Electronic Supplementary Material (ESI) for Soft Matter.
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Surface alignment of ferroelectric nematic liquid crystals

Electronic Supplementary Information (ESI)

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1. General information

LC cells are prepared by sealing glass surfaces treated in different ways, as detailed below. Rubbing direction, when present, is parallel on both the two plates and normal to the electrodes, that is in the same direction of the applied in-plane electric field. Cells are filled by capillarity at T = 180°C, corresponding to N phase. They are characterized by observations in Polarizing Optical Microscopy (PTOM) at various temperatures. The sign and the magnitude of the birefringence are evaluated using a Berek compensator.

2. Cell preparation: surface treatments

Rubbed C16 silanized surfaces

To prepare silanized surfaces, an ethanol:DI water (95:5) solution is acidified up to pH 4.5-5.5 using acetic acid. 2% v/v of hexadecyltrimethoxysilane (HDTMS) is added and the solution is stirred at room temperature for 5 minutes. Using a pipette, the silane solution is poured on tilted glass plates in order to uniformly wet the surface. Glass surfaces, once the solvent is evaporated, are put on a heating plate at a temperature T = 110°C for 10 minutes and stored at room temperature for one night. Glass plates are then rubbed in the direction of silanization using optical paper and ethanol, which also remove unreacted silane traces possibly present.

Teflon rubbed surfaces

Teflon rubbed surfaces are obtained by rubbing with a Teflon bar (RS-Components, www.rs-online.com) clean glass plates kept at a temperature T = 140°C. Rubbing speed is 2 mm/s. Glass plates are then allowed to cool down to room temperature before cell assembling.

Unrubbed Fluorolink surfaces

Unrubbed Fluorolink surfaces are coated by a solution of Fluorolink® MD700 and photoinitiator IRGACURE® 651 prepared as follows. IRG651 is dissolved into a tiny amount of $CHCl_3$, then MD700 is added into a ratio of initiator over monomer of 2% w/w. The solution obtained is diluted with $CHCl_3$ to a final ratio of 25% v/v of MD700 and chloroform and then spin-coated on glass plates carefully cleaned with acetone and air flow, at a speed of 3000 rpm, letting the solvent dry while spinning for 2 minutes. The thin film obtained is polymerized with a UV lamp in a nitrogen atmosphere for 40 minutes.

Unrubbed Hydroxylated glass surfaces

Hydroxylation is obtained by soaking the glass plates in a piranha solution for 90 minutes. Piranha solution is prepared by adding one volume of 35% hydrogen peroxide to three volumes of sulphuric acid under mild stirring. The plates are then rinsed three times with DI water and once with methanol prior to air drying. Cells are assembled immediately in order to avoid deterioration of the treated surfaces.

3. Videos

Video S1: N-N_F Zero Field Cooling phase transition in an 18 μm rubbed silanized cell, showing the real time formation of twisted polar domains in the direction of rubbing **R** and their slow shrinkage to a stationary configuration. As T is lowered, the N_F phase appears locally in multiple places in the cell. As long as it does not fill the whole space between the two plates, the cell texture is rather uniform, with faint lines, possibly marking the contact of the N_F phase with the surfaces. When the N_F phase grows to fill the space between the two plates, domain walls appear. As they develop, the cell becomes progressively more uniform, except for some domains having optical properties very similar to the rest of the sample, due to a good adiabatic following as discussed in the main text. Temperature is lowered from 180°C to 120°C.

Video S2: Real time electric field reversal in an 18 μm rubbed silanized cell. The pattern of defect lines developing during field reversal and the asymmetry of the LC response are clearly visible. The defect lines are orthogonal to the applied field and their time evolution leads to a double system of topological lines that are at different heights in the cell and thus move without intersecting, giving rise to textures as in Fig. 2f, right-hand side panel. Square wave, 50 mHz, E = 1 V/cm.

Video S3: N-N_F Zero Field Cooling real time phase transition in a 10 μm Teflon rubbed cell, showing the formation of polar domains in the direction of rubbing **R**. Domains form in a few tenths of seconds following the same dynamics as in silanized cells, but they do not shrink due to the stronger polar coupling with the confining surfaces. Moreover, contrary to domains in video S1, they are optically distinguished from the background because of the cell is thinner and the adiabatic rotation is incomplete. Temperature is lowered from 160°C to 120°C.

Video S4: N-N_F Field Cooling real time phase transition in a 10 μm Teflon rubbed cell, with E = 1 V/cm antiparallel to rubbing **R** ($\mathbf{u_E} = -\mathbf{u_R}$). In the latest stages of the transition, the N phase takes the shape of flexible filaments on a N_F background that disappear in a few seconds. As described in Ref. [5] of the main text, the orientation of the filaments does not appear to be strongly coupled to the director field in the ferroelectric phase. The final texture is that of a defect-free planar state uniformly aligned along the electric field. Temperature drops from 160°C to 120°C.

Video S5: N-N_F Zero Field Cooling real time phase transition in an 18 μm hydroxylated cell as temperature is lowered from 180°C to 120°C. The transition from homeotropic (N phase) to random planar alignment (N_F phase) initially appears through growing brightness, followed by a color sequence due to the increased phase retard associated with the growing planar orientation and terminating with the formation of polar domains having pale yellow color. In the final stages these domains couple to the surfaces adopting the distorted stationary configuration shown in Fig.5b of the main text.

Video S6: N_F-N real time phase transition in an 18 µm hydroxylated cell as temperature is increased from 120°C to 180°C, in the absence of an applied electric field. The observed reduction of phase retard is associated to the decreasing planar orientation, which gives rise to a color sequence opposite to that shown in video S5. The transition leads to the formation of a transient splayed state followed by the onset of homeotropic alignment. The development of the 2π splay-bend lines described in the main text is also visible.

Video S7: Effects of the application of an AC electric field (E = ± 1 V/cm, square wave, 1 Hz) to a 10 µm thick Teflon rubbed cell between crossed polarizers. The majority of the cell is aligned with $\mathbf{u_P} = -\mathbf{u_R}$ with domains having opposite polarity. Field inversion produces a rapid switch between a uniformly aligned and a twisted state that does not degrade even after thousands of cycles. Transient defect lines orthogonal to **E** appear during field reversal.

4. Figures

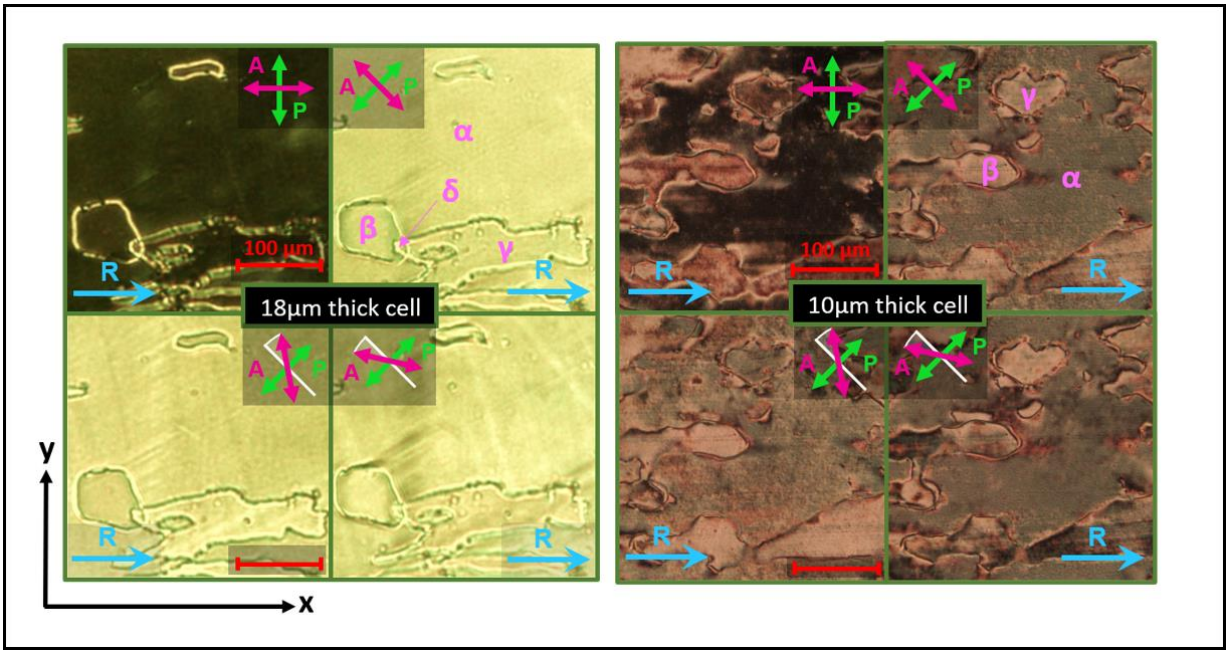

Figure S1: 18 µm (left panel) and 10 µm (right panel) thick silanized cells in NF phase after ZFC from the N phase. The domains shown in the right panel are of the same nature as those observed in the left panel and are described in detail in the main text. The similarity between the two domain textures is evident by comparing regions α, β and γ in the two panels. Regions α are uniformly aligned (i.e. untwisted), while β and γ are twisted with either right or left-handed rotation (see main text). The twisted polar domains exhibit the same brightness as the background in the thicker cell while they have a brighter appearance in the thinner one, which demonstrates the role of adiabatic rotation discussed in the main text. Indeed, due to the lower thickness of the cell shown in the right panel, the twist is tighter and the adiabatic rotation in the domains is incomplete.

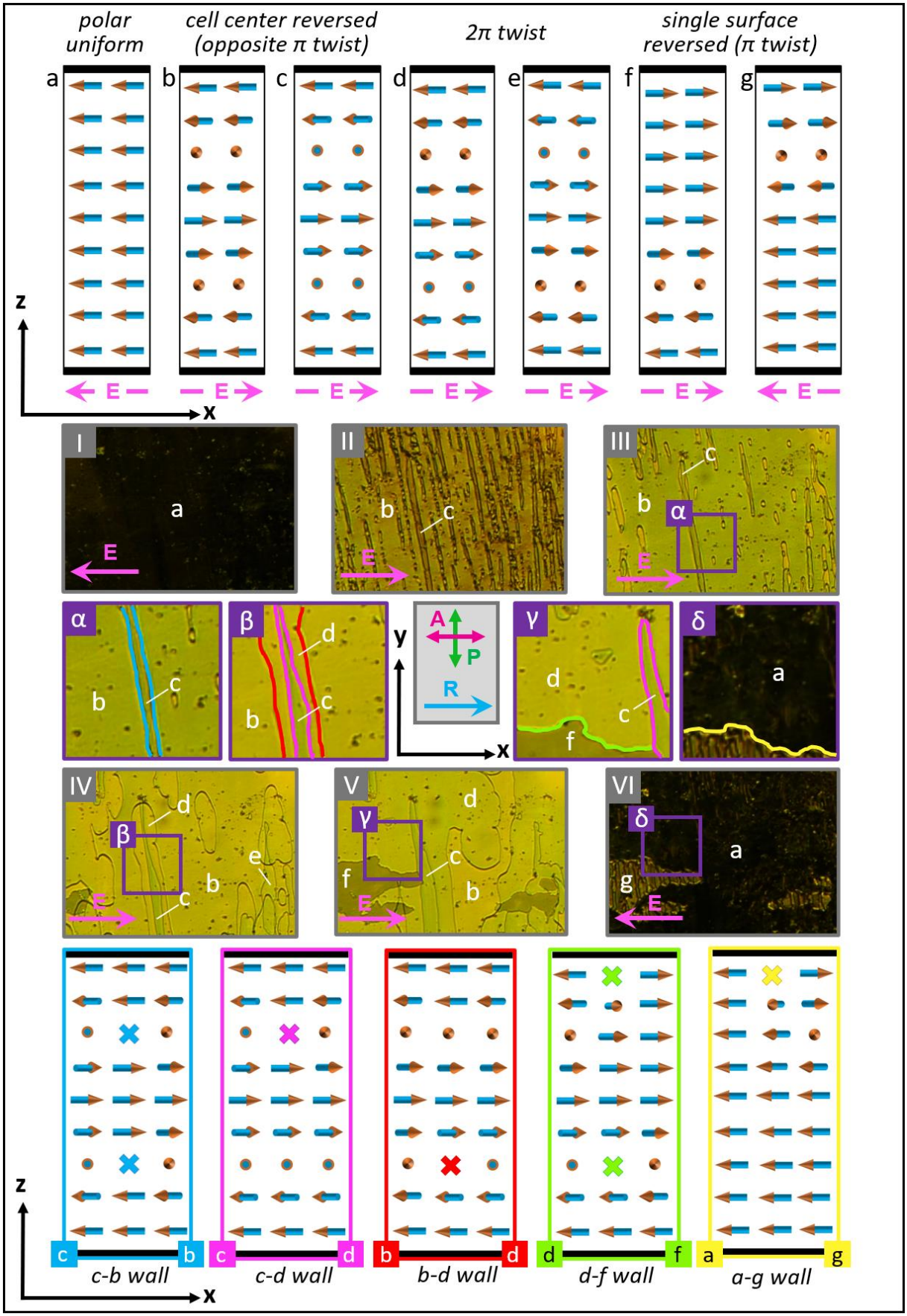

Figure S2 : Sequence of frames (I-VI) extracted from video S2 and magnification of their portions (α-δ) in which we marked domain boundaries and defect lines with colored lines whose structure is

described in the sketches (having frames of matching color) in the bottom of the figure.The frames show the behavior of the N_F phase during a $\boldsymbol{E}$ = 1 V/cm electric field reversal into an 18 μm rubbed silanized cell and the subsequent appearance of defect lines. Arrows: analyzer ($\boldsymbol{A}$), polarizer ($\boldsymbol{P}$), electric field ($\boldsymbol{E}$), rubbing direction ($\boldsymbol{R}$). The aim of the figure is to describe the variety of polarization orientations (a-g) and topological defects (colored frames) found upon switching the field. The time interval between subsequent frames is about 2s. Frame I) A polar uniform planar alignment (a) is achieved when $\boldsymbol{E}$ is opposite to $\boldsymbol{R}$. Frame II) Shortly after the field reversal, the bulk polarization becomes oriented along the field, while molecules in the proximity of the surfaces remain in their favorite -$\boldsymbol{R}$ direction; this leads to rod-shaped domains where the polarization, moving from the top to the bottom surface of the cell, undergoes two opposite π rotations within each domain, which can be of opposite handedness (b-c). Please note that since we cannot distinguish structures b and c, their assignment in frame II might be inverted. Such twisted structures produce bright states. When domains with structure b and structure c come in contact, a thick domain wall is formed. Frame III) In time, one of the two handedness tends to prevail and most of the lines disappear. The remaining domain walls start splitting into a pair of lines as become evident in frame IV. We interpret the doubling of the blue lines in panel α as drown in the blue-framed c-b wall sketch in the bottom of the figure. Frame IV) The displacement of the lines reveals that they can cross, generating new domains having structures (d-e) described in the top panels. One of these (structure d), over time, appears to be the most energetically favorable and grows in volume. Again, structures d and e could not be distinguished so their assignment might be inverted. The displacement of the defect lines generates new domain walls (red and pink lines in panel β) whose structures are described in pink- and red-framed sketches. According to our description the two lines are located at different height inside the sample and thus they can cross without merging (see for example bottom right portion of frame IV). Frame V) After a longer time, a new type of domain (f) is formed, which we interpret as the inversion of the polarity of the molecules in contact with one of the two surfaces. This inversion eliminates part of the twist deformation, making the sample uniform in half of the height of the cell, leading to a darker texture. The green defect line in panel γ, separating this new state from a twisted state, is sketched in green-framed panel. Frame VI) Upon reverting the field back to the original direction, the uniform planar alignment (a) is rapidly regained everywhere in the cell but where the domains (f) were observed. In these portions of the cell, where the surface anchoring was flipped, a new striped texture (g) is obtained, whose structure is analogous to (f), but inverted. Different stripes are due to opposite handedness of the π twists. The defect line slightly changes (yellow line in panel δ) and the new one is sketched in the yellow-framed panel.

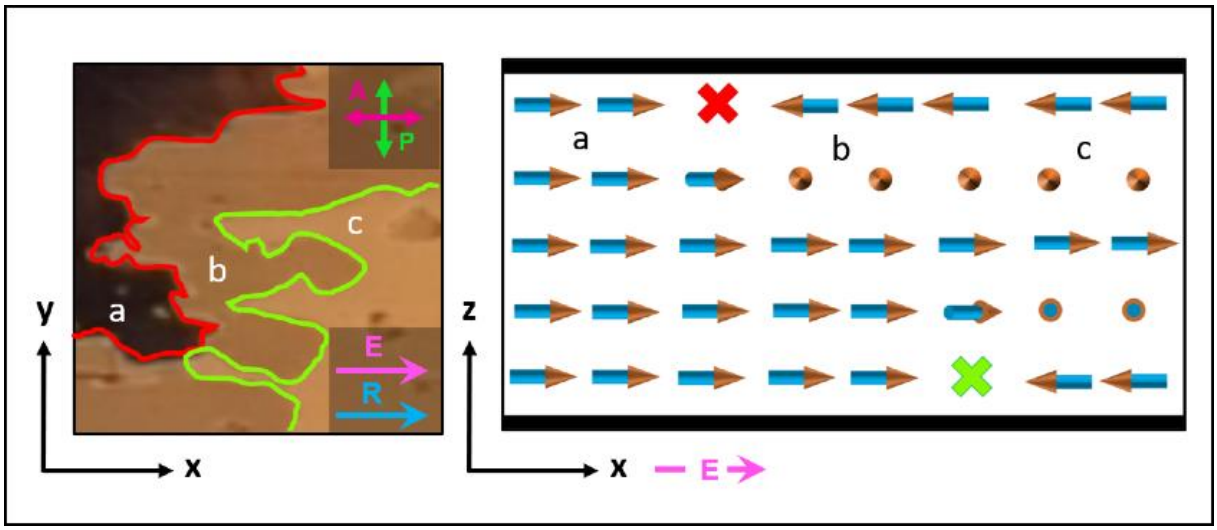

Figure S3: Analysis of the right panel of Figure 3h, with domain boundaries marked with colored lines whose structure is described in the panel in the right-hand side of this figure. The picture shows three different domains (a-c) formed upon field cooling ($\boldsymbol{E} = 1\ V/cm$, $\boldsymbol{u_E} = \boldsymbol{u_R}$) of a 10 µm thick RM734-filled cell with rubbed Teflon surfaces. Arrows: analyzer ($\boldsymbol{A}$), polarizer ($\boldsymbol{P}$), electric field ($\boldsymbol{E}$), rubbing direction ($\boldsymbol{R}$). We interpret the formation of three different domains as due to different polarities on the surfaces. a) The polarity of both surfaces is equal to the field direction leading to a dark, polar uniform phase. b) The polarity of the two surfaces is antiparallel, forming a π twisted structure compressed in half of the cell. The partial brightness is caused by a partial adiabatic rotation. c) The polarity of both surfaces is opposite to the field direction yielding a 2π twisted domain or a domain with two opposite π rotations which appears bright due to a stronger adiabatic rotation.