Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information

The interplay between spatial and heliconical orientational order in twist-bend nematic materials

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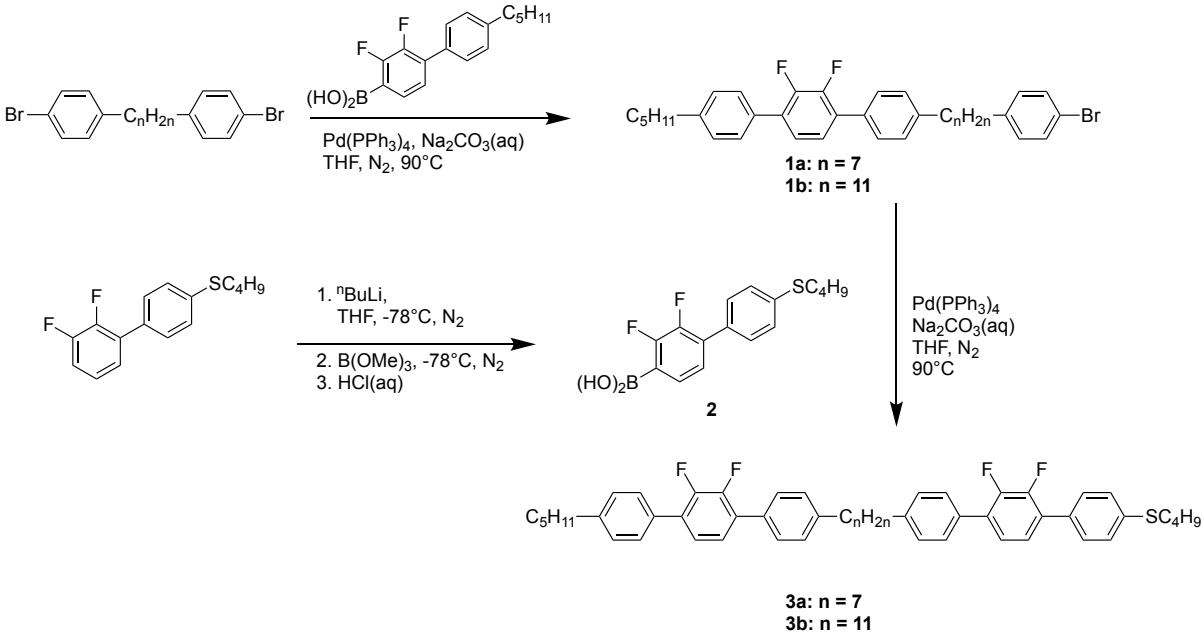
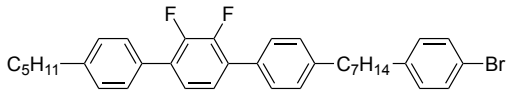
Scheme



Synthesis

4-(7-(4-bromophenyl)heptyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl, 1a



(2,3-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)boronic acid (0.64 g, 2.1 mmol) and 1,7-bis(4-bromophenyl)heptane (3.57 g, 8.7 mmol) were dissolved in 1,2-dimethoxyethane (40 mL) and a solution of aqueous sodium carbonate (2 mol.dm^{-3}, 10 mL) added. Dry nitrogen gas was bubbled through the resulting solution for 30 mins., $Pd(PPh_3)_4$ (74 mg, 0.06 mmol, 3 mol%) added in one portion and the reaction subsequently heated to 80°C for 16 hours under reflux conditions. After cooling to ambient temperature, water (100 mL) was added and the mixture extracted with diethyl ether (3 x 75 mL). The combined organic extracts were washed with water (2 x 100 mL) and dried over anhydrous $MgSO_4$ (s). After removal of the dessicant by filtration, the organics were concentrated *in vacuo* and the product isolated by column chromatography (Silica gel, eluent: Hexane / CH_2Cl_2, 97:3). Hot recrystallisation from a mixture of ethanol/ethyl acetate gave **1a** as white crystals. Yield 0.89g, 72%

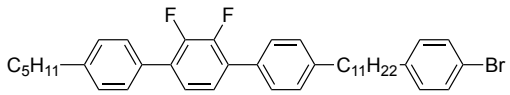
δ_H(400MHz; CD_2Cl_2) 7.53 (d, ^{3}J(H-H) = 7.8 Hz, 4H), 7.41 (d, ^{3}J(H-H) = 7.3 Hz, 2H), 7.36-7.25 (m, 6H), 7.09 (d, ^{3}J(H-H) = 7.8 Hz, 2H), 2.73-2.64 (m, 4H), 2.58 (t, ^{3}J(H-H) = 7.8 Hz, 2H), 1.75-1.51 (m, 6H), 1.45-1.28 (m, 10H), 0.94 (t, ^{3}J(H-H) = 6.4 Hz, 3H)

δ_C(100MHz; CD_2Cl_2) 148.90 (dd, ^{1}J(C-F) = 249.5 Hz, ^{2}J(C-F) = 15.4 Hz), 143.69 (d, ^{3}J(C-F) = 9.6 Hz), 142.48 (s), 132.29 (s), 131.58 (br s), 130.66 (s), 129.90 (br s), 129.14 (s), 129.10 (s), 125.09 (s), 119.52 (s), 36.05 (s),

δ_F(376MHz; CD_2Cl_2) -144.14 (s, 2F)

MS (APCI) *m/z* 588.2 $(M)^+$
HRMS : calculated for $C_{36}H_{39}BrF_2$: 588.2198, found 588.2186

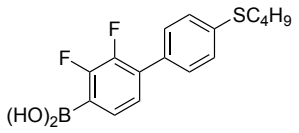
4-(11-(4-bromophenyl)undecyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl, 1b



1,11-bis(4-bromophenyl)undecane (3.60 g, 7.7 mmol) was dissolved in freshly distilled anhydrous THF and Na_2CO_3(aq) (0.41g in 15mL water) added followed by $Pd(PPh_3)_4$ (0.15 g, 0.05 mmol, 5 mol %). After heating to 50°C, dry nitrogen gas was bubbled through the reaction mixture for 30 minutes and then (2,3-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)boronic acid (0.79 g, 2.6 mmol) was added and the reaction heated to 90°C under reflux conditions for 24 hours. After cooling to ambient temperature, dichloromethane (100 mL) and water (100 mL) were added and the organics were separated and dried over anhydrous $MgSO_4$(s). Following filtration of the dessicant, solvents were removed under reduced pressure and the product **1b** isolated by silica gel column chromatography, eluent: (Hexane/DCM 95:5). Yield of white solid 1.02 g, 61 %

δ_H(400MHz; CD_2Cl_2) 7.51 (d, ^3J (H-H) = 8.2 Hz, 4H), 7.38 (d, ^3J (H-H) = 8.2 Hz, 2H), 7.34 - 7.25 (m, 6H), 7.07 (d, ^3J (H-H) = 8.2 Hz, 2H), 2.66 (t, ^3J (H-H) = 7.8 Hz, 4H), 2.55 (t, ^3J (H-H) = 7.8 Hz, 2H), 1.71 - 1.52 (m, 6H), 1.39 - 1.23 (m, 18H), 0.91 (t, ^3J (H-H) = 6.9 Hz, 3H)

(4'-(butylthio)-2,3-difluoro-[1,1'-biphenyl]-4-yl)boronic acid, 2



Butyl(2',3'-difluoro-[1,1'-biphenyl]-4-yl)sulfane (1.05 g, 3.8 mmol) was dissolved in freshly distilled anhydrous THF (40 mL) and the solution cooled to -78°C under an N_2 atmosphere. ^{n}BuLi (1.7 mL, 4.2 mmol, 1.1 equiv.) was added dropwise and the reaction stirred for one hour at -78°C before trimethyl borate (1.3 mL, 11.3 mmol, 3 equiv.) was added and the reaction stirred overnight, slowly rising to ambient temperature. The reaction mixture was acidified by addition of 10% HCl (40 mL) and stirred for one hour. DCM (100 mL) was added, the organic layer separated and solvents were removed *in vacuo*. The residue was dissolved in a minimum volume of DCM (~ 80 mL) and hexane was added until crystallisation was induced. The white crystals were filtered off and washed with hexane. A second crop was collected in the same fashion.

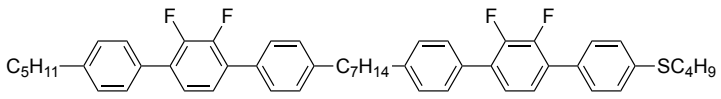
Yield : 879 mg (72.3 %)

δ_H(400MHz; CD_2Cl_2) 7.62 - 7.55 (m, 1H), 7.50 (d, ^3J (H-H) = 8.0 Hz, 2H), 7.39 (d, ^3J (H-H) = 7.8 Hz, 2H), 7.30 - 7.24 (m, 1H), 5.11 – 5.06 (m, 2H), 2.99 (t, ^3J (H-H) = 7.3 Hz, 2H), 1.73 - 1.63 (m, 2H), 1.53-1.44 (m, 2H), 0.94 (t, ^3J (H-H) = 6.9 Hz, 3H)

δ_C(100MHz; $(CD_3)_2CO$ 155.40 (dd, ^1J(C-F) = 246.6 Hz, ^2J(C-F) = 12.5 Hz), 148.36 (dd, ^1J(C-F) = 247.6 Hz, ^2J(C-F) = 15.4 Hz), 139.10(s), 132.84 (d, ^3J(C-F) = 9.6 Hz), 132.32 (br s), 131.30 – 131.00 (m), 130.17 (d, ^4J(C-F) = 2.9 Hz), 128.71 (s), 125.54 (br s), 32.72 (s), 31.90 (s), 22.54 (s), 13.90 (s)

δ_F(376MHz; CD_2Cl_2) -135.61 (d, ^3J(F-F) = 20.2 Hz, 1F), -145.72 (d, ^3J(F-F) = 20.2 Hz, 1F)

Butyl(4''-(7-(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)heptyl)-2',3'-difluoro-[1,1':4',1''-terphenyl]-4-yl)sulfane, 3a



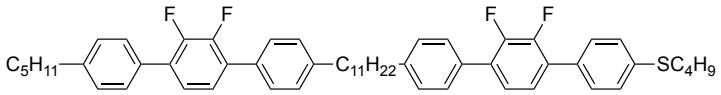
1a (105 mg, 0.18 mmol) and **2** (173 mg, 0.53 mmol) were dissolved in THF (40 mL) and Na_2CO_3(aq) (2M, 10 mL) added. Dry nitrogen was bubbled through the resulting mixture for 15 mins, after which time $Pd(PPH_3)_4$ (10 mg, 0.01 mmol, 6 mol %) was added and the reaction heated to 90°C for 16 hours, under a dry nitrogen atmosphere. After cooling to ambient temperature, water was added (100mL) and the organics extracted into dichloromethane (100 mL x 3). These were combined, washed with water (100 mL) and brine (100 mL). Solvents were removed under reduced pressure and the product isolated by column (silica gel, Hexane/DCM 9:1). Yield (white solid): 101 mg, 71 %

δ_H(400MHz; CD_2Cl_2) 7.55 – 7.47 (m, 8H), 7.43 - 7.37 (m, 2H), 7.34 - 7.24 (m, 10H), 2.99 (t, ^{3}J (H-H) = 7.3 Hz, 2H), 2.71 – 2.63 (m, 6H), 1.73 - 1.62 (m, 8H), 1.52 - 1.34 (m, 12H), 0.96 – 0.88 (m, 6H)

δ_C(100MHz; CD_2Cl_2) 148.82 (dd, ^{1}J(C-F) = 249.5 Hz, ^{2}J(C-F) = 15.4 Hz), 143.76 (s), 143.68 (s), 138.34 (s), 132.24 (br s), 132.05 (d, ^{2}J(C-F) = 25.1 Hz), 130.20 – 129.80 (m), 129.53 (s), 129.07 (s), 129.04 (s), 128.43 (s), 125.30 – 124.80 (m), 35.99 (s), 33.00 (s), 31.95 (s), 31.79(s), 31.54 (s), 29.67 (s), 29.57 (s), 22.96 (s), 22.40 (s), 14.22 (s), 13.82 (s)

δ_F(376MHz; CD_2Cl_2) -143.97 (s, 2F), -144.18 (s, 2F)

butyl(4''-(11-(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)undecyl)-2',3'-difluoro-[1,1':4',1''-terphenyl]-4-yl)sulfane, 3b



1b (105 mg, 0.16 mmol) and **2** (157 mg, 0.49 mmol) were dissolved in THF (40 mL) and Na_2CO_3(aq) (2M, 10 mL) added. Dry nitrogen was bubbled through the resulting mixture for 20 mins, and subsequently $Pd(PPH_3)_4$ (10 mg, 0.01 mmol, 6 mol %) was added and the reaction heated to 90°C for 15 hours, under a dry nitrogen atmosphere. After cooling to ambient temperature, water (100mL) and dichloromethane (200 mL) were added and the organics separated and washed with water (100 mL) followed by brine (100 mL). The solvents were removed under reduced pressure and the product isolated by column (silica gel, Hexane/DCM 9:1). Yield (white solid): 92 mg, 68 %

δ_H(400MHz; CD_2Cl_2) 7.55 – 7.47 (m, 8H), 7.40 (d, ^{3}J (H-H) = 8.5 Hz, 2H), 7.34 - 7.25 (m, 10H), 2.99 (t, ^{3}J (H-H) = 7.3 Hz, 2H), 2.67 (t, ^{3}J (H-H) = 7.6 Hz, 6H), 1.72 - 1.61 (m, 8H), 1.52 - 1.25 (m, 20H), 0.98 – 0.88 (m, 6H)

δ_C(100MHz; CD_2Cl_2) 148.82 (dd, ^{1}J(C-F) = 249.5 Hz, ^{2}J(C-F) = 15.4 Hz), 143.82 (s), 143.75 (s), 138.34 (s), 132.24 (s), 132.04 (d, ^{2}J(C-F) = 23.1 Hz), 130.20 – 129.72 (m), 129.53 (s), 129.07 (s), 129.04 (s), 128.43 (s), 125.25 – 124.80 (m), 36.02 (s), 32.99 (s), 31.95 (s), 31.88 (s), 31.57 (s), 31.54 (s), 30.01 (s), 29.96 (s), 29.88 (s), 29.84 (s), 29.73 (s), 29.70 (s), 22.96 (s), 22.40 (s), 14.22 (s), 13.82 (s)

δ_F(376MHz; CD_2Cl_2) -144.00 (s, 2F), -144.21 (s, 2F)