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Supplementary Information for

Investigating the Cusp between the Nano- and Macro-sciences in Supermolecular Liquid-Crystalline Twist-Bend Nematogens

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1.1. General Methods.

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) was purchased from Carbosynth UK, hydrogen gas was obtained from BOC and all other reagents were purchased from Sigma Aldrich and used without further purification. Solvents were purchased from Fisher Scientific UK and were dried *via* passage over activated alumina prior to use. The synthesis of 1,7-bis(4-hydroxyphenyl)heptane is described elsewhere. [1]

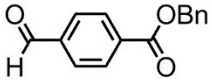
Reactions were monitored by thin layer chromatography (TLC) with DCM as the eluent. Silica coated aluminium TLC plates used were purchased from Merck (Kieselgel 60 F-254) and visualised using either UV light (254 nm and 365 nm), or by oxidation with either iodine or aqueous potassium permanganate solution. Yields refer to chromatographically (HPLC) and spectroscopically (^{1}H NMR, ^{13}C{^{1}H} NMR) homogenous material.

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^{1}H) or 100.5 MHz (^{13}C{^{1}H} as solutions in $CDCl_3$. Mass spectra were recorded on a Bruker micrOTOF MS-Agilent series 1200LC spectrometer. 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-20A solvent pump, a DGU-20A$_5$ 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 wavelengths of 230 and 255 nm. Reverse-phase HPLC was performed using an Alltech C18 bonded silica column with a 5 µm pore size, an internal diameter of 4.6 mm and a length of 250 mm, with neat acetonitrile used as the mobile phase. Chromatograms where only one peak was detected are quoted at >99% purity.

Elemental analysis data (CHN) were obtained using an Exeter Analytical Inc. CE-440 Analyser and Sartorius S2 analytical balance. Calibration was performed against acetanilide standards and checked by the use of S-benzyl thiouronium chloride as internal standard (analytical grade, Exeter Analytical). We extend our gratitude to Dr. Graeme Mcallister of the University of York for performing elemental analysis.

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} calibrated before use against indium and zinc standards under an atmosphere of dry nitrogen. DSC thermograms were processed in Matlab. Computational chemistry was performed using Gaussian G09 revision d01 on the York Advanced Research Computing Cluster (YARCC) at various levels of theory as described in the text. [2]

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 Kα (λ = 0.154056 nm) from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small angle and wide angle scattering data. Samples were filled into 0.9 mm OD glass capillary tubes and aligned with a pair of 1T magnets with the field perpendicular to the incident X-ray beam. Diffraction patterns were collected as a function of temperature (controlled to an accuracy of +/1 0.1 °C). Two dimensional diffraction patterns were radially averaged (0.05 ° step size) to give one dimensional profiles of scattered intensity as a function of two theta. Raw data are available upon request from the University of York data catalogue.



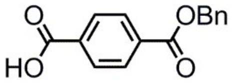
Benzyl 4-formylbenzoate

A suspension of 4-carboxybenzaldehyde (9 g, 60 mmol), benzyl alcohol (60 mmol, 6.5 g), EDAC (70 mmol, 13.4 g) and DMAP (100 mg) in DCM (100 ml) was stirred for 2h. The reaction was monitored by TLC, with the formation of a new compound at Rf_{DCM} = 0.5 noted. The solvent was removed *in vacuo* and the crude material purified by flash chromatography with DCM as the eluent, affording the title compound as a viscous, colourless oil that solidified upon standing. Spectra were in keeping with literature data. [3]

Yield:	12.2 g (85 %)
^{1}H NMR (400 MHz, $CDCl_3$):	5.35 (2H, s, Ph-C$\underline{H}_2$-OOCAr), 7.29 – 7.25 (5H, m, Bn), 7.88 (2H, ddd, $J_{\underline{H}-\underline{H}}$ = 1.5 Hz, $J_{\underline{H}-\underline{H}}$ = 2.3 Hz, $J_{\underline{H}-\underline{H}}$ = 8.4 Hz, Ar$\underline{H}$), 8.17 (2H,

ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.5 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.3 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 8.4 Hz, Ar$\underline{H}$), 10.02 (1H, s, ArC(=O)$\underline{H}$)

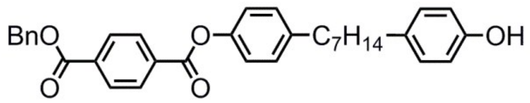
$^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CDCl_3$): 66.97 (Ph-$C$$H_2$-OOCAr), 128.06, 128.14, 128.42, 129.21, 129.93, 134.73, 135.34, 135.46, 138.92, 165.03 (Ar*C*OOBn), 191.33 (Ar-*C*(=O)H)



2: 4-((Benzyloxy)carbonyl)benzoic acid

Oxone (6.08 g, 40 mmol) was added in one portion to a stirred, cooled solution of benzyl 4-formylbenzoate (7 g, 29 mmol) in anhydrous DMF (60 ml). Once the exothermic reaction had subsided (<2 h) TLC analysis of the reaction showed complete consumption of the starting material (Rf_{DCM} = 0.5) and the formation of a new compound (Rf_{EtOAc} = 0.05). The solvent was removed *in vacuo*, and the resulting solid mass washed with dichloromethane (1000 ml). The filtrate was concentrated *in vacuo* and the crude material was purified by flash chromatography with ethyl acetate + 5% ethanol as the eluent. The chromatographed material was recrystalised from ethanol, affording the title compound as colourless crystals. Spectra were in keeping with literature data. [3]

Yield:	7.2 g (97%)
^{1}H NMR (400 MHz, $CDCl_3$):	5.40 (2H, s, Ph-C*H*$_2$-OOCAr), 7.34 – 7.52 (5H, m, Bn), 8.17 (4H, s, Ar*H*)
^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$):	67.23 (Ph-*C*H$_2$-OOCAr), 128.83, 128.46, 128.67, 129.77, 130.16, 132.93, 134.65, 135.57, 153.46, 165.51 (Ar*C*OOBn), 169.99 (Ar*C*OOH),



4: Benzyl (4-(7-(4-hydroxyphenyl)heptyl)phenyl) terephthalate

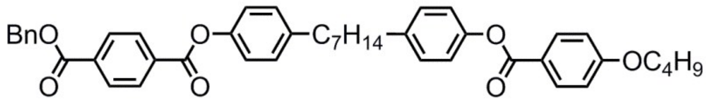
A suspension of 4-((benzyloxy)carbonyl)benzoic acid (2 g, 7.81 mmol) and EDAC (1.9 g, 10 mmol) was stirred in anhydrous dichloromethane (200 ml) for 5 minutes yielding a pale yellow, homogenous solution. This was added dropwise over the course of an hour to a stirred solution of *bis* 1,7-(4-hydroxyphenyl)heptane (8 mmol, 2.3 g) and DMAP (2.4 g, 20 mmol) in anhydrous dichloromethane (15 ml). The reaction was monitored by the formation of two new materials as evidenced by TLC analysis at Rf_{DCM} 0.6 (minor) and 0.2 (major) respectively. After 2 hours the reaction was deemed complete, the solvent removed *in vacuo* and the crude material purified by flash chromatography. The mono substituted title compound (Rf_{DCM} = 0.2) was obtained as a colourless, viscous oil that solidified upon standing.

Yield: 2.7 g (66 %)

^{1}H NMR (400 MHz, $CDCl_3$): 1.26 – 1.42 (6H, m, $Ar\text{-}CH_2\text{-}CH_2\text{-}(C\underline{H}_2)_3\text{-}CH_2\text{-}CH_2\text{-}Ar\text{-}OH$), 1.52 – 1.67 (4H, m, $Ar\text{-}CH_2\text{-}C\underline{H}_2\text{-}(CH_2)_3\text{-}C\underline{H}_2\text{-}CH_2\text{-}Ar\text{-}OH$), 2.54 (2H, t, $J_{H\text{-}H}$ = 7.6 Hz, $Ar\text{-}C\underline{H}_2\text{-}(CH_2)_5\text{-}CH_2\text{-}ArOH$), 2.63 (2H, t, $J_{H\text{-}H}$ = 7.6 Hz, $Ar\text{-}(CH_2)_6\text{-}C\underline{H}_2\text{-}ArOH$), 5.22 (1H, s, $ArO\underline{H}$), 5.46 (2H, s, $Ph\text{-}C\underline{H}_2O(O)C\text{-}Ar$), 6.74 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.4 Hz, $Ar\underline{H}$), 7.04 (2H, ddd, $J_{H\text{-}H}$ = 1.5 Hz, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 8.4 Hz, $Ar\underline{H}$), 7.13 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.4 Hz, $Ar\underline{H}$), 7.24 (2H, ddd, $J_{H\text{-}H}$ = 1.5 Hz, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 8.4 Hz, $Ar\underline{H}$), 7.36 – 7.51 (5H, m, $Bn\underline{H}$), 8.21 (2H, ddd, $J_{H\text{-}H}$ = 1.5 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.8 Hz, $Ar\underline{H}$), 8.27 (2H, ddd, $J_{H\text{-}H}$ = 1.5 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.8 Hz, $Ar\underline{H}$)

$^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): 28.95, 29.07, 29.20, 31.32, 31.56, 34.91, 35.28, 67.25, 115.00, 121.12, 128.29, 128.44, 128.65, 129.34, 129.37, 129.79, 130.09, 133.48, 134.33, 134.81, 135.51, 140.78, 148.52, 153.52, 164.64, 165.62

MS (ESI+, m/z): 523.2470 (calcd. for $C_{34}H_{35}O_5$: 523.2479, M + H)
545.2284 (calcd. for $C_{34}H_{34}NO_5$: 545.2298, M + Na)



6a: Benzyl (4-(7-(4-((4-butoxybenzoyl)oxy)phenyl)heptyl)phenyl) terephthalate

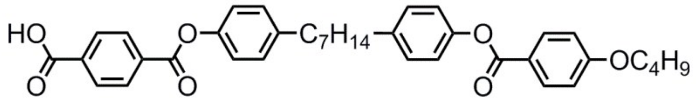
Quantities used: Compound **4** (500 mg, 0.957 mmol), 4-butoxybenzoic acid (1.2 mmol, 232 mg), EDAC (1.2 mmol, 229 mg), DMAP (<25 mg) and DCM (10 ml). The experimental procedure was as described in the synthesis of **4**. Column chromatography with 3:2 DCM/hexanes as the eluent afforded the title compound as a viscous, colourless oil (Rf$_{DCM}$= 0.3).

Yield: 620 mg (93%)

^{1}H NMR (400 MHz, CDCl$_3$): 0.99 (3H, t, $J_{\underline{H}\text{-}\underline{H}}$ = 7.0 Hz, ArO-CH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$), 1.28 – 1.41 (6H, m, Ar-CH$_2$-CH$_2$-(C$\underline{H}_2$)$_3$-CH$_2$-CH$_2$-Ar), 1.45 – 1.56 (2H, m, ArO-CH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$), 1.57 – 1.67 (4H, m, Ar-CH$_2$-C$\underline{H}_2$-(CH$_2$)$_3$-C$\underline{H}_2$-CH$_2$-Ar), 1.76 – 1.84 (2H, m, ArO-CH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 2.60 (2H, t, $J_{\underline{H}\text{-}\underline{H}}$ = 7.6 Hz, Ar-C$\underline{H}_2$-(CH$_2$)$_6$-Ar), 2.62 (2H, t, $J_{\underline{H}\text{-}\underline{H}}$ = 7.6 Hz, Ar-C$\underline{H}_2$-(CH$_2$)$_6$-Ar), 4.03 (2H, t, $J_{\underline{H}\text{-}\underline{H}}$ = 7.0 Hz, ArO-C$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$), 5.39 (2H, s, H$_5$C$_6$-C$\underline{H}_2$-OOCAr), 6.95 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.8 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.3 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 9.2 Hz, Ar$\underline{H}$), 7.06 – 7.14 (4H, m, Ar$\underline{H}$) 7.17 – 7.26 (4H, m, Ar$\underline{H}$), 7.33 – 7.49 (5H, m, $\underline{H}_5$C$_6$-CH$_2$-OOCAr), 8.12 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.8 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.3 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 9.2 Hz, Ar$\underline{H}$), 8.18 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.5 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.3 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 8.4 Hz, Ar$\underline{H}$), 8.25 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.5 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.3 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 8.4 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): 14.00, 19.35, 29.31, 29.48, 31.28, 31.58, 35.50, 53.60, 67.37, 68.12, 114.38, 121.34, 121.58, 121.83, 128.48, 128.62, 128.84, 129.43, 129.57, 129.96, 130.26, 132.37, 133.72, 134.52, 135.77, 140.38, 140.91, 148.77, 149.10, 163.59, 164.67, 165.28, 165.70

MS (ESI+, m/z): 721.3110 (calcd. for C$_{45}$H$_{46}$NaO$_7$: 721.3136, M + Na)



6: 4-((4-(7-(4-((4-Butoxybenzoyl)oxy)phenyl)heptyl)phenoxy)carbonyl)benzoic acid

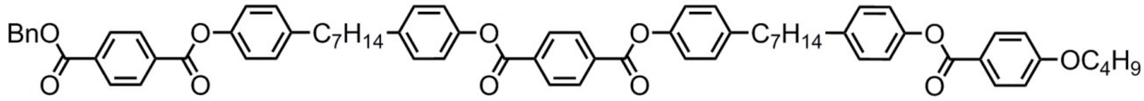
Compound **6a** (500 mg, 0.716 mmol) and palladium on carbon (<50 mg) were dissolved into freshly distilled THF (30 ml) with stirring, under an atmosphere of dry nitrogen. The reaction mixture was degassed using three vacuum/nitrogen cycles before replacing the nitrogen atmosphere with hydrogen. The reaction suspension was monitored by TLC analysis, with complete consumption of the starting material and formation of a new product (Rf_{EtOAc} = 0.1) noted after 6 h. The reaction mass was filtered through a pad of celite, eluting with DCM, the solvents removed *in vacuo* and the crude material recrystalised from ethanol, affording the title compound as a white powder.

Yield: 390 mg (89%)

^{1}H NMR (400 MHz, CDCl$_3$): 0.99 (3H, t, $J_{\underline{H}\text{-}\underline{H}}$ = 7.0 Hz, ArO-CH$_2$-CH$_2$-CH$_2$-C$\underline{H}_3$), 1.30 – 1.42 (6H, m, Ar-CH$_2$-CH$_2$-(C$\underline{H}_2$)$_3$-CH$_2$-CH$_2$-Ar), 1.47 – 1.57 (2H, m, ArO-CH$_2$-CH$_2$-C$\underline{H}_2$-CH$_3$), 1.58 – 1.69 (4H, m, Ar-CH$_2$-C$\underline{H}_2$-(CH$_2$)$_3$-C$\underline{H}_2$-CH$_2$-Ar), 1.77 – 1.85 (2H, m, ArO-CH$_2$-C$\underline{H}_2$-CH$_2$-CH$_3$), 2.59 – 2.67 (4H,m, Ar-C$\underline{H}_2$-(CH$_2$)$_5$-*C*$\underline{H}_2$-*Ar*), 4.04 (2H, t, $J_{\underline{H}\text{-}\underline{H}}$ = 7.0 Hz, ArO-C$\underline{H}_2$-CH$_2$-CH$_2$-CH$_3$), 6.97 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.5 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 3.0 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 8.4 Hz, Ar$\underline{H}$), 7.08 – 7.16 (4H, m, Ar$\underline{H}$) 7.19 – 7.25 (4H, m, Ar$\underline{H}$), 8.13 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.8 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.3 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 9.2 Hz, Ar$\underline{H}$), 8.26 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.8 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.8 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 8.8 Hz, Ar$\underline{H}$), 8.32 (2H, ddd, $J_{\underline{H}\text{-}\underline{H}}$ = 1.8 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 2.8 Hz, $J_{\underline{H}\text{-}\underline{H}}$ = 8.8 Hz, Ar$\underline{H}$)

^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): 13.82, 19.17, 29.12, 29.29, 31.11, 31.45, 35.33, 67.95, 114.20, 121.14, 121.41, 121.63, 129.26, 129.43, 130.20, 130.29, 132.21, 133.36, 134.27, 140.22, 140.81, 148.55, 148.90, 163.42, 164.43, 165.16, 170.69

MS (ESI+, m/z): 631.2672 (calcd. for $C_{38}H_{40}NaO_7$: 631.2666 , M + Na)



7a: Benzyl (4-(7-(4-((4-((4-(7-(4-((4-butoxybenzoyl)oxy)phenyl)heptyl)phenoxy)carbonyl)benzoyl)oxy)phenyl)heptyl)phenyl) terephthalate

Quantities used: Compound **6** (304 mg, 0.5 mmol), compound **3** (261 mg, 0.5 mmol), EDAC (191 mg, 1 mmol), DMAP (122 mg, 1 mmol), anhydrous DCM (10 ml). The experimental procedure was as described in the synthesis of **4**. Column chromatography with DCM as the eluent (Rf$_{\text{DCM}}$= 0.6) afforded the title compound as a white solid.

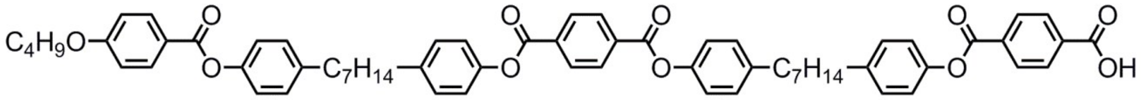
Yield: 440 mg (79%)

^{1}H NMR (400 MHz, CDCl$_3$): 0.98 (3H, t, $J_{H\text{-}H}$ = 7.5 Hz, ArO-CH$_2$-CH$_2$-CH$_2$-C$\underline{\text{H}}_3$), 1.27 – 1.42 (12H, m, 2x Ar-(CH$_2$)$_2$-(C$\underline{\text{H}}_2$)$_3$-(CH$_2$)$_2$-Ar), 1.44 – 1.54 (2H, m, ArO-CH$_2$-CH$_2$-C$\underline{\text{H}}_2$-CH$_3$), 1.57 – 1.70 (8H, m, 2x Ar-CH$_2$-C$\underline{\text{H}}_2$-(CH$_2$)$_3$-C$\underline{\text{H}}_2$-CH$_2$-Ar), 1.74 – 1.84 (2H, m, ArO-CH$_2$-C$\underline{\text{H}}_2$-CH$_2$-CH$_3$), 2.56 – 2.66 (8H, m, 2x Ar-C$\underline{\text{H}}_2$-(CH$_2$)$_5$-C$\underline{\text{H}}_2$-Ar), 4.02 (2H, t, $J_{H\text{-}H}$ = 7.5 Hz, ArO-C$\underline{\text{H}}_2$-CH$_2$-CH$_2$-CH$_3$), 5.39 (2H, s, PhC$\underline{\text{H}}_2$OOC-Ar [Bn]), 6.94 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.2 Hz, Ar$\underline{\text{H}}$), 7.05 – 7.15 (8H, m, Ar$\underline{\text{H}}$), 7.18 – 7.24 (8H, m, Ar$\underline{\text{H}}$), 7.30 – 7.47 (5H, m, Ar$\underline{\text{H}}$-CH$_2$ [Bn]), 8.12 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.2 Hz, Ar$\underline{\text{H}}$), 8.18 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.5 Hz, Ar$\underline{\text{H}}$), 8.23 (2H, ddd, $J_{H\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 2.3 Hz, $J_{H\text{-}H}$ = 8.5 Hz, Ar$\underline{\text{H}}$), 8.30 (4H, s, Ar$\underline{\text{H}}$)

^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): 14.01, 19.37, 29.34, 29.50, 31.31, 31.60, 35.54, 67.42, 68.16, 114.42, 121.37, 121.61, 121.87, 128.51, 128.66, 128.87, 129.46, 129.60, 129.62, 129.99, 130.29, 130.41, 132.41, 133.75, 134.13, 134.16, 134.57, 135.80, 140.42, 140.93, 140.98, 141.00, 148.81, 149.13, 163.63, 164.67, 164.73, 165.33, 165.74.

MS (ESI+, m/z): 1135.4981 (calcd. for $C_{72}H_{72}NaO_{11}$: 1135.4967, M + Na)

1151.4715 (calcd. for $C_{72}H_{72}KO_{11}$: 1151.4706, M + K)



7: 4-((4-(7-(4-((4-((4-(7-(4-((4-butoxybenzoyl)oxy)phenyl)heptyl)phenoxy)carbonyl)benzoyl)oxy)phenyl)heptyl)phenoxy)carbonyl)benzoic acid

Quantities used: Compound **7a** (440 mg, 0.395 mmol), palladium on carbon (<50 mg), THF (30 ml). The experimental procedure was as described for **6**, affording compound **7** as a white solid ($Rf_{DCM} = 0.05$).

Yield: 300 mg (74 %)

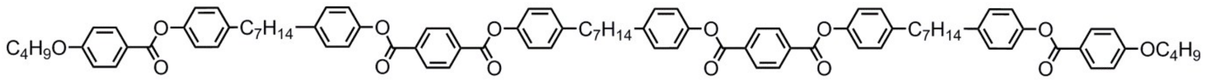
^{1}H NMR (400 MHz, $CDCl_3$): 0.92 (3H, t, J_{H-H} = 7.3 Hz, ArO-CH_2-CH_2-CH_2-$C\underline{H}_3$), 1.23 – 1.35 (12H, m, 2x Ar-$(CH_2)_2$-$(C\underline{H}_2)_3$-$(CH_2)_2$-Ar), 1.39 – 1.50 (2H, m, ArO-CH_2-CH_2-$C\underline{H}_2$-CH_3), 1.52 – 1.63 (8H, m, 2x Ar-CH_2-$C\underline{H}_2$-$(CH_2)_3$-$C\underline{H}_2$-CH_2-Ar), 1.71 – 1.80 (2H, m, ArO-CH_2-$C\underline{H}_2$-CH_2-CH_3), 2.53 – 2.62 (8H, m, 2x Ar-$C\underline{H}_2$-$(CH_2)_5$-$C\underline{H}_2$-Ar), 3.98 (2H, t, J_{H-H} = 7.3 Hz, ArO-$C\underline{H}_2$-CH_2-CH_2-CH_3), 6.89 (2H, ddd, J_{H-H} = 2.0 Hz, J_{H-H} = 2.8 Hz, J_{H-H} = 9.0 Hz, Ar$\underline{H}$), 7.00 – 7.10 (8H, m, Ar$\underline{H}$), 7.12 – 7.21 (8H, m, Ar$\underline{H}$), 8.05 (2H, ddd, J_{H-H} = 2.0 Hz, J_{H-H} = 2.8 Hz, J_{H-H} = 9.0 Hz, Ar$\underline{H}$), 8.11 (2H, ddd, J_{H-H} = 2.0 Hz, J_{H-H} = 2.8 Hz, J_{H-H} = 9.0 Hz, Ar$\underline{H}$), 8.18 (2H, ddd, J_{H-H} = 2.0 Hz, J_{H-H} = 2.8 Hz, J_{H-H} = 9.0 Hz, Ar$\underline{H}$), 8.25 (4H, s, Ar$\underline{H}$)

^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): 13.87, 19.22, 29.18, 29.34, 31.16, 31.46, 35.38, 67.99, 114.30, 121.23, 121.27, 121.47, 121.69, 129.32, 129.43, 129.47, 129.94, 130.03, 130.27, 132.24, 133.18, 134.00, 135.45, 140.28, 140.72, 140.85, 148.67, 148.72, 148.99, 163.51, 164.51, 164.74, 165.17, 167.65,

MS (ESI+, m/z): 1045.4472 (calcd. for $C_{65}H_{66}NaO_{11}$: 1045.4497, M + Na)

1061.4199 (calcd. for $C_{65}H_{66}KO_{11}$: 1061.4237, M + K)

Oligomeric Compounds:



O4$_7$: *bis*(4-(7-(4-((4-butoxybenzoyl)oxy)phenyl)heptyl)phenyl) O,O'-(heptane-1,7-diylbis(4,1-phenylene)) diterephthalate

Quantities used: compound **6** (50 mg, 82.2 µmol), compound **3** (10.9 mg, 40 µmol), EDAC (19.1 mg, 0.1 mmol), DMAP (1 mg) and DCM (3 ml). The experimental procedure was as described in the synthesis of **3**. Column chromatography with a gradient of DCM and ethyl acetate as the eluent as the eluent (Rf_{DCM} = 0.6) followed by recrystalisation from DCM/hexanes afforded the title compound as a white powder.

Yield: 34 mg (57%)

^{1}H NMR (400 MHz, CDCl$_3$): 0.99 (6H, t, $J_{H\text{-}H}$ = 7.6 Hz, ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.31 – 1.71 (34H, m, 2x ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$ + 3 x Ar-CH$_2$-(CH$_2$)$_5$-CH$_2$-Ar), 1.80 (4H, quintet, $J_{H\text{-}H}$ = 7.6 Hz, ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$), 2.59 – 2.67 (12H, m, 3 x Ar-CH$_2$-(CH$_2$)$_5$-CH$_2$-Ar), 4.04 (4H, t, $J_{H\text{-}H}$ = 7.6 Hz, ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$), 6.96 (4H, ddd, $J_{H\text{-}H}$ = 1.5 Hz, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 8.4 Hz, ArH), 7.10 (4H, ddd, $J_{H\text{-}H}$ = 1.5 Hz, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 8.4 Hz, ArH), 7.12 – 7.26 (18H, m, ArH), 8.13 (4H, ddd, $J_{H\text{-}H}$ = 1.5 Hz, $J_{H\text{-}H}$ = 3.1 Hz, $J_{H\text{-}H}$ = 8.4 Hz, ArH), 8.32 (8H, s, ArH)

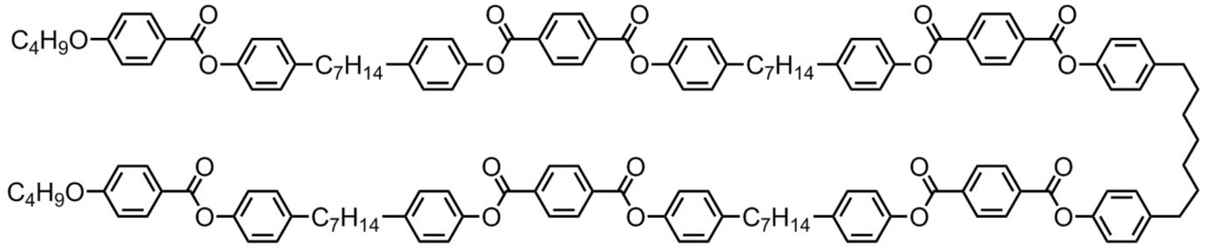
^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): 14.02, 19.38, 29.35, 29.51, 31.32, 31.62, 35.55, 68.16, 114.42, 121.38, 121.61, 121.88, 129.47, 129.63, 130.42, 132.41, 134.17, 140.43, 141.00, 148.81, 149.13, 163.63, 164.68, 165.33

MS (ESI+, m/z): 1487.7029 (calcd. for C$_{95}$H$_{100}$NaO$_{14}$: 1487.7005, M + Na)

Assay (RP-HPLC): >99%

Assay (CHN): calc: C 77.84 % H 6.88 % N 0.00% rest 15.48%

obs: C 77.45 % H 6.86 % N 0.00 % rest15.69%



O6$_7$: *bis*(4-(7-(4-((4-((4-(7-(4-((4-butoxybenzoyl)oxy)phenyl)heptyl)phenoxy)carbonyl)benzoyl)oxy)phenyl)heptyl)phenyl) O,O'-(heptane-1,7-diylbis(4,1-phenylene)) diterephthalate

Quantities used: Compound **7** (102 mg, 100 μmol), compound **3** (14 mg, 50 μmol), EDAC (38 mg, 200 μmol), DMAP (24 mg, 20 μmol) and DCM (5 ml). The experimental procedure was as described in the synthesis of **3**. The crude material was purified by passage through a silica plug; starting materials and reaction side products were eluted with dichloromethane, switching the eluent to ethyl acetate eluted oligomeric materials from the silica plug. The solvent was removed *in vacuo* and the crude oligomeric material purified by preparative TLC with neat dichloromethane as the eluent (Rf_{DCM} = 0.65). The chromatographed material was then redisolved in dichloromethane, filtered through a fine sinter (porosity 5) and concentrated *in vacuo* to an amorphous white solid. This solid was then twice dissolved in the minimum quantity of THF and precipitated by the addition of ethanol, affording the title compound as a fine white powder.

Yield 29 mg (13%)

^{1}H NMR (400 MHz, CDCl$_3$): 0.97 (6H, t, $J_{H\text{-}H}$ = 7.6 Hz, ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.30 – 1.42 (30H, m, 5 x Ar-CH$_2$--CH$_2$-(CH$_2$)$_3$-CH$_2$-CH$_2$-Ar), 1.46 – 1.54 (4H, m, 2x ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$), 1.56-1.70 (20H, m, 5x Ar-CH$_2$-CH$_2$-(CH$_2$)$_3$-CH$_2$-CH$_2$-Ar), 1.74 – 1.84 (4H, m, 2 x ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$), 2.56 – 2.66 (20H, m, 5 x Ar-CH$_2$-(CH$_2$)$_5$-CH$_2$-Ar), 3.99 (4H, t, $J_{H\text{-}H}$ = 7.6 Hz, ArOCH$_2$-CH$_2$-CH$_2$-CH$_3$), 6.94 (4H, ddd, $J_{H\text{-}H}$ = 1.9 Hz, $J_{H\text{-}H}$ = 2.5 Hz, $J_{H\text{-}H}$ = 8.9 Hz, ArH), 7.08 (4H, ddd, $J_{H\text{-}H}$ = 1.9 Hz, $J_{H\text{-}H}$ = 2.5 Hz, $J_{H\text{-}H}$ = 8.9 Hz, ArH), 7.10 – 7.16 (16H, m, ArH), 7.17 – 7.26 (20H, m, ArH), 8.12 (4H, ddd, $J_{H\text{-}H}$ = 1.9 Hz, $J_{H\text{-}H}$ = 2.5 Hz, $J_{H\text{-}H}$ = 8.9 Hz, ArH), 8.3 0 (16H, s, ArH)

^{13}C{^{1}H} NMR (100.5 MHz, CDCl$_3$): 13.98, 19.34, 29.31, 29.34, 29.47, 31.28, 31.58, 31.64, 35.51, 35.54, 68.12, 114.36, 114.39, 121.33, 121.39, 121.57, 121.61, 121.84, 129.43, 128.59, 129.63, 130.38, 130.41, 132.37, 132.42, 134.13, 140.39, 140.96, 148.77, 149.09, 161.15, 163.59, 164.63, 165.29

MS (ESI+, m/z): 2316.0641 (calcd. for $C_{149}H_{152}NaO_{22}$: 2316.0668, M + Na)

Assay (RP-HPLC): >99%

Assay (CHN):
calc: C 77.99 % H 6.68 % N 0.00 % rest15.33%
obs: C 77.95 % H 6.08 % N 0.00 % rest 15.97 %

Tabulated Calorimetry Data

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	mean	sd
Cr	154.0	154.0	153.9	153.9	153.9	153.9	-	-	-	-	-	-	-	-	153.9	0.06
Ntb-N	173.2	173.0	173.0	173.0	173.0	173.0	173.1	172.7	173.1	172.9	172.4	173.1	172.9	172.4	172.9	0.24
N-Iso	195.3	195.0	195.1	195.1	195.1	193.5	193.4	193.2	194.2	194.1	193.8	193.7	193.9	193.9	194.2	0.70

Table SI-1: Tabulated transition temperatures (°C) for the tetramer **O4$_7$**. Values for the Ntb-N and N-Iso are the mean of 14 cycles; those of the melting point are the mean of 6 cycles. Standard deviations from the mean are given. Values were obtained at a heat/cool rate 10 °C min^{-1} under an atmosphere of dry nitrogen.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	mean	sd
Cr	52.50	53.64	53.08	53.50	53.77	52.62	-	-	-	-	-	-	-	-	53.19	0.49
Ntb-N	0.80	0.77	0.78	0.79	0.80	0.81	0.81	0.73	0.83	0.83	0.84	0.84	0.84	0.83	0.81	0.03
N-Iso	0.78	0.80	0.78	0.77	0.80	0.66	0.78	0.77	0.77	0.77	0.79	0.77	0.79	0.79	0.77	0.03

Table SI-2: Tabulated associated enthalpies of transition (kJ mol^{-1}) for the tetramer **O4$_7$**. Values for the Ntb-N and N-Iso are the mean of 14 cycles; those of the melting point are the mean of 6 cycles. Standard deviations from the mean are given. Values were obtained at a heat/cool rate 10 °C min^{-1} under an atmosphere of dry nitrogen.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	mean	sd
Cr	14.78	15.10	14.95	15.07	15.14	14.82	-	-	-	-	-	-	-	-	14.98	0.14
Ntb-N	0.22	0.21	0.21	0.21	0.22	0.22	0.22	0.20	0.22	0.22	0.23	0.23	0.23	0.22	0.22	0.01
N-Iso	0.20	0.21	0.20	0.20	0.21	0.17	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.01

Table SI-3: Tabulated associated entropies of transition (ΔS/R) for the tetramer **O4$_7$**. Values for the Ntb-N and N-Iso are the mean of 14 cycles; those of the melting point are the mean of 6 cycles. Standard deviations from the mean are given. Values were obtained at a heat/cool rate 10 °C min^{-1} under an atmosphere of dry nitrogen.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	mean	sd
Cr	174.4	174.1	174.6	174.4	174.9	174.2	-	-	-	-	-	-	-	-	174.4	0.26
Ntb-N	159.0	159.1	159.1	159.1	159.2	159.0	158.9	158.9	159.1	159.0	159.0	158.7	158.9	159.0	159.0	0.11
N-Iso	188.1	188.2	188.1	188.4	188.1	188.2	188.2	188.1	188.2	188.0	188.1	188.2	188.1	188.2	188.1	0.09

Table SI-4: Tabulated transition temperatures (°C) for the hexamer **O6**$_7$. Values for the Ntb-N and N-Iso are the mean of 14 cycles; those of the melting point are the mean of 6 cycles. Standard deviations from the mean are given. Values were obtained at a heat/cool rate 10 °C min^{-1} under an atmosphere of dry nitrogen.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	mean	sd
Cr	30.13	29.26	29.67	29.71	29.95	29.84	-	-	-	-	-	-	-	-	29.761	0.271
Ntb-N	0.59	0.58	0.58	0.55	0.57	0.57	0.58	0.56	0.55	0.53	0.58	0.58	0.56	0.54	0.566	0.016
N-Iso	0.37	0.35	0.36	0.34	0.36	0.37	0.34	0.34	0.37	0.35	0.37	0.34	0.33	0.33	0.351	0.014

Table SI-5: Tabulated associated enthalpies of transition (kJ mol^{-1}) for the hexamer **O6**$_7$. Values for the Ntb-N and N-Iso are the mean of 14 cycles; those of the melting point are the mean of 6 cycles. Standard deviations from the mean are given. Values were obtained at a heat/cool rate 10 °C min^{-1} under an atmosphere of dry nitrogen.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	mean	sd
Cr	8.10	7.87	7.97	7.99	8.04	8.02	-	-	-	-	-	-	-	-	7.998	0.071
Ntb-N	0.16	0.16	0.16	0.15	0.16	0.16	0.16	0.16	0.15	0.15	0.16	0.16	0.16	0.15	0.158	0.004
N-Iso	0.10	0.09	0.09	0.09	0.09	0.10	0.09	0.09	0.10	0.09	0.10	0.09	0.09	0.09	0.092	0.004

Table SI-6: Tabulated associated entropies of transition (ΔS/R) for the hexamer **O6$_7$**. Values for the Ntb-N and N-Iso are the mean of 14 cycles; those of the melting point are the mean of 6 cycles. Standard deviations from the mean are given. Values were obtained at a heat/cool rate 10 °C min^{-1} under an atmosphere of dry nitrogen.

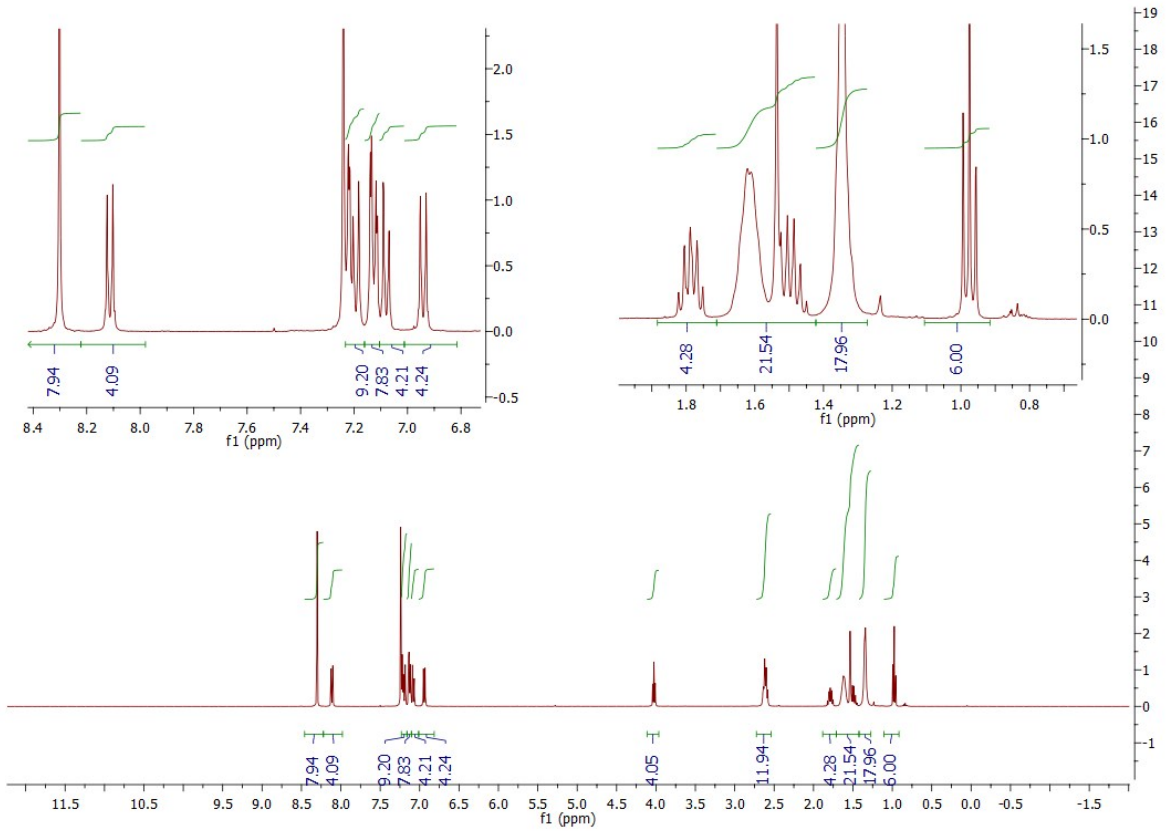


Figure SI-1: ^{1}H (400 MHz, $CDCl_3$) NMR spectra of the tetramer **O4$_7$**.

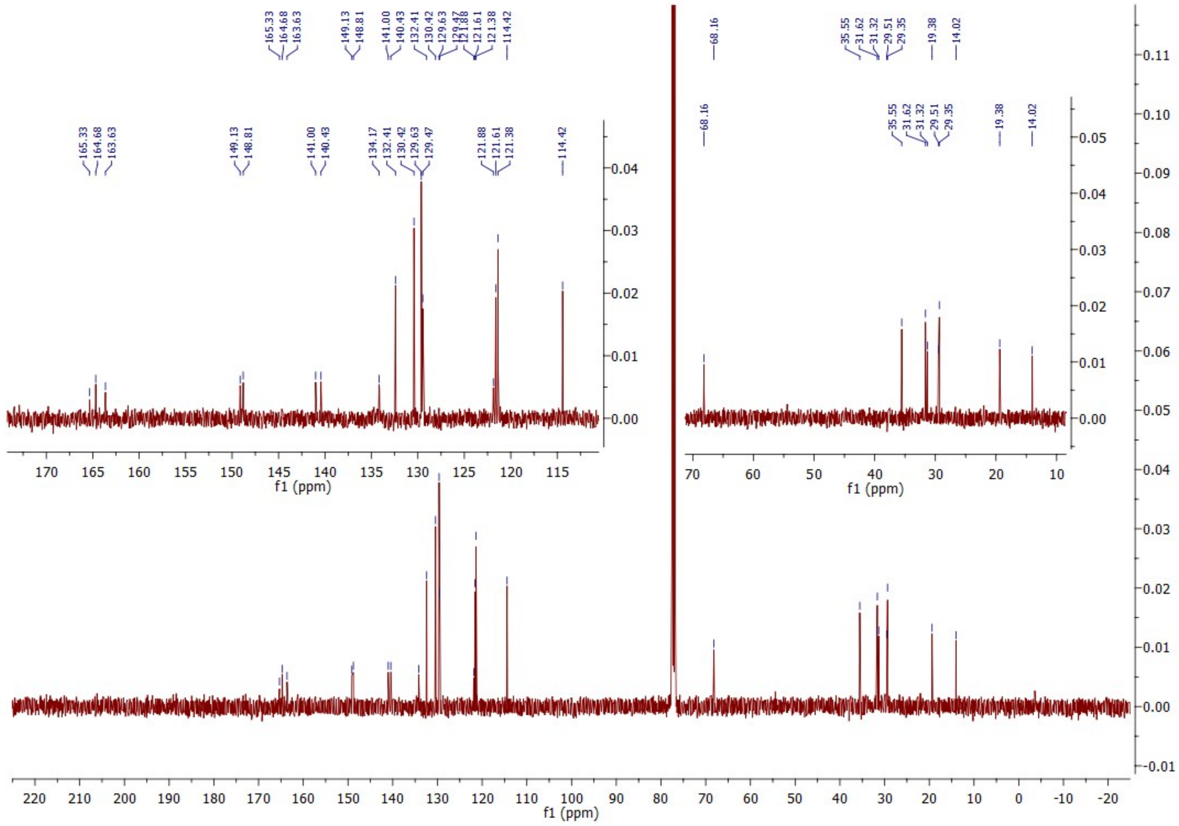


Figure SI-2: $^{13}C\{^1H\}$ (100.5 MHz, $CDCl_3$) NMR spectra of the tetramer **$O4_7$**.

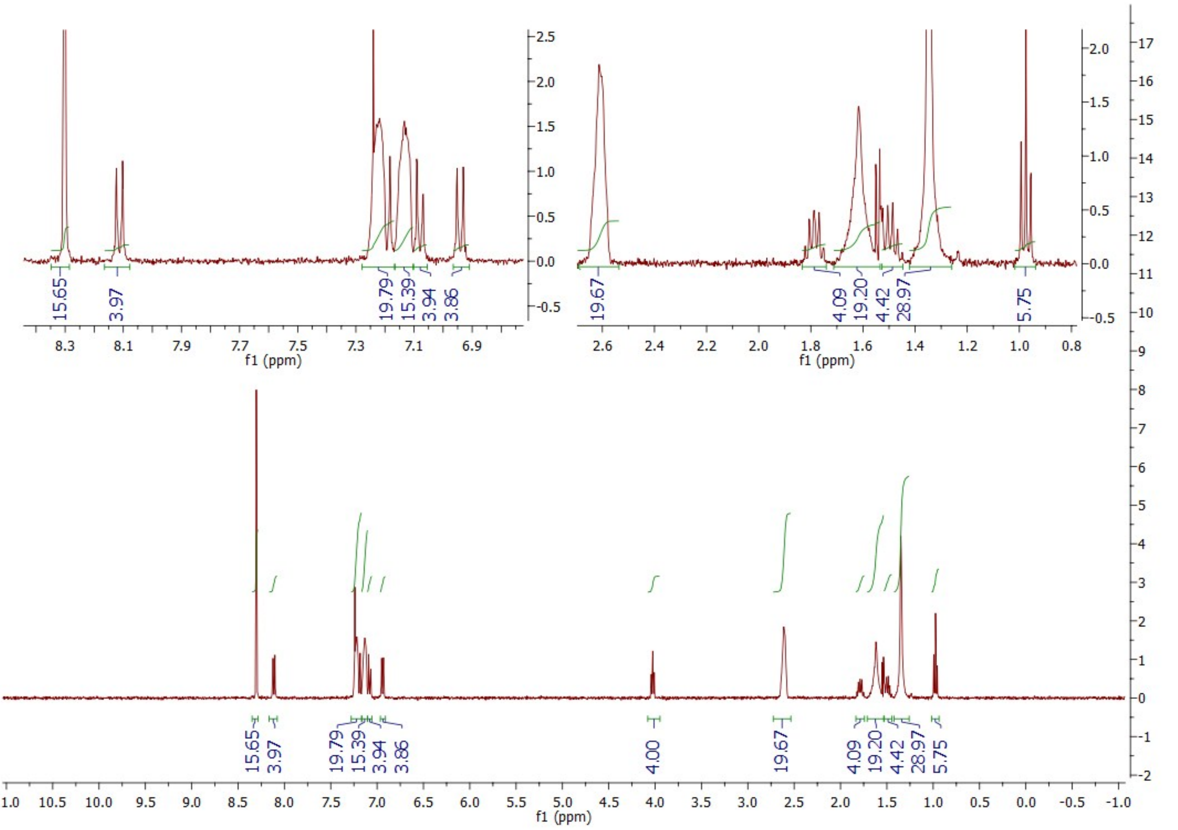


Figure SI-3: ^{1}H (400 MHz, $CDCl_3$) NMR spectra of the hexamer **O6$_7$**.

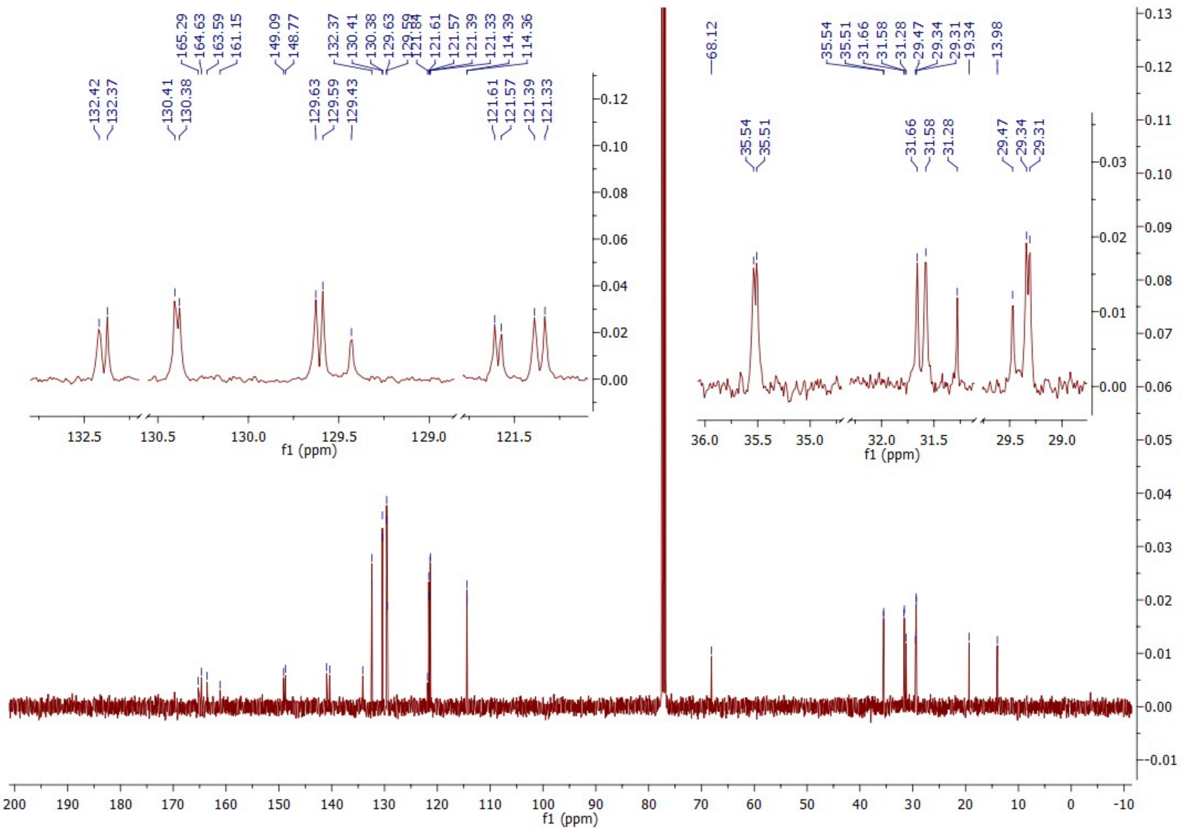


Figure SI-4: $^{13}C\{^1H\}$ (100.5 MHz, $CDCl_3$) NMR spectra of the hexamer **O6$_7$**.

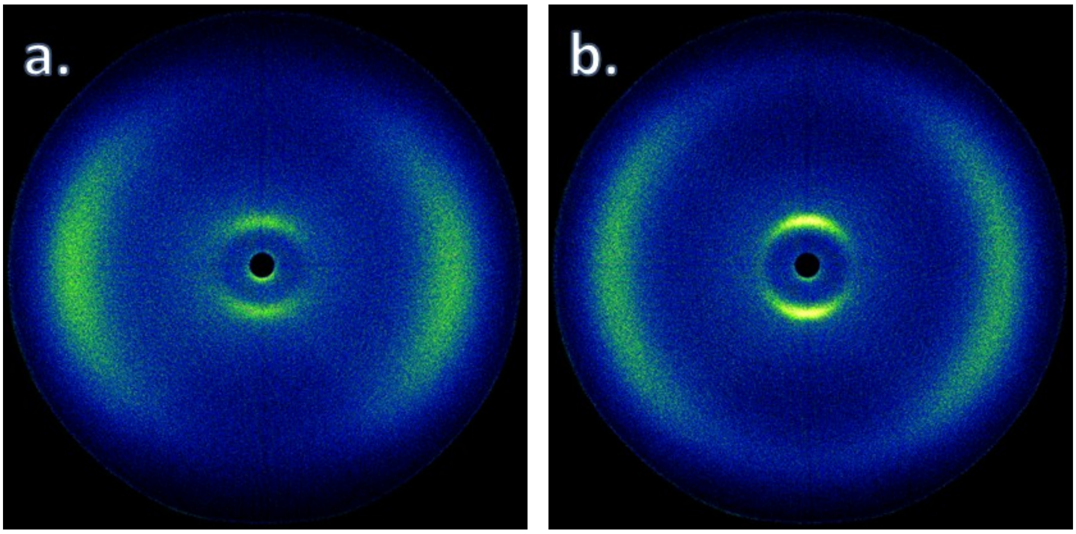


Figure SI-5: Magnetically aligned, two-dimensional small angle X-ray scattering patterns of the tetramer **O4$_7$** in (a) the nematic phase at 183 °C and (b) in the N$_{TB}$ phase at 122 °C

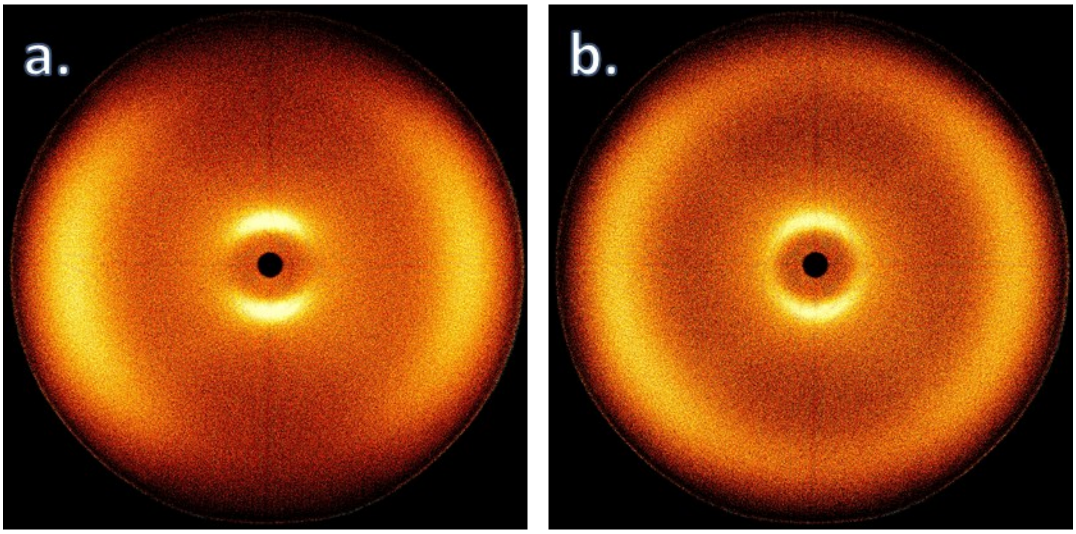
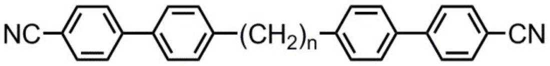


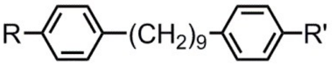
Figure SI-6: Two-dimensional small angle X-ray scattering patterns of the hexamer **O6$_7$** in (a) the nematic phase at 168 °C and (b) in the N$_{TB}$ phase at 154 °C. Both 2D SAXS patterns were collected under an external magnetic field, whereas the nematic phase was well aligned this alignment was only partially retained in the N$_{TB}$ phase.

Tabulated Transition Temperatures and Molecular Structures used in Figure 8:



No	Name	n	Cr		N_{TB}		N		Iso
SI-1	*CB7CB*	**7**	●	102	●	104.5	●	116	●
SI-2	*CB9CB*	**9**	●	83.0	●	105	●	119.8	●

Table SI-7



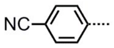
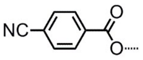
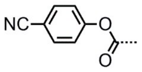
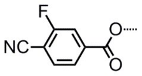
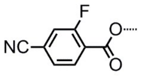
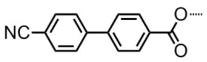
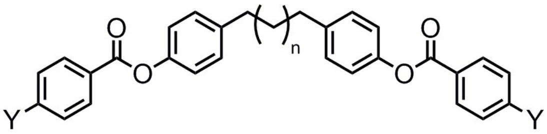
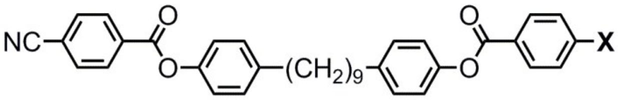
No	Name	R	Cr		N_{TB}		N		Iso
SI-3	*CB9CB*		●	83	●	105	●	119.8	●
SI-4	*PCB9PCB*		●	157.6	(●	114.5	●	146.6)	●
SI-5	*CPB9CPB*		●	125.2	(●	95.0)	●	138.4	●
SI-6	*n/a*		●	108.4	(●	- †	●	97.8)	●
SI-7	*n/a*		●	150.0	(●	108.6	●	128.5)	●
SI-8	*n/a*		●	165.5	●	179.6	●	324.0	●

Table SI-8



No.	**Y**	**n**	**Cr**		**N_{TB}**		**N**		**I**
SI-9	CN	5	●	149	(●	120.0	●	139.0)	●
SI-3	CN	7	●	157.6	(●	114.5	●	146.6)	●
SI-10	SCN	5	●	105.1	(●	103.3)	●	120.5	●
SI-11	SCN	7	●	97.7	●	103.7	●	127.4	●

Table SI-9



No.	**X=**	**Cr**		**N_{TB}**		**N**		**Iso**
SI-3	-CN	●	157.6	(●	114.5	●	146.6)	●
SI-12	-SCN	●	95.6	●	100.0	●	123.8	●
SI-13	-NO_2	●	115.4	(●	100.5)	●	124.9	●
SI-14	-F	●	86.2	(●	78.2)	●	95.9	●
SI-15	-CF_3	●	110.0	(●	69.6	●	78.3)	●
SI-16	-SF_5	●	102.2	(●	61.1	●	72.8)	●

Table SI-10

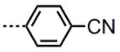
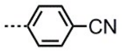
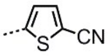
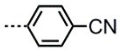
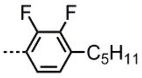
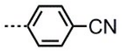
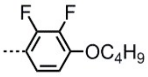
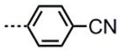
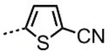
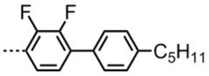
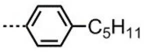
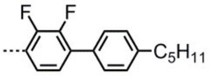
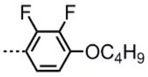
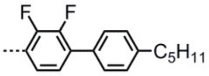
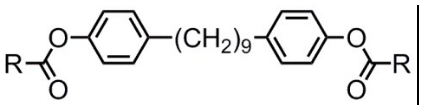
No.	R	R’	Cr		Smx		NTB		N		I
SI-17			●	83.0	-	-	●	105	●	119.8	●
SI-18			●	90.4	-	-	(●	89.5)	●	101.1	●
SI-19			●	40.6	-	-	(●	38.3)	●	43.8	●
SI-20			●	56.3	-	-	(●	54.9)	●	62.7	●
SI-21			●	89.7	-	-	(●	53.9)	●	114.7	●
SI-22			●	78.2	-	-	●	86.4	●	105.5	●
SI-23			●	69.5	(●	61.7)	●	82.8	●	103.4	●

Table SI-11



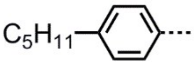
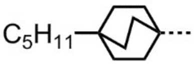
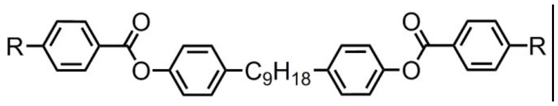
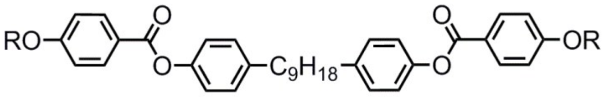
No	R	Cr		NTB		N		Iso
SI-24		●	72.8	(●	58.8	●	66.2)	●
SI-25		●	67.2	●	89.4	●	114.9	●

Table SI-12



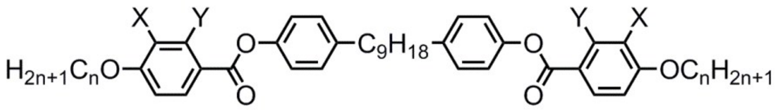
No	R	Cr		N_{TB}		N		Iso
SI-26	C_2H_5	●	66.8	(●	48.4	●	57.2)	●
SI-27	C_3H_7	●	77.6	(●	59.5	●	67.1)	●
SI-28	C_4H_9	●	67.3	(●	46.2	●	51.0)	●
SI-25	C_5H_{11}	●	72.8	(●	58.8	●	66.2)	●

Table SI-13



No	R	Cr		SmC_A		N_{TB}		N		Iso
SI-29	C_2H_5	●	119.6	-	-	(●	100.4	●	119.2	●)
SI-30	C_3H_7	●	110.4	-	-	(●	75.5	●	91.8	●)
SI-31	C_4H_9	●	83.3	-	-	●	84.7	●	99.5	●
SI-32	C_5H_{11}	●	71.8	-	-	●	76.0	●	86.6	●
SI-33	C_6H_{13}	●	78.2	●	78.4	●	85.2	●	97.1	●

Table SI-14



No	**n**	**X**	**Y**	**Cr**		**N_{TB}**		**N**		**Iso**
SI-29	2	H	H	●	119.6	(●	100.4	●	119.2	●)
SI-34	2	H	F	●	102.0	(●	84.5	●	101.9)	●
SI-35	12	H	CH_3	●	61.5	(●	28.7	●	33.3	●)
SI-36	12	H	OCH_3	●	60.3	(●	25.7	●	30.8	●)

Table SI-15

References

1. R. J. Mandle, E. J. Davis, C.C.A.Voll, C. T. Archbold, J. W. Goodby and S. J. Cowling, "The Relationship between Molecular Structure and the Incidence of the N_{TB} Phase", *Liq. Cryst.,* **2015**, *42*, 688-703, DOI: 10.1080/02678292.2014.974698
2. Gaussian 09, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
3. H. Hu, J.S. Mendoza, C.T. Lowden, L.M.Ballas and W.P. Janzen, *Biorg. Med. Chem.,* **1997**, *5*, 1873-1882.