

Supplemental Material

Spectroscopic characterization of oxadiazole based liquid crystals.

All derivatives were prepared using similar procedures to that described below. A table listing yields and elemental analyses data can be found at the end of this section.

OC12 Ph(Mono2MeODBP)

In a two-necked 250-mL round-bottom flask, 2-(4-hydroxyphenyl)-5-(4-hydroxy-2-methylphenyl)-1,3,4-oxadiazole (0.109 g, 0.41 mmol), 4-(dodecyloxy)benzoic acid (0.229 g, 0.756 mmol), and DMAP (0.0227 g, 0.186 mmol) were combined and placed under N₂. Dry CH₂Cl₂ (25 mL) was stirred into the reaction flask before the addition of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (0.149 g, 0.723 mmol). The reaction mixture was allowed to stir for 72 hours and was then quenched in DI H₂O (50 mL). The organic layer was washed two times with DI H₂O and one time with HCl (1 M). The aqueous layer was back-extracted with CHCl₃, and the organic layers were combined, dried over MgSO₄, filtered, and the solvents removed *in vacuo*. The crude product was recrystallized twice from Ethanol and a small amount of chloroform to give a chalky, white solid (0.204 g, 64.8% yield). ¹H NMR (400 MHz, CDCl₃) δ 0.87 ppm (6H, t, J = 6.9 Hz), 1.2 (32H, m), 1.42-1.51 (4H, m), 1.82 (4H, quintet, J = 6.4 Hz), 2.8 (3H, s), 4.0 (4H, t, J = 6.4 Hz), 6.98 (4H, dq, J = 8.9, 2.0 Hz), 7.22-7.26 (2H, mult. (obscured by chloroform)), 7.40 (2H, dt, J=8.9, 1.9 Hz), 8.11 (1H, d, J=8.5 Hz), 8.13-8.17 (4H, m.), 8.20 (2H, d, J=7.5 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 14.23, 22.41, 22.80, 26.08, 29.18, 29.46 (overlap), 29.66, 29.69, 29.74, 29.76, 32.02, 68.48, 114.48, 114.51, 119.94, 120.61, 121.02, 121.12, 121.45, 122.85, 125.16, 128.44, 130.42, 132.48, 132.51, 140.62, 153.19, 153.87, 163.71, 163.86, 163.90, 164.49, 164.55, 164.66.

OC12 3MePh(mono2MeODBP)

2-(4-hydroxyphenyl)-5-(4-hydroxy-2-methylphenyl)-1,3,4-oxadiazole (0.0662 g, 0.248 mmol), 4-(dodecyloxy)-3-methylbenzoic acid, (0.157 g, 0.488 mmol), DMAP (0.0150 g, 0.122 mmol), EDC (0.0963 g, 0.502 mmol). Recovery: 0.0964 g, 44.6% yield. ¹H NMR (400 MHz, CDCl₃) δ 0.88 ppm (6H, t, J = 6.4 Hz), 1.20-1.40 (32H, m), 1.50 (4H, quintet, CH₂, J = 6.8 Hz), 1.84 (4H, quintet, J = 6.4 Hz), 2.29 (6H, s, CH₃), 2.81 (3H, s, CH₃), 4.06 (4H, t, CH₂, J = 6.4 Hz), 6.89 (2H, d, J = 8.7 Hz), 7.22-7.26 (2H, m, obscured by chloroform), 7.40 (2H, d, J = 8.7 Hz), 7.99 (2H, s), 8.04 (2H, dt, J=8.7, 2.5 Hz), 8.11 (1H, d, J=8.2 Hz), 8.20 (2H, d, J=8.2 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 14.22, 16.33, 22.38, 22.79, 26.16, 29.21, 29.44 (overlap), 29.68 (overlap), 29.74, 29.75, 32.00, 68.39, 110.29 (overlap), 119.96, 120.37, 120.45, 120.56, 121.40, 122.87, 125.17, 127.25, 127.28, 128.42, 130.30, 130.35, 131.41, 132.64 (overlap), 140.58, 153.29, 153.96, 162.03, 162.10, 163.72, 164.51, 164.79, 164.90.

OC4 3MePh(Mono2MeODBP)

2-(4-hydroxyphenyl)-5-(4-hydroxy-2-methylphenyl)-1,3,4-oxadiazole (0.100 g, 0.373 mmol), 4-butoxy-3-methylbenzoic acid, (0.155 g, 0.745mmol), DMAP (0.0227 g, 0.186 mmol), EDC (0.147 g, 0.791 mmol). Recovery: 0.132 g, 57.0% yield. ¹H NMR (400 MHz, CDCl₃) δ 1.0 ppm (6H, t, J = 7.3 Hz), 1.50-1.58 (4H, mult.), 1.83 (4H, quintet, , J =

7.1 Hz), 2.28 (6H, s), 2.81 (3H, s), 4.07 (4H, t, J = 6.4 Hz), 6.89 (2H, d, J = 8.7 Hz), 7.22-7.25 (2H, m, obscured by chloroform), 7.40 (2H, dt, J = 8.7, 2.0 Hz), 7.97-7.99 (2H, m), 8.04 (2H, dt, J=8.5, 2.3 Hz), 8.11 (1H, d, J=8.5 Hz), 8.20 (2H, dt, J=8.8, 2.1 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 13.97 ppm, 16.34, 19.40, 22.41, 31.29, 68.07, 110.27 (overlap), 119.96, 120.36, 120.46, 120.55, 121.39, 122.88, 125.18, 127.25, 127.29, 128.43, 130.32, 130.36, 130.411, 132.64 (overlap), 140.59, 153.28, 153.96, 162.04, 162.09, 163.72, 164.51, 164.81, 164.92.

OC₄ Ph(mono2MeODBP)

2-(4-hydroxyphenyl)-5-(4-hydroxy-2-methylphenyl)-1,3,4-oxadiazole (0.125 g, 0.469 mmol), 4-butoxybenzoic acid (0.182 g, 1.04 mmol), DMAP (0.0274 g, 0.224 mmol), EDC (0.178 g, 0.929 mmol). Recovery: 0.149 g, 51.1% yield. ¹H NMR (400 MHz, CDCl₃) δ 0.98 ppm (6H, t, J = 7.4 Hz), 1.53 (4H, sextet, J = 8.3 Hz), 1.81 (4H, quintet, J = 6.9 Hz), 2.81 (3H, s), 4.06 (4H, t, J = 6.4 Hz), 6.98 (4H, dq, J=9.0, 2.0 Hz), 7.22-7.26 (2H, mult. (obscured by chloroform peak), 7.40 (2H, dt, J=8.9, 2.0 Hz), 8.11 (1H, d, J=8.2 Hz), 8.15 (4H, dd, J=9.0, 2.3 Hz), 8.20 (2H, dt, J=8.9, 2.1 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 13.94, 19.30, 22.41, 31.21, 68.14, 114.47 (overlap), 119.94, 120.60, 121.02, 121.13, 121.45, 122.85, 125.16, 128.44, 130.42, 132.48, 132.51, 140.61, 153.19, 153.87, 163.70, 163.86, 163.91, 164.49, 164.55, 164.66.

OC₄ Ph(mono3MeODBP)

2-(4-hydroxyphenyl)-5-(4-hydroxy-3-methylphenyl)-1,3,4-oxadiazole (0.2171 g, 0.812 mmol), 4-butoxy benzoic acid (0.3165 g, 1.62 mmol), DMAP (0.0510 g, 0.417 mmol), EDC (0.3216 g, 1.67 mmol). Recovery: 0.1028 g, 20.4% yield. ¹H-NMR (400 MHz, CDCl₃) δ 0.99 (6H, t, J=7.3 Hz), 1.52 (4H, sextet, J=7.6 Hz), 1.78 (4H, quintet, J=6.6 Hz), 2.33 (3H, s), 6.96-7.01 (4H, mult.), 7.33 (1H, d, J=8.5 Hz), 7.41 (2H, dt, J=8.7, 1.8 Hz), 8.02 (1H, dd, J=8.5, 2.0 Hz), 8.04 (1H, d, 1.0 Hz), 8.16 (4H, mult.), 8.21 (2H, dt, J=8.4, 1.7 Hz). ¹³C-NMR(400 MHz, CDCl₃) δ 13.93, 16.47, 19.29, 31.21, 68.15, 114.50, 114.54, 120.96, 121.03, 121.45, 121.52, 122.83, 123.26, 125.92, 128.43, 129.89, 131.95, 132.51 (overlap), 152.57, 153.87, 163.90 (overlap), 164.15, 164.31, 164.34, 164.55.

OC₁₂ Ph(3-MonoMeODBP)

4-dodecyloxy benzoic acid (0.1781 g, 0.581 mmol), DMAP (0.0198 g, 0.162 mmol), 2-(4-hydroxyphenyl)-5-(4-hydroxy-3-methylphenyl)-1,3,4-oxadiazole (0.0771 g, 0.2884 mmol), EDC (0.1055 g, 0.550 mmol). Recovery: 0.1283 g, 52.7 % yield. ¹H-NMR (400 MHz, CDCl₃) δ 0.88 (6H, t, J=6.6 Hz), 1.20-1.40 (32H, m) 1.44-1.60 (4H, m), 1.82 (4H, quintet, J=6.9 Hz), 2.34 (3H, s), 4.04 (4H, t, J=6.6 Hz), 6.96-7.02 (4H, mult.), 7.32 (1H, d, J=8.4 Hz), 7.41 (2H, dt, J=9.0, 2.4 Hz), 8.03 (1H, dd, J=8.5, 2.0 Hz), 8.08 (1H, d, J=1.3 Hz), 8.13-8.18 (4H, mult.), 8.21 (2H, dt, J=8.9, 2.0 Hz). ¹³C-NMR(400 MHz, CDCl₃) δ 14.22, 16.45, 22.78, 26.07, 29.18, 29.44 (overlap), 29.65, 29.68, 29.73, 29.75, 32.01, 68.49, 114.51, 114.55, 120.98, 121.05, 121.46, 121.53, 122.81, 123.25, 125.91, 128.42, 129.88, 131.93, 132.49 (overlap), 152.58, 153.88, 163.91 (overlap), 164.15, 164.29, 164.32, 164.53.

OC₄ 3-MePh(3-MonoMePh ODBP)

4-butoxy-3-methyl benzoic acid (0.1613 g, 0.775 mmol), DMAP (0.0261 g, 0.214 mmol), 2-(4-hydroxyphenyl)-5-(4-hydroxy-3-methylphenyl)-1,3,4-oxadiazole (0.1046 g, 0.391 mmol), EDC (0.1567 g, 0.817 mmol). Recovery: 0.1252 g, 49.8% yield. ¹H-NMR (400 MHz, CDCl₃) δ 1.00 (6H, t, J=7.3 Hz), 1.49-1.60 (4H, mult.), 1.84 (4H, quintet, J=6.9 Hz), 2.28 (3H, s), 2.29 (3H, s), 2.34 (3H, s), 4.07 (4H, t, J=6.4 Hz), 6.90 (2H, dd, J=8.7 Hz, 3.7 Hz), 7.31 (1H, d, J=8.2 Hz), 7.41 (2H, dt, J=8.7, 1.8 Hz), 7.97-8.10 (6H, m), 8.21 (2H, dt, J=9.0, 2.1 Hz). ¹³C-NMR(400 MHz, CDCl₃) δ 13.96, 16.33, 16.46, 19.40, 31.29, 68.08, 110.29, 110.32, 120.31, 120.37, 121.39, 121.48, 122.84, 123.29, 125.91, 127.28, 127.33, 128.41, 129.87, 130.31, 130.34, 131.99, 132.66 (overlap), 152.67, 153.96, 162.09 (overlap), 164.17, 164.35, 164.57, 164.80.

OC₁₂ 3-MePh(3-MonoMePh ODBP)

4-dodecyloxy-3-methyl benzoic acid (0.3090 g, 0.964 mmol), DMAP (0.0334 g, 0.273 mmol), 2-(4-hydroxyphenyl)-5-(4-hydroxy-3-methylphenyl)-1,3,4-oxadiazole (0.1307, 0.489 mmol), EDC (0.1964 g, 1.025 mmol). Recovery: 0.2037 g, 51.7% yield. ¹H-NMR (400 MHz, CDCl₃) δ 0.88 (6H, t, J=6.6 Hz), 1.27 (32H, m), 1.45-1.59 (4H, m), 1.84 (4H, quintet, J=6.9 Hz), 2.28 (6H, s), 2.34 (3H, s), 4.06 (3H, t, J= 6.2 Hz), 6.89 (2H, dd, J=8.5, 3.7 Hz), 7.32 (1H, d, J=8.2Hz), 7.40 (2H, d, J=8.5 Hz), 7.97-8.10 (6H, m), 8.21 (2H, d, J=8.5 Hz). ¹³C-NMR (400 MHz, CDCl₃) δ 14.23, 16.35, 16.47, 22.80, 26.16, 29.22, 29.45 (overlap), 29.68 (overlap) 29.76 (overlap), 32.02, 68.39, 110.30, 110.33, 120.30, 120.36, 121.39, 121.48, 122.84, 123.29, 125.91, 127.28, 127.33, 128.42, 129.87, 130.20, 130.35, 132.00, 132.66 (overlap), 152.67, 153.96, 162.09 (overlap), 164.17, 164.36, 164.58, 164.81.

OC₁₂ 2-MePh(3-MonoMePh ODBP)

4-dodoxy-2-methyl benzoic acid (0.4818 g, 1.503 mmol), DMAP (0.0461 g, 0.377 mmol), 2-(4-hydroxyphenyl)-5-(4-hydroxy-3-methylphenyl)-1,3,4-oxadiazole (0.2008 g, 0.751 mmol), EDC (0.2949 g, 1.538 mmol). Recovery: 0.336 g, 054.6% yield. ¹H-NMR (400 MHz, CDCl₃) δ 0.88 (6H, t, J=6.0 Hz), 1.22-1.40 (32H, m), 1.42-1.51 (4H, m), 1.81 (4H, quintet, J=7.1 Hz), 2.35 (3H, s), 2.67 (6H, s), 4.03 (4H, t, J=6.4 Hz), 6.80-6.84 (4H, m), 7.25 (1H, s), 7.30 (1H, d, J=8.5 Hz), 7.39 (2H, d, J=8.2 Hz), 8.02 (1H, d, J=8.2 Hz), 8.08 (1H, s), 8.17-8.24 (4H, m). ¹³C-NMR(400 MHz, CDCl₃) δ 14.22, 16.58, 22.69, 22.79, 26.08, 29.21, 29.45 (overlap), 29.66, 29.69, 29.74, 32.02, 68.30, 111.81 (overlap), 117.91, 117.96, 119.71, 119.74, 121.37, 121.45, 122.97 (overlap), 123.42, 125.90, 128.40, 129.87, 132.00, 133.79, 133.86, 144.80 (overlap), 152.64, 153.89, 162.93 (overlap), 164.17, 164.36, 164.55, 164.76.

OC₄ 2MePh(mono2MeODBP)

2-(4-hydroxyphenyl)-5-(4-hydroxy-2-methylphenyl)-1,3,4-oxadiazole (0.116 g, 0.433 mmol), 4-butoxybenzoic acid (.180 g, 0.866 mmol), DMAP (0.027 g, 0.217 mmol), EDC (0.172 g, 0.892 mmol). Recovery: 0.160 g, 57.2% yield. ¹H NMR (400 MHz, CDCl₃) δ 0.99 (6H, t, J=7.4 Hz), 1.45-1.57 (4H, m), 1.80 (4H, pentet, J=6.8 Hz), 2.66 (6H, s), 2.80 (3H, s), 4.04 (4H, t, J=6.6 Hz), 6.80-6.85 (4H, mult.), 7.20-7.25 (2H, m (obscured)), 7.38 (2H, d, J=8.5 Hz), 8.11 (1H, d, J=8.2 Hz), 8.16-8.22 (4H, m). ¹³C-NMR(100 MHz,

CDCl₃) δ 13.94, 19.30, 22.41, 22.71, 31.25, 67.96, 111.79 (overlap), 117.88 (overlap), 119.74, 119.84, 120.09, 120.52, 121.37, 123.00, 125.31, 128.41, 130.41, 133.86 (overlap), 140.59, 144.75, 144.81, 153.21, 153.89, 162.90, 162.93, 163.73, 164.52, 164.77, 164.91.

OC12 2MePh(mono2MeODBP)

4-dodecyloxy-2-methylbenzoic acid (0.1444 g, 0.455 mmol), 2-(4-hydroxyphenyl)-5-(4-hydroxy-2-methylphenyl)-1,3,4-oxadiazole (0.0615 g, 0.229 mmol), DMAP (0.0130 g, 0.106 mmol), EDC (0.0903 g, 0.471 mmol). Recovery: 0.136 g, 69.2% yield. ¹H NMR (400 MHz, CDCl₃) δ 0.88 (6H, t, J=6.8 Hz), 1.40-1.22 (32H, m), 1.50-1.42 (4H, m), 1.81 (4H, quintet, J=6.9 Hz), 2.67 (6H, s), 2.80 (3H, s), 4.03 (4H, t, J=6.8 Hz), 6.79-6.84 (4H, m), 7.26-7.20 (2H, m, obscured by chloroform), 7.38 (2H, d, J=8.3 Hz), 8.11 (1H, d, J=8.2 Hz), 8.21-8.16 ppm (4H, m). ¹³C NMR (100 MHz, CDCl₃): δ 14.23, 22.37, 22.68, 22.79, 26.07, 29.21, 29.43, 29.65, 29.68, 29.73, 29.75, 32.01, 68.27, 111.79 (overlapping), 117.91 (overlapping), 119.74, 119.87, 120.08, 120.53, 121.39, 123.00, 125.31, 128.40, 130.39, 133.83 (overlapping), 140.57, 144.72, 144.79, 153.23, 153.88, 162.90, 162.92, 163.71, 164.50, 164.75, 164.88.

Table S-1. Yields and Elemental Analysis Data for the ODBP Derivatives

Compound	Percent Yield	C% calc. (found)	H% calc. (found)	N% calc. (found)
OC4 Ph(mono2MeODBP)	51.1	71.6 (71.44)	5.85 (5.89)	4.51 (4.59)
OC4 Ph(mono3MeODBP)	60.0	71.6 (71.54)	5.85 (6.11)	4.51 (4.22)
OC12 Ph(mono2MeODBP)	64.8	75.32 (75.26)	8.11 (8.42)	3.31 (3.24)
OC12 Ph (mono3MeODBP)	52.7	75.32 (75.07)	8.11 (7.90)	3.31 (3.24)
OC4 2MePh(mono2MeODBP)	57.2	72.20 (72.15)	6.21 (6.12)	4.32 (4.28)
OC4 3MePh(mono2MeODBP)	57.0	72.20 (72.47)	6.21 (6.19)	4.32 (4.37)
OC4 2MePh(mono3MeODBP)	67.0	72.20 (72.00)	6.21 (6.27)	4.32 (4.24)
OC4 3MePh(mono3MeODBP)	49.8	72.20 (71.81)	6.21 (6.15)	4.32 (4.26)
OC12 2MePh(mono2MeODBP)	69.2	75.65 (75.63)	8.31 (8.40)	3.21 (3.18)
OC12 3MePh(mono2MeODBP)	44.6	75.65 (75.39)	8.31 (8.53)	3.21 (3.17)
OC12 2MePh(mono3MeODBP)	54.6	75.65 (75.62)	8.31 (8.44)	3.21 (3.17)
OC12 3MePh(mono3MeODBP)	54.7	75.65 (75.48)	8.31 (8.65)	3.21 (3.13)