Electronic Supplementary Information (ESI) for Soft Matter

From molecular biaxiality of real board-shaped mesogens to phase biaxiality ? On the hunt for the holy grail of liquid crystal science

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General

The solvents were distilled and if necessary dried by standard procedures. 2-Bromo-5-iodoanisol and (4-bromophenyl)trimethylsilane have been purchased from ABCR and 2,5-dibromothiophene from Aldrich and used as received. 2-Bromo-5-iodophenol has been prepared according to reference [1]. Compounds **14a**, **14b**, **16a** and **16b** have been synthesized according to references [2,3]. The silica 60 (0.063-0.2 mm / 70 - 230 mesh) has been purchased from Macherey-Nagel.

Equipment

Preparative recycling gel permeation chromatography was performed with the liquid chromatograph *LC-20A* (Shimadzu). The column set (PSS *SDV* 50 Å, 20·600 mm; PSS *SDV* 500 Å, 20·600 mm) was eluted with HPLC-grade CHCl₃ at a flow rate of 4.0 mL·min⁻¹. NMR spectra were recorded on a Bruker-Daltonics *Avance-400* spectrometer operating at 400 MHz (¹H) or 100 MHz (¹³C), with the residual protic

solvent used as the internal standard. Mass spectra were recorded on a Bruker-Daltonics *autflex II* (MALDI). Elemental analysis experiments were performed at the Institute of Inorganic Chemistry at the University of Würzburg. Polarised optical microscopy studies have been done with a Nikon *Eclipse LV100Pol* microscope equipped with a Linkam *LTS420* heating stage and a Linkam *T95-HS* system controller. Thermal analysis by differential scanning calorimetry (DSC) was performed on a TA instruments DSC Q1000 with a DSC refrigerated cooling system.

The temperature dependent X-ray scattering (XRS) at wide angles (WAXS; $2\theta = 1.0$ -22.5°) and middle angles (MAXS; $2\theta = 0.5-5.2^{\circ}$) were performed on a Bruker Nanostar (Detector Vantec 2000, Microfocus copper anode X-ray tube Incoatec). The measurements were carried out in Mark capillaries (Hilgenberg) positioned perpendicular to the incident X-ray beam. Investigations in the magnetic field has been performed in special home-made sample holders equipped with two Samarium ring magnets (1T) on both sides of the sample (Figure S2). The sample holder allowed the X-ray beam to lie along and perpendicular to the magnetic field. Sample 1a was originally prepared by slow cooling from the isotropic liquid to the nematic phase. For the samples 2a and 2b such a procedure would lead to the decomposition of the material. Thus these samples were first extruded from the LC phase with a miniextruder and subsequently heated to the nematic phase at 220°C and annealed in the magnetic field for 30 minutes in order to obtain the alignment. Alignment studies of **1a** (Figure S2) demonstrate that the sample also orients slowly in the magnetic field when heating from the crystalline non-oriented material to the nematic phase (Figure S2). All X-ray data was processed and evaluated with the program datasqueeze (http://www.datasqueezesoftware.com). Silver-behenate was used as calibration standard for the WAXS studies.

¹ S.-S. Jester, E. Sigmund, S. Höger, *J. Am. Chem. Soc.* **2011**, *133*, 11062–11065.

² a) J. Seltmann, M. Lehmann, *Liquid Crystals*, **2011**, *38*, 407–422. b) J. Seltmann, *Dissertation* **2011**, Chemnitz University of Technology.

³ M. Lehmann, S.-W. Kang, C. Köhn, S. Haseloh, U. Kolb, D. Schollmeyer, S. Kumar, *J. Mater. Chem.* **2006**, *16*, 4326-4334.

Complementary XRS data for compound 1a





Figure S1. WAXS and MAXS XRS pattern of compound **1a**. Charts A and B highlight the small angle part of the WAXS diffraction patterns during the crystallization process. Left: Pattern directly after cooling to 25 °C. Right: Patterns after partial crystallization (A) and complete crystallization (B). Chart C show the temperature-dependent MAXS patterns of the signal (i).

In chart A the nematic self-assembly and thus a very weak signal (i) is still present, while after the complete crystallization (chart B) the signal is completely absent. In contrast the signals (ii), (iii), (iv) and (v) transform in different sets of strong reflections in the crystal. Therefore, we propose, that signal (i) is mainly a consequence of the form factor of the molecule. With increasing positional order in the cluster the intensity of this signal decreases obviously as shown in the temperature-dependent study (chart C). Consequently, when the structure factor dominates in the crystal with perfect positional order the signal (i) is absent, owing to the crystal symmetry. Moreover, the signal (i) is not split, evidenced from chart C. The slight splitting in the χ -scan of figure 6G is a consequence of the attenuation of the weak intensity by the thin wire holding the beam stop.



Figure S2. Alignment studies of compound **1a** in a magnetic field (1T). **A**: Cr unoriented at 75 °C; **B**: Sample in the magnetic field (1T) at 100 °C (in the Cr-N transition), annealed prior to the measurement for 20 minutes. **C**: oriented sample at 110 °C; **D**: at 150 °C and **E**: after cooling at 25 °C. **F**: sample holder with the sample in a mark capillary, the direction of X-rays and the B-field.

The charts **A-E** demonstrate that compound **1a** is slowly oriented at the transition from the non-oriented crystal to the nematic phase with the molecular long axis along the magnetic field. At 110 °C in the nematic phase the alignment is complete. Heating to 150 °C and cooling to room temperature result in the same oriented pattern highlighted in Figure 6 without cooling from the isotropic liquid. The latter has been originally assumed to be necessary to guarantee the alignment of such a rather viscous nematic material.

Synthesis of the cores

1,4-Dibromo-5,8-dichloro-9,10-anthraquinone (3)

5,8-Dichloronaphthoquinone (200 mg, 0.88 mmol) [4] and 2,5-dibromothiophene (256 mg, 1.06 mmol) were dissolved in 10 ml CHCl₃, the reaction mixture was heated to 70 °C and 912 mg mCPBA (70-75%) were added slowly within two days. Subsequently, the mixture was poured in 50 ml of a saturated solution of Na₂CO₃ and the product was extracted with CHCl₃ (4 × 100ml). Column chromatography (silica; cyclohexane : ethyl acetate = 10 : 1 to 2 : 1) afforded 140 mg (322 µmol, 37 %) of a red solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.60 (s, 2 H, aromat. CH), 7.72 (s, 2 H, aromat. CH). The data is in agreement with the literature [5].

4-(Trimethylsilyl)phenylboronic acid (4)

The synthesis has been performed analogous to reference [6], however, starting with the commercial available (4-bromophenyl)trimethylsilane.

(4-Bromophenyl)trimethylsilane (10.91 g, 47.6 mmol) was dissolved in 600 ml THF, cooled to - 78 °C and 1.6 M *n*-BuLi in hexane (38.9 ml, 61.8 mol) was added dropwise. Subsequently, the reaction mixture was kept for 45 minutes at -20 °C. After cooling again to -78 °C, B(OMe)₃ (6.43 g, 6.90 ml, 61.9 mmol) was added. The reaction mixture was then stirred for 12 hours at ambient temperature and afterwards 200 ml of 2N HCl was added. After stirring for one hour at ambient temperature, the mixture was extracted twice with Et₂O (2 x 200 ml). The organic phases were washed with 100 ml H₂O and dried over MgSO₄. The solvent was removed under reduced pressure to afford a colorless solid, which was used directly without further purification.

¹H NMR (400 MHz, CDCl₃): δ = 0.26 (s, 9 H, Si((CH₃))₃), 7.37(AA'BB', 2 H, aromat. H), 7.48 (AA'BB', 2 H, aromat. H).

Spectral data from reference [7]:

⁴ K. Torssell, Acta Chemica Scandinavica **1976**, B 30, 353.

⁵ T. Thiemann, Y. Tanaka und J. Iniesta. *Molecules* **2009**, *14*, 1013.

⁶ M. S. Wong, P. F. Xia, X. L. Zhang, P. K. Lo, Y.-K. Cheng, K.-T. Yeung, X. Guo, S. Shuang, *J. Org. Chem.* **2005**, *70*, 2816-2819.

⁷ Hauke C. Schmidt, Christopher B. Larsen, and Oliver S. Wenger, *Angew. Chem. Int. Ed.* **2018**, 57, 6696 –6700.

¹H NMR (400 MHz, CDCl₃): δ = 0.33 (s, 9 H, Si((CH₃))₃), 7.66-7.70 (AA´BB´, 2 H, aromat. H), 8.18-8.22 (AA´BB´, 2 H, aromat. H).

The deviation from the literature known NMR results can be rationalized by the formation of a boroxine derivative.^[8] The NMR study of Snieckus et al. (supporting information) in CDCl₃ highlighted that the aromatic signals of phenyl boronic acid shifted strongly to larger ppm values when forming the boroxine derivatives.^[9] Consequently, we assume that our crude product, with lower chemical shifts for the AA'BB' system consisted of the 4-(trimethylsilyl)phenylboronic acid, while in reference [6] presumably the boroxine derivative had already been formed.

⁸ Y. Tokunaga, H. Ueno, Y. Shimomura, T. Seo, *Heterocycles* 2002, 57, 787-790.

⁹ A. Antoft-Finch, T. Blackburn, V. Snieckus, J. Am. Chem. Soc., 2009, 131, 17750–17752.

1,4,5,8-Tetrakis(4-iodophenyl)-9,10-anthraquinone (6)

Core **3** (3.59 g, 8.8 mmol), boronic acid **4** (10.23 g, 52.8 mmol) and Na₂CO₃ (28.00 g, 264 mmol) were dispersed in a mixture of 90 ml DME and 130 ml H₂O, degassed with N₂ and subsequently, Pd(PPh₃)₄ (1.02 g, 880 µmol) was added. The reaction mixture was heated to 80 °C for 14 hours and then 100 ml H₂O was poured into the flask. The aqueous phase was extracted three times with Et₂O (3 × 100 ml). The combined organic phases were dried over MgSO₄. After removing the solvent at reduced pressure, the product 1,4,5,8-tetrakis[4-(trimethylsilyl)phenyl]-9,10-anthraquinone **5** was isolated by column chromatography (silica, cyclohexane : toluene = 3 : 1) to furnish 2.47 g (3.1 mmol, 35 %) of a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 0.32 (s, 36 H, Si((CH₃))₃), 7.37(AA´BB´, 8 H, aromat. H), 7.52 (s, 4 H, aromat. H), 7.54 (AA´BB´, 8 H, aromat. H).

Compound **5** (150 mg, 187 µmol) was dissolved in 40 ml CHCl₃ and ICl (145 mg, 898 µmol) in 1 ml CHCl₃ was slowly added dropwise. The reaction mixture was stirred for one hour at room temperature and 10 ml saturated Na₂S₂O₅ was added and stirred for further 15 minutes. The organic phase was separated and washed twice with H₂O (2 × 20 ml). After removing the solvent under reduced pressure, the product was isolated by column chromatography (silica, cyclohexane : CH₂Cl₂ = 10 : 1). Yield: 180 mg (177 µmol, 95%)

¹H NMR (400 MHz, CDCl₃): δ = 6.98 (AA'BB', 8 H, aromat. H), 7.50 (s, 4 H, aromat. H), 7.68 (AA'BB',8 H, aromat. H); ¹³C NMR (100 MHz, CDCl₃): δ = 93.9 (C_q, aromat. C-I), 130.8, 134.6 (C_s, aromat. CH), 135.2 (C_q); 137.3 (C_s, aromat. CH); 138.6, 140.3 (C_q); 187.3 (C_q, C=O); HRMS (ESI): m/z (%): calc. 2049.5623 (100, [2M])⁺⁺), found: 2049.5541 (100, [2M]⁺⁺).

<u>Path A</u>

1-Bromo-2-hexyloxy-4-iodobenzene (8)

2-Bromo-5-iodophenol **7** (6.0 g, 20.1 mmol) was dissolved in 60 ml DMF and 1bromohexan (4.0 g, 3.38 ml, 24.1 mmol) and K_2CO_3 (3.3 g, 24.1 mmol) were added. The reaction mixture was stirred at 60 °C for 12 hours. Then K_2CO_3 was removed by filtration and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica, cyclohexane : ethyl acetate = 4 : 1). The product **8** (7.55 g,19.7 mmol) was isolated as a yellow liquid. Yield (two steps based on 2-bromo-5-iodoanisol) 84 %.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.91$ (t, 3 H, CH₃, ³*J* = 7.0 Hz), 1.35 (m, 4H, CH₂), 1.50 (m, 2H, CH₂), 1.82 (m, 2 H, CH₂), 3.98 (t, 2 H, OCH₂, ³*J* = 7.0 Hz), 7.13 (dd, 1 H, aromat. H, ³*J* = 8.1 Hz, ⁴*J* = 2.1 Hz), 7.15 (d, 1 H, aromat. H, ³*J* = 1.9 Hz), 7.22 (d, 1 H, aromat. H, ³*J* = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.2$ (CH₃), 22.7, 25.7, 29.0, 31.6 (C_s, CH₂), 69.6 (C_s, OCH₂), 92.5 (C_q, aromat. C-I), 112.4 (C_q, aromat C-Br), 122.4, 130.8, 134.6 (C_t, aromat. CH), 156.2 (aromat. C_q, C-O).

1-Hexyloxy-5-(triisopropylsilyl)ethynyl-2-(trimethylsilyl)ethynylbenzene (9)

Compound **8** (5.00 g,13.1 mmol) was dissolved in 60 ml piperidine and degassed by the pump-freeze-thaw procedure. Subsequently, $Pd(PPh_3)_4$ (754 mg, 653 µmol) and Cul (62 mg, 326 µmol) were added and the mixture was degassed by a nitrogen flow (10 minutes). Then TIPSA (2.4 g, 2.94 ml, 13.1 mmol) was injected in a nitrogen countercurrent and heated for 12 hours to 40 °C. Following dropwise addition of TMSA (1.68 g, 2.44 ml, 17.0 mmol) and heating for 24 hours to 65 °C finalized the reaction. The solvent was removed under reduced pressure and the product **9** was isolated by column chromatography (silica, cyclohexane) to yield 4.18 g (91.9 mmol, 70 %) of a yellow solid.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.25$ (s, 9 H, Si(CH₃)₃), 0.91 (t, 3 H, CH₃, ³*J* = 7.0 Hz), 1.12 (broad signal + m superimposed, 21 H, Si(*CH*(*CH*₃)₂)₃), 1.35 (m, 4 H, CH₂), 1.52 (m, 2, CH₂), 1.82 (m, 2 H, CH₂), 4.00 (t, 2 H, OCH₂, ³*J* = 6.3 Hz), 6.89 (d, 1 H, aromat. H, ⁴*J* = 1.3 Hz), 6.98 (dd, 1 H, aromat. H, ³*J* = 7.9 Hz, ⁴*J* = 1.3 Hz), 7.31 (d, 1 H, aromat. H, ³*J* = 7.9 Hz); ¹³C NMR (100 MHz, CDCl₃): $\delta = 0.0$ (Si(CH₃)₃), 11.4 (Si(*C*H(CH₃)₂)₃), 14.2 (CH₃), 18.8, 22.8, 25.8, 29.3, 31.7 (C_s, CH₂), 68.8 (C_s, OCH₂), 92.4, 100.2, 101.1, 106.9 (C_q, C≡C), 113.2 (C_q), 115.1, 124.4 (C_t, aromat. CH), 124.8 (C_q), 133.4 (C_t, aromat. CH), 159.9 (C_q, C-O); MS (MALDI-TOF, +): m/z (%): calc. for C₂₈H₄₆OSi₂ [M⁺⁺]: 454.85, found: 454.28 (24, M⁺⁺).

1-Hexyloxy-5-(triisopropylsilyl)ethynyl-2-ethynylbenzene (**10a**)

Compound **9** (4.18 g, 91.9 mmol) was subjected to a reaction with K_2CO_3 (1.83 g, 118 mmol) in 200 ml THF/MeOH (1 : 1) at room temperature for 12 hours. Subsequently, the solid was filtered off and the solvent was removed at reduced pressure. Alkyne **10a** was isolated by column chromatography to afford 3.52 g (91.0 mmol, 99 %) of a yellow oil.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.89$ (t, 3 H, CH₃, ³*J* = 7.3 Hz), 1.12 (broad signal + m superimposed, 21 H, Si(**CH**(**CH**₃)₂)₃), 1.36 (m, 4 H, CH₂), 1.52 (m, 2 H, CH₂), 1.82 (m, 2 H, CH₂), 3.32 (s, 1 H, C=**CH**), 4.02 (t, 2 H, OCH₂, ³*J* = 6.5 Hz), 6.92 (d, 1 H, aromat. H, ⁴*J* = 1.2 Hz), 7.00 (dd, 1 H, aromat. H, ³*J* = 7.7 Hz, ⁴*J* = 1.3 Hz), 7.35 (d, 1 H, aromat. H, ³*J* = 7.7 Hz); ¹³C NMR (100 MHz, CDCl₃): $\delta = 11.6$ (Si(**CH**(CH₃)₂)₃), 14.4 (CH₃), 19.0 (Si(CH(**CH**₃)₂)₃), 23.0 26.0, 29.3, 31.8 (C_s, CH₂), 69.2 (C_s, OCH₂), 80.1, 82.7 (C_t, C_q,

C≡C-H), 92.8, 106.9 (C_q, C≡C), 112.3 (C_q), 115.3, 124.6 (C_t, aromat. CH), 125.4 (C_q), 134.0 (C_t, aromat. CH), 160.1 (C_q, aromat. C-O).

<u>Path B</u>

(2-Bromo-5-iodophenoxy)(tert-butyl)dimethylsilane (11)

2-Bromo-5-iodophenol (2.87 g, 9.60 mmol) was dissolved in 25 ml DMF and TBDMS-Cl (2.17 g, 2.50 ml, 14.41 mmol) and 1.86 g (1.59 ml, 28.80 mmol) imidazole were added dropwise. The reaction mixture was stirred 12 hours. Then the solvent was removed under reduced pressure. The product **11** was isolated by column chromatography (silica, cyclohexane) and yielded 3.80 g (9.57 mmol, 99 %) of a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 0.25 (s, 6 H, OSi(CH₃)₂), 1.03 (s, 9 H, OSiC(CH₃)₃), 7.13 (dd, 1 H, aromat. H, ³*J* = 8.3 Hz, ⁴*J* = 2.0 Hz), 7.18 (d, 1 H, aromat. H, ⁴*J* = 2.0 Hz), 7.21 (d, 1 H, aromat. H, ³*J* = 8.3 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = -4.1 (OSi(CH₃)₂), 18.5 (C_q, OSiC(CH₃)₃), 25.8 (CH₃, OSiC(CH₃)₃), 92.0 (C_q, aromat. C-I), 115.8 (C_q, aromat. C-Br), 129.4, 131.6, 134.7 (C_t, aromat. CH), 153.6 (C_q, aromat. C-O).

1-[(tert-Butyldimethylsilyl)oxy]-5-(triisopropylsilyl)ethynyl-2-(trimethylsilyl)ethynylbenzene (**12**)

Compound **11** (3.80 g, 9.57 mmol) was dissolved in 45 ml piperidine and degassed by the pump-freeze-thaw procedure. Subsequently, $Pd(PPh_3)_4$ (553 mg, 479 µmol) and Cul (40 mg, 210 µmol) were added and the mixture was degassed by a nitrogen flow (10 minutes). Then TIPSA (1.75 g, 2.16 ml, 9.57 mmol) was injected in a nitrogen countercurrent and heated for 16 hours to 40 °C. Following dropwise addition of TMSA (1.23 g, 1.79 ml, 12.40 mmol) and heating for 24 hours to 65 °C finalized the reaction. The solvent was removed under reduced pressure and the product **12** was isolated by column chromatography (silica, cyclohexane) to yield 3.13 g (6.45 mmol, 67 %) as a yellow solid.

¹H NMR (400 MHz, CDCl₃): δ = 0.23 (s, 9 H, Si(CH₃)₂), 0.25 (s, 6 H, Si(CH₃)₃), 1.04 (s, 9 H, SiC(CH₃)₃), 1.13 (broad signal + m superimposed, 21 H, Si(**CH**(**CH**₃)₂)₃), 6.86 (dd, 1 H, aromat. H, ⁴*J* = 1.5 Hz, ⁵*J* = 0.4 Hz), 7.00 (dd, 1 H, aromat. H, ³*J* = 7.9 Hz, ⁴*J* =

1.4 Hz), 7.32 (dd, 1 H, aromat. H, ${}^{3}J$ = 7.9 Hz, ${}^{5}J$ = 0.4 Hz); ${}^{13}C$ NMR (100 MHz, CDCl₃): δ = -4.13 (C_p, OSi(CH₃)₂), 0.10 (C_p, Si(CH₃)₃), 11.4 (C_t, Si(**CH**(CH₃)₂)₃), 18.8 (C_q + C_p, Si**C**(CH₃)₃), SiCH(**CH₃**)₂)₃ superimposed), 25.9(C_p, SiC(**CH₃**)₃), 99.6, 102.1, 106.7, 116.3 (C_q, C=C), 123.0 (C_t, aromat. CH), 124.7 (C_q), 125.1, 133.9 (C_t, aromat. CH), 156.5 (C_q, aromat. C-O); MS (MALDI-TOF, +): m/z (%): calc. for C₂₈H₄₈OSi₃ [M⁺⁻]: 484.95, found: 441.23 (40, [M-C₃H₇]⁺⁻), 427.15 (18, [M-C₄H₉]⁺⁻).

5-((*Triisopropylsilyl*)ethynyl)-2-((trimethylsilyl)ethynyl)phenol (**13**)

Compound **12** (3.00 g, 6.19 mmol) was dissolved in 42 ml MeOH/THF (1:2) and HCl (3N, 6.98 ml) was added dropwise. The reaction mixture was stirred for 12 hours at 45 °C and the organic compounds were subsequently extracted with ethyl acetate (3 x 50 ml). The combined organic phases were washed with brine, dried over NaSO₄ and the solvent was removed under reduced pressure. The product was isolated by column chromatography (silica, cyclohexane : ethyl acetate = 100 : 1 to 50 : 1) and afforded 934 mg (2.90 mmol, 47 %) of **13** as yellow oil.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.28$ (s, 9 H, Si(CH₃)₃), 1.12 (broad signal + m superimposed, 21 H, Si(**CH**(**CH**₃)₂)₃), 5.80 (s, 1 H, OH), 6.97 (dd, 1 H, aromat. H, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz), 7.05 (dd, 1 H, aromat. H, ⁴*J* = 1.4 Hz, ⁵*J* = 0.2 Hz), 7.26 (dd, 1 H, aromat. H, ³*J* = 8.0 Hz, ⁵*J* = 0.3 Hz); ¹³C NMR (100 MHz, CDCl₃): $\delta = 0.06$ (C_p, Si(CH₃)₃), 11.4 (C_t, Si(**CH**(CH₃)₂)₃), 18.8 (C_p, Si(CH(**CH**₃)₂)₃), 93.0, 98.6, 104.1, 106.4 (C_q, C=C), 109.9 (C_q), 118.0, 124.2 (C_t, aromat. CH), 125.7 (C_q), 131.4 (C_t, aromat. C-O).

1-[(2-Ethylhexyl)oxy]-5-(triisopropylsilyl)ethynyl-2-(trimethylsilyl)ethynylbenzene (**10b**)

Phenol **13** (934 mg, 2.52 mmol) was dissolved in 60 ml DMF and 3-(bromomethyl)heptane (633 mg, 580 μ l, 3.28 mmol) and K₂CO₃ (453 mg, 3.28 mmol) were added. The reaction mixture was stirred two days at 60 °C. The organic phase was washed with H₂O (3×150 ml) und once with brine (150 ml) and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, petrolether : dichloromethan = 9 : 1) and afforded 500 mg (1.22 mmol, 48 %) of a yellow oil.

¹H NMR (400 MHz, CDCl₃): $\delta = 0.91$ (m, 3 H, CH₃), 0.94 (t, 3 H, CH₃, ³*J* = 7.4 Hz) 1.13 (m + broad signal superimposed, 21 H, Si(*CH*(*CH*₃)₂)₃), 1.33 (m, 4 H, CH₂), 1.50 (m, 4 H, CH₂), 1.78 (m, 1 H, CH), 3.30 (s, 1 H, C≡CH), 3.91 (d, 2 H, OCH₂, ³*J* = 5.7 Hz), 6.92 (d, 1 H, aromat. H, ⁴*J* = 1.3 Hz), 7.00 (dd, 1 H, aromat. H, ³*J* = 7.8 Hz, ⁴*J* = 1.4 Hz), 7.35 (d, 1 H, aromat. H, ³*J* = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃): 11.3 (C_t, Si-CH), 11.4 (C_p, CH₃), 14.2 (C_p, CH₃), 18.8 (C_p, Si(CH(*C*H₃)₂)₃), 23.2, 24.1, 27.1, 29.2, 30.7 (C_s, CH₂), 39.4 (C_t, aliphat. CH), 71.3 (C_s, OCH₂), 79.9, 82.5 (C_q, C_t, **C≡CH**), 92.6, 106.7 (C_q, C≡C), 112.2 (C_q), 115.0 (C_t, aromat. CH), 124.3 (C_t, aromat. CH), 125.1 (C_q), 133.7 (C_t, aromat. CH), 160.2 (C_q, aromat. C-O).

Ethyl 5-(4-{[4-ethynyl-2-(hexyloxy)phenyl]ethynyl}phenoxy)pentanoate (**16c**)

Compound **10a** (500 mg, 1.31 mmol) was dissolved in 30 ml piperidine and degassed by the pump-freeze-thaw procedure. Subsequently, $Pd(PPh_3)_4$ (75 mg, 65 µmol) and Cul (12 mg, 65 µmol) were added and the mixture was degassed by a nitrogen flow (10 minutes). Then iodoaryl **14a** (455 mg, 1.31 mmol) was added and heated for 16 hours to 45 °C. The solvent was removed under reduced pressure and the product **15a** was isolated by column chromatography (silica, cyclohexane : ethyl acetate = 15 : 1) to yield 608 mg (1.01 mmol) as a yellow oil. The oil was dissolved in 40 ml THF and TBAF (316 mg, 1.21 mmol) was added and stirred for one hour at ambient temperature. The solvent was removed at reduced pressure and the product **16c** was isolated by column chromatography (silica, cyclohexane : ethyl acetate = 10 : 1). Yield: 378 mg of a yellow solid. This precursor was still contaminated with 8 mol% iodoaryl **14a** and 41 mol% triisopropylsilylfluoride (NMR), which could not be further separated and was used as received in the next step. It has been removed after the preparation of the target mesogen **2a**. Corrected yield (NMR) of **16c** for two steps: 308 mg (0.69 mmol; 53 %).

¹H NMR (400 MHz, CDCl₃): $\delta = 0.90$ (t, 3 H, CH₃, ³*J* = 7.1 Hz), 1.26 (t, 3 H, CH₃), 1.36 (m, 4H, CH₂), 1.55 (m, 2 H, CH₂), 1.84 (m, 6 H, CH₂), 2.38 (t, 2 H, CH₂COO, ³*J* = 7.0 Hz), 3.14 (s, 1 H, C≡CH), 3.99 (t, 2 H, OCH₂, ³*J* = 5.9 Hz), 4.03 (t, 2 H, OCH₂, ³*J* = 6.4 Hz), 4.13 (q, 2 H, ³*J* = 7.0 Hz; COO**CH₂**CH₃), 6.85 (AA´BB´, 2 H, aromat. H), 6.98 (d, 1 H, aromat. H, ⁴*J* = 1.3 Hz), 7.05 (dd, 1 H, aromat. H, ³*J* = 7.8 Hz, ⁴*J* = 1.4 Hz), 7.39 (d, 1 H, aromat. H, ³*J* = 7.8 Hz), 7.44 (AA´BB´, 2 H, aromat. H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.2$, 14.4 (CH₃), 21.8, 22.8, 25.8, 28.7, 29.3, 31.7 (C_s, CH₂), 34.1 (C_s,

CH₂COO), 60.5 (C_s, COO**CH**₂CH₃), 67.6, 68.9 (C_s, OCH₂), 78.4 (C_q, C≡C), 83.7 (C_t, C≡**CH**), 84.3, 95.4 (C_q,C≡C), 114.5 (C_q), 114.6, 115.4 (C_t, aromat. CH), 115.6, 122.6 (C_q), 124.4, 132.9, 133.2 (C_t, aromat. CH), 159.1(6), 159.2(1) (C_q, aromat. C-O), 173.5 (C_q, COO).

Ethyl 5-(4-{[2-(2-ethylhexyl)oxy-4-(ethynyl)phenyl]ethynyl}phenoxy)hexanoate (16d)

Compound **10b** (571 mg,1.39 mmol) were dissolved in 25 ml piperidine and degassed by the pump-freeze-thaw procedure. Subsequently, $Pd(PPh_3)_4$ (80 mg, 0.07 mmol) and Cul (13 mg, 0.07 mmol) were added and the mixture was degassed by a nitrogen flow (10 minutes). Then iodoaryl **14b** (330 mg, 0.91 mmol) was added and heated for 16 hours to 45 °C. The solvent was removed under reduced pressure and the product **15b** was isolated by column chromatography (silica, cyclohexane : ethyl acetate = 50 : 1 to 20 : 1) to yield 466 mg (0.72 mmol) as a yellow oil. The oil was dissolved in 40 ml THF and TBAF (297 mg, 0.94 mmol) was added and stirred for one hour at ambient temperature. The solvent was removed at reduced pressure and the product **16d** was isolated by column chromatography (silica, cyclohexane : ethyl acetate = 10 : 1). Yield: 160 mg of a yellow solid. This sample was contaminated with 84 mol% triisopropylsilylfluoride (NMR), which could not be easily separated and was therefore used as received in the next step. Corrected yield (NMR) of **16d** after two steps: 123 mg (0.25 mmol, 28 %).

¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$ (t, 3 H, CH₃, ³*J* = 7.1 Hz), 0.96 (t, 3 H, CH₃, ³*J* = 7.5 Hz), 1.26 (t, 3 H, CH₃, ³*J* = 7.1 Hz), 1.25 – 1.65 (m, 10 H, CH₂), 1.71 (m, 2 H, CH₂), 1.81 (m superimposed, 3 H, CH, CH₂), 1.70 (m, 2 H, CH₂), 1.81 (m, 2 H, CH₂), 2.34 (t, 2 H, ³*J* = 7.4 Hz, CH₂COO), 3.14 (s, 1 H, C≡CH), 3.92 (m, 2 H, OCH₂), 3.97 (t, 2 H, OCH₂, ³*J* = 6.4 Hz), 4.13 (q, 2 H, ³*J* = 7.1 Hz; COO**CH₂**CH₃), 6.85 (AA´BB´, 2 H, aromat. H), 6.98 (d, 1 H, aromat. H, ⁴*J* = 1.4 Hz), 7.04 (dd, 1 H, aromat. H, ³*J* = 7.8 Hz, ⁴*J* = 1.4 Hz), 7.38 (d, 1 H, aromat. H, ³*J* = 7.8 Hz), 7.43 (AA´BB´, 2 H, aromat. H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 11.4$, 14.2,14.4 (CH₃), 23.2, 24.1, 24.8, 25.8, 29.0, 29.3, 30.8 (C₈), 34.4 (C₈, **CH**₂COO), 39.6 (C_t, aliphat. CH), 60.4 (C₈, COO**CH**₂CH₃), 67.8, 71.3 (C₈, OCH₂), 78.3, 83.8 (C_t, C_q, **C≡C**-H) 84.3, 95.4 (C≡C), 114.5 (C_q), 114.6, 115.2 (C_t, aromat. CH), 115.7, 122.5 (C_q), 124.3, 132.7, 133.1 (C_t, aromat. CH), 159.2, 159.4 (C_q, aromat. C-O), 173.8 (C_q, COO).

Board Mesogens

1,4,5,8-Tetrakis{(4-[(4-{4-[(5-ethoxycarbonyl)pentoxy]phenylethynyl}-2,5-bis(pentyloxy)phenyl)ethynyl]phenyl}-9,10-anthraquinone (**1a**)



A solution of core **6** (80.0 mg, 79 µmol) in 30 ml piperidine was degassed by the pumpfreeze-thaw procedure. After the addition of Pd(PPh₃)₄ (18.2 mg, 16 µmol) and Cul (1.5 mg, 8 µmol) the mixture was again degassed by a nitrogen flow and 5-(4-{[2,5-Bis(pentyloxy)-4-(ethynyl)phenyl]ethynyl}phenoxy)heptansäureethylester **16a** (252.0 mg, 461 µmol) was added after heating to 45 °C within four hours and stirred for further 12 hours. Subsequently, the solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, cyclohexane : ethyl acetate 4 : 1 to 0 : 1) and size recycling exclusion chromatography (chloroform) to afford 130 mg (51 µmol, 61 %) of **1a** as a yellow solid, mp. 98.3 °C (clearing temperature 208.1 °C).

¹H NMR (400 MHz, CDCl₃): δ = 0.91 (t, 12 H, CH₃, ${}^{3}J$ = 7.2 Hz), 0.93 (t, 12 H, CH₃, ${}^{3}J$ = 7.2 Hz), 1.26 (t, 12 H, CH₃, ${}^{3}J$ = 7.2 Hz), 1.34 (m, 24 H, CH₂), 1.50 (m, 24 H, CH₂), 1.67 (m, 8 H, CH₂), 1.81 (m, 24 H, CH₂), 2.32 (t, 8 H, ${}^{3}J$ = 7.4 Hz, **CH**₂COO), 3,92 (t, 8 H, OCH₂, ${}^{3}J$ = 6.4 Hz), 3.93 (t, 8 H, OCH₂, ${}^{3}J$ = 6.4 Hz), 3.96 (t, 8 H, OCH₂, ${}^{3}J$ = 6.5 Hz), 4.13 (q, 8 H, ${}^{3}J$ = 7.2, COO**CH**₂CH₃), 6.82 (AA´BB´, 8 H, aromat. H), 6.95 (s, 4 H, aromat. H), 6.97 (s, 4 H, aromat. H), 7.31 (AA´BB´, 8 H, aromat. H), 7.44 (AA´BB´, 8 H, aromat. H), 7.54, 7.55 (AA`BB' + s, superimposed, 12 H, aromat. H); 1³C NMR (100 MHz, CDCl₃): δ = 14.2(7), 14.2(9), 14.4 (C_p, CH₃), 22.7, 25.0, 25.9, 27.0, 28.4(3), 28.4(4), 29.0, 29.1(9), 29.2(2), 29.2(3) (C_s, CH₂), 34.4 (C_s, **CH**₂COO), 60.4 (C_s, COO**CH**₂CH₃), 68.0, 69.6(7), 69.7(4) (C_s, OCH₂), 84.9, 87.0, 94.7, 95.1 (C_q, C≡C), 113.6, 114.6 (C_q), 114.6 (C_t, aromat. CH, superimposed with C_q), 115.6 (C_q), 116.8, 116.9 (C_t, aromat. CH), 123.1 (C_q), 129.0, 131.4, 133.2 (C_t, aromat. CH), 134.9 (C_q), 135.3 (C_t, aromat. CH), 139.9, 141.3 (C_q), 153.6, 153.9, 159.3 (C_q, aromat. C-O), 173.9 (C_q, COO), 187.0 (C_q, C=O); HRMS (MALDI-TOF (+)): m/z: calc. 2689,4526 (M⁺⁻), found 2689,4440 (M⁺⁻).

1,4,5,8-Tetrakis(4-{[4-(4-cyanophenylethynyl)-2,5-bis(hexyloxy)phenyl]ethynyl}phenyl)-9,10-anthraquinone (**1b**)



A solution of core **6** (28 mg, 28 µmol) in 11 ml piperidine was degassed by the pumpfreeze-thaw procedure. After the addition of Pd(PPh₃)₄ (6 mg, 6 µmol) and Cul (5 mg, 27 µmol), the mixture was again degassed by a nitrogen flow and 1,4-bis(pentyloxy)-5-[(4-cyanophenyl)ethynyl]-2-ethynylbenzene **16b** (71 mg, 165 µmol) was added and the mixture was stirred for 14 hours at ambient temperature. Subsequently, the solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, dichloromethane) and size recycling exclusion chromatography (chloroform) to afford 25 mg (11 µmol, 41 %) of **1b** as a yellow solid, mp. 216.1 °C (clearing temperature 257.2 °C).

¹H NMR (400 MHz, CDCl₃): $\delta = 0.87$ (t, 12 H, CH₃, ³*J* = 7.2 Hz), 0.89 (t, 12 H, CH₃, ³*J* = 7.0 Hz), 1.34 (m, 32 H, CH₂), 1.52 (m, 16 H, CH₂), 1.82 (m, 16 H, CH₂), 3.91 (t, 8 H, OCH₂, ³*J* = 6.4 Hz), 3.94 (t, 8 H, OCH₂, ³*J* = 6.4 Hz), 6.94 (s, 4 H, aromat. H), 6.97 (s, 4 H, aromat. H), 7.31 (AA'BB', 8 H, aromat. H), 7.53(6), 7.54(4), 7.55 (2 AA'BB' + s, superimposed, 20 H, aromat. H), 7.59 (AA'BB', 8H, aromat. H); ¹³C NMR (400 MHz, CDCl₃): $\delta = 14.2(1)$, 14.2(5) (C_p, CH₃), 22.8, 25.9, 29.4(6), 29.4(8), 31.8 (C_s, CH₂), 69.5, 69.8 (C_s, OCH₂), 86.6, 90.9, 93.1, 95.4 (C_q, C≡C), 111.5, 112.7, 115.3 (C_q), 116.6, 116.9 (C_t, aromat. CH), 118.6 (C_q, CN), 122.9, 128.6 (C_q), 129.1, 131.4, 132.0, 132.1 (C_t, aromat. CH), 135.0 (C_q), 135.2 (C_t, aromat. CH), 140.0, 141.2 (C_q), 153.7, 154.1 (C_q, aromat. C-O), 187.0 (C_q, C=O); HRMS (ESI): m/z (%): calc. 2237.1127 (100, [M+1+Na]⁺), found 2237.0942 (100, [M+1+Na]⁺).

1,4,5,8-Tetrakis{4-[(4-{4-[(5-ethoxycarbonyl)butoxy]phenylethynyl}-3-(hexyloxy)phenyl)ethynyl]phenyl}-9,10-anthraquinone (**2a**)



A solution of core **6** (70 mg, 69 µmol) in 30 ml piperidine was degassed by the pumpfreeze-thaw procedure. After the addition of Pd(PPh₃)₄ (17 mg, 14 µmol) and Cul (1 mg, 5 µmol), the mixture was again degassed by a nitrogen flow and of the terminal arylethyne **16c** (215 mg, 483 µmol) was added. The mixture was stirred for 14 hours at ambient temperature. Subsequently, the solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, dichloromethane) and recycling size exclusion chromatography (chloroform) to afford 80 mg (35 µmol, 51 %) of **2a** as a yellow solid, mp. 179.1 °C (clearing temperature > 300 °C decomp.).

¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$ (t, 12 H, CH₃, ³*J* = 7.1 Hz), 1.27 (t, 12 H, CH₃, ³*J* = 7.1 Hz), 1.34 (m, 16 H, CH₂), 1.53 (m, 8 H, CH₂), 1.83 (m, 24 H, CH₂), 2.4 (t, 8 H, CH₂COOEt, ³*J* = 7.0 Hz), 3.96 (t, 8 H, OCH₂, ³*J* = 5.8 Hz), 3.98 (t, 8 H, OCH₂, ³*J* = 6.4 Hz), 4.14 (q, 8 H, ³*J* = 7.1 Hz; COO**CH₂**CH₃), 6.77 (AA'BB', 8 H, aromat. H), 6.99 (d + dd superimposed, 8 H, aromat. H), 7.29 (AA'BB', 8 H, aromat. H), 7.31 (d, 4H, aromat. H, ³*J* = 7.5 Hz), 7.42 (AA'BB', 8 H, aromat. H), 7.53 (AA'BB', 8 H, aromat.-H), 7.56 (s, 4H, aromat. H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.2$, 14.4 (C_p, CH₃), 21.8, 22.8, 25.9, 28.8, 29.3, 31.8 (C_s, CH₂), 34.1 (C_s, **CH**₂COO), 60.5 (C_s, COO**CH**₂CH₃), 67.5, 68.9 (C_s, OCH₂), 84.6, 90.4, 90.5, 95.4 (C_q, C≡C), 113.9 (C_q), 114.5, 114.7 (C_t, aromat. CH), 115.9, 122.7 (C_q), 123.7 (C_t, aromat. CH), 124.0 (C_q), 129.2, 131.4, 133.0, 133.2, 134.8 (C_t, aromat. CH), 135.3, 139.8, 141.0 (C_q), 159.0, 159.3 (C_q, aromat. C-O), 173.6 (C_q, COO), 187.3 (C_q, C=O); HRMS (ESI): m/z (%): calc. for C1₅₄H₁₅₂O₁₈ 2290.1012 (100, [M+1]⁺⁻); FA: calc. C 80.74 H 6.69, found: C 80.52 H 6.77.

1,4,5,8-Tetrakis{4-[(4-{4-[(5-ethoxycarbonyl)pentoxy]phenylethynyl}-3-(2ethylhexyloxy)phenyl)ethynyl]phenyl}-9,10-anthraquinone (**2b**)



A solution of core **6** (40.0 mg, 39 µmol) in 15 ml piperidine was degassed by the pumpfreeze-thaw procedure. After the addition of $Pd(PPh_3)_4$ (9.0 mg, 8 µmol) and Cul (0.8 mg, 4 µmol), the mixture was again degassed by a nitrogen flow and **16d** (115.0 mg, 236 µmol) was added and the mixture was stirred for 12 hours at ambient temperature. Subsequently, the solvent was removed under reduced pressure and the product was isolated by column chromatography (silica, dichloromethane) and recycling size exclusion chromatography (chloroform) to afford 49 mg (20 µmol, 51 %) of **2b** as a yellow solid, mp. 161.8 °C (clearing temperature > 300 °C decomp.).

¹H NMR (400 MHz, CDCl₃): $\delta = 0.87$ (t, 12 H, CH₃, ³*J* = 7.1 Hz), 0.95 (t, 12 H, CH₃, ³*J* = 7.5 Hz), 1.26 (t, 12 H, CH₃, ³*J* = 7.1 Hz), 1.25 – 1.65 (m, 40 H, CH₂), 1.72 (m, 8 H, CH₂), 1.81 (m superimposed, 12 H, CH, CH₂), 2.35 (t, 8 H, CH₂COO, ³*J* = 7.5 Hz), 3.90 (m, 8 H, OCH₂CH), 3.94 (t, 8H, OCH₂, ³*J* = 6.4 Hz), 4.14 (q, 8 H, ³*J* = 7.1 Hz, COOCH₂CH₃), 6.77 (AA'BB', 8 H, aromat. H), 6.97 (dd, 4 H, aromat. H, ³*J* = 7.8 Hz), 7.29 (AA'BB', 8 H, aromat. H), 7.39 (AA'BB', 8 H, aromat. H), 7.54 (AA'BB', 8 H, aromat. H), 7.56 (s, 4H, aromat. H); ¹³C NMR (100 MHz, CDCl₃): δ = 11.5, 14.3, 14.4 (C_p, CH₃), 23.2, 24.1, 24.9, 25.8, 29.1, 29.3, 30.8 (C_s, CH₂), 34.4 (C_s, CH₂COO), 39.6 (C_t, aliph.CH) 60.4 (C_s, COOCH₂CH₃), 67.8, 71.3 (C_s, OCH₂), 84.7, 90.4, 90.5, 95.3 (C_q, C=C), 114.0 (C_q), 114.5, 114.6 (C_t, aromat. CH), 115.9, 122.7, 123.6 (C_q), 124.0, 159.5 (C_q, aromat. C-O), 173.8 (C_q, COO); 187.3 (C_q, C=O); HRMS (MALDI-TOF (+)): calc. for C₁₆₆H₁₇₆O₁₈, m/z: 2457.2851 (M⁺⁺), found 2457.2832 (M⁺⁺); EA: calc. C 81.08 H 7.21; found C 80.69 H 7.30.

¹H NMR spectrum of compound **4** in CDCl₃



 ^{13}C NMR spectrum of compound 4 in CDCl_3



¹H NMR spectrum of compound **10a** in CDCI₃



¹³C NMR spectrum of compound **10a** in CDCI₃



¹H NMR spectrum of compound **10b** in CDCI₃



 ^{13}C NMR spectrum of compound 10b in CDCl_3



¹H NMR spectrum of compound **16c** in CDCI₃



 ^{13}C NMR spectrum of compound 16c in CDCl_3



¹H NMR spectrum of compound **16d** in CDCI₃



 ^{13}C NMR spectrum of compound 16d in CDCl_3



¹H NMR spectrum of compound **1a** in CDCl₃



¹³C NMR spectrum of compound **1a** in CDCl₃



¹H NMR spectrum of compound **1b** in CDCl₃



¹³C NMR spectrum of compound **1b** in CDCI₃



¹H NMR spectrum of compound **2a** in CDCl₃



 ^{13}C NMR spectrum of compound 2a in CDCl_3



¹H NMR spectrum of compound **2b** in CDCI₃



¹³C NMR spectrum of compound **2b** in CDCI₃



NMR relaxation: supporting equations

$$J^{(k)}(\omega, \Delta) = \sum_{m=0}^{2} J^{(m)}(\omega) f_{km}(\sin(\Delta))$$
(S1)

$$f_{km}(x) = \delta_{km} + \begin{bmatrix} -3x^2 + \frac{9}{4}x^4 & 18(x^2 - x^4) & \frac{9}{8}a^4 \\ \frac{1}{4}(x^2 - x^4) & -\frac{5}{2}x^2 + 2x^4 & \frac{1}{4}x^2 - \frac{1}{8}x^4 \\ \frac{1}{4}x^4 & 2(2x^2 - x^4) & -x^2 + \frac{1}{8}x^4 \end{bmatrix}$$
(S2)

with $\delta_{km} = 1$ for k = m and $\delta_{km} = 0$ for $k \neq m$.

Assuming the existance of domains with an uniform distribution of alignment directions it is possible to calculate S1 averaging over all possible orientations in the solid angle 4π

$$\overline{J^{(k)}(\omega,\Delta)} = \sum_{m=0}^{2} J^{(m)}(\omega) \overline{f_{km}(\sin(\Delta))}$$
(S3)

with

$$\overline{f_{km}(\sin(\Delta))} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} f_{km}(\sin(\Delta)) \sin(\Delta) d\Delta d\phi = \frac{c_k b_m}{30}$$
(S4)

with $c_k = 6$, 1, 4 and $b_m = 1$, 12, 3 and k, m = 0, 1, 2, respectively.

Rotations

In the case of BPP spectral densities $J^{(m)}(\omega) = c_m J^{(1)}(\omega)$, therefore we get $\overline{J^{(k)}(\omega, \Delta)} = \sum_{m=0}^{2} \overline{f_{km}(\sin(\Delta))} c_m J^{(1)} = c_k J^{(1)} \sum_{m=0}^{2} b_m c_m / 30 = c_k J^{(1)} = J^{(k)}(\omega)$.

Order director fluctuations

The spectral densities corresponding to order director fluctuations can be expressed in terms of the visco-elastic constants describing the nematic phase. Assuming, the Frank elastic constants:¹⁰ K_1 (splay), K_2 (twist), and K_3 (bend), and two Miesowicz viscosity coefficients:¹⁰,

¹⁰de Gennes, P.; Prost, J. The Physics of Liquid Crystals, 2nd Edition; Oxford University Press, 1993

 η_1 and η_2 ,

$$J^{(k)}(\nu) = f_{k1}(\Delta) \frac{\overline{|d_{00}^2(\alpha_{ij})|^2}}{r_{ij}^6} \frac{k_B T S^2 \eta_1^{1/2}}{2\pi^{3/2} K_1^{3/2}} \frac{1}{\sqrt{\nu}}$$

$$\sum_{p=1}^2 \frac{1}{2} \frac{K_1}{K_p} \sqrt{\frac{1}{U_p}} \left[h_p \left(U_p \frac{\nu_{cM}}{\nu}, \frac{\ell}{a} \right) - h_p \left(U_p \frac{\nu_{cm}}{\nu}, \frac{\xi_z}{\xi_\perp} \right) \right]$$
(S5)

with

$$U_p = \frac{K_3 \eta_1}{K_1 \eta_p} \tag{S6}$$

$$h_{p}(x,y) = \frac{1}{\pi} \left[tan^{-1} \left(\sqrt{2x} - 1 \right) + tan^{-1} \left(\sqrt{2x} + 1 \right) - tanh^{-1} \frac{\sqrt{2x}}{x+1} \right] \\ \pm \frac{1}{\pi} \sqrt{\frac{2}{V_{p}}} \left[\frac{1}{m_{\mp}^{p}} tanh^{-1} \frac{\sqrt{xV_{p}}m_{\mp}^{p}}{xV_{p}+n_{p}} - \frac{1}{m_{\pm}^{p}} \left(tan^{-1} \frac{2\sqrt{xV_{p}} - m_{\mp}^{p}}{m_{\pm}^{p}} + tan^{-1} \frac{2\sqrt{xV_{p}} + m_{\mp}^{p}}{m_{\pm}^{p}} \right) \right]$$
(S7)

$$\nu_{cM} = 2\pi K_1 / (\eta_1 \ell^2)$$

$$\nu_{cm} = 2\pi K_1 / (\eta_1 \xi_z^2),$$
(S8)

$$V_p = \left| 1 - \frac{K_p}{K_3} y^2 \right|, \tag{S9}$$

$$a_p = xy^2 \left(\frac{K_p}{K_3}\right), \tag{S10}$$

$$n_p = \sqrt{a_p^2 + 1} \tag{S11}$$

$$m_{\pm}^p = \sqrt{2\left(\sqrt{a_p^2 + 1} \pm a_p\right)},\tag{S12}$$

Here (+) sign is used if $K_p \ell^2 / a^2 < K_3$ or $K_p \xi_z^2 / \xi_{\perp}^2 < K_3$, otherwise (-) is used; S is the nematic order parameter, r_{ij} and α_{ij} are the inter-spin distance between (i, j) spin pair and the associated angle for the pair with respect to a long molecular axis, respectively. An average over all spin pairs is considered when calculating the overall spin-lattice relaxation contribution. These expressions are equivalent to those presented by Vold and Vold, ¹¹ and Dong, ¹² taking into account that the calculus was made taking into account both low and hight cut-off frequencies for the fluctuation modes. In particular, one can rewrite Eq. (S5) into two explicit terms when one wishes to consider two kinds of nematic director fluctuations for biaxial domains, one for director fluctuations of the director \mathbf{n} , the other for the minor director \mathbf{m} :

$$J^{(k)}(\nu) = J^{(k)}_{nDF}(\nu) + J^{(k)}_{mDF}(\nu)$$
(S13)

where

$$J_{nDF}^{(k)}(\nu) = f_{k1}(\Delta) \frac{\overline{|d_{00}^{2}(\alpha_{ij})|^{2}}}{r_{ij}^{6}} \frac{k_{B}TS^{2}\eta_{1}^{1/2}}{2\pi^{3/2} (K_{1})^{3/2}} \frac{1}{\sqrt{\nu}}$$

$$\frac{1}{2} \sqrt{\frac{K_{1}}{K_{3}}} \left[h_{1}\left(\frac{K_{3}}{K_{1}} \frac{\nu_{cM}}{\nu}, \frac{\ell}{a}\right) - h_{1}\left(\frac{K_{3}}{K_{1}} \frac{\nu_{cm}}{\nu}, \frac{\xi_{z}}{\xi_{\perp}}\right) \right]$$
(S14)

and

$$J_{mDF}^{(k)}(\nu) = f_{k1}(\Delta) \frac{\overline{|d_{00}^2(\alpha_{ij})|^2}}{r_{ij}^6} \frac{k_B T S^2 \eta_1^{1/2}}{2\pi^{3/2} (K_1)^{3/2}} \frac{1}{\sqrt{\nu}}$$

$$\frac{1}{2} \frac{K_1}{K_2} \sqrt{\frac{K_1 \eta_2}{K_3 \eta_1}} \left[h_2 \left(\frac{K_3 \eta_1}{K_1 \eta_2} \frac{\nu_{cM}}{\nu}, \frac{\ell}{a} \right) - h_2 \left(\frac{K_3 \eta_1}{K_1 \eta_2} \frac{\nu_{cm}}{\nu}, \frac{\xi_z}{\xi_\perp} \right) \right]$$
(S15)

Note that the above two expressions differs only in the usage of different viscoelastic constants. For an anisometric molecule such as the 1*a* compound where $L = \ell \sim 52$ Å and $a \sim 15$ Å or 5-6 Å, ℓ/a is between 3 and 5, therefore in eq. S7 the term devided by $\sqrt{V_p}$ might be considered small compared with the dominant term and an approximated expression can be obtained for $h_p(x, y) = h_p(x)$:

¹²Dong, R. Y. Nuclear Magnetic Resonance of Liquid Crystals; 2nd ed. Springer-Verlag, New York, 1997

¹¹Vold, R. R.; Vold, R. L. Chapter: *The Effects Of Director Fluctuations On Nuclear Spin Relaxation*, 1994, pp 207-231, in The Molecular Dynamics of Liquid Crystals, Proceedings of the NATO Advanced Study Institute, II Ciocco, Barga, Italy, September 11-23, 1989; Luckhurst, G. R., Veracini, C. A., Eds.; Springer Science+Business Media Dordrecht.

$$h_{p}(x) = \frac{1}{\pi} \left[tan^{-1} \left(\sqrt{2x} - 1 \right) + tan^{-1} \left(\sqrt{2x} + 1 \right) - tanh^{-1} \frac{\sqrt{2x}}{x+1} \right]$$

$$= g(x)$$
(S16)

In the case of a one-constant approximation, $K_1 \sim K_2 \sim K_3 \sim K$ and $\eta_1 \sim \eta_2 \sim \eta$ for a spherical integration domain in the wave modes space, the above spectral densities are written in the form

$$J_{\rm nDF}^{(1)} = f_{k1}(\Delta) \frac{\overline{(3\cos(\alpha_{ij})^2 - 1)^2}}{4r_{ij}^6} \frac{k_B T S^2 \eta^{1/2}}{2\pi^{3/2} K^{3/2}} \frac{1}{\sqrt{\nu}} \left[g\left(\frac{\nu_{\rm cM}}{\nu}\right) - g\left(\frac{\nu_{\rm cm}}{\nu}\right) \right]$$
(S17)

In the case of a polycristalline sample we have:

$$\overline{J^{(k)}(\omega, \Delta)} = \sum_{m=0}^{2} J^{(m)}(\omega) \overline{f_{km}(\sin(\Delta))} =$$

$$= \sum_{m=0}^{2} \frac{c_k b_m}{30} \delta_{m1} J^{(1)}(\omega) = \frac{2}{5} c_k J^{(1)}(\omega)$$
(S18)



Best model fits to the relaxation data

Figure S3. Best model fits obtained with to the experimental spin-lattice relaxation rate data as a function of the Larmos frequency for five temperatures in the nematic phase of compound 1a: a) T=150°C, b) T=145°C, c) T=140°C, c) T=135°C, and e) T=130°C, assuming a mono-domain nematic orientation, as explained in the main text.

fitteia Report (internet based fitter service) The Art of Model Fitting to Experimental Results¹

Subject	bola, t1all-20DFN-xhTdep-final1			
Date	Tuesday 16 th April, 2019, 19:51			
Affiliation	pj.sebastiao@gmail.com 194.210.229.54			
Abstract	Fit report produced with the fit results of function: y= ODFN_poli(f, A1 + A2*(T_2-Tref) + A3*(T_2-Tref)*(T_2-Tref) , (fM1 + fM2*(T_2-Tref))*h*h/(xL1*xL1), (fM1 + fM2*(T_2-Tref))*h*h/(L*L)) + BPP(f, 3.0/10.0*Kdd*Kdd/pow(ref1, 6), tau*exp(Ea/R*(1/T_2 -1/Tref))) + ODFN_poli(f, Ad1 + Ad2*(T_2-Tref) + Ad3*(T_2-Tref)*(T_2-Tref) , (fM1 + fM2*(T_2-Tref))*h*h/((T_1==1)? xh1*xh1:(T_1==2)? xh2*xh2:(T_1==3)? xh3*xh3:(T_1==4)? xh4*xh4:xh5*xh5), fM1 + fM2*(T_2-Tref)) to the 160 experimental points, considering 12 free parameters.			
	$A1 = 44054 \pm 5842$	$Ad1 = 34320 \pm 8348.8$		
$A1 = 44034 \pm 3042$ A2 = 39472 + 37714		$Ad2 = 378.06 \pm 510.94$		
A2 = 0 (fixed)		Ad3 = 0 (fixed)		
	$fM1 = 5.5788 \times 10^{+07} \pm 1.492 \times 10^{+07}$	h = 11 (fixed)		
$fM2 = -1.5406 \times 10^{+06} \pm 1.3313 \times 10^{+06}$		L = 50 (fixed)		
	$tau = 2.53 \times 10^{-10}$ (fixed)	$xh1 = 29.379 \pm 6.3031$		
	Tref = 423.15 (fixed)	$xh2 = 30.483 \pm 6.7431$		
	Ea = 1.0093 (fixed)	$xh3 = 38.768 \pm 9.3492$		
	R = 8.3145 (fixed)	$xh4 = 40.035 \pm 7.9099$		
	$ref1 = 2.41 \times 10^{-10}$ (fixed)	$xh5 = 46.595 \pm 11.684$		
	$Kdd = 7.55 \times 10^{-25} \text{ (fixed)}$	$xL1 = 300 \pm 170.34$		
$\begin{array}{ll} \chi^2[3] = 11.432 & \chi^2[5] = 5.59866 \\ \chi^2[2] = 11.8102 & \chi^2[1] = 10.1062 \\ \chi^2[4] = 6.0249 & \chi^2_t = 44.972 \end{array}$				
10°E				
10^{2}				
	(a) I=150 C	(b) I=145 C		
- <u></u> 10 ¹ ≡				
μĒ	μ μ μ μ μ μ μ μ μ μ μ μ μ μ μ μ μ μ μ			
-				
10 ⁰	10			
E	nDF	nDF S		
10 '	10^{6} 10^{7} 10^{8} 10^{10}	$10^6 10^7 10^8$		
$v_{L}(Hz)$ $v_{L}(Hz)$				
figure-1.pdf figure-2.pdf				

¹"The Art of Model Fitting to Experimental Results", P.J. Sebastião, Eur. J. Phys. **35** (2014) 015017





fitteia Report (internet based fitter service) The Art of Model Fitting to Experimental Results¹

Subject	bola, t1all-20DFN-xhTdep-final-mono			
Date	Tuesday 23 rd July, 2019, 17:34			
Affiliation	pj.sebastiao@gmail.com 194.210.229.102			
Abstract	$ \begin{array}{l} \label{eq:states} \hline \mbox{Instants} \\ \mbox{Fit report produced with the fit results of function:} \\ y= \mbox{ODFN}(f, \mbox{A1} + \mbox{A2}^*(\mbox{T}_2-\mbox{Tref}) + \mbox{A3}^*(\mbox{T}_2-\mbox{Tref})^*(\mbox{T}_2-\mbox{Tref}) , \ (f\mbox{M1} + \mbox{fM2}^*(\mbox{T}_2-\mbox{Tref}))^*\mbox{h}^*\mbox{h}^{-1}(\mbox{L}^1\mbox{xL}^1), \ (f\mbox{M1} + \mbox{fM2}^*(\mbox{T}_2-\mbox{Tref}))^*\mbox{h}^*\mbox{h}^{-1}(\mbox{L}^1\mbox{L}^1), \ (f\mbox{M1} + \mbox{fM2}^*(\mbox{T}_2-\mbox{Tref}))^*\mbox{h}^*\mbox{h}^{-1}(\mbox{L}^1\mbox{L}^1\mbox{L}^1)) + \mbox{ODFN}(f, \mbox{Ad1} + \mbox{Ad2}^*(\mbox{T}_2-\mbox{Tref}) + \mbox{Ad3}^*(\mbox{T}_2-\mbox{Tref})^*(\mbox{T}_2-\mbox{Tref})) + \mbox{ODFN}(f, \mbox{Ad1} + \mbox{Ad2}^*(\mbox{T}_2-\mbox{Tref}) + \mbox{Ad3}^*(\mbox{T}_2-\mbox{Tref})^*(\mbox{T}_2-\mbox{Tref}), \ (f\mbox{M1} + \mbox{fM2}^*(\mbox{T}_2-\mbox{Tref}))^*\mbox{h}^*\mbox{h}^{-1}(\mbox{T}_1==2)? \ \mbox{xh}^2\mbox{xh}^2\mbox{xh}^2\mbox{xh}^2\mbox{xh}^3\mbox{xh}^3\mbox{xh}^3\mbox{(T}_1==4)? \mbox{xh}^4\mbox{xh}^4\mbox{xh}^5\mbox{xh}^5\mbox{, f}\mbox{M1} + \mbox{fM2}^*(\mbox{T}_2-\mbox{Tref}), \ 0.0 \) \ \mbox{to the 160 experimental points, considering 12 free parameters.} \end{array}$			
	$A1 = 64471 \pm 7741.9$	$Ad1 = 48421 \pm 10177$		
	$A2 = 520.43 \pm 520.59$	$Ad2 = 463.97 \pm 660.88$		
	A3 = 0 (fixed)	Ad3 = 0 (fixed)		
	$fM1 = 3.669 \times 10^{+07} \pm 8.9843 \times 10^{+06}$	h = 11 (fixed)		
$fM2 = -9.496 \times 10^{+05} \pm 8.2705 \times 10^{+05}$ $L = 5$		L = 50 (fixed)		
	$tau = 2.53 \times 10^{-10}$ (fixed)	$xh1 = 31.593 \pm 6.2962$		
	$Tref = 423.15 \text{ (fixed)}$ $xh2 = 32.86 \pm 6.8321$			
	$Ea = 1.0093$ (fixed) $xh3 = 42.227 \pm 9.4538$			
	$R = 8.3145 \text{ (fixed)}$ $xh4 = 42.685 \pm 7.9819$			
	$ref1 = 2.41 \times 10^{-10}$ (fixed)	$xh5 = 49.142 \pm 11.759$		
	$Kdd = 7.55 \times 10^{-25} \text{ (fixed)}$	$xL1 = 300 \pm 159.52$		
$\begin{aligned} \chi^{2}[4] &= 6.2108 & \chi^{2}[1] = 10.2173 \\ \chi^{2}[5] &= 5.39747 & \chi^{2}[3] = 11.4263 \\ \chi^{2}[2] &= 11.9628 & \chi^{2}_{t} = 45.2146 \end{aligned}$				
3 3				
Ē	1a 🗍	E 1a 🗄		
10^2	$(a) = 150^{\circ} c$ = 10	$(b) T 145^{\circ}C$		
	(a) 1=150 C			
- 10 ¹ E				
μĒ		E S S		
- Pot				
10 [°]	10			
E	nDF	E ADF		
j-				
10 ⁻¹	10^{6} 10^{7} 10^{8} 10	10^6 10^7 10^8		
$v_{r}(Hz)$ $v_{r}(Hz)$ $v_{r}(Hz)$				
	-1 pdf			
	*	1		

¹"The Art of Model Fitting to Experimental Results", P.J. Sebastião, Eur. J. Phys. **35** (2014) 015017



