Tunable Mirrorless Lasing in Cholesteric Liquid Crystalline Elastomers**

By *Heino Finkelmann*, *Sung Tae Kim*, *Antonio Muñoz*, *Peter Palffy-Muhoray*,* and *Bahman Taheri*

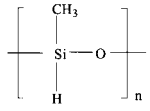
Cholesteric liquid crystals are chiral nematics, where the handedness of the constituent molecules causes the orientation of the local nematic director to vary in space. In the helical cholesteric structure, the director is perpendicular to the helix axis, and its orientation varies linearly with position along the helix axis. The spatial period of the structure is the pitch, which is determined by the concentration and the helical twisting power of the chiral constituents. As a consequence of the periodicity of the helical cholesteric structure and the birefringence of the liquid crystal, for a range of wavelengths, light propagation along the helix axis is forbidden for one of the normal modes. Since propagation is forbidden, incident light with a wavelength in this band and with the same helicity as the cholesteric is strongly reflected. The edges of this reflection band are at wavelengths that are equal to the refractive indices times the pitch.[1] Because of the existence of the selective reflection band, cholesteric liquid crystals are 1D photonic bandgap materials.

The bandgap structure of cholesteric liquid crystals allows for the possibility of lasing without external mirrors that usually form a laser cavity. When a fluorescent dye is dissolved in the cholesteric host so that the peak of the fluorescent emission of the dye is in the selective reflection band of the cholesteric, propagation of one normal mode of the emitted light is forbidden. As a consequence, at low pump intensities, the fluorescence spectrum of the dye is modified,[2] showing suppression of emission in the reflection band, and enhanced emission near the band edge. As the pump intensity is increased, the linewidth of the enhanced fluorescence at the band edge narrows, and, above a pump threshold, lasing occurs.[2] Thin samples, typically 15–30 μm in thickness, of low molecular weight cholesteric liquid crystals incorporating a variety of dyes[3] have been shown to lase. The primary role of the cholesteric liquid crystal in these systems is to act as a distributed cavity. Lasing occurs at the band edges,[2–4] as predicted for distributed feedback lasers.[5]

Lasing in dye-doped cholesterics has been proposed[6,7] and recently unambiguously demonstrated on nanosecond[4] and picosecond[4,8] time scales. More recently, UV lasing in pure liquid crystals was demonstrated in a system where the liquid crystal acts both as the active medium and the host.[9]

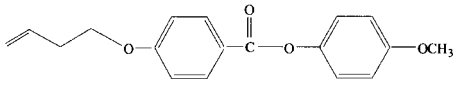
Very recently[10] the first cholesteric liquid single crystal elastomers (cholesteric LSCE) with a spontaneous and uniform orientation of the helical structure have become available. The most interesting aspect of these systems is that the helicoidal structure can be modified by external mechanical fields and that these materials do not need any mechanical support for a stable orientation of the helicoidal structure as compared to low molar mass liquid crystals. In this paper, we demonstrate that dye-doped cholesteric LSCE can act as mirrorless lasers, where the wavelength of the laser emission can be tuned by external mechanical deformations.

To investigate the possibility of lasing, we synthesized cholesteric LSCE according to the procedure described recently.[10] The networks are synthesized via a hydrosilylation reaction of poly[oxy(methylsilylene)] **1** with both an achiral nematogenic monomer **2**, a chiral cholesterylcarbonate **3** and the crosslinking agent **4**.



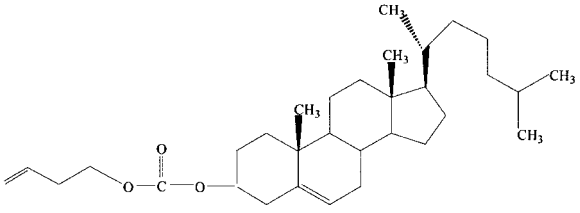
1

100 mol.%



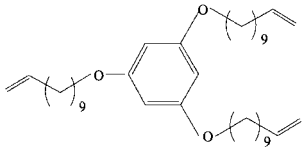
2

72 mol.%



3

18 mol.%



4

10 mol.%

Networks containing only monomer **2** exhibit a nematic phase. By adding co-monomer **3** induced cholesteric phases can be realized, where the pitch is determined by the concentration of the chiral component. For our experiments we chose the concentration of components indicated below the compounds. With this concentration of co-monomer **3** the network shows a selective reflection of left circularly polarized light with reflection maximum[10] at $\lambda_R = 590$ nm. The synthesis con-

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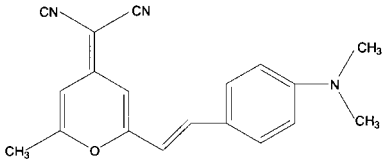
sists of two steps that result in an overall oblate chain conformation that causes a uniform orientation of the helix axis in the network. First, a weakly crosslinked gel is synthesized, whereby the crosslinking reaction is incomplete at this stage. The statistically averaged network chain conformation is assumed to be spherical here. Second, an anisotropic deswelling procedure is implemented, where the gel, swollen with the solvent toluene, is allowed to deswell only in one direction, keeping the dimensions in the two perpendicular directions to this constant. This anisotropic deswelling is equivalent to a uniaxial compression (or biaxial stretch), which gives rise to the oblate chain conformation. Due to the coupling between network chain conformation and the liquid crystalline order, the helix axis becomes aligned perpendicular to the directions along which the dimensions were held constant during the deswelling. Under these conditions, the crosslinking reaction is completed, resulting in a highly ordered macroscopic cholesteric liquid single crystal elastomer (LSCE).[10] To achieve lasing, the laser dye 4-(dicyanomethylene)-2-methyl-6-(4-dimethylamino styryl)-4-*H*-pyran (DCM) is dissolved in the LSCE.



DCM

In order to dope the elastomer with purified DCM, the network is simply swollen in toluene containing the dye and subsequently dried. The dye concentration in toluene was such that, when the solvent was removed, 0.2 wt.-% of DCM remained dissolved in the cholesteric LSCE.

The most important aspect for tunable lasing is to identify whether a mechanical deformation of the cholesteric LSCE causes a shift of the reflection band and consequently a shift of the wavelength of the laser emission. As in nematic elastomers[11] a strong coupling is expected between mechanical strain field and orientational order. In the case of cholesteric elastomers with an overall oblate chain conformation, a uniaxial strain perpendicular to the helix axis will cause director reorientation.[12] Only a biaxial extension perpendicular to or a uniaxial compression parallel to the helix axis leaves the helical structure unchanged. To determine whether this deformation directly changes the cholesteric pitch affinely with the macroscopic change of network dimension parallel to the pitch axis, we performed biaxial extension experiments as shown in Figure 1.

It has to be emphasized that in the simple experiment shown in Figure 1, a reasonable biaxial extension occurs only in the central region of the sample while in the other regions additional shear is imposed, which causes director reorientation. Nevertheless, the change in position of the reflection band with mechanical deformation can be seen clearly (Fig. 1). A scheme to accurately measure the local strain is currently under development.

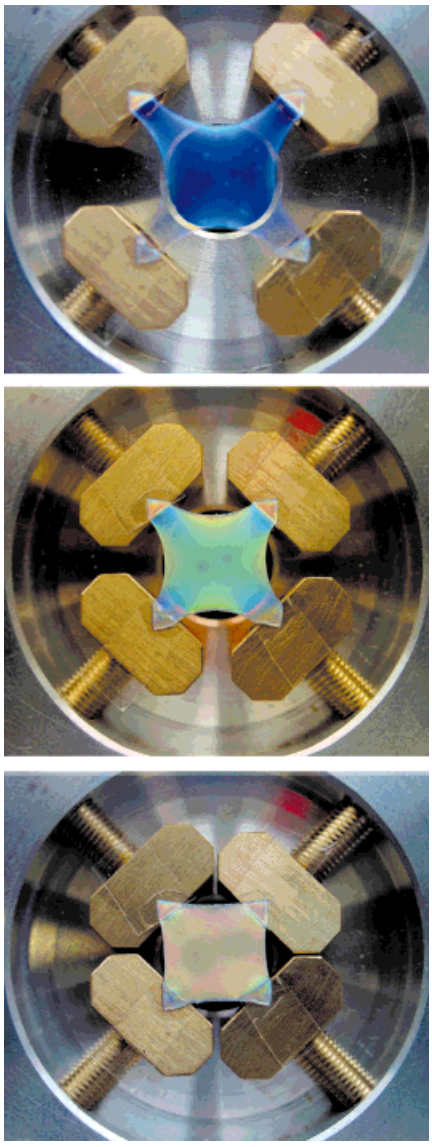


Fig. 1. Appearance of the cholesteric LSCE sample under white light illumination as a function of mechanical strain. The diameter of the large circular sample chamber is 3.5 cm; the thickness of the unstrained sample is 0.25 mm.

To quantify these observations, the thickness of the network is measured in the center of the sample by absorption measurements and simultaneously λ_R is determined.[10] The results are shown in Figure 2.

Within the accuracy of the experiments, λ_R is found to be proportional to the sample thickness. This result indicates that the cholesteric pitch affinely deforms with the macroscopic dimension of the network due to the strong coupling between network conformation and director orientation. Note that this effect does not occur with liquid cholesteric systems, i.e., low molar mass or non-crosslinked polymeric liquid crystals, where the pitch stays (nearly) constant with sample thickness.

The pitch of the cholesteric elastomer can be changed by modifying the dimension of the elastomer parallel to the pitch axis with a mechanical field. Consequently, if they are capable of lasing, cholesteric LSCEs can be used as a mechanically

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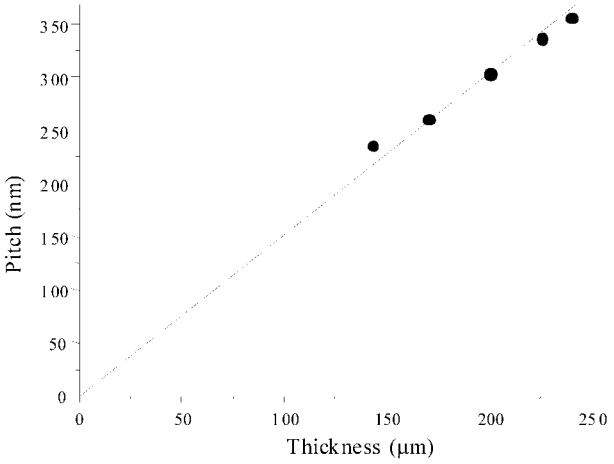

Fig. 2. Change of λ_R as function of the thickness of the cholesteric LSCE due to biaxial extension.

tunable laser sources. To carry out the lasing experiments, the free-standing dyed cholesteric LSCE samples are corner-mounted on the movable faces of a four-jaw chuck over an optical port, as shown in Figure 1. The pump beam is a frequency-doubled mode-locked Nd:YAG (Continuum PY61C) laser, with 35 ps pulses at a wavelength of λ = 532 nm. The experimental setup is shown in Figure 3.

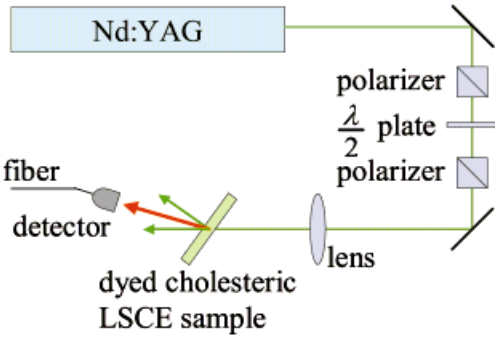

Fig. 3. Schematic of the experimental setup.

The pulse energy was controlled with a polarizer and half-wave plate. The pump beam was focused on the sample using an f = 20 cm, 2.5 cm diameter lens; the beam diameter at the sample was 300 μm. The emitted light was collected and focused onto the entrance slit of a TRIAX 550 (Jovin Yvon-Spex) spectrometer. The emission was recorded with an i-Spectrum One intensified CCD (JovinYvon-Spex) detector, operated in the continuous mode. The samples showed, under picosecond excitation at λ = 532 nm, fluorescence line-narrowing as a function of pump pulse energy. Lasing was observed in free-standing LSCE samples as shown in Figure 3. In non-deformed samples, lasing was observed above the pump threshold of ~280 μJ. Laser emission by a typical DCM-doped cholesteric LSCE sample is shown in Figure 4.

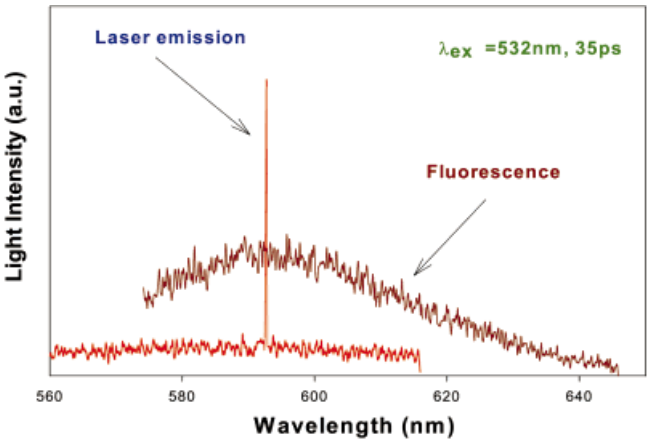

Fig. 4. Fluorescence spectrum of the DCM dye and laser line in a dye-doped LSCE sample.

As a biaxial distortion was applied to the sample, the laser line shifted. In Figure 5, three laser lines are shown. The wavelength of the emitted radiation depends on the distortion of the sample; lasing was achieved over the range of 544–630 nm. Observed line widths were ~3.5 Å.

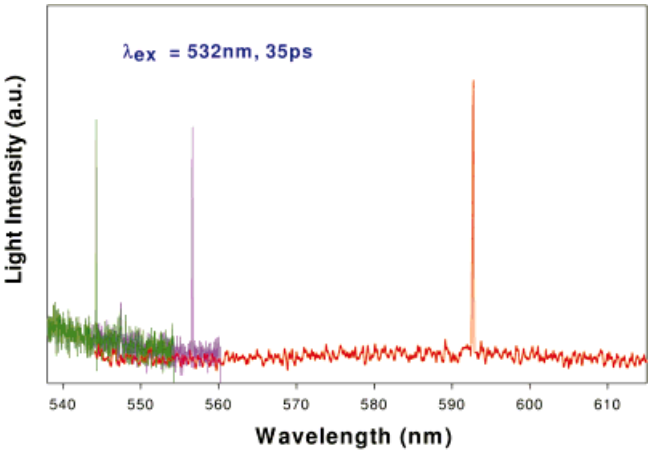

Fig. 5. Laser emission from the DCM-doped LSCE sample.

In summary, we have observed tunable low-threshold mirrorless lasing in free-standing cholesteric liquid single crystal elastomers. The linewidths are narrow, in the 3 Å range, and the position of the laser line shifts as a function of the mechanical strain applied to the sample. These preliminary observations are consistent with the model of strong coupling between a mechanical strain field and the pitch of the cholesteric structure, and suggest that cholesteric LSCEs may be useful as mechanically tunable laser sources. More detailed experimental results probing laser efficiency and accuracy and reproducibility of tuning, as well as a comparison between the experimental results and theoretical predictions will be published elsewhere.

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Polarized Electroluminescence in Double-Layer Light-Emitting Diodes with Perpendicularly Oriented Polymers**

By *Alberto Bolognesi*,* *Chiara Botta*, *Daniela Facchinetti*, *Markus Jandke*, *Klaus Kreger*, *Peter Strohriegl*, *Annalisa Relini*, *Raniera Rolandi*, and *Sylke Blumstengel*

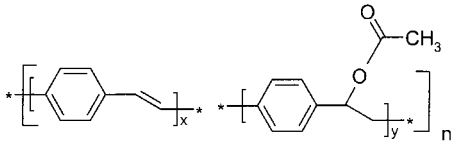
In recent years interest in organic light-emitting diodes (OLEDs) exhibiting polarized light has increased, thanks to the availability of low-cost techniques for chain alignment of the conjugated polymers[1] that are generally used as active materials in OLEDs. The strong anisotropy of the conjugated chains and their easy processability allow the preparation of well-oriented thin films emitting polarized electroluminescence (EL). Polarized EL is useful for applications such as back-lit liquid-crystal displays (LCDs),[2] as recently reported.[3] Methods commonly used to align polymeric films are the Langmuir–Blodgett technique,[4–6] rubbing of the film surface,[7,8] mechanical stretching of the film,[9] and orientation on pre-aligned substrates.[10,11] These methods are described and summarized in the recent review by Grell and Bradley.[10]

Depending on the optical properties of the polymers and the orientation technique used, different emission colors and EL polarization ratio (R_{EL}) are obtained. For emission in the blue, disubstituted polyfluorene aligned by LC self-organization on pre-oriented substrates[11] gives a polarization ratio of about 15 in EL. A further improvement in the orientation of polyfluorene has been obtained by orienting monodomains of poly(9,9-dioctylfluorene) on an alignment layer of segmented poly(*p*-phenylenevinylene) (PPV), reaching the highest anisotropy of 25 in EL.[12] For green emission, unsubstituted (PPV) oriented by the rubbing technique gives a value of $R_{EL} \approx 12$.[8] Red polarized emission with a dichroic ratio $R_{EL} \approx 8$ is obtained with a poly(3-alkylthiophene) derivative oriented by a combination of rubbing and thermal annealing.[13]

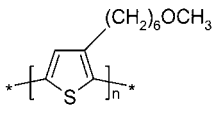
Until now the investigation of polarized EL has been focused on single active materials. The possibility of tuning EL emission associated with polarized emission represents a further development in this field.

In this communication we report the preparation and characterization of an LED in which the active material is formed by two polymer layers that are oriented perpendicularly to each other (Fig. 1a). The deposition and orientation of both the active polymer layers is obtained through a combination of the simple and low-cost spin-coating and rubbing techniques. This peculiar procedure permits the orientation of the two polymeric layers in any desired relative direction. The selected polymers emit in different regions of the visible spectrum. This introduces the possibility of providing polarized light in a large spectral region, extending from the green to the red. The EL observed through a polarizer can be changed from green to red simply by rotating the axis of the polarizer, yielding polarized light of different colors. This device design is particularly appealing as it can increase the versatility of organic LEDs able to provide polarized light with easily variable color.

The green-emitting polymer is a segmented PPV obtained as previously reported.[14,15]. As red-emitting polymer we used a regioregular poly[3-(6-methoxyhexyl)thiophene] (P6OMe) showing a thermal phase transition[16] from a three-dimensional ordered phase to an LC phase.[13] The LC properties, combined with the fact that the polymer can be oriented by the rubbing technique, permit high dichroic ratios to be achieved by performing an appropriate thermal treatment after the rubbing procedure.[13]



PPV



P6OMe

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