Supplementary Information (SI) for Soft Matter.

The Effect of Molecular Shape and Chemical Structure on the Photo-Physical Properties of Liquid Crystals

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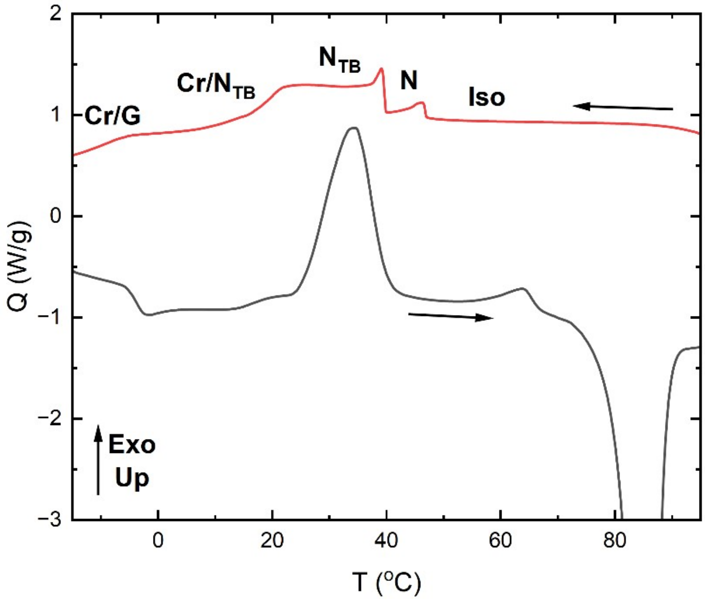


Fig. S1. DSC cycle of F-CB7CB at 10°/min. On cooling F-CB7CB exhibits a monotropic N phase at 46.9 °C followed by an N_{TB} phase at 39.8. A partial crystallisation event is then observed at 30.2 °C followed by vitrification of the uncrystallised remnant at -5.8 °C (taken from onset). On heating various cold crystallisation events are observed before melting of the entire sample at 82.4 °C.

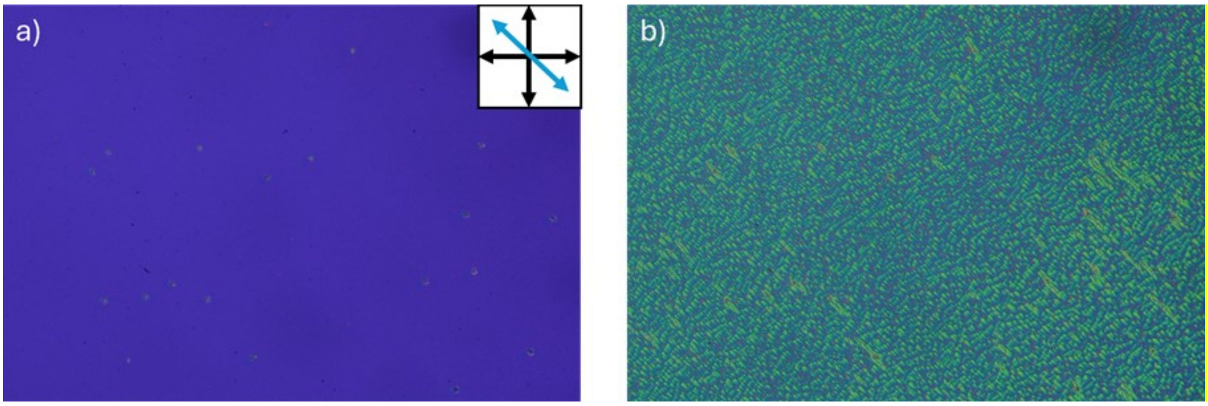


Fig. S2. POM textures of F-CB7CB in a 5 μm thick AP rubbed planar cell in the a) N phase at 45 °C and the b) N_{TB} phase at 35 °C. Black arrows indicate the polariser and analyser orientation while the blue arrow indicates the rubbing direction.

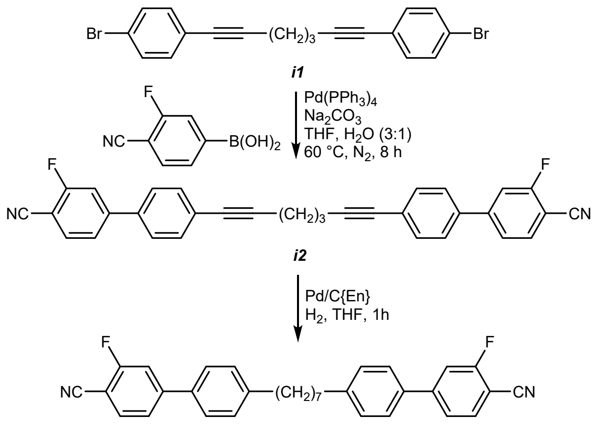
Synthesis

1.1 General

Chemical reagents were purchased from commercial suppliers and used without further purification, with the exception of 1,7-bis(4-bromophenyl)hepta-1,6-diyne (***i1***), which was prepared as described previously.[1,2] Miscellaneous solvents were purchased from Fisher Scientific dried by sequential percolation through columns of activated alumina and copper Q5 catalyst prior to use. Reactions were monitored by thin layer chromatography (TLC) using an appropriate solvent system. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using UV light at wavelengths of both 254 nm and 365 nm. Column chromatography was performed using flash grade silica from Fluorochem (40 - 63µm particle size). Yields refer to chromatographically (HPLC) and spectroscopically (^1H NMR, $^{13}C\{^1H\}$ NMR and ^{19}F NMR) homogenous material.

1.2. Synthetic Details

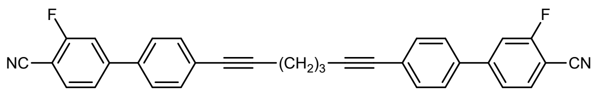
Suzuki-Miyaura coupling of either ***i1*** with 4-cyano-3-fluorobenzene boronic acid, to afforded the alkyne linked dimer ***i2*** in high yield and purity. Selective hydrogenation of the alkyne units of ***i2*** was achieved using palladium on carbon poisoned with diaminoethane, affording compound **1** (F-CB7CB).



1
3FCB7-CB3F

Scheme 1

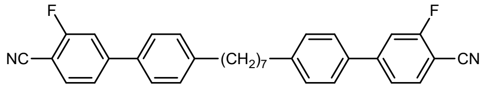
1.3. Chemical Synthesis



2: 4',4'''-(hepta-1,6-diyne-1,7-diyl)bis(3-fluoro-[1,1'-biphenyl]-4-carbonitrile)

A biphasic mixture of 1,7-bis(4-bromophenyl)hepta-1,6-diyne (***i1***, 4.0 g, 9.92 mmol), in 2M aqueous Na_2CO_3 (40 ml) and THF (40 ml), was degassed by sparging with argon whilst agitating in an ultrasonic bath for ~ 15 minutes. The degassed biphasic mixture was heated to reflux under an atmosphere of dry nitrogen gas. 4-Cyano-3-fluorobenzene boronic acid (3.6 g, 2.2 mol eqv., 21.8 mmol) was added as one portion, and the biphasic mixture stirred for 5 minutes. Next, $Pd(PPh_3)_4$ (<50 mg) was added and the solution was left to stir for 8 hours until the complete consumption of the starting aryl halide (***i1***, Rf_{hexane} ~ 0.45). The biphasic mixture was cooled, the organic layer was set aside and the aqueous washed with DCM (3 x 75 ml) and discarded. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude material was purified by flash chromatography with 1:1 hexanes/DCM as the eluent (Rf_{DCM} ~ 0.55) followed by recrystalisation from DCM/ethanol afforded the title compound as a colourless microcrystalline solid (Rf_{DCM} ~ 0.55)

Yield:	4.1 g (86%)
^{1}H NMR:	1.94 (2H, quintet, J = 7.0 Hz, Ar-CC-CH$_2$-CH_2-CH$_2$-CC-Ar), 7.63 (4H, t, J = 7.0 Hz, Ar-CC-CH_2-CH$_2$-CH_2-CC-Ar), 7.40 (2H, dd, J = 1.2 Hz, J = 10.6 Hz, Ar*H*), 7.45 (2H, dd, J = 1.2 Hz, J = 7.0 Hz, Ar*H*), 7.50 (8H, S, Ar*H*), 7.66 (2H, dd, J = 6.8 Hz, J = 8.0 Hz, Ar*H*)
^{13}C{^{1}H} NMR	18.93, 27.87, 80.82, 91.52, 100.11 (d, J = 15.8 Hz), 114.14, 114.76 (d, J = 20.2 Hz), 123.31 (d, J = 3.1 Hz), 125.16, 127.13, 132.53, 133.93, 137.13 (d, J = 1.8 Hz), 147.84 (d, J = 7.9 Hz), 163.60 (d, J = 258.8 Hz)
^{19}F NMR (376.4 MHz):	-105.86 (dd, J = 6.5 Hz, J = 9.9 Hz, Ar*F*)
MS (ESI+, m/z):	483.165653 (calcd. for $C_{33}H_{21}F_2N_2$: 483.166732, M + H) 505.147276 (calcd. for $C_{33}H_{20}F_2N_2Na$: 505.148676, M + Na)
Assay (RP-HPLC):	>99%
Assay (CHN) calcd:	C 82.14%, H 4.18% N 5.81%
Assay (CHN) obs:	C 82.13% H 4.10% N 5.64%



1: **4',4'''-(heptane-1,7-diyl)bis(3-fluoro-[1,1'-biphenyl]-4-carbonitrile)** (CB3F-7-CB3F)

A round bottomed flask was charged with 4',4'''-(hepta-1,6-diyne-1,7-diyl)bis(3-fluoro-[1,1'-biphenyl]-4-carbonitrile) (***i2***, 2.5 g, 5.19 mmol), 5% Pd/C poisoned with diaminoethane (50 mg) and THF (60 ml), in that order. The reaction suspension was sparged with hydrogen gas delivered *via* a balloon (approx. 5 L) over the course of one hour. After this time TLC analysis showed complete consumption of the starting alkyne (Rf_{DCM} ~ 0.55) and the formation of a new material (Rf_{DCM} ~ 0.58), with no reduction of the nitrile to benzylamine detectable (Rf_{DCM} ~ 0). The reaction suspension was filtered through a compacted pad of celite to remove catalyst, and the filtrate concentrated in vacuo to a white solid. This was redisolved into the minimum quantity of DCM, layered with ethanol and the two solvents were allowed to diffuse together slowly, affording the title compound as fine white crystals.

Yield:	2.1 g (83 %)
^{1}H NMR:	1.30-1.38 (10H, Ar-CH$_2$-CH$_2$-(C*H*$_2$)$_3$-CH$_2$-CH$_2$-Ar), 1.56-1.67 (4H, m, Ar-CH$_2$-C*H*$_2$-(CH$_2$)$_3$-C*H*$_2$-CH$_2$-Ar), 2.60-2.67 (4H, m, Ar-C*H*$_2$-(CH$_2$)$_5$-C*H*$_2$-Ar), 7.27 (4H, ddd, *J* = 2.2 Hz, *J* = 3.0 Hz, *J* = 8.8 Hz, Ar*H*), 7.39 (2H, dd, *J* = 1.3 Hz, *J* = 10.5 Hz, Ar*H*), 7.44 (2H, dd, *J* = 1.3 Hz, *J* = 8.4 Hz, Ar*H*), 7.47 (4H, ddd, *J* = 2.2 Hz, *J* = 3.0 Hz, *J* = 8.8 Hz, Ar*H*), 7.64 (2H, dd, *J* = 6.7 Hz, *J* = 8.0 Hz, Ar*H*)
^{13}C{^{1}H} NMR:	29.34, 29.48, 31.46, 35.76, 99.56 (d, *J* = 15.6 Hz), 114.33, 114.62 (d, *J* = 20.2 Hz), 123.23 (d, *J* = 3.0 Hz), 127.19, 129.45, 133.80, 135.48 (d, *J* = 1.5 Hz), 144.59, 148.64 (d, *J* = 8.1 Hz), 163.63 (d, *J* = 258.5 Hz)
^{19}F NMR:	-106.23 (dd, *J* = 6.9 Hz, *J* = 10.0 Hz, Ar*F*)
MS (ESI+, m/z):	491.228450 (calcd. for $C_{33}H_{29}F_2N_2$: 491.2293332, M + H) 513.210338 (calcd. for $C_{33}H_{29}F_2N_2Na$: 513.211276, M + Na)
Assay (RP-HPLC):	>99%

Assay (CHN) calcd:	C 80.79%,	H 5.75%	N 5.71%
Assay (CHN) obs:	C 80.55%	H 5.90%	N 5.61%

References

(1) Mandle, R. J.; Archbold, C. T.; Sarju, J. P.; Andrews, J. L.; Goodby, J. W. The Dependency of Nematic and Twist-bend Mesophase Formation on Bend Angle. *Sci Rep* 2016, *6*, 36682.

(2) Archbold, C. T.; Mandle, R. J.; Andrews, J. L.; Cowling, S. J.; Goodby, J. W. Conformational landscapes of bimesogenic compounds and their implications for the formation of modulated nematic phases. *Liq Cryst* 2017, *44*, 2079-2088.