Supplementary Material (ESI) for Chemical Communications

Enantioselective Segregation in Achiral Nematic Liquid Crystals

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Supplementary Information

Experimental

1. Materials and Characterisation

The reagents 4-benzyloxybenzoic acid, 4-dodecyloxybenzoic acid, 4-nonyloxybenzoic acid, 4-octyloxybenzoic acid, 2-fluoro-4-nonyloxybenzoic acid, and 2,3-difluoro-4-nonyloxybenzoic acid were available in the group. All other starting materials and solvents are commercially available, and were used as received. Column chromatography was performed over silica gel (ICN Silica 32-63, 60 Å).
The structures of the compounds prepared were confirmed by spectroscopic methods. ^{1}H NMR spectra were recorded on a JEOL JNM-LA 400FT 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 Ionization mass spectrometry was performed on a Thermo Quest LCQ instrument from Finnigan. Elemental analyses were carried out on a Fision Instruments Carlo Erba EA 1108 CHN analyser using acetanilide as the reference standard. A Perkin-Elmer DSC 7 differential scanning calorimeter calibrated against pure indium metal was used for determining transition temperatures; heating and cooling rates were 10 °C min^{-1}. The transition temperatures reported are the onset temperature values of transitions observed in the cooling cycles. An Olympus BH2 polarising microscope equipped with a JVC 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.

2. Synthesis

4- Benzyloxybenzoic acid pentafluorophenyl ester (1). A solution of 4-benzyloxybenzoic acid (12.45 g, 54 mmol), pentafluorophenol (10.00 g, 54 mmol), *N*-ethyl-*N`*-dimethylaminopropyl-carbodiimide hydrochloride (EDAC) (10.41 g, 54 mmol), and 4-dimethylaminopyridin (DMAP) (1.33 g, 10.8 mmol) in dichloromethane (400 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: 18.74 g (87%) colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.07-8.04 (m, 2H), 7.37-7.27 (m, 5H), 7.01-6.98 (m, 2H), 5.09 (s, 2H).

4-Hydroxybenzoic acid N`-(4-benzyloxybenzoyl)-hydrazide (2). A solution of 4- benzyloxy-benzoic acid pentafluorophenyl ester (**1**) (18.20 g, 46 mmol) and 4-hydroxybenzoic acid hydrazide (7.00 g, 46 mmol) in anhydrous DMF (160 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: 15.33 g (92%) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.26 (s, 1H), 10.18 (s, 1H), 10.14 (s, 1H), 7.90 (d, 2H, *J* 8.7), 7.80 (d, 2H, *J* 8.7), 7.48-7.34 (m, 5H), 7.12 (d, 2H, *J* 8.7), 6.85 (d, 2H, *J* 8.7), 5.19 (s, 2H).

5-(4-Benzyloxyphenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (3). A mixture of 4-hydroxybenzoic acid *N'*-(4-benzyloxybenzoyl)-hydrazide (**2**) (13.50 g, 37 mmol), thionyl chloride (40 g, 336 mmol), and pyridine (0.6 g, 7.5 mmol) was heated to reflux under nitrogen for 4h, cooled to room temperature, and poured onto ice (500 g). The colourless solid was filtered off, washed thoroughly with deionised water, and recrystallized from ethanol. Yield: 10.23 g (80%) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.26 (s, 1H), 7.95 (d, 2H, *J* 9.0), 7.86 (d, 2H, *J* 8.8), 7.41-7.27 (m, 5H), 7.15 (d, 2H, *J* 9.0), 6.89 (d, 2H, *J* 8.8), 5.13 (s, 2H).

5-(4-Benzyloxyphenyl)-2-[4-(4-dodecyloxybenzoyl)-phenyl]-1,3,4-oxadiazole (4). A solution of 4-dodecyloxybenzoic acid (2.66 g, 8.7 mmol), 5-(4-benzyloxyphenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (**3**) (3.00 g, 8.7 mmol), EDAC (1.67 g, 8.7 mmol), and DMAP (0.212 g, 1.74 mmol) in THF (350 mL) was stirred at room temperature for 4 days. After evaporation of the solvent the residue was purified by column chromatography on silica (ethyl acetate : hexane) and the product recrystallized from ethanol. Yield: 4.18 g (76%) colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.18 (d, 2H, *J* 8.8), 8.15 (d, 2H, *J* 9.0), 8.07 (d, 2H, *J* 9.0), 7.43-7.37 (m, 7H), 7.10 (d, 2H, *J* 9.0), 6.97 (d, 2H, *J* 9.0), 5.14 (s, 2H), 4.04 (t, 2H, *J* 6.6), 1.81 (quin, 2H), 1.48-1.44 (m, 2H), 1.35-1.25 (m, 16H), 0.87 (t, 3H, *J* 6.8).

5-(4-Benzyloxyphenyl)-2-[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (5). A solution of 4-heptylbenzoic acid (1.91 g, 8.7 mmol), 5-(4-benzyloxyphenyl)-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (**3**) (3.00 g, 8.7 mmol), EDAC (1.67 g, 8.7 mmol), and DMAP (0.212 g, 1.74 mmol) in dichloromethane (350 mL) was stirred at room temperature for 3 days. After evaporation of the solvent the residue was purified by column chromatography on silica (dichloromethane : hexane) and the product recrystallized from ethanol. Yield: 4.39 g (92%) 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, 8H), 0.89 (t, 3H, *J* 6.9).

5-[4-(4-Dodecyloxybenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (6). The benzyl protection group was removed in the usual way by hydrogenating a solution of compound **4** (4.10 g, 6.5 mmol) in a mixture of THF (300 mL) and ethanol (20 mL) at low pressure in the presence of Pd (10% on activated carbon) until no further hydrogen uptake was detectable (overnight). Removal of the catalyst by filtration through Celite and evaporation of the solvent yielded 3.14 g (89%) of **5a** as colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 8.17 (d, 2H, *J* 8.8), 8.12 (d, 2H, *J* 9.0), 7.95 (d, 2H, *J* 8.8), 7.42 (d, 2H, *J* 9.0), 7.01 (d, 2H, *J* 9.0), 6.97 (d, 2H, *J* 8.8), 4.07 (t, 2H, *J* 6.5), 1.82 (quin, 2H), 1.48-1.44 (m, 2H), 1.37-1.22 (m, 16H), 0.88 (t, 3H, *J* 6.9).

5-[4-(4-Heptylbenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (7). Hydrogenation of compound **5** (4.00g, 7.3 mmol) as described above for **6** provided compound **7**. Yield: 3.31 g (99%) colourless solid. ^{1}H NMR (DMSO-d_6) δ [ppm]: 10.40 (broad s, 1H), 8.17 (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, 8H), 0.83 (t, 3H, *J* 7.0).

Synthesis of 5-(4-(dodecyloxybenzoylphenyl)-2-(4-hydroxyphenyl)-1,3,4- oxadiazole esters.

General procedure. A solution of aromatic acid (1 equiv.), hydroxyphenyl oxadiazole (1 equiv.), EDAC (1 equiv.), and DMAP (20 mol%) in THF was stirred at room temperature for 48 h. After evaporation of the solvent the residue was purified by column chromatography on silica (ethyl acetate : hexane). 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 (THF : ethanol).

2,5-Bis[4-(4-Dodecyloxybenzoyl)-phenyl]-1,3,4-oxadiazole (8a). Reaction of 5-[4-(4-dodecyl-oxybenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (**6**) with 4-dodecyloxybenzoic acid provided **8a**. Yield: 69% colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.16 (d, 4H, *J* 9.0), 8.09 (d, 4H, *J* 9.0), 7.36 (d, 4H, *J* 8.8), 6.93 (d, 4H, *J* 9.0), 4.00 (t, 4H, *J* 6.5), 1.77 (quin, 4H), 1.46-1.36 (m, 4H), 1.32-1.20 (m, 32H), 0.82 (t, 6H, *J* 6.8). MS [m/z]: 831 (M^+, 100%), 633, 543. Calc. for $C_{52}H_{66}N_2O_7$: C, 75.15; H, 8.00; N, 3.37. Found: C, 75.14; H, 8.23; N, 3.40.

2-[4-(4-Dodecyloxybenzoyl)-phenyl]-5-[4-(4-nonyloxybenzoyl)-phenyl]-1,3,4-oxadiazole (8b). Reaction of **6** with 4-nonyloxybenzoic acid provided **8b**. Yield: 70% colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.16 (d, 4H, *J* 9.0), 8.09 (d, 4H, *J* 9.0), 7.35 (d, 4H, *J* 8.8), 6.92 (d, 4H, *J* 9.0), 3.99 (t, 4H, *J* 6.6), 1.76 (quin, 4H), 1.45-1.38 (m, 4H), 1.32-1.20 (m, 26H), 0.83-0.81 (m, 6H). MS [m/z]: 789 (M^+, 100%), 585. Calc. for $C_{49}H_{60}N_2O_7$: C, 74.59; H, 7.66; N, 3.55. Found: C, 74.33; H, 7.91; N, 3.59.

2-[4-(4-Dodecyloxybenzoyl)-phenyl]-5-[4-(4-octyloxybenzoyl)-phenyl]-1,3,4-oxadiazole (8c). Reaction of **6** with 4-octyloxybenzoic acid provided **8c**. Yield: 70% colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.15 (d, 4H, *J* 9.0), 8.09 (d, 4H, *J* 9.0), 7.34 (d, 4H, *J* 8.8), 6.92 (d, 4H, *J* 9.0), 3.98 (t, 4H, *J* 6.6), 1.76 (quin, 4H), 1.43-1.37 (m, 4H), 1.32-1.16 (m, 24H), 0.83-0.81 (m, 6H). MS [m/z]: 775 (M^+, 100%), 663, 607, 551. Calc. for $C_{48}H_{58}N_2O_7$: C, 74.39; H, 7.54; N, 3.61. Found: C, 74.53; H, 7.82; N, 3.67.

2-[4-(4-Dodecyloxybenzoyl)-phenyl]-5-[4-(4-pentylbenzoyl)-phenyl]-1,3,4-oxadiazole (8d). Reaction of **6** with 4-pentylbenzoic acid provided **8d**. Yield: 79% colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.18-8.13 (m, 4H), 8.09 (d, 2H, *J* 9.0), 8.06 (d, 2H, *J* 8.4), 7.36-7.33 (m, 4H), 7.27 (d, 2H, *J* 8.4), 6.92 (d, 2H, *J* 9.0), 3.98 (t, 2H, *J* 6.6), 2.64 (t, 2H, *J* 7.7), 1.76 (quin, 2H), 1.60 (quin, 2H), 1.45-1.38 (m, 2H), 1.32-1.20 (m, 20H), 0.84-0.81 (m, 6H). MS [m/z]: 717 (M^+, 100%), 633. Calc. for $C_{45}H_{52}N_2O_6$: C, 75.39; H, 7.31; N, 3.91. Found: C, 75.39; H, 7.54; N, 3.90.

2-[4-(4-Dodecyloxybenzoyl)-phenyl]-5-[4-(2-fluoro-4-nonyloxybenzoyl)-phenyl]-1,3,4-oxadia-zole (8e). Reaction of **6** with 2-fluoro-4-nonyloxybenzoic acid provided **8e**. Yield: 69% colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.23-8.20 (m, 4H), 8.16 (d, 2H, *J* 8.8), 8.06 (t, 1H, *J* 8.6), 7.43-7.40 (m, 4H), 6.99 (d, 2H, *J* 9.0), 6.79 (dd, 1H, *J* 8.8, 2.4), 6.71 (dd, 1H, *J* 12.8, 2.4), 4.05-4.02 (m, 4H), 1.84-1.80 (m, 4H), 1.48-1.41 (m, 4H), 1.36-1.27 (m, 26H), 0.90-0.88 (m, 6H). MS [m/z]: 807 (M^+, 100%), 631, 585. Calc. for $C_{49}H_{59}FN_2O_7$: C, 72.93; H, 7.37; N, 3.47. Found: C, 73.21; H, 7.63; N, 3.49.

2-[4-(4-Dodecyloxybenzoyl)-phenyl]-5-[4-(2,3-difluoro-4-nonyloxybenzoyl)-phenyl]-1,3,4-oxadiazole (8f). Reaction of **6** with 2,3-difluoro-4-nonyloxybenzoic acid provided **8f**. Yield: 69% colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.24-8.21 (m, 4H), 8.16 (d, 2H, *J* 9.0), 7.88-7.85 (m, 1H), 7.45-7.41 (m, 4H), 6.99 (d, 2H, *J* 9.0), 6.87-6.83 (m, 1H), 4.15 (t, 2H, *J* 6.6), 4.06 (t, 2H, *J* 6.6), 1.91-1.80 (m, 4H), 1.53-1.45 (m, 4H), 1.37-1.25 (m, 26H), 0.91-0.88 (m, 6H). MS [m/z]: 825 (M^+, 100%), 585. Calc. for $C_{49}H_{58}F_2N_2O_7$: C, 71.34; H, 7.09; N, 3.40. Found: C, 71.65; H, 7.39; N, 3.39.

2,5-Bis[4-(4-heptylbenzoyl)-phenyl]-1,3,4-oxadiazole (8g). Reaction of 5-[4-(4-heptylbenzoyl)-phenyl]-2-(4-hydroxyphenyl)-1,3,4-oxadiazole (**7**) with 4-heptylbenzoic acid provided **8g**. Instead of THF, dichloromethane was used as the solvent. Yield: 77% colourless solid. ^{1}H NMR ($CDCl_3$) δ

[ppm]: 8.22 (d, 4H, *J* 8.8), 8.13 (d, 4H, *J* 8.2), 7.42 (d, 4H, *J* 8.8), 7.34 (d, 4H, *J* 8.2), 2.71 (t, 4H, *J* 7.7), 1.69-1.64 (m, 4H), 1.34-1.28 (m, 16H), 0.89 (t, 6H, *J* 6.8). MS [m/z]: 659 (M^+, 100%). Calc. for $C_{42}H_{46}N_2O_5$: C, 76.57; H, 7.04; N, 4.25. Found: C, 76.80; H, 7.30; N, 3.96.

2-[4-(4-Heptylbenzoyl)-phenyl]-5-[4-(4-pentylbenzoyl)-phenyl]-1,3,4-oxadiazole (8h). Reaction of **7** with 4-heptylbenzoic acid provided **8h**. Instead of THF, dichloromethane was used as the solvent. Yield: 80% colourless solid. ^{1}H NMR ($CDCl_3$) δ [ppm]: 8.23 (d, 4H, *J* 8.6), 8.14 (d, 4H, *J* 8.2), 7.43 (d, 4H, *J* 8.6), 7.35 (d, 4H, *J* 8.2), 2.72 (t, 4H, *J* 7.7), 1.71-1.64 (m, 4H), 1.36-1.30 (m, 12H), 0.94-0.88 (m, 6H). MS [m/z]: 631 (M^+, 100%). Calc. for $C_{40}H_{42}N_2O_5$: C, 76.17; H, 6.71; N, 4.44. Found: C, 76.23; H, 7.00; N, 4.23.