

Supporting Information

Self-assembly of bent-core liquid crystals: Formation of a modulated smectic phase with $p2gg$ lattice to escape anticlinic tilt

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1. Additional Figures and Tables

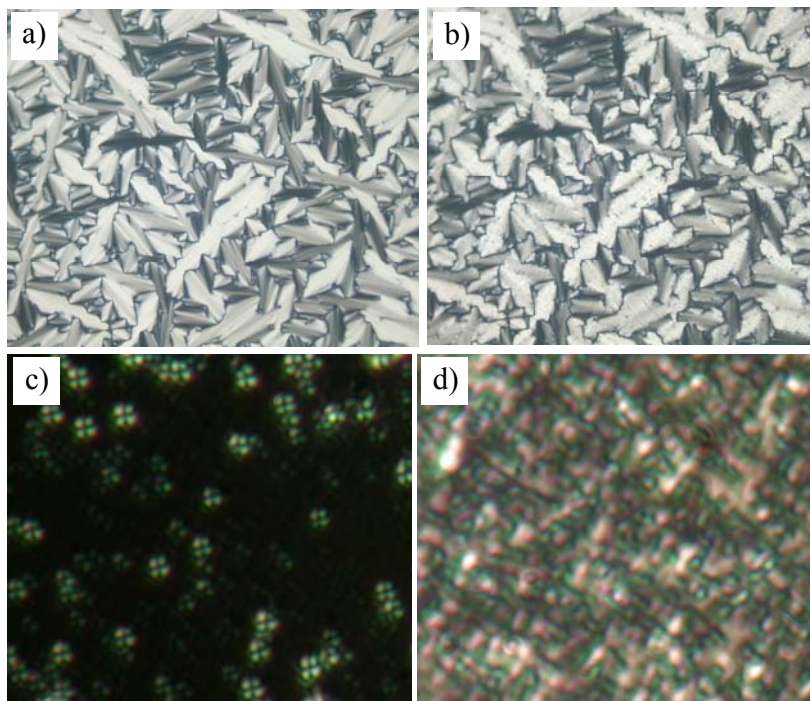


Figure S1. Optical photomicrographs obtained for compound **1** between crossed polarizers: a) fan-shaped texture of the high temperature smectic phase (SmC_R) at 132 °C; b) fan texture with stripes observed in the low temperature $Col_{rec}/p2gg$ phase at 123 °C; c) texture obtained after mechanical shear of the high temperature smectic phase, the dark areas are optically isotropic; d) same region the low temperature after transition to the $Col_{rec}/p2gg$ phase.



Figure S2. CPK model of compound **1** in the conformation used for determination of the molecular length ($L = 7.05$ nm).

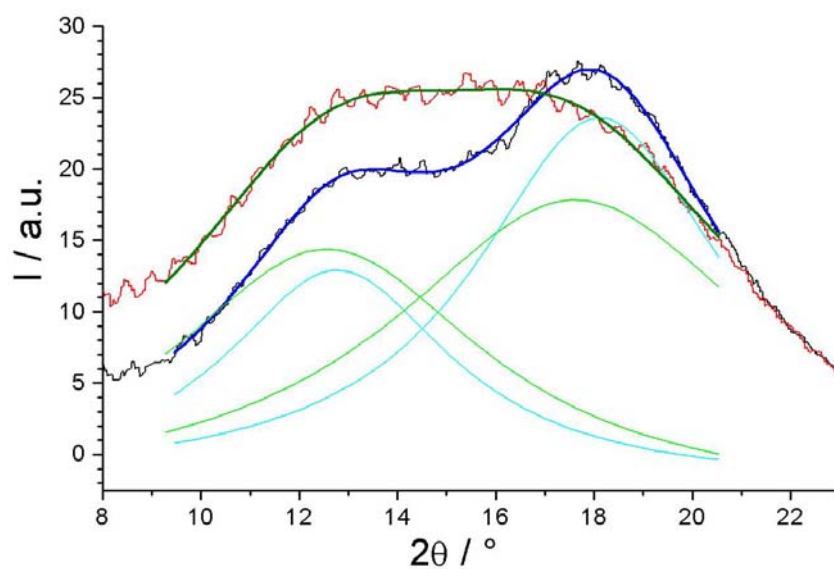


Figure S3. Theta scan for the diffuse wide angle X-ray scattering in the SmC_R phase at 130 °C and in the Col_{rec}/p2gg phase at 115 °C on cooling with Lorentzian fits for two maxima.

Colour code:	115 °C	130 °C
experimental curve:	black	red
Lorentzian fits	cyan	green
resulting fit	blue	olive

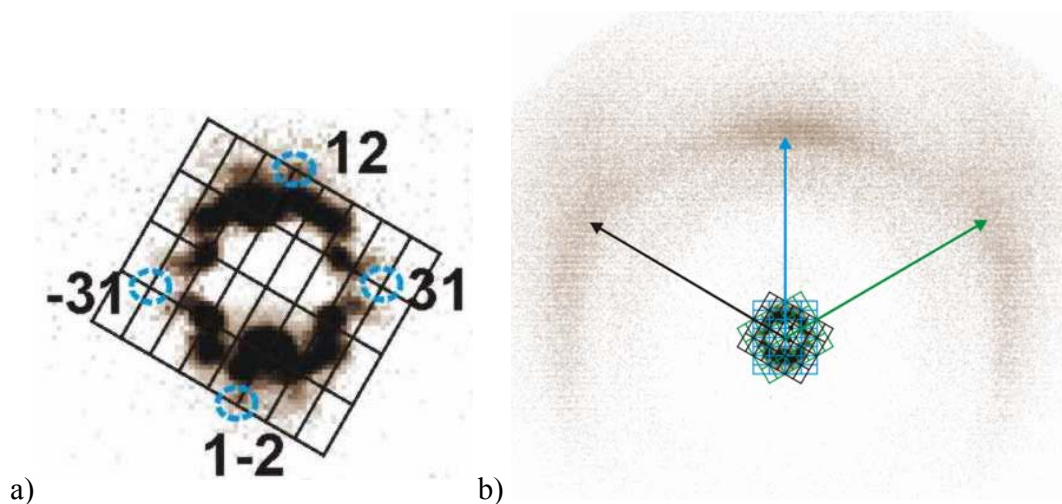


Figure S4. Confirmation of the $p2gg$ lattice: a) small angle region of the wide angle pattern with additional weak reflections assigned to 12 and 31; despite their very weak intensity and bad resolution they fit the extinction rules for $p2gg$ and support the proposed choice (in the small angle pattern, shown in Fig. 1f the 21 reflection is sufficiently strong to be no artefact and so the centred $c2mm$ can be excluded; the missing 01 or 10 and 03 or 30 reflections allow us to exclude $p2mm$ and $p2gm$ as well with high probability); b) correlation between the lattice orientation and the main directions of the diffuse wide-angle scattering (115 °C, arrows in a^* direction (see Fig. 1f) for the three lattice orientations).

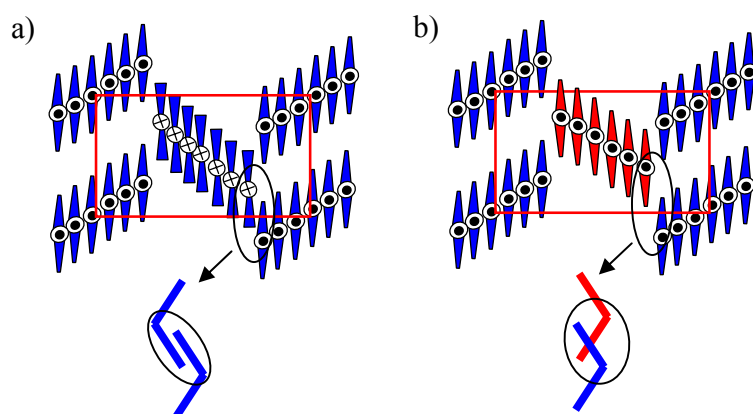


Figure S5. a) The $p2gg$ structure with synpolar order along the ribbon stacks and antipolar order in the other direction (antiferroelectric organization) is stabilized by the parallel alignment of the rod-like aromatic wings at the inter-ribbon interfaces; b) in the synpolar (ferroelectric) structure (after rotation of the molecules around the long axis) the aromatic wings at these interfaces would clash which destabilizes this structure.

Table S1. X-ray Data of Compound **1**.^a

Phase type	$\theta_{exp} / ^\circ$	d_{exp} / nm	n, hk	Lattice parameters / nm	d_{calc} / nm	$T / ^\circ\text{C}$
SmC _R	0.825	5.35	1	$d = 5.35$	5.35	130
	1.650	2.67	2		2.675	
Col _{rec} (<i>p2gg</i>)	0.738	5.99	11	$a = 12.0$ $b = 6.93$	6.00	115
	0.738	5.99	20		6.00	
	0.975	4.53	21		4.54	
	1.28 ^b	3.46	31		3.46	
	1.34 ^b	3.29	12		3.33	

^a $\theta_{exp} = \theta$ determined from Guinier powder patterns; d_{exp} = experimental d value according to the Bragg equation, $d_{calc} = d$ value calculated from the lattice parameters, d = layer distance in the smectic phase, n = order of the layer reflections, hk = Miller indices, ^breduced accuracy (very weak intensity, bad resolution)

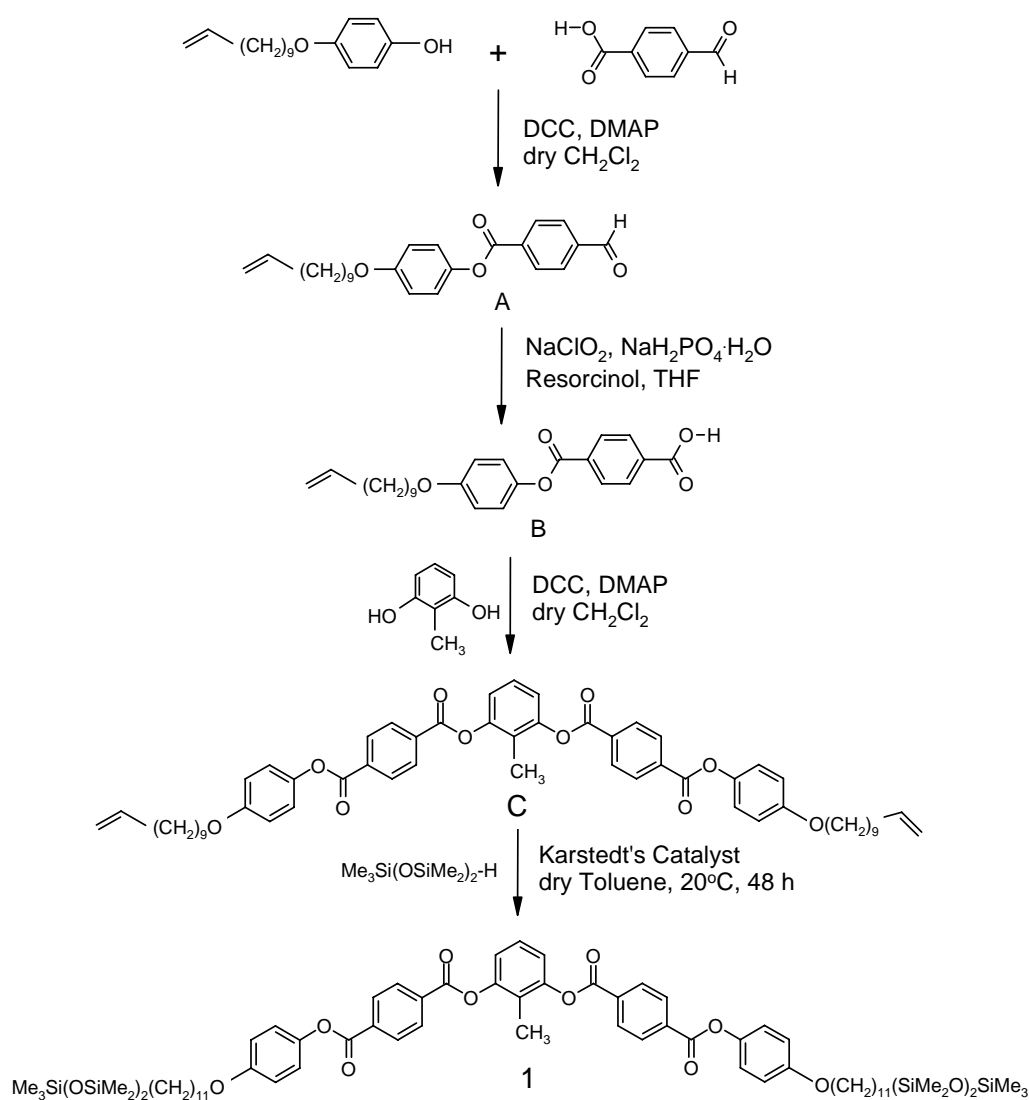
Table S2: Position (d) and FWHM (w) for the maxima of the diffuse wide angle X-ray scattering in the SmC_R phase at 130 °C and in the Col_{rec}/*p2gg* phase at 115 °C on cooling.

$T / ^\circ\text{C}$	$2\theta / ^\circ$	$d / \text{Å}$	$w / ^\circ$
115	12.8	6.9	5.7
	18.1	4.9	6.2
130	12.6	7.0	7.9
	17.6	5.0	9.2

2. Conditions for X-ray scattering

Powder X-ray investigations were carried out with a Guinier film camera (Huber) with samples kept in glass capillaries (\varnothing 1 mm) in a temperature-controlled heating stage using quartz-monochromatized CuK $_{\alpha}$ radiation (30 to 60 min exposure time, calibration with the powder pattern of Pb(NO₃)₂). 2D patterns for aligned samples on a glass plate on a temperature-controlled heating stage (alignment at the sample – glass or at the sample – air interface) were recorded with a 2D detector (HI-STAR, Siemens).

3. Synthesis and analytical data



Scheme S1. Synthesis of compound **1**.

4-(Undec-10-enyloxy)phenyl 4-formylbenzoate (**A**)

A mixture of 4-(undec-10-enyloxy)phenol (2.62g, 10 mmol), 4-formylbenzoic acid (1.5g, 10 mmol), 4-(*N,N*-dimethylamino)pyridine (DMAP) (0.12g, 1 mmol) and dry dichloromethane (60ml) was stirred for 10 minutes. To this mixture, *N,N'*-dicyclohexylcarbodiimide (DCC) (2.3 g, 11 mmol) was added and the stirring continued for 12 hours at room temperature. The precipitated *N,N'*-dicyclohexylurea was filtered off and washed with excess of dichloromethane (50 ml). The combined organic solution was washed with 5% aqueous acetic acid (2 × 50ml), cold 5% aqueous sodium hydroxide

(2 × 50 ml) and finally washed with water (3 × 50 ml) and dried over anhydrous sodium sulphate. The solvent was removed and the solid material obtained was purified by column chromatography on silica gel using chloroform as an eluent. Removal of solvent from the eluate afforded a white solid, which was crystallized from petroleum ether. Yield: 88%; m.p. 97 °C; ¹H-NMR (400 MHz, CDCl₃): δ 10.12 (s, 1H, Ar-CHO), 8.34-8.32 (dd, ³J=8.0Hz, ⁴J=1.2Hz, 2H, Ar-H), 8.0-7.98 (dd, ³J=8.4Hz, ⁴J=1.6Hz, 2H, Ar-H), 7.13-7.09 (m, 2H, Ar-H), 6.94-6.9 (m, 2H, Ar-H), 5.85-5.75 (m, 1H, -CH=C), 5.01-4.9 (m, 2H, -C=CH₂), 3.96-3.93 (t, ³J=6.4Hz, 2H, Ar-OCH₂), 2.06-2.00 (m, 2H, -CH₂), 1.81-1.74 (m, 2H, -CH₂), 1.57-1.24 (m, 12H, 6 × -CH₂).

4-[4-(Undec-10-enyloxy)phenoxy]benzoic acid (B)

Compound **A** (3.5 g, 8.88 mmol) and resorcinol (1.27 g, 11.54 mmol) were dissolved in 65 ml of tert. butyl alcohol. To this solution was added drop wise, over 30 min, a solution of sodium chlorite (NaClO₂, 4.8 g, 53.3 mmol) and sodium dihydrogen phosphate monohydrate (3.67 g, 26.6 mmol) in 48 ml water. The resulting pale yellow reaction mixture was then stirred overnight at room temperature. Volatile components were removed in vacuum and the residue dissolved in excess of water. The resulting aqueous solution was then acidified to pH 2 by adding 1M HCl. The white precipitate so obtained was filtered, washed several times with water, and dried. The white crystalline compound was crystallized from THF; Yield: 72%; transition temperatures (*T*/°C): Cr 160 SmC 230 Iso (>200 dec); ¹H-NMR (400 MHz, DMSO-*d*₆): δ 8.3-8.24 (m, 4H, Ar-H), 7.26-7.23 (m, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 5.86-5.76 (m, 1H, -CH=C), 5.02-4.9 (m, 2H, -C=CH₂), 4.02-3.98 (t, ³J=6.4Hz, 2H, Ar-OCH₂), 1.79-1.74 (m, 2H, -CH₂), 1.49-1.18 (m, 14H, 7 × -CH₂).

2-Methyl-1,3-phenylene bis{4-[4-(undec-10-enyloxy)phenoxy]benzoate} (C)

This was synthesized following a procedure described for the preparation of compound **A**, using 2-methylresorcinol and 4-[4-(undec-10-enyloxy)phenoxy]benzoic acid as the starting materials. Yield: 75%; m.p. 164 °C; ¹H-NMR (400 MHz, CDCl₃): δ 8.33 (s, 8H, Ar-H), 7.35-7.33 (m, 1H, Ar-H), 7.18-7.12 (m, 6H, Ar-H), 6.94-6.92 (d, ³J=6.8Hz, 4H, Ar-H), 5.84-5.77 (m, 2H, 2 × -CH=C), 5.00-4.90 (m, 4H, 2 × -C=CH₂), 3.97-3.94 (t, ³J=6.4Hz, 4H, 2 × Ar-OCH₂), 2.06-2.01 (q, ³J=6.4Hz, 4H, 2 × -CH₂), 1.80-1.76 (q, ³J=6.4Hz, 4H, 2 × -CH₂), 1.5-1.29 (m, 24H, 12 × -CH₂).

2-Methyl-1,3-phenylene bis(4-{4-[11-(1,1,3,3,5,5,5-heptamethyltrisiloxane-1-yl)undec-1-yloxy]phenoxy}benzoate) (1)

Compound **C** (0.30 g, 0.33 mmol) was dissolved in anhydrous toluene (5 ml) under an argon atmosphere. To this solution, was added 1,1,1,3,3,5,5-heptamethyltrisiloxane (0.162 g, 0.727 mmol) and a drop of Karstedt's catalyst (platinum-divinyltetramethylsiloxane complex in xylene). The resultant reaction mixture was stirred continuously at room temperature under argon till completion of the reaction, which was determined by TLC. The solvent was evaporated and the crude product was purified by chromatography on silica gel using CHCl₃ as an eluent. Yield: 71%, transition temperatures (*T*/°C): Cr 120 Col_{rec}/p2gg 127 SmC_R 135 Iso; ¹H-NMR (500 MHz, CDCl₃): δ 8.33 (s, 8H, Ar-H), 7.35-

7.33 (m, 1H, Ar-H), 7.18-7.12 (m, 6H, Ar-H), 6.94-6.92 (d, $^3J=6.8\text{Hz}$, 4H, Ar-H), 3.96-3.94 (t, $^3J=6.5\text{Hz}$, 4H, $2 \times \text{Ar-OCH}_2$), 2.13 (s, 3H, Ar-CH₃), 1.79-1.76 (q, $^3J=8.0\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2$), 1.53-1.43 (q, $^3J=7.5\text{Hz}$, 4H, $2 \times \text{OCH}_2\text{CH}_2\text{CH}_2$), 1.34-1.24 (m, 28H, $14 \times \text{CH}_2$), 0.52-0.50 (m, 4H, $2 \times \text{SiCH}_2$), 0.079-0.066 [s, 18H, $2 \times \text{Si}(\text{CH}_3)_3$], 0.056-0.045 [s, 12H, $2 \times \text{Si}(\text{CH}_3)_2$], 0.013-0.006 [s, 12H, $2 \times \text{Si}(\text{CH}_3)_2$]. $^{13}\text{C-NMR}$ (125 MHz, CDCl_3): δ 164.58, 163.76, 157.14, 150.16, 144.01, 134.29, 133.36, 130.35, 130.31, 126.85, 123.76, 122.21, 120.06, 115.19, 68.48, 33.45, 29.64, 29.59, 29.41, 29.39, 29.28, 26.05, 23.23, 18.3, 10.14, 1.81, 1.27, 0.21. $^{29}\text{Si-NMR}$ (99.3 MHz, CDCl_3): δ 7.48, 7.03, -21.07. Calcd for $\text{C}_{71}\text{H}_{108}\text{O}_{14}\text{Si}_6$: C, 62.98; H, 8.04. Found: C, 62.69; H, 8.12.