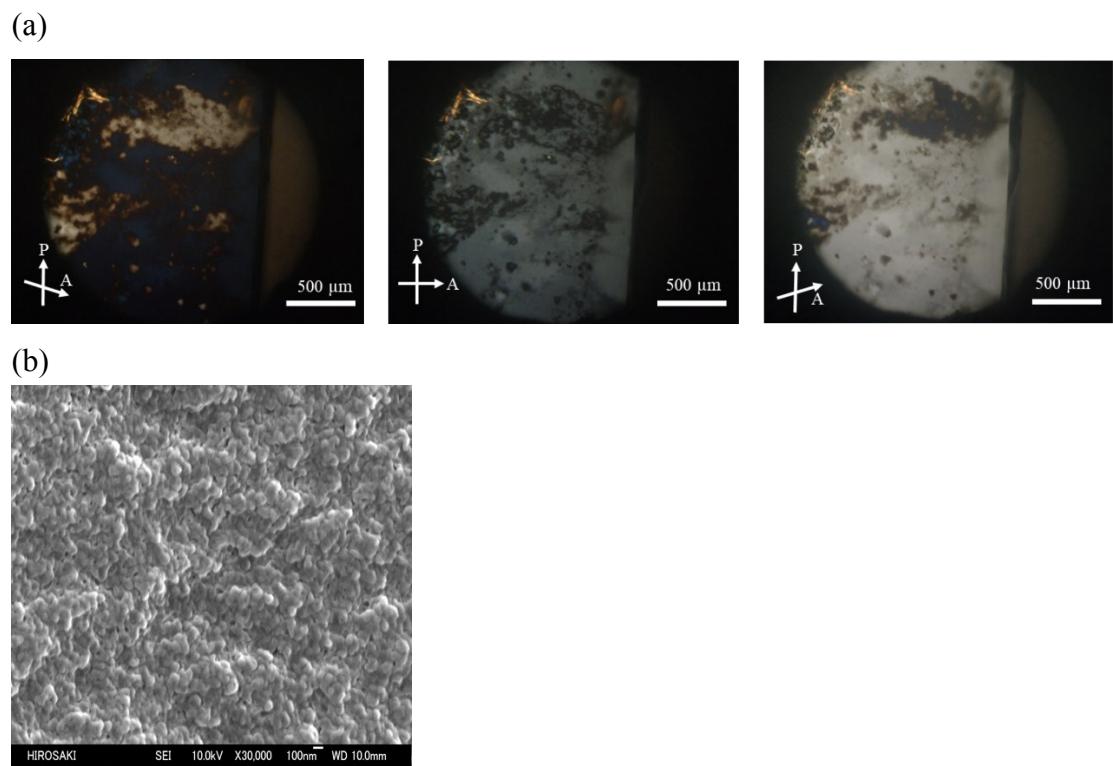


Fig. S5 (a) Optical textures at 124 °C and (b) SEM image of the cross section area of trimer I-9 with a sample thickness of 200 μm . The sample was cooled from the isotropic liquid at 136 °C.

7. Fig. S6

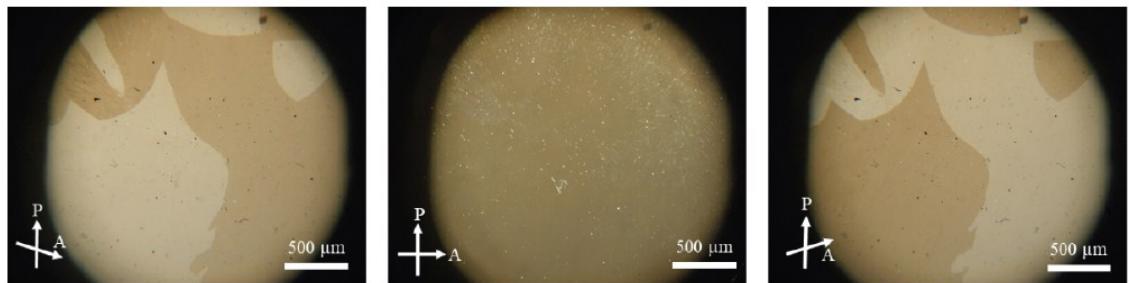


Fig. S6 Optical textures of an equimolecular mixture of **I-3** and **I-5** at 130 °C.

8. Fig. S7

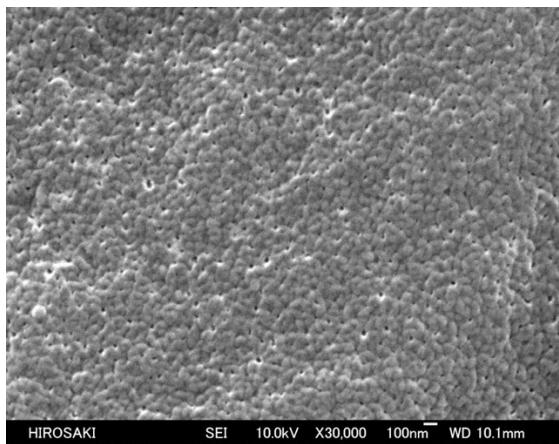


Fig. S7 SEM image of the surface structure of a mixture of **I-7** (50 mol%) and **I-11** (50 mol%).

9. Fig. S8



Fig. S8 SEM image of the surface structure of a mixture of **I-5** (50 mol%) and **I-7** (50 mol%).