Electrically Reconfigurable and Thermally Sensitive Optical Properties of Gold Nanorods Dispersed Liquid Crystal Blue Phase

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We report the electrically reconfigurable optical properties of gold nanorods (AuNRs) dispersed liquid crystal blue phase (BP). In principle, dispersing gold nanorods in a BP should not possess a critical concentration of the dispersant at the nanoscale, because the free-energy cost of disclination is negligible. Yet, the experimental results indicate that BP range reaches a plateau at a critical concentration of AuNRs. The mesophase range of the pure BP studied by polarizing optical microscopy is theoretically validated. The optical property of an AuNRs dispersed BP system is electrically and thermally reconfigurable.

1. Introduction

Cholesteric blue phase liquid crystals (BPLCs) are liquid crystals with self-aligned structures that exhibit mysterious intermediate phases first observed in 1888 by Reinitzer. The cholesteric blue phase has been extensively studied three decades ago—previous research characterizes BPLCs as a class of short-pitch chiral materials with a small doubly twisted structure, stabilized by the existence of disclination lines.

Blue phases appear within a narrow temperature range, due to the free-energy cost of disclination, usually less than one degree Celsius between the cholesteric and isotropic phases. The BP structure is formed by double twist cylinders of cholesteric liquid crystal molecules intersected at 45° to the helical axis that twists through the center of the cylinder. At the points where the three cylinders meet there is no avoiding defects. Therefore, the ideal packing of a series of double twist cylinders becomes a crystalline lattice of cylinders laced with disclination lines. Theoretically, the bend distortion energies at larger angles prevent the cylinder’s diameter from being greater than the pitch of a single twist helix. In principle, the cylinders can grow relatively long depending on the entropy of the self-assembled system, but their diameter is limited to approximately half of a pitch. Based on the packing structure of the cubic lattice, BPLCs are further classified into three categories: BPI, BPII, and BPIII corresponding to the body-centered, simple cubic, and an isotropic phase with uniform symmetry, respectively.

![POM images of (a) pure BP at 50 °C and (b) 0.06% AuNRs BP at 50 °C. The white scale bar is 20 μm and the cross-section of dark glass rod spacers in the photos is 10 μm.](Image)

The field-induced birefringence, Kerr effect, observed between a pair of polarizers crossed at 90 degrees is one of the important properties in a BPLC. The occurrence of this electro-optical effect, compared to a conventional nematic device, requires no alignment layers in the cell fabrication process. Furthermore, the response time of the Kerr effect appears in the sub-millisecond to millisecond range. Recently, interest in blue phase liquid crystal materials was renewed by their potential development as a new mode of operation in television sets, with the potential of enhancing motion picture image quality by the elimination of blurred images. Approaches in expanding the blue phase temperature range have been reported with a bimesogen chiral mixture and with a polymer stabilized blue phase liquid crystal. The primary issue related to the bimesogen chiral mixture is the field induced phase transition, while the challenges facing polymerized BP materials are high switching voltage, hysteresis, light scattering and stability for long term applications. Another study of sputtered gold particles has also shown an extended BP temperature range. Here we report the study of the dispersion of gold nanorods in a liquid crystal blue phase and investigate the fundamentals that may lead to the extended BP temperature range and enhanced electro-optical performance.

2. Results and discussion

2.1 Mesomorphic behavior

The mesomorphic behavior of pure BP and AuNRs dispersed BP samples was studied using a polarizing optical microscope and a computer controlled hot stage. Fig. 1 shows the textures of BPI of the pure and AuNRs dispersed BP samples. It was observed that red colored domains in the pure BP were smaller in size and nucleated at lower temperatures in comparison to the AuNRs dispersed BP samples; a sign of deformation of the cubic lattice, not observed in the pure BP sample. The photomicrographs, Fig. 1b, show that colored...
domains gradually grew to fill in the field of view as the temperature decreased in the AuNRs dispersed BPLC.

The AuNRs dispersed BP system enables thermally sensitive Bragg reflection wavelength in the visible spectrum. Reflection spectra of the samples were taken as the temperature was varied and kept at the reported temperature for a few minutes. Fig. 2 shows the reflection spectra of pure BP (Fig. 2a) and dispersed BP (Fig. 2b) while cooling the samples at a rate of 0.2 °C min⁻¹. We observed a red shift to longer wavelengths in the dispersed BP samples with respect to the pure BP, which is independent of the temperature. The longest shift was noticed in 0.06% AuNRs BP, which supports the reported POM image. The wavelength shift of the Bragg reflection as a function of temperature for the pure and AuNRs dispersed BPLCs is plotted in Fig. 2c. According to the results of the study, the highest concentration of 0.6% AuNR BP showed a decrease in the reflectance and peak maximum with respect to 0.06% AuNRs dispersed BP. This decrease may be due to the oversaturation of AuNRs in the void and defect regions of the cubic lattice. Broadening of spectral peaks was also noted with an increase in the concentration of AuNRs. This may be attributed to the non-uniform distribution of AuNRs in the samples which causes a large deformation of the blue phase lattice.

### 2.2 Theoretical rationale of temperature expansion

The temperature range of the BPLC can be estimated according to Melboom’s defect model.⁴ Based on the defect theory, the free energy of blue phase can be written as

\[
F = a(T_1 - T)\pi R^2 + 2\pi R - \pi K + \frac{1}{4}\pi K \ln \left( \frac{R_{\text{max}}}{R} \right) \tag{1}
\]

where coefficient \(a\) can be estimated from the latent heat of the cholesteric-isotropic phase transition. From de Gennes’ book,⁶ we adopted the value of \(a = 8 \times 10^4 \text{erg K}^{-1} \text{cm}^{-1}; T_1\) is the transition temperature of the BP-isotropic phase transition, \(T\) is the transition temperature of the BP-cholesteric phase transition, \(\sigma\) is the interfacial tension, which is about \(10^{-2} \text{erg cm}^{-2}\), \(R\) is the radius of the disclination core, \(R_{\text{max}}\) is the radius of the double twist cylinders, and \(K\) is the typical elastic constant of bend in the BP mixture (\(K = K_{b1}\)). In general, the bend distortion energies at larger angles prevent diameters greater than the length of a single twist. The blue phase would be stable when eqn (1) becomes negative. Because the \(2\pi R\) term is much smaller compared with other terms, for simplicity we ignore this term. Thus, the minimal free energy \(F\) can be obtained when

\[
\Delta T = T_1 - T = \frac{K}{8aR^2} \tag{2}
\]

From a provided estimate,⁴⁵ we can get the estimation of \(R\) in BPI,

\[
R = \frac{R_{\text{max}}}{33} = \frac{1}{33} \times \frac{P}{2} = \frac{1}{33} \times \frac{1}{2} \times \frac{1}{\text{HTP} \times C} \tag{3}
\]

where \(P\) is the pitch of the blue phase liquid crystal, \(\text{HTP}\) is the helix twisting power of the chiral dopant (defined as a combination of the reciprocal pitch and concentration of each enantiomer); and \(C\) is the weight concentration of the chiral dopant. The practical use of this is that, roughly speaking, adding more of a chiral dopant to an achiral nematic material will result in a more highly chiral mixture. Substituting eqn (3) into eqn (2), we can get the estimation of the BP temperature range,

\[
\Delta T = \frac{500 \times K \times \text{HTP}^2 \times C^2}{a} = \text{HTP}^2 K(1 - C)C^2 \tag{4}
\]

Taking a blue phase mixture BPLC-1 as an example, where \(C = 0.46,\) \(\text{HTP} = 9.8 \text{um}^{-1}\), then the temperature range is around 11 °C. The theoretically predicted value is close to the value of 12 °C of the pure BPLC that we obtained from experiments as the mixture 1 listed in Table 1.

In the case of AuNRs dispersed BP samples, the BP phase range expands to 3.2 °C with 0.004% AuNR doping. The BP phase becomes saturated with further increase in AuNRs concentration which counters the BP phase expansion. This phenomenon may arise from saturation due to the amount of AuNRs that can fit in the defects.

### Table 1 The composition and transition temperatures of neat BPLC and AuNRs dispersed BPLCs

<table>
<thead>
<tr>
<th>Mixture</th>
<th>AuNR wt%</th>
<th>Temp. range/°C</th>
<th>ΔT/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>43.9–55.9</td>
<td>12.0</td>
</tr>
<tr>
<td>2</td>
<td>0.004</td>
<td>43.6–58.8</td>
<td>15.2</td>
</tr>
<tr>
<td>3</td>
<td>0.01</td>
<td>43.4–58.4</td>
<td>15.0</td>
</tr>
<tr>
<td>4</td>
<td>0.06</td>
<td>43.6–58.53</td>
<td>14.9</td>
</tr>
<tr>
<td>5</td>
<td>0.6</td>
<td>42.8–57.2</td>
<td>14.4</td>
</tr>
</tbody>
</table>
2.3 Field-induced birefringence

The pure BPLC and 0.06% AuNRs dispersed BPLC were selected for the Kerr effect study. To determine the electro-optical properties of the BP samples, IPS cells with 5/5/5 (referring to a 5 µm electrode space, 5 µm line width, and 5 µm cell gap) were employed. Applying an in-plane voltage through the cells at a constant temperature of 50 °C allows the cells to switch between dark (field-off) and bright (field-on) states. Fig. 4 shows the optical properties and POM images of the pure and 0.06% AuNRs dispersed BPLC samples in response to the applied voltage. According to the quantitative analyses shown in Fig. 4a, the threshold voltage, \( V_{10} \) (voltage required for achieving 10% transmission of the cell) for the 0.06% AuNRs dispersed BP sample is 27.3 V, and the turn on voltage, \( V_{90} \) (voltage required for achieving 90% transmission of the cell), is 41.9 V. By contrast, the threshold voltage and the turn on voltage of the pure BPLC are 34.6 V and 49.4 V, respectively, which are much higher than those of the AuNRs dispersed BP sample. Compared to the high switching voltage, generally exceeding 140 V, of polymer stabilized BPLCs, the studied AuNRs dispersed BPLCs give a lower switching voltage (Fig. 4a). Furthermore, as seen in Fig. 4c the photomicrograph of AuNRs dispersed BPLC shows higher light transmittance at a lower switching voltage.

One of the advantages of BPLC is its fast response time. To measure the response time, we switched the pure and AuNRs dispersed BPLC samples between their corresponding voltages \( V_{10} \) and \( V_{90} \) obtained from Fig. 4a. The measured response time of the pure BPLC is 3.8 ms with the rise time, \( T_{\text{rise}} \) (switched between \( V_{10} \) and \( V_{90} \)), of 2.1 ms and the fall time, \( T_{\text{fall}} \) (switched between \( V_{90} \) and \( V_{10} \)), of 1.7 ms. Conversely, the measured response time for the 0.06% AuNRs dispersed BPLC is slightly higher at 21.2 ms with the rise time of 15.3 ms and the fall time of 5.9 ms. This phenomenon can be explained by a prior report. According to Gleeson and Coles, the rise and fall times can be expressed as eqn (5) and (6), respectively.

\[
T_{\text{rise}} = \frac{1}{\gamma_1 \varepsilon_0 \Delta \varepsilon} \left( \frac{V_{10}}{V_{90}} \right)^2 - 1
\]
\[
T_{\text{fall}} = \frac{1}{\varepsilon_0 \Delta \varepsilon} \left( \frac{V_{90}}{V_{10}} \right)^2
\]

Here, \( V_c \) is the critical voltage to unwind the cholesteric pitch, \( \gamma_1 \) is the rotational viscosity, \( E_c \) is the critical electric field (\( E_c = \frac{\pi^2 k}{p^2 \varepsilon_0 \Delta \varepsilon} \)), where \( p \) is the pitch and \( k \) is the twist elastic constant of the cholesteric phase), \( \varepsilon_0 \) is the dielectric permittivity at vacuum (\( \sim 8.85 \times 10^{-12} \)) and \( \Delta \varepsilon \) is the dielectric anisotropy of the BPLC. According to eqn (5) and (6), the rise time for the AuNRs dispersed sample would be slower if the applied voltage is close to \( V_c \). To speed up the turn on time, one should apply an overdrive voltage to the Kerr device. The analyses of fall times imply that the fall time of the AuNRs dispersed sample is about twice slower than that of the pure BPLC. We can speculate that this could be due to the increase in rotational viscosity arising from the inclusion of AuNRs at the deflections, which requires extra energy for local double twists to overcome the extra exclusive volume of the AuNRs.

Fig. 4c shows the POM images for both pure and dispersed BPs. In the case of pure BP, the POM image shows that the cell starts to...
switch from an initial dark state at 30 V and reaches a bright state at 50 V. The dark stripes are the regions on top of electrodes where the field is zero with a straight electrode pattern. With AuNR doping the BP is switched to a bright state at a lower voltage, where the field is applied in the direction normal to the stripes. The discontinued stripes arise from imperfect electrode patterning during the substrate preparation.

3. Materials and methods

A BPLC mixture was prepared using 55.0% of a nematic LC BL006 (dielectric anisotropy of +17.0 and optical birefringence of 0.289 at the wavelength of 589 nm purchased from Merck) and 45.0% of chiral dopant R811 (HTP of 9.8 µm⁻¹ purchased from Merck) to give a helical pitch around 160 nm. Alkylthio-decorated AuNRs dispersed in dichloromethane (DCM), with a size of 10 nm in diameter and 25–30 nm in length according to the information obtained from TEM study, were used as a nanoparticle additive. Due to the difficulty of measuring nanorods, AuNRs were dispersed in dichloromethane and measured on a micro-balance after the evaporation of solvent. AuNRs were transferred into sample vials and weighed with a microbalance capable of accuracy up to one microgram before the addition of the LC and chiral dopant to reduce the evaporation of the LC. The dispersed BPLC mixtures were prepared by adding 0.004 wt %, 0.01 wt %, 0.06 wt %, and 0.6 wt % of AuNRs in the BPLC.

Temperature and reflection spectra measurements were obtained in glass cells with a cell gap of 10 µm using ball spacers to separate the glass substrates. A computer-controlled hot stage and a polarization microscope (POM) were used to determine the BP phase range. All samples were heated to the isotropic phase and cooled at a rate of 0.2 °C min⁻¹ to room temperature. The reflection spectra were acquired with an Ocean Optics spectrometer as the temperature was varied.

Electro-optical (E-O) measurements of field induced birefringence required the use of in-plane-switching (IPS) cells with patterned indium tin oxide (ITO) of 5 µm electrode line and 5 µm electrode space on one glass substrate. The IPS cells were assembled with a second glass substrate, without ITO electrode, using ball spacers to separate the glass substrates with a cell gap of 5 µm (referring to a 5 µm electrode space, 5 µm line width, and 5 µm cell gap). Prior to filling the electro-optical cells, samples were agitated in a sonicator at a constant temperature of 30 °C for 90 minutes. Through the use of capillary action the BPLC samples were filled at an isotropic state and allowed to slowly cool to the cholesteric phase. An in-house E-O apparatus consisting of a helium-neon laser with light emission at 633 nm, a pair of polarizers crossed at 90° with respect to the polarization axes, a diode detector, a computer controlled function generator and an amplifier were used for data acquisition. The E-O measurements were carried out by aligning the stripes of electrode of the IPS cell at a 45° angle between the 90° crossed polarizers. The measurements of light transmittance as a function of applied voltage curves and response times were carried out at 50 °C, a constant BP state.

4. Conclusions

We have demonstrated an AuNRs dispersed BP system with expansion of the blue phase range and electrically thermally reconﬁgurable optical property suitable for applications as active optical elements. AuNRs dispersed BPLCs show a red shift of Bragg reﬂected wavelength as a function of temperature due to the perturbation of BP lattice. Theoretical estimations validate the BP temperature range. The AuNR dispersed BPLC system exhibits a low switching voltage, but slight increase in response time.

Acknowledgements

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Notes and References

1 F. Reinitzer, Monatsh. Chem., 1888, 9, 421–441.