

LETTER • OPEN ACCESS

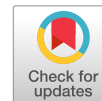
Selective phase transition of cholesteric blue phase I induced by pattern-controlled Grandjean–Cano disclinations

To cite this article: Kazuma Nakajima *et al* 2024 *Appl. Phys. Express* **17** 046002

View the [article online](#) for updates and enhancements.

You may also like

- [Multi-trace basis pursuit inversion with spatial regularization](#)
Rui Zhang, Mrinal K Sen and Sanjay Srinivasan
- [Confined cubic blue phases under shear](#)
O Henrich, K Stratford, D Marenduzzo et al.
- [Ultra-fast switching blue phase liquid crystals diffraction grating stabilized by chiral monomer](#)
Ramesh Manda, Srinivas Pagidi, Surjya Sarathi Bhattacharya et al.



Selective phase transition of cholesteric blue phase I induced by pattern-controlled Grandjean–Cano disclinations

Kazuma Nakajima[✉], Shogo Mitsuhashi, and Masanori Ozaki^{*}

Division of Electrical, Electronic and Infocommunications Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565-0871, Japan

^{*}E-mail: ozaki@eei.eng.osaka-u.ac.jp

Received March 11, 2024; revised March 26, 2024; accepted March 28, 2024; published online April 12, 2024

This study investigates the influence of Grandjean–Cano disclinations on the cholesteric-blue phase I (Ch-BPI) phase transition, revealing the pivotal role of defects in the phase transition of liquid crystals (LCs). We prepared the disclinations by wedge cells or parallel cells with an alignment pattern and demonstrated that the disclinations induce a phase transition in Ch-BPI. Furthermore, we demonstrated the control of the BPI appearance areas by utilizing this property. This defect-induced transition technique not only provides a novel method for controlling BPI orientation, but also offers insights into soft material crystal growth, suggesting potential applications in new BPLC-based device development.

© 2024 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

Various phase states of matter are known, such as solid, liquid, gas, plasma, and liquid crystals (LCs), each of which have further different phases. In solid and LC states, the freedom of the atom or molecule arrangement generates a diverse array of phases. Each phase exhibits specific physical and chemical properties. Therefore, phase transitions naturally allow the properties of materials to be tuned, and the thermodynamics and kinetics of phase transitions have attracted enormous research interest. Traditionally, studies on phase transitions have mainly focused on defect-free and homogeneous orientation states. However, in most real systems, defects are present in the material. In recent years, significant advances in theory and experimental techniques have enabled the understanding of the effects of defects on phase transitions.¹⁾

Generally, the term defect is used in crystalline solids to denote any interruption of the periodic atomic positional arrangement. Several types of defects are present in crystals, including point defects in zero-dimension, dislocation in one dimension, and grain boundary or stacking fault in two dimensions. However, defects in LCs mean interruptions in the positional or directional order of the molecules. Owing to their self-organization, LCs are classified into several phases based on their positional order, including nematic phases with no positional order, smectic phases with a layered order, and cholesteric (Ch) phases with a helical order. Moreover, in each of these LC phases, defects of various directional orders are formed.

Defects in LC devices, such as displays, have been known to diminish performance. Consequently, efforts have been made to uniformly control LC orientation to minimize defects. However, recent studies have shown useful properties of defects, such as trapping of particles^{2,3)} and generating optical vortex beams.⁴⁾ Several types of defects have been controlled in their presence and configuration by LC orientation techniques such as surface patterning,^{5–8)} confinement in geometrically designed cells,^{9,10)} and applying electric field.¹¹⁾ The ability to control the presence of defects is valuable in exploring their effect on LC phase transitions. Since the first experimental demonstration of defect-mediated phase transitions using lyotropic LC by Allain,¹²⁾ the effect

of defects on the LC phase transitions has primarily been observed in smectic-nematic¹³⁾ and nematic-isotropic (Iso)¹⁴⁾ phase transitions. However, the body of literature on this subject remains limited, both in the number of reports and the variety of LC phases explored.

The Ch phase appears in materials with chirality in the LC molecules or in materials in which non-chiral LC molecules are doped with chiral agents, and the LC directors form a uniaxial helical structure. The helical structure leads to the generation of various defects such as dislocations and disclinations, which are line defects. The most common defect in ChLC is the Grandjean–Cano disclination induced in wedge cells with a uniaxial horizontal alignment surface.¹⁵⁾ The disclination is formed owing to a discontinuous change in the number of helix layers in the cell thickness direction.

ChLC materials with strong helical twisting power, doped with a large number of chiral agents, appear with blue phases (BPs) between the Ch and Iso phases.¹⁶⁾ In BPs, the arrangement of LC molecules is biaxially twisted to form double-twisted cylinders (DTCs), which is a 2D quarter-skyrmion structure.¹⁷⁾ BPs are classified into three phases based on the arrangement of their DTCs: BPI with body-centered cubic symmetry, BP II with simple cubic symmetry, and BP III with amorphous symmetry, in order of decreasing temperature of appearance.¹⁸⁾ BPs have unique properties, including selective reflection of circularly polarized light,¹⁹⁾ a fast electro-optical response of sub-milliseconds,^{20,21)} and a large electro-optical Kerr effect.^{22,23)} While the temperature range for the appearance of BPs is inherently narrow (only a few degrees Celsius), the discovery of polymer-stabilized BPs (PSBPs) by Kikuchi et al. has significantly extended this temperature range to several tens of degrees Celsius.²⁴⁾ This has enabled the use of BPs at room temperature, leading to their study for applications such as displays,^{25–27)} polarization-independent phase modulators,^{28–30)} tunable lasers,^{31,32)} and biosensors.³³⁾ BPs, like other LC materials, are known to improve device performance when the lattice orientation is controlled in monodomains.^{34–37)} However, the orientation mechanism and phase transition of BPs have not been fully understood. The phase transitions between BP and Ch, BP



and Iso, and BPs are induced by temperature and electric field. In these phase transitions, the orientation state of the phase before the transition is known to affect the orientation state of the phase after the transition.^{38,39)} Nucleation of BPs in the phase transition is epitaxial growth, and studies have been reported on the fabrication of large single crystals using this process.⁴⁰⁾ The BPI-BPII phase transition is also known as a martensitic structural transition, which is interesting in terms of its analogy to crystal-crystal phase transitions.^{41,42)}

In this study, we demonstrated that the Ch-BPI phase transition is induced by Grandjean–Cano disclinations in wedge cells and that BPI nuclei grow from these disclinations. We focused this study on investigating the effect of disclinations on the phase transition and developed a technique to pattern the disclinations by photoalignment in cells with parallel substrates in order to eliminate the factor of the tilt angle between substrates in wedge cells. We found that the difference in the temperature of the Ch-BPI phase transition between the areas with and without the disclination is affected by the thickness of the cell, and that the smaller the cell thickness, the larger the temperature difference. Furthermore, we showed that densely patterned disclinations selectively induce the Ch-BPI phase transition, causing the appearance of BPI exclusively in the local area.

We fabricated two types of cells: wedge cells and cells with substrates parallel to each other. In the wedge cell, substrates were coated with a polyimide alignment agent (AL1254, JSR) and rubbed to give a uniaxial orientation easy axis. Two types of photo-curable adhesives with ball spacers of 2 and 20 μm diameters were used to attach the substrates with the easy axis direction matched. The dihedral angle of the wedge cell was $\sim 0.057^\circ$, meaning that the cell thickness varied by 1 μm per 1 mm in the inclined direction. In contrast, for parallel cells, one substrate was coated with a polyimide alignment agent and rubbed, and the other was coated with an azobenzene-based photoalignment agent (LIA-03, DIC) for photoalignment patterning. This parallel cell was used for patterning the Grandjean disclinations. Figure 1(a) shows a schematic of the disclination patterning and the easy axis distribution applied by photoalignment. Because one side had a uniaxial easy axis recorded by rubbing, the number of cholesteric helical layers depended on the direction of the easy axis patterned by the photoalignment at the other side. Therefore, the helix shifted by one layer when the easy axis direction changed by π , generating disclinations as in wedge cells. Outside the patterned area, a uniaxial easy axis was given, and areas with and without disclination were fabricated in one cell. Figure 1(b) is a schematic of the photoalignment system. In this system, a designed alignment pattern was applied by controlling the irradiation area using the projector, and the angle of the $\lambda/2$ plate was applied to control the linear polarization of the irradiation light. The projector had $1,024 \times 768$ pixels and the irradiated area was approximately $0.58 \times 0.43 \text{ mm}^2$. The system was computer-controlled to sequentially project light beams with different linear polarization angles. The linear polarization angle was varied in increments of 5° and light with intensity of $2.5 \times 10^2 \text{ mW cm}^{-2}$ was irradiated at each angle for 20 s.

The BPLC material was prepared by mixing two nematic LC materials (5CB and MLC-6849-100, both from Merck)

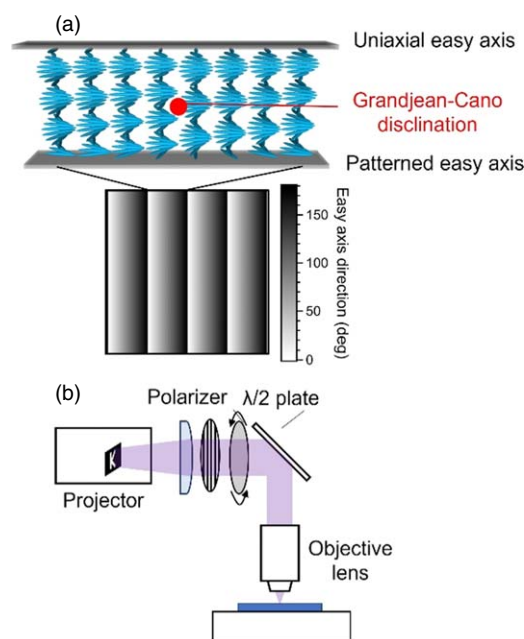


Fig. 1. (a) Schematic of disclination patterning in a cell with substrates attached in parallel. (b) Schematic of the photoalignment system.

and a chiral dopant (S-5011, HCCH) in a weight ratio of 48.5:48.5:3.0. The BPLC material underwent Ch, BPI, BPII, and Isotropic phases with increasing temperature. Specifically, for a non-alignment cell with a cell thickness of 5 μm , the phase transition temperatures were 46.0, 46.8, and 48.1 $^\circ\text{C}$, upon temperature increase.

After filling the BPLC material into the cell, disclinations were induced at room temperature, where the Ch phase appeared. Using a thermal controller (TS350, Linkam), the temperature was then gradually increased to 45.7 $^\circ\text{C}$, just before the Ch-BPI phase transition temperature. This temperature was maintained for 10 min to allow the entire system, including the temperature controller, to reach thermal equilibrium. Subsequently, the temperature was slowly raised at a rate of $0.01 \text{ }^\circ\text{C min}^{-1}$ until the Ch-BPI phase transitioned. The LC cell textures were observed using a polarized optical microscope (POM, Eclipse LV100-POL, Nikon) in reflection mode.

Figure 2 shows POM images depicting the Ch-BPI phase transition in the wedge cell. The temperature increased at a rate of $0.01 \text{ }^\circ\text{C min}^{-1}$ from the Ch phase. The cell thickness at the center of the observation area was $\sim 12 \mu\text{m}$. As is well known, Grandjean–Cano disclinations are generated in ChLCs confined in wedge cells. At 46.06 $^\circ\text{C}$, only the Ch phase appeared, and disclinations were observed as a discontinuous color change. The disclinations were observed at intervals of $\sim 130 \mu\text{m}$, corresponding to the region where the cell thickness changed by half the pitch of ChLC. Thus, the half pitch was calculated to be $\sim 130 \text{ nm}$, as the cell thickness varied by 1 μm per 1 mm in the inclined direction. At 46.08 $^\circ\text{C}$, BPI nuclei were generated in the areas where the disclinations existed before increasing temperature, indicating that the Ch-BPI phase transition had occurred. However, only a few BPI nuclei were generated in the disclination-free areas. As the temperature was further increased, BPI nuclei grew, and at 46.18 $^\circ\text{C}$, BPI expanded over the entire observation area.

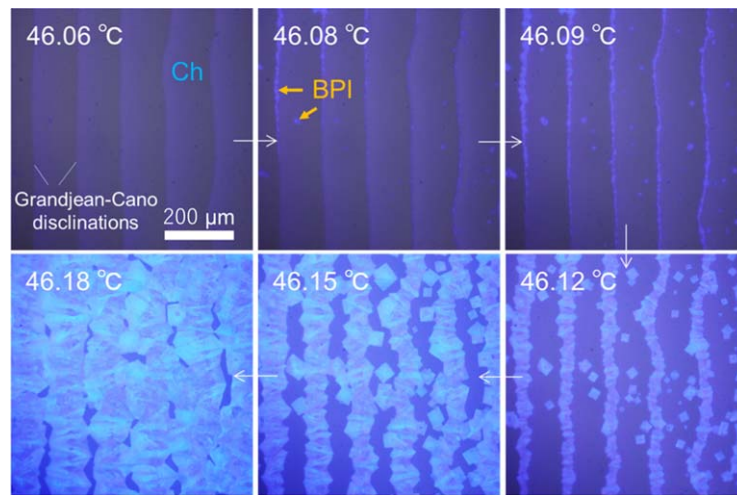


Fig. 2. POM images of Ch-BPI phase transition in the wedge cell with a dihedral angle of $\sim 0.057^\circ$.

Observations of the Ch-BPI phase transition in the wedge cell revealed a distinct difference in the phase transition temperature between areas with and without disclinations. To quantitatively evaluate this temperature difference, we developed a technique to control the cell thickness and location of the disclination. This involved using cells with two substrates attached in parallel and with the patterned easy axis, as shown in Fig. 1(b). Figure 3 shows a POM image of the patterned disclinations at 45.7°C . The white arrows in the image represent the easy axis, the direction of which changes with going horizontally in the image. The color of the POM image changed discontinuously from gray to purple in the position where the orientation of the easy axis was vertical. The gray area means that the reflection wavelength of Ch is in the ultraviolet region, indicating that the helix pitch is short. On the other hand, the purple area indicates that the helix pitch has expanded. Therefore, the disclinations are formed at intervals where the direction of the easy axis changes by π , and the orientation state would be as shown in Fig. 1(a). This result demonstrates that the disclinations, which previously could only be generated in wedge cells, can be controlled in cells with substrates attached parallel.

In Fig. 4(a), POM images show the Ch-BPI phase transition in a patterned cell with a thickness of $4.1\ \mu\text{m}$. Here, the period of the easy axis distribution was set to $\sim 41\ \mu\text{m}$. At 45.90°C , when only the Ch phase appeared, disclinations were intentionally generated with a width of $\sim 41\ \mu\text{m}$. At 45.91°C , BPI nuclei formed in the area with existing disclinations, and these nuclei grew with increasing temperature. Contrarily, in the disclination-free area, BPI nuclei did not emerge until 45.95°C and phase transitions occurred simultaneously from various positions at 45.96°C . This resulted in a phase transition temperature difference, denoted as $T_u - T_g$, measuring 0.05°C , where T_g and T_u represent the phase transition temperatures in the areas with and without disclination, respectively. The discrepancy in phase transition temperatures between Figs. 2 and 4(a) was attributed to the decrease in the phase transition temperature caused by the reduction in cell thickness.⁴³⁾

We investigated the effect of cell thickness on the phase transition temperature for both areas with and without disclination in parallel cells. The dependence of the phase

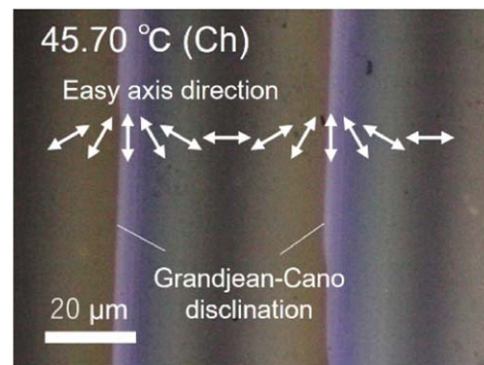


Fig. 3. POM image of patterned disclinations.

transition temperature difference $T_u - T_g$ on cell thickness is shown in Fig. 4(b). Eighteen cells with varying cell thicknesses were used, and the $T_u - T_g$ measured in each cell is shown as red circles in the figure. The red line is an auxiliary line fitted with an exponential function. The phase transition temperature difference increases significantly with decreasing cell thickness.

The structural transition from Ch to BPI requires breaking the one-dimensional helical structure and forming disclination networks. As Ch attempts to maintain its helical structure owing to the elasticity of the LC director, even when the most stable phase in terms of free energy becomes BPI, Ch maintains its structure without phase transition. Therefore, the phase transition requires additional energy to overcome the energy barrier to structural change. The disclinations, which have locally large elastic energy, will be the starting point of the phase transition because it gives the energy to overcome the energy barrier. As the cell thickness decreases, the rate of change in the number of Ch helical layers increases around the disclination, leading to greater distortions of Ch layer and an increase in the free energy. The increase in free energy facilitates the overcoming of the energy barrier, consequently leading to a larger phase transition temperature difference between areas with and without disclinations as the cell thickness decreases.

Finally, we demonstrated the control of BPI appearance areas using the defect-induced phase transition. The period of the easy axis distribution in the patterned cell shown in

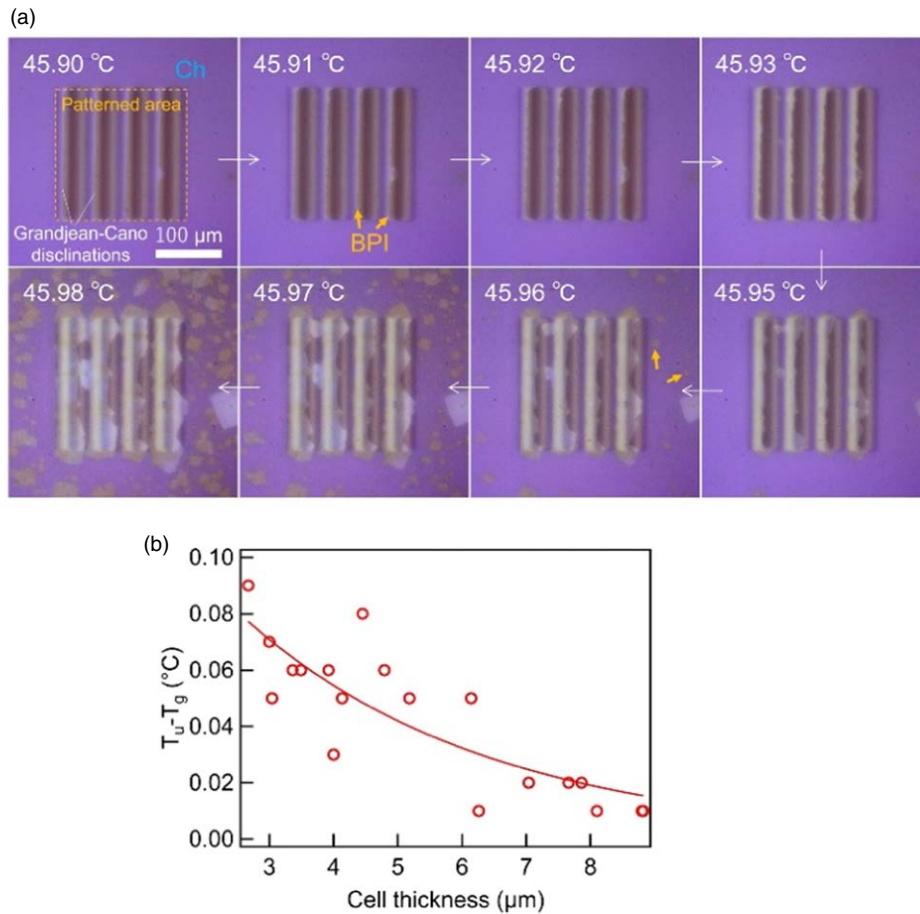


Fig. 4. (a) POM images of the Ch-BPI phase transition in a 4.1 μm thick cell with patterned disclinations. (b) Dependence of the phase transition temperature difference between areas with and without disclination, $T_u - T_g$, on the cell thickness in parallel cells.

Fig. 1(b) was decreased to generate the disclinations in density. Figure 5 shows POM images of BPI selective appearance in a cell with a cell thickness of 5.3 μm and patterned disclinations with a period of ~10 μm. The temperature increase stopped at 45.95 °C, where the phase transition started from the disclinations, and the temperature was kept constant. As shown in Fig. 4(b), for a cell thickness of 5 μm, the phase transition temperature difference was ~0.05 °C. Therefore, the area without disclination did not undergo a phase transition and remained in the Ch phase. In contrast, the BPI nuclei generated in the disclination grew such that the patterned area was covered with BPI at 15 min. Therefore, the BPI appearance areas were controlled by selective Ch-BPI phase transitions in cells with densely patterned disclinations.

In conclusion, we demonstrated that the Ch-BPI phase transition is induced by the Grandjean-Cano disclinations in the Ch phase. In the Ch-BPI phase transition, an energy

barrier is present to overcoming the structural change in the LC director arrangement from a one-dimensional to a three-dimensional helical structure. Disclinations, characterized by locally high free energy, effectively overcome this energy barrier at lower temperatures compared to disclination-free areas. Notably, in cells with smaller thicknesses, the energy around the disclination was greater, resulting in a more substantial difference in the phase transition temperature between areas with and without disclination. Furthermore, by segregating regions with densely patterned disclinations from disclination-free area within a single cell, we selectively induced the Ch-BPI phase transition, demonstrating control over the BPI appearance area. The technique of simultaneously maintaining two phases, Ch and BPI, which have different properties in terms of refractive index, electric field response, and selective reflection wavelengths, will contribute to the development of devices with new functions. The defect-induced phase transition in the BP provides an

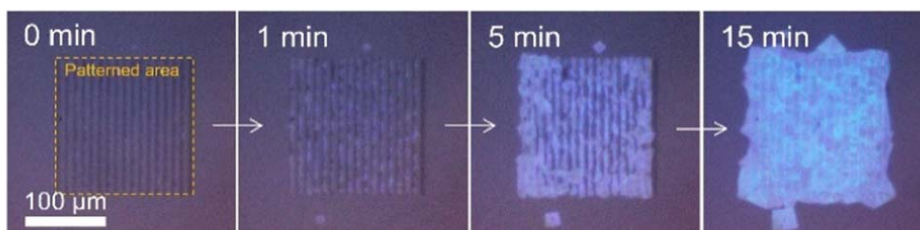


Fig. 5. POM images of selective phase transitions induced by densely patterned disclinations.

opportunity to study the effect of the defect on phase transitions and crystal growth on much longer length scales than in crystalline solids. The disclination patterning provides a platform for this purpose. This is expected to offer important insights into the crystal growth of soft materials, while also offering analogies to crystalline solids.

Acknowledgments We thank Prof. J. Fukuda of Kyushu University for the discussions. We thank DIC Co. for providing the alignment agent. This study was partly supported by MEXT KAKENHI (JP23H02038) and a Grant-in-Aid for JSPS Fellows (23KJ1507).

ORCID iDs Kazuma Nakajima  <https://orcid.org/0009-0004-4590-6428> Masanori Ozaki  <https://orcid.org/0000-0002-9556-4225>

- 1) X. Zhang, J. Zhang, H. Wang, J. Rogal, H.-Y. Li, S.-H. Wei, and T. Hickel, *Appl. Phys. Rev.* **9**, 041311 (2022).
- 2) T. Ohzono and J. Fukuda, *Nat. Commun.* **3**, 701 (2012).
- 3) B. Senyuk, J. S. Evans, P. J. Ackerman, T. Lee, P. Manna, L. Vigderman, E. R. Zubarev, J. Van De Lagemaat, and I. I. Smalyukh, *Nano Lett.* **12**, 955 (2012).
- 4) S. Slussarenko, A. Murauski, T. Du, V. Chigrinov, L. Marrucci, and E. Santamato, *Opt. Express* **19**, 4085 (2011).
- 5) H. Yoshida, K. Asakura, J. Fukuda, and M. Ozaki, *Nat. Commun.* **6**, 7180 (2015).
- 6) I. Nys, B. Berteloot, J. Beeckman, and K. Neyts, *Adv. Opt. Mater.* **10**, 2101626 (2022).
- 7) S. Wu, L. Ma, P. Chen, H. Cao, S. Ge, R. Yuan, W. Hu, and Y. Lu, *Adv. Opt. Mater.* **8**, 2000593 (2020).
- 8) M. Wang, Y. Li, and H. Yokoyama, *Nat. Commun.* **8**, 388 (2017).
- 9) M. Kim and F. Serra, *Crystals* **10**, 314 (2020).
- 10) D. S. Kim, S. Čopar, U. Tkalec, and D. K. Yoon, *Sci. Adv.* **4**, eaau8064 (2018).
- 11) Y. Sasaki, V. S. R. Jampani, C. Tanaka, N. Sakurai, S. Sakane, K. V. Le, F. Araoka, and H. Orihara, *Nat. Commun.* **7**, 13238 (2016).
- 12) M. Allain, *Epl* **2**, 597 (1986).
- 13) M. J. Gim, D. A. Beller, and D. K. Yoon, *Nat. Commun.* **8**, 15453 (2017).
- 14) N. J. Mottram and T. J. Sluckin, *Liq. Cryst.* **27**, 1301 (2000).
- 15) P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1995), 2nd ed..
- 16) D. Coates and G. W. Gray, *Phys. Lett. A* **45**, 115 (1973).
- 17) J.-S. Wu and I. I. Smalyukh, *Liq. Cryst. Rev.* **10**, 34 (2022).
- 18) D. C. Wright and N. D. Mermin, *Rev. Mod. Phys.* **61**, 385 (1989).
- 19) H. Yoshida, K. Anucha, Y. Ogawa, Y. Kawata, M. Ozaki, J. Fukuda, and H. Kikuchi, *Phys. Rev. E* **94**, 042703 (2016).
- 20) H. Kikuchi, H. Higuchi, Y. Haseba, and T. Iwata, *SID Symp. Dig. Tech. Pap.* **38**, 1737 (2007).
- 21) H. Choi, H. Higuchi, and H. Kikuchi, *Appl. Phys. Lett.* **98**, 131905 (2011).
- 22) Y. Hisakado, H. Kikuchi, T. Nagamura, and T. Kajiyama, *Adv. Mater.* **17**, 96 (2005).
- 23) L. Rao, J. Yan, S.-T. Wu, S. Yamamoto, and Y. Haseba, *Appl. Phys. Lett.* **98**, 081109 (2011).
- 24) H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, and T. Kajiyama, *Nat. Mater.* **1**, 64 (2002).
- 25) Z. Ge, S. Gauza, M. Jiao, H. Xianyu, and S.-T. Wu, *Appl. Phys. Lett.* **94**, 101104 (2009).
- 26) H. Kikuchi, Y. Haseba, S. Yamamoto, T. Iwata, and H. Higuchi, *SID Symp. Dig. Tech. Pap.* **40**, 578 (2009).
- 27) H. Chen, Y.-F. Lan, C.-Y. Tsai, and S.-T. Wu, *Liq. Cryst.* **44**, 1124 (2017).
- 28) F. Peng, Y.-H. Lee, Z. Luo, and S.-T. Wu, *Opt. Lett.* **40**, 5097 (2015).
- 29) N. Rong, Y. Li, X. Li, P. Zhou, S. Liu, J. Lu, and Y. Su, *J. Disp. Technol.* **12**, 1008 (2016).
- 30) E. Oton, E. Netter, T. Nakano, Y. D.-Katayama, and F. Inoue, *Sci. Rep.* **7**, 44575 (2017).
- 31) S. Yokoyama, S. Mashiko, H. Kikuchi, K. Uchida, and T. Nagamura, *Adv. Mater.* **18**, 48 (2006).
- 32) K. Kim, S.-T. Hur, S. Kim, S.-Y. Jo, B. R. Lee, M. H. Song, and S.-W. Choi, *J. Mater. Chem. C* **3**, 5383 (2015).
- 33) M.-J. Lee, C.-H. Chang, and W. Lee, *Biomed. Opt. Express* **8**, 1712 (2017).
- 34) P. Nayek, H. Jeong, S.-W. Kang, S. H. Lee, H.-S. Park, H. J. Lee, H. S. Kim, and G.-D. Lee, *J. Soc. Inf. Disp.* **20**, 318 (2012).
- 35) H.-S. Chen, Y.-H. Lin, C.-H. Wu, M. Chen, and H.-K. Hsu, *Opt. Mater. Express* **2**, 1149 (2012).
- 36) Y. Chen and S.-T. Wu, *Appl. Phys. Lett.* **102**, 171110 (2013).
- 37) Y. Kawata, H. Yoshida, S. Tanaka, A. Konkanok, M. Ozaki, and H. Kikuchi, *Phys. Rev. E* **91**, 022503 (2015).
- 38) M. Takahashi, T. Ohkawa, H. Yoshida, J. Fukuda, H. Kikuchi, and M. Ozaki, *J. Phys. D: Appl. Phys.* **51**, 104003 (2018).
- 39) S. Cho, M. Takahashi, J. Fukuda, H. Yoshida, and M. Ozaki, *Commun. Mater.* **2**, 39 (2021).
- 40) C. W. Chen et al., *Nat. Commun.* **8**, 727 (2017).
- 41) X. Li, J. A. Martínez-González, J. P. Hernández-Ortiz, A. Ramírez-Hernández, Y. Zhou, M. Sadati, R. Zhang, P. F. Nealey, and J. J. de Pablo, *Proc. Natl Acad. Sci.* **114**, 10011 (2017).
- 42) H. M. Jin, X. Li, J. A. Dolan, R. J. Kline, J. A. Martínez-González, J. Ren, C. Zhou, J. J. de Pablo, and P. F. Nealey, *Sci. Adv.* **6**, eaay5986 (2020).
- 43) E. Bukusoglu, J. A. Martinez-Gonzalez, X. Wang, Y. Zhou, J. J. de Pablo, and N. L. Abbott, *Soft Matter* **13**, 8999 (2017).