Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

Synthesis and characterization of room temperature columnar mesogens of cyclotriphosphazene with Schiff base unit

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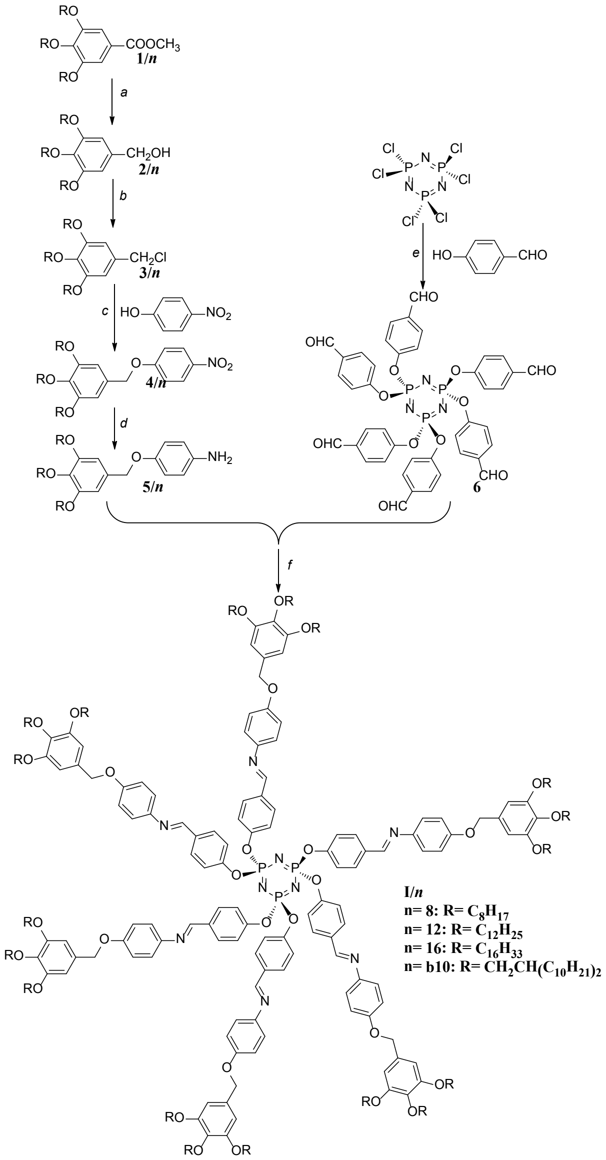
1. Syntheses and analytical data of the materials

1.1 Synthesis of the materials



Scheme S1. Chemical structure and synthetic pathway of the cyclotriphosphazenes **I/*n***: reagents and conditions: *a*) $LiAlH_4$, THF, 40 °C, 12 h; *b*) $SOCl_2$, THF, 25 °C 5 h; *c*) K_2CO_3, DMF, reflux, 12 h; *d*) Pd/C, H_2, 25 °C 14 h; *e*) K_2CO_3, toluene, reflux, 24 h; *f*) CH_3COOH, ethanol, 50 °C.

General procedure for the synthesis of 1/*n*: Methyl gallate (588 mg, 3.0 mmol) and the appropriate alkyl bromide (11.2 mmol) were dissolved in DMF (10 mL), K_2CO_3 (1.86 g, 13.5 mmol) was added. The mixture was stirred at 96 °C for 14 h. H_2O (15 mL) was added to dissolve the precipitate and then the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic phase was washed with brine (4×100 mL), dried over $MgSO_4$ and the solvent was removed under *vacuo*. The residue was purified by column chromatography (ethyl acetate:petroleum ether = 1:25). ^{1}H NMR data of **1/8**, **1/12** and **1/16** are in agreement with the literature data.[1]

1/b10: yellow liquid (2.91 g, yield 87.4 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.90 (t, *J*=6.3 Hz, 18H, CH_3), 1.18-1.55 (m, 108H, CH_2), 1.72-1.85 (m, 3H, CH), 3.86 (s, 3H, OCH_3), 3.88-3.89 (d, J=5.0 Hz, 6H, OCH_2), 7.24 (s, 2H, ArH).

General procedure for the synthesis of 2/*n*: 1/*n* (2.7 mmol) was dissolved in dry THF (9 mL), then $LiAlH_4$ (121 mg, 3.2 mmol) was added and the mixture was stirred vigorously at room temperature for 12 h. H_2O (30 mL) was added dropwise into the mixture, the precipitate was filtered and the residue was washed with ethyl acetate (120 mL). The organic phase was washed with brine (4×100 mL), dried over $MgSO_4$ and the solvent was removed under *vacuo*. The residue was purified by column chromatography (ethyl acetate:petroleum ether = 1:25) to yield **2/*n*** (83-88%). ^{1}H NMR data of **2/8**, **2/12** and **2/16** are in agreement with the literature data.

2/b10: light yellow liquid (2.47 g, yield 83.8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.90 (t, *J*=6.3 Hz, 18H, CH_3), 1.21-1.56 (m, 108H, CH_2), 1.70-1.83 (m, 3H, CH), 3.88-3.89 (d, J=5.0 Hz, 6H, OCH_2), 4.57 (s, 2H, $C\mathbf{H}_2OH$), 6.56 (s, 2H, ArH)

General procedure for the synthesis of 3/*n*: 2/*n* was dissolved in dry THF then 5 drops of $SOCl_2$ were added and the mixture was stirred at room temperature overnight. Solvent was removed under *vacuo* and the crude product was dried and used for the next reaction without further purification.

General procedure for the synthesis of 4/*n*: 4-nitrophenol (49 mg, 3.5 mmol) and **3/*n*** (2.4 mmol) was dissolved in dry DMF (6 mL), then K_2CO_3 (1.41 g,10.2 mmol) and KI (0.10 g, 0.6 mmol) were added and the mixture was stirred at 96 °C for 16 h. H_2O (15 mL) was added to dissolve the precipitate and then the reaction mixture was extracted with ethyl acetate (3×60 mL). The combined organic phase was washed with brine (4×100 mL), dried over $MgSO_4$ and the solvent was removed under *vacuo*. The residue was purified by column chromatography (ethyl acetate:petroleum ether = 1:30).

4/8: light yellow liquid (1.19 g, yield 81.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.90 (t, *J*=6.6 Hz, 9H, CH_3), 1.21-1.39 (m, 24H, CH_2), 1.41-1.51 (m, 6H, $OCH_2CH_2C\mathbf{H}_2$), 1.72-1.82 (m, 6H, $OCH_2C\mathbf{H}_2$), 3.93-3.97 (t, *J*=5.7 Hz, 6H, $OC\mathbf{H}_2CH_2$), 5.04 (s, 2H, $ArOCH_2$), 6.60 (s, 2H, ArH), 7.01-7.04 (d, *J*=9.3 Hz, 2H, ArH), 8.19-8.22 (d, *J*=9.3 Hz, 2H, ArH)

4/12: light yellow solid (1.23 g, yield 70.3%); m.p. 48-49 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.88 (t, *J*=6.6 Hz, 9H, CH_3), 1.21-1.38 (m, 48H, CH_2), 1.40-1.53 (m, 6H, $OCH_2CH_2C\mathbf{H}_2$), 1.70-1.84 (m, 6H, $OCH_2C\mathbf{H}_2$), 3.93-3.99 (t, *J*=6.6 Hz, 6H, $OC\mathbf{H}_2CH_2$), 5.04 (s, 2H, $ArOCH_2$), 6.60 (s, 2H, ArH), 7.01-7.04 (d, *J*=9.0 Hz, 2H, ArH), 8.19-8.22 (d, *J*=9.3 Hz, 2H, ArH)

4/16: white solid (1.46 g, yield 63.9%); m.p. 64-65°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.90 (t, *J*=6.6 Hz, 9H, CH_3), 1.24-1.40 (m, 72H, CH_2), 1.41-1.52 (m, 6H, $OCH_2CH_2C\mathbf{H}_2$), 1.70-1.84 (m, 6H, $OCH_2C\mathbf{H}_2$), 3.85-3.97 (t, *J*=6.3Hz, 6H, $OC\mathbf{H}_2CH_2$), 5.04 (s, 2H, $ArOCH_2$), 6.60 (s, 2H, ArH), 7.01-7.04 (d, *J*=9.0 Hz, 2H, ArH), 8.19-8.23 (d, *J*=9.3 Hz, 2H, ArH)

4/b10: brown liquid (2.35 g, yield 81.3%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.86-0.89 (t, *J*=6.6 Hz, 18H, CH_3), 1.16-1.50 (m, 108H, CH_2), 1.71-1.82 (m, 3H, CH), 3.81-3.83 (d, *J*=5.4 Hz, 6H, $OC\mathbf{H}_2CH_2$), 5.03 (s, 2H, $ArOCH_2$), 6.58 (s, 2H, ArH), 7.02-7.04 (d, *J*=9.3 Hz, 2H, ArH), 8.20-8.22 (d, *J*=9.0 Hz, 2H, ArH)

General procedure for the synthesis of 5/*n*: 4/*n* (0.9 mmol) was dissolved in dry THF (6 mL), palladium on carbon (70 mg) was added and the mixture was stirred at room temperature under H_2 atmosphere for 24 hours. The mixture was filtered, the filter was washed with ethyl acetate, and solvent of the filtrate was removed under *vacuo*. The product was purified by recrystallization from ethanol.

5/8: brown solid (452 mg, yield 84.2%); m.p. 31.5-32°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.88 (t, *J*=6.6 Hz, 9H, CH_3), 1.21-1.38 (m, 24H, CH_2), 1.40-1.52 (m, 6H, $OCH_2CH_2C\mathbf{H}_2$), 1.69-1.81 (m, 6H, $OCH_2C\mathbf{H}_2$), 3.45 (s, 2H, NH_2), 3.95-3.99 (t, *J*=6.3 Hz, 6H, $OC\mathbf{H}_2CH_2$), 4.86 (s, 2H, $ArOCH_2$), 6.56 (s, 2H, ArH), 6.63-6.66 (d, *J*=9.0 Hz, 2H, ArH), 6.80-6.83 (d, *J*=8.7 Hz, 2H, ArH)

5/12: light brown solid (502 mg, yield 72.5%); m.p. 38-39°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.90 (t, *J*=6.3 Hz, 9H, CH_3), 1.20-1.38 (m, 48H, CH_2), 1.40-1.52 (m, 6H, $OCH_2CH_2C\mathbf{H}_2$), 1.69-1.87 (m, 6H, $OCH_2C\mathbf{H}_2$), 3.94-3.99 (t, *J*=6.3 Hz, 6H, $OC\mathbf{H}_2CH_2$), 4.86 (s, 2H, $ArOCH_2$), 6.60 (s, 2H, ArH), 6.62-6.65 (d, *J*=8.7 Hz, 2H, ArH), 6.80-6.83 (d, *J*=9.0 Hz, 2H, ArH)

5/16: light brown solid (767 mg, yield 90.6%); m.p. 48-49°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86-0.90 (t, *J*=6.3 Hz, 9H, CH_3), 1.24-1.37 (m, 72H, CH_2), 1.40-1.52 (m, 6H, $OCH_2CH_2C\mathbf{H}_2$), 1.74-1.83 (m, 6H, $OCH_2C\mathbf{H}_2$), 3.43 (s, 2H, NH_2), 3.91-3.99 (t, *J*=6.6 Hz, 6H, $OC\mathbf{H}_2CH_2$), 4.86 (s, 2H, $ArOCH_2$), 6.60 (s, 2H, ArH), 6.63-6.66 (d, *J*=8.7 Hz, 2H, ArH), 6.80-6.83 (d, *J*=9.0 Hz, 2H, ArH)

5/b10: brown liquid (962 mg, yield 88.9%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.87-0.89 (t, *J*=6.5 Hz, 18H, CH_3), 1.18-1.60(m, 108H, CH_2), 1.71-1.83 (m, 3H, CH), 3.82-3.83 (d, *J*=5.0 Hz, 6H, $OC\mathbf{H}_2CH_2$), 4.86 (s, 2H, $ArOCH_2$), 6.59 (s, 2H, ArH), 6.64-6.66 (d, *J*=8.7 Hz, 2H, ArH), 6.82-6.83 (d, *J*=8.7 Hz, 2H, ArH)

Procedure for the synthesis of hexakis(4-formylphenoxy)cyclotriphosphazene 6. For compound 6 was prepared according to the literation 2 and ^{1}H NMR data is in agreement with the literature data.[2]

General procedure for the synthesis of I/*n*: 5/*n* (0.7 mmol) was dissolved in dry ethanol (10 mL) then 5 drops of acetic acid were added, finally **6** (62 mg) was added to the solution, and the mixture was stirred at 50°C for 4 days. The solvent was removed under *vacuo* and the residue was purified by recrystallization (ethanol/CH_2Cl_2 = 2:1).

I/8: brownish wax (244 mg, yield 80.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88 (br s, 54H, CH_3), 1.20-1.38 (m, 144H, CH_2), 1.40-1.54 (m, 36H, $OCH_2CH_2C\mathbf{H}_2$), 1.75-1.80 (m, 36H, $OCH_2C\mathbf{H}_2$), 3.95-3.97 (t, *J*=6.0 Hz, 36H, $OC\mathbf{H}_2CH_2$), 4.95 (s, 12H, OCH_2Ar), 6.61 (s, 12H, ArH), 6.93-6.96 (d, *J*=8.7 Hz, 12H, ArH), 7.09-7.11 (d, *J*=8.4 Hz, 12H, ArH) ,7.16-7.19 (d, *J*=8.4 Hz, 12H, ArH), 7.73-7.76 (d, *J*=8.1 Hz, 12H, ArH), 8.40 (s, 6H, CH=N). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 158.04, 157.17, 153.78, 152.80, 145.20, 138.53, 134.13, 132.18, 130.38, 122.71, 121.63, 115.85, 106.62, 73.84, 71.15, 69.59, 32.27, 30.80 ,30.00, 29.87, 29.83, 29.73, 26.56, 23.11, 14.51. Elemental analysis calcd (%) for $C_{264}H_{384}N_9O_{30}P_3$ (4256.84): C 74.49, H 9.09, N 2.96; Found C 74.32, H 9.03, N 2.89. GPC: single peak at Mn: 4675.5.

I/12: brownish wax (324 mg, yield 81.4%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (br s, 54H, CH_3), 1.18-1.38 (m, 288H, CH_2), 1.40-1.51 (m, 36H, $OCH_2CH_2C\mathbf{H}_2$), 1.72-1.85 (m, 36H, $OCH_2C\mathbf{H}_2$), 3.94 (s, 36H, $OC\mathbf{H}_2CH_2$), 4.94 (s, 12H, OCH_2Ar), 6.61 (s, 12H, ArH), 6.93-6.96 (d, *J*=8.7 Hz, 12H, ArH), 7.09-7.12 (d, *J*=8.7 Hz, 12H, ArH) ,7.15-7.18 (d, *J*=8.7 Hz, 12H, ArH), 7.73-7.76 (d, *J*=8.1 Hz, 12H, ArH), 8.40 (s, 6H, CH=N). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 158.06, 157.16, 153.78, 152.78, 145.19, 138.56, 134.11, 132.17, 130.39, 122.71, 121.62, 115.84, 106.63, 73.84, 71.15, 69.60, 32.36, 30.82, 30.10, 29.89, 29.81, 26.58, 23.11, 14.51. Elemental analysis calcd (%) for $C_{336}H_{528}N_9O_{30}P_3$ (5266.75) : C 76.62, H 10.10, N 2.39; Found C 76.55, H 10.04, N 2.34. GPC: single peak at Mn: 5702.1.

I/16: brown solid (369 mg, yield 77.7%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.85-0.87 (d, *J*=6.0 Hz, 54H, CH_3), 1.22-1.37 (m, 432H, CH_2), 1.40-1.52 (m, 36H, $OCH_2CH_2C\mathbf{H}_2$), 1.75-1.80 (m, 36H, $OCH_2C\mathbf{H}_2$), 3.94 (s, 36H, $OC\mathbf{H}_2CH_2$), 4.94 (s, 12H, OCH_2Ar), 6.61 (s, 12H, ArH), 6.93-6.96 (d, *J*=8.7 Hz, 12H, ArH), 7.09-7.12 (d, *J*=8.7 Hz, 12H, ArH) ,7.15-7.18 (d, *J*=8.4 Hz, 12H, ArH), 7.73-7.76 (d, *J*=8.4 Hz, 12H, ArH), 8.0 (s, 6H, CH=N). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 158.06, 157.15, 153.79, 152.82, 145.22, 138.58, 134.13, 132.16, 131.79, 130.37, 122.69, 121.60, 115.83, 106.65, 73.84, 71.17, 69.62, 32.35, 30.82, 30.15, 29.90, 29.79, 26.58, 23.10, 14.50. Elemental analysis calcd (%) for $C_{408}H_{627}N_9O_{30}P_3$ (6276.66) : C 78.07, H 10.79, N 2.01; Found C 78.01, H 10.75, N 1.97. GPC: single peak at Mn: 6719.0.

I/b10: dark brownish wax (459 mg, yield 78.6%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.87-0.89 (t, *J*=6.1 Hz, 108H, CH_3), 1.21-1.58 (m, 648H, CH_2), 1.75-1.80 (m, 18H, CH), 3.84 (br s, 36H, $OC\mathbf{H}_2CH$), 4.97 (s, 12H, OCH_2Ar), 6.62 (s, 12H, ArH), 6.98-7.00 (d, *J*=8.4 Hz, 12H, ArH), 7.15-7.17 (d, *J*=8.4 Hz, 12H, ArH) ,7.20-7.21 (d, *J*=8,2 Hz, 12H, ArH), 7.78-7.80 (d, *J*=8.2 Hz, 12H, ArH), 8.43 (s, 6H, CH=N). ^{13}C NMR (500 MHz, $CDCl_3$) δ: 158.12, 157.17, 154.00, 152.89, 145.25, 138.38, 134.13, 132.00, 130.36, 122.66, 121.54, 115.85, 106.28, 106.00, 76.91, 73.85, 72.02, 71.32, 39.70, 38.71, 32.36,31.79, 30.95, 30.72, 30.26, 30.17, 30.11, 29.80, 27.56, 23.11, 14.50. Elemental analysis calcd (%) for $C_{516}H_{888}N_9O_{30}P_3$ (7791.54) : C 79.54, H 11.49, N 1.62; Found C 79.50, H 11.46, N 1.57. GPC: single peak at Mn: 8067.5.

1.2 GPC graph

GPC was recorded on an Agilent 1100 GPC; eluent: THF; Flow rate: 1.0 ml/min; injection volume: 20 μ L; Detector: RI, column temperature: 20°C; detection temperature: 20°C; pressure: 48.0 bar; external PS standards were used for calibration.

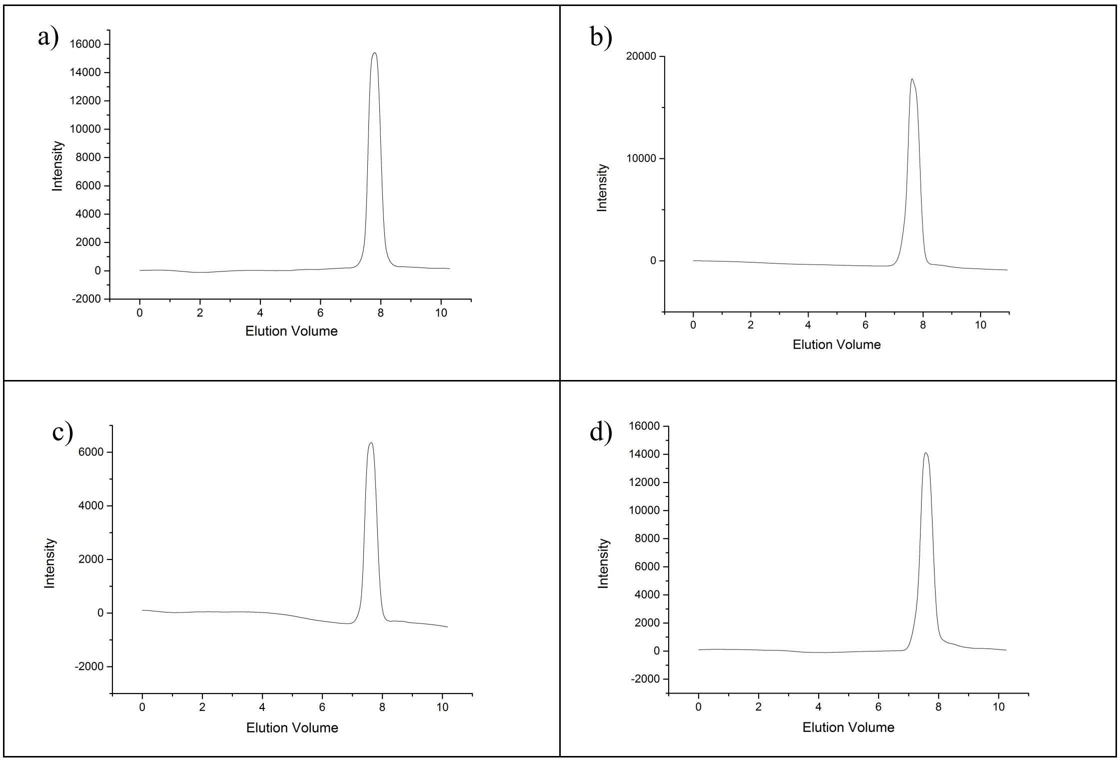
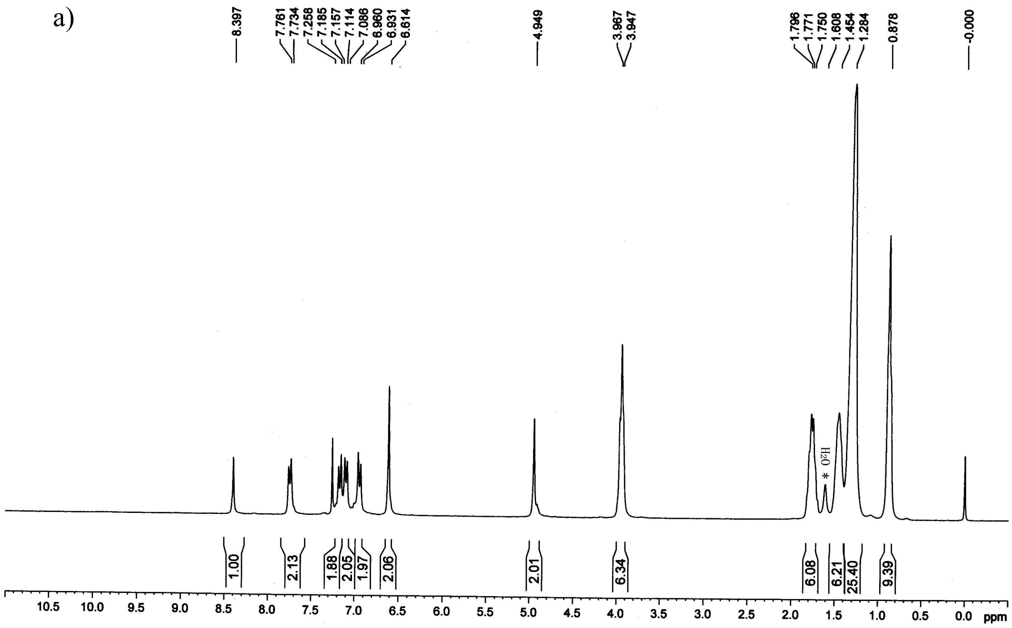
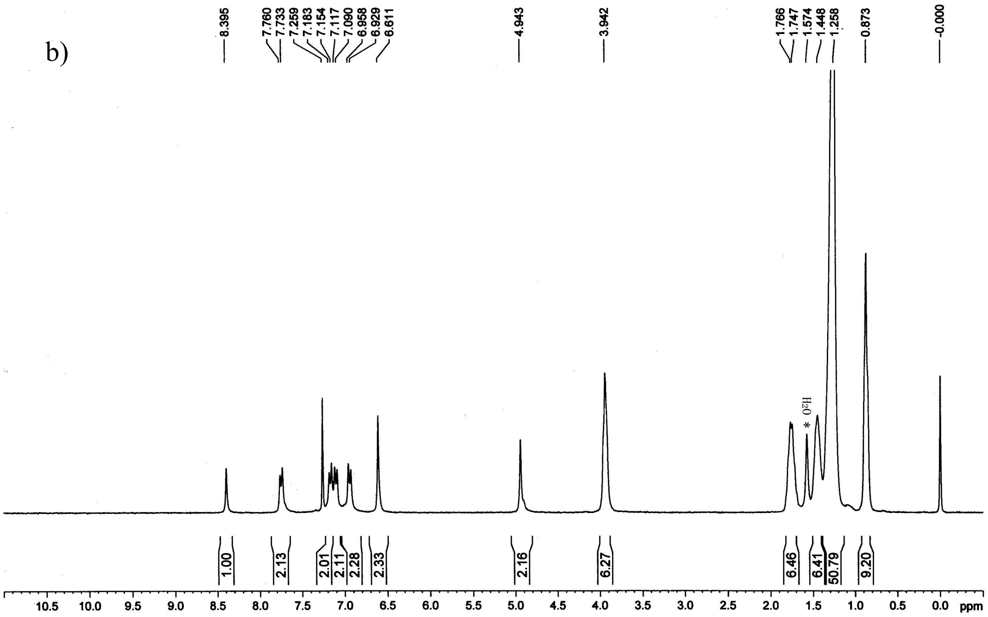


Fig. S1 GPC graphs of a) **I/8**, b) **I/12**, c) **I/16** and d) **I/b10** in THF (1 mL min^{-1}).

1.3 ^{1}H NMR spectra of compound I/8, I/12, I/16 and I/b10





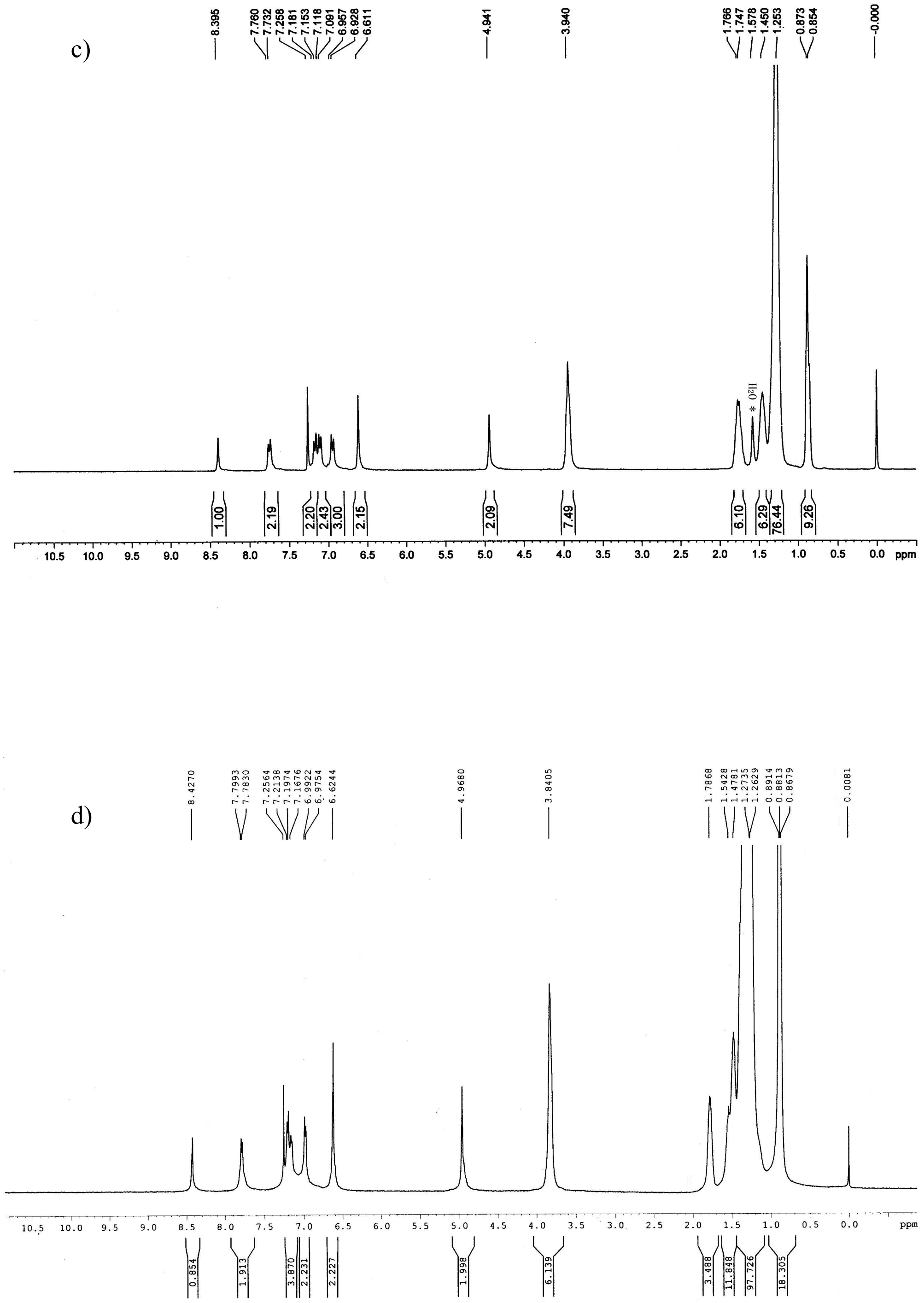


Fig. S2 H^1 NMR spectra of a) **I/8**, 300 MHz; b) **I/12**, 300 MHz; c) **I/16**, 300 MHz; d) **I/b10**, 500 MHz.

2. Experimental techniques

X-ray investigations on powder-like samples were carried out with a Mar 345 image plate detector, samples in glass capillaries (ϕ1 mm) in a temperature-controlled heating stage, quartz-monochromatized CuK$_\alpha$ radiation, 30 min exposure time, calibration with the powder pattern of a series of *n*-alkanes.

High-resolution small-angle powder diffraction experiments were recorded on station BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF), China. Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage with a thermal stability within 0.2 ºC was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. A MarCCD 165 detector was used. *q* calibration and linearization were verified using several orders of layer reflections from silver behemate and a series of *n*-alkanes. Positions and intensities of the diffraction peaks were measured using PeakSolve^{TM} (Galactic).

The 2-d electron density maps were reconstructed on the basis of the general Eqn. (1), using the relative electron densities *I*(*hk*):

$$E(xy) = \Sigma_{hk}\ \mathrm{sqrt}[I(hk)]\ \exp[i2\pi(hx+ky) + \phi_{hk}] \qquad \text{(Eqn. 1)}$$

For the centro-symmetric structures considered in this work the phase angle ϕ can take up the values of 0 or π. The choice of a phase combination was initially made on the merit of each reconstructed electron density map obtained using the most intense reflections, combined with the additional knowledge of the molecules (molecular shape, length, volume of each part and the distribution of electron density among the different moieties).

GISAXS experiments were carried out on station BL14B1 at Shanghai Synchrotron Radiation Facility (SSRF), China. Thin films were prepared from the melt on a silicon wafer. The thin film coated 5 x 5 mm^2 Si plates were placed on top of a custom built heater, which was then mounted on a six-circle goniometer. A MarCCD 225 detector was used. The sample enclosure and the beam pipe were flushed with helium.

3. Additional data

3.1 Optical property of compound I/12, I/16

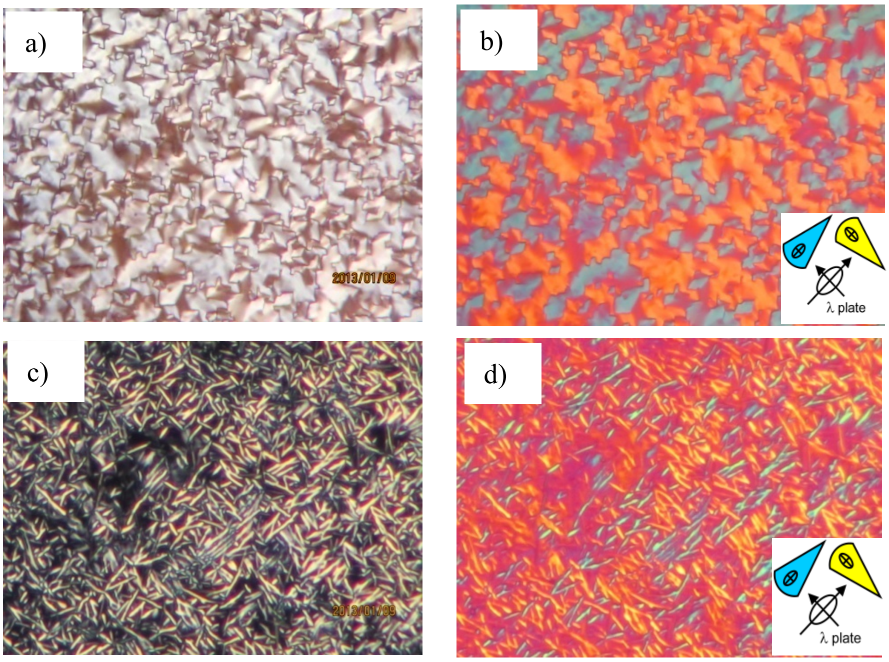


Fig. S3 Optical textures of the Col$_{hex}$ phase (cooling from isotropic state) of compounds a) **I/12** at T = 120 °C as observed between crossed polarizers; b) same texture with λ-retarder plate (the indicatrix orientation in the compensator is shown on the right); c) **I/16** at T = 100 °C as observed between crossed polarizers, d) same texture with λ-retarder plate.

3.2 XRD data

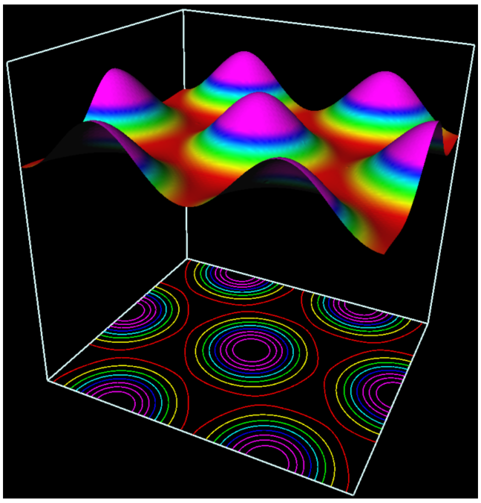


Fig. S4 The Col$_{hex}$/*p*6*mm* phase of compound **I/8**: the surface-and-contour plot of the electron density distribution in the plane normal to the column axis, reconstructed from diffraction pattern in Fig. 3a. The purple regions are the high electron density domains (polar columns), and the red regions are the low electron density areas (alkyl chains).

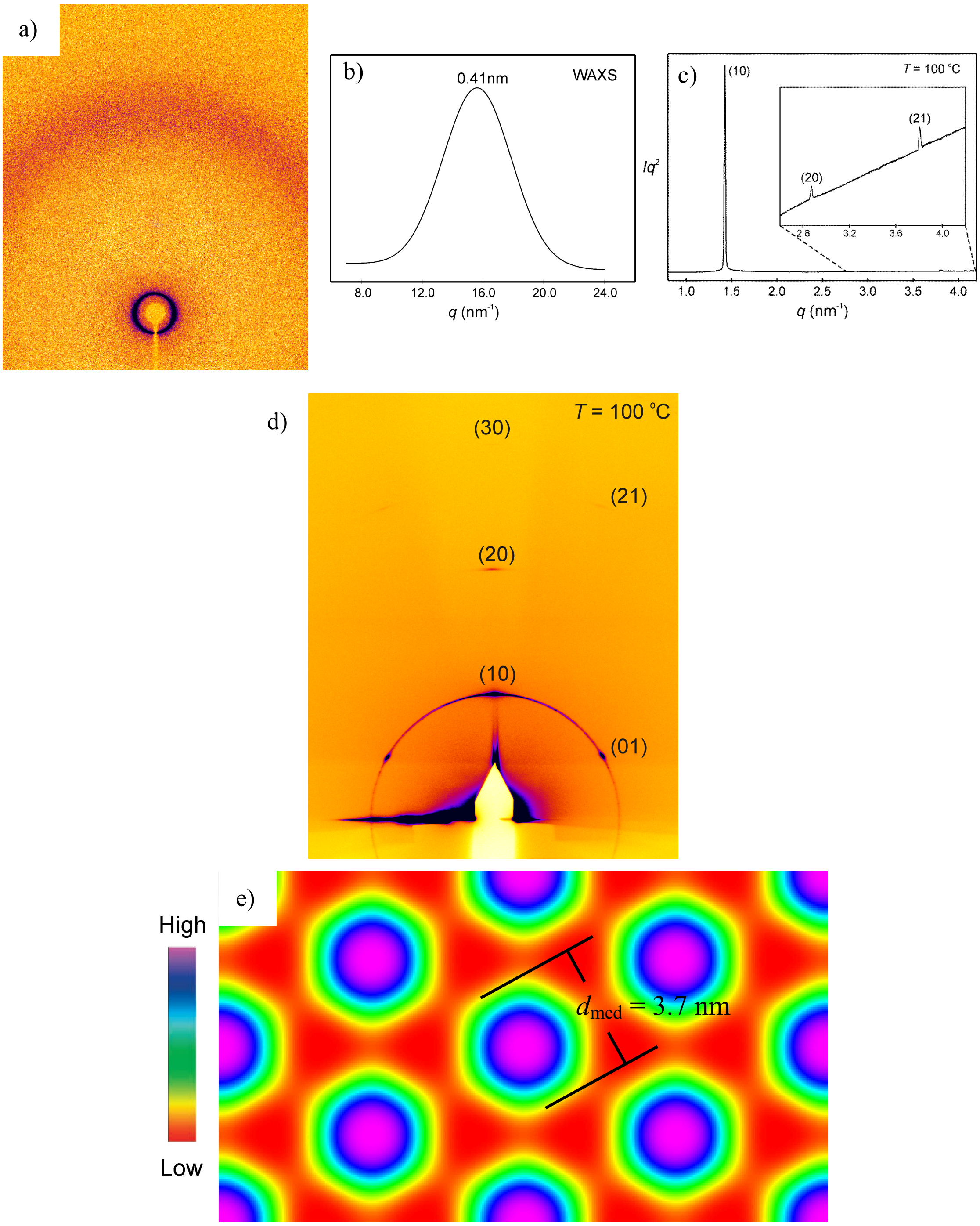


Fig. S5 The Col$_{hex}$/*p6mm* phase of compound **I/12**: a) 2D diffraction pattern at 100 °C; b) WAXS of the diffraction pattern with the *d* value for the maximum of the diffuse outer scattering; c) SAXS diffractogram (synchrotron source); d) GISAXS pattern of the *p6mm* phase at 100 °C; e) Electron density map reconstructed from diffraction pattern in Fig.S5c.

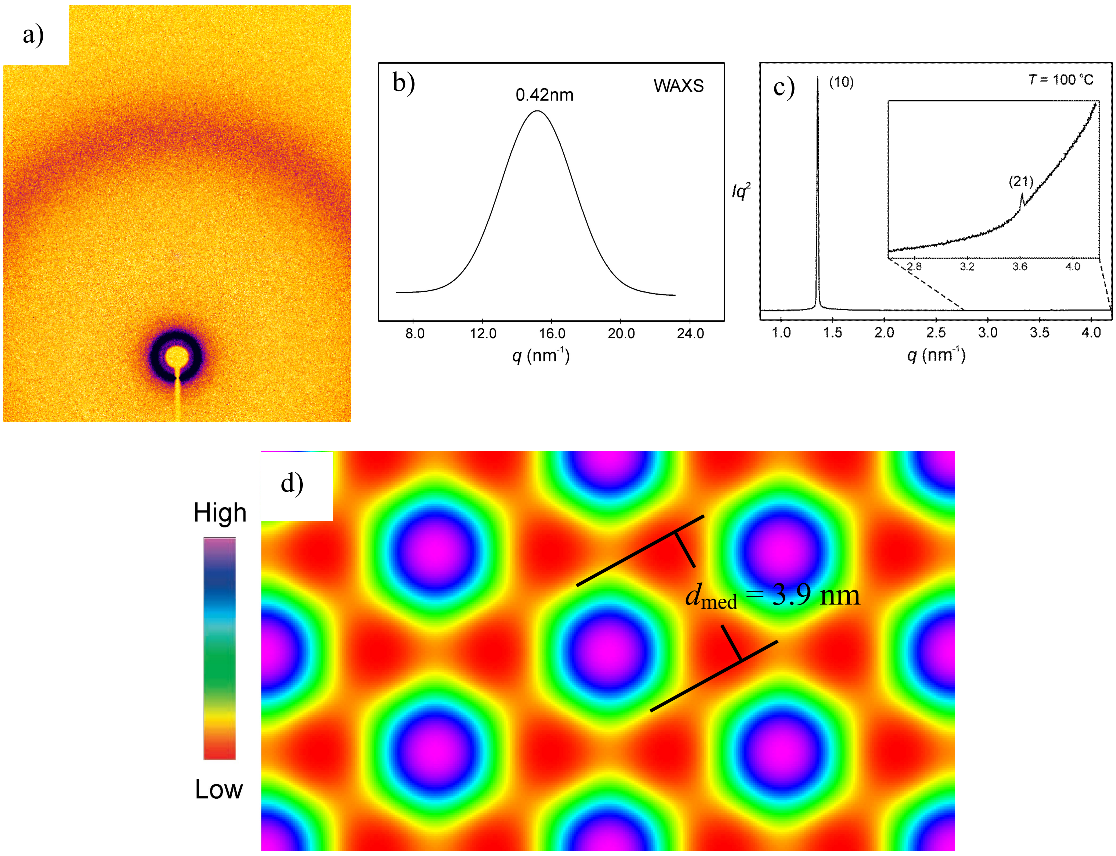


Fig. S6 The Col$_{hex}$/*p6mm* phase of compound **I/16**: a) 2D diffraction pattern at 100 °C; b) WAXS of the diffraction pattern with the *d* value for the maximum of the diffuse outer scattering; c) SAXS diffractogram (synchrotron source); d) Electron density map reconstructed from diffraction pattern in Fig.S6c.

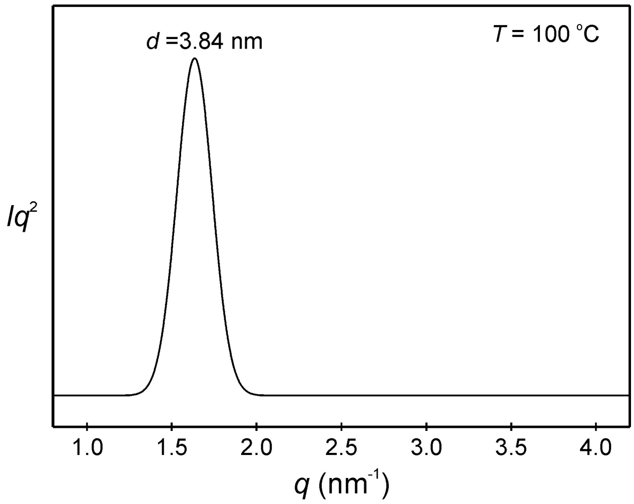


Fig. S7 SAXS diffractogram of **I/b10** (synchrotron source).

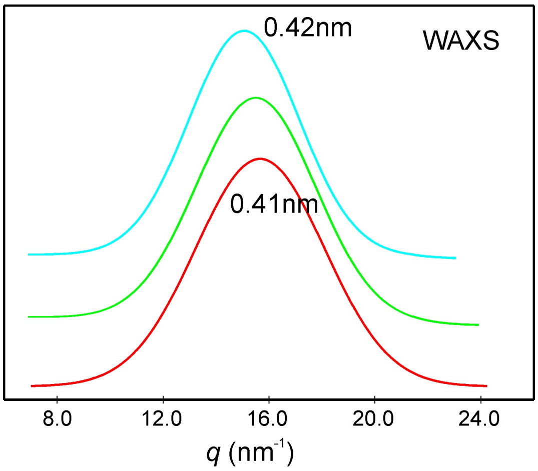


Fig. S8 WAXS diffractogram of **I/8**(red), **I/12**(green), **I/16**(blue).

Table S1 Experimental and calculated *d*-spacings of the observed SAXS reflections of the Col$_{hex}$/*p6mm* in compound **I/8** at 100 ºC. All intensities values are Lorentz corrected with correction for multiplicity.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*phase*
(10)	4.05	4.05	100.0	0
(11)	2.34	2.34	0.2	0
(20)	2.02	2.02	0.5	π
a_{hex} = 4.68 nm				

Table S2 Experimental and calculated *d*-spacings of the observed SAXS reflections of the Col$_{hex}$/*p6mm* in compound **I/12** at 100 ºC. All intensities values are Lorentz corrected with correction for multiplicity.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*phase*
(10)	4.40	4.40	100.0	0
(20)	2.19	2.20	0.2	π
(21)	1.65	1.66	0.3	π
a_{hex} = 5.08 nm				

Table S3 Experimental and calculated *d*-spacings of the observed SAXS reflections of the Col$_{hex}$/*p6mm* in compound **I/16** at 100 ºC. All intensities values are Lorentz corrected with correction for multiplicity.

(*hk*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*phase*
(10)	4.63	4.63	100.0	0
(21)	1.74	1.75	0.2	π
a_{hex} = 5.35 nm				

4. References

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