TWIST BEND AND DOUBLE TWIST IN LIQUID CRYSTALS

A dissertation submitted
to Kent State University in partial
fulfillment of the requirements for the
degree of Doctor of Philosophy

by

Jie Xiang

August, 2016

© Copyright
All rights reserved
Except for previously published materials
### TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. VI

LIST OF TABLES ..................................................................................................................... XVII

DEDICATION ............................................................................................................................... XVIII

ACKNOWLEDGEMENTS ............................................................................................................ XIX

CHAPTER 1 INTRODUCTION ................................................................................................. 1

1.1 Liquid Crystal Phases ........................................................................................................ 1

1.1.1 Nematic phase and twist bend nematic phase ........................................................... 1

1.1.2 Chiral nematic phase ..................................................................................................... 6

1.1.3 Blue phases .................................................................................................................... 11

1.2 Scope and Objectives of the Dissertation ........................................................................... 14

CHAPTER 2 NEMATIC TWIST BEND PHASE WITH NANOSCALE MODULATION OF MOLECULAR ORIENTATION ......................................................... 19

2.1 Introduction ........................................................................................................................ 19

2.2 Nanoscale Arrangement of Molecular Orientation in Twist Bend Nematic Phase .......... 20

2.2.1 Introduction ..................................................................................................................... 20

2.2.2 Materials .......................................................................................................................... 21

2.2.3 Optical textures and birefringence .................................................................................. 22

2.2.4 Dielectric reorientation of optic axis in N and Nb ......................................................... 24

2.2.5 Nanoscale periodic arrangement of molecular orientation ......................................... 27

2.2.6 Oblique helicoidal geometry of director ........................................................................ 30

2.2.7 Non-uniform Freeze-fracture transmission electron microscopy textures .... 31
2.3 Elastic Constants of Dimer Liquid Crystal Mixture with Negative Dielectric Anisotropy ........................................................................................................ 38

2.3.1 Introduction ............................................................................................. 38

2.3.2 Materials and methods .......................................................................... 41

2.3.3 Results and discussion .......................................................................... 47

2.4 Photo-responsive Twist Bend Nematic Phase ........................................ 50

2.4.1 Introduction ............................................................................................. 50

2.4.2 Material and methods ........................................................................... 50

2.4.3 Results and discussion .......................................................................... 51

CHAPTER 3 ELECTRICALLY CONTROLLED CHOLESTERIC HELICONICAL STRUCTURE ....................................................................................... 62

3.1 Introduction ................................................................................................ 62

3.2 Electrooptic Response of Chiral Nematic with Oblique Helicoidal Director .... 63

3.2.1 Introduction ............................................................................................. 63

3.2.2 Theoretical model .................................................................................. 63

3.2.3 Materials and methods .......................................................................... 66

3.2.4 Results and discussion .......................................................................... 68

3.2.5 Supplemental information ...................................................................... 76

3.3 Electrically Tunable Selective Reflection of Light from Ultraviolet to Visible and Infrared by Heliconical Cholesterics ....................................................... 79

3.3.1 Introduction ............................................................................................. 79

3.3.2 Materials and methods .......................................................................... 82
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.3</td>
<td>Results and discussion</td>
<td>84</td>
</tr>
<tr>
<td>3.4</td>
<td>Full Color Reflective Display Using Cholesteric Heliconical Structure</td>
<td>91</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Introduction</td>
<td>91</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Results and discussion</td>
<td>92</td>
</tr>
<tr>
<td>3.5</td>
<td>Electrically Tunable Laser based on Cholesteric Heliconical Structure</td>
<td>97</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Introduction</td>
<td>97</td>
</tr>
<tr>
<td>3.5.2</td>
<td>Materials and methods</td>
<td>98</td>
</tr>
<tr>
<td>3.5.3</td>
<td>Results and discussion</td>
<td>100</td>
</tr>
<tr>
<td>3.5.4</td>
<td>Supplementary information</td>
<td>106</td>
</tr>
</tbody>
</table>

**CHAPTER 4 FAST SWITCHING NEMATICS TEMPLATED BY THE POLYMER-STABILIZED BLUE PHASE**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>109</td>
</tr>
<tr>
<td>4.2</td>
<td>Materials and Sample Preparation</td>
<td>110</td>
</tr>
<tr>
<td>4.3</td>
<td>Results and Discussion</td>
<td>113</td>
</tr>
</tbody>
</table>

**CHAPTER 5 SUMMARY**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Summary</td>
<td>118</td>
</tr>
</tbody>
</table>

**REFERENCES**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>121</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

**Figure 1.1.** Schematics of local director arrangements in nematics. (a) Nematic N phase, uniaxial alignment, \( \theta_0 = 0 \), (b) Twist-bend N\(_{tb} \), with oblique helicoid \( 0 < \theta_0 < \pi / 2 \), and (c) Chiral nematic N\(^*\) phase, right-angle helicoid, \( \theta_0 = \pi / 2 \) (the twist is right-handed or left-handed, depending on molecular chirality)................................................. 3

**Figure 1.2.** Schematics of local director arrangements in chiral nematic under electric field. (a) Right-angle planar state, helical axis is perpendicular to the substrates, (b) right-angle fingerprint state, helical axis is parallel to the substrates, and (c) heliconical state. ......................................................................................................................... 9

**Figure 1.3.** (a) Blue phase formed by double-twist cylinders, the cylinders pack together to form body-centered cubic structure (BPI), and simple cubic structure (BPII); (b) the double twist cylinders are stabilized by the disclinations, which serving as a template for polymer-mesh trapped at the disclination cores [81]. ................................. 12

**Figure 2.1.** Properties of Ntb materials. (a) Structural formulae and phase diagrams of M1 and M2. (b) Temperature dependence of birefringence and dielectric anisotropy of M2. (c) Temperature dependence of \( K_1 \) and \( K_3 \) for M2......................................................... 22

**Figure 2.2.** Dielectric reorientation of the optic axis in the plane of homeotropic M2 cells. (a) PolScope texture of bend Frederiks transition in the N phase, showing the local optic axis projected onto the cell’s plane (black bars) and the local optical retardation of the cell (pseudocolors). Scale bar 10 \( \mu \)m. Inset shows bend-twist of
the director (red symbols; nails depict titled director). (b) PolScope texture of bend
Frederiks transition in the N\textsubscript{tb} phase showing only splay and saddle-splay
deformations of the optic axis. The inset shows the initial nucleating site in the
shape of an axially symmetric toroidal focal conic domain \[101\] with green lines
following the optic axis. Scale bar 10 \(\mu\)m. (c) Optical retardation of the realigned
N\textsubscript{tb} structure measured along the lines A and B shown in (b). (d) Threshold voltage
of expansion of a realigned N\textsubscript{tb} vs cell thickness \(d\), for \(T = 87^\circ C\) (filled symbols) and
\(T = 86^\circ C\) (open symbols).

**Figure 2.3.** FFTEM textures of Ntb with uniform and arched structures. (a, b) FFTEM
textures and corresponding fast Fourier transform (FFT) patterns of (a) M1 with
pitch \(p_{ib} = 8.05 \text{ nm}\) and (b) M2 with \(p_{ib} = 9.3 \text{ nm}\), viewed in the planes parallel to the
optic axis. The arrows in (a) point towards domain boundaries of average extension
26 nm, which are roughly perpendicular to the N\textsubscript{tb} layers. Presence of domains is
also revealed by a diffuse intensity pattern in FFT, marked by a white arrow in (a).
(c, d) FFTEM image of Bouligand arches in M1 formed as imprints of the oblique
helicoidal structure onto the fracture plane that is (c) almost perpendicular and (d)
almost parallel to the helicoid axis of N\textsubscript{tb}. The insets show the corresponding
schemes of Bouligand arches of two types in N\textsubscript{tb}, calculated for (c) \(\theta_0 = 17^\circ\), \(\psi = 5^\circ\)
and (d) \(\theta_0 = 20^\circ\), \(\psi = 57^\circ\). All scale bars are 100 nm.

**Figure 2.4.** FFTEM textures of non-uniform N\textsubscript{tb} samples. (a) M1 (CB7CB) quenched at
95\(^\circ\)C, showing layered structures of different orientations. The period of most
domains varies between 8.0-8.2 nm. Material: M1. (b) M1 with splay distortions of
the helix axis and atypical periodicity of 7.7 nm. Enlarged portions of the texture are displayed in (d). (c) M2, exhibiting domains with layered structure oriented along different directions. The period of the layered structure varies between 8.6-10.3 nm. Scale bar 200 nm in all images.

Figure 2.5. Scheme of oblique deposition onto the fracture surface of $N_{tb}$. (a) General case, the fracture surface corresponds to minimum density of molecules; period of replica $p_{tb}$; (b) Hypothetical limiting case, period of replica is two times smaller than the helix pitch; deposition direction is orthogonal to the wave-vector of the helix.

Figure 2.6. XRD results for M2 in the N and $N_{tb}$ phases. (a) Typical dependence of diffraction intensity vs. wave-vector $q$, presented in terms of the length scale $a$; inset shows the temperature dependences of $q$ and $\Delta q$, the full width at half maximum of scattered intensity; (b) 2D scattering pattern for the N phase; (c) 2D scattering pattern for the $N_{tb}$ phase.

Figure 2.7. Three types of Bouligand arches predicted by Eq. (2.2). (a) type I, alternating wide and narrow arches, with $\theta_0 = 0.3$, $\psi = 0.1$; (b) type II, $\theta_0 = 0.3$, $\psi = 0.35$; (c) type III, $\theta_0 = \psi = 0.3$.

Figure 2.8. Chemical structures and phase diagram of the dimeric LC mixture M3 with negative dielectric anisotropy.

Figure 2.9. Polarizing optical microscope textures of M3 in a planar cell on cooling: (a) isotropic phase, (b) N phase, (c) $N_{tb}$ phase near the N-$N_{tb}$ transition, (d) stripe texture in the $N_{tb}$ phase. The scale bar is 100 µm.
Figure 2.10. Measurement data of M3 mixture at temperature $T - T_n = -35^\circ C$: (a) Voltage-capacitance curve, (b) Magnetic field-capacitance curve of homeotropic cell with 9.9 µm thickness, to obtain $V_{bb3}$ and $B_{bb3}$, respectively; (c) Magnetic field-intensity curve, and (d) Magnetic field-capacitance curve of planar cell with 19.2 µm thickness, to obtain $B_{bb2}$ and $B_{bb1}$, respectively. The blue lines illustrate how the thresholds are determined by double extrapolation.

Figure 2.11. Temperature dependent dielectric constants of dimeric LC mixtures M3, measured at frequency of 10 kHz.

Figure 2.12. Temperature dependent elastic constants of dimeric LC mixture M3.

Figure 2.13. The temperature dependence of the elastic constants ratios (a) $K_1/K_3$ and (b) $K_1/K_2$ for M3.

Figure 2.14. DSC scans of CB6OABOBu obtained during (a) first cooling, (b) subsequent reheating, (c) second cooling to 100 °C without crystallization, (d) reheating immediately after (c). The insets magnify the weak N_{bb}-N peak seen (i) during the cooling trace shown in (c), and (ii) on reheating shown in (d). All heating and cooling rates: 10 °C/min.

Figure 2.15. Optical textures of CB6OABOBu in (a) the nematic phase at 151 °C, (b) the N_{bb} phase at 89 °C, and (c) N_{bb} phase at 103 °C, observed without the red color filter.

Figure 2.16. Optical textures of CB6OABOBu in a 12 µm PI-2555 planar cell with a red color filter (>600 nm light allowed through). (a) the isotropic phase at 160°C, (b) the
isotropic-nematic phase transition at 159.1°C, (c) the nematic phase at 119.8°C, (d) the nematic-twist bend nematic phase transition at 103.8°C, (e) deep within the twist bend nematic phase at 90°C, and (f) the crystal phase at 79.9°C. ........................................ 54

**Figure 2.17.** FFTEM images of the CB6OCBOBu samples prepared (a) without and (b) with ambient light. The insets correspond to fast Fourier transform patterns. The sharp bright spots (marked by arrows) indicate a well-defined 1D modulation with a periodicity of approximately 18 nm. ................................................................. 55

**Figure 2.18.** The optical textures of CB6OABOBu confined in a 12 μm planar cell obtained with a red color filter (>600 nm light allowed through). (a) The N\textsubscript{tb} phase at 90°C on cooling from the isotropic phase, (b) the N phase after about 30 seconds exposure to UV of intensity 1 mW/cm\textsuperscript{2}, and (c) the N\textsubscript{tb} phase after removing UV for 15 seconds. The textures are of the same area of the sample at 90 °C. .................... 57

**Figure 2.19.** The space filling molecular models for CB6OABOBu with the azobenzene moiety in the (a) trans and (b) cis conformations. ................................................................. 57

**Figure 2.20.** The UV-vis spectrum of CB6OABOBu in a 1.7 μm quartz cell at 90 °C (a) during irradiation by UV light of wavelength 365 nm and intensity 30 mW/cm\textsuperscript{2}, and (b) after turning the UV light off. ................................................................. 59

**Figure 2.21.** Dependence of (a) the time taken to drive the N\textsubscript{tb}-N and N-Iso phase transitions on the intensity of the UV light and (b) the time required for the back relaxation to form the N\textsubscript{tb} phase as a function of applied UV dosage using a UV source of intensity 12.8 mW/cm\textsuperscript{2}. The experiment was done in a 12 μm planar aligned cell, at 90°C. ............................................................................. 60
Figure 3.1. Effect of elastic properties of N* on (a) pitch, (b) cone angle of the field-induced heliconical structure. In (a) and (b), $E_C = \frac{2\pi}{P_0} \sqrt{K_2 / \varepsilon_0 \varepsilon_u}$.

Figure 3.2. Electric-field induced (a) unwound nematic with the director parallel to the electric field; (b) heliconical state with the director following an oblique helicoid with the axis along the electric field, and (c) right-angle helicoid state of the cholesteric, as seen under the polarizing optical microscope. All scale bars are 50μm. (d) First order diffraction angle of the heliconical state as a function of the applied electric field. (e) Optical phase retardance as a function of the applied electric field in the vicinity of nematic-to-heliconical transition.

Figure 3.3. Electric field dependence of (a) heliconical pitch; (b) cone angle, as deduced from the theory, numerical simulations and experiments.

Figure 3.4. (a) The director field in the cell with the homeotropic anchoring under the in-plane electric field, simulated for parameters $\kappa = K_3 / K_2 = 0.12$, $\kappa_1 = K_1 / K_2 = 2.2$, $E / E_{NC} = 0.6$ and $d / P_0 = 1.49$, demonstrating a heliconical structure with $P = 0.20P_0$. (b) In the heliconical state, the polar angle $\alpha$ (thin) and azimuthal angle $\psi$ (dashed) of the heliconical axis $\hat{h}$ as well as the cone angle $\theta$ (thick) are functions of $z$ coordinate across the cell.

Figure 3.5. Temperature dependent pitch $P_0$ of the chiral mixture CB7CB (99wt%) + S811 (1wt%).

Figure 3.6. Electric field in the in-plane switching cells: (a) patterned ITO electrodes at the bottom glass substrate with electrode gap 100μm, and applied voltage 100Vrms;
(b) aluminum foil electrodes between the glass substrates with electrode gap 140μm, and applied voltage 140Vrms. Electric fields strength in the patterned ITO cell (c) and aluminum electrodes cell (d), as a function of the \( z \) coordinate, for different values of the \( x \)-coordinate.

**Figure 3.7.** Field induced behavior of cholesterics structures. (a) Right-angle helicoidal cholesteric with a large bend constant and a positive local dielectric anisotropy in a planar cell. (b) Sufficiently strong vertical electric field \( \mathbf{E} \) realigns the cholesteric axis perpendicularly to itself, causing light-scattering fingerprint texture. (c) Heliconical structure in a cholesteric with a small bend constant and positive dielectric anisotropy stabilized by the vertical electric field \( \mathbf{E} \). (d) The pitch \( P \) and tilt angle \( \theta \) of the field-induced heliconical state both decrease as the electric field increases, \( \mathbf{E}_2 > \mathbf{E}_1 \). (e) As the field increases further, to some \( \mathbf{E}_3 > \mathbf{E}_2 \), it unwinds the helical structure completely and forms a homeotropic nematic state. The figures are not to scale, as the experimental cell thickness is typically 20-50 times larger than the cholesteric pitch \( P_0 \).

**Figure 3.8.** Electric field induced textures in cholesteric mixture M1. Polarizing optical microscope textures of field induced (a) unwound nematic; (b-g) heliconical states with reflected (b) blue, (c) green, (d) orange and (e) red colors, (f and g) two IR-reflective states; (h) fingerprint state. The RMS amplitude of the electric field is indicated on the figures.

**Figure 3.9.** Selective light reflection in M1 cell. (a) Typical reflection spectra of M1 cell at different electric fields, shown underneath the spectra in V/μm units. (b) Electric
field dependencies of the wavelength and bandwidth of the selective reflection peak.

................................................................................................................................. 86

**Figure 3.10.** Selective light reflection in double cell. (a) Reflection wavelength vs electric field for M2 and M3 cells. (b) State (I) transparent in visible and reflecting in IR. The electric field 4.9 V/μm acts on M2 cell and 0.5 V/μm on M3 cell; (c) state (II) transparent in IR and reflecting in visible; 0.9 V/μm at M2 cell and 3.1 V/μm at M3 cell; (d) State (III) reflecting in two different parts of spectrum; 0.9 V/μm at M2 cell and 0.5 V/μm at M3 cell. The textures are taken under a reflective optical microscope with crossed polarizers.......................... 87

**Figure 3.11.** Photographs of the reflective display (area 5 mm×5 mm, thickness 50±2 μm) controlled by an AC field. By changing the electric field, the reflected color changes between (a) blue, (b) green, (c) yellow, and (d) red. The RMS amplitude of the electric field is indicated in the figures.......................... 93

**Figure 3.12.** CIE1931 chromaticity diagram on the basis of 2° viewing angle and D65 illuminant. White open circle shows the color coordinates of the reflected color under different electric fields, calculated from the reflective spectra measured in Fig. 3.11. The white cross corresponds to the white chromaticity.................. 94

**Figure 3.13.** Electrooptic response of cholesteric structures. (a) Schematic illustration of the experiment setup. (b) Transient process when the sample switched from homeotropic state to heliconical state with red reflection color (λ<sub>p</sub>=632nm)......... 95

**Figure 3.14.** Schematic of electrically tunable lasing in dye doped cholesteric heliconical structure. (a) High electric field, unwound CLC helix, no lasing emission. (b)
electrically tunable tunable CLC<sub>OH</sub> structure with lasing emission. (c) Schematic of lasing cell with pump and laser emission beams. Spheres and ellipsoids represent dye molecules and liquid crystal molecules, respectively. ........................................ 97

**Figure 3.15.** Absorbance and fluorescence spectra of laser dyes in CLC mixtures: (a) DCM, (b) LD688. ................................................................. 99

**Figure 3.16.** Electric field controlled selective reflection of light in DCM-doped CLC mixture. Photographs in ambient light condition and corresponding polarizing optical micrographs (a) Electric field unwound homeotropic state; electric field induced CLC<sub>OH</sub> states reflecting (b) blue, (c) green and (d) red visible light. ....... 101

**Figure 3.17.** Electrically tunable lasing from CLC<sub>OH</sub> structure. (a) Reflection bands with associated lasing lines for LD688 dye (top row) and DCM dye (bottom) doped samples at different electric fields, shown underneath the spectra in V/μm units; (b) lasing emission beam profile with low pump energy and from a lasing spot of LD688-doped sample, E=0.78 V/μm, detected 25mm away from the sample; (c) the lasing emission beam from a DCM-doped sample observed on a projection screen, positioned 75 mm from the sample, E=1.05 V/μm for \( \lambda = 591 \text{ nm} \), and \( E=0.99 \) V/μm for \( \lambda = 630 \text{ nm} \). ........................................................................................................ 102

**Figure 3.18.** Lasing efficiency and electrically tunable lasing range. (a) Lasing emission intensity as function of pump energy at \( \lambda = 625 \text{ nm} \) for LD688 sample, and at \( \lambda = 610 \text{ nm} \) for DCM sample. (b) Electric field dependence of the lasing wavelength \( \lambda \) for LD688 and DCM dye doped CLC<sub>OH</sub> samples. (c) Lasing threshold and
intensity as function of lasing wavelength for LD688 sample. Error bars represent standard deviation of lasing emission energy for 40 consecutive pump pulses.

**Figure 3.19.** Spatial profiles of laser emission beam and fluorescence from LD688 sample mixture. (a) & (d) beam profile of 3rd lasing emission pulse, $\lambda = 650\text{nm}$; (b) & (e) beam profile of 7th lasing emission pulse, $\lambda = 650\text{nm}$; (c) & (f) spatial profile of fluorescence. 

**Figure 4.1.** Polarizing optical microscope textures of BP mixture (a) before and (b) after photo-polymerization, (c) after removing the LC; (d) SEM texture of BP-shaped polymer network; (e) 3D arrangement of disclinations in BPI; (f) 2D projection of the disclination network in (e). The scale bar is 100 $\mu$m in (a)-(c), and 2 $\mu$m in (d).

**Figure 4.2.** Polarizing optical microscope textures of BPTN E7 at different temperatures.

**Figure 4.3.** Polarizing microscope textures of BPTN E7 cell under AC electric field $(f = 10\text{ kHz})$ directed at 45 degree with respect to the two crossed polarizes labeled A and P.

**Figure 4.4.** Electro-optic performance of 3.8 $\mu$m IPS BP-templated E7 cell. (a) Phase retardation vs the applied AC field; $f = 10\text{ kHz}$; three cycles of driving at 25$^\circ$C. (b) Temperature dependence of Kerr constant. The line is a guide to an eye.

**Figure 4.5.** Electro-optic response of BP templated E7. (a) applied voltage profile with frequency 1 kHz and (b) corresponding light transmittance at 25$^\circ$C; (c) Temperature
dependence of the on- and off- response times for an applied voltage 100 V at different frequencies. .......................................................... 116
LIST OF TABLES

Table 2.1. Phase behaviour of CB6ABOBu\textsuperscript{a}................................................................. 52

Table 4.1. Comparison of pure BP, polymer-stabilized BP and BP-polymer-templated nematic approaches.................................................................................................................. 117
DEDICATION

To my family.

献给我的家庭
ACKNOWLEDGEMENTS

There are many people to whom I am indebted during the graduate study.

My deepest gratitude is to my advisor, Dr. Oleg D. Lavrentovich, from whom I learnt how to be a good scientist. Without his kind mentoring and support, my PhD study and research won’t be successful and so enjoyable.

I am thankful to my collaborators and lab members and for constant help, inspiration, encouragement and more importantly, criticisms: Dr. Sergij V. Shiyanovskii, Dr. Ming Gao, Dr. Andrii Glovin, Dr. Antal Jakli, Dr. Peter Palffy-Muhoray, Dr. Qihuo Wei, Dr. Corrie Imrie, Olena Iadlovsksa, Greta Cukrov, and Youssef Golestani. Also to Dr. Shuang Zhou, Dr. Volodymyr Borshch, Dr. Young-Ki Kim, Dr. Israel Lazo, Chenhui Peng, Bingxiang Li, Taras Turiv for fruitful discussions and fun memories.

It was a wonderful journey to study in the Chemical Physics Interdisciplinary Program, where I grow in a friendly and supportive environment created by the faculty, technical and administrative staff, and all students. I want to thank all of them for their kind help on numerous occasions. In particular, I am thankful to Dr. Liang-Chy Chien, who enlightens me the first glance of liquid crystal research as a curricular advisor.

I am deeply grateful to my wife, Tracy; my daughter, Alex; parents and friends who always stand by my side.

Jie Xiang

June 12, 2016 at Kent, Ohio
CHAPTER 1

INTRODUCTION

1.1 Liquid Crystal Phases

Liquid Crystals (LCs), also called mesophases, as their name implies, are a state of matter, in which molecules show a long-range orientational order and partial or no positional order [1-3]. LCs are anisotropic media and their optical properties change in the presence of external stimuli, such as electric/magnetic fields, surface anchoring, temperature, light, etc.. These fascinating features enabled the LCs to revolutionize the modern display technology [3,4]. All LCs can be divided into two large classes: thermotropics and lyotropics. The thermotropic LCs exhibit phase transitions into liquid crystal phases as the temperature changes. The lyotropic LCs require a solvent, in which the LC molecules self-assemble into mesogenic building blocks. Phase transitions of lyotropics depend on concentration and in some cases on temperature.

1.1.1 Nematic phase and twist bend nematic phase

In this dissertation, we explore the thermotropic nematic LCs. Nematic liquid crystals with fluid-like arrangements of molecules that pack parallel to each other are widely used in display and other applications because of the unique combination of orientational order and fluidity. In the uniaxial nematic (N) phase, rod-like molecules are on average parallel to the single director \( \hat{n} \), but their centers of mass are arranged
randomly, as in an isotropic fluid, Fig. 1.1a. The director is a non-polar entity, \( \hat{n} = -\hat{n} \), even if the molecules have dipole moments. Chiral molecules prefer to twist with respect to each other, forcing \( \hat{n} \) to follow a right-angle helicoid, either left-handed, or right-handed, thus forming the cholesteric phase (called also a chiral nematic \( N^* \)). In 1973, R.B. Meyer [5] predicted that polar molecular interactions that favor bend deformations might lead to a twist-bend nematic (\( N_{tb} \)) phase with the director bending and twisting in space, forming an oblique helicoid directed along some axis \( z \),

\[
\hat{n} = (\sin \theta_0 \cos \varphi, \sin \theta_0 \sin \varphi, \cos \theta_0),
\]

(1.1)

where \( \varphi = t_b z \) is the azimuthal angle, \( t_b = 2\pi / p_{tb} \), \( p_{tb} \) is the pitch of the helicoid, and \( 0 < \theta_0 < \pi / 2 \) is the angle that the local \( \hat{n} \) makes with the axis \( z \), Fig. 1.1b. Note that Eq.(1.1) describes also \( N \) (when \( \theta_0 = 0 \)) and \( N^* \) (when \( \theta_0 = \pi / 2 \)) phases, Fig. 1.1. Unlike the case of \( N^* \), formation of \( N_{tb} \) does not require molecular chirality, thus one should expect it to contain coexisting domains of left and right chirality [6]. Instead of chirality, \( N^* \) can be facilitated by bent (banana-like) shapes of molecules, as was demonstrated analytically by Dozov [6] and Shamid et al [7], and in molecular simulations by Memmer [8]. A similar structure, but with the hexatic order coupled to twist-bend deformation, has been predicted by Kamien [9].
Figure 1.1. Schematics of local director arrangements in nematics. (a) Nematic N phase, uniaxial alignment, \( \theta_0 = 0 \), (b) Twist-bend \( N_{tb} \), with oblique helicoid \( 0 < \theta_0 < \pi / 2 \), and (c) Chiral nematic \( N^* \) phase, right-angle helicoid, \( \theta_0 = \pi / 2 \) (the twist is right-handed or left-handed, depending on molecular chirality).

Experimentally, some unusual behavior, including a first-order phase transition between two seemingly uniaxial nematic phases, was detected in materials formed by polymer [10,11] and dimer molecules [12-23] in which rigid cores are connected by a flexible aliphatic tail with an odd number of methylene groups. While the high-temperature phase was easily identifiable as a standard uniaxial N phase, the nature of the low-temperature phase (often denoted \( N_x \)) became a subject of intensive exploration, revealing hints that are consistent with the \( N_{tb} \) structure. For example, X-ray diffraction (XRD) shows no periodic variation of the electronic density in the low-temperature phase \([14,17]\), suggesting that the molecular centers of mass are distributed randomly in space;
this excludes the smectic type of order. On the other hand, the optical textures show features such as focal conic domains. As demonstrated by Friedel in 1922 [24], focal conics appear in liquid crystals with one-dimensional positional order. This order can be caused by periodically changing density, as in smectics, or by “wave surfaces” of the director twist, as in N*, with no density modulation [2]. Focal conics should be expected [17] in N_{tb}, since its pitch $p_{tb}$ is fixed by the molecular interactions that favor twist-bend packing. Unlike the case of N*, in which the large pitch makes it possible to trace the helicoidal packing optically, no such clear evidence was presented prior to our research for the N_{tb} candidates. Macroscopic stripes with a period in the range of (1-100) μm often observed in dimer materials [13,14,17] do not represent a thermodynamically stable state, as the period depends strongly on the cell thickness [14]. Recently, N. Clark’s group established by the freeze-fracture transmission electron microscopy (FFTEM) a periodic director modulation in the N_{tb} phase of cyanobiphenyl material (Fig. 2.1a) [22]; the period of 8 nm was not associated with the smectic periodicity. Another important feature, a structural chirality of M1 (Fig. 2.1a) at the short time scales of NMR response, was demonstrated by L. Beguin et al [18]. The first goal of this thesis was to establish the very existence of the N_{tb} phase, in particular, that the director field in this phase does indeed follow the oblique helicoidal structure. In a parallel vein, the thesis also aimed to determine the basic material properties of the N phase at the temperatures above the N- N_{tb} transition temperature, in order to verify whether the driving force for the formation of the new phase is the tendency of the local director to bend.
After the establishment of the existence of the N_{tb} phase in the materials such as 1”,7”-bis(4-cyanobiphenyl-4’-yl)heptane (CB7CB), 1,5-Bis(2’,3’-difluoro-4”-pentyl- [1,1’:4’,1″-terphenyl]-4-yl)nonane (DTC5C9) mixed with 2’,3’-difluoro-4,4″-dipentyl-p- terphenyl (MCT5) [25] the world-wide research activities expanded to other materials. Currently, a number of liquid crystal dimers have been reported to show the N_{tb} phase. Other examples of twist-bend nematogens include two liquid crystal trimers [26,27] and a rigid bent-core liquid crystal [28]. Given such a small data set of molecular structures, our understanding of the empirical relationships between molecular structure and the formation of this fascinating new phase is at a very early stage of development. What appears to be clear, however, is that a bent molecular shape is essential [29] and that macroscopically it yields not only the thermodynamically stable N_{tb} phase but also a standard nematic with an anomalously small bend elastic constant $K_3$ [25,30,31]. The latter feature leads to interesting electro-optical effects in a nematic doped with chiral dopants, such as electrically controlled selective reflection of light [32-36], which will be studied in chapter 3.

In designing new twist-bend nematogens, there exists an intriguing possibility of manipulating molecular shape using external stimuli in order to control the N_{tb} and N phases and their elastic properties. A possible way of achieving this is to utilize the photo-chemically driven trans-cis isomerization seen for azobenzene-based compounds [37]. The well-known effect of trans-to-cis isomerization in these compounds results in lowering of the nematic-isotropic transition temperature; the phenomenon is easy to
explain by the extended shape of trans isomers and bent shape of cis isomers. However, other compounds exhibit an opposite behaviour, with cis isomers stabilizing the nematic phase [38]. These prior results, however, do not provide any definite clues as to what effect trans-cis isomerization might have on a phase transition between the standard nematic phase and its twist-bend counterpart, a transition that is accompanied by the spontaneous chiral symmetry breaking and is thus potentially more sensitive to the fine details of molecular structures than the nematic-to-isotropic transition. The second goal of the thesis was to explore whether the ability to form the N_{tb} phase can be controlled by light; in this study, we used azobenzene-based materials synthesized by Dr. Imrie (Scotland, UK) and his group.

1.1.2 Chiral nematic phase

The cholesteric (CLC), or chiral nematic (N*) phase is highly promising for optical and photonic applications including reflective displays [39], tunable lasers [40], smart windows [41], tunable color filters [42]. The selective reflection of light in the right-angle helicoid N* is a manifestation of the periodic helical organization of the phase which satisfies the condition for Bragg reflection. For light propagating parallel to the helical axis, the central wavelength of the reflection bandgap is defined as: \( \lambda_p = \frac{n}{P} \), where \( P \) is the pitch length of the helical twist of the director and \( n \) is the average refractive index of the liquid crystal. Assuming a constant pitch, the N* reflection bandwidth reads \( \Delta\lambda = \Delta n P \), where \( \Delta n \) is birefringence of the N*.
Dynamic response of the bandgap color and reflectivity can be induced by exposure to a variety of stimuli including electric field, heat, and light [43]. Considering the tuning speed, simplicity, and compatibility with other electrooptic devices, electric field tuning method could be the best choice. The field-induced modification of N* helicoid is typically of the two types: changing the pitch of the right angle-helicoid [1], Fig. 1.2a, (for example, in diffractive elements [44]) or realigning the helicoid axis as the whole [39], Fig. 1.2b. In these effects, the fundamental character of the right-angle helicoidal twist remains intact.

The direct electrical control of reflected color in N* is a nontrivial task due to the fact that the periodic structure becomes distorted in a non-uniform manner and induces a non-uniform coloration and reflectivity. In the case of an electric field applied parallel to the helix axis, the main reason for the disruption of the N* periodic structure is out-of-plane rotation of the helix from the uniform planar state to the disordered focal conic state [1]. Unwinding of the helix using an electric field perpendicular to the helix axis can lead to a change in the wavelength of the reflection band [45,46], but such an approach requires fringe-fields which locally distort the homogeneity of the structure. The Helfrich deformation [47-49] have also been shown to provide a means of change the reflection color with a narrow tuning range, in which the local tilting of helix leads to effective change of the pitch. However, the inhomogeneity of the pitch created by the deformation leads to a broadening of the reflection band and decreases the reflectance level.
There are also a number of reports on color tuning using polymer-stabilized N* and polymer-template of polymer-stabilized N*, utilizing either uniform planar state [50-52] or Helfrich deformation [49]. The difficulties in these techniques are large electric fields, short tuning range of the peak wavelength of the reflected light, and large spectrum bandwidth of the reflection peak. More recently, DC-driven technique has been used in polymer-stabilized N* to have a broadband and wide range color tuning [51]. The effect is due to the movement of locally trapped charges on the polymer surface in response to a DC field, which produce a large deformation of the polymer network leading to a nonlinear pitch extension. Another interesting DC-driven technique of color tuning of N* with negative dielectric anisotropy is the so called “electromechanical effect” [53], where the glass substrates bend due to the Maxwell’s stresses occurred during the application of the electric field, resulting in the blue tuning of the reflection bandgap. The cholesteric N* phase with a negative dielectric anisotropy aligns the helix along the applied electric field, allowing the preservation of the optical bandgap. By applying the DC field, the reflection bandgap shifts by 20% of the original notch position with little change in the quality of the bandgap due to the electromechanical effect [53]. However, DC field induces undesired electro-chemical process in liquid crystals.

Almost 50 years ago, R.B. Meyer [45] and P. G. de Gennes [54] predicted that there should exist a very distinct mode of electrically induced deformation of N*, with the director forming an oblique helicoid with the pitch and cone angle that depend on the applied electric field, Fig. 1.2c. This “heliconical” state was not proven to exist
experimentally for many decades, mainly because its existence requires the bend elastic constant $K_1$ to be much smaller than the twist constant $K_2$, a condition that is not satisfied in typical nematics formed by rod-like molecules. The principal feature of the heliconical structure is that the electric field controls the period of the heliconical structure but does not violate the uniformity of twist and does not create the “walls” inherent to the standard approach of field-unwound cholesterics [55]. These features of the field induced heliconical structure make it suitable for color tuning. The third important goal of the thesis was to establish experimentally the existence of the oblique helicoidal state in a cholesteric material with an anomalously small value of the bend elastic constant, using dimeric molecules similar to those that form the $N_{tb}$ phase, and demonstrate the electrooptic applications of cholesteric heliconical state in color tuning and reflective display.

Figure 1.2. Schematics of local director arrangements in chiral nematic under electric field. (a) Right-angle planar state, helical axis is perpendicular to the substrates, (b) right-angle fingerprint state, helical axis is parallel to the substrates, and (c) heliconical state.
In optically pumped thin layers of CLCs doped with fluorescent dyes, selective Bragg reflection of light gives rise to mirrorless lasing at the reflection band edges. Early demonstrations of lasing from CLCs [56-59] stimulated considerable interest in these easily produced micron-sized laser light sources due to their potential in spectroscopic, communications, sensing and display applications. One major appeal of CLC lasers is the tunability of the emission wavelength by controlling the pitch. This can be achieved by changing the temperature [59-61], composition or cell thickness [62-64], mechanical strain in cross-linked CLC elastomers [65-67], and using reversible photochemical reactions [68,69]. The most sought-after control is via an applied electric field, which, although possible in principle [70-76], has not yet achieved its full potential. The principal difficulty is created by the very geometry of CLC in which the molecules are oriented perpendicularly to the helical axis, as explained below.

CLC molecules tend to align parallel to an electric field $E$ if the local dielectric anisotropy is positive, $\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$ (the subscripts refer to the direction with respect to $\hat{n}$). When $E$ is parallel to the helical axis $\hat{h}$, it rotates the axis. Once $\hat{h}$ is perpendicular to $E$, the field expands the regions where $\hat{n}$ is parallel to $E$, thus introducing higher spatial harmonics into the structure. Such a distorted structure creates additional reflection bands at higher frequencies [77] and dramatically reduces the laser emission intensity [75,78]. Similar distortions occur not only in CLCs but also in chiral smectic C lasers when the applied field is perpendicular to the $\hat{h}$ axis [71]. The electric field tunability of CLC lasers is therefore severely limited [70]. An ideal electrically
tunable CLC laser would be one in which the electric field modifies only the pitch, but preserves the otherwise undistorted helical structure. The fourth goal of this thesis was to explore whether the electrically tunable lasing can be observed in the oblique helicoidal structure of cholesterics with a small bend elastic constant.

1.1.3 Blue phases

Blue phases (BPs) of liquid crystals (LCs) represent an example of a frustrated soft matter system [1,2]. They are formed by chiral molecules that tend to arrange locally into structures with the so-called double twist. Although locally the double-twist is preferable than the single-twist structure (typical of standard cholesteric LCs), it cannot extend itself to fill the entire volume and needs to be stabilized by a lattice of topological defects-disclinations [1,2]. At the cores of disclinations, orientational order is reduced, so that the material can be considered as partially melted. This is why the BPs are typically observed only within a close proximity (one-two degrees) of the isotropic phase. Depending on arrangements of ordered and disordered regions, one distinguishes three classes of the BPs: BPI (body-centered cubic structure), BPII (simple cubic structure) and BPIII (amorphous lattice) [1,2], Fig. 1.3a. In absence of an electric field, the BPs are optically isotropic, i.e., they show no birefringence. An applied electric field breaks the symmetry and causes birefringence \( \Delta n_e = \lambda KE^2 \) that is described as a Kerr effect with the Kerr constant \( K \), generally on the order of \( (10^{-10}-10^{-9}) \text{ m/V}^2 \); \( \lambda \) is the wavelength of probing light [79,80].
Figure 1.3. (a) Blue phase formed by double-twist cylinders, the cylinders pack together to form body-centered cubic structure (BPI), and simple cubic structure (BPII); (b) the double twist cylinders are stabilized by the disclinations, which serving as a template for polymer-mesh trapped at the disclination cores [81].

There are several advantages of using BPs as compared to traditional nematic LCs in practical devices, such as absence of alignment layers and fast (sub-millisecond) optical response to the electric field [79]. However, practical applications of BPs are hindered by intrinsic problems, the most serious of which is the narrow temperature range of BPs.

Two approaches have been demonstrated to extend the BPs temperature range [82-84]. The first one is a polymer-stabilized blue phase (PSBP) [82,83]. One of its drawbacks is the hysteresis of electro-optic response [85]. The second approach is to
search for new LC molecules, such as bimesogens and bent-core liquid crystals [84], that yield beneficial material parameters such as enhanced flexoelectricity [86] and a reduced bend elastic constant [87,88]. However, the bimesogenic and bent-core materials have a relatively low dielectric anisotropy and high viscosity [89], which leads to a longer response time and higher driving voltages [84]. One might hope to formulate a suitable PSBP or BP composition by using a broad-temperature range non-chiral nematic and doping it with a chiral additive, but the latter often reduces the temperature range of the resulting mixture and makes the electro-optic performance very temperature-sensitive [90]. The status of current research makes it clear that the material properties that are beneficial for the temperature stability of BPs are not necessarily beneficial for electrooptic performance. An ideal scenario would be to combine the features from both polymer-stabilized BP (temperature stability, and fast response) and pure BP mixture (hysteresis free) by using polymer-templating technique.

The general idea of mutual LC-polymer templating (transferring LC structure to polymers through photo-polymerization and imposing structural changes in the LCs by the polymer network) has been already explored, see, e.g., Refs.[91,92]. Experimentally, attraction of a polymerizing material to the disclination core has been demonstrated for disclinations in a twisted nematic [93]. Higashiguchi et al. [94] observed spatially periodic polymer networks formed in BPs. Guo et al. [95] described a washout refill method to create hyper-reflective chiral nematics, in which the unpolymerized components are washed out and the residual polymer network is refilled with another LC.
Castles et al.[96] used bimesogenic LCs to prepare a BP-templated polymer network and then refilled it with various nematics, to achieve unprecedented temperature stability (from -125 to 125 °C) and mirrorless lasing. The possibility of electro-optic switching was also demonstrated, although the merit parameters such as switching times and switching amplitude of optical retardance were not characterized. This BP-templated nematic technique has been confirmed by direct electron microscopy observations of the polymer mesh [97,98]. The fifth goal of this thesis was to use polymer template as a matrix for a broad-temperature range blue phase. The template is first polymerized within a normal blue phase; this blue phase material is then washed out and the polymer template is refilled with a new liquid crystal with properties appropriate for electrooptic applications and the structure being shaped by the polymer template to be of the blue phase type.

1.2 Scope and Objectives of the Dissertation

The scope of this dissertation is the study of the twist bend and double twist structures in the thermotropic LCs. The study involves various experimental techniques, such as polarizing optical microscopy, scanning electron microscopy, transmittance electron microscopy, LC-PolScope, electro-optics, and so on.

The objectives of the dissertation are: (i) to prove the very existence of the N_{tb} phase, and explain the driving force for the formation of oblique helicoidal director field in the N_{tb} phase; (ii) to explore the light-controlled formation of the N_{tb} phase using azobenzene-based liquid crystal dimers; (iii) to establish experimentally the existence of
the oblique helicoidal (heliconical) state in a cholesteric material placed in an external electric field, and demonstrate the electrooptic effects such as color tuning, suitable for reflective display application; (iv) to explore whether the electrically tunable lasing can be observed in the cholesteric heliconical structure; (v) to use polymer template as a matrix for a broad-temperature range blue phase with sub-millisecond response time.

The dissertation is organized as follows.

Chapter 2 describes the new type of orientational nematic order, twist bend nematics, in which achiral dimer molecules forms oblique helicoidal structure with nanoscale periodicity. In this chapter, we also present the elastic properties of the dimer LC mixture with negative dielectric anisotropy that forms the $N_{lb}$ phase. In addition, this chapter describes the photo-responsive $N_{lb}$ phase with the dimer molecules that contains azobenzene moieties.

Chapter 3 describes the new type of cholesteric structure, namely, the cholesteric heliconical structure, which was predicted 50 years ago but never observed before. In this chapter, we also present the applications of cholesteric heliconical structure in color tuning, reflective display, and tunable lasing.

Chapter 4 describes fast electrooptic switching (response time 0.1 ms) of a blue-phase-polymer templated nematic with a broad-temperature range of thermodynamic stability and hysteresis-free performance.

Chapter 5 summarizes the results in this dissertation.
The following publications cover the topics discussed in the dissertation:


The research also resulted in the following publications:


and four more manuscripts that are currently being prepared for submission:


CHAPTER 2
NEMATIC TWIST BEND PHASE WITH NANOSCALE MODULATION OF
MOLECULAR ORIENTATION

2.1 Introduction

As described in Chapter 1, the twist bend nematic (N_{tb}) phase was predicated by R.B. Meyer [5] in 1973, who stated that polar molecular interactions that favor bend deformations might lead to the director bending and twisting in space, forming an oblique helicoidal structure.

In this chapter, we demonstrate the existence of the N_{tb} phase through the freeze-fracture transmittance electron microscopy (FFTEM), electrooptic response, elastic constants measurement. We also explore the effects of photo-isomerization on the N-N_{tb} phase transition using an azobenzene-based non-symmetric liquid crystal dimer. The N_{tb} phase is confirmed by using polarizing optical microscopy and FFTEM. We observe an isothermal, reversible N_{tb}-N transition, which is attributed to a trans-cis photo-isomerization of the azobenzene fragment on UV irradiation. The cis isomers stabilizing the standard nematic phase and the trans isomers stabilizing the N_{tb} phase.

This chapter is organized as follows.

In section 2.2, we present the nanoscale arrangement of molecular orientation in the twist bend nematic phase. Section 2.3 presents the elastic constants of the dimer
liquid crystal mixture with negative dielectric anisotropy. Section 2.4 presents the photo-responsive twist bend nematic phase.

2.2 Nanoscale Arrangement of Molecular Orientation in Twist Bend Nematic Phase

2.2.1 Introduction

In this section, we present the result of a comprehensive experimental exploration of the nematic states in two different dimeric LC materials. The main result is that in addition to the N phase, both types of dimeric materials feature an \( N_{tb} \) phase with the local director (defined as the average orientation of the dimeric arms) shaped as an oblique helicoid, Fig. 1.1b. The oblique helicoidal structure of \( N_{tb} \) is evidenced by freeze-fracture transmittance electron microscopy (FFTEM) textures of Bouligand arches [99] of two distinct types. The local director is modulated along the helicoidal axis with a period \( p_{tb} \) of about (8-9) nm, which is 2-3 orders of magnitude shorter than typically found in the chiral \( N^* \) phase. Electrooptic response in an alternating current (AC) electric field shows that the field-induced reorientation of \( N_{tb} \) allows splay and saddle-splay of the optic axis but neither bend nor twist; as a result, the bend Frederiks transition is dramatically different in the two phases. The effect is a natural consequence of the equidistance of layers, \( p_{tb} = \text{const.} \) The tendency of the molecules to form local bend-twist configurations as a condition of the N-\( N_{tb} \) transition is confirmed by the temperature dependence of the bend modulus \( K_3 \) measured in the N phase: \( K_3 \) decreases near the
transition into the $N_{tb}$ phase to the anomalously low levels. We have published these results in [25].

### 2.2.2 Materials

The studied materials M1 and M2 are shown in Fig.2.1a. M1 material, $1''',7''''$-bis(4-cyanobiphenyl-4'-yl)heptane (CB7CB), was synthesized by the groups of G. Mehl and C. Imrie as described in Ref. [100]. The dimer has a longitudinal dipole moment at each arm. M1 shows a positive dielectric anisotropy $\varepsilon_a = \varepsilon || - \varepsilon \perp > 0$ in the $N$ phase (the subscripts indicate directions parallel to $\hat{n}$ and perpendicular to it). M2 is a mixture, of a dimer $1,1,1$-Di(2',3''-Difluoro-4-pentyl[1,1';4',1'']terphen-1''-yl)undecane (DTC5C9) and a monomer MTC5 (added in order to improve alignment, reduce viscosity and working temperatures); weight proportion is DTC5C9 (70wt%):MTC5(30%). The dielectric anisotropy of M2 is negative, $\varepsilon_a < 0$, which allows us to illustrate a dramatic difference of elastic properties and dielectric response of $N$ and $N_{tb}$ by exploring the bend Frederiks transition between the homeotropic and distorted state of the optic axis in both phases.
Figure 2.1. Properties of Ntb materials. (a) Structural formulae and phase diagrams of M1 and M2. (b) Temperature dependence of birefringence and dielectric anisotropy of M2. (c) Temperature dependence of $K_1$ and $K_3$ for M2.

2.2.3 Optical textures and birefringence

M1 and M2 show a similar phase diagram: A uniaxial N at high temperatures $T$ and a different phase N$_{tb}$ at lower $T$. In cells with homeotropic alignment (achieved by an inorganic passivation layer NHC AT720-A Nissan Chemical Industries, Ltd.), the N texture observed between two crossed polarizers is uniformly dark, as it should be, as the
optic axis $\hat{n}$ is along the direction of observation. In the $N_{tb}$ state, the texture remains dark, i.e., the material remains optically uniaxial.

In planar cells (aligned by rubbed polyimide PI2555 films (HD Microsystem)), the phase transition $N$-$N_{tb}$ upon the temperature decrease in both M1 and M2 is evidenced by a propagating front after which a texture of stripes is established. These range from faint stripes of sub-$\mu$m scale to macroscopic stripes, (10-100) $\mu$m wide. These stripes are not thermodynamically stable. By applying an AC electric field of a frequency 10 kHz (parallel to $\hat{n}$ in M1 and perpendicular to $\hat{n}$ in M2), we eliminate the stripes to achieve an optically homogeneous state. If the field is removed and the temperature is fixed or raised, the stripe pattern does not reappear. These uniform states were used to determine birefringence in both phases, Fig. 2.1b. By averaging the tilted director field in Eq. (1.1) for $\theta_0 > 0$, the effective birefringence $\Delta\bar{n}$ of the conical helix in $N_{tb}$ phase can be related to the corresponding quantity $\Delta n = n_e - n_o > 0$ ($n_e$ and $n_o$ are the extraordinary and ordinary refractive indices, respectively) in the $N$ phase with unwound helix $\theta_0 = 0$ (presumed to be at the same temperature)

$$\Delta\bar{n} = \sqrt{n_e^2 - \left(n_e^2 - n_o^2\right)}\sin^2\theta_0 - \sqrt{n_o^2 + \frac{1}{2}\left(n_e^2 - n_o^2\right)}\sin^2\theta_0 \approx \Delta n \left(1 - \frac{1}{2}\theta_0^2\right) \quad (2.1)$$

Equation (2.1) predicts that the birefringence of the $N_{tb}$ phase, as compared to the $N$ phase, decreases by a factor $\left(1 - 3\theta_0^2 / 2\right)$. For M2, the decrease of birefringence is about 7% from its maximum value in the N phase, which allows us to estimate the tilt as
\( \theta_0 \approx 17^\circ \) at 79\(^\circ\)C. If the temperature of the homogeneous sample is reduced, the stripes typically reappear. This behavior is consistent with the Helfrich-Hurault undulation (buckling) instability observed in smectics and N\(^*\), and caused by the temperature-induced decrease in layers periodicity (pitch) [2]. We conclude that the true layered nature of N\(_{tb}\) must be associated with (optically) invisible submicron features.

The elastic constants of M2 were determined by the Frederiks effect techniques, which will be discussed in details in the next section. As shown in Fig. 2.1c, behavior of \( K_1 \) is typical for N materials, while that of \( K_3 \) is not, as \( K_3 \) decreases to a very low value 0.77 pN as the temperature is lowered towards the N-N\(_{tb}\) transition; similarly small \( K_3 \) was recently measured for a mixture of dimers [23].

### 2.2.4 Dielectric reorientation of optic axis in N and N\(_{tb}\)

The behavior of homeotropic cells of M2 under a vertical AC field, which has been performed by Dr. Borshch, allowed us to trace an important difference in the Frederiks reorientation of the N and N\(_{tb}\) phases. In the N phase, Fig. 2.2a, once \( U > U_{th} \), the optic axis realigns gradually and everywhere, as in the second-order transition. Since the tilt direction is degenerate, it results in umbilics, i.e., defects of winding numbers -1 and +1, Ref. [1]. The +1 umbilics show an in-plane bend of \( \mathbf{n} \), which is expected, as \( K_3 \ll K_1 \). The same experiment in N\(_{tb}\) reveals a completely different scenario. Reorientation of the optic axis starts only at isolated sites of the sample, associated with dust particles or surface irregularities. The nucleating regions in the shape of
axisymmetric focal conic domains [101] coexist with the homeotropic surrounding (inset in Fig. 2.2b); they expand if the voltage is higher than some threshold \( \tilde{U}_{th} \). The deformations of the optic axis are of splay and saddle splay type, Fig. 2.2b.

The profile of optical retardation measured across the domain of reoriented \( N_{tb} \) reaches a maximum at the center of the domain, Fig. 2.2c, indicating that the tilt of the optic axis is at a maximum in the center. Thus the pattern is similar to the field-induced reorientation in smectic A [101] and \( N' \) [102] phases with \( \varepsilon_a < 0 \), in which the layers equidistance allows splay and saddle-splay, but prohibits bend and twist of the layers’ normal. The threshold voltage \( \tilde{U}_{tb} \) of expansion in layered liquid crystals is determined mostly by the balance of surface anchoring at the plates and the dielectric reorienting torque, so that [101,102] \( \tilde{U}_{tb} = 2 \frac{dW}{\varepsilon_0 |\varepsilon_a|} \propto \sqrt{d} \), where \( W \) is the surface anchoring strength and \( d \) is the cell thickness; the dependence \( \tilde{U}_{tb} \propto \sqrt{d} \) agrees with the experiment, Fig. 2.2d. In the N phase, the Frederiks voltage threshold does not depend on \( d \). The peculiar character of the dielectric response provides another argument in favor of periodic nature of \( N_{tb} \) at the scales much shorter than the visible scales.
**Figure 2.2.** Dielectric reorientation of the optic axis in the plane of homeotropic M2 cells. (a) PolScope texture of bend Frederiks transition in the N phase, showing the local optic axis projected onto the cell’s plane (black bars) and the local optical retardation of the cell (pseudocolors). Scale bar 10 μm. Inset shows bend-twist of the director (red symbols; nails depict titled director). (b) PolScope texture of bend Frederiks transition in the N_{tb} phase showing only splay and saddle-splay deformations of the optic axis. The inset shows the initial nucleating site in the shape of an axially symmetric toroidal focal conic domain [101] with green lines following the optic axis. Scale bar 10 μm. (c) Optical retardation of the realigned N_{tb} structure measured along the lines A and B shown in (b). (d) Threshold voltage of expansion of a realigned N_{tb} vs cell thickness d, for T = 87°C (filled symbols) and T = 86°C (open symbols).
2.2.5 Nanoscale periodic arrangement of molecular orientation

To prepare the replica specimens for FFTEM, we put ~0.6 μl of material between two copper planchettes. The sandwich structure was heated (125°C for M1, and 155°C for M2, respectively) to obtain isotropic phase, and then cooled down and kept at deep N_{tb} phase temperature for 5 minutes, 95°C for M1 (T_{M1}^{N_{tb}} = 103°C) and 80°C for M2 (T_{M2}^{N_{tb}} = 88°C). The sample was quenched by plunge freezing in liquid nitrogen, with a high cooling rate >1000°C/s, in order to avoid further phase transitions, and quickly transferred into a freeze-fracture vacuum chamber (BalTec BAF060) where the assembly is kept at -140°C. Inside the chamber, a built-in microtome was used to break the assembly and expose the fractured surface. ~4 nm thick Pt/C was then deposited onto the fractured surface at a 45° angle to create shadowing of the surface structure, followed by a ~20 nm thick C deposition from the top to form a continuous supporting film. The samples were then warmed up and removed from the freeze fracture machine. The liquid crystal material was dissolved in chloroform, while the replica film (often flakes) was picked up and placed onto carbon coated TEM grid and observed using room temperature TEM (FEI Tecnai F20).

The layered structure of N_{tb} phase is clearly evidenced in FFTEM images of Pt/C replicas of fractured M1 (Fig. 2.3a, Fig. 2.4a,b,d), and M2 (Fig. 2.3b, Fig. 2.3c). Most of them show a one-dimensional layered structure with a period ~$(8–9)$ nm, corresponding to the pitch $p_{tb}$ of director deformations, in agreement with the findings by Chen et al for
M1 [22]. In M1, the regularly observed value of \( p_{\text{ib}} \) is 8.05 nm, Fig. 2.3a, while in M2, \( p_{\text{ib}} = 9.3 \) nm, Fig. 2.3b. Frequent observation of layers that are perpendicular to the fracture plane, Fig. 2.3a,b, correlates with the theoretical predictions and experiments [103] on freeze-fractured N and N*, in which the fracture plane tends to be parallel to \( \mathbf{\hat{n}} \), as it minimizes the density of molecules in the cut surface. In the N\textsubscript{th} phase, the surface with the minimum molecular density is not flat, but modulated with a period \( p_{\text{ib}} \). This leads to a shadowing effect and explains why oblique deposition of the Pt/C film yields the period \( p_{\text{ib}} \), Fig. 2.5a. On rare occasions, FFTEM textures of M1 exhibit rather unusual patterns with a period smaller than 8 nm, e.g., 7.7 nm (Fig. 2.4b), 7.4, 4.8, and 3.4 nm (Fig. 2.4d). It is unlikely that all of these small periods can be explained by absence of shadowing effect when the oblique deposition direction happens to be perpendicular to the wave-vector \( t_{\text{ib}} \) of the N\textsubscript{th} helix, Fig. 2.5b. Most likely, these small periods are associated with packing of different conformers that are known [104] to exist in dimer materials similar to M1 and M2. The energy difference between the conformers is very small [104], thus some of them might form twist-bend structures with the period different from \( p_{\text{ib}} = (8-9) \) nm of the prevailing conformer.
Figure 2.3. FFTEM textures of Ntb with uniform and arched structures. (a, b) FFTEM textures and corresponding fast Fourier transform (FFT) patterns of (a) M1 with pitch $p_{tb} = 8.05 \text{ nm}$ and (b) M2 with $p_{tb} = 9.3 \text{ nm}$, viewed in the planes parallel to the optic axis. The arrows in (a) point towards domain boundaries of average extension 26 nm, which are roughly perpendicular to the N$_{tb}$ layers. Presence of domains is also revealed by a diffuse intensity pattern in FFT, marked by a white arrow in (a). (c, d) FFTEM image of Bouligand arches in M1 formed as imprints of the oblique helicoidal structure onto the fracture plane that is (c) almost perpendicular and (d) almost parallel to the helicoid axis of N$_{tb}$. The insets show the corresponding schemes of Bouligand arches of two types in N$_{tb}$, calculated for (c) $\theta_0 = 17^\circ$, $\psi = 5^\circ$ and (d) $\theta_0 = 20^\circ$, $\psi = 57^\circ$. All scale bars are 100 nm.
2.2.6 Oblique helicoidal geometry of director

The second important type of FFTEM textures is that of periodic arches, Fig. 2.3c,d. These arches are very different from the celebrated Bouligand arches [99] of the cholesteric N* liquid crystals. In N*, each arch corresponds to a rotation of \( \hat{n} \) by \( \pi \) and any two adjacent arches are indistinguishable from each other, as should be for a right-angle helicoid. In the N_{tb} phase, the geometry is very different, Fig. 2.3c,d and Fig. 2.7, since the underlying structure is an oblique helicoid rather than a right-angle helicoid. Little is known that in the Appendix of the original paper [99], in addition to the N* arches, Bouligand also considered asymmetric arches for a hypothetical fractured system of oblique helicoids. We extend his approach to the specific case of Eq. (2.1), written for the unit director field. Suppose that the plane of fracture (xy') is tilted around the axis \( x \), Fig. 1.1b, by an angle \( \psi \) measured between the new axis \( y' \) and the original axis \( y \).

The director components in the fracture plane are

\[ n_x = \cos t_{tb} \sin \theta_0 \]
\[ n_y = \sin t_{tb} \sin \theta_0 \cos \psi - \cos \theta_0 \sin \psi \]  

The local orientation of the director projection in the obliquely fractured N_{tb} phase is then given by the equation

\[ \frac{dx}{dy'} = \frac{\cos (t_{tb} y' \sin \psi) \sin \theta_0}{\sin (t_{tb} y' \sin \psi) \sin \theta_0 \cos \psi - \cos \theta_0 \sin \psi} \]

with the solution

\[ x - x_0 = \frac{2 \cos \psi \sin \theta_0 \left[ \sin (t_{tb} y' \sin \psi) - \tan \psi \cot \theta_0 \right]}{t_{tb} \sin \psi \cos \psi} \]  

(2.2)
Here $x_0$ is the shift of one arch with respect to the other. Equation (2.2) distinguishes three types of the Bouligand arches that should be observed in a material with oblique helicoidal structure: type I for $\psi < \theta_0$, Fig. 2.7a, with alternating wide and narrow arches, type II for $\psi > \theta_0$, with a wavy structure, Fig. 2.7b, and intermediate type III, with $\psi = \theta_0$, that is hard to distinguish from the classic symmetric $N^*$ arches, Fig. 2.7c. The type I and II arches, never seen in the chiral nematic $N^*$ phase, are readily distinguishable in the textures of the $N_{tb}$ phase, Fig. 2.3c and 2.3d, respectively. In type I, inset in Fig. 2.3c and Fig. 2.7a, the director imprint rotates in the entire range $(0-2\pi)$ of azimuthal angles in the fracture plane, but the odd and even arches are of a different width, $l_{0,2\pi} \neq l_{\pi,2\pi}$. Type II represents a wavy structure that extends in the direction normal to the helicoidal axis but do not explore the entire range of azimuthal orientations, Fig. 2.3d and Fig. 2.7b, in contrast to other types of Bouligand arches where the azimuthal reorientation is by $\pi$ within each arch. Observation of type I and type II arches provides a clear evidence of the oblique helicoidal structure of the $N_{tb}$ phase.

2.2.7 Non-uniform Freeze-fracture transmission electron microscopy textures

FFTEM textures show that the $N_{tb}$ structure is sometimes modulated not only in the direction of helix axis, but also along other directions, in particular, in the $xy$ plane perpendicular to the helix axis, Fig. 2.3a, and Fig. 2.4. For example, in Fig. 2.3a, the periodic arrangements of twist-bend director have a limited width of about 20-30 nm. The domains are separated by structure-less boundaries, with no clear periodicity on the
scales of $p_{tb}$, apparently of an N type. The modulation might be caused by defects such as grain boundaries, screw dislocations parallel to the helicoidal axis, and by coexistence of left-handed and right-handed twisted domains. Homochiral domains have been indeed observed in electro-optical studies [15,20,21], but at a much larger (supramicron) scale. One should expect that the spatial extension of the homochiral domains is determined by the kinetic history of sample preparation, confinement conditions, and other factors, such as presence of the electric field [15]. Further exploration is needed to understand the exact mechanisms behind the modulated structures seen in Fig. 2.3a. Such a work is in progress.

Besides the domain textures of $N_{tb}$ with abruptly changing orientation of the helix axes $t_{tb}$, Fig. 2.4a,c, one also observes regions with smooth splay type reorientation of $t_{tb}$, marked in Fig. 2.4b. Splay deformation seen in FFTEM textures at the nanoscale is consistent with the idea that the deformed $N_{tb}$ structure tends to preserve the pitch of helicoid and with the observation of splay and saddle-splay deformations on the optical (micrometer) scales, Fig. 2.2b. Predominance of splay and saddle splay in the distorted configurations of $t_{tb}$, combined with the very small (nanometers) period of the oblique helicoidal structure makes the polarizing microscope textures of the $N_{tb}$ phase very similar to those of the smectic phases.
Figure 2.4. FFTEM textures of non-uniform N_{16} samples. (a) M1 (CB7CB) quenched at 95°C, showing layered structures of different orientations. The period of most domains varies between 8.0-8.2 nm. Material: M1. (b) M1 with splay distortions of the helix axis and atypical periodicity of 7.7 nm. Enlarged portions of the texture are displayed in (d). (c) M2, exhibiting domains with layered structure oriented along different directions. The period of the layered structure varies between 8.6-10.3 nm. Scale bar 200 nm in all images.
Figure 2.5. Scheme of oblique deposition onto the fracture surface of N\(_{tb}\). (a) General case, the fracture surface corresponds to minimum density of molecules; period of replica \(p_{tb}\); (b) Hypothetical limiting case, period of replica is two times smaller than the helix pitch; deposition direction is orthogonal to the wave-vector of the helix.

The X-ray diffraction (XRD) study, performed by Dr. Jakli, shows that the pitch of (8-9) nm of the N\(_{tb}\) phase in M2 is not associated with the smectic-like modulations, as the intensity of X-ray scattering is featureless in the range 5 nm-14 nm, Fig. 2.6a. Smaller repeat distances of ~2.2 nm are observed in both N and N\(_{tb}\) phases, but the correlation length of these is relatively small, up to 9 nm, Fig. 2.6a, indicating that the long-range structure of both N and N\(_{tb}\) is nematic, Fig. 2.6b,c, rather than smectic-like. One should not exclude the possibility of cybotactic clusters, embedded into the N\(_{tb}\).
phase. Recently, Meyer, Luckhurst and Dozov [21] explored the flexoelectric effect in M1 and suggested that its features are consistent with an oblique helicoidal structure with $p_{tb} = 7$ nm, if one assumes standard values of the flexoelectric coefficients. This estimate is very close to the periodicities directly seen in Fig. 2.3a,b, and Fig. 2.4.

**Figure 2.6.** XRD results for M2 in the N and N$_{tb}$ phases. (a) Typical dependence of diffraction intensity vs. wave-vector $q$, presented in terms of the length scale $a$; inset shows the temperature dependences of $q$ and $\Delta q$, the full width at half maximum of scattered intensity; (b) 2D scattering pattern for the N phase; (c) 2D scattering pattern for the N$_{tb}$ phase.
Figure 2.7. Three types of Bouligand arches predicted by Eq. (2.2). (a) type I, alternating wide and narrow arches, with $\theta_0 = 0.3$, $\psi = 0.1$; (b) type II, $\theta_0 = 0.3$, $\psi = 0.35$; (c) type III, $\theta_0 = \psi = 0.3$.

The structural, elastic, optical, dielectric and electrooptical properties of the two different families of dimer compounds clearly demonstrate the existence of the N$_{tb}$ phase with a local twist-bend structure. The results underscore a complex interplay between the flexible nature of the achiral dimeric molecules with aliphatic chains containing an odd number of methylene groups, and their chiral nanoscale organization. The prevailing element of the twist-bend nematic order is an oblique helicoid, Fig. 1.1b, formed by the local director, associated with the average orientation of the dimers’ arms. The oblique helicoidal structure reveals itself in the unique shape of the Bouligand arches that are either asymmetric (type I, Fig. 2.3c, Fig. 2.7a) or not fully developed in the sense of director rotations in the fracture plane (type II, Fig. 2.3d and Fig. 2.7b). These two types of arches are different from the classic cholesteric arches that are always symmetric and fully developed [99]. The type I and II arches were originally proposed by Bouligand as
a hypothetical imprint of chiral fibrilles in chromosomes of Dinoflagellates [99], but were not observed so far.

The FFTEM measurements reveal that the periodic modulations of the director along the helical axis has a very short period, about 8-9 nm for both studied materials M1 and M2. These data compare well to the FFTEM data by Chen et al [22] and estimates based on electro-optic response [21] of M1. Although one does observe a typical period of (8-9) nm, there are also examples of much shorter periodicity, from 7.7 nm to 3.4 nm. Another aspect of nanostructural organization that deserves further studies is a modulation in the direction more or less perpendicular to the helicoidal axes, that can be caused by structural defects such as screw dislocations and by coexisting left- and right-twisted domains.

By exploring the dielectric response, we demonstrated that the classic Frederiks effect in the homeotropic cells is very different when staged in the normal N phase and in the N\textsubscript{tb} phase, because of the tendency of twist-bend director modulations to keep equidistance. The temperature dependence of the bend modulus and its very low value near the N-N\textsubscript{tb} phase transition put a new challenge to our understanding of molecular mechanisms of elastic properties of liquid crystals. A closely related issue is the relationship between the twist-bend N\textsubscript{tb} structure and double-twist structure of the blue phases that are known to be stabilized by the dimeric molecules [84]. Further studies of the N\textsubscript{tb} phase promise a dramatic improvement of our understanding of the long-range orientational order which shows new intriguing facets at the nanoscale.
2.3 Elastic Constants of Dimer Liquid Crystal Mixture with Negative Dielectric Anisotropy

2.3.1 Introduction

As already indicated, dimeric liquid crystals, formed by molecules with two rigid rod-like units connected by a flexible bridge, attracted a strong research interest because of their fascinating features [17,105]. In particular, dimeric mesogens with an odd number of methylene flexible links form oblique helicoidal director structures in the nematic phases, in which the local director experiences permanent and constant bend and twist. The complex interplay between the molecular structure and the macroscopic director field has been envisioned in the theoretical predictions of the twist-bend nematic phase [5-7] and field-induced oblique helicoidal structures [45]. In particular, Dozov [6] suggested that the twist-bend nematic could appear upon cooling of a uniaxial nematic formed by the molecules of a bent shape. The bent shape can result in spontaneous bend deformation of the director and a change of the sign of the bend elastic constant $K_3$ from positive to negative as one crosses the N-N_{ob} transition point. Uniform bend, however, cannot be realized in space without other types of deformations, either splay or twist. Thus two different variations of the nematic with spontaneous bend have been proposed by Meyer [5] and Dozov [6]: a twist-bend nematic and a splay-bend nematic (yet to be discovered experimentally). The relative stability of the two is controlled by the ratio of the splay to bend constants. Namely, in the twist-bend phase, $K_1/K_2 > 2$, while in the
splay-bend case, $K_1/K_2 < 2$ [6,7]. As for the oblique helicoidal cholesteric state, Meyer [45] predicted that it can be induced by an external electric or magnetic field in a cholesteric liquid crystal only when $K_3 < K_2$. In calamitic nematics formed by rod-like molecules, the latter condition is not satisfied; the expected and universally observed trend follows the inequalities $K_3 > K_1 > K_2$ [106].

The consideration above shows that the dimeric materials are expected to feature elastic properties that are very different from the elasticity of rod-like nematogens. So far, the elastic constants have been measured for a number of dimers. Atkinson et al. [107] demonstrated a strong odd-even effect in the behavior of the bend elastic constant. Two similar dimers, one with an even number of “links” in the bridge chain and another one with an odd number of links, were characterized by the splay Frederiks transition technique. In this approach, the splay constant $K_1$ is determined from the threshold field of the director reorientation, and the bend constant $K_3$ is obtained by exploring voltage dependence of capacitance far above the threshold field. $K_3$ of the odd homolog was found to be about (3-4) pN in a broad temperature range, much smaller (by a factor of 7) than the corresponding value for the even homolog; the results were in good agreement with the theoretical consideration of the odd-even effect by Cestari et al [16]. Yun [108] applied a similar technique to determine the elastic constants for the most studied dimer, abbreviated as CB7CB. It was found that in the temperature range (93.3-105) °C $K_3$ is significantly smaller than both $K_1$ and $K_2$, reaching a minimum value of about 0.3 pN;
the ratio $K_1/K_2$ was approximately constant in (93.3-105) °C range, at the level of 1.4, i.e., lower than 2. The latter result is somewhat surprising, as $K_1/K_2$ is expected to be larger than 2 in CB7CB, since this material does exhibit a twist-bend nematic phase rather than a splay-bend nematic, as demonstrated in the FFTEM studies in Section 2.2 and by the resonant carbon soft X-ray scattering [109]. Balachandran et al [110] used the splay Frederiks transition approach for another typical bimesogen, CB11CB, and found that as the temperature decreases, $K_3$ becomes smaller than $K_1$; near the transition to the N$_{tb}$ phase, $K_3=6$ pN, while $K_1=15.5$ pN. Adlem et al [23] explored multicomponent mixtures of dimeric materials by the dynamic light scattering; the latter allows one to extract all three bulk elastic constants of the material in the region close to the phase transition. They found even more dramatic difference, with $K_3=(0.3-2)$ pN and $K_1=(11-14)$ pN in the N phase at the temperature about one degree above the N-N$_{tb}$ phase transition; the ratio was determined to be somewhat higher than 2.

All the experiments listed above were performed on materials with a positive dielectric anisotropy, $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp > 0$, where the subscripts refer to the orientation of the field with respect to the director. The standard approach is to use a single uniformly aligned planar cell and apply the electric field across it. At some threshold, the director starts to deviate from the planar orientation by developing weak splay deformations in the center of the cell; this threshold determines the splay constant $K_1$. As the field increases, the distorted region expands and the director acquires bend deformations in addition to
the predominant splay. By extrapolating and fitting the response function (such as capacitance of the cell or transmitted light intensity), one can deduce the value of $K_3$. The approach is very reasonable when the elastic constant $K_3$ is comparable or larger than $K_1$. However, when $K_3 \ll K_1$, the extrapolation method is less reliable. A preferable method would be a bend Frederiks transition caused by an external field in a so-called homeotropic cell. To date, however, homeotropic alignment of dimeric nematics has been achieved only for the materials with negative dielectric anisotropy, $\varepsilon_a < 0$.

The goal of this work is to present the temperature dependence of the bend elastic constant of the N phase formed by dimeric molecules determined through the direct determination of the Fredericks threshold in homeotropic cells. The measurements are performed for two different materials with $\varepsilon_a < 0$. The temperature dependencies of $K_3$ are compared to those of $K_1$ and $K_2$; the latter two are determined by the combination of electric and magnetic field-induced effects. The results demonstrate that $K_3$ reaches very small values, about 0.5 pN when approaching the N-N_{tb} transition, while both $K_1$ and $K_2$ increase strongly when the temperature is lowered; the ratio $K_1/K_2$ remains larger than 2.

2.3.2 Materials and methods

We explore a dimeric LC mixture, with chemical structures shown in Fig. 2.8. The mixture, named M3, is comprised of a dimer 1,1,1-Di(2′,3″-Difluoro-4-propyl[1,1′;4′,1″]terphen-1″-yl)undecane (DTC3C11) and a monomer 2′,3′-difluoro-
4,4”-dipentyl-p-terphenyl (MCT5), mixed in weight proportion DTC3C11(65%) + MCT5(35%). The monomer is added to improve alignment, reduce viscosity and working temperatures. On cooling from the isotropic phase, M3 first shows a uniaxial nematic (N) at high temperatures and a twist-bend nematic phase N\_tb at lower temperatures. The presence of N\_tb phase in the M3 was established on the basis of the characteristic stripe and focal conic domains polarizing-microscopy textures, similar to those observed in other studies of the N\_tb phase [17,25,111-113].

The homeotropic alignment of M3 was achieved on glass plates coated with an inorganic passivation layer NHC AT720 (Nissan Chemical Industries, Ltd.). The N textures observed between two crossed polarizers are uniformly dark, as they should be, as the optic axis $\hat{n}$ is along the direction of observation. All textural observations were performed using a polarizing optical microscope (POM) [Nikon, Optiphot-2 Pol] equipped with a hot-stage LTS350 and a controller TMS94 (both Linkam Instruments) with the temperature control 0.01 °C. Conoscopy observations confirm the uniform homeotropic alignment. In the N\_tb state, the orthoscopic texture remains dark, that is, the material remains optically uniaxial with the optic axis oriented perpendicular to the bounding plates. We also prepared planar cells, using rubbed polyimide PI2555 layers (HD Microsystems). The characteristic textures of planar cells are shown in Fig. 2.9. On cooling the homeotropic and planar cells, the N-N\_tb transition is clearly evidenced by a propagating front that quenches fluctuations of the director in the N phase. All samples were first heated to the isotropic phase and then cooled down at a rate of 0.2 °C/min.
Figure 2.8. Chemical structures and phase diagram of the dimeric LC mixture M3 with negative dielectric anisotropy.

Figure 2.9. Polarizing optical microscope textures of M3 in a planar cell on cooling: (a) isotropic phase, (b) N phase, (c) N_{lb} phase near the N-N_{lb} transition, (d) stripe texture in the N_{lb} phase. The scale bar is 100 µm.

For dielectric characterization, we used an impedance gain analyzer HP4284A that measures complex values of impedance \( z = \text{Re}(z) + i\text{Im}(z) \). The effective dielectric permittivity across the cell of thickness \( d \) was calculated as \( \varepsilon = (C_\varepsilon \omega \text{Im}(z))^{-1} \), where
$C_e$ is the capacitance of the empty cell and $\omega$ is the angular frequency of the applied electric field. For these measurements we used planar cells of thickness $d = 19.2 \pm 0.5 \mu m$; and homeotropic cells of thickness $9.9 \pm 0.2 \mu m$. The AC electric field of frequency 10 kHz was applied parallel to the unperturbed director along the normal to the cell plates. The relatively high frequency of the field assured that the flexoelectric and surface polarization contributions [114] to the electrooptical response of the cell are minimized. The voltage was changed in the range 0-20 V with a typical step of 0.02 V; in this range, no electrohydrodynamic flows were observed. The dielectric permittivity coefficient $\varepsilon_\parallel$ was determined from the capacitance measured at low voltages, below the Frederiks threshold $V_{th3}$ of the bend deformation, Fig. 2.10a. The perpendicular component $\varepsilon_\perp$ was measured by extrapolating the voltage dependency of capacitance in the high voltage range, 10-20 V, to $V \to \infty$. The accuracy of dielectric permittivity coefficients $\varepsilon_\parallel$ and $\varepsilon_\perp$ is limited by the resolution of the impedance meter, which is better than 0.1%.

To determine the bend elastic constant $K_3$, we measured the voltage dependence of capacitance $C$ of a uniform homeotropic cell, as described by Deuling [115]. The bend constant is obtained by measuring the bend Frederiks threshold $V_{th3}$ and the relationship $K_3 = \varepsilon_0 \varepsilon_\perp V_{th3}^2 / \pi^2$, Fig. 2.10a. The accuracy of measurements is determined by how well one defines the threshold; we used the so-called double extrapolation approach [116,117]; the accuracy of $K_3$ measurements is 1.6% at $T - T_n = -35 ^\circ C$ for M3.
The bend Frederiks transition in homeotropic cell can also be triggered by the magnetic field directed perpendicularly to the director, as the diamagnetic anisotropy of M3 is positive, $\Delta \chi = \chi_0 - \chi_\perp > 0$. The magnetic threshold $B_{th3}$ was determined by measuring the cell’s capacitance vs magnetic field strength, Fig. 2.10b. Using the expression $K_3 = \left( \frac{dB_{th3}}{\pi} \right)^2 \Delta \chi / \mu_0$, where $\mu_0 = 4\pi \times 10^{-7}$ H/m; and comparing the bend constant to the value obtained in the electric Frederiks effect, we determined the diamagnetic anisotropy $\Delta \chi = \epsilon_0 \mu_0 \epsilon_a \left( V_{th3} / dB_{th3} \right)^2$. For example, $\Delta \chi = (0.79 \pm 0.03) \times 10^{-6}$ at $T - T_m = -35^\circ C$ for M3. The measured values of $\Delta \chi$ are used in measuring the splay and twist elastic constants in planar cells.

There are several approaches to measure $K_2$, such as the Frederiks transition in a twisted nematic (TN) cell, in-plane realignment in a planar cell, a dynamic light scattering method, etc. The measured value of $K_2$ in these methods is usually less accurate than those of $K_1$ and $K_3$, since the twist deformations are accompanied by bend and splay. For example, in the TN cell method, $K_2$ depends on $K_1$ and $K_3$, so that the errors in $K_1$ and $K_3$ are accumulated into the value of $K_2$. To avoid these complications, we use the twist Frederiks transition caused by the magnetic field acting on a planar cell in such a way that the field is perpendicular to the director but lies in the plane of the cell. At a certain threshold $B_{th2}$, the uniform cell experiences pure twist deformation, which allows us to determine the twist elastic constant,
$$K_2 = (dB_{th2}/\pi)^2 \Delta \chi / \mu_0.$$ The difficulty of this technique is that the cell capacitance does not change during the transition and one needs to resort to the optical characterization.

We used a planar sample placed between two crossed polarizers and tested transmittance of the He-Ne laser beam ($\lambda = 632.8$ nm). The beam impinged at an angle $7.6^\circ$ with respect to the surface normal (normal incidence does not allow to discriminate between the uniform and the twisted states because of the Mauguin effect) [118,119]. The output light intensity was measured as a function of the magnetic field to determine $B_{th2}$ and thus $K_2$, Fig. 2.10c. The accuracy of the latter was determined to be 5% at $T - T_{ni} = -35^\circ$C for M3. The main sources of the error are cell thickness error, $\Delta \chi$ error, and also fitting error of the threshold $B_{th2}$. The fitting error of $B_{th2}$ becomes large when the temperature is close to the iso-N transition.

The elastic constant of splay $K_1$ was obtained by determining the threshold $B_{th1}$ of the splay Frederiks transition in a planar sample caused by the magnetic field applied perpendicularly to the bounding plates, Fig. 2.10d. The director reorientation was monitored by measuring the capacitance. The splay elastic constant is found from the expression

$$K_1 = (dB_{th1}/\pi)^2 \Delta \chi / \mu_0.$$
Figure 2.10. Measurement data of M3 mixture at temperature $T - T_m = -35^\circ$C: (a) Voltage-capacitance curve, (b) Magnetic field-capacitance curve of homeotropic cell with 9.9 µm thickness, to obtain $V_{th3}$ and $B_{th3}$, respectively; (c) Magnetic field-intensity curve, and (d) Magnetic field-capacitance curve of planar cell with 19.2 µm thickness, to obtain $B_{th2}$ and $B_{th1}$, respectively. The blue lines illustrate how the thresholds are determined by double extrapolation.

2.3.3 Results and discussion

The temperature dependencies of dielectric permittivities for M3 are shown in Fig. 2.11. The data demonstrate clearly that the dielectric anisotropy $\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is negative in the entire N range.
Figure 2.11. Temperature dependent dielectric constants of dimeric LC mixtures M3, measured at frequency of 10 kHz.

In the N phase of the dimeric materials M3, both $K_1$ and $K_2$ increase with decreasing temperature, whereas $K_3$ shows a non-monotonous behavior, Fig. 2.12. As the temperature is reduced from the clearing point $T_{ni}$, $K_3$ first increases, reaching a maximum at about the ratio of $K_1/K_2$ is bigger than 2 in the entire N phase region. In conventional rod-like nematic liquid crystals, $K_3$ is usually larger than $K_1$, but $K_3$ for these dimeric LC materials is significantly lower than $K_1$, especially when approaching the N-N_{tb} transition.
The measured elastic properties of M3 dimeric materials agree with Dozov’s predication [6] that the $N_{tb}$ phase, rather than the splay-bend phase, is stable when $K_1/K_2 > 2$, Fig. 2.13.

**Figure 2.12.** Temperature dependent elastic constants of dimeric LC mixture M3.

**Figure 2.13.** The temperature dependence of the elastic constants ratios (a) $K_1/K_3$ and (b) $K_1/K_2$ for M3.
2.4 Photo-responsive Twist Bend Nematic Phase

2.4.1 Introduction

In this section, we explored the photo-isomerization effect on the N-N_{tb} phase transition, using a dimer liquid crystal material containing an azobenzene moiety, synthesized by Dr. Imrie (Scotland, UK) and his group. Upon UV irradiation, photo-isomerization of the azo moiety generates the cis isomer, which suppress the N_{tb} phase and in favour of the N phase. We have published these results in [120].

2.4.2 Material and methods

The azobenzene-based dimeric LC material used in this section is 1-(4-butoxyazobenzene-4'-yloxy)-6-(4-cyanobiphenyl-4'y)l)hexane, namely, CB6OABOBu.

\[
\text{NC-}
\begin{array}{c}
\text{-} \\
\text{(CH}_2\text{)}_9\text{O-}
\end{array}
\text{N-}
\begin{array}{c}
\text{-} \\
\text{OC}_4\text{H}_6
\end{array}
\]

To confirm the formation of the N_{tb} phase of CB6OABOBu, freeze fracture transmission electron microscopy (FF-TEM) was used. The procedure adopted is similar to the one described previously in details elsewhere [25,121] and is briefly outlined here. To prepare the replica specimens of CB6OABOBu for FF-TEM, ~0.6 µl of material was put on top of a copper planchette. The sample was first heated to 170 °C to obtain the isotropic (Iso) phase and then cooled to 90 °C at a rate of 2 °C/min, and kept at 90 °C (a temperature within the N_{tb} phase) for 5 min. The sample was then quenched by rapidly freezing in liquid N_{2} (rate >1000 °C/s) to avoid further phase transitions and quickly
transferred to a freeze-fracture vacuum chamber (BalTec BAF060), where the sample was kept at -165 °C. To ensure no photo-isomerization during sample preparation, the entire sample preparation process was performed in a dark environment. Only low intensity of light with λ>650 nm was used to observe the sample. Inside the chamber, a built-in microtome was used to cut the sample and expose a fractured surface. 4 nm thick of Pt was then deposited onto the fractured surface, followed by a 20 nm thick carbon deposition to form a supporting film. Samples were then slowly warmed to room temperature and removed from the freeze fracture chamber. Liquid crystalline material was removed by dissolving in chloroform and the replica film was placed onto the carbon coated TEM grid and observed at room temperature with TEM (FEI Tecnai F20).

The UV-vis spectra of CB6OABOBu were measured using a spectrophotometer Cary 50-Vis (Agilent) in transmission mode. The material was filled into a 1.7 µm planar quartz cell, and the spectra collected at 90 °C. The sample was initially in the N phase and the spectra collected for several UV on/off cycles.

2.4.3 Results and discussion

The phases, transition temperatures, and transition enthalpies of CB6OABOBu are listed in Table 2.1, and Fig. 2.14 shows the associated DSC traces. The enthalpy change associated with the N-N_{tb} transition is very small, Fig. 2.14. The N phase was identified on the basis of the polarizing microscopic observation of characteristic director fluctuations and Schlieren texture containing both two- and four-brush singularities, Fig. 2.15 and 2.16. On cooling, the Schlieren texture changed to give rise to regions of
fanlike textures with non-periodic stepped edges in coexistence with a striated texture characteristic of the N$_{tb}$ phase, Fig. 2.16b. In all cases, the formation of the N$_{tb}$ phase is accompanied by the cessation of optical flickering associated with director fluctuations of the conventional nematic phase.

**Table 2.1.** Phase behaviour of CB6ABOBu$^a$.

<table>
<thead>
<tr>
<th></th>
<th>$T_{Cr}$</th>
<th>$T_{N_{tb}-N}$</th>
<th>$T_{N-Iso}$</th>
<th>$\Delta H_{Cr}$</th>
<th>$\Delta H_{N_{tb}-N}$</th>
<th>$\Delta H_{N-Iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td>(°C)</td>
<td>(°C)</td>
<td>(kJ/mol)</td>
<td>(kJ/mol)</td>
<td>(kJ/mol)</td>
<td></td>
</tr>
<tr>
<td>104.8</td>
<td>105.5</td>
<td>152.7</td>
<td>49.40</td>
<td>0.06</td>
<td>1.43</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Data extracted from DSC measurements on heating at 10 °C/min.

**Figure 2.14.** DSC scans of CB6OABOBu obtained during (a) first cooling, (b) subsequent reheating, (c) second cooling to 100 °C without crystallization, (d) reheating immediately after (c). The insets magnify the weak N$_{tb}$-N peak seen (i) during the cooling trace shown in (c), and (ii) on reheating shown in (d). All heating and cooling rates: 10 °C/min.
Figure 2.15. Optical textures of CB6OABOBu in (a) the nematic phase at 151 °C, (b) the N_{tb} phase at 89 °C, and (c) N_{tb} phase at 103 °C, observed without the red color filter.

To study the optical textures of CB6OABOBu in the absence of the effects of UV light, a red color filter was used. Figure 2.16 shows the optical textures for a planar-aligned sample in a rubbed PI-2555 cell (d=12 μm) with a red color filter (>600 nm light allowed through). Uniform alignment of the sample in the N phase is seen in Fig. 2.16c. On entering the N_{tb} phase, a striped texture develops parallel to the rubbing direction, characteristic of the N_{tb} phase, Fig. 2.16d. The formation of the N_{tb} phase is visible as a propagating front that separates the conventional N phase with optical flickering of the textures, associated with director fluctuations, and flickering-free N_{tb} texture with “frozen” defects such as focal conic domains and stripes described for other N_{tb} materials [17,25]. We will return to a discussion of the effect of light on the phase behavior of CB6OABOBu later.
Figure 2.16. Optical textures of CB6OABOBu in a 12 μm PI-2555 planar cell with a red color filter (>600 nm light allowed through). (a) the isotropic phase at 160°C, (b) the isotropic-nematic phase transition at 159.1°C, (c) the nematic phase at 119.8°C, (d) the nematic-twist bend nematic phase transition at 103.8°C, (e) deep within the twist bend nematic phase at 90°C, and (f) the crystal phase at 79.9°C.

The layered structure of the N_{tb} phase is clearly evidenced in freeze fracture transmission electron microscopy (FFTEM) images of Pt/C replicas of the fractured sample, Fig. 2.17. The periodic pattern observed in the TEM textures corresponds to the variable director tilt with respect to the plane of view. The textures in Fig. 2.17a correspond to the field of view that is parallel to the heliconical axis of the N_{tb} phase. Variable tilt of the director results in local ridges and valleys of the fracture; their presence is visualized by the Pt/C deposits that form a thicker film on one side of the
ridges; the periodicity of the dark and fright regions of the replica corresponds to the pitch of the heliconical structure. The pitch determined from the TEM textures of the replicas is around 18nm, i.e., about twice the pitch measured for the $N_{tb}$ phase shown by CB7CB [22,25]. It is important to note that if the CB6OCBOBu samples are prepared under ambient light conditions (without red color filters), the corresponding fractures show no periodic features, Fig. 2.17b; the latter strongly suggests that ambient light causes a transformation of the $N_{tb}$ phase into the conventional uniaxial $N$ phase.

**Figure 2.17.** FFTEM images of the CB6OCBOBu samples prepared (a) without and (b) with ambient light. The insets correspond to fast Fourier transform patterns. The sharp bright spots (marked by arrows) indicate a well-defined 1D modulation with a periodicity of approximately 18 nm.
We now return to consider the effects of UV light on the phase behavior of CB6OABOBu. The reversible nature of this isothermal, photo-chemically driven N_{tb}-N phase transition is evident in Fig. 2.18. Fig. 2.18a shows the optical texture when viewed through the polarized light microscope with a red color filter on cooling the sample into the N_{tb} phase. The sample was irradiated using a UV light source of intensity 1 mW/cm². After about 30 s of light exposure, the sample had undergone a transition into the nematic phase, Fig. 2.18b. The light was switched off, and in about 15 s, the N_{tb} phase reappeared, Fig. 2.18c.

The N_{tb} textures in Fig. 2.18a,c exhibit focal conic domains similar to those observed in smectics and short-pitch cholesterics. Although the two textures are different in details, they have a common feature: the long axes of the elliptic based of the focal conic domains are parallel to the direction of rubbing. This alignment is dictated by geometry of the domains; the normal to the N_{tb} pseudo-layers lie in the plane of the elliptical base and run along the radial lines emanating from one of the two foci of the ellipse [2]. As a results, the in-plane surface anchoring energy is minimized when the long axis of the ellipse is parallel to the rubbing direction, Fig. 2.18a,c. Focal conic domain textures in other N_{tb} materials show similar alignment [111]. Because the UV irradiation does not change the direction of rubbing, the focal conic textures before and after irradiation show similarly arranged focal conic domains.
Figure 2.18. The optical textures of CB6OABOBu confined in a 12 μm planar cell obtained with a red color filter (>600 nm light allowed through). (a) The N_{1b} phase at 90°C on cooling from the isotropic phase, (b) the N phase after about 30 seconds exposure to UV of intensity 1 mW/cm², and (c) the N_{1b} phase after removing UV for 15 seconds. The textures are of the same area of the sample at 90 °C.

(a) 
(b) 

Figure 2.19. The space filling molecular models for CB6OABOBu with the azobenzene moiety in the (a) trans and (b) cis conformations.
The change in the phase behavior of azobenzene-based liquid crystals induced by UV light is attributed to the photo-isomerization of the azo-linkage and the concurrent change in molecular shape, Fig. 2.19. To verify that CB6OABOBu undergoes photochemical isomerization, we measured the UV-vis spectra of the material at 90 °C, i.e., in the N_{tb} phase, before and after exposure to UV light of wavelength 365 nm, Fig. 2.20. Prior to irradiation, the UV-vis spectrum contains a strong peak at around 365 nm associated with the $\pi-\pi^*$ transition of the trans form and a much smaller peak at around 450 nm associated with the weak, symmetry forbidden $\pi-\pi^*$ transition of the cis form. Irradiation causes the amplitude of the 365 nm peak to decrease and that of the 450 nm peak to increase, indicating trans-cis photo-isomerization of the azobenzene units, Fig. 2.20a. The peaks evolve with the exposure time and saturate after about 30 s. When the UV irradiation is switched off, a slow thermal cis-trans relaxation is observed, manifested by an increase in the intensity of the 365 nm peak and a simultaneous decrease of the 450nm peak, Fig. 2.20b.
Figure 2.20. The UV-vis spectrum of CB6OABOBu in a 1.7 μm quartz cell at 90 °C (a) during irradiation by UV light of wavelength 365 nm and intensity 30 mW/cm², and (b) after turning the UV light off.

Figure 2.21a shows the time taken for a given intensity of UV light to drive the N_{1b}-N and N-Iso phase transitions at 90 °C. For example, for a UV light intensity of 50.1 mW/cm², it takes around 9 s to convert the N_{1b} phase into the N phase and a further 8 s to obtain the isotropic phase. A considerably lower UV dosage is required to drive the N_{1b}-N than the N-Iso transition. Figure 2.21b shows the dependence of the time taken after applying a given dosage of UV radiation to drive the formation of the N phase to the reappearance of the N_{1b} phase. The time taken for the reappearance of the N_{1b} phase increases with the UV dosage applied and appears reach a limiting value, presumably the photo-stationary concentration. We note that throughout these cycling experiments no appreciable changes in the transition temperatures were observed after leaving the
samples overnight to relax, strongly suggesting that no chemical degradation had occurred during these experiments.

**Figure 2.21.** Dependence of (a) the time taken to drive the N\textsubscript{tb}-N and N-Iso phase transitions on the intensity of the UV light and (b) the time required for the back relaxation to form the N\textsubscript{tb} phase as a function of applied UV dosage using a UV source of intensity 12.8 mW/cm\textsuperscript{2}. The experiment was done in a 12 µm planar aligned cell, at 90°C.

It is clear that the isothermal phase transitions observed for CB6OABOBu when illuminated by UV light are driven by changes in the concentration of the cis isomer, Fig. 2.20. In particular, cis isomers destabilize the N\textsubscript{tb} phase toward a formation of the standard N phase and then destabilize the N phase by causing a transition to the isotropic phase. Although the second transition is not surprising and has been observed for other azobenzene-based nematics, destabilization of N\textsubscript{tb} is rather surprising. To explain it qualitatively, we must consider the shapes of the trans and cis isomers, Fig. 2.19. In the trans form, the molecular bend is governed by the geometry of the spacer giving a
spatially uniform bend. By comparison, in the cis isomer the bent fragments occur at two different locations (the azobenzene moiety and the spacer), causing a reverse in the bend polarity as one moves from one end of the molecule to the other end. Such a spatially varying bend is hardly compatible with local packing requirements of the \( N_{\text{th}} \) phase.

We have shown that CB6OABOBu exhibits the fascinating twist bend nematic phase, \( N_{\text{th}} \), and that this may be attributed largely to the bent shape of the trans isomer of the molecule. The material shows an isothermal \( N_{\text{th}} \)-N transition when illuminated by UV light that is driven by the photo-isomerization of the azo linkage generating the cis isomer. This transition is reversible on removing the light source driven by the thermal relaxation giving the trans isomers. At higher concentrations of cis isomers, one observes a classic effect of the nematic-isotropic phase transition, described for other azobenzene-based liquid crystals. In principle, one might expect the cis isomers to enhance the tendency to form the \( N_{\text{th}} \) phase because these are generally more strongly bent than the trans isomers. However, our findings indicate clearly that in the studied material with molecules that combine a flexible aliphatic bridge and the azobenzene moieties the cis isomer suppresses the \( N_{\text{th}} \) phase in favor of the N phase. We attribute this to the particular shape of the cis isomer of CB6OABOBu, in which the polarity of bend is different in the aliphatic and azobenzene parts of the molecule. This prompts the fascinating question, however, as to whether the photo-controlled shape of CB6OABOBu can be used to control the bend elastic constant in the nematic phase and selective reflection of light its chiral version; such studies are underway.
CHAPTER 3

ELECTRICALLY CONTROLLED CHOLESTERIC HELICONICAL STRUCTURE

3.1 Introduction

In this chapter, we demonstrate the existence of the oblique helicoidal state in a cholesteric LC formed by molecular dimers, in which the flexible aliphatic chain that links two rigid rod-like arms makes the ratio $\kappa = K_3 / K_2$ anomalously small [23,25,110]. Theoretical, numerical, and experimental analysis establishes that both the pitch and the cone angle of the oblique helicoid increase as the electric field decreases. The effect can enable many applications that require dynamically controlled transmission and reflection of light. We demonstrate the electrooptic applications using the cholesteric heliconical structure, such as the electrically tunable selective reflection of light, full color reflective display, and electrically tunable lasing.

This chapter is organized as follows.

In section 3.2, we present the electrooptic response of chiral nematic with oblique helicoidal director. Section 3.3 explores electrically tunable selective reflection of light from ultraviolet to visible and infrared using the cholesteric heliconical structure. Section 3.4 presents the full color reflective display application, and section 3.5 demonstrates the electrically tunable lasing application of the heliconical cholesterics.
3.2 Electrooptic Response of Chiral Nematic with Oblique Helicoidal Director

3.2.1 Introduction

In this section, we prove the existence of the cholesteric heliconical structure with the presence of the electric field, which is predicated by Meyer and de Gennes many years ago [45,54]. We expand the theory to describe how the cone angle of the heliconical structure changes with the electric field, and also describe the cholesteric states diagram when the electric field changes. We have published these results in [32,34].

3.2.2 Theoretical model

The field-induced director deformations are described within the framework of the Frank-Oseen free energy functional. Neglecting the effects of electric field non-locality, the energy density for a left-handed \(N^*\) writes

\[
f = \frac{1}{2} K_1 (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_2 (\hat{n} \cdot \nabla \times \hat{n} - q_0)^2 + \frac{1}{2} K_3 (\hat{n} \times \nabla \times \hat{n})^2 - \frac{1}{2} \epsilon_a \epsilon_0 (\hat{n} \cdot \mathbf{E})^2,
\]

where \(K_1\) is the splay elastic constant, \(q_0 = 2\pi / P_0\), \(P_0\) is the pitch of \(N^*\), \(\epsilon_a = \epsilon_\parallel - \epsilon_\perp > 0\) is the local dielectric anisotropy, representing the difference between the permittivity parallel and perpendicular to \(\hat{n}\); \(\mathbf{E}\) is the applied electric field. In absence of the field, the ground state is a right-angle left-handed helicoid \(\hat{n} = (\cos q_0 y, 0, \sin q_0 y)\). Suppose that the field is applied along the \(x\)-axis, \(\mathbf{E} = (E,0,0)\). When the field is very high, the director is parallel to it, \(\hat{n} = (1,0,0)\), because \(\epsilon_a > 0\). Suppose now that the field is reduced, so that
the tendency to twist caused by chiral nature of molecules can compete with the dielectric
torque. Below some threshold field \[ E_{NC} = \frac{2\pi}{P_0} \sqrt{\varepsilon_0 \varepsilon_a K_2}, \]
the unwound nematic transforms into a heliconical state with the director that follows an oblique left-handed
helicoid, \( \mathbf{n} = (\cos \theta, \sin \theta \sin \varphi, \sin \theta \cos \varphi) \) with the cone angle \( \theta > 0 \) and the angle of
homogeneous azimuthal rotation \( \varphi(x) = 2\pi x / P \). The heliconical pitch \( P \) is inversely
proportional to the field \[ \frac{2\pi}{P_0} \sqrt{\varepsilon_0 \varepsilon_a K_2}, \]
where \( \kappa = K_3 / K_2 \).

Minimization of the free energy functional based on Eq. (3.1) also relates the cone
angle \( \theta \) to the strength of the electric field:

\[
\sin^2 \theta = \frac{\kappa}{1 - \kappa} \left( \frac{E_{NC}}{E} - 1 \right).
\]  

(3.3)

Since \( \varepsilon_a > 0 \), it is clear, however, that the cone angle would not increase
continuously to its limiting value \( \theta = \pi / 2 \) as that would mean \( \mathbf{n} \) being perpendicular to
\( \mathbf{E} \) everywhere. One should thus expect a complete reorganization of the oblique helicoid
with an axis along \( \mathbf{x} \parallel \mathbf{E} \) into a right-angle helicoid with the axis perpendicular to \( \mathbf{E} \), at
fields lower than:

\[
E_{N^{PC}} \approx E_{NC} \frac{\kappa \left( 2 + \sqrt{2(1 - \kappa)} \right)}{1 + \kappa}.
\]  

(3.4)
The last expression is derived by balancing the energies of the right-angle and oblique helicoidal states with a small $\kappa$ in the external field. Further decrease of the field applied to the right-angle helicoid structure would decrease the helical pitch, which is a well-known effect [1].

In Fig. 3.1, we demonstrate by the numerical simulations how important is the value of the twist-bend elastic constants ratio $K_2/K_3$ for the field-controlled values of the structural parameters of the oblique helicoidal structure such as pitch, Fig. 3.1a, and the cone angle, Fig. 3.1b. The bigger the value of $K_2/K_3$, the wider is the field-tunable range of the heliconical structure. With this theoretical background, we now consider the experimental situation.

Figure 3.1. Effect of elastic properties of N* on (a) pitch, (b) cone angle of the field induced heliconical structure. In (a) and (b), $E_c = \frac{2\pi}{P_0} \sqrt{\frac{K_2}{\varepsilon_0 \varepsilon_a}}$. 
3.2.3 Materials and methods

We used a LC dimer material 1”,7”-bis(4-cyanobiphenyl-4’-yl)heptane (NC(C6H4)2(CH2)7(C6H4)2CN, CB7CB) which shows a uniaxial N phase between 116°C and 103°C with a positive dielectric anisotropy [17], sandwiched between the isotropic and the twist-bend nematic phase N\textsubscript{tb} [14,25]. We measured the dielectric permittivities parallel and perpendicular to the director as $\varepsilon_\parallel = 7.3$ and $\varepsilon_\perp = 5.9$, respectively; the elastic constants were determined by the Frederiks transition technique [54] to be $K_1 = 5.7 \text{ pN}$ and $K_2 = 2.6 \text{ pN}$. All data correspond to 106°C. To prepare the N* phase, we doped CB7CB with a small amount (1 wt%) of chiral (left-handed) dopant S811. The phase diagram is different from the case of an un-doped CB7CB: N* melts into an isotropic fluid at $T_{N^*I} = 112°C$ and transforms into a homochiral version of N\textsubscript{tb} at $T^* = 99°C$. The pitch $P_0$ of the N* phase, measured in the Grandjean-Cano wedge [54], decreases from 8.8 $\mu$m at $T^* + 1°C$ to 6.2 $\mu$m at $T_{N^*I} - 1°C$, see Supplement. The electro-optic experiments were performed at the temperature $T^* + 3°C$, at which $P_0 = (7.5 \pm 0.5) \mu$m.

We used flat glass cells of thickness $d = (11-16) \mu$m. The glass substrates were coated with polyimide PI2555 that sets a homeotropic (perpendicular) orientation of the molecules. When the cell is filled with N*, it shows a fingerprint texture with the helicoid axis in the plane $(x, y)$ of the cell. This geometry allows one to clearly visualize the periodic structure of both the heliconical and cholesteric structures, as the wave-
vector of director modulations in both cases is confined to the plane \((x, y)\). To assure a uniform alignment of the helicoid, the polyimide coatings were rubbed unidirectionally along the axis \(x\). For the polarizing optical microscopy (POM) study, two aluminum foil electrodes were placed between the glass plates to apply the electric field parallel to the rubbing direction \(x\). The distance between the electrodes was 140 \(\mu\)m. For optical diffraction and optical retardance mapping by PolScope [122], the cells with patterned indium tin oxide (ITO) electrodes on one of the substrates were used, and the distance between the electrodes was \(L=100\) \(\mu\)m. The AC field of frequency 3 kHz was used to explore the scenarios of structural transformations of the N* cells. Because of the cell geometry and in-plane arrangement of the electrodes, the electric field is inhomogeneous, being somewhat larger near the electrodes. To establish the spatial pattern of the electric field, we use COMSOL Multiphysics finite-element based solver, see Supplement. The simulations show that in the central part of the cell, the field is uniform and horizontal in the middle of the cell. For example, for the ITO case, for the applied voltage \(U=100\) V, the field is 0.7 \(V/\mu\)m with a 5% accuracy in the range \(-20\) \(\mu\)m \(\leq x \leq 20\) \(\mu\)m and across the entire extension of the LC slab along the \(z\)-direction. The field acting in the center of the cell can be calculated as \(E = \beta U / L\), where \(\beta\) is the correction coefficient, determined by numerical simulations to be 0.67 for ITO and 0.75 for aluminum electrodes.
3.2.4 Results and discussion

We start the experiment at a high field, $4 \text{ V/μm}$, at which the helical structure of $N^*$ is completely unwound with $\hat{n} \parallel \mathbf{E}$, showing no periodic modulations, Fig. 3.2a. The texture is dark when viewed between two crossed polarizers, one of which is parallel to $\mathbf{E}$. When the field is slowly decreased, the texture starts to brighten at $E_{NC}=(1.1 \pm 0.07) \text{ V/μm}$, showing a periodic modulation along the $x$-axis, Fig. 3.2b. The period increases with the decrease of the electric field, Fig. 3.3a. The effect is not transient, as for a fixed field, the structure relaxes to feature a well-defined period. Adjustment of the period to the varied electric field is achieved by nucleation and propagation of edge dislocations of Burgers vector equal to the single period of the structure. As the field is decreased further, at some other threshold $E_{N_{E}}=(0.35 \pm 0.07) \text{ V/μm}$, the structure changes completely, by nucleating regions with the wave-vector of periodic modulation that is perpendicular to $\mathbf{E}$, Fig. 3.2c. The new structure has a much larger period of about $9 \mu\text{m}$, which decreases as the electric field becomes smaller.
Figure 3.2. Electric-field induced (a) unwound nematic with the director parallel to the electric field; (b) heliconical state with the director following an oblique helicoid with the axis along the electric field, and (c) right-angle helicoid state of the cholesteric, as seen under the polarizing optical microscope. All scale bars are 50μm. (d) First order diffraction angle of the heliconical state as a function of the applied electric field. (e) Optical phase retardance as a function of the applied electric field in the vicinity of nematic-to-heliconical transition.

The described scenario corresponds to the transition from the nematic to oblique helicoid structure at $E_{NC}$, with a subsequent oblique-to-right angle helicoid first-order transformation with axis reorientation at $E_{N^{*}C} < E_{NC}$. To demonstrate the oblique helicoidal state in the range $E_{N^{*}C} < E < E_{NC}$, we use optical diffraction and PolScope. Optical diffraction experiment is performed with a He-Ne laser beam ($\lambda=633$ nm)
director normally to the cell. Polarization of incident light is varied by a rotating polarizer. The diffraction pattern is projected onto a screen 9.5 cm away from the sample. The heliconical state is a polarization-sensitive phase diffraction grating. For normal incidence, the diffraction condition is \(m\lambda = P\sin \Theta_m\), where \(m\) is the diffraction order, \(\Theta_m\) is the corresponding diffraction angle. For small cone angles \(\theta\), the first-order diffraction intensity \(\propto \sin^2 2\theta\) is expected to be higher than the second-order diffraction intensity \(\propto \sin^4 \theta\). This is indeed the case, as the values of \(P\) calculated from the field dependence of \(\Theta_1\), Fig. 3.2d, match the POM data very well, Fig. 3.3a.

The field dependence \(P(E)\) follows closely the theoretically expected behavior \([45]\) \(P \propto 1/E\), Fig. 3.3a, which allows one to extract an important information on the elastic constants of \(N^*\). According to Eq. (3.2), \(\kappa = EP/E_{NC}P_0\), which yields \(\kappa = K_3/K_2 \approx 0.12\) with the experimental data on \(P(E), E_{NC}\) and \(P_0 = 7.5 \mu m\). The smallness of \(\kappa\) satisfies the restrictions imposed by Meyer-de Gennes theory \([45,54]\). Moreover, the experimental \(E_{N^*C} = (0.35 \pm 0.07)\) V/\(\mu m\) agrees with the value \(E_{N^*C} = 0.39\) V/\(\mu m\) obtained from Eq. (3.4) when \(\kappa = 0.12\). The twist modulus is independently calculated from the definition of \(E_{NC}\) as \(K_2 = \varepsilon_0\varepsilon_a\kappa\left(\frac{P_0E_{NC}}{2\pi}\right)^2 = 2.6\) pN, the same as measured in the N phase 106°C. With the above data, one deduces a rather small value of the bend elastic constant in \(N^*\), \(K_3 = 0.3\) pN.
LC PolScope is used to characterize the oblique helicoid when the cone angle $\theta$ is small. PolScope maps the optical retardance $\Gamma(x, y)$ of the sample, $\Gamma = \int \Delta n_{\text{eff}} dz$, where $\Delta n_{\text{eff}}$ is the effective birefringence of the heliconical state. For a small $\theta$, one can use an approximation $\Delta n_{\text{eff}} \approx \Delta n \left(1 - \frac{3}{2} \sin^2 \theta\right)$ [25], where $\Delta n$ is the birefringence of the unwound $\hat{n} = (1, 0, 0)$ state. As a measure of $\Delta n$, we use the experimentally determined birefringence of pure CB7CB, $\Delta n = 0.15$ at 106°C. This value yields $\Gamma = 1690 \text{ nm}$ for the unwound state in the cell of thickness $d = 11.2 \mu \text{m}$, Fig. 3.2e. When the field is reduced, the nematic-to-oblique helicoid transition is manifested by a cusp in the dependency $\Gamma(E)$ followed by a decrease of $\Gamma$. Such a behavior is expected because of the departure of $\theta$ from its zero value at $E \leq E_{NC}$, Eq. (3.3). The direct comparison of Eq. (3.3) and the experimental data in Fig. 3.2e is difficult, as the director in the experiment is influenced by the boundary conditions; we resort to numerical simulations.

**Figure 3.3.** Electric field dependence of (a) heliconical pitch; (b) cone angle, as deduced from the theory, numerical simulations and experiments.
Simulations of the director field, carried out by Dr. S. V. Shiyanovskii, are performed by minimizing the free energy functional based on bulk density, Eq. (3.1) and surface anchoring, \( F = \int f_b dV + \int f_s dS \), where surface anchoring for homeotropic alignment is represented by the Rapini-Papoular potential \( f_s = \frac{1}{2} W \left[ 1 - (\hat{z} \cdot \hat{n})^2 \right] \); here \( W \) is the anchoring coefficient and \( \hat{z} \) is a normal to the substrates. The simulations are performed for the experimentally relevant values \( \kappa = K_3 / K_2 = 0.12 \), \( P_0 = 7.5 \mu m \), \( E_{NC} = 1.1 V/\mu m \), and assuming \( W = 10^{-4} J/m^2 \). The latter quantity does not influence the results much, as the typical contribution of the anchoring energy to the total energy is less than 0.1%. Minimization of \( F \) reveals that the oblique helicoid is the main structural element of the system in the range \( E_{NC} \leq E \leq E_{NC} \), Fig. 3.4a. The effect of finite cell thickness and surface anchoring is in introducing the \( z \)-dependence of the polar \( \alpha(z) \) and azimuthal \( \psi(z) \) angles characterizing the orientation of the heliconical axis \( \hat{h} = (\sin \alpha \cos \psi, -\sin \alpha \sin \psi, \cos \alpha) \), and in \( z \)-dependence of the cone angle \( \theta(z) \), Fig. 3.4b.
Figure 3.4. (a) The director field in the cell with the homeotropic anchoring under the in-plane electric field, simulated for parameters $\kappa = K_{3} / K_{2} = 0.12$, $\kappa_{1} = K_{1} / K_{2} = 2.2$, $E / E_{NC} = 0.6$ and $d / P_{0} = 1.49$, demonstrating a heliconical structure with $P = 0.20P_{0}$. (b) In the heliconical state, the polar angle $\alpha$ (thin) and azimuthal angle $\psi$ (dashed) of the heliconical axis $\hat{h}$ as well as the cone angle $\theta$ (thick) are functions of $z$ coordinate across the cell.

The field dependence of the pitch obtained in numerical simulations of the finite thickness cell reproduces the dependence $P \propto 1 / E$ found experimentally and predicted by Eq. (3.2) very closely, Fig. 3.3a. The simulations also allow us to trace the field dependence of $\theta$. Since the surface anchoring makes the cone angle $z$-dependent, we distinguish two parameters: the value $\theta_{m}$ in the middle of the cell, and the average value $\langle \theta \rangle_{num} = \sin^{-1} \sqrt{\int \sin^{2} \theta(z) dz / d}$. As shown in Fig. 3.4b, $\theta_{m}$ follows closely the behavior expected analytically, Eq. (3.3). The average value $\langle \theta \rangle_{num}$ is somewhat smaller.
because of the surface anchoring effect, and matches well its experimental equivalent, determined as \( \langle \theta \rangle_{\text{exp}} = \sin^{-1} \sqrt{\frac{2}{3} \left(1 + \frac{1}{\Delta n \cdot d} \right)} \), Fig. 3.3b.

In conclusion, we demonstrate the electric field-controlled oblique helicoidal state of a cholesteric LC with positive dielectric anisotropy, predicted many decades ago, but so far not proven experimentally because of lack of materials with a sufficiently small bend-to-twist moduli ratio. In the explored cholesteric, based on molecular dimers, the bend elastic constant \( K_3 = 0.3 \) pN is determined to be about 10 times smaller than the twist constant, \( K_2 = 2.6 \) pN, a very unusual result as compared to standard LCs formed by rod-like molecules. We establish the scenario of structural transitions in such a cholesteric, as the function of the applied electric field. At high fields, a uniaxial director parallel to the field is a stable state. At intermediate fields, the homochiral oblique helicoid forms with the axis parallel to the field. Both the pitch and the cone angle increase as the field is reduced. Finally, at low fields, the cholesteric right-angle helicoid emerges, with the axis perpendicular to the field.

Materials such as CB7CB have been connected to the twist-bend nematic phase [5-7,14,16] that was shown by TEM observations to exhibit a nanoscale periodicity [22,25] and the director field in the form of an oblique helicoid [25]. There are important differences between the oblique helicoidal structures induced by the electric field in the N* slab and the ground state of the \( N_{\text{tb}} \) phase. First, the period of the two structures is absolutely different, nanometers in \( N_{\text{tb}} \) vs microns in N* (the latter can be controlled by the electric field and concentration of chiral additives). Second, because of the chiral
dopant, the oblique helicoid in the N* case has the same chirality everywhere in the sample. In contrast, the N_{th} phase is formed by non-chiral molecules and thus should break into left-handed and right-handed domains [6]. As evidenced by TEM [25], these domains might be rather small, only 20-30 nm wide; generally, one expects the domain size to be dependent on the sample and its prehistory.

The observed homochiral oblique helicoidal state is close to the field-free chiral smectic C (SmC*) phase [1] and the phase observed in concentrated water suspensions of helical flagella isolated from Salmonella typhimurium [123]. In the latter case, the conical angle $\theta$ is fixed by the shape of relatively rigid flagellae. In the case of SmC*, $\theta$ is fixed by the molecular tilt within the smectic layers and the structure is modulated both in the sense of molecular orientation and materials density [1]. Absence of density modulation and the ability of the electric field to tune both the period and conical angle in the heliconical state of N* brings advantages in terms of proper alignment and electro-optical switching. Note also that each value of the pitch and cone angle is stable as long as the field is kept constant, which distinguishes the observed state from the transient structures that might occur in cholesteric cells when the field is abruptly removed [39].

One thus might expect that the electrically-controlled oblique helicoidal structure demonstrated will find applications in devices such as tunable diffraction gratings, color filters, light deflectors and scatterers, wide-angle beam steerers, etc.
3.2.5 Supplemental information

Pitch measurement using Grandjean-Cano wedge

A Grandjean-Cano wedge cell was produced by assembling two glass plates to form a wedge with an opening angle $\gamma = 0.6^\circ$. The uniform planar boundary conditions orient the $N^*$ helix perpendicularly to the cell walls. The number of half-pitches of $N^*$ increases as the wedge gap increases. The domains with different number of half-pitches are separated by dislocation lines. The pitch is calculated as $P_0 = 2 \cdot S \cdot \tan \gamma$, where $S$ is the distance between neighboring dislocations. The temperature dependence of $P_0$ is shown in Fig. 3.5. $T^* = 99^\circ C$ is the transition temperature from $N^*$ to homochiral version of $N_{th}$.

![Graph](image.png)

**Figure 3.5.** Temperature dependent pitch $P_0$ of the chiral mixture CB7CB (99wt%) + S811 (1wt%).
Electric field simulation

Electric fields in the cells with an in-plane electric field applied with the help of either patterned ITO electrodes or by two aluminum foil electrodes are generally nonuniform. To calculate the field configuration, we used commercial finite-element modelling simulator, COMSOL Multiphysics. We used the experimentally known parameters of the cell, cell thickness 12 \( \mu \text{m} \), electrode gap 100-140 \( \mu \text{m} \), ITO thickness 0.15 \( \mu \text{m} \), and glass plates thickness 1.1 \( \text{mm} \). The dielectric constant of glass is \( \varepsilon_{\text{glass}} = 3.9 \), and the dielectric constants of liquid crystal are \( \varepsilon_{||} = 7.3 \) and \( \varepsilon_{\perp} = 5.9 \). As shown in Fig. 3.6, in the central part of the cell, the field is uniform and horizontal. For example, for the ITO case, the field is 0.7 V/\( \mu \text{m} \) with a 5% accuracy in the range \(-20 \mu \text{m} \leq x \leq 20 \mu \text{m} \) and across the entire extension of the LC slab along the \( z \)-direction. For the aluminum electrodes, the field is 0.76V/\( \mu \text{m} \) with a 5% accuracy in the range \(-20 \mu \text{m} \leq x \leq 20 \mu \text{m} \), Fig. 3.6c,d.
**Figure 3.6.** Electric field in the in-plane switching cells: (a) patterned ITO electrodes at the bottom glass substrate with electrode gap 100μm, and applied voltage 100Vrms; (b) aluminum foil electrodes between the glass substrates with electrode gap 140μm, and applied voltage 140Vrms. Electric fields strength in the patterned ITO cell (c) and aluminum electrodes cell (d), as a function of the $z$ coordinate, for different values of the $x$-coordinate.
3.3 Electrically Tunable Selective Reflection of Light from Ultraviolet to Visible and Infrared by Heliconical Cholesterics

3.3.1 Introduction

Development of materials capable to dynamically control transmission and reflection of visible light and near infrared (IR) radiation is one of the most important directions of research with potential applications such as energy-saving smart windows [124], transparent displays, communications, lasers [40], etc. The most challenging problem is to formulate materials in which the transmission of light, or, more generally, electromagnetic radiation, can be performed dynamically and independently for different spectral bands, preferably by controlling reflection (as opposed to absorption). Among the oldest known materials capable of selective reflection of light are the so-called cholesteric liquid crystals (CLCs) formed by chiral elongated organic molecules in a certain temperature range between a solid crystal and an isotropic melt [1,40,125-129]. As described in section 1.1, the selectively reflected colors of CLCs are highly saturated, they add like colored lights and produce a color gamut greater than that obtained with inks, dyes, and pigments [125].

The pitch $P_0$ of CLCs and thus the wavelength $\lambda_p$ of reflected light can be controlled by exposure to a variety of stimuli including electric/magnetic field, heat, and light [43], thus enabling applications such as temperature indicators [1], sensors of minute quantities of gases [130,131], and optical switchable reflectors [132,133]. However, the most desirable mode to control light reflection, by an electric field applied
parallel to the helicoidal axis, Fig. 3.7a, has so far been elusive. The reason is that the field applied parallel to the axis, instead of changing the pitch while keeping the cholesteric axis intact to reflect light, rotates this axis perpendicularly to itself, as dictated by the dielectric anisotropy of the LC [39], causing a light scattering structure called a “fingerprint texture”, Fig. 3.7b. A limited range of electric tuning of right-angle cholesterics is still possible, with the help of special electrode geometry [42] or photopolymerization technique [50-52,134], at the expense of reduced levels of reflection and relatively high electric field. Because of these difficulties in electric tuning of the standard cholesterics, their use as materials for electrically-tunable large-area smart windows, mirrors, filters, displays, and lasers are not currently feasible.

In this work, in order to produce electrically tunable selective reflection, we use the so-called oblique helicoid structure of the cholesteric under low driving electric field, Fig. 3.7c, as opposed to the right-angle helicoid shown in Fig. 3.7a. In the oblique helicoid, the director is tilted, making some angle $\theta < \pi / 2$ with the helicoid axis. The electric field acting along the axis, realigns the molecules along itself and thus changes the pitch $P$ without reorienting the helicoid axis, Fig. 3.7c,d.
Figure 3.7. Field induced behavior of cholesterics structures. (a) Right-angle helicoidal cholesteric with a large bend constant and a positive local dielectric anisotropy in a planar cell. (b) Sufficiently strong vertical electric field $E$ realigns the cholesteric axis perpendicularly to itself, causing light-scattering fingerprint texture. (c) Heliconical structure in a cholesteric with a small bend constant and positive dielectric anisotropy stabilized by the vertical electric field $E_1$. (d) The pitch $P$ and tilt angle $\theta$ of the field-induced heliconical state both decrease as the electric field increases, $E_2 > E_1$. (e) As the field increases further, to some $E_3 > E_2$, it unwinds the helical structure completely and forms a homeotropic nematic state. The figures are not to scale, as the experimental cell thickness is typically 20-50 times larger than the cholesteric pitch $P_0$.

As already indicated, the oblique helicoidal (heliconical) state has been predicted by Meyer and de Gennes to occur in the applied electric field in a cholesteric in which the elastic constant $K_3$ of bend is much smaller than the elastic constant of twist [45,54]. For
a long time, the effect could not be explored because of lack of materials with the needed elastic properties. Recently, it was suggested [17] that the novel dimeric LCs, representing two rigid rod-like units connected by a flexible chain with an odd number of links, might have a small value of $K_3$, which was confirmed experimentally [23,25,110].

The heliconical state of the corresponding cholesterics was observed in Raman-Nath diffraction experiments [32], as described in the section 3.2, in which light propagates perpendicularly to the axis, and in Bragg reflection geometry [34], but only at very high temperatures above 100 °C and for a relatively short tuning range of the reflection band. In this section, by designing the cholesteric mixture with a broad temperature range of stability (that embraces the room temperatures) and with a small $K_3$ that assures the existence of the oblique helicoidal state, we demonstrate that the selective reflection of light can be tuned by relatively low electric fields (a few $V/\mu m$) within an exceptionally wide spectral range, from UV to near IR. We have published these results in [33].

### 3.3.2 Materials and methods

We formulated the broad temperature range cholesterics with the small $K_3$ by mixing two dimeric LCs (1’,7’-bis(4-cyanobiphenyl-4’-yl)heptane (CB7CB) and 1-(4-cyanobiphenyl-4’-yl)-6-(4-cyanobiphenyl-4’-yloxy)hexane (CB6OCB)), and a standard LC pentylcyanobiphenyle (5CB) (Merck). The mixtures were doped with a left handed chiral additive S811 (Merck) that determines $P_0$. Three mixtures were used, with composition CB7CB:CB6OCB:5CB:S811 (in weight units) being 30:20:46:4 (mixture
M1, cholesteric phase in the range (20-66.5 °C); 30.1:20:45.9:4 (M2, 22-68 °C); and 29:20:49:2 (M3, 21-69.5 °C). All mixtures demonstrated electrically tunable light reflection in the cholesteric phase at temperatures up to 45 °C; at higher temperatures, the effect disappears as $K_3$ in dimeric materials increases with temperature [23,25,110]. All data reported below were obtained at 25 °C. The temperature in the experiments was controlled by a hot stage LTS350 with a controller TMS94 (both Linkam Instruments) with 0.01 °C accuracy. In the experiments, the cholesteric is sandwiched between two glass plates with transparent indium tin oxide (ITO) electrodes and alignment polyimide PI-1211 (Nissan); the thickness of cholesteric layers was $d = 50±2 \, \mu m$. All cells in the selective reflection experiments were addressed with the AC electric field of frequency 3 kHz (square wave). Selective light reflection was characterized by two complementary approaches. First, the field-induced color changes were visualized under the polarizing microscope (Optiphot2-pol, Nikon) with two crossed linear polarizers, in the reflection mode, Fig. 3.8. Second, we measured the reflection spectra of the cholesteric heliconical structure using Ocean Optics spectrometers USB2000 (visible) and NIRQuest256 (near-IR). Note that the reflection of light can be tuned in cells thinner than 50 \, \mu m; however, the coefficient of reflection gradually decreases as $d$ becomes smaller.

The reflection coefficient $R$ at $\lambda_p = 632 \, \text{nm}$ was determined by measuring the transmitted intensity $I_{\text{trans}}$ and reflectance $I_{\text{reflect}}$ of a linearly polarized He-Ne laser beam of diameter 1.5 mm with intensity $I_{\text{in}} (\lambda = 632 \, \text{nm})$ through the cell. The incident beam
was tilted by 1 degree from the normal to the cell. We first characterized the cell in which the material was melted into the isotropic phase, to obtain the coefficient of reflection $R_{\text{glass}} = I_{\text{reflect}}/I_{\text{in}} = 0.064$ associated with the glass interfaces and $I_{\text{trans}}/I_{\text{in}} = 0.923$. For the heliconical state with red color reflection, we measured $I_{\text{reflect}}/I_{\text{in}} = 0.41$ and $I_{\text{trans}}/I_{\text{in}} = 0.564$, which implies that the coefficient of reflection caused exclusively by the periodic heliconical structure is $R_{hc} = 0.35$ (or 35%) and that the losses due to the light scattering are not significant, about 2.6%. The value of reflection coefficient caused by the interfaces and heliconical structure, $R = 0.41$, measured at 632 nm, was used to renormalize the reflection data measured by spectrometers for other wavelengths in Fig. 3.9 and 3.10.

### 3.3.3 Results and discussion

When a sufficiently strong electric field is applied, the material is switched into a uniform nematic with the director parallel to the field, Fig. 3.7e and Fig. 3.8a. Such a state is dark when viewed between crossed linear polarizers. When the field is decreased, the LC shows a sequence of changing wavelength of reflection, from UV to visible blue, then green, orange, red, and, finally, near IR, Fig. 3.8b-g. Below 0.7 V/μm, the LC transforms into the light scattering texture, Fig. 3.8h.
**Figure 3.8.** Electric field induced textures in cholesteric mixture M1. Polarizing optical microscope textures of field induced (a) unwound nematic; (b-g) heliconical states with reflected (b) blue, (c) green, (d) orange and (e) red colors, (f and g) two IR-reflective states; (h) fingerprint state. The RMS amplitude of the electric field is indicated on the figures.

Figure 3.9 presents reflection spectra, peak wavelength and bandwidth of reflection at various field strengths that further demonstrate a very broad range of controlled reflectance, from UV to IR, covering the entire range of visible light. As the field decreases, the peak wavelength shifts to IR, Fig. 3.9a,b. In absolute units, the reflection coefficient $R$ was measured to be 41\% for the reflection peak at 632 nm (field 1.1 V/$\mu$m). By controlling the chemical composition of the mixture, one can optimize the reflection efficiency for any given pitch, and adjust the bandwidth that narrows down at higher electric field, Fig. 3.9b.
Figure 3.9. Selective light reflection in M1 cell. (a) Typical reflection spectra of M1 cell at different electric fields, shown underneath the spectra in V/µm units. (b) Electric field dependencies of the wavelength and bandwidth of the selective reflection peak.

An important goal in the field of smart windows is to block visible and near-IR light selectively and independently, by varying the applied voltage [135,136]. Such a task can be performed by multilayered stacks of oblique helicoidal cholesterics with different concentration of chiral additive, since the materials are not absorbing. To demonstrate the principle, we stack the cells with short-pitch M2 and long-pitch M3 on top of each other, Fig. 3.10. The spectral tuning range is exceptionally wide, 360-1520 nm for M3, and somewhat shorter, 360-800 nm, for M2, Fig. 3.10a. Depending on the applied fields, the stack produces a variety of states: a state (I) transparent in the visible region and reflecting in IR (a stronger voltage is applied to M2 as compared to M3 cell), Fig. 3.10b; (II) transparent in IR and reflecting in the visible (stronger voltage applied to M3 cell), Fig. 3.10c; (III) reflecting in both visible and IR (moderate voltages), Fig. 3.10d; (IV) transparent in both the visible and IR part (high voltages). Importantly, the
electric field not only switches the two reflection bands on and off (as in standard cholesterics), it also tunes their spectral position, Fig. 3.10a. Using the rich arsenal of techniques developed previously for standard cholesterics, one can broaden the reflected bands by polymerization of the material [39,50,129,134], or increase the reflectivity to 100% by using optical compensators [125].

**Figure 3.10.** Selective light reflection in double cell. (a) Reflection wavelength vs electric field for M2 and M3 cells. (b) State (I) transparent in visible and reflecting in IR. The electric field 4.9 V/μm acts on M2 cell and 0.5 V/μm on M3 cell; (c) state (II) transparent in IR and reflecting in visible; 0.9 V/μm at M2 cell and 3.1 V/μm at M3 cell; (d) State (III) reflecting in two different parts of spectrum; 0.9 V/μm at M2 cell and 0.5 V/μm at M3 cell. The textures are taken under a reflective optical microscope with crossed polarizers.
Experimental results on the field dependence of $\lambda_p$, Fig. 3.9b, support the theoretical model [45] in which $P \propto 1/E$. For full description of the dependency $\lambda_p(E)$ one also needs to take into account a somewhat weaker field dependency of the refractive indices. For light propagating along the axis, the effective birefringence depends on the tilt angle $\theta$: 

$$\Delta n_{\text{eff}} = \frac{n_{\text{e}} n_{\text{o}}}{\sqrt{n_{\text{e}}^2 \cos^2 \theta + n_{\text{o}}^2 \sin^2 \theta}} - n_{\text{o}}.$$ 

As demonstrated in section 3.2, $\theta$ decreases as the field increases, so that $\Delta n_{\text{eff}}$ becomes smaller. This is why, for a given material, the reflectivity is typically weaker at high fields; it is also weaker at low fields, as the number of cholesteric layers in the cell of a fixed thickness decreases as the pitch increases, Fig. 3.9a.

When the light beam is not strictly perpendicular to the cell, the oblique helicoid produces reflection not only at $\lambda_p = \pi P$, but also at $\Lambda_p = 2\pi P$, since the molecules separated by $P/2$ are tilted in opposite directions [137]. In the presented experiments with normally incident beams of small divergence; the peak at $\Lambda_p = 2\pi P$, although observable, was about 10 times weaker than the main peak at $\lambda_p = \pi P$.

To change the color, the pitch needs to adjust to the field, either through slippage at the bounding plates or through nucleation and propagation of dislocations; some of these defect lines are seen in Fig. 3.8b-e. An important advantage of the heliconical cholesteric over similar structures in smectics is absence of positional order in molecular packing, which allows the system to adapt easily and reversibly to the changes of period;
all the color changes observed in our experiments are fully reversible and relatively fast. For example, the homeotropic state (at 5 V/μm) switches into the heliconical state with saturated (90% of the maximum reflection) reflective red color (1.1 V/μm) within 0.8 second; the time was measured by monitoring the transmission intensity of the He-Ne laser beam. Transition from the scattering state that exists at zero field, to the heliconical state with saturated (90% of the maximum reflection) red color reflection (1.1 V/μm) takes much longer time, about 120 seconds. The reasons is that this transformation involves motion of multiple linear defects that is strongly hindered in chiral structures, especially glide, as discussed for the case of standard cholesterics [138]. The transition from the scattering state (zero field) to homeotropic state (5 V/μm) is faster, 60 milliseconds, since the applied field is strong; thus the preferred mode of switching might be between the homeotropic states and color-reflecting states.

To conclude, we describe an electrically tunable selective reflection of light in UV, visible and IR by the heliconical cholesteric state that exist in a broad temperature range including the room temperatures. The tunable structural color is achieved in a simple sandwich geometry, in which the cholesteric is confined between two plates with transparent electrodes, thus implying a low cost and easy fabrication process. The color change occurs over the entire electrode area that can be designed as a desired pattern suitable, for example, for “see-through” color displays. The electrically tunable colors can be additionally controlled by the cholesteric composition and by employing reflective
stacks. The effect can be tuned to practically any spectral regions in UV, visible and IR by chiral additives of different twisting power or concentrations. The regular right-angle cholesterics are known to provide structural colors of certain birds, beetles [139] and plants [140]; it would be of interest to explore whether the oblique helicoidal states occur in the natural world.
3.4 Full Color Reflective Display Using Cholesteric Heliconical Structure

3.4.1 Introduction

There are several ways to prepare cholesteric-based reflective displays that show a broad tuning of the reflected color of light:

(i) By stacking multiple N* layers with different pitches on top of each other [141,142].

(ii) By placing N* pixels with different pitches side-by-side in one layer [143].

(iii) By electrical tuning of the period of N*.

The methods (i) and (ii) require a rather complicated technology of stacking and control/switching of colors. Method (iii) is potentially the most attractive, but its limitation is a very small range of tunable values of the pitch [49,50]. When the electric field is applied parallel to the helical axis, it abruptly realigns the axis in an orthogonal position (since the local dielectric permittivity along \( \hat{n} \) is higher than the permittivity perpendicular to \( \hat{n} \)) [39]. When the field is perpendicular to the axis, it distorts the helicoid [55] by expanding the regions where \( \hat{n} \) is parallel to the field; this alone makes the reflection band poorly defined. Besides, as the field increases, \( P_0 \) changes very little at first, and then it abruptly diverges [1,45]. As a result, applications such as reflective/transparent displays and large-area smart windows with selective light reflection controlled by the electric field are not feasible with the standard cholesteric materials.
In this section, by using the cholesteric heliconical structure, we demonstrate a single-layer full color reflective display. As demonstrated in section 3.2 and 3.3, the principal advantage of the heliconical structure as opposed to the standard right-angle cholesteric helicoid is that the electric field controls the period of the heliconical structure but does not alter the orientation of its axis and does not violate the uniformity of twist. These features of the field induced heliconical structure make it suitable for large-scale, single-layer, full-color reflective displays and other applications. We have published these results in [35].

3.4.2 Results and discussion

Section 3.3 already presents the results of electrically tuned color reflection under a microscope, Fig. 3.8, and in spectral measurement, Fig. 3.9. Here, we demonstrate the electrically tunable reflective color with a naked eye without any polarizers at ambient light conditions, Fig. 3.11, which demonstrates its suitability for reflective informational display. The electrically controlled color in Fig. 3.11 can be switched in any sequence among deep blue, green, yellow and red.
Figure 3.11. Photographs of the reflective display (area 5 mm×5 mm, thickness 50±2 µm) controlled by an AC field. By changing the electric field, the reflected color changes between (a) blue, (b) green, (c) yellow, and (d) red. The RMS amplitude of the electric field is indicated in the figures.

The color sensitivity of human eyes to a specific optical spectrum is usually characterized by a chromaticity diagram. We use the CIE1931 2° viewing angle basis with D65 illuminant [144] to characterize the colorimetric properties of the heliconical structure of N* samples. The chromaticity values (x, y) were calculated from the reflection spectra measured in Fig. 3.11. Each circle in Fig. 3.12 corresponds to the
reflection color obtained from heliconical structure under the applied electric field. The electrically switchable colors follow a clockwise fashion with the increase in applied field. The color gamut is around 19.9% of NTSC. The color gamut can be further improved by the following means: (i) tuning the concentration of chiral dopants to achieve the strongest Bragg reflection in the visible (as opposed to the near-infrared) part of the spectrum; (ii) by reflecting both circular polarizations of light, using double layers of N*; (iii) by broadening the reflection bandwidth, using mixtures with large birefringence.

**Figure 3.12.** CIE1931 chromaticity diagram on the basis of 2° viewing angle and D65 illuminant. White open circle shows the color coordinates of the reflected color under different electric fields, calculated from the reflective spectra measured in Fig. 3.11. The white cross corresponds to the white chromaticity.
We determined the characteristic times of electrooptic response by recording the transmittance change of the circularly polarized light through the cell and determining the levels of 10% and 90% of the maximum transmittance. The switching time is 0.8 second for switching from the homeotropic state (applied electric field $E = 5 \text{ V/μm}$) to the heliconical state with reflective red color ($E = 1.1 \text{ V/μm}$), Fig. 3.13. The switching time can be further improved by exploring alignment layers with different anchoring strengths, or chemistry/composition, such as using dimeric mesogen with low rotational viscosity.

![Diagram](image)

**Figure 3.13.** Electrooptic response of cholesteric structures. (a) Schematic illustration of the experiment setup. (b) Transient process when the sample switched from homeotropic state to heliconical state with red reflection color ($\lambda_p=632\text{nm}$).

In conclusion, we have demonstrated a single layer, high reflection full color display based on the cholesteric heliconical structure. The novelty of the technique is that the period of the heliconical structure is controlled by the electric field applied...
parallel to the helicoidal axis. The electric field changes the period of the structure in a
very broad range but does not change the orientation of the helicoidal axis. These
features make it possible to fabricate full color reflective/transparent displays and smart
windows with a simple electrode geometry, which implies a low cost and easy fabrication
process. The cholesteric heliconical structure also brings the advantage of low driving
electric field, wide tunable range, and large-scale uniformity of the reflected colors.
3.5 Electrically Tunable Laser based on Cholesteric Heliconical Structure

3.5.1 Introduction

In this section, we present the first realization of a high-efficient electrically tunable lasing with lasing wavelength $\lambda$ spanning an extraordinary broad range (>100 nm) of visible spectrum. The effect is achieved by using an electric-field induced oblique helicoidal state ($\text{CLC}_{\text{OH}}$) of CLCs in which the molecules form an acute angle with the helicoidal axis $\mathbf{h}$ rather than align perpendicularly to it as in a field-free CLC, Fig. 3.14b.

![Figure 3.14](image.png)

**Figure 3.14.** Schematic of electrically tunable lasing in dye doped cholesteric heliconical structure. (a) High electric field, unwound CLC helix, no lasing emission. (b) electrically tunable tunable $\text{CLC}_{\text{OH}}$ structure with lasing emission. (c) Schematic of lasing cell with pump and laser emission beams. Spheres and ellipsoids represent dye molecules and liquid crystal molecules, respectively.
3.5.2 Materials and methods

The CLC\textsubscript{OH} structure is formed in CLCs which have a very small bend elastic constant (\(K_3\)) under the influence of an electric field along the helical axis, as demonstrated in section 3.2 and 3.3. We have carried out the lasing experiments on CLC\textsubscript{OH} samples obtained by mixing dimeric LCs: 1’,7’-bis(4-cyanobiphenyl-4’-yl)heptane (CB7CB), 1-(4-cyanobiphenyl-4’-yl)-6-(4-cyanobiphenyl-4’-yloxy)hexane (CB9CB), the standard nematic LC pentylcyanobiphenyl (5CB) (Merck), a left-handed chiral additive S811 (Merck), and one of the laser dyes DCM or LD688 (Exciton). Laser dyes DCM and LD688 are known to exhibit high photoluminescence efficiency. Furthermore, these dyes are soluble in the liquid crystal mixtures. Two mixtures were used, with composition CB7CB:CB9CB:5CB:S811:DCM (in weight units) being 29.9:19.9:45.9:4:0.3 (mixture DCM, cholesteric phase in the range (21-64) °C); CB7CB:CB9CB:5CB:S811:LD688 being 29.9:19.9:45.6:4:0.6 (mixture LD688, 29.5-62.8 °C). The CLC mixtures were thoroughly mixed before they were capillary-filled into the homogeneous LC cells in an isotropic state. The thickness of all the LC cells was 50±2 µm. All data reported below were obtained at 25°C for mixture DCM, and 32.5 °C for mixture LD688. Experimentally measured fluorescence emission and absorption spectra of described mixtures are shown in Fig. 3.15. For the mixture DCM, the absorption peak is around 460 nm, and fluorescence peak is around 600 nm; for the mixture LD688, the absorption peak is around 525 nm, and fluorescence peak is around 650 nm.
Figure 3.15. Absorbance and fluorescence spectra of laser dyes in CLC mixtures: (a) DCM, (b) LD688.

The temperature of the samples during lasing experiments was controlled by a lab-made hot-stage with 0.1°C accuracy. All cells in the experiments were driven with the AC electric field of frequency 3 kHz (square wave). Flat cells were formed by glass plates with transparent ITO electrodes and alignment polyimide SE-1211 (Nissan). The field-induced color changes were visualized under the polarizing microscope (Optiphot2-pol, Nikon) with two crossed linear polarizers, in the reflection mode, Fig. 3.16a-d.

In order to obtain electrically tunable lasing emission, sample cells were optically pumped using pulsed frequency doubled Nd:YAG laser (Quantel YG682S-100) with wavelength of 532 nm. The pulse width and the repetition rate of a pump beam were 7.5 ns and 2 Hz, respectively. The pump beam was focused on the CLC layer to a ~50 µm waist at an oblique incidence of ~45° from the normal of the cell substrates. The output
lasing emission along the normal forward direction of the cell was collected into an optical fiber and analyzed using high-resolution spectrometer TRIAX 550 (Jobin Yvon Inc, USA) with optical resolution of 0.07 nm. The pump energy incident on the sample cell was controlled using polarizer and analyzer. The absorbance spectra were measured using a fiber spectrometer USB4000 (Ocean Optics), and fluorescence spectra were measured using TRIAX 550 spectrometer. Energies of the pump beam and laser emission were measured with Molecron energy meter OM4001.

3.5.3 Results and discussion

A strong electric field of magnitude \( \sim 2.0 \text{ V/\text{um}} \) above some critical threshold \( E_{NC} \) unwinds the CLC into a uniform homeotropic nematic texture with the director parallel to the field, Fig. 3.14a. Such a state appears dark between crossed polarizers as shown on Fig. 3.16a; it has no photonic bandgap for lasing. At smaller fields, \( E < E_{NC} \), the director twists into the CLC\textsubscript{OH} structure, which shows selective reflection of light, electrically tunable from near UV through visible to near IR range, Fig. 3.16b-d. Mirrorless lasing happens when the CLC\textsubscript{OH} photonic bandgap matches with the fluorescent emission band of the laser dye.
**Figure 3.16.** Electric field controlled selective reflection of light in DCM-doped CLC mixture. Photographs in ambient light condition and corresponding polarizing optical micrographs (a) Electric field unwounded homeotropic state; electric field induced CLC$_{OH}$ states reflecting (b) blue, (c) green and (d) red visible light.

The samples were pumped with 7 ns pulses at 532 nm from a frequency doubled Q-switched Nd:YAG laser. An obliquely incident pump beam produces lasing emission beam from a CLC$_{OH}$ sample in the direction of the helical axis. These can be seen as spatially separated on a projection screen, Fig. 3.14c. The absorption bands of both dyes allow optical pumping at 532 nm, and the fluorescence bands provide lasing in the red range of visible spectrum, Fig. 3.15.

Figure 3.17 illustrates the effect of lasing and electric tunability of emission wavelength for both laser dyes used as additives to the CLC mixture. For example, in the mixture with DCM, Fig. 3.17a, with an electric field of 1.08 V/µm, the reflection band of the sample is centered at 565 nm, and the lasing wavelength $\bar{\lambda}$ is at 575 nm. As the field
decreases to 0.92 V/µm, the reflection band center shifts to 664 nm and $\lambda$ increases to 675 nm. With optical pump, lasing emission with a typical full width at half maximum (FWHM) in the range 0.15nm-0.35nm occurs at the low-energy edge of CLC$_{OH}$ bandgap, Fig. 3.17a. The lasing emission beam profiles with low pump energy, 1µJ/pulse for LD688-doped sample, and 10 µJ/pulse for DCM-doped sample, observed with a profile meter and a black screen are shown in Fig. 3.17b and 3.17c, respectively.

Figure 3.17. Electrically tunable lasing from CLC$_{OH}$ structure. (a) Reflection bands with associated lasing lines for LD688 dye (top row) and DCM dye (bottom) doped samples at different electric fields, shown underneath the spectra in V/µm units; (b) lasing emission beam profile with low pump energy and from a lasing spot of LD688-doped sample, E=0.78 V/µm, detected 25mm away from the sample; (c) the lasing emission beam from a DCM-doped sample observed on a projection screen, positioned 75 mm from the sample, E=1.05 V/µm for $\lambda = 591$nm, and E=0.99 V/µm for $\lambda = 630$ nm.
The CLC\textsubscript{OH} laser emission intensity shows a clear threshold as a function of pump energy, Fig. 3.18a. The lasing threshold is $U_{th} = 1.55$ $\mu$J/pulse at $\lambda = 610$ nm for the DCM sample, and $U_{th} = 0.23$ $\mu$J/pulse at $\lambda = 625$ nm for the LD688 sample. With pump energies well above the threshold, laser emission can also appear at the high-energy band edge or even in the middle of the selective reflection band. Such behavior is explained by topological heterogeneities of the CLC director structure and possible thermal degradation of the distributed feedback cavity, as discussed in the supplementary information. The laser emission is left-circularly polarized, consistent with the chirality of CLC\textsubscript{OH} structure, thus indicating an optical feedback through internal Bragg reflection.

The use of an applied electric field to control the spectral location of the photonic bandgap in the CLC\textsubscript{OH} structure while preserving the periodic heliconical conformation of the director provides an efficient mechanism to tune the wavelength of laser emission as long as photonic bandgap overlaps the fluorescent emission spectrum of the laser dye, Fig. 3.17. In CLC\textsubscript{OH} samples, $p \propto 1/E$, see section 2.2. As the electric field decreases below $E_{KC}$, the pitch increases, and the emission wavelength $\lambda$ follows the spectral position of selective reflection band, moving toward longer wavelengths, Fig. 3.17a and 3.18b. The tunability is extraordinary broad, as $\lambda$ changes in the range 574-675 nm in a mixture with the DCM dye, and 594-722 nm in the LD688 mixture, Fig. 3.18b. The tunable lasing range covers a large portion of the fluorescence band for each of the laser dyes, see Fig. 3.15. In principle, with suitable laser dye and pump source there is no limitation to extend lasing into different regions of the spectrum.
Figure 3.18. Lasing efficiency and electrically tunable lasing range. (a) Lasing emission intensity as function of pump energy at $\lambda = 625$ nm for LD688 sample, and at $\lambda = 610$ nm for DCM sample. (b) Electric field dependence of the lasing wavelength $\lambda$ for LD688 and DCM dye doped CLC$_{OH}$ samples. (c) Lasing threshold and intensity as function of lasing wavelength for LD688 sample. Error bars represent standard deviation of lasing emission energy for 40 consecutive pump pulses.

To demonstrate high efficiency of electrical tuning of laser emission from the CLC$_{OH}$ structure, the lasing threshold was determined at different emission wavelength for LD688 samples. The threshold is lowest near the fluorescence peak of the laser dye.
and increases near the two edges of the fluorescence band, Fig. 3.18c. When the overlap of selective reflection and fluorescence band diminishes, lasing becomes inefficient and unstable, with large variations in energy output from consecutive pump pulses. Moving the selective reflection band away from the fluorescence band completely eliminates lasing, leaving only a broad fluorescence in the emission spectrum. The intensity of laser emission from CLC<sub>OH</sub> structure was measured as a function of emission wavelength for LD688 samples under fixed pump energy of 8.6±0.6 µJ/pulse. The energy of emitted laser pulses peaks near the center of the dye fluorescence band and decays as the selective reflection band is tuned away from it, Fig. 3.18c.

To conclude, we have demonstrated highly efficient electrically tunable lasing from the CLC<sub>OH</sub> structure at room temperature. The principal advantage of the electrically controlled CLC<sub>OH</sub> laser is that the electric field is applied parallel to the helical axis of the structure and thus changes the pitch but preserves the single-harmonic periodicity. The preserved single-harmonic periodicity explains why the efficiency of lasing is high in the entire tunable range of emission. The optically pumped CLC<sub>OH</sub> laser is very simple to fabricate and operate, as it represents a thin 50 µm slab of CLC material with dye, confined between two glass plates coated with transparent electrodes. Using two dyes, we achieved a very broad range of tunable lasing, 574-722 nm. The broad tuning range of CLC<sub>OH</sub> lasers, coupled with their microscopic size, and narrow line widths may enable new applications in areas such as labs-on-a-chip, medical diagnostics, dermatology, and holography.
3.5.4 Supplementary information

Light propagation in CLC$_{OH}$ structure

When the CLC$_{OH}$ is doped with fluorescent molecules, lasing is observed at the edges of selective reflection band, since there the photon group velocity approaches zero and the correspondingly long dwell time of the emitted photons supports simulated emission.

Light propagation in CLC$_{OH}$ is similar to that in right-angle helical cholesterics. By solving Maxwell’s equations in CLC$_{OH}$, the eigenvalues

\[ n^2 = \bar{\varepsilon} + \left( \frac{\lambda_0}{P} \right)^2 \pm \sqrt{\delta^2 + 4\bar{\varepsilon}\left( \frac{\lambda_0}{P} \right)^2}, \]

(3.5)

where \( \bar{\varepsilon} = \left( \varepsilon_\parallel + \varepsilon_\perp \right)/2 \) and \( \delta = \left( \varepsilon_\parallel - \varepsilon_\perp \right)/2 \). In CLC$_{OH}$, \( \varepsilon_\perp \) and \( \varepsilon_\parallel \) can be expressed as

\[ \varepsilon_\perp = n_o^2 \quad \text{and} \quad \varepsilon_\parallel = \left( n_e^{\text{eff}} \right)^2 = \frac{n_o^2 n_e^2}{n_e^2 \cos^2 \theta + n_o^2 \sin^2 \theta}, \]

respectively. \( \theta \) and \( P \) are the cone angle and pitch of the cholesteric heliconical structure, which are dependent on the applied electric field [32].

The eigenvalues, \( n^2 \), in Eq. (3.5) has two branches, the branch corresponding to the negative radical is negative for \( \sqrt{\varepsilon_\perp} < \frac{\lambda_0}{P} < \sqrt{\varepsilon_\parallel} \) and in this region, \( n \) is imaginary. This region therefore corresponds to the photonic bandgap, with the low-energy band edge at \( \lambda_0 = \sqrt{\varepsilon_\parallel} P \) and the high-energy edge at \( \lambda_0 = \sqrt{\varepsilon_\perp} P \).
Ignore the finite thickness of the CLC$_{OH}$ film, The photonic density of states (DOS) $\rho$ is can be calculated as [145]

$$\rho = \frac{\sqrt{\delta^2 + 4\varepsilon\left(\frac{\lambda_0}{P}\right)^2}}{cn} + \frac{2\left(\frac{\lambda_0}{P}\right)^2}{cn\sqrt{\delta^2 + 4\varepsilon\left(\frac{\lambda_0}{P}\right)^2}}.$$  \hfill (3.6)

Since $n^2$ is a smoothly varying function of $\lambda_0$, the DOS diverges at the band edges, where $n \rightarrow 0$. Photon emission by excited atoms and molecules and distributed feedback lasing is therefore expected at the band edges.

**Stability of lasing from CLC$_{OH}$ structure**

According to our observations, the lasing emission beam profile and wavelength change slightly during rapid sequential pump pulses (2 Hz). The lasing emission beam profile obtained with the first few pump pulses (i.e. a cold spot) of the sample has a nearly Gaussian profile. However, subsequent pump pulses lead to a heating induced change in pulse shape, eventually showing several distinct maxima.

Figure 3.19 shows 2- and 3D spatial profiles of emission intensity from a LD688 doped CLC sample. Emission from the first four pulses is with a single peak, as shown in Fig. 3.19a and 3.19d. Subsequently the pattern changes to that of Fig. 3.19b and Fig. 3.19e. Increasing the pump energy and continuing to pump, heating eventually results in loss of coherence, and fluorescent emission shown Fig. 3.19c and 3.19f. Lasing
emission profiles shown on Fig. 3.19(a, b, d, e) were obtained with pump energy of ~1 μJ/pulse, and spatial profile of fluorescent emission shown on Fig. 3.19(c, f) was obtained with pump energy of ~4 μJ/pulse.

Heating the CLC samples by the pump is known to create reversible thermal degradation of the distributed feedback cavity in dye doped CLC lasers [146]. In both CLC and CLC\textsubscript{OH} systems, if the pump rate/energy is reduced, stable emission at a constant wavelength occurs.

**Figure 3.19.** Spatial profiles of laser emission beam and fluorescence from LD688 sample mixture. (a) & (d) beam profile of 3rd lasing emission pulse, $\lambda = 650\text{nm}$; (b) & (e) beam profile of 7th lasing emission pulse, $\lambda = 650\text{nm}$; (c) & (f) spatial profile of fluorescence.
CHAPTER 4

FAST SWITCHING NEMATICS TEMPLATED BY THE POLYMER-STABILIZED BLUE PHASE

4.1 Introduction

As described in Chapter 1, BPs can become the materials of choice in the next generation liquid crystal displays (LCD), due to their distinctive advantages over the commonly used nematic phase: (1) self-assembled structure so no alignment layer is needed; (2) nanoscale (~100 nm) double twist cylinder structure which leads to sub-millisecond response time. However, practical applications are hindered by intrinsic problems, the most serious of which is a narrow temperature range of BPs. Two approaches have been demonstrated to extend the BPs temperature range [82-84]. The first one is a polymer-stabilized blue phase (PSBP) [82,83]. Its detrimental feature is hysteresis in electro-optic response[85]. The second approach is to search for new LC molecules with reduced bend elastic constants, such as bimesogens and bent-core LCs [84,87,88]. However, the bimesogenic and bent-core materials have a relatively low dielectric anisotropy and high viscosity [89], which leads to a longer response time and higher driving voltages [84]. The status of current research makes it clear that the material properties that are beneficial for the temperature stability of BPs are not necessarily beneficial for electro-optic performance.
In this chapter, we describe the fast electro-optic switching (response time 0.1 ms) of a blue-phase-polymer templated nematic with a broad-temperature range of thermodynamic stability and hysteresis-free performance. The nematic fills a polymer template that imposes a periodic structure with cubic symmetry and submicron period. In the field-free state, the nematic in polymer template is optically isotropic. An applied electric field causes non-zero optical retardance. The approach thus combines beneficial structural and optical features of the blue phase (cubic structure with submicron periodicity) and superior thermodynamic stability and electro-optic switching ability of the nematic filler. We have published these results in [97].

4.2 Materials and Sample Preparation

We propose an electro-optically switchable BP-polymer-templated nematic (BPTN) in which the specially formulated BP mixture is used only to create a polymer template, but is not used for the electro-optic switching; the latter function is performed by another filler in the polymer template, such as a broad-temperature range nematic, to achieve good electro-optic performance.

First, the BP was formed in a mixture of commercially available materials, a nematic MLC2048, chiral dopant S811 (both purchased from EM Industries), reactive monomers RM257 (BDH, Ltd) and TMPTA (Aldrich), and photoinitiator IRG651 (Aldrich) with weight percentages 51wt%, 36.1wt%, 7.3wt%, 5wt%, and 0.6wt%, respectively. The mixture was injected into the glass cell of thickness 3.8 µm in its
isotropic phase. The material was then cooled (0.2°C/min) to 24°C at which it shows a supercooled BPI phase. The mixture was irradiated with UV light (wavelength 365nm, intensity 1 mW/cm²) for 3 hours to induce photo-polymerization. The texture of the resulting PSBP under crossed polarizer is shown in Fig. 4.1b.

Second, the PSBP was placed in hexane for 20 hours, in order to remove the un-polymerized components, Fig. 4.1c. The residual hexane was evaporated by drying at room temperature.

To visualize the polymer network, we used a scanning electron microscope (SEM) Hitachi S-2600N, Fig. 4.1d. One of the plates of the cell was removed and a thin (~20 nm) layer of gold was deposited onto the polymer structure to enhance the contrast. The SEM texture clearly shows a periodic structure with a typical size of pores around 200 nm, as shaped by the original periodic cubic structure of BPI, Fig. 4.1e,f.

Finally, the template was refilled with a broad-temperature nematic mixture designed to perform electro-optic switching. The polymer template transfers the BP structural organization onto the nemtaic filler, resulting in a BPTN. Depending on the particular application, the filler can be designed to have a high dielectric anisotropy (to reduce the operational voltage), high birefringence (to increase the switchable phase retardance), extended temperature range of stability, etc. As an example, we use a standard nematic mixture E7 (EM Industries). The nematic phase of E7 is stable between -30°C and 58°C [147]. The material is nonchiral and does not form the BPs by itself. However, once E7 is inside the polymer template, it shows textures very similar to those
of the BPs, in a very broad temperature range, from -30°C (the lowest temperature we used in the experiments) to 60°C, Fig. 4.2, which is much wider than the range of the original BP (42°C-22°C on cooling).

Figure 4.1. Polarizing optical microscope textures of BP mixture (a) before and (b) after photo-polymerization, (c) after removing the LC; (d) SEM texture of BP-shaped polymer network; (e) 3D arrangement of disclinations in BPI; (f) 2D projection of the disclination network in (e). The scale bar is 100 µm in (a)-(c), and 2 µm in (d).
Figure 4.2. Polarizing optical microscope textures of BPTN E7 at different temperatures.

4.3 Results and Discussion

To study the electro-optic performance, we used in-plane-switching (IPS) cells. The IPS cells of thickness of 3.8 µm were formed by two parallel glass substrates, one with patterned indium tin oxide (ITO) electrodes (stripe electrodes of 10 µm width and 10 µm spacing). The textural response to the in-plane AC electric field (rectangular pulses of frequency $f = 10$ KHz) is shown in Fig. 4.3.
Figure 4.3. Polarizing microscope textures of BPTN E7 cell under AC electric field
\((f = 10 \text{ kHz})\) directed at 45 degree with respect to the two crossed polarizes labeled A and P.

Figure 4.4a shows the optical phase retardance of BPTN E7 cells as a function of the applied AC electric field \((f = 10 \text{ KHz})\) for three consecutive driving cycles. The retardance is measured by LC-PolScope (Cambridge Research and Instrumentation) [122,148] at wavelength \(\lambda = 546 \text{ nm}\). The electro-optic switching is practically hysteresis-free, which is a significant advantage as compared to the regular PSBP switching [85]. The hysteresis, defined as the voltage difference at half-maximum phase retardance change between forward and backward directions, is \(\Delta V = 0.77 \text{ V}\). As compared to the maximum applied voltage \(V_p\), it is very small, \(\Delta V/V_p = 0.64\%\). Figure 4.4b shows the temperature dependence of Kerr constant \(K\). It is of the same order as reported for the best PSBPs [83,149], with that advantage that the order of magnitude of \(K\) is preserved even at -10°C. As clear from the dependence [150] \(K \propto \Delta n \cdot \Delta \varepsilon\), Kerr
constant can be further increases by using a nematic filler with a large dielectric anisotropy $\Delta \varepsilon$ and field-free birefringence $\Delta n$[151]; for E7, these parameters are rather average, $\Delta \varepsilon = 13.8$ and $\Delta n \approx 0.2$; much higher values are currently available, e.g., $\Delta \varepsilon$ in excess of 100 [152].

![Figure 4.4](image)

**Figure 4.4.** Electro-optic performance of 3.8 $\mu$m IPS BP-templated E7 cell. (a) Phase retardation vs the applied AC field; $f = 10$ kHz; three cycles of driving at 25°C. (b) Temperature dependence of Kerr constant. The line is a guide to an eye.

We determined the characteristic times of the electro-optic response by recording the change of light transmittance through the cells and a pair of crossed polarizers and determining the levels of 10% and 90% of the maximum transmittance. Both switch-on $\tau_{on}$ and switch-off $\tau_{off}$ times are below 0.1 ms when the cells are driven by AC voltage (rectangular pulses) of amplitude 100 V and frequencies 1 KHz and 125 Hz, in the temperature range (30-50) °C, Fig. 4.5c and Table 4.1. Most importantly, these times remain shorter than 1 ms when the temperature is as low as (-20) °C, Fig. 4.5c. The response times are close to the record numbers achieved with PSBPs for oblique light
propagation and vertical electric addressing (e.g., $\tau_{\text{off}} = 39 \mu s$ at room temperature [149]), and are much smaller than the response times in standard BPs driven by IPS (~0.5 ms) [83,153].

![Figure 4.5](image)

**Figure 4.5.** Electro-optic response of BP templated E7. (a) applied voltage profile with frequency 1 kHz and (b) corresponding light transmittance at 25°C; (c) Temperature dependence of the on- and off- response times for an applied voltage 100 V at different frequencies.

To illustrate the advantages of our approach in terms of thermal stability and electro-optic switching, we compare the performance of BPTN with that of the original un-polymerized BP and PSBP (with the initial BP material remaining as a filler after the polymer network has been formed), Table 4.1. The response times in all three cases were measured in the same manner, by applying a rectangular-wave voltage with magnitude 100V and frequency 1 kHz in the IPS cells. As compared to the pure BP and PSBP, the BPTN approach offers the widest BP temperature range, the largest Kerr constant, and
also features a fast sub-millisecond electro-optic switching at temperatures at which BP
and PSBP are not switchable at all.

**Table 4.1.** Comparison of pure BP, polymer-stabilized BP and BP-polymer-templated
nematic approaches.

<table>
<thead>
<tr>
<th></th>
<th>BP range (°C)</th>
<th>Kerr constant (10^{-9} \text{ m/V}^2)</th>
<th>Response time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure BP</td>
<td>54-61 °C</td>
<td>0.14 (at 56 °C)</td>
<td>61 µs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>82 µs (at 56 °C)</td>
</tr>
<tr>
<td>PSBP</td>
<td>&lt;-30 °C - 56 °C</td>
<td>0.014 (at 25 °C)</td>
<td>154 µs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>180 µs (at 25 °C)</td>
</tr>
<tr>
<td>BPTN filled E7</td>
<td>&lt;-30 °C - 60 °C</td>
<td>0.16 (at 25 °C)</td>
<td>87 µs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>61 µs (at 25 °C)</td>
</tr>
</tbody>
</table>
CHAPTER 5

SUMMARY

Chirality is ubiquitous in the natural world and plays an important role in soft condensed matter, especially liquid crystals. In this dissertation, we investigated the twist bend and double twist structures in thermotropic liquid crystals. The summary of this dissertation is as follows:

1. We demonstrated experimentally a new type of orientational nematic order in which achiral dimer molecules follow the direction of oblique helicoids. The new phase, first considered theoretically by R.B. Meyer and I. Dozov as a twist-bend nematic (N_{tb}), is a structural link between the well-known uniaxial nematic (N) and chiral nematic (N'^{+}) phases. The oblique helicoidal structure of the N_{tb} phase is evidenced by asymmetric Bouligand arches in freeze-fracture transmission electron microscopy textures. The period of oblique helicoids is 8-9 nm. The unique nanostructure leads to new macroscopic properties of N_{tb}, such as first-order dielectric reorientation and expulsion of twist and bend deformations of the optic axis.

We measured the temperature dependence of the splay (K_1), twist (K_2), and bend (K_3) elastic constants of the uniaxial nematic (N) phase formed by dimeric liquid crystal
mixture with negative dielectric anisotropy. The material under study forms the nematic twist-bend (N_{tb}) phase when cooled down from the uniaxial nematic (N) phase. In the N phase, the bend constant $K_3$ decreases dramatically as the temperature is lowered towards the N-N_{tb} phase transition. Both $K_1$ and $K_2$ increase as the temperature is lowered; $K_1$ remains about 2-3 times higher than $K_2$ near the transition to the N_{tb} phase. The measured elastic properties are consistent with the tendency of the dimeric molecules to adopt bent configurations that eventually give rise to the N_{tb} phase.

We explored the effects of photo-isomerization on the N-N_{tb} phase transition using an azobenzene-based non-symmetric liquid crystal dimer. We observed an isothermal, reversible N_{tb}-N transition, which is attributed to a trans-cis photo-isomerization of the azobenzene fragment on UV irradiation. The cis isomers stabilize the standard nematic phase and the trans isomers stabilize the N_{tb} phase.

2. We observed experimentally an electrooptic effect in a cholesteric LC with a distinct oblique-helicoidal director deformation. The oblique helicoid, predicted in late 1960-ies, is demonstrated to exist in dimer materials with an anomalously small bend elastic constant. Theoretical, numerical, and experimental analysis establishes that both the pitch and the cone angle of the oblique helicoid increase as the electric field decreases. The effect can enable many applications that require dynamically controlled transmission and reflection of light. We demonstrated the electrooptic applications using the cholesteric heliconical structure, such as the electrically tunable selective reflection of
light from ultraviolet to visible and infrared, full color reflective display, and electrically tunable lasing. Further work can be done to achieve the cholesteric heliconical structure with the magnetic field, light irradiation, and surface confinement, besides the electric field. The cholesteric heliconical structure can also find applications in tunable optical filter, smart windows with transparent/opaque/tunable color states.

3. We reported on a fast electro-optic switching (response time 0.1 ms) of a blue-phase-polymer templated nematic with a broad-temperature range of thermodynamic stability and hysteresis-free performance. The nematic fills a polymer template that imposes a periodic structure with cubic symmetry and submicron period. In the field-free state, the nematic in polymer template is optically isotropic. An applied electric field causes non-zero optical retardance. The approach thus combines beneficial structural and optical features of the blue phase (cubic structure with submicron periodicity) and superior thermodynamic stability and electro-optic switching ability of the nematic filler. Further work can be done using liquid crystal twist bend structure as a template, such as N$_{tb}$ phase and cholesteric heliconical structure, to achieve the fast switching electrooptic performance.
REFERENCES


[99] Y. Bouligand, M. O. Soyer, and S. Puiseux-Dao, Chromosoma 24, 251 (1968).