Oriented fluorophore luminescent solar concentrators

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MASTER’S THESIS

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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

Christopher John Westcott
Abstract

Though the sun’s energy is the world’s most prominent renewable energy resource, technologies such as photovoltaics (PVs) have yet to become a significant factor in the energy market due in part to the sheer cost of unit deployment. Luminescent Solar Concentrators (LSCs) have been investigated since the late 1960s as a means of reducing the cost of PV arrays by replacing large areas of expensive PVs with cheaper materials such as glass or plastic. LSCs function by using fluorescent dyes embedded in a host matrix that absorb the sun’s rays and redirects the light through total internal reflection to small strips of PVs where it is converted into electrical current. This thesis describes a method by which LSC efficiencies can be improved through the use of modern materials and oriented fluorophores; allowing the direction in which the light is emitted by the dyes to controlled, reducing the primary mechanisms for light loss prevalent in other LSC designs. Projections of this technology suggest that further development of oriented fluorophores LSCs holds the potential of drastically reducing the world’s dependence on carbon based energy.
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Charles Wandler (Instrumentation)

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<td>TkWh</td>
<td>Tera-kilowatt hours</td>
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</tr>
<tr>
<td>TW</td>
<td>Terawatt</td>
<td>3</td>
</tr>
<tr>
<td>GW</td>
<td>Gigawatt</td>
<td>4</td>
</tr>
<tr>
<td>PW</td>
<td>Petawatt</td>
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<tr>
<td>PV</td>
<td>Photovoltaic</td>
<td>5</td>
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<tr>
<td>c-Si</td>
<td>Monocrystalline Silicon</td>
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<tr>
<td>mc-Si</td>
<td>Multicrystalline Silicon</td>
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<td>CdTe</td>
<td>Cadmium Telluride</td>
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</tr>
<tr>
<td>$/W_p$</td>
<td>Dollar per Watt peak</td>
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<td>TCPV</td>
<td>Traditional Concentrated Photovoltaic</td>
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<td>LSC</td>
<td>Luminescent Solar Concentrator</td>
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<td>TIR</td>
<td>Total Internal Reflection</td>
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<td>EQE</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<td>QD</td>
<td>Quantum Dots</td>
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<td>OF</td>
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<tr>
<td>OQE</td>
<td>Optical Quantum Efficiency</td>
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<tr>
<td>LC</td>
<td>Liquid Crystal</td>
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<tr>
<td>5CB</td>
<td>4-Cyano-4'-pentylbiphenyl</td>
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</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
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</tr>
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<td>rpm</td>
<td>revolutions per minute</td>
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<td>Symbol</td>
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<tr>
<td>nm</td>
<td>nanometer</td>
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<td>μm</td>
<td>micrometer</td>
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<td>AC</td>
<td>Alternating Current</td>
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<tr>
<td>V</td>
<td>Volt</td>
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</tr>
<tr>
<td>kHZ</td>
<td>Kilohertz</td>
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<tr>
<td>DMOAP</td>
<td>[3-(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride</td>
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<td>RM</td>
<td>Reactive Mesogen</td>
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<tr>
<td>w/w%</td>
<td>Weight Percent</td>
<td>53</td>
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<tr>
<td>mm</td>
<td>millimeter</td>
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<tr>
<td>MMA</td>
<td>methyl methacrylate</td>
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<tr>
<td>8CB</td>
<td>4′-Octyl-4-biphenyl-carbonitrile</td>
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<tr>
<td>Bis-Sebacate</td>
<td>Bis(2-ethylhexyl) sebacate</td>
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<tr>
<td>KG</td>
<td>Kilogauss</td>
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<tr>
<td>ppm</td>
<td>Parts per million</td>
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<tr>
<td>PI</td>
<td>Photo-initiator</td>
<td>91</td>
</tr>
<tr>
<td>ppt</td>
<td>Parts per Thousand</td>
<td>94</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal Quantum Efficiency</td>
<td>103</td>
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<tr>
<td>2D</td>
<td>2-Dimentional</td>
<td>104</td>
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Chapter 1: Introduction

1.1 Overview

This chapter presents the case for pursuing solar based energy generation. It first describes the imminent need for renewable energy to fill the gap in the future energy market and then describes why solar energy is the best candidate to meet this need. The chapter finishes by describing why solar power has yet to play such a prominent role.

1.1.1 World Energy Use

World energy consumption is projected to nearly double over the next 25 years, from 18.8 Tera-kilowatt hours (TkWh) in 2007 to 35.2 TkWh in 2035 (Fig. 1.1). Much of this increase is occurring in developing countries such as South and Central America, the Asia Pacific, Africa and the Middle East where improving living standards, highly correlated to per capita energy consumption, are increasing.¹

![Figure 1.1: Growth in world electric power generation and total energy consumption, 1990-2035](image)
Non-renewable sources of energy such as petroleum, natural gas, and coal accounted for 67.5% of all power produced in 2007, while nuclear made up an additional 13.8% of world power produced.\textsuperscript{1} It is thus evident that the world is ill prepared to meet the ever growing demand for energy in the near future without continuing its heavy reliance on these non-renewable sources. Fossil fuels by their nature are finite resources and while it is expected that coal, gas, and oil reserves will last for some time at current production levels,\textsuperscript{2} studies suggest that peak fossil fuel production will soon pass, if it has not done so already.\textsuperscript{3} This may leave the world in the precarious position of being unable to meet the energy demands of the future. The historical affordability as well as the high energy density of fossil fuels has helped prevent the development of other energy generation schemes.\textsuperscript{4} Yet the expected decline in the availability of these resources, in the face of their increasing demand, has made evident the need for energy sources that not only help fill the gap in power production, but have the potential to eventually displace non-renewable sources altogether.

\section*{1.2 The Potential of Renewable Energy}

In 2007 renewable energy sources accounted for 18% of all power produced worldwide, with the primary sources being hydroelectric (15.6%), wind (0.8%), geothermal (0.3%), solar (0.03%), and a few others (1.22%).\textsuperscript{1} Though renewable energy sources make up only a fraction of the world’s energy production, they may have vast untapped potential.
1.2.1 Hydroelectric Energy

Harnessing the kinetic energy of falling or moving water to turn an electric turbine, hydroelectric energy is an extremely effective renewable resource. The energy generated by dams can be adjusted to meet variable demand and is very reliable. However hydroelectric energy could never provide all that the world requires. Sites for hydropower plants are limited and most of those that could provide significant power generation have already been developed. The environmental impacts of hydroelectric can also be severe, resulting in land being submerged, ecosystems disrupted, and inhabitants displaced.

1.2.2 Wind Power

Using the energy of the wind to turn a turbine allows for a simple method for generating electricity. When placed on high resource sites, wind farms can generate electricity with relatively small impacts on the surrounding environment. It has been estimated that the amount of energy available from wind above an altitude of 100 m is around 1700 TW$^{5}$. While it would be impossible to harvest all this energy, obtaining a fraction of it would provide for all our current energy needs. However, variability and unpredictability of wind intensity have proven to be a large detriment to this form of energy generation.

1.2.3 Biomass

The production of biofuels and biomass as a means of generating electricity has been increasing in recent years. Biofuels such as ethanol, biodiesel and methane from processed biological products can be combusted to generate electricity. The burning of
biofuels such as wood chips or other feedstocks to produce steam to run a steam turbine is also a common method for generating electricity. This method has the benefit of being carbon neutral, since the biomass collects carbon dioxide as it grows and then releases it when burned. Unfortunately, generating biomass required to fuel the world’s energy needs would require a large amount of the earth’s surface area, resulting in reduced biodiversity, a negative effect on wildlife habitats, and potential impacts on other crop production.\(^6\)

### 1.2.4 Geothermal Energy

Heat, generally in the form of hot water, from below the earth’s surface has long been harvested as a means of heating buildings and running heat engines for energy generation. A conservative estimation of the amount of harvestable geothermal energy ranges from 70 to 140 GW.\(^5\) This amount lies well below the current energy demands of the world and has many issues associated with production. As a result, geothermal energy can play only a limited role in the world market.

### 1.2.5 Solar Energy

The sun continually bathes the earth with energy in the form of sunlight. It has been calculated that the amount of energy that reaches the surface of the planet in a year is 89 PW.\(^7\) Capturing a small fraction of this energy flux could easily provide for the demands of an ever growing and developing society.

Even with this potential there are several reasons that solar energy has not taken on a key role in the power market. The intermittent nature of solar power is problematic; as
these systems only function during daylight hours, evenings and darker winter months can prove to be a significant detriment to energy generation. Additionally, most solar concentrating systems (section 1.3.2) rely on direct sunlight, creating a dependency on maintenance prone tracking systems and clear, bright skies for functionality. While the location chosen for solar power plants can help reduce some of these limitations, they cannot be negated and must be accounted for when building electrical grids.

As fossil fuels and other cheap power generation methods are readily available, the primary hindrance for solar energy is cost. The price of power generated by coal is between 7-10¢ per kWh, wind between 4-10¢ per kWh, and natural gas between 5-7¢ per kWh. Over the lifespan of a standard photovoltaic (PV) system (section 1.3.1) in North America, the cost of generating power from a moderate size utility plant is currently above 20¢ per kWh; at least twice the cost of coal.\(^8\)\(^9\)

### 1.3 Solar Power Generation

Though solar electricity currently comprises a tiny fraction of world energy production, the amount of energy the sun imparts on the earth is truly astronomical: in an hour the sun provides the surface of the earth with as much energy as mankind uses in an entire year. No other energy source, finite or renewable, even comes close. This section reviews the most important solar energy technologies.
1.3.1 Photovoltaics

By harnessing the photovoltaic effect, first observed in 1839 by Alexandre-Edmond Becquerel, a semiconductor can be utilized to generate electricity. If an incident photon possesses enough energy it can excite an electron-hole pair within the P-N junction solar cell. An electric potential will separate the pair, producing an electric current. A typical P-N junction is shown in Figure 1.2. The development over the past thirty-five years of several PV technologies, expressed in terms of the percent of solar energy converted into electrical energy, is plotted in Figure 1.3.\(^\text{10}\)

![Figure 1.2: Basic solar cell architecture. An incident photon creates an electron-hole pair that is separated by the junction’s electric potential, generating a current.](image)
Though most semiconductor materials may be used for PV applications there are three dominate types of solar cells on the market today.

### Silicon Solar Cells

The most commonly used solar cells are those made from crystalline silicon (Fig 1.4), commanding 85% of the current PV market. Cells made from silicon come in two main forms:

- **Monocrystalline silicon (c-Si)** is a single crystal wafer cut from a silicon ingot, the highest efficiency yet achieved is 27.6% of solar energy into electrical energy. Commercially available c-Si converts solar energy at around 18% efficiency.
• Poly or multicrystalline silicon (poly-Si or mc-Si) are cast by carefully cooling and solidifying molten silicon in a square mold. This method is cheaper than that used for the production of c-Si but results in lower efficiency: the maximum conversion efficiency is reported at 20.3% with commercial cells around 14%.8,12

![Silicon Solar Cells. Monocrystalline (left) Polycrystalline (right)](image)

**Figure 1.4:** Silicon Solar Cells. Monocrystalline (left) Polycrystalline (right)

**Cadmium Telluride Thin Film Solar Cells**

Thin film photovoltaic cells are produced by depositing thin layers of a semiconductor material, a few nanometers to several micrometers thick, on a substrate. Recent developments in thin-film deposition methods have resulted in lower manufacturing prices and increased cell efficiencies, increasing the popularity of thin film modules in the PV industry. A prime example of this is the disruptive thin-film technology developed by U.S. based company First Solar, specializing in thin-film Cadmium Telluride (CdTe) solar cells. Possessing efficiencies around 12% and low costs, CdTe cells are likely to play a significant role in PV power generation for years to come.
Multi-Junction Solar Cells

Multi-junction solar cells contain two or more p-n junctions staked atop one another allowing the cell to capture more of the spectrum than a single p-n junction (Fig. 1.5). These cells, being far more complicated than single-junction cells, are much more costly but have achieved efficiencies up to 42.4% as of 2010.

The cost of multi-junction solar cells has largely limited their use to space based applications. However concentration of sunlight using low-cost optics and tracking systems can be used to make these cells more cost effective for terrestrial applications.
1.3.2 Traditional Solar Concentrators

Solar concentrators first appeared in the mid 1970’s and generally possess a primary concentrator, tracking system and possibly a second stage concentrator. Using primarily refraction and reflection, a wide variety of concentrator schemes have been devised.

Solar Thermal Power

Solar thermal power plants use mirrors or lenses to focus sunlight onto a single point, heating a working fluid to high temperature. A number of processes, utilizing steam, molten salt or heat engines, can be utilized to produce electricity. This method of power generation can have the added benefit of being able to store energy collected during the day, for use at night.\(^\text{14}\) There are three primary systems that use solar thermal power.\(^\text{15}\)

Parabolic Troughs

The parabolic trough, shown in Figure 1.6, consists of a long parabolic shaped reflector that focuses sunlight onto a receiver pipe, carrying a working fluid at the focal point of the parabola. Tracking the sun over the course of the day, the parabolic trough can focus sunlight up to 100x, with energy conversion between 24-26\% on a sunny day.\(^\text{16}\) The working fluid circulates through the receiver pipe, passing through a central heat exchanger to generate electricity by turning water into steam to turn a turbine.
A solar dish (Fig. 1.7) is comprised of a parabolic mirror that tracks the sun and focuses its light onto a central point, achieving concentration factors of 2000x or more. The dish generates electricity similarly to a trough, converting into mechanical power by heating a compressed working fluid, and expanding it through a piston or turbine that turns a generator.

**Figure 1.6:** (a) Light paths on Parabolic Troughs. Light reflected off the concentrator surface is focused on a receiver filled with a working fluid. This fluid is circulated thorough heat exchangers to generate electricity. (b) Luz System Collectors at Kramer Junction California

**Solar (Stirling) Dishes**

Figure 1.7: (a) Light paths on Solar Dishes. Light from the reflector is focused on a single point where a working fluid or gas is used to run a turbine to generate electricity. (b) SCE-Stirling project in Albuquerque, New Mexico
Solar Power Tower

The solar power tower (Fig 1.8) is a large area concentrator that generates electricity by reflecting sunlight off hundreds to thousands of sun-tracking mirrors, called heliostats, concentrating solar light by over 1,500x onto a central tower-mounted heat exchanger that utilizes either steam or molten salt for power generation or storage energy. Reflecting light using heliostats minimizes thermal energy losses by reducing the distance that the working material must travel before performing work.

Figure 1.8: (a) Light paths on Solar Power Towers. Light reflected off of sun-tracking heliostats concentrate light on a fixed tower where a working fluid like molten salt is used to generate or store energy. (b) Abengoa solar array near Seville, Spain

Photovoltaic Concentrators

As the widespread use of highly efficient multi-junction PVs is cost prohibitive, the use of light concentrating schemes can permit this PV material to be used economically in terrestrial applications. Though many traditional concentrator schemes exist for PVs, most are variations of two primary designs:
Fresnel Lens

While tracking the sun, a Fresnel lens (Fig. 1.9) concentrates light in the same manner that a traditional convex optical lens would, but requires much less material, resulting in a thinner, larger and flatter surface that may be bent to accommodate different geometries. Concentration factors of 250x have been reported by Alpha Solarco.\(^\text{18}\)

![Figure 1.9:](image)

**Figure 1.9:** (a) Fresnel Lens architecture (top) and rational convex lens. (b) Simulation of light concentration by a Fresnel lens onto a small area PV.

Parabolic Dish

Functioning in a manner identical to solar (Stirling) dishes (1.4.1), a parabolic mirror is used to concentrate light onto a small area, high efficiency PV. Concentration factors in excess of 2000x can be achieved.
1.4 Economics of Solar Power

The U.S. Department of Energy (DOE) has stated:\textsuperscript{19}:

\textit{The U.S. Department of Energy (DOE) estimates that a $1/watt installed photovoltaic solar energy system – equivalent to 5-6 cents/kWh – would make solar without additional subsidies competitive with the wholesale rate of electricity, nearly everywhere in the US. A solar energy system priced at $1/Watt would unlock the potential of the sun to provide low-cost, clean limitless electricity to the U.S. and the rest of the world, at the same cost of coal-based generation. At this price, solar generated electricity combined with affordable storage technologies could then meet all conventional electricity energy needs, providing solar energy potentially 24 hours a day. Meeting this challenge would result in a revolution in the world’s generation and use of energy.}

\textit{Preliminary DOE analysis on required component costs to reach a $1/watt installed PV system implies the following breakdown: 50 cents/watt for the module, 40 cents/watt for the balance-of-system and installation, and 10 cents/watt for the power electronics.}

The value of ‘dollar per Watt’ ($/W_p), is the cost of generating power given a standard AM1.5G light incidence. As stated above, the cost of $1/W for a solar power system has long been held as the benchmark by which solar energy will be competitive to conventional energy.

1.4.1 Silicon PVs

Currently, residential scale PV modules, generally using silicon PVs, produce power at a rate of around $4 per Watt-peak, commercial scale systems can be as low as $2.5/W_p.\textsuperscript{12, 19} The cost of the rest of the system (installation, inverters etc.) can account for nearly half the total system cost.\textsuperscript{19} Thus the total cost of solar power generation is priced at $5-7/W, or 30-40¢ per kWh, a price far higher than other prevalent power sources.\textsuperscript{11}
DOE projections suggest that for c-Si modules to cost less than $0.50/W, wafers would need to achieve an efficiency of around 23% (maximum theoretical efficiency is 29%) and a thickness of 80 μm (wafers are 180 μm thick today). Unfortunately, this degree of improvement in c-Si cells is unlikely to transpire, a more practical lower limit for c-Si being around $0.80/W.\textsuperscript{11} Taking into account other system costs, this makes sheets of c-Si PVs an unlikely source of competitive energy without significant government subsidies.

1.4.2 Cadmium Telluride Thin Film PVs

In recent years thin film cadmium telluride (CdTe) cells manufactured by First Solar have changed the landscape of solar energy generation. Currently these modules can generate energy at $0.76/W_p$, with projections showing further reductions in cost, down to $0.55/W_p$ by 2014. While significantly cheaper than any other PVs, these thin film modules have a relatively low efficiency, 11.2%.\textsuperscript{20} Though laboratory efficiencies of 17% have been achieved, projections of large scale development suggest achieving values significantly greater than 12% would be exceedingly difficult.\textsuperscript{19} In the long term, cost analysis studies have shown that the high extraction cost and the relative rarity of CdTe will significantly limit its potential in the energy market; beyond 0.3 TW per year, material scarcity likely becomes a limiting factor in product deployment.\textsuperscript{9}

1.4.3 Thermal Concentrators

To date thermal concentrators have yet to achieve power generation costs close to conventional methods. Even when factoring in heavy tax credits (up to 30%), values less than 20¢ per kWh are rarely observed.\textsuperscript{16} The new parabolic troughs in Spain, Andasol 1-3,
will generate power at nearly 40¢ per kWh after feed-in tariffs.\textsuperscript{14} While solar thermal methods provide the opportunity for energy storage, allowing power conversion during the evening, the systems are hardly cost effective when compared to non-renewable sources. However, the DOE projects that additional materials research could lower the cost of power generation by thermal concentrators to below 7¢ per kWh by 2030, after a 10% tax credit.\textsuperscript{16}

### 1.4.4 Traditional PV Concentrators

Concentrating light onto multi-junction PVs has generated significant conversion efficiencies, up to 42.5%. A mature commercially available multi-junction PV concentrator would have module efficiency around 38% resulting in a system cost between $1 and $3/W, translating into 6-18¢ per kWh.\textsuperscript{8,21} While the lower limits of this projection places traditional concentrated photovoltaic (TCPV) power on comparable footing to that of conventional power sources, several economic forces have prevented its entrance to the market.

One of these is the persistent low prices of conventional power, making the introduction of technology for a new, high capital cost, system difficult. The paralleled success of flat-plate PVs has also off set the use of TCPV systems, as flat-plate PVs have found markets in remote locations where low wattage, high reliability and near zero maintenance are important attributes. This leaves TCPVs in a situation where few market opportunities exist that would allow it to mature into a cost effective power generation method.\textsuperscript{21}
1.5 Summary

With the increasing demand for and scarcity of non-renewable energy sources it is becoming evident that renewable energy must represent a greater proportion of the worldwide energy portfolio if future power demands are to be met. Though it currently plays a minor role in the energy market, the vast untapped energy from the sun could be used to generate most, if not all, of the world’s energy needs. While the historically high cost of PV production has hindered its acceptance in the marketplace, developments over the past several years show that the world is on the verge of competitive PV based solar power. Unfortunately CdTe thin films, perhaps the most promising current PV technology, are likely to be limited by material scarcity over the long term. TCPVs possess the potential of generating power competitively, but high initial capital and high maintenance costs have all but negated its acceptance into the market. If a PV based concentrating technology could be developed with a smaller initial capital costs, higher concentration factors, and lower maintenance costs, solar energy could make significant gains in the energy marketplace.
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Chapter 2: Luminescent Solar Concentrators

2.1 Overview

This chapter describes the fundamental mechanisms and material requirements of luminescent solar concentrators (LSCs). The thermodynamic limits, reported performances, and design advantages of LSCs are given. This is followed by a detailed description of the material requirements of LSC as well as an outline of the primary efficiency loss mechanisms that have, to date, hindered LSCs acceptance into the energy market.

2.1.1 LSC Fundamentals

First proposed in the latter half of the 1970s, the luminescent solar concentrator, also referred to as a luminescent greenhouse collector, was envisioned as a means of reducing the cost of solar energy generation. An LSC typically consists of a sheet of glass or plastic coated or impregnated with photoluminescent (PL) dyes that absorb solar flux. The dyes then emit red-shifted light, a portion of which becomes trapped within the host matrix through total internal reflection (TIR). This trapped light can then travel the length of the sheet, which acts as a waveguide, until it reaches an edge where a thin strip of photovoltaic cells (PV) converts light into electrical energy (Fig. 2.1). \(^1,2,3,4,5\)
By replacing a large area of PV cells with inexpensive materials such as glass or plastic, LSCs offer the potential for a major reduction in the cost of solar energy generation. Using only small areas of PVs along the edge of the concentrator, significant concentration factors can be realized in proportion to the geometric gain $G$, defined as the ratio of the area of the front surface face $A_{Face}$ to the area of the edge $A_{Edge}$; the greater the geometric gain the greater the concentration factor of the LSC:

$$G = \frac{A_{Face}}{A_{Edge}}$$  \hspace{1cm} (eq. 2.1)

Since the ultimate goal of LSCs is to provide a lower cost source of energy than PVs alone, it is useful to define a measure of comparison between the two. Here we use the unit ‘Dollar per Peak Watt’ ($$/W_p$). Up to a few years ago the most economic PVs were
crystalline silicon modules with a conversion efficiency around 16% producing electricity at around $4/W_p$. Within the past year developments in thin film cadmium telluride cells have reduced the price of PV cells to $0.76/W_p$, though at the expense of conversion efficiency, which for CdTe cells is currently around 11.2%.\(^6\)

Though a significant reduction in the cost of solar energy has been achieved in recent years, there is still much room for improvement. The cost of electricity generated by LSCs has been projected to potentially be less than $1/W_p$, and thus competitive with even the cheapest PV systems.\(^8\) Since LSCs also are made primarily from abundant substances such as glass and plastic, and do not require large amounts of increasingly rare elements such as Tellurium and Cadmium, systems prices are less likely to fluctuate with increasing demand.

2.1.2 LSC Design Advantages

The fluorescence-based mechanism by which LSCs concentrate sunlight also gives rise to one of its primary advantages. By not relying on mirrors or lenses, LSCs are capable of concentrating diffuse light, a significant advantage over traditional solar concentration schemes and ideal for northern latitudes, such as areas in Europe and North America, where as much as 60% of all solar energy is scattered by cloud cover.\(^6\) Since direct sunlight is not needed tracking systems and heat sinks, both of which can be prone to malfunction, normally required for traditional concentrator systems are also no longer necessary, adding additional reliability and reducing system cost.
There has also been much interest in LSCs by architects and architectural firms. Since the structure of LSCs is generally flat and “colorful”, their as building sidings and possibly window tinters is attractive to groups trying to incorporate “green” technologies into building designs. The color of LSCs can even be tuned at the cost of system solar conversion efficiency.

2.1.3 LSC Performance: Historical and Theoretical

Despite being in development for well over thirty years, LSCs have thus far had little practical impact. This is due in part to the significant reduction in optical efficiency that occurs as the size of a concentrator increases. Consequently the highest concentration factors achieved so far are $\leq 10^x$. These values are well below the theoretical thermodynamic limits of $10^4x – 10^5x$ and several times smaller than what is needed to provide a significant impact of the cost of solar energy.

 Though it is difficult to compare one group’s results to another due to large variations in testing and reporting methods, the most effective manner is by comparing the overall efficiency of a system, known as the external quantum efficiency (EQE): defined as the fraction of energy delivered by incident light (usually the AM1.5G solar spectrum) converted into usable electrical energy:

$$EQE = \frac{E_{LSC}}{E_{\text{Incident Light}}} \quad \text{(eq. 2.2)}$$

To date, the highest EQE reported, by van Sloof et al. in 2008, was 7.1% using a PMMA concentrator, organic dyes, GaAs solar cells and a geometric gain of 2.5. With a small gain
and the use of expensive GaAs cells, this system is hardly capable of providing real savings in the solar energy market. The use of cheaper c-Si PVs has given yields of EQE = 2.7% as reported by Sark et al in 2008, using organic dyes and a geometric gain of 12.5. Baldo et al. in 2008 a new LSC design based on ultra-large Stokes shift dyes that they projected could achieve an EQE of up to 14.5% at $G = 3$. Though these projections are promising for the future development of LSC technology, to date there are no published reports of actual devices able to achieve them.

2.2 Luminescent Solar Concentrator Materials

Ultimately LSC design must be tailored to optimize performance if high concentration factors and high EQEs are to be obtained. This section reviews some of the most important issues concerning concentrator materials and device architecture.

2.2.1 Waveguide Materials

A waveguide material suitable for LSC applications must satisfy several criteria:

- High optical clarity
- Low cost
- High environmental durability/stability
- Easily moldable
Several materials have been proposed to act as the waveguide for LSCs including a host of glass substrates and polymers. While glass possesses high transparency and relatively large index of refraction it suffers from fabrication issues and is generally much more expensive than other potential matrix materials. For these reasons most LSC research in the last ten years has focused on the use of polymers as the waveguide material. Polycarbonate mixtures, poly(methyl methacrylate) (PMMA), Polyvinyl alcohol and several other polymers have been investigated as possible waveguide matrices.\textsuperscript{8,18} Among these, PMMA has gained prominence due its ability to meet most criteria mentioned above. With a refractive index around 1.49, high optical clarity, superior weathering resistance and high solubility of organic dyes, it is a good candidate for many LSC designs.

2.2.2 Photoluminescent Dyes

The characteristics of PL dyes are also of vital importance. Dyes in LSCs must satisfy a number of conditions to be appropriate for use:

- Strong solar absorption
- High quantum yield
- Highly photostable
- Large Stokes shift
- Low cost

There are many classes of dyes that could be used in LSCs; unfortunately there is no single compound available that can meet all the criteria noted above, so combinations of dyes must be used to obtain the desired results.
**Inorganic Dopants**

Inorganic dopants have several features that make them attractive, including high stability, broadband absorption across the visible spectrum and large stokes shifts.\(^{19,20,21}\) Nd\(^{3+}\) was in fact the first dye used in an LSC.\(^4\) However, inorganic dyes generally possess low quantum yields and weak absorption.\(^{22,23,24}\) As a result, high concentrations of the dye are needed to absorb the incident solar flux, leading to aggregation and self-quenching, though steps have been taken to help reduce these issues.\(^{20,23}\)

**Quantum Dots/Rods**

Quantum dots (QDs) and quantum rods have also been investigated as PL dopants for LSCs.\(^{25,26,27}\) Figure 2.2 shows QD’s tunable absorption/emission bands as a function of size, a convenient feature when trying to engineer dye combinations capable of absorbing all solar flux.\(^{28}\) Additionally, semiconductor nano-particles have exceptional photostability.\(^{29}\) However, their relatively low quantum yields and small stokes shifts have prevented QDs from achieving high overall efficiencies in LSC applications.\(^{30}\)
Organic dyes have undergone significant development in recent years resulting in several families of dyes that possess many qualities desirable for LSCs. While organic dyes suffer from narrow absorption bands, low photostability and low stokes shifts, they also exhibit quantum yields approaching unity and absorb light very strongly. One series of dyes developed by BASF, the Lumogen series, has demonstrated these particular strengths as well as high photostability (upwards of 10 years under ambient exposure) and is able to absorb solar flux up to 600 nm. The chemical structure of Lumogen F Red 305 and Lumogen F Orange 240 are shown in Figure 2.3. Organic dyes that absorb beyond 600 nm are

**Figure 2.2:** Quantum Dot emission dependencies on particle size. Source: AIST Today (2006) 6, 26-27
available but their quantum yields begin to decrease at longer wavelengths, significantly reducing overall performance.\textsuperscript{33}

![Chemical structure](image)

**Figure 2.3:** Chemical structure of BASF Lumogen F Red 305 (Left) and Orange 240 (right)

Fluorescent dyes exhibiting large stokes shifts, such as dicyanomethylene (DCM)\textsuperscript{34}, and organic/inorganic phosphorescent dyes like Pt-tetraphenyltetrabenzoporphyrin have been investigated for their low self-absorption characteristics, though some of these compounds continue to suffer from low quantum yields.\textsuperscript{7}

### 2.3 Optical Mechanisms within Luminescent Solar Concentrators

#### 2.3.1 Overview

While the concept of an LSC is fairly easy to understand, the mechanisms underlying its function are rather complex. We can trace the light paths within an LSC with the aid of a flow chart (Fig 2.2).
Solar flux first interacts with the air/waveguide interface resulting in some reflection of light. Of the light that enters the waveguide some of the light is lost because its frequency does not correspond with the absorption band of the incorporated dye or dopant and is lost. That light that is absorbed may then be emitted by the dye in a manner corresponding with an efficiency, $\Phi$, corresponding to the quantum efficiency of the dye (section 2.4.7). The emitted photon then has a probability, $P$, of being emitted in a direction

**Figure 2.4:** Photon flow diagram. Light that enters a waveguide and is absorbed by a dye may undergo photoluminescence as described by its quantum yield, $\Phi$, and either be lost through the matrixes escape cone, probability $P$, or retained by TIR, a probability of 1-$P$. Emitted light has a probability of being reabsorbed, $r$ or $r'$, and will experience the aforementioned mechanisms again. Light traveling within the matrix may be through imperfections in the matrix or lost due to reflection off the interface between the waveguide and the attached PVs. The photons that are successfully coupled into the PV may then be converted into an electrical current. Dashed lines represent different materials. Adapted from Batchelder et al.\textsuperscript{5}
within the escape cone of the waveguide (section 2.3.2), as well as a probability, \( r' \), of being reabsorbed by another dye molecule before exiting the waveguide (section 2.4.5 and 2.4.6). Should the photon be emitted outside of the escape cone it also has a probability, \( r \), of being reabsorbed by a dye molecule before reaching the PV. Photons that undergo a reabsorption event (\( r \) or \( r' \)) will then undergo all the aforementioned mechanisms again.

Of the light that is trapped within the waveguide some will be lost to matrix absorptions, scattering or surface roughness (section 2.3.2). Some portion of the fraction of photons \( Q \) that reach the LSC/PV interface may also be reflected. The remaining photons, \( Q_c \), are converted to an electrical current with an efficiency determined by the PV’s responsivity.

### 2.3.2 Light, Matrix and Interface Interactions

**Refraction**

The interaction of light at the interface between materials with differing refractive indices leads to reflection and refraction as described by Snell’s law:

\[
\frac{\sin \theta_1}{\sin \theta_2} = \frac{v_1}{v_2} = \frac{n_2}{n_1} \tag{Eq. 2.3}
\]

where light traveling from a medium with refractive index \( n_1 \) encounters the surface of a material with refractive index \( n_2 \) at angle \( \theta_1 \) from normal incidence. This light then enters the second material and travels within it at angle \( \theta_2 \) in a process known as refraction.
Reflection, Total Internal Reflection, and the Escape Cone

Light traveling between two media with different refractive indices has an opportunity to undergo reflection at the interface. Even at normal incidence some reflection occurs. Materials such as PMMA reflect about 4% of normal incident light. As the angle of incidence becomes larger the probability of light reflecting off the interface grows. At an angle known as the critical angle, $\theta_c$, 100% of light can be reflected off the interface as follows from Snell’s law:

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$  \hspace{1cm} (Eq. 2.4)

Light traveling within the critical cone can escape and undergo refraction. However, light traveling at an angle greater than the critical angle will be reflected off the surface.

Within a traditional LSC a dye molecule emits light isotropically. Thus the fraction, $P$, of photons emitted within the escape cone is equal to the ratio of the area swept out by the solid angle of the escape cone to that of a whole sphere:

$$\Omega_{cone} = 2\pi(1 - \cos \theta_c)$$  \hspace{1cm} (Eq. 2.5)

$$P = \frac{\Omega_{cone}}{4\pi} = \frac{1}{2}(1 - \cos \theta_c)$$  \hspace{1cm} (Eq. 2.6)

Since both the top and the bottom of the LSC are possible directions for escaping light, $P$ is multiplied by two. Then substituting eq. 2.4 into eq. 2.6 and simplifying, we determine the fraction of escaping photons to be:
For a material such as PMMA \( (n_1=1.5) \) this corresponds to a value of \( \sim 25\% \) of photons being lost through the top or bottom escape cones, with the remaining, \((1-P)\), being trapped through total internal reflection.

Matrix Losses

While many matrices used for LSC applications exhibit high optical transparencies they can still be a source of inefficiencies. Losses within the matrix can arise from incorporated impurities and scattering off imperfect faces. While such losses are generally assumed to be negligible for small area LSCs, their cumulative effect must be taken into account for LSCs of larger areas.

2.4 Photonic Processes of Luminescent Solar Concentrators

2.4.1 Light Absorption

Light absorption by a dilute collection of molecules is governed by the Beer-Lambert law:\(^{35}\)

\[
A(\lambda) = -\log\left(\frac{I(\lambda)}{I_o(\lambda)}\right) = \varepsilon(\lambda)IC
\]

\( (\text{Eq. 2.8}) \)

where \( I_o(\lambda) \) is the wavelength dependent intensity of incident light and \( I(\lambda) \) is the wavelength dependent intensity of the light transmitted through a sample. The right hand
side of equation 2.8 is Beer’s Law where \( \varepsilon(\lambda) \) is the wavelength dependent molar absorptivity (L mol\(^{-1}\) cm\(^{-1}\)), \( l \) is the path length (cm), \( C \) is the concentration of the sample (mol L\(^{-1}\)), and \( A \) is the absorbance of the sample.

2.4.2 Non-Radiative Relaxation

Once a molecule has absorbed a photon, an event taking about \( 10^{-15} \) s, there are several paths by which it may return to its ground state (assumed to be its lowest vibrational and electronic energy levels). Excess vibrational energy can be shed most rapidly through thermal equilibration, taking about \( 10^{-14} \) to \( 10^{-12} \) s. This is accomplished via the release of infrared photons or through collisions with neighboring molecules.

Internal conversion, a transition which typically takes about \( 10^{-12} \) s, is also possible depending on the properties of the ground and excited electronic states. Should the higher vibrational levels of the ground electronic state overlap with the lower vibrational levels of the excited electronic state these two states are said to be in transient thermal equilibrium, allowing relatively rapid conversion from the excited state to the ground state through the overlapping vibrational modes. If the vibrational states do not overlap but are instead separated by a small gap, a tunneling mechanism can allow the transition to occur through classically forbidden modes.\(^{35}\)

2.4.3 Fluorescence

If the energy gap between the higher vibrational levels of the ground electronic state is significantly different from the lowest vibrational levels of the excited electronic
state, the emission of a large amount of energy may be necessary in order for the molecule to relax. This can be accomplished through the emission of a photon, a process known as fluorescence. Typical fluorescence lifetimes are on the order of $10^{-9}$ to $10^{-8}$ s.

Since the lifetime of fluorescence is so much longer than internal conversion, fluorescence essentially always occurs from the lowest vibrational level of the excited electronic state and terminates at a different vibrational level of the ground electronic state. As a result, the emission spectrum of a fluorescent molecule is typically not dependent on the wavelength that excites it. Since absorption nearly always occurs from the lowest vibrational level of the ground electronic state and terminates at various vibrational levels of the excited electronic state the two processes of absorption and fluorescence appear to be mirror images of each other. This symmetry arising from the similar shapes of the excited and ground electronic states and known as the Franck-Condon principle produces a mirror-like relationship between absorption and emission spectra.  

\textbf{2.4.4 Singlet-Triplet Intersystem Crossing and Phosphorescence}

As with other internal conversion mechanisms, a vibrational level in the excited singlet state can overlap with a vibrational level in the triplet state, allowing for conversion between the two. This requires a change in the angular spin momentum of the electron, singlet $\rightarrow$ triplet transitions are classically forbidden and hence give rise to states with very long lifetimes. While intersystem crossing is more common in transition-metal-containing dyes, it has also been observed in aromatic organic dyes.
Relaxation from a triplet state gives rise to phosphorescence. The mechanism for phosphorescence is similar to that of fluorescence, however the transition involves the lowest vibrational state of an excited triplet state relaxing to the ground electronic singlet state. Phosphorescence is usually a very slow, due to the long intersystem transition time ($10^{-8}$ s) and the even longer triplet to ground singlet decay time ($10^{-5}$ to $10^{-2}$ s). This and the previously discussed mechanisms are outlined in Figure 2.5.

**Figure 2.5:** Jablonski Energy Diagram depicts the electronic states and transitions of a photoluminescent molecule. A molecule is excited from the ground state to an excited state by absorption of a photon (green arrows). This may then relax (yellow arrow) to the lowest vibrational level of the excited state, followed by intersystem crossing (dark blue/teal arrow), quenching (purple arrow), non-radiative relaxation (light blue), or photoluminescence (red arrow). Source: Olympus Inc.
2.4.5 Stokes Shift

Most fluorescent dyes do not exhibit perfect mirror symmetry between their absorption and emission spectra, rather the lowest energy absorption band and highest energy fluorescent band are offset by a certain amount, known as the Stokes shift. The larger the Stoke’s shift, the smaller the chance that an emitted photon will be reabsorbed by another fluorophore in the LSC. For this reason, most research on LSCs over the last 30 years has focused on identifying and using dyes with the largest possible Stokes shift.

2.4.6 Reabsorption

Partial overlap between absorption and fluorescence bands gives rise to the phenomenon of self-absorption. This process, the probability of which is directly related to the size of the Stokes shift, can have a large impact on LSC performance.

As discussed in section 2.3.2, each time a photon is emitted by a dye in an isotropic LSC there is approximately a 25% chance it will be emitted within the escape cone and leave the waveguide. This process repeats with every reabsorption / re-emission event. The cumulative effect of this is illustrated in Figure 2.6. Assuming no other loss mechanisms, after just three absorption events a photon has around a 50% chance of leaving the LSC. After ten events there is slightly more than a 10% chance of reaching the edge. Reducing these so-called escape cone losses brought on by multiple reabsorption events has been the primary focus of recent research in LSCs.
2.4.7 Quantum Yield

Fluorescence competes with other relaxation mechanisms, not all excited molecules undergo fluorescence. The probability of fluorescence is described by the fluorescent quantum yield, $\phi$:

$$
\phi = \frac{k_e}{k_e + \sum k_d} = \frac{n_E}{n_A}
$$

(Eq. 2.9)

where $k_e$ is the probability of fluorescence, and $\sum k_d$ is the sum of all probabilities for all other relaxation mechanisms. The simplified form on the right reduces the other variables to the measurable values of photons emitted, $n_E$, over photons absorbed, $n_A$. 

**Figure 2.6:** The probability of a photon reaching a LSCs edge due to escape cone losses after $n$ re-absorption events assuming no other loss mechanisms
In Chapters 4 and 5 the quantum yield of fluorescent dopants was determined using the method of Isak and Eyring. Solutions of dopants and suitable standards were prepared in an appropriate solvent at $10^{-8}$ to $10^{-6}$ M concentrations; the quantum yield was calculated using:

$$\phi_f = \phi_{f,\text{ref}} \left( \frac{A_{\text{ref}}}{A} \right) \left( \frac{n}{n_{\text{ref}}} \right) \left( \frac{I}{I_{\text{ref}}} \right)$$

(Eq. 2.10)

where $\text{ref}$ denotes the fluorescence standard, $A$ is the absorbance at a chosen wavelength, $I$ is the integrated fluorescence intensity of the sample when excited at the chosen wavelength, and $n$ is the refractive index of the solvent.

### 2.4.8 Overall LSC Efficiency

Although the separate effects of these internal LSC processes can be difficult to measure individually, the overall system efficiency, $\eta_{\text{LSC}}$, is relatively easily measured, and can be expressed as:

$$\eta_{\text{LSC}} = \eta_{opt} \times \eta_{PV}$$

(Eq. 2.11)

where $\eta_{opt}$ is the optical efficiency of the LSC and $\eta_{PV}$ is the PV photon-electron conversion efficiency. $\eta_{opt}$ can be expanded in terms of individual loss mechanisms:

$$\eta_{LSC} = ((1-R)\eta_{abs}\eta_{QY}\eta_{Tr}\eta_{mat}(1-\eta_{Self})\eta_{TIR}) \times \eta_{PV}$$

(Eq. 2.12)
2.5 Summary

Though the basic concept of an LSC is simple, the underlying mechanisms affecting system efficiency are subtle and complex. Indeed, partly due to the difficulty in finding materials and architectures able to simultaneously satisfy all the aforementioned performance criteria (and partly due to a near complete cessation of funding for renewable energy research in the early 1980’s), by the end of the 1980’s research into LSC technologies had effectively ceased. Even following its recent revival due to the advent of modern materials such as improved host matrices and high quantum yield dyes, many hurdles remain to be overcome. Use of large Stokes shift dyes and high index of refraction glass has
improved LSC efficiencies in recent years, but to date no prototype has been developed that
demonstrates high conversion efficiency at large geometric gains using low cost materials. If
LSC technology is to make a significant contribution to future renewable energy generation,
new designs and new materials able to overcome these challenges will have to be found.
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Chapter 3: Oriented Fluorophores for LSC Applications

3.1 Overview

This chapter describes how homeotropic orientation of fluorophores can drastically improve LSC efficiencies. A brief overview of the transition dipole moments of fluorophores leads to a discussion of the how their orientation can significantly reduce escape cone losses in LSCs. Methods of aligning these fluorophores through the use of liquid crystals and reactive mesogens are explained. The chapter is concluded by introducing a method by which Legendre polynomials may be used to generate 2-dimensional distribution functions describing the orientation of the dyes transition dipole moment.

3.1.1 Transition Dipole Moments

A photon interacts with an organic molecule most strongly when its electric field vector is parallel to the absorption transition dipole moment of the molecule. Likewise a photon emitted by a molecule has its electric field vector parallel to the molecule’s emission transition dipole moment. The orientations of these transition moments are determined by the electronic structure of the molecule. While the relationship between transition moment orientation and molecular structure is complex, many planar fused ring polycyclic aromatic hydrocarbons such as naphthalene, anthracene, tetracene, pentacene, pyranine and their derivatives exhibit their strongest transition dipole moments along one of the molecule’s principle axes, as illustrated by two examples in Figure 3.1. Molecules based on perylene cores, such as the yellow, orange and red dyes from the BASF Lumogen F
series used in this work,\textsuperscript{8} have both their emission and absorption moments nearly parallel to the long molecular axis.\textsuperscript{9,10,11,12}

By controlling the physical orientation of photoluminescent dyes it is thus possible to control the direction of light emission. This capability can be used to greatly increase the efficiencies of LSCs. By aligning dye molecules in a preferential direction, their absorption and emission transition moments exhibit a degree of dichroism that may be harnessed to increase edge emission by lowering escape cone losses in LSCs.\textsuperscript{13,14,15,16}

3.2 Ideal and Obtainable Orientation

3.2.1 Ideal Orientation

The probability of a linearly polarized photon being absorbed by a molecule is proportional to the projection of the photon’s electric field vector on the transition vector.\textsuperscript{17}

For a large sample of molecules the average probability is proportional to:
where $\langle \cdot \rangle$ indicates sample averaging and $\theta$ is the angle between the electric field vector of the photon and the molecule’s transition moment.\textsuperscript{17} When the absorption and emission moments are perpendicular to one another light absorption is minimized, increasing as the angle between the two becomes smaller.

Thus, an ideal molecular orientation for LSC applications would be one in which the emission transition dipole moment was aligned perpendicular to the host matrix surface and the absorption transition dipole moment lay parallel to its surface (Fig. 3.2).

\begin{equation}
P \propto \langle \cos^2(\theta) \rangle
decx{3.1}
\end{equation}

\textbf{Figure 3.2:} Ideal oriented fluorophore configuration. Incident light (Blue wave) is strongly absorbed by the absorption transition moment (Blue vector). Traveling within the escape cone of the host matrix due to its steep angle, emitted light (Red wave) is unlikely to be reabsorbed by subsequent dyes due to small vector dot products.

The situation in described above is ideal for several reasons: Firstly due to its alignment relative to incident sunlight, the absorption transition dipole moment can absorb solar flux very strongly (Eq. 3.1 approaches a maximum). Secondly, the emission transition dipole moment is oriented to emit light nearly parallel to the plane of the LSC, resulting in the majority of the light being trapped by total internal reflection. Thirdly, the probability of
reabsorption by another oriented dye is reduced due to the orthogonality of absorption end
emission moments, (Eq. 3.1 approaches a minimum).

Although ideal, the situation illustrated in Figure 3.2 would be difficult to achieve in
practice, while simultaneously maintaining other requirements of LSC dyes such as high
quantum yields and high extinction coefficients. This follows from the Franck-Condon
principle, which states that the probability of an electronic transition is maximal when the
participating wave functions are most similar.\textsuperscript{18}

\textbf{3.2.2 Obtainable Orientations}

Since dyes with quantum yields near unity and possessing high extinction
coefficients are usually associated with a rigid molecular structure, they tend to exhibit high
fluorescence anisotropy.\textsuperscript{7,19} Additionally, dyes with rigid structures are most easily aligned.
Given this restriction on dye selection the best obtainable orientation is one that places the
emission transition dipole moment perpendicular to the surface of the host matrix, as
shown in Figure 3.3. However, from the preceding discussion it follows that the absorption
and emission transition dipole moments are nearly collinear. Consequently, compared to an
isotropic dye LSC, reabsorption is enhanced in an oriented fluorophore LSC, placing greater
importance on the use of dyes with high fluorescent quantum yields.
3.3 Illustration of the Effects of Alignment: Monte Carlo Simulations

To illustrate the potential advantages provided by fluorophore alignment, Fig. 3.4 presents results from a Monte Carlo simulation of photon transport and escape cone losses within an oriented fluorophore LSC (OF-LSC) conducted by our collaborators, McDowall, Johnson, and Patrick at Western Washington University. As can be seen in the figure, as the degree of orientational order increases, greater $P_2$, the number of photons lost through the escape cones decreases (the order parameter plotted on the x-axis in Figure 3.4 is formally defined later in this chapter). For order parameters $P_2 > \sim 0.75$, escape cone losses are virtually eliminated.

**Figure 3.3:** Obtainable oriented fluorophore configuration. Incident light (Blue wave) is absorbed by the absorption transition moment which overlaps with the emission transition vector (Yellow vector). Traveling within the escape cone of the host matrix due to its steep angle, emitted light (Red wave) observes a high probability of reabsorption due to large vector dot products.
The results of reduced escape cone losses are reflected as an increase in the optical quantum efficiency (OQE) defined as:

\[ OQE = \frac{n_{edges}}{n_{face}} \]

where \( n_{edges} \) is the number of photons collected along all LSC edges and \( n_{face} \) is the number of photons incident on the surface of a LSC. Simulations of LSC performance modeling devices containing a mixture of lumogen F violet, yellow, orange and red were performed to examine the effects of alignment on a OQE as a function of geometric gain. Some of these results are presented in Fig. 3.5, which compares the performance of two identical LSCs, one with oriented fluorophores, the other with isotropic (randomly oriented) fluorophores. In the case of alignment the terminal red dye was given homeotropic orientation, where the long axis of the molecule lies perpendicular with the matrix surface, with an order parameter \( \langle p_2 \rangle = 0.7 \), while the other dyes were treated as isotropic. The
results show that given a modest degree of alignment and geometric gain of $G > 70$, at least
50% more photons may be collected from a LSC based on oriented fluorophores (Fig. 3.5).

![Figure 3.5: Results from ballistic Monte Carlo simulations of OQE from isotropic fluorophores (Black line) and homeotropically oriented fluorophores (Red Line)](image)

3.4 Aligning Dyes

The above arguments point to the advantages of LSCs incorporating oriented fluorophores. While there are a variety of methods capable of aligning molecules, this thesis focuses on the use of liquid crystals and their polymerizable counterparts, often referred to as reactive mesogens.

3.4.1 Liquid Crystals

Liquid crystals (LCs) were discovered over a hundred years ago, but first studied in
detail during the 1960s when it was recognized they had potential for use in a number of applications, most notably liquid crystal displays. LCs exhibit a wide range of different phases, the most common of which are the nematic and smectic phases, where rod-shaped LC molecules self-align producing long-range directional order with their long axes roughly parallel (Fig. 3.6).²²

![Figure 3.6: Typical molecular orientation for a nematic phase liquid crystal](image)

There are many compounds known to form LC phases at room temperature, many of which are potentially capable of being used to dissolve and orient organic dyes. To control the orientation of the LC director, \( n \), several methods are commonly used:

- **Surface effects:**
  - rubbed poly(vinyl alcohol) or polyimide for planar alignment
  - surfactants for homeotropic alignment
- **An electric or magnetic field**
**Liquid Crystal Cell Construction**

Depending on the orientation being investigated, cells for LC alignment were constructed via two primary methods, described in the following. In all cases the LC 4-Cyano-4′-pentylbiphenyl (5CB; Aldrich or Frinton Laboratories Inc.), was used as the LC host.

**LC Planar Alignment**

A thin layer (~100 nm) of polyimide, PI2556 from HD MicroSystems, was spin coated using a Laurell Tech. Inc. spin coater (model: WS-400B-6NPP-LITE; 3 s 500 rpm, 30 s 4000 rpm) onto cleaned (sonicated in acetone, methanol, and iso-propanol baths for 30 min each) Indium Tin Oxide (ITO) glass (Delta Technologies, Ltd.) and baked (preheated to 130 °C, held for 15 min, ramp at 5 °C/min to 250 °C, held 30 min) to produce a thin polymer layer. The baked, coated ITO glass was rubbed lightly 10-15 times using a soft cloth and placed together with an identical substrate to form a cell, with anti-parallel rubbing. The cell was sealed using UV-cured Norland Optical Adhesive #63, and separated using Artus Shim Stock (25 – 200 µm thickness) as spacers (Fig. 3.7).

**Figure 3.7:** Schematic of typical 5CB LC cell. A polyimide layer spin coated onto ITO glass is rubbing with a soft cloth to provide an alignment layer. Two rubbed PI/ITO glass slides were aligned anti-parallel, spaced with shim stock and adhered together using Norland Adhesive. The cell was filled with the desired LC/dye solution and sealed.
A LC/dye solution was then drawn into the cell via capillary action until filled. It was sealed with Norland Optical Adhesive, heated beyond the LCs isotropic point and allowed to cool to room temperature where alignment was confirmed via cross-polarized optical microscopy.

**Homeotropic Alignment**

Some planar cells produced via the above method were induced into homeotropic alignment through the application of an AC electric field across the cell. Voltages ranging from 0.5 V to 2000 V were applied using a frequency of 3 kHZ.

Permanent homeotropic alignment was achieved using cleaned glass substrates (sonicated in acetone, methanol, and iso-propanol baths for 30 min each, followed by 15 min UV-ozone cleaning) sonicated in a 0.1% v/v of [3-(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride (DMOAP; Aldrich) in nanopure water for 5 min, followed by baking at 110 °C for 1 hr. Cells were fabricated from these substrates using the methods described above and their orientation confirmed via cross-polarized optical microscopy.

### 3.4.2 Reactive Mesogen Thin Films

The so-called ‘reactive mesogens’ (RMs) are liquid crystalline materials which with polymerizable end groups.\(^{23}\) Polymerizing these compounds while in a preferred orientation will produce a solid polymer that is permanently aligned.\(^{24}\) *In situ* photo-initiated polymerization of RMs is carried out with the RM in its desired alignment (usually
at elevated temperatures to maintain the LC state, producing a large area monodomain as shown in Figure 3.8. As with conventional LCs, elongated molecules embedded within this matrix align with the RM director.

Reactive mesogen mixtures RMM28B and RMM28A (Merck Chemicals Ltd.) were used to create RM films. These mixtures include several liquid crystalline acrylates as well as a surfactant that induces homeotropic alignment. RMM28B also contains a photoinitiator, whereas RMM28A does not. This difference became important in studies of dye stability as discussed in Chapter 4.

**Homeotropic Reactive Mesogen Thin Films**

Homeotropically aligned RM thin films ~3.2 μm in thickness were produced by spin coating (20 s at 3000 rpm) a 33% w/w solution of reactive mesogen in toluene on a clean glass substrate (usually BK-7 glass). Samples were allowed to air dry for 30 seconds followed by UV-curing under nitrogen for 30 seconds at room temperature. Orientation was checked via cross-polarized optical microscopy and film thicknesses were determined by
UV-Vis interferometry. Samples prepared in this way were generally found to exhibit a high degree of homeotropic alignment.

**Planar Reactive Mesogen Thin Films**

Planar aligned RM films were produced following the ITO substrate preparation outlined in section 3.3.1 involving rubbed PI. Orientation was checked via cross-polarized optical microscopy. In general the perimeters of these samples exhibited good alignment parallel to the direction of rubbing, although the center showed significant deviation; measurements of these samples were taken towards the edge where the best alignment was observed.

### 3.5 Measuring Orientation

#### 3.5.1 Coordinate Systems

Understanding molecular orientation requires a set of coordinates that can be measured from a laboratory frame of reference: $X,Y,$ and $Z$. However a fluorophore’s transition dipole moments are most conveniently expressed in relation to the molecule’s internal frame of reference: $X’,Y’$ and $Z’$. We use the Euler angles, $\alpha$ and $\theta$, to relate these two frames as shown in Figure 3.9.
The molecular absorption and emission transition dipole measurements, $\mu_a$ and $\mu_e$ respectively, orient at angles $\theta_a$ and $\theta_e$ from the molecular long axis. The angle between them, $\beta$, is related to the fundamental anisotropy (section 3.5.3).

Due to the uniaxial nature of nematic LCs there is rotational symmetry around the director, $n$ (Z axis in Fig. 3.9a). This also applies to rod-shaped dyes embedded within the LC and thus the absorption and emission transition moments, producing a conal distribution as shown in Figure 3.10.
3.5.2 Orientational Order of Liquid Crystals

For homogeneously aligned samples the orientational order parameter $P_2$ is defined by:

$$P_2 = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$  \hspace{1cm} (Eq. 3.2)

where $\theta$ is the angle between the absorption long molecular axis and the director and the brackets denote averaging over all molecules.\cite{25,27} $P_2$ can vary from a value of 1, corresponding to perfect molecular alignment parallel to the director, to -1/2, corresponding perfect molecular alignment perpendicular to the director.

By measuring the absorption of polarized light by a mode that lies parallel to the molecular long axis, the degree of orientation can be calculated from the dichroic ratio, $R$, 

\textbf{Figure 3.10:} Cone like distribution of Absorption ($\mu_a$) and emission ($\mu_e$) transition moments around the director, $n$, due to free rotational symmetry.
between the absorption coefficients, $A_{\parallel}$ and $A_{\perp}$, where \( \parallel \) and \( \perp \) denote incident light polarized parallel and perpendicularly to the direction of the sample alignment.\(^{27}\) We can thus relate the angle $\theta$ to $R$ by:\(^{28}\)

$$R = \frac{2(\cos^2 \theta)}{\sin^2 \theta} = \frac{(1+S_2)}{(1-S_2)}$$  
(Eq. 3.3)

and thus:

$$S_2 = \frac{(R-1)}{(R+2)} = \frac{A_{\parallel}-A_{\perp}}{A_{\parallel}+2A_{\perp}}$$  
(Eq. 3.4)

The order parameters of many liquid crystals have been determined experimentally using this method. For the family of mesogens based on 4-alkyl-4-cyanobiphenyl, order parameters around $P_2 = 0.8 $ ($<\theta> \approx 21^\circ$) can be achieved with relative ease.\(^{27}\)

3.5.3 Fundamental anisotropy

The fundamental anisotropy of fluorescence, $r_0$, is a physical quantity that depends on the orientations of the absorption and emission transition dipole moments of a fluorescent molecule and is defined as:\(^{29,30}\)

$$r_0 = \frac{1}{5} (3 \cos^2 \beta - 1)$$  
(Eq. 3.5)

where $\beta$ is the angle between the transition dipole moments. The fundamental anisotropy may range from -0.2 to 0.4, where the transition moments are, respectively, perpendicular ($\beta = 90^\circ$) and parallel ($\beta = 0^\circ$) to one another. Determination of the fundamental anisotropy of a molecule requires knowledge of several dye characteristics and is sensitive to its host solution.\(^{29}\) Since a large number of different dyes were investigated in this work, steps were
taken to simplify the procedure, and approximate the fundamental anisotropy through the use of dilute dye solutions in a highly viscous solvent (polypropylene glycol) at reduced temperature ($\leq 5 \, ^\circ C$). The anisotropy, $r$, calculated from a fluorescence measurement, is defined as:

$$r_0 \approx r = \frac{I_{VV} - G I_{VH}}{I_{VV} - G I_{VH}}$$

(Eq. 3.6)

where $I$ is the fluorescence intensity and the first and second subscripts refer to vertical, $V$, or horizontal, $H$, polarization of the excitation and emission polarizers. The factor $G$ is used to correct for differing instrumental responsivities to vertically and horizontally polarized light and is defined as, $G = I_{HV}/I_{HH}$.\textsuperscript{31}

An example of the kind of data generated by anisotropy measurements is shown in Fig. 3.11. The figure plots the wavelength dependent anisotropy calculated from the above equations. Note that the anisotropy is nearly constant over the entire emission range, a typical characteristic of the fluorophores used in this work.
3.5.4 Absorption Transition Dipole Moment Orientation

Since the absorption of light by a molecule is dictated by its transition dipole moment, the molecular orientation, \( \langle P_2 \rangle_a \), in an ordered system may be determined by measuring its absorbance of polarized light:

\[
\langle P_2 \rangle_a = \frac{A_{II} - A_{\perp}}{A_{II} + 2A_{\perp}} \left(1 - \frac{3}{2} \sin \theta_a \right)^{-1}
\]  
(Eq. 3.7)

where \( A \) is the extinction coefficient parallel, (II), or perpendicular, (\( \perp \)), to the polarizer and \( \theta_a \) is average angle between the absorption transition moment and the long molecular axis. Since the transition dipole moments of planar fused ring polycyclic aromatic hydrocarbons usually lie along the long axis of the molecule, which is also the axis that usually aligns parallel to the LC director, \( \theta_a \) is typically close to zero, in which case the above equation

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

Figure 3.11: Observed Wavelength dependent anisotropy, \( r \), of peak Coumarin-6 emission in PPG at 0 °C. Values of \( r \) near 0.4 demonstrate a small angle, \( \beta \), between the molecules absorption and emission transition moments.
simplifies to:

$$\langle P_2 \rangle_\alpha = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}$$  \hspace{1cm} (Eq. 3.8)

To measure the order parameter of guest dyes in 5CB, planar cells were constructed as outlined above using 25 – 50 $\mu$m spacers and non-saturated 5CB solutions containing the dye being measured. Using a pure 5CB cell as a blank, polarized optical spectroscopy measurements were taken with an Agilent 8453 Diode Array UV-visible spectrometer and an Olympus U-AN360P polarizer to determine the order parameter of the dye. A representative example of the resulting spectra is presented in Fig 3.12, which shows the absorption of the dye PBI-C6 (whose synthesis is described in section 4.1.2) when light is polarized parallel (0 Deg) and perpendicular (90 Deg) to the director.

![Figure 3.12](image)

**Figure 3.12:** Absorbance intensity of a 5CB cell containing PBI-C6 aligned parallel to (black) and perpendicular to (red) polarized light. This large change in absorption intensity suggests a high degree of alignment.
The reported $<P_2>_a$ value of the dye is the result of averaging the wavelength dependent $<P_2>_a$ values over the of the peak absorption range.

### 3.5.5 Emission Transition Dipole Moment Orientation

Experimental measurements of the degree of order based on the emission transition moment of a molecule is much more complicated than for the set of absorption dipoles because one has to take into account the influence of photoselection and corrections for instrumental response. To do this, we used a procedure introduced by Damerau and Hennecke. Two sets of fluorescence spectra are required, one from an isotropic sample, the second from a planar aligned sample.

First an isotropic sample is produced and anisotropy measurements are taken using the method described above. For a 5CB cell this was accomplished by the addition of a small amount of the nematic disruptant 1-phenyloctane to the LC/dye solution, while for RM films the isotropic state was induced by spin coating on un rubbed ITO/PI slides and heating the film above its isotropic transition point while polymerizing.

Next, the following fluorescent emission intensities were measured on a planar oriented sample:

$I_{hhv}, I_{hvh}, I_{hvv}, I_{vvh}, I_{vvv}$
The first subscript index indicates the orientation of the LC or RM director and the second and third indices indicate the orientation of the excitation and emission polarizers. The sample alignment axis had to be in the plane of the sample oriented either horizontally or vertically to avoid complications associated with birefringence, as shown in Figure 3.13.

![Experimental setup for determining $\langle P_2 \rangle_e$ and $\langle P_4 \rangle_e$. Sample was set at an angle, $\phi_{ex}$, from the polarized excitation source and light emitted from the sample at angle $\phi_{em}$, was passed through a polarizer before being detected.](image)

**Figure 3.13:** Experimental setup for determining $\langle P_2 \rangle_e$ and $\langle P_4 \rangle_e$. Sample was set at an angle, $\phi_{ex}$, from the polarized excitation source and light emitted from the sample at angle $\phi_{em}$, was passed through a polarizer before being detected.

This measurement allows for the determination of two coefficients that can be used to describe the order parameter for the emission moment of the guest dye:

\[
\langle P_2(\cos \theta_e) \rangle = \frac{1}{2} (3 \cos^2 \theta_e - 1) \quad \text{(Eq. 3.9)}
\]

\[
\langle P_4(\cos \theta_e) \rangle = \frac{1}{8} (35 \cos^4 \theta_e - 30 \cos^2 \theta_e + 3) \quad \text{(Eq. 3.10)}
\]
These coefficients may be determined by solving for the terms $\langle \cos^2 \theta_e \rangle$ and $\langle \cos^4 \theta_e \rangle$, defined as:

$$\langle \cos^2 \theta_e \rangle = \frac{1}{2} + \frac{1}{2} \langle \cos^4 \theta_e \rangle - \frac{16(1-p)(AB/C)+4p(1/C)+4p(1-p)}{(2-3p)^2(3-p)^2} \quad (Eq. 3.11)$$

$$\langle \cos^4 \theta_e \rangle = \frac{16(AB/C)+(12-10p)(1/C)+p(6-7p+3p^2)}{(2-3p)^2(3-p)^2} \quad (Eq. 3.12)$$

where:

$$p = \frac{\sqrt{10r-2}}{-3} \quad (Eq. 3.13)$$

$$A = G_1 \frac{l_{v vh}}{l_{v vv}} \quad (Eq. 3.14)$$

$$B = \frac{l_{h vv}(\cos^2 \phi_{em} \sin^2 \phi_{ex} - \cos^2 \phi_{ex} \sin^2 \phi_{em})}{G_1 l_{h vv} \sin^2 \phi_{ex} - G_2 l_{h vv} \sin^2 \phi_{em}} \quad (Eq. 3.15)$$

$$C = \frac{(3-2p)+8AB+4A(3-p)}{3-2p+p^2} \quad (Eq. 3.16)$$

$$G_1 = \frac{l_{h v v} \sin^2 (\phi_{ex}+\phi_{em})}{2l_{h h}} + \sqrt{\left(\frac{l_{h v v} \sin^2 (\phi_{ex}+\phi_{em})}{2l_{h h}}\right)^2 + \left(\frac{l_{h v v} \cos^2 (\phi_{ex}+\phi_{em})}{l_{h h} l_{v h}}\right)^2} \quad (Eq. 3.17)$$

$$G_2 = \frac{l_{v h} \sin^2 (\phi_{ex}+\phi_{em})}{2l_{h h}} + \sqrt{\left(\frac{l_{v h} \sin^2 (\phi_{ex}+\phi_{em})}{2l_{h h}}\right)^2 + \left(\frac{l_{v h} \cos^2 (\phi_{ex}+\phi_{em})}{l_{h h} l_{v h}}\right)^2} \quad (Eq. 3.18)$$

Because LC cells consisted of several layers, the path followed by a ray of light traveling at angles $\phi_{ex}$ and $\phi_{em}$ was determined by treating the sample as a multilayered
structure with refractive indices $n_{glass}$, $n_{ITO}$, $n_{PI}$ and $n_{LC}$. Using Snell’s law we calculated the relationship between the angles of incidence and refraction for each layer of the cell:

\[
\theta_{glass} = \sin^{-1}\left\{ \frac{n_{air}}{n_{glass}} \sin[90 - \theta_{in}] \right\} \quad \text{(Eq. 3.19)}
\]

\[
\theta_{ITO} = \sin^{-1}\left\{ \frac{n_{glass}}{n_{ITO}} \sin[\theta_{glass}] \right\} \quad \text{(Eq. 3.20)}
\]

\[
\theta_{PI} = \sin^{-1}\left\{ \frac{n_{ITO}}{n_{PI}} \sin[\theta_{ITO}] \right\} \quad \text{(Eq. 3.21)}
\]

\[
\theta_{LC} = \sin^{-1}\left\{ \frac{n_{PI}}{n_{LC}} \sin[\theta_{PI}] \right\} \quad \text{(Eq. 3.22)}
\]

We then solved for $\theta_{LC}$ (which is equal to $\phi_{ex}$) as a function of the other angles:

\[
\theta_{LC} = \phi_{ex} = \sin^{-1}\left\{ \frac{n_{PI} n_{ITO} n_{glass} n_{air}}{n_{LC} n_{PI} n_{ITO} n_{glass}} \sin[90 - \theta_{in}] \right\} \quad \text{(Eq. 3.23)}
\]

The intermediate refractive indices cancel out yielding a simplified equation for $\phi_{ex}$ that includes only the refractive indices of the terminal layers of the cell (air and LC). This reasoning may be extended to calculate $\phi_{em}$, yielding:

\[
\phi_{ex} = \sin^{-1}\left\{ \frac{n_{air}}{n_{LC}} \sin[90 - \theta_{in}] \right\} \quad \text{(Eq. 3.24)}
\]

\[
\phi_{em} = \sin^{-1}\left\{ \frac{n_{air}}{n_{LC}} \sin[\theta_{in}] \right\} \quad \text{(Eq. 3.25)}
\]

The refractive indices were found using:
\[ n_{air} = 1 \]  \hspace{1cm} (Eq. 3.26)

\[ n_{LC} = 1 + n_a + n_b \frac{\lambda^2 \lambda_b^2}{\lambda^2 - \lambda_b^2} + n_c \frac{\lambda^2 \lambda_c^2}{\lambda^2 - \lambda_c^2} \]  \hspace{1cm} (Eq. 3.27)

where \( \lambda \) is the wavelength and the constants \( n_x \) and \( \lambda_x \) for the extraordinary ray (parallel to the director) and ordinary ray (perpendicular to the director) at room temperature are given in Table 3.1.\(^{35}\) The approximation derived from the values in Table 3.1 for \( n_{LC} \) are valid over the wavelength range of 380 to 780 nm.\(^{35}\)

<table>
<thead>
<tr>
<th>Constant</th>
<th>Extraordinary ray</th>
<th>Ordinary ray</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_a )</td>
<td>0.4552</td>
<td>0.4136</td>
</tr>
<tr>
<td>( n_b )</td>
<td>2.33 \times 10^{-6} \text{ nm}^{-2}</td>
<td>1.35 \times 10^{-6} \text{ nm}^{-2}</td>
</tr>
<tr>
<td>( n_c )</td>
<td>1.4 \times 10^{-6} \text{ nm}^{-2}</td>
<td>0.47 \times 10^{-6} \text{ nm}^{-2}</td>
</tr>
<tr>
<td>( \lambda_b )</td>
<td>210 nm</td>
<td>210 nm</td>
</tr>
<tr>
<td>( \lambda_c )</td>
<td>282 nm</td>
<td>282 nm</td>
</tr>
</tbody>
</table>

**Table 3.1:** 5CB refractive index constants for Eq. 3.27

Values of \( \langle P_2(\cos \theta_e) \rangle \) and \( \langle P_4(\cos \theta_e) \rangle \) (hereafter written using the shorthand notation \( \langle P_2 \rangle_e \) and \( \langle P_4 \rangle_e \)) were calculated and then checked for mathematical consistencies using the following tests:

**Consistency Test #1** \(^{36}\)

For \( \langle P_2 \rangle < 0.6 \), \( \langle P_4 \rangle \) should be approximately \( \langle P_4 \rangle \approx \frac{5}{7} \langle P_2 \rangle^2 \)
Consistency Test #2 \(^{36}\)

\(\langle P_2 \rangle \) and \(\langle P_4 \rangle \) should obey the following inequalities

\[
\frac{35}{18} \langle P_2 \rangle^2 - \frac{5}{9} \langle P_2 \rangle - \frac{7}{18} \leq \langle P_4 \rangle \leq \frac{5}{12} \langle P_2 \rangle + \frac{7}{12}
\]

Consistency Test #3 \(^{34}\)

The Damereau and Hennecke method allows for several combinations of \(\phi_{ex} \) and \(\phi_{em} \) allowing for an internal consistency check.

As with the anisotropy data, the reported \(\langle P_2 \rangle_e \) and \(\langle P_4 \rangle_e \) values are the result of the averaged peak emission wavelength dependent \(\langle P_2 \rangle_e, \langle P_4 \rangle_e \). An example of the type of data resulting from this analysis is shown in Figure 3.14. Further interpretation of this data is provided in the next section.

**Figure 3.14:** Wavelength dependent \(\langle P_2 \rangle_e, \langle P_4 \rangle_e \) values for Lumogen F Orange 240 in RMM28B
3.6 Orientational Distribution Functions

To obtain a more physically intuitive understanding of the numerical values of $\langle P_2 \rangle_a$, $\langle P_2 \rangle_e$, and $\langle P_4 \rangle_e$ it is useful to express orientational order in terms of a probability distribution function, $f(\theta)$. The full orientational distributions can be described in terms of an expansion in Legendre polynomials $P_L(\cos \theta)$:

$$
\text{f}_{\text{abs (or em)}}(\theta) = \sum_{L=0}^{\infty} f_L P_L(\cos \theta) \quad (L \text{ even}) \quad \text{(Eq. 3.28)}
$$

where

$$
f_L = \frac{(2L+1)}{2} \langle P_L(\cos \theta) \rangle \quad \text{(Eq. 3.29)}
$$

The curve generated by Eq. 3.29 describes the probability of a transition moment being aligned at a particular angle from the molecular long axis and is normalized such that it integrates to a value of 1 from 0° to 360°.

The coefficients of the distribution each contain the term $\langle P_L(\cos \theta) \rangle$, which comprise a set of order parameters. The first few non-zero terms (order parameters) are (all $L = \text{odd terms are zero}$):

$$
\langle P_0(\cos \theta) \rangle = 1 \quad \text{(Eq. 3.30)}
$$

$$
\langle P_2(\cos \theta) \rangle = \frac{1}{2} (3\cos^2 \theta - 1) \quad \text{(Eq. 3.31)}
$$
\[ \langle P_4(\cos \theta) \rangle = \frac{1}{8} (35\cos^4 \theta - 30\cos^2 \theta + 3) \]  

(Eq. 3.32)

The second term \( \langle P_2(\cos \theta) \rangle \) is the most commonly measured order parameter for LCs and other uniaxial systems. To fully describe the orientational distribution function, \( f_{abs} \) or \( f_{em} \) however, one has to measure the complete, infinite set of order parameters \( \langle P_0 \rangle, \langle P_2 \rangle, \ldots, \langle P_\infty \rangle \). Unfortunately, the higher rank order parameters are not easily determined and in practice we have only \( \langle P_0 \rangle \) and \( \langle P_2 \rangle \) (and for emission, \( \langle P_4 \rangle \)) to work from. One approach to estimating the orientational distribution functions from this limited amount of information would be to simply truncate the series in Eq. 3.27 after \( \langle P_2 \rangle \) (or after \( \langle P_4 \rangle \) in the case of emission) and use this as an approximation for \( f \). It turns out however that this does not give very good results.\(^{36}\) A better approach is to estimate the distribution based on the maximum entropy principle.\(^{37}\) To do this, we treat the dye molecules as if oriented in the LC or RM by a potential of the form:\(^{38}\)

\[ -\frac{U(\theta)}{kT} = c_2 P_2(\cos \theta) + c_4 P_4(\cos \theta) \]  

(Eq. 3.33)

where \( c_2 \) and \( c_4 \) are constants and compute the distribution function, \( f(\theta) \), using statistical mechanics:

\[ f(\theta) \approx \frac{\exp\left[-\frac{U(\theta)}{kT}\right]}{\int_0^\pi \sin \theta \exp\left[-\frac{U(\theta)}{kT}\right] d\theta} \]  

(Eq. 3.34)
To use this formula we have to know the coefficients, \( c_2 \) and \( c_4 \). If only \( \langle P_2 \rangle \) is known, as is the case for absorption moments, \( c_2 \) is found by satisfying the condition:

\[
\langle P_2(\cos \theta) \rangle = \frac{\int_0^\pi \sin \theta P_2(\cos \theta) \exp[c_2 P_2(\cos \theta)] d\theta}{\int_0^\pi \sin \theta \exp[c_2 P_2(\cos \theta)] d\theta} \tag{Eq. 3.35}
\]

If both \( \langle P_2 \rangle \) and \( \langle P_4 \rangle \) are known, as is the case for emission moments, \( c_2 \) and \( c_4 \) are found by satisfying the conditions:

\[
\langle P_2(\cos \theta) \rangle = \frac{\int_0^\pi \sin \theta P_2(\cos \theta) \exp[c_2 P_2(\cos \theta)+c_4 P_4(\cos \theta)] d\theta}{\int_0^\pi \sin \theta \exp[c_2 P_2(\cos \theta)+c_4 P_4(\cos \theta)] d\theta} \tag{Eq. 3.36}
\]

\[
\langle P_4(\cos \theta) \rangle = \frac{\int_0^\pi \sin \theta P_4(\cos \theta) \exp[c_2 P_2(\cos \theta)+c_4 P_4(\cos \theta)] d\theta}{\int_0^\pi \sin \theta \exp[c_2 P_2(\cos \theta)+c_4 P_4(\cos \theta)] d\theta} \tag{Eq. 3.37}
\]

To graph this distribution in two dimensions it is necessary to normalize by \( \sin(\theta)d\theta \), accounting for the difference in the area of the unit sphere swept out by a small angle at the equator versus at the poles.\(^{37,38}\) The distribution function was then found for the dyes relative to the alignment direction of the LC. An example is presented in Fig 3.15, which shows the \( <P_2>_a \) and \( <P_2>_e \), \( <P_4>_e \) distributions for PBI-C6 in 5CB and RMM28B respectively.
The curves generated in these graphs provide a probabilistic distribution of the aligned dye around the director, 0 degrees, normalized for 360 degree distribution.

**3.7 Summary**

Exploiting the unique properties of planar organic fluorophores, a method for improving LSC efficiency based on engineered orientation of absorption and emission dipole moments within the waveguide has been described. Methods for inducing alignment in LC and RM samples have been demonstrated to orient dopants incorporated within the host. Both planar and homeotropic orientations could be achieved at various thicknesses, allowing for the determination of the degree of orientation of absorption and emission.
transition moments within the aligned matrix. An intuitive method of expressing the degree of orientation is described based on the use of the maximum entropy principle, rendering the numerical values associated with alignment into a distribution function.
References


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Chapter 4: Towards Reactive Mesogen Oriented Fluorophore LSCs

4.1 Overview

This chapter works to describe a method by which sheets of reactive mesogen (RM) may be polymerized as to possess good homeotropic alignment for thicknesses up to 1 mm. First a description of dyes, both commercial and custom synthesized, thought suitable for oriented fluorophore LSCs is given. The method by which sheets of RM were produced is then given, followed by observations of dye degradation within the produced sheets.

4.1.1 Dye Investigation: Commercial dyes

In addition to a set of custom-synthesized dyes discussed below, the spectral, orientational, and solubility characteristics of a number of commercially available dyes were investigated for possible use in oriented fluorophore LSC devices. These dyes, along with a summary of their measured properties, are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Dye Name</th>
<th>Structure</th>
<th>Optical properties</th>
<th>Note</th>
</tr>
</thead>
</table>
| NIR-628                   | ![NIR-628](image)                               | $\lambda_{\text{Abs}}^{\text{max}} = 610 \text{ nm}$  
                           | | $\lambda_{\text{Em}}^{\text{max}} = 658 \text{ nm}$  | Very limited solubility in LC                 |
| 7-Pentyloxy-3-phenoxazone | ![7-Pentyloxy-3-phenoxazone](image)            | $\lambda_{\text{Abs}}^{\text{max}} = 464 \text{ nm}$  
                           | | $\lambda_{\text{Em}}^{\text{max}} = 540 \text{ nm}$  | Temperature sensitive; notable decomposition after periods of exposure to high (55°C) temperature. |

**Table 4.1:** List of commercial dyes investigated for use in oriented fluorophore LSCs. Chemical name or shorthand, structure, optical properties and relevant attributes of note are listed.
Of the commercially available dyes examined, 3-(2-Benzothiazolyl)-7-octadecyloxy-coumarin (a Coumarin-6 derivative) exhibited the best overall physical characteristics for oriented fluorophore LSCs. Some of its most important properties are summarized in Table 4.2 and its orientational distribution functions in a reactive mesogen matrix are shown in Figure 4.1.
Although Coumarin-6 possesses a relatively low quantum yield and only a modest degree of orientation in 5CB, its relatively large stokes shift, commercial availability and well documented characteristics made it a good candidate for initial testing.¹,²,³,⁴

### 4.1.2 Dye Synthesis

In addition to Coumarin-6, several new dyes were designed and synthesized with the goal of showing improved alignment properties, higher quantum yield, and better solubility.

**PBI-C6:** To obtain longer wavelength emission, dye compounds based on Perylene-3,4,9,10-tetracarboxyedianhydride (PTCDA) were investigated. As with perylene, the unprotected conjugated Pi system of PTCDA posed solubility and aggregation issues. To improve solubility and increase the degree of alignment, the molecule N,N'-bis-(hexyl)-perylene-
$3,4,9,10$-tetracarboxydilimide (perylene bis-imide hexylamine; PBI-C6, Fig 4.2 was synthesized by the author from PTCDA and purified using methods outlined by F. Donati et al.$^5$

![Chemical structures of PBI-C6 (Left) and Lumogen F Orange 240 (Right)](image)

**Figure 4.2:** chemical structures of PBI-C6 (Left) and Lumogen F Orange 240 (Right)

The PBI-C6 core has almost the same electronic structure as lumogen F Orange 240 and the two dyes exhibit nearly identical spectral properties (Fig 4.3). Unlike Lumogen Orange however, PBI-C6 was found to be highly oriented in LC solvents (refer to Table 4.3 and Fig. 4.4), a characteristic attributable to the substitution of the two $2,6$-diisopropylaniline groups with n-hexyl tails.$^5,6$

![Normalized absorption and emission intensities of a) PBI-C6 and b) Lumogen F Orange 240](image)

**Figure 4.3:** Normalized absorption and emission intensities of a) PBI-C6 and b) Lumogen F Orange 240
Unfortunately the increased orientability of PBI-C6 came at the cost of decreased solubility. Replacing the bulky 2,6-diisopropylaniline groups with more sterically compact n-hexyl chains permits dyes to more readily undergo \( \pi-\pi \) stacking interactions, driving the formation of aggregates and decreasing solubility.

**Table 4.3:** Physical Attributes of PBI-C6 and Lumogen F Orange 240. Absorption and emission spectra were taken in Toluene, LC 5CB was used to determine \(<P_2>_a\) and RMM28B thin films used for \(<P_2>_e, <P_4>_e\). * denotes BASF reported value.

<table>
<thead>
<tr>
<th>Dye</th>
<th>QY</th>
<th>r</th>
<th>( \lambda_{Abs}^{max} )</th>
<th>( \lambda_{Em}^{max} )</th>
<th>(&lt;P_2&gt;_a)</th>
<th>(&lt;P_2&gt;_e)</th>
<th>(&lt;P_4&gt;_e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI-C6</td>
<td>0.98</td>
<td>0.355</td>
<td>526nm</td>
<td>540nm</td>
<td>0.764</td>
<td>0.673</td>
<td>0.654</td>
</tr>
<tr>
<td>Lumogen F Orange</td>
<td>&gt;0.95*</td>
<td>0.345</td>
<td>532nm</td>
<td>542nm</td>
<td>0.232</td>
<td>0.010</td>
<td>0.320</td>
</tr>
</tbody>
</table>

**Figure 4.4:** 2D distribution of the optical transition moments of a) PBI-C6 and b) Lumogen F Orange 240 relative to the RM director.

**PBI-Perk11** A second dye, PBI-Perk11 was synthesized for us by collaborators working in the laboratory of Dr. J. Gilbertson at WWU. PBI-PERK11 shares the same electronic structure as PBI-C6 and Lumogen F Orange 240 but contains polymerizable olefin groups, included to
allow incorporation into polymer chains and thereby potentially increasing alignment while reducing orientational motion.\textsuperscript{7,8} The structure of PBI-Perk11 is shown in Figure 4.5.\textsuperscript{9}

![Chemical structure of PBI-Perk11. Polymerizable acrylate groups should allow incorporation into polymer chains.](image)

**Figure 4.5:** Chemical structure of PBI-Perk11. Polymerizable acrylate groups should allow incorporation into polymer chains.

Although studies with PBI-PERK11 showed a significant improvement in solubility, its alignment in 5CB, mechanically-stretched PMMA and PVA polymer films, and RM films was observed to be almost negligible. The alignment and optical properties in 5CB are summarized in Table 4.4.

<table>
<thead>
<tr>
<th>Dye</th>
<th>QY</th>
<th>r</th>
<th>$\lambda_{\text{max}}^{\text{Abs}}$</th>
<th>$\lambda_{\text{max}}^{\text{Em}}$</th>
<th>$&lt;P_2&gt;_a$</th>
<th>$&lt;P_2&gt;_e$</th>
<th>$&lt;P_4&gt;_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI-Perk11</td>
<td>0.976</td>
<td>0.352</td>
<td>527nm</td>
<td>540nm</td>
<td>-0.046</td>
<td>0.0455</td>
<td>-0.046</td>
</tr>
</tbody>
</table>

**Table 4.4:** Physical properties of PBI-Perk11. Absorption and emission spectra were taken in toluene, LC 5CB was used to determine $<P_2>_a$ and RMM28B thin films used for $<P_2>_e$, $<P_4>_e$

**PBI-C8-Phenoxy** In an attempt to produce dyes with longer wavelength emission, and improved solubility PBI-C8-Phenoxy was synthesized, also by collaborators in the Gilbertson group. The chemical structure of PBI-C8-Phenoxy, Figure 4.6, shares a very similar
electronic structure to Lumogen F Red and as seen in Figure 4.7 they possess nearly identical spectral properties.

![Chemical structures of PBI-C8-Phenoxy and Lumogen F Red 305](image)

**Figure 4.6:** Chemical structures of PBI-C8-Phenoxy (Left) and Lumogen F Red 305 (Right)

![Normalized absorption and emission intensities of PBI-C8-Phenoxy and Lumogen F Red 305 in Toluene](image)

**Figure 4.7:** Normalized absorption and emission intensities of a) PBI-C8-Phenoxy and b) Lumogen F Red 305 in Toluene

In addition to producing longer wavelength emission, the addition of phenoxy groups at the bay positions of the PTCDA core helps sterically shield the core pi system, greatly reducing aggregation and increasing dye solubility. The addition of octylamine to the molecule leads to good alignment in LCs and RMs, whereas Lumogen F Red, as seen in Figure 4.8, exhibits essentially no alignment. The alignability, high quantum yield, red
emission, and high solubility of PBI-C8-Phenoxy make it well suited for future testing in oriented LSC systems (Table 4.5).

\[ \text{Table 4.5: Physical Attributes of PBI-C8-Phenoxy and Lumogen F Red 305.} \]

<table>
<thead>
<tr>
<th>Dye</th>
<th>QY</th>
<th>( r )</th>
<th>( \lambda_{\text{Abs}}^{\text{max}} )</th>
<th>( \lambda_{\text{Em}}^{\text{max}} )</th>
<th>( &lt;P_2&gt;^a )</th>
<th>( &lt;P_2&gt;^e )</th>
<th>( &lt;P_4&gt;^e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBI-C8-Phenoxy</td>
<td>0.97</td>
<td>0.355</td>
<td>567nm</td>
<td>597nm</td>
<td>0.223</td>
<td>-0.015</td>
<td>0.362</td>
</tr>
<tr>
<td>Lumogen F Red</td>
<td>0.98</td>
<td>0.351</td>
<td>577nm</td>
<td>599nm</td>
<td>-0.095</td>
<td>-0.053</td>
<td>0.093</td>
</tr>
</tbody>
</table>

\[ \text{Figure 4.8: 2D distribution of the optical transition moments of a) PBI-C8-Phenoxy and b) Lumogen F Red 305 relative to the LC director.} \]

4.2 RMM28B Sheets

Because RMs can be oriented and polymerized homeotropically\(^\text{10}\) (Section 3.4.2) they are an attractive model system for the testing of oriented fluorophore LSC concepts.\(^\text{11}\)
RM mixture RMM28B is specifically designed to produce homeotropically oriented thin films when spin coated onto an appropriate substrate, such as glass or treated polymers (section 3.4.2).  

The RM28 series of reactive mesogens were originally formulated by Merck for use as optical correction layers in liquid crystal displays, designed to be applied as thin films a few microns in thickness. However due to the limited solubility of some organic dyes RMs it was desirable to be able to produce sheets of RMs having a thickness much greater than this. Toward this end a rectangular cell for RM polymerization was constructed with a 1 mm high Teflon rim that was clamped on glass slides as illustrated in Figure 4.9.

**Figure 4.9:** Illustration of Teflon rimmed cell for sheet polymerization. The cell had a well depth of 1 mm and was firmly clamped to the glass to avoid solution leaks.

Filling this cell with the same 33% w/w RM / toluene solution used for thin films showed however that a different approach would be needed for producing thicker RM sheets, since the resulting thick sheets were too strongly light scattering when polymerized. It was evident that new methods of inducing RM alignment would need to be identified in
order to obtain thick homeotropic RM sheets.

4.2.1 Differential Scanning Calorimetry

While Figure 4.10, a thermogram of raw RMM28B, shows a nematic phase between 40 and 60 °C, experimentation (section 4.2.2) suggested that the addition of a solvent stabilized the polymerization process thus yielding better sheets. Additionally a RM solution in its nematic phase at room temperature would be more convenient to work with.\textsuperscript{13,14,15} To this end several mixtures were investigated with the intent of developing such as state.

![Figure 4.10: DSC of raw RMM28B. The nematic and isotropic phases can be seen at 37.24 and 66.36 °C with thermal polymerization $\approx$140 °C.](image)

A number of different weight percent solutions of RM were investigated with solvents such as toluene, 5CB, 4’-Octyl-4-biphenyl-carbonitrile (8CB), methyl methacrylate (MMA), and Bis(2-ethylhexyl) sebacate (Bis-Sebacate). Differential scanning calorimetry and
polarized optical microscopy showed that while the addition of liquid crystals 5CB and 8CB to solid RM lowered the temperature of the nematic phase onset, they also lowered the temperature of the isotropic state, producing mixtures with a very narrow nematic range. Additionally, upon polymerization the LC would undergo phase separation from the RM, producing films of poor optical quality. Similarly MMA and Bis-Sebacate solutions did not yield a workable separation between the nematic and isotropic phases and were also expelled from the RM matrix upon polymerization.

While no mixture yielded a nematic phase RM at room temperature, the best workable solvent was found to be toluene, which provided a window of ~15 °C between the nematic and isotropic phases up to 46 w/w% toluene, at which point the nematic phase could no longer be isolated. The relationship between phases and thermal polymerization onset are outlined in Figure 4.11.

![Figure 4.11: Phase and thermal polymerization onsets for different weight percent’s of toluene mixed with RMM28B](image)
4.2.2 Self-Alignment Using Surfactants

Though one of the components in RMM28B is a surfactant for inducing homeotropic alignment in thin films,\textsuperscript{16} it was uncertain if thicker sheets, in excess of 200 \( \mu \text{m} \), could be aligned by this surface effect alone. To check this, several attempts at achieving homeotropically aligned sheets were performed utilizing the Teflon rim. The reservoir was filled with solutions of RM and toluene ranging from 95 - 60 w/w\% RM and heated to and maintained at \( \sim 50 \degree \text{C} \) for 1 minute before UV-polymerization for 45 seconds.

Solutions with a RM w/w\% greater than 80 consistently exhibit strong light scattering upon polymerization. Attempts to improve this result by varying the heating rates and holding temperatures up to and beyond the isotropic point did not resolve the problem. While solutions with RM w/w\% equal to or less than 80 showed significantly better results, splotches of opaqueness continued to occur in these samples and a general cloudiness was observed throughout the sample. Upon sitting overnight, samples with w/w\% less than 70 exhibited notable shrinking and cracking likely due to the evaporation of toluene trapped within the matrix.

4.2.3 Alignment by Magnetic and Electric Fields

From the solutions investigated the general trend indicated mixtures containing around 80 w/w\% of RM in toluene offered the most promise for obtaining aligned films with low light scattering. In an attempt to improve the degree of orientational order even further, several experiments using electric and magnetic fields were performed.\textsuperscript{17}
Cells constructed from ITO glass were prepared using shim stock ranging from 25 µm to 500 µm and filled with an 80 w/w% of RM in toluene solution. At a temperature of ~50 °C, an AC potential of 1000 V at a frequency of 3 kHZ was applied to the cell while exposed to UV light for 30 seconds. The resultant cells exhibited a marginal improvement over initial experiments at shim stock thickness less than 100 µm, but at greater thicknesses the cells were completely opaque.

Using a Maghion Inc. Ventron electromagnet a magnetic field of up to 6 KG was used in an attempt to induce homeotropic alignment in a sample. It was found that regardless of field strength, hold temperature or RM w/w%, alignment of samples could not be achieved.

4.2.4 Cell Cast RMM28B Sheets

While RMM28B exhibited negligible alignability under an applied electric or magnetic field, additional experiments and literature searches suggested that homeotropic alignment could be achieved by surface effects alone if films were sandwiched between two glass slides pre-treated with a surfactant. Using two clean glass substrates treated with DMOAP (section 3.4.1), alignment of samples could be obtained by a method similar to cell casting. The detailed procedure eventually developed was as follows:

An 80% w/w mixture of RMM28B and toluene was prepared and thoroughly mixed through sonication at 45 °C for 1 hour. Dye was then added to the solution in concentrations ranging from 20 – 250 ppm and the mixture homogenized by vortex mixing for 10 s followed by sonication at 45 °C for 30 min. In some cases, solutions were centrifuged for 1 min at 10,000 rpm and decanted to remove insoluble particulates. RM
sheets were cast by filling cells constructed using treated glass and shim stock (100 – 500 μm in thickness) or 1 mm thick microscope slides as spacers followed. Filled cells were polymerized in situ by UV irradiation while the temperature was held at ~50 °C for 20 – 45 s, depending on sheet thickness. Polymerization was performed under nitrogen atmosphere.

An example of a film prepared in this way is presented in Figure 4.12. The RM layer was 1 mm thick and contained PBI-C6 at a concentration of ~250 ppm, with dimensions of 50 mm x 50 mm. Figure 4.13 depicts a polarized optical microscopy observations of a cross section of the film used to confirm alignment.

**Figure 4.12:** Homeotropic RMM28B sheet doped with 250 ppm PBI-C6. Sheet dimensions are 50 mm x 50 mm x 1 mm.
Experimentation on sheets of RMM28B revealed an anomaly that was not observed in thin films and can be seen in Figure 4.14. Upon extended exposure to UV irradiation sheets of RM doped with dyes exhibited a notable hypsochromic shift when compared to their freshly made counterparts.

**Figure 4.13:** RMM28B sheet viewed through cross-polarizers. The sheet surface (a) is almost perfectly black at all angles. A sliver cut from the sheet and placed on its edge exhibits near blackness at 0 degrees, from the top polarizer, and high intensity at 45 degrees (characteristic of alignment).
Figure 4.14: Lumogen F Red 305 doped RMM28B sheets photo-polymerized from a stock solution for 2 min (right) and 15 min (Left). A significant blue shift in absorption and emission is observed for longer polymerization times.

Figure 4.14 shows two sheets polymerized from the same solution of Lumogen F Red 305 in 80 w/w% RM in toluene exposed to UV light for different periods of time. The sheet on the right was exposed for two minutes, while the one on the left was exposed for 15 minutes. The sheet exposed for a longer period of time showed a significant hypsochromic shift in both its absorbance and emission spectra. Even for exposure times less than one minute, the minimum time necessary to achieve complete RM polymerization, the resulting sheets still exhibited this effect to some degree, ultimately leading to complete photobleaching. Even exposure to white light from an incandescent lamp as seen in Figure 4.15 was found to cause the exposed area to become bleached.
Since the only compound in RMM28B that interacts strongly with light is the photo-initiator (PI) 2-methyl-1-(4-methylthiophenyl)-2-morpholinopropan-1-one it seemed likely to be responsible for the dye degradation. To test this, a closely related PI, 2,2-dimethoxy-1,2-diphenyl-ethanone, was used to perform photobleaching tests with Lumogen F Red in toluene. Figure 4.16 compares two solutions of this mixture. The one on the left was exposed to high intensity UV light for 45 min, while the other was kept in a darkened vial, shielded from light. The vial exposed to UV light (Fig 4.16, Left) exhibited an orange color similar to that observed in RMM28B sheets exposed to long polymerization times, while the control (Fig 4.16, right) retained its original, unchanged, red color similar to that of RMM28B sheets with short exposure times. UV-Vis absorbance data shown in Figure 4.17 of the two solutions show a significant broadening, hypsochromic shift and intensity change in the absorbance of light as a result of UV exposure.
**Figure 4.16:** Effect of UV irradiation on PI doped Lumogen F Red 305 in Toluene solution. The UV exposed vial (left) shows a blue shift in absorption and emission when compared to its non-UV exposed control (right).

**Figure 4.17:** Effect on absorbance due to UV irradiation on PI doped Lumogen F Red 305 in Toluene solution. High exposure to UV irradiation (Black, 45 minutes) exhibits broadening, hypsochromic shift and intensity change when compared to un-exposed Lumogen F Red 305 (Red)
Though the precise photodegradation mechanism is unknown, this hypsochromic shift suggests that the bay substituted phenoxy groups were being removed by the PI. To test the integrity of the PTCDA core two sheets of PBI-C6 were cast from the same stock solution and exposed to UV light for 2 and 20 minutes, resulting in a notable degradation in the absorption and fluorescence intensity for the long exposure sample as seen in Figure 4.18. The results suggest that the PTCDA core is just as susceptible to degradation by the PI as its bay substituted counterpart.

![Figure 4.18](image-url): PBI-C6 doped RMM28B sheets photo-polymerized from a stock solution for 2 min (right) and 20 min (Left). Significant dye degradation is observed for long periods of polymerization.

To mitigate these negative effects several experiments were performed in an attempt to reduce the effective concentration of the PI through the addition of the inhibitors 4-tert-butylicatechol or hydroquinone monomethyl ether. The inhibitor was dissolved in toluene and used as the 20 w/w% toluene present in standard sheet casting
mixtures. Following the procedure outlined in section 4.2.4 cells were filled with solution and exposed to UV irradiation. Though several concentrations, ranging from ppm to ppt, of PI where investigated sheets either continued to exhibit dye degradation or would not polymerized even after 45 min of UV light exposure.

4.3 RMM28A Sheets

The RM mixture RMM28A contains the same compounds as RMM28B except that it has no PI. This allowed us to add our own initiators and to investigate PI concentrations far below those in RMM28B, where the concentration reported by the manufacturer is in the range 2 - 5 w/w%. Two types of PIs were investigated: thermal initiators and photiniators.

4.3.1 Thermal Polymerization

The thermal polymerizer 2-2’-azobisisobutyronitile (AIBN) is commonly used to initiate free-radical polymerization in plastics such as PMMA and polystyrene. Experiments similar to those described in section 4.2.3 using toluene solutions suggested that AIBN does not photobleach dyes. To test the use of AIBN in polymerized RMM28A films, solutions with PI concentrations of 0.05 to 1% were investigated by dissolving in RM/toluene solutions followed polymerization through cell casting at 45 to 55 °C under nitrogen atmosphere for 4 to 24 hours.

Unfortunately it was found that high concentrations of AIBN (0.3-1 w/w%) resulted in sheets with incorporated bubbles, likely nitrogen from the AIBN radical mechanism, and
various degrees of transparency. Concentrations less than 0.3 w/w% AIBN resulted in long polymerization times (upwards of 12 hours) and opaque sheets.

4.3.2 Low Photo-Initiator concentrations

The PI 2,2-dimethoxy-1,2-diphenyl-Ethanone was also investigated for use in the polymerization of RMM28A sheets. Several concentrations of the PI were tested using the cell cast method described in section 4.2.5. Experiments revealed that the addition of 0.05 w/w% to a 80 w/w% RM / Toluene solution could produce small (10 mm x 10 mm) sheets of lightly doped homeotropicaly aligned and RMM28A of thicknesses up to 1 mm with very little light scattering. UV-Vis measurements on these samples show no evidence of dye degradation over several hours of UV exposure.

Research on these films is currently ongoing, with efforts focused on increasing the dye concentration and size of these sheets for use in oriented fluorophore LSC prototypes.

4.4 Summary

The development of orientable fluorophores such as PBI-C6 and PBI-C8-Phenoxy as well as the use of commercially available dyes like coumarin-6 are expected to permit improved system efficiencies by significantly reducing escape cone losses observed in traditional LSCs. Toward this end the use of RMs in oriented fluorophore LSCs may hold significant promise. Continued development of RM sheets is needed enable the creation of optically dense, highly ordered systems with low light scattering that can take advantage of
the improved light trapping characteristics of ordered dyes. While issues of dye degradation so far have prevented the construction of large area films, significant progress has been made in addressing this problem and in improving film quality.
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Chapter 5: Investigations of Homeotropic Alignment for LSCs

5.1 Investigations of an Oriented Fluorophore LSC Using 5CB

This chapter describes methods by which the effect of homeotropic alignment was tested through the use of available commercial materials. To this end 50 µm thick 5CB cells were constructed from ITO glass and rubbed PI using the methods described in section 3.3.1. One edge of the cell was UV-cured with a glass slide attached to its face and notches removed from the opposite end to allow electrical contact to be made to the ITO glass. (Fig. 5.1)

Figure 5.1: Illustration of 5CB cell architecture. The director, \( \hat{n} \), induced from rubbed PI on ITO coated ITO aligns LCS. Inset Picture is of a prototype coumarin-6 cell of 3 cm width.

Cells were filled with solutions containing fluorescent dye in 5CB. With an applied voltage the 5CB could be induced into homeotropic orientation from planar orientation,
thus allowing measurement of the two configurations in a single cell.\textsuperscript{1,2} Measurements were performed at room temperature (nematic phase) and 55 °C (isotropic phase).

### 5.1.1 Escape Cone Losses

By inducing homeotropic alignment, escape cone losses should be significantly reduced. Using the method from Reference 3 the effect of aligned PBI-C8-Phenoxy on bottom surface losses was investigated using 5CB cells. The experimental setup used to perform escape losses is shown in Fig. 5.2. Measurements were taken by placing the surface of the 30 mm X 40 mm cells against a 5 mm hole in a port plug of a Newport 4” integrating sphere. Cells were exposed to white light coupled from a Horiba FL3-11 spectrofluorometer using a F4-3000 Fiber-Optic Adaptor. Light was collected from the integration sphere by a fiber-optic with a ocean optics CC-3 cosine corrector lens attached. A blank cell, containing only 5CB, was used as a background.

**Figure 5.2:** Illustration of escape cone losses experimental setup. Light coupled from the source was used to excite a small area of a waveguide. Emitted light was collected with an integration sphere and coupled to the detector.
To account for the different refractive indices represented by the different layers of the LC cells, as well as scattering and related losses induced by the aligned LC layer versus its isotropic state, a lumogen F Red 5CB cell was used as a baseline. Lumogen F Red was selected for this purpose because it exhibits no alignment in 5CB and is expected to emit light in the same manner regardless of the LC state. This allowed for a correction of the differences between the two states by comparing surface losses of the isotropic state to that of the aligned state. A representative spectrum from the baselined data is presented in Figure 5.3. By integrating area 1 the number of photons absorbed by the cell may be calculated and by integrating area 2 the number of photons lost through the bottom surface may be determined, the ratio of the two giving the percent of photons lost out the bottom escape cone. The results of these calculations are listed in Table 5.1.

Figure 5.3: Emission spectrum from the surface of 5CB PBI-C8-Phenoxy cell. Area 1 and 2 are proportional to the number of photons absorbed and emitted, respectively.
### Table 5.1: Bottom Surface Losses (% Photons)

<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>Isotropic State</th>
<th>Homeotropic State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lumogen F Red 305</td>
<td>15.3</td>
<td>20.5</td>
</tr>
<tr>
<td>PBI-C8-Phenoxy</td>
<td>12.6</td>
<td>9.3</td>
</tr>
</tbody>
</table>

The data in Table 5.1 reveals a 25.3% increase in the number of photons lost through the bottom surface as a result of LC alignment when comparing the isotropic state to the homeotropic state of Lumogen F Red 305 cell. Because Lumogen F Red 305 does not align in 5CB this increase must be due to mechanisms associated with the LC and not the dye. Assuming these mechanisms are same for both cells this relationship can be applied as a correction factor to the PBI-C8-Phenoxy cell data to account for the effects of LC alignment:

\[
\varepsilon_{\text{Actual}}^{\text{PBI-C8 Homeotropic}} \propto \varepsilon_{\text{Observed}}^{\text{PBI-C8 Homeotropic}} \times \frac{\varepsilon_{\text{Observed}}^{\text{Lum F Red Isotropic}}}{\varepsilon_{\text{Observed}}^{\text{Lum F Red Homeotropic}}} \quad (\text{Eq. 5.1})
\]

where \( \varepsilon \) is the percent of photons lost for a given cell and phase. Applying this correction to the PBI-C8-Phenoxy data reveals a reduction of 45%, from 12.6% to 6.9%, in the number of photons lost out of the bottom surface of the cell as a result of dye alignment.

#### 5.1.2 Effect of Alignment on Absorption

The average orientation of the fluorophore absorption transition moment affects the amount of light absorbed by the LSC.\(^4,5\) This is illustrated in Figure 5.4, which shows the dependence of cell absorptivity on applied voltage for a representative LSC based on
coumarin-6. Increasing the applied voltage from 0 V causes a change in the director orientation (and hence dye orientation) from planar to homeotropic. Similar results were obtained for other aligned dye systems.

To properly compare the relative performance of isotropic and oriented fluorophore LSCs described in the following sections, the internal quantum efficiency (IQE) was calculated to account for the difference in absorption:

\[
IQE = \frac{\text{QE}}{\%A}
\]  
(Eq. 5.2)

where \%A is the fraction of incident photons absorbed.

**Figure 5.4**: Absorption profile of coumarin-6 in 5CB cell. As homeotropic alignment takes hold the absorbance falls by 45% due the absorption transition dipole moment becoming more orthogonal relative to the electric field vector of the incident light.
5.1.3 2D-Edge Emission: Polar Intensity Distribution

With the onset of alignment it becomes possible to observe its effects on the edge emission of a LSC. Using the method described by Bendig et al.\textsuperscript{6} a 2-dimentional (2D) cross section of light was collected from the edge of the cell while the LSC was excited at a small point 25mm away using a fiber optically coupled Halogen/Deuterium Lamp with an Ocean Optics P400-1-UV-VIS Fiber optic cable with 74-VIS Collimating Lens. Emitted light from the LSC was observed through a PMMA hemisphere (diameter of 3.5”, Fig. 5.5) with several electrical potentials applied to the cell, as well as with cells in the isotropic state. Photons were collected by an Angstrom Sun Technology SR300 fiber connected to a CCD detector with an Ocean Optics P1000-2-UV-VIS Fiber optic cable with 74-VIS Collimating Lens.

\textbf{Figure 5.5:} Experimental setup for 2D cross section measurements. Light emitted from the sample cell is coupled into the attached PMMA hemisphere, allowing for angle dependent measurements to be obtained.
Figure 5.6: Normalized angular dependence on cell edge emission for a) PBI-C8-Phenoxy while homeotropic (2000 V, Black) and isotropic (Red) and for b) coumarin-6 while homeotropic at 20 V (Black) and 2000 V (Red).

Figure 5.6 shows the normalized emission intensity from the edge of PBI-C8-Phenoxy and coumarin-6 cells as a function of the angle from normal emission. A drop in emission intensity is observed for the homeotropically aligned samples at angles less than ≈20°. At first this result may seem counterintuitive, since for homeotropic alignment one would expect the majority of photons to be emitted in the sample plane, i.e. at an angle of 0°.

While there are probably a number of mechanisms involved, one possible explanation is that light travelling close to 0° spends relatively more time in LC layer than in the glass walls of the cell, leading to significantly higher scattering losses. Accounting for the birefringence of 5CB, light emitted by a guest fluorophore in a homeotropicaly aligned LC host will observe a critical angle of ≈65 °C with a glass interface. This means that light emitted at shallower angles is trapped within the LC layer, where it is more strongly scattered, and undergoes more self-absorption than in the glass. To illustrate, the difference in path length for photons emitted at different angles in a hypothetical
homeotropic 5CB cell illuminated at a point 25 mm from the emission edge is calculated in Figure 5.7. Photons emitted at angles > 25° spend far less time in the LC layer than those emitted at shallower angles.

![Distance Traveled in LC Layer vs Emission Angle](image)

**Figure 5.7:** Emission angle dependence on the distance a photon travels within the 5CB LC layer for a spot illuminated 25mm from emission edge

Consequently, at low emission angles a photon is trapped within the LC layer where scattering and self-absorption losses are much stronger than in the glass. This may explain the results of Figure 5.6 where light emitted at angles less than 25° has a much lower chance of reaching the edge of the LSC than light traveling at larger angles. As the voltage increases from 20 V to 2000 V the induced homeotropic alignment becomes stronger, reducing the effects of thermal fluctuations in the LC director which are the primary source
of light scattering and increasing the chance of light trapped within the LC layer escaping through the LSC edge.

While the use of a large applied voltage helps reduce light scattering by suppressing fluctuations in the LC director, it cannot fully eliminate this effect. Since $\langle P_2 \rangle_a = 0.605$ for Coumarin-6 in 5CB the majority of photons are emitted at angles less than 25°. Even for a dye such as PBI-C8-Phenoxy, with much redder emission wavelengths, scattering still exhibits a noticeable effect on edge emission from 5CB cells.

By integrating the edge emission over all angles, the total edge emission can be measured. The results are shown in Figure 5.8, which shows the IQE of a 5CB cell (relative to the isotropic state) as a function of applied voltage. At low applied voltage the cell is in a planar state. Above the Fredericks transition at ~20 V the cell switches to the homeotropic state and the IQE increases dramatically. When fully homeotropic (2000 V) the cell exhibits an 86% greater transport efficiency than in the isotropic state.

**Figure 5.8:** IQE of the aligned states normalized to the IQE of the Isotropic state (Dashed Line) of coumarin-6 cell. Solid line used to illustrate the effects on IQE due to the onset of homeotropic alignment (Fredericks transition at ~20 V).
5.1.4 Edge Emission: Polar and Azimuthal Intensity Distribution

Overview

While useful, 2D-edge emission measurements are limited to providing information about emission from the edge of a LSC along a single angular coordinate. To measure both polar and azimuthal emission, an apparatus was constructed to allow emission to be observed over the entire hemisphere.

![Apparatus](image1)

**Figure 5.9:** a) Apparatus used to obtain Polar and Azimuthal Intensity distribution measurements. b) Coordinate system for measurements taken over hemisphere (X-Y) relative to 5CB cell orientation.

This apparatus shown in Fig. 5.9 utilizes a rotating cylinder and a sliding rail to position an Ocean Optics P1000-2-UV-VIS fiber optic cable with a 74-VIS collimating lens over the surface area of an optically transparent PMMA hemisphere (diameter of 3.5”). Light travels from the edge of the LSC into the coupled hemisphere and fiber optic cable where, using the same instrumentation used in section 5.2.2, the intensity of light is measured. Cells were made in the same manner described above. A small amount of index
of refraction matching fluid (Cargille Laboratories; Series A, n=1.518) was used to optically match the cell with the PMMA hemisphere.

Measurements were taken by rotating the cylinder to a desired angle; the detector was then moved to various angles along the rail to map out a cross section on the hemisphere. This was repeated by moving the cylinder to the next angle until measurements over the entire hemisphere were collected. Data are expressed in terms of the notation X-Y, where X is the angle in degrees that the cylinder was rotated from vertical and Y is the angle in degrees the detector was moved in the plane of the LSC.

Experimentation

A 50 mm X 30 mm cell was constructed from ITO coated glass with 50 µm spacers and filled with a solution of coumarin-6 in 5CB. Homeotropic alignment was achieved at room temperature with a 2000 V AC potential; the isotropic phase was induced by warming the LSC to 55°C with no applied voltage. Three sets of measurements were taken with the cell illuminated at different distances from the emission edge, 13mm, 26mm, and 40mm.
The distribution of light emitted from both isotropic and homeotropic LSCs is expressed in Cartesian coordinates in Figure 5.10, where the data is from cells illuminated 13 mm from the emission edge. The isotropic state, Figure 5.10a, shows a single intense peak at X-90 corresponding to light of normal emission. The shoulders of this peak, corresponding to 90-Y, show some TIR light from the BK-7 surface. Figure 5.10b, in contrast to the results of the isotropic state, shows the homeotropic state exhibiting a strong anisotropy in the angular emission profile. When the detector is observing the face of the BK-7 glass substrate (90-Y), it observes two intense peaks corresponding to light trapped by TIR within the glass substrate. As was observed in 2D cross section data, a significant drop in light intensity is observed at normal incidence, corresponding to light lost through LC scattering.

Figure 5.10 Angular emission Intensity of Coumarin-6 cell while a) isotropic and b) homeotropic (2000 V).
5.1.5 Edge Emission: Excitation Distance

Though 2D-Edge emission measurements showed an improvement of up to 97% at certain angles (section 5.1.3), the most important performance metric is the total light output, integrated over all angles. Utilizing an experimental the instrumentation as in 5.1.1 the edge emission of PBI-C6 in 5CB was therefore measured using integration, with the LSC excited by white light coupled from the spectrofluorometer at varying distances from the cell edge as outlined in Figure 5.11.

Figure 5.11 Illustration of excitation distance experimental setup. Light coupled from the source was used to excite the surface of the LSC whose edge emission was collected by an integrating sphere and coupled a detector.
The results are presented in Fig. 5.12, which show a continual decrease in edge emission as excitation distance increases. Figure 5.13 shows the total edge emission as a function of excitation distance, computed as the integrated counts over the full emission range of the dye.

**Figure 5.12:** Emission spectra of a) isotropic and b) homeotropic PBI-C6 at excitation distances 8-38 mm from emission edge.

**Figure 5.13:** Integrated edge emission intensity for PBI-C6 5CB cell in its homeotropic (Black Points) and isotropic (Red Points) state
The results indicate a small reduction in the rate of light loss as a function of excitation distance. Correcting for differences in the absorption efficiency, a reduction of 36% from isotropic to homeotropic, and computing $\text{IQE}_{\text{Aligned}}/\text{IQE}_{\text{Isot}}$, Figure 5.14, shows a significant improvement in transport efficiency for the homeotropic device vs the same device in an isotropic state, reaching nearly 60% at an illumination distance of 28 mm. This substantial increase in transporting efficiency is due solely to the application of oriented fluorophores within an alignable host matrix.

**Figure 4.14:** IQE for integrated edge emission of aligned PBI-C6 cell normalized to its isotropic state. A maximum improvement of 58.8% in the transporting efficiency of the cell is observed.
5.2 Summary

Characterization of vertically oriented devices based on 5CB provides insights into the performance of aligned fluorophores for LSC applications. While alignment has demonstrated the importance of matching different optical systems as to avoid internal inefficiencies it has also been seen to reduce escape cone (surface) losses by 45% and increase transport efficiency by at least 60%. These observed improvements stand to drastically improve LSC efficiencies by reducing the primary mechanisms for which light is lost in traditional LSC systems.
References


Conclusions

Faced with steadily increasing demand for energy and limited quantities of non-renewable energy sources, significant effort has been invested over the past several decades aimed at reducing our dependency on carbon-based energy sources. Though hydroelectric, wind, and geothermal power have grown to represent a larger share of overall energy production, solar energy has yet to make a significant contribution, due in large part to its high cost.

This thesis has presented studies of a new concept for reducing the cost of solar energy based on oriented fluorophore luminescent solar concentrators. Based on the use of oriented matrices such as liquid crystals and reactive mesogens, methods were demonstrated to control the directional properties of fluorophore emission, providing a mechanism to trap a greater proportion of light within the waveguide. By confining dye emission to the plane of the LSC, escape cone losses have been shown to be reduced by up to 45% when compared to an isotropic LSC. Similarly, edge emission from oriented fluorophore LSCs demonstrated improvements in photon transport efficiency of nearly 60%..

Experimental work included the screening of a large number of dyes as oriented fluorophore candidates, as well as the synthesis of custom dyes designed specifically for LSC applications. Reactive mesogen (RM) mixtures were studied for use as low light scattering oriented host matrices and methods were developed to produce large surface area,
optically dense, and homeotropically aligned sheets up to 1 mm thick. The spectral and light concentrating properties of reactive mesogen devices were investigated in prototype LSCs and progress was made toward increasing dye lifetime and stability in reactive mesogen hosts. Additional work involved thermotropic liquid crystal-based LSCs, which were studied in isotropic, planar, and homeotropic alignment, with devices switchable between orientational states by application of an external field. Facial and edge emission measurements using custom-built optical systems, as well as escape cone transport losses, quantum yields, and overall external quantum efficiencies have been measured and compared to theoretical predictions.

More broadly, the work reported in this thesis represents a first step toward a drastic reduction in the cost of PV based energy generation. Utilizing low cost materials to cover large areas, appreciable concentration factors can be obtained with LSCs allowing relatively small amount of PVs to generate large amounts of energy. With the application of oriented fluorophores mature LSC technology has been projected to be competitive with conventional energy generation methods such as coal, natural gas, and petroleum. Successful development and adaptation of oriented fluorophores LSCs grants the potential to end the worlds reliance on carbon based energy, and thus change the way the world perceives and uses energy.