Supplementary Material (ESI) for Chemical Communications

Probing the Structural Factors Influencing Columnar Mesophase Formation and Stability in Triphenylene Discotics

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General methods – see Cammidge *et al* **J. Am. Chem. Soc., 2005, *127*, 16382.**

2,3,6,7-Tetrakis(hexyloxy)-10,11-diphenyltriphenylene 14

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), benzeneboronic acid (0.23 g, 1.9 mmol), palladium (II) chloride (0.002 g, 0.012 mmol) triphenylphosphine (0.028 g, 0.11 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 2:3) to give the pure title compound (0.31 g, 62%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.90-0.96 (12 H, m), 1.34-1.41 (16 H, m), 1.52-1.61 (8 H, m), 1.89-1.99 (8 H, m), 4.20 (4 H, t, *J* 6.4 Hz), 4.26 (4 H, t, *J* 6.6 Hz,), 7.28-7.33 (10 H, m), 7.86 (2 H, s), 8.02 (2 H, s), 8.47 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.1, 22.6, 22.7, 25.8, 25.9, 29.4, 29.5, 31.7, 31.8, 69.6, 69.8, 107.3, 123.7, 124.6, 125.1, 126.8, 128.2, 128.5, 130.4, 138.9, 142.2, 149.5, 149.9; *m/z* (EI) 780.7 (M^+, 100%); HRMS. Calcd for $C_{54}H_{68}O_4$: 780.5112. Found: 780.5115.

2,3,6,11-Tetrakis(hexyloxy)-7,10-diphenyltriphenylene 15

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), benzeneboronic acid (0.23 g, 1.9 mmol), palladium (II) chloride (0.002 g, 0.012 mmol) triphenylphosphine (0.028 g, 0.11 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:1) to give the pure title compound (0.37 g, 74%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.85-0.96 (12 H, m), 1.32-1.60 (16 H, m), 1.81-1.84 (8 H, m), 1.95-1.99 (8 H, m), 4.19 (4 H, t, *J* 6.3 Hz), 4.28 (4 H, t, *J* 6.4 Hz), 7.38 (4 H, d, *J* 7.3 Hz), 7.45 (2 H, dd, *J* 7.7, 7.3 Hz), 7.69 (4 H, d, *J* 7.7 Hz), 7.88 (s, 2 H), 7.96 (2 H, s), 8.48 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.8, 13.9, 22.5, 22.6, 25.7, 25.8, 29.1, 29.3, 31.4, 31.6, 68.7, 69.6, 105.1, 107.6, 123.4, 124.5, 125.6, 127.1, 128.0, 129.3, 129.9, 131.1, 138.8, 149.7, 155.1; *m/z* (EI) 780.7 (M^+, 100); HRMS. Calcd for $C_{54}H_{68}O_4$: 780.5112. Found: 780.5117.

2,3,6,7-Tetrakis(hexyloxy)-10,11-bis(4-methoxyphenyl)triphenylene 16

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-methoxy-phenylboronic acid (0.29 g, 1.9 mmol), palladium (II) chloride (0.002 g, 0.012 mmol) triphenylphosphine (0.028 g, 0.11 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:1) to give the pure title compound (0.40 g, 75%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.86-0.95 (12 H, m), 1.34-1.40 (16 H, m), 1.52-1.62 (8 H, m), 1.88-1.97 (8 H, m), 3.83 (6 H, s), 4.20 (4 H, t, *J* 6.8 Hz), 4.26 (4 H, t, *J* 6.6 Hz), 6.86 (4 H, d, *J* 8.8 Hz), 7.24 (4 H, d, *J* 8.8 Hz), 7.86 (2 H, s), 8.01 (2 H, s), 8.42 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.1, 22.6, 22.7, 25.8, 25.9, 29.4, 29.5, 31.7, 55.4, 69.6, 69.8, 107.4, 113.7, 123.8, 124.6, 124.9, 128.2, 131.4, 134.7, 138.5, 149.4, 149.8, 158.7; *m/z* (EI) 840.7 (M^+, 50%); HRMS. Calcd for $C_{56}H_{72}O_6$: 840.5323. Found: 840.5318.

2,3,6,11-Tetrakis(hexyloxy)-7,10-bis(4-methoxyphenyl)triphenylene 17

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-methoxy-phenylboronic acid (0.29 g, 1.9 mmol), palladium (II) chloride (0.002 g, 0.012 mmol) triphenylphosphine (0.028 g, 0.11 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:1) to give the pure title compound (0.33 g, 62%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.87-0.96 (12 H, m), 1.34-1.62 (24 H, m), 1.82-1.85 (4 H, m), 1.95-1.99 (4 H, m), 3.88 (6 H, s), 4.19 (4 H, t, *J* 6.4 Hz), 4.28 (4 H, t, *J* 6.6 Hz), 6.99 (4 H, d, *J* 8.8 Hz), 7.64 (4 H, d, *J* 8.8 Hz), 7.87 (2 H, s), 7.95 (s, 2 H), 8.46 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.8, 13.9, 22.5, 22.6, 25.8, 29.2, 29.3, 31.4, 31.6, 55.2, 68.7, 69.6, 105.1, 107.6, 113.5, 123.4, 124.5, 125.3, 128.9, 130.6, 131.0, 131.2, 149.7, 155.1, 158.9; *m/z* (EI) 840.7 (M^+, 50%); HRMS. Calcd for $C_{56}H_{72}O_6$: 840.5323. Found: 840.5321.

2,3,6,7-Tetrakis(hexyloxy)-10,11-bis(4-ethylphenyl)triphenylene 18

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-ethyl-phenylboronic acid (0.28 g, 1.9 mmol), palladium (II) chloride (0.002 g, 0.012 mmol) triphenylphosphine (0.028 g, 0.11 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:1) to give the pure title compound (0.41 g, 77%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.89-0.95 (12 H, m), 1.24-1.59 (30 H, m), 1.88-1.97 (8 H, m), 2.68 (4 H, quartet, *J* 7.4 Hz), 4.17-4.27 (8 H, m), 7.14 (4 H, d, *J* 8.0 Hz), 7.24 (4 H, d, *J* 8.0 Hz), 7.86 (2 H, s), 8.02 (2 H, s), 8.45 (s, 2 H); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.0, 14.1, 15.5, 22.7, 22.8, 25.8, 25.9, 28.5, 29.4, 29.5, 31.7, 69.6, 69.8, 107.2, 107.4, 123.7, 124.6, 125.1, 127.7, 128.3, 130.3, 138.8, 139.5, 142.7, 149.4, 149.8; *m/z* (EI) 836.7 (M^+, 100%); HRMS. Calcd for $C_{58}H_{76}O_4$: 836.5738. Found: 836.5728.

2,3,6,11-Tetrakis(hexyloxy)-7,10-bis(4-ethylphenyl)triphenylene 19

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-ethylphenylboronic acid (0.28 g, 1.9 mmol), palladium (II) chloride (0.002 g, 0.012 mmol) triphenylphosphine (0.028 g, 0.11 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:1) to give the pure title compound (0.35 g, 66%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.85-0.97 (12 H, m), 1.21-1.61 (30 H, m), 1.83-1.87 (4 H, m), 1.94-1.99 (4 H, m), 2.74 (4 H, quartet, *J* 7.4 Hz), 4.20 (4 H, t, *J* 6.4 Hz), 4.28 (4 H, t, *J* 6.6 Hz), 7.30 (4 H, d, *J* 8.1 Hz), 7.63 (4 H, d, *J* 8.1 Hz), 7.88 (2 H, s), 7.96 (2 H, s), 8.50 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.8, 13.9, 15.5, 22.5, 22.6, 25.7, 28.6, 29.1, 29.3, 31.4, 31.6, 68.7, 69.6, 105.1, 107.6, 123.4, 124.5, 125.6, 127.5, 129.1, 129.8, 131.0, 136.1, 143.1, 149.7, 155.2; *m/z* (EI) 836.8 (M^+, 100%); HRMS. Calcd for $C_{58}H_{76}O_4$: 836.5738. Found: 836.5735.

2,3,6,7-Tetrakis(hexyloxy)-10,11-bis(4-benzaldehyde)triphenylene 20

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-benzaldehydeboronic acid (0.45 g, 3.0 mmol), palladium (II) chloride (0.007 g, 0.04 mmol) triphenylphosphine (0.04 g, 0.15 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene and water (3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:1) to give the pure title compound (0.20 g, 38%) as a yellow solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.84-0.97 (12 H, m), 1.33-1.63 (24 H, m), 1.91-2.00 (8 H, m), 4.22-4.30 (8 H, m), 7.49 (4 H, d, *J* 8.0 Hz), 7.83-7.88 (6 H, m), 8.02 (2 H, s), 8.50 (2 H, s), 10.04 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.8, 13.9, 22.5, 22.6, 25.7, 25.8, 29.3, 29.6, 31.5, 31.6, 69.6, 107.0, 107.3, 123.0, 124.9, 125.2, 128.9, 129.6, 130.8, 134.9, 137.0, 147.9, 149.5, 150.3, 192.0; *m/z* (ES) 859.5 ([M^++Na], 100%); HRMS. Calcd for $C_{56}H_{68}O_6Na$ [M^++Na]: 859.4908. Found: 859.4909.

2,3,6,11-Tetrakis(hexyloxy)-7,10-bis(4-benzadehyde)triphenylene 21

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-benzaldehydeboronic acid (0.45 g, 3.0 mmol), palladium (II) chloride (0.007 g, 0.04 mmol) triphenylphosphine (0.04 g, 0.15 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene and water (3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:1) to give the pure title compound (0.17 g, 32%) as a yellow solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.86-0.97 (12 H, m), 1.32-1.63 (24 H, m), 1.81-2.00 (8 H, m), 4.23 (4 H, t, *J* 6.6 Hz), 4.29 (4 H, t, *J* 6.5 Hz), 7.87-7.89 (6 H, m), 7.90-7.99 (6 H, m), 8.48 (2 H, s), 10.09 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.7, 13.8, 22.4, 22.5, 22.7, 29.0, 29.2, 29.5, 31.3, 31.6, 68.7, 69.6, 105.0, 107.6, 123.1, 124.4, 125.5, 129.4, 129.6, 130.1, 130.6, 135.0, 145.2, 150.1, 155.0, 192.2; *m/z* (ES) 837.5 ([M^++H], 100%); HRMS. Calcd for $C_{56}H_{69}O_6$ [M^++H]: 837.5089. Found: 837.5071.

10,11-Bis(4'-cyanophenyl)-2,3,6,7-tetrakis(hexyloxy)triphenylene 22

4-Cyanobenzeneboronic acid (0.24 g, 1.59 mmol), 2,3-dibromo-6,7,10,11-tetrakis(hexyloxy) triphenylene (0.50 g, 0.63 mmol), sodium carbonate (0.13 g, 1.27 mmol), palladium chloride (0.004 g, 0.02 mmol) and triphenylphosphine (0.01 g, 0.038 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (eluting with petroleum ether / dichloromethane, 1:1) and recrystallisation from propan-2-ol to give the pure title compound as a yellow solid (0.71 g, 75%).

Anal. Found: C, 80.94; H, 8.00; N, 3.24. $C_{56}H_{66}O_4N_2$ requires C, 80.93; H, 8.00; N, 3.37%; ν_{max}(Nujol)/cm^{-1} 2225 (CN); δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.92 (12 H, t, *J* 6.7 Hz), 1.33-1.59 (24 H, m), 1.88-2.01 (8 H, m), 4.20-4.29 (8 H, m), 7.40 (4 H, d, *J* 8.5 Hz), 7.63 (4 H, d, *J* 8.5 Hz), 7.86 (2 H, s), 7.98 (2 H, s), 8.44 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.1, 22.6, 22.7, 25.8, 25.9, 29.4, 31.7, 31.8, 69.7, 107.1, 107.4, 111.1, 118.9, 122.9, 125.1, 125.4, 129.3, 130.9, 132.3, 136.4, 146.3, 149.6, 150.6.

2,11-Bis(4'-cyanophenyl)-3,6,7,10-tetrakis(hexyloxy)triphenylene 23

4-Cyanobenzeneboronic acid (0.24 g, 1.59 mmol), 2,11-dibromo-3,6,7,10-tetrakis(hexyloxy)-triphenylene (0.50 g, 0.63 mmol), sodium carbonate (0.13 g, 1.27 mmol), palladium chloride (0.004 g, 0.02 mmol) and triphenylphosphine (0.01 g, 0.038 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 50 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (eluting with petroleum ether / dichloromethane, 1:1) and recrystallisation from propan-2-ol to give the pure title compound as a yellow solid (0.83 g, 79%).

Anal. Found: C, 80.47; H, 7.99; N, 3.11. $C_{56}H_{66}O_4N_2$ requires C, 80.93; H, 8.00; N, 3.37%; ν_{max}(Nujol)/cm^{-1} 2225 (CN); δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.89 (12 H, t, *J* 7.0 Hz), 1.25-1.64 (24 H, m), 1.80-2.01 (m, 8 H), 4.21-4.30 (8 H, m), 7.75 (4 H, d, *J* 8.8 Hz), 7.80 (4 H, d, *J* 8.8 Hz),7.89 (2 H, s), 7.94 (2 H, s), 8.40 (s, 2 H); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.0, 14.1, 22.6, 22.7, 25.9, 29.2, 29.4, 31.5, 31.7, 68.9, 69.8, 105.2, 107.7, 110.8, 119.3, 123.2, 124.6, 125.5, 129.1, 130.5, 130.7, 131.9, 143.7, 150.4, 155.1;

2,3-Bis(4-pyridyl)-6,7,10,11-tetrakis(hexyloxy)triphenylene 24

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-pyridineboronic acid (0.31 g, 2.5 mmol), palladium (II) chloride (0.009 g, 0.05 mmol) triphenylphosphine (0.06 g, 0.23 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum

ether, 3:7 changing to ethyl acetate / petroleum ether, 1:4) to give the pure title compound (0.21 g, 42%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.90-0.97 (12 H, m), 1.35-1.44 (16 H, m), 1.54-1.64 (8 H, m), 1.90-2.00 (8 H, m), 4.23 (4 H, t, *J* 6.8 Hz), 4.27 (4 H, t, *J* 6.6 Hz), 7.24 (4 H, d, *J* 4.6 Hz), 7.86 (2 H, s), 7.99 (s, 2 H), 8.46 (2 H, s), 8.58 (4 H, d, *J* 4.6 Hz); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.5, 13.6, 22.1, 22.2, 25.3, 25.4, 28.8, 31.1, 69.2, 106.5, 106.7, 122.4, 124.6, 124.8, 128.8, 134.9, 148.7, 149.1, 149.5, 150.0; *m/z* (EI) 782.6 (M^+, 60%); HRMS. Calcd for $C_{52}H_{66}N_2O_4$: 782.5017. Found: 782.5017.

2,3-Bis(3-pyridyl)-6,7,10,11-tetrakis(hexyloxy)triphenylene 25

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 3-pyridineboronic acid (0.31 g, 2.5 mmol), palladium (II) chloride (0.009 g, 0.05 mmol) triphenylphosphine (0.06 g, 0.23 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 3:7 changing to ethyl acetate / petroleum ether, 1:4) to give the pure title compound (0.31 g, 62%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.90-0.96 (m, 12 H), 1.38-1.60 (24 H, m), 1.91-2.00 (8 H, m), 4.23 (4 H, t, *J* 6.6 Hz), 4.27 (4 H, t, *J* 6.4 Hz), 7.23-7.27 (2 H, m), 7.52 (2 H, d, *J* 7.7 Hz), 7.87 (2 H, s), 8.00 (2 H, s), 8.49 (2 H, s), 8.57 (2 H, d, *J* 4.7 Hz), 8.70 (2 H, d, *J* 2.0 Hz); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.0, 14.1, 22.6, 22.7, 25.8, 25.9, 29.4, 31.7, 31.8, 69.6, 69.7, 107.1, 107.2, 123.1, 123.2, 124.9, 125.5, 129.1, 134.8, 137.2, 137.8, 148.4, 149.6,

150.3, 150.8; *m/z* (EI) 782.7 (M^+, 100%); HRMS. Calcd for $C_{52}H_{66}N_2O_4$: 782.5017. Found: 782.5013.

3,6-Bis(4-pyridyl)-2,7,10,11-tetrakis(hexyloxy)triphenylene 26

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), 4-pyridineboronic acid (0.31 g, 2.5 mmol), palladium (II) chloride (0.009 g, 0.05 mmol) triphenylphosphine (0.06 g, 0.23 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with ethyl acetate / petroleum ether, 1:1, changing to ethyl acetate) to give the pure title compound (0.38 g, 76%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.89-0.96 (12 H, m), 1.33-1.64 (24 H, m), 1.81-1.88 (4 H, m), 1.93-1.99 (4 H, m), 4.21 (4 H, t, *J* 6.3 Hz), 4.27 (4 H, t, *J* 6.6 Hz), 7.64 (4 H, d, *J* 4.0 Hz), 7.86 (2 H, s), 7.91 (2 H, s), 8.45 (2 H, s), 8.70 (4 H, d, *J* 4.0 Hz); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.0, 14.1, 22.6, 22.7, 25.9, 29.2, 29.4, 31.6, 31.7, 68.8, 69.7, 105.0, 107.6, 123.1, 124.5, 124.8, 125.3, 128.1, 130.6, 146.6, 149.7, 150.3, 155.1; *m/z* (EI) 782.3 (M^+, 100%); HRMS. Calcd for $C_{52}H_{66}N_2O_4$: 782.5017. Found: 782.5024.

2,3-Bis(thiophene-2-)-6,7,10,11-tetrakis(hexyloxy)triphenylene 27

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), thiophene-2-boronic acid (0.24 g, 1.9 mmol), palladium (II) chloride (0.007 g, 0.04 mmol) triphenylphosphine (0.04 g, 0.16 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with

dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 3:7) to give the pure title compound (0.33 g, 66%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.91-0.96 (12 H, m), 1.39-1.61 (24 H, m), 1.90-1.97 (8 H, m), 4.20-4.27 (m, 8 H), 7.04-7.07 (4 H, m), 7.35 (2 H, d, *J* 4.5 Hz), 7.84 (2 H, s), 7.98 (2 H, s), 8.54 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.0, 22.7, 25.8, 25.9, 29.4, 29.5, 31.7, 69.6, 69.7, 107.2, 123.3, 124.8, 125.7, 126.3, 127.3, 127.6, 128.6, 131.7, 143.4, 149.4, 150.1; *m/z* (EI) 792.5 (M^+, 100%); HRMS. Calcd for $C_{50}H_{64}O_4S_2$: 792.4241. Found: 792.4240.

2,3-Bis(thiophene-3-)-6,7,10,11-tetrakis(hexyloxy)triphenylene 28

2,3-Dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), thiophene-3-boronic acid (0.24 g, 1.9 mmol), palladium (II) chloride (0.007 g, 0.04 mmol) triphenylphosphine (0.04 g, 0.16 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 25 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 3:7) to give the pure title compound (0.25 g, 50%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.90-0.95 (12 H, m), 1.39-1.59 (24 H, m), 1.91-1.97 (8 H, m), 4.20-4.27 (8 H, m), 6.95 (2 H, d, *J* 4.8 Hz), 7.25-7.28 (4 H, m), 7.85 (2 H, s), 8.00 (2 H, s), 8.49 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.0, 22.7, 25.9, 29.4, 31.7, 69.6, 69.7, 107.3, 123.3, 123.5, 124.6, 125.0, 128.4, 129.5, 133.6, 142.7, 149.4, 149.9; *m/z* (EI) 793.4 (M^+, 100%); HRMS. Calcd for $C_{50}H_{64}O_4S_2$: 792.4241. Found: 792.4243.

3,6-Bis(thiophene-2-)-2,7,10,11-tetrakis(hexyloxy)triphenylene 29

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), thiophene-2-boronic acid (0.24 g, 1.9 mmol), palladium (II) chloride (0.007 g, 0.04 mmol) triphenylphosphine (0.04 g, 0.16 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:4) to give the pure title compound (0.29 g, 58%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.93-0.96 (12 H, m), 1.37-1.65 (24 H, m), 1.92-2.03 (8 H, m), 4.25 (4 H, t, *J* 6.6 Hz), 4.29 (4 H, t, *J* 6.3 Hz), 7.18 (2 H, dd, *J* 5.1, 3.7 Hz), 7.42 (2 H, d, *J* 5.1 Hz), 7.72 (2 H, d, *J* 3.7 Hz), 7.86 (2 H, s), 7.92 (2 H, s), 8.77 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.1, 22.6, 22.7, 25.9, 26.1, 29.4, 29.5, 31.7, 31.8, 69.0, 69.7, 104.6, 107.7, 123.1, 123.3, 124.5, 125.8, 127.0, 129.2, 140.1, 149.9, 154.3; *m/z* (EI) 792.5 (M^+, 100%); HRMS. Calcd for $C_{50}H_{64}O_4S_2$: 792.4241. Found: 792.4243.

3,6-Bis(thiophene-3-)-2,7,10,11-tetrakis(hexyloxy)triphenylene 30

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), thiophene-3-boronic acid (0.24 g, 1.9 mmol), palladium (II) chloride (0.007 g, 0.04 mmol) triphenylphosphine (0.04 g, 0.16 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 1:4) to give the pure title compound (0.23 g, 46%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.90-0.96 (12 H, m), 1.36-1.60 (24 H, m), 1.88-1.98 (8 H, m), 4.22-4.29 (8 H, m), 7.42 (2 H, dd, *J* 5.1, 4.2 Hz), 7.63 (2 H, d, *J* 5.1 Hz), 7.78 (2 H, d, *J* 4.2 Hz), 7.85 (2 H, s), 7.91 (2 H, s), 8.64 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.0, 14.1, 22.6, 22.7, 25.9, 26.0, 29.4, 29.5, 31.6, 31.7, 68.8, 69.7, 104.9, 107.7, 123.3, 123.7, 124.4, 124.5, 124.6, 125.3, 129.1, 138.8, 149.9, 155.2; *m/z* (EI) 793.6 (M^+, 100%); HRMS. Calcd for $C_{50}H_{64}O_4S_2$: 792.4241. Found: 792.4250.

2,3-Bis(furan-2-)-6,7,10,11-tetrakis(hexyloxy)triphenylene 31

2,3-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), furan-2-boronic acid (0.28 g, 2.5 mmol), palladium (II) chloride (0.009 g, 0.05 mmol) triphenylphosphine (0.06 g, 0.23 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 3:7) to give the pure title compound (0.16 g, 33%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.92-0.95 (12 H, m), 1.36-1.60 (24 H, m), 1.91-1.97 (8 H, m), 4.23-4.27 (8 H, m), 6.16 (2 H, d, *J* 3.3 Hz), 6.52 (d, 2 H, *J* 3.4 Hz), 7.57 (2 H, s), 7.83 (2 H, s), 8.01 (2 H, s), 8.68 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.9, 22.5, 25.7, 29.3, 31.6, 69.5, 69.7, 107.0, 107.3, 108.5, 111.6, 123.3, 123.6, 124.6, 126.7, 128.5, 141.9, 149.3, 150.0, 153.5; *m/z* (ES) 783.5 ([M^++Na], 100%); HRMS. Calcd for $C_{50}H_{64}O_6Na$ [M^++Na]: 783.4595. Found: 783.4593.

2,3-Bis(furan-3-)-6,7,10,11-tetrakis(hexyloxy)triphenylene 32

2,3-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), furan-3-boronic acid (0.28 g, 2.5 mmol), palladium (II) chloride (0.009 g, 0.05 mmol) triphenylphosphine (0.06 g, 0.23 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 3:7) to give the pure title compound (0.23 g, 48%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.85-0.96 (12 H, m), 1.25-1.58 (24 H, m), 1.92-1.98 (8 H, m), 4.21-4.27 (m, 8 H), 6.47 (2 H, s), 7.47 (s, 2 H), 7.54 (2 H, s), 7.84 (2 H, s), 7.98 (2 H, s), 8.42 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 13.0, 21.6, 24.8, 28.4, 28.7 30.7, 68.5, 68.7, 106.2, 111.1, 122.4, 123.4, 123.6, 125.3, 127.3, 128.6, 139.5, 141.7, 148.3, 148.9; *m/z* (ES) 783.4 ([M^++Na], 100%); HRMS. Calcd for $C_{50}H_{64}O_6Na$ [M^++Na]: 783.4595. Found: 783.4580.

3,6-Bis(furan-2-)-2,7,10,11-tetrakis(hexyloxy)triphenylene 33

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), furan-2-boronic acid (0.28 g, 2.5 mmol), palladium (II) chloride (0.009 g, 0.05 mmol) triphenylphosphine (0.06 g, 0.23 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 3:7) to give the pure title compound (0.11 g, 23%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.92-0.97 (12 H, m), 1.40-1.66 (24 H, m), 1.91-2.06 (8 H, m), 4.23-4.34 (8 H, m), 6.58 (2 H, d, *J* 3.3 Hz), 7.13 (2 H, d, *J* 3.3 Hz), 7.64 (2 H, s), 7.80 (2 H, s), 7.87 (s, 2 H), 9.12 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.1, 22.7, 22.8, 25.9, 26.1, 29.5, 31.8, 68.4, 69.6, 103.9, 107.4, 110.4, 112.0, 119.4, 120.5, 123.1, 124.5, 128.6, 141.4, 149.6, 151.0, 153.8; *m/z* (ES) 783.4 ([M^++Na], 100%); HRMS. Calcd for $C_{50}H_{64}O_6Na$ [M^++Na]: 783.4595. Found: 783.4593.

3,6-Bis(furan-3-)-2,7,10,11-tetrakis(hexyloxy)triphenylene 34

3,6-Dibromo-2,7,10,11-tetrakis(hexyloxy)triphenylene (0.50 g, 0.63 mmol), furan-3-boronic acid (0.28 g, 2.5 mmol), palladium (II) chloride (0.009 g, 0.05 mmol) triphenylphosphine (0.06 g, 0.23 mmol) and sodium carbonate (0.20 g, 1.8 mmol) were stirred in a refluxing mixture of toluene, ethanol and water (3:3:1 respectively, 30 mL) under nitrogen for 24 h. The mixture was cooled down, water added and the mixture extracted with dichloromethane (3×100 mL). The solvent was removed *in vacuo* to leave a dark-brown solid which was purified by column chromatography (eluting with dichloromethane / petroleum ether, 3:7) to give the pure title compound (0.20 g, 41%) as a white solid.

δ_H (400 MHz, $CDCl_3$, 25 °C, TMS) 0.93-0.97 (12 H, m), 1.37-1.63 (24 H, m), 1.91-2.00 (8 H, m), 4.20-4.24 (8 H, m), 7.02 (2 H, d, *J* 3.3 Hz), 7.56 (2 H, d, *J* 3.3 Hz), 7.69 (2 H, s), 7.79 (2 H, s), 8.16 (2 H, s), 8.53 (2 H, s); δ_C (75.45 MHz, $CDCl_3$, 25 °C, TMS) 14.1, 22.7, 22.8, 25.9, 26.1, 29.5, 31.8, 68.4, 69.6, 103.9, 107.4, 110.4, 112.0, 119.4, 120.5, 123.1, 124.5, 128.6, 141.4, 149.6, 151.0, 153.8; *m/z* (ES) 783.4 ([M^++Na], 100%); HRMS. Calcd for $C_{50}H_{64}O_6Na$ [M^++Na]: 783.4595. Found: 783.4593.

Crystal structure analysis of 2,11-bis(C_6H_4CN-4)-3,6,7,10-tetrakis(O-n-C_6H_{13})-triphenylene

Crystal data: $C_{56}H_{66}N_2O_4$, *ca* 0.7(H_2O), M = 843.7. Triclinic, space group P-1 (no. 2), a = 11.215(1), b = 12.998(2), c = 17.424(4) Å, α = 77.29(3), β = 80.52(1), γ = 80.53(1) °, V = 2422.0(7) $Å^3$. Z = 2, Dc = 1.157 g cm^{-3}, F(000) = 910, T = 140(1) K, μ(Mo-Kα) = 0.7 cm^{-1}, λ(Mo-Kα) = 0.71069 Å.

Crystals are very pale yellow plates. From a sample under oil, one, *ca* 0.7 x 0.45 x 0.10 mm, was mounted on a glass fibre and fixed in the cold nitrogen stream on a Rigaku R-Axis IIc image plate diffractometer equipped with a rotating anode X-ray source (Mo-Kα radiation) and graphite monochromator. Using 4° oscillations, 48 exposures of 56 min. each were made. Total no. of reflections recorded, to θ_{max} = 25.4°, was 13816 of which 8194 were unique (Rint = 0.063); 5686 were 'observed' with $I > 2\sigma_I$.

Data were processed using the DENZO/SCALEPACK (A) programs. The structure was determined by the direct methods routines in the SHELXS program (B1) and refined by full-matrix least-squares methods, on F^2's, in SHELXL (B2). There is disorder in two of the hexyl chains; alternative sites were identified for several carbon atoms and these partially occupied atoms were refined freely. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their Uiso values were set to ride on the Ueq values of the parent carbon atoms. Two partially occupied water sites were also identified and the oxygen atoms of these molecules were refined isotropically; no hydrogen atoms were included here. At the conclusion of the refinement, wR_2 = 0.165 and R_1 = 0.082 (B2) for all 8194 reflections weighted $w = [\sigma^2(F_o^2) + (0.0989P)^2]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; for the 'observed' data only, R_1 = 0.058.

In the final difference map, the highest peaks (to *ca* 0.47 $eÅ^{-3}$) were close to the water molecules.

Scattering factors for neutral atoms were taken from reference (C). Computer programs used in this analysis have been noted above or in Table 4 of reference (D), and were run on a Silicon Graphics Indy at the University of East Anglia, or a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

References

(A) Z. Otwinowski and W, Minor, 'Processing of X-ray diffraction data collected in oscillation mode', Methods in Enzymology, Vol. 276; Macromolecular Crystallography, Part A, p. 307-326; Eds C. W. Carter, Jr and R. M. Sweet, Academic Press (1997).

(B) G. M. Sheldrick, SHELX-97 - Programs for crystal structure determination (SHELXS) and refinement (SHELXL), University of Göttingen, Germany (1997).

(C) *`International Tables for X-ray Crystallography'*, Kluwer Academic Publishers, Dordrecht (1992). Vol. C, pp. 500, 219 and 193.

(D) S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans*., (1986) 245.

Notes on the structure

The triphenylene ring system is essentially planar and the side chains lie close to this plane. There is rotation of the substituent phenyl rings about the C(12)-C(13) and C(62)-C(63) bonds of *ca* 38.2 and 42.7°. In the O-hexyl chains:

the torsion angles about C(22)-O(23) are *ca* 0°, then the chain is all-*trans*;

the torsion angles about C(32)-O(33) are *ca* 4°; the arrangement about C(34)-C(35) is *cis*;

the torsion angles about C(42)-O(43) are *ca* 10°, and *cis* about C(44)-C(45);

the torsion angles about C(52)-O(53) are *ca* 1.5°. One of the disordered chains has an all-*trans* arrangement; the other has *cis* conformations about C(54a)-C(55a) and C(56a)-C(57a); C(59) is common to both chains.

The molecules are all parallel and are stacked, about centres of symmetry, in 'slipping' columns, *i.e.* there is a progressive offset between the centres of the triphenylene systems in the columns. Each molecule has an inverted neighbour on each side; on one side, the perpendicular distance between the centre rings is 3.465(3) Å, on the other 3.538(3) Å

In the triphenylene ring system, with approximately *3m* symmetry, there are patterns of bond dimensions, *e.g.*

the three bonds as C(1)-C(2) have a mean value of 1.410(3) Å,

the three bonds as C(1)-C(6) . . . 1.462(3) Å,

the six bonds as C(1)-C(11) . . . 1.415(2) Å,

the six bonds as C(11)-C(12) . . . 1.378(2) Å,

the three bonds as C(12)-C(22) . . 1.416(3) Å,

the six angles as C(2)-C(1)-C(11) have a mean value of 118.4(2) °,

. . . C(6)-C(1)-C(11) . . . . 121.6(4) °,

. . . C(1)-C(11)-C(12) . . . . 122.4(4) °,

the two angles C(11)-C(12)-C(22) and C(61)-C(62)-C(52) have a mean value of 117.22(7)°, and the four angles as C(21)-C(22)-C(12) . . 120.1(4) °.

There are two partially occupied sites of the oxygen atoms of water molecules in the structure; the hydrogen atoms have not been located. These atoms might be hydrogen bonded together, with an O...O distance of 2.64(2) Å, but they do not appear to be connected to the principal molecule.