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ABSTRACT

In this paper we demonstrate laser emission from emulsion-based polymer dispersed liquid crystals. Such lasers can be easily formed on single substrates with no alignment layers. Remarkably, it is shown that there can exist two radically different laser emission profiles, namely, photonic band-edge lasing and non-resonant random lasing. The emission is controlled by simple changes in the emulsification procedure. Low mixing speeds generate larger droplets that favor photonic band edge lasing with the requisite helical alignment produced by film shrinkage. Higher mixing speeds generate small droplets, which facilitate random lasing by a non-resonant scattering feedback process. Lasing thresholds and linewidth data are presented showing the potential of controllable linewidth lasing sources. Sequential and stacked layers demonstrate the possibility of achieving complex, simultaneous multi-wavelength and "white-light" laser output from a wide variety of substrates including glass, metallic, paper and flexible plastic.

Keywords: liquid crystal, photonic band-gap, laser, random laser, printable

1. INTRODUCTION

Photonic band-edge lasers, where laser emission occurs at a wavelength in the vicinity of a photonic band-gap edge due to a divergence in the density of available photon states, have been extensively examined.[1-3] Research has shown that band-edge lasers can be formed from either inorganic or organic materials; an organic system of particular recent interest has been the dye-doped chiral nematic liquid crystal. [4-6] In chiral nematic liquid crystals (LCs), the helical rotation of the liquid crystal director generates the requisite photonic band-gap due to a periodic dielectric tensor. When a gain medium is added to the system, for example through the addition of a laser dye to the LC host, optically pumped laser sources can be formed with laser emission at the edge of the photonic band-gap. Some of the advantages of these devices are readily selectable emission wavelengths, simultaneous lasing emission at different wavelengths and the ability to have multiple sources within a given layer.[7-9] A further mode of lasing operation is the random laser.[10-14] In these lasers, localised optical micro-cavities can be formed in strongly scattering gain media giving enhancement of spontaneous light emission. [11, 15]

Polymer dispersed liquid crystals (PDLCs) are composite materials that are formed by the immiscibility between a liquid crystal and a polymeric matrix. PDLCs can be formed in a variety of ways, for example by UV radiation and solvent/temperature induced phase separation methods.[16] A further approach is by direct emulsification of the liquid crystal within a polymeric solution such as polyvinyl alcohol (PVA) dissolved in water. Emulsified systems are readily coated onto 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 of well defined thickness can be obtained. Applications inlcude displays and switchable or smart windows.[16 17, 18]

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In this study, we demonstrate emulsion-based LC laser devices that, unlike conventional liquid crystal systems, do not require pre-treatment of the substrates with alignment layers.[19] Remarkably, it is shown that two very different kinds of laser emission profile, namely photonic band edge lasing and non-resonant random lasing, can be obtained in compositionally identical materials with simple processing modifications.[20] The nature of the laser output is determined by the sample preparation, specifically in the size and number density of the suspended droplets. Band-edge lasing is observed for large droplets (~ 30 µm) and low number densities. On the other hand, the combination of small droplets (< 6 µm) and high number densities appears to exhibit an emission profile that resembles non-resonant random lasing.

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 PROCEDURE

In this work, two studies were undertaken to examine, firstly, the role of different lasing mechanisms within the same host material, and, secondly, the creation of printable laser films possessing complex, multi-color (e.g. red, green and blue; RGB) output. For the study on lasing mechanisms using the same host material (Section 2.1), two samples, with large and small droplets respectively, were prepared using the same component ingredients. The base dye-doped chiral nematic mixture consisted of 5.5 % w/w of the chiral dopant BDH1305 in the achiral nematic LC BL093 (Merck), and 1 % w/w of the laser dye Pyrromethene-597 (Exciton). This mixture has previously been shown to exhibit very high lasing efficiencies.[21] In order to achieve efficient lasing the laser dye peak fluorescence should coincide with the chiral nematic long wavelength photonic band-edge; Fig. 1 shows the position of the band-edge close to the peak fluorescence of the dye. The lasing mixture was added to 20 % w/w aqueous solution of polyvinyl-alcohol (PVA) (Sigma-Aldrich, 10,000 amu) at a concentration of 10 % w/w (small droplet sample) or 5 % w/w (large droplet sample). The mixtures were then emulsified at 100 rpm or 1000 rpm respectively, for 10 minutes at room temperature, using an overhead stirrer. The emulsions were then immediately coated onto untreated glass substrates, at 80 µm wet film thickness, using a *k*-bar coating system (RK Print-Coat Instruments). A schematic of the sample preparation process is shown in Fig. 2.
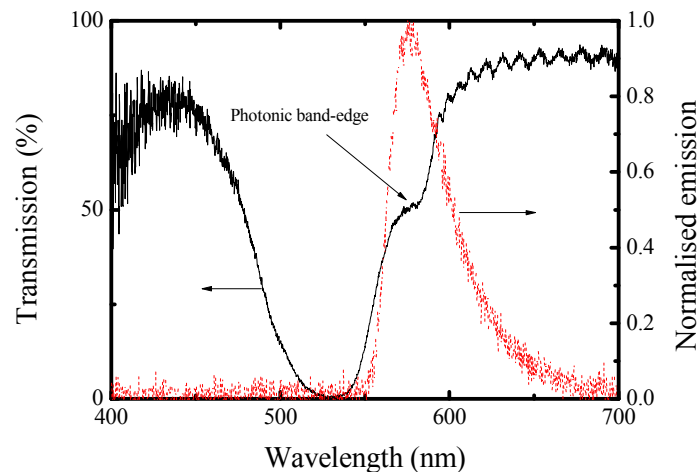

Figure 1 Transmission and emission spectra of the pre-emulsified dye-doped chiral nematic mixture, indicating dye absorbance around 532 nm and the long band-edge coinciding with the fluorescence gain maximum.
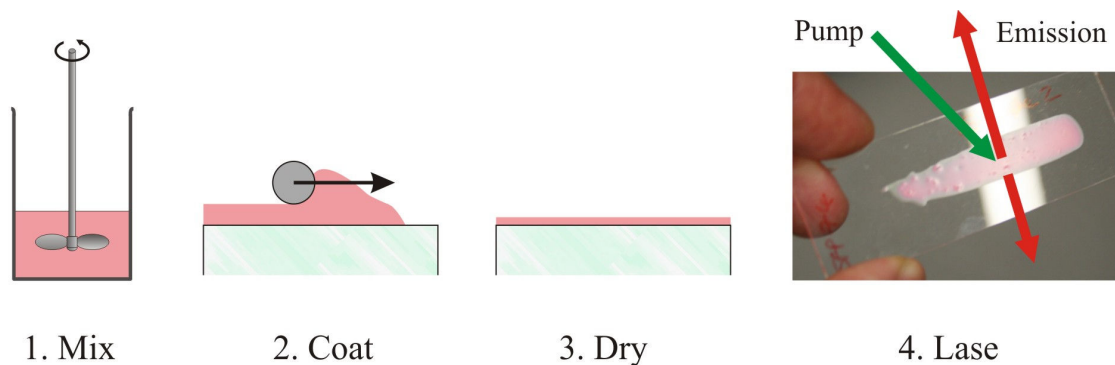
Figure 2 Schematic of the sample film preparation procedure.

For the multi-color red, green and blue (RGB) printed laser films the dyes (DCM, Coumarin 540A and Coumarin 504; supplied from Exciton) were added at approximately 1 % w/w, in a 3.5 % to 5.5 % w/w BDH1281 in BL006 host mixture. The emulsification conditions, subsequent processing conditions, and film thicknesses were identical to the large droplets sample discussed above.

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 doublet and meniscus lens combination.

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 DISCUSSION

3.1 Band-edge and random lasing

Following preparation, the coated films containing the large and small droplets were examined. Fig. 3 shows polarized microscopy images of the dried films. The emulsion prepared at higher mixing speeds resulted in smaller average droplet sizes (typically < 6 µm), Fig. 3 (d), whilst the more gently mixed sample resulted in larger droplets (30-50 µm), Fig. 3 (c). It is noteworthy that the process of the wet film drying leads to de-swelling, thus changing the droplet shape from spherical to oblate. This is a well-known phenomenon in emulsified LC films and can lead to preferential in-plane alignment of the nematic director.[16]. This process is depicted in Fig. 3 (a) and (b).
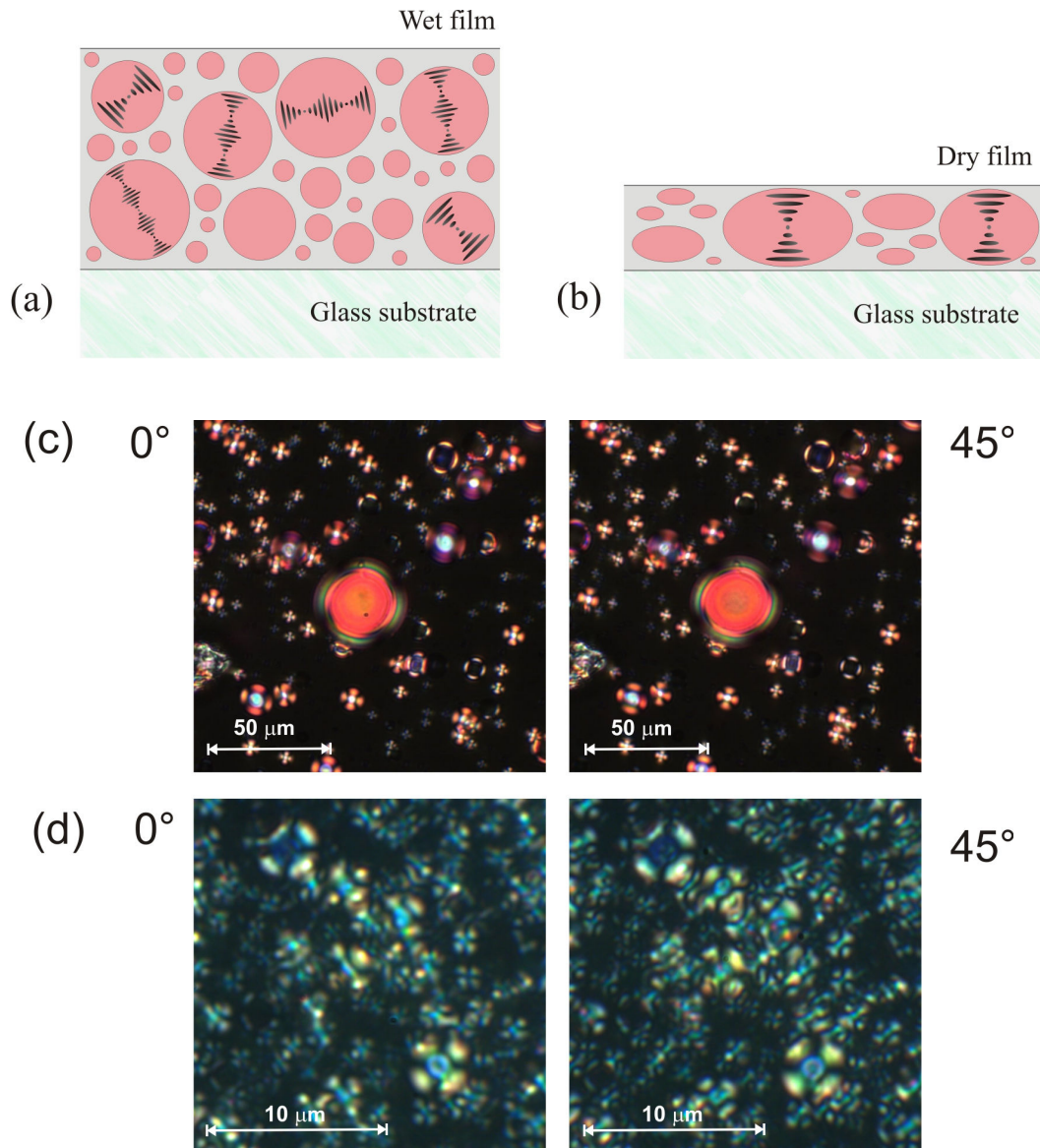
Figure 3 The formation of the Grandjean texture in large chiral nematic droplets contained within emulsified samples. Pictorial representation of the drying and film-shrinkage mechanism by which initially spherical liquid crystal droplets (a) become oblate (b). This leads to standing helix (Grandjean) texture alignment in the large droplets sample, and is confirmed experimentally by viewing the sample between crossed polarisers through a microscope. The texture shows no apparent change when the crossed polariser axis is rotated through 0° and 45° (c). The small droplet sample is shown in d).

Determination of the alignment of chiral nematic liquid crystals within droplets is a complex problem.[16] It depends upon surface alignment conditions, chiral twisting power, droplet shape, and in this case, film shrinkage. Recent literature concerning spherically confined chiral nematics, without shrinkage, suggest "Bragg Onion" alignment.[22] However, for the large droplets in Fig. 3 c), the majority of the area appears to have a uniform and rotationally invariant texture when viewed between crossed-polarizers. This is strong evidence of a standing helix (Grandjean) arrangement. A different alignment is visible around the edges of the larger droplets, where surface alignment effects dominate.

Polarizing microscopy images of the small droplets sample are shown in Fig. 3 d). They display characteristic extinction cross patterns and show no rotational changes in their appearance, indicating a rotationally symmetric director profile. There is no evidence of Grandjean alignment. Consequently, interface surface anchoring effects are thought to dominate LC alignment over the alignment that would be induced through film shrinkage.

The emission properties of both samples were also examined and the results are presented in Fig. 4 and Fig 5. Typical emission spectra are shown in Fig. 4 a) and Fig. 5 a) for the small and large droplet emulsions, respectively. The samples show strong evidence of laser emission at 574.1 nm and 574.7 nm. However, the lasing linewidths differ considerably between the two samples. Small droplets show much broader Lorentzian emission profiles, with linewidths of 5.049 (± 0.014) nm. The large droplets show a very narrow linewidth of 0.403 (± 0.008) nm (calculated from Gaussian curve-fitting). This provides clear evidence of different lasing mechanisms between the two samples.
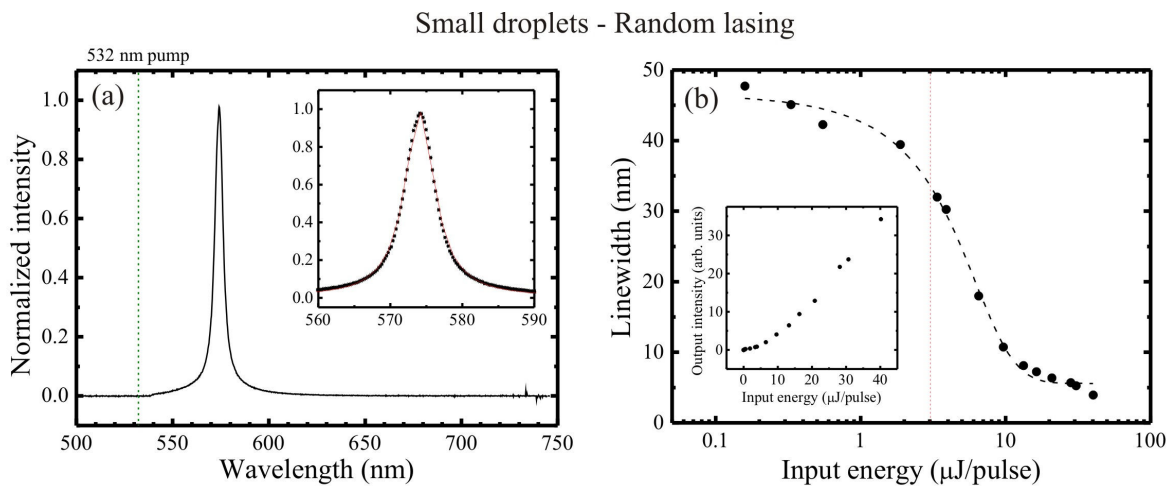

Figure 4 (a) Emission linewidth of the small droplets (random lasing) sample; the inset shows the Lorentzian fit; (b) laser threshold plot.
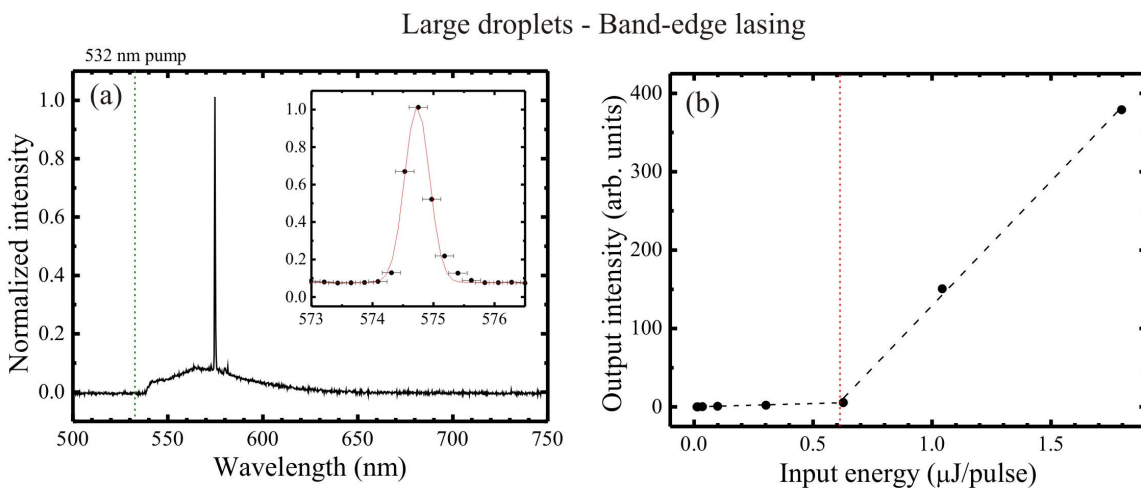

Figure 5 (a) Emission linewidth of the large droplets (photonic band-edge lasing) sample; the inset shows the Gaussian fit; (b) laser threshold plot for the band-edge laser sample showing well defined threshold.

Narrow linewidth emissions with Gaussian spectral profiles are usually indicative of optically resonant structures. Combined with the coincidence of the emission to the long band-edge (and the Grandjean texture), this provides strong evidence that band-edge lasing is occurring in the large droplet sample. The 10-20 μm droplet thickness also provides an optimum cavity size for band-edge lasing.[23] However, the broader lasing linewidth from the small droplet sample is not consistent with the same physical mechanism. In this case, it is suggested that emission here is due to a random lasing mechanism.[24] This type of lasing achieves optical feedback through propagation in a strongly scattering medium, provided in this case by the refractive index mismatch between the polymer host and the LC droplets. The small droplet emulsion has a high number density of droplets of less than 2 μm in size. The transport mean free path for photons (i.e. the distance over which scattering is randomized) will therefore be considerably smaller than the bulk film thickness; a primary requirement for random lasing.[24] In comparison, the large droplet emulsion will only contain one or two droplets within the 30 μm dried film thickness, and so the transport mean free path will be larger than the film thickness.

Further significant evidence comes from analysis of the polarization of the laser emission. The emission from the large droplets sample was right circularly polarized while the small droplets sample was unpolarized, indicating fundamentally different lasing mechanisms.

Considering further the small droplets sample, the emission does not display the discrete micro-resonances from localized modes seen in materials with sub-micron scattering particulates.[11, 25] Instead the emission appears to collapse into a broader extended mode, synonymous with diffusive materials.[26] It is important to note that due to the polydispersity of our sample, scattering is considered to be non-resonant, in contrast to the resonance-driven random lasing observed from monodisperse particulates.[27]

Further investigations into the lasing mechanisms were made with lasing threshold measurements [Fig. 4 (b) and Fig. 5(b)]. The larger droplet sample, Fig. 5 (b) displayed thresholds of between 0.6–1.0 μJ/pulse (6.3–10.5 mJ/cm^2/pulse) at different spatial positions across the sample. This range is due to LC droplet polydispersity. It is noteworthy that band-edge lasing measurements of the non-emulsified mixture, measured on the same equipment, gave thresholds of 0.1 μJ/pulse (1.1 mJ/cm^2/pulse). The increased threshold in the emulsified sample is most likely due to reducing light input coupling into the droplet since the lateral size of the droplet is much less than the pump spot size.

The smaller droplet sample did not show the same distinct threshold behavior as the large droplet sample. A measurement for threshold was instead made by determining the energy at which the linewidth collapses; a common technique adopted for random lasers.[28] The point of inflection to a sigmoidal fit to the data in Fig. 4 (b) shows this threshold to be 3.08 (± 0.80) μJ/pulse (32.4 mJ/cm^2/pulse). Therefore, random lasing from small droplet emulsions shows higher thresholds than band-edge lasing from large droplet emulsions.
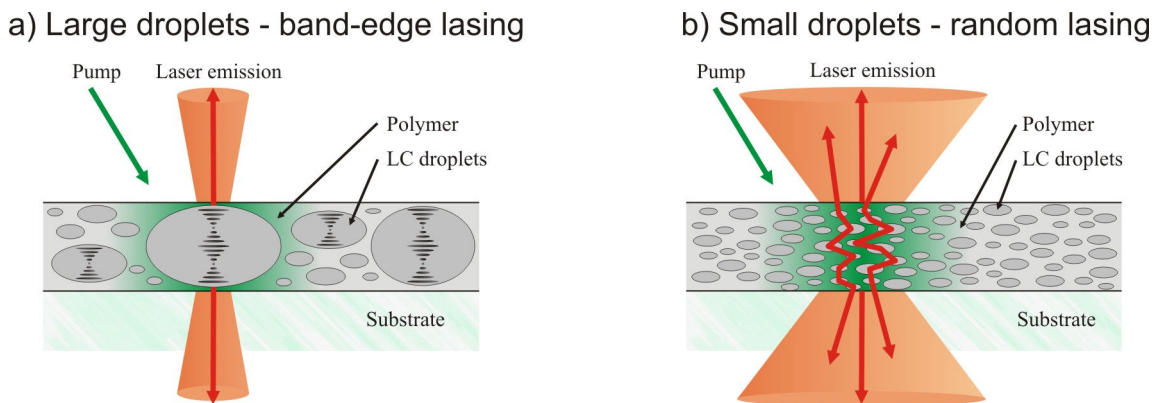

Figure 6 Schematic of random lasing and photonic band-edge lasing in printable liquid crystal emulsions; (a) large droplets form a Grandjean alignment suitable for band-edge lasing; (b)Small droplets give rise to non-resonant random lasing.

A schematic summary of the observations are presented in Fig. 6. It is remarkable that compositionally identical chiral nematic LC emulsions can be made to exhibit lasing by either band-edge or diffuse non-resonant random lasing mechanisms simply by altering the processing conditions. A straightforward variation of mixing speed, corresponding to a change in droplet size, allows differentiation between these two lasing mechanisms.

3.2 Paintable multi-color (RGB) band-edge lasers

A possible key advantage of the approach undertaken i.e. using an emulsion procedure to generate individual laser droplets in a readily coatable film, is the potential to formulate complex films with unique optical signatures. Such films would be of significant potential application in areas ranging from counter-forgery to authentication.

Red, green and blue lasing emulsions were prepared following the procedure and materials outlined in Section 2. The wet emulsions were coated onto glass substrates, shown in Fig. 7, and allowed to dry. The absorbance (using unpolarized light) and fluorescence spectra of the three lasing emulsions were measured, and found to match spectra observed in for equivalent non-emulsified dye-doped chiral nematic mixtures.[7] It is noteworthy that a common pump wavelength (430 nm) was used for all the samples. The dyes were chosen for their common absorbance properties at this wavelength while possessing fluorescence at the desired RGB wavelengths. Subsequently, when optically pumped, the LC emulsions gave rise to circularly polarized laser emissions (Fig. 7 (b)) at wavelengths that matched the locations of the long band-edges observed in the pure chiral nematic samples.

The inset to Fig. 7 (b) shows the blue, green, and red output profiles from the laser emulsions recorded approximately 30 cm from the sample. The emission wavelengths were found to occur at 480 nm, 528 nm, and around 615 nm, respectively.
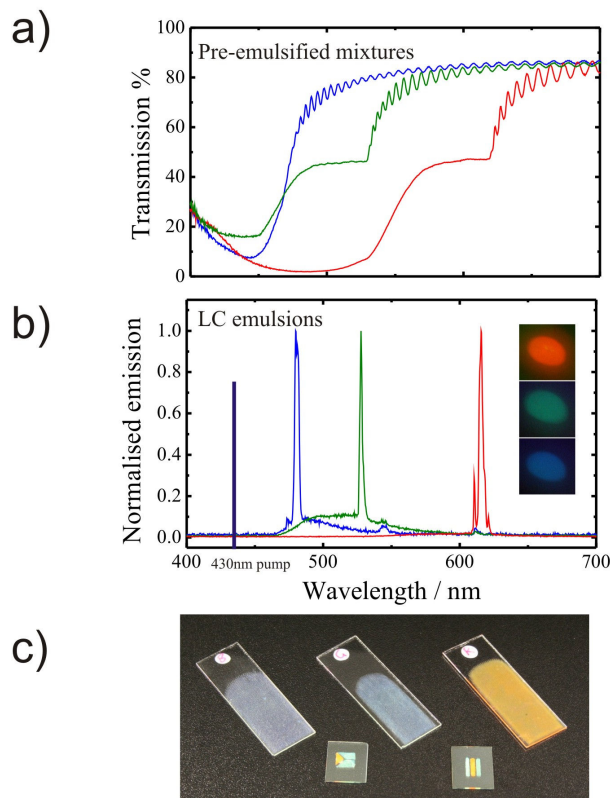

Figure 7 Red, green and blue (RGB) lasing LC emulsions. Shown are the pre-emulsified mixtures (a), laser emission from the emulsified films (b) and the coated films on glass slides (c).

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 as well as sequential adjacently printed RGB coatings (Fig. 8). For the stack of RGB layers the generation of "white" laser emission is shown (Fig. 8 b)). The sample was pumped with the red layer foremost so as to eliminate possible re-absorption of laser emission.

(a) Sequentially printed blue, green, red lasers

Glass substrate
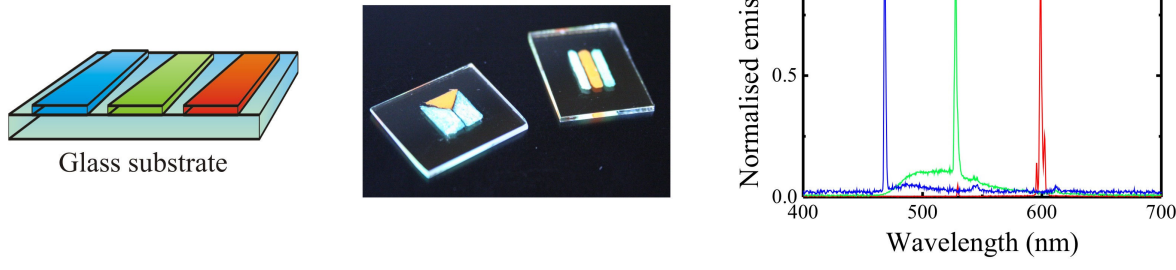
(b) Stacked blue, green, red layers

Glass substrate
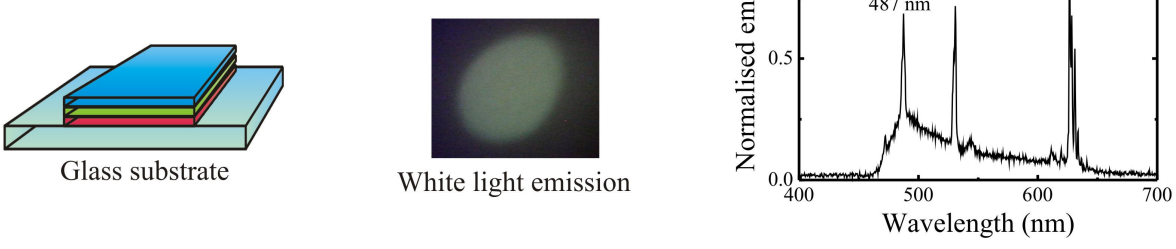
White light emission

Figure 8 Paintable "white light lasers". Adjacent coatings of RGB emitting layers are shown in (a). A stack of red, green and blue laser emulsions (b), when pumped with a single optical excitation source at 430 nm, gives three simultaneous laser emissions (b), including the combined RGB "white light" emission recorded in the far-field.

For the sequential coatings, (Fig. 8 (a), simultaneous emission could be obtained using a two-dimensional array-based pumping approach, for example. [7, 8] One notable benefit with the method employed here is that, unlike the pitch gradient approach used in, no unwanted diffusion occurs between the samples, and hence the output remains static with time.[7] 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. In principle, a large number of different emission wavelengths could be simultaneously probed to generate a unique, complex optical emission profile ideally suited for security coatings and applications. Furthermore, a random laser approach could similarly be implemented using coated smaller droplet films.

The paintable laser samples are not merely restricted to glass substrates. Fig. 9 demonstrates some of the functionality of these paintable lasers on different surfaces, including flexible polyethylene terephthalate (PET), aluminium and paper. 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. 9 (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.
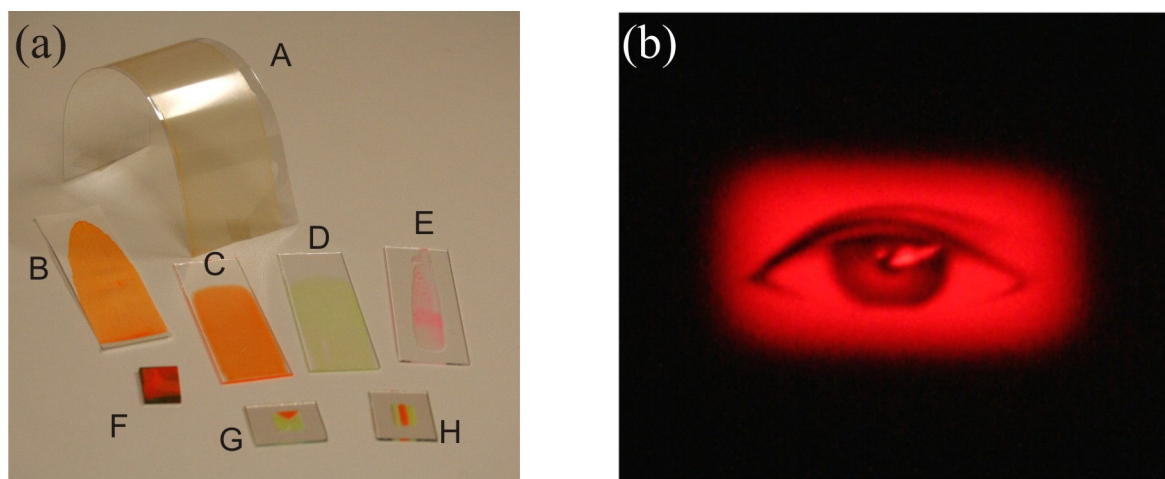
Figure 9. Examples of coated substrates in a) including flexible PET (A), paper (B), glass (C, D and E), aluminium-coated glass (F), and patterned red, green and blue laser emulsions on glass (G and H). The emission from the red LC emulsion laser on an aluminium-coated glass substrate (F) is then used to illuminate a multi-phase hologram, and the replay field is illustrated in image (b).

4. SUMMARY AND CONCLUSIONS

In summary, it has been shown that it is possible to create printable lasers using dye-doped chiral nematic liquid crystals emulsified within a polymer matrix. Two different laser mechanisms, photonic band edge lasing and non-resonant random lasing were exhibited. The output is determined by simple processing modifications. 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 is a 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.

5. ACKNOWLEDGEMENTS

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