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Abstract: In this paper we demonstrate photonic band-edge laser emission from emulsion-based polymer dispersed liquid crystals. The lasing medium consists of dye-doped chiral nematic droplets dispersed within a polymer matrix that spontaneously align as the film dries. Such lasers can be easily formed on single substrates with no alignment layers. The system combines the self-organizing periodic structure of chiral nematic liquid crystals with the simplicity of the emulsion procedure so as to produce a material that retains the emission characteristics of band-edge lasers yet can be readily coated. Sequential and stacked layers demonstrate the possibility of achieving simultaneous multi-wavelength laser output from glass, metallic, and flexible substrates.

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1. Introduction

There has been considerable recent work investigating photonic band-edge lasing in dye-doped chiral nematic liquid crystals (LCs) [1–6]. These band-edge lasers are of particular interest because they self-organize into regular helical structures, generating a periodic refractive index and a photonic band-gap ideally suited to efficient lasing. Such systems have been shown to offer wavelength-tunable and low-threshold laser emission across a wide proportion of the spectrum from the ultraviolet through to the near infra-red. Further functionality has also been demonstrated in the form of flexible LC lasers and free-standing films [7–9]. As an example, Matsui and associates showed that it was possible to produce a flexible free-standing film based upon a photopolymerizable cholesteric LC [7,8]. Upon deformation of the film, it was noted that laser emission was still observed and this demonstrated that the helical structure was maintained even when the film was subjected to stress. In addition, reports have shown that it is possible to tune the laser wavelength through stretching of cholesteric liquid crystalline elastomers [9] and cholesteric polymer films [10]. Alternative approaches using polymeric networks and, more recently, polydimethylsiloxane-enclosed LCs have also been considered [11,12].

In this study, we demonstrate emulsion-based LC band-edge laser devices that, unlike conventional liquid crystal systems, do not require pre-treatment of the substrates with alignment layers. Furthermore, owing to simple water-based emulsion processing they can be readily coated onto almost any surface (flexible or rigid) without the need for a second substrate. The lasers are formed through the emulsification of dye-doped chiral nematic LC droplets that are dispersed within a polymeric binder. The pre-requisite liquid crystal alignment is achieved by a de-swelling mechanism as the film is dried. Remarkably, these emulsions retain the emission characteristics that are observed for dye-doped LCs in aligned glass cells. Under optical excitation, it is shown that it is possible to generate single-mode photonic band edge lasing from such systems. The preparation, characterization and optical output of the sources are discussed, as well as the functionality of the coatings in the form of multi-layer, multi-color "white" lasers on glass, metallic, and flexible substrates. Finally, it is suggested that new application areas for such "plastic" laser sources may be obtained, for example into mass manufacturable, flexible and disposable laser devices. Specific applications could include integrated optical devices for point-of-care diagnostics, display technology and optically active films for security and friend-or-foe identification purposes.

2. Sample preparation and experimental description

For this study, we focus on emulsified polymer-dispersed liquid crystals (PDLCs) which are well known composite materials formed by the immiscibility between an LC and a polymeric matrix [13]. Unlike PDLCs formed by phase-separation techniques, such as UV radiation, solvent and/or temperature phase-separation methods, emulsified systems are readily coated onto single substrates using a variety of means, e.g. doctor-blading, roll-coating or screen-printing. After the coating step and evaporation of the water solvent, a rugged film can be obtained. The evaporation of the solvent has an added benefit in that it results in shrinkage of the film, which compresses the droplets from an initial spherical configuration in the wet film to an oblate arrangement in the dry film. This process forces the helical axis of the chiral nematic droplets to align perpendicular to the substrate.

The sample laser films, consisting of dye-doped chiral LC dispersed in polymeric binder were prepared in the following manner. To form the chiral LC host, a low concentration of the chiral additives, either BDH1281 or BDH1305 (3.5 to 5.5% w/w), were added to the achiral nematic liquid crystals BL006 or BL093. These materials were chosen as they are wide temperature range nematogen mixtures with clearing temperatures around 100 °C. The width

of the photonic band gap ($\Delta\lambda$) is related to the birefringence, (Δn), and the chiral nematic pitch (P), by $\Delta\lambda = \Delta nP$. For the threshold and circular polarization study, using a concentration of 5.5% BDH1305 in BL093, the laser dye Pyrromethene-597 (obtained from Exciton, and used without further purification) was added to the chiral nematic mixture at a concentration of 1% w/w. For the red, green and blue laser films the dyes (DCM, Coumarin 540A and Coumarin 504; supplied from Exciton) were used at a similar concentration by weight, in a 3.5% to 5.5% w/w BDH1281 in BL006 host mixture. All mixtures were placed in an oven for a period of 24 hours at 10 °C above the nematic to isotropic transition temperature to ensure sufficient thermal diffusion of the constituents. In order to confirm the position of the photonic band gap with respect to the laser emission wavelength, these non-emulsified mixtures were capillary filled into 10 μm thickness glass cells, which had antiparallel rubbed polyimide alignment layers, and thus gave a standing helix, or Grandjean, texture.

To form the emulsions, the dye-doped chiral nematic lasing materials were added at a concentration of 5% w/w to poly-vinyl alcohol (PVA) solution (Sigma-Aldrich Ltd, molecular weight 10,000 amu, 20% w/w in deionized water) and emulsified at the required rate. This was 100 rpm for 10 minutes using an overhead stirrer (Eurostar, IKA). Experiments were carried out to determine the optimum conditions for band-edge lasing, and was found to occur for large droplets (ranging from 30 μm to 50 μm in diameter), corresponding to low mixing speeds (~100 rpm). Coated films, on a wide variety of substrates, were prepared by a simple "k-bar" bar-coating method (RK Printcoat Instruments). The wet thicknesses of films described here were all 80 μm. Samples were allowed to dry at room temperature for a minimum of one hour. Images of LC orientation within emulsified droplets were obtained with the use of a polarizing microscope (Olympus BX-60) equipped with a digital camera.

To measure the excitation laser threshold and the polarization of the emission from the pyrromethene emulsion samples, coated films were photo-pumped by the second harmonic (532 nm) of a neodymium yttrium aluminium garnet (Nd:YAG) laser (Polaris II, New Wave Research), which had a 3-4 ns pulse duration and a repetition rate of 1 Hz. The input energy was modulated by a built-in attenuation system and monitored using a pyroelectric head connected to a calibrated energy meter. In both cases, so as to ensure that the pump beam did not interact with the photonic band gap, the linear polarization was converted to circular polarization of the opposite handedness to the helix of the chiral nematic LC using a quarter-wave plate. The pump beam was then focused to a spot size of 110 μm at the sample using a bi-convex lens. The output from the LC samples was collected and focused onto an HR2000 universal serial bus (USB) spectrometer (Ocean Optics, resolution 0.3 nm) using a lens combination consisting of a doublet and a meniscus lens.

For the red-green-blue (RGB) laser samples, an optical parametric oscillator, pumped by the third harmonic of a Nd:YAG laser (Spitlight, Innolas), was used to excite the samples at the shorter wavelength of 430 nm. The set-up consisted of similar elements to that used in the above experiment, except that the spot size at the sample was of the order of 300 μm.

3. Results and discussions

A key result from the use of emulsified systems is the induction of the standing helix (Grandjean) arrangement within the droplets. An illustration of the drying procedure, along with microscope images of the LC alignment within the droplets, after the film is formed, is presented in Fig. 1. In this case, a chiral nematic sample, consisting of a wide temperature range nematogen and a high twisting power chiral additive, was dispersed within an aqueous solution of the polymer PVA, and was coated onto a glass substrate. Following coating and the subsequent evaporation of water, the film volume shrinks to a level determined by the initial solvent content of the sample, in this case by approximately two-thirds. After drying, the sample was examined between crossed polarizers to confirm that a Grandjean texture (standing helix alignment) had been obtained. This was achieved by rotating the sample in the plane of the crossed polarizers. There was no observable change in the texture within the droplets, irrespective of orientation; confirming that the helical axes of the droplets were aligned along the normal of the substrates, and that the LC director was in-plane. For

illustrative purposes, the textures obtained at 0° and 45° rotations are shown in Fig. 1(c) and 1(d). This is in accordance with previous work on nematic and cholesteric LC emulsions [14–19], which have shown that a de-swelling mechanism can induce improved in-plane alignment when compared to mechanisms such as UV polymerization-induced phase separation.
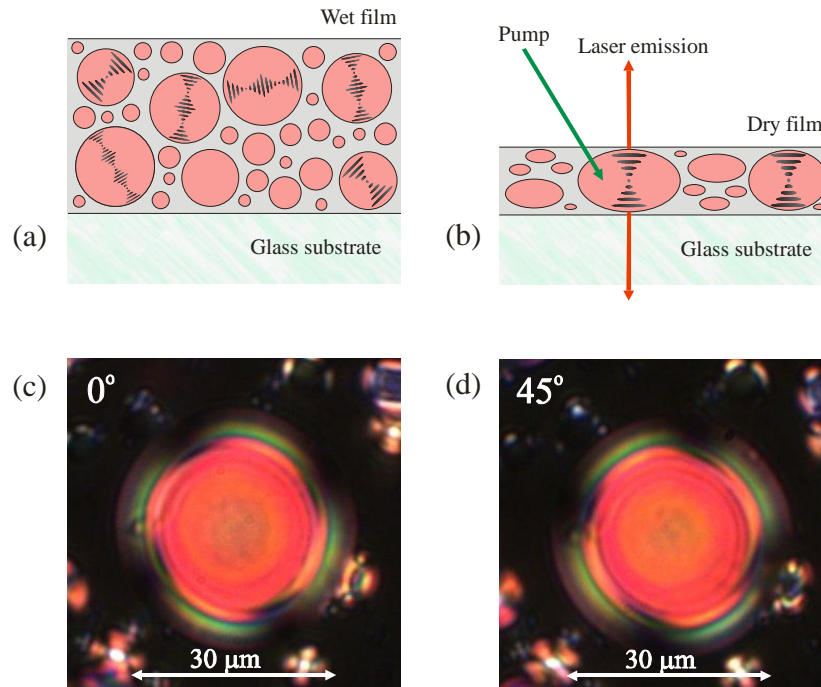

Fig. 1. The formation of the Grandjean texture in chiral nematic droplets contained within emulsified samples. Pictorial representation of the drying and film-shrinkage mechanism by which initially spherical liquid crystal droplets (a) become oblate (b), leading to a uniform alignment of the helical axis normal to the substrate. This standing helix (Grandjean) texture is confirmed experimentally by viewing the sample between crossed polarizers through a microscope. The texture shows no apparent change when the sample is rotated through 0° (c) and 45° (d).

To examine band-edge laser emission from the samples when optically excited, a dye-doped chiral nematic emulsion was prepared using a pyrromethene laser dye, which has previously been shown to exhibit high gain and high slope efficiencies in liquid crystalline media for laser emission at the long-wavelength band-edge [20]. The resulting films, coated onto glass substrates, were optically pumped by a pulsed solid-state laser at a wavelength corresponding to the absorbance maximum of the dye (532 nm). Successful laser emission was then observed (Fig. 2). As further evidence for the Grandjean alignment, laser emission was observed only within a narrow cone perpendicular to the substrate. Furthermore, this narrow emission cone was found to be consistent as the pump laser was moved to all positions across the emulsion coating, indicating uniform LC alignment within the sample. This high degree of directionality can only be achieved in a band-edge laser if the helical axis itself is oriented perpendicular to the substrate. This is because the photonic band gap only exists in one dimension, i.e. parallel to the axis of the helix. If the helical axis were instead lying parallel to the substrate, or in a random direction, then band-edge lasing would be expected to be emitted in-plane to the substrate, or along a correspondingly random axis.

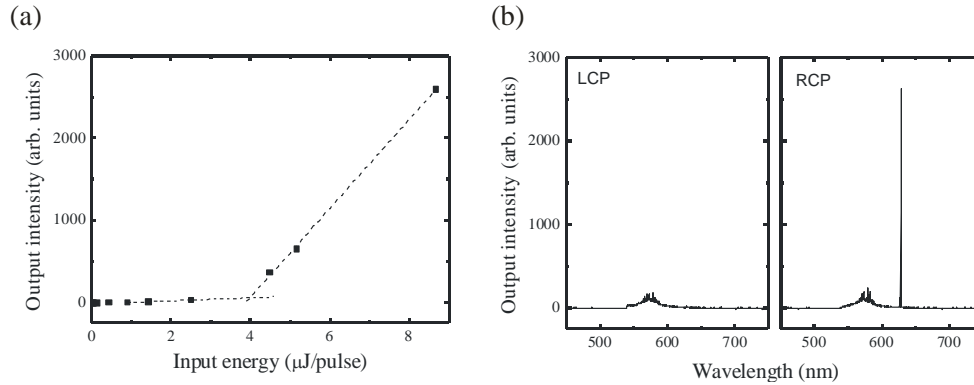(a)   (b)

Fig. 2. Band-edge lasing from an emulsified dye-doped chiral nematic liquid crystal. Input-output characteristics of the liquid crystal laser when optically excited at 532 nm (a), indicating a threshold of around 4 µJ/pulse, and the emission spectrum for both left and right circularly polarized light (LCP and RCP) (b), showing that the laser output is circularly polarized and indicative of band-edge lasing.

Figure 2(a) shows the output as a function of the input energy for a 30-50 µm droplet, similar to that shown in Fig. 1. The input-output characteristics show a typical threshold indicative of laser action, and in this case the laser threshold energy was found to be 4 µJ/pulse. The value of the excitation threshold is larger than that observed previously for conventional LC band-edge lasers [20] due to several factors: Firstly, the observed emission wavelength (630 nm) is at a longer wavelength than that of the gain maximum, which for the pyrromethene dye is at 590 nm, leading to a slightly reduced lasing efficiency. Secondly, the pump spot size of the pump laser is larger than the typical droplet size. The latter implies that some of the incident pump light does not enter the droplet leading to an increased threshold over the case where all the incident pump light contributes to the lasing process.

Figure 2(b) shows the emission spectra for both right and left circular polarizations (RCP and LCP). A laser emission line is only observed for right circularly polarized light. This polarized output matches the right-handed helical structure of the chiral nematic and thus provides strong evidence that emission is provided by a photonic band-edge lasing mechanism [1].

In order to demonstrate the functionality of these paintable lasers, samples for red, green and blue emission were prepared. Here the same polymer binder, class of nematogen host and chiral additive were used. The concentration of the latter was adjusted so as to match the band-edge with the fluorescence maximum of the corresponding laser dye. Three separate dyes were selected for the red (DCM), green (C540A), and blue (C504) lasers. These dyes were the same as those used in an earlier study on polychromatic laser arrays [5] and were used at around 1% w/w. The concentration of chiral additive BDH1281 was 4.05% (red), 4.77% (green) and 5.41% (blue) w/w in BL006, respectively. Significantly, due to the coincidence of the absorption bands of these three dyes, all three samples can be optically excited simultaneously using a common pump wavelength between 420 nm and 440 nm. This is made possible by the fact that the red dye (DCM) has wide-band absorbance and a large Stoke's shift.

Following preparation, red, green and blue lasing emulsions were coated onto glass substrates, shown in Fig. 3(a). The absorbance (using unpolarized light) and fluorescence spectra of the three lasing emulsions were measured, and found to match spectra observed in [5] for equivalent non-emulsified dye-doped chiral nematic mixtures indicating negligible changes to the optical properties due to the emulsification process. Furthermore, when optically pumped, the LC emulsions gave rise to circularly polarized laser emissions (Fig. 3(b)) at wavelengths that matched the locations of the long band-edges observed in pure chiral nematic samples. Although the short band-edges were obscured by dye absorption, measurements from non-dye-doped samples gave $\Delta\lambda$ of 96 nm (red, P = 370 nm), 82 nm

(green, P = 315 nm) and 78 nm (blue, P = 300 nm). Figure 3(c) depicts the blue, green, and red output profiles from the laser emulsions that were recorded approximately 30 cm away from the sample. Here the emission wavelengths were found to occur at 480 nm, 528 nm, and 599 nm for the blue, green, and red samples respectively. However, there is little change in the linewidth of the samples relative to non-emulsified samples studied previously and is therefore strong evidence that, within the resolution range of the spectrometer (<1.5 nm in this case), the quality factor of the periodic structure is unchanged when the chiral nematic is confined in the droplets. Overall, these results demonstrate that it is possible to encapsulate the liquid crystalline samples in a polymer binder using a facile approach that negates the need for alignment layers, but which at the same time retains the essential features of the dye-doped chiral nematic band-edge laser.
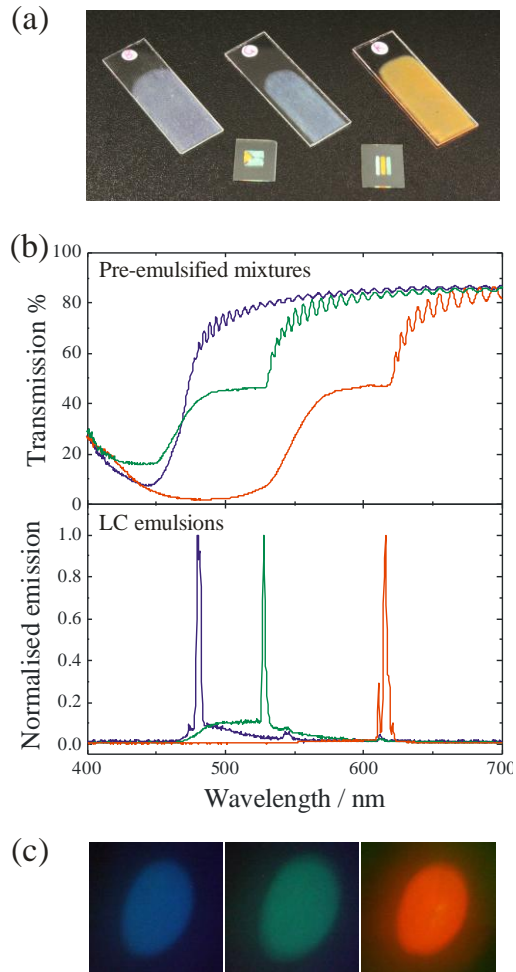

Fig. 3. Red, green and blue lasing LC emulsions. The emulsions can be painted and patterned onto glass substrates (a) without surface pre-treatment or alignment layers. When optically excited with a common pump at 430 nm, laser emission is observed in the red, green and blue (b), at wavelengths that coincide with the long-wavelength band-edges observed in pre-emulsified samples. Far-field emission spots of the red green and blue lasing emulsions are shown in (c).

By virtue of the versatility and ease-of-use of these paintable laser sources, a wide-range of combinations exist with which to obtain red, green and blue emission simultaneously. Typical examples of such combinations include an RGB stack (Fig. 4) as well as sequential adjacently printed red-green-blue (RGB) coatings (Fig. 5(a), samples G and H). For the stack

of RGB layers the generation of "white" laser emission is shown (Fig. 4). The sample was pumped with the red layer foremost so as to eliminate possible re-absorption of laser emission. The emission spectrum shown on the right hand side of the figure demonstrates the simultaneous RGB output that was observed when optically pumped with a single spot, 300 µm diameter, at a wavelength of 430 nm. The output in the far-field was clearly of a white appearance.
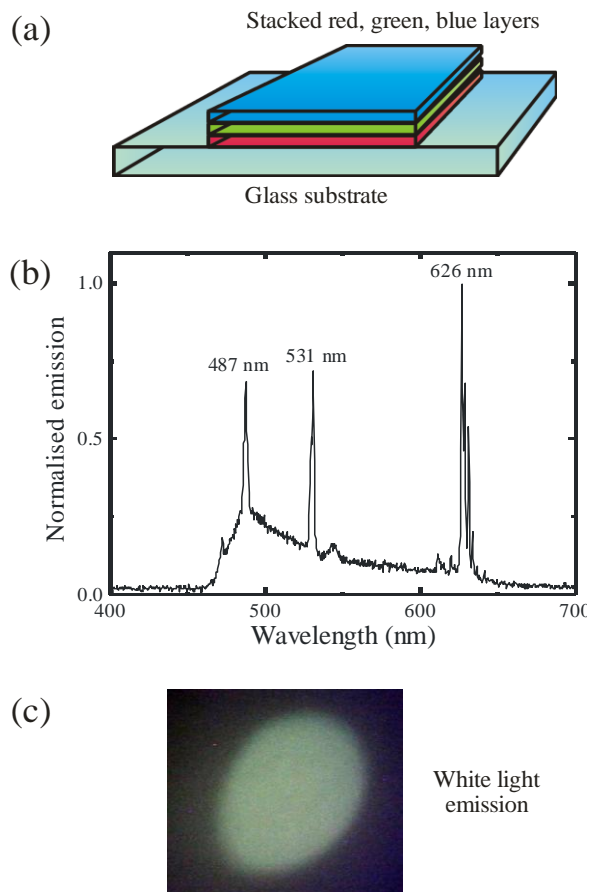

Fig. 4. Paintable "white light lasers". A stack of red, green and blue laser emulsions (a), when pumped with a single optical excitation source at 430 nm, gives three simultaneous laser emissions (b). The corresponding red, green and blue emissions combine, resulting in white light emission recorded in the far-field (c).

For the sequential coatings, (Fig. 5(a)), samples G and H), RGB emission could be obtained using raster scanning, or alternatively using a two-dimensional array-based pumping approach [4,5]. One notable benefit with the method employed here is that, unlike the pitch gradient approach used in [5], no unwanted diffusion occurs between the samples, and hence the output remains static and does not vary with time. It is important to further note that, as for the single layer coating case, no alignment layers are required between the separate layers and, in practice, it should be possible to deposit complex samples using screen, ink-jet or other forms of printing, in addition to simple k-bar coating.
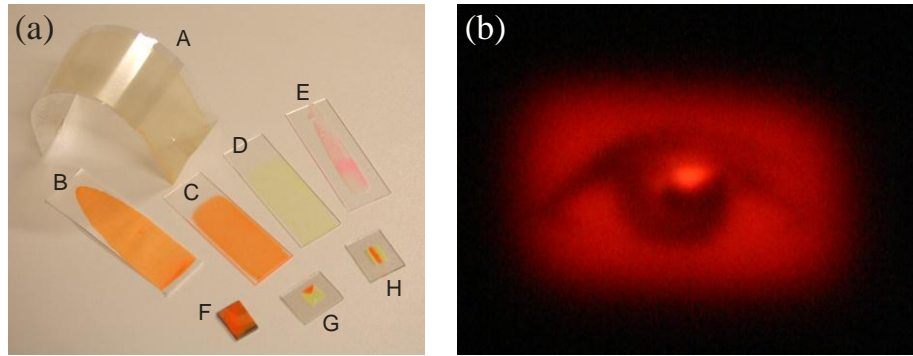
Fig. 5. Examples of the functionality of paintable lasers. Image (a) shows different LC laser emulsions painted onto a variety of substrates, including flexible PET (A), paper (B), glass (C, D and E), aluminium-coated glass (F), and patterned red, green and blue laser emulsions on glass (G and H). The emission from the red LC emulsion laser on an aluminium-coated glass substrate (F) is then used to illuminate a multi-phase hologram, and the successful replay field is illustrated in image (b).

The paintable laser samples are not merely restricted to glass substrates. Figure 5(a) demonstrates some of the functionality of these paintable lasers on different surfaces, including flexible polyethylene terephthalate (PET), aluminium and paper, which would otherwise be incompatible with conventional LC device fabrication procedures that require alignment layers and a uniform device thickness. The coatings can be uniformly deposited over large areas, with lasing occurring anywhere over the coated area, and can be easily scaled to a roll-to-roll manufacturing process. Furthermore, Fig. 5(b) consists of a photograph of the replay field of a multi-phase hologram illuminated with the emission from a paintable LC laser that is coated onto a metallic surface. Despite such a simple mixing and painting fabrication technique, the coherence of the resulting laser is sufficient to render a clear image in the holographic replay field.

4. Summary

In summary, it has been shown that it is possible to create printable band edge lasers using dye-doped chiral nematic liquid crystals emulsified within a polymer matrix. These lasers can be easily coated onto glass, plastic and metal substrates. The ability to coat films readily and cheaply onto flexible substrates, without the need for conventional liquid crystal alignment layers, through roll-to-roll coating or screen printing, and yet retain all the emission characteristics of photonic band-edge lasers is an obvious key benefit. Furthermore, it is envisaged that the use of such printable laser systems can extend applications of laser sources into new areas where flexibility or disposability may be required, such as display technology, lab-on-a-chip, and friend-or-foe identification. Further work is currently in progress to optimize the system and to introduce electro-optic functionality in the films.