

Supporting Information

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

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Calculation of electron density maps

The electron density $\rho(hk)$ of a liquid crystal is linked to its structure factor $F(hk)$ by inverse Fourier transformation:

$$\rho(hk) = \sum_{hk} F(hk) e^{2\pi i(hx+ky)}$$

In this formula h and k are the *Miller Indices* and x , y the fractional coordinates in the unit cell. To calculate the electron density, the complex structure factor $F(hk)$ has to be written as the product of the phase $\phi(hk)$ and the modulus $|F(hk)|$ which is proportional to the square root of the Intensity $I(hk)$ of the observed reflection:

$$F(hk) = |F(hk)|e^{i\phi(hk)} = \sqrt{I(hk)}e^{i\phi(hk)}$$

While the Intensity $I(hk)$ can easily be obtained from the X-ray diffraction experiment, the phase $\phi(hk)$ is unknown, which is called *phase problem*. For centrosymmetric groups the structure factor is real and thus the phase can only be 0 or π . For non-centrosymmetric groups the phase may take every value between 0 and 2π . To find the correct choice of phase, the different phase combinations have to be compared by means of physical and chemical feasibility. For instance, the volume fractions of the different parts of the molecule are calculated as well as their electron density and compared with the histogram of the obtained electron density map, to find out in which cases a good separation of high- and low-density regions occurs.

The indices (hk) , observed d -spacings $d_{\text{obs.}}$, calculated d -spacings $d_{\text{cal.}}$, multiplicity corrected intensities $I(hk)$ and phases $\phi(hk)$ used for the calculated electron density maps are found in the following Tables S1 to S3. The histograms for the chosen electron density maps with marked volume fractions are given in Figures S1 to S3. The low-electron density region of the histogram arises from the alkyl chains, the intermediate region from the aromatic cores and the high-density region from the diol headgroup including the water. The hydrophilic headgroup and the water cannot be detected separately as they mix very well. It has to be noted that due to the low water concentration in all liquid crystalline phases of the diol **1**, the water cannot be treated as bulk water.

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Tab. S1 *p2* phase at 64 °C with $a = 9.51$ nm, $b = 8.06$ nm, $\gamma = 117.2^\circ$.

(hk)	$d_{\text{obs.}} / \text{nm}$	$d_{\text{cal.}} / \text{nm}$	$I(hk)$	$\phi(hk)$
(1-1)	6.39	6.38	39.76	π
(11)	4.54	4.54	70.02	0
(20)	4.23	4.23	100	0
(02)	3.59	3.59	15.99	π
(3-1)	3.15	3.16	11.89	π
(22)	2.29	2.27	2.11 ¹	π
(31)	2.29	2.29	61.98	0

To perform X-ray diffraction experiments with the *p2* phase, a sample was used containing about 10 wt% of water. For this concentration the volume fraction of the alkyl chain is ~37 vol%, that of the aromatic core is ~34 vol% and that of the diol headgroup including the water is ~29 vol%. The histogram of the *p2* phase (Fig. S1)

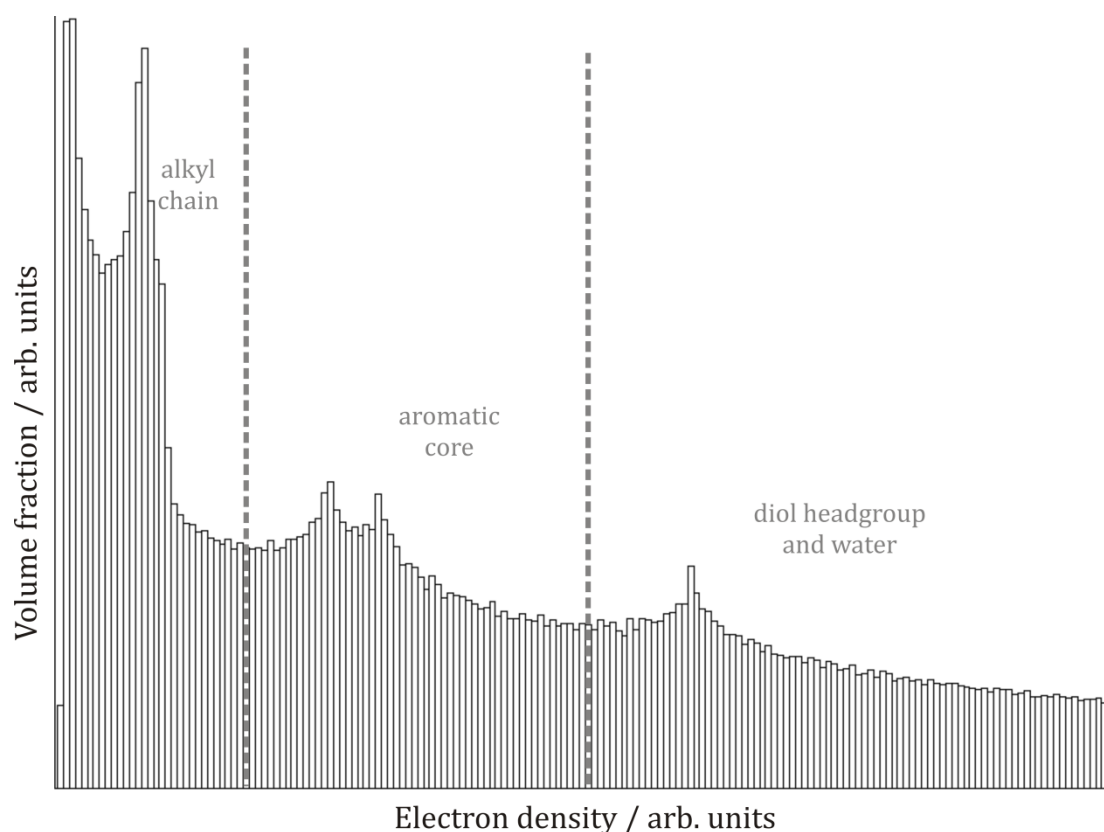


Fig. S1 Histogram of the *p2* phase. The volume fractions of the different parts of the molecule are marked with dashed lines.

¹ Value is estimated by the intensities of the oriented diffraction pattern.

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shows a sharp separation of the different parts of the molecule. Both the alkyl chains and the aromatic cores cause two peaks in the histogram, which may be explained by the different packing densities in the middle of a ribbon and in areas where two ribbons meet.

Tab. S2 Hexagonal $p6mm$ phase at 100 °C with $a = 7.4$ nm.

(hk)	$d_{\text{obs.}} / \text{nm}$	$d_{\text{cal.}} / \text{nm}$	$I(hk)$	$\phi(hk)$
(10)	6.35	6.38	16.2	π
(11)	3.70	3.68	100	0

For the hexagonal phase a sample with about 50 wt% of water was used. Thus, the volume fractions are ~24 vol% for the aliphatic part, 23 vol% for the aromatic part and ~53 vol% for the hydrophilic part. Again, the aliphatic and the aromatic parts show sharp peaks. The hydrophilic part is smeared due to thermal motion, but a small buckling is seen which is probably caused by the difference between strongly and weakly solvating water.

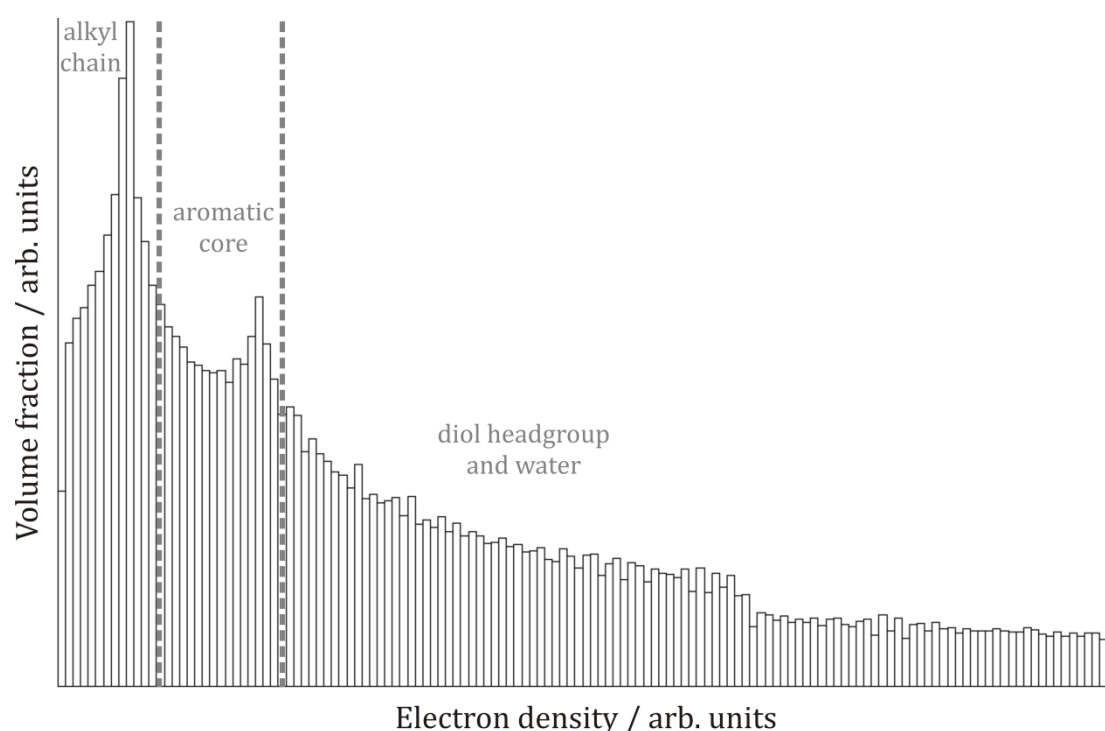


Fig. S2 Histogram of the hexagonal phase. The volume fractions of the different parts of the molecule are marked with dashed lines.

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Tab. S3 Pseudo-*c2mm* phase at 64 °C with $a = 19.5$ nm, $b = 5.5$ nm.

(hk)	$d_{\text{obs.}} / \text{nm}$	$d_{\text{cal.}} / \text{nm}$	$I(hk)$	$\phi(hk)$
(20)	9.74	9.74	32.8	0
(11)	5.30	5.30	44.2	0
(31)	4.19	4.20	32.5	π
(02)	2.75	2.75	100.0	0

For the X-ray diffraction experiments of the pseudo-*c2mm* phase, the same sample was used as for the hexagonal phase. The buckling in the high-electron density region of the histogram is increasing and the peak of the aromatic cores splits. This may be explained by the increasing difference between the two kinds of columns occurring in this phase.



Fig. S3 Histogram of the pseudo-*c2mm* phase. The volume fractions of the different parts of the molecule are marked with dashed lines.