# High Birefringence Liquid Crystals and Wide-View Electronic Lens

## Title and Subtitle
High birefringence liquid crystals and wide-view electronic lens

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## Abstract
The main objective of this program is to develop high birefringence liquid crystal (LC) materials and tunable-focus LC lens. A higher birefringence enables a thinner LC layer to be used which results in a faster response time. Low viscosity is always favorable as it helps to reduce the response time. We have developed several new LC compounds and mixtures exhibiting birefringence higher than 0.6. In parallel, we have demonstrated several device configurations for the tunable-focus spherical and cylindrical lenses, and microlens arrays. A flat spherical LC lens with 6-mm aperture and tuning range from infinity to 0.6 m has been demonstrated.

## Subject Terms
High birefringence liquid crystals, tunable-focus lens, electronic lens
1. List of papers submitted or published under ARO sponsorship during reporting period.
(a) Manuscripts submitted, but not published

1. H. Ren, Y. H. Fan, S. Gauza, and S. T. Wu
   “Tunable-focus flat liquid crystal spherical lens”
   Appl. Phys. Lett. (Accepted, 2004)

2. H. Ren, Y. H. Fan, and S. T. Wu
   “Liquid crystal microlens arrays using patterned polymer networks”

3. Y. Huang, G. Siganakis, M. G. Moharam, and S. T. Wu
   “All-optical display using photo-induced anisotropy in a bacterio-rhodopsin film”

   “Dual-frequency liquid crystal gels with submillisecond response time”
   Appl. Phys. Lett. (Accepted, 2004)

   “In-plane switching liquid crystal gel for polarization independent light switch”
   J. Appl. Phys. (Accepted, 2004)

   “UV stable high birefringence liquid crystals”

   “Super high birefringence isothiocyanato biphenyl-bistolane liquid crystals”

8. C. H. Wen, S. Gauza, and S. T. Wu
   “Ultraviolet stability of liquid crystals containing cyano and isothiocyanato terminal groups”
   Liq. Cryst. (Accepted, 2004)

   “Tunable-focus cylindrical liquid crystal lenses”

10. Papers published in peer-reviewed journals

1. Y. H. Fan, H. W. Ren and S. T. Wu
   “Normal mode anisotropic liquid crystal gels”,

2. H. W. Ren, Y. H. Fan and S. T. Wu
   “Prism grating using polymer-stabilized liquid crystal”,

   “High birefringence isothiocyanato tolane liquid crystals”
“The effect of olefinic terminal chains on the mesomorphic properties of 4,4’-disubstituted diphenyl-diacylenes”,

5. F. Du and S. T. Wu,
“Curing temperature effects on liquid crystal gels “

“Tunable Fresnel lens using nanoscale polymer-dispersed liquid crystals”,

7. F. Du, S. Gauza and S. T. Wu
“Influence of curing temperature and high birefringence on the properties of polymer-stabilized liquid crystals“
Optics Express 11, 2891-6 (Nov. 3, 2003).

8. Y. H. Fan, H. W. Ren and S. T. Wu
"Switchable Fresnel lens using polymer-stabilized liquid crystals,"
Optics Express 11, 3080-6 (Nov. 17, 2003).

“Tunable microarrays using polymer network liquid crystal”

10. H. Ren, Y. H. Fan, S. T. Wu
“Polymer network liquid crystals for tunable microarrays”

11. H. Ren, Y. H. Fan, S. Gauza and S. T. Wu
“Tunable-focus cylindrical liquid crystal lens”

12. Y. Huang, S. T. Wu and Y. Zhao
“All-optical switching characteristics in bacteriorhodopsin and its applications in integrated optics”
Optics Express 12, 895-906 (March 8, 2004)

13. Y. Huang, S. T. Wu, and Y. Zhao
“Photonic switching based on the photo-induced birefringence in bacteriorhodopsin film”
Appl. Phys. Lett. 84, 2028-30 (March 22, 2004)

“Tailoring the physical properties of some high birefringence isothiocyanato-based liquid crystals”

15. Y. H. Lin, H. Ren and S. T. Wu
“High contrast polymer-dispersed liquid crystal in a 90° twisted cell”

“High birefringence nematic liquid crystals for display and telecom applications”

11. Papers published in non-peer-reviewed journals or in conference proceedings


10. Papers presented at the meetings, but not published in conference proceedings


2. Demographic Data for this Reporting Period:
   (a) Number of Manuscripts submitted during this reporting period: 31
   (b) Number of Peer Reviewed Papers submitted during this reporting period: 22
   (c) Number of Non-Peer Reviewed Papers submitted during this reporting period: 9
   (d) Number of Presented but not Published Papers submitted during this reporting period: 1

3 Demographic Data for the life of this agreement:
   (a) Number of Scientists Supported by this agreement (decimals are allowed): 0
   (b) Number of Inventions resulting from this agreement: 0
   (c) Number of PhD(s) awarded as a result of this agreement: 0
   (d) Number of Bachelor Degrees awarded as a result of this agreement: 0
   (e) Number of Patents Submitted as a result of this agreement: 1
   (f) Number of Patents Awarded as a result of this agreement: 0
   (g) Number of Grad Students supported by this agreement: 4
(h) Number of FTE Grad Students supported by this agreement    0
(i) Number of Post Doctorates supported by this agreement    3
(j) Number of FTE Post Doctorates supported by this agreement    0
(k) Number of Faculty supported by this agreement    2
(l) Number of Other Staff supported by this agreement    0
(m) Number of Undergrads supported by this agreement    1
(n) Number of Master Degrees awarded as a result of this agreement    0

4 “Report of inventions” (by title only)
  1. Adaptive liquid crystal lens

5. “Scientific progress and accomplishments” (Description should include significant theoretical or experimental advances)
  1. Developed novel fluorinated isothiocyanato-tolane single compounds and mixtures with high birefringence and low viscosity.
  2. Formulated a new LC mixture which exhibits a high birefringence ($\Delta n>0.6$) and wide nematic range.
  3. Developed some tunable-focus spherical and cylindrical lenses, and microlens arrays.

6 “Technology transfer” (any specific interactions or developments which would constitute technology transfer of the research results). Examples include patents, initiation of a start-up company based on research results, interactions with industry/Army R&D Laboratories or transfer of information which might impact the development of products.
  1. We shipped a high birefringence liquid crystal mixture to Dr. Teresa Ewing of Boulder Nonlinear Systems for testing her spatial light modulator. Telephone number: 303-604-0077.
  2. We developed a high birefringence and fast response time mixture for Dr. William Ray Folks of College of Optics and Photonics, UCF for testing his infrared scene projection system. Telephone number: 407-823-6842

c. “Copies of technical reports,” which have not been previously submitted to the ARO, must be forwarded with the Interim Progress Report. (See page 5 “Technical Reports” section for instructions)
HIGH BIREFRINGENCE LIQUID CRYSTALS AND WIDE-VIEW ELECTRONIC LENS

1. Objectives:
The main objective of this program is to develop high birefringence liquid crystal materials and to demonstrate tunable-focus liquid crystal lens.

2. Status of Effort:
We have synthesized several new LC single compounds and formulated a high birefringence (∆n~0.4) eutectic mixture. In addition, we have developed several new device structures of flat spherical lens with focal length tunable from infinity to 0.6 m. A demo kit was shipped to DARPA for evaluation.

3. Accomplishments
3.1 Motivation
The motivation of this program is to develop high birefringence liquid crystal (LC) materials for tunable-focus LC lens applications. A higher birefringence enables a thinner LC layer to be used which results in a faster response time. Low viscosity is always favorable as it helps to reduce the response time. However, high birefringence compounds usually exhibit a high melting temperature. Thus, we need to formulate eutectic mixtures in order to lower the melting temperature. We have developed several new LC compounds and mixtures exhibiting birefringence around 0.4-0.6. In parallel, we have demonstrated several device configurations for the tunable-focus spherical and cylindrical lenses, and micro-lens arrays. A flat spherical LC lens with 6-mm aperture and tuning range from infinity to 0.6 m has been demonstrated.

3.2 Tunable-focus spherical lens
Figure 1 illustrates the fabrication procedures for a positive LC lens. The concave surface of the bottom glass substrate is coated with a transparent indium-tin-oxide (ITO) electrode, as shown in Fig. 1(a). Next, the sag area could be matched by a convex glass lens with the same curvature or filled with a polymer having the same refractive index as the employed glass substrate to form a planar substrate, as shown in Fig. 1(b). For the demonstration purpose, we filled the sag area with a UV curable prepolymer. To simplify the fabrication process, we used an empty LC cell to seal the prepolymer. The glass substrate which is in contact with the prepolymer has d2=0.55 mm, but no ITO electrode. When the prepolymer was cured by UV, the lens and the LC cell were attached together. The inner surfaces of the LC cell are coated with polyimide alignment layers and rubbed in anti-parallel direction. The pretilt angle is ~3°. When a LC mixture is injected into the cell, homogeneous alignment is induced by the buffed polyimide layers, as shown in Fig. 1(c).

Fig. 1 Procedures for fabricating the spherical LC lens. (a) Deposit ITO on a concave glass lens, (b) fill the sag area with polymer, and (c) assemble the LC lens cell with another flat glass substrate.

Based on the abovementioned procedures, we fabricated a positive lens LC cell. The concave lens with radius R=−9.30 mm, aperture D=6 mm, and sag d1=0.34 mm was purchased from Edmund Industrial Optics (BK7 glass, nG=1.517). The refractive index of the filled polymer NOA65 (nP=1.524, Norland Optical Adhesive) would affect the initial focal length of the LC lens. If nP ≈ nG , then the LC device would not focus light in the voltage-off state. If nP is much smaller than nG , then the device would have an initial focus. A home-made high birefringence LC mixture designated as UCF-2 (∆n=0.4 at λ=633 nm) was used to fill the 40-µm cell gap.

To evaluate the optical properties of the spherical lens, we investigated the profile of the phase retardation by observing the interference fringes between the ordinary and extraordinary rays using a white light under crossed polarizers. The rubbing direction of the lens cell is oriented at 45° with respect to the fast axis of the linear polarizer.

To characterize the light focusing properties of the lens cell, we measured the 3D profiles of the outgoing beams (He-Ne laser, λ=633 nm) using a CCD camera. The CCD camera was set at ~80 cm behind the LC lens cell. The intensity profiles were measured at
V=0, 23 and 35 \text{V}_\text{rms}, and results are shown in Fig. 2. At V=0, the observed He-Ne laser beam is not very uniform due to the Gaussian nature of the input laser beam. The peak intensity is \(\sim6\times10^3\) arbitrary units. As the voltage increases to 23 \text{V}_\text{rms}, the focusing effect manifests. The measured intensity at the CCD focal plane exceeds 6.5\times10^4\) arbitrary units. As the voltage is further increased, the peak intensity of the outgoing beam tends to decrease. At V=35 \text{V}_\text{rms}, the peak intensity drops to 1.7\times10^4\) arbitrary units. This is because the LC molecules in the bulk are reoriented by the electric field. The curvature of the refractive index profile is gradually flattened. As a result, the focal length of the lens increases and the measured light intensity at the CCD focal plane decreases.

![Fig. 2: CCD images of the measured He-Ne laser beam intensity profile at V=0, 23, and 35 \text{V}_\text{rms}, respectively.](image)

The voltage-dependent focal length of the lens was investigated and results are plotted in Fig. 3. At V=0, LC directors are aligned homogeneously due to the surface anchoring effect from the substrates. Thus, no focusing effect occurs or the focal point is at infinity. As the voltage increases, the focal length is reduced accordingly. At V=40 \text{V}_\text{rms}, the focal length reaches a minimum (f~0.6 m). Further increasing the voltage would cause the focal length to bounce back, but at a different rate.

![Fig. 3: Voltage-dependent focal length of the LC lens. Lens aperture D=6 mm, LC: UCF-2, cell gap d=40 \mu m and \lambda=633 nm.](image)

The focal length of an LC lens can be evaluated using the Fresnel’s approximation:

\[
f = \frac{r^2}{2\delta n_d L C},
\]

where \(r = D/2\) (D is the lens aperture), \(d_{LC}\) is the LC layer thickness, and \(\delta n\) is the refractive index difference between the lens center and border. From Fig. 1, \(\delta n\) is determined by the electric field difference between the lens center and the border. When a voltage \(V\) is applied to the lens cell, the electric field in the center \((E_{\text{Center}})\) and at the border \((E_{\text{Border}})\) is expressed as:

\[
E_{\text{Center}} = \frac{V}{\varepsilon_{LC}} - \frac{d_{LC}}{\varepsilon_2} - \frac{d_1}{\varepsilon_1},
\]

\[
E_{\text{Border}} = \frac{V}{\varepsilon_{LC}} - \frac{d_{LC}}{\varepsilon_2} + \frac{d_2}{\varepsilon_1},
\]

where \(\varepsilon_{LC}\), \(\varepsilon_2\), and \(\varepsilon_1\) represent the dielectric constant of the LC, medium 2, and 1, respectively. In an ideal case, we would like to eliminate the glass substrate which is closer to the spherical electrode, i.e. \(d_2 = d_1\). In such condition, the electric field shielding effect due to the glass substrate is reduced and the required operating voltage is lowered. From Eq. (1), the shortest focal length occurs when \(\delta n = \Delta \eta\), i.e. the LC molecules in the border are completely aligned by the electric field while those in the center are not yet reoriented owing to the weaker electric field.

In comparison with other tunable lens technologies, the major advantages of our lens are in simple fabrication process, uniform LC cell gap, plano-substrate surface, and simple electrodes. In addition, the lens has a very wide range of tunable focal length without light diffraction and scattering. In theory, the light throughput can reach 100\% for a linearly polarized laser beam. The response time
of the lens depends on the LC cell gap. In our experiment, we used a high \( \Delta n \) LC mixture and 40 \( \mu \)m cell gap. The switching speed is \(~1\)s at room temperature.

3.3 High birefringence, fast-response time and relatively high resistivity liquid crystal medium

The LC single compounds we developed contains a highly polar isothiocyanato (-NCS) terminal group. The rigid core of the compounds contains the phenyl rings linked by carbon-carbon triple bond, called tolane. This kind of structure exhibits a high birefringence (\( \Delta n \)) due to the elongated \( \pi \)-electron conjugation length. Those compounds typically show \( \Delta n \sim 0.35-0.40 \) at \( \lambda = 633 \) nm wavelength and room temperature. The lateral fluoro substitution near the NCS group serves for two purposes: it increases the resistivity of the compounds, and 2. it increases the dielectric anisotropy, i.e. reduces the operating voltage. However, it also reduces the birefringence and increases the viscosity. The general structures of the single compounds we prepared are shown as follows:

![General structures of single compounds](image)

Table I shows the compositions and percentages of the compounds used in BOSS-1 mixture. The CPTP-NCS compounds are useful for enhancing the clearing temperature of the mixture. The other compounds except the difluoro substituted isothiocyanato-terphenyl (comp. # 3) exhibit poor mesomorphic properties but are desirable for low viscosity. The highly conjugated linear structure of the rigid core exhibit large optical anisotropy. The compounds contain saturated cyclohexane ring exhibit a larger rotational viscosity than that of simple tolanes because of the increased molecular mass and momentum of inertia. Our high birefringence compositions are calculated based on the Schroder-Van Laar equation. The selection of compounds takes into account the need for high birefringence, low viscosity, high resistivity, and wide nematic range.

Table I. The LC compositions of BOSS-1 mixture. R1, n, P1, P2 – according to general structures listed above. PTT – phase transition temperatures in Celsius. Wt% - weight percentage of each single compound at the mixture

<table>
<thead>
<tr>
<th>No</th>
<th>Name</th>
<th>R1</th>
<th>n</th>
<th>P1</th>
<th>P2</th>
<th>PTT</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CPTP (3F) 2NCS</td>
<td>2</td>
<td>1</td>
<td>F</td>
<td>H</td>
<td>Cr 108.5 N 239.7 Iso</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>CPTP (3F) 4NCS</td>
<td>4</td>
<td>1</td>
<td>F</td>
<td>H</td>
<td>Cr 77.5 N 239.2 Iso</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>PPP (3, 5F) 3NCS</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Cr 107.3 N 199.5 Iso</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>PTP (3F) 2NCS</td>
<td>2</td>
<td>0</td>
<td>F</td>
<td>H</td>
<td>Cr 73.6 Iso</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>PTP (3F) 4NCS</td>
<td>4</td>
<td>0</td>
<td>F</td>
<td>H</td>
<td>Cr 38.6 Iso</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>PTP (3F) 5NCS</td>
<td>5</td>
<td>0</td>
<td>F</td>
<td>H</td>
<td>Cr 49.2 Iso</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>PTP (FF) 02NCS</td>
<td>2(O)</td>
<td>0</td>
<td>F</td>
<td>F</td>
<td>Cr 94.5 Iso</td>
<td>5</td>
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<tr>
<td>7</td>
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<td>Cr 68.3 Iso</td>
<td>6</td>
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<tr>
<td>8</td>
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<td>5(O)</td>
<td>0</td>
<td>F</td>
<td>F</td>
<td>Cr 49.5 N 56.6 Iso</td>
<td>5</td>
</tr>
</tbody>
</table>
The BOSS-1 LC mixture we developed exhibits a very wide mesomorphic property. The melting point (measured by DSC) is below -50°C while the clearing point appears at 95°C.

To characterize electro-optical performance of BOSS-1 nematic mixture, we measured its birefringence, visco-elastic coefficient, and then calculated its figure-of-merit. For practical applications of SLM, we need to consider both phase change and response time simultaneously. To make a fair comparison, we define a Figure-of-Merit as: \( FoM = \frac{K_{11}(\Delta n)^2}{\gamma_1} \). Figures 4 and 5 plot the wavelength and temperature-dependent birefringence of BOSS-1, compared with a commercial high birefringence Merck mixture TL-216. From Figs. 4 and 5, the birefringence of BOSS-1 is about 2X higher than that of TL-216.

A high birefringence LC usually exhibits a higher viscosity because of its longer molecular conjugation. However, from Fig. 6, BOSS-1 has about the same viscosity as TL-216, although its birefringence is 2X higher. This is because the NCS group not only elongates the conjugation length but also exhibits a relatively low viscosity.
Fig. 6: Temperature dependent visco-elastic coefficient for BOSS-1 and TL-216 mixtures. \( \lambda = 633 \) nm.

Figure 7 plots the temperature dependent FoM of BOSS-1 compared with TL-216. The maximum FoM of BOSS-1 reaches ~23 at \( T \approx 70^\circ C \). At room temperature, the FoM of BOSS-1 is 4X higher than that of TL-216.

4. The Future Plan to Be Performed

We will continue to develop high birefringence and low viscosity LC mixtures for BOSS program. To achieve high resistivity, we need to develop purification method dedicated for NCS based LC medium. The LC-based lens system has a relatively slow response time and aberration that would reduce the resolving power. In the BOSS Phase II program, we will apply our high birefringence LC mixtures to a transmissive spatial light modulator for demonstrating foveated imaging. By adjusting the voltage of each pixel, the SLM functions as a phase compensator. The aberration problem would be eliminated.