Supramolecular Liquid Crystals
Exhibiting a Chiral Twist-Bend Nematic Phase

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ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis
Butoxybenzoic acid was purchased from Sigma Aldrich and purified for use in mixtures by recrystallisation from ethanol (10 mL per g).

4OBA: M.P. = 147 °C. 1H NMR (300 MHz, CDCl3) δ ppm: 1.01 (t, J = 7.35 Hz, 3 H. CH3CH2CH2CH2OAr), 1.39 - 1.67 (m, 2 H. CH3CH2CH2CH2OAr), 1.71 - 1.99 (m, 2 H. CH3CH2CH2CH2OAr), 4.06 (t, J = 6.50 Hz, 2 H. CH3CH2CH2CH2OAr), 6.82 - 7.14 (m, 2 H. Ar), 7.90 - 8.31 (m, 2 H. Ar).

(S)-(2-Me)4OBA: 4-Hydroxybenzoic acid (1 eq.) and potassium hydroxide (3 eq.) were dissolved in ethanol and stirred for 1 h at room temperature. (S)-1-Bromo-2-methylbutane (1 eq.) was added dropwise and the resulting mixture heated under reflux for 17 h. The resulting potassium salt was hydrolysed by addition to H2O and concentrated HCl yielding a white precipitate which was collected by vacuum filtration. The crude product was purified by recrystallisation from hexane. Yield of 54 % was obtained.

M.P. = 105 °C. IR ν cm⁻¹: 2963, 2914, 2860, 1668 (C=O carboxylic acid), 1601 (para di-substituted benzene), 1426, 1295, 1168, 847, 774. 1H NMR (300 MHz, CDCl3) δ ppm: 0.93 - 1.02 (m, 3 H. CH3CH2CH2CH2OAr), 1.05 (d, J = 6.78 Hz, 3 H. CH3CH2(CH2)CHCH2OAr), 1.23 - 1.40 (m, 1 H. CH3CH2(CH2)CHCH2OAr), 1.51 - 1.69 (m, 1 H. CH3CH2(CH2)CHCH2OAr), 1.84 - 2.00 (m, 1 H. CH3CH2(CH2)CHCH2OAr), 3.66 - 4.09 (m, 2 H. CH3CH2(CH2)CHCH2OAr), 6.83 - 7.09 (m, 2 H. Ar), 7.90 - 8.26 (m, 2 H. Ar). 13C NMR (75 MHz, CDCl3) δ ppm: 11.32, 16.50, 26.08, 34.62, 73.06, 114.21, 121.32, 132.34, 163.87, 172.17.
Scheme 2. Synthesis of nOS, where R = C₄H₉ or CH₂CH(CH₃)CH₂CH₃.

4-[(E)-2-(Pyridin-4-yl)ethenyl]phenol, HOS: A stirred mixture of 4-methylpyridine (10 ml, 0.103 mol) and 4-hydroxybenzaldehyde (15.270 g, 0.125 mol) in acetic anhydride (21.5 ml, 0.226 mol) was heated under reflux for 23 hr. After cooling to room temperature, the mixture was poured into ice water (600 ml) and stirred for 1 h. The resulting precipitate was collected using vacuum filtration and refluxed in alcoholic potassium hydroxide (0.75 N) for 2 h. Acetic acid (20 ml) was added to precipitate the crude product, which was recrystallised from ethanol to give the title compound as a dark yellow solid. Yield: 6.852 g, 33.7 %.

M.P. = 282 °C. IR ν cm⁻¹: 3250-2000 (broad, OH), 1636 (C=C), 1581, 1512, 1250, 1192, 973, 829, 547.

1H NMR (300 MHz, DMSO-d₆) δ ppm: 6.80 (d, J = 8.67 Hz, 2 H), 7.01 (d, J = 16.58 Hz, 1 H. ArCHCHAr), 7.39 - 7.53 (m, 5 H. ArCHCHAr, Ar), 8.46 - 8.54 (m, 2 H. Ar, adj. to N), 9.77 (s, 1 H. OHAr).

13C NMR (75 MHz, CDCl₃) δ ppm: 115.64, 120.45, 122.43, 127.17, 128.63, 133.02, 144.76, 149.86, 158.18.

4-[(E)-2-(4-Alkoxyphenyl)ethenyl]pyridines, nOS (n = 4 and (S)-(2-Me)4): A stirred mixture of 4-hydroxystilbazole (1 eq.), n-bromoalkane (1 eq.) and potassium carbonate (3 eq.) in acetone was heated under reflux for 96 h. After cooling to room temperature, undissolved inorganic solid was removed by vacuum filtration and the filtrate removed in vacuo to yield a dark red solid. The crude product was purified by first passing through silica, washing through with copious amounts of ethyl acetate and subsequent recrystallisation from a mixture of ethyl acetate and hexane.

4OS: M.P. = 95 °C. IR ν cm⁻¹: 2939, 2876, 1604, 1589, 1257, 1176, 970, 836, 544.

1H NMR (400 MHz, CDCl₃) δ ppm: 8.55 (d, J = 5.1 Hz, 2H, Ar adj. to N), 7.46 (d, J = 8.2 Hz, 2H, Ar), 7.35 – 7.17 (m, 3H, Ar, ArCHCHAr), 6.96 – 6.79 (m, 3H, Ar, ArCHCHAr), 3.98 (t, J = 6.5 Hz, 2H, OCH₂CH₂CH₂CH₃), 1.79 (p, J = 6.8 Hz, 2H, OCH₂CH₂CH₂CH₃), 1.51 (h, J = 7.5 Hz, 2H, OCH₂CH₂CH₂CH₃), 1.00 (t, J = 7.3 Hz, 3H, OCH₂CH₂CH₂CH₃).

13C NMR (101 MHz, CDCl₃) δ ppm: 159.79, 150.10, 144.98, 132.76, 128.65, 128.38, 123.52, 120.61, 114.81, 67.78, 31.28, 19.25, 13.88. Elemental Analysis: Calculated for C17H19NO: C 80.60 %, H 7.56 %, N 5.53 %, Found: C 80.76 %, H 7.76 %, N 5.38 %.

(S)-(2-Me)4OS: M.P. = 101 °C. IR ν cm⁻¹: 2966, 2877, 1588, 1251, 1020, 971, 832, 814, 546.

1H NMR (400 MHz, CDCl₃) δ ppm: 8.57 (d, J = 5.0 Hz, 2H, Ar adj. to N), 7.48 (d, J = 8.2 Hz, 2H, Ar), 7.39 – 7.22 (m, 3H, Ar, ArCHCHAr), 6.98 – 6.84 (m, 3H, Ar, ArCHCHAr), 3.91 – 3.74 (m, 2H, OCH₂CH₂CH₂CH₃), 1.90 (h, J = 6.6 Hz, 1H, OCH₂CH₂CH₂CH₃), 1.67 – 1.52 (m, 1H, OCH₂CH₂CH₂CH₃), 1.30 (m, 1H, OCH₂CH₂CH₂CH₃), 1.05 (d, J = 6.8 Hz, 3H, OCH₂CH₂CH₂CH₃), 0.98 (t, J = 7.5 Hz, 3H, OCH₂CH₂CH₂CH₃). 13C NMR (101 MHz, CDCl₃) δ ppm: 159.97, 150.10, 144.98, 132.76, 128.65, 128.38, 123.52, 120.61, 114.81, 67.78, 31.28, 19.25, 13.88. Elemental Analysis: Calculated for C18H21NO: C 80.86 %, H 7.92 %, N 5.24 %, Found: C 80.84 %, H 8.11 %, N 5.06 %.

CB6OBA¹, CB6OS² and 1OB6OS³ were synthesized by procedures described elsewhere.
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1OB6OS M.P. = 139 °C. IR $\tilde{\nu}$ cm$^{-1}$: 2914, 2849, 1671, 1605, 1588, 1499, 1254, 1177, 1019, 972, 822, 545. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 1.40 - 1.62 (m, 4 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 1.65 - 1.77 (m, 2H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 1.78 - 1.91 (m, 2 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 2.68 (t, $J = 7.63$ Hz, 2 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 3.86 (s, 3 H. CD$_2$OAr), 4.01 (t, $J = 6.50$ Hz, 2 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 6.85 - 6.95 (m, 3 H. Ar, OArCHCHAr), 6.98 (d, $J = 8.85$ Hz, 2 H. Ar), 7.22 - 7.33 (m, 3 H. Ar, OAr-CHCH-Ar), 7.38 (d, $J = 6.22$ Hz, 2 H. Ar), 7.49 (dd, $J = 8.38$, 1.60 Hz, 4 H. Ar), 7.51 - 7.57 (m, 2 H. Ar), 8.57 (d, $J = 5.84$ Hz, 2 H. Ar (adj. to N)). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 25.90, 28.95, 29.12, 31.38, 35.43, 55.34, 68.00, 114.15, 114.83, 120.65, 123.55, 126.60, 127.98, 128.40, 128.68, 128.81, 132.81, 133.68, 133.82, 134.22, 141.16, 145.05, 150.09, 158.92, 159.75. Elemental Analysis: Calculated for C$_3$I$_2$H$_4$O$_2$: C 82.90 %, H 7.17 %, N 3.02 %, Found: C 82.61 %, H 7.15 %, N 2.99 %.

CB6OS M.P. = 129 °C. IR $\tilde{\nu}$ cm$^{-1}$: 2929, 2858, 2225 (C≡N stretch), 1592, 1251, 1174, 814, 535. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm: 7.43 (d, $J = 5.1$ Hz, 2H, Ar), 7.71 (q, $J = 8.2$ Hz, 4H, Ar), 7.51 (m, 4H, Ar), 7.42 - 7.20 (m, 5H, Ar, ArCHCHAr), 7.00 - 6.82 (m, 3H, Ar, ArCHCHAr), 4.01 (t, $J = 6.5$ Hz, 2H, ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 2.71 (t, $J = 7.7$ Hz, 2H, ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 1.84 (p, $J = 6.8$ Hz, 2H, ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 1.73 (p, $J = 7.6$ Hz, 2H, ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 1.65 - 1.38 (m, 4H, ArCH$_2$CH$_2$CH$_2$CH$_2$OAr). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm: 159.72, 150.12, 145.56, 145.00, 143.52, 136.53, 132.75, 132.57, 129.20, 128.75, 128.39, 127.48, 127.11, 123.63, 120.62, 119.04, 114.83, 110.57, 67.98, 35.52, 31.27, 29.15, 28.97, 25.91. Elemental Analysis: Calculated for C$_3$I$_2$H$_4$O$_2$: C 83.81 %, H 6.59 %, N 6.11 %, Found: C 83.33 %, H 6.76 %, N 5.88 %.

CB6OBA M.P. = 162 °C; T$_{M1}$ = 197 °C; T$_{NTBN}$ = 159 °C. IR $\tilde{\nu}$ cm$^{-1}$: 3000-2250 (broad, OH), 2932, 2853, 2228 (C≡N stretch), 1679 (C=O carboxylic acid), 1606 (para di-substituted benzene), 1430, 1295, 1255, 1168, 982, 845, 813, 769, 646, 545. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm: 1.40 - 1.62 (m, 4 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 1.72 (p, $J = 7.58$ Hz, 2 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 1.79 - 1.92 (m, 2H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 2.71 (t, $J = 7.63$ Hz, 2 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 4.05 (t, $J = 6.40$ Hz, 2 H. ArCH$_2$CH$_2$CH$_2$CH$_2$OAr), 6.90 - 7.00 (m, 2 H. Ar), 7.31 (d, $J = 8.29$ Hz, 2 H H, Ar), 7.53 (d, $J = 8.29$ Hz, 2 H. Ar), 7.65 - 7.77 (m, 4 H. Ar), 8.02 - 8.10 (m, 2 H. Ar). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm: 25.84, 28.90, 28.98, 31.24, 35.49, 68.13, 110.56, 114.19, 119.06, 121.40, 127.12, 127.48, 129.20, 132.35, 132.59, 136.55, 143.47, 145.56, 163.61, 171.65.

References

