This is a repository copy of *Electrically tunable refractive index in the dark conglomerate phase of a bent-core liquid crystal.*.

Version: Published Version

Article:

Nagaraj, M, Görtz, V, Goodby, JW et al. (1 more author) (2014) Electrically tunable refractive index in the dark conglomerate phase of a bent-core liquid crystal. Applied Physics Letters, 104 (2). 021903. ISSN 0003-6951

https://doi.org/10.1063/1.4861837

APPLIED PHYSICS LETTERS **104**, 021903 (2014)

Electrically tunable refractive index in the dark conglomerate phase of a bent-core liquid crystal

M. Nagaraj,[1,a)] V. Görtz,[2,3] J. W. Goodby,[2] and H. F. Gleeson[1]
[1]*School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, United Kingdom*
[2]*Department of Chemistry, University of York, York YO10 5DD, United Kingdom*
[3]*Department of Chemistry, University of Lancaster, Lancaster LA1 4YB, United Kingdom*

(Received 5 December 2013; accepted 24 December 2013; published online 13 January 2014)

Here we report an electrically tunable refractive index observed in an isotropic liquid crystal phase known as the dark conglomerate (DC) phase. This unusual change in the refractive index which has not been reported before in the DC phase of other bent-core liquid crystals occurs because of a series of electric-field-driven transformations that take place in the DC phase of the studied bent-core liquid crystal. These transformations give rise to a decrease in the refractive index of the system, when an electric field is applied across the device, and no change in the birefringence is seen during such behavior. The electro-optic phenomenon is described in detail and the possibility of exploiting this for a number of liquid crystal based device applications is discussed. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4861837]

Liquid crystals are widely accepted as one of the best opto-electronic materials. The method of controlling the orientation of nematic liquid crystal director by an external electric field and thereby tuning the effective refractive index has found profound applications for liquid crystals in optical devices.[1–5] However, due to the very nature of the nematic phase, this liquid crystal phase is not ideal for all photonic device applications. Some of the major limitations associated with using liquid crystals in their nematic phase in photonic devices include, first, difficulty in obtaining control over the surface anchoring, second, in the nematic phase the director fluctuations result in strong scattering effect. Therefore, damping of the light beam travelling through the liquid crystal is large. Polarization-related sensitivity of the material is another issue in the preparation of some of the nematic liquid crystal based electro-optical devices. These difficulties could be overcome if the nematic media is substituted by an optically isotropic medium, whose refractive index can still be tuned by external fields. One such class of liquid crystal phase known at present encompasses the blue phases.[6–8]

In this Letter, we report an interesting phenomenon where the average refractive index of an isotropic liquid crystal phase can be tuned over a remarkably wide range by an external electric field applied across the device. The isotropic phase under study is known as the dark conglomerate phase or the DC phase. The electro-optic phenomenon reported here could be exploited for number applications, where the applied electric field modulates the refractive index of the liquid crystal phase which in turn changes the nature of the propagating light wave. As the DC phase is optically isotropic (or exhibits very low birefringence in some cases) the advantages of the devices based on the DC phase mainly include no power loss due to scattering, no requirement of an alignment layer therefore ease of fabrication, and no polarization sensitive effects.

We have further investigated the behavior of the DC phase under an electric field by polarizing optical microscopy. This Letter also presents remarkable textural transformations that occur during the refractive index change and suggests the physical mechanism behind it. The temperature dependency of the average refractive index across the DC phase temperature range has also been measured and surprisingly a decrease in the refractive index on decreasing the temperature is noted.

The dark conglomerate phase or the DC phase is an optically isotropic phase observed in bent-core liquid crystals.[9–15] It is usually found to occur below the isotropic phase. Under polarizing microscopy, when the polarizers are crossed, the texture of this phase appears completely dark or exhibits very low birefringence. However on uncrossing the polarizers, usually chiral domains of opposite handedness are seen. Several studies have been carried out to understand the structure of the DC phase and it has been established that the phase consists of tilted polar smectic layers (SmCP type) with relatively short interlayer correlation length. There are four distinct structures possible in SmCP: $\mathrm{SmC_sP_S}$, $\mathrm{SmC_sP_A}$, $\mathrm{SmC_aP_S}$, and $\mathrm{SmC_aP_A}$, where the orientation of the tilt and the polar direction between adjacent layers are syn/anti-parallel and are represented by the letters s/S or a/A (Fig. 1). In the DC phase, the layers curve continuously due to the spontaneous saddle-splay (negative saddle-splay elastic constant, K_{24}) and three-dimensionally form a sponge-like structure. It is this spatial organization of the layers that makes the texture to appear dark under crossed polarizers. The origin of the optical activity in the DC phase formed by achiral mesogens has been discussed in detail in the literature and is attributed to the layer chirality or to the coupling of layer chirality with molecular conformational chirality.[16–19]

The liquid crystal material under investigation is an oxadiazole-based achiral bent-core mesogen, OC12-Ph-ODBP-Ph-C5 (Fig. 2). The DC phase in this material exists below a nematic phase for ∼60 K temperature range. It is to be noted that the nematic phase of this material exhibits low splay (K_{11}), twist (K_{22}), and bend (K_{33}) elastic constants

---

[a)] Author to whom correspondence should be addressed. Electronic mail: mamatha.nagaraj@manchester.ac.uk.

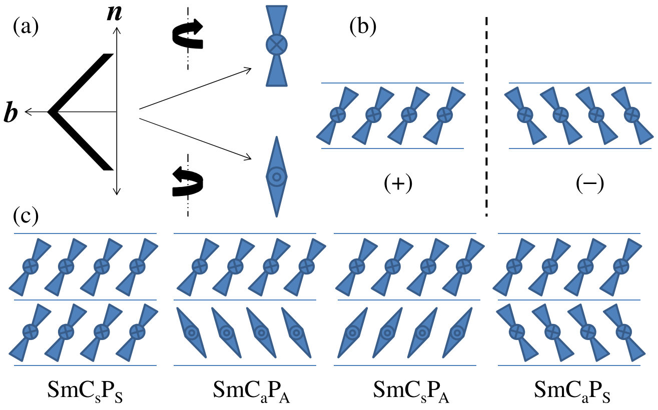

FIG. 1. Cartoon representation of (a) bent-core molecule with it major molecular director, ***n***, and the arrow direction, ***b***; (b) In-layer molecular arrangement in a SmCP phase and its mirror image constituting a chiral system; and (c) molecular arrangement in adjacent layers in four possible SmCP phases.

compared to other structurally similar materials.[20,21] It also has much lower twist and bend elastic constants compared to calamitics.[21] The material exhibits negative dielectric anisotropy throughout the nematic mesophase temperature range. All the experiments mentioned in this Letter are carried out on 5 μm thick planar sandwich cells (30 mm^2 indium tin oxide (ITO) electrode area, SE-130 high temperature polymer alignment layer with antiparallel rubbing). However, the phenomena seen are independent of the alignment conditions or device thickness. The temperature of the LC sample is controlled to an accuracy of ± 0.1 K using a Linkam THMS600 hot-stage connected to T95 temperature controller. The devices are capillary filled in the nematic phase of the material. Experiments are carried out on slow cooling (<0.5 K/min) of the sample from the isotropic phase.

For the refractive index measurements the thickness of the empty device, averaged over a 2 mm^2 field of view, is measured to an accuracy of ± 0.002 μm (by fitting the whole visible spectrum). The apparatus used to measure the refractive indices comprises a reflective polarizing microscope linked to a UV-Vis spectrometer.[22] An objective with numerical aperture of 0.25 is used for effective normal incidence. The reflection spectra are recorded between 400 nm to 700 nm with an accuracy of ± 0.1 nm.

The refractive indices are determined by analysing the reflection spectra by Berreman method.[22,23] The refractive index values obtained here are for the wavelength of 589 nm. An Agilent 33220A signal generator connected to home-built amplifier is used to apply an alternating electric field (of frequency $f = 550$ Hz) across the sample.

The average refractive index, n_{avg} $(= \sqrt{(n_e^2 + 2n_o^2)/3}$, where n_{e} and n_{o} are the extraordinary and the ordinary refractive indices of the material in an anisotropic phase) has been measured across the DC phase regime and also under an alternating electric field applied perpendicular to the substrate of the device. The temperature dependence of the n_{avg} in the DC phase shows an unusual behavior (Fig. 3). As the temperature is lowered below the nematic to DC phase transition temperature, the n_{avg} decreases from 1.656 at $T - T_{\text{N-DC}} = -1$ K to 1.632 at $T - T_{\text{N-DC}} = -48$ K. The coefficients of the Sellmeier's equation, $\left(n^2 = 1 + \left(\frac{A\lambda^2}{\lambda^2 - B^2}\right)\right)$, A varies from 1.56 to 1.48 and B remains almost constant $(180 \pm 1\,\text{nm})$ over this temperature range. Based on Vuks equation[24] the relationship between the average refractive index, n_{avg}, the average molecular polarizability, α_{avg}, and the molecular packing density, N, can be written as $n_{avg} = \frac{7}{2\sqrt{10}} + \frac{\frac{2\sqrt{10}}{5}\pi N \alpha_{avg}}{1 - \frac{4}{3}\pi N \alpha_{avg}}$. The term $\frac{4}{3}\pi N \alpha_{avg}$ is much smaller than 1, therefore, can be neglected. Thus, a decrease in the n_{avg} as the temperature decreases in the DC phase indicates that there is a decrease in either the molecular density (N) or/and in the average molecular polarizability (α_{avg}) of the system on reducing the temperature. The decrease in N or/and α_{avg} on reducing the temperature is not an obvious phenomenon and there is no straight forward explanation of such behavior. One of the possibilities that could explain such a behavior is that some form of molecular association (into small units) analogous to that observed in the B4 phase, occurs in the DC phase, and a decrease in the density or/and polarizability of such associated units occurs on decreasing the temperature.[25] However, the X-ray investigations carried out to date do not indicate any such molecular association in the DC phase.[26] The other possibility is that a spectral blue shift occurs on reducing the temperature, instigating a decrease in the average refractive index. In the latter case, we expect a strong change in the Sellmeier coefficient, B, but, as mentioned, no significant change in B is observed as the n_{avg} decreases. Further from the above equation it can be deduced that the $n_{\text{avg}}{}^2$ is approximately linearly proportional to n_{avg} according to $n_{avg}{}^2 + 2 \approx \sqrt{10} * n_{avg} - 0.5$.[27] Our experimental data is in very good agreement with this relation (Fig. 3 inset).

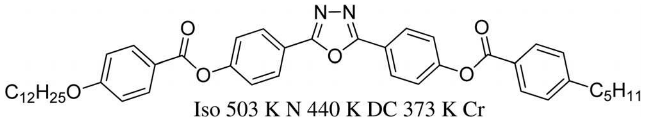

FIG. 2. Molecular structure, phase sequence, and phase transition temperatures of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal; Iso: isotropic; N: nematic; DC: dark conglomerate; and Cr: crystalline phase.

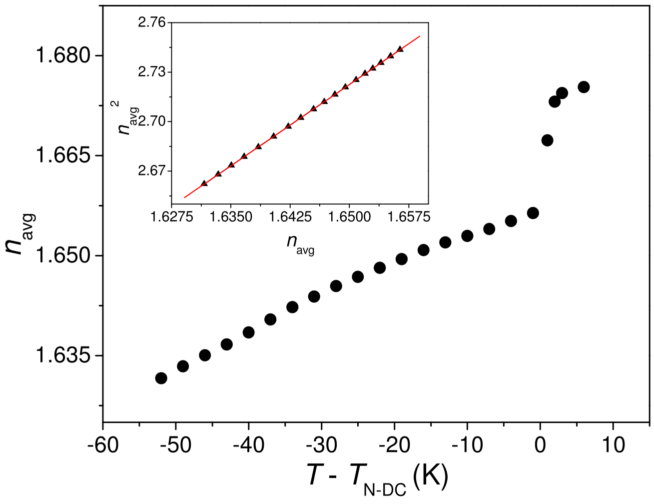

FIG. 3. Plot of temperature dependence of the average refractive index, determined by analyzing the reflection spectra. A decrease in the average refractive index of the DC phase on reducing the sample temperature is observed. Inset: Plot of $n_{\text{avg}}{}^2$ versus n_{avg} fitted to a straight line.

Generally, when an electric field is applied across a device containing a liquid crystal material in the DC phase, the optically isotropic structure is seen to transform to a synclinic (s) synpolar (S) structure ($\mathrm{SmC_sP_S}$) with long range correlations leading to the removal of the sponge-like structure. This results in a very high birefringence texture observable under crossed polarizers. However in our material, the behavior of the DC phase is completely different. There is no field induced birefringence observed even under sufficiently strong electric field (22 V/μm). Figure 4 shows the electric field dependence of the average refractive index at $T-T_{\mathrm{N-DC}} = -3$ K.

On increasing the applied electric field, initially n_{avg} increases slightly from 1.655 to 1.660 between $\boldsymbol{E} = 0$ to $\boldsymbol{E} \sim 14$ V/μm ($=\boldsymbol{E}_{\mathrm{th1}}$). For $\boldsymbol{E} > 14$ V/μm, the n_{avg} starts to decrease and surprisingly reduces to 1.61 ($\sim n_o$ at the nematic to the DC phase transition) at $\boldsymbol{E} \sim 21$ V/μm.

We see no significant change in the Sellmeier coefficient B ($=180 \pm 1$ nm) and A follows the refractive index behavior under electric field. The unusual behavior of the average refractive index can be investigated by analyzing the textural transformations that occur during these changes. Interestingly, unlike the DC phase commonly known in the literature, the DC phase of OC12-Ph-ODBP-Ph-C5 possesses no spontaneous chiral domains of opposite handedness at $\boldsymbol{E} = 0$. However, a constant increase in the electric field yields a set of field induced states which have not been seen in the DC phase of other bent-core materials. These changes involve a set of threshold electric fields which are temperature and frequency dependent.

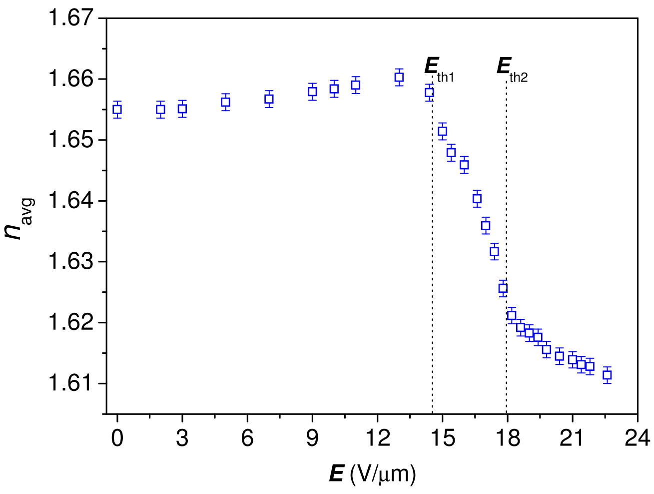

FIG. 4. Electric field dependence of the average refractive index in the DC phase. 8 V/μm $< \boldsymbol{E} <$ 11 V/μm corresponds to an optically uniform very low birefringent state, $\boldsymbol{E} > 14$ V/μm corresponds to domains of opposite handedness and $\boldsymbol{E} > 18$ V/μm corresponds to an achiral state.

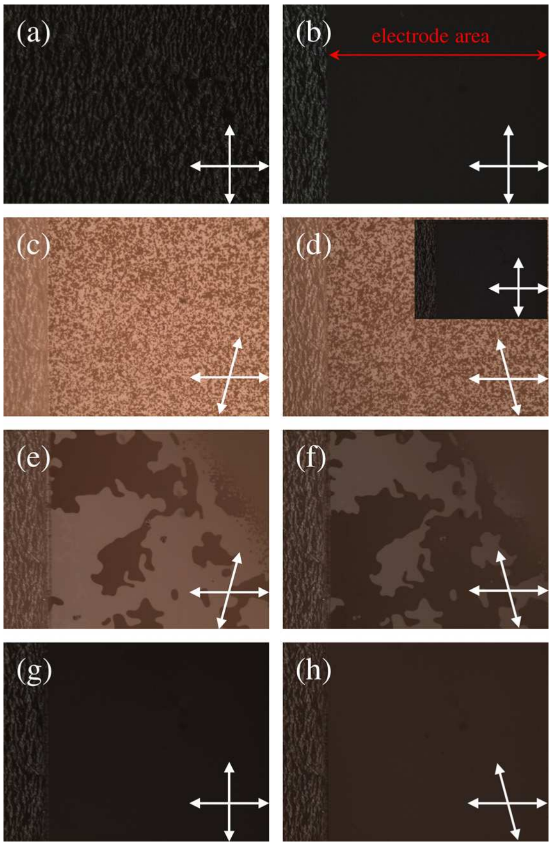

FIG. 5. Polarizing optical microscope textures in the DC phase at $T-T_{\mathrm{N-DC}} = -3$ K under various electric fields. (a) and (b) Under crossed polarizers at $\boldsymbol{E} = 0$ and $\boldsymbol{E} = 8$ V/μm, respectively. (c) and (d) Under uncrossed polarizers at $\boldsymbol{E} = 14$ V/μm—small chiral domains of opposite handedness are visible. (d) Inset: Under crossed polarizers at $\boldsymbol{E} = 14$ V/μm. (e), (f) at $\boldsymbol{E} = 17$ V/μm—disappearance of the chiral domains and (g), (h) at $\boldsymbol{E} = 18$ V/μm—an achiral uniform texture is seen. White arrows indicate the polarizer and the analyzer directions. The red arrow drawn on (b) indicates the area up to which the ITO electrodes extend. Beyond that arrow on the left hand side has no ITO or no electrodes. This is applicable to all photographs.

The polarizing optical microscope textures of the DC phase under electric field are given in Fig. 5. In all these photographs, there is a small area on the left hand side where there is no ITO coating and this is presented to show that the transformations that occur are due to the applied electric field and not because of temperature induced effects such as super cooling. For a particular temperature ($T-T_{\mathrm{N-DC}} = -3$ K) and for a particular frequency (550 Hz) of the applied waveform, on increasing the magnitude of the electric field, initially, no change in the texture occurs for $\boldsymbol{E} < 8$ V/μm. At $\boldsymbol{E} \sim 8$ V/μm, under crossed polarizers, the initial texture with low birefringence domains [Fig. 5(a)] changes to a uniform texture which also has a very low birefringence [Fig. 5(b)]. On further increasing the applied electric field to $\sim$14 V/μm, the texture remains uniform with low birefringence, however, uncrossing the polarizers reveals domains of opposite handedness [Figs. 5(c) and 5(d)] (from the refractive index data, $\boldsymbol{E} \sim 14$ V/μm corresponds to a point where the n_{avg} starts to decrease. See Fig. 4). Further increase in the magnitude of the electric field assists the growth of the chiral domains, in other words, the chiral domains grow as the field increases. At $\boldsymbol{E} \sim 18$ V/μm ($\boldsymbol{E}_{\mathrm{th2}}$), the texture of domains of opposite handedness slowly transforms to a uniform texture or the chiral domains disappear [Figs. 5(e)–5(h)]. These field induced states occur irrespective of the type of the waveform applied (sine, square, and triangular), the sample thickness (1.6 μm to 15 μm) and the geometry of the device (planar and twisted cells) used.

A more detailed description of these transformations and the physical phenomenon responsible for the field induced behavior in the DC phase will be given elsewhere.[26] In short, the above mentioned electric field driven transformations indicate that in the ground state the DC phase of OC12-Ph-ODBP Ph-C5 bent-core liquid crystal has $\mathrm{SmC_aP_A}$

(a-anticlinic and A-antipolar) structure. In SmC_aP_A the layers are homochiral; therefore, any chiral domains in the ground state must be smaller than the wavelength of the visible light. When an electric field is applied to the DC phase, for fields between 8 V/μm and 11 V/μm it appears that the distortion in the sponge structure is eliminated giving rise to a uniform, very low birefringence texture under crossed polarizers. The chiral domains which are initially smaller than the wavelength of visible light continuously grow on increasing the electric field and become visible for $\boldsymbol{E} \sim 14$ V/μm. Once the chiral domains become visible, turning the field off does not cause any change in the size of these domains. One of the possible explanations for the growth of chiral domains under electric field is that the applied electric field reduces the free energy of the system by eliminating the distortion of the director at the boundary between the right and left handed domains. However, as this is commonly true for in-layer boundaries only the exact nature of the free-energy-relevant mechanism responsible for the effect of electric field on the boundaries between the chiral domains needs further investigation.

Further, the process of growth of chiral domains does not stop at 14 V/μm; instead, they continue to grow for further increase in the electric field and at $\boldsymbol{E} > 18$ V/μm, an achiral state is achieved. The whole set of electric field driven transformations observed in the DC phase could be due to a switching from the ground state antiferroelectric arrangement of the layers to the ferroelectric arrangement (i.e., SmC_aP_A to SmC_aP_S) at very high electric fields, taking us through the intermediate states. This is different than the electric-field-induced chirality flipping observed in smectic liquid crystals.[28] The above suggestion is supported because the switching between SmC_aP_A to SmC_aP_S occurs by the rotation of the molecules around their molecular director. This is in line with our experiments where we see no strong birefringence induced during this processes. Also, the SmC_aP_S is a racemic structure, which explains the absence of chirality for $\boldsymbol{E} > 18$ V/μm. During the field-induced transformations, the average refractive index initially increases slightly from 1.655 to 1.660 between $\boldsymbol{E} = 0$ and $\boldsymbol{E} \sim 14$ V/μm. This could be due to the elimination of achiral defects and/or the alignment of the in-layer polarization to the electric field direction. Once the domains of opposite handedness become visible and further grow under electric field, the corresponding n_{avg} starts to decrease. On further increasing the electric field, n_{avg} reduces to 1.61 ($\sim n_o$ at the nematic to the DC phase transition) at $\boldsymbol{E} \sim 21$ V/μm. At this point, one possible description that can explain this behavior ($n_{avg} \sim n_o$) is that the DC phase under very high electric field transforms to a state, where the average molecular director is perpendicular to the substrates and the secondary directors form a twisted structure. A more detailed discussion is given in Ref. 26.

In summary, our results show that in the DC phase an electric field ($\boldsymbol{E}_{th1} = 14$ V/μm $< \boldsymbol{E} < \boldsymbol{E}_{th2} = 21$ V/μm) could be employed to tune the refractive index between the n_{avg} and the n_o without inducing any birefringence in the system and this happens due to a set of rare transformations that occur in the DC phase of OC12-Ph-ODBP-Ph-C5 bent-core liquid crystal. Even though the electric fields involved in these transformations appear relatively higher, they are comparable to the magnitudes involved in the electro-optic effects of other optically isotropic phases, for example the Kerr effect in blue phases.

As discussed before, the electro-optic phenomenon corresponding to an unusual change in the refractive index without changing the birefringence of an optically isotropic phase could be exploited for number applications, where the applied electric field, by modulating the refractive index of the liquid crystal, changes the nature of the propagating light wave. These mainly include integrated optical modulators such as optical waveguides and for fibre-optic core, liquid crystal phase gratings (in the in-plane switching mode) and liquid crystal based tunable lenses. Unlike regularly used nematic liquid crystal infiltrated devices, due to the optically isotropic nature of the DC phase, the advantages of the devices based on the DC phase essentially are no power losses due to scattering, no requirement of alignment layer therefore ease of fabrication, and no polarization sensitive effects. Even though the change in the refractive index (~0.05) achieved during the electro-optic effect in the DC phase is relatively low compared to that achieved during the Freedericks transition in very high birefringence nematic liquid crystals (>0.1) proper molecular design could overcome such limitations.

M.N. thanks the Royal Commission for the exhibition of 1851 for a research Fellowship and L. Tian for useful discussions.

[1] I. C. Khoo and H. Li, Appl. Phys. B **59**, 573 (1994).
[2] A. d'Alessandro, R. Asquini, M. Trotta, G. Gilardi, R. Beccherelli, and I. C. Khoo, Appl. Phys. Lett. **97**, 093302 (2010).
[3] G. Strangi, V. Barna, R. Caputo, A. De Luca, C. Versace, N. Scaramuzza, C. Umeton, R. Bartolino, and G. N. Price, Phys. Rev. Lett. **94**, 063903 (2005).
[4] J. G. Cuennet, A. E. Vasdekis, L. De Sio, and D. Psaltis, Nat. Photonics **5**, 234 (2011).
[5] J. Du, Y. Liu, Z. Wang, B. Zou, B. Liu, and X. Dong, Opt. Lett. **33**, 2215 (2008).
[6] D. C. Wright and N. D. Mermin, Rev. Mod. Phys. **61**, 385 (1989).
[7] Y. Hisakado, H. Kikuchi, T. Nagamura, and T. Kajiyama, Adv. Mater. **17**, 96 (2005).
[8] H. J. Coles and M. N. Pivnenko, Nature **436**, 997 (2005).
[9] G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl, and C. Tschierske, Angew. Chem. Int. Ed. **41**, 2408 (2002).
[10] J. Thisayukta, Y. Nakeyama, S. Kawauchi, H. Takezoe, and J. Watanabe, J. Am. Chem. Soc. **122**, 7441 (2000).
[11] J. Ortega, C. L. Folcia, J. Etxbarria, N. Gimeno, and M. B. Ros, Phys. Rev. E **68**, 011707 (2003).
[12] Y. Zhang, U. Baumeister, C. Tschierske, M. J. O'Callaghan, and C. Walker, Chem. Mater. **22**, 2869 (2010).
[13] W. Weissflog, M. W. Schröder, S. Diele, and G. Pelzl, Adv. Mater. **15**, 630 (2003).
[14] I. Wirth, S. Diele, A. Eremin, G. Pelzl, S. Grande, L. Kovalenko, N. Pancenko, and W. Weissflog, J. Mater. Chem. **11**, 1642 (2001).
[15] S. K. Lee, L. Shi, M. Tokita, H. Takezoe, and J. Watanabe, J. Phys. Chem. B **111**, 8698 (2007).
[16] S. Kawauchi, S.-W. Choi, K. Fukuda, K. Kishikawa, J. Watanabe, and H. Takezoe, Chem. Lett. **36**, 750 (2007).
[17] D. Earl, M. A. Osipov, H. Takezoe, Y. Takanishi, and M. R. Wilson, Phys. Rev. E **71**, 021706 (2005).
[18] H. S. Jeong, S. Tanaka, D. K. Yoon, S.-W. Choi, Y. H. Kim, S. Kawauchi, F. Araoka, H. Takezoe, and H.-T. Jung, J. Am. Chem. Soc. **131**, 15055 (2009).
[19] L. E. Hough, H. T. Jung, D. Krüerke, M. S. Heberling, M. Nakata, C. D. Jones, D. Chen, D. R. Link, J. Zasadzinski, G. Heppke, J. P. Rabe,

W. Stocker, E. Körblova, D. M. Walba, M. A. Glaser, and N. A. Clark, Science **325**, 452 (2009).

[20] S. Kaur, J. Addis, C. Greco, V. Ferrarini, V. Görtz, J. W. Goodby, and H. F. Gleeson, Phys. Rev. E **86**, 041703 (2012).

[21] S. Kaur, H. Liu, J. Addis, C. Greco, V. Ferrarini, V. Görtz, J. W. Goodby, and H. F. Gleeson, J. Mater. Chem. C **1**, 6667 (2013).

[22] H. G. Yoon, N. W. Roberts, and H. F. Gleeson, Liq. Cryst. **33**, 503 (2006).

[23] D. W. Berreman, J. Opt. Soc. Am. **62**, 502 (1972).

[24] M. F. Vuks, Opt. Spektrosk. **20**, 644 (1966).

[25] F. Araoka, T. Otani, K. Ishikawa, and H. Takezoe, Phys. Rev. E **82**, 041708 (2010).

[26] M. Nagaraj, K. Usami, Z. Zhang, V. Gortz, J. W. Goodby, and H. F. Gleeson, “Unusual electric-field-induced transformations in the dark conglomerate phase of a bent-core liquid crystal,” Liq. Cryst. (submitted).

[27] J. Li and S. T. Wu, J. Appl. Phys. **96**, 6253 (2004).

[28] M. Nakata, R.-F. Shao, J. E. Maclennan, W. Weissflog, and N. A. Clark, Phys. Rev. Lett. **96**, 067802 (2006).