Electronic Supporting Information

Development of polar order in liquid crystalline phases of a banana compound with a unique sequence of three orthogonal phases

Christina Keith,[a] Marko Prehm,[a] Yuri. P. Panarin,[b] Jagdish K. Vij[b] and Carsten Tschierske*

1. Used methods

Investigation of the mesomorphic properties was carried out by polarizing microscopy (Optiphot-2, Nikon) on a hot stage (FP 82 HAT, Mettler), differential scanning calorimetry (DSC, DSC-7, Perkin-Elmer), X-ray diffraction (XRD) of surface aligned samples (HI-Star, Siemens; alignment was achieved by slow cooling a drop of the isotropic liquid below the clearing temperature on a glass substrate; the incident X-ray beam was nearly parallel to the glass plate) as well as electrooptical experiments using a home built setup.

2. Additional XRD data

2.1 Compound 1a

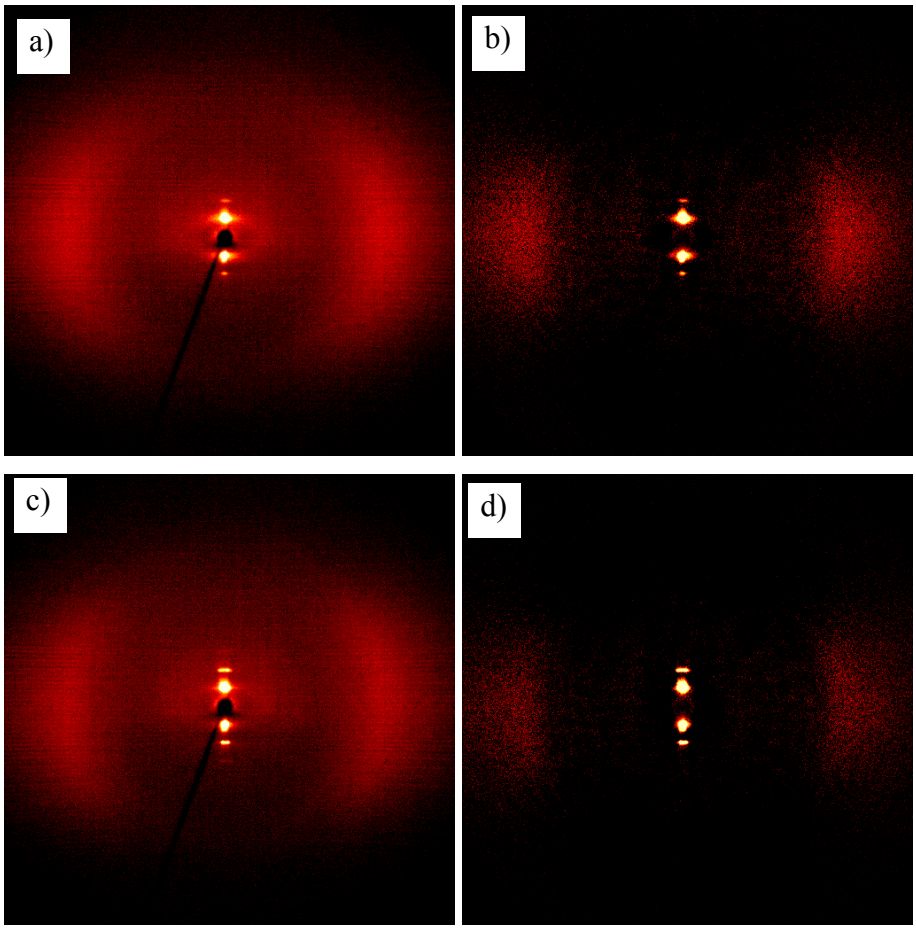


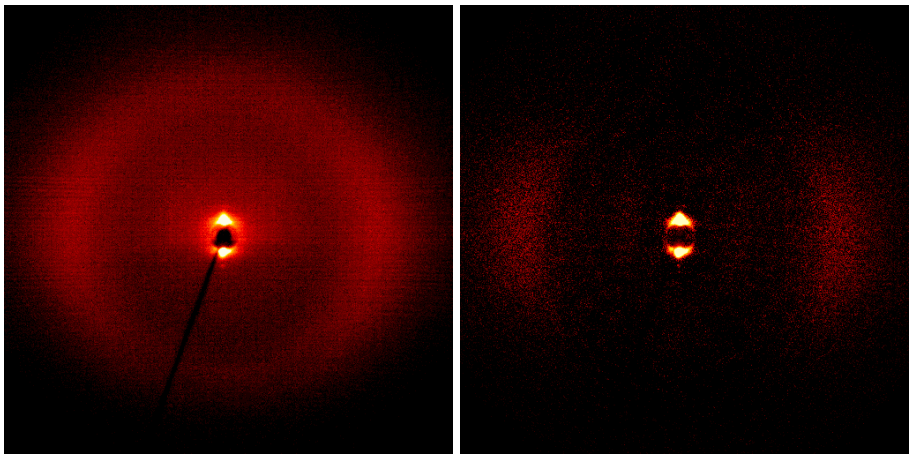
Figure S1. a-d) X-ray diffraction pattern of a oriented sample (surface alignment) of compound **1a**; a,b) SmA phase at T = 140 °C; c,d) $SmAP_A$ phase at T = 90 °C; a,c) show the

original diffraction patterns, b,d) diffraction patterns after subtraction of the isotropic liquid state (at T = 156 °C) from the original diffraction patterns.

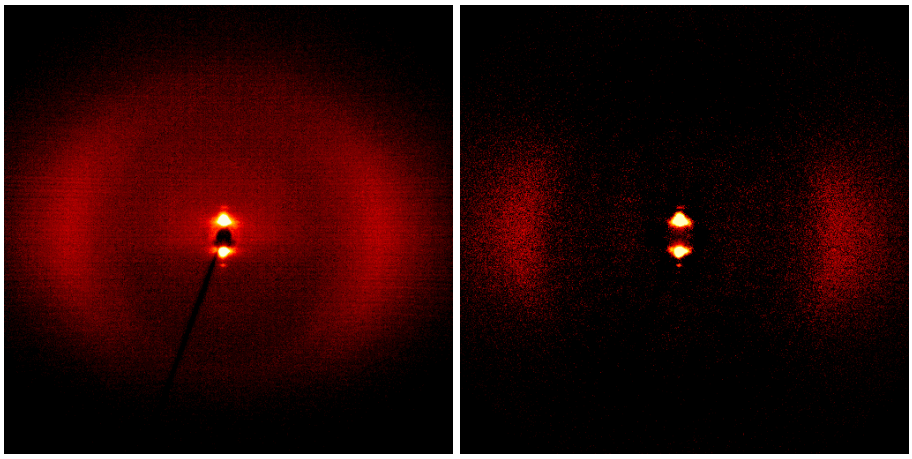
Table S1. Crystallographic data of compound **1a** at different temperatures.

	Small angle reflections		Wide angle reflections	
T / °C	θ / °	d/nm	θ / °	d/nm
140	1.139	3.88	9.236	0.48
130	1.137	3.89	9.290	0.48
110	1.131	3.91	9.349	0.48
100	1.132	3.90	9.375	0.47
90	1.134	3.90	9.412	0.47

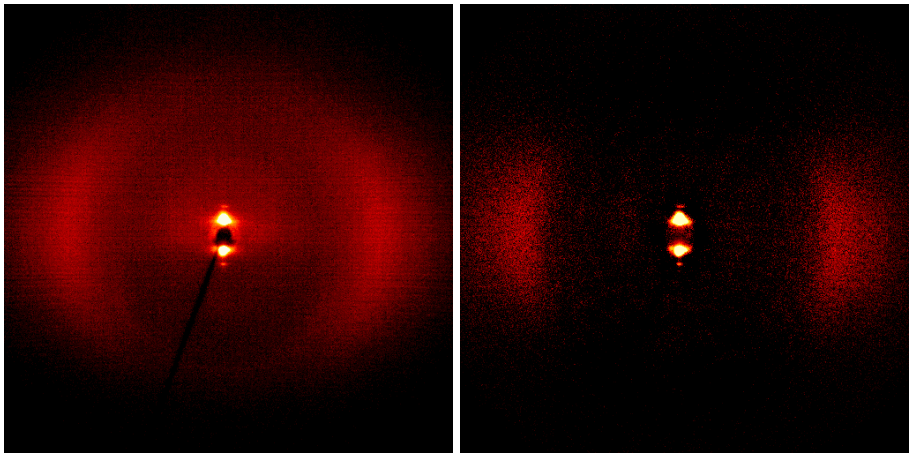
2.2 Compound 1b



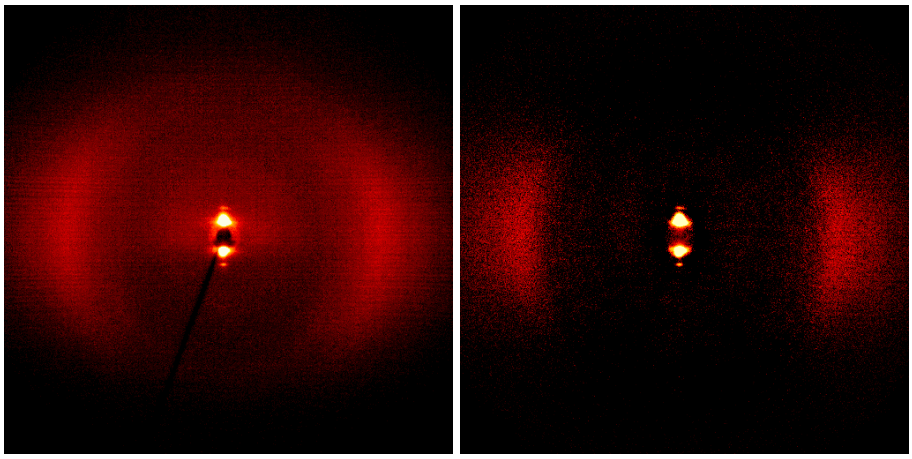
a) 160 °C



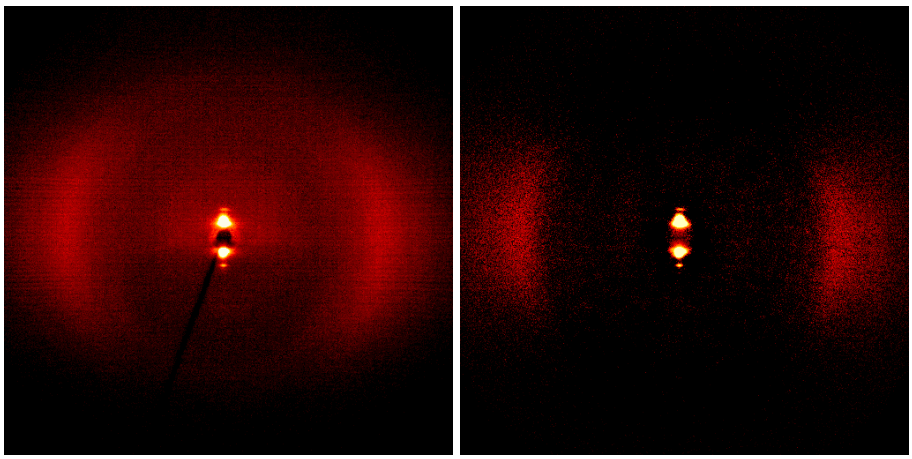
b) 140 °C



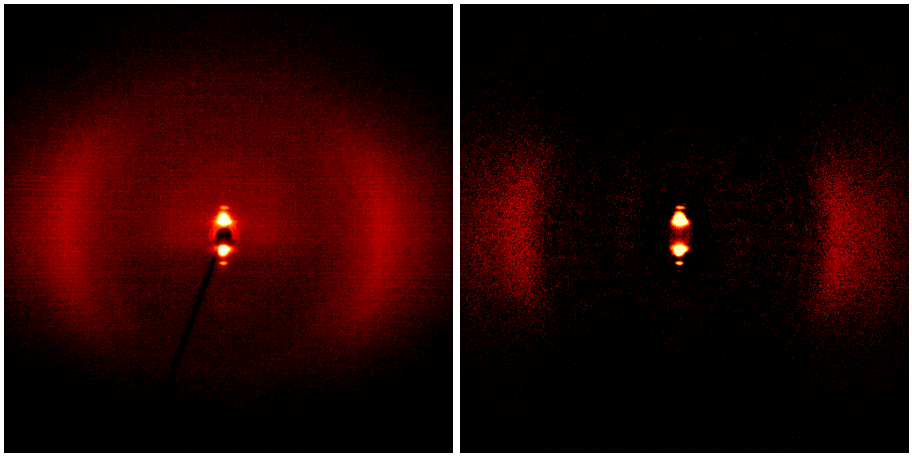
c) 130 °C



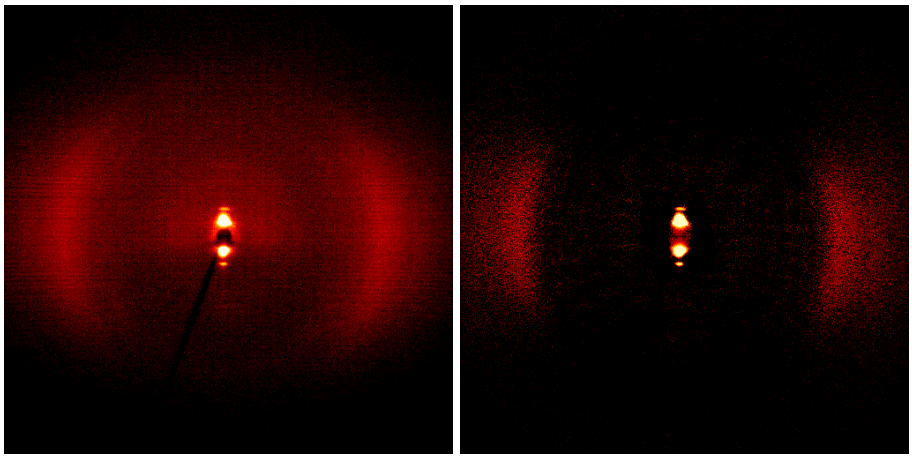
d) 110 °C



e) 100 °C



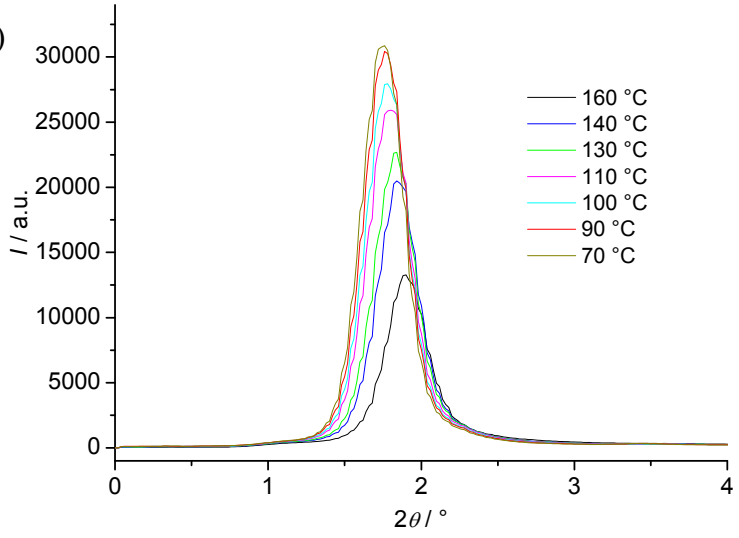
f) 90 °C



g) 70 °C

Figure S2. X-ray diffraction pattern of a oriented sample of compound **1b** (original diffraction pattern at the left, diffraction patterns after subtraction of the isotropic liquid state at T = 178 °C from the original diffraction pattern at the right); a) SmA phase, b,c) $SmAP_R$ phase at 140 and 130 °C and d-g) $SmAP_A$ phase at 110, 100, 90 and 70 °C.

a)



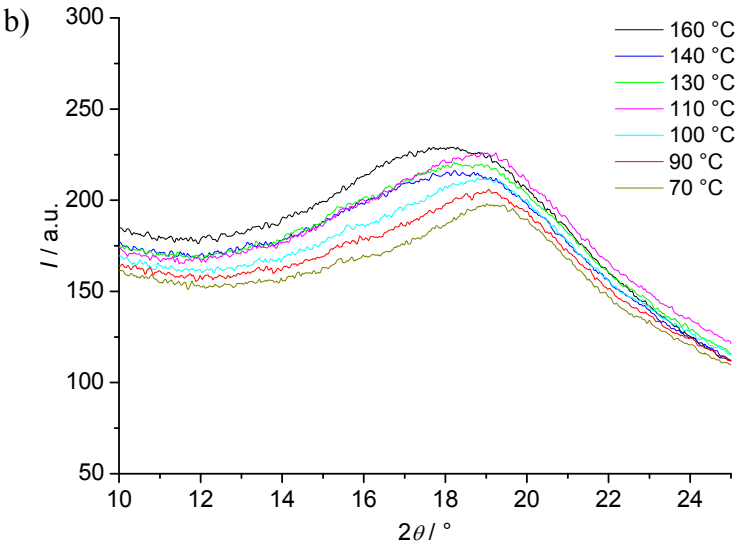


Figure S3. θ–scans over a) the small angle scattering and b) the wide angle scattering of compound **1b** at different temperatures.

Table S2. Crystallographic data of compound **1b** at different temperatures.

	Small angle reflections		Wide angle reflections	
T / °C	θ / °	*d*/nm	θ / °	*d*/nm
160	0.954	4.63	9.163	0.48
140	0.926	4.77	9.208	0.48
130	0.915	4.83	9.272	0.48
110	0.896	4.93	9.346	0.48
100	0.889	4.97	9.377	0.47
90	0.883	5.00	9.411	0.47
70	0.876	5.05	9.528	0.47

3. Electrooptical investigations

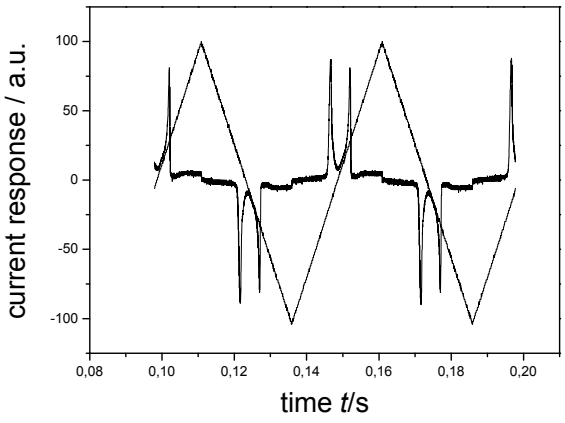


Figure S4: Switching current response of compound **1a** in a 6 µm ITO cell (400 V_{pp}, 10 Hz, 5 kΩ) on applying an triangular wave field at T = 100 °C; spontaneous polarization P_s ca. 770 nC/cm^2.

4. Textures and DSC

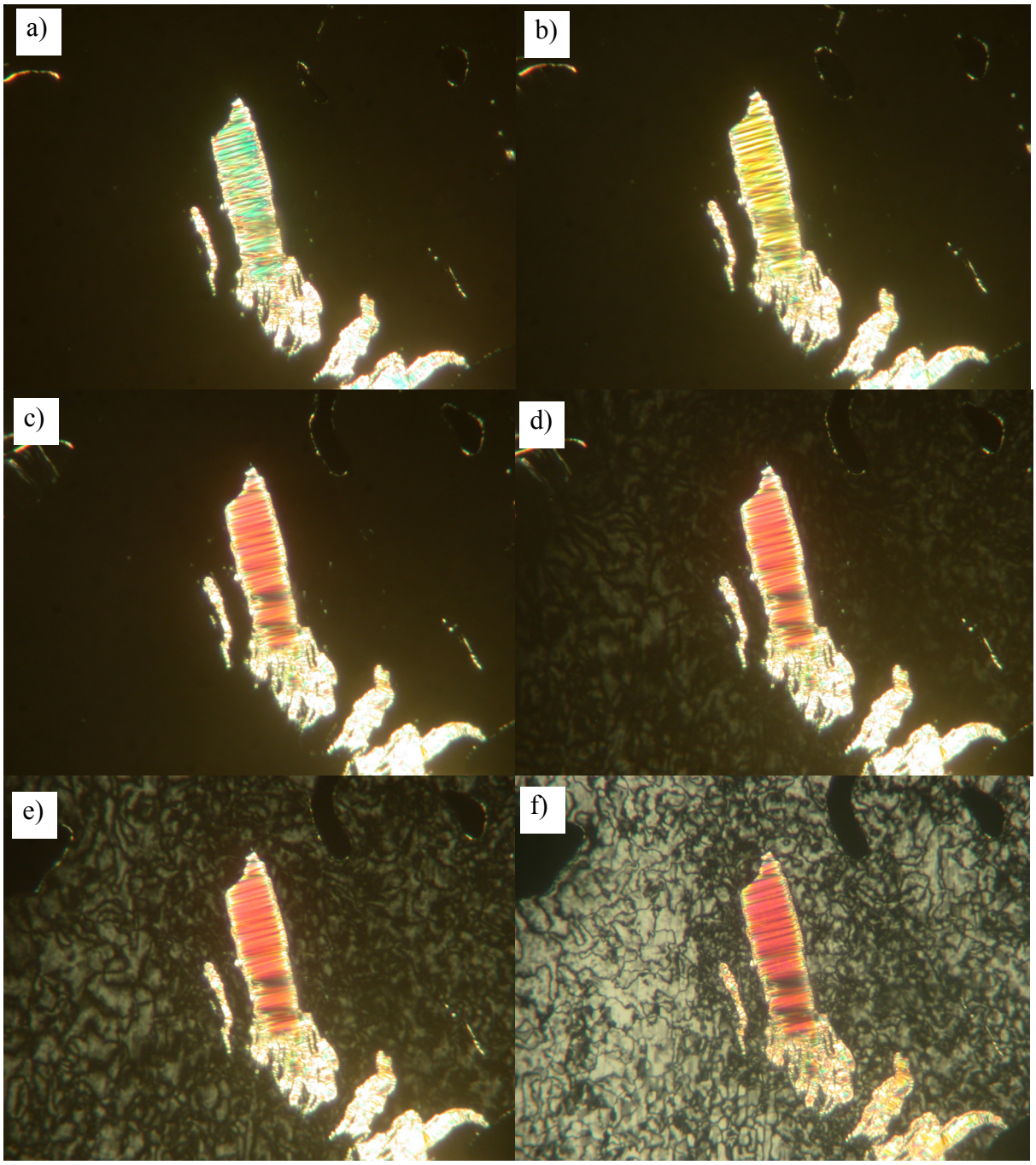


Figure S5: Textures of compound **1b** at different temperatures; a) SmA at T = 165 °C; b) $SmAP_R$ at T = 155 °C; c) $SmAP_R$ at T = 112 °C; d) $SmAP_A$ at T = 111 °C; e) $SmAP_A$ at T = 109 °C; f) $SmAP_A$ at T = 104 °C (same area).

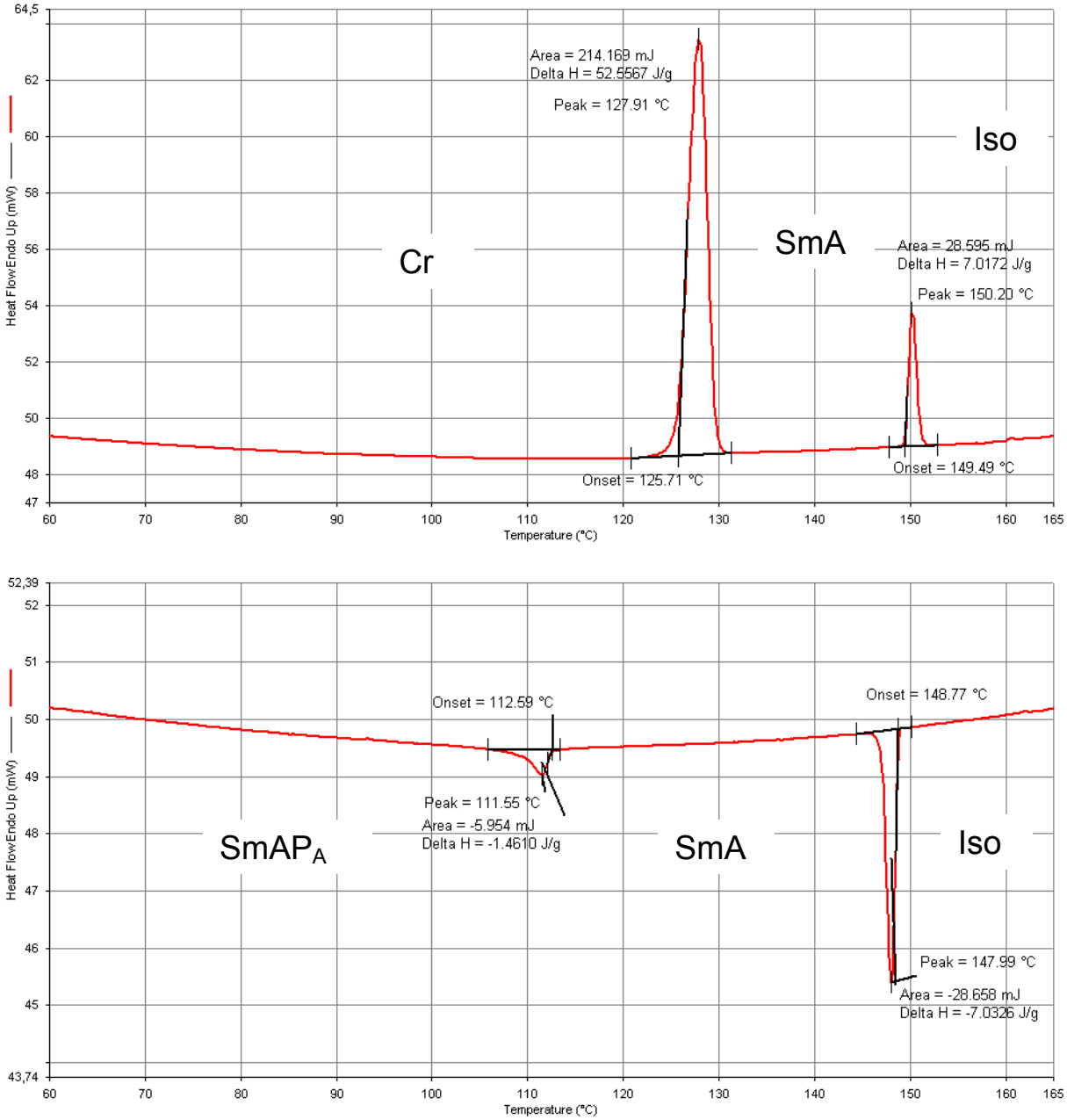
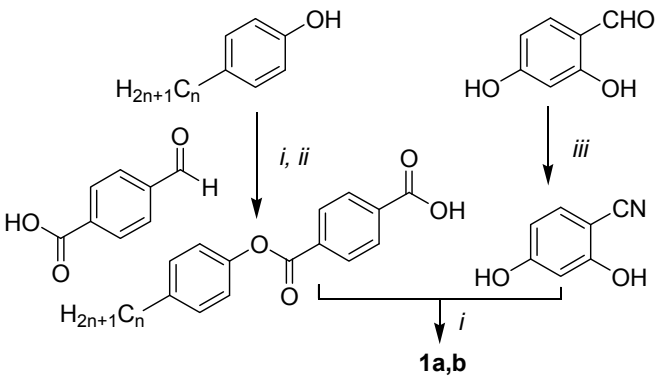


Figure S6. DSC heating (top) and cooling (bottom) curves as obtained for compound **1a** (10K min^{-1}).

5. Synthesis and analytical data



Scheme 1 Synthesis; *reagents*: *i*: DCC, DMAP, CH_2Cl_2; *ii*: $NaOCl_2$, NaH_2PO_4, resorcinol, *t*-BuOH;[S1] *iii*: 1. H_2NOH, 2. Ac_2O, 3. NaOH.[S2]

General procedure
The 4-substituted benzoic acid (1 eq.), 4-cyanoresorcinol (0.5 eq.), DCC (1.1 eq.) and DMAP (cat.) were dissolved in anhydrous CH_2Cl_2 (ca. 20 ml/mmol benzoic acid) and stirring is continued for 24 hrs. The reaction mixture is then filtered to remove solids, evaporated and purified by column chromatography and crystallization from CH_2Cl_2/EtOH (9:1). 4-Cyanoresorcinol was prepared according to ref.[S2]; 4-(4-*n*-alkylphenoxycarbonyl)benzoic acids were prepared according to reported procedures.[S3]

1a Prepared from 4-cyanoresorcinol (0.2 g, 1.5 mmol), 4-(4-hexylphenoxycarbonyl)benzoic acid (1.0 g, 3.06 mmol), DCC (0.64 g, 3.13 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml), purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.09) to yield 0.7 g (0.72 mmol, 36 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.35 (m, 8H, Ar-H), 7.82 (d, 1H, *J* 8.5, Ar-H), 7.37 (s, 1H, Ar-H), 7.35 (d, 1H, *J* 8.5, Ar-H), 7.24 (m, 4H, Ar-H), 7.13 (d, 2H, *J* 8.5, Ar-H), 7.12 (d, 2H, *J* 8.5, Ar-H), 2.62 (t, 4H, *J* 7.7, Ar-CH_2), 1.62 (m, 4H, CH_2), 1.31 (m, 12H, CH_2), 0.88 (t, 3H, *J* 6.8, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.08, 163.05, 162.73, 154.54, 153.23, 148.58, 148.55, 140.94, 140.89, 134.93, 134.81, 134.06, 132.57, 132.18, 130.61, 130.45, 130.38, 129.40, 129.38, 121.10, 121.07, 120.09, 117.24, 114.50, 104.58, 35.53, 31.84, 31.52, 29.08, 22.74, 14.21. EA, calc. for $C_{47}H_{45}O_8N$, 751.8677 g/mol:, C 75.08, H 6.03, N 1.86, found: C 75.08, H 6.11, N 1.70

1b Prepared from 4-cyanoresorcinol (0.16 g, 1.2 mmol), 4-(4-dodecylphenoxycarbonyl)-benzoic acid (1.0 g, 2.5 mmol), DCC (0.52 g, 2.5 mmol), DMAP (20 mg) in dry CH_2Cl_2 (50 ml) purified by column chromatography (silica gel, $CHCl_3$, R_f: 0.09) to yield 0.7 g (0.72 mmol, 36 %) of the product. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.34 (m, 8H, Ar-H), 7.82 (d, 1H, *J* 8.5, Ar-H), 7.58 (d, 1H, *J* 2.1, Ar-H), 7.36 (d, 1H, *J* 8.5, Ar-H), 7.22 (m, 4H, Ar-H), 7.13 (d, 2H, *J* 8.5, Ar-H), 7.12 (d, 2H, *J* 8.5, Ar-H), 2.62 (t, 4H, *J* 7.7, Ar-CH_2), 1.62 (m, 4H, CH_2), 1.31 (m, 12H, CH_2), 0.88 (t, 3H, *J* 6.8, CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 164.13, 163.09, 162.76, 154.56, 153.25, 148.60, 148.57, 140.97, 140.91, 134.93, 134.81, 134.07, 132.57, 132.17, 130.61, 130.46, 130.39, 129.40, 129.38, 121.09, 121.06, 120.09, 117.23, 114.50, 104.54, 35.43, 31.95, 31.47, 29.69, 29.67, 29.62, 29.53, 29.37, 29.32, 22.71, 14.12. EA, calc. for $C_{59}H_{69}O_8N$, 920.1893 g/mol:, C 77.01, H 7.56, N 1.52, found: C 76.97, H 7.62, N 1.42.

6. References

S1 G. S. Lee, Y.-J. Lee, S. Y. Choi, Y. S. Park and K. B. Yoon, *J. Am. Chem. Soc.*, 2000, **122**, 12151.

S2 J. L. Serrano, T. Sierra, Y. Gonzalez, C. Bolm, K. Weickhardt, A. Magnus, G. Moll, *J. Am. Chem. Soc*., 1995, **117**, 8312-8321.

S3 W. Weissflog, L. Kovalenko, I. Wirth, I., S. Diele, G. Pelzl, H. Schmalfuss, H. Kresse, *Liqu. Cryst.*, 2000, **27**, 677; L. Kovalenko, M. W. Schröder, R. A. Reddy, S. Diele, G. Pelzl, W. Weissflog, *Liqu. Cryst.*, 2005, **32**, 7, 857-865.