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Electronic Supplementary Information

Unfolding multistranded PBI bisimide LC columns to two-dimensional LC arrays – A mesogen design for efficient nanoscale multilayer self-assembly

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1. Materials and methods

Reagents were purchased from commercial suppliers and used as received without further purification. *N*,*N*'-dicyclohexylcarbodiimide (DCC) was freshly distilled prior to its use. Solvents were distilled and dried by standard procedures. All reactions were carried out under nitrogen atmosphere. Column chromatography was performed with commercial glass columns using silica gel 60M (particle size 0.04-0.063 mm; Macherey-Nagel GmbH & Co. KG, Germany) as stationary phase.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on an Avance III HD 400 or 600 MHz spectrometer (Bruker-Daltonics GmbH, Germany). The chemical shifts (δ) are reported in parts per million (ppm) and are internally referenced to the residual proton solvent rresonances or the the natural abundance carbon resonances. Multiplicities for proton signals are abbreviated as s, d and m for singlet, doublet and multiplet, respectively.

High resolution mass spectra (HRMS) were recorded on an ESI micrOTOF focus spectrometer (Bruker Daltonic GmbH, Germany).

UV-Vis absorption spectra in solution were recorded using a Lambda 35 spectrometer (Perkin Elmer Inc., USA). The spectra were measured in quartz glass cuvettes using spectroscopic grade solvents. Temperature control was accomplished by a PTP-1+1 Peltier system. Extinction coefficients were calculated according to the Beer-Lambert law.

Fluorescence spectroscopy in solution was carried out with an PTI QM4-2003 fluorescence spectrometer. Fluorescence quantum yields of the monomers in solution were determined as average value of four different excitation wavelengths using *N*,*N*'-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-3,4:9,10-perylenetetracarboxylic acid bisimide as a fluorescence standard[S1] by applying high dilution conditions (OD_{max} < 0.05). The signals were corrected for the different refractive indices according to common procedure.

UV/Vis of thin films was carried out with an Axio Imager 2 (Carl Zeiss AG, Germany) polarizing optical microscope equipped with a Hg arc lamp and a cooled CCD spectrometer MCS-CCD PCI (Carl Zeiss AG, Germany).

Optical textures of the liquid-crystalline materials were examined with an Nikon Eclipse *LV100Pol* optical polarizing microscope equipped with a Linkam LTS420 heating stage and a Linkam T95-HS system controller. Thermal analyses by differential scanning calorimetry were performed on a TA instrument *DSC Q1000* with a DSC refrigerated cooling system.

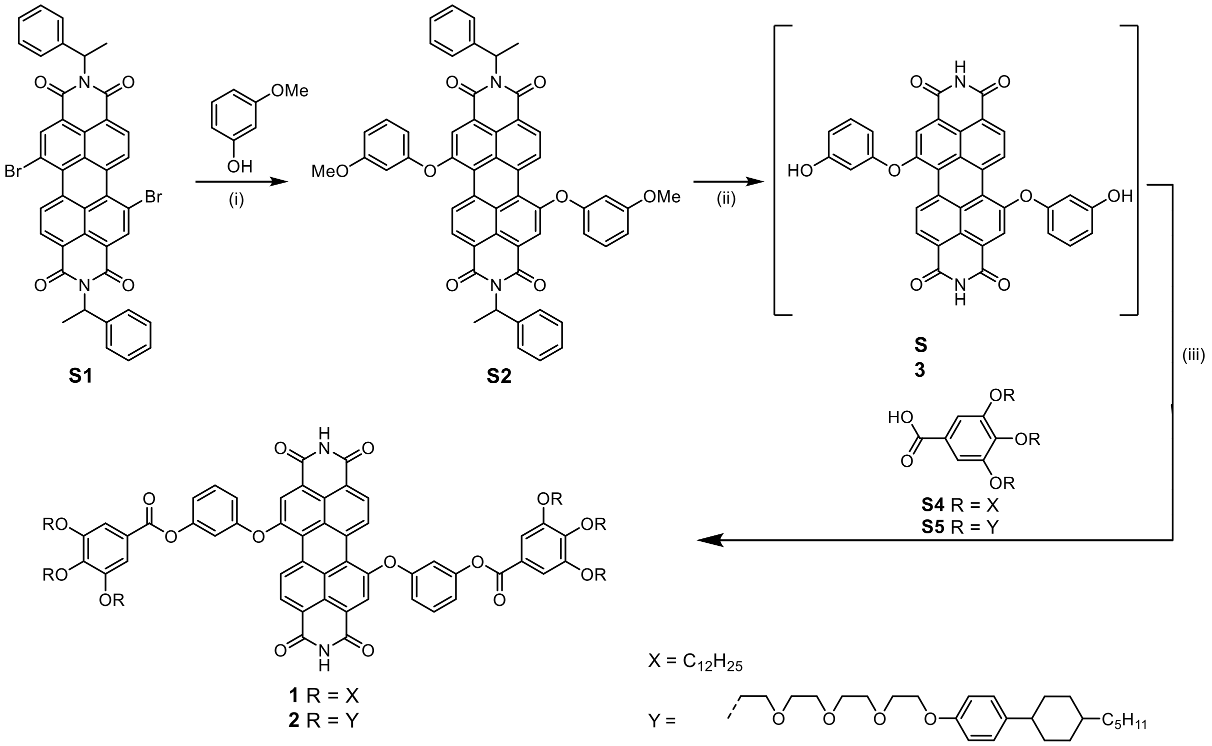
Polarized FT-IR spectra were recorded with an AIM-8800 infrared microscope connected to an IRAffinity FT-IR spectrometer (Shimadzu Corp., Japan). The sample was prepared as a thin film on a KBr substrate (thickness 2 mm) which was placed on a THMS600 heat stage with a TP94 controller (Linkam Scientific Instruments Ltd., UK). Polarization dependent FT-IR spectra were measured by using a precision automated polarizer (ZnSe) (PIKE Technologies, USA). This includes the PIKE Technologies Motion Control Unit and AutoPro software.

Temperature-dependent WAXS and MAXS measurements were performed on a Bruker Nanostar (Detector Vantec2000, Microfocus copper anode X-ray tube Incoatec). Liquid-crystalline samples were prepared by fiber extrusion using a mini-extruder. The measurements were carried out in Mark capillaries (Hilgenberg) positioned perpendicular to the incident X-ray beam. WAXS experiments were performed at a sample-detector distance of 21 cm, with the detector tilted by 14° upwards in order to study the angular range of $2\theta = 0.8° - 28°$. This allowed only the investigation of a section of the XRS pattern, therefore samples with lying and standing extruded fibres have been prepared to study the equatorial and the meridional signals in detail. Silver behenate was used as calibration standard for WAXS.

STM measurements were performed with a commercial Bruker AXS Multimode Nanoscope IV scanning probe microscope using mechanically cut PT/Ir (90:19) tips (MakTecK GmbH, Germany) For the samples adlayer of PBI solutions in 1-phenyloctane on HOPG surfaces ($c_0 = 5 \times 10^{-6}$ M) were prepared.

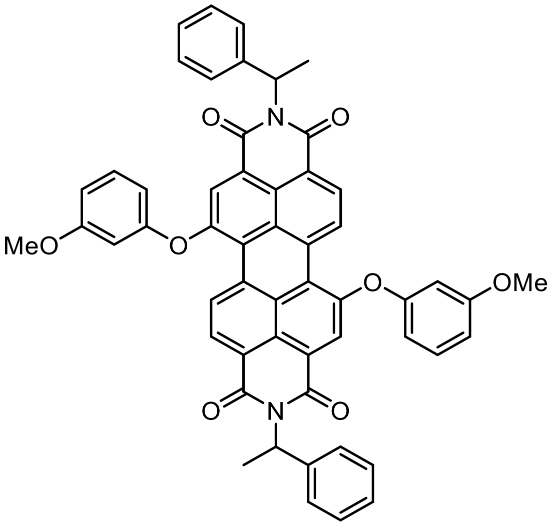
2. Synthesis and characterization

1 and **2** were prepared according to Scheme S1. Compounds **S1**[S2], **S4**,[S3] and **S5**[S4] were synthesized according to literature procedure.



Scheme S1. Synthetic route to **1** and **2**. i) K_2CO_3, NMP, 115 °C, 1 h; ii) BBr_3, CH_2Cl_2, 0 °C – rt., 3 h; iii) DCC, DPTS; DMF/CH_2Cl_2, rt – 35 °C.

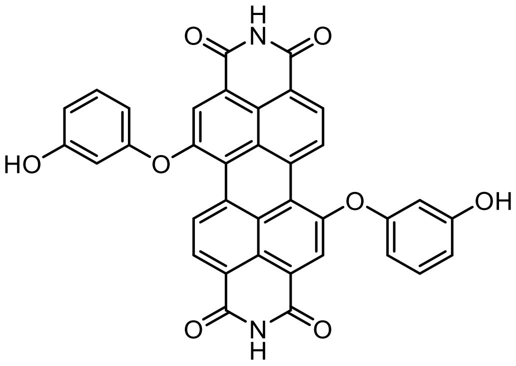
N,N’-Bis(α-methylbenzyl)-1,7-bis(3-methoxyphenoxy)perylene-3,4:9,10-bis(dicarboximide) (S2)



S1 (661 µmol, 1.0 Eq., 500 mg) and freshly distilled *N*-methyl-2-pyrrolidone (NMP, 6 mL) were stirred for 5 minutes. Afterwards, 3-methoxyphenol (1.98 mmol, 3.0 Eq., 246 mg) and potassium carbonate (1.98 mmol, 3.0 eq., 274 mg) were added and the reaction mixture was stirred at 115 °C for 1 h while the color of the solution changed to dark violet. After complete conversion, the reaction mixture was allowed to cool to room temperature. Then, the solution was slowly added into ice-cooled 1 N HCl_{aq} (50 mL) which caused the precipitation of a dark violet solid, which was filtered and purified by column chromatography (silica gel, CH_2Cl_2) to yield **S1** (396 mg, 470 µmol, 71 %).

^{1}H NMR (400 MHz, $CDCl_3$, 295 K, ppm): δ = 9.55 (d, 2H, ^3J = 8.3 Hz, Ar*H*), 8.58 (d, 2H, ^3J = 8.3 Hz, Ar*H*), 8.30 (s, 2H, Ar*H*), 7.48 (m, 4H, Ar*H*), 7.31 (m, 6H, Ar*H*), 7.23 (m, 2H, Ar*H*), 6.79 (m, 2H, Ar*H*), 6.70 (m, 4H, Ar*H*), 6.50 (q, 2H, ^3J = 7.0 Hz, C*H*), 3.81 (s, 6H, OCH_3), 1.97 (d, 6H, ^3J = 7.0 Hz, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, 295 K, ppm): δ = 163.6, 163.0, 161.6, 156.2, 155.3, 140.6, 133.5, 131.1, 130.7, 129.4, 129.0, 128.3, 127.3, 127.2, 125.4, 124.6, 124.4, 124.1, 122.6, 111.8, 110.6, 106.2, 55.7, 50.5, 16.3. **HRMS** (ESI, acetonitrile/$CHCl_3$ 1:1, pos. mode): *m*/*z* calculated for $C_{54}H_{38}N_2O_8Na$: 865.2526 $[M+Na]^+$, found: 865.2528. **m.p.** 287 °C.

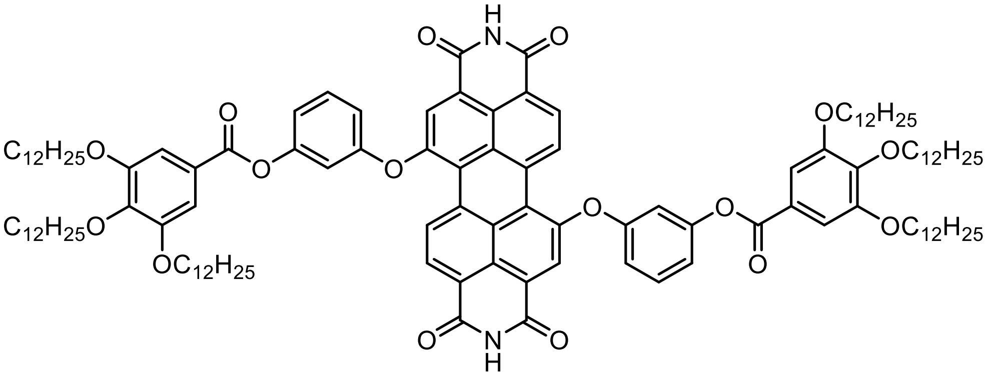
1,7-bis(3-hydroxyphenoxy)perylene-3,4:9,10-tetra-bis(dicarboximide) (S3)



A solution of **S2** (463 µmol, 1.0 Eq., 390 mg) and dry CH_2Cl_2 (40 mL) was cooled to 0 °C. A solution of BBr_3 (9.25 mmol, 20.0 Eq., 2.32 g) in CH_2Cl_2 (10 ml) was added dropwise. The mixture was stirred at 0 °C for 1 h and another 2 h at room temperature. The solvent and excess of BBr_3 were distilled under atmospheric pressure (oil bath: 55 °C). The residue was treated with MeOH-water mixture (1 : 4) at 0 °C and subsequently treated in a supersonic bath for 30 min. The solid was filtered off and washed with MeOH. 289 mg of a violet solid of **S3** were obtained. Due to the low solubility of **S3**, the material was used without further purification.

m.p. >400 °C.

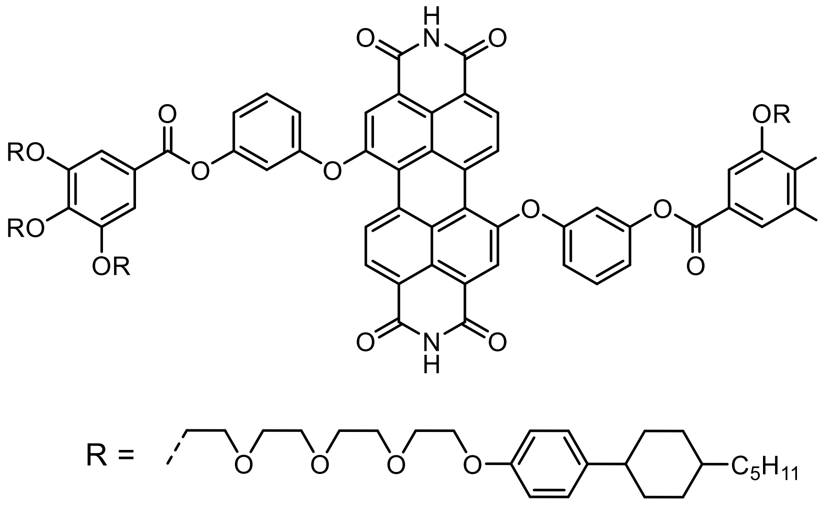
Synthesis of 1



S3 (49.5 µmol, 1.0 Eq., 30.0 mg) and 4-(dimethyl-amino)pyridinium 4-toluene-sulfonate (DPTS, 99.0 µmol, 2.0 Eq., 29.1 mg) were dissolved in dimethylformamide (0.4 mL). **S4** (148 µmol, 4.0 Eq., 134 mg) and *N*,*N*'-dicyclohexylcarbodiimide (DCC, 148 µmol, 4.0 Eq., 41.0 mg) were each added into a vial and dissolved in 0.3 mL and 0.1 mL dry CH_2Cl_2, respectively. Both solutions were subsequently added into the reaction mixture. The mixture was stirred at 35 °C for 3 d. The solvent was evaporated and the crude product was separated and purified by column chromatography (silica gel, $CHCl_3$) to yield **1** as a dark blue-violet solid (17.1 mg, 8.9 µmol, 18 %).

^{1}H NMR (600 MHz, *d*-$CDCl_3$, 323 K, ppm): $\delta = 9.58$ (d, 2H, $^3J = 8.4$ Hz, Ar*H*), 8.65 (d, 2H, $^3J = 8.4$ Hz, Ar*H*), 8.41 (m, 4H, Ar*H*), 7.49 (m, 2H, Ar*H*), 7.39 (s, 4H, Ar*H*), 7.13 (m, 4H, Ar*H*), 7.04 (m, 2H, Ar*H*), 4.05 (m, 12H, OCH_2), 1.79 (m, 12H, OCH_2CH_2), 1.48 (m, 12H, $O(CH_2)_2CH_2$), 1.38-1.24 (m, 96H, alkyl), 0.88 (m, 18H, CH_3). **^{13}C NMR** (600 MHz, *d*-$CDCl_3$, 323 K, ppm): $\delta =$ 164.7, 162.8, 162.5, 156.0, 154.9, 153.3, 153.1, 144.0, 133.9, 131.2, 130.5, 130.1, 129.4, 126.8, 125.0, 124.4, 124.3, 123.6, 122.7, 119.0, 116.6, 113.8, 109.3, 73.8, 69.8, 32.1, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.8, 14.2. **HRMS** (ESI, acetonitrile/ $CHCl_3$ 1:1, pos. mode): *m*/*z* calculated for $C_{122}H_{174}N_3O_{16}$: 1937.2889 $[M+NH_4]^+$, found: 1937.2882. **m.p.** >400 °C. **UV/Vis** ($CHCl_3$): λ_{max} (ε) = 539 nm (42000 M^{-1} cm^{-1}). **Fluorescence** ($CHCl_3$): λ_{max} = 565 nm, $\Phi_{Fl} = 0.95$.

Synthesis of 2



S3 (165 µmol, 1.0 Eq., 100 mg) and DPTS (330 µmol, 2.0 Eq., 97.0 mg) were dissolved in a mixture of DMF (1.0 mL) and CH_2Cl_2 (0.5 mL). **S5** (165 µmol, 1.0 Eq., 243 mg) and DCC (495 µmol, 3.0 Eq., 102 mg) were each added into a vial and dissolved in dry CH_2Cl_2 (0.5 mL). Both solutions were subsequently added into the reaction mixture. The mixture was stirred at 25 °C for 7 d. The solvent was evaporated and the crude product was separated and purified by column chromatography (silica gel, CH_2Cl_2/MeOH 50:1 with 1 % triethylamine) and preparative TLC ($CHCl_3$/MeOH 99:2) to yield **2** as a dark blue-violet solid (50 mg,14.9 µmol, 9%).

^{1}H NMR (600 MHz, *d*-$CDCl_3$, 295 K, ppm): δ = 9.57 (d, 2H, ^3J = 8.6 Hz, Ar*H*), 8.63 (d, 2H, ^3J = 8.6 Hz, Ar*H*), 8.55 (s, 2H, N*H*), 8.38 (s, 2H, Ar*H*), 7.48 (m, 2H,Ar*H*), 7.42 (s, 4H, Ar*H*), 7.08 (m, 18H, Ar*H*), 6.80 (m, 12H, Ar*H*), 4.25 (m, 4H,OCH_2), 4.19 (m, 8H, OCH_2), 4.07 (m, 12H, OCH_2), 3.85 (m, 8H, OCH_2), 3.80 (m, 16H, OCH_2), 3.69 (m, 24H, OCH_2), 3.65 (m, 24H, OCH_2), 2.36 (m, 6H, C*H*), 1.82 (m, 24H, CH_2), 1.27 (m, 66H, CH_2), 1.00 (m, 12H, CH_2), 0.88 (m, 18H, CH_3). **^{13}C NMR** (600 MHz, *d*-$CDCl_3$, 295 K, ppm): δ = 164.4, 162.9, 162.5, 157.0, 156.9, 155.9, 154.8, 152.7, 152.6, 143.6, 140.5, 140.4, 133.8, 131.2, 130.4, 129.9, 129.4, 127.7, 126.6, 124.9, 124.2, 124.1, 123.7, 122.5, 118.9, 116.8, 114.5, 113.7, 109.7, 72.7, 71.0, 70.9, 70.8, 70.7, 69.9, 69.7, 69.1, 67.5, 43.8, 37.5, 37.4, 34.7, 33.8, 32.4, 26.8, 22.9, 14.3. **HRMS** (ESI, acetonitrile/$CHCl_3$ 1:1, pos. mode): calculated for $C_{200}H_{266}N_2NaO_{40}$ 3358.8734 [M+Na]$^+$, found 3358.8718 and m/z calculated for $C_{200}H_{266}N_2Na_2O_{40}$ 1690.93132 [M+2Na]$^{2+}$, found 1690.93077. **m.p.** >260 °C decomposition. **UV/Vis** ($CHCl_3$): λ_{max} (ε) = 535 nm (45000 M^{-1} cm^{-1}). **Fluorescence** ($CHCl_3$): λ_{max} = 566 nm, Φ_{Fl} = 0.60.

3. NMR spectra

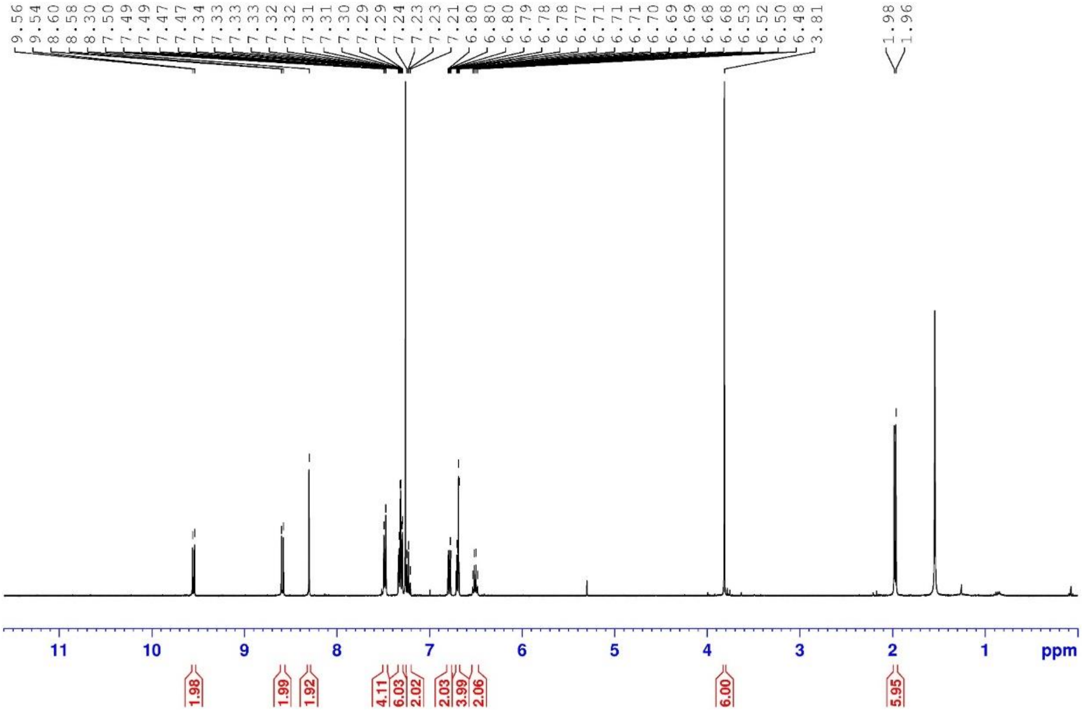


Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz, 295 K) of compound **S2**.

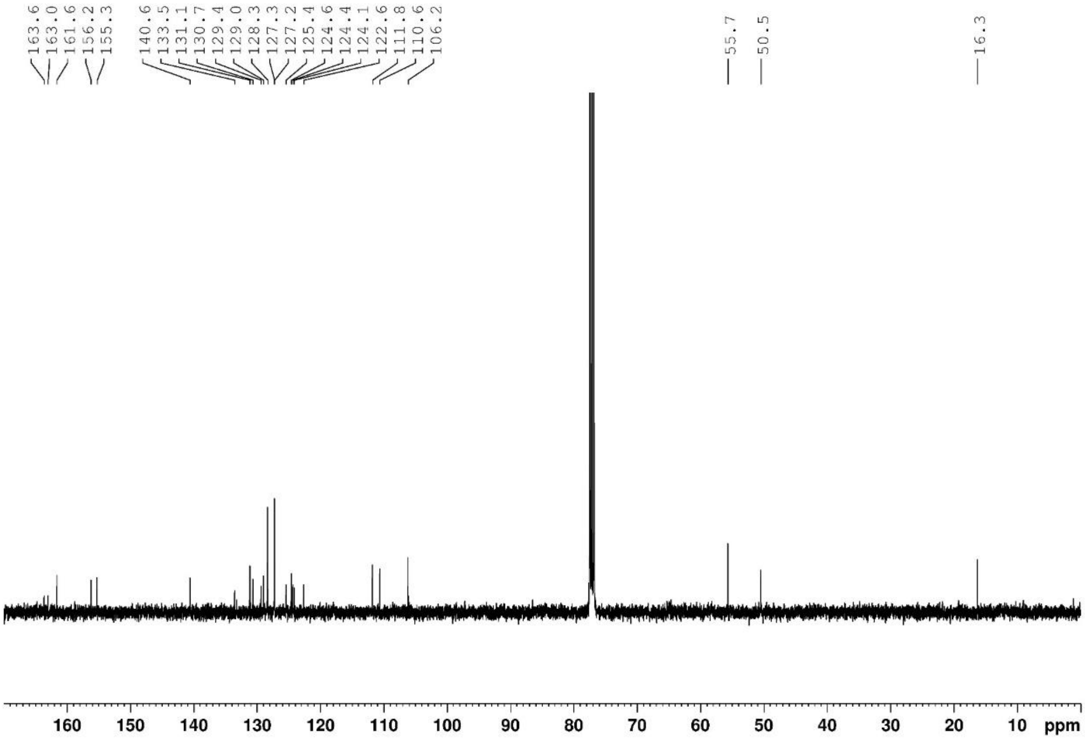


Figure S2. ^{13}C NMR ($CDCl_3$, 100 MHz, 295 K) of compound **S2**.

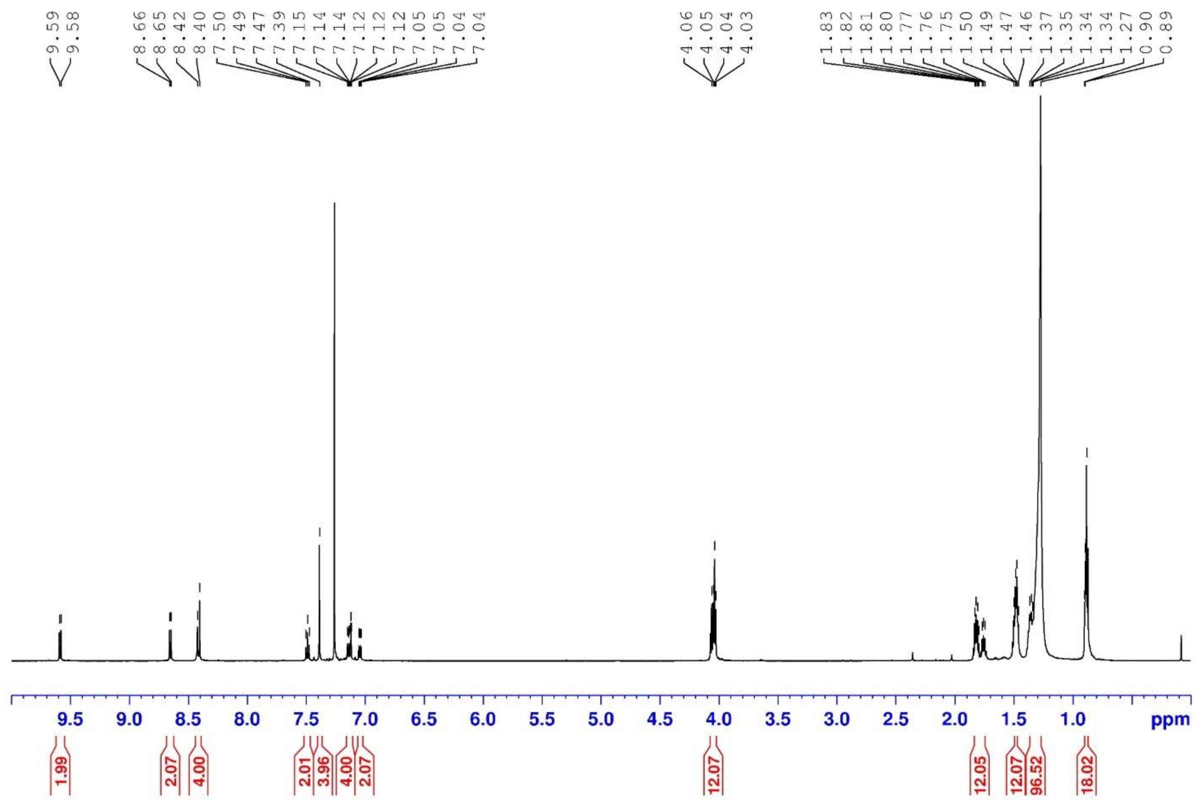


Figure S3. ^{1}H NMR ($CDCl_3$, 600 MHz, 323 K) of **1**.

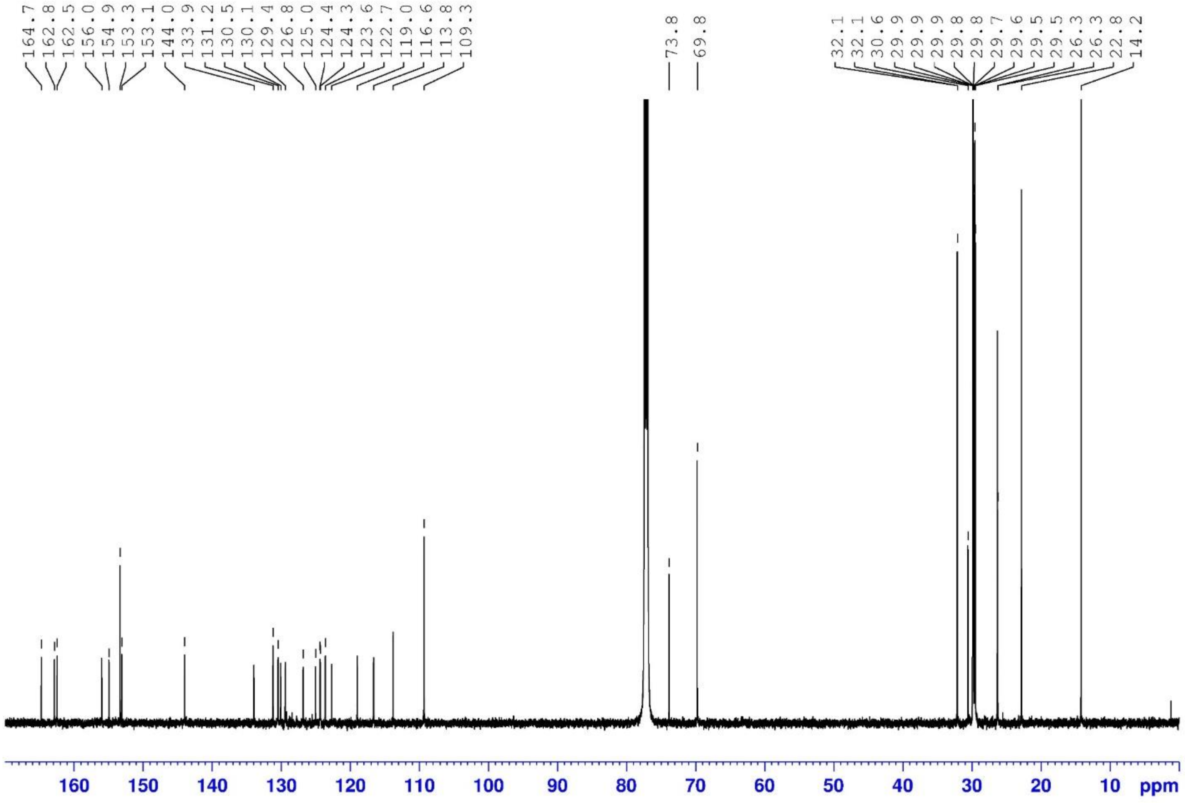


Figure S4. ^{13}C NMR ($CDCl_3$, 150 MHz, 323 K) of **1**.

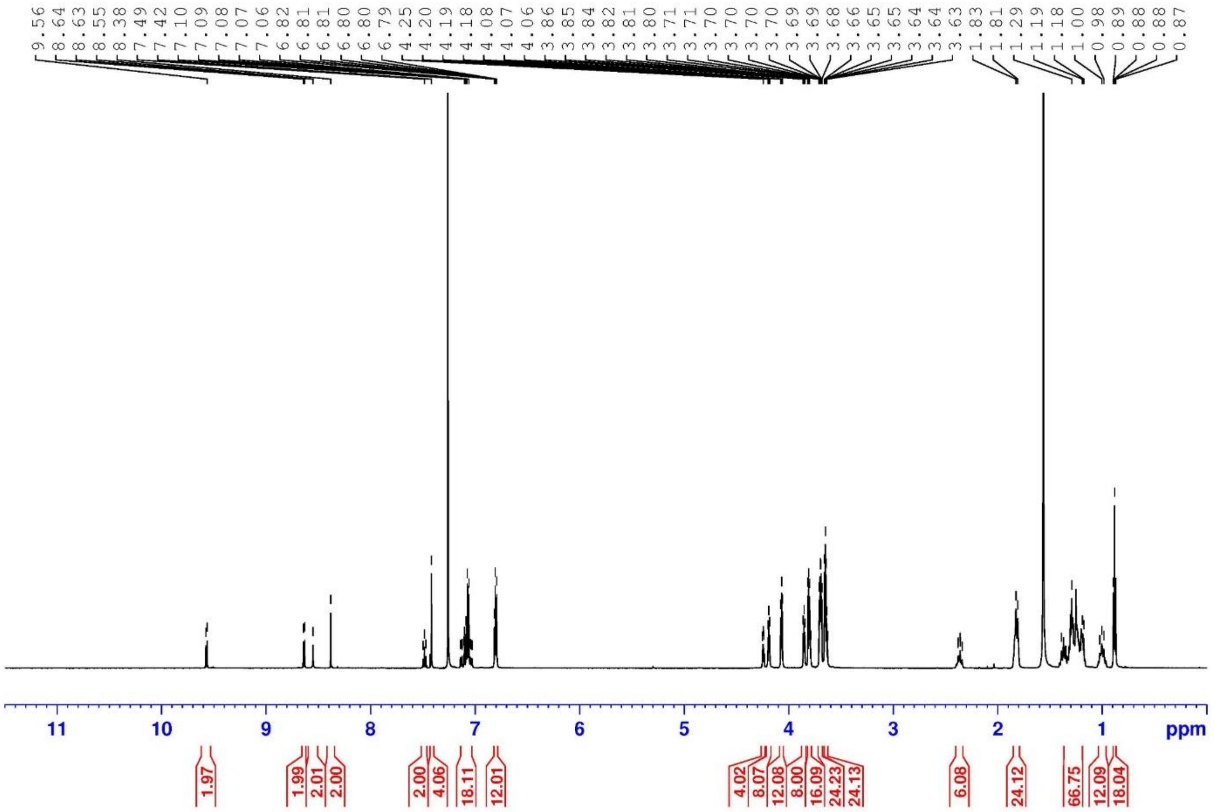


Figure S5. ^{1}H NMR (CDCl$_3$, 600 MHz, 295 K) of **2**.

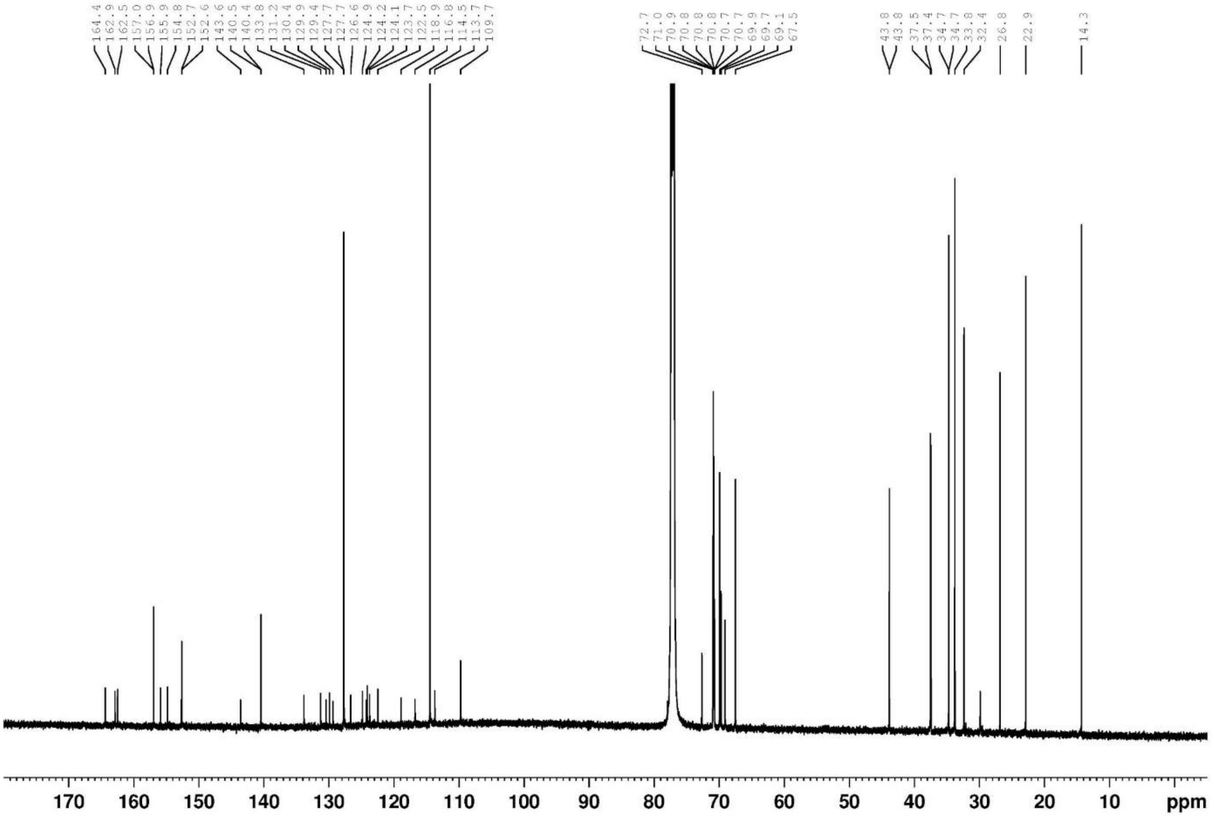


Figure S6. ^{13}C NMR (CDCl$_3$, 600 MHz, 295 K) of **2**.

4. DSC heating and cooling cycles

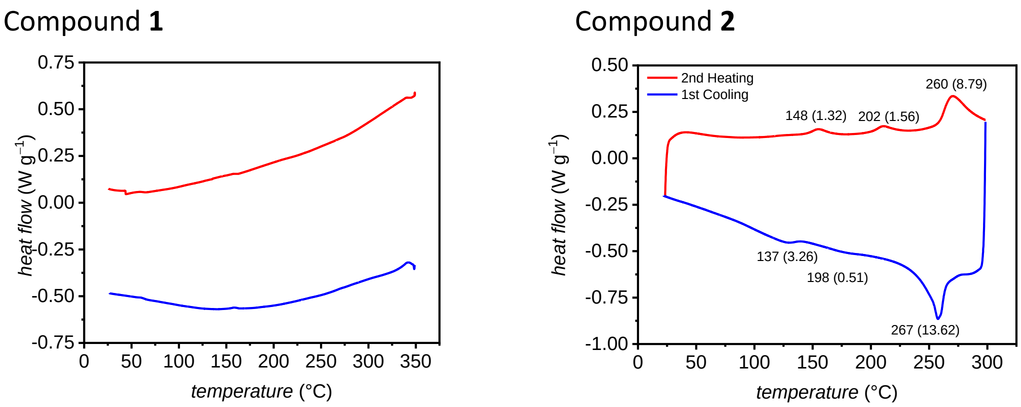


Figure S7. DSC traces of compounds **1** and **2** in the second heating (red) and first cooling (blue) cycles, respectively. The heating and cooling rates were 10 °C/min. Above 260 °C the samples slowly decompose. While compound **1** shows no transitions in the given temperature range compound **2** exhibit three transitions for which the onset temperatures are given in °C and the transition enthalpies in kJ/mol in parenthesis.

5. Polarised optical microscopy

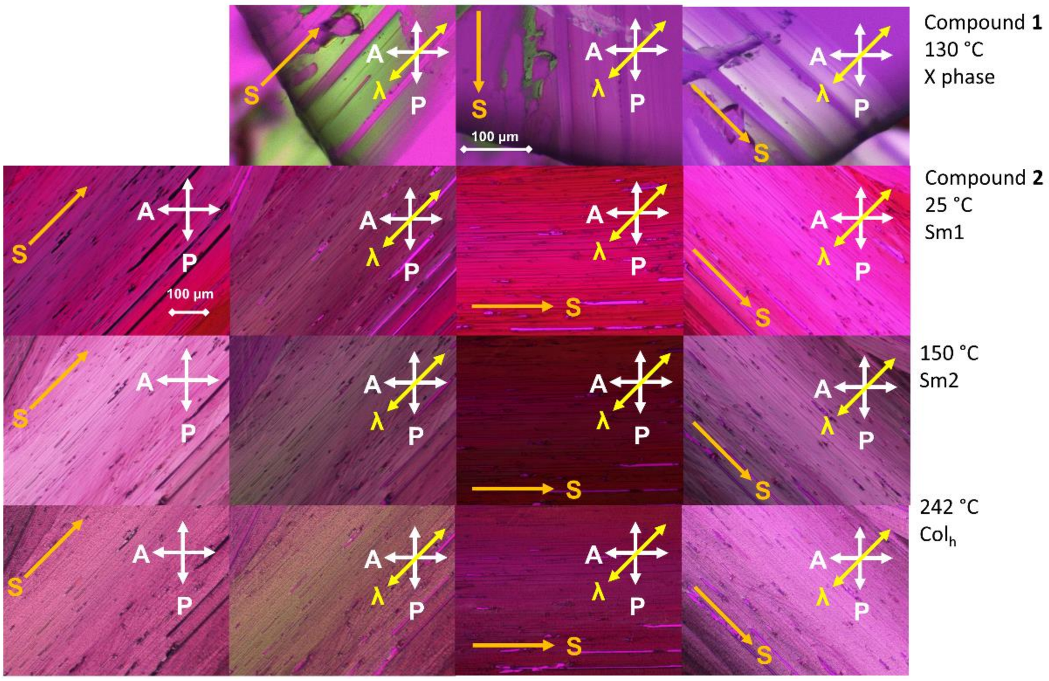


Figure S8.POM textures of shear-aligned thin LC films. S: shearing direction; A, P: position of analyser and polariser; λ: direction of the slow axis of the λ compensation plate.

6. UV-Vis- spectroscopy in solution

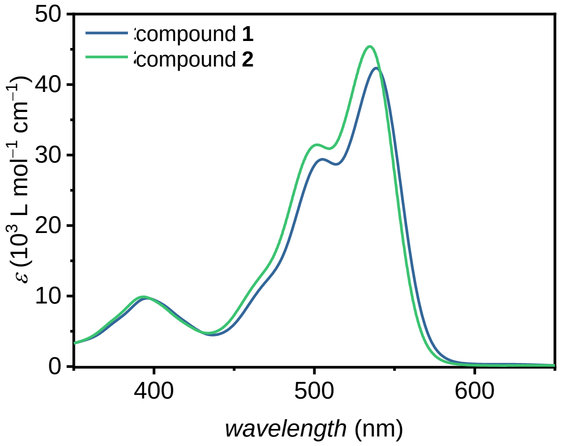


Figure S9. UV-Vis ($c_0 = 10^{-5}$ mol L^{-1}) and spectra of **1** (blue) and **2** (green) in $CHCl_3$.

7. STM image of compound 1

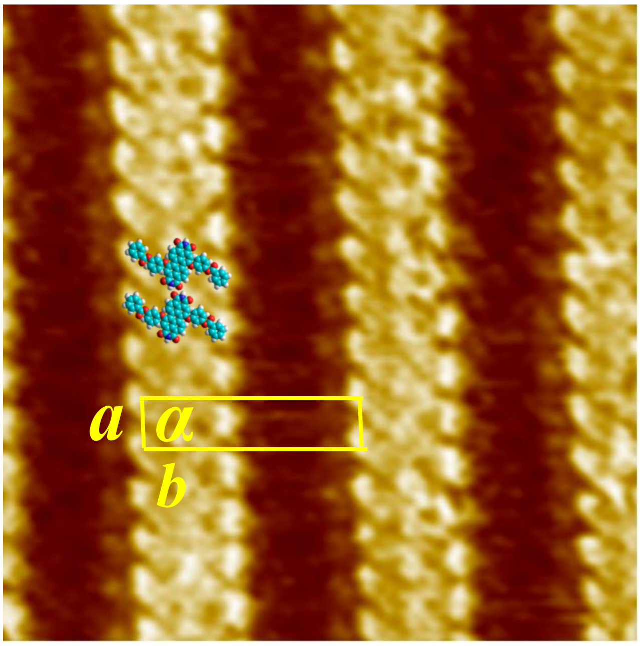


Figure S10. STM image of adlayer formed from **1** solution in 1-phenyloctane on HOPG surface, $c = 5.0 \times 10^{-5}$ M; Tunneling current: $I_t = 0.5$ pA, Bias voltage: $U_b = -500$ mV. Scan size: 14.5 nm × 14.5 nm. Two molecular structures (without showing alkyl chains) are superimposed on the STM image. The unit cell parameters are $a = 1.3 \pm 0.3$ nm; $b = 5.0 \pm 0.3$ nm; $\alpha = 91 \pm 5.0^{\circ}$.

8. X-ray results

Table S1. X-ray results.

Compound **1**						
X, 120 °C						
	h	**k**	**l**	$\mathbf{d}_{\mathbf{exp}}$ / Å	$\mathbf{d}_{\mathbf{calc}}$ / Å	**Δ** / Å
equator	-	-	-	41.5	-	-
	-	-	-	14.7	-	-
	-	-	-	10.1	-	-
	π–π (broad)			3.3		
meridian	halo			4.4	-	-
	intra lamellar (i)			3.5	-	-
Small angle signals are all very broad and cannot be attributed clearly to any periodic long range order. Based on the principle reflection at 41.5 Å, a lamellar phase should reveal reflections at 20.8 Å (002, absent), 13.9 Å (003, large deviation by 0.8 Å) and 10.4 (004, deviation by 0.3 Å). Therefore, an unknown local order has been assumed for this mesophases.						
Compound **2**						
Sm1, 90 °C	c = 65.4 Å, a = 27.6 Å b = 13.6 Å, Z = 5, ρ_{xrs} = 1.13 g/cm^3 ρ_{exp} = 1.12 g/cm^3 #					
	h	**k**	**l**	$\mathbf{d}_{\mathbf{exp}}$ / Å	$\mathbf{d}_{\mathbf{calc}}$ / Å	**Δ** / Å
equator	0	0	1	65.1	65.4	0.3
	0	0	2	32.9	32.7	0.2
	0	0	3	22.0	21.8	0.2
	0	0	4	16.5	16.4	0.1
	0	0	5	13.2	13.1	0.1
	0	0	6	11.0	10.9	0.1
	0	0	7	9.5	9.3	0.1
	0	0	8	8.2	8.2	0.1
	π–π broad reflection			3.4	-	-
meridian	halo			4.7	-	-
	halo			4.3	-	-

	intra lamellar (i)			3.5	-	-
	intra lamellar (diffuse reflections on the layer line (ii))			13.8	-	-
Sm2, 165 °C			c = 56.9 Å, a = 27.5 Å b = 16.5 Å, Z = 5, ρ_{xrs} = 1.07 g/cm^3; ρ_{exp} = 1.07 g/cm$^{3\,\#}$			
	h	**k**	**l**	$\mathbf{d_{exp}}$ / Å	$\mathbf{d_{calc}}$ / Å	**Δ** / Å
equator	0	0	1	56.6	56.9	0.27
	0	0	2	28.7	28.4	0.25
	0	0	3	19.2	19.0	0.26
	0	0	4	14.3	14.2	0.04
	0	0	5	11.5	11.4	0.16
	0	0	6	9.6	9.5	0.09
	π–π (broad)			3.4	-	-
meridian	halo			4.8	-	-
	halo			4.1	-	-
	intra lamellar (i)			3.5	-	-
	layer line (diffuse signals (ii))			13.7(4)		
Col$_h$, 230 °C			a = 55.6 Å, h = 14.1 Å, Z = 7, ρ_{xrs} = 1.03 g/cm^3, ρ_{exp} = 1.03 g/cm$^{3\,\#}$			
	h	**k**	**l**	$\mathbf{d_{exp}}$ / Å	$\mathbf{d_{calc}}$ / Å	**Δ** / Å
equator	1	0	0	48.4	48.2	0.27
	1	1	0	27.7	27.8	0.14
	2	0	0	23.9	24.1	0.13
	2	1	0	18.0	18.2	0.19
	3	0	0	15.9	16.1	0.11
	3	1	0	13.3	13.4	0.04
	π–π (broad)			3.4	-	-

meridian	halo	5.1	-	-
	halo	4.2	-	-
	intra columnar (i)	3.5	-	-
The diffuse and very weak signals (ii) could not be evaluated.				

[#] Experimental densities have determined by the buoyancy method, which is described in section 9.

9. Experimental determination of the density at 24 °C and extrapolation to 90 °C

Density measurements were carried out by the buoyancy method at 24 °C in mixtures of aqueous sodium chloride solution (20 wt% and 25 wt%). Sodium chloride (*pro analysi*) was dried under reduced pressure (1×10^{-3} mbar). The solutions were degassed by ultrasonication prior to the measurement. **2** was heated to 230 °C under reduced pressure and extruded in order to minimize the inclusion of air bubbles within the sample. The fiber was cut into several pieces of varying size (0.1-0.6 mg). The samples were put in a sealed vial containing aqueous sodium chloride solution (20 wt%) at 24 °C and aqueous sodium chloride (25 wt%) solution was added in small portions. The mixture was allowed to equilibrate between additions until the sample started floating in the center of the vial. The necessary weight percentage of sodium chloride was determined and the density was calculated according to literature.[S5] The density of **2** at 24 °C was determined to be $\rho = 1.156 \pm 0.001$ g cm^{-3}. Please note that for materials with much lower clearing temperatures and high thermal stability in the isotropic liquid, the samples can be prepared by melting them under reduced pressure to eliminate the inclusion of air bubbles.[S6] However, as **2** starts decomposing at very high temperatures, the probability of air inclusion can only be limited but not eliminated. Therefore, this density value displays a lower limit.

The molecular volume V_{mol} can be calculated using the following equation:

$$V_{\mathrm{mol}} = \frac{M}{\rho * N_{\mathrm{A}}}, \tag{S1}$$

with M being the molecular mass and N_{A} Avogadro's constant.

In order to estimate the density at an elevated temperature it is convenient to calculate the molecular volume as follows:

$$V_{\mathrm{mol}} = V_{\mathrm{ar}} + V_{\mathrm{aliph}} + V_{OEG}, \tag{S2}$$

with V_{ar}, V_{aliph} and V_{OEG} corresponding to the molecular volume of the aromatic and aliphatic as well as the oligoethyleneoxy parts, respectively. As discussed previously, the change of V_{ar} upon increasing temperature is negligible.[S7] Thus for the estimation of V_{mol} at higher temperatures the aromatic volume can be kept constant.

Calculating the change in molecular volume of the alkyl and oligoethyleneoxy part according to procedures reported in literature,[S8,S9] one obtains values that are summarized in Table S2.

Table S2. Summary of the values corresponding to the temperature-dependent density calculation for **2**.

T (°C)	V_{ar} (Å^3)	V_{aliph} (Å^3)	V_{OEG} (Å^3)	V_{mol} (Å^3)	ρ (g cm^{-3})
23	1921.37	1731.47	1143.71	4796.555	1.156
90	1921.37[a]	1833.76	1203.46	4958.59	1.118

[a] Assuming a negligible gradient for the expansion of V_{ar} as described above.

10. Modelling

General

The Sm1 phase was modelled with the program *BIOVIA Materials Studio 2017 R2*. The modelling is performed in the P1 unit cell without restrictions by symmetry elements. After the set-up of the unit cells the geometry optimization was performed using the module “Forcite Plus (2017R2)” with the force field “COMPASSII” and the Ewald summation method. An annealing step has been introduced, before a final geometry optimisation gave large negative non-covalent interactions (electrostatic and van der Waals interactions).

Sm1 phase

In a preliminary study, ten sheet-like conformers have been added to the unit cell of 160 Å length (c), 27.6 Å (a) breath and 13.6 Å depth (b) to form two layers with five mesogens each. Two perylene bisimides were hydrogen bonded along the *a* axis to guarantee a continuous periodical H-bonding strand. A second strand has been added in the pi-distance and a fifth single mesogen was needed to full-fill the density requirement. This assembly have been stepwise reduced to the experimental layer thickness of 2 * 65.4 Å. The resulting structure visualised a conformational change of the perylenes to a chair-like conformer. On the basis of these findings, the chair conformer (see Figure 5) has been generated first and a unit cell of 130.8 Å length (c), 27.6 Å (a) width and 13.6 Å depth (b) has been constructed. The H-bondend perylene strands were established along *a*. The second strand have been positioned with a distance of 3.4 Å on top, shifted by 3.5 Å along the perylene long axis and 3.5 Å along the perylene short axis to avoid steric interactions of the peripheral branches. Similarily, the fifth mesogen has been positioned. The described geometry optimisation resulted in strong negative non-bonding interactions (van der Waals and electrostatic interactions), thus rationalising the stability of the assembly.

Subsequently, the Powder X-ray diffraction of this structure have been calculated with the module “Reflex” of the Materials Studio program suite. The relative intensities I_{00l} in % with l = 1,2,3,4,5,6,7 have been determined to be 100; 4.76; 6.97; 0.43; 0.88; 0.31; 0.046. These intensities are similar to the experimental Intensity profile and thus, substantiate the similarity between the experimental and the modelled structure.

11. Supporting references

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