Published in final edited form as:

ACS Appl Mater Interfaces. 2012 December ; 4(12): . doi:10.1021/am301952f.

IMPROVING LIQUID CRYSTAL-BASED BIOSENSING IN AQUEOUS PHASES

Wilder Iglesias^a, Nicholas L. Abbott^b, Elizabeth K. Mann^c, and Antal Jákli^{a,d,*}

^aLiquid Crystal Institute, Kent State University, Kent, OH, 44242, USA

^bChemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI, 53706, USA

^cPhysics Department, Kent State University, Kent, OH, 44242, USA

^dInstitute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences H-1525 Budapest, P.O. Box. 49, Hungary

Abstract

Liquid crystal (LC)-based biological sensors permit the study of aqueous biological samples without the need for the labeling of biological species with fluorescent dyes (which can be laborious and change the properties of the biological sample under study). To date, studies of LC-based biosensors have explored only a narrow range of the liquid crystal/alignment layer combinations essential to their operation. Here we report a study of the role of LC elastic constants and the surface anchoring energy in determining the sensitivity of LC-based biosensors. By investigating a mixture of rod-shape and bent-shape mesogens, and three different alignment layers, we were able to widen the useful detection range of a LC-based sensor by providing an almost linear mapping of effective birefringence with concentration between 0.05 and 1mM of an anionic surfactant (model target analyte). These studies pave the way for optimization of LC-based biosensors and reveal the importance of the choice of both the LC material and the alignment layer in determining sensor properties.

Keywords

biosensing; anchoring energy; surfaces; liquid crystals; bent-core molecules; elastic constants

I. INTRODUCTION

Studies of interfacial phenomena involving liquid crystals (LCs) near solid surfaces have been pivotal in the development of a range of electro-optical devices (including LC displays).^{1–3} Surface science tools have yielded important details regarding molecular level interactions that couple the structure of the solid surface to the ordering of mesogens at the interface, which in turn transfer their organizational information to the bulk LC via long-range orientational order of the LC. The sensitivity of LCs to surface properties is also the basis of a more recent series of studies of interfaces formed between LCs and immiscible aqueous phases. A remarkably diverse range of ordering transitions occurs as amphiphilic molecules (surfactants and lipids), polymers, or proteins assemble at interfaces between LCs and aqueous phases. The interfacial phenomena can be monitored using the macroscopic

*Corresponding author: ajakli@kent.edu.

alignment of the LC director as an imaging tool for sensing key molecular and nanoscopic events at the LC/biomaterial-laden interface.⁴⁻⁹

An experimental setup that has been widely used for LC-based sensing of biological samples in water is shown in Figure 1. It involves an interface between an aqueous phase and a water-immiscible thermotropic LC in its nematic phase. Most studies to date have used the LC 4'-pentyl-4-cyanobiphenyl (5CB) at room temperature. The LC is placed in the holes of a gold transmission electron microscopy (TEM) grid that is supported on a glass microscope slide treated with different homeotropic alignment layers,⁹ most often octadecyltrichlorosilane (OTS). Immersion of this simple set-up into an aqueous phase leads to the formation of a stable interface between the aqueous phase and the LC.

By performing the study reported in this paper, we aimed to advance current bio-sensing techniques based on LCs by manipulating the bulk elastic constants and surface anchoring properties of the surface/mesogen combinations. The bulk elastic properties are determined by K_1 , K_2 and K_3 , which are “elastic constants” that dictate the changes in the Frank free energy per unit volume F_d , when the nematic liquid crystal is splayed, twisted or bent, respectively:¹⁰

$$F_d = \frac{1}{2}K_1(\vec{\nabla} \cdot \vec{n})^2 + \frac{1}{2}K_2(\vec{n} \cdot \vec{\nabla} \times \vec{n})^2 + \frac{1}{2}K_3(\vec{n} \times \vec{\nabla} \times \vec{n})^2 \quad (1)$$

Where $\vec{n}$ is the liquid crystal director. These constants are unique and characteristic of the hundreds of thousands of different LC materials synthesized and characterized to date. The director distortion in the bulk transfers a torque to the surfaces of the LC, and the equilibrium bulk configuration is determined by the torque balance at the surfaces. The surface interactions can be approximated by the Rapini-Papoular expression¹¹ for the energy per unit area

$$\Phi_s^\pm = \frac{1}{2}W^\pm \sin^2(\theta^\pm - \theta_e^\pm) \quad (2)$$

where $W^\pm > 0$ are the anchoring strengths at the different surfaces and $\theta_e^\pm$ are the surface easy tilt angles, i.e., the directions imposed by external surface conditions.

An additional key concept used to describe the anchoring of LCs at surfaces is the extrapolation length. The extrapolation length $b = K/W$ can be related to the distance from the surface where θ would reach the easy axis value without disturbing the $d\theta/dz = \text{constant}$ dependence valid in the bulk (see Figure 2.) When $b \ll L$ (strong anchoring), the bulk elastic properties govern the director profile, whereas when $b/L \sim 1$ (weak anchoring), the alignment surfaces will also play an important role.

In this paper, we advance the use of LCs for biosensing by identifying new LC materials and alignment methods that provide a wider sensing range for a surfactant (used as a model analyte). We note that sensing-range linearity is generally a highly desired attribute of a biosensor. We also note that, whereas past studies have generally interpreted the orientational response of LCs to adsorbates at aqueous-LC interfaces as resulting from changes in the easy axis of the LCs,⁴⁻⁹ in this paper, we offer an interpretation of our experimental results in terms of a reduction in the anchoring energy (without a change in the easy axis). We conclude that a complete description of the operation of LC-based sensors will likely need to include consideration of both changes in the easy axis and anchoring energies of LCs, as induced by targeted analytes. Overall, the results reported in this paper enable new approaches for investigations of the self-assembly of molecules at interfaces, as

well as opportunities for technological advances in areas such as chemical and biological sensing and the design of stimuli-responsive materials.

II. MATERIALS AND METHODS

II.1 Alignment Layers

In addition to the previously tested OTS-treated glass, two other homeotropic alignment surfaces, polyimide (PI) and a bent-core layer of amphiphilic molecules (Z4), were used to probe the role played by the anchoring energy of the bottom surface. All these alignment layers were deposited on glass slides cleaned in water by using an ultrasonic cleaner (Branson B200), and washed with a solution of isopropanol/water and placed immediately in an oven at 80°C for 15 minutes. For the OTS coating, the clean glass slides were immersed in an OTS/heptane solution at 0.5mM for 30 minutes, rinsed with dichloromethane (DCM or methylene chloride) three times and dried with nitrogen. For the PI coating, a drop of Nissan SE-1211 was placed in the center of the glass slide and spin coated for 20 s at 2500 rpm. Next, this slide was soft-baked for 1–2 minutes at 90°C on a hot plate and then hard-baked in an oven for one hour at 108°C. For the bent-core surface layer, a monolayer of the banana shaped liquid crystal molecules, Z4¹² (shown in Figure 3), spread on water in a Langmuir trough was transferred to a clean glass slide using the inverse Langmuir/Schaefer deposition. To achieve homeotropic alignment, the material is deposited at high surface pressure (~30mN/m) as described in earlier papers.¹³

II.2 Gold Grids

The alignment layer-coated glass slides were used to form the base of optical cells. Gold-coated TEM grids (obtained from Electron Microscopy Sciences; Figure 1.) were placed onto the coated glass slides. Square gold-coated meshes with 50 and 75 lines/inch were tested, giving similar results; the former one was chosen since the edge effects are less important for larger hole sizes.¹⁴ Grids were used more than once and stored in ethanol. Before each use, they were washed by rinsing three times with ethanol, three times with methanol, and three times with either chloroform or dichloromethane.

II.3 LC Mesogens

Bent-core liquid crystal molecules (BCLC) have been shown¹⁵ to possess distinctively lower bend elastic constants due their favorable molecular shape for bend distortions. This lower bend elastic constant makes BCLC interesting candidates for biosensing. On the other hand, the banana shape promotes molecular locking into layers that favor smectic structures. Although a nematic phase of BCLCs can be achieved by frustrating this locking mechanism by bulky substitutions in the central ring of a bent-shape molecule, the nematic phase usually occurs at high temperatures where thermal fluctuations are sufficient to break the locking. This presents a challenge for biosensors, which require a LC material with a nematic phase between room temperature and 37°C. Fortunately, the nematic phase range of BCLCs can be lowered by mixing them with calamitic mesogens,¹⁶ where the calamitic mesogens frustrate the locking of the bent-cores and the thermal energy necessary to induce a nematic phase is smaller.

To achieve the appropriate temperature range and low elastic constants, mixtures of, a bent-core mesogen with a CN substitution (CN6)¹⁷ with the well-known 5CB (see molecular structures in Figure 4) were studied. Since in a nematic phase the elastic constant values diminish as we approach the Iso-N transition temperature,¹⁸ we aimed to find a mixture of these two components such that the isotropic-nematic transition was close to the working temperatures, and the concentration of bent-shaped liquid crystal was large enough to lower the elastic constants of the blend.

III. MEASUREMENTS

III.1 Elastic Constants

To find the Frank elastic constants, the Freedericksz transitions were measured in magnetic and electric fields following the procedure described in reference [15]. Thick ($d=22\mu\text{m}$) homogeneously aligned (planar) films of 5CB and CN6/5CB were placed in a temperature-regulated oven mounted between the pole faces of a large electromagnet in orientations shown in Figure 5. One direction of the magnetic field corresponds to a field-induced splay-bend deformation, and the other one to a pure twist distortion. A 4mW HeNe laser, normally incident on the sample, together with a polarizer-analyzer combination and an amplified photodetector (Thorlabs, model PDA55), were used to detect optically the threshold field B_t for the onset of the director deformations. The magnetic field, monitored with a small Hall probe mounted near the sample, could be varied continuously from 0 to 1.3T, and was highly uniform over the sample cell volume. In addition to the optical transmission data, the cell capacitance was also recorded as a function of the applied magnetic field using a precision capacitance bridge (Andeen-Hagerling, model 2500A) with a probe voltage of 0.1V at 1 KHz frequency. Finally, the change of B_t as a function of an AC voltage ranging from 0 to 2 V_{rms} at 1kHz was determined using the optical transmission method in the splay-bend configuration.¹⁵

The measurements were analyzed by equations valid for aligned uniaxial nematics;¹⁹ the elastic constants determined in this way are shown in Table 2. The results obtained for 5CB at 24°C are in good agreement with values published in the literature.^{20–23} It can be seen that all three elastic constants are smaller for the mixture than for pure 5CB.

III.2 Surface Anchoring Energy

There are several methods of determining the anchoring strength (energy per unit area), most directly by finding the voltage necessary to overcome the preferred orientation of LC molecules at the surface. Below this voltage, the director will realign quickly (in several milliseconds) with a characteristic relaxation time given by the viscosity and elastic properties of the LC. Above the anchoring threshold, however, the realignment is gradual (taking several seconds or minutes), as dictated by a surface nucleation process whereby the mesogens adsorbed at the surface return to their original orientations. The threshold voltage to break the anchoring can be related to the surface anchoring energy per unit area W_o , by

equating it with the dielectric energy density $\frac{1}{2}\Delta\epsilon E^2$ ($\Delta\epsilon$ is the dielectric anisotropy, $E=V/d$ is the electric field and V is the voltage applied across the electrodes separated by a distance

d), multiplied by the electric coherence length,²⁴ $\xi_3 = \frac{1}{E} \sqrt{\frac{K_3}{\Delta\epsilon}}$, so that

$$W_o = \frac{V}{2d} \sqrt{\Delta\epsilon \cdot K_3} \quad (3)$$

Since the materials we studied have positive dielectric anisotropies, we used an in-plane switching (IPS) liquid crystal cell with homeotropic substrates. It was found that the anchoring for the Nissan SE-1211 PI breaks at $V \sim 107\text{V}$ for 5CB and $\sim 93\text{V}$ for 5CB/CN6 with a $d=20\mu\text{m}$ gap between electrodes. These provide $W_o \sim 1.4 \times 10^{-4} \text{J/m}^2$ for 5CB and $W_o \sim 0.9 \times 10^{-4} \text{J/m}^2$ for the 5CB/6CN, respectively. The anchoring energy measurements for 5CB coincide with those published in the literature.^{25–27}

III.3 Polarizing Optical Microscopy (POM)

The TEM grid filled with the LC material, supported on a homeotropic alignment layer is dark in POM between crossed polarizers (viewed in air), because the LC film adopts a homeotropic orientation at the interface with air (see left column of Figure 6). Immersion of the sample in deionized water results in a hybrid alignment, since the water promotes planar alignment at the top interface of the LC, while the bottom surface is homeotropic. This hybrid alignment leads to a LC samples that exhibits a bright appearance and a typical defect structure (second column on Figure 6). When a surfactant, sodium dodecyl sulfate (SDS), is added to the water, the adsorbed layer reduces the effective birefringence due the interaction of the SDS with the LC interface (third column on Figure 6). As described by Lockwood et al.,^{6,8} the pretilt angle at the top surface continuously increases with surfactant concentration until homeotropic alignment is achieved. To calculate the effective birefringence Δn_{eff} of the LC film, we measured the transmitted intensity of light, I , under monochromatic ($\lambda=550\text{nm}$) illumination with the optical axis of the sample at 45° from the two crossed polarizers, and determined an effective refractive index contrast Δn_{eff} using equation Eq. (4), which is exactly valid with $\Delta n_{eff}=\Delta n$ for a uniform cell

$$I=I_0 \sin^2 \left(\pi \Delta n_{eff} \frac{d}{\lambda} \right) \quad (4)$$

where I_0 is the incoming light intensity, and $d=22\mu\text{m}$ is the thickness of the LC cell. I_0 can be found by measuring I when the LC is under pure water and the bottom alignment layer also produces a planar alignment. For this configuration the birefringence is $\Delta n_{eff}=n_e-n_o$, which can be independently determined: The value of Δn_{eff} for 5CB can be found in the literature;^{18–21} and it can be found for both 5CB and 5CB/CN6 from our Freedericksz transition measurements. The measured light intensity, obtained by analyzing images at different surfactant concentrations with the software ImageProPlus, was used to calculate an effective birefringence according to Eq. (4), thus allowing the effective birefringence versus SDS concentration curves to be constructed. We used the average intensity of the whole image, which averages over all defects in the individual grid cells and avoids any observer bias but includes both the dark grid and the bright lines due to perpendicular alignment near that grid. For this reason, Δn_{eff} will always be greater than a minimum value due to the bright lines and less than a maximum value due to the dark grid.

IV. RESULTS

The effective birefringence of the LCs, measured as a function of the surfactant concentrations, are compared for the 5CB and the selected 5CB/CN6 mixtures for the three different alignment layers in Figure 7–9. In Figure 7, we compare the curves when using the PI alignment layer, at two temperatures: 24°C and 30°C .

There are several important features to be seen in Figure 7.

- a. The effective birefringence at pure water is larger for the mixture, which (considering that the birefringence of the mixture, $\Delta n=0.14$, is smaller than for the pure LC), means that the alignment is more nearly tangential to the interface for the mixture.
- b. The decline of Δn_{eff} appears at lower concentrations of SDS when using the pure 5CB than when using the mixture.
- c. The Δn_{eff} curve for the LC mixture is less abrupt (especially at 24°C). The more gradual the transition is, the wider is the sensing concentration range, which is an important factor for a sensor. Comparing the sensing range for the two different

temperatures, we see that the sensing range increases at higher temperatures for both LCs.

- d. The effective birefringence does not drop to zero even in the homeotropic state, because the interaction of the gold frame prevents homeotropic alignment at the edges. This effect is larger for the pure 5CB, indicating that the anchoring between the gold and LC is stronger for the 5CB than for the mixture.

Figure 7 shows the same type of graphs as Figure 6, but now with OTS alignment layers beneath the LCs.

We see several notable similarities and differences with respect to the PI coating. The value of the transmitted intensity of light in the absence of SDS is about 40% larger for the OTS coating, indicating that the OTS/LC anchoring energy is smaller than the PI/LC anchoring energy for both LCs. The sensing range is also 3 to 4 times wider for both LCs at 24°C (30°C) when using the OTS-coated surfaces, and again it is about 40% wider for the mixture than for the pure 5CB. These almost linear correlations between birefringence and SDS concentration make the sensors useful from 0.1mM up to 0.9mM for 5CB, and 0.1 mM and 1.2mM for the 5CB/CN6 mixture.

As a final test, we used a monolayer of the bent-core Z4, prepared at a high surface pressure with the inverse Langmuir/Schaefer technique,¹³ as the alignment layer. The birefringence in the sensor using Z4 as the alignment layer, as shown in Figure 8, shows an additional 10% increase of the upper limit of the sensing range. This observation implies a slightly smaller anchoring strength of Z4 compared to OTS, although they behave much more similarly to each other than to PI, due to their similar amphiphilic nature.

V. DISCUSSION

The continuous transition from the hybrid configuration to uniform homeotropic alignment has been the subject of a number of prior studies. Both the easy axis and the anchoring strength of the surface alignment at the upper water/surfactant interface may vary during the transition we report in this study. Rey, emphasizing changes in the easy axis, has reported a thermodynamic model that relates the orientation of a LC to the areal density of the surfactant absorbed at the water LC interface.²⁸ The Rey model has been extended to include bulk elastic distortion and estimating the surface anchoring energy as $w_o \sin^2(\theta_s - \varphi(x))$, where w_o is assumed constant, independent from the fraction $\times$ of saturation monolayer coverage; θ_s is the tilt of LC at the interface; and φ is the angle of the easy axis of the LC.⁶ This extension yielded a phase diagram with a two-phase region, with coexisting planar and homeotropic states of the LC. This region of coexistence, however, decreased upon heating towards the isotropic phase. We, on the contrary, find an increased range of concentrations over which changes in the LC occur as a function of surfactant concentration.

In contrast to the above interpretation of the adsorbate-induced orientational transition in the LC film as resulting from a change in the easy axis of the LC, here we consider an alternative interpretation of our experiments in terms of a change in anchoring energy (without a change in easy axis). In our experiments, we find a uniform variation between the hybrid configuration and uniform homeotropic alignment, with a transitional range that increased with temperature. In addition, we find that the anchoring strength of the bottom surface influences the transition at the top surfaces as well. This latter effect has not previously been reported, and it motivated us to propose a simple model that can explain both observations by focusing on the anchoring strength, rather than the angle of the easy axis.

For our model, we need an estimate of the anchoring energy at the OTS-treated glass and Z4-monolayer decorated interfaces. To this end, we use Barbero and Barberi's analysis,²⁹ which predicts that the tilt angle in the center of the film (at $z=L/2$), θ_{center} , is proportional to the ratios of the anchoring strengths at the opposite surfaces (see Figure 2). Moreover, θ_{center} can be calculated from the measured effective birefringence, and the ordinary and extraordinary refractive indices of the materials, as

$$\sin^2 \theta_{center} = \frac{n_o^2}{n_e^2 - n_o^2} \left[\frac{n_e^2}{(\Delta n_{eff} + n_o)^2} - 1 \right] \quad (5)$$

Thus, values of θ_{center} can be found from Δn_{eff} measured for pure water, without SDS, for all three alignment layers with both 5CB and the 5CB/CN mixture. Furthermore, we have independent measurements of the anchoring strength at the PI/5CB and PI/(5CB/CN6) interfaces, as reported in section III.2. We can then find the anchoring strength W_i at the LC/alignment layer interface i from the anchoring strength W_{PI} at the LC/PI alignment layer interface and the center angles θ_{center}^{PI} and θ_{center}^i measured (for the same liquid crystal and upper interface) for the PI and the i alignment layers respectively:

$$W_i = W_{PI} \frac{\theta_{center}^i}{\theta_{center}^{PI}} \quad (6)$$

The results of this calculation are shown in Table 3.

Inspection of Table 3 reveals that the anchoring energies of the mixtures are smaller than those of the pure 5CB. This is probably the result of the different positions of the cyano groups in 5CB and CN6. In 5CB it is along the molecular axis, whereas in the CN6 it is about 60° away, thus decreasing the interactions between the amphiphilic surfaces.

These anchoring energies at the bottom solid surface remain moderately strong, leading to a short extrapolation length $b_b \ll L$ (see Figure 2.) The model of Barbero and Barberi²⁹ states that a transition from the hybrid configuration to the homeotropic alignment happens when the differences of the extrapolation lengths at the top and bottom surfaces (b_t and b_b , respectively) become larger than the film thickness, L , i.e.,

$$b_t \geq L + b_b = L(1 + b_b/L) \quad (7)$$

In case of the observed relatively strong anchoring at the bottom, at the transition the anchoring strength at the top interface can be approximated as

$$W_t = \frac{K}{L(1 + b_b/L)} \approx \frac{K}{L}(1 - b_b/L) \quad (8)$$

In this expression K is the effective Frank elastic constant of the LC (K can be well approximated with the bend elastic constant K_3 , since hybrid alignment imposes a bend in the director.) Similar to Rey's model²⁸ for the surfactant concentration of the anchoring strength (see Eq. (4)), near the transition we write that

$$W_t \approx W_0(1 - c/c_s), \quad (9)$$

where c_s is the saturated surfactant concentration. Combining this with Eq. (9), the surfactant concentration, c , where the transition happens, can be written as

$$c=c_s \left(1 - \frac{b_t}{L} + \frac{b_b b_t}{L^2} \right) \quad (10)$$

In accordance with our observations, the surfactant concentration at which the alignment of the LC on the top surface becomes homeotropic depends on the bend elastic constant of the LC, and the anchoring strengths on both interfaces. Considering the role of the bottom interface, we see that c increases as b_b increases, i.e., with larger K and/or smaller W . Indeed, we found experimentally that the Z4 alignment layer, which has the lowest anchoring strength, gave the largest range. Our simple model also explains the observed increase of the upper limit of the sensing range of the mixture, which has a smaller bend elastic constant (thus smaller b_t) than of the pure 5CB.

To summarize, our results highlight the importance of the elastic and anchoring properties of the LCs used in biosensors. Specifically we have shown that a mixture of rod-like and bent-shape molecules provide a wider sensing range with an almost linear relation between the surfactant concentration and the effective birefringence. Our results also suggest that the anchoring strength at the bottom surface plays a key role in the response of the LC. We found that the anchoring strength affects the sensing range, providing an improved range for the weakest anchoring. In order to qualitatively explain this improved range, and its increase with increasing temperature, we have introduced a simple model in which the switch from hybrid alignment at low surfactant concentrations to a uniform cell at high concentrations is dominated by the anchoring energy at the surfactant/liquid crystal surface. As noted above, however, both the anchoring strength and the easy axis should be functions of surfactant concentration, and both models and experiments exploring their interplay would be valuable in optimizing the range and sensitivity of the sensors.

Acknowledgments

This work was supported by NSF grants DMR-0907055. The synthesis of the bent-core liquid crystal was supported by NSF DMR 0964765, and the material was provided by R. Brackon and R. Twieg at Kent State University. We acknowledge technical assistance of Ms. Mir Lim in characterizing phase transitions of 5CB/CN6 mixtures. NLA acknowledges partial support from the NSF under awards DMR-1121288 (MRSEC), the National Institutes of Health (CA108467 and AI092004), and by the ARO (W911-NF-11-1-0251 and W911-NF-10-1-0181).

REFERENCES

1. de Gennes, PG.; Prost, J. *The Physics of Liquid Crystals*. Second Edition. Vol. Vol.1. Oxford: Clarendon Press; 1993. p. 34-35.
2. Cognard J. *Mol. Cryst. Liq. Cryst.* 1982; 51:1-77.
3. Jerome B. *Rep. Prog. Phys.* 1991; 54:391-397.
4. Brake JM, Daschner MK, Luk Y-Y, Abbott NL. *Science*. 2003; 302:2094-2097. [PubMed: 14684814]
5. Brake JM, Abbott N. *Langmuir*. 2007; 23:8497-8507. [PubMed: 17595119]
6. Gupta J, Meli M-V, Teren S, Abbott N. *Phys. Rev. Lett.* 2008; 100 048301-1-4.
7. Lockwood N, Abbott N. *Curr. Opin. Colloid Interface Sci.* 2005; 10:111-120.
8. Bai Y, Abbott N. *Langmuir*. 2011; 27:5719-5738. [PubMed: 21090596]
9. Lockwood N, Gupta J, Abbott N. *Surf. Sci. Rep.* 2008; 63:255-293.
10. Frank FC. *Discuss. Faraday Soc.* 1958; 25:19-28.
11. Rapini A, Papoular M. *J. Phys. Colloq.* 1969; 30:C4-C54.

12. Kardas D, Prehm M, Baumeister U, Pocięcha DR, Reddy A, Mehl GH, Tschierske C. *J. Mater. Chem.* 2005; 15:1722–1733.
13. Iglesias W, Smith TJ, Basnet PB, Stefanovic SR, Tschierske C, Lacks DJ, Jákli A, Mann EK. *Soft Matter*. 2011; 7:9043–9050.
14. Brake JM, Abbott NL. *Langmuir*. 2002; 18:6101–6109.
15. Majumdar M, Salamon P, Jákli A, Gleeson JT, Sprunt S. *Phys. Rev. E*. 2011; 83 031701-1-8.
16. Nair GG, Bailey CA, Taushanof S, Fodor-Csorba K, Vajda A, Varga Z, Bóta A, Jákli A. *Adv. Mater.* 2008; 20:3138–3142.
17. Keith C, Lehmann A, Baumeister U, Prehm M, Tschierske C. *Soft Matter*. 2010; 6:1704–1721.
18. Tjpto-Margo B, Evans GT, Allen MP, Frenkel D. *J. Phys. Chem.* 1992; 96:3942–3948.
19. Stewart, IW. *The Static and Dynamic Continuum Theory of Liquid Crystals: A Mathematical Introduction*. First Edition. Vol. Vol.1. New York: Taylor and Francis; 2004. p. 57-132.
20. Chen GP, Takezoe H, Fukuda A. *Liq. Cryst.* 1989; 5:341–346.
21. Faetti S, Gatti M, Palleschi V. *J. Physique Lett.* 1985; 46:881–886.
22. Breddels PA, Mulkens JCH. *Mol. Cryst. Liq. Cryst.* 1987; 147:107–112.
23. Bradshaw MJ, Raynes EP, Bunning JD, Faber TE. *J. Phys. (Paris)*. 1985; 46:1513–1520.
24. Jákli A, Markscheffel S, Saupe A. *J. Appl. Phys.* 1996; 79:1891–1894.
25. Peng Y, Miyamoto T, Naito H, Kuze M, Sugimura A, Iwamoto M. *Mol. Cryst. Liq. Cryst.* 1997; 304:253–258.
26. Seo DS, Kobayashi S. *Mol. Cryst. Liq. Cryst.* 2000; 339:1–10.
27. Bechtold IH, Oliveira E. *Liq. Cryst.* 2005; 32:343–347.
28. Rey AD. *Langmuir*. 2004; 20:11473–11479. [PubMed: 15595772]
29. Barbero G, Barberi R. *J. Phys. (Paris)*. 1983; 44:609–616.

Figure 1.

Schematic illustration of the experimental system used to study the adsorption of amphiphiles at the aqueous-liquid crystal interfaces. TEM gold grids (50 lines/inch-square mesh) obtained from Electron Microscopy Sciences.

Figure 2.

LC director profile sketch in a cell of thickness L . Left: hybrid configuration with different anchoring energies at the surfaces. Right: equivalent LC cell with a uniform director angle through the z direction based on the hybrid cell director angle at $L/2$ position.

Figure 3. Amphiphilic bent-core molecule with 4 carbons between the carboxylic head group and aromatic core. The molecule was used as a successful homeotropic alignment layer for 5CB in Ref. 13.

Figure 4.

Chemical structures of mesogens used in this work. Left: A nitrile-substituted nematic bent-core liquid crystal (CN6). Right: A standard rod-like liquid crystal (5CB) that forms a nematic phase at room temperature.

Figure 5.
Schematic illustrations for the Freedericksz transition measurements.

Figure 6.

Liquid crystal at aqueous interfaces. Top: schematic illustration of the nematic director in the TEM grid. Bottom: texture captured by POM of the illustration above. First column: LC at the air interface. Second column: LC at the pure water interface. Third column: LC at the water interface with a high concentration of surfactant.

Figure 7. Birefringence and transmitted light for two different nematic liquid crystals, 5CB and the 5CB/CN6 mixture discussed in the text, versus surfactant concentration using the PI alignment layer. Left: SDS sensing at 24°C; Right: SDS sensing at 30°C.

Figure 8. Birefringence and transmitted light for two different nematic liquid crystals, 5CB and the 5CB/CN6 mixture discussed in the text, versus surfactant concentration using OTS as the alignment layer. Left: SDS sensing at 24°C; Right: SDS sensing at 30°C.

Figure 9. Birefringence and transmitted light for two different nematic liquid crystals, 5CB and the 5CB/CN6 mixture discussed in the text, versus surfactant concentration using ILS monolayers of Z4 as alignment layer at 24°C.

Table 1

shows that a blend of 5CB/CN6 at 57/43 wt. % was a good candidate for our study, since the nematic-isotropic phase transition temperature is similar to that of 5CB and the concentration of the bent-core mesogen is sufficiently high to lower the elastic constant of the blend.

5CB(wt. %)	CN6 (wt. %)	N-Iso heating (°C)	Iso-N cooling (°C)
100	0	35.5	35.2
65	35	36.4	35.8
57	43	38.8	37.9
34	66	45.1	41.9
0	100	101	98

[†] Iso = isotropic fluid, N = nematic phase.

Table 2

Elastic constant results for 5CB and mixtures of 5CB/CN6 at 57/43 wt.% measured at 24°C and 30°C

Parameter	5CB at 24°C	5CB at 30°C	5CB/CN6 at 24°C	5CB/CN6 at 30°C
K_1 (pN)	6.5	5.3	5.5	4.9
K_2 (pN)	3.5	3.2	2.9	2.7
K_3 (pN)	9.8	5.8	8.3	5.6

Table 3

Approximate anchoring energy values for the different surfaces used in this work; the values for PI are found by the method described in III.2, while the remaining values are found from these values and θ_{center}^i (from Eq. 6) in the grid with the pure water upper surface, using Eq. 7.

Alignment Layer	Anchoring Energy 5CB (J/m ²)	Anchoring Energy 5CB/CN6 (J/m ²)
PI	1.4×10^{-4}	0.9×10^{-4}
OTS	0.8×10^{-4}	0.5×10^{-4}
Z4	0.7×10^{-4}	0.4×10^{-4}