2. Sample preparation and experimental setups

A CLC host with left chirality is prepared by mixing 74.2*wt*% NLC (MDA-03-3970, from Merck) and 12.5*wt*% chiral material (S811, from Merck). The CLC host is then mixed with 12.6*wt*% photoisomerizable chiral agent (AzoM, left-handedness) and two laser dyes, 4-dicyanmethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM, from Exciton) and pyrromethene 567 (P567, from Exciton), in proportions 0.5 and 0.2*wt*%, respectively, to form a DDCLC mixture with AzoM. Details of the synthesis of AzoM can be found elsewhere [19,20]. A mixture of DDCLC with AzoM is injected into the empty cell and uniformly dispersed to form a 4cm-long × 0.5cm-wide planar DDCLC cell with AzoM. The empty cell is pre-fabricated by combining two indium-tin-oxide glass slides, separated by two narrow 23μm-thick plastic strips (cell gap). Homogeneously-aligned PVA films are individually pre-coated on the glass slides of the cell and pre-rubbed in the same direction.

Figure 1 displays the experimental setup for measuring the lasing spectra in the visible region at various cell positions. The pulse light source that is employed to pump the DDCLC cell is a Q-switched Nd:YAG second harmonic generation (SHG) pulse laser (wavelength: 532nm) with a pulse duration of 8ns and a pulse energy, E. A single pumped pulse is focused using a lens (focal length = 20cm) on the cell at an incident angle of approximately 20° and the generated lasing signal, which is emitting perpendicular to the CLC planes of the cell, can be measured. A half-wave plate (λ/2 for 532nm) and polarizing beam splitter (PBS) are placed in front of the lens to modify the pulse energy of the laser beam that impinges on the cell. To analyze the measured lasing signal at a certain cell position, the corresponding reflection spectrum (in the visible region), which indicates the CLC band structure at that position, is also measured. Both the lasing and the reflection spectra of the cell are recorded using a fiber-optic probe of a fiber-based spectrometer system (USB2000-UV-VIS, Ocean Optics, optical resolution: ~1.4) that is placed at a distance of l = 1cm behind the cell. Notably, the DDCLC cell is fixed on a sample holder on a translation stage, which can be moved to enable the spatial tuning feature of the obtained lasing and corresponding reflection spectra of the cell to be investigated.

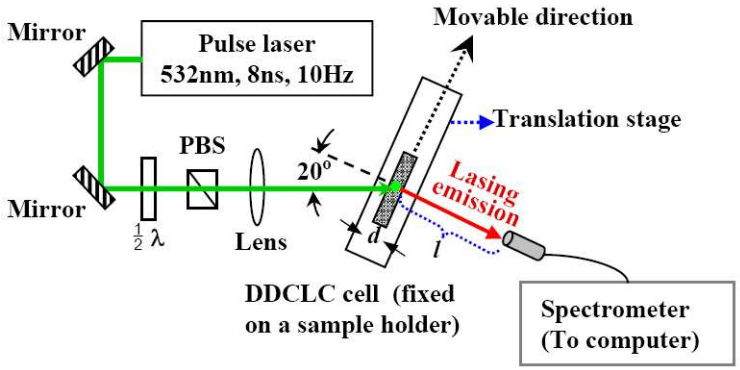

Fig. 1. Experimental setup for measuring lasing spectra of DDCLC cell at various positions of the cell. The DDCLC cell (cell gap: d) is fixed on a sample holder, which is removable on a translational stage, such that the incident single pumped pulse can excite the cell at various cell positions. The spectrometer probe is placed at a distance of l = 1cm behind the cell to receive lasing emission along the cell normal. PBS: polarizing beam splitter, λ/2: half-wave plate for 532nm.

3. Results and discussion

A pitch gradient in the AzoM-added DDCLC is pre-formed before the lasing and reflection spectra of the cell are measured. As displayed in Fig. 2(a), an expanded and collimated UV beam with a uniform intensity of 3mW/cm^2 passes through a rectangular photomask (5.08cm-length × 2.54cm-width) with a position-dependent transmittance to illuminate the AzoM-

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added DDCLC cell for 20 minutes by the UV-irradiation-gradient method. Figure 2(b) reveals that the transmittance of the UV light via the photomask monotonically increases as the cell position shifts from x = 0 to x = 40mm. Figures 2(c) and 2(d) present homogeneous and inhomogeneous image colors of a white beam reflected from the cell before and after UV irradiation, respectively. Apparently, in Fig. 2(d), the CLC reflection band (CLCRB) of the cell can be observed by naked eye gradually to red-shift from green to red as x increases. Figure 3(a) directly shows the gradual red-shift in the measured CLCRB as the cell position shifts from x = 6 to x = 34mm, establishing a CLCRB gradient. Experimental results in Figs. 2(d) and 3(a) reflect the formation of the pitch gradient on the cell by the UV irradiation. Since a separate experiment demonstrated the pitch-invariance of the DDCLC cell without AzoM following the above UV irradiation (data not shown), the UV-induced pitch gradient on the AzoM-added DDCLC cell, shown in Fig. 2(d), is certainly established by the effect of the UV-excited AzoM on the cell pitch. The mechanism is described as follows.

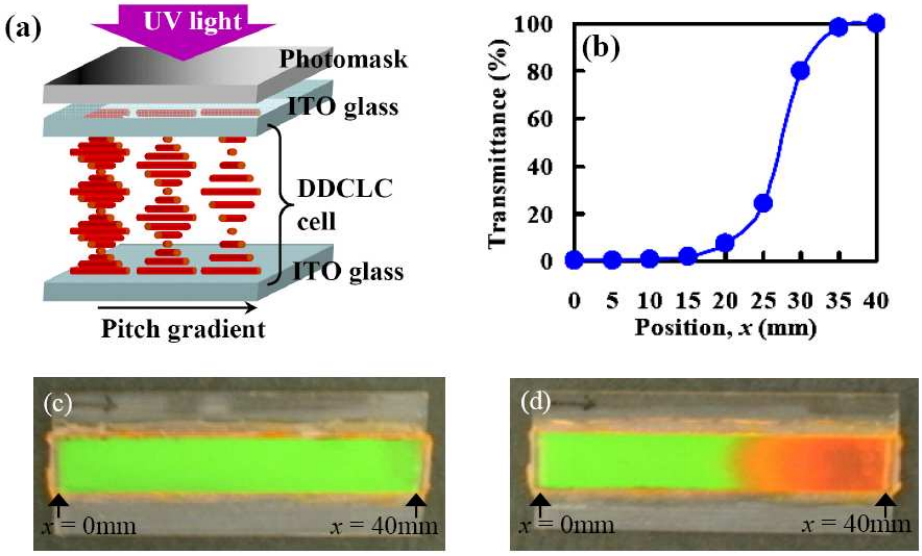

Fig. 2. (a) Pitch gradient in the AzoM-added DDCLC cell formed upon irradiation by one uniform UV beam with an intensity of 3mW/cm^2 for 20min through a transmittance-gradational photomask. (b) Gradient of transmittance of UV light through the photomask from 0 to 100% as cell position changes from x = 0 to x = 40mm. Reflection images of one white beam from AzoM-added DDCLC cell (c) without and (d) with a pitch gradient.

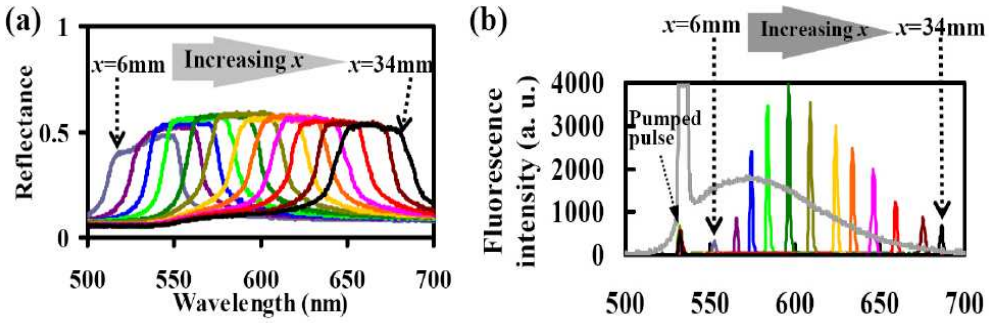

Fig. 3. Red-shifts of (a) measured CLCRB and (b) measured lasing signal at LWE as position of AzoM-added DDCLC cell varies from x = 6 to x = 34mm. The grey curve represents the fluorescence emission spectrum of the cell in the isotropic state.

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The authors' associates, Liu *et al.,* provided the AzoM chiral dopant that was used in this work. It is a photoisomerizable chiral dopant and is crucial to the tunability of the CLC pitch and thus that of the lasing feature of the AzoM-added cell. The details of the evolution of the UV-visible spectra of the AzoM in chloroform under UV irradiation can be found in Liu *et al*'s previous reports [19,20]. The AzoM has two absorption bands in the UV (around 365nm) and visible (around 450nm) regions, associated with π-π* and *n*-π* transitions, respectively. Figure 4(a) presents the molecular structures of the *trans*- and *cis*-AzoM and associated isomerization reactions [19]. Generally, the AzoM is stable in the rod-like *trans*-state in the dark. When excited by light with a short wavelength (photon energy hν, such as UV light), the AzoM can rapidly transform to bent *cis*-isomers. However, the *cis*-AzoM can convert back to the *trans*-state rapidly under irradiation by light with a long wavelength (photon energy hν', such as blue-green light) or slowly via a thermal reaction (represented by Δ). Experimental results (data not shown) confirm that the *trans*- and *cis*-AzoM in nematic LC (NLC), MDA-03-3970, have HTP values of approximately −12.26 and $-5.90\mu m^{-1}$ (at room temperature), respectively. The drop in the HTP value (absolute value) for *cis*-AzoM in NLC is probably caused by a disturbance of the bent structure of the *cis*-isomers upon the local order of the NLC director [19]. Since AzoM chiral dopant has the same left-handedness as the CLC host (S811 + NLC), doping with the AzoM increases the resultant HTP value of the DDCLC cell. As the intensity of the UV light that is used to irradiate the cell increases, the concentration of *cis*-AzoM in the cell increases, and the resultant HTP value of the cell declines for the aforementioned reason, established the UV-induced pitch gradient and thus the CLCRB gradient, as displayed in Figs. 2(d) and 3(a), respectively.

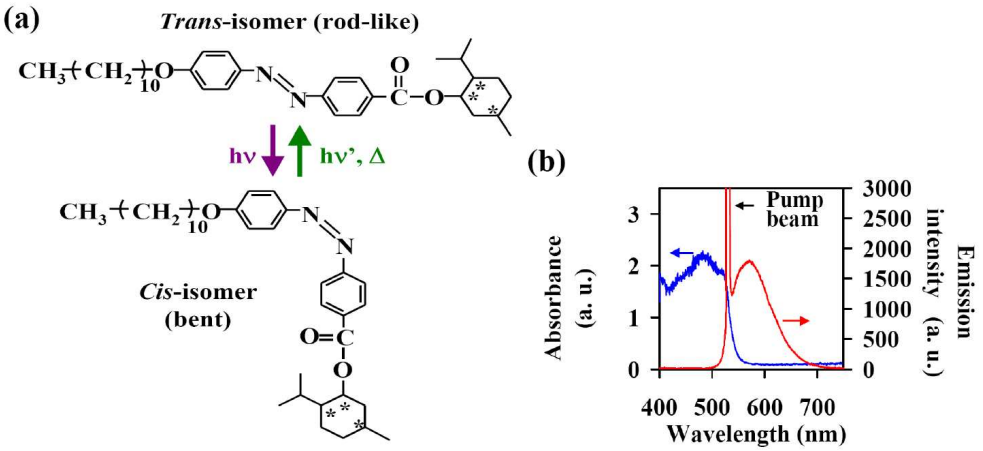

Fig. 4. (a) Two reversibly transformed isomeric structures of AzoM in rod-like *trans*- and bent *cis*-states and associated isomerization reactions. (b) Fluorescence emission (red curve) and absorption (blue curve) spectra of DDCLC cell in isotropic state. More of the fluorescence of the cell is emitted between 540 to 700nm.

Figure 4(b) presents the absorption and fluorescence emission spectra of the DDCLC cell in the isotropic state; the latter is distributed mostly between 540 and 700nm. Based on photonic band-edge lasing theory for a 1D PC-like planar DDCLC, lasing can occur at the edges of the CLCRB of the cell if the region of the spontaneously emitted fluorescence effectively overlaps the band edges [12,13]. Since the fluorescence emission spectrum of laser dyes (540-700nm) entirely overlaps the region of the spectrum associated with the CLCRB gradient of the AzoM-added DDCLC cell with the pitch gradient [Fig. 3(a)], a spatially-tunable edge lasing emission can be stimulated. Figure 3(b) presents the experimental results: the lasing emission can be excited at the long wavelength edge (LWE) of each position-dependent CLCRB when stimulated by a single pumped pulse with E = 18μJ/pulse. Accordingly, the lasing wavelength at the edge can be spatially tuned from 553 to 687nm at

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cell positions from x = 6 to x = 34mm. The gray fluorescence spectrum curve of the cell in the isotropic state in the region of 500-700nm is also displayed in Fig. 3(b). Apparently, the strongest lasing emission (~596 nm) does not exactly occur at the wavelength (~575 nm) at which the fluorescence emission of the cell is highest. This is possibly due to the weak re-absorption effect of the fluorescence photons with the wavelength of ~575nm, where the tail of the absorption spectrum curve of the cell overlaps [Fig. 4(b)].

Figures 5(a)–5(f) show the obtained color-changeable lasing patterns (from green to deep red) on the screen, as well as the corresponding lasing wavelengths (from 553 to 687nm) as the pumping position of the cell is varied from x = 6 to x = 34 mm. Hence, a large spatially-tunable range of lasing wavelengths with a width of 134nm in a length of 28mm on the cell, based on the AzoM-added DDCLC laser with a UV-induced pitch gradient, can be obtained. As shown in Fig. 4(b), lasing emission does not easily occur outside the range 553-687nm because of the strong loss caused by the strong re-absorption of fluorescence at λ<553nm or the negligible fluorescence emission at λ>687nm.

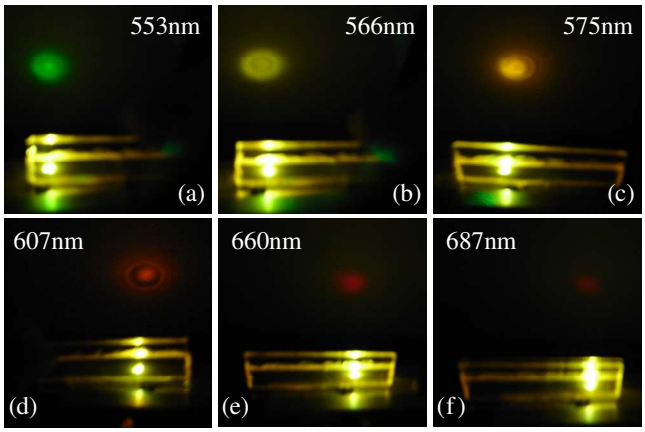

Fig. 5. (a)-(f) Lasing patterns with lasing wavelengths of 553 to 687 nm (green to deep red) at the LWE of the CLCRB obtained as pumping position of AzoM-added DDCLC cell increases from x = 6 to x = 34mm.

This study also elucidates the photoerasability and thermal stability of the formed pitch gradient and, thus, the spatial tunability of the laser. A pitch gradient is produced from x = 6 to x = 34mm in the AzoM-added DDCLC cell in response to UV-irradiation-gradient method for 40min. The wavelength at the LWE (λ_{LWE}) of the measured CLCRB of the cell varies from 561 to 745nm as the cell position varies from x = 6 to x = 34mm, as displayed in Fig. 6(a) (black curve). This result is similar to that shown in Fig. 3(a). Next, an expanded and uniform green beam (from a diode-pumped solid state laser, output power <1W, λ: 532nm) with an intensity of 20mW/cm^2 is applied to irradiate the cell with the pitch gradient for t_G = 0 to t_G = 90s, such that the black curve gradually shifts to the red line. Therefore, λ_{LWE} at x>19mm and x<19mm gradually blue-shift and red-shift, respectively, to an identical value, 581nm, as t_G increases from 0 to 90s. This result reflects the fact that the pitch gradient and thus the spatial tunability of the DDCLC laser mentioned above can be erased in 90s. The erasing time may be reduced by increasing the irradiated intensity of the green beam. This photoerasibility of the spatial features of the DDCLC laser is attributable to the green-beam-induced photoisomerization reaction of AzoM in the cell. In the *cis*-AzoM-rich region (x>19mm), the green beam can cause the *cis*-AzoM to enter the *trans*-state at a high *cis*→*trans* isomeirzation rate, causing the resultant HTP value to increase such that both the CLCRB and its LWE exhibit a large blue-shift. In contrast, in the *trans*-AzoM-rich region (x<19mm), the green beam transform the *trans*-AzoM into the *cis*-state at a low *trans*→*cis* isomerization rate, reducing the HTP value, such that both the CLCRB and its LWE are slightly red-shifted. Under continued irradiation of the green beam, a uniform dynamic equilibrium with a high

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concentration of *trans*-AzoM and a low concentration of *cis*-AzoM in the whole cell can be achieved such that the λ_{LWE} at each cell position can eventually reach a stable value.

In the absence of irradiation by a green beam, the pre-formed pitch gradient of the cell can naturally relax to the original uniform pitch value. Figure 6(b) presents related experimental results. When the AzoM-added cell with the pitch gradient is placed in a dark room at constant room temperature (~23°C) from t = 0 to t = 38hr, the *cis*-AzoM slowly transforms back to the *trans*-state by thermal *cis-trans* back-isomerization at each cell position, such that the pitch at each position slowly returns to the original value that prevailed before UV irradiation. Experimental results (data not shown) also indicate that the pitch gradient can be photorewritten using the UV-irradiation-gradient method. Before now, the AzoM-added DDCLC cell had undergone more than 100 cycles of photoerasing and photorewriting processes without decay or damage.

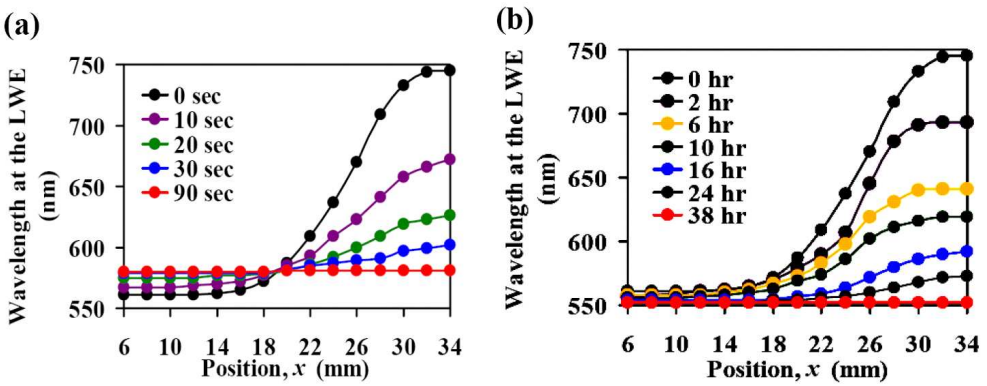

Fig. 6. Photoerasibility and thermal relaxation of the pitch gradient and thus the associated spatial tunability of laser. A pitch gradient is pre-written in the cell by the UV-irradiation-gradient method, yielding a position-dependent wavelength distribution at the LWE of the measured CLCRB (black curves in (a) and (b)). (a) The wavelengths at the LWEs at all cell positions shift to a single value (black curve → red line) as the duration of irradiation of one uniform green beam with an intensity of 20mW/cm^2 on the cell with a pitch gradient increases from 0 to 90s. (b) The wavelength at the LWE at each cell position slowly relaxes to the original value (black curve → red line) as the relaxation time increases from 0 to 38hr.

4. Conclusion

This work demonstrates, for the first time, a photoerasable and photorewritable spatially-tunable laser that is based on a DDCLC cell doping with a photoisomerizable chiral dopant (AzoM). UV irradiation through a photomask with a transmittance-gradient can establish a pitch gradient in the AzoM-added DDCLC cell such that the generated edge lasing wavelength can be spatially tuned over a wide band from green to deep red (553 to 687nm) in a cell length of 28mm. The pitch gradient is formed by the UV-irradiation-induced gradient of the concentration of the *cis*-AzoM and therefore the induced gradient of the HTP value of the cell, resulting in the spatial tunability of the DDCLC laser. Additionally, the laser is photoerasable and photorewritable. The spatial tunability of the laser can endure more than 100 cycles of photoerasing and photorewriting processes without decay or damage. The total thermal relaxation of the spatial-tunability of the laser does not take as long as 38 hours. Other methods, such as polymer-network stabilized method, will be employed to improve the thermal stability of the tunable laser in the future work.

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