Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

"Synthesis and characterisation of an unsymmetrical, ether-linked, fluorinated bimesogen exhibiting a new polymorphism containing the N_{TB} or 'twist-bend' phase"

Electronic Supplementary Information

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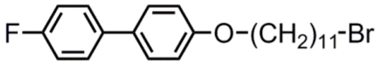
General Information

Compound **1** was obtained from TCI, 11-bromoundecan-1-ol was obtained from Sigma Aldrich and compound **3** was prepared *via* literature methods. [1] All solvents and general reagents were obtained from Fisher Scientific and used as received, with the exception of THF, which was dried by passage through a column of activated alumina prior to use. Column chromatography was performed using Fluka silica gel 60 (70-230 mesh) as the stationary phase, with a plug of neutral alumina at the base of the column to remove ionic impurities.

Analytical and Physical Property Measurements

Chemical Analyses: NMR spectra were recorded on a JEOL ECX spectrometer operating at 400 MHz (^{1}H), 100.5 MHz (^{13}C) or 376.4 MHz (^{19}F), with the residual protic solvent used as the internal standard for ^{1}H NMR. FTIR spectroscopy was performed using a Shimadzu IR Prestige-21 with Specac Golden Gate diamond ATR IR insert. High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20AT high pressure pump, a DGU-20A$_5$ and DGU-20B degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector. The column used was an Alltech C18 bonded reverse-phase silica column with a 5 μm pore size, an internal diameter of 10 mm and a length of 250 mm. Polarized optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Photomicrographs were captured with aid of an InfinityX-21 MP digital camera. Differential scanning calorimetry was performed on a Mettler DSC822^{e} fitted with an autosampler operating with Mettler Star^{e} software and calibrated before use each day using an indium standard (onset = 156.55 ± 0.2 °C, $\Delta H = 28.45 \pm 0.40$ Jg^{-1}) under an atmosphere of dry nitrogen.

Electrooptical Measurements: In order to assess the behavior of the materials under applied electric fields, cells were placed within a Metter FP82HT hotstage, which was controlled by a Mettler FP90 temperature controller. The hotstage was mounted on a Ziess Universal microscope, which was fitted with crossed polarizers and an 8/0.2 lens. The waveform was generated by a Hewlett Packard 33120A arbitrary waveform generator and amplified by a QinetiQ custom built linear x20 amplifier. The electrical response from the cell was amplified by a nano-current amplifier (20 kΩ or 100 kΩ impedance) and fed into a Hewlett Packard 54600B oscilloscope. The antiparallel buffed polyimide cells used were purchased from Linkam; they had spacings of approx. 5 ± 0.1 μm and were constructed from ITO-coated glass. In all cases, the cells were filled by capillary action at atmospheric pressure with the sample in the isotropic liquid.



4-((11-Bromoundecyl)oxy)-4′-fluorobiphenyl (2)

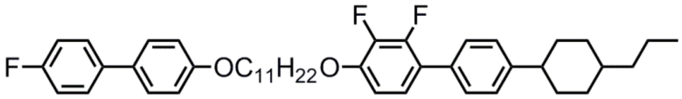
DIAD (10.7 g, 10.5 ml, 53.18 mmol) was added dropwise to a stirred solution of compound **1** (5 g, 26.6 mmol), PPh_3 (8.4 g, 31.91 mmol) and 11-bromoundecan-1-ol (8.7 g, 34.57 mmol) in anhydrous THF (150 ml) under an atmosphere of dry nitrogen. The reaction was followed *via* TLC until complete consumption of **1** was noted after 8 h. The solvents were removed *in vacuo* and the title compound isolated *via* dry vacuum flash chromatography with 2:1 DCM/hexanes as the eluent (Rf_{DCM} = 0.90), followed by low temperature (-100 ºC) crystallisation of the resulting oil from toluene/petroleum ether, giving the title compound as a fine white solid.

Yield: 11 g (98%)

^{1}H NMR: 1.22 – 1.50 (14H, m, CH_2-($\underline{CH_2}$)$_7$-CH_2-), 1.74 – 1.88 (4H, m, CH_2-$\underline{CH_2}$-(CH_2)$_7$-$\underline{CH_2}$-CH_2-), 3.93 (2H, t, J=7.0, Br-$\underline{CH_2}$-CH_2), 3.97 (2H, t, J=7.0, ArO-$\underline{CH_2}$-CH_2), 6.94 (2H, ddd, J=2.1, J=3.1, J=8.9, Ar), 7.08 (2H, dddd, J=2.1, J=3.1, J=8.9, J=17.7), 7.44 (2H, ddd, J=2.1, J=3.1, J=8.5, Ar), 7.47 (2H, dddd, J=2.1, J=3.1, J=5.5, J=8.5, Ar)

^{19}F NMR: -116.71 (1F, septet, J=4.6)

IR (cm^{-1}): 509, 563, 656, 725, 818, 957, 1011, 1034, 1126, 1165, 1242, 1288, 1396, 1474, 1605, 2847, 2916



4-((11-((4'-Fluoro-[1,1'-biphenyl]-4-yl)oxy)undecyl)oxy)-2,3-difluoro-4'-(4-propylcyclohexyl)-1,1'-biphenyl (4)

A stirred suspension of compound **2** (500 mg, 1.7064 mmol), compound **3** (560 mg, 1.7604 mmol), potassium carbonate (470 mg, 3.41 mmol) and potassium iodide (250 mg) in acetone (60 ml) was heated under reflux for 17 hours until the complete consumption of compounds **2** and **3**, as evidenced by TLC analysis. The insoluble matter was removed *via* filtration and the solvent removed *in vacuo* to give a white solid. The title compound was obtained *via* dry vacuum flash chromatography over silica gel with 3:1 DCM/hexanes as the eluent (Rf_{DCM} = 0.9). The solvents were removed *in vacuo* to yield a viscous oil, this was dissolved into DCM and passed through a short plug of neutral alumina to remove ionic impurities. The solvent was removed *in vacuo* and the resulting oil recrystallised from toluene, giving the title compound as fine white crystals.

Yield: 0.62 g (54%)

^{1}H NMR: 0.98 (3H, t, CH_3), 1.06 (2H, m), 1.19 – 1.60 (20H, m), 1.76 – 1.96 (8H, m), 2.49 (1H, t, J=11.9), 3.97 (2H, t, J=6.41, CH_2O), 4.05 (2H, t, J=6.41, CH_2O), 6.76 (1H, t, J=7.6, Ar), 6.94 (2H, d, J=8.5, Ar), 7.02 – 7.12 (3H, m, Ar), 7.26 (2H, d, J=8.2, Ar), 7.37 – 7.49 (6H, m, Ar)

^{13}C NMR: 14.40, 20.01, 25.85, 26.02, 29.12, 29.25, 29.28, 29.35, 29.45, 29.47, 29.50, 33.52, 34.26, 36.98, 36.69, 44.31, 68.06, 69.81, 109.44, 114.78, 115.46 (d, J=20.7), 122.95 (d, J=10.9), 123.42 (t, J=3.8), 127.47 (d, J=96.1), 128.13 (d, J=7.7), 128.56 (d, J=3.1), 132.33, 132. 53, 136.99 (d, J=3.1), 141.84 (dd, J=15.3, J=246.3), 147.37, 147.51 (d, J=2.3), 147.62 (t, J=2.3), 150.06 (d, J=11.5), 158.65, 160.79, 163.23

^{19}F NMR: -158.80 (1F, dd, J=6.9, J=19.5, Ar-F), -141.80 (1F, dd, J=6.9, J=19.5, Ar-F), -116.69 (1F, septet, J=5.1)

IR (cm^{-1}): 532, 594, 632, 725, 802, 894, 964, 1018, 1080, 1219, 1296, 1411, 1465, 1496, 1604, 1627, 2846, 2916

Assay (HPLC, 230/255 nm): 99.60% / 99.95%

References

[1] M. Hird, K.J. Toyne, A.J. Slaney and J.W. Goodby, *J. Mater. Chem.*, 1995, **5**, 423-430.