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Evidence of a polar cybotactic smectic A phase in a new fluorine substituted bent-core compound

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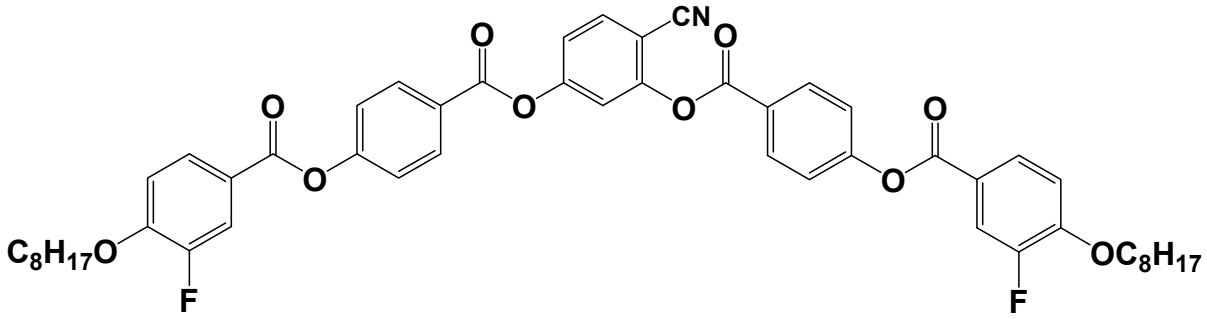
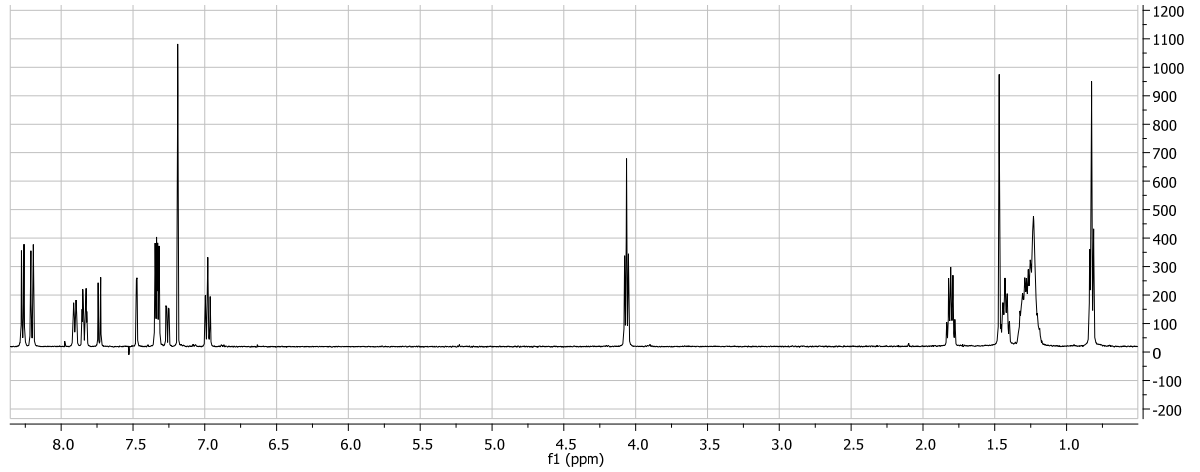
Supporting Information

1. Synthesis and analytical data

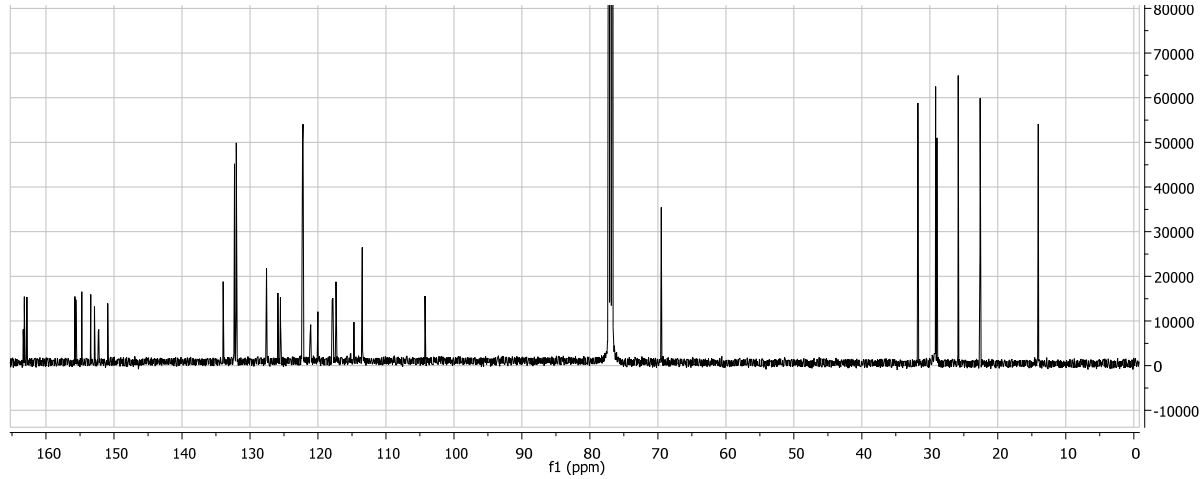


4-(3-Fluoro-4-octyloxybenzoyloxy)benzoic acid (0.15 g, 0.39 mmol) was stirred with thionyl chloride (10 ml) at 65 °C for 1 h to obtain a clear solution. After removing the excess thionyl chloride under reduced pressure the resulting acid chloride was dissolved in CH_2Cl_2 (8 ml) followed by adding a solution of 4-cyanoresorcinol (0.03 g, 0.21 mmol), Et_3N (0.07 ml, 0.50 mmol) and pyridine (0.01 ml) in CH_2Cl_2 (10 ml). The reaction mixture was refluxed for 3 h. Water was added and the phases were separated, followed by the extraction of the aqueous phase with CH_2Cl_2. The combined organic phases were washed with HCl solution (10%), a saturated $NaHCO_3$ solution and water. After drying the solution over anhydrous $MgSO_4$ the solvent was removed. The crude product was purified by column chromatography (silica gel, 6 nm, CH_2Cl_2) and crystallisation from $CHCl_3$/ EtOH (1:9) to yield 117 mg (0.133 mol, 69 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, 2H, Ar-H), 8.20 (d, J = 8.8 Hz, 2H, Ar-H), 7.90 (d, J = 8.6 Hz, 2H, Ar-H), 7.84 (dt, J = 11.4, 2.4 Hz, 2H, Ar-H), 7.73 (d, J = 8.5 Hz, 1H, Ar-H), 7.47 (d, J = 2.2 Hz, 1H, Ar-H), 7.34 (d, J = 8.8 Hz, 2H, Ar-H), 7.33 (d, J = 8.8 Hz, 2H), 7.26 (dd, J = 8.5, 2.2 Hz, 1H, Ar-H), 6.98 (t, J = 8.3 Hz, 2H, Ar-H), 4.06 (t, J = 6.6 Hz, 4H, Ar-OCH_2), 1.86 – 1.73 (m, 4H, CH_2), 1.45 – 1.38 (m, 4H, CH_2), 1.35 – 1.17 (m, 16H, CH_2), 0.83 (t, J = 6.9 Hz, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.35, 163.33, 163.31, 163.29, 163.18, 162.80, 155.74, 155.60, 154.73, 153.41, 152.89, 152.36, 152.32, 152.28, 152.24, 150.92, 133.94, 132.27, 132.02, 127.56, 127.54, 125.90, 125.52, 122.26, 122.21, 121.14, 121.08, 121.07, 121.02, 120.00, 117.94, 117.92, 117.78, 117.76, 117.35, 114.71, 113.48, 104.25, 69.50, 31.75, 29.24, 29.15, 28.95, 25.83, 22.61, 14.05. ^{19}F NMR (470 MHz, $CDCl_3$) δ -133.67 (ddd, J = 27.3, 11.2, 8.2 Hz). $C_{51}H_{51}F_2NO_{10}$, calculated: C 69.93 %, H 5.87 %, N 1.60, found: C 69.71 %, H 5.82, N 1.55.

^{1}H NMR



^{13}C NMR



^{19}F NMR

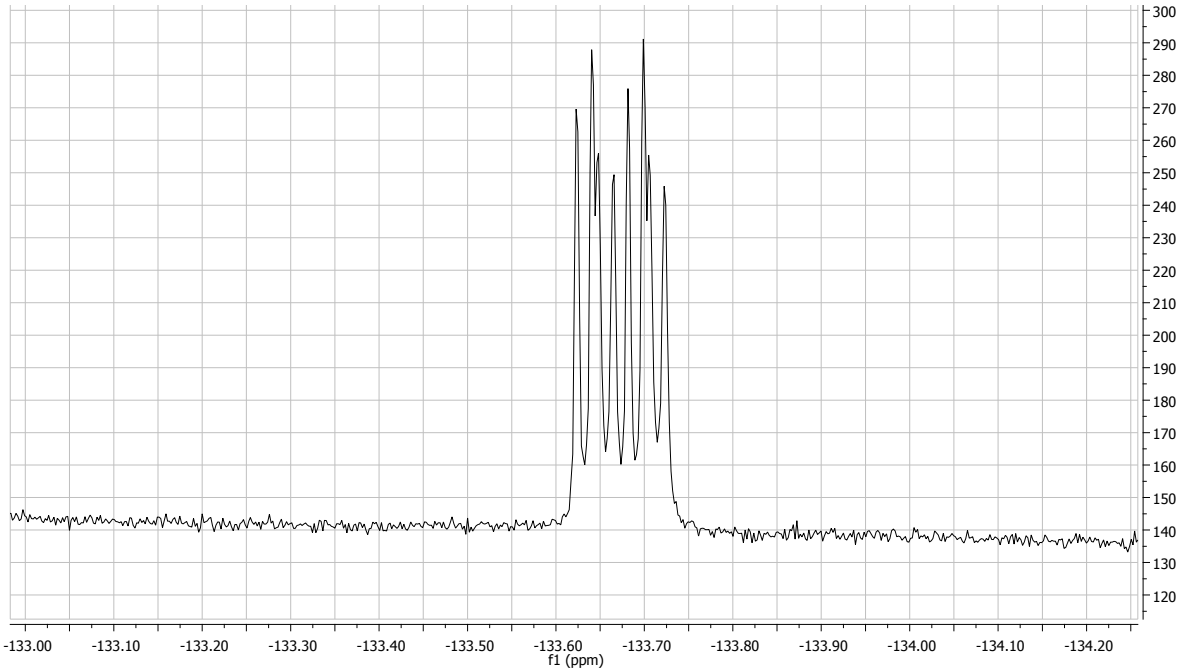


Fig. S1. ^{1}H-, ^{13}C- and ^{19}F-NMR spectra ($CDCl_3$) of **PAL 21**.

2. Additional data

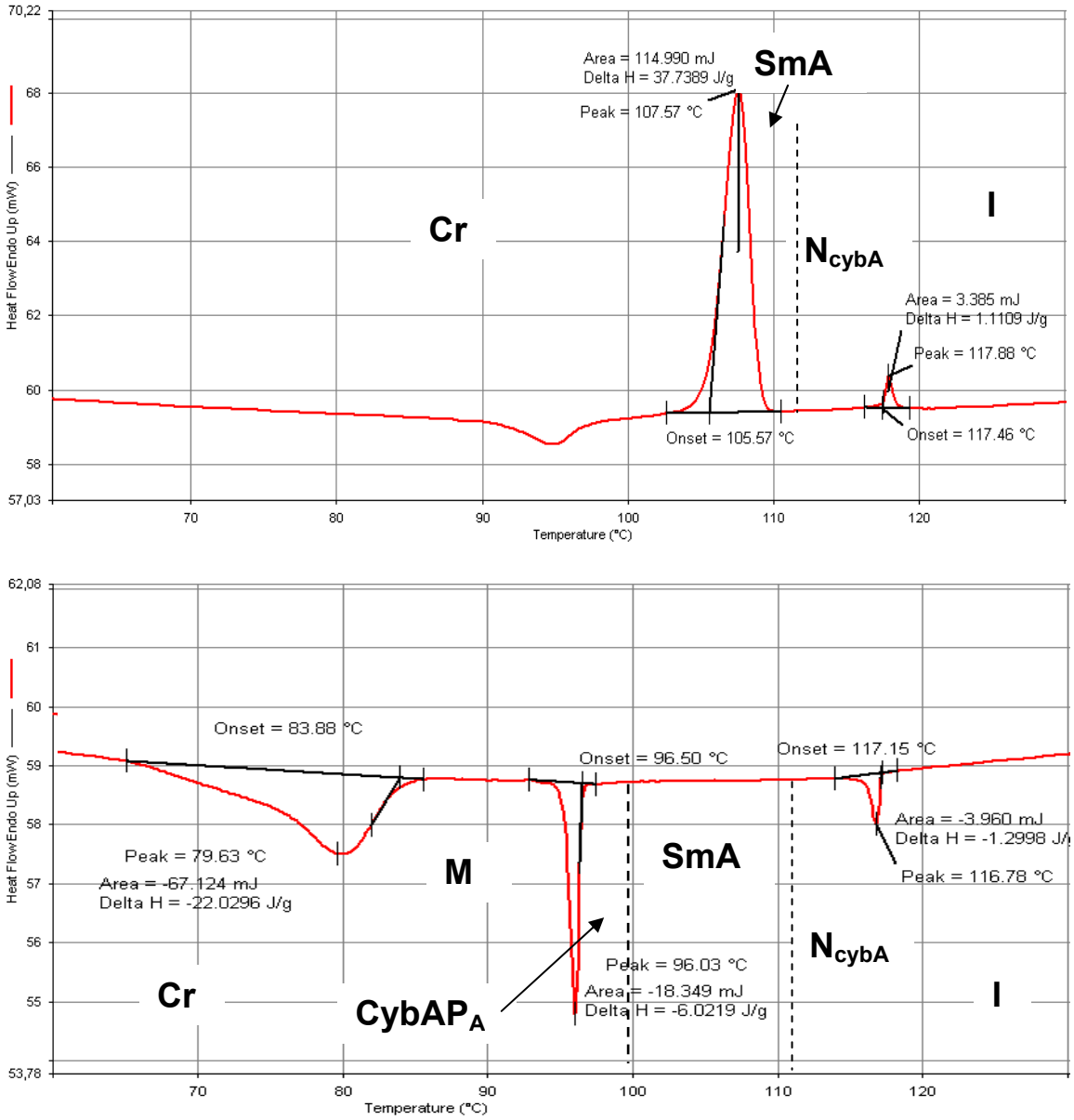


Fig. S2. DSC second heating (a) and cooling scans (b) of **PAL21** at 10 K min^{-1}.