View Article Online View Journal

# ChemComm

## Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Lehman, M. Prehm, C. Chen, F. Liu, X. Zeng, G. Ungar and C. Tschierske, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC06281A.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Published on 17 September 2018. Downloaded by Rensselaer Polytechnic Institute on 9/17/2018 11:00:39 PM

www.rsc.org/xxxxx

# **ARTICLE TYPE**

## Transition between tangential and co-axial liquid crystalline honeycombs in the self-assembly of Y-shaped bolapolyphiles

Anne Lehmann,<sup>a</sup> Marko Prehm,<sup>a</sup> Changlong Chen,<sup>b</sup> Feng Liu,<sup>b,\*</sup> Xiangbing Zeng,<sup>c</sup> Goran Ungar,<sup>c,\*</sup> Carsten Tschierske<sup>a,\*</sup>

65

70

s Received (in XXX, XXX) Xth XXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

*p*-terphenyl based Y-shaped bolapolyphiles self-assemble into liquid crystalline honeycombs with co-axial organization of the  $\pi$ -conjugated rods around columns filled by alkyl 10 sidechains. In this new hexagonal honeycomb with *P6/mmm* symmetry the orientation of the  $\pi$ -conjugated rods is perpendicular to the tangential honeycombs formed at lower temperature or with longer chain length.

Liquid crystals (LCs) are nowadays indispensible for display- and <sup>15</sup> information technology.<sup>1</sup> The architecture of the industrially used LCs is relatively simple, but in the recent decades the complexity of LC molecules and their self-assembly has been significantly increased.<sup>1,2</sup> Columnar LC phases, for example, were found for a wide range of molecular shapes from disc-like, via taper-shaped, 20 and star-shaped to rod-like.<sup>1,3</sup> The usual mode of organization of the mesogens in these columnar LCs is by stacking in columns, arranged on a 2d lattice, in most cases with hexagonal symmetry and embedded in the fluid continuum formed by the attached flexible chains. The orientation of the molecules is perpendicular 25 to the columns or slightly tilted to the normal of the column long axis, as shown in Fig. 1a for the multi-chain (polycatenar<sup>4</sup>) rodlike molecules. In the recent two decades T-shaped and X-shaped polyphiles have paved the way to new modes of columnar selfassembly, namely the LC honeycombs, having an inverted 30 structure with the flexible chains inside the columns and the nano-segregated rod-like mesogens forming the framework around them (Fig. 1c). In these liquid honeycombs the ratio of the volume of the alkyl chains to the length of the rods determines the number of rods arranged in the polygonal circumference of

<sup>35</sup> each alkyl-filled cell. <sup>5,6,7</sup> The orientation of the mesogens is perpendicular to the column axis  $z^6$  or tilted.<sup>8</sup> Only recently have the co-axial rod-bundle phases, with the molecules parallel to *z*, been reported (Fig. 1b).<sup>9</sup> Herein we report a structure (Fig. 1d) with  $\pi$ -conjugated rods oriented co-axially in honeycombs, thus

- <sup>40</sup> being inverted to structures (b) and (c) in Fig. 1 either with respect to the position or orientation of the rods, respectively. This mode of honeycomb self-assembly with co-axial rods was observed for the *p*-terphenyl based compounds **An** with two polar glycerol end groups and a peripheral lateral chain (see formula in
- <sup>45</sup> Table 1). These compounds were synthesized as described in the ESI (Scheme S1<sup>+</sup>) and their data are collated in Table 1.

Lamellar LC phases (SmA+) are dominant in most An compounds (n = 5-13) and additional non-lamellar LC phases can

be observed for all compounds with  $n \ge 8$ . For compound A11, as <sup>50</sup> a representative example, optical micrographs taken between crossed polarizers are shown in Fig. 2. The lamellar LC phase (SmA+) has a typical birefringent fan-like texture (Fig. 2a). On cooling the birefringence increases (green to second order orange) due to an increasing orientational order parameter of the <sup>55</sup> rods, and at the next transition a highly viscous mosaic-like texture develops (Fig. 2b), indicative of layer stiffening in the phase designated as *P6/mmm*. At the subsequent phase transition to the low temperature (LT) phase (*p4mm*) the mosaics become broken and fluid again, accompanied by a significant decrease in <sup>60</sup> birefringence (color change from 2<sup>nd</sup> order orange via 1<sup>st</sup> order green to blue, see Fig. 2c), meaning that either the degree of order or the orientation mode of the  $\pi$ -conjugated rods had changed.



**Figure 1**. Hexagonal columnar organizations in LC phases. (a) formed by polycatenar molecules<sup>4</sup> and (b-d) formed by bolapolyphiles with lateral <sup>80</sup> chains; (b) co-axial rod-bundle phase;<sup>9</sup> (c) tangential hexagonal honeycomb,<sup>6</sup>, and (d) the co-axial honeycomb (*P6/mmm*) reported herein.

In homeotropically aligning cells smectic layers form parallel to the surfaces. In this case the lamellar phase (SmA+), appearing at the highest temperature, is completely dark between crossed spolarizers. This indicates that, on average, the terphenyls are perpendicular to the layers. Under these conditions the phase transition to the next LC phase (*P6/mmm*) is difficult to recognize; the texture remains dark and only the viscosity increases (Fig. S2a, b†). This is the first hint that another 90 optically uniaxial mesophase has formed A low birefringent (gray) "spherulitic" texture, typical of columnar phases, with



An	Phase transitions $T/^{\circ}C [\Delta H/k \text{Jmol}^{-1}]$	SmA+: $d_1$ , $d_2$ (nm)	P6/mmm: $a_{hex}$ , $c$ (nm)	$p4mm: a_{squ}(nm)$
A5	Iso 203 [6.7] SmA+ 114 [18.2] Cr	2.16, 1.83	-	-
A7	Iso 191 [6.6] SmA+ 105 [16.2] Cr	n.d.	-	-
A8	Iso 187 [6.0] SmA+ 116 [0.8] P6/mmm 101 [18.1] Cr	2.20, 2.2	2.44, 2.20	-
A9	Iso 182 [5.2] SmA+ 130 [0.8] <i>P6/mmm</i> 95 [-] M 65 [2.4] Cr	2.19, 2.32	2.64, 2.23	-
A10	Iso 182 [4.7] SmA+ 157 [1.0] P6/mmm 115 [1.8] Col <sub>squ</sub> /p4mm 78 [11.3] Cr	2.13, 2.51	2.84, 2.17	2.81
A11	Iso 179 [4.0] SmA+ 164 [1.2] <i>P6/mmm</i> 136 [2.4] Col <sub>squ</sub> / <i>p4mm</i> 84 [13.4] Cr	2.16, 2.66	3.05, 2.22	2.86
A12	Iso 178 [3.5] SmA+ 169 [1.4] <i>P6/mmm<sup>b</sup></i> 131 [2.3] Col <sub>squ</sub> / <i>p4mm</i> 98 [17.1] Cr	2.14, 2.83	3.27, 2.21	2.86
A13	Iso 177 [3.0] SmA+ 172 [1.7] <i>P6/mmm<sup>b</sup></i> 141 [3.2] Col <sub>squ</sub> / <i>p4mm</i> 107 [18.4] Cr	2.12, 2.84	3.28, 2.20	2.83
A14	Iso 179 [6.2] Col <sub>rev</sub> /p2gg 129 [26.0] Cr	-	-	7.00, 6.58 $(p2gg)^c$

<sup>*a*</sup> Values determined on cooling with rate 10 K min<sup>-1</sup> by DSC (peak temperatures); abbreviations: Cr = crystalline solid, Iso = isotropic liquid, SmA+ = orthogonal lamellar phase with diffuse small angle scattering; *P6/mmm* = 3D hexagonal LC phase with co-axial rod orientation in a hexagonal honeycombs;  $Col_{squ}/p4mm$  = tangential square honeycomb LC phase;  $Col_{rec}/p2gg$  = pentagonal honeycomb LC phase; M = unknown mesophase; n.d. = not determined; for transitions on heating, more details and calculations, see Tables S1 and S8<sup>+</sup>, for DSC traces, see Fig. S1<sup>+</sup> and for XRD data see Figs S7-S15 and Tables S2-S7<sup>+</sup>; <sup>*b*</sup> phase coexists with  $Col_{squ}/p4mm$ ; <sup>*c*</sup> parameters *a* and *b* of the Col<sub>rec</sub>/p2gg phase.



Published on 17 September 2018. Downloaded by Rensselaer Polytechnic Institute on 9/17/2018 11:00:39 PM

**Figure 2.** Textures of **A11** as observed between crossed polarizers (white arrows); a-c) in planar aligning cells (terphenyls parallel to the substrate surface, 5 µm PI coated cells) and d) in homeotropic alignment (terphenyls perpendicular to the surfaces, between non-treated microscopy glass plates) as observed on cooling. The insets show textures with additional  $\lambda/2$  plate at the same temperatures, the blue arrows indicate the direction of the slow axis; for more details and explanations, see Figs. S2-S5†.

columns in the parallel to the surface, develops on further cooling at the transition to the fluid LT phase (*p4mm*, Fig. 2d).

For all **An** compounds in the whole temperature range down to crystallization, the WAXS pattern is diffuse with a maximum at d = 0.45-0.47 nm, confirming true LC phases without fixed

- positions of individual molecules (see Section S2.3 in ESI<sup>†</sup>). In the high temperature phases of surface-aligned **A5-A13** there is a weak 1<sup>st</sup>- and a stronger 2<sup>nd</sup>-order layer reflection on the meridian, confirming a homeotropic lamellar phase with a layer to thickness of  $d_1 = 2.13-2.20$  nm (Fig. 3a and Table 1). The *d*-value
- is almost identical for all compounds and is close to the length of the bolaamphiphilic core, measured between the secondary OH groups in a compact conformation ( $L_{mol,min} = 2.3$  nm, see Fig. S17a<sup>+</sup>). This indicates a smectic phase with monolayer structure.
- <sup>15</sup> In contrast to the layer reflections, the diffuse WAXS maximum is on the equator, confirming an on average non-tilted parallel organization of terphenyls and a significant part of the alkyl chains perpendicular to the layers.

An unusual feature of this SmA phase is an additional diffuse 20 scattering with relatively high intensity in the SAXS pattern (SmA+). In a homeotropically aligned sample with the X-ray beam parallel to the layers (Figs. 3a and S8b<sup>†</sup>) the maximum of this diffuse scattering  $(d_2)$  is on the equator, i.e. perpendicular to the layer reflection. It indicates additional strong short range in-25 plane density fluctuations with a mean distance between 1.8 and 2.8 nm. This distance increases with alkyl chain length (Table 1). This extra feature is likely to be due to the average distance between domains arising from local segregation of the flexible lipophilic alkyl chains from the polar and rigid bolaamphiphilic 30 cores. The volume fraction of the lateral chains increases from 0.20 to 0.39 between A5 to A13 (Table S8<sup>†</sup>), thus the chains represent the minor component in all cases. This phase, designated as SmA+,<sup>5,6</sup> can thus be considered as a mesh phase<sup>10,11</sup> with the layers irregularly penetrated by alkyl chain 35 domains. The relatively small meridional spread of the diffuse SAXS maxima on the equator suggests that the alkyl domains are columns perpendicular to the layers and cutting through several of them, on average (see Fig. 4c).

At the next phase transition, observed in compounds A8-A13, 40 this diffuse scattering condenses into a sharp Bragg peak on the equator (Figs. 3b and S8<sup>†</sup>) and then it can be indexed as the (100) reflection of a 3D hexagonal lattice, spacegroup P6/mmm, with  $a_{\text{hex}} = 2.44$  to 3.18 nm (Table 1). The positions of the (100) and (200) layer reflections on the meridian are almost unchanged and 45 become the (001) and (002) reflections of periodicity c = 2.17-2.22 nm). The GISAXS pattern in Fig. 3c confirms this assignment. The positions of the diffuse equatorial WAXS maxima do not change, indicating that the orientation of pterphenyls and alkyl chains remains parallel to the column long 50 axis (Fig. 3b). The proposed structure, depicted in Fig. 4b, is corroborated by the reconstructed electron density (ED) map in Fig. 3d, where the alkyl chains forming infinite low ED columns (red) are arranged on a regular hexagonal lattice and are embedded in a high ED lamellar continuum (purple) with slightly 55 modulating ED due to the alternation of glycerols and terphenyls in the penetrated layers. The ED difference between glycerols and terphenyls is small, hence the weak (001) reflections. The fact that Published on 17 September 2018. Downloaded by Rensselaer Polytechnic Institute on 9/17/2018 11:00:39 PM

(002) is stronger than (001) (Figs. 3c and S9b<sup>†</sup>) indicates a local ED minimum in the middle of the layers, attributed to the fact that the alkyls are tethered to the ends of the terphenyl cores (note the weak modulation in diameter of alkyl columns in Fig. 3d).

The  $a_{\text{hex}}$  parameter of the *P6/mmm* in-plane lattice increases significantly with increasing chain length, from 2.44 nm for **A8** to 3.28 nm for **A13**. This is due to the expansion of the lipophilic columns, amplified by a concomitant increase in the number of molecules per unit cell from  $n_{\text{cell}} = 14$  for **A8** to 22 for **A13** <sup>10</sup> (Tables 1 and S8†), The number of molecules in the lateral cross section of these honeycomb walls is  $n_{\text{wall}} = 2.6-2.7$  for all compounds (for calculation, see section S2.5 in the ESI†). Thus two to three (1.7-2.7) molecules are arranged side-by-side along each of the six sides of a hexagonal cell around each alkyl

<sup>15</sup> column. This structure can be considered as a co-axial honeycomb (Figs. 1d and 4b), having the rod-like mesogens arranged parallel to the column axis instead of perpendicular to it, as in the previously reported tangential honeycombs (Fig. 1c).<sup>6</sup> Due to this inverted organization the periodicity provided by the <sup>20</sup> bolaamphiphilic core structure leads to a periodicity along the column axis (*z*) instead of fixing the honeycomb shape in the *x-y* 



**Figure 3**. a,b) XRD patterns (obtained after subtraction of the scattering <sup>25</sup> pattern in the isotropic liquid state, for original patterns, see Fig. S10†) of a surface aligned sample of compound **A10** in (a) SmA+ and (b) *P6/mmm* phases; c) GISAXS pattern of the *P6/mmm* phase of **A13** at 165 °C on a Si surface with either the (100) or the (001) axis perpendicular to the substrate surface d) electron density (ED) map of the *P6/mmm* phase of **3**<sup>30</sup> compound **A9** (red = low ED, purple = high ED; see also Section S2.3 in the ESI†).

For compounds **A9-A13** there is an additional phase transition from *P6/mmm* to a LT phase. Its SAXS and GISAXS patterns for compounds **A10-A13** can be indexed to a square lattice with <sup>35</sup> *p4mm* phase group (Figs. S11 and S12). The lattice parameters of the *p4mm* phases of all four compounds are almost identical ( $a_{squ}$ = 2.81-2.86 nm, Table 1), being only slightly larger than the molecular length in the most stretched conformation ( $L_{mol,max}$  = 2.6 nm, see Fig. S17b†). This is typical of tangential honeycombs <sup>40</sup> with square cells. The phase structure is corroborated by ED

<sup>40</sup> with square cens. The phase structure is contobulated by ED maps (see Figs. S11d and S14<sup>†</sup>) and is in line with the negative birefringence (see inset in Fig. 2c and Fig. S2e,f<sup>†</sup>). This confirms that the intramolecular  $\pi$ -conjugation pathway, i.e. the rod orientation, is perpendicular to the columns. The structure is <sup>45</sup> depicted in Fig. 4a. For compounds A12 and A13 with longer chains the transition from *P6/mmm* to *p4mm* is not complete, i.e. *p4mm* and *P6/mmm* coexist in the *P6/mmm* range (Fig. S13c†). **A9** rapidly crystallizes and therefore its LT phase (M) could not be investigated. No LT phase is observed in **A8**, while even the <sup>50</sup> *P6/mmm* phase is absent in **A7** and **A5**, leaving only the SmA+ phase (Table 1, Fig. 5a). Extension of the lateral chain of **A13** by just one more CH<sub>2</sub> unit (**A14**) leads to a sudden and simultaneous loss of the SmA+, *P6/mmm* and *p4mm* phases. Only a rectangular columnar phase with *p2gg* lattice (*a* = 7.0 nm, *b* = 6.6 nm) is left <sup>55</sup> in **A14**, representing a honeycomb composed of slightly deformed pentagonal cells (Table 1, Fig. 5a, for details, see Figs. S6, S15 and S20†).



**Figure 4.** Schematic models of the three LC phases in compounds An: (a) square tangential honeycomb p4mm; (b) hexagonal coaxial 3D phase P6/mmm; (c) random mesh perforated layer phase SmA+. Grey = terphenyl, blue = glycerol, white = alkyl.

In the series of isomeric compounds **B***n* (Fig. 5b), having the lateral alkyl chain at the central benzene ring, the SmA+ phase is formed over a much smaller chain-length (n = 5,6) and temperature range and the *P6/mmm* phase is completely absent.<sup>12</sup> Instead, **B***n* compounds exhibit a series of more conventional tangential honeycombs, as follows (Fig. 5b): a centred rectangular (*c2mm*) phase consisting of rhombic cells in **B8**; a ro high-temperature square *p4mm* phase with square cells in **B9**, **B10** and **B11**, preceded in **B9-B11** at lower temperature by a rectangular *p2mm* phase. Finally, in **B12** and **B14** we see the *p2gg* phase made up of pentagonal cells, as in **A14**.

Why has the transfer of attachment point from the central (**B***n*) 75 to the terminal benzene ring (An) caused such unusual phase behaviour in An? As the side-chain volume increases, either due to increased temperature or to addition of extra CH<sub>2</sub> groups, the squares of the p4mm phase would be expected to turn into pentagons or hexagons, as in the **B***n* and other T-shaped <sup>80</sup> amphiphiles. However, in that case the chains in **Bn** compounds emanating from the corners of such polygons would have a problem reaching the centre of the cell. Even though geometrically possible, stretching of alkyl chains to maintain high density at the centre of pentagonal or even square cells at higher 85 temperatures would be entropically disfavoured. Hence an alternative solution is adopted by the Y-shaped An molecules, abandoning the tangential in favour of axial alignment of the cores. There must, however, be a free energy penalty for this inversion, as in most other cases the tangential structure prevails. <sup>90</sup> A possible penalty is the dilution of hydrogen bonding glycerol groups in (perforated) 2D layers in P6/mmm and SmA+ phases, in contrast to their concentration in well segregated 1D columns in tangential honeycombs. Thus, as in many other examples, a relative minor alteration in molecular design leads to frustration 95 resolved by the system adopting novel and potentially advantageous mesostructures.



**Figure 5**. Comparison of the LC phases on cooling (10 K min<sup>-1</sup>) a) of the Y-shaped (**A***n*) and b) the T-shaped bolapolyphiles **B***n*<sup>12</sup> depending on the 5 length of the lateral chain *n*; abbreviations: see Table 1 and 3D-Hex = P6/mmm; Col<sub>rec</sub>/c2mm = rhombic honeycomb; Col<sub>rec</sub>/p2mm = rectangular honeycomb; Col<sub>sq</sub> = Col<sub>squ</sub> in brackets were only observed on cooling.

A similar sequence SmA+  $\rightarrow$  *P6/mmm* has been observed for facial amphiphiles with exchanged positions of alkyl chains and <sup>10</sup> polar groups at the *p*-terphenyl core.<sup>13</sup> In this *P6/mmm* phase the polar lateral groups form the columns on the hexagonal lattice and the alkyl chains separate the layers of the coaxially aligned *p*terphenyl rods ("channelled layer phase", ChL<sub>hex</sub>).<sup>13</sup> In another related structure, the so-called "tubular nematic columnar phase", <sup>15</sup> formed by hairy-rod polymers<sup>17</sup> and some oligomesogens,<sup>14</sup> the mesogens are also co-axial to lipophilic columns, but have only orientational order. This indicates that co-axial honeycombs represent a general mode of LC self-assembly.

In summary, a new kind of LC honeycombs with co-axial rod <sup>20</sup> orientation is reported, occurring at the transition from lamellar phases to tangential honeycombs and competing with the triangular and square honeycombs as well as with the bicontinuous cubic phases<sup>15</sup>. This work shows that an inversion of rod orientation in the honeycombs from tangential<sup>6</sup> via tilted<sup>8</sup>

- <sup>25</sup> to co-axial provides a source of new complex LC phases, similar to the orthogonal (SmA), tilted (SmC)<sup>1</sup> and in-plane (Lam) versions of lamellar phases.<sup>16</sup> From an application point of view the reported molecules represent simple generic model compounds for the understanding and tailoring of the self-
- $_{30}$  assembly of larger  $\pi$ -conjugated molecules and lateral substituted rod-like macromolecules  $^{17}$  into well-defined superstructures, as required for advanced organic electronic and light harvesting applications.  $^{18}$

This work is supported by DFG (392435074), NSFC 35 (21761132033, 21374086) and EPSRC (EP-P002250). We thank Beamlines BL16B1 at SSRF, I22 at Diamond Light Source and BM28 at ESRF for providing the beamtime. There are no conflicts of interact to dealers.

There are no conflicts of interest to declare.

#### Notes and references

- <sup>40</sup> <sup>a</sup> Department of Chemistry, Martin Luther University Halle-Wittenberg, Kurt-Mothes-Str. 2, 06120 Halle, Germany. E-mail: carsten.tschierske@chemie.uni-halle.de
  - <sup>b</sup> State Key Laboratory for Mechanical Behavior of Materials, Xi'an
  - Jiaotong University, Xi'an 710049, P. R. China. E-mail:
- 45 feng.liu@xjtu.edu.cn
- <sup>c</sup> Department of Materials Science and Engineering, Sheffield University, Sheffield S1 3JD, UK. E-mail: g.ungar@sheffield.ac.uk

† Electronic Supplementary Information (ESI) available: [Synthesis, analytical data, experimental techniques, DSC and XRD data, structural 50 models and additional discussions]. See DOI: 10.1039/b000000x/

- J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. F. Gleeson, P. Raynes, Eds.; *Handbook of Liquid Crystals*, 2nd Ed.; Wiley-VCH, Weinheim, Germany, 2014.
- 2 C. Tschierske, Angew. Chem. Int. Ed., 2013, **52**, 8828; T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno and M. Funahashi, Nat. Rev. Mater., 2017, **2**, 17001; I. M. Saez, and J. W. Goodby, J. Mater. Chem. 2005, **15**, 26; W. Li, Y. Kim and M. Lee, Nanoscale, 2013, **5**, 7711.
- 3 S. Kumar, *Chemistry of Discotic Liquid Crystals*, CRC Press, Boca Raton, 2011; T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann and S. Laschat, *Chem. Rev.*, 2016, **116**, 1139.
- 4 H.-T. Nguyen, C. Destrade and J. Malthete, Adv. Mater., 1997, 9, 375.
- 5 X. H. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume and C. Tschierske, J. Am. Chem. Soc., 2003, 125, 10977.
- 6 a) C. Tschierske, *Chem. Soc. Rev.*, 2007, **36**, 1930; b) C. Tschierske, C. Nürnberger, H. Ebert, B. Glettner, M. Prehm, F. Liu, X. B. Zeng and G. Ungar, *Interface Focus*, 2012, **2**, 669.
- 7 a) A. J. Crane, F. J. Martinez-Veracoechea, F. A. Escobedo and E. A. Muller, *Soft Matter*, 2008, **4**, 1820; (b) X. Liu, K. Yang and H. Guo, *J. Phys. Chem. B*, 2013, **117**, 9106.
- 8 M. Poppe, C. Chen, F. Liu, M. Prehm, S. Poppe, C. Tschierske, Soft Matter, 2017, 13, 4676.
- 9 a) M. Prehm; F. Liu, X. Zeng, G. Ungar, and C. Tschierske, J. Am. Chem. Soc., 2011, 133, 4906; (b) F. Liu, M. Prehm, X. Zeng, C. Ungar and C.Tschierske, Angew. Chem. Int. Ed., 2011, 50, 10599.
- 10 M. Leaver, A. Fogden, M. Holmes and C. Fairhurst, *Langmuir*, 2001, 17, 35.
- 11 N. K. Oh, W.-C. Zin, J.-H. Im and M. Lee, *Polymer*, 2006, 47, 5375.
- 12 A. Lehmann, A. Scholte, M. Prehm, F. Liu, X.B. Zeng, G. Ungar and C. Tschierske, *Adv. Funct. Mater.*, 2018, DOI: 0.1002/adfm.201804162
- 13 a) B. Chen, X. B. Zeng, U. Baumeister, S. Diele, G. Ungar and C. Tschierske, *Angew. Chem. Int. Ed.* 2004, **43**, 4621; b) B. Chen, U. Baumeister, G. Pelzl, M. K. Das, X. B. Zeng, G. Ungar and C. Tschierske, *J. Am. Chem. Soc.*, 2005, **127**, 16578.
- 14 I. M. Saez, J. W. Goodby and R. M. Richardson, *Chem. Eur. J.*, 2001, 7, 2758.
- 15 M. Poppe, C. Chen, H. Ebert, S. Poppe, M. Prehm, K. Kerzig, F. Liu, and C. Tschierske, *Soft Matter*, 2017, **13**, 4381; M. Poppe, C. Chen, F. Liu, S. Poppe and C. Tschierske, *Chem. Eur. J.*, 2017, **23**, 7196.
- 16 M. Prehm, X. H. Cheng, S. Diele, M. K. Das, C. Tschierske, J. Am. Chem. Soc., 2002, 124, 12072.
- 17 J. Watanabe, N. Sekine, T. Nematsu and M. Sone, *Macromolecules*, 1996, **29**, 4816.
- 18 T. Brixner, R. Hildner, J Köhler, C. Lambert and F. Würthner, Adv. Energy Mater., 2017, 7, 1700236.

4 | Journal Name, [year], [vol], 00-00

**ChemComm Accepted Manuscript**