Wavelength-tuneable liquid crystal lasers from the visible to the near-infrared


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ABSTRACT

The study of band-edge lasing from dye-doped chiral nematic liquid crystals has thus far been largely restricted to visible wavelengths. In this paper, a wide range of commercially available laser dyes are examined for their suitability as infrared emitters within a chiral nematic host. Problems such as poor solubility and reduced quantum efficiencies are overcome, and successful band-edge lasing is demonstrated within the range of 735–850 nm, using the dyes LD800, HITC-P and DOTC-P.

This paper also reports on progress towards widely tuneable liquid crystal lasers, capable of emission in the region 460–850 nm. Key to this is the use of common pump source, capable of simultaneously exciting all of the dyes (both infrared and visible) that are present within the system. Towards this aim, we successfully demonstrate near-infrared lasing (800 nm) facilitated by Förster energy transfer between the visible dye DCM, and the infra-red dye LD800, enabling pump wavelengths anywhere between 420 and 532 nm to be used.

These results demonstrate that small and low-cost tuneable visible to near-infrared laser sources are achievable, using a single common pump source. Such devices are envisaged to have wide-ranging applications including medical imaging (including optical coherence tomography), point-of-care optical medical diagnostics (such as flow cytometry), telecommunications, and optical signatures for security coatings.

Keywords: Liquid crystal laser, photonic band gap, wavelength tuneable laser, visible, near-infrared, Förster transfer.

1. INTRODUCTION

Photonic band-edge lasers made from dye-doped chiral nematic liquid crystals (LCs) have been a subject of detailed academic interest in recent years. Their periodic micro-molecular structure is self-organizing, allowing mirror-free lasing with low thresholds and high slope efficiencies in simple and low-cost device architectures. More recently, they have even been implemented into paintable materials, without the need for encapsulation. Thus far, LC lasing experimentation has been restricted to wavelengths within the ultra-violet and visible regions of the spectrum, whilst longer wavelengths have only been speculated upon in theory. In the first section of the paper, a wide range of commercially available organic dyes are examined for their suitability within an LC host as coherent light emitters in the near-infrared (NIR). Extending emission into this wavelength region offers the opportunity of developing a new range of low-cost optical sources, with applications including sub-dermal medical imaging, point-of-care medical diagnostics tools, telecommunications, and unique optical signatures for security coatings.

Recent work has also shown that polychromatic (simultaneous multi-color emission) or widely tuneable laser sources are achievable in liquid crystal form. Through careful choice of dyes and a gradient chiral pitch, a single common pump

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source can be used to generate laser emission that is selectable across the entire visible spectrum, within a single device. In the second section of this paper, we present the latest results towards extending this work, by achieving polychromatic emission across the visible and NIR, from a single device, whilst pumped with a single common pump source. This presents some unique challenges, as the infrared (IR) dyes do not share common absorbance bands with the visible dyes. We therefore attempt to solve this problem through the use of Förster energy transfer techniques.

2. THEORY

All laser systems share the same three basic separate components: an input energy pump source; a gain medium; and a resonant cavity. This can make many laser systems relatively complex, especially in terms of their construction and optical alignment. LC lasers have the advantage that their resonant cavity is formed spontaneously and intrinsically, in the form of a self-assembled chiral nematic helix, and thus greatly simplifies construction. This chiral structure gives rise to a periodic refractive index profile (similar to a Bragg grating), enabling it to behave as a distributed feedback system for circularly polarized light of a specific wavelength. Such materials, which exhibit selective reflection as these, are referred to as photonic band-gap (PBG) materials. In the case of chiral nematics, the photonic band-gap is one dimensional, existing along the helical axis. An organic laser dye is then dissolved into the chiral nematic LC host, which acts as the gain medium. When optically excited by a suitable pump source (close to the absorbance maximum of the dye), the dye will fluoresce and emit light at a range of wavelengths. However, above a certain threshold, selective reflection from the LC provides resonance at a specific wavelength, enabling stimulated emission to occur. The emission wavelength of the corresponding laser output will therefore be determined by the chiral pitch (and refractive index) of the LC. Alignment of the dye to the LC directors will determine if the emission occurs at the long (parallel alignment) or short (perpendicular alignment) band edge of the photonic band-gap, where the photonic density of states is at a maximum.

When constructing an LC laser, one must ensure that the laser dye being used has a fluorescence spectrum that is co- positioned with the (usually long) band-edge of the chiral nematic. To achieve this reliably, and for a wide range of different dyes, chiral dopant is added to nematic LCs, rather than using intrinsically chiral (cholesteric) LCs. By varying the concentration of the dopant the chiral pitch can be controlled, and with suitable choice of dyes a wide and continuous range of liquid crystal laser emission is possible. In theory, this technique can be used to extend the emission of LC lasers into the IR. However, IR emission presents a challenge due to the relatively poor solubility of organic IR dyes in LC hosts. Furthermore, quantum efficiencies of IR dyes are frequently lower than their visible counterparts, due to the coincidence of hydrogen vibration resonances, which will offer competing non-radiative decay mechanisms.

LC lasers have previously been demonstrated exhibiting spatially dependent visible LC laser emission from red to blue wavelengths within the same cell\textsuperscript{6,7}, and even into the ultra-violet\textsuperscript{8,9}. Such devices use multiple laser dyes (preferably all with common absorbance spectra characteristics) dissolved in the same LC cell, with a spatial distribution of the position of the photonic band-gap across the device. Some previous authors have achieved such a band-gap distribution through photopolymerization techniques\textsuperscript{7,10}. An alternative simpler way to achieve this is to use two different chiral nematic mixtures of different pitch, which are then filled into the same cell from opposite sides, and allowed to slowly diffuse together within the cell\textsuperscript{6}. A gradient in the chiral pitch is thus formed, enabling laser emission to occur at arbitrary wavelengths, as determined by the spatial location of the focused pump beam. Unwanted continued diffusion can be circumvented by use of optically-induced polymer stabilization techniques at the appropriate stage of the diffusion process. Unfortunately, IR dyes do not share common absorbance wavelengths with the visible dyes used in these experiments, making a tuneable visible to IR LC laser a difficult task to accomplish. However, it has been previously demonstrated that Förster energy transfer between two separate dyes can be used to enable emission from one dye when pumped close to the absorbance maximum of another\textsuperscript{7,9,11,12}. It is therefore theorized that such a technique might be used to achieve visible to NIR tuneable lasing in a gradient pitch cell whilst pumped with a single wavelength common excitation source.
For this study, a wide range of commercially available organic laser dyes (supplied by Exciton) were canvassed. The choices were limited to those that displayed fluorescence in the IR or NIR, but yet had absorbances that were within the deliverable range of our optical pump source (420–690 nm). Given this restriction, a short-list of eleven dyes was chosen, containing examples of indoles, benzoazoles, benzothiazoles and rhodamines. The commercial names and structures of these dyes are detailed in Table 1.

Table 1. Infrared laser dyes tested for LC lasing, and their solubility in the LC host BL093. (Dyes marked with an asterix (*) were found to be photo or thermally unstable).

<table>
<thead>
<tr>
<th>Soluble</th>
<th>Insoluble</th>
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<tbody>
<tr>
<td>DOTCP</td>
<td>IR125</td>
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<tr>
<td>HITCP</td>
<td>IR140</td>
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<tr>
<td>LD800</td>
<td>IR144</td>
</tr>
<tr>
<td>HTC-4 *</td>
<td>Ox750-P</td>
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<tr>
<td>DMOTC-I *</td>
<td>DOTC-I *</td>
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<td>DTTC-I *</td>
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The solubility of these dyes was first assessed by mixing them (without further purification) into a nematic LC host (BL093 and BL006) (Merck KGaA) at 1% concentrations by weight (% wt/wt). These particular LC hosts was chosen for their wide temperature range of their nematic phase and their moderately high birefringence, which has been shown to be important for low lasing thresholds and high slope efficiencies. Attempts to dissolve the dyes into the liquid crystal host were first made by a thermal diffusion mixing process. Mixtures were heated into the isotropic phase (~ 100 °C) for a period of 24 hours. If required, further assistance was given by immersion in an ultrasonic bath at 95 °C. For dyes that still were unable to dissolve, a few drops of dichloromethane or acetone were also added to the mixture, and later allowed to evaporate away. This assisted the mixing process by increasing solvation energy and providing a medium of molecular interaction.

Successfully dissolved mixtures were then tested for their order parameter and their absorbance and fluorescence spectra. Dye-doped nematic mixtures were capillary-filled into prefabricated test cells (Instec), consisting of anti-parallel planar alignment layers and a cell-spacing of 5 µm. Samples were placed on a polarizing microscope (Olympus BH2) equipped with a hot-stage (Linkam THMS600 with TP94 controller), heated into the isotropic phase, mechanically sheared, and then slowly cooled until a mono-domain texture was formed. Absorbance and fluorescence spectra of each sample were obtained using a polarized microscope equipped with a spectrometer (Ocean Optics USB2000+ VIS-NIR, 1.5 nm resolution FWHM, with Spectra-Suite software). The order parameter ($S_T$) of each dye within the nematic LC host was obtained from absorbance measurements in directions both parallel ($A||$) and perpendicular ($A\perp$) to the director, and was calculated from the equation: $S_T = (A|| - A\perp)/(A|| + 2A\perp)$. A positive (or negative) value for the order parameter was used to determine if the position for most efficient lasing was at the long (or short) edge of the photonic band-gap.

An appropriate concentration (in the range 4.1–4.4 % w/w) of the high twisting power chiral dopant BDH1305 or BDH1281 (Merck KGaA) was then added to fresh dye-doped nematic mixtures. This enabled the coincidence of the (long) band-edge with the fluorescence maximum of the dye, where most efficient lasing is likely to occur. The positions of the photonic band-gaps of each of these mixtures were then verified by analyzing their transmission spectra. Mixtures were capillary-filled into prefabricated cells (LG Displays) with anti-parallel planar alignment layers and cell-spacing of

approximately 10 µm (found to be around the optimum thickness for lasing\(^4\)). Again the cells were thermally cycled and sheared until a uniform monodomain Grandjean texture (standing helix) was obtained. The resulting cells were then illuminated with a broadband white light source (400–1100 nm) (Ocean Optics), circularly polarized to oppose the chiral nematic helix, whilst the aforementioned spectrometer recorded transmitted light intensity through the sample.

The same dye-doped chiral nematic cells described immediately above were then tested for lasing. The pump source was a pulsed Nd:YAG frequency-tripled (355 nm) laser (Spotlight, Innolas) connected to an Optical Parametric Oscillator (OPO) (GWU) generating 5 ns pulses at a repetition rate of 2 Hz, in the range 400–690 nm. Pump wavelengths were chosen to be as close as possible to the absorbance maxima of each dye. The pump laser beam was first passed through a spatial filter and then through a 50:50 beam splitter to allow both the input and output wavelengths and energies to be measured simultaneously. Pulse energies were measured using pyroelectric detectors (Ophir). The output of the laser was linear polarized, and so was passed through a quarter waveplate to achieve circular polarization that had the opposite handedness of rotation to that of the liquid crystal helix. One arm of the beam was focused at normal incidence onto the dye-doped chiral nematic cell using a plano-convex lens to produce a spot that was measured (by knife-edge method) to be 300 µm diameter. A series of low and high pass filters at appropriate cut-off wavelengths were used to remove the pump signal from the output laser spectrum, and ensured that only the emission from the LC laser (and not the transmitted pump laser) was recorded. The LC laser emission was collected using a 10× microscope objective focused onto an optical fiber connected to the VIS-NIR USB spectrometer (resolution 1.3 nm).

Förster transfer lasing was performed in mixtures consisting of 1 % w/w DCM and 1 % w/w LD800 in the nematic BL006. 3 % w/w of the chiral dopant BDH1281 was added to provide a long photonic band-edge at around 800 nm. The mixture was filled as described previously into planar-aligned cells (10 µm thickness). Optical pumping was provided in a similar manner to that described above, but using a fixed-wavelength (532 nm) frequency-doubled Nd:YAG laser (New Wave Research Polaris II). This laser was used instead of the tuneable OPO pump source, as it provided a more optimized pump beam in terms of both improved optical quality and a smaller spot size (110 µm diameter). The OPO was later used to verify successful pumping at other wavelengths.

4. RESULTS AND DISCUSSION

4.1 Solubility of infrared dyes

Table 1 shows a summary of the solubility of the eleven dyes chosen for this study, which indicates that only four were compatible with the liquid crystal host: DOTC-P, HITC-P, LD800 and HITC-I. The generally poor solubility is thought to be largely due to the charged ionic nature of the dyes, which are largely incompatible with non-ionic liquid crystal media. The dyes instead show better solubility within more protic solvents, displaying high degrees of polarizability, such as hydrogen bonding within ethanol or water.

In order to obtain an absorbance in the long-wavelength part of the visible spectrum and beyond into the NIR, dye compounds must contain a high degree of conjugation. In this study, the most soluble dyes tended to have long hydrocarbon conjugated chains (HITC-I, HITC-P, DOTC-P). The less soluble dyes mostly consisted of aromatic conjugation (IR125, IR140, IR144, Ox750-P). Such condensed ring systems can result in π-π stacking and thus lead to the aggregation of dye molecules. The rhodamine dye LD800 is an exception to this trend however. It is thought that its peripheral saturated ring structures have a more flattened molecular configuration, leading to reduced π-π interactions, and thus improving its solubility. Sulphur-containing compounds (DTTC-I, IR125, IR140, IR144) will also induce aggregation from sulphur-sulphur interactions, thus further hindering their solvation in the LC host.

In general, the iodide-containing dyes (HITC-I, DMOCT-I, DOTC-I) were found to be unstable. At the elevated temperatures required for thermal mixing, the dyes tended to thermally decompose, leading to iodine deposits and a biphasic texture. HITC-I seemed to suffer from this problem less than the others, and could be successfully dissolved providing temperatures did not exceed 90 °C. However, it instead showed photo-decomposition during subsequent absorbance, fluorescence and lasing experiments.
4.2 Band-edge liquid crystal lasing in the near-infrared

Order parameter studies showed positive values in the range of 0.3–0.4 for all four of the successfully dissolved dyes within the LC host. This indicates relatively good alignment of the dyes’ transition dipole moments with respect to the LC directors. Corresponding dye-doped chiral nematic systems were therefore designed to have the long wavelength edge of their photonic band-gaps located close to the fluorescence maximum (Figure 1), where lasing thresholds are predicted to be lowest.

With the exception of HITC-I (which as described previously was found to be unstable), lasing was successfully achieved with all of the dyes which successfully dissolved in the LC host; HITC-P, DOTC-P and LD800. A range of band-edge lasing emissions were obtainable in the NIR, which spanned the range of their fluorescence spectra, from 738–850 nm. Typical examples of these are shown in Figure 1.

Of the three dyes that successfully lased, LD800 showed the most efficient performance. The performance of HITC-P was probably limited by the non-optimal pump wavelength used, which at 690 nm was slightly shorter than its absorbance maximum of around 750 nm. All three dyes are observed to have very small Stokes shifts, with overlap between their absorbance and fluorescence spectra. This overlap may limit their lasing performance, as some emitted light may be reabsorbed by the dye. The broader fluorescence of LD800 (and slightly reduced overlap) is thought to explain its greatest efficiency of the three dyes. Indeed, both DOTC-P and LD800 were observed to lase most efficiently when emitting at wavelengths slightly beyond their fluorescence maxima, where re-absorbance is reduced.

Figure 1. Absorbance and fluorescence spectra for three successfully dissolved NIR laser dyes in a nematic liquid crystal host (upper figures), and corresponding typical photonic band-gaps and lasing emission spectra (co-located at the long band-edge and fluorescence maximum) when in chiral nematic form (lower figures). Pump wavelength for lasing was 690 nm in each case.
Exact values of efficiency are not given here, but will be reported in a future publication, once further experimental optimization is completed. However, comparative values were obtained. Studies show that slope efficiencies for NIR lasing are comparable to their visible counterparts, with values very similar to the visible dye DCM (Figure 2). It is encouraging to see strong lasing from these systems. The NIR dyes have smaller Stokes shifts (and therefore possibly fewer non-radiative decay processes), which are thought to compensate for their reduced quantum efficiencies.

Roll-off behavior in the output energy with increasing input energies is commonly observed in the slope efficiency data for all LC laser systems. As input energies get too high, effects such as triplet quenching, reorientation of LC directors through thermally or photo-induced torques, or bleaching of the dye can occur. These are detrimental to the lasing process, leading to a roll-off in emission energies as input energies are increased. Although other techniques can be used to circumvent these problems, such as array-based pumping\textsuperscript{15}, it is preferable to use materials that are intrinsically less susceptible. Interestingly, Figure 2 shows that LD800 suffers less from roll-off at high input energies than the DCM system. Indeed the linear relationship between input and output energies was maintained up to the laser’s maximum of approximately 20 µJ/pulse, whereas for DCM, deviation from linear behavior occurs beyond 3 µJ/pulse. Infrared dyes are thought to have shorter-lived triplet states than their shorter wavelength counterparts, which may be accountable for the improvement in performance here.

4.3 Förster energy transfer

To test if lasing in the NIR was possible by Förster transfer, the rhodamine dye LD800 was chosen, as it was found to be the most efficient dye to lase in earlier tests. The visible laser dye 4-(dicyanomethylene)-2-methyl-6-(4-dimethylamino) styryl-4H-pyran (DCM) was chosen to couple energy into LD800. DCM has previously shown high efficiency lasing within a chiral LC host in the region of approximately 600–650 nm, when pumped in the range of 430–532 nm. It has a broad fluorescence spectrum (550–700 nm), which overlaps significantly with the absorbance of LD800 (550–750 nm), as can be seen in Figure 3(a).

An equimolar mixture consisting of DCM and LD800, at a total concentration of 2 % w/w in BL006, was prepared, and the chiral dopant BDH1281 added (3%) to give a long photonic band-edge at around 800 nm. This provided a medium from which band-edge lasing ought to occur close to the optimum wavelength for LD800. As can be seen from the absorbance spectrum in Figure 3(a), the 532 nm pump source is positioned to excite the DCM dye. Meanwhile, as Figure 3(b) shows, the presence of the LD800 completely suppressed and reabsorbed the fluorescence emission from the DCM. Lasing was exclusively observed at 800 nm, indicating that successful band-edge lasing was occurring, enabled by Förster transfer between the DCM and LD800. The same emission was also observed when pumped at 430 nm, although the larger spot size and lower pump energy associated with the non-optimized OPO system meant that efficiencies were not as good, and are not shown here, despite being pumped at a more appropriate wavelength for absorbance by DCM.
Figure 3. (a) Förster energy transfer within the mixture DCM/LD800/BL006 is possible due to the overlap of DCM fluorescence and LD800 absorbance spectra (data taken in nematic host). (b) After adding chiral dopant (3% BDH1281), successful lasing from LD800 is then observed at the band-edge when pumped at 532 nm.

Figure 4. A comparison of slope efficiencies and lasing thresholds between the directly pumped mixture DCM/BL006 (emission at 609 nm) and the Förster transfer enabled lasing mixture DCM/LD800/BL006 (emission at 800 nm). Both systems are pumped using the same excitation source and wavelength (532 nm). Förster transfer causes a rise in threshold, and a slight reduction in efficiency.
A comparison was made of lasing efficiency between the directly pumped DCM system and the DCM/LD800 Förster transfer system. Both were pumped at 532 nm using the same experimental arrangement, and their slope efficiencies and thresholds plotted in Figure 4. As one might expect, efficiency is reduced and thresholds are increased for the Förster transfer lasing system compared to the directly pumped system. The quantum efficiency of the two dye system is predicted to be considerably lower. Competing energy loss (non-radiative decay) mechanisms are also more likely to occur in the more complex system, where the energy difference between pump and emission photons is larger. Nevertheless, slope efficiencies and thresholds are perfectly attainable in a practical system.

The next logical stage to this research is to create a gradient pitch cell, consisting not only of directly-pumped visible dyes, but also of Förster transfer enabled NIR dyes. It is predicted that a tuneable LC laser could therefore be successfully demonstrated, pumped at a common wavelength of 430 nm (or possibly even shorter), with coherent emission anywhere in the range of 460–850 nm. Selection of the LC laser emission to arbitrary wavelengths would then be made possible by spatially tuning the location of the pump spot across the gradient pitch cell. Example spectra of individual LC lasers, using various dyes, all successfully pumped at 430 nm (either directly or by Förster transfer), are shown in Figure 5. Variations in efficiencies between the dyes could also be compensated for by control of concentration within the host. We therefore see no obstruction to the successful realization of a widely-tuneable LC laser over a 400 nm range, and hope to report on it in due course.

![Example spectra from a range of LC lasers, from the visible to near-infrared. All of the dyes can be pumped at a common wavelength of 430 nm either directly or by Förster transfer, enabling a visible to near-infrared tuneable LC laser to be realized.](image)

**5. CONCLUSIONS**

A range of commercially available organic laser dyes have been assessed for their suitability as gain media within a chiral nematic host for band-edge liquid crystal lasing. Many dyes were found to be either insoluble or unstable. However three of the dyes (HITCTP, DOTCTP and LD800) all showed successful lasing emission in the range of 735–850 nm, when pumped at 690 nm. Efficiencies of these directly-pumped NIR lasers are comparable to their visible counterparts, despite having lower quantum efficiencies. Furthermore, these efficiencies are maintained at high input powers, suggesting that they are capable of higher power outputs than are capable by equivalent shorter wavelength dye-doped systems.

Successful demonstration of NIR lasing has also been achieved from LD800, enabled by Förster transfer from the visible dye DCM, pumped in the range 430–532 nm. It is envisaged that this will enable the successful realization of a widely-tuneable LC laser, capable of emission anywhere between 460–850 nm, whilst pumped with a single common pump source. Such devices are expected to find numerous applications as low-cost and compact tuneable or fixed wavelength laser sources, especially in areas such point-of-care optical medical diagnostics and sub-dermal medical imaging.

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7. REFERENCES