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Molecular Factors Responsible for the Formation of the Axially Polar Columnar Mesophase Col_hP_A

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Abstract: The structure of hexacatenar bent-shape molecules has been systematically modified in order to determine the main molecular factors responsible for the appearance of the axially polar columnar mesophase. It was found that the stability of the polar phase is very sensitive to the subtle modifications of the molecular shape: the phase is solely preserved if the modification is made at the terminal parts of the mesogenic core, whilst any other modifications destabilize the phase. It can be concluded that the main factor driving the transition between the phase made of flat supramolecular discs and the axially polar phase made of the cone-like units is the ability to fulfill close packing conditions in order to eliminate voids between neighboring molecular rigid cores.

Keywords: liquid crystals · self-assembly · supramolecular chemistry · X-ray diffraction

Introduction

Generally, there are two broad classes of polar fluids. In the first class there are materials made of chiral rod-like or disc-like molecules; these materials have been studied for nearly 30 years[1] and the principles of their molecular designing are rather well understood today. The materials of the second class, discovered a few years ago,[2] are made from achiral, bent-core ("banana") molecules, in which the self-organization into polar structures appears spontaneously as a result of broken orientational symmetry. Achiral bent-core molecules form an unexpectedly rich variety of structures, a result of the interplay between polarity, nanoscopic chirality and density modulations.[3,4] The most important research in the field of "banana" molecules concentrates on studies of lamellar and broken-layer-type columnar phases that have been showed to be polar and switchable under electric field. However, recently it has been demonstrated that the polarly ordered phases can be also formed by a "supramolecular chemistry" approach in which bent-core molecules interact through noncovalent intermolecular forces to form cone-like self-assemblies.[5] This supramolecular approach is the first successful attempt to obtain polar, electrically switchable phase, despite several attempts to apply the same principle to columnar phases made of dendrimers[6] and different types of nonflat objects (mainly macrocycles).[7–17]

The columnar phases of studied bent-core polycatenar materials[5,17,18] are formed by the self-organization of few molecules packed into an overall flat discoid assembly (Col_h phase) or into a conical-shape unit (Col_hP_A phase); in both cases these elementary building blocks are stacked to form columns, which are arranged into a hexagonal lattice. The structure of the Col_h phase is non-polar while the Col_hP_A phase has antiferroelectric properties with electric polarization vectors oriented along the column axis. Inconsistency between hexagonal lattice of columns and antiferroelectricity of the whole structure is solved by appearance of additional superstructure: the columns are broken along their axis into blocks having ferroelectric order and the direction of polarization alternates between the blocks.[5,17,18] In an external electric field the polarization vectors switch by the collective re-orientation of the molecules forming supramolecular cones, the measured value of spontaneous polarization being typically $\approx 200\,nC\,cm^{-2}$. The Col_h–Col_hP_A phase transition can be easily detected by the optical methods (Figure 1). There is a pronounced decrease of the optical birefringence for the light propagating perpendicularly to the column axis, as the deformations of flat discs into cones in-

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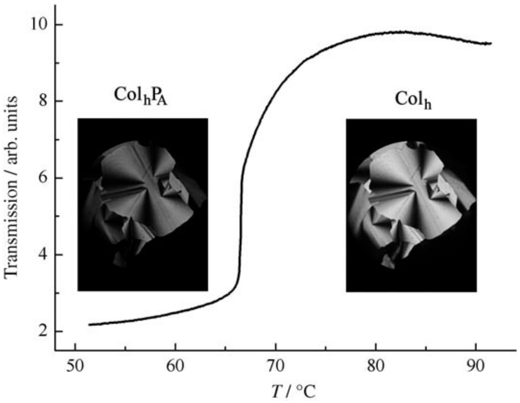


Figure 1. Light transmission through the circular domain, measured as a function of temperature for compound **9b** in three micron cell, reveals a decrease of optical birefringence at Col$_h$–Col$_h$P$_A$ phase transition. In the inset the texture of Col$_h$ and Col$_h$P$_A$ phases.

creases the refractive index along the columnar axis but decreases the refractive index perpendicular to the columnar axis.[18] The phase transition is also accompanied by noticeable softening of the dielectric response in the Col$_h$ phase due to the formation of the polarly ordered lower temperature phase.[18]

Our current aim was to identify some of the molecular factors driving the formation of the conical phase as well as describing the influence of the molecular modifications on the phase stability. In order to carry out this systematic study, 28 new polycatenar bent-shaped compounds were prepared, grouped into three main families (compounds **1**–**8**, **9** and **10**), depending on the structural modifications.

Results and Discussion

The phase sequences, phase transition temperatures and thermal effects, as well as the crystallographic unit cell parameters for the studied compounds are given in Table 1. The molecules of the basic homologues series, compounds **1a**–**f**, have a pyridine central ring linked by ethylene spacers to four-ring phenyl-biphenyl-phenyl branches. At the terminal phenyl ring three alkyl chains are attached, to ensure the tendency for large curvature of the column interface. Based on the X-ray diffraction (XRD) data and assuming a density close to 1 g cm^{-3} in the mesophase for these compounds, it was deduced that about 3–4 molecules self-assemble to form the elementary columnar stratum, which corresponds to 18–24 alkyl chains in the outer coat of the column. The dependence of column diameter, D, on the number of carbon atoms in terminal alkyl chains, n, $-\mathrm{d}D/\mathrm{d}n \approx 1$ Å suggests that there is roughly constant ratio of interdigitated part of the chains with respect to their overall length. All homologues, **1a**–**f**, show the Col$_h$–Col$_h$P$_A$ phase transition at which the diameter of the column decreases in accordance with the proposed model for this phase transition.[5] Moreover, electron density maps computed from XRD data, in which all the structure factors were taken positive, as $F = I^{1/2}$, reveal much sharper profiles in Col$_h$P$_A$ phase than in Col$_h$ phase. This shows that in Col$_h$P$_A$ phase concentration of the mass increases near the column axis (Figure 2).

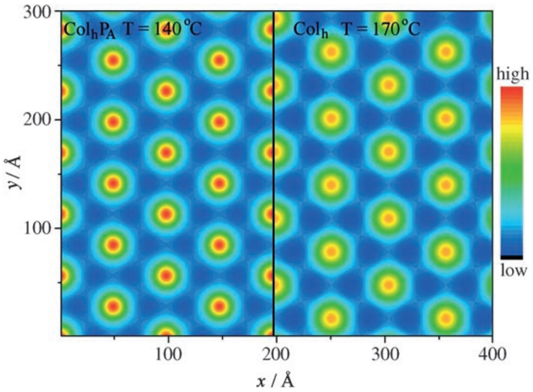


Figure 2. Electron density maps obtained in the plane perpendicular to the column axis in Col$_h$ and Col$_h$P$_A$ phases for compound **1a**. The relative intensities of XRD signals used for electron density calculations were, in Col$_h$ phase: $I_{10}/I_{11}/I_{20}$ 130:1:2; in Col$_h$P$_A$: $I_{10}/I_{11}/I_{20}/I_{21}$ 130:10:10:2.

In order to recognize and identify the possible factors responsible for the "conical" phase formation, several modifications were made at the basic molecular structure level, though preserving the overall molecular motif of **1**. The outer, inner and central parts of molecule were independently modified, the modifications included selective chlorination (**2**–**4**, **6**), methylation (**5**) and changes of terminal alkyl chain number (**7**) or the length of "banana" branches (**8**). It was found that the only modification preserving the "conical" phase is the substitution at the most outer part of molecular core. If one halogen atom is substituted at each outer phenyl ring, compounds **2a** and **2b**, the phase transition temperatures subtly decrease and the phase sequence remains unchanged. This substitution only slightly increases the column diameter of both the Col$_h$ and the Col$_h$P$_A$ phases, showing that the basic structure of the column stratum is not affected. Moreover, while the substitution of two halogen atoms at each of the most outer rings (compound **3**) does not change the columnar structure and phase sequence, the phase transition temperatures being significantly lowered, the substitution of halogen atom at any inner ring of the molecular branch (compounds **4a**–**c**) destabilizes totally the conical phase: the apolar columnar hexagonal phase is observed exclusively over a broad temperature range. The presence of a methyl group at the central ring at position 4 (compounds **5a** and **5b**) or halogen atom at position 3 (compound **6**) also prevents the conical phase appearance, likely due to steric hindrances. Decreasing the number of terminal alkyl chains (compounds **7a** and **7b**) makes the melting and clearing temperatures very high, that forbids further systematic studies of these tetracatenar materials, but it seems that the conical phase is also formed in this case. Finally, decreasing the banana branch length by one phenyl ring (com-

Table 1. Phase sequence with phase transition temperatures (°C) and thermal effects (in parentheses, $J\,g^{-1}$) for studied compounds. Also crystallographic unit cell parameters are given. Col_X is unidentified columnar phase.

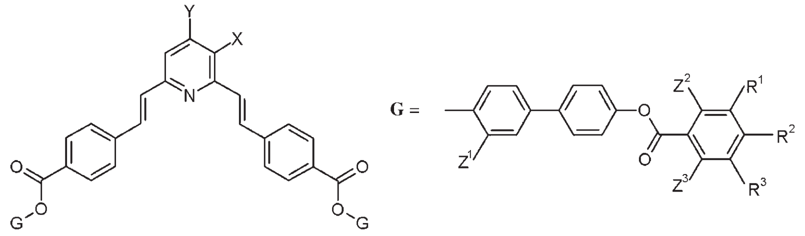
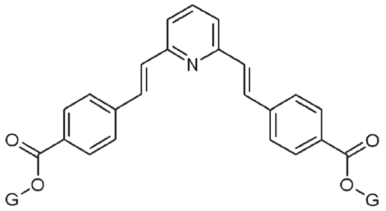
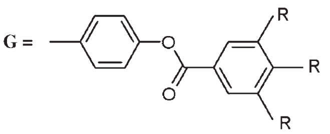
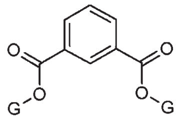
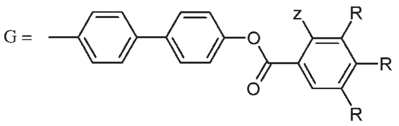
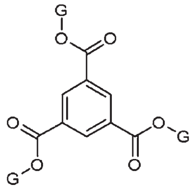
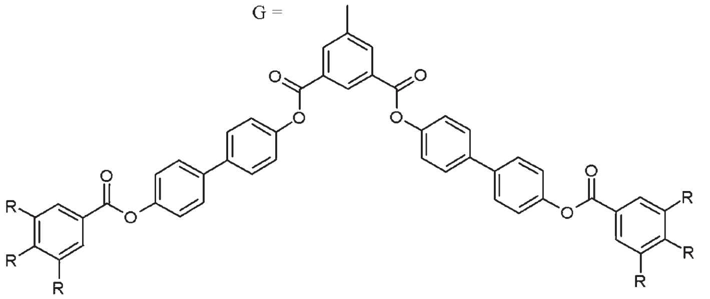
	R	Phase sequence	Unit cell parameters
			
$X=Y=H$, $R^1=R^2=R^3=R$, $Z^1=Z^2=Z^3=H$			
1a	OC_8H_{17}	Cr 89.6 (11.6) Col_X 128.1 (0.1) Col_hP_A 147.3 (1.8) Col_h 189.5 (1.0) I	Col_h: $a=61.4$ Å Col_hP_A: $a=56.5$ Å
1b	$OC_{10}H_{21}$	Cr 72.1(3.1) Col_X 82.2 (0.1) Col_hP_A 118.5 (2.0) Col_h 196.4 (0.4) I	Col_h: $a=63.0$ Å Col_hP_A: $a=61.7$ Å
1c	$OC_{12}H_{25}$	Cr 65.0 (15.5) Col_X 83.8 (6.6) Col_hP_A 137.2 (1.5) Col_h 197.4 (1.2) I	Col_h: $a=63.5$ Å Col_hP_A: $a=59.7$ Å
1d	$OC_{14}H_{29}$	Cr 34.0 (17.1) Col_X 83.7 (6.5) Col_hP_A 122.5 (1.1) Col_h 187.3 (0.9) I	Col_h: $a=64.4$ Å Col_hP_A: $a=61.3$ Å
1e	$OC_{15}H_{31}$	Cr 62.5 (25.6) Col_X 88.6 (7.7) Col_hP_A 128.5 (1.8) Col_h 187.2 (1.0) I	Col_h: $a=66.6$ Å Col_hP_A: $a=63.3$ Å
1f	$OC_{16}H_{33}$	Cr 58.2 (20.3) Col_X 90.2 (8.2) Col_hP_A 123.2 (1.5) Col_h 174.0 (0.9) I	Col_h: $a=68.5$ Å Col_hP_A: $a=65.0$ Å
$X=Y=H$, $R^1=R^2=R^3=R$, $Z^1=Z^2=H$, $Z^3=Cl$			
2a	$OC_{12}H_{25}$	Cr <50 Col_hP_A 135.6 (1.1) Col_h 192.4 (1.1) I	
2b	$OC_{14}H_{29}$	Cr 54.6 (0.4) Col_X 101.7 (0.05) Col_hP_A 123.5 (0.9) Col_h 185.8 (1.1) I	Col_h: $a=66.1$ Å Col_hP_A: $a=65.2$ Å
$X=Y=H$, $R^1=R^2=R^3=R$, $Z^1=H$, $Z^2=Z^3=Cl$			
3	$OC_{14}H_{29}$	Cr 80.2 (20.6) Col_X 95.5 (0.1) Col_hP_A 109.8 (0.5) Col_h 139.6 (0.3) I	Col_h: $a=64.9$ Å Col_hP_A: $a=61.8$ Å
$X=Y=H$, $R^1=R^2=R^3=R$, $Z^1=Z^2=Cl$, $Z^3=H$			
4a	$OC_{12}H_{25}$	Cr 101.4 (17.8) Col_h 140.1 (1.0) I	Col_h: $a=57.7$ Å
4b	$OC_{14}H_{29}$	Cr 98.6 (17.3) Col_h 138.4 (1.0) I	Col_h: $a=66.8$ Å
4c	$OC_{16}H_{33}$	Cr 89.4 (9.5) Col_h 119.1 (1.3) I	Col_h: $a=68.5$ Å
$X=H$, $Y=CH_3$, $R_1=R_2=R_3=R$, $Z_1=Z_2=Z_3=H$			
5a	$OC_{14}H_{29}$	Cr 100.1 (6.5) Col_h 168.4 (2.2) I	
5b	$OC_{16}H_{33}$	Cr 93.9 (3.4) Col_h 161.6 (0.9) I	Col_h: $a=66.8$ Å
$X=Cl$, $Y=H$, $R^1=R^2=R^3=R$, $Z^1=Z^2=Z^3=H$			

Table 1. (Continued)

	R		Phase sequence	Unit cell parameters
6	OC_8H_{17}		Cr 43.2 (9.6) Col$_h$ 160.1 (0.5) I	Col$_h$: $a=66.8$ Å
$X=Y=H, R^1=R^2=R, R^3=H, Z^1=Z^2=Z^3=H$				
7a	$OC_{12}H_{25}$		Col$_h$P$_A$–Col$_h$ >250 I	
7b	$OC_{14}H_{29}$		Col$_h$P$_A$–Col$_h$ >250 I	
 				
8a	OC_8H_{17}		Cr 97.5 (13.9) [Col$_h$ 94.6 (0.6)] I	
8b	$OC_{12}H_{25}$		Cr 85.3 (6.7) Col$_h$ 108.8 (0.9) I	Col$_h$: $a=56.7$ Å
 				
9a	OC_8H_{17}	Z=H	Cr 104.0 (48.2) I	
9b	$OC_{10}H_{21}$	Z=H	Cr 46.4 (20.0) Col$_h$P$_A$ 66.4 (1.2) Col$_h$ 107.4 (2.1) I	Col$_h$: $a=51.1$ Å Col$_h$P$_A$: $a=49.2$ Å
9c	$OC_{12}H_{25}$	Z=H	Cr 39.4 (25.6) Col$_h$P$_A$ 62.0 (1.0) Col$_h$ 109.1 (1.8) I	
9d	$OC_{15}H_{31}$	Z=H	Cr 53.4 (10.9) Col$_h$P$_A$ 63.3 (0.8) Col$_h$ 105.1 (0.9) I	Col$_h$: $a=55.5$ Å Col$_h$P$_A$: $a=55.5$ Å
9e	$OC_{16}H_{33}$	Z=H	Cr 46.4 (20.0) Col$_h$P$_A$ 66.4 (1.2) Col$_h$ 107.4 (2.1) I	
9f	$OC_{14}H_{29}$	Z=Cl	Cr 61.1 (49.0) Col$_h$P$_A$ 63.3 (0.5) Col$_h$ 103.9 (2.0) I	
 				
10a	OC_8H_{17}		Cr 148.1 (2.1) Col$_h$ 240.7 (4.8) I	Col$_h$: $a=49.9$ Å
10b	$OC_{10}H_{21}$		Cr 139.4 (4.9) Col$_h$ 236.9 (1.6) I	
10c	$OC_{12}H_{25}$		Cr 69.9 (27.7) Col$_h$ 200.5 (0.3) I	Col$_h$: $a=54.8$ Å

pounds **8a** and **8b**) results in the monotropic appearance of the apolar hexagonal phase, whilst the conical phase is completely destabilized.

The liquid crystalline behavior of this first family, compounds **1**--**8**, brings some interesting preliminary conclusions. It seems that the formation of the "conical", Col$_h$P$_A$ phase is driven mainly by the tendency of molecules to ensure the optimal close packing conditions. At higher temperature, the molecules self-assemble into supramolecular discs, leaving some voids between the molecular branches (these voids are obviously filled by the lower and upper molecular strata), whereas lowering the temperature results in the filling up of these voids by bringing the branches together, which is achieved by the deformation of the flat discs into supramolecular cones (Figure 3). This is consistent with obtained electron density profiles (Figure 2). Apparently, any bulky substituent at the banana branches renders the tilting, which is necessary for cone formation, difficult due to the steric hindrances. On the contrary, structural modifications at the outer part of the molecule, where the packing of molecular fragments in the column stratum is more flexible, provide still favorable conditions for creation of supramolecular cones.

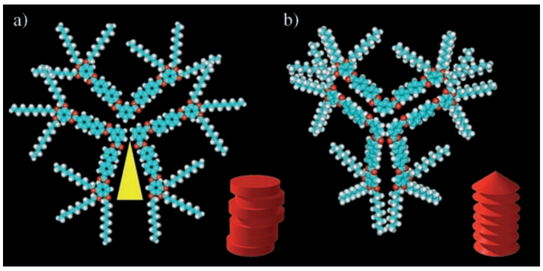


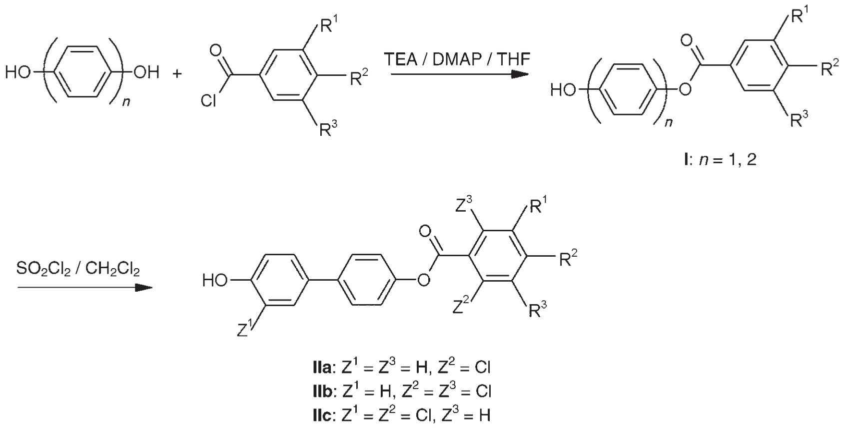
Figure 3. Supramolecular assemblies of molecules forming column stratum in the Col$_{\mathrm{h}}$ (a) and the Col$_{\mathrm{h}}$P$_{\mathrm{A}}$ (b) phases. Note that the voids between molecules, marked as yellow triangle in a) are considerably smaller due to tilting of the molecules and forming conical structure in b). The schematic side views of the columns in Col$_{\mathrm{h}}$ and Col$_{\mathrm{h}}$P$_{\mathrm{A}}$ phases are also shown.

Formation of the cones is only possible if there is some flexibility in the molecular arrangement. In order to prove this statement the compounds **9** and **10** were prepared. Compounds **9** are also bent-core hexacatenars, having the banana branches linked with the central phenyl ring by ester groups. Similarly to compounds **1a–f**, the Col$_{\mathrm{h}}$–Col$_{\mathrm{h}}$P$_{\mathrm{A}}$ phases sequence is restored. The clearing and melting temperatures are much lower for materials **9a–e** than for compounds of basic series **1a–f**, likely due to the smaller size of the branches. The XRD studies show that for compounds **9** the column diameter decrease at the phase transition from Col$_{\mathrm{h}}$ to Col$_{\mathrm{h}}$P$_{\mathrm{A}}$ phase is much less pronounced than in materials **1** and **2**. The number of molecules forming the elementary columnar stratum in both phases is about 3–4, the same as in compounds **1** and **2**.

If, instead of a supramolecular arrangement into discs or cones, the overall shape of the columnar unit is imposed by a single molecule, that is, results from the covalent linking of three banana units (compounds **10a–c**) through an trivalent core (trimesic acid), the "conical" phase is not formed and only a columnar hexagonal phase is observed in a broad temperature range, as expected.[19] Apparently covalently bonded banana shaped molecular fragments have not enough flexibility to tilt and to form cones.

Synthesis

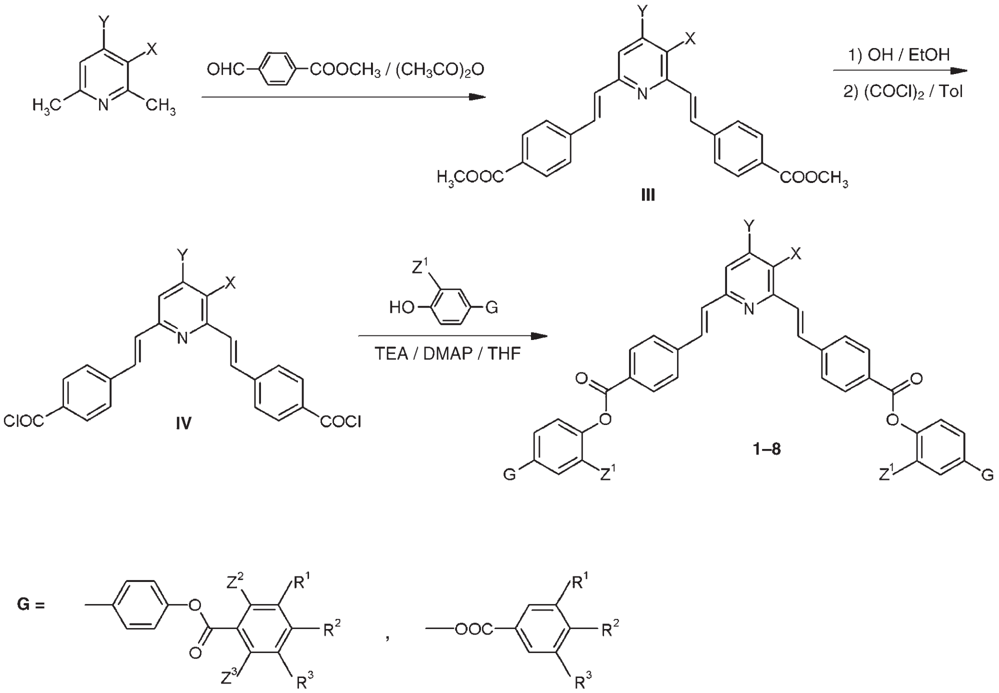
Synthetic route of banana branches is described in Scheme 1. Esterification of hydroquinone or 4,4′-dihydroxybiphenyl with 3,4,5-trialkoxybenzoyl chloride in standard conditions gave different arms segments (**I**). The lateral chlorine substituents were introduced in phenylene rings by electrophilic substitution by the action of sulfuryl chloride. The chlorination reaction was very interesting and surprising. In this case, reversed regioselectivity was observed and as a result, the chloro substituent was mainly attached into the position 2 in phenylene ring of gallic acid moiety. Beside the major monosubstituted product **IIa**, two disubstituted compounds were also obtained: the first one with two chlorine atoms in the phenyl ring of the gallic acid part (Z2 and Z3, **IIb**), and the other one, 3′-chloro-4′-hydroxybiphenyl-4-[2-chloro-3,4,5-tri(alkoxy)] benzoate, with the chlorine atoms in Z1 and Z2 positions (**IIc**). This regioselectivity can be explained by the formation of the sulfuryl ester intermediate in the first step of the reaction concomittant with the decreasing activity of hydroxy group; thereby new reaction center becomes active.



Scheme 1. Synthesis of the bent-shape molecules side-arms.

Compounds of the first family, namely compounds **1–8** were obtained according to the synthetic route shown in Scheme 2. The first step of the synthesis was the condensation of 2,6-lutidine derivatives with methyl 4-formylbenzoate, followed by the transformation of the resulting diester **III** into the acid chloride **IV**; the final compounds **1–8** were synthesised by esterification of the bent-core acid chlorides with the appropriate hydroxy group-conatining side arms (**I** and **II**). Detailed of this procedure was described in a previous paper.[5]

The chloro substituent (compound **6**) was attached to the central core according to the procedure reported in the liter-



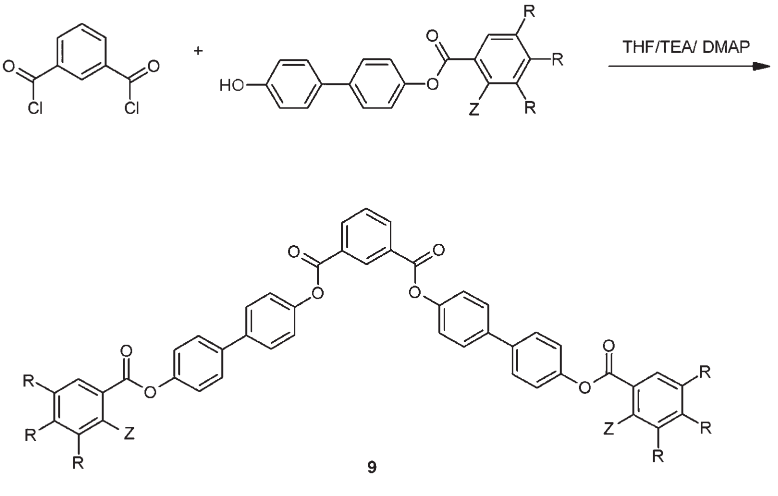
Scheme 2. Synthetic procedures of bent-shape molecules **1**–**8**.

ature,[20] while 4-methylpyridine (for compound **5**) is commercially available.

The synthesis of compounds **9** was based on the esterification of the side-arms **I** ($n=2$) and **IIa** with isophthaloyl chloride (Scheme 3). Scheme 4 outlines the reaction chain leading to discotic compounds **10**. In the first step, the hydroxy group of dimethyl 5-hydroxyisophthalate was protected and the ester moieties were then hydrolyzed. The obtained organic salt was converted into acid chloride and this compound was esterified with the beforehand synthesised branches (**I**, $n=2$) to yield bent-shape compounds **VI**. After removal of the protecting benzyl group by catalytic hydrogenation, the resulting hydroxy-containing bent-shape molecules **VII** were connected with benzene-1,3,5-tricarbonyl chloride to give the mesogenic star-shaped compounds **10**.

Conclusion

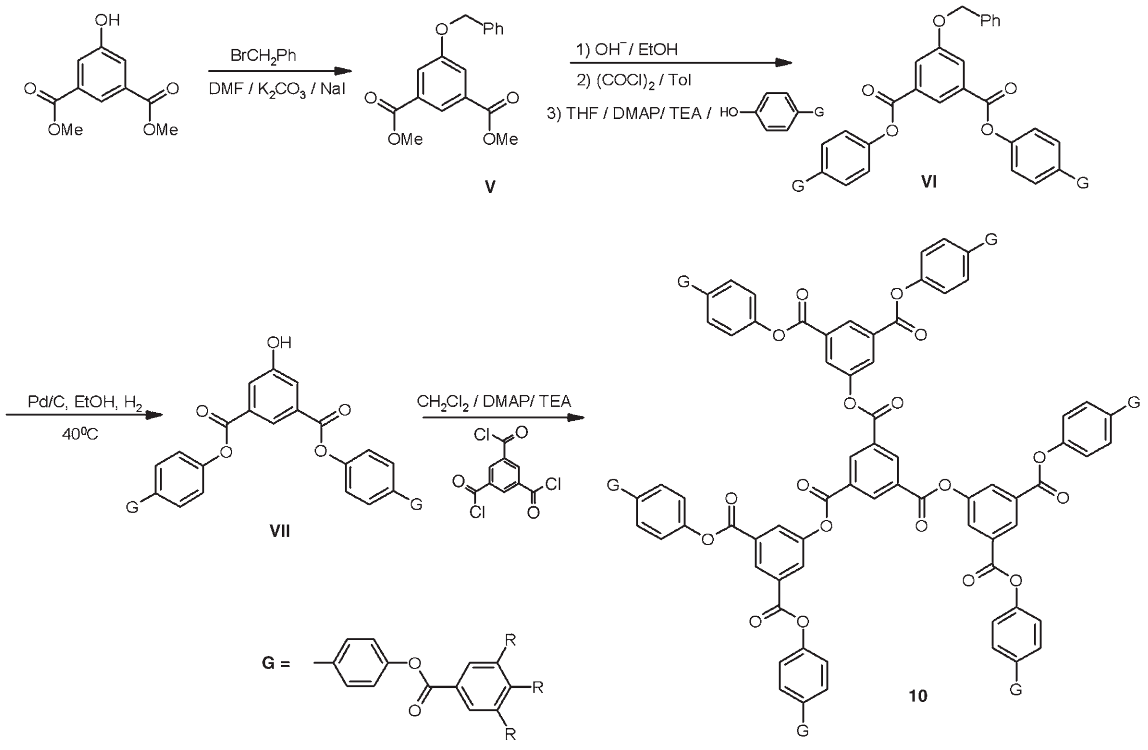
In order to form the axially polar $\mathrm{Col_hP_A}$ phase, a few banana molecules have to self-organize into units able to fill the column stratum. If the shape of the molecule does not allow for an efficient filling of a disc space, then at lowering temperature the molecules tilt to form cones to assure the close molecular packing. This is however only possible if the molecules form supramolecular, flexible aggregates and if the steric hindrances between the molecules are weak.



Scheme 3. Synthesis of bent-shape materials **9**.

Experimental Section

General methods: Compounds structure and purity were confirmed by TLC chromatography, ^{1}H NMR, ^{13}C NMR spectroscopies and elemental analysis. NMR spectra were recorded on the Varian Unity Plus spectrometer operating at 200 or 500 MHz for ^{1}H NMR and at 50 or 125 MHz for ^{13}C NMR. Tetramethylsilane was used as an internal standard. Chemical shifts are reported in ppm. TLC analyses were performed on Merck 60 silica gel glass plates and visualized using iodine vapor and UV light. Column chromatography was carried



Scheme 4. Synthetic procedures of star-shaped molecules **10**.

out at atmospheric pressure using silica gel (100–200 mesh, Merck). Elemental analyses were performed to confirm the expected molecular structure.

The following synthetic procedures are shown for representative compounds. The other compounds of the same series were obtained analogously under the same reaction conditions and mol ratio of substrates. The ^{1}H and ^{13}C NMR spectra and elemental analyses were performed for all compounds but only representative results are quoted.

Representative procedure for synthesis side-arms (I)

4′-Hydroxybiphenyl 4-[3,4,5-tri(tetradecyloxy)]benzoate (I, *n*=2): 4,4′-Dihydroxybiphenyl (14.9 g, 0.08 mol) and DMAP (40 mg) were dissolved in the mixture of tetrahydrofuran (100 mL) and triethylamine (20 mL), then 3,4,5-tri(tetradecyloxy)-benzoyl chloride (38.84 g, 0.05 mol) was added slowly. The reaction mixture was heated under reflux for 6 h. After removal of the solvents under vacuum the product was separated on column chromatography, on silica gel eluted with toluene. The pure compound was obtained (22.9 g, 52 %). ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.56 (d, 2 H, J=8.4 Hz), 7.46 (d, 2 H, J=8.8 Hz), 7.42 (s, 2 H), 7.23 (d, 2 H, J=8.4 Hz), 6.88 (d, 2 H, J=8.4 Hz), 4.96 (s, 1 H), 4.08–4.02 (m, 6 H), 1.87–1.73 (m, 6 H), 1.57–1.10 (m, 66 H), 0.7 ppm (m, 9 H); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 165.25, 155.18, 152.97, 149.99, 143.50, 138.57, 133.12, 128.39, 128.37, 127.76, 127.36, 123.87, 121.98, 121.89, 115.68, 108.57, 73.61, 69.27, 31.95, 31.93, 30.35, 29.77, 29.76, 29.72, 29.70, 29.67, 29.65, 29.58, 29.41, 29.40, 29.38, 29.30, 26.09, 26.07, 22.70, 14.13 ppm; elemental analysis calcd (%) for $C_{61}H_{98}O_6$ (927.44): C 79.00, H 10.65; found: C 78.91, H 10.75.

Representative procedure for introducing lateral chlorine substituents to side-arms (II)

4′-Hydroxybiphenyl 4-[2-chloro-3,4,5-tri(tetradecyloxy)]benzoate (IIa), 4′-hydroxybiphenyl 4-[2,6-dichloro-3,4,5-tri(tetradecyloxy)]benzoate (IIb) and 3′-chloro-4′-hydroxybiphenyl 4-[2-chloro-3,4,5-tri(tetradecyloxy)]benzoate (IIc): Sulfuryl chloride (1.0 mL, 13 mmol) was added to a stirred solution of 4′-hydroxybiphenyl 4-[3,4,5-tri(tetradecyloxy)]benzoate (10.0 g, 10.8 mmol) in dichloromethane (250 mL). Stirring was continued for 12 h. Solvent was evaporated and products were isolated on column chromatography, on silica gel eluted with toluene. Compounds were eluted in sequence **IIc**, **IIb** and **IIa**. The last compound was the main product and it was obtained in 36 % yield (3.73 g). Products **IIb** and **IIc** was separated in 5 % (0.53 g) and 10 % (1.08 g) yield, respectively.

Analytical data for compound **IIa**: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.55 (d, 2 H, J=9.0 Hz), 7.42 (d, 2 H, J=8.5 Hz), 7.37 (s, 1 H), 7.26 (d, 2 H, J=8.5 Hz), 6.85 (d, 2 H, J=8.5 Hz), 4.09 (t, 2 H, J=6.5 Hz), 4.05 (t, 2 H, J=7.0 Hz), 4.03 (t, 2 H, J=6.5 Hz), 3.50 (s, 1 H), 1.88–1.76 (m, 6 H), 1.54–1.44 (m, 6 H), 1.40–1.26 (m, 60 H), 0.90–0.86 ppm (m, 9 H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 164.48, 155.39, 151.53, 150.52, 149.65, 146.81, 138.89, 132.86, 128.34, 127.77, 123.79, 122.06, 121.89, 115.70, 111.01, 74.31, 74.16, 69.19, 31.96, 31.95, 30.30, 30.20, 29.76, 29.72, 29.69, 29.65, 29.63, 29.53, 29.49, 29.41, 29.39, 29.21, 26.09, 26.04, 26.01, 22.71, 14.14 ppm; elemental analysis calcd (%) for $C_{61}H_{97}ClO_6$ (961.87): C 76.17, H 10.16, Cl 3.69; found: C 76.25, H 10.25, Cl 3.55.

Analytical data for compound **IIb**: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.57 (d, 2 H, J=9.0 Hz), 7.44 (d, 2 H, J=8.5 Hz), 7.33 (d, 2 H, J=8.0 Hz), 6.88 (d, 2 H, J=8.5 Hz), 4.08–4.03 (m, 7 H), 1.84–1.74 (m, 6 H), 1.50–1.46 (m, 6 H), 1.40–1.22 (m, 60 H), 0.89–0.86 ppm (m, 9 H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 163.40, 155.29, 149.43, 149.32, 149.14, 139.30, 133.06, 128.50, 128.45, 127.93, 121.74, 120.97, 115.72, 74.66, 74.61, 30.24, 29.76, 29.75, 29.74, 29.72, 29.70, 29.68, 29.66, 29.51, 29.48, 29.41, 26.03, 25.98, 22.74, 14.16 ppm; elemental analysis calcd (%) for $C_{61}H_{96}Cl_2O_6$ (996.32): C 73.54, H 9.71, Cl 7.12; found: C 73.43, H 9.60, Cl 7.05.

Analytical data for compound **IIc**: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.58–7.54 (m, 3 H), 7.39 (dd, 1 H, J_1=8.5, J_2=2.5 Hz), 7.36 (s, 1 H), 7.29 (d, 2 H, J=8.5 Hz), 7.08 (d, 1 H, J=8.5 Hz), 5.61 (s, 1 H), 4.09 (t, 2 H, J=7.0 Hz), 4.05 (t, 2 H, J=6.5 Hz), 4.03 (t, 2 H, J=7.0 Hz), 1.87–1.75 (m, 6 H), 1.52–1.46 (m, 6 H), 1.43–1.22 (m, 60 H), 0.90–0.86 ppm (m, 9 H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 164.19, 151.54, 150.88, 150.52, 150.13, 146.79, 137.53, 134.06, 127.79, 127.49, 127.14, 123.81, 122.08, 121.98, 120.32, 116.57, 110.96, 74.28, 74.14, 69.18, 31.95, 31.94, 30.30, 30.20, 29.76, 29.73, 29.69, 29.64, 29.63, 29.53, 29.49, 29.41, 29.39, 29.21, 26.09, 26.04, 26.01, 22.71, 14.14 ppm; elemental analysis calcd (%) for $C_{61}H_{96}Cl_2O_6$ (996.32): C 73.54, H 9.71, Cl 7.12; found: C 73.40, H 9.65, Cl 7.30.

Representative procedure for synthesis distyrylopyridine derivatives (III)

2,6-Di-(4′-carbomethoxystyryl)pyridine (III, X = Y = H): 2,6-Lutidine (5 g, 0.046 mol) and methyl 4-formylbenzoate (23 g, 0.14 mol) were dissolved in acetic anhydride (50 mL) and the reaction mixture was stirred and refluxed for 40 h. Precipitate was filtered off, washed with methanol and pure product was dried under vacuum over potassium hydroxide (4.1 g, 22 %). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.05 (d, 4H, J = 8.4 Hz), 7.74 (d, 2H, J = 7.2 Hz), 7.67–7.62 (m, 5H), 7.31 (d, 2H, J = 1.4 Hz), 7.25 (d, 2H, J = 7.0 Hz), 3.92 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 166.81, 154.90, 141.15, 137.18, 131.86, 130.45, 130.04, 129.58, 127.00, 121.44, 54.14 ppm; elemental analysis calcd (%) for $C_{25}H_{21}NO_4$ (399.44): C 75.17, H 5.30, N 3.51; found: C 75.01, H 5.38, N 3.41.

Representative procedure for synthesis of acid chlorides

Dichloride IV (X = Y = H): Sodium hydroxide (4 g, 0.1 mol) was added to a stirred and refluxed solution of 2,6-di-(4′-carbomethoxystyryl)pyridine (**III**, X = Y = H) (4 g, 0.01 mol) in ethanol (1 L). The reaction was continued for 10 h. Precipitate was filtered and dried in vacuum over phosphorus pentoxide. Obtained sodium salt was suspended in dry toluene (500 mL) and excess of oxalyl chloride (10 mL) was added. The reaction mixture was refluxed for 18 h and inorganic salt was filtered off from a hot solution. Filtrate was cooled down and yellow crystals precipitated. The crude product (3.2 g, 72 % yield) of dichloride was used for the following reaction.

Representative procedure for synthesis compounds 1–8

Compound 2b: 4′-Hydroxybiphenyl 4-[2-chloro-3,4,5-tri(tetradecyloxy)]-benzoate (2 g, 2.1 mmol), catalytic amount of DMAP and triethylamine (3 mL) were dissolved in tetrahydrofuran (70 mL) and heated at reflux for ca. 30 min. The appropriate dichloride **IV** (0.42 g, 1.0 mmol) was added and the reaction was continued for 10 h. The solvents were removed under vacuum and the crude product was purified by column chromatography using CH_2Cl_2 as eluent. After that the product was recrystallized twice from ethyl acetate. Yield was 60 % (1.36 g). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.26 (d, 4H, J = 8.0 Hz), 7.87–7.79 (m, 7H), 7.65 (d, 8H, J = 8.5 Hz), 7.39–7.30 (m, 14H), 4.09 (t, 4H, J = 6.5 Hz), 4.07–4.03 (m, 8H), 1.88–1.75 (m, 12H), 1.50–1.45 (m, 12H), 1.38–1.23 (m, 120H), 0.90–0.86 ppm (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 164.84, 164.17, 151.55, 150.52, 150.46, 150.28, 149.32, 146.77, 138.36, 138.23, 128.40, 128.32, 128.27, 128.25, 123.86, 122.08, 122.05, 121.97, 121.89, 74.59, 74.28, 74.14, 69.18, 31.95, 31.94, 31.93, 30.31, 30.20, 29.75, 29.71, 29.67, 29.64, 29.62, 29.53, 29.49, 29.45, 29.41, 29.39, 29.21, 26.09, 26.04, 26.01, 25.95, 22.79, 14.14 ppm; elemental analysis calcd (%) for $C_{145}H_{207}Cl_2NO_{14}$ (2259.10): C 77.09, H 9.24, Cl 3.14, N 0.62; found: C 77.17, H 9.20, Cl 3.20, N 0.87.

Dimethyl-5-benzyloxyisophthalate (V): Benzylbromide (6.0 mL, 0.05 mol) was slowly added to a stirred suspension of dimethyl 5-hydroxyisophthalate (10 g, 0.05 mol), potassium carbonate (7 g, 0.05 mol) and sodium iodide (9 g, 0.06 mol) in DMF. The reaction mixture was stirred at 80 °C for 10 h and then was cooled down to room temperature. After pouring the solution onto an ice-water mixture, the crude product was precipitated and purified by recrystallization from ethanol (11 g, 77 %). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.29 (t, 1H, J = 1.5 Hz), 7.84 (d, 2H, J = 1.5 Hz), 7.47–7.34 (m, 5H), 5.14 (s, 2H), 3.94 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 167.01, 161.80, 140.99, 130.05, 128.80, 127.39, 123.25, 119.67, 77.77, 50.09 ppm; elemental analysis calcd (%) for $C_{17}H_{16}O_5$ (300.10): C 67.99, H 5.37; found: C 67.85, H 5.45.

Representative procedure for esterification of isophthaloyl or 5-benzyloxyisophthaloyl dichloride with side-arms

Compound VI ($R = OC_{10}H_{21}$): 4′-Hydroxybiphenyl 4-[3,4,5-tridecyloxy)]-benzoate (7,5 g, 10 mmol), and catalytic amounts of DMAP and triethylamine (1 mL) were dissolved in THF (100 mL). To the stirred and refluxed solution, 5-benzyloxyisophthaloyl dichloride, obtained according to the general procedure for the synthesis of acid chlorides, (1.5 g, 5 mmol) was added dropwise and the reaction was continued for 5 h. The solvent was evaporated and the residue was purified by chromatography on silica gel eluting with CH_2Cl_2 (5 g, 59 %). M.p.. 61–62 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.68 (t, 1H, J = 1.6 Hz), 8.09 (d, 2H, J = 1.7 Hz), 7.69–7.63 (m, 8H), 7.52–7.26 (m, 17H), 5.25 (s, 2H), 4.11–4.03 (m, 12H), 1.94–1.71 (m, 12H), 1.57–1.18 (m, 84H), 0.91–0.85 ppm (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.27, 164.36, 159.30, 153.19, 150.82, 150.43, 143.26, 138.69, 138.22, 136.04, 131.67, 128.98, 128.63, 128.50, 128.42, 127.89, 124.44, 124.02, 122.37, 122.16, 121.60, 108.79, 32.12, 30.56, 29.94, 29.85, 29.80, 29.61, 29.56, 29.51, 26.29, 22.89, 14.32 ppm; elemental analysis calcd (%) for $C_{113}H_{156}O_{15}$ (1754.44): C 77.36, H 8.96; found: C 77.25, H 9.05.

Representative procedure for catalytic hydrogenation

Compounds VII ($R = OC_{10}H_{21}$): A reaction mixture containing compound **VI** with decyloxy terminal chains (5 g, 2.9 mmol), catalytic amount of Pd/C and ethanol 99.8 % (250 mL) was stirred and heated to 40 °C for 20 h under hydrogen atmosphere. CH_2Cl_2 (100 mL) was added and the solution was filtered through Celite. The solvent was removed under vacuum and the residue was recrystallized from methanol (4.3 g, 91 %). M.p. 134–135 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.58 (t, 1H, J = 1.4 Hz), 7.88 (d, 2H, J = 1.4 Hz), 7.65–7.56 (m, 8H), 7.44 (s, 4H), 7.32–7.24 (m, 8H), 6.70 (s, 1H), 4.13–4.03 (m, 12H), 1.82–1.75 (m, 12H), 1.53–1.22 (m, 84H), 0.91–0.85 ppm (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 165.24, 164.16, 156.73, 152.97, 150.53, 150.19, 142.87, 138.39, 138.04, 131.40, 128.28, 128.22, 123.89, 122.13, 121.93, 108.57, 73.76, 69.29, 31.92, 30.31, 29.74, 29.68, 29.65, 29.60, 29.41, 29.36, 29.29, 26.09, 22.69, 14.12 ppm; elemental analysis calcd (%) for $C_{106}H_{150}O_{15}$ (1664.32): C 76.50, H 9.08; found: C 76.15, H 9.05.

Representative procedure for synthesis star-shaped compounds 10

Compound 10b: Compound **VII** with decyloxy terminal chains (1 g, 0.6 mmol) was dissolved in CH_2Cl_2 (50 mL), DMAP (catalytic amount) and triethylamine (0.5 mL) was added. After 1 h, benzene-1,3,5-tricarbonyl chloride was added dropwise. The reaction mixture was stirred at room temperature over night. The solvent was evaporated and the crude compound was purified by column chromatography on silica gel using CH_2Cl_2 (1.0 g, 32 %). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 9.40 (s, 3H), 9.05 (t, 3H, J = 1.4 Hz), 8.46 (d, 6H, J = 1.6 Hz), 7.70–7.63 (m, 24H), 7.43 (s, 12H), 7.34–7.25 (m, 24H), 4.09–4.03 (m, 36H), 1.88–1.74 (m, 36H), 1.52–1.22 (m, 252H), 0.91–0.83 ppm (m, 54H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 164.05, 164.00, 152.90, 152.00, 142.87, 135.42, 133.42, 132.09, 130.91, 128.50, 128.22, 127.83, 123.43, 121.95, 108.47, 72.32, 70.29, 32.41, 30.62, 30.39, 29.88, 29.40, 29.36, 29.53, 26.39, 23.01, 14.02 ppm; elemental analysis calcd (%) for $C_{327}H_{450}O_{48}$ (5149.04): C 76.28, H 8.81; found: C 76.15, H 8.95.

The phase sequence, phase transition temperatures and thermal effects for the studied materials were determined by optical microscopy (Nikon Optiphot2-Pol polarizing microscope equipped with Mettler FP82HT heating stage and photodiode FLCE PIN-20 for quantitative monitoring the light transmission) and confirmed by differential scanning calorimetry (Perkin Elmer DSC-7). The structure of the mesophases was confirmed by X-ray measurements performed with powder samples. $Cu_{K\alpha}$ radiation (1.5401 Å) was used; the patterns were registered with Inel CPS 120 curved counter or with imaging plates when the Guinier geometry was applied. Samples for dielectric and electrooptic studies were prepared in 3–5 μm thick glass cells with ITO electrodes and planar aligning surfactant layers.

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