





Topological defects in cholesteric liquid crystals induced by monolayer domains with orientational chirality†

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Unless stabilized by colloids or confinement with well-defined boundary conditions, defects in liquid crystals remain elusive short-lived objects that tend to disappear with time to minimize the medium's free energy. In this work we use multimodal three-dimensional imaging to visualize cholesteric director structures to show that self-assembled chiral molecular monolayer domains can stabilize topologically constrained defect configurations when in contact with a cholesteric liquid crystal. The cholesteric liquid

$\hat{n}(\mathbf{r})$, the LC director $\mathbf{n}(\mathbf{r})$ follows the local in-plane orientation of the surfactant monolayer (Fig. 1).

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^{18,20,22} The anchoring angle with respect to the surface normal is similar throughout the LB \hat{n} lm (35–45°), but outside the domains surfactant molecules are disordered, and the LC director adopts an in-plane alignment set by the complementary plate. Matching of the boundary conditions on the circular disk and on the planar far-field leads to a defect healing scenario that results in the formation of either single twist-escaped or double singular arch-like

disclinations in

was patterned by LB transfer of monolayers of the surfactant 4-[4-[4-octylphenyl/azo]-phenoxy]butanoic acid (8Az3COOH), previously self-assembled at the air/water interface in the form

regions with different elastic energy, depending on whether the local handedness has the same or opposite sign as that of the intrinsic pitch of the chiral mesogen. We employ a combination of two-dimensional and three-dimensional polarizing microscopy techniques, and reveal that the single arch and double arch disclinations obtained in nematic LC cells transform into different strength (Burgers vector) edge dislocations, characteristic of cholesteric LC and other lamellar materials. We begin by studying the continuous transformation from nematic to cholesteric LC cells by employing a mixture of mesogens with a strong temperature dependence of the cholesteric pitch around a compensation point.

Materials and methods

Sample preparation

Glass substrates of an area of a few square centimeters were cleaned with fresh piranha solution composed of 30% aqueous H_2O_2 and 70% of concentrated H_2SO_4 . The cleaning solution was kept at 70 °C in a water bath for 1 h. The plates were subsequently cooled, rinsed with abundant Milli-Q water and dried thoroughly with a stream of nitrogen. One of the plates

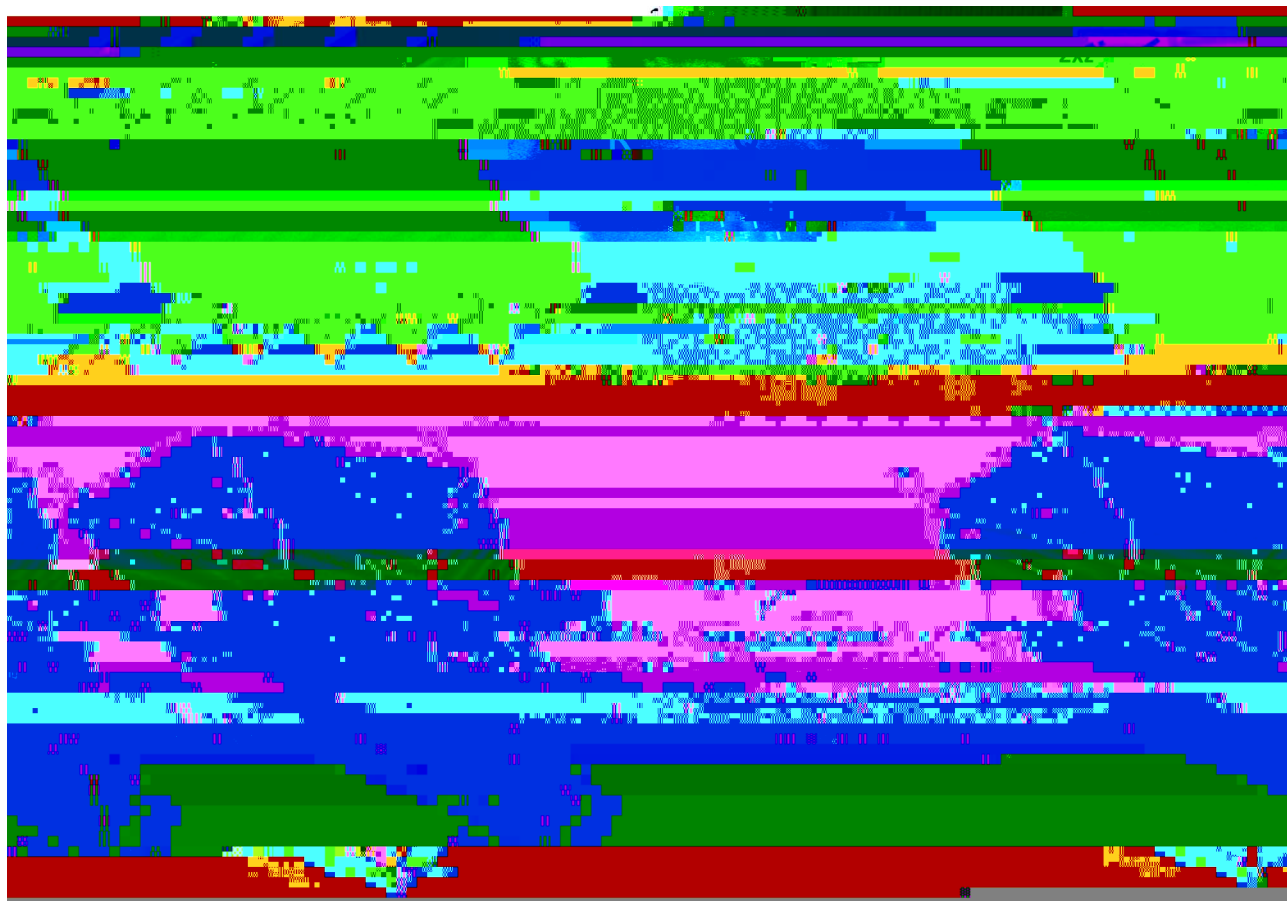


Fig. 5 In plane and different vertical 2PEFPM and 3PEFPM cross sections in the vicinity of a circular domain in the LB-coated top plate, after filling the cell with the CLC from right to left, parallel to the far-field orientation imposed by the buffed poly-imide layer on the bottom complementary plate. Surfactant molecules on the surface domain are ordered with CCW handedness. Vertical cross-sections across the paths indicated in (a) are presented in different panels. Data for two orthogonal polarizations are combined by means of color-coding, as indicated. A sketch of the director field in the OP XZ-cross section is included. For comparison, both the 2PEFPM and 3PEFPM OPQR vertical cross-sections are presented.

multiphoton excitation microscopy we used the same laser scanning device without confocal unit. Laser excitation was performed with a femtosecond Ti:sapphire oscillator (140 fs, 80 MHz, Chameleon Ultra-II, Coherent). This pulsed laser allows for wavelength tunability within 680–1080 nm. Two-photon excitation in 2PEFPM was performed with a 980 nm wavelength and by placing a band pass filter transmitting between 510 and 560 nm in front of the detector. For 3PEFPM, excitation was performed at 860 nm and a detector band pass filter transmitting between 387 and 447 nm. Excitation intensity was kept minimal in all cases to avoid altering the photosensitive LB films and the director structures in the LC. Although the precursor monolayer has been proven to be photosensitive at the air/water interface under irradiation at similar wavelengths,²⁵ steric hindrance inside the ordered domains and slow diffusion of surfactant molecules on the LB film allows observations to be performed without detectable alterations in the LC patterns.

Imaging was performed with colinear polarization directions for excitation and detected fluorescence light. The transition dipole moments of absorption and emission of the anisotropic BTBP dye molecules follow the liquid crystal director $\mathbf{n}(\mathbf{r})$.

Therefore, in the case of polarized epifluorescence signals, fluorescence intensity in the images scales as $\cos^4 \theta$ in FCPM, as $\cos^6 \theta$ in 2PEFPM, and as $\cos^8 \theta$ in 3PEFPM (for polarized fluorescence detection), where θ is the angle between the polarization of probing light and $\mathbf{n}(\mathbf{r})$; note that unpolarized detection in these techniques is also often used, in which case the detected signals scale as $\cos^2 \theta$ in FCPM, as $\cos^4 \theta$ in 2PEFPM, and as $\cos^4 \theta$ for 3PEFPM.^{26,27} Information about the spatial variation in the orientation of $\mathbf{n}(\mathbf{r})$ is extracted by comparing images acquired for different polarization directions of probing light. Using 2PEFPM and 3PEFPM is advantageous with respect to FCPM, particularly in thick samples, given their improved sensitivity and deeper penetration into the sample.²⁶ ImageJ and Mathematica were used for data analysis and presentation.

Results and discussion

Introduction of cholesteric order in hybrid nematic cells

In order to gradually introduce cholesteric lamellar-like order in the nematic system we employ the mixture 8OCB-CC (1 : 1) that

features a cholesteric phase with a compensation temperature $T_c = 56\text{--}60\text{ }^\circ\text{C}$ at which the pitch diverges (the material becomes nematic), and a strong temperature-dependence of the pitch above and below this temperature (p is right-handed above T_c and left-handed below T_c).²³ Typical values are $|p| \approx 45\text{ }\mu\text{m}$ for $|T - T_c| \approx 1.0\text{ }^\circ\text{C}$. Following previously described procedures,²⁰ we prepared nematic samples on hybrid cells featuring the single arch configuration (single twist-escaped disclination)

characteristic equilibrium angle of the disclination line as the boojum on the periphery circumnavigated. This angle was directly related to the pitch, as elastic energy in the untwisted and overtwisted regions on both sides of the disclination balance.³⁰ Although a similar equilibrium configuration as a function of the temperature-dependent CLC pitch exist in the present case, the complex three-dimensional nature of $\mathbf{n}(\mathbf{r})$

cell is filled right-to-left. Cross section data include two orthogonal polarizer configurations, and are combined in the presented color coded images. These are RGB color images, 8 bit per channel, with the G channel set to zero and the R and B channels incorporating data for each of the complementary (orthogonal) polarizer configurations, as indicated in each panel. While deep red regions correspond to $\mathbf{n}(\mathbf{r})$ oriented roughly along the X axis and deep blue regions correspond to $\mathbf{n}(\mathbf{r})$ oriented roughly along the Y axis, intermediate orientations appear with a purple hue, as both the R and B channels are

- 6 E. Pairam, J. Vallamkondu, V. Koning, B. C. van Zuiden, P. W. Ellis, M. A. Bates, V. Vitelli and A. Fernandez-Nieves, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 9295–9300.
- 7 M. E. McConney, A. Martinez, V. P. Tondiglia, K. M. Lee, D. Langley, I. I. Smalyukh and T. J. White, *Adv. Mater.*, 2013, **25**, 5880–5885.
- 8 B. Senyuk, Q. Liu, S. He, R. D. Kamien, R. B. Kusner, T. C. Lubensky and I. I. Smalyukh, *Nature*, 2013, **493**, 200–205.
- 9 T. Ohzono, J.-i. Fukuda, K. Suzuki and T. Yamaguchi, *Phys. Rev. E*, 2012, **86**, 030701.
- 10 P. Poulin, H. Stark, T. C. Lubensky and D. A. Weitz, *Science*, 1997, **275**, 1770–1773.
- 11 M. Zapotocky, L. Ramos, P. Poulin, T. C. Lubensky and D. A. Weitz, *Science*, 1999, **283**, 209–212.
- 12 J. C. Loudet, P. Barois and P. Poulin, *Nature*, 2000, **407**, 611–613.
- 13 T. Lopez-Leon, V. Koning, K. B. S. Devaiah, V. Vitelli and A. Fernandez-Nieves, *Nat. Phys.*, 2011, **7**, 391–394.
- 14 Y. Choi, T. Atherton, S. Ferjani, R. G. Petschek and C. Rosenblatt, *Phys. Rev. E*, 2009, **80**, 060701.
- 15 J. H. Kim, M. Yoneya and H. Yokoyama, *Nature*, 2002, **420**, 159–162.
- 16 J.-i. Niitsuma, M. Yoneya and H. Yokoyama, *J. Appl. Phys.*, 2012, **111**, 103507.
- 17 M. Cavallaro Jr, L. Botto, E. P. Lewandowski, M. Wang and K. J. Stebe, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 20923–20928.
- 18 J. Y. Fang, U. Gehlert, R. Shashidar and C. M. Knobler, *Langmuir*, 1999, **15**, 297–299.
- 19 M. C. Petty, *Langmuir-Blodgett films: an introduction*, Cambridge University Press, Cambridge, New York, 1996.
- 20 N. Petit-Garrido, R. P. Trivedi, J. Ignés-Mullol, J. Claret, C. Lapointe, F. Sagues and I. I. Smalyukh, *Phys. Rev. Lett.*, 2011, **107**, 177801.
- 21 N. Petit-Garrido, J. Claret, J. Ignés-Mullol and F. Sagues, *Nat. Commun.*, 2012, **3**, 1001.
- 22 W. Iglesias, T. J. Smith, P. B. Basnet, S. R. Stefanovic, C. Tschierske, D. J. Lacks, A. Jáklí and E. K. Mann, *Soft Matter*, 2011, **7**, 9043.
- 23 A. Dequidt and P. Oswald, *Europhys. Lett.*, 2007, **80**, 26001.
- 24 C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nat. Methods*, 2012, **9**, 671–675.
- 25 F. Sagues, R. Albalat, R. Reigada, J. Crusats, J. Ignés-Mullol and J. Claret, *J. Am. Chem. Soc.*, 2005, **127**, 5296–5297.
- 26 R. P. Trivedi, T. Lee, K. A. Bertness and I. I. Smalyukh, *Opt. Express*, 2010, **18**, 27658.
- 27 R. P. Trivedi, I. I. Klevets, B. Senyuk, T. Lee and I. I. Smalyukh, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 4744–4749.
- 28 P. Guillamat, F. Sangués and J. Ignés-Mullol, *Phys. Rev. E.*, 2014, **89**, 052510.
- 29 M. Stalder and M. Schadt, *Opt. Lett.*, 1996, **21**, 1948–1950.
- 30 S.-W. Suh, K. Joseph, G. Cohen, J. S. Patel and S.-D. Lee, *Appl. Phys. Lett.*, 1997, **70**, 2547.
- 31 I. Smalyukh and O. Lavrentovich, *Phys. Rev. E*, 2002, **66**, 051703.