Light controllable tuning and switching of lasing in chiral liquid crystals

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Abstract: A new approach based on the use of cholesteric liquid crystals (CLCs) and dye-doped light-sensitive chiral dopants was employed to create lasing materials with reversible tuning and switching. The lasing wavelength of optically-pumped dye-doped cholesteric liquid crystals (CLCs) is shifted by irradiation with UV light. The shift depends on the UV light exposure. Lasing is switched off at high levels of UV light irradiation. A qualitative model describing different lasing regimes is proposed.

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References and links

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1. Introduction

The lasing properties of cholesteric liquid crystals (CLCs) have attracted considerable recent attention [1-12]. CLCs are self-organized materials capable of forming planar helical structures when placed between glass plates covered with rubbed polyimide. Planar CLCs are one-dimensional, photonic band-gap (PBG) structures for light with the same sense of polarization as the cholesteric helix. The selective reflection band (SRB) is centered at the wavelength $\lambda = nP$ while the width of the band is $\Delta \lambda = (\Delta n/n)\lambda$, where $P$ is the pitch of the chiral liquid crystal [6], $n = (n_e+n_o)/2$ is the average refractive index of the cholesteric planes which have a birefringence of $\Delta n = n_e - n_o$.

Lasing in dye-doped CLCs occurs at long-lived modes at the edge of optical stop band [2-6]. This opens new possibilities for creating responsive lasing materials with tunable lasing wavelength as a result of the sensitivity of the helical pitch to external stimuli. Potential stimuli are electromagnetic fields and temperatures [13], and changes in the pH of the chemical environment [8].

The helical pitch can also be altered by UV irradiation of CLCs polymers containing light-sensitive molecules with variable chirality controlling the pitch [13]. In a typical experiment two optical sources may be used: a pump laser for exciting dye molecules and a UV lamp for inducing helical transformations and tuning the position of the SRB. Several groups have recently demonstrated non-reversible light-tunable lasing. In Ref. [9], this was achieved by polymerizing a chiral monomer that had been added to a cholesteric mixture. The polymerized monomer served as a chiral dopant and the SRB was tuned by varying the intensity and/or exposure time of the UV radiation. The polymerization resulted in irreversible changes of the cholesteric pitch. In Ref. [10] the chiral pitch in dye-doped CLC cells was controlled by irradiation with UV light, leading to a photolysis reaction of chiral cholesteryl iodide dissolved in the CLC sample. This irreversible reaction led to a profound shift of the selective reflection band and lasing wavelength (c.a.100nm). Recently, photo-tunable lasing from dye-doped CLCs containing an optically active dopant undergoing photo-rearrangement (photo-Fries rearrangement) was reported [11]. However, the transformation was not reversible and the mechanism for the observed changes was not established. Photo sensitive chiral dopants were used in study of lasing emission in Ref. [12], but very high intensity of UV irradiation damaged CLC and reversible tuning was not achieved.

In the present paper, we demonstrate a new strategy for producing light-tunable CLC lasers, in which chiral light-sensitive molecules undergo reversible trans-cis- isomerization at low intensity of UV light and study the mechanism of structural changes accompanying the isomerization process.

2. Results and discussion

Light-controllable lasing was achieved with two types of chiral dopants. Molecules of the first type have a light-sensitive fragment undergoing reversible trans-cis- isomerization under UV illumination and a chiral group attached to this fragment. Two isomers of the first type of chiral dopants have different values of the twisting power (which is a quantitative measure of
the twist of chiral molecules in the nematic phase) and their concentrations depend on the wavelength and dose of the UV irradiation. Molecules of the second type are not light-sensitive, but have high twisting power that brings the SRB into the visible part of the spectrum.

Reversible changes in the helical pitch and consequently in the wavelength of the SRB of the CLCs were achieved by using light sensitive chiral azo-molecules (LSAZ) with the isomers shown in Fig. 1. Under UV irradiation, these molecules undergo trans- to cis-isomerization. The azo fragment is a structural part of the chiral molecules. UV irradiation at 350nm stimulates the transition of rod-shaped trans-molecules into bent-shaped cis-molecules. This phenomenon is known to change the twisting power of chiral dopants of this type [13]. Changes in twisting power are translated into changes of the cholesteric helix, and hence the PBG structure of the CLCs. This transition is reversible. The backward transition (from cis- to trans- isomer) can be achieved by optical irradiation at a longer wavelength or by turning off the UV light. The rate of forward (from trans- to cis-) and backward transformation depends

Fig. 1. Structure of light sensitive chiral azo dopants and trans–cis isomerization.

Fig. 2. (a) Tuning of lasing wavelength towards shorter wavelengths with increasing time, t, of UV irradiation, (b) Backward shift of lasing wavelengths after turning UV irradiation off and keeping sample in the dark for t minutes. The arrows point to the direction of changes of the lasing peaks with time.
on the material properties of the matrix and is highest in matrices in which the viscosity is small.

The CLC mixture contained three components: liquid crystal E63, liquid chiral dopant C41 (both supplied by Merck), and light-sensitive chiral dopant LSAZ. Chiral dopant LSAZ has a relatively high melting temperature (about 55°C) and a twisting power of about 1-2 µm⁻¹. This twisting power produces a left-handed helical pitch of about 20µm at a concentration of about 5%. The tighter pitch requires a higher concentration of chiral dopant. This significantly changes the thermodynamic properties of the liquid crystals and depresses the mesophase. In order to avoid using high concentrations of chiral dopant LSAZ, a third component, chiral dopant C41, was added at a concentration of 42%, to yield a tighter right-handed pitch without causing an appreciable change in the thermodynamic properties of the liquid crystalline mixture.

The lasing properties of the cholesteric mixture were studied at two concentrations of chiral dopants LSAZ and different doses of UV irradiation. The cholesteric liquid crystal was placed between two glass plates with a rubbed polyimide layer. This arrangement provided an almost planar cholesteric layer with planarity determined by the wedge between the two glass plates. Changes in the helical structure were induced by low intensity UV light (Model 22-UV Lamp, 365nm) and high intensity UV light (High Pressure Mercury Lamp, 50W, 365 nm). A bandpass filter was used to select radiation at 365nm. The second harmonic of a Q-switched Nd-YAG laser (150ns pulse duration, average energy of 100 µJ per pulse) was used in order to pump the cholesteric samples and excite the laser dyes dissolved in the CLC samples. Laser emission occurred at the edge of the SRB centered at the wavelengths determined by the UV irradiation dose. The position of the SRB and the lasing emission were tuned by changing the intensity of UV irradiation. UV irradiation resulted in trans- to cis- isomerization which increased the twisting power of LSAZ molecules and resulted in a tighter pitch.
At low UV irradiation levels, lasing is characterized by a shift of the lasing wavelength of about 15-20 nm for a concentration of LSAZ molecules of about 4.5%. For lower concentration of LSAZ (1.5%) the shift of lasing wavelength is much smaller, about several nanometers. The shift of the lasing wavelength is shown in Fig. 2a for different time intervals of UV irradiation and concentration of LSAZ of about 4.5%. Lasing occurs in modes at the edge of the SRB. The shift of the lasing wavelength toward shorter wavelengths reflects the spectral shift in the SRB (Fig. 3(a)). The planar CLC structure does not change during this transition and the intensity of lasing remains approximately the same at the same pumping power. For the CLC cell parameters specified above, the center of the SRB shifts from 620 nm to 605 nm after three minutes of irradiation at 365 nm with intensity of ca. 20 µW. These changes are accompanied by typical changes in the absorption spectrum at 370 nm due to the increased concentration of cis-isomer [7]. The shift of the SRB and lasing wavelengths are reversible. The lasing wavelength returns back to its original wavelength after UV irradiation is turned off (Fig. 2(b)). This process is slower than a shift towards shorter lasing wavelength and typically requires 20 min. The complete restoration of the SRB also requires 15-20 min (Fig. 3b).

For higher UV intensity (c.a. 150 µW), the number of lasing modes typically increases by more than a factor of two. Multimode lasing is also accompanied by structural changes in the part of the sample closer to the source of the UV light. The morphology of the sample immediately after UV irradiation is shown in Fig. 4(a).

The regular chiral domains (“cholesteric spherulitic domains” or “cholesteric bubbles”) appear inside the sample and give rise to increased light scattering and multimode lasing. Since the transformation of planar cholesteric structure to chiral domain structure results from the higher intensity of UV irradiation, this phenomenon should be governed by

![Image](https://via.placeholder.com/150)

The absorption by the azo dye of UV light. No changes were observed in CLC samples without the presence of LSAZ molecules. The morphological changes are totally reversible when the size of the new domains is much smaller than the interdomain distance. Cholesteric bubbles gradually disappear after the UV irradiation (Fig. 4(b)). Most of the bubbles disappear within the three minutes after the UV irradiation is turned off. Bubbles are completely absent after 15-20 minutes. Two-dimensional domain structures were previously observed in cholesteric polymers [13] and in cholesteric liquid crystals in an electric field [13]. With further increase of UV intensity to 2 mW/cm² the cholesteric bubbles coalesce and form a stable structure. This also results in termination of lasing. We suggest the following qualitative model describing the properties of a CLC laser cavity.

![Image](https://via.placeholder.com/150)

**Fig. 4.** Morphology of the sample after low intensity UV irradiation: (a) Immediately after irradiation at 365 nm, (b) Restoration of the structure 180 s after irradiation.
At a relatively low concentration of LSAZ (in our experiments we used concentration of about 4.5%) dopants and at a low intensity of UV light irradiation, the absorption of UV light occurs near the surface close to the light source. The concentration of the cis-isomers is relatively uniform across the sample due to the relatively high rate of diffusion of cis-isomers from irradiated areas. This results in small but uniform changes of helical pitch across the sample and shift of the SRB and lasing wavelength. After the UV light is switched off, the helical pitch slowly returns back to the initial level because of the isomerization of cis-isomers back into trans-isomers.

At a higher intensity of UV light irradiation, the absorption of UV light by azo-dopants and the concentration of cis-isomers are not uniform across the sample, since the rate of conversion of trans-isomers into cis-isomers is much higher than the diffusion of cis-isomers away from irradiated area. This results in the non-uniform helical pitch across the sample. Most of the changes occur near the substrate close to the UV light source where the concentration of cis-isomers is the highest. These changes in the pitch result in the formation of cholesteric bubbles near the substrate with distorted planarity of cholesteric layers and a smaller helical pitch. These distortions result in termination of optically pumped lasing.

3. Conclusions

Reversible tuning of the wavelength of band-edge lasing in CLCs over a wide spectral range is observed with mild UV irradiation. At higher levels of UV irradiation an irreversible change in the structure occurs in which lasing is not possible. The observation of reversible tuning of the SRB and lasing wavelength open new possibilities for the design of optically tunable linear and nonlinear optical devices using the isomerization of novel chiral azo-dyes. The synthesis and study of novel optically tunable chiral dopants is currently underway in the laboratories of the authors.

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