

## Supplementary material: Chemical Leslie Effect in Langmuir Monolayers: a complete experimental characterization

Félix Bunel, Jordi Ignés-Mullol, Francesc Sagués and Patrick Oswald

April 11, 2018

### Compounds

In our experiment, we used multiple ferroelectric chiral liquid crystals, whose formulas are given in Figure S1. Among these products, four of them [1, 2] (referred to as A, B, C and D) were previously studied by Nitoń and co-workers [3, 4]. The Polish group observed the Leslie effect for only two of them (B and C) and gave an interpretation of why the two others were not presenting the rotation. According to them, the Leslie effect requires the chiral group to not be immersed in the subphase. This explains why A and D are not rotating since for these two molecules, the chiral part is close to the polar group that is presumably attached to the water.

However, we were able to make them rotate by increasing the temperature of the subphase. We believe nonetheless that the reason why these compounds are not rotating at room temperature is different for the two.

At room temperature, compound D creates a 2D solid on water surface even at a low surface pressure. Similarly to the observation made by Nitoń on the C compound [5], there is a phase transition between a solid phase and a rotating phase that occurs at a certain temperature. This temperature is around 12°C for the C compound but is much greater for D (around 40°C according to our experiments). This is probably why Nitoń and co-workers did not observe the rotation during their experiment at 23°C. The fact that the isotherms of C and D given by Nitoń [4] are very similar below the transition temperatures support this interpretation.

The reason why compound A is not rotating is different. As explained by Nitoń [3], this compound forms a monolayer in which coexist two phases. One of the phase is a planarly oriented phase where the molecules are still lying flat on the water, without any sign of order. And the other is a tilted phase where the molecules are raised from the monolayer. We believe that this phase separation refrain the molecular rotation. Our experiment showed that heating the subphase at 40°C favored the homeotropic ordered phase which then manifested the Leslie rotation of the molecules.

Beside these products, we also tested two other chiral liquid crystals that also presented the rotation at room temperature which are VE8/10 and BC110/6 [6, 7]. The compound BC110/6 also has his chirality center close to the polar group that is presumably attached to water which seems suggest that the Leslie rotation can be achieved with a wide array of compounds, regardless of the position of the chiral center within the molecule.

Although we found the rotation for multiple compounds, most of the experiments were performed using the compound B, which is the one presented in the main text. We used this product for two main reasons. The first one is that it creates the rotating phase at room temperature so we don't need to heat the subphase, which induces problematic flows at the surface. The other reason is that this compound forms a nice uniform monolayer after compression, which was useful to create the large area we wanted. One of the downside of this product is that it does not form a stable monolayer on glycerol so we were only able to perform experiments on water. Using glycerol could have allowed us to reverse the flux of water and thus the rotation.

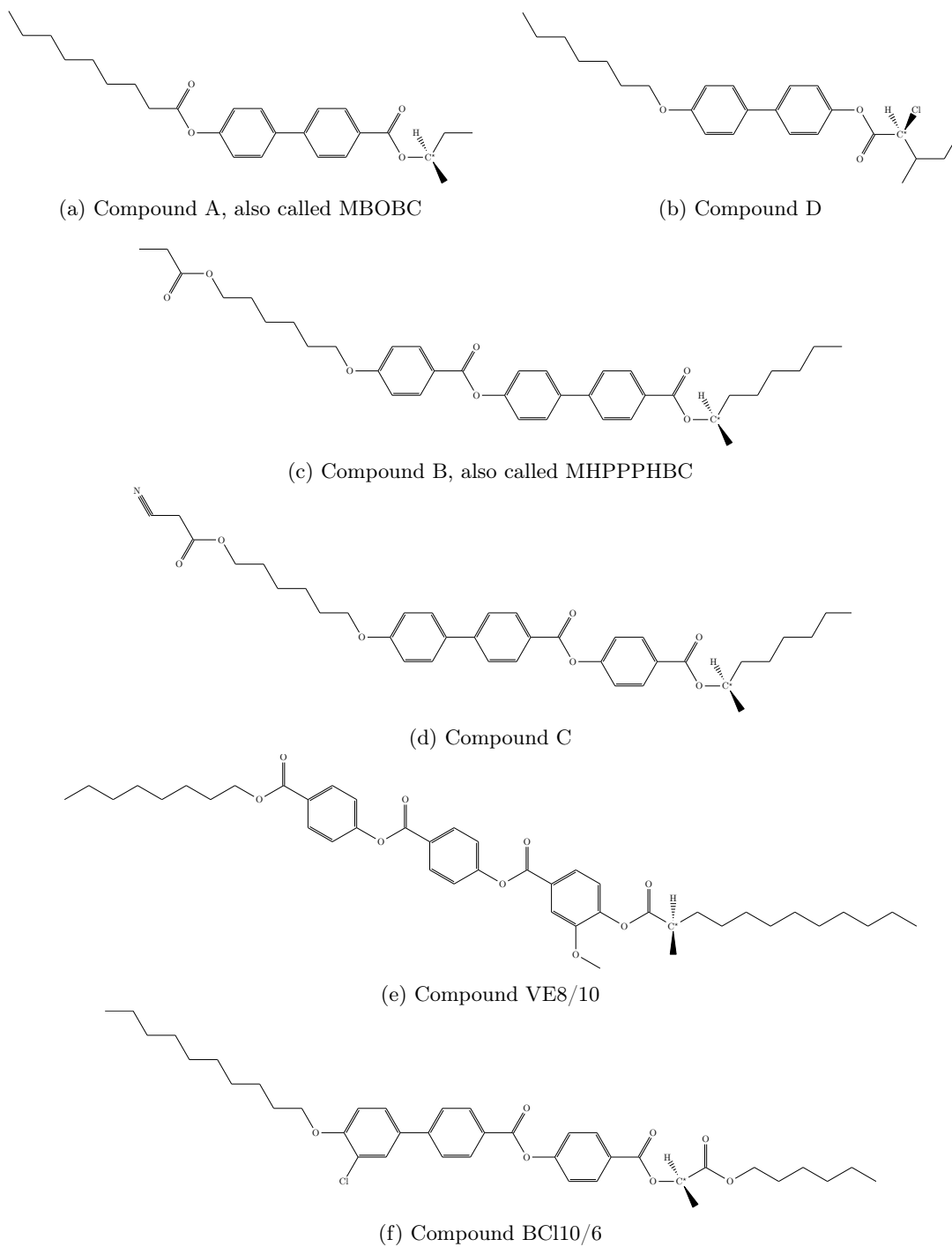


Figure S1: Molecules for which we observed the Leslie rotation.

## Homogeneity of the field

As explained in the main text, the electric field was applied to the monolayer with four  $1.8 \times 0.5 \times 0.5$  cm<sup>3</sup> parallelipedic electrodes. The four electrodes were fixed in a square insulated frame of size  $d = 2$  cm and supplied with appropriate voltages. More precisely, a potential difference of  $\Delta V_x = V_0 \cos \Phi_E$  was applied between the two electrodes facing each other in the  $x$ -direction and a voltage of  $\Delta V_y = V_0 \sin \Phi_E$  to the two electrodes opposed in the  $y$ -direction.

We have computed numerically the resulting field in Mathematica by solving the Laplace equation in 3D for our geometry. The boundary conditions are set by the potential applied to each electrode and the change of medium at the air-water interface and on the insulated frame that holds the electrodes are also taken into account.

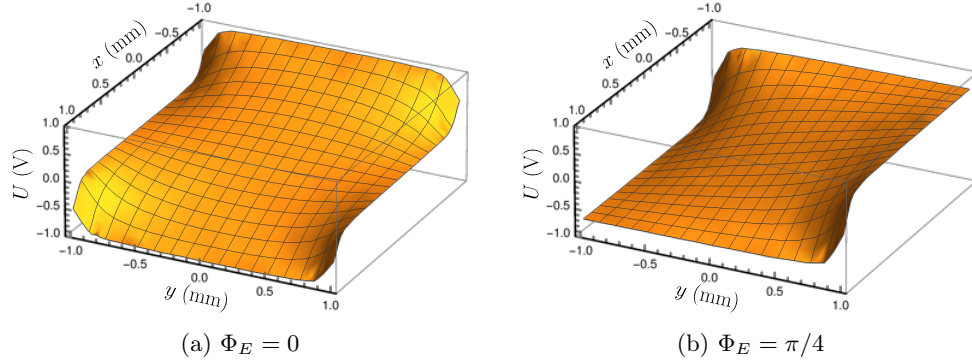


Figure S2: Electric potential created at the air-water interface in the  $1.8 \times 1.8$  cm<sup>2</sup> region between the electrodes. The applied voltage is  $V_0 = 2$  V.

The calculated potentials for two different values of  $\Phi_E$  are given in Fig. S2. From the potential, we can see that the electric field is diverging at the corner of the frame because of the high potential gradients. However, the region in the middle of the electrodes is homogeneously tilted, which suggests that the associated electric field is uniform.

Computation of the field show (see Fig. S3) that it is uniform both in orientation and intensity in the central region to  $\pm 1\%$ . The created field makes an angle  $\Phi_E$  with the  $x$ -direction as desired and the intensity is given by  $0.85V_0/d$ . This factor 0.85 is dependent of the geometry and must be taken into account to calculate the field created by the applied voltages.

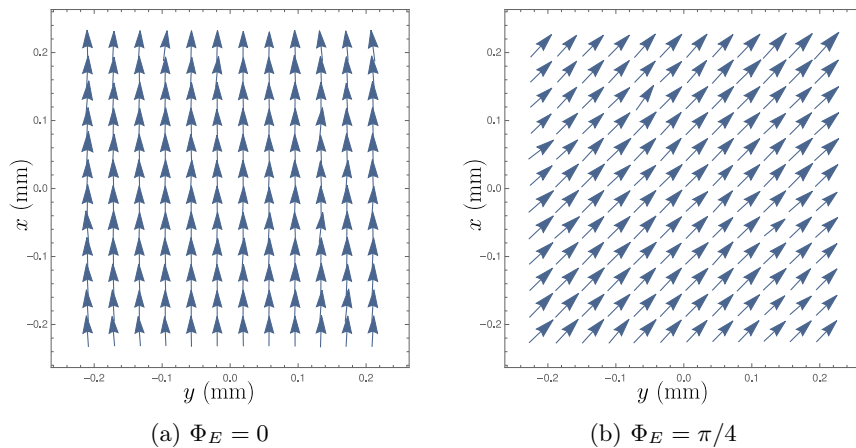


Figure S3: Electric field orientation at the air-water interface in the  $0.4 \times 0.4$  cm<sup>2</sup> region in the middle of the electrodes.

# Link between the relative humidity and the chemical potential

The chemical potential in the water is the standard chemical potential at a given temperature  $T$ :

$$\mu_{liq}(T) = \mu_{liq}^0(T). \quad (1)$$

Above the interface, the chemical potential can be written as a function of a standard potential and of the partial pressure of water in the air  $p$ :

$$\mu_{vap}(p, T) = \mu_{vap}^0(P_{sat}, T) + RT \ln(p/P_{sat}). \quad (2)$$

Here  $P_{sat}$  is the saturated vapour pressure of water at a given temperature. The saturated vapour pressure is by definition the pressure at which the vapor is at equilibrium with its liquid phase. At equilibrium, the chemical potential of the different phases are equal and thus we have a relation between the standard potentials:

$$\mu_{vap}(P_{sat}, T) = \mu_{liq}(T), \quad \text{that gives:} \quad \mu_{vap}^0(P_{sat}, T) = \mu_{liq}^0(T). \quad (3)$$

Finally, we see that the difference in chemical potential applied to the monolayer can be written as:

$$\Delta\mu = RT \ln(p/P_{sat}). \quad (4)$$

The ratio  $p/P_{sat}$  is by definition the relative humidity  $R_H$  that is measured by an hygrometer.

## References

- [1] Z. Raszewski, J. Kedzierski, P. Perkowski, J. Rutkowska, W. Piecek, J. Zieliński, J. Zmija, and R. Dąbrowski. Influence of Quadrupolar Ordering Factor on Supermolecular Structure in Ferroelectric Sm C\*. *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 328(1):255–263, August 1999.
- [2] J Dziaduszek, R Dąbrowski, K Czupryński, and N Bennis. Ferroelectric compounds with strong polar cyano group in terminal position. *Ferroelectrics*, 343(1):3–9, 2006.
- [3] Patrycja Milczarczyk-Piowarczyk, Andrzej Żywociński, Krzysztof Noworyta, and Robert Hołyst. Collective rotations of ferroelectric liquid crystals at the air/water interface. *Langmuir*, 24(21):12354–12363, 2008. PMID: 18826262.
- [4] Patrycja Nitoń. *Langmuir monolayers of ferroelectric and bolaamphiphilic liquid crystal at the air–water interface*. PhD thesis, IPCh PAS, Warsaw, 2012.
- [5] Patrycja Nitoń, Andrzej Żywociński, Marcin Fiałkowski, and Robert Hołyst. A "nanowindmill" driven by a flux of water vapour: a comparison to the rotating atpase. *Nanoscale*, 5:9732–9738, 2013.
- [6] Alexej Bubnov, Miroslav Kašpar, Vladimíra Novotná, Věra Hamplová, Milada Glogarová, Nadia Kapernaum, and Frank Giesselmann. Effect of lateral methoxy substitution on mesomorphic and structural properties of ferroelectric liquid crystals. *Liquid Crystals*, 35(11):1329–1337, 2008.
- [7] Alexej Bubnov, Věra Hamplová, Miroslav Kašpar, Milada Glogarová, and Přemysl Vaněk. New series of chiral smectic chlorinated liquid crystals. *Ferroelectrics*, 243(1):27–35, May 2000.