Supporting information

Synthesis and properties of oxadiazole based V-shaped, shape persistent nematogens

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Contents:

I. General Information

The compounds were purified by column chromatographic technique using silica gel as a stationary phase, whereas the target molecules were purified by recrystallisation technique. IR spectra were recorded using a Perkin-Elmer 1000 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Varian Inova (400MHz) spectrometers. For ^{1}H NMR spectra, the chemical shifts are reported in ppm relative to tetramethylsilane as an internal standard. Mass spectra were recorded on a MAT 95 (Finnigan) spectrometer. Elemental analyses were carried out using a. The thermotropic behaviour of target molecules were investigated with the aid of an optical polarizing microscope (Zeiss Axioscop 40) equipped with a programmable hot stage (Linkam, THM 600). The transition temperatures and associated enthalpies were determined by differential scanning calorimetry (Perkin Elmer). Optical observations were made using either clean untreated glass slides or treated with antiparallel rubbed polyimide alignment layers.
X-ray diffraction patterns on magnetic field aligned samples were recorded using a standard copper anode (2.2 KW) source with pinhole collimation equipped with a X-ray mirror (Osmic typ CMF15-sCu6) and a Bruker detector (High-star) with 1024x1024 pixels and the X-ray patterns were analysed with the software package Datasqueeze written by Prof. Paul Heiney.
Dielectric measurements were performed using the Solartron Schlumberger impedance analyzer SI 1260 in the frequency range between 0.1 Hz and 10^7 Hz. The substance was put in a golden-plated capacitor with a distance of 100 μm and oriented in an external magnetic field of 0.6 T. The raw data were fitted to the real and imaginary part of equation (1)

$$\varepsilon^* = \varepsilon_2 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (j\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (j\omega\tau_2)^{1-\alpha_2}} - \frac{jA}{f} + \frac{B}{f^N} \qquad (1)$$

with ε_i low and high frequency limits of the dielectric permittivity, $\omega=2\pi f$ (f - frequency), τ_i - relaxation times, α - Cole-Cole distribution parameters, the conductivity term A as well as B and N as further fit parameters describing the capacity of the double layer.[1]

II. Experimental

General Procedure for the Sonogashira-Hagihara coupling
Under nitrogen atmosphere 1 mmol of the halogenaryl derivative, 10 mol% $Pd(PPh_3)_4$ and 5mol% CuI were mixed with 20 ml piperidine. Oxygen was removed by a freeze-pump-tough procedure. Subsequently, 1 mmol of the terminal alkyne was added against nitrogen flow at rt. In case of bromoaryl compounds the temperature was raised to 80 °C. The reaction mixtures were stirred for 12 hours. After removing the solvent under vacuum, the crude products were purified by column chromatography.

2-{4-[2-(3-cyanophenyl)ethynyl]-2,5-bis(hexyloxy)phenyl}ethyne 2c: Compound **2c** was synthesised analogous to **2a,b**[2] using 3-bromobenzonitril as the arylhalogenid component of the Sonogashira-Hagihara coupling reaction. The crude product was purified by column chromatography (silica, hexane : CH_2Cl_2 =2 : 1); yield: 78 % of a yellow solid; mp. 80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.5 Hz, 3H, CH_3); 0.90 (t, *J* = 6.5 Hz, 3H, CH_3); 1.35 (m, 8H, CH_2); 1.50 (m, 4H, CH_2); 1.82 (m, 4H, CH_2); 3.36 (s, 1H, HC≡C); 3.99 (t, ^3J = 6.4 Hz, 2H, OCH_2); 4.00 (t, ^3J = 6.4 Hz, 2H, OCH_2); 6.97 (s, 1H, aromat. H); 6.98 (s, 1H, aromat. H); 7.46 (dd, ^3J = 8.0 Hz, ^3J = 7.8 Hz, 1H, aromat. H); 7.60 (ddd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 7.72 (ddd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 7.79 (dd, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3); 22.5, 22.6, 25.5, 25.7, 29.0, 29.1, 31.5 (CH_2); 69.5, 69.6 (OCH_2); 79.7, 82.7, 88.2, 92.1 (C≡C); 113.3, 113.4 (aromat. C_q); 116.7, 117.5 (aromat. CH); 118.0 (C_q, CN), 125.0 (aromat. C_q); 129.2, 131.3, 134.7, 135.5 (aromat. CH); 153.6, 154.0 (C_qO); FD-MS: m/z [%]: 427.3 (100, $M^{+\bullet}$); elemental analysis calc for $C_{29}H_{33}NO_2$: C 81.46, H 7.78, N 3.28; found C 81.51, H 7.62, N 3.27.

{4-[2-(4-deuteriophenyl)ethinyl]-2,5-bis(hexyloxy)phenyl}ethyne 2d: The synthesis was performed according to a modified general procedure. 0.27 g (2.61 mmol) *p*-deuteriophenylethyne[3] was added to a mixture of 1.27 g (2.61 mmol) 2,5-bishexyloxy-1-bromo-4-iodobenzene, 10 ml piperidine, 30.0 mg $Pd(PPh_3)_4$ and 18.0 mg CuI at rt. The reaction mixture was stirred for 2h at rt. After heating to 50 °C, 0.25 g (2.61 mmol) TMSA inserted and the slurry was stirred further for four hours. The crude product was purified by column chromatography (silica, hexane : CH_2Cl_2 =2 : 1, R_f = 0.4); yield 1.03 g (83%) of a yellow solid. 0.66 g (1.39 mmol) of the product were exposed to a deprotection procedure by dissolving it in 15 ml dry THF and adding 0.36 g (1.39 mmol) tetra-*n*-butylammonium fluoride (TBAF) at 0 °C under nitrogen atmosphere. After stirring four hours, the reaction mixture was diluted with 50 ml CH_2Cl_2,

[1] H. Kresse, H. Schlacken, U. Dunemann, M. W. Schroeder and G. Pelzl, *Liq. Cryst.*, **2002**, *29*, 1509.
[2] M. Lehmann, S.-W. Kang, Ch. Köhn, S. Haseloh, U. Kolb, D. Schollmeyer, Q. Wang, S. Kumar, *J. Mater. Chem.* 2006, **16**, 4326.
[3] W. D. Wulff, K. A. Korthals, R. Martinez-Alvarez, M. Gomez-Gallego, I. Fernandez, M. A. Sierra, *J. Org. Chem.* 2005, **70**, 5269.

washed successively with a solution of NH_4Cl and water and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, hexane : CH_2Cl_2 =4 : 1, R_f = 0.2); yield 0.41 g (73 %; overall yield for the two steps 57 %) of a yellow solid, mp. 68.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (2t, 6H, CH_3); 1.35 (m, 8H, CH_2); 1.50 (m, 4H, CH_2); 1.82 (m, 4H, CH_2); 3.36 (s, 1H, C≡CH); 3.99 (t, ^3J = 6.6 Hz, 2H, OCH_2); 4.00 (t, ^3J = 6.6 Hz, 2H, OCH_2); 6.97 (s, 1H, aromat. H); 6.99 (s, 1H, aromat. H); 7.34 (AA'BB', 2H, aromat. H); 7.53 (AA'BB', 2H, aromat. H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3); 22.5, 22.6, 25.5, 25.7, 29.0, 29.2, 31.4, 31.5 (CH_2); 69.6 (OCH_2); 79.9, 82.3, 85.6, 94.8 (C≡C); 112.4, 114.6 (aromat. C_q); 116.7, 117.7 (aromat. CH); 123.3 (aromat. C_q); 128.1, 131.5 (aromat. CH); 153.4, 154.1 (C_qO). FD-MS: m/z (%): 403.6 (100, $M^{+\bullet}$); 404.6 (27, $[M+1]^{+\bullet}$); elemental analysis calc. for $C_{28}H_{33}DO_2$: C 83.33, H 8.74; found C 83.32, H 8.75.

2-(4-bromophenyl)-5-({[2,5-bis(hexyloxy)-4-(phenylethynyl)phenyl]ethynyl}phenyl)-1,3,4-oxadiazole 4a: Following the general procedure the oxadiazole derivative **3** was coupled to arm **2a**[2] at rt. The crude product was purified by column chromatography (silica, CH_2Cl_2, R_f = 0.2); yield: 93 % of a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 7.0 Hz, 3H, CH_3); 0.90 (t, ^3J = 7.0 Hz, 3H, CH_3); 1.36 (m, 8H, CH_2); 1.57 (m, 4H, CH_2); 1.86 (m, 4H, CH_2); 4.04 (t, ^3J = 6.3 Hz, 2H, OCH_2); 4.05 (t, ^3J = 6.3 Hz, 2H, OCH_2); 7.03 (s, 1H, aromat. H); 7.04 (s, 1H, aromat. H); 7.35 (m, 3H, aromat. H); 7.54 (m, 2H, aromat. H); 7.69 (AA'XX', 4H, aromat. H); 8.02 (AA'XX', 2H, aromat. H); 8.12 (AA'XX', 2H, aromat. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3); 22.6, 25.7, 29.2, 29.3, 31.5, 31.6 (CH_2); 69.5, 69.6 (OCH_2); 85.8, 89.3, 93.8, 95.2 (C≡C); 113.0, 114.6 (aromat. C_q); 116.7, 116.9 (aromat. CH); 122.7, 123.3 (aromat. C_q); 126.8 (aromat. CH); 127.2 (aromat. C_q); 128.3, 131.5 (aromat. CH); 131.9, 132.0 (aromat. C_q); 132.1, 132.4 (aromat. CH); 153.5, 153.8 (C_qO); 163.9, 164.3 (C_qN).

2-(4-bromophenyl)-5-({[4-(3-cyanophenylethynyl)-2,5-bis(hexyloxy)phenyl]ethynyl}phenyl)-1,3,4-oxadiazole 4b: Following the general procedure the oxadiazole derivative **3** was coupled to arm **2c** at rt. The crude product was purified by column chromatography (silica, CH_2Cl_2, R_f = 0.5); yield: 63 % of a yellow solid; mp. 166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.0 Hz, 3H, CH_3); 0.91 (t, ^3J = 7.0 Hz, 3H, CH_3); 1.37 (m, 8H, CH_2); 1.55 (m, 4H, CH_2); 1.86 (m, 4H, CH_2); 4.04 (t, ^3J = 6.3 Hz, 2H, OCH_2); 4.05 (t, ^3J = 6.3 Hz, 2H, OCH_2); 7.01 (s, 1H, aromat. H); 7.03 (s, 1H, aromat. H); 7.46 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1H, aromat. H); 7.60 (ddd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 7.68 (AA'XX', 4H, aromat. H); 7.73 (ddd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 7.79 (dd, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 8.01 (AA'XX', 2H, aromat. H); 8.11 (AA'XX', 2H, aromat. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3); 22.6, 25.7, 29.2, 31.5 (CH_2); 69.5 (OCH_2); 88.3, 89.0, 92.4, 94.2 (C≡C); 105.0, 112.8, 113.3, 114.0 (aromat. C_q); 116.6, 116.7 (aromat. CH); 118.0 (C_q, CN), 122.6, 123.0, 125.0 (aromat. C_q); 126.8, 128.3, 129.2, 131.3, 132.1, 132.4, 134.7, 135.5 (aromat. CH); 153.7, 153.8 (C_qO); 163.9, 164.3 (C_qN); FD-MS: m/z [%]: 725.4 (92, $M^{+\bullet}$); 726.5.3 (48, $[M+1]^{+\bullet}$); 727.4 (100,$[M+2)^{+\bullet}$]; 728.4 (47, $[M+3]^{+\bullet}$).

2-({4-[2-(3-cyanophenyl)ethynyl]-2,5-bis(hexyloxy)phenyl}ethynyl)-5-({2-[4-(2-phenyl-ethynyl)-2,5-bis(hexyloxy)phenyl]ethynyl}phenyl)-1,3,4-oxadiazole 1a (X = H):[4] Following

[4] The mesogen **1a** with X = H was first synthesised, however, due to the promising properties and with respect to the planned solid state NMR investigations which can substantiate further phase biaxiality, only the selectively deuterated derivative **1a** (X = ^{2}H) was prepared for all further investigations including elemental analysis, POM, DSC, X-ray and dielectric measurements.

the general procedure the oxadiazole derivative **4b** was coupled to arm **2c** at 80 °C. The crude product was purified by column chromatography (silica, CH_2Cl_2, R_f = 0.2); yield: 56 % of a yellow solid, mp: 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (m, 12H, CH_3); 1.37 (m, 16H, CH_2); 1.56 (m, 8H, CH_2); 1.86 (m, 8H, CH_2); 4.05 (t, ^3J = 6.3 Hz, 4H, OCH_2); 4.05 (t, ^3J = 6.3 Hz, 4H, OCH_2); 7.02 (s, 1H, aromat. H); 7.03 (s, 1H, aromat. H); 7.04 (s, 1H, aromat. H); 7.05 (s, 1H, aromat. H); 7.35 (m, 3H, aromat. H); 7.47 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1H, aromat. H); 7.54 (m, 2H, aromat. H); 7.61 (ddd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 7.69 (AA'XX', 4H, aromat. H); 7.73 (ddd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 7.80 (dd, ^4J = 1.6 Hz, ^4J = 1.6 Hz, 1H, aromat. H); 8.14 (AA'XX', 4H, aromat. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3); 22.6, 25.5, 25.7, 29.0, 29.2, 29.3, 29.6, 31.5, 31.9 (CH_2); 69.5, 69.6 (OCH_2); 85.7, 88.3, 88.9, 89.2, 92.4, 93.8, 94.3, 95.2 (C≡C); 112.8, 113.0, 113.3, 114.0, 114.6 (aromat. C_q); 116.6, 116.7, 116.8 (aromat. CH); 118.0 (C_q, C≡N); 122.9, 123.1, 123.3 (aromat. C_q); 125.0, 126.8 (aromat. CH); 126.9, 127.1 (aromat. C_q); 128.3, 129.2, 131.3, 131.5, 132.1, 134.7, 135.5 (aromat. CH); 153.5, 153.7 (C_qO); 164.2, 164.3 (C_qN); FD-MS: m/z [%]: 1047.3 (100, $M^{+\bullet}$); 1048.3 (65, $[M+1]^{+\bullet}$); 1049.4 (17,$[M+2)^{+\bullet}$].

2-({4-[2-(3-cyanophenyl)ethynyl]-2,5-bis(hexyloxy)phenyl}ethynyl)-5-[4-(2-{4-[2-(4-deuteriophenyl)ethynyl]-2,5-bis(hexyloxy)phenyl}ethynyl)phenyl]-1,3,4-oxadiazole 1a (X = ^{2}H):[4] Following the general procedure the oxadiazole derivative **4c** was coupled to arm **2d** at 75 °C. The crude product was purified by column chromatography (silica, CH_2Cl_2, R_f = 0.2); yield: 45 % of a yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87-0.91 (m, 12H, CH_3); 1.33-1.40 (m, 16H, CH_2); 1.56 (m, 8H, CH_2); 1.87 (m, 8H, CH_2); 4.04 (t, J = 6.3 Hz, 4H, OCH_2); 4.05 (t, J = 6.3 Hz, 4H, OCH_2); 7.02 (s, 1H, aromat. H); 7.03 (s, 1H, aromat. H); 7.04 (s, 1H, aromat. H); 7.05 (s, 1H, aromat. H); 7.35 (AA'BB', 2H, aromat. H); 7.47 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz , 1H, aromat. H); 7.54 (AA'BB', 2H, aromat. H); 7.61 (ddd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz 1H, aromat. H); 7.69 (AA'XX', 4H, aromat. H); 7.73 (ddd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz 1H, aromat. H); 7.80 (dd, ^4J = 1.6 Hz, ^4J = 1.6 Hz 1H, aromat. H); 8.13 (2AA'XX', 4H, aromat. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.01, 14.02, 14.04 (CH_3); 22.62, 22.63, 22.64, 25.72, 25.73, 29.22, 29.24, 29.26, 29.29, 31.54, 31.56, 31.57, 31.58, (CH_2); 69.52, 69.57, 69.63 (OCH_2); 85.8, 88.4, 89.0, 89.3, 92.4, 93.9, 94.3, 95.2 (C≡C); 112.8, 113.1, 113.3, 114.0, 114.6 (aromat. C_q); 116.69, 116.71, 116.73, 116.75, 116.9 (aromat. CH); 118.0 (C_q, C≡N); 122.9, 123.1, 123.3, 125.0 (aromat. C_q); 126.77, 126.79 (aromat. CH); 126.9, 127.1 (aromat. C_q); 128.2, 129.2, 131.5, 132.08, 132.12, 134.8, 135.5 (aromat. CH); 153.6, 153.7, 153.77, 153.79 (C_qO); 164.2, 164.3 (C_qN); FD-MS: m/z [%]:1048.9 (100, $M^{+\bullet}$); 1049.9 (71, $[M+1]^{+\bullet}$); 1050.9 (25, $[M+2]^{+\bullet}$); elemental analysis calc. for $C_{71}H_{72}DN_3O_5$: C 81.26, H 7.11, N 4.00; found C 81.14, H 7.09, N 3.89.

2-({4-[2-(4-cyanophenyl)ethynyl]-2,5-bis(hexyloxy)phenyl}ethynyl)-5-(4-{2-[4-(2-phenyl-ethynyl)-2,5-bis(hexyloxy)phenyl]ethynyl}phenyl)-1,3,4-oxadiazole 1b: Following the general procedure the oxadiazole derivative **4a** was coupled to arm **2b** at 80 °C. The crude product was purified by column chromatography (silica, CH_2Cl_2, R_f = 0.4). The resulting product was recrystallized from methanol; yield: 36 % of a yellow solid, mp: 115-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 6H, CH_3, ^3J = 7.0 Hz), 0.91 (t, 6H, CH_3, ^3J = 7.0 Hz), 1.37 (m, 16H, CH_2), 1.55 (m, 8H, CH_2), 1.86 (m, 8H, CH_2), 4.04 (t, 4H, OCH_2, ^3J = 6.2 Hz), 4.05 (t, 4H, OCH_2, ^3J = 6.2 Hz), 7.02 (s, 1H, aromat. H), 7.03 (s, 1H, aromat. H), 7.03 (s, 1H, aromat. H), 7.04 (s, 1H, aromat. H), 7.35 (m, 3H, aromat. H), 7.54 (m, 2H, aromat. H), 7.62 (AA'BB', 4H, aromat. H), 7.69 (AA'XX', 4H, aromat. H), 8.14 (AA'XX', 4H, aromat. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

= 14.0 (CH_3); 22.6, 25.7, 25.7, 29.2, 29.6, 31.5 (CH_2); 69.4, 69.5, 69.6 (OCH_2); 85.7, 88.9, 89.2, 90.3, 93.2, 93.8, 94.4, 95.2 (C≡C); 111.4, 113.0, 113.2, 114.2, 114.6 (aromat. C_q); 116.6, 116.7, 116.8 (aromat. CH); 118.5 (C_q, C≡N); 122.9, 123.1, 123.3 (aromat. C_q); 126.8 (aromat. CH); 126.9, 127.1 (aromat. C_q); 128.3, 131.5, 131.9, 132.0, 132.1 (aromat. CH); 153.5; 153.7, 153.8 (C_qO); 164.2, 164.3 (C_qN); FD-MS: m/z [%]: 1047.2 (100, $M^{+\bullet}$); 1048.2 (77, $[M+1]^{+\bullet}$); 1049.2 (29, $[M+2]^{+\bullet}$).

2,5-bis[4-(2-{4-[2-(3-cyanophenyl)ethynyl]-2,5-bis(hexyloxy)phenyl}ethynyl)phenyl]-1,3,4-oxadiazole 1c: Following the general procedure the oxadiazole derivative **4b** was coupled to arm **2c** at 80 °C. The crude product was purified by column chromatography (silica, CH_2Cl_2 : THF = 4 : 3, R_f = 0.25). The resulting product was recrystallized from methanol; yield: 35 % of a yellow solid, mp. 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.0 Hz, 6H, CH_3), 0.91 (t, ^3J = 7.0 Hz, 6H, CH_3), 1.37 (m, 16H, CH_2), 1.56 (m, 8H, CH_2), 1.87 (m, 8H, CH_2), 4.05 (t, ^3J = 6.3 Hz, 4H, OCH_2), 4.05 (t, ^3J = 6.3 Hz, 4H, OCH_2), 7.02 (s, 2H, aromat. H), 7.04 (s, 2H, aromat. H), 7.48 (ddd, ^3J = 7.9 Hz, ^3J = 7.8 Hz, ^5J = 0.6 Hz, 2H, aromat. H), 7.61 (ddd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, ^4J = 1.3 Hz, 2H, aromat. H), 7.69 (AA'XX', 4H, aromat. H), 7.74 (ddd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, ^4J = 1.3 Hz, 2H, aromat. H), 7.80 (ddd, ^4J = 1.6 Hz, ^4J = 1.6 Hz, ^5J = 0.6 Hz, 2H, aromat. H), 8.15 (AA'XX', 4H, aromat. H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3); 22.6, 25.7, 29.2, 31.5 (CH_2); 69.5 (OCH_2); 88.3, 88.9, 92.4, 94.2 (C≡C); 112.8, 113.3, 114.0 (aromat. C_q);); 116.6, 116.7 (aromat. CH); 118.0 (C_q, C≡N); 123.1, 125.0 (aromat. C_q); 126.8, 126.9, 129.2, 131.4, 132.1, 134.7, 135.5 (aromat. CH); 153.7 (C_qO); 164.2 (C_qN); FD-MS: m/z [%]: 1072.5 (100, $M^{+\bullet}$); 1073.5 (80, $[M+1]^{+\bullet}$); 1074.5 (31, $[M+2]^{+\bullet}$).

2,5-bis(4-{2-[2,5-bis(hexyloxy)-4-(2-phenylethynyl)phenyl]ethynyl}phenyl)-1,3,4-oxadiazole 1d: Following the general procedure the oxadiazole derivative **4a** was coupled to arm **2a** at 80 °C. The crude product was purified by column chromatography (silica, CH_2Cl_2); yield: 60 % of a yellow solid, mp. 120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (m, 12H, CH_3); 1.37 (m, 16H, CH_2); 1.55 (m, 8H, CH_2); 1.87 (m, 8H, CH_2); 4.04 (t, ^3J = 6.3 Hz, 4H, OCH_2); 4.05 (t, ^3J = 6.3 Hz, 4H, OCH_2); 7.03 (s, 4H, aromat. H); 7.35 (m, 6H, aromat. H); 7.54 (m, 4H, aromat. H); 7.70 (AA'XX', 4H, CH); 8.14 (AA'XX', 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (CH_3); 22.6, 25.7, 29.2, 29.3, 31.5 (CH_2); 69.5, 69.6 (OCH_2); 85.8, 89.2, 93.8, 95.2 (C≡C); 113.1, 114.7 (aromat. C_q); 116.7, 116.9 (aromat. CH); 123.0, 123.3 (aromat. C_q); 126.8 (aromat. CH); 127.1 (aromat. C_q); 128.3, 131.5, 132.1 (aromat. CH); 153.5, 153.8 (C_qO); 164.3 (C_qN); FD-MS: m/z [%]: 1022.56 (100, $M^{+\bullet}$); 1023.56 (77, $[M+1]^{+\bullet}$); 1024.57 (29, $[M+2]^{+\bullet}$).

III. POM: thermotropic behaviour of 1b.

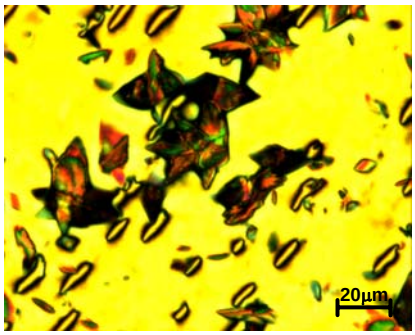

Figure S1. Photograph of a texture of compound **1b** annealed for 5 min at 91.8 °C. Many crystallites are visible in the nematic texture. The relatively fast crystallisation of this compound prevents the investigation of the nature of its nematic phase.

IV. DSC curves of 1a (X = ^{2}H)

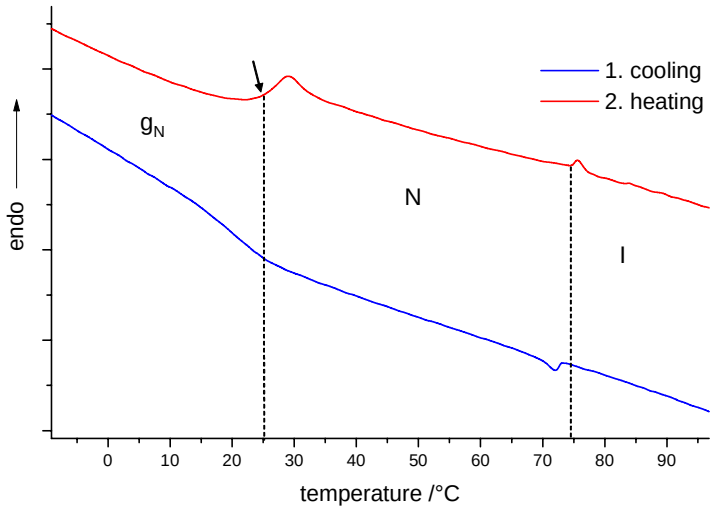

Figure S2. DSC curves of **1a**. The glass temperature T_g is indicated by the arrows.

V. X-ray integration along the equator of the diffraction pattern of 1a (X = ^{2}H)

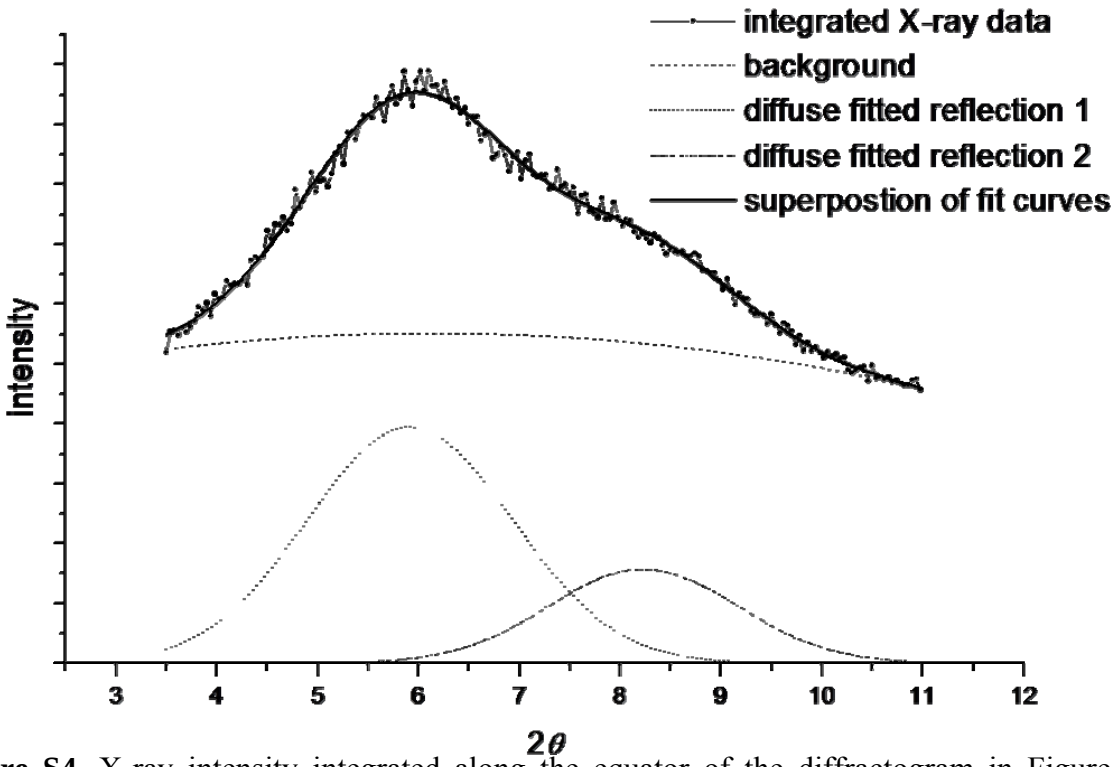

Figure S4. X-ray intensity integrated along the equator of the diffractogram in Figure 3, fit curves (background, reflections 1 and 2) and the superposition of the fit curves. The graph shows clearly that the diffraction pattern is composed of two diffuse reflections centred at 2θ = 5.9° (14.9 Å) and 2θ=8.3 (10.7 Å).

VI. X-ray of a shear aligned sample of 1a (X = ^{2}H)

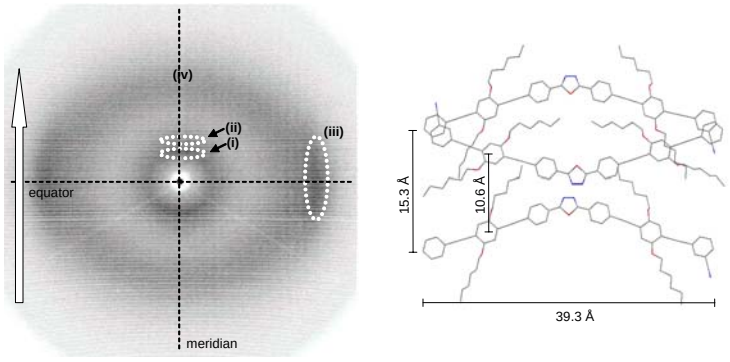

Figure S5. (a) X-ray diffractogram of a shear aligned sample **1a** at 25 °C (the white arrow shows the direction of extrusion). The pattern equals the one of the sample oriented in the magnetic field. However, extrusion aligns the bisect of the molecule, thus, the pattern is rotated by 90 °. **(b)** Possible model rationalising reflections (i) and (ii) with short range order along the bisect of the molecules.