

Supporting Information for

An “on-off” switching cubic phase with exceptional thermal stability and water sorption capacity

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Experimental. A pyridinium salt of 4 - [3,4,5 -tris(octyloxy)benzoyloxy] azobenzene-4-sulfonate (**C8Pyr**) was synthesized following the literature procedure [1-3]. The optical textures and thermal properties of **C8Pyr** were reported previously [3]. According to polarized microscopy, the isotropization temperature of the **C8Pyr** compound was found to be 210 °C [3].

Thin films of **C8Pyr** were prepared by spin-coating solutions in CHCl₃ (20mg/ml) on silicon substrates at 1000 rpm.

Grazing-Incidence Small-Angle X-ray scattering (GISAXS) experiments were performed at the BM26 and ID10 beamlines of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The energy of X-ray photons was 12 and 10 keV for BM26 and ID10 beamlines, respectively. The modulus of the scattering vector \mathbf{s} ($|\mathbf{s}| = 2\sin\theta/\lambda$, where θ is the Bragg angle and λ - the wavelength) was calibrated using silver behenate. The incidence angle was comprised between 0.18 and 0.20°. The sample size was approximately 5×10 mm². The temperature-resolved GIWAXS experiments were carried out under the atmosphere of water or methanol vapours using a specially designed variable-temperature environmental chamber described in an earlier paper [4].

Evaluation of water uptake λ . In a first approximation, one can assume that during swelling the water channels are separated by a bilayer of the amphiphile having thickness h and interfacial area S . The latter value is proportional to the square of the lattice parameter a . Therefore, the volume occupied by the mesogen $V_{mesogen}$ reads as:

$$V_{mesogen}(a) = \gamma \cdot h \cdot a^2 \quad (1),$$

where γ is a constant. In the experiments, $a = 117 \text{ \AA}$ corresponds to a completely dry sample, i.e. $V_{mesogen}(a = 117 \text{ \AA}) = a^3$. This results in $\gamma \cdot h = 117 \text{ \AA}$. Consequently, for any value of the lattice parameter the volume fraction of water molecules φ_{water} can be estimated as follows:

$$\varphi_{water} = \frac{a^3 - V_{mesogen}(a)}{a^3} = 1 - \frac{\gamma \cdot h}{a} \quad (2)$$

According to Eq(2), the content of water φ_{water} is 0.13 and 0.18 for the RH values of 33% (room humidity) and 100%, respectively.

The value of λ was estimated using the following equation:

$$\lambda = \frac{N_{water}}{N_{mesogen}} = \frac{\frac{V_{water} \cdot \rho_{water}}{M_{water}}}{\frac{V_{mesogen} \cdot \rho_{mesogen}}{M_{mesogen}}} = \alpha \cdot \frac{V_{water} \cdot M_{mesogen}}{M_{water} \cdot V_{mesogen}} = \alpha \cdot \frac{\varphi_{water}}{(1 - \varphi_{water})} \cdot \frac{M_{mesogen}}{M_{water}} \quad (3),$$

where N_{water} and $N_{mesogen}$ – the number of water and amphiphile molecules, M_{water} and $M_{mesogen}$ – molar weights of water and amphiphile, respectively ($M_{mesogen}$ for **C8Pyr** equals

844 g.mol⁻¹). Here we suppose that the mass density of dry Cub phase is close to 1.0 g/cm³ [5]. For the analysis of water uptake λ it was decided to introduce coefficient α which is equal to the ratio between the mass densities of water and the amphiphile. It should be mentioned that α slightly exceeds 1. This assumption was made according to our previous paper [6] where the electron density of similar compounds was studied. Based on the analysis of X-ray data it was shown that the local density maximum in the structure is located at the focal point of the wedge due to the sodium counter-ion. Likewise, alkyl areas have lower density than the channels filled with water molecules. In a second approximation based on the Gauss–Bonnet theorem [7] the volume fraction of the mesogen $\varphi_{mesogen}$ can be obtained from the following equation:

$$\varphi_{mesogen} = 2A_0 \cdot \left(\frac{l}{a}\right) + \frac{4\pi\chi}{3} \left(\frac{l}{a}\right)^3 \quad (4)$$

where $A_0 = 3,091$ and $\chi = -8$ are constants for the gyroid structure with symmetry Ia3d. The thickness of the molecular layer l is assumed to be 25.5 Å. Fig. S0 shows the mesogen volume fraction as a function of the lattice parameter. It can be seen that the initial approximation based on simple scaling arguments is relatively close to the result obtained by taking into account the curvatures of the surfaces displaced from the basal surface of the mesogen bilayer with the help of the Gauss–Bonnet theorem.

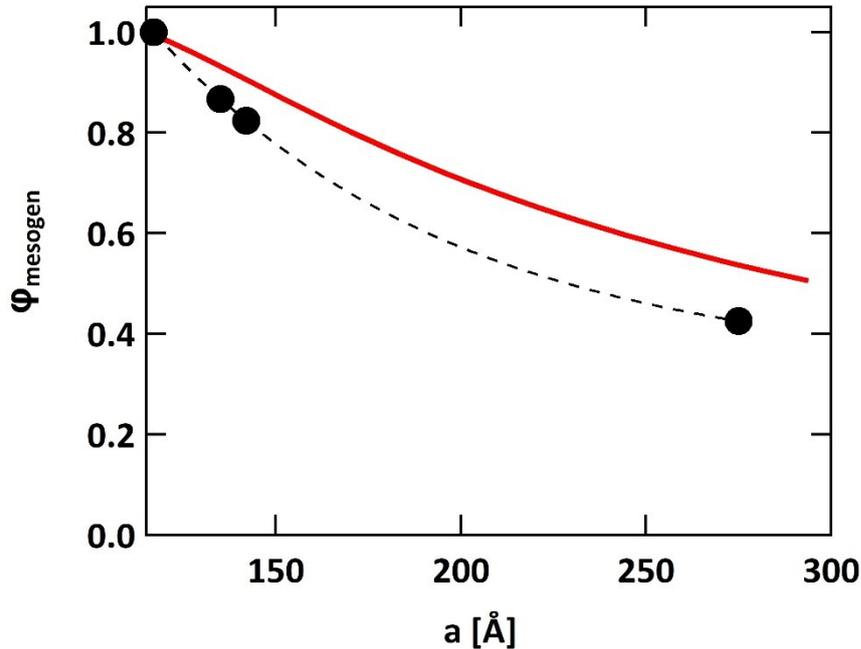


Fig. S0. Dependence of the mesogen volume fraction on the lattice parameter for $l = 25$ Å computed with Eq(4) (red curve). Black dots indicate the mesogen volume fraction estimated using Eq(2). The dashed line is a guide for the eye.

The average radius of water channels can be evaluated by:

$$r_{water} = \sqrt{\frac{A_0}{2\pi|\chi|}} a - l \quad (5)$$

Table S0 gives the calculated r_{water} for four different values of the experimentally observed lattice parameter.

Table S0 – Morphological parameters of the gyroid phase as a function of the lattice parameter.

$\varphi_{mesogen}$	$a_{gyr}, \text{Å}$	$r_{water}, \text{Å}$
1	117	3.5
0.87	135	8.0
0.82	142	9.8
0.68	275	42.7

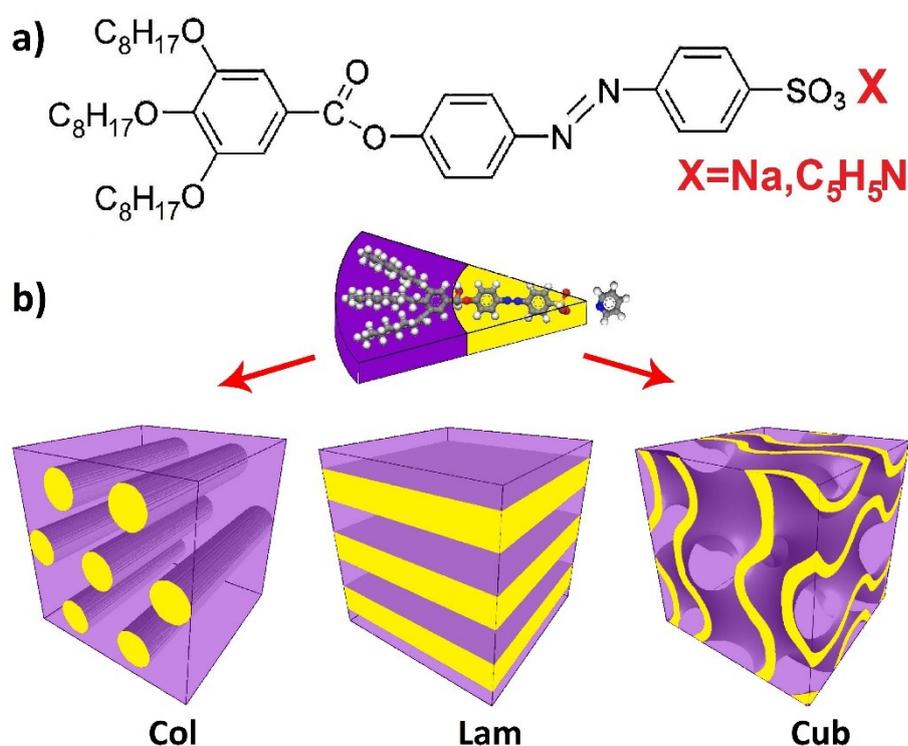


Fig. S1. Chemical structure of the **C8Pyr** compound (a). Examples of self-assembly of wedge-shaped mesogens (b). The violet and yellow colors represented the hydrophobic and hydrophilic parts of the molecules, respectively.

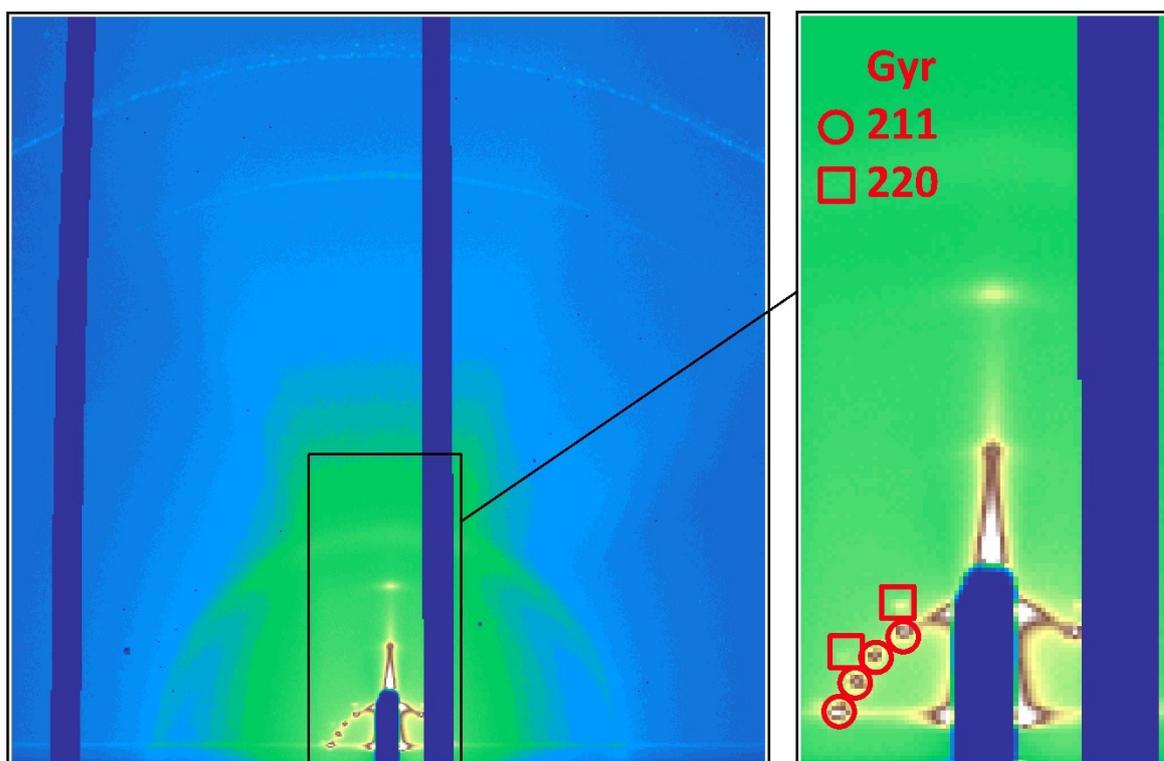


Fig. S2. 2D GIWAXS patterns in wide and small angles of the **C8Pyr** thin film in gyroid phase after storing at ambient humidity and temperature for several months. Inset show the indexation of the gyroid phase (red circles – 211, red squares - 200).

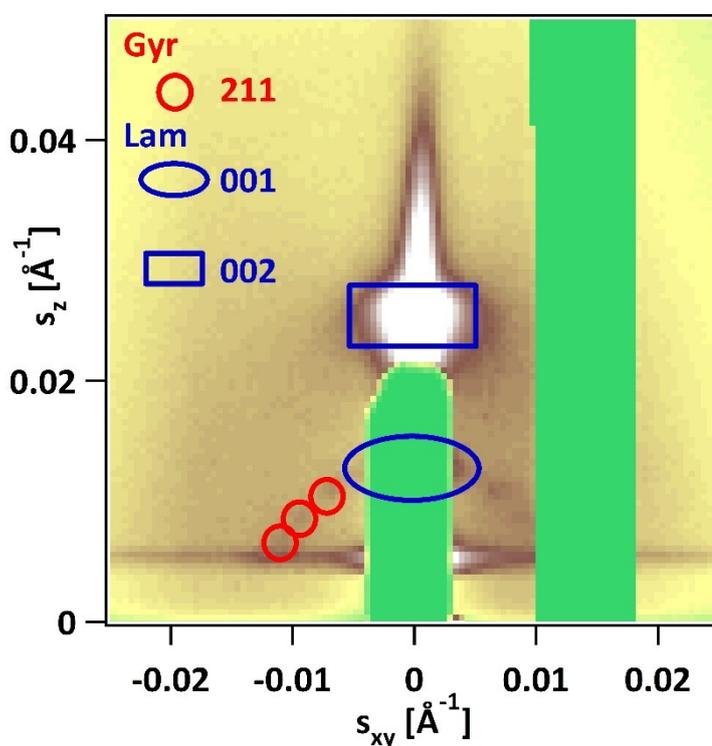


Fig. S3. 2D GIWAXS pattern of the **C8Pyr** thin film in the gyroid phase after cooling to 16 °C.

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