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PAPER

The 2D-correlated structures of a lyotropic liquid crystalline diol with a phenylpyrimidine core[†]

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Even though the fluid tilted smectic C (SmC) phase is one of the most common phases in thermotropic liquid crystals, the lyotropic analogue to SmC is practically unknown so far. One of the rare examples, a lyotropic liquid crystalline diol, which was reported in 1991 to show this phase, was re-examined by means of detailed X-ray diffraction and polarised optical microscopy. Although the diol possesses a smectic C promoting phenylpyrimidine core, it was not possible to verify the existence of a SmC-analogue lyotropic phase. Instead, the phase diagram shows the existence of five different lyotropic phases identified as nematic, lamellar L_{α} and hexagonal as well as two novel complex 2D-correlated lyophases. Results obtained by electron density calculations and X-ray diffraction data strongly suggest that the structure of one of these phases possesses a pseudo-*c2mm* symmetry and is built up of two different kinds of columns, whereas the other one is a ribbon phase of the oblique plane group *p*2.

Introduction

In thermotropic liquid crystals the SmC phase, known since the pioneering work of Arnold and Sackmann in 1959,¹ is one of the most common phases. The SmC as well as the SmA phases are 1D-stacks of 2D-fluid layers in which the molecules are orientationally ordered along a common direction, the so-called director. The SmC phase is distinguished from the orthogonal SmA phase by a temperature dependent tilt of the director with respect to the smectic layer normal. Since the 1980s the chiral variant, denoted as SmC*, has attracted considerable scientific interest due to its unique macroscopic chirality effects,² such as helicity of the tilt direction and spontaneous electric polarisation of the smectic layers, which render SmC* to be ferroelectric.³

Even though the SmC and SmC* phases are very common in thermotropic liquid crystals, they are practically unknown in lyotropic liquid crystals, which are formed by aggregates of amphiphilic molecules in the presence of a solvent. Indeed, the well-known lamellar $L_{\beta'}$ phase is tilted (like SmC); however this phase is not fluid but rather gel-like.⁴ So far, undoubted evidence of the existence of the SmC-analogue lyotropic phase has only

been given by Schaffheutle and Finkelmann⁵ using X-ray diffraction and by Ujiie and Yano⁶ by means of optical textures.

However, the important questions about the stability of SmCanalogue structures in lyotropics as well as the presence and characteristics of chirality effects on these structures are yet unresolved. Due to the substantial similarities of biological membranes to lamellar phases,⁷ these points could for instance lead to a better understanding of chirality related membrane processes, *e.g.* inclusion of chiral proteins or steroids.

In search of a lyotropic SmC-analogue phase, we started to investigate the diol 5-[4-(5-*n*-heptylpyrimidine-2-yl)phenoxy] pentane-1,2-diol/water system (Fig. 1), which has formerly been reported to exhibit a nematic, a lamellar L_{α} (SmA-analogue) and a lyotropic SmC-analogue phase, identified by texture investigations using polarised optical microscopy.⁸ This diol combines the typical structural properties of a thermotropic calamitic mesogen and a lyotropic amphiphile with its aromatic core and diol headgroup, respectively. The phenylpyrimidine is known as a SmC promoting motif⁹ and therefore it should be an ideal candidate for the formation of a fluid lamellar tilted phase. But in



Fig. 1 Chemical structure of 5-[4-(5-*n*-heptylpyrimidine-2-yl)phenoxy] pentane-1,2-diol. For the investigations the racemic mixture (**rac-1**) as well as the S-enantiomer (S-1, ee = 66%) were used.

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the course of our investigations, doubts grew about the correct assignment of the SmC-analogue phase. Hence, we reinvestigated the phase behaviour of the diol/water system in detail.

Herein we now report the results of these investigations including several new 2D-correlated structures. Next to a revised phase diagram, the paper covers extensive X-ray investigations and calculations of electron density maps for a comprehensive characterisation of all liquid crystalline phases formed by the diol/water system.

Results and discussion

Phase sequence and textures

The phase diagram of the diol/water system was revised by polarised optical microscopy. For this investigation the S-enantiomer (S-1) was used, but several points of the phase diagram were checked against samples of the racemic mixture (rac-1) and no difference could be detected within the measurement accuracy. The result is shown in Fig. 2a. The pure diol does not form any thermotropic liquid crystalline phase but the addition of only about 1 wt% water leads to the appearance of a nematic or chiral nematic phase, respectively (Fig. 2b). Further addition of water results in the formation of a lamellar L_{α} phase which is stabilised by increasing water concentration. In the phase diagram the stabilisation of the L_{α} phase settles at a temperature of 107 °C over a wide water concentration range (~ 3 to 40 wt%). By increasing the water concentration above roughly 40 wt%, a phase transition from the L_{α} phase to a hexagonal phase is observed. The L_{α} phase shows typical fan shaped (Fig. 2c) or homeotropic textures. By cooling, the $L_{\boldsymbol{\alpha}}$ phase turns into a further phase, which was previously identified as SmCanalogue.8 It is the most stable phase in the phase diagram and exists over a very broad concentration and temperature range, down to about 45 °C. In areas with planar alignment of the L_{α} phase this mesophase exhibits a platelet texture (Fig. 2d), while a pseudo-focal conic texture is seen in areas where the L_{α} phase was oriented homeotropically (Fig. 2e). This indicates that this mesophase cannot be a SmC-analogous phase as a textural change from a fan texture into a broken fan texture or from a homeotropic texture into a schlieren texture would be mandatory for such a phase transition. The appearance of the pseudo-focal conic texture rather suggests the existence of a 2D-correlated structure consisting of some kind of columns. As will be presented later this mesophase belongs to the plane group p2 and will therefore be called p2 phase in the following.

Increasing the water concentration over 40 wt% leads to the formation of two further so far unreported mesophases of the diol/water system. At temperatures between 105 °C and 88 °C a hexagonal phase forms which shows the typical pseudo focal conic textures (Fig. 2f). At lower temperatures the phase changes into a structure of pseudo-c2mm symmetry as identified by the results presented later in this paper. This phase shows fairly regular and remarkable textures consisting of differently sized trapezoid planes (Fig. 2g).

Properties of the nematic and the lamellar phases

The nematic phase formed by the racemic mixture of the diol (**rac-1**/water) exhibits an optical positive and uniaxial behaviour



Fig. 2 (a) Schematic phase diagram of the diol/water system. Textures under crossed polarisers of (b) the N* phase, (c) the L_{α} phase, (d) the *p*2 phase (formerly planar region in the L_{α} phase; assumed to be SmC-analogue), (e) the *p*2 phase (formerly homeotropic), (f) the hexagonal phase and (g) the pseudo-*c*2*mm* phase.

(Fig. 3). The birefringence is about $\Delta n = 0.1$, which is remarkably high for a lyotropic liquid crystal and close to the values of thermotropic liquid crystals. This is also reflected in the colourful textures (*cf.* Fig. 2) and is caused by the high diol concentration. Due to the large polarisability along the aromatic system the higher refractive index should be parallel to the long molecular axis independently of the aggregate's shape. Thus, the nematic phase may possibly be built up by single molecules or oblate micelles. The existence of cybotactic groups, as revealed by X-ray diffraction experiments, suggests oblate micelles to be more likely. Due to the low concentration of water they are most probably inverted.

Depending on water concentration and temperature the layer spacings in the lamellar L_{α} phase range from 3.5 nm to 4.2 nm. Since the length of the diol is l = 2.36 nm¹⁰ a partial double layer



Fig. 3 Optical properties of the nematic phase in the **rac-1**/water system: (a) measured refractive indices of the isotropic phase n_{iso} , the extraordinary refractive indices n_{eo} and the ordinary refractive indices n_o of the nematic phase as well as the calculated mean refractive indices \bar{n} ; (b) picture obtained by conoscopy on a homeotropic oriented sample.

arrangement for the structure of the lamellar L_{α} phase is reasonable.

The structure of the *p*2 phase

By performing X-ray diffraction experiments on the p2 phase, the typical diffuse reflections of a liquid crystal are observed in the wide angle region (Fig. 4a). In the small angle region a complex two-dimensional diffraction pattern is found which shows an exceptionally large number of reflections (Fig. 4b). Due to the good alignment of the sample it is possible to index the reflections in this pattern as shown in Fig. 4b. An indexation of all reflections may be obtained when assuming that the diffraction pattern originates from two oriented domains of a highly ordered 2D-correlated structure. The supposed unit cell is oblique and



Fig. 4 X-ray diffraction pattern of the *p*2 phase (a) in the WAXS area and (b) in the SAXS area with indexation for one domain; (c) lattice parameters *a* (circles $\bigcirc \bullet$), *b* (diamonds $\diamond \bullet$) and γ (squares $\Box \bullet$) for 7 wt% (closed symbols) and 31 wt% water (open symbols) respectively.

centred, thus its structure belongs to the plane group p2. The calculated lattice parameters a, b and γ are plotted in Fig. 4c for different temperatures and two water concentrations, showing that a change of the latter has the biggest impact on the value of a and only minor influence on b and γ . It also appears that the unit cell is quite large and therefore a very sophisticated SAXS setup is needed to separate the single reflexes. This may explain why the earlier phase assignment was incorrect, as the WAXS measurement might be mistaken for a SmC-analogue phase.

To determine the structure of the p2 phase the electron density map (Fig. 5a) was reconstructed using the powder diffraction data of the small angle reflections (see ESI[†]).¹¹ In this representation the high electron density region of the solvated hydrophilic headgroups is pictured in purple, while the intermediate electron density of the aromatic cores is visualized in green and the low density regions of the alkyl chains in orange. The map shows that the p2 phase consists of ribbons or deformed columns, respectively. These ribbons may either be described as normal with the alkyl chains aligned towards the center or as inverted with the diol headgroups including the water molecules arranged in the middle of the ribbons. Due to the small water to diol ratio between 1:1 and 10:1, inverted columns appear to characterise the structure more properly. The ribbons still reflect the former layers of the lamellar L_{α} phase in the direction of **b**, but are staggered in the direction of a. The ribbons are tilted with an angle of approximately 16° with respect to **b**.

The formation of the p2 phase and the observed textural change may be explained compellingly with the structure based on the calculated electron density map. By cooling from the lamellar L_{α} phase the solvation sphere of the diol headgroups decreases and thereby reduces the volume of the hydrophilic sublayer, which is expressed by gradual layer shrinkage. Reaching the transition temperature, a negative interface curvature around the hydrophilic regions is enthalpically favoured, causing the layers to break into the ribbons of the p2phase. As the ribbons are staggered there are two possible main directions in which the layers may break. At the phase transition the p2 phase propagates along both directions as observed in an aligned sample using polarised optical microscopy (Fig. 6). The angle between these directions has the same value as the angle γ of the unit cell.

This also explains the observation of domains with two different orientations emerging from a single domain in the L_{α} phase regarding the X-ray diffraction pattern.



Fig. 5 The structure of the p^2 phase: (a) calculated electron density map and (b) schematic model in which the sketched columns include the hydrophilic parts and the aromatic core of the diol.



Fig. 6 (a) Picture as seen through crossed polarisers at the phase transition of an aligned sample from the lamellar L_{α} phase to the oblique p2 phase. The two domains of the growing p2 phase are emphasised with arrows and include the angle γ . The layers of the lamellar phase are indicated with a dashed line. (b) Schematic model of the two domain's unit cells with the diagonals as the growing direction.

According to the symmetry the p2 phase is indeed of tilted and polar nature just like the thermotropic SmC* phase. However, it has a highly ordered structure and the tilt is not referring to single molecules, but to entire ribbons. Therefore electrical switching between the two orientations might not be possible.

The hexagonal and the pseudo-c2mm phases

The one dimensional X-ray diffraction patterns of the hexagonal and the pseudo-*c2mm* phases are plotted in Fig. 7a and b, respectively. Due to the increased water concentration it has not been possible to align the samples.

The indexation of the hexagonal phase is based upon the plane group p6mm with a lattice parameter a of 8.2 nm to 7.3 nm



Fig. 7 Powder diffraction pattern of (a) the hexagonal phase and (b) the pseudo-*c2mm* phase.



Fig. 8 (a) Electron density map and (b) schematic model of the hexagonal phase; (c) electron density map and (d) schematic model of the pseudo-*c2mm* phase.

between 88 °C and 100 °C and excess water. The reconstructed electron density map (Fig. 8a) shows that the hexagonal phase is built up of inverted columns, taking into account the still small water to diol ratio of about 19 : 1 for a lyotropic liquid crystal. However, in contrast to the p2 phase, the hexagonal phase holds two different kinds of columns (Fig. 8b). The column in the origin of the unit cell contains only little water while the water concentration in the other two columns is significantly higher. This is probably caused by the low solubility of the diol in water whereupon the smaller columns mark the maximum uptake of solvating water.

The low temperature phase is indexed on the plane group c2mm. But as the experiments were performed with the racemic as well as with the enantiomeric diol **rac-1** and **S-1**, respectively, the plane group of this phase is at least in the case of **S-1** not allowed to contain any reflection symmetry. Hence, this phase is only centered apparently and is therefore termed pseudo-c2mm phase. The reconstructed electron density map (Fig. 8c) demonstrates the close relation of this phase to the hexagonal phase. The pseudo-c2mm phase results from the high temperature phase by elongation of the unit cell in the direction of **a** and compression in the direction of **b**. The lattice parameters *a* and *b* at 64 °C and excess water were found to be 19.5 nm and 5.5 nm, respectively.

Experimental

General information

Samples for polarised optical microscopy were prepared by quickly heating the desired diol/water mixture above the melting point between two glass plates followed by sealing the sample with the UV curable adhesive NOA73 to avoid a loss of water. Due to the low solubility of the crystalline diol in water it was not possible to determine the exact concentration in the samples. Therefore the phase diagram in Fig. 2 has to be understood as a qualitative description. The samples were examined with a polarised optical microscope (BHS, Olympus) equipped with a hot stage (LTS 350, Linkam). Optical properties were measured using reflectometric interference spectroscopy (Alton Instruments Lambda LS 2000)¹² or a λ -compensator,¹³ respectively.

Samples for the X-ray diffraction experiments were prepared in Mark capillaries (Hilgenberg, 0.7 mm diameter) and measured with a Bruker Nanostar system applying CuK α radiation ($\lambda = 1.5418$ Å). Alignment of the samples was achieved by slowly cooling in a magnetic field (~1 T) using an integrated temperature controller (TCPU H, MRI Physikalische Geräte GmbH).

NMR spectra were recorded on a Bruker DPX 300. Infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FTIR spectrometer as ATR signals on a ZnSe crystal. Mass spectra were taken on a Finnigan MAT Incos 50 Galaxy System (low resolution), a Finnigan MAT 900 S (high resolution, CI) or a Bruker Daltonics micrOTOF-Q (high resolution, ESI). CHN-combustion analyses were measured using an Elementar Vario EL Instrument. The enantiomeric excess was determined by analytic HPLC (Daicel Chiralcel OJ, hexane/2-propanol 90 : 10 at 1.00 nl min⁻¹).

Synthesis of 5-[4-(5-*n*-heptylpyrimidine-2-yl)phenoxy]pentane-1,2-diol

(rac)-5"-[4'-(5-*n*-Heptylpyrimidine-2-yl)phenoxy]pentane-1,2-diol (**rac-1**) was synthesised according to the procedure described in ref. 14.

The chiral compound S-1 was obtained by a sequence of etherification of the commercially available 4-(5-heptylpyr-imidin-2-yl)phenol (3, Synthon Chemicals GmbH) with 5-bro-mopent-1-ene followed by an asymmetric dihydroxylation as outlined in Scheme 1.

5-Heptyl-2-[4'-(pent-4"-en-1"-yloxy)phenyl]pyrimidine (4). In a sealable 10 ml microwave vessel, 270 mg (1.0 mmol) 4-(5-hep-tylpyrimidin-2-yl)phenol (3) were solved in 6 ml acetone. 164 mg (0.13 ml, 1.1 mmol) 5-bromopent-1-ene (2), 460 mg (2.0 mmol) tripotassium phosphate monohydrate and 17 mg (0.1 mmol)



Scheme 1 Synthesis of (S)-5"-[4'-(5-*n*-heptylpyrimidine-2-yl)phenoxy] pentane-1,2-diol (S-1). (a) K₃PO₄·H₂O, KI, acetone, microwave, 100 °C, 2 h, 97% and (b) AD-mix α , *t*-BuOH, H₂O, 6 °C, 72 h, r.t., 48 h, 93%.

potassium iodide were added, the vessel was sealed and microwaved for 2 hours at 100 °C. The solution was filtered, the solvent was removed and the residue was purified chromatographically (SiO₂, 3 : 1 *c*-Hex/EtOAc, $R_f = 0.56$) yielding 327 mg (97%) of 4 as a colourless solid. mp (DSC): Cr 44.4 SmC 59.4 N 60.1 I (from *c*-Hex–EtOAc). $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.56 (2H, s; 4-H and 6-H), 8.36 (2H, d, J 8.9; 2'-H and 6'-H), 6.97 (2H, d, J 8.9: 3'-H and 5'-H). 5.86 (1H. ddt. J 16.9, 10.1, 6.6: 4"-H). 5.07 (1H, ddt, J 17.1, 1.7, 1.7; cis-5"-H), 5.01 (1H, ddt, J 10.2, 1.5, 1.5; trans-5"-H), 4.04 (2H, t, J 6.4; 1"-H), 2.58 (2H, t, J 7.6; CH₂CH₂(CH₂)₄CH₃), 2.32-2.18 (2H, m; 3"-H), 1.96-1.86 (2H, m; 2"-H), 1.64 (2H, p, J 7.4; CH₂CH₂(CH₂)₄CH₃), 1.40-1.24 (8H, m; CH₂CH₂(CH₂)₄CH₃), 0.94–0.83 (3H, t, J 6.8; CH₂CH₂(CH₂)₄CH₃). δ_C (75 MHz, CDCl₃) 162.67 (s; C2), 161.26 (s; C4'), 157.01 (d; C4 and C6), 137.87 (d; C4"), 132.15 (s; C5), 130.50 (s; C1'), 129.56 (d; C2' and C6'), 115.31 (t; C5"), 114.60 (d; C3' and C5'), 67.43 (t; C1"), 31.85 (t; CH₂CH₂(CH₂)₃CH₂CH₃), 30.88 (t; CH₂CH₂(CH₂)₃CH₂CH₃), 30.28 (t; CH₂CH₂(CH₂)₃CH₂CH₃), 30.22 (t; C3"), 29.12 (t; $CH_2CH_2(CH_2)_3CH_2CH_3), 28.62$ (t; C2''), 22.72 (t: CH₂CH₂(CH₂)₃CH₂CH₃), 14.13 (q; CH₂CH₂(CH₂)₃CH₂CH₃). $\nu_{\rm max}/{\rm cm}^{-1}$ 3077 (w), 3017 (w), 2994 (w), 2951 (m), 2924 (s), 2853 (m), 1640 (w), 1606 (m), 1583 (s), 1540 (m), 1513 (m), 1467 (m), 1429 (s), 1393 (m), 1327 (m), 1299 (m), 1251 (s), 1167 (m), 1106 (m), 1054 (m), 1028 (m), 991 (m), 935 (m), 910 (m), 845 (m), 822 (w), 796 (s), 759 (w), 721 (w), 701 (w), 653 (m); LRMS (EI, 70 eV) m/z: 69 (20%) [C₅H₉⁺], 119 (12) [C₇H₄NO⁺], 158 (19) $[C_9H_6N_2O^+]$, 185 (100) $[M^+-C_6H_{13}-C_5H_9]$, 199 (12) $[M^+-C_5H_{11}-C_5H_{12}-C_5H_{13}-C_5H_{$ C_5H_9], 253 (7) [M⁺-C₆H₁₃], 270 (24) [M⁺-C₅H₉], 338 (33) [M⁺]. HRMS (EI, 70 eV) m/z calcd. for C₂₂H₃₀N₂O: 338.2358. Found: 338.236. Anal. calcd for C₂₂H₃₀N₂O: C, 77.82; H, 8.90; N, 8.21. Found: C, 78.06; H, 8.93; N, 8.28%.

(S)-5"-[4'-(5-n-Heptylpyrimidine-2-yl)phenoxy]pentane-1,2-diol (S-1). 327 mg (0.97 mmol) of 4 were solved in 7 ml tert-butanol and dropped slowly into a cooled solution of 1.4 g AD-mix- α ¹⁵ in 7 ml water. The reaction mixture was stirred for 72 hours at 6 °C and for 48 hours at room temperature. The mixture was extracted twice with ethyl acetate, the organic phase was dried over magnesium sulfate and the solvent was evaporated. The residue was purified chromatographically (SiO2, EtOAc) yielding 334 mg (0.88 mmol, 93%) of S-1 as a colourless solid; ee 66%. $\delta_{\rm H}$ (300 MHz, CDCl₃) 8.56 (2H, s; 4-H and 6-H), 8.33 (2H, d, J 8.7; 3'-H and 5'-H), 6.97 (2H, d, J 8.8; 2'-H and 6'-H), 4.06 (2H, t, J 5.9; 5"-H), 3.87-3.74 (1H, m, 2"-H), 3.68 (1H, dd, J 10.9, 3.1; 1"-H_a), 3.48 (1H, dd, J 11.0, 7.5; 1"-H_b), 2.85–2.00 (2H, bs; OH), 2.59 (2H, t, J 8.2; CH₂CH₂(CH₂)₄CH₃), 2.05–1.80 (2H, m; 4"-H), 1.77-1.50 (4H, m; 3"-H and CH₂CH₂(CH₂)₄CH₃), 1.44-1.19 (8H, m; CH₂CH₂(CH₂)₄CH₃), 0.87 (3H, t, J 6.4; CH₂CH₂(CH₂)₄CH₃). δ_C (75 MHz, CDCl₃) 162.50 (s; C2), 160.96 (s; C1'), 157.09 (d; C4 and C6), 132.35 (s; C5), 130.48 (s; C4'), 129.57 (d; C3' and C5'), 114.54 (d; C2' and C6'), 71.99 (d; C2"), 67.99 (t; C5"), 66.91 (t; C1"), 31.86 (t; CH₂CH₂(CH₂)₃CH₂CH₃), 30.94 (t; CH₂CH₂(CH₂)₃CH₂CH₃), 30.27 (t; CH₂CH₂(CH₂)₃CH₂CH₃), 29.98 (t; C3"), 29.14 (t; CH₂CH₂(*C*H₂)₃CH₂CH₃), 25.58 (t; C4"), 22.75 (t; CH₂CH₂(CH₂)₃CH₂CH₃), 14.21 (q, CH₂CH₂(CH₂)₃CH₂CH₃). $\nu_{\rm max}/{\rm cm}^{-1}$ 3450 (bw), 2951 (m), 2924 (m), 2853 (m), 2779 (w), 1738 (m), 1667 (w), 1656 (w), 1606 (m), 1583 (m), 1541 (m), 1512



Fig. 9 Liquid crystalline phases of the diol/water system: (a) nematic phase, (b) lamellar phase, (c) p2 phase, (d) hexagonal phase and (e) pseudo-c2mm phase.

(w), 1430 (s), 1371 (m), 1327 (m), 1298 (m), 1236 (s), 1167 (m), 1106 (m), 1030 (m), 982 (w), 937 (w), 845 (m), 816 (w), 796 (s), 722 (w), 701 (w), 653 (m), 611 (s). LRMS (EI, 70 eV) *m/z*: 158 (19%) $[C_9H_6N_2O^+]$, 185 (87) $[M^+-C_5H_{11}O_2-C_6H_{13}]$, 270 (100) $[M^+-C_5H_{11}O_2]$, 341 (19) $[M^+-CH_2O]$, 372 (18) $[M^+]$. HRMS (pos. ESI) *m/z* calcd for $[C_{22}H_{32}N_2O_3 + Na]^+$: 395.2311. Found: 395.2302. Anal. calcd for $C_{22}H_{32}N_2O_3$: C, 70.94; H, 8.66; N, 7.52. Found: C, 70.96; H, 8.66; N, 7.51%.

Conclusions

We found that the lyotropic phase of 5-[4-(5-*n*-heptylpyrimidine-2-yl)phenoxy]pentane-1,2-diol, which was previously assumed to be SmC-analogue, is indeed a rather complex 2Dcorrelated structure. Thus, this is another striking example of the unresolved problem why tilted fluid structures – even though quite common in thermotropics – are rarely found in lyotropics.

Nevertheless the diol/water system exhibits a very rich and interesting polymorphism with five different mesophases, the structures of which are summarised in Fig. 9. All meosphases are of inverted nature, reflecting the uncommon molecular composition of the diol, *i.e.*, an aromatic core structure, typical of thermotropics, linked to a hydrophilic headgroup, typical of lyotropics. At low water concentrations the nematic phase is formed of discotic micelles. Increasing the water concentration, the micelles fuse into the layers of the lamellar phase. These layers then break into the ribbons of the p2 phase on cooling. By increasing the water concentration further the ribbons turn into the circular columns of the hexagonal phase, which are able to include a bigger amount of water molecules than the rather flat ribbons. Finally cooling leads to the more ordered pseudoc2mm phase by elongating the hexagonal phase in one dimension. Summing up, the diol/water system shows the typical phase sequence of a lyotropic liquid crystal, regarding the nematic, the lamellar and the hexagonal phases. However these conventional phases are mediated by rather uncommon 2Dcorrelated phases, which seem to be a distinctive feature for mesogens on the borderline of thermotropic and lyotropic liquid crystals.

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