## Rapid reversible phototuning of lasing frequency in dye-doped cholesteric liquid crystal

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Lasing in induced cholesteric liquid crystal (CLC) containing highly photosensitive azo chiral dopant (ChD) and pyrromethene laser dye was investigated. Due to the absence of excitation energy transfer from the dye molecules to the molecules of ChD in such a system, a low lasing threshold was achieved. When using violet and green light-emitting diodes, reversible frequency tuning was obtained in the range of about 30 nm with a tuning time 1–2 orders of magnitude smaller than in conventional CLC laser systems based on azo and azoxy photosensitive compounds. Further increase of the intensity of the excitation light by using a green laser pointer allowed us to achieve a record phototuning speed (~21 nm in 148 ms). © 2014 Optical Society of America

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Distributed feedback (DFB) lasers based on dye-doped cholesteric liquid crystals (CLCs) were first established in 1980 [1]. Based on the characteristics reported to date, such as threshold excitation intensity, linewidth, and energy efficiency, they can actually be used for development of high-brightness laser displays [2]. Perfection of components for these devices, e.g., development of dye activators with minimal triplet–triplet absorption, CLCs with a high melting point and temperature-independent pitch length make it possible to produce lasing under continuous excitation [3].

Since the creation of the DFB laser, a practical problem is to develop a method for tuning of its frequency, which would provide high speed and reversibility of this process. In practice, the tuning is achieved by changing the pitch of the CLC's helix, impacting on it by mechanical, thermal, electrical, or light factors [4]. The last process, photocontrolling of helical pitch, is of particular interest due to the remote, spatial, and temporal activation advantages of light stimulus. The method of tuning the lasing frequency based on this effect, which more generally is seen as a method of controlling light by means of light, is considered the most promising in terms of the above requirements of the process of tuning [4].

Variation of the helical pitch under the influence of light is due to a change in the helical twisting power of chiral molecular switches in CLCs as a result of the photoconversion of molecules of the chiral dopant (ChD) [5–9], or liquid crystal host [10–13]. Often, these phototransformations (photo-Fries reaction, photolysis reaction, etc.) cause irreversible changes in the helical pitch [5,6]. However, some phototransformations (such as a *trans–cis* isomerization of azo and azoxy compounds) are generally reversible; the photoexcited *cis* isomers of such molecules relax to initial trans form when heated or exposed to light of a different wavelength. The case of *cis-trans* photoisomerization is the most interesting, because it allows one to change the frequency of lasing in two opposite directions by means of the same, quite a technological factor, i.e., light.

Note that the efficiency of *trans-cis* and *cis-trans* photoisomerization and, consequently, the efficiency of lasing frequency tuning, depends on a number of factors, such as overlapping of the absorption spectra of *trans* and *cis* isomers, the lifetime of the *cis* form, and the excitation wavelength in the direct and reverse processes of photoisomerization. An unfortunate combination of these factors in many systems previously used may explain the rather small number of works on the reversible phototuning of the lasing frequency of CLC lasers. These works are mainly related to systems based on photosensitive nematic matrices from the class of azo and azoxy compounds [10,12,13] and, to a lesser extent, CLCs based on chiral azo dopants [7]. However, the dynamic characteristics of such systems are far from perfect. Typically, the time of reverse *cis-trans* photoisomerization is considerably less than the time of direct trans-cis photoisomerization, and for incoherent UV irradiation it reaches even tens of minutes. To our knowledge, the minimum time of reverse tuning (tens of seconds) was achieved by the irradiation of CLCs with a green laser beam  $(\lambda = 532 \text{ nm})$  [12]. In practice, for the application of CLC lasers in optoelectronic devices, it is necessary to reduce the time to tens of milliseconds.

Some recent studies provide hope that an essential reduction of the phototuning time will be achieved in the transition from a 1D helical structure to a 3D structure of the blue phase (BP). In [14], photoswitching between BP1 and BP3 was achieved for only 120 ms. Despite the fact that the color tuning was not attained, this work indicates the amount of time, which can be achieved in the tuning process. On the other hand, phototuning of the color of the BP throughout the visible spectral range was recently attained in [15], but for considerably longer time (tens of seconds). A significant disadvantage of the BP is its existence in only a narrow range of elevated temperatures, which would require temperature stabilization of the sample. A cardinal expansion of the temperature range of the BP (up to room temperatures and even lower) can be achieved by its polymer stabilization. However, this process significantly reduces the possibility of

structural manipulation, which is necessary for the tuning of color [16].

In view of these challenges of the BP approach, we have chosen a conservative method associated with perfection of the helical CLC structure by using more efficient ChDs, which provide expansion of the range of helical pitch as well as speed-up of the tuning process. As such a dopant we used our synthesized highly efficient azo ChD 1 (see the inset in Fig. 1) with very high helical twisting power and high photosensitivity that has recently been successfully used for photocontrol of helical pitch of the BP of CLCs [15]. As was found in [15], ChD 1 was subjected to the process of *trans-cis* photoisomerization, and radiation with wavelengths of 408 and 532 nm can effectively guide the process, respectively, in the direction of *trans-cis* or *cis-trans* transformation.

To fabricate the CLCs, first the nematic matrix was doped with a left-handed ChD S811 (Merck) in an amount of 15 wt. %. Thus the selective reflection band (RB) of the induced CLC was placed in the infrared area (>1100 nm). Subsequent addition of 1.3 wt. % of the left-handed ChD 1 to the above mixture shifted the RB to 550 nm. This CLC was finally activated with pyrromethene dye (PM 567 from Exciton) at a concentration of 0.3 wt. %. The resulting dyedoped photoresponsive CLC was filled into LC cells on glass substrates coated with rubbed polyimide layers to ensure uniform planar alignment. The cell thickness was 15 µm. For spectral measurements (transmission, fluorescence, and laser generation) an Ocean Optics USB 2000 spectrometer with resolution of 1 nm was used. For illumination of samples for the purpose of initiation of transcis and cis-trans izomerization of the molecules of ChD 1, 3 W violet and green light-emitting diodes (LEDs) were used without focusing their radiation on a sample. The average wavelength of the violet diode was 398 nm with a bandwidth of 14 nm, and the average wavelength of the green diode was 519 nm with a bandwidth of 34 nm. The divergence angle of the light beams was 10°, and the LEDs



Fig. 1. Transmission spectra of the CLC activated by PM 567 dye before (curve 1) and after (curve 2) illumination for 3 s with a violet LED. Curve (3) is the emission spectrum of the PM 567 dye in CLC. The pictures above show images of the cell before (left) and after the illumination (right). The inset of the spectral plot presents the chemical formula of ChD 1.

were placed at a distance of 10 cm from the sample. The radiation intensities were 12 and 10 mW/cm<sup>2</sup> for the violet and green diodes, respectively, which were measured using a Melles Griot 13PEM001 diode energy meter.

Figure 1 shows the transmission spectra of the induced CLC before (curve 1) and after (curve 2) 3 s irradiation by a violet LED. The minimum in the transmission spectrum of the CLC at 524 nm is due to the absorption band of the dye. As can be seen, the long-wave edge of the RB of the CLC after 3 s irradiation with a violet LED is redshifted from 567 to 593 nm, which corresponds to the long-wave edge of the fluorescence spectrum of the dye with a maximum at 554 nm (curve 3). The reverse tuning of the helical pitch upon irradiation with a green LED was attained in a similar time.

A green laser pointer (BOB Laser, BGP-3010, 532 nm, 50 mW) with a radiation intensity of 634 mW/cm<sup>2</sup> was used in the study of rapid phototuning associated with reverse *cis*-*trans* isomerization of the molecules of the photosensitive ChD 1. The exposure time was set by a mechanical shutter and changed in discrete portions with a duration of 8 ms. At this, the time of spontaneous *cis*-*trans* transition (the lifetime of the *cis* form) of ChD 1 was  $\approx$ 7 h, i.e., 4–5 orders of magnitude higher than the time used for light irradiation.

Note that since ChD 1 has an absorption band in the green region of the spectrum (with a center at 530 nm), in our system transmission of excitation energy from the dye molecules to the ChD 1 molecules is possible. This may result in weakening of the fluorescence of the dye activator and, hence, an increase in lasing threshold. This negative impact we minimized by restricting the weight of the photosensitive ChD 1 and choosing a dye with a high quantum yield of fluorescence in LCs ( $\approx$ 98, 5%).

The experiment on laser generation was carried out according to the standard scheme by pumping the samples with single pulses of the second harmonic of a Nd:glass laser ( $\lambda = 530$  nm) with a duration of  $\approx 20$  ns. The pumping beam was focused by a lens with a focal length of 21 cm and directed to the sample so that the incidence angle was 20°. To minimize the lasing threshold, a circularly polarized pumping light with a nondiffracting right circular polarization was used. This was done using a phase plate  $\lambda/4$  at 530 nm. The threshold excitation energy of the CLC was measured by a powermeter (IMO-2) and regulated by neutral density filters. The threshold excitation energy of lasing was quite low; it ranged from 20 to 36 µJ/pulse depending on the position of the wavelength of lasing with respect to the center of the emission band of the dye.

Figure 2(a) shows the lasing spectra of the sample. Note that the spectra were placed near the right edge of the selective reflection band of the studied CLC. At an excitation energy of 36  $\mu$ J/pulse, we obtained a spectrum of lasing located on the long-wave edge of the reflection band of the CLC, which initially (before irradiation with the LED) consisted of a single line at  $\lambda = 567$  nm, attributable to the lowest index longitudinal mode. When irradiated by a violet diode for 3 s, the lasing spectrum was shifted to longer wavelengths and, in addition to the above mentioned mode at 580 nm, it contained a new longitudinal mode at  $\lambda = 586$  nm. Judging by the intensity, this additional mode has a lower



Fig. 2. Tuning of the lasing spectra of the dye-activated CLC (a) in a course of illumination with a violet LED and (b) subsequent illumination with a green LED. Curves 1, 2, and 3 in (a) correspond to 0, 3, and 4 s of illumination. Similarly, curves 1, 2, and 3 in (b) correspond to 0, 3, and 5 s of illumination.

threshold. When exposure time was increased to 4 s, the lasing spectrum further shifted toward longer wavelengths and, with a major mode at 593 nm, it had an additional longitudinal mode at 586 nm. The claim that the weaker lines in spectra 2 and 3 in Fig. 2(a) are longitudinal modes is sustained by the same distance (equal to 7 nm) between two lines in each of these two spectra.

Figure 2(b) presents the lasing spectra of the sample in the reverse phototuning process when irradiated with a green LED. Restoration to the initial wavelength of lasing was achieved in 5 s. As seen from this figure, the structure of the spectrum is completely reproduced so that two longitudinal modes on the long-wave edge of the tuning range and a single mode on the short-wave edge of the tuning range are observed. Reducing the number of longitudinal modes on the short-wave edge of the tuning range can be explained by reabsorption of the emitted light by the dye molecules. This reabsorption increases the lasing threshold on the short-wave edge of the range of tuning. Indeed, for PM 567, strong overlap is characteristic of the absorption and fluorescence spectra; the corresponding Stokes shift in the studied samples was only 28 nm. Thus, the difference in the magnitude of the gain at wavelengths of 567 and 590 nm is leveled by increasing the reabsorption by the dye molecules and, as a result, the conditions for lasing at the long-wave edge of the tuning range are the best, as evidenced by the increase in the number of longitudinal modes.

As can be seen, phototuning in the range of 26 nm for 4 and 5 s, respectively, in the long-wave and short-wave directions was reached. The corresponding tuning speed is 1 order of magnitude higher than for the known CLC structures based on azo and azoxy materials [5-9]. The range of phototuning from the short-wave side was limited by the strong reabsorption of dye. However, it could be significantly enhanced by using activating dye with a larger Stokes shift. As shown in [15], the reflection band of the non-dyed CLC induced by ChD 1 can be phototuned across the whole visible range in a couple of seconds.

Figure 3 presents dependence of the lasing wavelength  $\lambda_g$  in the dye-activated CLC on the time of irradiation *t* by the violet (curve 1) and green (curve 2) LEDs. In order to

obtain a subsecond tuning time, we used a more powerful source of radiation—a laser pointer—for photoisomerization of ChD 1. Figure <u>4</u> shows the kinetic of the reverse phototuning of the lasing frequency for the case of irradiation by a green laser pointer ( $\lambda = 532$  nm). As can be seen, the phototuning is realized in the range from 596 to 575 nm in only 148 ms. It should also be noted that the dependence  $\lambda_g(t)$  is much more nonlinear than in the case of irradiation by a green LED (Fig. 3).

Note that acceleration of phototuning by use of highintensity light sources has clear restrictions, as the increase of the intensity of radiation leads to strengthening of destructive processes in the CLC. Therefore, adoption of other approaches is considered to be important. One of them may be an increase in the concentration of ChD 1 in the CLC. The low thresholds of lasing obtained allow one to increase the concentration of ChD 1 in the mixture and, presumably, to improve phototuning time.

In summary, the use of highly photosensitive ChD 1 allowed us to reduce the phototuning time of the lasing frequency by more than 1 order of magnitude compared with a previously used photosensitive CLC that was



Fig. 3. Kinetics of the direct (curve 1) and reverse (curve 2) phototuning of lasing wavelength, obtained, correspondingly, by using violet (curve 1) and green (curve 2) LEDs.



Fig. 4. Kinetics of the reverse phototuning of lasing wavelength in the case of irradiation with a green laser pointer.

manipulated by LED radiation. The important point is getting almost the same time of frequency tuning in both directions. Irradiation of the samples with a laser pointer can further reduce the phototuning time to 2 orders of magnitude, bringing it to tens of milliseconds.

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