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Abstract

Lasers are important components in the advanced imaging techniques that have enabled rapid progress in biomedical research. Tunable wavelength lasers provide control of sample illumination, desirable for efficient fluorophore excitation, but are currently large and expensive. Liquid crystal (LC) lasers can be continuously tuned across the visible spectrum and, although not commercially available, can be fabricated cheaply. The aim of this thesis is to develop LC lasers for, and demonstrate their use in, biomedical imaging, thus providing evidence for their commercial potential.

LC laser devices emit with much lower average power than is desirable for imaging. Two approaches to increasing the average power output were investigated, firstly using flowing LC droplets and secondly using a spinning LC cell. The spinning cell technique enabled emission at a pulse repetition rate of 10 kHz, with improved energy stability and acceptable wavelength stability. This is the highest repetition rate and highest average power (4.5 mW) achieved with a LC laser to date. This result means that LC lasers can be considered for use in biomedical imaging and a broader range of applications. The LC laser could be operated for 2 hours at 10 kHz with less degradation in power than in static cell systems, indicating improved commercial viability.

A stable emission wavelength, within ±2 nm, was demonstrated from a spinning cell with large, Grandjean domains. The quality of cells was therefore critical and large LC cells were required to maximise the benefits of the technique. Substrate surface flatness was found to be important in the fabrication of large, high quality cells.

A portable spinning cell LC laser system was developed and integrated into a fluorescence microscope. The system was successfully used to capture fluorescence images of a fixed tissue sample, and was the first use of LC lasers as a light source for imaging. Multi-wavelength LC laser cells allowed convenient, arbitrary wavelength selection or rapid wavelength switching in a pre-defined sequence. The LC laser system was also found to be more affordable than competing tunable wavelength laser technologies.

The flowing droplet approach was found to be a feasible method for achieving high repetition rate LC laser emission but did not result in sufficient intensity for imaging due to omnidirectional emission. Investigations into the effect of droplet shape on emission properties demonstrated a technique for manipulating laser light in microfluidic optical devices that could be used to enhance the sensitivity of LC droplet sensors.
Rapid progress in biomedical research has been enabled by developments in imaging techniques that rely on advanced optical systems. An important component of all imaging systems is the light source that illuminates the sample that is being studied. Advanced imaging techniques often have very specific illumination requirements, such as a specific wavelength of light, and often use lasers as light sources. Most lasers have a fixed emission wavelength so can only be used in certain experiments and hence multiple laser sources are often required, resulting in high equipment costs. Tunable wavelength lasers can be used instead but are currently large and very expensive. Liquid crystal (LC) lasers are not yet commercially available but could provide a solution to this problem as they are tunable and can be fabricated at low cost. The aim of this thesis is to develop LC lasers for, and demonstrate their use in, a biomedical imaging application. This would generate data that could be used as evidence for the commercial potential of LC lasers.

A typical LC laser device is not powerful enough for imaging. One objective of this research was therefore to design a LC laser system with higher output power. Two separate approaches were investigated, one using flowing LC laser droplets and one using a spinning LC laser cell. LC lasers emit pulses of light; both techniques were intended to allow pulses to be emitted with higher frequency, hence achieving higher power for a given pulse energy.

The spinning cell technique enabled a LC laser to emit pulses at relatively high frequency (10 kHz), resulting in the highest average power output reported from a LC laser to date (4.5 mW). The laser could be left running for 2 hours at full power without the catastrophic drop in power output seen without a spinning cell. These findings mean that LC lasers could be considered for biomedical imaging and other applications where stable emission of several milliwatts is required for an extended period. A stable emission wavelength, within ±2 nm, was also demonstrated. This was achieved through developments in LC laser cell fabrication methods; the properties of the glass used to make the cells were found to be particularly important. Fabrication of large or complex devices remains challenging, and would benefit from highly controlled manufacture processes.

A portable spinning cell LC laser system was built and fitted to a microscope. The system was successfully used to capture fluorescence microscopy images of a biological sample, and was the first use of a LC laser as a light source for imaging. The total
cost of the laser was much less than competing tunable wavelength laser technologies, meaning that the benefits of a tunable light source could be made more widely available. Methods of providing fast and convenient wavelength switching with a LC laser system were demonstrated.

The flowing droplet approach to high power LC laser emission was found to be unsuitable for use in imaging applications. However, it was demonstrated that a flowing droplet LC laser system is feasible and, with careful control of the droplet environment, may be suitable for use in microfluidic optical devices. This could be used to develop LC droplet sensors.
Declaration of authorship

I declare that the work presented in this thesis was undertaken by myself except in the instances listed below.

The laser emission and transmission spectra from droplets, presented in Figures 4.10 and 4.13, were collected by Mr Konstantinos Englezopoulos, who also prepared the DD-CLC mixture used for lasing droplets.

Confocal microscopy images in Figures 4.9(a), 4.11(a) and 4.12(a) were taken with assistance from Dr Anne Pawsey.

The images of the cell filling and cooling processes presented in Figures 5.12 and 5.11 were taken by Mr Zhihong Zeng, supervised by myself.

The portable laser prototype was initially constructed by Mr Andy Mullen in the School of Engineering mechanical workshop. Andy and Mr Steve Gourlay also contributed to the mechanical design by advising on suitable materials and fixtures.

This thesis has not, entirely or in part, been submitted for any other degree or professional qualification.

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Chapter 1: Introduction

1.1 Introduction to liquid crystal lasers

Liquid crystal (LC) lasers are small and versatile optical devices that have a large variety of potential applications, including medical diagnostics, imaging and laser displays [1]. Narrow line-width laser emission can be generated with high efficiency and with an emission wavelength that can be continuously tuned across the visible spectrum. The wavelength is determined by the molecular structure of the LC, which self-assembles, allowing ‘bottom-up’ fabrication processes similar to those used in LC displays. The device fabrication is consequently relatively inexpensive and highly scalable. LC lasers are not currently commercially available, but have the potential to be smaller and cheaper than other tunable wavelength laser technologies. A large body of experimental research, backed by thorough theoretical studies, has led to an advanced understanding of how laser light is generated within a LC laser and to some knowledge of the materials and processes that result in efficient generation of laser emission [2].

A LC laser is optically pumped at a wavelength that is absorbed by the gain medium which is usually a laser dye dissolved in the LC. The pump must be a Q-switched pulsed laser—typically costing £5000 to £20,000—and currently makes up a very high proportion of the cost of an LC laser system. However, the system cost is still considerably cheaper that most tunable lasers (see Section 1.2.2). Significant cost reductions could be realised if advances in the capabilities of lower cost lasers, such as diode lasers, allowed them to be used as pump lasers for an LC laser system. Pump laser costs could also be reduced if developments in LC lasers enabled the pump laser requirements to be relaxed, for example by developing extremely low threshold LC laser systems. LC lasers are currently suited to applications that require, or can tolerate, a relatively low repetition rate (<100 Hz) and low average power (<1 mW). Increasing the repetition rate and average power of LC laser systems would open up additional applications and is therefore another important area of investigation.

The research reported in this thesis aims to demonstrate some of the advantageous features of LC laser technology by developing a system that is optimised for a specific biomedical imaging application. The aims of this demonstration are both to provide...
benefit to the chosen application and to showcase the technology in order to attract interest from academic or industrial researchers who may benefit from using LC lasers in other applications. A compact, portable and versatile LC laser system was therefore envisaged. This thesis aims to provide evidence that the technology can be of practical use, specifically by improving the tools available for research involving biomedical imaging techniques. The collection of such example data is an important part of the early stages in the process of translating technology from fundamental research towards a commercial product.
1.2 Laser light sources in biomedical imaging

Developments in optical imaging techniques have enabled rapid progress in biomedical research and diagnostics. The study of microscopic organisms, cells and sub-cellular components have been enabled by technological advances in light sources, detectors and optical components such as lenses and filters. Samples are often illuminated with broadband light sources such as light emitting diodes (LED) or halogen bulbs. These can be used in combination with optical filters when narrow bandwidth illumination is required. However, lasers are now commonly used instead or in addition to these sources as they offer a number of advantages, as will be discussed in this section.

One universal advantage of using lasers in imaging systems is that the collimated beam emitted from a laser is much easier to expand to fill an aperture or focus to a small spot or thin sheet, leading to much more efficient and precise control of sample illumination. The coherence properties of laser light also enable some imaging techniques where contrast is achieved through phase differences. There are also some disadvantages; for example, laser light has a relatively long coherence length that can cause unwanted interference patterns in widefield imaging due to reflections from the surfaces of optical components. However, these issues can largely be solved by anti-reflection coatings, temporal scrambling techniques and increased exposure times.

1.2.1 Fluorescence-based imaging techniques

The most common use of lasers in imaging is in fluorescence-based techniques where the light source is used to excite fluorescent molecules (fluorophores) within the sample [3]. These fluorophores can be present naturally (autofluorescence) or can be added in order to label molecules within the sample, resulting in highly specific imaging. The development of a wide variety of small fluorescent molecules, many of which are biocompatible, has been very important in the proliferation of fluorescence imaging. These fluorophores can be conjugated to anti-bodies, bound to toxins or bound to DNA and introduced to cell samples that have been fixed, and have had their cell walls removed. Specific components of the cells are thus selectively highlighted, as demonstrated in Figure 1.1. Live cell imaging is possible with fluorescent proteins that can be expressed inside the live cell by modified DNA in the cell nucleus. Fluorescence-based techniques are now widely used to study the function and dynamics of proteins within cells (see [4], for example), identify chromosomes using fluorescence in-situ hybridisation (FISH), or study the cell environment [5].

Fluorescence-based imaging techniques are also used in medicine. For example, endoscopic procedures are used to detect cancerous tissue in the intestine or stomach [7]. Fluorescence imaging of the retina is used to aid diagnosis of diseases such as
CHAPTER 1. INTRODUCTION

Figure 1.1: An example fluorescence microscopy image, showing cultured cells from an Indian Muntjac deer. Three fluorophores have been used to highlight different parts of the cell: the nuclei are labelled with DAPI (blue), the actin is labelled with Alexa Fluor 488 (green) bound to the toxin Phalloidin and the mitochondria are labelled with Mitotracker Red CMXRos (red). Imaged with a $63\times$, NA = 1.4 objective lens, ApoTome.2 microscope Axiocam 702 mono and Axio Imager (Zeiss). The microscope uses an LED and several gas discharge lamps for sample illumination. [6]

age-related macular degeneration and diabetes [8].

The photodynamics of fluorescent molecules can be used as a quantitative method of studying dynamic systems with fluorescence lifetime imaging (FLIM) [9]. Lifetime information provides additional insight that cannot be obtained from the fluorescence intensity as it is strongly affected by the fluorophore environment. Fluorescence lifetime is also used to study dynamic events, such as protein-protein interactions with techniques such as fluorescence recovery after photobleaching (FRAP) [10]. Some super-resolution microscopy techniques [11, 12] also exploit photodynamics of fluorescent molecules to break the diffraction limit, for example in photoactivation localisation microscopy (PALM).

Three dimensional imaging of transparent samples is possible with confocal microscopy or light sheet microscopy, both of which require fluorescent molecules to be present in the sample and use laser light sources to excite these molecules. Confocal microscopy is most commonly achieved via a scanning technique and therefore requires a small spot of high repetition rate or continuous wave (CW) laser light to achieve
acceptable resolution and image acquisition time. Light sheet microscopy, also known as selective plane illumination microscopy (SPIM), is a newer technique that uses a very thin sheet of laser light to illuminate only the layer of the sample that is being imaged. This results in faster imaging and reduces the exposure of each area of the sample to light, thus minimising damage [13, 14].

1.2.2 Light source requirements

The light source used for fluorescence-based imaging techniques must be carefully selected and integrated into the microscope to optimise results. Different techniques have different requirements, and hence a source with variable emission properties can improve the versatility of an imaging system. Control of sample illumination is very important since fluorophores can be temporarily or permanently damaged by an intense light field, resulting in a much reduced signal. Additionally, most biological samples are sensitive to light and can be damaged by excessive illumination (phototoxicity), which can also lead to localised sample heating. Live cell imaging is particularly difficult since different cells within a sample can have different responses to illumination. The timing of cell processes can be affected by the sample temperature and phototoxicity, altering experimental results.

The fluorescence emission from the sample is very low intensity in comparison to the excitation light, therefore achieving sufficient contrast while minimising the unwanted effects of the light field on the sample is one of the main challenges when imaging biological samples [15]. The signal to noise ratio (SNR) can be maximised through illumination intensity, exposure time, wavelength and location. The use of fluorophores with high quantum efficiencies can minimise the intensity and exposure times required. The use of pulsed light sources can be beneficial as the period between pulses allows time for excited states in fluorescent molecules to decay back to the ground state. However, the repetition rate of pulsed sources limits image acquisition time in imaging techniques involving scanning systems, and so continuous wave (CW) sources are sometimes favoured.

The wavelength requirements for a light source in fluorescence imaging is determined by the absorption spectrum of the fluorophore used. For example, the naturally occurring molecule Green Fluorescent Protein (GFP) is commonly used for live cell imaging and requires excitation with wavelengths at the short end of the visible spectrum (450 nm to 500 nm). The optimum fluorophore for a given experiment depends on many factors, including photostability and quantum efficiency. Many samples have undesirable autofluorescence, which must be minimised by careful choice of illumination wavelength in order to maximise the SNR. Selection of fluorescent proteins for live cell imaging [16] is more difficult, partly because there are comparatively few fluorescent
proteins available, and partly because there are additional factors to consider such as the efficiency of protein expression and toxicity to the cell once expressed. It is also important to ensure that the influence of the fluorescent protein on the cell processes is minimised. The choice of illumination wavelength is even more important when more than one fluorophore is used in a single sample, so that the fluorophores can be independently excited with minimal cross-talk.

Control of the illumination wavelength in a microscope system is often provided by a selection of fixed wavelength lasers of any of the commercially available varieties, commonly including semiconductor lasers, solid state lasers and gas lasers. There are now a large number of different laser wavelengths available. However, having only fixed wavelength light sources means that the imaging system is inflexible as only fluorophores with suitable absorption spectra can be used. Increasing the number of light sources can increase flexibility but dramatically increases the cost of the system.

Tunable lasers would therefore be ideal light sources for fluorescence imaging to enable excitation of any fluorophore, and to enable the use of combinations of fluorophores whose excitation spectra partially overlap. However, commercially available tunable wavelength lasers are expensive and bulky, and require large and complex power supplies and cooling systems. Ti:Sapphire lasers allow tuning in the near infrared (IR) but require optical parametric oscillators (OPO) to achieve visible spectrum tuning. Dye lasers are complex to maintain and operate since they use dyes dissolved in toxic solvents that are pumped under high pressure. The smallest and most affordable tunable sources are supercontinuum white light sources. These are an attractive solution, but these cannot currently deliver much power over some wavelength regions. They are broadband sources so are inherently inefficient if a narrow wavelength range is required since all other wavelengths generated must be discarded with filters. Table 1.1 compares examples of tunable wavelength sources that are currently commercially available; tunable laser systems are clearly unaffordable to many potential users and have a footprint that is undesirably large.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Wavelength range (nm)</th>
<th>Repetition rate (kHz)</th>
<th>Size (m)</th>
<th>Mass (kg)</th>
<th>Cost (£)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super-continuum [17]</td>
<td>450–2400</td>
<td>20,000</td>
<td>0.3×0.2×0.9</td>
<td>4</td>
<td>15,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(no filter)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti:Sapphire with OPO [18, 19]</td>
<td>340–1200</td>
<td>80,000</td>
<td>0.8×0.4×0.2</td>
<td>&gt;40</td>
<td>200,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>plus cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dye laser [20]</td>
<td>570–900</td>
<td>100</td>
<td>1.1×0.5×0.3</td>
<td>30–80</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Examples of commercially available tunable lasers systems, highlighting the high cost and large footprint of this equipment.
1.3 Biomedical imaging with liquid crystal lasers

LC lasers could increase the capability of fluorescence-based imaging techniques and reduce phototoxicity by illuminating a sample with precise control of the wavelength and location. The versatility that a tunable wavelength source provides would enable biomedical imaging experiments to be designed based mainly on biological considerations, without having to take into account the capabilities of the available light source. This change in philosophy could accelerate the progress of biomedical research.

Discussions with microscope manufacturers [21] indicated that a typical laser light source suitable for microscopy would have the characteristics described in Table 1.2. Although the current state-of-the-art in LC laser technology could already have some of these properties, it was assessed that existing LC laser systems would not be able to meet enough of the requirements to enable fluorescence imaging, and therefore further development was required. It was particularly important to improve the average power output and pulse repetition rate so that the technology would be suitable for a wide range of imaging experiments. Wavelength stability was also considered an important parameter. The information gained from this discussion, and from discussions with microscope users, informed the design of the LC laser system discussed in Chapter 7. However, it was agreed that a LC laser system could be useful without having all of the generic properties listed in Table 1.2, as some trade-off in performance could be acceptable to end users if equipment costs were reduced. These properties should therefore not be considered to be strict design criteria, but provide a useful benchmark against which to compare the performance of a LC laser system for microscopy. It is also likely that optimisation of the sample excitation wavelength—possible with a tunable wavelength source—would reduce the power requirement for imaging to 3 mW to 4 mW.

After consideration of the requirements of laser light sources in various fluorescence-based techniques, in comparison to the likely achievable LC laser specifications, it was decided that a LC laser system should be constructed for wide-field fluorescence microscopy, with a target image acquisition time of <1 s per frame. Although its performance would primarily be assessed in this application, a versatile system would be advantageous to allow additional applications to be investigated in future research. A portable device with a small footprint could be easily transported to different research facilities and optically coupled to existing imaging equipment. Other advantageous features were identified, including the ability to switch wavelength in <1 s.
Property | Value
--- | ---
Average output power | 10 mW
Emission energy stability | 8 hours, <2 %
Wavelength range | Many wavelength in the region 460 nm to 850 nm are useful due to the wide range of available fluorophores.
Linewidth | <1 nm
Wavelength accuracy | ±2 nm
Wavelength stability | ±1 nm
Beam divergence | (1.2 ± 0.2) mrad
Operating temperature | 15 °C to 40 °C
Operating lifetime | > 15000 hours

Table 1.2: Typical requirements for lasers used in commercially available microscopy systems.
1.4 Summary

LC laser technology has the potential to improve tools for biomedical imaging, particularly in fluorescence-based techniques where precise control of sample illumination is essential. However, LC laser light sources are not currently available commercially so the potential benefits have not yet been realised. This research aims to advance the technology to meet the needs of a biomedical imaging application, and develop a low-cost, portable laser system to demonstrate the benefits that LC lasers can offer. The system will be primarily designed to meet the illumination requirements of wide-field fluorescence microscopy with multiple fluorophores, but with some flexibility to enable use in other imaging applications with minimal modification.
1.5 Thesis outline

The theoretical background necessary to understand LC lasers and their emission characteristics is given in Chapter 2. The optical experimental methods used throughout the project are described in Chapter 3. Two approaches to achieving the optical output required for fluorescence microscopy are then explored. Firstly, Chapter 4 describes research into a microfluidic laser system using LC droplets to form transportable microlasers. Secondly, Chapter 6 describes proof-of-concept spinning cell experiments, supported by the development of suitable liquid crystal cell fabrication processes reported in Chapter 5. The spinning cell approach was found to be more appropriate and therefore a portable spinning cell LC laser system was developed. Chapter 7 reports the design of this system and its use in fluorescence microscopy experiments. Conclusions are drawn in Chapter 8 regarding the benefits of using LC lasers in microscopy techniques, in comparison with competing technologies. Some future perspectives on the applications of LC lasers are also discussed.
Chapter 2: Theoretical background

2.1 Introduction to liquid crystals

2.1.1 Historical context

The existence of a phase of matter between solid and liquid was first discovered by Reinitzer in 1888 [22]. Naturally occurring cholesteryl materials were observed to appear cloudy in a certain temperature range; below this range the material was a crystalline solid, and at higher temperatures a clear liquid. The new phase of matter was described as a liquid crystal (LC) due to having some of the properties of a crystalline solid while being ‘soft’ like a liquid. The LC phase of matter is also sometimes described as a mesophase, leading to materials that can show liquid crystal behaviour to be called mesogens. Research into these materials accelerated in the 1960s when it became clear that they have many industrial applications, most notably in display technology. A detailed account of the development of LC research can be found in Reference [23]. Much of this research has been successfully commercialised and LC devices are now extremely common in everyday life. LC research is currently focused on exploiting the properties of LC materials for other applications such as spatial light modulators, optical interconnects, tunable filters and lasers [24].

2.1.2 Liquid crystal mesophases

For a material to be mesogenic, its molecules must have shape anisotropy, typically with an aspect ratio of 5 or greater [25]. Rod-like molecules, a few nanometres long, can exhibit the long-range order that gives rise to the crystalline properties of a LC, as illustrated in Figure 2.1. An essential feature of their molecular structure is a rigid core (typically aromatic) and a flexible tail. These materials are described as calamitic mesogens. Similar order is also possible in materials with flat ‘disc-like’ molecules, known as discotic mesogens, although these are less common and so will not be discussed in detail. A unit vector describing the average direction of the long-axes of molecules in a calamitic (or the short molecular axes in a discotic) is known as the director, \( \hat{n} \), and is useful in describing the molecular structure. In most cases (and in all materials...
discussed in this thesis), the short molecular axis has no preferential direction and the molecules can rotate freely about the director.

Example structures formed in a mesogenic material in solid, LC and liquid phases are illustrated in Figure 2.1, showing a decreasing degree of order. Many LC mesophases with different degrees of order have been observed and it is possible for one material to exhibit more than one mesophase between its liquid and solid states. Transitions between mesophases are caused either by temperature (thermotropic) or by density via the influence of solvents (lyotropic). The materials used in this thesis exhibit thermotropic transitions. The temperature at which a thermotropic mesogen transitions from solid to LC is the melting temperature, $T_M$, and the temperature of the LC to liquid transition is the clearing temperature, $T_C$.

The least ordered LC mesophase is nematic, $N$. In this mesophase molecules have orientational order (their directors are aligned) but no positional order (see Figure 2.1(b)). The degree of alignment is given by the order parameter, $S_{LC}$, which depends on $\theta$, the angle between the molecular long-axis and the director [25]:

$$S_{LC} = \left\langle \frac{1}{2} (3 \cos^2 \theta - 1) \right\rangle$$

(2.1)

$S_{LC} = 1$ describes a perfectly aligned nematic state whereas $S_{LC} = 0$ describes an isotropic material (no molecular alignment). Negative order parameters indicate different states to positive values, with $S_{LC} = -1/2$ indicating a state where the short molecular axes are aligned in a single plane but the long molecular axes are randomly orientated.

Chiral versions of nematic materials exist, where the director rotates about a helical axis. The rotation is caused by the twisted shape of some or all of the molecules in the material, and the twist can either be left or right handed. Chiral mesophases are denoted by an asterisk, for example $N^*$ describes a chiral nematic system, also known as a cholesteric because the first $N^*$ materials discovered were cholesteryl...
mixtures. Nematic materials can be made chiral with the addition of a chiral dopant, the concentration of which determines the pitch, $P$, of the resulting $N^*$ material. This relationship is described in Equation 2.2, where $x$ is the dopant concentration and $HTP$ is its helical twisting power. There are many other LC mesophases [26], however a full discussion is beyond the scope of this thesis, which will mainly concern $N^*$ materials.

$$P = \frac{1}{(HTP)x}$$ (2.2)

Bulk LC materials consist of ordered regions punctuated by line or point defects where the order is disrupted by a discontinuity in director orientation [27]. LC materials can be aligned to a surface [28], which influences the orientation of molecules in the bulk material. Surface alignment can be used to minimise the number of defects and control the position of defects. For these reasons, and to minimise scattering, most LC applications use thin films of LC material, such that the molecular structure is well controlled throughout. Surfaces can be treated so that the molecules preferentially align parallel (planar alignment) or perpendicular (homeotropic alignment) to the surface. In the case of planar alignment, the surface can be further conditioned so that the director is pointing in the same direction across the whole surface. LC structures under different alignment conditions are illustrated in two dimensions in Figure 2.2 for a $N$ material (a-c) and $N^*$ material (d-f). The nematic structure in 2.2(a) has uniform optical properties and can be used in LC displays. Planar alignment of a nematic 2.2(b) can either result in gradual changes in the director in the plane of the substrate, creating point defects, or a uniform texture, if the surface is conditioned so that one director orientation is favoured. This latter case is commonly used in LC displays. Without alignment, many point and line defects are present within a nematic sample, as illustrated in 2.2(c). In the $N^*$ case, planar alignment results in a standing helical structure where the helical axis is perpendicular to the surfaces, as illustrated in Figure 2.2(e). This structure is also known as Grandjean texture and is important for some lasing mechanisms. In the absence of strong alignment forces, small chiral regions form with randomly orientated helical axes (Figure 2.2(f)), known as a focal conic texture. This structure also has many defects. Under homeotropic anchoring conditions a $N^*$ LC can form several structures, including focal conic textures. A structure known as a uniform lying helix can also be formed [29], as shown in 2.2(d), normally in response to an applied electric field.

### 2.1.3 Optical properties of LC films

The molecules in mesogenic materials have optical anisotropy that gives LC mesophases distinctive optical properties. The long axes of the molecules have different refractive indices to the short axes, known as the ordinary and extraordinary refractive indices,
14 CHAPTER 2. THEORETICAL BACKGROUND

Figure 2.2: An illustration thin film liquid crystal structures between substrates (not to scale).
(a) Homeotropic alignment of a $N$ material, (b) planar alignment of a $N$ material, (c) a $N$ material with no surface alignment (d) an example structure for homeotropic alignment of a $N^*$ material (special case where a uniform lying helix is achieved), (e) planar alignment of an $N^*$ material (standing helix) and (f) a $N^*$ material with no surface alignment (focal conic texture). The pitch of the helix in the $N^*$ material, $P$, is defined.

$n_o$ and $n_e$, respectively. This property is known as birefringence and is exploited in optical applications of LC materials. Birefringent molecules experience a torque when a field is applied, and therefore fields can be used to control the molecular orientation and structure of mesogenic materials. Birefringence also allows the molecular structure of LC films to be probed with polarised light.

Polarising optical microscopy (POM) is the primary method used to investigate the structure of a LC film. White light is passed through a linear polariser, then through the sample, followed by another linear polariser (known as the analyser). The polariser and analyser are at 90° such that in the absence of a sample, all light is prevented from reaching the detector. Thus an isotropic sample appears dark whereas the intensity of an image of a birefringent sample depends on the orientation of the director field with respect to the plane of polarisation. A uniform planar-aligned nematic sample therefore appears bright if the director field is not aligned with the polariser, and dark if the polarisers are rotated by 90°. A Grandjean texture $N^*$ film appears bright, but in contrast to a nematic, does not change when the sample is rotated. Rotating the sample with respect to the polarisers is therefore helpful in identifying LC textures.

Example POM images of the common $N$ and $N^*$ structures illustrated in Figure 2.2 are shown in Figure 2.3. Homeotropic aligned $N$ samples appear dark, as in Figure
2.3(a), and can only be identified as birefringent if defects are present (or created by deforming the substrates). Planar alignment of a N material with no preferential director orientation results in the texture shown in 2.3(b). Poor alignment of a N material results in ‘marble’ textures; an example is shown in 2.3(c). A uniform lying helix with a N* material can be identified by the ‘fingerprint’ texture shown in 2.3(d). A N* film with Grandjean texture has line defects known as ‘oily streaks’ that are characteristic of this texture (see 2.3(e)). A focal conic texture is present in 2.3(f), with each ‘fan’ corresponding to a different orientation of the helix. The appearance of N* materials under POM often depends on whether the pitch of the helix can be resolved by the microscope system.

![Figure 2.3: Example POM images of LC structures, corresponding to the structures illustrated in Figure 2.2.](image)

---

Although there are some difficulties in inferring a 3-dimensional molecular structures from 2-dimensional POM images, many common structures can be easily identified if the material properties are known. POM is therefore used in this thesis as a method of understanding the structure in LC laser devices. A fuller discussion of nematic and...
$N^*$ textures is given in Reference [31], along with further example POM images. $N^*$ materials with Grandjean texture have particularly interesting optical properties. The rotation of the molecular director around the helical axis results in a periodic variation in the refractive index, which causes selective reflection of a range of wavelengths, as indicated in Figure 2.4. This photonic band gap (PBG) has a central wavelength ($\lambda_0$), determined by the helical pitch of the LC material, and width ($\Delta\lambda$), determined by its birefringence. These properties are described for an angle of incidence of 90° in Equations 2.3 and 2.4, respectively [32]. The PBG only exists along the helical axis (i.e. is one-dimensional) and for circularly polarised (CP) light of the same handedness as the helix. The minimum transmission in Figure 2.4 is approximately 50% because the sample was illuminated with unpolarised light.

![Figure 2.4: An example transmission spectrum of an $N^*$ material showing a partial PBG. The central wavelength ($\lambda_0$) and width ($\Delta\lambda$) of the PBG are indicated. Fabry-Perot interference fringes from the LC cell are also present in the transmission spectrum.](image)

\[
\lambda_0 = P\bar{n} \quad (2.3)
\]

\[
\Delta\lambda = P(n_e - n_o) = P\Delta n \quad (2.4)
\]
2.2 Liquid crystal lasers

2.2.1 Overview

The optical properties of LC materials can be used to create resonant cavities which emit laser light when combined with an appropriate optical gain medium and pump energy source (a pulsed laser). LC materials have the advantage that resonant cavities can self-assemble, under the right conditions, removing some of the challenges associated with fabricating resonant cavities such as the precise alignment of mirrors or diffraction gratings. LC lasers therefore have the potential to be manufactured at low cost. Another advantage is the tuneability of the self-assembled structure, which allows control of the laser wavelength through various mechanisms (see Section 2.2.6). The high efficiencies achievable with LC lasers mean that there is no need for large power supplies or cooling systems, making compact or even portable laser systems possible.

LC lasers can be classified into several types that describe the form of resonant cavity. The most common type is the distributed feedback (DFB) laser in which a periodic variation of the refractive index is used to reflect some wavelengths. These will be the focus of this project. Other types of LC lasers include random [33] and whispering gallery mode [34, 35].

2.2.2 Band edge lasing

Photonic band edge lasers fabricated from liquid crystal materials were first demonstrated by Kopp et al. [36] in 1998, using a N* LC material with a Granjean texture. The PBG in this structure provides a resonant cavity that supports laser modes at the edges of the PBG where there is a high density of photonic states. Laser modes can also exist between the PBG edges, if defects are present [34, 37].

Below a certain pump pulse energy ($E_{pump}$), known as the lasing threshold $E_{th}$, the emission is spontaneous, thus incoherent and random in direction. Above this threshold, coherent laser light is emitted via stimulated emission along the helical axis in both directions, in diverging cones. The divergence is caused primarily by diffraction and therefore depends on pump spot diameter [36]. The output energy increases linearly with the input energy, as shown in Figure 2.5. The slope efficiency of a LC laser, $\eta_s$, is defined as the gradient of a plot of the output energy against the input energy, above the lasing threshold (see Equation 2.5), and is often used as a performance metric. The slope efficiency is influenced by material and device properties and approaches to engineering a system with high efficiency are the focus of much of this Chapter. Low thresholds are also desirable and the value of $E_{th}$ also depends on both material and device properties. The lasing threshold is theoretically described by Equation 2.6,
where $\lambda$ is the laser wavelength, $k$ is an absorption coefficient and $L$ is the length of the LC cavity [38].

The laser light emitted from a band-edge LC laser is circularly polarised with the same handedness as the chiral structure [36, 39]. LC laser cells with one metallic reflective substrate result in linearly polarised emission due to the superposition of CP emission and the reflected CP emission of opposite handedness [40].

![Graph showing the emission pulse energy from a LC laser cell with increasing pump laser pulse energy. A linear relationship is fitted to data below the lasing threshold (dotted line) and to laser emission data (solid line). The lasing threshold (1.2 µJ) is identified as the intersection between these 2 lines and slope efficiency (11.6%) as the gradient of the solid line.](image)

**Figure 2.5**: A graph showing the emission pulse energy from a LC laser cell with increasing pump laser pulse energy. A linear relationship is fitted to data below the lasing threshold (dotted line) and to laser emission data (solid line). The lasing threshold (1.2 µJ) is identified as the intersection between these 2 lines and slope efficiency (11.6%) as the gradient of the solid line.

\[
E_{out} = \eta_s (E_{pump} - E_{th}) \tag{2.5}
\]

\[
E_{th} \propto \frac{\lambda^2}{\Delta n (1 - e^{-kL})L^2} \tag{2.6}
\]

Equation 2.6 indicates that LC materials with high birefringence should be chosen to achieve low threshold lasing. Morris et al. found that this was true when experimentally comparing LC lasers using different nematic host materials, and also demonstrated that high birefringence was linked to high slope efficiency [41]. Similarly, high LC order parameter was linked to low thresholds and high efficiencies. Both observations were attributed to a high density of photon states at the PBG edge.
2.2.3 Optical gain media

The optical gain in a LC laser is typically provided by an organic laser dye that is dissolved in the LC. The material can be modelled as a simple 4-level laser system as illustrated in Figure 2.6(a) [42]. The dye absorbs photons from the pump laser, promoting electrons from the ground state, $S_0$, to the first excited state, $S_1$. After some loss of energy via vibration, the electrons can decay radiatively to $S_0$: this is the highest probability transition and is responsible for the laser emission. It is also possible for electrons in $S_1$ to transition to a triplet state $T_1$, in a process known as inter-system crossing. Triplet states have a comparatively long lifetime and can also be excited by photons from the pump laser. The presence of triplet states is detrimental to laser efficiency as it reduces the number of photons that decay via the lasing transition.

![Figure 2.6](image)

Figure 2.6: (a) A Jablonski energy level diagram showing radiative (solid lines) and non-radiative (dashed lines) transitions between energy levels in a dye molecule. The lasing transition occurs between $S_1$ and $S_0$, whereas the triplet states ($T_1$ and $T_2$) provide competing processes. (b) An illustration of a dye molecule (red) aligned in a nematic LC (grey) showing the definition of $\theta$.

Laser dyes must have good solubility in the LC host, as aggregation of the dye molecules leads to less efficient absorption and can also disrupt the chiral LC structure, degrading the quality of the resonant cavity. Dyes must be therefore doped at a suitably low concentration to avoid aggregation and to ensure that the pump laser penetrates the full thickness of the LC film. However, very low concentrations do not provide sufficient optical gain. Studies have shown that 0.5% wt to 1% wt is an appropriate doping concentration [43]. Dye molecules are also typically anisotropic and emit preferentially along one axis. The alignment of a dye with the LC host molecules is
described by the dye order parameter, $S_{\text{dye}}$, analogous to the LC order parameter given in Equation 2.1. In this case, $\theta$ denotes the angle between the dye molecule emission dipole moment and the LC director, as shown in Figure 2.6(b). $S_{\text{dye}} = 1$ indicates perfect parallel alignment with the LC director whereas $S_{\text{dye}} = -1/2$ indicates perfect perpendicular alignment. The dye order parameter is of interest primarily because it determines which PBG band edge is preferred for lasing; positive values result in enhanced fluorescence and therefore preferential lasing at the long wavelength band edge whereas negative values result in a preference for the short wavelength band edge [44]. Highly ordered dyes are therefore thought to result in efficient lasers since one band edge is strongly favoured [45], a conclusion that is supported by the results in [41].

The absorption and emission spectra of the dye are extremely important and there are several features to consider. Firstly, the maximum of the dye absorption spectrum should be near the pump laser wavelength so that the pump energy is absorbed efficiently. Secondly, the emission spectra must overlap with the favoured edge of the PBG such that the emission is coupled into the resonant cavity. Lastly, the Stokes shift (wavelength difference between the absorption and fluorescence maxima) should be large enough to minimise re-absorption of the emitted photons. An ideal combination of pump wavelength, dye absorption, dye emission and PBG position is shown in Figure 2.7.

Other photophysical dye properties such as the fluorescence quantum yield also influence lasing efficiency. A variety of different commercially available dyes have been identified in previous studies as suitable for use in LC laser systems [43, 46–48], and the dyes used in this research have been selected from this range. Additional suitable dyes have been synthesised [49–51] however commercial materials were favoured in this project due to being reliably available in a repeatable form.

A further consideration is the resistance of a dye to photobleaching. Photobleaching occurs when triplet states are excited resulting in a temporary reduction in the number of photons decaying radiatively via the lasing transition. This effect means that a pulsed pump source is required, such that triplet states are allowed to decay to the ground state, and limits the pulse repetition rate and pulse durations that can be used. It is also possible to permanently damage dye molecules with extremely high input pulse energy, further reducing the efficiency of the LC laser emission [42].

Alternative gain media that do not have triplet states, such as fluorescent inorganic nanoparticles or quantum dots, are therefore being considered for future LC laser systems (see [52], for example) and could provide a route to achieving high repetition rates or even continuous wave (CW) lasing [53]. However, these are often insoluble in the LC host so can aggregate, preventing efficient absorption of the pump laser and distorting the LC structure [54]. Quantum dots typically have a lower quantum
efficiency than organic dyes, and have not yet resulted in low threshold, high efficiency lasing, when compared to dye-doped LC lasers.

2.2.4 Optical pumping

LC lasers are optically pumped using a nanosecond or picosecond pulsed laser with a pulse energy greater than the lasing threshold. Currently, a Q-switched diode pumped solid state (DPSS) laser is required to achieve sufficient energy in this short pulse duration. These pump lasers are relatively large and expensive so are a major contributor to the bulk and cost of any LC laser system, and negatively affect the case for commercialising the technology [40]. The input pulse energy and frequency must be limited and exceeding these limits results in reduced efficiency or complete cessation of laser emission [55]. At 1 Hz pump frequency, efficient laser dyes can emit up to 19\(\mu\)J per pulse [43]. However, LC lasers are rarely operated above 10 Hz, meaning that the average power output is typically low (<0.2 mW).

Experimental studies by Morris et al. concluded that the primary cause of performance degradation at high input power is the distortion of the CLC structure,
through optically induced rotation of the LC and dye molecules [56]. This was accompanied by a redshift in emission wavelength. The rotation of the molecules results in degradation of the resonant cavity and ultimately the cavity losses become too large for laser emission. A local rise in temperature caused by high power illumination contributes to distortion of the CLC structure [57], suggesting that thermal management strategies could improve output stability. Etxebarria et al. argued that thermal effects also increase scattering of the pump beam, which significantly reduces laser efficiency [58]. Polymer stabilization of the CLC may provide a mechanism for improved resistance to optically and thermally induced LC reorientation [59, 60], but introduces difficulties in achieving high quality LC alignment and thus efficient, low-threshold and narrow-linewidth laser emission.

The response of the dye molecules to the pump laser pulses also influences the maximum input pulse frequency and energy that can be used, as discussed in Section 2.2.3. Excitation with pump pulses with a duration $>0.1\text{ ms}$ is predicted to increase the triplet state population such that lasing is prevented [53]. Attempts to pump LC lasers with CW lasers (infinite pulse duration) or incoherent sources have only achieved enhanced fluorescence (amplified spontaneous emission) at the PBG edge, with no evidence of coherent laser output [60]. It is likely that, even with a gain medium that does not have triplet states, CW pumping would not be possible with the minimum lasing threshold energies achieved to date, since the intensity of light required would caused undesirable thermal effects [53].

There have been no detailed experimental studies on the effect of pump laser pulse duration (since this parameter cannot be easily varied in most commercial pump laser systems), but a comparison of results using picosecond-pulsed and nanosecond-pulsed pump lasers concluded that a shorter pulse results in lower lasing thresholds [61]. Theoretical studies have also suggested that longer pump pulses ($>10\text{ ns}$) result in reduced laser efficiency, due to the accumulation of triplet states in the laser dye [62], as discussed above.

The polarisation of the pump laser can be chosen to maximise the laser efficiency. If the pump wavelength is within the PBG, a circularly polarised pump with opposite handedness to the $N^*$ LC helix means that it is not reflected by the PBG and can therefore be absorbed by dye molecules along the full length of the cavity [63]. On the other hand, using circularly polarised light of the same handedness as the helix has been shown to enhance absorption if the pump laser wavelength is at the short edge of the PBG [64]. This method increased the laser efficiency and decreased the threshold so could be useful for optimising the laser performance. However, a LC laser system that included wavelength tuning with a single pump laser could not take advantage of this phenomenon at all wavelengths, and hence circular polarisation with opposite
handedness to the helix is the best strategy for a tunable system. This strategy also allows pumping at any angle of incidence; the pump angle affects the PBG position and therefore can be important if the pump is not circularly polarised to prevent reflection.

### 2.2.5 Overcoming output power limitations

Increasing the maximum average power output of a LC laser is desirable for some applications, including some imaging methods. Small improvements have been achieved by pumping the LC laser medium through a microlens array, and combining the output from the resulting array of LC laser emission [65]. This approach results in greater energy per pulse at a low pulse repetition rate, and also provides an opportunity for simultaneous polychromatic emission (see Section 2.2.6) [47]. An alternative method of increasing the average power output is to increase the pulse repetition rate, which is, in itself, desirable for some applications. In particular, imaging applications that require scanning lasers use high repetition rate or continuous wave (CW) lasers. However, high repetition rate pumping of LC lasers causes a reduction in laser efficiency, as discussed in Section 2.2.4. A method of maintaining a high efficiency at high pump repetition rates is required to enable LC lasers to be suitable for a broader range of applications.

Three different approaches have been reported:

- Moving the pump beam through dynamic holographic pumping, using a diffractive spatial light modulator, such that a new area of the LC cell is used for each laser pulse [66]. The movement of the input beam gives rise to displacement of the output beam, meaning that this method is unsuitable for microscopy or other applications where a consistent output beam position is required.

- Flowing the liquid crystal material such that new dye material is excited by each pulse [67]. This concept has been successfully used in commercial dye lasers [68]. Use of a 1 kHz pump laser was demonstrated in a flowing LC laser system but resulted in wavelength changes and will also have an upper flow rate limit where the CLC structure is destroyed through flow-induced alignment processes.

- Rotating the LC cell on a motorised stage such that a new area of the cell is excited by each pulse [69, 70]. This was primarily aimed at increasing the stability of LC laser emission over long time periods (days), but could also feasibly be used to enable higher pulse repetition rates. Similar methods have been used to achieve continuous wave emission in solid-state dye lasers [71].

### 2.2.6 Wavelength tuning

The ability to tune the wavelength of a LC laser is one of the main advantages of the technology for many applications, including biomedical imaging techniques. Several
possible tuning methods are outlined in this section. The tuning range, speed, precision
and ease of integration into a portable system are all important factors when assessing
the suitability of tuning methods for imaging applications.

The laser wavelength is determined by the pitch of the helical structure formed by
the chiral nematic LC material, as discussed in Section 2.2.2. This can be controlled
through the chemical composition of the CLC mixture; a higher concentration of chiral
dopant results in a shorter helical pitch. A reliable approach to making a tunable laser
system would be to make a large number of laser cells of different composition and select
the desired wavelength mechanically, or manually in a cartridge-style system. Although
not continuously tunable, this ‘selectable wavelength’ system could be customised to
an application and therefore offer the required flexibility over a very broad wavelength
range [72, 73].

Large changes in wavelength can be achieved within a single cell by allowing two
mixtures of different chiral dopant concentration to diffuse together, thus creating a
pitch gradient across the cell [46, 47, 74]. Translation of the cell across the pump
beam therefore results in ‘quasi-continuous’ tuning from chiral domains of different
pitch. Diffusion continues within the cell until it is homogeneous, a process that
takes days or weeks, and would be problematic if repeatable performance is was
required over a long period. Approaches to stabilising LC structures have included
polymerisation [75] which could allow an appropriate chirality gradient to be more
permanently fixed, although this has not yet been demonstrated. A stable gradient
pitch cell may also be possible by creating a polymer chiral template then filling with
a dye doped nematic mixtures [59, 76], which would have the advantages of removing
concerns about dye damage during the UV-activated polymerisation process. However,
both these approaches require further development before a gradient pitch cell could
be used reliably over a long period of time.

Reversible chemical tuning of the CLC chirality has been achieved by using a
photoactive chiral dopants [77, 78]. The emission wavelength of a LC laser cell
containing this material can be changed by illumination with an LED or CW laser.
The process can be slow, although the most recent studies have achieved 20 nm of
tuning in a few seconds.

The response of LC materials to electric fields provides another reversible method
of wavelength tuning. An applied electric field can be used to distort the helical
molecular structure of a planar aligned LC cell, thus changing the PBG position and
laser wavelength. This was first demonstrated with a chiral smectic (or ferroelectric,
FLC) laser [79], showing a tuning range of approximately 40 nm. This method has
the advantages of being very fast (taking only a few microseconds) and completely
reversible. However, when Choi et al. attempted to use the same mechanism with
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CLC materials, either using FLC layers at the substrates [80] or by doping with FLC [81], the response time was dramatically increased. These systems took over 100 s to tune over a range of 23 nm and 60 nm respectively. Schmidtke et al. showed that fine tuning over a small wavelength range (<4 nm) was possible with a pure CLC material [82], which could be useful in combination with another tuning technique in applications where high wavelength precision is required. However, if a wavelength change of more than 0.5 nm was induced, the distortion to the helix decreased the efficiency of the laser emission. Electric fields have also been used to create a selectable wavelength system by switching the lasing wavelength between the short and long PBG edges [83].

Some of the disadvantages of electrical tuning have recently been addressed by using oblique helicoidal CLCs [84]. In these materials, the molecular director forms an oblique angle with the helical axis, as opposed to the case of CLC materials where the angle is nearly perpendicular. Thus when an electric field is applied, tuning over a broad range (100 nm) can be achieved quickly with little loss in efficiency. Although this technique is promising, current systems have high lasing thresholds, relatively low efficiencies and limited cholesteric temperature ranges.

The wavelength of a CLC laser is also affected by the temperature of the LC mixture. Funamoto et al. observed a change in wavelength of nearly 50 nm for a 10°C rise in temperature, caused by a decrease in the length of the helical pitch [85]. Precise control of the temperature of the LC laser could be difficult in a portable LC laser system so this is unlikely to be the preferred tuning mechanism. Thermal management is an important consideration in LC laser system design to minimise undesirable wavelength fluctuations with changes in temperature. Morris et al. demonstrated that it is possible to eliminate temperature effects chemically by using two different chiral dopants in the LC laser mixture [86]. Dopants were chosen that had the opposite response to a change in temperature, such that a shortening in pitch in one dopant was counteracted by a lengthening in the other. This technique could be useful in a system where precise wavelength control is required outside of a laboratory environment.

2.2.7 LC cell fabrication

The emission properties of a LC laser are affected by the cell that contains the LC laser mixture. An optimised cell design can dramatically improve the efficiency, lasing threshold and repeatability of the laser. Cells can either be transparent, and therefore emit perpendicular to both substrates, or have one reflective substrate to direct the emission out of a single substrate only. A basic reflective LC laser cell is illustrated in Figure 2.8. One of the most important features of a LC laser cell is the internal surfaces of the substrates, as these should promote uniform planar alignment of the LC molecules in order to achieve a Grandjean structure with the helical axis perpendicular.
to the substrates. This is normally achieved by coating the surfaces with an alignment layer and rubbing to create a preferential direction for molecular alignment.

Figure 2.8: The basic construction of a LC laser cell with a reflective back plane. Dimensions are not to scale.

Variation of the director at the substrates of a planar aligned \( N^* \) cell results in many small Grandjean domains with slightly different helical pitches, leading to variations in laser emission wavelength. The domains are separated by oily streak defects. Changes in the helical pitch can also be caused by variations in the distance between substrates (cell gap), an inhomogeneous concentration of chiral dopant in the mixture or contamination in the cell. For a uniform planar aligned cell of constant cell gap, where the director is perfectly aligned at both substrates, only half-integer changes in the number of rotations of the director between the substrates are theoretically allowed. In this idealised case, the difference in pitch between adjacent Grandjean domains is relatively large, and depends on the cell gap. However, the domain size is much larger, with fewer oily streaks, and therefore LC laser cells should be fabricated with the aim of achieving perfectly uniform planar alignment in a cell with constant cell gap.

Alignment of LC materials with rubbed polymer layers was first studied in detail by Berreman in the 1970s, who proposed a theory that the alignment was caused by shape of the rubbed surface [87]. Subsequent work provided experimental evidence that the nematic director aligned with the grooves created on the surface of the substrate, as this configuration was energetically favourable [88]. Later, Geary et al. proposed an alternative theory that some of the molecules in a polymer layer were aligned by the rubbing process and that this promotes parallel LC alignment [89], and provided experimental evidence to support this theory. This latter theory has gained more support over the years, with several studies providing further experimental evidence [90–92]. However, there is still some evidence that substrate topology contributes to the LC alignment (see [93], for example), and it is often stated that both molecular alignment within the polymer layer and sub-micron scale grooves contribute to the alignment of a LC material.

The demands of the display industry drove the development of processes for
achieving high quality planar LC alignment, primarily of nematic materials. It became standard industry practice to coat substrates with a polyimide (PI) material and rub this layer using a cloth on a roller. The substrates were mounted on a stage that was moved under the rotating roller. The PI material used and the deposition process was found to affect the strength and quality of the LC alignment, as well as the tilt angle between the LC molecules and substrate [89, 94].

The rubbing process has many performance-critical variables such as the height of the roller, speed of the roller and cloth material. Uchida et al. attempted to characterise the rubbing process by defining a rubbing strength, \( R_s \), which is proportional to the total length of the cloth in contact with the substrate, \( L \) [95]:

\[
R_s = \gamma L
\]

\[
L = N l \left(1 + \frac{2\pi rn}{60v}\right)
\]

where \( \gamma \) is a constant that depends on the rubbing cloth, \( N \) is the number of passes of the roller over the substrate, \( l \) is the contact length between the cloth and the substrate when both are stationary (determined by the roller height), \( r \) is the radius of the roller, \( v \) is the stage speed and \( n \) is the roller speed (in r/min). The authors presented some evidence that this parameter could be related to the anchoring energy between the LC molecules and surface. For a given cloth and PI material, the equations therefore suggested that a fast, low roller with many passes would produce a higher anchoring energy. Although rubbing strength became a standard metric for describing a rubbing process, there was still limited understanding on the physical effect of different rubbing processes on the polyimide layer.

Later studies were able to take advantage of improved imaging techniques to study the topology of the rubbed PI layer. In particular, Kim et al. observed that the rubbing process aligned polymer molecules into chains, rather than clumps, resulting in grooves less than 50 nm wide and only a few nanometres deep [96]. The authors hypothesised that the grooves were formed by a combination of the shear forces exerted on the polymer by the cloth and local heating of the polymer. They found that as \( R_s \) was increased, the grooves became deeper and also wider, but did not offer comment on whether these larger, deeper grooves were better for LC alignment. It is also not clear which parameter was changed in order to increase \( R_s \). A similar study examined the surface roughness produced by different roller height settings and concluded that the mean surface roughness decreased (from 7.5 nm to 1.5 nm) as the roller was lowered (i.e. increasing \( R_s \)) [97]. This result at first seems to contradict the work by Kim et al., but could be explained if the parameter varied in the earlier study was roller speed rather than roller height.

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There is insufficient data published on this topic to reach a firm conclusion on the optimum rubbing process for producing defect-free planar alignment. It is likely that many studies have been conducted by display manufacturers but not published due to commercial sensitivities. Furthermore, alignment of chiral nematic LC mixtures is rarely mentioned in the published literature, with most studies focusing on nematic materials that are more relevant to the display industry. The LC and PI materials are likely to affect conclusions about the optimum rubbing process. For example, it is possible that the use of a chiral LC means that deep grooves in the alignment layer are not advantageous; these may result in discontinuities in the helix between high and low areas. The development of a consistent process for the fabrication of cells with high quality alignment layers therefore became a large part of this research (see Chapter 5). It should be noted that other techniques have been established for promoting planar LC alignment to a surface (as reviewed by Hoogboom et al. [98]), but these are either not sufficiently mature, or have other disadvantages, such as long processing times, that mean they were not chosen for this project.

Once substrates with appropriate alignment layers have been prepared, these must be assembled into cells with an appropriate gap between them for the LC laser mixture. There is evidence that the optimum cell gap is 14 µm, with a minimum of 8 µm required for lasing in a transparent cell [1, 99]. A minimum thickness of LC laser medium is necessary to allow sufficient absorption of the pump beam by the dye, and thus achieve a population inversion. Reflective cells are able to be thinner since the pump beam passes through the material twice. Increased scattering and reabsorption of stimulated emission photons reduce the laser efficiency if the cell thickness is >14 µm. The quality of the resonant cavity is also degraded in thick LC laser cells since the molecular alignment can only be influenced at the substrates. However, there have been some innovations in cell filling techniques such as using acoustic waves [100, 101], thermal annealing cycles [102] or electric fields [103] that could present opportunities to improve the efficiency of LC lasers made with thick cells.
Chapter 3: Optical experimental methods

3.1 Introduction

This chapter describes the experimental methods used in the analysis of LC laser mixtures, components of LC laser systems and in the optical characterisation of the emission from LC laser cells and droplets. These methods are referred to throughout this thesis. For LC laser mixture design, it was necessary to measure the PBG position of CLC mixtures in order to determine the concentration of chiral dopant required for a specific laser wavelength. Dye absorption and emission spectra depend on the solvent and therefore it was important to measure these in the nematic LC host material. Components such as in-house LC cells and the pump laser were also characterised optically, using techniques described in this chapter as well as standard techniques such as POM and confocal microscopy (see Sections 3.2.7 and 3.2.8, respectively). The emission characteristics of LC lasers were measured in order to evaluate the system performance.

Methods for measuring the following properties are described:

- PBG position;
- Dye absorption spectrum;
- LC cell gap;
- Pump laser spot diameter;
- Dye emission spectrum;
- LC laser emission spectrum;
- LC laser slope efficiency and lasing threshold;
- LC laser droplet emission spectrum.
3.2 Characterisation of LC laser cells and mixtures

3.2.1 Transmission and absorption spectra

The transmission spectra of CLC mixtures were measured by illuminating a small area of the cell, or droplets within a cell, with a tungsten halogen white light source (360 nm to 2400 nm HL-2000-HP-FSHA, Ocean Optics), that was collimated and the beam diameter reduced as much as was possible using three planar convex lenses. The diameter of the beam used to illuminate a LC cell was controlled with a variable aperture. A diagram of the set-up is shown in Figure 3.1. Transmission experiments with bulk CLC material used commercially available 20µm spaced cells with anti-parallel polyimide alignment layers (LC2-20.0, Instec), since these were low-cost and convenient in comparison to in-house cells. Droplet transmission measurements used 20µm or 100µm spaced plain glass cells fabricated in-house. Cells were mounted perpendicular to the incident light on a custom 3D-printed mount. The transmitted light was directed towards a spectrometer (USB4000, Ocean Optics). The resolution of this spectrometer was 1.5 nm full width half maximum (FWHM), and therefore was not suited to measuring the line-width of laser emission. The optical fibre that delivered the white light to the sample (P600-1-VIS-NIR, Ocean Optics) was designed with high transmission from 400 nm to 2100 nm, hence the SNR was poor below 400 nm. An identical set-up was used to measure the absorption spectra of laser dyes in nematic LC.

Figure 3.1: The optical set-up used to record the transmission spectra or absorption spectra of transparent cells.

3.2.2 Cell gap

The experimental set-up described in Figure 3.1 was also used to measure the cell gap between the substrates of an empty cell by measuring the Fabry-Perot interference fringes in the transmission spectrum. The interference fringes can be described by the
equation:

\[ m \lambda = 2d \sin \theta \] (3.1)

where \( m \) is the fringe number, \( \lambda \) is the peak wavelength, \( d \) is the cell thickness and \( \theta \) is the angle of incidence [104]. For this set-up, \( \theta = 90^\circ \), so \( m \lambda = 2d \). The peak wavelengths were determined manually from the transmission spectrum, and a graph of \( 2/\lambda \) against \( m \) was plotted, resulting in a straight line of gradient \( 1/t \). The thickness could therefore be calculated from the inverse of the gradient. The uncertainty on this measurement was propagated from the error on the gradient of the linear fit.

### 3.2.3 Emission spectra

The emission spectra of the laser dyes was collected by exciting the dye-doped nematic cells using a 532 nm Q-switched Nd:YAG laser (Crylas FDSS 532-Q2), as shown in Figure 3.2. The laser was operated at 100 Hz with a maximum energy of 5 \( \mu \)J per pulse. The pulse energy was attenuated via the rotation of a half wave plate (WPMH05M-532, ThorLabs) relative to a fixed Glan laser linear polariser (GT5-A, ThorLabs). The pump beam was expanded, reflected by a 550 nm cut-off dichroic mirror and focused onto a dye-doped nematic LC cell with an achromatic lens. The strongest fluorescence signals were achieved by moving the cell towards the lens, away from the focal plane, such that a larger area was excited and the collection lens received more of the resulting fluorescence.

The same pump laser was used in experiments to measure the emission spectra from dye-doped CLC laser cells. A rotatable half wave plate and a linear polariser were again used to control the energy per pulse of the linearly polarised pump beam. A quarter wave plate was used to circularly polarise the light with opposite handedness to the CLC helix to prevent reflection of the pump beam by the PBG. The 90° pump angle allowed easy alignment of the spectrometer (USB4000, Ocean Optics) or energy meter (PD10, Ophir). The LC laser cells were mounted either on a custom 3D printed static mount or spinning stage, as shown in Figure 3.3. The spinning stage was custom made from aluminium and controlled by a stepper motor (PKP546N18A2, Oriental Motors) with a step-angle of 0.72°, resulting in 500 steps per rotation. The motor was mounted on a 3-axis translation stage such that the pump spot could be offset from the axis of rotation and could also be placed at the focal point of the pump laser. The laser light emitted from the cell passed through the achromatic lens and dichroic mirror, and was focussed either towards the energy meter or spectrometer. A long pass edge filter (cut-off 550 nm, FEL0550, Thorlabs) was used to ensure that stray light from the pump laser was not incident on the energy meter.
Figure 3.2: The optical set-up used to record the fluorescence spectra from dye-doped nematic liquid crystal cells. The quarter wave plate was not necessary for this experiment, but was in place from experiments using CLC cells.

Figure 3.3: The optical set-up used for lab-based LC laser measurements.
3.2.4 Pump spot diameter

The diameter of the pump spot created by the optical set-up in Figure 3.3 was measured using a knife-edge method [105]. The energy meter was placed in the position that the LC cell would normally occupy. The beam diameter was found experimentally by moving the sharp edge of a blade across the pump beam, and measuring the distance between the position where 8% and 92% of the beam energy was incident on the energy meter. This beam diameter contained \(1/e\) of the pump energy. The process was repeated at different positions along the z-axis until the position of the focal point was found. The minimum pump beam diameter was found to be 100 \(\mu\)m (see Appendix C.1).

![Figure 3.4: The optical set-up used for measuring the pump spot size in lab-based LC laser experiments.](image)

3.2.5 Emission efficiency and lasing threshold

The pulse energy of the pump laser was measured using the set-up in Figure 3.4, but without the knife-edge. This allowed the angle of the half wave plate to be calibrated to the pump laser pulse energy. At least 500 pulses were measured at each half wave plate angle and an average value calculated. These measurements were repeated at different pump frequencies, as the pulse energy of the pump laser was found to depend on the pulse frequency. The slope efficiency of a LC laser could then be measured by recording the mean output energy for a minimum of 5 s at a series of different input pulse energies, from low to high, achieved by rotating the half wave plate. A pulse
repetition rate of 10 Hz was used for static cells, and at least 500 pulses recorded to obtain an average value for the output pulse energy. Average input and output energies were used because only one energy meter was available meaning it was not possible to simultaneously measure the input and output energy. The slope of the resulting linear plot gave a measurement of the LC laser cell efficiency. The optical arrangement was not designed to detect the less directional spontaneous emission and so emission below the lasing threshold was not always detectable. Where spontaneous emission was detected, the resulting graph had two distinct linear relationships, and hence the lasing threshold could be estimated from the intersection of the linear fits. A less precise method of estimating the lasing threshold was to use the spectrometer to find the minimum energy at which a laser line could be detected.

A similar method was used to evaluate spinning cells at repetition rates of up to 10 kHz. For low pulse repetition rates, the mean output energy was recorded over 1 full rotation (50 s). For higher repetition rates, the mean output energy was measured over a larger number of rotations for approximately 5 s.

### 3.2.6 Emission from LC laser droplets

The lasing properties of DD-CLC droplets were investigated by filling a transparent plain glass cell with a solution containing a dilute suspension of droplets. The edges were sealed with epoxy (Torr Seal, Agilent Technologies). This cell was then mounted at a 45° angle to the pump laser, as shown in Figure 3.5, using a custom 3D printed cell mount. The emission from the laser droplets was collected using a lens placed as close as possible to the LC cell, due to the high divergence expected. Two 550 nm long-pass filters were then used to prevent stray pump laser light from reaching the spectrometer.

![Figure 3.5: The optical set-up used for laser measurements with LC droplets.](image-url)
An energy meter could be substituted for the spectrometer in order to confirm that the emission from the droplet was pulsed, with the same repetition rate as the pump laser. However, this experimental set-up could not be used to quantify the energy emitted by the droplet because the lens only collected emission from a relatively small solid angle. Even if assumptions were made about the proportion of the emission energy collected by the lens, efficiency estimates could not be made as it was not possible to obtain an accurate measure of the energy incident on the droplet. The pump spot diameter was large in comparison to the droplet, and therefore much of the energy from each pump pulse could not be absorbed by the dye. Furthermore, it was not possible to confirm that a droplet was accurately aligned with the pump beam.

3.2.7 Polarising optical microscopy (POM)

Polarising optical microscopy (POM) is an imaging method used to investigate the birefringence of a sample. White light is passed through a linear polariser, then through the thin sample. Another linear polariser (known as the analyser), is placed before the detector, as illustrated in Figure 3.6(a). The polariser and analyser are at 90° such that in the absence of a sample, all light is prevented from reaching the camera. Thus an isotropic sample appears dark whereas the intensity of an image of a birefringent sample depends on the orientation of the optical axis with respect to the plane of polarisation.

![Figure 3.6: A simplified schematic of a typical POM set-up (a) and an upright confocal microscope (b), modified from [106].](image)
3.2.8 Confocal microscopy

Confocal microscopy is a high resolution three-dimensional imaging technique that can be used to image samples containing fluorescent molecules. Light from a laser is reflected by a dichroic mirror and focused onto the sample by an objective lens. The light emitted from the sample then passes through the same lens and is able to pass through the mirror as it has a longer wavelength than the laser beam (energy has been lost in non-radiative processes). The emitted light is focussed through a pinhole onto a detector (usually a photomultiplier tube or CCD). The pinhole is key to confocal microscopy as it prevents out of focus light from reaching the detector. By scanning the laser, an image of a thin plane of the sample is built up. An image of a different plane can then be acquired by adjusting the focal plane, and a three-dimensional image constructed. A simple confocal set-up shown in figure 3.6(b). Modern confocal microscopes often include multiple lasers to broaden the range of fluorescent molecules that can be used in the sample.
Chapter 4: Microfluidic droplet laser approach

4.1 Introduction

This chapter reports research into the feasibility of using a microfluidic channel filled with flowing DD-CLC droplets as a method of achieving high repetition rate lasing from a LC laser system. The degradation in the performance of LC lasers at high pump power, discussed in Section 2.2.4, is caused by the influence of the pump beam on the LC structure and dye photodynamics. A flowing gain medium has been used to overcome similar problems in dye lasers, as in these systems each pump pulse excites fresh dye molecules. It was therefore hypothesised that a flowing gain medium could increase the power and repetition rate operation limits of LC lasers. However, a method of maintaining the helical LC structure necessary for band edge lasing was required. It was hypothesised that discrete droplets of LC material could be moved in a microfluidic system with minimal change to the LC structure. A flowing droplet approach was therefore evaluated as a potential method of generating an average power output that was sufficient for fluorescence-based imaging techniques, whilst preserving the ability to easily adjust the laser emission characteristics to suit a particular imaging experiment.

The topic of LC droplet lasers will first be introduced, focusing on droplets of CLC materials. Techniques for generating CLC droplets will be discussed, along with a proposed method of manipulating the direction of the laser emission in order to direct light towards a microscopy sample. The experimental methods used to fabricate and analyse LC droplets will then be described, followed by a discussion of the optical properties of the resulting droplets and their behaviour under flow. Lastly, conclusions will be drawn regarding the suitability of flowing CLC droplet lasers as a light source for fluorescence imaging of biological samples.

4.1.1 LC droplets

Micron scale LC droplets immersed in an isotropic fluid have been studied since the 1980s as both a demonstration of the structural behaviour of LC materials and, more recently, with the aim of achieving practical devices such as lasers [107] and sensors [108–111]. The molecular structure of the LC inside a droplet is strongly influenced by
the anchoring at the droplet interface. Homeotropic anchoring at the droplet surface results in molecules orientated primarily towards the centre of the droplet whereas planar anchoring promotes an alignment in a plane perpendicular to the droplet radius. Structural defects are an inevitable consequence of forming droplets from LC materials. The director orientation and anchoring energy depends on the LC properties and the properties of the surrounding carrier fluid. The carrier fluid therefore performs the same role as an alignment layer in a LC cell. The surface tension between the droplet and carrier fluids determines whether droplets are stable in the surrounding medium.

Early investigations into the structure of CLC droplets showed that several, well-ordered structures were possible [112, 113]. With planar anchoring conditions on the droplet surface, CLC droplets were predicted to have either a radial defect (or ‘zip’ defect), two radial defects, a diametrical defect or two point defects at opposite poles (bipolar structure) [114], as illustrated in Figure 4.1. An in-depth experimental study by Orlova et al. found that a diverse range of structures were possible, depending on the droplet diameter and the ratio between diameter and helical pitch [115]. This work agreed with previous simulation studies that predicted a range of possible CLC structures [116, 117].

![Figure 4.1: Some example LC structures for droplets with planar anchoring. The illustrations are two-dimensional with lines to indicate the director field. (a) A bipolar droplet with two point defects, (b) a twisted bipolar droplet and (c) a concentric ring droplet. The latter has a radial or diametric defect in the a plane perpendicular to the illustration (out of page). Figure modified from [118]](image)

4.1.2 Droplet lasers

Spherical laser resonators were demonstrated very early on in the development of lasers [119], using the phenomenon of total internal reflection to produce the resonant cavity. This is known as whispering gallery mode (WGM) lasing, and can be achieved in a solid or liquid sphere if the material has a higher refractive index than its surroundings. Most droplet lasers have several WGM resonant modes and typically produce a series
of evenly spaced laser lines. The WGM lasing mechanism is thoroughly reviewed in Reference [120]. A notable use of WGM laser droplets was to create a flowing dye laser that could rapidly switch between two laser wavelengths through controlled droplet generation [121]. The high switching rates achieved (3.6 kHz) suggested that a high repetition rate laser from flowing LC laser droplets could also be achievable. A recent review of droplet lasers [122] concluded that LC droplet lasers may be able offer advantages over WGM droplet lasers, as they are more robust and it is easier to control their optical output.

The structure of the CLC laser droplets studied by Humar et al. [107], and illustrated in Figure 4.2(a), was a radial helical structure referred to as a ‘Bragg onion’ or ‘spherulite’ structure. Concentric rings of light and dark in a POM image, corresponding to rotation of the director, along the droplet radius, are indicative of this structure. At least one radial ‘zip’ defect is also present. Band-edge lasing was observed in 15 µm to 110 µm diameter droplets with this structure. The lasing threshold was lowest for droplets with a diameter greater than 50 µm. The Bragg onion structure creates a partial PBG (for circularly polarised light), similar to that of a Grandjean texture, but radial instead of one-dimensional. Consequently, the laser emission is radial along the helical axes. The omnidirectional nature of the emission from CLC droplets could be an attractive feature for some applications, for example in the field of telecommunications. Omnidirectional laser droplets could be used as light sources for an imaging system if the droplet was surrounded by the sample to be imaged. Implantable or embedded lasers made from microdroplets may open up some exciting new sensing and imaging possibilities, and have been recently demonstrated with CLC laser droplets [123]. However, for many sensing applications, including the fluorescence imaging applications that are the motivation for this work, directional emission would be preferred as this would be of higher intensity and could be more easily collimated and directed towards a sample or detector.

Directional lasing from CLC droplets has been reported in printed and painted LC emulsions [72, 124, 125]. In these cases, the droplets had an oblate shape after the surrounding polymer medium dried on the substrate. This change in geometry promoted a region of Grandjean texture within each droplet, with the helical axis aligned along the droplet’s minor axis. Accordingly, printed and painted lasers were found to emit laser light directionally, perpendicular to the substrate. However, in these painted and printed systems, lasing droplets are encapsulated within solidified polymeric films, and this approach is clearly not compatible with a flowing LC laser system.

It was hypothesised that a similar effect could be achieved by deforming a CLC droplet in a microfluidic channel to create a region of Grandjean texture, as
illustrated in Figure 4.2(b). This constrained droplet would emit in only two directions, perpendicular to the channel walls that it was constrained between, in a similar manner to well-aligned bulk DD-CLC material in a glass cell.

![Figure 4.2: An illustration of the arrangement of LC molecules in (a) a spherical droplet and (b) a droplet deformed by two surfaces (top and bottom of image).](image)

### 4.1.3 Droplet fabrication methods

Droplets can be fabricated inexpensively in large volumes with simple mixing (emulsification) processes [124, 126], however these methods produce polydisperse droplets of a wide range of diameters. Polydisperse droplets could have different LC structures, or require different conditions to achieve a suitable structure for lasing. The droplet diameter is also important to control for optimum absorption of pump laser light. Monodisperse droplet generation was therefore considered important in designing a LC droplet laser system where the lasing properties did not vary significantly from one droplet to another. Narrower droplet size distributions can be achieved with membrane emulsification [127] or, ideally, microfluidic techniques. Microfluidic methods of generating droplets have been studied extensively [128, 129] and successfully used to fabricate LC droplets [130, 131] in aqueous solutions. As well as producing droplets of consistent size which are likely to have repeatable laser emission characteristics, microfluidic systems allow precise control of droplet size and on-demand formation. If a polydisperse droplet sample is required, this can be generated by changing the flow rates during the sample collection. A microfluidic device was therefore thought to be the most suitable method of generating LC droplets for a high repetition rate flowing droplet laser system.

Microfluidics can also be used to form droplets of more than one liquid component,
and it is possible for one of these liquids to be completely enclosed by the other in a capsule. This approach has been successfully used to maintain stable planar alignment at the surface of a CLC droplet [132], by creating an alignment layer between the droplet and the carrier fluid. This has the advantage of preventing coalescence and also allows the capsules to be introduced to other fluids or elastomers without alignment changes. However, this technique may be problematic for laser applications, since it requires a UV curing step which can damage the laser dye.

### 4.1.4 Objectives

The research reported in this chapter had three objectives:

1. Design and assemble a microfluidic system for repeatable, on demand generation of LC laser droplets;

2. Study laser droplets while flowing and conclude whether this method is likely to enable high repetition rate operation with acceptable emission characteristics;

3. Test the hypothesis that laser emission from a LC droplet can be made bidirectional by changing droplet geometry.
4.2 Experimental methods

4.2.1 Droplet generation

Commercially available microfluidic chips were selected for this project to enable droplets be generated with diameters from 50µm to 110µm, as these dimensions are suitable for low threshold lasing when spherical, as well as being large enough for the droplet shape to be dramatically altered if confined in a 20µm cell or channel. Hydrophilic glass chips were chosen so that the LC droplets could be generated in an aqueous carrier fluid which would wet the surfaces and prevent the LC droplets from interacting with the channel walls. Droplets were generated using a droplet chip with either a 50µm etch depth X-junction (Dolomite Microfluidics, part no. 3200286) or a 100µm etch depth T-junction (Dolomite Microfluidics, part no. 3000158). The junctions were suitable for generating droplets of similar dimensions to the channel depth, and the larger T-junction was found to be less susceptible to channel blockages. The junction chips were connected to 1 ml syringes (Hamilton GasTight) via 250µm internal diameter (ID) fluorinated ethylene propylene (FEP) tubing. The precise droplet diameter, generation speed and inter-droplet spacing could be controlled by altering the LC and carrier phase flow rates using syringe pumps (KDS Legato 100). The syringes and syringe pumps were chosen to enable a wide range of flow rates, including flow rates that were sufficiently high to allow operation of a flowing droplet laser system at 10 kHz pump frequency. However, low flow rates were typically used to conserve materials and to improve the quality of video imaging. The experimental set-up is shown in Figure 4.3, along with detailed drawings of the droplet chip junctions.

For the laser droplets, a dye-doped chiral nematic liquid crystal mixture was prepared using the nematic MLC-2132 ($n_e=1.77$, $n_o=1.51$, Merck), 25%wt of the left handed chiral dopant S-811 (4-[(1-methylheptyl) oxy] carbonylphenyl-4-(hexyloxy) benzoate, Merck) and 0.5%wt of the laser dye 4- (Dicyanomethylene) -2-methyl-6- (4-dimethylaminostyryl) -4H-pyran (DCM, Exciton). This mixture is will be referred to as mixture ‘D1’. The chiral dopant was dissolved in the nematic at 140°C for 2 hours, then at 100°C for at least 8 hours. The dye was then added and dissolved at 100°C for 1 hour, aided by a magnetic stirrer. A similar mixture, ‘D2’ with a longer helical pitch (approximately 1.2µm) was made for microscopy experiments using the same process; this contained 4.3%wt S-811 and 0.5%wt DCM. Droplets of 50µm to 110µm diameter made from these DD-CLC mixtures would have a high pitch to diameter ratios (>40) and therefore could be expected to form Bragg onion structures under appropriate conditions.

The carrier fluid used in the microfluidic droplet generation was deionised water with 5%wt polyvinyl alcohol (PVA, Aldrich) to promote planar degenerate molecular
alignment at the droplet interface. This was filtered with a 0.2 µm syringe filter before use to reduce the risk of blockages in the microfluidic channels.

Figure 4.3: (a) The experimental set-up used to generate droplets. Junction details for the (b) 100 µm depth and (c) 50 µm depth microfluidic chips, taken from the product data sheets [133, 134]. All dimensions in millimetres.

4.2.2 Flowing droplets

Flow cells were fabricated from capillaries to allow imaging of droplets while flowing, either freely in a relatively large channel or while confined in a channel with one dimension smaller than the droplet diameter. The capillaries used were inserted into the 250 µm ID tubing and sealed with glue such that the fluid could be pumped through the capillary without the device leaking. A schematic of these flow cells is shown in Figure 4.4; the device shown in (a) and (b) was made using a square capillary for viewing spherical droplets (ID 100 µm x 100 µm, CM Scientific, part no. 8510) whereas the device shown in (c) and (d) was made using a rectangular capillary for viewing confined droplets (20 µm x 200 µm, CM Scientific, part no. 5002). The rectangular capillary dimensions were chosen based on the thickness that is optimal for bulk DD-CLC laser cells. It was important to clean the inside of the capillaries as contaminants affected the behaviour of LC droplets that were in contact with the channel walls. These flow cells were fabricated using the following process:

1. Clean a glass microscope slide to use as the base of the device and a 0.5 mm thick glass chip to use to support the capillary.
2. Glue the chip to slide and capillary to chip using optical adhesive (NOA 68, Agilent Technologies). Check capillary is correctly orientated and UV cure.

3. Use fine tweezers to slightly widen ID of FEP tubing.

4. Place end of tube on slide next to outlet end of capillary. Align under microscope and insert capillary approximately 5 mm by moving tube. Tape tubing to slide and repeat for inlet end of capillary.

5. Deposit a generous dot of glue over the capillary end of both pieces of tubing to seal the end. Glue the tubing to the slide further down to prevent bending. UV cure.

6. Connect a syringe to the inlet tubing and flush with acetone, potassium hydroxide (KOH) solution and 5% HCl solution, with a de-ionised (DI) water rinse between each cleaning step. Flush with DI water and dry as far as possible with nitrogen.

Figure 4.4: The flow cells used to view flowing droplets. (a) and (b) show cross-sections through a square capillary device from the side and perpendicular to the flow direction, respectively. (c) and (d) are the equivalent views for a rectangular capillary device. Dimensions are not to scale.

4.2.3 Imaging techniques

The droplet fabrication process was monitored using POM (see Section 2.1.3 and Section 3.2.7) with a high speed camera (MCT362, Mikrotron) attached to an inverted microscope (E800, Nikon) with a 10× NA 0.3 objective (Plan Fluor (PF), Nikon). This was used to image the droplets both during formation and whilst flowing in a microfluidic channel.

Droplets were collected in vials or capillary filled into untreated glass cells (100 µm spaced for spherical droplets and 20 µm spaced for constrained droplets, made in-house)
for imaging and lasing while stationary. Colour micrographs of stationary droplets were taken using an upright microscope *Nikon* and a colour camera (*Micropublisher 3.3, QImaging*). The experimental set-up obtaining transmission and emission spectra from stationary droplets is shown in Section 3.2.6.

Further insight into the LC structure within the droplets was obtained with confocal microscopy (see Section 3.2.8) using an inverted microscope (*Observer.Z1, Zeiss*) in conjunction with a scanning system (*LSM 700, Zeiss*). When available, a faster confocal microscope (*DMi8, Leica*) with a Plan Apochromat (PA) 63× NA 1.4 oil immersion objective, was also used. In both confocal systems, a 488 nm continuous wave solid state laser was used to excite the dye in the droplet.
4.3 Results and Discussion

4.3.1 Droplet generation

Stable DD-CLC droplets of a range of diameters were successfully generated with the 50µm X-junction and the 100µm etch depth T-junction. The droplets were not found to coalesce unless forced into close proximity, for example in a blocked channel. The X-junction was suitable for generating droplets of 42µm to 58µm diameter whereas the deeper T-junction was suitable for generating droplets of up to 110µm diameter.

An example of the droplet formation process, showing the gradual protrusion of CLC material and pinch-off into a droplet, is given in the sequence of images in Figure 4.5(a)-(e). As expected, increasing the ratio of the LC flow rate \(Q_{LC}\) to carrier fluid flow rate \(Q_{PVA}\) increased the droplet diameter, as shown by the data in Figure 4.6. If the flow rate ratio was too high, the LC material would not be broken up by the carrier fluid and would exit the junction in a continuous stream, or in long segments (‘jetting’). If this ratio was too low, the LC would not leave the inlet channel and no droplets were formed. The flow rates could also be used to control the inter-droplet spacing and it was demonstrated that this set-up could be used to generate flowing droplets with a small and regular spacing between them (see Figure 4.5(f)). This would be desirable in a flowing LC laser system, so that each pump laser pulse was incident on a new droplet.

![Figure 4.5](image)

Figure 4.5: POM images of the formation of spherical DD-CLC droplets (mixture D1) with the 50µm X-junction (a)-(e). (f) A chain of droplets generated using flow rates of 0.1 ml h\(^{-1}\) and 0.03 ml h\(^{-1}\) for the LC and PVA respectively. The scale bars indicate a distance of 100 µm.
Figure 4.6: The effect of increasing the flow rate ratio on the droplet diameter using the 50 µm X-junction chip. Data was collected using LC flow rates of 0.01 ml h\(^{-1}\) (black squares), 0.02 ml h\(^{-1}\) (open squares), 0.1 ml h\(^{-1}\) (black circles) and 0.15 ml h\(^{-1}\) (open circle).

The X-junction suffered from more frequent blockages, due to the small junction dimensions, which is likely to have caused discrepancies between the flow rate specified by the syringe pumps and the actual flow rate through the channels. Ensuring channels were clean and free from blockages was important in achieving reproducible droplet formation.

4.3.2 Spherical droplets: structure and lasing

Videos of droplet production revealed a defect-ridden internal molecular structure with an absence of any long range chiral structure, as shown in 4.7. The structure was continuously changing as the droplets moved along the channel. A video of droplet formation is provided via the link in Figure 4.8; this was taken through crossed polarisers and shows the defects in the droplet structure whilst flowing. It was hypothesised that defects may eventually clear as the droplet relaxed, but even after flowing through a length of 250 µm ID tubing for several minutes, a large number
of defects were still present. Due to the absence of a standing helical structure, these droplets were unlikely to exhibit a PBG and therefore would not perform as efficient band-edge lasers. Previous studies of DD-CLC laser droplets, such as Reference [107], were conducted on static droplets. It was therefore hypothesised that a static relaxation period was required in order to form a Bragg Onion structure in a CLC droplet.

Figure 4.7: POM images of spherical DD-CLC droplets (mixture D1). (a) A LC droplet generated in the 100 µm T-junction chip using flow rates of 0.69 ml h\(^{-1}\) and 0.31 ml h\(^{-1}\) for the LC and PVA respectively. (b) A droplet from the same batch after flowing through approximately 200 mm of tubing (250 µm internal diameter) into a 100 µm depth channel. Video available through the link in Figure 4.8.

A static storage step was subsequently added to the experiment to allow defects in the droplets to clear, leaving a more ordered CLC structure. This is consistent with the experimental methods used in Reference [115], where droplets were left for at least 30 min before imaging. Droplets with a helical pitch of approximately 1.2 µm
(mixture D2) were used as the pitch of lasing droplets could not be resolved with optical microscopy. After generation and collection in a vial of PVA solution, spherical droplets were observed to have the expected Bragg onion structure, confirming the hypothesis that a static storage period was required. A characteristic ‘zip’ defect is clearly visible in the resulting POM images, shown in Figure 4.9(b), and is also visible on the surface of some of the droplets in the confocal image 4.9(a).

The contrast in the confocal microscopy images is determined by the orientation of the DCM dye in the sample, rather than the orientation of the LC director (as observed in POM). Since the electric dipole moment of DCM has a tendency to align parallel to the LC director, this should be indicative of the director orientation, however there is some variation caused by the relatively low order parameter of DCM in typical nematic LC samples (0.21 to 0.47) [45, 135]. As discussed in Section 2.2.3, an order parameter of 1 would describe perfect alignment with the LC director whereas 0 would indicate no alignment. The imperfect ordering of the DCM dye molecules therefore effectively reduces the precision with which the LC director orientation can be determined.

Laser emission could be detected from the spherical droplets, although this was of low intensity, due to the omnidirectional emission characteristics of this type of droplet. A typical laser emission spectrum from the spherical droplet sample is included in Figure 4.10, along with the transmission spectrum and laser emission spectrum from a DD-CLC cell filled with the same mixture. The PBG of the bulk mixture is partially obscured by the dye absorption spectrum. The long band-edge of the PBG was located at 643 nm, coincident with laser emission from a bulk sample. The droplet laser emission wavelength was 630 nm, which is located inside the bulk material PBG. However, the emission was observed to be circularly polarised and therefore thought to be an instance of band-edge lasing. The slight difference in the laser wavelength between the droplet and bulk material could originate from the different boundary conditions resulting in different degrees of frustration in the helical structure.

4.3.3 Constrained droplets: structure and lasing

Droplets of a range of sizes were capillary filled into a 20 µm cell, resulting in ‘barrel’ shaped, constrained droplets. Their shape can be seen by viewing a confocal slice (y−z) perpendicular to the plane of the substrates, as shown in the right hand side of Figure 4.11(a). Both the confocal (a) and POM (b) images of the constrained droplets show a central region of uniform texture, which was invariant when the sample was rotated with respect to the polarisers. This is evidence for a large central area of Grandjean molecular structure.

Concentric rings of bright and dark are seen in the outer shell of the constrained droplets, suggesting that these areas remain substantially similar in structure to a
Figure 4.9: Images of spherical LC laser droplets with long helical pitch (approximately 1.2 µm, mixture D2) captured using (a) confocal microscopy (b) POM. A cross-section of the droplets in the x-z plane is included to the right hand side, and shows the position of the x-y plane displayed to the left. The polariser positions are indicated in the POM images.

spherical droplet. This structure is found in the regions of the droplets that do not touch either glass surface—as confirmed by y − z slices from the confocal microscopy—where the molecular structure remains dominated by planar anchoring at the curved interface between the droplet and PVA solution. A polydisperse droplet sample was generated,
and it was observed that the thickness of this outer shell of Bragg onion structure is consistent between droplets of different sizes, as can be seen in Figure 4.11(a). This shows that the size of the central Grandjean area can be readily controlled by altering the droplet diameter or channel dimensions.

The shorter-pitch droplets made for lasing experiments (such that the long band edge of the PBG would overlap with the DCM emission spectra) were also constrained in 20\µm cells and analysed using POM and confocal microscopy, as shown in Figure 4.12. Although the pitch is too short to be clearly resolved in these images, the uniform central area persists and suggests that the same structure is likely present.

The PBG of the constrained droplets could be measured by simultaneously illuminating several droplets, resulting in the transmission spectrum in grey in Figure 4.13. The PBG measurement was similar to the PBG of the bulk mixture in a cell with alignment layers. The peak emission was 645 nm, coincident with the long band-edge of the PBG. Additionally, polarising filters were used to establish that the laser emission from constrained droplets was circularly polarised with the same handedness as the CLC helix, as expected from a band-edge laser. These observations are evidence that the constrained droplets exhibited band-edge lasing in a similar manner to bulk
Figure 4.11: Images of confined DD-CLC droplets with long helical pitch (approximately 1.2 µm, mixture D2) captured using (a) confocal microscopy and (b) POM. A cross-section of the droplets in the x-z plane is shown to the right hand side with a line indicating the position of the $x-y$ plane that is displayed to the left. The polariser positions are indicated in the POM images.

Laser emission from the constrained droplets was far easier to detect with a
Figure 4.12: Images of constrained LC laser droplets with short helical pitch (mixture D1) captured using (a) confocal microscopy and (b) POM.

spectrometer or energy meter than emission from spherical droplets. This was partially because once constrained, the droplets had a larger diameter so could absorb more of the pump pulse energy. However, it was also observed that the laser emission was directional, emitted in a diverging cone, as it could be collimated and seen as spot on a screen placed approximately 100 mm behind the collimating lens.

Figure 4.13: The transmission spectrum (grey) and laser emission spectrum (bold grey) of a confined laser droplet, with a central region of Grandjean texture. The transmission spectrum (black solid) and emission spectra (black dashed) of the bulk DD-CLC mixture (D1) is included for comparison.
The experimental set-up used to measure the emission spectra from the LC droplets was not suitable for quantifying the slope efficiency, lasing threshold or emission cone angle, as discussed in Section 3.2.6. Detailed studies of these emission properties would be enabled by an experimental set-up that allowed the droplet to be imaged under magnification and immediately excited by a pump laser with a small spot that was precisely aligned with the droplet. This would allow the droplet structure to be related to the emission properties with more precision than was possible in the experiments reported here, which assumed that the structure of a population of identically prepared droplets did not vary between droplets and did not change during transport between laboratories.

4.3.4 Flowing spherical droplets

Having achieved laser emission from a LC droplet, and used the droplet geometry to control the emission direction, the next step was to experiment with flowing droplets. These were studied in large channels while spherical and in narrower channels that would constrain the droplets. A 100µm flow cell, as described in Section 4.2.2, was used to examine spherical droplets (<100µm diameter) that had been allowed to relax into a Bragg onion structure with the characteristic zip defect. The orientation of each droplet did not change unless the droplet was in contact with one of the channel side walls; in this case the drag force induced a rolling motion. Images from high speed video of droplets under different flow rates are shown in Figure 4.14 and provide evidence that the Bragg onion structure is maintained at flow rates up to 0.5 ml h⁻¹ and the zip defect is still visible. Omnidirectional emission from a flowing LC droplet laser system is therefore achievable.

The speed of the droplets at 0.5 ml h⁻¹ was measured from the video footage and found to be (17.2 ± 0.1) mm s⁻¹. Droplets of this diameter flowing in close proximity to each other through a pump beam at this speed would allow a pump pulse repetition rate of approximately 170 Hz to be used without more than one pulse being incident on each droplet. This approach could offer some advantages in emission stability over a static system, which are typically operated at repetition rates of 10 Hz or less. Higher droplet speeds would clearly be advantageous as this would allow higher repetition rates. For example, droplet velocities of 1 m s⁻¹ would allow pumping at 10 kHz. In a 100µm square channel this corresponds to a flow rate of 36 ml h⁻¹, which is achievable with the syringes and syringe pumps used in this experiment. However, it was not possible to determine whether a Bragg onion structure was present at higher flow rates with this camera and microscope due to motion blur.
4.3.5 Flowing constrained droplets

Droplets with a Bragg Onion structure were pumped into the 20 μm flow cell, such that they were constrained whilst flowing. The movement of a droplet constrained in a shallow channel was found to create a large number of defects, even at low flow rate. It was hypothesised that these were created by the drag forces on the interface between the LC droplet and glass channel walls, causing director re-orientation within the droplet. It is also possible that the differential flow rates between the carrier fluid and the constrained droplets—which were slowed by the aforementioned drag forces—would disrupt the planar LC alignment at the droplet surface. The defects, shown in Figure 4.15 for a pair of droplets flowing at 0.005 ml h\(^{-1}\), appeared initially as variations in intensity in the central Grandjean region of the droplet, orientated in the direction of flow (see (a)). Later, line defects that appear similar to oily streaks materialised at the leading edge of the droplet (right hand edge in figure) and extended gradually across the droplet towards the trailing edge as lines or loops, shown in both (b) and (c). The defect structure was continuously changing in response to the droplet movement and defect generation was faster at higher flow rates. An image of a droplet flowing at a higher flow rate (0.05 ml h\(^{-1}\)) is included in (d). This illustrates a typical defect density in a constrained droplet under flow. Defects in the constrained droplets slowly disappeared when the flow was stopped, after the droplet movement ceased. This was a gradual process that typically took 20 min to 30 min.

The rapid generation of defects within constrained droplets is highly likely to negatively affect the band-edge laser emission, or prevent band-edge lasing, since the central region of Grandjean texture is disrupted. It is unlikely that the flowing droplets could be used as a high repetition rate laser light source when constrained in small channels, and therefore directional band-edge lasing from flowing LC droplets could
Figure 4.15: POM images of constrained droplets of mixture D1 under flow. Images (a), (b) and (c) show defect generation in the same pair of droplets during the first 10 s after the syringe pump was switched on at a flow rate of 0.005 ml h\(^{-1}\). Image (d) shows a different pair of droplets (one large and one small) flowing at a faster flow rate (0.05 ml h\(^{-1}\)). This direction of flow is indicated by the arrows.

not be achieved with this method.
4.4 Conclusion and future perspectives

4.4.1 High repetition rate LC droplet lasers

LC droplets have been successfully generated and a suitable structure for lasing achieved after a period of static storage. A LC droplet laser system where droplets are generated and used on the same microfluidic chip would be the most desirable system for a high repetition rate laser, but would rely on the desired LC structure being present shortly after generation. This may be possible with further work to determine the optimum conditions for on-demand microfluidic generation of Bragg onion droplets. For example, alternative microfluidic generation methods, such as co-flow devices, may produce droplets with fewer initial defects that may require a shorter relaxation time. A thermal conditioning step could be introduced to encourage ordered structures to form. On-chip storage compartments could also be included in the chip design and could allow droplets to relax in a quasi-static environment.

The experiments using flow cells suggest that spherical LC laser droplets could be used as a high repetition rate LC laser, if the droplets are generated and placed in static storage so that a Bragg onion structure is present before use. Although this would be less flexible than an on-demand generation system, because the droplet properties and chemical composition would be more difficult to change, droplets could feasibly flow around closed-loop system and be re-used many times. Images were obtained to show that omnidirectional lasing would be possible at pulse repetition rate of at least 170 Hz, as the Bragg onion structure was still present in spherical flowing droplets. This is higher than the pulse repetition rates typically used with static LC laser cells (<100 Hz, as discussed in Section 2.2.4). Droplets may maintain a Bragg onion structure under much higher flow rates, allowing higher repetition rate pumping, but the upper limit could not be determined due to imaging limitations. Numerical simulation of CLC droplet structures under flow could provide additional insight into methods of producing fast-flowing and efficient LC lasers. Further work is also required to understand the thermal effects of high repetition rate pumping on the CLC droplet structure as well as practical considerations such as increased risk of droplet coalescence with temperature.

4.4.2 Directional emission from CLC droplets

The omnidirectional emission from a Bragg-onion CLC droplet was successfully changed to directional emission by using a shallow channel or cell that constrained the geometry of the droplet in one dimension, creating a barrel shaped droplet. This technique has the advantage of increasing the intensity of laser emission from a LC droplet and allowing it to be directed towards a sample or detector. However, these constrained droplets are
not suitable for flowing systems since the Grandjean structure rapidly becomes highly
defective under flow, and is therefore unlikely to support laser modes. Directional lasing
from a CLC droplet at high repetition rate was therefore not considered possible with
this technique. A method of controlling the CLC structure that creates a region of
Grandjean texture without contact with the channel walls would be necessary to achieve
directional lasing at high flow rates. A greater understanding of flow induced
alignment of CLC materials would contribute to this goal.

Despite the creation of defects under flow, a constrained CLC droplet could be
used as a mobile light source or sensor inside a microfluidic device, since the ordered
structure returns naturally if the droplet is allowed to remain stationary.

4.4.3 Applications of LC droplet lasers

The research in this chapter was designed to assess whether droplet lasers could meet
the requirements for a fluorescence microscopy light source. It is likely to be possible to
develop a high repetition rate LC laser using flowing CLC droplets which would have a
suitably high average power output. However, this system would have omnidirectional
emission and so would be difficult to integrate with a fluorescence microscope. When
the emission is directed by constraining the droplet, high repetition rate operation is
prevented. It was therefore concluded that this approach was not suitable for a portable
LC laser system for fluorescence microscopy applications.

CLC droplet lasers do show some promise in other applications, for example as a
tool in chemical sensing, as discussed in Reference [108]. The emission properties of a
droplet could be used as a highly sensitive method of detecting changes in the droplet
structure, caused by changes in the droplet environment. Further work is required to
understand the effect of structural changes on the droplet emission properties such as
the wavelength and linewidth. This would require an experimental set-up that allowed
near-simultaneous acquisition of POM and laser emission data, to ensure that the lasing
properties could be linked to a specific droplet structure.

Improving control of the LC droplet structure will be crucial for enabling applica-
tions of LC droplet lasers. Possible methods of influencing the droplet structure include
treating the surfaces of microfluidic channels with directional alignment layers, using
photo-alignment techniques instead of rubbing [98]. Alternatively, electric fields could
be used to control alignment in particular areas of a microfluidic device, which would be
an effective method of inducing planar alignment with negative dielectric LC materials.
Chapter 5: LC laser cell fabrication

5.1 Background and motivation

The aim of this chapter is to obtain LC laser cells suitable for use in a spinning cell system. A spinning cell is the proposed method of generating an average power output from the LC laser that is sufficient for fluorescence imaging. High quality cells were important in achieving emission characteristics from a LC laser system that met the requirements for biomedical imaging, as outlined in Section 1.3. This chapter will briefly describe the advantages and disadvantages of using commercially available cells, then describe the development of the processes used to make suitable cells in-house. The final process used to make cells used in the spinning LC laser system is detailed in Appendix B.

High quality cells were important because a highly efficient system was desirable to maximise output power. This requires optimised LC laser mixtures and cells that enable the self-assembly of LC molecules into a defect-free Grandjean texture that can be used as a low loss resonant cavity. In theory, this texture can be achieved by using an alignment layer to promote perfect planar LC alignment at the substrates.

The stability of the LC laser emission, both in wavelength and pulse energy, was very important in order to achieve repeatable imaging results. In a typical cell, finite domains of Grandjean texture are observed, separated by ‘oily streak’ line defects (see Figure 2.3). In static cell systems, optimum stability and efficiency can be achieved if the size of the Grandjean domains is larger than the pump laser spot (approximately 100 µm), enabling excitation of a single, defect free domain. In a spinning cell system it is necessary to minimise the number of domains excited during the cell rotation, since each different Grandjean domain may have a different efficiency and a slightly different wavelength due to changes in the chiral pitch. Additionally, some pump laser pulses may be incident on a domain boundary and therefore result in poor efficiency and/or multi-mode laser emission. An ideal cell for a spinning system would have Grandjean domains larger than the diameter of circle traced by the pump spot (the ‘pump ring’). Consequently, spinning cell systems introduce further demands on cell fabrication as the consistency of the LC laser cell over a larger area becomes important.
Developments to in-house cell fabrication processes consequently aimed to increase domain size and reduce the number of defects present, such that the emission properties of a cell remain stable when the cell is spun. The following factors were thought to influence domain size and defect density:

- Substrate properties (surface roughness, flatness)
- Anchoring of LC to substrate (alignment layer properties)
- Contamination of LC mixture or substrates
- Cell gap size and variation
- Chiral dopant dissolution and distribution within LC mixture
- Domain formation during filling with LC and post-filling thermal processes

Investigations into the importance of these factors and the development of processes that result in large domain sizes are reported in Section 5.4.
5.2 Commercially available cells

It was hypothesised that commercially available cells would not have the desired performance or geometry and therefore in-house cell fabrication would be necessary. LC cells are available from a small number of suppliers and range in price from £5 (LC2-20.0, Instec) to £180 (LCC1322-A, ThorLabs) each, depending on the quality and quantity ordered.

Cells made by Instec had the advantage of being cheap and available with several different designs. However, these were all made with spacer beads distributed across the full cell area. This is intended to ensure an even cell gap but also results small CLC domains and many defects, as seen in Figure 5.1(a). These cells were found to emit many different wavelengths, as described in Reference [136], and were therefore not considered suitable for spinning cell experiments.

Cells from ThorLabs were not evaluated since their high cost was considered prohibitive. LC cells had previously been acquired from the display manufacturer LG, but there were only a few of these remaining and it was not possible to order more. The LG cells were of high quality and showed that low defect densities were achievable (see Figure 5.1(b)). However, even if they had been available, these cells were not an ideal design for the spinning cell system; bespoke cells with novel geometries and features would maximise the benefits of using LC lasers.

An ideal scenario for this project would be to collaborate with a LC cell manufacturer that had fabrication facilities for making high quality cells with bespoke...
designs. In the absence of such an arrangement, it was concluded that fabricating cells in-house was the next best solution, as this would enable bespoke cell designs and reasonable cell quality at an acceptable cost to the project.
5.3 Cell fabrication process development methods

In-house LC cell fabrication processes would ideally be quick and produce cells at a similar cost to commercially available cells. The scalability of fabrication processes was therefore considered during development. LC cell fabrication can be broken down into the following steps, as illustrated in Figure 5.2:

- Substrate preparation (cleaning)
- Alignment layer deposition and treatment
- Glue deposition and cell assembly
- LC mixture preparation
- Cell filling, cooling and sealing

![Flow diagram of cell fabrication process](image)

Figure 5.2: A flow diagram to illustrate the basic steps of the cell fabrication process.

The detailed parameters of each of these steps were based on LC laser cell fabrication processes used in other research facilities as well as information gained from published literature and discussions with display manufacturers.

Individual process steps were evaluated qualitatively using optical microscopy. It was assumed that the presence of contaminants on a substrate, streaks in a coating or...
any other uneven features would negatively affect the performance of the LC cell by creating defects in the LC structure.

The thickness of the cell gap in empty cells was determined optically by the measuring the Fabry-Perot interference fringes on a transmission spectrum, as described in Section 3.2. This analysis was supported by a measurement of the spacer bead diameters in a microscope image, using image processing software (Fiji) to calibrate the image, set a threshold to isolate the beads and measure particle sizes. The presence of damaged beads or overlapping beads was also taken to indicate an uneven cell gap.

Cells were filled with LC laser mixtures that were designed to emit efficiently. The best combination of materials for a given excitation and emission wavelength was selected by reviewing literature. The filling technique also required optimisation to minimise defects and maximise domain size. Finally, the edges of cells used in spinning cell experiments had to be sealed to prevent leaking.

Filled cells were evaluated with POM to establish a typical domain size, when subject to an identical filling and cooling process. POM was not possible with reflective cells, but an assessment of the domain size was possible by viewing defects under a reflection microscope. Low magnification images were used to assess the consistency of the cells over large areas, and examine any edge effects.
5.4 Cell fabrication process development results

5.4.1 Substrate selection

LC laser cells are typically rectangular with lateral dimensions of 10 mm to 20 mm and, in a research laboratory, are often fabricated from substrate chips of this size. This approach was used during much of the process development to minimise waste material. However, it is usually more efficient and cost effective to fabricate devices on a larger scale, and results can often be more consistent as edge effects are minimised. There was therefore a desire to develop wafer-scale cell fabrication processes. In addition, large cells would allow fabrication of more sophisticated cell designs with multiple compartments containing different LC laser mixtures within a single cell. This would allow fast, automated wavelength switching, either arbitrarily or in a pre-determined sequence. It was consequently desirable to develop fabrication methods for large cells, including precision glue deposition techniques such that glue lines could be used to separate LC materials within a cell.

Substrates cut from 3” diameter glass and silicon wafers were used during the development of cell fabrication processes. These were typically 10 mm × 15 mm chips. In the case of transparent cells (required for POM analysis and transmission measurements), 0.5 mm thick borosilicate glass wafers (Compart Technologies) were initially used. For reflective cells, the reflective substrate was a 0.375 mm thick amorphous silicon wafer (Si MAT). Silicon wafers were sputter-coated with a thin aluminium layer resulting in a reflective surface.

It was difficult to coat these substrates evenly with an alignment layer, as discussed in Sections 5.4.2 and 5.4.3). Cells made from these substrates had regions focal conic textures (see Figure 2.3) that did not emit laser light. It was hypothesised that some of the alignment layer problems were caused by imperfections in the surface of the glass wafers. The scratch/dig (S/D) specification of the Compart Technologies wafers was 60/40, which is higher (i.e. more scratches and digs allowed) than normally acceptable for optical applications. As well as causing problems during spin-coating, scratches and digs were also likely to degrade the efficiency of the cell due to scattering and reflection of the pump laser. New glass wafers, polished to an S/D of 20/10 (fused silica, IBD Technologies), were therefore purchased. These wafers were also 1 mm thick to make the final cells more rigid and therefore easier to handle without damaging the cell or temporarily changing the thickness of the cell gap.

Cells made with these 1 mm fused silica wafers resulted in small Grandjean domains and many different emission wavelengths were observed. The transmission spectrum from a \( N^* \) cell made using the these substrates was measured using the method described in Section 3.2.1. The resulting spectrum did not have a steep PBG edge, as
shown in Figure 5.3(a), since the area illuminated contained many domains of different pitch lengths. The sum of emission spectra taken over a pump ring, in a cell with the same CLC mixture but including a laser dye, is also shown to indicate the many different emission wavelengths present, from 580 nm to 590 nm. In some cases, more than one wavelength was present simultaneously since the pump spot was larger than the domain size, as seen in the POM image in Figure 5.3(b).

![Image](image.png)

Figure 5.3: (a) An example transmission spectrum from a transparent CLC cell made with the 1 mm fused silica wafers. The edge of the PBG is not very steep due to the small size of the Grandjean domains. Emission from a reflective cell (made using similar processes and filled with a laser mixture of the same chirality) is included; the sum of 500 spectra taken over a pump ring is shown (bold), and includes many different lasing peaks along the PBG edge (580 nm to 590 nm). (b) POM of the transparent cell showing small domains and oily streaks.

A review of the possible causes of small Grandjean domains identified the poor bow/warp of glass and silicon wafers as a likely problem. Although their surface was polished, there could be micron-scale variations in the substrate flatness over a large area. Optically flat glass substrates were therefore tested. These had a minimum surface flatness of 4\(\lambda\) and could be purchased with or without an aluminium coating. The optical flats were also available in custom sizes and geometries and so could also be used to make slightly larger cells with multiple compartments.

Cells were made with 15 mm \(\times\) 15 mm optical flats using the same substrate preparation, cell assembly and filling processes used with the previous substrates. The resulting LC laser cells had much larger Grandjean domains and a much more consistent emission wavelength. This is demonstrated by comparing Figure 5.4 with Figure 5.3, although it should be noted that several of the improvements made to other steps in the cell fabrication process were implemented in the fabrication of cells with optical
flats. The PBG transmission spectra in Figure 5.4 has a much steeper edge than that shown in Figure 5.3(a) and the sum of the emission spectra taken over a small pump ring shows a single laser peak at the PBG edge. This spectrum would be suitable for repeatable excitation of fluorophores in a fluorescence microscopy experiment and is therefore an important result, demonstrating that in-house fabrication of acceptable cells is possible. The POM image in Figure 5.4(b) shows that the domain size was much larger than the pump spot, and much larger than domains in cells made from substrates cut from glass wafers (see Figure 5.3(b)).

![Figure 5.4: (a) An example transmission spectrum from a transparent CLC cell with large domains. The edge of the PBG is much steeper than in cells with small domains. Emission from a reflective cell (made using similar processes and filled with a laser mixture of the same chirality) is included; the sum of 500 spectra taken over a pump ring is shown (bold), showing consistent laser emission wavelength at 591 nm). (b) POM of the transparent cell showing large domains and few oily streaks.](image)

### 5.4.2 Substrate preparation

Reflective substrates made from silicon wafers were coated with an aluminium layer to improve their reflectivity for visible wavelength light. The silicon wafers were cleaned before aluminium deposition with a mixture of solutions known as ‘RC1’ (a volume ratio of 5:1:1 of DI water, ammonium hydroxide (27%) and hydrogen peroxide (31%)) at 60 °C for 20 minutes. The aluminium layer was sputter-coated after a 1 minute argon milling pre-cleaning step. A layer of approximately 100 nm was deposited during the process.

A polyimide (PI) alignment layer was deposited on the substrates by spin-coating. This process requires a very clean environment and clean substrate, otherwise the
resulting PI layer is not of even thickness. Early attempts to spin-coat glass substrates resulted in visible streaks, thought to be due to contamination, despite cleaning the glass in solvents (acetone and isopropyl alcohol (IPA)), potassium hydroxide (KOH) and hydrochloric acid (HCl). A more aggressive cleaning process was therefore introduced to ensure that the substrates were not contaminated with residues or particles. For glass substrates, this process was:

1. wipe with a dilute KOH solution;
2. rinse thoroughly in DI water;
3. immerse in ‘piranha’ solution (a mixture of concentrated sulphuric acid (96%) and hydrogen peroxide (30%) with a volume ratio of 3:1) for 10 minutes;
4. rinse thoroughly in DI water;
5. rinse with IPA and dry with $N_2$.

The best results were achieved if dried by surface tension gradient in a Marengoni drier but this was only practical with full wafers so smaller substrates were and dried manually with an $N_2$ gun. A reduction in the number of contaminants was visible under an inspection lamp or microscope as a result of this cleaning process.

A process was also developed to ensure that reflective substrates were extremely clean without damaging the aluminium layer. This process was:

1. place in acetone in an ultrasonic bath at 50°C for 10 min with at least 1 solvent change;
2. repeat with IPA;
3. brush from the centre outwards with a non-shedding swab soaked in IPA;
4. dry with $N_2$.

The best spin-coating results with reflective substrates were achieved when steps 3 and 4 of this process were carried out immediately before spin-coating.

5.4.3 Alignment layer deposition

The PI spin-coating process was refined in parallel with the cleaning process developments. A systematic study of different PI materials was impractical due to limited availability of display-grade materials in small quantities. The PI material was $SE-1410$ (Nissan Chemical Industries), chosen because it promotes planar alignment with a low tilt angle, and is sold for display applications. This was diluted with $N$-methyl-pyrrolidone (NMP) at $50\%_{\text{vol}}$ for spin-coating. Before use, the mixture was
stirred with a magnetic stirrer for at least 10 min and then filtered with a 0.22 \(\mu\)m polytetrafluoroethylene (PTFE) syringe filter (CM Scientific). The PI mixture was also left undisturbed for at least 1 hour before use to reduce the number of air bubbles present, as these could also result in streaks. Some early spin-coating problems could be attributed to the use of syringe filters that were not chemically compatible with the solvent and hence contaminated the PI solution with particles of filter material, resulting in the streaks shown in Figure 5.5(a).

![Microscope images of wafers subject to different cleaning and spin-coating processes resulting in non-uniform PI films: (a) spin-coating with a PI solution contaminated with particles and/or bubbles; (b) poor coverage at the wafer edge caused by insufficient volume of PI solution.](image)

Before spin-coating, the substrates were given a final clean with an ionised nitrogen gun. The PI was then poured onto the centre of the wafer, or a few drops deposited on the centre of the chip with a pipette. Improved PI coverage was observed when a generous quantity of PI was used, and the material allowed to spread to the edge of the substrate before spinning, preventing the edge effects seen in Figure 5.5(c). The substrates were spun at 500 r/min for 5 s then 4000 r/min for 60 s, with the aim of leaving a film approximately 50 nm thick. The NMP was immediately evaporated using an 80 \(^\circ\)C, 5 minute pre-bake. Glass substrates were additionally hard-baked at 220 \(^\circ\)C for 1.5 hours whereas silicon wafers were hard-baked at a lower temperature 140 \(^\circ\)C for 3 hours to avoid tarnishing the aluminium layer. When preceded by thorough cleaning, this spin-coating process resulted in uniform PI coverage across a 3” wafer, with few defects visible under a microscope.
5.4.4 Alignment layer rubbing

The PI layer was then rubbed with a velvet cloth (obtained through Forth Dimension Displays) using a bench-top rubbing machine (HO-IAD-BTR-01, Holmarc). Initial experiments into the optimum rubbing process were all conducted with the 50 mm diameter roller set at 900 r/min, and passing the substrate under the roller 2 or 3 times at 6 mm s$^{-1}$. A micrometer stage allowed the height of the substrate to be set, thus changing the contact pressure between the cloth fibres and PI layer. This process was seen to cause damage to the PI layer, resulting in a non-uniform finish, as shown by comparing Figure 5.6(a) and (b). A slower roller rotation speed of 200 r/min reduced the damage, as shown in (c). This method theoretically reduced the rubbing strength, and therefore may have resulted in reduced anchoring energy, as discussed in Section 2.2.7. However, it was considered more important to use a slow roller speed to prevent visible damage to the substrate.

![Figure 5.6: Microscope images of reflective substrates subject to different rubbing processes (a) no rub (b) 900 r/min, medium rub height (c) 200 r/min medium rub height.](image)

It was not possible to maintain a constant rub height across the diameter of a wafer with this rubbing machine due to a slight bow in the substrate plate when the vacuum chuck was activated. A modification to this equipment is therefore recommended for fabrication using large substrates.

5.4.5 Cell assembly

To control the gap between the substrates, silicon dioxide microspheres (Nanjing Jianzun Glass Microsphere Plant Co.) with diameter specifications of either (10.00 ± 0.05) µm (for all reflective cells and some transparent cells) or (20.0 ± 0.3) µm (for some transparent cells) were mixed into UV-curable optical adhesive (NOA68 or NOA68TH, Norland) at 2%wt. In theory, the variation in cell gap of cells made with these beads should be similar to, or even smaller than, the variation in bead diameter, since the distance between rigid substrates would be determined by the larger beads.
Glue patterns were deposited on one substrate using a precision dispenser (*Ultimus V*, *Nordson EFD*) fitted with a 0.2 mm diameter syringe tip, in conjunction with a desktop robot (*JR2000N*, *Janome*). The robot enabled lines or dots of glue to be dispensed, with reasonable control of the line thickness or dot size through adjustment of the dispensing pressure and line speed or dispense time. Continuous lines of width <1 mm could be reliably dispensed with this method. Co-ordinates for glue patterns could be imported from drawings using software provided by the manufacturer; this allowed complex cells to be easily designed and fabricated, as shown in Figure 5.7.

![Figure 5.7: (a) Wafer scale fabrication of rectangular transparent cells, before cleaving. (b) Glue pattern on a reflective wafer for 4 cells, each with 2 LC compartments for fast wavelength switching.](image)

The top substrate was placed on the glued substrate by hand, PI side down with the rubbing direction anti-parallel to the bottom substrate, with the aid of a wafer or chip holder for alignment. Where multiple cells were being fabricated using a single pair of wafers as substrates, the cuts were made into the wafers were after assembly, leaving 0.2 mm of the thickness of the wafer undamaged to prevent ingress of the dicing fluid between the substrates (see Figure 5.7(a)). In this case it was also necessary to ensure there was a continuous glue line around the edge of the wafer to prevent dicing fluid from entering the cell gap. The partially diced wafers were then cleaved into cells by hand using a straight edge. Fabricating small cells from larger wafers in this manner was very efficient during the early stages of fabrication since approximately 20 cells could be made by processing a single pair of wafers. However, the dicing process took several hours and, in the case of reflective cells, it was difficult to position the cutting blade accurately. A fully automated dicing process is therefore recommended for fabrication of multiple cells from large substrates; this was not possible with the available dicing tool.

A consistent cell gap was difficult to achieve with cells made from large wafers.
Microscope images showed that some spacer beads in the glue lines were overlapping and therefore the cell gap was larger than the bead diameter. This was thought to be due to the wafer warp (specification ±30µm) and was addressed by using a bonding machine to compress the substrates together. The glue was changed to one with a thermal curing ingredient (NOA68TH), as the bonding machine programme could include a heating step to partially cure the glue after compression but before the cells were moved to the UV oven for further curing (60 s at 20 mW cm⁻²). The compression force applied to the wafers was set based on the glue pattern (and therefore approximate number of spacer beads), but was typically below 200 N. Optical measurements of the cell gap showed this technique resulted a cell gaps that was constant across the wafer within ±0.1µm, similar to the uncertainty in the optical measurement technique (see Figure 5.8(b)). The bonding process was therefore thought to help ensure a consistent cell gap across large areas, if the spacer beads were not damaged. However, it was not possible to operate the bonding machine at low enough force to reliably prevent beads from being crushed—as shown in Figure 5.8(a)— and hence the yield of this process was unacceptably low. A bonding machine with a lower range of compression force settings is recommended for fabricating cells from wafers of this diameter.

The difficulties achieving cells with a consistent cell gap using full wafer substrates, combined with the issues with rubbing large substrates (discussed in Section 5.4.2), meant the best cell fabrication results were achieved with smaller substrates, typically <20 mm×20 mm. The quality of LC laser cells was considered more important than the efficiency of the fabrication process at this stage of research, and hence fabrication with small substrates was preferred.
5.4.6 LC mixture preparation

LC laser mixtures were prepared using the nematic mixture \textit{BL006 (Merck)}, which was chosen for its high birefringence [41] and high nematic-isotropic transition temperature (118.5 °C [137]). The high twisting power chiral dopant \textit{BDH1281 (Merck)}, in powder form, was added at a small weight percentage (typically 3 to 6%) and the resulting mixture heated in an oven to dissolve at 140°C for 2 hours, followed by 100°C for at least 8 hours. Uneven distribution of chiral dopant within the cell is a possible cause of variations in pitch between chiral domains so it was important to ensure the dopant was dissolved and evenly distributed. Figure 5.9 shows a POM image of a cell with poorly dissolved chiral dopant that had been mixed at <140°C.

![Figure 5.9: A POM image of a transparent cell filled with a DD-CLC mixture with poorly dissolved chiral dopant, which can be seen in crystalline form. The cell also has many small Grandjean domains of different colour, suggesting large variations in chirality.](image)

The PBG of the CLC mixtures was evaluated by filling a transparent cell and measuring the transmission spectrum (see Section 3.2). This data was compared to data from other sources to inform the necessary chiral dopant concentration for a desired PGB position (see Appendix A, Figure A.1). The position of the long band edge of the PBG was then used to predict the laser wavelength that would likely be emitted when a suitable dye was added. There were statistically significant differences between measurements made in by the author and data from other labs [138], suggesting a systematic difference in either the materials used, mixing processes
or optical measurement technique. Possible causes include absorption of water by the chiral dopant causing a mass increase, or a different method for measuring or defining the wavelength of the PBG edge. Commercial production of LC lasers would require more precise control of the laser wavelength than was possible when using a very small mass of CLC (<100 mg) via this technique. It is recommended that larger volumes of CLC material are prepared if a more precise laser wavelength is required, to reduce the percentage error arising from mass measurements. It is also important that mixtures are reheated for several hours before filling into cells to combat possible re-crystallisation and ensure they are thoroughly mixed.

A laser dye was then added to the CLC mixtures to enable laser emission and dissolved at 100°C for at least 1 hour. These were chosen based on their quantum efficiency, absorption spectrum, emission spectrum and previously published LC laser efficiency data (where available). All dyes have good solubility in the LC host material.

Detailed properties of the components of the LC laser mixtures are given in Appendix A.5. A list of the mixtures used in experiments reported in this thesis is given in Table A.1. Each mixture is given a unique ID and will be referred to using this description.

5.4.7 Cell filling & sealing

Cells were filled with LC laser mixture via capillary action. The best results were achieved with mixtures that had been freshly made or stored overnight at 100°C before use. This ensured that the LC mixture was inhomogeneous and reduced the appearance of domains of different emission wavelength.

It is known that the filling and cooling process is important for achieving a the Grandjean texture with few defects. A small study was therefore conducted to understand the most important parameters. Cooling processes were tested using a temperature controlled microscope stage (LTS420, Linkam) and the effects monitored with POM using an upright microscope (also provided by Linkam) with a 10x magnification objective lens. The study used two glass cells: a 20 µm cell made in-house from an early batch and a cell made by LG with a 9 µm cell gap. The cells from the in-house batch had much poorer alignment properties than the LG cell. The aim of this study was to determine a repeatable method of achieving a Grandjean structure with as few defects as possible, regardless of the cell quality. An ideal process would be quick and easily automated. The temperature stage was only on loan for a short period so the study was limited to an investigation of the following parameters:

- Filling temperature (above or below the LC clearing temperature);
- Influence of mechanical shearing processes during filling and cooling;
• Cooling rate (maximum 10 °C min⁻¹, minimum 0.1 °C min⁻¹).

**Filling temperature.** The temperature at which a cell was filled was found to be important with in-house cells; the LC texture was focal conic if filled above the clearing temperature, as shown in Figure 5.10(a). A Grandjean texture was observed if the cells were filled below the clearing temperature, as in the example in 5.10(b) (100 °C filling temperature). The LG cell exhibited a Grandjean texture regardless of filling temperature, and could be heated above the clearing temperature and re-cooled to a Grandjean texture. If an in-house cell was heated above the clearing temperature, a focal conic structure was seen on re-cooling.

![Figure 5.10: POM images of an in-house cell filled with a N* mixture and cooled at 0.5 °C min⁻¹. Image (a) shows a focal conic texture in a cell filled at 130 °C and (b) shows Grandjean texture in a cell filled at 100 °C.](image)

**Mechanical shearing.** A focal conic cell could be switched to Grandjean by manually applying mechanical shearing forces to the cell with plastic tweezers. This resulted in small domains and a high defect density if applied at room temperature. However, larger domains were obtained by shearing the in-house cells in the early stages of the cooling process. Large domains were also achieved by continuously shearing during a fast cooling process.

**Cooling rate** Slower cooling rates resulted in lower defect densities, as illustrated by the images of the in-house cells in Figure 5.11. Quantitative analysis of the defect density was not possible due to variations in sample illumination, however, Grandjean domains of larger dimensions were evident in cells that were cooled more slowly. This conclusion was confirmed with the LG cell, by heating the same cell above the clearing temperature and cooling at different rates; see Figure 5.12. This experiment removed the effect of cell-to-cell variations that could be a confounding factor in the in-house
cell experiments, and was only possible with the LG cell because it formed Grandjean
textures when cooled from above the LC clearing temperature, without the aid of
mechanical shearing. The largest domains were achieved with the \( \text{LG} \) cell cooled at
\( 0.1 \degree \text{C min}^{-1} \). No further reduction in defect density was seen in the 24 hours after a
cell reached room temperature.

Figure 5.11: POM images of the in-house cell filled with a \( N^* \) mixture at 100 \( \degree \text{C} \) and cooled at
different cooling rates: 4 \( \degree \text{C min}^{-1} \) (a), 1 \( \degree \text{C min}^{-1} \) (b) and (c) 0.5 \( \degree \text{C min}^{-1} \).

Figure 5.12: POM images of the \( N^* \) filled \( \text{LG} \) cell cooled from 130 \( \degree \text{C} \) at different cooling rates:
4 \( \degree \text{C min}^{-1} \) (a), 1 \( \degree \text{C min}^{-1} \) (b), 0.5 \( \degree \text{C min}^{-1} \) (c) and 0.1 \( \degree \text{C min}^{-1} \) (d).

The data from this study was used to inform the design of a programmable hotplate
for cooling LC laser cells and the development of a process that would achieve the
lowest defect density possible with any cell. Since mechanical shearing is labour
intensive and inconsistent, slow cooling rates of 0.1 \( \degree \text{C min}^{-1} \) to 0.5 \( \degree \text{C min}^{-1} \) were
specified. A hotplate (US150, \textit{Stuart}) was modified by postgraduate students [139]
to be controlled by a \textit{Raspberry Pi} computer. An example of the cooling profile of the
resulting equipment is shown in Figure 5.13. The hotplate initially had a cooling rate
of 0.8 \( \degree \text{C min}^{-1} \) and was later modified to achieve a cooling rate of 0.29 \( \degree \text{C min}^{-1} \), also
shown in Figure 5.13. Unless stated otherwise, this latter cooling profile was used in
the fabrication of all cells, in combination with mechanical shearing immediately after
filling and at 80 \( \degree \text{C} \) to 90 \( \degree \text{C} \), to aid the formation of a Grandjean texture with large
domains.
Figure 5.13: Typical cooling profile for a cell filled at 100 °C and cooled with the first iteration of the cooling program (grey circles) and the revised, slower cooling program (open circles). The faster cooling profile is quadratic however a linear fit (dashed black line) is included to allow comparison to the other cooling profile.

After cooling, the cell edges were sealed with epoxy adhesive (Torr Seal, Agilent Technologies). This was found to be extremely important when used in a spinning cell system as without a complete seal, the mixture was found to leak, and the remaining LC mixture moved away from the pump spot or ring. This resulted in a complete cessation of lasing within 30 min with a rapidly spinning cell (10 kHz stepper motor and pump laser frequencies). A thick reflective substrate had the advantage that it was easy to seal the edges without altering the flatness of the rear surface, allowing the cell to be mounted flat on the spinning disk.
5.5 Summary of cell fabrication developments

LC cells that were readily available at affordable prices were found to be unsuitable for a spinning cell system, primarily because the spatial variation in emission properties was too high. Cells therefore had to be fabricated in-house. The developments reported in this section have led to an in-house cell fabrication process capable of producing cells that are as good at the best available commercial cells, with the ability to customise the cell for the intended application. The biggest performance improvement was achieved by replacing the substrates cut from glass or silicon wafers with optically flat glass. However, these optical flats were much more expensive than the wafers, were only available with a minimum thickness of 2 mm and typically had a lead time of 6 weeks. It is therefore recommended that a review of glass available for LC cell fabrication is conducted and source of suitable material found that will reduce the cost of future high quality cells and, ideally, allow wafer-scale fabrication.

The final version of the cell fabrication process used in all spinning cell experiments is described in Appendix B and uses the materials and tools detailed in Appendix A. The materials cost of a producing a small LC cell using this method was estimated to be £35, with larger, multi-compartment cells costing in the region of £200 each. These materials costs would be significantly reduced by large volume production. However, if the cost of the labour and facilities required to manufacture cells were taken into account, the cost of the in-house cells would be higher than most commercial cells. Fabricating cells in house is therefore only recommended when suitable cells are not commercially available.

Several steps in the cells fabrication process could further improved. In particular, a more repeatable rubbing process would be beneficial as it is currently difficult to precisely control the rubbing direction. The rub height is also not constant across the area of a large cell, and therefore process is currently not suitable large cells or wafer-scale fabrication. Wafer scale fabrication would be further aided by a cell assembly machine that allowed the substrates to be pressed together and the glue cured without damage to the spacer beads. Equipment for faster dicing would also make wafer-scale cell fabrication more attractive.
Chapter 6:  Spinning cell laser approach

6.1 Introduction

The aim of this chapter is to determine whether a spinning cell approach can be used to achieve an average power output from a LC laser that is sufficient for fluorescence imaging. The approach uses a stepper motor to rotate a LC cell, such that the cell moves with respect to the stationary pump beam, in order to allow high repetition rate pumping. Proof of concept laboratory experiments to compare the emission from spinning LC laser cells with static cells are reported in this chapter. The objectives of these experiments were to investigate:

- the maximum pump frequency that could be used with stable emission energy over short periods of operation (within the limits of the available pump lasers);
- the wavelength stability of output from spinning LC laser cells;
- the maximum average power output achievable with spinning cells (within the limits of the available pump lasers);
- the stability of the power output of the spinning cell over longer periods of operation.

Cells made using the final iteration of the cell fabrication process developed in Chapter 5 were used in the proof-of-concept spinning cell experiments.
6.2 Experimental method

The optical set-up used to evaluate the spinning cell approach shown in Figure 6.1 and described in more detail in Section 3.2.3. The pump laser beam diameter was measured as described in Section 3.2.4, and found to be 100 µm. The stepper motor that rotated the cell was operated with a step size of 0.72° such that there were 500 steps per rotation. In spinning cell experiments, the motor was operated at a step frequency equal to the pump laser pulse frequency to ensure a new location for each pump pulse, meaning that there were also 500 pulses emitted per rotation. The motor was mounted on a translation stage such that the pump spot could be offset from the axis of rotation. This ensured that the pump beam was incident on the cell along the circumference of a circle of known diameter (the pump ring). The pump frequency of each spot on the pump ring was known as the effective pump frequency and was calculated by dividing the pump laser frequency by the number of spots (500). Thus, each spot on a cell spinning at 10 kHz would be subject to an effective pump frequency of 20 Hz.

Figure 6.1: The optical set-up used for the proof-of-concept spinning cell experiments.

Three cells were prepared identically, using the process outlined in Appendix B, and filled with LC mixtures (see Appendix A). Cells were mounted on the spinning disk using thin double-sided tape.

The energy of the input pump was measured at different pulse frequencies over a
period of 60 s to characterise the stability of the pump laser. The slope efficiencies of
the LC laser cells were then measured at a low pump frequency, that was very unlikely
to cause damage (10 Hz, an effective pump frequency of 0.02 Hz), and at the highest
possible pump frequency (10 kHz, an effective pump frequency of 20 Hz). The mean
output energy from static cells was recorded over a period of 10 s. The mean output
energy from spinning cells, at pulse and step frequencies of 10 Hz and 10 kHz, was
recorded over 1 full rotation (50 s) and 100 rotations (5 s), respectively.

An upper estimate of the lasing threshold was made during the slope efficiency
measurements. This information was used to select three different input pulse energies:
slightly above threshold \((E_1 = (0.53 \pm 0.04) \mu J \text{ per pulse})\), a moderate energy \((E_2 =
(2.8 \pm 0.6) \mu J \text{ per pulse})\) and near the maximum energy that the pump laser could
deliver \((E_3 = (4.9 \pm 0.1) \mu J \text{ per pulse})\).

The performance of the spinning system was compared to the static cell performance
with pump pulse energy \(E_1\) and a pump ring diameter, \(D_{\text{ring}} = 3\) mm. In static cell
experiments, each set of measurements was made using an unused area of the cell to
avoid potential cumulative damage. For spinning cell experiments, the same area of the
cell was used (as cumulative damage was not expected) but the lowest pump frequencies
measured first. The cell was covered for approximately 10 s between measurements at
different pump frequencies, to allow some heat dissipation and recovery of any triplet
states.

The spinning cell system was also left running for several hours to gain insight into
the longer term energy stability of the system. The maximum average power output
possible with this system was also explored by repeating the spinning cell experiments
with higher pump pulse energies \(E_2\) and \(E_3\).

The wavelength stability of the system was dependant on cell used and the diameter
of the pump ring. Stability was assessed by recording an emission spectrum for every
pulse in a single rotation by setting the spectrometer integration time to the inverse
of the pulse frequency and recording 500 spectra. The total emission spectrum of
pump ring could be represented by the sum of the emission spectra, which resulted in
a spectrum that could be described by a dominant peak wavelength and FWHM.
6.3 Results and discussion

The static cell emission properties of cells used in the spinning cell experiments in this chapter were measured and are summarised in Table 6.1, and the emission spectra shown in Figure 6.3. Cell A was then pumped at higher frequencies while static. As expected, the emission from a static LC laser cell (at the lowest input pulse energy, $E_1$) was not stable at pump frequencies above 100 Hz, whereby a significant decrease in output energy per pulse was seen in the first 60 s. Higher pump frequencies resulted in faster reduction of output energy, as shown in Figure 6.2(a). This reduction is likely due to a combination of optically induced distortions to the DD-CLC structure and cumulative thermal effects, as discussed in Section 2.2.4. The triplet state lifetime of the dye used in cell A (PM597) is approximately 0.1 ms, suggesting that accumulation of triplet states would not be significant using our pump laser which delivers 1.3 ns pulses below 10 kHz [53, 140].

<table>
<thead>
<tr>
<th>Cell</th>
<th>Mixture</th>
<th>Static efficiency (%)</th>
<th>Dominant emission $\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>19.8 ± 0.4</td>
<td>590</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>12.2 ± 0.5</td>
<td>583</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>4.4 ± 0.3</td>
<td>633</td>
</tr>
</tbody>
</table>

Table 6.1: A summary of LC cells used in this chapter. Slope efficiency measurements were taken with static cells at 10 Hz pulse frequency. The emission wavelength quoted is that observed in most pump spot locations in the central area of the cell.

The emission energy from a spinning cell is shown in Figure 6.2(b). In contrast to the static cell results, the output energy per pulse was constant over 60 s with all pump frequencies used. The spinning system was thus successful in allowing operation of a LC laser at 10 kHz. Over a 60 s period, there were negligible cumulative effects of operating the laser system at the upper end of the range of available pump frequencies when using this pulse energy ($E_1$). The maximum pump frequency that could be used while maintaining stable emission over 60 s could not be established due to the limitations of the pump laser (10 kHz).

The efficiency of a static cell (cell B) at low pump frequency (10 Hz,) was found to be 12% and is compared to the same cell spinning with step rates of 10 Hz and 10 kHz in Figure 6.4. Similar efficiency results were observed at all spin speeds. Lasing thresholds were below the limit of detection, but are less than 89 nJ per pulse (1.1 m J cm$^{-2}$).

The stability of the LC laser when operated at 10 kHz was then investigated by running the system for 2 hours and recording the mean energy per pulse over each 1 s
Figure 6.2: Emission spectra from the cells used in the spinning cell experiments. Data was recorded while the cells were static at a location emitting at the dominant wavelength.

period. The results, plotted in Figure 6.5(a), show that the laser was still operating effectively after 2 hours, but with approximately 65% of the original output energy per pulse. In the case of this 3 mm pump ring, consecutive pulses were overlapping, which is likely to have exacerbated optical and thermal distortions to the CLC structure. It was hypothesized that the long term stability at 10 kHz could be improved by increasing the pump ring diameter to prevent consecutive pump spots from overlapping, as illustrated in Figure 6.5(b) and (c). Results from an experiment using a larger pump ring diameter ($D_{\text{ring}} = 20 \text{ mm}$) are included in Figure 6.5(a), and show a small improvement in stability: the output energy per pulse was still at approximately 85% of the original output after 2 hours of operation at 10 kHz. Theoretically, each spot in this large diameter pump ring is subjected to an ‘effective pump frequency’ of 20 Hz (pump frequency / number of spots) and thus should be equivalent the behaviour of a static cell system at 20 Hz. The output energy from a static cell at 20 Hz remained within 96% of the original output after 2 hours (Figure 6.5(a)), close to the stability of the spinning cell with equivalent effective pump frequency.

The use of larger pump ring diameters had the side-effect of increasing the variation in output energy from pulse to pulse, due to variations in the imperfect polydomain CLC structure across the cell. These different chiral domains also affected the wavelength of
Figure 6.3: A comparison between the emission from cell A (a) when static and (b) when spinning, with different pump pulse frequencies, input energy $E_1$ and $D_{ring} = 3$ mm. The emission from a spinning cell was stable, even at 10 kHz (1200 rpm). The emission energy was normalized to the mean of the first ten data points recorded and down-sampled before plotting for clarity.

It may be possible to increase CLC domain sizes through greater control of the cell fabrication process, reducing both wavelength and energy variations, as discussed in Section 5.5. This may be achievable with further process development in an optimized commercial facility, and would allow the use of larger pump rings in combination with smaller step angles in order to increase the number of pulses per rotation without consecutive pump spots overlapping. For example, pumping at 100 kHz whilst maintaining an effective pump frequency at each spot of 20 Hz would be possible with an 8 cm diameter cell. There is clearly a limit to this approach, due to the size of equipment; a 1 MHz pump frequency would require an impractical 1 m diameter cell. Alternative solutions to managing thermal effects would therefore be required to achieve megahertz pulse frequencies. One possible approach is to stabilize the CLC structure to reduce distortion, for example with polymerization [60, 141].

The highest average power recorded for a spinning LC laser with a small wavelength variation ($D_{ring} = 3$ mm) was 3.5 mW. This value is likely to be high enough for use in fluorescence microscopy (see Section 1.3), providing the excitation wavelength and filters are chosen carefully. The highest output power was achieved by increasing the input pump energy to $E_3$, as shown in Figure 6.7. However, when using a high pulse
energy, the highest pump frequencies were no longer stable over a period of 60 s, as indicated by the large error bars on some high energy data points. This result agrees with the trends shown by Morris et al. [56], and shows that effect of increasing pulse energy is similar with the relatively low pulse energies used in our spinning cell experiments. It should be noted that high pulse energies resulted in some permanent degradation of cell performance, although the damage may have been exacerbated by LC mixture leaking from the cell (despite sealing attempts). The most effective strategy for achieving high average power output that is stable over 60 s or longer therefore appears to be to use a low pulse energy with a much higher pump frequency. With the 8 cm diameter cell discussed previously, allowing pump frequencies of 100 kHz, output power in excess of 10 mW would be possible with pump energy $E_1$, assuming a similar cell efficiency. Higher pulse energies could clearly be used to achieve much higher average power if a shorter period of stable emission was acceptable. In the case of microscopy applications, exposure times are typically $\sim 200$ ms so short emission periods could be acceptable if the pump laser was synchronised with the shutter on the camera such that the laser was only on when the shutter was open. This approach is also beneficial for reducing phototoxicity issues discussed in Section 1.2.2.

Figure 6.4: The slope efficiency of cell B when static compared to slowly spinning and spinning at 10 kHz ($D_{ring} = 3$ mm). For spinning cells, the motor step rate was equal to the pump repetition rate. Error bars show the standard deviation on the mean energy output. Note that spinning the cell had no detrimental effect on its efficiency.
Figure 6.5: (a) Emission from cell B at 10 kHz over 2 hours for two different pump ring diameters. In the case of non-overlapping pump spots, the data show similar stability to a static cell at 20 Hz (i.e. the same effective pump frequency). (b) Illustration of a pump ring with diameter large enough to prevent consecutive pump spots from overlapping. (c) A smaller pump ring with overlapping pump spots.

A video demonstration of the spinning cell system is available at the link provided in Figure 6.8.
Figure 6.6: Emission spectra from cell C while static (black, solid line) and the sum of all 500 emission spectra recorded during a single rotation of the spinning LC cell system at $D_{ring}=3\text{ mm}$ (bold black, dashed line) and $D_{ring}=6\text{ mm}$ (grey, short-dashed line).
Figure 6.7: The average power output of cell A with different pump frequencies, over a period of 60 s. Results from experiments with input pulse energies are shown ($E_1 =$ squares, $E_2 =$ circles, $E_3 =$ triangles). Error bars show the standard deviation in the output power over this period. The use of high energy input pulses was seen to damage the cell. A maximum average power of 3.5 mW was recorded.

Figure 6.8: A video of the spinning cell system, demonstrating operation at 10 kHz pump frequency and wavelength switching technique. https://doi.org/10.7488/ds/2407
6.4 Conclusions

The spinning cell technique outlined in this chapter has enabled higher repetition rate operation of a LC laser. A rapidly spinning stage was used to allow operation of a LC laser at 10kHz pulse repetition rate—two orders of magnitude greater than possible with a static cell—without a reduction in emission efficiency. This approach can enable stable operation at higher average power, with the optimum combination of pulse energy and frequency. For example, when used with a low pump pulse energy, the 10kHz emission was found to be stable over a period of 2 hours, suggesting that it would be feasible to use a spinning cell LC laser over an extended period of time in a microscopy facility. Average power outputs of up to 3.5 mW were achieved; the highest power output reported with a LC laser system. This is likely to be high enough for sample illumination in fluorescence microscopy techniques. Further average power and repetition rate improvements are likely to be possible by using this approach with a pump laser that can deliver much higher repetition rates.

The development of cell fabrication processes described in Chapter 5 was essential to achieve spinning cell results with acceptable wavelength and energy stability. Significant progress has been made towards highly controlled cell fabrication methods that minimize wavelength variation within a LC laser cell. These cells will be crucial in the successful use of spinning cell techniques, particularly with larger pump rings.

A spinning cell LC laser system is likely to meet the requirement for a laser light source in to fluorescence microscopy. In addition, the improved output demonstrated in this chapter may open up opportunities to use LC laser technology in other applications, such as laser displays, that would benefit from capabilities such as wavelength tuning or pre-programmed wavelength sequences, with low cost, compact equipment.
Chapter 7: A portable spinning cell LC laser for fluorescence microscopy

7.1 Introduction

The aim of this chapter is to demonstrate LC laser technology in a fluorescence microscope. As discussed in section 1.3, this application was chosen as it was likely to benefit microscope users and provide an opportunity to demonstrate some of the features of LC lasers. An LC laser system was therefore built with fluorescence microscopy in mind. Although the laser system performance is primarily assessed for this application, a versatile system was considered advantageous to allow additional applications to be investigated in future research. It was important that the LC laser system was small and portable so that it could be used in a variety of existing microscopy facilities where space is often limited. The system design specifications were developed by considering typical requirements for microscopy light sources, informed by discussions with a microscope manufacturer, and the characteristics of competing tunable light sources (see Section 1.3). The resulting design specifications for the a portable liquid crystal laser system for microscopy applications are given in Table 7.1.

The spinning cell approach was used to enable LC laser emission with high enough output power for imaging applications. Mechanical selection of LC laser mixtures with different emission wavelengths was chosen as the best method of achieving a broad wavelength range and fast wavelength switching. Cells with multiple compartments containing different LC laser mixtures were designed to facilitate rapid, convenient wavelength switching.

The objectives of this chapter are to construct a portable LC laser system with similar optical output to the laboratory bench system described in Chapter 6, integrate this system into a fluorescence microscope and use it to capture fluorescence microscopy images of biological samples. The construction and characterisation of this design is described in Sections 7.2 and 7.3, respectively. The portable system was then aligned with the epifluorescence port of a microscope, enabling wide-field fluorescence microscopy of biological test samples, as reported in Section 7.4. Modifications to the
<table>
<thead>
<tr>
<th>Property</th>
<th>Desired value</th>
<th>Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>0.3×0.2×0.9 m</td>
<td>Similar to a supercontinuum light source</td>
</tr>
<tr>
<td>Mass</td>
<td>&lt;15 kg</td>
<td>Similar to a supercontinuum light source and easily positioned by one person</td>
</tr>
<tr>
<td>Cost</td>
<td>&lt;£40,000</td>
<td>Cheaper than a supercontinuum light source</td>
</tr>
<tr>
<td>Average output power</td>
<td>10 mW</td>
<td>Typical requirement for a microscope light source (see Section 1.3)</td>
</tr>
<tr>
<td>Emission energy stability</td>
<td>8 hours, &lt;2%</td>
<td>Operational for a full working day</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>460 nm to 850 nm</td>
<td>To excite a wide range of commonly used fluorophores</td>
</tr>
<tr>
<td>Linewidth</td>
<td>&lt;1 nm</td>
<td>To allow fluorophore excitation with high specificity</td>
</tr>
<tr>
<td>Accuracy of wavelength selection</td>
<td>±2 nm</td>
<td>To allow fluorophore excitation with high specificity</td>
</tr>
<tr>
<td>Wavelength stability with time</td>
<td>±1 nm</td>
<td>To allow fluorophore excitation with high specificity and repeatability</td>
</tr>
<tr>
<td>Wavelength switching time</td>
<td>&lt;1 s</td>
<td>For convenient use with different fluorophores</td>
</tr>
<tr>
<td>Beam divergence</td>
<td>(1.2 ± 0.2) mrad</td>
<td>Typical illumination requirement for a microscope light source (see Section 1.3)</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>15°C to 40°C</td>
<td>For operation at all likely laboratory temperatures</td>
</tr>
<tr>
<td>Operating lifetime</td>
<td>&gt; 15,000 hours</td>
<td>Replacement frequency similar to competing technologies</td>
</tr>
</tbody>
</table>

Table 7.1: Design requirements for a portable LC laser system for microscopy applications.

LC laser system to improve performance and ease of use are suggested in Section 7.5.
7.2 Portable LC laser system: design & fabrication

7.2.1 Overview of design

The portable LC laser system consists of the laser head and a power and control unit that can be packed into a single, wheeled case for easy transport by one person. This section will highlight the most important design features, describe the selection of components and explain how these were integrated into a portable laser system. An overview of the system architecture is shown in Figure 7.1.

The laser head contained the pump laser head and all the optical components required for LC laser pumping, including the LC laser cells themselves. It also contained motors to spin and translate the LC cells, and to rotate the polarisation optics, along with the associated motor driver boards. All components were mounted on an 8 mm aluminium plate. Removable sides (butt-joint construction) and lid of the same material were fitted to provide a light-proof enclosure.

The power and control unit contained the pump laser power supply, a multi-voltage power supply to enable all components to be powered through a single mains socket, and a microcontroller for motor control. A Raspberry Pi computer with touch screen was initially included in the design with the aim of allowing the portable laser to be used without a PC. However, it became apparent that a laptop would require to control some of the devices chosen so the Raspberry Pi was not used. The touch screen was removed to allow the use of a smaller case but the Raspberry Pi was left for use in future design iterations.

A detailed list of the components used to build the system is given in Appendix C.2.
CHAPTER 7. A PORTABLE SPINNING CELL LC LASER FOR FLUORESCENCE MICROSCOPY

Figure 7.1: A schematic of the portable LC laser system showing the power connections (solid lines) and data connections (dashed lines).

7.2.2 Pump laser selection

The choice of pump laser was determined by the considerations listed in Table 7.2. A pump laser wavelength near the short end of the visible spectrum was desirable to maximise the system’s tuning range. However, many of the efficient laser dyes used in previous LC laser research are more optimally excited by wavelengths around 530 nm, so lasers up to 532 nm (a common solid-state laser wavelength) were also considered.

The energy per pulse had to be much greater than a typical LC laser threshold energy, to allow for some reflection losses from optical components. The combination of the energy per pulse and pulse repetition rate had to yield an average power greater than 20 mW, such that a cell with 50% efficiency could provide a 10 mW output, as specified in the design requirements (see Table 7.1).
### Value Comments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>400 nm–550 nm</td>
<td>To excite laser dyes</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>&gt;1µJ</td>
<td>≫ LC laser threshold</td>
</tr>
<tr>
<td>Pulse repetition rate</td>
<td>Variable</td>
<td>Must allow average power output requirements to be met</td>
</tr>
<tr>
<td>Maximum average power</td>
<td>20 mW</td>
<td>Theoretically allows 10 mW LC laser emission if 50 % efficiency is achieved</td>
</tr>
<tr>
<td>Dimensions</td>
<td>&lt;0.3 m×0.1 m×0.1 m</td>
<td>As small as possible, with a compact power supply, for portability</td>
</tr>
<tr>
<td>Cost</td>
<td>&lt;£20,000</td>
<td>System cost should be significantly less than a supercontinuum light source</td>
</tr>
</tbody>
</table>

Table 7.2: A summary of the pump laser requirements for the portable LC laser system.

A 440 nm Nd:YLF DPSS laser (QL440-025, Crystalaser) was selected as the most promising short wavelength source for a portable LC laser system. The specifications stated that this laser had an average power of 25 mW. Testing revealed that the maximum energy per pulse was 6.5 µJ, sufficient for a LC laser pump. The maximum repetition rate was 100 kHz, however the pulse energy decreased rapidly when the repetition rate was increased above 3 kHz, as shown in Figure 7.2. The energy per pulse was 1 µJ at 14 kHz, so the laser would only be useful as a high repetition rate LC laser pump in a low threshold system. The main disadvantage of this pump laser was the long pulse duration (30 ns) which caused high thresholds and poor energy stability, as discussed in Section 2.2.4. The effect of this pulse duration on the performance of a spinning cell system was not well characterised at the point of purchase, therefore the portable system was designed to also accommodate the better characterised 532 nm pump laser used in the previous chapter, which had similar dimensions. The energy per pulse emitted by this laser actually increased slightly with pulse repetition rate, as shown in Figure 7.2, up to a maximum repetition rate of 10 kHz. The disadvantage of the 532 nm pump was that the wavelength was too long to excite some fluorophores commonly used in biomedical imaging, including GFP.

#### 7.2.3 Optical system design

A schematic of the laser head, containing the pump laser head and all the optical and mechanical components of the system, is shown in Figure 7.3. The pump laser was mounted on aluminium plate to act as a heat sink and to set the beam height to...
CHAPTER 7. A PORTABLE SPINNING CELL LC LASER FOR FLUORESCENCE MICROSCOPY

Figure 7.2: The energy per pulse emitted from the 440 nm (filled circles) and 532 nm (open circles) pump lasers at different pulse repetition rates. The 440 nm laser emission energy decreased dramatically at high frequencies, whereas the 532 nm laser pulse energy increased with pulse repetition rate, but had a lower maximum repetition rate.

Controlling the pump laser polarisation and pulse energy. Both pump lasers had a linearly polarised output which was attenuated with a rotatable linear polariser according to Malus’ law. The beam was then circularly polarised with a quarter wave plate (specific to the pump laser wavelength). This was rotated with the linear polariser such that the circular polarisation of the pump beam was maintained. The wave plate was orientated such that the polarisation of the pump beam had opposite handedness to the CLC helix to maximise absorption by the dye molecules by preventing reflection. This is beneficial where the pump beam wavelength falls within the PBG, so was necessary to achieve high efficiency with a large range of LC laser mixtures (see Section 2.2.4). The optimum angle of the quarter wave plate with respect to the linear polariser was determined experimentally as the position that
resulted in lowest threshold lasing of a LC laser cell with PBG that overlapped with the pump laser wavelength. Rotating the linear polariser and quarter wave plate together removed the need for a half wave plate (as used in the methods described in Chapter 3), thus reducing losses from reflections as well as the cost and complexity of the system.

**Focusing the pump beam on to the spinning LC laser cell.** A concave mirror was used to focus the pump beam on to the LC laser cell. A mirror was preferable to a transparent optic since it allowed the pump beam to be folded towards the cell, resulting in a more compact layout. The pump beam was designed to be incident on the reflective LC laser cell at an angle of approximately 45°. This had the advantage that most reflected pump laser photons were spatially separated from the LC laser output. It also allowed control of the diameter of the collimated output from the LC laser by changing the collimating lens; this would be difficult with a 90° pump angle where the collimating lens also focusses the pump beam onto the cell. The concave mirror was mounted on a post that could be rotated to adjust the beam angle. A fold
mirror was added between the polarisation optics and focussing mirror to minimise the size of the laser head. This mirror was also mounted on a rotatable post. The geometry of the resulting layout meant that the minimum focal length of the concave mirror was determined by the diameter of the spinning disk on which the LC laser cell was mounted. A large disk and short focal length mirror would result in the disk blocking the pump beam before it reached the concave mirror (as evident in Figure 7.3). A focal length of 50 mm was chosen to allow a spinning disk diameter of up to approximately 50 mm. A long focal length was also beneficial as the larger depth of focus means the LC laser cell did not have to be positioned as precisely as with a short focal length mirror. The LC laser cells used in the portable LC laser system were made from optically flat substrates using the process summarised in Appendix B and filled with the mixtures detailed in Appendix A.5.3.

Collimating the LC laser emission. The LC laser emission was collected by an achromatic doublet lens with a broadband anti-reflective coating. An achromatic lens was required so that it was not necessary to adjust the lens position for different LC laser emission wavelengths. The focal length of the lens determined the diameter of the collimated beam. The diameter of the lens was chosen so that it was large enough to collect the majority of the LC laser emission but did not intersect with the pump beam when the lens was positioned a distance of one focal length away from the LC cell. The lens was mounted on a translation stage that allowed adjustment along the axis of emission such that the LC laser beam could be focussed. A 12.5 mm diameter lens with a focal length of 19 mm was used to achieve a collimated output beam of approximately 5 mm diameter. This could be swapped for a 25.4 mm diameter lens with a focal length of 30 mm, resulting in a larger beam diameter. Exchanging the collimating lens was a good method of expanding the beam as it took advantage of the natural divergence of the LC laser output rather than introducing additional lenses. The smaller diameter lens had the advantage of allowing fine adjustments to the beam position and direction as there was space to mount the lens on a \(x-y\) translation mount. Aligning the larger lens was more difficult as the height had to be adjusted using very thin spacers. In this case, the mirror and LC cell position were critical due to the lack of \(x-y\) adjustment of the collimating lens.

Blocking the pump beam from the laser system output. A long pass filter was placed over the LC laser output to prevent any reflected pump beam photons from exiting the laser head. The cut-off wavelength of this filter was chosen to be less that 20 nm longer than the pump laser emission wavelength, to maximise the output wavelength range. The long pass filter and quarter wave plate were the only optical
components that needed to be changed when the pump laser was changed.

7.2.4 Cell designs for wavelength switching

LC cells with multiple compartments were designed in order to allow fast, automated wavelength switching. Some example cell designs for wavelength switching are illustrated in Figure 7.4. The simplest multi-wavelength cell design (7.4(a)) enables rapid switching between two wavelengths by rotating the cell. This can be fabricated using the same methods as single wavelength cells. Introducing additional wavelengths, as shown in 7.4(b), requires different filling methods to ensure that each compartment is filled with the desired LC mixture without any air being within the cell. For capillary-filling, air must escape to enable the LC mixture to enter the cell, thus each compartment must have both an entrance and an exit in locations that minimise the risk of trapped air (caused by the exit being blocked by LC before all the air has escaped). This could be achieved by cutting out the central circle of one substrate of the cell shown in 7.4(b), but fabricating cells from such ‘doughnut’ shaped substrates is undesirable as the bespoke shape would increase the cost and lead time of substrates. An alternative method would be to drill or etch small holes through the reflective substrate in an area that is not required for emission. This approach could potentially allow any cell geometry, but it was not possible to achieve with the facilities available without unintended damage to the substrate. Substrates with pre-drilled holes could be ordered, but these would have the same disadvantages of high cost and long lead time discussed above. Furthermore, a substrate with holes through it could not be spin-coated effectively, and so a method of spray-coating a thin and even film of PI would be required. The simplest method for filling multi-wavelength cells is likely to be a vacuum-filling method, since each compartment would only require one entrance, which could be at the edge of the substrate. In the absence of facilities for vacuum-filling, multi-wavelength cells were made by preparing smaller cells and joining these together during the edge-sealing process.

Cells with concentric rings of different wavelengths, as shown in Figure 7.4(c), were designed to allow the use of a spinning cell for high power, stable emission while enabling convenient colour switching by translating the cell relative to the pump beam. Concentric ring cells were fabricated in two pieces from rectangular cells with semicircular glue lines, as shown in Figure 7.5, to allow edge-filling of all sections.

A method of preventing cross-contamination of compartments during the filling process was necessary for all multi-compartment cells. A small barrier was created on the edge of the substrate at the boundary of each compartment with the sealing adhesive, as shown in Figure 7.5. In this example, the adhesive was later removed to allow the 2 cells with semicircular compartments to be positioned close together to
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Figure 7.4: Spinning LC laser cell designs with several compartments for different LC laser mixtures. Cells are designed to rotate in the plane of the page, as indicated by the arrows. (a) A dual-wavelength cell for fast wavelength switching, (b) a multi-wavelength cell for fast wavelength switching and (c) a concentric ring multi-wavelength cell for convenient wavelength switching. The concentric ring cell can be translated to change the ring on which the pump laser is incident.

Figure 7.5: Photographs of the cell filling process for a concentric ring cell fabricated from 2 rectangular cells with semicircular glue lines. (a) An empty rectangular cell with semi-circular compartments showing adhesive barriers to prevent cross-contamination. (b) A partially filled cell with multiple compartments. The vials containing the LC laser mixtures, in holders designed to ensure even mixing via heating, are also shown.

7.2.5 Mechanical design

An important feature of the LC laser system was the spinning disk, which enabled high repetition rate operation. A small stepper motor (Oriental Motors CVK523AK) with a maximum step rate was higher than the pulse frequency was chosen, as this could be controlled precisely and synchronised with the pump laser pulses. A custom spinning disk was designed to fit tightly onto the motor axle and secured with grub screws,
allowing for a few millimetres of adjustment along the axle to optimise its position relative to the pump laser focus. The disk included a collar around its circumference that could be used to clamp large LC cells to the disk. The diameter of the disk had to be at least 25 mm to allow the use of pump rings with non-overlapping spots \( (D_{\text{ring}} > 16 \text{ mm}) \). A larger disk was desirable to allow more space for different LC mixtures, but increasing the disk size considerably increased the volume of the laser head. A design that was compatible with cells made from 50 mm (2 inch) wafers was chosen, as a compromise between size and performance. However, cells made from large wafers were not used due to the problems in achieving a consistent standing helix \( N^* \) LC structure discussed in Section 5.4.

A method of translating the LC cell relative to the pump beam was necessary to allow control of the pump ring diameter. The stepper motor and spinning disk were therefore mounted on a rail with a sliding carriage and attached to a linear actuator. Linear translation of the spinning cell also enabled cells with concentric rings of different LC mixtures to be used to allow convenient wavelength selection. The requirement for switching between emission wavelengths in under 1 s could be easily met by a low-cost linear actuator (Actuonix P16-P 50 mm) and slide (Actuonix 50 mm Micro Linear Slide Rail). Motorised linear translation solutions with more mechanical stability and higher precision were available from suppliers of optical components, but these were approximately 10 times the cost of the Actuonix components and had much slower translation. The use of a low-cost slide with poor mechanical tolerances meant that there was some undesirable movement of the stepper motor and therefore the spinning disk could move out of the plane of rotation, resulting in some displacement of the output laser beam. Beam displacement was minimised by ensuring that the LC laser cells were positioned in the middle of the disk such that the centre of mass was in line with the motor axle.

The linear polariser and quarter wave plate were mounted on a motorised precision rotation mount (Newport AG-PR100). This component was expensive, but it was important to enable precise and accurate control of the pump laser pulse energy, and slow rotation was acceptable.

### 7.2.6 Power and control systems

A power and control unit was designed to house electronic components that could not be easily included in the laser head, as shown in Figure 7.6. The optics rotation mount, linear actuator and stepper motor were supplied with individual driver boards (Newport AG-UC2, Actuonix LAC and Oriental Motors CVD518BR-K, respectively) that were mounted in the laser head, in an area inside the case that was not occupied by optical components. The main component in the power and control unit was the pump...
laser power supply. A commercially available multi-voltage power supply (TrackoPower TXL100-0534TI) was included to minimise the number of mains power cables required for the system. This provided a 24 V supply for the stepper motor driver board and a 12 V supply for the linear actuator control board. A micro-controller (Arduino Uno R3) was also powered from the 12 V supply. The micro-controller was used to set the pulse repetition rate of the pump laser and the stepper motor step rate (see Appendix C.3). Both devices required a 5 V square wave with a 50% duty cycle to trigger a pulse or step. The frequency of this square wave set the stepper motor or laser pulse frequency. The stepper motor frequency was increased or decreased gradually to avoid malfunction (the rate of change could be varied to suit the application). Turning the motor or laser off was achieved through setting the duty cycle to 0%. Serial commands were sent to the micro-controller from a PC via the USB port. The Arduino Uno has two timers (in addition to the built-in function timer) that were used to control the pulse frequency of the two devices independently. Devices could be easily synchronised by connecting them to output pins that use the same timers. If more than two devices are required with independent control, an Arduino Mega could be used, as this has additional timing chips.

![Figure 7.6: A schematic of the design of the power and control unit showing the power and data connections.](image)

Most power and data cables were bundled and run to the laser head in a single connection. However, the optics rotation mount required a USB connection to a PC to power the device and to send commands through the manufacturers software. An
OEM version of the rotation mount is available and could be used in future with the system power supply and controlled with the micro-controller. Similarly, the linear actuator was controlled using the manufacturer’s software via a USB connection to a PC. A 5 V supply was included in the design to allow future versions of the system to be controlled with a Raspberry Pi computer (gen. 3, model B) and Raspberry Pi touch screen interface, rather than a laptop PC. It should be noted that there must be a load on this ‘primary’ 5 V supply in order for the voltage from the other supplies to be properly regulated.
7.3 Portable LC laser system: evaluation

7.3.1 Overview

The performance requirements for an ideal microscopy light source, as outlined in Section 7.1, are repeated in Table 7.3 alongside a comment concerning the performance of the portable LC laser system. The output power, energy stability, wavelength range, linewidth, wavelength stability and operating lifetime of the portable LC laser system are discussed in this section, based on the results of initial characterisation tests.

<table>
<thead>
<tr>
<th>Property</th>
<th>Desired value</th>
<th>Comment on performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size</td>
<td>0.3×0.2×0.9 m</td>
<td>Laser head unit: 0.25×0.19×0.1 m, power &amp; control: 0.2×0.1×0.1 m. Acceptable for a prototype system.</td>
</tr>
<tr>
<td>Mass</td>
<td>&lt;15 kg</td>
<td>10.6 kg. Acceptable for a prototype system.</td>
</tr>
<tr>
<td>Cost</td>
<td>£40,000</td>
<td>Requirement met for both 440 nm and 532 nm pumped systems (£17,191.66 and £9087.67, respectively)</td>
</tr>
<tr>
<td>Output power</td>
<td>10 mW</td>
<td>4.5 mW achieved with a spinning cell</td>
</tr>
<tr>
<td>Emission energy stability</td>
<td>8 hours, &lt;2%</td>
<td>Not met, but improvements in stability over 2 hours achieved</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>460 nm to 850 nm</td>
<td>High power emission demonstrated between 570 nm and 650 nm</td>
</tr>
<tr>
<td>Linewidth</td>
<td>&lt;1 nm</td>
<td>Spinning cell typically 4 nm</td>
</tr>
<tr>
<td>Accuracy of wavelength selection</td>
<td>±2 nm</td>
<td>Not investigated in detail.</td>
</tr>
<tr>
<td>Wavelength stability with time</td>
<td>±1 nm</td>
<td>±2 nm with the best performing cells and a small pump ring</td>
</tr>
<tr>
<td>Wavelength switching time</td>
<td>&lt;1 s</td>
<td>Achieved with concentric ring cells, although cell fabrication refinements recommended.</td>
</tr>
<tr>
<td>Beam divergence</td>
<td>(1.2 ± 0.2) mrad</td>
<td>Depends on collimating lens.</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>15°C to 40°C</td>
<td>Not investigated in detail.</td>
</tr>
<tr>
<td>Operating lifetime</td>
<td>&gt; 15000 hours</td>
<td>Depends on input pump energy.</td>
</tr>
</tbody>
</table>

Table 7.3: Typical requirements for lasers used in commercially available microscopy systems.

Photographs of the portable LC laser system are shown in Figure 7.7 and Figure 7.8.
Both units could be easily transported by one person in a wheeled suitcase (Peli Storm iM2720) with adequate padding to protect the system during transit. The system dimensions (laser head unit: 0.25×0.19×0.1 m, power & control unit 0.2×0.1×0.1 m) were smaller than most tunable wavelength light sources. At 10.6 kg, the system was also lighter than competing laser systems.

7.3.2 System costs

The total cost of the commercially available components for the portable LC laser system was £9087.67 for the green pumped system or £17,191.66 for the blue pumped system. As discussed in Section 1.1, a large portion of these costs were the pump lasers.
themselves (£6,883 and £18,000\(^1\) respectively). The cost of the custom components, manufactured in-house, are not included in these values but would be very small in comparison to the pump laser costs.

The materials for in-house cells are estimated to cost £35 for a small cell and £200 for a larger, multi-wavelength cell. There would be significant facility and labour costs in manufacturing these cells commercially, and minimising these costs would be an important part of the commercialisation process. It would also be important to maximise the useful lifetime of each cell. Control systems designed to prevent use of a LC cell with high energy pump pulses for long periods are recommended to maximise the cell lifetime. It is unlikely that a LC laser cell of the quality required for consistent emission with a spinning cell would ever be considered a consumable item, due to the high cost of optically flat glass. However, LC laser applications that did not require spinning cells or did not required narrow linewidth could tolerate the use of much cheaper cell materials.

The cost of the portable LC laser system compares favourably with other tunable laser systems (see Table 1.1). A commercial LC laser system would likely be cheaper than the current cost of a supercontinuum light source, even with the cost of labour included. The system is slightly over-engineered to allow some versatility; a system with fewer features could be manufactured more cheaply if cost was more important than versatility. There would also be significant cost savings if devices were manufactured in bulk.

\(^1\)Including a discount from the supplier.
7.3.3 Output power & cell efficiency

The output power of the portable spinning LC laser was measured with a cell used Chapter 6 (cell B) in order to confirm that conclusions drawn from experiments with the laboratory set-up were valid for this system. The slope efficiency of cell B in the portable system was measured while static (10 Hz pump frequency) and spinning (10 kHz pump and step frequency, 3 mm pump ring). The spinning and static cell results were similar, as shown in Figure 7.9, and were in agreement with the results of experiments with the laboratory set-up discussed in Chapter 6 (data included in Figure 7.9 for comparison). The maximum average power output achieved with the portable laser system using cell B was 4.5 mW, which, although less than the desired 10 mW for an ideal microscopy light source, was considered sufficient for fluorescence imaging, particularly as the wavelength could be optimised for efficient absorption by a given fluorophore.

![Figure 7.9: Slope efficiency measurements using cell B, static and spinning (open and filled symbols, respectively), in the portable LC laser system and lab set-up (circles and diamonds, respectively). Spinning cell efficiencies were measured at 10 kHz pulse and stepper motor frequencies, with \( D_{ring} = 3 \text{ mm} \). Static measurements used a 10 Hz pump frequency. Error bars show the standard deviation on the mean energy output. Note the similarities between the spinning and static cell data for a given system, and the slightly higher maximum emission energy observed with the portable system.](image)

The slope efficiency of cell B in the portable system was similar to when measured in
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A slightly higher maximum emission energy was observed with the portable system. This could be explained for static cell measurements by a variation across the cell, as a different location was inevitably used in these two experiments. However, the fact that the result was replicated in the spinning cell experiments, where a much larger area of the cell was used, suggests that the optical arrangement of the portable system results in higher energy LC laser emission at high input pulse energies. The main changes made were the pump beam angle and focus spot size. The pump beam angle is not thought to affect absorption of energy by the dye in the CLC if the beam is circularly polarised with opposite handedness to the helix (see Section 2.2.4) and is therefore unlikely to have directly altered the output energy. Off-axis pumping does result in a larger, elongated, pump spot which allows a greater number of dye molecules to be excited. This can theoretically increase the LC laser output energy at high input pump energy, as the lasing threshold is exceeded over a larger area, and may be the cause of the higher output power achieved with the portable system. It was not possible to measure the pump spot diameter in the portable system due to its compact design, but the spot is expected to be larger than in the lab set-up due to the asymmetry introduced by the non-normal angle of incidence of the pump beam. Typical emission from the LC laser system, and the reflected pump beam, are shown in Figure 7.10.

Three additional cells with different emission wavelengths were used in the portable system, as summarised in Table 7.4. Cell E was designed to be the optimum wavelength for the fluorescence microscopy experiments discussed in Section 7.4. Cell F was designed to test the short wavelength limit of the portable system when fitted with the 532 nm pump laser. Cell R was a concentric ring cell that was made to test the

![Figure 7.10: A photograph of the emission from a LC laser cell in the portable system. A reflected pump beam spot from both substrates can also be seen.](image)
cell fabrication concepts in (see Section 7.2.4, and will be discussed further in Section 7.3.6.

The cell efficiencies varied considerably, as shown in Figure 7.11, depending on the wavelength of the PBG edge and the emission properties of the laser dye. Cells B, E and R had high efficiency, due to their emission wavelength being close to the maximum of the relevant dye emission spectrum. Cell F produced laser emission with low efficiency, demonstrating that although the green pumped system could be used at wavelengths around 550 nm, the available dyes did not result in high efficiency laser emission at this wavelength.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Mixture</th>
<th>Static slope efficiency (%)</th>
<th>Dominant emission λ (nm)</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>1 (PM597)</td>
<td>15.2 ± 0.3</td>
<td>572</td>
<td>Comparison with lab set-up</td>
</tr>
<tr>
<td>E</td>
<td>4 (PM597)</td>
<td>13.1 ± 0.4</td>
<td>599</td>
<td>For use in microscopy</td>
</tr>
<tr>
<td>F</td>
<td>5 (PM580)</td>
<td>0.42 ± 0.02</td>
<td>554</td>
<td>To investigate short wavelength limit</td>
</tr>
<tr>
<td>R</td>
<td>6 (PM580)</td>
<td>19.4 ± 0.1</td>
<td>575</td>
<td>To demonstrate a multi-wavelength cell</td>
</tr>
</tbody>
</table>

Table 7.4: A summary of the properties of LC laser cells used in this chapter. Data taken with static cells at at 10 Hz pulse frequency in the portable LC laser system. Uncertainties on the efficiency values are the uncertainty on the linear fit, and do not represent a measure of variation across the cell. See Appendix A.5.3 for mixture details.

7.3.4 Emission linewidth, wavelength stability and wavelength range

The emission spectra of these cells summed while spinning over a 3 mm pump ring is shown in Figure 7.12. The sum of the emission spectra from all spots on the pump ring was used to measure of the effective linewidth of a spinning cell system. Cells B, E and F all showed very little variation in wavelength over a small pump ring, due to the success of the cell fabrication methods developed in Chapter 5. The FWHM of the total emission spectrum was typically <4 nm for a central area in a high quality cell. The FWHM of the spectra from individual spots were considerably narrower and therefore the total spectrum is also a measure of the wavelength stability of the system over a short period. The linewidth and wavelength stability were both greater than desirable for an ideal microscopy light source, and greater than static cell LC laser emission. However, this compromise was necessary in order to achieve sufficient output power.
Figure 7.11: The emission energy from static LC laser cells in the portable system, with increasing pump laser energy, showing different slope efficiencies.

Laser emission was demonstrated with the 532 nm pump laser from 550 nm to 650 nm and longer wavelengths would be achievable with the addition of longer wavelength dyes, as in [48]. However, at wavelengths near the pump laser, cell efficiency was considerably reduced. A similar effect would be observed at long wavelengths and therefore the operating range of the system depends on the minimum power requirements of the application. Similarly, the 440 nm pump laser could be used to enable shorter wavelength emission, if the application did not require stable, high power operation.

7.3.5 Operating lifetime

The operating lifetime of the LC laser system is likely to be limited by the lifetime of the LC cells. The spinning cell results presented in Chapter 6 demonstrated that the spinning cell approach dramatically increased the time for which a LC laser cell could be continuously operated. Although experiments were not specifically conducted to measure the lifetime of a LC laser cell within the portable system, cumulative damage was observed in cells that were used repeatedly for microscopy experiments, as visible in
Figure 7.12: The emission spectra summed over 1 full rotation (500 spots) of a spinning LC laser cell in the portable system. The emission spectrum from the dye used in the LC laser mixture is also shown. Note the presence of multiple peaks in cell R, demonstrating the need for further development of fabrication processes for multi-wavelength cells.

Figure 7.13. This effect could be minimised by ensuring that the cell is always operated at moderate pump pulse energy when using a high repetition rate. Similarly, control systems could be designed to select a new area of the LC cell for use when the efficiency of the area being used drops below an acceptable value. Mechanisms such as these for maximising the lifetime of a LC laser cell would be necessary in a commercial system given the high cost of the substrates used in the LC laser cells.

7.3.6 Multi-wavelength cells for wavelength switching

Cells containing multiple mixtures were developed as a convenient wavelength switching method. A multi-wavelength cell with concentric rings containing different mixtures was tested in the portable system to evaluate these new cell fabrication methods. A microscopy image of this cell in Figure 7.14(a) shows that the glue lines were solid and <0.5 mm wide, and were successful in separating the different mixtures within the cell. This cell could be used while spinning and the emission wavelength changed by...
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Figure 7.13: A LC laser cell used for several spinning cell experiments, showing two concentric rings where the pump beam was incident for long periods.

using the linear actuator to translate the cell in less than one second, meeting the design specification. However, a high defect density was present in areas close to the glue lines, therefore a 1 mm band around the glue lines was not usable. The higher magnification microscopy images in (b), (c) and (d) show that reasonable alignment of the CLC material is possible with the fabrication processes used to make large, multi-wavelength cells, but the domain size was smaller than in the best single-wavelength cells. The domain size in the central compartment was smaller than the diameter of a typical pump spot (100 µm). The sum of the emission spectra from the ring area of the cell in Figure 7.12 (cell R) shows the presence of peaks of several different wavelengths from different chiral domains present along the ring. This resulted in a unacceptably large effective linewidth of 18 nm. Further work is therefore required to improve the filling processes for large, multi-wavelength cells, to make these cells suitable for applications that require narrow linewidth emission.

The spinning cell approach can also be used as a fast wavelength switching mechanism, by passing the pump beam over a pre-selected sequence of LC laser mixtures. This method was demonstrated with the laboratory set-up, as shown in Figure 7.15(a). This resulted in the wavelength switching performance shown in Figure 7.15(b), where a pump frequency and stepper motor frequency of 10 Hz was used to switch the pump laser between the 3 different LC laser cells positioned on the spinning disk. The number of pulses of each wavelength is determined by the size of the active area of the cell and the step angle; in the example shown, more pump pulses are incident on cell B than on the other cells, hence that cell’s wavelength is emitted for longer. The wavelength variation using cell B is greater than seen from the cells with smaller active area, due to variations in the CLC structure over large areas.
shape and position of the cells could be designed to minimize ‘dead-time’ between cells and enable faster switching. For example, a single cell with 2 mixtures separated by a single glue line approximately 1 mm thick would result in reduced dead-time in comparison to using separate cells. In this design, only 16 out of the 500 pump spots would be incident on the glue line (<3%). The shape and size of the different compartments within a cell could also be used control the number of wavelengths and their relative emission durations. Further research into this approach to wavelength switching, towards holography applications, can be found in [136].

Although demonstrated at a low pump frequency, this approach to wavelength switching is equally effective at high pump frequencies and could therefore allow high frequency switching between a pre-defined set of wavelengths. A video illustrating a higher switching frequency is available at the link provided in Figure 6.8. The difference in the intensity of emission from different cells is evident, and is caused by their differing slope efficiencies. Cell B had visibly higher emission energy per pulse, due to a high efficiency of 19% (in this set-up). The emission energy per pulse was lower for cells C and D under the same conditions due to their lower slope efficiencies (4% and 5% respectively), caused primarily by the misalignment of the absorption

\(^2\)Cell D was filled with mixture 3, which contained the laser dye PM650.
Figure 7.15: A demonstration of a wavelength switching technique using 3 cells mounted on a spinning disk. (a) A photograph of the cell positions. (b) A graph showing wavelength changes with the rotation of the disk (B = filled triangle, C = empty triangle and D = empty hexagon) mounted on a spinning disk. The cells had different active areas, resulting in slightly different output characteristics.

spectrum of the $PM650$ dye used in these cells with the 532 nm pump wavelength. Variations in efficiency between LC cells would be undesirable if this technique was used in fluorescence microscopy. However, the effect could be minimised with mixture design or pump pulse energy, or corrected with post-processing the microscopy images.
7.4 Application to fluorescence microscopy

7.4.1 Integration into a fluorescence microscope

The portable LC laser system was used with an Axioskop 2 upright microscope (Zeiss) with a monochrome camera (XM10, Olympus) and 10×, NA=0.5 objective (FLUAR, Zeiss). The 50 mm focal length collimating lens was used as this resulted in a larger beam diameter, closer to the diameter of the back aperture of the objective (approximately 25 mm). The collimated output from the LC laser was directed into the epifluorescence port at the rear of the microscope using 25 mm diameter mirrors, as shown in Figure 7.16. The beam was directed towards the sample by a 45° dichroic mirror through the objective lens onto the sample. Fluorescence emission from the sample was collected by the objective, allowed to pass through the dichroic mirror due to its longer wavelength, and was incident on the camera. An emission filter (long pass filter with a cut-off wavelength slightly longer than the dichroic mirror) was necessary to block LC laser light reflected by the sample, since this was of much greater intensity than the fluorescence emission, and the dichroic mirror transmission was > 0 at most wavelengths. Photographs of the set-up are shown in Figure 7.17.

![Diagram showing the optical alignment of a collimated beam from the LC laser with the epifluorescence port of the microscope.](image)

The maximum transmission of the LC laser to the sample was calculated to be 83%, based on the transmission properties of the mirrors, dichroic mirror and objective lens. However, this value decreased if the LC laser wavelength was not at the minimum of the dichroic mirror transmission spectrum.
Figure 7.17: Photographs of the portable LC laser system aligned with the raised epifluorescence port at the rear of the microscope, using 2 fold mirrors. (a) A side view, including the laser head and power supply. (b) A top view showing the laser head (lid removed) and alignment mirrors.
7.4.2 Imaging of biological samples

A fixed biological test sample was used to test that the LC laser would provide sufficient power for fluorescence imaging. The sample was a mouse kidney section (FluoCells Prepared Slide 3, Invitrogen) with actin labelled with Alexa Fluor 568 (AF568). This was imaged with LC laser cell E, which was reflected by a beamsplitter (83100BS, Chroma) and emission filter (83100em, Chroma). The reflection properties of these filters are shown in Figure 7.18, along with the absorption and emission spectra of the fluorescent label. When cell E was used with this dichroic mirror the transmission from the LC laser to sample was found to be 42%. The combination of filters was not perfect for the sample emission spectra because only approximately 50% of the light collected by the objective lens would reach the camera. However, this set-up would provide evidence that the LC laser was a suitable fluorescence imaging light source. Two other fluorophores with different excitation and emission spectra were also present in the sample, but the LC laser wavelength was chosen so that the AF568 would be selectively excited.

Images of the sample slide could be taken with an exposure time of 235 ms by illuminating the sample with a spinning cell at a pulse frequency of >5 kHz. It was not possible to detect sample fluorescence when illuminated with the emission from a static LC laser cell, demonstrating that the spinning cell approach allows LC laser technology to be used for imaging applications. The brightest images were taken with the maximum repetition rate 10 kHz, resulting in the image shown in Figure 7.19. This image is bright in regions where there is a high concentration of AF594 labelled actin in the sample. The actin concentration in the kidney is known to be inhomogeneous, with higher concentrations in the linings of the tubules and in glomeruli [142]. The bright rings in Figure 7.19 correspond to the expected actin distribution in cross-sections of tubules and the larger bright patches are consistent with the size of glomeruli. This image therefore provides evidence that the spinning LC laser has successfully and selectively excited the AF568 in the sample resulting in a fluorescence microscopy image.

7.4.3 Future microscopy studies

The next logical extension to this fluorescence microscopy demonstration was to use the wavelength selection capability of the LC laser system to selectively excite a sample containing multiple fluorophores. An experiment was designed with a sample containing the fluorescent dyes Alexa Fluor 594 (AF594) and Alexa Fluor 647 (AF647) with overlapping absorption spectra, as shown by the blue and orange lines in Figure 7.20. Precise control of the excitation wavelength would therefore enable the contrast between the two fluorophores to be maximised. A dichroic mirror with multiple transmission

The University of Edinburgh, 2019
Figure 7.18: The absorption and emission spectra of the AF568 fluorophore used in the biological test sample (green and red solid lines, respectively) combined with the transmission spectrum of the dichroic mirror (83100BS, solid black line) and emission filter (83100em, dashed black line). An emission spectrum from the LC laser cell used to excite the dye is included (solid orange line). The dichroic mirror transmission is $>0$ at the laser wavelength, hence the emission filter is required to block laser light reflected by the sample. Data obtained from the filter manufacturer (www.chroma.com)

The most suitable dichroic mirror available was not ideal for use with AF594, since much of the emission from this fluorophore was blocked. The mirror was well suited for use with AF647 as it the reflected wavelength range matched the fluorophore absorption peak and over half of the fluorescence could be transmitted. This experiment would therefore be best conducted with a high power LC laser at 550 nm and a less powerful laser at 650 nm. Unfortunately, the lasers made for 550 nm emission were of very low efficiency as this wavelength is at the edge of the emission spectra for the available laser dyes that could be pumped with the 532 nm laser. The combination of low power illumination, inefficient sample absorption and filtering of a large proportion of the sample fluorescence meant that it was not possible to image samples containing AF594.
with the 550 nm LC laser (cell F). A shorter wavelength pump laser and a more suitable dye (such as Courmarin 540A, Exciton) would be necessary for efficient emission at this wavelength.

This experiment highlights the importance of optical filters in fluorescence microscopes and shows that control of filter wavelengths is required to maximise the benefits of tunable wavelength light sources.
Figure 7.20: Optical properties of the filters and dyes for a microscopy experiment to demonstrate the benefits of precise wavelength selection. The absorption and emission spectra of the AF568 fluorophore (green and red solid lines, respectively) is shown with the transmission spectrum of the dichroic mirror (89100BS, Chroma, solid black line) and emission filters (ET605/52m, Chroma, dashed black line and ET605/52m, Chroma, dotted black line). Data obtained from the filter manufacturer (www.chroma.com).
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7.5 Recommended improvements

7.5.1 Optical design

A higher beam height is recommended for future systems for easy integration of the output with bench optics. A beam height of at least 50 mm would allow use of the standard 30 mm cage optic systems often used for alignment of optical components. A higher beam height would also allow the larger aperture collimating lens to be mounted on an $x-y$ stage for easy adjustment.

An achromatic waveplate could be used so that the pump laser could be exchanged without changing any of the other components in the laser head unit.

The pump beam was partially reflected by the front surface of the LC laser cell, as visible in the reflected pump beam (see Figure 7.10(b)). The front face of the LC laser cell could be coated with an anti-reflection coating to minimise the pump energy lost through reflection. However, this would increase the cost of cell fabrication.

7.5.2 Mechanical design

A casing made of thinner aluminium would result in a lighter system which would make transporting the system easier. The walls and lid of the case should be easily detachable from the base plate. Removable side walls were essential for optical alignment, but the current design requires many bolts to be removed which is time consuming. The design of the base plate should also be revised, as the plate became slightly warped after the side walls were removed.

The low-cost linear slide allowed some undesirable movement in spinning cell motor, out of the plane of rotation. This was minimised by ensuring that the load on the motor was evenly distributed. If unevenly loaded, vibrations in the linear slide caused the system to be noisy when spinning. Smoother operation would be possible with a more expensive, precision engineered linear slide, at the expense of translation speed.

The use of highly adhesive double-sided tape to mount LC cells was practical for the thick cells made of optical flats. However, thinner cells were difficult to remove if mounted with this method without damaging the cell. There was also a risk that the cell was not mounted flat on the disk, which would result in a slight change of emission angle as the cell rotated. To eliminate these problems, a quick and reliable method of securing small cells to a spinning disk should be designed. For example, a clamping plate with a variable aperture could be used. Thin steel components could allow the use of magnetic mounts and remove the need for bolts, thus speeding up the process of switching cells.
7.5.3 Power and control unit

The power unit was larger than intended, primarily due to the inclusion of a commercially available power distribution unit for 5 V, 12 V and 24 V components. A more compact solution to power distribution would be possible, particularly if fewer different voltages were required.

The micro-controller, optics rotation mount and linear actuator currently require individual USB connections to a laptop PC and are controlled through the software supplied with each component. The system could be made easier to operate by combining the control systems into a single piece of software, such as a LabView user interface. Integrating the control of the linear actuator and rotation mount into the same program as the laser and stepper motor would reduce the number of connections required and improve the user interface. It may be possible to control the entire system through a small computer such as a Raspberry Pi, resulting in a stand-alone portable system. Control systems that limited the pulse energy or exposure time for a particular LC laser cell would be desirable to prevent accidental cell damage by a non-expert user and to maximise the usable lifetime of each cell.

7.5.4 Integration with a fluorescence microscope

A more stable method for directing the LC laser emission into the epifluorescence port of the microscope would be desirable, but the design of this method would be dependant on the microscope model. The raised port at the rear of the microscope available for this research was less convenient than a bench-height port in the side of the microscope (see the Leica DMi8, for example). A method of securing the LC laser head to an optical table would help to ensure the laser was not accidentally moved and reduce the need for realignment.

A versatile alignment solution would be to couple the LC laser emission into a single-mode optical fibre designed to have low losses over a broad wavelength range. Such fibres are available, however, it would be difficult to achieve high coupling efficiencies across the full wavelength range. This would therefore only be a good approach if the LC laser was capable of producing much higher average power than the application required.
CHAPTER 7. A PORTABLE SPINNING CELL LC LASER FOR FLUORESCENCE MICROSCOPY

7.6 Summary

This chapter reports the construction of a spinning cell LC laser system with similar, or slightly better performance than predicted by the larger laboratory set-up. The system did not meet all of the requirements for an ideal LC laser system, but has been shown to be a capable light source for fluorescence microscopy applications, with far higher power output than a static cell LC laser system.

The LC laser system met the requirement for portability, being easily transported by one person. The size of the prototype system was acceptable but could be significantly reduced as part of a commercialisation process. The mass of the system (10.6 kg) was also less than the requirement set. The cost of the system was less than competing technologies and could be reduced mass production.

The maximum average power output achieved with the portable laser system was 4.5 mW, which, was less than the specified 10 mW for an ideal microscopy light source, but was considered sufficient for fluorescence imaging of biological samples. The system had the highest power and most stable output when fitted with the 532 nm pump laser with LC emission from 550 nm to 650 nm. Longer wavelengths, up to 850 nm would be achievable (see [48]) but were not demonstrated. The 440 nm pump laser could be used to enable shorter wavelength emission (from 500 nm), if the application did not require stable, high power operation. The linewidth (typically was typically <4 nm) was greater than desirable for an ideal microscopy light source and was caused by slight wavelength variations from different cell areas in a spinning cell. However, fluorescence imaging was still possible and this compromise was necessary in order to achieve sufficient output power.

The target wavelength switching time of less than one second was achieved. A wavelength switching technique, using multiple cells with different mixtures on the spinner, was a simple, low-cost switching mechanism. Cells with multiple compartments were also used, although these larger cells are much more challenging to fabricate and require further development. The spinning cell approach dramatically increased the time for which a LC laser cell could be continuously operated. However, cumulative damage was observed in cells that were used repeatedly for microscopy experiments. Control systems to prevent damage would be necessary in a commercial system given the high cost of the LC laser cells.

The portable LC laser has been successfully integrated into a fluorescence microscope and used to obtain a fluorescence microscopy image of a biological sample. Images could not be obtained using a static LC laser cell. This experiment was therefore the first practical demonstration of the benefits provided by the spinning cell technique. It was also the first use of LC laser technology in an imaging application.
Chapter 8: Conclusions

8.1 Motivation and approach

Many academic research topics in science and engineering have commercial applications and commercialisation is one of many ways that society can benefit from research. However, it is not guaranteed that a promising topic with commercial potential will be exploited in this way. In the case of liquid crystal laser research, great potential has been highlighted (see [40], for example) as it is possible to realise attractive features such as broad wavelength tuning in a small and relatively low-cost device. In the twenty years since the first demonstration of liquid crystal laser technology [36] there have been many advances in understanding and improvements in performance, as a result of research by physicists, chemists and engineers. However, it is still not possible to purchase a LC laser system, meaning that the impact of this technology on society has so far been small in comparison to other laser architectures. This thesis aims to progress LC laser technology towards commercialisation by demonstrating some of its features in an application that could benefit from the technology. This approach was designed to generate data that could be used as evidence for the commercial potential of LC lasers and therefore attract further interest and investment. Such exemplary data is currently scarce, with most literature focusing on a particular feature or mechanism rather than combining many features to yield a useful device.

For this approach to be successful, the chosen application must have a genuine need for new laser technology and have the potential to provide a market for a LC laser device. Biomedical imaging was thought to fulfil both these criteria since imaging techniques are central to this already large and expanding discipline. New imaging techniques are constantly being developed, and the hardware, including light sources, must keep up with the demands of increasingly sophisticated techniques. Furthermore, advances in tools than enable biomedical research to be more effective or faster have a positive impact on the outcomes of the research, and therefore also benefit society.

The first step in this research was to understand the general requirements for light sources in biomedical imaging and to compare these to the published performance of LC lasers. It was found that there were significant disparities; in particular, the
average power of a typical LC laser device was at least an order of magnitude lower than desirable for a biomedical imaging light source. The objective of much of the research in this thesis was therefore to improve the average output power through techniques that allowed the use of higher repetition rate pump lasers. Two separate approaches were investigated, one using flowing droplets and one using a spinning cell. Neither had previously been used to enable high repetition rate laser emission from dye-doped LC materials. Other objectives of this research were to improve the stability of the LC laser output, in terms of both power and wavelength, and to enable rapid or convenient switching between different laser wavelengths. The final stage in this research was to construct a system that enabled state of the art LC laser technology to be used in biomedical imaging.
8.2 Research achievements

The spinning cell approach was successful in enabling a LC laser cell to be operated with a pulse repetition rate of 10 kHz, with good energy and wavelength stability. This is the highest repetition rate achieved with a LC laser to date and the resulting average power output of 4.5 mW is also the highest reported. This result means that LC lasers can be considered for a much greater range of applications, including biomedical imaging. Provided a low pump pulse energy and a large pump ring was used, the LC laser could be left running for 2 hours at 10 kHz without the catastrophic drop in power output seen in static cell systems. This finding indicates that a LC laser system could function as a light source for imaging over an extended period, and is important in considering the commercial potential of the technology.

It was possible to demonstrate a stable emission wavelength, within $\pm 2 \text{ nm}$, in a spinning cell system if a cell with consistent LC structure was used. The cell fabrication developments described in Chapter 5 were therefore critical to the success of the technique, and this work has highlighted the importance of the substrate properties. LC cells have to be relatively large to realise the full benefits of a spinning cell system. With very large cells, it would theoretically be possible to increase the repetition rate and therefore average power output by a further order of magnitude, meaning that the output of the system would likely be limited by the capability of the pump laser, rather than the LC component. However, there are practical limits on cell size due to the difficulties in fabricating large cells with uniform structure.

A portable spinning cell LC laser system was developed and integrated into a fluorescence microscope. The system was successfully used to capture fluorescence microscopy images of a biological sample, and was the first use of LC laser emission as a light source for imaging. Imaging was not possible without spinning the LC cell, highlighting the success of this approach. The LC laser emission wavelength was chosen specifically for the sample; this is a known benefit of tunable wavelength light sources that enables far greater flexibility in the design of imaging experiments. The total cost of the LC laser system was much less than competing tunable wavelength laser technologies, meaning that the benefits of a tunable light source could be made more widely available. Additional imaging experiments are recommended, using combinations of wavelengths that not commonly available in low cost microscopes, in order to further demonstrate the value of LC lasers to microscopy users.

Novel LC laser cells with multiple compartments containing mixtures with different emission wavelengths were shown to be feasible methods of providing convenient wavelength switching with a LC laser system. These could be customised for a range of common experiments and would only need to be changed occasionally. A concentric
ring design was shown to enable arbitrary wavelength selection by translating the cell, whereas rapid wavelength switching in a pre-defined sequence was enabled in a colour wheel design. However, fabricating LC cells of this size and complexity was challenging and was only achieved with low yield.

The flowing droplet approach to high repetition rate LC laser emission was found to be unsuitable for use in imaging applications. However, it was demonstrated that LC droplets can be flowed under conditions that maintain their internal LC structure, providing they are not in contact with the channel walls. A flowing droplet LC laser system is therefore feasible and may be suitable for applications where omnidirectional emission is desirable. Investigations into the effect of droplet shape on the emission showed that it was possible to direct the laser emission from a droplet constrained in a narrow channel or cell. This novel approach to manipulating laser emission could be applied in microfluidic optical devices, for example in a sensor system to direct laser light towards a sample or detector.
8.3 Future perspectives

The pump laser remains the most expensive single component in a LC laser system and consequently strategies for minimising pump laser costs will be important to ensure LC laser systems can remain cheaper than competing technologies. The availability of suitable pump lasers currently places constraints on system design and therefore developments in solid state laser technology would benefit LC laser research and commercialisation. The portable LC laser system described in Chapter 7 did not have the wavelength range originally intended, due to the availability of suitable pump lasers that emit in the blue region. The 440 nm laser tested emitted long pulses which caused the system to be unstable at high repetition rates. Developments in LC laser materials, particularly gain media, that enable operation at longer pulse lengths, or reduce the threshold energy required for lasing, would both be highly beneficial as they would allow the pump laser requirements to be relaxed. It may be necessary to look beyond band-edge lasing towards other lasing mechanisms, such as defect mode, in order to achieve thresholds low enough to be pumped with very cheap lasers.

The success of the spinning cell technique reported in this thesis introduces a new requirement for pump lasers to have high repetition rates. Since the most stable method of achieving high output power was found to be to use a high repetition rate with a low pump energy, it follows that LC lasers with very low lasing thresholds would enable higher repetition rate operation. This work has therefore provided an additional motivation for research into reducing the lasing threshold of LC devices.

The wavelength selection method used in the portable LC laser system, requiring cells with multiple compartments, is a fairly coarse method of wavelength tuning, and was chosen to enable a broad wavelength range. However, it is not as flexible or as precise as some continuous tuning methods. An ideal system would be able to tune broadly across the visible spectrum in sub-nanometre wavelength steps, with a dynamic and reversible method, without loss of efficiency. Oblique helicoidal CLCs [84] are currently promising materials for broad, continuous wavelength tuning with an electric field, but further research is required to lower the lasing threshold of these systems. An intermediate solution would be to combine a coarse wavelength selection method with a fine-tuning mechanism, such as with an electrical field, in order to provide precision wavelength tuning over a relatively broad range. This engineering challenge should be addressed in future research or technology development projects and would have benefits in imaging applications of LC lasers. A commercial LC laser system should include a feedback loop to monitor the output pulse energy and adjust the pump pulse energy such that the output power does not vary with wavelength.

Poor cell quality and a lack of repeatability is one of the biggest problems
encountered in LC laser research and is consequently a barrier to commercialisation. Cell fabrication on a larger scale would dramatically reduce the cost of LC laser cells, if demand was high. This could allow them to be treated as consumables, which would remove the need for very long operating lifetimes and would provide a more regular income stream for a LC laser manufacturer. It is likely that fabrication techniques in use within the display industry, that are largely unpublished, would enable the large and complex cells suggested in this thesis to be manufactured with better results and a much higher yield. Collaboration with an industrial partner with this expertise and fabrication facilities is therefore highly recommended for any research projects with a commercialisation goal. It is also important to ensure that fabrication methods continue to take advantage of the self-assembling nature of the LC structure, to enable a rapid and low cost process.

Generating droplets of LC material is a much newer approach to LC laser fabrication that removes the need for high quality, carefully prepared substrates. A greater understanding of the structure of a CLC droplet on formation, and then how to manipulate the structure, will be necessary if these are to find an application. For example, the thermal conditioning steps used in cell fabrication could be investigated as a method of creating ordered structures within droplets. There is little known about the effects of flow on the structure of CLC droplets; studies that address this knowledge gap, either experimentally or through simulation, would make it possible to use LC droplet lasers as mobile light sources in microfluidic devices. The use of flowing droplet lasers is more likely to be beneficial in applications such as chemical sensing, than in biomedical imaging.
Bibliography


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Appendix A: Materials and tools

A.1 Laser system characterisation tools

**Pulse energy measurements** Laser energy meter PD10 (*Ophir*)

**Spectrometry** USB4000 spectrometer (*Ocean Optics*)

**White light source** HL-2000-FHSA (*Ocean Optics*)

A.2 Materials used in LC laser cell fabrication

**Adhesives** Norland Optical Adhesive (NOA) 68 or 68TH (*Norland*)

**Syringe tips** Precision stainless steel tips, clear, 0.2 mm (*EFD*)

**Alignment layer** Polyimide SE-1410 (*Nissan Chemical Industries*)

**Cleaning solvents** Acetone, Isopropyl alcohol (*Sigma Aldrich*)

**Cell sealant** Torr Seal epoxy adhesive (*Agilent Technologies*)

**Piranha cleaning solution** A 3:1 volume ratio of sulphuric acid (96%) and hydrogen peroxide (31%)

**RC1 cleaning solution** A 5:1:1 volume ratio of DI water, ammonium hydroxide (27%) and hydrogen peroxide (31%) at 60°C

**Spacer beads** 10µm or 20µm diameter silica beads (*Sinochem Nanjing Corporation*)

**Glass wafers** 0.5 mm thick borosilicate, S/D 60/40 (*Compart Technologies*) or 1 mm fused silica, S/D 20/10 (*IBD Technologies*)

**Silicon wafers** 0.375 mm thick amorphous silicon (*Si MAT*)

**Optical flats (transparent)** HK9L 15×30×3 uncoated (*CASIX*)

**Optical flats (reflective)** HK9L 15×30×3 coating S1 (*CASIX*)
A.3 Cell fabrication tools

**Adhesive curing**  UV oven (*Loctite*)

**Aluminium deposition on Si wafers**  Sputter coater BAS450PM (*Balters*)

**Alignment layer coating**  Spin coater Polos 150

**Alignment layer rubbing**  Benchtop rubbing machine HO-IAD-BTR-01 (*Holmarc*)

**Balance**  Analytical series, *PAS214C* (*Fisher Scientific*)

**Oxide growth on Si wafers**  3 inch oxide furnace

**Precision glue deposition**  Ultimus V dispenser (*Nordson EFD*) with JR2000N desktop robot (*Janome*)

**Substrate bonding**  Substrate bonder SB8e (*SUSS MicroTec*)

**Syringe filters**  0.22 µm PTFE, 25 mm (*CM Scientific*)

**Wafer rinsing and drying**  Marengoni drier

**Chip drying**  Model 251 ion gun (*Meech*)

A.4 Process analysis tools

**Optical microscopy**  DM12000 M inspection microscope (*Leica Microsystems*)

**Cooling stage**  LTS420 (*Linkham*)

A.5 LC laser mixtures

A.5.1 Chiral nematic materials

**Nematic LC**  BL006 Licristal, \( n_e = 1.815, n_o = 1.530 \), (*Merck*)

**Chiral dopant**  BDH-1281 for RMM-application (*Merck*)

**Nematic LC for droplet lasers**  MLC2132 Licristal, \( n_e = 1.77, n_o = 1.51 \), (*Merck*)

**Chiral dopant for droplet lasers**  S-811 ((4-[(1-methylheptyl) oxy] carbonylphenyl-4-(hexyloxy) benzoate, *Merck*)
Figure A.1: A graph of the concentration of the chiral dopant BDH1281 in LC BL006 against the position of the long edge of PBG. The solid line and equation describe a linear fit to the data obtained from large mixtures (>100 mg). This information was used in the design of LC laser mixtures. External data courtesy of P.J.W. Hands and D.J. Gardiner [138].

A.5.2 Laser dyes

**DCM** 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (*Exciton*)

**PM597** 1,3,5,7,8-pentamethyl-2,6-di-t-butylpyrromethene-difluoroborate (*Exciton*)

**PM597-89C** 2,6-di-tert-butyl-8-nonyl-1,3,5,7-tetramethylpyrromethene- BF₂ (*Exciton*)

**PM580** 1,3,5,7,8-pentamethyl-2,6-di-n-butylpyrromethene-difluoroborate (*Exciton*)

**PM650** 1,2,3,5,6,7-hexamethyl-8-cyanopyrromethene-difluoroborate (*Exciton*)

**Ph660** 9-(dimethylamino)-1H-benzo[a]phenoxazin-5-1 (*Exciton*)

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A.5.3 List of LC laser mixtures

A.6 Materials and tools used in LC droplet laser investigations

**Glass capillaries** 100\( \mu \)m x 100\( \mu \)m and 20\( \mu \)m x 200\( \mu \)m (CM Scientific, part numbers 8510 and 5002)

**Poly vinyl alcohol** Mw 9,000-10,000, 80% >hydrolyzed (Aldrich)

**Syringe pumps** Legato 100 (KDS)

**Syringes** GasTight 1 ml (Hamilton)

**Microfluidic chips** 50\( \mu \)m and 100\( \mu \)m etch depth (Dolomite microfluidics part numbers 3200286 and 3000158))
APPENDIX A. MATERIALS AND TOOLS

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Nematic LC</th>
<th>Chiral dopant</th>
<th>Dye</th>
<th>Pump laser wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>MLC-2132</td>
<td>S-811</td>
<td>DCM</td>
<td>440 or 532</td>
</tr>
<tr>
<td>D2</td>
<td>MLC-2132</td>
<td>S-811</td>
<td>DCM</td>
<td>440 or 532</td>
</tr>
<tr>
<td>1</td>
<td>BL006</td>
<td>BDH1281</td>
<td>PM 597</td>
<td>0.7 + 0.07</td>
</tr>
<tr>
<td>2</td>
<td>BL006</td>
<td>BDH1281</td>
<td>PM 650</td>
<td>0.6 + 0.07</td>
</tr>
<tr>
<td>3</td>
<td>BL006</td>
<td>BDH1281</td>
<td>PM 650</td>
<td>1.0 + 0.07</td>
</tr>
<tr>
<td>4</td>
<td>BL006</td>
<td>BDH1281</td>
<td>PM 597</td>
<td>1.0 + 0.07</td>
</tr>
<tr>
<td>5</td>
<td>BL006</td>
<td>BDH1281</td>
<td>PM 580</td>
<td>0.6 + 0.07</td>
</tr>
<tr>
<td>6</td>
<td>BL006</td>
<td>BDH1281</td>
<td>PM 580</td>
<td>1.0 + 0.07</td>
</tr>
</tbody>
</table>

Table A.1: A summary of LC laser mixtures used in this thesis.

Tubing Fluorinated ethylene propylene (FEP) 250µm I.D. (Dolomite microfluidics)

High speed camera MCI362 (Mikrotron)

Microscope E800 (Nikon) with plan fluor (PF) 10x NA 0.3 (Nikon) objective and Micropublisher 3.3 colour camera (QImaging)

Confocal microscopes Observer.Z1 inverted microscope with LSM 700 scanning system (Zeiss) or DMi8 with a plan apochromat (PA) 63x NA 1.4 oil immersion objective (Leica Microsystems)
Appendix B: Final LC laser cell fabrication process

B.1 Substrate preparation

2. Glass: Piranha clean then rinse thoroughly in DI water. Store in DI water until needed (same day).
3. Aluminium coated chips: IPA ultrasonic bath at 50°C for 10 min, change IPA after 5 min. Rinse with DI water. Store in DI water until needed (same day). Use IPA soaked non-shedding swab to gently clean surface.
4. Rinse with IPA and dry with anti-static $N_2$ gun. Use immediately.
5. If necessary, check cleanliness of one chip of each type under microscope.

B.2 Spin coating

1. Remove PI from freezer several hours before use.
2. Dilute PI in a volume ratio of 1:1 with NMP (approx. 1 ml for 10 cells), mix with magnetic stirrer (at least 10 min).
3. Syringe filter (0.2 μm) into clean vial. Leave to stand for at least 1 hour (preferably next to spinner).
4. Clean plastic pipette (anti-static $N_2$ gun).
5. Spin coat substrates: deposit a generous quantity of PI on the centre of chip with pipette – spread to edge if necessary. Spin at 500 rpm for 5 s then 4000 r/min for 60 s (1000 r/min/s).
6. Pre-bake: 80°C for 5 min.
7. Bake: 220°C for 1.5 hours (transparent substrates) or 140°C for 3 hours (reflective substrates).

8. If necessary, evaluate film quality under microscope.

B.3 Rubbing process

1. Ensure rubbing table is flat using spirit level.

2. Use test substrate to adjust roller to 0.1 mm rub depth. Should just be able to see daylight between test substrate and roller (between strands of cloth).

3. Place chip on table and set vacuum. Use \( N_2 \) gun to check vacuum and remove any dust.

4. Roller speed 200 rpm, 2 passes, 6 mm s\(^{-1}\).

5. Clean with anti-static \( N_2 \) gun.

B.4 Glue deposition

1. Mix NOA68 with 2% (wt) spacers, stir and de-gas.

2. Use 0.2 mm ID stainless steel precision tip (clear).

3. Suggested settings (NOA68): Pressure: 1.2 bar, point dispense 0.2 s, Line speed: 8 mm s\(^{-1}\), (for NOA68TH use 2 mm s\(^{-1}\)).

B.5 Cell assembly

1. If necessary, check glue lines are complete

2. Place another chip on glued chip (by hand – touch one edge and drop)

3. Apply pressure with tweezers, gently without much sideways movement.

4. Full UV cure (Loctite UV oven, >1 min, 25 mW cm\(^{-2}\))

5. Additional hardening (if required) – oven 12 hours at 50°C
Appendix C: Portable LC laser system

C.1 Pump spot diameter measurements

Measurements of the pump spot diameter were made in the laboratory set-up using the knif edge method. This is thought to be a lower limit on the spot diameter in the portable LC laser system. This data is presented in Figure C.1 and results summarised in Figure .

![Figure C.1: The spot diameter measurements taken at different positions along the z-axis of the 532 nm pump laser in the laboratory set-up. The legend shows the z-axis position in micrometers.](image)
APPENDIX C. PORTABLE LC LASER SYSTEM

Figure C.2: A summary of the spot diameter results from different positions along the z-axis of the 532 nm pump laser in the laboratory set-up, used to predict a lower limit to the LC laser system pump spot diameter.

C.2 List of parts for portable LC laser system

C.2.1 Commercially available parts (cost excl. VAT)

**Linear polariser** Glan-Taylor Polarizer, Coating: 350 nm to 700 nm (*ThorLabs* GT5-A) £380.00

**Linear polariser mount** SM05 Lens Tube Mount for 5 mm Mounted Polarizing Prisms (*ThorLabs* SM05PM5) £41.59

**Optics rotation mount** Piezo Rotation Stage (*Newport* AG-PR100) £486.00

**Optics rotation controller** 2 Axis Agilis Driver, PCB-Mountable (*Newport* AG-UC2-OEM) £320.00

**Linear translation motor** Linear Actuator P16-P 50 mm, 12V w/ feedback (*Actuonix*) £55.56

**Linear translation controller** Linear Actuator Control Board (*Firgelli Technologies*) £23.93
**Linear slide** Micro Linear Slide Rail 50mm (Firgelli Technologies) £27.78

**Spinning cell motor** Stepper motor (Oriental Motors CVK523AK) £101.70

**Spinning cell motor** Stepper motor driver board (Oriental Motors CVD518BR-K) £77.40

**Fold mirror** 1/2” Broadband Dielectric Mirror, 400 nm to 750 nm (ThorLabs BB05-E02) £36.31

**Focussing mirror** 1/2” Dielectric-Coated Concave Mirror, 400 nm to 750 nm, f = 50 mm (ThorLabs CM127-050-E02) £39.69

**Collection lens** f=19 mm, Ø1/2” Achromatic Doublet, SM05-Threaded Mount, ARC: 400-700 nm (ThorLabs AC127-019-A-ML) £56.67

**Collection lens** x − y adjustment Translating Lens Mount (ThorLabs LM05XY/M) £100.79

**Collection lens** z adjustment Dovetail Translation Stage (ThorLabs DT12/M) £56.01

**Collection lens mount** Adjustable Lens Tube, 0.8” Travel (ThorLabs SM05V10) £24.25

**Pulse generation** Arduino Uno (Arduino R3) £17.25

**Power supply** Triple Output Switch Mode Power Supply (TrackoPower TXL 100-0534TI) £77.09

**Power unit casing** Weatherproof ABS Box Light Grey, Clear Lid (Maplin N11GJ) £30.99

Total cost of commercially available parts (pump wavelength independent): £1897.90

C.2.1.1 Blue pump laser system

**Blue pump laser** 440 nm Nd:YLF DPSS (Crystalaser) £18,000

**Quarter wave plate (440 nm)** (Laser 2000 LAS-024533) £178

**Longpass filter 450 nm** 25 mm Premium Longpass Filter, Cut-On Wavelength: 450 nm (ThorLabs FELH0450) £115.76

Total cost of parts specific for a blue pumped system: £15,293.76
C.2.1.2 Green pump laser system

**Green pump laser** 532 nm Nd:YAG DPSS (Crylas FDSS 532-Q2) £6,883

**Quarter wave plate (532 nm)** Mounted Multi-Order Quarter-Wave Plate, 532 nm
*ThorLabs* £183.60

**Longpass filter 550 nm** 25 mm Premium Longpass Filter, Cut-On Wavelength: 550 nm
*ThorLabs* FELH0550 £123.17

Total cost of parts specific for a green pumped system: **£7189.77**

C.2.2 Custom parts

**Case for laser unit** Aluminium, 8 mm, bolted butt-joint construction.

**Laser heat sink** Aluminium block with tapped holes. Sets height of laser beam.

**Rotation mount block** Aluminium block. Sets height of polarisation optics.

**Mirror mounts** Aluminium posts in holders, angle adjustable.

**Cell mounting disks** Thin aluminium disks, detachable.

**Spinning disk** Axle mounted aluminium disk with clamping ring.

**Stepper munter to linear actuator interface** Aluminium plate on rear of motor with protruding bolt.

**Actuator mount** Aluminium plate with supports to hold linear actuator.

**Filter mount** 3D printed plate to cover laser aperture with long-pass filter.

**LC cells** See Appendix A.

C.2.3 Summary of materials costs (excl. VAT)

**Blue pump system:** £17,191.66

**Green pump system:** £9087.67

**Single-wavelength small LC laser cell:** £35 (small batch estimate)

**Multi-wavelength large LC laser cell:** £200 (small batch estimate)
C.3 Arduino code

The following code was used to control the pulse repetition rate of the blue pump laser and the stepper motor step rate with a micro-controller (Arduino Uno).

```c
#include <PWM.h>
#include <SoftwareSerial.h>

int reset;

// variables for stepper motor control
int stepper = 3; //pin number for stepper motor
int32_t SfreqNew = 0; //new (target) stepper motor frequency
int32_t Sfreq = 0; //current stepper motor frequency
int SChange = 0; //has a stepper motor frequency change been requested?
int incr = 10; //frequency increment by which stepper motor frequency is modified
unsigned long previousMillis = 0;
const long interval = 500; //time interval between stepper motor frequency modifications (ms)
int maxStepper = 30000; //maximum stepper motor frequency

//variables for laser pulse triggering
int32_t Lfreq = 0; //laser pulse frequency (Hz)
int32_t LfreqNew = 0; //New value of laser frequency
int change = 0; //
int New = 0;
int laser = 9; //pin number for laser
int maxLaser = 100000; // maximum laser frequency

//variables for serial communication
const int NUMBER_OF_FIELDS = 2; //how many comma-separated fields we expect
int fieldIndex = 0; //the current field being received
int values[NUMBER_OF_FIELDS]; //array holding integer values for all the fields
```

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```cpp
void setup(){
    Serial.begin(9600);
    pinMode(stepper,OUTPUT);
    pinMode(5,OUTPUT); //ground pin for stepper motor
    digitalWrite(5, LOW); // sets the ground pin for the motor
    InitTimersSafe();
    bool success= SetPinFrequencySafe(stepper,Sfreq);
    Serial.println("Please enter values: laser frequency, spin frequency");
}

void loop(){
    // void(* resetFunc) (void) = 0;
    if (Serial.available()){ //monitor serial port for user input
        Serial.println("Go");
        for(fieldIndex = 0; fieldIndex < 2; fieldIndex ++){
            values[fieldIndex] = Serial.parseInt(); // store a numeric value
        }
        for(int i=0; i < fieldIndex; i++){
            Serial.println("New value:");
            Serial.println(values[i]); //print values to check
        }
        fieldIndex = 0; // ready to start over
    }

    LfreqNew = values[0]; //sets new frequency for laser
    change=abs(Lfreq-LfreqNew);
    if (change < 0.005){ //monitors serial for changes in user input
    }
    else{
        Serial.println(change);
        Serial.println("New laser frequency:"); //confirms frequency change
        New=int(LfreqNew);
        Serial.println(New);
        Lfreq = LfreqNew;
        bool success = SetPinFrequencySafe(laser, Lfreq); //sets the frequency
        for the pin, if required
    }
pwmWrite(laser, 128); //turns laser on

    SfreqNew = values[1]; //sets new frequency for stepper motor
    if (Sfreq < incr + 1){
        pwmWrite(stepper, 0); //stops stepper motor (duty cycle =0)
    }
}
```
//Serial.println("Spinner stopped");
}

SChange = SfreqNew-Sfreq; //Determines whether freq increase or decrease
if (SChange < -0.01) { //if frequency decreases by significant amount
    unsigned long currentMillis = millis();
    if (currentMillis - previousMillis >= interval) {// wait for interval
        previousMillis = currentMillis;
        Sfreq = Sfreq - incr; // gradually decrease frequency
        SetPinFrequencySafe(stepper, Sfreq); //change pin to new frequency
        pwmWrite(stepper, 128);
        Serial.println("Lower spin frequency:");
        Serial.println(Sfreq);
    }
}

else if (SChange > 0.01) { //if frequency increases by significant amount
    unsigned long currentMillis = millis();
    if (currentMillis - previousMillis >= interval) {// wait for interval
        previousMillis = currentMillis;
        Sfreq = Sfreq + incr; // gradually increase frequency
        SetPinFrequencySafe(stepper, Sfreq);
        pwmWrite(stepper, 128);
        Serial.println("Higher spin frequency:");
        Serial.println(Sfreq);
    }
}
}
Appendix D: List of publications


