Supporting Information

Temperature-driven anchoring transitions at liquid crystal / water interfaces

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1 Temperature ramp on a homeotropic 5CB cell with solid boundaries

A small drop of 5CB was deposited between two glass slides treated with OTS so as to impose a strong perpendicular alignment of the molecules. Under crossed polarizers, a uniformly dark area was selected, and the sample was submitted to a $0.01\,°\mathrm{C}\cdot\mathrm{min}^{-1}$ temperature ramp. In the nematic state, conoscopy yielded a Maltese cross characteristic of homeotropic anchoring. A few tenths of degrees Celsius below the clearing point, we witnessed the rise of birefringence colors, signalling the presence of the isotropic/nematic interface. The colors and the way they nucleated were very reminiscent of our isotropic islands. However, while the island were nicely rounded by surface tension in the case of an all-fluid system, they were of a very irregular shape in the homeotropic cell, probably due to pinning on surface defects. Then fully black patches started appearing where the isotropic phase had reached both walls of the cell, until they took over the entire cell. This experiment in a more well-known situation validates the weakly out-of-plane nature of the anchoring between 5CB and its isotropic phase.

2 Supplementary movies

- SupMov1_HeatingFilmPVA: timelapse of the temperature-driven anchoring transition of a 5CB film in a 0.1 % PVA solution in water, corresponding to Fig. 2.
- SupMov2_HeatingHomeoCell: timelapse of a 5CB homeotropic cell heated quasi-statically in the vicinity of its clearing point.
- SupMov3_HeatingFilmPureWater: timelapse of the phase transition of a 5CB film in a solution with less than 0.1 % PVA in water, corresponding to Fig. 4A.
- SupMov4_HeatingShellPureWater: real-time movie of the phase transition of a 5CB shell without PVA in the inner and outer water phases, corresponding to Fig. 4B.
- SupMov5_HeatingShellPVA: timelapse of the temperature-driven anchoring transition of typical 5CB shells, with 1 % PVA in the outer and inner phases, corresponding to Fig. 5.
- SupMov6_HeatingCoolingShellsPVA: timelapse of the temperature-driven anchoring transitions of typical 5CB shells with 1 % PVA in the water phases as the sample is heated to isotropic then cooled back to nematic, corresponding to Fig. 6.

3 Supplementary figures

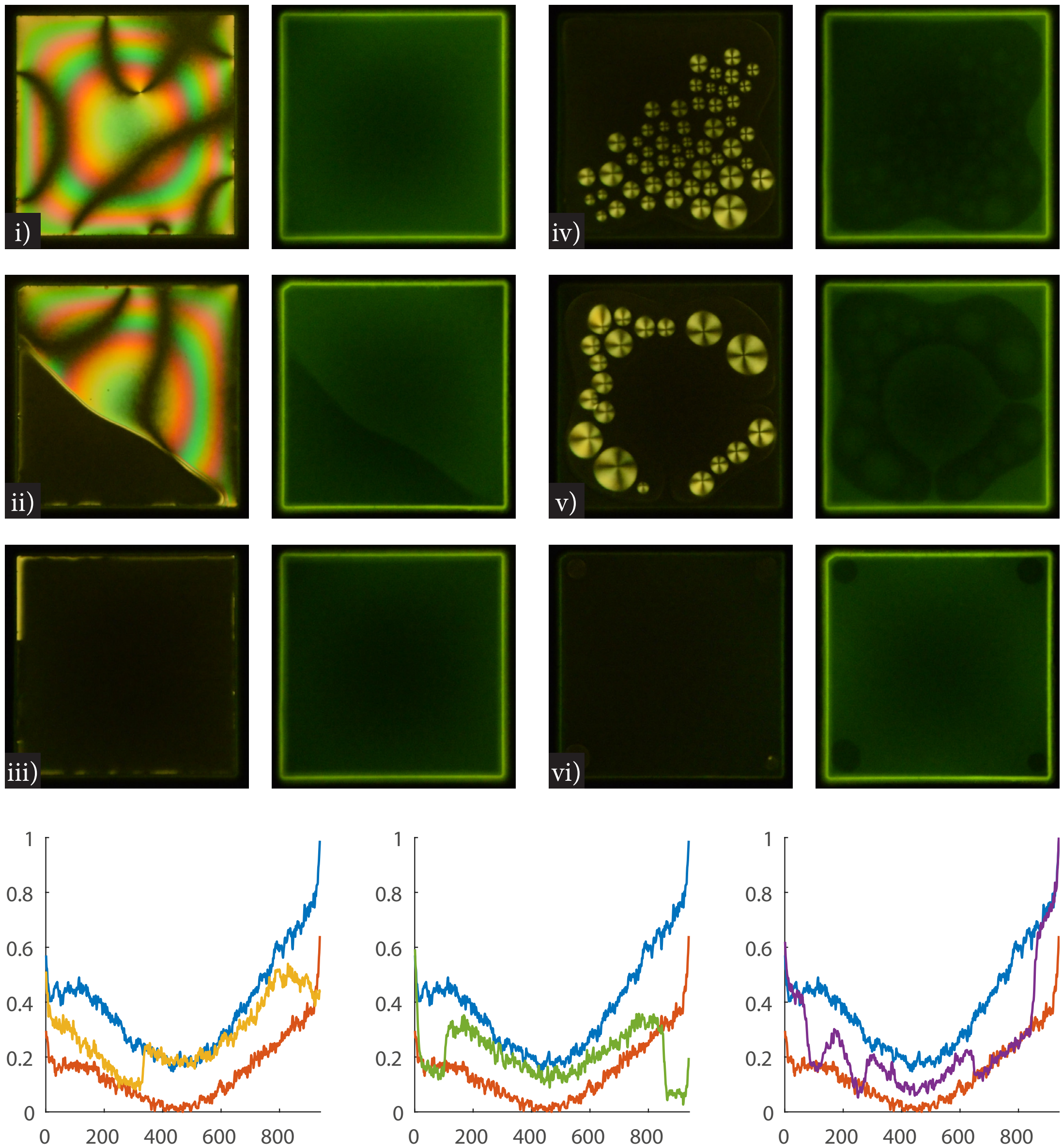

Figure S1: **5CB films doped with BTBP in a 0.1 % wt PVA solution undergoing a slow temperature ramp.** Left: micrographs between crossed polarizers, lit under both white light and near-ultraviolet light. Right: micrographs in fluorescence mode (single polarizer), lit under near-ultraviolet light. Bottom: average intensity profiles in a 25-pixel wide band along the SW-NE diagonal of the films. The U-shape of all the graphs is due to the concavity of the film: there is more material on the edges, hence more dopant, on the edges than in the center. Throughout, the films are 430 µm wide, about 10 µm thick close to the edges, about 5 µm thick in the center, and fixed on a suspended TEM grid. The temperature ramp has a rate of $0.01\,^{\circ}\mathrm{C}\cdot\mathrm{min}^{-1}$. The series of pictures depicts typical stages of the evolution of a film, as temperature is increased: i) planar state (blue curve), ii) transition from the planar to the homeotropic state (yellow curve), iii) homeotropic state (red curve), iv) early stage with the birefringent islands, v) late stage with the birefringent islands (purple curve), vi) almost all of the film has turned isotropic (green curve). The transition between planar and homeotropic levels shows a clear jump in fluorescence intensity. The isotropic profile shows intermediate values, about two thirds of the way between planar and homeotropic levels. The corners appear very dark due to remaining patches of homeotropic nematic phase. The late island stage profile shows a similar behavior as the isotropic profile; the peak on the left part corresponds to a birefringent island.

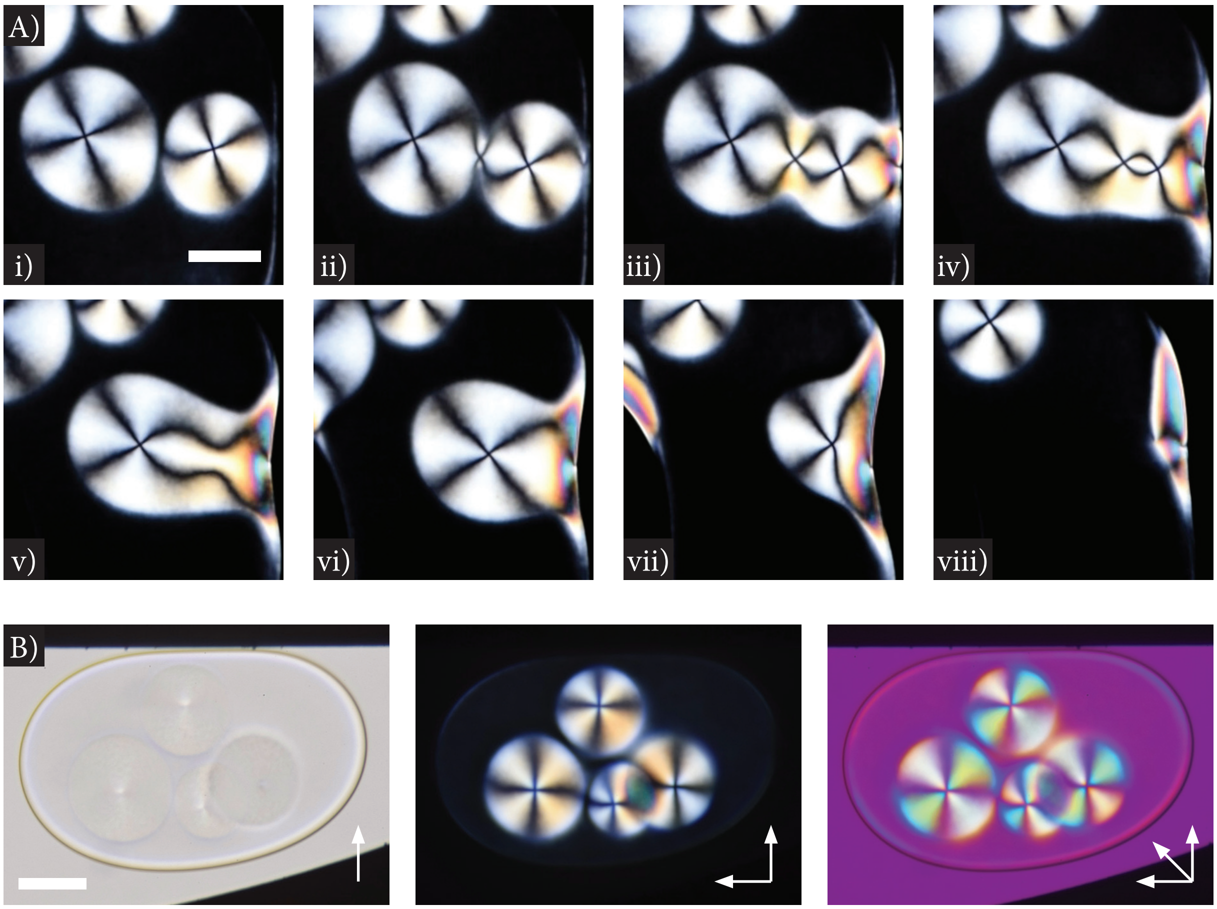

Figure S2: **Additional clues pertaining to the isotropic islands.** Micrographs showing isotropic islands on a 5CB film in a 0.1 % wt PVA solution in water, scale bars 50 μm. A) Coalescence of islands and merging into the isotropic phase. Time series as the temperature is linearly increased with a 0.01 °C $\cdot$ min^{-1} temperature ramp. Two isotropic islands are initially apart (i), they coalesce, creating a [-1] defect at the neck of the junction (ii-iii). The new defect then annihilates with one of the two [+1] initial defects (iv-v). Lastly, the remaining island fuses with the isotropic phase, growing from the right side of the image (vi-viii). B) Overlapping islands. Pictures in bright field, crossed polarizers, and crossed polarizers with first-order retardation plate. The temperature is a few tenths of degrees Celsius below the clearing point of pure 5CB. One island is located on one of the two interfaces of the film, while the other three islands are located on the second interface.