

Supplementary Information

Smectic Assemblies in C_3 -Symmetric Hexa-Alkylated Liquid Crystals: Transformation from Smectogen to Discogen via Hydrogen Bonding

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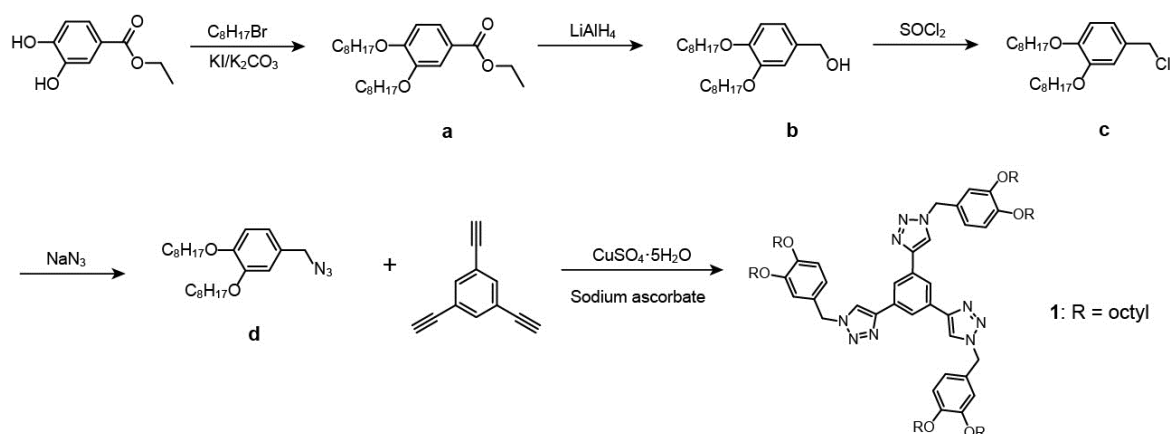
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Experimental Details

Materials. 1-Bromooctane, sodium azide (99.5%), 1,3,5-tribromobenzene, lithium aluminum hydride (95%), CuI (98%), 2-methyl-3-butyn-2-ol, (+)-sodium L-ascorbate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Sigma-Aldrich Chemical Co. Anhydrous MgSO_4 (min. 99%), anhydrous potassium carbonate (min.99%), potassium hydroxide (min.85%) were purchased from Duksan Pure Chemical, Korea. Bis(triphenylphosphine)palladium(II) dichloride, ethynyl-3,4-hydroxybenzoate, thionyl chloride were purchased from Tokyo Chemical Industry. Methyl ethyl ketone was stored over a type 4 Å molecular sieve. *N,N'*-Dimethylformamide (DMF) was distilled under vacuum, and stored over a type 4 Å molecular sieve. Tetrahydrofuran (THF) was dried by distillation from sodium metal, and stored over a type 4 Å molecular sieve. Triethylamine and pyridine were distilled from calcium hydride, and stored over a type 4 Å molecular sieve.

Methods. ^1H -, and ^{13}C -NMR spectra were recorded from a CDCl_3 solution using Varian 200 and Bruker AM 400 spectrometers. The purity of the compounds was checked by thin-layer chromatography (TLC; Merck, silica gel 60). Gel permeation chromatography (GPC) measurements were conducted in THF and *N,N'*-dimethylacetamide (99.9%) (40:1 volume ratio) using a Waters 401 instrument equipped with Stragel HR 2,3 columns and Shodex AT-8045 at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) measurements were performed using a Perkin Elmer DSC-7 with the 1020 thermal analysis equipment at a rate of 10 °C/min. Indium (melting temperature = 429 K and $\Delta H = 28.45$ J/g) was used as a calibration standard. 1D X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 9A beamline of the Pohang Accelerator Laboratory (PAL), Korea. The sample was held in an aluminum sample holder with polyimide films on both sides. 2D X-ray scattering experiments were also conducted at the 9A beamline of the PAL. For the 2D experiments, the surface-aligned samples were prepared by spin-casting the sample solutions (dissolved in chloroform, ~10 wt%) on Si-wafers functionalized with 3-aminopropyltriethoxysilane (APS). The aligned samples were held in vacuum chamber with temperature-controlled heating stage and the diffraction patterns were recorded with a 2-D imaging detector. The X-ray spectra were plotted against q value ($= 4\pi\sin\theta/\lambda$). Microanalyses were performed with a Perkin Elmer 240 elemental analyzer at the Organic Chemistry Research Center, Sogang University, Korea. A Nikon eclipse LV100 optical polarized microscopy equipped with a Linkam TMS 94 heating system was used to observe the thermal transitions and to analyze the anisotropic texture. IR spectra were recorded with a Perkin Elmer spectrum 100 FT-IR spectrometer. The density measurement was performed using a floating and sinking method in water/methanol mixture solutions. The density was determined when the particle was in the middle of the solution. By repeating the measurement several times, the average value (0.89 g/cm³ for **1**) was used. For the NMR titration experiments, the solution of **1** in CDCl_3 at 298 K was titrated by adding concentrated solutions of **TOBA**. The association constants K_1 and K_2 were obtained by fitting a plot of $\Delta\delta(\text{H}_b)$ versus the concentration of **TOBA**. In the graph fitting, a nonlinear least-squares fitting method (Graphpad prism 6) was used. The stoichiometry of the complex was further confirmed by a Job's plot. In this experiment, the two solutions of **1** and **TOBA** were mixed to produce a series of samples with an identical total concentration ($[\mathbf{1}] + [\mathbf{TOBA}] = 30$ mM) but different mole fractions ($\chi_1 = [\mathbf{1}] / ([\mathbf{1}] + [\mathbf{TOBA}])$). The ^1H -NMR spectrum of each sample

was obtained, and these NMR data were used to make a graph of $\Delta\delta(\text{H}_b)$ χ_1 versus χ_1 .



Scheme S1. Synthesis of C_3 -symmetric molecule **1**.

Synthesis. The synthetic procedures of **1** and **TOBA** are outlined in Scheme S1 and S2, respectively. 1,3,5-Triethynylbenzene was prepared by following a previous procedure.^{S1}

Synthesis of ethyl 3,4-bis(octyloxy)benzoate (a). Ethyl 3,4-dihydroxybenzoate (4.00 g, 21.96 mmol), 1-bromooctane (16.96 g, 87.83 mmol), potassium carbonate (18.21 g, 131.76 mmol) and potassium iodide (3.65 g, 21.96 mmol) were dissolved in 100 mL of dry methyl ethyl ketone. The reaction mixture was heated to reflux for overnight under N_2 atmosphere. After cooling to room temperature, the solvent was removed using a rotary evaporator. Then, the mixture was extracted with dichloromethane and deionized water, and dried over MgSO_4 . The organic solvent was removed using a rotary evaporator. The resulting mixture was purified by column chromatography (silica gel) using *n*-hexane:dichloromethane = 1:1 as the eluent, to yield 8.74 g (97.9%) of a white solid. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.64 (d, 1H, *Ar-H*), 7.53 (s, 1H, *Ar-H*), 6.86 (d, 1H, *Ar-H*, $J = 4.0$ Hz), 4.35 (q, 2H, $J = 3.6$ Hz, $\text{COOCH}_2\text{CH}_3$), 4.04 (t, 4H, $J = 6.4$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.85-1.72 (m, 4H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.48 (t, 3H, $J = 3.6$ Hz, $\text{COOCH}_2\text{CH}_3$), 1.48-1.33 (m, 20H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 0.91 (t, 6H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$).

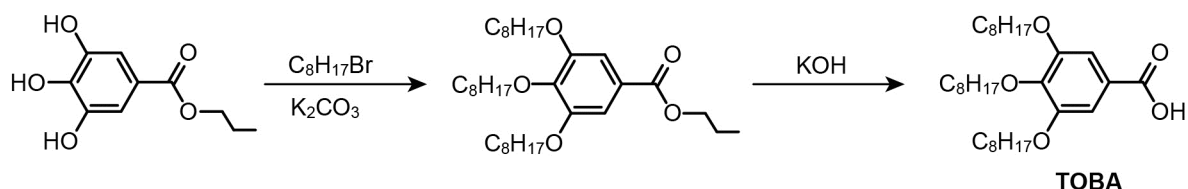
Synthesis of (3,4-bis(octyloxy)phenyl)methanol (b). To a stirred solution of compound **a** (8.74 g, 21.74 mmol) in dry THF 25 mL was added LiAlH_4 (1.65 g, 43.48 mmol) at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was quenched with a small amount of methanol and deionized water. The insoluble precipitate was filtered off. The filtrate was concentrated under a reduced pressure, to yield 6.53 g (82.4%) of a white solid. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 6.89 (d, 3H, $J = 13.6$ Hz, *Ar-H*), 4.60 (d, 2H, $J = 6.2$ Hz, CH_2OH), 3.99 (t, 4H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.82 (t, 4H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.47-1.33 (m, 20H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 0.90 (t, 6H, $J = 6.8$ Hz, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$).

Synthesis of 4-(chloromethyl)-1,2-bis(octyloxy)benzene (c). Compound **b** (5.82 g, 15.96 mmol), thionyl chloride (2.66 g, 22.35 mmol), and 2 mL of DMF were dissolved in 50 mL of dichloromethane. The mixture was stirred at room temperature under N_2 atmosphere. After 30 min, the resulting mixture was extracted with dichloromethane and deionized water, and dried over MgSO_4 . After removing dichloromethane by a rotary evaporator, the resulting compound was used for the next step without other purification.

Synthesis of 4-(azidomethyl)-1,2-bis(octyloxy)benzene (d). Compound **c** (5.59 g, 14.59

mmol) and sodium azide (9.49 g, 145.90 mmol) were dissolved in 50 mL of anhydrous DMF. The reaction mixture was heated at 100 °C for overnight under N₂ atmosphere. After cooling to room temperature, the solvent was removed by a rotary evaporator. The reaction mixture was extracted with dichloromethane and deionized water three times, and then dried over MgSO₄. After removing dichloromethane by a rotary evaporator, the resulting mixture was purified by a silica gel column chromatography using *n*-hexane:dichloromethane = 1:1 eluent, to yield 3.51 g (61.8%) of a white solid. ¹H-NMR (CDCl₃, δ, ppm): 6.83 (s, 3H, Ar-*H*), 4.25 (s, 2H, CH₂N₃), 3.99 (t, 4H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₅CH₃), 1.85-1.78 (t, 4H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₅CH₃), 1.46-1.26 (m, 20H, OCH₂CH₂(CH₂)₅CH₃), 0.90 (t, 6H, *J* = 6.8 Hz, OCH₂CH₂(CH₂)₅CH₃).

Synthesis of Compound 1. 1,3,5-Triethynylbenzene (0.20 g, 1.33 mmol), compound **d** (1.66 g, 4.26 mmol), (+)-sodium L-ascorbate (0.79 g, 4.00 mmol) and CuSO₄·5H₂O (0.50 g, 2.00 mmol) were dissolved in the mixture of 10 mL of THF and 1 mL of deionized water. The reaction mixture was stirred for 12 hours at room temperature. The solvent was removed by a rotary evaporator. The resulting mixture was extracted with dichloromethane and deionized water three times, and then dried over MgSO₄. After removing dichloromethane by a rotary evaporator, and the remaining compound **d** was removed by a silica gel column chromatography using dichloromethane:ethyl acetate = 10:1 as the eluent, to yield 0.98 g (60.5 %) of a white solid. ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 8.18 (s, 3H, Ar-*H*), 7.79 (s, 3H, *H*-triazole), 6.86 (d, 9H, ArCH₂, *J* = 19.2 Hz), 5.47 (s, 6H, benzyl-*H*), 3.97 (q, 12H, OCH₂CH₂(CH₂)₅CH₃, *J* = 6.4 Hz), 1.80–1.78 (m, 12H, OCH₂CH₂(CH₂)₅CH₃), 1.45–1.29 (m, 60H, OCH₂CH₂(CH₂)₅CH₃), 0.88 (t, 18H, *J* = 6.4 Hz, -OCH₂CH₂(CH₂)₅CH₃). ¹³C-NMR (100 MHz, CDCl₃, δ, ppm): 149.81, 149.79, 147.39, 131.74, 126.59, 122.21, 121.25, 120.16, 113.92, 113.73, 69.39, 54.46, 31.90, 29.46, 29.36, 29.35, 29.32, 26.12, 26.11, 26.09, 22.76, 14.20. Anal. Calcd for C₈₁H₁₂₃N₉O₆: C, 73.76; H, 9.40; N, 9.56. Found: C, 73.73; H, 9.44; N, 9.59. M_w/M_n = 1.01 (GPC).



Scheme S2. Synthesis of TOBA.

Synthesis of propyl 3,4,5-tris(octyloxy)benzoate. Propyl gallate (5.00 g, 23.6 mmol), 1-bromooctane (22.75 g, 117.8 mmol), potassium carbonate (16.28 g, 117.8 mmol) were dissolved in 75 mL of anhydrous methyl ethyl ketone. The reaction mixture was heated to reflux for 20 hours under an N₂ atmosphere. After cooling to room temperature, the solvent was removed by a rotary evaporator. The reaction mixture was extracted with dichloromethane and deionized water three times, and dried over MgSO₄. After removing dichloromethane by a rotary evaporator, the resulting compound was purified by a silica gel column chromatography using hexane:ethyl acetate = 20:1 as the eluent, to yield 10.29 g (79.5%) of a yellow liquid. ¹H-NMR (CDCl₃, δ, ppm): 7.26 (s, 2H), 4.25 (t, 2H, *J* = 6.8 Hz), 4.01 (t, 6H, *J* = 6.6 Hz), 1.84-1.70 (m, 8H), 1.46-1.28 (m, 30H), 1.02 (t, 3H, *J* = 7.2 Hz), 0.88 (t, 3H, *J* = 6.6 Hz).

Synthesis of TOBA. Propyl 3,4,5-tris(octyloxy)benzoate (2.18 g, 4.0 mmol) and potassium hydroxide (0.45 g, 8.0 mmol) were dissolved in 10 mL of ethanol and 2 mL of water. The reaction mixture was stirred for 4 hours under N₂ atmosphere. Then, a diluted HCl solution was added to the reaction mixture. The reaction mixture was extracted with dichloromethane and a diluted HCl solution, and dried over MgSO₄. After removing dichloromethane by a rotary evaporator, the resulting compound was purified by a silica gel column chromatography using dichloromethane:ethyl acetate = 8:1 as the eluent, to yield 1.70 g (83.5%) of a white solid. ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 7.32 (s, 2H), 4.06-4.01 (m, 6H), 1.84-1.74 (m, 6H), 1.49-1.29 (m, 30H), 0.90-0.87 (m, 9H). ¹³C-NMR (100 MHz, CDCl₃): 171.84, 152.85, 143.12, 123.61, 108.50, 73.56, 69.17, 31.91, 31.84, 30.33, 29.51, 29.38, 29.36, 29.30, 29.27, 26.08, 26.04, 22.71, 22.69, 14.12. Anal. Calcd for C₃₁H₅₄O₅: C, 73.47; H, 10.74. Found: C, 73.49; H, 10.54. M_w/M_n = 1.03 (GPC).

Reference

(S1) M.-H. Ryu, J.-W. Choi and B.-K. Cho, *J. Mater. Chem.*, 2010, **20**, 1806-1810.

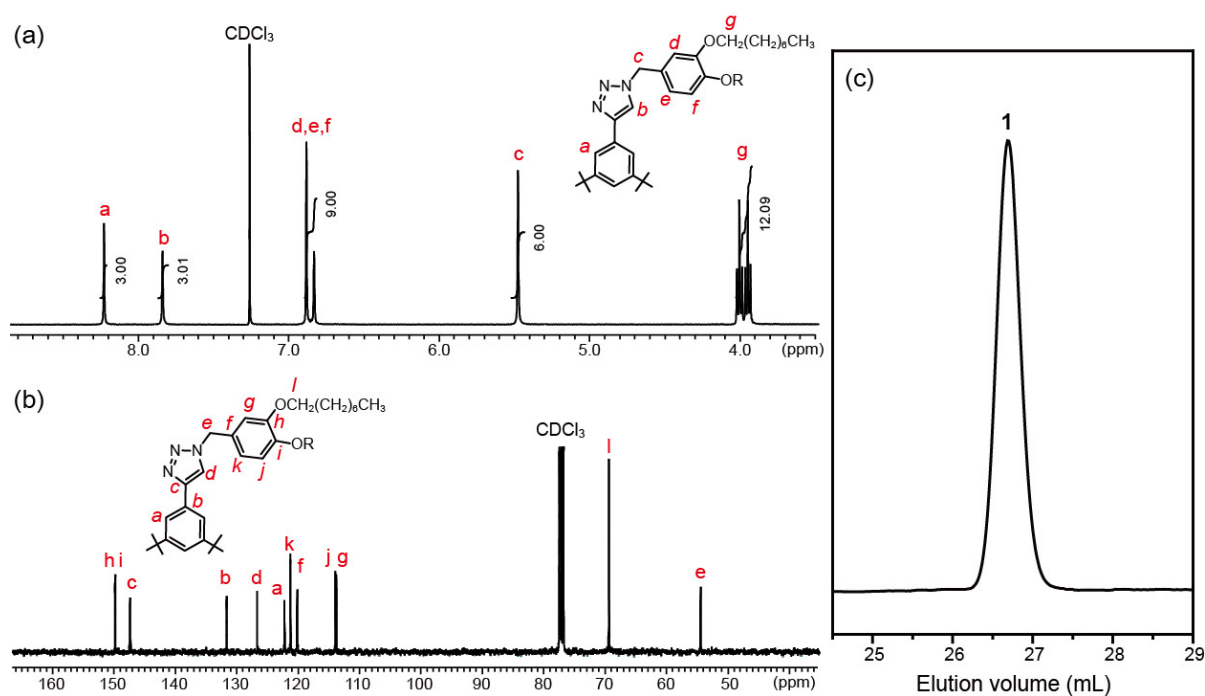


Fig. S1 (a) ^1H -NMR and (b) ^{13}C -NMR spectra, and (c) GPC elugrams of **1**.

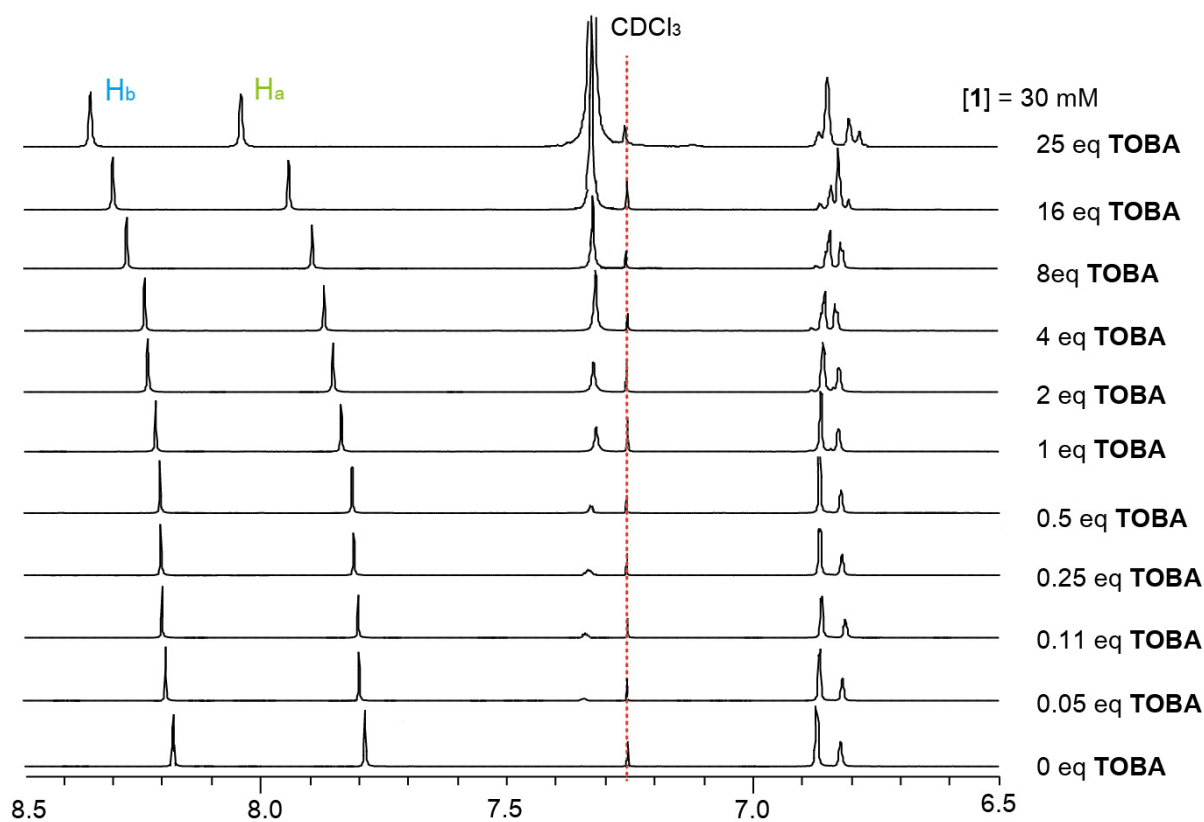


Fig. S2 Partial ^1H -NMR spectra of **1** upon addition of TOBA.

Table S1. Summary of the conformational states and LC morphologies of C_3 -symmetric analogues with sixfold alkyl peripheries.

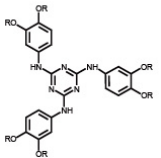
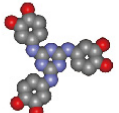
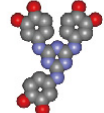
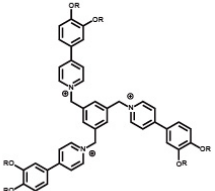
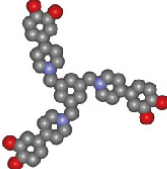
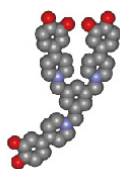
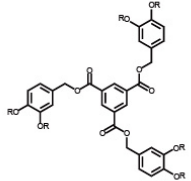
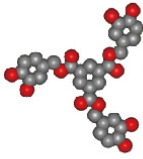
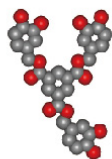
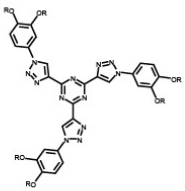
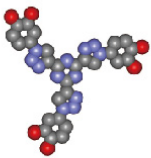
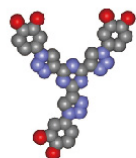
research group	molecular structure	conformational states		LC morphology
		C_3 -symmetric conformer	stretched conformer	
Janietz				hexagonal columnar
	<i>J. Mater. Chem.</i> , 2004, 14 , 1521-1525.			
Kato				rectangular columnar
	<i>J. Am. Chem. Soc.</i> , 2012, 134 , 5652-5661.			
Percec				hexagonal columnar
	<i>J. Am. Chem. Soc.</i> , 2011, 133 , 2311-2328.			
Giménez				hexagonal Columnar
	<i>Org.Lett.</i> , 2010, 12 , 7, 1404-1407.			

Table S2. Characterization of the X-ray data of **1**.

	$d_{cal}/\text{\AA}$	$d_{exp}/\text{\AA}$	hkl	Lattice parameters
30 °C	27.4	27.4	(001)	$a = 17.5 \text{\AA}$ $\gamma = 82^\circ$ $b = 10.1 \text{\AA}$ $d = 27.4 \text{\AA}$
	13.7	13.7	(002)	
	9.1	9.1	(003)	
	8.7	8.7	(200)	
	6.9	6.8	(004)	
	5.5	5.5	(005)	
	5.0	5.0	(020)	
	4.3	4.3	(400)	
	4.2	4.2	(410)	
95 °C (cooling)	28.3	28.3	(001)	$d = 28.3 \text{\AA}$
	14.2	14.2	(002)	
	9.4	9.4	(003)	

d_{cal} , calculated lattice spacing; d_{exp} , experimental lattice spacing.

Table S3. Structural characterization of the Smec_{ord} phase of **1**.

	M.W (g/mol)	ρ (g/cm ³)	V_{mol} (\AA ³)	d (\AA)	L_{total} (\AA)	L_{aro} (\AA)	S (\AA ²)	V_{lat} (\AA ³)	N $= V_{lat}/V_{mol}$
1 at 30 °C	1318.9	0.89	2433.1	27.4	41.5	18.5	173.3	4797.8	1.97

ρ , density measured at RT; V_{mol} , molecular volume; d , lamellar thickness; L_{total} , stretched molecular length of the Y-conformer; L_{aro} , aromatic length of the Y-conformer; S , area of the oblique unit cell; V_{lat} , volume of an arbitrary 3D lattice ($= d \times S$); N , number of molecules in a unit cell.