Magnetically tunable selective reflection of light by heliconical cholesterics

S. M. Salili,1 J. Xiang,1 H. Wang,1 Q. Li,1 D. A. Paterson,2 J. M. D. Storey,2 C. T. Imrie,2 O. D. Lavrentovich,1 S. N. Sprunt,3 J. T. Gleeson,3 and A. Jákli1,4

1Chemical Physics Interdisciplinary Program & Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA
2Department of Chemistry, University of Aberdeen, AB24 3UE Scotland, United Kingdom
3Department of Physics, Kent State University, Kent, Ohio 44242, USA
4Complex Fluid Group, Wigner Research Centre, Budapest, Hungary

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We present studies of chiral nematic liquid crystals composed of flexible dimeric molecules subject to large dc magnetic fields between 0 and 31 T. We observe that these fields lead to selective reflection of light depending on temperature and magnetic field. The band of reflected wavelengths can be tuned from ultraviolet to beyond the IR-C band. A similar effect induced by electric fields has been presented previously, and was explained by a field-induced oblique-heliconical director deformation in accordance with early theoretical predictions. The use of magnetic field here instead of electric field allows precise measurements of some material constants and holds promise for wireless tuning of selective reflection.

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I. INTRODUCTION

Flexible bent-core dimeric liquid crystal molecules are reminiscent of nunchaku fighting sticks: two rigid rodlike arms linked by a flexible, alkyl chain. These materials have recently taken center stage in liquid crystal science due to their extraordinary physical and electro-optical properties and novel states of orientational order [1–16]. In particular, many dimers with an odd number of carbons in the alkyl chain exhibit a “twist-bend” nematic (Ntb) phase, which was predicted by Dozov [17] assuming a negative bend-elastic constant that promotes spontaneous director bend. Since a pure director bend cannot fill space continuously, it must couple to a twist or splay. In the case of twist-bend coupling, the result is a heliconical director modulation, where the helical axis is the average optical axis of the medium.

Recent experiments verified the existence of the Ntb phase with a surprisingly short heliconical pitch of order 10 nm [7,18,19]. The temperature-variation of this nanoscale pitch (“pseudolayers”) results in a Helfrich-Hurault type buckling instability [20] causing optically observable stripes and/or elongated focal conics similar to smectic phases. However, the Ntb does not have the periodic density modulation like true, layered smectics. Most of the flexible dimers with Ntb phase also exhibit a higher temperature uniaxial nematic (N) phase.

The effect of chirality on the N phase of flexible bent-core dimers has been investigated recently both experimentally [21,22] and theoretically [23]. Experiments on chiral, asymmetric dimers indicate a sequence of up to seven distinct nematic phases. As the constituent molecules are intrinsically chiral, the highest-temperature mesophase is either the cholesteric phase (N*) or one of the blue phases. Stable phases observed at lower temperatures are variants of modulated nematic phases with apparently much larger pitch than in achiral Ntb dimers [10]. The addition of chiral dopants to achiral dimers [24,25] with a N-Ntb phase sequence results in a wide temperature range blue phase even at low concentrations. Interestingly, the chiral dopant-induced helical structure in the N* phase is expelled upon cooling to the Ntb* phase.

Depending on chiral dopant concentration, spontaneous formation of different stripe textures occurs in the N* phase above Ntb*. This phenomenon has been explained as a consequence of the bend elastic constant $K_3$ being sufficiently smaller than the twist constant $K_2/K_3 > 2$ [26]. Theoretically, it was predicted almost 50 years ago by Meyer [27] and de Gennes [28] that chiral N* materials with $K_3 < K_2$ should have very distinct responses to external influences. While in the conventional N* state, where $K_3 > K_2$, the director n is perpendicular to the helix axis, in the case of $K_3 < K_2$, the director makes an acute angle with the helix axis above a certain electric or magnetic threshold field. Experimentally Xiang et al. have demonstrated the existence of such a heliconical state by using electric fields [14,15]. In mixtures containing odd-numbered flexible dimers they demonstrated selective reflection of light between 400 and 1000 nm. However, because of finite polarizability and conductivity, as well as the need to use conducting electrodes, the effects caused by electric fields on liquid crystals are substantially more complex than those caused by magnetic fields. Therefore, it is desirable to study the magnetic analog of the electrically induced selective reflection effect, which we present here.

II. EXPERIMENTS

The molecular structures of the liquid crystal materials used are shown in Fig. 1(a). The rod-shaped compound pentyl cyanobiphenyl (5CB) has a nematic phase between 21 and 35.5°C. It has the same core structure as the arms of the two, symmetric dimers liquid crystals (LCs) 1-(4-cyanobiphenyl-4′-yl)-6-(4-cyanobiphenyl-4′-oxyloxy) hexane (CB7CB) and 1′,9′-bis(4-cyanobiphenyl-4′-yl) nonane (CB9CB). On cooling from the isotropic phase, CB7CB forms a uniaxial nematic phase at 116°C and then transitions to a twist-bend nematic phase at 103°C [29]. CB9CB forms the phase sequence $I(122.4°C)N(104.9°C)N_{tb}(40.5°C)Cr$. The left-handed chiral dopant S811 (Merck) was added to the above materials to make two chiral mixtures, M1 and M2. The composition of M1 is 45:20:32:3 wt % 5CB:CB9CB:CB7CB:S811, and its phase sequence is Iso (64.8°C) N* (30.0°C) Ntb*. The corresponding properties of M2 are 44:20:32:4 wt % 5CB:CB9CB:CB7CB:S811 composition and Iso (65.0°C)
$N^*$ (32.0°C)$N_{\text{th}}^*$ phase sequence. The helical pitch of M1 and M2 at 35°C and $B = 0$ are $p_o \sim 4 \mu m$ and $p_o \sim 3 \mu m$, respectively.

Magneto-optical experiments were carried out in the split-helix, resistive, solenoid magnet at the National High Magnetic Field Laboratory (NHMFL) [30]. The mixtures were loaded in $10 \times 10 \text{ mm}$ planar glass cells, whose inner surfaces are treated with a unidirectionally rubbed polyimide PI2555 (HD Micro Systems) that promotes molecular alignment parallel to the substrates (planar alignment) and along the rubbing direction. The separation $d$ between substrates was $30 \mu m$. Each filled liquid crystal cell is inserted into a Teflon-insulated, temperature-controlled oven (temperature stability $\pm 0.05 \degree C$) with optical access parallel to the magnetic field direction. Two high-precision temperature sensors are embedded in the oven; one is a glass-encapsulated thermistor and the other a platinum resistive temperature device. Neither showed any drift during application of high magnetic fields. The oven is inserted into the magnet bore and positioned 5 cm above the center line where the maximum achievable field is 31 T.

Optical measurements were carried out with the optical path oriented parallel to the field and to the heliconical axis of the sample. A standard optical spectroscopy setup [see Fig. 1(b)], incorporating a nonpolarized tungsten halogen light source (Ocean Optics LS-1) and visible or infrared spectrometers (Ocean Optics USB2000 and NIRQUEST), was used to measure the intensity spectrum of the reflected light as a function of wavelength from 400 to 1700 nm. The reflectance is the ratio of the reflected intensity from the LC cell and from a mirror. The background intensity was deducted by using a matt black surface representing the zero level.

Prior to each reflection measurement, the samples were heated to the isotropic phase, and cooled (at 0 T) at 1°C/min until the desired temperature within the $N^*$ phase is reached. The director structure of this initial alignment is shown in the left hand side of Fig. 1(c). The helix axis is normal to the substrates and has a pitch $p_o$. The magnetic field was then increased (at 5 T/min) to 31 T, and maintained for 3 min. This field was enough to unwind the helix and rotate the director along the magnetic field as shown in the middle of Fig. 1(c). The field was then decreased (5 T/min) to various levels, and kept constant at each level for 3 min before the reflection spectrum was recorded. When the field was smaller than a threshold $B_c$, a heliconical director structure forms with a pitch $p$ being different from $p_o$ of the initial $N^*$ structure. This is shown schematically on the right hand side of Fig. 1(c).

**III. RESULTS**

Figure 2 presents reflection spectra for the mixture M1 for various magnetic field levels and for three different temperatures in the $N^*$ range. The peaks could be well fitted by Lorentzian distribution.

As one can see, decreasing the field leads to a shift of the reflection spectrum toward the IR. At 38°C, a sharp reflection appears first at $B_1 = 16.1$ T with peak position at 410 nm. When the field is stepped down to 9.9 T, the peak shifts to 650 nm. Below 9.9 T, it disappears. At lower temperatures, the onset of selective reflection occurs at lower fields (e.g., $B_1 (35\degree C) = 11.2$ T and $B_1 (32\degree C) = 7.4$ T), and the peak position shifts over a broader range with decreasing field levels, before eventually disappearing at low field. In particular, at 35°C, selective reflection spans the range 420–1300 nm for field levels between 11.2 and 3.7 T. At 32°C the span ranges

![Reflection spectra](image-url)
from 450 to 1600 nm for fields between 7.4 and 2.5 T, and
reaches notably further into the IR. Below 2.5 T the peak shifts
outside the limit of our spectrophotometer (λmax = 1700 nm),
so the tunable wavelength certainly exceeds 1700 nm. We
note that in this range, the field necessary to induce tuning
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approaches that achievable with permanent magnets. At all
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values can be considered as the lower limit of the selective reflection and show that they
start in the UV range. Unfortunately, we could not follow the
peaks in the UV range due to the spectral limitations of our
light source and the absorption of the glass substrates.

As the peak positions depend both on the magnetic field and temperature, one can also tune the spectra by fixing the magnetic field and varying the temperature. For example, for
M1 at B = 7.4 T the peak can be shifted from 450 nm to
950 nm by heating the sample from 32 to 39°C. Both λp and
Δλ increase with temperature, the former linearly with T and
the latter approximately so.

Although the height of the reflected peaks shows non-
monotonous behavior, the area A under the peaks increases
with λp as A = a(λp − λo). The fitted parameters are α ≈
0.02−0.025 (when the transmittance is normalized to 1)
for both materials (indicating that only 2–3% of the total
light intensity is reflected), and λo ≈ 250 nm for M1 and
λo≈350 nm for M2. These latter values can be considered

Figure 3 presents reflection spectra for the M2 mix-
ture at various fields and for different temperatures.
The characteristics of the spectra are similar to those for M1,
except that for M2 the reflection band is limited to the
visible range. As seen for M1, the field level for onset of
selective reflection in M2 decreases with decreasing tempera-
ture [B1(40°C) = 18.6 T, B1(38°C) = 17.4 T, B1(36°C) =
13.6 T and B1(34°C) = 9.9 T], and decreasing the field shifts
the reflection to higher peak wavelength and larger width.

The magnetic field dependencies of the peak positions
(λp) and the full width at half maximum (Δλ) at various
temperatures are plotted in Figs. 4(a) and 4(b) for M1 and
Figs. 4(c) and 4(d) for M2. For both materials and at all mea-
sured temperatures, we fit the peak positions and widths to the
following forms: λp(B) = a(T)/B and Δλ(B) = b(T)/B2.

The fitted values of the parameters a and b are the following:
For M1: a(32°C) = 3867, a(35°C) = 4666, a(38°C) = 6465
in units of nm T; b(32°C) = 703, b(35°C) = 1265, b(38°C) =
1267 in units of nmT2. For M2: a(34°C)=4152,a(36°C) =
5660 , a(38°C) = 7044; a(40°C) = 7585; b(34°C) = 851,
b(36°C) = 1410, b(38°C) = 1734, b(40°C) = 1551. The fit
for peak position describes our data slightly better than that
for peak width.

As the peak positions depend both on the magnetic field and temperature, one can also tune the spectra by fixing the magnetic field and varying the temperature. For example, for
M1 at B = 7.4 T the peak can be shifted from 450 nm to
950 nm by heating the sample from 32 to 39°C. Both λp and
Δλ increase with temperature, the former linearly with T and
the latter approximately so.

Although the height of the reflected peaks shows non-
monotonous behavior, the area A under the peaks increases
with λp as A = a(λp − λo). The fitted parameters are α ≈
0.02−0.025 (when the transmittance is normalized to 1)
for both materials (indicating that only 2–3% of the total
light intensity is reflected), and λo ≈ 250 nm for M1 and
λo≈350 nm for M2. These latter values can be considered

Figure 3. Reflection spectra recorded from the M2 mixture for
various magnetic fields at temperature of 34°C, 38°C, and 40°C.

IV. DISCUSSION

The magnetic field induced director deformation of a chiral
nematic liquid crystal can be described by using the Frank-
Oseen free energy functional. The elastic component of free
energy density of the N° phase is

\[
F = \frac{1}{2}K_1(\vec{V} \cdot \vec{n})^2 + \frac{1}{2}K_2(\vec{V} \times \vec{n} - q_0)^2 
\]

\[
+ \frac{1}{2}K_3(\vec{n} \times (\vec{V} \times \vec{n}))^2 - \frac{1}{2}\mu_o \Delta \chi H^2, 
\]

where K_{1−3} are the splay, twist, and bend elastic constants,
respectively, q_0 = 2π/p_0 where p_0 is the helical pitch, μ_o =
4π10^{-7} Vs/(Am) is the permeability of free space, Δχ ∼
10^{-6} (SI) is the diamagnetic susceptibility anisotropy, and H
is the magnetic field.

When a strong enough field \( H = (0, 0, B/\mu_o) \) is applied
along the \( z \) axis, the helix becomes unwound with the
director pointing everywhere along the field, i.e., \( \vec{n} = (0, 0, 1) \).
As the field is reduced, the tendency to twist due to the
chiral molecular content can compete with the diamagnetic
interaction, and below a threshold field \( H_t = B_t/\mu_o = \frac{(2\pi/p_o)(K_2/\mu_o\Delta \chi K_3)}{4} \) a heliconical state forms where the
director follows an oblique left-handed helicoid, \( \vec{n} =
(sin \theta \cos \phi, sin \theta \sin \phi, cos \phi) \) with a cone angle \( \theta > 0 \) and
ϕ(x) = 2πx/\rho. Note that \( B_t \) is the highest magnetic field
where the modulated structure with the heliconical director
appears, whereas \( B_1 \) is the highest magnetic field where
the selective reflection is observed experimentally. Since
our measurements did not work in UV, where the selective
reflection starts, \( B_t > B_1 \). The tilt angle \( \theta \) depends on B
as sin^2θ = \frac{1}{1−(\frac{B}{B_t})^2} \) [14], and the heliconical pitch is
inversely proportional to the magnetic induction \( B = \mu_o H \) \[27\]
as \( \frac{1}{\rho} = \frac{\mu_o}{\mu} K_3/K_2 \).

If the heliconical pitch is in the UV-VIS-IR range, the
material selectively reflects light with peak value \( \lambda_p \approx \frac{\rho}{\mu} \).
Here \( \rho = \sqrt{(2n_o^2 + n_{e,eff}^2)/3} \), where
n_{e,eff} = \frac{n_n n_o}{\sqrt{n_n^2 \cos^2 \theta + n_o^2 \sin^2 \theta}}
is the average refractive index (\( n_n \) and \( n_o \) are extraordinary
and ordinary refractive index, respectively). The effective
refractive index at very small cone angles can be assumed to
be field-independent; i.e., \( \rho \approx n_o \). Under this assumption,
The peak wavelength should be inversely proportional to $B$; specifically,
\[ \lambda_p = \frac{\bar{n}}{\Delta n} \sqrt{\frac{K_3}{\mu_0 \Delta \chi}} \approx \frac{a}{B}. \]
As noted above, this prediction is indeed observed, with the coefficient increasing with temperature. This is likely due to the increase of $K_3$ with $T$, in accord with the independently measured values of elastic constants above the $N$- $N_{tb}$ phase transition [6,7,14,31–33].

Assuming $\bar{n} \sim 1.6$ and $\Delta \chi \sim 5 \times 10^{-7}$ SI, a typical value of $a \sim 4 \times 10^4$ nm T gives $K_3 \sim 2.5$ pN, which compares reasonably well with other determinations of $K_3$ [6,7,14,31–33].

The width of the peak $\Delta \lambda = \Delta n_{\text{eff}} p$, where $\Delta n_{\text{eff}} = n_{e,\text{eff}} - n_o$ is the effective birefringence. It clearly increases with decreasing magnetic fields, where the pitch increases, and where $\theta$ increases, i.e., $\Delta n_{\text{eff}}$ is increasing. As M1 could be tuned up to a larger pitch, on average the width of the reflection pitch appears larger, but when comparing the $\Delta \lambda$ of M1 and M2 at the same $\lambda_p$ they are very similar. For small $\theta$ the effective birefringence can be approximated as $\Delta n_{\text{eff}} \approx \frac{\Delta \chi_p}{2n_e^2(1-\kappa)} \theta^2$.

This means that for an ideally field-adjustable heliconical structure with a uniform pitch,
\[ \Delta \lambda \approx \frac{\kappa B_p n_o}{B} \frac{\Delta n(n_e + n_o)}{2n_e^2(1-\kappa)} \left( \frac{B_i}{B} - 1 \right). \]

At low magnetic fields when $B \ll B_t$, this equation predicts $\Delta \lambda \propto 1/B^2$. As can be seen in Figs. 4(b) and 4(d), this behavior is indeed found experimentally for small $B$ values. Deviations from this behavior are observed only at high magnetic fields.

The observed collapse of the selective reflection at a critical magnetic field $B_c$ is due to the positive local diamagnetic anisotropy of the quasinematic order that opposes the increase of the angle between the director and the magnetic field. As explained for the electrically tuned selective reflection of materials with positive dielectric anisotropy [14], as the field decreases below some critical value that can be recast for the diamagnetic response as
\[ B_c \approx B_t \frac{(2 + \sqrt{2(1-\kappa)})}{(1-\kappa)^2} \frac{1}{\kappa}, \]
the heliconical structure, with the axis parallel to the applied field is no longer stable, and transforms into a regular cholesteric right-angle helicoid with the axis being perpendicular to the applied field. Measuring $B_i/B_c$ one therefore can obtain $\kappa$. Since we could not measure in the UV range, we could only measure $B_1 < B_t$, thus we can only give an upper limit for $\kappa = K_3/K_2$, which we find to decrease from 0.18 to 0.1 as the temperature decreases from 38 to 32°C. In the case of the M2 mixture, the upper limit of $K_3/K_2$ varies from 0.25 to 0.18 from 40 to 34°C, indicating that increasing chiral concentration lead to an increase of $\kappa$. 

FIG. 4. Magnetic field dependence of the wavelength and full width at half maximum (FWHM) of the selective reflection peak observed at different temperatures. (a) $\lambda_p(B)$ [Inset 1/$\lambda_p(B)$] for M1, (b) $\Delta\lambda(B)$ [Inset 1/$\Delta\lambda(B^2)$] for M1, (c) $\lambda_p(B)$ [Inset 1/$\lambda_p(B)$] for M2, and (d) $\Delta\lambda(B)$ [Inset 1/$\Delta\lambda(B^2)$] for M2.
Future experiments will be done in a wider UV-VIS-IR region to be able to measure $B_t$ and $B_c$. With these we will be able to measure both $K_1/K_2$ and the cone angle $\theta$.

To summarize, we have demonstrated that magnetic fields can induce a heliconical state in the cholesteric phase of LC dimers above the twist-bend nematic phase, as was predicted long ago. The heliconical state exhibits a wavelength band of reflected light, and this band can be selectively tuned over a wide range from the UV to over 1700 nm in the IR. Measurements of the threshold and critical fields, and of the field-dependent peak positions, can provide the twist to bend elastic constant ratio and the cone angle $\theta$. The ability to tune reflection band using temperature as well as magnetic fields offers intriguing possible applications for novel magneto-optical devices.

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