Supplementary Information for

Isomeric Oligomesogens Exhibiting Modulated Nematic Mesophases

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1.1.1. General Methods

All chemicals were purchased from commercial suppliers and used as received, without further purification with the exception of solvents which were dried via percolation through active alumina and deoxygenated with Q5 copper catalyst prior to use. Intermediate compounds \textit{i1}, \textit{i4} and \textit{i8} were prepared as described previously. Reactions were monitored by thin layer chromatography (TLC) using an appropriate solvent system, with a stationary phase of silica coated aluminium plates (purchased from Merck, Kieselgel 60 F-254). TLC plates were visualised using either UV light (254 nm and 365 nm), or by oxidation with either iodine or aqueous potassium permanganate solution. Yields refer to chromatographically (HPLC) and spectroscopically (\textit{1H} NMR, \textit{13C\{1H\}} NMR and where appropriate \textit{29Si\{1H\}} NMR) homogenous material. Liquid crystalline materials were dissolved into a minimum quantity of dichloromethane and filtered through 0.2 µm PTFE syringe filters (Whatman Puradisk, part no. WHA67842502) in order to remove insoluble matter – chiefly silica gel - prior to recrystallization.

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (\textit{1H}), 100.5 MHz (\textit{13C\{1H\}}) or 76.4 MHz (\textit{29Si\{1H\}}) as solutions in CDCl\textsubscript{3}, unless stated otherwise. Atmospheric pressure chemical ionisation (APCI) mass spectra were acquired on a Bruker COMPACT instrument. We are grateful to Mr. Karl Heaton of the University of York for acquiring mass spectra. High-performance liquid chromatography (HPLC) was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A quaternary solvent pump, a DGU-20A\textsubscript{5} degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven, and a SPO-20A dual wavelength UV-vis detector operating at 230/255 nm. 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. The mobile phase used was neat acetonitrile that was sparged with nitrogen before use.

Computational chemistry was performed using the using Gaussian G09 revision e01 on the York Advanced Research Computing Cluster (YARCC) as described in the text. 2
1.1.2. Characterisation of Mesomorphic Behaviour

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 DSC822e calibrated before use against indium and zinc standards under an atmosphere of dry nitrogen. In all cases a heat/cool rate of 10 °C min\(^{-1}\) was used, with presented values being the average of three runs.

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. The radiation used was copper K\(\alpha\) (\(\lambda = 0.154 \text{ nm}\)) from a 1 \(\mu\)S microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector at a distance of 121 mm from the sample, allowing simultaneous observation of both the wide angle (\(2\theta = 15 – 25\)) and small angle (\(2\theta = 3 – 15\)) scattering. Samples were filled into 1mm capillary tubes and aligned with a pair of 1 T magnets, the field strength at the sample position being approximately 0.6 T. Diffraction patterns were collected as a function of temperature and the data processed using Matlab. Raw data are available upon request from the University of York data catalogue.
1.1.3. Synthetic Schemes

Scheme 1

Scheme 2
1.2. Characterisation of chemical intermediates

Solid tertbutyldimethylchlorosilane (4.44 g, 29.5 mmol) was added in portions to a solution of \( i1 \) (8.8 g, 24.5 mmol) and imidazole (2.2 g, 31.9 mmol) in anhydrous DCM (100 ml) under an atmosphere of dry nitrogen. The reaction was stirred for 8 h, until the complete consumption of \( i-1 \) (Rf\(_{\text{DCM}}\) = 0.15). The solvent was removed \( \text{in vacuo} \) and the crude material purified by flash chromatography with DCM as the eluent. The chromatographed material was recrystallised from ethanol, affording the title compound as a white solid.

**Yield:** 10.4 g (90 %)

**Rf:** 0.80 (DCM)

**\(^1H\) NMR:** 0.20 (6H, S, \((\text{CH}_3)_3\text{CSi(\text{CH}_3)_2OAr})\), 0.98 (9H, S, \((\text{CH}_3)_2\text{CSi(\text{CH}_3)_2OAr})\), 1.65 – 1.75 (2H, m, Ar-CC-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{OCH}_2\)-Ph), 1.75 – 1.85 (Ar-CC-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{OCH}_2\)-Ph), 2.45 (2H, t, \( J = 6.9 \) Hz, Ar-CC-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{OCH}_2\)-Ph), 3.53 (2H, t, \( J = 6.9 \) Hz, Ar-CC-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{OCH}_2\)-Ph), 4.51 (2H, s, Ar-CC-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{CH}_2\)-\( \text{OCH}_2\)-Ph), 6.88 (2H, ddd, \( J = 1.8 \) Hz, \( J = 2.1 \) Hz, \( J = 8.5 \) Hz, Ar\( \text{H} \)), 7.22 – 7.50 (11H, m, Ar\( \text{H} \)+ Bn\( \text{H} \)).

**\(^{13}\text{C}\{^1\text{H}\}\) NMR:** -4.24, 18.39, 19.46, 25.66, 25.83, 29.11, 70.02, 73.05, 80.93, 90.56, 120.54, 122.34, 126.54, 127.67, 127.78, 128.07, 128.52, 132.03, 133.67, 138.71, 140.07, 155.61

**\(^{29}\text{Si}\{^1\text{H}\}\) NMR:** 21.67 (S, OSi(\( \text{CH}_3 \))\(_2\)C(\( \text{CH}_3 \))\(_3\))

**MS (APCI):** 471.270484 (calcd. for C\(_{31}\)H\(_{39}\)O\(_2\)Si: 471.271383, M + H)
i3: 6-(4'-(tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-4-yhexan-1-ol

A suspension of i2 (6.03 g, 12.8 mmol) and 10% palladium on carbon (0.1 g) in THF (150 ml) was degassed thoroughly by stirring under vacuum and refilling with hydrogen gas 3 times. The reaction was then allowed to stir under an atmosphere of hydrogen gas for 24 hours, at which point it was noted that the starting material had been consumed entirely. The reaction suspension was filtered through a bed of celite and purified by flash chromatography with DCM as the eluent, affording the title compound as a colourless oil that solidified upon standing overnight.

Yield: 4.0 g (81 %)

Rf: 0.24 (DCM)

^1^H NMR: 1.36 – 1.44 (4H, m, -CH_2-CH_2-CH_2-CH_2-) 1.52 – 1.72 (4H, m, Ar-CH_2-CH_2- (CH_2)_2-CH_2-CH_2-CH_2-OH), 2.64 (2H, t, J = 7.3 Hz, Ar-CH_2-CH_2-), 3.65 (2H, t, J = 7.3 Hz, -CH_2-CH_2-OH), 6.88 (2H, ddd, J = 2.1 Hz, J = 2.7 Hz, J = 8.4 Hz, ArH), 7.22 (2H, ddd, J = 2.1 Hz, J = 2.7 Hz, J = 8.4 Hz, ArH), 7.42 – 7.48 (4H, m, ArH)

^{29}Si^{1}H NMR: 21.73 (S, OSi(CH_3)_2C(CH_3)_3)

MS (APCI): 385.2563 (calcd. for C_{24}H_{37}O_2Si: 385.2557, M + H)
DIAD (~1 ml, 1024 mg, 5.07 mmol) was added in one portion to a stirred solution of 4-hydroxy-4'-cyanobiphenyl (0.79 g, 4.06 mmol), i4 (1.3 g, 3.38 mmol) and triphenylphosphine (1.33 g, 5.03 mmol) in anhydrous THF (20 ml). The solution was stirred for 1 h until TLC analysis showed complete consumption of the starting alcohol i4. The solvent was removed in vacuo and the crude material purified by flash chromatography with DCM/hexanes (3:2) as the eluent. Recrystallisation from ethanol afforded i5 as a white powdery solid.

Yield: 1.53 (81 %)

Rf: 0.56 (DCM)

\[^{1}\text{H NMR:}\]
0.22 (6H, s, OSi(CH\(_3\))\(_2\)C(CH\(_3\))\(_3\)), 1.00 (9H, s, OSi(CH\(_3\))\(_2\)C(CH\(_3\))\(_3\)), 1.38 – 1.55 (4H, m, -CH\(_2\)-(CH\(_2\))\(_4\)-CH\(_2\)-), 1.65 – 1.73 (2H, m, Ar-CH\(_2\)-CH\(_2\)-CH\(_2\)-), 1.77 – 1.87 (2H, m, ArO-CH\(_2\)-CH\(_2\)-CH\(_2\)-), 2.65 (2H, t, J = 6.5 Hz, Ar-CH\(_2\)-CH\(_2\)-), 4.00 (2H, t, J = 6.5 Hz, ArO-CH\(_2\)-CH\(_2\)-), 6.88 (2H, ddd, J = 2.1 Hz, J = 2.4 Hz, J = 8.9 Hz, ArH), 7.19 (2H, ddd, J = 1.8 Hz, J = 2.1 Hz, J = 8.9 Hz, ArH), 7.22 (2H, ddd, J = 1.8 Hz, J = 2.1 Hz, J = 8.9 Hz, ArH), 7.40 – 7.45 (4H, m, ArH), 7.53 (2H, ddd, J = 2.1 Hz, J = 2.4 Hz, J = 8.9 Hz, ArH), 7.62 (2H, ddd, J = 1.8 Hz, J = 2.1 Hz, J = 8.9 Hz, ArH), 7.68 (2H, ddd, J = 1.8 Hz, J = 2.1 Hz, J = 8.9 Hz, ArH)

\[^{29}\text{Si}\left({}^{1}\text{H}\right)\text{NMR:}\] 21.55 (S, OSi(CH\(_3\))\(_2\)C(CH\(_3\))\(_3\))

MS (APCI): 562.313166 (calcd. for C\(_{37}\)H\(_{44}\)NO\(_2\)Si: 562.313583, M + H)
A solution of TBAF (3.64 ml, 1 M in THF, 3.64 mmol) was added to a stirred solution of \textit{i5} (0.48 g, 0.91 mmol) in THF (10 ml) under an atmosphere of dry nitrogen and stirred. TLC analysis showed complete consumption of the starting material within 20 minutes. The solvent was removed \textit{in vacuo} and the crude material purified by flash chromatography with DCM as the eluent. Precipitation of the chromatographed material from DCM by adding ethanol afforded a white powder.

**Yield:** 390 mg (96 %)

**Rf:** 0.18 (DCM)

**\(^1\)H NMR:**
\begin{align*}
1.38 – 1.55 & \text{ (4H, m, } -\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{CH}_2\text{-}), \\
1.65 – 1.73 & \text{ (2H, m, Ar-CH}_2\text{CH}_2\text{CH}_2\text{-CH}_{2}\text{-CH}_2\text{-)}, \\
1.77 – 1.87 & \text{ (2H, m, ArO-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-CH}_{2}\text{-)}, \\
2.66 & \text{ (2H, t, J = 7.0 Hz, Ar-CH}_2\text{CH}_2\text{-CH}_{2}\text{-CH}_2\text{-}), \\
4.01 & \text{ (2H, t, J = 7.0 Hz, ArO-CH}_2\text{CH}_2\text{CH}_2\text{-CH}_{2}\text{-}), \\
6.88 & \text{ (2H, ddd, J = 2.1 Hz, J = 2.4 Hz, J = 8.9 Hz, ArH),} \\
6.97 & \text{ (2H, ddd, J = 1.8 Hz, J = 2.1 Hz, J = 8.9 Hz, ArH),} \\
7.22 & \text{ (2H, ddd, J = 2.1 Hz, J = 2.4 Hz, J = 8.9 Hz, ArH),} \\
7.43 & \text{ - 7.48 (4H, m, ArH),} \\
7.52 & \text{ (2H, ddd, J = 2.1 Hz, J = 2.4 Hz, J = 8.9 Hz, ArH),} \\
7.63 & \text{ (2H, ddd, J = 1.8 Hz, J = 2.4 Hz, J = 9.2 Hz, ArH),} \\
7.69 & \text{ (2H, ddd, J = 1.8 Hz, J = 2.4 Hz, J = 9.2 Hz, ArH).}
\end{align*}

\[\text{**\(^{13}\)C\{\(^1\)H\} NMR:**} \]
\begin{align*}
26.07, & \text{ 29.08, 29.41, 31.37, 35.69, 68.11, 115.66, 115.91, 116.59, 119.14,} \\
128.25, & \text{ 128.34, 128.96, 129.64, 130.26, 131.24, 133.04, 133.79, 139.41,} \\
141.22, & \text{ 144.83, 157.68, 158.40}
\end{align*}

\[\text{**MS (APCI:** 448.226467 (calcd. for C}_{31}\text{H}_{30}\text{NO}_{2}: 448.227106, M + H)}\]
1.3. Characterisation of Liquid Crystalline Materials

\[ \text{NC}---\text{C}_6\text{H}_{12}\text{O}---\text{C}_6\text{H}_{12}\text{O}---\text{CN} \]

**A6**: 4’-((6’-(4’-cyano-[1,1’-biphenyl]-4-yl)hexyl)oxy)-[1,1’-biphenyl]-4-carbonitrile

Quantities used: \(\text{i6} \) (218 mg, 0.5 mmol), \(\text{i7} \) (168 mg, 0.6 mmol), \(\text{PPh}_3 \) (262 mg, 1 mmol), DIAD (202 mg, 1 mmol), THF (15 ml). The experimental procedure was as described for compound \(\text{i5} \). Column chromatography with 5:2 hexane/DCM as the eluent followed by recrystallisation from ethanol gave the title compound as a powdery white solid.

**Yield:** 300 mg (81%)

**Rf:** 0.56 (DCM)

**\(^1\)H NMR:**

- 1.41 – 1.60 (8H, m, 2x -CH\(_2\)-(CH\(_2\))\(_2\)-CH\(_2\)), 1.65 - 1.73 (4H, m, 2x Ar-CH\(_2\)-CH\(_2\)-(CH\(_2\))\(_2\)-CH\(_2\)), 1.76 – 1.86 (4H, m, 2x ArO-CH\(_2\)-CH\(_2\)-(CH\(_2\))\(_2\)-CH\(_2\)), 2.66 (2H, t, \(J = 7.7 \text{ Hz}, \text{CH}_2\text{-O-Ph-Ph-CH}_2\text{-CH}_2\)), 2.70 (2H, t, \(J = 7.7 \text{ Hz}, \text{NC-Ph-Ph-CH}_2\text{-CH}_2\)), 2.98 (2H, t, \(J = 7.7 \text{ Hz}, \text{CH}_2\text{-Ph-PhO-CH}_2\text{-CH}_2\)), 4.01 (2H, t, \(J = 7.7 \text{ Hz}, \text{NC-Ph-PhO-CH}_2\text{-CH}_2\)), 6.93 (2H, ddd, \(J = 2.1 \text{ Hz}, J = 2.9 \text{ Hz}, J = 8.9 \text{ Hz}, \text{ArH}\)), 6.98 (2H, ddd, \(J = 1.8 \text{ Hz}, J = 3.1 \text{ Hz}, J = 8.9 \text{ Hz}, \text{ArH}\)), 7.22 (2H, ddd, \(J = 2.1 \text{ Hz}, J = 2.9 \text{ Hz}, J = 8.9 \text{ Hz}, \text{ArH}\)), 7.28 (2H, ddd, \(J = 1.8 \text{ Hz}, J = 3.1 \text{ Hz}, J = 8.9 \text{ Hz}, \text{ArH}\)), 7.43 – 7.55 (8H, m, ArH), 7.62 – 7.73 (8H, m, ArH)

**\(^{13}\)C\(^{1}\)H NMR:**

- 26.02, 29.01, 29.07, 29.23, 29.31, 31.39, 31.50, 35.55, 35.60, 67.99, 68.17, 110.13, 110.64, 114.82, 115.20, 119.21, 119.29, 126.67, 127.20, 127.23, 127.61, 128.04, 128.46, 128.93, 129.34, 131.38, 132.70, 133.61, 136.63, 138.35, 141.26, 143.67, 145.40, 145.70, 158.67, 158.76, 159.88

**MS (APCI):** 709.380493 (calcd. for C\(_{50}\)H\(_{49}\)N\(_2\)O\(_2\): 709.378855, M + H)

**Assay (HPLC):** 99.4%
B6₃: 4',4'''-(([1,1'-biphenyl]-4,4'-diylbis(oxy))bis(hexane-6,1-diyl))bis([1,1'-biphenyl]-4-carbonitrile))

Quantities used: \textit{i7} (168 mg, 0.6 mmol), \textit{i8} (56 mg, 0.3 mmol), PPh₃ (262 mg, 1 mmol), DIAD (202 mg, 1 mmol), THF (5 ml). The experimental procedure was as described for compound \textit{i5}. Column chromatography with 3:2 hexane/DCM as the eluent followed by recrystallisation from ethanol gave the title compound as a powdery white solid.

Yield: 191 mg (90 %)

Rf: 0.51 (DCM)

\textsuperscript{1}H NMR: 1.40 – 1.60 (8 H, m, 2 x -CH₂-(CH₂)₂-CH₂-), 1.65 – 1.75 (4H, m, 2 x -CH₂-CH₂-CH₂-Ar), 1.79 – 1.86 (4H, m, 2 x -CH₂-CH₂-CH₂-OAr), 2.68 (4H, t, J = 7.1 Hz, 2 x -CH₂-CH₂-OAr), 3.98 (4H, t, J = 7.1 Hz, 2 x -CH₂-CH₂-OAr), 6.93 (4H, ddd, J = 1.8 Hz, J = 3.2 Hz, J = 8.7 Hz, ArH), 7.28 (4H, ddd, J = 1.8 Hz, J = 2.4 Hz, J = 8.4 Hz, ArH), 7.43 (4H, ddd, J = 1.8 Hz, J = 3.2 Hz, J = 8.7 Hz, ArH), 7.50 (4H, ddd, J = 1.8 Hz, J = 2.4 Hz, J = 8.4 Hz, ArH), 7.66 (4H, ddd, J = 1.9 Hz, J = 2.2 Hz, J = 9.2 Hz, ArH), 7.70 (4H, ddd, J = 1.9 Hz, J = 2.2 Hz, J = 9.2 Hz, ArH).

\textsuperscript{13}C\{\textsuperscript{1}H\} NMR: 26.02, 29.02, 29.31, 31.39, 35.61, 68.01, 110.62, 114.85, 119.20, 127.23, 127.60, 127.77, 129.34, 132.70, 133.41, 136.62, 143.67, 145.70, 158.30

MS (APCI): 709.376987 (calcd. for C₅₀H₄₉N₂O₂: 709.378855, M + H)

Assay (HPLC): 99.7%
1.4. Supplemental NMR data

Figure SI-1: $^1$H NMR (400 MHz, CDCl$_3$) of the trimer A$_6$$_3$
Figure SI-2: $^{13}$C($^1$H) NMR (100.5 MHz, CDCl$_3$) of the trimer A$6_3$. 
Figure SI-3: $^1$H NMR (400 MHz, CDCl$_3$) of the trimer B6$_3$
Figure SI-4: $^{13}$C($^1$H) NMR (100.5 MHz, CDCl$_3$) of the trimer B$_6$$_3$
Figure SI-5: Photomicrograph (x100) of the N\textsubscript{2} phase of B\textsubscript{6} at 115 °C showing an unusual optical texture.
Figure SI-6: Photomicrograph (x200) of a region of A6 showing the rope-like texture.
1.6. Supplemental SAXS Data

**Figure SI-7:** Plot of integrated SAXS intensity (Arb) as a function of $Q$ (Å$^{-1}$) for the trimer A6$_3$ in the nematic (145 °C) and N$_{TB}$ (125 °C) mesophases.
1.7. References
