- Supporting Information -

Frustration in a Non-chiral Ordered Fluid

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A real time video clip of the development of filaments at the transition from the nematic phase for compound **1** is available under the URL: http://www-users.york.ac.uk/~vg501 (follow the link to the avi video file "Verena Gortz filamentary growth")

Experimental Procedures

1. General Methods, Instrumentation and Characterisation

A Zeiss Axioskop 40 Pol transmission and epiluminescence polarising microscope (or an Olympus BH2 polarising microscope) equipped with a colour digital camera, a Mettler FP82 hot stage, and a Mettler Toledo FP90 central processor was used to observe thermal transitions and defect textures of the liquid crystalline phases using the transmission mode of the microscope. For the microscopy studies thin preparations of samples sandwiched between untreated glass slides and cover slips and preparations of samples in commercial Linkam 5 µm antiparallel buffed polyimide alignment cells were used.

A Mettler DSC 822^e differential scanning calorimeter calibrated against pure indium metal was used for determining the phase transition temperatures and enthalpy values. The heating and cooling rates were 10 °C min^{-1} for the determination of transition temperatures as reported in Figure 1, and 0.5 °C min^{-1} for experiments with slow rate as shown in Figure 2 (d) and Figure 4 (b). The transition temperatures reported in Figure 1 are the onset temperature values of transitions observed in the cooling cycles.

The x-ray scattering experiments were carried out on station 2.1 at the SRS, Daresbury Laboratory. X-rays of wavelength 1.54 Å were incident on samples, held in a hot stage, and constrained between 15 µm glass slides, coated with rubbed polyimide for alignment. The scattered x-rays were detected using an area detector, at 0.5 °C intervals across the liquid crystal phase range. The sandwiched cells used in the X-ray studies were made from glass substrates spin-coated with high temperature Liquicoat© Polyimide ZLI-2650; purchased from Merck and quoted to induce ~3° of pretilt. Photomicrographs were taken with direct reference to the X-ray diffraction studies, as shown in Figure 5 (a) to (d).

The calculated molecular length of compound **2** was obtained from the minimised structure using PC Spartan Pro 1.08^{TM}.

The structures of the compounds prepared were confirmed by spectroscopic methods. ^{1}H NMR spectra were recorded on a JEOL ECX400 spectrometer using the signal of the deuterated solvent as lock and internal standard for chemical shift data in the δ-scale relative to TMS. Coupling constants are given in Hz.

Atmospheric Pressure Ionisation mass spectrometry was performed on a Thermo Quest LCQ instrument from Finnigan.

For the HPLC purity analysis of final compounds a Shimadzu Prominence HPLC instrument with a Prevail silica 5µm column of a length of 150 mm and an internal diameter of 4.6 mm was used. Samples were eluted with solvent gradient 100 % chloroform to 95 % chloroform / 5 % isopropanol in 15 min; to 90 % chloroform / 10 % isopropanol after 17 min, and the percent purity was determined from the UV detector signals (254 nm and 270 nm).

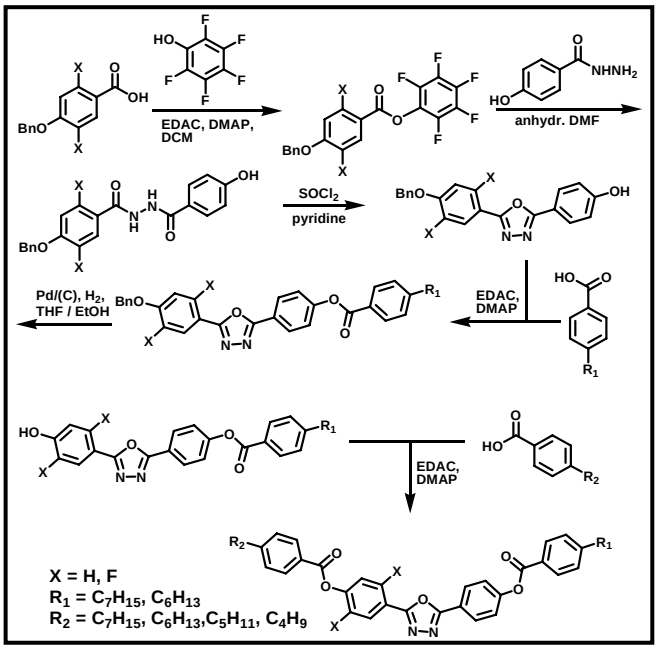
2. Synthetic Procedures

2.1. Reagents and Purification

The syntheses of the intermediates 4-benzyloxybenzoic acid pentafluorophenyl ester, 4-hydroxybenzoic acid N`-(4-benzyloxybenzoyl)-hydrazide, 5-(4-ben-zyloxyphenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole, 5-(4-benzyloxyphenyl)-2-[4-(4-heptylbenzoyl)-phe-nyl]-1,3,4-oxadiazole, 5-[4-(4-heptylbenzoyl)-phenyl] -2-(4-hydroxyphenyl)-1,3,4-oxadiazole, and the final compounds 2-[4-(4-heptylbenzoyl)-phenyl]-5-[4-(4-pentylbenzoyl)-phenyl]-1,3,4-oxadiazole (compound **1**) and 2,5-*bis*[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (compound **2**) have already been described elsewhere.[7]

The reagents 4-benzyloxybenzoic acid, 4-benzyloxy-2-fluorobenzoic acid, and 4-benzyloxy-2,5-difluorobenzoic acid were available in the group. All other starting materials and solvents are commercially available, and were used as received.

Column chromatographic purification was carried out using silica gel (Fluka 220-440 mesh, 35-70Å) and analytical TLC was performed on aluminium sheets precoated with silica gel (60 F-254 from Merck) and visualized with UV light.



2.2. Syntheses of precursors.

4-Benzyloxy-2-fluorobenzoic acid pentafluorophenyl ester. A solution of 4-benzyloxy-2-fluorobenzoic acid (5.00 g, 20.3 mmol), pentafluorophenol (3.74 g, 20.3 mmol), N-ethyl-N`-dimethylaminopropyl-carbodiimide hydrochloride (EDAC) (3.89 g, 20.3 mmol), and 4-dimethylaminopyridin (DMAP) (0.50 g, 20 mol %) in dichloromethane (100 mL) was stirred at room temperature for 24 h. After evaporation of the solvent the residue was purified by column chromatography on silica (dichloromethane : hexane, 4:1). Yield: 7.25 g (87 %) colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.05 (t, 1H, *J* 8.5), 7.41-7.33 (m, 5H), 6.87 (dd, 1H, *J* 8.8, 2.2), 6.78 (dd, 1H, *J* 12.5, 2.2), 5.14 (s, 2H).

4-Benzyloxy-2,5-difluorobenzoic acid pentafluorophenyl ester. A solution of 4-benzyloxy-2,5-difluorobenzoic acid (5.00 g, 18.9 mmol), pentafluorophenol (3.48 g, 18.9 mmol), N-ethyl-N`-dimethylaminopropyl-carbodiimide hydrochloride (EDAC) (3.62 g, 18.9 mmol), and 4-dimethylaminopyridin (DMAP) (0.46 g, 20 mol %) in dichloromethane (150 mL) was stirred at room temperature for 24 h. After evaporation of the solvent the residue was purified by column chromatography on silica (dichloromethane : hexane). Yield: 6.23 g (77 %) colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 7.81 (dd, 1H, *J* 10.8, 6.6), 7.42-7.36 (m, 5H), 6.84 (dd, 1H, *J* 11.6, 6.7), 5.23 (s, 2H).

4-Hydroxybenzoic acid N`-(4-benzyloxy-2-fluorobenzoyl)-hydrazide. A solution of 4- benzyloxy-2-fluorobenzoic acid pentafluorophenyl ester (7.20 g, 17.5 mmol) and 4-hydroxybenzoic acid hydrazide (2.70 g, 17.5 mmol) in anhydrous DMF (100 mL) was stirred at room temperature for 48 h. The solution was poured into deionised water (600 mL). The colourless precipitate was filtered off, washed thoroughly with water, then diethyl ether, and dried. Yield: 6.61 g (99 %) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.26 (s, 1H), 10.10 (s, 1H), 10.02 (s, 1H), 7.81-7.78 (m, 2H), 7.72-7.65 (m, 1H), 7.45-7.34 (m, 5H), 7.04-6.96 (m, 2H), 6.84-6.82 (m, 2H), 5.19 (s, 2H).

4-Hydroxybenzoic acid N`-(4-benzyloxy-2,5-difluorobenzoyl)-hydrazide. A solution of 4- benzyloxy-2,5-difluorobenzoic acid pentafluorophenyl ester (6.20 g, 14.4 mmol) and 4-hydroxybenzoic acid hydrazide (2.20 g, 14.4 mmol) in anhydrous DMF (100 mL) was stirred at room temperature for 48 h. The solution was poured into deionised water (600 mL). The colourless precipitate was filtered off, washed thoroughly with water, then diethyl ether, and dried. Yield: 5.51 g (96 %) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.30 (s, 1H), 10.12 (s, 2H), 7.85 (d, 2H, *J* 7.9), 7.69 (m, 1H), 7.49-7.36 (m, 6H), 6.84 (d, 2H, *J* 7.9), 5.27 (s, 2H).

5-(4-Benzyloxy-2-fluorophenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole. A mixture of 4-hydroxybenzoic acid N`-(4-benzyloxy-2-fluorobenzoyl)-hydrazide (6.55 g, 17 mmol), thionyl chloride (70 mL), and pyridine (2 mL) was heated to reflux under nitrogen for 4h, poured onto ice (500 g) whilst still hot, and left stirring for 1.5 h. The colourless solid was filtered off, washed thoroughly with deionised water and then cold diethyl ether, dried, and recrystallized from ethanol. Yield: 4.00 g (65 %) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.39 (s, 1H), 8.02 ("t", 1H, $J_{av.}$ 8.6), 7.89 (d, 2H, *J* 8.8), 7.47-7.35 (m, 5H), 7.19 (dd, 1H, *J* 12.8, 2.4), 7.07 (dd, 1H, *J* 8.9, 2.4), 6.95 (d, 2H, *J* 8.8), 5.22 (s, 2H).

5-(4-Benzyloxy-2,5-difluorophenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole. A mixture of 4-hydroxybenzoic acid N`-(4-benzyloxy-2,5-difluorobenzoyl)-hydrazide (5.40 g, 13 mmol), thionyl chloride (70 mL), and pyridine (2 mL) was heated to reflux under nitrogen for 4h, poured onto ice (500 g) whilst hot, and left stirring for 1.5 h. The colourless solid was filtered off, washed thoroughly with deionised water and then cold diethyl ether, dried, and recrystallized from ethanol. Yield: 2.98 g (60 %) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.41 (s, 1H), 7.99 (dd, 1H, *J* 11.3, 6.7), 7.93 (d, 2H, *J* 8.8), 7.54 (dd, 1H, *J* 12.2, 7.0), 7.50-7.38 (m, 5H), 6.96 (d, 2H, *J* 8.8), 5.29 (s, 2H).

5-(4-Benzyloxy-2-fluorophenyl)-2-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole. A solution of 4-heptylbenzoic acid (0.486 g, 2.20 mmol), 5-(4-benzyloxy-2-fluorophenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (0.800 g, 2.20 mmol), EDAC (0.422 g, 2.20 mmol), and DMAP (0.053 g, 20 mol %) in dichloromethane (100 mL) was stirred at room temperature for 5 days. After evaporation of the solvent the residue was recrystallized from ethanol. Yield: 1.08 g (87 %) colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.22-8.19 (m, 2H), 8.13-8.11 (m, 2H), 8.08 (("t", 1H, $J_{av.}$ 8.6), 7.44-7.33 (m, 9H), 6.94 (dd, 1H, *J* 8.8, 2.4), 6.87 (dd, 1H, *J* 12.2, 2.4), 5.15 (s, 2H), 2.71 (t, 2H, *J* 7.7), 1.66 (m, 2H), 1.34-1.28 (m, 8H), 0.89 (t, 3H, *J* 7.0).

5-(4-Benzyloxy-2,5-difluorophenyl)-2-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole. A solution of 4-heptylbenzoic acid (0.463 g, 2.1 mmol), 5-(4-benzyloxy-2,5-difluorophenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (0.800 g, 2.1 mmol), EDAC (0.402 g, 2.1 mmol), and DMAP (0.050 g, 20 mol %) in dichloromethane (100 mL) was stirred at room temperature for 5 days. After evaporation of the solvent the residue was recrystallized from ethanol/THF. Yield: 0.98 g (80 %) colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.19-8.17 (m, 2H), 8.12-8.09 (m, 2H), 7.86 (dd, 1H, *J* 11.0, 6.4), 7.45-7.30 (m, 9H), 6.89 (dd, 1H, *J* 11.3, 6.7), 5.19 (s, 2H), 2.69 (t, 2H, *J* 7.7), 1.62 (m, 2H), 1.32-1.26 (m, 8H), 0.87 (t, 3H, *J* 7.0).

5-(4-Benzyloxyphenyl)-2-[4-(4-hexylbenzoyl)-phenyl]-1,3,4-oxadiazole. A solution of 4-hexylbenzoic acid (1.19 g, 5.8 mmol), 5-(4-benzyloxyphenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole[7] (2.00 g, 5.8 mmol), EDAC (1.11 g, 5.8 mmol), and DMAP (0.142 g, 20 mol %) in dichloromethane (200 mL) was stirred at room temperature for 3 days. After evaporation of the solvent the residue was purified by column chromatography on silica (ethyl acetate: hexane, 2:3) and the product recrystallized from ethanol. Yield: 2.21 g (71 %) colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.19 (d, 2H, *J* 8.8), 8.12 (d, 2H, *J* 8.2), 8.08 (d, 2H, *J* 9.0), 7.47-7.39 (m, 7H), 7.34 (d, 2H, *J* 8.2), 7.12 (d, 2H, *J* 9.0), 5.16 (s, 2H), 2.71 (t, 2H, *J* 7.7), 1.68-1.63 (m, 2H), 1.34-1.28 (m, 6H), 0.89 (t, 3H, *J* 6.9).

5-[4-(4-Heptylbenzoyl)-phenyl]-2-(2-fluoro-4-hydroxyphenyl)-1,3,4-oxadiazole. The benzyl protective group was removed in the usual way: A stirred mixture of 5-(4-benzyloxy-2-fluorophenyl)-2-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (1.00 g, 1.77 mmol) and Pd (10 % on activated carbon, spatula tip) in THF (100 mL) and ethanol (20 mL) was evacuated, ventilated with hydrogen, and the process repeated 3 times. The mixture was then pressurized with hydrogen in a hydrogenator against a head of water, and left stirring at room temperature until no further hydrogen uptake was detectable (overnight). The removal of the catalyst by filtration through Celite, followed by evaporation of the solvent, yielded 0.85 g (quant.) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.89 (s, 1H), 8.16 (d, 2H, *J* 8.7), 8.06 (d, 2H, *J* 8.2), 7.99 ("t", 1H, J_{av} 8.7), 7.55 (d, 2H, *J* 8.7), 7.43 (d, 2H, *J* 8.2), 6.86-6.80 (m, 2H), 2.69 (t, 2H, *J* 7.7), 1.60 (m, 2H), 1.34-1.24 (m, 8H), 0.85 (t, 3H, *J* 6.6).

5-[4-(4-Heptylbenzoyl)-phenyl]-2-(2,5-difluoro-4-hydroxyphenyl)-1,3,4-oxadiazole. Hydrogenation of 5-(4-benzyloxy-2,5-difluorophenyl)-2-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (0.88 g, 1.51 mmol) as described above provided 0.78 g (98 %) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 8.26-8.24 (m, 2H), 8.13-8.11 (m, 2H), 8.01 (dd, 1H, *J* 11.3, 7.0), 7.62-7.60 (m, 2H), 7.50-7.48 (m, 2H), 7.03 (dd, 1H, *J* 11.9, 7.3), 2.74 (t, 2H, *J* 7.7), 1.66 (m, 2H), 1.34-1.28 (m, 8H), 0.90 (t, 3H, *J* 6.8).
5-[4-(4-Hexylbenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole. Hydrogenation of 5-(4-benzyloxyphenyl)-2-[4-(4-hexylbenzoyl)-phenyl]-1,3,4-oxadiazole (1.10 g, 2.06 mmol) as described above provided 0.86 g (94 %) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.39 (s, 1H), 8.18 (d, 2H, *J* 8.8), 8.04 (d, 2H, *J* 8.2), 7.96 (d, 2H, *J* 8.8), 7.53 (d, 2H, *J* 8.8), 7.41 (d, 2H, *J* 8.2), 6.97 (d, 2H, *J* 8.8), 2.66 (t, 2H, *J* 7.6), 1.61-1.56 (m, 2H), 1.30-1.22 (m, 6H), 0.85 (t, 3H, *J* 7.0).

2.3. Syntheses of final compounds 3 - 8.
General procedure. A solution of the alkylbenzoic acid (1 equiv.), hydroxyphenyl oxadiazole (1 equiv.), EDAC (1 equiv.), and DMAP (20 mol %) in DCM was stirred at room temperature for 48 h. After evaporation of the solvent the residue was purified by column chromatography on silica (dichloromethane/ethyl acetate). For further purification the product was dissolved in THF, the solution filtered through a microfilter (Whatman Puradisc 25 TF), the solvent evaporated, and the residual colourless solid recrystallized twice from ethanol/THF.
2-[4-(4-Hexylbenzoyl)-phenyl]-5-[4-(4-pentylbenzoyl)-phenyl]-1,3,4-oxadiazole (3). Reaction of 5-[4-(4-hexylbenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole with 4-pentylbenzoic acid provided 77 % colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.20 (d, 4H, *J* 8.5), 8.11 (d, 4H, *J* 8.2), 7.40 (d, 4H, *J* 8.5), 7.31 (d, 4H, *J* 8.2), 2.69 (t, 4H, *J* 7.7), 1.65 (m, 4H), 1.35-1.31 (m, 10H), 0.91-0.87 (m, 6H). HPLC: > 99.9 %.
2-[4-(4-Heptylbenzoyl)-phenyl]-5-[4-(4-hexylbenzoyl)-phenyl]-1,3,4-oxadiazole (4). Reaction of 5-[4-(4-hexylbenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole with 4-heptylbenzoic acid provided 78 % colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.21 (d, 4H, *J* 8.6), 8.11 (d, 4H, *J* 8.2), 7.40 (d, 4H, *J* 8.6), 7.32 (d, 4H, *J* 8.2), 2.69 (t, 4H, *J* 7.7), 1.63 (m, 4H), 1.31-1.27 (m, 14H), 0.88-0.84 (m, 6H). HPLC: > 99.9 %.
2-[4-(4-Butylbenzoyl)-phenyl]-5-[4-(4-hexylbenzoyl)-phenyl]-1,3,4-oxadiazole (5). Reaction of 5-[4-(4-hexylbenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole with 4-butylbenzoic acid provided 84 % colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.21 (d, 4H, *J* 8.5), 8.12 (d, 4H, *J* 8.2), 7.41 (d, 4H, *J* 8.5), 7.32 (d, 4H, *J* 8.2), 2.73-2.67 (m, 4H), 1.69-1.62 (m, 4H), 1.44-1.31 (m, 8H), 0.97-0.86 (m, 6H). HPLC: > 99.9 %.
2-[4-(4-Butylylbenzoyl)-phenyl]-5-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (6). Reaction of 5-[4-(4-heptylbenzoyl)-phenyl] -2-(4-hydroxyphenyl)-1,3,4-oxadiazole[7] with 4-butylbenzoic acid provided 85 % colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.20 (d, 4H, *J* 8.5), 8.10 (d, 4H, *J* 8.2), 7.40 (d, 4H, *J* 8.5), 7.31 (d, 4H, *J* 8.2), 2.72-2.67 (m, 4H), 1.69-1.58 (m, 4H), 1.43-1.27 (m, 10H), 0.96-0.85 (m, 6H). HPLC: > 99.9 %.
2-[4-(4-Heptylbenzoyl)-2-fluorophenyl]-5-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (7). Reaction of 5-[4-(4-heptylbenzoyl)-phenyl]-2-(2-fluoro-4-hydroxyphenyl)-1,3,4-oxadiazole with 4-heptylbenzoic acid provided 74 % colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.25-8.21 (m, 3H), 8.13-8.09 (m, 4H), 7.42-7.40 (m, 2H), 7.34-7.32 (m, 4H), 7.27-7.24 (m, 2H), 2.70 (t, 4H, *J* 7.7), 1.65 (m, 4H), 1.33-1.27 (m, 16H), 0.88 (t, 6H, *J* 7.0). HPLC: > 99.9 %.
2-[4-(4-Heptylbenzoyl)-2,5-difluorophenyl]-5-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (8). Reaction of 5-[4-(4-heptylbenzoyl)-phenyl]-2-(2,5-difluoro-4-hydroxyphenyl)-1,3,4-oxadiazole with 4-heptylbenzoic acid provided 77 % colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.21 (d, 4H, *J* 8.6), 8.11-8.09 (m, 4H), 8.02 (dd, 1H, *J* 9.5, 6.1), 7.40 (d, 2H, *J* 8.6), 7.34-7.28 (m, 5H), 2.69 (t, 4H, *J* 7.6), 1.64 (m, 4H), 1.32-1.27 (m, 16H), 0.87 (t, 6H, *J* 7.0). HPLC: > 99.9 %.