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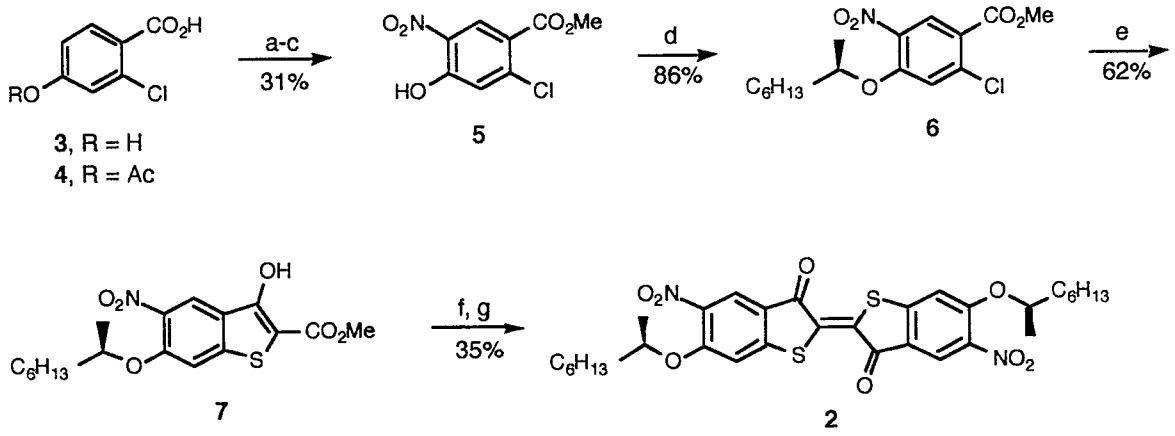

(a) Ac_2O; (b) HNO_3, AcOH; (c) CH_3OH, H_2SO_4; (d) (*S*)-2-octanol, DIAD, Ph_3P, CH_2Cl_2; (e) $HSCH_2CO_2Me$, LiOH, DMF, 25 °C; (f) 15% KOH, EtOH, H_2O; (g) $K_3Fe(CN)_6$

General. ^1H and ^{13}C NMR spectra were recorded on a Bruker ACF-200 NMR spectrometer in deuterated chloroform or deuterated acetone. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low-resolution EI and CI mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer; peaks are reported as m/e (% intensity relative to the base peak). High-resolution EI mass spectra were performed by the University of Ottawa Regional Mass Spectrometry Center. UV-visible spectra were recorded on a Varian Cary 3 spectrophotometer in benzene. Melting points were measured on a Mel-Temp II melting point apparatus and are uncorrected.

Materials. All reagents were obtained from commercial sources and used without further purification unless otherwise noted. Dimethylformamide (DMF) was distilled from BaO under reduced pressure and stored over molecular sieves. Methylene chloride (CH_2Cl_2) was distilled from P_2O_5 under N_2. 2-Chloro-4-hydroxybenzoic acid (**3**) was prepared according to the published procedure (Molnar, I.; Wagner-Jauregg, T. *Helv. Chim. Acta* **1969**, *52*, 401), and shown to have the expected physical and spectral properties.

Methyl 2-chloro-4-hydroxy-5-nitrobenzoate (5). A solution of **3** (1.55 g, 9.0 mmol) in acetic anhydride (5 mL) was heated on a steam bath for 30 min, then poured over ice and filtered in a Buchner funnel. The solid residue was washed with water and air dried to give 1.76 g of the acetoxy derivative **4**. Without further purification, compound **4** was dissolved in a mixture of 95% HNO_3 (15 mL) and glacial AcOH (15 mL) and stirred at 25 °C for 24 h. The mixture was then concentrated *in vacuo*, and the yellow residue was dissolved in a mixture of MeOH (20 mL) and conc. H_2SO_4 (0.5 mL) and refluxed overnight. After cooling, the mixture was poured into H_2O and extracted with ether (2×). The combined extracts were washed with H_2O, brine, then dried ($MgSO_4$) and concentrated. Purification by flash chromatography on silica gel (30% EtOAc/toluene) gave 0.64 g (31%) of **5** as a yellow solid: mp 94-95 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 3.91 (s, 3H), 7.36 (s, 1H), 8.64 (s, 1H), 10.8 (s, OH); ^{13}C NMR (50 MHz, acetone-d_6) δ 52.9, 122.3, 122.9, 130.0, 134.0, 142.3, 157.0, 164.1; MS (EI) m/e 233 (M+2, 6), 231 (M+, 18), 202 (35), 200 (100), 170 (5), 156 (15), 154 (38), 142 (8), 126 (13), 113 (6), 97 (12); HRMS (EI) calcd for $C_8H_6NO_5{}^{37}Cl$: 232.9905. Found: 232.9888.

Methyl (*R*)-2-chloro-4-(1-methylheptyloxy)-5-nitrobenzoate (6). Under a N_2 atmosphere, diisopropylazodicarboxylate (DIAD, 202 mg, 0.99 mmol) was added dropwise to a stirred solution of **5** (153 mg, 0.66 mmol), Ph_3P (260 mg, 0.99 mmol) and (*S*)-2-octanol (90 mg, 0.69 mmol) in dry CH_2Cl_2 (10 mL). After stirring at 25 °C for 2 h, the solvent was removed *in vacuo*, and the oily residue was purified by flash chromatography on silica gel (30% EtOAc/toluene) to give 195 mg (86%) of **6** as a yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 6.6 Hz, 3H), 1.20-1.80 (m, 10H), 1.38 (d, J = 6.0 Hz, 3H), 3.92 (s, 3H), 4.56 (m, J = 6.0 Hz, 1H), 7.10 (s, 1H), 8.45 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.3, 22.5, 25.0, 29.0, 31.6, 36.0, 52.6, 77.6, 117.6, 120.5, 129.5, 138.0, 140.3, 154.0, 163.6; MS (CI) m/e 346 (M+3, 32), 344 (M+1, 100), 316 (22), 314 (67), 301 (13), 299 (36), 279 (17), 262 (35), 260 (96), 234 (25), 232 (69), 201 (6), 149 (4), 91 (16); HRMS (EI) calcd for $C_{15}H_{19}NO_4{}^{35}Cl$ (M–OCH_3): 312.1001. Found: 312.1004.

Methyl (*R*)-3-hydroxy-6-(1-methylheptyloxy)-5-nitrobenzo[*b*]thiophene-2-carboxylate (7). Under a N_2 atmosphere, a mixture of **6** (197 mg, 0.57 mmol), anhydrous LiOH (48 mg, 2 mmol) and methyl thioglycolate (91 mg, 0.86 mmol) in dry DMF (10 mL) was stirred overnight at 25 °C. The mixture was poured into H_2O (40 mL), acidified with 3M HCl and extracted with EtOAc (3×). The combined extracts were washed with 1M HCl (2×), brine, dried ($MgSO_4$) and concentrated to give a yellow oil. Purification by flash chromatography on silica gel (30% EtOAc/toluene) gave 135 mg (62%) of **7** as a yellow waxy solid: mp 54-55 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 6.7 Hz, 3H), 1..24-1.80 (m, 10H), 1.39 (d, J = 6.2 Hz, 3H), 3.95 (s, 3H), 4.54 (m, J = 6.0 Hz, 1H), 7.26 (s, 1H), 8.31 (s, 1H), 10.1 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.2, 22.6, 25.2, 29.1, 31.7, 36.1, 52.3, 77.0, 101.5, 107.8, 120.1, 122.3, 140.0, 143.5, 151.7, 159.2, 166.8; MS (CI) m/e 382 (M+1, 3), 270 (100), 232 (98), 212 (18), 202 (48), 149 (12), 113 (19); HRMS (EI) calcd for $C_{18}H_{23}NO_6S$: 381.1246. Found: 381.1252.

(*R,R*)-6,6'-Bis(1-methylheptyloxy)-5,5'-dinitrothioindigo (2). A suspension of **7** (153 mg, 0.36 mmol) in a 15% solution of KOH in 1:1 EtOH/H_2O (15 mL) was heated to reflux for 5h. After cooling to room temperature, the mixture was treated with 300 mg of $K_3[Fe(CN)_6]$ dissolved in H_2O (2 mL) and stirred for 1 h. After removing the alcohol *in vacuo*, the mixture was extracted with $CHCl_3$ (2×), and the combined extracts were washed with H_2O, dried ($MgSO_4$) and concentrated to a red solid. Purification by flash chromatography on silica gel (benzene) gave 40 mg (35%) of **7** as a red solid. The compound was further purified for doping experiments by recrystallization from 15% $CHCl_3$/hexanes: mp 189-190 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 6H), 1.15-1.85 (m, 20H), 1.44 (d, J = 6.1 Hz, 6H), 4.66 (m, J = 6.0 Hz, 2H), 7.12 (s, 2H), 8.37 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.3, 22.5, 25.1, 29.0, 31.6, 36.0, 78.1, 109.0, 120.3, 124.4, 133.1, 139.6, 154.6, 157.6, 186.8; MS (EI) m/e 642 (M^+, 1), 418 (100), 388 (4), 372 (5), 359 (2), 326 (2), 253 (2), 208 (4), 165 (16), 111 (26), 83 (59); HRMS (EI) calcd for $C_{32}H_{38}N_2O_8S_2$: 642.2070. Found: 642.2044.