Supplementary Information for

Chiral Dopants and the Twist-Bend Nematic Phase – Induction of Novel Mesomorphic Behaviour in an Apolar Bimesogen.

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1.1 General Methods.

NMR spectra were recorded on a JEOL ECX spectrometer operating at 400 MHz (¹H), 100.5 MHz (¹³C). FT-IR 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-20A liquid chromatograph, a DGU-20A₅ 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 μ m pore size, an internal diameter of 10 mm and a length of 250 mm. Polarised 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 via an InfinityX-21 MP digital camera mounted atop the microscope. Differential scanning calorimetry was performed on a Mettler DSC822^e fitted with an autosampler operating with Mettler Star^e software and calibrated before use against an indium standard (onset = 156.55 \pm 0.2 °C, Δ H = 28.45 \pm 0.40 Jg⁻¹) under an atmosphere of dry nitrogen. Small angle X-ray diffraction was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. Samples were filled into 1mm capillary tubes and aligned magnetically with a 1T magnet. Diffraction patterns were collected as a function of temperature and the data processed using Bruker DIFFRAC.SUITE EVA software.

1.2 Synthetic Procedures

Dianhydro-d-glucitol, EDAC and DMAP were purchased from Sigma-Aldrich and used as received, without further purification. Anhydrous DCM was obtained by percolation of HPLC grade solvent through a column of activated alumina. 4-((4-(Hexyloxy)benzoyl)oxy)benzoic

acid was prepared as reported previously. [1] Compound **1** and CB9CB were prepared as described previously. [2,3] Compound **2** was prepared as follows:



4-((4-(Hexyloxy)benzoyl)oxy)benzoic acid (600 mg, 1.75 mmol), dianhydro-D-glucitol (122 mg, 0.875 mmol), EDC (382 mg, 2 mmol) and DMAP (5 mg) were dissolved into anhydrous DCM (10 ml) and stirred under an atmosphere of dry nitrogen for 4 hours, at which point TLC analysis showed complete consumption of dianhydro-D-glucitol. The reaction mixture was loaded onto celite and eluted through a plug of silica gel with DCM as the eluent. The solvent was removed and the crude residue purified by recrystalisation from ethanol/THF (4:1) affording the title compound as an amorphous white solid.

Yield: 480 mg (69%)

¹H NMR: 0.899 (6H, dd, *J* = 6.87, 7.33 Hz), 1.336 (8H, sex, *J* = 7.33 Hz), 1.463 (4H,ddt, *J* = 6.87, 7.33, 7.79 Hz), 1.804 (4H, ddt, *J* = 6.41, 7.33, 7.79 Hz), 3.991-4.140 (8H, m), 4.674 (1H, d, *J* = 5.04 Hz), 5.059 (1H, dd, *J* = 5.04, 5.50 Hz), 5.420 (1H, dt, *J* = 5.04, 5.50 Hz), 5.491 (1H, s), 6.957 (4H, dd, *J* = 1.83, 9.16 Hz), 7.289 (4H, dddd, *J* = 1.83, 2.75, 7.79, 8.24 Hz), 8.064-8.159 (8H, m)

¹³C NMR: 14.015, 22.567, 25.637, 29.022, 31.520, 68.352, 70.764, 73.472, 74.588, 78.497, 81.148, 86.172, 114.376, 120.907, 120.945, 121.975, 126.780, 126.828, 131.366, 131.385, 132.386, 155.117, 155.174, 163.774, 164.299, 164.337, 164.880, 165.214.

FT-IR: 665, 688, 727, 759, 842, 883, 968, 1008, 1016, 1056, 1093, 1122, 1159, 1199, 1247, 1315, 1348, 1377, 1392, 1413, 1467, 1510, 1579, 1602, 1716, 2349, 2870, 2933, 3078, 3741, 3851.

MS: 817.3028 (C46H50O12Na, [M+Na]+)

	Transition Temperatures / °C															
No.	wt% Comp.															
	2	\mathbf{Cr}_{1}		Cr ₂		X		N _{TB}		N*		BPIII		Iso		Iso
M1	0.9	•	71.5	•	80.9	-		٠	82.2	•	83.4	٠	95.3	•	98.6	•
M2	2.1	•	70.0	•	80.5	-		•	82.4	•	82.5	•	95.3	•	98.4	•
M3	4.7	٠	70.2	•	79.5	-		٠	82.1	•	82.3	•	91.6	•	98.1	•
M4	5.2	٠	70.5	٠	79.5	(•	62.1)	٠	83.5	٠	83.6	•	92.7	٠	97.3	•
M5	5.4	•	70.5	•	79.5	(•	66.1)	•	83.3	•	83.4	•	88.6	•	96.6	•
M6	5.5	٠	70.6	•	79.4	(•	67.2)	٠	83.2	-	-	-	-	٠	96.8	٠
M7	6.5	٠	70.2	•	79.3	(•	66.4)	٠	83.4	-	-	-	-	٠	96.4	٠
M8	7.1	٠	70.6	٠	79.4	(•	67.2)	٠	82.3	-	-	-	-	٠	96.4	•
M9	8.4	٠	70.1	•	79.1	(•	68.3)	٠	81.9	-	-	-	-	٠	95.3	٠
M10	9.8	•	70.2	•	79.2	(•	69.6)	•	79.2	-	-	-	-	•	96.5	•

 Table i: Cooling data used for phase diagram (Figure 5). Obtained via POM and DSC.

	Transition Temperatures / °C												
	wt%												
No.	Comp.												
	2	Cr		N _{TB}		N*		BPIII		Iso		Iso	
M1	0.9	•	80.6	•	82.29	•	96.7	-		•	96.85	•	
M2	2.1	•	80.5	•	80 44	•	95.8	-		•	96.5	٠	
M3	4.7	•	79.6	•	81	•	90.6	•	93.8	•	94 3	•	
M4	5.2	•	79.5	•	80.63	•	84	•	92.2	•	93 83	•	
M5	5.4	•	79.6	•	82 14	•	83	•	86.5	•	91 41	•	
M6	5.5	•	79.3	•	82 37	•	82.5	•	83.1	•	90.83	•	
M7	6.5	•	79.3	•	82.61	-	-	-	-	•	91.92	•	

M8	7.1	•	79.5	•	81.59	-	-	-	-	•	90.22	٠
M9	8.4	•	79.2	٠	81.56	-	-	-	-	•	88.4	•
M10	9.8	٠	79.1	٠	81.63	-	-	-	-	•	86.7	•

 Table ii: Heating data used for phase diagram (Figure 5). Obtained via POM and DSC.

SI References

- 1) G. Mohan Reddy *et. al., Australian Journal of Chemistry*, **2013**, *66*, 667-675.
- 2) R. J. Mandle et. al., Chem. Eur. J., **2015**, 21, 8158-8167
- 3) R. J. Mandle et. al., Liq. Cryst., **2015**, in press.