Electronic Supplementary Information for:

The detection of chiral perturbations in ferroelectric liquid crystals induced by dopants with axially chiral 2,2'-spirobiindan-1,1'-dione cores

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1. EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers; chemical shifts are reported in δ (ppm) relative to tetramethylsilane. Low-resolution mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer or an Applied Biosystems/MDS Sciex QSTAR XL QqTOF mass spectrometer. Peaks are reported as *m/z* (percent intensity relative to the base peak). High resolution EI mass spectra were recorded on a Waters/Micromass GCT mass spectrometer, and high resolution ESI mass spectra were recorded on an Applied Biosystems/MDS Sciex QSTAR XL QqTOF mass spectrometer. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Flash chromatography was performed using 60 Å silica gel (Silicycle Inc., Quebec) as the adsorbent. All final dopant molecules were recrystallized from HPLC grade hexanes after being passed through a 0.45μm PTFE membrane.

***Trans*-4-(4-chlorophenyl)cyclohexanecarbonitrile (6)**.[1] Conc. H_2SO_4 (10 mL) was slowly added at room temperature to a solution of *trans*-4-(4-chlorophenyl)cyclohexanecarboxylic acid (**5**, 5.0 g, 21 mmol) in MeCN (100 mL). The mixture was heated to reflux for 4h, then concentrated and diluted with $CHCl_3$ (200 mL). The solution was washed with water and 5% aq. $NaHCO_3$, dried ($MgSO_4$) and concentrated. Recrystallization from $CHCl_3$ and hexanes gave 2.53 g (55%) of **6** as an off-white solid: m.p. 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8 Hz, 2H), 7.12 (d, J = 8 Hz, 2H), 2.50 (m, 2H), 2.28 (m, 2H), 1.72 (m, 2H), 1.39 (m, 2H); MS (TOF-MS) *m/z* 219 (M^+, 41), 221 (M+2, 14); HRMS (TOF-MS) calc'd for $C_{13}H_{14}NCl$ 219.0815, found 219.0813.

4-(4-Chlorophenyl)-1-hexylcyclohexanecarbonitrile-d_2 (7). Under an Ar atmosphere, a 2.0 M solution of LDA in hexanes (10 mL, 20 mmol) was added dropwise to a solution of **6** (2.5 g, 11 mmol) in THF (80 mL) cooled to -15 °C. After stirring for 10 min at -15 °C, 1-bromohexane-1,1-d_2 (2 mL, 17 mmol) was added, and the mixture was allowed to warm to room temperature over 12 h, and further heated to 60 °C for 2 h. The mixture was concentrated, poured into 10% aq. HCl and extracted with Et_2O (3 × 100 mL). The combined extracts were washed with H_2O (2 × 100 mL), brine (2 × 100 mL), dried ($MgSO_4$) and concentrated to give an orange oil. Purification by flash chromatography on silica gel (4:1 hexanes/CH_2Cl_2) and recystallization from hexane gave 2.5 g (75%) of **7** as a white solid: m.p. 53-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8 Hz, 2H), 7.17 (d, J = 8 Hz, 2H), 2.46 (m, 1H), 2.14 (d, J = 13 Hz, 2H), 1.84 (m, 4H), 1.53 (m, 2H), 1.38 (m, 8H), 0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 22.9, 24.7, 29.6, 29.6, 31.1, 31.9, 36.1, 38.9, 43.5, 123.8, 128.5, 128.9, 132.3,144.7; MS (TOF-MS) *m/z* 305 (M^+, 80), 307 (M+2, 22); HRMS (TOF-MS) calc'd for $C_{19}H_{24}D_2NCl$ 305.1879, found 305.1890.

4-(4'-Heptyl[1,1'-biphen]-4-yl)-1-hexylcyclohexanecarbonitrile-d_2 (NCB76-d_2).[2] Under an Ar atmosphere, a 100 mL Schlenk flask was charged with $Pd(OAc)_2$ (22 mg, 0.1 mmol), 2-(dicyclohexylphosphino)biphenyl (60 mg, 0.2 mmol), 4-heptylphenylboronic acid (2.2 g, 10 mmol), **7** (2.0 g, 6.7 mmol), and K_3PO_4 (4.2 g, 20 mmol). Toluene (30 mL) was added to the flask after the second evacuation/backfill cycle. The mixture was evacuated and backfilled with Ar for another three cycles and was stirred at room temperature for 4 h and then heated to 110 °C overnight. The reaction mixture was cooled to room temperature, diluted with ether, and filtered through a short plug of silica gel. The solid residue was washed with ether and the combined filtrate was washed with aq. NaOH (1M, 200 mL), water, brine, dried ($MgSO_4$) and concentrated. Purification by flash chromatography on silica gel (4:1 hexanes/CH_2Cl_2) gave **NCB76-d_2** as a yellow oil (3.0 g, 60 %). The product was recrystallized from absolute EtOH three times and was filtered through a 0.45 μm PTFE filter before a final recrystallization to give a white solid: Cr 66 SmC 73 SmA 117 N 125 I; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 8 Hz, 2H), 7.52 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 7.26 (d, J = 8 Hz, 2H), 2.66 (t, J = 8 Hz, 2H), 2.54 (m, 1H), 2.18 (d, J = 13 Hz, 2H), 1.94 (m, 4H), 1.67 (m, 2H), 1.55 (m, 2H), 1.41 (m, 16H), 0.92 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 14.5, 23.0, 23.1, 24.8, 29.6, 29.8, 31.3, 31.9, 32.0, 32.2, 36.0, 36.4, 39.0, 43.9, 124.0, 127.2, 127.5, 127.6, 129.2, 138.7, 139.7, 142.3, 145.1; MS (TOF-MS) *m/z* 445 (M^+, 100); HRMS (TOF-MS) calc'd for $C_{32}H_{43}D_2N$ 445.3678, found 445.3682.

1-Octanol-2,2-d_2. Under an Ar atmosphere, a solution of octanoic acid-2,2-d_2 (0.15 mL, 0.57 mmol) in Et_2O (16 mL) was added dropwise to a suspension of $LiAlH_4$ (110 mg, 2.87 mmol) in Et_2O (8 mL), and the reaction mixture was refluxed for 24 h. Note: octanoic acid-2,2-d_2 was stored under an Ar atmosphere over 3 Å molecular sieves overnight prior to use. After cooling to room temperature, the mixture was quenched (1:2 MeOH/Et_2O), acidified with 5 % aq H_2SO_4 and extracted with Et_2O (3×). The combined organic extracts were washed with water, 5 % aq $NaHCO_3$, dried ($MgSO_4$) and concentrated to give 45 mg (60 %) of 1-octanol-2,2-d_2 as a clear oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 2H), 1.28 (s, 10H), 0.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.5, 29.3, 29.3, 31.8, 32.0 (quintet, J = 19 Hz), 63.0.

(*RS*)-6,6'-Dioctyloxy-2,2'-spirobiindan-1,1'-dione-d_2 ((*RS*)-3-β-d_4). Under an Ar atmosphere, a solution of 1-octanol-2,2-d_2 (77 mg, 0.58 mmol) in THF (2 mL) was added to a stirred solution of (*RS*)-6,6'-dihydroxy-2-2'-spirobiindan-1,1'-dione[3] (59 mg, 0.21 mmol) and Ph_3P (131 mg, 0.50 mmol) in THF (5 mL). After 5 minutes, DIAD (101 mg, 0.50 mmol) was added and the solution was stirred at room temperature overnight. The solution was concentrated and the residue purified by flash chromatography on silica gel (4:1 hexanes/EtOAc), then recrystallized from hexanes after filtration through a 0.45 μm PTFE membrane to give 71 mg (66 %) of (*RS*)-**3**-β-d_4 as a white solid: m.p. 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 9 Hz, 2H), 7.22 (m, 2H), 7.15 (s, 2H), 3.95 (s, 4H), 3.61 (d, J = 16 Hz, 2H), 3.09 (d, J = 16 Hz, 2H), 1.41 (m, 4H), 1.28 (m, 16H), 0.88 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.8, 28.3 (quintet, J = 18 Hz), 29.2, 29.2, 31.8, 37.5, 66.7, 68.4, 106.6, 125.1, 126.9, 136.6, 146.5, 159.2, 202.8; MS (TOF-MS) *m/z* 508 (M^+, 100); HRMS (TOF-MS) calc'd for $C_{33}H_{40}D_4O_4$ 508.3491, found 508.3470.

References

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