

Evaluation of Structural and Physical Properties

1 Phase Identification by Optical and Thermal Methods:

Phase identifications and determination of phase transition temperatures were carried out by thermal polarized light microscopy using a Zeiss Axioskop 40 Pol polarizing transmitted light microscope equipped with a Mettler FP82HT microfurnace in conjunction with an FP90 Central Processor. Differential scanning calorimetry was used to determine enthalpies of transition and to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms (scan rate $10\text{ }^{\circ}\text{C min}^{-1}$) were obtained using a Mettler DSC822e running on the Stare software. The results obtained were standardised to indium (lit. value $156.60\text{ }^{\circ}\text{C}$, ΔH 28.45 Jg^{-1}).[1]

2 Electrooptical Measurements:

The parallel and perpendicular dielectric permittivities of the materials in their nematic phases were determined using the "one-cell method" which was first reported by Clark,[2-4] and utilised an INSTEC ALCT Property Tester. In order to measure the dielectric permittivities of a material with a negative dielectric anisotropy, a relatively thin (at least $4\text{ }\mu\text{m}$) empty cell with patterned electrodes coated with a homeotropic aligning agent was used. The thickness of the cell, d , was measured using uv-vis interferometry, and the capacitance of the empty cell was then determined. The cell was then filled with a target synthesized material, and the capacitance was measured as a function of the applied voltage. For applied voltages lower than the threshold voltage for switching, V_{th} , the capacitance measured gave $C_{||}$ which was used to determine $\epsilon_{||}$ ($C_{||} = \epsilon_0 \epsilon_{||} A/d$). At applied voltages above the Fredericksz transition ($V > 3V_{th}$), the capacitance was plotted as a function of V_{th}/V . Linear fitting of the data gave the intercept $V_{th}/V = 0$ and the value for the capacitance C_{\perp} , which was used to determine ϵ_{\perp} . The errors for this technique were determined to be $\pm 2\%$.

For electrical field studies on ferroelectric liquid crystals, the test cells were contained within a Mettler FP82HT hot-stage oven in conjunction with a Mettler FP90 temperature controller. The hot-stage was mounted on a Zeiss Universal microscope fitted with crossed-polarizers and an 8/0.2 lens. The applied waveform was supplied

by a Hewlett Packard 33120A Arbitrary Waveform Generator into a linear x20 amplifier (custom-built by QinetiQ). The electrical response from the cell was fed into a nano-current detector (20 k Ω or 100 k Ω impedance) and to a Hewlett Packard 54600B oscilloscope, which was connected to a PC, see Figure 1. The types of cells used were constructed from ITO-coated glass which had separations of $5 \pm 0.1 \mu\text{m}$ (Linkam), with the internal surfaces coated with a polyimide aligning agent which is antiparallel buffed. The cells were filled by capillary action.

Alignment of the ferroelectric liquid crystals was achieved by differing procedures. In the cases where the materials exhibited both smectic A* and smectic C* phases, alignment was achieved by slowly cooling into the smectic A* mesophase from the isotropic state, and applying a high electric field in the form of a square wave (typically $16\text{-}20 \text{ V } \mu\text{m}^{-1}$) at a frequency of 50 Hz to 1 kHz depending on the material. Once the material was aligned in the cell, the voltage was removed and the cell cooled down into the smectic C* mesophase. For the case where the material only exhibited a smectic C* phase, alignment was achieved by cooling slowly ($0.1 \text{ }^\circ\text{C min}^{-1}$) into the smectic C* phase, and using the same procedure described previously but with the addition of an underlying DC voltage (typically 10 V). For comparison of results, measurements were determined as a function of the reduced temperature, $T_c - T$, where T_c is the Curie point.

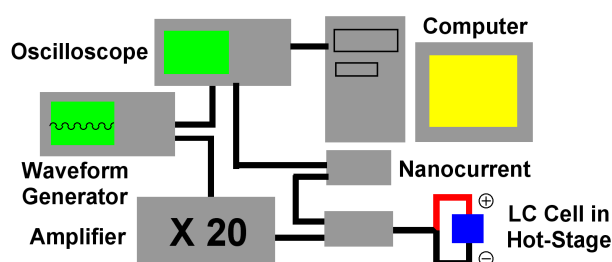


Figure 1. Experimental apparatus for electrical field studies

3 Measurement of Spontaneous Polarization (Using the 5 μm cells):

Upon alignment of the liquid crystal, the spontaneous polarization in the tilted phases was determined, on cooling, using a triangular waveform current reversal technique. An AC field in a triangular waveform (typically $10 \text{ V } \mu\text{m}^{-1}$ at 30 Hz) was applied to the cell. As the polarization is inverted by the field, a current pulse was observed. The

magnitude of the spontaneous polarization was determined from the area under the current-reversal peak.

4 Measurement of Tilt Angles:

The determination of tilt angle was achieved by measuring the optical transmission of the switched states using a photodiode (RS303-674; 1 cm² active area, high speed >50 ns) in an apparatus custom built by QinetiQ. The equipment was fitted with a green-eye response filter (Coherent-Ealing, 26-7617-000, 1 inch diameter, transmittance 400-700 nm, maximum transmittance 539.5 nm). The transmission values were determined using a Thurlby Thandar Instruments 1604 Digital Multimeter.

5 Computational

Molecular orbital calculations were performed on three different substituted tetrafluoroterphenyls and one trifluoroterphenyl using the TURBOMOLE 5.9 suites of programs.[5] Geometry optimisation calculations were conducted on two conformers of each terphenyl using density functional theory (DFT) with second order resolution of the identity Moller-Plesset perturbation theory (RIMP2)[6] providing higher level optimisations for the methyl and methoxy substituted variants of the tetrafluoroterphenyls. In addition, analytical vibrational frequency calculations were conducted on the smaller tetrafluoroterphenyls at the DFT level in order to obtain zero point corrected energies for the most stable structures and to determine whether or not they represented true minima as opposed to saddle points. The basis sets used were the doubly polarised triple zeta def2-TZVPP basis sets of Ahlrichs[7-8] whilst the functional used in the DFT calculations was B3-lyp.

Detailed Synthesis

2,3-difluoro-4''-pentyl-4-(pent-4-eneyloxy)terphenyl (5)

Potassium carbonate (4.7 g, 34.0 mmol) was added to a solution of compound **4a** (4.0 g, 11.4 mmol) and 5-bromo-1-pentene (1.7 g, 11.4 mmol) in butanone (100 ml). The reaction mixture was left to stir under reflux overnight. The product was washed with water, extracted into dichloromethane, dried over MgSO₄. The product was purified by column chromatography (silica gel, hexane) and recrystallized from ethanol to give

a white solid. Yield 3.2 g (67 %). Transitions/°C: Cr 101.31 SmC 139.37 SmA 151.95 N 169.41 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.89 (t (*J* = 7.23 Hz), 3H), 1.27-1.38 (m, 4H), 1.64(m, 2H), 1.95 (m, 2H), 2.28 (m, 2H), 2.63 (t (*J*= 7.41 Hz), 2H), 4.08 (t (*J*=6.70 Hz), 2H), 4.97-5.10 (m, 2H), 5.86 (m, H), 6.79 (m, H), 7.12 (m, H), 7.27 (m, 2H), 7.54 (m, 4H), 7.65 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.1 (CH₃), 22.8 (CH₂), 29.0 (CH₂), 30.0 (CH₂), 31.1 (CH₂), 31.6 (CH₂), 36.0 (CH₂), 69.1 (CH₂), 112.4 (arom. -CH), 115.8 (CH₂), 123.4 (arom. - quat. C), 126.9 (arom -CH), 127.1 (arom - 2x CH), 128.9 (arom - 2x CH), 129.0 (arom - 2x quat. C), 129.1 (arom - 2x quat. C), 133.6 (arom - quat. C), 137.5 (-CH), 137.8 (arom - 2x quat. C), 140.4 (arom - quat. C), 142.4 (arom - quat. C), 147.6 (arom - quat. C), 147.7 (arom - quat. C) ppm; ¹⁹F NMR (400 MHz, CDCl₃) δ -158.5, -141.5 ppm; IR(solid) ν_{\max} 621, 721, 794, 894, 1076, 1107, 1195, 1296, 1396, 1465, 1496, 1727, 2854, 2927 cm⁻¹; Ms *m/z* 420 (M⁺), 352, 295, 41.

2,3-difluoro-4''-pentyl-4-(hept-6-eneyloxy)terphenyl (6)

Compound **6** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **4a** (2.0 g, 5.7 mmol), potassium carbonate (2.4 g, 17.0 mmol) and 7-bromo-1-heptene (1.0 g, 5.7 mmol). Yield 1.6 g (63 %). Transitions/°C: Cr 89.87 SmC 136.85 SmA 146.37 N 159.94 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.89 (t (*J* = 7.10 Hz), 3H), 1.29-1.39 (m, 4H), 1.42-1.54 (m, 4H), 1.64 (m, 2H), 1.84 (m, 2H), 2.10 (m, 2H), 2.63 (t (*J*= 7.50 Hz), 2H), 4.06 (t (*J*=6.58 Hz), 2H), 4.92-5.05 (m, 2H), 5.82 (m, H), 6.79 (m, H), 7.12 (m, H), 7.26 (m, 2H), 7.54 (m, 4H), 7.64 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.1 (CH₃), 22.8 (CH₂), 26.2 (CH₂), 29.6 (CH₂), 29.9 (CH₂), 31.1 (CH₂), 31.8 (CH₂), 34.1 (CH₂), 35.5 (CH₂), 69.2 (CH₂), 112.0 (arom. -CH), 115.0 (CH₂), 124.4 (arom. - quat. C), 125.7

(arom –CH), 127.7 (arom – 2x CH), 128.3 (arom – 2x CH), 128.4 (arom – 2x quat. C), 128.7 (arom – 2x quat. C), 133.9 (arom – quat. C), 135.4 (arom – 2x quat. C), 137.9 (–CH), 137.6 (arom – quat. C), 144.8 (arom – quat. C), 146.3 (arom – quat. C), 146.9 (arom – quat. C) ppm; IR(solid) ν_{\max} 621, 721, 798, 894, 1080, 1103, 1195, 1300, 1396, 1465, 1496, 1631, 2854, 2924 cm^{-1} ; Ms m/z 448 (M⁺), 352, 295, 55, 41.

2,3-difluoro-4''-heptyl-4-(pent-4-eneyloxy)terphenyl (7)

Compound **7** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **4b** (2.0 g, 5.3 mmol), potassium carbonate (2.2 g, 15.8 mmol) and 5-bromo-1-pentene (0.8 g, 5.3 mmol). Yield 1.65 g (70 %). Transitions/ $^{\circ}\text{C}$: Cr₁ 45.65 Cr₂ 89.39 Cr₃ 96.91 SmC 140.48 SmA 157.76 N 162.80 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.88 (t (J = 7.14 Hz), 3H), 1.27-1.40 (m, 8H), 1.65 (m, 2H), 1.96 (m, 2H), 2.27 (m, 2H), 2.65 (t (J = 7.51 Hz), 2H), 4.06 (t (J =6.68 Hz), 2H), 4.96-5.10 (m, 2H), 5.85 (m, H), 6.82 (m, H), 7.15 (m, H), 7.30 (m, 2H), 7.56 (m, 4H), 7.67 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.1 (CH₃), 22.7 (CH₂), 29.0 (CH₂), 29.3 (CH₂), 29.5 (CH₂), 29.9 (CH₂), 31.3 (CH₂), 31.8 (CH₂), 36.1 (CH₂), 69.0 (CH₂), 112.1 (arom. –CH), 115.6 (CH₂), 124.5 (arom. – quat. C), 125.6 (arom –CH), 127.7 (arom – 2x CH), 128.4 (arom – 2x CH), 128.5 (arom – 2x quat. C), 128.7 (arom – 2x quat. C), 133.7 (arom – quat. C), 135.2 (–CH), 135.5 (arom – 2x quat. C), 137.7 (arom – quat. C), 144.3 (arom – quat. C), 146.2 (arom – quat. C), 146.9 (arom – quat. C) ppm; IR(solid) ν_{\max} 636, 721, 798, 894, 1076, 1107, 1195, 1300, 1396, 1469, 1496, 1635, 2850, 2920 cm^{-1} ; Ms m/z 448 (M⁺), 380, 295, 41.

2,3-difluoro-4''-heptyl-4-(hept-6-eneyloxy)terphenyl (8)

Compound **8** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **4b** (2.0 g, 5.3 mmol), potassium carbonate (2.2 g, 15.8 mmol) and 7-bromo-1-heptene (0.93 g, 5.3 mmol). Yield 1.6 g (64 %). Transitions/ $^{\circ}\text{C}$: Cr1 67.51 Cr 85.26 SmC 141.71 SmA 152.18 N 155.27 Iso. ^1H NMR (400MHz, CDCl_3) δ 0.87 (t ($J=7.15$ Hz), 3H), 1.21-1.36 (m, 8H), 1.43-1.55 (m, 4H), 1.64 (m, 2H), 1.84 (m, 2H), 2.10 (m, 2H), 2.63 (t ($J=7.52$ Hz), 2H), 4.07 (t ($J=6.52$ Hz), 2H), 4.92-5.04 (m, 2H), 5.82 (m, H), 6.79 (m, H), 7.12 (m, H), 7.25 (m, 2H), 7.55 (m, 4H), 7.65 (m, 2H) ppm; ^{13}C NMR (400MHz, CDCl_3) δ 14.1 (CH_3), 22.7 (CH_2), 26.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 31.3 (CH_2), 32.0 (CH_2), 34.0 (CH_2), 36.1 (CH_2), 69.0 (CH_2), 112.4 (arom. $-\text{CH}$), 115.5 (CH_2), 124.5 (arom. $-\text{quat. C}$), 125.6 (arom $-\text{CH}$), 125.7 (arom $-\text{CH}$), 127.7 (arom $-\text{2x CH}$), 128.2 (arom $-\text{2x CH}$), 128.5 (arom $-\text{2x quat. C}$), 128.6 (arom $-\text{2x quat. C}$), 132.9 (arom $-\text{quat. C}$), 135.6 (arom $-\text{quat. C}$), 136.9 ($-\text{CH}$), 137.6 (arom $-\text{quat. C}$), 144.5 (arom $-\text{quat. C}$), 146.1 (arom $-\text{quat. C}$), 146.4 (arom $-\text{quat. C}$) ppm; IR(solid) ν_{max} 624, 721, 802, 894, 1083, 1107, 1199, 1300, 1396, 1469, 1496, 1635, 2850, 2924 cm^{-1} ; Ms m/z 476 (M^+), 380, 295, 55, 41.

2,2',3,3'-tetrafluoro 4''-pentylterphenyl (15a)

n-Butyllithium (15.4 ml, 2.5M in hexanes, 38.5 mmol) was added dropwise to a stirred, cooled (-78 $^{\circ}\text{C}$) solution of compound **11a** (10 g, 38.5 mmol) in dry THF (250 ml) under an atmosphere of dry nitrogen. The reaction mixture was stirred for 2 hours and solution of trimethyl borate (8.2 g, 77 mmol) in dry THF (50 ml) was added dropwise at -78 $^{\circ}\text{C}$. The reaction was allowed to warm up to room temperature

overnight and then stirred for 1 h with hydrochloric acid (25 ml, 10 %). The product was extracted into diethyl ether (twice) and the combined extracts washed with water and dried over MgSO₄. The solvent was removed *in vacuo* to yield colourless crystals of boronic acid (7.2 g, 65 %). The obtained boronic acid (**12a**) (7 g, 24.4 mmol), 1-Bromo-2,3-difluorobenzene (**13**) (4 g, 19 mmol), tetrakis(triphenylphosphine) palladium(0) (0.74 g, 0.64 mmol), aqueous sodium carbonate (58 ml, 2M) and 1,2-dimethoxyethane (150 ml) were heated under reflux for *ca.* 24 h under an atmosphere of dry nitrogen. The product was extracted into diethyl ether (twice) and washed with brine and dried over MgSO₄. The solvent was removed *in vacuo*. The product was purified by column chromatography [silica gel; petroleum ether (b.p. 40-60 °C) to yield colourless crystals (7.3 g, 80 %); mp 77.4 – 77.7 °C. ¹H NMR (400MHz, CDCl₃) δ 0.89 (m, 3H), 1.34 (m, 4H), 1.65 (t, (*J*=7.43 Hz), 2H), 2.65 (m, 2H), 7.18 (m, 4H), 7.27 (m, 3H), 7.49 (m, 2H) ppm; IR(solid) ν_{\max} 787, 913, 1087, 1265, 1467, 2861, 2929 cm⁻¹; Ms *m/z* 372 (M⁺), 315.

2,2',3,3'-tetrafluoro 4''-heptylterphenyl (15b)

Compound **15b** was prepared using the same method as for the preparation of compound **15a**. The following quantities were used: compound **11b** (9 g, 31.3 mmol), *n*-butyllithium (12.5 ml, 2.5M in hexanes, 31.3 mmol) and trimethyl borate (6.5 g, 62.5 mmol). Yield of boronic acid (**12b**) 7.6 g (73 %). Compound **12b** (7 g, 21.1 mmol), compound **13** (3.7 g, 19.2 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.63 g, 0.55 mmol). Yield 5.9 g (70 %); mp 79.4 – 80.0 °C. ¹H NMR (400MHz, CDCl₃) δ 0.87 (m, 3H), 1.25-1.35 (m, 8H), 1.64 (m, 2H), 2.65 (m, 2H), 7.18 (m, 4H), 7.27 (m, 3H), 7.48 (m, 2H) ppm; IR(solid) ν_{\max} 783, 979, 1087, 1269, 1450, 2850, 2920 cm⁻¹; Ms *m/z* 400 (M⁺), 315.

2,2',3,3'-tetrafluoro 4''-pentylterphenyl (17a)

a) n-Butyllithium (7.5 ml, 2.5M in hexanes, 18.8 mmol) was added dropwise to a stirred, cooled (-78 °C) solution of compound **15a** (7.0 g, 18.8 mmol) in dry THF (250 ml) under an atmosphere of dry nitrogen. The reaction mixture was stirred for 2 hours and solution of trimethyl borate (3.9 g, 37.6 mmol) in dry THF (50 ml) was added dropwise at -78 °C. The reaction was allowed to warm up to room temperature overnight and then stirred for 1 h with hydrochloric acid (25 ml, 10 %). The product was extracted into diethyl ether (twice) and the combined extracts washed with water and dried over MgSO₄. The solvent was removed *in vacuo* to yield colourless crystals of boronic acid (5.87 g, 75 %).

b) Hydrogen peroxide (11 ml, 30 %) was added dropwise to a stirred solution of the boronic acid (5.0 g, 12.0 mmol) in diethyl ether (100 ml) and the reaction was heated under reflux for 2 h. Once cooled, the product was extracted into ether, washed with water and dried over MgSO₄. The solvent was removed *in vacuo* and the product was recrystallized from ethanol to give the phenol (17a) as a white solid. Yield 4.2 g (90 %); mp 110.0 – 110.9 °C. ¹H NMR (400MHz, CDCl₃) δ 0.75 (t, (*J*=7.17 Hz), 3H), 1.13-1.24 (m, 4H), 1.50 (m, 2H), 2.51 (t, (*J*=7.32 Hz), 2H), 6.80 (m, H), 7.01 (m, H), 7.23 (m, 3H), 7.30 (m, H), 7.40 (m, 2H), 10.76 (s, H) ppm. IR(solid) ν_{\max} 803, 909, 1084, 1265, 1476, 2851, 2922, 3446 cm⁻¹; Ms *m/z* 388 (M⁺), 331.

2,2',3,3'-tetrafluoro 4''-heptylterphenyl (17b)

a) Compound **17b** was prepared using the same method as for the preparation of compound **17a**. The following quantities were used Quantities: compound **15b** (5 g,

12.5 mmol), n-butyllithium (5 ml, 2.5M in hexanes, 12.5 mmol) and trimethyl borate (2.6 g, 25 mmol). Yield of boronic acid 4.5 g (81 %).

b) Boronic acid (4 g, 9 mmol) and hydrogen peroxide (8.2 ml, 30 %). Yield 3.41 g (90.1 %); mp 148.9 – 149.8 °C. ¹H NMR (400MHz, CDCl₃) δ 0.84 (m, 3H), 1.24-1.29 (m, 8H), 1.58 (m, 2H), 2.61 (m, 2H), 6.91 (m, H), 7.13 (m, H), 7.30 (m, 3H), 7.41 (m, H), 7.53 (m, 2H), 10.77 (s, H) ppm; IR(solid) ν_{\max} 798, 968, 1033, 1199, 1454, 2850, 2924, 3441 cm⁻¹; Ms *m/z* 416 (M⁺), 331.

2,2',3-trifluoro-4''-pentyl-4-(pent-4-eneyloxy)terphenyl (18)

Compound **18** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **16a** (4.0 g, 10.3 mmol), potassium carbonate (4.3 g, 30.9 mmol) and 5-bromo-1-pentene (1.54 g, 10.3 mmol). Yield 4.11 g (91 %). Transitions/°C: Cr 48.44 (SmC 35.90) SmA 117.06 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.89 (t, 3H, *J* = 7.02 Hz), 1.32-1.35 (m, 4H), 1.64 (m, 2H), 1.94 (m, 2H), 2.26 (m, 2H), 2.63 (t (*J* = 7.63 Hz), 2H), 4.08 (t, 2H, *J* = 6.41 Hz), 5.0-5.09 (m, 2H), 5.85 (m, H), 6.79 (m, H), 7.06 (m, H), 7.26 (m, 2H), 7.34-7.43 (m, 3H), 7.51 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.0 (CH₃), 22.5 (CH₂), 28.5 (CH₂), 30.0 (CH₂), 31.1 (CH₂), 31.5 (CH₂), 35.6 (CH₂), 68.9 (CH₂), 110.0 (arom. –CH), 115.5 (CH₂), 122.5 (arom –CH), 124.6 (arom – quat. C), 114.0, 114.2 (arom –CH), 126.8 (arom – 2x CH), 129.0 (arom – 2x CH), 131.6 (arom –CH), 131.1 (arom – quat. C), 134.1 (arom – quat. C), 134.5 (–CH), 137.0 (arom – quat. C), 137.6 (arom – quat. C), 144.2 (arom – quat. C), 146.3 (arom – quat. C), 147.0 (arom – quat. C), 158.8 (arom – quat. C), 161.2 (arom) ppm; ¹⁹F NMR (400 MHz, CDCl₃) δ -158.6, -137.8, -114.9 ppm; IR(solid) ν_{\max} 632, 725, 798, 914, 1072, 1095, 1199, 1296, 1396, 1469, 1492, 1620, 2870, 2927 cm⁻¹; Ms *m/z* 438 (M⁺), 370, 313, 69, 41.

2,2',3-trifluoro-4''-pentyl-4-(hept-6-eneyloxy)terphenyl (19)

Compound **19** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **16a** (4.0 g, 10.3 mmol), potassium carbonate (4.3 g, 30.9 mmol) and 7-bromo-1-heptene (1.83 g, 10.3 mmol). Yield 4.52 g (94 %). Transitions/°C: Cr 46.09 SmA 109.42 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.91 (t (*J* = 7.02 Hz), 3H), 1.34-1.37 (m, 4H), 1.49-1.55 (m, 4H), 1.66 (m, 2H), 1.86 (m, 2H), 2.11 (m, 2H), 2.65 (t (*J* = 7.63 Hz), 2H), 4.09 (t (*J* = 6.71 Hz), 2H), 4.95-5.05 (m, 2H), 5.83 (m, H), 6.81 (m, H), 7.08 (m, H), 7.26 (m, 2H), 7.36-7.43 (m, 3H), 7.53 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.0 (CH₃), 22.6 (CH₂), 25.4 (CH₂), 29.0 (CH₂), 29.9 (CH₂), 31.1 (CH₂), 31.5 (CH₂), 33.4 (CH₂), 35.7 (CH₂), 69.5 (CH₂), 106.4 (arom. -CH), 114.5 (CH₂), 116.3 (arom. -CH), 121.0 (arom -CH), 123.0 (arom - quat. C), 124.1 (arom -CH), 127.1 (arom - 2x CH), 128.7 (arom - 2x CH), 131.0 (arom -CH), 131.5 (arom - quat. C), 132.5 (arom - quat. C), 137.6 (arom - quat. C), 138.5 (arom - quat. C), 139.4 (-CH), 143.0 (arom - quat. C), 146.0 (arom - quat. C), 147.2 (arom - quat. C) 164.5 (arom - quat. C) ppm; IR(solid) ν_{\max} 632, 736, 798, 910, 1076, 1095, 1199, 1292, 1396, 1465, 1492, 1620, 2854, 2927 cm⁻¹; Ms *m/z* 466 (M⁺), 370, 313, 55, 41.

2,2',3-trifluoro-4''-heptyl-4-(pent-4-eneyloxy)terphenyl (20)

Compound **20** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **16b** (1.0 g, 2.5 mmol), potassium carbonate (1.0 g, 7.5 mmol) and 5-bromo-1-pentene (0.4 g, 2.5 mmol). Yield 0.83 g (69 %). Transitions/°C: Cr 30.39 SmC 69.95 N 111.38 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.86 (t (*J* = 6.71 Hz), 3H), 1.21-1.38 (m, 8H), 1.63 (m, 2H), 1.94

(m, 2H), 2.26 (m, 2H), 2.64 (t ($J=7.63$ Hz), 2H), 4.08 (t ($J=6.56$ Hz), 2H), 5.00-5.09 (m, 2H), 5.85 (m, 1H), 6.79 (m, 1H), 7.06 (m, 1H), 7.26 (m, 2H), 7.40 (m, 3H), 7.51 (m, 2H) ppm; ^{13}C NMR (400MHz, CDCl_3) δ 14.1 (CH_3), 22.6 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 30.0 (CH_2), 31.4 (CH_2), 32.0 (CH_2), 36.3 (CH_2), 68.7 (CH_2), 112.2 (arom. $-\text{CH}$), 114.6 (CH_2), 117.1 (arom $-\text{CH}$), 124.1 (arom $-\text{CH}$), 124.6 (arom. $-\text{quat. C}$), 125.7 (arom $-\text{CH}$), 127.7 (arom $-\text{2x CH}$), 128.8 (arom $-\text{2x CH}$), 130.0 (arom $-\text{CH}$), 130.5 (arom $-\text{quat. C}$), 133.9 (arom $-\text{quat. C}$), 135.0 ($-\text{CH}$), 137.0 (arom $-\text{quat. C}$), 137.7 (arom $-\text{quat. C}$), 145.0 (arom $-\text{quat. C}$), 146.1 (arom $-\text{quat. C}$), 147.0 (arom $-\text{quat. C}$) 160.0 (arom $-\text{quat. C}$) ppm; IR(solid) ν_{max} 632, 798, 910, 1095, 1199, 1300, 1396, 1473, 1492, 1639, 2850, 2920 cm^{-1} ; Ms m/z 466 (M^+), 398, 313, 284, 58.

2,2',3-trifluoro-4''-heptyl-4-(hept-6-eneyloxy)terphenyl (21)

Compound **21** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **16b** (1.0 g, 2.5 mmol), potassium carbonate (1.0 g, 7.5 mmol) and 7-bromo-1-heptene (0.45 g, 2.5 mmol). Yield 0.87 g (70 %). Transitions/ $^{\circ}\text{C}$: Cr 28.15 SmC 71.18 N 107.02 Iso. ^1H NMR (400MHz, CDCl_3) δ 0.86 (t ($J=7.24$ Hz), 3H), 1.21-1.38 (m, 8H), 1.44-1.51 (m, 4H), 1.63 (m, 2H), 1.84 (m, 2H), 2.09 (m, 2H), 2.63 (t ($J=7.43$ Hz), 2H), 4.07 (t ($J=6.50$ Hz), 2H), 4.92-5.05 (m, 2H), 5.82 (m, H), 6.79 (m, H), 7.06 (m, H), 7.27 (m, 2H), 7.40 (m, 3H), 7.49 (m, 2H) ppm; ^{13}C NMR (400MHz, CDCl_3) δ 14.1 (CH_3), 22.8 (CH_2), 26.2 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 30.0 (CH_2), 31.3 (CH_2), 32.0 (CH_2), 33.9 (CH_2), 36.8 (CH_2), 68.9 (CH_2), 112.4 (arom. $-\text{CH}$), 114.9 (CH_2), 117.0 (arom $-\text{CH}$), 124.1 (arom $-\text{CH}$), 124.7 (arom. $-\text{quat. C}$), 125.6 (arom $-\text{CH}$), 127.8 (arom $-\text{2x CH}$), 128.8 (arom $-\text{2x CH}$), 130.0 (arom $-\text{CH}$), 131.0 (arom $-\text{quat. C}$),

132.9 (arom – quat. C), 137.0 (arom – quat. C), 137.8 (arom – quat. C), 138.0 (–CH),
145.0 (arom – quat. C), 146.0 (arom – quat. C), 147.0 (arom – quat. C) 160.5 (arom –
quat. C) ppm; IR(solid) ν_{\max} 536, 632, 794, 910, 1072, 1103, 1300, 1400, 1469, 1496,
1635, 2854, 2924 cm^{-1} ; Ms m/z 494 (M+), 398, 313, 284, 58.

2,2',3,3'-tetrafluoro-4''-pentyl-4-(pent-4-eneyloxy)terphenyl (22)

Compound **22** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **17a** (2.0 g, 5.2 mmol), potassium carbonate (2.1 g, 15.2 mmol) and 5-bromo-1-pentene (0.77 g, 5.2 mmol). Yield 2.1 g (89 %). Transitions/ $^{\circ}\text{C}$: Cr 56.90 N 108.78 Iso. ^1H NMR (400MHz, CDCl_3) δ 0.91 (m, 3H), 1.26-1.37 (m, 5H), 1.66 (m, 2H), 1.97 (m, 2H), 2.29 (m, 2H), 2.66 (t ($J=7.63$ Hz), 2H), 4.11 (t ($J=6.41$ Hz), 2H), 5.01-5.12 (m, 2H), 5.87 (m, H), 6.83 (m, H), 7.09 (m, H), 7.15 (m, H), 7.30 (m, 2H), 7.36-7.49 (m, 2H) ppm; ^{13}C NMR (400MHz, CDCl_3) δ 14.0 (CH_3), 22.6 (CH_2), 28.3 (CH_2), 29.9 (CH_2), 31.5 (CH_2), 31.8 (CH_2), 35.6 (CH_2), 68.9 (CH_2), 109.3, 109.4 (arom. –CH), 115.5 (CH_2), 122.9, 130.0 (arom. – quat. C), 124.5 (arom –2x CH), 126.6 (arom –CH), 127.7 (arom – 2x CH), 128.7 (arom – 2x CH), 131.8 (arom – 2x quat. C), 133.3 (arom – quat. C), 137.1 (–CH), 139.3 (arom – quat. C), 143.7 (arom – quat. C), 145.3 (arom – 2x quat. C), 147.5 (arom – quat. C), 148.4 (arom – quat. C) ppm; IR(solid) ν_{\max} 640, 798, 837, 914, 991, 1076, 1199, 1300, 1404, 1450, 1469, 1492, 1639, 2854, 2927, 2958 cm^{-1} ; Ms m/z 457 (M+), 338, 297, 183, 142, 89.

2,2',3,3'-tetrafluoro-4''-pentyl-4-(hept-6-eneyloxy)terphenyl (23)

Compound **23** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **17a** (2.0 g, 5.2 mmol),

potassium carbonate (2.1 g, 15.2 mmol) and 7-bromo-1-heptene (0.9 g, 5.2 mmol). Yield 2.0 g (80 %). Transitions/°C: Cr 63.76 N 101.08 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.90 (m, 3H), 1.30-1.38 (m, 4H), 1.42-1.50 (m, 4H), 1.65 (m, 2H), 1.86 (m, 2H), 2.10 (m, 2H), 2.65 (t (*J*= 7.63 Hz), 2H), 4.08 (t (*J*=6.71 Hz), 2H), 4.93-5.04 (m, 2H), 5.82 (m, H), 6.81 (m, H), 7.07 (m, H), 7.15 (m, H), 7.29 (m, 3H), 7.47-7.50 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.0 (CH₃), 22.5 (CH₂), 26.8 (CH₂), 28.6 (CH₂), 28.7 (CH₂), 31.2 (CH₂), 31.8 (CH₂), 33.7 (CH₂), 37.1 (CH₂), 68.4 (CH₂), 111.0 (arom. -CH), 115.4 (CH₂), 124.2 (arom. - quat. C), 125.6 (arom -2x CH), 125.8 (arom -CH), 127.7 (arom - 2x CH), 128.5 (arom - 2x CH), 131.6 (arom - 2x quat. C), 132.7 (arom - quat. C), 136.8 (-CH), 137.4 (arom - quat. C), 144.2 (arom - quat. C), 145.5 (arom - quat. C), 147.0 (arom - 2x quat. C), 149.0 (arom - quat. C) ppm; IR(solid) ν_{\max} 644, 798, 829, 910, 1056, 1087, 1195, 1292, 1450, 1469, 1492, 1639, 2850, 2931 cm⁻¹; Ms *m/z* 485 (M⁺), 391, 338, 291, 167, 114.

2,2',3,3'-tetrafluoro-4''-heptyl-4-(pent-4-enyloxy)terphenyl (24)

Compound **24** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **17b** (1.5 g, 3.6 mmol), potassium carbonate (1.5 g, 11 mmol) and 5-bromo-1-pentene (0.54 g, 3.6 mmol). Yield 1.3 g (74 %). Transitions/°C: Cr 53.05 N 103.08 Iso.; ¹H NMR (400MHz, CDCl₃) δ 0.87 (t (*J* = 7.21 Hz), 3H), 1.21-1.31 (m, 8H), 1.58-1.69 (m, 2H), 1.94 (m, 2H), 2.28 (m, 2H), 2.64 (t (*J*= 7.42 Hz), 2H), 4.09 (t (*J*=6.60 Hz), 2H), 4.97-5.02 (m, 2H), 5.83 (m, H), 6.81 (m, H), 7.06 (m, H), 7.16 (m, 2H), 7.28 (m, 2H), 7.49 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.0 (CH₃), 22.6 (CH₂), 29.0 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.8 (CH₂), 31.3 (CH₂), 31.9 (CH₂), 36.1 (CH₂), 69.1 (CH₂), 111.4 (arom. -CH), 115.5 (CH₂), 124.5 (arom. - quat. C), 125.5 (arom - 2x CH), 125.7 (arom -

CH), 127.7 (arom – 2x CH), 128.7 (arom – 2x CH), 131.6 (arom – 2x quat. C), 132.5 (arom – quat. C), 135.1 (–CH), 137.6 (arom – quat. C), 144.0 (arom – quat. C), 146.1 (arom – quat. C), 146.1 (arom – 2x quat. C) 147.1 (arom – quat. C) ppm; IR(solid) ν_{\max} 632, 721, 806, 894, 1087, 1141, 1192, 1296, 1396, 1454, 1469, 1643, 2850, 2920 cm^{-1} ; Ms m/z 484 (M⁺), 416, 331, 69.

2,2',3,3'-tetrafluoro-4''-heptyl-4-(hept-6-eneyloxy)terphenyl (25)

Compound **25** was prepared using the same method as for the preparation of compound **5**. The following quantities were used: compound **17b** (1.5 g, 3.6 mmol), potassium carbonate (1.5 g, 11 mmol) and 7-bromo-1-heptene (0.64 g, 3.6 mmol). Yield 1.32 g (71 %). Transitions/°C: Cr 64.84 N 97.06 Iso. ¹H NMR (400MHz, CDCl₃) δ 0.87 (t (J = 7.20 Hz), 3H), 1.22-1.37 (m, 8H), 1.42-1.51 (m, 4H), 1.63 (m, 2H), 1.85 (m, 2H), 2.09 (m, 2H), 2.64 (t (J = 7.52 Hz), 2H), 4.08 (t (J = 6.48 Hz), 2H), 4.93-5.05 (m, 2H), 5.82 (m, H), 6.80 (m, H), 7.07 (m, H), 7.15 (m, H), 7.28 (m, 3H), 7.49 (m, 2H) ppm; ¹³C NMR (400MHz, CDCl₃) δ 14.0 (CH₃), 22.8 (CH₂), 26.0 (CH₂), 29.0 (CH₂), 29.4 (CH₂), 29.9 (CH₂), 30.0 (CH₂), 31.4 (CH₂), 32.0 (CH₂), 33.8 (CH₂), 37.1 (CH₂), 69.4 (CH₂), 110.4 (arom. –CH), 114.5 (CH₂), 124.5 (arom. – quat. C), 125.6 (arom – 2x CH), 125.7 (arom –CH), 127.8 (arom – 2x CH), 128.7 (arom – 2x CH), 131.5 (arom – 2x quat. C), 132.9 (arom – quat. C), 137.6 (arom – quat. C), 138.1 (–CH), 143.0 (arom – quat. C), 146.1 (arom – quat. C), 147.1 (arom – 2x quat. C) 148.5 (arom – quat. C) ppm; IR(solid) ν_{\max} 632, 736, 794, 837, 1076, 1134, 1215, 1300, 1404, 1438, 1473, 1635, 2854, 2924 cm^{-1} ; Ms m/z 512 (M⁺), 416, 331, 55.

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