

## Supporting Information

### **Added Alkane Allows Thermal Thinning of Supramolecular Columns by Forming Superlattice – an X-Ray and Neutron Study**

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## 1. Synthesis of the compounds and preparation of the mixtures

All reagents used were of analytical grade and were purchased from Sigma Aldrich. 1-Bromododecane (97%), 1-bromooctadecane (98%), methyl 3,4,5-trihydroxybenzoate (98%), LiOH (98%), RbOH (99%, 50% wt in H<sub>2</sub>O) were used as received. The solvents were used without further purification other than drying over molecular sieves. The benzene (anhydrous, 99.8%) for preparing the mixtures by freeze-drying was also purchase from Sigma Aldrich.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds were recorded on a Jeol JNM-ECP (400 MHz) spectrometer. CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were used as solvents and tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Autoflex Speed MALDI TOF/TOF MSMS instrument. Elemental analyses of products were carried out using an EA 1108 CHNS analyzer. All reactions were monitored by thin-layer chromatography on silica gel plates (60 F254). The purification by column chromatography was performed using silica gel 60 (35-70µm) as sorbent.

**Methyl 2-ethoxy-7-hydroxybenzo[d][1,3]dioxole-5-carboxylate (1).** A mixture of methyl gallate (31 g, 0.168 mol), amberlite IR 120 (1.5 g), triethylorthoformate (36.21 g, 41 ml, 0.244 mol), freshly ground 4 Å molecular sieves (40 g) and toluene (550 ml) was heated at reflux for 6.5 hours. Ethanol was removed by means of a Dean-Stark trap. The reaction mixture was cooled to r.t., the solid was filtered and the toluene and excess of triethylorthoformate was evaporated under reduced pressure. The product was obtained as yellow oil (24.0 g, 0.1 mol, 62%) which was used without further purification for the next step.

<sup>1</sup>H-NMR (400 MHz) CDCl<sub>3</sub>/δ [ppm]: 7.33 (d, 1H, H<sup>ar</sup>), 7.23 (s, 1H, CH), 6.94 (d, 1H, CH<sup>ar</sup>), 4.11 (t, 2H, -O-CH<sub>2</sub>-), 3.88 (s, 3H, -COO-CH<sub>3</sub>), 0.87 (t, 3H, -CH<sub>3</sub>).

**Methyl 3,4-dihydroxy-5-(octadecyloxy)benzoate (3).** To a mixture of **1** (7.2 g, 30 mmol), K<sub>2</sub>CO<sub>3</sub> (24.87 g, 0.18 mol), KI (0.63 g, 3.8 mmol) and dry 4Å molecular sieves (10g) in dry butanone (100 ml) was added 1-bromooctadecane (12.8 g, 38.4 mmol). The reaction mixture was heated under reflux until the reaction was completed (16 hours) and then was filtered and the butanone distilled off. After drying the residue solvent in vacuum slightly orange oil was obtained, which could be used in the next reaction without further purification. A mixture of methyl 2-ethoxy-7-(octadecyloxy)benzo[d][1,3]dioxole-5-carboxylate (**2**) (14.8 g, 30 mmol), *p*-toluenesulfonic acid (5.7 g, 30 mmol), water (50 ml) and methanol (350 ml) was stirred at room temperature overnight. The reaction mixture was diluted with a NaHCO<sub>3</sub> solution, the methanol was evaporated and the aqueous mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 30 ml). The combined organic layers were washed with water and brine, dried over anhydrous MgSO<sub>4</sub> and the solvent was distilled off. The crude product was purified by column chromatography SiO<sub>2</sub> (eluent CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 9.5/0.5 v/v) yielded (91.7%) a white powder (12.0 g, 27.5 mmol).

<sup>1</sup>H-NMR (400 MHz) CDCl<sub>3</sub>/δ [ppm]: 7.31 (d, 1H, H<sup>ar</sup>), 7.18 (d, 1H, H<sup>ar</sup>), 4.08 (t, 2H, -O-CH<sub>2</sub>-), 3.85 (s, 3H, -COO-CH<sub>3</sub>), 1.81 (q, 2H, -CH<sub>2</sub>-), 1.19-1.47 (overlap, 32H, -CH<sub>2</sub>-), 0.87 (t, 3H, -CH<sub>3</sub>). Anal. Calcd. for C<sub>26</sub>H<sub>44</sub>O<sub>5</sub> (436.63): C, 71.52; H, 10.16. Found: C, 71.46; H, 10.20 %.

**Methyl 3,4-bis(dodecyloxy)-5-(octadecyloxy)benzoate (4).** To a mixture of **3** (12.0 g, 27.5 mmol), K<sub>2</sub>CO<sub>3</sub> (49.75 g, 0.36 mol), KI (1.26 g, 7.6 mmol) and dry 4Å molecular sieves (30 g) in dry butanone (300 ml) was added 1-bromododecane (19.14 g, 76.8 mmol). The reaction mixture was heated under reflux until the reaction was completed (43 hours) and then was filtered and the butanone distilled off. The crude product was purified by column chromatography SiO<sub>2</sub> (eluent CH<sub>2</sub>Cl<sub>2</sub>/hexane = 8/2 v/v) yielded (70.5%) a white powder (15.0 g, 19.04 mmol).

<sup>1</sup>H-NMR (400 MHz) CDCl<sub>3</sub> [ppm]: 7.25 (d, 2H, H<sup>ar</sup>), 4.01 (m, 6H, -O-CH<sub>2</sub>), 3.88 (s, 3H, -COO-CH<sub>3</sub>), 1.77 (m, 6H, -CH<sub>2</sub>-), 1.35 (m, 66H, -CH<sub>2</sub>-), 0.88 (t, 9H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz) CDCl<sub>3</sub> [ppm]: 166.9 (COO), 152.8 x 2, 142.3, 124.6, 107.9 x 2, (6 X C<sup>ar</sup>), 73.5 (*p*-O-CH), 69.1(2 X *m*-O-CH), 52.1 (-COO-CH<sub>3</sub>), 31.9, 30.2, 29.2-29.7, 26.1, 26.0, 22.7 (-CH<sub>2</sub>-), 14.1 (2 X CH<sub>3</sub>). MS: m/z = 773; Anal. Calcd. for C<sub>50</sub>H<sub>92</sub>O<sub>5</sub> (773.28): C, 77.66; H, 11.99. Found: C, 77.48; H, 12.04 %.

**Lithium 3,4-bis(dodecyloxy)-5-(octadecyloxy)benzoate (5).** A mixture of **4** (1.2 g, 1.55 mmol), LiOH (0.185 g, 7.75 mmol) and 90% EtOH (50 ml) was stirred at 95°C for 10 hours. The compound was purified by recrystallization from 90% EtOH (3 x 100 ml) as a white powder (0.55 g, 45.9%).

<sup>1</sup>H-NMR (400 MHz) CDCl<sub>3</sub> + DMSO-d<sub>6</sub> [ppm]: 7.28 (s, 2H, H<sup>ar</sup>), 3.93 (t, 4H, *m*-O-CH<sub>2</sub>), 3.88 (t, 2H, *p*-O-CH<sub>2</sub>), 1.72 (m, 6H, -CH<sub>2</sub>-), 1.2-15 (overlap, 66H, -CH<sub>2</sub>-), 0.87 (t, 9H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz) CDCl<sub>3</sub> [ppm]: 166.9 (C=O), 152.8 x 2, 142.3, 124.6, 107.9 x 2, (6 X C<sup>ar</sup>), 73.5 (*p*-O-CH), 69.1(2 X *m*-O-CH), 52.1 (-COO-CH<sub>3</sub>), 31.9, 30.2, 29.2-29.7, 26.1, 26.0, 22.7 (-CH<sub>2</sub>-), 14.1 (2 X CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz) CDCl<sub>3</sub> + DMSO-d<sub>6</sub> [ppm]: 174, 156 X2, 142, 139, 112X2, 77, 73, 31, 29.7, 28.5-29, 25.5, 25, 21.9, 13.5. Anal. Calcd. for C<sub>49</sub>H<sub>89</sub>O<sub>5</sub>Li (765.19): C, 76.91; H, 11.72. Found: C, 76.83; H, 11.80 %.

**12-12-18Li** was included to test the behavior of asymmetric dendrons with non-equal chain lengths. Other than showing a larger intercolumnar spacing (Figure 1c) and a higher melting point (Figure S3), **12-12-18Li** behaves very similarly to **12-12-12Li**.

The synthesis of 12-12-12Li and 12-12-12Rb was carried out according to ref. S1.

The mixtures (alkali metal salts and n-alkanes) were prepared by freeze-drying from benzene in order to avoid inhomogeneities forming during evaporation of liquid solvent.

## 2. Differential scanning calorimetry

DSC thermograms of the pure compounds and the alkane mixtures were recorded using a Perkin Elmer DSC 6 instrument with a heating and cooling rate of 5 °C/min.

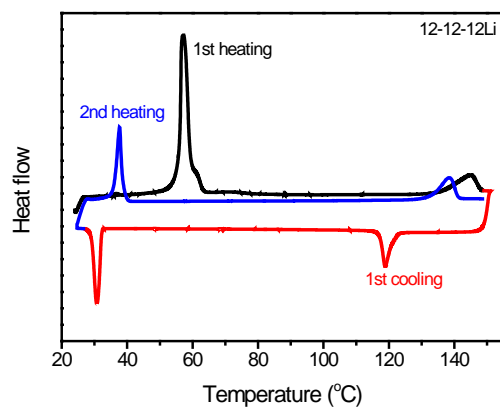


Figure S1. DSC thermograms of pure 12-12-12Li (1<sup>st</sup> heating, cooling and 2<sup>nd</sup> heating).

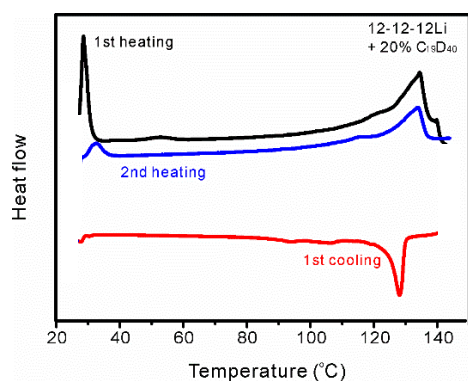


Figure S2. DSC thermograms of the 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 mixture (1<sup>st</sup> heating, cooling and 2<sup>nd</sup> heating).

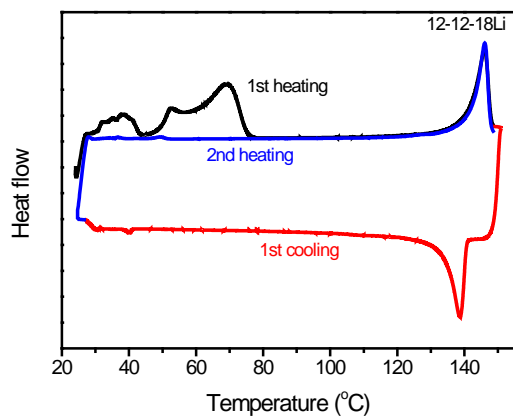


Figure S3. DSC thermograms of pure 12-12-18Li (1<sup>st</sup> heating, cooling and 2<sup>nd</sup> heating).

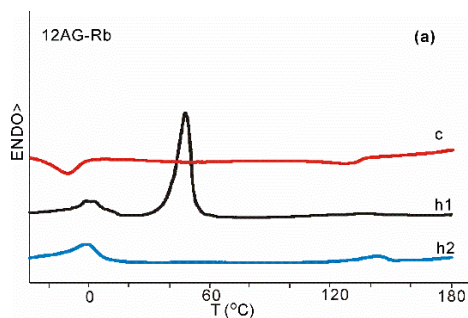


Figure S4. DSC thermograms of 12-12-12Rb (1<sup>st</sup> heating, h1, cooling, c, and 2<sup>nd</sup> heating, h2).

### 3. X-ray and neutron diffraction experimental details

In order to obtain samples with orientation, fibre specimens were prepared. Fibres were extruded using a home-built temperature-controlled piston-and-barrel mini-extruder. The powder sample is inserted in the barrel, the temperature is adjusted to allow extrusion but kept as low as possible to maximize the orientation. For 12-12-12Li and its mixture, all fibres were extruded at room temperature.

Single frame powder SAXS patterns, such as those in Figure S6, were recorded using a laboratory beamline. A Xenocs GeniX microfocus Cu X-ray source was used, coupled with FOX 3D Cu 12-INF infinity focus multilayer mirrors and a two scatterless slits collimator. A home-built furnace for capillaries connected to a Eurotherm temperature controller via a suitable transformer. Temperature could be controlled within  $\pm 0.5^\circ\text{C}$ . The powder samples were placed in 0.5 mm thin-wall glass capillaries and sealed under vacuum for SAXS experiments. A Bruker Vantec 2000 microstrip 2-D detector was used to record the diffraction patterns.

Multiframe powder SAXS patterns were recorded during continuous heating (e.g. Figures 1c or S5) at beamline I22 of Diamond Light Source. A Rapid II multiwire proportional 2-D detector was used. Samples in 1 mm X-ray capillaries were held in a Linkam hot stage. The temperature was calibrated with standard substances, such as the melting point of n-tetracontane. Sample-to-detector distance was calibrated by silver behemate and n-tetracontane.

Fibre WAXS experiments were done using a Rigaku MicroMax 007 system comprising a Cu rotating anode X-ray generator and Osmic Varimax HighRes multilayer optics. An Oxford Cryosystems Cryostream nitrogen cooler/heater was used to control the temperature of the fibre. Fibre samples were packed into 0.5 mm glass capillaries. The fibre axis could be tilted by a goniometer. Some diffraction patterns were recorded by tilting the fibre axis by angle  $\delta$  away from  $90^\circ$  to the beam to allow the meridional reciprocal point to intersect the Ewald sphere. The detector was a Mar345 image plate system.

The reason for using perdeuterated n-C<sub>19</sub>D<sub>40</sub> is that it can be clearly distinguished from the hydrogenous alkyl tails of the dendrons; while the neutron scattering length density (SLD) of a CH<sub>2</sub> group is nearly zero ( $-0.45 \times 10^{-6} \text{ \AA}^{-2}$ ), that of a CD<sub>2</sub> group is  $6.93 \times 10^{-6} \text{ \AA}^{-2}$ .<sup>2</sup> In this study

neutron scattering and SAXS studies give mutually complementary information. The calculated X-ray ED and neutron SLD values for different regions of the present compounds are listed in Table S3.

Small-to-intermediate angle neutron scattering experiments were performed at Station D16 at Institut Laue-Langevin, Grenoble, France. The  $q$ -range from 0.01 to 2.5  $\text{\AA}^{-1}$  could be covered. The primary beam was focused by a pyrolytic graphite monochromator. The take-off angle of  $90^\circ$  was chosen and the corresponding wavelength of the neutron beam was 4.7  $\text{\AA}$ . The samples were packed in aluminium DSC pans that were then inserted into a holder temperature-controlled to within  $\pm 0.5^\circ\text{C}$  by a Eurothem. A MILAND detector was used, which is a He gas-filled proportional detector covering a  $320 \times 320 \text{ mm}^2$  area. The pixel size was  $1 \times 1 \text{ mm}^2$ . For the calibration of resolution and detector response,  $\text{D}_2\text{O}$  data were used as reference.

#### 4. Additional X-ray and neutron diffraction data

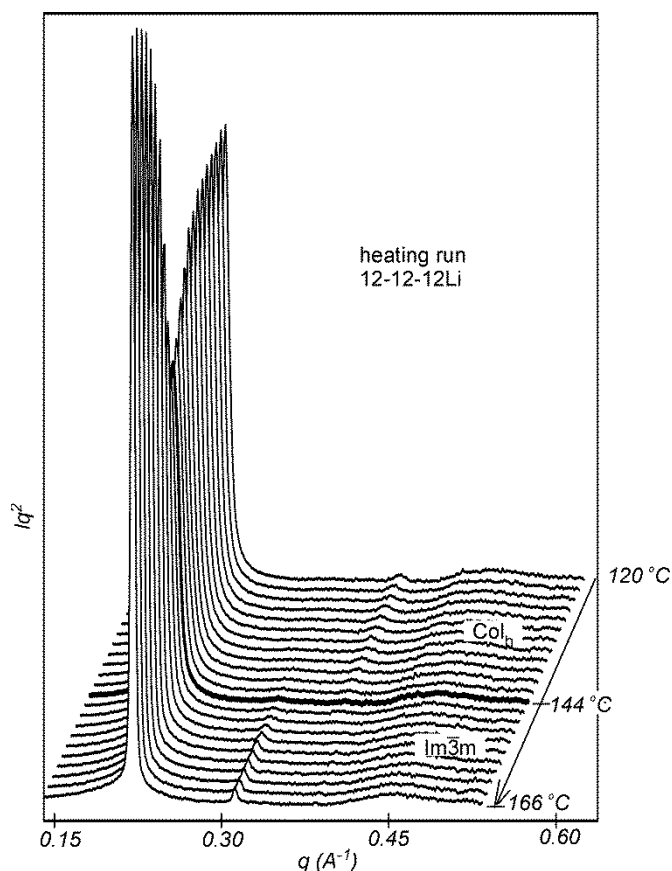


Figure S5 Powder SAXS curves of 12-12-12Li recorded during first heating, showing the hexagonal columnar phase  $\text{Col}_h$  and the BCC cubic phase ( $\text{Im}3m$ ). Visible reflections:  $10_{\text{Col}_h}$  (vs),  $11_{\text{Col}_h}$  (w),  $20_{\text{Col}_h}$  (vw),  $110_{\text{BCC}}$  (vs),  $200_{\text{BCC}}$  (w),  $211_{\text{BCC}}$  (vw).

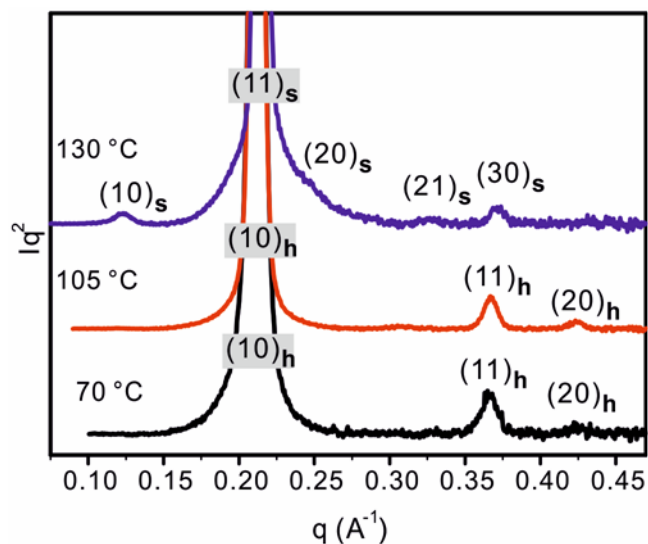


Figure S6 SAXS traces of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 at selected temperatures

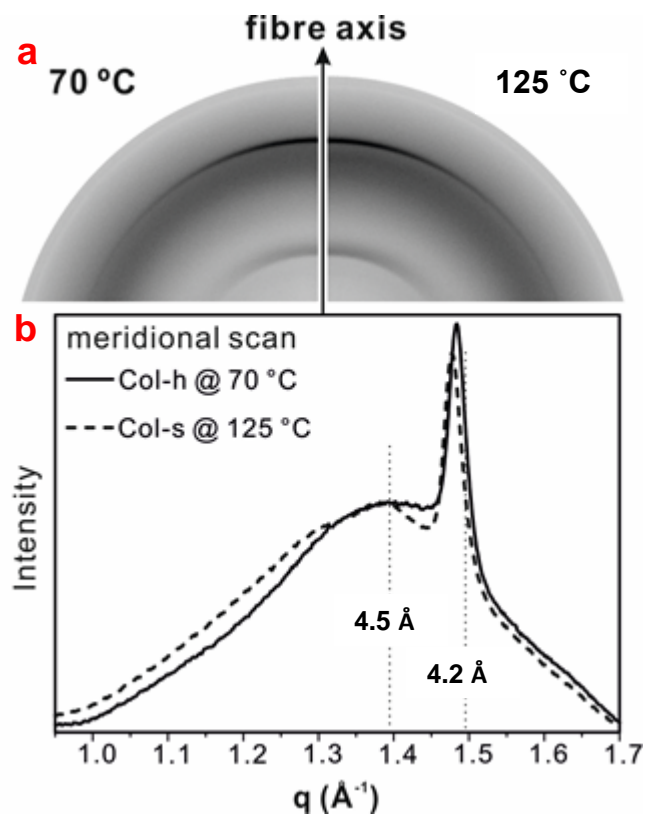


Figure S7. (a) Wide angle fibre X-ray diffraction patterns of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 in the Col<sub>h</sub> (left) and the Col<sub>s</sub> phase (right). Fibre axis is vertical. Only the top part of the patterns is

shown. (b) Radial meridional (vertical) scan of the two patterns in (a). The sharp reflection with d-spacing of 4.2 Å corresponds to the  $\pi$ - $\pi$  stacking of the benzene rings, while the broad peak with the maximum at 4.5 Å is due to correlation scattering of the disordered alkyl chains.

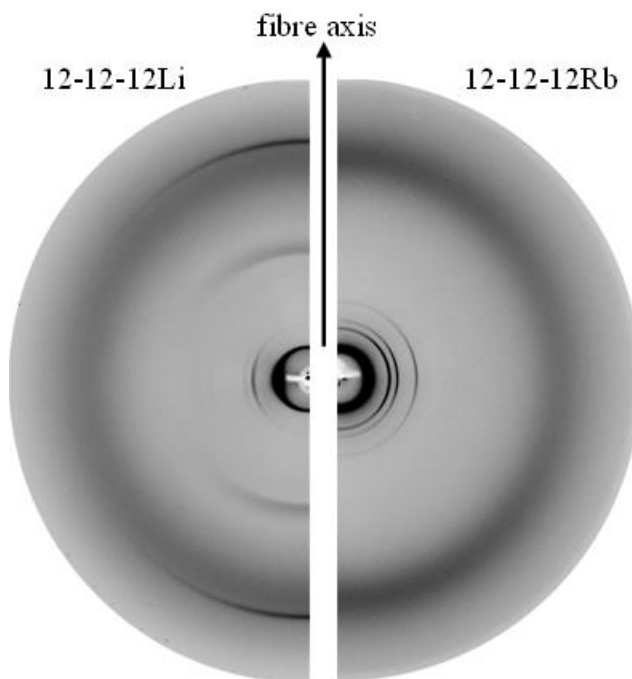


Figure S8. Wide angle fibre X-ray diffraction of a partially oriented fibre of 12-12-12Li (left) and 12-12-12Rb (right) in the Col<sub>h</sub> phase, both recorded at 70 °C. Fibre axis is vertical.

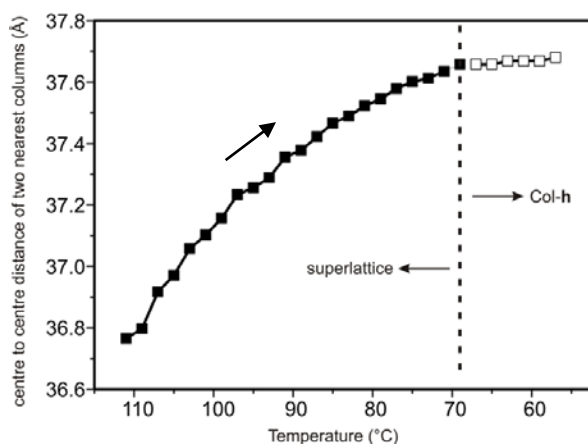


Figure S9. Centre to centre distance between nearest columns of 12-12-18Li + C<sub>19</sub>H<sub>40</sub> 85/15 recorded during cooling.



Table S1 Measured d-spacing of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20

12-12-12Li + C <sub>19</sub> D <sub>40</sub> 80/20				
phase	T (°C)	(hk)	$d_{(hk)}$ (Å)	$a$ (Å)
Col <sub>h</sub>	70	(10)	29.7	34.3
		(11)	17.2	
		(20)	14.8	
	90	(10)	29.8	34.4
		(11)	17.2	
		(20)	14.9	
	100	(10)	29.8	34.4
		(11)	17.2	
		(20)	14.8	
	105	(10)	29.7	34.3
		(11)	17.1	
		(20)	14.8	
Col-s	120	(10)	51.5	59.1
		(11)	29.6	
		(20)	25.6	
		(21)	19.5	
		(30)	17.1	
		(22)	14.8	
	130	(10)	51.1	58.6
		(11)	29.3	
		(21)	19.2	
		(30)	16.9	

Table S2 Bragg peaks and their intensities used for reconstruction of density maps for 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 the chosen phase combination is shown alongside.

		SAXS intensity	phase	SANS intensity	phase
Col <sub>h</sub> @ 70 °C	(10)	100.00	0	10.32	$\pi$
	(11)	4.13	0	100.00	0
	(20)	0.92	0	12.34	0

		SAXS intensity	phase	SANS intensity	phase
Col <sub>s</sub> @ 130 °C	(10)	2.33	$\pi$	36.52	0
	(11)	100.00	0	4.70	$\pi$
	(20)	1.37	$\pi$	28.08	$\pi$
	(21)	1.40	$\pi$	23.92	$\pi$
	(30)	3.61	0	100.00	0
	(22)	0.29	0	12.32	0

## 5. Electron densities and scattering length densities

Table S3 The electron density and neutron scattering length density of different parts of 12-12-12Li and C<sub>19</sub>D<sub>40</sub>. calculated from partial molecular volumes

12-12-12Li	molecular V (10 <sup>3</sup> Å <sup>3</sup> )	Total no. of electrons	electron density (10 <sup>-3</sup> /Å <sup>3</sup> )	Total coherent neutron scattering length (fm)	neutron scattering length density (10 <sup>-6</sup> /Å <sup>2</sup> )
Li gallate part (benzoate + ether oxygens)	0.17*	87.00	520.65	65.85	3.94
alkyl tails	0.91*	291.00	318.56	-41.10	-0.45
C <sub>19</sub> D <sub>40</sub>	0.57**	154.00	271.56	393.19	6.93

\*Molecular volumes were estimated by the unitary crystal volume method.<sup>S3</sup> Molecular volumes were calculated by summing up unitary crystal volumes of each atom. The volume of each atom was determined according to its coordination number.

\*\*Assuming that the molar volume of C<sub>19</sub>D<sub>40</sub> is the same as that of C<sub>19</sub>H<sub>40</sub>. At room temperature, the molar volume of C<sub>19</sub>H<sub>40</sub> is 341.63 cm<sup>3</sup> S<sup>4</sup>.

Electron density was obtained by dividing the total number of electrons with the molecular volume. The neutron scattering length density was calculated by dividing the sum of coherent neutron scattering lengths of all atoms with the molecular volume.

The mixture shows the hexagonal columnar (Col<sub>h</sub>) phase at low temperatures and the hexagonal columnar superlattice (Col<sub>s</sub>) phase at higher temperatures. Both phases are centrosymmetric and the phase angle of each diffraction peak can only be 0 (+) or  $\pi$  (-). In the Col<sub>h</sub> phase, only three peaks, (10), (11), (20), were observed in X-ray and neutron diffraction experiments. The ED maps of the eight possible phase combinations are shown in Figure S11. Maps (-++), (-+-), (--+) and (---) can be excluded because in these tapered dendrons the high-ED aromatic parts are in the centre and the low-ED aliphatic at the periphery of the column. Next we consider the volume ratio of Li gallate part to the aliphatic part (including added alkane), which is 1:8. The hi-ED centres should thus be considerably smaller than the low-ED periphery. This excludes map (+--). Map (++-) has unreasonable maxima at the interstitial points at the centre of the triangles defined by three neighbouring columns where. Map (+++), in contrast, has unreasonably sharp and deep minima at those same interstices, that are especially difficult to justify in blends, where the added alkane can plug such density gaps. Hence, the only remaining phase combination (+++) was selected in this case. It also has the advantage of containing a uniform density aliphatic continuum and circular columns, both typical features of columnar liquid crystals.

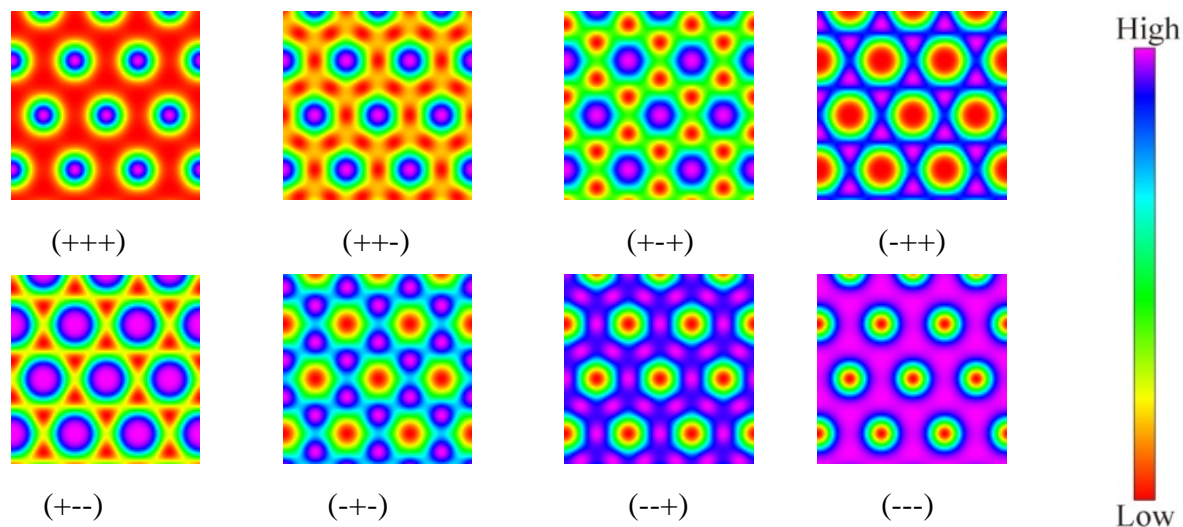


Figure S10. Electron density maps of the Col<sub>h</sub> phase of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> mixture for all phase combinations. Maps are projections on plane perpendicular to column axis. The chosen map is (+++).

Perdeuterated n-alkanes are fully miscible with their hydrogenous counterparts in liquid, rotator and crystalline phases, and are thus ideal labels. (ref: Ungar, G.; Keller, A. *Colloid Polym. Sci.* **1979**, 257, 90-94). Neutron scattering length density maps of the eight possible phase combinations for the Col<sub>h</sub> phase of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 are shown in Figure S12. Similar to the ED map, the columns in the neutron SLD map should have a maximum in the column centre, which excludes combinations (+++), (++-), (--+) and (---). (++-) and (--+) can also be dismissed due to their unexplicable sharp features which have no counterpart in the ED maps. Thus, only phase combination (-++) and (+++) are possible. They both have the same qualitative features, only the interstitial triangular maxima in (-++) are higher than in the (+++) map. Considering that the neutron SLD of deuterated alkane is the highest of all moieties in the system, and that C<sub>19</sub>D<sub>40</sub> is most likely preferentially occupying the interstitial positions, we expect high density there. Also, it is not easy to account for the sharp corners of the low-density (red) hexagon in the (+++) map. Hence, the phase combination (-++) was selected.

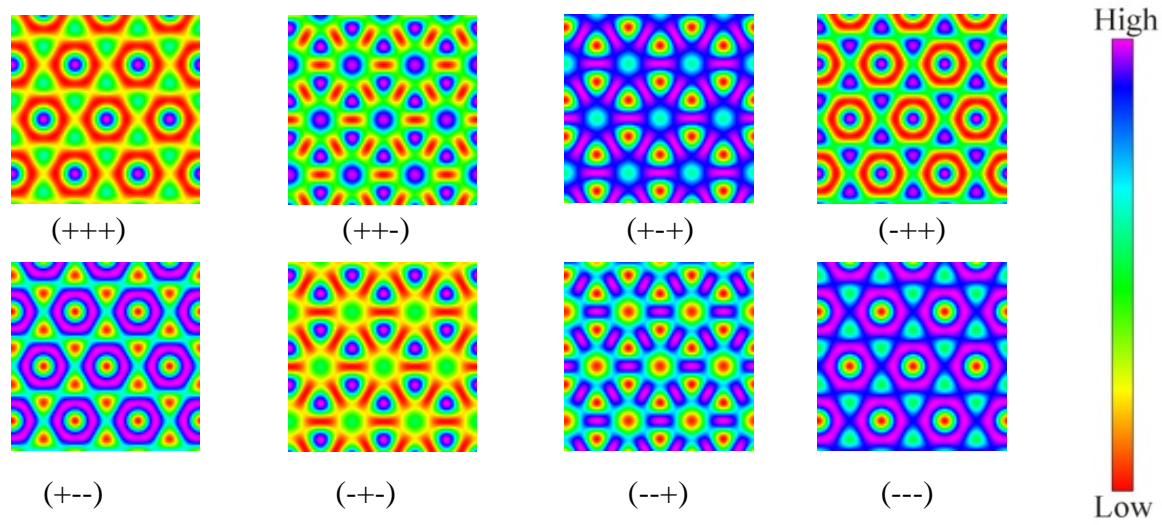
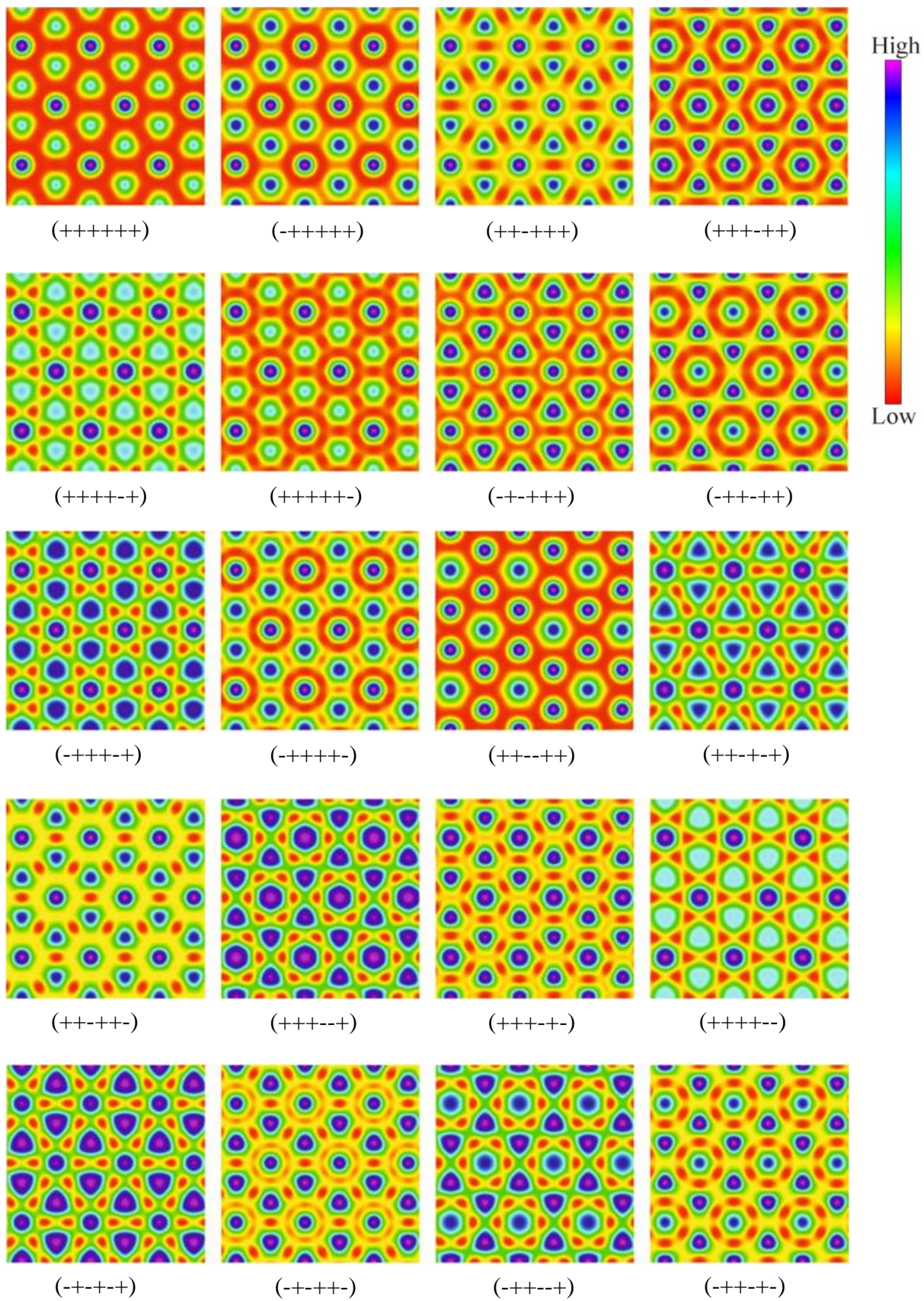


Figure S11. Reconstructed neutron scattering length density maps of the Col<sub>h</sub> phase of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 mixture for all phase combination. The chosen map is (-++).

In the superlattice phase, six peaks, (10), (11), (20), (21), (30), (22), were observed in X-ray diffraction pattern. Based on the criterion that the columns should have high density in the core of the columns, half of the 64 possible maps were deemed non-viable. The remaining 32 maps are shown in Figure S13. The criteria that the lowest density areas should be much larger than the high density ones, and that they should be continuous, leave only phase combinations (+++++), (-----), (++---), and (-+---) in the shortlist. Further, we consider that the number of dendrons in a unit cell is 8, a number not divisible by 3, hence all three columns cannot be equal. On this ground maps (-----) and (++---) were excluded, having central ED maxima of equal size. Both of the remaining phase combination (+++++) and (-+---) are possible. With the number of dendrons per supercell  $\mu'$  closer to 7, as is the case of 12-12-18Li + C<sub>19</sub>D<sub>40</sub> 70/30 near the top of the Col<sub>s</sub> temperature range, the (+++++) map (1 wide + 2 narrow columns, or “1\*3+2\*2”) is more likely, simply because there are not enough dendrons in the supercell for the alternative. However for the cases where  $\mu' \geq 8$ , as in the case of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20, based on X-ray intensities alone we cannot distinguish between the two alternative models of the superlattice cell: 2 wide + 1 narrow column (“2\*3+1\*2”), or 1 wide + 2 narrow columns (“1\*3+2\*2”). Fortunately the choice can be made based on neutron SLD maps, as explained below







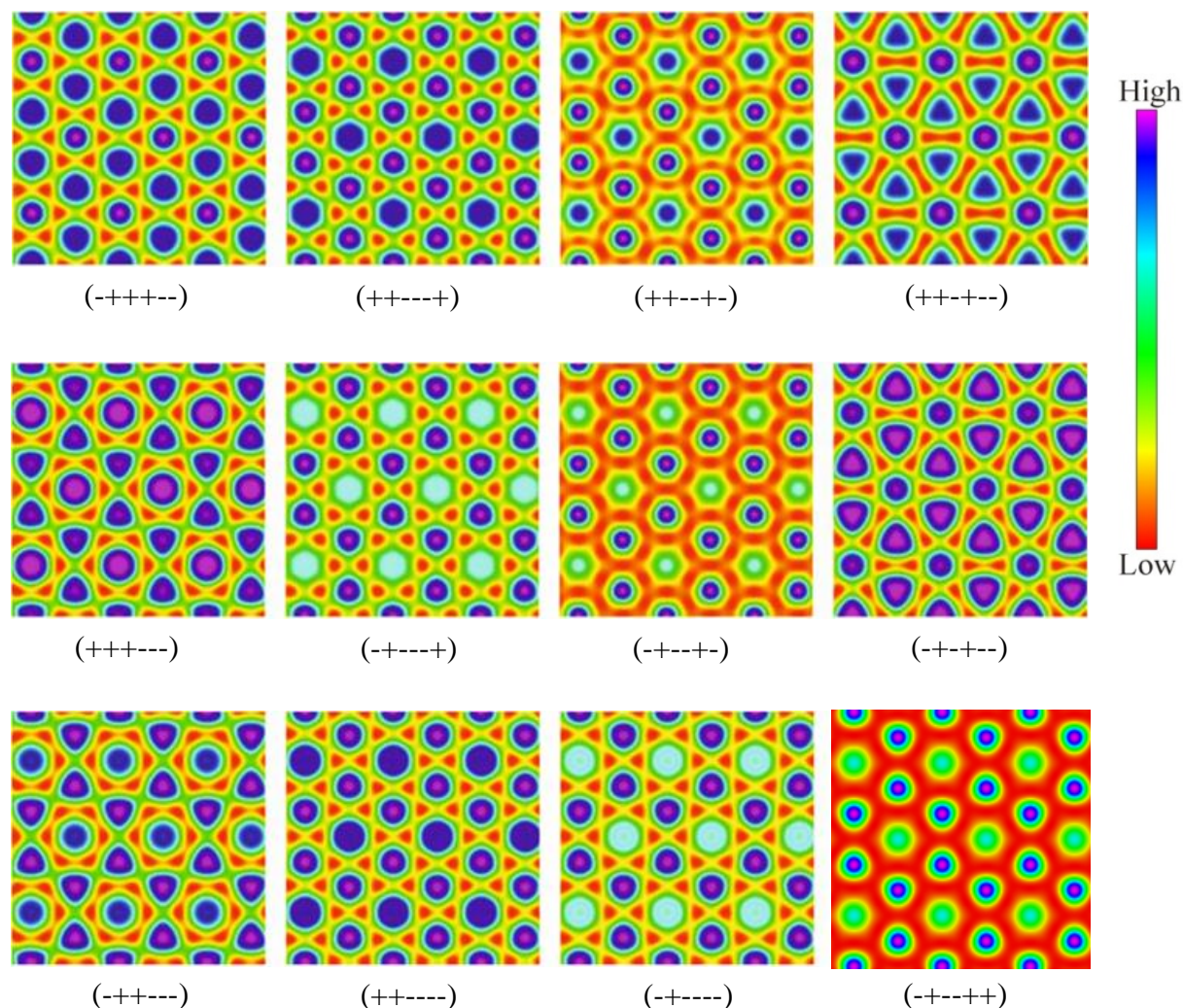


Figure S12. Electron density maps of the superlattice phase of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 for all possible phase combination giving positive maxima at column positions.

In the superlattice phase, six peaks, (10), (11), (20), (21), (30), (22), were observed in the neutron scattering pattern. The different SLD maps with positive maxima in the column centres are displayed in Figure S13. Based on the comparison with the selected ED map of the superlattice and the SLD map of the Colh phase, only three phase combinations are shortlisted:  $(+---++)$ ,  $(-+---)$  and  $(-+---)$ . The key feature, i.e. the replacement of the missing dendron by the alkane, is upheld in all three cases. The  $(+---++)$  corresponds to the “2 dendron-rich + 1 dendron-poor column” ( $2 \times 3 + 1 \times 2$ ) case, while the other two correspond to the “1 dendron-rich + 2 dendron-poor column” ( $1 \times 3 + 2 \times 2$ ) case. Whereas ED maps could not decide between these two cases, SLD maps are more helpful. By combining the data in Tables S3 and S4 we can see that the integrated neutron scattering length from the deuterated alkane is nearly 3 times that of the aromatic parts. This makes the maps  $(-+---)$  and  $(-+---)$  very unlikely, as they are dominated by the aromatic maxima. In contrast, in map  $(+---++)$  the maxima due to interstitial deuterated alkane are more fairly represented, giving the expected balance between aromatic and C<sub>19</sub>H<sub>40</sub> contributions to the map. Thus the  $(+---++)$  is our preferred choice. In fact the

distribution of high-SLD areas in this map is very similar to that in the SLD map of the Col<sub>h</sub> phase (map -++ in Figure S12). As a matter of fact, the phases of the strongest neutron diffraction peaks in the SLD maps of the Col<sub>h</sub> and Col<sub>s</sub> phases are the same, since the 2<sup>nd</sup>, 5<sup>th</sup> and 6<sup>th</sup> peak of Col<sub>s</sub> correspond to the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> peaks of Col<sub>h</sub> – see Figures 2a,b of the main text. Thus there is little doubt that the “2\*3+1\*2” scheme is the correct one for the superlattice phase in the 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 blend.

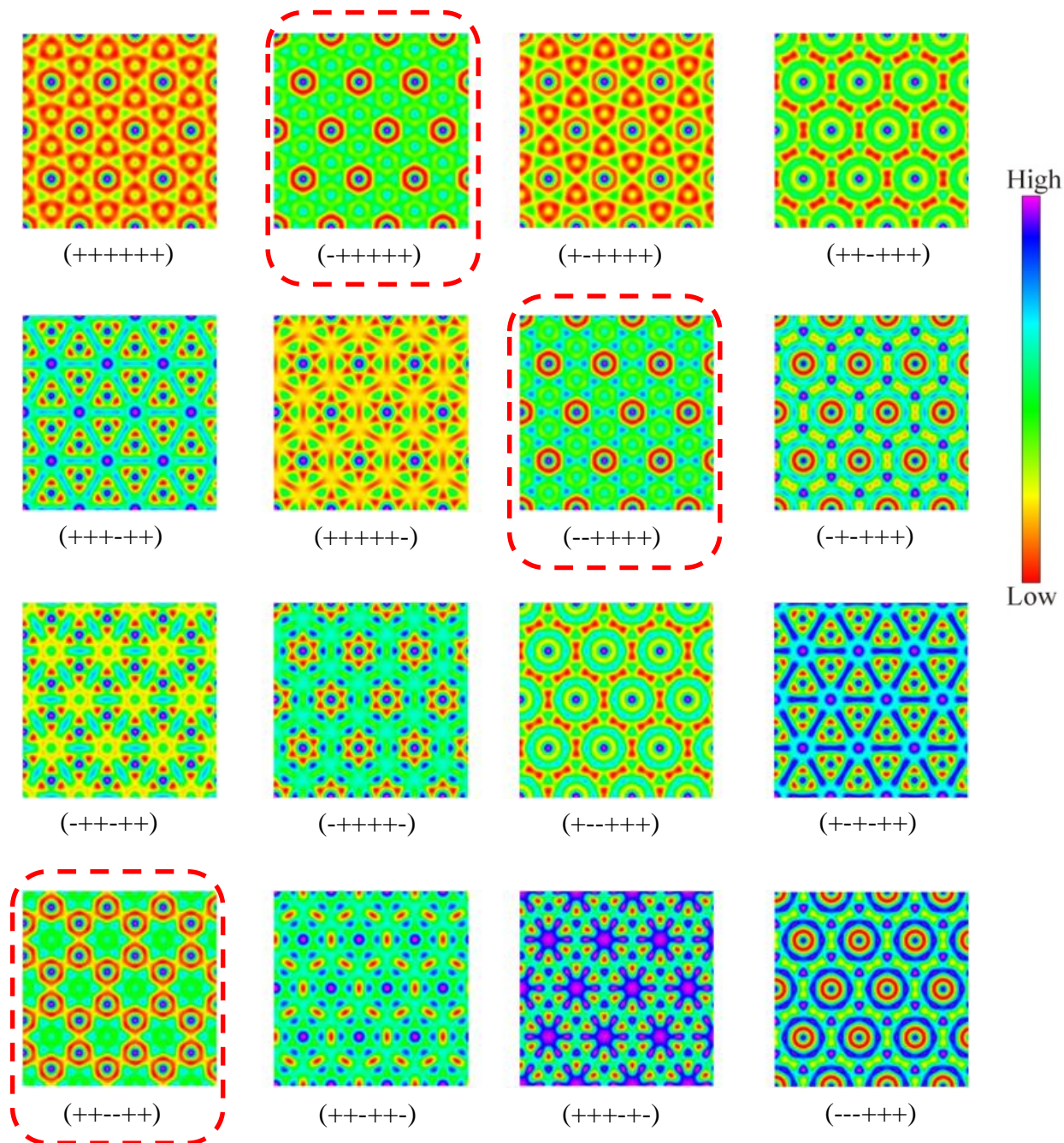


Figure S13 (continued overleaf)



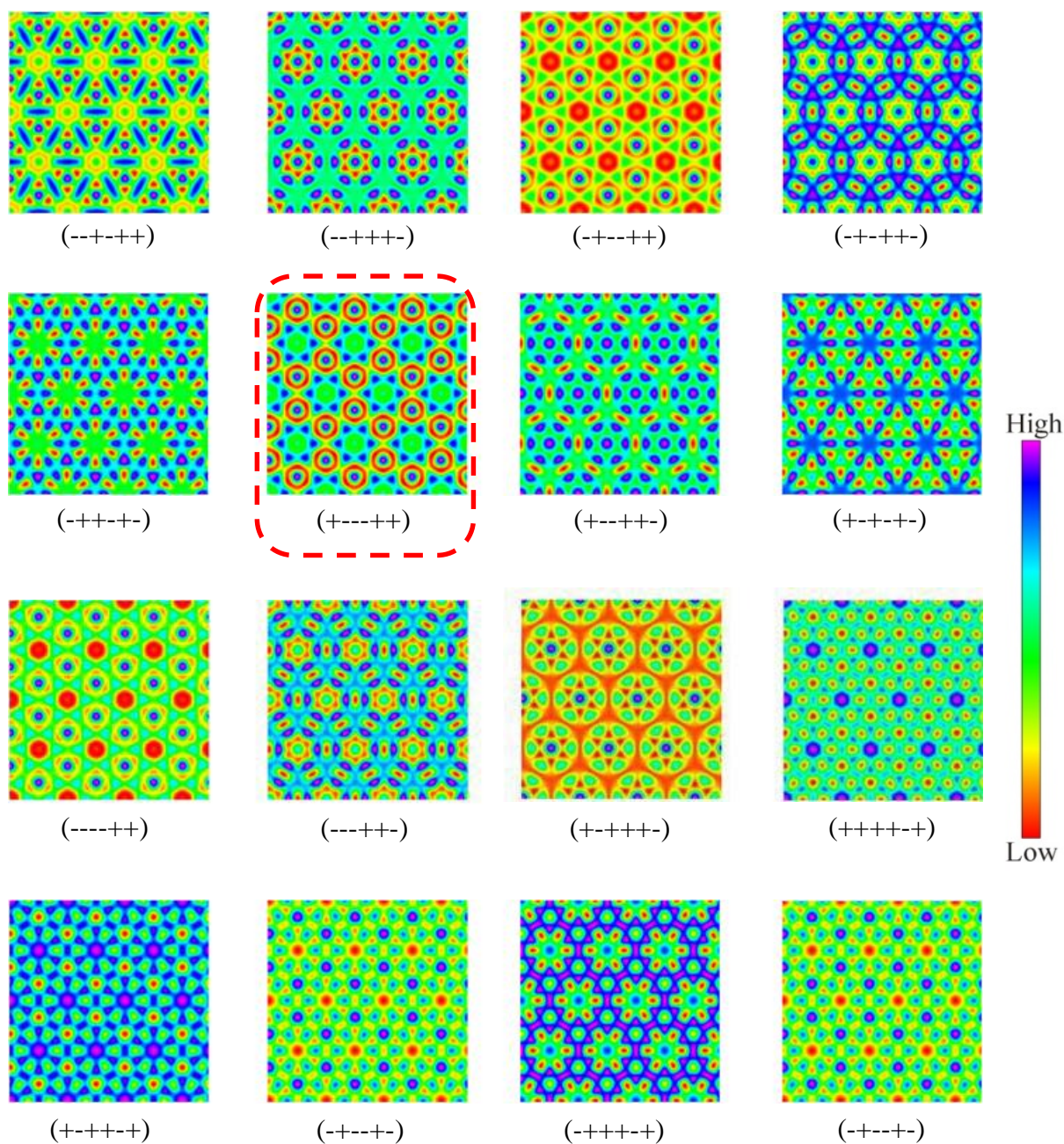


Figure S13. Reconstructed neutron scattering length density maps of the superlattice phase of 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 for all phase combination giving positive maxima in the column centres. The three circled maps are the only ones compatible with a columnar LC with columns of a viable size. The three shortlisted maps are circled, the chosen one with full line.

## 6. Number of molecules in unit cell and in a column stratum

The number of molecules 1 and 2 in a hexagonal unit cell of the blend can be determined by:

$$n_1 = \frac{\sqrt{3}}{2} \frac{N_A a_h^2 c}{M_1 \left( \frac{1}{\rho_1} + \frac{C_2}{C_1} \cdot \frac{1}{\rho_2} \right)}$$

$$n_2 = \frac{\sqrt{3}}{2} \frac{N_A a_h^2 c}{M_2 \left( \frac{1}{\rho_2} + \frac{C_1}{C_2} \cdot \frac{1}{\rho_1} \right)}$$

where  $N_A$  is the Avogadro number,  $a_h$  and  $c$  the lateral and longitudinal unit cell parameters,  $\rho_1$  and  $\rho_2$  the densities of the respective compounds, and  $C_1$  and  $C_2$  the weight fractions of the respective compounds in the blends. Here  $c$  is the spacing between adjacent layers (strata) in the column, obtained from the meridional reflection in the fibre diffraction pattern – see Figure S8

Table S4 Calculated number of molecules in a unit cell of Col<sub>h</sub> phase of pure 12-12-12Li at 70°C

Volumes	
$a$ (Å)	32.1
$c$ (Å)	4.2
V of unit cell (10 <sup>3</sup> Å <sup>3</sup> /molecule)	3.74
V of 12-12-12Li* (10 <sup>3</sup> Å <sup>3</sup> /molecule)	1.16
Number of 12-12-12Li (μ)	
in unit cell	3.2
(rounded)	3

\* Experimental density of 1.02 g/cm<sup>3</sup> for 12-12-12Li measured at R.T.<sup>S1</sup> was extrapolated to 70 °C using thermal expansivity  $9.49 \times 10^{-4} + 1.35 \times 10^{-6}T - 0.53 \times 10^{-8}T^2 + 6.28 \times 10^{-11}T^3$  K<sup>-1</sup>, where T is temperature, reported for alkane n-C<sub>12</sub>H<sub>26</sub>.<sup>S4</sup>

Table S5 Molecular and cell volume and estimated number of 12-12-12Li and C<sub>19</sub>D<sub>40</sub> molecules in a unit cell of Col<sub>h</sub> and superlattice phases in the 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 blend

Volumes		
	Col <sub>h</sub> (at 70 °C)	superlattice (at 130 °C)
<i>a</i> (Å)	34.2	58.6
<i>c</i> (Å)	4.2	4.2
V of unit cell (10 <sup>3</sup> Å <sup>3</sup> )	4.26	12.42
V of 12-12-12Li (10 <sup>3</sup> Å <sup>3</sup> /molecule)*	1.16	1.22
V of C <sub>19</sub> D <sub>40</sub> (10 <sup>3</sup> Å <sup>3</sup> /molecule)**	0.59	0.62
Numbers of molecules		
in unit cell		
12-12-12Li	μ = 2.9	μ' = 7.9
C <sub>19</sub> D <sub>40</sub>	ν = 1.6	ν' = 4.4
in column stratum (rounded)		
12-12-12Li (μ)	3	2, 3, 3***
C <sub>19</sub> D <sub>40</sub> (ν)	1.6	2.4, 1, 1****

\* Using a density of 1.01 g/cm<sup>3</sup> for 12-12-12Li measured at R.T.,<sup>S1</sup> and a density of 0.79 g/cm<sup>3</sup> for n-C<sub>19</sub>H<sub>40</sub>.<sup>S5</sup> The densities were extrapolated to the appropriate temperatures using thermal expansivity,  $9.49 \times 10^{-4} + 1.35 \times 10^{-6}T - 0.53 \times 10^{-8}T^2 + 6.28 \times 10^{-11}T^3$  K<sup>-1</sup>, where T is temperature, reported for alkane n-C<sub>12</sub>H<sub>26</sub>.<sup>S6</sup> Thermal expansivities of 12-12-12Li and C<sub>12</sub>H<sub>26</sub> were assumed to be the same.

\*\*Molar volume and thermal expansivities of C<sub>19</sub>D<sub>40</sub> and C<sub>19</sub>H<sub>40</sub> were assumed to be the same, i.e.  $7.63 \times 10^{-4} + 2.36 \times 10^{-6}T - 7.78 \times 10^{-9}T^2 + 1.91 \times 10^{-11}T^3$  K<sup>-1</sup>, where T is temperature<sup>S4</sup>.

\*\*\* See discussion.

\*\*\*\* Rough estimate

At 70 °C, the volume of Col<sub>h</sub> unit cell is  $3.74 \times 10^3$  Å<sup>3</sup> in pure 12-12-12Li and is  $4.26 \times 10^3$  Å<sup>3</sup> in 12-12-12Li + C<sub>19</sub>D<sub>40</sub> 80/20 mixture. The expansion of the volume of Col<sub>h</sub> unit cell in the mixture is  $0.52 \times 10^3$  Å<sup>3</sup>, which can be accounted for by the added volume of C<sub>19</sub>D<sub>40</sub>. The molecular volume of C<sub>19</sub>D<sub>40</sub> is  $0.59 \times 10^3$  Å<sup>3</sup>, which means that an average unit cell contains just over one added alkane.

## 7. References

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<sup>S1</sup> Percec, V.; Holerca, M. N.; Uchida, S.; Cho, W. D.; Ungar, G.; Lee, Y. S.; Yeardley, D. J. P. *Chem. Eur. J.* **2002**, 8, 1106

<sup>S2</sup> <https://www.ncnr.nist.gov/resources/n-lengths/> (last accessed 3<sup>rd</sup> November 2015)

<sup>S3</sup> Immirzi, A.; Perini, B. *Acta Cryst* **1977**, A33, 216.

<sup>S4</sup> Orwoll, R. A.; Flory, P.J. *J. Am. CSoc.* **1967**, 89, 6814.

<sup>S5</sup> [http://www.chemicalbook.com/ChemicalProductProperty\\_EN\\_CB0269216.htm](http://www.chemicalbook.com/ChemicalProductProperty_EN_CB0269216.htm). (last accessed 3<sup>rd</sup> November 2015)