Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supporting information

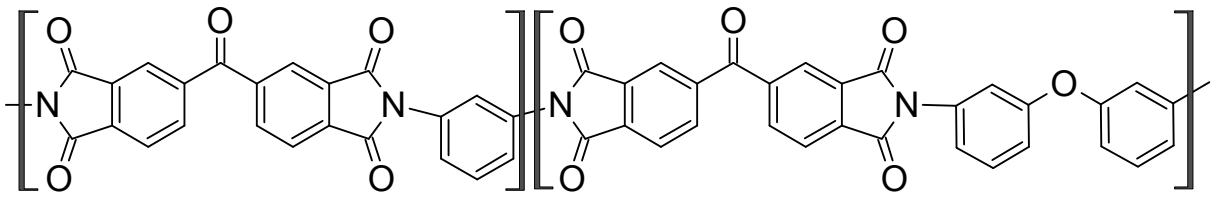
In situ laser-imprinted surface realignment of a nematic liquid crystal

Giorgio Mirri, Miha Škarabot and Igor Muševič

1. Experimental methods and materials

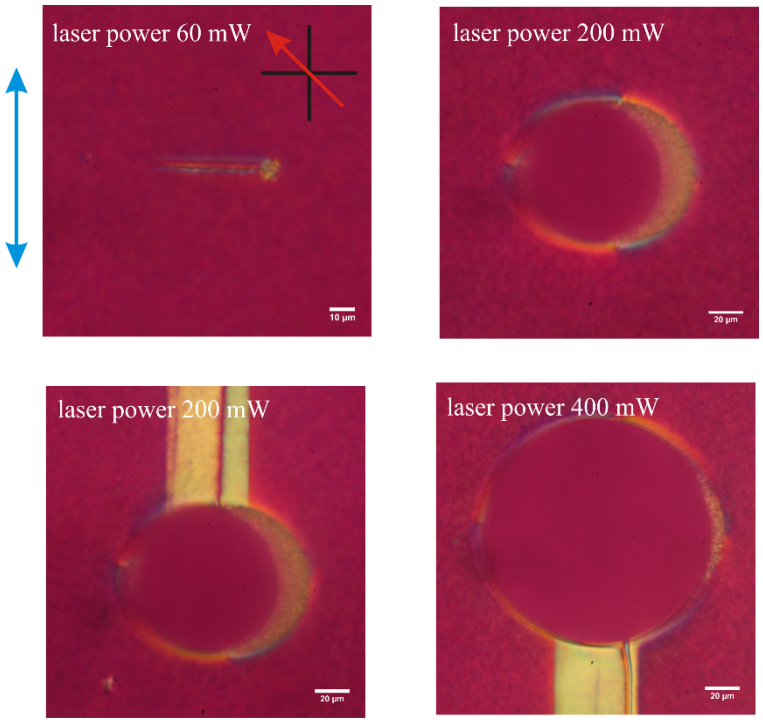
We have used the laser tweezers setup (LTMN2000-A, Aresis), built around inverted optical microscope (Nikon Eclipse TE2000-U), equipped with a motorized stage (Prior OptiScan II), high numerical aperture water immersion objective (Nikon NIR Apo 60x/1.0w), halogen lamp and CW IR solid state laser source (Tweez 200si laser unit). The laser beam was spatially controlled with a pair of acousto-optic deflectors (AA Optoelectronic DTSXY-400-532), driven by a beam steering controller (BSC-01, Aresis), which enables creation of multiple optical traps and their precise positioning. Beam steering controller was operated by a custom software (Tweez v2.1, Aresis), running on a personal computer. Colour images and videos were acquired by digital camera (Canon EOS 550D). The maximum power of a diffraction limited 1064 nm Gaussian laser beam in the sample plane was varied between 400 and 800 mW.

The surface of the indium tin oxide (ITO) covered glass substrates was cleaned in an ultrasonic bath and thoroughly rinsed with deionized water and iso-propanol. After drying in an oven at 80 °C for 20 min, the substrates were spin-coated with a polyamic acid solution of PI-2555 (Nissan Chemicals), to produce a 100 nm thick layer. The coated substrates were soft-baked at 80 °C for 45 min to evaporate the solvent and subsequently hard-baked at 250 °C for 90 min to finalize the imidization reaction. Finally, the polyimide coating was unidirectionally rubbed several times with a velvet cloth to obtain a homogeneous planar alignment of MLC2132 and 5CB nematic liquid crystals (LCs). The structure of PI-2555 molecule is shown below.



S.1 Molecular structure of PI monomers.

We carried out the experiments using a liquid crystal with a relatively high N-I transition temperature (MLC 2132 – Merck Southampton, UK), because we need to use a rather high power of the laser (400 to 800 mW) in order to obtain the imprinting of the PI layer. Under these conditions, using common LC, e.g. 5CB, it would not be possible to control the realignment and to confine it to only one glass side of the cell. As shown in S.2, the isotropic island generated by the laser at high power in 5CB is too big and gives rise to defects.



S.2 Isotropic island, generated by the laser in a cell filled with 5CB at different laser powers. Blue double headed arrow indicates the original rubbing direction; black lines the orientation of the polarizer and analyzer and red arrow the direction of the optical axis of the retardation (full wave) plate.

2. Measurements of LC orientation using lambda retardation plate (red plate)

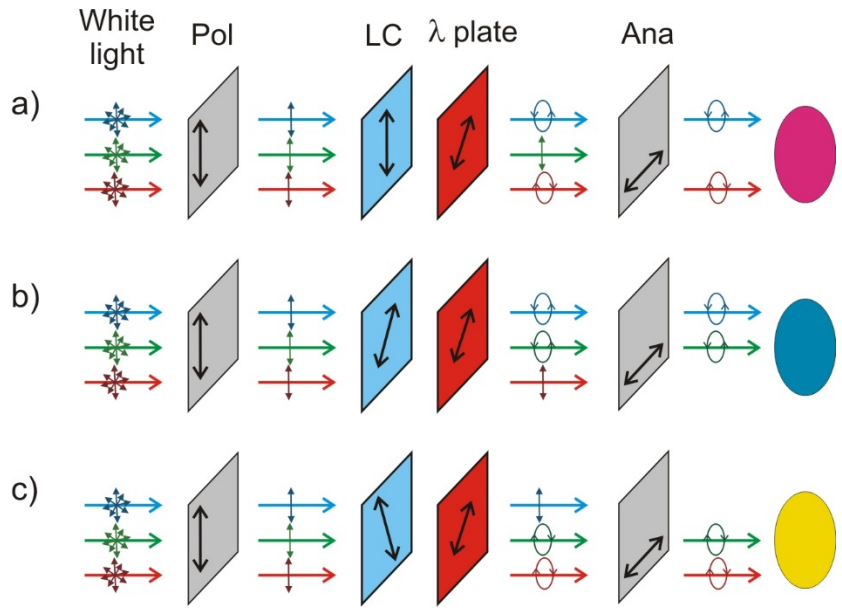
A nematic liquid crystal is an optically anisotropic (birefringent) material, with an optical axis along the direction of long axis of molecules, defined as the LC director. When the birefringent LC is placed between crossed polarizers, with the optical axis not coinciding with the direction of polarizers, the light travels through the NLC as a combination of two eigenwaves: the ordinary wave, travelling with the light velocity defined by the ordinary index of refraction and the extraordinary wave, travelling with slower velocity, due to larger extraordinary index of refraction. At the exit, both linear waves combine into an optical wave with the polarization that is in general elliptical and some light is transmitted through the analyser. In a planar cell, the optical axis of the NLC is lying in the plane of the cell and along the rubbing direction, which defines the director. Using only crossed polarizers, it is not possible to determine the direction of orientation of NLC in a planar cell, because it will appear dark, if the polarizer is oriented either along the long molecular axis (exciting extraordinary wave) or perpendicular to the molecular axis (exciting the ordinary wave).

However, one can determine the direction of the optical axis in a planar cell by using an optical microscope and optical technique, which is called “red plate” or “full wave retardation” method. In order to discriminate the difference between the ordinary and the extraordinary waves, one uses the full wave retardation plate, or λ-plate (usually λ = 530nm). For a linearly polarized optical wave, this λ-plate induces optical retardation equal to 2π for green light (λ = 530nm) and the polarization of this wavelength does not change after passing the retarder. Depending on the LC orientation, different colours can be observed under polarizing microscope with λ-plate (Fig. S.3).

We start with a situation, where the optical axis of LC is oriented along the polarizer and the axis of the λ-plate is oriented at 45° (Fig. S.3.a). The sample is illuminated with polarized white light, which passes through the LC with no change of polarization. For green light of the spectrum, the λ-plate preserves the polarization, and the green light is blocked by the crossed analyser. On the other hand, the blue and the red light are elliptically polarized after passing the λ-plate. They are partially transmitted through the crossed analyser and the transmitted light is of magenta colour, i.e. the combination of blue and red light.

If the LC molecules are turned slightly towards the axis of the retardation plate (Fig. S.3.b), the overall retardation is increased compared to the first case. The red light becomes linearly polarized and is blocked by crossed analyser, while the blue and green light are transmitted and the resulting light is bluish.

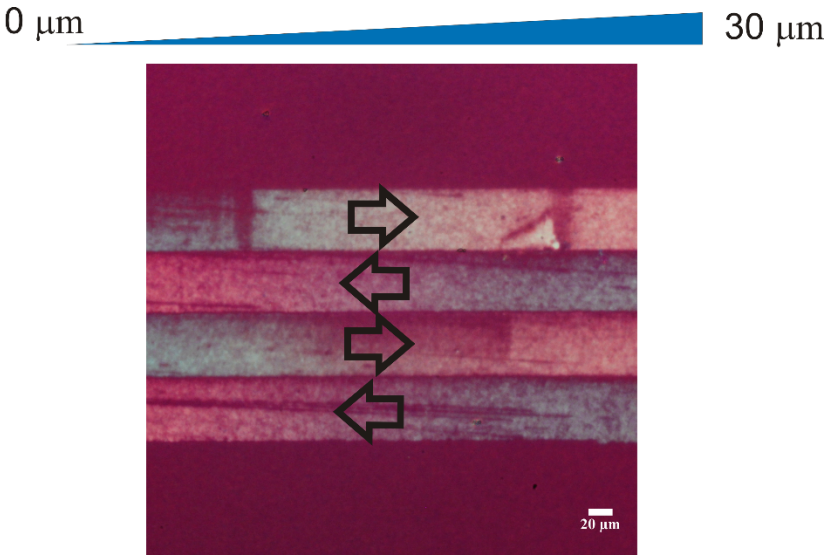
If the LC molecules are turned in the opposite direction (Fig. S.3.c), the overall retardation is decreased compared to the first case. The blue light is linearly polarized and blocked by the analyser, while the green and the red light are transmitted and the resulting light is yellowish.



S.3 Schematic representation of the effect of crossed polarizers, LC and the λ-plate on the incoming white light. a) The director of the LC is oriented along the polarizer, the axis of the λ-plate (λ=530nm) is oriented at 45° degrees, only the green part of the white light is linearly polarized and blocked by the analyser, the transmitted light is red. b) If the LC is oriented along the direction of the axis of the λ-plate, the retardation is increased, the red light is blocked and the resulting light is bluish. c) If the LC is turned in the direction opposite to the axis of the λ-plate, the retardation is decreased, the blue light is blocked and the resulting light is yellowish.

By observing a planar NLC between crossed polarizers and red plate, we can have the information on the local direction of the optical axis and the deviation of the realignment with respect to the original rubbing direction. However, the above explanation for observed colours is valid only for small LC induced retardation. If the thickness of the LC is large, the retardation is bigger and the colours for the same LC orientation can be reversed. This is clearly seen in the experiment, shown in Figure S.4, where the realigned stripes were induced along a wedged cell, each in the direction indicated by the

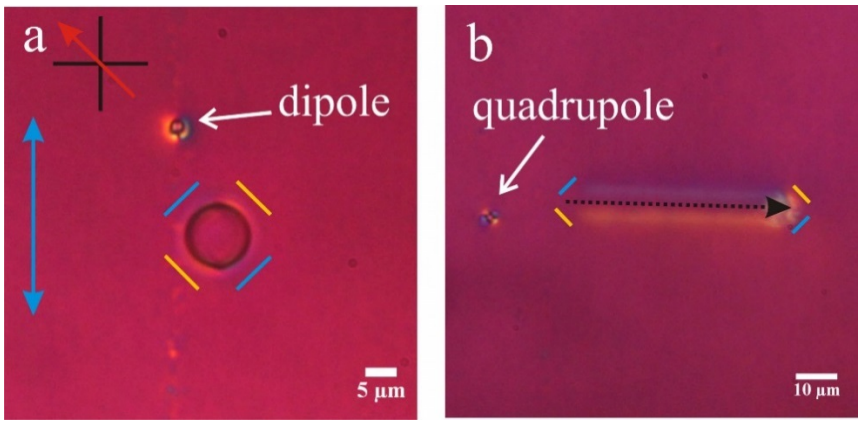
arrows (the alignment direction is the same in each whole stripe). It is clear that the colour changes depending on the thickness of the cell till a complete inversion (from blue to yellow and vice versa).



S.4 Optical appearance of realigned cell. The realignment was performed in stripes, oriented along a planar wedge cell, filled with nematic LC and observed under a microscope with crossed polarizers and full wave retardation plate. The arrows indicate the direction of the realignment.

Without knowing the exact optical retardation of the NLC, optical observations using the retardation plate can only give relative information on the director alignment. We can only claim that scanning the laser line in opposite directions induces alignment with a +45° or -45° offset with respect to the original rubbing direction.

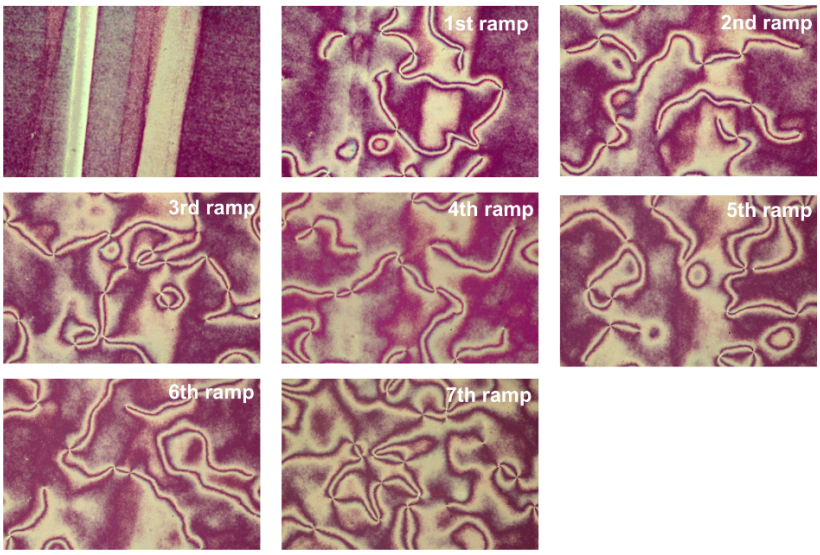
We therefore need an absolute reference to assign the correct direction of the liquid crystal in the realigned regions and around the isotropic island. To do so, we use colloids with perpendicular orientation of the LC at their surface as a reference. By comparing the colours observed around the colloidal particles and around the isotropic island, we are able to correctly assign the direction of the realignment, as shown in Figure S.5.



S.5 (a)The orientation of the liquid crystal around the isotropic island is determined by comparing the colours (yellow, blue) around that island, with the colours of the NLC around a small colloidal particle with perpendicular surface alignment of the LC. In this case, the particle shows the dipolar symmetry of the NLC around it with well-known director structure. (b) In this case, the colloidal particle shows the quadrupolar symmetry with known director field around it. This enables us to determine the direction of NLC molecules along the realignment line from the colours of that line.

3. Thermal stability of the surface memory effect in the absence of imprinting process

The permanent imprinting of the new orientation is due to the action of the laser on the polymer that aligns the NLC and seems to be more stable than just ordinary surface memory effect (SME) of the NLC. To analyse that, we carried out cycles of heating and cooling on an unrubbed PI cell without laser imprinting, to verify the strength of SME arising merely from the LC used. The cell was heated to temperatures way higher than the isotropic-nematic transition temperature, the ramps were from 80 °C to 130 °C and backwards and the last ramp up to 150 °C. As shown in S.6, the original surface pattern, generated by the polyimide spin-coating process, is cleared by the repetition of heating-cooling cycles. On the contrast, laser-imprinted alignment is stable for more than 9 cycles, as shown in the manuscript.



S.6 Texture of a 12 µm thick planar cell of unrubbed PI. The images are taken after each heating-cooling cycle. The stripe-like local alignment is induced by the spin coating process, and is presented in the first panel. This surface pattern is completely erased by 6th repetition of the heating-cooling cycles.

Video: Realignment process. Laser line parallel to the rubbing direction