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Liquid crystalline properties of unsymmetrical bent-core compounds containing chiral moieties

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7-Benzyloxy-2-hydroxynaphthalene, 1

A mixture of 2,7-dihydroxynaphthalene (5g, 31.25 mmol), benzyl chloride (4.0g, 31.62 mmol), butan-2-one (100 ml) and anhydrous potassium carbonate (13.0g, 93.75mmol)was stirred and refluxed for about 25 hours. Excess butan-2-one was distilled off and the reaction mixture was poured into ice-cold water and extracted with ether (3 × 50 ml). The combined organic solution was thoroughly washed with water and dried over anhydrous sodium sulphate. The crude product obtained after the removal of solvent was passed through a column of silica gel using 2% acetone in chloroform as eluant and the product isolated was crystallized from toluene. Yield 4.2g (54%); m.p. 151-152^{o}C; IR (Nujol) ν_{max}: 3200, 2924, 2855, 1628, 1608 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.72(s, 1H, Ar-OH, exchangeable with D_2O), 7.84-7.80(m, 2H, Ar-H), 7.67-7.65 (d, ^{3}J7.4 Hz, 2H, Ar-H), 7.56-7.45(m, 3H, Ar-H), 7.34-7.33 (d, ^{4}J2.4 Hz, 1H, Ar-H), 7.26-7.25 (d, ^{4}J2.32 Hz, 1H, Ar-H), 7.16-7.10 (m, 2H, Ar-H), 5.33 (s, 2H, $ArCH_2O$-).

[R]-[+]-7-(Benzyloxy)-2-naphthyl-2-[4-(benzyloxy)phenyloxy]propionate, 4

Compound **1** (4g, 16 mmol) and compound **3** (4.35g, 16 mmol) were dissolved in dry dichloromethane (75ml). After the addition of N, N^{l} - dicyclohexylcarbodiimide (DCC),

(4g, 18.5 mmol) and a catalytic amount of 4-(N, N-dimethylamino)pyridine (DMAP), the mixture was stirred at room temperature for about 12 hours. The precipitated dicyclohexylurea was filtered off and the filtrate was diluted with chloroform. This solution was washed with 2% aqueous acetic acid solution (3 ×100 ml) and 5% ice-cold sodium hydroxide solution (3 × 100 ml) and finally washed with water and dried over anhydrous sodium sulphate. The residue obtained after removal of solvent was chromatographed on silica gel using chloroform as an eluant. Removal of solvent from the eluate afforded a white material which was crystallized from a mixture of chloroform and alcohol. Yield 5.7g (71%); m.p. 83-85^{o}C; $[\alpha]_D^{25}$ = +55.5^{o}; IR (Nujol) ν_{max}: 2922, 2854, 1767, 1630, 1605, 1456, 1244 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 7.76-6.68(m, 20H, Ar-H), 5.16(s, 2H, Ar-CH_2O-), 5.04(s, 2H, Ar-CH_2O-), 4.98-4.88(q, ^{3}J6.8 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.81-1.80(d, ^{3}J6.8 Hz, 3H, Ar-O-CH(C<u>H$_3$</u>)-).

[R]-[+]-7-Hydroxy-2-naphthyl-2-(4-hydroxyphenyloxy)propionate, 5

Compound **4** (5.0g) was dissolved in 1,4-dioxane (50ml) and 5% Pd-C catalyst (1.0g) was added to it. The mixture was stirred at 50^{o}C in an atmosphere of hydrogen till the required quantity of hydrogen was absorbed. The mixture was filtered hot and the solvent removed under reduced pressure. The residue was chromatographed on silica gel and eluted with a mixture of 5% acetone in chloroform. Removal of solvent from the eluate gave the required product as a gummy material, which was directly used for further reaction. Yield 2.8g (89%); $[\alpha]_D^{25}$ = +27.2^{o}; IR (Nujol) ν_{max}: 3450, 3296, 2924, 2854, 1732, 1715, 1620, 1601, 1456, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.78(s, 1H, Ar-OH, exchangeable with D_2O), 8.06(s, 1H, Ar-OH, exchangeable with D_2O), 7.97-7.92(m, 2H,

Ar-H), 7.43-7.29(d, 1H, ^4J2.16 Hz, Ar-H), 7.39-6.82(m, 7H, Ar-H), 5.08-5.03(q, ^3J6.76 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.86-1.84(d, ^3J6.76 Hz, 3H, Ar-O-CH(C<u>H</u>$_3$)-).

[R]-[+]-7-(3-Fluoro-4-benzyloxybenzoyloxy)-2-naphthyl-2-[4-(3-fluoro-4-benzyl-oxybenzoyloxy)phenyloxy]propionate, 6

This was synthesized following a procedure described for the preparation of compound **4** using [R]-[+]-7-Hydroxy-2-naphthyl-2-(4-hydroxyphenyloxy)propionate, **5** and 3-fluoro-4-benzyloxy- benzoic acid. Yield 68%; m.p. 185-186^{o}C; $[\alpha]_D^{25}$ = + 41.2^o; IR (Nujol) ν_{max}: 2924, 2854, 1776, 1730, 1716, 1616, 1458, 1298 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.99-6.77(m, 26H, Ar-H), 5.26(s, 2H, Ar-CH_2O-), 5.24(s, 2H, Ar-CH_2O-), 5.05-4.96(q, ^3J6.72 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.86-1.84(d, ^3J6.72 Hz, 3H, Ar-O-CH(C<u>H</u>$_3$).

[R]-[+]-7-(3-Fluoro-4-hydroxybenzoyloxy)-2-naphthyl-2-[4-(3-fluoro-4-hydroxy-benzoyloxy)phenyloxy]propionate, 7

This was prepared following a procedure similar to that described for compound **5**. Yield 85%; m.p. 156-158 ^{o}C; $[\alpha]_D^{25}$ = + 34.3^o; IR (Nujol) ν_{max}:3329(br), 2924, 2854, 1772, 1757, 1732, 1616, 1446, 1284 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 9.9(s, 1H, Ar-OH, exchangeable with D_2O), 8.19-7.95(m, 7H, Ar-H), 7.81-7.80(d, 1H, ^4J2.16 Hz, Ar-H), 7.61-7.58(d, 1H, ^3J8.88 Hz, ^4J2.32 Hz, Ar-H), 7.46-7.27(m, 7H, Ar-H), 5.44-5.39(q, ^3J6.76 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.97-1.95(d, ^3J6.76 Hz, 3H, Ar-O-CH(C<u>H</u>$_3$).

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl-3-(benzyloxy)benzoate, 12

This was synthesized following a procedure described for the preparation of compound **4**. Yield 72%; m.p. 99-100^{o}C; $[\alpha]_D^{25}$ = + 16.1^o; IR (Nujol) ν_{max}: 2924, 2854, 1732, 1605, 1458,1261 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.16-8.13(d, 2H, ^3J8.9 Hz, Ar-H),

7.84-7.80(m, 2H, Ar-H), 7.48-7.33(m, 6H, Ar-H), 7.27-7.25(m, 5H, Ar-H), 6.98-6.95(d, 2H, ^3J8.9 Hz, Ar-H), 5.15(s, 2H, Ar-CH_2O), 4.5-4.45(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.82-1.3(m, 13H, 5×-CH_2-, 1 × -CH_3), 0.9-0.87(t, 3H, ^3J6.68 Hz, 1 × -CH_3). C_{35} H_{36} O_6 requires C, 76.06; H, 6.57; found: C, 75.6; H, 6.53%.

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl-3-hydroxybenzoate, 13

This was prepared following a procedure similar to that described for the preparation of compound **5**. Yield 85%; m.p. 108-109^{o}C; $[\alpha]_D^{25}$ = + 8.2^o; IR (Nujol) ν_{max}: 3445, 2924, 2854, 1730, 1715, 1709, 1605, 1456, 1292 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.99(s, 1H, Ar-OH, exchangeable with D_2O), 8.28-8.25(d, 2H, ^3J8.6 Hz, Ar-H), 7.83-7.78(m, 2H, Ar-H), 7.59-7.51(m, 5H, Ar-H), 7.34-7.32(d, 1H, ^3J8.0 Hz, Ar-H), 7.25-7.23(d, 2H, ^3J8.6 Hz, Ar-H), 4.8-4.77(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.56-1.44(m, 13H, 5 × -CH_2- ,1 × -CH_3), 1.01-0.98(t, 3H, ^3J6.92 Hz, 1 × -CH_3). C_{28} H_{30} O_6 requires C, 72.71; H, 6.54; found: C, 73.05; H, 6.69%.

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl-3-(4-benzyloxybenzoyloxy) benzoate, 14

This was synthesized following a procedure described for the preparation of compound **4**. Yield 70%; m.p. 125-126^{o}C; $[\alpha]_D^{25}$ = +13.9^o; IR (Nujol) ν_{max}: 2924, 2854, 1730, 1607, 1458,1261cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.19-8.04(d, 5H, Ar-H), 7.6-7.56(t, 1H, ^3J7.96 Hz, Ar-H), 7.51-7.26(m, 10H, Ar-H), 7.09-7.07(d, 2H, ^3J8.8 Hz, Ar-H), 6.96-6.94(d, 2H, ^3J8.8 Hz, Ar-H), 5.17(s, 2H, Ar-CH_2O-), 4.51-4.46(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.94-1.3(m, 13H, 5 × -CH_2- ,1 × -CH_3), 0.9-0.87(t, 3H, ^3J6.52 Hz, 1 × -CH_3). C_{42} H_{40} O_8 requires C, 74.98; H, 5.99; found: C, 74.98; H, 6.19%.

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl-3-(4-hydroxybenzoyloxy)-benzoate, 15

This was synthesized following a procedure similar to that described for the preparation of compound **5**. Yield 87%; m.p. 163-164^{o}C; $[\alpha]_D^{25}$ = + 5.1^{o}; IR (Nujol) ν_{max}: 3385, 2930, 2854, 1734, 1709, 1701, 1605, 1458, 1290 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 9.57(s, 1H, Ar-OH, exchangeable with D_2O), 8.27-8.20(d, 6H, Ar-H), 7.87-7.78(m, 2H, Ar-H), 7.58-7.50(m, 4H, Ar-H), 7.25-7.23(d, 2H, ^3J8.8 Hz, Ar-H), 7.18-7.15(d, 2H, ^3J8.68 Hz, Ar-H), 4.81-4.77(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 1.91-1.44(m, 13H, 5 × -CH_2- ,1 × -CH_3), 1.01-0.98(t, 3H, ^3J6.96 Hz, 1 × -CH_3). C_{35} H_{34} O_8 requires C, 72.15; H, 5.88; found: C, 72.28; H, 5.98%.

[R]-[+]-7-[4-(4-*n*-Tetradecyloxybenzoyloxy)3-fluorobenzoyloxy]-2-naphthyl-2-[4-{4-(4-*n*-tetradecyloxybenzoyloxy)3-fluorobenzoyloxy}phenyloxy]propionate, A1

This was synthesized following a procedure described for the preparation of compound **4**. Yield 65%; m.p. 130.5^{o}C; $[\alpha]_D^{25}$ = + 32.2^{o}; IR (Nujol) ν_{max}: 2924, 2854, 1750, 1740, 1608, 1510, 1256, 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.15-8.0(m, 8H, Ar-H), 7.91-7.86(t, 2H, ^3J9.56 Hz, Ar-H), 7.666-7.661(d, 1H, ^4J2.04 Hz, Ar-H), 7.48-7.32(m, 4H, Ar-H), 7.19-7.16(m, 3H, Ar-H), 7.07-7.05(d, 2H, ^3J9.04 Hz, Ar-H), 6.98-6.96(d, 4H, ^3J8.84 Hz, Ar-H), 5.04-5.0(q, ^3J6.70 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 4.05-4.02(t, 4H, ^3J5.52 Hz, 2 × Ar-OCH_2-), 1.99-1.77(m, 7H, 1 × Ar-O-CH(C<u>H</u>$_3$), 2×Ar-OCH_2-C<u>H</u>$_2$-), 1.49-1.25(m, 44H, 22 × -CH_2-), 0.88-0.86(t, 6H, ^3J6.52 Hz, 2 × -CH_3).

[R]-[+]-7-[4-(E-4-*n*-Octadecyloxycinnamoyloxy)3-fluorobenzoyloxy]-2-naphthyl-2-[4-{4-(E-4-*n*-octadecyloxycinnamoyloxy)3-fluorobenzoyloxy}phenyloxy]propionate, B1

Yield 69%; m.p. 142°C; $[\alpha]_D^{25}$ = + 24.4°; IR (Nujol) ν_{max}: 2920, 2851, 1759, 1738, 1637, 1604, 1510, 1254, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.09-8.01(m, 4H, Ar-H), 7.92-7.87(m, 4H, Ar-H), 7.674-7.673(d, 1H, ^4J1.96 Hz, Ar-H), 7.67-7.5(m, 5H, Ar-H), 7.42-7.34(m, 3H, Ar-H), 7.20-7.18(m, 3H, Ar-H), 7.09-7.06(d, 2H, ^3J8.88 Hz, Ar-H), 6.94-6.92(d, 4H, ^3J8.44 Hz, Ar-H), 6.53-6.49(d, 2H, ^3J15.88 Hz, Ar-H), 5.07-5.02(q, ^3J6.76 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 4.02-3.99(t, 4H, ^3J6.36 Hz, 2 × Ar-OCH_2-), 1.87-1.77(m, 7H, 1 × Ar-O-CH(C<u>H</u>$_3$), 2 × Ar-OCH_2-C<u>H</u>$_2$-), 1.46-1.11(m, 60H, 30 × -CH_2-), 0.89-0.86(t, 6H, ^3J6.4 Hz, 2 × -CH_3).

[R]-[+]-7-[4-(E-4-*n*-Tridecyloxy-α-methylcinnamoyloxy)3-fluorobenzoyloxy]-2-naphthyl-2-[4-{4-(E-4-*n*-tridecyloxy-α-methylcinnamoyloxy)3-fluorobenzoyloxy} phenyloxy]propionate, C1

Yield 75%; m.p. 123.5°C; $[\alpha]_D^{25}$ = + 16.1°; IR (Nujol) ν_{max}: 2922, 2852, 1759, 1734, 1635, 1605, 1508, 1248, 1176 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.1-8.01(m, 4H, Ar-H), 7.93-7.88(m, 4H, Ar-H), 7.675-7.670(d, 1H, ^4J2.04 Hz, Ar-H), 7.50-7.34(m, 8H, Ar-H), 7.2-7.18(m, 3H, Ar-H), 7.09-7.06(d, 2H, ^3J8.96 Hz, Ar-H), 6.96-6.94(d, 4H, ^3J7.72 Hz, Ar-H), 5.07-5.02(q, ^3J6.6 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 4.02-3.99(t, 4H, ^3J6.44 Hz, 2 × Ar-OCH_2-), 2.285-2.282(d, 6H, ^4J1.16 Hz, 2 × -CH=C(C<u>H</u>$_3$)COO-), 1.89-1.77(m, 7H, 1 × Ar-O-CH(C<u>H</u>$_3$), 2 × Ar-OCH_2-C<u>H</u>$_2$-), 1.47-1.26(m, 40H, 20 × -CH_2-), 0.89-0.87(t, 6H, ^3J6.36 Hz, 2 × -CH_3).

[R]-[+]-7-[4-(E-4-*n*-Octadecyloxy-α-methylcinnamoyloxy)3-fluorobenzoyloxy]-2-naphthyl-2-[4-{4-(E-4-*n*-octadecyloxy-α-methylcinnamoyloxy)3-fluorobenzoyloxy} phenyloxy] propionate, C2

Yield 72%; m.p. 127°C; $[\alpha]_D^{25}$ = + 24.4°; IR (Nujol) ν_{max}: 2920, 2852, 1757, 1736, 1635, 1607, 1508, 1256, 1176 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.1-8.01(m, 4H, Ar-H), 7.94-7.88(m, 4H, Ar-H), 7.68-7.67(d, 1H, ^4J2.12 Hz, Ar-H), 7.51-7.34(m, 8H, Ar-H), 7.2-7.17(m, 3H, Ar-H), 7.09-7.07(d, 2H, ^3J9.08 Hz, Ar-H), 6.96-6.94(d, 4H, ^3J7.36 Hz, Ar-H), 5.06-5.04(q, ^3J6.8 Hz, 1H, Ar-O-C<u>H</u>(CH_3)-), 4.02-3.99(t, 4H, ^3J6.32 Hz, 2 × Ar-OCH_2-), 2.284-2.281(d, 6H, ^4J1.32 Hz, 2 × -CH=C(C<u>H</u>$_3$)COO-), 1.87-1.77(m, 7H, 1 × Ar-O-CH(C<u>H</u>$_3$), 2 ×Ar-OCH_2-C<u>H</u>$_2$-), 1.47-1.26(m, 60H, 30 × -CH_2-), 0.89-0.86(t, 6H, ^3J6.6 Hz, 2 × -CH_3).

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl-3-[4-(4-*n*-decylbiphenyl-4-carbonyloxy) benzoyloxy]benzoate, D1

Yield 60%; m.p. 117°C; $[\alpha]_D^{25}$ = + 33.0°; IR (Nujol) ν_{max}: 2922, 2852, 1734, 1710, 1701, 1603, 1508,1256, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.32-8.31(d, 2H, ^3J8.76 Hz, Ar-H), 8.27-8.24(d, 2H, ^3J8.52 Hz, Ar-H), 8.14-8.06(m, 4H, Ar-H), 7.75-7.72(d, 2H, ^3J8.52 Hz, Ar-H), 7.62-7.51(m, 5H, Ar-H), 7.42-7.40(d, 2H, ^3J8.76 Hz, Ar-H), 7.30-7.24(m, 5H, Ar-H), 6.95-6.93(d, 2H, ^3J8.92 Hz, Ar-H), 4.49-4.45(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 2.67-2.63(t, 2H, ^3J7.6 Hz, 1 × Ar-CH_2-), 1.79-1.25(m, 29H, 13 × -CH_2- , 1 × -CH_3), 0.88-0.83(m, 6H, 2 × -CH_3). C_{58} H_{68} O_9 requires C, 77.14; H, 6.92; found: C, 77.33; H, 6.98%.

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl-3-[4-(4-*n*-undecylbiphenyl-4-carbonyloxy) benzoyloxy]benzoate, D2

Yield 63%; m.p. 120°C; $[\alpha]_D^{25}$ = + 40.3°; IR (Nujol) ν_{max}: 2922, 2854, 1740, 1732, 1716, 1700, 1603, 1506,1257, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.32-8.30(d, 2H,

^3J8.72 Hz, Ar-H), 8.27-8.24(d, 2H, ^3J8.48 Hz, Ar-H), 8.14-8.06(m, 4H, Ar-H), 7.75-7.72(d, 2H, ^3J8.48 Hz, Ar-H), 7.62-7.51(m, 5H, Ar-H), 7.42-7.40(d, 2H, ^3J8.76 Hz, Ar-H), 7.30-7.24(m, 5H, Ar-H), 6.95-6.93(d, 2H, ^3J8.96 Hz, Ar-H), 4.49-4.45(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 2.67-2.63(t, 2H, ^3J7.68 Hz, 1 × Ar-CH_2-), 1.79-1.25(m, 31H, 14 × -CH_2- , 1 × -CH_3), 0.88-0.83(m, 6H, 2 × -CH_3); C_{59} H_{70} O_9 requires C, 77.27; H, 7.03; found: C, 76.8; H, 7.11%.

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl-3-[4-(4-*n*-dodecylbiphenyl-4-carbonyloxy)benzoyloxy]benzoate, D3

Yield 65%; m.p. 122.5°C; $[\alpha]_D^{25}$ = + 36.7°; IR (Nujol) ν_{max}: 2922, 2852, 1742, 1734, 1715, 1701, 1605, 1506, 1257, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.32-8.30(d, 2H, ^3J8.68 Hz, Ar-H), 8.27-8.24(d, 2H, ^3J8.36 Hz, Ar-H), 8.14-8.06(m, 4H, Ar-H), 7.75-7.72(d, 2H, ^3J8.36 Hz, Ar-H), 7.62-7.51(m, 5H, Ar-H), 7.42-7.40(d, 2H, ^3J8.72 Hz, Ar-H), 7.30-7.24(m, 5H, Ar-H), 6.95-6.93(d, 2H, ^3J8.92 Hz, Ar-H), 4.49-4.46(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 2.67-2.63(t, 2H, ^3J7.64 Hz, 1 × Ar-CH_2-), 1.79-1.25(m, 33H, 15 × -CH_2- , 1 × -CH_3), 0.88-0.82(m, 6H, 2 × -CH_3); C_{60} H_{72} O_9 requires C, 77.39; H, 7.14; found: C, 77.85; H, 7.23%.

[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl 3-[4-(4-*n*-tetradecylbiphenyl-4-carbonyloxy)benzoyloxy]benzoate, D4

Yield 62%; m.p. 122.5°C; $[\alpha]_D^{25}$ = + 55.7°; IR (Nujol) ν_{max}: 2924, 2854, 1742, 1734, 1712, 1701, 1605, 1506, 1257, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.32-8.30(d, 2H, ^3J8.8 Hz, Ar-H), 8.27-8.24(d, 2H, ^3J8.52 Hz, Ar-H), 8.14-8.06(m, 4H, Ar-H), 7.75-7.72(d, 2H, ^3J8.52 Hz, Ar-H), 7.62-7.51(m, 5H, Ar-H), 7.42-7.40(d, 2H, ^3J8.76 Hz, Ar-H), 7.30-7.24(m, 5H, Ar-H), 6.95-6.93(d, 2H, ^3J8.92 Hz, Ar-H), 4.49-4.46(m, 1H, Ar-O-C<u>H</u>(CH_3)-

), 2.67-2.63(t, 2H, ^3J7.68 Hz, 1 × Ar-CH_2-), 1.79-1.24(m, 37H, 17 × -CH_2- , 1 × -CH_3), 0.88-0.83(m, 6H, 2 × -CH_3); C_{62} H_{76} O_9 requires C, 77.63; H, 7.36; found: C, 77.34; H, 7.43%.

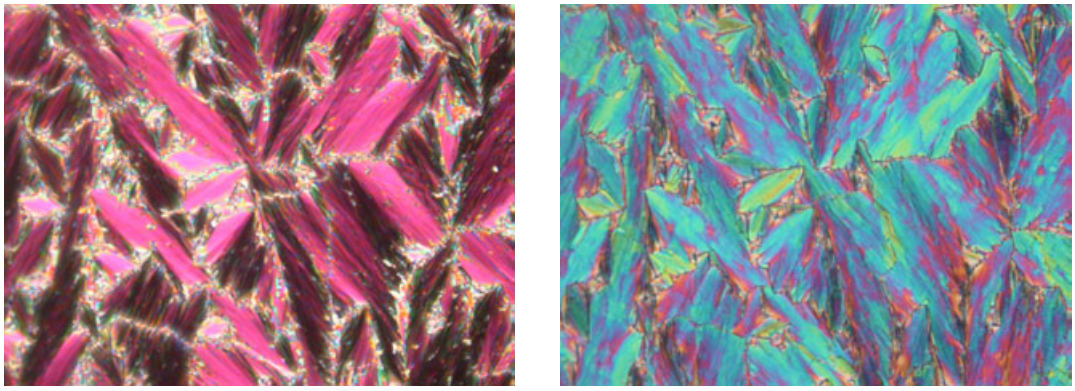
[S]-[+]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl 3-[4-(4-*n*-dodecyloxybiphenyl-4-carbonyloxy)benzoyloxy]benzoate, E1

Yield 68%; m.p. 114.5°C; $[\alpha]_D^{25}$ = + 25.7°; IR (Nujol) ν_{max}: 2922, 2852, 1738, 1720, 1705, 1605, 1510, 1252, 1175 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 8.32-8.30(d, 2H, ^3J8.64 Hz, Ar-H), 8.25-8.23(d, 2H, ^3J8.36 Hz, Ar-H), 8.14-8.06(m, 4H, Ar-H), 7.71-7.69(d, 2H, ^3J8.32 Hz, Ar-H), 7.61-7.51(m, 5H, Ar-H), 7.42-7.40(d, 2H, ^3J8.64 Hz, Ar-H), 7.30-7.22(m, 3H, Ar-H), 7.0-6.98(d, 2H, ^3J8.72 Hz, Ar-H), 6.95-6.93(d, 2H, ^3J8.84 Hz, Ar-H), 4.48-4.45(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 4.02-3.98(t, 2H, ^3J6.56 Hz, 1 × Ar-OCH_2-), 1.82-1.25(m, 33H, 15 × -CH_2- , 1 × -CH_3), 0.88-0.84(m, 6H, 2 × -CH_3). C_{60} H_{66} O_{10} requires C, 76.10; H, 6.98; found: C, 76.29; H, 7.14%.

[±]-4-[4-(1-Methylheptyloxy)benzoyloxy]phenyl 3-[4-(4-*n*-dodecyloxybiphenyl-4-carbonyloxy)benzoyloxy]benzoate, F1

Yield 60%; m.p. 114°C; IR (Nujol) ν_{max}: 2920, 2850, 1740, 1720, 1706, 1602, 1510, 1250, 1176 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ(ppm): 8.32-8.30(d, 2H, ^3J8.9 Hz, Ar-H), 8.25-8.23(d, 2H, ^3J8.8 Hz, Ar-H), 8.14-8.06(m, 4H, Ar-H), 7.71-7.69(d, 2H, ^3J8.4 Hz, Ar-H), 7.61-7.51(m, 5H, Ar-H), 7.42-7.40(d, 2H, ^3J8.8 Hz, Ar-H), 7.26-7.24(m, 3H, Ar-H), 7.0-6.98(d, 2H, ^3J8.8 Hz, Ar-H), 6.95-6.93(d, 2H, ^3J8.8 Hz, Ar-H), 4.48-4.46(m, 1H, Ar-O-C<u>H</u>(CH_3)-), 4.02-3.99(t, 2H, ^3J6.6 Hz, 1 × Ar-OCH_2-), 1.82-1.23(m, 33H, 15 × -CH_2- , 1 × -CH_3), 0.89-0.85(m, 6H, 2 × -CH_3). C_{60} H_{66} O_{10} requires C, 76.10; H, 6.98 found: C, 75.98; H, 7.03%.

Supplementary material (ESI) for Journal of Materials Chemistry



(a) 0V (b) ± 50 V

Fig. S1: Optical photomicrographs obtained in the SmC_s phase; (a) 0V; (b) ± 50 V, independent of the sign of the applied field.