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Electronic Supporting Information

The Influence of Alkoxy Chain Length on the Ferroelectric Properties of Chiral Fluorenol Liquid Crystals

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1. General Information

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise indicated) using a Bruker AV-400 spectrometer. Chemical shifts (δ) are reported as parts per million (ppm) relative to tetramethylsilane internal standard. Low resolution mass spectrometry (LRMS) and high resolution mass spectrometry (HRMS) were performed using either a Waters/Micromass GC-TOF system for electron ionization (EI) or an Applied Biosciences / MDS Sciex QSTAR XL QqTOF spectrometer for chemical ionization (CI). Differential scanning calorimetry analyses were performed using a Perkin-Elmer DSC-7 instrument with a scanning rate of 5 K/min. Texture analyses were performed using a Nikon Eclipse E600 POL polarized microscope fitted with a Linkam LTS 350 hot stage and TMS 93 temperature controller. Chiral liquid crystal materials were introduced into rubbed-polyimide coated ITO glass slides with a 4.0 μm spacing and a 0.16 cm^2 addressed area. As described in the main report, samples were aligned by slow cooling from the isotropic phase (1 K/min) while applying a 3 V/μm dc field. Spontaneous polarization measurements were measured as a function of temperature using the triangular wave method (6 V/μm, 100 Hz; application of higher fields at slower frequencies gave no change to the reported values). Tilt angles (θ) were determined by polarized microscopy as half the rotation between the two extinction positions corresponding to opposite signs of the applied field. The sign of P_S along the polar axis was assigned from the relative configuration of the electric field and the switching position of the sample according to the established convention.

2. Synthesis and Characterization

(a) 1-(4-Alkoxybenzoyl)benzotriazoles.

All benzotriazoles were synthesized using the procedure for 1-(4-undecyloxybenzoyl)-benzotriazole described in our previous report.[1] Yields were on the order of 60-70%, and characterization data are provided below.

1-(4-Butyloxybenzoyl)benzotriazole. ^{1}H NMR: δ 8.37 (d, J = 8.3 Hz, 1H), 8.29 (d, J = 9.1 Hz, 2H), 8.16 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.3 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 4.09 (t, J = 6.6 Hz, 2H), 1.83 (m, J = 7.1 Hz, 2H), 1.53 (m, J = 7.5 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H); ^{13}C NMR: δ 165.7, 163.9, 145.6, 134.4, 132.6, 130.1, 126.1, 123.1, 120.0, 114.8, 114.3, 68.1, 31.1, 19.2, 13.8; LRMS (EI): m/z 295 (M^{+}, 5), 211 (39), 121 (100); HRMS (EI): 295.1321 (calculated), 295.1321 (found).

1-(4-Hexyloxybenzoyl)benzotriazole. ^{1}H NMR: δ 8.30 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.9 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.3 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.76 (m, J = 7.3 Hz, 2H), 1.41 (m, J = 7.3 Hz, 2H), 1.28 (m, 4H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR: δ 165.7, 163.9, 145.7, 134.4, 132.6, 130.2, 126.1, 123.1, 120.1, 114.8, 114.4, 68.5, 31.5, 29.0, 25.7, 22.6, 14.0; LRMS (EI): m/z 323 (M^{+}, 4), 295 (20), 211 (100), 205 (74), 138 (21), 121 (61); HRMS (EI): 323.1634 (calculated), 323.1635 (found).

1-(4-Octyloxybenzoyl)benzotriazole. ^{1}H NMR: δ 8.36 (d, J = 8.3 Hz, 1H), 8.28 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 8.1 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 8.6

Hz, 2H), 4.07 (t, J = 6.6 Hz, 2H), 1.83 (m, J = 7.0 Hz, 2H), 1.48 (m, 2H), 1.30 (m, 8H), 0.90 (t, J = 6.5 Hz, 3H); ^{13}C NMR: δ 165.7, 163.9, 145.7, 134.4, 132.6, 130.1, 126.1, 123.1, 120.1, 114.8, 114.3, 68.4, 31.8, 29.3, 29.2, 29.0, 26.0, 22.6, 14.1; LRMS (EI): m/z 351 (M^+, 50), 323 (43), 233 (100), 211 (88), 121 (89), 91 (62), 64 (60); HRMS (EI): 351.1947 (calculated), 351.1954 (found).

1-(4-Tridecyloxybenzoyl)benzotriazole. ^{1}H NMR: δ 8.28 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.1 Hz, 1H), 7.57 (t, J = 8.1 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.6 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 1.75 (m, J = 7.0 Hz, 2H), 1.40 (m, 2H), 1.20 (m, 18H), 0.79 (t, J = 6.5 Hz, 3H); ^{13}C NMR: δ 165.7, 163.9, 145.7, 134.4, 132.6, 130.1, 126.1, 123.1, 120.1, 114.8, 114.3, 68.4, 31.8, 30-29 several overlapping peaks, 26.0, 22.6, 14.1; LRMS (EI): m/z 421 (M^+, 30), 395 (67), 322 (74), 304 (86), 212 (100), 121 (86); HRMS (EI): 421.2729 (calculated), 421.2720 (found).

1-(4-Pentadecyloxybenzoyl)benzotriazole. ^{1}H NMR: δ 8.28 (d, J = 8.3 Hz, 1H), 8.20 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.1 Hz, 1H), 7.57 (t, J = 8.1 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.6 Hz, 2H), 3.99 (t, J = 6.6 Hz, 2H), 1.75 (m, J = 7.0 Hz, 2H), 1.40 (m, 2H), 1.18 (m, 22H), 0.79 (t, J = 6.5 Hz, 3H); ^{13}C NMR: δ 165.7, 163.9, 145.7, 134.4, 132.6, 130.1, 126.1, 123.1, 120.1, 114.9, 114.4, 68.5, 31.9, 30-29 several overlapping peaks, 26.0, 22.7, 14.1; LRMS (EI): m/z 449 (M^+, 22), 331 (100), 211 (94), 121 (97); HRMS (EI): 449.3042 (calculated), 449.3024 (found).

(b) 2-Hydroxy-7-alkoxy-fluoren-9-ones (**7a-f**)

2-hydroxy-7-octyloxy-fluoren-9-one (**7a**). To a dry flask containing **6** (0.67 g, 3.2 mmol) was added 1-bromooctane (0.61 g, 3.2 mmol), K_2CO_3 (0.44 g, 3.2 mmol) and DMF (25 mL). The

resulting dark red solution was stirred overnight (17 h) at room temperature. The reaction mixture was quenched by adding saturated aqueous NH_4Cl solution (25 mL), then poured into a separatory funnel with water (50 mL) and ethyl acetate (100 mL). The layers were separated, and the aqueous portion was extracted with ethyl acetate (2 x 50 mL). The combined organics were washed with brine (2 x 50 mL), dried with $MgSO_4$, and concentrated to give a red residue. Purification by flash chromatography on silica (33% ethyl acetate / hexanes) provided the desired monoalkylated product as a red solid (0.39 g, 34 %). The characterization of this compound has been reported previously.[2] The other five 2-hydroxy-7-alkoxy-fluoren-9-ones were prepared using the same procedure, and their characterization data are reported below.

2-Hydroxy-7-undecyloxy-fluoren-9-one (**7b**). ^{1}H NMR: δ 7.27 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.92 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 6.87 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 1.78 (m, J = 7.0 Hz, 2H), 1.45 (m, 2H), 1.20 (m, 14H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR: δ 193.7, 160.4, 158.8, 138.3, 137.1, 136.8, 136.6, 121.9, 121.7, 121.3, 112.0, 110.8, 69.1, 32.6, 30.3, 29.3, 28.9, 26.7, 23.3, 14.3; LRMS (EI): m/z 366 (M^+, 17), 212 (100); HRMS (EI): 366.2195 (calculated), 366.2198 (found).

2-Hydroxy-7-hexyloxy-fluoren-9-one (**7c**). ^{1}H NMR: δ 7.27 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.92 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 6.87 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 1.77 (m, 2H), 1.44 (m, 2H), 1.20 (m, 4H), 0.87 (t, 3H); ^{13}C NMR: δ 193.7, 160.4, 158.8, 138.3, 137.1, 136.8, 136.6, 121.9, 121.7, 121.3, 112.0, 110.8, 69.1, 32.6, 30.3, 26.7, 23.3, 14.3; LRMS (EI): m/z 296 (M^+, 32), 212 (100); HRMS (EI): 366.2195 (calculated), 366.2198 (found).

2-Hydroxy-7-tridecyloxy-fluoren-9-one (**7d**). ^{1}H NMR: δ 7.27 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.92 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 6.87 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 1.78 (m, J = 7.0 Hz, 2H), 1.45 (m, 2H), 1.20 (m, 18H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR: δ 193.7, 159.5, 156.3, 137.4, 137.3, 136.2, 135.8, 121.0, 120.9, 120.6, 120.4, 112.0, 110.2, 68.6, 31.9, 30.2, 30-29 several overlapping peaks, 26.0, 22.7, 14.1; LRMS (EI): m/z 394 (M^{+}, 34), 212 (100); HRMS (EI): 394.2508 (calculated), 394.2502 (found).

2-Hydroxy-7-butyloxy-fluoren-9-one (**7e**). ^{1}H NMR (acetone-d_6): δ 8.83 (s, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.96 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 6.87 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 1.73 (m, J = 7.3 Hz, 2H), 1.48 (m, J = 7.3 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (acetone-d_6): δ 193.8, 160.4, 158.7, 138.3, 137.2, 136.9, 136.6, 121.9, 121.5, 121.2, 120.6, 112.0, 110.8, 68.8, 32.0, 19.9, 14.2; LRMS (EI): m/z 268 (M^{+}, 44), 212 (100), 155 (30); HRMS (EI): 268.1099 (calculated), 268.1097 (found).

2-Hydroxy-7-pentadecyloxy-fluoren-9-one (**7f**). ^{1}H NMR: δ 7.27 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.92 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 6.87 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.4 Hz, 1H), 3.97 (t, J = 6.5 Hz, 2H), 1.78 (m, J = 7.0 Hz, 2H), 1.45 (m, 2H), 1.20 (m, 22H), 0.87 (t, J = 6.6 Hz, 3H); LRMS (EI): m/z 422 (16), 212 (100); HRMS (EI): 422.2821 (calculated), 422.2827 (found).

(c) (*R*) and (*S*)-2-Hydroxy-7-(alkoxy)fluoren-9-ols (**8a**-**f**)

(*R*)- and (*S*)-2-Hydroxy-7-octyloxy-fluoren-9-ol ((*R*)- and (*S*)-**8a**). To a solution of **7a** (290 mg, 0.86 mmol) in 1:1 Et_2O:MeOH (20 mL) was added solid $NaBH_4$ (65 mg, 2.0 equiv). The red solution was stirred for 30 min at room temperature, then diluted with saturated aqueous NH_4Cl solution and extracted twice with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated to give a colorless solid. Purification by flash chromatography on silica gel (30% ethyl acetate / hexanes) gave (*RS*)-**8a** (240 mg, 99%) as a colorless solid. The characterization of this compound has been reported previously.[2] The other five (*RS*)-2-hydroxy-7-alkoxy-fluoren-9-ols were prepared using the same procedure, and their characterization data are reported below. Resolution of each pair of enantiomers was achieved by preparatory scale HPLC on a Daicel Chiralpak AS column with a 55 mL/min flow rate. Isopropanol (IPA) - hexanes mixtures were used as eluants in all cases (20% IPA/hexanes for **8a**, **8b**, **8c**, **8e**, 10% IPA/hexanes for **8d** and **8f**), giving the (*S*)- (first eluted, >99% ee) and (*R*)-fluorenols (second eluted, >99% ee).

(*R*)- and (*S*)-2-Hydroxy-7-undecyloxy-fluoren-9-ol ((*R*)- and (*S*)-**8b**). ^{1}H NMR (methanol-d_4): δ 7.42 (d, J = 8.1 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 7.01 (d, J = 2.2 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 6.75 (d, J = 8.1 Hz, 1H), 5.37 (s, 1H), 4.00 (t, J = 6.3 Hz, 2H), 1.81 (m, 2H), 1.50 (m, 2H), 1.30 (m, 14H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (methanol-d_4): δ 159.8, 157.8, 148.8, 148.5, 134.4, 133.2, 120.7, 120.4, 116.5, 115.9, 113.4, 112.5, 75.3, 69.3, 33.1, 30-29 several overlapping peaks, 27.2, 23.7, 14.5; LRMS (EI): m/z 368 (M^+, 53), 214 (100), 197 (22); HRMS (EI): 368.2351 (calculated), 368.2356 (found).

(*R*)- and (*S*)-2-Hydroxy-7-hexyloxy-fluoren-9-ol ((*R*)- and (*S*)-**8c**). ^{1}H NMR (acetone-d_6): δ 8.22 (s, 1H), 7.33 (d, J = 8.3 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.00 (d, J = 2.1 Hz, 1H), 6.94 (d, J = 2.1 Hz, 1H), 6.74 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.2 Hz, 1H), 6.67 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.2 Hz, 1H), 5.29 (d, J = 7.8 Hz, 1H), 4.49 (d, J = 7.8 Hz, 1H), 3.89 (t, J = 6.6, 2H), 1.65 (m, J = 7.0, 2H), 1.36 (m, J = 7.6, 2H), 1.23 (m, 4H), 0.78 (t, J = 6.9 Hz, 3H); ^{13}C NMR (acetone-d_6): δ 159.4, 157.6, 149.4, 149.1, 133.8, 132.6, 120.6, 120.2, 116.0, 115.4, 113.3, 112.3, 75.2, 68.8, 32.4, 30.2, 26.51, 23.3, 14.3; LRMS (EI): m/z 298 (M^+, 90), 282 (50), 214 (100), 213 (75), 212 (63), 198 (76), 197 (85), 149 (43); HRMS (EI): 298.1569 (calculated), 298.1574 (found).

(*R*)- and (*S*)-2-Hydroxy-7-tridecyloxy-fluoren-9-ol ((*R*)- and (*S*)-**8d**). ^{1}H NMR (acetone-d_6): δ 7.43 (d, J = 8.3 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.13 (d, J = 2.3 Hz, 1H), 7.03 (d, J = 2.2 Hz, 1H), 6.87 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.3 Hz, 1H), 6.77 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.2 Hz, 1H), 5.39 (s, 1H), 4.01 (t, J = 6.3, 2H), 1.80 (m, J = 6.8, 2H), 1.48 (m, J = 7.6, 2H), 1.30 (m, 18H), 0.91 (t, J = 6.6 Hz, 3H); ^{13}C NMR (methanol-d_4): δ 159.9, 157.9, 148.9, 148.6, 134.5, 133.2, 120.8, 120.4, 116.5, 116.0, 113.4, 112.6, 75.3, 69.3, 33.1, 31-30 several overlapping peaks, 27.2, 23.8, 14.5; LRMS (EI): m/z 396 (M^+, 44), 394 (67), 212 (100); HRMS (EI): 396.2664 (calculated), 396.2663 (found).

(*R*)- and (*S*)-2-Hydroxy-7-butyloxy-fluoren-9-ol ((*R*)- and (*S*)-**8e**). ^{1}H NMR (acetone-d_6): δ 8.42 (s, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.16 (d, J = 2.1 Hz, 1H), 7.11 (d, J = 2.1 Hz, 1H), 6.88 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.2 Hz, 1H), 6.83 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.2 Hz, 1H), 5.44 (d, J = 7.8 Hz, 1H), 4.72 (d, J = 7.8 Hz, 1H), 4.02 (t, J = 6.6, 2H), 1.77 (m, J = 7.1, 2H), 1.52 (m, J = 7.6, 2H), 0.99 (t, J = 6.9 Hz, 3H); ^{13}C NMR (acetone-d_6): δ 159.4, 157.6, 149.4, 149.0, 133.8, 132.6, 120.6, 120.2, 116.1, 115.4, 113.3, 112.3, 75.1, 68.5, 32.2, 20.0, 14.2; LRMS (EI): m/z 270

(42), 214 (68), 213 (35), 197 (33), 43 (100); HRMS (EI): 270.1256 (calculated), 270.1261 (found).

(*R*)- and (*S*)-2-Hydroxy-7-pentadecyloxy-fluoren-9-ol ((*R*)- and (*S*)-**8f**). ^{1}H NMR (acetone-d_6): δ 8.85 (s, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 1.8 Hz, 1H), 7.09 (d, J = 1.5 Hz, 1H), 6.87 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.1 Hz, 1H), 6.77 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.1 Hz, 1H), 5.41 (d, J = 7.6 Hz, 1H), 5.00 (d, J = 7.5 Hz, 1H), 4.02 (t, J = 6.6 Hz, 2H), 1.80 (m, J = 6.6 Hz, 2H), 1.48 (m, 2H), 1.20 (m, 22H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (acetone-d_6): δ 159.3, 158.0, 149.5, 149.2, 133.9, 132.3, 120.5, 120.1, 116.1, 115.4, 113.4, 112.4, 75.1, 68.8, 32.7, 31-30 several overlapping peaks, 26.9, 23.4, 14.4; LRMS (EI): m/z 424 (M^{+}, 100), 214 (92), 84 (52), 66 (80); HRMS (EI): 424.2977 (calculated), 424.2968 (found).

(d) (*R*)-7-(1-Alkoxy)-2-((4-alkoxybenzoyl)oxy)fluoren-9-ols ((*R*)-**3a**-**f**)

All (*R*)-7-(1-Alkoxy)-2-((4-alkoxybenzoyl)oxy)fluoren-9-ol liquid crystals were synthesized from the corresponding (*S*)-2-Hydroxy-7-alkoxy-fluoren-9-ols using the procedure for (*R*)-**3a** described in our previous report.[2] Yields were on the order of 60-70%, and characterization data are provided below.

(*R*)-7-(1-Undecyloxy)-2-((4-octyloxybenzoyl)oxy)fluoren-9-ol ((*R*)-**3b**). ^{1}H NMR: δ 8.06 (d, J = 8.9 Hz, 2H), 7.46 (d, J = 8.2 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.36 (d, J = 1.7 Hz, 1H), 7.11 (d, J = 1.5 Hz, 1H), 7.08 (dd, ^{3}J = 8.3 Hz, ^{4}J = 2.0 Hz), 6.90 (d, J = 9.0 Hz, 2H), 6.84 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.3 Hz, 1H), 5.44 (s, 1H), 3.97 (t, J = 6.6 Hz, 2H), 3.93 (t, J = 6.6 Hz, 2H), 1.84 (s, 1H), 1.73 (m, 4H), 1.42 (m, 4H), 1.20 (m, 22H), 0.83 (m, 6H); ^{13}C NMR: δ 165.2, 163.6, 159.5, 150.0, 147.7, 146.7, 137.7, 132.3, 131.8, 122.4, 121.5, 120.7, 119.6, 119.0, 115.7, 114.3, 111.2, 74.9, 68.4, 68.3, 31.9, 31.8, 30-29 several overlapping peaks, 26.04, 25.97, 22.7, 22.6, 14.10, 14.08;

LRMS (EI): m/z 600 (M^+, 21), 233 (100), 213 (10), 121 (80); HRMS (EI): 600.3815 (calculated), 600.3791 (found).

(*R*)-7-(1-Hexyloxy)-2-((4-tridecyloxybenzoyl)oxy)fluoren-9-ol ((*R*)-**3c**). ^{1}H NMR: δ 8.07 (d, 8.9 Hz, 2H), 7.47 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 1.8 Hz, 1H), 7.12 (d, J = 1.8 Hz, 1H), 7.10 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, 1H), 6.91 (d, J = 8.9 Hz, 2H), 6.85 (dd, ^{3}J = 8.2 Hz, ^{4}J = 2.1 Hz, 1H), 5.45 (s, 1H), 3.97 (t, J = 6.6 Hz, 2H), 3.94 (t, J = 6.5 Hz, 2H), 1.75 (m, 4H), 1.41 (m, 4H), 1.20 (m, 22H), 0.85 (t, J = 6.9 Hz, 3H), 0.81 (t, J = 6.8 Hz, 3H); ^{13}C NMR: δ 165.2, 163.6, 150.0, 147.7, 146.7, 137.8, 132.3, 131.9, 122.5, 121.5, 120.7, 119.6, 119.0, 115.7, 114.3, 111.3, 75.0, 68.4, 68.3, 31.9, 31.6, 30-29 several overlapping peaks, 26.0, 25.8, 22.7, 22.6, 14.1, 14.0; LRMS (EI): m/z 600 (25), 303 (100), 212 (63), 121 (73); HRMS (EI): 600.3815 (calculated), 600.3813 (found).

(*R*)-7-(1-Tridecyloxy)-2-((4-hexyloxybenzoyl)oxy)fluoren-9-ol ((*R*)-**3d**). ^{1}H NMR: δ 8.06 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 8.3 Hz, 1H), 7.36 (d, J = 1.5 Hz, 1H), 7.11 (s, 1H), 7.9 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.9 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 6.84 (dd, ^{3}J = 8.3 Hz, ^{4}J = 2.2 Hz, 1H), 5.44 (s, 1H), 3.97 (t, J = 6.6 Hz, 2H), 3.93 (t, J = 6.5 Hz, 2H), 1.84 (s, 1H), 1.73 (m, 4H), 1.45 (m, 4H), 1.20 (m, 22H), 0.85 (t, J = 6.9 Hz, 3H), 0.81 (t, J = 6.9 Hz, 3H); ^{13}C NMR: δ 165.2, 163.6, 159.5, 150.0, 147.7, 146.8, 137.8, 132.3, 131.8, 122.4, 121.5, 120.7, 119.6, 119.0, 115.7, 114.3, 111.3, 75.0, 68.4, 68.3, 31.9, 31.6, 30-29 several overlapping peaks, 26.1, 25.7, 22.6, 14.2, 14.0; LRMS (EI): m/z 600 (13), 396 (99), 214 (100), 197 (98), 121 (45); HRMS (EI): 600.3815 (calculated), 600.3801 (found).

(*R*)-7-(1-Butyloxy)-2-((4-pentadecyloxybenzoyl)oxy)fluoren-9-ol ((*R*)-**3e**). ^{1}H NMR: δ 8.07 (d, J = 8.9 Hz, 2H), 7.48 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 1.7 Hz, 1H), 7.12 (d, J = 1.5 Hz, 1H), 7.08 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.8 Hz), 6.91 (d, J = 8.9 Hz, 2H), 6.82 (dd, ^{3}J = 8.4 Hz, ^{4}J = 2.3 Hz, 1H), 5.42 (d, J = 8.6 Hz, 1H), 3.97 (t, J = 6.6 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 2.06 (d, J = 8.6 Hz, 1H), 1.73 (m, 4H), 1.43 (m, 4H), 1.20 (m, 22H), 0.92 (t, J = 6.8 Hz, 3H), 0.81 (t, J = 6.6 Hz, 3H); ^{13}C NMR: δ 165.2, 163.6, 159.6, 150.1, 147.7, 146.8, 137.8, 132.3, 131.9, 122.5, 121.5, 120.7, 119.7, 119.0, 115.8, 114.4, 111.3, 75.1, 68.4, 68.1, 32.0, 31.4, 30-29 several overlapping peaks, 26.0, 22.7, 19.3, 14.1, 13.9; LRMS (EI): m/z 600 (6), 331 (100), 212 (15), 121 (87); HRMS (EI): 600.3815 (calculated), 600.3820 (found).

(*R*)-7-(1-Pentadecyloxy)-2-((4-butyloxybenzoyl)oxy)fluoren-9-ol ((*R*)-**3f**). ^{1}H NMR: δ 8.07 (d, J = 8.9 Hz, 2H), 7.48 (d, J = 8.2 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 1.6 Hz, 1H), 7.12 (d, J = 1.6 Hz, 1H), 7.10 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.0 Hz), 6.91 (d, J = 8.8 Hz, 2H), 6.84 (dd, ^{3}J = 8.1 Hz, ^{4}J = 2.0 Hz, 1H), 5.45 (s, 1H), 3.99 (t, J = 6.6 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 1.74 (m, 4H), 1.44 (m, 4H), 1.19 (m, 22H), 0.93 (t, J = 7.3 Hz, 3H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 165.2, 163.6, 159.5, 150.0, 147.7, 146.8, 137.8, 132.3, 131.8, 122.4, 121.5, 120.7, 119.6, 119.0, 115.7, 114.3, 111.3, 74.9, 68.4, 68.0, 32.0, 31.2, 30-29 several overlapping peaks, 26.1, 22.7, 19.2, 14.2, 13.8; LRMS (EI): m/z 600 (2), 177 (100), 121 (28); HRMS (EI): 600.3815 (calculated), 600.3810 (found).

(e) 7-(1-Alkoxy)-2-((4-alkoxybenzoyl)oxy)fluoren-9-ones (**4a**-**f**).

7-(1-Octyloxy)-2-((4-undecyloxybenzoyl)oxy)fluoren-9-one (**4a**). To a solution of (*R*)-**3a** (70 mg, 0.12 mmol) in CH_2Cl_2 (10 mL) was added solid pyridinium chlorochromate (38 mg, 0.17 mmol). The solution was allowed to stir at room temperature for two hours, then diethyl ether

(30 mL) was added and the mixture was filtered through a short column of silica. The resulting yellow solution was concentrated to give **4a** as an orange solid (49 mg, 70 %), which was recrystallized from ethyl acetate / hexanes. The characterization of this compound has been reported previously.[2] The other five fluorenones were prepared using the same procedure, and their characterization data are reported below.

7-(1-Undecyloxy)-2-((4-octyloxybenzoyl)oxy)fluoren-9-one (**4b).** ^{1}H NMR: δ 8.05 (d, J = 8.9 Hz, 2H), 7.36 (s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.18 (dd, ^{3}J = 7.9 Hz, ^{4}J = 2.2 Hz, 1H), 7.11 (d, J = 2.5 Hz, 1H), 6.90 (d, J = 8.9 Hz, 3H), 3.97 (t, J = 6.5 Hz, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.72 (m, 4H), 1.38 (m, 4H), 1.20 (m, 22H), 0.82 (m, 6H); ^{13}C NMR: δ 192.8, 164.8, 163.8, 160.3, 151.0, 142.2, 136.4, 136.2, 135.8, 132.4, 127.7, 121.3, 121.1, 121.0, 120.2, 118.4, 114.4, 110.2, 68.6, 68.4, 31.9, 31.8, 30-29 several overlapping peaks, 26.0, 22.7, 14.1; HRMS (CI): 599.3736 (calculated for $[M+H]^{+}$), 599.3763 (found).

7-(1-Hexyloxy)-2-((4-tridecyloxybenzoyl)oxy)fluoren-9-one (**4c).** ^{1}H NMR: δ 8.05 (d, J = 8.8 Hz, 2H), 7.35 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.17 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.1 Hz, 1H), 7.11 (d, J = 2.1 Hz, 1H), 6.90 (d, J = 8.6 Hz, 3H), 3.97 (t, J = 6.5 Hz, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.72 (m, 4H), 1.39 (m, 4H), 1.20 (m, 22H), 0.81 (m, 6H); ^{13}C NMR: δ 192.8, 164.8, 163.8, 160.3, 151.0, 142.3, 136.4, 136.2, 135.8, 132.4, 127.7, 121.3, 121.1, 121.0, 120.2, 118.4, 114.4, 110.2, 68.6, 68.4, 32.0, 31.6, 30.9, 30-29 several overlapping peaks, 26.0, 25.7, 22.7, 22.6, 14.1, 14.0; HRMS (CI): 599.3736 (calculated for $[M+H]^{+}$), 599.3762 (found).

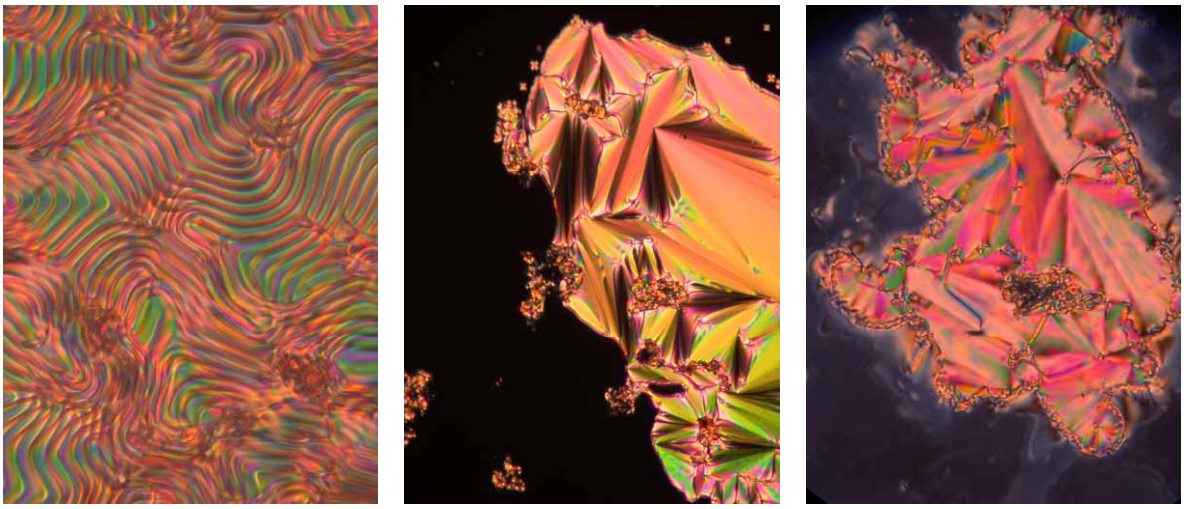
7-(1-Tridecyloxy)-2-((4-hexyloxybenzoyl)oxy)fluoren-9-one (**4d).** ^{1}H NMR: δ 8.05 (d, J = 8.8 Hz, 2H), 7.36 (s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.18 (dd, ^{3}J = 8.0 Hz, ^{4}J

= 2.1 Hz, 1H), 7.11 (d, J = 2.1 Hz, 1H), 6.90 (d, J = 8.7 Hz, 3H), 3.98 (t, J = 6.5 Hz, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.73 (m, 4H), 1.39 (m, 4H), 1.19 (m, 22H), 0.85 (m, 6H); ^{13}C NMR: δ 192.8, 164.8, 163.8, 160.3, 151.0, 142.2, 136.4, 136.2, 135.8, 132.4, 127.7, 121.3, 121.1, 121.0, 120.2, 118.4, 114.4, 110.2, 68.7, 68.4, 32.0, 31.6, 30-29 several overlapping peaks, 26.0, 25.7, 22.7, 22.6, 14.1, 14.0; HRMS (CI): 599.3736 (calculated for $[M+H]^+$), 599.3759 (found).

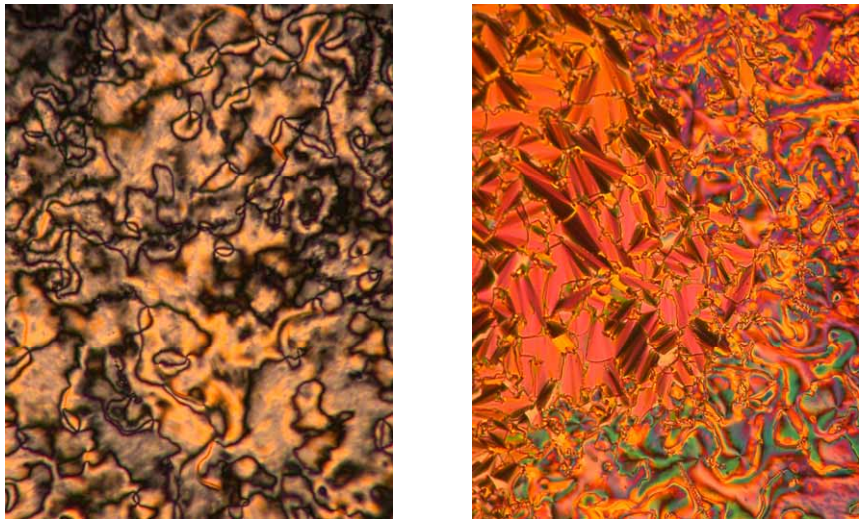
7-(1-Butyloxy)-2-((4-pentadecyloxybenzoyl)oxy)fluoren-9-one (**4e).** ^{1}H NMR: δ 8.05 (d, J = 8.7 Hz, 2H), 7.36 (s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 8.1 Hz), 7.18 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.2 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 6.90 (d, J = 8.8 Hz, 3H), 3.97 (t, J = 6.5 Hz, 2H), 3.94 (t, J = 6.5 Hz, 2H), 1.72 (m, 4H), 1.42 (m, 4H), 1.19 (m, 22H), 0.92 (t, J = 7.4 Hz, 3H), 0.81 (t, J = 6.9 Hz, 3H); ^{13}C NMR: δ 192.8, 164.8, 163.8, 160.3, 151.0, 142.3, 136.4, 136.2, 135.8, 132.4, 127.7, 121.3, 121.1, 121.0, 120.2, 118.4, 114.4, 110.2, 68.4, 68.3, 32.0, 31.2, 30-29 several overlapping peaks, 26.0, 22.7, 19.2, 14.1, 13.8; HRMS (CI): 599.3736 (calculated for $[M+H]^+$), 599.3760 (found).

7-(1-Pentadecyloxy)-2-((4-butyloxybenzoyl)oxy)fluoren-9-one (**4f).** ^{1}H NMR: δ 8.05 (d, J = 8.9 Hz, 2H), 7.36 (s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 8.1 Hz), 7.18 (dd, ^{3}J = 8.0 Hz, ^{4}J = 2.2 Hz, 1H), 7.11 (d, J = 2.2 Hz, 1H), 6.91 (d, J = 8.8 Hz, 3H), 3.98 (t, J = 6.5 Hz, 2H), 3.92 (t, J = 6.5 Hz, 2H), 1.73 (m, 4H), 1.44 (m, 4H), 1.19 (m, 22H), 0.93 (t, J = 7.4 Hz, 3H), 0.81 (t, J = 6.9 Hz, 3H); ^{13}C NMR: δ 192.8, 164.8, 163.8, 160.3, 151.0, 142.2, 136.4, 136.2, 135.8, 132.4, 127.7, 121.3, 121.1, 121.0, 120.2, 118.4, 114.4, 110.2, 68.1, 68.4, 32.0, 31.2, 30-29 several overlapping peaks, 26.0, 22.7, 19.2, 14.1, 13.8; HRMS (CI): 599.3736 (calculated for $[M+H]^+$), 599.3779 (found).

3. Liquid Crystal Texture Micrographs



(a) Fluorenols (*R*)-**3a-f**: chiral nematic phase (N*, left), chiral smectic A phase (SmA*, center), and chiral smectic C phase (SmC*, right).



(b) Fluorenones **4a-f**: nematic phase (N, left) and smectic C phase (SmC, right).

4. Differential Scanning Calorimetry Data

(a) Fluorenols (*R*)-**3a**-**f**: Phase transition temperatures (^{o}C) and enthalpies of transitions (kJ mol^{-1}, in parentheses).

Compound	m / n	Cr		Cr'		SmC*		SmA*		N*		I
(*R*)-3a	8 / 11	•	83 (38)		-	•	180 (10)		-			•
(*R*)-3b	11 / 8	•	88 (31)		-	•	179 (8)		-			•
(*R*)-3c	6 / 13	•	88 (18)		-	•	178 (8)		-			•
(*R*)-3d	13 / 6	•	102 (38)		-	•	175*		-	•	176 (7)	•
(*R*)-3e	4 / 15	•	97 (17)	•	102 (6)	•	172*	•	175 (6)			•
(*R*)-3f	15 / 4	•	102 (20)	•	117 (11)	•	164*	•	169*	•	173 (6)	•

* Broad phase transition overlaps with higher-temperature DSC peak(s); phase transition temperatures determined by polarized microscopy

(b) Fluorenones **4a**-**f**: Phase transition temperatures (^{o}C) and enthalpies of transitions (kJ mol^{-1}, in parentheses).

Compound	m / n	Cr		SmC		N		I
4a	8 / 11	•	94 (31)	•	147 (3)	•	158 (2)	•
4b	11 / 8	•	106 (36)	•	145 (2)	•	158 (2)	•
4c	6 / 13	•	81 (42)	•	140 (2)	•	155 (1)	•
4d	13 / 6	•	97 (31)	•	134 (2)	•	156 (2)	•
4e	4 / 15	•	84 (41)	•	124 (2)	•	150 (1)	•
4f	15 / 4	•	94 (38)	•	111 (1)	•	148 (1)	•

5. References

1. J.A. McCubbin, X. Tong, R. Wang, Y. Zhao, V. Snieckus, and R.P. Lemieux, *J. Am. Chem. Soc.* **2004**, *126*, 1161-1167.

2. J.A. McCubbin, X. Tong, Y. Zhao, V. Snieckus, and R.P. Lemieux, *Chem. Mater.* **2005**, *17*, 2574-2581.