Supplemental Information

Extended conjugated mesogens: synthesis and mesomorphic properties of **H-shaped** mesogens based on 3,3',5,5'-tetrasubstituted 2,2'-bithiophene with **oligo(1,4-phenyleneethynylene)** arms

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Synthesis of compound **9a**

To a solution of 2,2'-bithiophene (0.783 g, 4.71 mmol) in CH_3Cl -acetic acid (1:1, 50ml) was added *N*-iodosuccinimide (5.22 g, 23.2 mmol). The mixture was stirred for 80°C for 4 h. The reaction mixture was cooled to room temperature, and the precipitate was filtered and washed with EtOH (20 ml). The resulting solid was recrystallised from CS_2 -EtOH and then from CH_3Cl -EtOH to give 1.51 g (48%) of **9a** as white crystals, m.p. 189–190°C (lit.[20] m.p. 188–190°C). ^1H NMR (CDCl_3): δ = 7.29 (s, 2H). ^{13}C NMR (CDCl_3): δ = 77.80, 85.26, 140.07, 144.16.

Synthesis of compounds **12a**, **12b**, **13a** and **13b**

Compound **12a**

To a solution of **9b** (205 mg, 0.425 mmol) and **10c** (388 mg, 1.09 mmol) in *i*-Pr₂NH (25 ml) were added Pd(PhCN)₂Cl₂ 30 mg (0.078 mmol), PPh₃ 51 mg (0.19 mmol) and CuI (30 mg, 0.16 mmol). The mixture was stirred for 21 h at room temperature. MeOH (100 ml) was added to the reaction mixture, and the solid was filtered and washed with EtOH (20 ml). The resulting solid was chromatographed on silica gel using hexane–CH₂Cl₂ (3:1). Recrystallisation from hexane–EtOH gave 324 mg (73%) of **12a** as an orange solid, m.p. 128–129°C. ¹H NMR (CDCl₃): δ = 0.88 (t, *J* = 7.1 Hz, 6H), 1.24–1.36 (m, 28H), 1.58–1.65 (m, 4H), 2.62 (t, *J* = 7.7 Hz, 4H), 2.81 (q, *J* = 7.6 Hz, 4H), 2.85 (q, *J* = 7.6 Hz, 4H), 7.18 (AA'BB', 4H), 7.22 (s, 2H), 7.36 (s, 2H), 7.38 (s, 2H), 7.44 (AA'BB', 4H). ¹³C NMR (CDCl₃): δ = 14.10, 14.64, 14.73, 22.66, 27.15, 27.16, 29.16, 29.23, 31.81, 35.95, 85.24, 87.40, 94.92, 95.20, 111.88, 120.42, 121.03, 123.63, 125.61, 128.54, 129.48, 131.45, 131.48, 131.56, 134.52, 143.48, 143.56, 143.67.

Compound **12b**

To a solution of **9b** (364 mg, 0.755 mmol) and **11b** (715 mg, 1.99 mmol) in *i*-Pr₂NH (40 ml) were added Pd(PhCN)₂Cl₂ 48 mg (0.013 mmol), PPh₃ 77 mg (0.29 mmol) and CuI (47 mg, 0.25 mmol). The mixture was stirred for 21 h at room temperature. MeOH (120 ml) was added to the reaction mixture, and the solid was filtered and washed with MeOH (25 ml) and with hexane (75 ml). The resulting solid was chromatographed on silica gel (hexane/CH₂Cl₂ 3:1) and then recrystallised from hexane to give 612 mg (78%) of **12b** as an orange solid, m.p. 108–109°C. ¹H NMR (CDCl₃): δ = 0.88 (t, *J* = 6.9 Hz, 6H), 1.23–1.36 (m, 36H), 1.58–1.65 (m, 4H), 2.62 (t, *J* = 7.7 Hz, 4H), 2.81 (q, *J* = 7.6 Hz, 4H), 2.85 (q, *J* = 7.6 Hz, 4H), 7.18 (AA'BB', 4H), 7.23 (s, 2H), 7.36 (s, 2H), 7.38 (s, 2H), 7.44 (AA'BB', 4H). ¹³C NMR (CDCl₃): δ = 14.12, 14.64, 14.73, 22.68, 27.14, 27.16, 29.27, 29.32, 29.50, 29.55, 31.29, 31.90, 35.95, 85.23, 87.39, 94.92, 95.20, 111.87, 120.42, 121.03, 123.63, 125.60, 128.54, 129.48, 131.44, 131.49, 131.55, 134.52, 143.48, 143.55, 143.67.

Compound **13a**

To a solution of **9b** (170 mg, 0.353 mmol) and **10e** (352 mg, 915 μmol) in *i*-Pr₂NH (20 ml) were added Pd(PhCN)₂Cl₂ 26 mg (0.068 mmol), PPh₃ 59 mg (0.22 mmol) and CuI (30 mg, 0.16 mmol). The mixture was stirred for 20 h at room temperature. MeOH (60 ml) was added to the reaction mixture, and the solid was filtered and washed with EtOH (60 ml) and with hexane (60 ml). The resulting solid was chromatographed on silica gel using hexane–CH₂Cl₂ (4:1). Recrystallisation from hexane–EtOH twice gave 339 mg (88%) of **13a** as an orange solid, m.p. 155–156°C. ¹H NMR (CDCl₃): δ = 0.91 (t, *J* = 7.1 Hz, 6H), 1.29 (t, *J* = 7.6 Hz, 6H), 1.30 (t, *J* = 7.6 Hz, 6H), 1.32–1.38 (m, 8H), 1.76–

1.83 (m, 4H), 2.81 (q, $J = 7.6$ Hz, 4H), 2.84 (q, $J = 7.6$ Hz, 4H), 3.98 (t, $J = 6.6$ Hz, 4H), 6.89 (AA'BB', 4H), 7.22 (s, 2H), 7.36 (s, 2H), 7.37 (s, 2H), 7.45 (AA'BB', 4H). ^{13}C NMR (CDCl_3): $\delta = 14.04, 14.62, 14.73, 22.61, 25.70, 27.15, 29.16, 31.58, 68.12, 85.17, 86.69, 94.87, 95.25, 111.86, 114.60, 115.14, 120.81, 123.80, 125.63, 129.45, 131.42, 131.45, 132.97, 134.49, 143.30, 143.54, 159.37$.

Compound **13b**

To a solution of **9b** (363 mg, 0.753 mmol) and **11e** (767 mg, 1.91 mmol) in *i*-Pr₂NH (40 ml) were added Pd(PhCN)₂Cl₂ 48 mg (0.013 mmol), PPh₃ 79 mg (0.30 mmol) and CuI (48 mg, 0.25 mmol). The mixture was stirred for 6 h at room temperature. MeOH (120 ml) was added to the reaction mixture, and the solid was filtered and washed with MeOH (25 ml). The resulting solid was chromatographed on silica gel (hexane/CHCl₃ 3:1) and then recrystallised from hexane gave 724 mg (86%) of **13b** as an orange solid, m.p. 126–127°C. ^1H NMR (CDCl_3): $\delta = 0.89$ (t, $J = 7.0$ Hz, 6H), 1.24–1.40 (m, 32H), 1.42–1.50 (m, 4H), 1.76–1.83 (m, 4H), 2.80 (q, $J = 7.6$ Hz, 4H), 2.84 (q, $J = 7.6$ Hz, 4H), 3.98 (t, $J = 6.6$ Hz, 4H), 6.89 (AA'BB', 4H), 7.22 (s, 2H), 7.36 (s, 2H), 7.37 (s, 2H), 7.45 (AA'BB', 4H). ^{13}C NMR (CDCl_3): $\delta = 14.12, 14.62, 14.73, 22.68, 26.02, 27.15, 29.20, 29.27, 29.40, 29.54, 31.88, 68.13, 85.16, 86.69, 94.87, 95.25, 111.86, 114.61, 115.14, 120.81, 123.81, 125.64, 129.45, 131.42, 131.45, 132.97, 134.49, 143.30, 143.54, 159.38$.