

Electronic Supporting Information

1D, 2D and 3D liquid crystalline phases formed by bent-core mesogens

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Experimental

To confirm the molecular structure and purity of the synthesized compounds the following analytical methods were applied: analytical thin-layer chromatography (TLC), ¹HNMR, ¹³CNMR spectroscopy and elemental analysis. NMR spectra were recorded on the Varian Unity Plus spectrometer operating at 50 MHz and 200 MHz for ¹³CNMR and ¹HNMR respectively. Tetramethylsilane was used as an internal standard. Chemical shifts are reported in ppm. TLC analyses were performed on Merck 60 silica gel glassplates and visualized using iodine vapor and UV light. Column chromatography was carried out at atmospheric pressure using silica gel (100–200 mesh, Merck). Elemental analysis were performed to confirm the expected molecular structure.

Temperatures and thermal effects of the phase transitions were determined by calorimetric studies using TA Q200 calorimeter, samples of mass 1-3 mg were sealed in aluminum pans and kept in nitrogen atmosphere during measurement. Both heating and cooling scans with rate 5-10 K/min were applied, the data from heating are reported.

Optical textures of LC phases were observed using Zeiss Imager A2m polarizing microscope equipped with Linkam heating stage, samples were sandwiched between two glass plates.

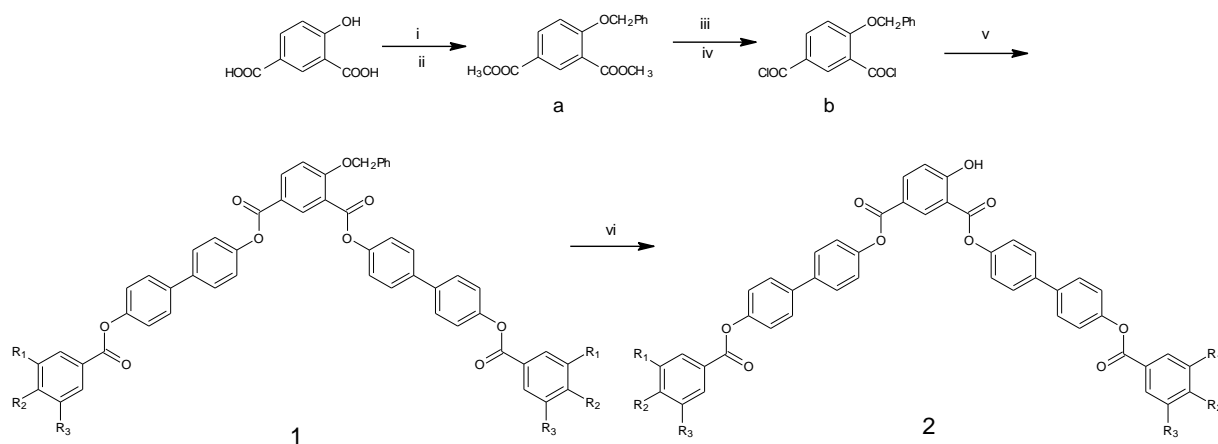
Dielectric studies were performed with Solartron SI1260 Impedance analyser. Samples were prepared in glass cells having transparent ITO electrodes, cells with thickness 3 and 5 microns were used.

The X-ray diffraction measurements in small angle range were performed with the Bruker Nanostar system (CuK α radiation, cross-coupled Goebel mirrors, area detector VANTEC2000) for the powder as well as partially aligned samples. The temperature of the sample was controlled with precision of 0.1 K. Samples were prepared either in thin-walled glass capillaries or as droplets on heated surface. Wide angle diffractograms were obtained with Bruker D8 GADDS system (CuK α line, Goebel mirror, point beam collimator, Vantec2000 area detector).

Synthesis

Synthetic road leading to obtain compounds of Series 1 and 2 is outlined in Scheme 1. Starting material for central ring was isophthalic acid; at first, hydroxy group was protected, then dichloride derivative **b** was obtained. Esterification of dichloride **b** with appropriate arms yielded the studied banana-shaped molecules of Series 1. Details of synthesis of three-ring side arms were described in our previous papers.¹⁻³ Compounds **2** were obtained from compounds **1** by de-protecting the hydroxyl group at the central ring.

Synthesis of banana molecules containing one dodecyloxy terminal chain in each arm is described as a general method to obtain studied materials. The other molecules of the same series were obtained analogously under the same reaction conditions and molar ratio of substrates.



Scheme 1. Reagents and conditions: (i) MeOH / H⁺; (ii) benzyl bromide, K₂CO₃, KI, DMF, 10h, 80°C; (iii) EtOH, KOH, reflux; (iv) (COCl)₂, toluene, reflux, 8h; (v) appropriate phenol arms, THF, TEA, DMAP, reflux, 8h; (vi) EtOH (99.8%), H₂, THF, Pd/C

Synthesis of dimethyl-4-benzyloxy-isophthalate (a)

A solution of 4-hydroxyisophthalic acid (25 g, 0.14 mol) and methanol saturated with hydrogen chloride (250 ml) was stirred and refluxed for 20 h, then the reaction mixture was concentrated under reduced pressure. After cooling the product was precipitated with yield 70%.

In the next step dimethyl-4-hydroxyisophthalate (10 g, 0.05 mol), sodium iodide (9g, 0.06 mol), potassium carbonate (7 g, 0.05 mol) and benzyl bromide (6 ml, 0.05 mol) was suspended in DMF (200 ml). The reaction mixture was stirred and heated to 80 °C during 10h, then was added to ice-water mixture and filtered off. The crude product was purified by crystallization from ethanol. Yield 75%.

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 8.51 (1H, d, J=2.2Hz), 8.12 (1H, dd, J₁=2.3Hz, J₂=8.8Hz), 7.50-7.31 (5H, M), 7.04 (1H, d, J=8.8Hz), 5.25 (2H, s), 3.92 (3H, s), 3.89 (3H, s),

¹³C-NMR (CDCl₃, 50 MHz): δ (ppm) 166.88, 165.89, 157.24, 136.23, 134.80, 128.90, 128.45, 127.80, 127.63, 119.75, 112.24, 70.41, 52.30;

Elemental analysis (C₁₇H₁₆O₅, M=300.31) - Calculated: C(67.99%), H(5.37%). Found: C(68.45%), H(5.10%).

Synthesis of 4-benzyloxy-isophthaloyl dichloride (b)

To a stirred suspension of compound (a) (5g, 0.017 mol) in ethanol (150 ml) solution of sodium hydroxide (2 g, 0.05 mol) in ethanol was added and the mixture was refluxed for 6h. After cooling down the precipitate was filtered off and dried under vacuum over phosphorus pentoxide. Dry sodium salt was suspended in toluene and oxalyl chloride (5ml) was added. That prepared suspension was stirred and refluxed for 7 h, afterward solvents was evaporated under vacuum. To the next reaction crude compound (b) was used without any purification.

Representative synthesis for compounds of Series 1:

Synthesis of 4-(benzyloxy)-isophthalic acid bis[4'-(4-dodecyloxybenzoyloxybiphenyl-4-yl)] ester (1a)

To a mixture of 4'-hydroxybiphenyl-4-[4-dodecyloxy]benzoate (4.8 g, 0.01mol), DMAP (0.02 g) and triethylamine (4 mL) in tetrahydrofuran (150 mL) 4-benzyloxy-isophthaloyl dichloride (b) (1.6 g, 0.005 mol) was added. Reaction was heated and leaded for 12h and then solvents were evaporated to dryness. The crude product was purified by column chromatography on silica gel, using toluene as eluent. Yield 75 %.

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 8.63 (1H, d, J=2.4 Hz), 8.22 (dd, 1H, J₁=2.0 Hz, J₂=8.6 Hz), 8.15 (4H, d, J=8.8 Hz), 7.67-7.53 (10H, m), 7.41-7.21 (12H, m), 6.98 (4H, d, J=8.9 Hz), 5.35 (s, 2H), 4.05 (4H, t, J=6.6 Hz), 1.90-1.79 (4H, m), 1.50-1.26 (36H, m), 0.89 (6H, t, J=6.8Hz);

¹³C-NMR (CDCl₃, 50 MHz): δ (ppm) 168.25, 164.40, 164.13, 159.90, 157.08, 153.40, 136.79, 134.72, 136.54, 132.19, 128.92, 128.41, 127.92, 126.62, 121.64, 119.77, 114.54, 112.20, 69.58, 68.02, 32.14, 29.56, 29.31, 26.20, 22.91, 14.35;

Elemental analysis (C₇₇H₈₄O₁₁, M=1185.48) - Calculated: C(77.00%), H(7.14%). Found: C(77.65%), H(7.05%).

Analytical data for other compounds of series 1**1b; Yield 81 %**

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 8.92 (1H, d, J=2.2 Hz), 8.39 (1H, dd, J₁=2.2 Hz, J₂=8.8 Hz), 8.17 (4H, d, J=9.0 Hz), 7.67-7.52 (10H, m), 7.40-7.26 (12H, m), 6.98 (4H, d, J=9.0 Hz), 5.35 (s, 2H), 4.05 (4H, t, J=6.6 Hz), 1.89-1.76 (4H, m), 1.52-1.20 (52H, m), 0.88 (6H, t, J=6.6 Hz);

Elemental analysis (C₈₅H₁₀₀O₁₁, M=1297.70) - Calculated: C(78.67%), H(7.77%). Found: C(78.73%), H(7.70%)

1c; Yield 78 %

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 8.92 (1H, d, J=2.2 Hz), 8.40 (1H, dd, J₁=2.2 Hz, J₂=8.8 Hz), 7.85 (2H, dd, J₁=2.0 Hz, J₂=8.4 Hz), 7.69-7.53 (12H, m), 7.45-7.27 (12H, m), 6.95 (2H, d, J=8.8 Hz), 5.36 (s, 2H), 4.08 (4H, t, J=6.6 Hz), 4.10 (4H, t, J=6.6 Hz), 1.93-1.78 (8H, m), 1.54-1.24 (72H, m), 0.92-0.84 (12H, m);

Elemental analysis (C₁₀₁H₁₃₂O₁₃, M=1554.12) - Calculated: C(78.06%), H(8.56%). Found: C(78.14%), H(8.49%)

1d; Yield 85%

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 8.92 (1H, d, J=2.2 Hz), 8.40 (1H, dd, J₁=2.6 Hz, J₂=8.8 Hz), 7.68-7.52 (10H, m), 7.43 (4H, s), 7.38-7.26 (12H, m), 5.36 (s, 2H), 4.12-4.04 (12H, m), 1.91-1.71 (12H, m), 1.58-1.20 (108H, m), 0.91-0.85 (18H, m);

Elemental analysis (C₁₂₅H₁₈₀O₁₅, M=1922.76) - Calculated: C(78.08%), H(9.44%). Found: C(78.00%), H(9.49%)

1e; Yield 72%

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 8.92 (1H, d, J=2.6 Hz), 8.39 (1H, dd, J₁=2.4 Hz, J₂=8.9 Hz), 7.68-7.53 (10H, m), 7.43-7.26 (16H, m), 5.36 (s, 2H), 4.09-4.03 (12H, m), 1.80-1.73 (12H, m), 1.57-1.22 (156H, m), 0.91-0.85 (18H, m);

Elemental analysis (C₁₄₉H₂₂₈O₁₅, M=2259.40) - Calculated: C(79.21%), H(10.17%). Found: C(79.05%), H(10.12%)

Representative synthesis for compounds of Series 2*Synthesis of 4-(hydroxy)-isophthalic acid bis[4'-(4-dodecyloxybenzoyloxybiphenyl-4-yl)] ester (2a)*

Compound **1a** (3.6g, 3.1 mmol) was dissolved in mixture of solvents: absolute ethanol (100mL) / dried tetrahydrofuran (25 mL) and catalytic amount of Pd/C (20 mg) was added. That prepared mixture was stirred under hydrogen atmosphere at room temperature for 12h. After that time reaction was finished; inorganic residue was filtrated out on celite pad, solvent was removed under vacuum and the product was crystallized from methanol to afford 3.2g pure compound **2a**.

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 11.06 (1H, s), 9.02 (1H, d, J=2.2 Hz), 8.40 (dd, 1H, J₁=2.2 Hz, J₂=8.6 Hz), 8.17 (4H, d, J=8.8 Hz), 7.71-7.62 (8H, m), 7.36-7.26 (8H, m), 7.19 (1H, d, J=8.7 Hz), 6.98 (4H, d, J=8.8 Hz), 4.06 (4H, t, J=6.8 Hz), 1.86-1.76 (4H, m), 1.58-1.19 (36H, m), 0.89 (6H, t, J=6.9 Hz);

¹³C-NMR (CDCl₃, 50 MHz): δ (ppm): 168.35, 164.41, 164.15, 162.17, 159.93, 153.22, 132.15, 131.85, 129.89, 128.41, 127.55, 126.79, 121.70, 120.98, 114.50, 112.00, 68.35, 32.32, 29.56, 29.38, 28.79, 26.20, 22.51, 14.08;

Elemental analysis (C₇₀H₇₈O₁₁, M=1095.36) - Calculated: C(76.76%), H(7.18%). Found: C(76.90%), H(7.30%).

Analytical data for other compounds of series 2**2b; Yield 95%**

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 11.06 (1H, s), 9.02 (1H, d, J=2.4 Hz), 8.40 (1H, dd, J₁=2.4 Hz, J₂=8.9 Hz), 8.16 (4H, d, J=8.7 Hz), 7.68-7.61 (8H, m), 7.30-7.22 (8H, m), 7.19 (1H, d, J=8.8 Hz), 6.97 (4H, d, J=8.8 Hz), 4.08 (4H, t, J=6.7 Hz), 1.80-1.71 (4H, m), 1.59-1.20 (52H, m), 0.89 (6H, t, J=6.7 Hz);

Elemental analysis (C₇₈H₉₄O₁₁, M=1207.57) - Calculated: C(77.58%), H(7.85%). Found: C(77.68%), H(7.79%)

2c; Yield 95%

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 11.07 (1H, s), 9.02 (1H, d, J=2.2 Hz), 8.40 (1H, dd, J₁=2.2 Hz, J₂=8.6 Hz), 7.84 (2H, dd, J₁=2.0 Hz, J₂=8.4 Hz), 7.71-7.63 (10H, m), 7.36-7.29 (8H, m), 7.19 (1H, d, J=8.8 Hz), 6.95 (2H, d, J=8.6 Hz), 4.09 (4H, t, J=6.4 Hz), 4.08 (4H, t, J=6.8 Hz), 1.88-1.78 (8H, m), 1.54-1.24 (72H, m), 0.92-0.85 (12H, m);

Elemental analysis (C₉₄H₁₂₆O₁₃, M=1463.00) - Calculated: C(77.12%), H(8.67%). Found: C(77.22%), H(8.59%)

2d; Yield 96%

¹H-NMR (CDCl₃, 200 MHz): δ (ppm) 11.07 (1H, s), 9.02 (1H, d, J=2.2 Hz), 8.41 (1H, dd, J₁=2.2 Hz, J₂=8.8 Hz), 7.72-7.64 (8H, m), 7.44 (4H, s), 7.37-7.18 (9H, m) 4.10-4.04 (12H, m), 1.89-1.72 (12H, m), 1.59-1.22 (156H, m), 0.92-0.86 (18H, m);

Elemental analysis (C₁₄₂H₂₂₂O₁₅, M=2169.27) - Calculated: C(78.62%), H(10.32%). Found: C(78.55%), H(10.25%)

References

1. E. Gorecka, D. Pocięcha, J. Mieczkowski, J. Matraszek, D. Guillon and B. Donnio, *J. Am. Chem. Soc.*, **126**, 15946 - 15947, (2004).
2. J. Matraszek, J. Mieczkowski, D. Pocięcha, E. Gorecka, B. Donnio and D. Guillon, *Chem. Eur. J.*, **13**, 3377, (2007).
3. M. Wojcik, W. Lewandowski, J. Matraszek, J. Mieczkowski, J. Borysiuk, D. Pocięcha, E. Gorecka, *Angew. Chem. Int. Ed.* **48**, 5167-5169, (2009)

Table S1 Observed and calculated positions of xrd signals for cubic phase of compound **1c** at T = 110 °C. For indexing and calculations a crystallographic lattice with Ia3d symmetry and unit cell parameter a = 124.8 Å was assumed.

d_{obs}	(hkl)	d_{calc}
50.94	(211)	50.94
44.14	(022)	44.12
33.26	(321)	33.35
31.17	(004)	31.20
27.92	(042)	27.90
26.62	(332)	26.60
25.53	(422)	25.47

Table S2 Observed and calculated positions of xrd signals for two LC phases of compound **2a**, B₇ at T = 220 °C and simple lamellar at T = 175 °C. For indexing of B₇ phase pattern an oblique crystallographic unit cell was assumed, with parameters a = 166.0 Å, c = 50.6 Å and β = 111.2 deg.

T = 220 °C, B₇ phase			T = 175 °C, lamellar phase		
d_{obs}	(hl)	d_{calc}	d_{obs}	(hl)	d_{calc}
156.2	(10)	154.8	48.31	(01)	
50.70	(-11)	50.53	24.22	(02)	24.16
47.23	(01)	47.20			
40.80	(11)	41.18			
24.83	(-12)	24.70			
23.57	(02)	23.60			

Table S3 Observed and calculated positions of xrd signals for LC phases of compound **2c**. Unit cell parameters: in Col_h phase – $p6$ symmetry (2D), $a = 56.73\text{Å}$; in B_{3D} phase – $P1$ symmetry (3D), $a = 83.67\text{Å}$, $b = 61.79\text{Å}$, $c = 50.6\text{Å}$, $\alpha = 95.66\text{ deg.}$, $\beta = 122.84\text{ deg.}$ and $\gamma = 96.71\text{ deg.}$; in B_{1rev} phase – $p2$ symmetry (2D), $a = 72.5\text{Å}$, $c = 54.8\text{Å}$ and $\beta = 113.7\text{ deg.}$

T = 130 °C, Col_h phase			T = 120 °C, B_{3D} phase			T = 95 °C, B_{1rev} phase		
d_{obs}	(h l)	d_{calc}	d_{obs}	(hkl)	d_{calc}	d_{obs}	(h l)	d_{calc}
49.13	(10)	49.13	68.84	(100)	68.83	66.54	(10)	66.40
24.41	(11)	28.36	60.20	(010)	60.20	50.9 ^a	(-11)	51.16
24.52	(20)	24.56	54.13	(-101)	54.08	50.20	(01)	50.23
			50.76	(-110)	50.72	34.02	(11)	34.02
			45.08	(001)	45.08	33.21	(20)	33.20
			39.04	(-111)	38.84	27.43	(-12)	27.42
			34.58	(2-1-1)	34.58	25.12	(02)	25.11
				(200)	34.41	22.23	(30)	22.13
			33.07	(011)	33.13			
				(2-10)	32.90			
			26.17	(-102)	26.20			
			22.54	(002)	22.54			

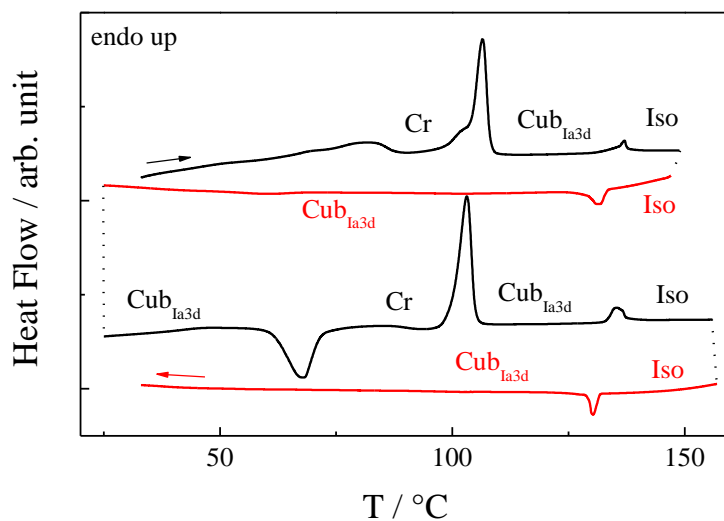


Figure S1. DSC scans for compound **1c**. The first and second heat/cool cycles are presented, evidencing that cubic phase can be easily supercooled to room temperature – it recrystallizes on consecutive heating run.

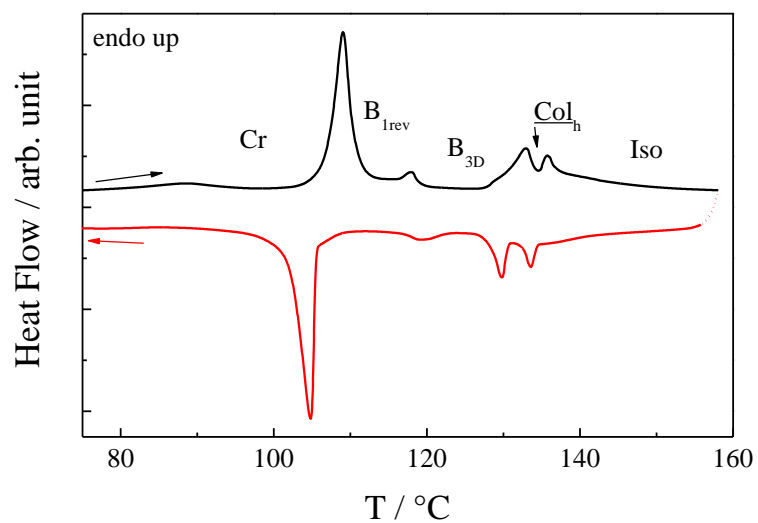


Figure S2. DSC scans for compound **2c**. It should be noted that no pronounced differences in the temperature ranges of LC phases were detected in calorimetric studies, however during x-ray diffraction experiments, performed on slow cooling ($\sim 1\text{K} / \text{hour}$) the phase transitions $B_{3\text{D}} - B_{1\text{rev}}$ and $B_{1\text{rev}} - \text{Cr}$ were shifted to lower temperatures (see Fig. 6a in the manuscript).

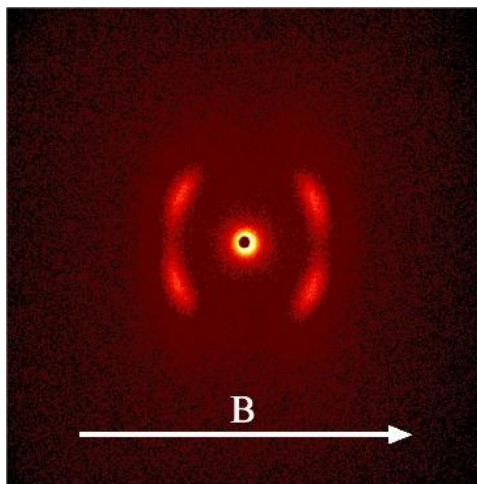


Figure S3. Small angle part of XRD pattern of compound **1a** in nematic phase, at $T = 171^\circ\text{C}$. The sample was aligned in magnetic field.

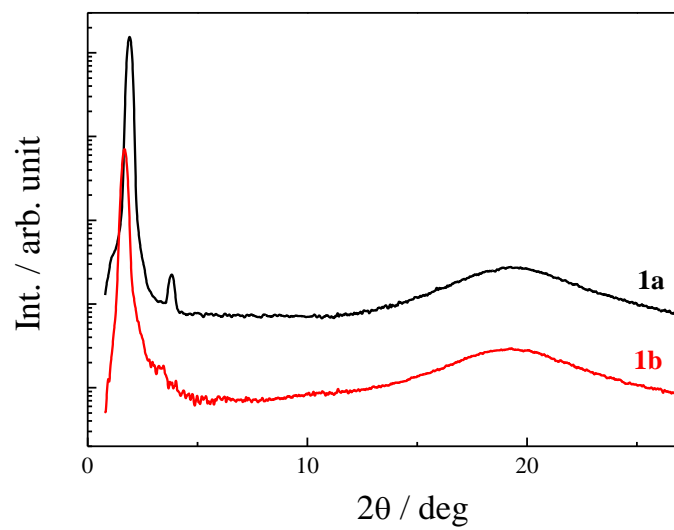


Figure S4. Broad angle x-ray diffractograms of compounds **1a** and **1b** in smectic C phase.

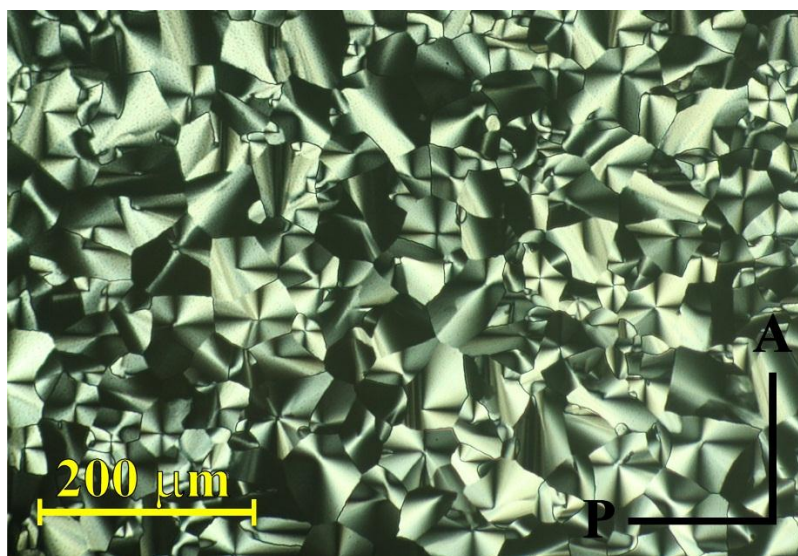


Figure S5. Optical texture of the Col_h phase of compound **1d** at $T = 100^\circ\text{C}$.

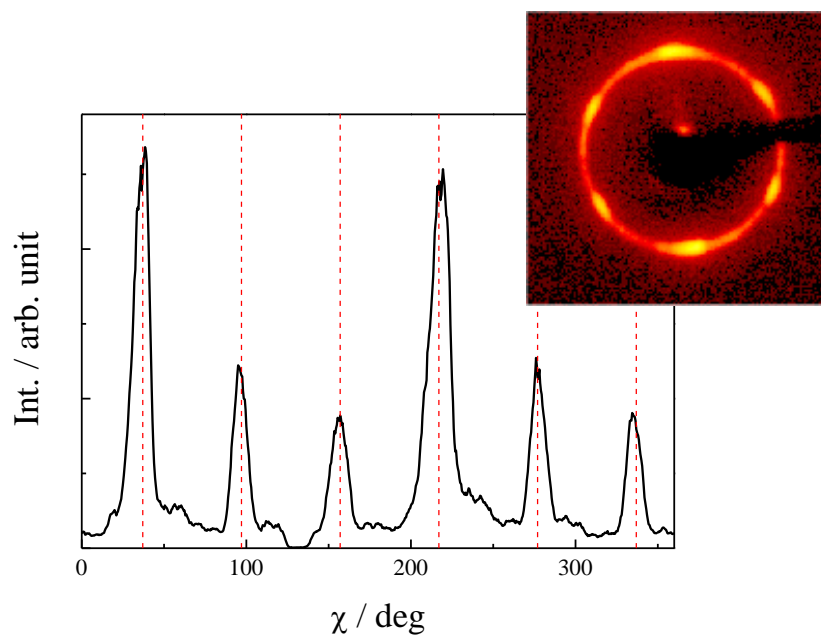


Figure S6. Intensity vs. azimuthal angle for the low angle xrd signal (10) of the Col_h phase of compound **1d**. In the inset part of the related 2D xrd pattern

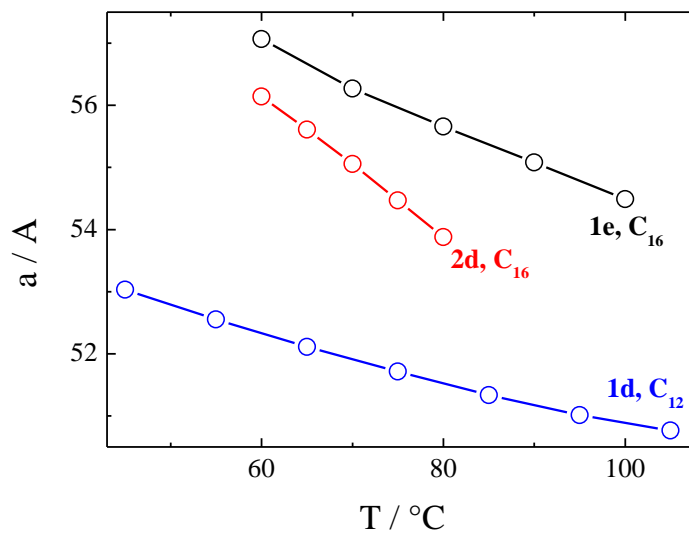


Figure S7. Temperature dependence of unit cell parameter a of the Col_h phase of compounds having three terminal chains at each banana arm.

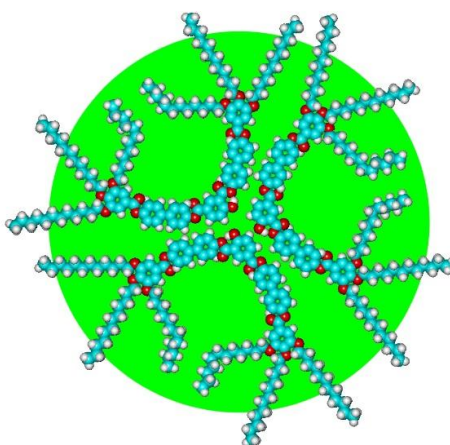


Figure S8. Schematic drawing illustrating packing of bent-core molecules into disc-like object – stacking of such objects forms columns in Col_h phases of compounds **1d**, **1e**, **2c** and **2d**.

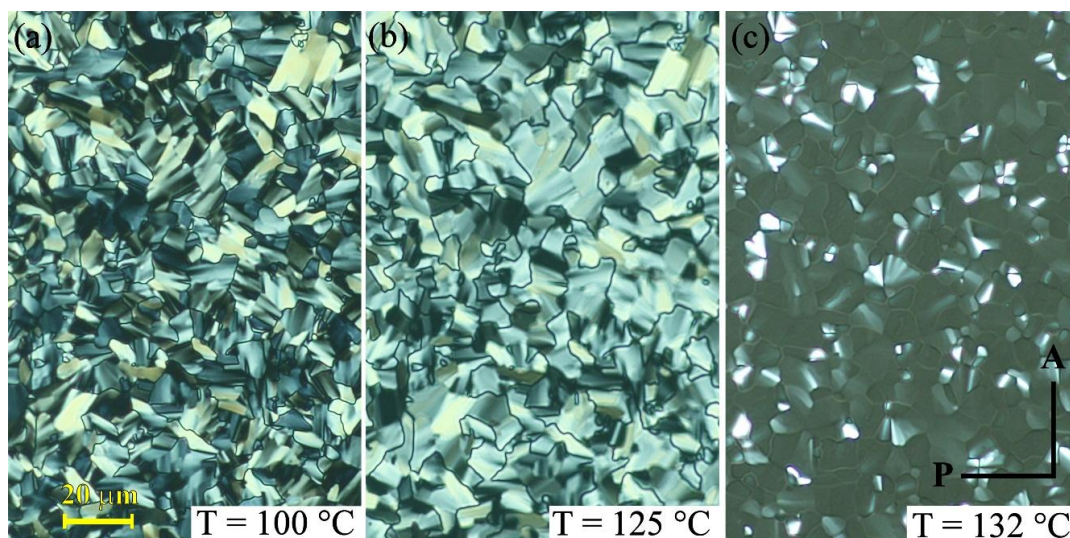


Figure S9. Optical textures of compound **2c** in 3-micron thick cell at (a) $T = 100\text{ °C}$ ($B_{1\text{rev}}$ phase), (b) $T = 125\text{ °C}$ (B_{3D} phase) and (c) $T = 132\text{ °C}$ (Col_h phase).

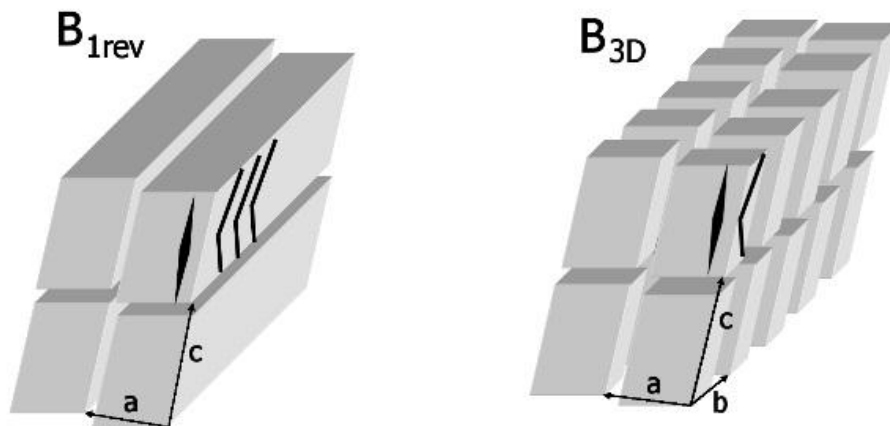


Figure S10. Schematic drawing of possible arrangement of molecular blocks in $B_{1\text{rev}}$ and B_{3D} phases.