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Band-edge and random lasing in paintable liquid crystal emulsions

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Lasing mechanisms within paintable dye-doped chiral liquid crystal emulsions are investigated. Evidence shows that by variation in liquid crystal droplet size, by simple control of mechanical mixing speeds, a change in the lasing mechanism from band-edge lasing (large droplets) to diffuse nonresonant random lasing (small droplets) can be facilitated. This approach represents a facile technique for the variation in lasing mechanism, within a self-organizing, flexible, and conformable system, and offers the opportunity of developing controllable linewidth laser sources. © *2011 American Institute of Physics*. [doi:10.1063/1.3574915]

Dye-doped chiral nematic liquid crystals (LCs) have proved particularly useful as self-organized resonant structures for low-threshold, photonic band-edge lasers with selectable emission across the visible waveband.[1,2] In a recent development, paintable and flexible sources in emulsified films were demonstrated,[3] illustrating a facile approach to LC laser fabrication, without alignment layers, and exhibiting band-edge lasing at red, green, and blue wavelengths simultaneously in a printed film. In this letter, we present results relating to emulsion-based chiral LC lasers, and provide evidence of two different lasing mechanisms (diffuse nonresonant random lasing and band-edge lasing) in compositionally identical mixtures, differentiated only by the size of LC droplets within the emulsions. We therefore present a unique and simple way to achieve lasing through the two different mechanisms by simple control of the sample preparation, notably mixing speeds.

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 been shown to exhibit very high lasing efficiencies.[4] Fig. 1 confirms the coincidence of the long band-edge of the photonic band gap with the gain maximum of the dye, thus ensuring optimized conditions for band-edge lasing.[2] This lasing mixture was then added to 20% w/w aqueous solution of polyvinyl-alcohol (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 min 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). After drying for 1 h at room temperature, water evaporation resulted in film shrinkage to approximately a thickness of 30 μm (i.e., 35%–40% of the wet film thickness).

Figures 2(b) and 2(d) show polarized microscopy images of the two dried emulsion films. Both emulsions are polydisperse. The emulsion prepared at higher mixing speeds resulted in smaller average droplet sizes (typically <6 μm) while the more gently mixed sample resulted in larger droplets (30–50 μm). However, deswelling of the film causes LC droplets to become oblate, and thicknesses are therefore estimated to be 35%–40% of these values (<2 μm and 10–20 μm).

Determination of the alignment of chiral nematics within spheroidal droplets is a nontrivial problem.[5] It will depend upon surface alignment preferences, chiral twisting power, droplet shape, and in this case, film shrinkage. Recent literature concerning spherically confined chiral nematics, without shrinkage, suggest "Bragg Onion" alignment.[6] However, for the large droplets in Fig. 2(d), 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. Smaller droplets in Fig. 2(b) display extinction cross patterns and show no rotational changes, indicating a rotationally symmetric director profile. There is no evidence of Grandjean alignment. Interface surface anchoring effects are thought to dominate LC alignment throughout these droplets.

The emission characteristics of the LC emulsions were examined by photoexcitation with a neodymium-doped yttrium aluminum garnet (Nd:YAG) pump laser (New Wave Research Polaris II, frequency-doubled to 532 nm, 3–4 ns pulse, 1 Hz repetition), at a wavelength coinciding with the

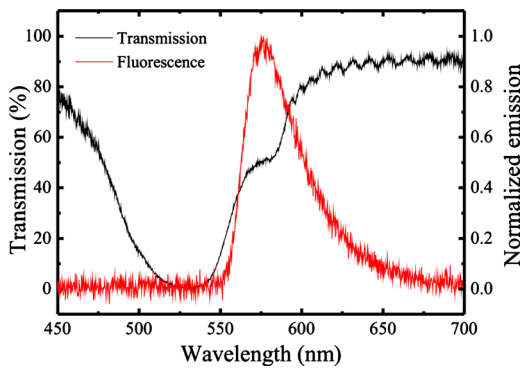

FIG. 1. (Color online) Transmission and emission spectra of the pre-emulsified dye-doped chiral nematic mixture, indicating dye absorbance around 532 nm and the long band-edge coinciding with the fluorescence gain maximum.

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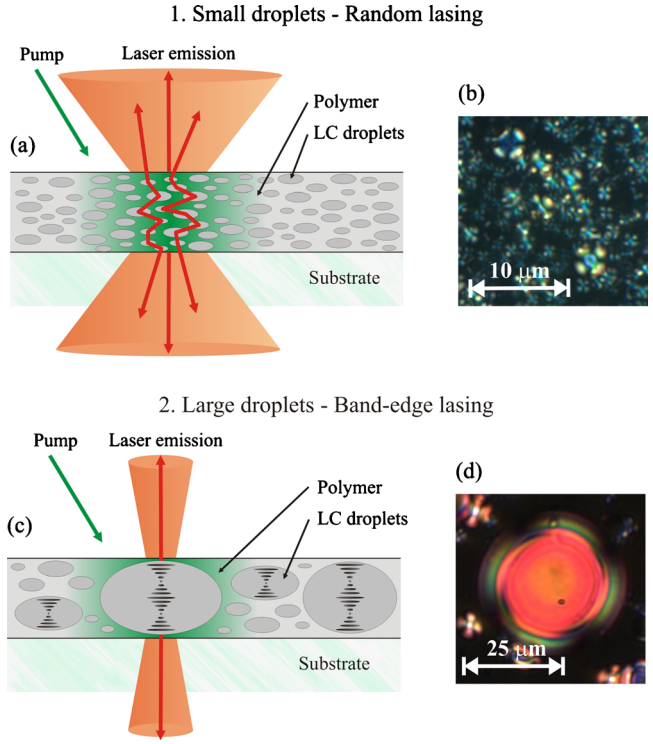

FIG. 2. (Color online) Deswelling of LC emulsion films forms oblate LC droplets. Small droplets give rise to nonresonant random lasing (a) while large droplets form a Grandjean alignment suitable for band-edge lasing (c). Polarized microscopy images of the droplets are shown in (b) and (d).

absorbance maximum of the laser dye (Fig. 1). The beam was circularly polarized to the opposite handedness of the chiral nematic (maximizing pump efficiency for band-edge lasing), and was focused onto the emulsion with a spot size of 110 μm. Emission was collected by focusing the output onto an HR2000 USB spectrometer (Ocean Optics, 0.3 nm resolution).

Figures 3(a) and 3(b) show typical emission spectra from both the small and large droplet emulsions. The samples show strong evidence of laser emission at 574.1 nm and 574.7 nm, respectively. The lasing linewidths of the two samples differ considerably. The large droplets show a very narrow linewidth of 0.403($\pm$0.008) nm (calculated from Gaussian curve-fitting). Small droplets show much broader Lorentzian emission profiles with linewidths of 5.049($\pm$0.014) nm. A narrower Gaussian fit indicates a linewidth governed by homogeneous (collisional) broadening while the broader Lorentzian fit indicates inhomogeneous (Doppler) broadening.[7] This provides clear evidence of different lasing mechanisms between the two samples.

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.[8] The broader linewidth from the small droplet sample is clearly not consistent with the same resonant mechanism. Small droplets are insufficient in size (and show no appropriate evidence from microscopy) for the formation of suitable internal cavities for band-edge lasing. We believe that emission here is due to a random lasing mechanism.[9] 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.[9] In comparison, the large droplet emulsion will only contain one or two droplets within the 30 μm dried film thickness, and

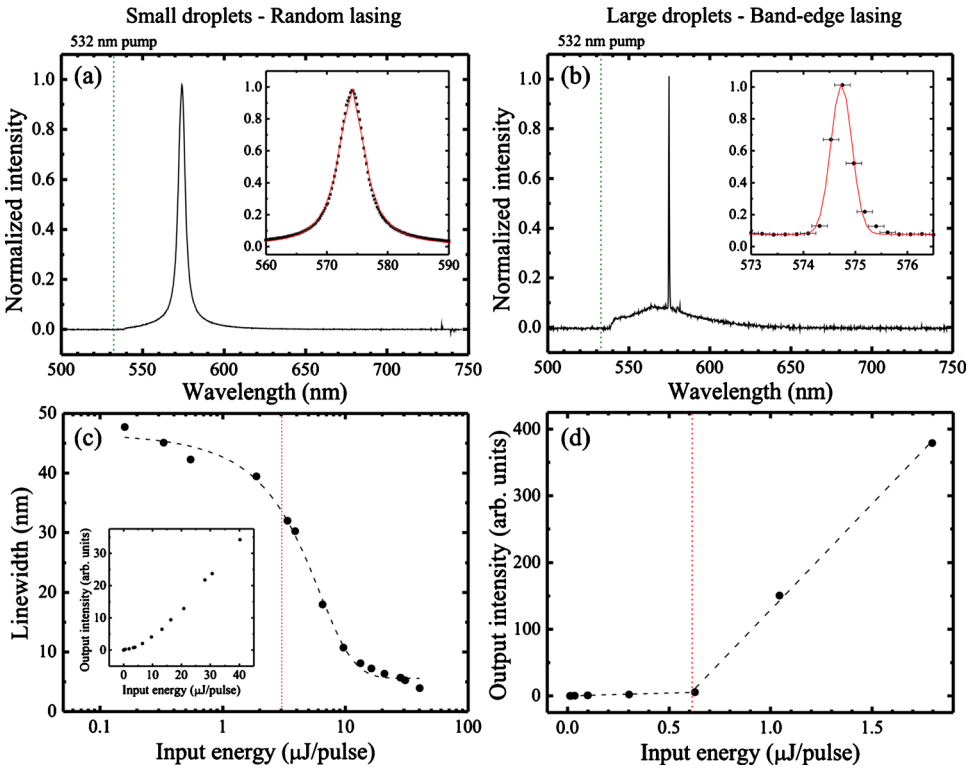

FIG. 3. (Color online) Emission spectra for broad linewidth random lasing from small droplets (a) and narrow linewidth band-edge lasing from large droplets (b). Insets show Lorentzian and Gaussian fitting, respectively. Lasing thresholds are shown in (c) and (d).

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so the transport mean free path will be larger than the film thickness.

The emission from small droplet emulsions does not display the discrete microresonances from localized modes seen in materials with submicron scattering particulates.[10,11] Instead the emission appears to collapse into a broader extended mode, synonymous with diffusive materials.[12] It is important to note that due to the polydispersity of our sample, scattering is considered to be nonresonant, in contrast to the resonance-driven random lasing observed by Gottardo *et al.*[13] from monodisperse particulates.

Further evidence of different lasing mechanisms is provided with polarization analysis. Larger droplets were found to emit purely circular polarized light of only right-handedness, matching the helicity of the chiral nematic. Emission is also restricted to a narrow cone perpendicular to the substrate on both sides. This is direct evidence of a band-edge lasing mechanism. Conversely, in the small droplet sample, the emitted laser light shows neither circular, nor indeed linear polarization, but yet it emits perpendicular to the substrate but with a far broader cone of emission. This further elucidates a diffuse nonresonant random lasing mechanism.

Large droplet samples displayed a variety of single emission wavelengths (within the fluorescence range of the dye) at different spatial positions across the sample. Polychromatic emissions were also observed when multiple large droplets were simultaneously photoexcited. Such multimode emission is a result of droplet polydispersity. LC anchoring at the droplet boundaries restricts the number of director rotations within the Grandjean regions to an integer or half-integer value. This restriction will be in frustration with the natural helicity of the LC, causing each different sized droplet to have a unique chiral pitch, band-edge position, and emission wavelength. Conversely, in the small droplet sample, despite droplet polydispersity, homogeneity is far greater over the length scale of the active volume, and the peak emission wavelength is therefore consistent at all points across the sample. This is consistent with a diffusive nonresonant random lasing mechanism, facilitated by scattering over a large number of LC droplets. Wavelength is determined only by the gain length, which is a minimum at the gain maximum while the transport mean free path is wavelength independent.

Further investigations into the lasing mechanisms were made with lasing threshold measurements [Figs. 3(c) and 3(d)]. The larger droplet sample 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 again due to LC droplet polydispersity. As the pump spot size exceeds typical droplet diameters, pump light wastage will result. Different input energies will therefore be delivered to different sized droplets, at different spatial locations in the sample, despite a constant pump source, leading to the observed range in lasing thresholds. Band-edge lasing measurements of the nonemulsified mixture, measured on the same equipment, gave thresholds of 0.1 μJ/pulse (1.1 mJ/cm^2/pulse), implying that potentially only 17% of the pump energy is incident upon a single droplet. Significant reductions in threshold are therefore expected when a more tightly confined pump spot is used, matching the size of the large droplets. 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.[14] The point of inflection to a sigmoidal fit to the data in Fig. 3(c) shows this threshold to be 3.08($\pm$0.80) μJ/pulse (32.4 mJ/cm^2/pulse). As one might expect, random lasing from small droplet emulsions shows higher thresholds than band-edge lasing from large droplet emulsions.

The uncertainty in the energy incident upon single droplets meant that the slope efficiency of the large droplet emulsion laser was not measured here. However, previously reported (nonemulsified) LC band-edge lasers with almost identical materials and geometries have been measured at up to 30%,[4] (60% for samples with reflective substrates). There seems little reason why similar efficiencies could not be achieved in emulsified samples also, provided an appropriately confined pump spot were used.

In summary, compositionally identical chiral nematic LC emulsions, made by a simple mixing, coating, and deswelling technique, have been shown to exhibit lasing by either band-edge or diffuse nonresonant random lasing mechanisms. A simple variation in mixing speed, corresponding to a change in droplet size, is all that is required to switch between these two lasing mechanisms. These flexible emulsions are wavelength selectable, can be painted onto arbitrary substrates, and require no pretreatment with alignment layers. This may facilitate low-cost, semidisposable laser sources for wide-ranging applications, including point-of-care biomedical analysis, optical security coatings and displays. Furthermore, they may find uses in systems, where a controllable linewidth is desirable, for example, in reducing speckle in holographic displays. Future work will study the effect of electrical switching upon lasing characteristics, and investigate the threshold at which lasing changes between random and band-edge mechanisms.

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