

Supporting Information

Liquid crystalline self-assembly of mixtures of rod- and wedge-shaped MIDA boronates

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Table of Contents

1.	General Methods	S2
2.	Syntheses	S3
3.	DSC Traces	S8
4.	POM Textures of mixtures	S14
5.	X-ray data	S15
6.	References	S20

1. General Methods

Nuclear magnetic resonance spectroscopy:

¹H-NMR spectra were recorded at frequencies of 400/ 500/ 700 MHz, broadband decoupled ¹³C-NMR spectra were recorded at frequencies of 100/ 125/ 176 MHz on Bruker AVANCE 300/ ASCEND 400/ AVANCE 500/ AVANCE 700 spectrometers, respectively. Chemical shifts were given in parts per million (ppm) and referenced to the peak of the deuterated solvents if not indicated otherwise. Multiplicities were given in Hz and abbreviated as following: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m).

Differential Scanning Calorimetry (DSC):

DSC measurements were performed on a DSC822^e by Mettler Toledo in standardized 40 μ L aluminum crucibles and evaluated with the software STAR^e 14.0. Phase transition temperatures are given as onsets of the corresponding peaks.

Polarizing Optical Microscopy (POM):

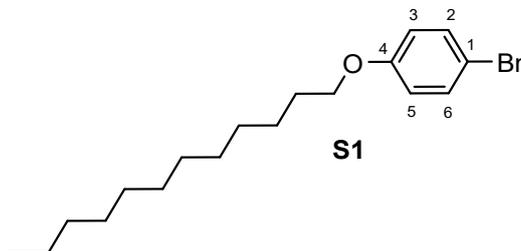
A polarizing optical microscope Olympus BX50 equipped with a variable temperature sample holder LTS350 (control unit: TP39 and LNP, $\Delta T = \pm 1$ K) by Linkam Scientific was used to investigate the mesomorphic properties of our compounds. Micrographs were taken with a Zeiss Axiocam 105 color camera module and the software ZEN core. The samples were investigated on regular glass slides and in polyimide coated cells.

Wide (WAXS) and small angle (SAXS) Xray diffraction:

For Xray diffraction studies, the samples were sealed in glass capillaries supplied by Hilgenberg GmbH (external diameter of 0.7 mm, wall thickness 0.01 mm). Two dimensional Xray diffraction (2D-WAXS and 2D-SAXS) studies were carried out on a Bruker AXS Nanostar C equipped with a ceramic tube generator (CuK α radiation, $\lambda = 1.5405$ Å, 1500 W) and a Bruker Vantec 500 detector. The diffractograms were processed using SAXS software and calibrated to the diffraction pattern of silver behenate at 25 °C.

2. Syntheses

1-Dodecyloxy-4-bromobenzene (S1)



4-Bromophenol (5.00 g, 27.5 mmol, 1 eq.), K_2CO_3 (10 g, 72.3 mmol, 2.5 eq.) and dodecylbomide (6.60 mL, 27.5 mmol, 0.95 eq.) were dissolved in abs. THF (50 mL) and stirred for 16 h at 80 °C. The reaction mixture was poured in an aqueous NaOH solution (200 mL, 1 M) and extracted with pentane (2×100 mL). The combined organic phases were washed with water (100 mL), brine (50 mL) and dried ($MgSO_4$). After evaporating the solvent, the desired product **S1** was obtained as a colorless solid in quant. yields without further purifications.

1H -NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.8 Hz, 3H, CH_3), 1.22–1.49 (m, 18H, CH_2), 1.73–1.82 (m, 2H, OCH_2CH_2), 3.91 (t, J = 6.6 Hz, 2H, OCH_2), 6.75–6.80 (m, 2H, 3-H, 5-H), 7.34–7.39 (m, 2H, 2-H, 6-H) ppm.; ^{13}C -NMR (101 MHz, $CDCl_3$): δ = 14.3 (CH_3), 22.8, 26.1, 29.3, 29.50, 29.53, 29.72, 29.74, 29.8, 29.8, 32.1 (CH_2), 68.4 (OCH_2), 112.7 (C-1), 116.4 (C-3, C-5), 132.3 (C-2, C-6), 158.4 (C-4) ppm. The spectroscopic data are in good agreement with those reported in ref¹.

1,2-Bis(dodecyloxy)-5-bromobenzene (S2)

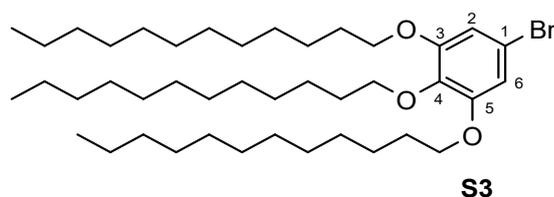


To a degassed solution of 4-bromocatechol (0.80 g, 4.27 mmol) dissolved in DMF (35 mL), K_2CO_3 (3.50 g, 25.6 mmol) and dodecylbomide (2.26 mL, 9.40 mmol) were added and the

suspension stirred over night at 80 °C. After completion the solvent was evaporated, the residue was taken up in Et₂O (100 mL) and washed with water (2 × 150 mL). The organic phase was dried (MgSO₄), the solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel using hexanes as eluent. The desired product **S2** was obtained as colorless solid in 98 % yield

¹H-NMR (CDCl₃, 300 MHz) δ = 0.88 (m, 6 H, CH₃), 1.23-1.51 (m, 36 H, CH₂), 1.74-1.86 (m, 4 H, OCH₂CH₂), 3.90-4.10 (m, 4 H, OCH₂), 6.71-6.76 (m, 1 H, 6-H), 6.96-7.00 (m, 2 H, 2-H, 3-H) ppm; ¹³C NMR (CDCl₃, 75 MHz) δ = 14.3 (CH₃), 22.8, 26.1, 29.3, 29.4, 29.5, 29.6, 29.77, 29.81, 29.85, 32.1 (CH₂), 69.5, 69.7 (OCH₂), 112.9 (C-2), 115.3 (C-6), 117.1, 123.6 (C-1, C-3), 148.5, 150.2 (C-4, C-5) ppm; The spectroscopic data are in good agreement with those reported in ref¹.

1,2,3-Tris(dodecyloxy)-5-bromobenzene (**S3**)



1,2,3-Trihydroxy-5-bromobenzene (1.40 g, 6.66 mmol) and K₂CO₃ (6.90 g, 50.0 mmol) were dissolved in DMF (30 mL) and the solution was degassed by flushing nitrogen through it for 30 min. After the addition of the respective 1-bromoalkane (4.80 mL, 5.16 g, 23.3 mmol) the solution was stirred for 14 h at 80 °C. The reaction mixture was poured into water (200 mL) and the aqueous phase was extracted with Et₂O (100 mL). After the organic phase was washed with water (2 × 150 mL) and dried (MgSO₄) the solvent was removed and the crude product was purified by flash chromatography on silica gel using mixtures of hexanes and ethyl acetate (60 : 1) as eluents.

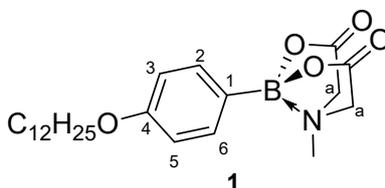
¹H-NMR (400 MHz, CDCl₃): δ = 0.88 (t, *J* = 7.1 Hz, 9H, CH₃), 1.21–1.40 (m, 36H, CH₂), 1.40–1.50 (m, 6H, OCH₂CH₂CH₂), 1.68–1.84 (m, 6H, OCH₂CH₂), 3.89–3.96 (m, 6H, OCH₂), 6.67 (s, 2H, 2-H, 6-H) ppm. ¹³C-NMR (101 MHz, CDCl₃): δ = 14.1, 14.2 (CH₃), 22.83, 22.84, 26.18, 26.24, 29.4, 29.49, 29.51, 29.54, 29.73, 29.77, 29.82, 29.9, 30.4, 32.1, 32.1 (CH₂), 69.5 (*m*-OCH₂), 73.6 (*p*-OCH₂), 110.3 (C-6, C-2), 115.7 (C-1), 137.6 (C-4), 154.0 (C-3, C-5) ppm. The spectroscopic data are in good agreement with those reported in ref¹.

General procedure for the syntheses of MIDA boronates (1-3) (GP1)

The respective alkoxy-bromo-benzene (2.5 mmol) was dissolved in abs THF (20 mL) cooled to -78 °C. After addition of *n*BuLi (4 mmol) the solution was stirred for 30 min at -78 °C. Triisopropyl borate (4.25 mmol) was added and the reaction was allowed to slowly warm to room temperature over 2 h. Then, a solution of MIDA (5 mmol) in abs. DMSO (10 mL) was added and the mixture was refluxed for another 2 h. After completion the reaction mixture was poured in to water (150 mL) and Et₂O (50 mL) was added.

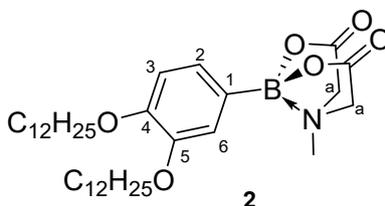
Purification Method A: Between the aqueous and the organic phases, a colourless solid precipitated. This was collected via a Büchner funnel, washed with Et₂O (50 mL) and water (100 mL) and dried in high vacuum yielding the pure product as a colourless solid.

4-Dodecyloxyphenyl-MIDA boronate (1)



Synthesis according to GP1, purification method A, colourless solid in 45 % yield; $R_f = 0.1$ (hexanes / ethyl acetate 1 : 1); ¹H-NMR (500 MHz, CDCl₃) $\delta = 0.84\text{--}0.93$ (m, 3H, CH₃), 1.22–1.50 (m, 18H, CH₂), 1.72–1.82 (m, 2H, OCH₂CH₂), 2.52 (s, 3H, NCH₃), 3.76 (d, $J = 16.6$ Hz, 2H, a-H), 3.91–3.98 (m, 2H, OCH₂), 4.04 (d, $J = 16.6$ Hz, 2H, a-H), 6.89 (d, $J_{3-2} = 8.5$ Hz, 2H, 3-H, 5-H), 7.41 (d, $J_{2-3} = 8.5$ Hz, 2H, 2-H, 6-H) ppm; ¹³C-NMR (126 MHz, CDCl₃) $\delta = 14.1$ (CH₃), 22.7, 26.1, 29.27, 29.35, 29.43, 29.59, 29.62, 29.64, 29.67, 31.9 (CH₂), 47.5 (NCH₃), 61.7 (C-a), 67.9 (OCH₂), 114.5 (C-3, C-5), 133.7 (C-2, C-6), 160.6 (C-4), 168.0 (O=C) ppm. The spectroscopic data are in good agreement with those reported in ref¹.

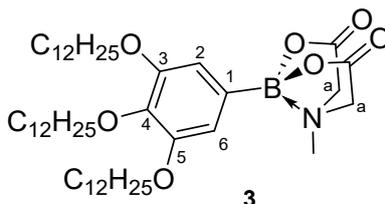
3,4-Bis(tetradecyloxy)phenyl-MIDA boronate (2)



Synthesis according to GP1, purification method A, colourless solid in 20 % yield; $R_f = 0.1$ (hexanes / ethyl acetate 1 : 1); ¹H-NMR (500 MHz, CDCl₃) $\delta = 0.82\text{--}0.95$ (m, 6H, CH₃), 1.18–1.54 (m, 44H, CH₂), 1.72–1.88 (m, 4H, OCH₂CH₂), 2.54 (s, 3H, NCH₃), 3.75 (d, $J = 16.4$ Hz,

2H, a-H), 3.92 (d, $J = 16.4$ Hz, 2H, a-H), 3.95–4.06 (m, 4H, OCH₂), 6.85–6.95 (m, 1H, 3-H), 6.95–7.07 (m, 2H, 2-H, 6-H) ppm; ¹³C-NMR (126 MHz, CDCl₃) $\delta = 14.1$ (CH₃), 22.7, 26.1, 29.28, 29.38, 29.46, 29.51, 29.65, 29.67, 29.72, 29.74, 31.9 (CH₂), 47.4 (NCH₃), 61.7 (C-a), 68.9 (*m*-OCH₂), 69.7 (*p*-OCH₂), 113.5 (C-3), 117.8 (C-6), 125.5 (C-2), 149.1 (C-5), 150.9 (C-4), 167.4 (O=C) ppm; The spectroscopic data are in good agreement with those reported in ref¹.

3,4,5-Tris(hexadecyloxy)phenyl-MIDA boronate (3)



Synthesis according to GP1, purification method B, colourless solid in 59 % yield, $R_f = 0.1$ (hexanes / ethyl acetate 1 : 1); ¹H-NMR (500 MHz, CDCl₃) $\delta = 0.82$ –0.94 (m, 9H, CH₃), 1.18–1.51 (m, 54H, CH₂), 1.68–1.83 (m, 6H, OCH₂CH₂), 2.56 (s, 3H, NCH₃), 3.72–3.79 (m, 2H, a-H), 3.89–3.99 (m, 8H, a-H, OCH₂), 6.65 (s, 2H, 2-H, 6-H) ppm; ¹³C-NMR (126 MHz, CDCl₃) $\delta = 14.1$ (CH₃), 22.7, 26.2, 29.38, 29.40, 29.49, 29.56, 29.63, 29.67, 29.68, 29.71, 29.73, 29.75, 29.77, 30.4, 31.9 (CH₂), 47.4 (NCH₃), 61.7 (C-a), 69.4 (*m*-OCH₂), 73.4 (*p*-OCH₂), 110.4 (C-2, C-6), 140.0 (C-4), 153.5 (C-3, C-5), 167.5 (O=C) ppm. The spectroscopic data are in good agreement with those reported in ref¹.

General procedure for the preparation of the mixtures 1 / 2 or 1 / 3

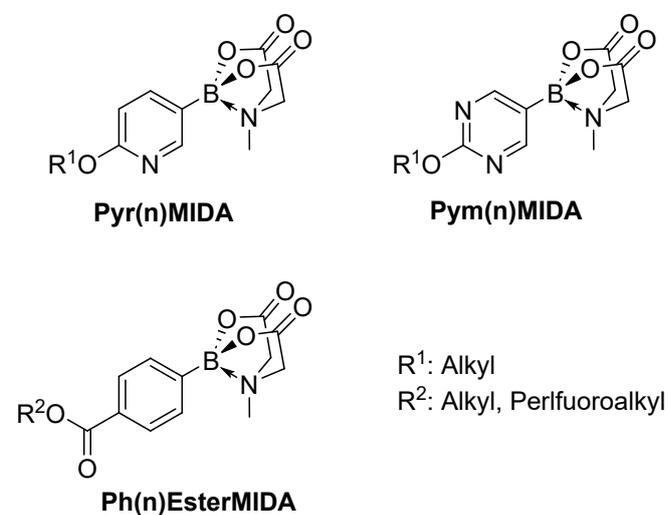
First, stock solutions of the neat MIDA boronates were prepared by dissolving those in THF according to Table S1. To prepare the mixtures, a certain amount of the respective stock solutions (depending on the molar fraction; an example is shown in Table S2 for **1 / 2 [0.25]**) was combined and stirred for 15 min. The solvent was removed under reduced pressure and the obtained mixtures were dried under high vacuum to remove any solvent residues.

Table S1. Preparation of stock solutions of **1**, **2** and **3**.

	M [g/mol]	m [mg]	n [mmol]	V _{THF} [ml] ^b	c [mol/l]
1	417.353	125.21	0.3	15	0.02
2	601.676	120.34	0.2	10	0.02
3	785.999	157.20	0.2	10	0.02

^b filled up to this volume.**Table S2.** Preparation of the mixture **1 / 2 [0.25]** with the stock solutions of Table S1.

1 / 2 [0.25]	1	2
M [g/mol]	417.353	601.676
c [mol/l]	0.02	0.02
X ₁ = [0.25]	n (1) = 0.025 mmol	n (2) = 0.075 mmol
V _{stock} [ml]	1.25	3.75
m [mg]	10	45

Structure overview of Pyr(n)MIDA, Pym(n)MIDA, Ph(n)EsterMIDA^{2,3}**Figure S1.** Pyr(n)MIDA, Pym(n)MIDA, Ph(n)EsterMIDA.^{2,3}

2. DSC traces

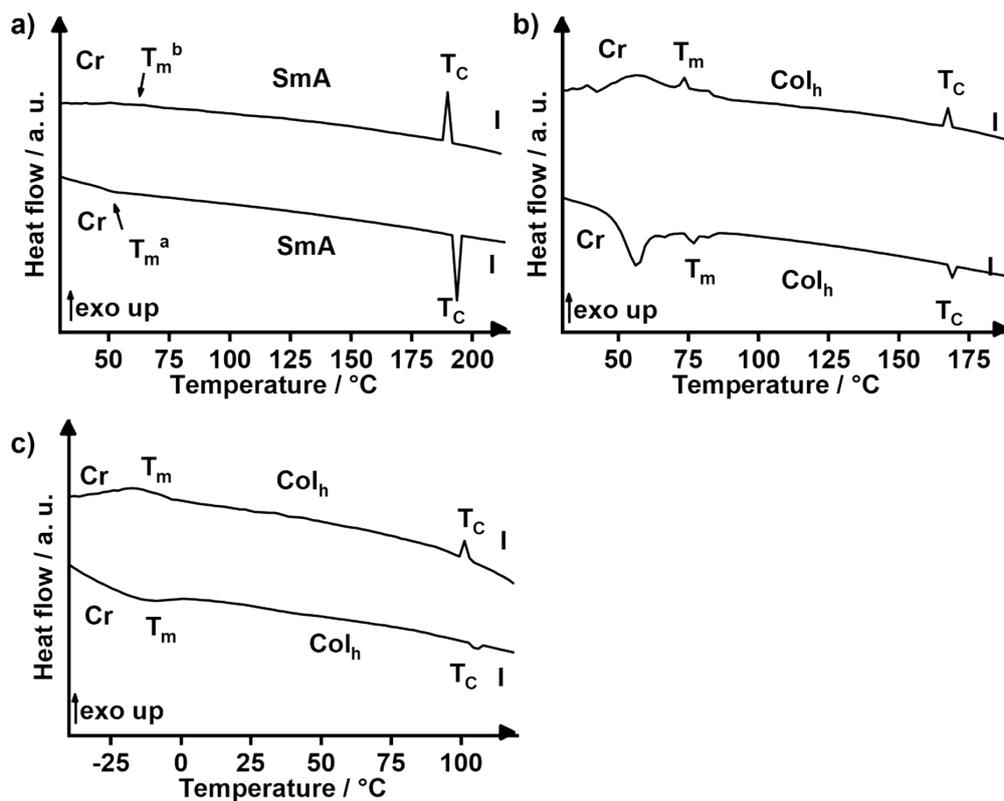


Figure S2. DSC traces of the neat MIDA boronates a) **1**; b) **2** and c) **3**; 2nd heating (bottom), 2nd cooling (top), heating / cooling rate 5 K·min⁻¹, ^b melting points were determined via POM. The data were taken from ref.¹ for comparison.

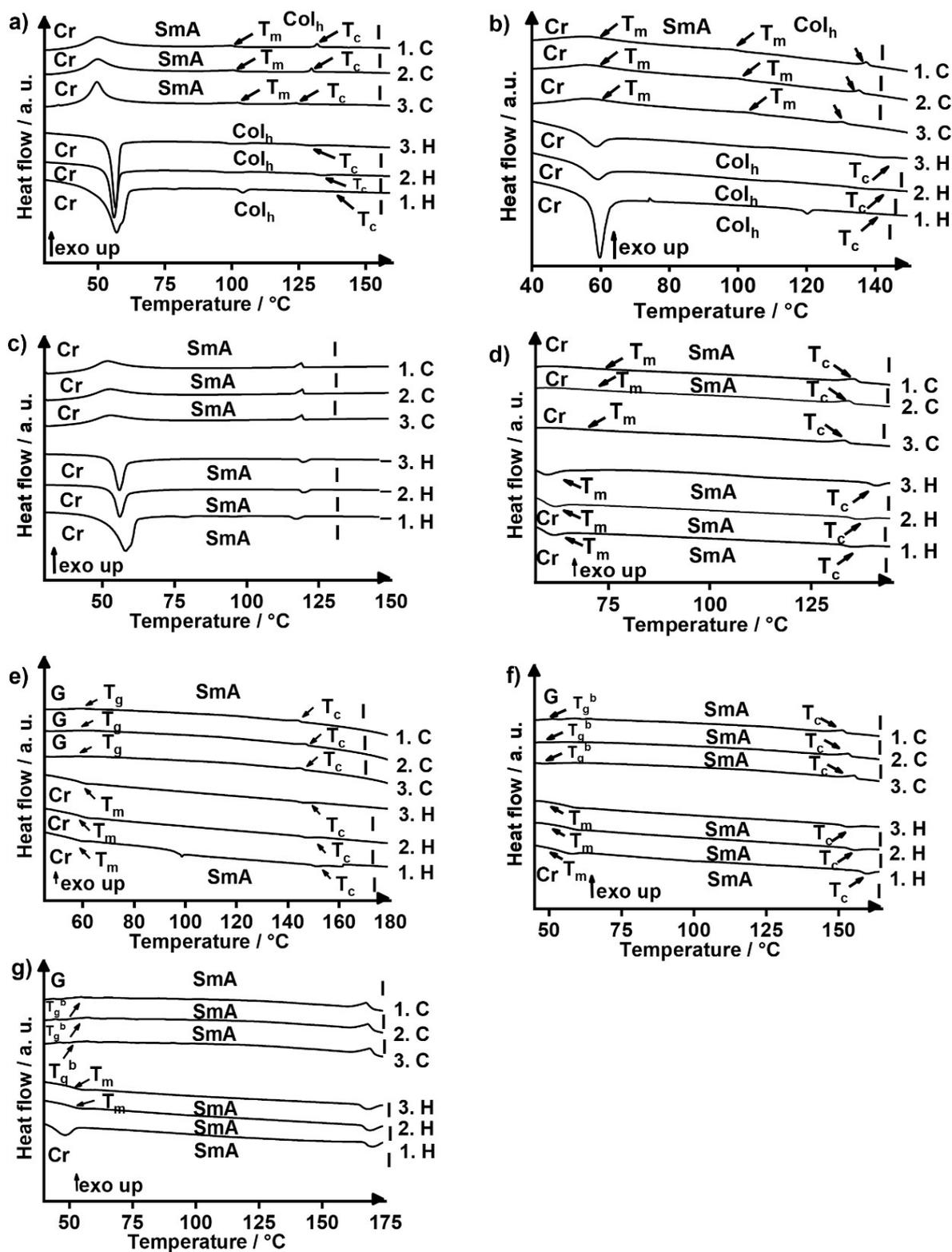


Figure S3. DSC traces of the mixture 1 / 2 in the ratios a) [0.15], b) [0.2], c) [0.25], d) [0.40], e) [0.5], f) [0.6], g) [0.8]; All heating and cooling cycles; heating / cooling rate 10 K min⁻¹).
^b melting points were determined via POM.

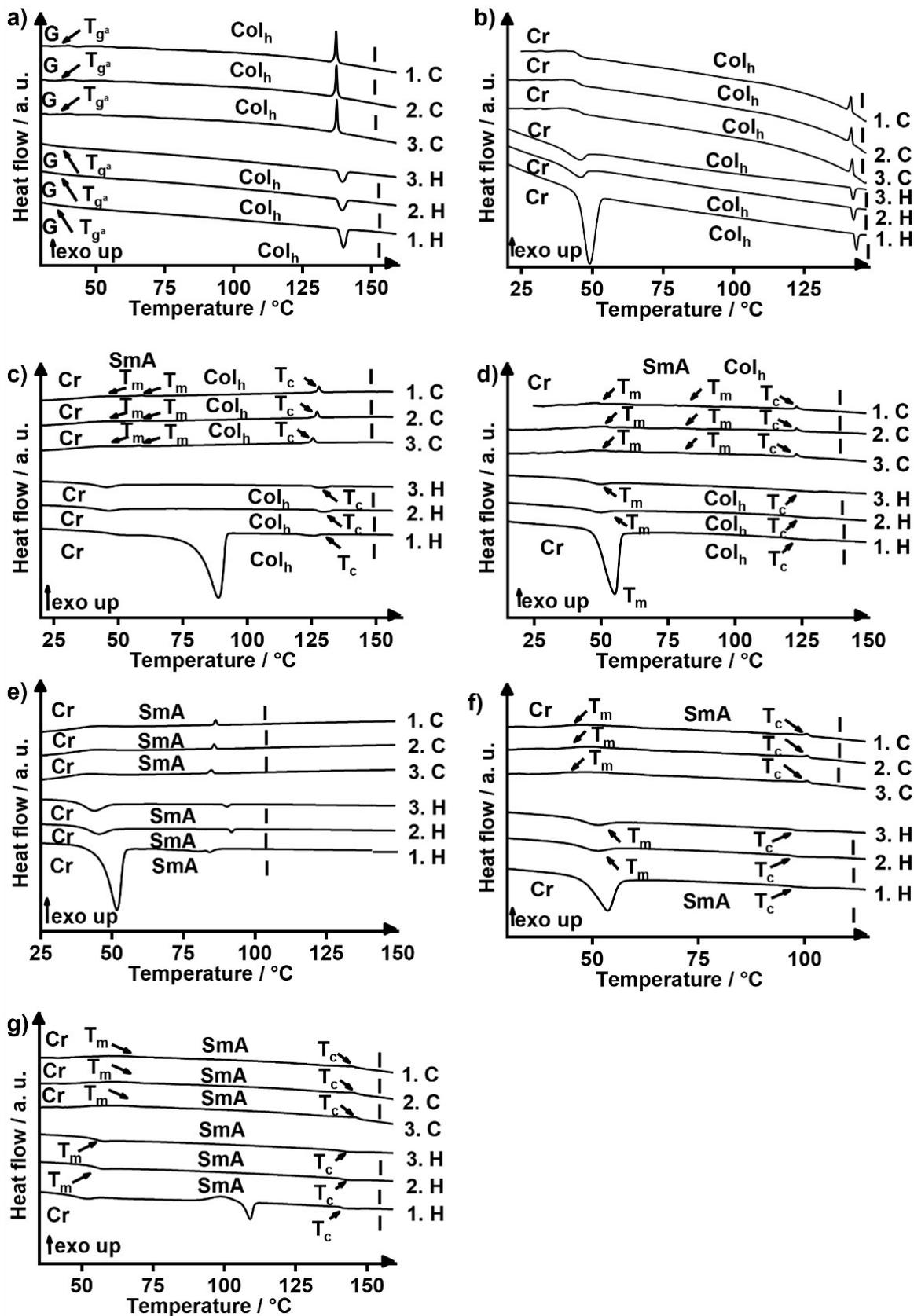


Figure S4. DSC traces of the mixture 1 / 3 in the ratios a) [0.2], b) [0.4], c) [0.45], d) [0.5], e) [0.55], f) [0.6], g) [0.8]. All heating and cooling cycles; heating / cooling rate 10 K min⁻¹.
^a melting points were determined via POM.

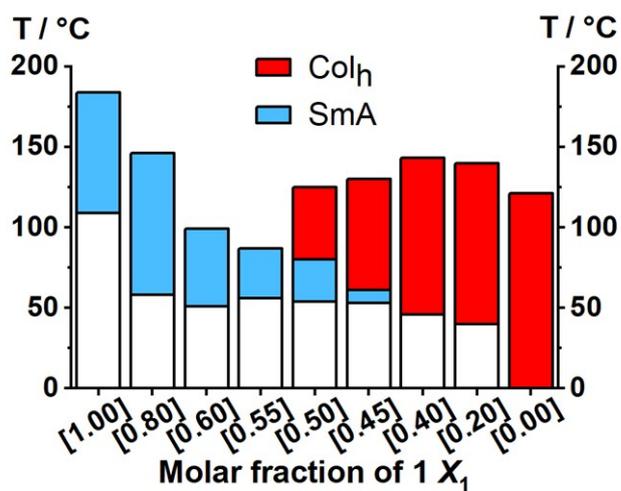
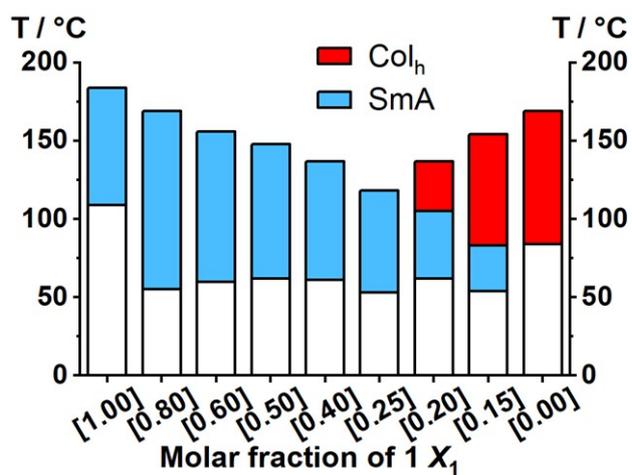


Figure S5. Partial phase diagram of binary systems 1 / 2 [X₁] (top) and 1 / 3 [X₁] (bottom) determined by DSC (2nd heating cycle, with exception of the SmA to Col_h transition temperature for 1 / 2 [0.20], 1 / 3 [0.45] and 1 / 3 [0.50] which were extracted from the 2nd cooling). Blue: SmA phases; red: Col_h phases.

Table S3. Phase transition temperatures and enthalpies of the pure MIDA boronates **1** and **2** as well as for their respective mixtures **1** / **2** [X_1] at given molar fraction [X] of **1**. The mean molar mass M is given in g mol⁻¹, melting temperatures T_m , mesophase transition temperatures T_M and clearing temperatures T_c are given in °C, molar enthalpies ΔH are given in kJ mol⁻¹.

[X]	M	Cr	T_m (ΔH)	SmA	T_M (ΔH)	Col _h	T_C (ΔH)	I	Cycle
[1.00] ^d	417.35	• ^a	109 (-)	•			194 (-1.8)	•	2 nd H
		• ^b	79 (-)	•			192 (1.7)	•	2 nd C
[0.80]	454.22	•	42 (-2.7)	•			167 (-1.0)	•	2 nd H
		• ^b	46 (-)	•			156 (1.1)	•	2 nd C
[0.60]	491.08	•	51 (-2.7)	•			153 (-1.0)	•	2 nd H
		• ^b	51 (-)	•			156 (1.1)	•	2 nd C
[0.50]	509.52	•	55 (-1.2)	•			145 (-0.5)	•	2 nd H
		• ^b	49 (-)	•			146 (0.5)	•	2 nd C
[0.40]	527.95	•	57 (-4.0)	•			134 (-0.9)	•	2 nd H
		•	72 (2.9)	•			136 (1.7)	•	2 nd C
[0.25]	555.60	•	53 (-9.4)	•			119 (-0.4)	•	2 nd H
		•	67 (7.2)	•			121 (0.4)	•	2 nd C
[0.20]	564.81	•	56 (4.7)	- ^c	- ^c	• ^a	133 (-)	•	2 nd H
		•	62 (1.8)	•	105 (0.4)	•	137 (0.3)	•	2 nd C
[0.15]	574.03	•	54 (-11.3)	•	96 (-0.4)	•	125 (-0.2)	•	2 nd H
		•	60 (8.6)	•	104 (0.4)	•	131 (0.2)	•	2 nd C
[0.00] ^d	601.68	•	84 (-)				169 (-0.9)	•	2 nd H
		•	84 (-)				169 (0.9)	•	2 nd C

^a Transition found under POM; ^b Glass transition; ^c no transition found; ^d The data were taken from ref.¹ for comparison.

Table S4. Phase transition temperatures and enthalpies of the pure MIDA boronates **1** and **3** as well as for their respective mixtures **1** / **3** [X_1] at given molar fraction [X] of **1**. The mean molar mass M is given in g mol⁻¹, melting temperatures T_m , mesophase transition temperatures T_M and clearing temperatures T_c are given in °C, molar enthalpies ΔH are given in kJ mol⁻¹.

[X]	M	Cr	T_m (ΔH)	SmA	T_M (ΔH)	Col _h	T_c (ΔH)	I	Cycle
[1.00] ^d	417.35	• ^a	109 (-)	•			194 (-1.8)	•	2 nd H
		• ^b	79 (-)	•			192 (1.7)	•	2 nd C
[0.80]	491.08	•	53 (-1.0)	•			140 (-0.2)	•	2 nd H
		•	73 (0.8)	•			153 (0.8)	•	2 nd C
[0.60]	564.81	•	45 (-2.0)	•			96 (-0.3)	•	2 nd H
		•	55 (1.1)	•			102 (0.1)	•	2 nd C
[0.55]	583.24	•	38 (-2.8)	•			89 (-0.2)	•	2 nd H
		•	56 (1.6)	•			87 (0.2)	•	2 nd C
[0.50]	601.68	•	47 (-0.4))	•	n.d. ^c	(•)	121 (-0.4)	•	2 nd H
		•	54 (0.4)	•	80 (0.04)	•	125 (0.2)	•	2 nd C
[0.45]	620.11	•	37 (-1.8)	•	n.d. ^c	(•)	126 (-0.5)	•	2 nd H
		•	53 (0.8)	•	61 (0.1)	•	130 (0.5)	•	2 nd C
[0.40]	638.54	•	39 (-4.6)				142 (-0.9))	•	2 nd H
		•	47 (1.9)				143 (0.9)	•	2 nd C
[0.20]	712.27	• ^a	40 (-)				138 (-1.4)	•	2 nd H
		• ^a	40 (-)				139 (1.3)	•	2 nd C
[0.00] ^d	786.00	•	-15 (-10.5)				106 (-1.6)	•	2 nd H

^a Transition found under POM; ^b Glass transition; ^c not determinable; ^d The data were taken from ref.¹ for comparison.

3. POM textures

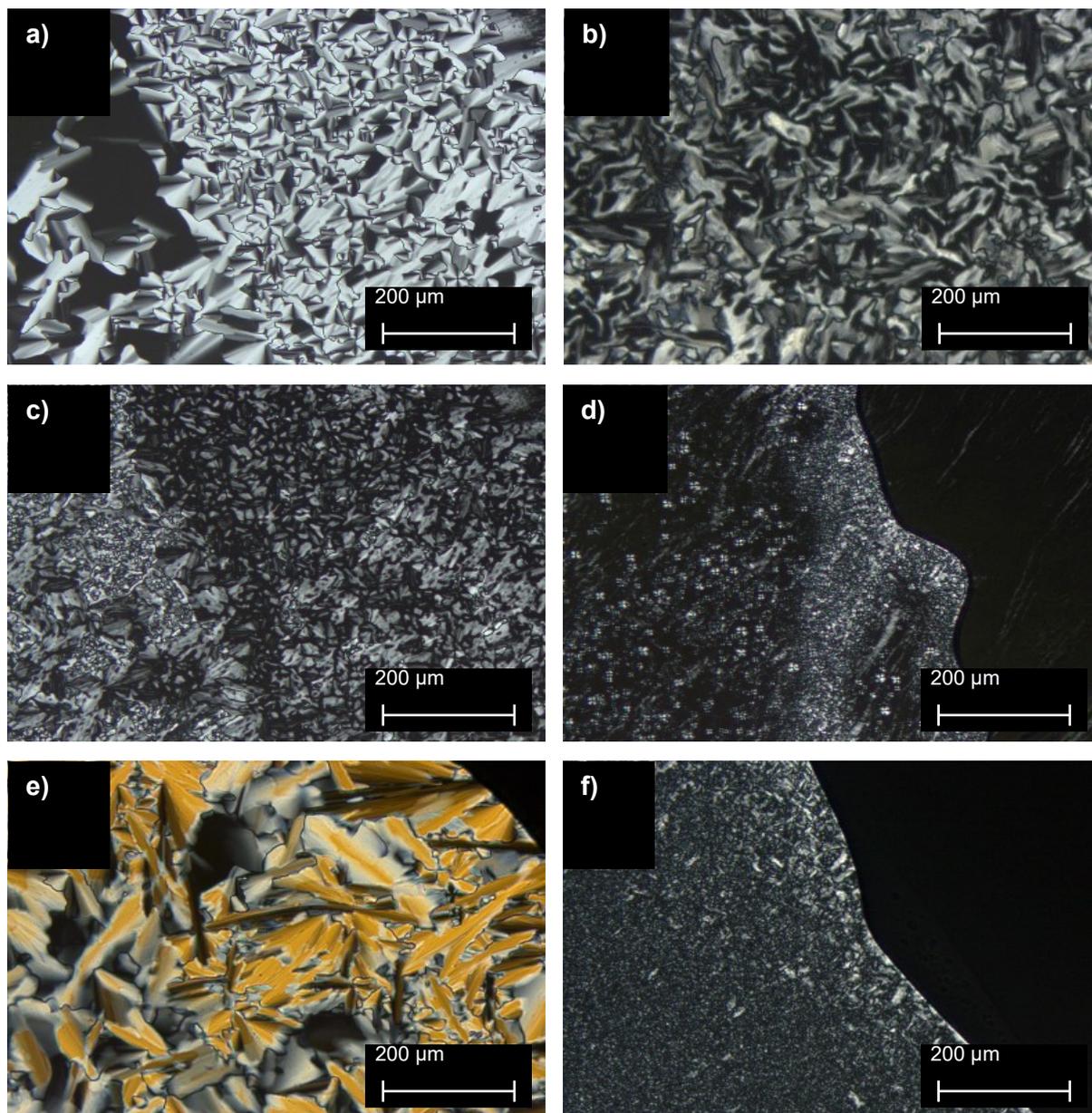


Figure S6. POM textures by a cooling rate of 5 K min^{-1} and a magnification of 10 of a) $1/2 [0.15]$ at $120 \text{ }^\circ\text{C}$, b) $1/2 [0.15]$ at $100 \text{ }^\circ\text{C}$ (cooling rate of 0.1 K min^{-1}), c) $1/2 [0.15]$ at $85 \text{ }^\circ\text{C}$, d) $1/2 [0.25]$ at $100 \text{ }^\circ\text{C}$, e) $1/3 [0.45]$ at $100 \text{ }^\circ\text{C}$, f) $1/3 [0.55]$ at $70 \text{ }^\circ\text{C}$.

4. X-ray data

Table S5. X-ray diffraction data for neat **1** and binary mixture **1 / 2 [0.5]**. The measurements were performed during cooling from the isotropic liquid phase. The halo was determined from WAXS. Data for **1** were taken from ref ¹.

Compound	Mesophase	Layer spacing $d / \text{\AA}$ d_{exp}	Miller Indices
1	SmA at 150 °C	33.9	(001)
		4.9	halo
1 / 2 [0.5]	SmA at 108 °C	36.0	(001)
		4.8	halo

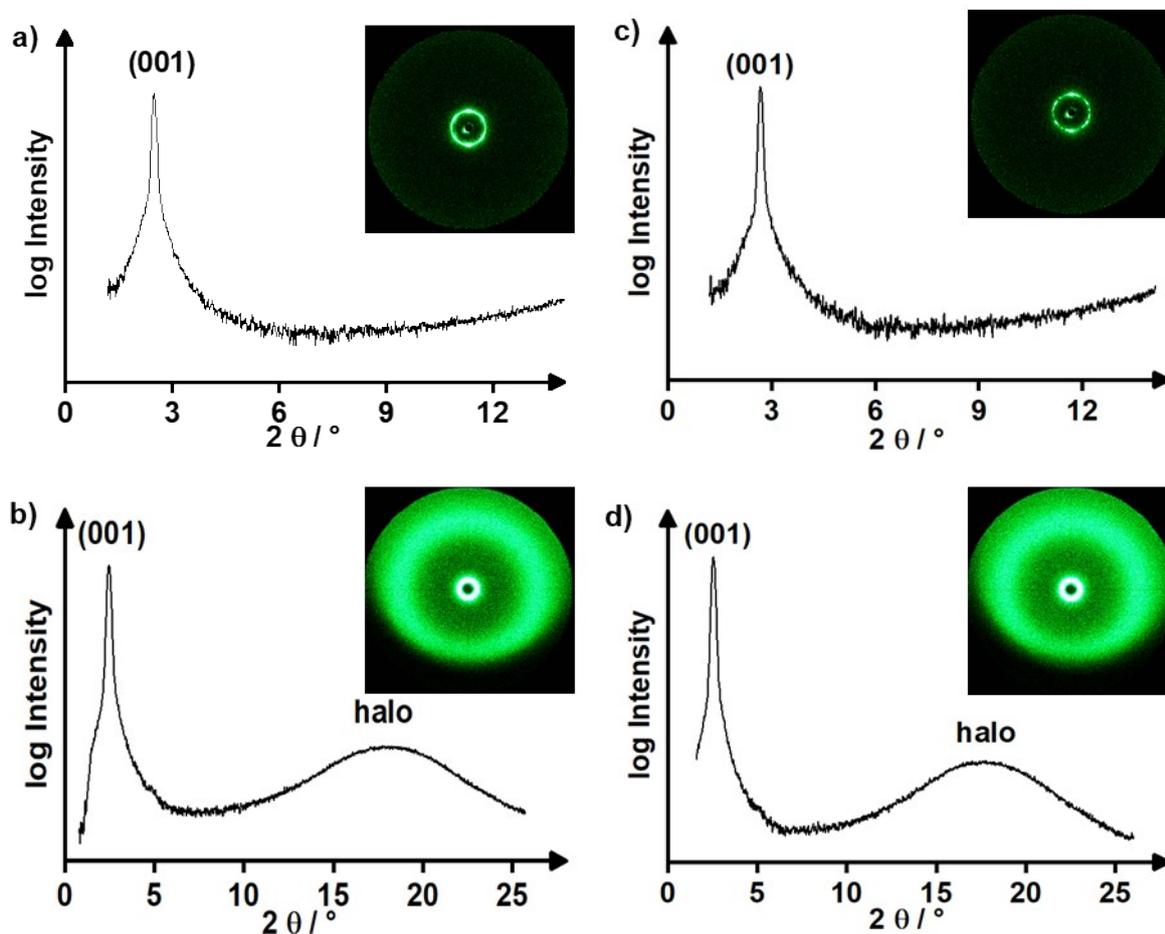


Figure S7. XRD patterns of **1 / 2 [0.15]** at 85 °C, a) SAXS, b) WAXS; at 120 °C, c) SAXS, d) WAXS.

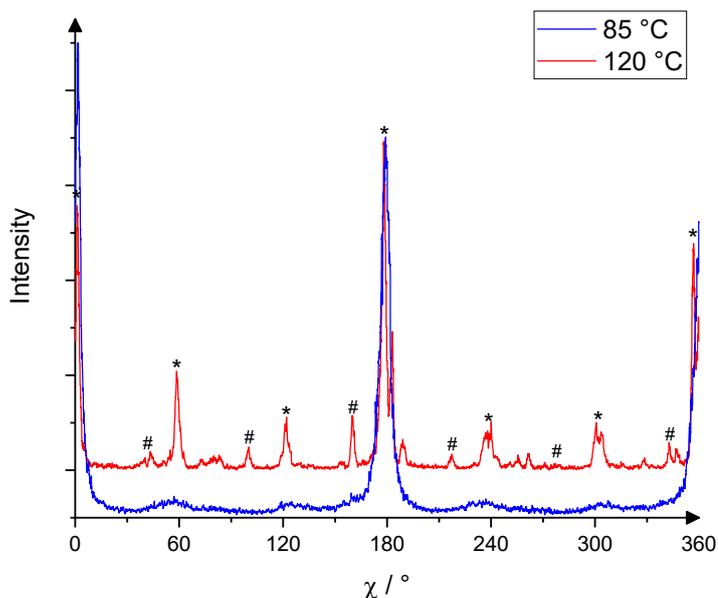


Figure S8. Scattering intensities of $1/2 [0.15]$ measured at 85 °C (cf. Figure S7a) and 120 °C (cf. Figure S7c) plotted versus the azimuthal angle χ . The symbols * and # indicate scattering maxima which originate from the same domain in the Col_h phase (cf. Table S6).

Table S6. Azimuthal angle χ of the scattering maxima in Figure S8 indicated with the symbols * and # as determined by fitting with the Lorentz function. The differences between consecutive maxima of approximately 60° suggest that the respective scattering maxima originate from the same hexagonal domain whose director is aligned parallel to the incident X-ray beam.

$\chi(*) / ^\circ$	Difference / $^\circ$		$\chi(\#) / ^\circ$	Difference / $^\circ$
1.3	57.5		43.7	56.2
58.8	62.9		99.9	60.2
121.7	56.6		160.1	57.1
178.3	60.0		217.2	60.7
238.3	63.8		277.9	65.0
302.1	59.2		342.9	60.8

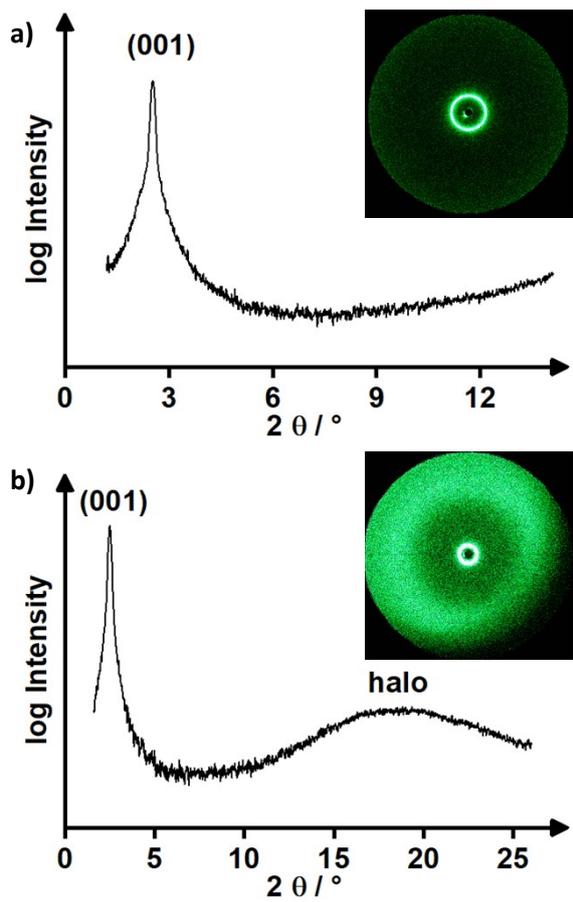


Figure S9. XRD patterns of $1/2 [0.25]$ at 100°C , a) SAXS, b) WAXS.

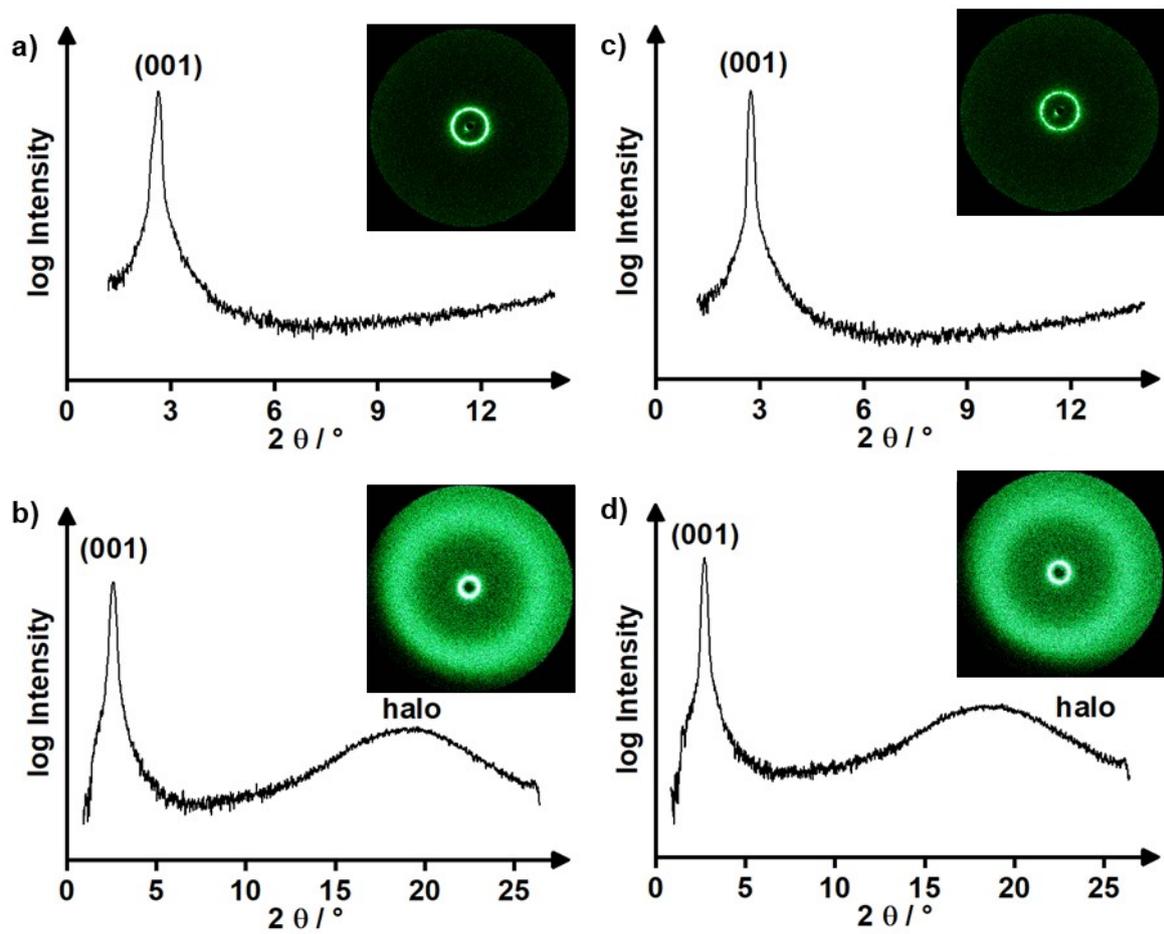


Figure S10. XRD patterns of $1/3 [0.45]$ at 57 °C, a) SAXS, b) WAXS. at 100 °C, c) SAXS, d) WAXS.

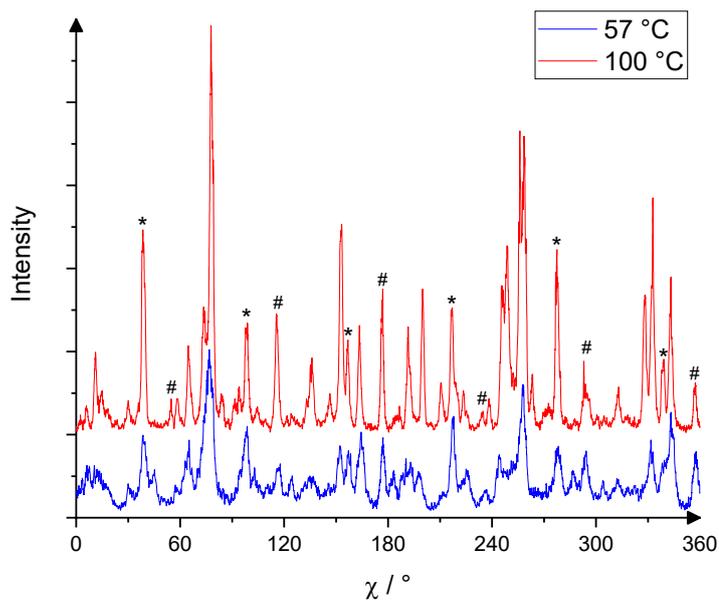


Figure S11. Scattering intensities of $1/3 [0.45]$ measured at 57 °C (cf. Figure S10a) and 100 °C (cf. Figure S10c) plotted versus the azimuthal angle χ . The symbols * and # indicate scattering maxima which originate from the same domain in the Col_h phase (cf. Table S7).

Table S7. Azimuthal angle χ of the scattering maxima in Figure S11 indicated with the symbols * and # as determined by fitting with the Lorentz function. The difference between consecutive maxima of approximately 60° suggest that the respective scattering maxima originate from the same hexagonal domain whose director is aligned parallel to the incident X-ray beam.

$\chi(*) / ^\circ$	Difference / °		$\chi(\#) / ^\circ$	Difference / °
38.8	59.6		54.8	61
98.4	58.3		115.8	60.8
156.7	60.1		176.6	57.8
216.8	60.7		234.4	59.8
277.5	61.2		294.2	63
338.7	60.1		357.2	57.6

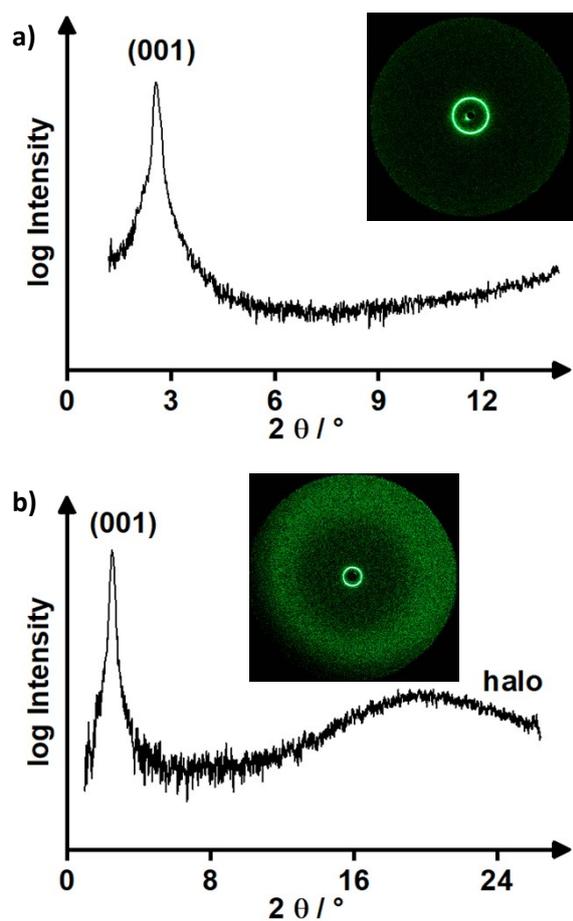


Figure S12. XRD patterns of 1/3 [0.55] at 70 °C, a) SAXS, b) WAXS.

5. References

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