Title: Amphiphile Induced Phase Transition of Liquid Crystals at Aqueous Interfaces

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Abstract: Monolayer assemblies of amphiphiles at planar interfaces between thermotropic liquid crystals (LCs) and an aqueous phase can give rise to configurational transitions of the underlying LCs. A general assumption has been that the hydrophobic tails of amphiphiles interdigitate with the molecules of the LC at the interface to trigger a reconfiguration of the LC phase. A different mechanism is discovered here, whereby reorientation of the LC systems is shown to occur through lowering of the orientation-dependent surface energy of the LC due to formation of a thin isotropic layer at the aqueous interface. Using a combination of simulations and experiments, we demonstrate that a monolayer of specific amphiphiles at an aqueous interface can cause a local nematic-to-isotropic phase transition of the LC by disturbing the antiparallel configuration of the LC molecules. These results represent new insights into the interfacial, molecular-level organization of LCs that may be exploited for rational design of biological sensors and responsive systems.

Main Text: Monolayer assemblies of amphiphiles at the interfaces of thermotropic liquid crystals (LCs) and an aqueous phase can be used to reconfigure LCs, thereby providing the basis for applications in biosensors, responsive soft matter, and molecular devices (1-3). Micrometer-thick LC films confined between an aqueous phase and a functionalized glass substrate typically adopt a hybrid configuration, with perpendicular (homeotropic) orientation at the glass interface and parallel (planar) orientation at the aqueous interface. Adsorption of amphiphiles such as sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) at the aqueous interface triggers a transition from the hybrid configuration into a uniform configuration, in which the LC is oriented perpendicular to both surfaces throughout the LC film (*1, 4*). Similarly, in LC droplets dispersed in water, amphiphiles localized at the aqueous interface (*5*) or in topological defects of the LC droplets (*2, 6*) can trigger a configurational transition from one state into another (*4, 7, 8*). Such transitions commonly generate distinct optical signals that can be monitored with polarized light (*7*) or angle-dependent light scattering (*5*). In the presence of foreign molecular species such as biological toxins and proteins, specific biomolecular interactions between amphiphiles and the toxins can lead to a "secondary" reorganization of the LC. These observations have enabled design of label-free biological sensors, drug delivery systems, and other microdevices (*9-11*).

The molecular mechanisms responsible for reconfiguration of LCs at aqueous interfaces are thought to be fundamentally different from those occurring at solid interfaces, due to the softness and mobility of the interface and the specific interactions of LC molecules with water (*3, 4, 12, 13*). The nanoscale details pertaining to interfacial organization of LCs at these aqueous interfaces, however, remain poorly understood. Past attempts to decipher these mechanisms have mainly involved manipulations of the molecular structure of the amphiphiles adsorbed at the interface (*4, 11, 14-16*). For example, past studies reported that surfactants with linear and branched hydrophobic tails cause distinct orientations of LCs at aqueous interfaces (*4*). Such studies and others (*1*, *10*, *17*) have supported the conclusion that the interdigitation of mesogens (molecules forming liquid crystal phase) with the hydrophobic tails of amphiphiles changes the preferred orientation of the LC molecules - known as the easy axis - at the interface with water, into a perpendicular orientation at the amphiphile-laden aqueous interface. In this work, we report a different mechanism that involves a nematic-to-isotropic phase transition of the LC phase within a narrow, disordered region near the interface.

In continuum descriptions of LCs (*18*, *19*), the orientation-dependent surface free energy, or the so-called surface anchoring energy, of a nematic LC is the free energy required to distort the orientation of the molecules at a surface from their preferred average alignment. The free energy penalty associated with a given distortion is generally quantified using a so-called "anchoring strength", whose magnitude depends on several parameters, including the type and the chemical structure of the surfaces. Two types of limiting anchorings are generally defined; homeotropic anchoring, in which the LC is aligned perpendicular to the surface, and planar anchoring, wherein the LC assumes a parallel orientation with respect to the surface. The equilibrium configuration of a LC system can then be estimated by minimizing the sum of elastic and anchoring contributions to the free energy. In a film confined between a homeotropic substrate and a planar aqueous interface, the anchoring strength at these conflicting surfaces is typically sufficiently strong to lead to a gradual change in the alignment of the LC, as described by the so-called nematic director, from homeotropic at the substrate to planar at the aqueous interface. This distortion leads to accumulation of elastic energy in the LC film. In contrast, the elastic energy stored in a LC film with a uniform homeotropic or planar configuration would be zero. In this work, we show that the configuration of a LC film induced by amphiphiles can also change via a nematic-to-isotropic phase transition that is localized at the aqueous interface, as opposed to a change in the easy axis. We propose the view that this localized phase transition weakens the anchoring strength, because the anchoring strength of 4-cyano-4′-pentylbiphenyl (5CB) in the *isotropic* phase essentially approaches zero. The film then transitions to a uniform configuration to release the stored elastic energy. At a molecular level, we show that the interfacial phase transition is triggered because the amphiphiles disturb the antiparallel orientation of the 5CB molecules near the aqueous interface. Within this isotropic layer, the 5CB molecules reorient freely, allowing the molecules throughout the rest of the film to align in a direction that minimizes elastic distortions. Because this phenomenon can be coupled to biological binding events at aqueous interfaces, the principles presented here provide new perspectives that may be of use for rational design of biological sensors, drug delivery systems, and molecular devices.

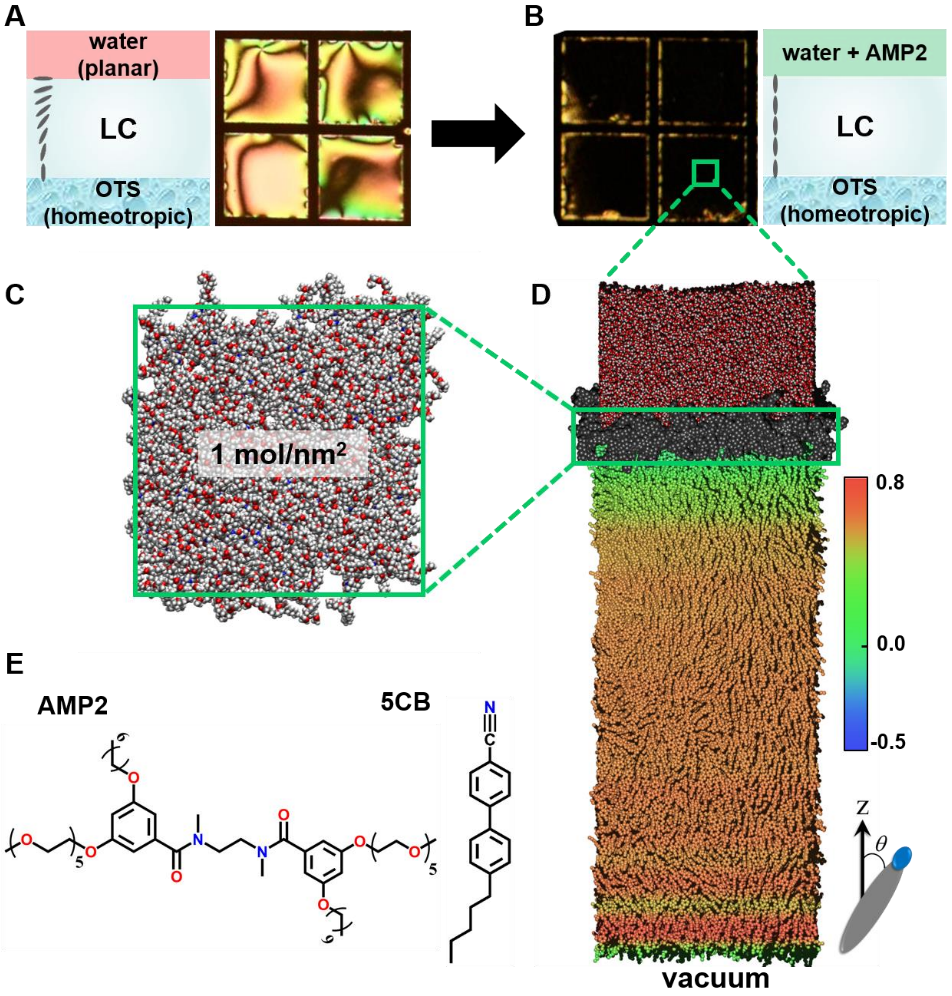

Fig. 1. Dynamic optical response of a 5CB thin film to the self-assembly of amphiphiles at aqueous interfaces, and molecular dynamics simulations. (**A, B**) Optical images of a LC thin film, and schematic representations of the molecular orientation within the LC phase, before addition of an amphiphile (A), and after addition of a 150 μM solution of the amphiphile AMP2 (B). The LC film assumes a hybrid configuration before addition of AMP2, and transforms to a uniform configuration upon formation of an amphiphile monolayer. (**C, D**) Setup for molecular dynamics simulations (C), and a top-view snapshot of the AMP2-monolayer at the LC-water interface (D). A thin film of 5CB is primarily confined between vacuum and pure water. The monolayer-assembly of AMP2 is created by adding 1 mol/nm^2 of the amphiphiles to the LC-water interface. The snapshot shows the color-coded profile of the second Legendre polynomial $P_2(z) = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2}\rangle$. (**E**) Molecular structure of a 5CB molecule and the amphiphile molecule AMP2.

To illustrate these ideas, 20 μm-thick nematic LC films were prepared by depositing 5CB into a transmission electron microscopy (TEM) grid supported on a glass substrate coated with octadecyltrichlorosilane (OTS). Consistent with past studies, the LC film immersed under an aqueous phase assumed a hybrid configuration (Fig. 1A) (*1*, *20*). This configuration of the LC leads to in-plane birefringence, thereby altering the polarization of incident light passing through the LC film and generating a bright optical appearance between crossed polarizers (Fig. 1A) (*21*, *22*). Next, we investigated the adsorption of the non-ionic amphiphile AMP2 (Fig. 1E) on the LC-aqueous interface and the influence of the adsorbed AMP2 molecules on the configuration of the LC film. We used a charge-neutral amphiphile molecule to avoid strong electrostatic interactions between the amphiphiles, the LC, and the water phase. Following exposure to an aqueous solution containing 150 μM AMP2, the LC film adopted a dark appearance between crossed-polars (Fig. 1B), consistent with a transition from a hybrid configuration into a configuration where the LC is uniformly oriented perpendicular to both the OTS-coated substrate and the aqueous interface (Fig. 1B).

To understand the detailed mechanisms underlying the configurational transition of the LC, we performed atomistic molecular dynamics simulations of amphiphile-laden aqueous interfaces. We initially brought a thin film of 5CB in contact with vacuum and water to stabilize a hybrid configuration (Fig. 1D); vacuum induces a perpendicular orientation of LCs similar to that of the OTS-coated glass substrate (*13*). When a monolayer of the amphiphiles (1 mol/nm^2) is assembled at the aqueous interface (Fig. 1C, D), however, the system exhibits an ordering transition. Specifically, analysis of the molecular orientation with respect to an axis normal to the film, i.e. calculation of the second Legendre polynomial $P_2(z) = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$ (where θ is the angle between the long molecular axis of 5CB and the $\hat{\boldsymbol{z}} = (0,0,1)$ direction (*19*)), indicates that the LC film assumes a nearly uniform configuration throughout its entire thickness (Fig. 1D). The profile of the vertical component of the nematic director (n_z) remains close to unity throughout the film, which further supports formation of a LC film with uniform orientation (Fig. 2A). Here we note an interesting observation; the nematic director is undefined within a thin region of approximately 2 nm thickness in the vicinity of the aqueous interface (red box in Fig. 2A). In this region, the scalar order parameter S is computed to be low ($S < 0.2$), suggesting a nematic-to-isotropic phase transition (Fig. 2B), while the average value of S remains ~0.55 in the bulk regions of the LC film (Fig. 2B). We note that the simulation results regarding profiles of n (Fig. 2A) and S (Fig. 2B) are significantly different from those reported in a recent study of pure LCs (*13*).

Our analysis of molecular orientation suggests that the mechanisms responsible for the amphiphile-induced interfacial phase transition are related to: i) the amphiphilic nature of 5CB and ii) specific interactions between 5CB and water molecules. Past studies have shown that, at aqueous interfaces, 5CB assumes a tilted orientation that permits hydration of the polar nitrile group (*13*). Furthermore, 5CB molecules exclusively adopt an antiparallel orientation in the bulk nematic phase, as well as at the interface, because of strong dipole-dipole repulsions between the polar heads (Fig. 1E) of the adjacent molecules (*13, 23, 24*). Upon assembly of the amphiphile molecules, however, our simulations reveal that 5CB molecules near the aqueous interface are no longer aligned in the antiparallel fashion. Figure 2C shows the probability distribution ($P(z, \cos\theta)$) of the molecular orientation in the LC film. At the AMP2-rich aqueous interface, $P(z, \cos\theta)$ has its maximum near $\cos\theta = 1$, revealing that the hydrophilic heads of 5CB molecules are oriented towards an overlying aqueous phase, due to favorable electrostatic interactions, and are interdigitated with the nonpolar tails of the amphiphiles. In the immediate sub-interface layer, therefore, 5CB molecules are not able to align their molecular dipoles next to those molecules, and therefore fail to maintain their liquid crystalline order, leading to the formation of a thin isotropic layer (Fig. 2B). This isotropic layer remains narrow (~2nm thick) in order to impose a minimal free energy penalty on the system.

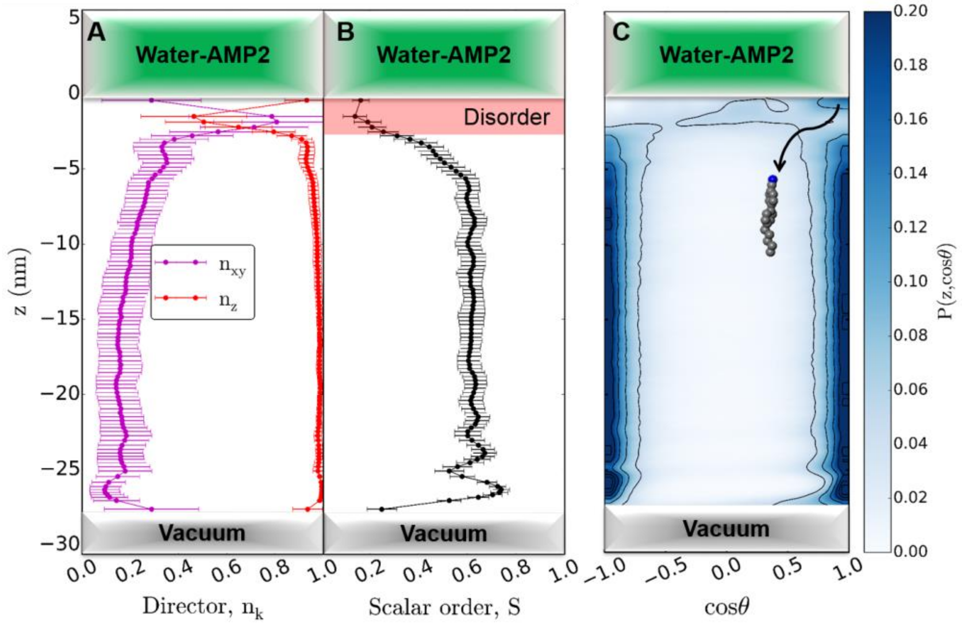

Fig. 2. Analysis of the molecular orientation at the amphiphile-laden aqueous interface. (A) Components of the nematic director n_z and $n_{xy} = \sqrt{(n_x^2 + n_y^2)}$ as a function of distance from the aqueous interface. The LC film assumes a nearly uniform configuration with perpendicular orientation throughout the film. (**B**) The profile of the scalar order parameter *S*. A thin layer of ~2nm thick with $S < 0.4$ is formed in the vicinity of the aqueous interface because the amphiphiles disrupt the nematic LC order. (**C**) The two-dimensional histograms of the molecular orientation. A peak at $\cos\theta = 1$ at the AMP2-rich aqueous interface indicates that 5CB molecules tend to maintain their hydrophilic head in proximity of the water phase. The probability of the molecular orientation shows that the LC molecules assume no preferred orientations within the thin isotropic layer near the aqueous interface. Beneath that isotopic region, the 5CB molecules adopt the antiparallel orientation throughout the rest of the film. The error-bars in panels (A) and (B) correspond to the standard deviations of the computed values.

To further test the proposition that the amphiphiles trigger a configurational transition of the LCs via a weakening of the anchoring strength, as opposed to a transition through reorientation of the easy axis of the LC (from planar to homeotropic orientation), we also simulated a LC film in which the lower plane is in contact with water, and the upper plane is in contact with a monolayer of AMP2 at the aqueous interface (Fig. 3A). We hypothesize that if the amphiphiles reorient the easy axis of LCs at the aqueous interface from a planar to a homeotropic orientation, then the LC film must have a hybrid configuration. The simulation results, however, reveal that the LC film assumes a uniform planar orientation, which indicates that the anchoring strength at the amphiphile-laden interface is extremely weak (Fig. 3B, C). A thin isotropic layer is similarly formed here at the AMP2-laden aqueous interface.

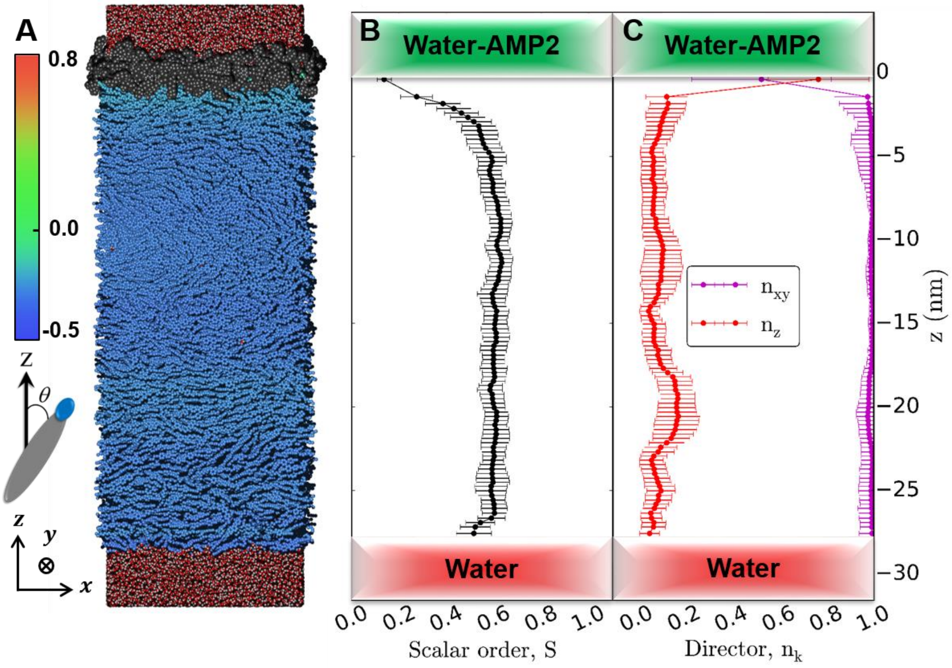

Fig. 3. Analysis of the molecular orientations of an LC film in contact with pure water and a monolayer of amphiphiles. (A) The color-coded profile of the second Legendre polynomial $P_2(z) = \langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \rangle$. The blue color shows a uniform planar (parallel) orientation of the LC molecules throughout the film. (**B**) The profile of the scalar order parameter S. (**C**) The profile of the nematic director n_z and $n_{xy} = \sqrt{(n_x^2 + n_y^2)}$.

We performed additional experiments to test the above predictions. Specifically, a 10 µm-thick film of 5CB was formed on a glass substrate coated with a polyimide (PI) layer that imparts planar anchoring of the LC. The PI interface was rubbed prior to contact with the LC to induce a unidirectional in-plane orientation of the LC. When characterized in air, the LC film exhibited a colorful birefringent optical texture, consistent with the homeotropic orientation of the LC at the air interface, and revealing a hybrid configuration in the LC film supported on the planar PI substrate (Fig. 4A). When the 5CB film was immersed in pure water, the optical appearance of the LC transformed to a uniform yellow color (Fig. 4B). The change in optical appearance (from bright birefringence colors to a uniform yellow color) indicates an increase in the optical retardance associated with planar anchoring of the LC at the aqueous interface (and thus a planar orientation of the LC across the entire LC film). Finally, we added AMP2 to the aqueous phase (Fig. 4C). If the adsorption of AMP2 at the aqueous-LC interface were to cause the LC at the aqueous interface to reorient into a homeotropic orientation, the LC films would recover the optical features of the hybrid configuration (colorful birefringent texture, Fig. 4A). The LC film, however, remains unchanged in its optical appearance following the addition of AMP2, indicating that a planar orientation of the LC is preserved in the presence of AMP2 (consistent with the simulations in Figs. 3). This result, when combined with the results in Fig 1B obtained with the LC film supported on the OTS-coated substrate, serves to establish that the transition between hybrid and uniform configurations in Fig 1B is due to a weakening of the anchoring of the LC by the adsorbed AMP2 molecules. As noted above, the LC configuration within the LC film is determined by a competition between the elastic energy associated with strain of the LC ($K \cdot d$) and anchoring energy of the LC interfaces ($W \cdot d^2$), where K is a characteristic Frank elastic constant of the LC, W is the surface anchoring energy density, and d is the thickness of the LC film (*19, 25, 26*). In the strong anchoring regime ($W \cdot d^2 > K \cdot d$ and thus $d > K/W$), the LC film confined between two surfaces that impose competing orientations (homeotropic and planar orientation) will adopt a hybrid LC configuration (Figs. 1A and 4A). When the anchoring strength is weakened (and thus $W \cdot d^2 < K \cdot d$), however, the hybrid configuration is no longer energetically favourable, and the LC will assume the orientation that corresponds to the surface with the highest anchoring energy (Figs. 1B and 4C). Using $K = 7.3$ pN at $T = 25$ °C (*27*) and the results in Fig 4, we estimate that $W < 7.3\cdot10^{-7}$ J/m^2 following adsorption of AMP2 at the aqueous interface. We note that this value of W is smaller than past estimates of $W = 10^{-5}$-10^{-6} for other molecules at the LC-aqueous interface (*2*, *28*).

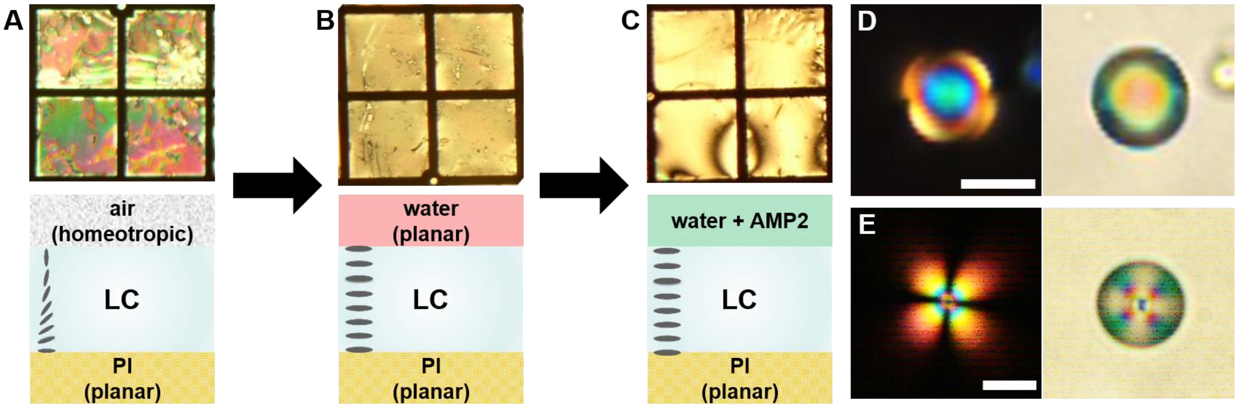

Fig. 4. Dynamic optical response of LC film and LC droplets to the self-assembly of AMP2. (**A**) Optical micrographs and schematic representation of a hybrid LC film confined between a glass substrate modified with rubbed polyimide (PI) and air. (**B, C**) Optical microscopy images and schematic representations of the molecular orientation in a 5CB film hosted on a planar rubbed PI surface and in contact with pure water (B), and AMP2-adsorbed aqueous interface (C). The optical features of the AMP2-rich interface are similar to those of amphiphile-free system, and the film retains its uniform orientation after addition of the AMP2. (**D, E**) Optical micrographs (crossed and parallel polars) of LC droplets after 0 (D) and 4 hours (E) of contact with aqueous AMP2 (150 μM). Scale bar, 10μm.

Past studies of LC ordering at "hard" interfaces, such as treated silica and alumina, suggest planar orientation of LCs at high surface densities (*12*). Overall, dense packings of amphiphiles at an interface tend to hinder penetration of liquid crystals into the amphiphile layers, which then causes a planar orientation at the interface. These assemblies, however, are not the same as "soft" aqueous interfaces, because the latter allow for dynamic adjustments of the surface concentration through the exchange of the amphiphiles with the aqueous phase and formation of micelles in water. As such, the aqueous medium imposes minimal conformational constraints on the molecules, which prohibit dense-packing of the amphiphiles at these interfaces. We believe it is unlikely, therefore, that the experimental observation of planar orientation of the LC observed in the presence of AMP2 arises from dense packing of this amphiphile at the interface.

AMP2 has the molecular architecture of a dimeric surfactant, with two aliphatic tails and two non-ionic head groups. The detailed mechanism identified in simulations, which gives rise to weak anchoring by AMP2, involves LC-water interactions. Future experiments will seek to further explore the influence of molecular surfactant architecture on the mechanisms by which anchoring transitions occur. In addition, it is possible for the mechanism reported in this paper to cause configurational transitions in LC emulsions dispersed in an aqueous phase. LC droplets dispersed in pure water assume a so-called bipolar configuration, with a tangential orientation at the droplet surface and two point defects, called “boojums”, at the poles of the droplets (*22, 29-31*). However, droplets with radii (R) below 1 μm were observed to have a “radial” configuration with perpendicular orientation at the surface (*32*). Gupta *et al.* (*32*) estimated a critical radius $R_c = (K_{24} - 3/2\, K_{11})/W$ below which a bipolar-to-radial transition occurs, where K_{24} and K_{11} are the saddle-splay and splay elastic constant, respectively. The results presented in this paper indicate that W can approach zero upon assembly of monolayers of AMP2 (i.e., $R_c \rightarrow \infty$), suggesting that one can introduce a radial configuration of the LC droplets across the entire range of droplet sizes (Fig. 4D, E)

In summary, our experiments and simulations have served to establish that specific amphiphiles, at aqueous interfaces, do not change the lowest free energy orientation of LCs (easy axis) but instead they greatly reduce the surface anchoring energy. This weakening of the anchoring strength facilitates the release of the stored elastic energy and induces a transformation of the LC system into a new state with minimum stored elastic energy. This mechanism enables fresh thinking of the design responsive LC systems for biological sensors and molecular devices.

References and Notes:

1. J. M. Brake, M. K. Daschner, Y. Y. Luk, N. L. Abbott, Biomolecular interactions at phospholipid-decorated surfaces of liquid crystals. *Science* **302**, 2094-2097 (2003).

2. I. H. Lin *et al.*, Endotoxin-induced structural transformations in liquid crystalline droplets. *Science* **332**, 1297-1300 (2011).

3. J. S. Patel, H. Yokoyama, Continuous anchoring transition in liquid crystals. *Nature* **362** 525-527 (1993).

4. Y. Q. Bai, N. L. Abbott, Recent Advances in Colloidal and Interfacial Phenomena Involving Liquid Crystals. *Langmuir* **27**, 5719-5738 (2011).

5. D. S. Miller, X. G. Wang, J. Buchen, O. D. Lavrentovich, N. L. Abbott, Analysis of the Internal Configurations of Droplets of Liquid Crystal Using Flow Cytometry. *Anal. Chem.* **85**, 10296-10303 (2013).

6. D. S. Miller, N. L. Abbott, Influence of droplet size, pH and ionic strength on endotoxin-triggered ordering transitions in liquid crystalline droplets. *Soft Matter* **9**, 374-382 (2013).

7. R. J. Carlton *et al.*, Chemical and biological sensing using liquid crystals. *Liq. Cryst. Rev.* **1**, 29-51 (2013).

8. E. Bukusoglu, M. B. Pantoja, P. C. Mushenheim, X. Wang, N. L. Abbott, Design of responsive and active (soft) materials using liquid crystals. *Annual Review of Chemical and Biomolecular Engineering* **7**, 163-196 (2016).

9. M. Sadati *et al.*, Liquid Crystal Enabled Early Stage Detection of Beta Amyloid Formation on Lipid Monolayers. *Adv. Funct. Mater.* **25**, 6050-6060 (2015).

10. S. J. Woltman, G. D. Jay, G. P. Crawford, Liquid-crystal materials find a new order in biomedical applications. *Nat. Mater.* **6**, 929-938 (2007).

11. M. Khan, A. R. Khan, J. H. Shin, S. Y. Park, A liquid-crystal-based DNA biosensor for pathogen detection. *Sci. Rep.* **6**, 22676 (2016).

12. G. P. Crawford, R. J. OndrisCrawford, J. W. Doane, Systematic study of orientational wetting and anchoring at a liquid-crystal-surfactant interface. *Phys Rev E* **53**, 3647-3661 (1996).

13. H. Ramezani-Dakhel *et al.*, Understanding Atomic-Scale Behavior of Liquid Crystals at Aqueous Interfaces. *J. Chem. Theory Comput.* **13**, 237-244 (2017).

14. J. M. Brake, A. D. Mezera, N. L. Abbott, Effect of surfactant structure on the orientation of liquid crystals at aqueous-liquid crystal interfaces. *Langmuir* **19**, 6436-6442 (2003).

15. N. A. Lockwood, J. J. de Pablo, N. L. Abbott, Influence of surfactant tail branching and organization on the orientation of liquid crystals at aqueous-liquid crystal interfaces. *Langmuir* **21**, 6805-6814 (2005).

16. C. D. Ma *et al.*, Liquid Crystal Interfaces Programmed with Enzyme-Responsive Polymers and Surfactants. *Small* **11**, 5747-5751 (2015).

17. P. D. I. Fletcher, N. G. Kang, V. N. Paunov, UV Polymerisation of Surfactants Adsorbed at the Nematic Liquid Crystal-Water Interface Produces an Optical Response. *ChemPhysChem* **10**, 3046-3053 (2009).

18. I. W. Stewart, *The static and dynamic continuum theory of liquid crystals : a mathematical introduction*. The liquid crystals book series (Taylor & Francis, London, 2004), pp. xi, 360p.

19. M. Kleman, O. D. Lavrentovich, *Soft Matter Physics: An Introduction*. (Springer, New York, 2003).

20. P. Popov, E. K. Mann, A. Jakli, Accurate Optical Detection of Amphiphiles at Liquid-Crystal-Water Interfaces. *Phys Rev Appl* **1**, 034003 (2014).

21. R. Ondriscrawford *et al.*, Microscope Textures of Nematic Droplets in Polymer Dispersed Liquid-Crystals. *J. Appl. Phys.* **69**, 6380-6386 (1991).

22. P. G. de Gennes, J. Prost, *The Physics of Liquid Crystals*. (Clarendon Press, Oxford, 1993).

23. M. Sadati *et al.*, Molecular Structure of Canonical Liquid Crystal Interfaces. *J. Am. Chem. Soc.* **139**, 3841-3850 (2017).

24. A. Pizzirusso, R. Berardi, L. Muccioli, M. Ricci, C. Zannoni, Predicting surface anchoring: molecular organization across a thin film of 5CB liquid crystal on silicon. *Chem. Sci.* **3**, 573-579 (2012).

25. Y.-K. Kim, S. V. Shiyanovskii, O. D. Lavrentovich, Morphogenesis of defects and tactoids during isotropic nematic phase transition in self assembled lyotropic chromonic liquid crystals. *J. Phys.: Condens. Matter* **25**, 404202 (2013).

26. T. A. Wood, J. S. Lintuvuori, A. B. Schofield, D. Marenduzzo, W. C. K. Poon, A self-quenched defect glass in a colloid-nematic liquid crystal composite. *Science* **334**, 79-83 (2011).

27. A. Bogi, S. Faetti, Elastic, dielectric and optical constants of 4'-pentyl-4-cyanobiphenyl. *Liq. Crysts.* **28**, 729-739 (2001).

28. R. J. Carlton, J. K. Gupta, C. L. Swift, N. L. Abbott, Influence of Simple Electrolytes on the Orientational Ordering of Thermotropic Liquid Crystals at Aqueous Interfaces. *Langmuir* **28**, 31-36 (2012).

29. G. E. Volovik, O. D. Lavrentovich, Topological dynamics of defects: Boojums in nematic drops. *Sov. Phys. JETP*. **58**, 1159-1167 (1983).

30. X. Wang *et al.*, Experimental Insights into the Nanostructure of the Cores of Topological Defects in Liquid Crystals. *Phys. Rev. Lett.* **116**, 147801 (2016).

31. X. Wang, D. S. Miller, E. Bukusoglu, J. J. de Pablo, N. L. Abbott, Topological defects in liquid crystals as templates for molecular self-assembly. *Nat. Mater.* **15**, 106-112 (2016).

32. J. K. Gupta, S. Sivakumar, F. Caruso, N. L. Abbott, Size-Dependent Ordering of Liquid Crystals Observed in Polymeric Capsules with Micrometer and Smaller Diameter. *Angew. Chem.-Int. Edit.* **48**, 1652-1655 (2009).

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Supplementary Materials: