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Title: Wide tunable lasing in photoresponsive chiral liquid crystal emulsion

A new kind of tunable laser is achieved by coating a photoresponsive chiral liquid crystal emulsion on a glass substrate. The laser wavelength is reversibly tuned by light within a wide spectral range, from 566 nm to 678 nm.

# As featured in:



See Zhi-gang Zheng, Dong Shen *et al.,* J. Mater. Chem. C, 2015, **3**, 2462.

www.rsc.org/MaterialsC



Registered charity number: 207890

# Journal of Materials Chemistry C

# PAPER



Cite this: J. Mater. Chem. C, 2015, 3, 2462

Received 9th December 2014 Accepted 15th January 2015

DOI: 10.1039/c4tc02832e

www.rsc.org/MaterialsC

# Introduction

Liquid crystals (LCs) are a type of organic material with significant self-assembly. Due to the strong van der Waals interactions between the molecules, LCs can form some ordered arrangements, such as the common nematic and smectic phases, without the aid of any external stimulus. By introducing the chiral center in the molecules or doping some chiral agents into LCs, the molecules are twisted and self-assembled into a helical structure, forming chiral liquid crystals (CLCs). Such CLCs have a specific selective reflection characteristic for circular polarized light with the same rotation sense as other CLCs because their wavelength is of the order of the helical pitch. Therefore, photons that match well with the CLC helix will be forbidden to propagate through the medium, which is called the effect of the photonic band gap (PBG). The group velocity of photons in the vicinity of the band-edge is the minimum; thus, the photon density of state (DOS) correspondingly reaches the maximum. If some fluorescent dyes are doped into the CLCs, and provided that the emission spectrum of the dye overlaps the band-edge of PBG, lasing will be found at the edge under certain pumping conditions, that is, the so-called band-edge CLC laser, which is promising for use in the next generation laser displays or can be



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A new tunable laser based on a photoresponsive chiral liquid crystal emulsion is reported. Such a laser can be reversibly photo-tuned in a wide spectral range of 112 nm (566–678 nm), and it simultaneously possesses stable emission performance and quasi-continuous tunability. Typically, unlike the conventional liquid crystal laser, the proposed laser can be fabricated by simply coating the material on a single substrate, which will simplify the production process and broaden the application of liquid crystal laser. In addition, the mechanisms of tunability are explored on a molecular scale. The studies reveal that the molecular conformation transition of a photosensitive chiral switch during isomerization leads to changes in not only the molecular geometry and the direction of dipole moment, but also the molecular interactions and the miscibility of the materials. These changes cause the rearrangement of liquid crystals, thus rendering the variation of helical twisted power and achieving tuning on the photonic band-edge of the chiral liquid crystal, consequently forming a photo-tunable laser.

directly embedded on the silicon to fabricate the lab-on-chip devices.<sup>1</sup>

The phenomenon of lasing in CLCs was first observed by Kopp et al.<sup>2</sup> Then, the theoretical work of Schmidtke et al. analyzed the lasing characteristics and discussed their correlations with the helical structure of CLCs.3 To decrease the emission threshold as well as increase the lasing efficiency, a great deal of effort has been made from the viewpoint of materials; e.g., some types of polymer laser dyes and dyes with extremely high quantum efficiency were synthesized.4,5 In addition, LCs with higher anisotropy, better orderliness and larger elasticity were adopted.6 Moreover, the glass substrates of the LC cell were replaced by the high reflection silicon wafer7 or the polymer CLCs layer<sup>8,9</sup> to increase the optical gain length, and consequently decrease the emission threshold. The pumping conditions, including the incident angle,<sup>10</sup> the polarization<sup>11</sup> as well as the temperature,<sup>12</sup> were also optimized in theoretical and experimental studies.

An excellent property of LCs is their response under a stimulus of external fields, such as mechanical force, temperature, electric field and light, which facilitates the tunability of LC laser. In general, a large wavelength tuning range and a fast response are preferred for the LC laser. The largest wavelength shift of about 80 nm by biaxially stretching CLC elastomer has been achieved.<sup>13</sup> As one of the most convenient tuning methods, the electrical tunability of the emission intensity and wavelength has been widely studied, *e.g.*, the switching on and off of the lasing in polymer stabilized CLCs with less than 10 V has been reported recently;<sup>14</sup> a wavelength-shift of the laser, normally less than 40 nm, has also been achieved in a defect mode device,<sup>15</sup> devices filled with some special LCs,<sup>16,17</sup> and CLCs

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<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c4tc02832e

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embedded nanopore networks.18 A light tuning method always attracts widespread attention because of its advantages of easy and remote on demand control, no need of electrodes on the substrate of cells, and high accuracy, as compared to electric-field tuning. The wide wavelength tuning, realized from the photo-Fries rearrangement of chiral agent S811 or the photolysis of certain chirals, has been reported earlier; however, its disadvantage is the irreversibility of such tuning.<sup>19,20</sup> Azo derivatives have a special reversible photoisomerization characteristic, which has been widely adopted in light responsive materials and devices.<sup>21-23</sup> The nematic azo- and azoxy-components were mixed with a conventional photo-insensitive chiral dopant to form a photosensitive helical superstructure, resulting in a 70 nm shift of the laser.<sup>24</sup> Doping a small amount of azo material in the CLCs can resolve this problem,<sup>25</sup> and a wider wavelength tuning range of 104 nm based on a rod-like azo chiral was achieved in the work of Lin et al.26 Nevertheless, the response time for the tuning is long; it generally takes a few to tens of minutes. By combining the photoisomerous azo dyes and the high excitation efficiency quantum dots, photo-tunable lasing with approximately 40 nm spectral shift were realized as well.27 Besides, a special tunable laser was proposed by introducing the helical pitch gradient in the cell, and tunable lasing from 577 to 670 nm was obtained.28 A three-layered structure, containing two CLC cells sandwiching an isotropic photoluminescence dye, with a wide tuning range was reported recently.29 Temperature variation is often considered another convenient tuning method. The tunable mode competition of the LC laser using temperature variation was reported a few months ago, indicating the prospect for the CLC laser to be used in the display.<sup>30</sup> For widening the wavelength tunable range further, more than three types of laser dyes were doped in CLCs. By combining the effect of Förster energy transfer between the dyes with the spatial gradient of helical pitch, an ultra-wide tuning that covered the whole visible spectrum band was achieved. However, such a system is not stable because of the diffusion between the dyes and the differences in the solubility; in addition, the interaction of the transition moment between the dyes will decrease their quantum efficiency, leading to the weakening or even the disappearance of the lasing.<sup>31-34</sup>

Based on the mechanism of the band-edge lasing of CLCs, some new types of three-dimensional (3D) CLC lasers were developed, such as the lasing in cubic blue phase liquid crystals (BPLCs),<sup>35,36</sup> and in the spherical CLC droplets, the dispersions which can be tuned through temperature as well as other external fields.<sup>37,38</sup> Recently, Chen *et al.* reported a phototunable 3D laser formed by the azo chiral doped CLC microshell, whereas a wavelength-shift of only about 50 nm was found.<sup>39</sup> In addition, the lasing induced by whispering-gallerymode (WGM) resonances inside the LCs microstructures<sup>40,41</sup> and the lasing pumped by two coherent beams<sup>42</sup> have been found recently.

Due to the fluidity of LCs and the dispersions, such materials should be sandwiched between two substrates in real practice; furthermore, the pre-treatments of the substrates are necessary and complex, thus restricting the miniaturization and simplification of LC laser devices. Gardiner *et al.* prepared an

emulsion by mixing the CLCs with an aqueous solution of polyvinyl alcohol (PVA), and then coated the syrup on a planar glass to form a wet-film with randomly dispersed CLC droplets.43 Unlike the traditional random laser in polymer dispersed liquid crystal (PDLC), due to the feedback loops formed by the dispersed tiny LCs scatterers,44 such a wet-film shrink in thickness because of the deswelling, leading to the geometrical deformation of the dispersed LC droplets from sphere to oblate sphere with the diameter of tens of micrometers or more; moreover, it forces the randomly aligned helical axis within the droplet to change to a uniform alignment vertical to the substrate. Consequently, the PBG effect, which is a requirement for the laser emission, was observed in the single substrate sample, similar as that of CLCs confined in pre-aligned cells. The CLC emulsion is independent of the LC cells, and therefore it simplifies the process of fabricating the LC laser. However, with regard to the tunability of such a single-substrate LC laser, there has been no report on this topic at present, which is the motivation of the studies herein.

To date, a great number of studies on the tunable LC laser have been reported as mentioned above; however, the first problem that the CLC emulsion laser faces is which tuning method is the most appropriate. Using mechanical force or ambient temperature as the stimuli is inapposite because of the requirement of complex, large and heavy accessories. Electrical tunability appears more convenient than the above mentioned two; however, two electrodes are necessary, thus limiting such manner to be adopted in the CLC emulsion laser with only one or no electrode coated on the single substrate. Tunability due to the spatial helical pitch gradient is also restricted because such an arrangement of LCs is very difficult in the single substrate without sufficient anchoring. Therefore, on the basis of the above discussions, photo-tuning is the most convenient way to realize the tunability of CLC emulsion laser. Second, because CLCs are normally photo-irresponsive, the most common way to resolve the problem is doping a certain amount of photoisomerous guest materials into the CLC host. Azo dyes are generally preferred because of their better photosensitivity, fast trans-to-cis transition, and good solubility with CLCs. Although studies on photo-tunable CLC PBG by doping azobenzene derivatives have been reported, the tuning performance was not satisfied. Li et al. proposed another azo based binaphthyl derivative with higher photo-tunable chirality, which is referred to as a light-driven chiral switch.<sup>45-49</sup> A series of reports concerning the photo-tunability of CLCs doped with this type of chiral switch has indicated an excellent photo-tunability performance, showing a rather wide shift of PBG from the ultraviolet, including the whole visible band, to the near infrared.47,48,50 Third, the wide emission band of laser dyes is another key point for obtaining wide tunable lasing. As aforementioned, Förster energy transfer in a multi-dye-doped system appears effective for wide tunable lasing, while accompanied by many problems, which are contrarily harmful for the performances of the laser. Therefore, in view of these aspects, doping with single laser dyes with a wide emission band and good solubility in CLCs is the most preferable way.

This paper reported wide photo-tunable lasing in a CLC emulsified film coated on a single substrate. Photo-tunability was obtained by mixing a small amount of an azo-based binaphthyl chiral molecular switch within the CLC emulsion, which makes the emulsion possess high photosensitivity, thus realizing the wide shifting of PBG, and consequently achieving the wide photo-tunability of the band-edge laser. To the best of our knowledge, such a wide tunable emulsion laser utilizing a photosensitive chiral switch has not been reported previously. Moreover, previous studies on tunable CLC laser mainly focus on tuning performances and little on the tuning mechanism. In this study, the mechanism of photo-tuning and the relevant influences on lasing performances were also investigated through molecular simulations. The results coincided well with the experiments.

# Experiments and molecular simulation methods

#### Sample preparation and testing

The conventional nematic LCs XH07-X (supported by Xianhua Chemical Co. Ltd., China) and the commercial chiral agent R811 (supplied from Merck, Germany) were mixed for preparing the CLCs. Simultaneously, some amount of photosensitive azo based binaphthyl chiral switch (Fig. 1), with the same helical sense as R811, denoted as QL55, was doped into the CLCs, forming the photoresponsive CLC system with the significant characteristic of photo-tunable PBG. The synthetic route of QL55 as well as the <sup>1</sup>H NMR (400 MHz) and high resolution mass spectroscopies used to identify the chemical structure of QL55 are given in ESI.† The optimized contents for R811 and photosensitive chiral switch QL55 are 19.5 wt% and 2.5 wt%, respectively, and 0.5 wt% of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostryl)-4H-pyan (DCM, supplied from Sigma-Aldrich) was doped as the laser dye. The helical twisted power (HTP) for the system can be tested through the common method of Grandjean-Cano wedge (supplied by Instec Co., Ltd.). This mixture was blended with the aqueous solution of polyvinyl alcohol (PVA, supplied from Sigma-Aldrich) to obtain the emulsion with a uniform CLC droplet dispersion. Subsequently, the emulsion was coated onto a clean glass, the CLC emulsion wet film was formed, and the dry film was obtained after deswelling (Fig. S1<sup>†</sup>). The size of the CLC droplets dispersed in the matrix of the dry film was 40-50 µm estimated through the scale bar fixed in the microscope, as shown in Fig. 2(a).

The sample was excited by a second-harmonic Q-switched Nd:YAG pulsed laser (supplied by Beamtech Co., Ltd., Canada) with the output wavelength of 532 nm. The emission characteristics were detected by an optical fiber connected



Fig. 1 Chemical structure of QL55.



Fig. 2 Microscope image of CLC emulsion film after the deswelling (a); the texture for the single CLC droplet in the white dashed box at  $\text{PSS}_{\text{UV}}$  (b) and  $\text{PSS}_{\text{VIS}}$  (c), and their corresponding transmittance spectrums (d).

spectrometer (Avaspec-2048 from Avantes, Netherland), and the photo-tunability was conducted by the irradiation of LEDs with a narrow spectral line width of 10 nm (Fig. S2†).

#### Molecular simulation methods

The complete atomistic model was adopted for more accurate and comprehensive analyses of the molecular characteristics. The optimization of molecular geometry was carried out through the semi-empirical molecular orbit algorithm, AM1, which is an ideal choice when making the tradeoff between the short calculation time and the accuracy, and has been proved to be effective and suitable for organic molecules.<sup>51,52</sup> Both the optimized geometrical configuration and the molecular dipole moment can be obtained in the calculation. Subsequently, some amounts of molecules were settled into a cubic box and molecular dynamic (MD) methods were conducted under the restraint of periodic boundary conditions to simulate the macroscopic real material system. After the entire system reached thermal equilibrium, the characteristics of the materials, such as the molecular interaction energy, the solubility, the director and the order parameter of LCs, at different situations were calculated. Some details of MD simulations, settings, and the calculation methods are presented in ESI.†

### **Results and discussions**

#### Characteristics of photosensitive CLC emulsion film

The emulsion containing QL55 was coated on a glass substrate and observed through the microscope with the reflection mode. As shown in Fig. 2(a), many green spherical zones randomly distribute throughout the view field. The green color is caused by the selective Bragg reflection of the CLCs with the standing helix, while the blurry halation around the green zone is resulted from the anchoring of the PVA interface, which influences the original arrangement of LCs. Due to the reversible photoisomerization of QL55, the reflective color of the CLC

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droplets red-shifted during the irradiation of 365 nm LED and recovered after exposure with 480 nm LED. When the photoisomerization reached thermal equilibrium, the color shifting stopped; thus, the sample attained a photo-stationary state (PSS). Herein, the PSS obtained through the UV (365 nm) and visible (480 nm) light irradiation is denoted by PSS<sub>UV</sub> and PSS<sub>VIS</sub>, respectively. In addition, it can be estimated from the scale bar that the size distribution of LC droplets is 30-100 µm, which approximately satisfies the normal distribution, with the statistical average of 72.4 µm. It should be noted that the droplet size not only is the size of the central Bragg reflection parts, but also includes the size of the halation parts around the center. Fig. 2(b) shows the PSS<sub>UV</sub> of the droplet encircled in the white dash frame after exposure with 365 nm LED for 1 minute with the intensity of 9.2 mW  $cm^{-2}$ . The reflection color changes from the original green to red due to the trans-to-cis photoisomerization of the chiral switch OL55. In contrast, the recovery of the reflection color can be realized though a thermodynamic process within a relative long time or promoted by the irradiation with blue-green visible light. Fig. 2(c) shows PSS<sub>VIS</sub> as the same droplet was exposed by 480 nm LED with the intensity of 7.3 mW cm<sup>-2</sup> for 1 minute. It is easily found that the reflection color comes back to the original green, which is similar to that in the initial state. The spectra of the sample in two PSS states, shown in Fig. 2(d), present the evident reflection stop bands with the long wavelength band-edge (LWBE) at 566 nm and 680 nm corresponding to  $PSS_{VIS}$  and  $PSS_{UV}$ , respectively; thus, indicating a good tunability of the band-edge within the range from 566 nm to 680 nm by light, which is crucial for the performance of the tunable laser. The HTPs of QL55 at the initial state and two PSS states were tested and calculated as well (eqn S1<sup>†</sup>), which indicate a remarkable decrease from 49.0  $\mu$ m<sup>-1</sup>, for the initial state, to 17.1  $\mu$ m<sup>-1</sup>, for the PSS<sub>UV</sub>; however, an opposite increase from the PSS<sub>UV</sub> to the PSS<sub>VIS</sub> with the HTP of 40.1  $\mu$ m<sup>-1</sup> is found. As a result, *cis*-QL55 cannot completely transform into the trans-isomer within a short time after exposure to visible light and HTP at  $PSS_{VIS}$  is a little smaller than that at the initial state. Such phenomena can also be inferred from the differences in the UV-visible absorbance between PSS<sub>UV</sub> and PSS<sub>VIS</sub> (Fig. S3<sup>†</sup>).

Although the photo-tunable band-edge was achieved by doping QL55, some issues, such as why and how does the HTP change, are still not clear. To explore the hidden mechanisms, a molecular simulation was carried out. The optimized configurations for the two QL55 isomers were obtained first. Fig. 3 shows the atomistic models of the trans-QL55 (the left-side) and the cis-QL55 (the right-side) isomers. Obviously, the two naphthalenes included in the QL55 molecule are not coplanar, but at a certain angle, irrespective of the trans or cis configurations. In addition, the calculation results reveal that the naphthalenes rotate with the axis of the  $\sigma$  bond, connecting two naphthalenes, during the photoisomerization. If we define the two naphthalenes as "A" and "B", as labeled in Fig. 3, when trans-tocis transition occurs, the A-unit rotates clockwise, while counter clockwise to the B-unit (as labeled by the arrow with violet color on the left side), forming the *cis*-isomer; however, the opposite rotations (labeled by the cyan-color arrow on the right side) for



**Fig. 3** Molecular conformation transformation of QL55 between the *trans* and *cis* isomers. The inset at the lower center depicts the rotation of the direction of the dipole moment; the blue arrow indicates the direction of the dipole moment for *trans*-QL55, while the green one indicates that for *cis*-QL55.

the two units lead to the recovery from cis-isomer to the trans one. Therefore, the original helical arrangement of LCs is disturbed by such rotations under the effect of molecular cooperation, which then transforms to the other helical arrangement. Simultaneously, the dipole moment of QL55 rotates in the same direction as that in the case of isomerization, leading to the realignment of the LC director due to the dipole interactions between LCs and QL55 molecules. As shown in the central inset of Fig. 3, the blue arrow denotes the direction of the dipole moment at trans-configuration, while the green one corresponds to that at *cis*-configuration. One noteworthy result is that the direction of dipole moment left-handedly rotates during trans-to-cis isomerization, thus rendering the LCs nearby to rotate in the same manner to maintain a parallel dipole moment between LCs and QL55 molecules. Such left-handed rotation causes the unwinding of the right-handed helical structure of LCs; thus, the HTP of the CLC system is diminished gradually; however, in the recovery process, the dipole moment rotates in the opposite direction, causing the HTP to increase. These results agree with the experimental ones.

The LC arrangements influenced by *trans*-QL55 and *cis*-QL55 were calculated in accordance with the MD methods. As shown in Fig. 4(a), there is an evident twist of the LC director when the QL55 molecules are *trans*-isomer (left-side); such a twist is



**Fig. 4** LC arrangements as the QL55 switch are *trans*-configuration and *cis*-configuration, respectively (a) and the direction of LC director denoted in the Cartesian coordinate system (b).

significantly weakened in the case in which trans-QL55 is replaced by cis-QL55. The extent of the twist can be evaluated by calculating the angle between the LC directors, near the top and bottom of the simulated box, and the LC director can be calculated through the statistical average for the direction of every LC molecular long axis (director of LC molecule). For the convenience of comparison, the directors are expressed as a vector containing azimuth angle ( $\varphi$ ) and polar angle ( $\theta$ ). Fig. 4(b) presents the LC directors near the bottom and top of the Cartesian coordinate system. The left-side of Fig. 4(b) corresponds to the case of the trans-QL55/LC system, showing that LC directors near the bottom and top are  $n_{\text{bottom}} = (\varphi, \theta) =$  $(45.0^{\circ}, 89.5^{\circ})$  and  $n_{top} = (\varphi, \theta) = (84.9^{\circ}, 89.3^{\circ})$ . Note that the polar angle,  $\theta$ , is almost unchanged in the helical arrangement; thus, the twisted angle can be simply calculated by the difference in the azimuth angle,  $\varphi$ , which is 39.9°. In addition, it is found that the LC director from the bottom to the top rotates clockwise, thus proving that trans-QL55 presents the characteristic of R-chirality, which is consistent with the fact. Similarly, LC directors in the system containing cis-QL55, shown on the right-side of Fig. 4(b), are  $n_{\text{bottom}} = (\varphi, \theta) = (61.0^{\circ}, 89.5^{\circ})$  and  $n_{\text{top}} = (\varphi, \theta) = (70.9^{\circ}, 89.6^{\circ})$ . Moreover, the twisted angle is 9.9°, which indicates a weak twisted helix and the invariability of the *R*-chirality. Another interesting aspect of the calculation is that the HTP of trans- or cis-QL55 can be estimated through the results obtained above. For instance, by combining the twisted angle of the trans-QL55/LC system, 39.9°, and the dimension of the corresponding cubic box, 80.52 Å, the helical pitch (P) can be calculated as  $80.52 \times 360^{\circ}/39.9^{\circ} = 72.65$  nm, while the mass percentage (C) of trans-QL55 can be calculated by the number of molecules in the cubic box (960 5CB LCs and 128 trans-QL55) and the molecular weight  $(249.36 \text{ g mol}^{-1} \text{ for 5CB molecule and})$ 634.82 g mol<sup>-1</sup> for *trans*-QL55), thus obtaining the mass percentage of trans-QL55 as (128 × 634.82)/(960 × 249.36 + 128  $\times$  634.82) = 25.34 wt%; therefore, the HTP of *trans*-QL55 is 1/  $(PC) = 1/(72.65 \times 25.34 \text{ wt\%}) \text{ nm}^{-1} = 54.3 \text{ }\mu\text{m}^{-1}$ . With the same method, the HTP of cis-QL55 is calculated to be 1/(292.80  $\times$ 25.34 wt%)  $nm^{-1} = 13.5 \ \mu m^{-1}$ . The estimated values are approximately consistent with the experimental results obtained through the Grandjean-Cano wedge, *i.e.*, 49.0  $\mu$ m<sup>-1</sup> for *trans*-QL55 and 17.1  $\mu$ m<sup>-1</sup> for *cis*-QL55, with only a deviation of 10-20%. Such deviation occurs due to the impurity of QL55 isomers in the system; that is, the trans-QL55 may contain some small amounts of cis-QL55 and vice versa; while in the simulated model, the QL55 isomer is completely pure.

Subsequently, the interaction energy  $(E_{int})$  between LCs and QL55 isomers were calculated (eqn S2<sup>†</sup>) to explore the interaction variations of the system caused by the configuration transformation due to the photoisomerization. Table 1 shows the interaction energies between the QL55 isomers and the LCs; besides, the interaction energy between the LC molecules is listed for comparison. The minus sign of the calculated results implies that the blend systems of QL55 and LCs are stable, while the strength of the interaction is represented by the corresponding absolute value. It is evident that the interaction between the *trans*-QL55 and the LCs is about 75 kcal mol<sup>-1</sup> stronger than that between the *cis*-QL55 and the LCs, which

indicates the weakening of the twisted power during the isomerization of QL55. It is also found by comparing these interactions with LC molecular interactions that the energy between the LCs is significantly weaker than that between the LCs and QL55, irrespective of the configuration. In general, the nematic alignment of LCs is maintained by the molecular interaction, while the stronger interactions between trans-(cis-)QL55 and LCs may be due to the contribution from the helical twisted energy. The static electric energy part  $(E_{ele})$  and the van der Waals part  $(E_{vdw})$  expressed by the 9-6 Lennard-Jones function<sup>53,54</sup> are also listed, respectively, in the third and fourth rows of Table 1, and it can be noted that the major factor that causes the weakening of the interaction energy in the trans-to-cis isomerization is the decrease in the static electric energy part. This decrease is attributed to the lengthening of molecular spacing because the static electronic energy is inversely proportional to the molecular spacing.

The total quantity of electronic charge for the system is constant during the isomerization; therefore,  $E_{ele}$  is only determined by the molecular spacing,  $r_{ij}$ .

Furthermore, from the viewpoint of molecular geometry, the azo groups in trans-QL55 show a rod-like configuration, which is very similar to that of the conventional LC molecules, while the corresponding cis-isomer presents a distinct configuration of a bent shape. Therefore, it can be predicted that the miscibility between trans-QL55 and the LCs is better. To prove it, the solubility parameters of two QL55 isomers were respectively calculated (eqn S3<sup>†</sup>) and then compared with the solubility of 5CB (the solubility of our LCs is considered to be similar to that of 5CB because the major component of our LCs is 5CB, >60 mol%) reported in the previous studies.<sup>54</sup> As the results show, the solubility parameter of *trans*-QL55 is 18.10 (J cm<sup>3</sup>)<sup>0.5</sup>, which is 3.8 (J cm<sup>3</sup>)<sup>0.5</sup> higher than that of *cis*-QL55, whereas only 0.8 (J cm<sup>3</sup>)<sup>0.5</sup> lower than that of 5CB, thus indicating a significantly better miscibility between the trans-QL55 isomer and the LCs owing to their closer solubility parameters. The decrease in the miscibility when the rod-like trans configuration transforms into the bent-shaped cis one may influence the helical structure from two aspects. On the one hand, the higher solubility of trans-QL55 leads to a stronger twisted power of the CLCs, thus shortening the helical pitch; in contrast, the lower solubility of cis-QL55 results in a lengthening of the pitch because of the weakening of the twisted power. On the other hand, the good miscibility of the trans-QL55/CLC system causes a better dispersion of trans-QL55 in CLCs, which decreases the molecular spacing and leads to stronger molecular interactions, thus shortening the helical pitch.

#### Tunable lasing in CLC emulsion

As aforementioned, the helical axes of the CLC droplets randomly arrange in the wet-film, causing the light scattering; thus leading to the disappearance of the PBG effect, consequently influencing the lasing performances of the film. However, after the deswelling of the wet-film, a standing helix is formed in the CLC droplet due to the shrinkage of the film, which thus establishes the fundamental structure of 1D PBG

Table 1	Molecular	interaction	energies	calculated	through	MD
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Interactions (kcal mol <sup>-1</sup> )	$E_{ m int} = E_{ m ele} + E_{ m vdw}$	$E_{ m ele} = \sum_{i>j} rac{q_i q_j}{arepsilon r_{ij}}$	$E_{ m vdw} = \sum_{i>j} \left[ rac{A_{ij}}{r_{ij}^9} - rac{B_{ij}}{r_{ij}^6}  ight]$
trans-QL55/LC cis-OL55/LC	-385.98 -310.69	-286.23 -235.13	-99.75 -75.56
LC/LC	-273.08	-211.76	-61.23

<sup>*a*</sup>  $q_i$  and  $q_j$  represent the electronic charge of molecule *i* and *j*, respectively;  $r_{ij}$  is the distance between the corresponding molecules;  $A_{ij}$  and  $B_{ij}$  are the van der Waals interaction parameters and  $\sum$  denotes the summation of energy between the molecules contained in the system.

laser chamber. This standing helix was confirmed first by observing the texture of the CLC droplet and comparing the texture as the sample was rotated with the central vertical axis of the objective stage. As shown in Fig. 5(a), there are many concentric circles from the center to the edge of the droplet, and these become increasingly obscure because of the oblate spherical surface of the CLC droplets. Similarly, the halation around the edge caused by the interfacial anchoring is still visible. As the sample is rotated by 90° from the original position  $(0^{\circ})$ , the textures before and after the rotation are compared; no differences are discerned in terms of the color, brightness or the profile, which indicates that the standing helix is established in the CLC droplets. Moreover, the laser emission in the normal direction of the substrate, detected in the front and 50 mm away from the sample, further proves the formation of the standing helix.

Subsequently, the lasing performance and the phototunability were tested. Fig. 5(b) shows the spectra of the laser *versus* the duration of irradiation by 365 nm LED with the intensity of 9.2 mW cm<sup>-2</sup>. At the initiation, laser emission with the wavelength of 566 nm, corresponding to the position at



Fig. 5 Textures of CLC droplets observed with transmission mode (a); the spectra of lasers during the photo-tuning (b); the relationships of pumping energy *versus* emission intensity of 566 nm laser and 678 nm laser (c); and the digital images of laser spots at 566 nm, 620 nm, and 678 nm, respectively (d).

LWBE of PSS<sub>VIS</sub>, is found (spectrum I); as the irradiation continues, the emission wavelength red-shifts gradually, passing through 594 nm (spectrum II) for a 2 second exposure, 620 nm (spectrum III) for a 7 second exposure, and 652 nm (spectrum IV) for a 23 second exposure, until it reaches the position at 678 nm (spectrum V), which is very close to the LWBE of  $PSS_{UV}$ , ~680 nm, after irradiation for 50 seconds. In contrast, if the exposure source is replaced by 480 nm LED, the wavelength of the laser blue-shifts, starting from 678 nm and finally returning to the original position at 566 nm within 55 seconds because the exposure intensity is 7.3 mW cm<sup>-2</sup>, thus achieving a photo-tunable laser, which can be tuned back and forth in a wide range of 112 nanometers, from 566 nm to 678 nm. The emission intensity is determined by the quantum efficiency at the corresponding wavelength if the pumping energy is constant; in other words, equal emission intensity for the laser with different wavelengths can be obtained by modulating the pumping energy. The laser emission thresholds (LETs) were tested, as shown in Fig. 5(c). The LET values of 566 nm laser and 678 nm laser are 1.05  $\mu$ J per pulse and 1.12  $\mu$ J per pulse, respectively. Such thresholds are very close to each other, with a value of less than 0.1 µJ per pulse higher, comparing the LET of 678 nm laser with that of 566 nm-laser; however, as the pumping energy exceeds the thresholds, a great difference in the slopes of the curves is generated, showing the evidently higher slope of the 566 nm laser than that of the 678 nm laser. This difference is considered to be attributed to the higher quantum efficiency of DCM at 566 nm. The line width  $(\Delta \lambda)$  of the laser is estimated to be 1.4-1.5 nm; however, considering that the value is very close to the resolution limit of the spectrometer, 1.4 nm, the real line width of the laser is supposed to be narrower. Fig. 5(d) presents three CCD images of laser spots, with the color of yellow-and-green, orange red and bright red, corresponding to the wavelength of 566 nm, 620 nm, and 678 nm. The brightness profiles of the spots are very similar to the Gaussian distribution, which coincides with the characteristic of the laser. However, the interference ring around the spot, usually found in the conventional CLC laser, is not found because the thickness of the dry-film, 50-60 µm, is considerably larger than that of other conventional CLC cells, 10 µm, which results in the weak interferences. It is noteworthy that such a better lasing performance is closely dependent on the size of the LC droplet, especially the size of the central Bragg reflection part. The larger the LC droplet is, the better are the lasing performances, and consequently the wider is the spectral shift of the laser. It was found that the emission intensity became increasingly weaker with the decreasing droplet size, and it disappeared as the droplet size became smaller than 20  $\mu$ m. To obtain the dispersion with large droplets, a slower stirring rate of 90 rpm (the details are given in ESI†) was maintained. As shown in Fig. 2(a), the film containing larger droplet size, with the central Bragg reflection parts of 40–50  $\mu$ m, was used in the experiments.

Note that the wavelength of the pumping source is 532 nm, which is also contained in the absorption spectral range of the azo material, rendering the cis-to-trans isomerization of the azo group. Thus, the photosensitivity for the CLC system doped with pure azo-derivatives is very strong, which is not beneficial for the stability of the material under ambient light. A previous study reported that the laser emission was generally accompanied by an evident wavelength-shifting in the pure azo-dye doped CLC laser.39 To confirm whether such shifting occurs in the CLC emulsion laser mentioned herein, the material was modulated to the PSS<sub>UV</sub> first, followed by pumping the material with the energy of about 3.0 µJ per pulse under the dark condition and simultaneously detecting the wavelength of the laser. However, it is interesting to note that no obvious wavelength shift was found, even after the sample was pumped for 20 times. Such good photo-stationary may be related with the low content of the photosensitive azo-derivative, QL55. Besides, the lower pumping energy is another factor when such energy is determined by the LET, which increases with the increase of the LET; a higher LET directly leads to a higher pumping energy, and thus decreases the photo-stability of the sample. Therefore, it can be considered that the lower LET is one of the requirements for obtaining an ideal photo-stationary CLC emulsion laser.

In addition, as Lin et al. reported, another weak laser appears at the short wavelength band-edge (SWBE) as the pumping energy is about three times of the threshold.26 The lasing position, either at LWBE or SWBE, is determined by the direction of the transition moment of the laser dye molecule with respect to the direction of the LC director, in accordance with a previous theoretical study.3 When the transition moment is parallel to the LC director, lasing at LWBE occurs; however, when they are perpendicular to each other, lasing at SWBE appears. Considering that the laser dye used in Lin's and our experiments is the same, DCM, and that many experimental results have already proved that the preferred orientation of the transition moment for DCM is parallel to the LC director,<sup>55</sup> it can be inferred that the emission energy of LWBE lasing could be lower than that of SWBE lasing. Therefore, the possible reason for the appearance of SWBE lasing may be related to the disordered alignment of LCs, occurring in the photoisomerization, which distorts the original direction of the transition moment. Thus, causing the transition moment perpendicular to the LC director in some parts of the system, and consequently decreasing the laser emission threshold at SWBE. This facilitates the pumping out of SWBE laser at a lower pumping energy. Whereas, unlike the previous report, SWBE lasing was not observed in the tunable lasing presented herein

because the pumping energy was controlled to 3.0 µJ per pulse (about three times of the threshold energy). The strong interaction between the LCs and the QL55 isomers is considered to be a possible interpretation. Under such strong interaction, the distribution of the LC director is constrained, thus maintaining an ordered alignment of LCs during the photo-tuning, and thus increasing the threshold emission energy at SWBE. To make the analysis more understandable, the order parameter of LCs near the QL55 isomers was calculated. The helical alignment of LCs can be simply approximated to be well-aligned and nematic because the effective interaction distance between QL55 and the LCs is considerably smaller than the helical pitch of the CLCs. However, in such a small range, the helical structure can be ignored and replaced by a well-aligned nematic alignment. Under such an approximation, the order parameters of LCs in the systems of trans-QL55/LC (LCs mixed with trans-QL55), trans + cis-QL55/LC (LCs mixed with trans- and cis-QL55) and cis-QL55/LC (LCs mixed with *cis*-QL55) were calculated to be 0.60, 0.59 and 0.57, respectively, indicating that the influence of photoisomerization on the order of LC alignment is so weak that it can be neglected. To further explore this phenomenon from an experimental viewpoint, the transmittance spectra of the deswelling film were detected during the UV and visible light irradiations (Fig. S4<sup>†</sup>) because the arrangement of LCs can be reflected from the changes in the spectrum. Interestingly, although there is an evident shift of the spectra, the features of the spectra, such as the shape, the transmittance at the stop band and the band width, are almost invariable during the photo-tuning; therefore, it can be speculated that the welldefined helical structure was maintained, except for the variation of the pitch. The suppression of SWBE lasing is obviously an improvement for the smooth application of such a tunable laser.

The continuous tuning of the wavelength of laser has always been a concern for researchers because it is difficult to achieve in the conventional CLCs encapsulated in the antiparallel proceeded planar cells.<sup>56</sup> The reason for this difficulty is that the strong anchoring on the inner surfaces of two substrates compels the LCs near the surfaces to align in parallel, causing a discrete pitch-tuning following the relationship, in which the cell gap is equal to the integer times of half of the pitch. Thus, the continuity of photo-tuning for the deswelling film was explored by detecting the shifting of LWBE where the laser emission occurs during the light irradiation. The light intensities for 365 nm LED and 480 nm LED sources are the same as the aforementioned, 9.2 mW  $cm^{-2}$  and 7.3 mW  $cm^{-2}$ , respectively. Considering the rapid shifting of LWBE under the corresponding intensities, the time step for auto-saving a spectrum was set as 200 milliseconds. As shown in Fig. 6, basically, a better continuous photo-tuning is obtained, irrespective of the red-shifting triggered by 365 nm LED, or the blue-shifting promoted by 480 nm LED, only with some unobvious jumps of the LWBE within 10 to 30 seconds duration of irradiation, labeled by the dashed frames with the violet color and the cyan color, respectively. The extent of such jumps is very small, about 2-3 nm. Therefore, it can be considered that the phototuning of the CLC emulsion laser is quasi-continuous. Such



Fig. 6 LWBE *versus* the irradiation time. The jumps are denoted in the dashed frames.

quasi-continuity might be closely related to the weak anchoring of the substrate because there is only one substrate without the orientational process and the thickness of the film is several times greater than that of the conventional CLC layer confined in the cell, which causes the weakening of the surface tension to the LCs. Therefore, the surface tension is inversely proportional to the distance between the LCs and the substrate. Such weak anchoring causes the aforementioned small jump of LWBE.

## Conclusions

A wide tunable laser in the photoresponsive CLC emulsion is demonstrated in this paper. The wavelength of the laser can be tuned reversibly in a wide spectral range, from 566 nm to 678 nm, by the irradiation with UV and visible light sources. The mechanisms for photo-tunability, explored from the molecular viewpoints through the MD simulations, indicate that the molecular conformation of the photosensitive chiral switch QL55 changes reversibly due to photoisomerization, and simultaneously causes the variation of molecular geometry and the rotation of the direction of the dipole moment, thus rendering the rearrangement of LCs compelled by the strong molecular interaction energy, and finally leads to the change of HTP under the long range interaction between LCs. In addition, the change of molecular structure simultaneously causes the different miscibility of QL55 isomers that blended into the LCs, *i.e.*, the *trans*-isomers have a better miscibility with LCs than the cis-isomers, which influences the molecular interactions and the HTP as well. Due to the strong interactions, the well-defined helical structure of CLCs is maintained during the phototuning, which ensures the stable laser emission at LWBE. The quasi-continual tuning is also achieved because of the weak surface anchoring in the system. This study provides a new material with a wide photo-tunable and well-performed laser emission based on photoresponsive CLC emulsion, and typically molecular simulations are adopted for a good understanding of the mechanisms of photo-tuning. The results also reveal that such a wide photo-tunable laser can be fabricated by simply coating the material onto the single substrate, which will be promising in the future photonic devices or the low-cost laser displays.

# Acknowledgements

This work is sponsored by the National Science Foundation of China (grant no. 61435008, no. 61108065), the Chen-guang Talent Foundation of Shanghai Education and Development Committee (grant no. 12CG32), and the Foundation of Laboratory of Solid State Microstructures, Nanjing University (grant no. M27005).

## Notes and references

- 1 H. Coles and S. Morris, Nat. Photonics, 2010, 4, 676.
- 2 V. I. Kopp, B. Fan, H. K. M. Vithana and A. Z. Genack, *Opt. Lett.*, 1998, 23, 1707.
- 3 J. Schmidtke and W. Stille, Eur. Phys. J. B, 2003, 31, 179.
- 4 F. Araoka, K. Shin, Y. Takanishi, K. Ishikawa, H. Takezoe, Z. Zhu and T. M. Swager, *J. Appl. Phys.*, 2003, **94**, 279.
- 5 M. Uchimura, Y. Watanabe, F. Araoka, J. Watanabe, H. Takezo and G. Konishi, *Adv. Mater.*, 2010, **22**, 4473.
- 6 S. M. Morris, A. D. Ford, M. N. Pivnenko, O. Hadeler and H. J. Coles, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2006, 74, 061709.
- 7 C. Mowatt, S. M. Morris, T. D. Wilkinson and H. J. Coles, *Appl. Phys. Lett.*, 2010, **97**, 251109.
- 8 K. Amemiya, M. H. Song, Y. Takanishi, K. Ishikawa, S. Nishimura, T. Toyooka and H. Takezoe, *Jpn. J. Appl. Phys.*, 2005, **44**, 7966.
- 9 Y. Zhou, Y. Huang and S. T. Wu, Opt. Express, 2006, 14, 3906.
- 10 L. Penninck, J. Beeckman, P. De Visschere and K. Neyts, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2012, **85**, 041702.
- 11 Y. Matsuhisa, Y. Huang, Y. Zhou, S. T. Wu and R. Ozaki, *Appl. Phys. Lett.*, 2007, **90**, 091114.
- 12 S. M. Morris, A. D. Ford, M. N. Pivnenko and H. J. Coles, *J. Appl. Phys.*, 2005, **97**, 023103.
- H. Finkelmann, S. T. Kim, A. Munoz, P. Palffy-Muhoray and B. Taheri, *Adv. Mater.*, 2001, 13, 1069.
- 14 B. Liu, Z. Zheng, X. Chen and D. Shen, *Opt. Mater. Express*, 2013, **3**, 519.
- M. H. Song, B. Park, K. C. Shin, T. Ohta, Y. Tsunoda, H. Hoshi, Y. Takanishi, K. Ishikawa, J. Watanabe, S. Nishimura, T. Toyooka, Z. Zhu, T. M. Swager and H. Takezoe, *Adv. Mater.*, 2004, 16, 779.
- 16 T. H. Lin, H. C. Jau, C. H. Chen, Y. J. Chen, T. H. Wei, C. W. Chen and A. Y. G. Fuh, *Appl. Phys. Lett.*, 2006, 88, 061122.
- 17 M. Kasano, M. Ozaki, K. Yoshino, D. Ganzke and W. Haase, *Appl. Phys. Lett.*, 2003, **82**, 4026.
- 18 Y. Inoue, H. Yoshida, K. Inoue, Y. Shiozaki, H. Kubo, A. Fujii and M. Ozaki, *Adv. Mater.*, 2011, 23, 5498.
- 19 A. Chanishvili, G. Chilaya, G. Petriashvili, R. Barberi, R. Bartolino, G. Cipparrone, A. Mazzulla and L. Oriol, *Adv. Mater.*, 2004, 16, 791.
- 20 S. Furumi, S. Yokoyama, A. Otomo and S. Mashiko, *Appl. Phys. Lett.*, 2004, **84**, 2491.
- 21 H. Yu and T. Ikeda, Adv. Mater., 2011, 23, 2149.

- 22 H. Yu, C. Dong, W. Zhou, T. Kobayashi and H. Yang, *Small*, 2011, 7, 3039.
- 23 L. Yu, Z. Cheng, Z. Dong, Y. Zhang and H. Yu, *J. Mater. Chem. C*, 2014, **2**, 8501.
- 24 G. Chilaya, A. Chanishvili, G. Petriashvili, R. Barberi, R. Bartolino, G. Cipparrone, A. Mazzulla and P. V. Shibaev, *Adv. Mater.*, 2007, **19**, 565.
- 25 A. Y. G. Fuh, T. H. Lin, J. H. Liu and F. C. Wu, *Opt. Express*, 2004, **12**, 1857.
- 26 T. H. Lin, Y. J. Chen, C. H. Wu, A. Y. G. Fuh, J. H. Liu and P. C. Yang, *Appl. Phys. Lett.*, 2005, **86**, 161120.
- 27 L. J. Chen, J. D. Lin and C. R. Lee, *J. Mater. Chem. C*, 2014, 2, 4388.
- 28 Y. Huang, Y. Zhou and S. T. Wu, *Appl. Phys. Lett.*, 2006, 88, 011107.
- 29 G. Petriashvili, M. A. Matranga, M. P. De Santo, G. Chilaya and R. Barberi, *Opt. Express*, 2009, **17**, 4553.
- 30 J. H. Lin, P. Y. Chen and J. J. Wu, Opt. Express, 2014, 22, 9932.
- 31 A. Chanishvili, G. Chilaya, G. Petriashvili, R. Barberi,
  R. Bartolino, G. Cipparrone, A. Mazzulla, R. Gimenez,
  L. Oriol and M. Pinol, *Appl. Phys. Lett.*, 2005, 86, 051107.
- 32 K. Sonoyama, Y. Takanishi, K. Ishikawa and H. Takezoe, *Jpn. J. Appl. Phys.*, 2007, **46**, L874.
- 33 P. J. W. Hands, C. A. Dobson, S. M. Morris, M. M. Qasim, D. J. Gardiner, T. D. Wilkinson and H. J. Coles, *Proc. SPIE*, 2011, 8114–8128.
- 34 A. Chanishvili, G. Chilaya, G. Petriashvili, R. Barberi,
  R. Bartolino, G. Cipparrone, A. Mazzulla, R. Gimenez,
  L. Oriol and M. Pinol, *Appl. Phys. Lett.*, 2005, 86, 051107.
- 35 W. Cao, A. Munoz, P. Palffy-Muhoray and B. Taheri, *Nat. Mater.*, 2002, 1, 111.
- 36 S. T. Hur, B. R. Lee, M. J. Gim, K. W. Park, M. H. Song and S. W. Choi, *Adv. Mater.*, 2013, 25, 3002.
- 37 M. Humar and I. Musevic, Opt. Express, 2010, 18, 26995.
- 38 J. D. Lin, M. H. Hsieh, G. J. Wei, T. S. Mo, S. Y. Huang and C. R. Lee, *Opt. Express*, 2013, 21, 15765.
- 39 L. Chen, Y. Li, J. Fan, H. K. Bisoyi, D. A. Weitz and Q. Li, *Adv. Opt. Mater.*, 2014, 2, 845.

- 40 M. Humar, M. Ravnik, S. Pajk and I. Musevic, *Nat. Photonics*, 2009, **3**, 595.
- 41 K. Peddireddy, V. S. R. Jampani, S. Thutupalli, S. Herminghaus, C. Bahr and I. Musevic, *Opt. Express*, 2013, **21**, 30233.
- 42 Z. V. Wardosanidze, A. Chanishvili, G. Petriashvili and G. Chilaya, *Opt. Lett.*, 2014, **39**, 1008.
- 43 D. J. Gardiner, S. M. Morris, P. J. W. Hands, C. Mowatt, R. Rutledge, T. D. Wilkinson and H. J. Coles, *Opt. Express*, 2011, **19**, 2432.
- 44 S. Gottardo, S. Cavalieri, O. Yaroshchuk and D. S. Wiersma, *Phys. Rev. Lett.*, 2004, **93**, 263901.
- 45 Y. Wang and Q. Li, Adv. Mater., 2012, 24, 1926.
- 46 Q. Li, Y. Li, J. Ma, D. K. Yang, T. J. White and T. J. Bunning, *Adv. Mater.*, 2011, **23**, 5069.
- 47 T. H. Lin, Y. Li, C. T. Wang, H. C. Jau, C. W. Chen, C. C. Li, H. K. Bisoyi, T. J. Bunning and Q. Li, *Adv. Mater.*, 2013, 25, 5050.
- 48 T. J. White, R. L. Bricker, L. V. Natarajan, N. V. Tabiryan, L. Green, Q. Li and T. J. Bunning, *Adv. Funct. Mater.*, 2009, 19, 3484.
- 49 H. K. Bisoyi and Q. Li, Acc. Chem. Res., 2014, 47, 3184.
- 50 J. P. Vernon, A. D. Zhao, R. Vergara, H. Song, V. P. Tondiglia, T. J. White, N. V. Tabiryan and T. J. Bunning, *Opt. Express*, 2013, **21**, 1645.
- 51 D. L. Cheung, S. J. Clark and M. R. Wilson, *Chem. Phys. Lett.*, 2002, **356**, 140.
- 52 Z. Zheng, D. Shen and P. Huang, New J. Phys., 2010, 12, 113018.
- 53 M. J. Hwang, T. P. Stockfisch and A. T. Hagler, J. Am. Chem. Soc., 1994, 116, 2515.
- 54 Z. Zheng, J. Ma, Y. G. Liu and L. Xuan, *J. Phys. D: Appl. Phys.*, 2008, **41**, 235302.
- 55 A. D. Ford, S. M. Morris, M. N. Pivnenko, C. Gillespie and H. J. Coles, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, **76**, 051703.
- 56 K. Funamoto, M. Ozaki and K. Yoshino, *Jpn. J. Appl. Phys.*, 2003, **42**, L1523.