2012

Performance of oriented fluorophore luminescent solar concentrators

Tristan Butler
Western Washington University

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Tristan Butler
11/19/12
Performance of Oriented Fluorophore

Luminescent Solar Concentrators

A Thesis Presented

To the Faculty of

Western Washington University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

By

Tristan Butler
Abstract

Solar power is likely to play a significant role in the future of fossil fuel alternatives. In order to maximize its impact, the cost of solar power must be competitive with fossil fuels on the global energy market. Luminescent Solar Concentrators are an attractive technology that can potentially reduce the cost of solar power. LSCs utilize cheap materials and no moving parts to concentrate light, however the amount of solar concentration is limited by loss mechanisms inherent in LSCs.

One potential method to improve the efficiency of LSCs is through the use of oriented fluorophores. Based on theory presented in this thesis, homeotropically oriented fluorophores preferentially emit light within the plane of the LSC, which increases the probability of total internally reflection. D8 and Lumogen Orange oriented fluorophore LSCs were fabricated using reactive mesogens and liquid crystals to achieve homeotropic orientation. The orientation of these devices was measured using UV-Vis and fluorescence spectroscopy. The number of photons emitted from the edge of the LSC compared to the number of photons absorbed by the LSC, or optical quantum efficiency (OQE) was determined by measuring emission intensity at varying excitation distances from the detector. The OQE was then fit to a theoretical model and the light trapping efficiency of each LSC was determined. It was found that D8 homeotropic LSCs have ~100% higher OQE than isotropic LSCs and approximately 12%-17% higher light trapping efficiencies within the excitation distances tested.
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90
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<td>Tera-kilowatt hours</td>
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<td>kWh</td>
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<td>$W_p$</td>
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<td>Multiexciton generation</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
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Chapter 1: Introduction

1.0 Overview

This chapter discusses the growing demand for cheaper solar energy. It describes the world’s dependence on energy generated by fossil fuels and discusses the economic costs and efficiencies of solar power. This chapter also presents the case for the development of solar concentrator technologies and describes some existing solar concentrator systems.

1.1 Global Energy Consumption and the Need for Alternative Fuel Sources

Energy is being consumed at a record pace worldwide. In 2007, 18.8 Terakilowatt hours (TkWh) were consumed alone.\(^1\) Current projections expect that the total power consumed per year worldwide will double, to 35.2 TkWh in within the next 25 years (Fig. 1.1).\(^1\)

![Figure 1.1 Growth in world electric power generation and total energy consumption, 1990---2035.](image-url)
Over 85% of the energy consumed worldwide comes from the burning of fossil fuels including: coal, natural gas, and petroleum (Fig. 1.2). Fossil fuels are not clean burning and have well documented environmental effects.\textsuperscript{1,2,3,4,5} Furthermore, they are finite resources and will eventually run out.\textsuperscript{3} While this is not expected to happen for sometime, peak production levels in some parts of the world have most likely passed and will continue to decline.\textsuperscript{4,5}

\textbf{Figure 1.2} Contributions of various energy sources to total worldwide energy consumption.\textsuperscript{2}

Renewable energy sources make up only 7% of energy consumed worldwide, with 6% coming from hydroelectric and about 1% from geothermal, solar, wind, and wood combined.\textsuperscript{2} Currently the majority of power produced form carbon-neutral sources comes from hydroelectric power. However, there are relatively few sites where hydroelectric power is viable and most of these are already developed. Thus it is
unreasonable to expect that the amount of hydroelectric power generated to grow substantially.²

Like hydroelectric power, the amount of growth that can be expected from wind power is limited because suitable locations for wind farms are scarce. Yet it is estimated that the amount of energy available from wind above an altitude of 100 m is around 1700 TW (Tera-Watts).⁶ It is impossible to harvest all this energy, and wind is often unpredictable, making wind power less attractive than some other forms of alternative energy generation.

Solar energy has the largest potential growth prospects among renewable energy sources. The amount of energy that reaches the earth from the sun is estimated to be 89 PW (petawatts). If even a small portion of this energy were collected, it would generate enough power to meet growing worldwide energy demands.⁷

While there is much room for growth in the solar energy market, it suffers from some of the same drawbacks as other renewable energy technologies. For example sunlight is often intermittent, and solar energy is only produced during daylight hours.

But the most significant drawback to solar power is the cost. In 2007, farm scale solar energy cost $0.20/kWh whereas the price of energy produced form coal was $0.05/kWh, over 4 times less. In order for the solar energy market to grow, the cost of must be competitive with fossil fuels on the global energy market.⁷

1.2 Economics of Solar Power

In 2007 the Department of Energy instituted the $1/Wp (“dollar per peak watt”)
initiative. The unit $1/W_p$ is a measure of the cost of electricity produced from a solar cell given a standard AM 1.5 G incidence. $1/W_p$ module cost is the benchmark where solar energy would be competitive with fossil fuels on the global energy market. Currently the cost of solar energy produced by a standard Si solar cell is $3.40/W_p$ (Fig. 1.3) so significant cost reductions need to be achieved before the $1/W_p$ goal is met.$^2$

![Figure 1.3 Contributions from different expense factors to the overall cost of solar energy.]

The cost of solar energy can be divided into of three separate areas: material costs ($1.70/W_p$), balance of system (BOS) and installation ($1.48/W_p$), and power electronics ($0.22/W_p$). For a typical Si solar module, the materials make up 50% of the overall cost. These materials include, metal conductor strips, an antireflection coating, p-doped and n-doped Silicon layers, and a metal backing.

The second largest contributor to the overall cost of solar energy is installation and
BOS costs. The installation costs include installing the module and connecting it to the power grid. Balance of system costs are comprised of the value of the land that solar modules occupy. The smallest contributor to the cost of solar power is the power electronics. This expense includes the electronic components that convert the DC output of the solar panels to usable AC current.

Supposing the cost of the solar module contributed nothing to the total price, the cost of solar power would be $1.70/W; greater than the $1/W goal. Thus, cost reductions in all three areas are needed to achieve the $1/W initiative.²

1.3 Methods of Reaching $1/Wₚ

There are two methods to reduce the cost of solar energy. The efficiency of the solar cells can be increased, or cheaper materials can be used to generate solar power. It is likely that a combination of the two methods must be used in order to reach the $1/Wₚ benchmark.

1.3.1 Increasing the Efficiency of Photovoltaic Cells

The cost of solar energy can be reduced through the development of more efficient solar cells. Currently the most efficient solar cell is a three-junction device made by Solar Junction measuring 43.5%.⁸ Its record setting-efficiency is achieved by stacking three different semiconductor materials on one another. Each layer has a different band gap that allows for a larger portion of the solar spectrum to be collected. While these cells are much more efficient than the most efficient single-junction cells
(29.1% GaAs semiconductor made by Alta Devices), it is much more costly to produce.\(^8\)

Figure 1.5 plots the efficiencies of 3 different photovoltaic technologies as a function of time. In general, all the technologies follow a similar “S-shaped” development curve, but the trend is most pronounced in the development curve of two-junction solar cells. From 1983-1990 the efficiency increased from 16%-17%, which corresponds to 1% increase in efficiency over 7 years. From 1990-1994, the efficiency improved to 30%; corresponding 13% increase in efficiency over 4 years. Over the next 15 years, the efficiency of Two-junction solar cells reached a maximum of 32.1%, corresponding to only a 2.1% increase over that time period.\(^8\)

![Figure 1.4](image)

**Figure 1.4** Development trend of CdTe (diamond), two junction (square), and multicrystalline Si (triangle) solar cells form 1976-2011.\(^8\)

This “S-Shaped” trend can be explained the following way: In the initial development phase for two junction solar cells, the efficiency increased slowly due to the development of new materials and experimental methods (1983-1990). As the
technology matured, the efficiency increased rapidly because the technology was better understood and advancements were made more quickly (1990-1994). Finally, progress leveled off because it was approaching a maximum theoretical limit.

For single junction solar cells, like multicrystalline Si, the theoretical maximum is referred to as the Shockley-Qiesser limit. The Shockley-Qiesser limit of a solar cell is a theoretical limit that is based on the bandgap of the semiconductor material used in the solar cell. Photons with lower energy than the bandgap are not collected by the photovoltaic and are either reflected or transmitted through the device. Photons with energy greater than the bandgap generate an electron hole pair, or exciton that can be converted into electrical current. Excess photon energy is dissipated in the form of heat, which decreases the amount of light absorbed. Thus, for a given photovoltaic, there is a fixed portion of incident sunlight that can be converted into electrical current. If the photovoltaic converted this entire wavelength range into electrical current, the device still would not be 100% efficient. This maximum efficiency is the Shockley-Qiesser limit.9

Since most current semiconductor materials are approaching their theoretical limits, the $1/W_p$ benchmark cannot be achieved by simply improving existing photovoltaic technologies. New semiconductor materials and methods must be developed that can either be made cheaply, (organic and CdTe semiconductors, solar concentration) or exceed their theoretical maximum (for example, through multi-exciton generation). These technologies are called generation III photovoltaics.10

Multi-exciton solar cells are an example of a generation III photovoltaic. In a
typical solar cell, a photon with energy greater than the bandgap produces an exciton that can be converted into current. In certain semiconductors, high energy photons can generate more than one exciton through is a process called multi-exciton generation (MEG). A group led by Nozik and Beard working at NREL in Golden Colorado has observed MEG in lead selenide nanocrystalline solar cells reporting 1.14 carriers collected from photons four times the energy of the band gap. While this technology doesn’t have a high efficiency yet, it offers the potential for higher efficiencies.¹⁰

1.3.2 Using Cheaper Materials To Achieve $1/W_p

Thin film photovoltaics are made by depositing thin layers of semiconductor onto a conducting substrate. This minimizes the amount of semiconductor material used such that these devices can be made for a fraction of the cost of other photovoltaic materials. Currently the company First Solar produces Cadmium Telluride (CdTe) thin film photovoltaics that produce power at $0.76/W_p; below the $1.00/W_p goal. Projections indicate that the cost could be reduced even further to $0.55/W_p by 2014. The record efficiency of CdTe thin film photovoltaics is currently 17.3% indicating that the small relative cost is due to the low cost of the device, not especially high efficiency.

While CdTe thin films are expected to play a major role in solar power generation for many years, long term projections indicate that high extraction costs of Te and its limited abundance will limit the impact of CdTe thin film solar cells.⁸,¹¹

Organic solar cells use semiconducting organic polymers that absorb incident UV and visible light to generate excitons. A common semiconducting polymer studied in
these applications is poly-phenylene vinylene, or PPV (Fig. 1.6), which allows for charge-carrier mobility through conjugated sp² hybridized carbon atoms. Charge-carrier mobility in OPVs is not as large as it is in their inorganic counterparts, limiting the overall efficiency of organic solar cells. However, the lack of efficiency is somewhat offset by a semiconducting polymer’s relatively high absorption coefficient (usually on the order of $10^5 \text{cm}^{-1}$). Organic solar cells are also amorphous as opposed to crystalline like inorganic semiconductors. This allows for deposition on flexible substrates that can be used for various applications.¹² While there is still much work to be done, organic solar cells have the potential to be made cheaply on a large scale and could be a factor in the global energy market.¹²

![Figure 1.5 Structure of poly-phenylene vinylene.](attachment:image.png)

The cost of solar power can also be reduced through solar concentration. Focusing sunlight incident on the photovoltaics can reduce the total area of solar cells used to generate power. Sunlight can also be concentrated onto a working fluid that is heated and used to turn a turbine that generates power.¹³ This type of energy is called solar thermal power. Both of these methods reduce the total cost of the power produced. There are many different methods used for solar concentration, which will be discussed
in the following section.

1.4 Methods of Solar Concentration

There exist many different types of solar concentration but most of these technologies can be separated into two main categories: high gain and low gain solar concentrators where gain represents the amount of solar concentration. High gain solar concentrators have gains exceeding 1000x and low gain solar concentrators are defined to have gains less than that. High gain solar concentrators concentrate more light onto a smaller area of photovoltaic or working fluid, but the machinery used to achieve this is often much more expensive than low gain systems. In order to reach the $1.00/W_p goal, the total cost of the system must be minimized. A few examples of each type of solar concentrator are presented in this section.

1.4.1 High Gain Solar Concentrators

Solar Dishes

Solar dishes use parabolic mirrors to focus light onto either a photovoltaic, or working fluid that turns a turbine or moves a piston to generate electricity. Solar dishes utilize solar tracking systems to achieve gains over 2000x.

Solar Tower

The solar tower generates electricity by using mirrors called heliostats to reflect sunlight onto a central tower. The concentrated sunlight heats a heat exchanger that
uses steam to power a turbine, generating electricity. Each heliostat is equipped with a solar tracking system that allows it to achieve gains exceeding 1500x.\textsuperscript{13}

\subsection*{1.4.2 Low Gain Solar Concentrators}

\textbf{Scattering Grid Concentrator}

A scattering grid solar concentrator uses numerous small beveled lenses distributed across a large substrate. The lenses use solar tracking to concentrate light onto even smaller angled mirrors which reflects the light to a photovoltaic surrounding the edge.\textsuperscript{14}

\textbf{Holographic Concentrators}

Holographic solar concentrators use a holographic diffraction grating to deflect the light so it can be trapped in a thin waveguide. The light is then harvested by a bi-facial solar cell located at the middle of the device achieving gains of 2.5x. Holographic solar concentrators do not require solar tracking but, like all the concentrators mentioned so far, do require direct sunlight.\textsuperscript{15}

\textbf{Luminescent Solar Concentrators}

Luminescent solar concentrators (LSCs) use fluorescent dyes to redirect light in the plane of a thin waveguide (fig. 1.7). Incident light is absorbed by a dye imbedded in the waveguide, and reemitted in the plane of the device where it is collected by photovoltaics lining the edge of the concentrator. LSCs need no solar tracking to
concentrate sunlight and have achieved gains of up to 10x. LSCs will be described in more detail in Ch.2.

Figure 1.6 A schematic of a general LSC. Fluorophores (red spheres) embedded in a waveguide absorb sunlight and subsequently emit it in the plan of the waveguide. The light is concentrated along the edges of the device where it is then collected by solar cells.

1.5 Summary

Solar power is likely to play a significant role in the future of fossil fuel alternatives. In order to maximize its impact, the cost of solar power must be competitive with fossil fuels on the global energy market. The U.S. Department of Energy has determined that this will happen if the efficiency of solar power can reach the benchmark of $1.00/W_p$. Cost reduction can be achieved by several methods including further development of generation III photovoltaics like MEG solar cells or by developing more efficient solar concentration schemes. Regardless of the approach, an emphasis must be placed on using cheap and abundant materials as well as maximizing efficiency.
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Chapter 2: Luminescent Solar Concentrators

2.0 Overview

This chapter discusses the underlying theory of luminescent solar concentrators, the materials used in their fabrication, and the efficiencies of current LSC technologies. Design concepts based on oriented fluorophore LSCs are introduced, and an improved model is presented that more accurately describes escape cone losses, the major loss mechanism in LSCs.

2.1 Description of LSCs

Research on LSCs began in the 1970s with early work centering on screening dyes for various properties including quantum yield, stokes shift, and photostability. However, this effort eventually stalled because no suitable dyes for LSC applications were found, and their performance was low. More recently, new generations of fluorophores have been synthesized offering the potential for improved performance, and research into LSCs has resumed with encouraging results.

LSCs consist of a waveguide, usually made from glass or plastic, which is either embedded or coated with a fluorescent material (Fig. 2.1). Incident sunlight is absorbed by the fluorophores and emitted through fluorescence. A portion of the emitted light is trapped within the waveguide and it is concentrated at the edges of the device. The light is then collected by photovoltaics along the perimeter of the device and converted into electrical current. LSCs use cheap waveguide materials to replace large areas of expensive solar cells, allowing for potential reduction in the cost of solar power.
LSCs offer several advantages over alternative solar concentrator systems. Other solar concentrators like scattering grids or parabolic mirrors require solar tracking systems that involve moving parts that can be expensive to maintain. LSCs consist of a single waveguide with no moving parts minimizing installation and maintenance costs.¹¹ They do not require mirrors or lenses to focus sunlight, thus direct sunlight is not needed to concentrate light. This advantage makes LSCs ideal for use in diffuse climates where sunlight is scattered by cloud cover.¹¹ A characteristic unique to LSCs is their color; this gives LSCs an artistic quality that makes them useful for “green” architectural applications.

2.2 Efficiencies of LSCs

LSCs are an example of a low gain solar concentration technology that does not use a mirror or a lens to concentrate sunlight. Instead they use fluorescent dyes to

![Figure 2.1 Schematic of an LSC. The fluorophores absorb a fraction of incident sunlight according to the absorption of the fluorophores. A portion absorbed light is emitted and totally internally reflected (TIR) to the edge of the waveguide where it is harvested by solar cells.](image)
collect light over a large area and concentrate it at the edges where it is collected by a photovoltaic. Consequently, the concentration metric used to describe LSCs is geometric gain, $G$, which is defined as the ratio of the surface area of the LSC, $A_{Surface}$, to the area of the edges, $A_{Edge}$ (2.1). 

$$G = \frac{A_{Surface}}{A_{Edge}}$$

The highest reported geometric gains in LSCs are less than 10, by far the lowest gain of any solar concentration technology discussed in the previous chapter. The efficiency of LSCs decreases as the area of the device increases because loss mechanisms in LSCs depend on the size of the waveguide. This limits the overall size and geometric gain of an LSC. Low geometric gains of current devices have limited the commercial viability of LSCs, but the thermodynamic maximum suggests that geometric gains of $10^4$-$10^5 \times$ could be reached. 

The performance of different LSCs are difficult to compare due to differences in, design and experimental testing. However, the two most common types of efficiencies reported in the literature are the optical quantum efficiency (OQE) and the external quantum efficiency (EQE). The OQE is the ratio of the number of photons absorbed by the LSC, $\varepsilon_{abs}$, compared to the number of photons collected at the edge of the device, $\varepsilon_{edge}$ (2.2). The EQE is a ratio that compares the fraction of energy incident, $\varepsilon_{incident}$ on the LSC to the amount of energy generated by the PVs lining the edge of the LSC, $\varepsilon_{LSC}$ (2.3).
\[ OQE = \frac{E_{abs}}{E_{edge}} \]  \hspace{1cm} (2.2)

\[ EQE = \frac{E_{LSC}}{E_{incident}} \]  \hspace{1cm} (2.3)

For the purposes of this discussion, previously reported LSC efficiencies will be compared using EQE since it is a measure of the total efficiency of the system. Currently, the highest reported EQE, by Van Sloof et. al. in 2008, was 7.1\%.\textsuperscript{15} Their system used a PMMA (poly methylmethacrylate) waveguide embedded with organic dyes surrounded by GaAs photovoltaic cells. The geometric gain was reported to be 2.5x. The use of expensive GaAs cells and small geometric gain makes it unlikely that this system will make a significant impact on the global energy market. If cheaper c-Si cells were used, the EQE of the system drops to 2.1\%.\textsuperscript{16}

Baldo et. al. developed an LSC using high stokes-shift dyes to limit reabsorption and increase efficiency.\textsuperscript{1} It was projected that these devices were capable of an EQE of 14.5\% at a \( G = 3x \), with EQE decreasing at larger \( G \). While these projections are encouraging, no publications reporting experimentally determined EQEs for these devices have been published.

2.2.1 The Shockley Queisser Limit for LSCs.

In the previous chapter the Shockley Queisser limit for the maximum efficiency of single junction solar cell was discussed. This idea can be extended to calculate the maximum efficiency of an LSC by starting with an expression for the cost per peak watt:
\[
\frac{\$}{W_p} = \frac{\text{module cost}}{\text{electrical power produced}}
\] (2.4)

\[
\frac{\$}{W_p} = \frac{(C_{\text{LSC}} + \frac{1}{G}C_{\text{PV}})}{(I_{\text{sun}} \eta_{\text{LSC}} \eta_{\text{PV}})}
\] (2.5)

Where \(C_{\text{LSC}}\) is the cost of the LSC, \(C_{\text{PV}}\) is the cost of the photovoltaic, \(G\) is the geometric gain, \(I_{\text{sun}}\) is the irradiance of the sun (1000 W/m\(^2\)), \(\eta_{\text{LSC}}\) is the efficiency of the LSC, and \(\eta_{\text{PV}}\) is the efficiency of the photovoltaic. The terms \(\eta_{\text{LSC}}\) and \(\eta_{\text{PV}}\) are expressed more generally below. While these expressions are not entirely correct, they are an approximation that allows for easy computation.

\[
\eta_{\text{LSC}} = \frac{N_{\lambda_1 - \lambda_2} \text{OQE}_{\text{LSC}}(A)}{I_{\text{sun}}} \left( \frac{hc}{\lambda_{\text{em}} \lambda_{\text{red}}} \right)
\] (2.6)

\[
\eta_{\text{PV}} = \frac{E_{\text{PV}}(\lambda_{\text{em}} \lambda_{\text{red}}) Y_{\text{FF}}}{c} \left( \frac{hc}{\lambda_{\text{em}} \lambda_{\text{red}}} \right)
\] (2.7)

\[
N_{\lambda_1 - \lambda_2} = \int_{\lambda_1}^{\lambda_2} \frac{\lambda}{hc} N_{\text{AM1.5G}}(\lambda) d\lambda
\] (2.8)

In (2.6), \(N_{\lambda_1 - \lambda_2}\) (2.2 \times 10\(^{20}\) photons m\(^{-2}\) s\(^{-1}\) calculated from (2.8)) corresponds to the flux of incident photons (photons m\(^{-2}\) s\(^{-1}\)) within the wavelength range \(\lambda_1\) to \(\lambda_2\). (The range over which the dyes absorb light). Devices studied in this lab use dyes analogous to the Lumogen series from BASF. The Lumogen dyes absorb over a wavelength range
from 300 nm to 600 nm (Fig. 2.2). The function $OQE_{LSC}(A)$ is the optical quantum efficiency of the LSC, which is dependent on the area of the LSC. It is assumed the OQE is independent of wavelength over this range.

In (2.7), the term $E QE_{PV}$ is the external quantum efficiency of the photovoltaic coupled to the LSC. The terms $FF$, and $V_{oc}$ are the fill factor and open circuit voltage of the photovoltaic respectively, and $C$ is the number of electrons in a coulomb ($6.242 \times 10^{18}$ electrons).

If an LSC were perfectly efficient at directing captured light to the edges, then $OQE_{LSC}(A) = 1$. Assuming the terminal dye is Lumogen Red ($\lambda_{red}^{em} = 625$ nm), the maximum efficiency is $\eta_{LSC} \approx 26\%$. GaAs solar cells have a high $\eta_{PV}$ at 625nm, where $\eta_{PV} = 0.46$. If GaAs solar cells were used in this system, the overall power efficiency would be calculated by multiplying $(\eta_{PV})(\eta_{LSC}) = (0.26)(0.46) = 12\%$.

Figure 2.2 The absorption spectra of the Lumogen dyes overlaid with the AM 1.5G solar spectrum. The lumogen dyes have overlapping absorption and emission spectra allowing for a cascade of light to the terminus dye.


2.3 Materials Used in LSCs

This section discusses some of the common materials used in LSC design, including materials used for waveguides and properties required of potential dyes for use in LSCs.

2.3.1 Waveguide Materials

There is a wide range of publications studying waveguide materials for use in LSCs.\textsuperscript{12,11,14} In general all materials used for waveguides have the following qualities:

• High optical clarity
• Highly durability
• Low production cost
• Suitable refractive index

The most common waveguide materials currently used in LSCs are PMMA (poly methylmethacrylate), polycarbonate (polycarbonate), and glass. Waveguides made from glass offer high optical clarity but are much less durable than their polymer counterparts. Furthermore, glass is relatively expensive which increases the overall cost of the LSC. However, glass has low oxygen and water permeability – which helps extend dye lifetime – and the refractive index of glass can be tuned to increase light trapping ability.\textsuperscript{17}

Most LSCs are designed using polymers as waveguide materials, because they are durable and can be made for a fraction of the cost of glass. The most prominent waveguide polymers are PMMA and various forms of PC.\textsuperscript{1,18} Both these materials satisfy
the requirements for use in LSCs. PMMA has particularly high optical clarity and can withstand long exposure to sunlight.\textsuperscript{17} While the properties of PMMA most closely match the waveguide requirements, PC liquid crystal cells were studied in this lab because its refractive index (1.58) is larger than PMMA (1.49), which increases light trapping (Chapter 4).\textsuperscript{17}

2.3.2 Dye Materials

Fluorophores must be screened for the following characteristics before use in LSCs. For devices studied in this lab, the order parameter of a fluorophore is measured in addition to these properties.

- Quantum Yield
- Solubility
- Photostability
- Molar Absorptivity
- Stokes Shift

While there are many different types of fluorophores including: quantum dots/rods and inorganic dopants the fluorophore used in this work were organic.\textsuperscript{17} Organic dyes are highly versatile and can be engineered to meet many of the aforementioned requirements.\textsuperscript{18,19}

Perylene dyes are known for their high quantum yields, molar absorptivities, and photostabilities, but have low solubilities, small Stoke’s Shifts, and low order parameters in liquid crystal hosts.\textsuperscript{20,21} However several modifications can be made to perylene dyes
to increase their alignability and solubility.\textsuperscript{21} In particular, the alignability and solubility of Lumogen Orange, (Fig. 2.3), can be increased without changing the electronic characteristics of the dye by functionalization at the imide nitrogen, which is along the long axis of the molecule.\textsuperscript{21}

Alkyl groups can be substituted at position A to increase both solubility and alignability of Lumogen Orange. Substitution of position B with octylamine or other alkyl chains can increase alignability. Solubility can also be increased through substitution at positions C, the bay positions.\textsuperscript{17,20,21} The dyes synthesized by the Gilbertson group used in this work, along with the members of the Lumogen series and their properties are listed below (Table 2.1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_3.png}
\caption{Structure of Lumogen Orange. Lumogen Orange is a perylene dye, the properties of which can be modified by substitutions at positions A, B, and C.}
\end{figure}
The absorption and emission spectra are shown Fig. 2.4 for D8 in dichloromethane. The absorption and emission spectra for the perylene dyes in Table 2.1 are virtually identical with the exception of Lumogen Red and LR-C8.
Solubility of Perylene Dyes

LSCs use fluorophores to absorb solar energy, thus they must be highly soluble in order to maximize absorbance. Perylene dyes for the most part are highly insoluble due to the propensity of dye molecules aggregate through π-stacking. Since aggregation generally decreases the quantum yield of the dye, approaches for increasing solubility are required if perylenes are to be used in LSCs. Aggregation can be inhibited through substitution at position A (Fig 2.3) with alkyl substituents such as isopropyl and methyl groups. These groups add steric bulk that prevents π-stacking and increases solubility.

Solubility can also be increased by substitution at the bay position (position C). In this case π-stacking is prevented through the use of steric bulk, but substitution at
position C also affects the amount of conjugation in the π-system of the dye, which changes the absorption and emission spectra (Lumogen Red).

**Orientation of Perylene dyes Based on Molecular Structure**

The solubility of perylene dyes is increased through the addition of steric bulk, but this also affects the aspect ratio of the dyes and thus their alignability. In general, a fluorophore is alignable if it has a large aspect ratio. Substitution of perylene at position A with a bulky isopropyl group decreases the aspect ratio and hence its alignability. However, a compromise between alignability and solubility can be made by substituting only some of these positions. For example, the dye used most often in this study, D8, has isopropyl groups in opposing A positions allowing higher solubility (0.86 mg/mL in 5CB) and alignability ($P_2 = 0.66$) than Lumogen Orange (0.22 mg/mL in 5CB and $P_2 = 0.11$).

### 2.4 Loss Mechanisms/Photonic Processes

The light trapping efficiency of an LSC drops precipitously as the size of the device is increased due to several loss mechanisms. It is therefore crucial that losses are well understood in order to develop better performing LSCs.

#### 2.4.1 Fates of an Absorbed Photon

Once light is absorbed by a fluorophore in an LSC, it can be lost in several different ways (Fig. 2.5). Light can be lost through non-unity quantum yields, where excited energy is dissipated through a mechanism other than fluorescence (i.e. non-
radiative decay) (Mechanism 1, Fig. 2.5). Light can also be lost out the escape cone (Mechanism 2). Escape cone losses occur when the wave vector of an emitted photon makes an angle less than the critical angle of the LSC with the surface normal. If this occurs, light is lost out the top or bottom of the waveguide. Escape cone losses are described in more detail in Section 2.4.3. The waveguide itself also contributes to the inefficiency of an LSC since light can be absorbed or scattered by the matrix (Mechanism 3). Emitted light can also be reabsorbed by subsequent fluorophores encountered as it propagates toward the edges of the waveguide. Loss mechanisms 1-3 occur repetitively depending on the number of reabsorption events.

![Figure 2.5](image)

**Figure 2.5** Light can be lost in an LSC through non-unity quantum yields (1), out the escape cone (2), or absorbed or scattered by matrix (3). Light can be reabsorbed by another fluorophore and is subject to the same loss mechanisms (4).

### 2.4.2 Quantum Yield

Once a photon is absorbed by a fluorophore, there are several different mechanisms by which excited energy may be dissipated. Energy can be lost non-radiatively, through the release of infrared photons or through collisions with other molecules. Excited energy can also be lost through phosphorescence and fluorescence. Fluorescence occurs when excited energy relaxed from an excited singlet state ($S_1$) to
the ground singlet state \( (S_0) \) through emission of a photon. Phosphorescence occurs when there is overlap between an excited singlet state \( (S_1) \) and an excited triplet state \( (T_1) \). In this mechanism, energy is transferred from an excited singlet state to a triplet state through intersystem crossing. Once in the triplet state, energy can be relaxed back to the ground singlet state through the release of a photon. (Fig 2.6).

![Jablonski Diagram](image)

*Figure 2.6* Jablonski diagram electronic transitions between electronic states

The probability that an excited molecule will undergo fluorescence is defined as the fluorescence quantum yield, \( \phi \):

\[
\phi = \frac{k_f}{k_f + \sum k_d} = \frac{n_E}{n_A}
\]  

(2.9)
Where $k_e$ is the probability of fluorescence, $\sum k_d$ is the sum of the probabilities for all other relaxation mechanisms, $n_E$ is the number of photons emitted, and $n_A$ is the number absorbed.

The quantum yields of the dyes shown in Table 2.1 were determined by comparison to a standard with a known quantum yield. For the dyes in Table 2.1, Lumogen Orange was used as the standard, which has a quantum yield of 1.0. Dilute solutions ($10^{-6} - 10^{-5}$ M) of both Lumogen Orange, and the dye to be measured were prepared in order to minimize reabsorption. Absorption and emission spectra of both solutions were gathered and the fluorescence quantum yield was computed using the (2.10):

$$\phi_f = \phi_{f,\text{ref}} \left( \frac{A_{\text{ref}}}{A} \right) \left( \frac{n}{n_{\text{ref}}} \right) \left( \frac{l}{l_{\text{ref}}} \right)$$  \hspace{1cm} (2.10)

Where $\Phi_{f,\text{ref}}$ denotes the fluorescence standard, $A$ is the absorbance at excitation wavelength, $I$ is the integrated fluorescence intensity of the sample when excited and $n$ is the refractive index of the solvent.\textsuperscript{22}

### 2.4.3 Escape Cone Losses

The probability of losing light through the escape cone can be derived using Snell’s Law, assuming illumination from all sides. This model has been used to calculate escape cone loses in previous LSC research.\textsuperscript{7} In practice however, LSCs are illuminated by the sun, which implies illumination primarily from one direction. This leads to photoselection, a phenomenon where the probability of absorption depends on the
dye’s orientation. In this section, escape cone losses are modeled two different ways: using Snell’s Law, and a more complete treatment accounting for photoselection. The latter model was developed by Dr. Stephen McDowall and tested experimentally by our lab.\textsuperscript{23}

**Escape Cone Losses Using Snell’s Law**

Light traveling between different media can be refracted or reflected depending on the angle of incidence of the light, and the refractive indices of the two media. This interaction can be summarized using Snell’s Law:

\[
\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1}
\]

(2.11)

Where \(n_1\) and \(n_2\) are the refractive indices of the two materials and \(\theta_1\) and \(\theta_2\) are the angles of light from normal incidence in the two materials. If the angle of incident light is below a critical angle, \(\theta_{\text{crit}}\), light is reflected off the interface. If the angle of incident light is above \(\theta_{\text{crit}}\), light is refracted into the new medium. The critical angle is defined in (2.12):

\[
\theta_{\text{crit}} = \sin^{-1} \left( \frac{n_2}{n_1} \right)
\]

(2.12)

Assuming illumination from all angles, emission would be isotropic and emanate equally in all directions, resulting in a spherical emission profile (Fig. 2.7). The escape cone is defined as the cone swept out by the critical angle, \(\Omega_{\text{cone}}\), and the fraction of
photons lost through the escape cone, \( P \), is then the volume of the escape cone circumscribed on the volume of the whole sphere.

\[ \Omega_{cone} = 2\pi (1 - \cos \theta_c) \quad (2.13) \]

\[ P = \frac{\Omega_{cone}}{4\pi} = \frac{1}{2} (1 - \cos \theta_c) \quad (2.14) \]

**Photoselection**

Fluorophores embedded in a polymer matrix, as in an LSC, have fixed orientations and are unable to rotate within typical excited state lifetimes. If an LSC is illuminated from a single direction, fluorophores will absorb differently depending on the dye’s orientation. Absorption dipoles aligned parallel to the electric field of incident light will be preferentially excited over dyes with absorption dipoles aligned at other angles (Fig 2.8). Fluorophore orientation also has an effect on light trapping efficiency, as dyes in certain orientations are more likely to emit light within the escape cone.
Figure 2.8 Photoselection in an LSC. Planarly aligned fluorophores (blue dye) absorb more light than dyes in other orientations (red dye). Planarly aligned dyes also preferentially emit light out the escape cone.

Escape Cone Losses Accounting for Photoselection

In this treatment, escape cone losses are quantified by determining the probability a photon with a given polarization will be emitted within the escape cone, $P(esc)$, given that it is absorbed by a dye with a specific absorption moment $\mu_a$, (2.15).

$$P(esc) = \int P(esc|abs \ by \ \mu_a) \ P(abs \ by \ \mu_a) \ d\mu_a$$  \hspace{1cm} (2.15)

Photoselection was accounted for in (2.15) by weighting the probability a photon is lost out the escape cone given that it was absorbed by a dye with a specific orientation, $P(esc|abs \ by \ \mu_a)$, by the probability of absorption by a dye with that orientation, $P(abs \ by \ \mu_a)$. The probabilities are then summed over every possible orientation. These calculations lead to an equation of the form.$^{23}$
\[ P(esc) = -a \cos(2\alpha) + c \] (2.16)

Where \( a \), and \( c \), are dimensionless coefficients that are calculated individually for each LSC based on a given device geometry and materials properties, and \( \alpha \) is the polarization angle of incident light.

To test this model, experimental data were generated by illuminating a PMMA block with a low concentration of Lumogen Red with polarized light. The intensity of light emitted out the escape cone as a function of polarizer angle, \( \alpha \), was measured and the data fit to (2.16) (Fig. 2.9).

The least squares regression of the data fit to (2.16) yielded coefficients \( a \) and \( c \) equaling 8566.2 and 39206, respectively. Coefficients \( a \) and \( c \) based on theoretical calculations were 8081 and 39207, respectively. These two curves lie within the 95% confidence interval.
confidence interval based on the experimentally determined data and accurately and completely describe escape cone losses in LSCs.\textsuperscript{23}

This model is of particular importance in this study, because it accurately describes the effect of fluorophore orientation on escape cone losses. Using this model, $P(esc)$ can be calculated for successive reabsorption/emission events for dyes with specific P2 order parameters (described in detail in Chapter 3). For example, in a PMMA LSC with dye molecules aligned normal to the plane of the waveguide, a photon absorbed by a dye with a P2 order parameter of 0.8 has a 16% chance of escape for the first absorption/emission event. The previous model, derived using Snell's Law, assumes isotropic emission. A photon emitted within an isotropic PMMA LSC has approximately a 25.9% chance of escape based on this model. These results indicates that escape cone losses can be mitigated through fluorophore alignment\textsuperscript{23}

**Experimental Procedure for Validating the Model**

Rectangular PMMA samples (10 x 10 x 27 mm$^3$) containing 100 ppm Lumogen Red were fabricated using methyl methacrylate monomer from Aldrich and 0.04 wt.% AIBN thermal initiator. The monomer was poured into a scintillation vial, capped, and placed into a water bath at 60°C for 24 hrs. Rectangular samples were cut and polished from PMMA cylinders. Light scattering off PMMA samples was reduced by coating the polished block with a small amount 1.518 refractive index matching fluid from Cargille Labs.
All sample faces were blackened with the exception of two adjacent faces, one with a rectangular opening (4.4 x 4.9 mm$^2$) for illumination and the other, a circular opening (d= 5.5 mm) for emission. The samples were excited with 492 nm light using a Horiba FL3-11 spectrofluorometer with a F4-000 fiber-optic adaptor and Xe lamp light source. Prior to illumination, light was passed through a collimating lens and an Olympus U-AN360P rotatable polarizer. Light lost out the escape cone was measured by a fiber-optic placed along a sample face perpendicular to the illumination direction. The fiber-optic cable was terminated with a 3.2 mm diameter cosine corrector 1.2 mm from the sample face to allow for collection of the widest possible range of escaping light rays (Fig. 2.10),

**Figure 2.10** Experimental setup for testing escape cone loss theory.
2.4.4 Matrix Losses

Waveguide materials used in LSCs are mostly optically transparent but can still contribute to inefficiencies in LSCs. Common waveguide materials like PMMA or polycarbonate are weakly absorbing in the visible spectrum and impurities at the surface, or imbedded within those materials can scatter light. These losses are considered negligible for small LSCs, but can be significant if they are suitably large.

2.5 Summary

LSCs are inexpensive solar concentrators that use fluorescent dyes to concentrate light. Although they offer the potential to reduce the cost of solar power, current efficiencies are not high enough to make a significant impact on the global energy market. The efficiencies are low because LSCs suffer from several loss mechanisms that limit the geometric gain of the device. The major loss mechanism in LSCs is escape cone loss, where light is lost out the top and bottom of the waveguide. Escape cone losses must be minimized in order to maximize the efficiency of LSCs. Based on the model described above, escape cone losses can be reduced through fluorophore alignment.
Reference


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Chapter 3: Oriented Fluorophores

3.0 Overview

This chapter discusses the effects of fluorophore orientation on the performance of LSCs by mathematically describing molecular orientation and its effect on the absorption and emission of light. Experimental methods are presented for controlling molecular orientation and measuring order parameters for dyes in anisotropic media. Oriented single dye LSCs were fabricated and characterized using polarized absorption and fluorescence spectroscopy.

3.1 The Effect of Orientation on Absorption and Emission

The probability of light absorption by a molecule is determined by the orientation of the molecule’s absorption transition dipole with respect to the polarization of incident photons. Absorption is maximized when the absorption dipole is oriented parallel to the electric field vector of incident light, and minimized when oriented orthogonally.\(^1,2\) The molecular axis along which a fluorophore’s absorption moment is oriented is determined by the electronic structure of the molecule.\(^3,4,5,6,7\) For perylene, the absorption dipole lies along the long axis of the molecule and interacts with light most strongly when the long axis is oriented perpendicular to the propagation direction of incident sunlight (Fig. 3.1).\(^8,9,10,11,12\)
Fluorophores emit photons that are polarized with their electric field vectors oriented parallel to the emission transition moment of the dye. The angle, $\beta$, between the emission moment, $\mu_e$ and the absorption moment $\mu_a$ is determined by the dyes fundamental anisotropy in a given medium.\textsuperscript{13,14} Most perylene dyes exhibit uniaxial symmetry so the absorption and emission dipoles have a conal distribution about the long axis of a molecule (Fig. 3.2). Based on this model, the emission direction of perylene dyes can be controlled through orientation of the long axis of the molecule.\textsuperscript{15,16}

**Figure 3.1** The transition moment of perylene is located along the long axis of the molecule and interacts with light when it is parallel to the electric field vector of incident sunlight.

**Figure 3.2** Conal distribution of emission moment, $\mu_e$ and the absorption moment $\mu_a$ for uniaxial dyes along their director, $n$. 
The effect of orientation on LSCs has been studied in planar and homeotropic systems (Fig. 3.3).\textsuperscript{17,18,19,20,21} Planar systems have dyes oriented parallel the plane of the waveguide. In liquid crystal and reactive mesogen matrices, rubbed polyimide or polyvinyl alcohol are often used as surface treatments to achieve planar alignment.\textsuperscript{17,18} Homeotropic systems have dyes oriented with the long axis orthogonal to the plane of the waveguide. For liquid crystal LSCs made in this lab, homeotropic alignment was achieved using an applied electric field. A surfactant was used for homeotropic alignment in reactive mesogen LSCs.\textsuperscript{19,20,21}

![Figure 3.3 Homeotropic alignment (left) and planar alignment (right). Darkly shaded shapes represent liquid crystal molecules and lightly shaded shapes represent dye molecules.](image)

The effect of fluorophore alignment on LSC efficiencies has been investigated previously. Debije et. al. have studied both planar and homeotropic oriented LSCs with DFSB-k160 dye using rubbed polyvinyl alcohol to achieve planar alignment and polyimide for homeotropic alignment.\textsuperscript{17} Planar LSCs lost nearly 50% of absorbed energy out the escape cone, whereas homeotropic devices lost only 5%. These results were attributed to preferred emission in homeotropically LSCs.\textsuperscript{17}
Baldo et al. have also studied the effect of homeotropic on LSC efficiency.\textsuperscript{22} They fabricated homeotropic LSCs with coumarin-6 dye, using reactive mesogen mixture UCL018 and surfactant FC-4430 as a director. Light trapping efficiency in these homeotropic LSCs was 81% compared to 66% for isotropic PMMA LSCs. The OQE was also reportedly 5% better for homeotropic devices.\textsuperscript{22}

The results of both groups indicate that homeotropic LSCs trap light more efficiently than isotropic or planar devices. However, increased efficiency comes at the expense of reduced absorption because the absorption dipole lies outside the plane of polarization of incident light.

### 3.2 Methods for Controlling Alignment

The effect of homeotropic alignment on the efficiency of LSCs was investigated in this study using perylene dyes that were highly alignable, soluble, and had high quantum yields. Dyes were aligned using liquid crystals and reactive mesogens to orient dye molecules.

#### 3.2.1 Liquid Crystals

Liquid crystals were discovered over 100 years ago but were not studied in detail until the 1960’s.\textsuperscript{23} The unique properties of liquid crystals make them ideally suited for a wide range of applications, particularly liquid crystal displays. Depending on temperature, liquid crystals can exist in a wide range of phases, the two most common of which are the nematic and smectic phases.\textsuperscript{23} When in these phases, liquid crystals
self-align with their long molecular axis roughly parallel (Fig. 3.4). As the temperature is increased, liquid crystals eventually enter an isotropic phase where no alignment is observed.\textsuperscript{23}

\textbf{Figure 3.4} Typical molecular orientation for a nematic phase liquid crystal

There are many compounds known to form liquid crystal phases at room temperature, almost all of which are capable of guest-host orientation. The liquid crystals used in this study were 4-cyano-4′-pentylbiphenyl, 5CB and 4-trans-pentylcyclohexylcyanobenzene, 5PCH (Fig. 3.5).

\textbf{Figure 3.5}: Liquid crystals 5PCH (top) and 5CB (bottom)
5CB was used to measure order parameters of dyes in Table 2.1 and 5PCH was used for dye alignment in polycarbonate LSC devices. The orientation of the liquid crystal director, n, was controlled using an applied electric field or rubbed polyimide.

3.2.2 Reactive Mesogens

Reactive mesogens are liquid crystalline materials with polymerizable end groups. As with conventional liquid crystals, elongated molecules embedded within this matrix align with the director. By polymerizing in the liquid crystalline state, the orientation becomes permanent. In situ photo-initiated polymerization of reactive mesogens was carried out with the reactive mesogen in its desired alignment, producing a large area monodomain (Fig. 3.10).

![Figure 3.6 Schematic of polymerizable liquid crystals before and after photopolymerization.](image)

The RM28 series of reactive mesogens were originally formulated by Merck for use as optical correction layers in liquid crystal displays. These reactive mesogen mixtures include several liquid crystalline acrylates as well as a surfactant that induces homeotropic alignment.
3.3 Experimental Methods for Fabricating Liquid Crystal and Reactive Mesogen LSCs

Planar Liquid Crystal Cells

Order parameters calculated in Table 2.1 were measured using planarly oriented liquid crystal cells. The cells were fabricated by spin coating a thin layer (~100 nm) of polyimide, PI2556 from HD MicroSystems, using a Laurell Tech. Inc. spin coater (model: WS-400B-6NPP-LITE; 3 s 500 rpm, 30 s 4000 rpm) onto 1mm thick BK7 glass microscope slides. Prior to spin coating, the glass slides were cleaned by sonication for 20 min in dichloromethane, methanol, and isopropanol. The polyimide coated slides were subsequently baked in an oven preheated to 130°C for 15 min. The temperature was then heated to 250°C with a 5°C/min ramp rate and held for another 30 min. The baked ITO slides were rubbed with a soft cloth 10-15 times to induce planar alignment. Two identical slides were placed anti-parallel on top of one another separated by a 100 μm spacer. The cell was sealed using UV-cured Norland Optical Adhesive #63 (Fig 3.6).

![Diagram](Spacer Polyimide Coated Glass 5CB/Dye Mixture)

**Figure 3.7** Schematic of planarly aligned Liquid crystal cells.

Liquid crystal solutions made with dyes in Table 2.1 were then drawn into the cell via capillary action until filled. The cell was sealed using Norland Optical Adhesive
#63. The cell was heated beyond the isotropic transition temperature of 5CB inducing the liquid crystal into an isotropic phase. The cells were cooled to room temperature where planar alignment was checked via cross polarization optical microscopy.

**Homeotropic Polycarbonate Cells**

Polycarbonate was used as the waveguide material in homeotropic cells because it has a refractive index of 1.58, the largest among suitable polymer materials. The combination of polycarbonate and liquid crystal 5PCH, (ordinary refractive index, n_o=1.48 and extraordinary refractive index n_e = 1.60) have closely matching refractive indices, which promotes efficient light propagation between layers. ITO coated polyethylene terephthalate (PET, n = 1.575) was adhered to the polycarbonate waveguide using Norland Optical Adhesive 1625(n = 1.625). The refractive index of ITO varies significantly as a function of wavelength, but has a value of 1.96 at 540 nm corresponding to the peak emission of D8 in liquid crystal (Fig. 3.7).

<table>
<thead>
<tr>
<th>Poly Carbonate (n =1.58)</th>
</tr>
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<tbody>
<tr>
<td>PET (n =1.575)</td>
</tr>
<tr>
<td>ITO (n =1.95)</td>
</tr>
<tr>
<td><strong>Dye/SPCH (n_o = 1.48, n_e = 1.60)</strong></td>
</tr>
<tr>
<td>ITO</td>
</tr>
<tr>
<td>PET</td>
</tr>
<tr>
<td>Poly Carbonate</td>
</tr>
</tbody>
</table>

*Figure 3.8 A schematic of the device is shown above depicting the different layers along with the refractive indices of each layer*
Polycarbonate cells were fabricated by cutting and polishing polycarbonate slabs with dimensions 12.2 cm by 3.0 cm. Norland Optical Adhesive 1625 was applied to the polycarbonate and the ITO/PET was gently rolled onto the polycarbonate cell with the ITO facing upwards. The cells were then placed under vacuum for 5-10 minutes to allow any air bubbles trapped in the adhesive layer to escape. The adhesive was cured for 1 hour using a UV lamp and the excess ITO/PET was removed. Pieces of polycarbonate were glued together using Loctite 5 Minute Epoxy with the ITO layers facing each other, separated by a 250 µm thick spacer of electrical tape. A glass microscope slide was glued to the polished end of the device using Norland Optical Adhesive 1625 (Fig. 3.8)

\[\text{Figure 3.9} \] Polycarbonate liquid crystal cells were made in a “key” shape so that electrodes could be easily attached to the tabs of the cell.

The D8/5PCH mixture for homeotropically aligned cells was made by adding D8 to 0.216 g 5PCH until saturation. The solution was subsequently diluted with 5PCH to a total mass of 0.654 g. The D8/5PCH solution was sonicated for 1 hour and then poured into the cell.
D8/5PCH/phenyloctane solution for chemically induced isotropic cells was made by adding 20% phenyloctane/5PCH (phenyloctane, n=1.484) solution to 0.217 g of previously saturated 5PCH/D8 mixture until the resulting mixture had a mass of 0.656 g. The isotropic D8/5PCH/phenyloctane solution was poured into an identical polycarbonate cell made as described above.

Phenyloctane was added to disrupt alignment of liquid crystal molecules. The D8/5PCH/phenyloctane solution looked isotropic to the eye but was verified by cross-polarized optical microscopy. The chemical structure of phenyloctane and D8 are shown below (Fig. 3.9).

![Chemical structures of phenyloctane (top) and the alignable perylene based dye D8 (bottom).](image)

**Figure 3.10** Chemical structures of phenyloctane (top) and the alignable perylene based dye D8 (bottom).

**Homeotropically Aligned Reactive Mesogen LSCs**

Homeotropically aligned RM thin films, ~1-4 μm in thickness, were produced by spin coating from a toluene solution. Spin coating parameters varied from 200-3000 rpm for 15 sec. depending on the desired thickness. Reactive mesogen LSCs were spin cast at 3000 rpm for 15 sec. unless otherwise specified.
Reactive mesogen solutions (33% w/w solution of reactive mesogen in toluene) were spun on clean glass substrates (1 mm. thick BK-7 glass or 140-160 μm. thick VWR soda glass microscope cover slips). Photo-initiator CIBA A (0.0045 wt.%) was added to reactive mesogen solution prior to polymerization.

Solutions were filtered through 0.2 μm Fisher Scientific PTFE syringe filters before spin coating. After spin coating, the samples were allowed to air dry for 30 seconds followed by UV-curing under nitrogen for 30 min. at room temperature. Orientation was checked via cross-polarized optical microscopy and film thicknesses were determined by UV-Vis interferometry.

3.4 Measuring Alignment

The orientational order of a uniformly oriented sample is described using the second order Legendre Polynomial, $P_2$ averaged of all molecules:

$$P_2 = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

(3.1)

The angle $\theta$ is the angle between the absorption moment of a molecule and the director of the alignable matrix. The value of $P_2$ can range from $P_2 = 1$ to $P_2 = -1/2$. When $P_2 = 1$, the angle $\theta = 0^\circ$, corresponding to alignment parallel to the director. When $P_2 = -1/2$, the angle $\theta = 90^\circ$, indicating alignment perpendicular to the director.$^{26,27}$

3.4.1 Measuring Alignment in Planar Liquid Crystal Cells

Molecular orientation can be determined by measuring the absorbance of an LSC with different polarizations of light. Order parameters were calculated from absorption
spectra collected using a V-670 Jasco UV visible spectrometer. In planar LSCs, the order parameter is often calculated by measuring the absorption of polarized light parallel and perpendicular to the director of the sample.\(^{28}\)

\[
\langle P_2 \rangle_a = \frac{A_{||}-A_{\perp}}{A_{||}+2A_{\perp}} \left(1 - \frac{3}{2} \sin \theta_a \right)^{-1}
\]

(3.2)

where \(A_{||}\), and \(A_{\perp}\), are the absorbance with incident light polarized parallel and perpendicular to the director of the sample. The angle \(\theta_a\) is the average angle between the absorption transition moment and the long molecular axis. The absorption dipole of perylene dyes lies along the long axis of the molecule so, \(\theta_a \approx 0\), in which case the above equation simplifies to:

\[
OP = \frac{A_{||}-A_{\perp}}{A_{||}+2A_{\perp}}
\]

(3.3)

The spectra used to calculate the planar order parameter of D8 (\(OP = 0.66\)) in 5CB are shown below (Fig. 3.11). The absorbance of the sample with the director aligned parallel to the polarizer angle is greater than when the sample is aligned perpendicular. This is consistent with the model, as the interaction with incident light is favored molecules are aligned in this direction.\(^{15,16}\)
Only order parameters of planarly aligned samples can be calculated using (3.3) because the transition moments of the dyes lie within the plane of polarization. Homeotropically aligned samples cannot be measured with this method since the transition moments of the dyes lie outside the plane of polarization.

3.4.2 Measuring Alignment in Homeotropic Liquid Crystal Cells

As in planar liquid crystal cells, the order parameter is calculated by measuring the absorbance of aligned liquid crystal cells. In a homeotropic cell though, the order parameter is calculated by measuring the absorbance of the aligned, $A_{Homeo}$ and isotropic, $A_{iso}$ states:\(^{28}\)

\[
OP = 1 - \frac{A_{Homeo}}{A_{iso}}
\]  

(3.4)
$A_{iso}$ is measured from UV vis gathered at temperatures above the isotropic transition temperature of the liquid crystal. Alternatively, $A_{iso}$ can be measured using a separate sample chemically induced into the isotropic phase. The latter method was used to measure order parameters in polycarbonate liquid crystal cells because they degraded at elevated temperatures. Isotropic reactive mesogen samples could not be made using either method thus, order parameters are not reported in reactive mesogen.

Using the spectra of isotropic and homeotropic D8 in 5PCH, an order parameter of 0.56 was measured (Fig. 3.12). These spectra were baselined by subtracting an exponential function fit to the background of the spectra. Homeotropic alignment was achieved by applying a 600 V electric field oscillating at 1 kHz. (An electric field this size was used to achieve homeotropic alignment in all LSCs made using this method).

**Figure 3.12** Absorption spectra of isotropic (darkly shaded line) and homeotropic (lightly shaded line) polycarbonate liquid crystal cells.
The use of individual homeotropic and isotropic samples in calculating the order parameter for homeotropic LSCs is not ideal as there is potential for error in the composition and concentration of the polycarbonate cells. However the order parameter of D8 in 5PCH (0.56) is consistent with the order parameter calculated for D8 in 5CB (0.66) shown in Table 2.1.

3.5 Polarized Edge Emission

Homeotropically aligned LSCs have polarized edge emission according to the emission moment of the dye. Dyes with higher order parameters exhibit higher polarization. Polarization in LSCs was measured by monitoring edge emission intensity as a function of polarizer angle. For homeotropically aligned cells, emission intensity is at a maximum when the polarizer is oriented parallel to the director and a minimum when oriented perpendicular.

Polarized edge emission of homeotropic D8/polycarbonate and D8/reactive mesogen LSCs and isotropic D8/PMMA, D8/polycarbonate and LO/reactive mesogen LSCs was measured using the experimental setup shown below (Fig. 3.13). A rotatable polarizer was placed in front of an LSC such that light was polarized prior to collection by the integration sphere. The configuration and equipment used for this measurement is described in chapter 2. The D8 and Lumogen Orange LSCs were excited at 492 nm and the PMMA LSCs were excited at 465 nm. The edge emission intensity of each sample was measured as the orientation of the polarizer was varied in 10° increments from 0°-
170° where 0° corresponds to vertically polarized light and 90° refers to horizontally polarized light.

**Figure 3.13** Experimental setup for measuring the polarization of edge emission of homeotropic and isotropic LSCs.

### 3.5.1 Polarized Edge Emission of Polycarbonate Liquid Crystal Cells

Emission intensity as a function of polarization angle, θ, was measured for isotropic and homeotropic D8/polycarbonate LSCs and compared to commercially available dyed PMMA (Fig. 3.14). Polycarbonate liquid crystal samples were chosen for initial testing because homeotropic order parameters were measured using absorption spectroscopy.
Isotropic D8/polycarbonate LSCs have scattered emission intensities as a function of polarizer angle due to high uncertainty in emission intensity, however there is a definite trend in the data with minimum emission intensities at $\theta = 30^\circ$ and $\theta = 170^\circ$ and maxima at $\theta = 70^\circ$. Dyed PMMA LSCs have very little scatter in emission intensity relative to isotropic D8/polycarbonate LSCs that is reflected by their relatively low uncertainty. Dyed PMMA samples have minimum emission intensities at $\theta = 0^\circ$ and $\theta = 170^\circ$ and maxima at $\theta = 90^\circ$. The uncertainty in emission intensity for homeotropic D8/polycarbonate cells is much greater than in both isotropic LSCs, yet despite the...
uncertainty the opposite trend can be observed with maxima at $\theta = 0^\circ$ and $\theta = 170^\circ$ and a minimum at $\theta = 70^\circ$.

The homeotropically aligned polycarbonate cell had maxima when the polarizer was oriented at $\theta=0^\circ$ and $\theta=170^\circ$ corresponding to vertically polarized light. This is consistent with our model, as homeotropic D8/polycarbonate LSCs have an order parameter of 0.56, indicating the majority of dye molecules are aligned homeotropically. Thus the edge emission of homeotropic LSCs should consist of mostly vertically polarized light. According to the model, it is expected that minimum edge emission should occur at $\theta = 90^\circ$, corresponding to horizontally polarized light, however the minimum edge emission occurs at $\theta = 70^\circ$, but both intensities are encompassed within the uncertainty. The same argument can be made for the maxima and minima in each of the samples and their expected values based on theory.

The isotropic PMMA and D8/polycarbonate LSCs showed the same general profile where the emission maximum occurs near $\theta = 90^\circ$ and the minimums occur at $\theta = 0^\circ$ and $\theta = 170^\circ$. One might expect that the isotropic samples would exhibit no polarization dependence since all orientations are equally favorable, however since the samples were illuminated from a single direction photoselection preferentially excites planarly oriented dyes leading to larger emission intensity when the polarizer is oriented horizontally as opposed to vertically.
3.5.2 Polarized Edge Emission of Reactive Mesogen Thin Films

Reactive mesogen LSCs containing 1000 ppm of Lumogen Orange or D8 were made on VWR BK7 microscope slides using the procedures described in section 3.2.2. Lumogen Orange has a small order parameter (OP=0.11) in 5CB compared D8 (OP=0.66) making it an ideal isotropic comparison to the homeotropic D8 samples. The polarized edge emission of both samples was measured using the same apparatus shown in Figure 3.13 and the results are shown below (Fig 3.15).

Isotropic Lumogen Orange LSCs have maximum edge intensity at θ = 90° and minima at θ = 0° and θ = 170°. Homeotropic D8 LSCs, have maxima at θ = 0° and θ = 170° and minima at θ = 90°. Alignment in reactive mesogen LSCs can be confirmed using the emission intensity profile of liquid crystal polycarbonate LSCs. D8 reactive
mesogen LSCs are homeotropically aligned because edge emission is maximized when the polarizer is vertically oriented and minimized when the polarizer is oriented horizontally. Conversely, Lumogen Orange reactive mesogen LSCs are isotropic because edge emission is maximized when the polarizer is oriented horizontally and minimized when oriented vertically.

3.6 Characterizing the Orientation of Reactive Mesogen Thin Films

3.6.1 Thickness of Reactive Mesogen Samples.

According to Beer’s Law (3.5) absorbance depends on three parameters: the concentration of the sample, $c$, the path length, $b$, and the molar absorptivity, $\epsilon$.

$$A = \epsilon bc$$  \hspace{1cm} (3.5)

In reactive mesogen LSCs, the path length of light corresponds to the thickness of the reactive mesogen layer. Thus absorbance can be maximized by fabricating thicker reactive mesogen layers. Reactive mesogen LSCs with varying thicknesses were made using 1000 ppm D8 reactive mesogen solutions, and various spin coating parameters. Each LSC was spun for 15 seconds at a different rate. The speeds used were 3000, 2000, 1000, 500, 300, 250, and 200 rpm. The thicknesses of the LSCs were calculated by measuring absorbance spectra and fitting the interference fringes that arise between the reactive mesogen and the glass substrate to (3.6).\textsuperscript{29}
\[ d = \frac{1}{2\sqrt{n^2 - \sin^2 \phi}} \times \frac{p}{r_1 - r_2} \times 10^4 [\mu m] \]  

(3.6)

Where \( d \) is the thickness of the film, \( n \) is the refractive index of reactive mesogen (\( n_e = 1.667 \)), \( \phi \) is the angle of incident light (\( \phi = 0^\circ \)), \( p \) is the periodicity of the interference wave, and \( r_1 \) and \( r_2 \) are the peak and valley wavelengths respectively. The film thickness as a function of rpm is shown below fit to an exponential decay function (Fig. 3.16).

![Graph showing film thickness as a function of RPM.]

**Figure 3.16** Film thickness as a function of spin coating RPM. The thickness were fit to an exponential decay function.

D8 reactive mesogen LSCs have a maximum film thickness of 4.4 µm at 500 rpm, and a minimum thickness of 1.9 µm at 3000 rpm. The data were fit to an exponential function with \( R^2 = 0.98 \) (3.8)

\[ t = 3.76e^{-\frac{x}{947.3}} + 0.33 \]  

(3.7)
Where t is the film thickness, and x is the spin coating RPM. For films spun at 250 and 200 rpm, the interference fringes were too small to be calculated using (3.6). Alignment in LSCs was determined by measuring \( R = \frac{I_{90^\circ}}{I_{0^\circ}} \) for each LSC at a fixed distance from the integration sphere using the apparatus shown in Figure 3.13. The absorbance and R are plotted as a function of rpm (Fig. 3.17).

From 3000-300 RPM, the order parameter of the LSCs remained above \( R = 1 \), indicating homeotropic alignment. Along this same segment, the absorbance gradually increases from 0.0063 at 3000 rpm, to 0.0193 at 300 rpm. From 300 - 200 rpm the absorbance increases dramatically to a maximum of 0.047 AU at 200 rpm. At 200 rpm \( R = 0.36 \) demonstrating that the samples are isotropic.
At spin rates less than 300, R decreases below the isotropic threshold, R = 1, indicating that the samples are no longer homeotropically aligned which accounts for the rapid increase in absorbance. These results along with the film thickness calculations shown in Figure 3.16, demonstrate that the maximum thickness that can be achieved while maintaining alignment is approximately 4.5 μm. However, the optical quality of the samples degrades as the thickness is increased. To maintain the highest optical quality and alignment, reactive mesogen samples used in proceeding measurements were spun at 3000 rpm.

3.7 Summary

The Alignment of fluorophores can be used to control the emission direction of photons in LSCs. For LSCs with homeotropically aligned perylene dyes, emission is directed within the plane of the waveguide. Based on the theoretical model discussed in Chapter 2, emission from oriented fluorophores reduces the probability of emission within the escape cone and increases the probability of total internal reflection. This leads to increased overall efficiencies in LSCs. Oriented fluorophore D8 and Lumogen Orange LSCs were made to confirm this theory using liquid crystals and reactive mesogens to control orientation. Order parameters were measured using UV-Vis spectroscopy for liquid crystal LSCs and orientation was confirmed in reactive mesogen LSCs using polarized fluorescence spectroscopy. The absorbance of aligned reactive mesogen LSCs was maximized by fabricating the thickest possible LSC while still
maintaining alignment. The maximum thickness was measured to be approximately 4.5 µm.
References


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Chapter 4: Single Dye Device Characterization

4.0 Overview

This chapter describes the performance of D8 and Lumogen Orange reactive mesogen and PMMA thin film LSCs. Absorption and emission spectra of reactive mesogen LSCs are presented and their performance in oriented and isotropic fluorophore LSCs is discussed. The results are then used to estimate the light trapping efficiency of the devices. Finally, the performance of reactive mesogen thin film LSCs is described using a simple but accurate model.

4.1 Absorption and Emission Spectra of Reactive Mesogen Thin Film LSCs

D8 is ideal for use in homeotropic reactive mesogen thin film devices because it has a large order parameter (0.66) and exhibits high solubility in organic solvents. Conversely, Lumogen Orange has a low order parameter in 5CB and the ratio between the emission intensity at vertical and horizontal polarization in reactive mesogen is less than 1. These results indicate that Lumogen Orange exhibits no measureable orientation in anisotropic media. Thus Lumogen Orange reactive mesogen LSCs can be used as an isotropic comparison to homeotropically aligned D8 reactive mesogen devices.

4.1.1 Absorption Spectra of Reactive Mesogen Thin Films

Lumogen Orange and D8 reactive mesogen thin films were made by spin coating either 1000 ppm D8 or 835 ppm Lumogen Orange reactive mesogen solutions at 3000
rpm for 15 sec onto glass coverslips. The solutions were made using the procedure described in section 3.2.2. 3000 rpm was chosen as the spin speed in order to ensure that reactive mesogen films were highly aligned and optically transparent. The absorbance of these devices was measured using an V-670 Jasco spectrophotometer. The raw absorbance spectrum of Lumogen Orange in reactive mesogen is shown below normalized by the peak absorbance, 0.0044 AU (Fig. 4.1).

![Normalized Absorbance vs Wavelength](image)

**Figure 4.1** UV-Vis spectrum of Lumogen Orange in reactive mesogen.

The absorbance of the Lumogen Orange reactive mesogen thin films was very small because the thickness of the film was less than 2 μm, thus the spectrum above must be background corrected to remove interference oscillations. The baseline is comprised of two component functions: an exponential decay function and an oscillation function. The oscillation in the baseline is due to optical interference that arises between the reactive mesogen and the glass substrate. The function describing
the oscillation in the background depends on the refractive indices of the reactive mesogen and the glass substrate and layer thickness. Presumably, scattering in the reactive mesogen layer causes the exponential decay observed in the baseline (Fig. 4.2).

![Image](image.png)

**Figure 4.2** UV-Vis spectrum of Lumogen Orange (dashed line) in reactive overlaid with exponential (dotted line) and oscillatory (solid line) components of the background correction function.

The exponential and oscillatory components (4.1) of the background can be fit to individual functions that can be subtracted from the raw signal (4.2). The absorbance of the Lumogen Orange device is taken from the resultant spectrum (Fig. 4.3).

\[
T = \frac{A}{B - C \cos \frac{4\pi n D}{w} + D^2} \quad \text{(4.1)}
\]

\[
\text{Background Subtraction} = 10^{-T} + Fe^{-G\lambda} \quad \text{(4.2)}
\]
In (4.1) and (4.2) the terms $A$, $B$, $C$, $D$, $F$ and $G$ are fitting constants, $t$ is the film thickness and $\lambda$ is wavelength.

The same procedure was used to baseline D8 reactive mesogen devices, however the process was more difficult because of the decreased absorbance signal in D8 reactive mesogen devices.

![Baseline corrected absorption spectrum of Lumogen Orange in reactive mesogen](attachment:Figure_4.3.png)

**Figure 4.3** Baseline corrected absorption spectrum of Lumogen Orange in reactive mesogen.

The baseline corrected absorption spectrum for a representative Lumogen Orange reactive mesogen LSC is shown above. The baseline remains constant from 575 nm to 850 nm, however there is a small amount of oscillation in the baseline from 350 nm to 400 nm. Despite oscillation in this range, the baseline remains close to 0 absorbance. This indicates that the exponential fit closely approximates the data at all wavelengths but the function describing the oscillation in the background deviates from
the data at shorter wavelengths. The function used to model the oscillation in these samples uses a constant refractive index, however the refractive index varies with wavelength. This likely explains the discrepancy in the model at shorter wavelengths.

While this method can be used to produce accurate baselines for absorbance spectra of Lumogen Orange in reactive mesogen LSCs, it is labor intensive and tedious. Furthermore the result is less accurate for D8 thin films. The excitation spectra of D8 and LO reactive mesogen thin films closely approximate the shape of the absorption spectra of the two devices (Fig 4.4). The excitation spectra of each device require no background correction and have a much higher signal to noise ratio than the absorption spectra. The excitation spectra were gathered using a Horiba FL3-11 spectrofluorometer while monitoring emission at 580 nm.

![Graph](image)

**Figure 4.4** The excitation and absorption spectra of Lumogen Orange are shown above normalized by their peak value.
The normalized excitation and absorption spectra of Lumogen Orange in reactive mesogen are shown in Figure 4.4. The shape and intensity of each spectrum is nearly identical at the 0->1 transition, but the spectra begin to slightly diverge from one another at shorter wavelengths. For calculations that don’t require absolute absorption values to compute, (i.e. overlap fraction between absorption and emission) the absorption spectrum can be replaced by the excitation spectrum, making the calculations easier.

The peak absorption wavelength for perylene based dyes occurs at the 0->1 transition. Since the excitation and absorption spectra are nearly identical for this transition, the excitation spectra can be used to calculate where the peak absorption occurs. The excitation spectra for Lumogen Orange and D8 reactive mesogen thin films are shown below (Fig. 4.5).

![Figure 4.5](image)

*Figure 4.5* The excitation of D8 (dotted line) and Lumogen Orange (solid line) normalized by peak excitation.
The shape of both spectra is nearly identical and the peak intensities at each transition are the same. However the peak absorption of D8 (531 nm) is red shifted relative to the peak absorption of Lumogen Orange (527 nm). This red shifting is likely caused by the orientation of D8 reactive mesogen because no red shift is observed in isotropic solvents.

4.1.2 Emission Spectra of Reactive Mesogen Thin Films

The emission spectra of D8 and Lumogen Orange thin films were acquired using a Horiba FL-3 spectrofluorometer with an excitation wavelength of 480 nm. The samples were measured using a scattering background in order to achieve the largest possible signal. The emission spectra of 1000 ppm D8 and Lumogen Orange reactive mesogen LSCs is shown below normalized by peak emission (Fig. 4.6)

![Normalized Emission vs Wavelength](image)

**Figure 4.6** Normalized excitation spectra of D8 (dotted line) and Lumogen Orange (solid line) are shown below.
Like the absorption spectra, the peak emission of D8 in reactive mesogen (541 nm) is red shifted relative to the peak emission of Lumogen Orange (536 nm). However, the relative peak intensities vary significantly between the two spectra. These differences are illustrated through the examination of relative peak intensities. The peak intensity of the 2->0 transition relative to peak emission for D8 and Lumogen Orange LSCs are .77 and .54 respectively. This difference in intensity can be attributed to self-absorption losses.

Self-absorption causes a change in relative peak intensity because a percentage of light is lost during each reabsorption event. The relative peak intensity increases because the 0->1 peak is attenuated due to a higher probability of self-absorption over this wavelength range. Despite having a path length of approximately 2 μm, both LSCs have a high enough concentration that self-absorption is observed. To quantify the probability of self-absorption in D8 and Lumogen Orange LSCs, the self-absorption in the emission spectra must be minimized. This can be achieved by measuring the emission of less concentrated samples decreases, because the probability of self-absorption is minimized.

The spectra of 1000 ppm D8 and Lumogen Orange LSCs are shown below compared to samples made with the lowest concentration of dye detectable using this method (Fig 4.7). 100 ppm D8 and 50 ppm Lumogen Orange. Because the absorption of D8 is smaller due to alignment, a larger concentration was required to maintain a strong signal above the detection limit.
In the spectra of low concentration Lumogen Orange and D8 LSCs, the relative peak intensity is reduced compared to the 1000 ppm LSCs. For D8 LSCs, the relative peak intensity decreased from 0.77 to 0.53. The relative peak intensity for Lumogen Orange LSCs decreased from 0.54 to 0.47. At low concentrations, the relative peak intensities have approximately the same value, 0.53 for D8 and 0.47 for Lumogen Orange LSCs. While the relative peak intensities are not identical, these results indicate that self-absorption is roughly the same in either LSC. Using these emission spectra along with the excitation spectra of D8 and Lumogen Orange reactive mesogen LSCs, self-absorption can be calculated.

4.1.3 Quantifying Self-Absorption

Perylene based dyes, like Lumogen Orange or D8, undergo self-absorption because they have overlapping absorption and emission spectra. Photons emitted at
wavelengths within the overlapping region can be reabsorbed by the same dye. The probability of reabsorption is related to the fraction of the total emission spectrum contained within the overlapping region.

The fractional overlap is calculated using the excitation and emission spectra of D8 and Lumogen Orange. For reasons presented above, the excitation spectra of each sample were used instead of absorption spectra. Due to the detection limits of our method it is impossible to measure a spectrum for both Lumogen Orange and D8 samples where some reabsorption has not already been observed. As an approximation, the emission spectra of 100 ppm D8 and 50 ppm Lumogen Orange reactive mesogen samples were used to calculate the overlap area between the absorption and emission spectra for each sample (Fig. 4.8).

**Figure 4.8** The excitation spectra of Lumogen Orange (double solid line) and D8 (dashed line) are overlaid with the emission spectra of Lumogen Orange (solid line) and D8 (dotted line). The overlap region represents the available wavelengths that can be reabsorbed (shaded region).
The fractional overlap for each LSC is defined as the area encompassed between the absorption and emission spectra of an LSC compared to the total area of the emission spectrum for that LSC. The fractional overlap of the D8 sample is 0.30 compared to 0.33 for Lumogen Orange. While there is a 0.03 difference between the two values, it is important to note that the emission spectrum of D8 used to calculate the fractional overlap still exhibits signs of reabsorption. Baldo et al. uses a ratio, S, to quantify self-absorption. S is defined as the ratio of the absorption coefficients at the absorption and emission maxima (4.1). \(^2\)

\[
S = \frac{A_{\text{max}}}{I_{\text{max}}}
\]  

(4.3)

Where \(A_{\text{max}}\) and \(I_{\text{max}}\) are the absorption values at peak absorption and peak emission emission respectively. Large S values indicate small fractional overlap. S values reported by Baldo et. al. ranged 80 to 500 depending on the parameters of the LSC system. \(^1\)

When calculating the S value for Lumogen Orange and D8 reactive mesogen it is appropriate to use excitation spectra instead of absorption spectra because the approximation is close within this wavelength range. The S value for Lumogen Orange reactive mesogen is 1.60 compared to 1.27 for D8.

There are small differences between the S values and fractional overlap integral between the Lumogen Orange and D8 reactive mesogen samples. However the emission spectra used in these calculations exhibit signs of self-absorption even at these
low concentrations. Given the uncertainty in the emission spectra, it is reasonable to assume that there is very little difference in the probability of self-absorption for Lumogen Orange and D8 in reactive mesogen thin films based on spectral overlap alone. Taking into account the fact that D8 molecules are co-aligned with approximately parallel absorption moments in RM films, one anticipates that self-absorption should be higher in D8 samples. This has implications for computed light trapping efficiencies, discussed in the next section.

4.2 Light Trapping Efficiency Measurements

Homeotropic LSCs absorb less light than isotropic devices because the absorption dipoles of the dyes are oriented such that the interaction with incident light is reduced. However the decrease in absorbance comes with a corresponding increase in light trapping efficiency. The light trapping efficiency, $\varepsilon_{\text{trap}}$ is the probability a photon will be trapped within the waveguide given the loss mechanisms of an LSC. For a single absorption and emission event $\varepsilon_{\text{trap}}$ can be expressed as a product of the loss mechanisms in an LSC (4.4).

$$\varepsilon_{\text{trap}} \sim \varepsilon_{\text{matrix}} \times \varepsilon_{\text{TIR}} \times \varepsilon_{\text{QY}}$$  \hspace{1cm} (4.4)

Where $\varepsilon_{\text{QY}}$ is the quantum yield of the dye, $\varepsilon_{\text{TIR}}$ is the probability that light is totally internally reflected and not lost out the escape cone, and $\varepsilon_{\text{matrix}}$ is the probability that light is transported through the matrix without being scattering or
absorbed. Lumogen Orange and D8 can undergo self-absorption and $\varepsilon_{TIR}$ and $\varepsilon_{QY}$ depend on the number of reabsorption events so these quantities are raised to the power $\tau$ (the number of reabsorption events). Predicted total internal reflection trapping efficiencies, $\varepsilon_{TIR}$ can be approximated using (4.5):

$$\varepsilon_{TIR} = 1 - \frac{2 \int_0^{2\pi} \int_0^{\theta_{\text{crit}}} \sin \theta \, d\theta \, d\varphi}{4\pi}$$  \hspace{1cm} (4.5)$$

$\varepsilon_{TIR}$ in isotropic LSCs is calculated using (4.5) by computing the area the solid angle the escape cone makes with the spherical emission profile of an isotropic dye. For isotropic reactive mesogen LSCs (i.e. Lumogen Orange reactive mesogen) $\varepsilon_{TIR} \sim 0.78$ and for PMMA LSCs $\varepsilon_{TIR} \sim 0.75$. The difference in trapping efficiency is due to the different critical angles of the LSCs, which are calculated, using the refractive indices of the waveguide materials.

$$\varepsilon_{TIR} = 1 - \frac{2 \int_0^{2\pi} \int_0^{\theta_{\text{crit}}} \sin^2 \theta \sin \theta \, d\theta \, d\varphi}{4\pi}$$  \hspace{1cm} (4.6)$$

Predicted $\varepsilon_{TIR}$ values for homeotropically oriented LSCs were estimated using (4.6) assuming an order parameter of $P2 = 1$. Equations (4.5) and (4.6) are identical with the exception of an additional $\sin^2 \theta$ term, which accounts for the emission profile of an oriented emitter.
The light trapping efficiency of 835 ppm Lumogen Orange and 1000 ppm D8 reactive mesogen and PMMA LSCs was tested by measuring the emission intensity at the edge of the LSCs as a function of distance, D, from the detector. The reactive mesogen samples were made on glass microscope coverslips using the procedure described in section 3.2.2. PMMA samples were made by spin coating 1 mm thick VWR glass microscope slides with a 10 wt.% PMMA/chloroform/dye solution. The samples were illuminated with 485 nm light and the distance from the integration sphere was varied in 0.254 cm. increments. The experimental setup used is described in detail in section 2.4.2 (Fig 4.8).

**Figure 4.8** Experimental setup used in for light trapping efficiency measurements.
4.2.1 Emission as a Function of Distance From the Integration Sphere

The emission spectra at increasing excitation distances from the integration sphere are shown below for individual D8 and Lumogen Orange reactive mesogen thin film LSCs.

![Figure 4.9 Emission spectra at different distance of D8 (A) and Lumogen Orange (B).](image)

For both D8 and Lumogen Orange samples, the emission intensity decreases as the excitation distance is increased. At the shortest excitation distance (0.254 cm), the peak emission is more intense for Lumogen Orange (9600 CPS) than for D8 (4750 CPS) due to the larger absorbance in the Lumogen Orange LSCs. In both samples, the relative peak intensities diminish as the excitation distance is increased due to increased self-absorption at longer excitation distances.

Self-absorption in LSCs causes a red-shift in the average energy of photons collected at the edge of the LSC. During self-absorption, there is attenuation on 1->0 transition lowering the average photon energy. The average photon energy is
calculated from the above spectra by converting wavelength to KJ/mol and integrating over the wavelength range. The average photon energy as a function of excitation distance is shown below for D8 and Lumogen Orange PMMA and reactive mesogen LSCs (Fig 4. 10).

**Figure 4.10** The average photon energy as a function of distance from the integration sphere is shown for D8 (filled diamonds) and Lumogen Orange (filled squares) in reactive mesogen and D8 (open diamonds) and Lumogen Orange (open squares) in PMMA.

The average photon energy of each LSC decreases as the excitation distance from the integration sphere is increased. The average photon energy loss in Lumogen Orange and D8 PMMA LSCs is ~5 KJ/mol given initial average energies of 216.5 KJ/mol and 216.0 KJ/mol respectively. For reactive mesogen LSCs, the change in average energy is ~5 KJ/mol with a 214.1 KJ/mol initial average photon energy for Lumogen Orange and ~6 KJ/mol with a 206.0 KJ/mol initial average photon energy for D8 LSCs. The rate of average photon energy loss is roughly the same for all LSCs and gradual given the initial average energy for each LSC.
The average photon energy in D8 reactive mesogen LSCs is lower at all excitation distances than the other LSCs measured. According to Figure 4.6 the peak emission of D8 in reactive mesogen is red shifted ~5 nm relative to Lumogen Orange in reactive mesogen and D8 and Lumogen Orange in PMMA. This slight red shift accounts for the lower average photon energy in D8 reactive mesogen LSCs.

4.2.2 Measuring OQE

In this section, the light trapping efficiency of an LSC is calculated by from measurements of the OQE at varying distances from the integration sphere. The OQE is described by the trapping efficiency of an LSC as a function of reabsorption. One would expect greater light trapping efficiency in the D8 samples because the emission from homeotropically aligned fluorophores is directed in the plane of the waveguide.

The OQE of 1000 ppm D8 and 835 ppm Lumogen Orange reactive mesogen and PMMA thin film LSCs was measured by collecting the edge emission from an LSC at increasing distances from the integration sphere. The emission intensity was detected using the apparatus described in Figure 4.8. Rather than using the peak emission intensity at each distance, the integrated emission intensity was used because the peak emission of the D8 reactive mesogen LSCs varies as the distance from the integration sphere is increased. In order to account for the difference in absorbance, the integrated emission intensities were divided by the quantity 1-T, where T is the transmittance of the samples.
Often it is convenient to express OQE in terms of geometric gain, G, instead of excitation distance. Distance can be represented in terms of geometric gain by approximating the dimensions of the LSC with a disk of radius $d$, where $d$ is the distance of excitation from the integration sphere. $G$ is then equal to the ratio of the surface area of the LSC to the thickness of the device. However emission is collected form only a small portion of the total area of edge. This is corrected for by multiplying the edge emission by the correction factor $g$. Multiplication by $g$ calculates the OQE of an LSC if light were being collected along all edges of the LSC.

$$g = \frac{\pi}{\tan^{-1}A/2d} \quad (4.7)$$

Where $d$ is the distance of excitation from the integration sphere and $A$ is the diameter of the integration sphere aperture ($7.1 \; \text{e}^{-3} \; \text{m}$). The correction factor $g$ also accounts for the light dilution at increasing excitation distances (Fig. 4.11).

**Figure 4.11** Diagram used for the derivation of the correction factor.
The power efficiency as a function of excitation distance is shown below for a single group of devices. Power efficiency is a ratio of the power incident on the LSC compared to the power of light emitted from the edge of the LSC. The power of incident light and the power of light emitted from the LSC was measured a Newport model 1916-C power meter. In order to measure the incident power, the excitation light source, 485 nm, was shined directly on the power meter. To measure the power of emission, 555 nm light was shined on the chip and the excitation and emission monochrometer slit widths were adjusted such that the intensity of light on the power meter was on the same order as the emission intensity of the LSCs (Fig 4.12).

**Figure 4.12** The power efficiency as a function of excitation distance from the integration sphere for D8 (filled diamonds) and Lumogen Orange (filled squares) in reactive mesogen and D8 (open diamonds) and Lumogen Orange (open squares) in PMMA.
The power efficiency for all LSCs decreases exponentially at longer excitation distances from the integration sphere. The power efficiency of the Lumogen Orange reactive mesogen LSC is larger than all other LSCs at every excitation distance. D8 in reactive mesogen has the lowest power efficiency at all excitation distances and the power efficiencies of the PMMA LSCs are in between the reactive mesogen LSCs.

All LSCs in Figure 4.11 have low power efficiencies because the absorbance at excitation wavelength of the LSCs is weak. In the reactive mesogen LSCs, the Lumogen Orange device absorbs only 1.1% of the incident sunlight, and the D8 device absorbs only 0.3%. At all excitation distances, more light is reaching the detector for Lumogen Orange devices than for D8 devices, thus the power efficiency is higher in Lumogen Orange LSCs. In Figure 4.11, the power efficiency is dominated by the absorbance of the LSC and not by the light trapping efficiency of the LSCs.

The OQE*g of Lumogen Orange and D8 LSCs is shown below as a function of excitation distance from the integration sphere (Fig 4.13). The conversion of emission intensity to OQE accounts for the difference in absorption between D8 and Lumogen Orange LSCs. The OQE is multiplied by g to account for the dilution of light at longer excitation distances from the integration sphere and limited collection along only a small section of the LSC.
Figure 4.13 OQE as a function of distance for D8 (filled diamonds) and Lumogen Orange (filled squares) in reactive mesogen and D8 (open diamonds) and Lumogen Orange (open squares) in PMMA.

The OQE of all LSCS is roughly constant over the excitation distances measured so the average OQE can be used to compare each device (Table 4.1). The isotropic LSCs (D8 in PMMA, Lumogen Orange in PMMA or reactive mesogen) have similar OQEs that are within the error of the measurement and lower than D8 in reactive mesogen, the homeotropically oriented LSC. D8 in reactive mesogen has a larger OQE at all distances than other types of LSCs, indicating that it is trapping light more efficiently than the other devices.
### Table 4.1

<table>
<thead>
<tr>
<th>Type of LSC</th>
<th>Average OQE*g</th>
</tr>
</thead>
<tbody>
<tr>
<td>D8/Reactive Mesogen</td>
<td>0.64</td>
</tr>
<tr>
<td>LO/Reactive Mesogen</td>
<td>0.35</td>
</tr>
<tr>
<td>D8/PMMA</td>
<td>0.33</td>
</tr>
<tr>
<td>LO/PMMA</td>
<td>0.32</td>
</tr>
</tbody>
</table>

D8 in reactive mesogen is trapping light more efficiently than the other LSCs, presumably because D8 is homeotropically oriented within this LSC. However there are several factors other than orientation that could contribute to increased light trapping efficiency within D8/reactive mesogen LSCs.

As shown in Figure 4.8 there is a difference in fractional overlap between the excitation and emission spectra for D8 and Lumogen Orange reactive mesogen LSCs. This overlap represents the probability an emitted photon can undergo self-absorption. The fractional overlap for reactive mesogen LSCs were 0.30 for D8 and 0.33 for Lumogen Orange. While these numbers indicate that Lumogen Orange LSCs can undergo more self-absorption than D8 LSCs, the difference in fractional overlap is small and unlikely to account for the increased trapping efficiency observed in the D8/reactive mesogen device.

Further evidence for this conclusion comes from comparison of PMMA devices, which showed essentially identical performance for D8 and Lumogen Orange.
conclude that the improved light trapping efficiency of D8 / reactive mesogen devices is due solely to homeotropic orientation of the dye.

4.2.3 Calculating Light Trapping Efficiency

The amount of photons that are measured at the edge of the LSC depends on the light trapping efficiency of the LSC, $\varepsilon_{\text{trap}}$. Assuming unity quantum yield, the OQE can be approximated at large edge illumination distances in terms of $\varepsilon_{\text{trap}}$ using (4.8).

$$\text{OQE} \approx \varepsilon_{\text{trap}}^\tau \quad (4.8)$$

$\varepsilon_{\text{trap}}$ can be described as the product of the efficiencies associated with each loss mechanism, $\varepsilon_{\text{TIR}}, \varepsilon_{\text{QY}},$ and $\varepsilon_{\text{Matrix}}$ (4.2). For the D8 and Lumogen Orange LSCs, matrix losses and quantum yield losses have little effect on light trapping efficiency. Both D8 and Lumogen Orange have unity quantum yields and the waveguide materials (reactive mesogen and PMMA) are optically transparent over the wavelength range measured. Thus the light trapping efficiency depends mostly on the probability of total internal reflection, $\varepsilon_{\text{TIR}}$.

$$\varepsilon_{\text{trap}} \sim \varepsilon_{\text{TIR}}^\tau \quad (4.9)$$

Using (4.8) and (4.9), an expression for $\varepsilon_{\text{TIR}}$ can be written in terms of OQE to yield (4.10).

$$\text{OQE} = \varepsilon_{\text{TIR}}^\tau \quad (4.10)$$
OQEs of each device as a function of distance are shown in Fig. 4.11 and can be used to calculate $\varepsilon_{TIR}$ as a function of $\tau$, the number of reabsorption events. Equations (4.10) and (4.11) can be used to estimate $\tau$ using the absorbance of Lumogen Orange reactive mesogen LSCs. This calculation assumes that self-absorption has no effect on the total number of reabsorption events (i.e. it neglects red-shifting of emitted light) and that the number of reabsorption events is constant for all LSCs regardless of dye orientation and waveguide material.

$$\tau = \frac{d}{l} + 1 \quad (4.11)$$

$$\tau = \frac{dA}{b} + 1 \quad (4.12)$$

Here $d$ is the distance from the edge of the LSC and $l$ is the mean path length between reabsorption events. Using Beer’s law, $l$ can be replaced with the quantity $A/b$ where $A$ is the peak absorbance (0.00803) of the 1->0 transition (540 nm) and $b$ is the path length of the sample ($b=160 \mu m$). The peak absorbance of the 1->0 transition was used because this transition encompasses the wavelength range of photons that can undergo self-absorption. The initial absorption event was accounted for by adding a single reabsorption event to (4.11) and (4.12). The predicted number of reabsorption events as a function of distance from the integration sphere is shown below (Fig 4.14). The number of reabsorption events increases linearly and has an intercept at 1.0, representing the initial reabsorption event.
**Figure 4.14** Plot of the number of reabsorption events as a function of distance from the integration sphere.

The total internal reflection trapping efficiency, $\varepsilon_{TIR}$ for homeotropic and isotropic LSCs was determined by fitting 4.9 to the OQE* data as a function of distance for each LSC using the predicted number of reabsorption events calculated by (4.12) (Fig 4.15).

**Figure 4.15** The OQE* as a function of excitation distance was fit to (4.9) for D8 (blue) and Lumogen Orange (red) PMMA (A) and D8 (blue) and Lumogen Orange (red) reactive mesogen (B) LSCs.
For the PMMA LSCs, the fit lines of both Lumogen Orange and D8 LSCs lie virtually on top of one another suggesting that both samples have identical $\varepsilon_{TIR}$. Since D8 and Lumogen Orange have identical spectroscopic characteristics in isotropic media, this result is as expected. For the reactive mesogen LSCs, the fit lines indicate that homeotropic D8 LSCs have a larger $\varepsilon_{TIR}$ than isotropic Lumogen Orange LSCs. The measured $\varepsilon_{TIR}$ for each device is shown below compared to the predicted light trapping efficiency calculated using (4.5) and (4.6).

<table>
<thead>
<tr>
<th>LSC</th>
<th>Measured $\varepsilon_{\text{trap}}$</th>
<th>Predicted $\varepsilon_{\text{trap}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LO+PMMA (isotropic)</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>D8+PMMA (isotropic)</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>LO+RM (isotropic)</td>
<td>0.79</td>
<td>0.78</td>
</tr>
<tr>
<td>D8+RM (oriented)</td>
<td>0.92</td>
<td>0.94</td>
</tr>
</tbody>
</table>

**Table 4.2** Measured and Predicted values for $\varepsilon_{TIR}$ and $\varepsilon_{\text{trap}}$ for each

For PMMA LSCs, the measured and predicted values of $\varepsilon_{TIR}$ and $\varepsilon_{\text{trap}}$ are 0.75. Since the measured and predicted values agree, this supports the approximation that $\varepsilon_{TIR} \sim \varepsilon_{\text{trap}}$. Lumogen Orange reactive mesogen LSCs are also isotropic but has a measured $\varepsilon_{\text{trap}}$ of 0.79. This is higher than the PMMA LSCs because reactive mesogen has a higher refractive index. This result is also reflected in the higher predicted $\varepsilon_{\text{trap}}$ (0.78) in Lumogen Orange reactive mesogen LSCs. The predicted trapping efficiency of homeotropically oriented D8 reactive mesogen LSCs, $\varepsilon_{TIR}$ is 0.92 compared to a
predicted $\varepsilon_{\text{trap}}$ of 0.94 (The predicted $\varepsilon_{\text{trap}}$ was calculated assuming an OP =1 whereas the measured OP=0.66).

While this model is relatively simple, it predicts $\varepsilon_{\text{trap}}$ for D8 and Lumogen Orange LSCs within 2% of the theoretically calculated values. Furthermore, these results indicate that oriented D8 LSCs have approximately 12% - 17% higher trapping efficiencies than other D8 and Lumogen Orange isotropic LSCs. Since $\varepsilon_{\text{trap}} \sim \varepsilon_{\text{TIR}}$, these results show that escape cone losses can be significantly reduced through the use of homeotropically oriented fluorophores.

4.3 Summary

Measuring the peak absorbance of reactive mesogen LSCs is crucial because proper interpretation of LSC performance relies on accurately measured optical densities. Complex background correcting procedures were developed to obtain an accurate value. The peak absorption, and the emission intensity as a function of excitation distance were used to calculate the OQE for homeotropic and isotropic LSCs. D8 homeotropic LSCs have $\sim$100% higher OQE than isotropic LSCs within the excitation distances tested, indicating that homeotropic LSCs have larger light trapping efficiencies. Light trapping efficiencies of isotropic and homeotropic LSCs were estimated using a model derived from Beer’s Law. The OQE data were fit to the model and the light trapping efficiencies were determined. These results indicate that oriented D8 LSCs have approximately 12% - 17% higher trapping efficiencies than isotropic LSCs.
References


Concluding Remarks

The goal of this thesis was to show theoretically and experimentally that light trapping efficiencies in LSCs could be improved through fluorophore alignment. Theoretical models quantifying escape cone losses in LSCs were developed by computing the probability a photon, with a given polarization, will be emitted within the escape cone, given that it is absorbed by a dye with a specific absorption moment $\tilde{\mu}_a$. Based on this model, a photon absorbed by a dye with a P2 order parameter of 0.8 has a 16% chance of escape for the first absorption/emission event compared to 25.9% for an isotropic system. This indicates that light trapping efficiency can be improved through fluorophore orientation. To test this model, escape cone losses were measured for an isotropic PMMA sample doped with Lumogen Red dye. The model accurately predicted escape cone losses within the 95% confidence level.

The light trapping efficiency in LSCs was measured experimentally by fabricating homeotropically aligned D8 reactive mesogen LSCs, and comparing their performance to otherwise identical isotropic LSCs using both nematic liquid crystal and reactive mesogen alignment matrices. LSC performance was quantified by measuring emission intensity as a function of excitation distance from the integration sphere. It was found that D8 homeotropic LSCs have $\sim$100% higher OQE and 12% - 17% higher light trapping efficiencies than their isotropic counterparts. These findings represent a significant improvement in trapping efficiency for homeotropically aligned LSCs, demonstrating that LSC performance can be improved through fluorophore orientation.

The work described in this thesis represents a step toward improved efficiency in
LSCs. Fluorophore orientation, along with other developments such as increased Stoke’s shift, have the potential to improve light trapping efficiencies, possibly enough for LSCs could be competitive with fossil fuels. The implementation of alternative energy technologies, like LSCs, could help usher the world into an era where the majority of power is produced from non-fossil fuel based energy sources.