

## Supplementary Material

# Self-assembly, condensation, and order in aqueous lyotropic chromonic liquid crystals crowded with additives

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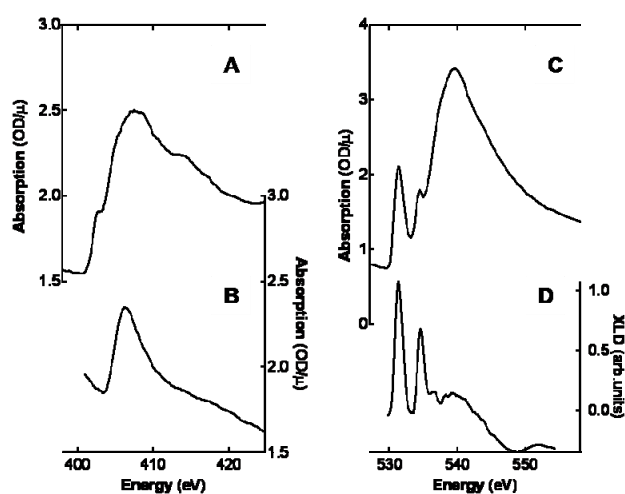
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### Scanning Transmission X-ray microscopy

Linearly polarized soft x-ray light emitted by an undulator was monochromatized to 5000 energy resolving power and focused by Fresnel zone plate to a focal spot  $\sim 50$  nm in diameter. The images were obtained by monitoring the photon flux through the sample while it was raster-scanned across the focus at fixed photon energy. The images were normalized (by a negative logarithmic ratio) to the intensity of the incoming flux transmitted through an empty portion of  $\text{Si}_3\text{N}_4$  window to produce the optical density (OD) map at a given energy. Near edge x-ray absorption fine structure (NEXAFS) spectral analysis was performed in two ways, either by focusing the beam to a spot of interest in the sample while scanning the photon energy across a particular absorption edge or by combining several OD maps taken at different energies and extracting the spectra at each pixel. Energy scale was verified by x-ray transmission through residual air during STXM chamber pumping prior to the sample measurements; N  $1s \rightarrow p^*$  ( $\nu=1$ ) transition was set to 401.1 eV [1] and O  $1s \rightarrow p^*$  transition (main peak) to 530.75 eV [2]. A combined measurement across N and O K edges permits quantitative derivation of the effective thickness of the film comprised of the two components of interest, an oxygen rich DSCG and a nitrogen rich Spm or TBABr.

The N edge NEXAFS spectra of Spm and TBABr, Supplementary Fig. S1 (A,B), are similar to the spectra of other saturated amino compounds [4]. The O edge NEXAFS for DSCG clearly shows three peaks at 531.4, 534.5, and 539.5 eV, Supplementary Fig. S1 (C). Prior studies of small organic molecules assign unambiguously the sharp peaks in the 530-534 eV range to O  $1s \rightarrow \pi^*$  excitation [4, 5]. X-ray structure data [5-7] reveal that the carboxyl group COOH is typically coplanar with the adjacent aromatic ring. Therefore, by measuring the polarization dependence of the  $1s \rightarrow \pi^*$  peak, one can determine orientation of the DSCG molecular planes and thus derive the spatial variation of both the direction and degree of orientational order.

For linearly polarized light the intensity of the NEXAFS resonances also depends on the relative orientation of x-ray



**Supplementary Figure S1.** NEXAFS spectra of (A) Spm, (B) TBABr across the nitrogen K-edge and (C) DSCG across the oxygen K-edge. (D) The x-ray linear dichroic (XLD) signal measured as a difference for the x-ray polarization along and perpendicular to the shear direction in DSCG oriented film.

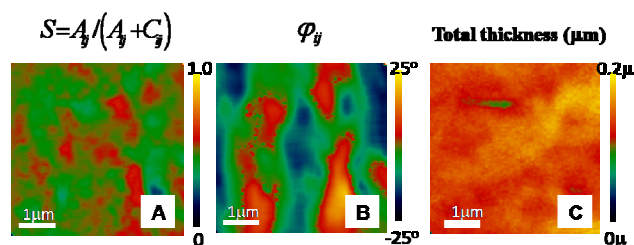
polarization and molecule dipole transition. For K-edge absorption, where core electron density distribution is atomic-like and the dipole transition moment polarization selection rules are dictated by the symmetry of the unoccupied orbital (i.e.  $\pi^*$  in the  $1s \rightarrow \pi^*$ , and  $\sigma^*$  in the  $1s \rightarrow \sigma^*$  transitions), the linear dichroic NEXAFS signal provides a direct measurement of a given bond orientation, Supplementary Fig. S1 (D).

By measuring the sequence of images with varying X-ray light polarization, the spatial variation of the linear dichroism signal can be mapped and inverted as to give information about the average orientation of molecules or an order parameter at a spatial resolution below 100 nm. The orientation of the sample plate was set to be perpendicular to incoming x-ray light, so only in plane LC orientation can be probed.

For each orientation  $\theta$  of X-ray linear polarization, two images (at 531.4 eV and at 530 eV (a “pre edge” background))

were recorded, converted to an OD map by normalizing to the intensity of X-ray passed through the empty position of Si<sub>3</sub>N<sub>4</sub> cell and subtracted. The intensity of dichroic signal at 531.4 eV is maximum when the **E**-vector of the X-ray beam is perpendicular to molecular plane (and parallel to  $\hat{\mathbf{n}}(\mathbf{r})$ ), and as angular orientation  $\theta$  of x-ray polarization varies, it should follow the  $A_{ij} \cos^2(\theta - \varphi_{ij}) + C_{ij}$  law at each  $ij$ -th image pixel, Fig. 7. The ratio  $S = A_{ij}/(A_{ij} + C_{ij})$  defines the relative magnitude of orientational order (Fig. 9 (A,D) and Supplementary Fig. S2 (A)), while  $\varphi_{ij}$  determines orientation of  $\hat{\mathbf{n}}(\mathbf{r})$  in  $ij$ -th image pixel (Fig. 9 (B,E) and Supplementary Fig. S2 (B)) [3].

Small twist between two aromatic rings might result in a finite intensity of  $1s \rightarrow \pi^*$  peak even if the **E**-vector is in the plane of DSCG molecule; the effect would manifest itself as an orientational disorder. However, we keep the above framework of analysis, as it is evident from the experimental data that the effect is small and does not affect qualitative conclusions. As a reference, we used dried films of DSCG solutions with no additives, oriented by shear flow (Supplementary Fig. S2).



**Supplementary Figure S2.** (Color) Dried film cast out of  $c = 0.34$  mol/kg DSCG. (A) spatial map of relative magnitude of the in-plane scalar order parameter, (B) false color image of spatial map of in-plane LC director orientation; the zero value of the angle  $\varphi_{ij}$  corresponds to the horizontal director, (C) DSCG film thickness.

The resulting “herring-bone” texture is similar to the one of thin films in the C phase of other LCLCs [3]. For  $0.15 \mu\text{m}$  thick film, the in-plane  $\hat{\mathbf{n}}(\mathbf{r})$  smoothly undulates within a  $\pm 15$  deg (FWHM) angle, creating elongated  $2.5 \mu\text{m}$  wide domains perpendicular to the shear direction. The scalar order parameter defined as  $A_{ij}/(A_{ij} + C_{ij})$  varies  $\sim 15\%$  across the area, mostly due to the domain structure (Supplementary Fig. S2 (A)).

The differential image constructed for the N K-edge, as a difference between the signals at 402 eV and 407 eV, is proportional to the effective thickness of additives, or to the amount of Spm and TBABr molecules along the direction of X-ray propagation (normal to the film). Similarly, the data for the O K-edge result in the “DSCG thickness”, see Supplementary Figure S2 (C). The logarithm of the ratio of the “additive thickness” to the “DSCG thickness” yields a measure of the concentration ratios  $c_{\text{Spm}}/c$  and  $c_{\text{TBABr}}/c$ . The ratio, although dimensionless, still depends on choice of units for atomic cross-sections. A normalized thickness is employed instead, and logarithm of thickness ratio is chosen to show

relative concentration as false color image with equal color variation for rich and depleted regions (Fig. 9 C,F).

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